Formation mechanism of complex organic molecules in the interstellar medium

Department of Chemistry



Reetu

Supervisor: Prof. Dr. Anthony J. H. M. Meijer

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Abstract

The abundance of atomic hydrogen (H) in the interstellar medium (ISM) makes it a key player in its thermal balance. The formation of molecular hydrogen (H₂) in the ISM has long been a topic of interest, as gas-phase models alone cannot account for its large abundance. It is widely believed that carbonaceous dust grains catalyze the formation of H₂ through surface-catalyzed reactions. The adsorption of hydrogen on a grain surface is a crucial step in this process, and therefore, plays an important role in interstellar chemistry. While carbon, oxygen, and nitrogen are also major elements in the ISM, their adsorption on carbonaceous materials and suitable models for their reaction remains uncertain. These elements can also react to form H₂O and NH₃, which have been observed in the ISM. The presence of isomers in different regions of the ISM has also been reported, but the reaction mechanism for their formation is still under investigation. To study the adsorption and reaction of these atomic species on carbonaceous dust grains, density functional theory (DFT) has been used.

Previous studies have shown that the adsorption energy of H atoms on graphitic surfaces can be accurately described using either the full graphene sheet or polycyclic aromatic hydrocarbons (PAHs). For this study, we selected coronene, hexabenzocoronene, and bilayer graphite as models of carbonaceous grain surfaces. We also investigated the impact of dispersion interactions on the adsorption energetics of C, O, N, and H. Our results showed that vdW-DF significantly affects the physisorption energy, the binding energy, and the energy barrier between physisorption and chemisorption, but the precise effect depends on the gas type and the specific adsorption site.

In the second part, we examine the influence of surface relaxation and grain defects on the adsorption and desorption of atoms within bi-layer graphite surfaces. This is accomplished by substituting one carbon atom from the top graphene layer with H, O, N, Fe, Si, and Mg defects. Adsorption of a hydrogen atom on a pristine graphite surface requires a target carbon atom to move out of the plane by ~ 0.35 Å and introduces an energy barrier of 0.2 eV. Our findings show that the presence of surface defects significantly decreases or even removes this energy barrier.

In the third part, we employ our initial calculations to investigate the hydrogenation of oxygen and nitrogen adsorbed on a grain mimic to create water and ammonia, respectively. We also explore the formation of ammonia and water on an oxygenated surface. Our results reveal that a single water molecule physisorbs on a graphitic surface and that water clusters further reduce the binding energy due to an increase in H-bonding within the water molecules. However, in contrast, the presence of a defect increases the binding energy of a water dimer with the graphitic surface.

A single ammonia molecule also physisorbs on a graphite surface. However, the presence of epoxy and hydroxyl functional groups increases the binding energy of ammonia with the graphitic surface.

In the final chapter, we investigate the gas-phase reaction of atomic oxygen with small molecules such as acetylene, ethylene, and propyne. Additionally, we studied the potential energy profile for the formation of various isomers in the presence of a carbonaceous surface (hexabenzocornene and bi-layer graphite) to assess the effect of such grain surfaces on the barrier heights and relative stability of isomers. Our results show that the potential energy profile follows a similar pattern in the gas phase and on a grain surface. However, the presence of a surface does result in reduced energy barriers for some reaction pathways.

Dedicated to

my parents

Mrs. Shakuntla Devi

&

$Mr. \ Dharam \ Singh$

for being a source of endless love and motivation

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Glossary

- **DFT** Density functional theory
- D3BJ Becke Johnson damping
- DZ double-zeta
- **ER** Eley Rideal
- **EC** Electron correlation
- FFF Completely restricted surface and incoming atom
- FFT Surface atoms can move in z-axis with restricted incoming atom
- **GGA** Generalized gradient approximation
- **GMC** giant molecular cloud
- ${\bf GTO}\,$ Gaussian Type Orbitals
- **BE** Binding energy
- **GO** Graphene Oxide
- **HP** Hartree product
- HF Hartree Fock
- HK Hohenberg-Kohn
- **ISC** Inter-System Crossing
- **ISM** Interstellar medium
- KS Kohn Sham
- LH Langmuir Hinselwood
- LDA Local density approximation
- LSDA Local spin density approximation
- **BO** Born Oppenheimer
- **MCSCF** Multi configurational self consistent field
- **MBPT** Many body perturbation theory
- PAHs Polycyclic aromatic hydrocarbons
- PBC Periodic boundary condition

- PAW Projector augmented wave
- **PEC** Potential energy curve
- **rhs** Right hand side
- SE Schrödinnger equation
- SCF Self-consistent field
- **STO** Slater type orbitals
- **CASSCF** Complete active space self consistent field
- SCTST Semiclassical Transition State Theory
- **TTT** Surface atoms can move in x, y, and z-direction with lateral movement of incoming atom
- UV Ultraviolet
- **USPP** ultrasoft pseudo-potential
- vdW van der Waals
- **VASP** Vienna *ab initio* simulation package
- **CC** Coupled Cluster
- CCSD(T) Coupled Cluster single double with perturbative triple
- **CASPT2** Complete active space second order perturbation
- **CASPTn** Complete active space nth order perturbation
- CGTO Contracted Gaussian Type Orbital
- **CI** Configuration interaction

Chapter 1

Introduction

1.1 Background

The Universe is about 13.6 billion years old and has a radius of $\approx 10^{26}$ m.¹ During the Big Bang, the temperature changed from 10^{32} K to 10^9 K within three seconds along which the high temperatures led to collisions between high-energy photons that formed electrons, protons, and neutrons. These led to the formation of atomic nuclei such as hydrogen, deuterium, helium, and lithium through nucleosynthesis (fusion of protons and neutrons) within the first 3 minutes of the formation of the Universe. No heavy elements were formed at this time² because the temperature and density dropped so rapidly that further nucleosynthesis was impossible. These small nuclei coalesced into gas clouds which can be recognized as proto-galaxies. As the Universe further developed, these further combined and transformed into galaxies,² where most baryonic matter is concentrated. Our Milky Way is one of these galaxies, which has a spiral shape¹ with a total mass of approximately 10^{10} solar masses $(M \odot)$.^{3,4} There are many stars in the Milky Way, but also much empty space, which is occupied by diffuse matter and radiation. This diffuse matter is called the Interstellar medium (ISM).

1.1.1 The interstellar medium

The ISM consist of 99 % gas and 1 % dust.⁵ The gas largely consists of hydrogen in both atomic and molecular form along with He. Other, heavier, elements are also present but in trace amounts.¹ The nature and density of the ISM is also closely related to the operation of stars, where light elements (H and He) transform into heavier elements (*e.g.* C, N, O) through nuclear fusion⁶ as shown in Fig. 1.1 panel (a). These heavy elements return to the ISM at the end of a star's life.⁷ The life of a star (in the present-day Universe) is driven by fuel which is produced in a sequence of nuclear reactions. In the early Universe, or in low-mass stars the dominant process is hydrogen-burning in which the fusion of hydrogen nuclei generates helium. There are two possible routes for the formation of He *via* hydrogen fusion (Eqn. 1.1 and 1.2) and the carbon-nitrogen-oxygen (CNO) cycle, see Fig. 1.1 panel (b).



Figure 1.1: (a)-Layers of material evolved at the end-of-life of massive stars.⁶ Image is taken from Ref. [6] with permission, (b)Carbon-nitrogen-oxygen (CNO) cycle.⁸

$${}^{2}_{1}\mathrm{H} + {}^{1}_{1}\mathrm{H} \rightarrow {}^{3}_{2}\mathrm{He} + \gamma \tag{1.1}$$

$${}^{3}_{2}\text{He} + {}^{3}_{2}\text{He} \to {}^{4}_{2}\text{He} + {}^{1}_{1}\text{H}$$
 (1.2)

After its hydrogen runs out, a high-mass star can burn helium, carbon, and neon in the inner layers of a star as shown in Fig. 1.1 (a), which releases energy. Conversion of helium atoms into carbon occurs through the triple-alpha process. In this process, two helium nuclei transform into one ⁸Be. Because of the short half-life of ⁸Be, it can easily decay back to two ⁴He at low temperatures (Eqn. 1.3). But, at temperatures of $\approx 10^8$ K and by addition of a third ⁴He atom one ¹²C atom can be formed, whereby the formation of ¹²C is faster than decay back to ⁴He (Eqn. 1.4).⁸

$${}^{4}_{2}\text{He} + {}^{4}_{2}\text{He} \Longrightarrow {}^{8}_{4}\text{Be} + \gamma \tag{1.3}$$

$${}^{8}_{4}\mathrm{Be} + {}^{4}_{2}\mathrm{He} \rightarrow {}^{12}_{6}\mathrm{C} + \gamma \tag{1.4}$$

From carbon, one can form oxygen and neon through α -capture. Higher mass elements are formed through carbon or neon burning. For the heaviest stars elements up to iron can be formed in the core of the star. The explosion of a massive star (supernova) at the end of its life can generate elements heavier than iron up to uranium.⁹ These elements are then returned to the ISM where they can participate in chemistry or be part of a new star. Thus, the ISM plays a key role in the evolution of galaxies and its chemistry. As noted above, the ISM is mainly composed of gas and dust which is now discussed in more detail.

1.1.2 Interstellar gas

In the previous section, we indicated that the composition of diffuse matter in the ISM depends upon the life cycle of stars. Because of the high temperatures inside a star, the matter inside is plasma. Thus, when a star releases its matter into the ISM, it will be

a charged gaseous. Therefore, it was initially thought that all matter in the ISM was mainly gaseous and atomic in nature with some simple diatomic molecules. However, the advent of astronomical spectroscopy has shown this is not the case and to date, more than 200 different molecules have been detected, varying from diatomic molecules to complex species such as fullerenes.^{10,11} It should be noted that the temperature in the ISM varies considerably with location. As a consequence, baryonic matter in the ISM can be present in as plasma as well as a solid form.¹² The latter are often referred to as dust grains, which are an important component of interstellar clouds, not in the least because of the role they play in the formation of molecules.

As mentioned above, the most abundant element in the ISM is hydrogen. Its average abundance is one hydrogen atom per cm^{3} .¹² Relative to this, the number density of other elements is much smaller, as reported in Table 1.1. It is assumed that half of the total gas in the ISM is distributed over 98 % of the space, *i.e.* gas densities are very low.¹⁵ The rest of the gas occupies the remaining space in the form of interstellar clouds. Thus, the ISM is not homogeneous and there are variations in density and temperature with location.^{15,16} The temperature can be close to absolute zero or can be thousands of K,⁴ whereas the density can vary from 0.1 to 10^6 particles cm⁻³. As hydrogen is the most abundant element in the ISM, regions of the ISM are named after the most abundant form of hydrogen. Thus, these are referred to as HI (neutral atomic hydrogen) or HII (ionized hydrogen) clouds.

Table 1.1: Abundance ratio of the elements in the ISM relative to one hydrogen atom per cm^{3} .^{13,14}

Element	composition
He	0.1
0	$5.6 imes10^{-4}$
С	3.3×10^{-4}
Ν	5.8×10^{-5}
S	2.6×10^{-5}
Na	2.0×10^{-7}
Si	$7.0 imes 10^{-9}$
Mg	$7.0 imes 10^{-9}$
Cl	2.0×10^{-9}
Li	1.5×10^{-9}

Interstellar clouds can also be sub-divided into diffuse

and dense clouds.⁷ The density of matter in diffuse clouds is 10 cm^{-3} to 100 cm^{-3} with a temperature range of 50 K–100 K. Here, the nature of the gas is mainly atomic. The density in dense clouds is $10^3 \text{ cm}^{-3}-10^6 \text{ cm}^{-3}$ with temperatures below 50 K. Within these dense clouds, complex molecules and dust particles are found.¹⁷ On the basis of the ionized state of the gas, the density, and the temperature, the ISM is divided further into different phases¹⁷ as shown in Table 1.2. Our research will focus on molecular clouds at low temperatures to study the formation of molecules.

Table 1.2: Different phases of the $ISM^{15,16}$ with different temperature ranges and densities of matter.

ISM phase	$n(cm^{-3})$	T(K)	hydrogen state	vol. filling $factor(\%)$
cold neutral	20 - 50	50 - 100	HI	4
warm neutral	0.25 - 0.5	6000 - 10000	HI	30
molecular	$100 - 10^{6}$	10 - 20	molecular	1
hot ionized	6×10^{-3}	10^{6}	HII	50
warm ionized	0.2 - 0.5	8000	HII	15

1.1.3 Interstellar dust

Dust has already been mentioned a few times above. It was first positively identified in 1994 and contributes less than 1% of the total mass of matter in the ISM.¹⁸ Dust grains are solid particles and have a size ranging from nanometers to micrometers.¹⁹ Despite

their small size, dust is arguably one of the most complex components of the ISM. The temperature of these small dust grains²⁰ can be as low as 5-6 K but will increase to ~ 75 K close to bright stars (HII region).¹² Most importantly, dust grains provide a surface on which different species can be adsorbed, meet, and react with each other.¹² The existence of dust was observed through 'reddening' and 'extinction' of starlight^a in *dark clouds*²¹ and has been postulated since 1980.²² In particular, these dust particles absorb and scatter light that comes from stars behind them. It leaves a dark space in which stars appear to be absent.³ An example of this is shown in Fig. 1.2, 'Eagle Nebula'.



Figure 1.2: Eagle Nebula, a cloud of gas and dust which block starlight behind it. Image Credits: NASA, ESA, and R. Sahai (Jet Propulsion Laboratory); Processing: Gladys Kober (NASA/Catholic University of America). Picture taken by Hubble Telescope.²³

The extent of absorbance and scattering depends on the wavelength of the incident light and the size of the dust particle.¹⁹ Moreover, near bright stars dust clouds can also reflect the light, so-called reflection nebulae.¹⁹ The major dust components are C, O, Mg, Si, and Fe with minor contributions from Na, Al, Ca, and Ni and trace amounts of K, Cr,

^aIf the light is partially scattered and dims to some extent, this is known as extinction.¹⁹ If the dust is thick, it can block the light completely which leads to a dark area and these regions are known as dark nebulae. Partial scattering of light depends upon the wavelength of light and thickness of dust. Scattering is inversely proportional to (wavelength)⁴. As a result, red light (higher wavelength) scatter less than blue light (shorter wavelength). In conclusion, scattering affects blue light more. This means the dust scatter more blue light and as a consequence, we observe more red light. This is known as reddening.¹⁹

and Co.^{24} Dust grains have the form of a mixture of carbonaceous and silicaceous solids generally covered with ices at low temperatures. A cartoon of this is shown in Fig 1.3.⁶



Figure 1.3: A cartoon of a typical interstellar dust grain.⁶ Image is taken from Ref. [6] with permission.

In hot gas regions, solid carbon degrades to polycyclic aromatic hydrocarbons (PAHs), such as coronene, circumcoronene, and graphite. These might then combine to give e.g. fullerenes and carbon nanotubes.²⁵

Amorphous carbon					
Diamond					
Silicon carbide					
Graphite					
Silicates					
Polycyclic aromatic hydrocarbons(PAH)					
Soot					
Fullerene					
Hydrogenated amorphous carbon (HAC)					
Carbynes					
Diamond-like carbon (DLC)					

Table 1.3:	Forms	of	interstellar	dust	$qrains^{21,26}$
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Spectroscopic studies confirm that PAHs are an important component of interstellar dust grains, which can readily interact with atomic radicals (H, C, O, and N) to generate new species in the ISM.²⁷ Table 1.3 highlights some of the identified forms of interstellar dust grains. The complexity of these means that graphite and small polycyclic aromatic hydrocarbons are commonly used as simple models for the dust grain surface. This is what we have chosen to do in this thesis as well. It is important to note that dust grains are neither inert nor eternal. They can react easily with the radicals and they can easily be destroyed by interstellar shocks²⁸ (stellar winds, supernova explosion, photons, high energy particles *etc*). Most importantly the properties of dust grains change when they interact with radiation or gas. Therefore, it is important to understand them²⁹ and their chemistry.

Carbonaceous grains

As is clear from Table 1.1, the abundance of carbon atoms is lower than that of H, He, and O atoms. However, its capacity for condensation at low temperatures and for polymerization to form chain and ring molecules is high. Thus, a higher abundance of carbon bearing molecules and carbonaceous materials can be expected.³⁰ These materials can be characterized as aromatic and "flat". Thus, their structure and geometry can be rationalized in terms of hybrid orbitals that are formed by a linear combination of the atomic orbitals of carbon. Carbon has a total of six electrons and out of these six, four are valence electrons, leading to an electronic configuration of $1s^22s^22p_x^12p_y^12p_z^0$. Carbon can be sp, sp^2 , or sp^3 hybridized. If carbon atoms in the sp^2 hybridization combine, they form a planar honeycomb-like structure, which ties 3 valence-p electrons with the fourth electron delocalized over the layer. If this is a monolayer, then this is generally referred to as graphene. However, the size and shape of the molecule are affected by the extended π system. Van der Waals interactions are the short range intermolecular forces that occur because of the fluctuations in electron distribution around atoms and molecules. The fourth electron of the carbon atoms in the graphene layer is no longer bound to particular carbon atoms. This means the interactions between two adjacent layers of graphene are weak, van der Waals, interactions. However, graphene is not the only compound with this general structure. PAHs such as coronene and hexabenzocoronene also have sp^2 hybridized carbon. However, in this case, the peripheral atoms are hydrogen to fulfill the valency of carbon. Graphene or PAHs are idealized forms of sp^2 -carbon lattices. In reality, it has been reported that the structure of carbonaceous compounds depends on their location in ISM.^{31,32} Moreover, the majority of carbonaceous solids show defects and are present in a mixture of sp, sp^2 , and sp^3 hybridizations.³³ Moreover, carbonaceous dust is not the only material present in the ISM. In addition to carbonaceous dust, silicaceous dust is also present in the ISM. These are amorphous silicate grains along with metal ions such as Mg or Fe^{21}

For our research, a bi-layer graphite model was chosen as a model for carbonaceous dust grains. Moreover, PAHs are widely accepted as a molecular model for graphene.^{34–36} On the basis of this, we have chosen coronene and hexabenzocoronene as a mimic for a graphene surface.

1.2 Chemical reactions in the ISM

In any region of the ISM, chemistry depends on the density of matter, the temperature, pressure, the availability of atoms and molecules, and their physical and chemical state. The physical and chemical processes are driven by energy sources such as cosmic rays, radiation, and magnetic fields. Chemical processes in the gas phase often happen at low temperatures (T<<50 K) whereby it is noted that an extremely low temperature of about 10 K favours the chemistry between gas and dust.³⁷ However, these processes are also influenced by the stellar radiation field, which depends on the type of star involved. Magnetic fields in ISM contribute towards the total pressure of interstellar gas and control the distribution of cosmic rays and the density of gas in the ISM.^{38,39}

More specifically, a detailed consideration of dense clouds is important as this is the main region where stars and planets can form and where most chemistry happens. Different types of reactions occur in cold dense clouds, because of the interaction of gas with dust, including catalytic surface reactions at very low temperatures (approximately 10-15 K). Such temperatures provide a favourable situation for molecule formation as well as freezeout onto the dust surface. Consequently, different molecules such as CH₄, H₂O, NH₄, and CO_2 are reported to form both in the gas phase and on dust grains with some molecular ions, isomers and unsaturated species such as $HC_{11}N$. Ions form because cosmic rays, energetic electrons, and protons are sources of ionization in the ISM. However, the main gas-surface reaction is the formation of H₂. This is not just because it has the highest abundance in the ISM, but also because it is a key molecule for the formation of other molecules and other pathways to formation are limited and relatively low.⁴⁰

Generally, interstellar chemistry can be divided into four different classes of processes. The first process is the interaction of gas, dust, and stars with cosmic rays (MeV to GeV). This induces ionization or photodissociation processes and can produce photons. The second process is the interaction of photons produced in the above process with dust grains in the ISM. The third process is bi-molecular gas-phase reactions. The fourth process is the interaction of gas with dust grains.⁴¹ Our research is focused on the third and fourth classes.

1.2.1 Gas phase reactions

Gas-phase reactions in the ISM occur in the gaseous environment between stars. These reactions form, evolve, and destroy molecules. In the ISM mostly only two-body collisions occur, because of the low densities. However, the formation of a diatomic molecule is less probable through the collision of two atoms, because of the short interaction time and the need to dissipate energy. As a consequence, two hydrogen atoms can not form an H₂ molecule (H + H \rightarrow H₂) in the gas phase. Formation of molecules is possible through a radiative association reaction (Eqn. 1.5) but, its efficiency is low and requires the presence of a dipole moment.

$$X + Y \to XY + h\nu. \tag{1.5}$$

During a collision, atoms use their kinetic energy to cross any barriers toward the formation of products. The rate of reaction depends heavily on both the temperature and the height of any barrier as shown in the Arrhenius equation (Eqn. 1.6),

$$k = A \mathrm{e}^{-\frac{E_a}{k_B T}}.$$
 (1.6)

Here, k is the rate constant, A is the pre-exponential factor, E_a is the activation energy, k_B is the Boltzmann constant, and T is the temperature. From this, it is clear that even with a small activation barrier, the reaction rate will be low at low temperatures. However, some reactions occur without an activation barrier such as ion-molecule reactions, where routes to the formation of ions are available through ionization⁴² or electron attachment. For example, H₂, after it has formed on a dust grain and has been returned to the gas phase can easily be ionized by cosmic rays (Eqn. 1.7),

$$H_2 + \text{cosmic ray} \longrightarrow H_2^+ + e^- + \text{cosmic ray}.$$
 (1.7)

The H_2^+ ion generated by this is reactive and can easily react with H_2 to form H_3^+ , which has been detected⁴³

$$H_2^+ + H_2 \to H_3^+ + H$$
 (1.8)

 H_3^+ is important because it acts as a proton donor. H_3^+ reacts with neutral atoms or molecules present in the ISM.⁴⁴ The product of this reaction can then react further with H_2 . For example

$$\mathrm{H}_{3}^{+} + \mathrm{O} \to \mathrm{OH}^{+} + \mathrm{H}_{2}, \tag{1.9}$$

$$OH^+ + H_2 \to OH_2^+ + H.$$
 (1.10)

The protonated OH⁺ species, formed in Eqn. 1.9, is more reactive than the neutral species and can lead to an ion-neutral chain reaction. This can lead to the formation of OH_3^+ , but also e.g. CH_3^+ . Hence, these chain reactions can lead to polyatomic molecular ions, which eventually recombine with electrons to form small neutral molecules.⁴⁴ The chain reaction to form hydrocarbons like CH_3^+ can also be initiated by C^+ , as the presence of C^+ is also reported in the ISM,⁴⁵ along with neutral carbon. The major products that can be obtained from these reactions are CH₃ and CH₄. These can then transform into more complex molecules via various reactions.⁴⁶ For example, they can react further with $C \text{ or } C^+$ to form larger molecules. Other significant reactions are condensation, in which a hydrocarbon ion reacts with a neutral hydrocarbon to form a larger molecule, ion-molecule reactions in which ionic hydrocarbons react with neutral molecules such as H_2 , or neutralneutral reaction in which two neutral hydrocarbons can react or a neutral atom reacts with a hydrocarbon. It is to be noted that the ISM is far from thermal equilibrium, but for the simple model calculation, the calculations are performed at uniform temperature.⁴⁷ Reactions and rates of these types detected in the ISM are available at https://kida. astrochem-tools.org.

1.2.2 Gas surface reactions

Gas-phase reactions appear to be more important for the ISM. Here, we know much more about these reactions. However, gas phase reactions are unable to explain the formation of many molecules detected in the ISM. Thus, it is important to study gas-surface reactions and gas-surface interactions. It has been widely accepted that H_2 forms through the adsorption of H atoms on dust grains.^{48–50} However, there are still questions about the adsorption of other atomic gases (O, C, and N) on dust surfaces and also the formation of small molecules through the reaction of these adsorbed species.

The first step in a reaction on a surface is the adsorption of gaseous species. Experimental studies⁵¹ show that the majority of adsorbates attain thermal equilibrium after a reasonable time and undergo adsorption. The ratio of the number of adsorbates undergoing adsorption to the total number of adsorbates colliding with the surface is known as the sticking coefficient. The sticking coefficient, also known as the sticking probability is used to determine the probability of a gaseous atom remaining on the dust surface. It changes with the temperature of the gas, the nature of the surface and the interaction of the surface with the gas. Generally, the sticking coefficient decreases with an increase in temperature and the value of the sticking coefficient lies between 0 (no atoms adsorb) and 1 (all atoms adsorb).^{52,53} In astrophysics, the assumption is usually made that this should be of the order of unity. Previous studies reported the sticking coefficient of unity during simulated adsorption of hydrogen atoms on amorphous ice within a temperature range of 10 K-100 K. However, the sticking coefficient reduced with temperature above 100 K. Thus, the conclusion was drawn that, once the hydrogen atom adsorbs on the surface, it diffuses over the surface until it binds to a minimum energy site. As a consequence, H atoms sometimes do not get close enough to each other to form e.g. H₂.
1.3

The sticking coefficient for H_2 adsorption has been well studied on a variety of substrates.⁵⁴ However, there are still questions around the sticking probability for heavier atoms and molecules such as O, N, H₂O, CH₄, NH₃, CH₃OH, CH₃CHO. Moreover, there are questions around the final state *i.e.* whether the product remains on the surface or whether it returned to the gas phase. If it returned to the gas phase it is not clear whether this would be as the saturated hydride such as H₂O, CH₄, or NH₃ or in an unsaturated form such as NH, OH, NH₂, CH₃, CH₂.⁵⁴

1.3 Reaction mechanisms

The previous section gave a general overview of the chemistry of the ISM and the uncertainties surrounding it. However, to understand the chemistry better, it is crucial to understand in particular the chemical reactions that occur on the surface of dust grains. Such reactions could also be classed as heterogeneous catalysis.⁵⁵ So far, it is still unclear which chemical mechanism describes the interstellar surface catalysed—reactions best, but a typical surface—catalyzed reaction should follow the following steps: firstly, adsorption of adsorbate onto the surface, secondly, diffusion of the adsorbate to the active site of the surface where it can be physisorbed or chemisorbed. Thirdly, the reaction of two adsorbate molecules or the reaction of an adsorbed molecule with a colliding atom. Fourthly, desorption of the product from the surface.⁵⁶

The energy budget is not the only criterion for a chemical reaction on a dust grain in the ISM. For example, it is also important whether adsorbed species can get close enough to interact during their residence on the surface. Hereby, the mode of adsorption (chemisorption vs physisorption) is important (see below for a more extensive discussion). The most important reaction where this comes into play is the formation of H₂.⁵⁷ However, the acting mode depends strongly on temperature and temperature change can lead to changes in adsorption. Thus, particularly at high temperatures, species could desorb from the surface before a reaction happens.

1.3.1 Adsorption

For reactions on surfaces, the initial step is the collision of a gas species with a dust grain. The outcome of this collision depends on the interaction potential between the adsorbate and the surface. The resulting adsorption may either be associative, where the adduct is formed without fragmentation, or it may be dissociative, where after adsorption, the molecule dissociates. In an adsorption process, a bond is formed between the potential adsorbate and the surface. Therefore, these adsorption processes can be further divided into two different categories, physisorption or chemisorption, depending on the type of bond formed. These will be discussed below.

When atoms or molecules interact with a dust surface, they first encounter a weak attractive force which results in a weak interaction ($\sim 50 \text{ meV}$) with the surface, *i.e.* physisorption. The physisorption process involves weak, van der Waals-type, interactions between adsorbate and adsorbent. Physisorption interactions tend to be weak, so the process is entirely reversible⁵⁸ and the adsorbate layer is in equilibrium with the gas-phase molecule. Physisorption is fast since it is a non-activated process,⁵⁹ *i.e.* there is no barrier to physisorption.

In contrast to the weak bond formed during physisorption, an actual chemical bond is formed between the adsorbate and surface during chemisorption, Therefore, the bond strength is significantly stronger, because a redistribution of electron charge density takes place upon the formation of the covalent bond. The binding energy depends on the extent of the adsorbent surface covered by the adsorbate and the amount of charge transfer. In addition, high coverage can also lead to adsorbate-adsorbate interactions,⁵⁹ and reduce the binding strength between adsorbate and the surface. The formation of the chemical bond can also lead to a reorganization of the surface. This means that chemisorption can be an activated process, which will be slower than physisorption. However, this also means that the residence time for a chemisorbed moiety is significantly higher than for a physisorbed species.

1.3.2 Reactions on surfaces

The mechanism and mode of adsorption define how chemical reactions happen at the surface. There is a range of potential reaction mechanisms. Of these, the Eley-Rideal mechanism and the Langmuir-Hinshelwood mechanism form the two extremes. Which of these describes the reaction of gases on surfaces in the ISM best is still unclear, so both will be discussed below.

The first mechanism to discuss is the Langmuir–Hinshelwood mechanism (LH). In this mechanism, both reacting elements are initially adsorbed on the surface on different sites and in thermal equilibrium with the surface. Migration of the mobile species across the surface occurs until they meet and react to form the product (see Fig. 1.4).



Figure 1.4: Schematic representation of the Langmuir-Hinshelwood, Eley-Rideal, and Kasemo Haris mechanisms.

This mechanism operates at relatively low coverages with physisorbed mobile species and will depend on the temperature and structure of the surface.^{60,61}

The other extreme mechanism is called the Eley-Rideal mechanism. In this mechanism, one of the reacting elements first chemisorbs on the surface and equilibrates to the surfaces. The other gas molecule interacts directly with this pre-adsorbed molecule to react and form the product (see Fig. 1.4). In this case the coverage will need to be higher to yield a significant amount of product. This is enabled by the longer residence time of such species on the surface. It is noted that this mechanism depends less on the temperature of the surface, but allows efficient energy transfer into the surface.^{60,61}

Generally, the ER and LH mechanisms are considered two extremes of potential mechanisms for surface reactions. The Kasemo Haris mechanism is an intermediate mechanism between the ER and LH mechanisms. In this mechanism, the approaching atom does not directly adsorb on the surface due to inefficient energy transfer between the atom and the surface. However, before complete dissipation of its incident energy and thermal equilibration with the surface, it reacts with an atom that is already adsorbed on the surface and desorbs as a product species.^{59,61}

1.3.3 Desorption from surfaces

Once atomic or molecular species have adsorbed on a surface, they will remain adsorbed, especially in the denser region of ISM and especially if they are chemisorbed. During the lifetime of a cloud ($\sim 10^6$ yr) atoms and molecular species freeze out on a dust surface and evolve to form interstellar ices.⁶² However, the interaction of these grains with cosmic rays, UV radiation or highly energetic photons, may lead to the desorption of these molecules, if the temperature of the surface increases sufficiently. Then, small molecules such as H₂, H₂O, CO₂, CH₃OH^{63,64} *etc*, which were trapped in the interstellar ice on the dust surface, can return to the ISM.

Such desorption processes can happen either thermally or non-thermally. However, in addition, these interactions with radiation, cosmic rays, or photons can increase the internal energy of any absorbed species. This could then be sufficient to overcome a barrier to reaction to give products that either stay on the surface or desorb from the surface.⁶⁵

First of all such desorption can happen thermally. In this case, the adsorbed species gains energy, because of an increase in temperature of the surface leading to a return of the species to the gas phase. The rate of desorption can be expressed by a rate law of nth order⁶⁵

$$R_{\rm des} = -\frac{d\theta}{dt} = k\theta^n. \tag{1.11}$$

Here, n is the order of desorption, k is the rate constant of the desorption process, and θ is the surface covered by the adsorbate on the adsorbent. The rate constant k can be described by the Arrhenius equation⁶⁵ (Eqn. 1.6), where E_a is the activation energy for desorption. The pre-exponential factor is also considered a desorption frequency (ν) which may be equated with the frequency of the adsorbate-substrate bond. Thus, every time a bond stretches during the vibrational cycle, it can be considered as an attempt to break the bond for desorption.⁶⁵ Thus, the rate of desorption can also be written as⁶⁵

$$R_{des} = -\frac{d\theta}{dt} = \nu e^{-\frac{E_a}{K_B T}} \theta^n.$$
(1.12)

The alternative to thermal desorption is non-thermal desorption, which is the process of returning of the adsorbate species into the gas phase when the system is not in thermal equilibrium such as through photodissociation or chemical desorption. In a photodissociation process, the surface absorbs a UV photon which leads to phonon or electronic excitation in the solid. This energy can then be transferred into an adsorbate–surface bond, which can lead to the desorption of a nearby molecule from the surface.⁶⁶

An alternative is chemical desorption. Here, reaction occurs on the surface and transfer of the energy released by the reaction into the surface is slow. Thus, the energy will stay in the molecule and does not dissipate. This can lead to desorption of the molecule.^{67,68}

A lack of detailed information on diffusion and desorption processes in the ISM limits our understanding of astronomical processes.^{63,64} A key piece of information in this area is the binding strength of molecules on the surface, which we will discuss next.

1.3.4 Binding Energies

The adsorption process of gas on a dust grain surface is described by a potential energy curve, which represents the variation in the potential energy value with a change in the distance between the adsorbate and adsorbent. A general potential energy curve is shown in Fig. 1.5. During the process of adsorption of a molecule on a surface, one must consider the changes in the bond length and bond angle of the adsorbent, the orientation of the adsorbate, and surface distortion of the adsorbent, since they all can influence the adsorption process.



Figure 1.5: Potential energy curve between adsorbate and adsorbent as a function of internuclear distance.

Fig. 1.5 shows that adsorption can be described as a combination of physisorption and chemisorption. Physisorption involves van der Waal forces which give a small potential energy gain at a large distance from the surface (see Sec. 1.3.1). As the molecule approaches the surface, repulsive forces arise from overlapping of electron clouds. This creates an energy barrier, E_S .⁶⁹ A chemisorption well will then form because of the formation of a chemical bond between adsorbate and adsorbent. The energy value at the bottom of the chemisorption well represents the adsorption energy corresponding to the equilibrium bond distance of the adsorbate from the surface.⁶⁹ The physisorption energies can be up to 0.5 eV. For chemisorption the binding energy is up to 10 eV.

1.4 Research objectives

As stated above, hydrogen is the most abundant element in the ISM. The reactions of H atoms with other gas and dust species directly affect the thermal balance of ISM. Many previous studies have shown that the mechanism for the formation of H_2 in the interstellar clouds is through surface-catalyzed reaction on dust grains. The key step in this reaction

is the adsorption of the first H atom on dust grains. In addition to hydrogen, other gases such as C, O and N are also present in atomic and ionic forms in the ISM. These elements can further react with each other to form molecules. More than 200 different molecules already have been detected in the ISM. But their formation mechanisms are still not always clear. Therefore, the objective of our research is to study the formation of small molecules such as H₂, H₂O, NH₃, and various isomers of C_2H_4O , C_2H_2O , and C_3H_4O and how their formation is affected by the presence of a dust surface. This will be done using electronic structure theory.

First, we have studied the adsorption of atomic species such as H, C, O, and N (Chapter 4) on the dust surfaces (bi-layer graphite and coronene). These calculations formed the basis for further calculations on the formation of molecules in Chapters 5, 6, 7, and 8. These results are also a key to understanding where these atoms adsorb on a surface and how that is influenced by the presence of other defects. Thus, in Chapter 5, we will consider the adsorption of H in the presence of a defect within the graphite surface. H, O, N, Si, Fe, and Mg were chosen as defects based on their abundance in the ISM. Adsorption and desorption of up to 2 hydrogen atoms on a graphite surface with a defect have been studied to find a favourable path for the recombination of hydrogen atoms and their desorption in the form of H_2 .

Third, the formation of H_2O and NH_3 molecules from the reaction H with O and N atoms was studied on a pristine graphite surface as well as on an oxygenated graphite surface (Chapters 6 and 7, respectively). Finally, the reaction pathways for the reaction of ethylene, acetylene, and propyne with atomic oxygen in the gas phase and on a dust surface (bi-layer graphite and hexabenzocoronene) were studied (Chapter 8).

Chapter 2

Theory

2.1 Introduction

This chapter is a brief introduction to the different theoretical methods used in this study. Theoretical chemistry aims to calculate the total energy, frequencies, potential energy surfaces, dipole moments, and other physical and chemical properties of atoms and molecules using mathematical modelling and computational programs. In this thesis, these will be largely based on quantum mechanics. The methods used in this thesis are particularly useful to study those elements of a chemical reaction that are difficult to study experimentally, such as transition states. Moreover, in the ISM the majority of reactions occur at low temperatures and with low densities. Such experimental conditions are difficult to replicate in laboratories. Therefore, computational methods are crucial to understand the reaction mechanisms for the formation of molecules in the ISM.

In the early 20th century, quantum mechanics was developed to solve problems with the physical description of atomic particles. One noteworthy contribution came from Louis de Broglie⁷⁰ in 1923, who proposed that matter could exhibit both particle-like and wave-like behaviour. This concept, known as particle-wave duality, was later incorporated by Erwin Schrödinger in 1926 in the time-independent Schrödinger equation.⁷¹ This equation, which takes the form of a partial differential equation, is considered a fundamental component of quantum mechanics and can be expressed as⁷¹

$$\hat{H}\Psi = E\Psi. \tag{2.1}$$

Here, \hat{H} is a differential operator representing the total energy, called the Hamiltonian. E corresponds to the total energy of the system and Ψ represents a many-particle wave function that depends on both Cartesian and spin coordinates of all the particles. There is no physical meaning to Ψ per se, but $|\Psi|^2$ represents the probability of finding a particle at a given position. The Hamiltonian operator can be defined as the sum of the kinetic energy operator (\hat{T}) and the potential energy operator \hat{V} for a system⁷²

$$\hat{H} = \hat{T} + \hat{V}. \tag{2.2}$$

Here, \hat{T} represents the kinetic energy operator which can be written for an *n*-particle system as,⁷³

$$\hat{T} = \sum_{i}^{n} -\frac{\hbar^2}{2m_i} \hat{\nabla}_i^2, \qquad (2.3)$$

where $\hbar = h/2\pi$, *h* is Planck's constant, *m* refers to the mass of particle, and $\hat{\nabla}_i^2$ is the Laplacian operator for particle *i*. This means that $\hat{\nabla}_i^2 = -\frac{\hbar^2}{2m} \left(\frac{\partial^2}{\partial x_i^2} + \frac{\partial^2}{\partial y_i^2} + \frac{\partial^2}{\partial z_i^2}\right)$, if Cartesian co-ordinates are to be used. The potential energy operator \hat{V} is a multiplicative operator and represents the interaction between the particles. It will be assumed that this interaction is solely Coulombic in this thesis. Therefore, if *A* and *B* are two arbitrary particles with charge Q_A and Q_B , which are separated by a distance of R_{AB} , then the potential energy within a set of particles can be written as:⁷³

$$\hat{V} = \frac{1}{4\pi\epsilon_0} \sum_{A>B}^{N} \frac{Q_A Q_B}{R_{AB}},$$
(2.4)

 $\mathbf{2.1}$

where ϵ_0 is the electrical permittivity of the vacuum. Thus, the potential energy for two nuclei A and B with electrons i and j as shown by a molecular coordinate system⁷⁴ in Fig. 2.1, can be written in terms of nuclear-electron, nuclear-nuclear, and electron-electron interactions.



Figure 2.1: Molecular coordinate system, here A and B represent the nuclei whereas i and j refer to the electrons. Image is taken from Ref. [74] with permission.

For a given nucleus, its charge will be Ze (Z is the atomic number of that atom) and for an electron, the charge will be -e. Thus, the potential energy can be written as,

$$\hat{V} = \underbrace{-\sum_{Ai} \frac{Z_A e^2}{4\pi\epsilon_0 r_{Ai}}}_{nuclear-electron} + \underbrace{\sum_{A>B} \frac{Z_A Z_B e^2}{4\pi\epsilon_0 R_{AB}}}_{nuclear-nuclear} + \underbrace{\sum_{i>j} \frac{e^2}{4\pi\epsilon_0 r_{ij}}}_{electron-electron},$$
(2.5)

where Z_A and Z_B correspond to the atomic numbers of nuclei A and B, respectively, vector \vec{r}_{Ai} and \vec{R}_{AB} is the distance between position of nucleus A from position of electron i, and nuclei B, respectively, and \vec{r}_{ij} refers to the distance between two electrons i and j. By inserting Eqn. 2.3 and Eqn. 2.5 into Eqn. 2.2 and reverting to atomic units ($m_e=1$ [mass of electron], e=1, $\hbar=1$, $4\pi\epsilon_0=1$) we get^{73,74}

$$\hat{H} = -\underbrace{\frac{1}{2}\sum_{i}\hat{\nabla}_{i}^{2}}_{\hat{T}_{e}} - \underbrace{\frac{1}{2M_{A}}\sum_{A}\hat{\nabla}_{A}^{2}}_{\hat{T}_{N}} - \underbrace{\sum_{Ai}\frac{Z_{A}}{r_{Ai}}}_{\hat{V}_{eN}} + \underbrace{\sum_{A>B}\frac{Z_{A}Z_{B}}{R_{AB}}}_{\hat{V}_{NN}} + \underbrace{\sum_{i>j}\frac{1}{r_{ij}}}_{V_{ee}}.$$
(2.6)

Here, the first and second terms on the right-hand side of Eqn. 2.6 correspond to the kinetic energy of the electrons and nuclei, respectively. The third term corresponds to the attractive interactions between the nuclei and electrons, whereas the fourth and fifth terms represent repulsion between the nuclei and repulsion between the electrons, respectively. Finally, M_A refers to the mass of nucleus A. Equation 2.6 can be written more compactly as⁷⁴

$$\hat{H} = \hat{T}_e(\vec{r}) + \hat{T}_N(\vec{R}) + \hat{V}_{eN}(\vec{r},\vec{R}) + \hat{V}_{NN}(\vec{R}) + \hat{V}_{ee}(\vec{r}).$$

$$(2.7)$$

Here, the positions of electrons and nuclei are represented collectively by vector \vec{r} and \vec{R} , respectively. This Hamiltonian can be used to solve the Schrödinger equation for a general system.

The second element of the Schrödinger equation is the wave function, whose square is a probability density as noted above. The wave function can have many forms. However, not all wave functions are allowed as there are some restrictions. First, the wave function must be normalizable, in other words, the square of the wave function must integrate to 1. The wave function will also need to be single-valued, finite, and continuous.⁷³ In the case of bosons (particles that have integer spin), the wave function must remain unchanged on the interchange of coordinates. Thus, the wave function is said to be symmetric. On the other hand, in case of fermions (particles that have half-integer spin such as electrons), the sign of the wave function must change on an interchange of particles, so the wave function is said to be anti-symmetric. Equation 2.1 can only be solved analytically for "simple" problems, such as the hydrogen atom (*i.e.* a one-electron system). Thus, for molecules, it is impossible to solve the Schrödinger equation exactly. Therefore, we need approximations to simplify the problem. Some of these will be discussed below.

2.2 Born-Oppenheimer approximation

The first approximation used to help solve the Schrödinger equation is called the adiabatic or **Born-Oppenheimer approximation** (BO). Born and Oppenheimer developed the Born-Oppenheimer approximation⁷⁵ using the assumption that the motion of the electrons and nuclei in a molecule are decoupled, because of the difference between the mass of an electron and a nucleus (as $m_p = 1836 m_e$). This means that electrons move faster than the nuclei, even if they have the same kinetic energy. Thus, the electron distribution is assumed to be dependent only on the position of the nuclei rather than also their velocities. Hence, to solve the Schrödinger equation for all particles in a molecule, one assumes the nuclei are fixed in a particular arrangement. The time-independent Schrödinger equation can then be solved for the electrons only. Within this approximation the second term of Eqn. 2.7 can be neglected $(\hat{T}_N(\vec{R}) = 0)$, and the repulsion between the nuclei $V_{NN}(\vec{R})$, can be considered constant.⁷⁵ The remaining terms of Eqn. 2.7 are collectively called the electronic Hamiltonian (\hat{H}_{elec}) . It describes the motion of electrons in a field of fixed nuclei⁷⁴

$$\hat{H}_{elec} = \hat{T}_e(\vec{r}) + \hat{V}_{eN}(\vec{r}, \vec{R}) + \hat{V}_{ee}(\vec{r}).$$
(2.8)

Using this assumption, the solution of the Schrödinger equation in terms of the *electronic* Hamiltonian can be written as⁷⁴

$$\hat{H}_{elec}\Psi_{elec}(\vec{r}; \ \vec{R}) = E_{elec}(\vec{R})\Psi_{elec}(\vec{r}; \ \vec{R}).$$
(2.9)

This form makes it clear that the motion of electrons and their energy E_{elec} depends on both electronic and (fixed) nuclear coordinates. Thus, one will get a different Ψ_{elec} and E_{elec} for different arrangements of the nuclei. The total energy for fixed nuclei is the sum of the electronic energy and the constant nuclear repulsion.

$$E_{tot, \ elec}(\vec{R}) = E_{elec}(\vec{R}) + \hat{V}_{NN}(\vec{R}).$$
(2.10)

From this, one can generate the Hamiltonian operator for the motion of nuclei in the average field of the electrons 74

$$\hat{H}_{nucl} = \hat{T}_N(\vec{R}) + E_{tot, \ elec}(\vec{R}).$$
(2.11)

The total electronic energy $E_{tot, elec}(\vec{R})$ provides a potential for nuclear motion and constitutes a potential energy surface. \hat{H}_{nucl} is now used to solve the *nuclear Schrödinger* equation⁷⁴

$$\hat{H}_{nucl}\Psi_{nucl}(\vec{R}) = E_{tot}\Psi_{nucl}(\vec{R}).$$
(2.12)

Here, E_{tot} is the Born-Oppenheimer approximation to the total energy of Eqn. 2.1. It describes the electronic, rotational, and vibrational energy.⁷⁵ The total wave function within the Born-Oppenheimer approximation is given as

$$\Psi(\vec{r}, \ \vec{R}) = \Psi_{elec}(\vec{r}; \ \vec{R})\Psi_{nucl}(\vec{R}).$$
(2.13)

The Born-Oppenheimer approximation has been found to be a reasonable approximation, that works well for many cases for chemical reactions. However, it breaks down, if electronic and nuclear motion are coupled *i.e.* if the electronic wave function changes rapidly with small changes in the nuclear coordinates.⁷⁶

Even after applying the BO approximation, finding the exact solution of the Schrödinger equation for a one-electron system is still very complicated. Moreover, having more than one electron in the molecule also adds the inter-electron repulsion term to the Hamiltonian, which makes an exact solution impossible. Thus, we need additional approximations to calculate the ground state energy and the wave function for many-body problems which will be discussed below.

2.3 Hartree-Fock self-consistent field method

The first approximation to simplify the electronic Schrödinger equation was suggested by Hartree in 1928.⁷⁷ It is also known as the orbital or independent particle approximation. In this approximation, each electron is assumed to occupy in its own one-electron orbital. Indeed, if we assume that there is no interaction between electrons, *i.e.* $\hat{V}_{ee} = 0$, and consider that each electron is moving under the action of nuclei only, then the electronic wave function for electrons can be written as the product of N one-electron wave functions. This is known as the Hartree Product:⁷⁷

$$\Phi^{HP}(r_1, r_2, r_3, \dots, r_N) = \phi_1(r_1)\phi_2(r_2)\phi_3(r_3), \dots, \phi_N(r_N) = \prod_i^N \phi_i(r_i).$$
(2.14)

Here, ϕ_i are normalized, mutually orthogonal, one-electron wave functions depending on coordinates $r_i = (x_i, y_i, z_i)$, where *i* labels the electron. However, this wave function ignores the spin of the electrons. As electrons are fermions, they have three spatial degrees of freedom and an intrinsic spin coordinate, which can be denoted by $\omega = \alpha$ or $\omega = \beta$ when electron is present in the form of spin up or spin down $(m_s = \pm \frac{1}{2})$, respectively. Thus, the set of space-spin coordinates can be represented by $\tau = (r, \omega)$. Thus, we change notation from $\phi(r)$ to $\chi(\tau)$, which is a spin orbital. Spin orbitals are defined as⁷⁸

$$\chi(\tau) = \begin{cases} \phi(r)\alpha \\ \text{or} \\ \phi(r)\beta \end{cases}$$
(2.15)

Then, Eqn. 2.14 can be written as^{78}

$$\Psi^{HP}(\tau_1, \tau_2, \tau_3, \dots, \tau_N) = \chi_1(\tau_1)\chi_2(\tau_2)\dots,\chi_N(\tau_N).$$
(2.16)

However, the electrons are indistinguishable. Thus, they must follow the Anti-symmetry Principle, which states that the sign of a wave function for fermions must change if coordinates of a pair of electrons are interchanged.⁷⁹ For a two-electron system, the antisymmetry principle can be easily illustrated as follows:

$$\Psi(\tau_1, \tau_2) = -\Psi(\tau_2, \tau_1)$$

$$\chi_1(\tau_1)\chi_2(\tau_2) = -\chi_1(\tau_2)\chi_2(\tau_1)$$
(2.17)

However, the Hartree product obtained in Eqn. 2.16 is an uncorrelated wave function, which implies that electrons are distinguishable. As such, it does not satisfy the Antisymmetry Principle. Thus, for systems with more than one electron the Hartree product cannot form a valid wave function. Therefore, to obtain the correct anti-symmetric wave function, for a two-electron system, the wave function will now be written as:

$$\Psi(\tau_1, \tau_2) = \frac{1}{\sqrt{2!}} [\chi_1(\tau_1)\chi_2(\tau_2) - \chi_1(\tau_2)\chi_2(\tau_1)].$$
(2.18)

This can also be written as in the form of a determinant, known as a Slater determinant,⁸⁰

$$\Psi(\tau_1, \tau_2) = \frac{1}{\sqrt{2!}} \begin{vmatrix} \chi_1(\tau_1) & \chi_2(\tau_1) \\ \chi_1(\tau_2) & \chi_2(\tau_2) \end{vmatrix}.$$
 (2.19)

Here $\frac{1}{\sqrt{2!}}$ is the normalization constant to ensure the square of the wave function integrates to unity. A Slater determinant satisfies the condition of anti-symmetry as $\Psi(\tau_1, \tau_2) = -\Psi(\tau_2, \tau_1)$. The wave function obtained from a Slater determinant also satisfies the Pauli exclusion principle, which states that, if two electrons occupy the same spatial orbital, they must have opposite spins. In particular, if two electrons occupy the same spin-orbital then two columns in the determinant become equal and the determinant becomes zero. For an N-electron system, the Slater determinant can be written as

$$\Psi(\tau_1, \tau_2, ..., \tau_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \chi_1(\tau_1) & \chi_2(\tau_1) & ... & \chi_N(\tau_1) \\ \chi_1(\tau_2) & \chi_2(\tau_2) & ... & \chi_N(\tau_N) \\ \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot \\ \chi_1(\tau_N) & \chi_2(\tau_N) & ... & \chi_N(\tau_N) \end{vmatrix}$$
(2.20)

Alternatively, an anti-symmetrizing operator⁸¹ (\hat{A}) can be used to obtain the same result and to enforce anti-symmetry on the Hartree Product,

$$\hat{A} = \frac{1}{N!} \sum_{\hat{\pi} \in S_n} \epsilon_{\pi} \hat{\pi}.$$
(2.21)

Here, $\hat{\pi}$ is the permutation operator that exchanges the coordinates of a pair of identical particles and ϵ_{π} refers to the sign associated with the permutation. The wave function obtained by using the anti-symmetrizer (\hat{A}) is equivalent to the Slater determinant and can be written as:

$$\Psi(\tau_1, \tau_2, ..., \tau_N) = \sqrt{N!} \hat{A} \chi_1(\tau_1) \chi_2(\tau_2) \chi_N(\tau_N).$$
(2.22)

To solve the Schrödinger equation for the many-body problem, we need to collect the terms of the Hamiltonian operator (Eqn. 2.7). It will be advantageous to write the Hamiltonian in the form of 1-electron terms and 2-electron terms as⁷⁸

$$\hat{H}_{elec} = \overbrace{-\frac{1}{2}\hat{\nabla}_{i}^{2} - \sum_{A} \frac{Z_{A}}{r_{iA}}}^{1-electron} + \overbrace{j>i}^{2-electron} \overbrace{ij}^{1-ij} = \sum_{i} \hat{h}_{i} + \sum_{j>i} \hat{v}_{i,j}.$$

$$(2.23)$$

Here, \hat{h}_i refers to the one-electron operators acting on electron i and \hat{v}_{ij} refer to the twoelectron operator acting on electrons i and j ($i \neq j$). It represents the electron-electron repulsion term. To simplify the discussion below, Dirac notation⁸² which is also known as 'bra-ket' notation $(\langle bra | ket \rangle)$ is introduced here. If n and m are a row and a column vector, respectively then these can be written as $\langle n |$ and $|m \rangle$. Their scalar product can be written as:

$$< n ||m> \equiv < n|m> = n^{\dagger}m = \begin{bmatrix} n_1^{\dagger}n_2^{\dagger}...n_N^{\dagger} \end{bmatrix} \begin{bmatrix} m_1\\m_2\\\vdots\\\vdots\\m_N \end{bmatrix} = \sum_{i=1}^N n_i^*m_i \tag{2.24}$$

In quantum mechanics, if n and m represent vectors then changing a bra into a ket or *vice versa* is doing a conjugate transpose. Using bra-ket notation, the electronic energy for Hamiltonian (\hat{H}) can now be written as:

$$E_{elec} = \int \Psi^* \hat{H}_{elec} \Psi d\tau = <\Psi |\sum_i \hat{h}_i + \sum_{j>i} \hat{v}_{i,j} |\Psi> = <\Psi |\hat{H}_{elec} |\Psi>.$$
(2.25)

By applying the anti-symmetrizing and permutation operator the above 1-electron terms can be simplified to:

$$<\Psi|\sum_{i}\hat{h}_{i}|\Psi>=\sum_{i}<\chi_{i}|\hat{h}|\chi_{i}>, \qquad (2.26)$$

and the 2-electron term to:

$$<\Psi|\sum_{j>i}\hat{v}_{ij}|\Psi> = \frac{1}{2}\sum_{ij} <\chi_i\chi_j|\hat{v}_{ij}|\chi_i\chi_j> - <\chi_i\chi_j|\hat{v}_{ij}|\chi_j\chi_i>,$$
(2.27)

Combining the 1-electron and 2-electron terms gives the following expression for the electronic energy

$$E = \sum_{i} \underbrace{<\chi_i | \hat{h} | \chi_i >}_{h_i} + \frac{1}{2} \sum_{ij} (\underbrace{<\chi_i \chi_j | \hat{v}_{ij} | \chi_i \chi_j >}_{J_{ij}} - \underbrace{<\chi_i \chi_j | \hat{v}_{ij} | \chi_j \chi_i >}_{K_{ij}}).$$
(2.28)

Here, the second term J_{ij} is called the Coulomb integral and the third term K_{ij} is called the exchange integral. K_{ij} arises, because electrons of the same spin will try to avoid each other. The method to split these 1-electron and 2-electron terms in this way is referred to as the Slater-Condon rules,^{83,84} which are exact within the Born-Oppenheimer and independent particle approximations.

At this point, a further approximation can be made to the Coulomb and exchange integrals by defining Coulomb and exchange operators as,

$$\hat{J}_j(1)\chi_i(1) = \left[\int d\tau_2 \chi_j^*(2) \frac{1}{r_{12}} \chi_j(2)\right] \chi_i(1), \qquad (2.29)$$

and

$$\hat{K}_{j}(1)\chi_{i}(1) = \left[\int d\tau_{2}\chi_{j}^{*}(2)\frac{1}{r_{12}}\chi_{i}(2)\right]\chi_{j}(1).$$
(2.30)

Here, the Coulomb operator \hat{J}_j and exchange operator \hat{K}_j are pseudo 1-electron operators. Approximation of the 2-electron integrals through pseudo 1-electron integrals J_{ij} and K_{ij} is the basis of the Hartree-Fock method. Thus, we re-write Eqn. 2.28 as,

$$E_{HF} = \sum_{i} h_{i} + \frac{1}{2} \sum_{ij} \langle \chi_{i} | \hat{J} | \chi_{j} \rangle - \langle \chi_{j} | \hat{K} | \chi_{i} \rangle .$$
(2.31)

Here, E_{HF} is the Hartree-Fock energy.

So far we have an expression for the HF energy (E_{HF}) . However, this clearly depends on the wave function and the quality of E_{HF} will depend on the quality of Ψ . Thus, to get a better approximate wave function and to obtain the best approximation to the electronic energy, the Variational theorem is used. To explain this, first, consider the approximate ground state wave function Θ . The energy value associated with this can be calculated as

$$E_{\Theta} = \frac{\langle \Theta | \hat{H}_{el} | \Theta \rangle}{\langle \Theta | \Theta \rangle}.$$
(2.32)

The Variational theorem now states that, for all values of Θ

$$E_{\Theta} \ge E_0, \tag{2.33}$$

where, E_0 corresponds to the exact ground state energy, *i.e.* it is a lower bound energy to the energy calculated. Thus, we need a set of orbitals that minimizes the energy in a variational manner whilst keeping the orbitals orthonormal. This can be done by the method of Lagrangian multipliers,⁸⁵ see Ref. 85 for more details. Ultimately, this leads to a set of equations to solve, which are given as

$$\hat{f}(\tau_i)\chi_i(\tau_i) = \epsilon_i\chi_i(\tau_i), \qquad (2.34)$$

$$\hat{f} = \hat{h}_i + \sum_i (\hat{J}_i - \hat{K}_i).$$
 (2.35)

Here, \hat{f} is the Fock-operator which is obtained from pseudo 1-electron operator, \hat{h} , \hat{J} , and \hat{K} . ϵ_i refers to the orbital energy and χ_i is a spin orbital.

The common approach to solve the HF equations is by introducing a basis set. This transforms the HF equations into the HF-Roothaan equations.⁸⁶ In this form the spin orbitals χ_i are expanded in basis functions ξ_{μ} through coefficients C_{μ} .

$$\chi_i = \sum_{\mu} C_{\mu i} \xi_{\mu} , \qquad (2.36)$$

where $C_{\mu i}$ represents the coefficient ("contribution") of basis function ξ_{μ} in spin orbital *i*. Introducing this expansion into Eqn. 2.34 we obtain the expression,

$$\hat{f}(\tau_i) \sum_{\nu} C_{\nu i} \xi_{\nu}(\tau_1) = \epsilon_i \sum_{\nu} C_{\nu i} \xi_{\nu}(\tau_1).$$
(2.37)

If we multiply both sides from the left with $\xi^*_{\mu}(\tau_1)$ and integrate we get⁷⁸

$$\sum_{\nu} C_{\nu i} \int dx_1 \xi^*_{\mu}(\tau_1) \hat{f}(\tau_1) \xi_{\nu}(\tau_1) = \epsilon_i \sum_{\nu} C_{\nu i} \int dx_1 \xi^*_{\mu}(\tau_1) \xi_{\nu}(\tau_1).$$
(2.38)

This can be simplified using matrix notation

$$\sum_{\nu} F_{\mu\nu} C_{\nu i} = \epsilon_i \sum_{\nu} C_{\nu i} S_{\mu\nu}$$

$$\mathbf{FC} = \epsilon \mathbf{SC} .$$
(2.39)

Here, ϵ is a diagonal matrix containing the orbital energies ϵ_i . **F** is the Fock matrix, **S** is the overlap matrix, and C is the matrix of coefficients. Eqn. 2.39 is known as the HF-Roothaan equation.

The HF-Roothaan equation solves for a set of coefficients \mathbf{C} . However, the Fock matrix itself also depends on them. Therefore, the HF-Roothaan equations need to be solved iteratively. We need to select basis functions and trial coefficients to generate the Fock matrix, which is then diagonalized. This will give a new set of coefficients, which is used to build a new Fock matrix. These steps are followed until the coefficients do not change anymore. This is why this theory is also referred to as self-consistent field theory (SCF).

In summary, HF theory gives the exact solution for a 1-electron system only. For manybody problems it uses pseudo one-electron Coulomb and exchange operators \hat{J} and \hat{K} , and neglects the electron correlation to give an approximate electronic energy. To include electron correlation, post-HF methods are introduced for multi-electron wave functions, which will be discussed in Section 2.6.

2.4 Density functional theory

Before moving on to post-Hartree Fock methods we will discuss the most popular method of solving the electronic Shrödinger equation for multi-electron systems, **Density Func***tional Theory* (DFT). DFT is based on calculating the electron density $\rho(r)$ rather than the molecular wave function $\Psi(r)$.

In DFT, the key component is the electron density which is a function of space and time. If a given system is composed of N electrons, then at a point r in space the electron density can be written as $\rho(r)$. DFT is based on the **Hohenberg-Kohn theorems**,⁸⁷ which were introduced in 1964. The first Hohenberg-Kohn (HK) theorem states that the ground state electronic energy of a molecule is determined by the ground state electron density. Thus, if E is the ground state electronic energy, it can be written as $E[\rho]$ to indicate that it is a functional *i.e.*, a function of a function of the electron density. It should be noted that the HK theorem is just an existence theorem and does not define a procedure for calculating the energy or obtaining a functional.

2.4.1 Kohn-Sham equation

In 1965, Kohn and Sham⁸⁸ developed a method to calculate E from ρ . In this approach they tried to avoid the multi-dimensional wave function and only considered the threedimensional electron density. They used a reference system of non-interacting electrons which contained the same number of electrons N as the real system. Therefore, the Hamiltonian could be expressed as a sum of one-electron operators. Moreover, the energy in terms of the density could be written $as^{89,90}$

$$E[\rho(r)] = T_{ni}[\rho(r)] + V_{ne}[\rho(r)] + V_{ee}[\rho(r)] + \Delta T[\rho(r)] + \Delta V_{ee}[\rho(r)].$$
(2.40)

Here, the r.h.s. terms represent the kinetic energy of non-interacting electrons, the potential energy due to nucleus-electron interactions and electron-electron repulsion, a correction to the kinetic energy due to the interacting nature of electrons and the non-classical correction to the electron-electron repulsion energy.

For a system of non-interacting electrons, the total kinetic energy is the sum of individual electronic kinetic energies. Thus, for an N-electron system the energy in terms of the density can be written as⁸⁹

$$E[\rho(r)] = \sum_{i}^{N} (\langle \chi_{i} | -\frac{1}{2} \hat{\nabla}_{i}^{2} | \chi_{i} \rangle - \langle \chi_{i} | \sum_{A}^{nuclei} \frac{Z_{A}}{|r_{i} - R_{A}|} | \chi_{i} \rangle) + \sum_{i}^{N} \langle \chi_{i} | \frac{1}{2} \int \frac{\rho(r')}{|r_{i} - r'|} dr' | \chi_{i} \rangle + E_{xc}[\rho(r)]. \quad (2.41)$$

The density used is $simply^{89}$

$$\rho = \sum_{i=1}^{N} \langle \chi_i | \chi_i \rangle,$$
 (2.42)

Here, $|\chi_i\rangle$ are spin orbitals.

The terms $\Delta T[\rho(r)]$ and $\Delta V_{ee}[\rho(r)]$ in Eqn. 2.40 can be written together in the form of E_{xc} . This is referred to as the exchange-correlation energy. This term includes the effects of quantum mechanical exchange and correlation. It also includes the difference in kinetic energy between the reference system and the real one.

$$E_{xc}[\rho] = \underbrace{\left(T[\rho] - T_{ni}[\rho]\right)}_{kinetic-energy} + \underbrace{\left(V_{ee}[\rho] - V_{ni}[\rho]\right)}_{electron-interaction}.$$
(2.43)

Here, the first term on r.h.s. refer to the difference in the kinetic energy of the interacting and non-interaction electrons and the second term corresponds to the difference in electronelectron repulsion in the real system and in the reference system. The orbitals, χ , that minimize E in Eqn. 2.41, satisfy the Kohn-Sham eigenvalue value equation⁸⁹

$$\hat{h}_i^{KS} \chi_i = \varepsilon_i \chi_i, \qquad (2.44)$$

where ε_i represents the Kohn-Sham (KS) orbital energies. The KS one-electron Hamiltonian operator is now defined as⁸⁹

$$\hat{h}_{i}^{KS} = -\frac{1}{2}\hat{\nabla}_{i}^{2} - \sum_{A}^{nuclei} \frac{Z_{A}}{|r_{i} - R_{A}|} + \int \frac{\rho(r')}{|r_{i} - r'|} dr' + V_{xc}, \qquad (2.45)$$

where

$$\mathbf{2.4}$$

$$V_{xc} = \frac{\delta E_{xc}}{\delta \rho}.$$
(2.46)

In Eqn. 2.46, V_{xc} is a functional derivative of the exchange energy and called the exchangecorrelation potential.⁸⁹ Similar to the HF equations, the KS equations can be solved using the self-consistency approach. Thus, a guess electron density is used as an input to solve the KS equations and to get an initial set of KS orbitals. These orbitals are then used to compute an improved density. This procedure is repeated until the convergence of the density and E_{xc} .⁸⁹ Finally, the electronic energy can be calculated using Eqn. 2.41.

2.4.2 Exchange correlational functionals

The exchange correlational energy functional (E_{xc}) is described as the differences in kinetic energy and the electron-electron repulsion potential between the reference system and the real system. Therefore, a good approximation to E_{xc} will determine the accuracy of the KS method.⁹¹ However, the exact expression for E_{xc} is still unknown. There are some different approximations, which can give desirable results for a wide range of systems. These are discussed below.

The first approximation for E_{xc} was proposed by Kohn and Sham.⁸⁸ It is called the *local density approximation* (LDA). It assumes that the density locally can be treated as a homogeneous electron gas as it varies slowly. Thus, for a spin-unpolarised system the exchange-correlation functional can be expressed as,

$$E_{xc}^{LDA}[\rho] = \int \rho(r)\epsilon_{xc}[\rho(r)]dr. \qquad (2.47)$$

Here, ρ is the electron density and $\epsilon_{xc}[\rho(r)]$ is the exchange-correlation energy density, which depends only on the electronic density at each point in space. This approximation gives good results for many atomic systems. The limitation of LDA is that it is valid only in the case of a uniform electron density or a system in which the variation in density is very slow, such as solid-state materials.⁹²

For spin-polarized systems, the local spin density approximation is used. This is particularly useful for open-shell systems or radicals where the spin densities are different for spin-up and spin-down electrons. In these systems the exchange-correlation energy will depend upon both the spin density and the total electron density.⁹³ Now, the exchange-correlation functional can be defined as,⁹²

$$E_{xc}^{LSDA}[\rho(r), n(r)] = \int \rho(r) \epsilon_{xc}[\rho(r), n(r)] dr \qquad (2.48)$$

Here, n(r) is the spin density, which describes the distribution of the spin-up and spindown electrons in the system. $\epsilon_{xc}[\rho(r), n(r)]$ is the exchange-correlation energy density, which depends on both the electronic density and the spin density at each point in space.

LDA works less well for molecules because the density can vary considerably across a molecule. Thus, more advanced approximations were developed, so-called generalized gradient approximations (GGA) for a non-uniform electron gas. In these approximations E_{xc} not only depends on the electron density ρ , but also depends upon the gradient of the density $\nabla \rho$. Thus,

$$E_{xc}^{GGA}[\rho] = \int \rho(r) \epsilon_{xc}(\rho(r), |\nabla \rho(r)|) dr.$$
(2.49)

There are many GGA functionals. The majority of GGA functionals are obtained by adding a correction term to the LDA functional. For our work, we used the GGA functional PBE by Perdew, Burke, and Ernzerhof.^{91,94}

Another set of functionals is the hybrid functionals. These are known to improve DFT results as these mix HF-like exchange terms with exchange-correlation functionals. A well-known example of a hybrid functional is B3LYP.^{93,95,96} In this hybrid functional, the exchange functional B88 is combined with the correlation functional LYP. For the exchange functional B88, some exchange energy is replaced by the exact HF exchange energy⁹⁷ (about 20-25 %).

2.4.3 Van der Waals interactions

Density functional theory is used to study various chemical properties with a reasonable computational cost and accuracy. However, DFT also has some drawbacks. In particular, it does not treat van der Waals (vdW) interactions, also known as dispersion interactions, well.^{98,99} These are attractive interactions caused by fluctuations in the electron cloud of one molecule near another molecule. They are crucial for adsorption processes as well as in surface reactions.^{100,101} The dispersion energy (E_{dis}) between two atoms or molecules at a long distance can be written as¹⁰²

$$E_{dis} = -\frac{C_6}{R^6},$$
 (2.50)

where R is the distance between the two systems and C_6 is the dispersion coefficient. In DFT dispersion interactions were first included in 2004.¹⁰³ For our calculations, we included vdW interactions through Grimme's dispersion correction scheme with Becke Johnson damping 'D3BJ'¹⁰⁴ to ensure that the correction term behaves correctly at small values of R.

2.5 Post Hartree-Fock theory

So far we discussed DFT and Hartree-Fock methods. As discussed above, the HF method uses an average electron-electron interaction instead of the real electron interaction for the calculation of the total energy. Moreover, it is based on the use of a single Slater Determinant. This results in a difference between the HF energy E_{HF} and the lowest possible energy E_{exact} . This difference in energies is due to the lack of electron correlation (EC) and can be expressed as, ($E_{EC} = E_{exact} - E_{HF}$). As the Hartree-Fock energy is always higher than the exact energy, E_{EC} will always be negative. Physically, EC corresponds to the correlated motion of the electrons. The correlation energy consists of two parts, static correlation and dynamic correlation.⁹² Dynamic correlation comes from the interaction of electrons in the same spatial orbital. The static part is more complicated as it is a contribution from the electrons avoiding each other when they are in different spatial orbitals.

To include the effect of electron correlation various methods have been developed which are known as post-Hartree-Fock methods. For these, the HF wave function is used as a starting point. The HF method uses a single determinant wave function and can therefore calculate occupied orbitals accurately, but not unoccupied orbitals. As a consequence, excited state properties and excitation energies are not determined well. Hence, to improve on the HF energy, the wave function must contain more than one Slater determinant Φ , which is generated by promoting electrons from occupied to unoccupied orbitals. A number of methods have been developed to study electron correlation such as Configuration Interaction (CI), Many-Body Perturbation theory (MBPT), and Coupled Cluster (CC). In the present study, we have used the complete active space second order perturbation method (CASPT2) and the coupled cluster single double with perturbative triples (CCSD(T)) method.

2.5.1 Multi configurational self-consistent field (MCSCF)

Promotion of electrons from an occupied molecular orbital of the HF determinant to an unoccupied molecular orbital generates a series of excited state determinants. Promotion of a single electron is known as a single excitation and promotion of two electrons is known as a double excitation and so on. A so-called full CI expansion can be obtained by promoting all the electrons from ground-state occupied orbitals to all excited orbitals. In general, a multi-determinant wave function is written as,

$$|\Psi\rangle = c_0|\Phi_0\rangle + \sum_{ai} c_i^a |\Phi_i^a\rangle + \sum_{a < b, i < j} c_{ij}^{ab} |\Phi_{ij}^{ab}\rangle + \sum_{a < b < c, i < j < k} c_{ijk}^{abc} |\Phi_{ijk}^{abc}\rangle \dots, \quad (2.51)$$

where, c is a variational coefficient. In the first term of the r.h.s. of Eqn. 2.51, c_0 , the contribution of the ground state determinant, is usually close to one. Φ_0 represents the HF reference determinant. Φ_i^a in the second term represents the Slater determinants formed by replacing spin-orbital *i* from the reference determinant Φ_0 with virtual spin-orbital *a*. Similarly, the third and fourth terms represent double and triple excitations. These sets of orbital occupancies are known as configuration state functions (CSFs) and one can construct a total wave function by a linear combination of these CSFs. If one only varies the coefficients, c, then this is generally referred to as configuration interaction (CI).

Multi-configurational self-consistent field (MCSCF) calculations are in their setup similar to CI calculations.¹⁰⁵ Thus, the MCSCF wave function Ψ is constructed from a linear combination of Slater determinants as in Eqn. 2.51. However, unlike in CI, in MCSCF the orbitals and the expansion coefficients are *both* optimized variationally. Thus, for a set of CI expansion coefficients one solves for the molecular orbitals and then from a set of molecular orbitals, one solves for a new set of expansion coefficients until self-consistency is obtained. It should be noted here that MCSCF still uses the HF approximation for Coulomb and exchange operators. Thus, within the MCSCF framework correlation energy is added by adding flexibility to the wave function to lower the total energy. The simplest way of doing this is through the complete active space self-consistent field (CASSCF) method, which includes all possible CSFs within a given "active" space of orbitals. Thus, the molecular orbitals are divided into subsets to build the wave function. These subsets are called - inactive, active, and virtual. A schematic representation of these orbitals is shown in Fig. 2.2. In this, the inactive MOs are those that are completely filled (*i.e.*, (i)) containing 2 electrons). At all times the highest occupied and lowest unoccupied MOs are called the active MOs or active space, whereas the rest of the orbitals are in virtual orbitals which will remain unoccupied throughout the calculation.¹⁰⁶ Excitations are only allowed between orbitals in the active space.



Figure 2.2: Schematic representation of inactive, active, and virtual orbitals for CASSCF. This Figure was adapted from Ref. [109].

If all possible CSFs within a given active space are used within a calculation, then these are referred to as complete active space self-consistent field (CASSCF) calculations. On the other hand, if only selected CSFs are used, then these are called restricted active space self-consistent field (RASSCF) calculations. A full valence CASSCF calculation is difficult to manage and a selection of active space molecular orbitals must be done manually. Moreover, for the accuracy of the calculations it is important to choose which orbitals will be included in the calculation. Poor selection of orbitals leads to inaccurate results.

Perturbation theory

Additional electron correlation can be included in MCSCF by performing a perturbation theory calculation on top of an MCSCF calculation. This is referred to as CASPTn, where *n* refers to the order of perturbation theory. Perturbation method is a size-extensive and non-variational method, which is based on the idea that one can calculate the overall Hamiltonian (\hat{H}) of the system by adding a small perturbation $(\Delta \hat{H})$ to a reference Hamiltonian (\hat{H}_0) as:¹⁰⁷

$$\hat{H} = \hat{H}_0 + \lambda \Delta \hat{H}. \tag{2.52}$$

Here, λ is a variable that determines the strength of the perturbation ($0 < \lambda < 1$). For an unperturbed Hamiltonian $\lambda=0$, for the full perturbed Hamiltonian $\lambda=1$. It is assumed that we know the exact solution for the reference system for which the Schrödinger equation is written as:

$$\hat{H}_0 \Psi_i^{(0)} = E_i^{(0)} \Psi_i^{(0)}, \qquad (2.53)$$

Thus, when $\lambda = 0$, then $\hat{H} = \hat{H}_0$, $\Psi_i = \psi_i^0$, and $E_i = E_i^0$. Here, $\psi^{(0)}$ and $E_i^{(0)}$ refer to the unperturbed eigenstate and corresponding energy.¹⁰⁷ Moreover, a small perturbation value means that the wave function and energy can be written in the form of a Taylor expansion:

$$\Psi = \lambda^{(0)}\psi_i^{(0)} + \lambda^{(1)}\psi_i^{(1)} + \lambda^{(2)}\psi_i^{(2)} + \lambda^{(3)}\psi_i^{(3)}\dots$$
(2.54)

$$E = \lambda^{(0)} E_i^{(0)} + \lambda^{(1)} E_i^{(1)} + \lambda^{(2)} E_i^{(2)} + \lambda^{(3)} E_i^{(3)} \dots$$
(2.55)

Here, $\psi^{(1)}$, $\psi^{(2)}$, $\psi^{(3)}$... and $E^{(1)}$, $E^{(2)}$, $E^{(3)}$... are the 1st-order, 2nd-order, and 3rd-order corrections to the wave function and energy, respectively. Moreover, the total energy up to the first-order correction, E^{1st} can be written as¹⁰⁷

$$E_i^{1st} = E_i^{(0)} + \lambda^{(1)} E_i^{(1)}, \qquad (2.56)$$

This 1st-order energy correction depends on the perturbation Hamiltonian and the ground state wave function and can be written as in the form of an expectation value as,

$$E_i^{(1)} = \langle \psi_i^{(0)} | \Delta \hat{H} | \psi_i^{(0)} \rangle .$$
(2.57)

If it is assumed that the perturbed wave functions are orthogonal to the unperturbed wave functions, then the first-order correction to the wave function can be written as,

$$\psi_i^{(1)} = \sum_{j \neq i} \frac{\langle \psi_j^{(0)} | \Delta \hat{H} | \psi_i^{(0)} \rangle}{E_i^{(0)} - E_j^{(0)}}.$$
(2.58)

In the same way, the total energy for the second-order correction E^{2nd} can be expressed as,

$$E_i^{2nd} = E_i^{(0)} + \lambda^{(1)} E_i^{(1)} + \lambda^{(2)} E_i^{(2)}, \qquad (2.59)$$

Here, the second-order energy correction involves a 1st-order correction to the wave function and can be re-written as,

$$E_i^{(2)} = \langle \psi_i^{(0)} | \Delta \hat{H} | \psi_i^{(1)} \rangle = \sum_{j \neq i} \frac{|\langle \psi_j^{(0)} | \Delta \hat{H} | \psi_i^{(0)} \rangle|^2}{E_i^{(0)} - E_j^{(0)}}$$
(2.60)

For our work we used CASPT2 to calculate the correlation energy up to 2nd order.

2.5.2 Coupled cluster method

Another method to calculate electronic correlation is the Coupled cluster (CC) method. This method is similar to the CI method as the wave function is a linear combination of many determinants. However, the selection of determinants is more involved. There are various orders of CC expansions such as CCSD (couple cluster single and double excitation), CCSDT (couple cluster single, double and triple excitation), and so on. Coupled cluster is a size-extensive method and provides more accurate results than other similar methods.¹⁰⁷ In coupled cluster theory, the wave function is written as,

$$\Psi = e^T \Phi_0. \tag{2.61}$$

Here, Φ_0 represents the reference wave function and \hat{T} represents the cluster operator. For n electrons it is written as¹⁰⁷

$$\hat{T} = \hat{T}_1 + \hat{T}_2 + \dots + \hat{T}_n, \tag{2.62}$$

where \hat{T}_i generates all possible determinants with *i* excitations. The exponential part in Eqn. 2.61 can be written in terms of a Taylor expansion,

$$e^{T} = (1 + \hat{T}_{1} + \frac{\hat{T}_{2}^{2}}{2!} + \frac{\hat{T}_{2}^{3}}{3!} + ...)\Phi_{0}.$$
 (2.63)

For double excitations,

$$\hat{T}_2 = \sum_{i < j}^{occ} \sum_{a < b}^{virt} t_{ij}^{ab} \Phi_{ij}^{ab},$$
(2.64)

where t_{ij}^{ab} are known as amplitudes.

The truncated CC method uses a reduced number of \hat{T} operators. For example, if $\hat{T} = \hat{T}_2$ then only double excitation are included (CCD), and if $\hat{T} = (\hat{T}_1 + \hat{T}_2)$ then both single and double excitations are included (CCSD), and so on.

For this work, we used the CCSD(T) method. In CCSD(T), triple excitations are included perturbatively rather than exactly. The accuracy of CCSD(T) is close to full CI with a difference in the energy of a few kJ mol⁻¹. However, a strong dependence on the basis and a slow convergence of energy for electron correlation with bigger basis sets limits the use of CCSD(T). This behaviour can be improved by using the CCSD(T)-F12 method. In this method some explicitly correlated terms are added to the wave function. Previous studies have reported that the correlation energy obtained using CCSD(T)-F12 method with an augmented triple-zeta basis set is equal to the correlation energy obtained with an augmented quintuple-zeta basis set using the CCSD(T) method.^{108,109} For the CCSD(T)-F12 method, for example, the double excitation operator is written as

$$\hat{T}_{2} = T_{ab}^{ij} \hat{E}_{i}^{a} \hat{E}_{j}^{b} + \tau_{\alpha\beta}^{ij} \hat{E}_{i}^{\alpha} \hat{E}_{j}^{\beta}.$$
(2.65)

Here, i, j and a, b refer to the occupied and virtual orbitals respectively. \hat{E}_i^{α} represents electron excitation operator from orbital i to α . For the F12 method the additional term $\tau_{\alpha\beta}^{ij}$ is included which is written as,

$$\tau_{\alpha\beta}^{ij} = T_{mn}^{ij} F_{\alpha\beta}^{mn}, \qquad (2.66)$$

where,

$$F_{\alpha\beta}^{mn} = \langle mn | \hat{F}_{12} \hat{Q}_{12} | \alpha\beta \rangle.$$
 (2.67)

Here, F_{12} is a short-range correlation factor, for example, a Slater function. T_{mn}^{ij} refers to the actual amplitude used in the F12 treatment, and \hat{Q}_{12} ensure the orthogonality of the

 F_{12} configuration to the HF reference function. This explicitly correlated term improves the wave function description of electrons. A more detailed explanation can be found in Refs. [108, 109].

2.6 Density functional theory for the solid state

In the above sections, we discussed different methods which can be used for molecular systems or small clusters. However, these are not generally useful for the study of crystalline solids. A crystalline solid can be described as the periodic arrangement of fundamental units, unit cells, and by a lattice of points invariant under translation. A vector used to join these lattice points is known as the lattice vector and can be represented by $\overline{a_1}$, $\overline{a_2}$, $\overline{a_3}$ in case of a 3-dimensional unit cell. Then each lattice point can be written as:

$$R = n_1 \overline{a_1} + n_2 \overline{a_2} + n_3 \overline{a_3}, \qquad (2.68)$$

where n_1, n_2, n_3 are integers. The combination of these lattice vectors leads to the formation of a Bravais lattice. On the basis of the Bravais lattice and the symmetry point group crystalline solids can be classified into 230 space groups. As crystalline solids can have an infinite number of electrons within an infinitely repeating unit cell, calculation of these systems is computationally expensive. However, this problem can be overcome if we use **Bloch's theorem**.¹¹⁰ This theorem connects the properties of electrons in the infinite periodic system with the properties of the electrons in the unit cell.

According to Bloch's theorem, the wave function of an electron in an external periodic potential can be expressed as the product of a plane wave and function $u_k(\vec{r})$ which has the same periodicity as the crystal:

$$\psi_k(\vec{r}) = e^{i\vec{k}\vec{r}} u_k(\vec{r}), \qquad (2.69)$$

where

$$u_k(\vec{r}) = u_k(\vec{r} + \vec{a}_i). \tag{2.70}$$

This means that if the position r of the electron is shifted by a unit vector $\vec{a_i}$ then the wave function takes the form of:

$$\psi_k(\vec{r} + \vec{a}_i) = e^{i\vec{k}\cdot\vec{a}_i}\psi_k(\vec{r}).$$
(2.71)

This means that the probability density $|\psi_k(\vec{r})|^2$ is the same at both points due to cancellation of the complex phase vector. For a more detailed description, the reader is referred to Ref. 113.

For every given set of lattice points we can construct a reciprocal lattice with lattice vectors b_1, b_2, b_3 . These are defined as, $\vec{a}_i \vec{b}_j = 2\pi \delta_{ij}$. Thus, these reciprocal lattice vectors take the form of:

$$\vec{b}_1 = 2\pi \frac{\vec{a}_2 \times \vec{a}_3}{\Omega}; \vec{b}_2 = 2\pi \frac{\vec{a}_3 \times \vec{a}_1}{\Omega}; \vec{b}_3 = 2\pi \frac{\vec{a}_1 \times \vec{a}_2}{\Omega},$$
(2.72)

where Ω represents the volume of the unit cell and \times refer to the outer product. A unit cell formed by the reciprocal lattice is known as the Brillouin zone. The wave function ψ_k , can now be calculated using Bloch's theorem for an infinite periodic system based on the wave function for the electrons within the unit cell of the reciprocal lattice or \vec{k} vector. As nearby \vec{k} vectors contain nearly identical information, it is possible to construct a suitable wave function using only a finite number of \vec{k} vectors.

A further simplification happens through the use of *periodic boundary conditions* (PBCs). They allow for the calculation of *macroscopic* properties from a simulation with a reduced size system. This reduces the cost of the simulation, since by using periodic boundary conditions one can perform simulations using a small number of atoms, molecules, or particles. With PBCs the modelled system is assumed to be an infinite collection of 2D tiles or 3D boxes. For the 2D tile approach, each tile will be surrounded by eight identical neighbours; for a 3D box approach, each box will be surrounded by adding or subtracting integral multiples of the box sides.¹¹¹ During the simulation the total number of particles and the mass within each image will remain constant.⁹² This means that if a particle leaves from a box or tile. Hereby, it is noted that the size of the box/tile should be large enough to avoid the interaction of a particle with its own image in a neighbouring box/tile.

According to Bloch's theorem, each electronic wave function for a periodic solid can be written as the product of a cell-periodic and a wave part as noted above. The cell-periodic part can be expanded using a basis set of plane waves, whose wave vectors are the reciprocal lattice vectors of the crystal. Thus, the electronic wave function can be written as a sum of plane waves¹¹²

$$\Psi_{i}^{k}(\vec{r}) = \sum_{G} c_{i,k+G} \exp(i(\vec{k} + \vec{G}).\vec{r}), \qquad (2.73)$$

where \vec{k} is the wave vector that characterizes the wave function, \vec{G} is the reciprocal lattice vector, and \vec{r} is a general position vector. At each \vec{k} point the electronic wave function can be expanded in terms of a discrete plane wave basis set in the same way. However, the coefficients $c_{i,k+G}$ in Eqn. 2.73 associated with a small kinetic energy are more important than others with a higher kinetic energy.¹¹² Thus, the plane wave basis set includes only those plane waves which have a kinetic energy less than the energy cutoff. This will lead to an error in the value of the total energy, which can be reduced by increasing the cutoff energy.

However, to perform an all-electron calculation a large number of plane waves and a long computational time would be required. Instead, we use the so-called pseudopotential approximation^{113–115} together with a small number of plane waves. This is a valid approximation as the physical properties of solids depend more strongly on the valence electrons, and less strongly on the core electrons. In the pseudo-potential approximation one replaces the strong ionic potential of the nucleus and the core electron by a pseudo-potential, which will give a wave function which is identical to the valence electron wave function outside the core region. This reduces the number of terms required for the plane wave expansion of the wave function and the computational demand.¹¹² These pseudo-potentials are available in various forms. *Soft* pseudo-potentials are computationally more attractive due to the requirement of fewer plane waves. *Ultrasoft* and *supersoft* pseudo-potentials require even fewer plane waves. However, the selection of suitable potentials is crucial for the accuracy of calculations, as the softer potentials are less transferable between atomic environments.

An alternative approach is the projector augmented wave (PAW) method.¹¹⁶ The PAW method assumes that core electrons and the valence electrons can be treated differently.

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For the bonding region a smooth wave function is obtained, but rapid oscillations are observed in the wave function closer to the nucleus. This is due to the fact that atomic orbitals closer to the nucleus electrons have high kinetic energy. Therefore, this method divides the wave function into two parts, a partial-wave expansion within an atom centred sphere and an envelope function outside the sphere. In general, PAW potentials are more accurate than their ultrasoft pseudo-potential (USPP) counterparts.¹¹⁷

2.7 Localised Basis sets

Above we discussed various methods to find the electronic wave function to solve the Schrödinger equation for any atoms or molecules. However, we have not really discussed the functional form this wave function takes. To discuss this, the reader is reminded that the solutions of the atomic Schrödinger Equation are the atomic orbitals. It stands to reason that these atomic orbitals can be used as a starting point for a calculation of molecules. This is the idea behind the linear combination of atomic orbitals (LCAO) approach. Here, atomic orbitals, as described by atom-centred functions, are used as basis functions in a molecular calculation. In particular, the molecular orbitals are calculated using linear combinations of the atomic orbitals (or plane waves in solid state calculations). The accuracy and performance of a simulation depend on choice of basis function.¹¹⁸

There are various possible basis functions. These can be e.g. hydrogenic functions (Slater type orbitals), Gaussian functions (Gaussian Type Orbitals), plane wave functions or delta functions. Slater type orbitals (STO) are of the form $e^{-\alpha r}$, similar to the solution of the hydrogenic Schrödinger (Eqn. 2.1). On the other hand, Gaussian Type Orbitals (GTOs) are of the form $e^{-\alpha r^2}$. STOs will give a more accurate result than GTOs. However, the calculations will take longer because the integrals are more complicated. Hence, GTOs are generally preferred over STOs in calculations on molecules. However, GTOs have the wrong dependence on distance from the nucleus and will therefore not give physically correct answers. Thus, a linear combination of GTOs is required to attain a similar level of accuracy compared to STOs. These are known as Contracted Gaussian Type Orbitals (CGTOs). If the number of STOs or CGTOs are equal to the core and valence atomic orbitals of the atom then these are known as a minimal basis. If the number of STOs or CGTOs orbitals are twice the core and valence atomic orbitals of the atom, then those are known as a double-zeta (DZ) basis, etc.

These basis sets can be further improved by polarization or diffuse functions. When two atoms approach each other, then the orbitals of an atom change. This is known as polarization. Thus, an s-orbital polarizes in one direction *i.e.*, becomes p-like and a porbital polarizes in two directions. To account for this, polarization functions are added to the basis set. These have a higher angular momentum quantum number than one would normally use, *e.g.*, d-functions for a carbon basis set or f-functions for an iron one or even d and f functions for oxygen, *etc.* Diffuse functions are necessary for anionic systems to get accurate binding energies and consist of GTOs with very small exponents.

There are many different families of basis sets that have evolved over the years, obtained in a variety of ways. For this research project we have used 6-311 G(d,p), a split-valence triple zeta basis set due to Pople,^{119,120} cc-pVDZ (correlation consistent polarized and valence double zeta), cc-pVTZ¹²¹ (correlation consistent polarised valence triple zeta) both of which are due to Dunning, and def2-TZVP^{122,123} (valence triple-zeta polarisation) due to Ahlrichs. For periodic systems plane waves were used.

2.8 Semi-classical transition state theory

So far, we have concentrated our discussion on solving the electronic Schrödinger equation, in which the nuclei are clamped within the B.O. approximation. However, we are also interested in obtaining rates from our calculations. We could obtain these through the use of the Arrhenius equation, Eqn. 1.6, but that would exclude the potential quantum effects. So, instead we have studied the rate constants for polyatomic chemical reactions using Semiclassical Transition State Theory.

In 1935, to get a better understanding of reaction processes Eyring proposed Transition State Theory (TST), which is also known as Activated Complex Theory¹²⁴ (ACT). The rate in this theory is given as,

$$k_{TST} = \frac{kTQ^{\ddagger}}{hQ^R} \exp(-\frac{\Delta V_f^0}{kT}).$$
(2.74)

Here, kT/h refers to the collision frequency, Q^{\ddagger} and Q^{R} refers to the partition functions of transition state and reactant, respectively. ΔV_{f}^{0} represents the adiabatic barrier height in the forward direction. The partition functions include vibrational motion which is normally included using a harmonic oscillator model. Thus, to calculate the rate constant we need the barrier height and the vibrational frequencies both at the transition state and for the reactant from calculations.

Transition state theory is inherently a classical theory, similar to the theory proposed by Arrhenius¹²⁵ in 1888. However, in particular at low temperatures, quantum tunnelling could play an important role, particularly for reactions with relatively small barriers, especially in case of hydrogen transfer reactions. Such tunnelling pathways can be included in the calculation of the rate constant through semiclassical rate theories.

Semiclassical Transition State Theory (SCTST) was developed by Miller *et al.*.^{126–128} It is an effective way to study the rate constant of chemical reactions including nuclear quantum effects, such as tunnelling, through a combination of classical and quantum mechanics. In this theory the motion of atoms within a molecule is treated using classical mechanics and the motion of the electrons is described using quantum mechanics. SCTST calculations require (2+2F) Hessian calculations and expansion of a force field around the transition state, where, F represents the number of degrees of freedom for a given system. Since the initial development of this method, various improvements have been suggested by different groups. Wang and co-workers, Wagner, Santon, and Greene *et al.*^{129–131} introduced various improvements for the calculation of the anharmonic density, tunnelling at low energy, and a one-dimensional form. This 1-dimensional form (by treating the reaction coordinate separately) reduces the computational cost significantly compared with a full-dimensional calculation. However, the literature shows that the results obtained by this approach still give a good agreement with experimental results.^{129,132–134}

Chapter 3

Computational details

3.1 Gaussian09

Molecular calculations were performed using the SMP version of the Gaussian09 software package¹³⁵ revision E.01. Gaussian was compiled using Gaussian-supplied versions of BLAS and ATLAS on the EMT64 architecture.^{136,137} The optimization and scan calculations in Chapter 1 used Kohn-Sham density functional theory (DFT) using density functionals BLYP,^{96,138} B3LYP,^{93,95,96} B3PW91,^{95,139} CAM-B3LYP,¹⁴⁰ and PBE⁹⁴ with the 6-311G(d, p)^{119,120} basis set. To generate a reasonable input geometry we used GaussView 5.0.¹⁴¹ We performed spin unrestricted calculations to allow for spin polarization and to allow α and β spin densities to be different. All ground-state optimizations were carried out for a neutral species. The scan calculations were performed with a complete relaxation of geometry.

For the optimization, transition state, and intrinsic reaction coordinate^{142,143} (IRC) calculations in Chapter 8, we used the density functional B3LYP with basis sets - 6-311 G(d,p), cc-pVDZ, cc-pVTZ,^{144,145} def2-TZVP.^{122,123} We also performed all these calculations using the density functional PBE⁹⁴ with def2-TZVP. Van der Waals interactions were introduced via the method developed by Grimme with Becke Johnson damping (D3BJ)^{104,146} with a unit value of S6 coefficient. All the optimization calculations were performed without any restrictions. The transition state calculations were done using the QST3 and QST2¹⁴⁷ approaches. Presence of one imaginary frequency confirmed the existence of a transition state. To connect the obtained transition state structure with two minimum energy structures IRC calculations were performed.

3.1.1 VASP

The calculations on extended systems were performed using the Vienna *Ab initio* Simulation Package¹⁴⁸ (VASP), version 5.4.4. This software package is capable of performing *ab initio* quantum-mechanical molecular dynamics (MD) simulation and electronic structure calculations using various pseudopotentials or using the projector-augmented wave (PAW)¹⁴⁹ method with a plane wave basis set^{150–152} within the DFT framework. For the benchmarking calculation, we used the functionals: PW91,^{94,153} PBE,¹⁵⁴ RPBE,^{154,155} revPBE,^{154,156} PBEsol,¹⁵⁷ B3LYP.^{95,96} Van der Waals interactions were introduced *via* the method developed by Grimme with Becke Johnson damping (D3)^{104,146} with a unit value of S6 coefficient for PBE, PBEsol, RPBE, revPBE, PW91, and B3LYP. For the optimization calculations, all atoms were allowed to move freely. Adsorption of atoms and

molecules on the surface was studied with some restrictions. All restriction schemes are explained in each chapter, separately. In Chapter 8, we performed Nudged Elastic Band calculations¹⁵⁸ to find the minimum energy path between the initial and final state of a reaction. To analyze the electronic charge density we have performed the Bader charge analysis code developed by the Henkelman group^{159–162}

3.2 Molpro

Multiconfigurational self-consistent field (MCSCF) calculations were performed using Molpro¹⁶³ version 2012. We performed single point energy calculations using the CASPT2,¹⁶⁴ CCSD(T),¹⁶⁵ and CCSD(T)-F12¹⁰⁹ methods with cc-pVDZ and cc-pVTZ basis sets. For these calculations, we used the optimized geometry generated with Gaussian09.

3.3 PySCTST software

To perform semiclassical transition state theory (SCTST) we used the Python package $pySCTST^{166}$ which was modified to take account of local variation in Python libraries. To perform the SCTST calculations we used the output files generated with the Gaussian09 program.

3.4 Visualization and plotting

In Chapters 6, 7, and 8 the initial geometries for VASP calculations were created using Atomic Simulation Environment¹⁶⁷ (ASE). For the VASP result visualization, VMD^{168–171} was used and for all Gaussian result visualization, JMOL¹⁷² was used. For plotting the energy profiles Gnuplot and Python 3.4,¹⁷³ Numpy,¹⁷⁴ and Matplotlib¹⁷⁵ were used.

Chapter 4

Adsorption of atoms on dust analogues

4.1 Introduction

Hydrogen is the most abundant element in the ISM. Many previous studies have therefore focused on the adsorption of hydrogen atoms on dust analogues.^{27,100,176,177} These studies have reported that the adsorption of hydrogen on the graphite and graphite-like systems is an activated process that requires overcoming an energy barrier of ~0.2 eV. Our study focuses, in contrast, on the adsorption of other atomic species, such as C, O, and N on dust analogues, as well as the reaction mechanism for the formation of molecules by the reaction of adsorbed species. To model the dust grains, we have chosen an 18-C atom graphene supercell as a model, since it is reported in the literature,^{12,19,24} dust grains in the ISM are partly carbonaceous.



Figure 4.1: Potential energy curves for adsorption of gas phase atomic species (X_{GP}) on grain surface as a function of internuclear distance.

In this Chapter, the second and third sections present a benchmarking study to decide the influence of the density functionals used for the adsorption of atomic gases on coronene and graphene, respectively. The adsorption of atomic gases on graphite is discussed in the fourth section.

The adsorption of atomic gases on the dust surface is either an activated chemisorption process *via* an activation energy barrier or a non-activated adsorption process. These are discussed in more detail in Chapter 1, Section 1.3. A general example of

both these scenarios is shown in Fig. 4.1. Here, the change in potential energy is described as a function of the internuclear distance between the adsorbate and the grain surface. This shows that the adsorption of the adsorbate can result in barrierless chemisorption (shown by the green curve). Alternatively, it can show a van der Waals interaction at a long distance (physisorption). However, as the molecule gets closer to the surface, repulsive forces arise from the overlapping of electron clouds, creating an energy barrier. A chemisorption well can subsequently form because of the formation of a chemical bond between adsorbate and substrate. The energy value at the bottom of the chemisorption well represents the adsorption energy, E_a corresponding to the equilibrium bond distance of the adsorbate from the surface¹⁷⁶ (shown by the purple curve).

The energy at each point in the potential energy curve has been calculated as the difference between the total energy of the bound system minus the sum of the total energies of individual non-bound species. Thus, for the interaction between coronene and an atom A, the binding energy is calculated as¹⁷⁶ shown in Eqn. 4.1.

$$E_{\text{Binding}} = E_{\text{coronene+A}} - [E_{\text{coronene}} + E_{\text{A}}] \tag{4.1}$$

The potential energy curves obtained by these calculations can include the motion of atoms on the surface, which will be done adiabatically.

4.2 Adsorption of atomic gases on coronene

Understanding adsorption on dust grains requires a model for a grain surface, whose actual structure is unknown. In many previous studies^{176–178} for the adsorption of hydrogen atoms, coronene has been considered as a model for graphene. Therefore, neutral coronene was chosen as a mimic for carbonaceous dust gains. The Gaussian09 software package¹³⁵ was used for these calculations. For additional computational details see Chapter 3. Within the coronene ring the C-C bond length was initially 1.421 Å, and the bond length of peripheral C-H bonds was 1.1 Å. For these calculations, the surface was fully relaxed, and the adsorption calculations were performed along a vector perpendicular to the surface plane. To ensure this perpendicular approach appropriate dihedral angles of the incoming atom with the surface were frozen *e.g.*, for the adsorption of the gas phase atomic species (X_{GP}) at the top site (A) three dihedral angles were frozen. For each dihedral includes the A-X bond and further two neighbouring bonds of A.

4.2.1 Method benchmarking

The adsorption behaviour of **hydrogen** atoms on coronene (and graphene) has been studied previously. Thus, we performed benchmarking calculations to find an accurate density functional for adsorption of any atom. Thus, we tested BLYP,^{96,138} B3LYP,^{93,95,96} B3PW91,^{95,139} CAM-B3LYP,¹⁴⁰ and PBE⁹⁴ with the 6-311G(d, p)^{119,120} basis set. Surface adsorptions are also affected by weak long-range interactions.¹⁷⁹ Thus, we performed another set of calculations including Grimme's long-range correction with Becke-Johnson damping (D3BJ)¹⁰⁴ to study the long-range interactions of these atoms with the surface. For our benchmarking calculations, we investigated the adsorption of hydrogen and carbon atoms on a coronene surface.

The potential energy curves (PECs) for the adsorption of a hydrogen atom with and without empirical dispersion are shown in Fig. 4.2 panels A and B, respectively. Comparing panel A with panel B shows that the inclusion of dispersion has a small effect on the energy barrier and the chemisorption well, but that the physisorption well becomes more pronounced. In contrast, the difference between the different DFT functionals is relatively minor. The exact energy values for the stationary points are summarized in Table 4.1. Previous studies have reported that chemisorption occurs only if the target carbon atom is allowed to pucker out of the surface. Thus, the height of the puckering will vary with the site of adsorption and the incoming atom.¹⁸⁰ Puckering causes a change in the hybridization of the target carbon atom from sp^2 to sp^3 , i.e. from a trigonal planar to a tetrahedral geometry, breaking the π conjugation. Consequently, the C-C bond associated with the adsorbate carbon atom in the substrate will show an increase in bond length and smaller bond angle, reflecting a move to a tetrahedral carbon environment³⁵ and indicating a loss of aromaticity with distortion of the ring. Puckering happens in our calculations as well as is evident from the inset in Fig. 4.2.



Figure 4.2: Potential energy curves for adsorption of H_{GP} on top position of coronene. Panel (A): With different DFT functionals and panel (B): with the effect of empirical dispersion. The insets show the side and top view of the minimum energy geometry. The atoms are color-coded in hydrogen (white), carbon (gray).

Table 4.1: Physisorption energies (E_{ph}) , adsorption energies (E_a) , and energy barriers (E^{\sharp}) all are in eV for the adsorption of hydrogen on coronene with different density functional, without and with empirical dispersion

DFT-F	-			D3BJ		
	E_{ph}	E_a	E^{\sharp}	E_{ph}	E_a	E^{\sharp}
B3LYP	-	-0.63	0.29	-0.03	-0.65	0.19
CAM-B3LYP	-0.005	-0.68	0.30	-0.02	-0.68	0.26
B3PW91	-	-0.65	0.30	-0.03	-0.67	0.20
BLYP	-	-0.62	0.24	-0.03	-0.64	0.13
PBE	-	-0.64	0.25	-0.01	-0.66	0.19

The results obtained from these calculations are in good agreement with previous studies.^{27,100,176,177} However, the results are insensitive to the choice of functional and to the inclusion of dispersion interactions, although it is noted that B3LYP gives consistently the lowest chemisorption energy. To investigate this further we have chosen to study the effect of carbon adsorption on coronene with the previously selected DFT functionals, without and with the inclusion of D3BJ empirical dispersion correction.

Atomic carbon can exist in the ground state triplet and excited singlet state.¹² Initially, we chose to keep carbon in its triplet spin state. DFT results in the form of PECs are shown in Fig. 4.3. We found barrierless adsorption of a triplet carbon atom at the top site of coronene. Moreover, with B3LYP and CAM-B3LYP, C_{GP} shows strong long-range interactions with coronene rather than pure chemisorption. The energies are summarized in Table 4.2. We found that in comparison to the hybrid exchange-correlation functional B3LYP and CAM-B3LYP, the GGA functional PBE and BLYP lead to an

increased adsorption energy with B3PW91 close to the BLYP curve. The effect of empirical dispersion is more pronounced for the hybrid functionals than for the GGA functionals for the adsorption of $H_{\rm GP}$ and $C_{\rm GP}$. B3LYP appears to be taking a middle ground here and due to the unavailability of previous theoretical and experimental data for the adsorption of carbon atom on coronene surface so, we have chosen B3LYP for all calculations.



Figure 4.3: Potential energy curves for adsorption of triplet C_{GP} at the top position of coronene with different density functionals, without and with empirical dispersion. The inset shows the minimum energy geometry.

Table 4.2: Physisorption energies (E_{ph}) and adsorption energies (E_a) are all in eV for the adsorption of triplet carbon at coronene with different density functional, without and with empirical dispersion.

DFT-F	-	-	D3BJ		
	E_{ph}	E_a	E_{ph}	E_a	
B3LYP	-0.14	-0.10	-0.34	-0.26	
CAM-B3LYP	-0.13	-0.03	-0.24	-0.10	
B3PW91	-	-0.31	-0.42	-0.45	
BLYP	-	-0.34	-0.48	-0.53	
PBE	-	-0.79	-	-0.87	

4.2.2 Site-dependence of adsorption of atomic gases on coronene



Figure 4.4: Geometrical structure of coronene with top, centre, and midbond sites of adsorption.

So far we have shown the results for a single adsorption site for the adsorption of hydrogen or carbon atoms. However, there are multiple sites on coronene where an atom (X_{GP}) can adsorb. Thus, naturally, our next step was to investigate these other adsorption sites. To study the adsorption of atomic gases, we considered three symmetric sites of coronene: top, midbond, and centre as shown in Fig. 4.4. Throughout the discussion of the results we will refer to the incoming gas atoms as X_{GP} , where X corresponds to H, C, O, and N.

Adsorption of atomic hydrogen

We first investigated the adsorption of H_{GP} on the top, centre, and midbond sites of the coronene surface. The results for the adsorption of H_{GP} at these sites in the form of PECs are shown in Fig. 4.5. Here, panels A and B represent the calculation with B3LYP and B3LYP-D3BJ, respectively. All stationary points are summarized in Table 4.3.



Figure 4.5: Potential energy curves for adsorption of H_{GP} at the top, centre, and midbond site of coronene surface, panel (A): with B3LYP/6-311G(d,p), panel (B): with B3LYP-D3BJ/6-311G(d,p), panel (C and D): minimum energy structure for the adsorption of H_{GP} at the top and centre site, respectively panels (E): intermediate structure obtained for adsorption at the midbond site at point Q. All structures are calculated with the B3LYP/6-311G(d,p).

It is noted that hydrogen is in a doublet state, so the entire calculation was performed as a doublet.³⁵ Until a distance of 3 Å the hydrogen atom does not show any interaction with the coronene surface in either calculation. Moving to the top site at 2.6 Å, we find a physisorption well of -0.03 eV. At shorter distances, the surface carbon atom (shown by X in Fig. 4.5 panel C) puckers out from the surface. This creates an energy barrier of ~ 0.29 eV at a distance of 1.74 Å, the inclusion of dispersion interaction lowers this to 0.2 eV and shortens it to 1.7 Å. At this point, the target carbon atom is completely puckered which favours the formation of a σ bond between C and H. This leads to a decrease in

Table 4.3: Physisorption energies (E_{ph}) , adsorption energies (E_a) , and energy barriers (E^{\sharp}) are all in eV for the adsorption of H_{GP} at coronene with density functional B3LYP/6-311G(d,p) and B3LYP-D3BJ/6-311G(d,p).

Ads-site	B3LYP		B3I	LYP-D3BJ		
	E_a	E^{\sharp}	E_{ph}	E_a	E^{\sharp}	
Top	-0.63	0.29	-0.03	-0.65	0.2	
Centre	-	-	-	-	-	
Midbond	-0.02	0.6	-0.03	-0.03	0.53	

energy with a further approach. Thus, a chemical bond is formed at the top site with an equilibrium distance of 1.1 Å with an adsorption energy of -0.63 eV, the inclusion of dispersion changes that to -0.65 eV. Simultaneously, the bond length with neighbouring carbon atoms XY and XZ (Fig. 4.5 panel C) changes from 1.421 Å to 1.53 Å with a change in bond angle \angle ZXY from 120° to 113°, which is in agreement with a previous study.³⁵ Upon shortening the distance further, because of the repulsion of electron clouds, the curve then rises steeply (Fig. 4.5 panel A). These results show a good agreement with a previous study¹⁷⁷ for the top site adsorption. In the ISM environment within diffuse clouds, the temperature varies from 10 K–100 K. This is not high enough to overcome the chemisorption energy barrier of 0.2 eV. However, H atom chemisorption may still occur in photon-dominated and shock wave regions, which have a temperature range of 500 K–5000 K.¹⁸¹ It should be noted that, of course, other factors such as surface relaxation and defects will play an important role in adsorption as well, and we will cover some of these below.

Our calculations of adsorption at the centre site show that the adsorption of a hydrogen atom is not favourable at the centre of the ring in both cases with and without dispersion corrections. This can be expected due to the monovalent nature of hydrogen atom.³⁵

On the other hand, absorption of H_{GP} at the midbond site shows a completely different energy profile from the other two absorption sites. Here, we also find a physisorption well of 0.04 eV at a distance of 2.6 Å. In particular, a steady increase in energy upon the approach of the surface is found initially. However, at an internuclear distance of 1.51 Å, a sharp and abrupt drop in energy is obtained, followed by another steady increase in energy. Inspection of the geometry around 1.51 Å shows a sudden restructuring of the surface at this point from a transition state at point P (see panel D of Fig 4.5) to a minima at point Q (see panel E of Fig. 4.5). The consequence of this is that one of the bridging carbon atoms (C1) is pushed towards the incoming H atom, allowing the H atom to chemisorb at the top site with puckered down of the other midbond carbon atom (C2) simultaneously. At this point the $\angle YXZ$ was found as 117.8°, showing the stress induced in the coronene molecule by the adsorption of H_{GP} .¹⁸² A similar energy profile is obtained by adding the effect of empirical dispersion and the obtained results are shown in Fig. 4.5-B.

Adsorption of atomic carbon

Hydrogen is a monovalent element. As a consequence its bonding modes are limited. In contrast, other elements can bind in more than one way. These can form a single bond at the top site or two single bonds with two carbon atoms at the midbond site. The first such element investigated was carbon. After H, He, and O, carbon is the fourth most abundant element in the ISM. Previous studies have shown that it is present in both singlet and triplet spin states in the ISM.^{183,184} Based on these findings we have performed

adsorption simulations with both spin states for carbon on coronene. It is noted that the ground state of the carbon is a triplet. The energy difference in the triplet and 1^{st} singlet excited state is 0.41 eV. However, C_{GP} migrates during adsorption and prefers to form a stable cyclopropane-like configuration for which a singlet configuration is expected to have the lowest energy. As a consequence, it is important to study both spin states. It is noted that there is no electronegativity difference between the surface and the adsorbate. Therefore, there should not be any charge transfer. Previous study¹⁸⁵ reported that the adsorbed carbon atom transfers only 0.04 e charge to the surface carbon atom it binds to. This small value indicates a covalent bonding between adsorbate and adsorbent.

Results for the adsorption of **singlet** atomic carbon at three different sites of the coronene ring are shown in Fig. 4.6 with B3LYP and B3LYP-D3BJ in panels A and B, respectively. All energies are summarized in Table 4.4. A barrierless chemisorption of C_{GP} is obtained at the top site with a binding energy of -1.79 eV at an internuclear distance of 1.46 Å. Hereby, the target surface carbon atom ends up significantly puckered as could be expected (see in the inset of Fig. 4.6-A). This leads to a change in the bond length of the target carbon atom with neighbour carbon atoms within the surface from 1.42 Å to 1.47 Å with a change of bond angle from 120° to 116°.



Figure 4.6: Potential energy curves for adsorption of a singlet carbon atom at top, centre and midbond of coronene. Panel (A): With B3LYP/6-311G(d,p) and the inset shows minimum energy geometry for adsorption of a carbon atom at the top site. Panel (B): With B3LYP-D3BJ/6-311G(d,p) and the inset shows the geometry for the adsorption of a carbon atom at centre position at point P (top view). Panel (C): Geometry for adsorption of a carbon atom at centre position at point P (side view). Panel (D): Minimum energy geometry for adsorption of a carbon atom at the centre site at point Q, and panel (E): Minimum energy structure for adsorption of C_{GP} at the midbond site. All structures are calculated with the B3LYP/6-311G(d,p).

Adsorption at the centre site shows a long-range attractive interaction from an internuclear distance of 3.4 Å to 2.3 Å with a physisorption well of -0.038 eV without dispersion correction and -0.21 eV with dispersion correction. However, a decrease in the internuclear distance leads to an energy barrier of ≈ 0.25 eV at a distance of 2.09 Å from the surface coupled with puckering of the surface. Dispersion lowers this to 0.073 eV. From that point (shown by point P), the surface restructures leading to a sharp decrease in energy (shown

Table 4.4: Physisorption energies E_{ph} , adsorption energies E_a , and energy barriers (E^{\sharp}) are all in eV for the adsorption of singlet C_{GP} at coronene with density functional B3LYP/6-311G(d,p) and B3LYP-D3BJ/6-311G(d,p).

Ads-site	B3LYP			B3I	LYP-D3BJ		
	E_{ph}	E_a	E^{\sharp}	E_{ph}	E_a	E^{\sharp}	
Top	-	-1.79	-	-	-1.89	-	
Centre	-0.04	-0.55	0.25	-0.21	-0.63	0.08	
Midbond	-	-2.29	-	-	-2.30	-	

by point Q). Thus, a further approach leads to the formation of a cyclopropane-like structure as a transition state with bridging carbon atoms (1 and 6) as shown in the inset of panel B (top view) and in panel C (side view) of Fig. 4.6 with a binding energy of -0.55eV and -0.63 eV with dispersion inclusion. This eventually leads to the incorporation of the incoming carbon atom within the ring and forms a cyclopropane unit with two carbon atoms (2 and 5, Fig. 4.6-D) at *para* position at each other within the same six-membered ring. This causes strain within the surface. As a consequence, the full coronene ring is no longer flat but becomes concave instead.

Similar to the top adsorption site, barrierless adsorption of C_{GP} is obtained at the midbond site with chemisorption in the form of a cyclopropane configuration at a distance of 1.88 Å as shown in Fig. 4.6 panel E. This configuration has a binding energy of -2.29 eV with a change in bond length of a carbon atom number 3 and 4 to 1.5 Å with a change in $\angle C_3C_{GP}C_4$ to 64.6°. The inclusion of dispersion lowers this to -2.30 eV with similar changes in distances and angles. The resulting bond length and angle are similar to a stable cyclopropane ring.¹⁸⁶ When C_{GP} comes in closer, it leads to an increase of the bridging bond angle and a decrease of bond length of C_3-C_{GP} and C_4-C_{GP} , which causes deformation of the surface and repulsion between the atoms. As a result, the energy increases as shown in Fig. 4.6 panel A. A comparison of the adsorption of atomic carbon between the top site and the midbond site shows that adsorption at the midbond site is 0.5 eV more favourable. This suggests that midbond site is the favourable site for the adsorption of the singlet carbon atom. As noted above and shown in Fig. 4.6 panel B, the inclusion of empirical dispersion has only a qualitative effect on the characteristics of the PECs.

Adsorption of carbon in its lowest electronic **triplet** state, ³P was investigated next. DFT results for the adsorption of triplet carbon on the selected sites of a coronene ring are shown in Fig. 4.7 and the energy values are summarized in Table 4.5. It is worth noting that at a long internuclear distance, singlet C_{GP} shows a site-independent barrierless physisorption with a similar energy value.

A long-range interaction is observed for the adsorption of triplet carbon for the top and midbond sites as shown in Fig 4.7 panels A and B. At the top site a physisorption well, of -0.14 eV is obtained at an internuclear distance of 2.3 Å. Inclusion of dispersion deepens the physisorption well to -0.34 eV at 2.3 Å. Upon further approach, the target carbon atom starts to pucker out due to the re-hybridization of its valence orbital. As a consequence, the energy value increases to form plateau X and Y in panels A and B, respectively. Thus, an adsorption energy of -0.105 eV is obtained at a distance of 1.67 Å (Fig. 4.7 panel C). We want to point out here that the inclusion of dispersion actually means that chemisorption does not lead to a stable minimum for the top site.

For the adsorption of triplet carbon at the centre site of the coronene ring with a physisorp-

4.2

tion well of -0.005 eV is found. The potential energy increases with further moving in of C_{GP}, because of the repulsion of the electron cloud in the ring (Fig. 4.7 panel D). Dispersion significantly increases the physisorption well to -0.13 eV, in line with expectations. This suggests that there will be possibilities for physisorption across the surface and increases the residence time.



Figure 4.7: Potential energy curves for adsorption of triplet C_{GP} on top, centre and midbond sites of coronene ring. Panel (A): With B3LYP/6-311G(d,p), panel (B): with B3LYP-D3BJ/6-311G(d,p). Panel (C, D, and E): Minimum energy structures for the adsorption of C_{GP} at top, centre, and midbond site, respectively. All structures are calculated with the B3LYP/6-311G(d,p).

Table 4.5: Physisorption energies (E_{ph}) and adsorption energies (E_a) are all in eV for the adsorption of triplet C_{GP} at coronene with density functional B3LYP/6-311G(d,p) and B3LYP-D3BJ/6-311G(d,p).

Ads-site	B3L	YP	B3LYF	P-D3BJ
	E_{ph}	E_a	E_{ph}	E_a
Top	-0.14	-0.10	-0.34	-
Centre	-0.005	-	-0.13	-
Midbond	-0.10	-0.15	-0.29	-0.33

The midbond site, similar to the top site has a physisorption well of -0.1 eV at an internuclear distance of 2.4 Å. This well depth increases to -0.29 eV if dispersion corrections are included. The further approach of C_{GP} leads to a stable cyclopropane form with a binding energy of -0.15 eV at 1.88 Å combined with significant puckering of the surface (Fig. 4.7 panel E). Inclusion of dispersion interactions lowers this to -0.33 eV. This well depth is not much larger than the physisorption well depth reflecting the energetic penalty of distorting the surface upon chemisorption. Thus, the binding energy for the adsorption of a carbon atom at the midbond site is only 0.045 eV stronger than the binding energy at the top site because of the higher stability of the cyclopropane ring at the bridging site.
Adsorption of atomic oxygen

Similar to atomic carbon, atomic oxygen has been detected $^{185,187-189}$ in its singlet excited state O (¹D), along with a majority of triplet ground state oxygen O (³P). Therefore, we have considered both spin states of oxygen atoms for our calculations. We found that both electronic states of the oxygen atom show site-independent physisorption. Moreover, an oxygen atom is bi-valent, like carbon. Hence, it prefers to form a carbonyl or an epoxide at the top and midbond sites, respectively and shows higher adsorption energy at the midbond site compared to the top and centre sites for both spin states. The details for both spin states are discussed below.

The energy profile for adsorption of **singlet** O_{GP} on coronene with B3LYP and B3LYP-D3BJ is shown in Fig. 4.8 panel A and B, respectively. A barrierless adsorption of an oxygen atom is obtained at all sites under consideration. All the energy values are summarized in Table 4.6.



Figure 4.8: Potential energy curves for adsorption of singlet O_{GP} on top, centre and midbond of coronene ring. Panel (A): With B3LYP/6-311G(d,p), panel (B): with B3LYP-D3BJ/6-311G(d,p), panels (C, D, and E): top and side view of the minimum energy structure for adsorption of O_{GP} at the top, centre, and midbond site, respectively. All structures are calculated with B3LYP/6-311G(d,p).

At the top site, chemisorption of O (¹D) is found at an internuclear distance of 1.51 Å with an adsorption energy of -2.65 eV. The corresponding geometry is shown in Fig. 4.8 panel C. This results in a change in the C-C bond length of the target carbon atom with other bonded atoms from 1.421 Å to 1.45 Å and bond angle from 120° to 118° at the target site. This change and therefore the amount of puckering is significantly less than for the adsorption of C(¹D). It is not quite clear to us why this is the case, but it is assumed that the electronegativity difference between carbon and oxygen has a role to play here,

4.2

Ads-site	B3LYP	B3LYP-D3BJ
	E_a	E_a
Top	-2.65	-2.70
Centre	-1.04	-1.04
Midbond	-3.70	-3.87

Table 4.6: Adsorption energies (E_a) are in eV for the adsorption of singlet O_{GP} at coronene with density functional B3LYP/6-311G(d,p) and B3LYP-D3BJ/6-311G(d,p).

creating a positive charge on carbon. The effect of dispersion in this case is fairly minor with only a small change in the binding energy.

In contrast to the top site, the centre site first shows a long-range interaction. Further approach of O_{GP} , however, induces puckering in the coronene ring. This leads to chemisorption of oxygen atom at the midbond site in the form of an epoxide, but the oxygen atom is bent toward the centre of the ring (see Fig. 4.8 panel D). Again inclusion of van der Waals interactions has little effect. Therefore, a binding energy of -1.04 eV is obtained with both B3LYP and B3LYP-D3BJ.

Similar to the adsorption of atomic carbon the midbond site is found as the most stable site for adsorption of O_{GP} . Here, O_{GP} adsorbs in the form of an epoxy group with a binding energy of -3.7 eV at an internuclear distance of 1.67 Å with a change in C1-C2 bond length to 1.56 Å (see Fig. 4.8 panel E). The further approach of atomic oxygen lengthens the C1-C2 bond leading to insertion into the C1-C2 bond, leading to the formal formation of an ether. This also lifts the bonded surface carbon atoms slightly above the surface and reduces the flatness of surface^{190,191} as shown in Fig 4.8-E. Again, the effect of van der Waals interaction is small, although larger than for the other adsorption sites, leading to a chemisorption well depth of -3.87 eV.

PECs for the adsorption of **triplet** O_{GP} (³P) on a coronene surface with B3LYP and B3LYP-D3BJ are shown in Fig. 4.9 panels A and B, respectively. All energies are summarized in Table 4.7. Similar to singlet atomic oxygen, site-independent physisorption is found at all sites for O (³P) at longer distances followed by chemisorption for the top and midbond sites. For the centre site, only a physisorption well of -0.02 eV is found which increases to -0.11 eV upon inclusion of dispersion interactions.

Table 4.7: Physisorption energies (E_{ph}) , adsorption energies (E_a) , and energy barriers (E^{\sharp}) are all in eV for the adsorption of triplet O_{GP} at coronene with density functional B3LYP/6-311G(d,p) and B3LYP-D3BJ/6-311G(d,p).

Ads-sites	B3LYP			B3LYP-D3BJ		
	E_{ph}	E_a	E^{\sharp}	E_{ph}	E_a	E^{\sharp}
Top	-0.07	-0.52	0.26	-0.17	-0.13	0.18
Centre	-0.02	-	-	-0.11	-	-
Midbond		-0.15	-		-0.25	-

Looking at the top site we find that triplet oxygen shows a long-range interaction with an energy of -0.074 eV at 2.48 Å. But, in contrast to the adsorption of singlet oxygen, activated adsorption is obtained with a binding energy of -0.052 eV at 1.44 Å via an energy barrier of 0.26 eV at 1.79 Å (Fig. 4.9 panel C). These binding energies are much smaller than for singlet oxygen reflecting the stabilizing nature of the additional electron pair.



Figure 4.9: Potential energy curves for adsorption of triplet O_{GP} on top, centre and midbond site of coronene ring. Panel (A): With B3LYP/6-311G(d,p), panel (B): with B3LYP-D3BJ/6-311G(d,p), panel (C, D, and E): minimum energy structure for adsorption of O_{GP} at the top site, midbond site, and centre of the ring, respectively. All structures are calculated with B3LYP/6-311G(d,p).

Finally, adsorption on the midbond site leads to chemisorption with a binding energy of -0.15 eV (-0.25 eV with dispersion interaction) at 2.6 Å (Fig. 4.9 panel E). Again this energy is much smaller than for singlet oxygen. Concluding, it is noted that whilst triplet oxygen is the ground state asymptotically, adsorption at a coronene surface is much more favourable in the singlet state. However, this requires a non-adiabatic transition which under normal conditions will be slow and inefficient because of the weak spin-orbit coupling for light atoms, like oxygen.

Adsorption of atomic nitrogen

In line with carbon and oxygen, atomic nitrogen has also been detected in ground state quartet $({}^{4}S)^{187,192}$ and in excited state doublet $({}^{2}D).{}^{193}$ The energy difference between ground state quartet and 1^{st} excited state doublet is 2.81 eV. Therefore, we have considered both spin states of nitrogen atom for our calculations. In the quartet state, nitrogen has half-filled 2p-orbitals which can be expected to be more stable than the carbon and oxygen triplet states. As a consequence, no interaction of quartet nitrogen with the coronene surface is found, whereas doublet nitrogen prefers to adsorb at the midbond site. Adsorption of nitrogen atom at all considered sites for both spin states are discussed below.

First we will discuss the adsorption of ground state **quartet** nitrogen atom at three different sites of coronene. PECs for the adsorption of $N(^{4}S)$ at top, centre, and midbond sites on a coronene surface are shown in Fig. 4.10. All the stationary points are summarized in Table 4.8.



Figure 4.10: Potential energy curves for the adsorption of quartet N_{GP} at top, centre, and midbond sites of coronene ring. Panel (A): With B3LYP/6-311G(d,p), panel (B): with B3LYP-D3BJ/6-311G(d,p), panel (C, D, and E): geometry for the adsorption of N_{GP} at top, centre, and midbond of the ring at point P, Q, and R, respectively. All structure are calculated with B3LYP/6-311G(d,p).

Table 4.8: Physisorption energies (E_{ph}) , adsorption energies (E_a) , and energy barriers (E^{\sharp}) are all in eV for the adsorption of quartet N_{GP} at coronene with density functional B3LYP/6-311G(d,p) and B3LYP-D3BJ(d,p).

Ads-sites	B3LYP		B3LYP-D3BJ			
	E_a	E^{\sharp}	E_{ph}	E_a	E^{\sharp}	
Top	0.71	0.89	-0.06	0.60	0.78	
Centre	-	-	-0.06	-	-	
Midbond	-	-	-0.06	-	-	

At long-range internuclear distance no interaction is found for N_{GP} at all sites for B3LYP. Inclusion of van der Waals interactions leads to a small physisorption well of ~0.06 eV for all. Further approach of N_{GP} at the centre and midbond sites leads to a repulsive interaction and adsorption minimum. However, adsorption of N_{GP} at the top site results in a metastable adsorption with a binding energy of 0.71 eV via a barrier of 0.89 eV, i.e. a metastable adsorption energy of -0.18 eV. Inclusion of dispersion interaction lowers this to a binding energy of 0.6 eV with a barrier of 0.78 eV, *i.e.*, a metastable adsorption energy of -0.18 eV. The positive adsorption energy shows the repulsive nature of the nitrogen-coronene interaction.

PECs for the adsorption of **doublet** $N(^{2}D)$ on a coronene surface were studied next and are shown in Fig. 4.11. All the energies are summarized in Table 4.9. Similar to ground state quartet nitrogen, excited state doublet nitrogen also shows no interaction with coronene at long-range internuclear distances. However, with closer approach doublet nitrogen form a chemical bond at the top site with adsorption energy of -0.34 eV via an energy barrier of 0.34 eV. Inclusion of dispersion interaction lowers this barrier to 0.22 eV and a higher adsorption energy of -0.44 eV is obtained with physisorption of -0.084 eV.



Figure 4.11: Potential energy curves for the adsorption of doublet N_{GP} at top, centre, and midbond sites of coronene ring. Panel (A): With B3LYP/6-311G(d,p), panel (B): with B3LYP-D3BJ/6-311G(d,p).

Table 4.9: Physisorption energies (E_{ph}) , adsorption energies (E_a) , and energy barriers (E^{\sharp}) are all in eV for the adsorption of doublet N_{GP} at coronene with density functional B3LYP/6-311G(d,p) and B3LYP-D3BJ(d,p).

Ads-sites	B3LYP			B3LYP-D3BJ			
	E_{ph}	E_a	E^{\sharp}	E_{ph}	E_a	E^{\sharp}	
Top	-	-0.34	0.34	-0.08	-0.44	0.22	
Centre	-	-	-	-0.02	-	-	
Midbond	-0.03	-1.38	0.24	-0.08	-1.40	0.11	

At the centre site no interaction of nitrogen is observed with B3LYP, whereby inclusion of dispersion result a physisorption of -0.17 eV.

On the other hand, approach of nitrogen atom to the midbond site results in a long range interaction of -0.07 eV at a distance of 2.3 Å. Further approach of nitrogen atom cause puckering of the surface carbon atoms and results an energy barrier of 0.24 eV. This then favours the adsorption of nitrogen atom at the midbond site with a binding energy of -1.38eV at a distance of 1.65 Å by breaking the π conjugation. Beyond this atomic nitrogen adds more distortion in the coronene surface and insert itself into the C-C bond. This resulting in an increase in energy as shown in panel A. Inclusion of empirical dispersion reduces the energy barrier to 0.11 eV and results in physisorption well of -0.081 eV and chemisorption well of -1.4 eV. In conclusion, adsorption of nitrogen atom in quartet and doublet state results showed that a nitrogen atom in its ground state does not adsorb onto coronene, weak chemisorption only happens in the doublet state. This requires a nonadiabatic transition, which will be slow and inefficient as was the case for atomic oxygen. Results presented here agree with a previous study.¹⁹⁴

4.3 Adsorption of atomic gases on graphene

In the previous section, we considered adsorption of atomic gases on coronene since this is often used as a mimic for interstellar dust grains. However, graphene is used similarly and therefore adsorption on graphene was studied next.

To study the adsorption of atomic gases on graphene and bi-layer (AB) graphite surface

we used VASP v.5.4.4^{150–152,195,196} and performed spin-polarized calculations. To enforce the spin-polarization by calculating both spin-up and spin-down electron density is defined by ISPIN and ICHARG. This is in contrast to the calculations for coronene, where spinunpolarized calculations were performed. Thus, we expect to find a combination of the effects due to spin, found for coronene. As mentioned in section 4.1 we used an 18 C atom graphene supercell as our standard dust grain model. Graphene is a 2-dimensional crystal, which possesses only a surface and no volume. It is a semi-metal with a zero band gap. Previous studies^{181,197,198} have reported that chemisorption of hydrogen atoms on a graphene surface is an endothermic process with an energy barrier of ≈ 0.2 eV, in accordance with the adsorption of hydrogen on a coronene surface as discussed in section 4.2.2.



Figure 4.12: Relaxation scheme for the adsorption process of atomic gases at the top site (C1) of graphene.

In the current section, benchmarking results are discussed for the adsorption of hydrogen and carbon atoms on the top site of graphene using various GGA functionals and the hybrid functional B3LYP. This is followed by a comparison between the adsorption of atomic hydrogen, carbon, oxygen, and nitrogen on graphene and coronene surfaces in the next section.

All calculations were performed using density functional theory with a plane wave basis set. A 4×4 unit cell has been used with a $6\times 6\times 1$ Γ -centred k-point mesh to study the adsorption of atomic

gases with an energy cutoff of 850 eV. For more details see Chapter 3. The adsorption profile of X_{GP} at the top site of a graphene surface was studied using the relaxation scheme as shown in Fig. 4.12. In this, the carbon atom C1 (shown by green colour) represents the top site. Thus, to study the adsorption of X_{GP} at the top of carbon atom C1, carbon atoms C1, C2, C3, and C4 were allowed to move in the x, y, and z directions (complete relaxation) during the approach of X_{GP} . Throughout the discussion, we will refer to the carbon atom at which adsorption will take place as C1. The other relaxed carbon atoms will be referred to as C2, C3 and C4.

4.3.1 Method benchmarking

Our benchmarking calculations aimed to determine the influence of the choice of functional for the adsorption energy profile of atomic hydrogen and carbon on graphene. Thus, the GGA functionals: PBE (Perdew-Burke-Ernzerhof),¹⁵⁴ PW91,^{94,153} revPBE,^{154,156} RPBE (revised Perdew-Burke-Ernzerhof with Pade Approximation),^{154,155} PBEsol (Perdew-Burke-Ernzerhof revised for solids),¹⁵⁷ and the hybrid functional B3LYP^{95,96} were used in this study. Separately, the influence of van der Waals interactions was studied by using Grimme's third-generation van der Waals corrections with Becke Johnson damping (D3-BJ).^{104,146}

Previous studies^{35,180,199} have reported that the chemisorption binding energy of atomic hydrogen on graphene depends upon the degree of surface relaxation. In fact, it can be between -0.5 and -1.09 eV with an energy barrier of ≈ 0.2 eV. For our work, we found a similar potential energy curve for the adsorption of atomic hydrogen on graphene with

all GGA functionals as shown in Fig. 4.13. The exact values of long-range interactions, binding energies, activation energy barriers and puckering values are summarized in Table 4.10.



Figure 4.13: Potential energy curves for adsorption of H_{GP} at the top site of graphene. Panel (A): With various DFT functionals, panel (B): with the inclusion of dispersion effects. The insets show the top and side view of minimum energy structure with H_{GP} adsorbed.

Table 4.10: Physisorption energies (E_{ph}) , adsorption energies (E_a) , and energy barriers (E^{\sharp}) are all in eV and puckering (D) of top site carbon atom is in Å for adsorption of H_{GP} on graphene with different density functionals, without and with empirical dispersion.

DFT-F	-			D3BJ			
	E_a	E^{\sharp}	D	E_{ph}	E_a	E^{\sharp}	D
PBE	-0.73	0.17	0.34	-0.04	-0.76	0.09	0.34
PW91	-0.81	0.18	0.35	-0.02	-0.91	0.06	0.34
PBEsol	-0.98	0.05	0.33	-0.04	-0.98	0.01	0.33
revPBE	-0.78	0.22	0.35	-0.04	-0.86	0.05	0.35
RPBE	-0.78	0.22	0.34	-0.04	-0.86	0.01	0.34
B3LYP	-1.52	-	0.36	-	-1.56	-	0.35

All GGA functionals show an activated chemisorption of atomic hydrogen. This requires a puckering of C1 by ~0.34 Å at an internuclear distance of 1.9 Å. All GGAs show very similar results with all binding energies (apart from the PBEsol functional) within 0.08 eV of each other. The GGA functional PBEsol shows a notably higher binding energy with an energy barrier of approximately one-third lower than other GGA functionals. However, the hybrid functional B3LYP shows barrierless adsorption with a binding energy of approximately double than that of others (-1.52 eV) and considerably more than any of the literature values. This is an indication of the failure of B3LYP for periodic systems in line with previous studies.^{140,200} In particular, these studies report that B3LYP shows an inaccurate atomization energy and fails to attain the homogeneous gaseous limit in case of metals and semiconductors with small band gaps. Inclusion of empirical dispersion leads to a reduction in the energy barrier to values that are lower than the experimentally determined values²⁰¹ and a small increase in the magnitude of the binding energy as shown in Fig. 4.13 panel B. we turned our attention to the adsorption of atomic carbon on the top site of graphene as indicated in Fig. 4.14. All adsorption energies and puckering values are summarized in Table 4.11.



Figure 4.14: Potential energy curves for adsorption of C_{GP} at the top site of graphene. Panel (A): With various DFT functionals and the inset shows the geometry at point X. Panel (B): with inclusion of dispersion effect and the inset shows the geometry at point Z.

Table 4.11: Physisorption energies (E_{ph}) , adsorption energies (E_a) , and barriers (E^{\sharp}) all in eV and puckering (D) is in \hat{A} of adsorption of C_{GP} on graphene with different density functionals, without and with empirical dispersion.

DFT-F	-		D3I	3J
	E_a	D	E_a	D
PBE	-0.76	0.10	-0.90	0.08
PW91	-0.69	0.08	-0.86	0.08
PBEsol	-1.05	0.09	-1.13	0.09
revPBE	-0.47	0.09	-0.78	0.08
RPBE	-0.45	0.10	-0.88	0.08
B3LYP	-0.97	0.09	-1.20	0.09

A barrierless adsorption of C_{GP} is observed with all GGA functionals. Interestingly, for the adsorption of C_{GP} on top of C1, a double well potential is (X and Z) obtained *via* energy barrier Y with all GGA functionals as shown in Fig. 4.14 panel A. Here the first well 'X' refers to the chemisorption of C_{GP} on the top site (see image in Fig. 4.14 panel A). As C_{GP} further approaches, C1 is required to move out of the surface an approximately 0.09 Å. This causes a change in hybridization of C1 from sp^2 to sp^3 . It also adds distortion to the surface. As a consequence, the potential energy increases to form energy barrier Y. Finally, further approach of C_{GP} starts to push C1 below the graphene plane (see image in Fig. 4.14 panel B). This results in a reorganization of the graphene surface and gives a lower potential energy in the form of the second well, Z.

In contrast to the adsorption of atomic hydrogen, the adsorption of atomic carbon leads to significant differences between the different GGA functionals. In particular, the PBEsol functional shows significantly stronger chemisorption than the other GGA functionals and gives even stronger binding than B3LYP. The reason for this is not entirely clear to us, but it suggests that the PBEsol functional is not the right one to use for the study of this process. This conclusion is strengthened by the calculations with included empirical dispersion that show PECs that are closer together, but still the PBEsol functional binds more strongly than the other functionals including B3LYP. Other than that, the influence of empirical dispersion interactions is mainly felt through the stronger binding and lower absolute barrier between the two chemisorption minima.

To explore our results further, we have performed benchmarking calculations using B3LYP and PBE for both coronene and graphene.

4.3.2 Comparison of PBE and B3LYP for coronene and graphene

In section 4.2.1 and section 4.3.1, benchmarking calculations of different density functionals for the adsorption of hydrogen and carbon atom on coronene and graphene were presented. In this section, a comparison of potential energy curves for the adsorption of atomic species on graphene and coronene using PBE and B3LYP is discussed. For ease of presentation earlier presented PECs will be repeated here.



Adsorption of atomic hydrogen

Figure 4.15: Potential energy curves for the adsorption of hydrogen. Panel (A): On graphene surface with PBE/plane-wave, PBE-D3BJ/plane-wave. Panel (B): On coronene with PBE/6-311G(d,p), PBE-D3BJ/6-311G(d,p). Panel (C): On graphene with B3LYP/plane-wave, B3LYP-D3BJ/plane-wave and panel (D): on coronene with B3LYP/6-311G(d,p), B3LYP-D3BJ/6-311G(d,p). The insets in panels A, C and B, D show the top and side view of the minimum energy structure for the adsorption of a hydrogen atom on graphene and coronene, respectively.

The C-C bond length in graphene (1.42 Å) and coronene (1.421 Å) are equivalent. This is one of the reasons, why coronene has been used as a model for interstellar dust grains. The

Table 4.12: Physisorption energies (E_{ph}) , adsorption energies (E_a) , and barriers (E^{\sharp}) for the adsorption of atomic hydrogen on coronene and graphene. All energies are in eV. The puckering (D) of the graphene surface is given in Å. The density functionals PBE and B3LYP, without and with empirical dispersion.

DFT-F		Graphene			Coronene		
	E_{ph}	E_a	E^{\sharp}	D	E_{ph}	E_a	E^{\sharp}
PBE	-	-0.73	0.17	0.34	-	-0.64	0.25
B3LYP	-	-1.52	-	0.36	-	-0.63	0.29
PBE-D3BJ	-0.04	-0.76	0.09	0.34	-0.01	-0.66	0.19
B3LYP-D3BJ	-	-1.56	-	0.35	-0.03	-0.65	0.19

literature shows that similar results are obtained for the adsorption of a hydrogen atom on both coronene and graphene. Thus, in the following, we will investigate whether this holds for other gases as well. PECs for the adsorption of atomic hydrogen on graphene and coronene with PBE and B3LYP are shown in Fig. 4.15. The physisorption energy, adsorption energy and energy barrier are summarized in Table 4.12.

Comparison of panels A, B, and D shows that the adsorption of atomic hydrogen on coronene with PBE and B3LYP shows similar results. Both functionals show activated adsorption with a binding energy of -0.64 eV at an internuclear distance (C-H) of 1.1 Å. Similar geometrical structural changes are observed as well. For the minimum energy structure, the C1-C2 bond length changes to 1.50 Å. In addition, the energy barrier to adsorption is also similar with both functionals.

For adsorption of graphene, (panel A), PBE gives an adsorption energy of atomic hydrogen of -0.73 eV with a lower energy barrier of 0.17 eV at an equilibrium distance of 1.26 Å. Simultaneously, the target carbon atom (C1) puckers out of the surface by 0.34 Å, and the C1-C2 bond length changes to 1.52 Å for the minimum energy structure. The inclusion of van der Waals interactions does not really change the results. Thus, PBE shows equivalent structural distortion in coronene and graphene in agreement with the literature.^{35,180,199} Panel C shows the adsorption of atomic hydrogen on graphene surface by B3LYP. As already discussed B3LYP shows non-activated adsorption with a binding energy, which is approximately twice as high as obtained with PBE (Fig. 4.15 panel C). This is both quantitatively and qualitatively different from the coronene results and the results obtained with PBE on graphene. This suggests that B3LYP is not well suited for solid-state calculations, as we noted above.

Adsorption of atomic carbon

In our Gaussian calculations, we have investigated the adsorption of singlet and triplet carbon atom on the coronene surface. However, in VASP we have chosen not to use well-defined spin states. Instead, a spin-polarized calculation was run, which yields the lowest spin state at any geometry. A comparison of the adsorption of atomic carbon on graphene and on coronene is shown in Fig. 4.16. As explained in section 4.3.1 adsorption of carbon on the graphene surface gives a double well potential (see Fig. 4.16 panels A and C). First chemisorption is found on the surface. Upon decreasing the height of C_{GP} above the surface C1 moves below the graphene plane and forms a complex with C_{GP} (see panel (A-i) of Fig. 4.16). Inclusion of dispersion interactions leads to qualitatively a similar curve. A similar adsorption scenario is observed with B3LYP, but with higher chemisorption energy as shown in panel C (Fig. 4.16) although the order of the well depth



is now reversed.

Figure 4.16: Potential energy curves for the adsorption of C_{GP} . Panel (A): On graphene surface with PBE/plane-wave and PBE-D3BJ/plane-wave. Panel (B): On coronene with PBE/6-311G(d,p) and PBE-D3BJ/6-311G(d,p), panel (C): on graphene with B3LYP/plane-wave and B3LYP-D3BJ/plane-wave, and panel (D): on coronene with B3LYP/6-311G(d,p), B3LYP-D3BJ/6-311G(d,p). The inset (A-i, and C-ii) shows the intermediate geometrical structure for the adsorption of C_{GP} at the top site of graphene at points Z and X, respectively.

Table 4.13: Physisorption energies (E_{ph}) and adsorption energies (E_a) for the adsorption of atomic carbon on coronene and graphene are in eV. The puckering of the graphene surface carbon atom C1, the bond length of C1-C_{GP} and C1-(C2, C3, C4) are in Å with the density functionals PBE and B3LYP, without and with empirical dispersion.

system	PBE	PBE-D3BJ	B3LYP	B3LYP-D3BJ
Graphene				
E_a	-0.76	-0.90	-0.97	-1.20
D	0.10	0.09	0.09	0.09
$C1-C_{GP}$	1.77	1.77	1.82	1.82
C1-(C2, C3, C4)	1.43	1.43	1.44	1.44
Coronene(s, t)				
E_a	-1.07, -0.79	-1.46, -0.87	-1.79, -0.10	-1.89, -0.26
E_{ph}	-	-	-, -0.14	-, -0.34
$C1-C_{GP}$	1.60	1.60	1.60	1.60
C1-(C2, C3, C4)	1.48	1.48	1.48	1.48

Comparing the coronene results in panels B and D to the graphene results in panels A and C shows a similar non-activated chemisorption in all cases. It is clear that the spinpolarized calculations are most comparable with the singlet calculations for the adsorption on coronene. It is also clear that the adsorption on coronene is not leading to a double chemisorption well. We suspect that due to deformation of the surface as atomic carbon is approaching leads to that pathway not being available in the calculations. However, in contrast to the adsorption of atomic hydrogen, there are now considerable differences between B3LYP and PBE for adsorption on coronene and graphene. In contrast, PBE gives a chemisorption energy on graphene which is similar to the triplet adsorption energy on coronene. The comparison between PBE and B3LYP also shows the increased singlettriplet splitting caused by the inclusion of HF-like exchange into the functional.

Adsorption of atomic oxygen

PECs for the adsorption of O_{GP} on graphene and coronene are shown in Fig. 4.17 and the energies are summarized in Table 4.14.



Figure 4.17: Potential energy curves for adsorption of O_{GP} . Panel (A): On graphene surface with PBE/plane-wave and PBE-D3BJ/plane-wave, panel (B): on coronene surface with PBE/6-311G(d,p) and PBE-D3BJ/6-311G(d,p), panel (C): on graphene with B3LYP/plane-wave and B3LYP-D3BJ/plane-wave, and panel (D): on coronene with B3LYP/6-311G(d,p) and B3LYP-D3BJ/6-311G(d,p) and the inset (A-i, B-ii, and C-iii): show the -minium energy structure for the adsorption of O_{GP} on graphene with PBE-D3BJ, on coronene with B3LYP-D3BJ, and on graphene with B3LYP-D3BJ, respectively.

We found barrierless adsorption of O_{GP} at the top site of the graphene surface with an

Table 4.14: Physisorption energies (E_{ph}) , adsorption energies (E_a) , and energy barrier E^{\sharp} for the adsorption of atomic oxygen on coronene and graphene are in eV. The puckering (D) of surface carbon atom C1, the bond length of C1-O_{GP} and C1-(C2, C3, C4) are in Å with the density functionals PBE and B3LYP, without and with empirical dispersion.

system	PBE	PBE-D3BJ	B3LYP	B3LYP-D3BJ
Graphene				
E_a	-1.10	-1.20	-1.51	-1.62
D	0.33	0.33	0.34	0.34
$C1-O_{GP}$	1.49	1.49	1.50	1.50
C1-(C2, C3, C4)	1.51	1.51	1.51	1.51
Coronene(s, t)				
E_a	-1.59, -0.59	-1.61, -0.61	-2.65, -0.05	-2.70, -0.13
E_{ph}	-	-	-,-0.07	-,-0.17
E^{\sharp}	-	-	-,0.26	-,0.18
$C1-O_{GP}$	1.44, 1.39	1.44, 1.39	1.44	1.44
C1-(C2, C3, C4)	1.50, 1.52	1.50, 1.52	1.51	1.51

adsorption energy of -1.1 eV using PBE. This chemisorption required the target carbon atom (C1) to pucker up by 0.33 Å. A C-O bond of 1.49 Å was found with a lengthening of the C1-C2 bond to 1.51 Å and an increase of the bond angle to 113.8° (Fig 4.17 panel A-i). The higher level of distortion compared to atomic carbon adsorption is caused by the charge transfer between C1 and O because of the adsorption of more electronegative oxygen atom. A similar adsorption scenario is observed with B3LYP with higher adsorption energy of -1.51 eV. The adsorption energy is further increased by adding empirical dispersion in the calculation, even though qualitatively the PEC does not change significantly.

On comparing these results with coronene (Fig. 4.17 panel B and D). It is clear that PBE consistently gives barrierless adsorption, even though the adsorption is less energetically favourable for the triplet state. The overall chemisorption energy calculated with coronene is approximately 33% lower at -1.6 eV, suggesting a final singlet state for this system. As for PBE the addition of van der Waals interaction has little effect.

On the other hand, B3LYP shows considerable differences between graphene and coronene, whereas the graphene result is similar to the PBE coronene result, the binding energy for singlet oxygen is -2.65 eV. As for carbon adsorption the energy difference between singlet and triplet is larger for B3LYP than for PBE. Interestingly, B3LYP calculations for graphene show a puckered-down structure rather than a puckered-up structure (see inset C-iii of Fig. 4.17).

Adsorption of atomic nitrogen

Lastly, we considered the adsorption of atomic nitrogen on graphene and coronene with density functional PBE, B3LYP and with empirical corrections. PECs for the adsorption of N_{GP} at the top site of graphene and coronene surface are shown in Fig. 4.18.

We found that adsorption on the top site of graphene leads to physisorption with an energy of -0.02 eV at an internuclear distance of 2.9 Å. Further, approach to the surface of atomic nitrogen leads to an activated metastable adsorption with an energy of 0.14 eV through an energy barrier of 0.3 eV with a C-N bond length of 1.56 Å. To facilitate this adsorption the target carbon atom moves out of the graphene plane by 0.25 Å. Inclusion of dispersion effects leads to a stronger physisorption of -0.09 eV with PBE-D3BJ and

a metastable chemisorbed state at 0.04 eV with a barrier of 0.22 eV. A similar pattern is observed by the interaction of quartet nitrogen with coronene as shown in Fig. 4.18-B with PBE and PBE-D3BJ. However, in the case of adsorption of nitrogen studied with B3LYP, graphene shows a slight stronger adsorption as shown in panel C.



Figure 4.18: Potential energy curves for adsorption of N_{GP} . Panel (A): On graphene surface with PBE/plane-wave, panel (B): on coronene surface with PBE/6-311G(d,p), panel (C): on graphene surface with B3LYP/plane-wave, panel (D): on coronene surface with B3LYP/6-311G(d,p) and the inset shows the minimum energy structure for the adsorption of N_{GP} on graphene and coronene surface.

On contrary, doublet nitrogen paints a different picture and result a strong chemisorption of nitrogen atom at the top site of coroenene. As shown in panel D with B3LYP an adsorption energy of -0.34 eV is obtained *via* an energy barrier of 0.34 eV. By adding the effect of van der Waals interaction a physisorption well of -0.084 eV is obtained first at a distance of 2.7 Å and result a higher adsorption energy of -0.44 eV with a lower energy barrier of 0.22 eV. Similar to C and O, the PBE results show a higher adsorption energy of -0.7 eV with a smaller barrier of 0.03 eV, whereby this barrier disappears in the presence of empirical dispersion and a higher adsorption energy of -0.8 eV is obtained as shown in panel B. All these energies are summarized in Table 4.15.

Comparing the PBE and B3LYP results shows that B3LYP is not suitable for solid state calculations which is consistent with results of previous studies.^{140,200} Here, it is also interesting to note that the PBE results are more consistent between coronene and graphene. Moreover, whereas B3LYP consistently finds asymptotically excited spin as the most appropriate description of behaviour close to the surface in the graphene calculations, this

Table 4.15: Physisorption energies (E_{ph}) , adsorption energies (E_a) , and energy barrier E^{\sharp} for the adsorption of atomic nitrogen on coronene and graphene are in eV. The puckering (D) of graphene carbon atom C1, bond length of C1-N_{GP} and C1-(C2, C3, C4) are in Å with the density functionals PBE and B3LYP, without and with empirical dispersion.

system	PBE	PBE-D3BJ	B3LYP	B3LYP-D3BJ
Graphene				
E_a	0.14	0.04	-0.57	-0.74
E_{ph}	-0.02	-0.09	-0.07	-
E^{\sharp}	0.30	0.22	0.06	-
D	0.25	0.24	0.24	0.24
$C1-N_{GP}$	1.56	1.56	1.56	1.56
C1-(C2, C3, C4)	1.49	1.49	1.47	1.47
Coronene(q,d)				
E_a	0.26, -0.70	0.20, -0.80	0.71, -0.34	0.60, -0.44
E_{ph}	-0.02, -0.05	-0.06, -0.08	-	-0.06, -0.08
E^{\sharp}	0.50,0.03	0.44,-	0.89, 0.34	0.77, 0.22
$C1-N_{GP}$	1.53	1.53	1.54	1.54
C1-(C2, C3, C4)	1.50	1.50	1.50	1.51

is not the case for PBE, where *e.g.*, for atomic nitrogen the quartet state appears to be the most stable in the graphene calculations. Thus, we have chosen the GGA functional PBE for all solid-state calculations going forwards.

4.4 Adsorption of atomic gases on bi-layer graphite surface

To test the reliability of the graphene single-layer calculations, we also performed doublelayer calculations. For this, we used two layers of graphene stacked in an AB arrangement. We note that there are two different top sites in this arrangement. First, carbon atom above a hexagonal ring of the bottom layer as shown by C1 in Fig. 4.19-A. Second, carbon atom above the top of bottom layer carbon atom as shown by C2 in Fig. 4.19-B. For our adsorption calculations we have chosen to use both top sites (C1 and C4), midbond, and centre sites through necessity. We used a different relaxation scheme for different sites as shown in Fig. 4.19.

We performed the adsorption calculations at C1 by relaxing the C2, C3, and C4 (panel A) and at C4 by relaxing the C1, C2, and C3 (panel B). However, an identical potential energy curve is obtained in both cases. Hence, only one site will be discussed for more simplification. But, the energy values for both adsorption schemes are summarized in the respective Tables. At the midbond and centre sites the associated relaxed carbon atoms will be referred to as C1, C2, C3, C4, C5, and C6. An interlayer distance of ~ 3.74 Å is used. This was obtained after the optimization of the bi-layer system. This is slightly larger than the bulk distance $(3.35 \text{ Å}).^{202}$



Figure 4.19: Relaxation scheme of graphite surface for adsorption of atomic gases. Panel (A): Adsorption at top site C1 atom which lies at centre of the bottom layer hexagonal ring by relaxing four carbon atoms, panel (B): adsorption at top site C4 which lies above carbon atom of bottom layer by relaxing four carbon atoms, panel (C): adsorption of atom at the centre of the ring by relaxing six carbon atoms, and panel (D): adsorption at midbond between C1 and C2 by relaxing six associated carbon atoms.

4.4.1 Adsorption of atomic hydrogen

Potential energy curves for the adsorption of H_{GP} on graphite with PBE and PBE-D3BJ are shown in Fig. 4.20. All the stationary points are summarized in Table 4.16. The adsorption profiles of H_{GP} on graphite follow a similar adsorption pattern as obtained on the coronene molecule. Fig. 4.20 illustrates that similar to the coronene surface, H_{GP} does not show any interactions at longer distances until 3.5 Å. Further, moving in of H_{GP} to the top site the surface carbon atom C4 puckers by 0.3 Å and creates an energy barrier of 0.16 eV. This favours the chemisorption of H_{GP} at the top site with binding energy of -0.72 eV at an internuclear distance of 1.5 Å. Addition of van der Waals interaction adds a physisorption well, but the PEC qualitatively stays the same. However, the barrier drops to 0.08 eV, which is lower than for coronene.

Similar to the coronene surface, when H_{GP} moves onto the centre site the six relaxed carbon atoms recede into the graphene plane by -0.05 Å. The overall, adsorption profile is repulsive for both PBE and PBE-D3BJ. Adsorption of H_{GP} at the midbond site on graphite is similar to adsorption on coronene. The energy profile in Fig. 4.20 panel A shows no interaction of H_{GP} at the midbond site until a distance of 2.5 Å, where metastable adsorption is found with an energy of 0.28 eV (marked by X), accompanied by a puckering of C2 by 0.44 Å and C1 by only 0.06 Å. A similar energy profile is obtained with a lower energy metastable state by adding the effect of empirical dispersion as shown in Fig. 4.20 panel B.



Figure 4.20: Potential energy curves for adsorption of H_{GP} at top, centre and midbond sites of graphite. Panel (A): With PBE/plane-wave, panel (B): with PBE-D3BJ/plane-wave, panel (C, D, and E): minimum energy structures for the adsorption of hydrogen at top, centre, and midbond respectively.

Table 4.16: Geometrical structural change by adsorption of hydrogen at the top, centre, and midbond sites. Physisorption energies (E_{ph}) , adsorption energies (E_a) , and barriers (E^{\sharp}) all are in eV. D and D_n are the puckering value of the target surface carbon atom and other corresponding relaxed carbon atoms in Å, bond length of hydrogen atom and target carbon atom (C-H), and bond length of the corresponding relaxed carbon atoms to the surface target carbon (C-C) are in Å.

- Top (C1, C4)		Centre		Midbond		
-	PBE	PBE-D3BJ	PBE	PBE-D3BJ	PBE	PBE-D3BJ
E_{ad}	-0.72	-0.75	-	-	0.28	0.27
E^{\sharp}	0.16	0.08	-	-	0.47	0.38
E_{ph}	-	-0.04	-	-0.04	-	-0.04
D	0.3	0.33	-	-	0.44, 0.06	0.43, 0.06
D_n	0.06	0.09	-0.05	-0.05	-0.09	-0.09
C-H	1.30	1.30	-	-	1.37	1.37
C-C	1.50	1.50	1.43	1.43	1.45	1.45

In conclusion, our results show that the top site is the most favourable position for hydrogen adsorption on a graphite layer. However, it will be difficult to obtain the required energy to overcome the energy barrier in the cold temperature regions of ISM. In addition, physisorption energy values show a site-independent nature as expected, given their distance from the surface.

4.4.2 Adsorption of atomic carbon

Potential energy curves (PECs) for adsorption of C_{GP} on a graphite surface with PBE and PBE-D3BJ are shown in Fig. 4.21.



Figure 4.21: Potential energy curves for adsorption of C_{GP} at top, centre and midbond site of graphite. Panel (A): With PBE, panel (B): with PBE-D3BJ. Panel (C, D, and E): Minimum energy structure for the adsorption of C_{GP} at top, centre, and midbond sites respectively.

As discussed above, the adsorption of a carbon atom at the top site of graphene surface generates a double well potential energy surface. A similar energy profile is obtained for the adsorption of C_{GP} at the top site of an AB graphite surface (Fig. 4.21 panel A). In this 'X' is associated with adsorption of C_{GP} at the top site. This requires the top carbon atom to move out of the graphene plane by 0.1 Å with additional puckering of associated carbon atoms by 0.034 Å. Further approach of C_{GP} starts to push the bonded top carbon atom into the graphene plane. This leads to the second well 'Z' via the barrier Y, ultimately. For more simplicity, only the binding energies of the first chemisorption well (X) are noted in Table 4.17.

Table 4.17: Structure change by adsorption of C_{GP} at top centre, and midbond site. Adsorption energies (E_a) , are in eV. D and D_n refer to the puckering value of the target carbon atom and other corresponding relaxed carbon atoms in Å, bond length of target carbon atom and incoming carbon atom $(C-C_{GP})$, and bond length of the corresponding relaxed carbon with target carbon atom (C-C) are in Å.

-	Top (C	C1, C4)	(Centre	Midbond		
-	PBE	PBE-D3BJ	PBE	PBE-D3BJ	PBE	PBE-D3BJ	
E_a	-0.70, -0.84	-0.71, -0.85	-	-	-1.22	-1.30	
E_{ph}	-	-	-0.08	-0.22	-	-	
D	0.10, 0.12	0.09			0.32	0.31	
D_n	0.034	0.028	-0.02	-0.02	0.10	0.10	
$C-C_{GP}$	2.03	2.03	-	-	2.01	2.01	
C-C	1.43	1.43	1.44	1.44	1.43	1.43	

Similar to coronene and graphene adsorption of atomic carbon atom is found to be unfavourable at the centre site of bi-layer graphite. Only a physisorption energy well of $-0.08~{\rm eV}$ and $-0.22~{\rm eV}$ is obtained with PBE and PBE-D3BJ, respectively at a distance of 2.8 Å from the surface.

In contrast, as expected, the midbond site is found to be the most favourable site for the adsorption of C_{GP} in a cyclopropane form with a binding energy of -1.22 eV (Fig 4.21 panel E). Adsorption at this site requires the puckering of C1 and C2 by 0.1 Å and increases the C1-C2 bond to 1.43 Å. The resulting C-C_{GP} bond forms at a longer distance of 2.03 Å on graphite than on coronene (1.6 Å). As a consequence, the distortion of the C-C bond within the graphite layer is small. Please note that the obtained energy values of adsorption show more resemblance to singlet carbon atom adsorption on coronene. Inclusion of empirical dispersion leads to an increase in the binding energy coupled with a decrease in surface carbon atom puckering. The energies and structural changes are summarized in Table 4.17.

4.4.3 Adsorption of atomic oxygen

Results for the adsorption of atomic oxygen on a bi-layer are shown in Fig. 4.22. All the energy data is summarized in Table 4.18. These results are qualitatively similar to the results for atomic oxygen adsorption on coronene.



Figure 4.22: Potential energy curves for adsorption of O_{GP} at top, centre and midbond site of graphite. Panel (A): With PBE, panel (B): with PBE-D3BJ, panel (C, D, and E): minimum energy structure for the adsorption of O_{GP} at top, centre, and midbond sites respectively.

Adsorption of O_{GP} at the centre site shows only a physisorption well of -0.13 eV with PBE and -0.22 eV with PBE-D3BJ at a distance of 2.5 Å. A closer approach just leads to repulsive interactions and no chemisorption. These energy values are similar to the adsorption of triplet oxygen on coronene.

In contrast, chemisorption of O_{GP} at both top sites (C1 and C4) is shown to be barrierless with a binding energy of -0.96 eV. This is facilitated by the puckering of top carbon atom (C1 or C4) by 0.33 Å with additional puckering of the neighbour carbon atoms by 0.09

Table 4.18: Structure change by adsorption of O_{GP} at top centre and midbond site. Physisorption energies (E_{ph}) , adsorption energies (E_a) are in eV. D and D_n are the puckering value of adsorbed surface carbon atom and other corresponding relaxed carbon atoms are in Å, bond length of oxygen and target carbon atom (C-O), and bond length of the target carbon atom with corresponding relaxed carbon atoms (C-C) are in Å.

-	Top (C1, C4)		(Centre	Midbond		
-	PBE	PBE-D3BJ	PBE	PBE-D3BJ	PBE	PBE-D3BJ	
E_a	-0.96	-1.04	-	-	-1.78	-1.87	
E_{ph}	-	-	-0.13	-0.22	-	-	
D	0.33	0.32			0.32	0.32	
D_n	0.09	0.08	-0.09	-0.09	0.05	0.05	
C-O	1.50	1.50, 1.46	-	-	1.63	1.53	
C-C	1.51	1.50	1.44	1.44	1.47	1.47	

Å. At both sites a C-O bond with a bond length of 1.5 Å is formed. At shorter distances, atomic oxygen pushes the top site carbon atom below the plane, leading to increases in the energy due to the surface distortion. Comparing these results with the coronene results we conclude that the bond length parameters are identical to ground-state triplet oxygen adsorption. However, the adsorption energy value obtained here is approximately 60 % of the value for singlet oxygen adsorption and much higher than the value for triplet oxygen adsorption in line with results reported in Fig. 4.17. The addition of the additional layer leads to a chemisorption value which is ~ 20 % smaller than the adsorption on graphene.

The midbond site is found to be the most advantageous location for adsorption of atomic oxygen onto graphite as expected from previous results discussed above. The PECs are initially identical to the top site PECs, with deviation starting around 2 Å. Ultimately, binds to the midbond carbon atoms C1 and C2 with a binding energy of O_{GP} in this case, -1.78 eV and a C-O bond length of 1.63 Å. This is accompanied by puckering of C1 and C2 by 0.2 Å. As a consequence, the C1-C2 bond stretches slightly to 1.47 Å. This is in agreement with our coronene results. Adding empirical dispersion interactions leads to a negligible change in energy values as summarized in Table 4.18.

4.4.4 Adsorption of atomic nitrogen

PECs for the adsorption of atomic nitrogen to bi-layer graphite with PBE and PBE-D3BJ are shown in Fig. 4.23 panels A and B, respectively. All the stationary points are reported in Table 4.19. In contrast to atomic oxygen a site-independent physisorption well is obtained for the adsorption of N_{GP} at an internuclear distance of ~ 3 Å with an energy of -0.02 eV with PBE and ~ -0.1 eV with PBE-D3BJ for all initial geometries. For adsorption on the centre site no chemisorption is found.

At both top sites C1 and C4, N_{GP} shows metastable chemisorption with an energy of $\approx 0.14 \text{ eV}$ via an energy barrier of 0.34 eV similar to adsorption on coronene combined with puckering of C1 or C4 by 0.23 Å. The bridging site is the most advantageous site for the adsorption of atomic nitrogen with a binding energy of -0.75 eV and -0.83 eV for PBE and PBE-D3BJ, respectively with an energy barrier of 0.34 eV (PBE) and 0.2 eV (PBE-D3BJ). Comparing graphite results with coronene conclude that the adsorption of N_{GP} at the top and centre positions are in good agreement with the coronene results for the adsorption of doublet nitrogen.



Figure 4.23: Potential energy curves for adsorption of N_{GP} at top, centre and midbond site of graphite. Panel (A): With PBE, panel (B): with PBE-D3BJ. Panel (C, D, and E): minimumm energy structures for the adsorption of N_{GP} at top, centre, and midbond site respectively.

Table 4.19: Structure change by adsorption of N_{GP} at top centre and midbond site. Physisorption energies (E_{ph}) , adsorption energies (E_a) , and barriers (E^{\sharp}) all in eV. D and D_n are the puckering value of the target carbon carbon atom and other corresponding relaxed carbon atoms in Å, bond length of the target carbon atom with nitrigen (C-N) and bond length of target carbon atom with corresponding relaxed carbon atoms (C-C) are in Å.

-	Top $(C1, C4)$		(Centre	Midbond			
-	PBE	PBE-D3BJ	PBE	PBE-D3BJ	PBE	PBE-D3BJ		
E_a	0.14, 0.15	-0.04, -0.05	-	-	-0.75	-0.83		
E^{\sharp}	0.34	0.24	-	-	0.34	0.20		
E_{ph}	-0.02	-0.09	-0.02	-0.12	-0.03	-0.09		
D	0.23, 0.24	0.23, 0.24			0.34	0.35		
D_n	0.04,0.05	0.04,0.05	-0.05	-0.05	0.06	0.06		
C-N	1.53, 1.54	1.53,1.53			1.51	1.51		
C-C	1.53, 1.54	1.53, 1.54	1.43	1.43	1.49	1.49		

4.4.5 Conclusion

Up to this point, we have chosen the methods to study the adsorption of these atomic species on grain analogues. For the molecular system such as coronene, we have found that the results obtained with B3LYP are consistent with previous studies. These results also show an agreement for the adsorption of these atomic species in periodic systems such as graphene with the GGA functional PBE. On the other hand, energies are overestimated with B3LYP in the periodic system and PBE in the molecular system. Therefore we have chosen B3LYP/6-311G(d,p) method for the molecular systems and PBE/plane-wave for the periodic systems.

We then studied the adsorption of all considered atomic gases at various sites of coronene, graphene and bi-layer graphite surface. In all systems, each carbon atom is bonded to three other carbon atoms with sp² hybridization by leaving the one valence electron in π -orbital along the z-direction. The formation of extra bonds then leads to a transformation up to sp^3 hybradization and a change in the structure of the surface. We would expect the most optimum mode of binding to reflect the number of valence electrons. A hydrogen atom only has one electron and therefore shows favorable adsorption at the top site. On the other hand, carbon and oxygen need four and two electrons to fulfil the octet, respectively. Thus, these can form bonds with one carbon atom at the top site and two carbon atoms at the midbond site. However, as expected the midbond site is the most stable. Following on, a nitrogen atom would expected to form 3 bonds with three carbon atoms at the centre site or a single one at the top site. However, a long C-N bond is formed showing a weak interaction between carbon and nitrogen. A similar effect is found for the top sites. Thus, unexpected wide adsorption of N is found to be more stable than adsorption at the top or centre sites. This is also consistent with previous study²⁰³ Thus, from these calculations we have found the preferable site of adsorption for atomic species on bi-layer graphite surface. For further investigation, we will use this information to study the adsorption of hydrogen atoms in the presence of a substitutional defect in the bilayer graphite surface and also to study the formation of water and ammonia molecules on graphite.

First, the adsorption of a hydrogen atom on the bi-layer graphite surface has been studied with substitutional defects (H, N, O, Fe, and Si). These results are discussed in Chapter 5.

Chapter 5

The effect of graphite surface carbon atoms substitution on the formation of H₂

5.1 Introduction

Formation of H_2 molecules in the ISM has been a prominent area of research for a long time,²⁰⁴ since molecular hydrogen is the most abundant molecule in the ISM. However, its formation is less than straight forward. It is widely acknowledged that radiative association of H atoms in the gas phase is an inefficient way of forming H_2 .²⁰⁵ Because given that H_2 does not have a dipole moment to allow efficient emission of a photon, and the allowed quadruple transition would be too slow on the time scale of a general collision. An alternative way for H_2 formation involves the adsorption and recombination of hydrogen atoms on dust grains.^{47,178,206} This process can be described by a whole spectrum of mechanisms of which the two extremes are the Eley-Rideal (ER) and the Langmuir-Hinshelwood (LH) mechanism. In the ER mechanism, the reaction happens when gaseous atoms collide directly with adsorbed atoms on a dust grain. Meanwhile, in the LH mechanism, the incident gaseous atoms first adsorb on the surface and attain thermal equilibrium before diffusion and ultimately recombination happens. Previous studies indicate that the surface and its motion play a significant role in the formation of H_2 .^{207,208}

The precise nature of dust grains is complex (see Ref. 2 and 12 for more details), but carbonaceous surfaces have been extensively studied as dust grain mimics in the context of the formation of hydrogen molecules. However, it has been observed that H atoms do not stick to defect-free graphene surfaces at low temperatures (<10 K).^{209–212} Instead, the adsorption of a hydrogen atom on pure graphene typically requires overcoming an energy barrier of ≈ 0.2 eV, which necessitates the first H atom to have a kinetic energy greater than 0.2 eV.^{211,213–215} This barrier is caused by the fact that by forming a C-H bond (at *e.g.*, site C in Fig. 5.1-A), the hybridization of carbon changes from sp^2 to sp^3 which breaks a C-C π bond.^{180,216} Therefore, the surface must be flexible for chemisorption, as a rigid surface will only result in metastable adsorption.¹⁸⁰ Conversely, dust grains are thermodynamic entities that can convert collision energy into thermal energy, increasing the sticking probability of H atoms on the grains. Highly hydrogenated graphene has also been observed^{217,218} which would facilitate the recombination and desorption of hydrogen in the form of H₂.²⁰⁶ Adsorption of a single H atom creates spin density on neighbouring atoms leading to the preferred adsorption of a second atom on such sites. In particular,

studies^{213,219} have reported that *ortho* and *para* dimers are crucial for recombination and the formation of molecular hydrogen on pristine graphene or graphitic-type surfaces. Furthermore, these studies reported that the binding energy of the second hydrogen atom is more than double the binding energy of a single H atom on a graphene surface at the *ortho* and *para* sites. Previous studies also show that physical and electronic phenomena aid chemisorption.²²⁰

In the present work, we are interested in the role of defects within the graphite surface for the formation of molecular hydrogen, building on previous work in the group. Our approach involved using a bi-layer graphite model of 36 carbon atoms, with single substitutional impurities (where one carbon atom is replaced by a different defect atom at site C as shown in Fig. 5.1-A). We selected impurities (defects) including H, N, O, Fe, Si, and Mg based on their prevalence in the ISM.^{221–223} The introduction of these elements can result in *p*-type or *n*-type doping, which can alter the chemical reactivity and electronic structure (including band gap, charge density, spin density, and magnetic moment). To ensure accurate results, we include the relaxation of the active sites and their surrounding atoms in our calculations. This relaxation step was crucial for obtaining realistic reaction energies.²²⁰



Figure 5.1: Panel (A): Pure bi-layer graphite surface with top layer atoms are shown in cyan color and bottom layer atoms in gray color. Site C is the one chosen for substitution. Carbon atom sites A, D, and F represent the ortho position, carbon atom sites H, E, B, and J represent the meta position. Finally, carbon atom sites G and I represent the para position relative to the defect site within the substituted graphite surface. Panel (B): Schematic bi-layer graphite surface to show the positively and negatively puckered states.

In this study, we explore the potential roles of defects in dust grains by considering three distinct adsorption scenarios for hydrogen on a single substituted bi-layer graphite system as depicted in Fig 5.2. The first scenario involves the direct adsorption of hydrogen on top of the defect. The second scenario involves the adsorption of hydrogen at the carbon atoms *ortho*, *meta* and *para* from the defect site, as shown in Fig 5.1-A. Adsorption of a hydrogen atom at the top of the defect site creates two different *ortho* and *meta* sites, because of the AB geometry of the graphite sheet. Thus, for the third scenario, we use the optimized structure obtained from the adsorption of H on the top of the defect site as the initial structure to investigate the potential initial stage of formation of H₂ by adsorbing the 2^{nd} H atom at the *ortho1*, *ortho2*, *meta1*, *meta2*, and *para* carbon atoms (see Fig. 5.24 for a schematic representation).



Figure 5.2: Flow chart for the adsorption of a hydrogen atom on a single substituted bi-layer graphite system.

5.2 Single substitution of carbon atom



Figure 5.3: Bi-layer graphite system without and with substitution (point) defect. Panel (A): Reference graphite system. Panel (B): Graphite with a single vacancy (point defect). Panel (C): Graphite with a single carbon atom replaced by hydrogen. Panel (D): Graphite with a single carbon atom replaced by nitrogen. Panel (E): Graphite with a single carbon atom replaced by oxygen. Panel (F): Graphite with a single carbon atom replaced by magnesium. Panel (G): Graphite with a single carbon atom replaced by iron. The atoms are colour-coded as follows: carbon (cyan), hydrogen (white), nitrogen (blue), oxygen (red), magnesium (purple), silicon (yellow), and iron (coral).

Substituting elements do not necessarily have the same atomic radius as the carbon atom they replace. Therefore, one of the goals of our study was to investigate the preference

5.2

of substitutional defects to stay within the plane, pucker-up from the surface (out-ofplane), or pucker-down (recede) into the surface. To study this, we performed two types of optimizations for all substitutional defects. Specifically, we added a positive puckering of 0.5 Å or a negative puckering of 0.5 Å before each optimization, as shown in Fig. 5.1-B. All these optimized geometries are shown in Fig 5.3. In the case of pure bi-layer graphite, the C-C bond measures 1.42 Å (AB=AC=1.42 Å) as shown in Fig. 5.1-A. In contrast, graphite with a single vacancy shows a minor contraction of the nearest C-C bond to 1.39 Å (AB and DE in Fig. 5.1-A).

Creating a vacancy or replacing a carbon atom comes with an energy cost/benefit. The energy of formation for single atom vacancy (E_V) can be defined as²²⁴

$$E_V = E_{graphite+vacancy} - \frac{N-1}{N} E_{graphite}.$$
(5.1)

Here, N is the number of carbon atoms in the graphite model. Similarly, the binding energy for the defect substituted atom in the graphite surface E_{sub} is calculated by using the relation²²⁴

$$E_{sub} = E_{graphite+sub} - \frac{N-1}{N} E_{graphite} - E_{sub\ atom}.$$
(5.2)

Here, $E_{graphite+sub}$, $E_{graphite}$, and $E_{dopedatom}$ are the energy of bi-layer graphite + substituted atom, bi-layer graphite, and substituted atom, respectively. The binding energy of all considered defects within the graphite system is shown in Fig 5.4.



Figure 5.4: Stability of bi-layer graphene by substitution of one carbon atom with one defect atom (Fe, H, N, O, Mg, and Si). The binding energy of puckered-up and puckered-down optimized structures are shown by up and down bars.

Within pristine graphite, all carbon atoms are in the sp^2 hybridization. Replacing one carbon with a defect also attains a similar configuration, but because of the difference in size and the nature of the defect atom result a difference in the binding energy of these substituted atoms in the graphite surface. Considering the fact that nitrogen and oxygen atoms are nearly similar in size but more electronegative than carbon atoms. Therefore, a charge transfer from carbon to these atoms can be expected. By Bader charge analysis, a charge transfer of 0.5 e and 0.3 e is obtained from neighbouring carbon atoms to nitrogen and oxygen site, respectively. On the other hand, Mg, Si, and Fe have larger atomic radii and are less

electronegative than carbon atoms. Thus, a charge transfer of 0.4 e, 0.3 e, and 0.2 e is obtained from Mg, Si, and Fe to neighbouring carbon atoms, respectively.

The energy of substitution (binding energy) does not strongly depend on whether an atom is initially puckered up or down. In particular, for O, N, and H a negligible change was obtained in the E_{sub} after forming positive and negative puckering. In fact, these atoms will revert back to being in the surface. This is probably due to the similarity in size. Hence, only one structure was used as a starting point for the adsorption calculations below. In contrast, for Mg, Si, and Fe puckering has an effect on E_{sub} and the elements stay in a puckered state. In particular, a unfavourable substitution is obtained in case of Mg in the puckered-up state, but this is not the case for Fe and Si. Thus, for Si and Fe both puckered up and down optimized structures were considered for the adsorption of H_{GP} atop of the defect and at the *ortho, meta*, and *para* sites. For Fe, Si, and Mg the minimum energy optimized structure was found with a negatively puckered defect where Fe, Si, and Mg moved 1.34 Å, 1.16 Å, and 1.79 Å below the top layer and showed a strong interaction

with the bottom layer. This was particularly clear for the Mg defect. Such extensive puckering adds distortion within the graphite surface and reduces the binding energy of the substituted atom. As a consequence substitution with the atomic magnesium leads to the smallest substitution energy. Moreover, for both positive and negative puckering of the substituted atom bond distance with nearest neighbours were similar. These findings agree with previous studies^{225–227} and are summarized in table 5.1.

Table 5.1: Optimized energies of the substituted bi-layer graphite system, for the 'up' (positive puckering), 'down' (negative puckering), C-X is the bond length between the substituted defect and neighbour carbon atom in Å, and charge obtained on the substituted defect atom.

Defect (X)	$E_{up} eV$	$E_{\rm down}~eV$	$E_{sub-up} eV$	$E_{sub-down} eV$	C-X (Å)	Charge (e)
Н	-319.60	-319.59	-0.55	-0.54	1.14	0.05
Ν	-330.53	-330.53	-3.25	-3.25	1.41^{224}	-1.26
Fe	-325.65	-325.76	-1.25	-1.36	$1.76^{225-227}$	0.37
0	-325.08	-325.09	-2.09	-2.09	1.50	-0.91
Si	-324.05	-324.06	-1.70	-1.71	1.76	1.15
Mg	-316.93	-317.24	0.10	-0.21	2.14	1.21

5.3 Adsorption of hydrogen at various sites on substituted bi-layer graphite

Adsorption of hydrogen can happen on different sites on substituted graphene. Thus, adsorption of hydrogen is discussed for two different scenarios: first, when a single H atom is adsorbed on top of a defect (see this section), and second, when the H atom is adsorbed at sites *ortho*, *meta*, and *para* to the defect (see section 5.4). In these discussions we will be using the following notation: H_{GP} refers to the gas-phase H atom, C^{*} is the active site for H_{GP} adsorption, and X is the substituted atom replacing a surface carbon atom in the bi-layer graphite system (X= H, Fe, Si, Mg, N, O).

For these calculations, we followed two different relaxation schemes. In the **TTT** scheme, the x, y, and z-coordinates of the



Figure 5.5: Relaxation scheme for the adsorption of H_{GP} at the top of a defect atom (C). Here, the atoms A, D, F, and C were allowed to move in and out of the surface.

active surface site and three other bonded atoms (A, D, and F as shown in Fig. 5.5) are completely relaxed, while the incoming H_{GP} is relaxed laterally, but frozen in its z-

position. In the **FFT** scheme, the C, A, D, and F atoms are only relaxed in the z-direction with a complete freeze of all co-ordinates for H_{GP} , unless stated otherwise.

All calculations were performed with and without empirical dispersion correction (D3-BJ). For most defects, similar potential energy curves were obtained for both cases. Therefore, we will only discuss the dispersion-corrected results below otherwise stated separately. However, all other results will be summarized in the respective tables.

5.3.1 Adsorption on top of a hydrogen defect

Hydrogen, being the most abundant element in the interstellar medium (ISM), is likely to be present as a defect in a bi-layer graphite surface. When a carbon atom is replaced with hydrogen, the H atom moves slightly below the graphene layer by -0.04 Å, due to the small difference in atomic radii between H (0.53 Å) and C (0.7 Å). In this case, H is bonded to atom A and so the AH bond length is 1.14 Å whilst the HD and HF distances are 1.79 Å. Carbon atoms A, D, and F are puckered down by 0.01 Å with almost no distortion of other surface carbon atoms. Substitution with H creates unsaturated carbon atoms (D and F) with dangling bonds available for reaction (edge sites C^{*}).

The energy profile for the binding of H_{GP} was studied through desorption and adsorption pathways. The neighbouring carbon atom (F) was chosen as the binding site referred to as C^{*} for H_{GP} instead of the doped site. This should be more advantageous, given the dangling bond at F (and D), whereas for adsorption at A, carbon will hybridize from sp^2 to sp^3 with a concomitant loss of aromaticity, which will lead to an energetic penalty. The movement of the edge site was also studied with investigated by relaxing C^{*} (*i.e.* C^{*}-free) or freezing C^{*} (*i.e.* C^{*}-fix) within a TTT and FFT scheme as outlined above. For the TTT scheme within C^{*}-fix, only H_{GP} was relaxed laterally, while for the FFF calculation, a series of single point energy calculations were performed by changing the distance of incoming H_{GP} from the binding site only. The potential energy curves are given in Fig. 5.6. All the stationary points are summarized in Table 5.2.

Fig. 5.6, panel A shows desorption of H_{GP} from the equilibrium structure of H adsorbed to carbon atom F. This structure has a strong C-H bond with a binding energy of -3.96eV as evidenced by removing the H atom through desorption. This can be expected on an edge site with a dangling bond C^{*} in this case is puckered by 0.4 Å because otherwise it would clash with the defect already present. To avoid that the defect H atom moves approximately ~ 1 Å into the surface. Desorption of H_{GP} leads to similar curves in all relaxation schemes with a small residual energy left in the surface upon complete desorption as clear from Fig. 5.6-A, whereby the repulsive part of the PECs is most affected by the precise relaxation schemes used. For a fully relaxed surface, movement inwards of H_{GP} leads to both being underneath the top graphite layer at a distance of 1.2 Å from each other. If the defect atom allowed to move it moves back into the surface as shown in panel D and the slightly flat curve is observed due to the interaction of H and H_{GP} , whereby it is not the case within complete restriction such as C^{*}-fix (FFF) where a steep curve is obtained by desorption of H_{GP} .



Figure 5.6: Potential energy curves for the desorption and adsorption of H_{GP} on top of C^* in the presence of H defect with PBE-D3BJ. Panel (A): desorption of H_{GP} , panel (B): adsorption of H_{GP} , panel (C): optimized structure for H_{GP} adsorption at C^* , panel (D): intermediate structure for the desorption of H_{GP} from the binding site, panel (E): minimum energy structure for the adsorption of H_{GP} within TTT framework (C*-fix), and panel (F): minimum energy structure for the adsorption of H_{GP} within FFF framework (C*-fix).

Table 5.2: Adsorption energies (E_a) , energy barriers E^{\sharp} , physisorption energies E_{ph} are in eV, puckering of C^* (D) is in Å for desorption and adsorption of H_{GP} , and puckering of other three bonded atoms (N_p) are in Å for the adsorption of H_{GP} atom at the top of C^* defect in bi-layer graphite system. C^* -free and C^* -fix indicate the active carbon atom is free or fixed for the binding of H_{GP} .

-		Desorption			Adsorption						
Defect	Scheme	PBE		PBE-D3BJ	PBE				PBE-D3BJ		
Н	-	E_a	D	E_a	E_a	E^{\sharp}	D	N_p	E_a	E^{\sharp}	E_{ph}
C^* -free	TTT	-3.93	0.87	-3.96	-3.89	-	0.80	0.26	-3.93	-	-
C^* -free	\mathbf{FFT}	-4.04	0.90	-4.09	-2.8	0.02	0.93	0.30	-2.85	-	-
C^* -fix	TTT	-4.10	-	-4.15	-3.11	0.15	-	-	-3.16	0.09	-0.02
C*-fix	\mathbf{FFF}	-4.12	-	-4.16	-1.78	0.15	-	-	-1.82	0.09	-0.02

Fig. 5.6, panel B shows adsorption of H_{GP} onto an edge site, created by a carbon defect. For the most relaxed optimization, the PEC (pink curve in panel B) is very similar to the desorption curve. This would correspond to a low-energy collision and adsorption. The relaxation of the defect site and C^{*}, as well as the lateral movement of H_{GP} , support adsorption of H_{GP} . The most complete relaxation scheme leads to a strong C-H bond with a distance of 1.08 Å and a binding strength of -3.93 eV combined with barrierless adsorption of H_{GP} , as shown by the red curve in Fig 5.6-B. Restricting relaxation, *i.e.* a scenario where the incoming H_{GP} moves fast, leads to barrierless adsorption. It also restrict the potential motion of H_{GP} and H_X , thus leading to the defect H atom remaining in the graphite plane and a smaller binding energy of -2.85 eV, as shown by the blue

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curve in Fig 5.6-B. Interestingly, by restricting the entire surface and only allowing lateral relaxation to H_{GP} (C*-fix (TTT) scheme), a stronger binding energy of -3.16 eV (pink curve) is obtained with H and H_{GP} moving out of each other's way as shown in panel E (Fig 5.6). When the surface and H_{GP} are completely restricted, the lowest binding strength is obtained *via* an energy barrier of 0.09 eV, as shown by the orange curve in Fig 5.6 panel B.

Structurally, it is clear that relaxation of C^{*} is needed to bind H_{GP} . For pristine graphite, this means a puckering of the carbon atom by 0.34 Å is required. This is similar in the presence of an H-defect, as a C^{*}-H bond of 1.08 Å is formed by puckering of C^{*} by 0.8 Å and 0.96 Å within the TTT and FFT framework, respectively, showing that vertical motion can be compensated for by lateral motion. Comparing the relaxation effect between the desorption and adsorption scenarios reveals that allowing more relaxation for the surface and H_{GP} increases surface distortion which allows for agreement between adsorption and desorption scenarios. This relaxation allows H_{GP} and the hydrogen defect atom to occupy a favourable position and avoid repulsion between them, resulting in a stronger binding strength. Conversely, by restricting the surface or to the adsorbate (H_{GP}), the binding energy is significantly reduced, as a consequence.

5.3.2 Adsorption on top of a nitrogen defect

Nitrogen doping has been extensively studied in graphene/graphite systems because of its potential to modify the electronic and chemical properties of carbon-based materials.^{228–233} Nitrogen's similar atomic size to carbon and the five valence electrons make it behave similarly to carbon. Thus, it remains in the plane of the graphitic surface and causes minimal distortion within the π -electron system. However, substituting a nitrogen atom for a carbon atom will alter the charge distribution of surface carbon atoms and create an activated region in graphene/graphite.²³⁴



Figure 5.7: (Panel A): Optimized state of bi-layered graphite with N defect, (panel B): Bader charge distribution of nitrogen substituted graphite.

Additionally, doping with nitrogen can lead to different bonding configurations. These include *pyridinic*-N, *pyrrolic*-N, and *graphitic*-N. Here, we replaced a carbon atom with nitrogen in the hexagonal ring of graphite to create graphitic-N, where the N atom is sp^2 hybridized as shown in Fig. 5.7 panel A. In this configuration, each C atom in the graphene layer contributes one electron to the π -electronic system, while the substituted N contributes 2 electrons. This extra electron can enter into the π^* state, resulting in a π -doping effect. Thus, the N-defect exhibits n-type conductivity by contributing ~0.5 electrons to the graphite system, 233,235 as calculated by Bader charge analysis. Adsorption of hydrogen at the top of a nitrogen atom would be expected to give a strong covalent

N-H bond given the charge distribution between N and C as illustrated in Fig. 5.7 panel B.

Substituting nitrogen for carbon does not lead to noticeable distortion in the graphite surface as shown in Fig. 5.7-A. Indeed, the C-N bond length of 1.41 Å, is only slightly different from the C-C bond length of 1.42 Å. Similar to our studies of the H-defect we studied the effect of relaxation on our calculation by conducting **N-free** simulations where N was allowed to relax using either the TTT or FFT schemes. We also performed **N-fix** simulations where the entire surface, including nitrogen was not relaxed, using both TTT and FFT pathways. Here, we allowed lateral relaxation of H_{GP} in the TTT scheme and no relaxation for the FFT scheme. The potential energy curves red and blue obtained for the adsorption of H_{GP} on top of nitrogen for the FFT and TTT pathways are shown in Fig 5.8 panels A and B, respectively. The curves reflect the N-free and N-fix schemes, respectively. All the numerical data is reported in Table 5.3.



Figure 5.8: Potential energy curves for the adsorption of H_{GP} atop of an N defect in bi-layer graphite. Panel (A): With PBE-D3BJ using the FFT relaxation scheme. Inset shows the intermediate adsorption structure, panel (B): with PBE-D3BJ using the TTT relaxation scheme. Inset shows optimized structure for the adsorption of H_{GP} on top of a nitrogen atom defect.

Table 5.3: Physisorption energies (E_{ph}) , adsorption energies (E_a) , and energy barrier E^{\sharp} are all in eV, puckering of Nitrogen (D) and other three bonded atoms (N_p) are in Å for the adsorption of H_{GP} on top of the N defect in a bi-layer graphite system.

Defect	Scheme	PBE			PBE-D3BJ				
-	-	E_a	E^{\sharp}	D	E_a	E^{\sharp}	E_{ph}	D	
N (free)	TTT	-0.53	0.27	0.42	-0.58	0.20	-0.031	0.43	
N (free)	FFT	-0.42	0.28	0.40	-0.48	0.20	-0.034	0.41	
N (fix)	\mathbf{FFT}	1.20	1.36	-	1.16	1.30	-0.04	-	
N (fix)	FFF	1.20	1.36	-	1.16	1.30	-0.04	-	

Upon approaching the surface layer, within the TTT framework, the incoming H_{GP} first pushes nitrogen below the top layer's plane by 0.19 Å. However, upon closer approach of H_{GP} , nitrogen puckers out of the plane by ≈ 0.66 Å to accommodate H_{GP} . This causes neighbouring carbon atoms to be pulled out by ~ 0.14 Å. The puckering has an energy barrier of 0.2 eV, which is larger than that for the adsorption of H_{GP} on a carbon atom (0.16 eV) in a bare graphite system, as discussed in Chapter 4. However, otherwise, the structure and energetics of the adsorption process are similar. At the minimum energy geometry, an N-H_{GP} bond length of 1.05 Å is obtained with a binding strength of -0.58 eV and a C-N bond length of 1.50 Å.

Within the **FFT** framework, a reduced chemisorption of -0.48 eV is obtained with an energy barrier of 0.2 eV. Here, the minimum energy structure has a C-N bond length of 1.47 Å and an N-H bond of 1.06 Å, consistent with previous studies.^{231,236}

Relaxing nitrogen during the approach of H_{GP} leads to similar results as adsorption of H_{GP} on pristine graphite. Similarly, restricting relaxation of the graphite surface including the defect atom leads to metastable adsorption of H_{GP} in both the TTT and FFT schemes. These results are also in close agreement with previous studies carried out on a pure graphene surface.¹⁸⁰

5.3.3 Adsorption on top of an oxygen defect

Oxygen is the third most abundant element in the ISM after H and He and as such will be a likely candidate for substitutions in a graphite surface. After substitution of carbon with oxygen, the oxygen atom has moved below the graphite layer by 0.3 Å. As a consequence the three adjacent carbon atoms are pulled down by 0.12 Å as shown in Fig 5.9-A. This results a C-O bond length of 1.5 Å (AB and BC in Fig 5.9 panel A), which is slightly longer than a standard C-C bond in graphite due to the larger atomic radius of oxygen compared to carbon. Bader charge analysis shows that the electronegative oxygen atom pulls charge from the adjacent carbon atoms, resulting in an overall negatively charged oxygen (-0.91) and positively charged carbon atoms, as shown in Fig 5.9-B. However, since the oxygen atom already has 3 bonding partners and is forced in a sp^2 -like hybridization, forming an O-H_{GP} bond is expected to be unfavourable.



Figure 5.9: (Panel A): Optimized structure of oxygen defects within bi-layer graphite system. (panel B): Bader charge distribution of oxygen substituted graphite.

Our calculations indeed bear this out. Within PBE calculations introducing H_{GP} on top of the oxygen defect site causes the oxygen atom to sink to further into the plane by 0.12 Å, whilst the neighbouring carbon atoms pucker up by 0.03 Å in the FFT framework allowing only movement in the z-direction decreases puckering to 0.08 Å, since neighbouring carbon atoms are not allowed to move laterally. This results in an O-H bond of 2.34 Å and 2.48 Å for the TTT and FFT calculations, respectively, for the minimum energy structure (see in the inset of Fig. 5.10 panel A). The O-H bond length is significantly larger than the "natural" O-H bond length of 0.96 Å,²³⁷ in H₂O, indicating physisorption of H on the oxygen defect rather than chemisorption. This results in the binding energy of only -0.05 eV and -0.03 eV for the TTT and FFT scenarios, respectively. All the numerical data is summarized in Table 5.4.



Figure 5.10: Potential energy curves for the adsorption of H_{GP} at the top of oxygen defect. Panel (A): With PBE and the inset shows the intermediate structure for the adsorption of H_{GP} at the top of the oxygen defect. Panel (B): With PBE-D3BJ and the inset shows the minimum energy structure for the adsorption of H_{GP} at the top of oxygen defect.

Table 5.4: Adsorption energies (E_a) in eV, puckering of O(D) and other three bonded carbon atoms (N_p) are in Å for the adsorption of the H_{GP} atom on top of the O defect in a bi-layer graphite system.

Defect	Scheme		PBE		PBE-D3BJ		
-	-	E_a	D	N_p	E_a	D	N_p
Ο	TTT	-0.05	-0.12	0.03	-0.13	-0.13	0.03
0	\mathbf{FFT}	-0.03	-0.08	0.01	-0.11	-0.09	0.01

Furthermore, within the TTT framework, a closer approach of the H atom causes the oxygen defect to recede further into the surface, while the carbon atom bonded to oxygen puckers up. This leads to the formation of a weak C-H_{GP} bond (inset of Fig. 5.10 panel B). A similar effect is not found within the FFT relaxation scheme showing that lateral movement of adjacent carbons is crucial for this physisorption interaction to become apparent. Adding dispersion corrections to these calculations leads to qualitatively the same energy profile. However, the binding energy increased to more than double, as shown in Fig 5.10 panel B.

5.3.4 Adsorption on top of a silicon defect

In the interstellar medium, Silicon is the 5th most abundant element. Researchers have identified thirteen different silicon-containing molecules,²³⁸ including SiC, SiH₄, SiO, SiC₂, Si₂C, SiCN, SiNC, and SiS, among others. These molecules play a crucial role in the formation of complex organosilicon molecules like SiC₃ and SiC₄, ultimately leading to SiC on dust grains.^{239,240} Therefore, we have included it into our calculations here. Potential energy curves for the adsorption of H_{GP} at the top of puckered-up and puckered-down silicon defect in bi-layer graphite with FFT and TTT relaxation schemes is shown in Fig. 5.11 panels A and B, respectively. All the stationary points are summarized in Table 5.5.



Figure 5.11: Potential energy curves for the adsorption of H_{GP} on top of the Si-defect. Panel (A): With PBE-D3BJ in the FFT relaxation, panel (B): with PBE-D3BJ in the TTT relaxation, panel (C): Bader charge analysis for Si substituted graphite system, panels (D, E): optimized structure for bi-layer graphite with Si puckered-up and puckered-down, and panels (F and G): Minimum energy structures with adsorbed H atom on top of silicon puckered-up and puckered-down defect in bi-layer graphite.

Table 5.5: Adsorption energies (E_a) , energy barrier E^{\sharp} are in eV, puckering of Si (D) and other three bonded carbon atoms (N_p) are in Å for the adsorption of H_{GP} atom on top of Si defect in the bi-layer graphite system. \uparrow and \downarrow indicate the positive and negatively puckered silicon.

Defect	Scheme		P	BE	PBE-D3BJ			
-	-	E_a	E^{\sharp}	D	N_p	E_a	D	N_p
Si (\uparrow)	TTT	-2.90	-	0.12	0.04	-2.93	0.11	0.04
Si (\uparrow)	\mathbf{FFT}	-2.89	-	0.12	0.04	-2.91	0.12	0.04
Si (\downarrow)	TTT	-1.01	0.04	-0.02	-0.01	-1.06	-0.02	-0.01
Si (\downarrow)	FFT	-0.94	0.058	-0.02	-0.01	-1.03	-0.02	-0.01

When silicon replaces carbon in the sp² hybridized structure of graphene, the structure of the material changes. This is because the atomic radius of Si is larger than that of C. Thus, Si-doped graphene shows significant distortion of the geometry, with the Si atom receding 1.16 Å below the top carbon plane and 3.3 Å above the bottom plane. The bond length between Si and neighbouring carbon atoms is 1.75 Å, which is longer than the C-C bond in graphene (1.42 Å). The Bader charge analysis in Fig 5.11 panel C shows a significant charge difference between Si and neighbouring carbon atoms (a similar charge distribution is obtained for both puckered-up and puckered-down Si-defect), *i.e.* a charge transfer from the defect to its carbon neighbours. This results in a positively charged Si atom (1.15) and negatively charged C atoms. As a result, the silicon will be an electron-deficient site in the graphite surface, making it a likely site of attack for H. The lowest energy structure has Si puckered down as noted above. However, Si could also puckered-up. This is just 0.01 eV higher in energy. However, this will make the Si atom more available for reaction

5.3

with H.

Figure 5.11 (panels D and F) shows the optimized bi-layer graphite system with Si atoms in both puckered-up and puckered-down states. For both sites, the adsorption of H on top of the defect was considered, and similar energetic profiles were obtained for both FFT and TTT relaxation schemes, with a negligible energy difference as shown in Fig 5.11 (panels A and B). Fig. 5.11 only shows our PBE-D3BJ results. The PBE results (without dispersion) are very similar and for reasons of clarity of presentation have been omitted. However, the energy values for all relaxation schemes and functionals used are summarized in Table 5.5.

When an out-of-plane Si defect is present, chemisorption of hydrogen on top of the Si defect is barrierless without any evidence of physisorption. To form a Si-H bond the Si defect further puckers out by 0.12 Å. As a consequence three carbon atoms bonded to the silicon atom are pulled out of the plane by ≈ 0.04 Å. The resulting Si-H_{GP} bond has a length of 1.57 Å and strength of -2.93 eV. This is longer and weaker bond than for Si-H in SiH₄ 1.48 Å and 4.07 eV, respectively.²⁴¹ When the H atom approaches the surface, the Si atom moves into the graphene plane resulting in a significant increase in energy.

In the optimized Si-down state, the Si atom prefers to stay close to the top layer, 1.17 Å from the top layer. Introducing a hydrogen atom causes the Si defect to recede slightly by 0.018 Å. The resulting Si-H_{GP} bond length is 1.63 Å, with a binding energy of -0.94 eV. In addition, chemisorption of H_{GP} occurs through an energy barrier of 0.04 eV.



Figure 5.12: Diffusion of Si defect atom from puckered-up to puckered-down state in bi-layer graphite system.

Comparing the potential energy profiles for the adsorption of H_{GP} at the top of a silicon defect for either puckered state, it is evident that in the puckered-up state, the silicon atom defect site is more active towards adsorption of H_{GP} . Conversely, when the silicon is moved through the plane (*i.e.* puckered down) adsorption is weaker. Moreover, because of the difference in the size of carbon (0.7 Å) and silicon atom (1.1 Å), diffusion of silicon atom

from the puckered-up state to puckered-down state adds a significant distortion within the graphite surface. As a consequence, an energy barrier of 2.76 eV is obtained as shown in Fig. 5.12.

However, in comparison to the puckered-up state where the defect site is favourable for the adsorption of H_{GP} . On the other hand, in puckered-down state edges open up for the adsorption of H_{GP} at the *ortho* site relative to the defect. This effect is discussed in sections 5.4 and 5.5.

5.3.5 Adsorption on top of an iron defect

Substitution of iron into the graphite plane causes significant distortion. Like silicon, Fe can take up two positions within the graphite layer, pucker-down and puckered-up as noted above. In the optimized structure for Fe puckered-down, the Fe atom is located ~1.22 Å below the top layer and 3.4 Å above the bottom layer (Fig. 5.13 panel C). The three neighbouring carbon atoms are depressed by 0.3 Å. In the other form Fe can be puckered-up and stay at 1.07 Å above the top layer of the graphite surface (Fig. 5.13 panel F). This is due to the large difference in atomic radius between Fe (1.26 Å) and carbon (0.7 Å). However, the resulting C-Fe bond length of 1.76 Å remains the same for both positively and negatively puckered states, consistent with previous studies.^{226,227} Potential energy curve for the adsorption of H_{GP} at the top of Fe in puckered-down and puckered-up state with FFT and TTT relaxation scheme is given in Fig. 5.13 panels A and B, respectively. All the numerical data is reported in Table 5.6.



Figure 5.13: Potential energy curves for adsorption of H_{GP} at the top of Fe defect in bi-layer graphite. Panel (A): With PBE-D3BJ in FFT relaxation scheme, panel (B): with PBE-D3BJ in TTT relaxation scheme. Panel (C): Optimized structures for bi-layer graphite with Fe puckered-down, panel (D): intermediate structure for H_{GP} adsorption atop of the Fe in puckered-down state, and panel (E): optimized structure for H_{GP} adsorption atop of the Fe defect in puckered-down state, panel (F): Optimized structures for bi-layer graphite with Fe puckered-up, and panel (F): optimized structure of H_{GP} adsorption atop of the Fe in puckered-up, state in bi-layer graphite system.
Table 5.6: Adsorption energies (E_a) and energy barrier E^{\sharp} are in eV, puckering of Fe (D) and other three bonded carbon atom (N_p) are in Å for adsorption of H_{GP} atom on the top of Fe defect in bi-layer graphene system.

Defect (X)	Scheme		PB	Е		PB	E-D3E	зJ
-	-	E_a	D	N_p	E^{\sharp}	E_a	D	N_p
Fe (\uparrow)	TTT	-2.52	0.20	0.07	-	-2.55	0.20	0.07
$\operatorname{Fe}(\uparrow)$	\mathbf{FFT}	-2.51	0.20	0.08	-	-2.55	0.19	0.08
Fe (\downarrow)	TTT	-1.37	0.04	0.07	0.05	-1.44	0.04	0.05
$\overline{\text{Fe}}(\downarrow)$	FFT	-1.33	0.03	0.06	0.05	-1.40	0.06	0.05

Introducing H_{GP} on top of the defect site (puckered-down) within FFT scheme leads to the formation of an Fe-H bond of 1.52 Å with binding energy of -1.4 eV. Adding more relaxation to the system in the TTT framework causes the defect to recede further by 0.06 Å. As shown in Fig. 5.13 panel D, this leads to the formation of a C-H bond (1.08 Å) as an intermediate, which then leads to the formation of a Fe-H bond of 1.53 Å as the minimum energy structure (see Fig. 5.13-E). Here, a C-H interaction of 1.61 Å is also observed with the three surrounding carbon atoms. The binding energy of -1.44 eV is obtained by blue lines as shown in Fig 5.14 panel B. Both more restricted relaxation scheme as well as the omission of van der Waals interactions have very little effect on the overall profile for this reaction.

On the other hand, in the positively puckered iron defect system, H_{GP} is adsorbed barrierlessly onto the defect site, resulting in the formation of a Fe-H bond with a bond length of 1.57 Å(Fig. 5.13-G), similar to the Fe-H (1.56) bond in Mg₂FeH₆.²⁴² An identical binding energy of -2.55 eV is obtained for both the TTT and FFT schemes. As with silicon, the substitution of Fe in puckered-down state is found as energetically more favourable than the puckered-up state with an energy difference of 0.16 eV as discussed in section 5.2. In contrast, as with silicon the adsorption of H_{GP} in the puckered-up state has a stronger adsorption energy -2.55 eV compared to the puckered-down state (-1.44 eV). Therefore, on the basis of substituion of Fe in puckered up and down scenario and adsorption of H_{GP} in puckered up and down scenario, both forms of defects are feasible. However, based on silicon diffusion results, diffusion of iron from puckered-up to puckered-down state will be an activated process because of the difference in atomic radii between iron and carbon.

5.3.6 Adsorption on top of magnesium defect

Like for Si and Fe the larger atomic radius of Mg (1.45 Å) compared to carbon (0.7 Å), is expected to cause significant surface distortion. As discussed in section 5.2, the geometry obtained by Mg in puckered down state is 0.31 eV smaller in energy than Mg in puckered up state. On the basis of binding strength we have considered only Mg puckered-down geometry for our further calculations. In the optimized puckered-down state, Mg is found to move below the plane of the top layer of the graphite surface by 1.78 Å. It sits in between the two graphene layers, forming a C-Mg bond of 2.13 Å with an \angle CMgC of 76.4° with the top layer, as shown in the inset of Fig. 5.14-A. This causes a hollow in the graphene layer and opens up edges. This makes the edge sites more active than the defect site. Potential energy curves for the adsorption of H_{GP} on top of negatively puckered Mg atom with FFT and TTT relaxation schemes is shown in Fig. 5.14 panel A. All the numerical data is reported in Table 5.7.



Figure 5.14: Panel (A): Potential energy curves for adsorption of H_{GP} at the top of Mg defect with PBE-D3BJ in FFT and TTT relaxation scheme and the inset shows optimized structure of Mg substituted graphite surface, panel (B): minimum energy structure for H_{GP} adsorption atop of Mg defect with FFT scheme, and panel (E): optimized structure for H_{GP} adsorption atop of negatively puckered Mg defect in bi-layer graphite system.

Table 5.7: Adsorption energies (E_a) in eV, puckering of Mg(D), and other three bonded atoms (N_p) are in Å for adsorption of H_{GP} atom on the top of Mg defect in bi-layer graphite system.

Defect	Scheme		PBE		PBI	E-GD3	BJ
-	-	E_a	D	N_p	E_a	D	N_p
Mg (\downarrow)	TTT	-3.30	0.10	0.17	-3.33	0.10	0.16
Mg (\downarrow)	\mathbf{FFT}	-2.63	0.08	0.14	-2.67	0.09	0.14

The energy profile for the adsorption of a hydrogen atom at the top of a magnesium defect in Fig. 5.14-A demonstrates the barrierless adsorption of H_{GP} atop the Mg defect. This requires the three bonded carbon atoms to pucker up by ~ 0.17 Å, leading to the formation of an Mg-H bond of 1.78 Å along with a C-H bond of 1.08 Å that causes Mg to move further down by -0.08 Å as shown in Fig. 5.14-B. The Mg-H bond length obtained in this is slightly shorter than the Mg-H bond length in MgH₂ (1.87 Å).²⁴³ As expected the C-H bond is energetically stronger than the MgH bond, lateral movement may lead to the formation of a C-H bond instead of MgH, as shown in Fig 5.14 panel C.

5.4 Adsorption of a hydrogen atom *ortho*, *meta* & *para* to the substitution

So far we have concentrated on the adsorption of a hydrogen atom on top of a defect. However, it is worth noting that defects on a surface may not only enhance the adsorption of hydrogen atoms directly on the defect site but also influence the electronic structure of the surrounding area, making adsorption or desorption more favourable near defect sites. To explore this further, we conducted calculations on the adsorption of hydrogen atoms at the carbon atoms ortho, meta, and *para* to the original defect. These locations are designated as "active sites" (as shown in Fig 5.15). The TTT and FFT relaxation schemes are used for the adsorption of H_{GP} at ortho, meta, para sites. For TTT, we fully relaxed the active site (C^*) and its three bonded atoms and included lateral relaxation of H_{GP} . For FFT, we only relaxed the z-coordinates of the active site and its neighbouring bonded atoms, with H_{GP} held completely fixed. For H_{GP} adsorption at the ortho carbon position, both the defect and two adjacent carbon atoms were fully relaxed. For adsorption at the *meta* and *para* positions, all four



Figure 5.15: Scheme for the adsorption of H_{GP} at the carbon atoms ortho, meta and para relative to the defect atom within the same ring.

adjacent carbon atoms were relaxed. As stated above all the calculations were performed with and without empirical dispersion correction (D3-BJ). For most defects, similar potential energy curves were obtained for both cases. Therefore, we will only discuss the dispersion corrected results below unless stated otherwise. However, all other results will be summarized in the respective tables.

5.4.1 Adsorption of H_{GP} ortho, meta & para to a hydrogen defect

Potential energy curves for the adsorption of H_{GP} at the ortho, meta & para site to the hydrogen defect using the FFT and TTT schemes are shown in Fig. 5.16 panels A and B, respectively. All the stationary points are summarized in Table 5.8. In section 5.2, we discussed that the substitution of a carbon atom with hydrogen on a surface creates a hollow and exposes edges on the three adjacent ortho carbon atoms. These edges have a significant impact on the adsorption of H_{GP} at the ortho-carbon atom. Due to the consideration of the same active site (C^*) was used for the adsorption of H_{GP} at the top of the defect (in section 5.3.1) the same energy profile as discussed in section 5.3.1 and shown in Fig. 5.6-B by C^{*}-free(TTT) and C^{*}-free(FFT) schemes was obtained for adsorption at the ortho site. Within the FFT framework, a small barrier of 0.03 eV is obtained. Adding the effect of empirical dispersion and surface relaxation results barrierless adsorption of H_{GP} at the ortho site within both FFT and TTT frameworks as shown in Fig. 5.16 panels A and B, respectively. Within TTT framework when H_{GP} is laterally relaxed, both hydrogen atoms move down into the surface, resulting in an H-H_{GP} interaction of 1.2 Å as shown in the inset of panel B. The optimized structure for the adsorption of H_{GP} at the ortho site is shown in panel C. This show that chemisorption of H_{GP} causes the hydrogen defect to recede below the surface, creating space for H_{GP} .



Figure 5.16: Potential energy curves for the adsorption of H_{GP} at the ortho, meta and para carbon atom positions relative to the hydrogen defect in a bi-layer graphite system. Panel (A): with PBE-D3BJ in FFT scheme, panel (B): with PBE-D3BJ in TTT scheme and the inset shows an intermediate structure for H_{GP} adsorption at the ortho position, Panel (C): Optimized structure of the adsorption of H_{GP} at the ortho carbon position to the defect site, panel (D): optimized structure of H_{GP} adsorption at the meta position, and panel (F): optimized structure for H_{GP} adsorption at the para position.

Table 5.8: Binding energies (E_a) , activation energy E^{\sharp} , physisorption energy (E_{ph}) are all in eV, for the adsorption of the H_{GP} atom at the ortho, meta, and para carbon atom sites relative to the hydrogen defect in the bi-layer graphite system.

Defect			PB	Е					PB	E-D3B	J		
-	orti	ho	meta para			$\cdot a$	or tho		meta			para	
-	E_a	E^{\sharp}	E_a	E^{\sharp}	E_a	E^{\sharp}	E_a	E_a	E_{ph}	E^{\sharp}	E_a	E_{ph}	E^{\sharp}
H(FFT)	-2.80	0.03	-0.69	0.14	-1.88	0.09	-2.85	-0.71	0.08	0.03	-1.90	0.04	0.03
H(TTT)	-3.89	-	-0.73	0.13	-2.09	0.08	-2.93	-0.77	-0.03	0.08	-2.13	-0.03	0.03

In contrast, the adsorption of H_{GP} at the meta and para carbon atom sites is an activated process. At these sites for the adsorption of H_{GP} , C^{*} is required to pucker from the graphite surface, resulting in more distortion in the surface and creating an energy barrier. In particular adsorption of H_{GP} at the meta site result in a higher distortion than the para site adsorption as shown in the optimized structure of meta and para adsorption in panels D and E, respectively. This is due to the involvement of the carbon atom bonded to the hydrogen defect in the relaxation scheme at the meta site adsorption, but this is not the case for the para site adsorption. By incorporating the effect of empirical dispersion this energy barrier reduced significantly. Moreover, adding more relaxation to the calculation framework *i.e.* from FFT to TTT this energy barrier is further reduced and a stronger binding energy of H_{GP} is obtained at both meta and para carbon atoms sites. All these energies are summarized in Table 5.8.

5.4.2 Adsorption of H_{GP} ortho, meta & para to a nitrogen defect

Introduction of a nitrogen defect in the graphite has a significant effect on the charge distribution across the surface, as discussed in section 5.3.2. In particular, according to Bader charge analysis, there is a noticeable depletion of charge from the *ortho* and *para* carbon atoms, and an accumulation of charge on the *meta* carbon atom. This obviously will affect the adsorption of H_{GP} , as shown through the potential energy curves in Fig. 5.17. All the numerical data is reported in Table 5.9.



Figure 5.17: Potential energy curves for H_{GP} adsorption at the ortho, meta and para carbon atom positions relative to the nitrogen defect in a bi-layer graphite system. Panel (A): With PBE-D3BJ in FFT scheme and the inset shows optimized structure for the adsorption of H_{GP} at the ortho carbon atom, panel (B): with PBE-D3BJ in TTT scheme and the inset shows optimized structure for the adsorption of H_{GP} at the meta carbon atom.

Table 5.9: Adsorption energies (E_a) , activation energy E^{\sharp} , and physisorption energy (E_{ph}) are all in eV, for the adsorption of H_{GP} atom at the ortho, meta, and para sites relative to the nitrogen defect in bi-layer graphite system.

Defect			PE	BΕ						PBI	E-GD3E	3J			
-	ort	ho	$\begin{array}{c c c c c c c c c c c c c c c c c c c $				ortho			meta			para		
-	E_a	E^{\sharp}	E_a	E^{\sharp}	E_a	E^{\sharp}	E_a	E_{ph}	E^{\sharp}	E_a	E_{ph}	E^{\sharp}	E_a	E_{ph}	E^{\sharp}
N (FFT)	-1.71	0.08	-1.14	0.11	-1.55	0.08	-1.74	-0.04	0.001	-1.17	-0.03	0.04	-1.59	-0.03	0.01
N (TTT)	-1.80	0.07	-1.2	0.11	-1.63	0.08	-1.82	-0.04	0.001	-1.22	-0.03	0.04	-1.65	-0.03	0.01

Comparison of Fig. 5.17 panels A and B show that adsorption at all sites is activated with a slightly higher energy barrier of 0.04 eV at the *meta* site in Fig. 5.17 panel A for the FFT relaxation scheme and of 0.04 eV in Fig. 5.17 panel B for TTT relaxation scheme as outlined in Table 5.9. This barrier is weakly dependent on the relaxation scheme used but dependent on the surface distortion and van der Waals interaction, which reduce the barrier by 0.07 eV. Adsorption of H_{GP} at the *ortho* carbon leads to puckering up of the N defect by 0.2 Å with C* to accommodate the incoming hydrogen atom. C* moves out of the surface by ~ 0.75 Å. As a consequence, the C-N bond length changes from 1.41 Å to 1.49 Å, while the C-C bond changes from 1.42 to 1.51 Å. The potential energy profile for the adsorption of H_{GP} at the top of the *para* carbon is similar to the adsorption at the *ortho* carbon, but the final adsorption energy is 0.17 eV smaller. Here, similar structure of the surface is found as well, with the *para* carbon atom puckering of 0.75 Å along with the three bonded atoms, which move by 0.2 Å. A C-H bond of 1.49 Å is formed, with the change in C-C bond length from 1.42 to 1.51 Å.

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The *meta* site is clearly much less favourable, with a higher barrier and smaller adsorption energy. On the other hand, structurally a similar minimum energy geometry is found. The omission of van der Waals interactions leads to a small change in the potential energy curves and structural data with the major change in the disappearance of the physisorption well as shown in Fig. 5.17 panels A and B.

5.4.3 Adsorption of H_{GP} ortho, meta & para to an oxygen defect

In section 5.3.3, it was noted that oxygen prefers to pucker downwards by 0.3 Å upon adsorption of hydrogen, whilst maintaining sp² hybridization as evidenced by the three equivalent C-O bonds. This would open up edges at the *ortho* carbon atom sites. Conversely, this suggests that the C-O bond is relatively weak, which could lead for restructuring upon H_{GP} adsorption, *ortho* to the oxygen defect. As shown in Fig. 5.9-B, the Bader charge distribution does not show a significant redistribution of charge following oxygen insertion into the surface. The potential energy curves for all three adsorption sites and two relaxation schemes for the PBE-D3BJ calculations are shown in Fig. 5.18-A and 5.18-B. All energetic data is summarized in Table 5.10. When H_{GP} is introduced on top of the *ortho* carbon atom, the C^{*} atom must pucker up by 0.9 Å and 1.1 Å in FFT and TTT systems.



Figure 5.18: Potential energy curves for H_{GP} adsorption at the ortho, meta and para carbon atom sites in the presence of an O-defect in a bi-layer graphite system. Panel (A): With PBE-D3BJ in FFT scheme, panel (B): with PBE-D3BJ in TTT scheme, panel (C, D, and E): optimized structure for the adsorption of H_{GP} at the ortho, meta, and para.

In both cases, a C-H bond of 1.11 Å is formed at the minimum energy stage, and a C^{*}-O bond of 1.59 Å and 1.82 Å is observed in the FFT and TTT systems, respectively. Exclusion of dispersion corrections result the chemisorption of H_{GP} with a binding energy of -2.2 eV and -2.63 eV with an energy barrier of 0.07 eV and 0.02 eV in case of the FFT and TTT relaxation schemes, respectively. Inclusion of the dispersion correction reduces the barrier to 0.03 eV and also makes a physisorption well appear, while barrierless adsorption is observed in the TTT calculation setup. This clearly shows the impact of the defect atom, dispersion correction, and relaxation in the system. The optimized structure

Defect			PB	Е					PBE-C	GD3BJ		
-	ortl	ho	met	ta	par	a	orth	10		meta		para
-	E_a	E^{\sharp}	E_a	E^{\sharp}	E_a	E^{\sharp}	E_a	E^{\sharp}	E_a	E_{ph}	E^{\sharp}	E_a
O(FFT)	-2.2	0.07	-0.77	0.13	-1.43	0.07	-2.22	0.03	-0.8	-0.05	0.04	-1.46
O(TTT)	-2.63	0.02	-0.83	0.11	-1.51	0.07	-2.67	-	-0.85	-0.04	0.03	-1.53

Table 5.10: Adsorption energies E_a , activation energy E^{\sharp} , and physisorption energy E_{ph} are all in eV, for the adsorption of H_{GP} atom at the ortho, meta, and para sites relative to the oxygen atom defect in the bi-layer graphite system.

for the adsorption of H_{GP} at the ortho site is shown in Fig. 5.18-C.

However, when H_{GP} is adsorbed at the *meta* carbon atom site, the oxygen atom is fixed in position and not relaxed, causing the *meta* carbon atom to pucker out of the graphene plane by ~ 0.52Å and 0.57 Å within the FFT and TTT schemes, respectively. This distortion also affects the two neighbouring carbon atoms, causing them to pucker out of the graphene plane by 0.1 Å, while the third bonded carbon, *ortho* to the oxygen defect puckers by ~0.04 Å. This distortion leads to higher energy barriers of 0.13 eV and 0.11 eV within the FFT and TTT relaxation schemes. Including the effect of dispersion correction this energy barrier reduced significantly to 0.04 eV and 0.03 eV within the FFT and TTT relaxation schemes, respectively. The presence of the oxygen defect weakens the binding of the hydrogen atom at the *meta* site by introducing more distortion because of the changes in the electronic structure.

In contrast, there is less distortion at the *para* carbon atom than at the *meta* carbon atom. C^{*} still puckers by ~ 0.77 Å, causing the other three bonded carbon atoms to pull up by 0.21 Å. Additionally, a smaller energy barrier of 0.07 eV is found with a higher adsorption energy of -1.43 eV and -1.51 eV in FFT and TTT relaxation schemes, respectively. Similar to the above results inclusion of empirical dispersion results the barrierless adsorption of H_{GP} at the *para* site with binding energy of -1.46 eV and -1.53eV with FFT and TTT schemes, respectively and the optimized geometry for this is shown in panel E. Interestingly, adding more relaxation to the surface carbon atoms and H_{GP} in the TTT framework makes the *ortho* carbon atom site more favourable for adsorption than the *meta* and *para* carbon atom sites.

5.4.4 Adsorption of H_{GP} ortho, meta & para to a silicon defect

To examine the adsorption behaviour of H_{GP} at the *ortho*, *meta*, and *para* carbon atoms in the presence of a silicon defect, we considered both optimized silicon defect geometries. Thus, the defect can be puckered up or down in a bi-layer graphite system. The potential energy curves for all three adsorption sites and two relaxation schemes in Si puckereddown and Si puckered-up PBE-D3BJ are shown in Fig. 5.19 and Fig. 5.20, respectively. All the important stationary points are summarized in Table 5.11.

As stated in section 5.3.4, in the lowest energy geometry, the silicon atom moves down by a distance of 1.16 Å below the plane of the top layer, pulling down three bonded carbons by 0.33 Å and creating a hollow in the surface. This will affect the subsequent binding of H_{GP} , particularly, at the *ortho* site. However, its effect should depend upon the precise relaxation scheme used. Considering the FFT relaxation schemes and *ortho* adsorption first, we find that C^{*} puckers by 0.35 Å and the neighbour carbon atoms by only ~0.03 Å. This structural reorganization leads to an energy barrier of 0.08 eV as shown in Fig. 5.19 panel A. Furthermore, the silicon atom moves down by -1 Å, which leads to even more distortion in the surface. This causes the C*-Si bond to lengthen to 1.97 Å. As a result, a small binding energy of -0.63 eV was obtained. However, allowing lateral relaxation of H_{GP} and fully relaxing the active site and the bonded atom using the TTT relaxation scheme, means the incoming hydrogen atom tilts over the hollow towards the Si atom at an angle of 10° (Fig 5.19 panel B). The decrease in surface distortion leads to a stronger C-H bond with a binding energy of -1.97 eV.



Figure 5.19: Potential energy curves for the adsorption of a hydrogen atom at ortho, meta and para position relative to silicon defect (puckered-down) in bi-layer graphite system. Panel (A): with PBE-D3BJ in FFT scheme, panel (B): with PBE-D3BJ in TTT scheme and the inset shows optimized structure for the adsorption of H_{GP} at the ortho carbon atom.

As expected, the presence of the hollow left by Si in the surface makes the *ortho* site more favourable for binding than either the *meta* or *para* sites. Indeed, in the absence of an edge effect for the FFT relaxation, the energy barrier increased to 0.09 eV at the *meta* and *para* positions. The resulting binding energies were smaller as well, -0.75 eV and -1.02 eV for *meta* and *para* adsorption, respectively. Additional relaxation in the TTT relaxation schemes has less of an effect here as expected, with similar barrier heights and a slight increase in the binding energy. This effect is also apparent when looking at surface distortion. At the *meta* position in the FFT relaxation schemes C^* puckers out of the surface by 0.42 Å, and at the *para* adsorption, it puckers by 0.35 Å, with additional puckering of the three neighbouring carbon atoms by 0.04 Å. In the TTT scheme, this changes to 0.4 Å and 0.3 Å for the *meta* and *para* carbon atoms, respectively. It is noted that in both relaxation schemes, the silicon defect does not relax, so that the distortion stays local, leading to smaller binding energies than otherwise would be obtained.

Table 5.11: Adsorption energies (E_a) , activation energy E^{\sharp} , physisorption energy (E_{ph}) are all in eV, for the adsorption of H_{GP} atom at ortho, meta, and para carbon atom site relative to silicon defect in bi-layer graphene system.

Defect			PI	ЗE						PB	E-GD3E	ЗJ			
-	ortl	ho	me	ta	a para			ortho			meta			para	
-	E_a	E^{\sharp}	E_a	E^{\sharp}	E_a	E^{\sharp}	E_a	E_{ph}	E^{\sharp}	E_a	E_{ph}	E^{\sharp}	E_a	E_{ph}	E^{\sharp}
Si $(\downarrow)(FFT)$	-0.59	0.08	-0.73	0.15	-1.01	0.16	-0.63	-0.04	0.01	-0.75	-0.02	0.09	-1.02	-0.02	0.09
Si $(\downarrow)(TTT)$	-1.93	0.03	-0.96	0.16	-1.13	0.15	-1.97	-	-	-1.00	-0.02	0.09	-1.16	-0.02	0.09
$Si(\uparrow)(FFT)$	-0.85	-	-0.26	0.17	-1.36	0.04	-0.92	-	-	-0.29	-0.06	0.11	-1.39	-	-
$Si(\uparrow)(TTT)$	-2.88	-	-0.65	0.12	-1.45	0.024	-2.93	-	-	-0.67	-0.06	0.03	-1.48	-	-



Figure 5.20: Potential energy curves for the adsorption of a hydrogen atom at the ortho, meta and para carbon atom positions relative to the silicon defect (puckered-up) in bi-layer graphite system. Panel (A): With PBE-D3BJ in FFT scheme, panel (B): with PBE-D3BJ in TTT scheme and the inset shows the optimised structure for the adsorption of H_{GP} at the para carbon atom, panel (C): intermediate structure for the adsorption of H_{GP} at the ortho carbon atom with FFT scheme, panel (D): intermediate structure for the adsorption of H_{GP} at the ortho carbon atom with TTT scheme, panel (E): optimised structure for the adsorption of H_{GP} at the meta carbon atom.

As noted before in section 5.3.4, the silicon atom puckers out of the surface and creates a convex site for adsorption. Whilst this is higher in energy, the formation history of the defect may make this state accessible, because of the high barrier for the interconversion of the puckered-up to the puckered-down state.

All potential energy curves are given in Fig. 5.20 with important data in Table 5.11. As shown above, in the puckered-down state adsorption on the *ortho* site is activated, because of the creation of a hollow site by the Si defect. In contrast, when the Si atom is puckered-up, the *ortho* site shows non-activated adsorption of H_{GP} in both the FFT and TTT relaxation schemes. In the TTT relaxation scheme, the Si atom puckers up by 0.22 Å to accommodate H_{GP} , which lifts the *ortho*-carbon atom by 0.15 Å. This creates a global minimum and a binding energy of -2.93 eV where the H atom forms an **Si-H** bond with a length of 1.43 Å, similar to the bond length in silane H_3SiH (1.49 Å)²⁴⁴ and not a C-H bond. Hereby, it can be constructed as bending towards the *ortho* carbon atom, which is at a distance of 2.65 Å, as shown in Fig 5.20 panel B. This leads to depression of the active site C^{*} by 0.74 Å, which in turn pulls down the other two bonded carbon atoms by 0.3 Å and the Si defect by 0.38 Å (see Fig. 5.20 panel D). As the H atom moves further towards the *ortho* carbon atom, the surface distorts, and the Si-H bond dissociates, resulting in a plateau (P). Thus, rather than binding on the *ortho* site, here H_{GP} binds to the puckered-up Si.

In the FFT scheme, the adsorption of an H atom follows the same qualitative path as in the TTT scheme. However, here C^{*} and Si are only allowed to relax in the z-direction, while H_{GP} remains fully rigid, the Si atom puckers up by 0.058 Å to form a Si-H bond as

shown in Fig 5.20 panel C. The loss of lateral relaxation leads to a smaller binding energy of -0.92 eV rather than -2.93 eV in the TTT scheme.

The Si atom has less effect on introducing H_{GP} at the *meta* and *para* carbon sites, given the distance between Si and these carbon sites and the fact that the Si atom is fixed. Therefore, an activated adsorption is expected at the *meta* and *para* carbon atoms as in the puckered-down scenario. Indeed, for *meta* adsorption a barrier of 0.11 eV is found for the FFT relaxation scheme and 0.03 eV for the TTT relaxation scheme. However, for adsorption at the *meta* site, C^{*} needed to pucker by 0.76 Å and 0.52 Å for the FFT and TTT schemes, respectively.

On the other hand, for the *para* site, C^{*} lifted up by 0.7 Å in both scenarios, but no major other distortion in the surface was observed. Therefore, no barrier was found for adsorption in the *para* position in either relaxation scheme. It is noted that, as shown in Table 5.11 this is dependent on the inclusion of dispersion effects. However, these results show that surface distortion cannot be viewed in isolation from electronic effects in predicting the presence of a barrier. As Si is electropositive, the carbon atom becomes more electronegative and more active, leading to the barrierless adsorption of H_{GP} at the *para* position.

5.4.5 Adsorption of H_{GP} ortho, meta & para to an iron defect

In the case of an iron defect, we considered both optimized geometries *i.e.*, with Fe puckered-down and Fe puckered-up, since either could be accessible given a specific formation history. We will discuss the case of Fe puckered-down first. The PECs for this are shown in Fig. 5.21 panels A and B with relevant numerical data in Table 5.12. Section 5.3.5 discusses how an iron defect site on the surface of the material recedes by 1.22 Å, creating a hollow space that can be expected to be important for the adsorption of H_{GP} at the *ortho* position to the defect. The FFT scheme shows activated adsorption at all three sites with similar binding energies, as illustrated by the potential energy curves in Fig 5.21 panel A. However, due to the presence of the Fe defect, the *ortho* carbon atom site shows a reduced energy barrier, with the formation of a C-H bond measuring 1.13 Å, at the minimum energy site. At the minimum energy geometry, C^{*} is puckered up by 0.3 Å and Fe is puckered down further to 1.2 Å below the surface plane. Furthermore, the effect of empirical dispersion significantly reduces the energy barrier at all sites, as shown in Table 5.12.

On the other hand, the TTT calculation setup as shown in Fig. 5.21-B, where more relaxation is given to the surface and H_{GP} atom, leads to enhanced C^{*} puckering to 0.77 Å, whereas the Fe defect moves further into the surface by 0.18 Å. This resulted in an increase in the C-Fe bond length from 1.76 Å to 1.9 Å. Additionally, the incoming hydrogen atom's lateral relaxation allows it to bend over the iron atom at an angle of 12° with a Fe-H distance of 2.54 Å. As a consequence the overall binding energy of *ortho* adsorption increases to -2.33 eV and the adsorption becomes barrierless.

For the *meta* and *para* carbon atoms sites, which are bonded to only three other carbon atoms and are two and three bonds away from the Fe defect, respectively, the effect of the defect and relaxation was less. This is apparent from the fact that similar curves were obtained for both relaxation schemes. It is worth noting that inclusion of dispersion had the largest influence on barrier heights as is clear from Table 5.12.



Figure 5.21: Potential energy curves for H_{GP} adsorption at the ortho, meta and para carbon atoms site with Fe defect puckered down, panel (A): With PBE-D3BJ in FFT scheme, panel (B): with PBE-D3BJ in TTT scheme and the inset shows an optimized structure for the adsorption of H_{GP} at the ortho carbon atom.

Table 5.12: Adsorption energies (E_a) , activation energy E^{\sharp} , and physisorption energy (E_{ph}) are all in eV, for the adsorption of H_{GP} atom at the ortho, meta, and para carbon atom sites relative to the iron defect in a bi-layer graphite system.

Defect			PB	E						PB	E-GD3E	BJ			
-	ortl	10	me	ta	pai	ra		ortho			meta			para	
-	E_a	E^{\sharp}	E_a	E^{\sharp}	E_a	E^{\sharp}	E_a	E_{ph}	E^{\sharp}	E_a	E_{ph}	E^{\sharp}	E_a	E_{ph}	E^{\sharp}
$Fe(\downarrow)(FFT)$	-1.16	0.09	-1.16	0.11	-1.17	0.12	-1.17	-0.04	0.01	-1.21	-0.03	0.07	-1.20	-0.04	0.08
$Fe(\downarrow)(TTT)$	-2.28	0.11	-1.35	0.16	-1.28	0.16	-2.33	-0.02	-	-1.38	-0.04	0.08	-1.30	-0.04	0.08
$Fe(\uparrow)(FFT)$	-1.71	-	-0.81	-	-1.07	0.07	-1.74	-	-	-0.83	-	-	-1.09	-	-
$Fe(\uparrow)(TTT)$	-2.52	-	-1.06	0.03	-1.19	0.04	-2.56	-	-	-1.10	-	-	-1.09	-	-

We also examined the adsorption of H_{GP} at meta and para carbon atom sites using both FFT and TTT setups, with additional lateral relaxation of the Fe atom. In both cases, a similar energy profile was observed, as earlier for the TTT scheme. We assume that this is because the edge effect is more effective at the ortho carbon atom site than the other two carbon atoms, which are further away. It is interesting to note that the adsorption of H_{GP} at the ortho, meta, and para carbon atoms in the presence of a negatively puckered iron atom (within FFT) exhibits a similar pattern to that of the pristine graphite surface, as discussed in Chapter 4.

As noted above, we also considered the Fe puckered-up geometry. The PECs for this are shown in Fig. 5.22 with important data summarized in Table 5.12. As is clear from comparing Fig. 5.22 to Fig. 5.20, there are many similarities with the Si puckered-up scenario, including the differential effect of relaxation on adsorption at the *ortho* position vs adsorption at the *meta* and *para* positions. In the TTT relaxation for *ortho* adsorption the Fe atom further puckered by 0.18 Å, and C^{*} by 0.1 Å. This leads to the formation of a C-H bond and an Fe-H bond. The optimized structure shows Fe-H bond length of 1.65 Å similar to that in FeH₃ (1.589 Å)²⁴⁵ with a binding energy of -2.56 eV. In the FFT system, a binding energy of -1.74 eV was obtained with a similar puckering of C^{*} and Fe, with H_{GP} adsorbed directly on top of C^{*}.



Figure 5.22: Potential energy curves for adsorption of H_{GP} at the ortho, meta and para carbon atom sites with Fe defect puckered-up. Pmael (A): With PBE-D3BJ in FFT scheme, panel (B): with PBE-D3BJ in TTT and the inset shows optimized structure for ortho adsorption of H_{GP} .

The binding energy of H_{GP} adsorption at the *meta* and *para* carbon atom sites is smaller due to the reduced effect of the Fe defect atom. The Fe atom remains fixed in both TTT and FFT schemes, resulting in H_{GP} being positioned straight on top of the C^{*} atom with a stronger binding energy at the *para* carbon atom compared to the *meta* site. The *para* adsorption shows a larger puckering of C^{*} and the three other bonded carbon atoms. The puckering of the *meta* carbon atom site is more limited due to the restricted motion of neighbouring carbon atoms, which are bonded to the frozen Fe defect site. Adsorption at all sites is barrierless when the empirical dispersion effect is included in the calculations.

5.4.6 Adsorption of H_{GP} ortho, meta & para to a magnesium defect

As described in section 5.3.6, the atomic radius of Mg (1.45 Å) is over twice that of carbon atom (0.7 Å). Hence, Mg will either recede into or sit on top of the graphite surface. The lowest energy confirmation is obtained by the magnesium atom receding into carbon plane by 1.78 Å, placing it in the centre of the bilayer graphite structure. This configuration is 0.31 eV lower in energy relative to the puckered-up geometry. Therefore, we have only considered the negatively puckered Mg substituted graphite surface for our calculations. Potential energy curves for all three adsorption sites relative to Mg site with two relaxation schemes FFT and TTT are shown in Fig. 5.23 and the important stationary points are reported in Table 5.13.

The location of the magnesium defect makes the *ortho* carbon atom site more active as the edges are exposed. In the FFT scheme using empirical dispersion correction introducing H_{GP} at the *ortho* site results in a puckering of C^{*} out of the carbon plane by 1.3 Å, this elevates the neighbouring carbon atoms by 0.4 Å and the Mg atom by 0.1 Å. As a result barrierless adsorption of the hydrogen atom is obtained with a C-H bond of 1.12 Å in the minimum energy state, with a binding strength of -2.06 eV. At this point, the Mg atom moves slightly, remaining 1.68 Å away from the top layer, as shown in the inset of Fig 5.23-A. However, the Mg-H interaction of ~ 3.64 Å is observed which is significantly greater than the natural Mg-H bond in MgH₂ (2.14 Å)²⁴⁶ suggesting that there is a very weak Mg-H interaction. Simultaneously, in the TTT scheme, C^{*} can move out of the graphene plane by 1.27 Å and the Mg defect atom moves up by 0.68 Å. In addition, the neighbouring carbon moves by 0.4 Å to accommodate H_{GP}. The Mg defect still stays

below the top layer, 1.58 Å away from it and a strong C-H bond is formed with a more negative binding energy of -3.44 eV. This confirms that adding relaxation to the defect site is crucial for describing the adsorption process. Chemisorption of H_{GP} at the *ortho* carbon atom site in this case is also barrierless, but the binding strength increases by 1.38 eV. Interestingly, the large hollow created by the Mg receding allows H_{GP} to bend over Mg by about 20° as shown in the inset of Fig 5.23-B.



Figure 5.23: Potential energy curve for adsorption of H_{GP} at the ortho, meta, and para relative to the Mg defect. Panel (A): with PBE-D3BJ in FFT scheme and the inset shows the minimum energy structure for the adsorption of H_{GP} at the ortho site within FFT scheme, panel (B): with PBE-D3BJ in TTT scheme and the inset shows the optimized structure for the adsorption of H_{GP} at the ortho site. Panel (C, D): minimum energy structure for the adsorption of H_{GP} at the meta and para site with FFT scheme, panel (E, F) optimized structure for the adsorption of H_{GP} at the meta and para site.

Table 5.13: Adsorption energies (E_a) , activation energy E^{\sharp} , and physisorption energy (E_{ph}) are all in eV, for the adsorption of H_{GP} atom at ortho, meta, and para site relative to Mg defect in bi-layer graphene system.

Defect			PB	Е					PB	E-D3B	J		
-	ortl	ho meta para				a	ortho		meta			para	
-	E_a	E^{\sharp}	$E_a E^{\sharp} E_a E^{\sharp}$			E_a	E_a	E_{ph}	E^{\sharp}	E_a	E_{ph}	E^{\sharp}	
$Mg(\downarrow)(FFT)$	-2.02	0.01	-1.24	0.1	-1.25	0.12	-2.06	-1.28	-0.03	0.07	-1.26	-0.03	0.07
$Mg(\downarrow)(TTT)$	-3.43	0.03	-1.45	0.09	-1.39	0.1	-3.44	-1.48	-0.03	0.04	-1.42	-0.03	0.07

It is clear that the formation of an edge enhances adsorption ortho to Mg. Thus, when H_{GP} adsorbed at the meta and para carbon atom sites, the edge effects are expected to become smaller. Indeed, both sites show an identical pattern for chemisorption of H_{GP} . For the FFT relaxation scheme for both meta and para adsorption, C^{*} puckers up by ~ 0.7 Å and lifts the three bonded carbon atoms by 0.2 Å, resulting in an energy barrier of 0.07 eV. The chemisorbed species has a binding energy of -1.28 eV and -1.26 eV for the meta and para sites, respectively. The minimum energy structure obtained for the adsorption H_{GP} at meta and para site within FFT scheme is shown in Fig. 5.23 panels C

and D, respectively. Introducing extra relaxation in the TTT relaxation scheme shows the interaction of Mg has a small influence on the adsorption profile as expected. However, there is a slight increase in the binding energy.

5.5 Adsorption of a second hydrogen atom on graphite surface with various defects

Finally, we investigated the adsorption of a second hydrogen atom near the X-H bond (X=defect atom). Previous studies have examined these calculations in the absence of a defect.^{247–250} They have shown that adsorption of a second hydrogen atom at the *meta* carbon atom site relative to the X-H bond results in a significant energy barrier of more than 0.2 eV. However, barrierless adsorption is found at the *para* carbon atom site. The *ortho* position, on the other hand, behaves differently. Adsorption of the 2nd hydrogen atom next to X-H could result in an unstable product which may lead to the formation of an H₂ molecule. In addition, there is a potential energy barrier in the entrance channel.^{27,177} Therefore, the primary objective of these calculations is to examine the energetics of the second adsorption process in the presence of defect atoms.



Figure 5.24: Five different sites for the adsorption of the 2^{nd} hydrogen atom in the presence of oxygen defect with a pre-chemisorbed hydrogen atom (H_{GP}), purple = ortho1, pink = ortho2, green = meta1, orange= meta2, yellow = para

To study the adsorption of a second hydrogen atom we have only considered the minimum energy substituted graphite system, *i.e.*, form the Fe, Si, and Mg defects only the puckereddown optimized geometry was chosen for this step. We refer to the second hydrogen atom as H' and the carbon atom onto which it adsorbs as C'. The already adsorbed hydrogen atom on the defect site is referred to as H_{GP} as shown in Fig 5.24. To study the adsorption of H' we followed the FFT scheme for all calculations. In this, the z-coordinate of C' and the three other bonded atoms were allowed to relax, with H' being completely restricted. In contrast to the single adsorption process, there are now five different sites for adsorption of the second hydrogen atom. These include two *ortho*, two *meta* and one *para* site as shown in Fig. 5.24 panels A and B.

As discussed above in section 5.3, in case of a hydrogen defect, instead of the defect site we have chosen the *ortho* site for the adsorption of H_{GP} . This then shows a different electronic environment at the neighboring *ortho* and *meta* sites of the hydrogen defect as shown in Fig. 5.24-A. Similar to the hydrogen defect, in the presence of O, Si, Fe, and Mg the incoming H_{GP} was found to adsorb at the neighbouring edge carbon atom site instead of the defect site. This also results in a different electronic environment at the *ortho* and *meta* neighbouring sites as shown in Fig. 5.24 panel B. Thus, instead of three sites as discussed in section 5.4, five different sites are obtained after the first hydrogenation at the defect site.

In our calculations, the initial step involved the optimization of the structure with hydrogen on top of the substitution defect. To further understand the interaction of the second hydrogen atom, both adsorption and desorption studies were carried out. The starting point for the latter calculations was the optimized structures of H_{GP} bound to the defect site on the graphite surface with a second hydrogen atom (H') at ortho, meta, or para to the defect site. It should be noted that the optimized structures generated for investigating the desorption processes were different from the minimum energy structures obtained from the adsorption processes, because of the more restrictive relaxation scheme we had to follow. Moreover, when studying the desorption energy profile of H' from a graphene surface with a silicon, iron or magnesium defect, the optimized structures revealed that H_{GP} had migrated from the top of the defect site to the ortho carbon position to take advantage of the exposed edges of the graphite sheet as observed in section 5.3. On the other hand, investigating the desorption energy profile of H' from a graphite surface containing a nitrogen defect showed that in the optimized structure H_{GP} was still bonded to the defect site, but both the C-H' bond and the N-H_{GP} bond bent away from each other.

5.5.1 Second hydrogen adsorption on a hydrogen substituted surface

As explained above, we performed both adsorption and desorption of a second hydrogen atom on a hydrogen-substituted surface. First, we have discussed the adsorption of a second hydrogen atom at *ortho1*, *ortho2*, *meta1*, *meta2* and *para* sites relative to H-H_{GP}. The potential energy curve for these adsorptions are shown in Fig. 5.25 panel A and the relevant stationary points are summarized in Table 5.14.

To study the adsorption of H', the optimized structure of H_{GP} on a hydrogen-substituted bi-layer graphite was considered as an initial geometry as shown in the inset in panel A. In this H_{GP} adsorbed at the dangling ortho carbon atom to the hydrogen defect and remains tilted over the hydrogen defect. This results in the hydrogen defect receding into the surface by ≈ 1 Å. Two relaxation scenarios were employed to study the adsorption of H' at both the ortho1 and ortho2 sites. First, by completely freezing H_{GP} and second, by allowing H_{GP} to relax in the z-direction within the FFT relaxation scheme. For both relaxation scenarios, H' chemisorbs at ortho1 site through an energy barrier of 0.035 eV via puckering of C' and hydrogen defect by 1.26 Å and 1.23 Å, respectively as shown by the orange curve in Fig. 5.25-A. For the minimum geometry, a C'-H' bond of 1.12 Å is observed with a binding strength of -1.53 eV as shown in panel B. A smaller chemisorption energy is obtained at ortho1 (-1.53 eV) compared to ortho2 (-2.7 eV), which is understandable as at the ortho1 site, H' adsorbs at the active site (C') that is bonded to a hydrogen defect. Within the optimized geometry the defect atom recedes slightly below the plane of the graphene surface and the space left by this was occupied by tilted H_{GP} (inset of Fig 5.25-A) with H-H_{GP} of 2 Å. With the approach of H', C' and the defect hydrogen atom pucker out of the plane, resulting in a reduced $H-H_{GP}$ distance to a minimum of 1.12 Å. Within the minimum energy geometry an interaction of 1.53 Å is observed between H_{GP} , H', and H-defect atom as shown in panel Fig. 5.25-B.

In contrast, the adsorption of H' at the *ortho2* site requires overcoming a higher energy barrier (0.07 eV). This might be because of the distant position of the *ortho2* carbon

atom from the substituted hydrogen atom and the presence of H_{GP} at the top of neighbouring carbon atom. When H' adsorbs, the C' puckers out by 1.1 Å and also pulls up the neighbouring carbon atoms and the defect hydrogen atom by 0.33 Å. But, the defect site puckers up only by 0.014 Å, perhaps because of the presence of H_{GP} above it. As a consequence, the surface distortion increases, which also increases the H-H_{GP} repulsion. Within the minimum energy geometry (see Fig. 5.25-C), all three hydrogen atoms remain at a distance of more than 2 Å from each other, which reduces repulsion and favours chemisorption of H' at the *ortho2* position.

5.5



Figure 5.25: Panel (A): Potential energy curves for the adsorption of a second hydrogen H' in the vicinity of a hydrogen defect on the bi-layer graphite surface with PBE-D3BJ in the FFT scheme and the optimized geometry of the adsorption of H_{GP} at the orthosite to the defect atom. Panel (B): minimum energy geometry for the adsorption of H' at ortho2 site, panel (C): minimum energy geometry for the adsorption of H' at ortho2 site, panel (D): minimum energy geometry for the adsorption of H' at meta1 site, panel (E): minimum energy geometry for the adsorption of H' at meta1 site, panel (E): minimum energy geometry for the adsorption of H' at meta1 site, panel (E): minimum energy geometry for the adsorption of H' at meta2 site, and panel (F): minimum energy geometry for the adsorption of H' at para site.

Accommodating H' at the *meta1* position, one bond away from the substituted hydrogen atom, requires the puckering of active site C' by 0.58 Å, two neighbour carbon atoms by 0.14 Å and the carbon atom bonded to the defect atom by 0.65 Å. Whereby, for the *meta2* site, C' puckers up by 0.68 Å and the neighbouring atoms by 0.2 Å. In this case, there is no effect on the defect site is observed. This result is a smaller binding energy of H' at the *meta1* site (-0.37 eV) than at the *meta2* (-0.44 eV) site.

The effect of the defect diminishes from the *meta* to the *para* position. Thus, activated chemisorption of H' at the *para* carbon atom has a binding energy of -1.67 eV, through an energy barrier of 0.025 eV as shown by purple curve in panel A. The minimum energy

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Table 5.14: Adsorption energies (E_a) , activation energy E^{\sharp} , and physisorption energy (E_{ph}) are all in eV, and puckering of C' is in Å for the adsorption of second hydrogen (H') atom at the ortho1, ortho2, meta1, meta2 and para sites relative to H defect in the bi-layer graphite surface.

_			Ads	sorption					Desc	orption		
Defect		PBE		P	PBE-D3	BJ		PBE		P	BE-D3	BJ
H (FFT)	E_a	E^{\sharp}	d	E_a	E^{\sharp}	E_{ph}	E_a	E^{\sharp}	d	E_a	E^{\sharp}	E_{ph}
Ortho1	-1.5	0.1	1.26	-1.53	0.035	-0.04	-2.76	0.06	1.16	-2.79	-	-
Ortho 2	-2.66	0.13	1.1	-2.7	0.07	-0.04	-4.13	0.14	0.78	-4.19	0.06	-0.023
Meta1	-0.35	0.27	0.58	-0.37	0.19	-0.035	-2.1	0.01	0.52	-2.15	-	-
Meta2	-0.41	0.28	0.68	-0.44	0.16	-0.035	-0.96	0.14	0.63	-0.99	0.09	-0.04
Para	-1.67	0.09	0.71	-1.72	0.025	-0.036	-2.19	0.063	0.64	-2.22	-	-

geometry is shown in panel F.

To provide more clarity, the study also investigated the desorption of H'. The corresponding potential energy curves are given in Fig. 5.26 panel A and the optimized geometries for these are shown in panels B to F and the stationary energy points are reported in Table 5.14.



Figure 5.26: Panel (A): Potential energy curves for the desorption of a second hydrogen atom in the vicinity of H-defect on the bi-layer graphene system within the FFT framework. Panel (B to F): Optimized structure for the adsorption of H' at ortho1, ortho2, meta1, meta2, and para site, respectively.

Interestingly, the potential energy curves for desorption follow a similar pattern to the adsorption system, as shown in Fig. 5.25 panel A. Within the optimized geometries an

 $H'-H_{GP}$ bond of 1.57 Å and 1.42 Å is obtained at *ortho1* and *ortho2* positions, respectively. This short distance might contribute to the barrier observed for both sites. Similar to the adsorption results, a stronger binding energy is obtained for the *ortho2* site than for *ortho1*, due to the presence of more active *ortho2* carbon atoms with dangling bonds. Activated chemisorption is observed at all sites, but with a reduced barrier height at the *meta1* and *para* sites. At the *meta1* site, the hydrogen defect atom moved down by an angle of roughly more than 45° during desorption (Fig 5.26-D). However, this is not the case at the *meta2* site since C' was further away from the defect site. As a consequence, a more negative binding energy is obtained at the *meta1* site compared to *meta2* site. Furthermore, chemisorption of H' at both *ortho* sites seems to be a possible route for the potential recombination of hydrogen atoms and the formation of H₂ molecules.

5.5.2 Second hydrogen adsorption on a nitrogen substituted surface

In section 5.3.2 we showed that the adsorption of H_{GP} on top of an N-defect resulted in a puckering of the nitrogen atom by 0.38 Å and the neighbouring carbon atoms by 0.15 Å, leading to an N-H bond of 1.04 Å as shown in Fig 5.27 panel A. Again, below we cover both adsorption and desorption calculations. In these calculations, identical energy profiles were obtained for both *ortho* sites and both *meta* sites. Therefore, only one of the adsorption profiles for the *ortho* and *meta* sites is discussed. All adsorption potential energy curves are shown in Fig. 5.28 panel A and desorption PECs in Fig. 5.28 panel B. All relevant numerical data is given in Table 5.15.



Figure 5.27: Optimized structure for the adsorption of first hydrogen atom (H_{GP}) on top of the nitrogen defect.

Considering adsorption first, we can see in Fig. 5.28 panel A that the *ortho* carbon atom (C') undergoes barrierless adsorption of H', resulting in C' puckering by 0.61 Å and the nitrogen atom by 0.02 Å, with two neighbouring carbon atoms by 0.13 Å. A C'-H' bond of 1.1 Å is formed (see inset in panel A), but the binding energy of -0.83 eV is smaller than that of C-H' bond formation on an unsubstituted graphite surface (-2.02 eV).²⁵¹ This is due to H-H repulsion, as relaxation of the z-coordinate of H_{GP} while restricting H' leads to a minimum energy structure with H_{GP} and H' at a distance of 1.47 Å.

At the *para* position, barrierless chemisorption of H' occurs, resulting in C' puckering by 0.64 Å, along with the other three bonded carbon atoms by 0.17 Å. In the minimum energy geometry, the two H atoms remain at a distance of 2.85 Å (Fig. 5.28-D). Bader charge analysis shows stronger binding energy at the *para* site due to the accumulation of charge at the *para* carbon atom position and depletion of charge at the *ortho* and *meta* carbon sites (Fig 5.27-B). Overall, this makes the *para* site more active for the adsorption of H'. Moreover, the longer H-H distance will lead to stronger binding strength because of less repulsion between the hydrogen atoms. Adsorption at the *meta* carbon leads to position a smaller binding energy of 0.53 eV through an energy barrier of 0.11 eV. For

this C' puckers up by 0.69 Å and the two hydrogen atoms sit at a distance of 2.45 Å in the minimum energy structure (Fig. 5.28-C).



Figure 5.28: Potential energy curves for the adsorption of a 2^{nd} hydrogen atom at the ortho, meta, and para sites relative to the nitrogen defect. Panel (A): Adsorption profile with PBE-D3BJ in FFT with minimum energy geometry with H' at ortho site with FFT scheme, panel (B): desorption profile with PBE-D3BJ in FFT with optimized geometry with H' at ortho site, panel (C, D): minimum energy geometry with H' at meta and para site, respectively with FFT scheme, panel (E, F): optimized geometry with H' at meta and para site, respectively.

Table 5.15: Adsorption energies (E_a) , activation energy E^{\sharp} , and physisorption energy (E_{ph}) are all in eV, and puckering of C' is in Å for the adsorption and desorption of a second hydrogen atom (H') at the ortho1, ortho2, meta1, meta2 and para sites relative to the nitrogen atom in bi-layer graphite system.

-			Ads	orption					Des	orption		
Defect		PBE		PE	BE-GD	3BJ		PBE		PE	BE-GD	3BJ
N (FFT)	E_a	E^{\sharp}	d	E_a	E^{\sharp}	E_{ph}	E_a	E^{\sharp}	d	E_a	E^{\sharp}	E_{ph}
Or tho	-0.8	0.02	0.61	-0.83			-1.79	-	0.6	-1.82	-	-
Meta	-0.53	0.11	0.69	0 -0.54 0.04 -0.047			-0.53	0.11	0.69	-0.54	0.04	-0.047
Para	-1.32	0.01	0.64	-1.35	-	-	-1.61	-	0.68	-1.64	-	-

To confirm the H' adsorption profile at the *ortho* and *para* sites, H' desorption was studied as well. Corresponding potential energy curves are shown in Fig. 5.28 panel B with relevant numerical data in Table 5.15.

Thus, we first optimized the minimum energy structure for all dimer adsorptions. Interestingly, for the *ortho* geometry both hydrogen atoms repel each other in the minimum energy structure, as in the case of pristine graphite.²⁵¹ Thus, causes the C-H and N-H bonds to bend away (H-H distance 1.92 Å) as shown in the inset in Fig 5.28 panel B. Additionally, the C-N bond length increases from 1.41 Å to 1.57 Å. In contrast, adsorption of H['] at the *para* carbon atom leads to the C-H and N-H bonds remaining parallel, with an H-H distance of 2.81 Å. However, relaxation leads to a considerable increase in binding energy for the *ortho* geometry. Desorption of H' from the optimized geometry leads to the recovery of the original H_{GP} on top of N-defect again similar to the pristine graphite case. At the *meta* position similar potential energy curves are obtained for both adsorption and desorption of H_{GP} with a barrier towards creating/destroying the C-H bond.

5.5.3 Second hydrogen adsorption on an oxygen substituted surface

In section 5.3.3 we showed that the initial hydrogen atom H_{GP} was weakly physisorbed onto an oxygen defect. As a result, the *ortho* site was found to be unstable for the adsorption of a second hydrogen atom H' due to the immediate formation of H₂. Thus, both C' and the oxygen defect reverted back into the graphene plane after H₂ formation, as shown in the inset of Fig 5.29-B. Therefore, no further investigation was conducted on the adsorption of a second hydrogen atom at the *ortho* site. Instead, the adsorption of a second hydrogen atom at the *meta* and *para* carbon atom positions was explored. The potential energy curves for the adsorption and desorption of H' in the presence of an oxygen defect at the *meta* and *para* sites are displayed in Fig 5.29 panels A and B, respectively. All the numerical data is summarized in Table 5.16.



Figure 5.29: Potential energy curves for the adsorption and desorption of a second hydrogen atom from the vicinity of an O-H bond in the bilayer graphite with PBE-D3BJ in FFT framework. Panel (A): Adsorption profile, panel (B): desorption profile and the inset shows an optimized geometry for the adsorption of 2nd hydrogen atom at the ortho position to the defect, panel (C, D): minimum energy structure for the chemisorption of 2nd H atom at the meta and para site, respectively with fully rigid, and panel (E, F): optimized structure for the chemisorption of 2nd H atom at the meta and para site, respectively.

Both *meta* and *para* sites show activated adsorption, with the *para* site having a stronger binding strength compared to the *meta* site. As a shorter H-H distance is observed in the case of *meta* adsorption (2.46 Å) than in the case of *para* adsorption (2.85 Å), but is more likely to be due to the fact that adsorption of a second H atom leads to further

Table 5.16: Adsorption energies (E_a) , activation energy E^{\sharp} , and physisorption energy (E_{ph}) are all in eV, and puckering of C is in Å for the adsorption of second hydrogen atom H at ortho1, ortho2, meta1, meta2 and para site relative to the oxygen defect in bi-layer graphite system.

-			Adso	orption				De	sorptic	n
Defect		PBE		PB	E-GD3	BBJ		PBE		PBE-D3BJ
O (FFT)	E_a	E^{\sharp}	d	E_a	E^{\sharp}	E_{ph}	E_a	E^{\sharp}	d	E_a
Meta	-1.13	0.11	0.54	-1.18	0.03	-0.07	-1.49	0.02	0.45	-1.51
Para	-1.52	0.10	0.62	-1.57	-	-	-2.10	0.03	0.61	-2.15

degradation of the graphite π -system. The *para* site, leads to the formation of a single localized double bond between the *ortho* and *meta* carbons, on the other hand, this is not possible for adsorption at the *meta* site. A similar trend is observed in graphene with a nitrogen defect, where the binding energy is stronger for the *para* position compared to *ortho* and *meta* positions for identical reasons. To investigate the influence of our chosen relaxation scheme on H₂ molecule formation at the *meta* and *para* sites, further relaxation was applied to the surface.

Thus, lateral relaxation is allowed to H_{GP} , allowing it to move along the x and y directions for both the *meta* and *para* adsorption scenarios. The potential energy curves for the *para* position remained unchanged as shown in Figure 5.29 panel A. However, for *meta* adsorption the H_{GP} drifted onto the *ortho* carbon atom but stayed bent over the O defect, as shown in Figure 5.29 panel C. A similar potential energy profile was observed but with a slightly more negative binding energy due to the relaxation effect.

Fig. 5.29 panel B shows desorption calculations. An interesting arrangement is found in the optimized structures for the adsorption of H' at the *meta* and *para* carbon atom positions. In the optimized structures, H_{GP} shifts towards *ortho* carbon atom next to the *meta* active site but remains angled over the oxygen defect by an angle of ~ 10° as shown in Fig 5.29 panel E. To avoid H-H repulsion, H' bends away in the opposite direction, so the two hydrogen atoms remain at a distance of 2.4 Å. Similarly, for the *para* system, again H_{GP} is found in this case angled over the oxygen atom but bound to on the *ortho* carbon (Fig. 5.29-F). As a result, the oxygen defect further recedes into the surface, and the two hydrogen atoms remain at a distance of 3.43 Å apart with no additional lateral movement of H'. Overall, an activated adsorption was observed with a smaller energy barrier at both sites, which is entirely due to the puckering of carbon atoms.

5.5.4 Second hydrogen adsorption on a silicon substituted surface

Adsorption of a hydrogen atom on top of a silicon defect was discussed in section 5.3.4. Summarizing, adsorption of a hydrogen atom on top of a Si defect causes the Si defect to move into the graphite surface by 1.4 Å, while the neighbouring carbon atom puckers up by 0.06 Å. Potential energy curves for the adsorption and desorption of a second hydrogen atom (H') in the vicinity of such a Si-H defect are given in Fig. 5.30 panels A and B, respectively with relevant numerical data in Table 5.17.

For the adsorption of H' at the ortho1 site, H_{GP} bends towards the ortho1 carbon atom and shows the formation of a CH_2 group as an intermediate structure (Fig 5.30 panel A). At the minimum energy stage, the H-H distance of ≈ 1.88 Å is observed. Consequently, a barrierless chemisorption with an adsorption energy of -1.53 eV is observed. However, for the ortho2 scenario, a minimum energy structure with a longer H-H distance of 1.97 Å is obtained, as shown in Fig 5.30 panel C. Moreover, CH_2 formation was not observed in the *ortho2* scenario, instead an activated adsorption was observed. These observations may be an artifact of the calculations, and thus, further investigation may be needed.



Figure 5.30: Potential energy curves for the adsorption and desorption of a second hydrogen atom H' in the vicinity of a Si-H bond in the bi-layer graphite with PBE-D3BJ in FFT scheme. Panel (A): Adsorption profile, inset shows an intermediate structure of 2nd hydrogen adsorption (H') at the ortho1 site with FFT scheme, panel (B): desorption profile, inset shows an optimized structure for adsorption of H' at the ortho1 site, panel (C, D, and E): minimum energy structure for the adsorption of 2nd hydrogen atom at the ortho2, meta1, and para sites, respectively with FFT scheme and panels (E, F): optimized structure for the adsorption of 2nd H atom at the meta1 and para sites, respectively.

Table 5.17: Adsorption energies (E_a) , activation energy E^{\sharp} , and physisorption energy (E_{ph}) are all in eV, and puckering of C is in Å for the adsorption of H at the ortho1, ortho2, meta1, meta2 and para sites relative to Si defect in bi-layer graphite system.

-			Ads	orption					Deso	rption		
Defect		PBE		P	BE-D3B	J		PBE		PI	BE-D3	BJ
$\operatorname{Si}(\downarrow)(\operatorname{FFT})$	E_a	E^{\sharp}	d	E_a	E^{\sharp}	E_{ph}	E_a	E^{\sharp}	d	E_a	E^{\sharp}	E_{ph}
Ortho1	-1.50	-	1.20	-1.53	-	-	-2.92	-	0.01	-2.96	-	-
Ortho2	-1.09	0.12	1.07	-1.53			-2.93	-	0.006	-2.96	-	-
Meta1	-0.86	0.14	0.71	-0.88	0.06	-0.03	-1.33	0.07	0.70	-1.37	0.04	-
Meta2	-0.76	0.16	0.77	-0.78	0.09	-0.04	-1.33	0.10	0.70	-1.37	0.05	-0.05
para	-1.30	0.09	0.60	-1.33	0.02	-0.04	-1.80	0.03	0.55	-1.84	-	-

For the adsorption of H' at the *meta* and *para* carbon atom positions, the defect site is not involved in the relaxation scheme. As a result, activated adsorption of H' is observed at the *meta*1, *meta*2 and *para* positions, with an energy barrier due to the puckering of the carbon atoms.

Desorption of H' is shown in Fig. 5.30 panel B. For this optimization calculations of double hydrogenation at *ortho1*, *ortho2*, *meta1*, *meta2* and *para* sites in the presence of a Si defect were performed. The optimized structures generated showed that H_{GP} migrates

from the top of the defect site to the *ortho* carbon position for the *ortho*1, *meta*1, and *para* scenarios (see Fig 5.30 panel B, F, and G). In addition, identical potential energy profiles were obtained from the desorption of H' from both the *ortho*1 and *ortho*2 carbon atom positions as well as from the *meta*1 and *meta*2 positions. Thus, care needs to be taken with the results from the adsorption calculations, since the relaxation restrictions have a clear influence on the final results. Hence, only one site for each is discussed here. The presence of an edge effect makes the *ortho* carbon atom more active. For desorption from the *meta* carbon, H_{GP} and H' are positioned at three bond lengths away from each other (Fig 5.31 panel F). Thus, the edge effect is expected to diminish as the adsorption position is moved further away from the defect site. For double adsorption at the *meta* and *para* carbon atom positions, C' puckers up by 0.7 Å, pulling up the neighbouring carbon atoms by 0.2 Å. As a consequence, excess energy of ~ 0.04 eV is needed for desorption at the *meta* meta position. But, for the *para* site due to the less severe surface distortion activation barrier was found to be equal to the desorption energy.

5.5.5 Second hydrogen adsorption on an iron substituted surface

Re-optimization of the position of H_{GP} on top of an iron defect in a bi-layer graphite system leads to the formation of an Fe-H bond of 1.51 Å with a Fe-C bond length of 1.80 Å. Here, the iron atom is displaced below the top layer of graphene by roughly 1.25 Å, causing the neighbouring carbon atoms to be pulled down by ~ 0.02 Å. The re-optimized geometry shows that the hydrogen atom is found to be bent towards the *ortho* carbon atom. This re-optimized structure was then used to investigate the adsorption of a second hydrogen atom (H') at the *ortho1*, *ortho2*, *meta1*, *meta2* and *para* positions relative to the Fe-H bond. Similar to the investigation of the Si defect, both adsorption and desorption profiles were studied for a complete understanding. The potential energy curves for both the adsorption and desorption scenarios are shown in Fig 5.31 panels A and B, respectively. All relevant numerical data is in Table 5.18.

If we consider adsorption first, then it is clear that the movement of the iron atom below the graphene plane, opens up the edges at the *ortho* carbon atom positions, making the *ortho* site more active than the *meta* and *para* sites, as mentioned above in section 5.3.5. As before, puckering of C' is required for the adsorption of the hydrogen atom at both *ortho* positions, which is made easier by the presence of the Fe defect site. The amount of surface distortion in this case is reduced in comparison to the puckering needed at the *meta* and *para* carbon atoms. Similar potential energy profiles are obtained when H' moves in at the two *ortho* positions (*ortho1*, *ortho2*) and *meta* positions (*meta1*, *meta2*) with minor differences in the energy barrier and the binding energy. Therefore, only one site is discussed here from either position.

For the ortho carbon atom position, C' puckers out of the graphene plane by ~ 1 Å, pulling up the neighbouring carbon atoms by 0.23 Å and the Fe atom by 0.15 Å, respectively. At the minimum, a C-H bond of 1.1 Å is formed with a H-H interaction of 1.85 Å. This is equivalent to the structure obtained for the system containing a Si defect. The Fe-C' bond also increases from 1.80 Å to 2.06 Å, as shown in the inset of Fig 5.31-B. This process has a small activation barrier of 0.01 eV for ortho1 and no barrier for adsorbing at ortho2.

In contrast, for adsorption at both the *meta* and *para* positions activated adsorption is found. This is caused by the need for C' to pucker from its equilibrium position. This puckering leads to the *ortho* carbon to pucker out of the graphene plane by 0.2 Å. This means an additional loss of surface planarity with its consequent effects on its electronic structure. Thus, the adsorption energy is found to be smaller at the *meta* position than

at the *para* position. It is noted that moving from the *ortho* to the *meta* to the *para* positions, the H-H interaction distance increases and therefore any H-H repulsion will be decrease as well.



Figure 5.31: Potential energy curves for the adsorption of a 2^{nd} H atom at the ortho1, ortho2, meta1, meta2 and para relative to Fe-H in bi-layer graphite with PBE-D3BJ in FFT scheme. Panel (A): Adsorption profile, panel (B): desorption profile, inset shows an optimized geometry for adsorption of H' at the ortho1 site, panel (C, D, and E): minimum energy geometry for the adsorption of H' at the ortho1, meta1 and para sites, respectively with FFT scheme, and panel(E, F): optimized geometries for the adsorption of H' at the meta1 and para site, respectively.

Table 5.18: Adsorption energies E_a , activation energy E^{\sharp} , and physisorption energy E_{ph} are all in eV, and puckering of C' is in Å for the adsorption of a second Hydrogen atom at the ortho1, ortho2, meta1, meta2 and para sites relative to Fe defect in the bi-layer graphite system.

-	adsorption							desorption				
Defect	PBE			PBE-D3BJ			PBE		PBE-D3BJ			
$Fe(\downarrow)(FFT)$	E_a	E^{\sharp}	d	E_a	E^{\sharp}	E_{ph}	E_a	E^{\sharp}	E_a	E^{\sharp}	E_{ph}	
Ortho1	-1.27	0.03	1.01	-1.30	0.01	-0.04	-3.18	0.02	-3.20	-	-	
Ortho2	-1.34	0.02	1.04	-1.36	-	-	-3.18	0.02	-3.20	-	-	
Meta1	-1.0	0.10	0.70	-1.03	0.04	-0.04	-1.93	0.10	-1.96	0.04	-0.04	
Meta2	-1.00	0.09	0.75	-1.02	0.01	-0.05	-1.66	0.08	-1.69	-	-	
para	-1.22	0.09	0.63	-1.26	0.03	-0.05	-1.62	0.07	-1.64	0.01	-0.04	

To develop further understanding, the desorption of H' was also studied starting from the optimized equilibrium structures, which are slightly different from the minimum energy structures obtained in the adsorption scenario. Structural changes in the presence of the Fe defect were found similar to the system containing a silicon defect. In the optimized structure, H_{GP} shifts from the top site of the defect to the neighbouring *ortho* carbon atom. Moreover, the Fe defect prefers to move below the top layer of the graphene plane by more than 1 Å, leaving a hollow behind. Adsorption of H_{GP} on top of the Fe defect

and H' at the ortho position to the defect site does not affect the position of the iron atom significantly. In this case, both H_{GP} and H' adsorbed at the ortho positions to the defect site and bent over Fe atom roughly by 10°, but both remain at a distance of 1.87 Å away from each other. Even though it was not part of our investigation, it seems possible that this geometry could be a potential intermediate for the H atoms to recombine and form H_2 .

As seen in all simulations, the presence of 'edges' facilitates the adsorption of H' to the *ortho* position. Adsorption requires some excess energy at all positions, but less so at *ortho* position compared to the *meta* and *para* positions.

5.5.6 Second hydrogen adsorption on a magnesium substituted surface

As explained in the previous section a Mg defect atom prefers to sit in between the two graphene layers because of the difference in atomic radii between C and Mg. Introducing H_{GP} on top of the magnesium atom only pulls up the Mg atom slightly, but it remains at a distance of more than 1.6 Å below the top layer of graphene. As a consequence, in the optimized structure H_{GP} forms a bond with the carbon atoms at the *ortho* position instead of the magnesium atom and tilts over the magnesium defect. For this system, we also performed adsorption and desorption calculations, which are shown in Fig. 5.32 panels A and B, respectively. All relevant numerical data is given in Table 5.19.



Figure 5.32: Potential energy curves for the adsorption and desorption of hydrogen atom H' in the vicinity of Mg-H bond at the ortho1, ortho2, meta1, meta2 and para site in the bi-layer graphite system with PBE-D3BJ in FFT scheme. Panel (A): Adsorption profile, panel (B): desorption profile, inset shows optimized structure of adsorption of H' at the ortho1 site, panel (C, D): minimum energy structure for the adsorption of 2nd hydrogen atom at the ortho1 and meta1 carbon atom, panels (E, F): optimized structure for the adsorption of 2nd the meta1 and para carbon atom, respectively.

The movement of H_{GP} in the re-optimization means that nomenclature becomes slightly more complicated. For clarity, we use the original designation even though the movement of H_{GP} turns, *e.g. meta* desorption into either *ortho* or *para* desorption. Overall, activated

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-	Adsorption						Desorption			
Defect	PBE			PBE-D3BJ			PBE			PBE-D3BJ
$Mg(\downarrow)(FFT)$	E_a	E^{\sharp}	d	E_a	E^{\sharp}	E_{ph}	E_a	E^{\sharp}	d	E_a
Ortho1	-1.81	0.02	1.30	-1.80	-	-	-3.68	-	0.91	-3.72
Ortho 2	-1.80	0.01	1.28	-1.79	-	-	-3.68	-	0.91	-3.72
Meta1	-0.78	0.15	0.52	-0.81	0.07	-0.04	-1.50	0.04	0.7	-1.54
Meta2	-0.78	0.15	0.5	-0.81	0.06	-0.04	-1.50	0.04	0.70	-1.54
Para	-1.42	0.10	0.62	-1.44	0.03	-0.04	-1.96	0.02	0.54	-1.98

Table 5.19: Adsorption energies (E_a) , activation energy E^{\sharp} , and physisorption energy (E_{ph}) are all in eV, and puckering of C' is in Å for the adsorption of second hydrogen atom H' atom at the ortho1, ortho2, meta1, meta2 and para positions relative to the Mg defect in bi-layer graphite system.

adsorption is found at all positions with a smaller energy barrier at both *ortho* sites (Fig 5.32 panel A). Here, C' puckers out of the graphene plane by ~ 1.3 Å, while the magnesium atom further recedes into the bi-layer by 0.005 Å further opening up the edge site. A similar scenario is observed for the *meta* system. For the adsorption of H' at the *meta* position C' puckers out by 0.52 Å, along with the *ortho* carbon atom. This leads to a high degree of surface distortion and a weaker binding strength. However, for the *para* carbon atom position, edge effects diminish. Thus, adsorption of H' at the *para* position has smaller energy barrier (0.1 eV) and stronger binding energy (-1.44 eV).

For the next step desorption of H' from an optimized equilibrium structure, was studied in all cases. When the hydrogen atom are originally *ortho* to each other, the optimized structure shows that both H' and H_{GP} cover the space originally left by Mg defect as shown in the inset of Fig 5.32 panel B. In this case, the two hydrogen atoms end up at a distance of only 1.45 Å. Thus, the H atoms could combine through this generally to form H₂. For the *meta* and *para* systems the magnesium atom further recedes below the graphene plane. Activated desorption is observed, but small excess energy is observed for the *para* position system when compared to the *meta* position. This might be due to the involvement of the *ortho* carbon atom in the relaxation scheme for the *meta* system, hence more distortion is present in the *meta* system than in the *para* system, which will not be released because of the restrictions that are put in during the calculation.

5.6 Conclusion

It has been accepted that the formation of H_2 molecule occurs *via* adsorption of hydrogen atoms on the surface of grains. Adsorption of the first hydrogen atom on a pristine graphite surface is an activated process with an energy barrier of 0.2 eV. The subsequent adsorption can then be barrierless depending upon the precise relative position of the H atoms.

In the present work, we have investigated the effects of substitutional defects on the adsorption and desorption characteristics of hydrogen atoms on a graphite surface. Some of these defects modulate both the energy barrier to adsorption and the binding energy. The absolute energy profiles for single adsorption for each system are given in Fig. 5.33. Substitution using Fe, Si, H, and Mg opens up the edge sites in a layer of graphite, making these sites more reactive. But the extent of the edge effects is largest within the systems containing hydrogen and magnesium defects. Adsorption of a hydrogen atom (H_{GP}) on top of these defects (H and Mg) led to the formation of strong C-H bonds at the *ortho* carbon atom position. This will increase the residence time of the hydrogen atom on the

In contrast, in the presence of an oxygen defect physisorption of H on top of the oxygen defect is observed. The H atom then moves towards the *ortho* carbon atom away from the oxygen defect. Second adsorption in the presence of a nitrogen defect activated adsorption of a hydrogen atom is observed similar to pristine graphite (Fig 5.28). Subsequent adsorptions have similar characteristics to pristine graphite. For Fe and Si defects we investigated both the puckered-up and puckered-down defects, since both may be accessible depending on the formation history of the defect, even though the puckered-down geometry is significantly smaller in energy. In the puckered-down systems, activated adsorption is observed with a small energy barrier, whereas barrierless adsorption is observed within the puckered-up systems. However, these puckered-up Si and Fe defects also make adsorption at the *ortho* position unstable. In contrast, adsorption of a hydrogen atom on top of a puckered-down defect will likely convert into the *ortho* adsorption system due to the activation of the edges. In general, the largest binding energy is found for Mg, which also exposes the edge sites the most.



Figure 5.33: Energy profile for the adsorption of first hydrogen on top of the defect site with (1) Presence of H at far from the surface, (2) Transition state energy, and (3) Adsorption energy for the chemisorption.

The absolute energy profiles for double hydrogenation are given in Fig. 5.34. As adsorption

of first hydrogen at the top of the defect site result a different electronic environment to the *ortho*, *meta*, and *para* sites. Due the puckering of the defect site in case of H, Si, Fe, and Mg the first hydrogen atom adsorbed at the *ortho* carbon atom instead of defect site and create two *ortho* and two *meta* sites within the neighbour hexagonal ring. Thus instead of three sites we have chosen five different sites for the adsorption of 2^{nd} hydrogen atom.

Adsorption of a 2^{nd} hydrogen atom at the *ortho1*, *ortho2*, *meta1*, *meta2*, and *para* sites relative to bond X-H (X represents the defect atom) follows a similar trend as observed in the case of the first hydrogen atom adsorption at the *ortho*, *meta*, and *para* carbon atom sites relative to the defect site, with higher barriers at the *meta* sites combined with small binding energies. *Ortho* adsorption is generally most favourable with the lowest barriers. This is borne out in the absolute energy profile for double adsorption which are shown in Fig. 5.34. Interestingly, the comparison with the formation of H₂ shows that stronger binding at the surface will actually means that H₂ formation is an endothermic process. Particularly from the favourable *ortho* double adsorption.



Figure 5.34: Energy profile for the double hydrogenation on the pure and substituted graphite surface with (1)-adsorption of first hydrogen atop of the defect site, (2, 3, and 4)-double hydrogenation at ortho, meta and para in the vicinity of the defect- H_{GP} , (5)-formation of H_2 molecule atop of the pristine and substituted bi-layer graphene.

Chemisorption of a 2nd hydrogen atom at the *ortho* positions, in the presence of H or Mg defect, leads to strong C-H bond formation as shown in Fig. 5.34. This is due to the edge

effect and shows the formation of hydrogen molecule in these would be an endothermic process. It is notable that in the presence of an oxygen defect, *ortho* adsorption leads to a probable scenario for the formation of an H_2 molecule due to the weak binding of the first adsorbed hydrogen atom on top of oxygen defect. In the case of pristine graphite and the graphite system containing N, Fe, and Si defects, a hydrogen molecule can be formed on the graphite surface *via* an exothermic reaction.

Overall, our results show that defects modulate the adsorption and desorption process on a graphite surface. Thus, *e.g.* the energy barrier reduces for a first adsorption, which can completely vanish for subsequent adsorptions in some cases. The final H-substrate bond strength can vary from -0.4 eV to -4.1 eV depending upon the availability of edge sites. This increases the chances for further adsorption of hydrogen atoms increasing the reaction probability to form a H₂ although in some cases that may require additional H atoms since the formation of H₂ from the double adsorption is endothermic.

Chapter 6

The effect of graphite/substituted graphite surface on the formation of water

6.1 Introduction

Water is an ubiquitous molecule in the ISM. It has been reported that it is present everywhere in the cosmos, either in gas or solid form, although not in the liquid²⁵² form. Studies have reported that at low temperatures (T<50 K), ice forms an amorphous layer in grains.^{253,254} However, the ice film crystallizes because of the interaction with UV radiations or photons.^{253–255} The abundance of water in the ISM varies from $<10^{-8}$ cm⁻³ in the coldest regions, where it is present on the grains in ice form, to $>10^{-4}$ cm⁻³ in warmer regions, where it evaporates from grains.^{256,257} Water was first detected within diffuse clouds²⁵⁸ of ISM, but it also as a major component of ices that coat the dust grains (carbonaceous and silicate) in dense clouds of ISM.^{259–262} Finally, water is, as far as we know essential for life, which makes it a suitable subject for study.

First of all, we will consider the formation of water in diffuse clouds, where gas-phase reactions are key to its formation. Ion-neutral reactions at low temperatures (10 K-100 K) have been considered experimentally in this context.²⁵² In these reactions, water is formed *via* a series of barrierless exothermic chain reactions (shown in Eqn. 6.1 to Eqn. 6.4). They initiate by reaction of O^+ with molecular hydrogen (H₂) and form H₂O by addition of electrons to the intermediate product H₃O⁺.

$$\mathrm{H}_2 + \mathrm{O}^+ \to \mathrm{OH}^+ + \mathrm{H} \tag{6.1}$$

$$\mathrm{H}_{2} + \mathrm{OH}^{+} \to \mathrm{H}_{2}\mathrm{O}^{+} + \mathrm{H}$$

$$\tag{6.2}$$

$$\mathrm{H}_{2}\mathrm{O}^{+} + \mathrm{H}_{2} \rightarrow \mathrm{H}_{3}\mathrm{O}^{+} + \mathrm{H}$$
 (6.3)

$$\mathrm{H}_{3}\mathrm{O}^{+} + \mathrm{e}^{-} \to \mathrm{H}_{2}\mathrm{O} + \mathrm{H}$$

$$\tag{6.4}$$

All these intermediate ionic species have been detected in the ISM.^{263,264} However, it is widely accepted that these gas-phase reactions are incapable of explaining the amount of water present in the dense ISM. Thus, it is crucial to study the formation of water on dust grain analogues.²⁶² Some previous experimental and theoretical studies^{262,265–267} suggested three possible reaction pathways for the formation of water by reaction networks of atoms and molecules on a grain surface, as shown by reaction pathways R1, R2, and R3 in Fig. 6.1. In the first reaction pathway (R1), atomic oxygen is sequentially hydrogenated to lead to the formation of H₂O. The second reaction pathway (R2) can be initiated by the reaction of atomic hydrogen with an oxygen molecule, leading to the formation of H₂O *via* the intermediate products HO₂, H₂O₂ and OH.



Figure 6.1: Three different reaction pathways R1, R2, and R3 to form water molecule by neutral-neutral reaction

The third possible reaction pathway (R3) is initiated by the hydrogenation of an ozone molecule, leading to the formation of O_2 and OH. The OH formed in this pathway can further react with a hydrogen molecule to form H_2O . All of these intermediate products have also been detected in the ISM.²⁶⁸ However. the energy barriers for these reactions on a grain surface are still not clear. We note here that as mentioned before, the precise nature of a dust surface is unclear. However, graphene has been considered a model of a carbonaceous dust grain in many previous studies. Therefore, for this work, we have used bi-layer graphite as a model for a dust grain.

Before the formation of water is considered, we should first consider the interaction of a water molecule with a

graphene surface. The adsorption energy of a water molecule on a graphene surface is a representation of carbon-water interaction.²⁶⁹ It has been reported that graphene is hydrophobic in nature, which means that water does not form a chemical bond with the graphene surface and shows only physisorption towards surface sites.^{270,271} Moreover, it attains a configuration of minimum energy at a height of \approx 3-4 Å above the surface without distorting the graphene surface.²⁷²

A recent study²⁷³ reported that water can adsorb on a graphene surface in three different orientations: 0-leg (when oxygen is pointed towards the surface), 1-leg (when one hydrogen is pointed towards the surface), and 2-leg (when both hydrogens are pointed towards the surface). It was found that, if the oxygen atom points towards the graphene surface, there will be a charge transfer from oxygen to graphene. On the other hand, if hydrogen points towards the surface in a 2-leg orientation, then charge transfer occurs from graphene to hydrogen.²⁷¹ Moreover, adsorbed water has a strong preference for the interaction of its hydrogen atoms with the surface rather than the lone pair of the oxygen atom, since this interaction could affect the hybridization of the carbon atoms within the graphene surface.²⁷⁴ Thus, 2-leg would be the favourable geometry with a higher binding energy than the 0-leg and 1-leg orientations.

Previous studies also suggest that pre-adsorbed and freeze-out of gaseous atomic species on a graphene surface can facilitate the adsorption of water on a graphene surface.^{275–277} In particular, the adsorption of a water molecule on oxygenated graphite surfaces was explored by Pogorelyi *et al.*.²⁷⁶ They found that previously chemisorbed atomic oxygen on a graphene surface increases the binding energy of water to graphene surface sites.²⁷⁶ Moreover, the sequential hydrogenation of graphite oxide (GO) could lead to the formation of carbonyl, carboxyl, and hydroxyl functional groups on a graphene surface and create hydrophilic sites. To our knowledge, the formation of water by hydrogenation of these functional groups on GO has not been studied yet. Thus, for our work, we studied the formation of a single water molecule and small water clusters up to four water molecules *via* sequential hydrogenation of a partially oxidized bi-layer graphite surface (section 6.2). In addition to this, the presence of defective carbon structure has also been reported in the ISM.^{21,278–280} Therefore, the formation of a water dimer on a substituted graphite surface is discussed in section 6.3.

6.2 Formation of water on a graphite surface

In this section, we will discuss the formation of up to four water molecules from graphite oxide (GO), a partially oxidized bi-layer graphite surface *via* sequential hydrogenation of oxygen atoms. For all sequential hydrogenation calculations, full relaxation was allowed for the top layer of the graphite surface. The other adsorbed atomic species (*i.e.*, the other adsorbed oxygen and hydrogen atoms) were allowed to move in the x, y, and z directions.

6.2.1 Formation of a single water molecule



Figure 6.2: Four different sites for the formation of a single water molecule at bi-layer graphite surface.

First, calculations for the adsorption of a single oxygen atom and the sequential hydrogenation of this oxygen to form OH and H_2O at the centre, midbond, top-C1, and top-C4 sites were performed as shown in Fig. 6.2. The relative energy profiles and the optimized structures for these sequential hydrogenation steps are given in Fig. 6.3 and 6.4, respectively. These relative energies are calculated as follows:²⁸¹

$$E_{rel} = E_{Gr+func} - (E_{Gr} + \sum E_{func}) \quad (6.5)$$

graphite surface. Here, $E_{Gr+func}$ is the total energy of the system (*i.e.*, bi-layer graphite surface with all the functional groups), E_{Gr} is the total energy of the bi-layer pristine graphite surface, and $\sum E_{func}$ is the sum of the energy of the individual functional groups. As discussed in Chapter 4, an oxygen atom can form a bond with one carbon atom at the top site to form a carbonyl functional group or with two carbon atoms at the midbond site to form an epoxy functional group, which is expected to be the preferable site for adsorption of an oxygen atom, since oxygen atom has six valence electrons. This allows it to bind with the two carbon atoms at the midbond site straight forwardly.

Fig. 6.3 shows that the oxygen atom has indeed only a weak van der Waals interaction with the centre site of the graphite surface. The corresponding geometry in Fig. 6.4 panel A-i shows physisorption as well. The midbond site is found to be the most favourable site for adsorption of an oxygen atom with a binding energy of -1.99 eV, and two equivalent CO bonds with a bond length of 1.46 Å (Fig 6.4 panel B-i).



Figure 6.3: Relative energy profile for the formation of a single water molecule at centre, midbond, top-C1, and top-C4 sites of bi-layer graphite through sequential hydrogenation of oxygen atom.



Figure 6.4: Optimized structures (top and side view) for the adsorption of O, OH, and H_2O at (Centre)-panel A (i, ii, iii), (Mid)-panel B(i, ii, iii), (Top-C1)-panel C(i, ii, iii) and (Top-C4)- panel D(i, ii, iii) sites of bi-layer graphite surface.

Finally, adsorption of the oxygen atom at the top site leads to the formation of a carbonyl functional group (see panel C-i and D-i in Fig. 6.4) with a C-O bond of 1.42 Å, which is not much stronger than the epoxide bond shown in Fig. 6.4-B(i). However, adsorption at this site requires the target carbon atom to move out of the surface, resulting in higher surface distortion in comparison to midbond site adsorption. As a consequence, the binding energy at the top site is lower than at the midbond site.

The reaction of the first hydrogen atom with an oxygen atom at all sites leads to the formation of a hydroxyl group (OH). At both top sites, the target atom puckers up further leading to a longer C-O bond of 1.51 Å. Moreover, at the top-C1 site, the O-H bond is formed with the hydrogen pointing towards the carbon atom (panel C-ii), and at the top-C4 site, the hydrogen atom of the O-H bond points towards the centre of the hexagonal ring (panel D-ii). In both cases, an identical relative energy of -3.39 eV is obtained, which is in good agreement with previous studies.²⁸¹ At the midbond site, the OH bond is formed with the hydrogen pointing towards the centre of the hexagonal ring at a distance of ~2.25 Å from the nearest surface carbon atoms of the graphite layer (panel B-ii) with a binding energy of -1 eV.

As noted, the midbond site is the preferable site for the adsorption of atomic oxygen but was found the least preferable for the adsorption of OH. To investigate this further, we also studied the potential energy profile for the migration of OH from the top-C1 to the top-C4 site. For this, a full relaxation was given to the top layer of the graphite surface, while the oxygen and hydrogen atoms were allowed to move laterally *i.e.*, in the x and y direction but frozen along the z-direction. This results in the adsorption of OH at the midbond site as a transition state structure, as shown in Fig. 6.5. We found that the diffusion of OH from top-C1 to top-C4 occurs via weak physisorption of OH at midbond site through an energy barrier of ~0.33 eV. This is in good agreement (0.32 eV) with a previous study performed by Ghaderi *et al.*.²⁸¹



Figure 6.5: Diffusion of OH from top-C1 site to top-C4 site via the intermediate state of OH at midbond site of bi-layer graphite surface.

Similar to the midbond site, a physisorption interaction is obtained for the formation of OH at the centre site with hydrogen pointing toward the carbon atom of the hexagonal ring where it remains at a distance of ≈ 3.2 Å from the nearest surface carbon atom.

Finally, further hydrogenation leads to the formation of H₂O at all sites at a distance of

more than 3 Å from the nearest surface carbon atom, as shown in Fig. 6.3 panel A-iii, B-iii, C-iii, and D-iii. The binding energies for the adsorption of H_2O at each site are summarized in Table. 6.1. These binding energies are defined as:

$$E_b = E_{Gr+ads} - E_{Gr-ads}.$$
(6.6)

Here E_{Gr+ads} is the optimized energy of the bi-layer graphite surface with an adsorbed molecule, and E_{Gr-ads} is the optimized energy of the geometry with the molecule placed at a specific position from the graphitic surface where no interaction observed between them.

At the centre, top-C1, and midbond site, H_2O is formed in the 1-leg orientation, with one O-H pointing towards the surface. On the other hand, at the top-C4 site, water is formed in the 2-leg orientation, with both O-H bonds pointing towards the surface and both lone pairs of electrons away from the surface, resulting in a higher binding energy of -0.19 eV at the top-C4 site. This suggests that the 2-leg orientation is the most favourable geometry for adsorption of a water molecule at a graphite surface. It is in close agreement with the study conducted by Brandenburg.²⁷³ Thus, the adsorption of a water molecule on graphite surface depends on the orientation of the water molecule which is in agreement with previous studies.^{271,272,274,276,277,282–284}

Table 6.1: Binding energy for the adsorption of a single water molecule at centre, mid, top-C1, and top-C4 sites in eV, orientation of water molecule, 'd' is the distance of water molecule from the surface carbon atom, as measured to the O atom.

Sites	Centre	Mid	Top-C1	Top-C4
B.E.	-0.10	-0.11	-0.15	-0.19
orientation	1-leg	1-leg	1-leg	2-leg
d	3.52	3.32	3.17	3.6



Figure 6.6: Relaxation scheme for the adsorption of OH and H_2O at top-C1 site of bi-layer graphene surface

To further understand these reactions within the ISM environment, we have also studied the full potential energy profile for the adsorption of OH and H_2O . As discussed above the adsorption of a water molecule at all considered sites of our bi-layer graphite surface led to similar adsorption energies. Therefore, we considered the top-C1 site only here. For the first hydrogenation step (*i.e.*, to form OH at top-C1 site), full relaxation was given to carbon atom C1 and its three neighbouring carbon atoms C2, C3, and C4 as shown in Fig. 6.6. In

addition to this, the already adsorbed oxygen atom was also allowed to move in the zdirection (*i.e.*, to move in and out of the surface). For the second hydrogenation step, we used the same relaxation scheme and also allowed the previously adsorbed hydrogen to move in and out of the surface.

The potential energy curves for the formation of OH and H_2O are shown in Fig. 6.7 panels A and B, respectively. As we know, the adsorption of a hydrogen atom on a pristine

graphite surface is an activated process with an energy barrier of ~0.2 eV (discussed in Chapter 4). However, in the presence of either an epoxy or a hydroxyl functional group barrierless reaction is obtained to form either OH or H₂O, respectively. However, the formed water molecule only shows physisorption at a distance of ~ 3.2 Å from the top-C1 site. This is in agreement with previous studies which reported that, for graphene oxide (GO), the oxygen atoms act as a precursor for the adsorption of other species on the surface and can increase the binding energy²⁸⁵ of these on the surface. Therefore, it is essential to study the effect of multiple adsorbed oxygen atoms on the formation of water clusters.



Figure 6.7: Potential energy curves for the adsorption of H_{GP} to form OH (panel A) and H_2O (panel B) on bi-layer graphite surface at the top-C1 site.



6.2.2 Formation of two water molecules

Figure 6.8: Optimized structure for the adsorption of two oxygen atoms at meta and para position to each other on graphite surface. Side and top view for the meta dioxide (panel A) and for para dioxide (panel B).

After hydrogen and helium, the oxygen atom is the third most abundant element in the ISM and shows barrierless adsorption on carbonaceous surfaces as discussed in Chapter 4 and section 6.2.1. Hence, the presence of multiple oxygen atoms on dust surfaces can be expected. Below, we consider the presence of two, three and four oxygen atoms on a bilayer graphite surface.

Our calculations show that the two oxygen atoms cannot adsorb on adjacent sites of a single six-membered ring in the graphite surface. Hence, we only considered the presence of two oxygen atoms at *meta* and *para* positions to each other to form *meta* dioxide and *para* dioxide, as shown in Fig. 6.8 panels A and B, respectively. Our calculations show that *meta* dioxide is 0.74 eV lower in energy than *para* dioxide. For *meta* dioxide

(Fig 6.8 panel A), the carbon atoms bonded to a particular oxygen were non-equivalent. In particular, the two adjacent oxygen-connected carbons (C2/C3) are chemically differ-
ent from the oxygen-connected carbons, which are separated by a formal double bond (C1/C4). No distortion was observed for the C5-C6 bond, which is one bond length from the oxygenated site. The adsorption of oxygen atoms within *para* dioxide introduces a large distortion within the graphite surface, resulting in a weaker C1-C2 bond of 1.53 Å. Because of this, the adsorption of two oxygen atoms in the form of *meta* dioxide is energetically more favourable than for *para* dioxide. This is also consistent with the previous study conducted by Zhu *et al.*²⁸⁶ which reported that adsorption of oxygen atoms at different sites of graphite surface results in changes in the electronic structure of graphite. As a consequence, a large band gap of 0.279 eV for *meta* dioxide and a smaller band gap of 0.056 eV for *para* dioxide is obtained.

To study the formation of water dimer, we performed sequential hydrogenation of *meta* and *para* dioxides on a graphite surface. As discussed above, sequential hydrogenation will lead to the chemisorption of hydroxyl (OH) group and physisorption of H₂O on graphite surface. For the first hydrogenation step, we optimized all possible structures. However, only the minimum energy structure was considered for the next step. For further hydrogenation steps, we considered the previous optimized structure as an initial structure. Optimized structures and relative energy profiles for the formation of two water molecules at different sites of bi-layer graphite surface through sequential hydrogenation of oxygen atoms of *meta* dioxide and *para* dioxide are shown in Fig. 6.9 and 6.10, respectively.



Figure 6.9: Structures for sequential hydrogenation steps of a meta oxygen dimer (M-1 to M-5) and para oxygen dimer (P-1 to P-5) to form water dimer on bi-layer graphite surface.



Figure 6.10: Relative energy profile for the formation of two water molecules at different sites of bi-layer graphite surface through sequential hydrogenation of oxygen atoms of meta dioxide (pink lines) and para dioxide (blue lines).

The first hydrogenation leads to the transformation of one epoxy functional group into a hydroxyl functional group in both meta and para systems. The optimized geometries for these transformations are shown in Fig 6.9, panels M-1 and P-1, respectively. The optimized structures obtained for this shows that during this process the oxygen atom moves from the midbond site to the top of one of the bonded carbon atoms. This requires further puckering of that target carbon atom to form a C-OH bond with a C-O bond length of 1.5 Å and 1.49 Å as shown in panels M-1 and P-1, respectively. In panel M-1, the hydroxyl bond is formed at the *ortho* position to the epoxy functional group with the hydrogen atom pointing towards the centre of the ring. This results in the formation of H-bond of 1.88 Å between hydroxyl and epoxy functional group. On the other hand, in panel P-1, the hydroxyl functional group is formed *meta* to the epoxy functional group, with again the hydrogen pointing towards the centre of the hexagonal ring. The distance to the epoxy functional group is 1.97 Å in this case. Additionally, the formation of OH at the *meta* and *para* positions to the epoxy functional is obtained as an endothermic step and the geometry obtained in panel P-1 is found to be 0.12 eV higher in energy than that in panel M-1.

The second hydrogenation can lead to two possible scenarios. When a second hydrogen is added to the geometries as depicted in panels M-1 and P-1, it can either react with the hydroxyl group and lead to the formation of a water molecule, or it can react with the epoxy group and lead to the formation of two hydroxyl groups. Our results show that for both initial geometries, the formation of a water molecule in the presence of an epoxy group is energetically more favourable than the formation of two hydroxyls. After water is formed, it desorbs from the surface and leaves the surface undistorted, as shown in panels M-3 and P-3, respectively. In both cases, H₂O is formed in a 0-leg orientation and only shows weak van der Waals interaction with the GO, remaining at a distance of 3.19 Å and 3.26 Å in the *meta* and *para* geometry, respectively from the nearest surface carbon atom. The main interaction is a hydrogen bond with the remaining epoxy group. Identical energies are obtained for both geometries. On the other hand, the optimized geometry for the formation of two hydroxyl groups shows a different picture in each case, as shown in Fig. 6.9 panels M-2 and P-2, respectively. In the former case, two hydroxyls are formed at adjacent carbon atoms, with both O-H bonds parallel to the surface C-C bond. However, the short distance between these two means that the hydroxyl groups are bent away from each other, leading to an H-bond of 1.75 Å. Moreover, extensive puckering is found in this case. On the other hand, when both hydroxyls are formed *para* to each other significantly less distortion is found as shown in panel P-2. Thus, this hydroxyl dimer is 0.37 eV lower in energy than the geometry shown in panel M-2. Overall, the second hydrogenation is exothermic relative to the first hydrogenation. Compared to the initial oxidized surface it is isoenergetic to the *meta* geometry if water is formed, but the formation of two hydroxyl groups is still endothermic.

The third hydrogenation step has only one reaction possibility which leads to the formation of a hydroxyl group in the presence of a physisorbed H₂O molecule, as shown in panels M-4 and P-4. The optimized geometry in panel M-4 shows a hydroxyl group with a C-O bond of 1.5 Å, and an O-H bond is optimized parallel to the surface C-C bond. The optimized H₂O molecule is formed at a distance of 3.35 Å from the nearest surface carbon atom with a 1-leg orientation towards the surface. This results in an interaction distance of 1.87 Å between H₂O and OH, as shown in panel M-4. The optimized geometry, shown in panel P-4 has the hydroxyl bond formed with its hydrogen pointing to the centre of the hexagonal ring with a C-O bond length of 1.49 Å. In this case physisorbed H₂O is optimized in a more favourable 2-leg orientation at a distance of 3.15 Å from the surface with OH acting as H-bond donor at 1.92 Å. The more favourable 2-leg orientation of the water molecule means that the geometry in panel P-4 is 0.11 eV lower in energy than the geometry in panel M-2. Formation of the OH-H₂O group on the surface is exothermic relative to all earlier discussed scenarios.

Finally, the fourth hydrogenation step completely hydrogenates both oxygen atoms, resulting in the formation of two water molecules as shown in Fig. 6.9 panels M-5 and P-5, respectively. In both cases, one water molecule is formed in a 2-leg orientation, and the second water molecule is formed with one O-H bond pointing away from the surface and a second O-H bond parallel to the surface. The distance between the two H₂O molecule is 1.9 Å and 1.87 Å as shown in panels M-4 and P-4, respectively. In both cases, the water dimer is formed at a distance of more than 3 Å from the surface and shows only a weak interaction with the graphite surface, resulting in a similar energy of water dimer formation. The binding energies obtained for the adsorption of water dimer are weaker than the adsorption of a single water molecule in the presence of an epoxy group. In contrast, this final hydrogenation step is endothermic as is clear from the energies reported in Table 6.2.

Table 6.2: Binding energy (E_b) in eV for the formation of single water in the presence of epoxy and hydroxyl functional and for the formation of water dimer in meta and para systems on bi-layer graphite surface.

Eb	meta	para
$O-H_2O$	-0.24	-0.25
$OH-H_2O$	-0.36	-0.47
$2H_2O$	-0.12	-0.09

Concluding, the presence of oxygen atoms on a graphite surface makes the graphite surface hydrophilic. Thus, stronger binding energies are obtained for the adsorption of a single water molecule in the presence of epoxy or hydroxyl groups compared to the adsorption of a single water molecule on the hydrophobic pristine graphitic surface. For panels M-5 and

P-5 water dimer result a smaller binding energy with the surface and shows H-bonding within the water dimer. This is consistent with previous studies.^{287,288} These studies reported that as the number of water molecules on the surface increases, a water layer is formed and the binding energy within the set of water molecules is found to be stronger than the binding energy of a water molecule with the graphite surface.²⁷²

6.2.3 Formation of three water molecules

For the next step, we considered the presence of three oxygen atoms on a bi-layered graphite surface located within one hexagonal ring. Similar to the single and double oxygenation of a graphite surface as discussed above, adsorption of three oxygen atoms is found to be an exothermic step. The optimized geometry for the adsorption of three oxygen atoms on the graphite surface showed equivalent C-C, C-O, and O-O bonds in the hexagonal ring, as shown in Fig. 6.11 panel-A. As above, we will discuss the sequential hydrogenation of these oxygen atoms. The optimized structures for each of these calculations are shown in Fig. 6.11 from panels B to J. The relative energy profile for the hydrogenation steps is shown in Fig. 6.12.



Figure 6.11: Structures for sequential hydrogenation steps of three oxygen atoms on a bi-layer graphite surface (panels A to J) to form three water molecules.



Figure 6.12: Relative energy profile for the formation of three water molecules at different sites of bi-layer graphene surface through sequential hydrogenation of oxygen atoms. Blue and pink color shows the energy of structures with equivalent hydrogenation.

The first hydrogen atom has an equal probability of hydrogenating any of the oxygen atoms, transforming one epoxy group into a hydroxyl group (Fig. 6.11 panel B). As before, the epoxy oxygen moves from the midbond site of the C-C bond to the top of one of the carbon atoms (in this case, at C3), forming a C-O bond of 1.48 Å with the O-H bond pointing towards the centre of the hexagonal ring. This requires C3 to pucker up, and C4 to revert into the graphite plane by dissociation of the C-O bond. This also adds strain to the C2-C3 bond, because C2 is still bonded to an epoxy group. Formation of two hydroxyl groups results in the formation of a C-O bond of 1.47 Å and the formation of two O-H bonds, with one O-H pointing to the centre of the ring and the second O-H bond parallel to the surface C-C bond. On the other hand, formation of a water molecule (panel D) only shows a weak interaction with the graphite surface and stays at a distance of 3.24 Å from the surface. This also releases the distortion from the surface, and the remaining distortion is observed because of the epoxy functional group. Thus, similar to the discussion in section 6.2.2, for the second hydrogenation step, the formation of a water molecule in the presence of two epoxy groups is found as 0.14 eV lower in energy than the formation of two hydroxyl groups in the presence of one epoxy group. The corresponding geometries are shown in Fig. 6.11 panels C and D.

The third hydrogenation step shows two possible reaction pathways resulting in the formation of either a physisorbed H₂O in the presence of an epoxy and a hydroxy group (panel E) or the formation of three hydroxyls groups (panel F). The optimized geometry in panel E shows the formation of a hydroxy group at a carbon atom next to the epoxy group with a C-O bond length of 1.45 Å, and an O-H bond parallel to the surface C-C bond. However, the epoxy group also shifts in this case from the midbond site to one of the carbon, As a consequence, it is more like a carbonyl group. One C-O bond has a length of 1.41 Å and the other is 2.15 Å. There is also a bond of 1.6 Å between the hydroxyl and carbonyl functional groups. Meanwhile, the water molecule stays at a distance of 3.06 Å from the surface leaving it undistorted with both O-H bonds parallel to the graphite surface.

Panel F shows the formation of three hydroxyl functional groups with C-O bond lengths of 1.46 Å, 1.49 Å, and 1.5 Å. Two of these hydroxyl functional groups are formed at

6.2

adjacent carbon atoms with one O-H bond pointing along the surface C-C bond with a distance of 1.71 Å between them, whilst the C-C bond underneath these hydroxyls group is elongated to 1.58 Å. The third hydroxyl bond is formed at two and three bonds apart from the other two with the O-H bond pointing to the centre of the hexagonal ring. However, the obtained relative energy profile shows that whilst adsorption of these species on the surface is energetically more favourable than desorption, this hydrogenation step is endothermic relative to the previous step and as a result, the formation of 3OH groups is more favourable than the other scenario.

The fourth hydrogenation step generates two possible reaction pathways. This can either form one water molecule in the presence of two hydroxyl groups or the formation of two water molecules with a remaining epoxide (panels G and H in Fig. 6.11, respectively). Within the optimized geometry shown in panel G, the water molecule is at a distance of 3.12 Å from the surface. The two hydroxyl functional groups are formed at adjacent carbon atoms lengthening the C-C bond to 1.57 Å. In this configuration, one O-H bond is formed parallel to the surface C-C bond, with a C-O bond of 1.5 Å. The other O-H bond is formed pointing to the centre of the ring with a stronger C-O bond of 1.46 Å. Thus, the two hydroxyl functional groups end up 1.73 Å apart. This geometry is energetically less favourable than the geometry shown in panel H. Here, two water molecules end up at a distance of more than 3.3 Å from the surface. The relative energy obtained in this case shows that the interaction between two water molecules is stronger than between one water molecule and hydroxyl group. Thus, the presence of an epoxy functional group on the surface favours the interaction of water molecules. In panel H, this epoxy functional group is transformed into a hydroxyl group with O-H in parallel to a C-C bond and relatively long C-O bond of 1.53 Å. In this geometry, one water molecule is formed in a 2-leg orientation and the other in a 0-leg orientation. This results in a distance of 1.83Å between these two and a distance of 1.85 Å with the hydroxyl group. However, the higher relative energy obtained for this shows that the interaction of two water molecules with an epoxy group is more favourable than the interaction with a hydroxyl group.

Finally, the complete hydrogenation of all three oxygen atoms led to the formation of a water trimer (panel J of Fig. 6.11). These water molecules show only a weak interaction with the surface and have an equilibrium distance of more than 3.4 Å, leaving the surface completely undistorted. This lack of distortion results in relatively low energy. This result a lower binding energy of -0.12 eV with the graphite surface, which is identical to the binding energy obtained for the formation of water dimer. Overall hydrogenation of three oxygen atoms to three water molecules is exothermic. However, there are endothermic steps in this process and therefore, it would be possible for hydrogenation to stop, because the energy budget for further reaction is not present.

6.2.4 Formation of four water molecules

Finally, we studied the formation of four water molecules on a graphite system *via* sequential hydrogenation of four adsorbed oxygen atoms. As four oxygen atoms cannot adsorb on a single hexagonal ring, we consider the adsorption of three oxygen atoms on a single six-membered ring with the fourth oxygen atom on the neighbouring hexagonal ring. The optimized bi-layer graphite with four oxygen atoms is shown in Fig. 6.14 panel A. The results show that all oxygen atoms are adsorbed at the midbond site of alternate C-C bonds of the hexagonal ring in the form of epoxy groups. All four oxygen atoms were found to be equivalent, and the C-C bond lengths underneath the oxygen atoms and the neighbouring C-C bonds were also found to be equivalent with a bond length of 1.48 Å. It is noted that adding a fourth oxygen atom makes that not all C-O distances are the

K)

З

C1-C2=1.45, C2-C3=1.48

C3-C4=1.47,C5-C6=1.43

C4-C5=C6-C7=1.40

C-C=1.41, C7-C8=1.51

C2-C3=C3-C4=1.51



same. All relevant distances are reported in Table 6.13.

Figure 6.13: Structures for sequential hydrogenation steps of four oxygen atoms on bilayer graphite surface (panels A to O) to form four water molecules.

C-C=1.42, C2-C3=1.48

C-C=1.42, C-OH=1.51

C2-C3=C3-C4=1.49

C-C=1.42, C-H₂O=3.38



Figure 6.14: Relative energy profile for the formation of four water molecules at different sites of bi-layer graphite surface via sequential hydrogenation of oxygen atoms. Blue, pink, and green colors show the energy of structures with equivalent hydrogenation.

The optimized structure for the sequential hydrogenation of four oxygen atoms is shown in Fig. 6.13 panel B to panel O, and the relative energy profile for these is shown in Fig. 6.14. Similar to the previous systems, the first hydrogenation leads to the transformation of any epoxy functional group into a hydroxyl group *via* the breakage of one C-O bond. This requires one of the bonded carbon atoms to move out and simultaneously the other carbon atom to move back in the graphite plane resulting O-H bond is formed with hydrogen pointing to the centre of the hexagonal ring, as shown in Fig. 6.14 panel B.

Similarly to the two-oxygen and three-oxygen systems, further hydrogenation leads to a competition to form either a hydroxyl functional group or a water molecule. For the second (panels C and D), third (panels E and F), and fourth hydrogenation step (panels G, H, and I), hydrogenation of a hydroxyl group to form a water molecule is found to be energetically more favourable than the hydrogenation of an epoxy group to form a hydroxyl group. This is expected because, after the formation of a water molecule, it desorbs from the surface and physisorbs at a distance of more than 3 Å. This also removes the distortion from the surface, whilst formation of a hydroxyl group adds distortion to the surface.

The fourth hydrogenation could be done through three possible reaction pathways. First, the formation of two water molecules in the presence of two epoxy groups (panel G). These water molecules remain at a distance of ~ 3.16 and 3.61 Å from the surface and show two possible H-bonding interactions. In that case, the formation of four hydroxyl functional groups is not stable as shown in panel I. This results in the formation of one physisorbed water molecule and two hydroxyl groups. This geometry shows three H-bonding interactions (H(O3)-O1=1.9 Å H(O2)-O1=1.46 Å, H(O4)-O1=1.56 Å) and has almost identical energy to the geometry shown in panels H, because of similar surface distortion. Here, one can also form 1 water molecule, 2 hydroxyl groups and an epoxy group. This geometry is shown in panel H. The final geometry has all hydroxyl groups *meta* to each other.

6.3

The fifth hydrogenation step has two pathways. First, the formation of three hydroxyl functional groups (panel J) with one H₂O molecule in 2-leg orientation at a distance of 3.61 Å from the nearest surface carbon atom. The hydroxyl groups form with a C-O bond length of 1.5 Å with the O-H bonds pointing towards the centre of the hexagonal ring. This results in different interactions between the functional groups, $(H_2O)-O3=2.02$ Å, $H(H_2O)-O2=2.26$ Å, $H(O_2)-O3=1.91$ Å, and $O(H_2O)-H(O4)=1.66$ Å. This hydrogenation step is endothermic relative to the previous one. The second possibility is the formation of two water molecules in the presence of a hydroxyl group (panel K). This process ends up in a 1-leg form and the other with both O-H bonds parallel to the surface, resulting in a distance of 1.84 Å between these water molecules. Here, there is also a distance of 2.43 Å between H (H₂O) and O2, and a distance of 1.71 Å between H(O4) and O1. These interactions combined with the smaller amount of surface distortion makes this geometry more favourable than the 3 OH and 1 water geometry and makes it exothermic relative to the previous hydrogenation step.

Further hydrogenation hydrogenates the hydroxyl groups and leads to the formation of water molecules. The optimized geometries for the sixth and seventh hydrogenation steps are shown in panels L, M, and N, respectively. The optimized geometry obtained in panel L shows the formation of two water molecules in the presence of two hydroxyl functional groups, which were found to be higher in energy because of more distortion in the surface. Thus, the formation of water molecules was found to be energetically favourable, as water molecules have only a weak interaction with the graphite surface with the associated lower energy penalty from desorption. The complete hydrogenation of four oxygen atoms leads to the formation of four water molecules, as shown in panel O. In this case, water molecules are formed at a distance of ~ 3.38 Å from the graphite surface. These four water molecules clusters have three H-bonding interactions with a distance of 1.83 Å, 1.79 Å, and 2.65 Å respectively. They leave the graphite surface completely undistorted. However, this step is endothermic and results in the binding energy of -0.17 eV. The binding energy obtained in this case is higher than the binding energy obtained for the formation of water dimer (-0.12 eV) and trimer (-0.13 eV) but still lower than the adsorption of a single water molecule (-0.19) eV. This shows that water can form an ice layer on a dust surface, as within the ice layer water molecules show strong H-bonding interactions. However, they need to be anchored to the surface through either hydroxyl or epoxy groups. This suggests that achieving the surface through defects may help in the formation of a water layer. Thus, in the next section, we show the effect of defects within the surface on the formation of water molecules.

6.3 Formation of a water dimer on a doped graphite surface

Previous studies have reported that the chemical properties of a graphene surface change dramatically when doped with B, N, Si, and S. Adsorption of gas molecules (O₂, NO₂, CO₂, and NH₂) has also been studied on doped graphene surfaces.^{289–293} However, the formation of water clusters on Si and Fe-doped graphitic surface has not been studied yet.

In this section, we present the results of the reaction of adsorbed species to form water dimers on single Si and Fe-doped bilayer graphite. We only consider Fe and Si as defects given their abundance in the ISM.^{221–223} A substituted graphite surface was formed by replacing one carbon atom from the graphite surface with a single alternative defect atom (Fe and Si). Site A of bi-layer graphite surface (Fig. 6.15).



Figure 6.15: Pure bi-layer graphite surface. Site A was chosen for substitution, while the midbond site of carbon atoms B-C and D-E represent the adsorption of two oxygens atoms at the meta position to each other in the form of H an epoxy group. Similarly, the midbond site of carbon atoms B-C, and E-F represents the adsorption of two oxygens atoms para to each other.

As discussed in Chapter 4, the substituted Si and Fe atoms prefer to stay in either positively or negatively puckered states because either atom is larger than the carbon atom it replaces. Considering this, we re-optimized the substitution of Fe and Si in graphite surface by adding a positive or negative puckering of 0.5 Å before each optimization. The binding energy E_{sub} for the defect substitution was calculated using the relation²²⁴

$$E_{sub} = E_{graphite+sub} - \frac{N-1}{N} E_{graphite} - E_{sub\ atom}.$$
(6.7)

Here, $E_{graphite+sub}$, $E_{graphite}$, and $E_{sub\ atom}$ are the energy of bi-layer graphite + substituted atom, bi-layer graphite, and substituted atom, respectively. N is the The binding energies of Fe and Si atoms

number of carbon atoms in the graphite model. The binding energies of Fe and Si atoms in the graphite surface are shown in Table 6.3.

Table 6.3: Total optimized energies and the substitution energy of the substituted bi-layer graphite system, for 'up' (positive puckering), and 'down' (negative puckering) are in eV, C-X is the bond length between the substituted defect atom and neighbour carbon atoms in Å.

Defect (X)	E_{up}	E _{down}	E _{sub-up}	$E_{\rm sub-down}$	C-X (up)	C-X (down)
Fe	-329.38	-330.74	-1.23	-1.36	$1.77^{225-227}$	1.76
Si	-327.72	-327.83	-1.70	-1.81	1.81	1.77

The substitution energy shown in Table 6.3 demonstrates the effect of positive and negative puckering of these atoms within the graphite surface at site A. This indicates a higher binding energy of these defects within the puckered-down configuration. This is equal to the result obtained in Chapter 5. To study the formation of a water dimer in the presence of these defect atoms, we considered the presence of two oxygen atoms in the form of a *meta* dioxide and a *para* dioxide within the same hexagonal ring. The formation of the water dimer was studied by sequential hydrogenation of these oxygen atoms, similar to our discussions in section 6.2.2.

6.3.1 Formation of a water dimer on a silicon doped graphite surface

As discussed in section 5.3.4, Si is the 5th most abundant element in the ISM. The reader is reminded that substituting one carbon atom from the graphite surface with one Si atom dramatically distorts the graphite surface to form a silicon-substituted graphite surface (SiG). Thus, as expected due to the large atomic radius of Si in comparison to C as before, to release the stress, the Si atom either moves below (puckered-down) the carbon plane by ~1.16 Å, or moves above the plane by ~1.18Å (puckered-up). For our work, we considered both geometries for the formation of water dimers. To study the formation of



a water dimer, we first optimized two oxygen atoms at the *meta* and *para* positions to each other within a substituted six-membered ring.

Figure 6.16: Optimized structures for the substitution of a negatively puckered Si atom as a defect in bi-layer graphite surface, $Si \downarrow G$ (panel A), adsorption of two oxygen atoms meta to each other (panel B), and para to each other (panel C) on $Si \downarrow G$.

First of all, we consider the puckered-down Si geometry $(Si\downarrow G)$. The structures of $Si\downarrow G$ with two oxygen atoms at *meta* and *para* positions to each other are shown in Fig. 6.16, panels B and C, respectively. The presence of the Si atom in a negatively puckered configuration creates edges at the two bonded carbon atoms, C1 and C5, making these sites more reactive. Chemisorption of oxygen atoms requires the target carbon atoms to pucker up. As a consequence, the Si-C1 bond length increases to 1.83 Å. Our calculations for the adsorption of oxygens *meta* to each other show that, due to the edge effect, the first oxygen atom (O1) slightly shifts to the defect site, as shown in panel B of Fig. 6.16. However, no effect of the defect is observed for oxygen atom O2, which is located further from the defect site. On the other hand, adsorption of two oxygen atoms *para* to each other in the same hexagonal ring on the Si \downarrow G surface is found to be 0.43 eV higher in energy than the *meta* scenario (see Fig. 6.16, panel C). Because of the edge effect, both oxygen atoms shift from the midbond site towards the defect site, introducing more distortion in the surface leading to a higher energy in comparison to the *meta* dioxide geometry.

For the formation of a water dimer, we studied all the possibilities of hydrogenation at each step, but only the minimum energy-optimized structures are reported here. The structures for the *meta* starting point are shown in panels M-1 to M-5 of Fig. 6.17. The corresponding structures starting from the *para* geometry are shown in Fig. 6.17 panels P-1 to P-5. The relative energy profile is shown in Fig. 6.18.

The first hydrogenation step for *meta* dioxide has a hydrogenation at the far oxygen atom O2 instead of the near oxygen atom O1. This results in the formation of a hydroxyl group at the carbon atom C3 with the O-H bond pointing towards the defect site (Fig. 6.17 panel M-1). In the case of the *para* dioxide, both oxygen atoms are found to be chemically equivalent and equally reactive towards the hydrogen atom. Therefore, in the structure presented here the incoming hydrogen atom reacts with oxygen atom O1, resulting in the formation of a hydroxyl group on top of the edge carbon atom C1 with a relatively short C-O bond of 1.39 Å (Fig. 6.17 panel P-1). The transformation of the epoxy group to a hydroxyl group requires the target carbon atom C1 to move out of the graphite plane, resulting in a longer Si-C1 bond of 2.1 Å. Moreover, the geometry in panel P-1 also shows

that the O-H bond is formed pointing towards the centre of the hexagonal ring, and the more electronegative oxygen atom is bent $\approx 10^{\circ}$ towards the defect site. The interaction between the defect site and the hydroxyl functional group in panel P-1 is probably the reason for the lower energy of this geometry in comparison to the geometry found in panel M-1.



Figure 6.17: Structures for sequential hydrogenation steps starting from an epoxy dimer, either meta (panels M-1 to M-5) or para (panels P-1 to P-5), to each other on a negatively puckered $Si \downarrow G$ to form water dimer.

Similar to the discussion in section 6.2, two reaction pathways are possible for the second hydrogenation step. Interestingly, for the second hydrogenation, the formation of two hydroxyl groups is found to be more favourable for both *meta* and *para* starting points rather than the formation of a single water molecule. This shows a clear effect of the substitution, as it is opposite to what we found on the unsubstituted graphite surface, as discussed in section 6.2.2. The optimized geometries for the formation of water molecules in both systems are shown in panels M-3 and P-3, respectively. Similar to previous results, it is shown that after the formation of the water molecule, it is released from the surface and stays at a distance of more than 3.1 Å from the Si \downarrow G surface, as shown in panels M-3 and P-3. The formation of the water molecule leaves an epoxide group next to the defect and releases deformation from the surface. Thus, similar energies are obtained for

both geometries. The second reaction pathway leads to the formation of two hydroxyl groups, as shown in panels M-2 and P-2, respectively. The geometry in panel M-2 has one hydroxyl group at the *ortho* position to the defect site and one at *meta* to the defect site. As discussed before, the formation of a hydroxyl group requires the target carbon atom to pucker up. In this case this results in a longer Si-C1 bond length of 1.95 Å. As mentioned the second hydroxyl group is formed *meta* to the defect site with a longer C-O bond (1.51 Å). This is far enough from the defect site as to not affect the Si-C5 bond. In this case, the O-H bond is formed pointing towards the defect site with a resulting distance of 1.76 Å between the two hydroxyl groups. In panel P-2 both hydroxyl functional groups are formed *ortho* to the defect site with C-O bond lengths of 1.36 Å and 1.49 Å, respectively. This geometry also has a short distance of 1.5 Å between the hydroxyl groups. However, the adsorption of two hydroxyl functional groups *ortho* to the defect site forces the defect atom further down, resulting in longer Si-C bonds of 1.96 Å and 2.21 Å. This higher surface distortion means that the geometry shown in panel P-2 is 0.34 eV higher in energy than the geometry shown in panel M-2.



Figure 6.18: Relative energy profile for the formation of water dimer on $Si \downarrow G$ surface through sequential hydrogenation of meta (pink lines) and para (blue lines) oxygen dimer. Blue, pink, green, and red color shows the energy of structures with equivalent hydrogenation.

The third hydrogenation step, which forms physisorbed water molecules in the presence of one hydroxyl group is found to be endothermic for both *meta* and *para* starting points. The optimized structures obtained for both systems are shown in panels M-4 and P-4, respectively. Interestingly, in panel M-4, the hydroxyl group migrates to the position *meta* to the defect site instead of remaining *ortho* to the defect site. As a result, no effect of the defect is observed in this case with a C-O bond length of 1.50 Å, and the O-H bond forms parallel to the surface C-C bond. The water molecule is formed above the surface atom with a 1-leg orientation at a distance of 2.01 Å from the hydroxyl group. In contrast, the geometry in panel P-4 shows the formation of a water molecule in a 2-leg orientation at 2 Å from the hydroxyl group. Here, the hydroxyl group stays *ortho* to the defect site. Thus, the defect atom further recedes into the surface lengthening the Si-C bond to 1.97 Å. Moreover, the oxygen atom now bends over the space left by the defect atom. This makes this geometry 0.63 eV lower in energy compared to the geometry shown in panel M-4.

The fourth hydrogenation step results in the formation of two water molecules. This step is exothermic with respect to the previous step but endothermic to the formation of 2OH groups. The optimized geometries for this step are shown in Fig. 6.17 panel M-5 and P-5 with binding energies of -0.22 eV and -0.11 eV, relative to Si \downarrow G, respectively. The optimized geometry shown in panel M-5 shows the formation of one water molecule in the 2-leg form, while the other water molecule is formed with one O-H bond in parallel to the surface and the other O-H bond pointing away from the surface. The resultant distance between the two water molecules is 1.89 Å. On the other hand, the optimized geometry in panel P-5 shows the formation of one water molecule in the 1-leg form and the second water molecule with both O-H bonds in parallel to the surface with a distance of 2.77 Å between the water molecules. The release of both water molecules from the surface releases the distortion caused by previously adsorbed oxygen atoms in both cases. However, stronger H-bonding within the M-2 geometry leads to a more stable geometry (by 0.34 eV) compared to panel P-2. Overall, the two water molecules do not interact strongly with the negatively puckered $Si\downarrow G$ surface. However, a positively puckered $Si\uparrow G$ surface paints a different picture.

In the puckered-up stage, the defect atom remains at a distance of 1.81 Å from the bonded carbon atoms, as shown in Fig. 6.19 panel A. In general, the presence of a positively puckered Si atom makes the defect site more active than in the negatively puckered system, where the edges are more active than the defect site. Optimized structures of positively puckered Si \uparrow G with two oxygen atoms at either *meta* or *para* positions to each other are shown in Fig. 6.19, panels B and C, respectively.



Figure 6.19: Optimized structures for the substitution of a positively puckered Si atom as a defect in bi-layer graphite surface, $Si\uparrow G$ (panel A), adsorption of two oxygen atoms at meta to each other (panel B), and para to each other (panel C) on $Si\uparrow G$.

Our results show that in the *meta* system, oxygen atom O1 moves from the epoxy form to form a bond with the more active defect site, resulting in a Si-O bond of 1.56 Å, which is close to the length of a double bond (1.6 Å) between Si and O.²⁹⁴ To form this bond, the Si atom further puckers up. This increases the Si-C1 bond length to 1.83 Å. Meanwhile, the second oxygen atom O2 remains in the epoxy form. On the other hand, in the *para* system, both oxygen atoms are equivalent. Therefore, they have an equal probability to form the Si-O bond. The geometry shown in panel C shows the migration of oxygen atom

O2 from the epoxy form to form a Si-O bond, with a bond length of 1.56 Å, which is the same as for the *meta* system.

Optimized structures for the sequential hydrogenation of *meta* and *para* dioxide to form water dimer on positively puckered Si substituted bi-layer graphite $(Si\uparrow G)$ are shown in Fig. 6.20 panels M-1 to M-5 and P-1 to P-5, respectively. The relative energy profile for these are shown in Fig. 6.21.

The first hydrogenation step shown in Fig. 6.20 panels M-1 and P-1 leads to a hydroxyl group at the top of the defect site with a longer Si-O bond length than before the hydrogenation of 1.65 Å, which is equivalent to the single Si-O (1.68 Å) bond.²⁹⁴ Thus, this bond length is not significantly influenced by the hydrogenation. In panel M-1 the O-H bond is formed with hydrogen pointing parallel to the Si-C1 bond, while in panel P-1 this O-H bond is formed pointing toward the centre of the ring. The presence of the epoxy group next to the Si-O group leads to more distortion than having the epoxy group further away as in the geometry shown in panel M-1. Thus, the geometry shown in panel M-1 is 0.25 eV lower in energy than the geometry shown in P-1. However, in both cases the hydrogenation process is exothermic.



Figure 6.20: Structures for sequential hydrogenation steps starting from an epoxy dimer, either meta (panels M-1 to M-5) or para (panels P-1 to P-5), to each other on a positively puckered $Si\uparrow G$ to form water dimer.

As discussed before in sections 6.2.2 and 6.3.1, the second hydrogenation leads to the formation of either a water molecule in the presence of an epoxy group or the formation of a hydroxyl dimer. Similarly to the situation discussed earlier with the negatively puckered Si atom the formation of a hydroxyl dimer is found to be more favourable than the formation of a water molecule in both cases, as shown in Fig. 6.21, even though both processes are endothermic relative to the formation of a single hydroxyl group. In both cases, one hydroxyl bond is formed at the top of the defect site with a Si-O bond length of 1.66 Å. In panel M-2, the second hydroxyl functional group is formed at C4, which is two bonds apart from the defect site with the hydrogen pointing towards the centre of the neighbouring hexagonal ring and the two hydroxyl groups remain at a distance of 3.74 Å. In contrast, the position of the remaining epoxy group as shown in panel P-1 leads to the formation of OH dimers. The resulting geometries are shown in panels M-2 and P-2. The second hydroxyl functional group at the carbon atom next to the defect site as shown in panel P-2, requires puckering of both Si and carbon atom C1. This also results in the bending of the C-O bond by more than 10° away from the defect site, as a result, the distance between the two hydroxyl groups is 2.16 Å. This distance is smaller than the geometry pictured in panel M-2 (3.74 Å), which explains the lower energy of panel P-2 geometry compared to panel M-1.



Figure 6.21: Relative energy profile for the formation of water dimer on $Si\uparrow G$ through sequential hydrogenation of meta (pink) and para (blue) dioxide. Blue, pink, green, and red color shows the energy of structures with equivalent hydrogenation.

The second potential outcome of this hydrogenation step is the formation of water in the presence of an epoxy group. Geometries for this are shown in panels M-3 and P-3, respectively. The geometry obtained in panel M-3 shows the formation of H₂O as a ligand on top of the Si atom with a Si-O bond of 2.03 Å. Meanwhile, the epoxy group remains at the position *meta* to the defect site. Thus, there is only a weak van der Waals interaction between the two. For the *para* system, the presence of the epoxide close to the defect site means that formation of water leads to an unstable geometry, which immediately finds a lower energy structure in the form of a hydroxyl dimer, as shown in panel P-2. Thus, we modelled the second hydrogenation as the formation of H₂O away from the defect site in the presence of Si-O. The optimized structure obtained for that is shown in panel P-3. with the oxygen atom of Si-O of 1.74 Å. The relative energy profile also shows that the structure in P-3 could be an intermediate which will transform into the more favourable geometry, P-2. However, further calculations on the full potential energy surface will be needed to elucidate that.

For the third hydrogenation step, the minimum energy geometries show formation of a water molecule in the presence of a Si-OH bond in both cases as shown in Fig. 6.20 panels M-4 and P-4, respectively. Here, OH is attached to the Si atom with a Si-O bond length of 1.68 Å. The oxygen atom of this OH has an H-bonding distance of ~ 2 Å with the hydrogen atom of H₂O. The optimized H₂O ends up at distances of 3.83 Å and 3.66 Å, respectively, with one hydrogen pointing toward the surface and the other parallel to the carbon plane, in a similar geometry to panel P-3. Due to the equivalent configuration and similar amount of distortion in the surface, similar energies are obtained for both geometries, which are exothermic relative to the previous step but still endothermic relative to the situation depicted in panels P-1 and M-1.

For complete hydrogenation, an optimized water dimer is obtained on a positively puckered $Si\uparrow G$ and the optimized geometries are shown in panel M-5 and P-5, respectively. In both systems, one H₂O coordinated to the defect site and hydrogen bonded to the second water molecule, which ends up in the 2-leg orientation. In both cases this second water molecule ends up more than 3 Å from the surface. Moreover, the geometries in panels M-5 and P-5 are formed with binding energies of -0.82 eV and -0.6 eV, relative to Si $\uparrow G$, respectively. These binding energies are approximately four times the binding energy of water dimer obtained on negatively puckered Si $\downarrow G$. This might be because of the presence of interaction of Si and O in case of Si $\uparrow G$, but this is not the case in Si $\downarrow G$. Thus, the defect acts as an anchor for the adsorption of the water dimer which ultimately could lead to the formation of a water layer. It should be noted that this last step is endothermic to all steps.

6.3.2 Formation of a water dimer on an iron doped graphite surface

Similar to the substitution of carbon with silicon discussed in section 6.3.1, the substitution of one carbon atom for one iron atom adds significant distortion to the graphite surface due to the larger atomic radius of iron compared to carbon. As before, this requires iron to pucker in or out of the graphene plane. In either case, a Fe-C bond of ~ 1.76 Å is obtained, which is in close agreement with previous studies.^{226,227} Similar to when Si was substituted, a lower binding energy is obtained in the puckered-up form compared to the puckered-down form. However, a large surface distortion can be expected in the case of Fe substitution because of the large atomic radius of Fe (1.26 Å) than Si (1.1 Å). As a consequence lower binding energies are found for Fe substitution in both puckered-up and puckered-down than for Si. For our work, we used both structures to study the formation of water dimers.

The optimized structure of the negatively puckered FeG system (Fe \downarrow G) shows an opening of the edge at the carbon atoms bonded to the defect site, with a Fe-C bond length of 1.77 Å without any distortion for the rest of the surface (Fig 6.22 panel A). The optimized structures of the negatively puckered FeG with two oxygen atoms positions at *meta* or *para* to each other is shown in Fig. 6.22 panels B and C, respectively. Similar to section 6.3.1 the depression of the substitution below the graphene plane creates hollow and the active edge sites at C1 and C5. As a consequence, the oxygen atom adsorbed at the midbond site *ortho* to the defect site interacts more strongly with the active carbon atom edge site, resulting in non-equivalent C-O bonds for the epoxy group, *i.e.* a C1-O bond length of 1.44 Å, and a C2-O bond length of 1.49 Å. This also lifts up carbon atom C1 and lengthens the Fe-C1 bond to 1.81 Å. However, no effect of the defect is observed on the other oxygen atom, which remains in the middle of the C3-C4 bond.

On the other hand, in the *para* dioxide form, both oxygen atoms present at the *ortho* position to the defect site show a shift to the edge site, resulting in the formation of C-O bonds of 1.42 Å and 1.48 Å, respectively. This introduces more surface distortion in the surface and results in a longer Fe-C bond of 1.82 Å because the iron atom further recedes into the surface as shown in Fig. 6.22 panel B. Because of the edge effects, adsorption of an oxygen atom at the active edge sites in the form of *para* dioxide is found to be 0.91 eV lower in energy than *meta* dioxide.

As above, we will consider sequential hydrogenation next. The optimized structures starting from *meta* and *para* dioxide are shown in Fig. 6.23 panels M-1 to M-5 and P-1 to P-5, respectively. The relative energy profile for these hydrogenation steps is shown in Fig. 6.24.



Figure 6.22: Optimized structures for the substitution of a negatively puckered Fe atom as a defect in bi-layer graphite surface, $Fe \downarrow G$ (panel A), adsorption of two oxygen atoms meta to each other (panel B), and para to each other (panel C) in $Fe \downarrow G$.

As before, the first hydrogenation leads to the formation of one hydroxyl functional group in both the *meta* and *para* configurations. The final geometries obtained are shown in panels M-1 and P-1, respectively. The geometry shown in panel P-1 is energetically more stable than M-1. In both cases, the hydroxyl functional group is optimized at the carbon atom next to the defect site, with a C-O bond length of 1.37 Å. The hydroxyl group also shows H-bonding with the epoxy oxygen atom with bond distance of 1.73 Å and 1.75 Å for Fig. 6.23 panels M-1 and P-1, respectively. Hydrogenation of the epoxy group to form a hydroxyl group requires carbon atom C1 to pucker up, which increases the Fe-C1 bond length to 1.93 Å. The oxygen atom leans over into the space left by the iron atom, resulting in a bent C-O bond on the defect site by $\sim 10^{\circ}$. Again, the formation of the epoxy and hydroxyl functional groups at the active edge site makes the P-1 geometry more favourable than the *meta* system (M-1). However, both hydrogenations are exothermic compared to both dioxide geometries.

Similar to the discussion in section 6.3.1, the reaction of a second hydrogen results in the formation of a hydroxyl dimer as a more energetically stable geometry compared to the formation of a single water molecule in the presence of an epoxy group in both systems. The optimized geometries for the *meta* and *para* starting points are shown in Fig. 6.23

6.3

panels M-2–M-3 and P-2–P-3, respectively. The geometry shown in panel M-2 shows the formation of two hydroxyl groups with one hydroxyl bond formed next to the defect site (C1) with a C-O bond length of 1.43 Å. The second hydroxyl bond is formed meta (C4) to the defect site with a C-O bond length of 1.51 Å (see Fig 6.23 panel M-2). In this geometry, the hydroxyl bond formed at C1 has the O-H bond pointing towards the centre of the ring, whilst the hydroxyl bond formed at C4 has the O-H bond pointing towards the defect site, resulting in a hydrogen bond of 1.76 Å. On the other hand, the geometry shown in panel P-2 shows the formation of two hydroxyl groups at the edge sites with C-O bond lengths of 1.40 Å and 1.42 Å. However, these hydroxyl groups stay at a distance of 2.73 Å with two oxygen at 2.51 Å apart. Again because of the edge effect, the geometry shown in panel P-2 is found as 0.58 eV lower in energy than the geometry shown in panel M-2. Moreover, the formation of this geometry is exothermic relative to single hydrogenated species. For the formation of H_2O in the presence of an epoxy group edge effects dominate again. In addition, the epoxy group is formed *meta* or *ortho* to the defect site in panels M-3 and P-3, respectively. The presence of the edge effect and the more advantageous placement of the epoxy oxygen in panel P-3 means that the P-3 geometry is 0.84 eV lower in energy than the M-3 geometry.



Figure 6.23: Structures for sequential hydrogenation steps starting from an epoxy dimer, either meta (panels M-1 to M-5) or para (panels P-1 to P-5), to each other on a negatively puckered $Fe \downarrow G$ to form water dimer.

The third hydrogenation step leads to the formation of H₂O in the presence of a hydroxyl group. The water molecule ends up at a distance of 3.52 Å and 3.55 Å from the Fe \downarrow G surface as shown in panels M-4 and P-4, respectively. Formation of the hydroxyl group at the position *meta* to the defect site as shown in panel M-4 and formation of the hydroxyl group is formed with a C-O bond of 1.5 Å, with the O-H bond pointing to the centre of the ring. The distance to the H₂O molecule ends up as 1.88 Å. On the other hand, in panel P-4, the hydroxyl group formed at the more active edge site with a shorter C-O bond of 1.42 Å. This C-O bond is also bent approximately 10° towards the defect site. Overall, this hydrogenation step is endothermic to the previous configuration.



Figure 6.24: Relative energy profile for the formation of water dimer on $Fe\downarrow G$ through sequential hydrogenation of meta (pink) and para (blue) dioxide. Blue, pink, green, and red color shows the energy of structures with equivalent hydrogenation.

Finally, complete hydrogenation of oxygen atoms leads to the formation of a water dimer at a distance of more than 3.7 Å from the surface in both systems. The optimized geometry is shown in panels M-5 and P-5, respectively. Similar to negatively puckered $Si\downarrow G$, a lower binding energy of -0.18 eV and -0.07 eV is found for the formation of water dimer on Fe $\downarrow G$ for the *meta* and *para* starting point, respectively. As the water dimer shows only a weak interaction with the surface, the formation of the water dimer releases the distortion from the surface created by oxygen atoms. However, the geometry in panel M-5 shows evidence for H-bonding, whereas this is not the case in panel P-5, showing that the total energy in this system is largely dependent on the interaction between water molecules and not between water molecules and the surface. Overall, the formation of the water dimer is endothermic relative to the previous step.

As before, we also considered the case of starting with a positively puckered iron atom in FeG, Fe \uparrow G. The optimized structure for this is shown in Fig. 6.25 panel A. Here, the iron atom moves out of the plane by ~1.22 Å. In contrast to the puckered-down configuration, where the iron atom leaves a hollow within the surface which generates more active edge carbon atoms, in the puckered-up configuration the iron atom becomes more reactive, particularly towards electronegative atoms because of the presence of the unpaired d-electrons of the iron atom. This effect is clearly observed for adsorption of oxygen atoms at a position *para* to each other. The calculations show that both oxygen atoms have an interaction with the defect site and transform from epoxy groups into carbonyl-like

groups. As a consequence, they shift to the carbon atom *ortho* to the defect site (Fig. 6.25 panel C). As a result, the binding energy of two oxygen atoms for the *para* dioxide is found to be 2.96 eV more than for *meta* dioxide (Fig.6.25 panel B). In *meta* dioxide, only one oxygen atom has an interaction with the defect site. That oxygen atom bends towards the defect site and remains at a distance of 2.57 Å, but ultimately both oxygen atoms stay as an epoxide, *meta* to each other.



Figure 6.25: Optimized structures for the substitution of a positively puckered Fe atom as a defect in bi-layer graphite surface $Fe\uparrow G$ (panel A), adsorption of two oxygen atoms at meta to each other (panel B), and para to each other (panel C) in $Fe\uparrow G$.

The geometries for sequential hydrogenation for the *meta* dioxide and *para* dioxide scenarios are shown in Fig. 6.26 in panels M-1-M-5 and P-1-P-5, respectively. The relative energy profile for these are shown in Fig. 6.27.

Interestingly, the optimized geometries after the first hydrogenation step show a similar structure for both *meta* and *para* scenario, as shown in Fig 6.26 panel M-1 and P-1, respectively. In both cases, one epoxy group is transformed into a hydroxyl group and adsorbed at the defect site. The other oxygen atom remains in the carbonyl form with a C-O bond length of 1.37 Å. Thus, in the *meta* scenario the second epoxide moves across the surface to become a carbonyl group *ortho* to the defect site. As a consequence, this step is exothermic for both starting scenarios.

Again, as before in both systems, for the second hydrogenation step a higher binding energy is found if a hydroxyl dimer is formed on the surface, relative to the formation of a weakly bound H₂O as shown in panel M-2, M-3 and P-2, P-3, respectively. The geometry shown in panel P-2 particularly shows both OH groups are attached to the defect atom site with an Fe-O bond length of 1.83 Å in a tetrahedral arrangement with the surface. This attachment of both O-H groups to the defect atom further puckers up the iron atom (Fe-C bond length 1.94 Å). However, no further distortion is observed in the rest of the surface carbon atoms. On the other hand, in panel M-2, one hydroxyl group ends up on the top of the defect site at a distance of 1.77 Å. The other ends up *para* to the defect site with a C-O bond length of 1.49 Å (see Fig. 6.26 panel M-2), with the O-H bond pointing towards the centre of the ring. The adsorption of only one OH at the defect site leads to less puckering of the Fe atom. However, it also leads to more extensive distortion in the surface through the puckering of the carbon atom underneath the hydroxyl group, resulting in a higher energy for this geometry (panel M-2). As for SiG, this step is endothermic relative to the formation of a single hydroxyl group on the surface.



Figure 6.26: Structures for sequential hydrogenation steps starting from an epoxy dimer, either meta (panels M-1 to M-5) or para (panels P-1 to P-5), to each other on a positively puckered $Fe\uparrow G$ to form water dimer.

In the other scenario, the second hydrogenation step leads to the formation of H_2O in the presence of a carbonyl group, as shown in panels M-3 and P-3. In both cases, the carbonyl group ends up *ortho* to the defect atom with a C-O bond length of 1.39 Å. However, the position and orientation of the water molecule result in an energy difference of 0.68 eV between the two systems. In panel M-3, H_2O is formed at a distance of 3.44 Å from the nearest carbon atom of Fe†G with two O-H bonds parallel to the graphite plane. On the other hand, the geometry shown in panel P-3 is found to be more favourable than M-2. In P-3, we obtain a strong interaction between H_2O and the iron atom, as is clear from the short distance of 2.13 Å between them, H_2O here is optimized in the 0-leg geometry. As a result, the defect atom puckers up, leading to Fe-C bonds of 1.8 Å and 1.78 Å, as shown in Fig. 6.26 panel P-3. The geometry, shown in panel P-3, could be an intermediate stage toward forming a lower energy structure, such as the hydroxyl dimer shown in panel P-2. However, this requires a full potential energy surface calculation for a clear understanding.



Figure 6.27: Relative energy profile for the formation of water dimer on $Fe\uparrow G$ through sequential hydrogenation of meta (pink) and para (blue) dioxide. Blue, pink, green, and red color shows the energy of structures with equivalent hydrogenation.

The third hydrogenation step leads to the formation of a H_2O molecule in the presence of a hydroxyl group in both cases. Almost similar optimized geometries are obtained for both cases, with the hydroxyl group on top of the defect atom and the water molecule hydrogen bonded to it. Thus, due to these structural similarities, a similar energy is obtained, which is exothermic to the previous step relative to all structures except the one shown in panel P-2.

Complete hydrogenation leads to the formation of a water dimer for both the *meta* and para scenarios. The optimized geometries for these are shown in Fig. 6.26 panel M-5 and P-5, respectively. In panel M-5, one water molecule is adsorbed at the top of the defect site with both O-H bonds parallel to the surface. This lifts the defect atom and lengthens the Fe-C bond to 1.82 Å. The other H_2O is formed at a distance of 2.43 Å from the nearest surface carbon atom in a 1-leg orientation but clearly, is hydrogen bonded to the first. On the other hand, in panel P-5, both H_2O molecules are optimized in the 1-leg orientation facing away from each other. In this case, both oxygen atoms point their lone pair of electrons towards the defect atom, resulting in a lone-pair lone-pair repulsion between the two water molecules leading to FeO bonds (2.24 Å) equivalent to the Fe-O bonds²⁹⁵ in $[Fe(H_2O)_6]^{2+}$. The lack of hydrogen bonding is not quite compensated by the stronger Fe-O ligand interaction, meaning that the geometry in panel P-5 is slightly higher in energy than the one in M-5. However, the geometry of panels M-5 and P-5 results in a higher binding energy of -1.39 eV and -1.18 eV, respectively for the formation of a water dimer. By far the binding energy for the formation of water dimer in Fe \uparrow G is much larger than the formation of water dimer either on Si \downarrow G, Si \uparrow G, or bare graphite surface. This is because of the d-electrons transition metal binding like in $[Fe(H_2O)_6]$. It is to be noted that the final step is endothermic relative to all previous steps.

6.3.3 Conclusion

Water is ubiquitous in the cosmos, often taking the form of an ice layer in low temperature regions. However, our current understanding is that this ice layer cannot be simply explained by freeze-out of water on a surface. To explore alternative ways of gaining an ice layer we conducted a study on the adsorption and formation of $(H_2O)_n$ (where $n \leq 4$) on a bi-layer graphite surface *via* sequential hydrogenation of atomic oxygen.

Our findings revealed that the adsorption of a single water molecule is site independent. However, it is orientation dependent consistent with prior research.^{270,271} Notably, a higher adsorption energy was observed when H₂O adopted a 2-leg orientation. Nevertheless, a single water molecule exhibited only a weak van der Waals interaction with the surface, resulting in a binding energy of -0.19 eV for the adsorption of H₂O at a top site in a 2-leg orientation.

We also investigated the process of forming a single water molecule through sequential hydrogenation of atomic oxygen. This process was found to be exothermic and non-activated. However, when multiple oxygen atoms (2-4) were present on the graphite surface, the formation of water occurred *via* an endothermic step. This indicates that the hydrogenation of atomic oxygen might cease at this endothermic step, leading to the ultimate formation of epoxy or hydroxyl groups in combination with a single water molecule instead of two, three, or four water molecules.

On a bare graphite surface, we observed that the presence of an epoxy or hydroxyl group favoured the formation of a water molecule over the formation of two hydroxyl groups. This preference is attributed to the desorption of the water molecule, which alleviates the distortion on the graphite surface. However, when defects (Fe or Si) are introduced the energetics of water dimer formation change.

When the defect atom moves below the graphite surface plane (puckered-down), it creates active edge sites that facilitate the adsorption of oxygen atoms. As a result, unlike on the pristine graphitic surface, the adsorption of two hydroxyl groups becomes more favourable than the desorption of a single water molecule. In contrast, when the defect atom moves out of the plane (puckered-up), the defect site becomes more reactive toward the adsorption of atomic oxygen, hydroxyl group or water molecules. This behaviour is particularly in the puckered-up geometry, significantly enhancing the adsorption of the water dimer onto the surface. However, similar to the bare graphite surface, hydrogenation of atomic oxygen to form water occurs via an endothermic step. Consequently, the hydrogenation might halt at this endothermic step, leading to the formation of either two hydroxyl groups or a single water molecule in the presence of an epoxy or hydroxyl group.

In summary, the formation of a water layer through sequential hydrogenation of oxygen atoms on the bare graphite surface and in the presence of defect atoms is not a completely exothermic process. However, to understand the complete mechanism for the formation of water clusters on a bare graphite surface and on substituted graphite surfaces, a full potential energy profile is still needed.

Chapter 7

Formation of ammonia on a cosmic dust analogue

7.1 Introduction

After H, He, C, and O, nitrogen is one of the next most abundant elements in the ISM. Given the abundance of hydrogen in the ISM, a significant proportion of nitrogen can be expected to be in the form of nitrogen hydrides. As such, the discovery of ammonia in the ISM was first reported in 1968 by Cheung *et al.*,²⁹⁶ making it the first polyatomic molecule detected in the ISM. Subsequently, other nitrogen hydrides, such as NH,²⁹⁷ NH₂,²⁹⁸ NH₂D, but also molecular nitrogen, have been discovered. It is believed that once the ammonia molecule has formed, it may agglomerate with other species such as H₂O, CO, and CH₄ and freeze out on grain surfaces in the form of ammonia ice. The abundance of NH₃ in the ISM varies from 10^{-7} cm⁻³ to 10^{-5} cm⁻³ and depends on the physical and chemical environment.²⁹⁹

In some regions of the ISM, such as in cold dense clouds, exothermic gas-phase reactions dominate as these reactions can occur easily at low temperatures. Irrespective of that it is generally accepted that dust plays a fundamental role in the formation of more molecules. Various studies have reported that the reaction in solids starts at cryogenic temperatures by ionizing radiation,^{300–302} then hydrogen atoms can diffuse within the solids for a long distance at low temperatures (5 K–20 K) and can react through tunnelling with trapped atomic species on a grain surface, such as nitrogen and oxygen. This suggests that the high mobility of hydrogen atoms plays an important role in the formation of complex molecules on grain surfaces in dense clouds.

Previous studies explored the formation of NH_3 via various reaction pathways such as ionmolecule and neutral-neutral reactions. In the gas phase, the ion-molecule^{303–305} reaction pathway is found to be a non-activated process. They reported that the most common route for the formation of NH_3 in the gas phase is through dissociative recombination of NH_4^+ (ammonium ion) as shown in Eqn. 7.1.

$$\mathrm{NH}_4^+ + \mathrm{e}^- \to \mathrm{NH}_3 + \mathrm{H} \tag{7.1}$$

The ammonium ion can be formed *via* chain reactions from ionic nitrogen (N^+) at low temperatures. Ionic nitrogen (N^+) can be formed from the dissociation of N₂ as shown by reaction pathway R3 in Fig. 7.1.



Figure 7.1: Three different reaction pathways R1, R2, and R3 for the formation of ammonia molecule in the ISM.

Previous studies reported that the first step for the reaction to form NH⁺ is a slow and activated reaction with an energy barrier of approximately 0.1 $eV.^{303,304}$ Subsequent reactions are all reported to be barrierless. After NH₃⁺ or NH₄⁺ have formed, they can combine with electrons to give NH₂ and NH₃, respectively. This last step in the formation of NH₃ is reported to be the ratedetermining step.³⁰⁵

Previous experimental studies suggested two different reaction pathways for the formation of NH_3 through neutralneutral reactions. First, the reaction can start with a collision of atomic nitrogen with OH to form NO^{306} from which ammonia can form through successive hy-

drogenation (pathway R2). The presence of NO molecules in the gas phase has been reported in different regions of the ISM.³⁰⁷ However, the formation of NO is also reported to be an activated process with an energy barrier of 0.004 eV. Moreover, one experimental study³⁰⁷ reported that in the gas phase, NO is very reactive and can react further with nitrogen to form molecular nitrogen N₂. N₂ is very stable, but can react with He⁺ to form N⁺ which follows reaction path R3 to form NH₃. However, NO can also adsorb on a surface.³⁰⁷ Fedoseev *et al.*³⁰⁸ reported the formation of NH₃ by successive hydrogenation of NO on an ice surface at a temperature of 10 K. The reaction mechanism for this is shown by reaction path R2 in Fig. 7.1. Second, an ammonia molecule can be formed *via* sequential hydrogenation of nitrogen atoms. Hiraoka *et al.*³⁰⁴ studied the formation of ammonia in this way in a N₂ matrix at a temperature range of 33 K–35 K. The purposed reaction mechanism for this is shown by reaction path R1 in Fig. 7.1. However, the abundance of ammonia molecules can not be explained only by gas-phase reactions. Thus, it is important to study these reactions on dust grains.

A complete reaction mechanism for the formation of ammonia on grains is still unclear which is why we choose to study it in this chapter. For our work, we considered bi-layer graphite as a model of a dust grain, and we chose to follow the reaction pathways R1 and R2. For the first hydrogenation step, we optimized all possible structures. However, only the minimum energy structure was considered for the next step. For further hydrogenation steps, we considered the previous optimized minimum energy structure as an initial structure.

To start our investigation, we studied the adsorption and orientation of ammonia at different sites on a graphitic surface by calculating the binding energy and the amount of charge transfer which is discussed in section 7.2. Then we studied the formation of ammonia in the presence of other molecules on the graphite surface. In particular, we considered the co-presence of epoxy, carbonyl, and hydroxyl groups as well as water molecules on the surface. This is discussed in section 7.3.

7.2 Formation of ammonia on graphite surface

In this section, we discuss the results for the formation of a single ammonia molecule at different sites of a bi-layer graphite surface via sequential hydrogenation of an initially adsorbed nitrogen atom. For these calculations, the carbon atoms of the top layer graphite surface and the adsorbed atomic species were allowed to move in all directions (*i.e.*, a complete relaxation). The bottom layer of the graphitic surface was kept rigid in all calculations.



Figure 7.2: Four different sites centre, mid, top-C1, and top-C4 for the formation of single ammonia molecule at bi-layer graphite surface.

Similar to the formation of water, as discussed in Chapter 6, we chose four different sites on the bi-layer graphite surface to study the formation of ammonia, as shown in Fig. 7.2. Thus, we first performed calculations for the adsorption of atomic nitrogen at all considered sites: centre, midbond, top-C1, and top-C4. These were then further hydrogenated to form NH, NH_2 , and NH_3 . A nitrogen atom has five valence electrons and nitrogen's electronic configuration is more stable than carbon and oxygen atoms due to its half-filled 2*p*-orbitals. This makes it less reactive to the graphene surface compared to an oxygen atom. Moreover, nitrogen can form up to three covalent bonds and also has

the possibility to form one co-ordinate bond. Thus, it can form a bond with one carbon atom at the top site and two bonds with two carbon atoms at the midbond site. The potential energy curves for the adsorption of a nitrogen atom at all the considered sites have already been discussed in Chapter 4 and the potential energy curves for these are shown in Fig. 4.23. Metastable adsorption of a nitrogen atom was found at both top sites with an energy barrier of 0.24 eV see also Fig. 7.4 panel A. An activated chemisorption of nitrogen atom was obtained at the midbond site with an energy barrier of 0.22 eV, whereas physisorption of atomic nitrogen was found at the centre of a ring.

We considered the sequential hydrogenation of atomic nitrogen at all considered sites. Thus, potential energy curves were calculated for the adsorption of atomic nitrogen at the midbond of the C1-C2 bond on a bilayer graphite surface (see Fig. 7.3) and its further hydrogenation to form NH, NH₂, and NH_3 . In the first step, we allowed a complete relaxation to six carbon atoms C1, C2, C3, C4, C5, and C6, but the incoming nitrogen atom was only allowed to move laterally (*i.e.* to move in the x and y directions, but fixed along the z-direction). In the further hydrogenation steps to form NH, NH_2 , and NH₃ we followed the same scheme but also allowed the already adsorbed nitrogen atom



Figure 7.3: Relaxation scheme for the adsorption of a nitrogen atom at the mid-site of C1-C2 bond on bi-layer graphite surface.

complete freedom. The incoming atomic hydrogen was allowed to move in the x and y di-

rections only. The potential energy curves (PECs) obtained for these processes are shown in Fig. 7.4. The potential energy curve for the adsorption of atomic nitrogen is shown in panel A. It shows that at long internuclear distance atomic nitrogen has a physisorption interaction with the surface. Further approach of atomic nitrogen requires C1 and C2 to pucker out of the graphene plane. This adds distortion to the surface and results in an energy barrier of 0.22 eV and eventually leads to the chemisorption of nitrogen atom at the midbond with a C-N bond of 1.47 Å as shown in panel A (see section 4.4.4 for a more complete discussion). Thus, the C1 and C2 carbon atoms become sp^3 hybridized and the nitrogen atom adsorbs at the midbond by forming two σ bonds with these carbon atoms. At the minimum energy geometry, it still has one lone pair of electrons and one non-bonded electron.



Figure 7.4: Potential energy curves for the adsorption of atomic nitrogen at the midbond site of a pristine graphite surface (panel A), reaction of a hydrogen atom to the adsorbed nitrogen atom to form NH (panel B), reaction of a 2^{nd} hydrogen atom to form NH₂ (panel C), and reaction of a 3^{rd} hydrogen atom to form NH₃. Insets show the optimized structures for the adsorption of N, NH, NH₂, and NH₃, respectively.

For the first hydrogenation step, we used the optimized structure of adsorbed atomic nitrogen at the midbond (see inset of Fig. 7.4-A) as our initial structure. The PEC for the reaction of atomic hydrogen using the relaxation scheme as outlined above with adsorbed atomic nitrogen is shown in Fig. 7.4-B. We found that the presence of non-bonded electrons on the nitrogen atom favours the adsorption of atomic hydrogen *via* a radical-radical reaction. Therefore, the adsorption of atomic hydrogen to form NH bond is found to be a non-activated process. The minimum energy structure shows that the nitrogen atom remains at the midbond site of the C1-C2 bond with the hydrogen atom

pointing towards the centre of the hexagonal ring as shown in Fig. 7.4-B.

The optimized structure of NH at the midbond position (Fig. 7.4-B) was used as an initial structure for the reaction of NH with a 2^{nd} hydrogen atom. The PEC obtained is shown in panel C. We found that as NH₂ is formed the nitrogen atom shifts from the middle of the C1-C2 bond to be on the top of the C2 carbon atom. This was to be expected as in this scenario, the nitrogen atom forms two covalent bonds with hydrogen atoms and one with the surface carbon atom. Then it still has one lone pair of electrons pointing away from the surface, completing the tetrahedron. This reaction leads to a puckering of the target carbon atom by ~0.5 Å which distorts the surface. This leads to a small energy barrier of 0.0034 eV. This small energy barrier is surmountable in the cold temperature region of the ISM.

Finally, for the formation of NH₃ we used the optimized structure of NH₂ at the C4 position (see Fig. 7.4-C) as the initial structure. The reaction of the 3^{rd} hydrogen atom leading to the formation of NH₃ is a non-activated process, as shown in Fig 7.4 panel D. NH₃ is physisorbed on the surface and no surface distortion is found.

Summarizing we found that the first step, the adsorption of atomic nitrogen on graphite is an activated process. However, the hydrogenation steps to ultimately form NH₃ are either barrierless or have small energy barriers, which can be easily overcome in low-temperature regions. The final NH₃ product is then physisorbed on the surface. This is consistent with a previous study³⁰⁹ which reported that the adsorption of NH₃ at different sites of graphene surface is a non-activated process and results in small adsorption energy of ~ 0.1 eV.

To study the adsorption of N, NH, NH₂, and NH₃ at all considered sites and also in different orientations we performed optimization calculations. For these, the adsorbed atoms and all the carbon atoms of the top layer of graphite surface were allowed to move in all x, y, and z directions. The relative energy profile for the adsorption of N, NH, NH₂ and NH₃ is shown in Fig. 7.5. For this, the relative energies are calculated as follows:²⁸¹

$$E_{rel} = E_{Gr+ads} - (E_{Gr} + \sum E_{ads}).$$
 (7.2)

Here, E_{Gr+ads} is the total energy of the system (*i.e.*, the energy of bi-layer graphite surface and the adsorbed atoms or molecules), E_{Gr} is the total energy of bi-layer pristine graphite surface and $\sum E_{ads}$ refer to the sum of the energies of the isolated atomic species. For the two top sites top-C1 and top-C4, we obtained an identical energy profile, therefore, only one site is discussed here.

The optimized structures for the adsorption of N, NH, NH₂, and NH₃ at centre, midbond, and top sites are shown in Fig. 7.6. As expected the relative energy profiles show that the midbond site is the preferable site for the adsorption of atomic nitrogen and NH with relative energy -0.885 eV and -4.19 eV, respectively. On the other hand, the centre site is found to be the least preferable for the adsorption of atomic nitrogen with a repulsive energy of 0.783 eV, suggesting only a repulsive interaction with the nitrogen atom.



Figure 7.5: Relative energy profile for the formation of single NH_3 molecule at centre, midbond, and top site of bi-layer graphite through sequential hydrogenation of nitrogen atom.

A similar pattern is also found for adsorption of NH. Here, nitrogen remains adsorbed at the midbond site preferably while hydrogen points to the centre of the ring, as shown in Fig. 7.6 panel B-ii. On the other hand, at the top sites, NH is adsorbed with its hydrogen atom pointing to the centre of the hexagonal ring. Adsorption of NH at the top site has a smaller binding energy than at the midbond site, as expected from valency arguments. On the other hand, adsorption of NH at the centre site leads only to a weak physisorption interaction of NH to the graphitic surface as is clear from Fig. 7.6 panel A-ii.

The centre site stays the least favourable for the formation of NH₂ with relative energy of -3.8 eV. In this case, NH₂ is formed with hydrogen atoms pointing to the surface carbon atoms as shown in Fig. 7.6 panel A-iii. An identical geometrical structure is obtained for the adsorption of NH₂ at the top and midbond site, as shown in Fig. 7.6 panel (B-iii and C-iii). Hereby, the reaction with the 2nd hydrogen atom shifts the nitrogen atom from the midbond of C1-C2 onto the top of one of the carbon atoms. This results in the effective adsorption of NH₂ at the top site with both hydrogen atoms pointing toward the centre of neighbouring hexagonal rings. This requires the target carbon atom to move out of the plane and therefore adds surface distortion. The result is the formation of a C-N bond of 1.53 Å with relative energy of -4.47 eV at both sites. This is in agreement with the previous study,³¹⁰ which suggests that the lower binding energy of NH₂ is due to the formation of a weak semi-ionic C-N bond, because the carbon atom of graphene does not have an empty orbital to accept the extra electron present on the nitrogen atom.



Figure 7.6: Optimized structures (top and side view) for the adsorption of N, NH, NH_2 , and NH_3 at Centre (panels A-i, A-ii, A-iii, A-iv), Midbond (panels B-i, B-ii, B-iii, B-iv), and Top-C4 (panels C-i, C-ii, C-iii, C-iv) sites of bi-layer graphite surface.

Finally, the third hydrogenation leads to the formation of NH_3 at each site with different orientations at a distance of more than 3.3 Å from the nearest surface carbon atom, which leaves the graphite surface completely undistorted. The adsorption of NH_3 has been studied in different orientations at different sites. However, the energetically most stable structure is found with the two hydrogen atoms pointing toward the surface (2-leg) as shown in Fig. 7.6 panel A-iii. The binding energies for the minimum energy structures of NH_3 are reported in Table 7.1.

Table 7.1: Binding energy (E_b) in eV for the adsorption of NH_3 molecule in eV at centre, midbond, top-C1, and top-C4 sites. D is the distance between the nitrogen atom and the nearest surface carbon atom in Å.

Sites	$E_b (NH_3)$	Orientation	D
Centre	-0.132	2-leg	3.70
Midbond	-0.134	2-leg	3.40
Top-C1	-0.129	2-leg	3.35
Top-C4	-0.129	2-leg	3.35

These binding energies are defined as:

$$E_b = E_{Gr+ads} - E_{Gr-ads}.$$
(7.3)

Here E_{Gr+ads} is the optimized energy of the bi-layer graphite surface with adsorbed atom or molecule, and E_{Gr-ads} is the optimized energy of the geometry with the atom or molecule placed at a specific position far from the graphitic surface where no interaction observed between them. The binding energies reported in Table 7.1, illustrate that the binding energy is site-independent, in line with the expectation for a physisorption interaction through van der Waals interactions, which is in close agreement with previous work.³¹¹ We noted that the ammonia molecule can be formed in different orientations on the graphite surface. Leenart *et al.*²⁷¹ reported that the charge transfer within ammonia and graphene surface depends upon the orientation of the ammonia molecule. Therefore, we have studied the adsorption of ammonia in four different orientations at different sites on graphite. Our results are illustrated for the top site in Fig. 7.7.



Figure 7.7: Relative energy profile for the formation of NH_3 in N-up, N-down, 1-leg, and 2-leg form at the top site of pristine graphite surface.

Fig. 7.7 shows that the amount of charge does not strongly depend on the precise orientation of ammonia. If NH_3 is adsorbed with its nitrogen atom pointing away from the surface (N-up). Only a small charge transfer of 0.01 e is obtained from graphene to the hydrogen atoms of NH_3 . Adsorption of NH_3 in 1-leg orientation results in an optimized geometrical structure 0.54 eV lower in energy than the N-up orientation. However, this also shows a charge transfer of 0.02 e from the graphite surface to hydrogen atoms of ammonia. The third possible orientation has ammonia adsorbing in a 2-leg orientation with two hydrogen atoms pointing toward the surface. This orientation has a charge transfer of 0.013 e from graphite to NH₃. Finally, NH₃ can adsorb with its nitrogen atom pointing toward the surface (N-down). Here, a charge transfer of 0.0015 e from ammonia to graphite is found, which is consistent with the previous study.²⁷¹

The experimental study conducted by Corre *et al.*³¹² reported that the binding energy of ammonia can increase in the presence of acid and vacancies on the graphene surface at a constant temperature of 298 K. Some other studies also reported that the presence of defects on the surface can create active sites on the surface for the adsorption of atomic and molecular species and can effectively increase the binding energy of the adsorbate with the surface.^{285,313–315} Similar to Chapter 6, to understand the effect of defects we studied the formation of NH₃ in the presence of atomic oxygen on a graphitic surface. For this, we considered the presence of atomic oxygen and atomic nitrogen at position *meta* and *para* to each other and also in the form of N-O (*ortho*) where atomic N and atomic O adsorbed at the adjacent carbon atoms.

7.3 Formation of an ammonia molecule on oxygenated graphite surface

As discussed in Chapters 4 and 6, the adsorption of atomic oxygen on a bi-layer graphitic surface is non-activated. Therefore, the presence of single and multi-oxygenated graphitic surfaces can be expected in the low-temperature regions of the ISM. As noted above oxygen atoms on a graphitic surface can be found in the form of an epoxy (C-O-C) group at the midbond site or in the form of a carbonyl (C=O) group at the top site. These functional groups can react further with hydrogen atoms to form hydroxyl (OH) groups and H₂O. Previous studies report that the presence of an oxygen atom on a graphene surface can enhance the charge transfer from the nitrogen atom of ammonia to graphene.^{316,317} Therefore, the presence of O, OH, or H₂O on graphitic surface could lead to an increase in the binding energy of NH₃ as well as its molecular radicals³¹⁸ on bi-layer graphite. Thus, here, we investigated the formation of NH, NH₂ and NH₃ in the presence of either an epoxide (C-O-C) or a carbonyl group, a hydroxyl group, or H₂O on bi-layer graphite.

7.3.1 Adsorption of nitrogen at *ortho*, *meta*, and *para* to the oxygenated site on graphite

To study the formation of NH₃ via sequential hydrogenation of nitrogen we considered the presence of atomic nitrogen at positions meta and para to atomic oxygen as shown in Fig. 7.8. For this, the reference energy is taken from the geometry in which atomic nitrogen is present but does not have an interaction with the oxygenated bi-layer graphite surface. Here, both oxygen and nitrogen atoms adsorb at the midbond site. Both atoms remain sp^2 hybridized with two lone pairs of electrons at the oxygen atom and one lone pair and one non-bonded electron for nitrogen. As expected the highest binding energy is obtained for the adsorption of atomic nitrogen and oxygen in the form of NO as shown in Fig. 7.8. This relative energy profile show that the adsorption of atomic nitrogen or *tho* to oxygen is 1.67 eV and 1 eV lower in energy than adsorption at *para* or *meta*, respectively.



Figure 7.8: Relative energy profile for the adsorption of atomic nitrogen at para, meta, and ortho position to oxygen in bi-layer graphite surface.

For adsorption of nitrogen and oxygen, C-O and C-N bonds of 1.52 Å and N-O bond of 1.41 Å are formed. Moreover, the surface carbon atoms have moved out of the graphene plane by 0.5 Å to become more sp^3 hybridized. As a result, the underlying C-C bond elongates to 1.58 Å. In contrast, for *meta* and *para* adsorption the C-C bond length is found to be 1.49 Å and 1.54 Å, respectively.

In section 7.2.1, we showed that the adsorption of atomic nitrogen on a pristine graphite surface is an activated process with an energy barrier of 0.22 eV at the midbond site. To further understand the effect of the presence of oxygen, we also studied the PECs for the adsorption of atomic nitrogen in the presence of atomic oxygen at position *ortho*, *meta*, or *para* to nitrogen. For these calculations, oxygen atom was frozen either in the form of an epoxide or a carbonyl. For nitrogen, we used the same relaxation scheme as shown in Fig. 7.3, *i.e.*, a complete relaxation was given to the six carbon atoms and a lateral relaxation only for nitrogen.

For the adsorption of nitrogen *ortho* to oxygen a complete relaxation to the six surface carbon atoms underneath the resulted NO molecule was allowed. The incoming nitrogen atom was allowed to move in the x and y directions. The potential energy curves obtained for the adsorption of atomic nitrogen *para* or *meta* to the atomic oxygen are shown in Fig. 7.9, panel A. This shows a site-independent physisorption of the nitrogen atom at a distance of more than 3 Å from the surface for either geometry. Upon closer approach of the nitrogen atom the surface carbon atoms pucker. This creates an energy barrier of ~0.2 eV for both reaction geometries. However, a higher binding energy is obtained for the adsorption of nitrogen atom *meta* to the epoxy group than *para* to the epoxy group. This might be due to the fact that a double bond can form between the two spectator carbon atoms for the *meta* geometry, whereas this is not possible for the *para* geometry.



Figure 7.9: Potential energy curves for the adsorption of atomic nitrogen on graphite at a position meta or para to the epoxy group (panel A), ortho to the carbonyl group in the form of N-O (panel B).

On the other hand, the PEC for the adsorption of nitrogen next to a carbonyl group (C=O) is shown in Fig. 7.9 panel B. This results in non-activated adsorption and reaction of the nitrogen atom to form NO with a higher binding energy.

Within the cold temperature region of the ISM, it is difficult to envisage overcoming an energy barrier of 0.2 eV, as for the *meta* and *para* geometries. However, the absence of an energy barrier for the formation of N-O suggests that N-O could be a key for the formation of NH₃. Hence, it is essential to study the sequential hydrogenation of NO molecules for the formation of NH₃.

In Chapter 6, we showed that the hydrogenation of atomic oxygen to form OH and H_2O on graphite is a barrierless process. Thus, these functional groups are likely to be present on dust surfaces in the ISM. Therefore, we have included the formation of NH₃ via sequential hydrogenation of nitrogen in the presence of OH and H_2O in our studies. Fig. 7.10 panels A and B shows the potential energy curve for the adsorption of atomic nitrogen on graphite in the presence of OH and H_2O .



Figure 7.10: Potential energy curves for the adsorption of atomic nitrogen on graphite in the presence of a hydroxy group (panel A) and in the presence of H_2O (panel B).

In these calculations, OH and H_2O were kept fixed at a specific position. The same relaxation scheme as shown in Fig. 7.3 was used for the adsorption of atomic nitrogen. In

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both cases nitrogen first shows a physisorption interaction with the graphite surface at a distance of around 3 Å. Upon closer approach the surface puckers. Interestingly, attractive adsorption of nitrogen atom is observed in both cases. This attractive adsorption of atomic nitrogen suggests another pathway for the formation of NH_3 .

Thus, the formation of ammonia *via* sequential hydrogenation of atomic nitrogen at positions *ortho*, *meta* and *para* to a pre-adsorbed oxygen atom is explored by three pathways, as shown in Fig. 7.11.



Figure 7.11: Potential isomers for the hydrogenation of adsorbed nitrogen and oxygen atoms on a graphite surface.

First, we studied the formation of NH_3 via sequential hydrogenation of atomic nitrogen in the presence of atomic oxygen. Second, the formation of NH_3 via sequential hydrogenation of atomic nitrogen in the presence of OH and finally, the sequential hydrogenation of atomic nitrogen in the presence of H_2O was studied. In Fig. 7.11 the blue arrow indicates the hydrogenation of nitrogen whereas, the orange arrow is showing the alternative hydrogenation pathway of hydrogenating oxygen instead of nitrogen.

7.3.2 Formation of an ammonia molecule in the presence of O

Optimized structures for the formation of ammonia *via* sequential hydrogenation of nitrogen *meta*, *para*, and *ortho* (N-O) to atomic oxygen are shown in Fig. 7.12 panels M-1 to M-4, P-1 to P-4, and O-1 to O-4 respectively. The relative energy profiles for these are shown in Fig. 7.13.

In Chapter 6, we discussed that two oxygen atoms at *meta* to each other are not equivalent, whereas they are equivalent if they are *para* to each other. A similar observation can be made for the adsorption of oxygen and nitrogen atoms *meta* or *para* to each other as shown in Fig. 7.12 panels M-1 and P-1 respectively. In panel M-1 the C-O bonds are inequivalent (1.46 Å and 1.49 Å) as are the C-N bond (1.48 Å and 1.49 Å). On the other hand, in the *para* system both C-O bonds and both C-N bonds are 1.46 Å and 1.45 Å, respectively as
shown in panel P-1. More surface distortion is observed for *para* adsorption. Thus, the *meta* adsorption is more stable. The case of *ortho* adsorption is different, in this case the C-O and C-N bonds (1.52 Å) are larger and there is a bond of 1.4 Å between N and O. Whilst there is still surface distortion, it is less than for the other cases. Thus, the formation of NO is significantly more favourable than the other reaction geometries.

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Figure 7.12: Optimized structure for the sequential hydrogenation of atomic nitrogen to form NH, NH₂, and NH₃ para (panels P-1 to P-4), meta (panel M-1 to M-4) or ortho (panel O-1 to O-4) to pre-adsorbed oxygen. All the distances are in Å.



Figure 7.13: Relative energy profiles for the formation of ammonia in the presence of an epoxide group on bi-layer graphite surface through sequential hydrogenation of nitrogen atom. For the blue, pink, and red curves, the nitrogen and oxygen atoms were initially para, meta, and ortho to each other, respectively.

First, hydrogenation of the nitrogen atom of the geometries depicted in panels M-1 and P-1 leads to the formation of NH in all cases, as shown in Fig. 7.12 panels M-2 and P-2. The structures shown in panels M-2 and P-2 have an N-H bond of 1.03 Å, with the hydrogen atom pointing towards the centre of the ring. This results in O-H distances of 1.96 Å and 1.92 Å in panels M-2 and P-2, respectively. For these cases, the nitrogen atom remains at the midbond site. Again, in panel M-2, non-equivalent C-O and C-N bonds are obtained. In contrast, for panel P-2, all C-O and C-N bonds are found to be identical. However, the C-C bonds are longer (1.58 Å and 1.53 Å) than for the *meta* case (1.5 Å and 1.48 Å). This results in more extensive surface distortion in panel P-2, in comparison to M-2, which means that the geometry shown in panel M-2 is ~1.2 eV lower in energy than that depicted in panel P-2.

On the other hand, the first hydrogenation of the geometry in panel O-1 leads to the formation of HNO with C-O and C-N bonds of 1.49 Å and 1.53 Å, respectively and an N-H bond of 1.03 Å parallel to the C-C bond as shown in panel O-2. This increases the N-O bond to 1.49 Å, while the underlying C-C bond length reduces from 1.58 Å to 1.53 Å, without any significant distortion for the rest of the graphite surface. This decrease in surface distortion means that the geometry depicted in panel O-2 is energetically more favourable than that depicted in panel P-2. However, it is less favourable than the geometry depicted in panel M-2. The reason is not entirely clear but will be an interplay between the degree of surface distortion and the epoxide/imine interaction in panel M-2, compared to the stronger NO bond in panel O-2.

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Similar to what we have found before, the second hydrogenation results in the formation of NH_2 at the top of a carbon atom instead of at the midbond site for the *meta* and *para* geometries as shown in Fig. 7.12 panels M-3 and P-3. For the *meta* geometry, NH_2 is formed *ortho* to the epoxy group with both N-H bonds pointing to the centre of the rings, as shown in panel M-3. Whereas for the *para* geometry, NH_2 is formed two bonds apart from the epoxy group as shown in panel P-3. Here, one N-H bond is formed pointing to the centre of the ring and the second N-H bond is formed parallel to the surface C-C bond. For both systems, the C-N bond is 1.51 Å. In addition to this, for both the M-3 and P-3 geometries, a hydrogen bond with a length of 2.14 Å and 2.57 Å, respectively forms between the oxygen and one of the hydrogen atoms of NH_2 . Due to the position of the NH_2 group and its H-bonding interaction, the adsorption of NH_2 in the geometry shown in panel M-3 is 0.71 eV lower in energy than the geometry shown in panel P-3. However, in both cases, formation of NH_2 is endothermic compared to the formation of NH. This is likely due to the loss of one C-N bond in combination with the increase in surface distortion because of the puckering of the surface carbon atom underneath NH_2 .

The situation for the second hydrogenation of NO is somewhat different. Here, the second hydrogenation leads to the formation of physisorbed ONH_2 as shown in panel O-3. In this geometry oxygen and nitrogen atoms are 2.88 Å and 3.05 Å from the nearest surface carbon atom, respectively and no surface distortion is found. This step is endothermic, but the endothermicity is less than the *meta* and *para* geometries.

Finally, the third hydrogenation step for the *meta* and *para* geometries leads to the formation of NH₃ in the presence of an epoxy group, as shown in panels M-4 and P-4 of Fig. 7.12, respectively. In both cases, NH₃ has a van der Waals interaction with the surface at a distance of more than ~ 3.3 Å from the surface. In both cases, NH₃ is in the N-down orientation. Formation of NH₃ decreases the amount of the distortion in the surface and now the distortion is only observed around the epoxy group. The geometries in panels M-4 and P-4 also show an H-bonding of 2.58 Å and 2.64 Å between the hydrogen atom of NH₃ and the epoxy group, respectively. Because of the structural similarities between the *meta* and *para* geometries a similar energy is obtained for both cases.

The situation is quite different for the *ortho* geometry. The third hydrogenation of N-O does not show formation of NH₃. Instead, it leads to the formation of physisorbed HONH₂ as shown in panel O-4 with the lone pair of electrons of nitrogen atom pointing toward the surface. The relative energy profile shows that the formation of HONH₂ is exothermic relative to the formation of ONH₂. However, it is energetically less favourable than the formation of NH₃ in the presence of an epoxide as shown for the *meta* and *para* geometries.

7.3.3 Formation of an ammonia molecule in the presence of OH

For the second step, we investigated the formation of NH_3 by sequential hydrogenation of atomic nitrogen in the presence of a hydroxyl group. The geometries for the steps leading up to NH_3 are shown in Fig. 7.14 with the energy profile plotted in Fig. 7.15.

The final geometry for the adsorption of atomic nitrogen in the presence of hydroxyl group is shown in Fig. 7.14, panels M-1, P-1, and O-1 for the *meta*, *para*, and *ortho* geometries, respectively. In panel M-1, the OH group is formed at the top of a surface carbon atom located at the centre of the ring of the bottom graphene layer. Here, there is a hydrogen bond of 1.81 Å between OH and atomic nitrogen. However, the OH group is tilted away from the adsorbed nitrogen atom. This causes strain in the surface and lengthens the C6-C1 bond to 1.52 Å. For the *para* geometry as depicted in panel P-1, the C-O bond remains perpendicular to the surface. The hydrogen bond is slightly longer at a distance

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of 1.85 Å which allows for less distortion in the surface. However, the geometry depicted in panel M-1 is still 0.41 eV lower in energy than the geometry in panel P-1. This might be due to the presence of a stronger hydrogen bond between OH and atomic nitrogen, which is not counter-balanced by the increase in surface distortion.



Figure 7.14: Optimized structure for the sequential hydrogenation of nitrogen atom to form NH, NH_2 , and NH_3 at meta and para position to the hydroxyl functional (OH) are shown in panels M-1 to M-4 and P-1 to P-4 respectively and for N-O are shown in panels O-1 to O-4. All the distances are in Å.

In the case of HON (*ortho*), panel O-1 shows that HON adsorbs weakly on the graphite surface with an N-O bond of 1.286 Å, as shown in panel O-1, leaving the surface undistorted. The shorter distance of the nitrogen atom to the nearest surface carbon atom

compared to the oxygen-carbon distance suggests an interaction of the lone pairs on nitrogen with the graphite surface. Interestingly, the formation of HON is energetically more favourable than any OH-N geometry.



Figure 7.15: Relative energy profile for the formation of ammonia in the presence of hydroxyl group (OH) on bi-layer graphite surface through sequential hydrogenation of nitrogen atom. For the blue, pink, and red curves the nitrogen and OH were initially para, meta, and ortho to each other, respectively.

The first hydrogenation step for the *meta* and *para* geometries leads to the formation of an N-H bond of 1.03 Å at one bond and two bonds apart from the OH position, as shown in panels M-2 and P-2, respectively. The optimized geometry in panel M-2 shows that O-H bond points towards the centre of the ring, pointing at the nitrogen atom with a slight tilt from the perpendicular. The N-H bond forms pointing to the centre of the ring. As a result, an H-bond of 1.87 Å exists between the OH group and the nitrogen atom. For the *para* geometry in panel P-2, the N-H and O-H bonds have a similar geometry as in panel M-2 with a hydrogen bond of a very similar length and slightly less tilt from the perpendicular. Similar to adsorption of atomic nitrogen, the *meta* geometry is found to be 0.15 eV lower in energy than the *para* geometry. This energy gap is significantly smaller than the previous step, for the adsorption of atomic nitrogen due to the C-O bond being slightly tilted but less than in panels M-1 and M-2.

First hydrogenation of HON leads to the formation of physisorbed HONH. HONH can be present in two different forms: cis and trans, where the *trans* form is found to be more stable than the *cis* form by 1.26 eV. Interestingly, the relative energy of HONH is similar to that of the HONH attached to the surface shown in panel M-2. Clearly, the stronger binding in HONH is compensated by the additional surface strain evident in panel M-2.

Reaction of a second hydrogen leads to the formation of NH_2 at position *meta* and *para* to the OH group, as shown in panels M-3 and P-3, respectively. In panel M-3, NH_2 is formed at the surface carbon atom above the centre of the bottom layer hexagonal ring, Both hydrogens are pointing to the centre of rings in opposition to the OH bond, creating a hydrogen bond of 1.84 Å. On the other hand, in panel P-3, NH_2 is formed at the surface carbon atom in the bottom layer. Both hydrogens pointing to the centre of a ring in opposition to the OH bond, resulting in a hydrogen bond of 1.86 Å. The relative energy profile shows that positioning OH and NH_2 *para* to each other as in panel P-3 leads to a more stable situation than when they are at *meta* to each other in

panel M-3. The reason for this is the fact that in the latter case there is only one carbon atom between the adsorbed groups, whereas in the former case it is two, which means that there will be more conjugation in the former case compared to the latter.

In panel O-3, the reaction of a second hydrogen leads the desorption of HONH₂. This molecule is physisorbed on the graphite surface and stays at a distance of ~ 3.3 Å from the surface. It is worth noting that HONH₂ is formed so that both the OH groups and the lone pair of electrons of nitrogen have an interaction with the graphite surface as shown in panel O-3. The relative energy profile shown in Fig. 7.15 suggests that the geometry shown in panel O-3 is energetically less favourable than the *para* geometry in panel P-3. The decrease in surface distortion is therefore clearly not compensating for the absence of the C-N and C-O bonds.

The third hydrogenation leads to the formation of NH_3 for all systems. The optimized structures are shown in Panels M-4 and P-4. Here, a weakly adsorbed NH_3 is formed at a distance of more than 3.4 Å from the surface. NH_3 is formed in 2-leg orientation in panels M-4 and P-4, while in panel O-4, NH_3 is formed in 1-leg orientation. However, in all cases, NH_3 is formed as a hydrogen-bond acceptor. For the *ortho* geometry in panel O-4, the third hydrogenation leads to the dissociation of the N-O bond of HONH₂, resulting in the physisorption of NH_3 . Simultaneously, the OH group chemisorbs onto the surface. In panels M-4 and O-4, the OH points parallel to a surface C-C bond, whereas in panel P-4 the OH bond points to the centre of the ring, whilst the hydrogen bonds are all very similar. This minor difference leads to the slightly lower energy of the P-4 geometry.

7.3.4 Formation of ammonia in the presence of H_2O



Figure 7.16: Relative energy profile and the optimized structures for the sequential hydrogenation of atomic nitrogen to form NH, NH_2 , and NH_3 in the presence of H_2O on bi-layer graphite surface. All the distances are in Å.

It has been reported that H_2O acts as an electron acceptor on the graphene, while the nature of NH_3 depends upon its orientation on the graphene surface.³¹⁹ Therefore, for the final step, we investigated the formation of NH_3 in the presence of H_2O . In Chapter 6, we discussed that H_2O physisorbs on the pristine graphite. Obviously, the concept of *ortho*,

meta, and para no longer exists for this scenario. Thus, only one site is considered to place N, NH, NH₂, and NH₃. The relative energy profile for the sequential hydrogenation of atomic nitrogen to form NH₃ is shown in Fig. 7.16.

We found that the nitrogen atom adsorbs at the midbond site with a C-N-bond of 1.47 Å in the presence of physisorbed H₂O in the 2-leg orientation with a binding energy of -0.99 eV, which is larger than the adsorption of nitrogen on bare graphite (-0.88 eV). The presence of a non-bonded electron on nitrogen favours the reaction of atomic hydrogen to form NH. Thus, this process is exothermic. In this case water functions as a hydrogen bond donor with NH as the hydrogen bond acceptor with a geometry that matches this assignment. The resulting hydrogen bond has a length of 2.66 Å.

The second hydrogenation leads to the migration of nitrogen from the midbond site to the top site as before with a consequent puckering of the carbon underneath the nitrogen atom leading to more distortion of the surface. NH_2 still functions as a hydrogen bond acceptor. The increase in surface distortion does not counter-balance the additional NH bond or the loss of a C-N bond. As a consequence, this process is endothermic compared to the formation of NH.

Finally, the third hydrogenation leads to the formation of NH₃. Similar to the above cases NH₃ is formed in 1-leg orientation at a distance of 3.57 Å from the nearest surface carbon atom. Its geometry again shows it interacting as a hydrogen bond donor with an H-bond length of 1.83 Å, suggesting a strong interaction between H₂O and NH₃. The formation of this dimer is exothermic compared to the previous step.

7.3.5 Conclusion

Similar to previous studies we found that adsorption of atomic nitrogen on bare graphite is an activated process. However, we also found the subsequent steps for the formation of ammonia are barrierless. We also found that ammonia physisorbs on pristine graphite with a site-independent, but orientation-dependent binding energy. As NH_3 is reported to be electron-donating, the presence of electron-accepting species such as O and OH should help the adsorption of NH_3 on the surface. This is indeed what we found. The binding energies and orientations of the adsorbed NH_3 on pristine graphite surface and in the presence of an epoxy group, a hydroxyl group, and water are summarized in Table 7.2. All these binding energies are calculated using Eqn 7.2.

-	E_{b}	Orientation	d
Pristine-graphite	-0.134	2-leg	0.41
O (meta)	-0.23	N-down	3.28
O (para)	-0.26	N-down	3.47
OH (meta)	-0.55	2-leg	3.46
OH(para)	-0.62	2-leg	3.40
H_2O	-0.489	1-leg	3.57

Table 7.2: Binding energy (E_b) for the adsorption of NH_3 in eV, d is the distance between the nearest surface carbon atom and nitrogen atom of the ammonia molecule in Å.

In this chapter, we also studied the adsorption of NH_3 at positions ortho, meta, and para to a carbonyl group and a hydroxyl group. We found that the presence of a single oxygen atom increases the binding energy of NH_3 onto graphite, which physisorbed in the N-down orientation. However, at closer distances, NH_3 actually dissociates to form chemisorbed NH_2 and OH. The presence of a hydroxyl group on the surface significantly enhances the interaction with physisorbed NH_3 , resulting in approximately twice the binding energy compared to an epoxy group and a five-fold increase compared to bare graphite. Among the different orientations of NH_3 , the 2-leg orientation achieves the minimum energy-optimized geometry. The presence of H_2O on the surface leads to a more weakly bound dimer. In that case, both monomers are physisorbed on the surface, meaning that the binding energy to the surface will be low.

Our calculations show that the formation of NH_3 through the sequential hydrogenation is modulated by the presence of O, OH, or H_2O on the surface. The presence of O as either epoxide or carbonyl shows an endothermic step for the hydrogenation of NH, which means that hydrogenation may will stop here. Interestingly, the effect of a hydroxyl group is site-dependent. A hydroxyl group in the *para* position leads to the exothermic formation of NH_2 , whilst OH in the *ortho* or *meta* position is exothermic up to the formation of NH. Finally, the formation of NH_3 in the presence of H_2O also has an endothermic step and the hydrogenation may halt after the formation of NH. In all cases the step leading up to formation of NH_3 is endothermic. Overall our calculations show that the complete sequential hydrogenation of nitrogen to form ammonia requires an external energy source.

Chapter 8

Reaction of atomic oxygen with ethylene, acetylene, and propyne in the gas phase and on the dust analogues

8.1 Introduction

The most abundant elements in the ISM are H (93.38 %) and He (6.49 %), with the total contribution of C, N, and O at 0.11 % (O:C:N $\approx 8:4:1$).³²⁰ The relative dominance of H, C, and O atoms suggest that the chemistry of the ISM will be dominated by these atoms.^{321–324} Indeed, oxygen plays an important role in the chemistry of the ISM and leads to the formation of O-rich organic molecules³²¹⁻³²⁴ so-called complex organic molecules (COMS). Additionally, presence of unsaturated hydrocarbons such as ethylene,³²⁵ acetylene.^{326,327} and propyne^{328,329} has been reported in the ISM. The reaction of an oxygen atom with these unsaturated hydrocarbons not only breaks the C-C bond, but also leads to the formation of alcohols, aldehydes, and acids. Indeed, isomers of acetylene oxide (C_2H_2O) , ethylene oxide (C_2H_4O) , and propylene oxide (C_3H_4O) have been observed in different regions of the ISM, particularly in hot cores and star-forming regions.³³⁰ These isomers can be quite varied. Isomers of ethylene oxide (C_2H_4O) are reported e.g., in the form of vinyl alcohol, acetaldehyde, and c-ethylene oxide, 331-335 whereas acetylene oxide has been detected as ethynol, oxirene and ketene.^{336–338} Similarly, propylene oxide can exist in various linear and cyclic isomeric forms of C₃H₄O, but so far has only been detected in the form of acrolein.^{339–341} The abundance of these molecules varies within different regions of the ISM and depends on the temperature, pressure, and radiation sources.

It is worth noting that these molecules are not just interesting in themselves. Given that these are organic molecules, they are expected to play an important role in prebiotic astrochemistry.^{323,330} For example, acetaldehyde and c-ethylene oxide play a key role in the formation of amino acids.^{342,343} However, the pathways for the formation of these molecules in the interstellar environment are still unclear. Simple molecules like CO, CH₃OH, C₂H₂ (acetylene), and other small carbon chains have established gas-phase formation mechanisms in cold, dense clouds.^{17,344} Conversely, the accumulation and reaction of atomic and molecular species on dust surfaces can result in the creation of more complex organic molecules, which can later contribute to the interstellar gas.²⁶⁵ Thus, for COMs, both gas-phase and gas-surface formation pathways based on observation have been proposed.³⁴⁵ Some experimental and computational studies have explored the reaction of an oxygen atom with ethylene, ^{346–353} acetylene, ^{337,354,355} and propyne^{356–358} in the gas phase. Moreover, Ward *et al.* conducted a study³⁵⁹ on oxygenation reactions of alkene molecules on a graphite surface within an astrophysical context, at temperatures ranging from 12–90 K. Their findings indicated the formation of ethylene oxide and propene oxide when the surface temperature exceeded 12 K. Through the use of a kinetic model, the study demonstrated that the barriers for O+ethylene and O+propene reactions on the surface were lower than the corresponding gas phase values. However, to the best of our knowledge, there has been no theoretical exploration of these reactions on grain analogues.

Previous gas-phase studies have reported that these reactions initiate *via* the collision of a ground state triplet oxygen atom with ethylene, acetylene, and propyne. This results in the addition of a triplet oxygen atom to any of the double or triple-bonded carbon atom and lead to the formation of the first intermediate isomer *via* a small energy barrier. This then intersects to the singlet potential energy surface and shows the possible inter-system crossing (ISC) between triplet and singlet systems.³⁶⁰ Thus, to understand the reaction dynamics of ethylene, acetylene, and propyne molecules with an oxygen atom it is crucial to consider both the singlet (¹D) and triplet (³P) spin states of an oxygen atom, as the reaction between acetylene, ethylene, and propyne with O (³P) can proceed on a ground state triplet potential energy surface, thereby conserving the spin. On the other hand, to access a lower-lying singlet potential energy surface Inter-System Crossing (ISC) has to be included, *i.e.* couplings between molecular triplet and singlet states. Such ISC effects have been studied before for the O+C₂H₄ reaction^{350,352} and O+C₃H₄³⁵⁷ in the gas phase, but remain challenging for more complex systems.

Understanding the reactions of organic molecules in the interstellar medium requires knowledge of two key factors: (i) the energy profile for the formation of intermediate molecules and (ii) the rate constants of these reactions. This chapter focuses on investigating the energy profile for neutral-neutral reactions of oxygen atoms with small carbon-bearing molecules such as ethylene, acetylene, and propyne to study the formation of different isomers using a variety of methods for the formation of these isomers in the gas phase and on solid surfaces such as bi-layer graphite and hexabenzocoronene (PAH). Hexabenzocoronene is used as an example of a polycyclic aromatic compound with a higher number of π -sextets than coronene. Hence, it is more stable and also provides a large surface area for adsorption than coronene. Additionally, we focused our attention on the possible formation of some unknown species such as carbene which can be formed as a metastable isomer in the gas phase and transformed to a more stable isomer on the grains.

The first section here provides an introduction to the species and reactions, methods used for these calculations are discussed in the second section, while the third, fourth and fifth sections discuss the reactions of oxygen atoms with ethylene, acetylene, and propyne for the singlet and triplet spin states in the gas phase, on hexabenzocoronene, and bi-layer graphite surfaces. These sections also include an analysis of the importance of tunnelling for the interconversion of isomers.

8.2 Method

Our study employs various methods to analyze the energy profile for the reaction of oxygen atoms with ethylene, acetylene and propyne in the gas phase and on the surfaces. In the gas phase for the optimization of geometries, for harmonic vibrational frequencies of transition states, and for real frequencies of minimum energy structures we performed unrestricted

8.3

density functional theory (UDFT) with B3LYP-D3BJ/6-311G(d,p), B3LYP-D3BJ/def2-TZVP, PBE-D3BJ/def2-TZVP. Transition states were calculated using QST3 method in Gaussian. Intrinsic reaction coordinates (IRC) calculations have also been performed at the UDFT level to confirm and connect the local minima (intermediate isomers) *via* transitions state. These optimized structures were then used to perform the single point energy calculations with the CCSD(T) and CCSD(T)-F12 method with the cc-pVDZ and cc-pVTZ basis sets, and with CASPT2 with the cc-pVDZ and cc-pVTZ basis set. All CASPT2 level calculations were performed using a minimal active space. This will allow us to compare the results with previous studies.

We then used the Gaussian-optimized gas phase structures to study the formation of these species on hexabenzocoronene and bi-layer graphite surfaces. On hexabenzocoronene, we have performed UDFT calculations with B3LYP/6-311G(d,p) and PBE/def2-TZVP. For the bi-layer graphite surface, we have performed UDFT with PBE and a plane wave basis set. To find the transition states on the graphite surface we have performed Nudge Elastic Band¹⁵⁸ (NEB) calculations. The harmonic vibrational frequency calculations for the transition state on the graphite surface were also performed at the same level of theory as the minimum energy isomers. For these calculations, we restricted the bottom layer of the graphite surface, while all the carbon atoms of the top layer and isomer species were fully relaxed, while for hexabenzocoronene, both the surface and the isomers species were completely relaxed throughout the calculations.

In the gas phase and on the hexabenzocoronene surface both singlet and triplet states were considered. On the other hand, on the graphite surface, spin-polarized calculations were performed. To compare the formation of isomers in the gas phase and on dust analogues density functional theory results using PBE/def2-TZVP in the gas phase and on hexabenzocoronene, and PBE/plane-wave on graphite surface are discussed here.

To study the reaction rate for isomerization within a temperature range of 10 K to 100 K, we have performed TST and SCTST calculations using Gaussian09 program with PBE/def2-TZVP. In TST, the dynamics are considered classical. The barrier height, two partition functions and the vibrational frequency of the reactant, product and the transition states calculated at DFT level were then used to perform TST. On the other hand, SCTST required is an expansion of the force-field around the transition state. In doing this, SCTST removes the need to find distinct tunnelling paths by directly calculating the tunnelling probabilities from analytical formulae in terms of the action variables. These action variables are calculated using a perturbation theory analysis of the transition state and allowing for direct computation of rates from ab initio calculations.

8.3 Reaction of atomic oxygen with ethylene

In the case of C_2H_4O , it is worth noting that the abundance of acetaldehyde is higher than the abundance of c-ethylene oxide or vinyl alcohol.^{361,362} The formation of acetaldehyde in these clouds can occur through various reactions involving H, C, and O atoms on grain surfaces at 10 K^{206,363–365} via radical-radical reactions. For example, previous research has demonstrated that at 10 K, the mixture of CO and CH₄ can produce acetaldehyde by dissociating the H bond in methane through an interaction with cosmic radiation,³⁶⁶ as illustrated in Eqn. 8.1 and 8.2.

$$CH_4 \longrightarrow CH_3 + H$$
 (8.1)

$$C^{-} \equiv O^{+} \xrightarrow{+H} CHO^{-} \xrightarrow{+CH_{3}} H_{3}C - CHO$$

$$(8.2)$$

As the temperature increases, acetaldehyde can be released into the gas phase,³⁶⁷ but this alone cannot account for the amount of acetaldehyde present in the ISM. Whilst these reactions produce only acetaldehyde, they do not lead to the formation of c-ethylene oxide and vinyl alcohol.³⁶⁴ Therefore, other mechanisms are needed as well. In particular, the addition of an oxygen atom to ethylene *via* the π bond of ethylene can lead to the formation of acetaldehyde, ethylene oxide, or vinyl alcohol. Thus, it is important to study the energy profile for this addition reaction.

As discussed above various research groups have studied the reaction of atomic oxygen with ethylene experimentally *via* crossed molecular beam experiments^{346–349} and theoretically *via ab initio* methods.^{350–353} The majority of these studies explored the formation and dissociation of cyclic ethylene oxide.

A general reaction mechanism for the formation of c-ethylene oxide, acetaldehyde, and vinyl alcohol via formation of a bi-radical oxirane is shown in Fig. 8.1. These reactions are initiated by the collision of an ethylene molecule with a ground state triplet oxygen atom (³P). They form a bi-radical CH₂CH₂O (oxirane) intermediate, which is further transformed into different isomers via reaction pathways R1, R2, and R3.



Figure 8.1: Reaction mechanism for the formation of c-ethylene oxide, acetaldehyde, and vinyl alcohol from atomic oxygen and ethylene.

Spin states will be important for this reaction. To illustrate the oxirane molecule formed in the triplet and singlet systems is shown in Fig. 8.2 panels A and B, respectively. In both cases, oxirane is formed with one sp^3 carbon atom (C1) and one sp^2 carbon atom (C2). In the triplet system, this second CH₂ moiety has its C-H bonds at an angle of ~ 10° to the C-C bond, while, within the singlet system, this second CH₂ moiety is obtained with C-H bonds at an angle of ~ 60° to the C-C bond. This results in longer C-C and C-O bonds in the case of the triplet oxirane molecule (Fig. 8.2-A). We note that the oxirane molecule obtained for the singlet system is found to be 0.03 eV lower in energy than for the triplet system, which is because of electron pairing. The energy profile obtained from the reaction of ethylene with a singlet and triplet atomic oxygen for the formation of different isomers *via* various reaction paths is discussed below.



Figure 8.2: Minimum energy structure of oxirane obtained for the triplet system (panel (A)) and oxirane as a transition state for the singlet system (panel (B)). The atoms are color-coded in hydrogen (white), carbon (gray), and oxygen (red).

8.3.1 Reaction of oxygen $({}^{3}P)$ with ethylene in the gas phase and on hexabenzocoronene



Figure 8.3: Potential energy profile for the formation of oxirane from atomic oxygen $({}^{3}P)$ and ethylene.

The energy profile for $C_2H_4+O(^{3}P)$ in the gas phase and on hexabenzocoronene surface is shown in Fig. 8.4. These profiles start from a collision of an ethylene molecule with a ground state triplet oxygen atom (³P). This collision first shows a physisorption interaction at an internuclear distance of 2.4 Å. This further leads to the formation of minimum energy oxirane molecule I_0 via transition state TS0 as shown in Fig. 8.3.

Density functional theory results show the formation of TS0 as an exothermic step relative to an infinitely separated reactant. In contrast, CCSD(T) and CASPT2 results show this as an endothermic step relative to $C_2H_4+O(^3P)$ as shown by the blue line. This is consistent with previous studies.^{350,352} Interestingly, this intermediate state TS0 is not found when hexabenzocoronene is included.

Oxirane is the starting point for the formation of other isomers. First, oxirane can transform into dimethylene ether (I1) through an energy barrier of 2.17 eV via a transition state (TS1) by fission of C-C bond and dissociate oxirane into CH₂ and CH₂O moieties. This leads to the insertion of oxygen in between the two carbon atoms and transforms into isomer I1 (CH₂OCH₂). In the second pathway, oxirane can transform into dissociated species CH₂CHO+H (I7) via breaking of C-H bond and formed with 1.16 eV higher in energy than that of oxirane. This energy difference is only 0.5 eV on hexabenzocoronene surface. In the third pathway by breaking of C-C bond oxirane can also transform into another dissociated species CH_2+CH_2O (I8), ~0.5 eV higher in energy than oxirane. In the presence of hexabenzocoronene, both I7 and I8 are also formed as an endothermic step with 0.5 eV higher in energy than oxirane. The formation of these dissociated species in the gas phase is consistent with previous study³⁵⁰ conducted by Fu *et al.* at RCCSD(T)/augcc-pVTZ level. However, they have studied the energy profile only by fitting the energy of the obtained molecules and also showed the formation of these dissociated species via transition states whereby, we have performed the optimization for the minimum energy structure and vibrational frequency calculations for the transition states. Thus, we found no transition states to these dissociated species. The absence of transition states agrees with another study conducted by Talotta et al.³⁵² at CASPT2/NOL-VDZ level.

In the fourth pathway, oxirane transforms into the most stable isomer, acetaldehyde (I2), by 1,2-H transfer via transition state TS2 with an energy barrier of 1.02 eV. Alternatively, acetaldehyde can also be formed from syn-vinyl alcohol (I3) by keto-enol tautomerization with the migration of hydrogen from carbon to oxygen atom via transition state TS3 with an energy barrier of 1.23 eV in the gas phase and 0.07 eV in the presence of hexabenzocoronene. Similar to oxirane, acetaldehyde can also result in the formation of dissociated species CH_3 +HCO by dissociation of the C-C bond as an endothermic reaction step with an energy of 1.25 eV higher than that of acetaldehyde. This also agrees with the previous studies. Finally, anti-vinyl alcohol (I4) can also be formed from oxirane via transition state (TS2) by migration of a hydrogen atom from carbon to oxygen. Additionally, antivinyl alcohol (I4) can also transform to the lower energy syn-vinyl alcohol (I3) isomer via transition state TS4 through rotation of the O-H bond. In addition to these, we also found some additional isomers which were not discussed in the literature, such as I5 and 16. These are syn and anti forms of carbene with alcoholic functional groups. In the gas phase and on hexabenzocoronene both I5 and I6 are obtained with identical energy and can be easily transformed from syn to anti and vice-versa via rotation of OH bond with a small energy barrier of ~ 0.07 eV in the gas phase, which reduces to 0.05 eV on hexabenzocoronene. Moreover, in contrast to the gas phase, on the hexabenzocoronene surface, these are obtained as metastable isomers.

Fig. 8.4 also shows the reaction of $O({}^{3}P)+C_{2}H_{4}$ adsorbed on hexabenzocoronene, all isomers physisorbed onto the hexabenzocoronene surface at a distance of ~3.2 Å. The transformation pattern from one isomer to another on the surface is similar to that in the gas phase. Fig. 8.5 depicts the optimized geometry of these isomers and the transition





states connecting these on the hexabenzocoronene surface for the triplet system. This figure reveals that in general one of the carbon atoms of ethylene interacts with a top carbon atom of the hexabenzocoronene surface. On the other hand, the oxygen atom interacts with the centre of a hexagonal ring of the surface, except for dimethylene ether (I1). In that case one of the lone pairs of electrons of the oxygen atom interacts with a top carbon atom site of the hexabenzocoronene ring, and the carbon atoms of adsorbed dimethylene ether remain at the centre site of hexagonal rings.



Figure 8.5: *Minimum energy optimized isomers and transition state structures obtained by the reaction of ethylene and triplet oxygen atom on hexabenzocoronene surface. The atoms are color-coded in hydrogen (white), carbon (cyan and gray), and oxygen (red).*

It is noted that the presence of a grain surface provides an extra dimension to the system. This results in additional reaction pathways, particularly for the transformation of I2 to I5 *via* the migration of the hydrogen atom from C1 to the oxygen atom through transition state TS8, as shown in Fig. 8.4. Thus, the transformation of I2 into I5 can take place *via* a migration of the hydrogen atom below the molecule (*i.e.*, in between the surface and the molecule) or over the molecule. In the former case, the migrating hydrogen can interact more with the surface. This results in a lower energy barrier of 2.33 eV from I2 to TS8. In the latter case, the migrated species does not have any interaction with the surface and a higher energy barrier of 3.32 eV from I2 to TS8 is recorded. The two transition states obtained are shown in Fig. 8.5 panels TS8-in and TS8-down, respectively. A clear interaction of the moving hydrogen atom with the hexabenzocoronene surface can be seen in panel TS8-down.

Fig. 8.4 also allows us to ascertain the influence of the surface. Whilst the general trends are similar, the relative energies of the isomers I0, I5, and I6 show a destabilization in the presence of the surface. This might be because of the orientation of the molecule. In addition, we see a reduction in the energy of some barriers in particular, the energy barrier for the isomerization of acetaldehyde to vinyl alcohol *via* transition state TS3 was significantly lower going from 1.32 eV in the gas phase to 0.49 eV in the presence of the surface.

The energies obtained for the formation of these isomers using various methods relative

to $C_2H_4+O(^{3}P)$ are summarized in Table 8.1. We found a similar pattern for the transformation of isomers and the relative energy profiles across all methods in both the gas phase and on the surface. The energy profile for the isomerization of triplet C_2H_4O isomers using four different methods relative to the energy of isomer I1 (dimethylene ether) is shown in Fig. 8.6. This illustrates that an identical energy profile is obtained for the minima and transition states by using CCSD(T), CCSD(T)-F12, and CASPT2 methods. These results agree with the previous studies, as summarized in Table 8.1. However, the DFT method PBE/def2-TZVP underestimates the barriers for I1-I0, I0-I2, I2-I3, and I4-I5 pathways.

Table 8.1: Relative energy for the formation of different isomers by reaction of ethylene molecule with a triplet oxygen atom in the gas phase and on hexabenzocoronene surface by using different methods.

-	- Gas									H	Iex	Gas
-	B3LYP	B3LYP	PBE	CCS	D(T)	CCSDT-F12		CASPT2		B3LYP	PBE	others
Str	6-311G(d,p)	def2-TZVP	def2-TZVP	pVDZ	pVTZ	6-311G(d,p)	def2-TZVP	-				
TS0	-0.23	-0.22	-0.45	0.21	0.13	0.06	0.05	0.23	0.11	-	-	$0.143,^{350},0.08^{352}$
IO	-1.22	-1.26	-1.64	-0.71	-0.92	-1.0	-1.04	-0.63	-0.89	-1.34	-0.87	-0.93 , ³⁵⁰ -0.9^{352}
I1	-1.1	-1.16	-1.56	-0.55	-0.84	95	-0.99	-0.45	-0.78	-1.19	-0.74	
TS1	1.33	1.26	0.53	1.91	1.59	1.49	1.45	1.94	1.58	1.25	1.36	
TS2	0.16	0.11	-0.62	0.86	0.58	0.46	0.42	0.82	0.48	0.067	0.19	0.49^{350}
I2	-1.68	-1.70	-2.17	-1.14	-1.32	-1.42	-1.45	-1.24	-1.46	-2.55	-2.37	-1.32^{350}
TS3	-0.1	-0.14	85	0.48	0.22	0.10	0.06	0.44	0.16	-1.96	-1.88	0.178^{350}
13	-1.57	-1.61	-2.08	-1.0	-1.32	-1.45	1.49	-1.04	-1.4	-2.1	-1.95	-1.27^{350}
TS4	-1.32	-1.38	-1.82	-0.75	-1.09	-1.22	-1.26	-0.81	-1.18	-1.90	-1.73	
I4	-1.51	-1.57	-2.03	-0.96	-1.28	-1.41	-1.45	-1.0	-1.33	-2	-1.91	
TS5	0.7	0.65	-0.067	1.31	0.97	0.84	0.79	1.07	0.70	0.58	0.69	
15	-1.39	-1.41	-1.92	-0.95	-1.19	-1.31	1.34	-1.17	-1.22	-1.56	-1.15	
TS6	-1.32	-1.34	-1.85	-0.87	-1.13	-1.25	-1.29	-1.11	-1.15	-1.45	-1.13	
16	-1.39	-1.41	-1.92	-0.95	-1.19	-1.31	-1.34	-1.17	-1.22	-1.58	-1.16	
TS7	0.22	0.15	-0.48	0.80	0.48	0.36	0.31	0.81	0.45	0.14	0.35	0.35^{350}
TS8	-0.01	-0.04	-0.72	0.49	0.25	0.13	0.09	0.45	0.19	-0.12, 1.1	-0.04, 0.95	
TS9	0.70	0.69	-0.01	1.33	0.97	1.25	0.84	1.11	0.76	0.58, 0.57	0.65	
17	-1.17	-1.01	-1.13	-0.20	-0.33	-0.44	-0.47	-0.25	-0.38	-0.75	-0.364	-0.37, ³⁵⁰ -0.34 ³⁵²
I8	-0.16	-0.16	-0.48	-0.01	-0.07	-0.12	-0.14	-0.31	-0.39	-0.28	-0.37	$-0.05,^{350}-0.07^{352}$
19	-1.14	-1.19	-0.99	-0.77	-0.92	-1.01	-1.03	-0.71	-0.92	-1.25	-0.404	-0.88^{350}



Figure 8.6: A comparison of different methods for the isomerization of C_2H_4O in the gas phase.



Figure 8.7: Thermal rate constants as a function of temperature for the reaction of ethylene with atomic oxygen $({}^{3}P)$ in the gas phase computed using transition state theory (TST) and semi-classical transition state theory (SCTST). Panel A to panel D, rate for transformation I0–I1, I0–I2, I3–I4, and I5–I6 (top) and barrier for I0–I1, I0–I2, I3–I4, and I5–I6 transformation (bottom). 170

We have also calculated the reaction rates for isomerization reactions within a temperature range of 10 K to 100 K. The calculations were done with a purely classical and a semiclassical (SCTST) approach as explained in Chapter 2, Section 2.8. The results are shown in Fig. 8.7 panels (A) to (D).

In panels A1 to D1, the solid line represents the dependence of the rate of reaction with temperature for the semiclassical approach, while the dotted line shows the same dependence rate for a purely classical approach. The sub-panels (A2) to (D2) illustrate the energy barriers for the reactions along reaction coordinates. In this the reaction coordinates in atomic units (a.u.) shows the changes in the positions and configurations of atoms and molecules as they transition from reactants to products *via* transition state. The geometry of these transitions states were calculated using QST3 method.

Panel A shows the I0-I1 transformation (oxirane to dimethylene ether) which has a ≈ 2.4 eV barrier. The corresponding rate is very low at astronomically relevant temperatures. There is an effect of tunnelling, but it is small, in line with the heavy mass of the CH₂ unit that needs to tunnel for this transformation. Panel B shows the data for the I0-I2. Compared to the I0–I1 transformation a significantly lower energy barrier is shown in panel (B2) leading to a significant tunnelling effect at low temperatures leading to a predicted rate of 10^{-10} s⁻¹. We also found the transformation of I2 to I3 (acetaldehyde to vinyl alcohol) isoenergetic to I0–I2 and shows a similar barrier of ~1.2 eV leading to a low-temperature rate of 10^{-10} s⁻¹, suggesting that at a long time, equilibration between I2 and I3 should be achieved. The barrier between I3 and I4 (*syn*-vinyl alcohol to *anti*-vinyl alcohol) is very low as shown in panel C2. Therefore, even at very low temperatures, the rate is ~10² s⁻¹, largely through tunnelling. Finally, the transformation between I5 and I6 should be rapid again, particularly if tunnelling is included. On the other hand, similar to panels A and B other transformations were obtained with a large barrier leading to a small rate, even if tunnelling is included.

8.3.2 Reaction of oxygen (¹D) with ethylene in the gas phase, on hexabenzocoronene, and on graphite

All the isomers obtained in the triplet system are also obtained within the singlet system except isomer I1. In the triplet system, I1 is obtained in the form of dimethylene ether, which is not discussed in the literature. On the other hand, in the singlet system, I1 is obtained in the form of c-ethylene oxide. The energy profile for the reaction of C_2H_4+O (¹D) in the gas phase relative to the asymptotic energy for $C_2H_4+O(^{3}P)$ is shown in Fig. 8.8. As before, our consideration starts with the formation of oxirane (I0). In the singlet system the intermediate isomer oxirane (I0) is formed with identical geometry as in the triplet system, but with a rotation of CH_2 fragment to make it co-planar with the C-O bond. In contrast to the triplet system in which oxirane is obtained as a minimum energy structure, in the singlet system oxirane is obtained as a transition state, but 0.03eV lower in energy than the triplet form. This indicates that the formation of oxirane is crucial for inter-system crossing (ISC). ISC can happen once the energy for the singlet and triplet systems are similar. For the singlet system, oxirane (I0) connects the two minima c-ethylene oxide (I1) and acetaldehyde (I2). In the gas phase c-ethylene oxide is 2.43 eV lower in energy than oxirane by ring-closing of the oxygen atom. On the other hand, acetaldehyde is at 3.51 eV lower in energy than oxirane and forms via 1,2-H shift. The optimized acetaldehyde in the singlet system is formed with a C-O bond of 1.2 Å and a C-C bond of 1.51 Å. In contrast, in the triplet acetaldehyde, a longer C-O bond of 1.32 Å and a C-C bond of 1.52 Å are obtained.

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Acetaldehyde (I2) is the lowest energy isomer and can transform further via three different pathways. First, acetaldehyde can lead to the formation of the dissociated species CH_4+CO (I8) by breaking the C1-H and C-C bond. In the second pathway acetaldehyde can transform into syn-vinyl alcohol (I3) by the migration of a hydrogen atom from the C2 carbon atom to oxygen via transition state TS2 with an energy barrier of 2.67 eV. Finally, acetaldehyde can transform into the higher energy carbene isomer I5 via migration of a hydrogen atom from the C1 carbon atom to oxygen via transition state TS7. Similar to the triplet system, this can further transform to isomer I6 with identical energy by a rotation of the OH bond via transition state TS5. Moving further, syn-vinyl alcohol (I3) can also undergo two further transformations. First, the rearrangement of syn-vinyl alcohol (I3) to anti-vinyl alcohol (I4) by rotation around the OH bond via transition state TS3 with an energy barrier of 0.27 eV. Second, the isomerization of syn-vinyl alcohol I3 to carbene I6 by a 1,2-H shift via transition state TS8. In addition to isomers I5 and I6, we also found this metastable isomer I7 which is also not discussed in the literature. This can lead to the formation of *anti*-vinyl alcohol by migration of the OH group from carbon atom C1 to C2 via transition state TS6 with an energy barrier of 0.46 eV.

On the other hand, the optimized isomers are obtained on graphite and hexabenzocoronene surfaces at a distance of ~ 3.3 Å from the surface, leaving the surface initially completely undistorted. Interestingly, within the gas phase and on both surfaces the optimized isomers are obtained with identical bond angles and bond lengths, which is perhaps unsurprising given the fact that the molecules are physisorbed on the surface. Fig. 8.9 and 8.10 show the resultant structures on both bi-layer graphite and hexabenzocoronene, respectively.

Similar to the triplet system these molecules are optimized on hexabenzocoronene such that one of the carbon atoms of ethylene interacts with a top carbon atom of the hexabenzocoronene surface. On the other hand on the graphite surface, these optimized structures are formed with the C-C bond parallel to the C-C bond of the graphite system. However, the bond length and angles in both cases are found identical to the molecules obtained in the gas phase.



Figure 8.9: Minimum energy optimized isomers and transition state structures obtained by the reaction of ethylene and an oxygen atom on a bi-layer graphite surface.

As noted before in comparison to the gas phase, in the presence of a surface there are additional pathways for the transformation of one isomer into another because of the extra dimension added to the system. In particular, we have found two transition states, TS2-up and TS2-in, for the migration of hydrogen from C2 to oxygen during the transformation from acetaldehyde (I2) to *syn*-vinyl alcohol (I3) *via* either from the top or bottom of the molecule. On both surfaces the first pathway, *via* at the top of the molecule, has an energy barrier of 2.67 eV (see Fig.8.9 and 8.10 panel TS2-up), while the second pathway, *via* underneath the molecule, has an energy barrier of 2.65 eV (see Fig. 8.9 and 8.10 panel TS2-in), suggesting that the surface only has a small effect on the energy of this transformation. Similarly, a reduced energy barrier is obtained within some other pathways in the presence of a surface compared to the gas phase as shown in Fig. 8.8.



Figure 8.10: Minimum energy optimized isomers and the transition state structures obtained by the reaction of ethylene with a singlet oxygen atom on the hexabenzocoronene surface.

In addition to this, similar to the gas phase, isomer I7 was found as a metastable isomer on both surfaces. On hexabenzocoronene, this transforms into *anti*-vinyl alcohol with an energy barrier of 0.53 eV, which is higher than the gas phase (0.46 eV), whereas on graphite surface this energy barrier is reduced significantly as shown in Fig. 8.8. By comparing the energy profile of these reactions in the gas phase and on the surfaces, we found that in the presence of surface, the energy barrier was reduced but only in some pathways.

The energies obtained for transition states and the minimum energy isomers relative to the $C_2H_4+O(^{3}P)$ by various methods are summarized in Table 8.2. In contrast to the triplet isomers, for the singlet isomers, we obtained lower energies for the minima and transition states.

As discussed in Fig. 8.8, a similar pattern is obtained for the isomerization of the singlet C_2H_4O in the gas phase and on the surface. To compare our results with the previous studies, we have also studied these energy profiles with different methods. The energy profiles relative to isomer I1 for the comparison of four different methods in the gas phase calculations are shown in Fig. 8.11. This illustrates that similar to triplet C_2H_4O , the results

-	Gas									H	ex	Graphite	Gas
-	B3LYP	B3LYP	PBE	CCSI	D(T)	CCSD	T-F12	CAS	PT2	B3LYP	PBE	plane-wave	other
Str	6-311G(d,p)	def2-TZVP	def2-TZVP	pVDZ	pVTZ	pVDZ	pVTZ	pVDZ	pVTZ	6-311G(d,p)	def2-TZVP	plane-wave	
-	2.77	0.84	0.7	2.26	2.2	2.79	2.16	2.19	2.04	0.72	0.8	-	
TS0	0.93	0	-0.18	1.43	1.16	0.97	0.93	1.45	1.16	-	-	-	
I1	-3.58	-3.67	-4.28	-3.17	-3.57	-3.71	-3.76	-3.05	-3.41	-3.65	-3.42	-4.61	-3.56 , ³⁵⁰ , -3.37^{352}
TS1	-1.35	-0.96	-1.85	-1.74	-1.67	-1.88	-1.77	-0.72	-0.98	-0.95	-1.35	-2.14	$-1.07,^{350}-0.95^{352}$
I2	-4.87	-4.89	-5.36	-4.47	-4.73	-4.86	-4.89	-4.41	-4.65	-4.95	-4.54	-5.54	-4.83, 350 -4.7 352
TS2	-1.86	-1.91	-2.69	-1.35	-1.68	-1.81	-1.86	-1.34	-1.64	-1.95, -1.97	-1.87, -1.89	-2.85, -2.89	-1.69^{350}
I3	-4.4	-4.44	-4.92	-3.9	-4.29	-4.44	-4.49	-3.92	-4.22	-4.51	-4.12	-5.06	-4.28^{350}
TS3	-4.15	-4.21	-4.65	-3.66	-4.08	-4.24	-4.28	-3.63	-4.04	-4.30	-3.89	-4.91	
I4	-4.32	-4.38	-4.85	-3.81	-4.23	-4.39	-4.43	-3.75	-4.16	-4.46	-4.07	-5.16	
TS4	-1.54	-1.58	-2.20	-1.03	-1.41	-1.58	-1.63	-0.97	-1.29	-1.61, -1.65	-1.4, -1.36	-2.42, -2.41	-1.43^{350}
I5	-2.62	-2.64	-3.07	-2.22	-2.53	-2.67	-2.70	-1.95	-2.54	-2.72	-2.27	-3.31	-2.5^{350}
TS5	-1.43	-1.48	-1.89	-0.98	-1.34	-1.50	-1.55	-0.91	-1.19	-1.66	-1.23	-1.99	
I6	-2.49	-2.51	-2.99	-2.1	-2.38	-2.51	-2.55	-2.03	-2.31	-2.6	-2.15	-3.17	
TS6	-0.11	-0.17	-0.80	0.41	0.01	-0.13	-0.17	0.55	0.14	-0.15	0.11	-1.62	
I7	-0.68	-0.73	-1.26	-0.32	-0.67	-0.79	-0.84	-0.17	-0.53	-0.72	-0.42	-1.63	
TS7	-1.23	-1.27	-1.98	-0.837	-1.13	-1.27	-1.31	-0.64	-0.94	-1.48	-1.28	-2.17	-1.16^{350}
TS8	-1.43	-1.41	-2.07	-0.88	-1.24	-1.38	-1.43	-0.82	-1.16	-1.48, -1.52	-1.27, -1.25	-2.3, -2.4	
I7	-4.91	-4.89	-5.11	-4.84	-4.94	-5.03	-5.04	-5.11	-5.21	-4.97	-4.27	-5.03	-4.91^{350}

Table 8.2: Relative energy for the formation of different isomers by the reaction of ethylene with a singlet oxygen atom in the gas phase, on hexabenzocoronene, and on graphite surface by using different methods.

obtained from PBE show some inconsistency in comparison to the other three methods. On the other hand, the relative energies obtained by CCSD(T)-F12 and CASPT2 are in good agreement with the previous studies as summarized in Table 8.2. This suggests that CCSD(T)-F12 and CASPT2 methods determine the energy values equally accurately for these isomerizations.



Figure 8.11: A comparison of different methods for the isomerization of singlet C_2H_4O in the gas phase.

Similar to the triplet system we performed semiclassical transition state calculations for the singlet system as well. However, the higher energy barriers mean that these are generally small at astrochemically relevant temperatures. The only reaction that has a significant rate at low temperatures is the rotation of the OH bond, *i.e.*, rotation for the *syn* to *anti*-vinyl alcohol transformation (I3-I4). The dependence of this rate constant as well as the

corresponding barrier is shown in Fig. 8.12. This Figure shows that the tunnelling-aided rate levels out around 20 K at 10^{-2} s⁻¹.



Figure 8.12: Thermal rate constant as a function of temperature for the reaction of ethylene with atomic oxygen $({}^{1}D)$ in the gas phase computed using transition state theory and semiclassical transition state theory. Panels A1 and A2 show the rate for the transformation of $I_{3}-I_{4}$ and the barrier for $I_{3}-I_{4}$ transformation geometry, respectively.

8.4 Reaction of atomic oxygen with acetylene

The reaction between an oxygen atom and acetylene in the gas phase has been studied before.^{337,354,355,368} Similar to ethylene, the reaction of acetylene with atomic oxygen is initiated by a collision between acetylene and a triplet oxygen atom. This collision results in the formation of ketene (H₂CCO), ethynol/hydroxy acetylene (HCCOH), and oxirene (HC-O-CH). These isomers can be considered to be building blocks of COMs in the ISM. Ketene has two double bonds (C=C and C=O), while ethynol has one triple bond (C≡C) and a single C-O bond. A recent study published in March 2023, conducted by Wang et al.³³⁸ also reported the formation of oxirene in the gas phase at a temperature of 5K. Oxirene is believed to be an intermediate isomer in between the more stable isomers. However, within the ISM only ketene^{369,370} has been detected so far.

The reaction mechanism of acetylene and an oxygen atom is shown in Fig. 8.13. The

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reaction between these first forms the intermediate product cyclic oxirene, which can be considered crucial because this is where inter-system crossing (ISC) is most likely to happen (see below). ISC can lead to further reaction either on ground state singlet or excited state triplet potential energy surfaces. The reaction can follow three different pathways R1, R2, and R3 to form either oxyacetylene, ethynol, or ketene in the singlet and triplet spin state as shown in Fig. 8.13.



Figure 8.13: Reaction mechanism for the formation of oxyacetylene, ethynol, and ketene from atomic oxygen and acetylene.

The triplet and singlet oxirene obtained are shown in Fig. 8.14 panels A and B, respectively. Similar to the reaction of atomic oxygen with ethylene, triplet oxirene is obtained as a minimum energy structure, while singlet oxirene is obtained as a transition state structure, which minimizes to oxyacetylene. In singlet oxirene, weak C-O bonds of 1.503 Å are obtained, while the C-C bond of 1.262 Å is equivalent to a triple bond.³⁷¹ On the other hand, in triplet oxirene these C-O bonds have a bond length of 1.403 Å. Moreover, the C-C bond is found to be 1.434 Å which is equivalent to a single bond.³⁷¹ This makes singlet oxirene ~ 0.92 eV lower in energy than triplet oxirene.



Figure 8.14: Minimum energy structure of oxirene obtained for the triplet system (panel (A)) and oxirene as a transition state for the singlet system (panel (B)).

8.4.1 Reaction of atomic oxygen (³P) with acetylene in the gas phase and on hexabenzocoronene

The relative energy profile for the reaction of C_2H_2 with $O(^{3}P)$ in the gas phase and on hexabenzocoronene is shown in Fig. 8.15. The minimum energy and transition state structures on the hexabenzocoronene surface are shown in Fig. 8.16. The initial collision of acetylene with a triplet oxygen atom leads to the formation of c-oxirene (I1) as a minima in both gas phase and on hexabenzocoronene. This can then transform to higher energy oxiranylidene (I2) via transition state TS1 by 1,2-H shift with a barrier of 2.09 eV and 2.25 eV in the gas phase and on hexabenzocoronene, respectively. Oxiranylidene can further transform into alcoholic form *anti*-hydroxy-vinylidene (I3) via transition state TS2 by migration of hydrogen from carbon to oxygen. However, this requires overcoming an energy barrier of ≈ 3 eV in both gas phase and also in the presence of hexabenzocoronene. The other form of hydroxy-vinylidene is obtained as, *syn*-hydroxy-vinylidene (I4), which is 0.24 eV higher in energy than *anti*-hydroxy-vinylidene (I3) in both gas phase and on the hexabenzocoronene surface.

Syn-hydroxy-vinylidene (I4) can further transform to lower energy isomer ethynol (I5) via transition state TS4 by 2,1-H shift with a barrier 2.66 eV in the gas phase. Interestingly the energy barrier reduced significantly to 1.4 eV in the presence of hexabenzocoronene and a lower energy isomer ethynol is formed with both carbon atoms in the sp^2 hybridization as shown in Fig. 8.15 and 8.16. Ethynol further leads to the formation of energetically more stable ketene (I7) via intermediate isomer oxyacetylene (I6) in both the gas phase and in the presence of hexabenzocoronene. Ketene is found as a stable isomer, which is in agreement with a previous study.^{351,368}



Figure 8.15: Schematic representation of the energy profile for the reaction of acetylene with atomic oxygen $({}^{3}P)$ in the gas phase (shown by green lines) and on the hexabenzo-coronene surface (shown by purple lines). Relative energies (in eV) are computed relative to the collision geometry $O({}^{3}P)+C_{2}H_{2}$. All calculations are done with PBE/def2-TZVP.

Similar to C_2H_4O isomers, isomers of C_2H_2O were also optimized in different orientations on hexabenzocoronene and graphite surface. But, only the structures associated with the lowest energies were considered for the transition state calculations. All isomers were physisorbed and remained at a distance of ~ 3.2 Å from the surface. Optimized structures on hexabenzocoronene corresponding to minima and transition states are shown in Fig. 8.16. The geometries are found either with the C \equiv C bond of acetylene parallel to the surface C-C bond or with one carbon atom at the top of a surface carbon atom and a second carbon atom at the centre of the hexagonal ring.



Figure 8.16: *Minimum energy optimized isomers and transition state structures obtained by the reaction of acetylene and triplet oxygen atom on hexabenzocoronene surface.*

The energies obtained for minima and transitions state by different methods for triplet manifold in the gas phase and on hexabenzocoronene, relative to the $C_2H_2+O(^{3}P)$ are summarized in Table 8.3.

Table 8.3: Relative energies for the formation of different isomers by reaction of acetylene with a triplet oxygen atom in the gas phase and on hexabenzocoronene surface by using different methods.

-		He	ex								
-	B3LYP	B3LYP	PBE	CCS	D(T)	CCSD	CCSDT-F12		SPT2	B3LYP	PBE
Str	6-311G(d,p)	def2-TZVP	def2-TZVP	pVDZ	pVTZ	pVDZ	pVTZ	pVDZ	pVTZ	6-311G(d,p)	def2-TZVP
I1	-1.41	-1.21	-1.87	-0.73	-0.88	-0.98	-1.01	-0.68	-0.93	-1.17	-1.93
TS1	1.21	1.16	0.38	1.5	1.42	1.34	1.32	1.55	1.35	1.0	0.86
I2	-0.37	-0.45	-1.12	-0.06	-0.21	-0.33	-0.35	0.05	-0.22	-0.46	-1.4
TS2	2.79	2.73	1.86	3.12	3.02	2.94	2.92	3.29	3.07	2.62	1.68
I3	-0.97	-1.01	-1.46	-0.54	-0.65	-0.74	-0.77	-0.32	-0.54	-1.16	-1.72
TS3	-0.22	-0.19	-0.85	-0.03	-0.14	-0.24	-0.27	0.07	-0.22	-0.47	-1.05
I4	-0.72	-0.78	-1.22	-0.28	-0.42	-0.51	-0.54	-0.16	-0.34	-0.95	-1.49
TS4	2.17	2.13	1.44	2.54	2.42	2.34	2.32	2.87	2.69	0.67	-0.09
I5	-1.03	-1.07	-1.62	-0.60	-0.75	-0.86	-0.88	-0.11	-0.83	-1.21	-1.83
TS5	0.56	0.75	-0.06	1.04	0.88	0.79	0.76	1.01	0.21	0.44	-0.44
I6	-2.51	-2.54	-3.06	-2.16	-2.21	-2.31	-2.32	-2.09	-2.22	-2.62	-3.2
TS6	0.15	-0.71	-1.46	-0.13	-0.21	-0.32	-0.34	-0.12	-0.28	-0.79	-1.62
I7	-1.03	-3.43	-3.91	-2.95	-3.02	-3.13	-3.15	-2.89	-3.06	-3.52	-4.08

A comparison of different methods for the isomerization of triplet C_2H_2O is shown in Fig. 8.17. The energy profiles for these are obtained relative to the energy of isomer I1. Fig. 8.17 shows that similar to C_2H_4O , for triplet C_2H_2O inconsistent results are found with

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PBE/def2-TZVP in comparison to the other three methods. Similar to what we observed before, PBE shows underestimated barriers for the pathways I2–I3 and I6–I7.



Figure 8.17: A comparison of different methods for the isomerization of triplet C_2H_2O in the gas phase.

As the isomerizations in the triplet manifold occur via higher energy barriers. Thus, the result obtained by semiclassical transition state theory within temperature 10 K-100 K shows that the only reaction that will have a significant rate at low temperatures is I4–I3 (syn-anti hydroxy-vinylidene). The dependence of the rate constant and the corresponding energy barrier for I4–I3 is shown in Fig. 8.18 panels A1 and A2, respectively. I4–I3 involves the rotation of OH bond for the formation of syn-hydroxy-vinylidene to anti-hydroxyvinylidene. This result an energy barrier of ≈ 0.37 eV and predicted a tunnelling rate of 10^{-5} s⁻¹.



Figure 8.18: Thermal rate constants as a function of temperature for the reaction of acetylene with a triplet oxygen atom in the gas phase computed using the TST and SCTST. Panel A1 is the rate of transformation and panel A2 is the barrier for I4-I3.

8.4.2 Reaction of oxygen (¹D) with acetylene in the gas phase, on hexabenzocoronene, and on graphite

The energy profile for the reaction of C_2H_2 with $O(^1D)$ follows a similar pattern in the gas phase and on the surfaces. A comparison of the relative energy profile for the isomerization of these in the gas phase, on the hexabenzocoronene, and on the bi-layer graphite surface is shown in Fig 8.19. Similar to our approach above, the initial collision of acetylene with a triplet oxygen atom leads to the formation of c-oxirene as an intermediate isomer for both the singlet and triplet manifolds. ISC at this point would allow the further evolution of either a singlet or a triplet system. Similar to ethylene we found that all the isomers obtained for the triplet system are also present in the singlet system in the gas phase and on a hexabenzocoronene surface except *syn*-hydroxy-vinylidene. However, in the gas phase singlet system, we also found two additional metastable isomers I5 (oxiranylidene) and I6 (hydroxy-vinylidene) as shown in Fig. 8.19. 4

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Gas

Figure 8.19: Schematic representation of the energy profile for the reaction of acetylene with atomic oxygen $({}^{1}D)$ in the gas phase (shown by blue lines), on hexabenzocoronene surface (shown by purple lines), and on bi-layer graphite surface (shown by red lines). Relative energies (in eV) are computed relative to collision geometry $O({}^{3}P) + C_{2}H_{2}$. All calculations in the gas phase and on hexabenzocoronene are performed with PBE/def2-TZVP and on graphite are performed with PBE/plane-wave.

For the singlet manifold, c-oxirene (TS1) is formed in the gas phase as a transition state between two lower energy forms of oxyacetylene, which are the ring-opening forms of coxirene. These are 0.18 eV lower in energy, which is in agreement with the previous study (0.15 eV).³⁶⁸ This energy barrier increases to 0.21 eV on hexabenzocoronene and 0.24 eV on graphite surface. Oxyacetylene has an aldehyde functional group but is a carbene. Both I1 and I2 exist in the form of *anti*-oxyacetylene whereas oxirene for both singlet and triplet is found in the Z-configuration. Oxyacetylene can further transform into two different isomers. First, it can transform into hydroxy-vinylidene (I6) by the migration of a hydrogen atom from C1 to oxygen via a four-membered ring transition state (TS5). which requires overcoming an energy barrier of 1.6 eV. Again, similar to oxyacetylene (I2), hydroxy-vinylidene (I6) is also found in the *anti* form. Secondly, oxyacetylene (I2) can isomerize to ketene (I3) by a 1,2-H shift via transition state TS2 with an energy barrier of 0.44 eV. An identical energy barrier is obtained in the case of hexabenzocoronene. However, surface effects are observed in the case of graphite, since a significantly reduced energy barrier of 0.16 eV is found here. This might be due to the alignment of the oxyacetylene and ketene on the graphite surface (discussed below).

Similar to triplet manifold ketene is found as the energetically most stable isomer. Ketene can further undergo two endothermic pathways and lead to the formation of oxiranylidene (I5) and ethynol (I4). Higher energy oxiranylidene is formed *via* transition state TS4, in which the CO bond of ketene rotates and undergoes dissociation of the C-C bond forming CH_2 and CO as an intermediate. This reaction has an energy barrier of 3.79 eV. On the other hand, ethynol is found as energetically more stable than oxiranylidene. Formation of ethynol occurs *via* a higher energy barrier than the oxiranylidene as in this case the migrating hydrogen atom needs to travel three bonds away from the C-H site to form O-H. In the gas phase transformation of ketene into ethynol is observed *via* a three-

membered transition state TS3 with an energy barrier of 3.89 eV. On the other hand, this energy barrier was reduced to 3.67 eV and 3.7 eV in the presence of hexabenzocoronene or graphite. On the surfaces, the hydrogen atom migrates below the molecule and shows a physisorption interaction with one of the surface carbon atoms (see Fig. 8.20 and 8.21 panel TS3).

Similar to triplet C_2H_2O isomers, singlet C_2H_2O isomers are obtained as physisorbed and remained at a distance of ~ 3.2 Å from the surface. Optimized structures on graphite and hexabenzocoronene corresponding to minima and transition states are shown in Fig. 8.20 and 8.21, respectively. On the graphite surface, the geometries are obtained generally with the C=C of acetylene parallel to a C-C bond of the surface. On the other hand, on the hexabenzocoronene surface, geometries are found either with the C=C bond of acetylene parallel to the surface C-C bond such as I1 and I2 or with one carbon atom at the top of a surface carbon atom and second carbon atom at the centre of the hexagonal ring such as I3 and I4. Interestingly, we were not able to locate the metastable isomers hydroxy-vinylidene and oxiranylidine on both hexabenzocoronene and graphite. Instead, these optimized into the more stable isomers ethynol and ketene, respectively. Structurally identical oxyacetylene, ketene, and ethynol are found on the surfaces as well as in the gas phase.

In general, we found that the isomers of singlet C_2H_2O are of lower in relative energy compared to triplet C_2H_2O isomers. The barriers to the interconversion of isomers are also higher for the triplet than for the singlet manifold. However, in terms of structure, all intermediate isomers on singlet and triplet surfaces are almost identical except for ketene and ethynol. In the singlet system, both carbon atoms of ethynol (I5) are *sp* hybridized, while in the triplet system, both carbon atoms are sp^2 hybridized in both gas phase and on the surface, as shown in Fig. 8.16 panel I5. The optimized ketene in the singlet system has *sp* and sp^2 hybridized carbon atoms, whereas, in the triplet system, both carbon atoms are found in the sp^2 hybridized state. Interestingly, the formation of ketene in the singlet system is thermodynamically more stable and kinetically faster than in the triplet system.



Figure 8.20: *Minimum energy optimized isomers and transition state structures obtained by the reaction of acetylene and oxygen atom on the graphite surface.*



Figure 8.21: Minimum energy optimized isomers and transition state structures obtained by the reaction of acetylene and singlet oxygen atom on hexabenzocoronene surface.

The energies obtained for the singlet transition states and the minimum energy isomers in the gas phase, on hexabenzocoronene, and on graphite surface relative to the C_2H_2+O (³P) by various methods are summarized in Table 8.4.

Table 8.4: Relative energy for the formation of different isomers by acetylene with a singlet oxygen atom in the gas phase, on hexabenzocoronene, and on graphite surface by using different methods.

-			He	ex	Graphite							
-	B3LYP	B3LYP	PBE	CCS	CCSD(T)		T-F12	CASPT2		B3LYP	PBE	PBE
Str	6-311G(d,p)	def2-TZVP	def2-TZVP	pVDZ	pVTZ	pVDZ	pVTZ	pVDZ	pVTZ	6-311G(d,p)	def2-TZVP	plane-wave
-	0.73	2.76	2.90	2.26	2.21	2.19	2.16	2.24	1.91	0.72	0.82	-
I1	-2.19	-2.27	-2.97	-1.83	-1.97	-2.11	-2.14	-1.41	-1.88	-2.36	-3.14	-3.74
TS1	-1.98	-2.14	-2.79	-0.82	-1.15	-1.29	-1.34	-0.71	-1.11	-2.15	-2.93	-3.5
I2	-2.19	-2.27	-2.97	-1.82	-1.974	-2.11	-2.14	-1.41	-1.88	-2.36	-3.14	-3.78
TS2	-1.99	-2.08	-2.53	-0.89	-1.15	-1.32	-1.36	-1.59	-1.86	-2.19	-2.69	-3.62
I3	-5.68	-5.71	-6.26	-5.17	-5.36	-5.48	-5.51	-5.02	-5.26	-5.76	-6.36	-6.72
TS3	-1.41	-1.46	-2.37	-0.82	-1.15	-1.29	-1.34	-1.67	-1.21	-1.69	-2.69	-2.39
I4	-4.04	-4.06	-4.56	-3.53	-3.88	-4.0	-4.05	-4.41	-3.81	-4.23	-4.78	-5.31
TS4	-1.99	-1.79	-2.47	-1.66	-1.69	-1.79	-1.81	-1.54	-1.54	-	-	-
15	-2.79	-2.84	-3.45	-2.6	-2.76	-2.85	-2.88	-2.33	-2.49	-	-	-
TS5	-0.47	-0.53	-1.37	-0.29	-0.47	-0.61	-0.64	-0.19	-0.45	-	-	-
16	-1.87	-1.94	-2.32	-1.56	-1.77	-1.89	-1.92	-1.38	-1.64			

Comparison of different methods for the isomerization of singlet C_2H_2O relative to the energy of isomer I1 is shown in Fig. 8.22. Similar to what we found before CCSD(T),

CCSD(T)-F12, and CASPT2 methods result give identical energies for the minima and transitions states but PBE/def2-TZVP method show underestimated energy barriers. Again the energies obtained using CCSD(T)-F12 and CASPT2 methods are in good agreement with the previous studies.



Figure 8.22: A comparison of different methods for the isomerization of singlet C_2H_2O in the gas phase.

Similar to Section 8.3.1 ethene we have performed semiclassical transition state theory calculations to study the rate of reaction within the temperature range of 10 K–100 K for the acetylene oxide isomerization for the singlet manifolds. The only reactions that have significant rates at low temperatures in the singlet manifold are I1–I2 (formation of oxyacetylene) and I2–I3 (oxyacetylene to ketene). The dependence of the rate constant and the corresponding energy barriers are shown in Fig. 8.23 panels A and B, respectively. I1–I2 involves the migration of the heavy oxygen atom instead of hydrogen migration in I2–I3. As a result for a similar barrier a significantly reduced rate is obtained in panel A1 compared to panel B1.



Figure 8.23: Thermal rate constants as a function of temperature for the reaction of acetylene with a singlet oxygen atom in the gas phase computed using TST and SCTST. Panels A1 and B1, the rate of transformation of I1–I2 and I2–I3, respectively (top). Panel A2 and B2, barriers for I1–I2 and I2–I3 transformation (bottom).

8.5 Reactions of atomic oxygen with propyne

Propyne is structurally similar to acetylene. In propyne, one carbon atom is sp^3 hybridized and the other two are sp hybridized. The gas phase reaction of atomic oxygen with propyne has been studied before theoretically and experimentally.^{356–358} A complicating factor for the reaction of oxygen with propyne is that there are two equivalent potential reaction sites for atomic oxygen. A general reaction mechanism for the addition of oxygen at the C1 and C2 sites is shown in Fig. 8.24 panels A and B, respectively. Previous studies reported that similar to ethylene and acetylene the addition of the electrophilic oxygen atom to the triple bond of propyne is initiated by a collision of ground-state triplet oxygen atoms. The addition of oxygen to the C1 site forms a bi-radical ketocarbene (see Fig. 8.24 panels A and B) as an intermediate product, a structure that exists on the singlet and triplet surface and where ISC needs to happen to allow progression on the singlet surface. Moreover, ketocarbene can favour the migration of a hydrogen atom via 1,2 or 3,2-H shifts. This then provides four major routes R1, R2, R3, and R4 for the formation of products. Within the ISM in high-temperature regions, C₃H₄O has been detected in the form of acrolein (H₂CCHCHO), which has an aldehyde functional form. However, acrolein exists in two forms syn and anti, but only anti-acrolein has been detected in the ISM so far. For the singlet system syn-acrolein and anti-acrolein are found as isoenergic. Even though singlet and triplet methylketene is found as the energetically more stable form,³⁷² it has not been identified in the ISM. Similarly, the addition of an oxygen atom to the C2 site also leads to the formation of ketocarbene (see Fig. 8.24 panel B) as an intermediate product. This can further undergo three different pathways R1, R2, and R3 to form either propenol, ketone, or ketene.

As both sites are important to study these reactions, both reaction pathways for the reaction of ground state triplet atomic oxygen with propyne need to be considered.



Figure 8.24: Reaction mechanism for the formation of methylketene, acrolein, c-ketone, and ethylene by addition reaction of atomic oxygen at C1 site of propyne (Panel A), for the formation of propenol, ketone, and ketene by addition reaction of atomic oxygen at C1 site of propyne (panel B).

8.5.1 Reaction of oxygen (³P) with propyne in the gas phase and on hexabenzocornoene

As discussed above the reaction between triplet oxygen atom and propyne can result in the addition of an oxygen atom to either carbon atom of the triple bond. Therefore, the potential energy surface for both reaction pathways was investigated.



Figure 8.25: *Minimum energy structure of ketocarbene obtained for the triplet and singlet system in panels A and B, respectively.*

The reaction of $O(^{3}P)$ at the C1 site of propyne leads to the formation of biradical ke-

tocarbene CH_3CCHO (I0) *via* an intermediate state TS0. Surprisingly, unlike ethylene and acetylene, ketocarbene is obtained as a minimum for both the singlet and triplet systems. The optimized geometry of triplet and singlet ketocarbene is shown in Fig. 8.25 panels A and B, respectively. However, due to the presence of strong C-C bonds in singlet ketocarbene this geometry is 0.23 eV lower in energy than the triplet ketocarbene.

The energy profile for the reaction of $O({}^{3}P)$ at the C1 site of propyne is shown in Fig 8.26, with green lines representing the gas phase and purple lines indicating the presence of hexabenzocoronene. The minimum energy and transition state structures obtained from the reaction of propyne with triplet oxygen at carbon atom C1 on hexabenzocoronene are displayed in Figure 8.27. Geometries obtained in the presence of the surface exhibit a similar structural arrangement to that in the gas phase.

The addition of atomic oxygen $({}^{3}P)$ to C1 results in the formation of ketocarbene (I0) via an intermediate state TS0. The formation of TS0 is found to be exothermic using PBE/def2-TZVP, similar to ethylene *i.e.*, as a submerged barrier. On the other hand, CCSD(T) and CASPT2 methods show it to be an endothermic step as shown by the blue line in Fig. 8.26, consistent with a previous study.³⁵⁸ This structure is not obtained in the presence of a surface. Ketocarbene can undergo isomerization via three different pathways. First, an exothermic transformation to methylketene I4 by 1,2-H shift via transition state TS4 with an energy barrier of 1.69 eV and 1.67 eV in the gas phase and on hexabenzocoronene, respectively. Second, an endothermic transformation to an alcoholic isomer I9 by migration of a hydrogen atom from the methyl group to the oxygen via transition state TS9 with an energy barrier of 1.45 eV and finally, isomerization of ketocarbene to syn-acrolein by 3,2-H shift via transition state TS3 with an energy barrier of 1.68 eV. Syn-acrolein (I3) can further rearrange to anti-acrolein I2 by rotation around the COH bond via transition state TS2 with an energy barrier of 0.53 eV in the gas phase and 0.49 eV on hexabenzocoronene. I2 can further transform into I1 via transition state TS1 by 2,3-H shift with a relatively higher energy barrier of 1.92 eV.

Isomer I4 which has a ketone functional group can undergo two further endothermic transformations, I4 to I7 or I4 to I5 by 3,2-H shift. Interestingly, depending upon the migrating hydrogen atom which can either rotate the CO group leading to the formation of I7 *via* transition state TS7 or without CO rotation which leads to the formation of I5 *via* transition state TS5, respectively. These can further transform into an aldehyde functional form *syn*-acrolein (I8) and *anti*-acrolein (I6), respectively by 2,1-H shift.

Minimum energy and transition state structures obtained on the hexabenzocoronene surface are shown in Fig. 8.27. Similar to ethylene and acetylene the optimized isomers of propyne oxide are obtained with one carbon atom at the top of a surface carbon atom and the other two carbon atoms either at the top of the surface atom or at the centre of the hexagonal ring. Similar to ethylene and acetylene, the presence of a surface affects the energy barriers and result in reduced energy barrier for some pathways.






Figure 8.27: Minimum energy optimized isomers and transition state structures obtained by the reaction of a triplet oxygen atom with carbon atom (C1) of propyne on hexabenzocoronene surface.

Table 8.5 summarizes the relative energies for these pathways obtained using various methods in both the gas phase and in the presence of hexabenzocoronene.

A comparison of different methods for the isomerization of C_3H_4O is shown in Fig. 8.28. The energy profiles for different methods are relative to the energy of isomer I1. As noted before PBE shows the underestimated barriers for these isomerization pathways, whereas the other three methods show identical energies for the minima and transition states. Comparing the relative energies with the previous studies as summarized in Table 8.5, CCSD(T)-F12 shows a close agreement.

-				Gas						He	ex	Gas
-	B3LYP	B3LYP	PBE	CCS	D(T)	CCSD)T-F12	CAS	SPT2	B3LYP	PBE	Other
Str	6-311G(d,p)	def2-TZVP	def2-TZVP	pVDZ	pVTZ	pVDZ	pVTZ	pVDZ	pVTZ	6-311G(d,p)	def2-TZVP	-
TS0	0.022	0.002	-0.10	0.17	0.12	0.09	0.09	0.15	0.19	-	-	0.23^{358}
IO	-2.39	-2.43	-2.76	-2.29	-2.33	-2.38	-2.40	-2.35	-2.42	-2.85	-3.42	$-2.09,^{358}-2.31^{357}$
I1	-2.29	-2.35	-2.67	-2.19	-2.23	-2.29	-2.31	-2.32	-2.44	-2.76	-3.35	-2.31^{357}
TS1	-0.29	-0.38	-0.92	-0.01	-0.14	-0.21	-0.24	-0.39	-0.49	-0.76	-1.59	
I2	-2.50	-2.57	-2.83	-2.33	-2.41	-2.47	-2.49	-2.49	-2.54	-2.99	-3.52	
TS2	-1.92	-1.99	-2.27	-1.82	-1.9	-1.96	-1.98	-2.03	-2.09	-2.36	-2.93	
I3	-2.49	-2.55	-2.80	-2.32	-2.40	-2.45	-2.66	-2.69	-2.66	-2.97	-3.42	-2.18 , ³⁵⁸ -2.46^{357}
TS3	-0.42	-0.5	-1.08	-0.11	-0.25	-0.34	-0.37	-0.37	-0.62	-0.88	-1.73	$-0.065,^{358}-0.47^{357}$
TS4	-0.45	-0.51	-1.07	-0.22	-0.29	-0.36	-0.39	-0.72	-0.73	-0.93	-1.75	-0.16^{358}
I4	-3.14	-3.16	-3.47	-2.99	-3.04	-3.10	-3.12	-3.18	-3.18	-3.59	-4.15	-2.79^{358}
TS5	-1.25	-1.32	-1.82	-0.99	-1.12	-1.20	-1.24	-1.35	-1.45	-1.71	-2.48	
15	-2.54	-2.54	-2.86	-2.49	-2.55	-2.6	-2.62	-2.65	-2.67	-3.0	-3.52	
TS6	-1.09	-1.16	-1.71	-0.75	-0.89	-0.97	-1	-1.24	-1.32	-1.55	-2.36	
I6	-2.25	-2.31	-2.61	-1.98	-2.07	-2.10	-2.13	-2.05	-2.13	-3.11	-3.86	
TS7	-1.26	-1.33	-1.83	-1.02	-1.15	-1.23	-1.27	-1.34	-1.67	-1.71	-2.48	-0.95^{358}
I7	-2.58	-2.62	-2.89	-2.54	-2.58	-2.63	-2.65	-2.70	-2.69	-3.04	-3.54	-2.4^{358}
TS8	-1.17	-1.23	-1.78	-0.85	-0.98	-1.06	-1.09	-1.34	-1.41	-1.67	-2.44	
18	-2.28	-2.34	-2.65	-2.01	-2.11	-2.16	-2.18	-2.12	-2.18	-2.97	-3.26	
TS9	-0.68	-0.73	-1.31	-0.41	-0.54	-0.59	-0.63	-0.81	-0.89	-1.14	-1.97	
10	-254	-2.09	-2.44	-1.68	-1.92	-2.0	-2.04	-1.94	-2.12	-2.49	-3.12	-1 99357

Table 8.5: Relative energy for the formation of different isomers by reaction of C1 carbon atom of propyne with a triplet oxygen atom in the gas phase and on hexabenzocoronene surface by using different methods.



Figure 8.28: A comparison of different methods for the isomerization of singlet C_3H_4O in the gas phase.

Semiclassical transition state calculation for the isomerization of triplet propylene oxide shows that only one reaction pathway I2–I3 (rotation around CHO bond) is feasible at a low-temperature region of the ISM. The dependence of this rate constant as well as the corresponding barrier is shown in Fig. 8.29. The transformation of I2 to I3 involves the rotation of a heavy oxygen atom in addition to a hydrogen atom. As a result lower rate is obtained in the presence of a lower energy barrier of ≈ 0.5 eV.



Figure 8.29: Thermal rate constants as a function of temperature for the reaction of triplet oxygen with carbon atom C1 of propyne in the gas phase computed using the SCTST. Panel A1 shows the rate of transformation of I2-I3 and the barrier for this transformation is shown in sub-panel A2.

Addition of oxygen atom to C2

For propyne, the oxygen atom can also react with C2 instead of C1. Fig. 8.30 illustrates the energy profile for these pathways in the gas phase and on hexabenzocoronene surface relative to C_3H_4+O (³*P*). Moreover, the optimized minimum energy isomers and transition state structures obtained by the reaction of propyne with triplet oxygen at carbon atom C2 on hexabenzocoronene surface are presented in Fig. 8.31. In both cases, we observed structurally similar isomers, where the C-C bond of the isomers is parallel to the C-C bond of the surface, ensuring their stability, as shown in Fig. 8.31. This behaviour is analogous to ethylene and acetylene.

When an oxygen atom is added to C2, it leads to the formation of ketocarbene I1 *via* intermediate state TS0, which was not found in the presence of hexabenzocoronene. The formation of TS0 in the gas phase is exothermic, with a loss of energy of 0.08 eV by DFT/PBE, while other methods show this as an endothermic step as shown by blue line



in Fig. 8.30 and consistent with a previous study.³⁵⁸

Figure 8.30: Schematic representation of the energy profile for the reaction of propyne carbon atom C2 with atomic oxygen $({}^{3}P)$ in the gas phase (shown by green lines) and on hexabenzocoronene (shown by purple lines). Relative energies (in eV) are computed relative to the collision geometry $O({}^{3}P) + C_{3}H_{4}$. All calculations are done with PBE/def2-TZVP.



Figure 8.31: Minimum energy isomers and transition state structures obtained by the reaction of triplet oxygen atom with C2 carbon atom of propyne on hexabenzocoronene surface.

Ketocarbene (I1) can then follow two pathways: exothermic and endothermic, to form isomers I4 and I2, respectively. Through an endothermic step, I1 can transform into propenol by migration of hydrogen from C3 to oxygen *via* transition state TS1, forming a three-membered ring with energy barriers of 2.40 eV and 2.45 eV in the gas phase and in the presence of hexabenzocoronene, respectively. In contrast, through exothermic pathways, I1 can isomerize into the more stable ketone form I4 by 3,1-H shift *via* transition state TS5, with lower energy barriers of 1.56 eV and 1.54 eV in the gas phase and in the presence of hexabenzocoronene, respectively. Another form of propenol (I3) with identical energy of I2 is also found, which can be formed from I2 through a 3,1-H shift *via* transition state TS2, which can further undergo an exothermic step to form again isomer I4 by migration of hydrogen atom from oxygen to C3 site, forming a three-membered ring, as shown in transition state TS3 with an energy barrier of ≈ 1.3 eV in both gas phase and on hexabenzocoronene. Moreover, I4 can also be formed by the reaction of ketene and methylene (CH₂), I5 via transition state TS4 with a lower energy barrier of 0.07 eV in both gas phase and on hexabenzocoronene surface. This is an exothermic step and the barrier can be easily overcome at low temperatures. On the other hand, in the presence of hexabenzocoronene reduced energy barriers are obtained particularly for the reaction pathways I1–I4, I3–I4, and I4–I5.

The relative energies obtained for these pathways using different methods in the gas phase and on hexabenzocoronene are summarized in Table 8.6.

Table 8.6: Relative energy for the formation of different isomers by reaction of C2 carbon atom of propyne with a triplet oxygen atom in the gas phase and on hexabenzocoronene surface by using different methods.

-				Gas						He	ex	Gas
-	B3LYP	B3LYP	PBE	CCS	D(T)	CCSD	T-F12	CAS	SPT2	B3LYP	PBE	other
Str	6-311G(d,p)	def2-TZVP	def2-TZVP	pVDZ	pVTZ	pVDZ	pVTZ	pVDZ	pVTZ	6-311G(d,p)	def2-TZVP	-
TS0	0.06	0.05	-0.08	0.22	0.17	0.14	0.14	0.20	0.18	-	-	0.29^{358}
I1	-2.29	-2.32	-2.65	-2.28	-2.30	-2.35	-2.37	-2.34	-2.46	-2.75	-3.31	-2.29 , $^{357}-2.09^{358}$
TS1	0.36	0.28	-0.25	0.57	0.41	0.35	0.32	0.14	-0.03	0.05	-0.86	0.59^{358}
I2	-1.77	-1.84	-2.12	-1.66	-1.83	-1.91	-1.93	-1.88	-2.0	-2.27	-2.74	-1.53^{358}
TS2	0.18	0.12	-0.39	0.30	0.13	0.06	0.03	-0.05	-0.19	-0.31	-1.08	-1.46^{358}
I3	-1.85	-1.88	-2.16	-1.71	-1.85	-1.93	-1.95	-1.94	-2.02	-2.34	-2.84	-1.54^{358}
TS3	-0.24	-0.32	-0.87	0.02	0.14	-0.20	-0.23	-0.47	-0.63	-0.72	-1.54	0.05^{358}
I4	-2.90	-2.95	-3.12	-2.74	-2.81	-2.86	-2.89	-2.88	-3.22	-3.39	-3.82	-2.57^{358}
TS4	-0.57	-0.61	-0.93	-0.39	-0.47	-0.50	-0.52	-0.66	-0.69	-1.02	-1.60	-0.42^{358}
15	-0.76	-0.79	-1.0	-0.77	-0.80	-0.82	-0.83	-0.95	-0.96	-1.22	-1.68	-0.85^{358}
TS5	-0.53	-0.57	-1.09	-0.40	-0.45	-0.49	-0.52	-0.71	-0.73	-0.99	-1.77	-0.35^{358}



Figure 8.32: A comparison of different methods for the isomerization of triplet C_3H_4O in the gas phase.

The energy profile for the comparison of four different methods performed for the isomerization of triplet C_3H_4O relative to the energy of isomer ketocarbene (I1) is shown in Fig. 8.32. We found that except PBE/def2-TZVP, all other three methods show similar energies for the minima and barriers for the isomerization as before. Similar to what we have found before, PBE/def2-TZVP underestimates energy barriers. Hereby, the results obtained by CCSD(T) and CASPT2 methods are again obtained in agreement with previous studies as reported in Table 8.6.

Semiclassical transition state calculations for the isomerization of triplet propylene oxide show that only one reaction pathway I5–I6 (addition reaction of CH₂ to ketene) is feasible at a low-temperature region of ISM. The dependence of this rate constant as well as the corresponding barrier is shown in Fig. 8.33 panels A1 and A2, respectively. The transformation of I5 to I4 involves the addition of a heavy CH₂ group to ketene. As a result lower rate of $\approx 10^{-7}$ s⁻¹ is obtained in the presence of a lower energy barrier of ~ 0.07 eV.



Figure 8.33: Thermal rate constants as a function of temperature for the reaction of triplet oxygen with carbon atom C2 of propyne in the gas phase computed using the SCTST. Panels A1 and A2 show the rate of transformation of I5-I4 and the barrier for this transformation.

8.5.2 Reaction of oxygen (¹D) with propyne in the gas phase, on hexabenzocoronene, and on graphite

The energy profile for the propyne + $O(^{1}D)$ reaction for the gas phase and on the dust analogues is shown in Fig. 8.34. Additionally, the minimum energy isomers and transition state geometries on hexabenzocoronene and graphite surfaces are shown in Fig. 8.35 and 8.36, respectively. As discussed in the reaction mechanism, various intermediate isomers can be accessed *via* the migration of a hydrogen atom from C1 to C2, and from C3 to C1 and C2. In the singlet system, at the first step, two transformations were found from ketocarbene (I0).

First, metastable ketocarbene (I0) can transform into a more stable isomer, methylketene (I4) by 1,2-H shift via transition state TS4 with a barrier of 0.2 eV in the gas phase. This energy barrier reduces to 0.11 eV in the presence of hexabenzocoronene but increases to 0.45 eV in the presence of a graphite surface. Methylketne (I4) obtained in the previous step can further isomerize in three different ways by the migration of a hydrogen atom from the methyl group: (i) cyclization of I4 to cyclic ketone I3 by 3,2-H shift via transition state TS3, (ii) dissociation to C_2H_4 + CO (I8) by 3,2-H shift via transition state TS11, (iii) formation of *anti*-acrolein (I6) by 3,1-H shift via transition state TS9 and also rotate the CO bond. For all these reactions compared to the gas phase, a significantly reduced energy barrier is obtained in the presence of surface, in particular on hexabenzocoronene surface. The cyclic ketone I3 obtained by the first pathway can further transform into a cyclopropenol form I2 via transition state TS2 by migration of a hydrogen atom from C1 to the oxygen. This is required to overcome a higher energy barrier of ~ 3.5 eV in the gas phase and on dust analogues. This can further transform into another form of cyclopropenol (I1) by rotation of the OH bond. Again, a lower energy barrier is obtained for the transformation of I2 to I1 in the presence of a surface in comparison to the gas phase.

Secondly, I0 can also isomerize via a different route. For this pathway, I0 can transform into syn-acrolein (I5) by 3.2-H shift via transition state TS5 with an energy barrier of 0.35 eV, 0.27 eV, and 0.45 eV in the gas phase, in the presence of hexabenzocoronene, and graphite surface, respectively. Further rearrangement of syn to anti-acrolein isomer (I6) can take place via transition state TS6 by rotation of the HCO bond. This requires overcoming an energy barrier of 0.28 eV in the gas phase. On the surface, we found the rotation of this CHO bond via interaction of hydrogen with the surface. This results in an increase in energy barrier to 0.3 eV and 0.35 eV in the presence of hexabenzocoronene and graphite surfaces, respectively. This aldehyde functional isomer I6 can also lead to the formation of a higher energy isomer I7 by migration of hydrogen from C1 to oxygen and transforming into an alcoholic form (I7) with a relatively higher energy barrier of more than 3 eV. Again in comparison to the gas phase, a reduced energy barrier is obtained in the presence of the surface. In another pathway, I5 can also dissociate to C_2H_4+CO (I8) via transition state TS10 with a higher energy barrier of ~ 3.5 eV in all three cases. As reported in the literature only *anti*-acrolein has been detected in the ISM so far. We found that in the triplet manifold methyleketene is energetically more stable than syn and anti-acrolein. On the other hand, in the singlet manifold within the gas phase again formation of methylketene is more favourable than the formation of acrolein, but on the surface, acrolein is found to energetically more favourable than the methyleketene. However, formation of acrolein from ketocarbene requires overcoming a higher energy barrier ($\approx 0.35 \text{ eV}$) in comparison to methylketene ($\approx 0.2 \text{ eV}$).







Figure 8.35: Minimum energy isomers and transition state structures obtained by the reaction of propyne and singlet oxygen atom on hexabenzocoronene surface.



Figure 8.36: Minimum energy isomers and transition state structure obtained by the reaction of propyne with an oxygen atom on the bi-layer graphene surface.

Similar to ethylene, acetylene and triplet propyne the minimum energy structures of C_3H_4O are optimized with one carbon atom at the top of the hexabenzocoronene surface and with other two either at the top of the surface carbon atom or at the centre of the hexagonal ring. On the other hand optimization of isomers of C_3H_4O also follows the same pattern as obtained in the case of ethylene and acetylene. Thus, the C=C bond of C_3H_4O is found parallel to one of the C-C bonds of graphene. In general, identical geometrical structures are obtained for the minima in the gas phase and on the dust analogues.

The relative energy obtained by different methods for the formation of minimum energy isomers and the transition states by the reaction of propyne with singlet oxygen in the gas phase and also in the presence of hexabenzocoronene and graphite surfaces are summarized in Table 8.7. These show the formation of methylketene in the gas phase as an energetically more stable isomer in comparison to others, which agrees with the previous studis.^{356,372} Our study found that in the presence of hexabenzocoronene and graphite surface, *anti*-acrolein is found as energetically more favourable than methylketene as reported in Table 8.7.

Table 8.7: Relative energy for the formation of different isomers by the reaction of atomic oxygen $({}^{1}D)$ with propyne.

-	Gas							Hex		Graphite	Gas		
-	B3LYP	PBE	B3LYP	CCS	D(T)	CCSI	DT-F12	CAS	PT2	B3LYP	PBE	PBE	other
Str	6-311G(d,p)	def2-TZVP	def2-TZVP	pVDZ	pVTZ	pVDZ	pVTZ	pVDZ	pVTZ	6-311G(d,p)	def2-TZVP	plane-wave	-
-	2.89	2.6	2.90	2.20	2.1	2.11	2.07	3	3.07	2.56	2.0	0	
TS0	1.12	1.08	2.29	2.12	1.12	0.98	0.97	1.89	1.74	-	-	-	
IO	-2.09	-2.66	-2.18	-1.89	-2.06	-2.17	-2.19	-1.43	-1.68	-2.57	-3.28	-3.09	-2.18^{357}
I1	-3.06	-3.61	-3.12	-2.94	-3.23	-3.33	-3.37	-3.10	-3.31	-3.54	-4.29	-3.81	-2.28^{357}
TS1	-2.81	-3.34	-2.87	-2.68	-3.0	-3.11	-3.15	-2.87	-3.08	-3.35	-4.10	-3.62	-1.91^{357}
I2	3.06	-3.61	-3.11	-2.92	-3.23	-3.33	-3.37	-3.10	-3.31	-3.52	-4.27	-3.88	-2.27^{357}
TS2	-0.17	-1.14	-0.26	0.01	-0.31	-0.42	-0.46	-0.14	-0.36	-0.60	-1.76	-1.41	
I3	-4.13	-4.64	-4.17	-4.05	-4.23	-4.31	-4.34	-4.22	-4.33	-4.56	-5.28	-4.79	-2.27^{357}
TS3	-1.75	-2.41	-1.82	-1.61	-1.81	-1.89	-1.94	-1.84	-1.95	-2.21	-3.03	-2.77	
I4	-5.12	-5.48	-5.14	-4.96	-5.11	-5.19	-5.21	-5.26	-5.32	-5.54	-5.98	-5.58	-5.10^{357}
TS4	-2.06	-2.46	-2.15	-1.83	-2.0	-2.11	-2.14	-1.83	-2.02	-2.56	-3.17	-2.64	-2.19^{357}
TS5	-1.78	-2.31	-1.89	-1.63	-1.82	-1.94	-1.97	-1.42	-1.54	-2.25	-3.01	-2.53	-2.10^{357}
15	-4.96	-5.25	-5.0	-4.93	-5.05	-5.13	-5.16	-4.96	-5.09	-5.44	-5.93	-5.6	-5.13^{357}
TS6	-4.64	-4.97	-4.72	-4.63	-4.8	-4.89	-4.91	-4.77	-4.86	-5.08	-5.60	-5.20	
I6	-5.03	-5.35	-5.09	-4.98	-5.13	-5.22	-5.20	-5.0	-5.18	-5.51	-6.02	-5.63	
TS7	-1.39	-1.98	-1.48	-1.33	-1.54	-1.63	-1.66	-1.55	-1.70	-1.87	-2.59	-2.39	
17	-2.84	-3.11	-2.90	-2.79	-2.99	-3.08	-3.11	-2.91	-3.05	-3.29	-3.76	-3.55	
TS8	-1.38	-2.14	-1.45	-1.97	-1.99	-2.09	-2.08	-2.52	-2.55	-2.99	-3.17	-2.29	
TS9	-1.88	-2.59	-1.93	-1.71	-1.85	-1.93	-1.96	-1.97	-2.03	-1.61, -1.66	-2.54, -2.60	-2.97	
TS10	-1.36	-1.75	-1.25	-1.06	-2.29	-1.29	-1.31	-1.28	-1.36	-1.71	-2.43	-1.99	
TS11	-1.52	-2.29	-1.55	-1.50	-1.61	-1.69	4 - 1.72	-1.92	-1.98	-1.96	-2.95	-1.20	-1.88^{357}
18	-4.77	-4.79	-4.79	-4.98	-5.05	-5.14	-5.16	-5.02	-5.12	-5.21	5.5	-4.97	-5.12^{357}

The energy profile for the comparison of four different methods used for the isomerization of singlet C_3H_4O relative to the energy of isomer ketocarbene (I1) is shown in Fig. 8.37. As before all four methods show a similar relative energy for the minima I2, I3, and I4 and transition state TS1. Whereas PBE/defe2-TZVP shows a slight variation in energy for others as shown in Fig. 8.37. However, comparing the relative energies for the minima and transition states obtained by these methods with the literature as summarized in Table 8.7 is in good agreement with CCSD(T)-F12.



Figure 8.37: A comparison of different methods for the isomerization of singlet C_3H_4O in the gas phase.

Semiclassical transition state calculations for the singlet propylene oxide isomerization result in four possible reaction pathways at astronomically low temperatures. These are reaction pathways I1–I2 (rotation of OH in cyclopropenol) and I5–I6 (syn to anti-acrolein). The transformation of I1–I2 involves the rotation of only hydrogen atom around oxygen via energy barrier of 0.2 eV and results in the rate of 10^{-15} s⁻¹. On the other hand, the transformation of I5–I6 involves the rotation of a heavy oxygen atom in addition to hydrogen. As a consequence, a slight increase in energy barrier of ~0.3 eV reduces the rate of reaction significantly as shown in panel B. On the other hand, reaction pathways I0–I4 and I0–I5 are obtained by migration of hydrogen atoms and result in the transformation of ketocarbene to methylketene and acrolein, respectively. The presence of lower energy barriers results in the rate of ~ 10^0 s⁻¹ for both reaction pathways. This suggests that tunnelling is crucial for the formation of lower-energy acrolein rather than methylketene in low-temperature regions.



Figure 8.38: Thermal rate constant as a function of temperature for the reaction of a singlet oxygen atom with carbon atom C1 of propyne in the gas phase computed using TST and SCTST. Panels A1 to D1 are rate of transformation of I1-I2, I5-I6, I0-I4, and I0-I5 (top). Panels A2 to D2 are the barrier for these transformations (bottom).

8.5.3 Conclusion

In this chapter, we have investigated the reactions and isomerizations of ethylene, acetylene, and propyne with atomic oxygen in both the gas phase and on dust analogues. The energy profile obtained for these isomerizations in the gas phase aligns with previous studies. We have identified all the isomers discussed in the previous studies and have additionally discovered some other isomers.

Various methods were employed to study these reactions, and all of them yielded a similar isomerization pattern. The results from CCSD(T)-F12 and CASPT2 in the gas phase are consistent with the previous studies conducted at the same level. Similar to previous research, the reaction of ethylene, acetylene, and propyne with an oxygen atom initiates through the collision of a ground-state triplet oxygen atom with the double or triple-bonded carbon atoms. This collision forms biradical intermediate isomers-oxirane, oxirene, and ketocarbene for ethylene, acetylene, and propyne, respectively. These biradical intermediates play a crucial role in inter-system crossing. Subsequently, the reaction can proceed further on the singlet manifold. Generally, on the triplet manifold, higher-energy isomers are obtained, and the isomerization occurs *via* higher energy barriers compared to the singlet manifold. Additionally, the energy profile obtained in the gas phase and on the dust analogues shows a similar pattern for the isomerization.

In some pathways, we have observed the influence of surfaces, leading to lower energy barriers. Specifically, in the case of C_3H_4O , triplet methylketene is found to be energetically stable in the gas phase and on the hexabenzocoronene surface, compared to acrolein. However, on the graphite surface, *anti*-acrolein is found to be energetically more stable than methylketene. Although acrolein is formed from ketocarbene *via* a higher energy barrier, hydrogen atom tunneling can play a significant role in this process. These findings suggest a route for the formation of *anti*-acrolein in comparison to methylketene, which is not discussed in the literature.

In addition to isomerization, we have also identified some dissociation pathways, where energetically stable isomers break into higher energy fragments. This occurs particularly in the cases of C_2H_4O and C_3H_4O . In C_2H_4O , the dissociation of triplet oxirane and acetaldehyde leads to the formation of CH_2+CH_2O , CH_2CHO+H , and CH_3+HCO , respectively. The energetic values for the formation of these species align perfectly with previous experimental and theoretical studies. On the other hand, singlet acetaldehyde leads to the formation of CH_4+CO . In C_3H_4O singlet methylketene transforms into ethylene and CO, and the triplet isomer propeneone transforms into ketene and methylene fragments. Furthermore, these dissociation processes are endothermic and require overcoming higher energy barriers. This indicates that at higher temperature regions, these complex organic molecules may dissociate into higher energy simple molecules, which can adsorb and react with other species on the surface, leading to the formation of further complex organic molecules.

Chapter 9

Conclusion and future work

At the beginning of this project, our main goal was to explore how dust grain surfaces contribute to the formation of small organic molecules from atomic species on dust grains in the interstellar medium. Specifically, we focused on understanding the behavior of H, C, O, and N in this context.

The first results chapter, Chapter 4, presents the chosen methodology and investigates the adsorption of gaseous H, C, O, and N on different sites of carbonaceous grain mimics, which include coronene, graphene, and bi-layer graphite. Our findings indicate that hydrogen and nitrogen undergo activated adsorption, while carbon and oxygen undergo barrierless adsorption. This allowed us to identify the most favorable adsorption sites for these elements on the dust grain analogues.

In Chapter 5, we delve into the adsorption and desorption of hydrogen atoms and molecules on the surface of substituted graphite. Here, one of H, O, N, Fe, Si, or Mg replaces a carbon atom in the graphite surface. We optimized these substitutions either in the puckered-up or puckered-down state, especially for Si, Fe, and Mg. Our study reveals that substituting Si, Fe, and Mg in the puckered-down state leads to higher binding energy compared to the puckered-up state. This is explained through the observation these substitutions create active sites on the graphitic surface, resulting in the adsorption of atomic hydrogen with a lower energy barrier. Additionally, there is barrierless adsorption for the H, O, Fe (puckered-up) and Si (puckered-up) substituted graphite surfaces.

We also considered the adsorption of a second hydrogen atom. Here, we find that either two hydrogen atoms adsorb on the substituted graphite surface, or both hydrogen atoms desorb as an H_2 molecule. However, we have only considered the lower energy initial geometries for the adsorption of the second hydrogen atom (i.e., Fe, Si, and Mg in the puckered-down state). To obtain a more complete understanding of the double hydrogenation step, further investigation into the reaction of the second hydrogen atom in the case of the puckered-up geometries is needed.

Chapter 6 focuses on the formation of H_2O clusters on graphite. Formation of a single water molecule on pristine graphite is found to be a non-activated process. The binding energy was found to be site-independent but orientation dependent. However, when multiple water molecules form, the interactions are stronger between the water molecules themselves rather than with the graphite surface. As a result, the adsorption of multiple water molecules on graphite yields lower binding energy. Moreover, the process of forming more than one water molecule from multiple adsorbed oxygen atoms on the graphite surface is found to contain endothermic steps. Thus, instead of forming a water cluster on the graphite surface, the reaction could reach a point where it stops, resulting in the formation of a single water molecule in the presence of epoxide or hydroxyl groups.

This chapter also examines the impact of defects (Fe and Si) on the adsorption and formation of a water dimer. The sequential hydrogenation of *meta* and *para* dioxide on an Fe and Si substituted graphite surface results in the formation of a water dimer with higher binding energy compared to the pristine graphite surface. However, similar to pristine graphite, the formation of a water dimer on the substituted graphite surface also contains endothermic steps.

Thus, in contrast to pristine graphite, the reaction on the substituted surface could lead to the formation of either a hydroxyl group in the presence of an epoxide group or 2 hydroxyl groups instead of a water molecule. Nevertheless, to gain a complete understanding of the entire mechanism for the formation of water dimers in the presence of defects, a full potential energy profile is necessary.

Chapter 7 of the study is dedicated to investigating the formation of NH_3 on both pristine graphite and in the presence of O, OH, and H_2O . The study reveals that the adsorption of a nitrogen atom on a graphite surface is activated, while the subsequent steps for the formation of the NH_3 molecule are barrierless. Ammonia physisorbs on the graphite surface, with a site-independent, but orientation-dependent binding energy. Interestingly, the presence of O and OH functional groups on the graphite surface promotes the adsorption of NH_3 and enhances binding with the surface. However, the bonding energy of ammonia is reduced in the presence of a water molecule.

The results in this chapter further show that the formation of ammonia through successive hydrogenation of atomic nitrogen in the presence of O, OH, and H_2O has endothermic steps. As a result, the reaction for the formation of ammonia could halt at that endothermic step, leading to the formation of either NH in the presence of O, or H_2O or NH_2 in the presence of OH. Once again, a comprehensive potential energy profile is necessary to gain a complete understanding of the process.

In Chapter 8, we consider the reaction of ethylene, acetylene, and propyne molecules with oxygen atoms in both the gas phase and on dust analogues (hexabenzocoronene and graphite). If these reactions commence with the collision of a triplet oxygen atom with ethylene, alkene, or alkyne then they lead to the formation of intermediate isomers that further evolve on the singlet or triplet manifolds. Interestingly, we observe similar patterns in these energy profiles within the gas phase and on both surfaces. However, certain reaction pathways show a reduced energy barrier in the presence of surfaces compared to the gas phase. Additionally, we find that at low temperatures, hydrogen atom tunneling plays a crucial role in the isomerization process. However, our study on the rate of reactions was limited to the gas phase, and a comprehensive understanding of the reaction rates on dust analogues is still necessary.

Apart from isomerization, we also identify dissociation pathways where the resulting fragments exist in the form of neutrals or radicals. These fragments can either adsorb onto the surface and participate in subsequent reactions or be released as gas. While our primary focus in this work was on isomerization pathways rather than dissociation, understanding pathways, particularly on the grain surface, remains a topic that requires further investigation.

There is a continued need in astrochemistry to expand the available reaction information, whether through theoretical, experimental, or observational means, especially concerning gas-dust interactions. This study has focussed on several outstanding issues, such as the adsorption of atoms on grain surfaces, the reactivity of surface species, and the role of defects in adsorption modulation.

Chapter 10

Appendix

10.1 VASP input files

10.1.1 For geometry optimization

INCAR

SYSTEM=optimization ALGO=Fast #elecronic minimisation algorithm ISMEAR=0 #Gaussian smearing, to specify the partial occupancies for each orbital SIGMA=0.05 #width of smearing in eV LCHARG=.FALSE. #to generate CHGCAR file ISYM=2#turn on symmetry LREAL=AUTO #projection done in real space, fully automatic optimization of projection operators ISPIN=2#spin-polarized calculations NSW = 150#number of ionic steps IBRION =2#ionic relaxation with conjugate gradient algorithm LPLANE=.TRUE. #switches on the plane-wise data distribution in real space NPAR=2#number of cores #number of bands that are optimized simultaneously NSIM=4ISTART=0 #start from initial NELM = 200#electronic self-consistency step GGA=PE #exchange-correlational functional IVDW=12 #van der Waals interaction LWAVE=.FALSE. #do not generate WAVECAR file ENCUT=850 #cut-off energy for the plane-wave basis set in eV **PREC**=Accurate #precision mode EDIFF=1E-6 #global break condition for the electronic SC-loop EDIFFG=0.01 # break condition for the ionic relaxation loop

KPOINTS

Automatic mesh

0	! number of k-points automatic generation scheme
Gamma	! select Monkhorst-Pack (first letter is significant)
$6\ 6\ 1$! size of mesh (1x1x1 points along b1, b2, b3)

0. 0. 0. ! shift of the k-mesh

10.1.2 For transition state calculation

INCAR

```
SYSTEM=NEB-CALC
ALGO=Normal
             # Gaussian smearing, det. partial occupancies
ISMEAR=0
SIGMA = 0.05
LCHARG=.FALSE.
ISIF=2
ISYM=0
           # switch on symmetry
GGA=PE
ISTART=0
ICHARG=2
ISPIN=2
           \# disabled vasp default optimiser
NSW = 2500
IBRION=3
LPLANE=.TRUE.
MAXMOVE=0.2
NSIM=4
NELM = 650
ICHAIN=0
             # METHOD TO RUN NEB (ICHAIN=)
EDIFF=1E-6
              # ELECTRONIC CONVERGENCE
EDIFFG = -0.03
                \# \max forces
IMAGES=5
             # 5 INTERMEDIATE GEOMETRIES
             # SPRING CONSTANT
SPRING=-5
ENCUT=400
IVDW = 12
LCLIMB=.TRUE.
IOPT=3
POTIM=0
PREC=ACCURATE
LWAVE=.FALSE.
```

10.2 Molpro input file

```
***,CH3CHO CASSCF/cc-pvdz
memory,450,m
basis = default, vtz
!symmetry,nosym
geomtyp=xyz
angstrom
geom={
5
oh-rotate-final
С
    -0.23501
               1.34119
                        -0.12949
С
     0.38936 0.08639
                        -0.24567
```

Η	-0.96971	-0.74772	0.72221
Η	1.32857	-0.13989	-0.75355
0	-0.13856	-1.01756	0.28724
}			
set,	charge=0		
spin	n=2		
hf;v	vf,22,1,2		
ucc	$\rm sd(t)$		

10.3 IRC calculation



Figure 10.1: IRC calculation showing the confirmation of transition state of the singlet vinyl alcohol and acetaldehyde .

(A)

10.4 Charge density of substituted atom in graphite surface

Figure 10.2: Charge density obtained by substitution of (A) hydrogen, (B) nitrogen, (C) oxygen, (D) iron, (E) silicon, and (F) magnesium atom in graphite surface.

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