

# **First principles investigation of $\text{Ti}_2\text{C}$ MXene as catalyst and support in $\text{CO}_2$ activation and CO oxidation reactions**

A  
thesis submitted  
in partial fulfillment of the requirements for the degree of

**DOCTOR OF PHILOSOPHY**

by

**Aswathi Mohan T**

**Roll No.: 20163472**



**Indian Institute of Science Education and Research, Pune  
Pune 411008, Maharashtra, India**

**2023**

## Certificate

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Certified that the work incorporated in the thesis entitled “**First principles investigation of  $\text{Ti}_2\text{C}$  MXene as catalyst and support in  $\text{CO}_2$  activation and CO oxidation reactions**” submitted by **Aswathi Mohan T** was carried out by the candidate, under my supervision. The work presented here or any part of it has not been included in any other thesis submitted previously for the award of any degree or diploma from any other University or institution.



Date: 01-03-2023

(Dr. Prasenjit Ghosh)  
Thesis supervisor



## Declaration

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I declare that this thesis titled, **“First principles investigation of  $\text{Ti}_2\text{C}$  MXene as catalyst and support in  $\text{CO}_2$  activation and CO oxidation reactions”**, represents my ideas in my own words and where other’s ideas have been included, I have adequately cited and referenced the original sources. I also declare that I have adhered to all principles of academic honesty and integrity and have not misrepresented or fabricated or falsified any idea/data/fact/source in my submission. I understand that violation of the above will be cause for disciplinary action by the Institute and can also evoke penal action from the sources which have thus not been properly cited or from whom proper permission has not been taken when needed.



Aswathi Mohan T  
Roll No. 20163472  
Date: 01-03-2023

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*To my constants, amma and ettan*

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## List of Publications

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### Published

- Aswathi Mohan T, Nishamol Kuriakose, Krishnakanta Mondal, and Prasenjit Ghosh, “CO<sub>2</sub> capture, activation and dissociation on the Ti<sub>2</sub>C surface and Ti<sub>2</sub>C MXene: the role of surface structure”, *Physical Chemistry Chemical Physics*, **22(26)**, 14599-14612 (2020). (Chapter 4)
- Nishamol Kuriakose, Aswathi Mohan T, and Prasenjit Ghosh, “Coverage dependent CO<sub>2</sub> activation on Ti<sub>2</sub>C (111) surface: Effect of intrinsic subsurface Carbon vacancies.”, *Surface Science*, **706**, 121798 (2021). (Chapter 4)
- Aswathi Mohan T and Prasenjit Ghosh, “A low cost bimetallic AuCu<sub>3</sub> tetramer on Ti<sub>2</sub>CO<sub>2</sub> MXene as an efficient catalyst for CO oxidation: a theoretical prediction”, *Physical Chemistry Chemical Physics*, **24(32)**, 19512-19520 (2022). (Chapter 5)

## Synopsis

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Ever since its discovery a decade ago, MXenes have caused a stir in the realm of two-dimensional materials owing to their diverse compositions and countless applications. Broadly, the composition of this class is transition metal carbides, nitrides, or carbonitrides with additional flexibility offered in terms of the number of layers, terminations, etc, thus taking the number of members to practically infinite. The synthesis of these materials can be done either top-down route by chemical etching of A layer from the respective MAX parent phase, which invariably leads to surface terminations. A bottom-up approach through chemical vapor deposition (CVD) is also reported and this empowers us to use bare MXenes possessing several intriguing properties. They have been employed in fields ranging from energy storage, implantable devices, and spintronics to environmental remediation. The latter application was originally motivated by the indisputable role of transition metal carbides (TMCs) as catalysts in the area. This, in addition to having a higher surface-to-volume ratio, has made MXenes a popular choice (both as support and catalyst) in the field of heterogeneous catalysis, especially for environmental remediation. This constitutes the backdrop of this thesis, where we have investigated the performance of these novel catalysts for some environmentally relevant processes.

To design effective catalysts, it is pertinent to have an understanding of the reaction mechanisms and intermediates associated with the process. Computational techniques are commonly used as a complementary tool to gain better insight into the thermodynamic and kinetic aspects of heterogeneous catalysis. The processes we are interested in belong to the class of thermally activated processes, often referred to as rare events because of the large time intervals in between the transitions. This makes it inaccessible by molecular dynamics, hence we have explored the potential energy surface via elastic methods. Further, for an accurate description of the electrons, quantum chemical technique called density functional theory (DFT) is used, which provides a fine balance between computational cost and accuracy.

The thesis is divided into six chapters.

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**Chapter 1** briefly introduces the system we have studied throughout the thesis, MXenes. We look into the features that make it a unique member among the two-dimensional materials. The synthesis strategies used in the literature and the applications derived are discussed in detail. Additionally, we draw the origin and relevance of the bulk TMCs in the domain of heterogeneous catalysis. Further, we discuss the issues associated with computational methods used for studying heterogeneous catalysis. A brief account of the following chapters is also included.

The computational techniques encountered in our work are detailed in **chapter 2**. This includes Born-Oppenheimer approximation, the basis of density functional theory i.e., Kohn Sham equations, and exchange-correlation functional. Additionally, we have also glanced upon the theory of periodic supercells, and pseudopotential. Calculation of forces by Hellmann-Feynman theorem and deducing minimum energy paths via climbing image nudged elastic band (CI-NEB) are discussed in detail too.

In transition metal dichalcogenides (TMDs), the phases that merely differ in stacking of the atomic layers, 1T and 2H, are extensively studied, and so is the transition from one phase to another. This leads to a metal to insulator transition in group VI TMDs. Motivated by this, in the first work chapter of the thesis (**chapter 3**), we explored the plausibility of a structural phase transition from the most stable 1T to 1H phase of  $\text{Ti}_2\text{C}$  MXene. We have examined the structural, electronic, and magnetic properties of the most stable 1T phase of  $\text{Ti}_2\text{C}$  MXene along with a newly predicted metastable 1H phase. We also put forward the phase transition mechanism involving a barrier of 1.48 eV as the Ti-C-Ti stacking changes from ABC (1T) to ABA (1H). As a consequence of this phase transition, we find that while the 1T phase is an antiferromagnetic semiconductor, the metastable 1H phase is a ferromagnetic half metal. Monte Carlo simulations confirm that the magnetism is maintained well above room temperature.

$\text{CO}_2$  capture and utilization is a relevant technique to reduce the atmospheric  $\text{CO}_2$ . Direct dissociation of  $\text{CO}_2$  is one of the possible pathways and also the first step in redox pathway of reverse water gas shift reaction. The most difficult step in here is the activation of  $\text{CO}_2$  where the substrate transfers electrons to  $\text{CO}_2$  and make the structure bent. Bulk transition metal carbides (TMCs) have displayed good activity in this aspect with the stoichiometry, composition, etc having a profound effect. This sparked our interest in studying the same on  $\text{Ti}_2\text{C}$  MXene and  $\text{Ti}_2\text{C}\{100\}$  surface, enabling us to comprehend the impact of surface structure in the reaction steps, in **chapter 4**. Our studies indicate barrierless chemisorption for  $\text{CO}_2$  for both cases. MXene exhibit a lower activation energy

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for dissociation compared to the  $\{100\}$  surface, ascribed to a weaker  $\text{CO}_2$  binding on the former. As the coverage increases,  $\text{CO}_2$  molecules form clusters around C-vacancies present in the  $\{100\}$  surface while there is a uniform distribution on MXene.

CO is extremely poisonous once released into the environment, and its oxidation is the most simple and effective way to convert CO to  $\text{CO}_2$ . This, apart from being a model reaction, finds applications in automobile exhausts, proton-exchange membrane fuel cells, gas sensors etc. Gold nanoparticles deposited on oxide support is a prominent catalyst for the reaction but poses an issue due to sintering other than being expensive. Doping with copper is a popular strategy deployed to improve stability, increase oxyphilicity and decrease cost. Therefore, we designed a catalyst, detailed in **chapter 5**, composed of ultrasmall gold-copper bimetallic cluster,  $\text{AuCu}_3$ , deposited on O-terminated  $\text{Ti}_2\text{C}$  MXene. Our investigations predict that the first and second cycle of CO oxidation pass via Langmuir-Hinshelwood and Eley-Rideal pathways respectively. With a barrier of 0.56 eV, this catalyst is attractive in terms of cost, stability and activity compared to the ones reported in literature.

The thesis ends with **chapter 6**, where we summarise the outcome of the forementioned investigations, and additionally provide future directions to carry the research forward.



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# Chapter 1

## Introduction

---

MXenes are a novel and prominent class of two-dimensional materials composed of transition metal carbides, nitrides, or carbonitrides. The first of its members,  $\text{Ti}_3\text{C}_2\text{T}_x$ , was realized almost a decade ago by selectively removing Al atomic layers from its ternary carbide precursor  $\text{Ti}_3\text{AlC}_2$  at Drexel University [1]. This discovery was significant because, as opposed to what was done previously, extraction of a two-dimensional sheet did not require a parent phase bound by van der Waals interactions. The material displayed high metallic conductivity, hydrophilicity, and the capacity to intercalate cations, which sparked interest in MXenes for energy storage applications [2]. Owing to its diverse parent phases available, till date, over 30 MXenes have been synthesized experimentally and nearly 100 predicted theoretically, making it a prodigious family. It is of general formula  $\text{M}_{n+1}\text{X}_n\text{T}_x$  containing transition metal M, carbon and/or nitrogen X, surface terminations like -O, -OH, -F and/or -Cl as  $\text{T}_x$  and  $n$  ranging from 1 to 4. Adding to the abundance, the M site can be occupied by two metal atoms  $\text{M}'$  and  $\text{M}''$ , either following a random arrangement (called solid solution) or an ordered pattern giving rise to two classes: *i*-MXene if they exhibit an in-plane ordering forming chains of  $\text{M}'$  and  $\text{M}''$ , and *o*-MXene if  $\text{M}'$  and  $\text{M}''$  possess an out-of-plane ordering [3]. Thus, MXenes are unique in comparison to other layered materials for the ample features it can display arising from infinite possibilities by varying the elements M and X, and the number of layers (by changing  $n$ ) both of which depends on the parent MAX phase and terminations dependent of the synthesis conditions and reagents.

As discussed for the first member of the MXene family, the conventional synthetic strategy is top-down where chemical etching of A atoms (group 13/14 element) from the MAX phase is carried out and further intercalation and exfoliation follows. Typically, the etchant used is concentrated hydrofluoric acid (HF) but it possesses the safety risk of being

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extremely corrosive and toxic. A popular alternate route is reagents that are HF-producing such as LiF, KF, or NaF in hydrochloric (HCl) acid solution [4]. Other pathways are also being explored in isolated studies like using molten KF, NaF, and LiF for  $\text{Ti}_4\text{N}_3\text{T}_x$  [5] or ultraviolet ray-induced etching using phosphoric acid for  $\text{Mo}_2\text{CT}_x$  [6]. A disadvantage associated with this method is that the surface is inevitably covered with terminations which makes it difficult to control the composition and properties of the MXenes. The bottom-up approach, chemical vapor deposition (CVD) was used to synthesize bare  $\text{Mo}_2\text{C}$  MXene crystal on graphene with Mo-Cu alloy catalyst [7]. This technique, although in the budding stage shows promise for obtaining high quality crystals on a larger scale with controlled thickness and composition.

Outside of energy storage applications such as batteries, supercapacitors and wearable devices, MXenes have proved promising in areas of biomedical applications like drug delivery, cancer theranostics, and implantable devices, optical uses such as solar cells, electrochromic devices, and photonic diodes, sensors, spintronics, electromagnetic interference shielding, wireless communication, environmental remediation etc, to name a few [3]. In this thesis, we are primarily interested in the last application which predominantly happen via catalysis. This field of study is growing at a rapid pace, partly because of the reputation three-dimensional transition metal carbides (TMCs) possess in the field of heterogeneous catalysis. Transition metal carbides (TMCs) gained interest in heterogeneous catalysis since a study by Levy and Boudart in the 1970s showed that tungsten carbide, exhibited Pt- like features, because of their similarities on the density of states (DOS) near Fermi level arising from metal bonds in this region [8]. Noble metals like Pt are known for their catalytic activity but was often limited by stability and high cost. Apart from overcoming these issues, TMCs also have improved electrical conductivity, corrosion resistance etc, making it an ideal alternative to precious metals in catalysis [9]. This has resulted in tremendous research utilizing TMCs for reactions like hydrogen evolution reaction (HER) ( $\text{Mo}_2\text{C}$ ), Fischer-Tropsch ( $\text{Fe}_2\text{C}$ ), methane reforming (WC), etc. Apart from use as catalyst itself, TMCs are also good support material [10].

We note that C-based MXenes are similar to TMCs in terms of the constituting chemical elements, viz. transition metal and carbon. However, TM:C stoichiometry and structure of both of them differ. Since MXenes also possess a layered structure, they exhibit higher surface-to-volume ratio and are also capable of stabilising atoms and nanoparticles on the surface. Hence, the focus has now shifted to this family. For example,  $\text{Mo}_2\text{CT}_x$  showed good stability and activity towards water gas shift reaction (WGS) with a selectiv-

## Introduction

ity  $> 99\%$  [11]. Similarly, Pd atom on  $\text{Ti}_3\text{CO}_2$  is predicted to be a trifunctional catalyst for hydrogen evolution reaction (HER), oxygen evolution reaction (OER) and oxygen reduction reaction (ORR) [12]. Many more related works showcasing MXene as active phase and support will be discussed in the upcoming chapters.

The process of catalysis starts with the adsorption of one/more species of which at least one must remain adsorbed on the surface of the catalyst throughout the reaction. There can be two ways of adsorption physisorption, which utilizes the weak dipole (permanent and induced) and quadrupole interactions and has  $-0.10 - -0.40$  eV energy released, and chemisorption which is strong enough through the overlap of electron clouds to break/make bonds with an enthalpy of  $-0.80 - -4.00$  eV. When a molecule approaches the surface, it can scatter back or undergo physisorption which further can lead to chemisorption. Upon adsorption, further reaction happens at particular locations called active sites, which may or may not be different from adsorption sites. After adsorption and diffusion to the active site, the reaction happens and then the product formed is desorbed away from the system thus freeing the catalyst to be ready for the next cycle. Hence for a catalyst to be cyclable, the active site must follow Sabatier principle, i. e., adsorbate-surface interaction should be optimal, neither too weak nor too strong. Manipulating the interactions at the active site, which happens at the nanoscale, for enhancing certain aspects of the catalyst is difficult for heterogeneous catalysts though its macroscopic nature is very advantageous in industries [13].

A catalyst is evaluated based on three primary parameters activity, stability, and selectivity, with the goal being to achieve higher values of all three at a cheaper price. Activity determines how much products are formed per unit time volume while selectivity dictates which ones are formed [14]. Stability essentially determines the lifetime of catalysts, which can vary from months to years. Instability against sintering has diminished the use of pure metals, which was the most prominent candidate in the budding years of catalysis, in addition to the high cost and a low number of active sites. Hence for the past 60 years or so, the metal particles are dispersed on supports like alumina, silica, titania, zeolites, and mixed oxides. Apart from enabling stability, the support can participate in the process by providing an active interface or can act as promoter/inhibitor or can influence the properties of the active site directly by migrating to it, called as strong metal-support interaction (SMSI). The size of the metal particles (usually in the order of nms) formed is sensitive to preparation conditions, interaction with support, etc and can significantly alter the reaction mechanisms [15].

## *Introduction*

In this thesis, we are interested in heterogeneous catalysis via thermal route, which comes under the broad category of thermally activated processes. It is defined as a process that needs to surpass an activation barrier to progress. Thus, thermally activated processes are often characterized by long intervals between transitions from one minimum energy state to another. They are also regarded as rare events, with timescale varying from milliseconds to minutes (orders of magnitude higher in comparison with atomic vibrations) [16]. A few other examples of these processes include but are not limited to recrystallization, ionic conductivity, and diffusion. It is therefore interesting to note that many pertinent characteristics of solids are governed by these processes, which in turn are directly influenced by their microscopic structure [17].

Studying the dynamic evolution of the system of interest undergoing such transitions goes beyond the affordability of molecular dynamics (MD). In MD simulations, we follow the trajectory of the constituent atoms and molecules by calculating the forces and modifying their positions and velocities accordingly after definite time steps. Typically, time steps are given in the order of femtoseconds. The rare events we are focusing on occur on a timescale of at least milliseconds, which requires a minimum of trillion MD steps to monitor one such transition. This is impossible to implement even with the best supercomputer facilities available to date [18]. Also, long MD can create errors during numerical integration steps. Exploring the potential energy surface (PES) directly is an alternate technique in this scenario. There are several computational techniques available for use depending on the nature of PES being investigated [16]. Provided we have the final state of the system, and if the landscape is smooth with only a limited number of local minima, then the reaction pathway can be scanned via the single-ended elastic band or string methods. This is the type of PES we encounter both in chapter 4 which deals with CO<sub>2</sub> dissociation on Ti<sub>2</sub>C MXene, and chapter 5, that explores CO oxidation on an AuCu bimetallic cluster adsorbed on Ti<sub>2</sub>CO<sub>2</sub> substrate. The method we have used in these cases unanimously is explained in detail in chapter 2. Complicated double-ended sampling methods of the kinds of discrete path sampling, milestoning, finite-temperature string, etc can be helpful in case of rough landscapes. Investigating PES is harder if the final state evolves during the course of the reaction and this is still an active area of research.

Computational techniques of varying levels of complexity are available for use today, and as we see the choice has to be made depending on the nature of the process and its time scale. For example, in the catalytic processes, we are interested in, bond making and breaking occur in many steps. This requires accurate prediction of properties at the elec-

tronic level with affordability. Thus, a quantum mechanical method, density functional theory (DFT) is the routinely used tool in this field as it provides a fine balance between accuracy and computational cost. Though in the early days, it was used to explain experimental observations by providing details at a microscopic level, now we are so far ahead in technology that the same method is now used for prediction [19]. In fact, DFT has gained more interest recently due to the development of machine learning (ML) in catalysis since the data used in ML is predominantly from DFT [20]. Hence, in the current work, we use DFT for total energy calculations and harmonic transition state theory (hTST) for computing the kinetic parameters.

## 1.1 Outline of the thesis

In this thesis, I present the results of my investigations of CO<sub>2</sub> capture and activation, and CO oxidation to CO<sub>2</sub> using DFT. We have considered two materials, namely, Ti<sub>2</sub>C MXene surface and small bimetallic AuCu clusters. Here MXene acts as a catalyst for CO<sub>2</sub> capture and activation, while for CO oxidation, it acts as a support for the bimetallic cluster. The rest of the thesis is divided as follows:

**Chapter 2:** Contains details of the computational methods used in the thesis. In this chapter we briefly describe the Born-Oppenheimer approximation, Kohn-Sham equations, density functional theory, exchange-correlation functionals, periodic supercells, electron-ion interactions and nudged elastic band.

**Chapter 3:** Before studying the chemical reactions, in this chapter we present the structure and electronic properties of Ti<sub>2</sub>C MXene. Transition metal dichalcogenides with similar layered structures, are known to exhibit structural phase transition when the stacking is changed. Here we have explored the possibility of similar phase transition in Ti<sub>2</sub>C MXene.

**Chapter 4:** CO<sub>2</sub> adsorption, activation and dissociation have been studied on two-dimensional Ti<sub>2</sub>C MXene. In addition to adsorption of a single CO<sub>2</sub> molecule, we have also studied the CO<sub>2</sub> coverage dependence on adsorption on this surface.

**Chapter 5:** This chapter proposes a promising novel catalyst composed of bimetallic AuCu clusters on Ti<sub>2</sub>CO<sub>2</sub> MXene, for the CO oxidation reaction. We have explored LH and ER mechanism for first and second cycles of the process.

Finally, in **Chapter 6**, we review the findings from all chapters of this thesis and suggest a few possible directions for future investigations.

## Chapter 2

### Computational methods

---

The development and advancement of quantum mechanics is the most radical scientific breakthrough that twentieth century has witnessed. This has enabled quantum mechanical modeling a go-to tool for many researchers, blanketing almost the entirety of chemical, biological, and physical domains. Over the last century, enhanced computing facilities and better algorithms have made doing experiments computationally a cheaper and definitely an easier option compared to its counterpart. To give a perspective, only performing total energy calculations can provide us a number of physical properties including but not limited to lattice constants, dielectric constants and bulk modulus but the same via physical experiment require their corresponding apparatuses. Computing also provides additional advantages of modeling experiments where the physical analog is impossible or difficult to perform.

Applying quantum mechanical modeling to a system essentially begins with solving the Schrödinger equation for the atoms and electrons belonging to that system. This equation,  $H\Psi = E\Psi$ , although appears deceptively simple, is impossible to solve exactly even for a three-particle system like He atom because of the coupled interaction terms. As explained by Paul Dirac, “The fundamental laws necessary for the mathematical treatment of a large part of physics and the whole of chemistry are completely known, and the difficulty lies only in the fact that application of these laws leads to equations that are too complex to be solved” [21]. Then the question arises; how are systems (containing hundreds of atoms) modelled quantum mechanically in the thousands of papers published each year. And the answer is, we solve Schrödinger equation not exactly but by utilising a bunch of approximations that works surprisingly well in most of the cases and these are discussed as follows.

## 2.1 Density functional theory

### 2.1.1 Born-Oppenheimer approximation

For a system having  $n$  nuclei and  $n''$  electrons, the Schrödinger equation needs to be solved contain Hamiltonian;

$$H = - \sum_i \frac{\hbar^2 \nabla_i^2}{2m_i} - \sum_{i''} \frac{\hbar^2 \nabla_{i''}^2}{2m_e} + \frac{1}{4\pi\epsilon_0} \sum_{i'' > j''} \frac{e^2}{|\mathbf{r}_{i''} - \mathbf{r}_{j''}|} - \frac{1}{4\pi\epsilon_0} \sum_{i,i''} \frac{Z_i e^2}{|\mathbf{r}_{i''} - \mathbf{r}_i|} + \frac{1}{4\pi\epsilon_0} \sum_{i > j} \frac{Z_i Z_j e^2}{|\mathbf{r}_i - \mathbf{r}_j|} \quad (2.1)$$

Here,  $m_i$  ( $m_e$ ) is the mass of nucleus (electron),  $\mathbf{r}_i$  ( $\mathbf{r}_{i''}$ ) is the position of the nucleus (electron),  $Z_i$  is its charge and  $\epsilon_0$  is the permittivity of vacuum. In eq. 2.1, the first two terms on the right denote kinetic energy of nucleus and electron respectively. The third and fifth terms represent repulsive interactions of electron-electron and nucleus-nucleus. The fourth one corresponds to electron-nucleus attractive potential.

Since each of  $n$  and  $n''$  needs to have 3 coordinates each, the Schrödinger equation corresponding to the above Hamiltonian is a partial differential equation with  $3(n + n'')$  variables and the minimum computational power (CPU time) needed to solve it is proportional to the square of variables  $9(n + n'')^2$ . The Born-Oppenheimer approximation helps to reduce this. Nucleus is orders of magnitude heavier than electrons, hence correspond to a different timescale of movement i.e., electron moves faster than nuclei. Mathematically, this helps to separate the nuclear part from the above hamiltonian thereby decoupling the electronic and nuclear terms. The approximation is implemented in two steps; first, for a fixed nuclear position, we optimise the electronic configuration by solving electronic Schrödinger hamiltonian. This step is then repeated for all possible positions of the nucleus. The electronic Hamiltonian  $H_e$  is given by,

$$H_e = - \sum_{i''} \frac{\hbar^2 \nabla_{i''}^2}{2m_e} + \frac{1}{4\pi\epsilon_0} \sum_{i'' > j''} \frac{e^2}{|\mathbf{r}_{i''} - \mathbf{r}_{j''}|} - \frac{1}{4\pi\epsilon_0} \sum_{i,i''} \frac{Z_i e^2}{|\mathbf{r}_{i''} - \mathbf{r}_i|}. \quad (2.2)$$

Via this two-step process, the required computational power for the above-mentioned equation (2.1) drops significantly to  $3n''^2 + 3n^2$ . But the most important issue that we face in solving the Schrödinger equation still persists; the electron-electron interaction term in this equation.



### 2.1.2 Kohn Sham equations

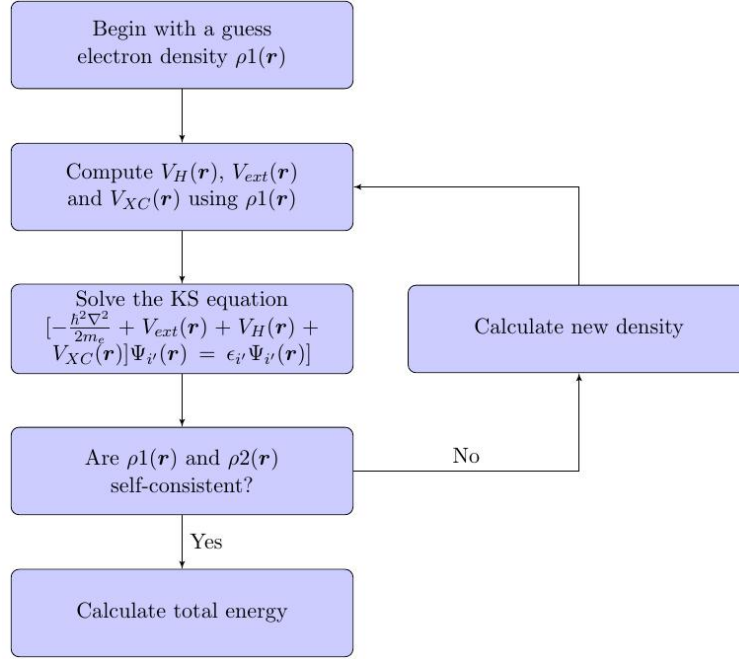
Kohn and Hohenberg (1964) introduced a breakthrough theorem which states, “The ground-state energy from Schrödinger equation is a unique functional of the electron density” [22]. Hence, to determine the ground state electronic properties of the system, it is sufficient to calculate its density. This shifts the focus from wavefunction ( $\Psi_{i'}$ ) to an observable property like density ( $\rho(\mathbf{r}) = 2 \sum_{i'} \Psi_{i'}^*(\mathbf{r}) \Psi_{i'}(\mathbf{r})$ ) for solving the Schrödinger equation and reduced the dimensionality from  $3n''$  to just 3. Their second theorem in 1965 explained the properties of the energy functional computed from this density i.e., “The electron density that minimizes the energy of the overall functional is the true electron density corresponding to the full solution of the Schrödinger equation” [23]. Further, Kohn and Sham laid out a set of single-electron equations (2.3), thus solving for a system of non-interacting electrons in a collective potential of others rather than a system of mutually interacting electrons.

$$\left[ -\frac{\hbar^2 \nabla^2}{2m_e} + V_{ext}(\mathbf{r}) + V_H(\mathbf{r}) + V_{XC}(\mathbf{r}) \right] \Psi_{i'}(\mathbf{r}) = \epsilon_{i'} \Psi_{i'}(\mathbf{r}), \text{ where} \quad (2.3)$$

$$V_H(\mathbf{r}) = e^2 \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3\mathbf{r}', \text{ and} \quad (2.4)$$

$$V_{XC}(\mathbf{r}) = \frac{\delta E_{XC}(\mathbf{r})}{\delta \rho(\mathbf{r})} \quad (2.5)$$

In eq. 2.3 first term represents the kinetic energy of the electron and  $V_{ext}(\mathbf{r})$  is the potential between electron and combined nuclei interaction.  $V_H(\mathbf{r})$ , known as Hartree potential, shows the interaction of the chosen electron with the density created by all electrons. This (eq. 2.3) looks exactly like the eq. 2.2 written above, except for the summation because earlier the coupled terms prevented this simplification. This leads inevitably to a self-interaction error as this potential includes the electron’s interaction with itself. These three terms constitute the well-defined part of Kohn-Sham (KS) equations and the  $V_{XC}(\mathbf{r})$  (exchange-correlation potential) is regarded as the unknown and the trickiest part of all. Exchange (correlation) energy corresponds to the lowering of the repulsion by keeping same-spin (different-spin) electrons apart. The  $V_{XC}(\mathbf{r})$  includes a correction for self interaction, exchange and correlation. Even since the two HK theorems have laid the foundation for DFT, the research to find the exact form of XC functional began and it still continues, almost 50 years later. In order to solve the one-electron KS equations for wavefunction  $\Psi_{i'}$ s, we need to determine the potential terms. This in turn depends



**Figure 2.1:** Flowchart showing the process of self-consistently solving Kohn-Sham equation.

on the electron density which is obtained from the wavefunction  $\Psi_{i'}$ s. Hence in order to solve for the unknown (density) we need to know unknown-dependent terms (potential), which seems impossible. But a self-consistent procedure, demonstrated in Fig. 2.1, helps to achieve this.

### 2.1.3 Exchange-correlation functional

$$V_{XC}^{LDA}(\mathbf{r}) = V_{XC}^{electron\ gas}[\rho(\mathbf{r})] \quad (2.6)$$

As described earlier, the true form of exchange-correlation functional is unknown and we have been using several approximations to deal with it. The simplest of them all is called LDA (local density approximation), given by Kohn and Sham in 1965 (eq. 2.6) [23]. According to this, we approximate the exchange- correlation potential at every point  $\mathbf{r}$  of the system by that of a homogenous electron gas of corresponding density at  $\mathbf{r}$ . This may appear as a far-fetched approximation for real systems however, this works well for the cases where electron density varies slowly.

For systems having inhomogenous electron density, further improvement can be done

through generalised gradient approximation (GGA) [24], where the  $V_{XC}(\mathbf{r})$  is given as,

$$V_{XC}^{GGA}(\mathbf{r}) = V_{XC}[\rho(\mathbf{r}), \nabla\rho(\mathbf{r})]. \quad (2.7)$$

Here apart from the local density, we also consider its gradient to give a better picture of the chemical bonds in materials. Perdew group has developed several routinely used functionals like PBE, PW91 based on this approximation [25]. These are often found to outperform many LDA-based functionals although exceptions do exist. Because of some drawbacks observed in these functionals such as incorrect bandgap (GGA and LDA), magnetization (LDA), many advanced approximations like meta-GGA, hybrid-GGA, are further being researched.

## 2.2 Periodic supercells

The solution to the KS equation above (eq 2.3), are expanded in a basis set, preferably of plane waves in solids. The benefits of using plane waves are multifold i.e., they are easy to differentiate, delocalised over the entire solid, a single parameter controls the size of the basis set, and since they are independent of nuclear positions, forces can be computed smoothly. Since we are interested in solids with a periodic arrangement of atoms, the wavefunction is given by Bloch's theorem. According to this [26], it is a product of a wave-like part and a crystal-periodic part of which the latter is further expanded using a set of plane waves,

$$\Psi_{n,\mathbf{k}}(\mathbf{r}) = e^{i(\mathbf{k} \cdot \mathbf{r})} f_{n,\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{G}} C_{n,\mathbf{k}+\mathbf{G}} e^{i(\mathbf{k}+\mathbf{G}) \cdot \mathbf{r}} \quad (2.8)$$

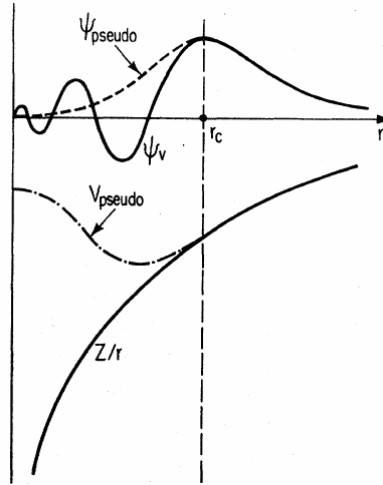
Here,  $n$  is band index,  $\mathbf{k}$  is wave vector and  $\mathbf{G}$  is reciprocal lattice vector.

Ideally, the above wavefunction needs to be determined for infinite  $\mathbf{k}$  points belonging to the first Brillouin Zone (unit cell in the reciprocal lattice). Applying the Born-von Karman periodic boundary condition restricts this to certain  $\mathbf{k}$ -points, whose density is proportional to the solids volume. The total potential the electron sees depends on the electron density. This is contributed by each occupied state at each  $\mathbf{k}$ -point. Additionally, the wavefunctions are similar for  $\mathbf{k}$ -points which are closely located, hence calculating at a single  $\mathbf{k}$  point in such regions suffices the purpose. Thus through this process of  $\mathbf{k}$ -point sampling, the infinite calculations are numerically brought down to a great extend. Of the several sampling schemes employed, the most commonly used is regular-grid-

based Monkhorst-Pack approach developed in 1976. For insulating and semiconducting materials a small number of  $k$  points can provide good accuracy while for metallic systems a dense set is needed. This is due to the drastic change in occupancy at the Fermi surface, which makes it difficult to integrate. One of the approaches to overcome this issue is to use smearing that eases the discontinuity at this region. Basically, the step function is replaced by a smearing function like Fermi-Dirac, which is smooth enough to do the integration and also doesn't add any significant unphysical contribution. The next approximation dictates how to truncate the basis set in the Bloch function although in ideal case this should be an infinite summation over  $\mathbf{G}$  vectors. As  $e^{i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}}$  corresponds to kinetic energy, and since we need to consider only low values of kinetic energy, we choose a cut-off for it [27]. Thus above equation now modifies to,

$$\Psi_{n,\mathbf{k}}(\mathbf{r}) = \sum_{|\mathbf{k}+\mathbf{G}| < G_{cut}} C_{n,\mathbf{k}+\mathbf{G}} e^{i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}}. \quad (2.9)$$

## 2.3 Electron-ion interaction



**Figure 2.2:** Schematic depiction of real potential and pseudopotential along with their wavefunctions. (Taken from ref. [26] with permission.)

Chemical bonding and several physical properties of materials are dominantly dependent on the valence electrons than the core electrons. This is because the core electrons are highly localized to the nucleus, experience very strong electrostatic interactions, and the corresponding energy states are much lower in comparison with the valence electrons.

Hence to reduce the computational cost, we do not consider the core electrons explicitly. Rather we assume that the valence electrons experience an effective nuclear potential that is screened by the core electrons. This is called the "frozen core" approximation.

Moreover, the valence electron wavefunctions closer to the core region exhibits huge oscillations to satisfy the orthogonality condition with the electron wavefunctions. With the basis set entirely composed of plane waves, these oscillations demand more number of plane waves to represent it. This results in an increase in the basis set size, thereby increasing the computational cost. Additionally, the effective core potential that the valence electrons experience diverges at the core.

To circumvent these issues, we use pseudopotential approximation. In this approximation, a pseudo smooth potential replaces the actual potential inside the core region (Fig. 2.2). Outside the core region, it matches the actual potential. Similarly, a smoothly varying pseudowavefunction takes the place of real wavefunction inside while both remain identical outside the core region. This pseudopotential can be created empirically or via first-principles calculation on isolated atoms. The latter is preferred to the prior because of its better transferability (a property that provides the pseudopotential more flexibility to be used in different chemical conditions). Among the *ab initio* pseudopotentials, frequently used ones are norm-conserving and ultrasoft. Norm-conserving pseudopotentials are formulated based on two conditions: 1) inside the chosen cutoff radius  $r_{cut}$ , the norm of both true and pseudowavefunctions are identical and 2) outside  $r_{cut}$ , the wavefunctions are identical [28]. The norm-conserving constraint limits the pseudopotential generation for first row and transition elements as their valence orbitals are strongly localised, thus making it impossible to create a pseudowavefunction smoother than the all-electron one. This led to the development of ultrasoft pseudopotentials, that offer enhanced smoothness due to norm-conservation relaxation and improved transferability and accuracy from good scattering properties over range of occupied states. This also allows the freedom to use higher values of  $r_{cut}$ , which translates to having smaller basis set. Here, the norm inside  $r_{cut}$  is maintained by adding an augmented charge density in the core regions [29].

## 2.4 Hellmann-Feynman theorem

Quantum mechanical calculation of force is important in DFT for optimizing the position of nuclei (to get an accurate estimate of bond lengths and angles) in static calculations and determines the trajectory in dynamics. Earlier this was done by calculating energy for

## Computational methods

different geometries and then taking the slope of energy vs position. Hellmann-Feynman theorem helped to severely reduce the computational cost by enabling estimation of force for a single configuration [30]. The derivation is as follows,

$$\mathbf{F}(\mathbf{r}_i) = -\frac{dE}{d\mathbf{r}_i} = -\frac{d\langle \psi_{i'} | H_e | \psi_{i'} \rangle}{d\mathbf{r}_i} - \frac{dE_{ion-ion}}{d\mathbf{r}_i}, \text{ where} \quad (2.10)$$

$E$  is the total energy of the system and  $E_{ion-ion}$  is obtained from ion-ion interactions.

$$\mathbf{F}(\mathbf{r}_i) = -\langle \frac{d\psi_{i'}}{d\mathbf{r}_i} | H_e | \psi_{i'} \rangle - \langle \psi_{i'} | \frac{dH_e}{d\mathbf{r}_i} | \psi_{i'} \rangle - \langle \psi_{i'} | H_e | \frac{d\psi_{i'}}{d\mathbf{r}_i} \rangle - \frac{dE_{ion-ion}}{d\mathbf{r}_i}, \quad (2.11)$$

Since  $\psi_{i'}$  is independent of nuclear coordinates, the derivatives in the first and third term go to 0. Hence,

$$F(\mathbf{r}_i) = -\langle \psi_{i'} | \frac{dH_e}{d\mathbf{r}_i} | \psi_{i'} \rangle - \frac{dE_{ion-ion}}{d\mathbf{r}_i} \quad (2.12)$$

and this is called the Hellmann-Feynman theorem.

## 2.5 Minimum energy path and saddle point

The quantities that can be obtained from theoretical calculations and can also be directly observed in experiments such as the rate in chemical reactions, are especially important considering the direct comparison it provides. For studying dynamics of reactions, a purely statistical method like Transition State Theory (TST) proves to be very useful. It works on two assumptions; a) there is a thermodynamic equilibrium established throughout the reaction and b) there is a dividing surface, called transition state, crossed once as reactants evolve into products. As we concentrate only on solids, we use a harmonic approximation of TST (hTST) assuming that the temperatures of interest are significantly lower than the melting point [31]. According to hTST, the rate constant  $k$  is given by,

$$k = \frac{\prod_{j=1}^{3N} \omega_j^{in}}{\prod_{j=1}^{3N-1} \omega_j^*} e^{-(E^* - E^{in})/k_B T} \quad (2.13)$$

showing the exponential dependence of  $k$  on temperature and activation energy (difference between  $E^{in}$  and  $E^*$ ). Here,  $E^*(E^{in})$  is the energy of the saddle point (initial state) and  $\omega_j^*(\omega_j)$  represent normal modes of saddle point (initial state). Since the initial state is known to us, all that is required is to find the transition state, identified as a first-order

saddle point in potential energy surface. Hence identification of saddle point becomes the bottleneck of the whole calculation. Further, the normal mode with imaginary frequency at the saddle point is the reaction coordinate direction which helps us to map the entire reaction pathway, also known as the minimum energy path (MEP). MEP is a unique path connecting initial and final state and have the highest probability on the configuration space. All points on MEP have zero force perpendicular to their tangent and thus only have components along the direction of the path.

Initially, locating the saddle point was done only using the initial state and going forward either by the method of steepest ascent or tracing the normal modes. An upgrade over these led to techniques that utilize both the initial and final geometries, which are normally known. One example is the 'drag' method, whereby a reaction coordinate chosen via interpolation or intuition is incremented in a series of steps, relaxing the rest of the coordinates in each step. Here however the choice of the coordinate is extremely crucial and if not done right, saddle point is easily missed [32].

A popular other technique is the 'chain of states', that breaks down continuous MEP into a chain of equally-spaced states (or images) and thereafter each image is optimized so that the perpendicular force,  $\mathbf{F}_\perp(\mathbf{R}_i) = 0$ . Since these images are optimized simultaneously this method unlike others can benefit from parallel computing. However this inevitably leads to sliding-down problem, where the images disperses in energetically high regions and finally collapses into one of the two minimas. Hence a fictitious spring force is introduced between these images of rest length zero, thus resembling an elastic band. This force term can create unphysical forces in the orthogonal direction in curved regions of MEP (corner-cutting). A force projection that operates by separating the true force (from external potential) and spring force, also called as nudging, can help overcome the issues of corner-cutting and sliding down. Thus in nudged elastic band method (NEB), the total force experienced by each image  $i$  is a sum of true force in direction perpendicular to that of tangent and spring force along the tangent,

$$\mathbf{F}(\mathbf{R}_i) = \mathbf{F}_\parallel^s(\mathbf{R}_i) + \mathbf{F}_\perp(\mathbf{R}_i), \text{ where} \quad (2.14)$$

$$\mathbf{F}_\perp(\mathbf{R}_i) = -\nabla E(\mathbf{R}_i) + \nabla E(\mathbf{R}_i) \cdot \hat{\boldsymbol{\tau}}_i \hat{\boldsymbol{\tau}}_i \text{ and} \quad (2.15)$$

$$\mathbf{F}_\parallel^s(\mathbf{R}_i) = k(2\mathbf{R}_i - \mathbf{R}_{i+1} - \mathbf{R}_{i-1})\hat{\boldsymbol{\tau}}_i. \quad (2.16)$$

Here,  $E$  is the total energy,  $k$  is the spring constant,  $\mathbf{R}_i$  is the reaction coordinate of  $i$ th image and  $\hat{\boldsymbol{\tau}}_i$  is the unit tangent vector for  $i$ th image. This ensures that the optimization

### Computational methods

of the images to reach MEP is not influenced by the condition to maintain equidistant images along the path, which is important for convergence of MEP. Further, to converge the highest energy point exactly to the transition state, a correction was introduced to NEB, called as climbing image NEB (CI-NEB) [33]. After running NEB for a while, we choose the highest energy image,  $i_m$ , and the force applied on it is modified as

$$\mathbf{F}(\mathbf{R}_{i_m}) = -\nabla E(\mathbf{R}_{i_m}) + 2\nabla E(\mathbf{R}_{i_m}) \cdot \hat{\boldsymbol{\tau}}_{i_m} \hat{\boldsymbol{\tau}}_{i_m}. \quad (2.17)$$

Compared to other images,  $i_m$  does not experience any spring force and instead an additional true force inverted along the tangent direction, thus moving up along the tangent and down orthogonal to it. Also, this adds no significant computational cost and helps the convergence better.

The tangent  $\boldsymbol{\tau}_i$  plays a very crucial part in the working of the NEB, as in evident from the eq. 2.15 - 2.17. Previously this was calculated for image  $i$ , from the difference with two neighboring images  $i + 1$  and  $i - 1$ , i.e,

$$\boldsymbol{\tau}_i = \frac{\mathbf{R}_{i+1} - \mathbf{R}_i}{|\mathbf{R}_{i+1} - \mathbf{R}_i|} + \frac{\mathbf{R}_i - \mathbf{R}_{i-1}}{|\mathbf{R}_i - \mathbf{R}_{i-1}|}, \text{ and } \hat{\boldsymbol{\tau}}_i = \frac{\boldsymbol{\tau}_i}{|\boldsymbol{\tau}_i|}. \quad (2.18)$$

This estimation made sure that images are equally spaced even in areas of high curvature. But this falls short when there is a huge parallel force component as compared to perpendicular and also many images exist in the path, leading to kinks. A new scheme was devised to overcome this issue. Here,  $\boldsymbol{\tau}_i$  is given by,

$$\boldsymbol{\tau}_i = \begin{cases} \boldsymbol{\tau}_i^+, & E_{i+1} > E_i > E_{i-1} \\ \boldsymbol{\tau}_i^-, & E_{i+1} < E_i < E_{i-1}, \text{ where} \end{cases} \quad (2.19)$$

$$\boldsymbol{\tau}_i^+ = \frac{\mathbf{R}_{i+1} - \mathbf{R}_i}{|\mathbf{R}_{i+1} - \mathbf{R}_i|} \text{ and } \boldsymbol{\tau}_i^- = \frac{\mathbf{R}_i - \mathbf{R}_{i-1}}{|\mathbf{R}_i - \mathbf{R}_{i-1}|} \quad (2.20)$$

Now, if  $i + 1$  and  $i - 1$  are both higher or lower in energy than  $i$ , a weighted average (decided by energy) of  $\boldsymbol{\tau}_i^+$  and  $\boldsymbol{\tau}_i^-$  are used instead given by eq. 2.21 for switching smoothly between  $\boldsymbol{\tau}_i^+$  and  $\boldsymbol{\tau}_i^-$  [34].

$$\boldsymbol{\tau}_i = \begin{cases} \boldsymbol{\tau}_i^+ \Delta E_i^{max} + \boldsymbol{\tau}_i^- \Delta E_i^{min}, & E_{i+1} > E_{i-1} \\ \boldsymbol{\tau}_i^+ \Delta E_i^{min} + \boldsymbol{\tau}_i^- \Delta E_i^{max}, & E_{i+1} < E_{i-1}, \text{ where} \end{cases} \quad (2.21)$$



### *Computational methods*

$$\Delta E_i^{max} = \max(|E_{i+1} - E_i|, |E_i - E_{i-1}|) \text{ and } \Delta E_i^{min} = \min(|E_{i+1} - E_i|, |E_i - E_{i-1}|). \quad (2.22)$$

Another important aspect of NEB is the optimization scheme that takes the initial guess provided for the reaction path to MEP by bringing down the total force for each image in each iteration below a set threshold. One of the most common methods used is based on the velocity Verlet algorithm. In each iteration, velocity and positions of images are updated following the force at that point. This can further be improved by keeping the velocity component parallel to this force. As velocity and force become antiparallel, velocity is made zero. Setting the velocity to zero changes this scheme to the steepest descent, which is the simplest technique for force minimization.

## Chapter 3

# Antiferromagnetic semiconducting 1T to ferromagnetic half metallic 1H phase transition in $\text{Ti}_2\text{C}$ MXene: A theoretical prediction

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### 3.1 Introduction

It has been more than a decade since the first member in the family of two-dimensional materials, graphene, was successfully isolated by Geim and Novoselov [35]. The intriguing mechanical and electronic properties of graphene [36–39], in contrast to its bulk counterpart graphite, motivated the research community to explore many more materials with the same dimensionality. This quest has resulted in the discovery of a wide range of 2D materials such as hexagonal boron nitride (h-BN), transition metal dichalcogenides (TMDs), graphitic carbon nitride (g- $\text{C}_3\text{N}_4$ ), phosphorene, borophene, germanene, silicene etc. with applications spanning over electronics, photovoltaics, medicine, catalysis, energy storage, biological engineering, sensors etc [40–45]. One of the recent additions to this family is MXenes.

Like 2D TMDs, a single sheet of MXene can exist in two polymorphs, namely the 1T phase where the M-X-M layers are stacked in a ABC fashion (for eg.  $\text{Ti}_2\text{C}$ ) or the 1H phase where the M-X-M layers are stacked in a ABA fashion (for eg.  $\text{Mo}_2\text{C}$ ). In TMDs structural phase transitions from the 1T to 1H phases and vice-versa are known to give rise to several intriguing properties. For example in Group V TMDs electrically activated metal-to-metal structural phase transitions have been observed in multilayer  $\text{TaS}_2$  [46] and  $\text{TaSe}_2$  [47]. In contrast, in Group VI TMDs one of the above mentioned structural phases is semiconducting while the other one is metallic [48–50]. Since this metal to insulator transitions (MIT) are structural in nature, it is expected that there will be considerable

metastability and hysteresis. We note that in the conventional way of achieving MIT by using large macroscopic strains to a semiconducting phase, the above mentioned features of metastability and hysteresis are not available. Further, these being monolayers, they also provide opportunities for flexible devices.

Though these phase transitions are extensively studied in transition metal dichalcogenides (TMDs), in MXenes, which are structurally similar to TMDs, not much is explored. To the best of our knowledge, the only study of the 1H phase was reported very recently by Chen *et al.* where they have studied the thermodynamic stability of the 1H and 1T phases of different MXenes, both in their pristine form and when functionalized with O, F and OH [51]. However, they have not explored the possibilities of structural transitions and MITs associated with them. Another investigation in this direction was done by the group of Luo [52], but they contained majority of the investigation to most stable 1T phase of  $\text{Ti}_2\text{C}$  MXene.

In this work we have explored the possibility of the structural phase transition and its influence on the electronic properties of the most commonly studied MXene  $\text{Ti}_2\text{C}$  using first principles density functional theory (DFT) based calculations. The rest of the chapter is divided as follows: in section 3.2 we discuss the computational methods employed to obtain the results, section 3.3 explains how we deduced the ground state magnetic structure and further details the structural, electronic, magnetic and vibrational properties associated with both 1T and 1H phase. The mechanism proposed for the phase transition along with the energy barrier and transition state is discussed also discussed. Finally, in section 3.4, we summarise the results so obtained in this study.

## 3.2 Computational Details

The calculations were carried out using plane wave based DFT as implemented in the Quantum ESPRESSO [53] software. The electron-ion interactions were described by using ultrasoft pseudopotentials [54]. We have used kinetic energy cutoffs of 55 Ry and 480 Ry for wavefunction and charge density respectively. The electron-electron exchange-correlation functional was described using the spin-polarized generalized gradient approximation as parametrized by Perdew-Burke-Ernzerhof (GGA-PBE [55]). Since conventional GGA functionals are known to underestimate the band gap [56, 57], we have performed the band structure and density of states (DOS) calculation using the singularity free Gau-PBE hybrid functional [58], which was then interpolated by maximally localised

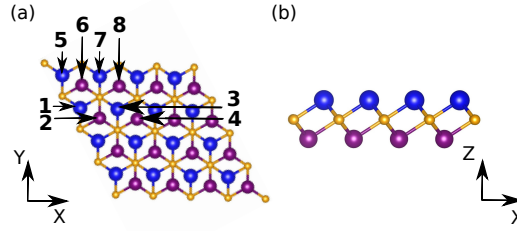
wannier functions [59,60] using wannier90 [61] to plot the band structure. To evaluate the matrix elements of the Fock exchange operator, we have expanded the wave functions in a plane wave basis set defined by a kinetic energy cutoff of 480 Ry and a  $(5 \times 5 \times 1)$  q-mesh. Brillouin zone (BZ) integrations were done using a  $15 \times 15 \times 1$  Monkhorst-Pack [62] k-point mesh for  $(1 \times 1)$  unit cell. To speed up convergence we have used Marzari-Vanderbilt smearing [63], with a smearing width of 0.007 Ry. To minimize the fictitious interactions between the periodic images, we have used a vacuum of 15 Å in the direction perpendicular to the plane of the MXene sheet. CI-NEB [64, 65] method was applied to identify the minimum energy path for the phase transition mechanism in which a total of 11 images were considered for the path. In order to ascertain the dynamic stability of the two phases, phonon spectra were computed using density functional perturbation theory [66] employing a  $3 \times 3 \times 1$  q-grid. VESTA [67] software was used for the visualisation of the structures.

## 3.3 Results and Discussion

### 3.3.1 The 1T phase

The structure of  $\text{Ti}_2\text{C}$  MXene was derived from that of  $\text{Ti}_2\text{AlC}$  (MAX phase) by removing the Al atoms. This results in a hexagonal unit cell of  $\text{Ti}_2\text{C}$  with the C layer sandwiched between two Ti layers. The three atomic layers are stacked in ABC pattern, similar to the 1T structure of  $\text{MoS}_2$  (space group  $\text{p}\bar{3}\text{m1}$ ). In this structure, as shown in Fig. 3.1, each of the C atoms is bonded to six Ti atoms forming an edge-sharing octahedra around C while each Ti is bonded to three C atoms. This phase of  $\text{Ti}_2\text{C}$  MXene is mostly reported to have the ferromagnetic ground state in the literature [68–71]. To the best of our knowledge, there are very few studies that have actually looked into all the possible magnetic structures [68, 69, 72]. Only recently Chakraborty *et al.* have reported an antiferromagnetic (AFM) configuration that is more stable than the ferromagnetic one. Hence, to eliminate this ambiguity related to the magnetic structure, we have considered all different possible magnetic configurations of this phase to find out the ground state configuration.

Table 3.1 shows the magnetic configurations that has been considered in this study [73]. The atoms labelled 1-8 in Table 3.1 are marked in Fig. 3.1. The unit cell used to determine the lattice parameters for each of these configurations was decided by the nature of the spin alignment, i.e.,  $(1 \times 1)$  unit cell was used for ferromagnetic (FM), non



**Figure 3.1:** 1T phase of  $\text{Ti}_2\text{C}$  MXene, projected on (a) the  $xy$  plane and (b) along  $z$  direction. In this figure and as well as in the subsequent figures in the manuscript Ti atoms in top and bottom layer are represented by blue and purple colour respectively and the C atoms by yellow colour.

magnetic (NM) and AFM-1,  $(1 \times 2)$  supercell was used for AFM-5, while for AFM-2, AFM-3 and AFM-4 we have used a  $(2 \times 2)$  supercell. Upon optimizing the lattice parameters and geometry, we find that AFM-1, with a lattice parameter of  $3.06 \text{ \AA}$ , to be the most stable configuration in which the spins on the Ti atoms within the layer are aligned parallel to each other (ferromagnetic) while those between two layers are aligned antiparallel (antiferromagnetic), giving rise to A-type antiferromagnetism. The AFM-1 configuration is about  $33 \text{ meV/formula unit}$  lower in energy compared to the mostly reported ferromagnetic phase (FM) [69, 74], which is in excellent agreement with that reported by Chakraborty *et al.* For all the magnetic states considered, the stability follows the following order:  $\text{AFM-1} > \text{FM} > \text{AFM-3} > \text{AFM-2} = \text{AFM-4} = \text{AFM-5} > \text{NM}$ .

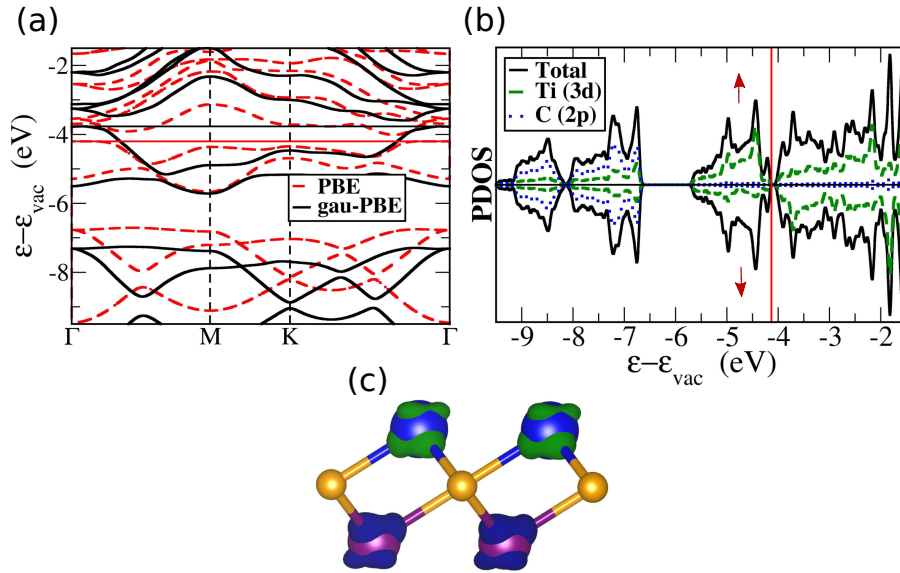
**Table 3.1:** Alignment of spins on atoms labelled 1-8 in Fig. 1 along with the energy and cell parameters for the magnetic configurations studied in 1T  $\text{Ti}_2\text{C}$  MXene. The energies are given with respect to the AFM-1 ground state.

| Config. | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | Energy<br>(meV/f. u.) | Cell param.<br>( $\text{\AA}$ ) |
|---------|---|---|---|---|---|---|---|---|-----------------------|---------------------------------|
| AFM 1   | + | - | + | - | + | - | + | - | 0.00                  | $a = 3.06$                      |
| FM      | + | + | + | + | + | + | + | + | 33.00                 | $a = 3.08$                      |
| AFM 3   | + | - | + | + | - | + | - | - | 102.00                | $a = 6.12$                      |
| AFM 2   | - | - | + | + | + | + | - | - | 107.00                | $a = 6.11$                      |
| AFM 4   | - | + | + | - | + | - | - | + | 107.00                | $a = 6.11$                      |
| AFM 5   | + | + | - | - | + | + | - | - | 107.00                | $a = 6.10$<br>$b = 3.07$        |
| NM      | - | - | - | - | - | - | - | - | 142.00                | $a = 3.04$                      |

As mentioned in the previous paragraph, the cell parameter for the AFM-1 phase is found to be  $3.06 \text{ \AA}$  (in close agreement with  $3.04 \text{ \AA}$  reported by ref [52]). The separation between the Ti atom on one layer with that of the C atom on the second layer (with that of

the Ti atom on the third layer) is 1.14 Å (2.28 Å). We obtain a Ti-C bond length of 2.10 Å.

Since the most commonly reported state is the ferromagnetic one, we compared our results for this state with those reported in literature. For the ferromagnetic phase our calculations yield a cell parameter of about 3.08 Å and a magnetic moment of  $1.90 \mu_B$ . We find that these values are in excellent agreement with those reported in ref [69]. Further, in comparison to ref [75] where they report the distance between Ti atoms in different layers as 2.90 Å and between Ti and C atoms as 2.10 Å, our studies give 2.85 Å and 2.10 Å respectively. Also, our computed value of the Ti-C bond length of 1.12 Å matches very well with the reported value of 1.13 Å [74]. Hence, we can confirm that our results are in reasonably good agreement with the literature, which guarantee reliability in our study.



**Figure 3.2:** (a) Band structure computed from PBE and Gau-PBE with corresponding VBM marked by solid horizontal lines, (b) DOS computed from PBE, and (c) magnetisation density isosurfaces for the 1T phase of  $\text{Ti}_2\text{C}$  MXene. The green and blue isosurfaces represent spin up and spin down density respectively. Energy levels are shifted with respect to vacuum energy.

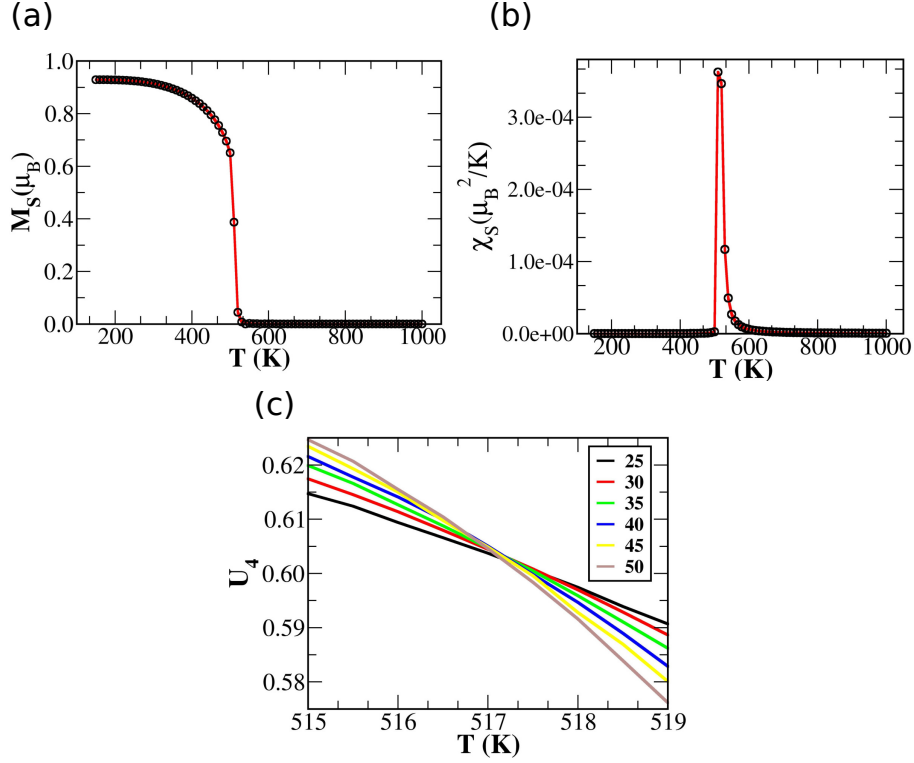
The band structure (BS) and the density of states (DOS) for the AFM 1 configuration of the 1T phase from PBE are shown in Fig. 3.2 (a) and (b) respectively. In both the figures the Kohn-Sham eigenvalues are shifted with respect to the vacuum energy. Hence the valence band maxima (VBM) gives the work function of the 1T phase. We find the work function for the 1T phase to be 4.20 eV. Since the ground state is antiferromagnetic, the spin up and spin down channels are degenerate and this phase turns out to be a semiconductor with a bandgap of 0.19 eV, consistent with that reported in ref [72].

In Fig. 3.2 (b), along with the total DOS, we have also plotted the DOS projected onto the  $d$  states of Ti and  $p$  states of C. The valence band extends from about -6.00 eV to -4.20 eV and is predominantly from Ti 3d orbitals, since in this case the Ti atoms are not terminated/passivated and they give rise to dangling bonds. The valence band maxima (VBM) is formed primarily from the Ti- $d_{z^2}$  states. The states arising due to the hybridization between the Ti- $d$  and C- $p$  states lie between -9.50 to -6.50 eV. Since PBE is known to underestimate the band gap, we have also computed the band structure with Gau-PBE hybrid functional. The same is also plotted in Fig. 3.2 (a). The hybrid functional acts differently on the different bands compared to PBE. While for the low energy states arising from the hybridization of the Ti-C atoms, Gau-PBE pushes them further lower in energy with band dispersion similar to that of PBE, the valence band is affected in a different way. For example, with Gau-PBE the VBM is moved upward, resulting in lowering of work function (from 4.20 eV for PBE to 3.77 eV for Gau-PBE). Similarly the conduction band is also moved upward. However, the band gap remains unchanged and is similar to that observed with PBE. The magnetisation density plot is shown in Fig. 3.2 (c). From our calculations we find that the magnitude of the magnetic moments on the Ti atoms are  $0.93 \mu_B$  ( $1.19 \mu_B$  with Gau-PBE) while those on the C atoms are  $0.00 \mu_B$ . This differs from the reported value of  $0.63 \mu_B$  for Ti atoms by [52], possibly due to the inclusion of Hubbard U correction in the report.

Since the ground state is antiferromagnetic in nature, calculating the coupling constants and thus Néel temperature will impart an idea of the stability of the magnetism with respect to temperature. The coupling constants are calculated by employing the Heisenberg Hamiltonian,

$$H = H_0 + \sum_{i>j} J_{ij} S_i S_j,$$

where  $H_0$  is the spin-independent part,  $S_i$  and  $S_j$  are the magnetic moments on the  $i^{th}$  and  $j^{th}$  atoms respectively and  $J_{ij}$  is the coupling constant between them [76]. In the 1T phase, since we have three layers consisting of Ti-C-Ti stacked in an ABC pattern, there are two coupling constants,  $J_{wl}$  and  $J_{bl}$ , to denote the coupling within a layer and between layers respectively. Here, we consider the nearest and next nearest neighbour interactions. Thus there are six neighbouring atoms within a layer and three in the next layer for a single Ti atom. So using the above equation in our system and avoiding the double counting, we find that the difference in energies between a magnetic and non magnetic configuration is



**Figure 3.3:** The plots of (a) staggered magnetization, (b) susceptibility ( $\chi_s$ ), and (c) Binder's fourth order cumulant against temperature, obtained from Monte Carlo simulations for the 1T phase of  $\text{Ti}_2\text{C}$  MXene. In (a) and (b) the red line is used to join the data points (black circles), obtained from simulation.

given by [77],

$$E_{mg} - E_{nm} = -12J_{wl}S^2 - 5J_{bl}S^2,$$

where  $E_{mg}$  and  $E_{nm}$  are the energies of the magnetic and the non-magnetic configurations respectively. The  $S$  values are taken from our PBE calculation. We need two such equations to solve for the two unknowns  $J_{wl}$  and  $J_{bl}$ ; hence we have considered two lowest energy magnetic structures, FM and AFM-1, solving for which we get  $J_{wl} = 11.24$  meV and  $J_{bl} = -2.52$  meV. Thus, within the layer, we get a positive  $J$  or ferromagnetic coupling and between them a negative  $J$  or an antiferromagnetic coupling further reconfirming that the intralayer exchange coupling is ferromagnetic while the interlayer one is antiferromagnetic in AFM-1. The coupling constants we obtained are slightly lower compared to ref [52]. This can be because 1) inclusion of Hubbard  $U$ , 2) they have considered an additional coupling constant, and 3) an additional  $J_{bl}$  interaction term is also added.

To find out the Néel temperature for the antiferromagnetic to paramagnetic phase tran-



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sition, we have performed Monte Carlo simulations using a  $(50 \times 50 \times 1)$  bipartite hexagonal lattice of 1T phase. The interactions between the spins are modelled within Ising model where the above mentioned coupling constants have been used. Periodic boundary conditions have been applied only along X and Y directions. In Ising model, usually a magnetic transition is traced by the variation in magnetisation and magnetic susceptibility with temperature. Since the 1T phase ground state is antiferromagnetic in nature, the magnetisation values fluctuate around zero, thereby making it difficult to predict the Néel temperature. Hence, here we have computed the staggered magnetisation ( $M_s$ ) and the corresponding staggered susceptibility ( $\chi_s$ ) to provide more clarity to the phase transition region. The  $M_s$  and  $\chi_s$  are given by,

$$M_s = \langle m_s \rangle,$$

where

$$m_s = \frac{1}{N} \sum_{upperlayer} S_i - \sum_{lowerlayer} S_i,$$

and

$$\chi_s = \frac{\langle m_s^2 \rangle - \langle m_s \rangle^2}{k_B T^2}$$

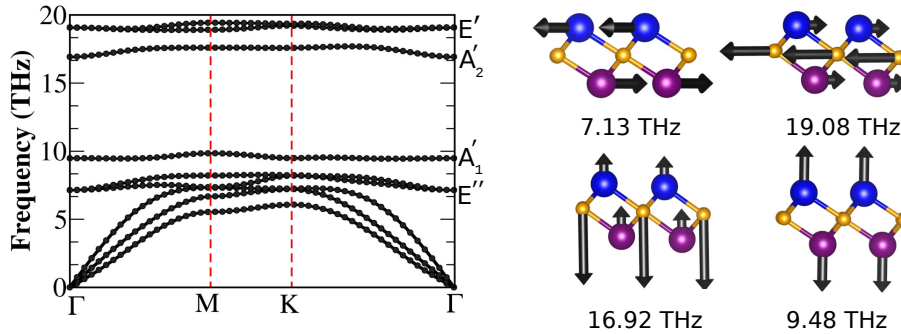
Fig. 3.3 (a) and (b) show the plots of  $M_s$  and  $\chi_s$  as a function of temperature respectively. More accuracy in predicting Néel temperature was achieved by calculating Binder's fourth order cumulant [78] given by,

$$U_4 = 1 - \frac{\langle m_s^4 \rangle}{3 \langle m_s^2 \rangle^2},$$

for a series of  $(n \times n)$  lattices with  $n = 25, 30, 35, 40, 45$  and  $50$  and then using the cumulant crossing method [79]. The Néel temperature was determined to be  $517.12$  K ( $243.97^\circ$  C). Thus our calculations predict that the pristine 1T phase will remain as an antiferromagnet even at temperatures much higher than the room temperature. The work of Luo et. al. ([52]) predicts a higher transition temperature of  $875$  K, arising dominantly from difference in calculation of coupling constants.

The dynamic stability of the 1T phase of  $\text{Ti}_2\text{C}$  MXene was investigated by computing the phonon spectra, which alongside the displacement patterns associated with the optical modes at the  $\Gamma$  point, is shown in Fig. 3.4. It matches extremely well with the reported one in ref [52]. Phonon spectra do not show any imaginary frequency throughout the Brill-

lounin zone, which proves the dynamical stability of the structure. The hexagonal unit cell we employed has three atoms and hence we observe nine branches in the phonon spectra. The first three denotes acoustic modes, namely, ZA (out-of-plane transverse polarisation), LA (in-plane longitudinal polarization) and TA (in-plane transverse polarization) in the increasing order of energy and the remaining six branches denote the optical modes. Although near  $\Gamma$  point, LA and TA clearly shows a linear dependence, ZA shows slightly quadratic one which reflects the two-dimensional nature of the material. The point group of 1T phase is  $D_{3h}$ , hence the optical modes at  $\Gamma$  point consist of  $A'_1$ ,  $A''_2$ ,  $E'$  and  $E''$ . The optical branches at 7.13 THz and 19.08 THz are doubly degenerate  $E''$  and  $E'$  and correspond to in-plane motions. In  $E''$ , the C layer remains static and Ti layers move out of phase. In  $E'$ , both the Ti layers move in phase and the layer containing C atoms move in a direction opposite to that of both the Ti layers. The remaining two optical branches at 9.48 THz and 16.92 THz are non-degenerate  $A'_1$  and  $A''_2$  respectively, which denotes out-of-plane motions with a static C and out of phase Ti atoms in  $A'_1$  and C and Ti atoms moving out of phase with respect to each other in  $A''_2$ . There is a phonon bandgap of 8 THz between  $A'_1$  and  $A''_2$ .

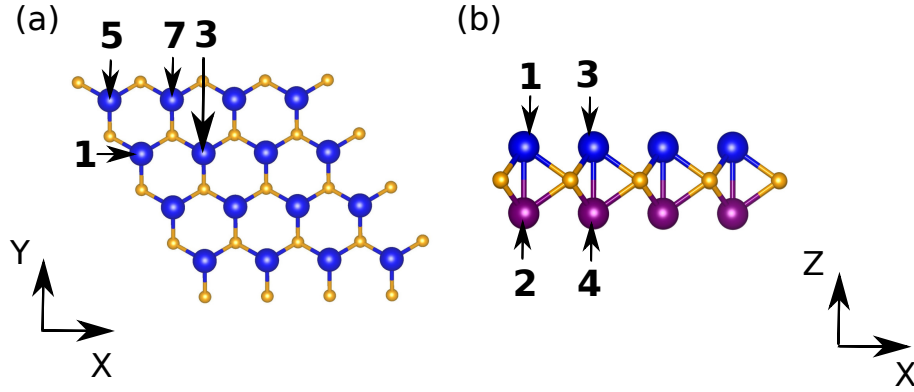


**Figure 3.4:** Phonon spectra and optical modes (at  $\Gamma$  point of the BZ) of 1T phase of  $\text{Ti}_2\text{C}$  MXene. The black arrows show the displacement patterns of the atoms. The length of the arrows is proportional to the magnitude of the displacement.

### 3.3.2 The 1H phase

As mentioned earlier, this dynamically stable ground state of  $\text{Ti}_2\text{C}$  MXene is structurally similar to the metastable 1T phase of  $\text{MoS}_2$ . The ground state of  $\text{MoS}_2$  is the 1H phase, in which Mo-S-Mo is stacked in ABA fashion and behaves as a direct band gap semiconductor. It was only recently found that upon rhenium doping [80],  $\text{MoS}_2$  undergoes phase transition to the 1T phase, which is metallic nature. This kind of polymorphism, caused

by only change in stacking and leading to such diverse electronic properties, was shown to be useful for preparing nanoscale heterostructure for electronic devices [81]. The possibility of such phase transition in  $\text{Ti}_2\text{C}$  MXene, because of the similarity in structures, prompted us to explore the possibility of the existence of the 1H phase where the stacking changes from ABC to ABA. The new phase of  $\text{Ti}_2\text{C}$  MXene that we report here, has similarly hexagonal unit cell with Ti-C-Ti layers but stacked in ABA pattern, as shown in Fig. 3.5. The coordination around C atom is still 6 but now the geometry is trigonal prismatic, just like the the 1H phase of  $\text{MoS}_2$ .



**Figure 3.5:** 1H phase of  $\text{Ti}_2\text{C}$  MXene in projected on (a) the xy plane and (b) along z direction respectively.

In order to investigate the magnetic ground state of this 1H phase, we used similar magnetic structures that were employed earlier for the 1T phase. The alignment of the spins on atoms 1-8 (Fig. 3.5) is same as given in Table 3.1 and unit cells used for the different structures are same as that reported in the previous section. We find the FM configuration to be lowest in energy. The energies of the other configurations, with respect to this ferromagnetic ground state of 1H phase and their cell parameters are given in Table 3.2. We find that the cell parameters in these configurations are similar to that found for the 1T phase. However, the order of stability of the different magnetic configurations is altered,  $\text{FM} > \text{AFM-1} > \text{AFM-2} = \text{AFM-5} = \text{AFM-3} = \text{AFM-4} > \text{NM}$ . Thus, in contrast to the 1T phase, the 1H phase have a ferromagnetic ground state, the latter being 1.29 eV/f. u. higher in energy than the 1T phase. Moreover, we find that the AFM-1 phase of the 1H state, which is the ground state for the 1T phase, is about 20 meV/f. u. higher in energy than the FM state.

The ferromagnetic state so reported, has a cell parameter of 3.05 Å. The Ti-C bond length is 2.16 Å and the separations between Ti atoms in the first layer with carbon atom

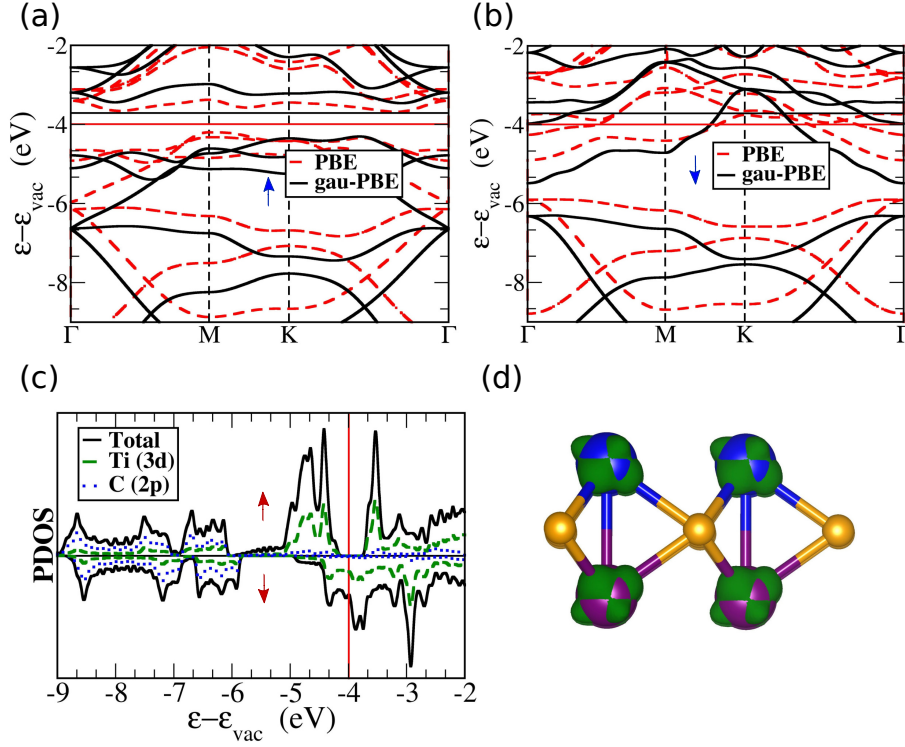
**Table 3.2:** Energies and cell parameters of the different magnetic configurations of 1H phase. Energies are given with respect to ferromagnetic ground state.

| Configuration | Energy<br>(meV/f. u.) | Cell parameters<br>(Å) |
|---------------|-----------------------|------------------------|
| FM            | 0.00                  | a = 3.05               |
| AFM 1         | 20.00                 | a = 3.04               |
| AFM 2         | 110.00                | a = 6.08               |
| AFM 3         | 110.00                | a = 6.07               |
| AFM 4         | 110.00                | a = 6.07               |
| AFM 5         | 110.00                | a = 6.06, b = 3.03     |
| NM            | 120.00                | a = 3.02               |

in the second layer and Ti atom in the third layer are 1.25 Å and 2.49 Å respectively. Though the change in the bond lengths with respect to the 1T phase is small, the cell has slightly shrunk along  $xy$  direction and expanded along  $z$  direction as a result of the change in stacking. This is because now the Ti atoms of one layer is on top of Ti atoms of the other layer.

Fig. 3.6 (a) and (b) show the band structure for the spin up and spin down channel obtained from PBE and Gau-PBE respectively, shifted with respect to vacuum energy. By virtue of the ferromagnetic ground state, we observe non-degenerate spin up and spin down channels in the bandstructure of the 1H phase. Using PBE, the Fermi energy is at -3.99 eV resulting in an work function of 3.99 eV. We note that this is about 0.20 eV lower than the work function for the 1T phase. Further, compared to the 1T phase, this novel 1H phase is half-metallic with the spin-up channel to be semiconducting with an indirect PBE band gap of about 0.52 eV and the spin-down channel to be metallic. The DOS and PDOS are shown in Fig. 3.6 (c). Similar to the 1T phase, the states arising from the hybridization of the C- $p$  and Ti- $d$  orbitals are lower in energy while those near the Fermi level is primarily from the Ti- $d$  states. Computing the band structure with the Gau-PBE hybrid functional (solid black lines in Fig. 3.6 (a) and (b) shows that the qualitative picture of the electronic properties remain same as that obtained with PBE. However, with Gau-PBE, the band gap for the spin up channel increases to 0.86 eV. This further reconfirms that indeed the 1H phase is half metallic. The magnetisation density plot in Fig. 3.6 (d) shows same polarizations on the two Ti atoms at the bottom and top layers and a small amount of polarization on C atom. The magnitude of the magnetic moments on each Ti atom is  $0.96 \mu_B$  and  $0.94 \mu_B$  from Gau-PBE and PBE respectively while that on the C

atom is  $0.12 \mu_B$  and  $0.03 \mu_B$ .



**Figure 3.6:** Band structure computed using PBE and Gau-PBE functionals for the spin up channel (a) and spin down channel (b), (c) DOS from PBE and (d) magnetisation density for the 1H phase of  $\text{Ti}_2\text{C}$  MXene. The green isosurfaces represent spin up density. Energy levels are shifted with respect to vacuum energy.

As done earlier, the stability of the magnetism in 1H phase was investigated by calculating coupling constants and thereafter the Curie temperature, since now we have a ferromagnetic system. In the 1H phase, the Ti-C-Ti layers are stacked in a ABA fashion and thus each Ti has six nearest neighbours within a layer and one in the other layer. Applying the Heisenberg Hamiltonian in this system gives,

$$E_{mg} - E_{nm} = -12J_{wl}S^2 - J_{bl}S^2,$$

where  $E_{mg}$  and  $E_{nm}$  are the energies of the magnetic structure and the non-magnetic structure respectively. Here also we took the two most stable structures, FM and AFM-1, thus giving two equations, which on solving gives  $J_{wl} = 8.12 \text{ meV}$  and  $J_{bl} = 32.86 \text{ meV}$ . As we can see both the constants are positive which is consistent with FM configuration. Further, the interlayer coupling is stronger than the intralayer coupling. This is attributed to the fact that the interlayer Ti-Ti distance ( $2.49 \text{ \AA}$ ) is smaller than the intralayer Ti-Ti

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distance (3.05 Å). The Curie temperature was computed using Ising model with Monte Carlo sampling for  $(50 \times 50 \times 1)$  bipartite hexagonal lattice of 1H phase using these coupling constants. The magnetization( $M$ ) and magnetic susceptibility( $\chi$ ) are given by,

$$M = \langle m \rangle,$$

where

$$m = \frac{1}{N} \sum_{i=1}^N S_i,$$

and

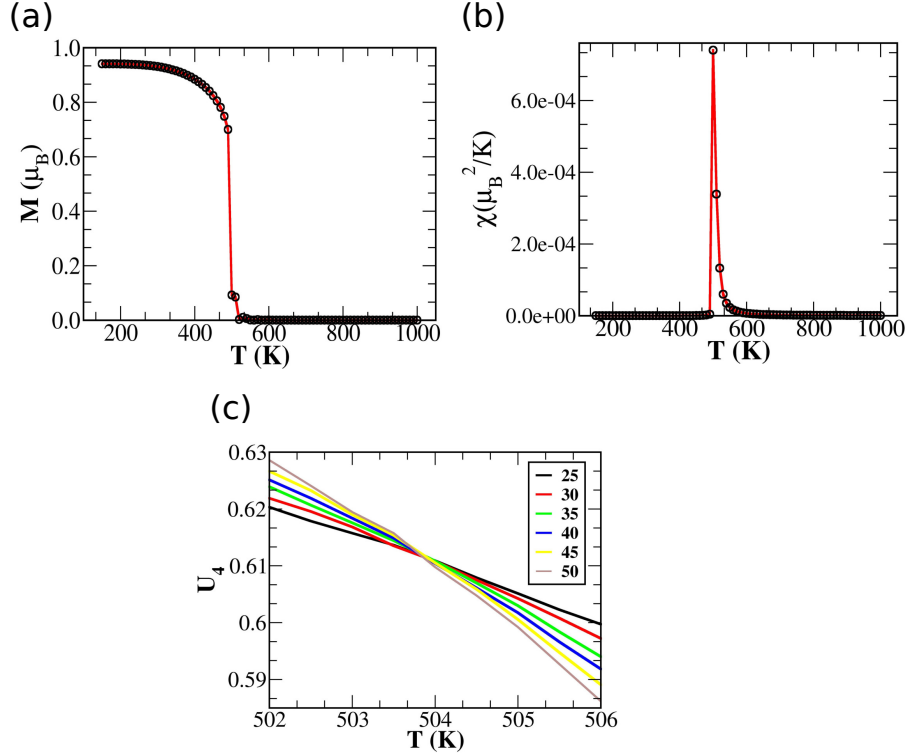
$$\chi = \frac{\langle m^2 \rangle - \langle m \rangle^2}{k_B T^2}.$$

Fig. 3.7 (a) and (b) shows the plots of  $M$  and  $\chi$  respectively. The phase transition is characterised by a peak in magnetic susceptibility. As done for the 1T phase, in order to pin down the Curie temperature more accurately, Binder's fourth order cumulant [78],

$$U_4 = 1 - \frac{\langle m^4 \rangle}{3 * \langle m^2 \rangle^2},$$

was computed for a series of lattices, 25, 30, 35, 40, 45 and 50 and the Curie temperature was identified to be 503.80 K (230.65 °C). Similar to the 1T phase, the 1H phase also remains magnetic upto temperatures well above the room temperature.

The phonon spectra of the 1H phase along with the displacement patterns corresponding to the optical vibrational modes are given in Fig. 3.8. The absence of any imaginary frequency in the BZ establishes the dynamic stability of this newly reported phase. Since the number of atoms in the unit cell is same as that for the 1T phase, 9 branches can be seen in the spectra, where the first three correspond to acoustic modes and the remaining six corresponds to the optical modes. Moreover the point group of 1H is  $D_{3d}$ . Hence at  $\Gamma$ -point of the BZ the modes that had  $A'_1$ ,  $A''_2$ ,  $E'$  and  $E''$  symmetries in the 1T phase, now corresponds to  $A_{1g}$ ,  $A_{2u}$ ,  $E_u$  and  $E_g$  respectively. Compared to the 1T phase, for the 1H phase we find that there is an overall softening of the optical modes except for  $A_{1g}$ . This implies a weakening in the Ti-C bond upon phase transition. For  $A_{1g}$  branch, the upshift is explained by a decreased Ti-Ti bond length of 2.49 Å as compared to 2.88 Å in the 1T phase. Since  $A_{1g}$  and  $A_{2u}$  has undergone upshift and downshift respectively, the gap between these non-degenerate bands is now significantly reduced and so is the gap between the two highest energy degenerate and non-degenerate optical branches, which

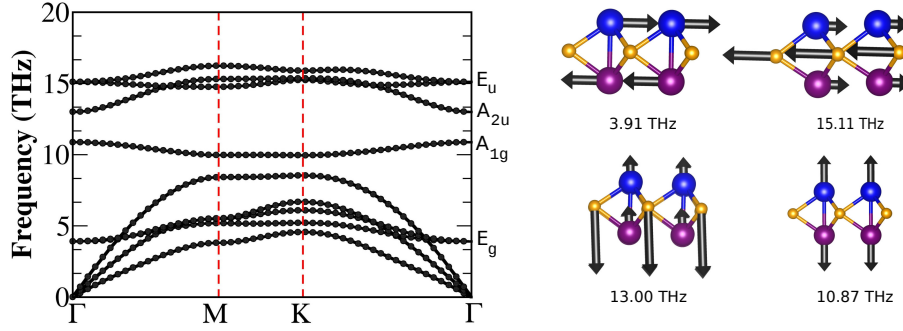


**Figure 3.7:** The plots of (a) magnetisation, (b) magnetic susceptibility and (c) the Binder's fourth order cumulant plotted as a function of temperature, obtained from Monte Carlo simulation for the 1H phase of  $\text{Ti}_2\text{C}$  MXene. The red line is used to join the data points (black circles), obtained from simulation.

now crosses each other at K, after K and before M.

### 3.3.3 1T to 1H phase transition

We predict a possible mechanism for the phase transition to happen. The mechanism involve one layer of Ti atoms gliding over the other until it comes exactly above the other layer so that stacking is changed from ABC to ABA. In this mechanism, the Ti atoms in the lower layer (purple in Fig. 3.9 (b) glide along the  $[11]$  direction of the 2D hexagonal unit cell till it is above the Ti atoms in the upper layer (blue). Similarly the upper layer can also glide and move over to the bottom layer forming the ABA stacking. Moving any one of these is equivalent by symmetry. Since the phase transition is from an antiferromagnetic 1T phase to a ferromagnetic 1H phase, we performed NEB calculations for two cases: (a) antiferromagnetic 1T phase to antiferromagnetic 1H phase and (b) ferromagnetic 1T phase to ferromagnetic 1H phase, the potential energy curves of which are shown in Fig. 3.9 (a).



**Figure 3.8:** Phonon spectrum of the 1H phase and the displacement patterns of the corresponding optical modes (at  $\Gamma$  point of the BZ). The black arrows show the displacement patterns of the atoms. The length of the arrows is proportional to the magnitude of the displacement.

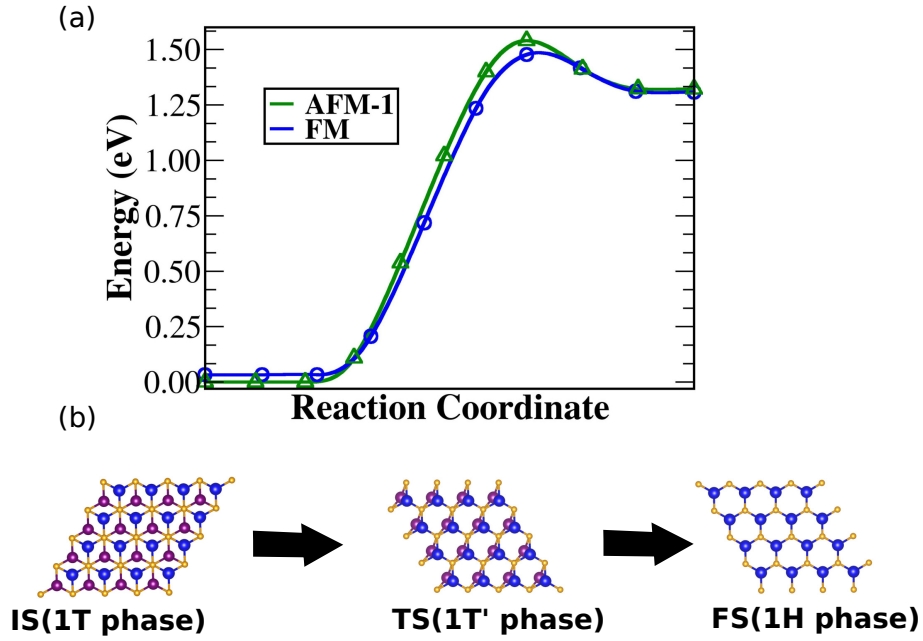
Our calculations suggest that at first there will be a switch from the antiferromagnetic state to a ferromagnetic one that will require an energy of 0.03 eV. This is followed by gliding of the Ti layer, which at the transition state (TS)  $\text{Ti}_2\text{C}$  forms a structure analogous to the 1T' state of  $\text{MoS}_2$ . This involves a barrier of 1.45 eV. Hence the net barrier for transition from 1T to 1H is 1.48 eV.

We note that while in our study we have considered pristine  $\text{Ti}_2\text{C}$  surfaces, in reality, when synthesized by chemical etching of the MAX phase, there are presence of functional groups like -OH, -F, -O, etc. This rises the question that as to whether our results will hold true for a realistic  $\text{Ti}_2\text{C}$  monolayer. To this end we would like to draw attention to recent reports in literature where MXenes have also been synthesized using chemical vapour deposition techniques [82]. In these methods the above mentioned problem of the presence of the functional groups can be avoided resulting in pristine MXene surfaces.

### 3.4 Conclusion

Using first principles DFT based calculations we predict a structural phase transition in  $\text{Ti}_2\text{C}$  MXene. Our results show that while the 1T phase is an antiferromagnetic semiconductor, the novel 1H phase is a ferromagnetic half metal. The latter is about 1.29 eV/f.u. higher in energy than the 1T phase. The phonon calculations show that both the phases are dynamically stable. This suggests that though it is possible to form the 1H phase, its practical realization and stabilization against the 1T phase will require special experimental considerations. Using Monte Carlo simulations, our estimates of the Néel and the Curie temperature of the above two phases show that the magnetic properties of





**Figure 3.9:** (a) The potential energy curve of the 1T to 1H phase transition. (b) Geometries of the initial state (IS), transition state (TS) and final state (FS).

both the phases can be retained at temperatures much higher than the room temperature. Further, we show that the transition from 1T to 1H involves a barrier crossing and will occur through a gliding motion of the Ti layer (either the top or the bottom one) along the [11] direction.

## Chapter 4

### CO<sub>2</sub> capture, activation and dissociation on Ti<sub>2</sub>C surface and Ti<sub>2</sub>C MXene: Role of surface structure

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#### 4.1 Introduction

Mitigation of CO<sub>2</sub> in the atmosphere, which is regarded as the main component of greenhouse effect, is a scientific problem of supreme importance in recent times. In this regard, carbon capture and utilisation (CCU) is a well-known strategy in which CO<sub>2</sub> is utilised via converting it into value added products, hence called as a “two birds, one stone approach” [83]. CCU has benefits of higher efficiency, low cost and convenience over other approaches employed for the same. One way to utilise CO<sub>2</sub> is to convert it to CO which can then be converted to a wide range of chemicals like methanol, acetic acid, etc. The issue that most of the catalysts face for conversion of CO<sub>2</sub> in general is its chemical stability arising from the two CO double bonds [84]. However, CO<sub>2</sub> has a significant amount of quadrupole moment that enables it to interact with a suitable catalyst [85]. In spite of this, the quest for a catalyst is impeded due to the low activity [86] or due to the need for expensive and scarce metals [87, 88].

Transition metal carbides (TMCs) are widely investigated due to their high chemical and mechanical stability with high electrical and thermal conductivity [89–92]. The chemical stability of the TMCs depends on the stoichiometry of the systems. TMCs have attracted attention recently as catalysts for a wide range of reactions like CO hydrogenation [93], water gas shift (WGS) [94] reaction, and CO<sub>2</sub> hydrogenation [95]. Another interesting report in this regard is the activation of CO<sub>2</sub> using TiC{001}, leading to a higher CO<sub>2</sub> to methanol conversion compared to Cu{111} surface [95]. Moreover, TMCs can contribute in two ways towards CO<sub>2</sub> reduction; they can either act as a catalyst themselves or they can be used as an “active” support for small metal clusters that catalyze

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CO<sub>2</sub> capture and conversion [87].

In addition to the conventional TMCs, there has emerged a new class of layered TMCs, MXene. Although through the common synthesis protocol, they usually end up having O-, OH- and/or F-surface terminations, it is possible to obtain bare MXenes via chemical vapour deposition (CVD) method [96]. These two dimensional counterparts have an advantage of enhanced surface to volume ratio compared to the bulk carbides, hence are employed as catalysts in reactions like hydrogen evolution reaction (HER), N<sub>2</sub> fixation, water gas shift (WGS) [97] etc. In a CO<sub>2</sub> abatement study conducted on different M<sub>2</sub>C MXenes, Illas *et al.* found that the Ti<sub>2</sub>C could not only activate CO<sub>2</sub> but also had the highest uptake of CO<sub>2</sub>, 8.25 mol/Kg, even better than the zeolites which are typically used for this purpose [98]. Hence, it would be interesting to understand the CO<sub>2</sub> dissociation process in these systems.

There have been many studies to understand the role of different surface terminations of TMCs in CO<sub>2</sub> hydrogenation. These were primarily focused on TiC, MoC and Mo<sub>2</sub>C surfaces [99]. In a recent study Quesne *et al.* investigated the co-adsorption of CO<sub>2</sub> and water on low-indexed surfaces of conventional carbides of Ti, V, Zr and Nb with 1:1 stoichiometry using density functional theory (DFT) based calculations to understand the role of the transition metal [100]. However, in addition to the chemical nature of the catalyst, the surface structure is also crucial. To the best of our knowledge, there are no systematic studies on the role of the surface structure. In the existing studies, either the metal:C stoichiometry is different or the chemical constituents are different. In this work, in order to highlight the role of the surface structure in the adsorption and decomposition of CO<sub>2</sub>, we have studied CO<sub>2</sub> adsorption on different Ti<sub>2</sub>C surfaces. Here, for each of the cases the bulk has a Ti:C stoichiometry of 2:1. In particular we have chosen the low indexed {100} surface of the cubic phase of Ti<sub>2</sub>C and the Ti<sub>2</sub>C MXene.

The rest of the chapter is divided as follows: Section 4.2 contains the details of the DFT calculations and procedure adopted to determine the stable terminations of the different surfaces. In Section 4.3 we present our results and discuss their implications. Finally, we conclude in Section 4.4. It is to be noted that the calculations on Ti<sub>2</sub>C{100} surface part was carried out by my colleague Dr. Nishamol Kuriakose.

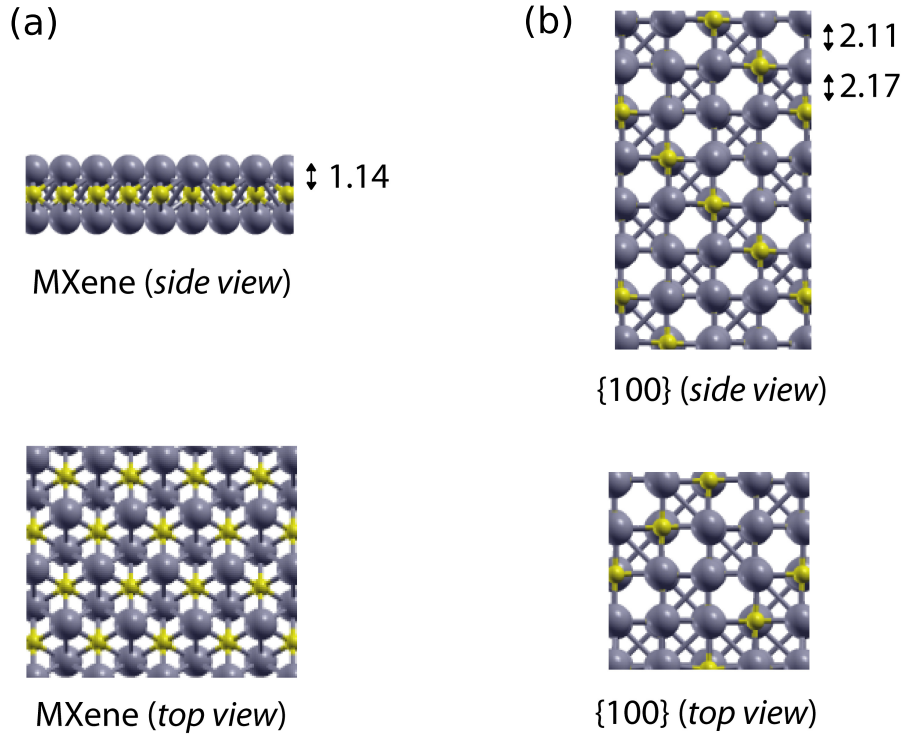
## 4.2 Computational Details

The calculations were carried out using plane wave based DFT as implemented in the Quantum ESPRESSO (QE) package [101, 102]. Ultrasoft pseudopotentials have been used to describe the electron-ion interactions [54]. In our calculations we have used the Perdew-Burke-Ernzerhof (PBE) [55] parametrization of the generalized gradient approximation (GGA). To include the van der Waals correction we have used Grimme’s dispersion (DFT-D2) correction as implemented in QE [103]. The calculations were performed employing kinetic energy cut offs of 55 and 480 Ry for the wave function and charge density, respectively. To speed up the convergence, we have used the Marzari-Vanderbilt smearing with a smearing width of 0.007 Ry [104].

All calculations were spin polarised for  $\text{Ti}_2\text{C}$  MXene as the ground state is an antiferromagnetic configuration. A vacuum separation of 15 Å was used to separate the periodic images. The Brillouin zone (BZ) was sampled using a  $9 \times 9 \times 1$  Monkhorst-Pack k-point mesh for a  $(1 \times 1)$  surface unit cell. For  $\text{Ti}_2\text{C}\{100\}$  surface, the BZ was sampled using a  $8 \times 8 \times 1$  Monkhorst-Pack k-point mesh for  $(1 \times 1)$  unit cell and a vacuum separation of 16 Å was used between the periodic images. It is to be noted that, for the adsorption study using  $\text{Ti}_2\text{C}\{100\}$  surface, we have used a  $6 \times 6 \times 1$  Monkhorst-Pack k-point mesh to reduce the computational cost (see k-point convergence plot in Fig. B.1 in appendix). The energy difference between a spin-polarized and non-spin polarized calculation of the  $\text{Ti}_2\text{C}\{100\}$  surface is less than 1.00 meV, which is within the error bar of our calculations, suggesting that these surfaces are non-magnetic. In these  $\text{Ti}_2\text{C}\{100\}$  non-magnetic and spin-polarized cases, we have also observed very close  $\text{CO}_2$  adsorption energy (see Table B.2 in appendix). Hence, for further studies of the  $\{100\}$  surface we have performed non-spin polarized calculations.

### 4.2.1 Surface model

The MXene belongs to  $\text{P}\bar{3}\text{m}1$  space group and from our studies we find the lattice constant and Ti-C bond length to be 3.06 Å and 2.10 Å, matching well with reported values (3.03 Å and 2.10 Å [105]). It has three layers with C-layer between Ti-layers and Ti-C-Ti arranged in a ABC fashion (Fig. 4.1 (a)). MXene is one of the most stable surfaces, as per the surface energy calculations performed on seven surfaces created from the most stable cubic and higher energy trigonal phase ( $\Delta E = 0.05$  eV/f. u.) of  $\text{Ti}_2\text{C}$ . This is followed by  $\{100\}$  and  $\{111\}$ - $\text{Ti}_{\text{highC}}$  surface (created by cleaving the cubic phase along  $\{111\}$



**Figure 4.1:** Optimised geometry of (a)  $\text{Ti}_2\text{C}$  MXene and (b)  $\{100\}$  surface. The Ti and C atoms are represented by grey and yellow spheres respectively. The inter-planar distances are given in Å.

direction in between Ti layer and C layer containing lower number of atoms) at C-poor and C-rich conditions respectively [106]. For the purpose of the study we choose  $\{100\}$  surface because of its contrasting surface structure to MXene.  $\{100\}$  is modelled with symmetric slab consisting of 8 layers. Each layer consists of a chain of octahedral carbon vacancies ( $\text{Oh}_\text{C}$ ) in  $[1\bar{1}]$  direction in addition to both C and Ti atoms present in the same plane with a Ti:C ratio of 2:1, as evident in Fig. 4.1 (b). Here, the spacing between the top layer and the second layer is 2.11 Å, which is about 0.05 Å lower than that observed for any two consecutive layers in the bulk. This indicates that the top layers are compressed as compared to the bulk layer spacing, which is 2.16 Å. As we move towards the bulk, we observe inter-planar distances that are similar to the bulk, 2.17 Å. All the layers are interconnected through Ti-Ti and Ti-C bonding interactions, where the bond lengths were found to be 2.91 Å and 2.11 Å respectively.

### 4.2.2 Adsorption

For the adsorption of CO<sub>2</sub> we have calculated the adsorption energy ( $E_{CO_2-ads}^n$ ) using the equation 4.1:

$$E_{CO_2-ads}^n = (E_{total} - E_{surf} - nE_{CO_2})/n, \quad (4.1)$$

where  $n$  is the number of CO<sub>2</sub> molecules adsorbed on the surface. Since we are also interested in the dissociation of CO<sub>2</sub> to carbon monoxide (CO) and oxygen (O), we have computed the co-adsorption energy ( $E_{CO-O-ads}$ ) of CO and O which is given by

$$E_{CO-O-ads} = E_{total} - E_{surf} - E_{CO} - 0.5E_{O_2} \quad (4.2)$$

In Equations 4.1 and 4.2,  $E_{total}$ ,  $E_{surf}$ ,  $E_{CO}$ ,  $E_{O_2}$  and  $E_{CO_2}$  are the energies of the total system consisting the surface and the adsorbed species, only surface, CO, O<sub>2</sub> and CO<sub>2</sub> in the gas phase, respectively.

### 4.2.3 Determination of barriers

Climbing image nudged elastic band (CI-NEB) method was applied to identify the minimum energy path for CO<sub>2</sub> dissociation. In case of MXene ({100}), a minimum of 13 (16) images were employed to the NEB path search. To reduce the computational cost, a 4-layer Ti<sub>2</sub>C{100} model surface has been used for CI-NEB path search using  $6 \times 6 \times 1$  k-point mesh (model validation in section 4.3.2).

## 4.3 Results and Discussion

### 4.3.1 CO<sub>2</sub> dissociation on Ti<sub>2</sub>C MXene

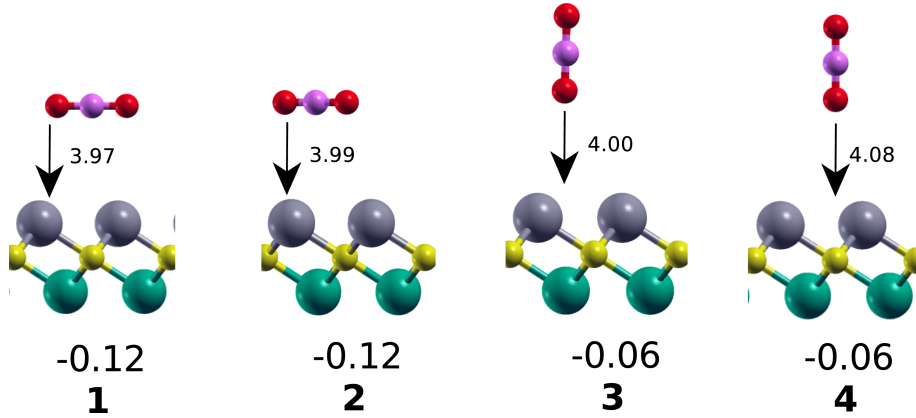
In this section we study the adsorption and dissociation of CO<sub>2</sub> to CO and O on the MXene surface.

#### 4.3.1.1 CO<sub>2</sub> adsorption

In MXene, for adsorption of any species, there are three sites available i.e., top site (on top Ti atom), hcp site (on hollow site above middle C atom) and fcc site (on hollow site above bottom Ti atom). In a previous study Junkaew *et al.* [107] showed that on MXene

surface, functional groups and adsorbate bind to only hollow sites; hence we proceed with the adsorption on fcc and hcp sites. We have considered both horizontal and vertical alignments of the molecule on the surface.

**Physisorption:** In all the horizontal configurations (see structure **1** and **2** in Fig. 4.2), the CO<sub>2</sub> remains linear. The separation between the adsorbed CO<sub>2</sub> and the top Ti-layer is about 4.00 Å and the calculated adsorption energy is -0.12 eV. There are no significant changes in C-O bond length and O-C-O bond angle with respect to the gaseous CO<sub>2</sub> (1.17 Å and 180.00°), which clearly indicate physisorption. For the vertically aligned cases, we have studied two geometries for physisorption, **3** and **4** from Fig. 4.2, where the CO<sub>2</sub> molecule is on two different hollow sites, namely hcp and fcc respectively. For both the cases we find that the separation of CO<sub>2</sub> with the surface and bond lengths remain same as in horizontal.

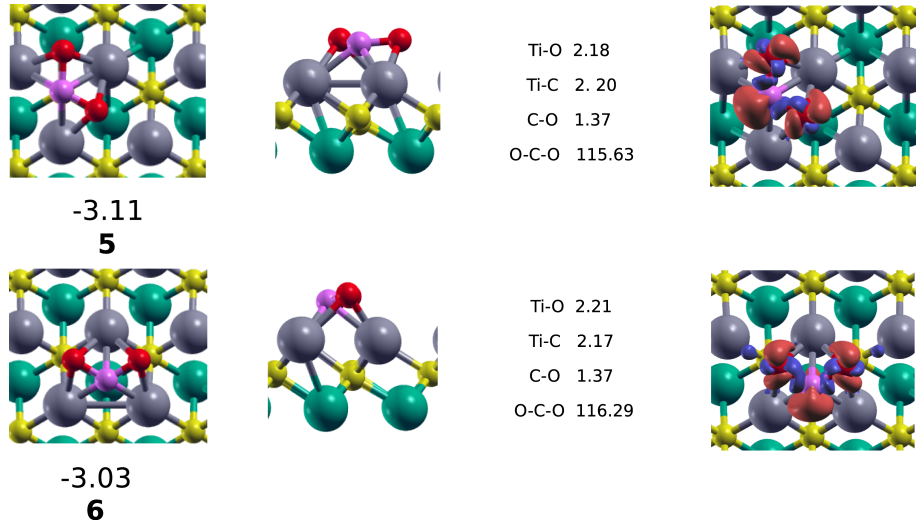


**Figure 4.2:** Stable structures of physisorbed CO<sub>2</sub> on MXene. Adsorption energy (in eV/CO<sub>2</sub> molecule) and important bond lengths (in Å) are given. Grey, green, yellow, pink and red spheres denote top Ti, bottom Ti, C, C and O of CO<sub>2</sub> respectively.

**Chemisorption:** We have obtained two distinct geometries with bent CO<sub>2</sub> (**5** and **6**) as shown in Fig. 4.3. The relative energies for different magnetic configurations suggest that MXene surface is antiferromagnetic even in the presence of adsorbed CO<sub>2</sub>, see Table B.1 in appendix. Out of these, the configuration **5** where C (O atoms) of CO<sub>2</sub> is on hcp (fcc) site(s) is the most stable one having an adsorption energy of -3.11 eV. The O and C atoms of the adsorbed molecule are at a distance of 2.18 Å and 2.20 Å respectively from the nearest surface Ti atom. Similar structure was reported by Garcia et. al. [98] for non magnetic MXene. In this adsorption configuration the C-O bond length and O-C-O bond angle is changed to 1.37 Å and 115.63° respectively from that of the gaseous CO<sub>2</sub>. From BADER charge analysis, we see a charge transfer of 1.81 e<sup>-</sup> from the surrounding

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surface Ti atoms to  $\text{CO}_2$ , mainly concentrated on C and O atoms, which elongates the C-O bond and causes structural changes in  $\text{CO}_2$ . The other bent geometry (**6**) is 0.08 eV higher in energy with  $\text{C}_{\text{CO}_2}$  at fcc and  $\text{O}_{\text{CO}_2}$  at hcp sites yet possessing similar geometry (C-O bond length of 1.37 Å, O-C-O bond angle of 116.29°, Ti-O and Ti-C bond lengths of 2.21 Å and Ti-C 2.17 Å respectively) with a charge transfer of 1.85  $e^-$  to  $\text{CO}_2$ . On Ti-terminated  $\text{TiC}\{111\}$ , a similar structure of chemisorbed  $\text{CO}_2$  was obtained with an adsorption energy of -3.05 eV, charge transfer of 1.79  $e^-$  and C-O bond length of 1.21 Å [100].

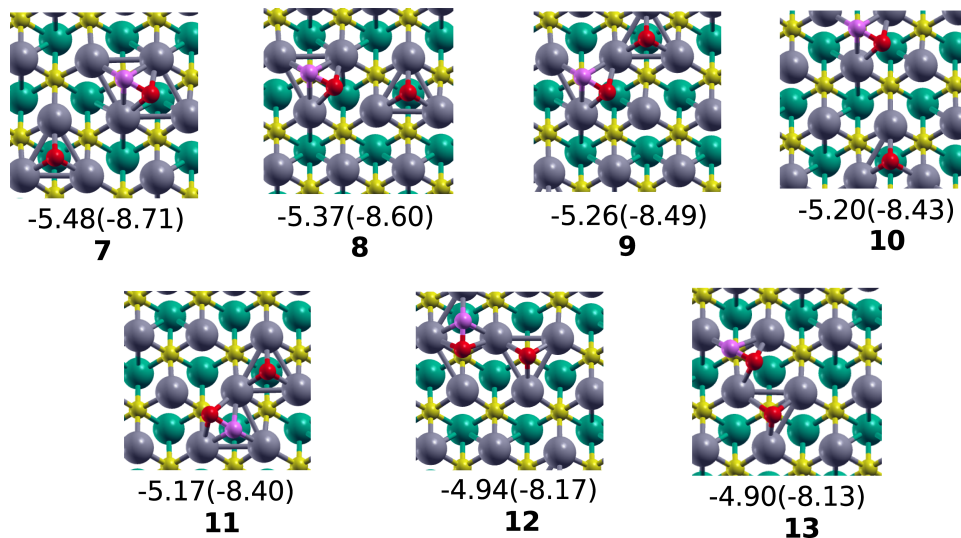


**Figure 4.3:** Stable structures of activated  $\text{CO}_2$  on MXene with the corresponding charge transfer plot (right panel). Adsorption energy (in eV/ $\text{CO}_2$  molecule), important bond lengths (in Å) and bond angles (in °) are given. Grey, green, yellow, pink and red spheres denote top Ti, bottom Ti, C, C and O of  $\text{CO}_2$  respectively.

### 4.3.1.2 CO and O co-adsorption

CO and O bind to the hollow sites rather than top site due to increased free electrons in these sites [107], as in case of chemisorbed  $\text{CO}_2$ . We obtain a set of structures (**7-10**), which are thermodynamically more stable ones, with C of CO binding at hcp and O occupying fcc site. Among these, depending on the average separation between CO and O on the surface (3.12 Å -5.21 Å) adsorption energies vary from -5.48 eV to -5.20 eV, as shown in Fig. 4.4. In these cases C-O bond length varies from 1.36 Å -1.38 Å, which is elongated with respect to gas phase CO (1.13 Å). For the other geometries (**11-13**) we find that the adsorption energy corresponding to the binding sites of  $\text{C}_{\text{CO}}$  and O atoms follow as: fcc and fcc < fcc and hcp < hcp and hcp respectively.



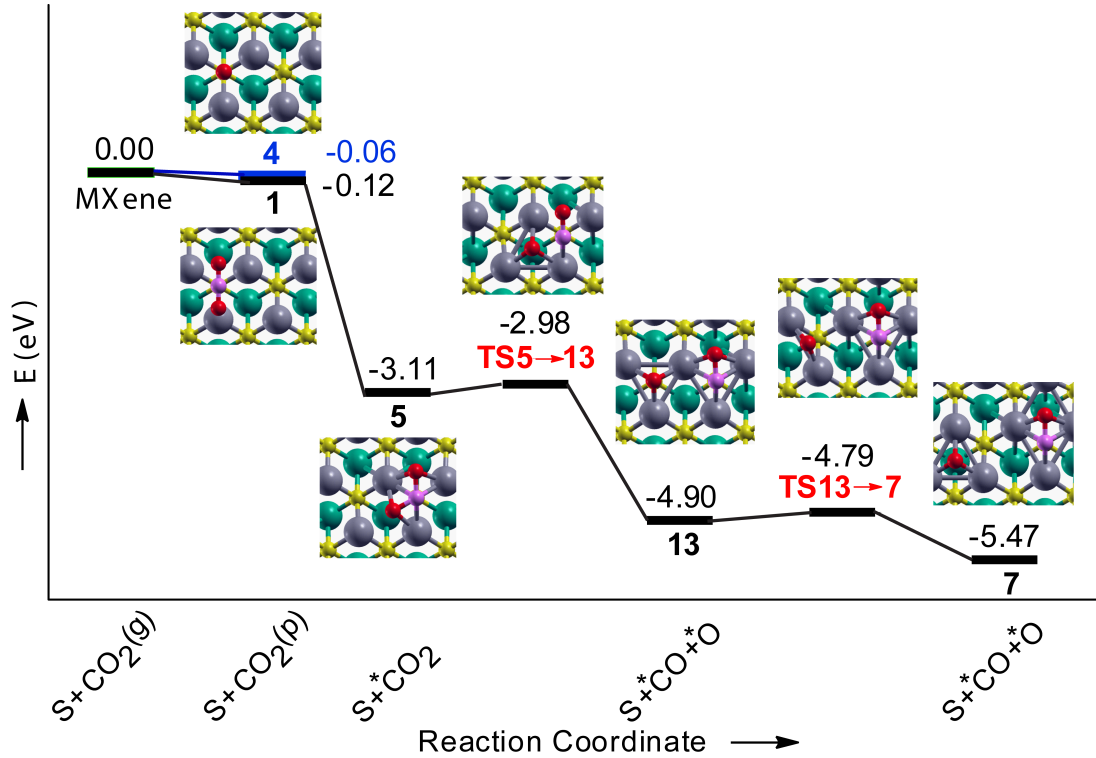


**Figure 4.4:** Stable structures of CO and O co-adsorbed on MXene. Adsorption energy with respect to CO<sub>2</sub> (CO and O<sub>2</sub>) in eV/CO<sub>2</sub> molecule (CO + O<sub>2</sub>) are given. Grey, green, yellow, pink and red spheres denote top Ti, bottom Ti, C, C and O of CO<sub>2</sub> respectively.

#### 4.3.1.3 CO<sub>2</sub> dissociation

CO<sub>2</sub> dissociation to CO and O on MXene was studied using the NEB method to understand the reaction mechanism and barriers associated with them. Here, we have performed this on all the physisorbed CO<sub>2</sub> cases (1-4) discussed earlier, which serve as the reactants, and dissociate it to the most stable dissociated CO<sub>2</sub> cases 7 or 11. We have studied a two-step dissociation process, going from physisorbed to the dissociated case via a chemisorbed bent CO<sub>2</sub> structure. The different cases and the investigation of the path for each of them are detailed in the following discussions.

**1→5→13→7:** Here we have considered path connecting 1 to 7 via 5 and 13. The reaction energy profile along with the geometries of the initial state (IS), transition state (TS) and final state (FS) for this case is shown in Fig. 4.5. In the first step, i.e., from physisorbed to bent geometry, there is no barrier involved. This is observed for all the cases discussed below. We see CO<sub>2</sub> getting systematically activated and turning into bent structure 5, as it moves closer to the substrate. In Ti-terminated TiC{111} also, there was no barrier associated with the activation of CO<sub>2</sub> [100]. From 5, one of the C-O bonds breaks leading to an elongation in that bond by 0.31 Å and the dissociated O atom moves to the fcc site in **TS5→13** with a barrier of 0.13 eV. In this geometry, O-Ti (2.14 Å) and C<sub>CO</sub>-Ti (2.08 Å) bond lengths decrease while that of O<sub>CO</sub>-Ti (2.26 Å) increases with respect to 5. O<sub>CO</sub> atom further diffuses through a bridge site to reach hcp site in 13, going



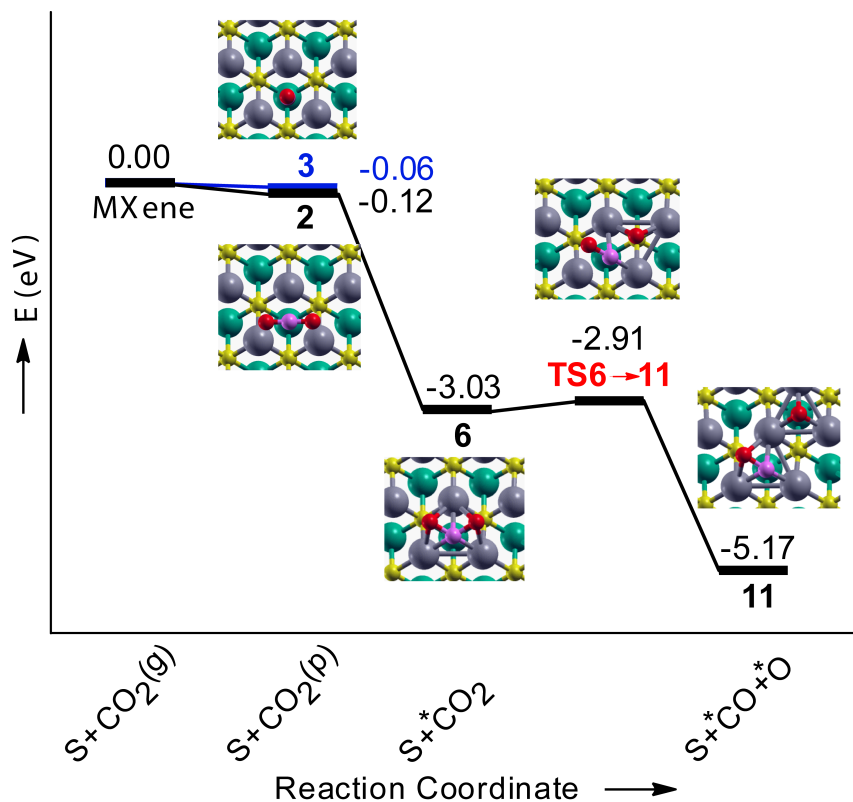
**Figure 4.5:** Reaction energy profile for CO<sub>2</sub> dissociation on MXene for paths **1**→**5**→**13**→**7** and **4**→**5**→**13**→**7**.

downhill in energy reflecting on the repulsive interaction of CO and O. Further diffusion to reach fcc site, as in **7**, is achieved by crossing a bridge site (TS**13**→**7**) with 0.11 eV barrier.

**4**→**5**→**13**→**7**: Here we have studied a pathway connecting vertical geometry **4** to **7**. The activation of CO<sub>2</sub> takes place without any barrier (blue line in Fig. 4.5) and results in bent geometry **5**. The reaction then proceeds further to the stable geometry **7** as discussed in the previous paragraph.

**2**→**6**→**11**: From horizontal geometry **2**, a barrierless activation leads to **6** in this case. As discussed earlier, in **6** C<sub>CO<sub>2</sub></sub> atom and O<sub>CO<sub>2</sub></sub> atoms occupy fcc and hcp sites respectively while in **7** C<sub>CO</sub> atom binds at hcp and O<sub>CO</sub> at the fcc site. Hence moving C<sub>CO<sub>2</sub></sub> from bent structure in **6** to the dissociated one in **7** for the second step requires either a rotation of CO or migration of CO on the surface, both of which involve breaking of C and O bonds with the top site. This, we expect to have a significant energy cost because of strong interaction of surface with CO, making it unlikely to happen. Hence here our final geometry is **11**, 0.31 eV higher in energy than **7**, where the position of CO is maintained. In this path we

see that C-O bond breaking happens upon overcoming a barrier of 0.12 eV as O occupies the hcp site (**TS6**→**11** in Fig. 4.6), increasing C-O distance to 1.67 Å. In **TS6**→**11** O-Ti is 2.07 Å, C<sub>CO</sub>-Ti is 2.15 Å and O<sub>CO</sub>-Ti is 2.31 Å. Further, by diffusing across the bridge site it occupies the fcc site (**11**), going downhill in energy.



**Figure 4.6:** Reaction energy profile for CO<sub>2</sub> dissociation on MXene for paths **2**→**6**→**11** and **3**→**6**→**11**.

**3**→**6**→**11**: In this path, only the initial few steps differ for **3** with respect to **2**, otherwise the trend follows the same in the sense that there is a barrierless gradual activation happening till it becomes **6** and further **6** to **11** happens as explained earlier (blue line in Fig. 4.6).

### 4.3.2 CO<sub>2</sub> dissociation on Ti<sub>2</sub>C{100} surface

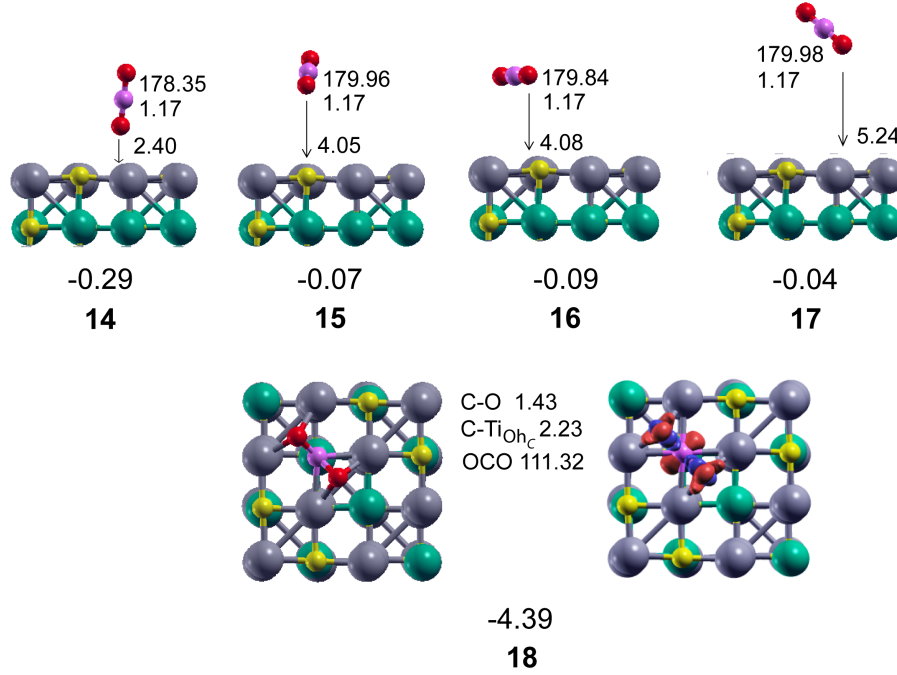
In this section we have discussed the dissociation of CO<sub>2</sub> on Ti<sub>2</sub>C{100} surface and compared the results with those obtained on MXene.

### 4.3.2.1 CO<sub>2</sub> adsorption

In the physisorbed geometries, the adsorbate retained its O-C-O bond angle of 180.00°. The vertical alignment of CO<sub>2</sub> over top Ti atom (see **14** in Fig. 4.7) with Ti-O distance of 2.40 Å was found to be slightly favoured (-0.29 eV) than the horizontal CO<sub>2</sub> alignment over top Ti (**15**) or top C atoms (**16**) (see Fig. 4.7). In these two horizontally aligned cases the adsorbate is located approximately 4.00 Å away from the surface, resulting in negligible adsorption energy of -0.07 eV and -0.09 eV respectively as shown in Fig. 4.7. The chemisorption on these sites ultimately led to a bent or dissociated CO<sub>2</sub> moiety adsorbed on the nearby Oh<sub>C</sub> site. The adsorption energy of a physisorbed structure where the CO<sub>2</sub> is aligned horizontally above Oh<sub>C</sub> sites around 5.24 Å away as in **17** is found to be -0.04 eV. In its chemisorbed state CO<sub>2</sub> binds to the surface with a bent geometry as shown in **18** having an adsorption energy of -4.39 eV (Fig. 4.7). The O-C-O bond angle is changed to 111.24° and the C-O bond length is elongated to 1.43 Å, which is 0.25 Å longer than in the physisorbed system (1.17 Å). Similar to MXene, here also the BADER charge analysis shows a surface to adsorbate charge transfer of 2.25 e<sup>-</sup> with a charge accumulation of 0.87 e<sup>-</sup> at the O<sub>CO<sub>2</sub></sub> atoms and 0.51 e<sup>-</sup> at the C<sub>CO<sub>2</sub></sub> atom (see Fig. 4.7 for the charge transfer plot). The charge transfer in {100} surface is slightly higher than that in MXene (1.81 e<sup>-</sup>), which resulted in a stable structure (-4.39 eV) with an elongated C-O bond (1.43 Å) with respect to **5** (1.37 Å and -3.11 eV). In a previously reported CO<sub>2</sub> adsorption study on TiC{001} surface shows the adsorption energy corresponding to the bent structure as -0.83 eV, much higher than that in **18**, with a C-O bond length of 1.29 Å and O-C-O angle of 122.6°. Here, O atoms are located above the top Ti sites rather than the bridge site as in **18** [108]. In these physisorbed and chemisorbed configurations **14** - **18**, spin-polarization brings negligible changes in the CO<sub>2</sub> adsorption energy, which further supports the non-magnetic nature of the {100} surface (see Table B.2 of the appendix).

### 4.3.2.2 CO and O co-adsorption

To locate the most favourable sites for the co-adsorption of O<sub>CO<sub>2</sub></sub> and CO<sub>CO<sub>2</sub></sub> moiety on the {100} surface, we have optimized eight different configurations (see geometries **19-26** in Fig. 4.8). We found that the most favourable site for O<sub>CO<sub>2</sub></sub> and CO<sub>CO<sub>2</sub></sub> co-adsorption is one of the Oh<sub>C</sub> sites. In **19**, the C<sub>CO<sub>2</sub></sub> interacts with the Ti atom below the Oh<sub>C</sub> site and the corresponding bond length is 2.24 Å. The C-O<sub>CO<sub>2</sub></sub> bond length is 1.46 Å, the longest among the eight configurations considered in this study. We note that this C-O bond length is also longer than that observed in MXene. This is the most stable

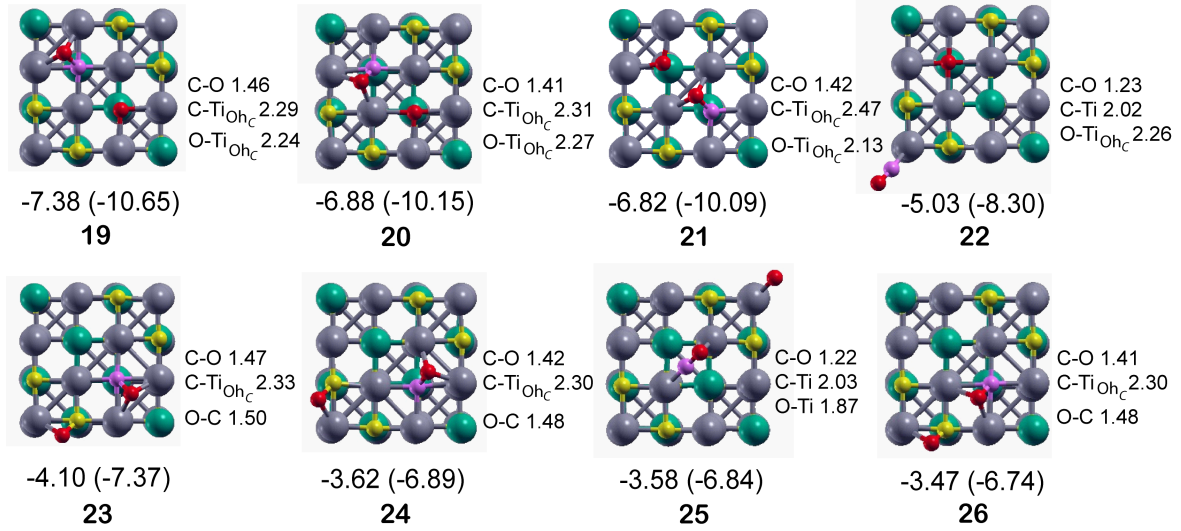


**Figure 4.7:** Physisorbed and chemisorbed CO<sub>2</sub> configurations on Ti<sub>2</sub>C{100} surface along with the charge transfer plot; adsorption energy (in eV/CO<sub>2</sub> molecule), important bond lengths (in Å) and bond angles (in °) are given. Grey, green, yellow, pink and red spheres denote top Ti, Ti in second layer, C, C and O of CO<sub>2</sub> respectively.

geometric configuration we found in our study with a co-adsorption energy of -7.38 eV. The adsorption energy of the remaining configurations range from -3.47 eV to -6.88 eV. In these cases also the lowest energy configurations have co-adsorption occurring at the Oh<sub>C</sub> sites. In **20** and **21** the CO<sub>CO2</sub> and O<sub>CO2</sub> species adsorb at the Oh<sub>C</sub> sites, leading to an adsorption energy which is very close to that of **19**, -6.88 eV and -6.82 eV respectively. In addition, the interaction of CO moiety with the Oh<sub>C</sub> site also affect the adsorption energy. In these two systems (**20** and **21**), the O atom is making a bond distance of 2.27 Å and 2.13 Å respectively and the C<sub>CO</sub> to Ti (below Oh<sub>C</sub> site) bond length is 2.31 Å and 2.47 Å respectively. The C-O bond length is slightly shorter in these two cases, 1.41 Å and 1.42 Å respectively.

#### 4.3.2.3 CO<sub>2</sub> dissociation

Similar to MXene, we have explored the CO<sub>2</sub> dissociation barrier through similar path. The most stable physisorbed structure **14**, where the adsorption taking place at the top Ti sites, leads to a chemisorbed geometry as in **25** (-3.58 eV), relatively unstable co-



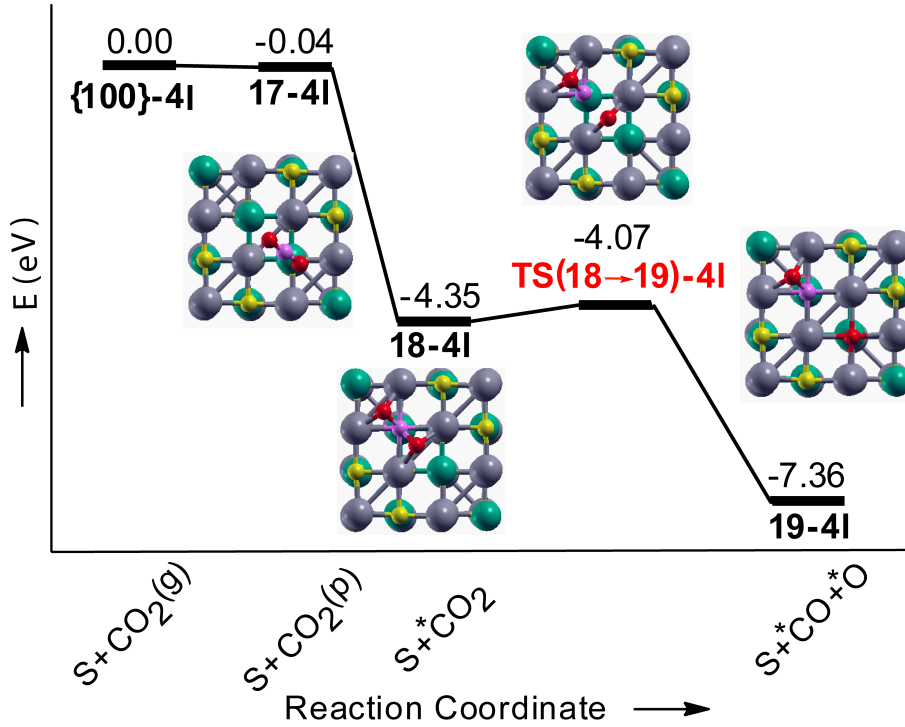
**Figure 4.8:** Co-adsorption of CO and O on  $\text{Ti}_2\text{C}\{100\}$  surface; adsorption energy with respect to  $\text{CO}_2$  (CO and  $\text{O}_2$ ) (in eV/ $\text{CO}_2$ ), important bond lengths (in Å) and bond angles (in °) are given. Grey, green, yellow, pink and red spheres denote top Ti, Ti atom in second layer, C, C and O of  $\text{CO}_2$  respectively.

adsorbed structure with respect to **19**. Since **19** is the most stable chemisorbed structure, we have considered path for the same connecting **17** via bent structure **18**. For the transition state search, we considered a relatively small 4-layer  $\text{Ti}_2\text{C}\{100\}$  model surface. The physisorbed and chemisorbed structures were fully optimised. To assess the model reliability, we have compared the adsorption energies of the most stable geometric variants **18**, **19** and **20** with the 4-layer model. The  $E_{\text{CO}_2-\text{ads}}$  for the **18-4l** (-4.35 eV), **19-4l** (-7.36 eV) and **20-4l** (-6.86 eV) geometric configurations were found to be very close to its 8l analogues (-4.39 eV, -7.38 eV and -6.88 eV respectively).

For the path **17-4l**→**18-4l**→**19-4l**, the first step involving the chemisorption of  $\text{CO}_2$  to form an activated  $\text{CO}_2$  with O-C-O bond angle of  $111.34^\circ$  (**18-4l**) was found to be barrierless whereas the same for  $\text{TiC}\{001\}$  surface required a barrier of 0.25 eV [100]. Subsequent dissociation of bent  $\text{CO}_2$  required an activation barrier of 0.28 eV, 0.15 eV higher than that of MXene. An illustration of the path from physisorbed **17-4l** to the dissociated **19-4l** via an activated chemisorbed **18-4l** is shown in Fig. 4.9. The C-O bond length in transition state **TS(18-19)-4l** is 1.80 Å, longer by 0.37 Å from **18-4l** and 0.12 Å from the **TS5**→**13**. Here the dissociated O atom occupies the bridge site between two top Ti atoms with a Ti-C distance of 1.94 Å.

A comparison of the adsorption energies and geometries of  $\text{CO}_2$  in the chemisorbed state, amount of charge transfer and  $\text{CO}_2$  dissociation barriers on these two surfaces are





**Figure 4.9:** CO<sub>2</sub> dissociation path on Ti<sub>2</sub>C{100} surface.

interesting. From our study, we find that the adsorption energy of the activated CO<sub>2</sub> is correlated with the amount of charge transferred to CO<sub>2</sub>, i.e., higher the amount of charge transfer (more is the reduction of CO<sub>2</sub>) stronger is the CO<sub>2</sub> adsorption energies. In order to associate these behaviour observed on the two surfaces with their properties, we have computed the work function ( $\phi$ ) of the clean surfaces. We note that the redox property of a surface is connected to its work function. Usually surfaces with low  $\phi$  typically acts as good electron donors. For our case, we find that the Ti terminated MXene surface ( $\phi=4.13$  eV) has a higher work function compared to that of the {100} surface ( $\phi=3.79$  eV); hence, one observes a larger amount of charge transfer to CO<sub>2</sub> from the {100} surface than from MXene.

In addition to the difference in adsorption energies of CO<sub>2</sub> on these surfaces, their adsorption geometries, in particular, the orientation of the chemisorbed CO<sub>2</sub> molecule on the two surfaces are significantly different. While on the MXene the O-C-O plane is almost parallel to the surface, on Ti<sub>2</sub>C{100} the O-C-O plane is normal to that of the surface, with the O atoms pointing away from the surface. Apart from this the C-O bond length for the latter is about 0.07 Å longer than that observed for CO<sub>2</sub> on MXene. While the elongation in the C-O bond length can be understood from the accumulation of larger

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amount of electron on the LUMO of the bent CO<sub>2</sub> molecule on the {100} surface, the differences in the orientation arises from the surface structure. In case of MXene, the surface has only Ti atoms and CO<sub>2</sub> can only bind on the top-Ti or the hollow sites. Hence it prefers a flat orientation to maximize the interaction with the substrate. This is also corroborated by the fact that when we try a vertical adsorption configuration of bent CO<sub>2</sub> on this surface, after geometry optimization, it prefers to go back to the horizontal one. In contrast, on Ti<sub>2</sub>C{100} surface there are rows of intrinsic C vacancies. Hence the bent CO<sub>2</sub> molecule adsorbs vertically such that the C of CO<sub>2</sub> can easily occupy the C vacancy. This results in an enhancement of the coordination number of the Ti atoms around the vacancy occupied by CO<sub>2</sub>, which usually prefers to be in an octahedral coordination with the C atoms (for eg. in TiC), thereby stabilizing the system. To verify this we have decomposed the  $E_{CO_2-ads}$  into two parts: (a) the deformation energy ( $E_{def}^X$ ,  $X$  can be surface or CO<sub>2</sub>) and (b) the interaction energy ( $E_{int}$ ).  $E_{def}^X$  is a measure of the energy cost for the surface and the CO<sub>2</sub> molecule to undergo deformation to bind together and is given by the energy difference between the total energies of  $X$  in the chemisorbed geometry and in its relaxed geometry.  $E_{int}$  is the energy gained due to the binding of the CO<sub>2</sub> with the surface and is given by:

$$E_{int} = E_{CO_2+surf} - E_{CO_2}^d - E_{surf}^d \quad (4.3)$$

where  $E_X^d$  is the energy of  $X$  (CO<sub>2</sub> or surface) in the same geometry as in the chemisorbed state. While the  $E_{def}^{surface}$  is small,  $E_{def}^{CO_2}$  on both the surfaces are quite large, 4.61 eV (5.87 eV) on MXene (Ti<sub>2</sub>C{100}). However,  $E_{int}$  is much larger than the deformation energy for both the cases. Albeit on MXene the surface-CO<sub>2</sub> interaction energy is about -7.91 eV, on the Ti<sub>2</sub>C{100} surface, as envisaged, it is significantly larger than on MXene and is about -10.44 eV. We note that similar large values of  $E_{int}$  have also been observed for CO<sub>2</sub> adsorption on different polar surfaces of ZnO [109]. The large value of  $E_{int}$  compared to the deformation energy results in thermodynamically favourable adsorption of CO<sub>2</sub> on these surfaces.

Based on the trends observed in the adsorption energies and geometries, it would be expected that the reaction barrier to be smaller on the {100} surface compared to the MXene. However, instead, as mentioned above, the barrier on the {100} surface is about 0.15 eV higher than that observed on MXene. This can be attributed to the fact that the barrier associated with this reaction is primarily due to the diffusion of the dissociated O atom. We find that since the {100} surface tends to bind adsorbates strongly, and



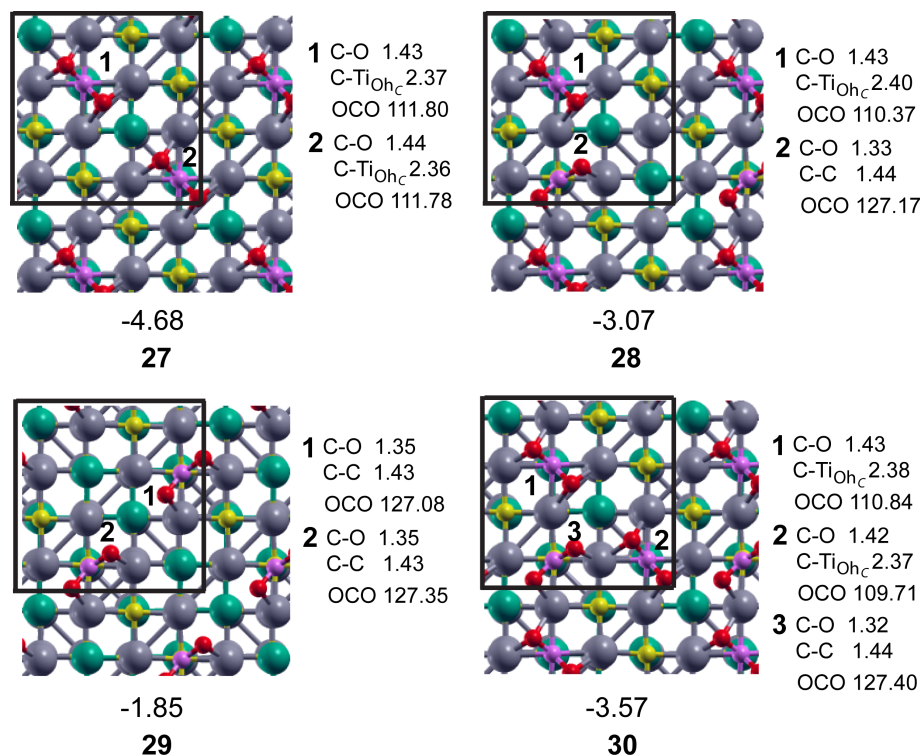
the diffusion of O involves breaking of surface-O bonds, the reaction barrier is higher on the  $\{100\}$  surface. We note that since the reaction rate depends exponentially on the reaction barrier, slight changes in the reaction barrier can result in significant changes in the reaction rate. For example, in our case, a difference of about 0.15 eV in the reaction barrier on the two surfaces will result in reaction rates that differ by a factor of four hundred at room temperature.

### 4.3.3 Coverage dependent chemisorption of CO<sub>2</sub>

It is well known that CO<sub>2</sub> chemisorption depends on the CO<sub>2</sub> coverage and the nature of the surface on which it is adsorbing. For example, previous studies have shown that while on calcium oxide (CaO), cerium oxide (CeO<sub>2</sub>) and hydroxylated Kaolinite (001) surfaces the CO<sub>2</sub> adsorption energy increases as a function of coverage [110–112], on TiO<sub>2</sub> the adsorption energy decreases slightly from 1/12 to 1/2 monolayer (ML) and increases further as the coverage is increased [113]. Therefore in order to understand the effect of CO<sub>2</sub> coverage and the nature of the surfaces on the former's adsorption energy, we have computed the adsorption energies per CO<sub>2</sub> molecule on both the surfaces by placing up to three CO<sub>2</sub> molecules (up to four in the case of MXene) on the surface. As discussed below, this is the minimum number of CO<sub>2</sub> molecules the surface can adsorb before the interaction between them becomes repulsive.

**Ti<sub>2</sub>C{100} surface:** Two CO<sub>2</sub> molecules on the Ti<sub>2</sub>C{100} surface amounts to a coverage of 0.25 ML (Here 1 ML is defined as the density of the surface Ti atoms). On this surface the CO<sub>2</sub> molecules can adsorb either at the Oh<sub>C</sub> defect sites or on the Ti-C (top Ti or C sites) surface. Hence for adsorption of 2 CO<sub>2</sub> molecules there are three possibilities based on the adsorption sites, namely, both CO<sub>2</sub> adsorbing either at the Oh<sub>C</sub> site or on the surface and one CO<sub>2</sub> at the surface and the second one at the Oh<sub>C</sub> site. 27-29 of Fig. 4.10 shows the lowest energy configurations of the above three possibilities along with their adsorption energies. The other configurations considered are shown in Fig. B.2 of appendix. We find that the case where both the CO<sub>2</sub> molecules are bound to the Oh<sub>C</sub> site (27) has the lowest adsorption energy (-4.68 eV/CO<sub>2</sub> molecule). We note that this value of adsorption energy is 0.33 eV lower than that observed when a single CO<sub>2</sub> molecule binds to one such site (as in 18-41 where the  $E_{CO_2-ads}^1$  is -4.35 eV). The distance between two closest O atoms of the two CO<sub>2</sub> molecules is about 3.70 Å. The adsorption of second CO<sub>2</sub> molecule brings negligible changes in the CO<sub>CO<sub>2</sub></sub> bond length and OCO bond angle of first CO<sub>2</sub> and both the adsorbed CO<sub>2</sub> molecules are found to have similar bond param-

eters (see Fig. 4.10). The increase in the adsorption strength compared to that of one CO<sub>2</sub> molecule suggests that the interactions between two CO<sub>2</sub> molecules is attractive in nature. Similar to the case of one CO<sub>2</sub> molecule adsorption, we find that there is a charge transfer of 2.25 e<sup>-</sup> from the surface to each of the CO<sub>2</sub> molecules (Figure B.3 of appendix).



**Figure 4.10:** Chemisorption of two (27-29) and three CO<sub>2</sub> molecules (30) on Ti<sub>2</sub>C{100} surface; adsorption energy (in eV/CO<sub>2</sub> molecule), important bond lengths (in Å) and bond angles (in °) are given. Grey, green, yellow, pink and red spheres denote top Ti, Ti in second layer, C, C and O of CO<sub>2</sub> respectively.

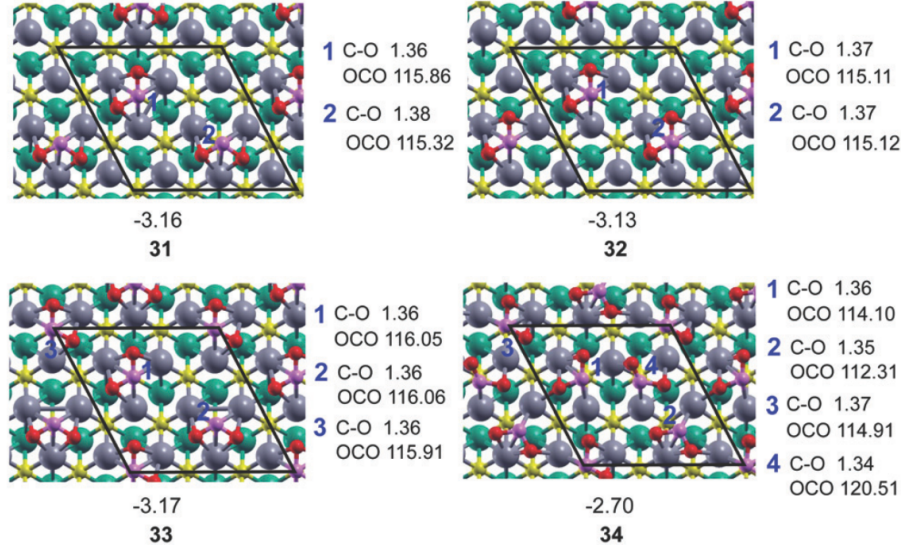
For the case where one CO<sub>2</sub> is at the Oh<sub>C</sub> site while the other one is on the surface, in the lowest energy configuration, the CO<sub>2</sub> adsorption energy is -3.07 eV/CO<sub>2</sub> molecules (28 of Fig. 4.10). The total energy gained by the system by adsorbing 2 CO<sub>2</sub> molecule in this case (-6.14 eV, i.e. twice the adsorption energy of CO<sub>2</sub> molecule) is about 0.07 eV lower in energy than the sum of the adsorption energies when the two adsorbed CO<sub>2</sub> molecules are infinitely apart from each other (i.e. sum of  $E_{CO_2-ads}^1$  of a CO<sub>2</sub> molecule on the surface (-1.86 eV) and at the Oh<sub>C</sub> site (-4.35 eV)). The minimum distance between two CO<sub>2</sub> molecules in this case is 2.76 Å. This indicates that at these distances the interactions between CO<sub>2</sub> molecules become repulsive in nature. The other configurations for this combination of adsorption sites are shown in Fig. B.2 of appendix. When both the CO<sub>2</sub>

molecule are on the surface, we find that  $E_{CO_2-ads}^2$  is -1.85 eV/CO<sub>2</sub> molecule (**29** of Fig. 4.10). This is same as the adsorption energy of a single CO<sub>2</sub> molecule at the same site. We note that for this case, the smallest distance between the O atoms of two CO<sub>2</sub> molecule is 3.66 Å, which is comparable to that observed for the most stable adsorption configuration on this surface. This implies that in contrast to adsorption of CO<sub>2</sub> molecules at the C-vacancies, on the surface the lateral interactions between the two CO<sub>2</sub> molecules are negligible even though the separation between them are similar.

Upon adsorbing the third CO<sub>2</sub> molecule (0.38 ML) on the surface, we find that it prefers to bind on the surface site rather than at the defect site, as shown in structure **30** of Fig. 4.10, with an adsorption energy of -3.57 eV/CO<sub>2</sub> molecule. The shortest distance between two CO<sub>2</sub> molecules is 2.69 Å (between the O atoms of the second and third CO<sub>2</sub> molecule). Further, we find that all the CO<sub>2</sub> molecules gain electrons from the surface, with the CO<sub>2</sub> molecules at the defect site gaining about 2.16 e<sup>-</sup> each, while that on the surface gains 1.12 e<sup>-</sup>, see Fig. B.3 of appendix.

**MXene:** Similar to that on the Ti<sub>2</sub>C{100} surface we have studied adsorption of up to four CO<sub>2</sub> molecules on MXene. Based on the studies done for adsorption of one CO<sub>2</sub> molecules in Section 4.3.1.1, we have placed the first CO<sub>2</sub> molecule lying horizontally on the surface at the centre of a (3 × 3) surface unit cell, with the C on the hcp site and the two O atoms occupying the neighbouring fcc sites. The second CO<sub>2</sub> molecule (amounting to a coverage of 0.22 ML) has been positioned in one of the remaining eight vacant hcp sites. Moreover, we have also considered different relative orientations of the two CO<sub>2</sub> molecules. In particular, we have considered cases where the two CO<sub>2</sub> molecules are either parallel to each other or the second CO<sub>2</sub> is rotated by 120° (based on the symmetry of the surface), either clockwise or anti-clockwise, with respect to the central one. All the possible configurations are shown in Fig. B.4 of appendix. In the most stable configuration, we find that the second CO<sub>2</sub> molecule prefers to occupy the hcp site along the long diagonal of the unit cell, with the O atoms on two fcc sites (**31** of Fig. 4.11). Moreover, in this configuration the molecule is rotated by about 120° with respect to the first one. For this case the adsorption energy is -3.16 eV/CO<sub>2</sub> molecule. We note that, the CO<sub>2</sub> adsorption energy in this case is slightly lower than the adsorption energy of -3.11 eV/CO<sub>2</sub> molecule observed for one CO<sub>2</sub> molecule adsorption. This suggest a weak attractive interaction of about 0.10 eV between two CO<sub>2</sub> molecules on this surface. Moreover, similar to the case of one CO<sub>2</sub> adsorption, here also we find that each of the CO<sub>2</sub> molecules gains about 1.74 e<sup>-</sup> each. Additionally, there is another configuration

(32), where the two CO<sub>2</sub> molecules are parallel to each other that is only 0.03 eV higher in energy than the most stable one.

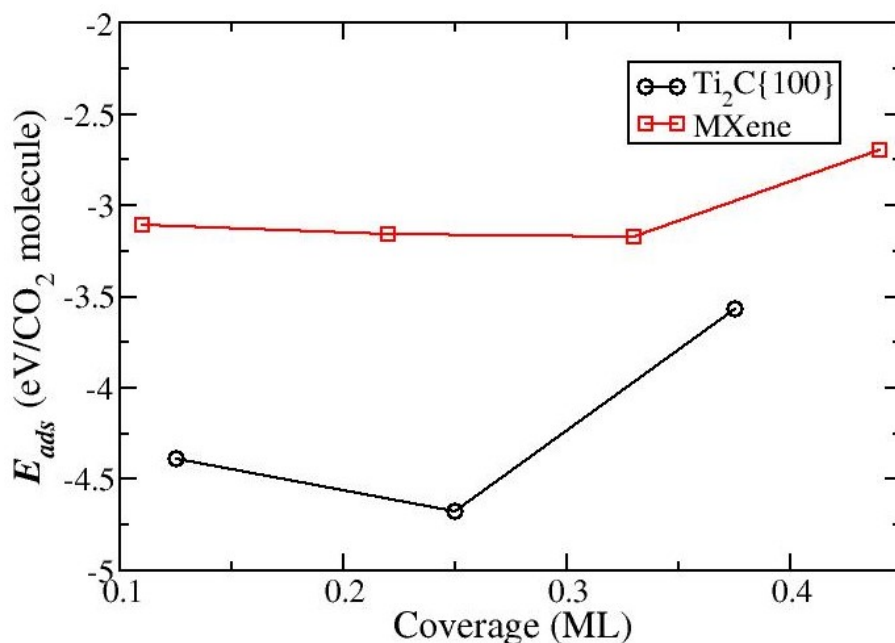


**Figure 4.11:** Chemisorption of two (31-32), three (33) and four (34) CO<sub>2</sub> molecules on MXene surface; adsorption energy (in eV/CO<sub>2</sub> molecule). Grey, green, yellow, pink and red spheres denote top Ti, Ti in second layer, C, C and O of CO<sub>2</sub> respectively.

When three CO<sub>2</sub> molecules (0.33 ML coverage) are adsorbed on this surface, we find that all the molecules occupy the hcp-fcc sites along the long diagonal of the unit cell. Similar to that observed in the case of adsorption of two CO<sub>2</sub> molecule, here also, the relative orientations of the CO<sub>2</sub> molecules are not so important and results in configurations that are very close in energy. In the lowest energy configuration (33), the binding energy is about -3.17 eV/CO<sub>2</sub> molecule and is almost same as that observed when there are two CO<sub>2</sub> molecule on the surface. The similar values of adsorption energies with two and three CO<sub>2</sub> molecules can be understood from the fact that in these two cases, the distance between two CO<sub>2</sub> molecules remain similar. The smallest O-O distances between two CO<sub>2</sub> molecules for both the cases (i.e. two and three CO<sub>2</sub>) molecules remain similar and is about 3.50 Å. Charge transfer calculations shows that each of the CO<sub>2</sub> molecules gains about 1.69 e<sup>-</sup> from the surface.

Upon adsorbing 4 CO<sub>2</sub> molecules, i.e. at a CO<sub>2</sub> coverage of 0.44 ML, we observe a decrease in adsorption energy. In the most stable configuration, three CO<sub>2</sub> molecules occupy the long diagonal fcc sites, as observed earlier, and the fourth one occupies an off diagonal site. The adsorption energy for this case is -2.70 eV/molecule and a charge transfer of around 1.52 e<sup>-</sup> is observed from the surface to each of the CO<sub>2</sub> molecules. The

weakening of the adsorption strength suggests that the CO<sub>2</sub> molecules are now close to each other (smallest distance between two CO<sub>2</sub> molecules is about 2.74 Å). Unlike earlier cases, here the relative orientation of the CO<sub>2</sub> molecules does affect the adsorption energy, which is why the next two stable geometries differ by 0.08 eV from each other (see Fig. B.4 of appendix for the other geometric variants with 3 and 4 CO<sub>2</sub> molecules and Fig. B.5 for the charge transfer plots).



**Figure 4.12:** Coverage dependent adsorption energy of CO<sub>2</sub> on Ti<sub>2</sub>C{100} and MXene.

Fig. 4.12 shows a comparison of the coverage dependence chemisorption of CO<sub>2</sub> on these two surfaces. The plot shows that the two surfaces behave in very different ways. At all the coverages considered in this study, the CO<sub>2</sub> adsorption is weaker on MXene compared to that on Ti<sub>2</sub>C{100}. For the {100} surface, the C-vacancies play a very crucial role. This results in significantly strong binding of CO<sub>2</sub> molecules, even at an increased coverage, compared to that observed on MXene. Moreover, on MXene, till a coverage of 0.33 ML, the lateral interactions of CO<sub>2</sub> molecules are weakly attractive and then becomes repulsive in nature. In contrast on Ti<sub>2</sub>C{100} surface, first the interactions are attractive and once the C-vacancy site starts filling up, the interactions become repulsive in nature. Further, till the coverages considered in this study, we find that on Ti<sub>2</sub>C{100} surface there is clustering of the CO<sub>2</sub> molecules around the defect sites. In contrast, on MXene, the CO<sub>2</sub> molecules are more or less uniformly distributed on the surface.

## 4.4 Conclusions

To understand the role of surface composition and structure on  $\text{CO}_2$  adsorption and dissociation we have studied the same on  $\{100\}$  surface of cubic  $\text{Ti}_2\text{C}$  and MXene. Our results show that on both these surfaces,  $\text{CO}_2$  shows a barrier less chemisorption with a preferential binding on the  $\{100\}$  surface. The reason for this has been attributed to the lower work function and hence greater reducing capability of the  $\{100\}$  surface compared to that of MXene. However, our calculations show that dissociation of  $\text{CO}_2$  to CO and O has a lower barrier on MXene. Our results suggest that the MXene is the better candidates for  $\text{CO}_2$  dissociation. A coverage dependent adsorption studies on both the surfaces show that while on the  $\text{Ti}_2\text{C}\{100\}$  surface the  $\text{CO}_2$  molecules tend to cluster around the C vacancies, on MXene, they are more uniformly spread.

## Chapter 5

### **Economic bimetallic AuCu<sub>3</sub> tetramer on Ti<sub>2</sub>CO<sub>2</sub> MXene as an efficient catalyst for CO oxidation: A theoretical prediction**

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#### **5.1 Introduction**

Conversion of carbon monoxide (CO) to carbon dioxide (CO<sub>2</sub>) is not only an important reaction but also one of the most studied ones. CO is fatal for living organisms, and thus oxidation to CO<sub>2</sub> is often regarded as the simplest and most effective way to abate it. Automobile exhaust contributes to 90 % of the CO release in big cities and 50 % in ground-level ozone [114]. Therefore, three-way catalytic converters were launched in 1974 (United States) to carry out CO oxidation to CO<sub>2</sub> along with NO<sub>x</sub> to N<sub>2</sub> and hydrocarbon also to CO<sub>2</sub> [115]. CO oxidation is also beneficial in proton-exchange membrane fuel cells (PEMFC) [116] in order to purify traces of CO present in the incoming hydrogen stream. Moreover, it is considered a model reaction in the field of heterogeneous catalysis by virtue of its simplicity.

Catalysis by gold on oxide support attracted attention especially in this domain, after Haruta discovered the incredible activity of gold nanoparticles on TiO<sub>2</sub> for low temperature CO oxidation [117]. However, some of the disadvantages associated with this catalyst are the high price limiting its commercial use and also steep decline in activity due to instability against sintering [118]. A detailed mechanistic study of this reaction shows different mechanisms for active or reducible (for example, TiO<sub>2</sub>) and inactive support (SiO<sub>2</sub>, for instance). For active case, the support or the metal-support interface is responsible for adsorbing and breaking O<sub>2</sub> as Au particles have a high barrier for O<sub>2</sub> activation and dissociation [119]. One way to overcome this limitation for inactive support is to make



it bimetallic by doping the cluster with an oxophilic metal like Cu, which as we see in literature, also addresses the issues with stability in addition to cost.

Compared to monometallic counterpart, a bimetallic catalyst offers flexibility in enhancing the activity or selectivity of a desired reaction by tweaking the composition. For example, Pt-Ir clusters when used in petrochemical industries for refining process to produce high-octane-number hydrocarbons like toluene and xylenes, overcame the limitations set by Pt cluster of performance degradation due to carbonaceous residues and Ir cluster of formation of undesired light gaseous substances [120]. This alteration of properties brought by the combination of metals is attributed to either ligand or strain effect of electronic origin or to ensemble effect of geometric origin. Often what we observe is a cumulative effect resolving which is cumbersome.

Experimentally, Au-Cu nanoparticles on  $\text{Al}_2\text{O}_3$  enhanced the selectivity of CO oxidation over  $\text{H}_2$  oxidation through electronic effect in all the temperature ranges and is extremely useful for PEMFC as discussed earlier [121]. Another report on  $\text{TiO}_2$  nanotubes shows that Au-Cu synergy enhanced the activity and lowered the conversion temperature of the bimetallic catalyst compared to pure Au counterpart [122]. Along similar lines, upon depositing the bimetallic clusters on SBA-15 (mesoporous silica), the nanoparticles so-formed were stable and had significantly higher activity than the monometallic due to reduced particle size and improved oxygen activation by gold [123]. A computational study detailing the mechanism of Au-Cu nanocluster on  $\text{CeO}_2(111)$  concluded a bifunctional mechanism for the system where  $\text{O}_2$  and CO prefers to bind at Cu-rich and Au-rich sites of the cluster respectively [124]. This intelligent engineering avoided the competition of CO and  $\text{O}_2$  species for the binding sites and thereby increased the overall rate by five orders of magnitude compared to pure Au.

Thus, deriving motivation from the forementioned investigations, we study CO oxidation on Au-Cu bimetallic tetramers. These model catalytic systems are the smallest ones that can shed light on the fluxionality (involving three-dimensional and two-dimensional geometries) of the nanoclusters. As support, we have used  $\text{Ti}_2\text{CO}_2$  MXene. MXenes have advantages of large surface area with a composition similar to transition metal carbides, which are rigorously employed for heterogeneous catalysis. These attributes have introduced MXenes in recent times to the field of heterogeneous catalysis, both as a catalyst and support for metal catalysts in the form of single atom, nanoparticles or monolayers. For CO oxidation, single atom catalyst (SAC) of Ti/ $\text{Ti}_2\text{CO}_2$  [125] and Zn/def- $\text{Mo}_2\text{CO}_2$  [126] were used and they performed the conversion with a barrier of 0.25 eV and 0.15 eV re-



spectively. Also when  $\text{Cu}_3$  was deposited on perfect and defective  $\text{Mo}_2\text{CO}_2$ , the cluster maintained its stability in defective cases and CO oxidation on the same was found to proceed by overcoming a barrier of 0.72 eV [127].

The remainder of the chapter is laid out as follows: the details of the methods employed in our computations are given in section 5.2. In section 5.3, we show and analyse the results of our computations. Finally, in section 5.4, we draw conclusions.

## 5.2 Computational Details

Spin-polarised calculations were carried out using plane wave-based density functional theory (DFT), as implemented in the Quantum ESPRESSO [53] software. The electron-ion interactions were described by using scalar relativistic ultrasoft pseudopotentials [54]. In this pseudopotential, the valence configuration of the elements considered is as follows: Ti ( $3s^2 3p^6 3d^2 4s^2$ ), Cu ( $3d^{10} 4s^1$ ), O ( $2s^2 2p^4$ ), C ( $2s^2 2p^2$ ), and Au ( $5d^{10} 6s^1$ ). We have used kinetic energy cutoffs of 55 Ry and 480 Ry for wavefunction and charge density respectively. The electron-electron exchange-correlation functional was described using the spin-polarized generalized gradient approximation as parameterized by Perdew-Burke-Ernzerhof (GGA-PBE [55]). Since GGA-PBE functionals do not describe van der Waals interaction, we have used semi empirical Grimme's DFT-D2 correction [128].

For the study of the clusters in gas phase they were placed in a cubic box that ensures a vacuum of 15 Å in all three directions to minimize the fictitious interactions between the periodic images. To study the clusters on support, they were deposited on a (4×4)  $\text{Ti}_2\text{CO}_2$  supercell. This ensured a minimum distance of 9 Å along the XY direction. A vacuum separation of minimum 13 Å was used along Z direction for this system.

To speed up convergence we have used Marzari-Vanderbilt [63] smearing with a smearing width of 0.007 Ry. For the calculations of the support and the clusters on the support we have performed Brillouin zone (BZ) integrations using a  $3 \times 3 \times 1$  k-point grid. For the isolated cluster BZ integrations were done at  $\Gamma$  point.

The binding energy of the isolated cluster is given by,

$$E_b^{Au_nCu_m} = (E_t^{Au_nCu_m} - nE_t^{Au} - mE_t^{Cu})/(n + m), \quad (5.1)$$

where  $E_t^{Au_nCu_m}$ ,  $E_t^{Au}$  and  $E_t^{Cu}$  are the total energy of  $\text{Au}_n\text{Cu}_m$  cluster, Au and Cu atom respectively, and  $n$  and  $m$  denote the number of Au and Cu atoms in the cluster. Mixing energy, the energy released/absorbed in forming the bimetallic cluster from the pure ones,

## Chapter 5

provides a comparison between clusters of same size but compositions. It is defined as,

$$E_{mix} = E_b^{Au_nCu_m} - \frac{n}{n+m} E_b^{Au_y} - \frac{m}{n+m} E_b^{Cu_y}, \quad (5.2)$$

where  $y = n + m$ ,  $E_b^{Au_nCu_m}$ ,  $E_b^{Au_y}$  and  $E_b^{Cu_y}$  is the binding energy of  $Au_nCu_m$ ,  $Au_y$  and  $Cu_y$  cluster respectively. A negative value of  $E_{mix}$  indicates that the mixed clusters are thermodynamically more stable than the pure ones.

Binding energy of the cluster on  $Ti_2CO_2$  is given by,

$$E_b^{Au_nCu_m/Ti_2CO_2} = (E_t^{Au_nCu_m/Ti_2CO_2} - E_t^{Ti_2CO_2} - nE_t^{Au} - mE_t^{Cu}), \quad (5.3)$$

and adsorption energy of the cluster on  $Ti_2CO_2$  is given by,

$$E_{ads}^{Au_nCu_m/Ti_2CO_2} = (E_t^{Au_nCu_m/Ti_2CO_2} - E_t^{Ti_2CO_2} - E_t^{Au_nCu_m}). \quad (5.4)$$

Adsorption energy of a species X adsorbed on  $Au_nCu_m/Ti_2CO_2$  is defined as,

$$E_{ads}^{X/Au_nCu_m/Ti_2CO_2} = E_t^{X/Au_nCu_m/Ti_2CO_2} - E_t^{Au_nCu_m/Ti_2CO_2} - E_t^X, \quad (5.5)$$

where  $E_t^{X/Au_nCu_m/Ti_2CO_2}$ ,  $E_t^{Au_nCu_m/Ti_2CO_2}$ ,  $E_t^X$  is the total energy of species X adsorbed on  $Au_nCu_m/Ti_2CO_2$ ,  $Au_nCu_m/Ti_2CO_2$  and species X.

In order to map the reaction profile and accurately determine activation energy, we have used climbing image nudged elastic band (CI-NEB) [64]. Depending on the length of the path, we have used 4-25 images to map the path.

## 5.3 Results and Discussion

### 5.3.1 Bimetallic clusters and the support in gas phase

For the four-atom clusters we have investigated, there are 4 geometries considered; planar structures like rhombus, Y-shaped and square, and three-dimensional tetrahedral structure. The ground state geometry is rhombus for pure  $Cu_4$  cluster with Cu-Cu of 2.42 Å (2.30 Å) for the peripheral (short diagonal) bond (Fig. 5.1 (a)). This matches well with the work of Zhao et. al. i.e., 2.39 Å (2.27 Å) bond length for the peripheral (short diagonal) bond [129]. Similarly, the lowest energy configuration for pure  $Au_4$  cluster is also a rhombus with long peripheral and short diagonal Au-Au bond lengths of 2.70 Å and 2.65

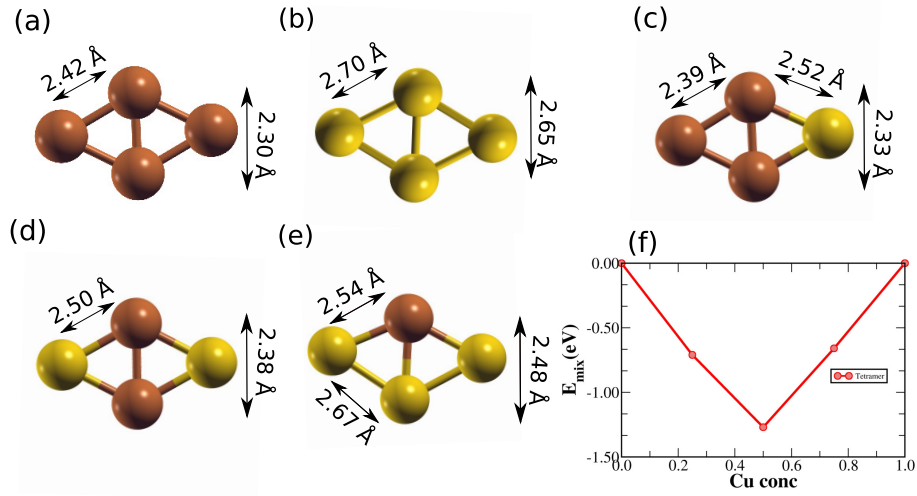
Å respectively (Fig. 5.1 (b)). These match well with the corresponding reported values of 2.69 Å and 2.63 Å [130]. The binding energy for clusters pure Au<sub>4</sub> is -1.55 eV/atom and pure Cu<sub>4</sub> is -1.48 eV/atom.

For the same size bimetallic clusters, three compositions are possible; AuCu<sub>3</sub>, Au<sub>2</sub>Cu<sub>2</sub>, and Au<sub>3</sub>Cu. The most stable configuration of AuCu<sub>3</sub> cluster is a kite having Au atom at one of the low coordination sites (Fig. 5.1 (c)). The Cu-Cu bonds are of length 2.39 Å (peripheral) and 2.33 Å (short diagonal). Each of the Cu-Au bonds is of length 2.52 Å. These values are close to the corresponding bond lengths reported in reference [129] i.e., 2.37 Å for peripheral Cu-Cu, 2.29 Å for short diagonal Cu-Cu and 2.53 Å for Cu-Au bonds).

The Au<sub>2</sub>Cu<sub>2</sub> composition favors rhombical geometry where Cu occupies the high coordination sites. The Au-Cu bonds are 2.50 Å long (2.51 Å [129]), and the single Cu-Cu bond is 2.38 Å long (2.33 Å [129]) (Fig. 5.1 (d)). The most stable Au<sub>3</sub>Cu cluster structure is kite with the Cu atom forming higher number of bonds (Fig. 5.1 (e)). The Au-Cu bond lengths here are 2.48 Å along the short diagonal, and 2.54 Å along the edges, and Au-Au bond length is 2.67 Å along the periphery. Again, the agreement with literature ([129]) is excellent (2.47 Å, 2.54 Å, and 2.71 Å respectively).

Thus for the four-atom bimetallic clusters, all of the compositions favor planar structure as in the monometallic case since Cu is isoelectronic with Au [131] and both having  $nd^{10}ns^1$  configuration. Also, magnetically the ground state is a singlet. This is in accordance with the literature report [131, 132]. Fig. 5.1 (f) shows the plot of mixing energy as a function of Cu concentration. All variants have negative mixing energies, indicating that the Au-Cu alloying is thermodynamically favorable. From the comparison of mixing energies, we find that the order of stability is Au<sub>2</sub>Cu<sub>2</sub> (-1.27 eV) > Au<sub>3</sub>Cu (-0.71 eV) > AuCu<sub>3</sub> (-0.66 eV). This trend correlates directly with the number of Au-Cu bonds in each composition.

Our support, MXene Ti<sub>2</sub>CO<sub>2</sub> has five atomic layers in the order O-Ti-C-Ti-O arranged in an ABCAB pattern in its lowest energy case, as visible in Fig. 5.2 (a) and (b). The unit cell parameter is 3.03 Å with Ti-C bond of length 2.19 Å and Ti-O bond of length of 1.97 Å. These matches excellently with a PBE based DFT-D3 study [133]. In addition, the system is non-magnetic and semiconducting in nature with a band gap of 0.34 eV, in agreement with reference [134].

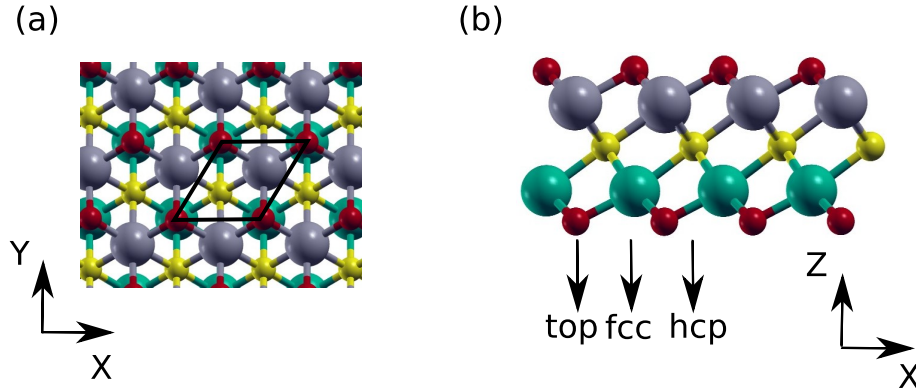


**Figure 5.1:** Lowest energy structures of (a)  $\text{Cu}_4$ , (b)  $\text{Au}_4$ , (c)  $\text{AuCu}_3$ , (d)  $\text{Au}_2\text{Cu}_2$  and (e)  $\text{Au}_3\text{Cu}$  and clusters in gas phase, and (f) plot of mixing energy vs Cu concentration. Golden and brown atoms denote Au and Cu respectively.

### 5.3.2 Bimetallic cluster on support

In this section, we highlight the results that we obtain upon depositing the above clusters on the  $\text{Ti}_2\text{CO}_2$  MXene support. There are three possible adsorption sites on the MXene surface i.e., top of O atom (top site), a hollow site created above the top Ti atom (fcc site), and a hollow site created above the C atom (hcp site) (Refer Fig. 5.2 (b)). For deducing the most favorable cluster/support configuration, we chose the ground state gas-phase rhombus and tetrahedral geometry for each case and placed it on the substrate with Cu/Au atoms above either of these three sites. Additionally, the clusters in rhombus geometry were placed both vertically and horizontally on the support. The interaction of clusters with support can favor three-dimensional geometry, hence we chose the tetrahedron [135]. From all the geometrical variants these considerations gave rise to, below, we delve deep into the lowest energy geometries among them. Other distinct local minimas obtained can be found in Fig. C.1 of appendix.

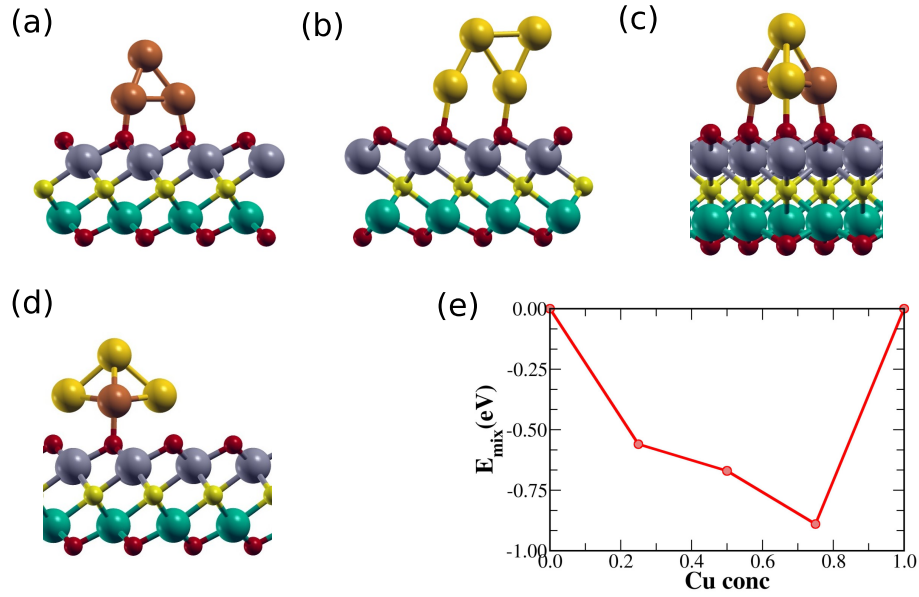
The gas-phase clusters are essentially a control system that depicts the dominant impact of heterometallic Au-Cu bonds in dictating its structure. In comparison on support, we see that the structure of pure metallic clusters is significantly distorted and is decided by a number of factors. In general, the geometry of a cluster on support is decided by the balance of support-metal and metal-metal interactions.  $\text{Cu}_4$  cluster is reported to assume a tetrahedral geometry on  $\text{Ti}_2\text{CO}_2$  MXene thereby forming 3 Cu-O bonds [135] of length



**Figure 5.2:** Lowest energy structure of  $\text{Ti}_2\text{CO}_2$  MXene in (a) top view and (b) side view. Red, grey (green), and yellow spheres denote O, Top Ti (bottom Ti), and C atoms respectively.

1.89 Å. This is because a Cu atom adsorbs on this MXene releasing 1.85 eV energy, which is lower than Cu-Cu interaction in the isolated dimer (-1.05 eV). With dispersion correction, adsorption energy is -3.56 eV and there is a slight elongation in Cu-Cu bonds to a maximum of 2.45 Å at the base triangle (Fig. 5.3 (a)). Herein, we note that on  $\text{TiO}_2(110)$  also,  $\text{Cu}_4$  adopts a tetrahedral geometry forming three Cu-O bonds (of length 2.01 Å and 2.12 Å) with an adsorption energy of -3.60 eV [136]. However, rhombus and tetrahedron  $\text{Cu}_4$  are isoenergetic on hydroxylated  $\text{Al}_2\text{O}_3$  with former being 0.02 eV lower in energy. Binding occurs via two -OH groups and an O atom (contrary to our case) releasing an energy of 1.96 eV [137].

In stark contrast,  $\text{Au}_4$  cluster has a distorted rhombus geometry linking the support through two Au-O bonds (2.12 Å and 2.18 Å) in a vertically aligned fashion with an adsorption energy of -2.08 eV, suggesting weaker binding to the support than  $\text{Cu}_4$  (Fig. 5.3 (b)). This is a direct consequence of Au-Au (binding energy is -1.14 eV for dimer) being stronger than Au-O bond (adsorption energy of Au atom on MXene is -0.63 eV). This leads to a longer Au-Au bond (2.88 Å) at the bottom, and slightly longer peripheral Au-Au bonds of length 2.61 Å (2.72 Å) at the sides (top) from the gas phase. This is in fact a peculiarity of gold clusters, demonstrated on  $\text{Au}_n$  ( $n=1-7$ ) clusters deposited on perfect  $\text{MgO}(100)$  surface, where small Au clusters prefer upright configurations over horizontal isomers because bonds in this favourable orientation are stronger [138]. On  $\text{MgO}(100)$ , the ground state (distorted rhombus) of  $\text{Au}_4$  resembles closely with our study with Au-O bonds (2.18 Å and 2.28 Å) and an associated adsorption energy -1.75 eV [139]. Upright Y-shaped configuration, though more distorted, is observed in both  $\text{TiO}_2(101)$  and  $\text{ZrO}_2(101)$  surfaces with corresponding adsorption energies of -2.39 eV and -3.81

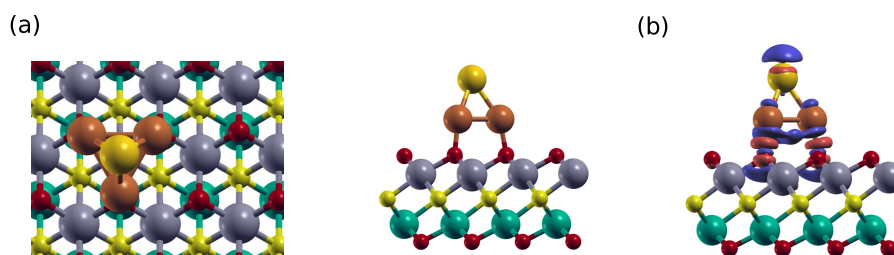


**Figure 5.3:** Lowest energy structures of (a) Cu<sub>4</sub>, (b) Au<sub>4</sub> (c) Au<sub>2</sub>Cu<sub>2</sub>, and (d) Au<sub>3</sub>Cu clusters deposited on Ti<sub>2</sub>CO<sub>2</sub> MXene, and (e) plot of mixing energy vs Cu concentration. In this and the following figures, golden, brown, red, grey (green), and yellow spheres denote Au, Cu, O (Ti<sub>2</sub>CO<sub>2</sub>), Top Ti (bottom Ti), and C atoms respectively.

eV [140].

In the bimetallic clusters, there is a structure dependence on composition, as illustrated in Fig. 5.3 (c) and (d). We obtain a tetrahedral geometry with triangle Cu-Cu-Cu positioned above the fcc site in the case of AuCu<sub>3</sub> and it has an adsorption energy of -3.41 eV (Fig. 5.4 (a)). From isolated cluster, the Cu-Cu bond length increases to 2.51 Å, Cu-Au maintains 2.52 Å and the Cu-O bond formed is 1.87 Å long (very close to Cu<sub>4</sub> cluster). The ground state remains tetrahedral for Au<sub>2</sub>Cu<sub>2</sub> (adsorption energy = -2.23 eV) with each atom in the base triangle Cu-Au-Cu occupying the top site and the triangle resides over the fcc site (Fig. 5.3 (c)). Compared to the ground state gas phase cluster, the bond lengths of apical Au-Cu (basal Au-Cu) increase to 2.55 Å (2.62 Å), Cu-Cu increases to 2.52 Å and the newly formed Au-Au bond is of length 2.68 Å. Further Au-O and Cu-O bonds resemble that of corresponding pure clusters. For Au<sub>3</sub>Cu, the ground state is an oblique kite conformer binding to the surface O atom with Cu atom in a bond of length 1.91 Å and -2.31 eV adsorption energy. Au-Au bonds maintain the same length, diagonal (peripheral) Au-Cu elongates to 2.56 Å (2.55 Å) (Fig. 5.3 (d)), in compared with gas phase cluster.

The composition-dependent geometric variants we obtain are essentially a transition



**Figure 5.4:** Lowest energy structure of (a) AuCu<sub>3</sub> (top view and side view) on Ti<sub>2</sub>CO<sub>2</sub> MXene along with the corresponding charge transfer isosurface with isovalue of 0.003 electron/Å<sup>3</sup> (b). In (b), red isosurfaces show accumulation and blue one show depletion of charges.

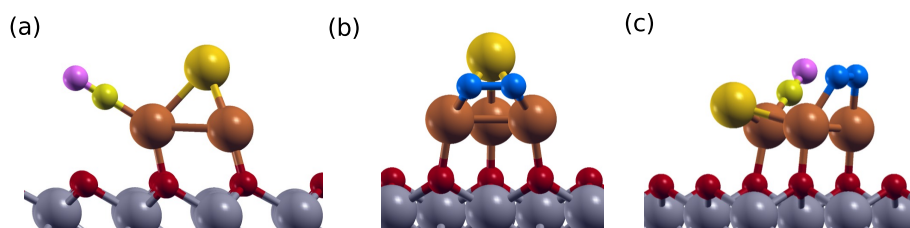
going from one pure composition to the other i.e., from Cu<sub>4</sub> tetrahedron, increasing the substitution of Au leads to the minimas favoring less three-dimensional tetrahedral geometry to more planar structure like in the Au<sub>4</sub> scenario. As previously discussed, the mixing energy was calculated in order to pin down the dependence of stability on the constitution. As Fig. 5.3 (e) shows, the trend of stability has completely changed from the gas phase; now it follows AuCu<sub>3</sub> (-0.89 eV) > Au<sub>2</sub>Cu<sub>2</sub> (-0.67 eV) > Au<sub>3</sub>Cu (-0.56 eV). This is not accredited to the number of the heterometallic bonds as in the gas phase but stems from the fact that Cu-O has a higher strength of bond compared to Au-O, as we stated previously in this section.

Amongst the clusters of different composition considered in this study, since AuCu<sub>3</sub> is the most stable cluster on Ti<sub>2</sub>CO<sub>2</sub>, we have studied CO oxidation on this supported cluster going forward. Bader analysis on this system shows a transfer of 0.29 e<sup>-</sup> and 0.37 e<sup>-</sup> from Au and Cu atom to O atom respectively. This is consistent with the electronegativity of each element from the Pauling scale. As evident in Fig. 5.4 (b), the charge transfer is concentrated on the Cu-O bonds. Pure Cu<sub>4</sub> cluster on Ti<sub>2</sub>CO<sub>2</sub> MXene is reported to have the bottom Cu atoms electron-deficient by 0.48 e<sup>-</sup> and top Cu almost neutral [135]. The positively charged top atom in our case arises from the heterometallic Au-Cu bond and can be beneficial since cationic gold plays a major role in CO oxidation on MgO, TiO<sub>2</sub>, CeO<sub>2</sub>, etc [141].

### 5.3.3 CO and O<sub>2</sub>: individual and co-adsorption

For the catalyst system, AuCu<sub>3</sub>/Ti<sub>2</sub>CO<sub>2</sub>, top sites (Au/Cu) and bridge sites (Au-Cu/Cu-Cu) are available for adsorption of any species. CO adsorption was tried both end-on and side-on on these sites to deduce the minimum energy geometry. The binding of CO





**Figure 5.5:** Optimized structures for (a) CO, (b) O<sub>2</sub> and (c) CO and O<sub>2</sub> co-adsorption on AuCu<sub>3</sub>/Ti<sub>2</sub>CO<sub>2</sub>. In this and the following figures pink and blue spheres denote O (CO) and O (O<sub>2</sub>) atom respectively.

happens unanimously end-on through C atom, as observed for Au-Cu bimetallic surfaces and isolated clusters [142, 143]. Out of all possible configurations we have tried, upon relaxation, we obtain two different scenarios; one where the cluster remains tetrahedral and the other where it dissociates to Cu atom and Cu-Cu-Au triangle. CO can bind to the Au/Cu atom in the former case while it binds to the dissociated Cu atom in the latter situation. The former case (where cluster remains intact and CO is adsorbed on Cu atom) is the most stable one here with an adsorption energy of -1.26 eV and has zero magnetic moment. CO binds to the tetrahedral cluster via C-Cu bond of length 1.85 Å and C-O of distance 1.14 Å, as in Fig. 5.5 (a). The C-O bond length is close to the gas phase molecule (1.13 Å). A similar configuration was obtained for Cu<sub>3</sub>/Mo<sub>2</sub>CO<sub>2</sub>(defective) system with an adsorption energy of -1.57 eV [127] and on isolated Cu<sub>4</sub> cluster with C-Cu bond distance of 1.92 Å [142]. Binding to the Cu atom is preferred over the Au atom in tetrahedra by 0.44 eV. The higher energy geometries for this and other cases can be found in Fig. C.2 of appendix.

O<sub>2</sub> can bind side-on as well as end-on, and the most stable case here is side-on adsorption of O<sub>2</sub> using O-Cu bonds at Cu-Cu bridge site (Fig. 5.5 (b)). This happens with the release of -0.83 eV energy. The O<sub>2</sub> bond elongates to 1.35 Å, compared to gas phase 1.23 Å, with a magnetic moment of 1.01  $\mu_B$  (indicative of superoxo bond). The Cu-O bond is 1.97 Å long. This geometry is seen in isolated Cu<sub>4</sub> cluster also [142]. Adsorption energy reported there is -1.24 eV and Cu-O bond length is 1.92 Å long. A stronger activation is observed for Cu<sub>3</sub>/Mo<sub>2</sub>CO<sub>2</sub>(defective), by virtue of adsorption at hollow site created by Cu-Cu-Cu triangle possessing lower adsorption energy of -2.57 eV and longer O-O bond distance of 1.51 Å [127]. This is followed in energy by adsorption via single O-Cu (O-Au) bond which is 0.11 eV (0.43 eV) higher in energy. Upon comparing different CO and

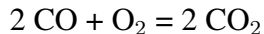


O<sub>2</sub> adsorption geometries, we find that both prefer to bind to Cu atom at the base and CO adsorption is mostly preferred over O<sub>2</sub>.

For co-adsorption of CO and O<sub>2</sub>, the lowest energy structure is quasi-planar kite and aligned horizontally on the MXene with the Au atom slightly pointing up. This cluster structure is not stable otherwise i.e., without either of the adsorbed species. Transitioning between structural isomers in order to achieve the ground state is an inherent feature of small clusters. For example, Au<sub>8</sub> cluster geometry transforms from bicapped octahedral to bicapped trigonal prismatic structure upon O<sub>2</sub> adsorption [144]. Going forward, we also see that this quasi-planar geometry helps in providing good active sites, thus enhancing the activity. CO adsorbs on the Cu site and O<sub>2</sub> horizontally on the Cu-Cu bridge site with an energy of -2.16 eV, similar to that in individual adsorption cases, in Fig. 5.5 (c). C-O and O-O bond lengths are 1.15 Å and 1.38 Å, again very close to individual adsorption. Also, here the co-adsorption energy is more negative compared to the sum of the individual ones, suggesting an attractive interaction between the two.

### 5.3.4 CO oxidation

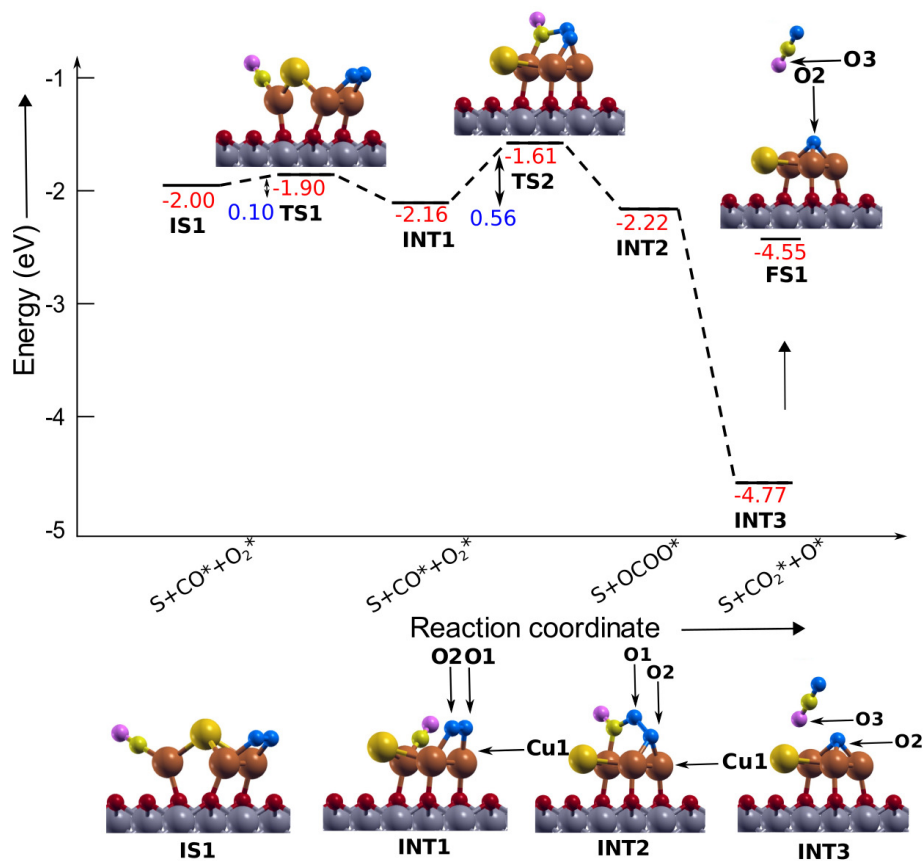
The oxidation of CO to CO<sub>2</sub> is represented by the following chemical reaction:



Thus the full reaction requires two CO molecules to be oxidized to two CO<sub>2</sub>. The oxidation of each CO is hereafter called a reaction cycle. For each of the cycles we have studied three mechanisms for the process of CO oxidation on AuCu<sub>3</sub>/Ti<sub>2</sub>CO<sub>2</sub>; 1) Langmuir-Hinshelwood (LH) mechanism - CO and O<sub>2</sub> adsorbs on the cluster and then interact with each other, 2) Eley-Rideal (ER) mechanism - O<sub>2</sub> interacts with already adsorbed CO on the cluster (since CO has lower adsorption energy), and 3) Mars van Krevelen (MvK) mechanism - CO adsorbed on cluster attacks the O atom from the Ti<sub>2</sub>CO<sub>2</sub> surface. The reaction is carried out in two steps; first, a molecule of CO reacts with O from O<sub>2</sub> in the first cycle and, in the following step the remaining O atom is removed through reaction with another CO (second cycle). In the discussion below, **IS**, **TS**, **FS** and **INT** refer to initial state, transition state, final state and intermediate respectively.

#### 5.3.4.1 First cycle

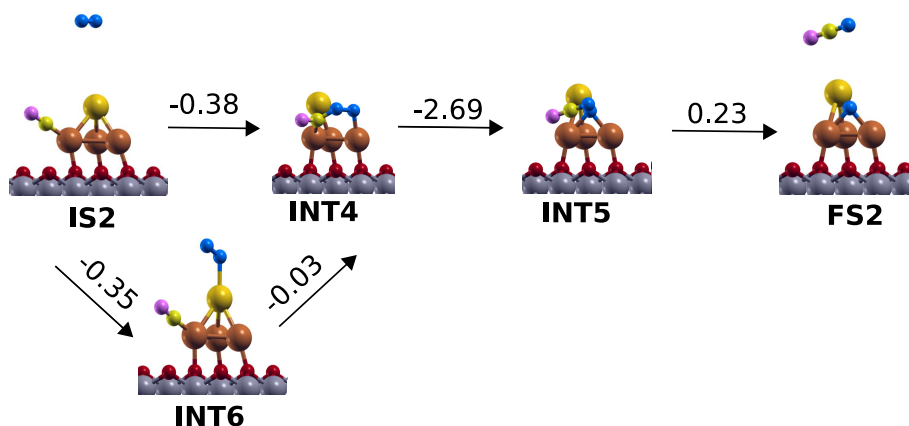
**LH mechanism:** The reaction energy profile for LH mechanism in the first cycle is given in Fig. 5.6. Although LH mechanism usually begins with the most stable CO and O<sub>2</sub>



**Figure 5.6:** First cycle of CO oxidation via LH mechanism on  $\text{AuCu}_3/\text{Ti}_2\text{CO}_2$ . Golden, brown, red, grey, and yellow denote Au, Cu, O, Top Ti, and C atoms respectively. Reference energy is  $2\text{CO} + \text{O}_2 + \text{AuCu}_3/\text{Ti}_2\text{CO}_2$ . Activation energy is given in blue color.

co-adsorption geometry, here we wanted to address the possibility of moving from a tetrahedral geometry (ground state for the cluster/support system) to a rhombus-like geometry upon CO and  $\text{O}_2$  co-adsorption. Hence we start with a less stable but tetrahedral (slightly distorted) CO and  $\text{O}_2$  co-adsorption (**IS1**), which is higher in energy than the most stable (**INT1**) by 0.16 eV. Here, CO and  $\text{O}_2$  are at the same sites as **INT1** and the bond lengths are very close to the most stable case as well as single molecule adsorption case. **IS1** to **INT1** is favored thermodynamically and kinetically via overcoming a barrier of 0.10 eV. The reaction mainly involves movement of Au atom from the center of the tetrahedron to one side along with only change in the alignment of CO. The transition state is breaking of the Au-Cu1 bond (**TS1**). At **INT1**, as CO approaches  $\text{O}_2$ , and it moves vertically by

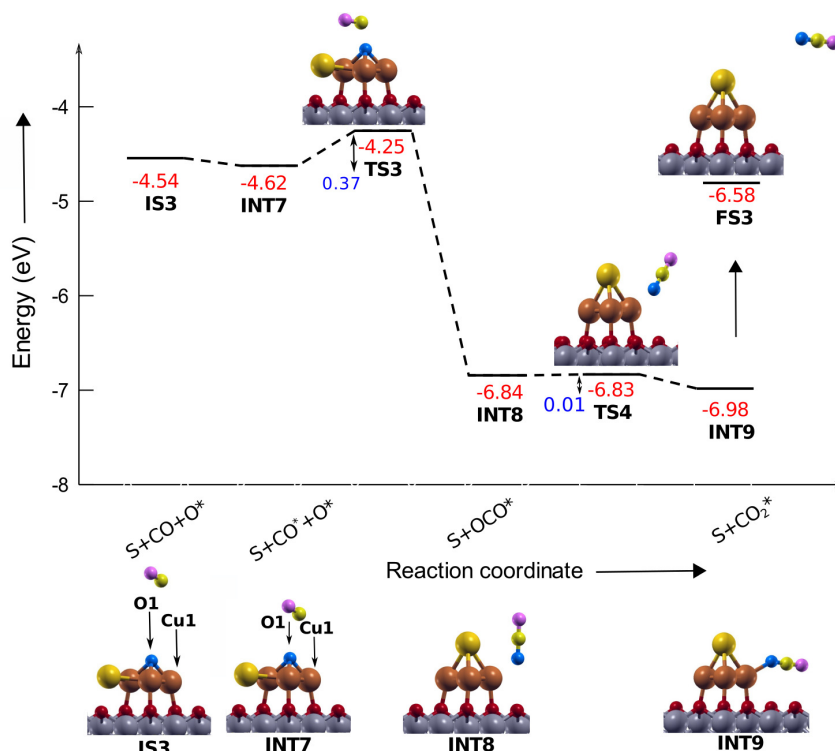
breaking O1-Cu1 bond, an intermediate (**INT2**) is formed, which is 0.06 eV lower in energy than **INT1**. The bond distance O1-O2 increases by 0.12 Å in this structure and a new C-O1 bond of length 1.38 Å is formed between them. This step requires a barrier of 0.56 eV and in the transition state (**TS2**), we observe a simultaneous O1-Cu1 bond breaking and C-O1 bond forming. A similar intermediate over triangular Cu<sub>3</sub> was obtained for Cu<sub>3</sub>/Mo<sub>2</sub>CO<sub>2</sub>(defective) but the lowest barrier obtained for this step was 0.76 eV [127]. On Au nanoclusters also, the triangular Au<sub>3</sub> site helps to stabilize the OCOO intermediate and thus significantly bringing down the barrier of O-O bond breaking [145]. From **INT2**, O1-O2 bond breaks, and as CO<sub>2</sub> forms, O2 occupies the hollow site of Cu1-Cu-Cu in structure **INT3**. This is an exothermic process (releasing 2.55 eV) with no barrier. From here, CO<sub>2</sub> desorbs to vacuum (**FS1**), 0.22 eV endothermically and during this, the distance of O3-O2 increases from 2.97 Å to 5.05 Å. The reaction energy profile for each step in first and second cycle is shown in appendix (Fig. C.4 - Fig. C.16).



**Figure 5.7:** First cycle of CO oxidation via ER mechanism on AuCu<sub>3</sub>/Ti<sub>2</sub>CO<sub>2</sub>. Golden, brown, red, grey, and yellow denote Au, Cu, O, Top Ti, and C atoms respectively. The reaction energies in eV are marked above the arrow for each step.

**ER mechanism:** Fig. 5.7 depicts the first cycle via ER mechanism. In here, reaction happens step wise; initially one species adsorbs which in our system is CO because of its lower adsorption energy, followed by attack from gaseous O<sub>2</sub>. From a distance of 5.00 Å from the cluster (**IS2**), O<sub>2</sub> approaches the CO adsorbed on Cu atom to form a OCOO intermediate (**INT4**), releasing an energy of 0.38 eV. From here CO<sub>2</sub> dissociates and O atom moves to Cu-Cu bridge site in **INT5**, which is 2.69 eV lower in energy. Further desorption of CO<sub>2</sub> to vacuum is an uphill process that requires 0.23 eV energy. Although thermodynamically the whole process is favourable releasing 2.85 eV energy, from the barrier calculations we find that in the first step, as O<sub>2</sub> approaches CO from the

vacuum, it prefers to bind to the cluster (**INT6**) rather than attacking CO directly. Hence ER mechanism is not kinetically feasible for this system. Similarly, MvK mechanism was found thermodynamically not viable from our studies (see Fig. C.3 in appendix) .

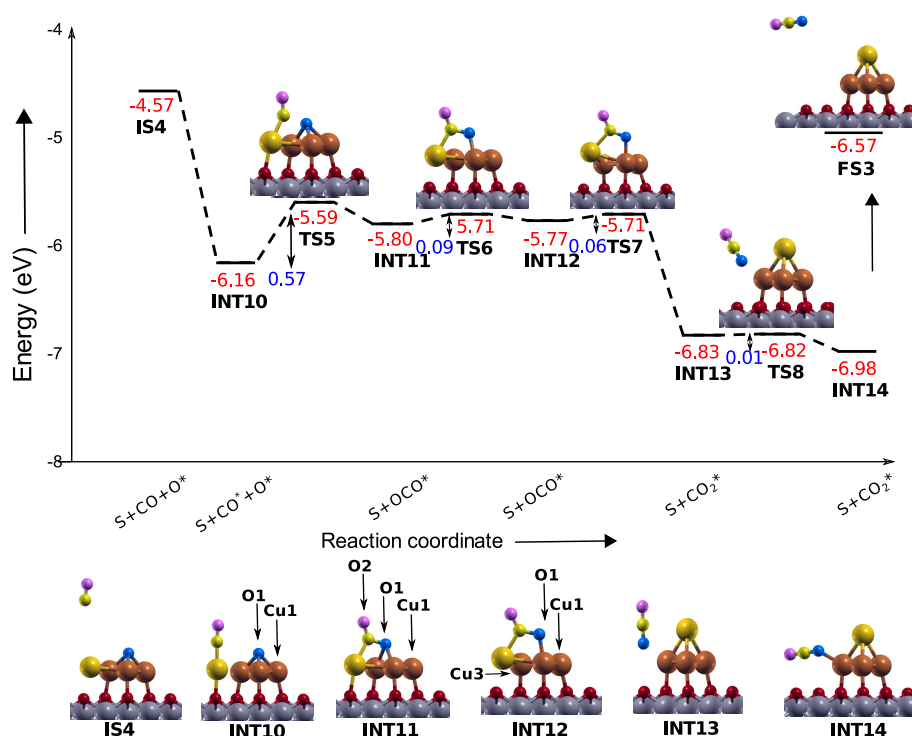


**Figure 5.8:** Second cycle of CO oxidation via ER mechanism on  $\text{AuCu}_3/\text{Ti}_2\text{CO}_2$ . Golden, brown, red, grey, and yellow denote Au, Cu, O, Top Ti, and C atoms respectively. Reference energy is  $2\text{CO} + \text{O}_2 + \text{AuCu}_3/\text{Ti}_2\text{CO}_2$ . Activation energy is given in blue color.

### 5.3.4.2 Second cycle

For the entire reaction of CO oxidation to complete and to regenerate the catalyst, the O atom which remains on the cluster after the first cycle needs to be removed. Here also the process can happen via LH or ER mechanism, hence we are considering both.

**ER mechanism:** For ER mechanism (shown in Fig. 5.8) we have initially the remaining O1 atom, in the hollow site formed by Cu1-Cu-Cu triangle, approached by CO from vacuum, leading to **INT7**, where the C-O1 distance decreases to  $2.85 \text{ \AA}$  compared to  $5.10 \text{ \AA}$  in **IS3**. This structure is lower by  $0.08 \text{ eV}$  and involves a zero barrier reaction. As CO moves closer, O1 elevates from this site and  $\text{CO}_2$  is formed along with a change in cluster



**Figure 5.9:** Second cycle of CO oxidation via LH mechanism on AuCu<sub>3</sub>/Ti<sub>2</sub>CO<sub>2</sub>. Golden, brown, red, grey, and yellow denote Au, Cu, O, Top Ti, and C atoms respectively. Reference energy is 2CO + O<sub>2</sub> + AuCu<sub>3</sub>/Ti<sub>2</sub>CO<sub>2</sub>. Activation energy is given in blue color.

geometry to tetrahedral. However, CO<sub>2</sub> is bounded to the cluster through non-covalent interactions (adsorption energy = -0.30 eV) in a vertical alignment in **INT8**, releasing 2.22 eV energy. The C-O bond length is 1.17 Å in this structure. The transition state is C-O1 bond formation and the barrier associated is 0.37 eV. From **INT8**, CO<sub>2</sub> rearranges to the most stable **INT9** and further desorbs into vacuum. So the entire cycle proceeds exothermically by 2.04 eV with an overall barrier of 0.37 eV.

**LH mechanism:** In LH mechanism, given in Fig. 5.9, CO translates from the vacuum to the O-adsorbed system and binds to Au atom (**INT10**) in a barrierless downhill reaction ( $\Delta E = -1.59$  eV). C-O2 is 1.14 Å, C-O1 is 3.40 Å and Cu1-O1 is 1.92 Å in this configuration. From here, O1 moves to the bridge site as CO moves towards it forming a bent CO<sub>2</sub> intermediate (**INT11**) where C-O1 and C-O2 is of length 1.41 Å and 1.20 Å respectively. This step is uphill by 0.36 eV (and requires activation energy of 0.57 eV) with C-O1 forming and Cu1-O1 breaking simultaneously in **TS5**. Further, CO<sub>2</sub> dissipation requires slight reordering by breaking the Cu3-O1 bond (length of which increases from 2.05 Å to 3.05 Å) in **INT12**, 0.03 eV higher in energy. This transition state (**TS6**) is 0.09

eV higher in energy. From **INT12**, Au atom elevates along with the CO<sub>2</sub> molecule leading to **INT13**, thus restoring the original tetrahedral geometry. The following steps proceed similar as earlier. Thermodynamically, both LH and ER is favorable almost equally ( $\Delta E = -0.04$  eV). Considering the activation energies, we find that LH requires a 0.20 eV higher barrier in comparison with ER for the completion of the second cycle.

Based on our calculations, we observe that while the first CO oxidation on this cluster follows the LH mechanism, the second CO oxidation occurs according to the ER mechanism. The rate limiting step for the first CO oxidation is the formation of the OCOO species and involves a barrier of 0.56 eV. For the second CO the oxidation the barrier is 0.37 eV. Hence, for the complete cycle the maximum barrier that needs to be overcome is 0.56 eV.

To get a better perspective on the performance of the catalyst support system proposed in this work, we compare our results with some of the similar studies carried out on a wide range of systems including single atom catalyst (SACs) and small clusters on perfect and defective oxide support and also metal surfaces. These are shown in Table 5.1. Our computed barriers are almost half of those observed on noble metal surfaces like Pt [146], Pd [147] etc, which serve as a benchmark in this area. The single atom catalysts reported in Table 5.1, namely Ti/Ti<sub>2</sub>CO<sub>2</sub> [125] and Zn/def-Mo<sub>2</sub>CO<sub>2</sub> [148], exhibit lower barrier than our system. However, in SAC stability against agglomeration is an issue [125, 148]. Particularly for Zn/def-Mo<sub>2</sub>CO<sub>2</sub>, we observe that the Zn atom is weakly bound to the support. Amongst the few atoms clusters on different support, those that have barriers smaller than ours are either pure Au clusters or are composed of other precious metals like Pd, Pt, etc. Amongst the Au-Cu bimetallic clusters most of them have larger concentration of Au than Cu. The only exception is that of Au<sub>7</sub>Cu<sub>23</sub> on MgO(100) surface with defect [149] where the CO oxidation barrier is of 0.31 eV. However, we note that the size of this cluster is much larger than the one considered in this study. All other systems have barriers larger than that observed in our system. Hence, we believe it would be interesting to explore the novel catalyst-support system proposed in this study as a cheaper catalyst with moderately low barrier for CO oxidation.

## 5.4 Conclusions

In summary, through DFT based calculations, we propose a novel sub-nanometer few atom bimetallic cluster of AuCu<sub>3</sub> supported on O-terminated Ti<sub>2</sub>C MXene as a catalyst

## Chapter 5

**Table 5.1:** Comparison of catalytic performance of various systems towards CO oxidation. The one in bold is the system proposed in this work.

| System                                                        | A. E.<br>(eV) | Rate Determining step                          | Mechanism | Barrier<br>(eV) |
|---------------------------------------------------------------|---------------|------------------------------------------------|-----------|-----------------|
| <b>AuCu<sub>3</sub>/Ti<sub>2</sub>CO<sub>2</sub></b>          | <b>-3.41</b>  | <b>CO* + O<sub>2</sub>* → OCOO*</b>            | <b>LH</b> | <b>0.56</b>     |
| Ti/Ti <sub>2</sub> CO <sub>2</sub> [125]                      | -7.68         | CO + O <sub>2</sub> * → CO <sub>3</sub> *      | ER        | 0.25            |
| Au <sub>4</sub> /TiO <sub>2</sub> (110) [141]                 | -             | OCO* → CO <sub>2</sub> + O*                    | LH        | 0.38            |
| Pt <sub>2</sub> Au/MgO(100) [150]                             | -2.98         | 2CO + O <sub>2</sub> * → 2CO + 2O*             | ER        | 0.22            |
| Pd <sub>4</sub> Au/TiO <sub>2</sub> (110) [151]               | -3.50         | CO* + 2O* → CO <sub>2</sub> + O*               | ER        | 0.69            |
| RuPt <sub>7</sub> /TiO <sub>2</sub> (101) [152]               | -             | CO* + O <sub>2</sub> * → CO <sub>2</sub> + O*  | LH        | 0.59            |
| Au <sub>7</sub> Cu/TiO <sub>2</sub> (101) [153]               | -0.98         | CO* + O <sub>2</sub> * → CO <sub>2</sub> + O*  | LH        | 0.48            |
| Au <sub>7</sub> Cu <sub>3</sub> /CeO <sub>2</sub> (111) [124] | -             | CO* + O* → CO <sub>2</sub> *                   | ER        | 0.23            |
| Zn/def-Mo <sub>2</sub> CO <sub>2</sub> [148]                  | -1.73         | CO + O <sub>2</sub> * → CO <sub>2</sub> * + O* | ER        | 0.15            |
| Cu <sub>3</sub> /def-Mo <sub>2</sub> CO <sub>2</sub> [127]    | -3.75         | 2CO* + O <sub>2</sub> * → OCOO* + CO*          | bLH       | 0.72            |
| Au <sub>3</sub> /def-CeO <sub>2</sub> (111) [154]             | -6.93         | CO* + O* → CO <sub>2</sub> *                   | MvK       | 0.65            |
| Au <sub>7</sub> Cu <sub>23</sub> /def-MgO(100) [149]          | -6.35         | CO* + 2O* → CO <sub>2</sub> + O*               | ER        | 0.31            |
| Pt(111) [146]                                                 | -             | CO* + O* → CO <sub>2</sub>                     | LH        | 1.05            |
| Pd(111) [147]                                                 | -             | CO* + O* → CO <sub>2</sub>                     | LH        | 0.93            |

for CO oxidation. The first and second cycle proceeds through an LH mechanism and ER mechanism respectively. The rate determining step is the formation of the OCOO species adsorbed on the cluster in the first cycle and involves a barrier of about 0.56 eV. Moreover, compared to the other similar sized catalysts reported in literature, our proposed one is the cheapest catalyst showing excellent catalytic properties. We hope that our study will encourage experimentalist to further explore this catalyst as a plausible candidate for CO oxidation.

## Chapter 6

### Summary and outlook

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To summarise, we have primarily investigated, using first-principles calculations, the performance of different forms of  $\text{Ti}_2\text{C}$  MXene as a catalyst itself and also as a support for ultrasmall bimetallic clusters, for environmentally relevant reactions. Before this investigation, we look into a probable phase transition possible on bare  $\text{Ti}_2\text{C}$  MXene, motivated by a similar transition on transition metal dichalcogenides (TMDs). As the MXene phase changes from 1T to 1H based on the stacking of the atomic layers, we observe remarkably distinct magnetic and electronic properties. We also predict the minimum energy path corresponding to this process. In the following chapter, we examine the role of surface structure in the processes of  $\text{CO}_2$  activation and dissociation on two distinguishable  $\text{Ti}_2\text{C}$  surfaces. Although researchers have explored the effect of transition metal, stoichiometry, surface terminations, etc, this aspect has been overlooked in the literature. Our work shows a noticeable influence of the surface in these reactions as activation is stronger on  $\{100\}$  whereas dissociation is easier on the MXene surface. In the final work chapter, we show a possible new catalytic Au-based bimetallic cluster system for CO oxidation reaction because Au clusters deposited on oxide support are a well-known catalyst for this reaction. For substrate, we have employed O-terminated  $\text{Ti}_2\text{C}$ . Considering the cost, stability, and activity associated with the system, it proves to be a good alternative.

Similar to MXenes, TMDs are a class of quasi-2D material containing three layers of atoms. Two common phases exist in this group, based on the arrangement of these layers, known as 1T and 2H phases. This can lead to polar opposite properties in the material, for instance, 1T-MoSe<sub>2</sub> displayed 100 times better performance in activity and turnover frequency (TOF) in comparison with the 2H phase [155]. In a similar manner, distinct electronic properties corresponding to these phases lead to the metal to insulator phase transition in Group VI TMDs [156]. MXenes can also exist in these two phases. 1T is



the ground state for Ti-based carbides and nitrides while 1H is preferred for Mo-based carbides and nitrides. But being a relatively new class, such studies are scarce in MXenes. In our work on  $\text{Ti}_2\text{C}$  MXene (**chapter 3**), we have explored the electronic, magnetic, and vibrational properties of both structures. The ground state 1T phase exists in an A-type antiferromagnetic state having an intralayer and interlayer same spin and opposite spin coupling respectively. Heisenberg Hamiltonian reveals a stronger intralayer coupling and Monte Carlo (MC) simulations hint at Néel temperature of 517 K. It is a semiconductor of 0.19 eV bandgap. The metastable 1H phase is 1.29 eV/formula unit higher in energy than 1T. In addition, the spins are ferromagnetically coupled at the intralayer and interlayer. MC simulations predict that the magnetism is maintained till 503.8 K. Interestingly, 1H is a half-metallic structure with a spin-up bandgap of 0.86 eV. The dynamical stability of both of these phases was also established. The transition of 1T to 1H first involves a magnetic crossover with an energy of 0.03 eV. Further, a layer of Ti atoms glides over the other in [11] direction until both layers completely overlap. This step needs to overcome a barrier of 1.45 eV. Although, this transition is possible, future work can look into ways of achieving it through experiments, as the change in properties associated is extremely relevant.

The surface layer of  $\text{Ti}_2\text{C}$  MXene contains only Ti atoms while the  $\{100\}$  surface of bulk  $\text{Ti}_2\text{C}$  has Ti atoms and C atoms in addition to C vacancies. Through the calculations performed in **chapter 4**, we observe that due to a lower work function of  $\{100\}$  surface, higher activation of  $\text{CO}_2$  takes place on this surface. Nevertheless, this process cost no energy in either case. The process of  $\text{CO}_2$  dissociation to CO and O is more favorable on MXene, almost half the barrier as that of  $\{100\}$  surface. In this study, however, we have not included the possibility of other gaseous molecules being present. From a practical point of view, the catalyst applied for  $\text{CO}_2$  conversion must perform unaffected if not better in presence of gaseous compounds, like water vapor, nitrogen, and sulfur oxides in the flue gas. Of these, water is particularly interesting since it was found to exhibit promotional effects by reducing the barrier in reactions like  $\text{CO}_2$  hydrogenation to methanol [157]. An investigation in this regard carried out for  $\text{CO}_2$  activation showed promising results on Ti-terminated  $\text{TiC}\{111\}$ , which closely resembles the MXene surface [158]. Thus, it will be interesting to look at how the  $\text{CO}_2$  dissociation, in particular, modifies in presence of  $\text{H}_2\text{O}$ . Further, recent studies have probed into doping in MXenes to modify their electronic, magnetic, and catalytic properties (leading to a new subclass called hetero-MXenes) [159]. Research carried out in  $\text{TiC}\{001\}$  in this regard showed

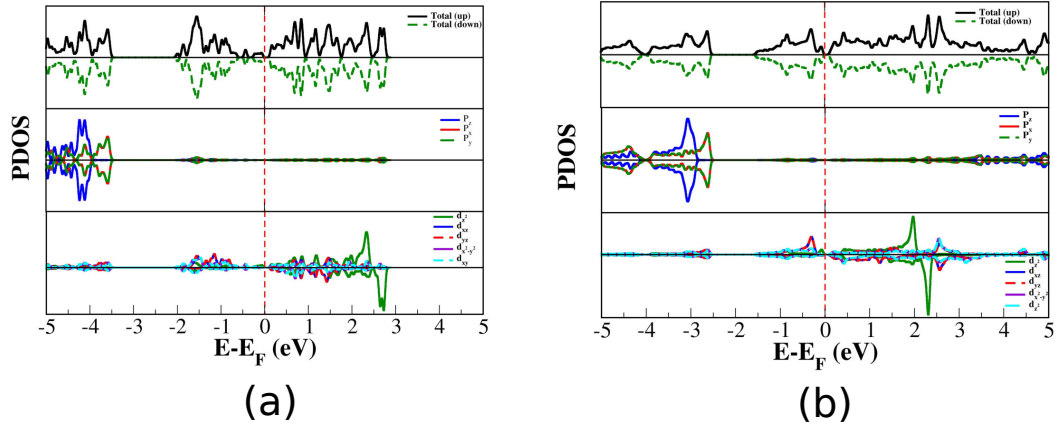
## Chapter 6

a significant impact on  $\text{CO}_2$  activation and desorption where they used a series of elements belonging to s block, p block, f block, early [160] and late transition series [161]. Thus along similar lines, one can examine doping on  $\text{Ti}_2\text{C}$  MXene with respect to  $\text{CO}_2$  dissociation reaction.

In CO oxidation reaction, the Au-based catalysts face issues of stability and cost, combating which is possible via Cu doping. Thus, we evaluate the performance of the AuCu bimetallic cluster of four atoms deposited on  $\text{Ti}_2\text{CO}_2$  MXene in **chapter 5**. On the support, the lowest energy composition is  $\text{AuCu}_3$  with a tetrahedral structure having strong binding through basal Cu-O bonds. With the possible mechanisms included, the first cycle prefers the LH mechanism and OCOO formation is the rate-limiting step. For completing the reaction, ER mechanism shows a lower barrier than LH for the second cycle. In this work, we only have the favorable composition researched, and it will be intriguing to look at the impact of bimetallic composition on the thermodynamics and kinetics of CO oxidation reaction. An extensive computational investigation in this regard was carried out on  $\text{Au}_{15}\text{Cu}_{15}$ ,  $\text{Au}_{23}\text{Cu}_7$ , and  $\text{Au}_7\text{Cu}_{23}$  clusters on perfect and defective  $\text{MgO}\{100\}$  by Akola et al. [149]. Composition indeed played a major role in the adsorption of reactants as well as reaction barriers. Hence, a similar study in our system can help corroborate these findings if not additional useful insights. Additionally, apart from the mechanisms we have deployed, a DFT study on a series of Au gas-phase clusters shows significantly reduced O-O bond-breaking barrier through CO self-promoting mechanism or trimolecular LH mechanism (one additional CO) as compared to bimolecular LH [145]. This offers an incredible advantage from a practical standpoint since it was observed experimentally and theoretically alike that many CO molecules bind to the active sites of Au clusters, especially at low temperature and high CO pressure. Therefore, future studies can shed light on this mechanism.

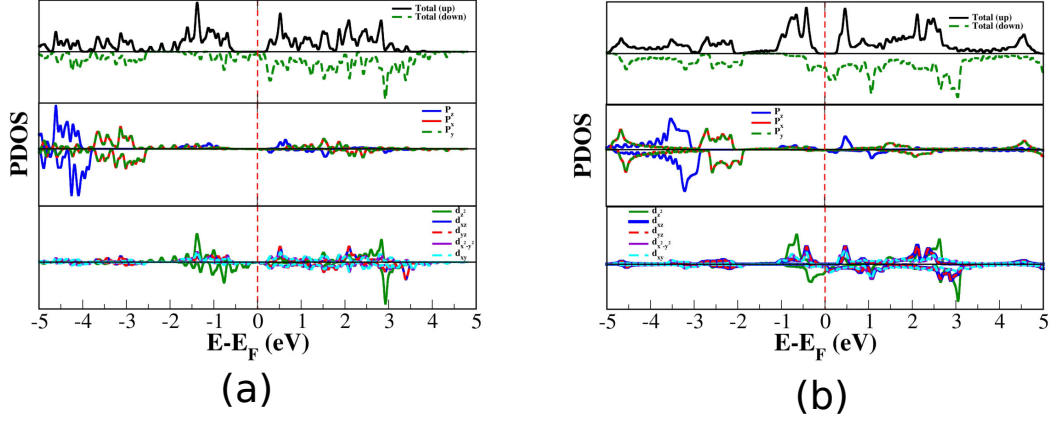
## Appendix A

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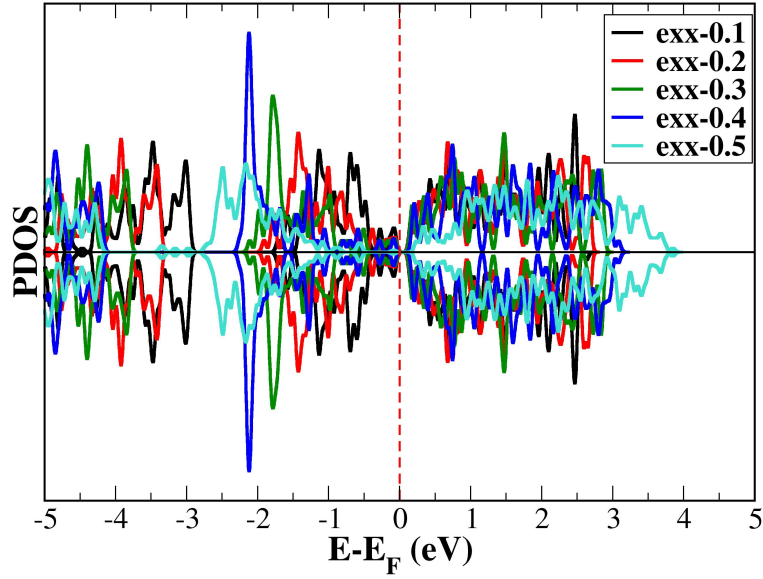


**Figure A.1:** DOS of 1T phase of  $\text{Ti}_2\text{C}$  MXene computed using (a) Gau-PBE and (b) PBE. The spin up and spin down channels are plotted in the top and bottom half of the figure respectively.

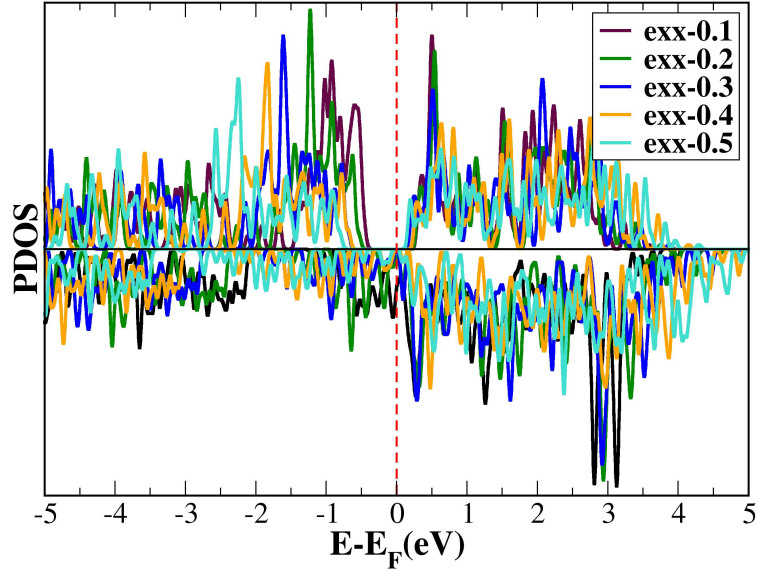
## Appendix A



**Figure A.2:** DOS of 1H phase of  $\text{Ti}_2\text{C}$  MXene computed using (a) Gau-PBE and (b) PBE. The spin up and spin down channels are plotted in the top and bottom half of the figure respectively.



**Figure A.3:** DOS of 1T phase of  $\text{Ti}_2\text{C}$  MXene computed using hybrid functional Gau-PBE for different exchange fractions. The spin up and spin down channels are plotted in the top and bottom half of the figure respectively.



**Figure A.4:** DOS of 1H phase of  $\text{Ti}_2\text{C}$  MXene computed using hybrid functional Gau-PBE for different exchange fractions. The spin up and spin down channels are plotted in the top and bottom half of the figure respectively.

## Appendix B

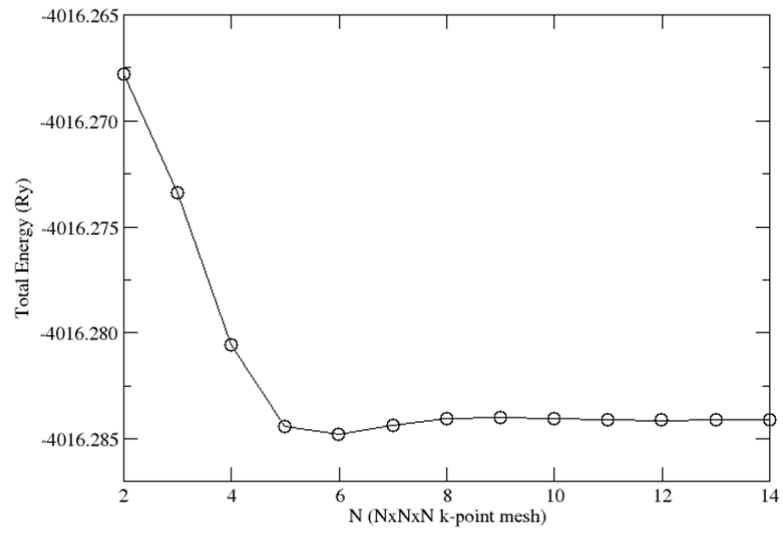
**Table B.1:** Relative energies for different magnetic configurations of chemisorbed CO<sub>2</sub> on Ti<sub>2</sub>C MXene.

| Configuration <b>5</b> (Fig. 6 of the manuscript)<br>(Fig. 6 of the manuscript) |                      | Configuration <b>6</b> (Fig. 6 of the manuscript)<br>(Fig. 6 of the manuscript) |                      |
|---------------------------------------------------------------------------------|----------------------|---------------------------------------------------------------------------------|----------------------|
| Magnetic configuration                                                          | Relative energy (eV) | Magnetic configuration                                                          | Relative energy (eV) |
| AFM                                                                             | 0.00                 | AFM                                                                             | 0.00                 |
| FM                                                                              | 0.12                 | FM                                                                              | 0.23                 |
| NM                                                                              | 0.81                 | NM                                                                              | 0.93                 |

**Table B.2:** Adsorption energy of CO<sub>2</sub> on magnetic and non-magnetic Ti<sub>2</sub>C{100} surfaces. All energies are given in eV.

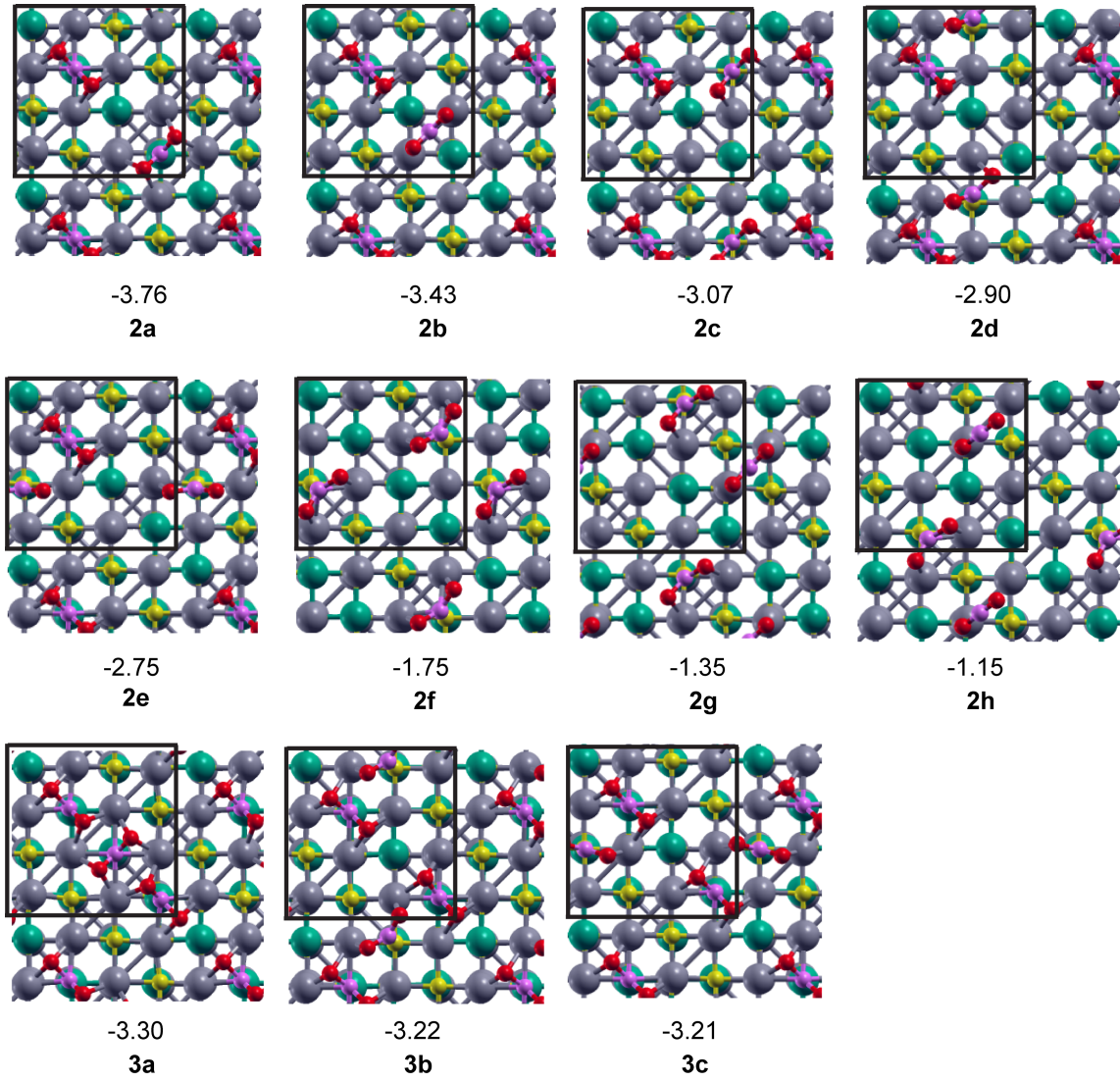
| surfaces  | $E_{mag}$ | $E_{non-mag}$ | $E_{diff}$ |
|-----------|-----------|---------------|------------|
| <b>14</b> | -0.29     | -0.29         | 0.0        |
| <b>15</b> | -0.07     | -0.07         | 0.0        |
| <b>16</b> | -0.09     | -0.09         | 0.0        |
| <b>17</b> | -0.04     | -0.04         | 0.0        |
| <b>18</b> | -4.39     | -4.39         | 0.0        |

## Appendix B



**Figure B.1:** k-point convergence plot for  $\text{Ti}_2\text{C}\{100\}$  surface.

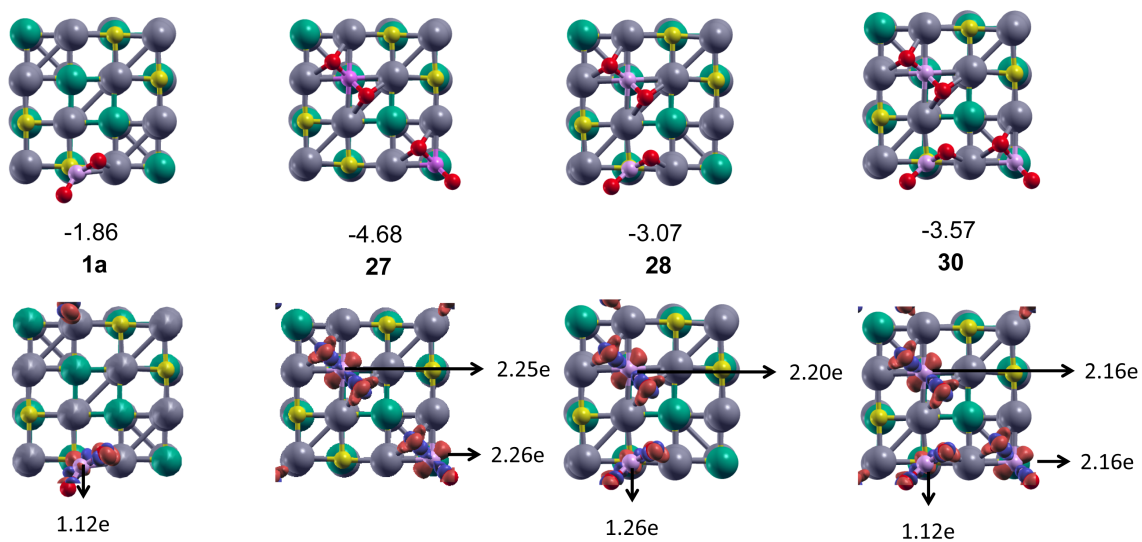
## Appendix B



**Figure B.2:** Geometric variants corresponding to the adsorption of two (geometries **2a-2h**) and three (geometries **3a-3c**)  $\text{CO}_2$  molecules on  $\text{Ti}_2\text{C}\{100\}$  surface; adsorption energy given in  $\text{eV}/\text{CO}_2$ .

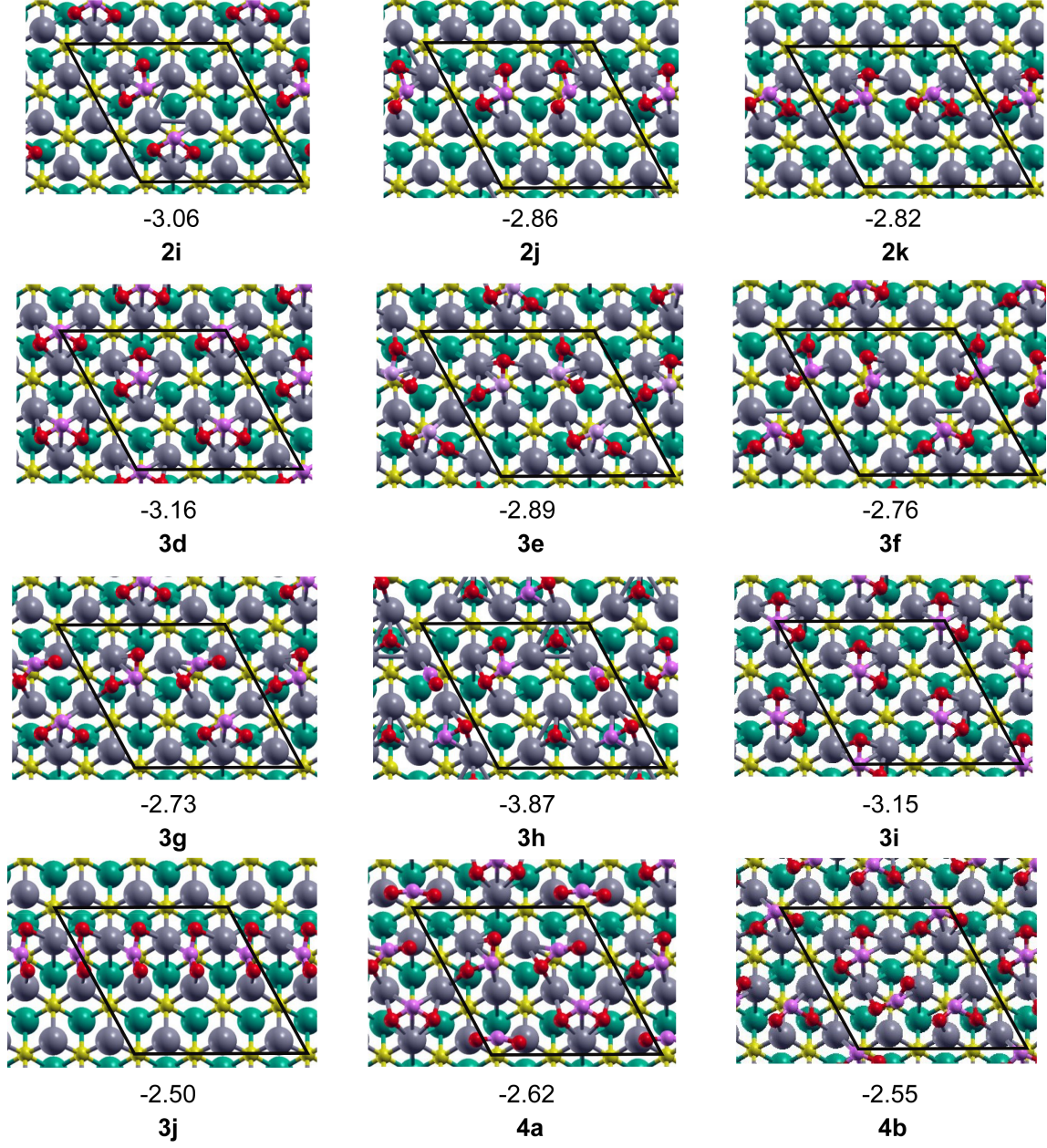


## Appendix B

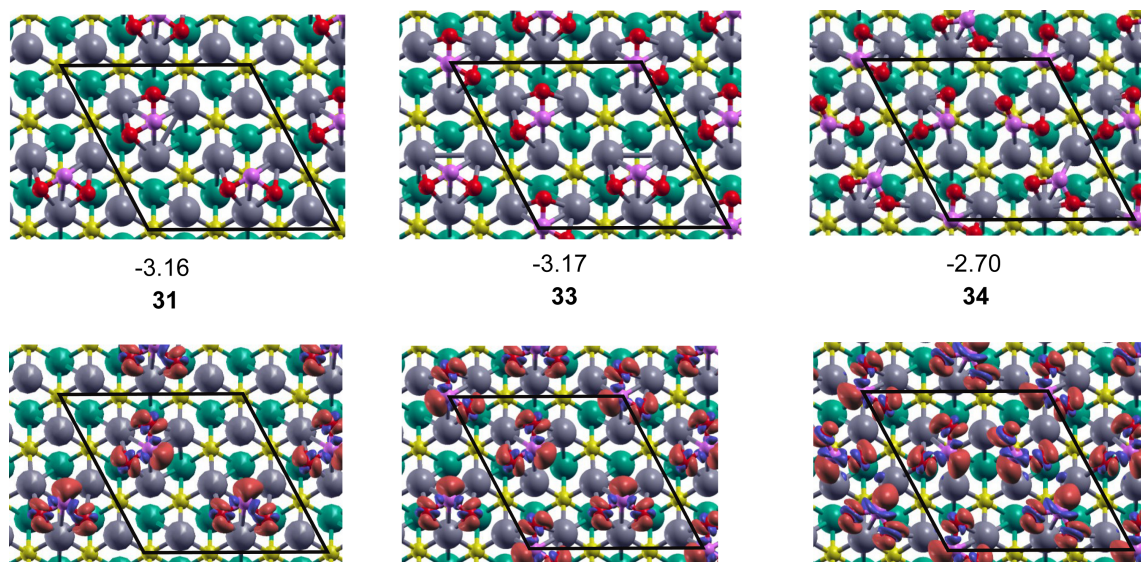


**Figure B.3:** Charge transfer plots for structures **27**, **28**, and **30**.

## Appendix B



**Figure B.4:** Geometric variants corresponding to the adsorption of two (geometries **2i-2k**) three (geometries **3d-3j**), and four (geometries **4a** and **4b**)  $\text{CO}_2$  molecules on MXene surface; adsorption energy given in  $\text{eV}/\text{CO}_2$ .



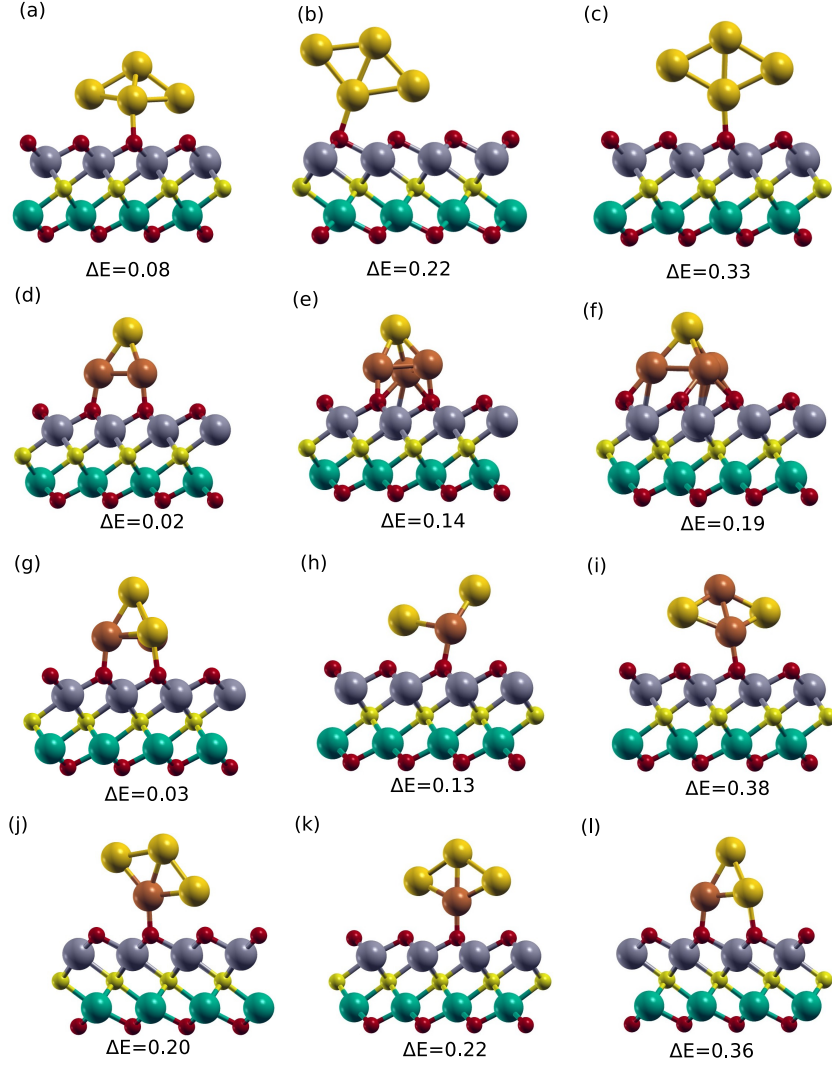
**Figure B.5:** Charge transfer plots for structures **31**, **33**, and **34**.

## Appendix C

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***MvK mechanism:*** A crucial factor decisive of this path is oxygen vacancy formation energy. For  $\text{Ti}_2\text{CO}_2$ , it was found to be 3.27 eV [162], which is comparable to substrates like rutile  $\text{TiO}_2(110)$  (around 3.00 eV) that is known for facile oxygen vacancy formation [163]. Hence to investigate the MvK mechanism for CO oxidation, we take the most stable CO adsorption geometry (**IS4** in Fig. C.3). From the reaction thermodynamic studies, we find that CO attacks an O atom from the top layer of  $\text{Ti}_2\text{CO}_2$ , forming a  $\text{CO}_2$  intermediate (**INT12**), 2.23 eV higher in energy. The next step of  $\text{CO}_2$  desorption is also endothermic, making the whole mechanism unlikely to happen.

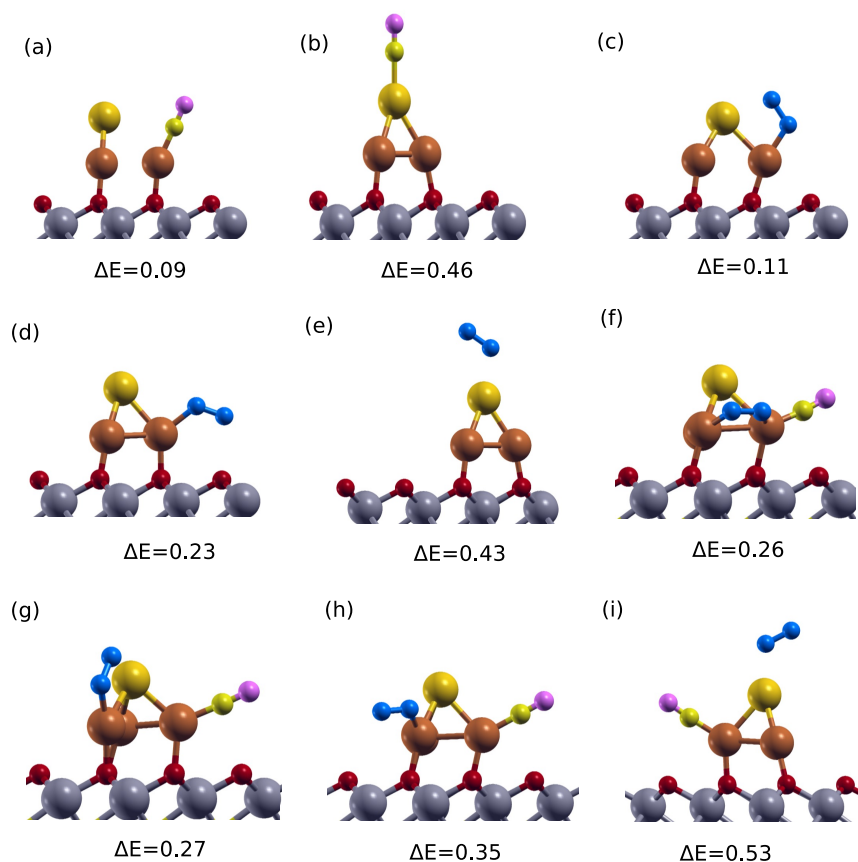
## Appendix C



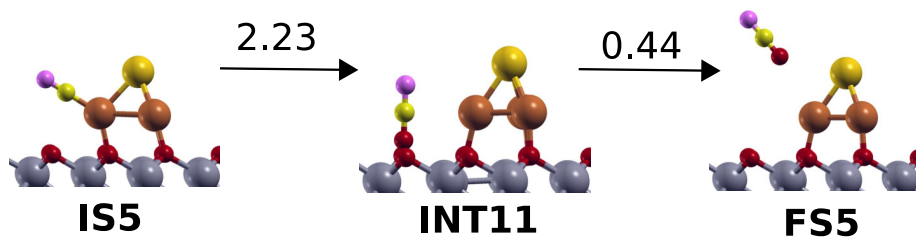
**Figure C.1:** Stable higher energy structures of a)-c)  $\text{Au}_4$ , d)-f)  $\text{AuCu}_3$ , g)-i)  $\text{Au}_2\text{Cu}_2$  and j)-l)  $\text{Au}_3\text{Cu}$  clusters deposited on  $\text{Ti}_2\text{CO}_2$  MXene. Relative energy with respect to the corresponding most stable geometry given in eV.



## Appendix C

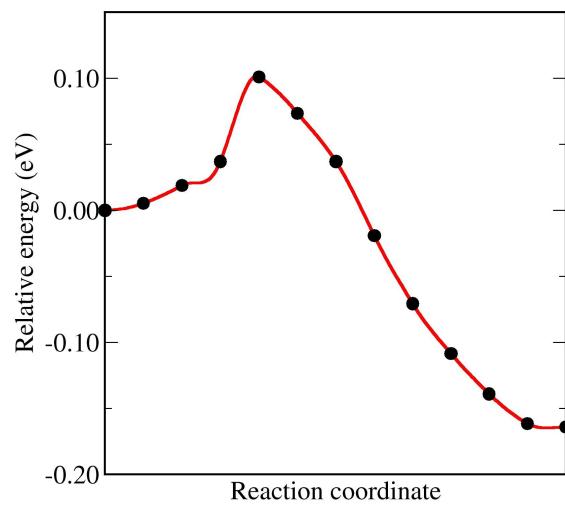


**Figure C.2:** Stable higher energy structures of a)-b) CO, c)-e) O<sub>2</sub> and f)-i) CO and O<sub>2</sub> co-adsorption on AuCu<sub>3</sub>/Ti<sub>2</sub>CO<sub>2</sub>. Relative energy with respect to the corresponding most stable geometry given in eV.

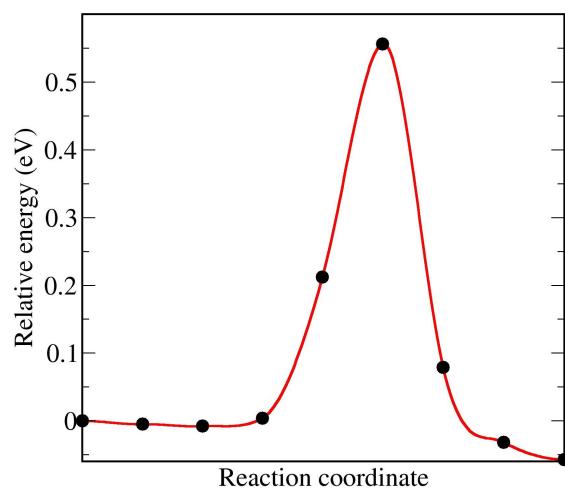


**Figure C.3:** First cycle of CO oxidation via MvK mechanism on AuCu<sub>3</sub>/Ti<sub>2</sub>CO<sub>2</sub>. The reaction energies in eV are marked above the arrow for each step.

## Appendix C

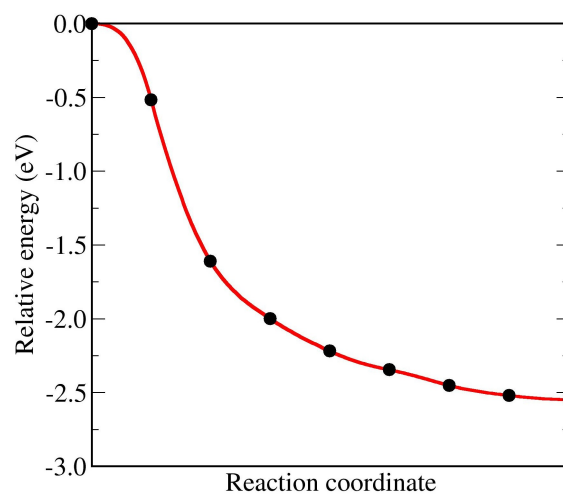


**Figure C.4:** Reaction energy profile of IS1 to INT1.

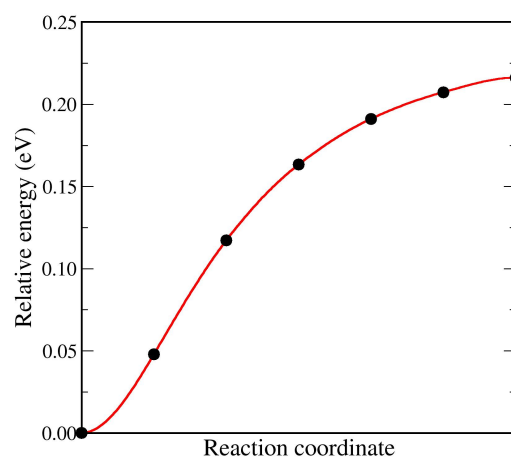


**Figure C.5:** Reaction energy profile of INT1 to INT2.

## Appendix C



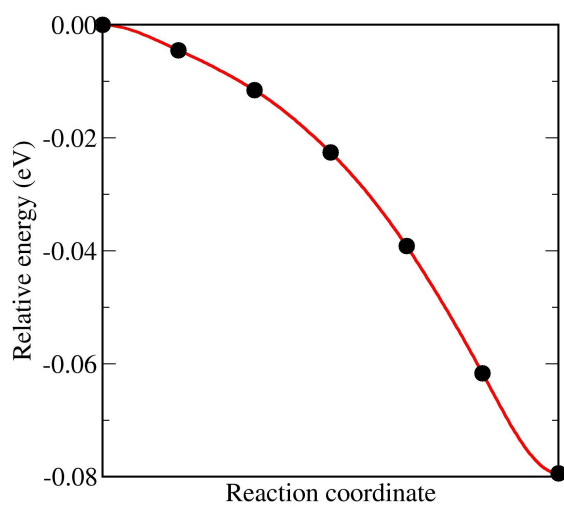
**Figure C.6:** Reaction energy profile of INT2 to INT3.



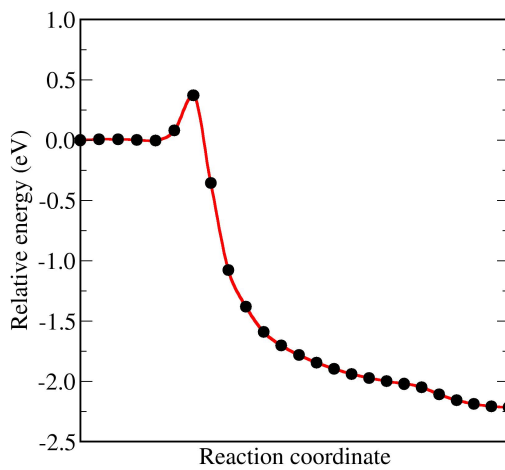
**Figure C.7:** Reaction energy profile of INT3 to FS1.



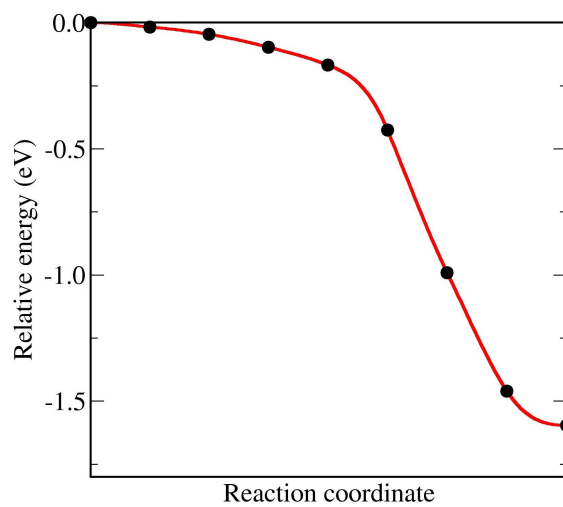
## Appendix C



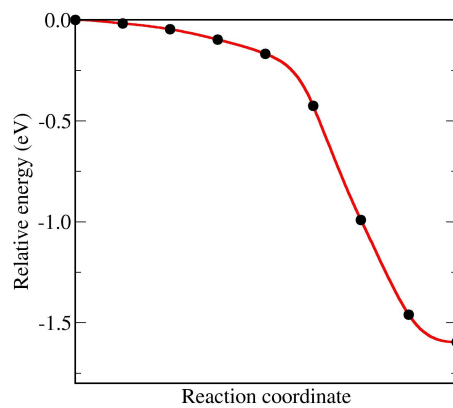
**Figure C.8:** Reaction energy profile of **IS2** to **INT4**.



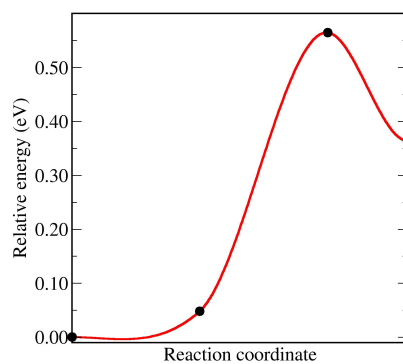
## Appendix C



**Figure C.10:** Reaction energy profile of INT4 to INT5.

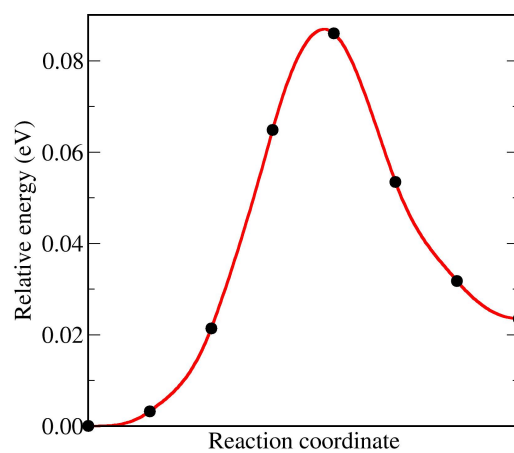


**Figure C.11:** Reaction energy profile of IS3 to INT7.

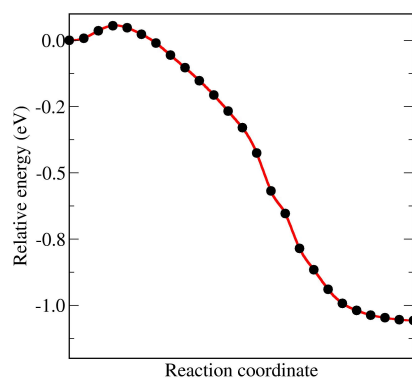


**Figure C.12:** Reaction energy profile of INT7 to INT8.

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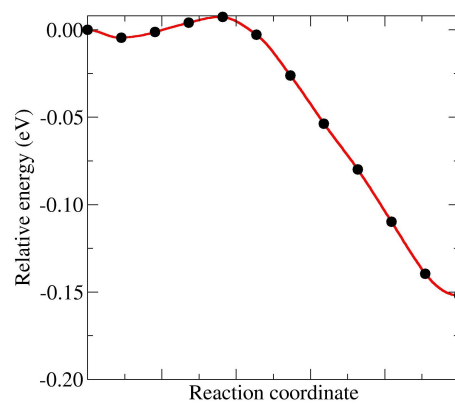


**Figure C.13:** Reaction energy profile of **INT8** to **INT9**.

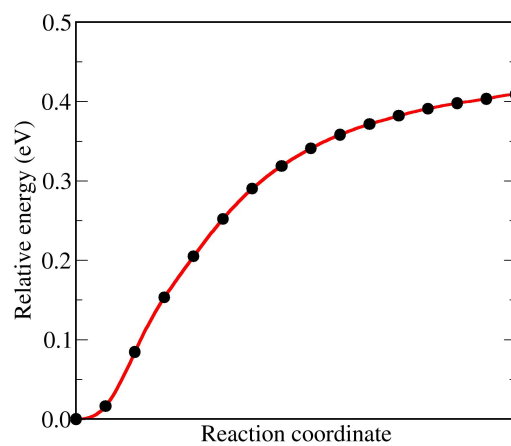


**Figure C.14:** Reaction energy profile of **INT9** to **INT10**.

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**Figure C.15:** Reaction energy profile of INT10 to INT11.



**Figure C.16:** Reaction energy profile of INT11 to FS3.

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