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Surface functionalization of H-terminated diamond with NH and NH$_2$ on the (1 0 0), (1 1 0) and (1 1 1) surface planes using Density Functional Theory

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Abstract

The adsorption energy of aminated diamond surfaces on the (1 1 1), (1 1 0) and (1 0 0) diamond surfaces have been calculated with density functional theory (DFT). The resulting values show that bridging is favoured before on-top nitrogen at low coverage for all the low index planes. The trend is even more pronounced as the coverage increases, most likely due to sterical hindrance. As expected, the imidogen (NH) and amidogen (NH$_2$) groups are bonded to the surface planes in the order (1 0 0)>(1 1 1)>(1 1 0) as decrease in energy is the highest on the (1 0 0) plane and lowest on the (1 010) plane. The effect of sterical hindrance is largest at the (1 1 0) surface while the (1 0 0) surface is almost unaffected by neighbouring functional groups. Also, double bonded on-top imidogen (NH) is the least stable group at the (1 0 0) surface at low coverage while it is almost as stable as bridging NH when having a full mono-layer. Moreover, on-top imidogen (NH) was highly distorted and forced a change in surface geometry

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Contents

1 Goal

The goal of this study was firstly to find out which one of amidogen (NH_2) and imidogen (NH, on-top or bridge) is theoretically most strongly bonded to a diamond surface. Secondly to find out whether NH_2 or NH (on-top or bridge) is theoretically best attached to a (1 0 0), (1 1 0) or (1 1 1) oriented diamond surface.

2 Introduction

2.1 Background

Diamond, and in particular nanodiamond, has become a promising candidate for several fields of application. One of those applications is to use it in medical and biological sciences as it possess biocompatibility as well as good chemical and electrical properties. It also has a large electro-potential window, which may be further enhanced or inhibited by modifying the surface. Furthermore, even though diamonds show good physical/chemical stability, the surfaces are still easily modified or functionalized by photochemical reactions [1].

To use diamond for medical purposes such as the growing of bones, proteins and DNA must first be successfully attached to the diamond surface. One way to enhance the attachment of these types of molecules is functionalizing surfaces with various biologically common functional groups before trying to bind the specific molecule to the surface. Amine-based groups in particular may be a good step on the way to so this since both imidogen (NH-) and amidogen (NH_2) are part of many well known biochemical and organical reactions. This has already been done as preliminary step in binding DNA to a diamond surface. Aminating the surface by UV-radiation will also make the surface pH sensitive depending on the amount of UV-radiation. Furthermore, amidogen (NH_2, on-top) groups produced by long-term UV-radiation have proven to be stable under exposure to air. [2]. It has also been reported that diamond has high stability and sensibility as well as compatibility with microelectronic processing technology. All of these properties also make diamond a promising candidate for biological integration of microelectronics as well as biological modification [3].

There are also several well established ways to produce diamond in industrial and laboratory settings aside from CVD (Chemical Vapor Deposition). Naturally, the surface chemistry will vary depending on chosen method. Specifically, nano-diamonds can for example be produced using shock waves (so called shock-wave diamond) or explosives

(detonation diamond) on carbon materials. The surface of shock-wave diamond is graphitized and detonation diamond is covered with various oxygen containing groups. The surface of detonation diamond have been successfully homogenised using oxidative (yielding for example mostly keto- and carboxyl-groups) or reductive methods with the latter yielding, for example, an H-terminated or OH-terminated surface. CVD-diamond will, generally, yield an H-terminated surface without further cleaning or homogenisation.[4] Also, several studies have already been made concerning low-index planes of diamonds, mostly practical work, but also some purely computational studies. Some of those cover the adsorption of amines on diamond. One of these are a relatively early study that regarded the full coverage (mono-layer) of NH_2 on the (1 1 1), (1 1 0) and (1 0 0) planes of diamond surfaces. They used MM (Molecular Mechanics). The results showed that full coverage meant great distortion of the structure at the (1 1 0) and (1 1 1) cleavage of the diamond surface. Although the report did not report either enthalpies or adsorption energies, this may indicate that full coverage is unlikely. The (1 0 0) surface did not show any significant distortion. [5]

Another, slightly more recent study has been done regarding adsorption of NH_2 on a reconstructed (1 0 0)-diamond surface using DFT (Density Functinal Theory) with the GGA (General Gradient Approximation) approximation. The resulting energies, while comparing a structure with two nearby NH_2 groups with one with hydrogen instead, showed that the energy levels were lower in the latter case. It is hence unlikely that two amino-groups will form in two nearby reaction sites at the reconstructed (1 0 0) diamond surface. [6]

Amidogen (NH) and Amine (NH_2) adsorption has also been found to be energetically favoured around room temperature on the (1 0 0), (1 1 0), and (1 1 1) planes of nanodiamond using density functional tight binding simulations. [7]

3 Theory

3.1 Surfaces of diamond

3.1.1 General surface theory

The reactivity of a crystal surface is known to be dependent of the surface structure and morphology, which do not only depend on the crystal lattice, but also the orientation of the intersection in relation to the crystal lattice. Both coordination numbers and numbers of possible reaction sites differ depending on plane (orientation of the

Figure 1: A description of the (1 0 0), (1 1 1) and (1 1 0) planes. This picture was picked from an online glossary [10], but the same information can be found in any book pertaining basic solid state chemistry

intersection) and surface morphology. The specific plane is formally described using miller indexes where the numbers represent the intersection through the three mayor crystallographic axes of the lattice. The three most simple surface planes are (1 1 1), (1 1 0) and (1 0 0) but it is possible to use higher indexes. The (1 1 1), (1 1 0) and (1 0 0) planes are demonstrated in figure 1. Naturally, properties that generally leads to larger surface energy such as large surface areas and low coordination numbers on surface atoms generally means a higher reactivity and a stronger binding of an adsorbate. Another property that affect surface energy, and thus its reactivity, is how close-packed the surface atoms are. The direction of free bonds at the radical surface also plays a role in how well an adsorbate can be bonded to the surface [8, 9].

3.1.2 Structure of the low index surfaces of diamond

For simplicity, this study only explores the adsorption of ammonia on diamond at the three low-index surfaces (1 1 1), (1 1 0) and (1 0 0). The overall structure of diamond is a derivative of the zinkblende-structure where all atoms are the same (se figure 2). In other words, all carbon atoms in the bulk have the coordination number 4 meaning sp^3-hybridisation and a tetrahedral symmetry around the atoms (se figure 2). A closer look at the three planes show that the surface atoms has the same coordination number, which is three, but the rest is different. The (1 0 0) plane does not keep perfect tetrahedral symmetry around the carbon atoms at the surface and are less close-packed than the other two planes studied and is therefore expected to have the largest surface energy. One might even speculate that it is possible for a bond to break between two neighbouring surface atoms, creating lower coordination numbers. In comparison, the (1 1 0) and (1 1 1)

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HM:F-43M #216
a=5.434Å
b=5.434Å
c=5.434Å
α=90.000°
β=90.000°
γ=90.000°
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Figure 2: The general lattice of diamond. This picture was generated on a free, online resource center, but the same information can be obtained in many ways and the diamond structure as well as the that of zinkblende are both to be considered general nowledge.

planes do keep the tetrahedral symmetry around the carbon atoms. One can also see that while the surface of the (1 1 1) plane seem more close-packed than the (1 1 0), the free bonds of the latter is actually closer to each other in the latter case. A schematic illustration displaying the free bonds (refererred to as dangling bonds) of the three planes is shown in figure 3.

3.2   General compuional theory

Molecular modelling is a good way to get a further understanding of the workings of chemical systems and molecules. Not only can one study reactions that are either strictly theoretical or either to dangerous or hard to study in a practical experiments. Environments can easily be strictly defined (thus isolating problems and trend factors

Figure 3: Schematic illustration displaing the dangling bonds of the (1 1 1), (1 1 0) and (1 0 0) plane from the side (top) and from above (bottom).

from each other) from other factors) and properties that would otherwise be very hard, impossible or very expensive might be studied. There is however, no perfect model simulating an exact replica of the real world, which gives all the answers. It is, specifically, impossible to get an exact and true electron configuration.

There are hence several different approaches and methods developed for modelling chemical systems, each using their own approximations that have their own pros and cons. Those use quantum mechanics, molecular mechanics or a statistical approach. Quantum mechanical methods are, in essence, solving the problem by approximate solutions of the Shcrödinger equation. Molecular mechanics uses classical mechanics and replace the electrons with a fixed force field that represent them. Molecular mechanics might generate properties such as temperature dependence, different kinetical properties and even information about systems that are not in equilibrium. The statistical approach uses the inherent statistical properties that exist within all systems and will therefore only give information about systems in equilibrium, which those methods are very good at. Both molecular mechanics and methods that use statistics are cheap in computational time and requirement, so very large systems can be simulated at a short time. They do not, however, give any information about electron configuration (which is what this study wanted) [11]. Hence the quantum mechanical approach had to be used here.

3.3 Quantum mechanical methods

3.3.1 General

As mentioned earlier, quantum mechanical methods calculates the total energy of a system by 'solving' the Schrödinger equation with the help of various approximations. Those approximations are needed as it is very hard to successfully calculate all interactions between two or more particles. There are therefore not one, but several different approaches for that, and the area is still under development.

The Schrödinger equation in its most basic form is stated below (see equation 1). H is an operator which operates on a mathematical function, Ψ is the wave-function and E the energy of the system. Ψ is actually a set of functions with each specific function Ψ_i corresponding to an allowed E_i. The functioanal of the Schrödinger equation (H) is what is referred to the Hamiltonian. The Hamiltonian is composed of two parts, the part that comes from the kinetic energy of the system ($\hat{T}$) and the external potential energy of the system ($\hat{S}$). Wave-functions that satisfy the Schrödinger equation are normally called orbitals, which will be used henceforth.

$$H\Psi = (\hat{T} + \hat{S})\Psi = E\Psi \tag{1}$$

This is a many-body problem and therefore not solvable (one can not get an exact replica of reality), the computational cost will also increase rapidly as the size of the core and number of electrons increase. Therefore, the Born-Oppenheimer approximation will be used from know on in the text.

Explanation: The Born-Oppenheimer approximation: The BO-approximation states that the mass of the nuclei are so much larger than that of the electrons that the mass of the electrons is negligible and can be approximated to a fixed field while studying the nuclei. It also states that the movements of the nuclei are so small compared to that of the electrons that the core can be described as fixed points while studying the electrons. In this study, the electrons are studied, so the nuclei will be fixed.

The orbitals are not known for poly-electron atoms and molecules, hence the use of approximate orbitals. As it is, when implementing orbitals in a model, a starting set of wave-functions that satisfy equation 1 are used leading to a starting energy. The wave-functions are themselves a linear combination of so called basis functions that are picked from a set of pre-defined functions. The total set of basis functions used in a calculation is referred to the basis set of the calculation.

Explanation: A basis set is a set of predefined functions that are used to describe the wave-functions of the system that is being studied. Each wave-function is a linear combination of basis functions. [12] A plane-wave basis set is a set uses plane wave-functions.

Explanation: A plane wave-function A plane wave-function is a wave-function that is a whole plane rather than a single line. Those can be described using a wave-function and a vector that shows the direction of the plane wave-function. Specific 3-D surfaces can be obtained by combining several non-parallel plane-waves.

3.3.2 Plane wave basis sets and cut-off energy

Plane wave basis functions are, as the name implies, a set of basis functions that uses plane waves instead of ordinary waves. In principle, to get a perfect result, an infinite number of plane waves are needed. Naturally, the accuracy of the result increases while using more functions. That does not prevent good results as one apply

Bloch's theorem as well as truncate by only including the most important plane-waves. It has been found that the plane-waves with the smallest kinetic energy is most important. That means that only the plane-waves with a kinetic energy that is below a pre-specified value, the so called cut-off-energy, is needed to be included.

There is, generally, necessary to use more basis functions than those needed to just describe the electrons surrounding the lone atoms. Naturally, a large basis set both increases the accuracy of the calculation as well as creating a great increase in computational requirement. There are also different methods to get the energy by solving and optimizing the equation [11].

There are both several basis set and methods to chose from, and the purpose of this study was not to write a book about quantum chemical methods, so no more descriptions of all combinations that were not used will follow.

3.4 Density Functional Theory (DFT)

The general concept behind DFT is to treat the electron as an inhomogeneous gas of electrons rather than discreet orbitals. That is, the electron density is calculated for the system as opposed to each electron on their own. DFT is therefore not just another way of solving the Schrodinger equation. [12] This is a good approach, as Kohn and Hohenberg proved with a simple contradiction in the year 1964 that the energy of a system is uniquely defined by its electron density and vice versa. That means that the potential, $\hat{S}$ in equation 1 can be replaced with a density. The methods for this where developed a year later by Kohn and Sham. The final expression for the energy of an interacting gas in a static potential $v(r)$ and electron density $(n(r))$ that was presented in that report is shown in equation 2. $G(n)$ is a universal functional of the density.

$$E = G(n) + \int v(r)n(r)dr + \frac{1}{2} \iint (\frac{n(r)n(r')}{|r - r'|})drdr' \qquad (2)$$

As an approximation of $G(n)$, Kohn and Sham define the universal functional $(G(n))$ as the sum of the kinetic energy,$T_s(n)$ and the major parts of the effects of the exchange and the correlation energy that stems from the electron-electron and core-electron interaction, $E_{xe}(n)$ (see equation 3).

$$G(n) \equiv T_s(n) + E_{xc}(n) \qquad (3)$$

The hard part of equation 3 is the correlation energy which can be approximated easily if the electron density does not vary much. Then

the correlation energy can be calculated simply as if each electron is in a homogeneous gas of electrons. (equation 4, ϵ_{xc} is the correlation and exchange energy per electron in a homogeneous gas with density n). This approach is referred to as the Local Density Approximation (LDA).

$$E_{xe}[n] = \int n(r)\epsilon_{xc}n(r)dr \qquad (4)$$

Equation 4 do not work well when the density is expected to vary so other solutions or further approximations for the correlation and exchange energy is needed. The solution that Kohn and Sham suggested were the Local Density Approximation (LDA) that can be extended to the General Gradient Approximation (GGA). [13][14]

Explanation: A functional is a real valued function on a vector space (usually of functions). The meaning of that is that it maps a set of functions (if that is what the vector space contains) to a set of numbers [15]. In DFT, a set of wavefunctions that represent the electron cloud is mapped to a set of unique eigenvalues [12] .

3.4.1 Local Density Approximation, LDA

Another explanation of equation 4, and hence LDA, is to say that LDA, as the name implies, calculate the energy by using the local density for each electron as if that was the universal density. This can be implemented by writing the functional as an integral over a function of the density at each point in space.

General Gradient Approximation, GGA In this study, the GGA (General Gradient Approximation,) which is an extension of LDA, was used. An oversimplified way of describing the General Gradient approximation is to say that each functional use a local functional that depend on the gradient, as opposed to the value, of the electron density at each point in space [12].

3.5 The super-cell approach

It is possible to use the fact that crystal structures, and therefore diamond, are periodical. This can be done using Bloch's theorem which states that each electron wave-function in a periodic system can be described as the product between a cell-periodic part and a wavelike part. One can, in other words, describe each electron wave-function at a given k-point as a function of a discrete plane-wave basis set. See equation Bloch's theorem 1

$$\Phi_r = f_i(r) \exp^{ir} \qquad \text{(Bloch's theorem 1)}$$

The cell-periodic part, $f(r)$ can be described using a plane wave basis set. A plane wave basis set is a basis set that consist of plane waves rather than ordinary waves. See equation Bloch's theorem (discrete part 1).

$$f_i(r) = \sum_G c_{i,G} exp^{iGr} \qquad \text{(Bloch's theorem (discrete part 1))}$$

Combining Bloch's theorem 1 and Bloch's theorem (discrete part 1) gives Bloch's theorem 2

$$\Phi_i(r) = \sum_G c_{i,k+G} exp^{i(G+k)*r} \qquad \text{(Bloch's theorem 2)}$$

3.5.1   K-point sampling

So far, when applying Bloch's theorem, one get a finite number of wave-functions for an infinite number of k-points. This is where the periodic nature of the system comes into use as the functions of k-points that are very similar will be almost identical. It is therefore possible to choose a limited region called a k-space that is copied lots of times. In every cycle, all wave-functions of each region can then be calculated as if the each and every wave-function in the other regions where there before. In the end of all cycles, the data of every region is set to the overall average of the regions. It is however, significantly more complicated than this, as the number of k-points needed for a specific amount of space differs depending on system. The theory surrounding the latter is to complicated and would take to long to include here. Further reading can be found in Paines article that is provided as source theory for CASTEP at the homepage of Materials Study [16]. CASTEP, which was used for all of the calculations in this study, is a software that was developed by BIOVIA in which it is possible to graphically define structures and then calculate energies and associated properties such as electron distribution, charge distribution and optimal structures as some examples.

3.5.2   Practical explanation

This is how it is done practically (for the person that uses CASTEP). A super-cell that has everything that is interesting is made and added as a starting point. That cell is then multiplied, creating a large
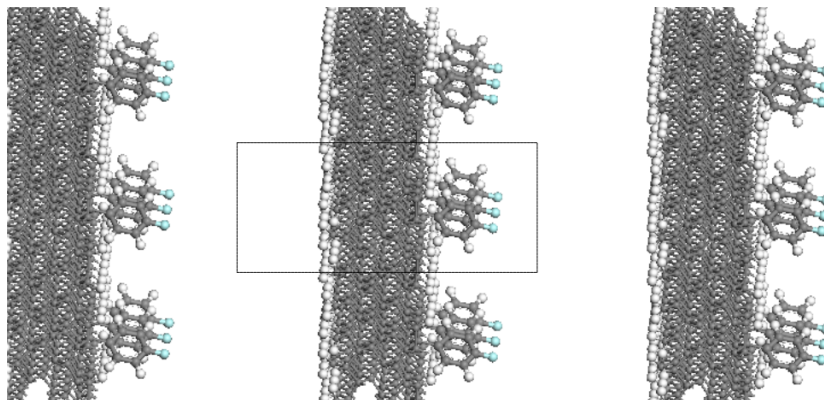
Figure 4: An easy illustration of the super-cell approach showing 9 cells. The vacuum between the sheets are chosen so that they do not interact. The only difference between this figure and the one in the study is the functional group. The structure inside the rectangle in the middle corresponds to roughly one cell.

bulk that represent the k-space. See the illustration in figure 4. The calculation of each cell is then done as if the others where there. After that, the set of values (and functions) for the crystal structure and electron density in each cell is set to the average value of the cells before the next cycle of the energy minimization is made.

4   Methods

All data were obtained doing geometry optimizations using DFT (Density Functional Theory) with GGA (General gradient approximation). Specifically Perdow–Burke-Erzhow density functional (PBE-DFT) were used in the program CASTEP [17]. Also, a super-cell approach was used. Band structure, density of states and population analyses were made as a complement to the energy calculations.

4.1   Implementation

4.1.1   The model

There are, theoretically, three possible ways for the nitrogen in ammonia to attach to the diamond surface.

Ammonia may attach in an on-top configuration either as amidogen (NH_2) with a single bond or as imidogen (NH) with a double bond. The latter is only possible at the (1 0 0) plane due to the position of
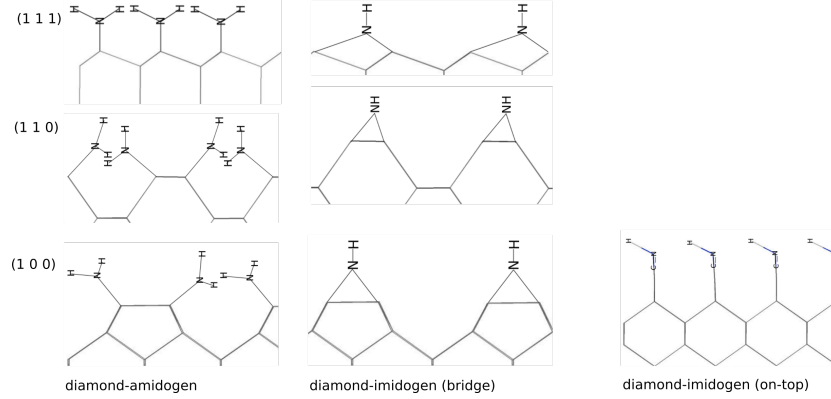
Figure 5: Shematic illustration of the three possible products in the reaction between a diamond surface on the (1 0 0), (1 1 1) and (1 1 0) surfaces of diamond. Double bonded NH (to the left) is only possible at the (1 0 0) plane.

dangling bonds. Another possible product between ammonia and a diamond surface is that the nitrogen attach in a bridge configuration as imidogen (NH). Also, figure 3 clearly shows that amidogen (NH_2) groups are unlikely to build a mono layer on the (1 1 0) plane as the hydrogen of the amidogen would have to either overlap with each other or create energetically less stable angles. The possible products of the reaction between a clean diamond surface and ammonia are illustrated in figure 5.

Theory The adsorption energies (E_a) were calculated by subtracting the energy of the amino-group (E_{NH_2}) and the energy of a surface lacking one hydrogen (E_{surf-H}) from the energy of the amino-terminated diamond surface (E_{D-NH_2})

$$E_a = E_{D-NH_2} - (E_{NH_2} + E_{surf-H}) \qquad (5)$$

Hence, the internal energy of both NH, NH_2, terminated surface lacking 1 or 2 hydrogen depending on calculation had to be calculated.

4.2 Calculations

The models were generated and modified to specify each specific surface using the materials study software before the calculations were carried out using CASTEP. The adsorption energy was calculated both at full coverage and with a single amidogen or imidogen per supercell. Also, additional calculations were made for amidogen where half of

the sites were covered so that amidogen (NH$_2$, on-top) could be compared with an equal amount of imidogen (NH, bridge) when having a monolayer of the latter. The size of the supercells where chosen so that the adsorbates of the supercells with only one amidogen (NH$_2$, on-top) or imidogen (NH, bridge) from different cells would not interact with each other. Rather than having the user of the CASTEP software manually set the calculation parameters that affect accuracy, a general quality of calculation is chosen depending on how accurate the calculation has to be. The specifics of each quality can be found at CASTEPS own homepage. In this study, all calculations where set to medium quality.

5 Results

At all surfaces: The adsorption energy was calculated at full coverage and at low coverage for imidogen (NH) and amidogen (NH$_2$) at all planes. For every plane an additional calculation was made with 50% coverage for amidogen (NH$_2$). Adsorption energies of on-top imidogen (NH, double bonded) on the (1 0 0) plane was calculated at 100%, 50% and single occupied. Single occupied groups are not truly single occupied due to the super-cell approximation, and real coverage will be written henceforth. All adsorption energies are demonstrated in figure ?? and summarised in table ??. Also, the resulting structures are shown in figure 6, 7, 8, 10, 11 and 9.

5.1 The (1 1 1) - plane

Table ?? and figure ?? show all adsorption energies at different coverage for all products on the (1 1 1) plane. The adsorption energy for imidogen (NH, bridge) is -5.0 eV at very low coverage (11 %) and -4.1 eV at 100% coverage. That is an 18% decrease in energy per imidogen when going from single occupied to full coverage. Amidogen (NH$_2$), on the other hand, has an adsorption energy of -3.6 eV at the low coverage (single occupied) and -2.3 eV at full coverage, which is a 36% decrease in energy. The adsorption energy of amidogen (NH$_2$) at 50% coverage is -3.4 eV, which is only 5% lesser than that of single occupied amidogen (NH$_2$).

The clean surface (H-terminated diamond) is showed in figure 9. As expected, the surface structure of a clean surface indicate stability. The angles between surface carbons are 109.5° and the distance between neighbouring carbons are 1.54 Å. Also, the hydrogen are pointed perfectly away from the surface, forming a perfect tetrahedra (every angle is 109.5°).
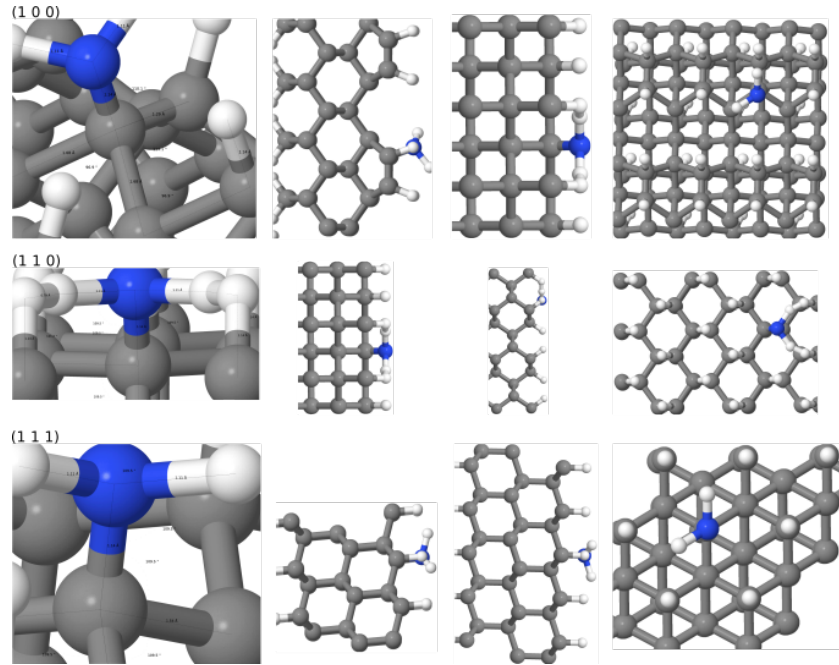
15

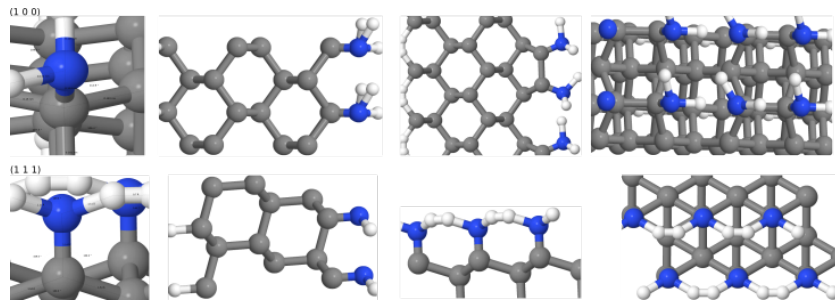Figure 6: The optimized structures of amidogen (NH₂) with low coverage coverage

Figure 7: The optimized structures of amidogen (NH₂) with half the sites covered coverage
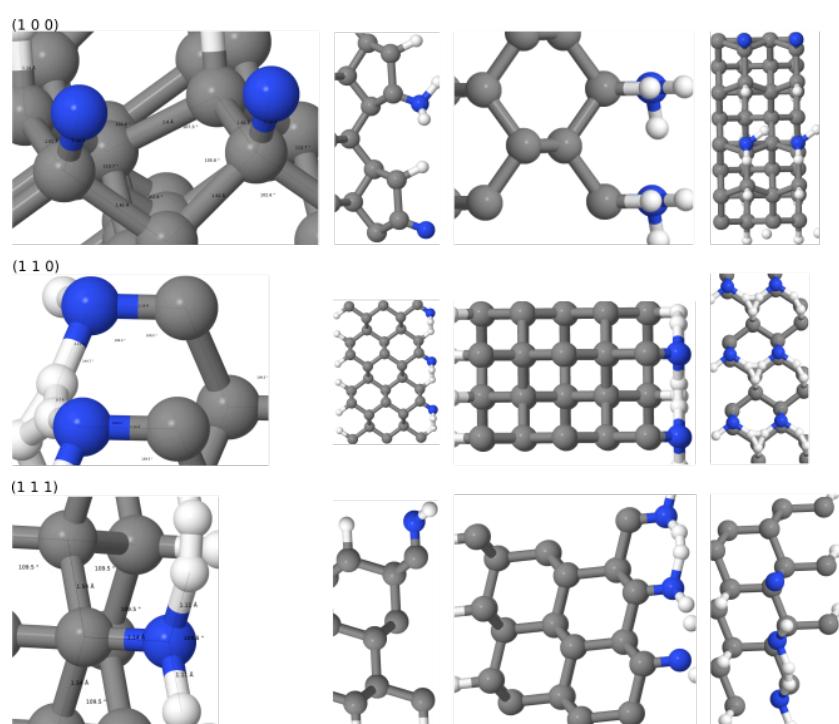
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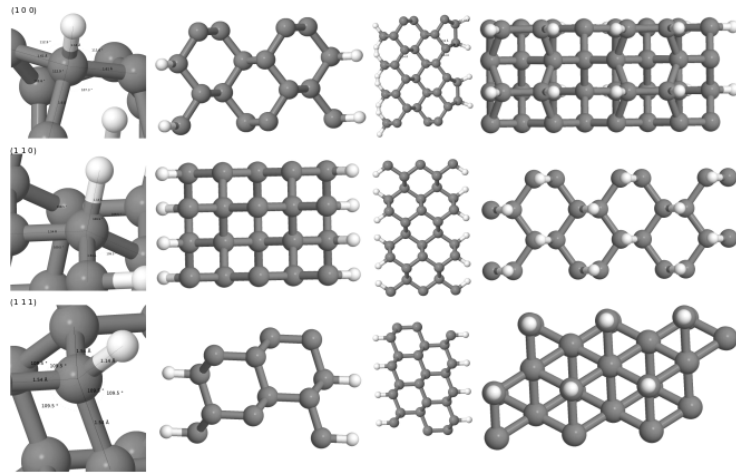Figure 8: The optimized structures of amidogen (NH₂) with a full monolayer

Figure 9: All resulting structures from the gemonetry optimization of H-terminated diamond with angels and distances displayed (to the left) as well as wieved from both sides (middle left, middle right) and from above (to the right).

The resulting structures of bridged imidogen (NH) is shown in figure 10 and the resulting structures for amidogen at different coverage are shown in figure 6, 7 and 8. Neither imidogen (NH, bridge) or amidogen (NH_2) force any changes between the hydrogen and the remaining carbons. This is also true for the angle between amidogen and nearby carbons. Naturally, imidogen loses the tetrahedral symmetry (angles 140° and 150°). Also, the distance between nitrogen and nearby carbons are 1.73 Å for imidogen (NH, bridge) and 1.14 Å for amidogen (NH_2). There is, however, only 0.7 Å between the hydrogen while occupying all sites with amidogen and the overlap is also clearly visibly in figure 7.

5.2 The (1 1 0) - plane

Table **??** and figure **??** show all adsorption energies at different coverage for all products on the (1 1 0) plane. The adsorption energy of imidogen (NH, bridge) is -4.1 eV at very low coverage (single occupied) and -3.6 eV at 100% which corresponds to a 12% decrease in energy per imidogen. Amidogen (NH_2), on the other hand, has an adsorption energy of -3.1 eV at the low coverage (single occupied) and not stable at all at full coverage (to the point where the geometry optimization failed). The adsorption energy of amidogen (NH_2) at 50% coverage is -2.6 eV, which is 12% lesser than that of the single occupied amidogen (NH_2).

The clean surface (H-terminated diamond) is showed in figure 9. As with the (1 0 0) - plane, the surface structure of a clean surface indicate stability. The angles between surface carbons are 109.5° and the distance between neighbouring carbons are 1.54 Å. The bonding distance for hydrogen in this geometry optimization is 1.14 Å. These angles and distances did not change while adding imidogen (figure 10) or amidogen (figure 6, 7, 8). The distance between a nitrogen and the nearest carbon was the same for both low and high coverage for both imidogen (NH) and amidogen (NH_2). The bonding distance for amidogen was 1.14 Å for amidogen, which is the same as the hydrogen-carbon distance. The imidogen bridge varied between 1.19 Å and 1.22 Å between nitrogen atoms and their nearest carbon atoms. Also, the hydrogen of the amidogen groups are clearly overlapping with neighbouring hydrogen (see figure 6, 7 and 8).

5.3 The (1 0 0) - plane

Table **??** and figure **??** show all adsorption energies at different coverage for all products on the (1 0 0) plane. The adsorption energy
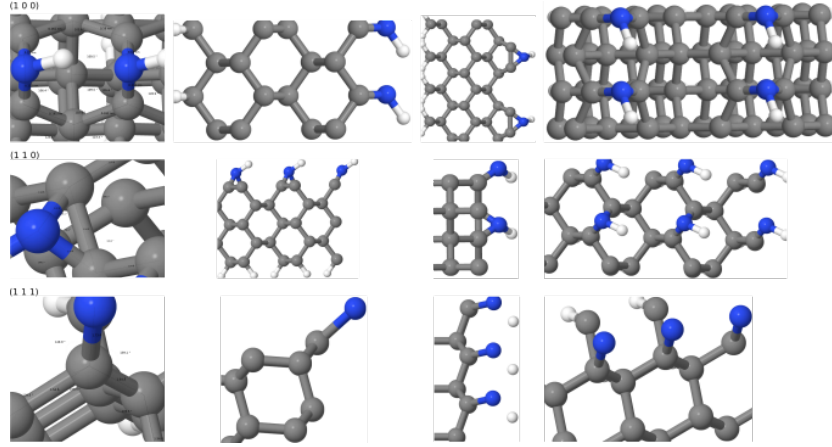
Figure 10: The optimized structures of imidogen (NH) with maximum coverage coverage

for imidogen (NH, bridge) is -5.1 eV at very low coverage (single occupied) and -5.0 eV at 100% coverage, which is a 2% difference. The adsorption of single occupied and fully occupied (100%) amidogen (NH_2 , on-top) is -3.9 eV and -3.1 eV respectively, which is a 21% difference. The adsorption energy of amidogen (NH_2) at 50% coverage is -3.7 eV, which is 5% lesser than that of the single occupied amidogen (NH_2). Also, the adsorption energy for on-top imidogen (NH, double bonded) is -3.5 eV for single occupied and, surprisingly, -4.9 eV at 100% coverage.

The bond distance between surface carbons near double bonded nitrogen is $1.54 - 1.55$ Å and the angles between those are $109°$ leading to increased symmetry compared to the hydrogen covered surface (figure 11).

As can be seen in figure 10 (for the bridge) and figures 6, 7, 8 (for NH_2) amidogen and bridge imidogen do not affect angles and distances between carbons any more or less than pure hydrogen, i.e. the angles vary between $102°$ and $113°$ and the distance between two nearby carbons (that are bonded) are 1.6-1.61 Å. The bonding distance between the nitrogen and the surface, which do not change with coverage, is 1.1 Å for the double bonded imidogen (NH), 1.3 Å for bridged imidogen (NH) and 1.14 for amidogen (NH_2). Note that the bonding distance for hydrogen is 1.14 Å.

5.4   Comparison between planes

The adsorption energies of single-site imidogen (NH, bridge) on the (1 0 0), (1 1 1) and (1 1 0) are -5.1 eV, -5.0 eV and -4.1 respectively.
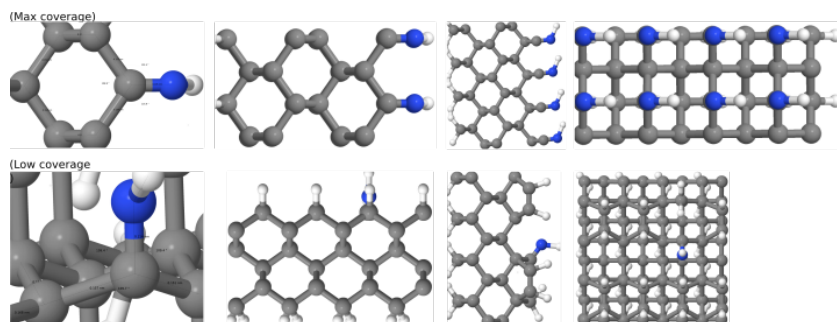
Figure 11: The optimized structures of on-top imidogen on the (1 0 0) surface with low coverage (below) and maximum coverage (on-top). Note that even the maximum coverage maintain stable angles in surface carbons (109°) and 1.54-1.55 Å between surface carbon which is the same as the bulk distance between carbons in diamond.

The corresponding values for imidogen at 100% coverage are -5.0 eV, -4.1 eV and 3.6 eV respectively. For amidogen (NH_2 , on-top), those values are -3.9 eV, -3.6 eV and -3.1 eV when having a single site at the (1 0 0), (1 1 1) and (1 1 0) planes (in that order). The corresponding values for 100% amidogen (NH_2 , on-top) coverage are -3.1 eV, -2.3 eV and not forming at all respectively (see figure 11).

6   Discussion and summary

6.1   General

The results are consistent with earlier reports concerning similar systems and shows that functionalization of diamond surfaces with amine-based compounds are a promising method of modifying the diamond surface. Drawn conclusions from calculations are also consistent with conclusions that can be drawn from common knowledge about diamond and general surface theory. Due to that, it can be concluded that nitrogen based compound might be used as an anchor for further bio-functionalization. It has, indeed, already been created successful attempts to get a relatively good coverage of NH and NH_2 groups, but never a mono-layer. The fact that creating a mono layer is difficult is actually explained by this study. The reason for these difficulties might be the hydrogen overlap that causes instability in all but the (1 0 0) plane. Scientists would have to try to create surfaces that are mostly of other planes than (1 1 1) and (1 1 0).

In addition to further proving that a mono-layer of NH_2 is very unlikely, especially at the (1 1 0) surface, this study concludes that NH_2 is less favourable than bridged NH. Bridged NH are further away from each other and hence less coverage dependent. It is also further proven that the (1 0 0) surface is easier to functionalize than the (1 1 1) and (1 1 0) surfaces. Furthermore, additional computations on the (1 0 0) surface indicated that imidogen (NH) is the least likely product at low coverage but almost as stable as bridging imidogen at full coverage.

6.2 Further studies needed

6.2.1 More calculations

This is not a full study and before fully going over to practical work, several more calculations could be made to get more information.

The most glaring calculation that is missing is the bonding energy of hydrogen that would enable a comparison between the products of the study and the standard case (These calculations were complete when I did this study, so that particular calculation was likely lost rather than not done at all).

It could also be beneficiary to do the same calculations, but on other planes with higher indexes. Also, more variations in coverage on the planes that are found to be the most favourable would give a more accurate picture of how the adsorption changes with coverage. Another factor that could play a role is whether the diamond is doped or not (doping of diamond is when one or more carbon in the bulk are exchanged with another atom). One could, for example, exchange a carbon with a nitrogen.

There is, furthermore, the next step. The reason for studying the adsorption of amidogen and imidogen was due to the potential in further fictionalization of the surface. Ideally, one would also calculate the adsorption of the target group (DNA, proteins or whatever it is) to a surface that already has a layer of amidogen or imidogen.

6.2.2 Practical work

This is only one step in the direction of using amine-terminated diamond as an intermediate in bio-functionalization of the surface of diamond. Someone has to examine the next step too, which is the reaction between the functionalized diamond surface and whatever that is to be used in the actual application.

Also, amines are only one type of functional groups that might be interesting to use as an intermediate in the functionalization of

diamonds.

All of this also need to be tested in practical experimentation rather than just theoretical computations.

7 Conclusions

The results show that a single bridging NH is more strongly attached to the diamond surface than a single NH_2 or NH in on-top positions for all three low index planes. This is even more noticeable as the coverage increases, which probably comes from the increased sterical hindrance due to lack of space between the NH_2 groups reported by [6]. One may also note that the on-top imidogen (NH) is the least stable product at low coverage at the (1 0 0) surface, but it is almost as stable as bridging imidogen (NH) under the same conditions. The cause of that is likely the increased symmetry that can be seen at the (1 0 0) surface when on-top imidogen is added as compared to the bridge that does not change anything between the carbons.

As in earlier reports, the effect of coverage is smallest in the (1 0 0) case and largest in the (1 1 0) case where half of the NH_2 -groups desorbed from the surface during the DFT calculation (although the system did not converge properly). The effect of the total coverage was also less pronounced at the (1 0 0) surface and the bridged NH-groups. These results were quite expected as they also could be derived from doing and looking at simple schematic sketches of the surface bonds.

Another thing to consider is that although the bridged NH is the most favourable per molecule, it is still less stable per bond than the NH_2 group while having a low coverage for all the low index surfaces. There are also half as many reaction sites for the bridge imidogen (NH) to consider as with the on-top position (see tables 2, 3 and 4). But that is only an issue while discussing low coverages, since NH_2 is strongly affected by neighbouring groups, especially in the (1 1 0) case where half of the amino groups desorbed during the geometry optimization. Amidogen also shows overlap between hydrogen on both the (1 1 0) and (1 1 1) plane while forming a mono-layer. This study also conclude that the 1 0 0-plane is favoured for both amidogen (NH_2 , on-top) and imidogen (NH, double bonded and bridged) which was expected. A summary for each plane follows below.

(1 1 1) Imidogen (bridge, NH) is favoured before amidogen at the (1 1 1) surface despite less stable angles due to higher adsorption energy and overlap between hydrogen as the coverage of amidogen becomes to high. Also, imidogen adsorption on the diamond surface is slightly

dependent on total coverage. Amidogen is much more dependent, but not until after the surface is more than 50% covered.

(1 1 0) Imidogen (bridge, NH) is favoured before amidogen at the (1 1 0) surface due to higher adsorption energy and severe overlap between the hydrogen atoms on the amidogen groups and nearby hydrogen atoms. Imidogen adsorption is slightly dependent on coverage, even though it is even less than at the (1 1 1) plane. According to this, amidogen is not likely to form a mono-layer, which is also in accordance to earlier reports. The results also indicate a dependence on coverage for the adsorption of amidogen, as the adsorption energy decreased while the coverage was increased.

(1 0 0) Bridged imidogen (bridge, NH) is favoured before double bonded imidogen (NH, on-top) and amidogen (NH_2, on-top) even though double bonded imidogen is almost as stable as bridged. Note that while bridged imidogen is almost unaffected by high coverage, the double bonded variant seem more stable at 100 % coverage as the on-top imidogen stabilise the diamond surface.

Acknowledgements

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