Ab initio study of molecular adsorption on hydrogenated diamond (001) surfaces

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Abstract. The interaction of molecules (HCl, NH₃ and H₂O) and the hydrogen-terminated diamond (001) surface is studied with ab initio simulation. Both the energy and the geometry indicate that the surface H atoms are more favourable to pull the H atoms of these polar molecules. The calculated charge redistribution reveals that a weak covalent interaction formed between H atom of adsorbate molecules and the H atom of the diamond surface.

1. Introduction
The hydrogenated diamond surface is of considerable interest because of its two outstanding features – a fairly high p-type surface conductivity [1] can be used for electronic devices and true negative electron affinity [2] – making diamond an efficient photo emitter and possibly a candidate in the field of cold cathode field emission. The p-type surface conduction is a unique property among semiconductors that has already proven its potential for electronic devices such as a diamond-based FET [3]. Since 1989 Landstrass and Ravi [4] observed a substantial surface conductivity in a hydrogenated diamond surface, much research has been done on this surface conductive layer [5,6,7]. The surface conductivity is as high as 10⁻⁴ to 10⁻⁵ Ω⁻¹ at room temperature with activation energy of as low as 50 meV at 80-450 K [8]. It has also been observed that the p-type conduction is enhanced in atmospheres rich in HCl and weakened in an NH₃ ambience [9]. There have been several proposed mechanisms for the origin of surface conduction based on the experimental observations. Landstrass and Ravi[4] proposed that the high-conductivity layer is due to passivation of deep levels by hydrogen that is incorporated in the region near the surface. Maki et al.[6] suggested that the high conductivity is attributed to holes generated by shallow acceptor levels related to hydrogen incorporated in the surface region. Kawarada [1] et al. suggested, on the basis of scanning tunnelling spectroscopy (STS) results, that the surface of as-deposited diamond films that are terminated by hydrogen, which makes the surface negatively charged, inducing a hole accumulation layer near the surface and causing surface band bending and high conductivity due to hole accumulation at the bent band. On the other hand, Hayashi et al. [8] proposed the model of the existence of acceptor levels in the subsurface region. Later, Maier et al. [10] suggested that hydrogen is not the only necessary requirement for the surface conductivity; exposure to air is also essential. And they proposed a mechanism in which a redox
reaction in an adsorbed water layer provides the electron sink for the subsurface holes accumulation layer.

Although there are numerous experimental and theoretical studies of the diamond surface, theoretical studies on the interaction between molecules and the diamond surface are still rare. Here we studied on the interaction of molecule adsorbates (HCl, NH₃, H₂O) and H-terminated diamond (001) surface within density-functional theory (DFT), give a clear picture of these polar molecular adstructures on the diamond surface, and the charge distribution are calculated to further understand these structures.

2. Calculation details

The ab initio study was carried out with the Vienna ab initio simulation package (VASP) [11,12] based on DFT. The electron-ion interaction is described by optimized ultrasoft pseudopotentials, and the generalized gradient approximation (GGA) by Perdew et al. [13] is used for the exchange-correlation potential. The plane-wave basis set included waves up to 300eV. And the optimizations of the atomic structures were obtained via a quasi-Newton quench based on the exact Hellmann-Feynman forces. The Monkhorst-Pack scheme with 2×2×1 k points has been used for integration in the surface Brillouin zone.

The periodic slab for the H-terminated C (001) surface consisted of ten carbon layers and a vacuum region equal to ten atomic layers (about 8 Å). The supercell has 16 (4×4) C atoms per layer. Every surface C atom is paired with another and the upper member of this pair is attached to one hydrogen atom resulting in a (2×1):H surface, which has been found in experiment [14] as well as in calculation [15,16]. A monolayer of hydrogen atoms ties up the dangling bonds on the bottom of the C layer. The bottom-most C layer and the H layer below it were fixed in the optimization position and the other atoms of the supercell were allowed to move freely in all of the computations. The theory lattice constant, 3.574 Å, is used. The molecule adsorbate is placed above the surface and also allowed to relax. The computation was stopped when the Hellmann-Feynman forces on all the relaxed atoms were less than 0.1eV/Å.

3. Results and discussion

The polar molecules HCl, NH₃ and H₂O are studied in our calculation. Their geometries before and after relaxation are shown in Fig.1, respectively.

![Figure 1](image)

**Figure 1.** Adsorption structures of (a) HCl, (b) NH₃, and (c) H₂O on the H-terminated diamond surface: before and after relaxation. The green, blue, red, white and gray balls represent Cl, N, O, H and C atoms, respectively.

To each molecule, the adsorption of the top site is more favoured than the bridge or hollow sites. For HCl, the molecule lies aslant on the surface with the H atom closer to the surface. The distances between the Hₐ(HCl) and the Hₗ(surface) is 2.07Å, and the adsorption energy is 55 meV. For NH₃, the molecule lies on the surface flatly, and the pyramid of the NH₃ turns upside down. The distances
between the three \( H_\text{m}(\text{NH}_3) \) and the \( H_\text{s} \) are all larger than 2.5 Å, and the adsorption energy is 21meV. For \( \text{H}_2\text{O} \), the molecule lies on the surface with one \( H \) atom pointing toward the surface. The distances between the \( H_\text{m}(\text{H}_2\text{O}) \) and the \( H_\text{s} \) is about 1.98 Å, and the adsorption energy is 85meV. All those adsorption geometries reveal that the \( H \) of the molecules has interaction with the \( H \) of the surface. Since the electronegativity of \( C (~2.5) \) is larger than that of \( H (~2.2) \), the \( H \) end of the \( C-H \) bond is positive pole. While \( \text{HCl} \), \( \text{NH}_3 \) and \( \text{H}_2\text{O} \) are all polar molecules, the \( H \) ends of these molecules are positive poles and the other atoms are negative poles. So it is involuntary supposed that the negative poles of the molecules point to the surface \( C-H \) bond. However our calculations show an opposite picture.

To apprehend this result further, the redistribution of electronic density of the surface region before and after the \( C-H \) bond formation was calculated. The difference density is defined as

\[
\Delta \rho = \rho[\text{H-terminated surface}] - \rho[\text{surface without H atoms}] - \rho[\text{H atoms}]
\]

The isodensity contours of the difference electron density for the \( H \)-terminated diamond (001) surface and the summation of difference electron density of planes paralleling to the surface are drawn as Fig 2 (a) and (b), respectively.

\[\text{Figure 2. (a) Isodensity contours for the difference electron density for the diamond (2×1): H surface. The contours have densities } \Delta \rho = \{0.9, 0.75, 0.5, 0.25, 0.1, 0.075, 0.05, -0.005, -0.0075, -0.01, -0.025, -0.05, -0.075, -0.1, -0.125, -0.14\}. \text{ Solid and dashed lines correspond to } \Delta \rho > 0 \text{ and } \Delta \rho < 0, \text{ respectively. (b) The difference electron density of planes paralleling to the surface corresponding to the distance from the plane to the surface } C \text{ atoms layer.}\]

It can be seen clearly in the two figures that the formation of the \( C-H \) bonding leads to electron transfer from the \( C \) atoms’ region (the dashed lines around the \( C \) atoms in Fig. 2 (a)) to the bonding region (the solid lines in Fig. 2(a)). This is because the dangling bond of the surface \( C \) atom forms a \( \sigma \) bond with \( H \) atom. The charge around the \( H \) atom increases comparing with isolated \( H \) atom. This is consistent with the electronegativity of \( C (2.5) \) and \( H (2.2) \). Since the difference of the two element’ electronegativity is not significantly large (comparing to the difference between \( O, N, F \) etc. and \( H \) element), the polarity of the \( C-H \) bond is much weaker than those typical polar bond (such as \( O-H \) bond). So when \( \text{HCl}, \text{NH}_3 \) and \( \text{H}_2\text{O} \) adsorbed on the surface, there is no visible attractive power between the surface \( H \) atoms and the negative poles of these polar molecules.

The charge redistribution of one \( \text{H}_2\text{O} \) adsorbed on the \( H \)-terminated diamond surface system is then calculated using similar method mentioned above to reveal what happened when polar molecule absorbed on the \( H \)-terminated diamond surface. The summation of difference electron density of planes paralleling the surface, corresponding to the distance from the plane to the surface \( C \) atoms layer, is shown in Fig. 3.
We can find that when H₂O adsorbed on the surface, electron between the surface and the H₂O molecule increased, that is, a weak covalent interaction formed between H atoms of H₂O and the surface C-H bond. At the same time, electron between the C-H bond and the O-H bond reduced. So the reason all the H ends of the three adsorbed molecules pointing to the H-terminated diamond surface is that a weak covalent interaction forming between them.

The energy and the distance obtained in our calculation about HCl and H₂O are similar to that of an unconventional hydrogen bonding, namely dihydrogen bonding [17, 18], in which the association energies situated in the range of 1.1-3.7 kal/mol [17], which is 50 to 161meV, and the noncovalently bonded H…H distances in the M-H…H-X (M= transition metals, Li, B etc.; X = O, N, halogen etc.) systems typically range from 1.7 Å to 2.4 Å [18]. Therefore, the H…H interaction between the polar molecules and the H-terminated diamond surface may be regarded as a kind of hydrogen bond.

Furthermore, the calculation reveals that the adsorbed molecules had little influence on the structure of the H-terminated C (001) surface. So we consider that the p-type surface conduction of the H-terminated C (001) surface is not due to the molecule adsorption on the H-terminated surface. The real origin of this particular property needs further study on the partly H-terminated surface.

4. Conclusion
In summary, we studied the interaction of the adsorbed molecules (HCl, NH₃ and H₂O) and the hydrogen-terminated diamond (001) surface via *ab initio* calculations. When these polar molecules adsorbed on the surface, the H-end of molecule points to the H atom on the surface. This is dramatically different from the usual supposed picture of adsorbates on the H-terminated diamond surface. Further calculation disclosed that a weak covalent interaction formed between H atoms of adsorbed molecules and the H atoms of the diamond surface. The adsorption energy and the H…H distance are similar to those of the dihydrogen bonding. Thus, we consider that the interaction found here is also a kind of hydrogen bond.

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