Letters

Differentiating between hydrogen and fluorine on a diamond surface

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Abstract. We have computed the interaction energies for pyridine (C_5H_5N) and $(CH_3)_3PO$ with H and F atoms on the surface of diamond(111) as a function of the type of neighboring surface atom. The pyridine-H and -F interaction energies differ by about 5 kcal/mol, which is only about one-third of that found for a one-dimensional model for the surface. The difference in the interaction energies for $(CH_3)_3PO$ is larger. However, the $(CH_3)_3PO$-neighbor interaction energy is larger than for pyridine, so that the $(CH_3)_3PO$—H interaction becomes repulsive for six neighboring F atoms. Substituting CN for F dramatically increases the repulsion between the surface atoms and molecules. The repulsion is sufficiently large that H/CN does not appear to be better than H/F as a possible way to store data on a surface. While pyridine shows some potential as a possible probe to differentiate between H and F on a diamond surface, it is not ideal.

Key words: Interaction energies – Pyridine – Hydrogen – Fluorine – Diamond(111) – Nanotechnology – Chemical storage of data

1 Introduction

We previously proposed storing binary data using H(=0) and F(=1) atoms bonded to a diamond(111) surface [1]. We investigated molecules that could be attached to the tip of an atomic force microscope (AFM) that could be used to differentiate between H and F. Pyridine (C_5H_5N) and $(CH_3)_3PO$ were both found to yield interaction energies (and forces) with H and F that were sufficiently different that it should be possible to read the data. We have also investigated a possible

mechanism to replace a surface H atom with an F atom [2], and hence write the data.

The biggest limitation in our previous study [1] was using a one-dimensional (1-D) model of the surface. Although a crude model, it did allow us to exclude some probe molecules from further consideration as the difference in their interaction energies with H and F was too small. In this work we test the two most promising probe molecules from the previous study using a 2-D model for the surface. In addition, we previously suggested that H and CN might be a better system for data storage as the difference in height above the surface for H and CN is larger than for H and F. Therefore, substituting CN for F should result in larger forces on the AFM tip for a constant height, or larger differences in height for a constant force. This should make reading H versus CN on a surface easier than H versus F. Therefore, we also investigate H and CN on diamond(111) using the same 2-D model as used for H and F.

2 Model

The hydrogenated diamond(111) surface is modeled using $C_{13}H_{22}$. There are seven surface C atoms in this cluster model of diamond (see Fig. 1). The central data storage atom has all six neighbors compared with only two in the previous [1] 1-D model. The pyridine (C_5H_5N) probe molecule is also shown in Fig. 1. The three C atoms on the top of the pyridine are where the probe molecule would be attached to the AFM tip, with the H atoms simulating atoms in the AFM tip. Three C—X bonds should attach the probe firmly to the AFM tip. An analogous mechanism is envisioned for attaching $(CH_3)_3PO$ to the AFM tip. The H atoms at the top of pyridine and $(CH_3)_3PO$ and on the sides and bottom of the diamond cluster model are used to tie up the dangling bonds. Pyridine approaches the surface with its C_2 axis coincident with the C—X bond axis of the central data storage site. For $(CH_3)_3PO$ the PO bond axis is coincident with the C—X bond axis. The probe molecule central data storage atom interaction energy is computed as a function of probe-diamond surface distance. This process is repeated for H and F and for three choices of

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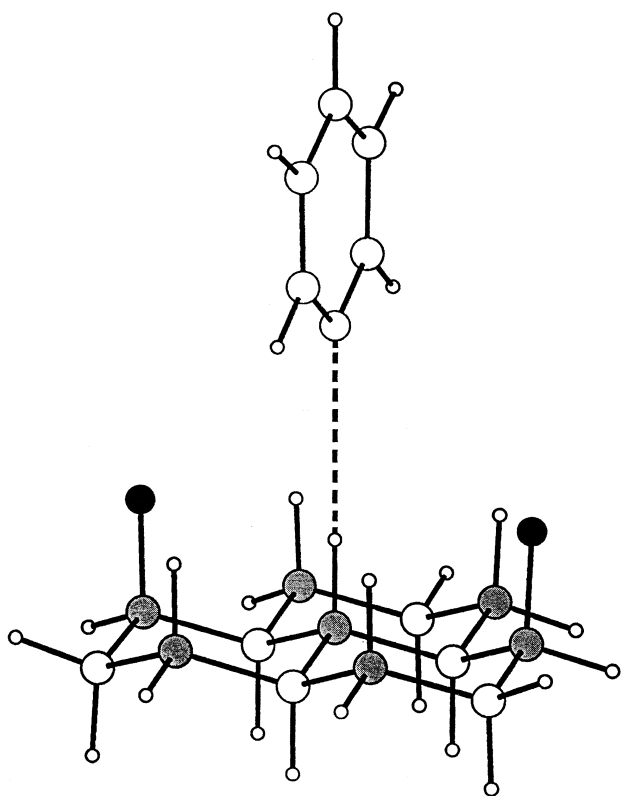*Correspondence to*: C.W. Bauschlicher

Fig. 1. An illustration of the diamond(111) surface with H and F atoms (the *two filled circles*) and the pyridine probe molecule approaching the central surface H atom

the surrounding surface atoms: six H atoms, four H atoms and two F atoms, and six F atoms. For a workable storage system, it must be possible to differentiate between the two data atoms for all possible combinations of surrounding atoms.

3 Methods

Density functional theory, using the hybrid [3] B3LYP functional [4], is used to fully optimize the geometries of the probe molecules and our models of the diamond surface. The interaction energy between the probes and the surface is computed as a function of the probe-surface distance, with the probe and surface geometries fixed. The 6-31 G(d) basis set [5] is used throughout. Our previous study [1] showed that improving the basis set or using second-order Møller-Plesset perturbation theory (MP2) [6] did not change the results significantly, thus only the B3LYP approach, in conjunction with the 6-31 G(d) basis set, is used in this work. All calculations are performed using Gaussian 94 [7].

4 Results and discussion

4.1 Cluster models

We first consider the model for diamond(111) with surface H and F atoms and surface CN molecules. It is

possible either to fully optimize the cluster geometry or constrain the location of the C and H atoms on the sides and bottom of the cluster. The former is easier and reduces the potential for some types of computational errors. It might be argued that the latter approach is more consistent with the real surface where the location of the C atoms is constrained by their neighbors. A complete optimization of $C_{13}H_{22}$ yields a structure where the central C surface atom is about 0.01 Å out of the plane of the other six surface atoms. The seven surface C—H bonds are nearly parallel; the surrounding H atoms bend 0.07 Å away from the center. That is, even without any constraints our cluster is sufficiently large that nonphysical distortions do not occur.

The distortion of the cluster where the central surface H atom has been replaced with an F atom or CN molecule is still very small. For F, the central C is now 0.02 Å out of the plane of the other six, while for CN the difference is 0.09 Å. For the central F atom case, the bending of the surrounding H atoms is the same as for the all-hydrogen cluster, while for a central CN the surrounding H atoms bend by 0.11 Å, or 0.04 Å more than for the all-hydrogen cluster or with a central F atom. The surface-CN binding energy of 118.8 kcal/mol is very similar to that for F (117.6 kcal/mol) and somewhat larger than for H (101.9 kcal/mol). That is, CN has about the same binding energy as F, but causes slightly larger distortions of the cluster.

Replacing all seven surface H atoms with F atoms yields a distortion of the cluster that is only slightly larger than observed for one F atom, while for seven CN molecules on the surface, the optimized cluster becomes an unreasonable model for the surface (see Fig. 2). It is probably not surprising that there is a large stabilization energy associated with the distortion of the $C_{13}H_{15}(CN)_7$ cluster. Idealizing the $C_{13}H_{15}F_7$ and $C_{13}H_{15}(CN)_7$ cluster geometries by replacing the surface H atoms in $C_{13}H_{22}$ with F atoms or CN molecules, setting the C—F and C—C—N bond distances to those in $C_{13}H_{21}X$ and constraining the C—F and C—C—N bond axes to be parallel to the central bond, increases the energy of $C_{13}H_{15}(CN)_7$ by 145 kcal/mol compared with only 15 kcal/mol for $C_{13}H_{15}F_7$. The CN—CN repulsive interaction is very large compared to the surface-CN binding energy; it only requires 45 kcal/mol to remove the central CN molecule in the idealized structure.
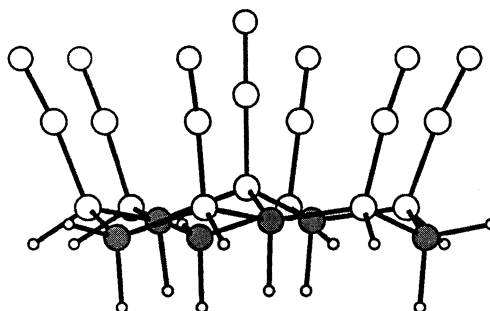

Fig. 2. The optimal B3LYP structure of $C_{13}H_{15}(CN)_7$

On the basis of these cluster calculations we do not study the H/CN system further as the CN—CN repulsive interaction is sufficiently large that it would appear to make its use as a data storage system questionable. On a more open face of diamond or on a material with a larger spacing between atoms, the H/CN system might be superior to H/F, but this is not the case for diamond(111). Since fully optimizing the cluster does not lead to any significant distortion, we adopt the computationally simpler approach of fully optimizing all of our diamond cluster models.

4.2 Cluster-probe interaction energies

The interaction energies for pyridine and $(CH_3)_3PO$ with the coated diamond surfaces are summarized in Table 1. We first consider the results for the pyridine probe. For $C_{13}H_{22}$, the optimal surface C—N probe distance is 3.8 Å. This produces an attractive interaction of 1.57 kcal/mol. For the same C—N distance the interaction decreases with two F atoms on opposite sides of the central atom; this arrangement is shown in Fig. 1. When all six neighbors are F atoms, the probe-H interaction is the most attractive of the three cases considered. The neighboring F atoms are all expected to withdraw charge from the cluster, and hence should affect the data-H atom-N probe interaction in the same way. While the N-data atom interaction is expected to be the largest, the pyridine C—H groups adjacent to the N atom also have some interaction with the surface. We have minimized this interaction by orienting the pyridine such that the C—H groups point between the F and H surface atoms; however, this interaction is not zero. Therefore, while replacing the two H atoms farthest from the pyridine C—H groups with F decreases the overall interaction strength, replacing the four H atoms nearest the C—H groups increases the interaction energy by introducing an attractive F—H interaction.

The pyridine-F interaction is repulsive. Adding two F neighbors increases the repulsion but when all six neighbors are F atoms, the interaction is the least repulsive of the three cases considered because it adds the attractive F—H interaction from the C—H groups of the pyridine. That is, the interaction of the pyridine with H and F follows the same trends. For the three choices of neighbors considered, the worst case would be to differentiate between F with six F neighbors and H with two F neighbors, where the difference in interaction energy is only 5.06 kcal/mol. This is about one-third the energy difference found for the 1-D model, and is sufficiently small that it might be difficult to differentiate between H and F, especially if the method of connecting the pyridine to the AFM tip involved a nanotube or other method that reduced the sensitivity by introducing some flexibility into the system.

We now consider the $(CH_3)_3PO$ probe. We previously noted that this probe molecule had about the same difference in interaction energies between H and F as pyridine, but that it was expected to be more directional as the adjacent C—H groups were eliminated. The results for this probe molecule are also summarized in Table 1. For the case of six H neighbors, we find that the central H-probe interaction is more attractive and the F-probe interaction is more repulsive than the analogous quantities for pyridine. Replacing the neighboring H surface atoms with F atoms increases the repulsion for both a center H or F. For six F neighbors, the central H now has a repulsive interaction. Thus the desirable feature of having one species attractive and the other repulsive is lost. The increased repulsion arises from the negative charge on the probe oxygen which has a repulsive interaction with the neighboring F atoms. For pyridine the unwanted C—H-surface interaction can be reduced by orienting the pyridine but, unfortunately, it is not possible to minimize the O-neighbor interaction. The problem is perhaps a little worse than indicated by the results in Table 1. The total interaction for the central H with six F neighbors is a superposition of the H—O attractive interaction with the F—O repulsive interaction. At long range the F—O repulsion is large and there is an overall repulsive interaction. At short range, the H—O attraction modifies the interaction potential to give an inner well, see Fig. 3. Thus, in addition to having both a repulsive and attractive interaction for H depending on
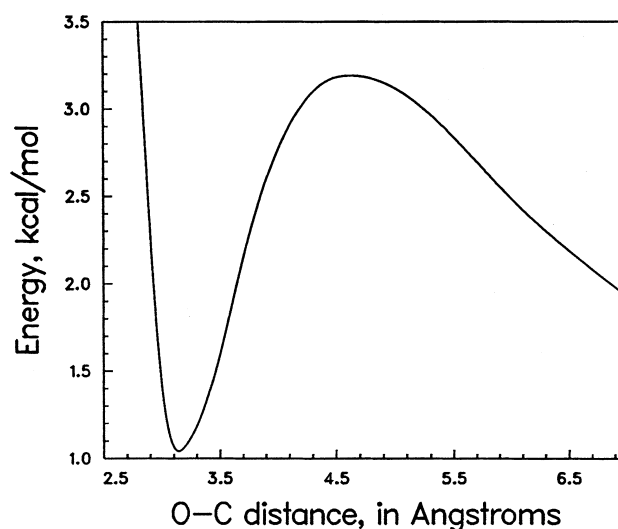
Table 1. Summary of B3LYP/6-31G* results. Interaction energies are in kcal/mol

Neighbors	Central H	Central F	ΔE
C_5H_5N probe N—C (surface) distance = 3.8 Å[a]			
6 H	1.57	−6.62	8.19
4 H 2F	0.64	−7.25	7.89
6 F	2.40	−4.42	6.82
$(CH_3)_3PO$ probe O—C (surface) distance = 3.5 Å[a]			
6 H	2.56	−12.57	15.13
4 H 2F	1.24	−12.85	14.09
6 F	−1.59	−13.57	11.98

[a] The optimal distance for $C_{13}H_{22}$, i.e. a central H with six surrounding H atoms

Fig. 3. The interaction energy for $(CH_3)_3PO$ approaching the central H atom in $C_{13}H_{16}F_6$

the number of F neighbors, the H-probe potential is repulsive at long range with an inner well. A potential of this form does not seem ideal for an AFM-based detection scheme.

5 Conclusions

The two most promising probe molecules from our previous 1-D model of the surface were tested using a 2-D surface model. Pyridine still has an attractive interaction for H and a repulsive interaction for F regardless of the type of neighboring data atoms. Unfortunately the difference in probe-H and probe-F interaction energies is only about one-third of that found using the 1-D model. The pyridine CH groups adjacent to the N have an interaction with the surface as expected. However, by orienting the pyridine so that these groups point between the surface atoms, this interaction is not prohibitively large. It was expected that $(CH_3)_3PO$ would have a smaller interaction with the neighboring surface atoms than pyridine because the PO points directly at the data atom, without side groups interacting with neighboring surface atoms. Unfortunately, this is not the case. The O-neighbor interaction is sufficiently large that the H-probe interaction becomes repulsive for six F neighbors.

Our previous suggestion for using H/CN instead of H/F to increase the difference in interaction energies between the two data atoms does not appear to be ideal for the diamond(111) surface, where the CN—CN interaction is large. The H/CN system might be superior to H/F on a surface with a larger separation between the neighbors.

The present study shows that there is significant room for improving the design of an atomic-level surface storage system. We are continuing these studies by considering other probe molecules as well as comparing the results obtained using a silicon surface with those obtained on a diamond surface.

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