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# Stability of Halogen-Terminated Diamond (111) Surfaces

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The adsorption of the different species X and $CX_3$ on an X-terminated diamond (111) surface (X = H, F, Cl, Br) has been investigated structurally and energetically, using a cluster approach and two different types of quantum mechanical methods: the ab initio molecular orbital (MO) method and the first-principle density functional theory (DFT) method, respectively. The halogen species F and Cl, as well as hydrogen H, were all shown to be able to sustain the $sp^3$ structural configuration of the surface carbon atoms. Furthermore, the adsorption energies were much larger for the H and F species than for other species like Cl and Br, indicating that H and F species stabilize the diamond (111) surface better than the Cl and Br species do. For Br large sterical hindrances are induced, and the diamond (111) surface cannot be stabilized. The adsorption of $CH_3$ or $CF_3$ to a radical carbon on a H- or F-terminated diamond (111) surface stabilizes also the $sp^3$ structural configuration of the radical carbon atom. The large difference in adsorption energy of the species $CH_3$ and $CF_3$ indicates that the probability for diamond growth, based on the $CF_3$ species as a dominant growth species on a F-terminated diamond (111) surface, is much lower than for growth based on the $CH_3$ species as a dominant growth species on a H-terminated surface. There is no tendency for the gaseous species $CCl_3$ and $CBr_3$ to adsorb on a Cl- or Br-terminated diamond (111) surface.

## Introduction

Considerable experimental and theoretical efforts have been made during the past decade toward obtaining a fundamental understanding of the low-temperature, low-pressure gas phase synthesis of diamond. For optimization of diamond growth processes a detailed understanding of the adsorption and nucleation on surfaces of different crystallographic orientations is needed. Diamond films are grown by a number of techniques including chemical vapor deposition (CVD) (filament-activated CVD, rf, and microwave plasma-activated CVD) and the combustion flame method. Both experimental and theoretical work have been concentrated on dilute gas mixtures of simple hydrocarbon species in an excess of hydrogen.[1−3]

Hydrogen has been considered to be a very important reactant for diamond growth.[1,4−6] One role for H during the growth process is to maintain the $sp^3$ configuration of surface carbon atoms on for example the diamond (111) surface in order to prevent the (1 × 1) structure from being reconstructed to the (2 × 1) structure. Computations based on the local-density theory have indicated that the $\pi$-bonded chain model proposed by Pandey, in which the C atoms form rows of $\pi$-bonded chains with $sp^2$ bond, is the energetically most favorable model of the various structures proposed for the reconstructed surface.[7] Other roles for H are to preferentially etch the graphitic phase of carbon, abstract hydrogen atoms from surface bonded C−H, and to initiate free radical reactions in the gas phase.

Some simple hydrocarbon species (e.g., acetylene and methyl radicals) have, in both experimental and theoretical work, been considered to be very important carbon-containing precursors for diamond growth.[8] In particular, the methyl radical has been assumed to be the dominant growth species during filament-activated deposition on the diamond (111) surface from a reaction mixture of methane and hydrogen.[9] However, some recent theoretical studies have also concluded that a combination of the methyl radical and the acetylene species will most probably act as dominant growth species during growth of the (111) surface.[10,11]

Several researchers have suggested that diamond can also be grown from gas mixtures of halogens or halogenated methane.[12−16] When halogen-containing species are added to the vapor, a lower substrate temperature can be used.[12,14,16] For instance, the presence of fluorine lowers the critical substrate temperature by several hundred degrees compared to hydrogen-based processes.[14] Reduction of the substrate temperature is strongly desired for growth of diamond on materials which cannot tolerate high temperatures. Furthermore, fluorine-terminated diamond films have been found to be very useful for solid lubrication.[17]

The adsorption step is very important in all vapor growth processes and affects both nucleation and growth. The purpose of the present work is to theoretically make a structural and energetic investigation of the adsorption of halogen (F, Cl, and Br) and halogenated methyl to a halogen-terminated diamond (111) surface and compare the results from corresponding investigations of the $H/CH_x$ system. The calculations use a cluster approach and two different types of quantum mechanical methods; the ab initio molecular orbital (MO) method and the first-principle density functional theory (DFT) method. Both methods have frequently been used in similar types of investigations. It would, hence, be of a great interest to make a comparison of the results obtained by using these different methods for one specific surface reaction process. The calculations based on the different methods should then involve identical clusters (modeling the diamond (111) surface) and type of geometry optimization, as well as very similar basis sets.

## Methods

The quantum mechanical calculations presented and discussed in the present work have used the ab initio MO method (using

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the program system Gaussian 92[18]) and different approximations within the DFT method (using the program system Dmol[19]), in calculating the total energies for the reactants as well as for the products of the adsorption process:

$$M^{\bullet} + A^{\bullet} \rightarrow MA \qquad (1)$$

where $M^{\bullet}$ is the template modeling the diamond (111) surface and $A^{\bullet}$ is one of the adsorbing gaseous species used in the investigation (H, F, Cl, Br, $CH_3$, $CF_3$, $CCl_3$, or $CBr_3$).

The ab initio MO method used is a self-consistent-field (SCF) method in which the true many-electron wave function is approximated as a single determinant of orthonormalized molecular orbitals by using the Hartree−Fock (HF) theory. Linear combinations of primitive Gaussian functions (contracted basis functions) are used as atomic orbitals in the linear combination of atomic orbitals to molecular orbitals (LCAO-MO). Moreover, due to inadequate treatment of the instantaneous correlation between motions of electrons in the HF theory, electron correlation treatments will be performed by using a second-order Møller−Plesset perturbation theory (MP2). It is well established that the quantum mechanical approaches based on the HF theory provide a successful and thorough method for calculating the electronic structure and energetics of different types of molecular systems.[20]

The most commonly applied approximation in DFT, the local density approximation (LDA),[22] assumes the charge density to vary slowly on an atomic scale. This LDA method may be regarded as a HF method, corrected for correlation effects. The total energy is then minimized within a SCF approach by the ground-state density $\rho(\mathbf{r})$. One of the most important deficiencies of the LDA exchange is that it does not have the correct asymptotic behavior. Numerically, this leads to a too large calculated chemical bond energy in the system under investigation. Improved functionals (i.e., Becke88, LYP, B-LYP) have been shown to give more accurate bonding energies.[23−25] All-electron LDA calculations, as well as calculations based on DFT with nonlocal Becke exchange, were performed in the present investigation.

The first-principle program system Dmol uses numerical spherical atomic orbitals, rather than analytical ones, in a LCAO-MO approach.[26,27] The success of the method has been shown in different applications. For instance, the adsorption energies of Cu and Ag atoms on Si(111) surfaces have been found to be in good agreement with experimental values.[28]

## Optimal Conditions in Describing the Electronic State

**A. Size of Template.** A necessary condition for obtaining a good description of the electronic state of the reactants and the products in the adsorption reaction is primarily to choose a model cluster describing the diamond surface well, to perform geometry optimizations, and to choose a highly flexible basis set. In an earlier work by the present authors,[29] it was concluded that a medium-sized diamond cluster $C_{13}H_{21}$ is adequate to use in the study of adsorption reactions involving different hydrocarbon species and hydrogen, using ab initio MO theory. This conclusion should also be valid for adsorption reactions involving fluorine, F. In preliminary calculations, the adsorption energy of F to a H-terminated template was found to increase by less than 0.5% when using a larger template $C_{22}H_{26}$ in the calculations. The number of carbon layers in this latter template (four layers) is a factor of 2 larger than the number of carbon layers in $C_{13}H_{21}$ (two layers). Hence, these two lower carbon layers in the larger template $C_{22}H_{26}$ do not noticeably influence the adsorption energy. Moreover, the six surface-bonded hydrogens in the medium-sized template $C_{13}H_{21}$ are for some specific types of calculations in the present investigation replaced by the halogens F, Cl, and Br. Hence, the template $C_{13}H_{21}$ will hereafter be denoted $C_{13}H_{15}X_6$ where X is H, F, Cl, or Br.

**B. Geometrical Optimization.** All geometrical parameters for the gaseous and the adsorbed species were fully optimized in the present investigation. For the medium-sized template $C_{13}H_{15}X_6$, with or without an adsorbed species, two different combinations of atoms were allowed to relax in the field of the fixed structure of its neighbors; (a) only the radical carbon atom and its six adjacent surface-bonded species X. These two types of combinations define the minimum and maximum, respectively, in adsorption energy obtained for the different adsorbing species in the present investigation. However, the more exact adsorption energy is expected to be somewhere in between on the energy scale since the adjacent surface-bonded species on a diamond (111) surface are not expected to be fully relaxed due to sterical hindrances induced by surface neighbors further out from the radical carbon atom. This will at least be the most probable situation for the adsorption of different species to a Cl- or Br-terminated diamond (111) surface due to the large size of Cl and Br. Furthermore, a geometry relaxation of the carbon neighbors to the radical surface carbon atom could also influence the adsorption energies. As a test, the three nearest C neighbors to the radical carbon atom on a F-terminated template $C_{13}H_{15}F_6$ were also allowed to relax in a Hartree−Fock energy calculation of the adsorption of F. A negligible change in adsorption energy of less than 1% was then observed.

**C. Basis Set.** The effect of different basis sets on the adsorption energy of different hydrocarbon species and hydrogen, H, was investigated systematically in an earlier work by the present authors.[29] A combination of two different basis sets was then used for the template $C_{13}H_{21}$ (modeling the H-terminated diamond (111) surface) with the more flexible basis set used near the region of adsorption. It was found that the adsorption energies, obtained at the Hartree−Fock MO level of theory, are rather similar for the different basis set combinations studied: 3-21G/STO-3G, 6-31G**/STO-3G, and 6-31G**/6-31G. The radical carbon atom and its three carbon neighbors, as well as the gaseous and adsorbed species, were all represented by the more flexible basis set. The remaining atoms, including the adjacent surface-bonding species, were then represented by the smaller basis set. A description of the different basis sets are given in ref 20. However, the adsorption of fluorine, F, to this hydrogen-terminated template $C_{13}H_{21}$ has been found to be very sensitive to the choice of basis set combination. The calculated adsorption energy for the different basis set combinations 6-31G**/STO-3G, 6-31G**/6-31G, and 6-31G**/6-31G** were found to be 349, 230, and 228 kJ/mol, respectively, using the Hartree−Fock method. These results indicate that the effects of the next-nearest carbon neighbors and the adjacent surface hydrogens on the adsorption process are not satisfactorily described by using the minimal basis set STO-3G for these atoms. Instead, split-valence basis sets, with or without polarization functions, must be used. The split-valence basis sets with polarization functions (6-31G**) for all atoms in the template $C_{13}H_{15}X_6$ were chosen in the ab initio MO calculations in the present investigations. Split-valence basis sets are able to give an improved description of the expansion or contraction of the valence shells in response to differing molecular environments. Furthermore, by adding polarization functions (p to H and d to C), the description of the charge rearrangement occurring around the atoms will be better. Hence, these polarization functions are, due to the large electronegativity of halogens (especially F), of great importance for the present investigation of adsorption of halogen species to a halogenated surface. The corresponding calculations within the DFT theory are based on the numerical dnp (double numeric plus polarization) basis set. This basis set is equivalent to the 6-31G** basis set in the sense that it is generated by doubling the minimal basis set and by including polarization functions.

Corrections for "basis set superposition errors" (BSSE) are also made for the adsorption of the different gaseous species at the MP2/6-31G** level of theory. These BSSE are due to overlap of basis functions located on the template and on the adsorbed species, leading to an artificial lowering of the energies of both the adsorbant and the template. The effect of the BSSE is that the calculated adsorption energies will be too large. Hence, the corrections for BSSE, commonly called "counterpoise correction",[36] are subtracted from the adsorption energy.

## Results and Discussion

**A. General.** The halogens F, Cl, and Br, as well as hydrogen, H, are all capable of forming a single bond with a carbon atom in the $sp^3$ configuration and on a diamond (111) surface. This single bond results from $\sigma$ overlap between the surface dangling bond perpendicular to the surface and a corresponding orbital of the adsorbent. However, due to large differences in size and electronegativity of the different halogens, structural geometries of a halogenated diamond (111) surface may be different. This is also the situation for the adsorption energies of a specific halogen to an otherwise halogenated surface. Within the halogens, fluorine is most reactive and bromine least reactive toward other elements and groups. Fluorine has the highest electronegativity (4.0) and the smallest covalent atomic radius (71 pm) which leads to strong bonds between fluorine and other atoms. On the other hand, chlorine and bromine atoms form weaker bonds because of their lower electronegativities (3.2 and 3.0, respectively) and larger sizes (99 and 114 pm, respectively). Compared to the halogens, hydrogen has the lowest electronegativity of 2.2.[30]

Fluorine termination of diamond surfaces has attracted a great interest in itself. These surfaces are very hard and have excellent tribological properties. The behavior of diamond crystal surfaces during heating in fluorine ($F_2$) gas has been investigated by means of thermodynamic methods in a work by Piekarczyk and Praver.[31] The obtained terminated surfaces were found to be very stable and could exist at very low fluorine partial pressures and/or high temperatures. Furthermore, the behavior of fluorine atoms on the diamond surfaces (100)-(2×1), (111)-(2×1), and (111)-(1×1) have been studied from both an experimental and a theoretical perspective.[32−34] Adsorption of fluorine on a partly H covered ($0.05 < \Theta < 1.0$) unreconstructed diamond surface (111)-(1×1) was performed by introducing $XeF_2$ vapor into the chamber with the diamond at room temperature.[32] XPS examinations indicated that one monolayer coverage of F and H was obtained. Complete thermal removal of F from this surface was easily achieved below 1300 K. Pederson and Picket[33] have performed local-density calculations in investigating the bonding situation of F to the diamond (100) surface. General conclusions regarding effect of particle size and electronegativity on the surface geometry have also been made. Diamond (100) and (111) surfaces have been exposed to beams of atomic and molecular fluorine and chlorine in an ultrahigh-vacuum environment in a work by Freedman.[34] It was then found that F will act similarly to H in that it will break surface $\pi$-bonded chains to form regions of (1 × 1) reconstructions, desorb from the surface at an appropriate temperature, and abstract surface-bonded hydrogens. The much larger chlorine atoms, on the other hand, are found to bond much more weakly to the diamond (100) surface, producing a saturation coverage of less than half a monolayer at 300 K, which monotonically decreases to almost zero at 400 K. In a recent theoretical work by Hukka, Pakkanen, and Dévelyn it has been indicated that adsorbed F and Cl should rather strongly bound to the dimer-reconstructed (100)-(2×1) surface, at least in the low coverage limit.[35] One of the purposes with the present work is to investigate the stabilizing effect of H, F, Cl, and Br on a diamond (111)-(1×1) surface. The adsorption process of a halogen (F, Cl, Br) and H to a halogen- and H-terminated diamond (111) surface, respectively, will then be investigated both structurally and energetically (see section B).

**TABLE 1: Binding Energy for Adsorbed Species ($\Delta E_{ads}$ (kJ/mol)) on a Template Modeling the Diamond (111) Surface, Calculated by Using Different Types of Quantum Mechanical Methods and Different Levels of Approximation; Neighboring Surface Species are Geometry Optimized**

| | $H^{\bullet}$ [a] | $F^{\bullet}$ [b] | $Cl^{\bullet}$ [c] | $Br^{\bullet}$ [d] | $CH_3^{\bullet}$ [a] | $CF_3^{\bullet}$ [b] |
|---|---|---|---|---|---|---|
| HF | 344 | 269 | 39 | | 194 | −31 |
| MP2+BSSE | 431 | 430 | 200 | | 341 | 105 |
| LDA (B88) | 413 | 421 | 173 | 95 | 276 | 32 |
| LDA | 450 | 550 | 270 | 253 | 418 | 205 |

[a] H-terminated diamond surface. [b] F-terminated diamond surface. [c] Cl-terminated diamond surface. [d] Br-terminated diamond surface.

It has been suggested by several authors that growth of diamond at lower temperatures may be obtained by including halogen or halogenated methane into the growth vapor during chemical vapor deposition of diamond.[12,14−16] For instance, Patterson et al. have used a thermally activated halogen-assisted CVD technique at low temperatures (525−1023 K).[14] They have reported that simple hydrocarbons such as methane can be used in combination with elemental fluorine to produce diamond at those low temperatures. Harris and Belton have performed molecular mechanics calculations in evaluating the growth of diamond on F-terminated diamond (111) surfaces.[15] Methyl radicals were then assumed to be the dominating growth species on an otherwise F-terminated template modeling the diamond (111) surface. Yamada et al. have studied the adsorption and subsequent surface processes of $CH_x$ with the (2 × 1) structure of the diamond (111) surface.[32] It was shown that H can react with and replace any preadsorbed $CH_x$, and vice versa. It would then be interesting to also investigate the role of the halogenated methanes in the adsorption process on an otherwise halogen-terminated diamond (111) surface. Piekaczyk and Prawer have investigated possible diamond crystal growth in an unactivated $CF_4$−$F_2$ gas mixture by means of thermodynamic methods.[31] They find that diamond cannot be deposited by any unactivated process in the binary carbon−fluorine system. However, if we start with radicals, i.e., an activated process, the situation will be different as will be shown in the present paper. The other purpose with the present work is, hence, to investigate, both structurally and energetically, the adsorption of halogenated methanes on an otherwise halogen-terminated diamond (111) surface. These adsorption processes (involving $CF_3$, $CCl_3$, and $CBr_3$) will be presented and discussed in section C.

**B. Stability of Halogen-Terminated Diamond (111) Surfaces. (i) Bonding Energies.** *Introduction.* The results of the Hartree−Fock and MP2 calculations for the adsorption of the species H, F, and Cl on the H-, F-, and Cl-terminated diamond (111) surface, respectively, are given in Table 1. As expected, the changes obtained when performing the calculations with electron correlation are large. These large changes are primarily due to the inadequate treatment in the Hartree−Fock theory of the instantaneous correlation between motions of electrons. The main part of the correlation energy comes from pairs of electrons with opposite spins. These effects are, hence, of special importance in the present investigation since a new bond is formed in the adsorption reaction. As an illustration, calculated energies for dissociation (the reverse of adsorption) of different A−B compounds have been compared with experimental values in ref 20, where both A and B are fluorine or hydrides of the first-period elements. The "adsorption" of various first-row fluorides or hydrides (B) to a methyl group (A) is of special interest for our investigation since the methyl group is closely related to the diamond template models in the present work. The results given in ref 20 show that the HF/6-31G** results in general are in very poor agreement with experiment, being typically in error by 110−190 kJ/mol. The theoretical results improve substantially when performing electron correlation treatments (MP2) with the 6-31G** basis set. The bond dissociation energies are then in error by less than 8 kJ/mol. This accuracy should be sufficient for the calculations of the adsorption energies in the present work.

Unfortunately, it was not possible to use the ab initio MO theory in calculating the energy of adsorption of Br to a Br-terminated diamond (111) surface. Instead, calculations based on the DFT theory were performed. However, before any complementary DFT calculations are to be performed, it is necessary to make a comparison of the corresponding adsorption processes regarding the X and $CX_3$ species (X is H, F, or Cl). The results of the DFT calculations for the adsorption of these different gaseous species on the diamond (111) surface are also shown in Table 1, in addition to the HF and MP2 levels of ab initio MO theory (including corrections for BSSE). Since the results obtained from calculations on the DFT level of theory include corrections for electron correlation effects, they should be compared numerically with results obtained from calculations on the MP2 level of theory (see Methods). As can be seen in Table 1, the ordering of the different adsorption energies is identical for the different quantum mechanical methods used. Numerically, there are large differences in results obtained by the two different types of first-principle DFT calculations, with the MP2 results somewhere in between. The two different DFT methods used are LDA and DFT with nonlocal Becke exchange. The results obtained by using the latter method are in much better agreement with the results obtained by the MP2 method, giving a more accurate bonding energy than the LDA method does for the system under investigation. One can then draw the conclusion that it is quite possible to use the DFT method with nonlocal Becke exchange in calculating the adsorption energy of Br to an otherwise Br-terminated diamond (111) surface. More generally, both of the two different quantum mechanical methods (ab initio MO and the first-principle DFT with nonlocal Becke exchange) were shown to be useful in investigating the relative adsorption energies in the present work.

*Fluorine*. As can be seen in Table 1, the adsorption energy of F to a F-terminated diamond (111) surface is similar to the adsorption energy of H to a corresponding H-terminated surface (430 and 431 kJ/mol, respectively, on the MP2+BSSE level of theory). The binding energy of 430 kJ/mol for the adsorption of one F species to a F-terminated diamond (111) surface is in agreement with a corresponding adsorption of one F species in the work by Harris and Belton (440 kJ/mol).[15] The heats of formation $H_f$ (decomposed into a bond enthalpy $H_{bond}$ and a strain energy $E_{strain}$), as well as entropies $S$, for different diamond (111) surface configurations were calculated performing group additivity and molecular mechanics. Free energy changes at 1200 K for selected reactions including adsorption processes of F and $CF_3$ species to a F-terminated diamond (111) surface were then obtained. Since the calculations in the present investigation do not include any temperature effect, a comparison in energy regarding the adsorption of F to a F-terminated diamond (111) surface has to be carried through using the enthalpy changes $\Delta H$ obtained in the work by Harris and Belton.[15] As can be seen in the work by Harris and Belton, this exclusion of any temperature effect might bring about an increase in adsorption energy of about 180 and 200 kJ/mol for the species F and $CF_3$, respectively, in comparison to the corresponding calculated adsorption energies at the temperature 1200 K. The large entropies $S$ of the gaseous species in the adsorption reactions (e.g., F, $CF_3$, H, $CH_3$) are responsible for a decrease in entropy during the adsorption reaction and, hence, for the present increase in the adsorption energies. Since the entropies $S$ of the gaseous species F, $CF_3$, H, and $CH_3$ in the work by Harris and Belton were found to be numerically similar, the effect of temperature on adsorption energy in the adsorption processes discussed in the present investigation will also be numerically similar. Hence, the order of the adsorption energies of the different species in the present investigation are assumed to be independent of temperature.

**TABLE 2: Binding Energy for Adsorbed Species ($\Delta E_{ads}$ (kJ/mol)) on a Template Modeling the Diamond (111) Surface, Calculated by Using HF Level of Theory and Not Allowing Neighboring Surface Species To Relax Their Positions**

| | | | |
|---|---|---|---|
| $H^{\bullet}$ [a] | 336 | $CH_3^{\bullet}$ [a] | 180 |
| $F^{\bullet}$ [a] | 251 | $CF_3^{\bullet}$ [b] | −64 |
| $Cl^{\bullet}$ [a] | −21 | | |

[a] H-terminated diamond surface. [b] F-terminated diamond surface. [c] Cl-terminated diamond surface.

*Chlorine and Bromine*. The effect of the considerably lower electronegativities and larger atomic radius of chlorine and bromine is demonstrated in Table 1. The adsorption energy of Cl to a Cl-terminated diamond (111) surface is much smaller than the corresponding adsorption energy of F to a F-terminated surface (200 vs 430 kJ/mol on the MP2+BSSE level of theory). As can be seen in Table 1, the calculated adsorption energy of Br to a Br-terminated diamond (111) surface was found to be somewhat smaller than the corresponding adsorption energy of Cl to a Cl-terminated surface (95 and 173 kJ/mol, respectively, based on the DFT method with nonlocal Becke exchange).

*Sterical Repulsions on the Surface*. All of the different adsorption energies in Table 1 are maximal since both the radical carbon, with its adsorbed halogen species, and the six adjacent surface-bonded species were allowed to relax fully in the calculations. On the other hand, if only the radical carbon atom, with its adsorbed halogen species, was allowed to relax in the calculations, the obtained adsorption energies were expected to become minimal (see Methods). These minimal adsorption energies on the HF//6-31G**/STO-3G level of theory are demonstrated in Table 2.

As can be seen in Tables 1 and 2, only a minor change in adsorption energy for F and H will be the result (from 264 to 251 kJ/mol and 344 to 336 kJ/mol, respectively) if the six adjacent surface-bonded species on the diamond template are not allowed to relax fully during the adsorption process. Steric repulsions between the surface-bonded species on a F-terminated diamond (111) surface are, hence, very small. Naturally, the steric repulsions induced by F atoms on a diamond (111) surface are somewhat larger than the corresponding repulsions induced by the smaller terminating H atoms.

The sterical effect induced by the larger, surface-bonded Cl species was found to decrease the adsorption energy of Cl by

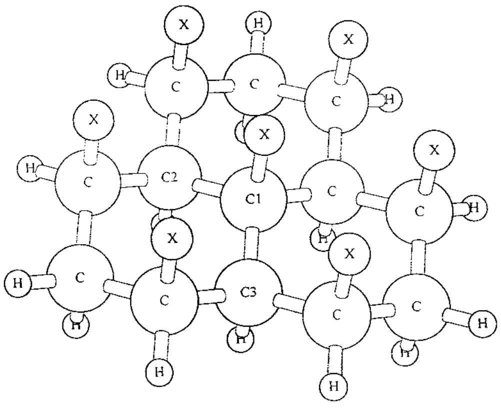

**Figure 1.** Template modeling the X-terminated diamond (111) surfaces (X = H, F, Cl, Br). The angle $\nu_{C_{neighbor}-C_{central}-C_{neighbor}}$ ($\nu_{C2-C1-C3}$) is 111.2°, 111.3°, 111.9°, and 112.9°, respectively.

about 60 kJ/mol (see Tables 1 and 2). The present investigation does then predict that steric repulsions between neighboring Cl atoms on the Cl-terminated diamond (111) surface are quite appreciable, especially in comparison with the steric repulsion between F atoms on a corresponding F-terminated diamond (111) surface.

The influence of the larger size of Br was also demonstrated by freezing the positions of the adjacent surface-bonded Br atoms in the DFT calculations. The sterical hindrances induced by these very large surface species were then found to be large enough to prevent the Br species to be adsorbed on a Br-terminated diamond (111) surface. As a further test, all surface terminating Br species were allowed to be vertically, and independently, relaxed in the calculations. No difference in the results was then observed. These large sterical hindrances are most probably responsible for the diamond (111) surface to be not stabilized by the Br element.

**(ii) Structural Geometries.** The geometries of the adsorption region of X to a X-terminated diamond (111) surface (X = H, F, Cl, Br) can be seen in Figure 1. Only the bonding surface carbon and the adsorbed species were allowed to relax fully. The bonding carbon atom on the template $C_{13}H_{15}X_6$ has sunk down into the fixed framework of the neighboring carbon atoms by only about 0.050 and 0.054 Å for the F- and H- terminated diamond (111) surfaces, respectively, and by the somewhat larger distance of 0.067 Å for the Cl-terminated surface. This hardly noticeable partial transition to $sp^2$ hybridization from a pure $sp^3$ hybridization of the surface carbon atom will result in a minor increase in the $\nu_{C2-C1-C3}$ from an ideal tetrahedral angle (109.4°) to 111.2°, 111.3°, and 111.9°, respectively, for H, F, and Cl termination. However, it has been proposed by Pandey[7] that if reconstruction occurs on the diamond (111) surface, $\pi$-bonded carbon chains will be formed. As a check, the tendency toward partial reconstruction of the F- and Cl-terminated diamond (111) surfaces has been investigated by allowing two neighboring surface carbon atoms, and their adsorbents, to relax geometrically using a larger template modeling the diamond (111) surface. No tendency for a $\pi$-bond formation between the two neighboring surface carbons was then observed for any one of the two different type of surfaces. The two carbon atoms have sunk down into the fixed framework of the neighboring carbon atoms by only about 0.075 and 0.095 Å, respectively. It is then obvious that F and Cl atoms, as well as H atoms, may sustain an almost ideal bulk truncated diamond (111) surface, with each surface carbon in the $sp^3$ configuration. The minor increase in the angle $\nu_{C2-C1-C3}$ (about 0.7°) for a Cl-terminated diamond (111) surface compared to a H or F surface is, however, accompanied by a significant decrease in adsorption energy for the species Cl compared to H and F of about 230 kJ/mol on the MP2 + BSSE level of theory (see section B; (i) Bonding Energies).

The bonding carbon atom on the Br-terminated template $C_{13}H_{15}X_6$ has sunk down into the fixed framework of the neighboring carbon atoms by as much as 0.11 Å, resulting in a relatively large increase in the $\nu_{C2-C1-C3}$ angle (to 112.9°) from the ideal tetrahedral angle (109.5°). This value is very similar to the corresponding angle (113.2°) for the situation where no adsorbant is bonded to the dangling bond on the radical carbon atom. For this situation the hybridization of the central radical atom has an appreciable influence of $sp^2$ hybridization. Hence, it is obvious that the element Br (in contrast to the elements H, F, and Cl) does not sustain a stabilizing, almost ideal $sp^3$ structural configuration of the carbon atoms on the halogenated diamond (111) surface, which otherwise would have been able to protect the outermost carbon layer from being transformed to a more graphitic-like geometrical structure. This conclusion is also supported by the fact that the large sterical hindrance, induced by the adjacent surface-bonded Br species, is shown to dramatically influence (decrease) the adsorption energy of a Br species on a Br-terminated diamond (111) surface (see section B; (i) Bonding Energies).

**C. Adsorption of Halogenated Methyl. (i) Bonding Energies.** Many investigations, both experimental and theoretical, have assumed the $CH_3$ species to be the dominant growth species during diamond deposition on the H-terminated diamond (111) surface.[9] The adsorption of $CX_3$ to a X-terminated diamond (111) surface (X = H, F, Cl, Br) has, hence, in the present work also been investigated both within the ab initio MO theory and within the first-principle DFT theory. As can be seen in Table 1, the calculated adsorption energy of the species $CH_3$ is found to be smaller than the adsorption energy of the corresponding species H by only 90 kJ/mol (341 vs 431 kJ/mol). On the contrary, the calculated adsorption energy of the $CF_3$ species is found to be much smaller than the corresponding adsorption energy of F by about 330 kJ/mol (105 vs 430 kJ/mol). These numbers were obtained from calculations on the MP2 level of theory using the 6-31G** basis set and including BSSE corrections. As can be seen in Tables 1 and 2, these differences in adsorption energies are almost independent of level of theory (MP2 or DFT), or allowance for the surface neighbors to be geometrically optimized. The minimum adsorption energy of $CF_3$ on the MP2+BSSE level of theory (85 kJ/mol) is comparable to the corresponding enthalpy change (120 kJ/mol) obtained by Harris and Belton (see section B).[15] The much lower adsorption energy of $CF_3$ compared to F does support the $CF_3$ group to be much less efficient as a dominant growth species, during deposition on a F-terminated diamond (111) surface, than the $CH_3$ group is on a corresponding H-terminated surface.

**(ii) Structural Geometries.** The structure of the adsorption region of $CX_3$ to an otherwise X-terminated diamond template $C_{13}H_{15}X_6$ (X = H, F) is demonstrated in Figure 2. The surface geometry in the immediate vicinity of an adsorbed $CF_3$ species on a F-terminated surface is very similar to the corresponding surface geometry close to an adsorbed $CH_3$ species on a H-terminated surface. Furthermore, the geometries of these different regions are both more similar to the geometry of bulk diamond than the surface geometry close to a corresponding H adsorbant is. The bonding carbon atom on the diamond template in Figure 2 has not sunk down into the rigid lattice as much as it did in the case of the adsorption of H to a H-terminated surface (0.02 Å ($CH_3$) and 0.01 Å ($CF_3$) compared to 0.054 Å (H)). The resulting C−C distance between the central (bonding) C

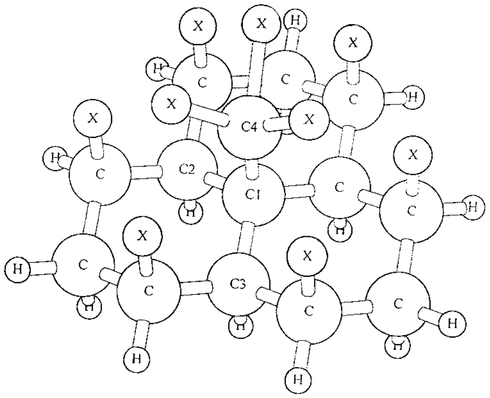

**Figure 2.** An X-terminated diamond (111) surface configuration with one adsorbed $CX_3$ group (X = H, F). The angle $\nu_{C_{neighbor}-C_{central}-C_{neighbor}}$ ($\nu_{C2-C1-C3}$) is 110.1° and 109.2°, respectively. The angle $\nu_{C_{neighbor}-C_{central}-C_{adsorbant}}$ ($\nu 2$) is 108.8° and 109.8°, respectively. The $C_{central}-C_{neighbor}$ distance ($r_1$) is 1.533 and 1.540 Å, respectively. The $C_{central}-C_{adsorbent}$ distance ($r_2$) is 1.527 and 2.250 Å, respectively.

and its closest C neighbor in the diamond template is 1.533 Å ($CH_3$) and 1.54 Å ($CF_3$), respectively. The angles are 108.8° ($CH_3$) and 109.8° ($CF_3$), respectively, for $C_{neighbor}-C_{central}-C_{methyl}$ and 110.1° ($CH_3$) and 109.2° ($CF_3$), respectively, for $C_{neighbor}-C_{central}-C_{neighbor}$. These numbers are also close to the bulk diamond C−C distance of 1.54 Å and C−C−C angle of 109.5°. The almost perfect "tetrahedral" angle of 110.1° and 109.2°, respectively, indicates that hardly any partial $sp^2$ hybridization is present. It is then obvious that both the $CF_3$ species and the $CH_3$ species will sustain an ideal bulk diamond (111) surface with each surface C in the $sp^3$ configuration.

Furthermore, the calculations indicate that there is energetically no possibility for a $CCl_3$ and $CBr_3$ species to be adsorbed on a Cl- and Br-terminated diamond (111) surface, respectively.

## Conclusion

The adsorption of different types of halogens and halogenated methyl species on a halogen-terminated diamond (111) surface has been structurally and energetically investigated, using a cluster approach and two different quantum mechanical methods. The halogens used in the investigation were F, Cl, and Br. These adsorption processes have then been compared with the corresponding processes involving hydrogen, H, and methyl, $CH_3$, adsorbed on a H-terminated diamond (111) surface.

The theoretical methods used in these calculations were the ab initio MO method and different first-principle DFT methods (LDA and DFT including nonlocal Becke exchange). The program systems used were the Gaussian92 and the Dmol programs. Both the DFT method including nonlocal Becke exchange and the ab initio MO method were found to be quite useful in investigating the relative order of adsorption energies of all the different species in the present investigation.

The calculations show that almost all species (e.g., H, F, Cl, $CH_3$, and $CF_3$) may sustain the bulk $sp^3$ structural configuration of the surface carbon atoms on a diamond (111) surface. It was also found that the structural region of adsorption of $CH_3$ and $CF_3$ to a H- and F-terminated diamond (111) surface, respectively, is more similar to the geometry of bulk diamond than the corresponding regions of adsorption of the different elements H, F, and Cl.

As expected from the large difference in electronegativity of F, on one hand, and the other halogens Cl and Br, on the other, the fluorine atom will induce a much larger atomic charge rearrangement near the surface with a large depletion of charge from the surface carbons, and, hence, an appreciable ionic character of the C−F chemical bond. This charge rearrangement in the structural region of adsorption is reflected in the adsorption energy of F to a F-terminated diamond (111) surface. This energy is much larger than the corresponding adsorption energy of Cl or Br to a Cl- and Br-terminated diamond (111) surface, respectively. The adsorption energy of F to a F-terminated diamond (111) surface is very similar to the corresponding adsorption energy of H to a H-terminated surface. Numerically, the calculated adsorption energies for the species H, F, Cl, and Br are 430 (413), 431 (421), 200 (173) and (95) kJ/mol, respectively. The numbers without parentheses are adsorption energies calculated on the MP2 level of theory by using the ab initio MO method and the basis set 6-31G**. The numbers within parentheses are adsorption energies calculated by using the DFT method including nonlocal Becke exchange and the numerical basis set dnp. These numbers are maximal in the sense that also the six adjacent surface-bonded hydrogens or halogens are allowed to relax in the calculations. Smaller adsorption energies are obtained by not allowing these neighboring species to relax. The numerical value of the "true" adsorption energies will be somewhere in between. The differences in energy between these two extremes are only appreciable for the larger species Cl and Br. In fact, the large sterical hindrances induced by the very large Br species are most probably responsible for the diamond (111) surface not being stabilized by the Br element. However, on the basis of these differences in adsorption energy, it is tempting to draw the conclusion that the elements H and F will stabilize the diamond (111) surface from being reconstructed from the (1 × 1) to the (2 × 1) structure more efficiently. Hence, it is expected that F- and H-terminated diamond (111) surfaces should passivate surfaces from being chemically attacked better than Cl- or Br-terminated surfaces do. Nevertheless, the element Cl is found to be capable in sustaining the $sp^3$ configuration of the surface carbon atoms, and in the absence of F and H in the gas phase, it is then predicted to protect the diamond surface (111)-(1*1) from being reconstructed to the (111)-(2*1) structure.

It was also predicted in the calculations that the adsorption of $CH_3$ to a H-terminated diamond (111) surface (being the first step in the diamond growth mechanism) occurs much more easily than the adsorption of $CF_3$ to a corresponding F-terminated surface (341 vs 105 kJ/mol on the MP2+BSSE level of theory). These results are in agreement with earlier experimental and theoretical work which claims that both hydrogen and the halogen F have to be present in the activated gas mixture during diamond growth at lower temperatures. These suggestions are based on thermodynamic arguments as well as thermodynamic calculations, which claim that halogen-based reactions will produce as a major byproduct HX molecules (where X is a halogen atom) instead of the less stable $H_2$ and $X_2$ molecules which are produced in gas mixtures containing only methane and hydrogen or fluorinated methane and fluorine. The very low adsorption energy of $CF_3$ to a F-terminated diamond (111) surface obtained in the present work is also in agreement with the recent work by Piekarzcyk and Prawer,[31] which states that diamond growth is not possible at all in unactivated $CF_4-F_2$ gas mixtures at a temperature of about 1200 K. According to the results of Harris and Belton,[15] if the effects of a temperature of about 1200 K on the adsorption process had been included in the present investigation, the adsorption energy of $CF_3$ to an F-terminated diamond surface should most probably have been decreased to a numerically negative value (no tendency for any adsorption). Furthermore, it was not possible to adsorb $CCl_3$ and $CBr_3$ to a Cl- and Br-terminated, respectively, diamond (111) surface due to large sterical hindrances.

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