Partial Electron Transfer during Vapor Growth of Diamond on a (111) Surface

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During diamond growth, surface vacancies are formed and diamond grows by adding carbon-carrying species to these vacancies. In the present investigation, the correlation between adsorption energies and accompanying partial electron transfer in the newly formed bond has been studied by using quantum mechanical calculations. Important CVD growth species were then allowed to adsorb on a H- or F-terminated diamond (111) surface. Correlations were obtained for different types of adsorbates. At an increase in electron transfer from a hydrocarbon adsorbate to the surface an increased bond strength was found. For the situation with fluorine-containing adsorbates, an increase in bond strength was associated with an increased partial electron transfer toward the adsorbate, i.e., the partial electron transfer occurs in the opposite direction as compared to the hydrocarbon adsorbates.

Introduction

Vapor growth of diamond is a dynamic process which involves the generation of surface vacancies and adsorption of different species (atomic hydrogen and growth species) to various radical surface sites. These surface reactions are chemical reactions which generally are accompanied by electron transfer (at least partially). Electron transfer reactions can be quite complicated, e.g., involving breaking and formation of chemical bonds.[1] However, one group of chemical reactions that has been studied (isotopic exchange) involves only the transfer of one electron.[1] This group is unique in chemistry in that no chemical bonds are broken and has been studied thouroughly.

Several authors have derived quantum mechanical models for reactions involving the transfer of one electron.[2] An example of a general result obtained with these models is the prediction of the dependence of the rate constant on the free energy difference of the reaction. The corresponding classical adiabatic model developed by Marcus predicts, essentially, the same relationships as the quantum mechanical models for the high-temperature limit. From the 1960s, the field has rapidly developed in many directions (e.g., electron transfer at electrodes, solar energy conversion, coupled electron transfer and proton transfer, electron transfer in solids and polymers).[3]

The purpose of the present study is to theoretically investigate the correlation between the partial electron transfer, occurring during an adsorption reaction, and the corresponding adsorption energy. Different important CVD growth species (ordinary, as well as halogenated hydrocarbons), and H and F, respectively, are then allowed to be adsorbed on a surface radical site on diamond (111).

Methods

The present study is an extension of the calculations performed in earlier investigations by the present authors.[4−7] These include the investigations of the adsorption of the gaseous species H and C_xH_y with different (x,y) combinations $((x,y)$: (1,2), (1,3), (2,1), (2,2)), as well as of CH_xF_y $((x,y)$: (0,3), (1,2), (2,1)) and CH_xCl_y $((x,y)$: (0,3), (1,2), (2,1)), on diamond (111) surface. The surface was then terminated by H or F. It was also found adequate to use the medium-sized template $C_{13}H_{21}$ in these earlier investigations.[4] As can be seen in Figure 1a, a surface radical site (to which the gaseous species will be adsorbed) is for this template surrounded by six terminating species X (X = H or F).

The influence of one already adsorbed neighboring CH_2 or CH_3 species (or an unterminated surface site) on the adsorption energy for a specific adsorbate was specifically investigated in ref 5. The larger template $C_{19}H_{28}$ was used when investigating these effects (Figure 1b). The framework of this specific template is different in that two neighboring radical surface sites have identical environments, five adjacent H species and one adjacent dangling bond. One of the radical sites is then assumed to be unterminated or terminated with CH_3 (or CH_2).

Some recalculations, regarding the adsorption energies of gaseous species to a radical surface site with an already adsorbed neighboring hydrocarbon species (or a neighboring dangling bond), have been performed in the present study. A combination of the basis sets 6-31G** and STO-3G was used in ref 5, while the 6-31G** basis set was used for all atoms in the other investigations present above.[4,6,7] Since the intention in the present work is to investigate the existence of correlations, it will be of crucial importance to be as careful as possible when choosing the method as well as the input parameters for the quantum mechanical calculations. This means, especially, that one has to use identical parameters in the different calculations (e.g., identical choice of basis sets). Hence, the ab initio molecular orbital (MO) method at the MP2 level of theory (Möller−Plesset perturbation theory of second order[8]) was finally used for the investigated correlations in the present work. The 6-31G** basis set was then used for all atoms in the templates. This split-valence basis set is able to give an improved description of expansion or contraction of the valence shell in response to differing molecular environments. Furthermore, by adding polarization functions (p to H and d to heavier atoms than He) the description of the charge rearrangement occurring around the atoms will be better.

For the different templates modeling the diamond (111) surfaces, different atoms were allowed to be relaxed. These include the adsorbate, as well as the surface carbon to which the
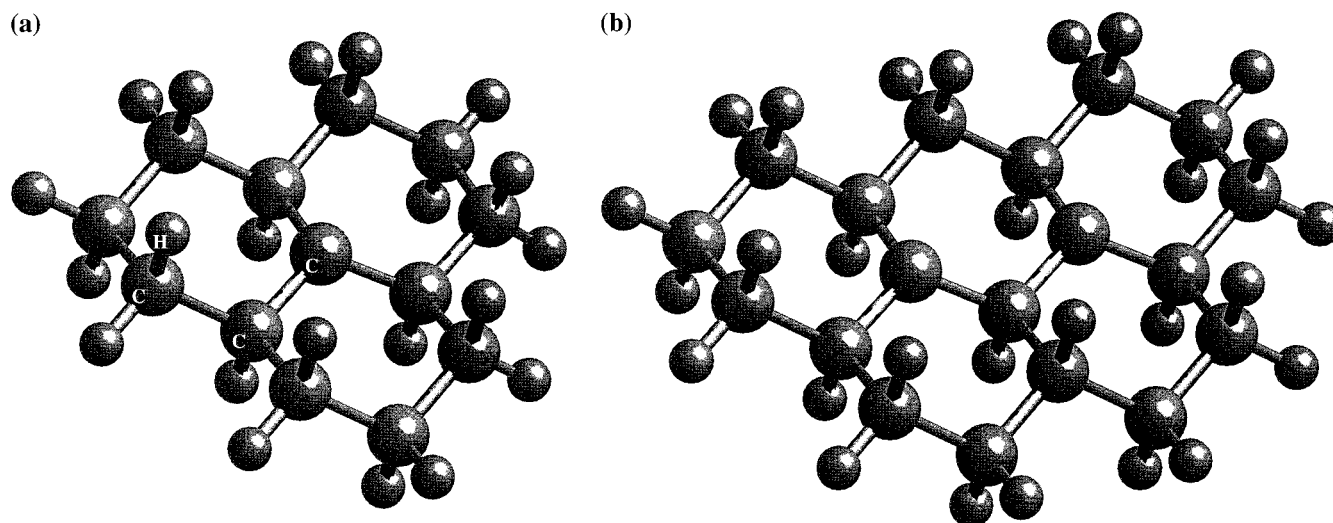
(a) **(b)**

Figure 1. Templates demonstrating the different diamond models. The closest neighbors to the radical carbon in the asymmetric unit in (a) are marked with atomic abbreviations.

adsorbate is bonded. Other underlayer atoms were kept fixed in order to hold the characteristics of the crystal. As a check, the three nearest neighbors to the central carbon on the template were also allowed to relax in a Hartree−Fock energy calculation of the adsorption of hydrogen. No change in adsorption energy was then observed.

The total energies were calculated for the reactants as well as for the products for the adsorption process,

$$M + A \rightarrow M-A \qquad (1)$$

where M is the template modeling the diamond (111) surface and A is the gaseous species that will adsorb to the surface. The different adsorption energies were calculated by using

$$E_{ads,A} = E_A + E_M - E_{M-A} \qquad (2)$$

Total atomic charges were, furthermore, calculated in order to investigate the charge distribution. Mulliken population analysis was then used, based on the MP2/6-31G** level of theory.[8] Split-valence basis sets with polarization functions, as well as corrections for electron correlation, are a demand when good Mulliken charges and dipole moments are desirable.

Results and Discussion

A. Introduction. The correlation between the partial electron transfer processes occurring during adsorption of halogen- or nonhalogen-containing species on a diamond (111) surface and the corresponding adsorption energy have been investigated in the present study. The combinations of adsorbed and terminated species are shown in Table 1.

The halogens included were F and Cl. They, as well as H, are capable of forming a single bond with a carbon atom in the sp³ configuration and on a diamond (111) surface. Within the halogens, fluorine is most reactive and chlorine least reactive toward other elements and groups. Fluorine has the highest electronegativity (4.0) and the smallest atomic radius (71 pm) which leads to strong bonds between the fluorine and the other atoms. On the other hand, chlorine forms weaker bonds because of its lower electronegativity (3.2) and larger size (99 pm). Hydrogen has, compared to the halogens, the lowest electronegativity of 2.2. Due to large differences in size of the different halogens (F and Cl), induced steric hindrances may occur on a terminated diamond (111) surface. This will be more pronounced

TABLE 1. Calculated Changes in Total Atomic Charges for the Adsorbate-bonding Surface Carbon, as Well as for the Atoms in the Adsorbate[f]

adsorbate	Δ_{charge} of $C_{surface}$ (au)	Δ_{charge} of adsorbate (au)	adsorption energy (kJ/mol)	series number in Figure 3	series number in Figure 4
H[a]	−0.14	+0.11	441	1	1
CH$_3$[a]	−0.11	0.00	338	1	1
H[b]	−0.05	+0.10	444	1	1
CH$_3$[b]	−0.08	−0.05	317	1	1
C$_2$H$_2$[b]	+0.01	−0.20	13	1	1
C$_2$H[b]	−0.35	−0.11	566	1	2
CH$_3$[c]	−0.08	−0.07	199	1	1
C$_2$H$_2$[c]	−0.09	−0.10	−97	1	1
C$_2$H[c]	−0.15	−0.12	475	1	2
H[d]	−0.31	+0.06	418	2	1
CH$_3$[d]	−0.26	−0.09	253	2	1
CH$_2$[d]	+0.02	−0.11	261	2	1
C$_2$H$_2$[d]	−0.15	−0.12	101	2	1
C$_2$H[d]	−0.34	−0.16	506	2	2
CH$_3$[e]	−0.27	+0.13	345	3	3
CF$_3$[e]	−0.26	+0.03	192	3	4
CHF$_2$[e]	−0.39	+0.15	196	3	3
CH$_2$F[e]	−0.34	+0.15	222	3	3
CF$_3$[a]	−0.26	+0.04	489	1	3
CCl$_3$[a]	−0.03	−0.26	91	4	4
CHCl$_2$[a]	−0.08	−0.14	338	4	4
CH$_2$Cl[a]	−0.14	0.00	226	4	4

[a] An H-terminated diamond (111) surface. [b] An H-terminated diamond (111) surface where one of the neighboring H atoms is being removed, leaving a dangling bond. [c] An H-terminated diamond (111) surface where one of the neighboring H atoms is being replaced by an CH$_3$ species. [d] An H-terminated diamond (111) surface where one of the neighboring H atoms is being replaced by an CH$_2$ species. [e] An F-terminated diamond (111) surface. [f] The sum over the adsorbate is presented in the table. These changes are induced by the adsorption process, for which the adsorption energy is also presented.

for the adsorption of an ordinary or halogen-containing methyl species, especially in the case of an otherwise halogenated surface.

The adsorbed hydrocarbon species (CH$_3$, CH$_2$, C$_2$H$_2$, and C$_2$H) have been found to be important precursors during diamond deposition in hot filament and plasma CVD reactors.[9] Halogenated methyl species have also been found to be important.[10−14] It has been suggested that growth of diamond at lower temperatures may be obtained by including halogen (F, Cl) or halogenated methane into the growth vapor. Hence,
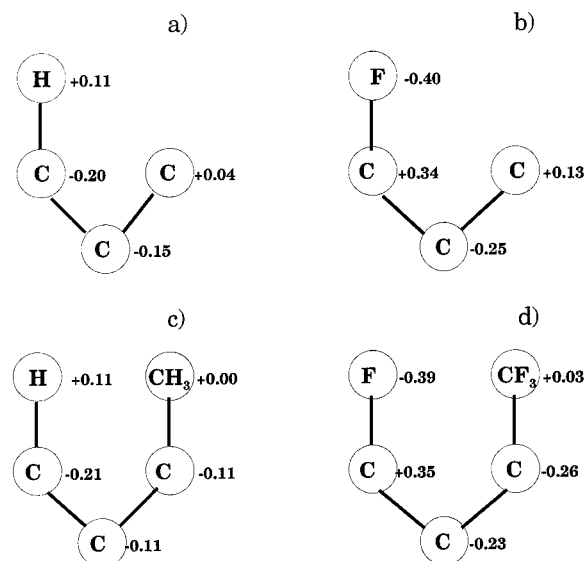
Figure 2. Calculated total atomic charges for H- and F-terminated diamond (111) surfaces, monoradical ones (a vs b) or with an adsorbed CH_3 and CF_3 species (c vs d). The sum of the total atomic charges is shown for the adsorbates. Only the radical surface carbon with its closest neighbors in the asymmetric unit are shown. These atoms are marked in Figure 1a.

it has been of large interest to investigate comparatively the adsorption of different hydrocarbon species, as well as of halogenated methyl.

The dangling bonds in, e.g., a diradical surface site are assumed to be created by abstraction reactions including species in the gas phase. An eventual adsorption of CH_3 to one of the radical sites may then occur, forming a radical site with a neighboring CH_3 species. The CH_3 species has been clearly shown to be one of the dominating growth species in the most common diamond CVD methods.[9] The adsorbed CH_3 may then undergo an H-abstraction reaction in the experimental hydrogen-rich environment, forming a CH_2 species.

B. Atomic Charges. The total atomic charges obtained for H- and F-terminated templates modeling diamond (111) surfaces are shown in Figure 2. The templates in parts a and b of Figure 2 (H and F terminations) demonstrate the surfaces obtained when abstraction reactions (involving gaseous species) have created monoradical surface sites. The templates in parts c and d of Figure 2 demonstrate the corresponding surfaces after the adsorption of a CH_3 and CF_3 species, respectively, to this monoradical site. As can be seen in parts a and b of Figure 2, the surface terminating F species have, compared to the terminating H species, an electron-withdrawing effect on the radical surface carbon. The total atomic charge on the radical surface carbon (C_{rad}) was calculated to be +0.04 and +0.13 for an H- and F-terminated surface, respectively.

However, this electron-withdrawing effect by the surface terminating F species has been counteracted by the adsorption of CF_3. As can be seen in parts c and d of Figure 2, the total atomic charge for the surface carbon bonded to the adsorbate has now become −0.11 and −0.26 as a result of the adsorption of CH_3 or CF_3 to an H− or F-terminated surface. Partial electron transfer processes have obviously occurred during the adsorption of CH_3 or CF_3 to a H- or F-terminated template. To clarify these accompanying partial electron transfer processes, the differences between the total atomic charges for all atoms in the adsorbate/template and the corresponding radical template is instead recommended to be used. Numerical values of

these charge differences are presented in Table 1 for all combinations of adsorbates and surface terminations. As can be seen in Figure 2, it is only the adsorbate-bonding surface carbon that will appreciable change the total atomic charge as an effect of the adsorption process. Hence, the adsorption processes are assumed to induce a very local influence on the diamond (111) surface.

The Mulliken population analysis is only applicable for systems that do not include highly polarized bonds, i.e., bonds formed by atoms with a large differences in electronegativity. This is due to the fact that the electrons in the bond are, within the Mulliken population analysis, equally shared between the two bonding atoms. In the present study, only the polarization in the bond between the adsorbate and the surface carbon (bonded to the adsorbate) will be of any interest to study. Since this bond is connecting two atoms with a small difference in electronegativity (C−C or C−H), the Mulliken population analysis is assumed to be applicable for the present system of interest.

C. Influence of Adsorption Processes on Surface Atomic Charges. Not only are differences in total atomic charges presented in Table 1 but also corresponding adsorption energies for all combinations of adsorbates/terminating species in the present study. The results are being grouped together with respect to type of terminating surface species. Furthermore, the correlations obtained for the calculated adsorption energies and accompanying electron processes are presented in Figure 3. Since only the adsorbate-bonding surface carbon will mainly be involved in a partial electron transfer process accompanying the adsorption (see previous section), the change in total atomic charges for this specific carbon atom will be used as a measure of the polarization in the bond between the adsorbate and the surface.

As can be seen in Figure 3, there is an obvious correlation regarding the calculated adsorption energies and accompanying partial electron-transfer processes. With one exception, the general tendency obtained is that the adsorption energy will increase with a resulting increase of negative charges on the adsorbate-bonding surface carbon. Hence, a partial electron transfer toward this surface carbon will accompany an increase in bond strength.

No common correlation was obtained for all types of surface terminations (H, F, or an H termination where one neighboring H species is removed or replaced by CH_3 (or CH_2)) (series 1 and 2 in Figure 3). The correlation obtained when using a fully H-terminated template does, however, coincide with the correlations obtained when using a template where one of the neighboring H-terminating species was removed (the presence of a neighboring dangling bond) or being replaced by CH_3. The correlation including an F-terminated surface differs significantly. It is then found that the adsorption energy will increase with a resulting decrease of negative charges for the adsorption of fluorine-containing methyl species (series 3 in Figure 3). The fluorinated methyl species will, hence, have an electron-withdrawing effect on the surface carbon due to the large electronegativity of F. Chlorinated methyl species will, however, not contribute to any correlation. The main reason for this is most probably the sterical hindrances induced on the surfaces by these very large molecular groups (series 4 in Figure 3).

D. Influence of Adsorption Processes on Atomic Charges of the Adsorbate. Correlations were observed for the adsorption energy and the partial electron transfer process in the previous section. The increase in negative total atomic charge of the adsorbate-binding surface carbon, as a result of the adsorption
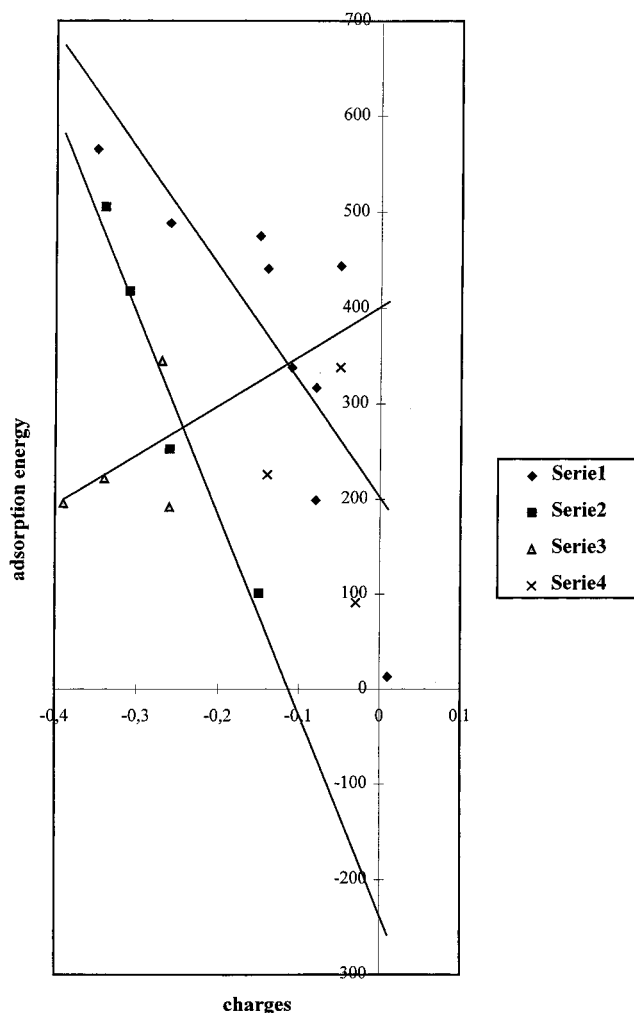
Figure 3. Correlations obtained between the adsorption energy and the induced change in atomic charge of the surface-binding C atom: series 1, H-terminated surfaces (6H, 5H + rad, 5H + CH_3); series 2, H-terminated surfaces (6H + CH_2); series 3, F-terminated surface; series 4, no correlation observed. The expressions within the parantheses describe the closest environment to a radical surface carbon (6 H atoms, or one of the H atoms has been removed or replaced by CH_2 or CH_3, respectively).
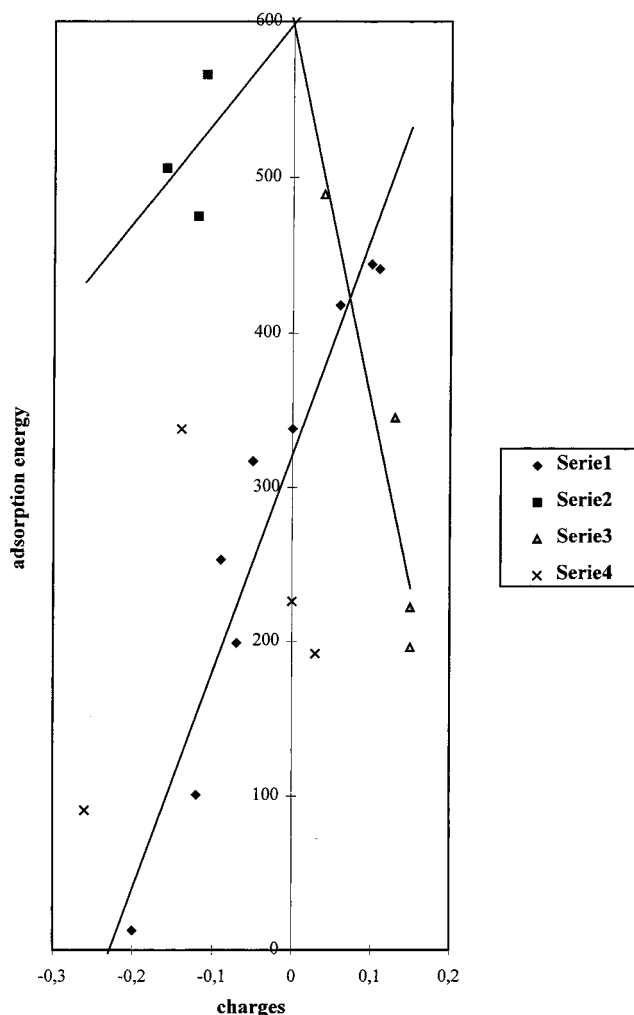

Figure 4. Correlations obtained between the adsorption energy and the sum of atomic charge for the adsorbates: series 1, H-terminated surfaces (6H, 5H + rad, 5H + CH_3, 6H + CH_2); series 2, H-terminated surfaces (5H + rad, 5H + CH_3, 6H + CH_2) with adsorbed C_2H species; series 3, adsorption including F species (either as a surface terminating species or as a fluorination in the methyl species); series 4, no correlation observed. The expressions within the parantheses describe the closest environment to a radical surface carbon (6 H atoms, or one of the H atoms has been removed or replaced by CH_2 or CH_3, respectively).

process occurring on a H-terminated surface, was then regarded to be a measure of the partial electron transfer process accompanying the adsorption. This increase in negative total charges is predominantly a result of a partial electron transfer in the bond formed between the surface and the adsorbate and in the direction from the latter to the former. On the other hand, a minor part of this change in atomic charges does also arise from partial electron transfer processes occurring within the template modeling the diamond (111) surface (see Figure 2). The sum of total atomic charges for the various adsorbates in the present investigation (and for different type of terminated surfaces) would, however, be a more direct measure of the partial electron transfer process occurring in the newly formed bond.

The sums of total atomic charges for the different adsorbates, as well as corresponding adsorption energies, are presented in Table 1. Correlations were also here obtained for different types of surface terminating species (Figure 4). In contrast to the situation described in the previous section, the correlation obtained when using a template that was totally H-terminated was found to coincide with the correlations obtained when using a template where one of the neighboring H-terminating species was removed or being replaced by a CH_3 (or CH_2) species.

The general tendency obtained for the correlations including hydrocarbon species adsorbed on H-terminated surfaces was that the adsorption energy will increase with a resulting decrease of the negative charges of the sum of total atomic charges of the adsorbate species. Hence, a partial electron transfer toward the adsorbate-bonding surface carbon (from the adsorbate) accompanies an enhancement in the bond strength. This result is supporting the result obtained in the previous section, where an increase in negative charges on the adsorbate-bonding surface carbon was also obtained for larger adsorption energies (series 1 in Figure 4).

There were a few exceptions to the trends of correlations obtained for the different types of H-terminated surfaces described above. The species that was found to be most strongly bonded to the surfaces (C_2H) was involved in all of these exceptions. As can be seen in Table 1, there is an unexpectedly large partial electron transfer from the surface atoms to the surface-binding C atom in C_2H. A similar observation is also made for the other C atom in C_2H. This atom has withdrawn the electrons from the H atom (to which it is bonded)

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unexpectedly effectively. The total atomic charges of the H atom (z_H) in C_2H is within the range $0.21-0.23$ for the different H-terminated surfaces investigated (one neighbor being a dangling bond, a CH_2 species, or a CH_3 species). This value of z_H is to be compared with the z_H values for the H atoms in the other hydrocarbon adsorbates in the present investigation. A range of z_H of about $(0.06-0.11)$ was observed for the combinations of hydrocarbon species/surface termination that resulted in clear correlations. As can be seen in Figure 4, the C_2H adsorbate with z_H of about 0.22 will form a separate group (series 2 in Figure 4).

A correlation between partial electron transfer and adsorption energy was also observed for fluorine-containing methyl adsorbates (series 3 in Figure 4). The template modeling the diamond (111) surface was then H- and F-terminated, respectively. The total atomic charges for F in the adsorbate is within the range $0.37-0.38$. For this correlation, the adsorption energy will increase with an increase in the negative sum of atomic charges for the adsorbate. Hence, the F atoms in the adsorbate, with its large value of electronegativity, will withdraw electrons from the surface, resulting in an increase in $C_{surface}-C_{adsorbate}$ bond strength. The adsorption process involving the CH_3 species adsorbed on an F-terminated surface did also fit into the correlation involving fluorine-containing adsorption species. The calculated atomic charge of H in CH_3, z_H, was almost identical to the corresponding values of z_H in CFH_2 and CF_2H, adsorbed on a F-terminated surface (0.17, 0.17, and 0.18, respectively).

As was the case in the previous section, the chlorine-containing methyl species adsorbed on totally H-terminated surfaces did not contribute to any correlation (series 4 in Figure 4). This is most probably due to large steric hindrances induced by the very large adsorbates (CCl_3, $CClH_2$, and CCl_2H). These steric hindrances are most probably also the underlying cause for the various numerical values of the total atomic charges of the Cl atom, z_{Cl}, in the adsorbate (0.016, -0.035, and -0.033, respectively). Large steric hindrances are also the most probable cause of the unexpectedly low atomic charge obtained for F in CF_3 adsorbed on a F-terminated surface ($z_F = -0.329$). This adsorption process will, hence, not fit into the correlation involving fluorine-containing adsorbates.

Summary

Correlation between adsorption energies and accompanying partial electron transfer in the newly formed bond has been investigated theoretically for different important CVD species. These include ordinary, as well as halogenated (F, Cl), hydrocarbon species adsorbed on H- or F-terminated diamond (111) surfaces. For three specific H-terminated surfaces, one of the neighboring H species (to the adsorbate) has been removed (leaving a dangling) or replaced by one CH_3 (or CH_2) species.

Besides the adsorbate, only the adsorbate-bonding carbon in the surface was found to predominantly be involved in partial electron transfer processes accompanying the adsorption. Cor-

relations were looked for in two different ways. First, the change, due to adsorption, in total atomic charges for the adsorbate-bonding surface carbon was studied as a function of adsorption energy. Second, the sum of atomic charges for the adsorbate was studied as a function of adsorption energy. The second approach resulted in much better correlations, with a few exceptions. Generally, ordinary hydrocarbon adsorbates resulted in one correlation where an increase of partial electron transfer from the adsorbate was found to accompany an enhancement in bond strength. On the other hand, fluorine-containing hydrocarbons resulted in another type of correlation where an increase of partial electron transfer toward the adsorbate was found to accompany an enhancement in bond strength. No correlations were obtained for chlorine-containing hydrocarbons, most probably due to steric hindrances induced by these large adsorbates.

It will then be possible to draw the conclusion that information about the bond strength for an adsorbed species may be estimated if information regarding atomic charges and/or bond polarization is known and vice versa.

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