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Nearest-neighbor influence on hydrocarbon adsorption on diamond (111) studied by *ab initio* calculations

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The influence of adjacent molecular groups on the adsorption of $H^{\cdot}$, $CH_3^{\cdot}$, $CH_2^{\cdot}$, $C_2H^{\cdot}$, and C_2H_2 on the diamond (111) surface has been investigated theoretically. *Ab initio* molecular-orbital theory was used in order to calculate the adsorption energies of these different species. The adsorption energies were found to be in the order $C_2H^{\cdot} > H^{\cdot} > CH_2^{\cdot} > CH_3^{\cdot} > C_2H_2$ (onefold adsorption) for all the different types of neighboring environments investigated. The adsorbed species are here either surrounded by only $H^{\cdot}$ atoms or one of these $H^{\cdot}$ atoms is being removed, leaving a diradical site, or replaced by a $CH_2^{\cdot}$ or $CH_3^{\cdot}$ species, respectively. Generally, the sterically hindering effects of the branched neighboring species $CH_2^{\cdot}$ and $CH_3^{\cdot}$ will decrease the adsorption energy by about 60 and 100 kJ/mol, respectively. An exception is the C_2H_2 species adjacent to a $CH_2^{\cdot}$ group, where the presence of the $CH_2^{\cdot}$ group *increases* the adsorption energy, due to a C-C bonding interaction between the two adsorbed species. This implies that C_2H_2 adsorption under these circumstances will be energetically competitive with $CH_3^{\cdot}$ adsorption.

I. INTRODUCTION

Considerable effort has been made during the last decade in developing methods to synthesize diamond films at low temperature and low pressure. This increase in interest can be traced to the unique properties of diamond (e.g., extreme hardness, high thermal conductivity and electric resistivity, optical transparency, and chemical inertness). Chemical vapor deposition (CVD) techniques have proven to be useful in producing diamond films on various substrates.

In order to succeed in a well-controlled growth of diamond, there is a need to achieve a detailed understanding at the molecular level of the adsorption and nucleation processes. The growth mechanism of diamond films by chemical vapor deposition has therefore become a subject of considerable interest in recent years. Unfortunately, the current understanding of the mechanisms and role of various molecular and radical species present during the CVD process is limited. However, it is generally accepted that the diamond (111) surface is hydrogen terminated.[1] It is also agreed that the growth process of diamond on the (111) surface is initiated by the activation of the surface (S) through reaction with atomic hydrogen: $SH+H^{\cdot}\rightleftarrows S^{\cdot}+H_2$. The radical surface site may then adsorb another hydrogen atom or hydrocarbon species. The adsorbed hydrocarbon species will act as growth species.

Different theoretical methods have been used to calculate the adsorption energy for a variety of hydrocarbon species adsorbed on a hydrogen-terminated diamond (111) surface. Semiempirical methods, used by Valone, Trkula, and Laia[2] and Mehandru and Andersson,[3] have yielded disparate results. More recently, Pedersen, Jackson, and Picket[4] and Mintmire *et al.*[5] have used local-density approximations in order to calculate the energy of adsorption of different hydrocarbon species, as well as hydrogen. The ordering of these species on the energy scale is in quantitative agreement with the results from a previous work by the present authors,[6] where *ab initio* molecular-orbital theory was used to calculate the relative adsorption energies of different species. An electron correlation treatment, using the second-order Møller-Plesset (MP2) model, resulted in the following order of the different species on the energy scale: $C_2H^{\cdot} > H^{\cdot} \approx CH_2$ (singlet) $> CH^{\cdot} > CH_2^{\cdot}$ (triplet) $> CH_3^{\cdot} > C_2H_2$ (onefold adsorption).

Vapor growth of diamond is a very dynamic process, since it involves the generation of surface vacancies, adsorption of atomic hydrogen, and addition of growth species to various radical surface sites. One important factor is the energetics during the growth, and adsorption energies are of specific importance. The adsorption energy, however, is influenced by the configuration and type of adsorbed species and vacancies surrounding a specific site.

In this investigation the influence of different neighbors (e.g., $H^{\cdot}$, radical site, $CH_3^{\cdot}$, $CH_2^{\cdot}$) on the adsorption energy for important species in a diamond CVD process will be investigated, using *ab initio* molecular-orbital theory. The gaseous species which are included in the calculations are $H^{\cdot}$, $CH_3^{\cdot}$, $CH_2^{\cdot}$, $C_2H^{\cdot}$, and C_2H_2. Both onefold and twofold site adsorption, respectively, of C_2H_2 will be considered. The two acetylenic carbons will in the latter case form a bridge over two adjacent surface carbon atoms. This type of five-membered carbon ring is quite common on the surface of diamond.[7]

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II. METHOD

The adsorption of different species to a radical carbon atom on a diamond (111) surface was investigated theoretically within *ab initio* molecular-orbital theory using the program system GAUSSIAN92,[8] applied to a number of different model systems. The adsorbed species are the four hydrocarbons $CH_3^{\cdot}$, $CH_2^{\cdot}$, $C_2H^{\cdot}$, and C_2H_2 and hydrogen $H^{\cdot}$. Different *in situ* experiments[9–11] and thermodynamic calculations[12] have shown that these hydrocarbons are present at equilibrium in the gas phase during diamond deposition in hot filament and plasma CVD reactors. Furthermore, the adsorbed species $CH_3^{\cdot}$, $CH_2^{\cdot}$, $C_2H^{\cdot}$, and C_2H_2 and hydrogen $H^{\cdot}$, are assumed to be surrounded by different configurations of adjacent neighbors in the present investigation. The configurations studied are when the adsorption site is (1) surrounded by only $H^{\cdot}$ atoms; or (2) when one of the closest $H^{\cdot}$ atoms is removed, leaving a diradical; or (3) when it is replaced by a $CH_2^{\cdot}$ or (4) by a $CH_3^{\cdot}$ species. These configurations modeling the diamond (111) surface will be referred to as $M^{\cdot}_{H}$, $M^{\cdot}_{rad}$, $M^{\cdot}_{CH2}$, and $M^{\cdot}_{CH3}$, respectively, in the present paper.

The $CH_2^{\cdot}$ species exists in two different low-lying electronic states, one singlet state ($^1A_1$) and one triplet state ($^3B_1$), where the triplet state is more stable by approximately 140 kJ/mol,[13] and hence the present calculations consider only the triplet state. For C_2H_2, a onefold site adsorption is generally assumed; i.e., C_2H_2 binds to the surface diradical carbon through one end only. The present paper will also investigate a twofold site adsorption of C_2H_2 for the situation where one of the six hydrogen atoms (adjacent to the radical carbon site) has been removed, leaving a diradical site. The two acetylenic carbons will then form a bridge over two adjacent surface carbon atoms.

The adsorption of $H^{\cdot}$, $CH_3^{\cdot}$, $CH_2^{\cdot}$, $CH^{\cdot}$, $C_2H^{\cdot}$, and C_2H_2 to an $M^{\cdot}_{H}$ site on a diamond (111) surface has been investigated earlier by the present authors.[6] A major part of that work was a methodological study in which the effects of electron correlation, template size, and basis sets on the relative adsorption energies were investigated systematically. A medium-sized template $C_{13}H_{21}^{\cdot}$ was one of the templates that was used in modeling the diamond (111) surface. The framework of this template consists of a central atom (the central carbon), the nearest three carbon atoms, the next-nearest six carbon atoms (surface carbons), and the next-nearest three hydrogen atoms [Fig. 1(a)]. Hydrogen atoms, together with three additional hydrogen-terminated carbon atoms, terminate the cluster. A terminal C-H distance of 1.10 Å was used. Hence the template $C_{13}H_{21}^{\cdot}$ contains six hydrogen atoms adjacent to the carbon atom, with a dangling bond (i.e., the radical carbon site).

The largest template that modeled the diamond surface in our previous work was the four-layer-thick $C_{22}H_{26}^{\cdot}$ template.[6] The difference between this template and the smaller $C_{13}H_{21}^{\cdot}$ consists of two carbon layers beneath the two surface carbon layers. It was shown that these two carbon layers have only a minor influence on the calculated adsorption energy, and it was concluded that the medium-sized $C_{13}H_{21}^{\cdot}$ template is adequate to use in the study of the adsorption reactions. This conclusion should also be valid for the case where one of the neighboring surface hydrogens is removed or replaced by a different hydrocarbon species. The two lower carbon layers in the larger $C_{22}H_{26}^{\cdot}$ template are in these cases not supposed to influence the effect of different adjacent surface species on the adsorption energy noticeably. The medium-sized template $C_{13}H_{21}^{\cdot}$ was, hence, chosen in the present investigation to model the diamond (111) surface, and also when one of the adjacent surface hydrogens is

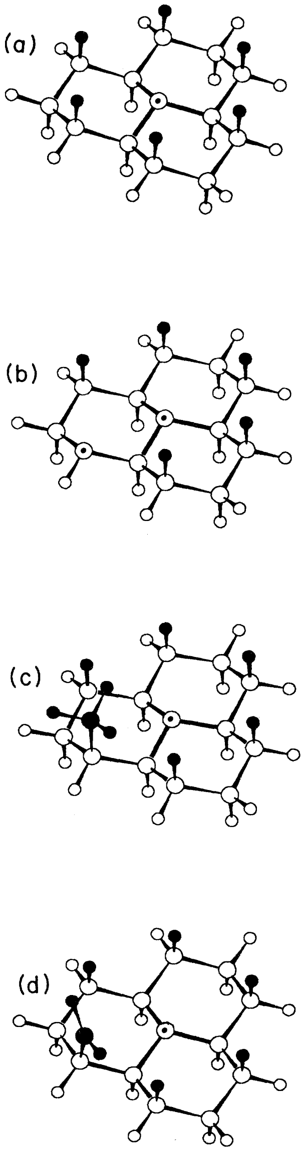

FIG. 1. The template $C_{13}H_{21}^{\cdot}$ (a) with one of the adjacent $H^{\cdot}$ atoms being removed (b) or replaced by a $CH_3^{\cdot}$ group (c) or a $CH_2^{\cdot}$ group (d), respectively. The marked atom in the center is the radical surface carbon on which the different hydrocarbon species are adsorbed.

being removed (the $M^{\cdot}_{\rm rad}$ type of surface configuration) [Fig. 1(b)]. As will be shown in Secs. III B 2 and III A 3, a larger template was chosen for situations with a twofold site absorption of C_2H_2 to a $M^{\cdot}_{\rm rad}$ type of surface configuration, and for the situation of adsorption of different species to $M^{\cdot}_{\rm CH2}$ and $M^{\cdot}_{\rm CH3}$ types of configurations, respectively. The framework of these larger templates differs mainly from the template $C_{13}H^{\cdot}_{21}$ ($M^{\cdot}_{\rm H}$) in that the two adsorbants have identical environments, five adjacent hydrogen atoms, and one adjacent hydrocarbon species (Figs. 2 and 3).

The present work includes calculations of the total energies for the reactants as well as for the products of the adsorption process:

$$M^{\cdot}+C_XH^{\cdot}_Y \rightarrow M-C_XH_Y \ , \qquad (1)$$

where M is the template modeling the diamond surface for the various configurations investigated (i.e., $M^{\cdot}_{\rm H}$, $M^{\cdot}_{\rm rad}$, $M^{\cdot}_{\rm CH2}$, and $M^{\cdot}_{\rm CH3}$).

The adsorption energies were calculated by using

$$E_{{\rm ads},C_xH^{\cdot}_y}=E_{C_xH^{\cdot}_y}+E_{M^{\cdot}}-E_{M-C_xH_y} \ .$$

$E_{C_xH^{\cdot}_y}$, $E_{M^{\cdot}}$, and $E_{M-C_xH_y}$ are the total electronic energies for the different gaseous species and for the template M with and without an adsorbed species, respectively.

The ordering of the different adsorption energies was then investigated for different types of adjacent neighbors to the radical site on the diamond (111) surface.

A complication in these calculations is that the basis functions located on the template atoms partly overlap the adsorbed molecules, and vice versa. This will lead to an artificial lowering of the energies of both the adsorbate and the template; a basis set superposition error (BSSE).[14] Hence the calculated adsorption energies will be too large. To estimate the magnitude of BSSE's, additional calculations were carried out, where the complete basis sets of the supermolecule (template plus adsorbate) were also used to compute the energies of the separate adsorbate and template, respectively. The corrections of the total energies obtained in this way, commonly called counterpoise corrections, were then subtracted from the total binding energy.

The present calculations used a combination of two different basis sets for the diamond template. The atoms close to the region of adsorption were represented by a more flexible basis set called A, while the remaining atoms were represented by a slightly smaller basis set called B. The gaseous and adsorbed species were all represented by A. This division is due to practical considerations. The calculations would be very time consuming if calculations were performed using a highly flexible basis set for all atoms in the system. The basis sets that were examined are the STO-3G minimal basis set and the split-valence basis set 6-31G (B) in combination with the polarized split-valence basis set 6-31G** (A).[15]

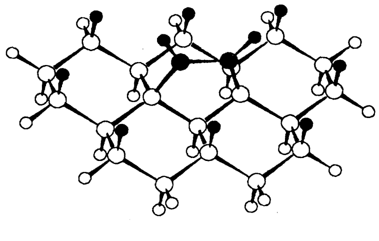

FIG. 2. A twofold site adsorption of the acetylene species to a $C_{19}H^{\cdot}_{28}$ template that models the diamond (111) surface.

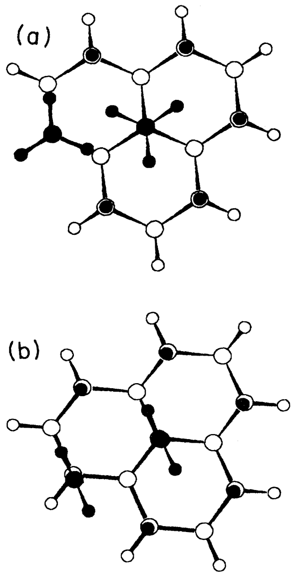

FIG. 3. (a) The surface configuration with an adjacent $CH^{\cdot}_3$ species in an eclipsed position in relation to the adsorbed $CH^{\cdot}_3$ species. (b) The surface configuration with two captured $CH^{\cdot}_2$ species.

The results in our previous work,[6] where the adsorption of different species to a $M^{\cdot}_{\rm H}$ type of diamond surface configuration was investigated, showed that there is a difference between the adsorption energies calculated by using the 6-31G**/6-31G combination of basis sets and the corresponding energies calculated by using the 6-31G**/STO-3G combination of basis sets. This shows that the influence of the next-nearest neighbors on the adsorption process is not satisfactorily described by using the STO-3G basis set for the latter. However, the ordering of the adsorption energies for the gaseous species $H^{\cdot}$, $CH^{\cdot}_3$, $CH^{\cdot}_2$, $C_2H^{\cdot}$, and C_2H_2 was the same for the two combinations of basis sets on the Hartree-Fock level of theory.

The two combinations of basis sets, 6-31G**/STO-3G and 6-31G**/6-31G, were also used in the Hartree-Fock calculations in the present work, where an adjacent hydrogen atom has been removed or replaced by a hydrocarbon species. The radical carbon atom(s) and its three nearest carbon neighbors were also represented here by the basis set 6-31G**, while the remaining atoms were represented by the smaller basis sets 6-31G or STO-3G, respectively. The gaseous and adsorbed species were all represented by 6-31G**.

It is well known that calculations of reactions, resulting in a pairing of electrons, on the Hartree-Fock (HF) level gives rather poor results since the instantaneous correlation between motions of electrons is inadequately treated in the HF theory. Electron correlation treatments have therefore been included in this study, since the reactions in the present cases generally result in a pairing of electrons. Second-order Møller-Plesset (MP2) perturbation theory was used in these correlation energy calculations.[15]

Calculated dissociation energies of different CH_3R compounds have been compared with experimental values in Ref. 15. The results show that HF/6-31G** energies for the dissociation of various hydrides from a methyl group are in very poor agreement with experiment, being typically in error by 108–188 kJ/mol. The methyl group is chemically similar to the radical site in the diamond template models in the present work. The theoretical results improve substantially when performing electron correlation treatments using MP2 perturbation theory. The bond-dissociation energies are then in error by less than 8 kJ/mol at the MP2/6-31G** level of theory. These results are also relevant for adsorption reactions since this latter type of reaction is the reverse of the dissociation of bonds. Hence the accuracy of 8 kJ/mol should be sufficient for calculations of the adsorption energies in the present work.

All geometrical parameters for the gaseous and adsorbed hydrocarbon species were fully optimized. For the template modeling the diamond (111) surface, with or without an adsorbed species, different combinations of atoms were allowed to relax in the field of a fixed structure of its neighbors. In one type of combination only the radical carbon atom of the different configurations studied ($M^{\cdot}_{\mathrm{H}}$, $M^{\cdot}_{\mathrm{rad}}$, $M^{\cdot}_{\mathrm{CH2}}$, and $M^{\cdot}_{\mathrm{CH3}}$), with or without an adsorbed species, was allowed to relax. As a check, the three nearest neighbors to the central carbon on the different templates were also allowed to relax in a Hartree-Fock energy calculation of the adsorption of hydrogen. No change in adsorption energy was then observed. It has also previously been shown to be sufficient to relax the central carbon atom during a corresponding adsorption of different hydrocarbons and hydrogen on a hydrogen-terminated (111) surface of diamond [the $M^{\cdot}_{\mathrm{H}}$ type of diamond (111) surface].[6]

III. RESULTS AND DISCUSSION

A. Effect of adjacent radical site on adsorption energy

1. General

We will presently investigate the influence of a neighboring radical site on the adsorption energies of the hydrocarbons $CH_3^{\cdot}$, $CH_2^{\cdot}$, $C_2H^{\cdot}$, and C_2H_2 and hydrogen $H^{\cdot}$. One of the hydrogen atoms on the hydrogenated diamond (111) surface surrounding the radical surface site, where the adsorption is assumed to occur, has then been removed [the $M^{\cdot}_{\mathrm{rad}}$ type of diamond (111) surface] [Fig. 1(b)]. It is assumed here that the diamond surface has been activated through reactions with atomic hydrogen from the gas phase (abstraction reactions).

A diamond surface covered by radical and diradical sites was studied by use of a Monte Carlo kinetic method in the work by Frenklach.[16] Two gas-surface reactions were then assumed to govern the formation of surface radicals: abstraction of a surface hydrogen atom by an impinging hydrogen atom, and the addition of a gaseous hydrogen atom to the surface radical formed. The results show that there is a large probability for a surface radical on a diamond (111) surface to have an adjacent radical site.

2. Results

The results of the Hartree-Fock calculations for the adsorption of the different gaseous species $H^{\cdot}$, $CH_3^{\cdot}$, $CH_2^{\cdot}$, $C_2H^{\cdot}$, and C_2H_2 on the diamond (111) surface are given in Table I. Adsorption energies are presented for the $M^{\cdot}_{\mathrm{H}}$ and $M^{\cdot}_{\mathrm{rad}}$ types of template, respectively, modeling the different configurations of a diamond (111) surface. The calculated adsorption energies of the different species on the $M^{\cdot}_{\mathrm{H}}$ type of template has already been predicted and discussed in an earlier work by the present authors.[17]

As can be seen in Table I, the ordering of the adsorption energies is identical at all levels of calculation used and for both types of neighboring environment to the central radical carbon atom. Hence the limitations of the basis set 6-31G**/STO-3G does not influence the ordering of hydrogen and hydrocarbon species on the energy scale. The $C_2H^{\cdot}$ species is predicted to adsorb stronger on the diamond (111) surface than $H^{\cdot}$ does. A onefold site adsorption of C_2H_2 is predicted to yield a significantly weaker adsorption than the other hydrocarbons. The ordering of the different species on the adsorption scale is now $C_2H^{\cdot} > H^{\cdot} > CH_2^{\cdot} > CH_3^{\cdot} > C_2H_2$ for both types of neighboring environments to the central radical carbon atom.

As can be seen in Table I, the results are also numerically very similar for both types of neighboring environments. The sterically hindering effect of neighboring hydrogen atoms on the surface is minor. The adsorption energies for the hydrocarbon species increase by less than 20 kJ/mol when removing the sterically hindering effect of one adjacent hydrogen atom, using the MP2/(6-31G**/STO-3G) level of theory. The results of the HF/(6-32G**/6-31G) calculations are very similar.

The effects of electron correlation can also be studied in Table I. The MP2 calculations, regarding the adsorption of the different gaseous species on the different types of diamond (111) surfaces, define a higher computational level compared to Hartree-Fock calculations (see Sec. II). As expected, the changes obtained when performing the calculations with electron correlation included are large. The correlation effect on the absolute adsorption energies varies between 23 and 243 kJ/mol (the quoted values exclude the BSSE corrections). However, the ordering of the adsorption energies is still identical for both types of neighboring environments to the central radical carbon atom.

The smallest values of the correlation corrections for the hydrocarbon species are related to the onefold adsorption of the C_2H_2 species. For the $M^{\cdot}_{\mathrm{H}}$ and $M^{\cdot}_{\mathrm{rad}}$ types of surface configurations, the corrections for electron correlation are 23 and 24 kJ/mol, respectively (−41 and

TABLE I. Effect of adjacent H atoms vs adjacent radical sites on adsorption energies in kJ/mol, calculated at the Hartree-Fock and MP2 levels of theory and corrected for basis-set superposition effects (BSSE's). Numbers within parentheses do not include the BSSE corrections.

	ΔE_{ads} (kJ/mol)					
	H[a]	RAD[a]	H[b]	RAD[b]	H[c]	RAD[c]
$C_2H^{\cdot}$	370 (383)	361 (388)	(362)	(362)	556 (628)	566 (630)
$H^{\cdot}$	341 (346)	343 (349)	(340)	(343)	428 (441)	431 (450)
$CH_2^{\cdot}$	232 (254)	250 (266)	(236)	(244)	334 (416)	340 (429)
$CH_3^{\cdot}$	201 (213)	194 (229)	(195)	(202)	315 (388)	317 (397)
C_2H_2 (onefold)	37 (49)	33 (80)	(32)	(52)	−4 (72)	13 (104)
C_2H_2 (twofold)		168 (227)		(207)		356 (451)

[a] HF/(6-31G**/STO-3G).
[b] HF/(6-31G**/6-31G).
[c] MP2/(6-31G**/STO-3G).

−20 kJ/mol with the BSSE correction included). It is quite understandable that the adsorption energy of this species to the diamond (111) surface is subject to the smallest electron correlation corrections since no additional pairing of electrons is expected during the adsorption reaction.

The largest electron correlation corrections of 243 ($M_{\mathrm{H}}^{\cdot}$) and 242 kJ/mol ($M_{\mathrm{rad}}^{\cdot}$) (186 and 205 kJ/mol with BSSE corrections) are related to the adsorption of $C_2H^{\cdot}$. In this species there is a short triple bond, and the bond length will be additionally shortened during the adsorption reaction ($\Delta r_{\mathrm{C\equiv C}} = -0.026(M_{\mathrm{H}}^{\cdot})$ and $\Delta r_{\mathrm{C\equiv C}} = -0.027(M_{\mathrm{rad}}^{\cdot})$. The $C_2H^{\cdot}$ group has also the shortest C-C bond of 1.487 ($M_{\mathrm{H}}^{\cdot}$) and 1.460 Å ($M_{\mathrm{rad}}^{\cdot}$), respectively, to the radical atom on the diamond (111) surface. The rather large value of the electron correlation correction can then be understood as an effect of the very short carbon bonds both within the $C_2H^{\cdot}$ species and to the diamond surface, and the resulting high electron density in the binding regions.

Corrections for the BSSE are made for the adsorption of the different gaseous species on the two different types of diamond (111) surfaces at the HF/(6-31G**/STO-3G) and MP2/(6-31G**/STO-3G) levels of theory (Table I). BSSE's at the MP2 level of theory are larger than BSSE's calculated at the Hartree-Fock level. The BSSE's for hydrogen $H^{\cdot}$ are 13 and 19 kJ/mol at the MP2 level of theory for surface types $M_{\mathrm{H}}^{\cdot}$ and $M_{\mathrm{rad}}^{\cdot}$, respectively. The corresponding ranges of BSSE's for the hydrocarbons are 72–82 and 64–91 kJ/mol. BSSE-corrected binding energies are normally more reliable than uncorrected ones, independent of the computational level used. The present corrections for BSSE's, although relatively large in absolute terms, do not change the ordering of the different adsorption energies calculated at the uncorrected HF/(6-31G**/STO-3G and MP2/(6-31G**/STO-3G) levels of theory. The ordering of the different species on the energy scale is still the following: $C_2H^{\cdot} > H^{\cdot} > CH_2^{\cdot} > CH_3^{\cdot} > C_2H_2$ for both types of neighboring environments to the central radical carbon atom.

3. *Twofold site adsorption of acetylene*

A onefold site adsorption was assumed in the above investigated adsorption of C_2H_2 to a central radical carbon atom surrounded by six or five neighboring hydrogen atoms, respectively. It was then found that the C_2H_2 species is very weakly bound to the surface by 72 and 104 kJ/mol, respectively, at the MP2/(6-31G**/STO-3G) level of theory. These adsorption energies decrease to −4 and 13 kJ/mol, respectively, when including the BSSE corrections (i.e., essentially no binding). As mentioned above, however, it is also of great interest to investigate the twofold site adsorption of C_2H_2 to a radical site, since it was found in the work by Frenklach[16] that there is a pronounced probability for a carbon radical on a diamond (111) surface to have an adjacent radical site. The two acetylenic carbons are then forming a bridge over two adjacent surface carbons atoms (Fig. 2).

The template that models the diamond (111) surface in the calculations is a modification of the template used for the investigation of the onefold site adsorption of the C_2H_2 species. The framework of this larger $C_{19}H_{28}^{\cdot}$ template differs mainly from the previous template (containing a diradical site) in that both surface radical sites have identical environments: five adjacent hydrogen atoms and one adjacent radical site (Fig. 2). It is then possible to optimize the geometry of the adsorbed C_2H_2 species under the influence of the surrounding hydrogen neighbors. However, the template $C_{19}H_{28}^{\cdot}$ is still a two-layer-thick carbon template. The carbon framework is also in this template terminated by hydrogen atoms at a distance of 1.10 Å.

For the template $C_{19}H_{28}^{\cdot}$, with or without an adsorbed species, only the two radical carbon atoms of the template were allowed to relax in the field of a fixed structure of its neighbors. As a check, the five nearest carbon neighbors to the diradical site, as well as the surrounding hydrogen atoms on the surface, were also allowed to relax in a Hartree-Fock energy calculation of the adsorption of hydrogen $H^{\cdot}$. A minor change of about 2% in the adsorption energy was then observed.

The results of the calculations of a twofold site adsorption of the species C_2H_2 to the template $C_{19}H_{28}^{\cdot\cdot}$ are given in Table I. Numerically, the results of Hartree-Fock calculations show that a twofold site adsorption is energetically favored by 227 kJ/mol at the HF/(6-31G**/6-31G) level of theory. Two surface dangling bonds have been stabilized by the C_2H_2 species during the adsorption process. This value of 227 kJ/mol is to be compared with the corresponding value of 80 kJ/mol obtained when performing HF/(6-31G**/6-31G) calculations on the onefold site adsorption.

Also at the more reliable MP2 level of calculation, a twofold site adsorption of C_2H_2 to a diradical template results in a larger adsorption energy than a corresponding onefold site adsorption of C_2H_2 does (451 kJ/mol for a twofold site adsorption and 104 kJ/mol for a onefold site adsorption). These adsorption energies decrease to 356 and 13 kJ/mol, respectively, when counterpoise corrections are included in the calculations.

In comparison with the previous results (Sec. III A 2) a twofold site adsorption of the species C_2H_2 to a diradical site on the diamond (111) surface gives the final ordering on the energy scale: $C_2H^\cdot > C_2H_2(\text{twofold}) > H^\cdot > CH_2^\cdot > CH_3^\cdot > C_2H_2(\text{onefold})$. Hence a twofold site adsorption is predicted to occur much more easily on a hydrogenated diamond (111) surface with two adjacent radical sites than a onefold site adsorption of $CH_3^\cdot$ or C_2H_2, respectively, does.

B. Effect of adjacent adsorbed methyl or methylene groups on adsorption energy

1. General

We also investigated the influence of one adjacent hydrocarbon species on the adsorption energies of the hydrocarbons $CH_3^\cdot$, $CH_2^\cdot$, $C_2H^\cdot$, and C_2H_2 and hydrogen $H^\cdot$. One of the six hydrogen atoms surrounding the radical surface site on the hydrogenated diamond (111) surface, on which adsorption is assumed to occur, is then replaced by the hydrocarbon species $CH_3^\cdot$ or $CH_2^\cdot$ (creating the $M^\cdot_{\text{CH2}}$ and $M^\cdot_{\text{CH3}}$ types of surface configurations) [Figs. 1(c) and 1(d)].

Earlier experimental results have supported a diamond growth mechanism based on the $CH_3^\cdot$ group as a dominant growth species during filament-assisted deposition on diamond (111) from a reaction mixture of methane and hydrogen.[18] The gas phase concentration of C_2H_2 was estimated to be almost equal to the gas-phase concentration of $CH_3^\cdot$ at these experimental conditions.[9,10] These species were also found to be dominating in the gas phase.[11] Moreover, earlier theoretical investigations[4,6] have predicted a much larger adsorption energy for the adsorption of the $CH_3^\cdot$ species, compared to the adsorption of the C_2H_2 species, to a hydrogenated diamond (111) surface. Hence there will be a large probability for the $CH_3^\cdot$ species to adsorb to a hydrogenated diamond (111) surface. It is therefore of a great interest to investigate the influence of the adsorbed $CH_3^\cdot$ species on the adsorption energies of a second adsorbing species. The gas phase concentrations of the hydrocarbon species $CH_2^\cdot$ is predicted to be about two orders of magnitude lower than the gas phase concentrations of the hydrocarbon species $CH_3^\cdot$ and C_2H_2.[11] Nevertheless, the influence of the $CH_2^\cdot$ species will also be of interest since the adsorbed $CH_3^\cdot$ species may undergo an H-abstraction reaction in the experimental hydrogen-rich environment, resulting in an adsorbed $CH_2^\cdot$ group as an adjacent species to the radical carbon site on the diamond (111) surface.

2. Geometry optimization

The nonlinear hydrocarbon species $CH_3^\cdot$ and $CH_2^\cdot$ may induce steric hindrances toward adsorption on an adjacent site. It is therefore of primary interest to study the effect of geometrical optimizations of both the adjacent hydrocarbon species $CH_3^\cdot$ and $CH_2^\cdot$, respectively, and the adsorbed species, on the adsorption energies.

A difference in adsorption energy of 408 kJ/mol was obtained when performing a full geometrical optimization of both the adsorbed $CH_3^\cdot$ species and an adjacent $CH_3^\cdot$ species, compared to a geometrical optimization of only the adsorbed $CH_3^\cdot$ species. The geometry of the adjacent $CH_3^\cdot$ species was in the latter case fixed in an eclipsed position to the initial geometry of the adsorbed $CH_3^\cdot$ species [Fig. 3(a)]. The absolute adsorption energies, calculated at the HF/(6-31G**/STO-3G) level of theory

TABLE II. Effects of adjacent CH_3 groups vs adjacent CH_2 groups on adsorption energy in kJ/mol, calculated at the Hartree-Fock and MP2 levels of theory. Numbers within parentheses are not corrected for BSSE effects.

Adsorbed	Nearest neighbor					
species	CH_3[a]	CH_2[a]	CH_3[b]	CH_2[b]	CH_3[c]	CH_2[c]
$C_2H^\cdot$	250 (292)	281 (344)	272	312	475 (549)	506 (591)
$H^\cdot$	324 (331)	334 (344)	325	340	409 (430)	418 (444)
$CH_2^\cdot$	136 (176)	143 (196)	161	177	257 (350)	261 (368)
$CH_3^\cdot$	67 (100)	105 (156)	85	131	199 (286)	253 (342)
C_2H_2	−80 (−38)	103 (172)	−56	111	−97 (−5)	101 (246)

[a] HF/(6-31G**/STO-3G).
[b] HF/(6-31G**/6-31G).
[c] MP2/(6-31G**/STO-3G).

were 100 and −308 kJ/mol, respectively (correlation and BSSE effects can be assumed to be constant in this comparison). Hence, due to sterical considerations, it is not possible to adsorb a $CH_3^{\cdot}$ species to a surface site near another CH_3 species without the possibility of geometry relaxation of the latter. A corresponding difference in adsorption energy of 44 kJ/mol was obtained when performing geometry optimizations of an adsorbed $CH_2^{\cdot}$ species with an adjacent $CH_2^{\cdot}$ species. The fixed geometry of the adjacent $CH_2^{\cdot}$ species in relation to the initial geometry of the adsorbed $CH_2^{\cdot}$ species is demonstrated in Fig. 3(b). The corresponding adsorption energies in this case were 188 and 144 kJ/mol.

Since the adjacent species $CH_3^{\cdot}$ and $CH_2^{\cdot}$ induce large (especially for $CH_3^{\cdot}$) sterical hindrances during the adsorption process of different hydrocarbon species, it is necessary to optimize also these adjacent hydrocarbon groups geometrically. Moreover, the geometry relaxation of these adjacent hydrocarbon species may also be influenced by adjacent hydrogen atoms that are situated further from the central radical carbon atom. The template that was used in modeling the diamond (111) surface in the present investigation is shown in Fig. 4. It is almost identical to the template $C_{19}H_{28}^{\cdot}$ that was used in the investigation of the twofold site adsorption of C_2H_2 to an $M_{\mathrm{rad}}^{\cdot}$ type of surface configuration (Sec. III A 3). The only difference is that one of the two radical sites is replaced by a $CH_3^{\cdot}$ or $CH_2^{\cdot}$ group.

It must therefore be of importance to optimize the geometry of both hydrocarbon species (the adsorbed and the adjacent ones) under the influence of all the surrounding hydrogen neighbors. As a further check, the effect of geometry optimization of these surrounding hydrogen neighbors on adsorption energy should also be investigated. This was studied for $CH_2^{\cdot}$ adsorption. However, a complete geometry optimization at the HF/(6-31G**/STO-3G) level of theory of both the two $CH_2^{\cdot}$ adsorbants and the surrounding hydrogen atoms resulted only in a minor increase (3%) of the adsorption energy of $CH_2^{\cdot}$.

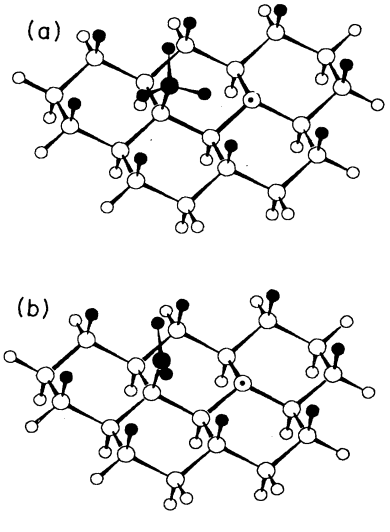

FIG. 4. The $C_{19}H_{28}^{\cdot}$ template with one of the adjacent H atoms being replaced by a $CH_3^{\cdot}$ group (a) or a $CH_2^{\cdot}$ group (b), respectively.

Furthermore, the surface carbon atom that is bonded to an adjacent $CH_2^{\cdot}$ species was allowed to relax in a HF/(6-31G**/6-31G) calculation of the adsorption of a $CH_2^{\cdot}$ species to the radical carbon atom. The three nearest neighbors to the central carbon on the template were also allowed to relax in a corresponding calculation. No change in adsorption energy was observed in either of these two tests. Hence the different results of the geometry optimizations of the different combination of atoms shows that it is sufficient to relax completely the central carbon atom and the adjacent hydrocarbon species.

3. Results

a. HF calculations. The results of the Hartree-Fock calculations for the adsorption of the different gaseous species $H^{\cdot}$, $CH_3^{\cdot}$, $CH_2^{\cdot}$, $C_2H^{\cdot}$, and C_2H_2 on the diamond (111) surface are given in Table II. Different adsorption energies are then presented for $M_{\mathrm{CH3}}^{\cdot}$ and $M_{\mathrm{CH2}}^{\cdot}$ types of surface configuration. For the $M_{\mathrm{CH3}}^{\cdot}$ type of surface configuration, the ordering of the different adsorption energies is identical for the two combinations of basis sets 6-31G**/STO-3G and 6-31G**/6-31G.

Generally, the ordering of the adsorption energies for the $M_{\mathrm{CH2}}^{\cdot}$ type of surface configuration is also identical for the two combinations of basis sets 6-31G**/STO-3G and 6-31G**/6-31G. The species $CH_3^{\cdot}$ and C_2H_2, whose adsorption energies were lowest on the energy scale, constitute an exception by having exchanged their relative positions on the energy scale (from 156 and 172 kJ/mol to 131 and 111 kJ/mol, respectively) when using the larger basis set combination 6-31G**/6-31G, instead of the smaller one. However, the HF/(6-31G**/STO-3G) results also predict $CH_3^{\cdot}$ to be more strongly bound when the BSSE correction is considered. (No BSSE corrections were calculated for the 6-31G**/6-31G basis, but they may be presumed to be smaller than for the 6-31G**/STO-3G basis, since the basis is more complete.)

The sterically hindering effect of the highly branched $CH_3^{\cdot}$ neighbor decreases the adsorption energy of the hydrocarbon species relative to a hydrogen neighbor by 70–130 kJ/mol. The steric effect on hydrogen atom adsorption is, however, low (about 15 kJ/mol). This will result in a slightly different order of adsorption energies ($H^{\cdot} > C_2H^{\cdot} > CH_2^{\cdot} > CH_3^{\cdot} > C_2H_2$) compared with the corresponding order of energies for a completely hydrogenated diamond (111) surface ($C_2H^{\cdot} > H^{\cdot} > CH_2^{\cdot} > CH_3^{\cdot} > C_2H_2$). As can be seen, the only difference in order of species on the energy scale is that $H^{\cdot}$ will exchange position with $C_2H^{\cdot}$ and, hence, adsorb more strongly to the diamond (111) surface that includes a $CH_3^{\cdot}$ neighbor to the adsorbant. It is no longer possible for a onefold site adsorption of the C_2H_2 species to occur with a $CH_3^{\cdot}$ group as an adjacent species. The results of the Hartree-Fock calculations shows that the adsorption energy of the C_2H_2 species will be negative.

The sterically hindering effect of the less-branched $CH_2^{\cdot}$ neighbor decreases the adsorption energies of the hydrocarbon species by 40–100 kJ/mol. One exception is the adsorption of the C_2H_2 species, for which the adsorption energy *increases* by 70–120 kJ/mol, depending on computational level. The very short distance (1.61 Å) formed between the C atom in the $CH_2^{\cdot}$ neighbor and the surface-bonding C atom in the adsorbing C_2H_2 species indicates the origin of this large increase in adsorption energy, namely the establishment of a C-C bond between the two adsorbed species (Fig. 5). Moreover, the steric effect on hydrogen adsorption is also very low in this case; about 1 kJ/mol. This effect will also influence the order of adsorption energies ($H^{\cdot} > C_2H^{\cdot} > CH_2^{\cdot} > C_2H_2 > CH_3^{\cdot}$), which is to be compared with the corresponding order of energies for a completely hydrogenated diamond (111) surface ($C_2H^{\cdot} > H^{\cdot} > CH_2^{\cdot} > CH_3^{\cdot} > C_2H_2$). Numerically, the adsorption of a C_2H_2 species to a radical site adjacent to a $CH_2^{\cdot}$ neighbor will result in the positive value of 111 kJ/mol (the basis set combination used is the more flexible 6-31G**/6-31G). Thus, in contrast to the case with a $CH_3^{\cdot}$ neighbor, there will be a finite probability for this adsorption process to occur.

b. Effects of electron correlation. The results of the MP2/(6-31G**/STO-3G) calculations for the coadsorption of the different species $CH_3^{\cdot}$, $CH_2^{\cdot}$, $C_2H^{\cdot}$, C_2H_2, and $H^{\cdot}$ are also given in Table II. The results are very interesting in that the ordering of the different adsorption energies now becomes identical for all four types and configurations of adjacent species investigated in the present work. The adsorbants are then either surrounded only by $H^{\cdot}$ atoms or one of the $H^{\cdot}$ atoms is removed or replaced by a $CH_2^{\cdot}$ or $CH_3^{\cdot}$ species.

The sterically hindering effect of the highly branched $CH_3^{\cdot}$ neighbor is, in these MP2 calculations, responsible for a decrease in adsorption energy by about 80 kJ/mol. As expected, the steric effect on the hydrogen atom $H^{\cdot}$ is lower (about 10 kJ/mol). Numerically, the results of the electron correlation corrections also show that the adsorption energy of the onefold adsorption of the C_2H_2 species will be negative and, hence, that this type of adsorption process is not predicted to occur.

The corresponding sterically hindering effect of the less branched $CH_2^{\cdot}$ neighbor has, with one exception, diminished the adsorption energies of the hydrocarbon species by about 40 kJ/mol. The exception is the adsorption energy of the C_2H_2 species, which has increased by 174 kJ/mol. Hence the effect of the C_{neighbor}-$C_{\text{adsorbant}}$ interaction on the adsorption energy of C_2H_2 is more pronounced in these MP2 results. The steric effect of the adjacent $CH_2^{\cdot}$ species diminishes the adsorption energy of the hydrogen species by 3 kJ/mol. Corrections for the BSSE are also made in the calculations at the HF/(6-31G**/STO-3G) and MP2/(6-31G**/STO-3G) levels of theory (Table II). As already mentioned, the BSSE's at the MP2 level of theory are larger than the BSSE's calculated at the HF level. The BSSE's for hydrogen $H^{\cdot}$ are 23 and 27 kJ/mol at the MP2/(6-31G**/STO-3G) level of theory for $CH_3^{\cdot}$ and $CH_2^{\cdot}$ neighbors, respectively. The corresponding range of BSSE's for the hydrocarbons are 75–119 and 85–145 kJ/mol, respectively. The relatively large corrections for BSSE's are, however, too small to alter the order of the different species on the energy scale. As expected, the energy of adsorption of the C_2H_2 species, adsorbed to a radical carbon site with an adjacent branched $CH_3^{\cdot}$ species, is still more negative when the effects of basis set superposition are taken into consideration (Table II). The final probability for a onefold adsorption of the C_2H_2 species to this type of site is, hence, infinitesimal.

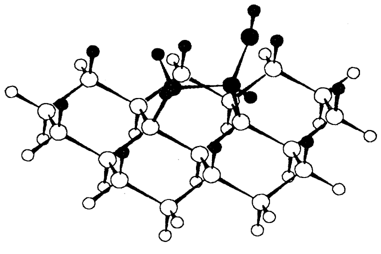

FIG. 5. The surface configuration with an adjacent $CH_2^{\cdot}$ species to the adsorbed C_2H_2 group. The C-C bond formed between the C atom in the $CH_2^{\cdot}$ neighbor and the surface-binding C atom in the adsorbing C_2H_2 molecule is marked with a line.

Pedersen, Jackson, and Picket used a local-density approximation in studying the effects of steric interference between neighboring adsorbants.[4] It was shown that islands of one, two, and three methyl radicals are all bound with respect to the bare surface. The binding energies for the different type of islands were 432, 403, and 317 kJ/mol, respectively. Their results suggested that the steric repulsions prevent the formation of a methyl-terminated diamond (111) surface. The binding energy for the adsorption of one $CH_3^{\cdot}$ species in the work by Pedersen, Jackson, and Picket is in agreement with the *ab initio* results of the adsorption of one $CH_3^{\cdot}$ species in the present work (388 kJ/mol). In fact, a quantitative comparison of the adsorption energies of all the species ($C_2H^{\cdot}$, $H^{\cdot}$, $CH_3^{\cdot}$, and C_2H_2) studied in the work by Pedersen, Jackson, and Picket (637, 473, 434, and 164 kJ/mol, respectively) shows a satisfactory agreement with the corresponding MP2 results in the present work (628, 441, 388, and 72 kJ/mol, respectively). Interestingly, the difference in adsorption energy between the MP2 and local-density-approximation (LDA) results is relatively large for the C_2H_2 species (92 kJ/mol) compared to the corresponding difference for the $C_2H^{\cdot}$ species (9 kJ/mol). The decrease in adsorption energy in the series $C_2H^{\cdot} > H^{\cdot} > CH_3^{\cdot} > C_2H_2$ is, hence, reflected in a corresponding increasing difference in the results obtained by the two different quantum-mechanical methods. It is well known that the density-functional calculations generally overestimate binding energies and, hence, adsorption energies for the adsorption of different species to a diamond (111) surface.[19] The LDA method used by Pedersen, Jackson, and Picket[4] would thus seem less reliable for calculations of weak adsorption energies, i.e., for compounds with inherently weak bonds.

Moreover, the estimated dissociation energy for a single methyl radical from an island of two methyl radicals is calculated to be 374 kJ/mol in the work by Pedersen, Jackson, and Picket.[4] This type of dissociation reaction can be regarded as the reverse of the adsorption of a second methyl to an adjacent methyl group. Hence this energy of 374 kJ/mol is to be compared with the adsorption energy of a second methyl to an adjacent methyl group in the present work (286 kJ/mol). However, the adsorbed methyl radical carbons were, in the work by Pedersen, Jackson, and Picket, tied off from below by hydrogens rather than a diamond surface in the template used in their work to study islands of two or three methyl species, respectively, on a diamond (111) surface. This means that no repulsions of adjacent surface hydrogen atoms were included in their LDA calculations regarding islands of more than two methyl species, which otherwise would have lowered their estimated energy of dissociation.

C. Adsorption energies in relation to growth species

During filament-assisted chemical vapor deposition of diamond from a reaction mixture of methane and hydrogen, there is a mixture of different hydrocarbon species present in the gas phase above the substrate surface. The C_2H_2 concentration has been measured in different *in situ* experiments to be almost equal to the $CH_3^{\cdot}$ concentration[9–11] in the gas phase. Furthermore, kinetic modeling also showed that the concentration of the species $CH_2^{\cdot}$ and $C_2H^{\cdot}$ is much lower than the concentration of $CH_3^{\cdot}$ and C_2H_2 (by about two and four orders of magnitude, respectively). The $CH_3^{\cdot}$ and C_2H_2 species are hence the most abundant ones.

The calculated adsorption energy of the gaseous species $CH_3^{\cdot}$ on the $M_H^{\cdot}$ type of surface configuration was predicted in earlier investigations to be much larger than the adsorption energy for the onefold adsorption of C_2H_2 (cf. Table I and Ref. 6). This is also, with one exception, the result in the present work, where the adsorption of different hydrocarbon species has been investigated for different situations: $M_{\mathrm{rad}}^{\cdot}$, $M_{\mathrm{CH2}}^{\cdot}$, and $M_{\mathrm{CH3}}^{\cdot}$. The calculations have also shown that there is no tendency for a onefold adsorption of C_2H_2 to occur adjacent to a $CH_3^{\cdot}$ group.

The significant difference in adsorption energy between $CH_3^{\cdot}$ and C_2H_2 (onefold adsorption), together with the fact that these species dominate the gas phase and that the concentrations of these species are about the same, thus support a diamond growth on the diamond (111) surface based on the $CH_3^{\cdot}$ group as a dominant growth species during filament-assisted diamond deposition from a relation mixture of methane and hydrogen. Earlier experimental studies of diamond growth mechanisms on the (111) crystal face of diamond have also indicated that the $CH_3^{\cdot}$ species is the dominant growth species under hot-filament CVD conditions for the (111) orientation of the diamond substrate. Competition studies by using carbon-13-labeled methane and carbon-12 acetylene were then made. The carbon-13 mole fraction of the diamond film indicated that the methyl radical is the dominant growth species.

The calculated adsorption energy of the $CH_3^{\cdot}$ species on a radical carbon site adjacent to a $CH_2^{\cdot}$ group is predicted to be only slightly larger than the corresponding adsorption energy for the onefold site adsorption of C_2H_2 (253 vs 101 kJ/mol) at the MP2 level of theory (including corrections for the BSSE) (Table II). The formation of a C-C bond between the adjacent hydrocarbon species $CH_2^{\cdot}$ and C_2H_2 on the diamond (111) surface explains the increase in adsorption energy of the C_2H_2 species for this particular configuration of diamond surface environment. An adjacent $CH_2^{\cdot}$ group on the diamond (111) surface thus makes the adsorption energy of C_2H_2 (onefold) approach that for $CH_3^{\cdot}$. Hence it is not possible to preclude the C_2H_2 species, in cooperation with $CH_3^{\cdot}$, from any role as a growth species only from these calculated adsorption energies. The situation with an adjacent $CH_2^{\cdot}$ group is easily accomplished by hydrogen abstraction of an already adsorbed $CH_3^{\cdot}$ species in the very dense hydrogen atmosphere during filament-assisted diamond deposition.

Furthermore, the calculations at the MP2 level of theory (including corrections for the BSSE) also predict a stronger bonding of a twofold site adsorption of C_2H_2 (356 kJ/mol), compared to the adsorption of $CH_3^{\cdot}$ (317 kJ/mol) and, particularly, a onefold site adsorption of C_2H_2 (13 kJ/mol), to a diradical site on a diamond (111) surface. This result, together with the fact that there is a pronounced probability found for a diradical site on a diamond (111) surface under the prevailing experimental conditions,[16] provides additional evidence that the C_2H_2 species should be considered as a possible growth species during diamond growth on a (111) surface.

IV. SUMMARY

The influence of adjacent molecular groups on the adsorption of $H^{\cdot}$, $CH_3^{\cdot}$, $CH_2^{\cdot}$, $C_2H^{\cdot}$, and C_2H_2 on the diamond (111) surface was investigated by the *ab initio* molecular-orbital method. The adsorption energies were found to be in the order $C_2H^{\cdot} > H^{\cdot} > CH_2^{\cdot} > CH_3^{\cdot} > C_2H_2$ for all different types of neighboring environments investigated. The adsorbed species is then either surrounded by only $H^{\cdot}$ atoms or one of these $H^{\cdot}$ atoms is removed, leaving a diradical site, or replaced by a $CH_2^{\cdot}$ or a $CH_3^{\cdot}$ species. Hence the $C_2H^{\cdot}$ and $CH_2^{\cdot}$ species are predicted to adsorb much easier to the radical carbon atom on the diamond (111) surface than $CH_3^{\cdot}$ and C_2H_2 do. For a twofold site adsorption of C_2H_2 the final ordering of species on the energy scale would be $C_2H^{\cdot} > C_2H_2$ (twofold) $> H^{\cdot} > CH_2^{\cdot} > CH_3^{\cdot} > C_2H_2$ (onefold). A stabilization of both surface dangling bonds by a C_2H_2 species has hence produced stronger bonding than the adsorption of $CH_3^{\cdot}$ or a onefold adsorption C_2H_2, respectively, does.

Numerically, the sterically hindering effects of the branched neighboring species $CH_3^{\cdot}$ and $CH_2^{\cdot}$ decrease the adsorption energy for the different hydrocarbon species by about 100 and 60 kJ/mol, respectively, on the MP2 level of theory (including corrections for the BSSE). An exception to this observation is the adsorption of the C_2H_2 species to an adjacent $CH_2^{\cdot}$ group. A C-C bonding interaction between the two adsorbed hydrocarbon species on the surface is most probably responsible for the increase in adsorption energy by about 100 kJ/mol, compared to the adsorption of a C_2H_2 species to an otherwise completely hydrogenated diamond (111) surface. It is then remarkable that the difference in adsorption energies between C_2H_2 and $CH_3^{\cdot}$ decreases dramatically by about 170 kJ/mol (from 319 to 152 kJ/mol) when one of the adjacent hydrogen atoms is replaced by $CH_2^{\cdot}$. The difference in adsorption energy at the MP2 level of theory (including corrections for the BSSE) between the species C_2H_2 and $CH_3^{\cdot}$ for the other types of surface configurations are 296 kJ/mol for the case with an adjacent $CH_3^{\cdot}$ species, and 304 kJ/mol for the case with a radical site neighbor.

The effect of the higher adsorption energies for $C_2H^{\cdot}$ and $CH_2^{\cdot}$ on the diamond growth is counteracted by the effect of the much lower gas-phase concentrations of these species during filament-assisted diamond deposition from a reaction mixture of methane and hydrogen. Generally, the significant difference in adsorption energy between $CH_3^{\cdot}$ and C_2H_2, together with the fact that the gas-phase concentrations of these species are about the same, will then support a diamond growth mechanism based on the $CH_3^{\cdot}$ group as a dominant growth species. This result is consistent with earlier experimental results. However, the calculated adsorption energy of a onefold site adsorption of C_2H_2 adjacent to a $CH_2^{\cdot}$ species is predicted to be smaller than the corresponding adsorption energy of $CH_3^{\cdot}$ by only about 150 kJ/mol. This is not to be regarded as a significant difference in adsorption energy. This result, together with the still stronger bonding of a twofold adsorption of C_2H_2 to a diradical surface site, makes it impossible to preclude the C_2H_2 species from any role as a growth species during filament-assisted diamond deposition from a reaction mixture of methane and hydrogen.

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