

## Ab Initio Calculation of Adsorption to $\beta$ -SiC Clusters

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The adsorption of gaseous H and CH<sub>3</sub> species to H-terminated  $\beta$ -SiC clusters of different sizes and shapes have been investigated theoretically using ab initio molecular orbital theory, including the effects of electron correlation by means of second-order Möller–Plesset (MP2) perturbation theory. Corrections for basis set superposition errors (BSSE) were also performed. An obvious dependence of cluster shape on the adsorption energy was found. The order of energies for H adsorption was found to be cluster I (478) > cluster II (398) > cluster III,a (365)  $\approx$  cluster III,b (366). (The unit of energies presented here is kJ/mol.) Cluster I and IV represent a smaller and a larger roundish cluster, while cluster II represents an (111) surface and cluster III (a,b) different sites of an (110) surface. The order of energies was somewhat different for CH<sub>3</sub> adsorption: cluster I (521) > cluster III,b (421) > cluster II (346) > cluster III,a (269). As a comparison, adsorption of F/CF<sub>3</sub> to corresponding F-terminated clusters was also studied at various levels of theory. The adsorption energies for the smallest cluster I were found to be 621 kJ/mol for F and 297 kJ/mol for CF<sub>3</sub> at the MP2/BSSE level of theory. More generally, a tendency was observed where the gaseous F was found to bind more strongly to the clusters than the H species does, while the gaseous CF<sub>3</sub> was found to bind more weakly to the clusters than the CH<sub>3</sub> species does (at the HF level of theory). Furthermore, bond strength was also influenced by cluster size. The H species was found to bind more strongly to the smaller roundish cluster I (484) than to the larger roundish cluster IV (369) (at the MP2 level of theory).

### I. Introduction

Silicon carbide (SiC) has a large technological potential for high-power devices and semiconductor materials. This is mainly due to properties such as extreme hardness, thermal conductivity, and chemical stability. To produce high-quality SiC, e.g., by CVD (chemical vapor deposition) methods,<sup>1</sup> it is important to find optimal growth parameters. One way of doing this is to obtain a deeper knowledge at the atomic level of these processes. This knowledge can in part be obtained from quantum mechanical calculations.

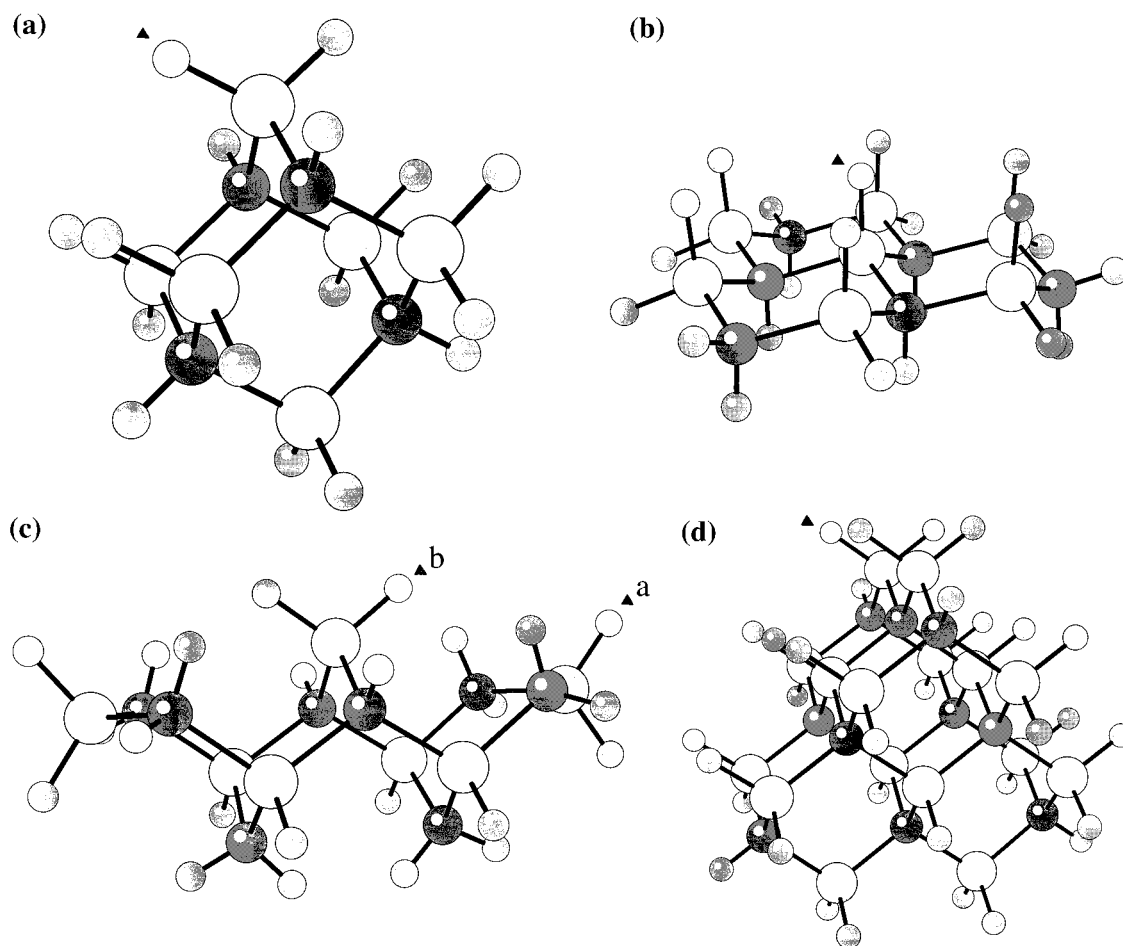
SiC exists in many polytypes that differ only in one dimension. More specifically, this means different stacking sequences of the Si and C planes along the *c*-axis. The numerous polytypes, representing hexagonal and rhombohedral modifications of SiC, are collectively referred to as  $\alpha$ -SiC.<sup>2</sup> The only cubic polytype, called  $\beta$ -SiC, is of the zinc blende structure.  $\beta$ -SiC is of special interest since (i) it can be prepared at much lower temperatures than the  $\alpha$ -SiC polytypes, (ii) it has a comparatively lower energy gap, and (iii) it has higher electron mobility.<sup>3</sup> Moreover,  $\beta$ -SiC has many characteristics in common with diamond. Structurally  $\beta$ -SiC is obtained by substituting every other C atom in diamond with Si in such a way that the Si atoms are only allowed to bond to C atoms. The bonds between the atoms in both diamond and SiC are strongly covalent. The electronegativity of C (e.n. = 2.55) is, however, much larger than that of Si (e.n. = 1.90).<sup>4</sup> This leads to a polarity of the Si–C bonds in SiC.

Clusters of various shapes and sizes may be obtained homogeneously in the gas phase during CVD. At high supersaturations, they are easily formed. The properties of these clusters generally differ from those of bulk materials.<sup>5</sup> Semiconductor clusters are of special interest since their inherent

properties (e.g., band gap) often differ from the corresponding bulk values. A size dependency of the band gap of clusters has been observed earlier.<sup>6</sup>

In vapor growth processes such as SiC CVD, carbon- and silicon-carrying gaseous species have to be deposited onto the growing surface. Precursors currently used in such processes are methyltrichlorosilane<sup>3,7,8</sup> as well as C<sub>3</sub>H<sub>8</sub><sup>1,9,10</sup> together with different silicon-containing species and with a large excess of H<sub>2</sub>. Upon thermal decomposition, many different gaseous species are formed (e.g., C<sub>2</sub>H<sub>2</sub>, CH<sub>3</sub>, CH<sub>2</sub>, CH, and C). Ohshita et al. found that CH<sub>3</sub> and CH<sub>2</sub> are the most likely carbon-containing reactants for growth of  $\beta$ -SiC clusters.<sup>9</sup> Lespiaux and Langlais found C<sub>2</sub>H<sub>2</sub> to be the major adsorbed species on a Si-terminated  $\beta$ -SiC(111) surface but that CH<sub>3</sub> is a competing species under certain conditions.<sup>11</sup>

The purpose of the present work is to make a comparative structural and energetic investigation regarding the adsorption of various species to  $\beta$ -SiC clusters of various shapes and sizes. The species included in the calculations are H and CH<sub>3</sub>, or in some cases F and CF<sub>3</sub>. The main reason for using a surface-terminating species, H (or F), was to maintain the sp<sup>3</sup> configuration of the surface silicon in order to prevent the surface from being reconstructed. The CH<sub>3</sub> was specially chosen since it is the geometrically largest of the precursors and we were interested in studying cluster shape effects on adsorption processes. A large gaseous species, such as CH<sub>3</sub>, will most probably induce steric hindrances at different degrees when adsorbed to clusters of various sizes and shapes (especially the latter). This will then influence the adsorption process, since a large adsorbate as CH<sub>3</sub> will be most sensitive to various neighboring environments to the adsorption site. Hence, it will be of great interest to investigate eventual cluster size and shape



**Figure 1.** Geometry of the clusters used in the calculations: (a) a small roundish cluster I; (b) a planar cluster II; (c) a planar cluster III, with the different adsorption sites marked by “a” and “b”; (d) a larger roundish cluster IV. The larger circles represent silicon atoms, the middle sized ones carbon atoms, and the smallest circles represent hydrogen atoms. Unfilled hydrogen atoms, marked with a triangle, denote the adsorption sites used.

effects on adsorption processes for various SiC surfaces. If there are such effects, tailor-made materials with desired properties could then be deposited from clusters of specific sizes and shapes.

## II. Method

The adsorption of various species to  $\beta$ -SiC clusters has been investigated within ab initio quantum molecular orbital theory using the program systems Gaussian94<sup>12</sup> and GAMESS.<sup>13</sup> Gaussian94 was used for the more extensive calculations. Total energies were calculated for the reactants as well as for the products in the adsorption process,



where  $M^*$  is the template modeling the actual  $\beta$ -SiC cluster and  $A^*$  is one of the adsorbing species (H, CH<sub>3</sub>, F, CF<sub>3</sub>). The adsorption energies were calculated by using

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

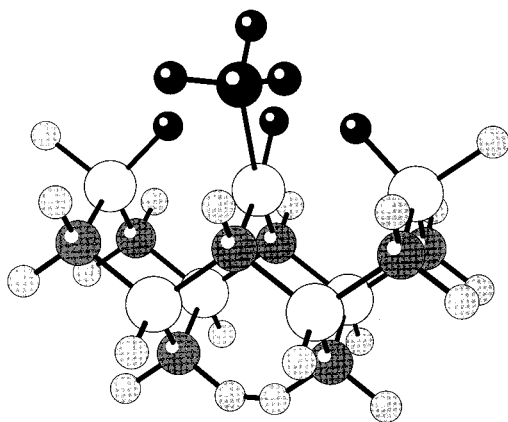
where  $E_A$ ,  $E_M$ , and  $E_{M-A}$  are the total energies for the different adsorbing species and for the cluster M with and without the adsorbed species, respectively.

The ab initio method used is the Hartree–Fock (HF) method.<sup>14</sup> Because of the inadequate treatment of the correlation of the motion of the electrons, additional calculations were performed using the second-order Möller–Plesset perturbation

(MP2) theory.<sup>14</sup> Corrections for the basis set superposition error (BSSE) were also made in the MP2 calculations.<sup>14</sup>

As mentioned above, clusters of different shapes and sizes are often obtained intentionally or unintentionally in the gas phase during CVD. They may, to some extent, deposit on the growing thin film surface<sup>5</sup> and thereby introduce defects as complex grain boundaries and voids. Clusters may also be grown heterogeneously and simultaneously with the film. The effects of cluster size and shape, respectively, on various adsorption processes on the  $\beta$ -SiC cluster surfaces were especially studied in the present investigation. Four different clusters were then prepared (Figure 1). Cluster I (Si<sub>6</sub>C<sub>4</sub>) has a roundish shape. Cluster II (Si<sub>7</sub>C<sub>6</sub>) is more planar and can also be regarded as modeling a part of the (111) surface. Cluster III (Si<sub>7</sub>C<sub>8</sub>) is, as cluster II, planar but is instead modeling a part of the (110) surface. Two different adsorption sites were considered for this model, “a” on the edge and “b” on the middle of the cluster. Some calculations were also performed on a larger roundish cluster IV (Si<sub>16</sub>C<sub>10</sub>). One of the silicon surface atoms has been selected as the adsorption site in this investigation. Furthermore, either hydrogen or fluorine was used (i) to terminate the cluster surfaces and (ii) as a ligand in CX<sub>3</sub> in order to investigate the influence of H versus F on the adsorption processes. Hydrogen is the most common surface-terminating species, but it is interesting to also study fluorine, which has been found to stabilize diamond surfaces well.<sup>15</sup>

All geometric parameters for the gaseous and adsorbed species were fully optimized in the present investigation. The



**Figure 2.** A model of the more restricted cluster III,b,"stiff" with an adsorbed CH<sub>3</sub> species. The black atoms are the ones which were allowed to relax during the geometry optimization.

clusters were, with one exception, also fully optimized. For Si<sub>7</sub>C<sub>8</sub>b, additional optimization calculations were performed where most atoms of the cluster were kept fixed. Only three surface-terminating hydrogen atoms around the silicon adsorption site were then allowed to relax (see Figure 2). The resulting model could be regarded as a cluster partly bonded to a  $\beta$ -SiC surface, or even more incorporated with the surface. It provides quite an inconvenient adsorption site. Adsorption of CH<sub>3</sub> to this type of cluster was simulated with the aim to get an idea of how much the adsorption process seems to be affected by the  $\beta$ -SiC clusters' ability to relax.

To obtain a good description of the electronic state of the reactants and the products in the adsorption reaction, it is important to use a flexible basis set for the optimization calculations. These calculations are, however, very computer demanding. By performing the optimization calculations using a smaller basis set, followed by a single-point calculation with a more flexible basis set, the computer time will decrease. To check the effect of the basis set on adsorption energy for H to cluster I, geometry optimizations with the minimal STO-3G basis set and with the 6-31G split valence basis set, respectively, were performed. Subsequent single-point calculations with the more flexible 6-31G\*\* split valence basis set with polarizing functions resulted in adsorption energies of 274 vs 276 kJ/mol. Hence, the STO-3G basis set was found to be adequate in performing the geometry optimizations. A flexible basis set is, however, very important for the single-point calculations, especially when the differences between the related energies turn out to be small. For this reason, 6-31G\*\* was chosen. Additional BSSE calculations were also made at the MP2/6-31G\*\* level of theory.

### III. Results and Discussion

**A. General.** Among the various physical and chemical steps involved in CVD, the adsorption of the gaseous species on the solid surface is frequently a rate-determining step, either by contributing to the growth rate or by blocking the available surface sites. In several recent investigations, the inhibiting or favorable effects of chlorine in CVD of SiC are described.<sup>7–11</sup> Chlorine is often a gaseous byproduct from the silicon source species. By adding HCl to the atmosphere during CVD experiments of  $\beta$ -SiC, Ohshita found the surface morphology to be improved.<sup>10</sup> Chlorine can also be expected to stabilize the surface. In an earlier investigation by one of the present authors,<sup>15</sup> chlorine was found to sustain the sp<sup>3</sup> structural configuration of the surface carbon atoms of diamond. This was

**TABLE 1: Binding Energies for Adsorbed H or CH<sub>3</sub> Species on the Various Clusters (see Figures 1 and 2), Calculated at Different Levels of Accuracy, All Using the 6-31G\*\* Basis Set ( $\Delta E_{\text{ads}}$ /(kJ/mol))**

	H			CH <sub>3</sub>		
	MP2+ BSSE	MP2	HF	MP2+ BSSE	MP2	HF
CH <sub>3</sub> Si <sub>6</sub> C <sub>4</sub> H <sub>16</sub> (I)	478	484	320	521	540	282
Si <sub>7</sub> C <sub>6</sub> H <sub>22</sub> (II)	398	405	377	346	371	275
Si <sub>7</sub> C <sub>8</sub> H <sub>24</sub> <sup>a</sup> (III <sup>a</sup> )	365	373	322	269	366	281
Si <sub>7</sub> C <sub>8</sub> H <sub>24</sub> <sup>b</sup> (III <sup>b</sup> )	366	373	323	421	442	268
Si <sub>7</sub> C <sub>8</sub> H <sub>24</sub> <sup>b</sup> , "stiff"				233	266	211
Si <sub>16</sub> C <sub>10</sub> H <sub>32</sub> (IV)		369	320			

also found to be the situation with fluorine and hydrogen. These species have large electronegativities (4.0 and 2.2, respectively, compared to 3.2 for Cl) but small atomic radii (71 pm and 37 pm, respectively, compared to 99 pm for Cl), thus inducing smaller steric hindrances compared to chlorine. Fluorine and hydrogen are, hence, assumed to be capable of forming single bonds with the surface atoms in SiC, then sustaining the sp<sup>3</sup> configuration. However, due to the large differences in size and electronegativity, structural geometries of a fluorinated cluster may be different from those of a hydrogenated cluster. This is also the situation for the adsorption energies. Moreover, several researchers have suggested that a mixture of F and H in the feed gas during growth of diamond will enhance the growth by reducing the required substrate temperature.<sup>16</sup> Due to the physical and chemical similarities between  $\beta$ -SiC and diamond, it is of interest to also investigate the effects of F vs H in the aforementioned adsorption studies. The carbon-containing growth species used in the present investigation were, hence, either hydrogenated (CH<sub>3</sub>) or fluorinated (CF<sub>3</sub>).

**B. Calculations on Different Levels of Accuracy.** The calculated adsorption energies for the adsorption of H and CH<sub>3</sub>, respectively, to the four H-terminated clusters (Figure 1) are shown in Table 1. The obtained order of adsorption energies for H is cluster I > cluster II > cluster III,a  $\approx$  cluster III,b (on the MP2 level of theory). The corresponding order for the CH<sub>3</sub> species turned out to be cluster I > cluster III,b > cluster II > cluster III,a > cluster III,b, "stiff". Cluster III,a and cluster III,b represent a cluster type with two different adsorption sites. The former provides an adsorption site on the edge of cluster III, and the latter provides an adsorption site on the central part of the cluster (see Figure 1). The more restricted cluster III,b,"stiff" (pictured in Figure 2), is originally identical to cluster III,b. However, during the geometry optimization, only the adsorbed species, plus the three hydrogens surrounding the adsorption site, were allowed to relax. This resulted in a more restricted adsorption site than the one in the totally relaxed cluster III,b.

As can be seen in Table 1, the orders of adsorption energies were not changed for adsorption of H when performing corrections for basis set superposition errors (BSSE). The individual results for the H-adsorption do not even seem to be affected by the BSSE, since corrections for the BSSE altered the different adsorption energies by only 6–8 kJ/mol. On the other hand, the adsorption energy of CH<sub>3</sub> to cluster III,a changed by about 100 kJ/mol for this refinement of the calculations. This implies that the BSSE corrections are not negligible, at least regarding the adsorption of CH<sub>3</sub>. However, as was the situation with H adsorption, the order of energies for adsorption of CH<sub>3</sub> was not altered when performing BSSE corrections compared to the nonrefined MP2 calculations. Furthermore, the differences in energies for the various clusters and a specific adsorbate (H or CH<sub>3</sub>) are small when calculated at the HF level of theory. They are in fact too small to draw any conclusions regarding trends. Hence, the more accurate MP2 calculations (including



BSSE) should be used while investigating trends in the adsorption energies.

The differences in adsorption energies, calculated on the HF respective MP2 levels of theory, were large. This can be explained by the new pairing of electrons taking place during the adsorption process. The largest differences in adsorption energies were found for H and  $\text{CH}_3$  adsorbed to cluster I, whether using the HF or the MP2 level of theory. An energy difference of 158 kJ/mol was obtained for the H species on the various levels of accuracy (320 (HF), 478 (BSSE/MP2) kJ/mol). The corresponding energy difference for the  $\text{CH}_3$  species was 239 kJ/mol (282 (HF), 521 (BSSE/MP2) kJ/mol). These results were expected, since the shortest bond lengths within the two series (for H and  $\text{CH}_3$  as adsorbates) were obtained for the open cluster I (1.38 Å (H), 1.86 Å ( $\text{CH}_3$ )). Short bonds result in high electron density in the binding region and consequently large values of electron correlation corrections.

For all the adsorbed hydrogen atoms, the calculated adsorption energies are strongly correlated to the bond lengths (1.38 (478)<sup>I</sup> < 1.42 (398)<sup>II</sup> < 1.47 (365)<sup>III,a</sup>  $\approx$  1.47 (366)<sup>III,b</sup>). The numbers in parentheses are energies calculated on the MP2 level of theory, and the exponents describe the cluster type in question. Hence, an increase in  $\text{Si}_{\text{surface}}\text{--H}$  bond length is followed by an expected decrease in bond energy. The corresponding bond lengths for  $\text{CH}_3$  adsorbates almost followed the order of adsorption energies (1.86 (521)<sup>I</sup> < 1.92 (421)<sup>III,b</sup> < 1.88 (346)<sup>II</sup> < 1.92 (269)<sup>III,a</sup> < 2.12 (266)<sup>III,b,"stiff"</sup>). The exception is the adsorption of  $\text{CH}_3$  to cluster II. The adsorption of  $\text{CH}_3$  to the more stiff cluster III,b yielded the lowest adsorption energy. However, this result was expected, since the induced steric hindrances within this model resulted in a bond length of 2.12 Å. Moreover, the surface silicons bonded to the adsorbed species (H or  $\text{CH}_3$ ) seem to be close to  $\text{sp}^3$  hybridized in all but one of the investigated cases. All the bond angles,  $\nu_{\text{C--Si(surface)--C}}$ , obtained are fairly close to the ideal 109.4° (106.9–113.1°). The exception is  $\text{CH}_3$  adsorbed to cluster II, for which the corresponding angle was found to be as large as 115.4°. The large bonding angle for  $\text{CH}_3$  adsorbed to cluster II implies much influence of  $\text{sp}^2$  hybridization for the surface adsorption site, something that could explain the relatively low adsorption energy obtained.

Lespiaux and Langlais<sup>11</sup> calculated the adsorption energy of H and  $\text{CH}_3$  to an Si site of the  $\beta$ -SiC(111) surface within the Langmuir model and without using any surface-terminating species. Their results, 296 and 368 kJ/mol, respectively, contradict our results since they found that  $\text{CH}_3$  adsorbs more strongly to the surface than H does. However, this difference in order is not strange since the differences in energy are small. The fact that they did not use surface-terminating atoms lowered to some extent the influence of steric hindrances and led to different adsorption conditions compared to our situation.

**C. H versus F in the Adsorption Process.** Calculations of F and  $\text{CF}_3$  adsorption to the F-terminated cluster I were performed in order to study the effect of cluster-terminating species. The results, shown in Table 2, can be related to the corresponding values for the H-terminated cluster (Table 1). As was the case with the hydrogenated cluster I, the MP2 calculations (including corrections for the BSSE) altered the energies significantly. An increase of 147 (158) kJ/mol was obtained in the case of F (H) adsorption. An exception was the adsorption of  $\text{CF}_3$  to the F-terminated cluster type I for which the correction for electron correlation resulted in a weak increase in adsorption energy of only 62 kJ/mol. This is to be compared with the corresponding correction for  $\text{CH}_3$  adsorbed on a

**TABLE 2: Binding Energies for Adsorbed F or  $\text{CF}_3$  on the Various Clusters (See Figure 1) Calculated on Various Levels of Accuracy, All Using the 6-31G\*\* Basis Set ( $\Delta E_{\text{ads}}$ /(kJ/mol))**

	X			$\text{CX}_3$		
	MP2+ BSSE	MP2	HF	MP2+ BSSE	MP2	HF
$\text{Si}_6\text{C}_4\text{F}_{16}$ (I)	621	656	474	297	349	235
$\text{Si}_7\text{C}_6\text{F}_{22}$ (II)		630	444			200
$\text{Si}_7\text{C}_8\text{F}_{24}^{\text{a}}$ (III <sup>a</sup> )			475			244
$\text{Si}_7\text{C}_8\text{F}_{24}^{\text{b}}$ (III <sup>b</sup> )			514			273
$\text{Si}_{16}\text{C}_{10}\text{F}_{32}$ (IV)			493			

H-terminated cluster I (increase of 239 kJ/mol). This difference is most probably attributed to the different bond lengths between the adsorbates and the surface (2.02 Å ( $\text{CF}_3$ ) and 1.86 Å ( $\text{CH}_3$ )).

For practical reasons, it was only possible to perform the demanding MP2 calculations with the 6-31G\*\* basis set for the smallest of the F-terminated clusters. The results from the HF calculations for all F- and H-terminated clusters used in the present study are shown in the Tables 1 and 2. They include adsorption of X and  $\text{CX}_3$  to X-terminated clusters of type I, II, III, and IV (X = H,F). As was shown in the previous section (B. Calculations on Different Levels of Accuracy), it is necessary to perform the calculations on the MP2 (BSSE) level of theory in order to receive any reliable information concerning reliable adsorption energies. However, with respect to this circumstance we find it informative to draw some conclusions from the HF calculations. F and  $\text{CF}_3$  seem to adsorb differently to the fluorinated clusters than H and  $\text{CH}_3$  do to the hydrogenated ones. This is expected since F is both larger and more electronegative than H. The fluorine atoms will induce a much larger atomic charge rearrangement near the surface than the hydrogen atoms do, with a large depletion of charge from the surface silicons. This also implies an ionic character of the Si–F chemical bond. The pronounced charge rearrangement in the region of adsorption is reflected in the adsorption energies of F to the different clusters. They are larger than the corresponding energies for H.  $\text{CF}_3$ , on the other hand, is prevented by steric hindrances to bind strongly to any of the F-terminated surfaces used in the present investigation. These trends obtained from the HF calculations are strongly supported by the more accurate calculations for cluster I.

**D. X versus  $\text{CX}_3$  in the Adsorption Processes.** The assumed mechanism for SiC growth is a very dynamic process since it involves a combination of surface abstraction (creation of surface vacancies) and adsorption of terminating species, as well as of growth species. The gaseous species  $\text{CH}_3$  is assumed to replace a hydrogen atom on a surface Si site, then acting as a growth species. The difference between the adsorption energies for  $\text{CH}_3$  and H is a measurement of how likely  $\text{CH}_3$  would be to replace H, and thereby extend the cluster. Numerically, these differences are 43 kJ/mol for cluster I, –52 kJ/mol for cluster II, –96 kJ/mol for cluster III,a and 55 kJ/mol for cluster III,b (Table 1). The values imply that the clusters I and III,b provide more favorable adsorption sites for methyl vs hydrogen than the other two clusters investigated. It is, however, important to remember that other influencing parameters, such as energy barriers and temperature, are not taken into account. Two different factors are generally expected to have a large effect on the bond strengths. One is the polarization of electrons within the newly formed bond between the adsorbate and the surface. A stronger bond is most often correlated with a higher degree of  $\text{sp}^3$ -hybridization (for the adsorbate-binding surface atom) and with a shorter bond length. Another factor is the steric hindrances induced by the adsorbate on the surface. The angles,  $\nu_{\text{C--Si(surface)--C}}$ ,

for H and CH<sub>3</sub> adsorbed to cluster I and cluster III,b, respectively, are both about 107°, something which implies the strong sp<sup>3</sup> hybridization of the adsorbate-binding surface silicon for these particular configurations. For the other two clusters, cluster II and III,a, the corresponding angles are between 110.7° and 115.4°. Furthermore, the distance between the adsorbate and its nearest neighbor (the nearest of the surrounding surface terminating hydrogens) was measured to be longer for CH<sub>3</sub> adsorption than for H adsorption in the cases of cluster I (2.68 (CH<sub>3</sub>) and 2.29 (H) Å), respectively, cluster III,a (3.02 (CH<sub>3</sub>) and 2.35 (H) Å), respectively. Since the CH<sub>3</sub> species in these cases experiences less steric hindrances from the surrounding species than H, this implies that cluster I and III,a provide comparatively favorable growth sites. However, this was energetically found to be true only for cluster I. The sp<sup>2</sup> character of the surface silicon of cluster III,a, bonded to the adsorbed CH<sub>3</sub> species, thus seems to have more impact on the strength of the bond created than the favorable geometric circumstances. While an sp<sup>3</sup> hybridized surface atom will form four strong  $\sigma$ -bonds with the surrounding atoms (inducing the adsorbed species), a partly sp<sup>2</sup> hybridized surface atom will form a weaker bond with an adsorbate. Furthermore, the distances from the adsorbates to their nearest surface-binding neighbors were found to be 2.61 (CH<sub>3</sub>) and 3.25 (H), for cluster II, and 2.33 (CH<sub>3</sub>) and 2.37 (H), for cluster III,b. The adsorption site provided on cluster II was apparently more accessible for the smaller H species than for CH<sub>3</sub>. In the case of cluster III,b, the corresponding adsorption site was found to be equally accessible for both adsorbates. The results in the present investigation hence show that both the steric factor, as well as the degree of sp<sup>3</sup> hybridization, will contribute to an increase in bond strength for CH<sub>3</sub> on cluster I and, to some extent, on cluster III,b (similar steric hindrances). Both factors were also found to cooperate in reducing the bond strength of CH<sub>3</sub> for cluster II. A positive effect of the lack of steric hindrances of CH<sub>3</sub> was opposed to the more negative effect of a large degree of sp<sup>2</sup> hybridization for the surface atom in cluster III,a. A less favorable growth site was then the result.

A trend has also been observed where F adsorbs stronger to the clusters than CF<sub>3</sub> does. For cluster I, the difference in adsorption energy between CF<sub>3</sub> and F was found to be 324 kJ/mol (at the MP2/BSSE level of theory), which is numerically much larger than the corresponding values obtained for any of the H-terminated clusters. The considerably stronger adsorption energy of F will for this situation irrecoverably result in a decrease in SiC growth rate when using F (instead of H) as a termination species.

**E. Effect of Cluster Size.** To investigate the influence of cluster size, calculations of adsorption energy of H to cluster I and IV were performed (see Figure 1). Both clusters have roundish shapes, and they provide similar adsorption sites. As can be seen in Table 1, the adsorption energies for H to cluster I and IV were found to be 484 vs 369 kJ/mol on the MP2 level of theory. This shows that adsorption of H to cluster I is significantly more favorable than adsorption of H to the larger cluster IV, something which was not expected because of the similarities in geometry. The bond distance for H to the clusters I and IV, calculated to be 1.38 and 1.43 Å, respectively, and the bond angle,  $\nu_{\text{C-Si(surface)-C}}$ , calculated to 107.4° and 108.7°, respectively, imply the strong sp<sup>3</sup> hybridization of the surface Si on both clusters. Moreover, the distance between the adsorbed H and its closest neighbor (a surface terminating H) was 2.3 (2.3) Å for cluster I (IV), inducing an almost identical degree of steric hindrances. However, the band gap energies obtained

(1415 and 1229 kJ/mol for cluster I and IV, respectively,) were quite different. (The band gap energy for bulk  $\beta$ -SiC is 231 kJ/mol.<sup>18</sup>) This is in accordance with earlier proposed inverse proportionality between band gap energies and cluster sizes.<sup>16</sup> There are significant differences in adsorption and band gap energies for the different cluster types (I and IV) and large similarities in geometry of these clusters. From these observations, one can draw the conclusion that there is a pure cluster size dependency of the adsorption processes investigated in the present study.

**F. Effect of Cluster Shape.** The calculations indicated that the shapes of the clusters affect the adsorption possibilities of the different species. As can be seen in Table 1, the adsorption energy is numerically larger for the roundish cluster I (478 (H)) than for the other clusters. However, the number of Si and C in each cluster type is not identical (10 in cluster I, 13 in cluster II, and 15 in cluster III). The decrease in adsorption energy for H adsorbed to types II, III,a, and III,b (compared to I) is almost as large as in the case of cluster IV (79<sup>II</sup>, 111,<sup>III,a</sup> and 111<sup>III,b</sup> vs 115<sup>IV</sup>). Hence, a pure size-dependent effect can be excluded. Most probably, the shape of the H-terminated clusters will be one cause of the variations in adsorption energy. With one exception, the order of adsorption energies obtained to H and CH<sub>3</sub> are cluster I > cluster II > cluster III,a > cluster III,b. The adsorption of CH<sub>3</sub> to cluster III,b seems to be much more favorable than adsorption to cluster III,a. This is a little strange, since the adsorption site is situated on the middle of cluster III,b while the corresponding site for cluster III,a is situated on the outer edge of the cluster (see Figure 1c). As discussed earlier, this is probably a result of the type of bond involved. The bonding angles,  $\nu_{\text{C-Si(surface)-C}}$ , were found to be 106.9°(cluster I), 106.3°(cluster III,b), 115.4°(cluster II), 112.2°(cluster III,a), and 109.5°(cluster III,b, "stiff"). The fact that the CH<sub>3</sub>-binding surface silicons on cluster I and III,b, respectively, are more sp<sup>3</sup> hybridized than to the corresponding Si atoms on the other clusters types (except cluster III,b, "stiff"), will further support the differences in adsorption energies.

By performing geometry optimizations for all atoms in a cluster, results realistic for very small clusters will be obtained. By optimizing only the atoms closest to the adsorbing site, something closer to a crystalline surface is achieved. The conditions for realistic clusters are somewhere between these two extreme cases. The clusters III,b and III,b, "stiff" are originally the same, but for the "stiff" variant only three of the terminating surface H atoms were allowed to relax (Figure 2). This is to be compared with the completely relaxed cluster (Figure 1). The more restricted geometry in this case provides a less available adsorption site, and the resulting adsorption energy (233 kJ/mol) is, hence, smaller than in the totally relaxed case (421 kJ/mol). The numerical value of the "true" energy for adsorption to a surface will then be somewhere in between, and it is interesting that the obtained range in adsorption energies is large (about 190 kJ/mol). The more stiff cluster III,b seems to have a strongly sp<sup>3</sup> hybridized surface silicon ( $\nu_{\text{C-Si(surface)-C}}$  (cluster III,b, "stiff") = 109.5°) bonded to the adsorbed CH<sub>3</sub> species. The distance to its nearest neighbor is, however, only 2.13 Å compared to 2.33 Å for the totally relaxed cluster III,b. Hence, the steric hindrances were most probably responsible for a reduction in adsorption energy of the more restricted cluster.

#### IV. Conclusion

The adsorption of the gaseous species H and CH<sub>3</sub> to H-terminated  $\beta$ -SiC clusters of various sizes and shapes has

been theoretically investigated, using the ab initio molecular orbital theory. The effect of different terminating species X (X = H, F) has also been included in the present investigation by performing a corresponding adsorption study using F and CF<sub>3</sub> instead of H and CH<sub>3</sub>. The models used were the roundish clusters I and IV and the more planar clusters II and III (Figure 1). Clusters II and III model parts of the (111) and (110) surfaces, respectively. The order of the adsorption energies for H to H-terminated clusters was found to be cluster I (478) > cluster II (398) > cluster III,a (365)  $\approx$  cluster III,b (366)  $\approx$  cluster IV (369). The open cluster I provided the most favorable adsorption site for the H atoms, something that was also found for the CH<sub>3</sub> clusters. The adsorption energies for the CH<sub>3</sub> species do not otherwise follow the order of the ones for the H species, cluster I (521) > cluster III,b (421) > cluster II (346) > cluster III,a (269) > cluster III,b,"stiff" (233). The results in the present study were, with some exceptions, calculated on the MP2 level of theory (with corrections for BSSE).

The possibility for CH<sub>3</sub> to replace a surface-terminating H species on the surface of a SiC cluster is a measurement of how good the combination H/CH<sub>3</sub> is for C growth on this specific material. In the present investigation,  $\Delta E_{\text{ads}}(\text{CH}_3) - \Delta E_{\text{ads}}(\text{H})$  was found to be 43 kJ/mol for cluster I, -52 kJ/mol for cluster II, -96 kJ/mol for cluster III,a, and 55 kJ/mol for cluster III,b. Hence, the cluster sites provided on the H-terminated models I and III,b were found to be favorable as growth sites, in contrast to the other sites investigated. The corresponding value for the F-terminated cluster I was found to be -324 kJ/mol. Moreover, a tendency was observed that supported the results obtained for the fluorinated cluster I, namely that CF<sub>3</sub> cannot be regarded as an effective growth species from a gaseous mixture of CF<sub>3</sub> and F. This tendency includes all the cluster types in the present study.

The following main conclusions can be drawn from the results presented in this study. (i) The initial stage of C growth on Si surface sites on SiC clusters are energetically more favorable using H, instead of F, as the terminating species. (ii) This adsorption process is also markedly ideal for small, roundish clusters instead of more planar ones. In designing SiC surfaces with improved adsorption properties, the above presented results (i) and (ii) can be of help. Hence, a rough SiC surface consisting of a large number of small and more roundish cluster-like SiC particles is to be preferred over a smooth and largely planar SiC surface. The rougher surface is, e.g., a consequence of

deposition of SiC from a gas phase consisting mainly of small, cluster-sized SiC particles.

The adsorption energy for H was found to be significantly greater for the smaller cluster I (484) than for the larger cluster IV (369) of the roundish shapes. This implies that the cluster size does affect the adsorption process and that self-termination of the cluster growth may occur for larger clusters.

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