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Empirical potential for hydrocarbons for use in simulating the chemical vapor deposition of diamond films

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An empirical many-body potential-energy expression is developed for hydrocarbons that can model intramolecular chemical bonding in a variety of small hydrocarbon molecules as well as graphite and diamond lattices. The potential function is based on Tersoff's covalent-bonding formalism with additional terms that correct for an inherent overbinding of radicals and that include nonlocal effects. Atomization energies for a wide range of hydrocarbon molecules predicted by the potential compare well to experimental values. The potential correctly predicts that the π-bonded chain reconstruction is the most stable reconstruction on the diamond $\{111\}$ surface, and that hydrogen adsorption on a bulk-terminated surface is more stable than the reconstruction. Predicted energetics for the dimer reconstructed diamond $\{100\}$ surface as well as hydrogen abstraction and chemisorption of small molecules on the diamond $\{111\}$ surface are also given. The potential function is short ranged and quickly evaluated so it should be very useful for large-scale molecular-dynamics simulations of reacting hydrocarbon molecules.

I. INTRODUCTION

Despite the tremendous technological advances made in the chemical vapor deposition (CVD) of diamond films, the underlying chemical and physical processes that allow diamond to be grown under apparently metastable conditions remain controversial. For example, it is unclear whether the primary species that adds to the surface is acetylene,[1] methyl radical,[2,3] or some mixture of hydrocarbon molecules,[4] and whether reaction occurs at a surface terrace[2,3] or step.[1] Other unresolved issues include the role(s) of hydrogen atoms, the influence of substrate temperature, and the initiation of defects such as stacking faults and twin planes.[5-8] Clearly the key to resolving these types of issues is an understanding of the atomic-scale dynamics that lead to the CVD of diamond films.

In the first quantum chemical total-energy calculations of a proposed reaction mechanism that leads to the CVD of diamond films, Tsuda *et al.* suggested that the attack of a methyl cation on a methyl-terminated diamond $\{111\}$ surface is responsible for the growth of diamond.[2] They used semiempirical modified intermediate neglect of differential overlap calculations to show that their reaction mechanism could proceed with relatively small potential-energy barriers. In a contrasting mechanism, Frenklach and Spear suggested that the addition of acetylene to a step is the primary reaction leading to diamond growth.[1] Using modified neglect of differential overlap (MNDO) calculations, Huang *et al.* showed that after the creation of a radical site at a step, two acetylene molecules can be added without any barriers to reaction.[9] More recently, Pederson *et al.*[10] have used local-density-functional methods and Valone *et al.*[11] have used semiempirical methods to calculate the energy and structure of a variety of hydrocarbon radicals chemisorbed on terrace sites on the diamond $\{111\}$ surface. While these techniques have been successful in quantifying the energetics of proposed reaction mechanisms and structures, they are relatively computer time intensive and are therefore somewhat restrictive in the size of the systems and the number of mechanisms that can be examined. Furthermore, these methods have not been able to address issues such as the influence of substrate temperature, and so other methods are needed to compliment total-energy calculations.

In related work, Yarbrough and Roy,[12] Machlin,[13] and Chen[14] have used empirical bond energies to estimate bonding configurations for various atomic structures, and have suggested that surface energetics plays a key role in the deposition of diamond films. Badziag *et al.* reached similar conclusions using both energies extrapolated from MNDO calculations and experimental heats of formation for small molecules.[15] They were able to demonstrate that diamond microcrystallites with hydrogen-terminated surfaces up to a few nanometers in diameter are more stable than graphitelike molecules with corresponding hydrogen-to-carbon ratios. This result suggests that the thermodynamic stability of diamondlike clusters at large hydrogen-to-carbon ratios may be a factor in the initiation of diamond films during CVD.

An alternate approach that has been used to model both the molecular beam and CVD growth of silicon films has been to use classical analytic potential-energy expressions in combination with molecular-dynamics simulation techniques.[16-25] Agrawal *et al.*, for example, have examined a number of key chemical processes in the CVD of silicon films,[21-24] and similar techniques should be useful for studying the CVD of diamond films. Crucial to the success of these types of studies is an analytic potential-energy expression that can capture the essential chemistry and physics. Although a number of classical potential-energy expressions have recently been proposed for carbon,[26–31] no potential-energy functions are currently available that can be used in molecular-dynamics simulations to model the CVD of diamond films from hydrocarbons.

As a first step toward using molecular dynamics to model the CVD of diamond films, we have developed an empirical potential-energy function that captures many of the essential features of chemical bonding in hydrocarbons. In particular, the goal of this work has been to develop a simple expression that (1) can reproduce the intramolecular energetics and bonding in solid diamond and graphite as well as a number of essential hydrocarbon molecules; (2) yields realistic energetics and bonding for structures not included in the data base; (3) allows for bond breaking and forming (i.e., chemistry); and (4) is not computationally intensive. While a number of classical expressions have been developed for studying the dynamics of hydrocarbon molecules, none are able to meet these criteria. For example, valence force fields and related approaches such as the molecular mechanics formalism developed by Allinger and co-workers[32] do not incorporate bond dissociation, and so cannot be used to model the chemical addition of molecules to diamond surfaces. The approach taken here is to use a highly parametrized Tersoff bond-order expression[33] as a fitting function for a number of small molecules as well as graphite and diamond lattices. Since a bond-order function is fit rather than, for example, a many-body expansion of the potential energy, the function should be reasonably transferable to structures not included in the fitting data set.

The organization of this paper is as follows. In the next section the Abell-Tersoff bonding formalism is outlined, and several problems associated with describing carbon and hydrocarbons are discussed. Two parametrizations of a Tersoff-type expression are then given which have been fit to the energetics of a relatively large number of hydrocarbon molecules. The first parametrization provides a good description of carbon-carbon bond lengths but has stretching force constants that are too small, while the second yields force constants that are in better agreement with experiment but produces bond lengths for double and triple bonds that are too long. Transferability of the expressions is tested by calculating energetics for diamond surfaces and hydrocarbons not used in the fitting data base. The energetics of a limited number of atomic configurations that are of direct relevance to the CVD of diamond films is then given.

II. POTENTIAL-ENERGY EXPRESSION

In an attempt to explain a universality relation observed in binding-energy curves,[34] Abell derived a general expression for binding energy that is a sum of near-neighbor pair interactions that are moderated by the local atomic environment.[35] Tersoff subsequently introduced an analytic potential-energy function based on the Abell expression that realistically describes bonding in silicon for a large number of solid-state structures.[33] Similar expressions have since been used for a range of applications, including other IV-IV (Refs. 28, 29, 36, and 37) and III-V compounds,[38] as a fitting function for the reactions $H+H_2$ and $O+O_2$,[29] and as a model for describing reactive collisions in molecular solids.[39]

The binding energy in the Abell-Tersoff formalism is written as a sum over atomic sites i,

$$E_b=\frac{1}{2}\sum_i E_i \ , \tag{1}$$

where each contribution E_i is written as

$$E_i=\sum_{j(\neq i)} [V_R(r_{ij})-B_{ij}V_A(r_{ij})] \ . \tag{2}$$

In Eq. (2), the sum is over nearest neighbors j of atom i, $V_R(r)$ and $V_A(r)$ are pair-additive repulsive and attractive interactions, respectively, and B_{ij} represents a many-body coupling between the bond from atom i to atom j and the local environment of atom i. As discussed by Abell and Tersoff,[33,35] if Morse-type functions are used for the repulsive and attractive pair terms, then B_{ij} can be considered a normalized bond order because the Pauling relationship between bond order and bond length is realized.[40]

Abell has suggested that to a first approximation B_{ij} can be given as a function of local coordination Z in the form

$$B_{ij}\propto Z^{-\delta} \ , \tag{3}$$

where δ may depend on the particular system. This analysis yields a relationship between bond length, binding energy, and coordination that is realized for a number of systems, including carbon-carbon bonds in diamond, graphite, and in hydrocarbon molecules.[27]

The procedure used by Tersoff to develop classical potentials for silicon, carbon, and germanium has been to fit the pair terms and an analytic expression for B_{ij} to a number of properties of the diatomic and solid-state structures (e.g., bond energies and lengths, bulk moduli, vacancy formation energies, etc.). His expression developed in this way appears to be relatively transferable to other solid-state structures not used in the fitting procedure such as surface reconstructions on silicon[33] and interstitial defects in carbon.[28] As discussed below, however, further analysis shows that this expression is unable to reproduce a number of properties of carbon such as a proper description of radicals and conjugated versus nonconjugated double bonds.

A. π-bonding in carbon

Since the Abell-Tersoff expression uses Pauling bond-order ideas, it can realistically describe carbon-carbon single, double, and triple bond lengths and energies in hydrocarbons and in solid graphite and diamond. In intermediate bonding situations, however, the assumption of near-neighbor interactions combined with the sum over atomic sites [Eq. (1)] results in nonphysical behavior. For example, if a carbon atom with three nearest neighbors is bonded to a carbon atom with four neighbors, Eqs. (1)–(3) interpolate the bond so that it is intermediate between a single and double bond. The formation of a double bond, however, results from the overlap of unbonded

$2p$ orbitals. Since the atom with a coordination of 4 does not have a free orbital, π overlap cannot occur and the bond is better described as a single bond plus a radical orbital. This overbinding of radicals results in a nonphysical description of bonding for carbon in a number of common situations. For example, the formation of a vacancy in diamond results in four radicals, and so this overbinding of radicals makes fitting the vacancy formation energy in diamond while maintaining a fit to graphite difficult if not impossible.[28]

Similar nonphysical behavior results when conjugated and nonconjugated double bonds are examined. For example, in graphite each atom has a local coordination of 3, and Tersoff-type potentials for carbon have been fit to yield a bond strength appropriate for graphite for this atomic environment.[28,29] A simple analysis of kekule' structures for graphite shows that due to the conjugation each bond has approximately one-third double-bond and two-thirds single-bond character. In the molecule $(CH_3)_2C{=}C(CH_3)_2$ the two carbon atoms connected by the central bond have the same local environment as in graphite, but because the bond is not conjugated it has an almost entirely double-bond character. Hence the potential cannot describe both situations unless nonlocal effects are included.

One way to correct both of these problems while maintaining the fit to diamond and graphite is to rewrite Eqs. (1)–(3) as a sum over bonds in the form

$$E_b=\sum_i \sum_{j(>i)} [V_R(r_{ij})-\bar{B}_{ij}V_A(r_{ij})] , \tag{4}$$

where

$$\bar{B}_{ij}=(B_{ij}+B_{ji})/2 . \tag{5}$$

The overbinding of radicals can now be fixed by adding corrections to Eq. (5) for bonds between pairs of atoms that have different coordinations. As described below, nonlocal effects can also be added to a first approximation to account for conjugated versus nonconjugated bonding.

B. Empirical potential-energy expression for hydrocarbons

Following the discussion given above, the binding energy for the hydrocarbon potential is given as a sum over bonds as

$$E_b=\sum_i \sum_{j(>i)} [V_R(r_{ij})-\bar{B}_{ij}V_A(r_{ij})] , \tag{6}$$

where the repulsive and attractive pair terms are given by

$$V_R(r_{ij})=f_{ij}(r_{ij})D_{ij}^{(e)}/(S_{ij}-1)e^{-\sqrt{2S_{ij}}\beta_{ij}(r-R_{ij}^{(e)})} \tag{7}$$

and

$$V_A(r_{ij})=f_{ij}(r_{ij})D_{ij}^{(e)}S_{ij}/(S_{ij}-1)e^{-\sqrt{2/S_{ij}}\beta_{ij}(r-R_{ij}^{(e)})} , \tag{8}$$

respectively. The function $f_{ij}(r)$, which restricts the pair potential to nearest neighbors, is given by

$$f_{ij}(r)=\begin{cases} 1, & r<R_{ij}^{(1)} \\ \left[1+\cos\left[\dfrac{\pi(r-R_{ij}^{(1)})}{(R_{ij}^{(2)}-R_{ij}^{(1)})}\right]\right]\Big/2, & R_{ij}^{(1)}<r<R_{ij}^{(2)} \\ 0, & r>R_{ij}^{(2)} . \end{cases} \tag{9}$$

The pair terms are of the same form as that used by Tersoff,[28,33,36] but rewritten to make the correspondence to a Morse function more apparent. If $S_{ij}=2$, then the pair terms reduce to the usual Morse potential. Furthermore, the well depth $D_{ij}^{(e)}$, equilibrium distance $R_{ij}^{(e)}$ and β_{ij} are equal to the usual Morse parameters independent of the value of S_{ij}.

The empirical bond-order function is given by the average of terms associated with each atom in a bond plus a correction as discussed above:

$$\bar{B}_{ij}=(B_{ij}+B_{ji})/2+F_{ij}(N_i^{(t)},N_j^{(t)},N_{ij}^{\mathrm{conj}}) , \tag{10}$$

where

$$B_{ij}=\left[1+\sum_{k(\neq i,j)} G_i(\theta_{ijk})f_{ik}(r_{ik})e^{\alpha_{ijk}[(r_{ij}-R_{ij}^{(e)})-(r_{ik}-R_{ik}^{(e)})]}+H_{ij}(N_i^{(\mathrm{H})},N_i^{(\mathrm{C})})\right]^{-\delta_i} . \tag{11}$$

The quantities $N_i^{(\mathrm{C})}$ and $N_i^{(\mathrm{H})}$ are the number of carbon and hydrogen atoms, respectively, bonded to atom i, $N_i^{(t)}$ is the total number of neighbors $(N_i^{(\mathrm{C})}+N_i^{(\mathrm{H})})$ of atom i, N_{ij}^{conj} depends on whether a bond between carbon atoms i and j is part of a conjugated system, $G(\theta_{ijk})$ is a function of the angle between bonds i—j and i—k, and the functions H_{ij} and F_{ij} are described below. The latter function, which is used for carbon-carbon bonds only, is the correction discussed above. Forms similar to that used by Tersoff to describe group-IV alloys were tried,[36] but because of the large difference in bonding characteristics between hydrogen and carbon (hydrogen is monovalent while carbon has a valency of up to 4), a set of parameters could not be found that could adequately describe bond energies for a large number of hydrocarbon molecules. Furthermore, as discussed above, radicals and nonconjugated double bonds are not well described.

To make the potential function continuous, the functions $f_{ij}(r)$ are used to define bonding connectivity in the system, and are therefore used to define values for $N_i^{(\mathrm{H})}$, $N_i^{(\mathrm{C})}$, $N_i^{(t)}$, and N_{ij}^{conj}. First, values for $N_i^{(\mathrm{H})}$, $N_i^{(\mathrm{C})}$, and $N_i^{(t)}$ for each of the carbon atoms i are given by

$$N_i^{(\mathrm{H})}=\sum_{j(=\text{hydrogen})} f_{ij}(r_{ij}) , \tag{12}$$

$$N_i^{(\mathrm{C})}=\sum_{j(=\text{carbon})} f_{ij}(r_{ij}) , \tag{13}$$

and

$$N_i^{(t)}=N_i^{(\mathrm{H})}+N_i^{(\mathrm{C})} . \tag{14}$$

Values of $N_i^{(t)}$ for neighbors of the two carbon atoms involved in a bond can be used to determine whether the bond is part of a conjugated system. For example, if any neighbors are carbon atoms that have a coordination of less than 4 ($N_i^{(t)}<4$), the bond is defined as being part of a conjugated system. The value of N_{ij}^{conj} for a bond between carbon atoms i and j is given by

$$N_{ij}^{\mathrm{conj}}=1+\sum_{\text{carbons } k(\neq i,j)} f_{ik}(r_{ik})F(x_{ik}) + \sum_{\text{carbons } l(\neq i,j)} f_{jl}(r_{jl})F(x_{jl}) \tag{15}$$

where

$$F(x_{ik})=\begin{cases}1, & x_{ik}\leq 2\\ \{1+\cos[\pi(x_{ik}-2)]\}/2, & 2<x_{ik}<3\\ 0, & x_{ik}\geq 3\end{cases} \tag{16}$$

and

$$x_{ik}=N_k^{\mathrm{tot}}-f_{ik}(r_{ik}) . \tag{17}$$

This function yields a continuous value of N^{conj} as bonds break and form and as second-neighbor coordinations change. For $N_{ij}^{\mathrm{conj}}=1$, a bond is not part of a conjugated system and the function yields appropriate values, and for $N_{ij}^{\mathrm{conj}}\geq 2$ the bond is part of a conjugated system and parameters fit to conjugated bonds are used. As a final step for making the potential continuous, two- and three-dimensional cubic splines are used for the functions H_{ij} and F_{ij}, respectively, to interpolate between values at discrete numbers of neighbors.

The procedure used to determine parameters for Eqs. (6)–(17) was to first fit to systems consisting of only carbon and only hydrogen. Parameters were then chosen for the mixed hydrocarbon system that reproduced additive bond energies. Since the pair terms are first fit to solid-state carbon structures, the equilibrium carbon-carbon distances and stretching force constants for hydrocarbons are completely determined by fitting to bond energies.

To determine appropriate energies for hydrocarbons with carbon-carbon bonds, additive bond energies for single, double, conjugated double and triple carbon-carbon bonds, and carbon-hydrogen bonds were determined from molecular atomization energies. Heats of formation at 0 K for acetylene, ethylene, ethane, benzene, and cyclohexane are 2.356, 0.629, −0.717, 1.041, and −0.868 eV, respectively.[41] Combining these values with binding energies of 7.3768 eV for graphite[42] and 2.375 eV for molecular hydrogen,[43] and neglecting corrections for zero point energy in the hydrocarbons, yields total atomization energies of 17.149, 23.626, 29.723, 57.472, and 73.634 eV for acetylene, ethylene, ethane, benzene, and cyclohexane, respectively. Assuming constant carbon-hydrogen and carbon-carbon single bond energies, energy values of 4.362, 8.424, 6.175, 5.216, and 3.547 eV can be derived for carbon-hydrogen and carbon-carbon triple, double, conjugated double (in benzene), and single bond energies.[44] For methane, the heat of formation at 0 K of 0.693 eV (Ref. 41) was used to determine carbon-hydrogen bond energies of 4.393 eV. Bond dissociation energies of 4.861 eV for methane[45] and 4.944 eV for methyl radical[46] were then used to determine bond energies of 4.237 eV for CH_3 and 3.833 eV for CH_2.

Two different parametrizations for Eqs. (6)–(18) for carbon and hydrocarbons have been determined. A similar function (without the corrections discussed above) has been fit to the binding energy of the C_2 diatomic molecule, and the binding energies and lattice constants of graphite, diamond, simple cubic, and face-centered-cubic structures,[29] and so the first parametrization was chosen to reduce to that function. The function $G_{\mathrm{C}}(\theta)$ is given by

$$G_{\mathrm{C}}(\theta)=a_0\{1+c_0^2/d_0^2-c_0^2/[d_0^2+(1+\cos\theta)^2]\} \tag{18}$$

and the carbon-carbon parameters are given in Table I. The potential yields binding energies and nearest-neighbor bond lengths of 7.3768 eV/atom and 1.42 Å, respectively, for graphite, and 7.3464 eV/atom and 1.54 Å for diamond. It also reproduces calculated values of 7.2 and 7.6 eV for the vacancy formation energies in diamond and graphite, respectively.[48] The predicted carbon-carbon bond lengths and stretching force constants given by this parametrization (denoted as potential I) for the bond energies derived above are given in Table II. The bond lengths agree very well with the experimental values, the largest difference being 0.02 Å for a single bond. The stretching force constants, however, differ from experimental values by as much as 60%. The carbon-hydrogen bond length given by the potential is 1.071 Å, which is slightly short of typical experimental values of 1.09 Å.[40]

Given in Table III are a second set of hydrocarbon parameters for Eqs. (6)–(18). This potential was again fit to the binding energies and lattice constants of graphite, diamond, simple cubic, and face-centered-cubic structures for pure carbon,[42] and the vacancy formation energies for diamond and graphite.[48] It yields binding energies and nearest-neighbor bond lengths of 7.3756 eV/atom and 1.45 Å, respectively, for graphite, and 7.3232 eV/atom and 1.54 Å for diamond. The predicted carbon-carbon bond lengths and force constants for hydrocarbons given by this parametrization (denoted by potential II) are given in Table II. The stretching force constants are closer to the experimental values than potential I, with the differences being reduced to 11%, 8%, and 26% for single, double, and triple bonds, respectively. The bond lengths for multiple bonds, however, are not as well described as with potential I, with the double and triple bonds being larger than the experimental values by 3.7% and 7.5%, respectively. A parametrization for the functions used for the pair terms could not be found that fit carbon-carbon stretching force constants and bond lengths simultaneously, although other forms may reproduce both sets of properties.

For hydrogen, the pair terms were fit to properties of the gas-phase diatomic.[43] The parameter δ_{H} was set equal to δ_{C}, and the remaining parameters were fit to

TABLE I. Parameters for Eqs. (4)–(18) for potential I. All parameters not given are equal to zero, $F(i,j,k)=F(j,i,k)$, $F(i,j,k>2)=F(i,j,2)$, and $\partial F(i,j,k)/\partial i=\partial F(j,i,k)/\partial i$. The partial derivatives are used in the multidimensional cubic splines.

Parameter		Value	Fit to
Carbon	$R_{\text{CC}}^{(e)}$	1.315 Å	Lattice constants of diamond and graphite
	$D_{\text{CC}}^{(e)}$	6.325 eV	Reference 29
	β_{CC}	1.5 Å^{-1}	Reference 29
	S_{CC}	1.29	Reference 29
	δ_{CC}	0.804 69	Reference 29
	α_{CCC}	0.0	
	$R_{\text{CC}}^{(1)}$	1.7 Å	Reference 29
	$R_{\text{CC}}^{(2)}$	2.0 Å	Reference 29
	α_0	0.011 304	Reference 29
	c_0^2	19^2	Reference 29
	d_0^2	2.5^2	Reference 29
	$F(2,3,1), F(2,3,2)$	−0.0465	E_{vac} for diamond
	$F(1,2,2)$	−0.0355	E_{vac} for graphite
Hydrogen	$R_{\text{HH}}^{(e)}$	0.74144 Å	Gas-phase diatomic
	$D_{\text{HH}}^{(e)}$	4.7509 eV	Gas-phase diatomic
	β_{HH}	1.9436 Å^{-1}	Gas-phase diatomic
	S_{HH}	2.3432	Barrier for reaction (19)
	δ_{HH}	0.804 69	Set equal to carbon value
	α_{HHH}	3.0	Remove spurious wells from (19)
	G_{HH}	4.0	Barrier for reaction (19)
	$R_{\text{HH}}^{(1)}$	1.1 Å	Near-neighbor interactions
	$R_{\text{HH}}^{(2)}$	1.7 Å	Near-neighbor interactions
Hydrocarbons	$R_{\text{CH}}^{(e)}$	1.1199 Å	Gas-phase diatomic
	$D_{\text{CH}}^{(e)}$	3.6422 eV	Gas-phase diatomic
	β_{CH}	1.9583 Å^{-1}	Gas-phase diatomic
	S_{CH}	1.7386	$(S_{\text{HH}}S_{\text{CC}})^{1/2}$
	$R_{\text{CH}}^{(1)}$	1.3 Å	Reaction (19)
	$R_{\text{CH}}^{(2)}$	1.8 Å	Reaction (19)
	$\alpha_{\text{HHC}}, \alpha_{\text{CHH}}, \alpha_{\text{HCH}}, \alpha_{\text{HCC}}$	3.0 Å^{-1}	H_3 value
	$H_{\text{CC}}(1,1)$	−0.0175	CC bond energy in benzene
	$H_{\text{CC}}(2,0)$	−0.0070	CC double bond in ethylene
	$H_{\text{CC}}(3,0)$	0.0119	CC single bond in ethane
	$H_{\text{CC}}(1,2)$	0.0115	CC single bond in isobutane
	$H_{\text{CC}}(2,1)$	0.0118	CC single bond in cyclohexane
	$H_{\text{CH}}(1,0)$	−0.0760	Atomization energy of CH_2
	$H_{\text{CH}}(2,0)$	−0.2163	Atomization energy of CH_3
	$H_{\text{CH}}(3,0)$	−0.3375	Atomization energy of methane
	$H_{\text{CH}}(0,1)$	−0.1792	CH bond energy in acetylene
	$H_{\text{CH}}(0,2)$	−0.2407	CH bond energy in benzene
	$H_{\text{CH}}(1,1)$	−0.2477	CH bond energy in ethylene

TABLE I. (*Continued*).

Parameter	Value	Fit to
$H_{\mathrm{CH}}(2,1)$	−0.3320	CH bond energy in ethane
$H_{\mathrm{CH}}(0,3)$	−0.3323	Tertiary-HC bond energy in isobutane
$H_{\mathrm{CH}}(1,2)$	−0.3321	CH bond energy in cyclohexane
$\frac{\partial H_{\mathrm{CH}}(1,1)}{\partial C}$	−0.128 05	Centered difference
$\frac{\partial H_{\mathrm{CH}}(2,0)}{\partial C}$	−0.076 55	Centered difference
$\frac{\partial H_{\mathrm{CH}}(0,2)}{\partial H}$	−0.130 75	Centered difference
$\frac{\partial H_{\mathrm{CH}}(1,1)}{\partial H}$	−0.0764	Centered difference
$F(1,1,1)$	0.1511	CC triple bond in acetylene
$F(2,2,1)$	0.075	Average energy of bonds in $(CH_3)_2C{=}C(CH_3)$ and $(CH_3)HC{=}CH(CH_3)$ equal double bond
$F(1,2,1)$	0.0126	Atomization energy of $HC{=}CH_2$
$F(1,3,1),F(1,3,2)$	−0.1130	Single bond in H_3C—CH
$F(0,3,1),F(0,3,2)$	−0.1220	Single bond in H_3C—C
$F(0,2,2)$	−0.0445	Conjugated double bond in $C{=}CH(CH_2)$
$F(0,2,1)$	0.0320	Double bond in $C{=}CH_2$
$F(0,1,1)$	0.1100	Atomization energy of C_2H
$F(1,1,2)$	0.0074	Atomization energy of CH_2CCH
$\frac{\partial F(3,1,1)}{\partial i}$	−0.1160	Centered difference
$\frac{\partial F(3,2,1)}{\partial i}$	−0.132 05	Centered difference
$\frac{\partial F(3,1,2)}{\partial i}$	−0.0610	Centered difference
$\frac{\partial F(2,3,2)}{\partial i}$	0.022 25	Centered difference
$\frac{\partial F(2,4,2)}{\partial i}$	−0.037 75	Centered difference
$\frac{\partial F(3,4,2)}{\partial i}$	0.0565	Centered difference
$\frac{\partial F(3,4,1)}{\partial i}$	0.0565	Centered difference
$\frac{\partial F(3,2,2)}{\partial i}$	−0.1065	Centered difference

reproduce the barrier of 0.425 eV for the ground-state linear exchange reaction

$$H+H_2 \rightarrow H_2+H \tag{19}$$

at the hydrogen-hydrogen distance of 0.93 Å as calculated by Liu and Seigbahn[49] and to remove spurious wells from this surface. For simplicity, angular dependence of the potential for hydrogen centers via the function $G_H(\theta)$ was replaced by the (constant) value of G_H used to fit reaction (19). The resulting parameters corresponding to hydrocarbon potential I are given in Table I, and those for potential II are given in Table III.

Some important points about the function, fitting procedure, and resulting structures need to be addressed. First, the angular function $G(\theta)$ associated with the carbon centers favors 180° bond angles and hence open structures. This is physically motivated by valence shell electron pair repulsion (VSEPR) theory,[50] which assumes that repulsions between pairs of valence electrons tend to maximize bond angles. This assumption, combined with the tendency to maximize the binding energy (i.e., num-

TABLE II. Carbon-carbon bond lengths R_e (in Å) and force constants F_c (in 10^5 dyn/cm) given by the two potentials based on bond energies of 3.547, 6.175, and 8.424 eV for single, double, and triple bonds, respectively, as derived in the text.

	Single bonds		Double bonds		Triple bonds	
	F_c	R_e	F_c	R_e	F_c	R_e
Potential I	2.6	1.56	4.5	1.33	6.1	1.20
Potential II	5.0	1.55	8.7	1.38	11.9	1.29
Experiment	4.5[a]	1.54[b]	9.5[a]	1.33[b]	16.0[a]	1.20[b]

[a] From Ref. 40.
[b] From Ref. 48.

TABLE III. Parameters for Eqs. (4)–(18) for potential II. All parameters not given are equal to zero, $F(i,j,k)=F(j,i,k)$, $F(i,j,k>2)=F(i,j,2)$, and $\partial F(i,j,k)/\partial i=\partial F(j,i,k)/\partial i$. The partial derivatives are used in the multidimensional cubic splines.

Parameter		Value	Fit to
Carbon	$R_{\mathrm{CC}}^{(e)}$	1.39 Å	Lattice constants of diamond and graphite
	$D_{\mathrm{CC}}^{(e)}$	6.0 eV	Fit to data in Ref. 42
	β_{CC}	2.1 Å^{-1}	Fit to data in Ref. 42
	S_{CC}	1.22	Fit to data in Ref. 42
	δ_{CC}	0.5	Fit to data in Ref. 42
	α_{CCC}	0.0	
	$R_{\mathrm{CC}}^{(1)}$	1.7 Å	Fit to data in Ref. 42
	$R_{\mathrm{CC}}^{(2)}$	2.0 Å	Fit to data in Ref. 42
	a_0	0.000 208 13	Fit to data in Ref. 42
	c_0^2	330^2	Fit to data in Ref. 42
	d_0^2	3.5^2	Fit to data in Ref. 42
	$F(2,3,1)$,$F(2,3,2)$	−0.0363	E_{vac} for diamond
	$F(1,2,2)$	−0.0243	E_{vac} for graphite
Hydrogen	$R_{\mathrm{HH}}^{(e)}$	0.74144 Å	Gas-phase diatomic
	$D_{\mathrm{HH}}^{(e)}$	4.7509 eV	Gas-phase diatomic
	β_{HH}	1.9436 Å^{-1}	Gas-phase diatomic
	S_{HH}	2.3432	Barrier for reaction (19)
	δ_{HH}	0.5	Set equal to carbon value
	α_{HHH}	4.0	Remove spurious wells from (19)
	G_{HH}	12.33	Barrier for reaction (19)
	$R_{\mathrm{HH}}^{(1)}$	1.1 Å	Near-neighbor interactions
	$R_{\mathrm{HH}}^{(2)}$	1.7 Å	Near-neighbor interactions
Hydrocarbons	$R_{\mathrm{CH}}^{(e)}$	1.1199 Å	Gas-phase diatomic
	$D_{\mathrm{CH}}^{(e)}$	3.6422 eV	Gas-phase diatomic
	β_{CH}	1.9583 Å^{-1}	Gas-phase diatomic
	S_{CH}	1.690 77	$(S_{\mathrm{HH}}S_{\mathrm{CC}})^{1/2}$
	$R_{\mathrm{CH}}^{(1)}$	1.3 Å	Reaction (19)
	$R_{\mathrm{CH}}^{(2)}$	1.8 Å	Reaction (19)
	$\alpha_{\mathrm{HHC}},\alpha_{\mathrm{CHH}},\alpha_{\mathrm{HCH}},\alpha_{\mathrm{HCC}}$	4.0 Å^{-1}	H_3 value

TABLE III. (*Continued*).

Parameter	Value	Fit to
$H_{CC}(1,1)$	−0.0226	CC bond energy in benzene
$H_{CC}(2,0)$	−0.0061	CC double bond in ethylene
$H_{CC}(3,0)$	0.0173	CC single bond in ethane
$H_{CC}(1,2)$	0.0149	CC single bond in isobutane
$H_{CC}(2,1)$	0.0160	CC single bond in cyclohexane
$H_{CH}(1,0)$	−0.0984	Atomization energy of CH_2
$H_{CH}(2,0)$	−0.2878	Atomization energy of CH_3
$H_{CH}(3,0)$	−0.4507	Atomization energy of methane
$H_{CH}(0,1)$	−0.2479	CH bond energy in acetylene
$H_{CH}(0,2)$	−0.3221	CH bond energy in benzene
$H_{CH}(1,1)$	−0.3344	CH bond energy in ethylene
$H_{CH}(2,1)$	−0.4438	CH bond energy in ethane
$H_{CH}(0,3)$	−0.4460	Tertiary-HC bond energy in isobutane
$H_{CH}(1,2)$	−0.4449	CH bond energy in cyclohexane
$\frac{\partial H_{CH}(1,1)}{\partial C}$	−0.173 25	Centered difference
$\frac{\partial H_{CH}(2,0)}{\partial C}$	−0.099 05	Centered difference
$\frac{\partial H_{CH}(0,2)}{\partial H}$	−0.176 15	Centered difference
$\frac{\partial H_{CH}(1,1)}{\partial H}$	−0.097 95	Centered difference
$F(1,1,1)$	0.1264	CC triple bond in acetylene
$F(2,2,1)$	0.0605	Average energy of bonds in $(CH_3)_2C{=}C(CH_3)$ and $(CH_3)HC{=}CH(CH_3)$ equal double bond
$F(1,2,1)$	0.0120	Atomization energy of $HC{=}CH_2$
$F(1,3,1)$,$F(1,3,2)$	−0.0903	Single bond in H_3C—CH
$F(0,3,1)$,$F(0,3,2)$	−0.0904	Single bond in H_3C—C
$F(0,2,2)$	−0.0269	Conjugated double bond in $C{=}CH(CH_2)$
$F(0,2,1)$	0.0427	Double bond in $C{=}CH_2$
$F(0,1,1)$	0.0996	Atomization energy of C_2H
$F(1,1,2)$	0.0108	Atomization energy of CH_2CCH
$\frac{\partial F(3,1,1)}{\partial i}$	−0.0950	Centered difference
$\frac{\partial F(3,2,1)}{\partial i}$	−0.108 35	Centered difference
$\frac{\partial F(3,1,2)}{\partial i}$	−0.0452	Centered difference
$\frac{\partial F(2,3,2)}{\partial i}$	0.013 45	Centered difference
$\frac{\partial F(2,4,2)}{\partial i}$	−0.027 05	Centered difference
$\frac{\partial F(3,4,2)}{\partial i}$	0.045 15	Centered difference
$\frac{\partial F(3,4,1)}{\partial i}$	0.045 15	Centered difference
$\frac{\partial F(3,2,2)}{\partial i}$	−0.087 60	Centered difference

ber of bonds times the bond strength), leads to, for example, a tetrahedral structure for methane and linear structure for acetylene. Because lone electron pairs are not explicitly treated in this empirical potential, however, some structures are linear that experimentally are bent, such as methylene.[51] Second, although the procedure for defining N_{ij}^{conj} incorporates conjugation in an approximate way, it will not give the subtle differences in bond orders for conjugated ring systems predicted by even simple molecular-orbital methods. This procedure, however, is able to include to a first approximation nonlocal effects without the need for diagonalizing a matrix or going beyond nearest-neighbor interactions, hence drastically reducing computational requirements for large systems. Third, the carbon-carbon single bond energies derived for hydrocarbons are smaller than those in diamond. This difference also occurs in more-elaborate least-squares-fitting procedures for determining carbon-carbon bond energies, and can be attributed to both the weakening of the bonds due to hydrogen and steric repulsions.[52] Fourth, barriers for rotation about carbon-carbon bonds (especially double bonds) and nonbonded interactions such as van der Waals forces have not been included. With the potential written as a sum over pairs, the former effects can be modeled, and methods for incorporating both types of interactions within this formalism are being developed. Finally, the price one pays for using a simple classical expression is that properties such as resonance effects[53] (i.e., $4n+2$ Hückel stability) and Woodward-Hoffman rules[53] may not necessarily be obeyed. Care should therefore be used when interpreting reaction mechanisms suggested by empirical potentials, and where possible they should be reexamined using other less-empirical techniques.

III. PREDICTED ENERGETICS AND BONDING

To test the transferability of the potential given in the preceding section, the energy and structure of a variety of small hydrocarbon molecules and the diamond $\{111\}$ and $\{001\}$ surfaces have been examined. Shown in Table IV are atomization energies given by the empirical potential and corresponding experimental values. The experimental values were derived from heats of formation without correcting for zero-point energy or other finite temperature effects. The overall agreement is good, with energies being reproduced to within 1% or better for 81% of the molecules tested. While this level of agreement may be somewhat fortuitous given the approximations made in estimating the experimental values, it does demonstrate that the potential can describe chemical bonding for a wide range of hydrocarbon molecules. The worst fits are for the molecules $CH_3CH=C=CH_2$ and $H_2C=C=CH_2$ for both potentials, and for cyclopropene using potential II. For the former two molecules the potential function treats the two double bonds as part of a conjugated system, and so the bond energies are reduced. This is an example of where our analytic approximation for defining conjugation breaks down.

In Table V the energetics predicted by the potential for the relaxed bulk-terminated, Pandey π-bonded chain,[54] and Chadi π-bonded molecule[55] reconstructions on the diamond $\{111\}$ surface are given along with values calculated by Vanderbilt and Louie using local-density-functional (LDF) methods.[56] The values given by the empirical potentials were calculated using a slab ten layers thick with 16 atoms per layer and periodic boundary conditions perpendicular to the surface. The bottom two layers were held rigid and the top eight layers were allowed to completely relax under the influence of each of the potentials to the minimum-energy configurations starting from the positions reported by Chadi for the various reconstructions.[55] The potentials predict that the (undimerized) π-bonded chain reconstruction is energetically preferred, in agreement with the LDF result[56] and with a number of experimental studies.[57,58] If radical energetics is not correctly described, the Tersoff-type potentials given in Refs. 28 and 29 incorrectly predict the relaxed bulk-terminated surface to be the most stable.[59]

Experimental studies have shown that upon exposure to atomic hydrogen the π-bonded chain reconstruction converts to a hydrogen-terminated surface with the carbon atoms reverting to positions that are characteristic of the bulk.[57,58,60] To test the potentials, a monolayer of hydrogen atoms was placed above the surface carbon atoms on the relaxed bulk-terminated surface and the π-bonded chain reconstruction and the systems were relaxed. Potential I predicts energies of -1.00 eV/(surface atom) and -0.61 eV/(surface atom) for the hydrogen-covered bulk-terminated surface and hydrogen-covered π-bonded chain reconstruction, respectively, relative to the clean π-bonded chain reconstruction plus gas-phase H_2 molecules. Potential II yields corresponding energies of -1.13 eV/(surface atom) for adsorption on the bulk-terminated surface and -0.63 eV/(surface atom) for adsorption on the π-bonded chain reconstruction. Hence the potentials correctly predict that hydrogen adsorption is energetically stable, and that adsorption on a bulk-terminated surface is favored over the reconstructed surface. Side views of the equilibrium structures for the two hydrogen-terminated surfaces are shown in Fig. 1.

The structure and energetics of the dimer reconstructed $\{001\}$ surface of diamond are also of interest, and detailed experimental studies have just recently been completed.[61] Potential I predicts a stabilization energy of -5.49 eV/dimer relative to the bulk-terminated surface, and a surface dimer bond length of 1.38 Å. Potential II predicts a slightly less stable reconstruction with an energy of -5.20 eV/dimer relative to the bulk-terminated surface, and a surface dimer bond length of 1.43 Å. These values were obtained using a slab eight layers thick with 32 atoms per layer. Periodic boundaries were used for the two directions perpendicular to the surface, the bottom two layers were held rigid, and the remainder of the system was relaxed to the minimum-energy structure starting from a surface reconstruction consisting of a 2×1 arrangement of surface dimers. The dimer length is stretched from the double bond distance in ethylene for both potentials, and the bond energy is correspondingly weakened. This is due to the strain induced by the lattice. The monohydride phase, where a hydrogen atom is bonded to each atom in a dimer pair, was also examined

TABLE IV. Atomization energies for various hydrocarbon molecules. Experimental values were derived from heats of formation using energies of 7.3768 eV for carbon and 2.375 eV for hydrogen.

	Molecule	Potential I (eV)	Potential II (eV)	Experimental value (eV)
Alkanes	methane	17.6	17.6	17.6[a]
	ethane	29.7	29.7	29.7[a]
	propane	42.0	42.0	42.0[a]
	n-butane	54.3	54.3	54.3[a]
	i-butane	54.3	54.3	54.4[a]
	n-pentane	66.5	66.5	66.6[a]
	isopentane	66.5	66.5	66.6[a]
	neopentane	66.8	66.8	66.7[a]
	cyclopropane	35.5	35.0	35.8[a]
	cyclobutane	48.7	48.5	48.2[a]
	cyclopentane	61.4	61.3	61.4[a]
	cyclohexane	73.6	73.6	73.6[a]
Alkenes	ethylene	23.6	23.6	23.6[a]
	propene	36.2	36.2	36.0[a]
	1-butene	48.5	48.5	48.5[b]
	cis-butene	48.8	48.9	48.6[b]
	isobutene	48.4	48.4	48.7[b]
	$(CH_3)_2C=C(CH_3)_2$	73.2	73.3	73.4[b]
	cyclopropene	28.2	27.3	28.8[b]
	cyclobutene	42.4	42.0	42.4[b]
	cyclopentene	55.7	55.7	55.6[b]
	1,4-pentadiene	55.0	55.0	54.8[b]
	$CH_2=CHCH=CH_2$	41.8	41.9	42.6[b]
	$CH_3CH=C=CH_2$	40.4	40.5	42.1[b]
	$H_2C=C=CH_2$	27.8	27.9	29.6[b]
Alkynes	acetylene	17.1	17.1	17.1[a]
	propyne	29.4	29.4	29.7[b]
	1-butyne	41.7	41.7	42.0[b]
	2-butyne	41.7	41.7	42.2[b]
Aromatics	benzene	57.5	57.5	57.5[a]
	toulene	69.6	69.6	70.1[b]
	1,4-dimethylbenzene	81.8	81.8	82.6[b]
	ethylbenzene	81.9	81.9	82.5[b]
	ethenylbenzene	76.2	76.2	76.5[b]
	ethynylbenzene	69.8	69.8	69.9[b]
	naphthalene	91.4	91.4	91.2[b]
Radicals	CH_2	7.8	7.8	7.8[c]
	CH_3	12.7	12.7	12.7[d]
	$H_3C_2H_2$	25.7	25.7	25.5[b]
	H_2C_2H	18.9	18.9	18.9[e]
	C_2H	12.2	12.2	12.2[f]
	CH_2CCH	24.5	24.5	25.8[b]
	n-C_3H_7	37.9	38.0	37.8[e]
	i-C_3H_7	38.3	38.3	38.0[e]
	t-C_4H_9	50.5	50.5	50.5[e]
	phenyl	52.7	52.7	52.7[e]

[a] From heat of formation at 0 K (from Ref. 41).

[b] From heat of formation at 300 K [from H. M. Rosenstock, K. Draxl, B. W. Steiner, and J. J. Heron, J. Chem. Ref. Data **6**, Suppl. 1, I-774 (1977)].

[c] Calculated from Ref. 46.

[d] Calculated from Ref. 45.

[e] From heat of formation at 300 K (from Ref. 52).

[f] From heat of formation at 0 K [from H. M. Rosenstock, K. Draxl, B. W. Steiner, and J. J. Heron, J. Chem. Ref. Data **6**, Suppl. 1, I-774 (1977)].

TABLE V. Energetics (in eV/surface atom) for various structures of the {111} surface of diamond.

	Ideal 1×1	Relaxed 1×1	π-bonded chain	π-bonded molecule
Potential I	0.0	−0.24	−1.10	−0.32
Potential II	0.0	−0.23	−1.03	−0.25
LDF[a]	0.0	−0.37	−0.68	0.28

[a] From Ref. 56.

using the potentials. The predicted carbon-carbon surface dimer bond length is 1.63 Å for potential I and 1.60 Å for potential II, both of which are stretched from the gas-phase single bond lengths. Potentials I and II predict changes in energy for hydrogen adsorption of −2.72 eV/dimer and −2.96 eV/dimer, respectively, relative to the clean dimer reconstructed surface and gas-phase H_2. Hydrogen adsorption is therefore predicted to be energetically stable, in agreement with experiment.[61]

The abstraction of hydrogen from hydrogen-terminated diamond surfaces has been proposed as being a rate-determining step in the CVD of diamond films,[1-3] so the potential-energy surface for the hydrogen abstraction reaction

$$CH_4+H\rightarrow H_3C-H-H\rightarrow CH_3+H_2 \qquad (20)$$

was examined using the empirical potentials. This reaction was chosen because the potential-energy surface has been well characterized in the gas phase. Following Walsh,[62] the reaction was examined for a linear configuration along the reaction coordinate assuming C_{3v} symmetry, with the energy at each point minimized with respect to the other carbon-hydrogen bond distances and angles. The barrier for reaction (20) is 0.52 eV using potential I, which agrees with the experimental energy threshold of 0.52 eV,[63] and which can be compared to the value of 0.58 eV for the barrier estimated by Walch using *ab initio* total-energy techniques.[62] The barrier along the linear reaction coordinate for potential I is at a carbon-hydrogen bond distance of 1.30 Å and a hydrogen-hydrogen bond distance of 1.02 Å. The values calculated by Walch are 1.47 Å for the carbon-hydrogen distance and 0.93 Å for the hydrogen-hydrogen distance. Potential II yields a barrier of 0.72 eV at a carbon-hydrogen bond distance of 1.19 Å and a hydrogen-hydrogen bond length of 1.14 Å. This barrier is somewhat higher than the experimental value, and so potential I should yield a better description of hydrogen abstraction.

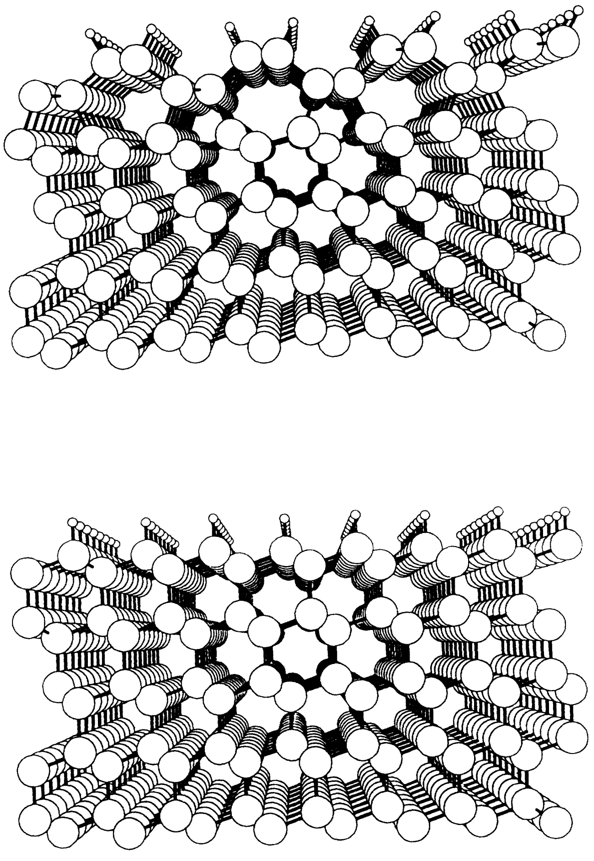

FIG. 1. Side views of hydrogen-terminated diamond {111} surfaces. The top picture is the π-bonded chain reconstruction and the bottom picture is the bulk-terminated surface.

IV. ENERGETICS FOR STRUCTURES RELATED TO DIAMOND CVD

To begin to quantify energetics for surface structures associated with the CVD of diamond films, we have calculated the energetics for hydrogen abstraction from the diamond {111} and {001} surfaces, and the energetics for the chemisorption of methane, acetylene, and their respective radicals at terrace sites on the {111} surface of diamond. More systematic studies of structures and dynamics of hydrocarbons reacting with diamond surfaces and their relevance to the CVD of diamond films are planned to be presented at a later time.

Removing a hydrogen atom from a hydrogen-terminated {111} surface was found to be endoergic by 4.13 eV for potential I and 4.15 eV for potential II. These numbers are close to the estimate obtained by subtracting the relaxation energy given in Table V for the relaxed bulk-terminated surfaces from the carbon-hydrogen bond strength of 4.36 eV. Combining these values with the gas-phase bond strength of 4.75 eV for H_2 yields a net exoergicity of ≈0.6 eV for abstraction of hydrogen from the {111} surface by a gas-phase hydrogen atom. Because of the bonding topology of this surface, the energy

TABLE VI. Predicted energetics and intramolecular carbon-carbon bond lengths for various single molecules chemisorbed on terrace sites on a hydrogen-terminated diamond {111} surface.

	Potential I		Potential II	
Molecule	Potential energy (eV)	Bond length (Å)	Potential energy (eV)	Bond length (Å)
Hydrogen atom	−4.1[a]		−4.2[a]	
Methyl radical	−3.7[a]		−4.0[a]	
Acetyl radical	−3.9[a]	1.20	−4.1[a]	1.29
Hydrogen molecule	−3.6[b]		−3.6[b]	
Acetylene	−5.0[b]	1.33	−4.9[b]	1.39
Ethylene	−4.3[b]	1.59	−4.3[b]	1.57

[a] Relative to a hydrogen-terminated surface with one radical site and the gas-phase molecule.

[b] Relative to a hydrogen-terminated surface with two adjacent radical sites and the gas-phase molecule.

required to remove a second adjacent hydrogen atom is essentially the same as that required to remove the first, so radical sites on this surface should be randomly distributed. Removing a hydrogen atom from the monohydride phase of the dimer reconstructed diamond {001} surface was found to be endoergic by 4.44 and 4.49 eV using potentials I and II, respectively, so abstraction by a gas-phase hydrogen atom is exoergic by ≈0.3 eV. Removing a second hydrogen atom from the other carbon in the surface dimer pair, however, is endoergetic by only 2.9 eV with potential I and 3.1 eV with potential II. This decrease in endoergicity is consistent with the formation of a partial double bond between the two surface carbon atoms. Hence the dimer reconstructed {001} surface with radical sites should be composed primarily of a mixture of hydrogen-terminated carbon-carbon dimers with single bonds and nonhydrogen-terminated double-bonded carbon-carbon dimers.

To quantity the energetics of adsorption on terrace sites on the {111} surface, chemisorption energies for both single molecules and monolayer coverages of acetylene and ethylene molecules and ethynyl and methyl radicals have been calculated using the empirical potentials. For the chemisorption of single radicals, a hydrogen atom on a hydrogen-terminated {111} surface was replaced with the molecule (with the carbon-carbon bond in the ethynyl radical perpendicular to the surface), and the systems were relaxed to the minimum-energy structures. For acetylene and ethylene, two hydrogen atoms bonded to adjacent surface carbon atoms were removed and the molecules were placed with the carbon atoms in each of the molecules approximately over the open sites (i.e., with the intramolecular carbon-carbon bonds parallel to the surface). The resulting energies and intramolecular carbon-carbon bond lengths for each of the molecules are given in Table VI. Energetics for hydrogen adsorption is given for comparison. The radicals C_2H and CH_3 both form carbon-carbon single bonds without large changes in bonding character within the molecules, which leads to the similar binding energies. For the adsorption of acetylene and ethylene each molecule forms two single bonds with the surface and the order of the carbon-carbon bond in the molecules is reduced by 1. The carbon-carbon bond in the chemisorbed acetylene is predicted to be equal to the gas-phase double bond length. Hence in contrast to the dimer reconstruction on the {001} surface the constraint of the lattice does not inhibit the formation of a double bond. The difference in energy between the chemisorption of acetylene and ethylene is consistent with their heats of hydrogenation. Hydrogenation of acetylene to ethylene is exoergic by 1.72 eV relative to H_2 plus acetylene, while the hydrogenation of ethylene to ethane is exoergic by 1.35 eV.

Given in Table VII are energies for the chemisorption of a monolayer of each of the molecules discussed above on the {111} surface. In each case the initial

TABLE VII. Predicted energetics and intramolecular carbon-carbon bond lengths for a monolayer of various molecules chemisorbed on the diamond {111} surface. The energies are relative to a relaxed clean surface and the gas-phase molecules.

	Potential I		Potential II	
Molecule	Potential energy	Bond length (Å)	Potential energy	Bond length (Å)
Hydrogen atom	−4.2 eV/atom[a]		−4.3 eV/atom[a]	
Methyl radical	−3.2 eV/molecule[a]		−3.0 eV/molecule[a]	
Acetyl radical	−4.2 eV/molecule[a]	1.20	−4.3 eV/molecule[a]	1.29
Hydrogen molecule	−3.7 eV/molecule[b]		−3.9 eV/molecule[b]	
Acetylene	−5.2 eV/molecule[b]	1.33	−5.2 eV/molecule[b]	1.39
Ethylene	−4.0 ev/molecule[b]	1.58	−3.9 eV/molecule[b]	1.57

[a] One surface atom per chemisorbed molecule.

[b] Two surface atoms per chemisorbed molecule.

configurations were generated by removing the hydrogen atoms terminating the surface bonds and translating the chemisorbed single molecules across the surface. Each configuration was then relaxed to the minimum-energy structure. The energies for adsorbed hydrogen, ethynyl radicals, and acetylene molecules decrease (i.e., become more strongly bound) from single molecules to monolayers, while because of the interactions between nonbonded hydrogen atoms the energies for methyl radicals and ethylene molecules both increase.

While a specific mode of CVD growth cannot be unambiguously deduced from these energies, they do suggest some possible trends. First, abstraction of a single hydrogen atom from a $\{111\}$ surface should be favored over abstraction from a dimer reconstructed $\{001\}$ surface. Abstraction of a second hydrogen atom, however, should be strongly favored on the reconstructed $\{001\}$ surface since the bonding topology of the surface reconstruction allows formation of double bonds on the surface. Second, displacement of a hydrogen atom from a hydrogen-terminated diamond $\{111\}$ surface by either ethynyl or methyl radicals is not strongly energetically favored. Ethylene and especially acetylene, however, can energetically displace hydrogen from terrace sites provided that a gas-phase hydrogen molecule is formed (rather than two H atoms). A reaction sequence that might lead to this, however, is unclear, although a sequence similar to that proposed by Frenklach and Spear may be possible.[1] Finally, the potential suggests that adsorption of a monolayer of methyl radicals on the $\{111\}$ surface is not an energetically favorable configuration compared to hydrogen adsorption. The predicted energies given here for a monolayer of methyl are uncertain at best since nonbonded steric interactions between hydrogen atoms have not been included in the potential. A better estimate could probably be made using other potentials such as Allinger's molecular mechanics.[32]

V. SUMMARY

As a first step toward using molecular-dynamics simulation techniques to study the CVD of diamond films, we have developed an empirical potential-energy function that can model intramolecular chemical bonding in a wide range of hydrocarbon molecules as well as diamond and graphite lattices. The analytic function is a highly parametrized version of Tersoff's empirical-bond-order formalism which includes terms that correct for an inherent overbinding of radicals. Nonlocal effects have been incorporated via an analytic function that defines conjugation based on the coordination of carbon atoms that neighbor carbon-carbon bonds. Because only nearest-neighbor interactions are incorporated, the function is very quickly evaluated and can therefore be used in large-scale molecular-dynamics simulations. Future refinements to the potential include incorporating barriers for rotation around carbon-carbon bonds and nonbonded interactions such as van der Waals forces.

Atomization energies predicted by the function compare well to experimentally derived energies for a wide range of hydrocarbon molecules. The function predicts the π-bonded chain reconstruction to be the energetically favored structure on a clean diamond $\{111\}$ surface in agreement with local-density-functional calculations, and correctly predicts hydrogen adsorption on a bulk-terminated surface to be favored over the π-bonded chain reconstruction. The structure and energetics of the dimer reconstructed diamond $\{001\}$ surface and its monohydride phase were also examined using the empirical potential.

Energetics for a limited number of static surface structures that are relevant to the CVD of diamond films were also calculated using the empirical potential. These structures included the energies required to abstract hydrogen atoms from diamond $\{111\}$ and dimer reconstructed $\{001\}$ surfaces, and energies for methyl and ethynyl radicals and acetylene and ethylene molecules adsorbed on terrace sites on the $\{111\}$ surface of diamond. More detailed and systematic studies of bonding energies and reactive dynamics using this potential will be presented in the future.

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