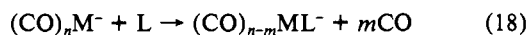


been reported recently. Observation of reaction 18 implies



$D[(\text{CO})_{n-m}\text{M}^- - \text{L}] \geq D[(\text{CO})_{n-m}\text{M}^- - m\text{CO}]$ . Thermochemical results that can be derived from such reactions include  $D[(\text{C}-\text{O})_3\text{Fe}^- - \text{L}] \geq 41.7 \pm 2.5$  kcal/mol for  $\text{L} = \text{SO}_2$  and  $(\text{CF}_3)_2\text{CO}$ ;  $D[(\text{CO})_2\text{Fe}^- - \text{C}_2\text{H}_2] \geq 42.4 \pm 3.5$  kcal/mol;<sup>63</sup>  $D[(\text{CO})_2\text{Fe}^- - \text{L}] \geq 84.1 \pm 4.3$  kcal/mol for  $\text{L} = 1,3$ - and  $1,4$ -dinitrobenzene,  $1,4$ -benzoquinone, and tetracyanoethylene;  $D[(\text{CO})\text{Fe}^- - \text{CS}_2] \geq 78.2 \pm 4.9$  kcal/mol;<sup>68</sup>  $D[\text{Fe}^- - \text{CS}_2] \geq 111.8 \pm 8.0$  kcal/mol;<sup>68</sup>  $D[(\text{CO})_2\text{Ni}^- - \text{L}] \geq 38.5 \pm 2.3$  kcal/mol for  $\text{L} =$  nitrobenzene;  $D[(\text{CO})\text{Ni}^- - \text{L}] \geq 81.9 \pm 5.8$  kcal/mol for  $\text{L} = 1,4$ -benzoquinone and tetracyanoethylene; and  $D[\text{Ni}^- - \text{L}] \geq 114.3 \pm 1.3$  kcal/mol for  $1,2$ - and  $1,4$ -bromonitrobenzene.<sup>66</sup> Further thermochemical implications for various aromatic compounds can be made from the data in ref 66.

Another method for deriving thermochemistry is to combine the measured enthalpy of disruption<sup>7</sup> of organometallic species containing metal carbonyl fragments, eq 19, with the metal-

$$\Delta H_{\text{disr}}[\text{M}(\text{CO})_n\text{L}_m] = \Delta H_f(\text{M}) + n\Delta H_f(\text{CO}) + m\Delta H_f(\text{L}) - \Delta H_f[\text{M}(\text{CO})_n\text{L}_m] \quad (19)$$

carbonyl bond strengths to derive bond strengths for the other ligands. The results derived using this procedure include  $D[(\text{CO})_4\text{Fe} - \text{C}_2\text{H}_4] = 36.5 \pm 3.6$  kcal/mol,<sup>69</sup>  $D[(\text{CO})_3\text{Fe} - \text{C}_4\text{H}_6] = 56.0 \pm 8$  kcal/mol,<sup>69</sup>  $D[(\text{CO})\text{Fe} - 2(\text{C}_4\text{H}_6)] = 103.4 \pm 5$  kcal/mol,<sup>69</sup>  $D[(\text{CO})\text{Fe} - 2(\text{C}_6\text{H}_8)] = 109.6 \pm 5$  kcal/mol,<sup>69</sup> and  $D[(\text{CO})_3\text{Fe} - \text{C}_8\text{H}_8] = 50.9 \pm 8.4$  kcal/mol<sup>70</sup> ( $\text{C}_4\text{H}_6 = 1,3$ -butadiene,  $\text{C}_6\text{H}_8 =$  cyclohexa-1,3-diene, and  $\text{C}_8\text{H}_8 = 1,3,5,7$ -cyclooctatetraene). Similar analyses have been carried out previously using mean metal-carbonyl bond strengths instead of the individual values.<sup>7,69,70</sup> These calculations give consistently lower metal-ligand bond strengths. The present values indicate that bonds from iron to one, two, or four alkene groups are slightly weaker than bonds to the corresponding number of carbonyl ligands. No analogous enthalpies of disruption are available for compounds containing nickel carbonyl fragments, but studies of substitution equilibria<sup>71</sup> indicate that nickel-olefin bond strengths

are in the 25-42 kcal/mol range, similar to the values encountered in the iron-containing systems.

The individual metal-carbonyl bond strengths can be used with heats of formation given in Table IV to derive values for the heats of formation of the metal carbonyl fragments. The heats of formation of  $\text{Fe}(\text{CO})_n^-$  ( $n = 1-3$ ) are calculated iteratively starting with the heat of formation of Fe.  $\Delta H_f(\text{Fe}(\text{CO})_4)$  is derived from the heat of formation of  $\text{Fe}(\text{CO})_5$  and  $D[(\text{CO})_4\text{Fe} - \text{CO}]$ . The results are given in Table V and may be useful for deriving additional metal-ligand bond energies when further calorimetrically determined heats of formation for  $\text{Fe}(\text{CO})_n^-$  and  $\text{Ni}(\text{CO})_n^-$ -containing species become available.

### Conclusions

Energy-resolved collision-induced dissociation has been used to determine the metal-carbonyl bond energies in  $\text{Fe}(\text{CO})_n^-$  ( $n = 1-4$ ) and  $\text{Ni}(\text{CO})_n^-$  ( $n = 2, 3$ ). These can be combined with literature thermochemistry to give  $D[\text{Ni}^- - \text{CO}]$ , ionization potentials and heats of formation for the neutral iron and nickel carbonyls and, perhaps most significantly, metal-carbonyl bond strengths in the neutral fragments. These results are compared to previous experimental and theoretical estimates. The results suggest that the thermochemistry determined from loss of one or two CO ligands is essentially unaffected by electron detachment, competitive shifts, or reaction barriers in excess of the dissociation endothermicities. The present results can be used to derive thermodynamic data for other organometallic species which contain metal carbonyl fragments, in particular species where one to four carbonyl ligands are replaced with alkene ligands.

The sequential M-CO bond strengths in the iron and nickel carbonyls deviate from the mean value by an average of up to 10 kcal/mol, emphasizing the importance of measuring sequential rather than average bond strengths. The deviation from the mean is particularly large for  $D[\text{Fe}^- - \text{CO}]$ , which is exceptionally low ( $8.1 \pm 3.5$  kcal/mol), in agreement with recent theoretical predictions. Further work in this laboratory will provide bond strength determinations for other metal carbonyls that should make any correlations between metal-carbonyl bond strengths and electron count, charge state, or number of ligands more apparent.

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## Structure and Energetics of Clean and Hydrogenated Diamond (100) Surfaces by Molecular Mechanics

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**Abstract:** The molecular mechanics (MM3) method has been applied to the clean and hydrogenated surfaces of diamond (100). Periodic boundary conditions are incorporated into the computational algorithm, permitting calculations comparable in size to modest-sized clusters but without complications from edge effects. The atomic structure and energetics of the clean (100)-(2×1), monohydride (100)-(2×1):H, full dihydride (100)-(1×1):2H, and intermediate dihydride (100)-(3×1):1.33H surfaces have been determined. Pairs of surface carbon atoms form symmetric dimers on the reconstructed diamond (100)-(2×1), (2×1):H, and (3×1):1.33H surfaces, with dimer bond lengths of 1.46, 1.63, and 1.59 Å, respectively, corresponding to strained double or single bonds. The full (1×1):2H dihydride, with two hydrogen atoms per surface carbon atom, is highly strained due to H-H repulsions, causing a reduction of the H-C-H bond angle and twisting about the surface normal, and is predicted to be thermodynamically unstable with respect to dehydrogenation to the monohydride. Some important gas-surface reactions involving hydrogen and the diamond (100) surface are discussed in light of the derived energetics.

Phenomenal progress has been made over the past few years in the low-pressure growth of diamond films by chemical vapor

deposition (CVD).<sup>1</sup> Hydrogen atoms are known to enhance the growth of diamond while suppressing graphite growth in the CVD

process<sup>2</sup> and are widely believed to play a critical role in stabilizing the diamond surface and in creating vacant sites by abstraction.<sup>3</sup> Significant progress has been made in understanding the gas-phase chemistry in diamond CVD,<sup>4</sup> but unfortunately, little is known about the surface chemistry of diamond. Of the two predominant crystal faces in polycrystalline diamond films, the properties of clean and hydrogenated diamond (111) are better understood than those of the (100) face.<sup>5</sup> Hydrogenated diamond (111) has an "ideal" structure, with the surface carbon atoms very near their bulk-terminated positions<sup>6</sup> and C-H bonds oriented along the surface normal.<sup>7</sup> When hydrogenated diamond (111) is heated above ~1200 K, hydrogen desorbs and the surface forms a (2×1) reconstruction,<sup>5,7,8</sup> with current evidence favoring a  $\pi$ -bonding chain model.<sup>9</sup> Nominally clean diamond (100) has been observed to have a (2×1) unit cell by low-energy electron diffraction.<sup>8b</sup> By analogy to the well-studied Si(100)<sup>10</sup> and Ge(100)<sup>11</sup> surfaces, the (2×1) unit cell suggests the formation of dimer bonds between pairs of surface carbon atoms. Hydrogen atoms are known to chemisorb on diamond (100),<sup>2,8b,12,13</sup> with either a (2×1) or nominally (1×1) unit cell. In the only detailed experimental study of hydrogen chemisorption on diamond (100) to date, Hamza, Kubiak, and Stulen<sup>13</sup> assigned the hydrogen-chemisorbed (2×1) surface to a monohydride and the (1×1) structure to a dihydride (one or two hydrogen atoms per surface carbon atom, respectively). The corresponding monohydride and dihydride species on Si(100) have a substantial literature, and it appears that a full dihydride can only be formed under conditions where SiH<sub>3</sub>(a) is also formed and some etching takes place, and that steric repulsion between the hydrogen atoms is important.<sup>14</sup> The existence of a stable dihydride on diamond (100) seems questionable, since the lattice constant of diamond is 34% smaller than that of silicon and hydrogen-hydrogen repulsion will be even more important. The

only experimental information about the relative energetics of the surfaces is the observation by Hamza et al. that hydrogen desorbs over the temperature range 700–1200 K with a kinetic order varying between 1 and 1.6 as the coverage increases and an activation energy in the range of 24–36 kcal/mol.<sup>13</sup> In contrast to the behavior of the (111) face, Hamza et al. concluded that the monohydride was stable up to a temperature of 1400 K,<sup>13</sup> which is also surprising in view of the fact that the hydrogen desorption temperature on Si(100) is nearly identical to that on Si(111).<sup>15</sup>

In this paper we focus on diamond (100), for which the picture seems more confusing, and which also provides a more challenging test for theory because of steric hindrance. Only a handful of theoretical papers have dealt with the structure and energetics of clean and hydrogen-covered diamond (100), and none have been at the level of the computationally demanding self-consistent pseudopotential/local density functional calculations which have been performed for Si(100)<sup>16</sup> and Ge(100)<sup>17</sup> surfaces. Several researchers have utilized semiempirical methods. Verwoerd<sup>18</sup> used the MNDO method on hydrogenated carbon clusters, and Bechstedt and Reichardt<sup>19</sup> investigated the clean (100) surfaces of group IV elements by a tight-binding method. Very recently, Mehndru and Anderson<sup>20</sup> applied their molecular orbital band and cluster methods (ASED-band and ASED-MO) to study the clean and hydrogenated diamond (100) surfaces as well as the adsorption of several simple hydrocarbons. Other researchers have turned to an empirical mechanical approach to investigate the diamond surfaces, because calculations based on these empirical methods are very efficient computationally and can easily deal with large systems such as solid surfaces. Appelbaum and Hamann<sup>21</sup> employed a Keating-type force field and calculated the atomic structure of clean diamond (100)-(2×1) surface down to the fifth layer. Brenner,<sup>22</sup> using a Tersoff-type force field, has studied clean, monohydride diamond surfaces as well as several important gas-surface reactions. Substantial discrepancies in both the dimer bond length ( $\pm 0.1$  Å) and the energetics were obtained in these studies, and a satisfactory description of hydrogen chemisorption on diamond (100), even at the qualitative level, is not yet possible.

In the present work, we extend the so-called molecular mechanics force field, developed by Allinger and co-workers<sup>23</sup> over the past two decades, to the study of diamond surface chemistry. The current version of the force field, MM3,<sup>24,25</sup> with parameters for saturated, unsaturated, and conjugated hydrocarbons, is claimed to be accurate to within approximately  $\pm 0.01$  Å in bond length,  $\pm 1^\circ$  in bond angle between atoms other than hydrogen, and  $\pm 4^\circ$  in torsional angles. Calculated heats of formation for a wide variety of compounds are consistently within "chemical accuracy",  $\sim \pm 1$  kcal/mol. The force field is successful in modeling not only small, simple molecules, but also large molecules and some highly strained molecules such as cubane, *exo,exo*-tetracyclo[6.2.1.1<sup>3,6</sup>.0<sup>2,7</sup>]dodecane, and its anhydride derivative.<sup>24a</sup>

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MM3 predicts a C–C bond length of 1.5431 Å in diamond, in excellent agreement with the experimental value of 1.5445 Å.<sup>24a</sup> Existing evidence suggests that the unsaturated dangling bonds on the clean diamond (100) surface form a  $\pi$ -bond-like dimer bond, and that chemisorbed hydrogen atoms form  $\sigma$ -bonds with the surface carbon atoms. Therefore, the bonding on both clean and hydrogenated diamond surfaces (a "large molecule limit") is qualitatively the same as that in discrete organic molecules, and the force field should be directly transferable. MM3 should be applicable to the description of saturated, unsaturated, and conjugated hydrocarbon species on any crystal face of diamond as long as the bond lengths, bond angles, and distances between nonbonded atoms are within the range of values in structures for which MM3 has demonstrated accuracy. MM3 parameters for radicals are tentative,<sup>25</sup> making calculations with open-shell species more uncertain, and MM3 cannot describe surface species with bonding configurations that have not been parameterized in molecules.

In the following, we first present the methodology adopted in our calculations. Results for the atomic structures and relative enthalpies of formation of diamond (100)-(2 $\times$ 1), diamond (100)-(2 $\times$ 1):H, diamond(100)-(1 $\times$ 1):2H, and diamond(100)-(3 $\times$ 1):1.33H surfaces are presented, and finally we discuss some gas-surface reactions important in diamond CVD.

### Theoretical Method

Briefly, the MM3 force field for hydrocarbon molecules is summarized by eq 1, where  $E$  is defined as the steric energy,  $E_s$  is the bond stretching energy,  $E_\theta$  is the angle bending energy,  $E_\omega$  is the torsional energy,  $E_{s\theta}$  is the stretch-bend energy,  $E_{\omega s}$  is the torsion-stretch energy,  $E_{\theta\theta'}$  is the

$$E = \sum E_s + \sum E_\theta + \sum E_\omega + \sum E_{s\theta} + \sum E_{\omega s} + \sum E_{\theta\theta'} + \sum E_{vdw} + \sum E_{dpl} \quad (1)$$

bend-bend coupling energy,  $E_{vdw}$  is the van der Waals interaction energy between two atoms which are bonded neither to each other nor to a common atom, and  $E_{dpl}$  is the dipole-dipole interaction energy between two bonds which do not share an atom. In the MM3 description of saturated hydrocarbons,  $E_{dpl}$  is taken to be zero, but for alkenes bond dipoles are assigned to C(sp<sup>2</sup>)-C(sp<sup>3</sup>) bonds. Specific equations and parameters for calculating each energy term can be found in the literature.<sup>24,25</sup>

Heats of formation in MM3 are calculated from eq 2,<sup>24,25</sup> where  $\Delta H_{\text{bond}}$  is the sum of the bond energy contributions,  $\Delta H_{\text{struct}}$  is the sum of structural energy contributions for functional groups such as methyl groups or five-membered rings,  $\Delta H_{\text{steric}}$  is the steric energy which is the result from eq 1 after minimization,

$$\Delta H_f^\circ = \Delta H_{\text{bond}} + \Delta H_{\text{struct}} + \Delta H_{\text{steric}} + \Delta H_{\text{thermo}} \quad (2)$$

and  $\Delta H_{\text{thermo}}$  is the partition function contribution. For hydrocarbons  $\Delta H_{\text{thermo}}$  is assumed to be 2.4 kcal/mol (to account for translation, rotation, and a correction for constant volume), and for alkanes in particular, an extra torsional correction of 0.4 kcal/mol is added for each bond about which there is a rotational barrier of less than 7 kcal/mol. As the surface species considered here have neither translational nor rotational degrees of freedom,  $\Delta H_{\text{thermo}}$  is not considered.

The computational advantages of working with a cluster without the complication of edge effects may be gained by calculating *changes* in the steric energy rather than the total energy. Upon reconstruction of or adsorption on the surface, the top few layers of substrate atoms as well as the adsorbed species relax while atoms in the bulk remain in their ideal positions. We define the surface steric energy as the steric energy of the top few layers of atoms, including adsorbed atoms, minus the steric energy of the clean ideal surface, i.e., with all the substrate atoms in their ideal bulk positions. Since substrate atoms more than a few atomic layers below the surface do not move, they make no energetic contribution and the thickness of the slab is immaterial. The choice of the ideal bulk-terminated surface as the reference structure is arbitrary and is made for convenience. However, in the case of diamond (100) the ideal bulk-terminated surface consists of surface "carbenes" with two extra electrons ("dangling bonds", if unpaired) per carbon atom. Since the MM3 force field has not been parameterized to describe molecular carbenes, it is clear that the energetics of the ideal bulk-terminated surface are not calculated correctly. This feature has the disadvantage that comparisons with high-level quantum chemical calculations of the energy of relaxation from the ideal surface to (2 $\times$ 1) dimerized surfaces cannot meaningfully be made. Comparisons with experimental results are not hampered;

however, the ideal reference surface is unobservable physically. It is energy *differences* between stable surface structures (e.g., the clean and monohydride surfaces) that are physically meaningful, and the reference energy cancels out in calculations of differences in steric energies or in enthalpies of formation. Comparisons between MM3 predictions and the results of high-level quantum calculations can therefore be made by determining the difference in enthalpy between two stable structures, taking zero-point energy and finite-temperature corrections into account.

The calculations are limited in the lateral directions by imposition of periodic boundary conditions. The total surface steric energy,  $E_{\text{total}}$ , is simply related to the surface steric energy within a unit cell,  $E_{\text{unit cell}}$ , by

$$E_{\text{total}} = N_0 E_{\text{unit cell}} \quad (3)$$

where  $N_0$  is the number of unit cells on a particular surface and the unit cell is taken to be (2 $\times$ 1), (1 $\times$ 1), or (3 $\times$ 1) as appropriate. Minimization of the total surface steric energy is therefore reduced to minimizing the surface steric energy in a unit cell restricted by surface periodicity. Conventional molecular mechanics calculations for molecules optimize all the atomic coordinates. For cluster calculations of highly strained structures such as the dihydride, unphysical distortions of the underlying "lattice" due to edge effects can result. In our calculations the bottom three layers of substrate atoms were fixed in position, preventing expansion or contraction of the unit cell in the lateral directions.  $E_{\text{unit cell}}$  includes interactions within the unit cell, counted once, plus all interactions with atoms outside the unit cell. As a side note, the important aspect of the periodic boundary conditions for these calculations is the location of atoms interacting with the unit cell, so that the energy of isolated adsorbates can be evaluated rather accurately by simply assuming the absence of the same adsorbate in adjacent unit cells. Put differently, the periodic boundary conditions can easily be taken to apply to the substrate but not to the adsorbate. In the calculations presented here, full periodic boundary conditions were applied on (3 $\times$ 1), (2 $\times$ 1), or (1 $\times$ 1) unit cells.

The slab chosen for the clean, monohydride (2 $\times$ 1) and the intermediate hydride (3 $\times$ 1) reconstructed diamond surfaces was 5 layers thick, consisting of 3 $\times$ 4 (2 $\times$ 1) unit cells or 3 $\times$ 3 (3 $\times$ 1) unit cells, with a total of 123 carbon atoms. The (1 $\times$ 1) dihydride surface slab was 5 layers thick, comprising 25 unit cells (5 $\times$ 5), with a total of 106 carbon atoms. In the calculations, the Cartesian coordinates of the carbon atoms are defined with respect to their ideal positions in the bulk, as determined by simple geometry using the diamond lattice constant of 3.5667 Å,<sup>26</sup> while those of the adsorbed hydrogen atoms are defined with respect to the carbon atom to which they are attached. The ideal C–C and C–H bond lengths in diamond and in hydrocarbon molecules are 1.54 and 1.11 Å,<sup>24a</sup> respectively ( $r_g$  bond lengths, as derived from electron diffraction). In the MM3 force field slightly different C–C bond parameters are used for three- to five-membered rings than for noncyclic molecules and six-membered rings. The (2 $\times$ 1) as well as (3 $\times$ 1) structures involve five-membered rings in the topmost layer and six-membered rings below, and so the appropriate parameters were used.

The surface steric energy for each of the three surfaces was calculated by including all the possible interactions defined in eq 1. For the dihydride surface, the hydrogen atoms as well as the topmost layer of carbon atoms were allowed to relax completely, while for the clean, monohydride (2 $\times$ 1) and intermediate hydride (3 $\times$ 1) surfaces the top two layers of carbon atoms were also allowed to fully relax. The minimization of the surface steric energy was carried out using the conjugate first-order derivative DFP algorithm,<sup>27</sup> a convenient and reliable method for minimizing a function with a modest number of variables. The program was written in FORTRAN, and all computations were carried out on an IBM RISC/6000-320 workstation.

### Results

The calculated atomic displacements of the top-layer carbon atoms and chemisorbed hydrogen atoms from their ideal positions on diamond (100)-(2 $\times$ 1), diamond (100)-(2 $\times$ 1):H, diamond (100)-(1 $\times$ 1):2H, and diamond (100)-(3 $\times$ 1):1.33H are tabulated in Table I. The surface structures are also drawn to scale in Figure 1, with selected bond lengths and angles given explicitly.

Enthalpies of formation for the diamond (100)-(2 $\times$ 1), diamond (100)-(2 $\times$ 1):H, diamond (100)-(1 $\times$ 1):2H, and diamond (100)-(3 $\times$ 1):1.33H surfaces, referenced to the unreconstructed surface as defined above, were found to be 59.27, 12.61, 30.88, and 11.11 kcal/mol per (2 $\times$ 1), (2 $\times$ 1), (1 $\times$ 1), or (3 $\times$ 1) unit cell,

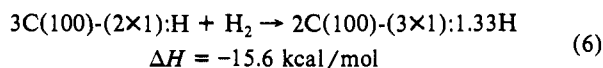
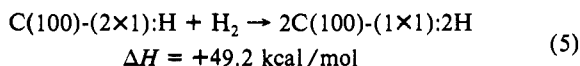
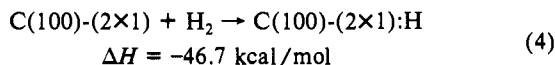
(26) Field, J. E. *The Properties of Diamond*; Academic Press: New York, 1979; p 643.

(27) Press, W. H.; Flannery, B. P.; Teukolsky, S. A.; Vetterling, W. T. *Numerical Recipes*; Cambridge University Press: Cambridge, 1986; p 307.

**Table I.** Displacements from Bulk-Terminated Positions of Clean and Hydrogenated Diamond (100) Surfaces

|                         | displacements (Å) along |                 |        |
|-------------------------|-------------------------|-----------------|--------|
|                         | [011]                   | [0 $\bar{1}$ 1] | [100]  |
| Diamond (100)-(2×1)     |                         |                 |        |
| C1                      | 0.532                   | 0.000           | -0.087 |
| C3                      | 0.073                   | 0.000           | 0.030  |
| Diamond (100)-2×1:H     |                         |                 |        |
| H1                      | -0.437                  | 0.000           | 1.021  |
| C1                      | 0.447                   | 0.000           | -0.057 |
| C3                      | 0.066                   | 0.000           | 0.027  |
| Diamond (100)-1×1:2H    |                         |                 |        |
| H1                      | -0.667                  | -0.331          | 0.786  |
| H2                      | 0.667                   | 0.331           | 0.787  |
| C1                      | 0.000                   | 0.000           | -0.010 |
| Diamond (100)-3×1:1.33H |                         |                 |        |
| H1                      | -0.850                  | 0.000           | 0.697  |
| H3                      | -0.369                  | 0.000           | 1.045  |
| C1                      | 0.465                   | 0.000           | -0.066 |
| C3                      | 0.070                   | 0.000           | 0.028  |
| C5                      | 0.000                   | 0.000           | -0.011 |
| C6                      | 0.000                   | 0.000           | 0.008  |

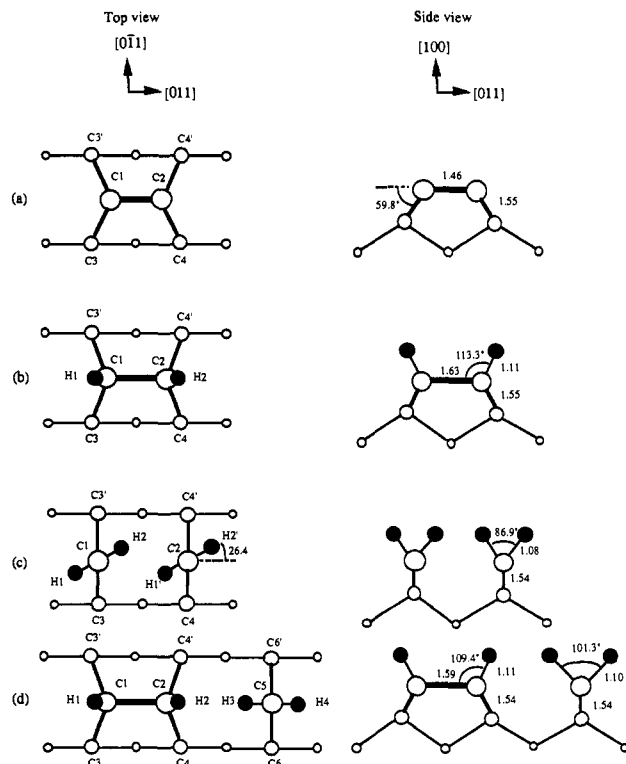
respectively (a (1×1) unit cell has a surface concentration of  $1.57 \times 10^{15} \text{ cm}^{-2}$ ). Substantial strain is present in each structure, as the steric energies of these structures are 46.37, 35.62, 40.06, and 43.30 kcal/mol per unit cell, respectively. MM3 bond energy and structural units present in the clean (2×1) surface unit cell are one C=C bond, two iso units, and conversion of four C(sp<sup>3</sup>)—C(sp<sup>3</sup>, neo) bonds to C(sp<sup>2</sup>)—C(sp<sup>3</sup>, *t*-Bu) bonds. The (2×1):H monohydride unit cell contains one C(sp<sup>3</sup>)—C(sp<sup>3</sup>) bond, two C(sp<sup>3</sup>)—H bonds, two cyclopentane rings, and two iso units, while the (1×1):2H dihydride unit cell contains two C(sp<sup>3</sup>)—H bonds and the (3×1):1.33H dihydride unit cell contains one C(sp<sup>3</sup>)—C(sp<sup>3</sup>) bond, four C(sp<sup>3</sup>)—H bonds, two cyclopentane rings, and two iso units. As noted previously, only differences in the reference energies can be used in making comparisons to quantum chemical calculations or (in principle) to experiment, and the values given imply the following heats of reaction:



The heats of reaction in eqs 4–6 are given per mole of H<sub>2</sub>; i.e., formally one C–C bond and the H–H bond are replaced by two C–H bonds in each equation. The corresponding heats of reaction with atomic hydrogen may be obtained by subtracting 104.20 kcal/mol (the heat of formation of two hydrogen atoms<sup>28</sup>) from the values in eqs 4–6.

### Discussion

**Diamond (100)-(2×1).** Surface carbon atoms C1 and C2 were found to relax inward by 0.09 Å, whereas the subsurface second-layer carbon atoms C3 and C4 expand outward by 0.03 Å. This result is in good agreement with the semiempirical study of Mehandru and Anderson,<sup>20</sup> who obtained vertical displacements for first- and second-layer carbon atoms of -0.12 or -0.14 Å and 0.03 or 0.05 Å, respectively, depending on whether the p-electrons on the dimer atoms were spin-unpaired or -paired. The contraction in Verwoerd's<sup>18</sup> semiempirical study was more pronounced, 0.24 Å. This is probably due to the small size of his model cluster (one surface unit cell), thereby reducing the restraint on relaxation due



**Figure 1.** Top and side views of atomic structures of clean and hydrogenated diamond (100) surfaces: (a) diamond (100)-(2×1); (b) diamond (100)-(2×1):H; (c) diamond (100)-(1×1):2H; and (d) diamond (100)-(3×1):1.33H. Bond lengths are given in angstroms. Large, medium, and small circles indicate carbon atoms in top, second, and third layers, respectively. Shaded circles indicate hydrogen atoms.

to the lattice, together with the fact that only the topmost layer was allowed to relax. The empirical calculation of Appelbaum and Hamann<sup>21</sup> also predicted contraction of the surface carbon atoms toward the bulk, but by a much smaller amount (0.04 Å). The tight-binding calculation of Bechstedt and Reichardt,<sup>19</sup> on the other hand, predicted that the surface carbon atoms expand outward in the [100] direction. Their result is almost certainly incorrect. Besides disagreeing with the other results cited, their study found the same outward expansion tendency on Si(100), which is at odds with high-level calculations,<sup>16</sup> a semiempirical cluster calculation,<sup>29</sup> an empirical force field study,<sup>21</sup> and experiment.<sup>10</sup>

We predict a dimer bond (C1–C2) length of 1.46 Å, significantly longer than the typical nonconjugated π-bond length in alkenes of 1.34 Å.<sup>24d</sup> Our dimer bond length agrees well with the results of Brenner<sup>22</sup> (1.38 or 1.43 Å for two sets of parameters in the empirical potential), Mehandru and Anderson<sup>20</sup> (1.40 Å for paired p-electrons), and Verwoerd<sup>18</sup> (1.43 Å), but disagrees with those of Appelbaum and Hamann<sup>21</sup> (1.67 Å) and Bechstedt and Reichardt<sup>19</sup> (1.54 Å). Mehandru and Anderson<sup>20</sup> argue that the p-electrons of the dimer atoms are unpaired on the clean surface, resulting in a longer dimer bond length (1.58 Å), but this seems very unlikely given the strong tendency of carbon to form π-bonds. The elongation of the dimer bond is clearly attributable to strain. Formation of the dimer bond distorts the back-bonds (C1–C3, etc.) considerably inward, and the back-bonds are bent downward from the horizontal plane containing the double bond by 60°. The outward force exerted by the strained back-bonds on the dimer atoms would be expected to stretch the dimer bond, precisely as seen. The bond length of the dimer back-bond (C1–C3 in Figure 1) was found to be 1.55 Å, which is about the same as that of the bulk C–C bond length but slightly longer than typical C(sp<sup>3</sup>)–C(sp<sup>2</sup>) bond lengths, 1.51 Å.<sup>24d</sup> Other researchers obtained 1.56 Å<sup>21</sup> and 1.52 Å<sup>20</sup> for this back-bond length. This bond-

(28) Wagman, D. D.; Evans, W. H.; Parker, V. B.; Schumm, R. H.; Halow, I.; Bailey, S. M.; Churney, K. L.; Nuttall, R. L. *J. Phys. Chem. Ref. Data* **1982**, *11* (Suppl. No. 2).

(29) Craig, B. I.; Smith, P. V. *Surf. Sci.* **1989**, *218*, 569.

stretching, like that of the dimer bond, is an obvious consequence of strain. Bond angles  $\angle C3C1C3'$  and  $\angle C2C1C3$  were found to be  $108.8^\circ$  and  $107.2^\circ$ , respectively, which are not unusual for alkenes.

The bond lengths and bond angles of the surface dimer represent an extrapolation from the database of molecular structures used to construct MM3, and so the accuracy of our predictions is difficult to assess. The same force field parameters are used for conjugated and nonconjugated hydrocarbons in MM3 (a separate SCF calculation is performed for the conjugated  $\pi$ -electrons),<sup>24d</sup> and so it seems justifiable to regard calculated  $C(sp^2)-C(sp^2)$  bond lengths in aromatic molecules as "tested" values which can be compared to the (nonconjugated) dimer bond length. MM3 predicts a  $C(sp^2)-C(sp^2)$  bond length of 1.409 Å for the strained molecule hexamethylbenzene, in good agreement with the experimental value of 1.417 Å.<sup>24d</sup> This value represents an increase of 0.08 Å over the normal  $C=C$  bond length, which is significantly less than the elongation of 0.12 Å predicted for the dimer bond. In addition, all four of the back-bonds to the dimer are bent downward, and we are unaware of any structurally-analogous molecule which has been synthesized and characterized. The overall agreement between the present calculation and previous work using other methods<sup>18,20,22</sup> is encouraging, but an unequivocal determination of the accuracy of the various predictions will likely await high-level quantum chemical calculations.

**Diamond (100)-(2×1):H.** Again the surface carbon atoms were found to contract toward the bulk, but by a smaller distance (0.06 Å) than on the clean surface. Reduced contractions relative to the clean surface were also predicted in earlier studies (0.08 Å<sup>18</sup> and 0.01 Å<sup>20</sup>). We obtained a dimer bond (C1-C2) length of 1.63 Å, longer than typical  $C(sp^3)-C(sp^3)$  single bond lengths—1.54 Å in alkanes<sup>24a</sup> and bulk diamond—and clearly attributable to strain induced by the lattice. This value agrees closely with that of Brenner<sup>22</sup> (1.63 and 1.60 Å for two sets of potential parameters) and fairly well with those of Verwoerd (1.67 Å)<sup>18</sup> and Mehandru and Anderson (1.73 Å).<sup>20</sup> The C-H bond length on the dimer is about 1.11 Å, typical for alkanes.<sup>24a</sup> The dimer back-bond (C1-C3) length is about 1.55 Å, in agreement with Mehandru and Anderson (1.56 Å).<sup>20</sup>  $\angle C2C1C3$  is  $104.3^\circ$ , indicating some angle strain, while  $\angle C3'C1C3 = 109.4^\circ$ , very nearly the ideal  $sp^3$  hybridization angle. The angle between the hydrogen atoms and the surface normal [100] is  $23.3^\circ$ , in good agreement with previous work ( $21^\circ$ <sup>20</sup> and  $20^\circ$ <sup>18</sup>).

In this case the bond lengths and bond angles are essentially within the range known to be well-described by MM3, and the structure should be quite accurate. The calculated C-C bond length in the dimer (1.63 Å) is nearly the same as that of the central C-C bonds in tri-*tert*-butylmethane (1.611 Å<sup>30</sup>), for which MM3 is quite accurate (we calculate 1.615 Å using a standard MM3 program<sup>31</sup>). The bond angles are not unusual for alkanes.

**Diamond (100)-(1×1):2H.** The first-layer carbon atoms remain in their ideal positions without much relaxation on this surface, consistent with previous results (0.02 Å<sup>18,20</sup>). If the hydrogen atoms remained in their ideal  $sp^3$  positions, the distance between neighboring (nonbonded) hydrogen atoms H2 and H1' would be only 0.71 Å, less than the H-H bond length in H<sub>2</sub>! Therefore, one can expect rather dramatic orientational changes in the C-H bonds in order to stabilize the surface. Indeed, our results show that the H-C-H bonds not only bend toward each other, reducing bond angle  $\angle H1CH2$  by more than  $22^\circ$  to  $86.9^\circ$ , but also twist about the surface normal by  $26.4^\circ$ . This bond reorientation is caused mainly by van der Waals repulsion between neighboring hydrogen atoms H2 and H1'. In the optimized structure, the distance between H2 and H1' is 1.36 Å, which is considerably more than the unrelaxed value but still much shorter than the shortest known nonbonded H-H distances, found in *exo,exo*-tetracyclo[6.2.1.1<sup>3,6</sup>.0<sup>2,7</sup>]dodecane and its anhydride derivative (1.75 and 1.70 Å, respectively),<sup>24a</sup> which bear a structural re-

semblance to the dihydride surface. The accuracy of the structure is rather uncertain due to the extent of the extrapolation (0.34 Å) from the range of nonbonded H-H distances known to be fit by MM3. We calculate a C-H bond length of 1.08 Å, which is shorter than typical C-H bond lengths (1.11 Å). Reduction of the H-C-H bond angle ( $86.5^\circ$ <sup>18a</sup>  $84^\circ$ <sup>20</sup>) and shortening of the C-H bond (1.10 Å,<sup>18a</sup> 1.08 Å<sup>20</sup>) has been predicted previously, but twisting about the [100] axis has not. As a result, the nonbonded H-H distances calculated previously are even shorter than our predictions (1.03 Å<sup>18a</sup> and 1.08 Å<sup>20</sup>).

**Diamond (100)-(3×1):1.33H.** The extreme steric hindrance in the (1×1) dihydride can be reduced by alternating monohydride and dihydride units, as noted previously for hydrogenated Si(100).<sup>14b</sup> We find that the structure of the dimer bond in the (3×1) unit cell is almost identical to that in the (2×1) unit cell: dimer bond length 1.59 Å (vs 1.63 Å in the (2×1) monohydride); back-bond C1-C3 length 1.54 Å (1.55 Å);  $\angle C2C1C3 = 104.9^\circ$  ( $104.3^\circ$ ); and  $\angle C3C1C3' = 109.5^\circ$  ( $109.4^\circ$ ). However, van der Waals repulsions between H2 and H3 reduce the angle between H2 and the surface normal to  $19.4^\circ$  (vs  $23.3^\circ$  in the monohydride). As would be expected, van der Waals repulsions also reduce  $\angle H3C5H4$  to  $101.3^\circ$ . Structural parameters for this surface have not been reported previously. As with the (2×1):H monohydride, because the calculated bond lengths and bond angles are within the range of values known to be well-described by MM3, we expect this structure to be accurate.

**Energetics.** Considerably more scatter is seen in the energetics of diamond (100) surfaces calculated by various researchers than in the structural parameters. For the monohydride, our heat of formation from the clean surface ( $-46.7$  kcal/mol, eq 4) compares reasonably well with that calculated by Brenner<sup>22</sup> ( $-68.2$  or  $-62.8$  kcal for two sets of parameters), whereas there are large discrepancies with the results of Verwoerd<sup>18b</sup> ( $-98.2$  kcal/mol) and of Mehandru and Anderson<sup>20</sup> ( $-202.5$  kcal/mol). Insight into the relative contributions of normal bond energies and strain to  $\Delta H$  for eq 4 may be gained by comparing this value to the heats of hydrogenation of molecular analogues 1 and 2, which bear some



structural similarities to the dimers on diamond (100)-(2×1).  $\Delta H$  for reaction of H<sub>2</sub> with the relatively strain-free molecule 2,3-dimethyl-2-butene (1),  $-25.9$  kcal/mol,<sup>24a,24e</sup> is not unusual for hydrogenation reactions of olefins but is much smaller in magnitude than the heat of hydrogenation of the clean diamond (100)-(2×1) surface. Much of the strain present on diamond (100)-(2×1) is also present in tricyclo[3.3.1]nonene (2).  $\Delta H$  for hydrogenation of 2,  $-44.6$  kcal/mol, as calculated using a standard MM3 program<sup>31</sup> since the molecule has not been synthesized, to the best of our knowledge, is nearly the same as that for hydrogenation of the clean (100) surface. The obvious conclusion is that nearly half the value of  $\Delta H$  for eq 4 is due to release of the strain associated with the stretched  $C=C$  bond and the out-of-plane distortions of the four  $C(sp^2)-C(sp^3)$  bonds as the dimer double bond is reduced, forming the monohydride.

Our calculations indicate that the (1×1):2H dihydride is thermodynamically unstable with respect to dehydrogenation to the monohydride ( $\Delta H$  for eq 5 is  $+49.2$  kcal/mol), in agreement with a previous calculation ( $\Delta H = +23.1$  kcal/mol<sup>18b</sup>). The fact that the calculated H-H nonbonded distance is 0.34 Å shorter than any known to be well-described by MM3 implies that our predictions of both the structure and energetics of this species are rather uncertain. Nonetheless, the magnitude of the positive heat of reaction and the qualitative agreement with the previous calculation provides evidence that it will not be present at high temperature under chemical vapor deposition growth conditions, although it may be metastable at lower temperatures:  $\Delta H$  for the reaction  $C(100)-(2\times 1):H + 2H \rightarrow C(100)-(1\times 1):2H$  is predicted to be  $-55.0$  kcal/mol.

The (3×1):1.33H dihydride, on the other hand, is reasonably

(30) Bartell, L. S.; Bürgi, H. B. *J. Am. Chem. Soc.* 1972, 94, 5239.

(31) MM3(89), Quantum Chemistry Program Exchange, University of Indiana, Bloomington, IN 47405, 1989.

stable and may be present under diamond CVD growth conditions if the surface temperature is not too high. The structure and energetics of this species, whether theoretical or experimental, have not been previously reported. Construction of a suitable molecular analogue is problematic, and we note simply that the net result of eq 6 is the replacement of C–C and H–H bonds by two C–H bonds. Heats of hydrogenolysis of saturated hydrocarbons generally lie in the range of  $-7$  to  $-11$  kcal/mol,<sup>24a</sup> and the difference between these values and  $-15.6$  kcal/mol may be taken as a rough estimate of the effect of strain and steric interactions. Some strain energy is released by opening a C–C dimer bond but is partly compensated by an increase in H–H steric repulsion.

Two additional observations about the  $(3\times 1):1.33\text{H}$  structure are noteworthy. Formation from the  $(2\times 1):\text{H}$  monohydride is nontrivial, as rearrangement of the dimer bonds between atoms not bonding to a second hydrogen atom is required. Also, the  $(3\times 1):1.33\text{H}$  structure represents an upper limit to the hydrogen coverage that may be achieved without significant van der Waals repulsion, but a whole family of  $(2n+1\times 1):(2n+2)/(2n+1)\text{H}$  structures, consisting of  $n$  dimers separated by a dihydride unit, are possible. Disorder in the long-range order of such structures is very likely, and could result in streaked half-order spots or, more probably, simply a  $(1\times 1)$  low-energy electron diffraction (LEED) pattern, as seen for the dihydride formed at 300 K on Si(100)<sup>14b,d</sup> and as observed by Hamza et al.<sup>13</sup> on diamond (100).

Of the relative energetics of the four species considered here, defined by eqs 4–6,  $\Delta H$  for eq 6 should be the most reliable, as both the  $(2\times 1):\text{H}$  monohydride and  $(3\times 1):1.33\text{H}$  partial dihydride have structural parameters in the range known to be well-described by MM3. Dimers on clean  $(2\times 1)$  surface are more strained than any known olefins, injecting some uncertainty into the value of  $\Delta H$  for eq 4. As just noted, the uncertainty in  $\Delta H$  is probably greatest for eq 5, due to the extreme steric hindrance in the  $(1\times 1):2\text{H}$  dihydride. However, the predictions of severe distortion and of thermodynamic instability seem unlikely to be incorrect. High-level quantum chemical calculations should be able to test our predictions and, ideally, enable the extension of the MM3 "database" to include these highly strained surface species.

Our prediction that the  $(1\times 1):2\text{H}$  dihydride is unstable calls into question one of the conclusions of Hamza et al.<sup>13</sup> namely, that the  $(1\times 1):2\text{H}$  dihydride is formed upon exposure of the surface to hydrogen atoms and eliminates  $\text{H}_2$  by desorption in the temperature range of 700–1200 K. While reduction of the  $(2\times 1):\text{H}$  monohydride by atomic hydrogen to form the  $(1\times 1):2\text{H}$  dihydride is predicted to be energetically favorable by 55 kcal/mol,  $\Delta H$  for desorption of  $\text{H}_2$  to reform the monohydride is calculated to be  $-49$  kcal/mol, in contrast to the positive heats of desorption for every other system of which we are aware. It seems very unlikely that the activation energy for desorption could be large enough for a thermodynamically unstable species (the dihydride) to be stable up to 700 K. Our result also indicates that the mechanism proposed by Harris<sup>3c</sup> for growth by chemical vapor deposition on diamond (100) is incorrect, at least in detail, in that it assumes the  $(1\times 1):2\text{H}$  dihydride as the starting point. At present the only direct evidence for a full two-monolayer coverage of hydrogen comes from the nuclear microanalysis results of Derry et al.<sup>12</sup> on polished diamond surfaces, which were sample-preparation-dependent, often complicated by the presence of oxygen, and certainly not definitive. As noted above, a disordered dihydride with local  $(2n+1\times 1)$  structure would most likely give rise to a  $(1\times 1)$  LEED pattern and would be consistent with the observations of Hamza et al.<sup>13</sup>

Our calculated heats of hydrogenation are consistent with the  $\text{H}_2$  desorption peak observed by Hamza et al.<sup>13</sup> in the range of 700–1200 K being from the monohydride, forming the clean surface, rather than from the dihydride. By detailed balance, the activation energy for desorption of  $\text{H}_2$  from the  $(2\times 1):\text{H}$  structure is simply  $\Delta H$  for the reverse of eq 4 plus the activation energy for dissociative adsorption of  $\text{H}_2$ , which is almost certainly nonzero since molecular hydrogen does not readily adsorb on diamond.<sup>5,7,8</sup> Assuming that desorption from the  $(2\times 1):\text{H}$  monohydride is first-order, by analogy to Si(100)- $(2\times 1):\text{H}$ ,<sup>32</sup> and taking 20

kcal/mol as a rough estimate of the activation energy for dissociative adsorption of  $\text{H}_2$ <sup>33</sup> and a value of  $10^{13}$  s<sup>-1</sup> for the preexponential factor, one predicts a peak temperature of  $\sim 1050$  K for a temperature-programmed desorption experiment with a heating rate of 6 K s<sup>-1</sup>,<sup>34</sup> in approximate agreement with the peak temperature observed by Hamza et al.<sup>13</sup> These researchers assigned the desorption peak as being due to the dihydride and concluded that the monohydride was stable up to a temperature of  $\geq 1400$  K.<sup>13</sup> However, assuming our heat of reaction is correct, this would require either an activation energy for hydrogen adsorption of  $\geq 50$  kcal/mol or an anomalously low preexponential factor. It is unclear why desorption of  $\text{H}_2$  from the monohydride on diamond (111), which takes place at  $\sim 1100$ – $1200$  K,<sup>5,7,8</sup> should be qualitatively more facile than desorption from the (100) face. The primary evidence for the stability of the monohydride above 1400 K was the persistence of  $\text{H}^+$  and  $\text{H}_2^+$  peaks in the electron-stimulated desorption spectrum, together with the lack of observable unoccupied electronic states in the band gap.<sup>13</sup> It seems possible that the electron-stimulated desorption peaks resulted from hydrogen in the bulk, as was recently observed on Si(111),<sup>35</sup> and/or from hydrogen at defect sites, which should exist in abundant concentration since diamond surfaces cannot be properly annealed without graphitization. However, existing calculations of the surface electronic structure are not able to determine the consistency of the photoemission results of Hamza et al.<sup>13</sup> with various structural models of diamond (100). Resolution of these questions will clearly require more experimental and theoretical work.

## Conclusions

We have demonstrated that molecular mechanics (MM3) is a very useful tool in understanding the surface chemistry of diamond. The structure and energetics of clean diamond (100)- $(2\times 1)$ , the  $(2\times 1):\text{H}$  monohydride, and the  $(1\times 1):2\text{H}$  and  $(3\times 1):1.33\text{H}$  dihydrides have been determined, identifying the effects of strain on the bond lengths and heats of hydrogenation of surface dimers. The  $(1\times 1):2\text{H}$  dihydride is found to be thermodynamically unstable and unlikely to exist under diamond chemical vapor deposition conditions, contrary to assumptions in previous experimental and modeling work. Application of the computationally-simple MM3 method to stable surface species, such as the  $(2\times 1):\text{H}$  and  $(3\times 1):1.33\text{H}$  surfaces and to a lesser extent the clean surface, with structural parameters comparable to molecules which are known to be well-described by MM3, should give results which are of chemical accuracy and superior to semiempirical methods and empirical potentials which are less well tested. The accuracy of the method for structures with parameters outside the database, such as the  $(1\times 1):2\text{H}$  dihydride, is obviously more uncertain, but the same is true for semiempirical quantum chemical methods. A disadvantage of the model is that accuracy of the force field is assured only near chemically-significant minima in the potential, thus excluding transition states, and so it may be unsuitable for molecular dynamics computer simulations of surface processes such as chemical vapor deposition.

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