

## $\pi$ bond versus radical character of the diamond (1 0 0)-2 $\times$ 1 surface

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### Abstract

The dimers on clean diamond (1 0 0)-2  $\times$  1 are linked by a  $\sigma$  bond and a highly strained  $\pi$  bond. The weakness of the surface  $\pi$  bond causes the reactivity of this surface to be intermediate between that of an alkene and a bi-radical. We illustrate this behavior by investigating two prototypical cycloaddition surface reactions using multiple-internal-reflection infrared spectroscopy. Adsorption of 1,3-butadiene occurs via [4 + 2] addition to surface dimers, analogous to Diels–Alder chemistry of alkenes. However, [2 + 2] cycloaddition of cyclopentene, a reaction that is symmetry-forbidden with alkenes, occurred with a sticking coefficient of  $\sim 10^{-3}$ . These reactions illustrate novel approaches to the functionalization of diamond surfaces. © 2001 Elsevier Science B.V. All rights reserved.

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### 1. Introduction

Realization of the full potential of diamond in various applications requires an understanding of its surface reactivity, as the surface chemistry plays a critical role in growth and also controls properties ranging from electron affinity and surface conductivity to wettability. An improved fundamental understanding of the surface reactivity of diamond will certainly help in improving the growth rate, quality, and surface characteristics of diamond grown by chemical vapor deposition (CVD). In addition, there is a unique opportunity for new insights into the general relationship between surface reactions of covalent materials and reactions of analogous molecular species. The molecular analogs to surface intermediates on diamond are organic molecules, for which an enormous database of mechanisms and kinetics is available. In addition, the low atomic weight of carbon makes diamond surface chemistry amenable to high-level quantum chemical calculations.

The dimer-reconstructed (1 0 0)-2  $\times$  1 surface displays a rich variety of chemistry that is beginning to be understood in some detail. C=C dimers on the clean surface are linked by a  $\sigma$  bond and a highly strained  $\pi$  bond [1–6] and might be expected to exhibit reactivity patterns similar to organic molecules with C=C bonds (alkenes or olefins). On the other

hand, some authors have argued that the dimers should behave essentially as bi-radicals, with one dangling bond at each surface carbon atom [7]. Why should the distinction matter? Because the Woodward–Hoffman [8,37] rules for the orbital symmetry of organic reactions make rather specific predictions about the selectivity of reactions of alkenes, but do not apply to bi-radicals if interconversion of singlet and triplet spin states is rapid, as might be expected on a surface. In addition, the presence of even weak  $\pi$  bonds will induce adsorbates such as H to pair up on dimers [6,9], whereas adsorption will be random if the  $\pi$  bond energy is very low.

For example, dissociative adsorption and recombinative desorption are analogous to molecular addition and elimination reactions [10], respectively, as illustrated in Fig. 1. Addition of a homonuclear diatomic molecule (i.e., A = B in Fig. 1) to an alkene is symmetry-forbidden, i.e., will have a high activation energy and, therefore, will proceed with a very low rate [8,37]. If the surface dimers on diamond (1 0 0)-2  $\times$  1 behave like alkenes, therefore, the dissociative sticking coefficients of such molecules would be very small. Indeed, dissociative adsorption of molecules such as H<sub>2</sub>, O<sub>2</sub>, or Cl<sub>2</sub> on clean C(1 0 0)-2  $\times$  1 *has not been reported to date* in high vacuum in the absence of dissociation or excitation by a hot filament, and adsorption of even the extremely reactive F<sub>2</sub> molecule occurs with a low sticking coefficient [11].

Hydrogen desorbs from the diamond (1 0 0)-2  $\times$  1:H monohydride with near-first-order kinetics, with an activation energy of about 80–88 kcal mol<sup>-1</sup> [12–15]. This value

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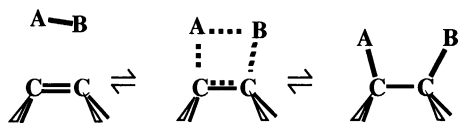


Fig. 1. Schematic representation of a simple adsorption/desorption reaction on diamond (100)- $2 \times 1$ .

is much smaller than the activation energy for elimination of  $H_2$  from ethane to form ethylene, ca.  $120 \text{ kcal mol}^{-1}$  [16]. The activation energy for *adsorption* of  $H_2$  is essentially the difference between the activation energy for the reverse process (desorption) and the enthalpy of desorption, estimated as  $74\text{--}85 \text{ kcal mol}^{-1}$  from high-level quantum chemical calculations [6]. This difference, a few  $\text{kcal mol}^{-1}$ , is much smaller than the activation energy for addition of  $H_2$  to  $H_2C=CH_2$ , ca.  $87 \text{ kcal mol}^{-1}$  [16], apparently indicative of a much weaker  $\pi$  bond on the surface. The simplest explanation for the near-first-order desorption kinetics is that the surface  $\pi$  bond causes preferential pairing of adsorbed H atoms [5,6,17]. However, bond strain will also tend to cause adsorbates to segregate into one- or two-dimensional islands [18,19], which would also lead to first-order kinetics. The detailed dynamical mechanism for  $H_2$  desorption on the closely related Si(100)- $2 \times 1$ :H surface is still under debate, and further study will be required for a complete understanding of this reaction on diamond (100)- $2 \times 1$ :H.

Cycloaddition reactions constitute a powerful method for formation of C–C bonds and could provide a means for well-defined functionalization of the diamond (100)- $2 \times 1$  surface, and exhibit rather specific reactivity patterns with olefins. Direct reaction of two C=C double bonds ( $2 + 2$  p electrons) to form a 4-membered ring,  $[2 + 2]$  cycloaddition, as shown for the analogous surface reaction in Fig. 2, is symmetry-forbidden and, therefore, proceeds with a very low rate [8,37].

On the other hand, reaction of two conjugated C=C bonds with another C=C bond to form a 6-membered ring ( $4 + 2$  p electrons),  $[4 + 2]$  cycloaddition, is facile. A prototype  $[4 + 2]$  surface cycloaddition reaction on a diamond (100) surface dimer is shown in Fig. 3. Both  $[4 + 2]$  [20,21] and  $[2 + 2]$  [22–24] cycloaddition reactions have been observed on the isostructural Si(100) surface.

We have investigated  $[4 + 2]$  and  $[2 + 2]$  cycloaddition reactions of diamond (100)- $2 \times 1$  surface with two prototypical olefins, 1,3-butadiene and cyclopentene. We show that the surface dimer behaves like a C=C double bond in the first case, forming a Diels–Alder adduct directly analogous

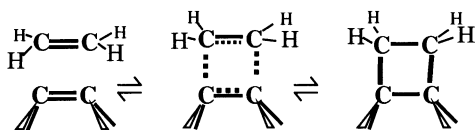


Fig. 2. Schematic representation of the  $[2 + 2]$  cycloaddition reaction of ethylene with diamond (100)- $2 \times 1$ .

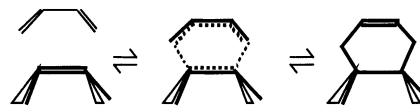


Fig. 3. Schematic representation of the  $[4 + 2]$  cycloaddition reaction of 1,3-butadiene with diamond (100)- $2 \times 1$ . For clarity, the carbon atoms are represented only as the vertices between bonds and hydrogen atoms are omitted.

to molecular cyclohexene, but the surface  $\pi$  bond is manifested in the second case only via a low sticking coefficient, behaving somewhat like a bi-radical.

## 2. Experimental

Experiments were performed at the Naval Research Laboratory in an ultrahigh vacuum (UHV) chamber with a base pressure of  $1 \times 10^{-10}$  Torr. Vibrational spectra of chemisorbed species were obtained by multiple-internal-reflection infrared spectroscopy (MIRIRS) with a trapezoidal, type IIa natural diamond ( $15 \times 3 \times 0.25 \text{ mm}^3$ ) prism, with the large faces oriented to within  $2^\circ$  of (100). Unpolarized infrared light from a Fourier transform infrared (FTIR) spectrometer was focused through a KBr window onto one beveled edge of the diamond internal reflection element within the UHV chamber. After undergoing 33 internal reflections, the transmitted light passed through another KBr window and was focused onto a liquid-nitrogen-cooled InSb detector. The diamond is opaque in the C–D stretch region due to two-phonon absorption in the bulk and the very long path length [13,25]. Prior to insertion into the UHV chamber, the diamond was treated in a series of acids to remove metals, non-diamond carbon, and Si/SiO<sub>2</sub> contaminants [26]. The sample was then exposed to a hydrogen microwave plasma for 30 min on each of the two large faces to produce a smooth (100)- $2 \times 1$ :H monohydride surface that is stable in air [27,28]. The sample was then transferred to the UHV chamber and heated to  $\sim 1360 \text{ K}$  to desorb the hydrogen, leaving a clean,  $2 \times 1$ -reconstructed surface [2,5].

## 3. Results and spectral assignments

### 3.1. Adsorption of 1,3-butadiene [29]

1,3-Butadiene,  $CH_2=CH-CH=CH_2$ , is capable of undergoing either  $[4 + 2]$  cycloaddition with C=C surface dimers, forming a  $-CH_2-CH=CH-CH_2-$  6-membered-ring species, or  $[2 + 2]$  cycloaddition, forming a 4-membered ring with a terminal  $-CH=CH_2$  group. Following exposure of the clean diamond (100)- $2 \times 1$  surface at room temperature to 1000L of 1,3-butadiene, the infrared spectrum shown in Fig. 4(a) was obtained. Several modes between  $2850$  and  $2970 \text{ cm}^{-1}$  are observed, characteristic of  $sp^3$ -hybridized  $>CH_x$  groups,

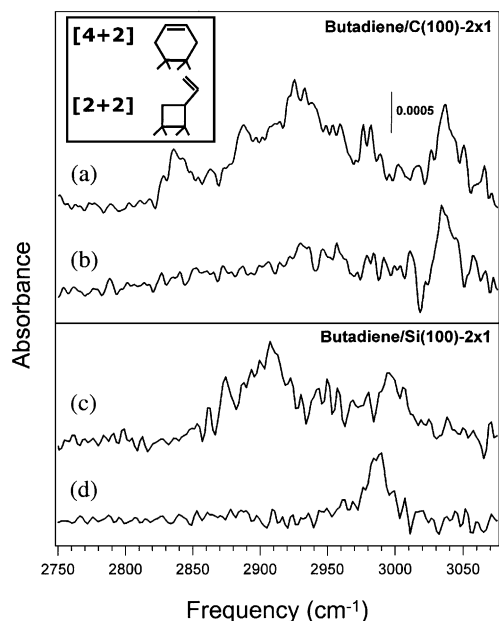


Fig. 4. Infrared spectra of: (a) 1,3-butadiene on C(100) (1000L); (b) 1,3-butadiene-1,1,4,4-d<sub>4</sub> (20,000L) on C(100); (c) 1,3-butadiene on Si(100) (1L); (d) 1,3-butadiene-1,1,4,4-d<sub>4</sub> (1L) on Si(100). All exposures and spectra were performed at room temperature.

and also a mode near 3035 cm<sup>-1</sup>, typical of sp<sup>2</sup>-hybridized C=CH<sub>x</sub> groups, indicating adsorption of the 1,3-butadiene.

The spectrum obtained after room temperature exposure to 1,3-butadiene is quite different than that of a multilayer condensed at 90 K, as shown in Fig. 5(a), indicating that the former species was chemisorbed rather than simply physisorbed. In particular, physisorbed 1,3-butadiene

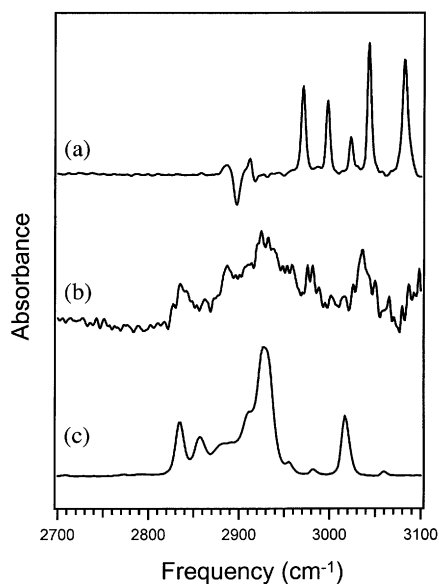


Fig. 5. Comparison of infrared spectra of: (a) a multilayer of 1,3-butadiene physisorbed at 90 K; (b) chemisorbed 1,3-butadiene; (c) a multilayer of cyclohexene physisorbed at 110 K.

lacks sp<sup>3</sup>-hybridized C–H modes at frequencies below 2960 cm<sup>-1</sup> that are present in the chemisorbed species, and possesses an extra mode at 3080 cm<sup>-1</sup> due to the terminal =CH<sub>2</sub> group. The absence of a sharp doublet at 2899 and 2919 cm<sup>-1</sup>, characteristic of hydrogen chemisorbed directly on the C(100) surface [30], further suggests that chemisorption is non-dissociative.

To distinguish the terminal and central hydrogen atoms in the adsorbed species, a comparative experiment was performed with 1,1,4,4-d<sub>4</sub>-butadiene (CD<sub>2</sub>=CH–CH=CD<sub>2</sub>). The only mode remaining in the C–H region with the deuterated, chemisorbed species appeared near 3035 cm<sup>-1</sup> (Fig. 4(b)), essentially unchanged from the spectrum with perhydro-butadiene. Together with the absence of the 3080 cm<sup>-1</sup> mode in physisorbed perhydro-butadiene (Fig. 5), this result precludes the presence of a terminal –CH=CD<sub>2</sub> group in the deuterated species and proves that [4 + 2] cycloaddition is the dominant adsorption mode of butadiene on diamond (100)-2 × 1. The spectra on diamond (100)-2 × 1 are very similar to previously observed spectra on the isostructural Si(100)-2 × 1 [20], as shown in Fig. 4(c) and (d). The structure of the [4 + 2] adduct, shown in the inset to Fig. 4, is very similar to that of molecular cyclohexene. The spectrum of a multilayer of physisorbed cyclohexene, shown in Fig. 5(c), is strikingly similar to that of chemisorbed 1,3-butadiene (Fig. 5(b)), providing further support for the spectral assignments.

### 3.2. Adsorption of cyclopentene [31]

With only a single C=C, cyclopentene is capable of only [2 + 2] cycloaddition, nominally symmetry-forbidden. Following exposure of the clean diamond (100)-2 × 1 surface to 10,000L of cyclopentene, the infrared spectrum shown in Fig. 6(a) was obtained. A large peak is observed at 2953 cm<sup>-1</sup> with shoulders at higher and lower frequency along with a second, smaller peak near 2880 cm<sup>-1</sup>. As described above, these frequencies are characteristic of sp<sup>3</sup>-hybridized C–H groups. Heating the sample to 573 K did not change the spectrum, indicating that the molecules were chemisorbed rather than being simply physisorbed. The sharp doublet at 2899 and 2919 cm<sup>-1</sup> associated with chemisorbed hydrogen [30] was not observed, indicating non-dissociative chemisorption. The spectrum of a multilayer of physisorbed cyclopentene, prepared by a 5L exposure at 90 K, is shown in Fig. 6(c). The 3040 cm<sup>-1</sup> peak in the physisorbed multilayer is due to an sp<sup>2</sup>-hybridized C=CH mode. The absence of a mode near 3040 cm<sup>-1</sup> in the chemisorbed species (Fig. 6(a)) indicates that the C=C bond in cyclopentene is directly involved in bonding to the surface so that all the C atoms are now sp<sup>3</sup>-hybridized, as expected for a [2 + 2] cycloaddition reaction. The similarity of the infrared spectrum to that of cyclopentene chemisorbed on Si(100), shown in Fig. 6(b), where [2 + 2] cycloaddition has been confirmed previously [24], provides further support for the spectral assignment.

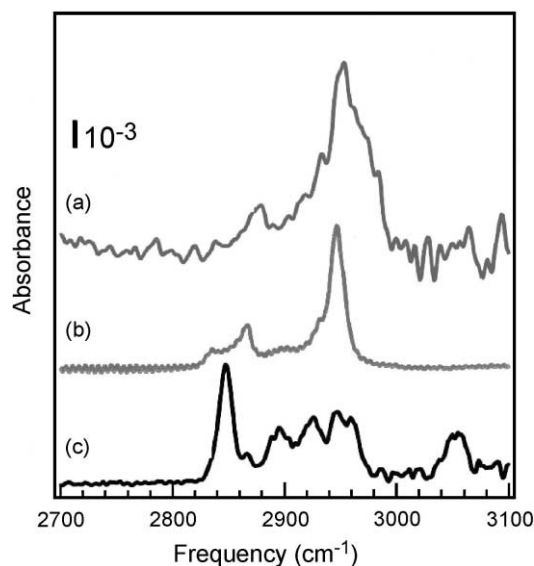


Fig. 6. Infrared spectra of: (a) C(100) after exposure to 10,000L of cyclopentene at room temperature; (b) Si(100) after exposure to 10L of cyclopentene at room temperature; (c) C(100) after exposure to 5L of cyclopentene at 90 K.

#### 4. Discussion

The observed Diels–Alder chemistry of 1,3-butadiene on diamond (100)-2 × 1 indicates that the surface dimers behave like an alkene — with bi-radicals one would expect roughly equal probabilities for [4 + 2] and [2 + 2] cycloaddition. The vibrational spectrum of the [4 + 2] adduct closely resembles that of its molecular analog, cyclohexene. The sticking coefficient for 1,3-butadiene was smaller than on Si(100) [20], which we suggest is due to a stronger  $\pi$  bond on diamond relative to silicon, together with a lower polarizability and shorter-ranged bonding interactions and, therefore, a lower trapping (physisorption) probability.

Formation of the symmetry-forbidden [2 + 2] cycloaddition product in the case of cyclopentene adsorption might be regarded as indicating that surface dimers behave more like a bi-radical than an alkene. However, it is noteworthy that the sticking coefficient is roughly three orders of magnitude smaller on diamond (100) than on silicon (100) [24]. We attribute the more alkene-like reactivity of the diamond surface relative to silicon to a stronger  $\pi$  bond and a symmetric [5–7] rather than a buckled geometry.

The reactivity of diamond (100)-2 × 1 appears to be very similar to that of a highly pyramidalized alkene, i.e., where the olefinic back bonds do not lie in a common plane [32,33]. The best molecular analog to the clean diamond (100) surface is tricyclo[3.3.1.0<sup>3,7</sup>]non-3(7)-ene, C<sub>9</sub>H<sub>12</sub>, shown in Fig. 7. This molecule has been used as a model for the surface in many theoretical papers [5–7] and has been synthesized by Borden and co-workers [34,35]. The “dimer” bond length of C<sub>9</sub>H<sub>14</sub>, the hydrogenated analog, calculated as 1.60–1.63 Å by many authors [5–7], is in

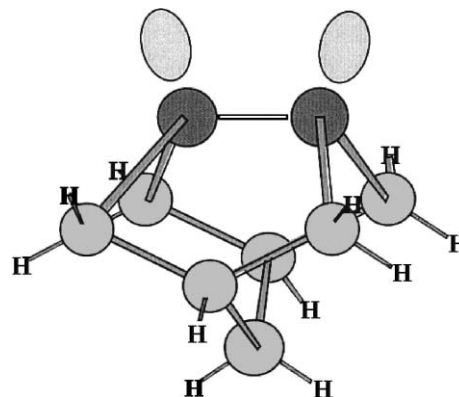


Fig. 7. Ball-and-stick diagram of C<sub>9</sub>H<sub>12</sub> — molecular analog of the C(100) surface. Carbon atoms are represented as shaded balls, with the darker balls representing the surface dimer. The p orbitals of the surface atoms, comprising a highly strained  $\pi$  bond, are indicated by the shaded ovals.

excellent agreement with the measured dimer bond length of diamond (100)-2 × 1:H, 1.60 Å [36]. C<sub>9</sub>H<sub>12</sub> readily undergoes [4 + 2] cycloaddition with a diene, but will also react with itself via nominally symmetry-forbidden [2 + 2] cycloaddition [33]. The vibrational frequency of the “dimer” bond stretch mode, 1496 cm<sup>-1</sup>, is intermediate between  $\nu_{C=C}$  for (CH<sub>3</sub>)<sub>2</sub>C=C(CH<sub>3</sub>)<sub>2</sub>, 1680 cm<sup>-1</sup>, and a C–C single bond frequency, ca. 1330 cm<sup>-1</sup> [34]. Both the vibrational frequency and reactivity pattern of C<sub>9</sub>H<sub>12</sub> indicate a very highly strained double bond.

In conclusion, we have demonstrated the surface dimers on diamond (100)-2 × 1 undergo reactions with simple olefins that can be understood using concepts from organic chemistry, but show behavior that is intrinsically different from unstrained alkenes due to the geometric deformation associated with the bonding structure of the surface. Cycloaddition reactions can be used for well-defined functionalization of the diamond surface.

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