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Hydrocarbon adsorption on Si(001): when does the Si dimer bond break?

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Abstract

We have used ab initio calculations to study the structural and electronic properties of two simple hydrocarbons, C₂H₄ and C₂H₂, adsorbed on the Si(001) surface. The hydrocarbons adsorb above surface dimers, saturating the dangling bonds and in the process weakening the carbon–carbon bond of the molecule. We found that the σ -bond of the silicon dimer remains intact but may be broken by post-hydrogenation of the surface. This resolves an apparent conflict between previous calculations and recent experiments. © 1997 Elsevier Science B.V. All rights reserved.

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1. Introduction

The adsorption of molecules at surfaces is important both for applications in catalysis and for semiconductor growth technologies which are reliant on surface deposition and processing techniques. New direct observations have become possible with the spectacular development of the scanning tunnelling microscope (STM) [1], which allows direct real-space imaging and manipulation of adsorbed systems.

Extensive experimental studies have been made of the adsorption of C₂H₄ and C₂H₂ on Si(001)-(2 × 1) surfaces, and of subsequent desorption [2,3], and of the dependence on prior H coverage

[4]. The conclusion is that the adsorption of C₂H₄ occurs by di-sigma attachment to Si₂ dimer sites. However, an active debate continues over whether the structure of the dimers is retained beneath the adsorbed molecules [5–8] (Fig. 1a) or whether the dimer bond is cleaved during adsorption [2,3,9,10] (Fig. 1b). The most recent theoretical paper [11] suggests that the dimer bond indeed continues to exist after the molecule is adsorbed. It was, however, difficult to reconcile this result with experiments reported recently [9] which showed that atomic hydrogen could be co-adsorbed onto surfaces already saturated with C₂H₄, and that Si–H bonds were formed in this process. It has been argued [9,10] that this was only possible if the dimer bond is *broken*. In this paper, we address the issue of hydrogen co-adsorption directly and show that the dimer bond is broken only *after* co-adsorption of hydrogen, thus remov-

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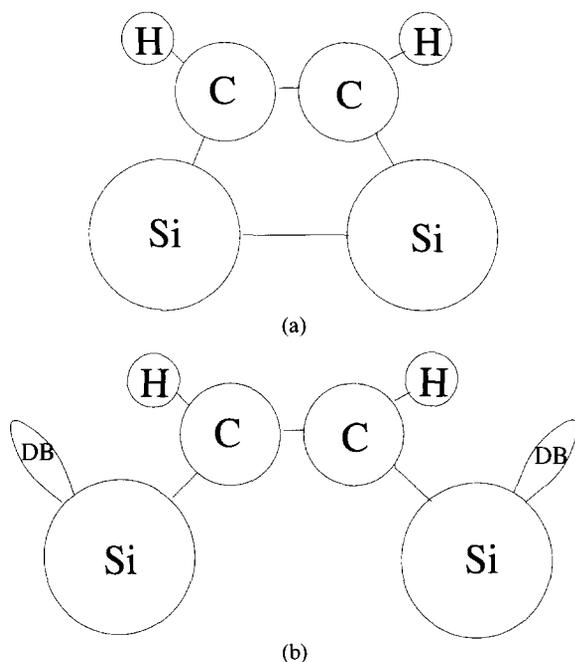


Fig. 1. Schematic diagram of the alternative bonding scenarios for C_2H_2 atop a dimer: (a) dimer bond retained; (b) dimer bond broken. "DB" denotes dangling bond.

ing the discrepancy between experiment and theory. After completion of our work, we received a preprint of another paper [12] reporting similar results.

Temperature-programmed desorption (TPD) studies [2] show that almost all C_2H_4 molecules come off intact between 550 and 600 K; the energy of adsorption, extrapolated to zero coverage, is 1.65 ± 0.07 eV per molecule (38.0 ± 1.5 kcal mol $^{-1}$). For C_2H_2 [3] the temperature for desorption is higher but less than 5% of a monolayer is desorbed as C_2H_2 . The remainder comes off as H_2 , leaving carbon on the surface. The adsorption energy of C_2H_2 cannot therefore be deduced but it is certain to be higher than that of C_2H_4 .

Surfaces exposed to C_2H_4 and C_2H_2 have been studied by STM [13,14] with the sample biased both negative and positive relative to the tip (± 2 V), thus imaging both the filled and the empty states. At +2 V sample bias the molecules stand out with strong contrast against the dip in the centre of the dimers associated with the node of

the antibonding orbital. At -2 V sample bias the molecules appear to have about the same height as the dimers but to be slightly smaller overall. Around 50% coverage the C_2H_4 molecules prefer to adsorb on alternate dimer sites [15], forming either (2×2) or $c-(4 \times 2)$ local periodicity, depending how the adsorption on adjacent dimer rows lines up. The order is short range, so that the domains are small, and the periodicity would not be picked up by any practical diffraction technique. The STM images are consistent with di-sigma attachment to Si dimers but do not reveal whether the dimer bond remains intact.

There have been previous semi-empirical calculations for adsorbed C_2H_2 [16] and C_2H_4 [17] using unrelaxed bulk positions for the Si atoms, and non-self-consistent cluster calculations for adsorbed C_2H_2 [18] and C_2H_4 [19] using symmetric dimer positions for the Si surface. There have also been MINDO calculations in a slab geometry [7,20] in which the positions of the adsorbate atoms and the top four layers of substrate were relaxed, and recent ab initio molecular dynamics calculations (in the generalized gradient approximation) on adsorbed C_2H_2 [11]. These most recent calculations showed that the dimer bond remains when ethylene is adsorbed and that the vibrational frequencies obtained in this situation are in good agreement with those measured experimentally.

2. Description of calculations

We have used relaxation of the atoms by the ab initio Car–Parrinello technique [21] to study this problem. The electronic states are treated within the local density approximation (LDA) to density functional theory [22–24]. We solved the Kohn–Sham equations by the projector-augmented wave (PAW) method [25] rather than by using pseudopotentials. By treating explicitly the core electrons and the correct nodal structure of the valence wavefunctions, the method makes possible an efficient treatment of first-row elements such as carbon while retaining the convenience and flexibility of a plane-wave based treatment of the electron wavefunctions.

If the generalized gradient approximation

(GGA) were to be used rather than the LDA, we should expect differences in the quantitative detail of our results (such as the molecular adsorption energies) but not in the qualitative features of bond formation and breaking which are our main focus. This expectation is supported by the previously published work [11] applying the GGA to the case of isolated C_2H_2 only; these results are very similar to ours on this system.

Our use of augmented plane waves constrained us to work with periodic boundary conditions in all three directions. The calculations were performed in a 4×2 unit cell containing eight surface atoms that are equivalent in the undistorted diamond lattice. We used the experimental cubic lattice constant of 5.43 Å. This is very close indeed to the LDA bulk lattice constant (5.44 Å) obtained using the PAW method with the same plane-wave cut-off. Molecules are adsorbed on only one side of the slab. We included four layers of silicon atoms perpendicular to the surface and the height of the unit cells in this direction is 10.86 Å, with a vacuum gap of approximately 6.9 Å between periodic images of the silicon slab. This is ample to allow the inclusion of an adsorbed hydrocarbon without introducing any significant interaction between the slabs in the total energy calculations. We checked that there is no significant change in the electronic state if the vacuum gap is increased to 12.3 Å. We estimate that the energy of the dipole–dipole interaction between the weakly polar Si–C bonds in adjacent cells is about 0.5 meV, much too small to be a significant source of error. All atoms in the slab were relaxed in the calculations. We checked that our results for the adsorption geometry and energetics do not depend on the number of layers used to represent the silicon surface by repeating the calculations for a silicon slab eight layers thick with hydrogen atoms saturating the dangling bonds on the lower surface. In this case, the two lowest silicon layers and the hydrogen layer were fixed. We used a plane-wave cut-off of 25.0 rydbergs for the electron wavefunctions and sampled only the Γ -point of the reduced Brillouin zone. The energy cut-off is considerably more than required for calculations on silicon but is necessary to give a good description of the adsorbates. We checked that the description of the

adsorbates is not improved by increasing the cut-off to 35.0 rydbergs.

3. Results

3.1. Isolated molecules

We first discuss the case of C_2H_4 . We found that the stable position for adsorption of a molecule is indeed directly above a dimer. The hybridization of the C atoms changes from sp^2 in free C_2H_4 to sp^3 (as in C_2H_6). Consequently, the bond length increases from 1.33 Å in the free molecules to 1.53 Å as in C_2H_6 . The H–C–H bond angle is 106.7° and the H–C–C bond angle is 113° , relatively close in each case to the 109° of ideal sp^3 bonding. The C atoms of the molecule form covalent bonds with the Si atoms of the dimer, of length 1.95 Å. The Si atoms (which were formerly sp^3 hybridized) become more sp^2 -like, with sp^2 bonds to the carbon and the sublayer Si atoms and the remaining p orbitals forming an Si–Si dimer bond.

The adsorption energy for a single C_2H_4 molecule in our 4×2 unit cell is 1.57 eV ($36.2 \text{ kcal mol}^{-1}$); this is consistent with the result of $1.65 \pm 0.07 \text{ eV}$ ($38.0 \pm 1.5 \text{ kcal mol}^{-1}$) from thermal desorption measurements, and indeed the agreement is unusually good for a calculation using the LDA. The adsorption energy for a second molecule at an adjacent site along a dimer row is lower: we found only 1.07 eV ($24.7 \text{ kcal mol}^{-1}$). We broke down the difference of 0.25 eV per nearest-neighbour pair ($5.8 \text{ kcal mol}^{-1}$) into contributions: 0.19 eV ($4.4 \text{ kcal mol}^{-1}$) can be accounted for by a combination of direct steric repulsion (0.02 eV or $0.5 \text{ kcal mol}^{-1}$), substrate-mediated elastic interaction [26] (0.10 eV or $2.3 \text{ kcal mol}^{-1}$) and electrostatic dipole interactions (0.07 eV or $1.6 \text{ kcal mol}^{-1}$).

We now proceed to C_2H_2 . The most favoured adsorption site is again above a dimer. Once again the carbon–carbon bond of the molecule lengthens, from 1.21 Å in the isolated molecule to 1.37 Å (as compared to 1.33 Å in free C_2H_4), and the C atoms change from sp hybridization to sp^2 . The H–C–C bond angle is reduced from 180° in the

free molecule to 123° , and the H–C–Si bond angle is 132° .

The adsorption energy for an isolated molecule of C_2H_2 is 2.38 eV or $54.9 \text{ kcal mol}^{-1}$ (obtained in a 4×2 surface unit cell). It is larger than the corresponding energy for C_2H_4 , as we would expect because it costs more energy to change a double bond to a single than to change a triple bond to a double. We found a repulsive interaction between molecules adsorbed along a dimer row of 0.19 eV ($4.4 \text{ kcal mol}^{-1}$) per nearest-neighbour pair. We cannot compare our result with a TPD measurement because dissociation of the molecules occurs on the surface before they can desorb. It might be interesting instead to measure the adsorption energy directly by surface calorimetry techniques which are capable of resolving heats of reaction from very small samples of adsorbed gases [27,28].

Our calculations show that the dimer bond beneath the adsorbates remains intact. There is only a small change in the Si–Si bond length on adsorption of either C_2H_4 or C_2H_2 . Furthermore, the bonding charge density is still present. Fig. 2a shows a (110) section through a plane including a dimer with an adsorbed C_2H_4 . There is a high density associated with the carbon atoms while the hydrogen atoms (which do not lie in this plane) are not visible. The charge density of the dimer bond is still clearly visible. Fig. 2b shows a (1 $\bar{1}$ 0) section through the structure, through a plane bisecting the dimer bond. The high density between the silicon atoms and the near-circular symmetry in Fig. 2b suggests a σ -bond. Fig. 2c shows the negative part of the change in charge density that occurs on adsorption, with a much more sensitive greyscale. Note the reduction in bonding charge above and below the main Si–Si dimer bond, which can be thought of as the destruction of the π component (but not the σ component) of the dimer bond.

3.2. Molecules with coadsorbed hydrogen

This completes our description of the bonding of C_2H_2 and C_2H_4 to the surface. Our conclusion that the dimer bond is unbroken in both cases supports the results of Imamura et al. [11] (for

C_2H_2 only); our energy difference between the broken-dimer and intact-dimer structures (see below) is also in reasonable agreement with their value of 1.08 eV (25 kcal mol^{-1}). However, as mentioned above, recent experimental evidence appears to contradict the picture we have presented: hydrogen co-adsorption experiments indicate the existence of unsaturated dangling bonds on the surface [29]. In contrast, we will now show that the dimer bond is broken *only* in the process of hydrogen co-adsorption and that hydrogen does not attach to *pre-existing* dangling bonds.

The experiments [9] involved exposing a Si(001)-(2 \times 1) surface saturated with deuterated C_2H_4 to atomic hydrogen. High resolution electron energy loss spectroscopy (HREELS) measurements gave a spectrum almost identical to that following initial C_2H_4 chemisorption, with the addition of a strong Si–H vibration at 2100 cm^{-1} . Temperature programmed desorption (TPD) experiments exhibited almost the same C_2H_4 desorption peak as without post-hydrogenation and isotopic mixing experiments showed no exchange between C_2H_4 and hydrogen to within the isotopic purity of the chemicals used. These results show that on post-hydrogenation the hydrogen attaches to Si dangling bonds. Each surface Si atom also has an Si–C bond and two Si–Si bonds to the layer below, so the dimer bond can no longer exist.

To reconcile this observation with our finding that the dangling bond is retained, we performed additional calculations on a surface with co-adsorbed C_2H_2 and H. We found that the dimer bond breaks in order to create Si–H bonds. Fig. 3a shows the electron density in the (110) plane before the hydrogen was added. The geometry and the charge distribution around the silicon is very similar to that shown for the case of C_2H_4 adsorption in Fig. 2a and, in particular, the Si–Si σ -bond is still present. On introducing two hydrogen atoms close to the dimer silicon atoms and relaxing the system the situation changes to that shown in Fig. 3b. Two changes are evident: the dimer atoms have moved apart (to a separation of 3.64 Å) and the electron density between them has almost vanished. The hydrogen atoms are attached to the dangling bonds on the silicon atoms, just as was

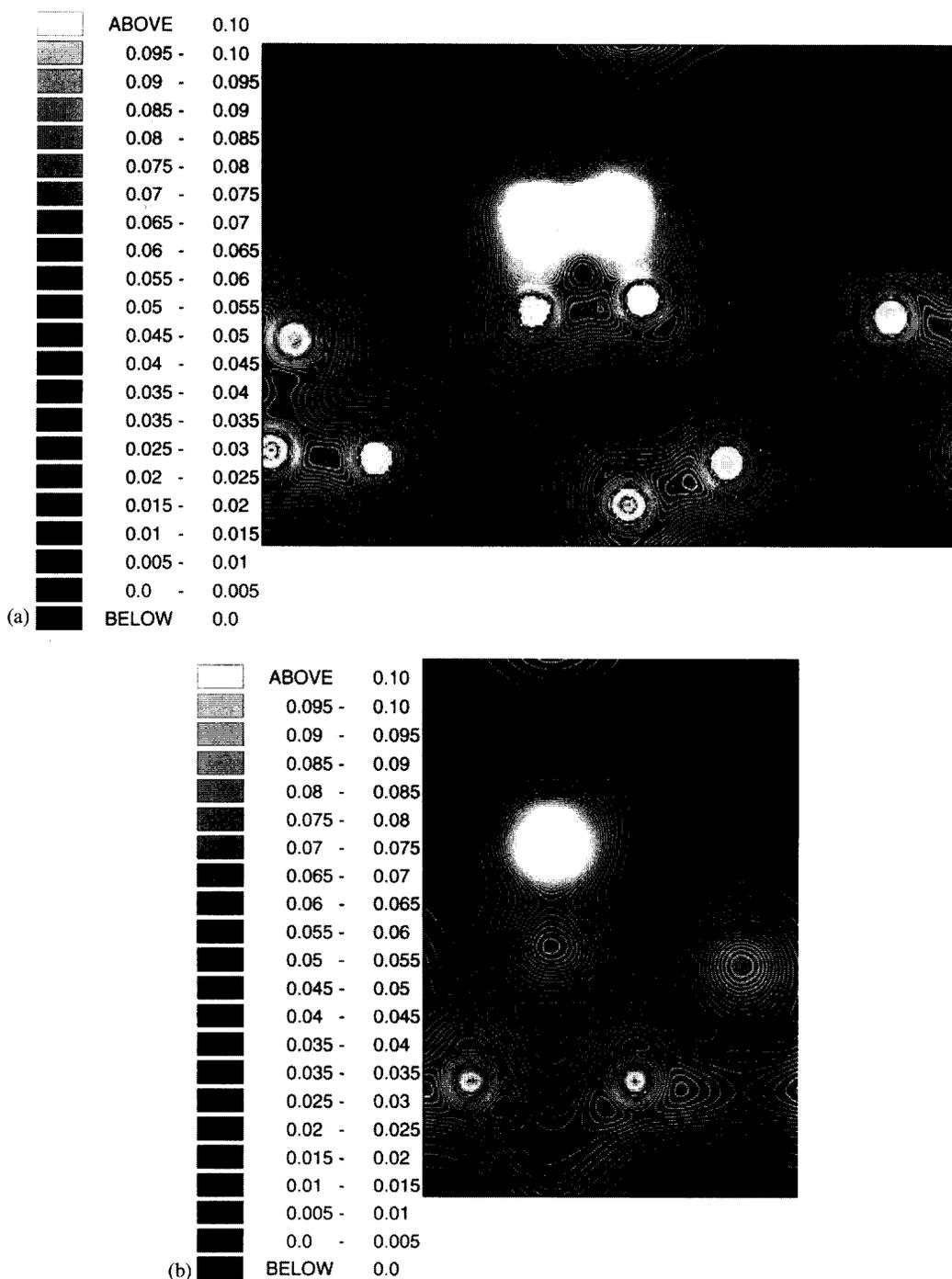


Fig. 2. Valence electron density: (a) in a (110) plane containing the C–C bond of a C_2H_4 molecule and silicon dimer; (b) same system in a $(1\bar{1}0)$ plane through the centre of the dimer bond; (c) the difference in the charge density in the $(1\bar{1}0)$ plane produced by adsorption. In (a) and (b) charge density contours are in steps of 0.05 atomic units from 0.00 (black) to 1.00 and above (white). In (c) contours are in steps of 2.5×10^{-4} atomic units from -0.005 (black) to 0.000 or above (white).

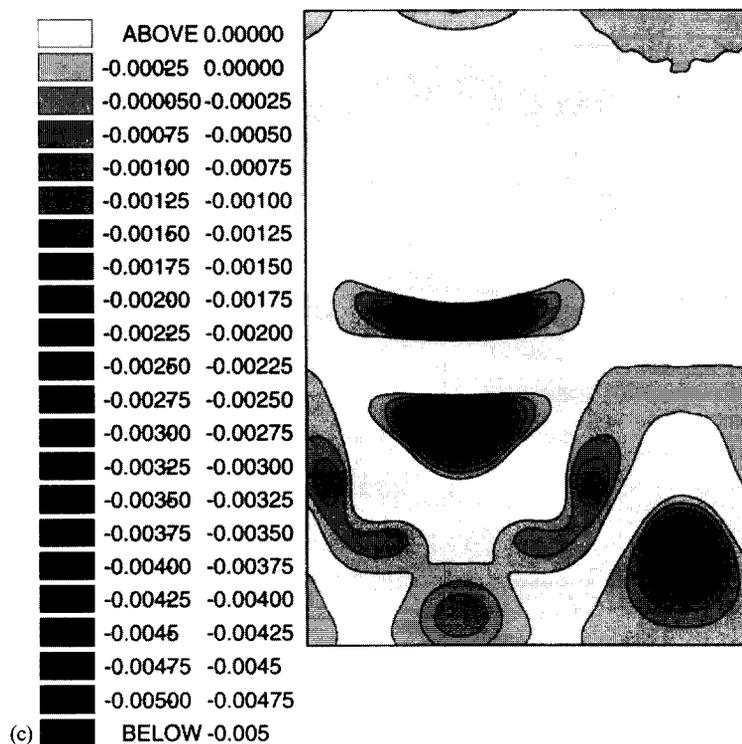


Fig. 2. (continued).

suggested by the experiments. These results indicate that the dimer bond is indeed broken in the presence of co-adsorbed hydrogen and C_2H_2 but that the bond cleavage occurs as a result of the post-adsorption of the hydrogen rather than of the initial adsorption of the hydrocarbon. When the hydrogen atoms are removed this broken-dimer structure has an energy 1.54 eV ($35.5 \text{ kcal mol}^{-1}$) higher than the structure of Fig. 3a; if the atoms are allowed to move, the dimer bond re-forms and the structure relaxes spontaneously back to that shown in Fig. 3a. We therefore predict that the broken-dimer structure is unstable. This finding agrees with the results presented in [12] but disagrees with the results of Imamura et al., who found that the broken-dimer structure was metastable.

We also performed total energy calculations for the case in which only a single hydrogen atom is co-adsorbed on the same dimer as the C_2H_2 molecule. In this case, we found an intermediate result: the silicon dimer bond is stretched to a separation

of 2.84 Å and some σ -bond charge density remains. This suggests that weakening of the dimer bond at low coverages of atomic hydrogen might provide a pathway leading to complete bond cleavage at higher coverages. It should be noted, however, that our calculations have addressed only the location of stable minima on the potential energy surface of the system and we have not considered their accessibility.

Our findings are supported further by the observation of a small downshift in the C–C stretching frequency of the hydrocarbon when hydrogen co-adsorbs (W. Widdra, private communication). This strongly suggests that co-adsorption takes place on the same dimers that are already occupied by the hydrocarbons.

4. Discussion

Our results are reminiscent of those for hydrogen adsorption on Si(001), which has been well studied

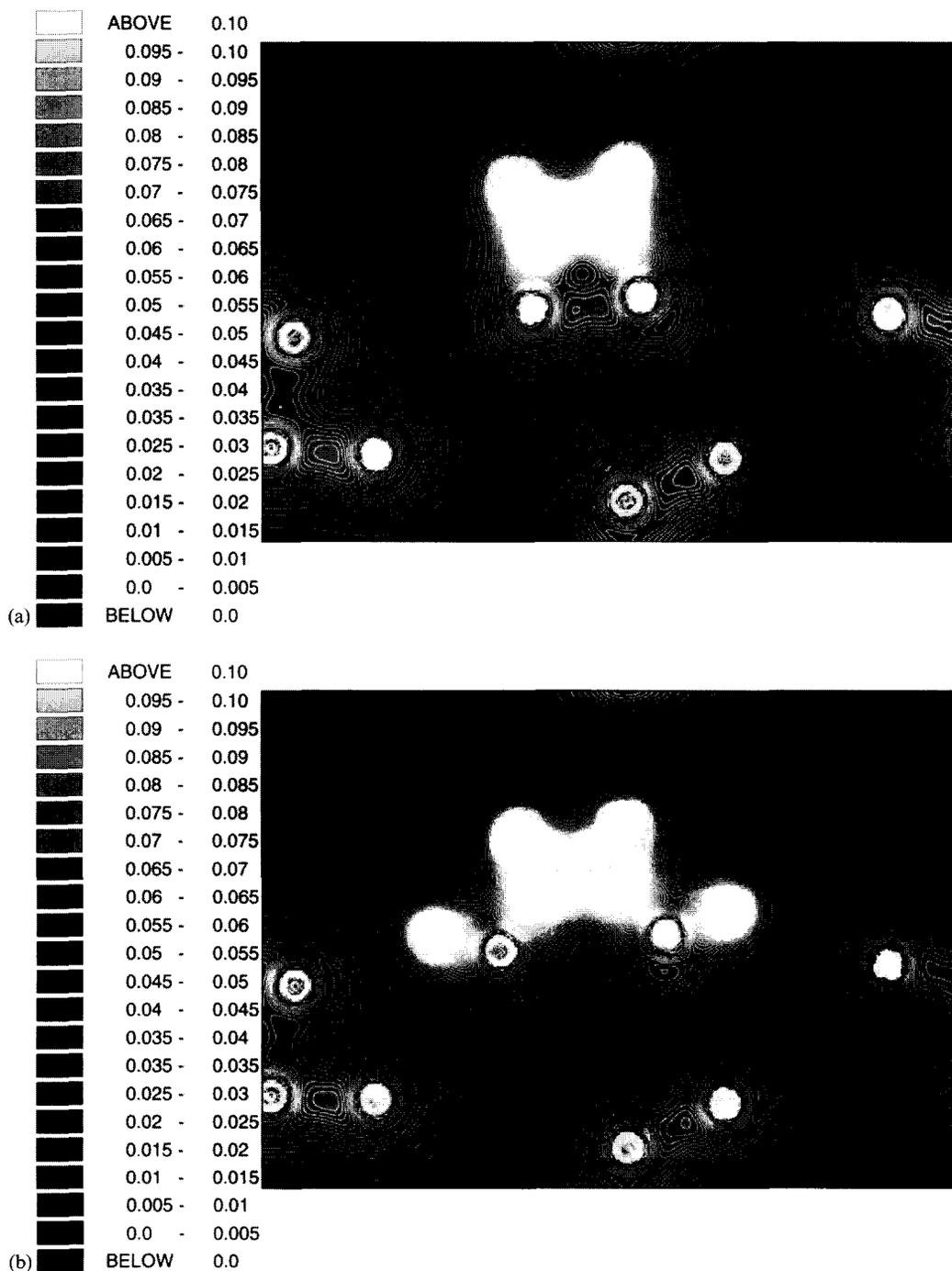


Fig. 3. Contour plots of valence charge density: (a) in a (110) plane containing the C–C bond of an adsorbed C_2H_2 molecule and a silicon dimer; (b) for the same system but with a co-adsorbed hydrogen atom attached to each silicon. Note the disappearance of the silicon dimer bond in (b). Charge-density contours are in steps of 0.05 atomic units from 0.00 (black) to 1.00 and above (white).

both experimentally [30] and theoretically [31,32]. The monohydride phase (i.e. two hydrogen atoms and therefore two covalent bonds per dimer) does not exhibit cleavage of the dimer σ -bond. Instead, higher coverages of hydrogen are required to break up the dimer structure and produce a 1×1 or 3×1 surface periodicity with up to two covalent bonds per surface atom. This is similar to our finding that hydrocarbon adsorption (two covalent bonds per surface dimer) is not sufficient to break the dimer bonds; an increase in the number of bonds per dimer to four by hydrogen co-adsorption is necessary to make this happen.

Another interesting comparison can be made with the adsorption of the same hydrocarbons on the As-rich GaAs(001) surface. Here, although a dimerization exists on the clean surface, there is an additional electron available to each As atom, which has the effect of converting its dangling bond into a much less reactive lone pair. In this respect the extra electron plays much the same role as co-adsorbed hydrogen in silicon. One would therefore expect that hydrocarbon adsorption on this surface would be very much more likely to proceed via cleavage of the dimer bonds. Total energy calculations confirm this [33]; although there is a metastable configuration in which the molecule is adsorbed atop an unbroken dimer bond, in the stable structure the dimer bond is indeed broken.

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