

Hydrocarbon adsorption on a diamond (100) stepped surface

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We present theoretical studies of various hydrocarbon radicals and molecules on the (100) surface of diamond. We use molecular dynamics and a dynamical quenching algorithm to calculate the energetics of different adsorption configurations, allowing for full relaxation of the underlying lattice. We use a parametrized many-body potential function that has been used for energetics calculations with a great deal of success [D. Brenner, *Phys. Rev. B* **42**, 9458 (1990)]. Our calculations show that adsorption of hydrocarbons on either the flat terraces or near different types of step edges give small variations of binding energies and equilibrium configurations. This reflects the strong covalent bonding pervasive in the carbon systems, which forces the strain fields and bonding energetics to be determined to a great extent by the local environments. We analyze the consequences of these results for the dynamics of growth under typical conditions.

I. INTRODUCTION

Synthesis of diamond and diamondlike films at low pressure and temperature has received increasing attention in recent years.¹ The interest in these materials originates from their useful properties, which include extreme hardness, high thermal conductivity, and chemical inertness.² Moreover, these films are found to be useful materials for commercial applications such as machine tools, optical coatings, thermal management in electronics, and even possibly high-temperature electronic devices.³ To improve or realize many of these applications, it is imperative to optimize the conditions under which films are fabricated so that well-controlled growth of diamond of good quality is achieved at high rates. It is therefore important to understand the nucleation and growth processes at the molecular level, so as to gain insight into ways to improve growth.

The incorporation of hydrocarbon species to surface radical sites is very likely responsible for the films' initial growth. It is therefore of great interest to study the details of the adsorption of various hydrocarbon molecules on the diamond surface.^{4,5,7-11} Recently, Larsson, Lunell, and Carlsson employed an *ab initio* molecular orbital technique to study the adsorption of H, CH₃, CH₂, C₂H, CH, and C₂H₂ on the (111) surface of diamond.¹¹ Mintmire *et al.*⁷ and Pederson *et al.*⁸ investigated the binding of various one- and two-carbon species to the (111) surface using a density functional scheme. Using a semiclassical potential, Brenner calculated binding energies of various hydrocarbons on the (111) surface,⁵ while Mehandru and Anderson employed a semiempirical tech-

nique to study the adsorption and migration of H, CH₃, CH₂, and C₂H₂ on both the (111) and (100) surfaces.^{4,9} However, these authors did not consider adsorption of C₂H and C₂H₄ on the (100) face, and these species may well be present in the gas phase during typical diamond deposition processes.

On the other hand, most of these theoretical efforts have provided no information about binding on stepped surfaces. Zhu *et al.*¹² explored the possibility that growth may occur at the steps, as evidence from scanning-tunneling-microscopy and atomic-force-microscopy experiments would seem to suggest.¹³ Despite the anticipated different reactivity of steps, little has been done theoretically to explore hydrocarbon binding near single-layer high steps on the diamond surface. Although adsorption of H and CH₃ near one specific type of stepped (100) surface has been analyzed,¹² the adsorption of other hydrocarbon species has not been reported.

In this paper, we investigate the adsorption and structures of hydrocarbons such as CH₃, CH₂, C₂H, C₂H₂, and C₂H₄ on the flat terraces and near step edges of diamond (100) surfaces. The admolecules considered in this work may be formed in the gas phase during film growth.¹⁴ Since *ab initio* methods are computationally intensive and therefore somewhat restricted in the size of the systems that can be examined, we use here molecular dynamics simulations with semiclassical potentials to assist our understanding with only modest demands on computer resources. An empirical potential function for the hydrocarbon system,⁵ in combination with a dynamical quenching technique,¹⁵ was employed to calculate the minimum energy configurations of the admolecule-

substrate systems.

Our results show that binding to radical sites is determined to a great extent by the local energetics. This high site-specificity is likely due to the strong covalent bonding between carbon atoms, and gives rise to small variations between binding on terrace sites and binding near step edges. In fact, we find that many times the binding to sites near edges is weaker than on equivalent sites on the flat terraces. This unfavorable situation is the result of strains built in the step itself, which tend to increase with adsorption of the studied hydrocarbon radicals. In other cases, however, the energetics of both configurations is nearly equivalent, which may give rise to an effectively preferential reactivity near edges, as steric hindrance for incoming molecules and radicals is greatly reduced near the edge.

The methodology is presented in Sec. II, while the results of the calculations are presented and discussed in Sec. III.

II. THEORETICAL METHOD

The binding energies and the resulting minimum energy structures of the various hydrocarbons on the flat and stepped diamond (100) surfaces were determined through molecular dynamics (MD) simulations. We employ an empirical many-body potential which realistically describes bonding in hydrocarbon systems and assumes the form⁵

$$U = \sum_{j>i} [V_r(r_{ij}) - B_{ij}V_a(r_{ij})], \quad (1)$$

where V_r and V_a are terms which represent pair-repulsive and pair-attractive interactions, respectively, while B_{ij} is a many-body bond order term which depends on atomic coordination and angles.⁵ This potential is based on a Tersoff bond-order expression which contains terms that correct for overbinding of radicals and consider nonlocal effects.¹⁶ The predicted energetics and dimer bond lengths for the case where the dimer reconstructed surface is H-terminated agree with predictions from molecular mechanics calculations.⁵ For molecules ranging from alkanes to large aromatic molecules to radicals, binding energies are within 1% or better for over 80% of the molecules considered. This same function also provides a good description of energetics and bonding of one- and two-carbon species on a diamond substrate. The predicted adsorption energies of molecules such as CH_3 and C_2H_2 on the (111) substrate are in good qualitative agreement with results from semiempirical calculations.^{4,5}

The simulation system used for calculating the energies on the flat (100) surface consists of an eight-layer-thick carbon slab with 18 atoms per layer. The (100) face is exposed, and naturally reconstructed into a (2×1) dimerized surface terminated by hydrogen. The energy calculations are performed with periodic boundary conditions in two dimensions. The bottom layer is held fixed and the remaining atoms plus the admolecule are allowed to move in the MD simulations. For the calculation of energies near step edges, the S_A and S_B step types were

created on a properly dimerized surface. According to Chadi's nomenclature,¹⁷ S_A indicates a single-atom step whose upper terrace contains dimers oriented perpendicular to the step edge, while S_B denotes a single-layer step with dimers on the upper terrace oriented parallel to the step edge (see Fig. 1). Notice that there are two types of S_B step structures. One is the nonbonded type with no rebonded atoms on the lower terrace, while rebonded atoms appear on the lower ledge for the bonded type. We consider these two types in this work, in order to study the effects of different local strain on the binding energies.

The S_A and S_B type stepped structures used in this work have horizontal dimensions of 6×4 and 8×4 atoms per layer, respectively (see Fig. 1). Periodic boundary conditions were used at the edges of the slab. To make sure that the atoms below the steps were in their proper state of stress, we initially fixed the bottom layer and let the remaining layers relax through MD techniques. During relaxation in the presence of an admolecule, the bottom four layers were kept to their fully relaxed configurations in the absence of the admolecule, allowing the remaining layers to move. While reducing the computational demands, we found that fixing these additional layers did not change our results in a significant fashion.

The minimum energy configurations of our system were achieved using the technique of dynamical quenching.¹⁵ The atoms are allowed to respond to internal forces and are accelerated accordingly. The resulting kinetic energy of the system increases as the atoms

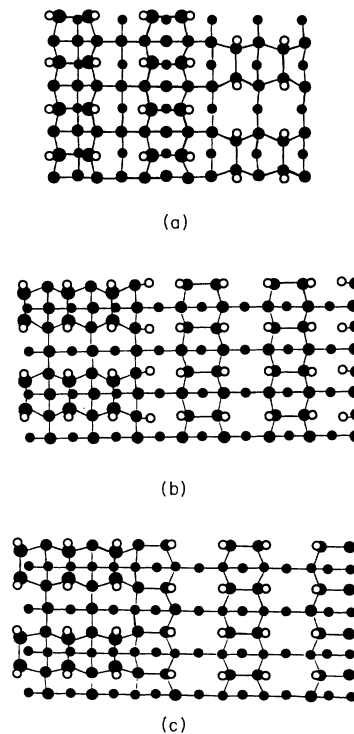


FIG. 1. The three types of diamond (100) stepped structures: (a) S_A , (b) $S_B(n)$, and (c) $S_B(b)$. Portions shown are unit cells used in this work for each step (periodic 6×4 for the S_A structure and periodic 8×4 for the S_B structure). Carbon atoms appear shaded.

accelerate until it reaches a maximum. The kinetic energy of the system is then removed by setting all the velocities to zero at one time, after which the atoms are allowed to accelerate again and the quenching process is repeated. Several quenching cycles (typically 20 per atom) are needed to obtain the minimum energy structures (determined to within a few meV). The adsorption energies quoted below are defined as the difference between the total energy of the surface-adsorbate system minus the total energy of the bare surface minus the energy of the isolated molecule. Notice that only one adsorbate molecule per unit cell (as defined above) was considered in our simulations. Higher relative coverage may indeed affect the adsorption probabilities,^{5,6} but typical growth conditions make that situation less likely. We will treat multiplicity and hyperthermal effects, possible in a molecular beam setup, in a future publication.

III. RESULTS AND DISCUSSION

A. Adsorption on the flat diamond (100) (2×1) surface

Table I and Fig. 2 summarize the results of the theoretical studies of single hydrocarbon molecule adsorption on the flat diamond (100) surface. The predicted energetics and structures for CH_3 and C_2H admolecules were obtained by removing a hydrogen atom from a H-terminated (100) surface and replacing it with the molecule, after the structure is allowed to relax completely. For CH_2 , hydrogen atoms attached to two carbon atoms belonging to a dimer pair were removed and replaced by the molecule. The molecule was placed such that it is above and lies in between the surface carbon-carbon bond. The carbon-carbon bond in the C_2H radical was placed such that it is perpendicular to the surface. In the case of C_2H_2 and C_2H_4 , two possible binding sites were considered. A *bridge* site where C_2H_2 or C_2H_4 bridges carbons belonging to the same dimer pair, and a *cave* or *trough* site where the two-carbon molecule bridges carbons belonging to two adjacent

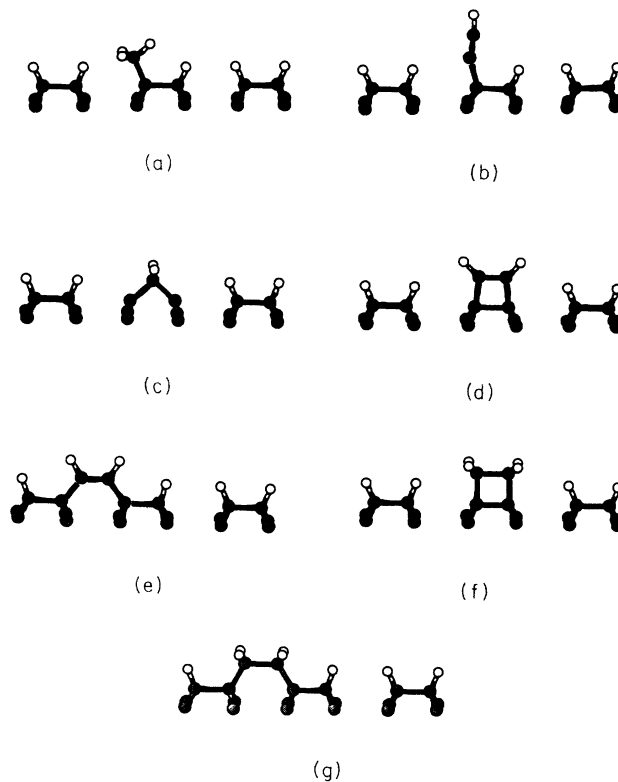


FIG. 2. Configurations of the various admolecules on the flat diamond (100) surface. (a) CH_3 , (b) C_2H , (c) CH_2 , (d) C_2H_2 (bridge site), (e) C_2H_2 (cave/trough site), (f) C_2H_4 (bridge site), and (g) C_2H_4 (cave/trough site). Dimer pairs shown are along the $[0\bar{1}1]$ direction. Carbon atoms appear shaded.

cent dimers (aligned with bonds end to end). In this configuration, the admolecule's carbon-carbon bond is parallel to the surface plane. We find that a vertical placement yielded either hydrogen detachment or/and higher energies. All the configurations were relaxed to their minimum energy structures using the dynamical quenching technique described above.

TABLE I. Adsorption energies and structures for various hydrocarbon molecules chemisorbed onto the diamond (100)-(2×1) surface. BE is the adsorption energy of the single hydrocarbon molecule on the surface. h is the height of the adsorbed C_xH_y carbon(s) with respect to the surface plane. $r(\text{C}_s-\text{C}_a)$ is the bond length between the surface carbon(s) and the adsorbed C_xH_y carbon(s). $r(\text{C}_a-\text{H}_a)$ denotes the C-H bond length of adsorbed hydrocarbon. $\theta(\text{H}-\text{C}-\text{H})$ refers to the H-C-H bond angle in the adsorbed CH_3 and CH_2 . $r(\text{C}_a-\text{C}_a)$ is the bond distance between the carbons of the adsorbed two-carbon molecule. θ_1 is the tilt of C- CH_x bond from the surface normal. θ_2 is the tilt of the C_2H_2 or C_2H_4 C-H bond away from the surface plane. The values in parentheses were obtained using semiempirical calculations (see Ref. 9). Values before and after a slash refer to binding energies on the bridge and trough site, respectively.

	CH_3	C_2H	CH_2	C_2H_2	C_2H_4
BE (eV)	4.18(3.38)	4.34	4.67(6.30)	3.62(3.20)/6.54(3.80)	2.85/4.88
h (Å)	1.48(1.47)	1.49	1.03(1.26)	1.48(1.51)/1.17(1.25)	1.56/1.34
$r(\text{C}_s-\text{C}_a)$ (Å)	1.55(1.59)	1.54	1.52(1.52)	1.53(1.52)/1.50(1.59)	1.58/1.55
$r(\text{C}_a-\text{H}_a)$ (Å)	1.07(1.09)	1.07	1.07(1.09)	1.06(1.09)/1.08(1.09)	1.07/1.07
$\theta(\text{H}-\text{C}-\text{H})$ (deg)	109(111)		106(116)		
θ_1 (deg)	21(19)				
θ_2 (deg)				46(46)/60(60)	
$r(\text{C}_a-\text{C}_a)$ (Å)		1.20		1.35(1.38)/1.34(1.38)	1.59/1.60

The trend in adsorption energies of CH_3 , CH_2 , and C_2H_2 given in Table I are in qualitative agreement with results from semiempirical calculations.⁹ The predicted structures of these molecules on the surface are also comparable with the values obtained there. The calculated energy and long bond length for CH_3 suggest that interaction of the radical with the surface dangling bond forms a strong *single* bond [indeed, typical single-bond energy is 4.1 eV (Ref. 18)]. We find that cave/trough site binding of C_2H_2 is clearly preferred over the bridge site. Unlike CH_3 , and not unexpectedly, we do not observe any stable onefold interaction of this admolecule to the substrate. In the case of CH_2 , we find that the configuration shown in Fig. 2(c) is the most stable one. The strained surface carbon-carbon bonds were released giving rise to twofold interaction of the molecule with the surface. We find that onefold adsorption of C_2H_2 to a dimer carbon with the carbon-carbon triple bond tilted away from the surface is not energetically favorable. This qualitative agreement with the semiempirical calculations indicates that the empirical potential can accurately predict trends in binding energies of the system considered in this work.

Various theoretical studies have shown that CH_3 may be a possible growth species during diamond deposition.¹⁹ Recent molecular dynamics simulations revealed that addition of CH_3 to a (100) radical site is a relevant growth mechanism.¹⁰ This suggestion is supported by experimental results showing that the methyl radical is the dominant species under hot filament chemical vapor deposition (CVD) for both the (100) and (111) diamond substrate orientations. Our results show that chemisorption of this radical to the surface is indeed strong, and produces a bond with the surface carbon radical tilted by about 21° with respect to the surface normal. Adsorption of CH_3 on the (100) face and subsequent abstraction of one of its hydrogens will promote β -scission which is a necessary condition for continued growth on this surface. Notice that adsorption of a methyl radical and the removal of one of its hydrogens is similar to the one-step process where CH_2 from the gas phase binds with a surface radical on the (100) surface. This would indicate that CH_2 is also an important growth precursor. Indeed, the molecular dynamics simulation studies support this suggestion.¹⁰ The stability of this and other adsorbed species to the addition of energetic hydrogen and other radicals will be the subject of a future publication.

Table I shows that the carbon-carbon bond lengths of the chemisorbed C_2H_2 on both adsorption sites lie between the double (1.34 Å) and triple (1.20 Å) bond lengths.¹⁸ This drop is due to the twofold interaction of acetylene with the surface. As noted before, adsorption on the bridge site is less favorable, as evidenced by its smaller binding energy. Notice also that, in contrast to binding on the cave site, the resulting configuration of acetylene over a bridge site is more strained due to the constraint of the underlying lattice. It is not clear whether these energies for the acetylene admolecule can support a growth mode on the (100) surface. Nevertheless, some useful conclusions can be drawn from

these results. First, at least two radical sites situated on two adjacent surface carbon or on carbons belonging to the dimer pair are required for stable chemisorption of C_2H_2 to occur. Adsorption of C_2H_2 over carbons on adjacent dimers is preferable. However, this adsorption mode is less probable since the surface conditions under a gaseous hydrogen atom environment make it unlikely that two radical sites would reside on dimers next to each other. Simulations predict that under common CVD conditions, the reconstructed (100) surface with radical sites is composed mainly of segregated regions of H-terminated and non-H-terminated double-bonded carbon-carbon dimers.⁵ This implies that bridge sites are more available than trough sites, except of course for the domain boundaries. It is nevertheless also possible that under some conditions the kinetics of the reactions may favor unstable populations of singly dehydrogenized dimers on this surface. This, together with a much larger binding energy, would tend to produce cave-adsorbed molecules on the surface. Unfortunately, further growth steps for this adsorption geometry are not easily accessible and may yield inactive regions on the surface.

C_2H_4 is predicted to be considerably less bound to the surface, compared to C_2H_2 on both adsorption sites. No onefold adsorption to the surface is observed in this case either. The decrease in energy relative to acetylene is clearly due to the presence of the extra hydrogen bonded to each carbon of the admolecule, providing for higher saturation and increased steric hindrance. Indeed, the resulting structure for the adsorbed ethene is more strained due to enhanced steric repulsion induced by the hydrogen. The trend in binding energies is similar to acetylene (i.e., binding over a cave site is preferred over a bridge site). Twofold interaction with the substrate occurs in this case, however, as evidenced by the admolecule's longer carbon-carbon bond length. The bond distance is typical of a single bond. Its lower binding energies and its low concentration under ordinary CVD conditions would likely preclude C_2H_4 from playing an important role in diamond deposition on the (100) surface.

In the case of C_2H , formation of a strong single bond with the substrate similar to the methyl radical is also observed. Analysis of these structures on the surface yields no significant changes in the bonding character within the molecule. This observation alone would suggest that its binding energy is comparable to the methyl radical, as indeed we find. Although there is no substantial difference between the binding energies, the gas phase concentration of C_2H is very much less than CH_3 . We therefore believe that C_2H plays no significant role in the growth processes on the (100) substrate.

B. Adsorption on stepped (100) surfaces

For stepped surfaces, we consider binding sites near step edges for the upper and lower terraces. For the one-carbon adsorption, a hydrogen is removed from a surface carbon near the step edge and replaced by CH_3 or C_2H . For CH_2 , the initial configuration as outlined above is

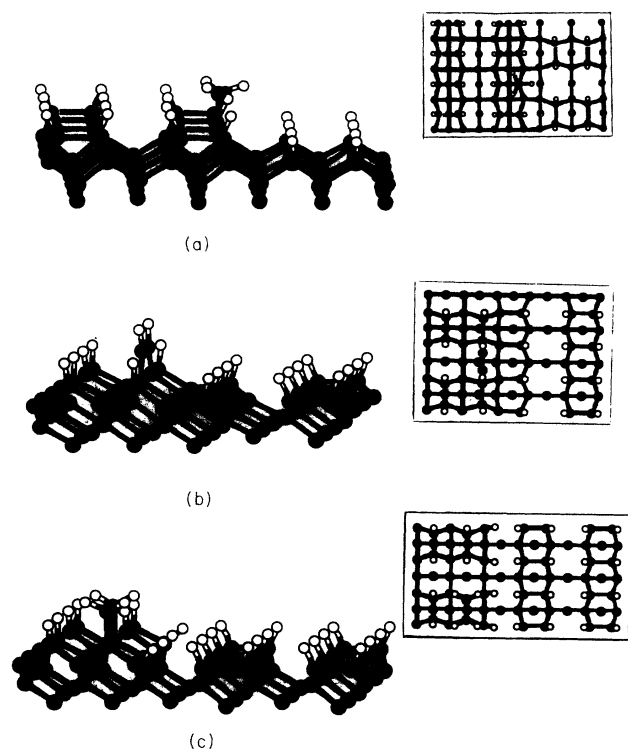


FIG. 3. Typical minimum energy configurations for admolecule-stepped surface systems. Clusters shown are portions of the unit cell employed in this work. (a) CH_3 on S_A , (b) C_2H_2 on $S_B(b)$ (trough site), and (c) C_2H_4 on $S_B(n)$ (bridge site). Carbon atoms appear shaded.

also employed. A trough site and a bridge site are created by the scheme mentioned above from carbon pairs near step edges. Figure 3 shows the one- and two-carbon binding sites for the three types of stepped surfaces considered in this investigation. The simulation systems were then relaxed to their equilibrium structures using the dynamical quenching technique.

Table II lists the energies of the various adsorbed hydrocarbons, while Fig. 3 shows typical minimum energy configurations for admolecule-stepped surface systems. Comparison of the S_A binding energies with the flat surface shows no significant differences (typically less than 4%), except for a near 10% increase of C_2H_2 on-bridge-site adsorption, and only a modest 5% increase for C_2H_4 on-bridge adsorption. A similar trend is also seen for the bonded type S_B surface, as we find an 8% increase in binding energy for C_2H_2 on-bridge adsorption, and an 8% drop for C_2H_4 on-trough binding. Notice that there is a generally weaker binding of admolecules to the surface near step edges, in a somewhat surprising result. This indicates that the built-in strains in creating the step itself prevent the admolecule from binding more strongly, even

TABLE II. Binding energies near step edges. Value inside parentheses denotes percentage difference of binding energies with respect to flat terrace site.

Molecule	S_A edges	$S_B(n)$	$S_B(b)$
CH_3	4.10 (-2%)	4.00 (-4%)	4.10 (-2%)
C_2H	4.29 (-1%)	4.00 (-8%)	4.22 (-3%)
C_2H_2^a	3.98 (+10%)	3.51 (-3%)	3.90 (+8%)
C_2H_2^b		6.44 (-2%)	6.65 (+2%)
C_2H_4^a	2.98 (+5%)	2.70 (-5%)	2.88 (+1%)
C_2H_4^b		4.80 (-2%)	4.50 (-8%)
CH_2	4.72 (+1%)	4.47 (-4%)	4.77 (+2%)

^aBridge site.

^bTrough site.

when the steric hindrances are reduced for the various geometries.

It is also of interest to analyze the built-in strains in the stepped structures. Comparison of the atomic positions across a step edge makes it evident that strain is localized around the first few rows of atoms on both sides of the step. In Fig. 3 it seems that the S_A and S_B (nonbonded) steps are basically strain-free, which explains the near equivalence of the binding energies of adsorbed atoms on the step to those on a flat terrace for these two steps (see Table I), although we find that most binding energies decrease near the step edge. On the other hand, S_B bonded steps exhibit a great deal of lattice distortion around the step which extends over a few atomic rows. It is for this step that C_2H_2 shows an increase in binding energy for both the bridge and the trough sites.

We should also point out that given that most entries in Table II are rather close in energy from one step to another and in comparison with the flat terrace, a set of first-principles calculations would perhaps determine these differences more precisely. We are confident that the qualitative results of little or no difference for some of those species would indeed stand, as the effects of strain, appropriate coordination, and changes in steric hindrances are reliably incorporated in our potential. We plan to report on some of these calculations currently in progress elsewhere.

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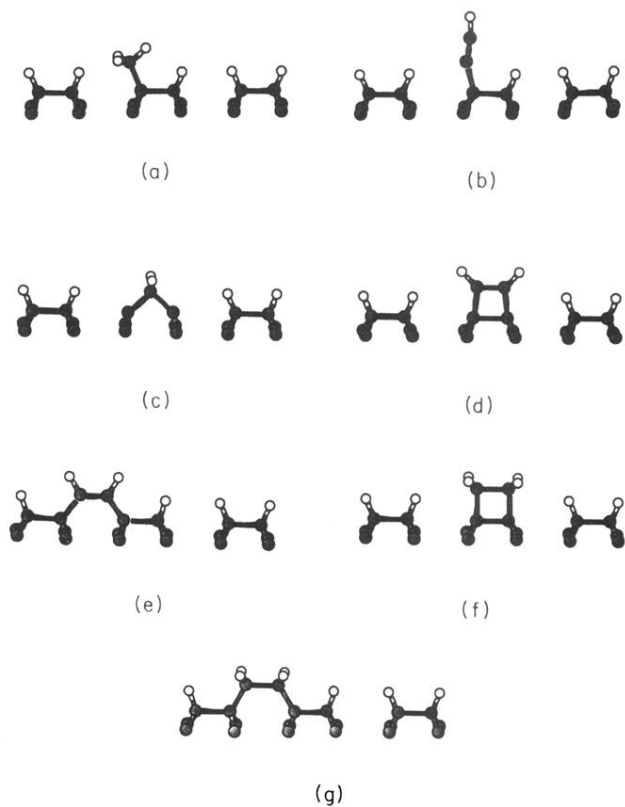


FIG. 2. Configurations of the various ad molecules on the flat diamond (100) surface. (a) CH_3 , (b) C_2H , (c) CH_2 , (d) C_2H_2 (bridge site), (e) C_2H_2 (cave/trough site), (f) C_2H_4 (bridge site), and (g) C_2H_4 (cave/trough site). Dimer pairs shown are along the $[0\bar{1}1]$ direction. Carbon atoms appear shaded.