Modeling of Surface Processes as Exemplified by Hydrocarbon Reactions

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I. Introduction

Examples of fascinating chemical reactions at solid surfaces abound in this issue of *Chemical Reviews*. It is only natural that theorists want to understand these reactions in order to obtain qualitative pictures of reaction mechanisms and to predict quantitative information that can be directly compared to experimental results. Moreover, given the complexity of these reactions, theoretical input is often desirable in order to choose judiciously the next set of experiments.

There are several categories of surface chemical reactions that are now amenable for theoretical modeling studies. Rather than detailing every reaction investigated for all possible systems, we have chosen to focus on hydrocarbon reactions in this review since there is now an extended library of information emerging from this type of chemistry. Moreover, hydrocarbon reactions often have a direct relationship to other fields and perhaps are more intuitive for a general audience. For some of the reactions such as adsorption and abstraction, the reaction products are known a priori and the modeling studies are performed to obtain quantitative information, e.g. adsorption probabilities. On the other hand, exploratory simulations have also been performed for reactions among surface species, collisions of energized molecules with surfaces and two surfaces sliding against each other. This delineation of reaction events is not meant to be all inclusive but rather to exhibit the dynamic range of events that occur at solid surfaces.

Let us first consider adsorption in which a gas-phase molecule impinges on a surface and sticks. Adsorption scenarios are shown in Figures 1 and 2 for CH_3 radical adsorption to the reconstructed diamond {001}(2×1) surface.[1] Depending upon the H coverage, the CH_3 radical can either adsorb to a π-bond site (Figure 1) or to an isolated radical (Figure 2). The adsorption probabilities and the consequences for diamond growth are different for the two structures. Molecular adsorption is also a common adsorption mode for CO on metal surfaces.[2] Depending on the orientation and energy of the molecule as it approaches the surface, it either adsorbs or reflects.

Another mode of adsorption is dissociative adsorption. Shown in Figure 2 is dissociative adsorption of H_2 on a π-bond. In this case a pair of sites near each other is needed before adsorption can occur. This is a very common mode for H_2 and O_2 adsorption on metal surfaces at room temperature.[2] A weakly bound molecular adsorption state may also exist but at room temperature the molecule readily dissociates to the more stable atomic state.

Abstraction or etching can occur when a gas-phase species removes part of the surface. Figure 2 depicts a gas-phase H-atom reacting with a C−H bond on the surface to form a gaseous H_2 molecule.[3] This abstraction reaction forms radical sites during diamond growth due to chemical vapor deposition. It is these radical sites to which C-containing species can adsorb.

Surface reactions occur when species on the surface rearrange. For example, the CH_3 species shown in Figure 1b can transfer a H atom to the adjacent C atom as shown in Figure 1c. The strained surface dimer then opens forming an ethylenic type configuration (Figure 1d). Finally the adsorbed CH_2 inserts into the dimer (Figure 1e). This is known as a β-scission reaction in small molecule chemistry and is a proposed reaction step in the growth of diamond.[4]

The surface reactions delineated above are relatively straightforward. There are processes, however, where many simple reactions take place simultaneously. For example, the structure of the clean diamond {111} surface has been proposed to be a π-bonded chain structure.[5] Although the π-bonded chain structure can be H-terminated,[6] the most stable H-terminated configuration shown at the right of Figure 3 is the bulk-terminated surface. Exposure of the clean π-bonded chain structure to a gas of H atoms induces a reaction in which the atoms rearrange to the bulk-terminated structure.[7] This process is some combination of H adsorption, H abstraction, and surface reaction. The sequence shown in Figure 3 is slightly different in that one starts with

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a partially H-terminated π-bonded chain structure (left of Figure 3). After 30 ps of heating at 800 K the surface has partially reverted to the bulk terminated structure (middle of Figure 3).[8]

Reaction events become even more complex as the experimental conditions stray from equilibrium. For example, in surface-induced dissociation (SID) experiments, the beam of gas ions striking the surface has up to a few hundred electronvolts of kinetic energy.[9] After the beam strikes the surface, the molecules can either reflect intact, break up and reflect, molecularly adsorb, dissociatively adsorb or

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pick up a piece of the solid and desorb. Several representative reaction channels for a phenyl radical[10] are shown in Figure 4. In ion-bombardment experiments such as secondary ion mass spectrometry (SIMS),[11] a beam of Ar^+ ions energized to several thousand electronvolts of kinetic energy strikes a surface and induces reactions in an organic overlayer[12] as shown in Figure 5. Obvious reaction products include H, C, and Pt atoms, H_2 and C_2H_2 molecules, and CH_3 radicals. Instead of distorting the system by using energized particles, friction between two surfaces sliding against each other may induce reactions. Shown in Figure 6 are two H-terminated diamond {111} surfaces with an ethyl radical adsorbed to the top surface.[13] In the simulation the top surface is moved to the right while a vertical force is applied. A series of basic organic reactions unfold in this environment.

The strategies for modeling surface reactions are based on the fact that the comparable studies of simple gas-phase reactions have been successful and led to insight of the important chemical events taking place. For example, there is now a remarkably good comparison between experiment and theory for the exchange reaction of $H + H_2 \rightarrow H_2 + H$.[14] The current level of agreement did not occur with the first experiment and calculation. Rather, success is based upon many incremental improvements in both experimental techniques and theoretical approaches over past decades. Given the plethora of interesting reactions at surfaces, we seriously doubt that any one process will become the benchmark system as $H + H_2$ is for gas-phase reactions. Consequently the approach is to adapt modeling techniques used to study gas-phase reactions and apply them to surface reactions.

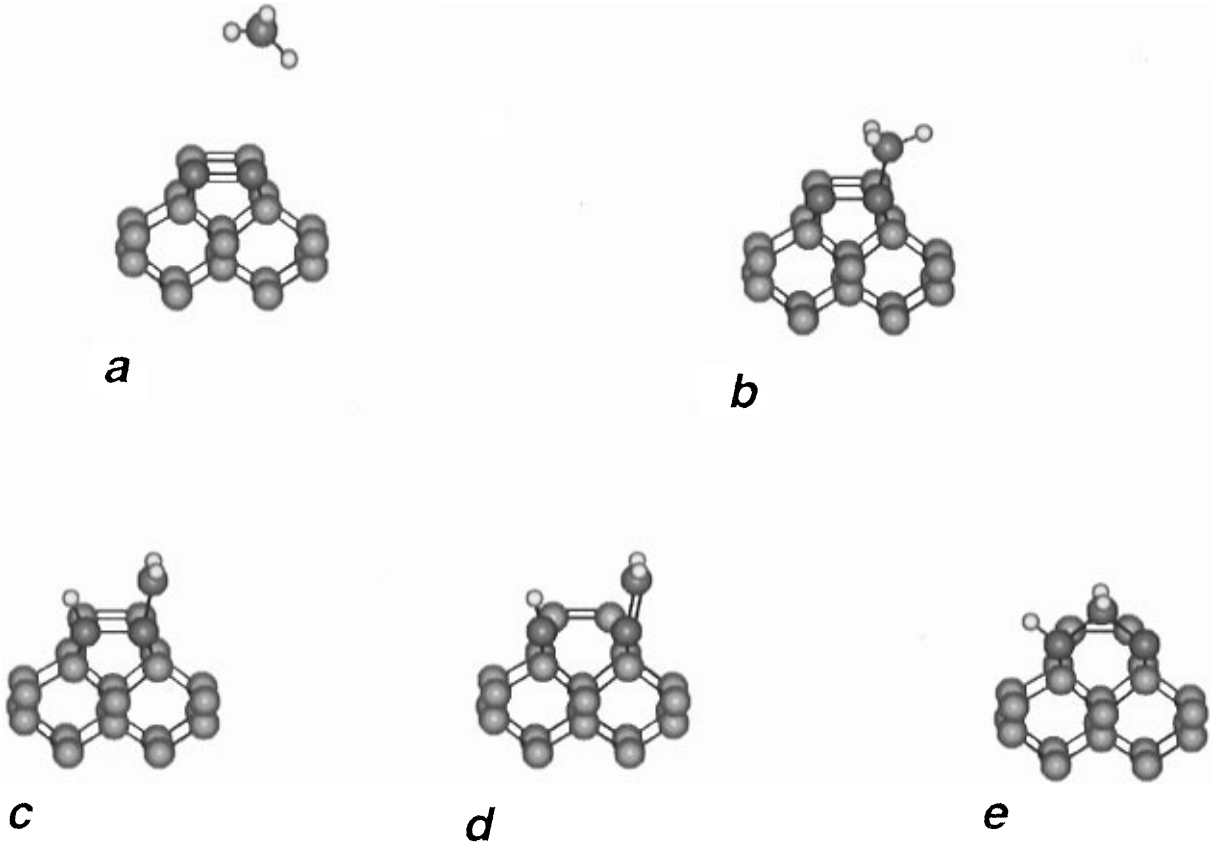

Figure 1. Steps in the insertion reaction of CH_2 into a surface dimer on diamond {001} (2×1): (a) gas-phase CH_3 radical, (b) adsorbed CH_3 species, (c) H migration, (d) ethylenic configuration, and (e) inserted CH_2. The modeling of the CH_3 adsorption process is discussed in ref 1 and the CH_2 insertion reaction in ref 4. The C atoms are represented by blue and pink spheres and the H atoms by smaller yellow spheres. This color representation is used throughout the figures.

Both classical and quantum mechanical theories have been used to model the H + H_2 reaction. Surprisingly the classical approximation has been shown to be sufficient to describe many of the experimental quantities.[14] This is fortunate as classical molecular dynamics (MD) simulations are tractable for thousands of atoms, whereas quantum modeling is not feasible for such systems. Thus we can follow the atomic-scale dynamics of surface reactions using MD simulations in which the classical equations of motion are integrated in time for all the atoms in the system of interest. In general, MD simulations provide the positions of the atoms as a function of time, so that it is relatively straightforward to deduce the reaction mechanism as well as the reaction dynamics. Energy and angular distributions of reactants and products may also be computed and compared directly with experimental measurements.

A necessary element for any MD simulation is a potential energy surface (PES) which describes the energy of the system for all possible configurations of the atoms. Herein lies the first major challenge. For the gas-phase H + H_2 exchange reaction, there are only three atoms. If the center-of-mass coordinates and motion are extracted, then there are only three coordinates or variables for the PES. In contrast, there are considerably more degrees of freedom in the examples shown in Figures 1−6. The challenge has been to obtain a reasonable functional form for the PES and, given the large number of atomic coordinates, also to find sufficient data from either experiment or high-quality electronic structure calculations to fit the parameters in the PES. The availability of or the ability to construct an appropriate PES dictates which systems can be modeled.

The scope of this review is modeling studies of surface reactions. As necessary background we first give a brief description and history of the molecular dynamics approach for surface reactions and the current status of PESs for reactions at solid surfaces. A discussion of the modeling studies of the processes shown in Figures 1−6 and others for hydrocarbons is given next. We stray from our theme in section IV by discussing a few simulations where quantum effects have been included. We wrap up with a commentary in section V.

II. Methodology

A. Classical Mechanics

The use of molecular dynamics simulations is pervasive throughout various fields of science and a thorough discussion is not warranted here. Briefly each atom in the system is treated as a particle and the classical equations of motion are integrated in time for an ensemble of atoms. The procedures and tricks for implementing the MD method are described in a text by Allen and Tildesley.[15] Aside from the daunting challenge of finding a suitable PES for surface reactions, there are other details that need to be addressed when applying MD to large systems of atoms.[16,17] These include protocols for mimicking

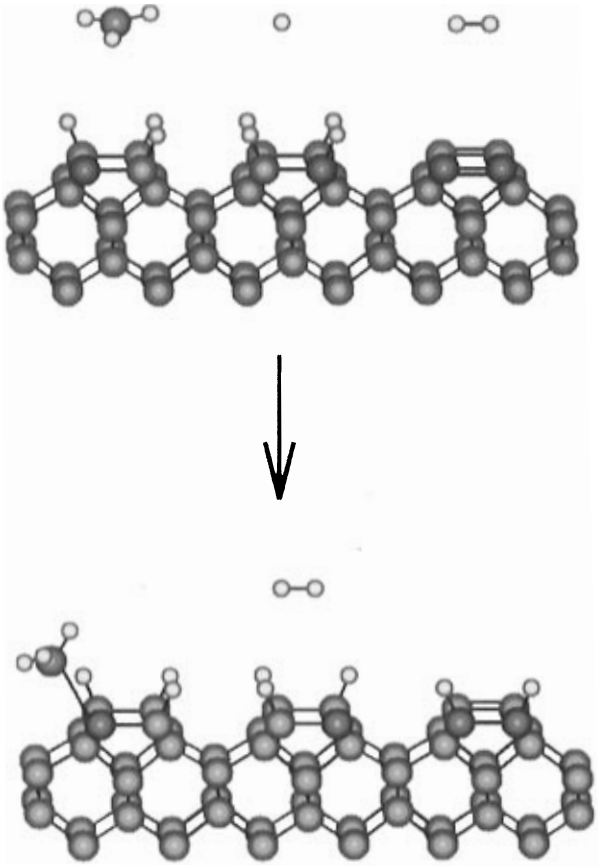

Figure 2. CH_3 adsorption, H abstraction, and H_2 adsorption. In contrast to Figure 1 the CH_3 radical adsorption event in this case is onto a surface radical site. The product of the H abstraction reaction is a gaseous H_2 molecule. Modeling of the CH_3 adsorption on a {001} radical site is discussed in ref 1. Modeling of H abstraction reactions are given in refs 3, 50, and 51.

an infinite solid and dealing with the long time scale of many surface processes. Each of these are described below.

A solid surface consists of $\sim 10^{15}$ atoms per cm^2 on the surface with a bulk heat bath of $\sim 10^{23}$ atoms per cm^3. Many of the reactions shown in Figures 1−6 appear to occur with only a few surface atoms but in fact the bulk atoms play an important role. For example, the adsorption from the gas phase of either H or CH_3 on the surface is exothermic by over 4 eV (~100 kcal/mol). There must be a heat bath to dissipate the excess energy. Moreover, there are cases such as shown in Figure 3, where one wishes to define and control the temperature of the system. How does one incorporate the effects of all the substrate atoms while not explicitly having 10^{23} atoms in the simulation? At this point, a historical perspective is appropriate. The initial studies of MD simulations of reactions on surfaces can be traced to McCreery and Wolken in the mid-1970s.[18] They modeled H_2 reactions on a rigid W{001} surface using a London−Eyring−Polyani−Sato potential. In this case the parameters in the potential which characterize the surface are periodic functions of the lateral position of the H atoms on the rigid surface. McCreery and Wolken went on to perform MD simulations in order to investigate a number of processes including molecular scattering,[19] adsorption of H_2 from the gas phase,[20] molecular desorption of H_2 from two H atoms on the surface,[21,22] and the Eley−Rideal pick up of one H atom on the surface by an incoming H atom.[23] Although the rigid surface approach might be appropriate in the case of light H atoms scattering from massive W atoms (184 amu), there needs to be moving substrate atoms for most reactions of interest.

The conceptual advance in this era was by Adelman, Doll, and co-workers in the mid-to-late 1970s.[24−29] They showed for a harmonic solid that one can rigorously define primary and heat bath zones of substrate atoms. The equations of motion of the primary zone of atoms are modified to include the influence of the dissipative and random forces in the heat bath zone. This approach has been called the generalized langevin equation (GLE) method. The dissipative force (friction integral) acts to remove excess energy, for example, from the exothermic adsorption of a species on the surface. The random force is determined from the fluctuation−dissipation theorem and is balanced with the dissipative force in order to maintain the temperature of interest. Due to limited computer resources most GLE-MD studies of this era were focused on how to define and evaluate the friction integral and random force so as to approximate the infinite solid by a small primary zone of 1−4 atoms.[30] This approach is exemplified by Tully's investigation of the Eley−Rideal reaction in which an incident gas-phase O atom reacts with a C atom adsorbed on a Pt{111} surface (four primary atoms) to yield a gaseous CO molecule.[31] He determined that the CO molecule quickly departs from the surface with considerable internal excitation.

An obvious simplification of the GLE approach is to get the friction and random forces farther away

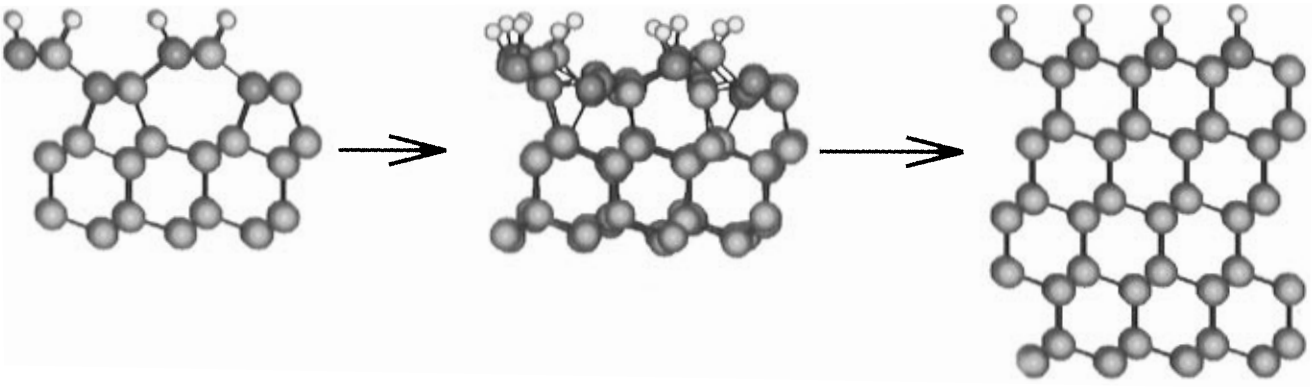

Figure 3. Conversion of H terminated diamond {111} (2×1) to {111} (1×1).

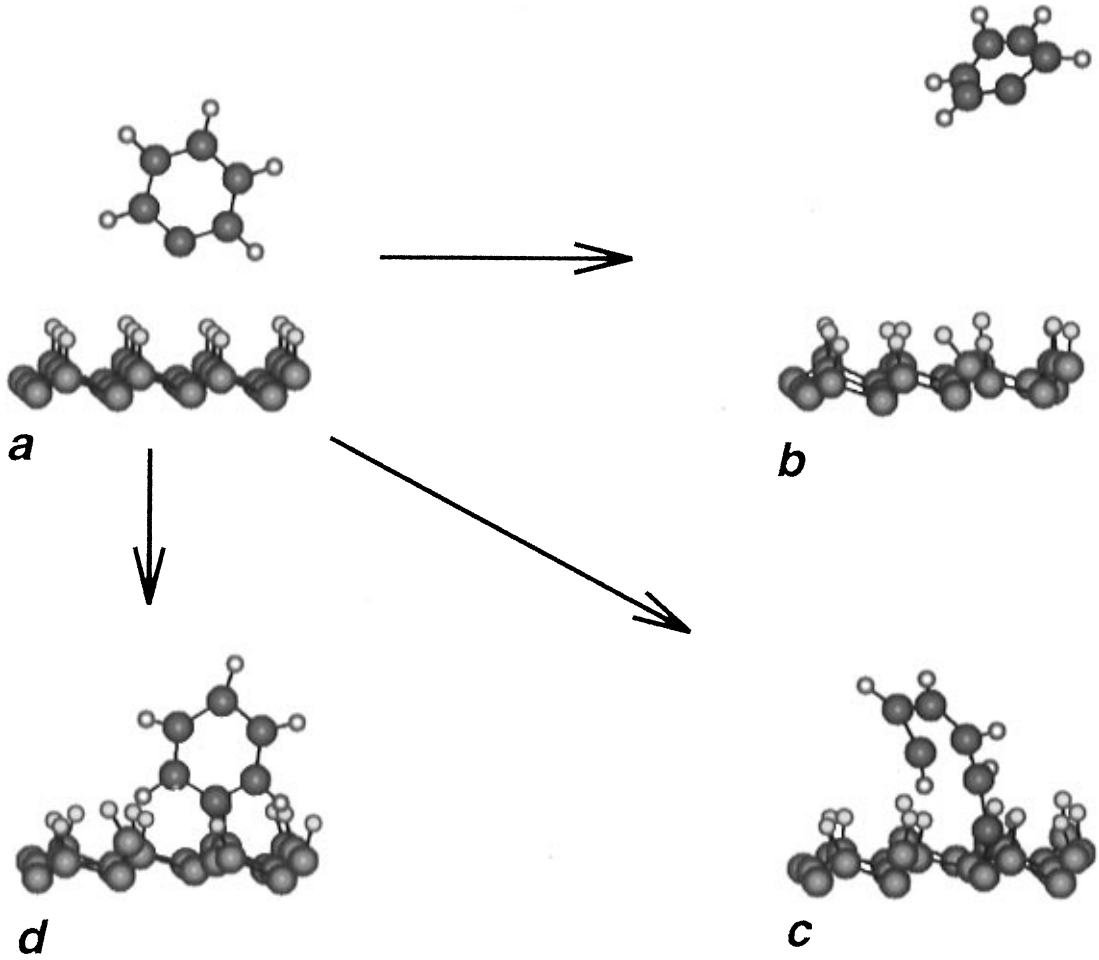

Figure 4. Surface-induced dissociation channels for a phenyl radical colliding with a H-terminated diamond {111} surface: (a) incoming molecule, (b) reflected molecule, (c) dissociative adsorption, and (d) molecular adsorption. These modeling studies are described in ref 10. Only a small subset of the atoms used in the simulation is shown in this figure.

from the atoms participating in the reaction of interest. Garrison and Adelman introduced the Brownian oscillator model for the heat bath where the primary surface atom interacted with a single Brownian oscillator.[29] The equation of motion for the Brownian oscillator only has simple friction (no integral) and Gaussian random noise. At about the same time Shugard, Tully, and Nitzan also separated the surface atoms into a primary zone and a secondary zone.[32] This conceptually moves in the same direction but still maintains an explicit coupling tensor.

As the speed of computers increased it became possible to have a large number of primary atoms. The general philosophy now[33−35] is to have a set of atoms (reaction zone) which experience the forces due to the interaction potential of the substrate and possible gas-phase or surface adsorbates. The reaction zone may be, for example, the top several layers of a slab (similar to one shown in Figure 3) in which periodic boundary conditions have been imposed in the horizontal directions. The next several layers comprise a stochastic zone of Brownian oscillators, where, in addition to the forces from the interaction potential, there is a frictional force and a Gaussian random noise term. Since this stochastic zone is well removed from the reaction site, the integral is replaced by a simple constant friction term ($-\beta\mathbf{v}$, where β is the friction constant[36] and $\mathbf{v}$ is the velocity vector of the individual atom). The random force is Gaussian white noise with width σ given by $\sigma^2 = 2m\beta k_B T/\Delta t$, where m is the mass of the particle, k_B is the Boltzmann constant, T is the desired temperature, and Δt is the integration time step. The stochastic zone may have a layer or two of rigid atoms beneath it in order to keep the bottom from reconstructing or moving.

While the above history outlines the development of MD simulations for chemical reactions at surfaces, there was work a decade previous by several groups aimed at modeling displacement of atoms in solids due to kiloelectronvolt particle bombardment. The initial simulations by the Brookhaven group[37,38] were aimed at modeling radiation damage. They used crystallites of almost 1000 atoms but only used repulsive pair potentials for the atoms with a constraining force to maintain the crystal. The major group working in this field during the late 1960s and early 1970s was Harrison and co-workers.[39−46] In 1978 we first started collaborating with them on the modeling process of particle bombardment[47−49] and an example of this work is given in Figure 5 and is discussed below.

The particle bombardment process exemplifies a different approach to modeling $\sim 10^{23}$ atoms per cm^3 in the solid. In this case the incident particle has hundreds to thousands of electronvolts of kinetic energy. The simulation is often aimed at modeling

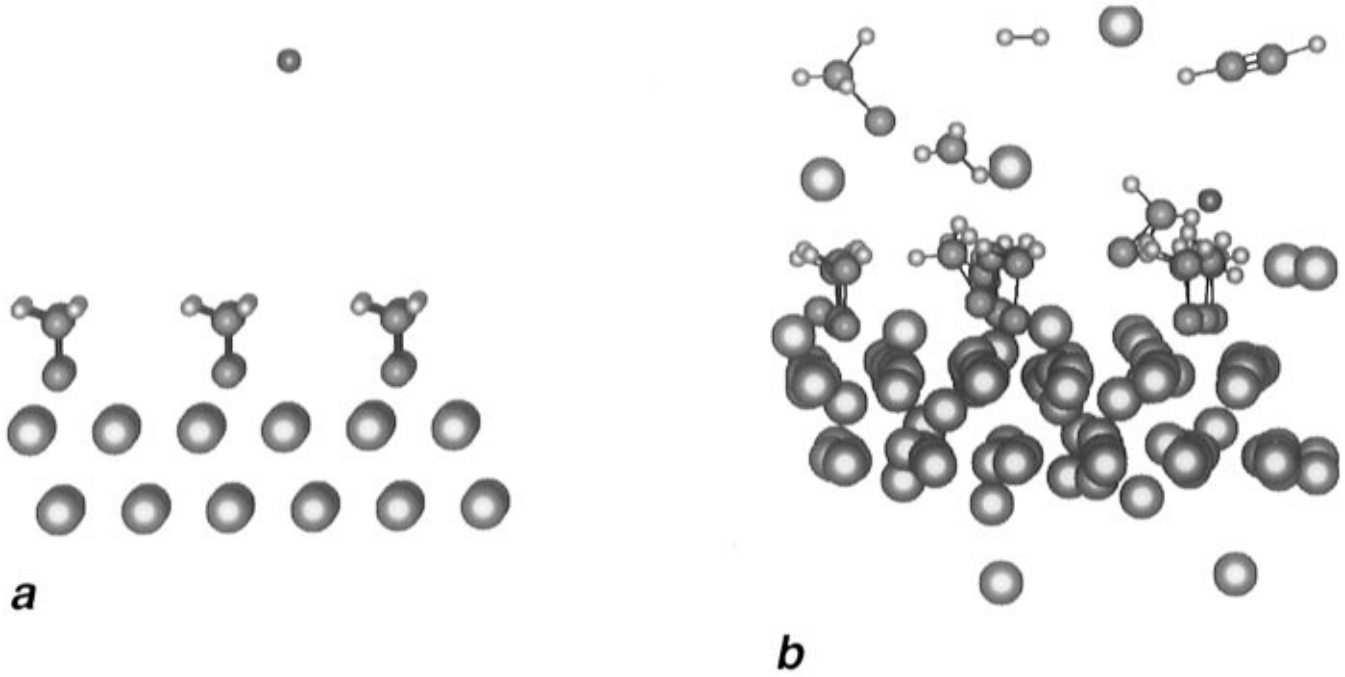

Figure 5. Ar bombardment (500 eV) of ethylidyne, C_2H_3, adsorbed on Pt[111}. The top is the initial configuration. The view angle perfectly aligns the atoms. The bottom gives the position of the atoms after ~500 fs. The metal atoms are represented by gold spheres, the C atoms are pink, the H atoms are green, and the Ar^+ ion is purple. These modeling studies are described in ref 12. Only a small subset of the atoms used in the simulation is shown in this figure. Some artistic license is used to have a diversity of reaction products in one figure. In reality usually only a few products arise from one Ar^+ ion impact.

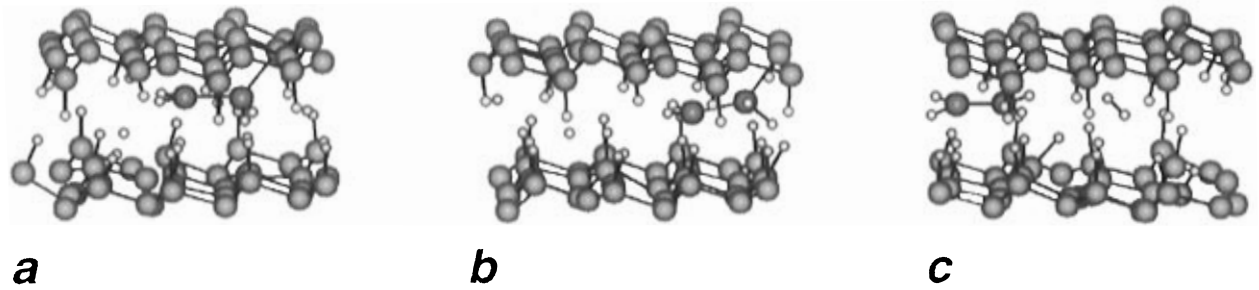

Figure 6. Friction reactions due to two surfaces rubbing together. These modeling studies are described in ref 13. Only a small subset of the atoms used in the simulation is shown in this figure. In particular we have removed one ethyl group in the interface from the original figure.

what ejects from the surface and not what damage occurs in the bulk. The time scale of the simulation is ~1 ps. Open boundary conditions are employed so that a particle can escape from the sides or bottom. It is not physically correct to have periodic boundary conditions in these simulations where an atom leaves one side of the crystal and reenters the other side with hundreds of electronvolts of energy. Stochastic forces can be omitted as the time scales of the vibrational periods (picoseconds) are longer than the physically interesting events, i.e., ejection.

Regardless of the approach used to mimic the infinite solid, one chooses a finite number of atoms to include. It is thus essential to test the robustness of a calculation with respect to variation in the size of the crystal.

The numerical integration of the classical equations of motion is performed by choosing a time step such that the forces on the atoms are approximately constant. For reactive systems the time step typically varies between 10^{-16} and 10^{-14} s. Practically one can only take 10^6 to 10^8 integration steps thus the MD simulations are limited to hundreds of nanoseconds. Processes such as adsorption, sputtering and SID easily occur in femtosecond to picosecond time scales and thus can be modeled with MD. Diffusion or desorption, on the other hand, can take milliseconds or microseconds between events especially for chemically bonded systems like H on diamond.[50−52] Diamond film growth, however, occurs at a rate of a few micrometers per hour.[53] The limitation of MD to be within hundreds of nanoseconds with the current computers does put a bound on what can be modeled with MD. Efforts at overcoming the time-scale limitation with Monte Carlo methods are described near the end of this article.

B. Potential Energy Surfaces

The potential energy surface is a necessary and critical input to the MD simulations. We have recently reviewed the available PESs for reactions at solid surfaces.[54] Although there has been considerable work developing potentials for surface reactions, the diversity of systems considered is quite

limited. There are a number of London−Eyring−Polanyi−Sato (LEPS) potentials for diatomic molecules reacting with metal surfaces. The face-centered-cubic (fcc) metals are reasonably well described by embedded atom method (EAM) potentials[55−57] and molecular dynamics/Monte Carlo-corrected effective medium (MD/MC-CEM) potentials.[58−60] A vast number of groups have developed potentials for silicon, with the two most popular being the Stillinger−Weber[61] and the Tersoff potentials.[62,63] Brenner has expanded the concept behind the Tersoff potential for Si and developed a potential for hydrocarbon reactions.[64,65] Except for the LEPS functions, all of the above-mentioned PESs can describe an arbitrary number of atoms without any redevelopment of the functional forms or any reparameterization.

Missing from this list of systems is the reaction of a hydrocarbon molecule with a metal surface as in the formation of ethylidyne on a Pt{111} surface from ethylene;[66,67] the formation of the (7×7) reconstruction of Si{111} and reactions of disilane, germanes, oxygen, water, etc., with silicon;[68] the reaction of alkanethiols with metal surfaces to produce adsorbed alkanethiolates and hydrogen in some form;[69] alkyne cyclotrimerization on TiO_2 surfaces;[70] and numerous other examples found in this issue of *Chemical Reviews*.

Since we are focusing on hydrocarbon reactions, we briefly describe the Brenner potential.[64,65] Based on a form developed by Tersoff[62] to model covalent solids, this potential function gives the binding energy E_b in a form reminiscent of a pair potential

$$E_b = \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} V_R(r_{ij}) - b_{ij} V_A(r_{ij})$$

where r_{ij} is the distance between pairs of atoms, V_R represents repulsion between atomic cores, V_A represents attraction due to valence electrons, and b_{ij} represents a bond-order function that modulates the bonding according to the local environment of each atomic pair. Based on chemical pseudopotential theory, this form assumes that the core−core repulsion and bonding due to valence electrons are both pair additive and independent of atomic hybridization, with all many-body bonding effects, including rehybridization due to bond breaking/forming, incorporated in the bond-order function. A recent article describes similar function in more detail.[71]

Figure 7 demonstrates the transferability of the pair terms between atomic hybridizations by plotting the equilibrium bond energies, stretching force constants, and equilibrium bond length versus the C−C bond type. The functional forms used for V_R and V_A are a screened Coulomb and sum of three exponentials, respectively. As is apparent from the figure, a single form for each interaction is able to accurately describe properties of chemical bonds over a very wide range of atomic hybridizations.

The central properties that determine the value of the bond order function b_{ij} are local atomic coordination and bond angles. A functional form is used for b_{ij} so that its value decreases as the local coordination increases; this weakens the attractive term, modeling

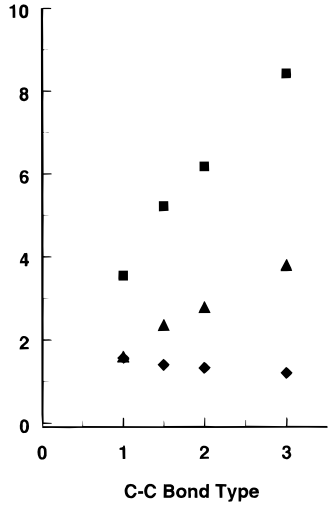

Figure 7. Bond length, bond energy, and force constant vs C−C bond type. A value of 1 for the bond type corresponds to a single bond (sp^3 hybridization); 1.5, a conjugated π system as in benzene; 2, a double bond (sp^2 hybridization) and 3, a triple bond (sp hybridization): ◆, bond length (Å); ■, bond strength (eV); ▲, force constant (10 eV/Å^2).

the finite number of valence electrons available for bonding. The bond-order function is also parameterized so that its value increases with increasing bond angles. This favors, for example, angles of 180°, 120°, and 109.5° for 2, 3, and 4-fold coordinations, in agreement with the expected hybridizations. The value of the bond order also depends on the presence of radicals, whether unsaturated bonds are part of a conjugated system, and the value of the dihedral angle for rotation about double bonds.

Parameters in the functional form are fit to a wide variety of solid-state and molecular properties. The solid-state properties include lattice constants, cohesive and defect energies, and elastic properties of diamond, single graphene sheets, and various high-pressure phases of carbon. Molecular properties include carbon−carbon and carbon−hydrogen bond lengths and energies as well as the barrier for rotation about the double bond in ethylene. Because solid-state and molecular properties are both fit on an equal basis, the function reproduces properties predicted by first-principle approaches for intermediate cases like surface reconstructions at a fraction of the computational cost.

The unique feature of this potential is that atomic hydridizations are not explicitly specified; instead the bonding characteristics are all determined by the local environment through the bond-order function coupled to highly transferable pair terms. This feature, which is absent in more traditional force fields, provides not only a good description of the structure and energetics of carbon in a variety of hybridizations with a single functional form, but it also allows bonding characteristics to change as bonds are formed and broken. This has made it an extremely useful tool for modeling a wide variety of phenomena, as discussed in this article, outside of that for which it was originally developed (namely diamond deposition).

A frequently asked question is, How well does it do for transition states? The answer is, it depends.

The potential reproduces general chemical trends such as the lowering and repositioning of chemical barriers earlier in the reaction path with increasing exothermicity along a series of related chemical reactions (the Polanyi−Semenov relations).[72] This means that one may only have to fit one or two known chemical barriers to produce relative agreement with barriers for related reactions. On the other hand, being a classical potential it has no knowledge of avoided crossings, Woodward−Hoffman rules,[73] or other phenomena that arise explicitly from electronic effects. Therefore we view dynamics produced by this potential more as a way to identify possible reaction mechanisms that may not be suggested with other more computationally demanding methods.

It is perhaps useful to compare and contrast the Brenner CH potential with the popular forms based on the molecular mechanics potential, MM3.[74−76] Both are empirical potentials with parameters fit to data either from experiments or electronic structure calculations. The functional forms are fundamentally distinct, and the criteria for choosing the data for fitting are also different. The MM3 potential is designed to calculate energetics, structures and vibrational properties for molecules in which the basic bonding configuration is prescribed and remains unchanged. For example, it must be specified a priori that a given C atom exhibits sp^2 bonding.

The Brenner potential has been designed to model reactions. The preferred energetics and geometries are parameterized as a function of the neighbors of a given atom. There is no a priori specification of a given bonding configuration so the bonding can dynamically change from sp^2 to sp^3 as shown in Figure 1. The ability to model reactions comes at a cost since the Brenner potential is not as good as the MM3 potential for computing highly precise structural and vibrational properties.

Because of the diversity of events that have been modeled, we have chosen to focus on the hydrocarbon reactions modeled by Brenner potential as the common thread for illustrating surface reactions in this article. We are not claiming that the CH empirical PES is perfect, rather it provides a starting point for examining reaction mechanisms via MD simulations. We specifically restrict our discussion to the use of MD simulations for reaction dynamics. In addition to the dynamical investigations there are numerous studies of energetics for similar systems in the literature. Some of these studies involve integration of the classical equations of motion mainly to obtain energetic minima and transition states and their structures but do not involve reaction dynamics. Such studies are outside the scope of this review. The reactions discussed below were performed using the Brenner hydrocarbon potential unless otherwise noted.

III. MD Simulations of Reactions of Hydrocarbons

A. Adsorption

A multitude of surface reactions from heterogeneous catalysis to diamond growth involve, as a first step, adsorption of a gas-phase species onto the surface. For atomic adsorption, several investigators have examined H atom reactions with the {111} and {001}(2×1) surfaces of diamond as a function of temperature.[3,50,51] In these cases the velocity of the initial gas atom is selected from a Boltzmann distribution which is set at the same temperature as that of the surface. The calculated adsorption probabilities per C radical site are shown in Figure 8 for these two surfaces. Several observations are clear.[51] First, the adsorption process is exothermic and unactivated, therefore the absolute value of the adsorption (or sticking) probability is relatively large. The H atom is found to stick in 40−80% of the trajectories. The difference in cross section between the two surfaces presumably arises from the fact that the radical on the {111} face is perpendicular to the surface, whereas on the {001}(2×1) face the radical is oriented at an angle. Hence, there is a greater angle of approach for the incoming H atom. Second, there is only a minor temperature dependence to the adsorption probability although the greater vibrational motion of the solid at higher temperatures does decrease the probability slightly. Third, there is a greater probability of adsorption onto a π-bond than of adsorption onto an isolated radical. This trend is the opposite to the relative exothermicities of the two processes since energy must be expended to break the π-bond. The major factor leading to a difference in π-bond adsorption vs isolated radical adsorption is that the available surface area for sticking on a π-bond is greater.

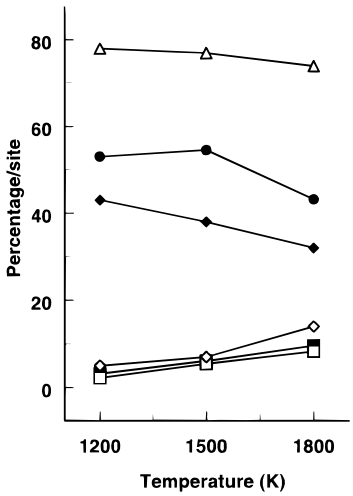

Figure 8. H adsorption and H abstraction probabilities: ◆, adsorption on a {111} radical; ●, adsorption on a {001} isolated radical; △, adsorption on a π-bond; □, abstraction from {001} to form an isolated radical; ■, abstraction from {001} to form a π-bond; ◇, abstraction from {111}. This figure is adapted from ref 50.

Other simulations of H atom adsorption have been performed. The adsorption probability at 1200 K for H addition to an adsorbed CH_2 on the {001}(2×1) surface has been determined to be 19%.[1] This value is lower than found for other surface sites because the flexibility of the CH_2 species makes it difficult for the H atom to adsorb. Perry and Raff have calculated the adsorption probabilities at 1250 K for the {111} terrace[77] and a {111} ledge (step) sites.[78] Finally, there is one study with a different potential that examines the detailed effect of the phonon frequencies on the H adsorption probability.[79]

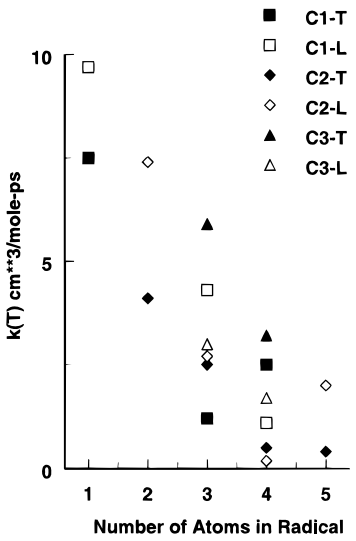

Figure 9. Rate coefficient for radical species chemisorbing on a diamond {111} terrace (T) and ledge (L) vs number of atoms in the radical. All rates are for 1250 K. C1 = {C, CH_2, CH_3}, C2 = {C_2, C_2H, C_2H_2, C_2H_3}, C3 = {C_3, C_3H}. The data are taken from refs 77 and 78, and the correlation discussion is from ref 77.

The next level of complication for an adsorption process involves a diatomic molecule such as H_2. There have been a plethora of MD simulations for H_2 adsorption on metal substrates, many of which are mentioned in ref 54. For H_2 adsorption on a metal surface there is generally a molecular adsorption state which is easily accessible to the gas molecule. There is a small barrier that leads to the atomic adsorption state. Consequently, it is relatively straightforward to model the adsorption of H_2 on a metal. For H_2 adsorption on diamond, however, the mechanism of the reverse reaction (H_2 desorption) may be important and is a topic of current investigation.[80−82] In particular there is a question of the nature of the transition state for adsorption/desorption and the Brenner potential does not suggest a reasonable pathway for this process. Consequently we turn to the next molecular adsorbate—the CH_3 radical.

The adsorption of the CH_3 radical on diamond is an unactivated process, but in contrast to H atom adsorption there are steric factors involved. In general, the simulations of adsorption have been performed for a H-terminated surface with one radical site. By examining adsorption on the {111} surface at 1250 K, Perry and Raff have found that the adsorption on a terrace site[77] is low, whereas for an exposed ledge site[78] the probability increases by a factor of 4. CH_3 radical adsorption on the {001}-(2×1) surface is found to be 10−100 times lower than that for H atom adsorption.[1]

Adsorption probabilities have also been calculated for C, CH_2, CH_3, C_2, C_2H, C_2H_2, C_2H_3, C_2H_4, C_3, and C_3H on a H-terminated diamond {111} terrace[77] and ledge by Perry and Raff.[78] They find that radicals adsorb more readily than nonradicals by 1−2 orders of magnitude. Interestingly they observe that the adsorption rate decreases as the number of atoms in a radical increases (Figure 9). In the radical−radical recombination reactions, the variation in the adsorption rates is due to steric hindrance as the molecule approaches the surface. As of yet these predictions have not been experimentally verified.

The molecule C_2H_2 deserves special note as it has been proposed as a key component for diamond growth on the {111} surface.[83−85] MD simulations of C_2H_2 adsorption on a clean, bulk-terminated {111} surface,[86] a H-terminated {111} surface with one radical site,[77] and a {111} ledge with two adjacent radical sites[78] have been performed. These simulations indicate that acetylene prefers two adjacent radical sites for effective chemisorption. If only one site is available there is a propensity for desorption from the surface.

Adsorption studies of C_2H_2 at a H-terminated diamond {111} surface with CH_2 adspecies were performed by Zhao et al. using an AM1 semiempirical potential.[87] They predict the existence of a trapped, physisorption state for the acetylene molecule. They also examined a limited number of H adsorption and H abstraction trajectories but, presumably due to the computational cost of using a semiempirical potential, they did not obtain averaged probabilities.

The effect of hyperthermal CH_3 radical deposition on a diamond {001} (2×1) surface with 50−75% H coverage has been examined by Alfonso and Ulloa.[88] They find that the adsorption probability increases as the kinetic energy of the CH_3 radical increases from 1 to 10 eV. In general the CH_3 radical adsorbs at a radical site on the surface. At 10 eV, however, the CH_3 radical can displace a bound H atom.

Pailthorpe has examined the deposition of C atoms with 1−100 eV on a diamond {111} surface.[89] He fit a carbon potential based on the Stillinger and Weber functional form.[61] For 15 eV C deposition Pailthorpe found that the atom hardly penetrates the surface and readily binds to a radical site. Deposition at 30 eV can produce surface disorder but the incident atom bonds to the surface radicals. The energy must be ∼80 eV before bonding occurs to the lower layers in the substrate. This value correlates well with the experimental atomic displacement energy in diamond of 75 eV.[90]

B. Etching

Etching or removal of atoms from the solid by a gas-phase species occurs in numerous environments. For example, H atoms react with surface CH species creating a surface radical and a gas-phase H_2 molecule (Figure 2). This is an activated and exothermic reaction. Shown in Figure 8 are the probabilities for H atom abstraction from the {111} and {001}(2×1) surfaces.[3,50,51] The values are identical within statistical limits although the values might be slightly higher for the {111} surface. The activation energy is in the range of 0.34−0.42 eV depending on the surface and the coverage. The transition state on both the surfaces is nearly a collinear configuration of the C atom and the two H atoms, and is the main reason for the low abstraction probabilities. As the temperature of both the gas and the surface increases, it becomes easier to overcome the activation barrier and the abstraction probability increases.

The calculations of the H-abstraction reaction on the diamond surfaces were performed in order to obtain quantitative estimates of the reaction prob-

abilities. There is a more exploratory series of simulations aimed at determining reaction mechanisms of etching of silicon by halogen atoms.[91−94] For example the MD simulations predict that an incoming F atom reacts with a surface−SiF_3 adspecies. An S_N2-like reaction, in which an Si−Si bond breaks and an Si−F bond forms, creates a gaseous SiF_4 molecule.[91] In addition the same simulations predict that tower-like structures are the surface species that react with an incoming F atom to form gaseous Si_2F_6.

C. Surface Reactions

The reaction products in the simulations of adsorption and abstraction events are generally known before performing the MD simulations. Exploration of the unknown is where we believe that MD simulations have and will continue to have an important role in surface science.

The CH_2 insertion reaction shown in Figure 1 is an example of such an exploratory MD simulation.[4] A simulation was performed in which there is a H-terminated diamond {001}(2×1) surface with a CH_2 species adsorbed to one of the surface dimers (Figure 1c). The MD simulations predict a two-step reaction mechanism. First the surface dimer opens (Figure 1d) and second the CH_2 species inserts into the dimer (Figure 1e). The initial configuration is a five-membered C ring, whereas the product is a six-membered ring. The final configuration shows all the C atoms at epitaxial positions. Hence, this mechanism was proposed as a growth mechanism for diamond.[4]

The activation barrier for this reaction is predicted to be 3.9 kcal/mol using the empirical potential. Subsequently using ab initio electronic structure techniques[95,96] an activation energy of 8.8 kcal/mol was determined. These values differ by a factor of 2; however, they are both sufficiently small that the reaction will proceed at diamond growth temperatures. Finally kinetic modeling studies indicate that it may indeed be one of the steps in the growth process.[95]

A class of surface reactions that is important to model involves surface reconstructions. For example, it is has been proposed that the (2×1) reconstruction of a diamond {111} surface is a π-bonded chain[5] as shown at the left of Figure 3 albeit without the adsorbed H atoms. Indeed the Brenner potential predicts that the π-bonded chain structure is lower in energy than the bulk-terminated structure as shown at the right of Figure 3 but without the adsorbed H atoms. Initial attempts to heat the bulk reconstructed surface result in the bonds breaking between the top layer and the second layer.[97] At this point, however, the surface atoms start taking on the character of a graphite sheet. Since the potential is short ranged, there is not sufficient attraction to form bonds to make the five- and seven-membered rings. Conversely, taking the H-terminated π-bonded chain structure at the left of Figure 3 and heating it to yield the bulk terminated structure at the right of Figure 3 is also probably beyond the capability of the MD method. In this case there must not only be rearrangement of bonding between the C atoms but also half of the H atoms must migrate from blue C atoms to pink C atoms.

Two simulations have been performed on this system. In the first case the clean π-bonded chain structure was exposed to a gas of H atoms.[7] There was H-atom deposition as well as H-atom abstraction. Some of the five- and seven-member rings were severed and six-member rings formed. In the second case, one quarter of the H atoms were selectively removed from the H-terminated π-bonded chain structure.[8] Heating caused the surface to convert partially to the bulk-terminated structure.

Sinnott et al. examined surface patterning by atomically controlled forces in a molecular dynamics simulation.[98] A proposal had been made by Drexler[99] that an ethynyl radical attached to the tip of a scanning tunneling microscope (STM) or atomic force microscope (AFM) could abstract hydrogen with atomic scale precision by the following reaction:

$$\text{tip}-\text{C}\equiv\text{C}^{\bullet} + \text{H}-\text{diamond} \rightarrow \text{tip}-\text{C}\equiv\text{C}-\text{H} + {}^{\bullet}\text{diamond}$$

By this process radicals at specific sites on a diamond surface could be created. To test the proposal Sinnott et al. constructed a H-terminated diamond {111} surface and also a diamond tip with a H coating except for the ethynyl radical at the tip. The two surfaces were brought together. An irreversible reaction was observed whereby a H atom from the diamond surface was transferred to the ethynyl radical. Repeated application of such reactions can lead to atomically precise patterns of reactive radical sites. This may be useful in generating atomically controlled surface structures for building nanodevices.

D. Surface-Induced Dissociation

Recently there has been interest in using energized beams of ions to collide with surfaces. The experiments are typically performed for molecules with tens to hundreds of electronvolts of kinetic energy. Ions rather than neutral molecules are used as the ions are easier to energize and collimate. This experiment is analogous to the gas-phase mass spectrometric technique of collision-induced dissociation (CID) except that the collision partner is now the surface (SID).[9−102] In general, the goal is to examine the structure and stability of the incident ion by varying either the energy of the incident particle or the nature of the surface. The scattered particles are detected.

There have been several MD simulations of fullerene collisions with surfaces. Although some of these simulations do not involve H atoms, we include them since they illustrate a category of surface reactions. In 1991 Mowrey et al. used the Brenner potential and examined collisions of 150−250 eV C_{60} with a H-terminated diamond surface.[103] At 150 eV they found that all of the collisions are nonreactive, i.e., the fullerene reflects from the surface. At 200 and 250 eV the molecule reacts with the surface. In a handful of cases, a dissociation product, C_{57} or C_{59}, reflects from the surface. In other trajectories reaction products of $C_{60}H$, $C_{60}H_2$, $C_{58}H$, $C_{59}H$, $C_{61}H$, or $C_{61}H_2$ are found to desorb. In addition, the fullerene chemisorbs to the surface. This simulation exempli-

fies the dynamic range of neutral reaction events that can occur in SID. Of note is that in one observed channel of the fullerene reaction is a chain of C atoms emanating from the molecule.

Using a semiempirical density functional potential, Blaudeck et al. examined the scattering of C_{60} from an H-terminated diamond {111} surface for collision energies of 150−300 eV.[104] They found that collisions at all energies are reactive in contrast to the Mowrey simulations. They compared the energy partitioning to the results of Mowrey et al. and found that more energy goes into the internal energy and less into the center of mass kinetic energy as compared to results from simulations with the Brenner potential.

Galli and Mauri used a tight binding potential derived from first principles quantum calculations to model the collisions of C_{60} with a clean diamond {111} (2×1) surface at nine energies between 60 and 400 eV.[105] They performed one trajectory per energy. For energies of 120 eV and less, the molecule reflects from the surface. For 120−240 eV collisions, bonds are formed between the molecule and the substrate, and surface defects are formed. Finally at the highest energies a considerable number of bonds are broken. One dissociation channel observed is also a chain of C atoms emanating from the fullerene, which is the same as observed for the Brenner potential.[103]

Smith, Webb, and co-workers[106−108] examined the scattering of C_{60} with graphite and silicon for energies up to 15 keV using the Tersoff potential.[109] Not surprisingly at the highest energies they observed considerable fragmentation of the fullerene, implantation of the fullerene into the substrate, and ejection of pieces of the substrate.

Beardmore et al.[110] examined the collisions of 10−30 eV H with C_{60} using the Brenner potential. They found that the H atom preferentially adsorbs to the outer surface of C_{60} but that it can also adsorb to the inside of the fullerene. This latter adsorption process, however, causes C−C bonds to break and ultimately allows the H atom to migrate to the outside of the fullerene.

From consideration of the above simulations, it is logical to examine the effect of two fullerene molecules hitting each other. Zhang et al.[111] calculated trajectories resulting from the collision of two C_{60} molecules using a tight-binding potential at collision energies between 10 and 110 eV. At lower energies the molecules are scattered from each other and at the highest energies they undergo fragmentation. In the intermediate region the two molecules are observed to fuse. The authors characterize the various structures formed.

All of the above-mentioned investigations are for fullerenes, whereas the SID experiments cover a wide variety of incident molecules. Sundararaman investigated collisions of benzene (C_6H_6) and phenyl radical (C_6H_5) with a H-terminated diamond {111} surface and a phenyl-terminated diamond {111} surface in order to examine the effect of the reactivity difference between the two molecules and the two surfaces.[10]

Two orientations of the molecules, one in which the molecule is flat with respect to the surface and one in which it strikes the surface in an upright configuration were examined. For the phenyl radical it is the radical end that approaches the surface. At a collision energy of 20 eV for the H-terminated diamond surface, all orientations of the two molecules reflect from the surface (Figure 4b) except for phenyl with the radical end down as shown in Figure 4a. In this orientation the C_6H_5 radical molecularly adsorbs to a surface C atom (Figure 4d). Since all C atoms in the surface are originally fully saturated, the adsorption results in the cleavage of a bond in the substrate. At higher energies dissociative adsorption occurs (Figure 4c).

Finally we have examined the collision of phenanthrene with a molecule of benzene physisorbed on a H-terminated diamond {111} surface.[112] We observe that the phenanthrene reacts with the benzene molecule and that the entire entity subsequently reflects from the surface.

E. Sputtering

The studies of 1−100 eV C deposition into diamond,[89] and the high-energy C_{60} scattering from surfaces,[106−108] lead to the simulations of kiloelectronvolt particle bombardment or sputtering of solids. In contrast to the SID experiments, in sputtering the initial particle is usually an atomic ion, e.g. Ar^+, and generally has thousands of electronvolts of kinetic energy.[11] The detected species are those that are ejected from the substrate due to a collision cascade initiated by the energized particle. Smith and Webb have examined the kiloelectronvolt particle bombardment of diamond and graphite.[113,114] They predict the energy and angular distributions of the ejected material along with the mechanisms of ejection.

Of direct relationship to the surface reactions discussed in the early part of this article are the MD simulations of 500 eV Ar bombardment of organic films such as CH, CH_2, CH_3, C_2H_3, C_3H_7, and C_5H_9 on a Pt{111} surface.[12,115−118] As shown in Figure 5 several reactions are predicted from the calculations. First there is molecular ejection, e.g. C_2H_3, from an ethylidyne (C_2H_3)-covered surface. There are direct cleavage reactions, for example, the most abundant ejected particles from the C_2H_3-covered surface are H atoms and the CH_3 radicals.[12] There are rearrangement reactions where an internally excited C_2H_3 ejects and within 1 ps rearranges to give stable acetylene (HCCH) and a H atom. To our surprise there are also H abstraction reactions such as shown in Figure 2. The atomic H forms from an energetic collision and then moves laterally across the surface. As it collides with an adsorbed C_2H_3 molecule, it abstracts a H atom and forms gaseous H_2.[115] These simulations provide insight into what is happening near the surface and help explain some of the products observed in the experiments.

F. Friction

Friction has been modeled by sliding two diamond slabs against each other. The slabs are moved in a horizontal direction while a force is applied in the vertical direction. When two H-terminated {111} diamond surfaces are moved under these circumstances no chemical reactions are observed.[119] When

one of the adsorbed H atoms on the surface is replaced by a functional group, such as C_2H_5 as shown in Figure 6, reactions occur.[13] In the sequence shown, first an H atom is sheared from the tail of the ethyl group (Figure 6a). The radical on the ethyl then bonds to the lower surface, adhering the two surfaces (Figure 6b). In this process, two H atoms form a H_2 molecule. As the surfaces continue to move, bonds break and a free ethylene molecule is formed (Figure 6c). The loose H_2 and C_2H_4 molecules in the interface form debris that can hinder smoothly sliding surfaces.

G. Time-Dependent Monte Carlo

Brute force MD simulations will probably never be stretched beyond the microsecond regime as required for many processes of experimental interest. As a complement to the MD approach several workers are developing Monte Carlo (MC) prescriptions that incorporate a real time clock and utilize reaction mechanisms and rates derived from MD simulations and otherwise. A recent comparison of different approaches is given in ref 50. In keeping with the spirit of this article, we mention here only those that deal with hydrocarbon reactions, i.e. diamond growth.

In one study, the diamond {001}(2×1) surface in the presence of gaseous H atoms and H_2 molecules was modeled with a time-dependent Monte Carlo (TDMC) approach.[50,51] The quantities of interest are the concentration and distribution of radical sites. The processes such as H atom and H_2 molecule adsorption and desorption, H-atom abstraction as well as H-atom diffusion were included in the TDMC calculations and equilibrium concentrations of radical and π-bonded sites were calculated as a function of temperature. Moreover, the time-related quantities such as the lifetime of radicals and π-bonds and the diffusion length of the radicals before they are destroyed were also determined.

This method has been extended to a three-dimensional growth of diamond.[1] In this simulation, reactions of gas-phase CH_3 radical with the diamond surface as well as surface reactions were included. Diamond films of 10−100 layers were grown in the simulations and the observed growth rate of ~0.5 μm/h at 1200 K is in agreement with experimental results. The overall growth rate is dominated by the CH_3 concentration in the gas mixture and is in agreement with predictions of Harris and Goodwin.[95] The predicted activation energy for diamond growth is 13 kcal/mol, whereas the experimental value is 8 kcal/mol.[53] For temperatures between 1000 and 1200 K the simulations predict that the H abstraction process is the rate-limiting step and for temperatures approaching 800 K a new trough-insertion process has been identified as the rate-limiting reaction.

There are three kinetic MC investigations of the processes related to diamond growth. Frenklach has modeled the concentration and distribution of radicals and diradicals on diamond[120] but has not included either the time domain or the energetics specific to π-bond sites. Frenklach also incorporated the tetrahedral diamond structure and adsorption of CH_3 and C_2H_2 onto an adamantane seed crystal.[121] He assumed that the surface reactions occur instantaneously. Consequently, the time in his simulation is related to the collision time of the various gas phase species. Finally Xing and Scott have modeled acetylene adsorption, desorption, and reaction with a diamond {111} surface.[122] They have based their MC moves on initial and final state energy differences which inherently assumes equilibrium at every step.

IV. Quantum Effects

At this point it is also relevant to mention efforts to include explicit quantum effects in the simulations of the dynamics of processes at surfaces. The examples discussed below, however, stray from our themes of reactions and hydrocarbons. Efforts to include explicit quantum effects have been few and are limited to systems of either low dimensionality or where specific approximations can be made regarding the physical or chemical process under investigation. This section is not intended to be comprehensive, but it is included in order to exemplify the challenges associated with describing nonclassical behavior.

An obvious example where quantum effects can be important are processes involving hydrogen. For example, diffusion of H atoms and H_2 dissociative chemisorption on metal surfaces has been investigated by transition-state theory and correlation function theory based methods.[123−127] The quantum effects due to H tunneling through reaction barriers at low temperature are significant. A factor of 8−10 difference in the classical and quantum reaction rates has been found in these simulations. These two methods, however, are not dynamical in the sense that the motion of the species are not followed. Rather the initial, final, and the transition state configurations of the system have to be known in advance and then the rate is calculated.

The kiloelectronvolt particle bombardment process results in neutral and ionic species being ejected, and there have been several efforts aimed at including quantum effects in MD simulations of bombardment. The first effort in this vein was by Sroubek and coworkers.[128,129] They developed an approximate electronic structure scheme which incorporates atomic orbitals for each atom and a time-dependent hopping integral. This work was followed by that of Lin and co-workers[130,131] who determined that the ionization probability at low velocities is dependent on the velocity of the particle right before it ejects rather than the measured velocity at the detector.[131] Even though the quantum mechanics is simplistic in these studies, it is still too computationally intensive to include for a large number of atoms.

An alternative approach is to model the quantum mechanical effects by a simple model and thus be able to incorporate thousands of atoms in the simulation. For example, in a recent study on the populations of Rh atoms ejected in the $^4F_{9/2}$ and $^4F_{7/2}$ fine-structure states due to kiloelectronvolt particle bombardment of the Rh{111} surface, we modeled the collisional excitation process as a function of the distance of closest approach and the local electronic environment.[132−134] We were able to explain that the anomalous velocity dependence of the excitation probability

was due to collisions of atoms in the 1−20 Å region above the surface. A similar approach had been used previously to examine the probability of Auger deexcitation in collision cascades.[135]

The methodology for explicitly including electron−hole pair transitions in semiclassical dynamics simulations of CO on Cu{100} has been recently developed by Head-Gordon, Tully, and co-workers.[136,137] They incorporate a frictional term describing nonadiabatic energy transfer from the nuclear motion to electronic excitations and a fluctuating force for the reverse reaction.[137] They express the electronic frictions by evaluation of matrix elements from molecular orbital electronic structure calculations.[136,138] From this approach they predict mode-specific vibrational lifetimes[137] and desorption yields due to femtosecond laser-induced desorption.[139] This method has been proposed as also being applicable for desorption induced by electron transfer (DIET) processes.[140] A similar approach incorporating the nonadiabatic electronic transitions with MD simulations has also been used by Li and Wahnström to study H-atom diffusion in Pd.[141]

V. Commentary

A diverse collection of reactions has been discussed above. In reflection, what does molecular dynamics modeling do well and where does it struggle? With an accurate interaction potential it is relatively straightforward to calculate reaction probabilities and mechanisms for direct reactions. An example of this application is the adsorption probability of atoms and small molecules on diamond surfaces. The trend that the adsorption probability decreases with increasing number of atoms in the incident radical due to steric hindrance makes good chemical sense.[77] The precision of the absolute value of the reaction (adsorption) probability, however, is not nearly as great as for the classic gas-phase $H + H_2$ exchange reaction. In fact, the experimental conditions are also not as clean and precise as for the gas-phase reaction. Virtually every surface has some steps, kinks, and defects. Consequently the experimental measurements contain averages over unspecified configurations. Perhaps we are doing as well as is justified in modeling adsorption phenomena on chemically reactive surfaces.

Another success arena has been in exploring reactions in regimes where the conditions are far from equilibrium such as SID, sputtering, friction, and nanoabstraction. Certainly qualitative factors in these reactions have been elucidated. Moreover, the approximate quantitative information such as the energy ranges where the incident molecules reflect from the surface, molecularly adsorb, and/or dissociatively adsorb has also been obtained. None of the investigators, however, have made quantitative predictions as to the absolute number and type of all the reaction products.

The extreme conditions of energy or pressure in the SID, sputtering, or friction studies induce reactions to occur on a time scale that is amenable to MD simulations. We dream, though, of being able to model reactions under more temperate conditions. An example of this is the CH_2 insertion reaction on the diamond {001}(2×1) surface. A specific step in the overall growth process has been predicted by MD simulations.[4] Ab initio calculations[96] and kinetic modeling[95] have confirmed its feasibility and importance in the diamond growth process on the {001} surface. The proposed insertion reaction is even sufficiently intriguing that a small molecule analog is being synthesized and analyzed for reaction mechanisms.[142] What has not been done in the MD simulations, however, is to grow multilayers of a diamond film because of the time scale of the real growth is micrometers per hour or angstroms per second.

Another type of reaction process which probably cannot be modeled with MD is the conversion of the diamond {111} surface from the (1×1) bulk terminated configuration to the (2×1) reconstruction. As discussed above, the Brenner potential is too short ranged for the critical interactions in the rearrangement reaction. The development of reactive hydrocarbon potential with suitable long-range interactions could, however, alleviate the problem in studying such phenomenon in the future.

Molecular dynamics modeling has demonstrated itself as a useful tool for understanding reactions at surfaces. Much of the technology, except for PESs, is available to employ the MD method for a vast array of phenomena. It is the PESs that are limited in diversity. As we conclude in our recent review article on PESs,[54] "large scale simulations are here to stay. The ultimate impact will depend on the availability of better and more diverse many-body PESs."

There has actually been a slowdown in the development of empirical PES. Rather, most development is toward PES based on electronic structure methods such as mentioned above for fullerene collisions.[104,105,111] The series of calculations of the fullerene molecules scattering from diamond surfaces exemplifies the current situation. First, even though different potentials have been used, the qualitative results are the same from all the simulations. Second, only one trajectory per energy has been calculated for the "best" potential,[105] whereas 50 trajectories per energy have been calculated for the empirical potential.[103] This reflects the computer time required for the evaluation of the forces. What may be gained in accuracy for one trajectory with a better potential is lost because experimental quantities are averages over many initial configurations. In fact, the studies by Mowrey et al.[103] and Blaudeck et al.[104] show clearly that the scattering outcome depends on the initial aiming point on the surface and the orientation of the molecule. One trajectory is thus insufficient for detailed comparisons to the experimental results. Many of the successes of the large-scale MD simulations have been for many trajectories of large numbers of atoms. Empirical PESs are still needed.

Resolving the time scale issue is trickier. The work on TDMC calculations mentioned earlier is promising. Like all MC calculations, however, a list of reactions must be delineated for the calculation. For example, the three-dimensional calculation of diamond growth[1] may have included all the important reactions for single-crystal diamond growth but did

not include graphitic or amorphous configurations. In contrast, a MD simulation allows the atoms to move anywhere in phase space. We are optimistic, though, that the TDMC approach will become a useful tool for taking microscopic information about reactions into the macroscopic time domain. Consequently it is a complementary approach to MD for modeling surface reactions.

The challenges of incorporating electronic effects will remain for some years. There are two extreme situations. The first corresponds to a relatively localized system such as CO on Cu{100}. In this case ab initio electronic structure calculations can be performed to provide the fundamental quantities (nonadiabatic crossing terms) which can be incorporated into the MD simulations.[136] The second situation is exemplified by the anomalous velocity dependence of the excitation probability of Rh atoms ejected in $^4F_{9/2}$ and $^4F_{7/2}$ fine structure states.[132] In this case, a simple excitation model was incorporated into MD simulations of thousands of atoms and the correlation of the observed phenomena to specific collision events was made. Both of these approaches will be needed in the future in order to fully understand reaction channels at solid surfaces.

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