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CHEMICAL DYNAMICS AT SURFACES

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The current status of molecular dynamics simulations of chemical processes at surfaces is assessed. Limitations of the method are discussed, and recent progress towards overcoming the limitations is described. The reliability and depth of understanding achievable through interplay between simulation and experiment is illustrated by a simple example, the trapping of Ar on a Pt(111) crystal surface. The prognosis for extending these techniques to chemically reacting systems in "real" environments is addressed.

Keywords: Molecular dynamics simulation of argon adsorption on Pt(111), state of molecular dynamics calculations to simulate surface chemical processes.

1. Introduction

Chemical Dynamics is the study of the atomic motions that occur as a chemical system evolves from reactants to products. As a molecule approaches a surface, what determines whether it will stick or bounce off? If it bounces off, how much energy will be transferred among its rotational, vibrational and electronic states, and among the phonon and electronic modes of the substrate? If the molecule sticks, how much time will it take to settle down into a binding site? Will it dissociate or remain intact? How far will it diffuse across the surface? Will it react with other adsorbates or with substrate atoms? Will it subsequently desorb from the surface, either thermally or via laser excitation? These processes involve the concerted motions of many atoms, and it is becoming increasingly clear that a proper understanding of them must take explicit account of this multidimensional behavior.

As an illustration, consider the conventional one-dimensional view of a molecule dissociating at a surface [1], as shown schematically in fig. 1a. According to this picture, the molecule approaches the surface on the lower molecular potential curve, and then makes a transition to the dissociative potential curve at the point of intersection. While this picture can and has been useful in categorizing dissociative adsorption, it provides a very misleading view of the actual dynamics of atomic motion. A somewhat improved picture is afforded by fig. 1b, which is a schematic two-dimensional view of the same process. It is clear from fig. 1b that the dissociative and molecular curves of fig. 1a do not intersect each other. In fact, they are not distinct curves at all, but rather are cuts across different regions

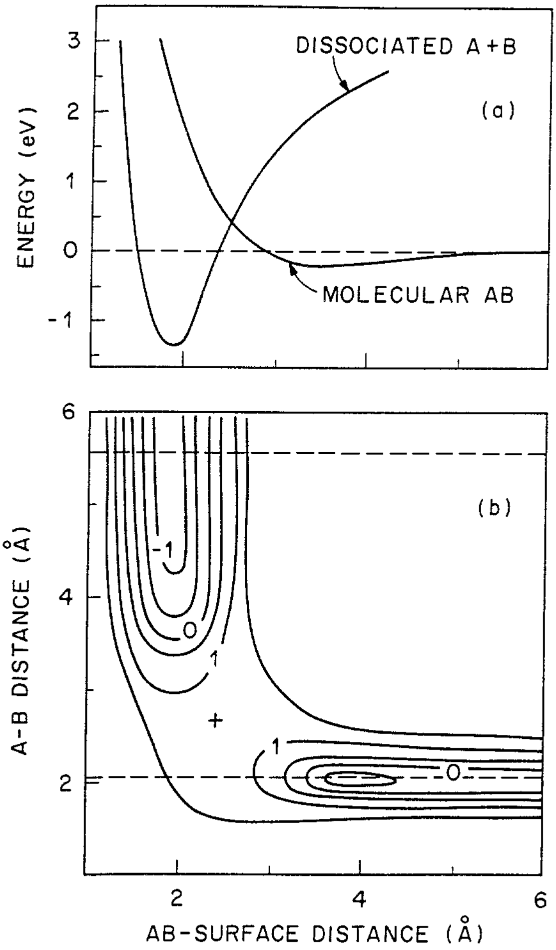

Fig. 1. (a) A schematic one-dimensional view of recombinative desorption and dissociative adsorption of a diatomic molecule AB on a surface. (b) A schematic two-dimensional view of the same process. Equal energy contours are in eV. The dashed lines in (b) denote the cuts across the potential energy surface that correspond to the curves shown in (a).

of the same multidimensional potential energy hypersurface. The dissociation of a molecule is better described by a concerted motion along this hypersurface than an artificial transition at a hypothetical localized crossing point. The two-dimensional view of fig. 1b begins to make clear that the reaction probability can be affected by the curvature of the reaction path, by the location as well as the height of the reaction barrier, and by the initial distribution of energy among molecular internal and translational modes. Even this view is over-simplified, of course. The roles of initial orientation of the molecule, of molecular rotational energy, of surface atom vibrations, of surface corrugation, etc., require a full multidimensional description of the reaction dynamics. It is for this reason that molecular dynamics, the simulation of atomic motions in full dimensionality, is beginning to play a central role in our search for a molecular level understanding of surface chemistry.

Our ability to simulate, on the computer, the detailed motions of individual atoms through the course of a surface chemical reaction has progressed substantially in recent years [2–5]. There have been a number of advances in the methodology of molecular dynamics simulation, some of which are briefly outlined below. The primary reason for the progress, however, is experimental. Until relatively recently, chemical reactions at surfaces were usually studied under conditions that were so complex that there was little hope of making direct contact with molecular level theory. Almost any theory, with an adjustable parameter or two, could fit the experiments. Now more and more studies are being carried out under controlled conditions using nearly perfect single crystal surfaces and quantitative probes not only of thermal reaction rates, but of molecular level details; energy and angular dependences, lifetimes, identity of intermediates, and even quantum state specificity [6,7]. These experiments provide a crucial testing ground for theory. Our ultimate goal, of course, is to be able to simulate complex chemical reactions under "real" conditions with quantitative and predictive success. But there is no hope of achieving this goal without first understanding the elementary steps that contribute to the complex process.

The availability of detailed and quantitative experimental data on well-characterized systems has provided the input required to challenge theory. Theory has answered with several important advances that enhance our ability to achieve a molecular level description of surface chemical reactions. Some of these advances are described, in qualitative terms, in the next section. An example of the use of computer simulation, in conjunction with experiment, to achieve a molecular level understanding of the dynamics of interaction of a gas with a surface is presented in section 3. The example chosen, the trapping of argon on a single crystal platinum surface, is a far cry from a catalytic chemical reaction. Nevertheless, the example serves well to illustrate the molecular dynamics technique, and perhaps there are some insights drawn from this study that may have much broader implications. The current status and future potential of the molecular simulation approach is summarized in the conclusion section.

2. Computer simulation of atomic motion

The standard technique for simulating the motions of a collection of interacting atoms is molecular dynamics [8]. Molecular dynamics in its usual form is based on two assumptions.

1. The interactions among the atoms are governed by some conservative force field, usually assumed to be derived from the electronic ground state adiabatic potential energy hypersurface. Additional assumptions about the form of the force field such as pairwise additivity are common, but are not central to the

method. In particular, pairwise additive forces are inadequate to accurately describe the breaking and forming of chemical bonds during chemical reactions at surfaces.

2. The motion of the atoms is governed by classical mechanics.

Molecular dynamics has been successfully applied in a great many contexts, including gas-phase chemistry, liquid state dynamics, diffusion in solids, phase transitions, and crystal growth, as well as in gas-surface interactions. There are some serious limitations of the method, however. Some of these have been at least partially overcome, but many challenges remain.

The first and most serious limitation is the availability of accurate force fields. Chemical reaction dynamics is generally particularly sensitive to quantitative details of the interaction potentials, such as the heights and locations of reaction barriers. If the assumed forces are not accurate, then the simulations will most likely be useless. *Ab initio* quantum chemical and local density methods, although very valuable for obtaining semiquantitative interaction potentials, have not yet been developed to the point that they can reliably produce force fields to the accuracy required to describe chemical reactivity. Completely empirical interactions are even less reliable. Empirical potentials can usually be constructed and optimized to fit most any finite set of experimental data. But except for very simple, nonreactive processes (see next section), such fits are by no means unique. The unreliability and absence of predictive value of empirical potentials has been a hard lesson in gas-phase chemical dynamics. Empirical interaction potentials that reproduce all previously existing results seem to almost always fail as soon as a new experiment is performed. In view of the increased complexity of chemistry at surfaces, the outlook is even bleaker here. That is not to say that dynamical studies based on empirical forces may not be useful for obtaining qualitative insights and elucidating trends. But if molecular dynamics is to become a predictive theory, the force fields must be based on a correct quantum mechanical foundation. However, they need not necessarily be obtained entirely by *ab initio* methods. Indeed, it appears that the most promising method, at least for the near future, is to intelligently introduce a minimum number of empirical normalization points or corrections into a legitimate quantum mechanical based theory. One promising attempt of this type are the approaches based on the "embedded atom" [9] or "effective medium" [10] methods. Future progress in generating accurate force fields is clearly the greatest challenge facing the development of quantitative and predictive methods for simulating chemical reactions at surfaces.

A second important limitation of the molecular dynamics method, as applied to surface chemistry, is the large number of atoms that may be involved. In most situations it appears correct to view chemical changes as local; the making and breaking of chemical bonds directly involves the motions of only a few, or perhaps a few dozen, nearby atoms. However, the local region is altered by virtue of being embedded in a large system. It is altered for two reasons. Firstly, the electronic properties of the local region are effected by the surroundings. Whether the substrate is metallic or insulating is a bulk property that can strongly effect the local chemistry. These electronic effects are, or should be, incorporated in the force fields employed in the simulations. A second way the surroundings can effect the local chemistry is a dynamic one. Energy can flow in and out of the local region through its connection to the bulk. In order to make the molecular dynamics simulation computationally tractable, it is important to develop a way to take account of this energy flow so that the motions of only a relatively small number of atoms need to be computed explicitly. This has been accomplished quite successfully using socalled "stochastic trajectory" techniques [11–13]. It has been shown that surrounding atoms that participate only as a "heat bath" can be removed from explicit consideration, by introducing in their place frictional terms and fluctuating forces at the outskirts of the local region. (The word "stochastic" refers to the random nature of the fluctuating force.) Roughly speaking, the frictional terms allow for the dissipation of energy from the local region to the omitted surroundings. The fluctuating forces take account of thermal fluctuations of the surroundings that are felt by the local atoms. The frequency spectra of the fluctuating forces and the memory kernels of the frictional forces can be chosen to accurately mimic the properties of the substrate, using knowledge of the bulk and surface phonon dynamics. The frictional and fluctuating forces are chosen to satisfy the "fluctuation-dissipation" theorem [14] so that energy dissipation balances thermal energy input. Thus even a very small number of atoms will acquire a temperature; i.e., the energy of the local region will fluctuate properly as though it were connected to the infinite system. In fact, the control of temperature afforded by the stochastic trajectory method allows one to examine the effect of changing temperature so that one can model, e.g., chemistry produced by rapid laser heating. The stochastic trajectory method has proved very successful in reducing the number of atoms needed for accurate simulation of surface chemistry to a tractable number, typically of order 20 to 100.

Another limitation to molecular dynamics involves time scales. The numerical integration of the classical mechanical equations of motion must be carried out on the timescale of the fastest atomic motion, usually a high frequency vibration. This imposes an integration time step of typically 10^{-15} seconds. It is straightforward to simulate processes that occur on the picosecond time scale, and tedious but possible for processes that occur in one nanosecond (10^6 time steps). Processes that occur on more typical laboratory time scales (10^{-6} to 10^0 seconds) would require prohibitive computational time to address directly. Fortunately, this limitation of molecular dynamics can be overcome for a very important subset of slow processes, those termed "infrequent events" [15–18]. Most slow chemical reactions take a long time to occur because they must surmount an energy barrier of height many times kT. For such cases, once the system is appropriately energized, passage to products or return to reactants proceeds very rapidly, usually on the subpicosecond timescale. It is the seemingly aimless wandering in phase space prior to energization that renders the reaction slow, i.e., the reaction is not really slow, but infrequent. For such situations, one can exploit the time-reversal symmetry of classical mechanics. One can initiate trajectories at or near the bottleneck to the reaction, i.e., the energy barrier, and then integrate both forward and backward in time. In a very short time the forward and backward paths will have trapped in the product and/or reactant valleys of the potential energy hypersurface. These very short trajectories contain all dynamical information about the reaction, provided one knows how to properly select the initial conditions of the trajectories in the bottleneck region. For reactions taking place under equilibrium conditions one can choose the initial conditions from an equilibrium ensemble. This method has proved to be both accurate and practical, and has been very valuable in extending the power of molecular dynamics to long timescales for equilibrium chemical reactions or reactions for which the reactants are equilibrated. There has even been progress in developing methods to treat infrequent events that are far from equilibrium [19]. Thus molecular dynamics is not limited to short timescales.

Another limitation of molecular dynamics is associated with one of its underlying assumptions, that atomic motion obeys classical mechanical equations of motion. Atomic motions evolve according to quantum mechanical laws of motion. Classical mechanics is an approximation to quantum mechanics. In fact, it is the most widely applicable approximation we know. However, it is not always accurate for describing atomic motion. Quantum effects associated with tunneling, zero-point motion and quantum interference can be important and in some cases even dominant in certain chemically reactive encounters. The main difficulty, in surface chemistry, occurs for reactions involving hydrogen. Heavier atoms (carbon, nitrogen, oxygen, etc.) are generally well described by classical mechanics. The accuracy of classical mechanics for reactions involving these atoms has been established in gas-phase studies. Classical mechanics is undoubtedly even more accurate for describing surface chemical reactions because of their complexity. Averaging over many degrees of freedom, many initial conditions and many pathways serves to reduce quantum interference effects and render results less sensitive to other quantum effects. Reactions that explicitly involve hydrogen atom motion, however, remain a problem. The most difficult problem is tunneling; at temperatures low compared to the reaction barrier, reaction rates can be dominated by classically forbidden tunneling. Accurate completely quantum mechanical methods in full dimensionality are as yet impractical, but semiclassical methods have been developed for including tunneling in multidimensional dynamics, with some success [20]. Nevertheless, this remains a serious limitation to our ability to quantitatively describe the dynamics of many important catalytic reactions.

The final limitation to molecular dynamics to be addressed here is associated with the other basic assumption of the method, that atomic motion is governed by a conservative force field. This assumption is generally justified by the Born-Oppenheimer approximation; atomic motion evolves so slowly that the electrons adjust adiabatically to the atomic motion. However, there are many situations in surface chemistry where this assumption breaks down, often dramatically. This is particularly true for chemistry at metal surfaces. Metals possess conduction electrons which can be excited via electron-hole pair formation to any arbitrarily small energy, providing a mechanism for energy dissipation that can be particularly effective for high-frequency vibrational motion. More importantly, transitions among different electronic states involving the adsorbates can be driven by atomic motion. Of particular note is electron transfer in either direction between the adsorbate and the metal. The work function of a typical metal is about 5 electron volts, giving the metal a larger electron affinity than a halogen atom and almost as small an ionization potential as an alkali atom. In addition, an ionic species near a metal surface is stabilized by the image charge. The result is that adsorbate-metal systems exhibit covalent and ionic states that lie close to each other energetically, frequently displaying avoided crossings. Even in thermal energy reactions, electronic transitions among these electronic states can be facile. To each electronic state corresponds a different potential energy hypersurface, i.e., when an electronic transition occurs the forces felt by the atoms are suddenly altered, frequently drastically. In order to treat such processes, molecular dynamics must be extended to motion on more than one potential energy hypersurface. But electronic transitions are quantum mechanical and must be described as such, so a mixed quantum-classical dynamics must be developed. Of course, a completely quantum mechanical description of both electrons and atoms would be preferable if possible, but as discussed above an accurate fully quantal molecular dynamics in full dimensionality is totally intractable for the foreseeable future. Two mixed quantum-classical methods have been proposed recently to address this problem [21,22]. Although different in some details, both methods allow electronic transitions to occur probabilistically when called for by the time-dependent electronic Schrödinger equation, with the required change in the forces that govern the atomic motion. Thus a single initial multidimensional trajectory can branch into a number of paths, each with a different history of electronic transitions. While these methods have yet to be demonstrated on a realistic surface chemistry problem, they show real promise. It should be cautioned, however, that the possibility of electronic transitions not only complicates the dynamics, it further complicates the most challenging part of molecular dynamics, obtaining accurate interaction potentials. For such cases, not only must one obtain the ground state potential, but also potentials corresponding to each relevant excited state as well as the couplings between pairs of excited states that promote transitions.

3. Trapping of Ar on Pt(111)

The objective of molecular dynamics simulation is not merely to reproduce experiment. Agreement with experiment is an important test of the validity of the calculation, of course. But molecular dynamics should be capable of accurate prediction for conditions (e.g., temperatures, pressures, etc.) far removed from those of the comparison experiments. Molecular dynamics should also provide insight into the dynamical mechanisms responsible for the experimental behavior. Finally, molecular dynamics should uncover underlying general principles that can be transferred to different systems so that one need not carry out calculations anew for each different chemical system.

To illustrate how molecular dynamics, in conjunction with modern experimentation, can enhance our understanding of chemical dynamics at surfaces, let us examine the following case study: the trapping of argon atoms on the (111) face of single-crystal platinum. The trapping of rare gases on metal surfaces has been examined in detail previously, both experimentally [6] and by molecular dynamics simulation [23]. If there is any gas-surface system that is completely understood, this most surely must be it. Thus some justification for re-investigating this system is in order. Our first motivation is that new and detailed molecular beam scattering results have been recently reported [24]. The gas-surface interaction potentials for rare gases on single crystal metal surfaces are so simple that it is difficult to imagine that standard empirical potentials are very far wrong. Furthermore, for the heavier rare gases classical mechanics should describe trapping and scattering with very high accuracy; quantum effects should be negligible. Thus this affords an unprecedented opportunity for a detailed and quantitative comparison between experiment and theory, even if it is for a relatively uninteresting system. But the system is not entirely uninteresting, either. As is discussed subsequently, rare gas scattering can provide insights into the dynamics of other short-lived, weakly bound adsorbates, such as precursors to chemisorption and adsorption at high temperatures. Our final motivation for choosing this system for study is that it has not been that well understood after all; as discussed below, there are some surprises.

The previous body of work on rare-gas scattering from smooth, close-packed single crystal surfaces largely confirmed that the simple hard-cube model provided an adequate description of the dynamics [6]. The hard-cube model asserts that there exist no forces on the adsorbate directed along the surface plane. Thus the component of adsorbate momentum in the surface plane is conserved during a collision; only the component of momentum normal to the surface is altered. If this is true, then trapping probabilities can depend only on the component of momentum normal to the surface, not on the total momentum. This behavior is termed “normal energy scaling”, and has been observed to hold approximately in both experiments [6] and simulations [25]. The recent experiments of Mullins et al. [24] on Ar trapping on Pt(111) also confirm this behavior at low surface temperatures, but at higher surface temperatures they observe a striking breakdown of normal energy scaling. While at higher temperatures the surface would be expected to become dynamically “roughened”, the magnitude of the deviation from normal energy scaling appears much too large to be accounted for by this effect.

The molecular dynamics simulations on this system were carried out by Head-Gordon, et al. [26] using the stochastic trajectory method discussed earlier to allow for energy flow into and out of the local region. A surface slab of three atomic layers with 36 atoms per layer was employed. Periodic boundary conditions were imposed in the x and y (surface plane) directions. Random forces and frictions were applied in the z (surface normal) direction only to the bottom (interior) layer of substrate atoms. Harmonic Pt-Pt interactions were taken from earlier work [13]. The Ar -surface interaction potential was taken to be a pairwise additive Morse potential. This form has been shown to accurately describe rare gas trapping at metal surfaces [25]. The Morse parameters were chosen to reproduce a large body of experimental results, including binding energy, angular and velocity scattering distributions, and low temperature trapping probabilities. The high temperature trapping probabilities which are the focus of study here were not included in the fitting. The gas-surface force field employed is blatantly empirical. It is only because of the simplicity of the rare gas, metal interaction and the wide body of data reproduced that we can be confident that the potential is approximately correct.

This system is not very demanding for molecular dynamics. The assumption that motion evolves on a single adiabatic potential energy hypersurface should be accurate in this case. Argon does not participate in charge transfer, and the excitation of electron-hole pairs is believed to be insignificant in this system [27]. Argon and platinum atoms are sufficiently massive that classical mechanics should be entirely adequate, particularly at the high temperatures of interest here. Trapping is prompt, and so can be simulated directly with no need for long timescale techniques. Frictional and fluctuating forces were employed in these calculations to account for energy flow in and out of the surface slab, but even this was not necessary. The energies deposited here are so small that the 108 atom slab provides an adequate heat-bath on its own.

At the lowest surface temperature examined, the simulations confirmed the experimental finding of approximate normal energy scaling of the trapping probability. At the higher temperatures, trapping is not uniquely defined. The residence time of trapped atoms on the surface is so short at these temperatures (e.g., 45 ps for $T_s = 273$ K) that the distinction between directly scattered and trapped atoms is somewhat blurred. A definition that proved satisfactory for this study was that a trajectory was designated "direct" if the atom scattered after only one encounter with the surface, and "trapped" if the trajectory bounced more than once on the surface before escaping. The usual assumption is that trapped molecules ultimately desorb with an angular distribution that is symmetric with respect to the surface normal; i.e., they lose memory of the angle and velocity at which they initially impinged on the surface. This, in fact, was the assumption on which the method for extracting trapping probabilities from the

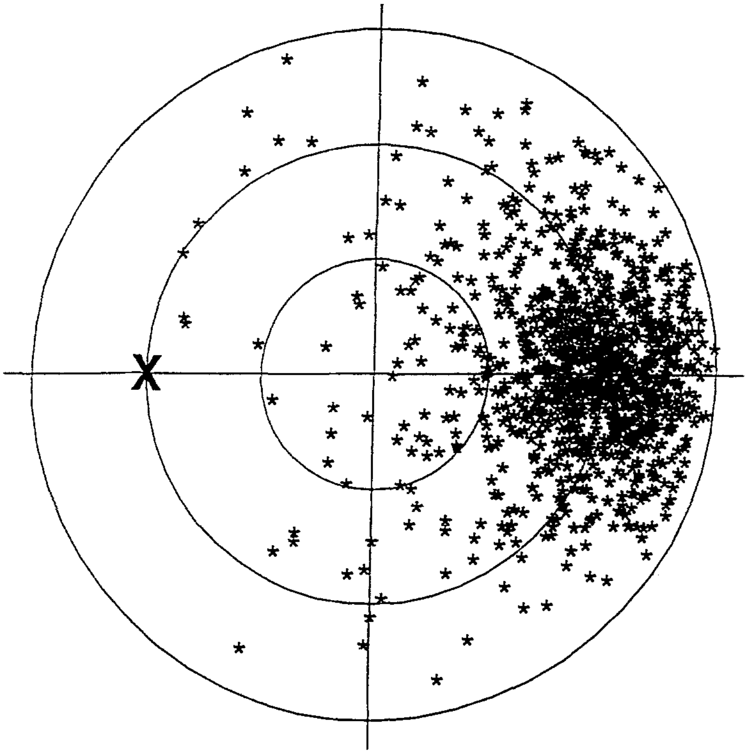

Fig. 2. A scatter diagram of the angular distribution of the desorbing flux associated with quasi-trapping (i.e. excluding atoms that scatter on the first bounce) for Ar atoms with 2 kJ mol^{-1} normal energy incident at 60° on a 273 K Pt(111) surface. Each point is calculated trajectory. The angle θ, $0 < \theta < 90°$, between the final velocity vector and the surface normal is plotted radially. The angle ϕ, $0 < \phi < 360°$, between the scattering plane and the plane formed by the surface normal and the final velocity vector is plotted as the polar angle. (From ref. [26]).

molecular beam experiments was based. The experimental trapping-desorption flux was determined from the intensity of scattering near the surface normal. Fig. 2 shows a calculated angular distribution for the trapped (multiple bounce) trajectories for Ar incident at 60 degrees from the normal on a 273 K platinum surface. The trapping-desorption flux is seen to be far from symmetric about the surface normal. Thus the trapped atoms desorb without complete loss of memory of their initial conditions. Complete loss of memory of the normal momentum occurs very quickly; the relaxation time for normal energy is calculated to be about 5 ps for this case. But the relaxation time for in-plane energy is calculated to be about 100 ps, longer than the mean residence time of 45 ps. Thus we are observing a kind of "quasi-trapping" in which the normal energy of the atoms thermalizes quickly and the atoms subsequently desorb in an ordinary thermal first-order process. But they continue to glide horizontally across the surface throughout their entire residence on the surface. The angular distribution of desorbing quasi-trapped atoms thus is not symmetric about the surface normal, but peaks somewhere between the specular reflection angle and the surface normal. As a result the initial experimental procedure of deducing trapping from the intensity near the surface normal under estimates trapping for atoms incident at large angles compared to those incident nearer the normal angle. This gives the appearance of a deviation from normal energy scaling toward total energy scaling. Thus the reported apparent deviation from normal energy scaling was not a result of the roughening of the surface at higher temperatures, but rather is due to the extreme flatness that produces the retention of memory of the in-plane momentum of trapped atoms.

This was a very simple example, chosen to illustrate the kind of insight that can be revealed by molecular dynamics simulations in conjunction with detailed experiments. More complex systems can and have been addressed successfully. For example, simulations of the effects of coverage on rare gas trapping, only a slight increase in complexity over the current example, have elucidated the role of enhanced energy transfer when an incoming atom strikes an atom of the same mass loosely bound on the surface [28]. Accurate simulations of non-dissociative interactions of molecules with surfaces have also been reported [29]. Initial applications [5] to chemical processes such as dissociative adsorption have been qualitatively illuminating, although uncertainties in the interaction potentials limit their reliability. Applications to surfaces with defects or impurities and at high pressures await only improvements in our ability to obtain the required interaction potentials.

4. Conclusions

The objective of this paper was to outline the current status of molecular dynamics simulation techniques, with emphasis on their application to chemical processes at surfaces. The example of the last section demonstrates that molecular dynamics can contribute significantly to our understanding of surface chemical processes. The simplicity of the example chosen, however, underlines the difficulties in carrying out similar studies for complex chemical reactions under real laboratory or industrial conditions. Reactions involving hydrogen pose a particularly difficult challenge, since they may display significant quantum mechanical effects. Numerical solution of fully quantal equations of motion, even with approximations, are feasible only for problems of greatly reduced dimensions. While such calculations may be illuminating, they are very limited. A full-dimensional classical mechanical simulation, even in situations where quantum effects are large, almost always provides a more realistic description of the true dynamics. A major goal, of course, is to develop tractable semiclassical methods for accurately including the essential quantum effects in an otherwise classical mechanical simulation.

The major limitation to molecular dynamics simulation of chemical reactions is the lack of accurate and predictive methods for computing the required potential energy hypersurfaces. Considerable progress has been made, but more is needed. Relatively little effort has been directed at developing semiempirical methods based on a legitimate and accurate theoretical framework. Methods based on very approximate theories such as tight-binding or extended Huckel, or on the bond-order-bond-energy method, cannot be expected to provide the required predictive and quantitative capability. But it is possible that more rigorously based semiempirical theories could be developed that do meet the quantitative and predictive criteria. This appears to be our best hope for significantly addressing the interaction potential problem over the next few years. In the meantime, application of molecular dynamics based on approximate or empirical force fields can continue to provide valuable qualitative guidance about chemical reaction dynamics, even for quite complex systems.

This paper has addressed methods for studying elementary chemical processes in well-characterized systems. The need to isolate and understand the fundamental steps, both experimentally and theoretically, cannot be overstated. But the ultimate goal is to address real chemical systems in their full complexity. This will require development of some kind of grand computer simulation scheme that incorporates all the simpler pieces. It is not too soon to begin in this direction.

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