Dynamics of Chemical Processes at Surfaces

JOHN C. TULLY

Bell Laboratories, Murray Hill, New Jersey 07974

Exciting progress is being made toward elucidating the dynamics of individual chemical events at the gas–surface interface.[1] Experiments are revealing or are on the verge of revealing incisive information such as angular and velocity distributions of gaseous products, residence times and lifetimes of intermediates, selective energy requirements for reaction, and energy disposal in products.[2] Efforts toward obtaining state-to-state probabilities and achieving alteration of chemical rates or pathways by selective laser excitation are planned. We are still not in sight of the ultimate goal of complete understanding of how electronic forces govern the evolution of atomic motion through a reactive encounter. Chemical processes at surfaces are too complex and perverse to relinquish their secrets readily. However, some valuable insights have been gained, and there is promise for much more.

Theories are gearing up to meet the challenge issued by the availability of detailed dynamical information about gas–surface processes.[3] "Stochastic classical trajectory" techniques have been developed to cope with the huge numbers of atoms involved in chemical events at surfaces. With these methods we are now able to achieve reliable computer simulations of the complicated maneuverings of individual interacting atoms as they search for favorable configurations, squeeze over potential barriers, get trapped in and escape from potential wells, and participate in the rupture and formation of chemical bonds.[4,5] An example, illustrated in Figure 1, is the dissociative adsorption of nitric oxide on a platinum surface. The sequences shown in Figure 1 are selected frames of a computer-generated movie[6] of recent stochastic trajectory studies of a variety of simple inelastic and reactive processes at surfaces. The movie illustrates a handful of "typical" events excerpted from the many hundreds of trajectories that were required to produce statistically reliable sticking probabilities, energy accommodation coefficients, surface residence times, reaction probabilities, product angular and velocity distributions, etc. In this Account we discuss the results of these studies, including a brief introduction to the stochastic trajectory approach. We will emphasize the physical insights gained and the implications to future experimental studies of gas–surface dynamics.

The first system we will discuss is a simple one, the scattering of rare gases from the (111) face of a platinum crystal. We have chosen this system because required gas–surface interaction potentials can be constructed

John Tully received his Ph.D. in Chemistry from the University of Chicago in 1968, working with R. Stephen Berry. He then performed molecular beam experiments with Richard Wolfgang as an NSF Postdoctoral Fellow at the University of Colorado and Yale University. Since 1970 he has a been a Member of Technical Staff at Bell Laboratories. He has been carrying out theoretical and experimental studies of simple gas-phase and gas-surface dynamical processes, with particular interest in electronically nonadiabatic phenomena.

without too much difficulty, and because very careful and detailed molecular beam studies have been carried out of sticking probabilities, surface residence times, and angular and velocity distributions. The stochastic trajectory studies duplicate the experimental results with quantitive accuracy. Furthermore, the calculations reveal information that is impossible to obtain experimentally, e.g., the dependence of sticking probability and accommodation coefficient on the position at which the atom first makes impact with the surface.

We next discuss thermal desorption of rare gases from platinum. The trajectory studies, employing the same interaction potentials that reproduced the scattering experiments, predict that rates of thermal desorption will be non-Arrhenius and that the mean kinetic energy of desorbing atoms will be markedly lower than that characteristic of a Maxwell–Boltzmann distribution at the surface temperature.

Finally, we will discuss a chemical reaction, the Eley–Rideal reaction of a gas-phase oxygen atom with an absorbed carbon atom on platinum. The trajectory studies predict that the newly formed carbon monoxide molecule will escape quickly from the surface and carry with it a substantial fraction of the reaction exothermicity. This suggests that it may be fruitful to design experimental efforts to uncover nonstatistical energy disposal in products of chemical reactions at surfaces.

Stochastic Classical Trajectory Approach

A chemical reaction at a surface is just one example of a great many situations in chemistry involving

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(2) M. Balooch, M. J. Cardillo, D. R. Miller, and R. E. Stickney, *Surf. Sci.*, 46, 358 (1974); C. A. Becker, J. P. Cowan, L. Wharton, and D. J. Auerbach, *J. Chem. Phys.*, 67, 3394 (1977); T. Engel and G. Ertl, *ibid.*, 69, 1267 (1978); R. J. Madix, *Acc. Chem. Res.*, 12, 265 (1979); J. T. Yates, J. J. Zinck, S. Sheard, and W. H. Weinberg, *J. Chem. Phys.*, 70, 2266 (1979); S. G. Brass and G. Ehrlich, *ibid.*, 70, 5244 (1979); S. J. Sibener and Y. T. Lee, *Rarefied Gas Dynam.*, 11, 1417 (1979); D. E. Tevault, L. D. Talley, and M. C. Lin, *J. Chem Phys.*, 72, 3314 (1980); S. L. Bernasek, *Adv. Chem. Phys.*, 41, 477 (1980).
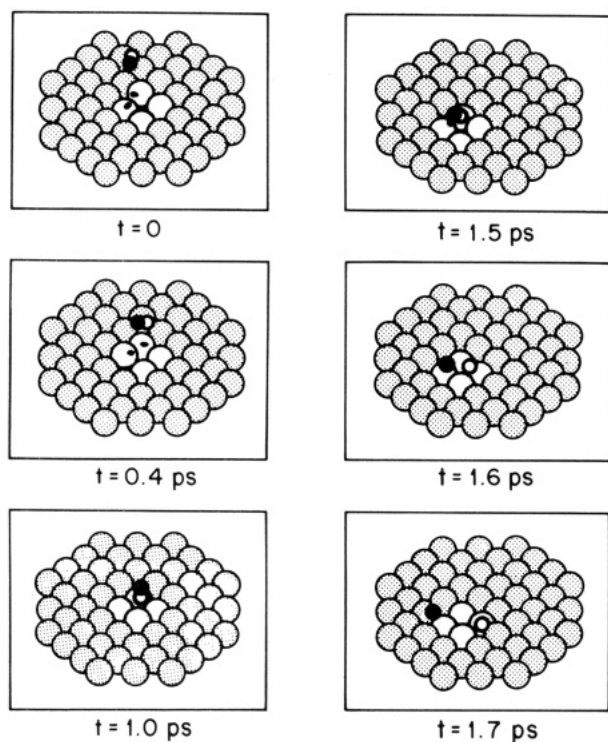
(3) J. C. Tully, *Annu. Rev. Phys. Chem.*, 31, 319 (1980).

(4) The ordinary classical trajectory method with explicit inclusion of many surface atoms has been employed for studies of gas–surface collisions, but it is cumbersome. See R. A. Oman, *J. Chem. Phys.*, 48, 3919 (1968); J. Lorenzen and L. Raff, *ibid.*, 52, 6134 (1970); J. D. McClure, *ibid.*, 57, 2823 (1972).

(5) A series of interesting classical trajectory studies employing motionless surfaces have been reported by McCreery, Wolken, and co-workers, and by Gelb and Cardillo. See J. H. McCreery and G. Wolken, *J. Chem. Phys.*, 64, 2845 (1976); J. H. McCreery and G. Wolken, *Chem. Phys. Lett.*, 39, 478 (1976); A. Gelb and M. J. Cardillo, *Surf. Sci.*, 75, 199 (1978).

(6) J. C. Tully and K. Knowlton, "Dynamics of Gas-Surface Interactions: A Computer Generated Movie", Bell Laboratories, Murray Hill, NJ, 1978.

Figure 1. Selected frames of a computer-generated movie[6] illustrating dissociative adsorption of nitric oxide on platinum. The dark atom is oxygen and the light atom is nitrogen. The four lightly shaded platinum atoms comprise the "active" surface zone. "Shadows" are cast directly beneath gas atoms.

localized events that take place in the midst of very large assemblies of atoms. Trans to gauche isomerization of polypropylene, photodissociation and recombination of I_2 in liquids, proton transfer in rhodopsin, and radiationless deactivation of F centers in sodium chloride are other examples. The stochastic trajectory technique allows one to eliminate the vast majority of "uninteresting" atoms and focus on the local region of action.

The approach is founded on the "generalized Langevin formalism" of Zwanzig,[7] Mori,[8] and Kubo,[9] and was developed for gas–surface phenomena by Adelman, Doll, and co-workers.[10] It has been further developed and applied to realistic three-dimensional studies of inelastic and reactive processes at surfaces by Tully and co-workers.[11–13] Preliminary applications to vibrational relaxation of impurity molecules in condensed phases and atom–atom recombination in liquids have also been reported.[14]

The objective of the stochastic trajectory approach is to accurately describe the flow of energy into and out of the local region of action (the "primary zone")

(7) R. Zwanzig, *Annu, Rev. Phys. Chem.*, **16**, 67 (1965).
(8) H. Mori, *Prog. Theor. Phys.*, **33**, 423 (1965).
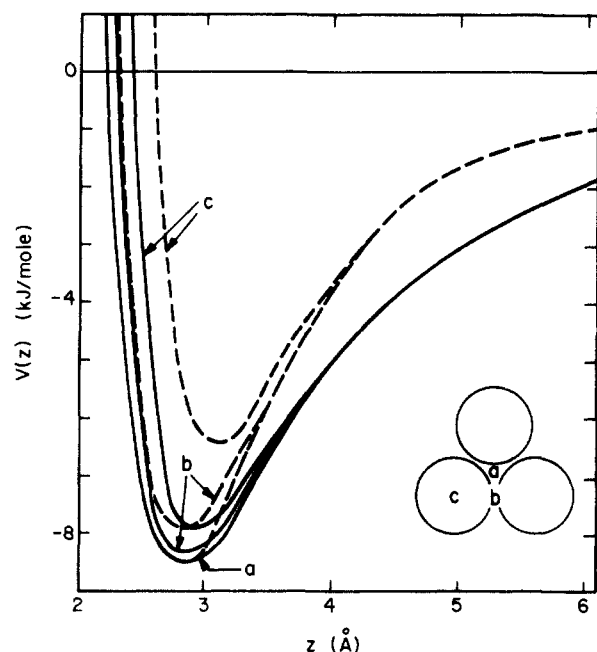(9) R. Kubo, *Rep. Progr. Theor. Phys.*, **29**, 255 (1966).
(10) S. A. Adelman and J. D. Doll, *J. Chem. Phys.*, **64**, 2375 (1976); S. A. Adelman and B. J. Garrison, *ibid.*, **65**, 3751 (1976); J. D. Doll and D. R. Dion, *ibid.*, **65**, 3762 (1976); S. A. Adelman and J. D. Doll, *Acc. Chem. Res.*, **10**, 378 (1977).
(11) M. Shugard, J. C. Tully, and A. Nitzan, *J. Chem. Phys.*, **66**, 2534 (1977).
(12) J. C. Tully, *J. Chem. Phys.*, **73**, 1975 (1980).
(13) A related "response function" technique has been described by J. A. Barker and W. A. Steele, *Surf. Sci.* **74**, 596 (1978); J. A. Barker, D. R. Dion, and R. P. Merrill, *ibid.*, **95**, 15 (1980).
(14) M. Shugard, A. Nitzan, and J. C. Tully, *J. Chem. Phys.*, **69**, 336 (1978); A. Nitzan, M. Shugard, and J. C. Tully, *ibid.*, **69**, 2525 (1978); C. L. Brooks, M. Berkowitz, and S. A. Adelman, *ibid.*, **73**, 4353 (1980).

without explicit inclusion of huge numbers of uninteresting atoms (the "secondary zone"). In the simple form of the theory as applied here, this is accomplished via a single assumption: interactions involving the secondary atoms are harmonic. With this assumption, the classical equations of motion for the primary and secondary atoms can be written

$$\ddot{\mathbf{y}} = F(\mathbf{y}) - \Omega^2 \mathbf{z} \tag{1}$$

$$\ddot{\mathbf{z}} = -\Omega^2 \mathbf{y} - \Omega_z^2 \mathbf{z} \tag{2}$$

Here the vectors $\mathbf{y}$ and $\mathbf{z}$ are the coordinates of the primary and secondary atoms, respectively, and Ω^2 and Ω_z^2 are the harmonic frequency matrices. $F(\mathbf{y})$ are the complicated anharmonic forces (divided by masses) acting among primary atoms. As shown in ref 12, eq 2 can be solved formally for the coordinates z of the secondary atoms, and the result substituted into eq 1 for the primary atoms. This produces a small set of coupled generalized Langevin equations of motion involving only the primary atoms:

$$\ddot{\mathbf{y}} = F'(\mathbf{y}) - \int_0^t \Lambda\,(t - t')\dot{y}(t')\mathrm{d}t' + R(t) \tag{3}$$

Equation 3 differs from eq 1 in the following ways: First, the forces $F'(\mathbf{y})$ have been slightly modified. Second, a friction integral, including memory effects, has been introduced. Qualitatively, the friction accounts for dissipation of energy from the primary zone to the secondary lattice. Third, a fluctuating force, $R(t)$, has been introduced to account for impulses to the primary atoms arising from thermal fluctuations of the secondary atoms.

Equation 3 is exact; i.e., the set of classical trajectories $\mathbf{y}(t)$ generated from eq 1 and 2, for a particular choice of initial primary atom conditions $\mathbf{y}(0)$ and $\dot{\mathbf{y}}(0)$ and for a canonical ensemble average over secondary atom initial conditions, is identical with the set of trajectories generated by eq 3 for the same primary atom initial conditions and for a canonical ensemble average of the fluctuating force $R(t)$ at the same temperature. Thus we have reduced the enormous number of equations of motion, eq 1 and 2, to an equivalent very small number of effective equations, eq 3, for only those atoms of direct interest. Of course, we have not performed any magic. Exact evaluation of the very complicated friction kernal $\Lambda(t)$ and fluctuating force $R(t)$ appearing in eq 3 would involve the same labor as solving the original enormous set of coupled equations for the secondary atoms, eq 2. The objective of this approach is then obvious: develop approximations to $\Lambda(t)$ and $R(t)$ which are easy to evaluate and yet which adequately represent the effects of the large number of secondary atoms that have been discarded.

Consider first the fluctuating force, $R(t)$. It represents the Gaussian fluctuations of an assembly of harmonic oscillators; thus $R(t)$ can be taken to be a Gaussian random force. It is because of the random impulses injected by $R(t)$ that the trajectories are termed "stochastic". Second, there exists a relationship (the "second fluctuation–dissipation theorem"[9]) between the friction kernal and the correlation function of the random force:

$$\Lambda(t) = kT\langle R(t)R^+(0)\rangle \tag{4}$$

This theorem is the quantitative expression of the

Figure 2. Interaction potentials for Ar on Pt(111), from ref 18. Dashed curves are Lennard-Jones potentials. Solid curves are "smoothed" potentials. Threefold, bridge, and on-top sites are designated a, b, and c, respectively.

Figure 3. Angular distributions of Ar scattered from Pt(111). The surface temperature is 700 K. The incident energy of Ar is 6 kJ/mol. (a) Incident angle is 45° with respect to the surface normal. (b) Incident angle is 75°. Points are experimental molecular beam results of Hurst et al.[17] Solid lines are stochastic trajectory results of ref 18 using "smooth" potential. Dashed lines are for Lennard-Jones potential.
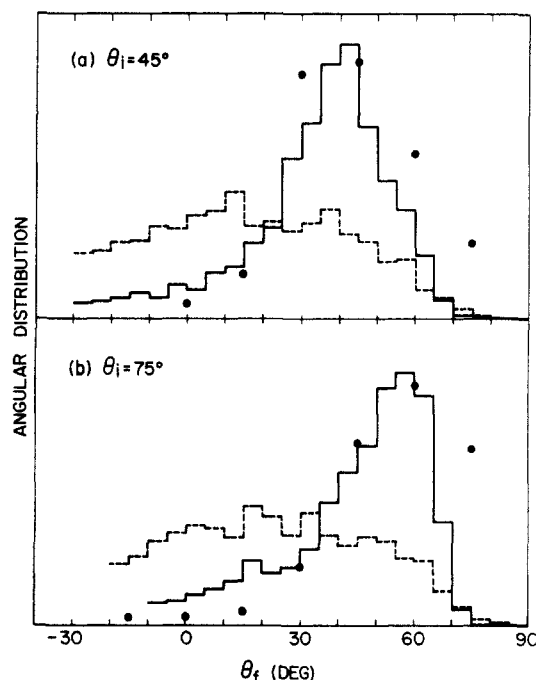
statement that the net energy dissipated via the friction must, on average, balance the net energy injected via the random force in order to maintain the primary zone at a temperature T. Equation 4 gives us a way to construct $R(t)$ once we have obtained $\Lambda(t)$ and allows us to perform simulations at any desired temperature, no matter how small the primary zone.

The friction kernal $\Lambda(t)$ can be related to the phonon spectrum of the solid. Our procedure has been to employ simple expressions for $\Lambda(t)$ with some adjustable parameters chosen to best reproduce known information about surface and bulk vibrational properties of the solid, obtained either from experiment or accurate lattice dynamics calculations. We have demonstrated that this procedure reproduces the motion of the surface atoms and their response to attack by gas atoms to quite adequate accuracy.[12] Furthermore, calculation of the friction and random forces in eq 3 by this procedure requires very little additional effort. Most of the computation time is expended in evaluating the forces, $F(y)$.

In the remainder of the Account we discuss results of realistic three-dimensional stochastic trajectory studies of the dynamics of some simple gas–surface processes. All of the processes studied are assumed to occur on the perfect (111) plane of a platinum crystal, with four active atoms in the primary zone. As shown in Figure 1, active surface atoms (lightly shaded) can be turned "on" and "off", with correct correlations, so that the active region can follow a mobile species across the surface.[12]

Scattering of Ar and Xe From Pt(111)

Molecular beam studies have been carried out of sticking probabilities[15] and angular and velocity scattering distributions[16,17] of Ar and Xe on the (111) face

of platinum. Stochastic trajectory studies of the same processes have been performed,[18] at first employing Lennard-Jones pairwise-additive gas–surface potentials (Figure 2). The pairwise contributions were summed over the four active surface atoms as well as the 10 atoms (assumed fixed) in the next surface shell. The sum over the remaining atoms in the semiinfinite solid was approximated by an integral. The range parameter in the Lennard-Jones interaction was taken to be the sum of the covalent radii of platinum and the rare gas. The energy parameter was adjusted to reproduce the experimental binding energies on Pt(111), 8.3 kJ/mol for Ar and 29 kJ/mol for Xe. Sticking probabilities computed using the Lennard-Jones potential were much larger than those obtained experimentally.[15] Angular distributions were shifted and much too broad, as shown in Figure 3. Large adjustments in the binding energy and in the parameters of the friction and random force could not bring calculations into agreement with experiment. Agreement could only be obtained by employing a potential with the same experimental binding energy, but much "smoother" than the Lennard-Jones potentials with respect to variation in potential energy as a function of the lateral position of the rare gas on the surface. A comparison of the Lennard-Jones and smooth potentials for Xe on Pt(111) are shown in Figure 2. With these smooth potentials, quantitative agreement is achieved between experimental and theoretical sticking probabilities, angular distributions (Figure 3), and velocity distributions. Lifshitz[19] argued a long time ago that screening due to

(15) A. G. Stoll, D. L. Smith, and R. P. Merrill, *J. Chem. Phys.*, **54**, 163 (1971).

(16) J. E. Hurst, C. A. Becker, J. P. Cowin, L. Wharton, D. J. Auerbach, and K. C. Janda, *Phys. Rev. Lett.*, **43**, 1175 (1979).

(17) J. E. Hurst, C. A. Becker, J. P. Cowin, L. Wharton, D. J. Auerbach, and K. C. Janda, to be published. I am grateful to these authors for making their results available prior to publication.

(18) J. C. Tully and E. K. Grimmelmann, to be published.
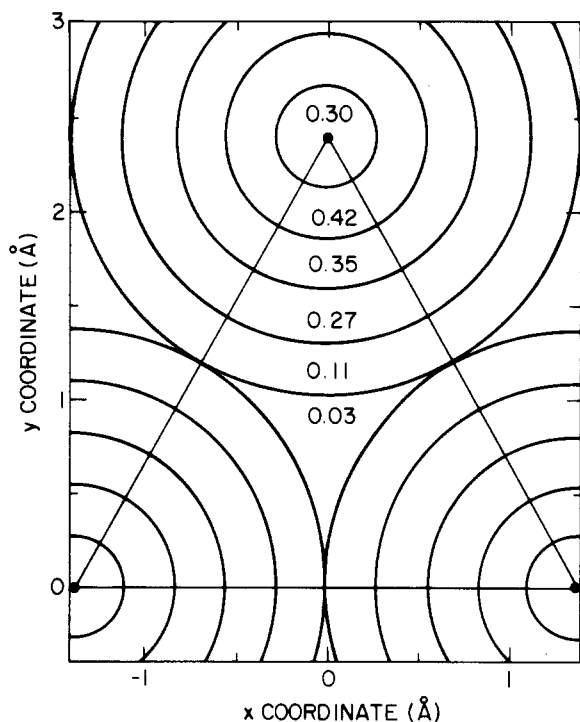
Figure 4. Variation of sticking probability of Ar on Pt(111) with position of impact computed by stochastic trajectory method.[18] Ar atoms are incident with 5 kJ/mol energy in the normal direction. Surface temperature 573 K. Regions are defined by radial distance to closest surface atom.
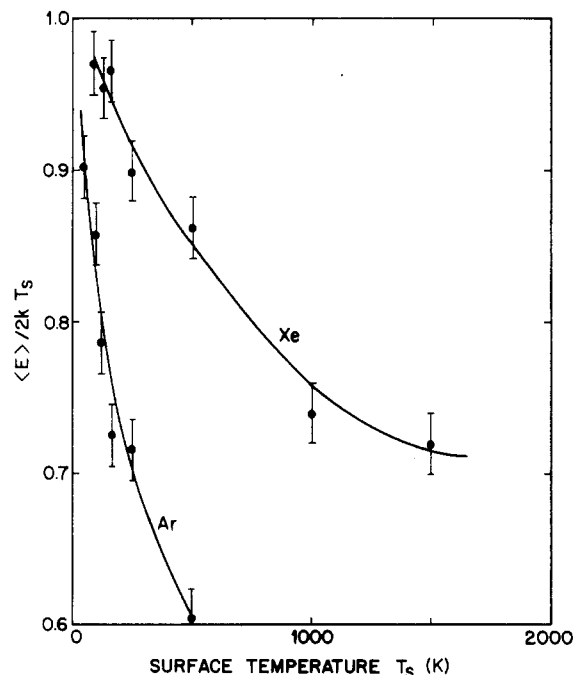

Figure 5. Mean kinetic energy $\langle E \rangle$ of Ar and Xe thermally desorbed from Pt(111), in units of $2kT_s$ where k is Boltzmann's constant and T_s is the surface temperature. Results are from stochastic trajectory studies of ref 22.

metallic conduction electrons will tend to smooth out the gas–surface interaction potential. The present studies provide a measure of the extent of this effect. It is obvious that a smoother potential will result in narrower angular scattering patterns, as in Figure 3. It is not so obvious that adjusting the potential to make it smoother without changing the binding energy will result in a dramatic decrease in sticking probabilities. This can be understood from Figure 4, which shows the sticking probability as a function of where the Ar first strikes the surface. Head-on collisions with a single surface atom do not result in maximum sticking probability. Energy exchange in a single collision is usually insufficient to result in trapping. Ar atoms stick with higher probability if they strike a sloping region of the potential and are thereby deflected laterally, subsequently experiencing multiple energy-exchanging collisions with the surface. For a smoother potential, this lateral deflection mechanism becomes less significant.

The smoothness of the potential influences the nature of energy accommodation of rare gas atoms striking the surface. Accommodation of motion in the direction perpendicular to the surface is much more rapid than accommodation of parallel motion. In fact, atoms incident on the surface at an angle may continue to glide several hundreds of angstroms downstream from their initial point of impact before they are finally thermalized.

Thermal Desorption of Ar and Xe from Pt(111)

The "smooth" interaction potentials of Figure 2 which produced good agreement with scattering experiments were also employed in simulations of thermal desorption. Thermal desorption presents a challenge

to the molecular dynamics approach because under usual experimental conditions it is slow. If the residence time of an atom on the surface is, say, 10 μs, then trajectories must be integrated on the computer for at least 10^8 vibrational periods. Furthermore, to obtain good statistics about desorption rates, angular distributions, and velocity distributions, hundreds or thousands of trajectories must be sampled. The task is hopeless by direct methods. Fortunately, there exist efficient techniques for simulating "infrequent events" of this type that render the problem quite tractable.[20,21] Simulations of thermal desorption of Ar and Xe from Pt(111) have been carried out by using such techniques, even at temperatures for which surface residence times exceed 1 s.[21,22]

An interesting result was obtained in these studies.[22] Figure 5 shows the mean kinetic energy of desorbed atoms divided by $2kT_s$, where k is Boltzmann's constant and T_s is the temperature of the surface. The atoms have been completely thermalized on the surface prior to desorption. Nevertheless, their mean kinetic energy is considerably less than the $2kT_s$ characteristic of a Maxwell–Boltzmann distribution at the surface temperature. In addition, angular distributions deviate somewhat from the expected $\cos \theta$ form, with wide angles enhanced relative to the surface normal direction. Arrhenius-type plots of the desorption rates exhibit curvature, with preexponential factors lower than characteristic vibrational frequencies.

This behavior can be understood qualitatively from detailed balance arguments. Referring to Figure 6, consider a surface and a gas in equilibrium at some temperature T. At steady state, the distribution of

(19) E. M. Lifshitz, *Soviet Phys. JETP*, **2**, 73 (1956).

(20) J. C. Keck, *Disc. Faraday Soc.*, **33**, 173 (1962); J. B. Anderson, *J. Chem. Phys.*, **58**, 4684 (1973); C. H. Bennett, *ACS Symp. Ser.*, **No. 46** (1977); D. Chandler, *J. Chem. Phys.*, **68**, 2959 (1978).

(21) E. K. Grimmelmann, J. C. Tully, and E. Helfand, *J. Chem. Phys.*, in press.

(22) J. C. Tully, submitted to *Surf. Sci.*
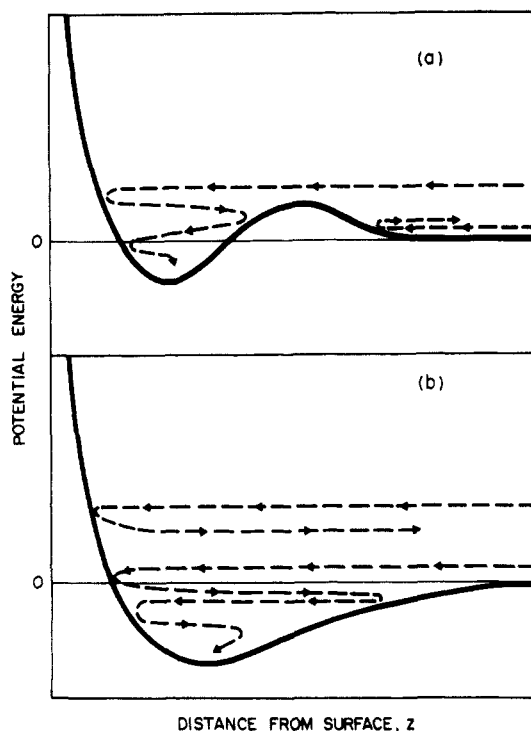
Figure 6. Schematic illustration of atom–surface interaction potentials as a function of the distance z from the surface. (a) Barrier to adsorption. (b) No barrier to adsorption (taken from ref 22).

kinetic energies of all atoms striking the surface (and leaving the surface) will be Maxwell–Boltzmann at temperature T. If the interaction potential exhibits a barrier as in Figure 6a, then that fraction of atoms belonging to the lowest energy part of the Maxwell–Boltzmann distribution will be unable to surmount the potential barrier and therefore will not adsorb. Only the higher energy particles will adsorb. By detailed balance, adsorbed atoms which subsequently desorb must come off with higher mean kinetic energy than kT, and with angular distribution peaked toward the surface normal. This is, of course, obvious from microscopic considerations, desorbing atoms which surmount the potential barrier will then roll down the hill and pick up kinetic energy as they leave. Experimental observations consistent with this picture have been discussed.[23]

Our simulations of rare gas desorption predict the opposite behavior; desorbing atoms are colder than the surface. The interaction potential is of the form illustrated in Figure 6b. Again picturing a gas in thermal equilibrium with the surface, we might now expect that those incident atoms in the high-energy tail of the Maxwell-Boltzmann distribution would stick with lower probability than would the low kinetic energy atoms. Thermally desorbing atoms would then, by detailed balance, come off with lower energy than the mean. Microscopically, this type of behavior arises from the fact that energy exchange between the atom and the surface is slow compared to the transit time of an atom once it has sufficient energy to escape. Thus the transition-state theory assumption of equilibration breaks down for atoms with energy near the top of the well.

Very recent experimental studies[24] confirm that the mean kinetic energy of Ar atoms thermally desorbing from Pt(111) is much less than $2kT_s$. Furthermore, Ceyer and co-workers[25] have reported that D_2O formed by reaction of adsorbed D with OD on Pt(111) comes off the surface with mean kinetic energy less than $2kT_s$, even though the reaction is exothermic. It may be that the D_2O remains on the surface sufficiently long for any excess energy to be dissipated, and then desorbs thermally.

Reaction of Gas-Phase O with Adsorbed C

Stochastic trajectory studies of the Eley–Rideal-type reaction of a gas-phase oxygen atom with adsorbed carbon on Pt(111) have been carried out.[26] This reaction was selected for study, in part, because formation of gas-phase CO is extremely exothermic, 5–6 eV. Our concern is not whether the reaction occurs. It will with high probability. Our major interest is what happens to the 5 or 6 eV liberated in the reaction? Does this energy dissipate into the solid, or is it deposited in specific ways in the CO molecule? The answer to this question hinges to some extent on whether the newly formed CO molecule escapes from the surface quickly or whether it remains trapped at the surface for many vibrational periods. (CO binds to Pt(111) by about 1 eV[27].)

Our interest in the possibility of specific energy disposal in this reaction stems from the general concern that energy equilibration at solid surfaces may be so rapid that prior state selection of reactants may be destroyed long before reaction occurs and specific partitioning of energy in product may be destroyed before products can be probed. If true, this would preclude the possibility of uncovering information about the dynamics of the reactive event.

The gas–surface interaction potential employed for this study was of the London–Eyring–Polanyi–Sato form,[28] with parameters chosen empirically. The potential incorporates experimental information about the gas-phase CO molecule and about C, O, and CO adsorbed on Pt(111). In particular, the most stable position of CO is assumed to be an on-top site, oriented normal to the surface with the carbon down. An only slightly less stable bridge site has also been incorporated. C–O stretch, C–Pt stretch, and bending frequencies have been chosen to approximately match experiment.[29] Unfortunately, available experimental information is by no means sufficient to define the entire multidimensional potential-energy hypersurface. Thus at present the interaction potential must be considered extremely uncertain, useful only to elucidate gross qualitative features of the reaction dynamics.

A two-dimensional cut of the many-dimensional potential-energy hypersurface is shown in Figure 7. Note the weakening of the CO bond as the molecule approaches the surface and the 1-eV well corresponding to adsored CO. With the exception of this 1-eV basin,

(23) M. J. Cardillo, M. Balooch, and R. E. Stickney, *Surf. Sci.*, **50**, 263 (1975).

(24) J. E. Hurst, C. A. Becker, J. P. Cowin, L. Wharton, D. J. Auerbach, and K. C. Janda, Unpublished results.
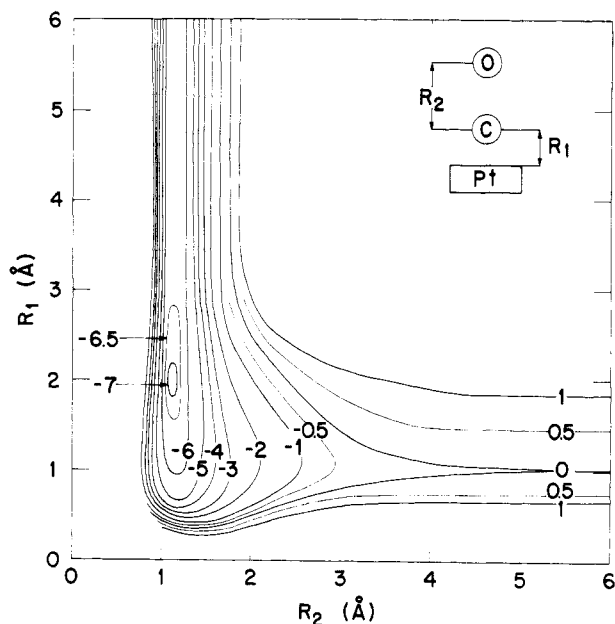
(25) W. L. Guthrie, S. T. Ceyer, and G. A. Somorjai, Second Continental Congress of the North American Continent, Las Vegas, NV, 1980. S. T. Ceyer, Ph.D. Thesis, Univeristy of California, Berkeley, 1979.

(26) J. C. Tully, *J. Chem. Phys.* **73**, 6333 (1980).

(27) P. R. Norton, J. W. Goodale, and E. B. Selkirk, *Surf. Sci.*, **83**, 189 (1979).

(28) C. A. Parr and D. G. Truhlar, *J. Phys. Chem.*, **75**, 1844 (1971).

(29) A. M. Baro and H. Ibach, *J. Chem. Phys.*, **71**, 4812 (1979).

Figure 7. Equal energy contours (eV) for C and O interacting with Pt(111). C and O atoms are both constrained to lie directly above the threefold site. Only their perpendicular distances R_1 and R_2 are varied. Platinum atom positions have been relaxed at every point. (Reprinted with permission from ref 26. Copyright 1980, American Institute of Physics.)
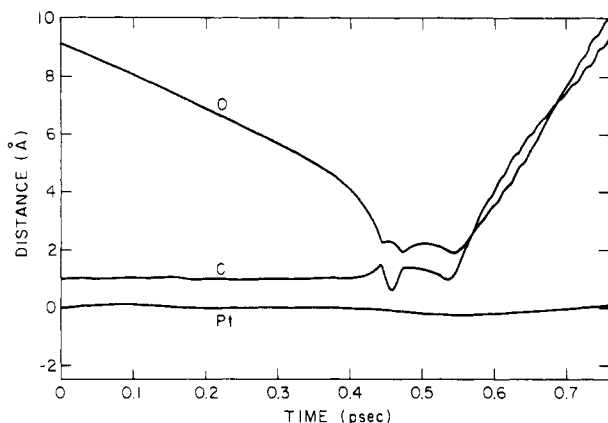

Figure 8. Representative reactive trajectory. Perpendicular distances from the surface of O, C, and closest Pt atom are plotted as a function of time. No information about lateral coordinates or about other nearby Pt atoms is given. CO is produced translationally and internally excited. Massive Pt atom is only slightly disturbed by the event. (Reprinted with permission from ref 26. Copyright 1980, American Institute of Physics.)

the path from reactants to gas-phase product CO is energetically downhill throughout.

For incident O atoms that strike within 2 Å of the adsorbed C atom, the reaction probability was found to be very high, ~98%. Furthermore, the vast majority of trajectories produced gas-phase CO within 5 ps (see Figure 8). The 1-eV basin in Figure 7 is apparently too shallow compared to the reaction exothermicity to result in trapping of a significant fraction of the product CO molecules.

As shown in Figure 9a, about 90% of the 6 eV of liberated energy is carried by the CO molecule. Only 10% is dissipated to the solid.[30] The largest share of

(30) Inclusion of energy dissipation via conduction electrons decreases the product energy somewhat, but does not change the qualitative conclusions.
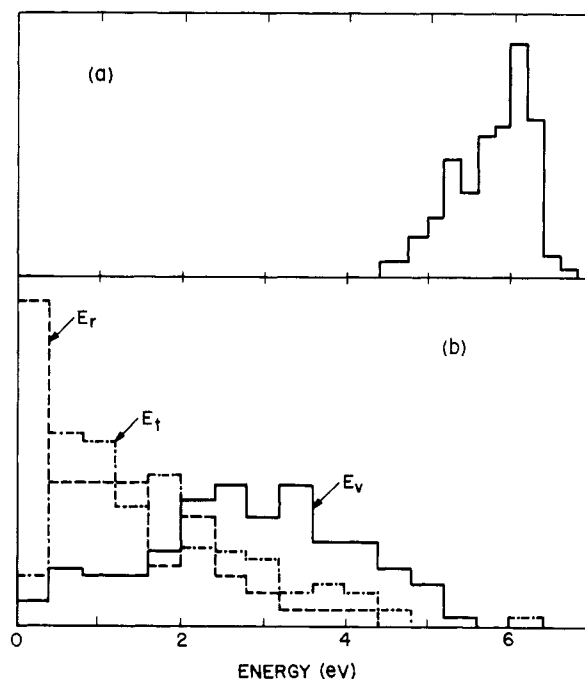
Figure 9. Distribution of energy in product CO molecule computed for O atom incident energy of 8 kJ/mol, incident direction normal, and surface temperature 500 K. (a) Total energy of CO. (b) Partitioning of energy into vibration (solid line), rotation (dashed line), and translation (dot–dash line). (Reprinted with permission from ref 26. Copyright 1980, American Institute of Physics.)

energy is deposited into CO vibration, (Figure 9b). Rotational motion was found to be anisotropic; i.e., molecules tend to tumble rather than rotate in the plane of the surface.[31] The angular distribution of CO was found to be quite broad, but definitely peaked toward the surface normal.

Because of the considerable uncertainty in the interaction potential employed to obtain these results, the calculations were repeated for a variety of potentials with quite different topographies. Significant differences in the relative partitioning of energy among translation, rotation, and vibration were obtained. However, the major conclusion—that the product CO molecule escapes quickly from the surface with substantial excitation—was unaltered.

The implication of these results that specific partitioning of energy might occur in products of reactions at surfaces is encouraging. Admittedly the reaction selected for study here is not an ordinary one. Recombination of O and C atoms on metals under usual experimental conditions is not believed to proceed via the Eley–Rideal mechanism invoked here. Rather a Langmuir–Hinshelwood process in which both atoms are initially adsorbed is thought to dominate. Preliminary trajectory simulations of the latter mechanism show very much reduced product excitation.[32] Nevertheless, it may be that experimental conditions can be designed so as to enhance the Eley–Rideal mechanism in order to provide information about the gas-surface interactions. There is experimental evidence for both H atom recombination[33] and N atom recom-

(31) A similar preference for tumbling motion was obtained in simulations of Eley–Rideal recombination of H atoms on tungsten: A. B. Elkowitz, J. H. McCreery, and G. Wolken, Jr., *Chem. Phys.*, **17**, 423 (1976).

(32) J. C. Tully, work in progres.

bination[34] on metals that internally excited molecules are produced. These hints that specific energy disposal can occur—that reaction products are not necessarily thermalized on the surface—may be a preview of exciting developments to come.

Concluding Remarks

Stochastic classical trajectory studies promise to be a valuable compliment to experiment in elucidating the dynamics of elementary chemical events at surfaces. In addition to the processes discussed in this Account, the approach has been applied to diffusion of rare gas atoms and clusters on surfaces.[35] Preliminary studies have been carried out of relaxation of vibrationally excited CO adsorbed on platinum,[26] of accommodation of translational, vibrational, and rotational energy of N_2 scattered from platinum,[6] and of dissociative adsorption of NO on platinum.[6]

The major obstacle is construction of accurate potential-energy hypersurfaces for chemically interesting systems. In the studies described above there was considerable uncertainty in the interaction potentials employed. As more reliable interaction potentials become available, either through experimental or theoretical input, exciting possibilities will arise. It should be feasible to examine a great variety of elementary chemical transformations not only at clean, flat surfaces but also at surfaces containing steps, imperfections, adlayers, or impurities.

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