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Dynamics of Molecular Motion at Single-Crystal Surfaces

J. C. Tully and M. J. Cardillo

Summary. Dramatic advances in our understanding of the motion of individual atoms and molecules at single-crystal surfaces have been made within the past 5 years. Recent experimental and theoretical studies of the interaction of nitric oxide with metal surfaces illustrate the depth of understanding now obtainable. General principles, applicable to a broader range of molecule-surface encounters, have begun to emerge out of the systematic and in-depth analyses of these and related studies.

Within the past few years our knowledge of the elementary dynamical steps that constitute molecular interactions with single-crystal surfaces has increased dramatically. Powerful experimental techniques coupled with sophisticated theories, particularly those of molecular dynamics, have revealed a detailed picture of the nature of the forces involved in molecule-surface encounters and the fundamental dynamical response of molecules to these forces. At present, this level of understanding is available only for a few systems. However, some general principles have begun to emerge which are applicable to a wider range of surface chemical phenomena. These principles underscore the significance of research carried out on idealized surfaces, such as single crystals, where a detailed understanding is potentially obtainable.

In this article we emphasize one particular class of gas-surface encounters: the nondissociative interactions of nitric oxide (NO) with selected transition metals, for which there is a substantial body of data, dynamical models, and detailed comparisons of experiment with theory. We use these examples to illustrate the extent of knowledge that can be extracted in the "idealized" studies of molecular interactions with single crystals.

Surface science, and in particular surface physical chemistry, has enjoyed vigorous growth in the past decade. In part this has been due to the availability of adequate high-vacuum equipment (pressures $\sim 10^{-10}$ torr, enabling surfaces to remain free of contamination for ~ 1 hour) and the extraordinary developments in analytical instrumentation. These developments allow the state of the surface and adsorbates, which may be present in only small fractions of a monolayer (one monolayer corresponds to $\sim 10^{15}$ atoms per square centimeter), to be well characterized and properly maintained at the atomic level. Another aspect of this growth has been the increasing awareness that chemical and physical processes at surfaces lie at the heart of a vast array of modern technologies. The fields of heterogeneous catalysis, electronic device development, and materials science, including synthesis, analysis, and protection, have benefited from research in surface chemistry. The electronics, telecommunications, and computer industries are continually extending advanced technologies based on new processes such as molecular beam epitaxy (solid-state electronic devices and lasers), high-resolution plasma etching (large-scale integrated circuits), and modified chemical vapor deposition (fiber optics). The development and ultimate optimization of these and other processes require a knowledge base that extends to the molecular level. As microelectronic devices continue to decrease in size, the surface-to-bulk atom fraction approaches unity and further developments become an extension of surface science, a situation that has always been true for dispersed catalysts.

Phenomenology of Molecule-Surface Dynamics

A useful guide with which to consider molecular interactions at surfaces is a flow diagram which proceeds from gas-phase "reactants" to adsorbates, through surface "intermediates," and subsequently back to gas-phase "products," as shown in Fig. 1. On the left side of this picture we consider molecules that approach the surface and are either scattered or adsorbed. In order to be adsorbed, a molecule must lose sufficient translational kinetic energy so that it cannot escape the attractive forces that will bind it to the surface. This loss of kinetic energy may involve surface excitations (phonons and electrons), exchange of energy from translational to internal energy within the molecule, and redirection of translational momentum from perpendicular to parallel to the surface. Alternatively, a molecule may be adsorbed by fragmenting "on the fly" as the surface is approached. This can occur, for example, in activated dissociative adsorption which is common for species with closed electron shells with weak attractive interactions with the surface. Examples include CX_4, SiX_4 (X = H, F, Cl, and so on), N_2, CO_2, and occasionally H_2 on most transition metal and semiconductor surfaces. These adsorptive and reactive collision processes are most effectively studied in depth with

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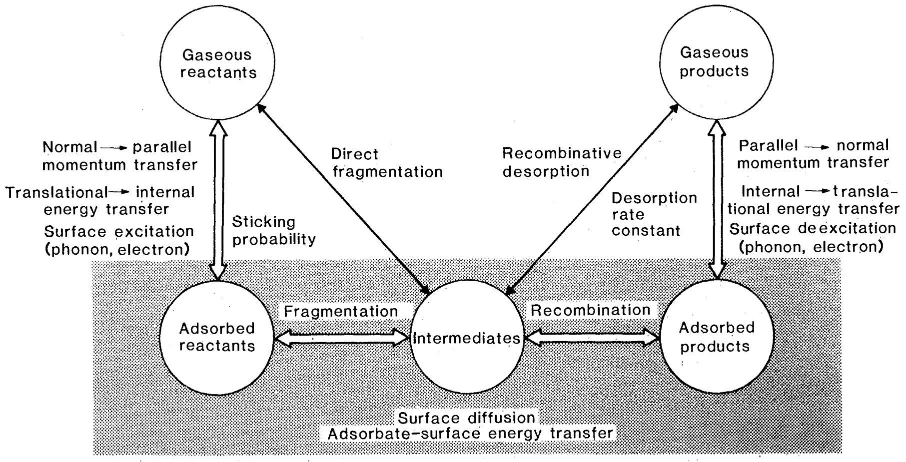


Fig. 1. Flow chart of a molecular interaction with a surface, showing initial adsorption, subsequent thermalization, diffusion and rearrangement on the surface, and final desorption.

molecular beam techniques, which allow the incident conditions (such as flux, energy, angle, and modulation frequency) to be varied in a controlled manner and the subsequent elementary rate processes to be followed without interference from the environment.

After a species is adsorbed on a surface, it may undergo a variety of elementary processes; these include lateral translation (two-dimensional diffusion), further exchange of energy with the surface, and elementary reactive steps (dissociation and recombination). The surface may play a variety of roles in reactive processes. For example, it may foster collisions of adsorbates in particular configurations, thereby generating specific products. Alternatively, the surface may function primarily as a means of concentrating species, with little direct structural influence. An important role of the surface frequently is to make intermediate molecular configurations available without the severe energetic and momentum restrictions that often dominate gas-phase reaction rates. In contrast to adsorption and desorption, the various dynamic events that may occur on surfaces have yet to be effectively investigated. It is difficult with present experimental capabilities to directly measure these molecular processes. It will be necessary to develop surface-sensitive, time-resolved measurement techniques in order to gain a fundamental understanding of the dynamics of surface reactions. In particular, the two-dimensional surface adsorbate analog of gas-phase reactive collisions has not been examined directly experimentally. However, static pictures of "frozen" intermediate species have been obtained by use of newly developed surface vibrational spectroscopies, and surface diffusion has been directly measured with the field ion microscope.

Finally, the desorption process, whether direct and based on surface deexcitations or concerted in conjunction with simultaneous recombination of intermediates, represents to a large extent the reverse of the processes considered in the adsorption direction. By using lasers as probes, detailed molecular quantum state distributions have been recorded and analyzed to elucidate the dynamics of desorption. Detailed balance arguments have proved useful in relating this information to sticking probabilities and thus complementing our understanding of molecular dynamics in both directions—adsorption and desorption.

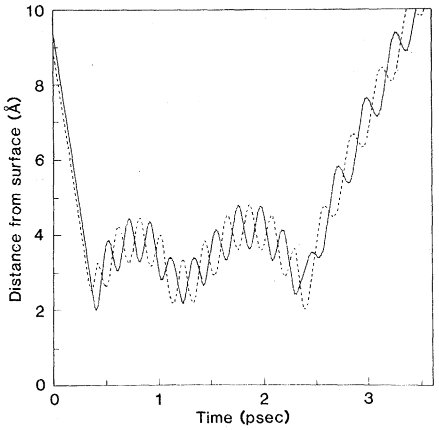
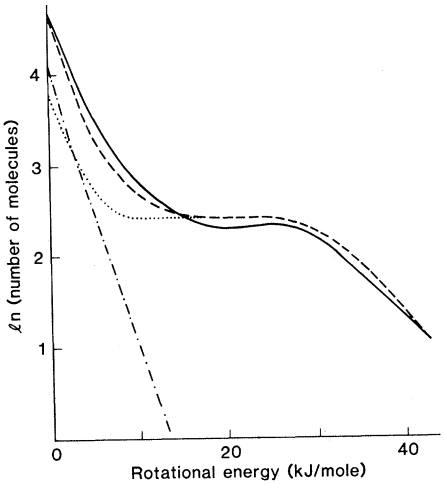


Fig. 2. Computed trajectory for intact NO molecule scattering from Ag(111). The solid and dashed curves are the vertical distances from the surface plane of the N and O atoms, respectively, plotted as a function of time. Lateral motion of the molecule and surface atom motion are not shown. The surface temperature is 650 K. The molecule is incident at 5° with respect to the surface normal, with an initial translational energy of 50 kJ/mole and zero initial rotational energy. The initial vibrational energy is 11.4 kJ/mole, corresponding to the zero-point energy of NO. (The high-frequency vibrational motion is barely discernible in the vicinity of the turning points/of the solid curve.)

On the theoretical front, it has become feasible, by direct numerical solution of the classical mechanical equations of motion on a high-speed computer, to simulate the motion of gas and surface atoms through a dynamic encounter (*1*). As an illustration, we show in Fig. 2 the results of a computation of the trajectories followed individually by the N and O atoms of an intact NO molecule as it approaches an Ag(111) surface (*2*). In this "typical" event the molecule is temporarily trapped at the surface after exchanging energy from translation into molecular rotation and surface vibration. The molecule is thermalized to some extent as it diffuses laterally along the surface, and then it is finally desorbed. By calculating a large number of such trajectories, with appropriately distributed initial molecular orientations, vibrational phases, impact sites, and so on, one can compute sticking probabilities, angular and velocity scattering patterns, surface diffusion coefficients, desorption Arrhenius parameters, and other quantities of experimental interest. By systematic variation of the parameters under control it is then possible to identify the effect of specific features of the interaction potential on the dynamics and to build a general understanding. Of course, these computations have validity only if the chemical forces employed in the trajectory calculations are realistic.

We have yet to achieve an accurate ab initio determination of the required multidimensional potential energy surface and thus the chemical forces even for simple gas-surface systems. At present, most of our knowledge of these interaction potentials is derived from experiment. Adsorbate binding energies can be obtained from adsorption-desorption experiments. Techniques commonly used are temperature-programmed desorption (*3*), molecular beam residence time measurements (*4*), and thermodynamic analysis of equilibrium coverages. Electron energy loss (*5, 6*) and infrared reflection (*6*) spectroscopies provide information about the adsorbate binding site, molecular configuration, and vibrational motion; that is, these measurements characterize the gas-surface potential energy hypersurface in the neighborhood of stable minima. Modulated molecular beam measurements yield rates of simple kinetic processes and insight into the dynamics through analysis of the temporal behavior of the interaction. In addition, topographic information can be derived for the gas-surface potential through analysis of the scattered angular distributions (*7*). Rotational energy distributions of scattered molecules contain information about the dependence of the interaction potential on the orientation of the molecule (*2*). By coordinating trajectory simulations with this wide array of experimental studies, an accurate empirical description of the gas-surface interaction potential can be approached. This interaction potential can then be used as the basis for computation of a great variety of other dynamic processes, either to obtain predictions to be tested by future experiments or to produce information that is difficult to obtain experimentally.



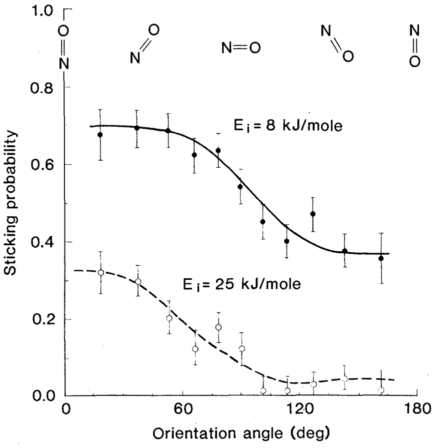


Fig. 3 (left). Distribution of final rotational energy of NO molecules scattered from Ag(111). Incident translational energy is 97 kJ/mole, incident angle is 15°, and surface temperature is 650 K. The solid curve is a fit to the experimental data of Kleyn *et al.* (*10*). The dashed curve was obtained from trajectory calculations (*2*). The dot-dash and dotted curves are the calculated distributions for molecules with an initial orientation angle of the molecular axis less than and greater than 60°, respectively. The orientation angle is defined as 0° for the molecule aligned along the surface normal with the nitrogen end toward the surface. Fig. 4 (right). Sticking probability of NO as a function of initial NO orientation angle, as defined in the caption of Fig. 3. Distributions of incident translational energies and angles are Maxwell-Boltzmann at the surface temperature, as indicated in the figure. Initial rotational energy is zero.

Interactions of Nitric Oxide with Metal Surfaces

With this outline of some of the phenomenology of gas-surface interaction dynamics in mind, we will examine in detail two specific cases for which a substantial amount of information has already been extracted: the interaction of NO with the (111) faces of silver and platinum. For these surfaces it has been demonstrated that NO does not dissociate to an appreciable extent. Thus we will examine the adsorption, diffusion, desorption, and scattering of intact NO molecules.

The NO molecule has an electronic structure that is convenient for laser-induced fluorescence (LIF) characterization of specific vibration-rotation quantum state populations. If a laser probe is tuned to the appropriate resonance, only NO molecules in a specific vibrational and rotational state will undergo a transition to the electronically excited state. The intensity of the subsequent fluorescence from this state is proportional to the initial quantum state population. A similar resonance condition applies to the first photon in a two-photon laser ionization of the NO molecule, with subsequent detection of the NO^+ ion.

Molecular beam studies utilizing these state-sensitive techniques (*8–13*) have provided new and provocative information about energy transfer at surfaces, as well as the detailed and quantitative data required to challenge theoretical models of the dynamics of scattering, adsorption, and desorption. A qualitative and general understanding of these fundamental processes is beginning to emerge from these experimental studies. A dominant factor that is found to influence the dynamics is the relative severity of constraint of the adsorbed state compared to that of the isolated gas molecule—that is, the change in entropy upon adsorption. An NO molecule in the gas phase has free translational motion in three dimensions and has two free rotational degrees of freedom. When the molecule is adsorbed on a metal, such as Pt(111), it makes frequent hops from one binding site to another. Nevertheless, it spends most of its time at the lowest energy binding sites on the surface (such as ontop or bridge sites). More important, the molecule is constrained to a particular orientation, with the nitrogen end bound to the surface and the oxygen pointing outward. The free rotational motion of the gas-phase molecule has been replaced by relatively low-amplitude bending vibrations (frustrated rotation). When the forces that orient molecules as they approach a surface are strong, as in the case of NO on transition metals, they have a direct influence on the motion of the molecule as it is scattered, adsorbed, or desorbed.

Consider, for example, the transfer of rotational energy upon direct scattering of an NO molecule from the surface. Kleyn *et al.* (*10*) directed a translationally energetic but rotationally cold ($T_{rot} \approx 20$ K) molecular beam of NO from a nozzle expansion at a Ag(111) surface. They then measured the rotational energy distribution of molecules scattered from the surface by using LIF. An example of their results is displayed in Fig. 3, which shows that large amounts of rotational energy can be imparted to the molecule. Also shown in Fig. 3 for comparison is the rotational energy distribution computed from an ensemble of 2000 trajectories for molecules having an interaction potential with the surface that is believed to well represent the NO-Ag(111) interaction (*2*). The interaction potential includes strong orientational forces that align the molecule perpendicular to the surface. The experimental and theoretical rotational energy distributions are in good agreement. In Fig. 3 separate theoretical distributions are shown for molecules that approach with the nitrogen end pointing toward the surface (the appropriate orientation for binding) and those with the oxygen end facing the surface (wrong-end approach). Essentially all of the events that produce high rotational excitation in the scattered molecule correspond to the wrong-end approach; the molecules are spun around by the strong orientational forces and continue to rotate as they leave the surface.

This mechanism of rotational energy exchange is illustrated by the trajectory shown in Fig. 2. In this case, the molecule initially approaches with the wrong end (oxygen) toward the surface. As the molecule nears the surface, it is spun around in order to obtain a favorable binding interaction with the nitrogen atom. However, the molecule may continue spinning through this orientation, whereupon it may subsequently leave the surface. Thus we expect that the probability that a colliding molecule will stick rather than scatter will depend on the orientation of the molecule as it strikes the surface. The prediction of trajectory calculations (*2*) is shown in Fig. 4. Experiments with oriented NO molecules are feasible and would provide an interesting direct test of this prediction.

An additional prediction of the trajectory simulations is that the sticking probability will decrease sharply as the rotational state of the incident molecule is increased. Consider a low-pressure gas in dynamic equilibrium with a surface at a temperature of T_s. The molecules striking the surface will have a distribution of rotational energies with a mean of kT_s. Molecules with high rotational energies will be more difficult to orient and hold in the most favorable binding configuration during a collision. Thus the adsorption probability in general will fall as the rotational state is increased, as exhibited by the trajectory results. Therefore, the rotational energy distribution of molecules that stick to the surface will be biased lower than kT_s and that of molecules that scatter will be biased higher than kT_s. Invoking detailed balance, we conclude that if the molecular desorption from the surface were isolated in this equilibrium situation, it would have a mean rotational energy lower than kT_s. The same dynamics of desorption are expected to hold for desorption into a vacuum. Experimental verification of "rotational cooling" (that is, a deficiency of high rotational states) upon desorption has been observed for NO from both Ag(111) (*14*) and Ru(001) (*11*), as well as CO from polycrystalline Pt (*15*), and has been reproduced by trajectory studies (*2*). These examples demonstrate how comparison of a high-resolution experiment and detailed theory leads to an understanding of important dynamical phenomena and their explanation in terms of specific features of the molecule-surface interaction potential, in this case the orientational anisotropy.

In contrast to the facile transfer of rotational energy described above, vibrational energy exchange upon impact of the NO molecule with the surface is predicted to be very inefficient. The high-frequency wiggles apparent in the trajectories of Fig. 2 correspond to the zero-point vibrational motion of NO. It is evident from Fig. 2 that this vibrational motion occurs on a much faster time scale than molecular rotation, translation, and surface-atom motion. The inefficiency of vibrational energy exchange is a result of this mismatch in characteristic times. In fact, it appears that the major mechanism for vibrational energy exchange when a stiff molecule with a permanent dipole is scattered from a metal surface involves excitation of electron-hole pairs. On the other hand, molecules with low-frequency, floppy vibrations can be expected to easily transfer vibrational energy to and from rotational, translational, and surface vibrational motion. The importance of matching characteristic times has been well documented in gas-phase energy transfer for some time.

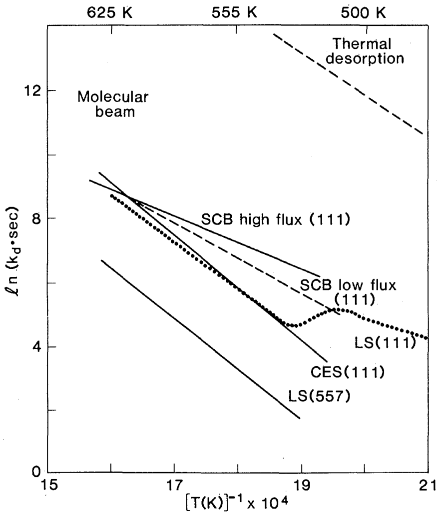


Fig. 5. Arrhenius plot of experimental rate constants for NO desorption from the Pt(111) surface. The highest rate constant, obtained by extrapolating the results of (*20*), corresponds to desorption from the (111) terrace by thermal desorption spectroscopy. The remaining rate constants are derived from molecular beam experiments. The curves labeled SCB high flux (*19*), SCB low flux (*19*), LS(111) (*17*), and CES (*18*) correspond to measurements of the nominal (111) surface; LS(557) is the rate constant for the stepped (557) surface (*17*).

Another interesting feature of a molecule-metal interaction potential, in contrast to the strong orientational anisotropy, is the smoothness of the potential with respect to lateral displacements along the surface. A general smoothness in gas-metal physisorption potentials has been well documented in molecular beam scattering experiments with inert gas atoms (helium, neon, and argon) and weakly binding molecules such as N_2 (*7*). For more strongly binding molecules such as NO, the small barrier to surface diffusion serves as an indication of a comparable smoothness. The origin of this smoothness is the delocalization of valence electrons and close packing of the metal surfaces with a low Miller index. Although molecules like NO have specific preferences for binding sites (for instance, on top, hollow, or bridge sites) they are dislodged and hop to another site with only a small activation energy. A useful and often cited rule is that the diffusion barrier $E_D \leqslant 1/4\ E_B$, where E_B is the binding energy (*16*).

This small diffusion barrier can have very important consequences for surface rate processes occurring on single crystals, as recently demonstrated in a series of molecular beam studies on the residence times of NO on Pt(111) (*17–19*). By modulating the incident molecular beam and monitoring the time delay of molecules leaving the surface, the temperature-dependent residence time distribution for the molecules on the surface is measured. (For a simple first-order desorption process, the mean residence time is the inverse of the desorption rate constant.) The characteristic residence times for NO on Pt(111) so obtained are orders of magnitude longer than those extrapolated from temperature-programmed desorption results (*20*). Furthermore, molecular beam results reported by the different laboratories (*17–19*) differ significantly from each other, as shown in Fig. 5.

These differences arise because the molecular beam studies are carried out at much lower surface coverages than the temperature-programmed desorption experiments. At low coverages, steps or other surface defect sites can play a dominant role, serving as traps for adsorbed species. Desorption at moderate or high coverages occurs while the steps remain saturated and is therefore insensitive to their presence. In contrast, at low coverages most molecules rapidly diffuse to step sites and are temporarily trapped, producing a lower effective desorption rate. The differences observed in the experiments reported in Fig. 5 can be accounted for quantitatively with a simple kinetic model (*21*) which utilizes a common set of rate constants and the appropriate flux and step density for each experiment. A principal conclusion of this work is that it is virtually impossible to have low-coverage thermal rate processes that are not influenced by steps and defects, no matter how well the surface is prepared. This general result is due to the lateral smoothness of the gas-surface interaction potential (low barriers to surface diffusion) and consequent very high diffusion rates compared to desorption rates.

Transition state theory (TST) provides a useful qualitative guide for the magnitudes and variations of the desorption rates observed in the different molecular beam experiments. The TST expression for a unimolecular rate constant k_d is (*22*)

$$k_d = \frac{kT}{h} e^{\Delta S/k - \Delta H/kT} = \frac{kT}{h} e^{-\Delta G/kT} \tag{1}$$

where k is Boltzmann's constant, h is Planck's constant, T is temperature, and the thermodynamic variables for enthalpy ΔH, entropy ΔS, and free energy ΔG represent the differences between an "activated complex" configuration and the reactant state. For NO desorption into the vacuum from Pt(111), the different rate constants reflect primarily the thermodynamics of the adsorbed (reactant) state. The transition state can be taken to be the free molecule and surface at large separation. Since the lowest energy binding site for the molecular beam experiments described above is at steps, the entropy difference in the rate constants can be associated with the probability of being at a step. At low coverage where steps are not saturated, this is just the configuration entropy $S = k \ln \Omega$, where Ω is the number of step sites. Thus the ratio of rate constants for the low-coverage experiments is approximately the ratio of step densities. This is consistent with experiment within the accuracy of the analysis.

Another interesting application of TST to desorption concerns the rate of desorption of NO from Pt(111) terraces, which was measured by Gorte *et al.* using temperature-programmed desorption (*20*). At the higher coverages employed in this kind of experiment, steps do not play a significant role. They obtained the desorption rate constant

$$k_d = 10^{16} \exp \left(\frac{-25 \text{ kcal/mole}}{kT} \right) \text{sec}^{-1} \tag{2}$$

The activation energy $E_a = 25$ kcal/mole is approximately the binding energy of NO on Pt(111) as expected. However, the prefactor A is measured to be 10^{16} sec^{-1}, about four orders of magnitude larger than the NO-Pt(111) vibrational frequency.

The large prefactor arises from the reduced entropy of the adsorption configuration, primarily due to the orientational alignment of the molecule on the surface. From Eq. 1, the TST prefactor is approximately

$$A = \frac{kT}{h} e^{\Delta S/k} = \frac{kT}{h} \frac{Q_f}{Q_a} \tag{3}$$

where Q_f and Q_a are the partition functions for the free molecule and the adsorbed molecule, respectively. The function Q_f can be computed from the molecular constants of NO, and Q_a can be approximated by assuming separable harmonic degrees of freedom on the surface, with frequencies of 306 cm^{-1} (NO–Pt stretch) (*23*), 465 cm^{-1} (frustrated rotation) (*23*), and 60 cm^{-1} (frustrated lateral translation, estimated). At 300 K, the prefactor *A* estimated by this procedure is 2×10^{16} sec^{-1}. Trajectory studies produce very similar results, without requiring the harmonic or separability assumption, that is, with an exact classical mechanical treatment of the molecular motion subject to an assumed force field (*2*). If the interaction potential is made orientationally isotropic but with the same binding energy as that for the favored NO orientation, the computed rate constant has approximately the same value of E_a but with the prefactor *A* reduced from 2×10^{16} to 5×10^{13}. The difference of 400 is thus a measure of the reduced entropy of the adsorbate due to constraining the NO to a specific orientation.

General Principles

The specific conclusions from these few studies cited suggest some general considerations which may underlie a wide range of molecule-surface rate processes.

1) *The influence of constrained adsorbate geometry on dynamics.* The fact that a molecule free to translate and rotate in the gas phase is constrained at the surface with a well-defined orientation at specific binding sites has significant consequences for both adsorption (sticking) probabilities and desorption rates. The entropy difference between an orientationally constrained adsorbed molecule and a free molecule produces a prefactor in the desorption rate constant that is much larger than characteristic adsorbate frequencies, as discussed above. Specific dynamical pathways that lead from the gaseous state to the adsorbed state must be followed. Thus sticking probabilities may depend strongly on initial molecular orientation and initial rotational energy as well as initial velocity. Correspondingly, thermally desorbed species are formed with specific nonthermal internal energies and velocities.

2) *The pervasive role of defects in molecule-surface encounters.* Surfaces are in general chemically active, in part because their constituent atoms have less than a full complement of bonding neighbors. They readily form bonds with most molecular adsorbates and their constituent fragments, thereby lowering energetic barriers for reaction. They are also impenetrable for thermal energy collisions and thus provide a region of two-dimensional concentration of intermediate species. Steps and other defect sites have even lower bonding coordination and generally provide sites of stronger interaction with adsorbates. Thus dissociation of molecular adsorbates may occur only at steps or defects. Steps provide a further (one-dimensional) concentration of species. The results cited above imply that surface diffusion is in general sufficiently fast that steps and defects will be sampled essentially on all single-crystal surfaces. They will fill first and desorb last. This means that low- and even medium-coverage rate processes can exhibit nonlinearities that depend on step or defect density. It also implies that at least one important role of surface poisons may simply be blocking of active defect or step sites where reactions occur. Conversely, a significant aspect of pretreating of surfaces may be to block unwanted reactions by the same mechanism.

3) *Utility of thermodynamic models of surface processes.* The value of statistical theories of reaction rates, such as transition state theory, is often primarily as a pedagogical tool due to the inability to define or observe the intermediate "transition state" configurations. However, for desorption into the vacuum, this restriction is essentially eliminated. The transition state can usually be taken to be the gas molecule and bare surface, for which the partition functions are known. Thus TST can be applied accurately. Dynamic corrections to the TST desorption rate will be appreciable only if the sticking probability deviates significantly from unity. For molecules with a sticking probability near unity, desorption rates can be quantitatively determined from the thermodynamics of the adsorbed state. Alternatively, thermodynamic properties of the adsorbed state can be inferred from analysis of desorption rates. For example, we have shown how the prefactor for the NO desorption rate constant (entropy term) at low coverage can be interpreted as a sensitive measure of (low) step or defect density. In contrast, for desorption at higher coverages the preexponential provides a measure of the orientational constraint of the adsorbed molecule. One may also anticipate dramatic effects in the desorption rate constant if the adsorbed molecules undergo phase transitions or any significant change in ordering during the desorption process. One expects such transitions to occur at approximately constant chemical potential (ΔG), which implies that the ΔH and ΔS terms in Eq. 1 would compensate, that is, desorption rates would be expected to remain continuous through a transition, but the prefactors and activation energies might change significantly.

Conclusion

We have highlighted a selected few of the many experimental and theoretical studies under way to reveal the underlying molecular phenomena which determine surface rate processes. We have specifically cited studies of nitric oxide sticking probabilities, energy transfer, and desorption rates on close-packed metal surfaces where specific and general conclusions about the molecular dynamics and interaction potential have been drawn. In order to attain this level of understanding, high-resolution experiments and detailed theories are combined. We anticipate a comparable level of understanding to unfold for elementary reactive processes at surfaces. Key to progress in this direction is the evolution of sensitive time-resolved measurements of the populations of adsorbed molecules and their intermediate configurations.

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A Replication Cycle for Viroids and Other Small Infectious RNA's

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Summary. Experimental data concerning viroid-specific nucleic acids accumulating in tomato plants establish, together with earlier studies, the major features of a replication cycle for viroid RNA in plant cells. Many features of this pathway, which involves multimeric strands of both polarities, may be shared by other small infectious RNA's including certain satellite RNA's and "virusoid" RNA's which replicate in conjunction with conventional plant viruses. The presence, in host plants, of an elaborate machinery for replicating these disease agents suggests a role for endogenous small RNA's in cellular development.

Viroids are infectious circular RNA molecules consisting of 250 to 400 nucleotides; these viroids replicate and cause disease in various economically important plants (*1–3*). We have analyzed the viroid-specific nucleic acids in tomato plants infected by potato spindle tuber viroid (PSTV) and have used these data to construct a model for PSTV replication. Our experiments presented in this article suggest that the pathway for PSTV replication proposed here may also apply to other viroids and to two nonviroid classes of small pathogenic RNA molecules found in plants. These additional species include (i) virus satellite RNA's that are packaged as linear molecules such as the satellite of tobacco ringspot virus, TobRV (*4–6*) and (ii) the small circular viral RNA's ("virusoids") that have recently been discovered (*7–10*). In light of experiments suggesting that viroids do not encode proteins (*11–14*), we propose possible host functions of the machinery used for viroid replication.

The early studies of viroid replication were directed toward detecting viroid-specific nucleic acids (minus strands) that could serve as the template for synthesis of mature, infectious RNA (plus strands). Minus strands composed of RNA were first discovered in 1978 by Grill and Semancik during their studies of citrus exocortis viroid (CEV) (*15*) and now have also been detected in plants infected by PSTV (*16–18*), avocado sunblotch viroid (ASBV) (*19*), and chrysanthemum stunt viroid (CSV) (*20*). In addition, double-stranded RNA has been found in association with the satellite of TobRV (*4*) and the virusoid of velvet tobacco mottle virus (VTMoV) (*21*). The minus strand RNA of PSTV appears to contain regions complementary to the entire plus strand and therefore could act as its template (*22*). Experiments by several groups of investigators have established that host plants do not contain detectable amounts of viroid-specific DNA (*23–25*). Thus, key experimental questions about viroid replication concern the size and structure of the RNA minus strands, the form of plus strand intermediates, and the composition of the replication complex.

Multimeric Minus Strands

Analysis of RNA filter hybridization (Northern blot) experiments (*26*) using two different denaturing gel electrophoretic systems established that multimeric minus strands accumulate during PSTV replication (*17*). To determine whether multimeric minus strands could be detected in an additional viroid system, hybridization experiments were carried out with nucleic acids extracted from tomato plants infected by CEV. The nucleic acids were denatured by treatment with glyoxal and dimethyl sulfoxide (*27*) and then separated by gel electrophoresis. The pattern of complementary nucleic acids detected after hybridization to ^{125}I-labeled CEV (Fig. 1B) was similar to the pattern of multimeric minus strands of PSTV (Fig. 1, A and C).

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