



PERSPECTIVES: SURFACE CHEMISTRY

Controlling the Rate of Reaction

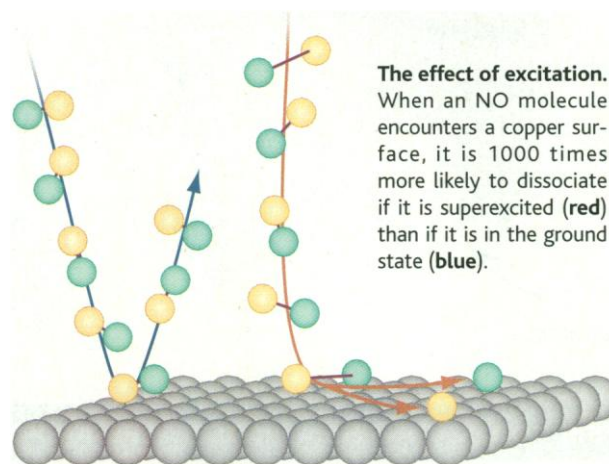
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One way in which chemists can tailor the outcome of a reaction is by controlling the reaction rate. For reactions that occur in the gas phase ($AB + C \rightarrow A + BC$), molecular beam studies have long been used to elucidate the relationship between the population of internal energy states of the molecules and the resulting reaction rates and products (1). These studies have been extended to surface reactions (2), and theoretical studies have been able to reproduce and explain the most salient features of the observations (3). Now, Hou *et al.* demonstrate on page 1647 of this issue that enhanced dissociation rates are observed when highly excited NO molecules encounter a copper surface (4). The results pose a challenge for both theorists and experimentalists.

Consider how energy is initially distributed in a diatomic molecule AB. Restricting our discussion to the ground electronic state, there are three independent energies that will define our reagent. The center of mass of AB moves with a velocity corresponding to a particular translational energy E_{trans} . The molecule can also rotate, and according to quantum mechanics this motion is quantized, with the rotational energy E_{rot} taking on discrete values. Finally, the molecule has a certain vibrational energy E_{vib} , which can only take on specific values related to the particular quantum state, v , that is occupied.

With the use of molecular beam technology, E_{trans} can be specified with some precision for a wide range of molecules. Recently, the combination of laser pumping with molecular beam technology has enabled well-collimated beams of H_2 in a particular rotational-vibrational or rovibrational (J, v) state to be produced (5, 6). With the use of such beams, the scattering and dissociation of hydrogen from the Cu(111) surface—a benchmark problem in surface reactivity research (2)—has been studied. It has even been possible to determine the effects of molecular rotational polarization on a reaction, and to show that molecules dissociate more readily when they approach the surface in a particular geometry (3).

In these earlier experiments, the amounts of energy selectively placed in the internal states of the molecules were relatively small. But in their study of NO scattering from Cu(111) (4), Hou *et al.* selectively placed no less than 300 kJ/mol (3.1 eV per molecule) into vibrational motion by stimulated emission pumping. This method, sometimes referred to as “pump and dump,” uses one laser to excite from the ground to an intermediate state and a second laser to induce emission from this state back down to a high vibrational state in the ground-state NO. Using this method, Hou *et al.* prepared states with v as high as



22. Their work marks a new chapter in the study of surface dynamical processes. Not only are they the first to adapt this experimental method to the study of highly excited molecules at surfaces; the results also provoke theorists to consider the complexity of the interactions.

Hou *et al.* (4) placed about 0.2% of the incident molecules in the $v = 13$ state, while the remainder stay predominantly in the $v = 0$ state. The beam was then scattered from the surface, and the reflected flux state was selectively measured. As time passed, the surface became oxidized as a result of the dissociation of $v = 0$ NO. At the same time, the fraction of $v = 13$ molecules that survived the encounter increased with time. Hou *et al.* considered two possible processes occurring when the surface is oxygen-free at the beginning of the experiment: (i) The vibrationally excited NO could be undergoing inelastic vibrational scattering, which would redistribute energy to a set of scattered molecules. (ii) The vibrationally excited v

$= 13$ NO molecules could be dissociating with enhanced efficiency over the $v = 0$ species. They found that since the intensities of all of the inelastically scattered molecules was independent of time, the first mechanism cannot possibly be operative. Hou *et al.* conclude that the second mechanism is operative, and that there is an 87% probability that an encounter of $v = 13$ NO with a Cu(111) surface results in reaction—an enhancement by a factor of 1000 over the encounter of a $v = 0$ molecule with the same surface. Additional experiments carried out with beams having differing translational energies and surfaces with increased temperatures gave essentially the same results.

No theory exists for the interaction of highly excited molecules with surfaces, and the results of Hou *et al.* essentially throw down the gauntlet to theorists. Issues to consider include energy dissipation into phonons and electron hole pairs in the surface. Previous work involving NO scattering from Ag surfaces (7) prompted theoretical work that suggested that both electrons (8) and phonons (9) provide energy to the incident molecule. If this is the case, then it seems unlikely that simply running classical trajectories (or quantum wave packets) on a single electronic potential energy surface will be sufficient to reproduce Hou *et al.*'s results (10). Perhaps

the insensitivity of the experiment to initial velocity and surface temperature is telling us more than simply helping us to rule out trapping as a dominant effect. We will need all the help that we can get in order to develop new theoretical methods to explain these intriguing experimental observations.

References and Notes

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