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Controlling an Electron-Transfer Reaction at a Metal Surface by Manipulating Reactant Motion and Orientation**

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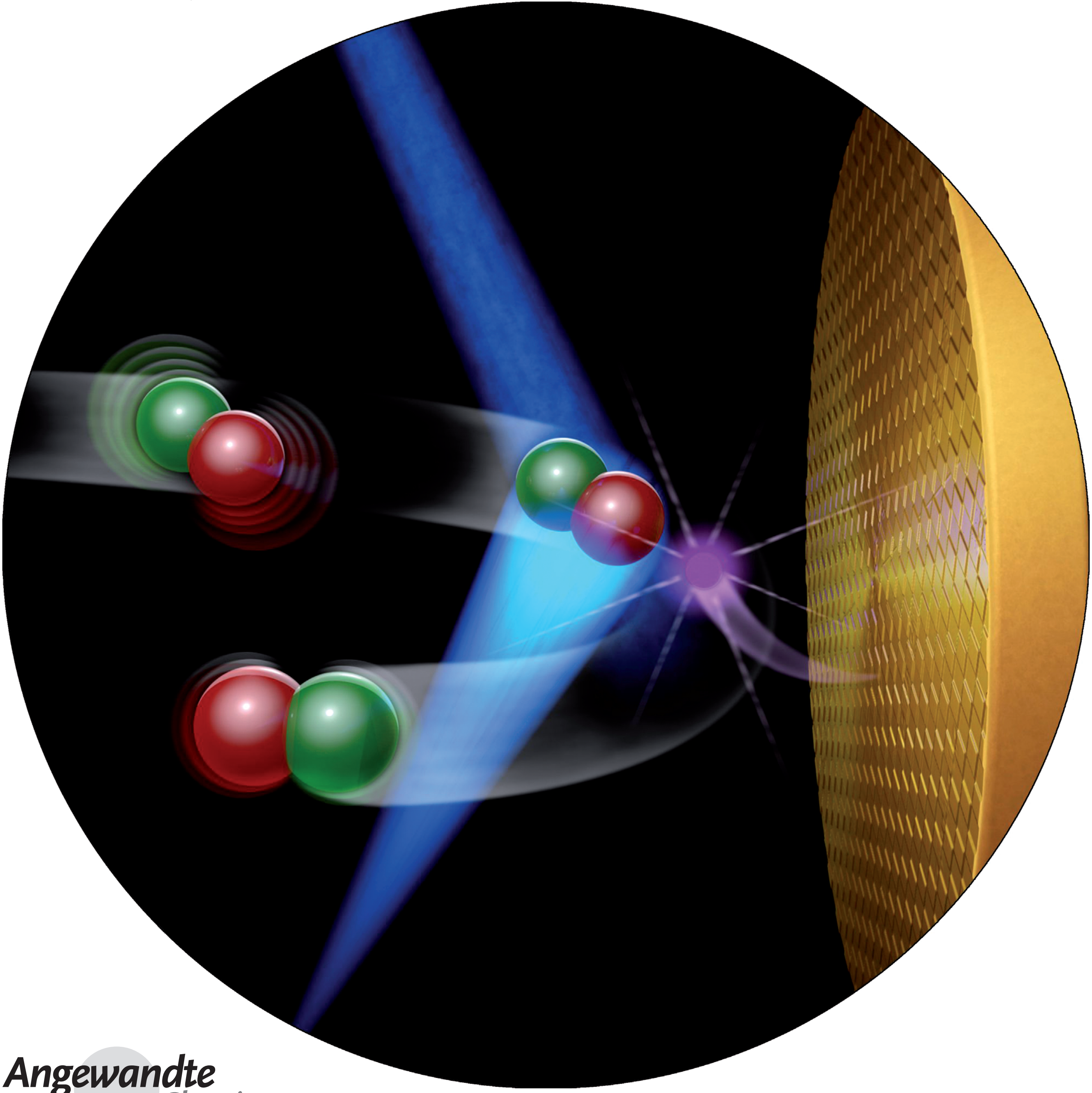

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Abstract: *The loss or gain of vibrational energy in collisions of an NO molecule with the surface of a gold single crystal proceeds by electron transfer. With the advent of new optical pumping and orientation methods, we can now control all molecular degrees of freedom important to this electron-transfer-mediated process, providing the most detailed look yet into the inner workings of an electron-transfer reaction and showing how to control its outcome. We find the probability of electron transfer increases with increasing translational and vibrational energy as well as with proper orientation of the reactant. However, as the vibrational energy increases, translational excitation becomes unimportant and proper orientation becomes less critical. One can understand the interplay of all three control parameters from simple model potentials.*

Electron-transfer reactions are important in a remarkably wide range of phenomena in biology, chemistry, physics, and technology and have been the subject of extensive scientific efforts.[1] A fundamental question is how reactant motion influences the probability for electron transfer. All degrees of freedom—including angular (i.e. orientation), vibrational, and translational—are thought to be important control parameters for electron transfer, making understanding their influence and interplay highly challenging.[1b] Furthermore, most studies investigate electron-transfer reactions in solution, where solvent effects and the difficulty associated with experimentally controlling these parameters further complicate matters.

Extensive experimental[2–3] and theoretical work[4] has revealed that the transfer of vibrational energy that occurs when an NO molecule collides with a metal solid is the result of a simple electron-transfer reaction. The electron-transfer event accompanies breakdown of the Born–Oppenheimer approximation, allowing the conversion of the vibrational energy of the molecule to the electronic excitation of the solid[3a,b] or even electron emission.[2,3c–f] This model system is in many ways dynamically equivalent to electron transfer in the condensed phase, but solvent effects appear in a much simpler way.[3a] Specifically, the interaction of the ion with the solvent is replaced by an interaction with its image charge in the metal, which is much more easily modeled.[4a–d]

By studying electron transfer in this way, we are able to remove the complicating effects of the solvent and to control all degrees of freedom of the molecule using modern dynamic methods. This work benefits from recent developments in the field of molecular beam surface scattering.[5] A new technique, called pump–dump–sweep[5a,b]—an extension of the better known stimulated emission pumping[6]—as well as improved overtone pumping[5c–e] enable us to prepare molecular beams of vibrationally excited NO over a wide range of initial translational energies with excellent quantum state purity, a crucial requirement for the present study. In addition, we have developed a new method for orienting molecules,[5f] which unlike hexapole focusing,[7] is applicable at high as well as low translational energies.

These recent experimental innovations allow us to examine the influence of NO's motion on the electron-transfer reaction in a comprehensive way: We independently control the molecule's initial vibrational motion, translational excitation, and orientation with respect to the electron donor. These three control parameters describe all degrees of freedom relevant to the electron-transfer reaction and can be varied independently. Thus, we determine the effect of each control parameter and also see how each degree of freedom affects the influence of the other kinds of motion.

This unprecedented experimental capability is applied here to electron-transfer chemistry for the first time. While the observations are excellent benchmarks for first-principles theories of electron transfer and the Born–Oppenheimer breakdown,[4a] we emphasize herein a simple model that helps us understand the influence of vibrational, translational, and rotational motion on electron transfer. The model describes an energetic barrier to electron transfer that is modified by the molecular vibrational state and orientation and can be overcome by translational energy.

Figure 1 shows experimental results for the vibrational relaxation of randomly oriented NO molecules scattered from Au(111) for three different incidence vibrational and five different translational energies. Scattered vibrational state distributions for high incident vibrational states of $v_\mathrm{I}=16$ and 11 are shown in Figure 1 A and B, respectively. We obtain these distributions by resonance-enhanced multiphoton ionization (REMPI) spectroscopy of surface-scattered molecules. The interested reader is referred to the Supporting Information where we show an example of a measured spectrum and describe its analysis. In Figure 1 C we show data for $v_\mathrm{I}=3$ which we recently measured in a similar experiment.[5e] We would like to bring several important observations to the reader's attention:

1. We find that the vibrational relaxation probability, that is, the probability that a molecule loses at least one quantum of vibrational energy, increases strongly with increasing incidence vibrational energy (see Figure 2). At low incidence translational energy, these probabilities range from 20% for $v_\mathrm{I}=3$ and 90% for $v_\mathrm{I}=11$ to essentially 100% for $v_\mathrm{I}=16$. This demonstrates the vibrational promotion of electron transfer.
2. Translational energy also enhances the vibrational relaxation probability. This finding contradicts predictions from both surface hopping[4a] and electronic friction[4e] theories and is opposite to the observed trend for the probability of electron emission promoted by collisions of vibrationally excited NO from a cesiated gold surface.[3d]
3. For both $v_\mathrm{I}=16$ and $v_\mathrm{I}=11$, the final vibrational distributions are remarkably similar, peaking around $v=6$, and

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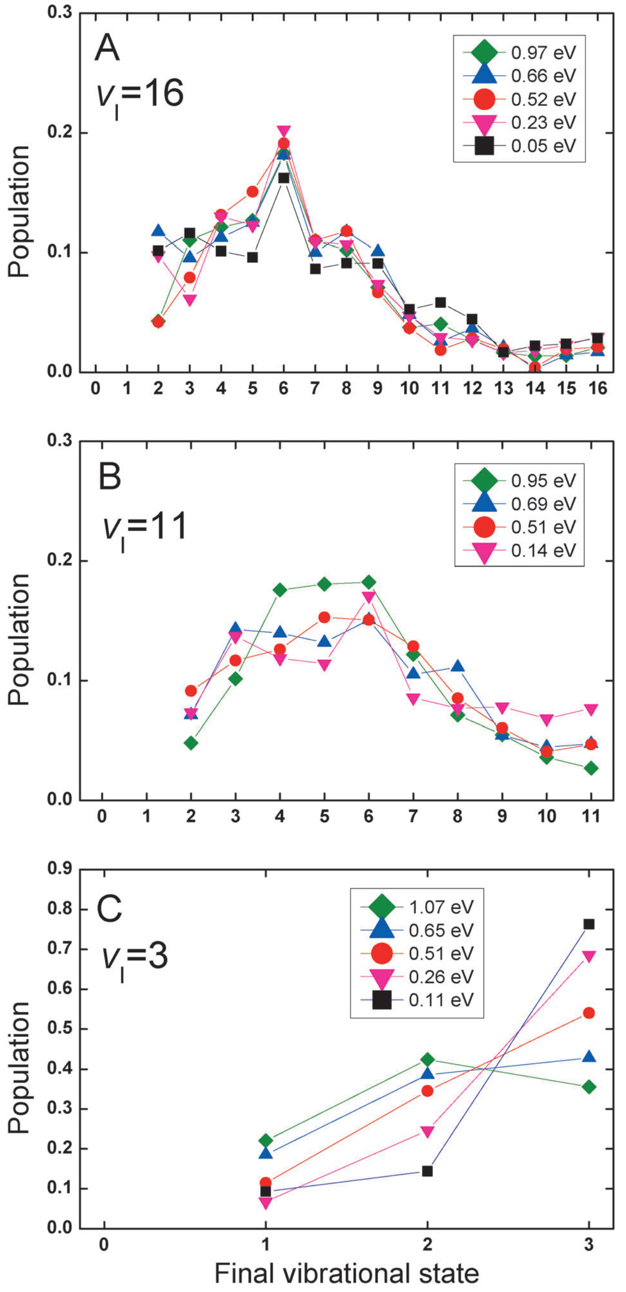

Figure 1. Experimental final vibrational state distributions of scattered NO from Au(111) for different incident vibrational states and incidence translational energies.

largely independent of the incidence translational energy. This independence does not mean that the scattered molecules lose their memory of the incident translational energy. In fact, the scattered molecules have distinct nonthermal rotational state distributions with rotational rainbows resulting from orientation-dependent collisions[6a,8] which are strongly affected by the incidence translational energy.

In order to elucidate the influence of the molecular orientation of NO with respect to the metal surface on the vibrational relaxation, we use a recently developed orientation method called optical state selection with adiabatic orientation.[5f] This method can be used to orient molecules preferentially pointing either with the O atom towards the surface or the N atom towards the surface. We recently published data for the scattering of oriented molecules in $v_I = 3$.[5b,9] Figure 3 shows how the incidence orientation affects the vibrational relaxation for higher incidence vibrational states. For $v_I = 11$ (Figure 3B) we find that the vibrational relaxation is significantly enhanced for molecules oriented with the N atom towards the surface. This is similar to our previous observations for $v_I = 3$. Interestingly, this effect disappears for

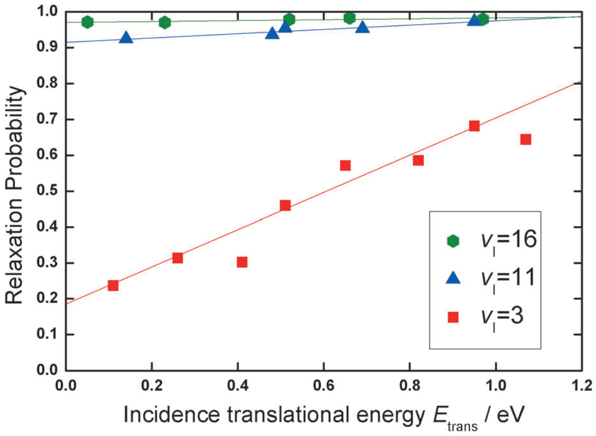

Figure 2. Relaxation probability for NO molecules initially prepared in different vibrational states (v_I) as function of the incidence translational energy. The relaxation probability increases with the incidence translational as well as with the incidence vibrational energy.

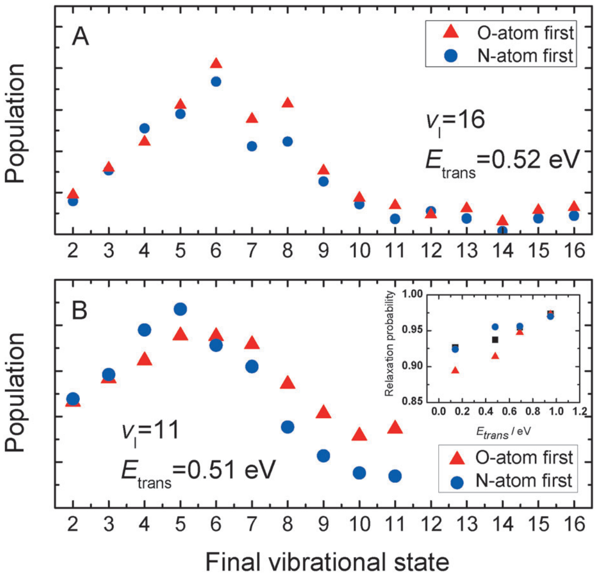

Figure 3. Final vibrational state distributions of highly vibrationally excited NO scattered from Au(111) for different incidence vibrational states ($v_I = 16$ top, $v_I = 11$ bottom) and incidence orientations. Molecules are either preferentially oriented with the O atom towards the surface (red triangles) or with the N atom towards the surface (blue dots). The inset in (B) shows the orientation-dependent relaxation probability for unoriented (black squares), N-atom-first, and O-atom-first collisions.

the very high incidence vibrational state $v_{\mathrm{I}}=16$ (Figure 3 A). In this case, the driving force for vibrational relaxation is so strong that the incidence orientation—just like the incidence translation—becomes less crucial.

Some trends in the observed vibrational state distributions can be understood by analyzing semiempirical electronic ground state model potentials of NO and NO^- species near the surface (see Figure 4). We approximate the interaction of the anionic species with the surface by Coulombic forces between the anion's charge and the image charge formed in the metal. We give parameters, references, and further details on the potentials in the Supporting Information. The energetically optimum bond length for electron transfer is at a high N–O separation close to the outer classical turning point of the vibration.[4a] Accordingly, in Figure 4 we compare the energetics for NO/NO^- bond lengths constrained to the outer classical turning points of the different incident vibrational states of $v_{\mathrm{I}}=3$, 11, and 16. Note that especially high vibrational states have a high probability density near the classical outer turning point, justifying their modeling as "stretched molecules".[6a] The anionic potentials are strongly affected by the molecular orientation, because the lowest unoccupied molecular orbital (LUMO) has higher probability density on the N atom than on the O atom. We thus plot the anionic potentials for different orientations of the angle θ between the surface normal and the NO bond, at the expectation values $\langle\theta_{\max}\rangle$ for side-on (isotropic), O-atom-first, and N-atom-first collisions of 68°, 90° and 112°, respectively.

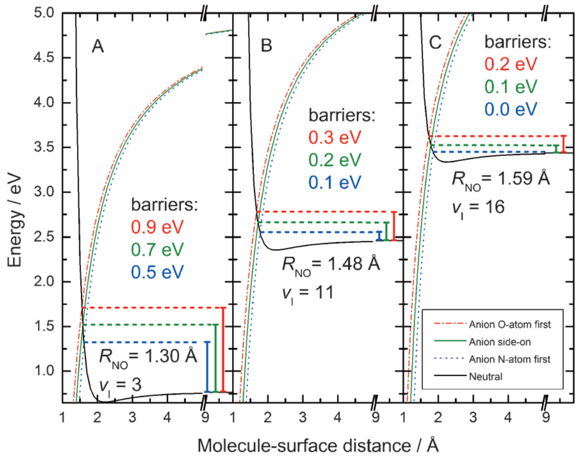

Figure 4. Affecting the barrier of an electron-transfer reaction by incidence vibration and orientation. We show neutral (black line) and anionic potential energy curves (green line: side-on collision, dashed-dotted line: collision with the O atom pointed towards the surface, dotted line: reverse orientation). The curves are constructed following the lines described by White et al. for vibrationally frozen molecules at the outer turning points of $R_{\mathrm{NO}}=1.30$, 1.48, and 1.58 Å for $v_{\mathrm{I}}=3$, 11, 16 (A, B, C) as a function of the molecule–surface distance.[2] The increase in vibrational energy reduces the energy barrier between neutral and anionic potential significantly. Additionally, the height of the barrier is influenced by orientation: A collision with the N atom pointing towards the surface results in a lower barrier. Please note that the neutral curves also show an orientation dependence that is much weaker than for the ionic curves, and are thus omitted from the figure. A corresponding figure can be found in the Supporting Information.

The existence of a barrier towards electron transfer when molecules approach the surface is apparent in Figure 4. In a diabatic picture, the top of the barrier occurs at the curve crossing between the NO and NO^- potentials and within this simple model decreases from 0.7 to 0.1 eV between $v_{\mathrm{I}}=3$ and 16 (side-on orientation) and is always lower for the N-first than for the O-first orientation. In other words, we can reduce the barrier towards electron transfer by increasing the incidence vibrational energy and by choosing the optimum incidence orientation.

This simple picture explains not only the orientation-dependent vibrational promotion of electron transfer but also the enhancement by incidence translational energy: the transition probability of crossing the potential energy barrier is significantly augmented at elevated translational energy. It should be mentioned that the electron transfered from the metal to the molecule may tunnel through the barrier and that the barrier width will affect the tunneling probability. However, the trends for tunneling are expected to be similar to those for crossing a classical barrier. The closer the particle approaches, the more likely tunneling will occur.

As pointed out already, it is intriguing that vibrational relaxation is enhanced by translational energy, whereas previous experiments have shown unambiguously that the vibrational promotion of electron emission depends inversely on the colliding molecule's velocity. However, we can easily explain these—at first sight—contradictory experimental observations within the same framework of the same simple model. The lowering of the surface work function from 5.3 eV to 1.6 eV (achieved by adsorbing Cs on the surface) causes the energy barrier between neutral and anionic potentials to vanish even when NO is at its equilibrium bond length (see Figure 9 in Ref. [2]). Thus, the relaxation process is barrier-free for any vibrational state. Instead, the inverse velocity dependence of electron emission arises from a vibrational autodetachment mechanism,[3d] whereby electron emission is possible only beyond a certain critical distance from the surface. Hence, the relaxation probability is determined by the interaction time between molecule and surface in the region only beyond the critical distance. The interaction time, and hence the electron emission probability, decreases at higher incidence translational energies. For vibrational relaxation, this critical distance plays no role, and thus vibrational relaxation is not affected in the same way.

In conclusion, our experiments demonstrate how to control a simple electron-transfer reaction between a molecule and a metal surface by manipulating the translational energy, vibrational energy, and orientation of the reactant molecule. These variables affect the reaction in a complex and interrelated manner, yet despite the seeming complexity, predictions of a simple model based on the shift of neutral and anionic potential energy curves are in qualitative agreement with the experimental findings. Further work is required to develop a quantitative first-principles description of the electron-transfer process.

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