

Observation of Direct Vibrational Excitation in Gas-Surface Collisions: NO on Ag(111)C. T. Rettner, F. Fabre,^(a) J. Kimman,^(b) and D. J. Auerbach
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Vibrationally excited NO molecules have been observed in the scattering of NO($v=0$) from Ag(111). A direct mechanism is inferred based on the observation of $v=1$ angular distributions, which are quasispecular, and rotational-state distributions, which depend on beam energy. Vibrational excitation is found to depend strongly on surface temperature, T_S , and relatively weakly on incident kinetic energy, E , reaching ($\sim 7 \pm 5$)% at $T_S = 760$ K and $E = 120$ kJ mol⁻¹. These results are discussed in terms of an electronic mechanism for vibrational excitation.

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The understanding of energy-transfer dynamics at the gas-surface interface is a prerequisite for any detailed model of the trapping and sticking of atoms and molecules at surfaces and is of fundamental importance to any comprehensive theory of gas-surface chemistry. Recent molecular-beam scattering and theoretical studies have probed many aspects of such interactions.¹⁻¹² In particular, there has been much recent experimental and theoretical²⁻⁴ interest in rotational excitation^{1,5} and vibrational deexcitation⁹⁻¹² at surfaces. Vibrational excitation at surfaces, however, has received relatively little attention. This is unfortunate since such excitations couple directly to dissociative-reaction coordinates, as has been pointed out by Holloway and Gadzuk,¹¹ who have considered both vibrational excitation and disassociation at surfaces. Previous experiments⁶⁻⁸ have all been concerned with excitation following surface trapping, whereby the vibrational populations approach the equilibrium at the surface temperature before desorption occurs. While such studies can reveal thermally averaged excitation rates, all memory is lost of the incident translational energy and angle, except to the degree that they affect the trapping probability. Thus such measurements provide only limited information on the dynamics and mechanism of vibrational excitation.

We report here the first unambiguous observation of *direct* vibrational excitation, whereby energy transfer occurs in essentially a single gas-surface encounter. The NO/Ag(111) system was chosen for study since it has been the subject of several previous direct rotational inelastic scattering studies^{1,5} and of considerable theoretical effort.¹⁻⁴ Measurements of distributions of scattered molecules with respect to angle, velocity, and rotational state and their dependence on incident energy, angle, and surface temperature are used to distinguish direct inelastic scattering events from trapping followed by equilibration and desorption. We find that the direct vibrational excitation probability is usually quite small but reaches several percent for high incident energies and surface temperatures, varying by

several orders of magnitude with surface temperature and by 1 order of magnitude with incident kinetic energy and angle. These experimental findings suggest an electronic mechanism for vibrational excitation.

The experimental setup is similar to that described previously,⁵ with the substitution of resonant-multiphoton-ionization detection^{6,12} for the previously employed laser-induced-fluorescence detection scheme. Briefly, a supersonic molecular beam of NO is directed at a single crystal of Ag(111) held on a manipulator in an ultrahigh-vacuum chamber. The beam is formed either in a pulsed-beam source or in a heatable continuous-beam source, and passed through four differential pumping stages. A high-speed chopper with a 1% duty cycle reduces the NO background pressure in the scattering chamber to a negligible level and permits time-of-flight distributions to be measured. Scattered NO molecules are detected by use of two-photon ionization in order to selectively ionize specific quantum states via one-photon resonances to the NO $A^1\Sigma^+$ state at around 225 nm. A Nd-doped yttrium-aluminum-garnet laser (Quanta-Ray, DCR2) at 1064 nm is doubled to 532 nm and used to pump a dye laser (Quanta-Ray, PDL1). This is frequency doubled to ~ 285 nm and then mixed with residual 1064-nm light to provide 1-3-mJ, ~ 8 -ns pulses of tunable radiation in the region of 225 nm with a bandwidth of ~ 0.5 cm⁻¹. This light is collimated to about 1 cm diameter, giving a peak power of ~ 0.2 - 0.5 MW/cm². For most of the measurements reported here, this beam is apertured to 5 mm and directed 1 cm from the crystal. Thus the detection volume is a 5-mm-diam cylinder parallel to the crystal face with its axis 1 cm from the surface, giving an effective angular resolution of $\sim 30^\circ$ for in-plane scattering and integrating over out-of-plane angles. This low angular resolution permits us to essentially integrate over a large range of scattering angles. Photoions are collected and detected by an electron multiplier (EMI, model 9642/3B). Rotational distributions are extracted by division of the observed (0,0) and (1,1) line intensities by the appropriate rotational

line strengths¹³ and by the laser intensity to the power of 1.8, in accordance with the measured power dependence. This procedure was checked against a 300-K static gas. Calibration experiments using both a static gas and a heated effusive beam were used to obtain $\text{NO}(v=1)$ to $\text{NO}(v=0)$ ratios.

Rotational distributions for scattered $\text{NO}(v=0)$ were found to be virtually identical to those reported previously.^{1,5} Similar rotational distributions were observed for NO scattered in $v=1$, but with a slightly lower degree of rotational excitation, corresponding to ≤ 100 K difference in the initial slopes of the familiar $\ln[N(J)/(2J+1)]$ vs E_J plots.⁵ For example, with NO beams of 10 and 100 kJ mol^{-1} , and incident and final scattering angles, θ_i and θ_f , of 15° , initial slopes of 280 ± 20 K and 450 ± 30 K, respectively, were obtained for $v=1$ and 380 ± 20 K and 500 ± 30 K for $v=0$ $^2\Pi_{3/2}$ molecules. These slopes are virtually independent of surface temperature, T_s , in the range 500 to 760 K. At the highest beam energy employed, 135 kJ mol^{-1} , the rotational distributions could be followed out to $J=66.5$ for $v=0$ and $J=46.5$ for $v=1$. Here the $v=1$ data were found to be highly non-Boltzmann, resembling the rotational rainbow¹⁻⁵ distribution exhibited by the $v=0$ data. In extracting these $v=1$ distributions, a small correction was made for the fraction of NO in $v=1$ in the incident beam, as measured by separate experiments on the beam itself, with the assumption that $\text{NO}(v=1)$ scatters identically to $\text{NO}(v=0)$.

By summing members of these rotational distribu-

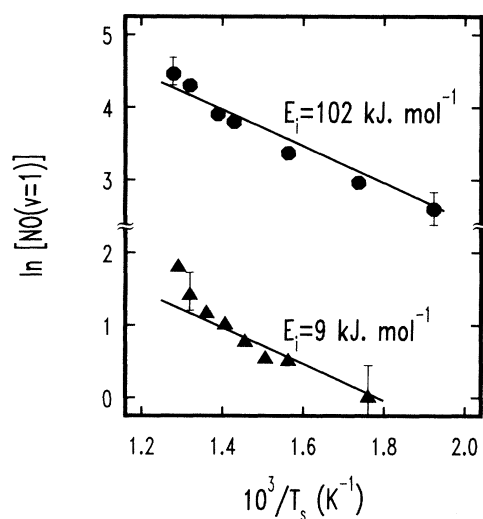


FIG. 1. Effect of surface temperature on the $\text{NO}(v=1)/\text{NO}(v=0)$ scattering ratio. The upper data points refer to a beam energy of 102 kJ mol^{-1} , while the lower ones were obtained at 9 kJ mol^{-1} , with $\theta_i=15^\circ$ in both cases. These two sets of data are arbitrarily scaled relative to each other.

tions, we are able to estimate the fraction of the beam that is excited into $v=1$ compared to the vibrationally elastic channel for a given set of conditions. This fraction is found to depend sensitively on both the incident kinetic energy and the surface temperature. Of these, the surface-temperature dependence is found to be the most dramatic. For a surface temperature of 273 K, the level of vibrational excitation of $\text{NO}(v=1)$ is indistinguishable from the $\text{NO}(v=1)$ concentration in the beam at all incident energies up to 135 kJ mol^{-1} . For $E_i=102$ and 53 kJ mol^{-1} , and $\theta_i=15^\circ$, we estimate the vibrational excitation probability to be $\leq 1 \times 10^{-3}$ and 5×10^{-4} , respectively. Heating of the sample increases the $v=1$ contribution to measurable levels, as shown in Fig. 1, where an Arrhenius plot of the $v=1$ fraction is displayed for beam energies of 9 and 102 kJ mol^{-1} .¹⁴ It is apparent that the form of the temperature dependence is insensitive to beam energy. The solid lines correspond to an activation energy of ~ 22 kJ mol^{-1} , the NO vibrational excitation energy.¹³ The data are roughly parallel to these lines with, however, some curvature, indicating a departure from a strict Arrhenius behavior.

The dependence of vibrational excitation on beam energy is also substantial. Figure 2 shows the observed fraction of vibrationally excited NO scattered for $T_s=760$ K as a function of beam energy. In both figures, the displayed error bars indicate approximate 95% confidence limits for the relative magnitudes. In addition there is an uncertainty of about a factor of 2 (again at $\sim 95\%$ confidence) in the absolute values. This reflects the uncertainty in the calibration of the relative sensitivity to $\text{NO}(v=0)$ and $\text{NO}(v=1)$. Thus

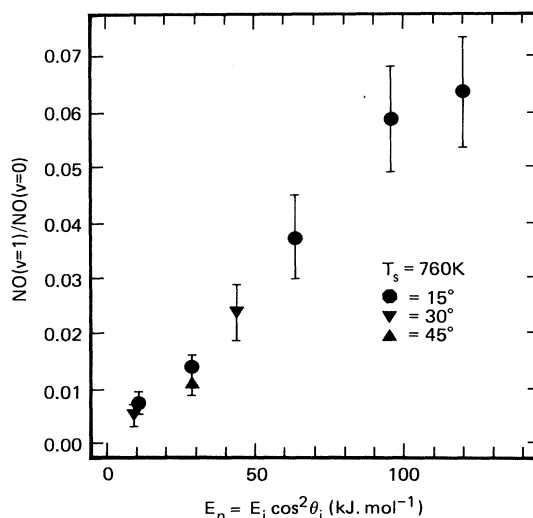


FIG. 2. Effect of incident energy on the $\text{NO}(v=1)/\text{NO}(v=0)$ scattering ratio for $T_s=760$ K and $\theta_i=15^\circ$, 30° , and 45° .

we conservatively estimate that the highest level of excitation reached is of the order of $(\sim 7 \pm 5)\%$. While most data were obtained at $\theta_i = 15^\circ$, several points were recorded for other incident angles where $\theta_i = \theta_f$ in every case. Approximately normal energy scaling is observed, where the normal energy is defined by $E_n = E_i \cos^2 \theta_i$. This is similar to the behavior reported previously for rotational excitation.^{1,5}

In experiments with $E_n = 120 \text{ kJ mol}^{-1}$ and $T_S = 760 \text{ K}$, a search was made for $\text{NO}(v=2)$ via the (2,2) band in the region of 221.6 nm. None was detected, giving $\text{NO}(v=2)/\text{NO}(v=0) \leq 5 \times 10^{-3}$, under these conditions.

The above results suggest a direct-inelastic, rather than trapping-desorption, origin for the vibrationally excited NO molecules. Calculations indicate that in this energy regime the trapping probability for NO on Ag(111) should *decrease* rapidly with increasing kinetic energy,⁵ whereas the $v=1$ intensity is found to *increase* with this energy. Furthermore, the rotational distributions for $v=1$ are found to vary with incident energy and angle. Trapped molecules would be expected to lose memory of the incident beam properties. To confirm the direct nature of the vibrational excitation observed, the in-plane angular resolution was improved to $\leq 5^\circ$ and the out-of-plane to $\leq 20^\circ$ by moving the detection distance to 7 cm from the crystal. Angular distributions for both $\text{NO}(v=0)$ and $\text{NO}(v=1)$ were quasispecular in all cases. For example, with $E_i = 80 \text{ kJ mol}^{-1}$, $\theta_i = 45^\circ$, and $T_S = 760 \text{ K}$, the in-plane angular distribution for $v=1$, $J=18.5$ was found to peak at $\theta_f \sim 40^\circ$ with a FWHM of $\sim 40^\circ$. These angular distributions are certainly inconsistent with a trapping-desorption process which would be expected to yield a cosine scattering pattern.^{6,7}

The above measurements were performed with the chopper spinning sufficiently slowly to minimize velocity selection of the scattered beam. By spinning the chopper more rapidly, time-of-flight distributions were recorded for scattered molecules by scanning of the delay between 10- μs chopper pulses and the firing of the laser. These measurements allow us to set a

limit of $\leq 10 \mu\text{s}$ for the surface-residence time of NO molecules contributing to our $v=1$ intensity. Measurements with the laser 7 cm from the crystal allow us to distinguish clearly the scattered velocity distributions from a Boltzmann distribution at T_S . Details of the velocity and angular distribution measurements for both $v=0$ and $v=1$ will be given elsewhere.¹⁵

The experimental findings outlined above place strong constraints on models for the vibrational excitation observed here. First, we must consider a direct mechanism and one which involves both the surface temperature and the incident *normal* kinetic energy. Furthermore, as indicated by Fig. 1, these two effects enter *independently*, i.e., the form of the surface temperature effect is not dependent on incident energy, at least to a first approximation. Finally, there must be a very strong coupling to surface temperature following a roughly Arrhenius behavior with activation energy equal to the NO vibrational energy spacing, E_{vib} . The energy for vibrational excitation appears to be coming from the coupling to the surface as evidenced by the observation of $v=1$ for $E_i < E_{\text{vib}}$ and by the quasispecular scattering observed even at low incident energies. This coupling could be via either phonons or electronic states of the silver. Preliminary calculations and intuitive considerations favor the latter process. It seems unlikely that a coupling to phonons would have the property of factoring into a term dependent on E_n and one dependent on T_S . It also seems unlikely that coupling to phonons would have the very unequal roles displayed here for the velocities of surface atoms and incident molecules.

We thus are led tentatively to suggest an electronic mechanism for the vibrational excitation. The NO excitation may be coupled to deexcitation of thermal electron-hole pairs in the metal. Here the role of increased E_n is to allow the molecules to penetrate further into the electron cloud above the surface, increasing the coupling to the molecule. Such an excitation process would involve transitions near the Fermi level between states in the high-energy tail of the Fermi distribution and lower-lying unoccupied states. If we calculate the product of the density of filled and empty states separated by E_{vib} , we obtain

$$N_{\text{NO}(v=1)} \sim \int_0^\infty f(E) \rho(E) [1 - f(E - E_{\text{vib}})] \rho(E - E_{\text{vib}}) \sigma(E) dE \sim \exp(-E_{\text{vib}}/kT_S) (E_{\text{vib}} - kT_S \ln 2),$$

where f is the Fermi function, and we have made the approximation that the density of states, ρ , and coupling, σ , are constant near the Fermi energy. Over the range of temperatures explored here, this function will give a linear Arrhenius plot with an effective activation energy equal to E_{vib} . This is roughly consistent with our data (see Fig. 1). We also note that the highest levels of $v=1$ excitation observed here [$(\sim 7 \pm 5)\%$] are of the order of the equilibrium value for the 760-K surface temperature ($\sim 3\%$).

So far we have said nothing about the nature of the coupling between the NO molecule and the electron-hole pairs. It is possible that direct electron-molecule scattering occurs close to the surface. It is well known that the cross section for molecular vibrational excitation via electron scattering is greatly enhanced by shape resonances corresponding to the formation of temporary negative ions, as has been described by a number of workers in considering vibrational excita-

tion probabilities in electron-molecule scattering.¹⁶⁻¹⁸ Since charge transfer is a relatively common feature of gas-surface interactions,¹⁹⁻²¹ and NO possesses convenient low-lying empty orbitals,²² such a mechanism is highly appealing. Indeed, Gadzuk²³ has specifically proposed that vibrational excitation may occur in gas-surface collisions as a result of temporary negative-molecular-ion formation, and has predicted that vibrational excitations should be seen in experiments such as ours. Moreover, Sanche and Michaud have directly observed such shape resonances in electron-induced vibrational excitation of N₂ multilayer films.²⁴ It is also possible that the dominant coupling is via dipole-dipole interaction as in Förster energy transfer.²⁵

Whatever the nature of the excitation mechanism, our observations demonstrate that it is possible for a molecule to become vibrationally excited in essentially a single gas-surface encounter. If an electronic mechanism is indeed responsible for this effect, this excitation process may be quite general for metal surfaces. In this case, such excitations may play an important role in a wide range of surface chemistry. For example, consider the case of activated dissociative chemisorption, where reaction is often driven by heating of the surface. Here a direct vibrational excitation mechanism could promote direct reaction paths. The alternative process of trapping followed by surface accommodation would be expected to become inefficient at high temperatures where the desorption rate may be too rapid for equilibration to occur. More detailed calculations are clearly necessary to understand these new observations quantitatively.

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Note added. We have recently received a preprint from Newns,²⁶ who has calculated vibrational excitation probabilities for the NO/Ag(111) system after hearing of our results. He is able to account for the principal features of our data (Boltzmann-type temperature factor plus linear dependence on incident energy) by considering negative-ion formation and electron-hole-pair deexcitation in a mechanism very similar to that outlined above.

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