Observation of Direct Multiquantum Vibrational Excitation in Gas-Surface Scattering: NH_3 on Au(111)

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Vibrationally excited NH_3 molecules are observed in the scattering of NH_3 ($v=0$) from Au(111). We observe up to three quanta of vibrational excitation in the ν_2 "umbrella" vibrational mode of NH_3. The vibrational excitation probability scales linearly with the kinetic energy of the incident beam above a threshold energy corresponding to the quanta excited, and is independent of the surface temperature, T_s, over the range 300 K $\le T_s \le$ 800 K. These results are discussed in terms of an electronically adiabatic collisional mechanism for vibrational excitation.

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Heterogeneous catalysis, corrosion, microelectronic fabrication, aerodynamic drag, and heat transfer are processes with great economic and technological importance. The detailed molecular dynamics of the interactions between molecules and surfaces form the microscopic basis for these macroscopic processes. Recently molecular-beam–surface scattering experiments and theoretical techniques have been utilized to study the fundamental aspects of rotational excitation[1-11] and vibrational relaxation[12-14] during gas-surface encounters. However, the detailed study of vibrational excitation via such encounters has received relatively little attention.[15-20] A detailed understanding of vibrational excitation at surfaces is requisite to a dynamical description of surface chemical reactions, since molecular vibrational degrees of freedom are directly coupled to the dissociative reaction coordinate. Most previous experimental studies[15-17] of vibrational excitation have been concerned with excitation following trapping. One important exception is an elegant study by Rettner *et al.*[20] on the NO/Ag(111) system in which significant vibrational excitation is observed in a direct encounter. These results have been interpreted with an electron-hole-pair deexcitation mechanism first proposed by Gadzuk[18] and more recently addressed by Newns.[19]

In this Letter we report the first observation of multiquantum vibrational excitation in a direct gas-surface encounter. The NH_3/Au(111) system was chosen for study since it has revealed interesting new dynamical information concerning rotationally inelastic scattering[11] and because NH_3 has several normal vibrational modes. The experiment consists of scattering of a well-collimated, rotationally cold (<20 K), supersonic NH_3 beam from an atomically clean Au(111) surface. The scattered angular, rotational, and vibrational distributions are detected in a quantum-resolved manner by use of two-photon–resonant, three-photon–ionization [(2+1)MPI] laser spectroscopy and molecular-beam scattering techniques. A detailed description of the experimental apparatus and the (2+1)MPI laser spectroscopy is published elsewhere.[10,21,22]

Up to three quanta of vibrational excitation in the ν_2 "umbrella" mode of NH_3 are observed in the scattered beam. In order to examine quantitatively the dependence of the observed vibrational excitation upon the energy and angle of the incident molecular beam, we measured a series of spectra probing the $\tilde{C}'(v_2'=0)\leftarrow\tilde{X}(v_2''=0,1,2,3)$ transitions. These transitions are not sufficiently resolved to determine the rotational distribution in the vibrationally excited NH_3. Thus, in order to extract the vibrational population we integrate the area under the rotational envelope of the transition. The $\tilde{C}\leftarrow\tilde{X}$ transitions are dominated by the zeroth-rank two-photon absorption tensor and hence appear as a rotational Q branch ($\Delta J=\Delta K=0$) with line-strength factors which do not depend on J or K.[21,23,24] Thus, the (2+1)MPI spectrum is simply a map of the rotational population in the electronic ground state. Recently, Ebata, Conaway, and Zare[25] have calculated the vibrational Franck-Condon factors for the $\tilde{C}'\leftarrow\tilde{X}$ two-photon transitions and we utilize their results in the vibrational population analysis.

Figure 1 displays the dependence of the observed vibrational excitation upon the incident molecular-beam kinetic energy for scattering from a 300-K Au(111) surface. The observed vibrational excitation probability is found to scale linearly with the energy associated with motion normal to the surface plane E_n ($E_n=E_i\cos^2\theta_i$) above a threshold which is very close to the energy of the vibrational level being excited. The energies of the $v_2=1$, 2, and 3 vibrational levels are shown as arrows in Fig. 1. The slopes of the data in Fig. 1 are different for the various vibrational levels ($v_2=1,2,3$) but deviate from each other by, at most, a factor of 2. This factor of 2 is within the combined absolute uncertainty of the experimental measurements and their subsequent analysis, and we are thus reluctant to ascribe a dynamical interpretation to the difference in slopes. Furthermore, the velocity distributions of the vibrationally inelastically scattered NH_3 have not been measured, and so Fig. 1

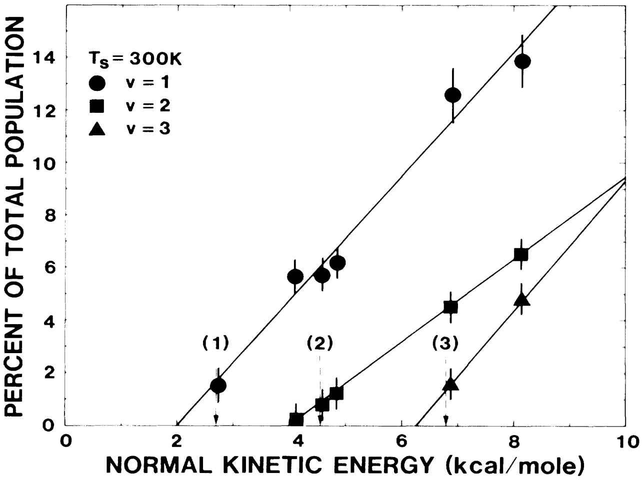

FIG. 1. NH_3 ν_2 vibrational excitation as a function of the normal incident-beam kinetic energy. The energies of the various ν_2 quanta are indicated by the arrows.

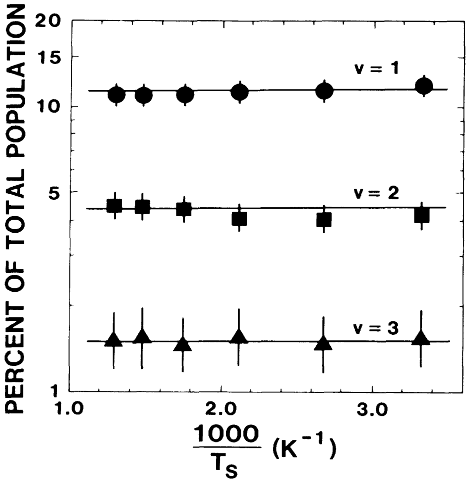

FIG. 2. Arrhenius plot of the observed vibrational excitation for the temperature range 300 K ≤ T_s ≤ 800 K at a normal incident kinetic energy of 6.9 kcal/mol.

does not necessarily represent the scattered-flux vibrational distribution. Quantum-resolved measurements of both the scattered angular and velocity distributions are under way and will be reported elsewhere.[26]

Both the nonzero threshold behavior and the linear normal energy scaling experimentally observed for the vibrational excitation probability strongly suggest a mechanism dominated by direct collision translational-to-vibrational ($T \rightarrow V$) energy transfer. This mechanism is further supported by the observed insensitivity of the vibrational excitation probability to the Au(111) surface temperature. Figure 2 displays an Arrhenius plot of the scattered NH_3 vibrational distribution for an incident normal kinetic energy of 6.9 kcal/mol. Over the experimentally examined surface-temperature range of 300 K ≤ T_s ≤ 800 K, the dominant vibrational excitation mechanism is clearly not a thermally activated process. Furthermore, a similar insensitivity of the vibrational excitation probability to surface temperature is observed for all normal kinetic energies examined experimentally.

As mentioned above, direct vibrational excitation in a gas-surface encounter has been previously reported[20] in a study of the NO/Ag(111) system by Rettner *et al.* In that study the probability for excitation into the $v=1$ level of NO was observed to scale linearly with normal kinetic energy with no energy threshold and to exhibit a strong dependence upon surface temperature. Furthermore, the surface-temperature dependence of the vibrational excitation probability was roughly Arrhenius in nature, with an activation energy equal to the NO vibrational excitation energy (5.3 kcal/mol). Rettner *et al.*[20] suggest that an electronic mechanism is responsible for the observed vibrational excitation. Gadzuk[18] has proposed that vibrational excitation may occur in gas-surface collisions as a result of temporary negative-molecular-ion formation with attendant electron-hole pair relaxation. Temporary negative-ion formation due to shape resonances is known to play an important role in vibrational excitation during gas-phase electron-molecule scattering.[27] Recent calculations by Newns[19] considering negative-ion formation and electron-hole-pair deexcitation on the NO/Ag(111) system semiquantitatively predict the experimental findings of Rettner *et al.*[20]

The lack of a surface-temperature dependence and the nonzero-energy excitation thresholds observed experimentally lead us to suggest that vibrational excitation in the NH_3/Au(111) system occurs predominantly via electronically adiabatic "mechanical" collisions between the NH_3 oscillator and the surface. To test the plausibility of this suggestion, we have performed classical trajectory calculations for the scattering of a 1D vibrator, 3D rotor model of the NH_3 molecule scattered from a structureless, rigid gold surface. In these model calculations, the three hydrogen atoms are constrained to be fixed at the corners of a rigid equilateral triangle. The ν_2 NH_3 "umbrella" motion is modeled via the motion of the nitrogen atom perpendicular to the plane of the hydrogen atoms along the molecular symmetry axis. The double-well potential of Manning[28] is used to describe the NH_3 umbrella motion. The classical trajectory calculations quantitatively predict the nonzero-energy threshold and semiquantitatively predict the magnitude of the vibrational energy transfer observed experimentally. This agreement strongly supports the proposed electronically adiabatic, mechanical vibrational excitation mechanism. The details of these classical trajectory calculations will be published elsewhere.[29]

In the classical trajectory calculations the longest-range part of the gas-surface interaction potential is the dipole–image-dipole term. This potential causes the molecule to reorient as it approaches the surface. This reorientation preferentially aligns the molecule with its symmetry axis perpendicular to the surface plane. Of the molecules striking the surface oriented along the surface normal, the calculations show that collisions in which the three hydrogen atoms are directed toward the surface give rise to facile vibrational energy transfer, while collisions in which the nitrogen atom is directed toward the surface are nearly vibrationally elastic. This finding is in agreement with a simple "light-heavy" impulsive collision model in which vibrational energy transfer is very efficient for impacts on the light end of the molecule directed along the molecular symmetry axis. Thus, the long-range potential orients the molecule to a favorable orientation for vibrational excitation. The excitation occurs during the nearly impulsive collision of the favorably oriented molecule against the short-range repulsive potential.

The NH_3/Au(111) system is fundamentally different from the NO/Ag(111) system. For the NO/Ag system there is very little preferential orientation from the long-range dipole–image-dipole potential because of the small dipole moment in NO. In addition, the nearly equal masses of the two atoms in NO reduces the impulsive vibrational-energy transfer probability for simple kinematic reasons. Furthermore, the energy of the NO vibration is over a factor of 2 greater than the energy of the umbrella mode in NH_3. For the reasons listed above, the "mechanical" excitation mechanism is much less important for the NO/Ag(111) system than for NH_3/Au(111).

From a variety of evidence outlined above, we conclude that NH_3 undergoes direct vibrational inelastic scattering from Au(111) for our experimental conditions. The results for this study have revealed an interesting dynamical finding heretofore unobserved, namely, the observation of direct multiquantum vibrational excitation dominated by an electronically adiabatic, "mechanical" collision excitation mechanism.

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