

Isotope and Quantum Effects in Vibrational State Distributions of Photodesorbed Ammonia

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A marked quantum effect has been observed in the vibrational state distribution of photodesorbed ammonia. Namely, for quantum numbers larger than zero, symmetric and antisymmetric levels in the ν_2 mode of the desorbed ammonia molecule are unequally populated. A strong propensity for symmetric levels is observed for NH_3 , whereas the reverse is found for ND_3 . Model calculations reproduce this effect. Moreover, it is found that the actual ratios probe the binding energy in the energetically less favorable inverted geometry with the H atoms pointing towards the surface. [S0031-9007(97)02386-7]

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Photostimulated desorption processes have attracted considerable interest in recent years due to their fundamental importance and their ability to provide complementary insights into molecule-surface interaction dynamics [1,2]. State resolved detection of desorbed molecules and isotopic substitution of adsorbates are powerful tools in unraveling the details of the microscopic events leading eventually to photodesorption [3–8]. The photodesorption of ammonia has been proven to be a system rich in detail, since the desorption dynamics follows a path which is multidimensional in canonical coordinates [9–11]. Ammonia is believed to adsorb in atop sites with the N atom bound to the surface and an only slightly perturbed pyramidal internal geometry [12]. An excitation to an electronically excited state of approximate planar geometry leads to rapid acceleration of motion in the out-of-plane bending (ν_2 -) mode when the molecule attempts to adopt the planar structure. After returning to the electronic ground state, which is expected to happen within less than a vibrational period, this motion is continued. This motion *directly* couples to the molecule-surface coordinate, since the H atoms are now approaching a highly repulsive region, thereby causing desorption of the entire molecule. Recently this system has been the subject of a number of theoretical attempts to model the desorption dynamics employing quasiclassical [13,14] and time-dependent quantum-mechanical methods [14–16].

In this Letter we report detailed vibrational state distributions of photodesorbed NH_3 and ND_3 from Cu(111). Some results for NH_3 have recently been published [11]. For the first time, we observe a marked isotope-dependent disparity of the population in the symmetry states in the ν_2 mode. Modeling shows that this feature probes the binding energy of the molecule in its inverted geometry which is not accessible by conventional spectroscopy.

The experiments have been carried out using a conventional molecular beam apparatus [17]. Most experimental

details have been discussed in a recent publication [11]. A pulsed excimer laser (193 nm, 17 ns) is used to illuminate an area of 6×8 mm (pulse fluence < 8 mJ/cm²) on the Cu surface. Ammonia is dosed between desorption laser pulses using a pulsed nozzle. The apparatus allows a dye laser beam to be aligned close (2.5 mm) to the sample [11]. $2 + 1$ photon resonance enhanced multiphoton ionization (REMPI) via the \tilde{B}_1E'' state of ammonia is used to detect photodesorbed ammonia molecules in a state specific manner [18]. Spectra were recorded with the delay between the desorption and the dye laser set such that predominantly molecules in the maximum of the time-of-flight distribution, 1000 and 850 m/s for NH_3 and ND_3 , respectively, we detected. Deuterated ammonia was obtained from Cambridge Isotope Laboratories with a specified purity of 99%.

Because of lateral interactions, ammonia forms a number of adsorbate states, which have been labeled α , β_1 , and β_2 [13]. In this Letter we will solely present results for the medium coverage β_1 state; this is not critical since no significant variation of the vibrational state distribution has been observed as a function of coverage. The sample was held at an elevated temperature at the onset of thermal desorption of the β_1 feature in order to achieve a near constant coverage resulting from equilibration between thermal and laser stimulated desorption and pulsed redosing between laser shots.

At the specified desorption laser fluences, about 10^{-3} ML were found to desorb per laser shot. In common with the original observation on GaAs(100), a marked isotope effect in the desorption cross section is found, with ratios ($\sigma_{\text{NH}_3}/\sigma_{\text{ND}_3}$) varying between 4.1 for low coverages and 1.9 for saturation coverage for $\text{NH}_3/\text{Cu}(111)$ [13]. Nonstate resolved time-of-flight measurements showed that NH_3 and ND_3 desorb with mean translational energies, $\langle E_{\text{trans}} \rangle$, of 102 ± 7 and 93 ± 9 meV, respectively. State-resolved time-of-flight measurements have confirmed these values and have shown

no evidence for a systematic dependence of the mean translational energy on the quantum state probed [19].

Quantum state-resolved measurements showed that NH_3 desorbs with a rotational temperature, T_{rot} , differing by not more than 20 K from the sample temperature [11]. Only for the very low coverage regime (α) does the rotational temperature exceed the value expected for accommodation with the sample temperature by 100 K. No evidence for deviations from Boltzmann statistics could be found. Hence, it can safely be concluded that the rotational degrees of freedom are not relevant in the desorption process, although this statement may need to be relaxed for the low coverage regime. The same data set showed that NH_3 desorbs with a vibrational temperature, T_{vib} , of about 820 K for the ν_2 mode (Fig. 1).

These findings corroborate a two-dimensional model put forward by Burns *et al.* [10] and Hertel *et al.* [13]. Accordingly, a ground state wave function is Franck-Condon transferred to an electronically excited state V_e , where it survives for an ultrashort lifetime τ . After return to the ground state V_g , the wave packet may split into a recaptured and a desorbing part (Fig. 2).

New data for ND_3 show that this molecule desorbs with a rotational temperature identical to that observed for NH_3 . However, the average energy in the ν_2 vibration is found to be significantly smaller at about 500 K.

In this Letter we focus on a finer detail of the vibrational state distributions than the more global mean energy in this degree of freedom. Namely, we have found a marked nonequal population of the states of different symmetry in the ν_2 manifold: For NH_3 the symmetric

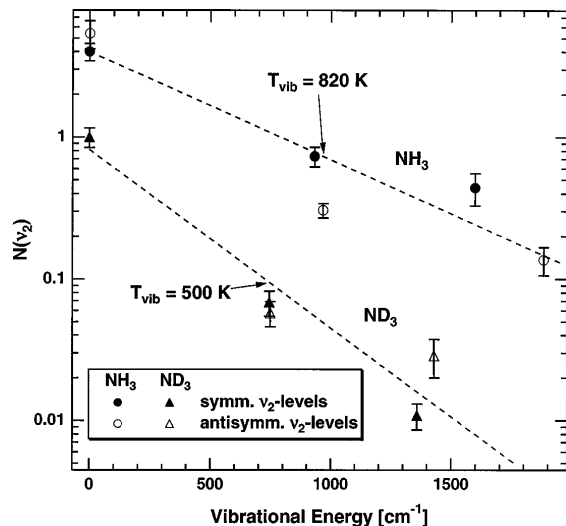


FIG. 1. Boltzmann graph for the population distribution in the symmetric and antisymmetric levels of the ν_2 mode for NH_3 (\circ , \bullet) and ND_3 (\triangle , \blacktriangle). The data have been obtained at a sample temperature of $T_s = 170$ K. The dashed lines indicate Boltzmann distributions with $T_{\nu_2} = 820$ and 500 K for NH_3 and ND_3 , respectively. Symmetric levels are marked by closed symbols, antisymmetric levels by open symbols.

levels for $\nu_2 > 0$ are more strongly populated than the antisymmetric ones.

We define the parity as

$$P(\nu_2) = \frac{N(\nu_2^+) - N(\nu_2^-)}{N(\nu_2^+) + N(\nu_2^-)}, \quad (1)$$

where $N(\nu_2^\pm)$ are the populations of the symmetric (+) and antisymmetric (-) levels for quantum number ν_2 . Using this definition we find that, for NH_3 , parities are -0.14 ± 0.14 , 0.41 ± 0.16 , and 0.53 ± 0.31 for $\nu_2 = 0, 1$, and 2, respectively.

The data for ND_3 show reversed parities, namely, 0.08 ± 0.15 and -0.45 ± 0.12 for $\nu_2 = 1$ and 2, respectively. For $\nu_2 = 0$ the value could not be measured, but we assume that it will be 0, as for NH_3 and as predicted by theory (see below).

Time-dependent two-mode two-state wave packet calculations have been carried out. Accordingly, we obtain numerically the nuclear wave function $\chi(x, z; t)$ for a Franck-Condon excited particle surviving in the excited

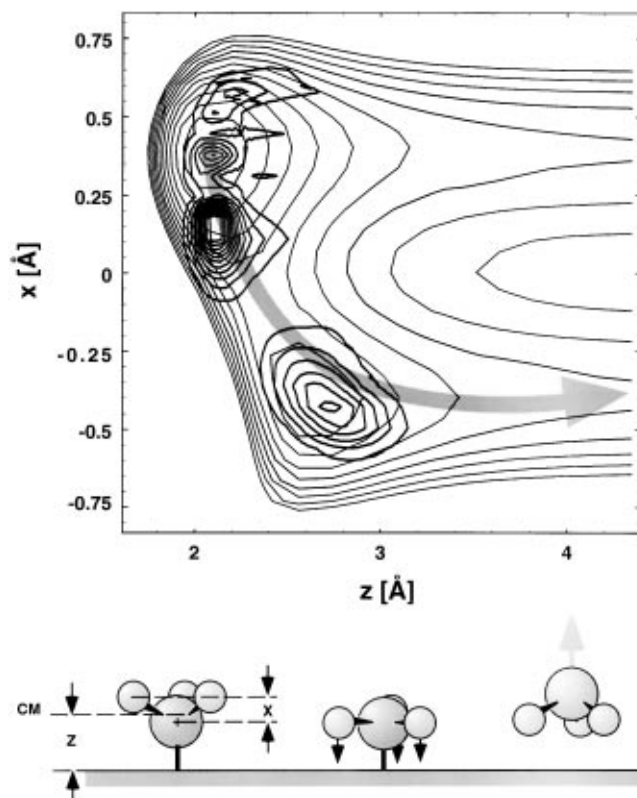


FIG. 2. Contour plot of the ground state potential energy surface used. z denotes the molecule-surface distance, x is the intramolecular ν_2 coordinate. Contour lines are drawn each 100 meV. A snapshot of the wave packet after 50 fs is depicted (after a residence time τ_R of 7.5 fs). Clearly, two parts can be distinguished, one being recaptured but vibrationally excited, the other approaching the exit channel towards desorption. The cartoon at the bottom sketches the classical motion of the molecule.

state for some residence time τ_R as

$$\chi(x, z; t; \tau_R) = e^{-i\hat{H}_g(t-\tau_R)/\hbar} e^{-i\hat{H}_e(t-\tau_R)/\hbar} \chi(x, z; 0). \quad (2)$$

Here, $\chi(x, z; 0)$ is the initial wave function in the x (inversion mode) and z coordinate, and \hat{H}_e and \hat{H}_g are the excited and ground state Hamiltonians, respectively. Expectation values for any observable \hat{A} are then obtained by running several quantum trajectories [Eq. (2)] and incoherently averaging according to [4]

$$\langle \hat{A} \rangle = \frac{\int_0^\infty d\tau_R e^{-\tau_R/\tau} \langle \chi(t; \tau_R) | \hat{A} \chi(t; \tau_R) \rangle}{\int_0^\infty d\tau_R e^{-\tau_R/\tau}}, \quad (3)$$

where τ is the electronic lifetime of the system.

As shown in [20], this procedure corresponds rigorously to the solution of an open system Liouville–von Neumann equation, when the quenching rate is coordinate independent and hence the decay exponential in time. $\tau = 1.5$ fs was determined by adjusting the theoretical isotope effect in the total desorption yields to agree with the experiment, and Eq. (3) was evaluated sampling 100 τ_R points between 0.25 and 25 fs. Other computational parameters and further details can be taken from Ref. [14,15].

Calculations using the potential energy surface proposed by Hertel *et al.* [13] predicted parities for NH_3 of opposite sign to the experiment. Careful inspection of the model potential showed that the only feature which could be modified without influencing the predicted isotope effect and average translational and vibrational energy severely was the depth of the potential in the region where the molecule approaches the surface with the hydrogen atoms toward the surface. All other aspects were either fixed by the experimentally observed vibrational frequencies of the adsorbed molecule and the asymptotic potential of the free molecule or led to results in conflict with the experiment. Systematic variation of the well depth in the inverted geometry showed that the calculated parities depend strongly on the choice made and even change sign. Using a binding energy of the potential in this region of 0.35 eV, which is half the value experimentally determined for the upright geometry (at low coverage), the measured parities for NH_3 could be reproduced (Fig. 3). Moreover, the calculated average vibrational energy, 132 vs 89 meV experimentally, and average translational energy, 122 vs 102 meV, are in broad agreement.

Applying the same model to ND_3 without varying any parameter gave desorbates vibrationally colder than NH_3 by a factor of 1.74 (experiment, 1.64). Moreover, the calculation predicts parities of 0.0, -0.05 , and -0.214 for $\nu_2 = 0, 1$, and 2, respectively, in close agreement with the experiment.

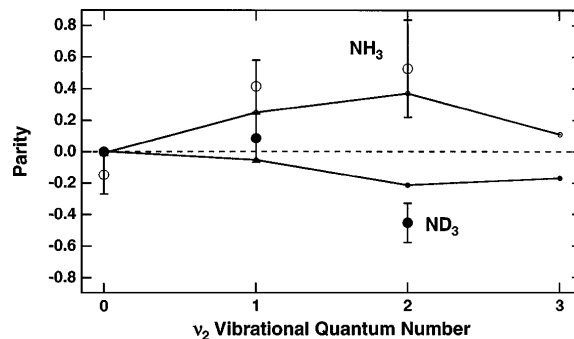


FIG. 3. Observed parity for individual levels in the ν_2 manifold (\circ : NH_3 , \bullet : ND_3). The lines represent the theoretical results.

In discussing these results, we first mention that it is not surprising that NH_3 and ND_3 show rotational state distributions of near identical temperature since the rotational degrees of freedom are accommodated to the sample temperature, indicating that no forces are acting in the desorption process which transfers energy into rotational degrees of freedom.

The lower average energy in the ν_2 vibration for ND_3 is expected, since, due to the higher reduced mass, energy transfer into this coordinate, which proceeds while the molecule is in the excited state, is less efficient. If the process is interpreted in *natural*, i.e., curvilinear, coordinates, which has been discussed as a semi-quantitative interpretation [11], the reduced vibrational temperature follows naturally from the different ratios of the molecular to the reduced internal mass for NH_3 and ND_3 .

The core of this Letter is the observed nonthermal population of the states of different symmetry and the isotope dependence of this effect. The first question arising is whether this effect arises from simple Frank-Condon arguments involving the initial and asymptotic wave functions or whether it is due to the dynamics. For this reason, calculations with the other isotopomer's initial wave function were carried out. The results for ND_3 , assuming the initial wave function from NH_3 , gave parities practically identical to the ones obtained for ND_3 with its proper initial wave function. Thus, the effect does not simply arise from the different initial wave functions or their overlap with the asymptotic ones.

Liu and Guo [21] have used the potential energy surface of Hertel *et al.* [13] to study NH_3 surface scattering. For a scenario where the NH_3 molecules were prepared in states of different symmetry, they found rather strong mixing of these states such that the scattering process totally scrambles the symmetry states. Since the photodesorption process is essentially a half-collision, this should also apply in our case.

Thinking in terms of time-independent scattering theory, each asymptotic eigenstate collects a certain phase

when scattered elastically. Since the symmetric and antisymmetric states have somewhat different asymptotic energies, they would adopt different phases. This phase difference governs the branching into the exit channels when these channels couple as described, e.g., in Landau-Zener theory. Calculating the parity for molecules of various fictional mass compositions we observed that, for NH_3 with a N atom mass of 17, the parities closely resemble the ones obtained for $^{14}\text{NH}_3$, while for a variation of the H atom mass between 1 and 2 (noninteger values), a smooth transition between the parities reported above is found. This finding clearly demonstrates that, indeed, a mass-dependent phase difference is responsible for the observed nonequal population of symmetry states.

This interpretation also explains our observation that, in the modeling, the parities obtained depend strongly on the assumed binding energy for the inverted molecule. In this region the molecular vibration and the translational motion are strongly coupled. The molecules transverse this region with different velocities depending on the depth of the potential minimum. Hence, the phase difference is varied.

The proposed large binding energy of NH_3 in the inverted geometry is in agreement with forthcoming potential energy calculations by Jennison and co-workers [22].

In summary, we have observed a marked quantum effect in the vibrational state distribution of a desorbed molecule which arises from the dynamics as the asymptotic wave functions are developed and adopt varying phases. These are strongly dependent on the potential in the region of the minimum for the inverted geometry. It is worth noting that in this sense these experiments enable us to probe the binding energy of ammonia in a configuration which is not stable enough to allow any conventional spectroscopy of it. This region is, in principle, also probed by molecular beam scattering, which has been performed by Kay *et al.* [23] for NH_3/Au . However, the information is much better isolated in a half-collision, photodesorption scenario due to the limited range of surface sites sampled.

We expect such effects for the large number of cases in which adsorption reduces the symmetry in a molecule. They should not be restricted to photodesorption but should also occur in the scattering of oriented beams, where orientation and final scattering angle result in the necessary reduction of sampled configuration space [24].

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