

Vibration-Mediated uv Photodesorption: Ammonia on GaAs

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A surprisingly large isotope effect is observed in nonthermal uv photodesorption of ammonia from GaAs(100). The cross section for NH₃ photodesorption is 4 times larger than for ND₃, a fact which cannot be explained using existing photodesorption models, e.g., the conventional Menzel-Gomer-Redhead model. We take this as the first evidence for uv-driven photodesorption from electronically quenched, vibrationally excited ground-state adsorbates.

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Fundamental questions regarding excited-state molecule-surface interactions, such as charge and energy transfer, can be investigated in pulsed-laser-induced desorption studies. uv-photon-driven desorption of adsorbates from metal and semiconductor surfaces is frequently described in terms of the Menzel-Gomer-Redhead (MGR) model [1] and its variations [2-4]. The MGR model, advanced originally to explain electron-stimulated desorption (ESD) from surfaces [1], employs an adiabatic approximation: An initial Franck-Condon transition is followed by nuclear motion on an excited potential-energy surface (PES). Efficient substrate-mediated relaxation (quenching) occurs on a metal or semiconductor surface and, in the MGR model, there is a critical adsorbate-substrate distance z_c on the excited-state PES. For $z < z_c$, quenching leads to the recapture of the ground-state adsorbate, whereas for $z > z_c$, quenching leads to desorption because the adsorbate has gained enough kinetic energy to overcome the ground-state barrier leading to desorption. The MGR model predicts an isotope effect because a lighter particle is accelerated in a shorter time on the excited PES and, thus, has a higher probability to desorb. Quantitatively, for two isotopically labeled species with masses m_1 and m_2 for the leaving particles, the isotope effect is given by [5,6]

$$\sigma_{m_1}/\sigma_{m_2} = (1/P_{m_1})^{(m_2/m_1)^{1/2}-1}, \quad (1)$$

where σ_{m_1} and σ_{m_2} are the desorption cross sections and P_{m_1} is the probability of photolysis. The latter is given by the ratio of σ_{m_1} to σ_{ex} , the excitation cross section. It is important to note that Eq. (1) is independent of the details of the PES, as well as the excitation and relaxation processes. It is given by Newton's law of motion, provided the potential-energy surfaces are the same for both isotopes. Strong isotope effects, consistent with the MGR model, have been observed in ESD [7] and in surface photon-driven processes [6]. Electronic states, and therefore σ_{ex} , can be taken as isotope independent in surface photochemical reactions [6].

In this Letter, we demonstrate that Eq. (1) fails to account for the surprisingly large isotope effect in the uv photodesorption of ammonia from GaAs(100) by $h\nu=6.4$ eV. We propose that desorption from vibrationally excit-

ed ground-state ammonia is important and, thus, that electronic-to-vibrational energy transfer is a central consideration in this system. This vibrational pumping mechanism is an alternative to the direct resonant intra-adsorbate vibrational excitation by ir photon absorption that has been found in ir-laser-induced desorption studies [8].

All experiments were conducted in a UHV chamber and involved temperature-programmed desorption (TPD), time-of-flight (TOF) mass spectroscopy, high-resolution electron energy-loss spectroscopy (HREELS), x-ray photoelectron spectroscopy (XPS), and low-energy electron diffraction (LEED). The GaAs(100) substrate ($15 \times 10 \times 1$ mm, $10^{15}/\text{cm}^3$ Si doped) was cleaned by standard procedures to yield a (4×6) LEED pattern, which corresponds to a Ga-rich surface [9]. Ammonia was dosed through a $2\text{-}\mu\text{m}$ pinhole doser onto the front face of the sample at 102 K. This surface temperature precludes the accumulation of multilayer ammonia. In the following, we define the saturation ammonia coverage at 102 K as 1 monolayer (ML). The light source was a pulsed (11 ns) ArF excimer laser (193 nm, $h\nu=6.4$ eV). A low pulse energy ($1 \text{ mJ}/\text{cm}^2$) was used to minimize transient surface heating. For postirradiation TPD measurements, the full front surface of the substrate was uniformly illuminated at normal incidence. In TOF measurements, only the center portion of the sample was irradiated with the laser light (diameter, 5 mm) 60° off the surface normal. The flight distance [sample to quadrupole mass spectrometer (QMS) ionizer] was 6 cm. The flight times were corrected for the QMS transit time (11 μs).

The right panel in Fig. 1 shows the TPD spectra for 1 ML ND₃ on GaAs(100) with and without irradiation of 6.4-eV photons at 102 K. With no irradiation, molecular ND₃ is the only desorption product and is characterized by a main desorption peak at 140 K and a broad peak between 200 and 400 K. The absence of other desorption products suggests that the adsorption of ammonia on GaAs(100) is reversible. Supporting this, XPS and HREELS showed no evidence of thermal dissociation [9].

With irradiation, a significant depletion of the ND₃ TPD area is evident, a result of mainly molecular photodesorption ($\geq 90\%$ of total photolysis). In addition to

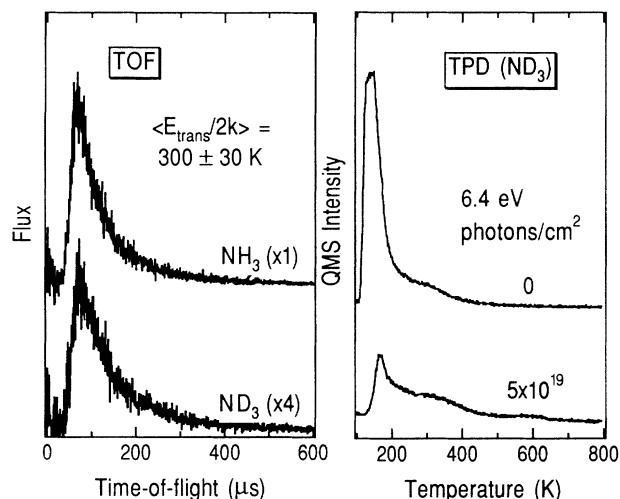


FIG. 1. Right panel: TPD spectra for ND_3 taken after a GaAs(100)-(4 \times 6) surface was dosed with saturation amounts of ND_3 at 102 K and irradiated with 0 and 5×10^{19} photons/cm 2 (6.4 eV), respectively. Left panel: Photon-driven time-of-flight (TOF) spectra of NH_3 and ND_3 ($\times 4$) averaged over a fluence of 1×10^{18} photons/cm 2 and saturated GaAs(100) surfaces at 102 K. The flux-weighted average translational energy for photodesorbing NH_3 or ND_3 , derived from numerical integration of the data, is $\langle E_{trans}/2k \rangle = 300 \pm 30$ K.

ND_3 desorption, there is a small amount of D_2 ($\sim 1\%$ of the intensity of ND_3) desorbed at 550 K. This D_2 arises from the thermal decomposition of ND produced by the photodissociation of ND_3 [9]. Quantitative XPS analysis confirms that photodissociation accounts for $\leq 10\%$ of the loss of molecular ND_3 . The TPD spectra for NH_3 are identical to those for ND_3 and, again, photodissociation accounts for $\leq 10\%$ of the photolysis [9].

Time-of-flight distributions of photodesorbing ammonia are shown in the left panel of Fig. 1. Desorption was initiated by a 6.4-eV laser pulse (1 mJ/cm 2 , 11 ns) and was monitored as a function of time with the QMS. For either a NH_3 - or ND_3 -covered surface, the signal was averaged over enough pulses to give a total photon fluence of 1×10^{18} /cm 2 . The flux-weighted average translational energy, derived from numerical integration of the data, is independent of the isotopic composition: $\langle E_{trans} \rangle = 52 \pm 5$ meV, or $\langle E_{trans}/2k \rangle = 300 \pm 30$ K. While this temperature is higher than the substrate temperature (100 K), consistent with a nonthermal desorption process, stronger evidence for the nonthermal character is provided by (1) the linear relation between the TOF intensity and the laser-pulse energy (0.5 to 11 mJ/cm 2) and (2) the independence of the mean translational energy on laser-pulse energy.

While the *translational energy* of photodesorbing ammonia is, within experimental error, independent of isotope substitution, the *intensity* of photodesorbing NH_3 is more than 4 times that for ND_3 , indicating a very strong

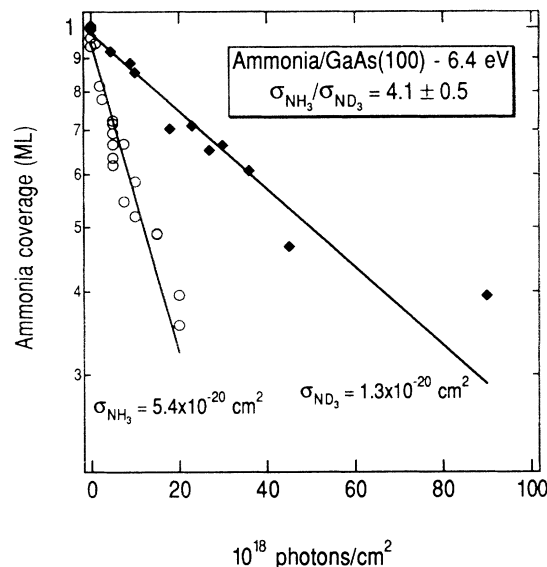


FIG. 2. Postirradiation TPD areas for NH_3 (open circles) and ND_3 (solid diamonds) as a function of photon fluence at 6.4 eV. Least-squares linear fits to the data result in photodesorption cross sections of 5.4×10^{-20} and 1.3×10^{-20} cm 2 for NH_3 and ND_3 , respectively. This gives an isotope effect, $\sigma_{\text{NH}_3}/\sigma_{\text{ND}_3}$, of 4.1 ± 0.5 .

isotope effect in the photodesorption cross section (note the scaling factor in Fig. 1). To confirm this, and to measure the cross sections quantitatively, we have plotted (Fig. 2) the molecular ammonia coverage, obtained from postirradiation TPD areas, as a function of photon fluence for both NH_3 and ND_3 . The photodissociation channel makes a negligible contribution; thus, the slopes measure the photodesorption cross sections. Least-squares linear fits to the data yield, for ammonia photodesorption from GaAs(100) at 6.4 eV, $\sigma_{\text{NH}_3} = 5.4 \times 10^{-20}$ cm 2 and $\sigma_{\text{ND}_3} = 1.3 \times 10^{-20}$ cm 2 , i.e., $\sigma_{\text{NH}_3}/\sigma_{\text{ND}_3} = 4.1 \pm 0.5$, in agreement with the TOF results presented in Fig. 1. We have also measured the isotope effect for coadsorbed NH_3 and ND_3 on GaAs(100) at 100 K and again obtained a ratio of ~ 4 for $\sigma_{\text{NH}_3}/\sigma_{\text{ND}_3}$.

We now demonstrate the inadequacy of the conventional interpretation of the MGR model. For ammonia photodesorption, the responsible potential-energy surfaces are those describing the substrate- NH_3 (- ND_3) interaction. Using Eq. (1) with a mass ratio for the leaving group of $m_{\text{NH}_3}/m_{\text{ND}_3} = 1.176$ and the measured isotope effect, $\sigma_{\text{NH}_3}/\sigma_{\text{ND}_3} = 4.1 \pm 0.5$, gives $P_{\text{NH}_3} = 5.5 \times 10^{-8}$. This results in a photoexcitation cross section, $\sigma_{ex} = \sigma_{\text{NH}_3}/P_{\text{NH}_3}$, of $\sim 1 \times 10^{-12}$ cm 2 or 10^4 Å 2 , which is not physically sensible. Since isotope substitution has a much larger effect on the N-H coordinate than the surface- NH_3 coordinate, we now examine how N-H excitation, i.e., vibrational excitation, might lead to desorption.

The proposed variation of the MGR model, shown

schematically in Fig. 3, involves uv photon excitation, either directly or through the substrate, to give an electronically excited molecule, assumed to be antibonding with respect to N-H (this naturally accounts for some photodissociation, as observed). Consistent with the MGR picture, most of the excited ammonia is quenched to give vibrationally excited NH_3 on the ground-state PES. This vibrational energy in the N-H coordinate (x) is coupled, perhaps through the umbrella mode, to the N-surface coordinate (z) and, if sufficient energy transfers, desorption follows. As a result of the mass difference in the stretching of N-H (-D), the vibrational energy distribution for quenched NH_3 is significantly hotter than that for ND_3 and leads to a large isotope effect in the photodesorption cross section. The vibrational energy-transfer process has already been demonstrated in ir-laser-induced desorption of NH_3 from metal and dielectric surfaces, where resonant excitation of the ν_s stretching mode of adsorbed NH_3 leads to molecular desorption [8(d)].

We introduce two critical distances in the stretch of N-H, x_c and x'_c . For deexcitation occurring at $x > x_c$, the kinetic energy E_k (in this case of the H atom) is greater than the barrier for dissociation, E_r , and the coordinate x is not bound. The reverse holds for $x < x_c$. We assume a *second* critical distance, x'_c : Deexcitation at

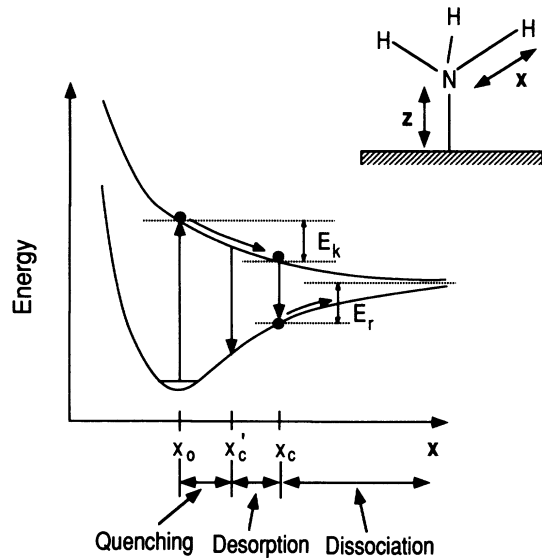


FIG. 3. Schematic energy diagram of the proposed model for vibration-mediated photodesorption. x corresponds to the N-H distance in NH_3 and z corresponds to the surface- NH_3 distance. The ground-state minimum is taken as the reference point x_0 . Photon-driven excitation moves the system to the excited PES, assumed to be repulsive with respect to the N-H bond, but can be of any shape. If deexcitation occurs at $x > x_c$, the H atom has gained enough kinetic energy to overcome the recapture barrier and lead to dissociation, with a escape probability of P_e . For $x'_c < x < x_c$, the N-H vibrational energy in the "recaptured" NH_3 is sufficient to overcome the thermal desorption barrier, provided it transfers to the z .

$x > x'_c$ results in a ground-state NH_3 adsorbate with sufficient *intramolecular* vibrational content to undergo the aforementioned vibrational energy transfer, and desorb. With a quenching rate of $R(x)$, which scales with the inverse of the excited-state lifetime $\tau(x)$, the probability of survival on the excited PES at x is given by [5]

$$P_e(x) = \exp \left[- \int_{x_0}^x \frac{R(x) dx}{v} \right], \quad (2)$$

where v is the velocity along the excited PES. Expressing v as a classical velocity, we have

$$P_e(x) = \exp \left\{ - \left[\frac{m}{2} \right]^{1/2} \int_{x_0}^x \frac{R(x) dx}{[V(x_0) - V(x)]^{1/2}} \right\}, \quad (3)$$

with $V(x)$ representing the excited-state potential and m the mass of the leaving particle. The integrand, depending on the form of the potential $V(x)$ and the recapture rate $R(x)$, is canceled out to give the isotope effect in dissociation, Eq. (1).

The probability of desorption P_d is equal to the fractional population that is formed by quenching within the range $x'_c \leq x \leq x_c$,

$$P_d = P_e(x'_c) - P_e(x_c). \quad (4)$$

Since the dissociation probability $P_e(x_c)$ is only $\leq 10\%$ of the desorption probability P_d , the second term in Eq. (4) can be neglected and the desorption probability (P_d) is given by $P_e(x'_c)$. Therefore, a modified form of Eq. (1) can be derived to give the isotope effect in ammonia photodesorption:

$$\sigma_{\text{NH}_3} / \sigma_{\text{ND}_3} = [1/P_d(\text{NH}_3)]^{(m_D/m_H)^{1/2} - 1}. \quad (5)$$

It is important to note that the masses entering Eq. (5) are not those for the leaving group, but the reduced masses in the N-H and N-D stretching coordinate which can be approximated by those of H and D atoms. This can be intuitively understood because the energy leading to NH_3 desorption is fed in through the N-H coordinate. From the measured isotope effect of $\sigma_{\text{NH}_3} / \sigma_{\text{ND}_3} = 4.1$, and the mass ratio of $m_D / m_H = 2$, we obtained a photodesorption probability of $P_d = 0.033$ for NH_3 . Therefore, the excitation cross section is $\sigma_{\text{ex}} = \sigma_{\text{NH}_3} / P_d = 1.6 \times 10^{-18} \text{ cm}^2$.

Clearly, while the above model can successfully explain the large isotope effect observed for NH_3 photodesorption from GaAs(100), it is oversimplified; a more rigorous treatment of this vibration-mediated model would require a detailed dynamical understanding of the electronic excitation and quenching processes, as well as the vibrational energy transfer, including resonant and nonresonant processes [8], which are not examined by our experiments. This transfer involves the modes of the adsorbed ammonia, the adsorbate-substrate bond, and the surface phonons. Although there has been significant progress in

the theoretical description of desorption induced by vibrational energy transfer within adsorbate-substrate systems [8], successful theories describing electronic excitation and relaxation on surfaces remain to be developed [2,3]. Experimentally, state-resolved detection of photodesorbing ammonia will certainly aid in the understanding of this fascinating system.

To summarize, a model involving electronic-to-vibrational energy transfer in uv-driven photodesorption is presented to account for an exceptionally large isotope effect observed in the photodesorption of ammonia from GaAs(100). The role of the electronically quenched but vibrationally "hot" ground-state adsorbate is evidenced for the first time for desorption induced by electronic excitation.

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