

Time-Resolved Mass-Spectrometric Study on Infrared Laser Photodesorption of Ammonia from Cu(100)

T. J. Chuang and Ingo Hussla

IBM Research Laboratory, San Jose, California 95193

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Pulsed-infrared-laser time-of-flight mass spectrometry has been applied to investigate photodesorption of NH_3 adsorbed on a Cu(100) surface at 90 K. Desorption from monolayer and multilayer surface coverages due to resonant ν_s stretching vibrational excitation has been observed. Both single-photon and multiphoton excitation processes are examined and the molecule-surface interaction dynamics associated with the desorption phenomenon is discussed.

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Photon-stimulated desorption is an important photochemical process in adsorbed phases, in particular when competing surface processes such as the reaction of adsorbates and surface migration happen on the same time scale. It is by now quite well established that desorption from dielectric and metal surfaces can be induced by resonant vibrational excitation of adsorbed molecules with infrared laser radiation.¹ By measuring the dependence of the desorption yield as a function of laser frequency, it has been shown that CH_3F molecules can be photodesorbed from NaCl surfaces by excitation of the stretching molecular vibration in the 10- μm region.² Likewise, resonantly excited desorption of pyridine from KCl³ and Ag^{4,5} surfaces due to molecular ring-mode vibrational activation has been reported. So far, the phenomenon of infrared (IR) laser photodesorption has been investigated exclusively with rather high-power CO_2 lasers.¹⁻⁵ The photon energy of the laser in the 9-11- μm region is quite small, i.e., about 12 kJ/mole per photon. For all systems that have been studied, it requires the absorption of multiple CO_2 laser photons to provide sufficient energy to promote the breaking of molecule-surface bonds. Multiphoton excitations substantially complicate the rate analyses and render the desorption kinetics rather difficult to understand. The high laser intensity requirements may also induce undesirable effects. Furthermore, there exist very few studies concerning the molecular dynamics involved in the desorption process. Questions such as surface accommodation in translational and internal modes of motion need to be answered. Although there are some theoretical studies of the IR photodesorption process,⁶⁻⁹ experimental investigation on the dynamic behavior is still lacking. In this Letter, we report the first time-resolved study of the photodesorption phenomenon for a relatively simple molecule adsorbed on a clean single-crystal metal

surface. Both single-photon and multiphoton excitation processes are examined. Specifically, we have used a tunable pulsed IR laser in the 2-4- μm region to excite NH_3 adsorbed on a Cu(100) surface. Time-of-flight (TOF) mass spectrometry is used to determine the velocity distribution of desorbed particles which reveals new and interesting characteristics of the desorption phenomenon.

The experimental apparatus consists of a UHV chamber equipped with an ESCA/Auger spectrometer, an ion gun, a quadrupole mass spectrometer, and an rf induction heater as described previously.⁵ A Q-switched Nd-doped yttrium aluminum garnet laser (Quante-Ray) is frequency doubled to pump a dye laser containing an Exciton LDS 7650 dye. The tunable IR pulses are generated from the frequency difference between the 1.064- μm radiation and the dye laser in a LiNbO_3 crystal. The polarized IR beam at 10 Hz (6-nsec pulse width) is focused and incident at 75° from the surface normal covering a surface area of about 5 mm². The laser beam enters and leaves the UHV chamber through sapphire windows. The mass spectrometer is placed in a line-of-sight arrangement along the surface normal and the ionizer is located about 45 mm from the sample. The TOF mass signal amplified with a fast preamplifier (3.3- μsec rise time)¹⁰ is recorded with a Tracor signal averager with 2- μsec time resolution which is triggered by the laser synchronization pulse. The Cu(100) crystal (10 mm diam \times 1 mm thick) is held with a manipulator and can be cleaned by Ar^+ bombardment, annealed by rf heater, and cooled to about 90 K with liquid N_2 . Gaseous NH_3 is dosed through a small copper tubing directly facing the crystal. The amount of surface coverage is determined from electron spectroscopy for chemical analysis intensity analyses and from the conventional thermal desorption spectra.

The adsorption behavior of NH_3 on Cu(100) at 90 K has been studied in detail by thermal desorp-

tion and x-ray photoemission spectroscopy.¹¹ We have observed from thermal-desorption spectra the presence of three different adsorbed states with desorption temperatures of about 143, 194, and 246 K, respectively. The two major chemisorbed states at submonolayer coverages have the estimated heats of adsorption of about 64 and 46 kJ/mole. The corresponding value for the physisorbed species present at a coverage greater than a monolayer is about 34 kJ/mole. At very high NH₃ exposures, solid NH₃ can be condensed on the metal showing a desorption peak around 109 K. The vibrational spectrum of ammonia adsorbed on Cu(110) has been investigated by Lackey, Surman, and King,¹² using electron energy-loss spectroscopy (EELS). It was shown that at low NH₃ coverages, the ν_s (N-H) stretching mode had vibrational frequencies at 3360 and 3430 cm⁻¹, which merged into a broad band centered around 3400 cm⁻¹ at more than 1 monolayer coverages. No evidence of dissociative adsorption on the Cu surface was observed. It was also suggested that the molecular adsorption involved the nitrogen lone-pair electrons interacting with the metal surface. Similar vibrational frequencies and configuration interactions were determined for NH₃ adsorbed on Ag surfaces.¹³

Our laser experiments involve the vibrational excitation of the ν_s stretching mode of adsorbed NH₃ molecules. As a first step, the IR laser is tuned to $\nu = 3340$ cm⁻¹. When the *p*-polarized light with intensity $I = 10$ mJ/cm² is incident at 75° onto the Cu(100) surface with about 1 monolayer of NH₃, molecular desorption is detected by the mass spectrometer. The *p*-polarized radiation is chosen because it is much more effective in promoting surface vibrational excitation and desorption than *s*-polarized light.⁴ The observed desorption yield (Y) per pulse strongly depends on the laser frequency (ν). As shown in Fig. 1(a), major desorption occurs in the laser frequency range between 3320 and 3370 cm⁻¹. The full width at half maximum of the laser absorption-desorption spectrum is about 33 cm⁻¹, much narrower than the vibrational spectrum of NH₃ adsorbed on Cu (110) obtained by EELS¹² which does not have the comparable high spectral resolution. When the laser is tuned off resonance from NH₃ vibrational bands, no desorption is detected for $I \leq 15$ mJ/cm². For the monolayer of adsorbate excited at 3340 cm⁻¹, the laser threshold for detecting the desorption is about 5 mJ/cm², i.e., about 0.85 MW/cm² or 7.5×10^{16} photons/cm². At this monolayer coverage ($\theta = 1$), the desorption yield increases nonlinearly with the laser intensity

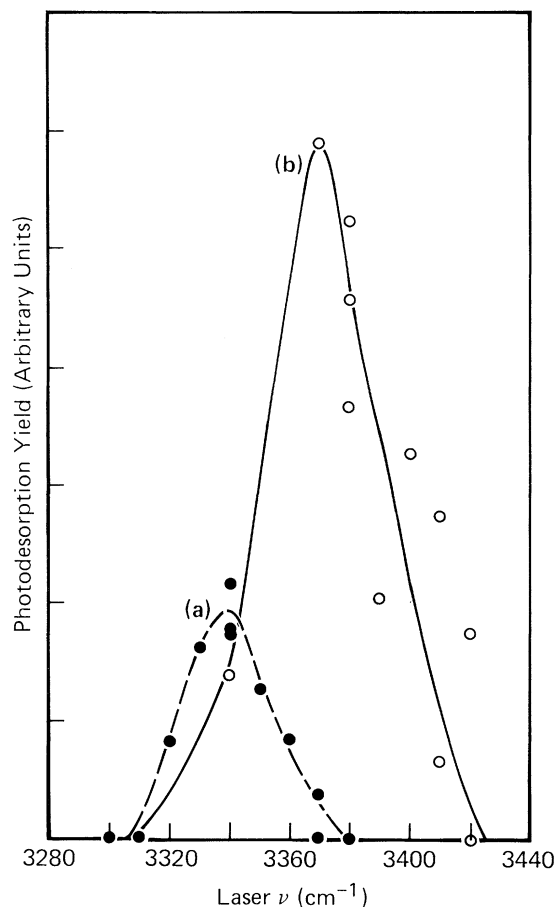


FIG. 1. IR photodesorption yields of NH₃ adsorbed on Cu(100) at 90 K as a function of laser frequency: (a) surface coverage about a monolayer, $\theta = 1$, and laser intensity $I = 10$ mJ/cm²; (b) multilayer coverage, $\theta = 3.4$, and $I = 4$ mJ/cm². The laser is *p* polarized and at 75° angle of incidence. Each datum point is an average of mass spectrometer signals due to 20 laser pulses.

[see Fig. 2(a)]. A plot of $\ln Y$ vs $\ln I$ yields a slope close to 2, indicating that two-photon absorption may be involved in inducing the desorption of chemisorbed species. In great contrast to the chemisorbed states, resonantly excited desorption is readily detected at a rather low laser intensity for the physisorbed species at $\theta > 1$. Figure 1(b) shows the photodesorption spectrum of multilayer NH₃ ($\theta = 3.4$) adsorbed on Cu(100) excited at $I = 4$ mJ/cm². The peak of the spectrum clearly shifts to a higher laser frequency ($\nu = 3370$ cm⁻¹) and the band is substantially broadened (full width at half maximum = 47 cm⁻¹). There is a significantly lower laser threshold for desorbing the multilayer adsorbate. Figure 2(b) shows the desorption yields as a function of laser intensity at $\nu = 3370$ cm⁻¹. The essentially linear dependence suggests that

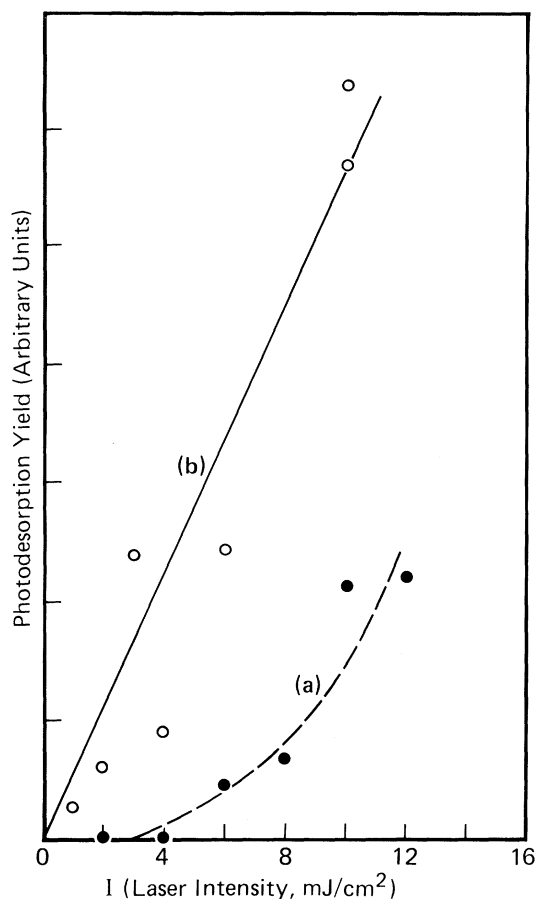


FIG. 2. Photodesorption yields of $\text{NH}_3/\text{Cu}(100)$ at 90 K as a function of laser intensity: (a) $\theta = 1$, $\nu = 3340 \text{ cm}^{-1}$, and (b) $\theta = 3.4$, $\nu = 3370 \text{ cm}^{-1}$, sampling average of 20 laser pulses.

single-photon excitation is involved in promoting the desorption. It is further observed that when the laser intensity is raised to $I > 20 \text{ mJ/cm}^2$, laser-induced thermal desorption due to direct substrate heating can overtake the resonant photodesorption effect for the multilayer adsorbate. This is because the physisorbed species is much more weakly bound than the chemisorbed species and an increase of the surface temperature of $\Delta T_s = 35 \text{ K}$ above 90 K due to substrate absorption of laser energy can readily desorb the physisorbed molecules thermally.

Figure 3(a) shows the NH_3 photodesorption signal as a function of time following a laser pulse at the surface coverage of about a monolayer. The laser excites the adsorbate at $\nu = 3340 \text{ cm}^{-1}$ and $I = 10 \text{ mJ/cm}^2$. From time-resolved mass-spectrometer signals, the translational temperatures of desorbing molecules can be calculated. A detailed description of the theoretical treatment, assuming

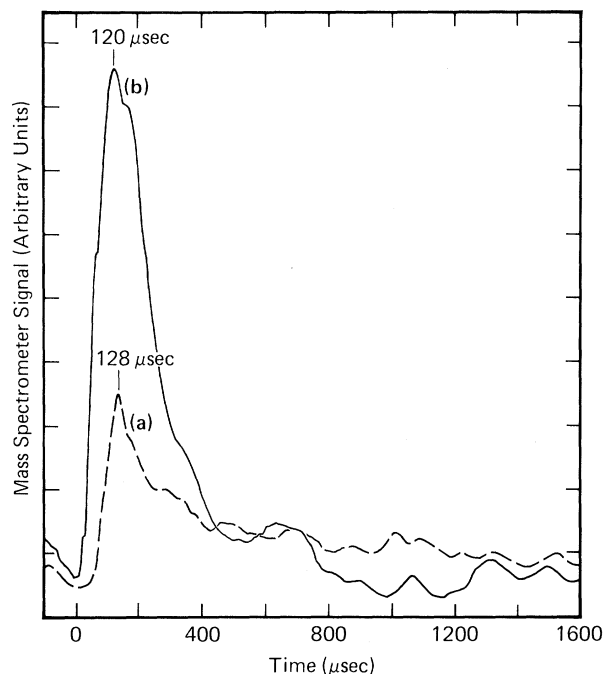


FIG. 3. Time-of-flight mass spectrometer signals of NH_3 photodesorbed from $\text{Cu}(100)$ at 90 K: (a) $\theta = 1$, $\nu = 3340 \text{ cm}^{-1}$, and $I = 10 \text{ mJ/cm}^2$; (b) $\theta = 3.4$, $\nu = 3370 \text{ cm}^{-1}$, and $I = 10 \text{ mJ/cm}^2$, sampling average of 20 laser pulses.

that the desorbed molecules leave the surface with a Maxwell-Boltzmann distribution, has been recently given by Wedler and Ruhmann.¹⁴ Following this approach, the translational temperature of the desorbing particles (T_d) can be calculated from the maximum of the TOF signal (t_m). From the observed t_m at $128 \mu\text{sec}$ as shown in Fig. 3(a) and with the correction of the drift time in the mass spectrometer, T_d for the photodesorbed NH_3 is estimated to be about $80 \pm 25 \text{ K}$. The large temperature spread is due to the finite length of the ionizer in comparison with the relatively short TOF distance. The maximum rise in the surface temperature due to laser heating of the substrate, which is highly reflective in the IR, is estimated to be about $\Delta T_s \leq 10 \text{ K}$ at the laser intensity of 1.7 MW/cm^2 . The observed translational temperature of the photodesorbed molecules apparently is about the same as or slightly below the substrate temperature (T_s). Since the ground-state molecules do not desorb at 90 K, the TOF results indicate that the desorbing species is likely to be in internally excited states during the photoexcited desorption process. Vibrational excitation has caused the molecular sticking probability to decrease and the desorbing translational temperature seems to be quite accommo-

dated to the temperature of the underlying substrate. Figure 3(b) shows the TOF signal for the multilayer adsorbate excited by laser pulses at $\nu = 3370 \text{ cm}^{-1}$ and $I = 10 \text{ mJ/cm}^2$. The desorption temperature calculated from $t_m = 120 \mu\text{sec}$ is about $90 \pm 25 \text{ K}$, also very close to T_s . From the line shapes of TOF spectra as shown in Fig. 3, it appears that the velocity distribution of the desorbed particles does not deviate far from the Maxwell-Boltzmann distribution.

From our experimental observations, it is clear that resonant vibrational excitation can promote molecular desorption from single-crystal metal surfaces at a coverage as low as a monolayer. The translational temperatures of the photodesorbed particles are close to or even slightly below the substrate temperature. This appears to be the case not only in resonantly excited photodesorption but also in laser-induced thermal desorption¹⁰ as well. An IR photon in the $3340\text{--}3370\text{-cm}^{-1}$ range has an energy of 40 kJ/mole per photon. By single-photon absorption, it would not be sufficient to induce the rupture of the chemisorption bond of 46 or 64 kJ/mole of bond energies. The observed photodesorption of the chemisorbed species is thus likely induced by the two-photon excitation as shown in the desorption yield dependence on the laser intensity. In contrast, the physisorbed species at multilayer coverages has a bond energy of about 34 kJ/mole . These more weakly bound molecules can apparently be more easily desorbed by the absorption of a single IR photon. Namely, if the bonding of the adsorbed phase is described with a Morse potential, the desorption continuum within this surface potential can be readily reached by transferring the absorbed photon energy in the ν_s stretching mode to these continuum states for desorption. The rate of this energy transfer from the molecular vibrational mode to the molecule-surface vibration resulting in the breakage of the surface bond should be quite high in comparison with the vibrational energy relaxation rate; otherwise desorption is not likely to be observed. This is consistent with the theoretical model considered by Kreuzer *et al.*⁷ In the model calculation, it was shown that phonon-mediated bound-state to bound-state transitions to channel the absorbed energy into the levels in the molecule-surface potential could play an important role in the photodesorption. In addition, the effects of "indirect substrate heating"^{1,5} or "resonant

heating,"⁸ involving transfer of the absorbed laser energy to the substrate atoms, on the desorption yields could be quite significant and the effects should be more thoroughly examined. For this purpose, we are doing further experiments on the photodesorption behavior for NH_3 and Xe coadsorbed on the metal surfaces. The results along with the photodesorption study of the isotope effects and molecular selectivity in the $\text{NH}_3\text{-ND}_3/\text{Cu}(100)$ system will be reported in detail later.

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