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Infrared laser-induced desorption of N₂O condensed on NaCl(100)

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Abstract

A study of infrared laser-induced desorption of N₂O condensed on NaCl(100) is presented. The comparison of the wavelength dependent desorption yield to the linear absorption spectrum shows that desorption of intact molecules occurs at the resonance frequencies of the symmetric stretching and the bending vibration of N₂O. The analysis of the time-of-flight spectra yields translational temperatures that are well above the substrate temperature and depend strongly on the applied laser fluence. In addition, the dependence of the desorption signal on layer thickness and substrate temperature is investigated. The results are discussed in the context of different desorption mechanisms, and it is concluded that a resonant heating process can best explain the experimental observations. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

The interaction of infrared radiation with an adsorbate-covered solid surface can lead to desorption of the adsorbed species if sufficient energy to overcome the desorption barrier is deposited in the adsorbate-surface bond. Several excitation and desorption scenarios are possible: (a) The laser energy can be transferred directly into the substrate, which leads to rapid heating and facilitates laser-induced thermal desorption of the adsorbate. This process is possible at all laser frequencies for

which the substrate possesses an appreciable absorption. (b) The laser light can be coupled into the adsorbate-substrate bond. The laser frequency has to match the eigenfrequency of one of the modes with which the molecule vibrates relative to the substrate and this process is therefore resonant in character. However, in most cases absorption of more than one photon will be required and owing to the anharmonicity of the adsorption potential and efficient energy loss processes to the substrate, desorption is expected to be difficult to induce. (c) Finally, the laser energy can be used to resonantly excite an internal vibrational mode of the adsorbed molecule. A molecule in the excited state can absorb other photons, and at some point the internal energy may become degenerate with a state in the desorption continuum, and desorption

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via direct coupling to the desorption coordinate can occur. Alternatively, the vibrationally excited molecule can relax to the ground state of the adsorbate-surface system under emission of phonons, thus heating the solid. This may finally result in a thermal desorption process and is here referred to as resonant heating.

The infrared laser-induced processes described above attracted experimental, see e.g. [1–8] as well as theoretical, see e.g. [9–14] interest in the past and are not reviewed here in detail. Most experiments used line-tunable CO₂ lasers and relied on accidental resonances of a molecular vibration with a laser line. Obviously, a widely tunable pulsed infrared laser would be beneficial in the investigation of infrared laser-induced desorption.

In this paper we will present results on the infrared laser-induced desorption of N₂O condensed on NaCl(100) using the free electron laser for infrared experiments (FELIX) as a continuously tunable source for infrared radiation over a wide wavelength range. The wavelength dependence of the desorption yield of N₂O in the frequency range of the symmetric stretching and the bending mode is investigated. Time-of-flight (TOF) distributions, as well as the dependencies of the desorption signal on surface coverage, laser fluence and substrate temperature are studied. The results are discussed in the context of the underlying desorption mechanism.

2. Experimental

The experiments reported herein are performed using a standard ultrahigh vacuum (UHV) apparatus operating at a base pressure $<3 \times 10^{-10}$ mbar. Single crystal NaCl(100) samples are prepared by cleavage under dry nitrogen atmosphere, mounted to the sample holder and immediately brought under vacuum. The sample can be cooled to temperatures as low as 25 K; between the measurements it is maintained at temperatures above 450 K in order to avoid contaminations. N₂O films are condensed on the NaCl(100) surface via background gas dosing under non-equilibrium conditions at low temperatures (30–40 K) and gas pressures in the range of 1×10^{-6} mbar.

Determination of the coverage is performed by means of linear absorption measurements using a FTIR spectrometer (Bruker IFS 66v) attached to the UHV chamber. Desorbing neutral species are detected normal to the surface plane using electron impact ionization (70 eV) for mass selective ion detection in a quadrupole mass spectrometer (Extrel Q50). The mass selected signal is recorded either with an analog current amplifier or by single ion counting as a function of time after the laser pulse.

The s-polarized laser light enters the UHV chamber through a KBr window, and irradiates the transparent NaCl sample under an angle of 45° relative to the surface normal. FELIX can provide continuously tunable light between 4.5 and 250 μm. The light output consists of macropulses of typically 5 μs time duration at a repetition rate of up to 10 Hz. Each macropulse contains a sequence of micropulses with an uniform spacing of 1 or 40 ns. In the experiments reported here the wavelength range between 7 and 17 μm is used at a micropulse spacing of 1 ns. The spectral width is transform limited and is kept below 0.5% (FWHM) of the central frequency. Macropulse energies can reach up to 100 mJ; the actual values in the measurement reported herein are measured directly in front of the KBr entrance window of the UHV chamber. The micropulse intensity as a function of time within a macropulse is critically dependent on the FEL tuning parameters [15]. In the experiments presented here the micropulse energy rises to its maximum value within 1 μs. At the end of the macropulse the cavity then decays with a decay time of 360 ns. The laser fluence is varied either by using fixed value attenuators or by changing the focussing conditions for the laser light onto the surface. In the latter case desorption yields are corrected for the changes in irradiated surface area.

3. Results and discussion

When FELIX irradiates the N₂O covered NaCl(100) surface, at some wavelength desorption of N₂O is observed. The desorbed molecules are recorded mass selectively using a quadrupole

mass spectrometer. In all cases the mass spectrum of the desorbed molecules is identical to the fragmentation pattern of gas phase N_2O , thus indicating desorption of intact N_2O molecules. Fig. 1 shows the desorption (upper trace) and the linear absorption spectrum (lower trace) of a 600 monolayers (ML) thick N_2O film condensed on $NaCl(100)$ at 38 K. The comparison of both spectra clearly shows that desorption is induced after excitation of the symmetric stretching (ν_1) or bending (ν_2) vibration of N_2O at 1293 and 589 cm^{-1} , respectively. Between the peaks no signal is found, independent of the laser fluence. In the linear absorption spectrum both resonances are observed to consist of two components. Such behavior is reported for other systems like $CO/NaCl(100)$ as

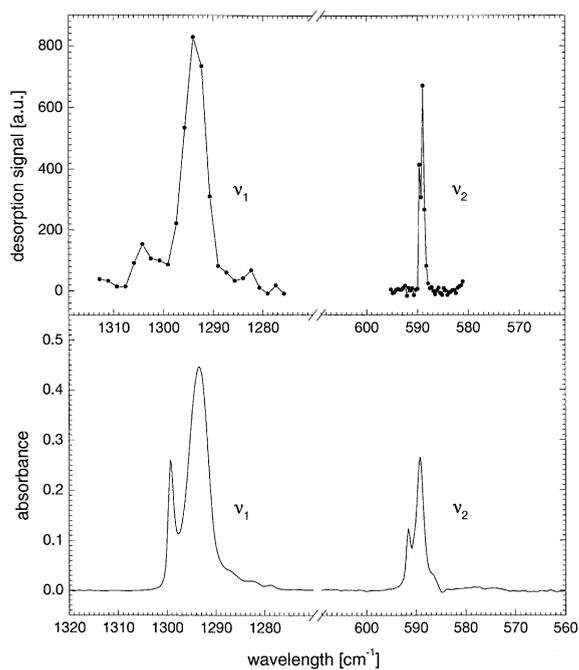


Fig. 1. Desorption spectrum (upper trace) and linear absorption spectrum (lower trace) of ~ 600 ML N_2O condensed on $NaCl(100)$ at 38 K when exciting the symmetric stretching (ν_1) and the bending mode (ν_2). Desorption of the condensed N_2O molecules is induced using FELIX at 1 GHz micropulse and 5 Hz macropulse repetition rate. Each data point of the desorption spectrum is averaged over 20 macropulses. The absorption spectrum is recorded using a Bruker FTIR spectrometer (IFS 66v) adapted for measurements in transmission geometry, using a MCT detector and a resolution of 0.5 cm^{-1} .

well and the high frequency component is attributed either to a longitudinal optical or a multi-reflection mode [16,17]. This mode is observable with p-polarized light only. The FTIR spectra presented here are recorded with unpolarized light and show therefore this component. The desorption spectrum is recorded with s-polarized light and accordingly each mode consists of only one line which corresponds to the low frequency component in the linear absorption spectrum. The peak widths of the modes in the different spectra are found to be comparable. In the linear absorption spectrum the resolution of the spectrometer is much higher than the observed peak width. In the desorption spectrum, however, the width of the observed peaks (5.2 and 1.2 cm^{-1} for the ν_1 and ν_2 mode, respectively) is given by the bandwidth of FELIX.

In Fig. 2 representative TOF spectra are shown for the ν_1 (upper trace) and ν_2 (lower trace) mode recorded for high (left) and low (right) laser fluences. TOF spectra can provide information on the translational temperature of the desorbing species. The TOF spectra at high fluences induce a higher signal and peak at an earlier time. The spectra shown here can be well described by a Maxwell–Boltzmann equation for a flux distribution [18]. From the fitted functions (shown in the graph as dotted lines) translational temperatures between 100 and 222 K can be derived, well above the temperature of the underlying $NaCl(100)$ substrate (38 K). For both vibrational modes under study the thus determined translational temperatures depend strongly on the laser fluence; for higher laser fluences a higher translational temperature is found.

In order to get more insight into the underlying desorption mechanism, the influence of the surface coverage as well as the substrate temperature is investigated. In Fig. 3 the dependence of the desorption signal on the surface coverage after excitation on the ν_1 mode is shown for different fluences, and is found to depend strongly on both: the yield increases with increasing layer thickness and increasing laser fluence. As can be seen from the inset in Fig. 3, the data indicate a threshold of the coverage for each laser fluence, below which no desorbing species are observed. For higher laser

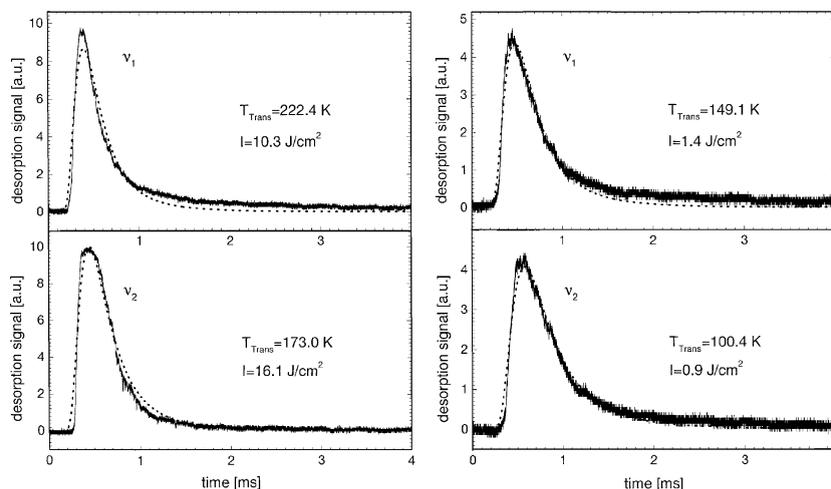


Fig. 2. TOF spectra recorded for high (left) and low (right) laser fluence I after resonant excitation of the ν_1 (upper trace) and ν_2 (lower trace) mode of N_2O condensed on $\text{NaCl}(1\ 0\ 0)$ (~ 600 ML; 38 K). The full lines give the experimental data, the dotted lines represent fits to a Maxwell–Boltzmann flux distribution. The laser fluences as well as the derived translational temperatures of the desorbing molecules are given in the figure.

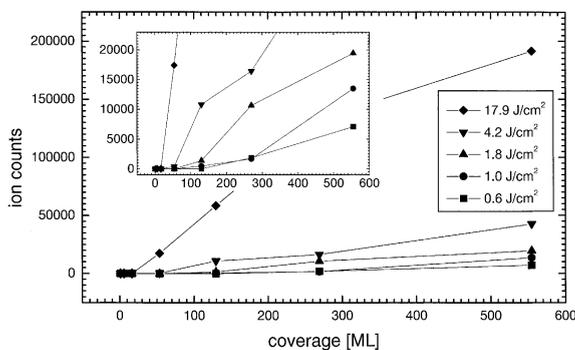


Fig. 3. Dependence of the desorption signal on the N_2O coverage. N_2O is resonantly excited via the ν_1 mode at $1293\ \text{cm}^{-1}$. The desorption signal is derived by means of the single ion counting detection scheme. TOF spectra (100 averages) are recorded for different laser fluences (given in the figure) by changing the focussing conditions of the laser beam. Each data point is recorded on a “fresh” surface spot.

fluences this threshold shifts to lower surface coverage.

In Fig. 4 the dependence of the desorption signal on the temperature of the substrate is shown. The layers are prepared at the highest temperature given in the figure and afterwards cooled stepwise to about 40 K. A significant dependence of the desorption signal on the substrate temperature

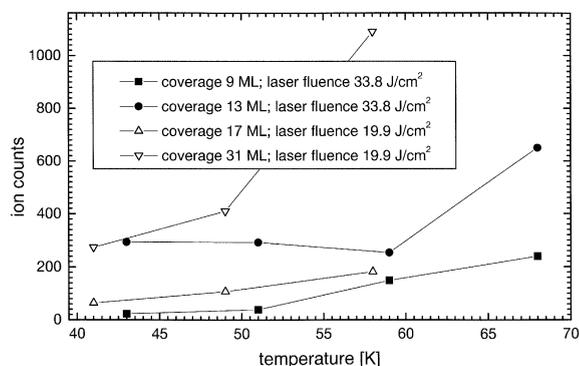


Fig. 4. N_2O desorption yield as a function of the $\text{NaCl}(100)$ temperature for different coverages and laser fluences after resonant excitation via the ν_1 mode. Each data point is averaged over 100 TOF spectra, and recorded on a “fresh” surface spot.

is found. The lower the sample temperature, the less desorbing molecules are detected. Warming the sample again to the starting temperature yields the original signals, thus showing that no irreversible processes are occurring. A similar effect, a dependence of the desorption cross-section when changing the surface temperature, was observed in the system $\text{NO}/\text{Cr}_2\text{O}_3(000\ 1)$ [19]. However, the initial excitation step via UV photons is different from that in the present investigation.

The question of the excitation and desorption mechanism now arises. In the desorption spectrum of Fig. 1 it is clearly observed that desorption only occurs when an internal molecular vibration is resonantly excited. Therefore case (c), as described in the introduction, applies to this study. For the desorption two different pathways are possible: In one, the vibrational energy may couple to the desorption coordinate directly while in the other pathway, desorption occurs after energy transfer to the solid. The analysis of the TOF spectra yields translational temperatures above the sample temperature. This points towards a resonant heating process. However, in case of a direct coupling to the desorption coordinate, the molecules leaving the surface can carry significant excess energy, which also could give rise to translational temperatures well above the sample temperature. However, such a direct coupling to the desorption coordinate is not expected to yield a TOF distribution that can be fit with a thermal Maxwell–Boltzmann distribution. In this case, rather, all molecules should leave the surface with the same excess energy, and a variation in fluence should influence only the total yield, but not the translational temperature. Thus the observation that the TOF spectra can be fit by a Maxwell–Boltzmann distribution and that the determined translational temperatures are strongly dependent on the laser fluence are indicative for the resonant heating process. This attribution is supported by the dependence of the desorption yield on the substrate coverage and the substrate temperature. The latter cannot be easily rationalized in the picture of a direct coupling to the desorption continuum, as in this case the desorption would mainly depend on the energy locally stored in the molecular bond. In the resonant heating case, however, the desorption can depend not only on the local energy storage but also on the total amount of energy stored in the layer. In addition, in a heating picture the thermal coupling of the heated layer to the substrate is important. This coupling will drain the energy of a thin layer much quicker than that of a thick layer and the latter is thus expected to yield higher desorption signals, as observed here.

Presently, model calculations for the resonant heating process, based on the solution of the heat

conduction equation, are in progress. Preliminary results show that the experimental data can be reproduced and explained within the model. Details will be presented in a forthcoming publication.

4. Conclusions

Studies on the infrared laser-induced desorption of N_2O condensed on $NaCl(100)$ show that desorption of N_2O is only observed after resonant excitation of the ν_1 and ν_2 modes. The desorption spectrum compares well to the linear absorption spectrum. The analysis of the TOF spectra yields translational temperatures above the surface temperature and exhibits a pronounced fluence dependence as well as a threshold for the desorption which depends on the laser fluence and on the layer thickness. In addition, the desorption yield depends on the initial temperature of the substrate. The experimental observations as well as first model calculations are indicative of a resonant heating process.

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