Resonance, Rate, and Quantum Yield of Infrared-Laser-Induced Desorption by Multiquantum Vibrational Excitation of the Adsorbate CH_3F on NaCl

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The linear infrared absorption spectra of CH_3F gas, multilayer film, and CH_3F adsorbate on NaCl crystal surfaces have been found to be distinctly different and significantly coverage dependent. On resonant infrared-laser excitation of the ν_3 internal vibration of the adsorbate CH_3F on NaCl, molecular desorption of CH_3F occurs. Measurement of the resonance, rate coefficient, and quantum yield has revealed high spectral selectivity and efficiency of the desorption due to multiphoton ($n > 2$) adsorbate vibrational excitation.

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In recent years desorption phenomena in heterogeneous systems have been studied by various techniques, e.g., thermal desorption, photodesorption, and electron-impact desorption.[1] The purpose of this communication is to report the selective frequency dependence and large efficiency of molecular desorption by resonant coupling of laser infrared into *internal* adsorbate vibrations. The phenomenon observed appears to be a process highly localized in the adsorbate. It is essentially different from the well-known illumination effects on desorption from semiconductors and insulators which are largely not surface processes, probably due to photon absorption by the solid and subsequent transfer of the excitation to the surface proper.[1] The photodesorption mechanism established in this work in continuation of our previous studies[2,3] has also been proposed in the recent theoretical work by Kreuzer and Lowy.[4]

To investigate the feasibility of resonant infrared-laser–induced desorption we studied the absorption system fluoromethane–sodium chloride, CH_3F-NaCl(100) film, for the following reasons:

(1) We have been able to discriminate distinctly between the vibrational infrared spectra of CH_3F multilayer film (solid CH_3F) and CH_3F adsorbate on NaCl surfaces by linear transmission absorption spectroscopy.[3,5,6]

(2) NaCl is highly transparent for CO_2 laser pulses, wave number $\omega \cong 1000\ \mathrm{cm}^{-1}$, fluence $\varphi \approx 0.1\ \mathrm{J\ cm}^{-2}$, pulse width 200 ns (full width at half maximum), the absorption coefficient at 77 K being $\leq 10^{-3}\ \mathrm{cm}^{-1}$.

(3) The yield of evaporation from multilayer CH_3F films on NaCl(100) crystals and films at 64 and 77 K by pulsed CO_2 laser radiation shows a sharp resonance around 990 cm^{-1} in coincidence with the obtained linear transmission infrared spectra.[3,5]

(4) The fundamental of the ν_3 internal vibration of the adsorption system CH_3F-NaCl(100) film at wave numbers of 980 and 960 cm^{-1}, respectively, is in resonance with some CO_2 laser lines in the R and P branch of the $00^\circ 1$-$10^\circ 0$ CO_2 laser transition.

Only the main features of the experimental setup and procedure are summarized here. An ultrahigh-vacuum (uhv) cryostat with flanged analyzer cell suitable for optical and infrared spectroscopy as well as laser-stimulated processes is equipped with a quadrupole mass spectrometer, 12 cm from the sample surface. The entire uhv system is pumped to a base pressure in the low 10^{-10}-mbar range by an ion getter and a titanium sublimation pump after bakeout at 420 K. NaCl films are evaporated *in situ* onto optically polished NaCl(100) single crystals, after cooling the substrate down to 77 K, at 5×10^{-9} mbar total pressure. A carefully purified CH_3F gas stream is directed towards the sample surface and controlled by an uhv leak valve. The beam of a transversely excited atmosphere CO_2 laser running in TEM_{00} mode is focused ($f = 71$ cm) onto the sample, angle of incidence 60°. The pulse energy is measured with a pyroelectric energy meter, the wavelength determined with a grating spectrum analyzer, giving energy 0.01 J in a pulse width ca. 200 ns. After each laser pulse the pressure rise was traced at mass 34 (CH_3F^+ ion current) with the mass spectrometer operated in time-of-flight mode. The CH_3F^+ ion current increase $i(\tau)$ for the time of flight τ of the desorbed CH_3F molecules to the ionization chamber of the mass spectrometer was measured and displayed on a storage oscilloscope and the integral $j = \int i(\tau)d\tau$

determined. The maximum value i_m of $i(\tau)$ turned out to be proportional to j within an error of ± 7%.

Figure 1 shows the resonance characteristics of laser-induced desorption (CH_3F^+ ion current) at 77 K for two different fluence values, both peak maxima around 975 cm^{-1}. The NaCl film on the NaCl(100) crystal was exposed to a CH_3F partial pressure of 1×10^{-6} mbar for 40 s; afterwards the pressure dropped to 1.6×10^{-9} mbar. At higher fluence values the characteristic becomes broader. After each laser pulse the beam was directed at a new spot on the sample thus ensuring constant coverage conditions. When we compare the linear infrared transmission absorption spectra of adsorbed CH_3F on NaCl film (Fig. 1) with the frequency dependence of the desorption yield of the adsorbed CH_3F, it may be inferred that the desorption spectra are due to the resonant excitation of the internal vibrational ν_3 normal mode of the CH_3F adsorbate.

Desorption is achieved by multiquantum absorption $nh\nu_3 > \epsilon$, ϵ being the activation barrier to desorption of the bound adsorbate. The activation energy ϵ has been estimated from thermodynamic measurements of adsorption isotherms to be ≥ 25 kJ mol^{-1}, equivalent to $n\approx 3$, and weakly increasing with decreasing coverage.[6] The higher internal vibrational states, $v_3 > 2$, degenerate with the continuum in the adsorption potential, are populated by stepwise multiphoton excitation and possibly by very fast intermolecular quasiresonant V-V energy transfer, in both processes anharmonicity compensation being assisted by low-frequency external adsorbate modes and/or adsorbent phonons. The fast transfer of the infrared-induced internal-vibrational adsorbate excitation into excitation of adsorption potential continuum states is probably stimulated by adsorbent phonons.

The dependence of desorption yield upon laser fluence is shown in Fig. 2. The desorption yield is given by $\ln(\theta_0/\theta)$, θ_0 and θ being the coverage before and after a laser pulse [if $(\theta_0-\theta)\ll\theta_0$, $\ln(\theta_0/\theta)\approx(\theta_0-\theta)/\theta_0$]. It has been determined from

$$\frac{\theta_0}{\theta}=\frac{\sum_{n=k}^{m} j_n}{\sum_{n=k+1}^{m} j_n}, \quad j_k \ll \sum_{n=k}^{m} j_n,$$

where $j_{n>m}\approx 0$ at fluences $\varphi > 100$ mJ cm^{-2}. This description relates the change of coverage $\theta_0-\theta$ by desorption to the surface coverage θ_0. A sequence of laser pulses $k,\ldots,m$ has been employed at constant wave number always striking the same spot of the sample until no more desorbed CH_3F

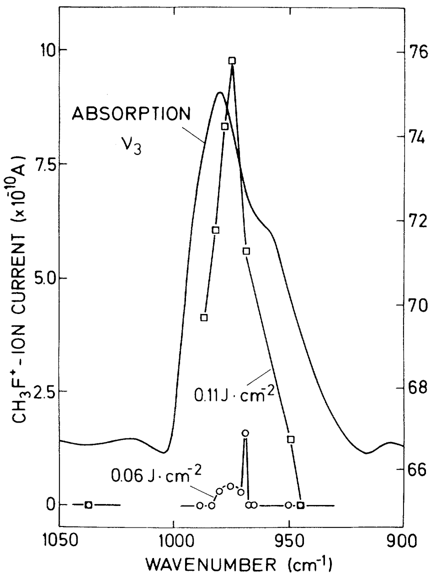

FIG. 1. Linear absorption spectrum of CH_3F adsorbed on NaCl and yield of molecular desorption (CH_3F^+ ion current i_m) at constant coverage and fluence, vs infrared-laser excitation frequency. Sample temperature 77 K, pressure after gas admission 1.6×10^{-9} mbar.

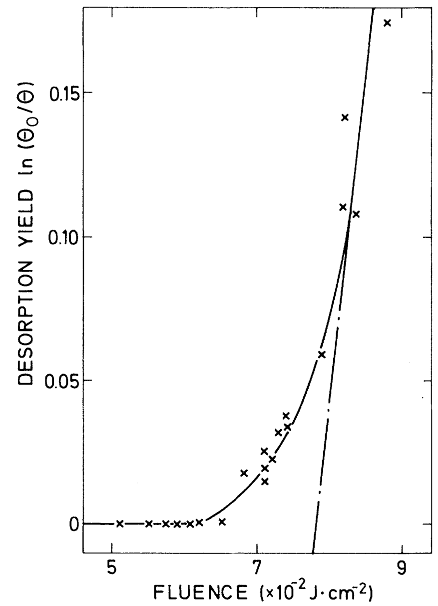

FIG. 2. Yield of CH_3F molecular desorption from CH_3F adsorbed on NaCl vs fluence at constant laser excitation, wave number $\omega = 975.9$ cm^{-1}. Sample temperature 77 K, pressure 1.6×10^{-9} mbar.

molecules could be detected. Thus the surface concentration of the adsorbate is determined by desorption.

The observed infrared-laser–induced desorption can be considered as an unimolecular process, the rate coefficient under conditions discussed by Quack[7] being defined by

$$-d\ln(\theta/\theta_0)/dt = k_u(\varphi, I, t),$$

where

$$\varphi = \int_0^t I(t')dt'$$

denotes fluence, I intensity, and t laser pulse length.

According to our experimental results (Fig. 2), at sufficiently high fluence values the rate equation can be written as

$$\frac{d\ln(\theta_0/\theta)}{d\varphi} = \frac{d\ln(\theta_0/\theta)}{I(t)dt} = \mathrm{const};$$

because of $k_u(I,t)/I(t) = \mathrm{const}$, $k_u \sim I$, which is theoretically expected for the intensity dependence of the steady-state rate coefficient k_u at intermediate intensities.[7] The rate coefficient was evaluated from the limiting slope (dot-dashed line in Fig. 2),

$$k_u/I = 1\times 10^7\ \mathrm{s^{-1}/(MW\ cm^{-2})},$$

within an error of factor 2.

It should be noted that the rate coefficient k_u for desorption could be dependent on coverage θ_0 also.

From the rate coefficient the desorption cross section

$$\sigma_D = (k_u/I)h\nu_3$$

can be estimated to be about 2×10^{-19} cm^2, only slightly smaller than the absorption cross section $\sigma_A = 3\times 10^{-18}$ cm^2, indicating the high efficiency of the desorption process. With the activation energy $\epsilon \approx 3\ h\nu_3$ taken into account, the quantum yield q has been estimated from $q = 3\Delta\theta/\Delta p$ to be 10^{-2}, with $\Delta\theta \simeq \theta_0(k_u/I)(\varphi - \varphi')$ being the number of molecules desorbed per pulse, $\Delta p \simeq \theta_0\sigma_A\varphi/h\nu_3$ the number of photons absorbed, and φ' the intercept on the φ axis in Fig. 2. The quantum yield of desorption stimulated by vibrational excitation may be compared with, e.g., the quantum yield for desorption stimulated by electronic excitation in the adsorption system carbon monoxide–tungsten,[1] given as 10^{-7}.

The results show that even at low laser fluence, $\varphi \lesssim 0.1$ J cm^{-2}, fast and frequency-selective desorption can be stimulated. Further we can clearly distinguish between solid and adsorbed CH$_3$F on the NaCl surface by means of infrared transmission spectroscopy as well as by the resonance characteristics of laser-induced sublimation and desorption. The agreement of the fragmentation patterns obtained from the stationary and laser-induced mass spectra indicates that the desorbed species are neutral CH$_3$F molecules.

Fast energy transfer between external and internal vibrational absorbate modes probably plays an important role also in adsorption, which is the reverse of the studied process, and in the activation of catalytic reactions. Further investigations on this subject and an extension to gas-metal systems are under study.[8]

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Oscillatory Relaxation of the Cu(110) Surface

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Complementary studies of the Cu(110) surface have been carried out by means of low-energy electron diffraction and high-energy ion scattering. The results obtained from the use of the two techniques are in acceptable agreement and indicate that the interlayer spacings in the Cu(110) surface exhibit a damped, oscillatory deviation from the bulk value, in qualitative agreement with the predictions of Landman, Hill, and Mostoller.

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In this Letter, we present briefly the results of complementary low-energy electron-diffraction[1] (LEED) and high-energy ion-scattering[2] (HEIS) studies of the surface structure of Cu(110). Both studies lead to the conclusion that the structure exhibits an oscillatory relaxation of the interlayer spacings in the surface, in qualitative agreement with the results of recent calculations of Landman, Hill, and Mostoller.[3]

Previous LEED studies of unreconstructed metal surfaces have indicated that the most significant deviation from bulk geometry occurs for bcc (100) and fcc (110) planes, where contractions of the first interlayer spacing of up to 10% of the bulk value have been reported.[4,5] The general nature of these results has been reproduced in some recent model calculations of surface-interlayer spacings.[3,6] An interesting additional feature of these calculations is the prediction that the deviation from bulk geometry is not limited to the first interlayer spacing but extends in a damped, oscillatory fashion into the bulk. This possibility does not appear to have been widely examined in the interpretation of experimental measurements of surface structure, and in the case of clean, unreconstructed metal surfaces, we are aware of only two systems where a relaxation (Δd_1 and Δd_2) of both first and second interlayer spacing has been reported. For Re$(0\bar{1}01)$, Davis and Zehner[7] obtained $\Delta d_1 = -17\%$ and $\Delta d_2 = +1$ to 2%. (The values are given as percentages of the bulk value. The minus sign indicates a contraction.) For V(100), Jensen *et al.*[8] obtained $\Delta d_1 = -7\%$ and $\Delta d_2 = +1\%$. In neither case, however, was the expansion of the second interlayer spacing regarded as being sufficiently large in comparison with the estimated uncertainty to be taken as conclusive evidence of an oscillatory relaxation of the interlayer spacings.

For the Cu(110) surface, Davis and co-workers[9-11] have considered the possibility of a relaxation of both the first (d_1) and second (d_2) interlayer spacing in their analyses of LEED data but have concluded that $\Delta d_2 = 0 \pm 2.5\%$, whereas $\Delta d_1 = -10 \pm 2.5\%$. The LEED results and interpretation presented in the present article are in reasonable agreement with those of Davis *et al.*, except that it has proved to be possible to establish the existence of a relaxation of both d_1 and d_2. This conclusion is confirmed and given extra weight by the complementary HEIS measurements, particularly in view of the fundamental differences between the LEED and HEIS techniques.

LEED study of Cu(110).—After preparation of