Rotational cooling and vibrational excitation of CO_2 molecules during desorption from a titanium surface

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An above-equilibrium excitation and a simultaneous rotational cooling have been observed during the desorption of CO_2 molecules from the surface of a titanium foil by diode-laser spectroscopy. The molecules were desorbed by a pulsed thermal method. The binding energy of the molecules with the surface is estimated to be 0.22 eV. For surface temperatures over the range 120–180 K, the rotational and vibrational temperatures of the desorbed molecules were 100 ± 10 K and 220 ± 20 K.

INTRODUCTION

Qualitatively new information on the mechanism by which molecules interact with surfaces can be found by studying the vibrational-rotational distribution of molecules during desorption from surfaces. A nonequilibrium vibrational excitation of the products of catalytic reactions has been observed in several studies,[1,2] but for systems with low binding energies, without a reaction, the effect has received little attention. A simultaneous study of the rotational distribution would make it possible to determine the excitation mechanism in detail. For example, in certain cases [one being the associative desorption of NO from Ir (111)], the rotational temperature is observed to rise above the surface temperature.[3] In the absence of a reaction, on the other hand, the rotational temperature decreases (this is "rotational cooling").[4]

Most experiments on rotational cooling have been carried out for NO, CO, and N_2 molecules[4] as they interact with a wide variety of surfaces. However, these particular molecules, which have been selected because of the capabilities of highly sensitive methods of laser-induced fluorescence and multiphoton ionization, have approximately equal rotational constants. Studies of rotational cooling during desorption, with the initial state of the molecules on the surface fully determined, and for polyatomic molecules with substantially smaller rotational constants would make it possible to distinguish in the process of interest effects which stem from the properties of the molecules from those of the surface.

In the present study we have observed an above-equilibrium vibrational excitation in the absence of a reaction and a simultaneous rotational cooling during the desorption of CO_2 molecules from the surface of a titanium foil by diode-laser spectroscopy. This method makes it possible to extend the study to a substantially larger group of molecules, including polyatomic molecules.

EXPERIMENTAL PROCEDURE

Figure 1 shows the experimental layout for the determination of the vibrational-rotational distribution of CO_2 molecules desorbed from the surface of a titanium foil. Analysis of the foil by x-ray photoelectron spectroscopy on a HP-5950A spectrometer[5] showed that the foil is coated with titanium dioxide, TiO_2. In the experiment, the foil was pressed through a Teflon insulating film of a material equivalent to to a copper cold conductor 3 cooled by liquid nitrogen. The carbon dioxide was adsorbed through an extended effusion source with slit dimensions 250 × 1 mm onto a titanium foil with dimensions of 250 × 6 mm. The foil temperature was 80 K. The thickness of the sorbed layer of CO_2 molecules was estimated to be less than a monolayer on the basis of geometric considerations and of the flow rate of gas from the effusion source. The CO_2 molecules were desorbed as the foil was heated by a current pulse. The pressure in the vacuum chamber (2), with a volume of 120 liters, was 10^{-3} Torr. This chamber was evacuated by a sorption pump. A diode-laser spectrometer was used for the spectral measurements.[6] The desorbed molecules were probed by a beam 5 mm in diameter and 5 mm from the surface from diode laser 1.

The foil temperature at any time during the desorption pulse could be determined from the ohmic resistance of the foil. This resistance is easily calculated from the known temperature dependences of the current and of the voltage applied to the foil. By changing the direction of the current one can change the rate at which the foil is heated. The optical density of the desorbed molecules was used to determine the desorption rate at various heating rates. The results of these measurements are shown in Fig. 2.

Woodruff and Delchar[7] have shown how to estimate the binding energy of absorbed molecules from a plot of the temperature corresponding to the maximum desorption rate versus the rate of change of the temperature. Using their

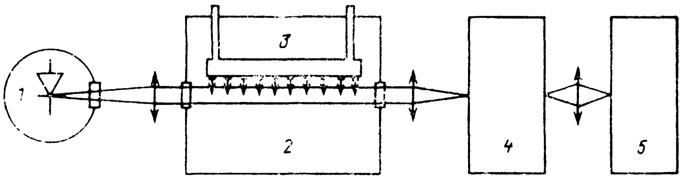

FIG. 1. Experimental layout. 1—Diode laser; 2—vacuum chamber; 3—copper cold conductor, on which the titanium foil is placed; 4—MDR-23 monochromator; 5—radiation detector.

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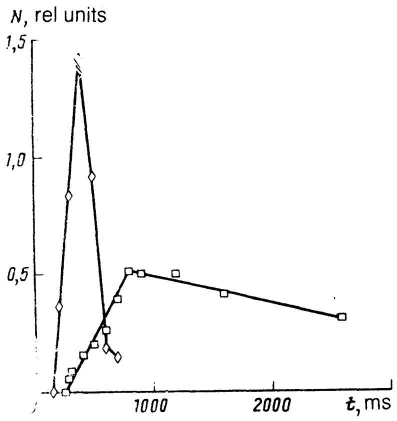

FIG. 2. Time evolution of the flux of desorbed molecules at various heating rates. Here N is the optical density.

method and the data found in this study, we find the binding energy of the CO_2 molecules with the titanium surface to be $D = 0.22$ eV.

The spectra of the desorbed CO_2 molecules were studied in the 16-μm region in the absorption band of a deformation mode. The laser beam passed through a tube through which nitrogen was blown. The adsorption of the laser light by carbon dioxide of the air was thus eliminated. The vibrational-rotational distribution of the molecules was determined from the intensity of spectral lines of the Q branches of the fundamental 00^00–01^10 band and the "hot" 01^10–02^20 band which correspond to the populations of the unexcited and first excited vibrational levels. Figure 3 shows a characteristic spectrum, measured after one desorption pulse. The time taken to record the spectrum of the entire Q branch, 500 μs, is comparable to the desorption time. In the determination of the vibrational-rotational distribution corresponding to a given temperature and a given surface coverage, the entire spectrum of the Q branch was therefore measured over several pulses, with the same delay time for each absorption line. The line intensities and the known oscillator strength[8] were used to determine the concentration of desorbed molecules. The corresponding time dependence (Fig. 3) was used to estimate the total number and, correspondingly, the surface density of adsorbed molecules. This density turned out to be $\sim 10^{15}$ cm^{-2}, or less than a monolayer.

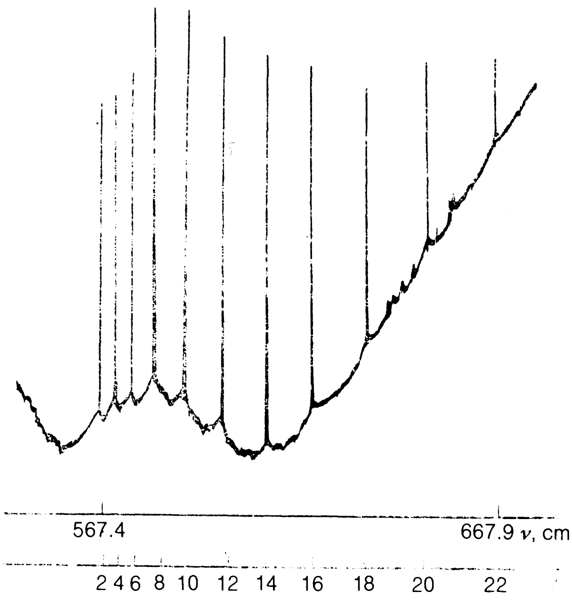

FIG. 3. Spectrum of the Q branch of the 00^00–01^10 band of the CO_2 molecules desorbed from the titanium surface.

The maximum concentration of molecules at the time of desorption was $5\cdot 10^{13}$ cm^{-3}. This figure indicates that the desorbing molecules do not collide with each other.

EXPERIMENTAL RESULTS AND DISCUSSION

The rotational distribution was determined from the relative intensities of the absorption lines of the fundamental band of the Q branch of the CO_2 molecules. This distribution is shown in Fig. 4 (curve b) as a plot of the logarithm of the relative population versus the energy of the corresponding rotational state. The distribution was measured for various surface temperatures over the range 120–180 K and for various degrees of surface coverage. It was found that this distribution is independent of these parameters and is of a non-Boltzmann nature, with overpopulated low-lying states with rotational numbers $J = 2$–6. The nonequilibrium nature of the distribution is important, since other experiments have yielded a Boltzmann distribution of desorbed molecules.[9] The rotational temperature determined by the method of least squares is $T_r = 100 \pm 10$ K.

In experiments using N_2, NO, CO, and HF, the surface temperature at which the rotational cooling begins is typically 300 K (Ref. 4). The rotational cooling for the CO_2 molecules, with a rotational constant B lower than those of the molecules which have been studied previously, is thus being observed at a lower surface temperature, in agreement with Ref. 10.

In Ref. 10, the rotational cooling for weakly bound molecules was explained in terms of a conversion of rotational energy into the translational energy required for de-

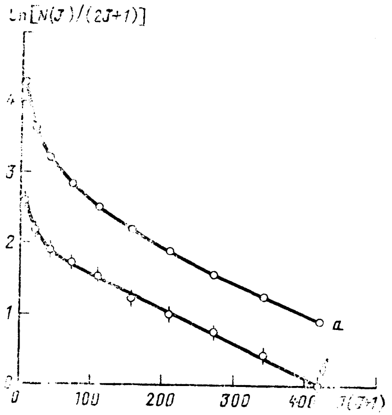

FIG. 4. Population distribution among J levels (the curves are displaced along the ordinate with respect to each other). a—Theoretical; b—experimental.

sorption. An expression was derived for the population of the rotational states of the desorbing molecules:

$$P(J)=[(2J+1)^2+4\Delta(T)/B]^{1/2}\times\exp(-\Delta/RT)\exp[-BJ(J+1)/RT]/Q_r(T), \quad (1)$$

where $\Delta(T)=D-\langle E\rangle$ is the energy required for desorption, and $\langle E\rangle$ is the average thermal energy of the vibrations of the molecule as a whole in the adsorbed state. This distribution is shown in Fig. 4a for a surface temperature $T=180$ K. The rotational temperature determined for the CO_2 molecules through a linear approximation of distribution (1) for rotational numbers 10–20 lies in the range 80–105 K for surface temperatures from 120 K to 180 K. This result agrees quite well with the experimental data.

This mechanism for rotational cooling[10] presupposes a free rotation of the molecules in the adsorbed state. This assumption is not valid for the CO_2 molecule, because the surface potential depends strongly on the orientation of the molecule. A nonspherical potential and a rotational relaxation of desorbed molecules by phonons were taken into account in Ref. 11. It can be suggested on the basis of that theory that a rotational relaxation of molecules by phonons initially occurs during the desorption, as a result of the nonspherical nature of the potential. The molecule then acquires the translational energy required for desorption at the expense of rotational energy, as suggested in Ref. 10.

Rotational relaxation also explains why the difference between the rotational distribution observed for the low-lying rotational states (Fig. 4b) and a Boltzmann distribution is much smaller than the calculated difference (Fig. 4a).

In the experiments, the population of the first vibrational level of the deformation mode with respect to the fundamental vibrational state was measured. The corresponding vibrational temperature is 220 ± 20 K. This parameter is also independent of the surface temperature over the range 120–180 K. The binding energies of vibrationally excited and ground-state molecules are the same, as was determined from the desorption rate. The rotational cooling of the molecules indicates that no reaction occurs at the surface. Furthermore, the vibrational excitation of the molecules does not occur as the result of a redistribution of thermal energy at the time of desorption. If such a redistribution *were* responsible, we would see a rotational cooling of the excited molecules going beyond that of the excited molecules.

The presence of such molecules in a concentration which is above the equilibrium concentration and independent of the surface temperature can apparently be explained in terms of a desorption of molecules which are present in a deformed state on the surface. According to the reversibility principle, deformed molecules form on a surface during the adsorption of vibrationally excited CO_2 molecules. This result confirms that the vibrational temperature of the desorbed molecules is close to room temperature, at which the adsorption occurred. It also confirms that this temperature is independent of the surface temperature at the time of desorption. Gdowski *et al.*[12] studied the dissociative adsorption of CO_2 molecules on a Ni surface and suggested that vibrationally excited CO_2 molecules play a governing role in the formation of deformed molecules on a surface. Confirmation of that suggestion may be found in experiments to determine the vibrational distribution of desorbed molecules which have been adsorbed at various molecular-beam temperatures.

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