Scattering of vibrationally and electronically excited CO molecules from a LiF(100) surface

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Abstract

Experiments are performed in which vibrationally and electronically excited $CO(a^3\Pi, v = 1)$ molecules are scattered from a LiF(100) surface. As there is originally no population in the vibrationless level of the metastable state, this experiment gives the unique possibility of probing the vibrationally inelastic channel in the scattering of vibrationally excited molecules. The vibrational deactivation probability can thus be accurately determined and is found to be below 10^{-3} for the system under study. © 1997 Elsevier Science B.V.

1. Introduction

The use of molecular beams in surface scattering enables a detailed investigation of the interaction potential between molecules and surfaces. The importance of the vibrational degree of freedom of molecules for the determination of the interaction potential has been reviewed by Houston and Merrill [1] in 1988, and more recently by Rettner et al. [2]. Unambiguous vibrational excitation has been observed for ground-state NO molecules scattered from a Ag(111) surface in essentially a single gas–surface encounter [3]. Molecular beam studies in which vibrationally excited molecules are scattered from surfaces are thus far limited in number [4–15]. An important parameter to be determined is the vibrational survival probability, or, alternatively, the vibrational deactivation probability. This is, however, a difficult observable as one has to average over

scattering angle, velocity distribution and final state-distribution to determine the total fraction of molecules in the vibrationally elastic channel. A large experimental error is intrinsic to this procedure.

The survival probabilities for vibrationally excited molecules scattering from clean, well-defined and atomically flat surfaces range from 0.6 up to almost unity, depending on the experimental conditions. For vibrationally excited NO $(X^2\Pi_{1/2}, v = 1)$ (seeded in He) scattered from a cleaved (room temperature) LiF(100) surface it is observed that the survival probability for molecules in the vibrationally excited state is 0.9 ± 0.1, i.e. as close to unity as could experimentally be determined [5].

The accuracy of the determination of the survival probability can be improved if also the vibrationally inelastic channel is probed. Normally this is impossible because only a small fraction of the molecules is prepared in the vibrationally excited state, and the

remaining ground-state molecules will dominate in such an experiment. If, however, both vibrationally and electronically excited molecules, or, alternatively, high(er) vibrationally excited molecules ($v \geqslant 2$) are scattered, the vibrationally inelastic channel can be probed and vibrational deactivation probabilities can be determined precisely.

In this Letter we report state-to-state scattering experiments with vibrationally and electronically excited $CO(a^3\Pi, v = 1)$ molecules from a LiF(100) surface. From recent scattering studies with metastable CO molecules in their vibrational ground state it is known that a few percent of these molecules survives the collision with a LiF(100) surface as a metastable molecule [16,17]. In the experiments reported here both the vibrationally elastic channel ($\Delta v = 0$) and also the vibrationally inelastic channel ($\Delta v = -1$) have been probed for the scattering process.

2. Experimental

The experimental apparatus for the scattering experiments consists of a pulsed molecular beam machine that is connected to an ultra high vacuum (UHV) system as schematically indicated in Fig. 1. The operation principles of this machine have been discussed in detail elsewhere [17,18]. To briefly summarize, a mixture of 20% CO in a rare gas is

expanded into vacuum to produce a pulsed supersonic beam. Metastable CO molecules are prepared by direct laser excitation. The + parity component of the $a^3\Pi_1(v = 1, J = 1)$ level is populated via excitation of the $Q_2(1)$ line of the spin-forbidden $a^3\Pi \leftarrow X^1\Sigma^+$ transition using pulsed 199 nm radiation (~ 0.5 mJ in a 150 MHz bandwidth). Subsequently, the molecular beam enters the hexapole chamber via a 0.8 mm diameter skimmer. Only the laser-prepared metastable CO molecules are bent around the beamstop with the electrostatic hexapole and are focused onto a 1.2 mm diameter diaphragm; an almost pure beam of metastable CO molecules, essentially free of carrier gas atoms and ground-state CO molecules, enters the UHV scattering chamber. The averaged kinetic energy of the metastable CO molecules is 78 meV.

A cleaved LiF(100) crystal is mounted on a manipulator in the UHV system, 72.5 cm downstream from the excitation region. The LiF surface is chosen for these experiments as it is known that part of the metastable $CO(a^3\Pi, v = 0)$ molecules retain their electronic energy (6.0 eV) after scattering from this surface [16,17]. The vibrational energy of CO (0.22 eV) might be conserved as well in the interaction with the surface, as high survival probabilities have been reported for the scattering of vibrationally excited NO molecules from this same surface [5].

After scattering, both the vibrationally elastic and inelastic channels are probed in a (1 + 1)-resonance
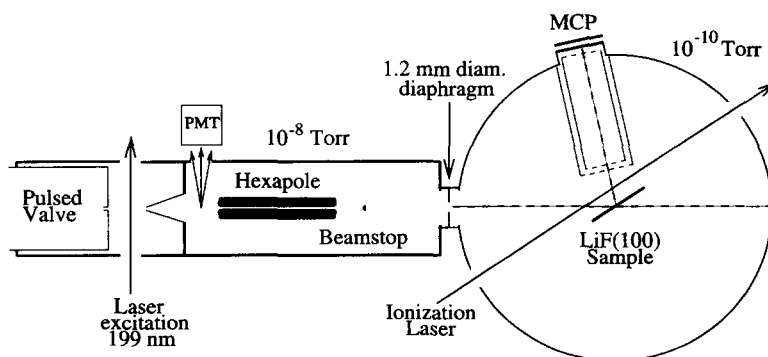

Fig. 1. Schematic view of the experimental apparatus. The 199 nm laser excitation in combination with the hexapole-beamstop-diaphragm apparatus allows the preparation of a pure beam of vibrationally excited metastable CO molecules in the UHV chamber. The production of metastable CO molecules is monitored with a photomultiplier (PMT). Internal state distributions are probed via a (1 + 1)-REMPI scheme from the $a^3\Pi$ state using an ionization laser around 280 nm. Mass selective ion detection is performed using the ion extraction assembly mounted in front of the MCP detector.

enhanced multi-photon ionization (REMPI) scheme. The extraction assembly used for mass-selective ion detection is depicted in Fig. 1. The $b^3\Sigma^+(v = 1) \leftarrow a^3\Pi$ ($v = 1$) transition around 279 nm is used as the resonant step in the REMPI process and probes the vibrationally and electronically elastic channel, while the corresponding $0 \leftarrow 0$ band around 283 nm [19,20] probes the vibrationally inelastic channel. Both 279 and 283 nm radiation are produced by frequency doubling the output of a pulsed dye laser system. Ions are produced in a volume close to the LiF surface and are extracted to impinge on a micro-channel plate (MCP) detector. The angle of incidence is chosen to be $\theta_i = 51°$, to allow free passage of the ionization laser close to the LiF surface.

3. Results and discussion

Fig. 2 shows experimental $(1 + 1)$-REMPI spectra of the incoming beam (upper trace) and the scattered beam (middle trace) of metastable CO molecules. The upper trace shows two features, both originating from the laser prepared $a^3\Pi_1(v = 1, J = 1)$ level. The middle trace shows the REMPI spectrum of the scattered metastable CO molecules that remain in the $v = 1$ state. The rotational redistribution within the $a^3\Pi(v = 1)$ state is evident. The experimental spectrum is fitted in a similar way as was accomplished previously for the spectra obtained for scattering CO molecules in the $a^3\Pi(v = 0)$ state [17]. The frequencies for the $b^3\Sigma^+(v = 1) \leftarrow a^3\Pi(v = 1)$ transition are taken from the literature [21,22]. From a least-squares fit of the contour of the experimental spectrum, the rotational temperature, as well as the relative population within the three different Ω-components of the $a^3\Pi$ state is obtained. The best fitting spectrum is shown in the lower trace of Fig. 2. Optimum agreement with the experimental spectrum is obtained for a rotational temperature of $T_{rot} = 290 \pm 25$ K. The weight of the total population in levels with $\Omega = 0$ and 2 character relative to the total population in levels with $\Omega = 1$ character [17] is found to be 0.7 ± 0.2. Both the rotational temperature and the observed overpopulation of levels in the initially prepared $\Omega = 1$ component is consistent with the results obtained for the scattering of $CO(a^3\Pi, v = 0)$ [17]. The part of the b ← a spectrum
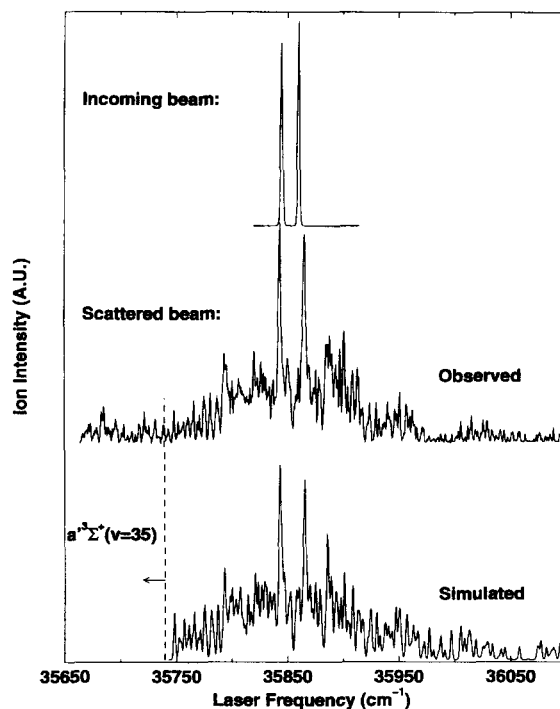

Fig. 2. Upper trace: REMPI spectrum showing the internal state distribution of the incoming beam of metastable CO molecules. The two features that are observed originate from the laser prepared $J = 1$ level in the $a^3\Pi(v = 1)$ state that is focused by the hexapole. Middle trace: REMPI spectrum reflecting the population of rotational levels in the $a^3\Pi(v = 1)$ state of the scattered CO molecules. The CO molecules that are probed have retained their electronic and vibrational energy. The spectrum is recorded for a gas mixture of 20% CO in Ar and $\theta_i = 51°$. Lower trace: Best fitting spectrum using $T_{rot} = 290$ K, and an overpopulation of the $\Omega = 1$ component with a factor 1.4 relative to the other Ω-components.

to the red of the dashed vertical line is omitted from the fit as it overlaps the $a'^3\Sigma^+(v = 35) \leftarrow a^3\Pi(v = 1)$ spectrum.

The vibrationally inelastic channel is investigated via probing of the scattered metastable molecules that end up in the $v = 0$ state. For a correct interpretation of the results it is essential to know what fraction of CO molecules in the $a^3\Pi$ state in the incoming beam has decayed to the $v = 0$ state by the emission of infrared (IR) photons. These vibrationally deexcited CO molecules are scattered from the LiF(100) surface as well and at least partly contribute to the observed signal in the $CO(a^3\Pi, v = 0)$ channel.

The left part of Fig. 3 shows the (1 + 1)-REMPI spectrum of metastable CO molecules in the incoming beam that reside in the lowest vibrational level ($v = 0$) of the $a^3\Pi$ state. A mixture of 20% CO in Ar is used. The spectrum is measured with the hexapole state selector on and the beamstop in place, thus selecting a pure beam of metastable CO molecules (the absolute intensity of this spectrum is more than two orders of magnitude lower than the intensity of the spectrum in the upper trace of Fig. 2). In zero electric field, only radiative (IR) transitions from the laser prepared $J = 1$ + parity level of the $a^3\Pi_1(v = 1)$ state to the − parity component of the $J = 0, 1$ and 2 levels of the different spin components of the $a^3\Pi(v = 0)$ state are allowed. From the Hönl–London factors for the IR $v = 1 \rightarrow v = 0$ transition [23] it is calculated that mainly the $J = 1$ and $J = 2$ levels of the $\Omega = 1$ component become populated. The peaks indicated by * (+), at least partially, originate from the + parity $\Omega = 1$ spin component of the $J = 1$ ($J = 2$) level. Transitions to the + parity components are possible in the electric field present inside the hexapole state-selector as the

wavefunctions of + and − parity components become mixed. Part of the molecules decay to the + parity component of the $a^3\Pi_1(v = 0, J = 1)$ level (with positive Stark effect) and can thus be focused, while the other molecules, decaying to levels with a small or negative Stark effect, are deflected much less efficiently or are even defocused by the hexapole. For this reason the peaks originating from the + parity component of the $a^3\Pi_1(v = 0, J = 1)$ level are strong and the spectrum deviates from that obtained for a field free situation.

From the REMPI spectrum in Fig. 3 the relative population in the different rotational levels of the $a^3\Pi(v = 0)$ state can be deduced. The ratio of the total population in the $v = 0$ state ($N_{v=0}$) to the total population in the $v = 1$ state ($N_{v=1}$) is obtained by comparing the corresponding REMPI spectra. The resonant step in the REMPI process is saturated and it is assumed that the ionization probability for the $a^3\Pi(v = 0)$ level (via the $b^3\Sigma^+(v = 0)$ level) is the same as that of the $a^3\Pi(v = 1)$ level (via the $b^3\Sigma^+(v = 1)$ level). After correction for the energy of the ionization laser and for the intensity of the metastable CO beam, the ratio $N_{v=0}/N_{v=1}$ is calculated to be $N_{v=0}/N_{v=1} = (4.2 \pm 1.0) \times 10^{-3}$.

From the time evolution of this ratio, now measured for the unfocused molecular beam (hexapole switched off and beamstop removed), the radiative (IR) vibrational relaxation rate for CO in the $a^3\Pi$ state can be determined for the field free situation. The time evolution can be probed by using different carrier gasses, i.e. different velocities of the molecular beam. The right part of Fig. 3 shows the experimentally determined ratio (circles with error bars) as a function of time delay between the preparation of metastable CO molecules and ionization in the UHV chamber 72 cm downstream from the excitation region.

From the rate equations for this system the ratio $N_{v=0}/N_{v=1}$ is calculated to be

$$N_{v=0}(t)/N_{v=1}(t) = \frac{\gamma_{10}}{\gamma_0 - \gamma_1 - \gamma_{10}}$$

$$\times\left(1 - e^{-(\gamma_0 - \gamma_1 - \gamma_{10})t}\right) \qquad (1)$$

in which γ_i is the radiative relaxation rate of metastable CO molecules in the vibrational level
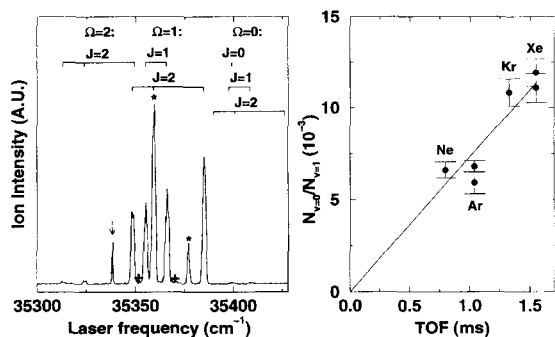
Fig. 3. Left: REMPI spectrum showing the relative population of the rotational levels in the $a^3\Pi(v = 0)$ state present in the incoming pure beam of metastable CO molecules (hexapole on, Ar seed gas). The (J, Ω) quantum numbers of the − parity levels of the $a^3\Pi$ state probed in the b ← a transition are indicated on top of the spectrum. The peaks indicated with * and + originates from the + parity levels of $J = 1$ and $J = 2$ in the $\Omega = 1$ component. The narrow peak indicated by an arrow is probably due to the much weaker (non-saturated) $a'^3\Sigma^+(v = 34) \leftarrow a^3\Pi(v = 1)$ transition. Right: The experimentally determined ratio of the total population in the $v = 0$ state ($N_{v=0}$) to the total population in the $v = 1$ state ($N_{v=1}$) of CO ($a^3\Pi$) in the incoming beam versus the time after laser preparation in the $v = 1$ state. The hexapole is switched off and the beamstop is removed.

$v = i$ to the electronic ground state, and γ_{10} is the radiative (IR) vibrational relaxation rate of metastable CO molecules in the $v = 1$ state to the $v = 0$ state. The electronic radiative relaxation rate of the $a^3\Pi$ state is expected to be large compared to the vibrational relaxation rate, and is calculated to be almost the same for the $v = 1$ and $v = 0$ levels ($\gamma_0 \approx \gamma_1 \approx$ 300 s^{-1} [24]). For this reason the term in the exponent is small and $N_{v=0}(t)/N_{v=1}(t)$ can be approximated by $\gamma_{10}t$. The straight line in the right-hand part of Fig. 3 is the best fit of this model through the experimental data points. The slope of this line corresponds to an IR vibrational relaxation rate of $\gamma_{10} = 7.4 \pm 1.1$ s^{-1}.

The vibrationally inelastic channel of the scattered metastable CO molecules is probed by performing a scan for the scattered beam. It is observed that only a small fraction of the scattered metastable molecules ends up in the $v = 0$ state. The spectrum is sampled by summing the ion signal over 10^4 laser pulses on top of and in between several bandheads. The data points of the sampled spectrum are indicated in Fig. 4 by the circles with error bars. For comparison, the solid line shows the REMPI spectrum that was measured for the scattering of metastable CO molecules in the vibrational ground state [16,17], recorded un-
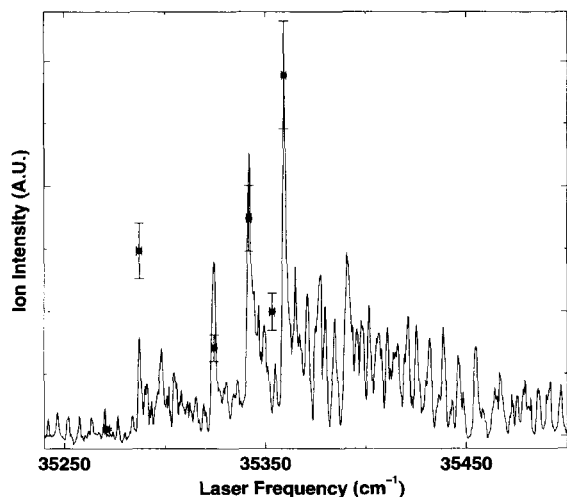

Fig. 4. The spectrum of vibrationally deexcited metastable CO molecules is sampled on top of, and in between a number of bandheads (indicated by the circles with error bars). For comparison, the b($v = 0$) ← a($v = 0$) spectrum recorded for the scattering of CO $a^3\Pi(v = 0)$ [16,17] is indicated by the solid line.

der otherwise identical experimental conditions. The sampled spectrum tends to follow the solid line well. The fact that the relative intensity of the sampled spectrum does not always match the solid line, is most probably caused by a small detuning from the top of the bandhead; the experimental error in the laser frequency, indicated by the horizontal error bar, has a relatively large effect on the ion intensity.

The ion intensity of scattered metastable CO molecules in the $v = 0$ level is approximately 200 times weaker than the ion signal of scattered metastable CO molecules in the $v = 1$ state. This signal can, assuming the same (electronical) survival probability for molecules in the $v = 1$ and $v = 0$ states, completely be attributed to the fraction of metastable CO molecules in the $v = 0$ level in the incoming beam that is scattered from the LiF surface. In this case, the b($v = 0$) ← a($v = 0$) spectrum recorded for excitation to the $a^3\Pi(v = 1)$ state of CO must be similar to that recorded for the scattering of CO($a^3\Pi$, $v = 0$) because mainly the lowest two rotational levels of the $a^3\Pi_1(v = 0)$ state are populated after IR relaxation.

Thus we conclude that the vibrational relaxation channel upon collision with the LiF surface is at least two orders of magnitude slower than the electronic relaxation channel. From the strength of the ion signal of metastable CO molecules in the $v = 1$ state it is concluded that the absolute (electronic) survival probability for metastable CO molecules in the $v = 1$ level is in the same range (of the order of a few percent) as the survival probability for scattered metastable CO molecules in the $v = 0$ level. This implies that the vibrational deactivation probability of CO($a^3\Pi$, $v = 1$) upon collision with the LiF surface is below 10^{-3}.

4. Conclusions

We have presented experiments in which vibrationally and electronically excited molecules are scattered from a LiF(100) surface. Both the vibrationally elastic and vibrationally inelastic channels for the scattered metastable CO molecules are probed. The vibrational deactivation probability for this system is shown to be below 10^{-3}, indicating that the

electronic relaxation channel is at least two orders of magnitude faster than the vibrational relaxation channel. The radiative (IR) vibrational relaxation rate γ_{10} for the relaxation of CO molecules prepared in the $a^3\Pi(v = 1,\ J = 1)$ level to the $v = 0$ state is determined to be $7.4 \pm 1.1\ \text{s}^{-1}$.

In scattering experiments with CO $(a^3\Pi)$ in its vibrational ground state it has been observed previously that the translational and rotational temperatures of the scattered beam depend on the kinetic energy of the incoming beam, thereby indicating a direct scattering mechanism, although the observed broad angular distribution [16,17] points to a trapping-desorption process. The experiments reported here are in support of a direct scattering process; the small vibrational deactivation probability makes a significant contribution of a trapping-desorption channel highly unlikely.

Acknowledgements

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