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Characterisation of desorbing molecules by REMPI-TOF spectroscopy: the system $H_2(D_2)-V(100)+O$

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Abstract

The internal state distribution (rotation, vibration) and the translational energy distribution of state selected molecules can be measured with the help of a REMPI (resonance enhanced multi-photon ionisation)-TOF (time-of-flight) spectrometer. We have performed measurements of this type on hydrogen and deuterium molecules desorbing from an oxygen covered V(100) surface. The rotational state population of the hydrogen and deuterium molecules in the vibrational ground state exhibits an overpopulation for J < 3 and an underpopulation for 3 < J < 8. In addition we observe a slight overpopulation for J > 9 for desorbing deuterium. The calculation of the mean rotational energy $\langle E_{rot} \rangle$ leads in all cases to values significantly below the respective thermal equilibrium values (rotational cooling). For the vibrational state distribution we observe in all cases an overpopulation for molecules in the first excited vibrational state (vibrational heating). The translational energy distribution of desorbing deuterium strongly depends on the surface quality. On the flat, well annealed oxygen covered V(100) surface the mean translational energy of desorbing deuterium is hyperthermal, whereas the translational energy of molecules desorbing from a rough surface is closer to thermal. \bigcirc 2003 Elsevier Science Ltd. All rights reserved.

Keywords: REMPI; TOF; Laser spectroscopy; Hydrogen; Desorption

1. Introduction

The interaction of hydrogen with vanadium oxide has become a subject of considerable interest. It is well known that vanadium is able to absorb huge amounts of hydrogen and deuterium so that it is an interesting candidate for energy storage [1]. On the other hand vanadium is an important metal for heterogeneous catalysis [2]. Unfortunately, cleaning of the vanadium sample is very difficult. Therefore contaminated surfaces are

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mostly used for practical applications. There exist several papers dealing with the characterisation of contaminated vanadium surfaces [3,4] and adsorption on these surfaces [5,6].

We have focused on the desorption behaviour of hydrogen and deuterium from an oxygen covered V(100) surface. Using the REMPI-(resonance enhanced multi-photon ionisation) technique we have studied the rotational and vibrational state distribution of desorbing hydrogen molecules. With the time-of-flight (TOF) unit we can also obtain information on the translational energy of the state selected molecules. This should give us information on the particular potential energy

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surface which governs the adsorption/desorption process.

2. Experimental

The experimental set-up for the REMPI TOF spectroscopy will only be described briefly. A more detailed description is given elsewhere [6,7]. The laser system consists of a Nd:YAG pump laser and a dye laser which yields a pulsed tunable laser light between 600 and 620 nm. By the use of two non-linear optical crystals (KDP and BBO) we can finally produce a tunable laser radiation between 201.6 and 206.6 nm. The pulse length is 8 ns and the pulse energy of the 200 nm radiation amounts to $350-800 \,\mu$ J. The laser beam is steered into the ultrahigh vacuum chamber via four dielectric mirrors and focused in front of the sample with an achromatic lens.

The desorbing molecules are excited by the UVlaser radiation (200 nm) in a two photon process from the electronic ground state $(X^{1}\Sigma_{g}^{+})$ into the electronically excited state $E,F^{1}\Sigma_{g}^{+}$ [8]. Photons from the 300 nm laser radiation then ionise the molecules and the ions are accelerated onto a channel plate. The resulting multiplier signal is fed into a fast digital storage oscilloscope. Subsequently the data are transferred to a desktop computer. With typical acceleration voltages of 50 V the state selected ions can be detected with high efficiency, but one gets no information about the initial velocity distribution of the molecules. Therefore we have constructed a TOF unit which allows to detect weakly accelerated state selected ions with high sensitivity. The whole unit is differentially pumped by a turbo pump and a titanium sublimation cryo panel to obtain a sufficiently high pumping speed for hydrogen and deuterium. The molecular beam enters the detection chamber via an aperture of 4 mm diameter which is positively biased. This prevents the entrance of stray ions from the main chamber into the detection unit. The laser radiation entering the vacuum chamber via a quartz glass window is focused by a plano-convex quartz lens with a focus length of 100 mm. This lens is mounted on a linear feed-through in order to

optimise the laser focus position behind the entrance aperture. Behind the laser focus and opposite the aperture a set of three electrodes accelerates the generated ions into the TOF tube. At the end of the tube a high transparency grid prevents the penetration of the high negative supplied the channel potential to plate (-2000 V). The Chevron channel plate is positioned 90° off-axis. This configuration guarantees the minimisation of the detection and amplification of stray laser light and thermal radiation from the sample or the Knudsen source. The flight time of the excited and ionised molecules is determined by the initial translational energy and the acceleration voltage. The advantage of this detector type is that one can distinguish between the directly desorbed molecules and the molecules entering the laser focus from the background which also increases during desorption.

The V(100) sample has been prepared as described earlier [5]. After extended sputtering and heating an oxygen covered surface exists showing the well known (5×1) LEED pattern.

The sample was first dosed with atomic deuterium or hydrogen using an appropriate high efficiency doser [9,10]. This dosing procedure led to adsorption on the surface but also to absorption in the bulk of the vanadium sample. Several hundred monolayer equivalents of deuterium (hydrogen) could be dissolved in the vanadium sample easily. Afterwards the sample was heated to 950 K and the absorbed deuterium was desorbed isothermally at this temperature during REMPI-TOF analysis. The spectra obtained were calibrated by comparison with the spectra of Maxwellian beams of H₂ and D₂ originating from a Knudsen source, which can be positioned in front of the TOF unit, instead of the sample.

3. Results and discussion

The integration of the beam contribution in the TOF spectra allows to determine the relative population of the individual rotational and vibrational states of desorbing molecules. We have measured and evaluated TOF spectra for rotational states between J = 0-8 for the vibrational

ground state (v = 0) and J = 0-3 for the first excited vibrational state (v = 1) for H₂ molecules desorbing isothermally from an oxygen covered V(100) surface at 950K (see Fig. 1). From the signal intensities of the individual rotational states we can deduce the mean rotational energy. To do this in a quantitative way we have to take into account the wavelength dependent laser pulse energy and the ionisation probability of the rotational states. The latter can be obtained from measurements on a Maxwellian beam effusing from a Knudsen cell. It is common to represent the rotational-vibrational distribution N(J) in the form of a Boltzman plot $(\ln (N(J)/(g_n(2J+1))))$ vs. $E_{rot}(J)$, with J being the rotational quantum number, $E_{rot}(J)$ the rotational energy of the rotational state J and g_n the nuclear spin degeneracy (H₂: $g_n = 1$ for even and 3 for odd J; D_2 : $g_n = 2$ for even and 1 for odd J). The straight line in Fig. 1 represents the rotational state

distribution of a thermalised hydrogen beam of 950 K. Apparently the rotational state distribution of hydrogen molecules desorbing from the oxygen covered vanadium surface deviates from the Boltzmann distribution. The low J states up to J = 2 are overpopulated, whereas the high J states are underpopulated. A mean rotational energy of $\langle E_{\rm rot} \rangle = 35$ meV can be obtained from $\langle E_{\rm rot} \rangle = \Sigma N(J)E(J)$, corresponding to a mean rotational temperature of 410 K (rotational cooling). On the other hand a clear overpopulation of rotational states in the first excited vibrational state can be observed (vibrational heating).

The same measurements were done for deuterium desorbing isothermally from the same oxygen covered V(100) surface at 950 K. In this case we have evaluated TOF spectra for the vibrational ground state from J = 0 to 12 and for the first excited vibrational state from J = 0 to 6. In Fig. 2 the results are presented once again in the form of





Fig. 1. Boltzmann plot of the rotational state distribution of H_2 molecules (v = 0, J = 0-8 and v = 1, J = 0-3) desorbing from V(100)+O. The straight line represents the distribution of a Maxwellian beam at 950 K.

Fig. 2. Boltzmann plot of the rotational state distribution of D_2 molecules (v = 0, J = 0-12 and v = 1, J = 0-6) desorbing from V(100)+O. The straight line represents the distribution of a Maxwellian beam at 950 K.

a Boltzmann plot. The results are similar to the hydrogen measurements. We obtain an overpopulation for the low J states (up to J = 3) and an underpopulation for the rotational states J = 4-8. For higher J states we can observe again an overpopulation. From this data a mean rotational energy of $\langle E_{\rm rot} \rangle = 50$ meV corresponding to a mean rotational temperature of 580 K can be calculated. From the measurements of the first excited vibrational states we obtain once again a significant vibrational heating.

The observed over-representation of low and high J states, but the underpopulation of the intermediate J states can be explained by the superposition of two effects [11]. On the one hand there exists a rotational hindering for adsorption and desorption of molecules in higher J states, because the residence time in the favoured position for dissociation (molecule axis parallel to surface) is decreased. This effect is dominant for molecules in the cartwheel mode (rotational axis parallel to surface). On the other hand this hindering effect of the rotational motion is counterbalanced by the transfer of rotational energy to translational energy along the reaction-path which is caused by the stretching of the molecular bond. The larger J is, this mechanism becomes more effective because then a larger amount of rotational energy can be transferred to the translational motion [12,13]. This latter effect is dominant for molecules in the helicopter mode.

The vibrational degree of freedom plays an important role in the adsorption and desorption process too. A reason for this behaviour is again a conversion from vibrational energy into translational energy [12,14].

To measure the translational energy for state resolved D_2 molecules desorbing from V(100) + Othe potentials supplied to the three electrodes are in the range of a few volts. In Fig. 3 three different TOF spectra for the v = 0, J = 5 state are shown. All of them show a clear bimodal form. The peak on the right-hand side of the TOF spectra stems from molecules, which have not entered the laser focus directly and can be assigned to the background. Curve A in Fig. 3 is obtained from measurements of a Maxwellian beam of D_2 effusing from a Knudsen cell at 950 K for



Fig. 3. Time-of-flight spectra for state selected deuterium molecules (v = 0, J = 5) effusing from a Knudsen source (curve A) and desorbing from different V(100) + O surfaces at 950 K (curve B and curve C). For details see text.

comparison. The TOF distribution of desorbing deuterium molecules from an oxygen covered V(100) surface at 950 K is represented by curve B. From these two curves we can calculate a flight time difference of 1 µs. From measurements of the Knudsen source at different temperatures one can calculate a temperature difference of 920 K from this flight time shift, so that a beam temperature of desorbing D₂ molecules of T = 1870 K is obtained. Due to this result we can state that the translational energy of desorbing deuterium from V(100)+O is hyperthermal.

Dosing the well annealed V(100)+O surface with atomic deuterium over long time most probably leads to a roughening of the initially flat surface resulting in a TOF distribution which is closer to thermal (see curve C). This corresponds to the well known effect, that on a rough surface the activation barrier for adsorption is reduced [15].

4. Summary

The translational, rotational and vibrational state distribution of H₂ and D₂ molecules desorbing isothermally from a V(100) + O surface at 950 K was investigated with REMPI-TOF spectroscopy. The rotational state distribution of the desorbing molecules exhibits a deviation from the Boltzmann distribution. For both systems we observed rotational cooling resulting in a mean rotational energy $\langle E_{\rm rot} \rangle = 35 \,\mathrm{meV}$ for hydrogen and $\langle E_{\rm rot} \rangle = 50 \,\mathrm{meV}$ for deuterium, respectively. On the other hand, the first excited vibrational states are overpopulated compared with the equilibrium population corresponding to the surface temperature. The translational energy is also found to be hyperthermal, at least for a well annealed smooth surface. We can state that the adsorption/desorption system $H_2(D_2) - V(100) + O$ behaves like most of the highly activated systems which are characterised by translational heating, rotational cooling and vibrational heating of the desorbing molecules.

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