

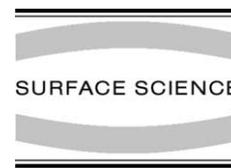


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Surface Science 537 (2003) L435–L441



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Surface Science Letters

Determination of the translational, rotational and vibrational degree of freedom for H₂ and D₂ desorbing from vanadium(1 0 0) + O

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Received 12 November 2002; accepted for publication 13 February 2003

Abstract

The rotational, vibrational and translational energy distribution for hydrogen (deuterium) molecules desorbing from a vanadium(1 0 0) + O surface have been determined using resonance enhanced multi-photon ionization time-of-flight spectroscopy. The translational energy has been found to be hyper-thermal for all selected internal states. However, the translational energy E_{kin} for molecules in $v = 1$ is smaller than for those in the vibrational state $v = 0$. The influence of the rotational states J on the translational energy is more complex: for low J -states E_{kin} increases with J , whereas for high J -states E_{kin} decreases with increasing J . We have also measured the population of the individual rotational and vibrational states of the desorbing H₂ (D₂) molecules: In both cases the first excited vibrational state is overpopulated. The population of the J -states is hyper-thermal for low and high J but sub-thermal for medium J .

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Keywords: Thermal desorption; Hydrogen molecule; Deuterium; Vanadium

1. Introduction

The detailed understanding of the microscopic processes governing adsorption and desorption is one of the most challenging goals in surface science. Recent progress in the experimental and theoretical treatment of this subject has revealed the influence of the translational, rotational and vibrational degrees of freedom in the interaction of gas molecules with solid surfaces. From the experimental point of

view resonance enhanced multi-photon ionization (REMPI) spectroscopy in combination with time-of-flight (TOF) spectroscopy has turned out to be a suitable method to obtain information on all degrees of freedom. It has been applied to several adsorption/desorption systems, but in particular to the model systems H₂ (D₂)–Pd(1 0 0) [1,2], D₂–Cu(1 1 1) [3,4] and H₂–Ag(1 1 1) [5]. On the other hand molecular dynamics simulations can be performed nowadays with high reliability which allow the determination of multi-dimensional potential energy surfaces (PES) governing the adsorption–desorption process. The state-of-the-art of these calculations has been described in several recent review articles [6–9].

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In this contribution we present experimental results concerning all degrees of freedom (translation, rotation, vibration) of H_2 and D_2 molecules following desorption from a $\text{V}(100) + \text{O}$ surface. The adsorption and desorption behavior of vanadium, vanadium alloys and vanadium oxides have recently attained considerable interest due to their promising properties for a number of modern technologies, like hydrogen storage [10], heterogeneous catalysis [11] or NEG pumping devices [12]. Vanadium surfaces are very difficult to prepare absolutely free of contaminants, in particular at elevated temperatures, due to the specific solution and segregation behavior. We therefore have focused on the oxygen covered $\text{V}(100)$ surface which should represent more closely the adsorption–desorption behavior of vanadium surfaces used for practical applications. In addition, this system has been shown to be highly activated with respect to hydrogen adsorption [13], which is a prerequisite to observe a significant influence of the individual degrees of freedom on adsorption/desorption. To our knowledge the investigation of all degrees of freedom of desorbing molecules, as described in this letter, has been performed in this completeness so far only by the IBM group for the activated adsorption systems $\text{H}_2\text{-Cu}(111)$ [3] and $\text{D}_2\text{-Cu}(111)$ [14].

2. Experimental

For the desorption experiments the $\text{V}(100)$ sample was first dosed with atomic deuterium or hydrogen using an appropriate high efficiency doser [15,16]. 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 (hydrogen) was desorbed isothermally at this temperature during REMPI-TOF analysis. The $\text{V}(100)$ sample was prepared and analysed as described earlier [13,17]. After sputtering and extended heating a stable oxygen covered surface is obtained exhibiting the well known (5×1) LEED pattern.

The experimental setup for the REMPI-TOF spectroscopy is described only briefly. More details can be found elsewhere [18,19]. The laser system consists of a Nd:YAG pump laser and a dye laser which yields pulsed tunable laser light in the 600 nm range. By frequency doubling and tripling with non-linear optical crystals we finally produce a tunable laser radiation in the 200 nm range. The hydrogen and deuterium molecules are excited by the 200 nm laser light in a two photon process from the electronic ground state ($X^1\Sigma_g^+$) into the electronically excited state $E, F^1(\Sigma_g^+)$ [20]. Photons from the 300 nm laser radiation finally ionize the molecules, which are entering the differentially pumped detection chamber via a 4 mm \varnothing aperture. The geometry of the sample-detector system is as follows: sample diameter: 10 mm, sample aperture distance: 15 mm, aperture–laser focus distance: 10 mm. Due to this design only molecules desorbing normal to the surface within an angle of less than $\pm 10^\circ$ are probed. The ions produced are weakly accelerated (few volts) by a specifically designed electrode system into the 27 cm long drift tube. After leaving the drift tube via a highly transparent grid the ions are detected by a Chevron channel plate, positioned 90° off-axis. The resulting multiplier signal is fed into a fast digital storage oscilloscope. The small acceleration of the ions yields a sufficiently high transmission probability, yet on the other hand the acceleration is small enough to get information on the initial translational energy distribution [5]. Moreover, one can clearly distinguish between molecules coming directly from the sample or from the randomized background.

3. Results and discussion

A typical state selected TOF spectrum for deuterium ($J = 4, v = 0$) desorbing from an oxygen covered $\text{V}(100)$ surface at 950 K is depicted in Fig. 1(a). One can clearly see the expected bimodal spectrum, resulting from the direct desorption flux and the randomized background gas. To discriminate between the direct beam signal and the background signal we have taken TOF spectra with the sample turned away from the detector aperture (Fig. 1(b)). The difference spectrum (after

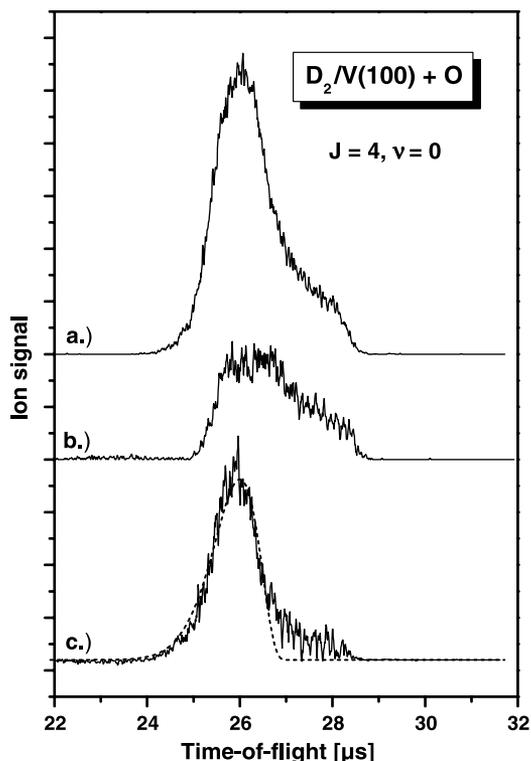


Fig. 1. (a) State selected time-of-flight (TOF) spectrum ($J = 4$, $v = 0$) for deuterium molecules desorbed from V(100)+O at 950 K. (b) TOF spectrum of background gas. (c) Difference spectrum representing the desorbed molecules only. The smooth curve in (c) is a best fit to the data, using a special function for the TOF distribution, yielding a beam temperature of $T = 1525$ K.

proper scaling of the background spectrum) yields the TOF spectrum for the desorbing molecules (Fig. 1(c)). At first sight it might look odd that the background spectrum is also made up of two contributions (bimodal curve). Monte Carlo simulations have shown, that the actual flight time of an ion produced in the laser focus not only depends on the initial velocity and on the acceleration voltage, but also on the initial velocity component with respect to the accelerating electric field (parallel or anti-parallel). This leads to a symmetric bimodal curve for an isotropic gas ionized in the laser focus. In our particular case, however, please have in mind that gas from the main chamber has to enter the detector chamber through the aperture to produce the “background

situation”. This leads to a non-isotropic distribution of deuterium molecules entering the laser focus, and therefore to the asymmetric bimodal spectrum for the background situation.

The smooth dashed line in Fig. 1(c) is a fit to the experimental data using an analytic expression for the TOF curve. The TOF distribution function $g(t)$ has been obtained by solving a cubic equation involving the initial velocity distribution $f(v)$, the acceleration voltage U and some geometric parameters describing the TOF unit. The calculations have been performed with the computer program *MATHEMATICA*, the resulting expression for $g(t)$, however, is too complex to be presented in this letter. Nevertheless, the shape of the calculated TOF spectrum, with T as the only fit parameter (apart from a scaling parameter for the Y -axis), reproduces the experimental data nicely. In this particular case the best fit is obtained with a beam temperature of 1525 K, with $\langle E \rangle = 2kT_{\text{beam}}$. Another frequently used characterisation of the mean energy is $\langle E \rangle = nkT_{\text{surface}}$, which yields $n = 3.2$ in the present case. This shows that the mean translational energy for desorbing deuterium in the rovibrational state $J = 4$, $v = 0$ is significantly larger than the thermal value corresponding to the surface temperature (950 K). In addition to the fit procedure as described above we have calibrated the obtained TOF spectra by comparing with TOF spectra of a thermalized beam originating from a Knudsen source.

Using these procedures we have measured and evaluated TOF spectra for desorbing hydrogen in the vibrational ground state ($v = 0$) and rotational states $J = 0$ through 8, as well as H_2 molecules in the first excited vibrational state ($v = 1$) and $J = 0$ through 3. In the same way we have studied desorbing deuterium for $v = 0$ and $J = 0$ through 12, as well as $v = 1$ and $J = 0$ through 6. From the data set obtained we can determine the relative population of the individual rovibrational states, in addition to the state selected translational energy. To do this in a quantitative way we have to take into account the wavelength dependent laser pulse energy and the ionization probability of the rotational states. The latter has been obtained from measurements on a Maxwellian beam effusing from a Knudsen cell. It is common to represent the

rovibrational distribution $N(J)$ in the form of a Boltzman plot $\ln(N(J)/(g_n(2J+1)))$ vs. $E_{\text{rot}}(J)$, with J being the rotational quantum number, $E_{\text{rot}}(J)$ the rotational energy of the rotational state J and g_n the nuclear spin degeneracy (H_2 : $g_n = 1$ for even and 3 for odd J ; D_2 : $g_n = 2$ for even and 1 for odd J). In Fig. 2 the Boltzmann plot for desorbing hydrogen is depicted. The straight line represents the rotational state distribution of a thermalized hydrogen beam of 950 K for comparison. Normalization of both data sets has been made in such a way that in both cases the sum of the molecules in all rotational states is unity. Apparently the rotational state distribution of hydrogen molecules desorbing from the oxygen covered vanadium surface deviates significantly 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 $\langle E_{\text{rot}} \rangle =$

35 meV can be obtained from $\langle E_{\text{rot}} \rangle = kT_{\text{rot}} = \sum N(J) \cdot E(J)$, corresponding to a mean rotational temperature of 410 K, at a surface temperature of 950 K (rotational cooling). On the other hand a clear overpopulation of the first excited vibrational state can be observed (ninefold overpopulation, vibrational heating). The mean translational energy for desorbing H_2 from $\text{V}(100) + \text{O}$ as a function of the rotational states in $v = 0$ is shown in Fig. 3. Interestingly, the mean kinetic energy not only is hyper-thermal in all cases, but additionally increases with increasing J -state.

The same data acquisition and evaluation procedure has been performed for desorbing deuterium molecules too. Due to the smaller spacing of the rotational energy levels a larger number of J -states can be investigated. In Fig. 4 the rotational state population is presented once again in form of a Boltzmann plot. The results are similar to the

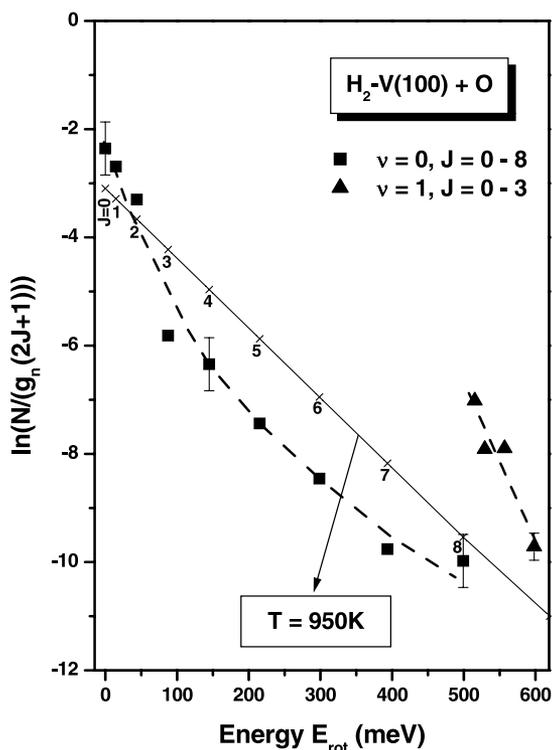


Fig. 2. Boltzmann plot for desorbing hydrogen from $\text{V}(100) + \text{O}$ in $v = 0$ and $v = 1$. The thin straight line represents the Boltzmann distribution for a 950 K gas. The dashed lines should guide the eye.

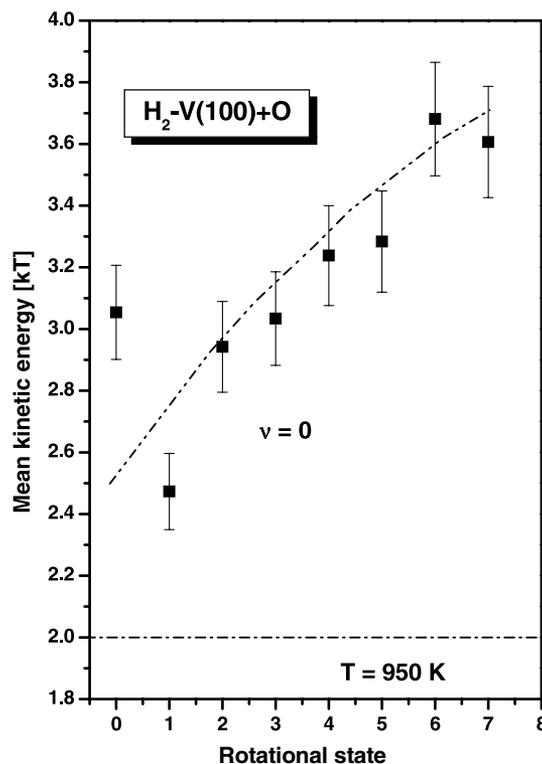


Fig. 3. Mean kinetic energy in terms of 2 kT for hydrogen molecules desorbing from $\text{V}(100) + \text{O}$, as function of the rotational state J .

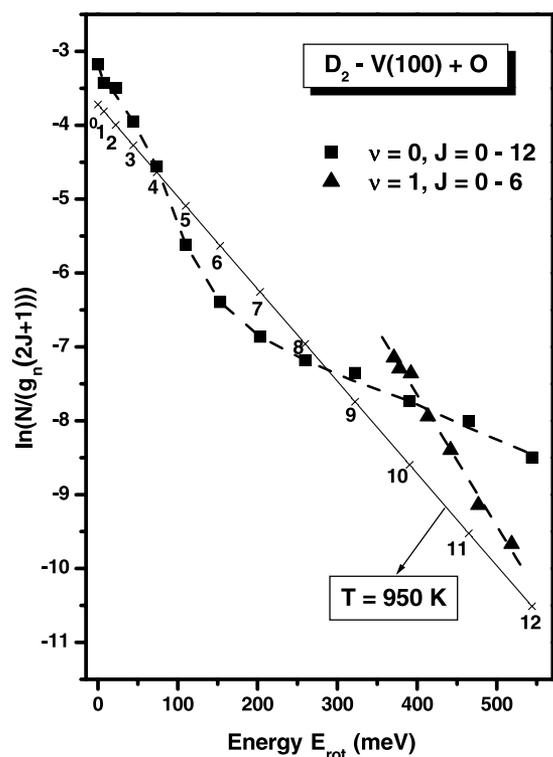


Fig. 4. Boltzmann plot for desorbing deuterium from V(100)+O in $v=0$ and $v=1$. The thin straight line represents the Boltzmann distribution for a 950 K gas. The dashed lines should guide the eye.

hydrogen measurements. We obtain an overpopulation for the low J -states (up to $J=3$) and an underpopulation for the rotational states $J=4$ through 8. However, for higher J -states we observe again an overpopulation. From these data a mean rotational energy of $\langle E_{rot} \rangle = 50$ meV corresponding to a mean rotational temperature of 580 K can be calculated (surface temperature 950 K). The first excited vibrational state again exhibits a clear overpopulation, compared with the thermal distribution (fourfold overpopulation). The state selected translational energies for deuterium from V(100)+O are summarized in Fig. 5. Qualitatively the results are similar to the hydrogen case; the mean kinetic energy again is hyper-thermal in all cases. However, interesting additional features can be observed, due to the population of more vibrational states. Whereas the mean kinetic energy increases again with increasing J -state up to $J=5$,

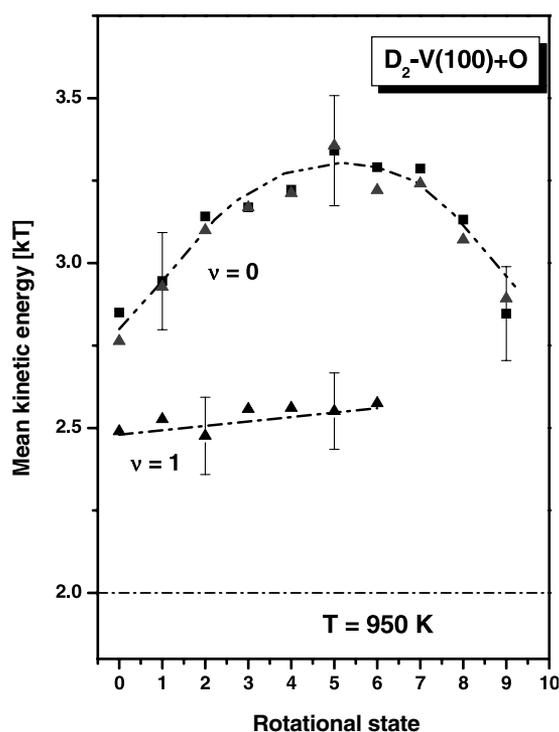


Fig. 5. Mean kinetic energy in terms of $2kT$ for deuterium molecules desorbing from V(100)+O, as a function of the rotational state J and vibrational state $v=0, v=1$.

the energy decreases in the higher J -state regime. The molecules in the first excited vibrational state (which in this case can also be evaluated with sufficient accuracy) exhibit clearly a lower, but still hyper-thermal mean translational energy.

The interpretation of these data is straightforward and can be done along the line of existing theoretical considerations (e.g. [6]): The adsorption-desorption system H₂ (D₂) on the oxygen covered V(100) is strongly activated. This is demonstrated by the low sticking coefficient for molecular hydrogen (deuterium) on this surface [13]. Therefore one can expect that all degrees of freedom should considerably influence the probability to overcome the activation barrier for adsorption-desorption. In terms of detailed balancing the enhancement of the sticking probability caused by a particular degree of freedom should correspond to an overpopulation of this degree of freedom in the desorption flux. The translational

energy in all cases observed so far for activated systems has a promoting effect in adsorption [4,21] and therefore a hyper-thermal population of the translational energy distribution has to be expected in the desorption flux. The dependence of the mean kinetic energy on the rotational and vibrational state exhibits a coupling of all degrees of freedom in the adsorption–desorption process. This is nicely demonstrated in the opposite trend of the rotational state population and the mean translational energy of the corresponding rotational states (Figs. 4 and 5). In the low J -state regime an increase of the rotational energy leads to a decrease in the rotational state population (Fig. 4). Invoking detailed balancing this corresponds to a decrease of sticking (increase of effective activation barrier). According to Darling and Holloway [6] this is caused by orientational hindering (geometric effect). It means that there is an increasing inability to follow the minimum path for dissociative adsorption with increasing rotational energy (hindered steering). However, this decrease of sticking can be compensated by an appropriate increase of translational energy, as seen in Fig. 5. For higher J -states the energy effect dominates the influence of rotation, in which rotational energy is converted into translational energy during traversing of the activation barrier. Therefore, in this J -range less translational energy is needed to overcome the barrier. It should be noted that the orientational hindering mostly effects molecules in the cartwheel mode, whereas the energy effect is more operative to molecules in the helicopter mode [6]. If we compare the results of Figs. 2 and 5 it is obvious that for the hindering or promoting effect the *rotational quantum number* is more important than the *rotational energy*. For example D_2 and H_2 molecules in the rotational state $J = 8$ are both underpopulated, with rotational energies of 499 meV (H_2) and 259 meV (D_2), respectively. On the other hand, the $J = 11$ state for deuterium, with $E_{\text{rot}} = 465$ meV (comparable to $J = 8$ of hydrogen), is already clearly overpopulated.

A similar explanation as to the correlation between rotation and translation can be given for the observed influence of vibration. Desorbing molecules in the first excited vibrational state exhibit

lower translational energy than those in the vibrational ground state, but the population of the first excited vibrational state is hyper-thermal. It has been shown both experimentally [22] and theoretically [7] that vibration helps to overcome a barrier for dissociative adsorption in all cases. It is again a result of the strong coupling between vibrational energy and translational energy in the reaction path close to the activation barrier. Therefore a molecule in an excited vibrational state needs less translational energy to overcome the barrier, and hence the mean translational energy in the desorption flux is smaller than for the ground state molecules. According to the same arguments the population of the $v = 1$ state in the desorption flux has to exceed that of the corresponding thermal population.

4. Summary

The results obtained in this work for the activated adsorption/desorption system H_2 (D_2)– $V(100)+O$ can be summarized as follows: Desorbing deuterium (hydrogen) molecules exhibit a hyper-thermal translational energy distribution. The mean translational energy is larger for molecules in the vibrational ground state than that for the first excited vibrational state, indicating the strong coupling between these two degrees of freedom. The relation between rotation and translation is more complicated. Whereas for low J -states the translational energy increases with increasing J , this correlation is reversed for high J -states. This is due to geometric hindering for low J and rotation–translation energy conversion for high J -states. All the results are comparable to those obtained for the adsorption system H_2 – $Cu(111)$ [3] and D_2 – $Cu(111)$ [14]. We would therefore like to stress that the observed features seem to be of general validity for activated adsorption–desorption systems.

Acknowledgements

This work has been supported by the Austrian “Fonds zur Förderung der wissenschaftlichen Forschung”, Project no. P13570 and S8102-PHY.

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