Rotational Alignment in Associative Desorption of $D_2(v'' = 0$ and 1) from Pd(100)

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We report the first measurement of the preferential steric orientation of D_2 molecules associatively desorbing from a metal surface. The flux of D_2 desorbing from Pd(100) is probed by laser induced fluorescence with linearly polarized tunable vacuum ultraviolet radiation in the $B\,^1\Sigma_u^+(v', J', M') \leftarrow X\,^1\Sigma_g^+(v'', J'', M'')$ Lyman bands. In $(v'' = 0)$ an increasing positive alignment with rotational quantum number is observed up to $J'' = 6$, establishing the preferred helicopter motion of the molecules. In $(v'' = 1)$ and also for $(v'' = 0, J'' = 7$ and 8) an isotropic J vector distribution is measured.

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The dynamical processes which govern the associative desorption and its counterpart, dissociative adsorption, of hydrogen on transition metal surfaces are of general interest for the understanding of catalytic reactions on surfaces. Molecular beam studies of the dissociative adsorption behavior on palladium [1,2], tungsten [3,4], and platinum [5] single-crystal surfaces show that the initial sticking probability exhibits a minimum as the kinetic energy of the hydrogen molecules is increased. This behavior is often interpreted as precursor mediated adsorption. Internal state selective studies revealed an enhanced vibrational population for desorption from Pd(100) [6], similar to the desorption of hydrogen from copper single-crystal surfaces [7,8]. This behavior could be reconciled by quantum mechanical calculations showing a late barrier in the dissociative adsorption potential, although with a considerably lower barrier height than in copper [6]. The rotational population distribution in the desorption flux has been measured earlier in our group [9]. It always showed lower rotational temperatures than the surface temperature. An interpretation of this behavior predicts a specific steric orientation of the molecular axis during desorption [10]. Similarly, interpreting the rotational state dependence of the velocity of H_2 and D_2 desorbing from Cu(111) [11], combined with the observed rotational-translational coupling, leads to the prediction of a preferential orientation of the molecular rotational axis parallel to the surface normal.

Very recently a potential energy surface for the H_2/Pd(100) system has been derived from density functional theory [12]. It shows activated as well as nonactivated pathways for dissociative adsorption, without any molecular precursor potential well. On this potential energy surface, Gross, Wilke, and Scheffler [13] performed the first six-dimensional quantum calculation for the dynamical behavior of a hydrogen/metal system. They could reproduce the main experimentally observed features very well: the decrease of the initial sticking coefficient with kinetic energy and the rotational cooling in desorption. A key element of this potential energy surface and their dynamical calculation is the steering of slow hydrogen molecules onto adsorption paths which do not show a barrier. In this calculation Gross, Wilke, and Scheffler predicted differences in the sticking coefficient of molecules with their rotational axis parallel and perpendicular to the surface normal, so-called helicoptering and cartwheeling rotational motion, respectively. This difference showing the preferred sticking of helicoptering molecules increases with rotational quantum number. In this study we report the first experimental proof of this prediction for a hydrogen/metal system.

A detailed description of the experimental setup has been given previously [9]. Briefly, the experiments are performed in an ultrahigh vacuum chamber pumped by turbomolecular and titanium getter pumps to a base pressure of less than 2×10^{-10} mbar. Order and cleanliness of the surface are determined by low-energy electron diffraction (LEED) and Auger spectroscopy, respectively. When necessary, adsorbates are removed by Ar^+ ion sputtering at low energy and current density. After sputtering the surface is annealed before an experimental run. Deuterium atoms are supplied to the surface by atomic permeation through the 1 mm thick Pd(100) single crystal. The sample is radiatively heated to constant temperatures of $T_s = 690$ and 900 K for measurements of vibrationally ground and excited state D_2 molecules, respectively. The continuous desorption flux from the permeation source gives rise to an average deuterium partial pressure in the chamber leading to a background signal from molecules which reenter the detection volume after having encountered wall collisions. Since the alignment of these molecules is different from those desorbing, this background has to be accounted for, which is achieved by moving the sample out of the measurement position under otherwise identical conditions.

Rotational state selective detection of desorbing molecules is performed by electronically exciting D_2 in the $B\,^1\Sigma_u^+(v', J', M') \leftarrow X\,^1\Sigma_g^+(v'', J'', M'')$ Lyman bands with vacuum ultraviolet (VUV) light tunable around $\lambda = 106$ and 110 nm. The tunable VUV radiation is generated by nonresonant frequency tripling of tunable UV laser radiation in xenon or krypton gas

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[9]. The polarization of the VUV radiation is linear and parallel to that of the generating UV light. Changing thus the polarization of the UV light with a half-wave plate will concurrently change the polarization of the VUV probe laser radiation. The laser beam intersects the desorption flux at a distance of 15 mm in front of the palladium surface, propagating parallel to the surface. In the interaction region about 1×10^{10} VUV photons per pulse are available with a spectral bandwidth of about $2.0\ \mathrm{cm}^{-1}$. The fluorescence from the B state is detected without polarization selection at right angles to the laser beam and the surface normal by a solar blind photomultiplier (EMR, 542 G-08-17). Figure 1 specifies the excitation and detection geometry. The surface normal **n** serves as quantization axis. The output of the photomultiplier is processed by a photon counting system and then transferred to a microcomputer.

The experimental setup is tested by measuring the relative fluorescence intensities of several rotational lines in isotropic gas phase D_2 at various angles between the probe laser electric vector **E** and the surface normal **n**. Measurements at every 10° of their relative angle show the theoretically predicted angular dependence, which arises due to the polarization insensitive fluorescence detection. The deviations between the measured and the predicted intensities are less than 5% at each individual angle setting and rotational line [14]. Information about the rotational alignment of the desorbing molecules is obtained by measuring the fluorescence intensity with the VUV probe laser polarized parallel ($I_\parallel$) and perpendicular ($I_\perp$) to the surface normal. This yields the molecular polarization P given by $P = (I_\parallel - I_\perp)/(I_\parallel + I_\perp)$. Following Greene and Zare [15] these intensities are related to the alignment factors for cylindrical symmetry $A_0^{(k)}$ via

$$I = SC \sum_{k_a,k_d,k} A_0^{(k)} \varepsilon(k_a, k_d, k, 0; \Omega)\, \omega(k_a, k_d, k; J_i, J_e, J_f)\,, \tag{1}$$

where S is the product of the Hönl-London factors of the participating transitions from the initial state J_i to the electronically excited state J_e, and further from this state to the final rotational state J_f populated via the fluorescence. C is proportional to the population in the initial state, and ω denotes the angular momentum coupling factor, which can be obtained from Eqs. (8) through (12) of Ref. [15]. The $\varepsilon(\Omega)$ factors are based on the excitation and detection geometry for cylindrical symmetry and are tabulated in Ref. [15]. The summation runs over all possible combinations of the multipole moments k_a and k_d of the absorbed and detected photons, respectively. k is the multipole moment of the combined transition. When the emitted fluorescence is not analyzed with respect to its polarization, as in this case, one has to sum over the two polarization directions of $\varepsilon(\Omega)$. Equation (1) has to be evaluated for $I_\parallel$ and $I_\perp$. The quadrupole alignment factor $A_0^{(2)}$ is then connected to the experimentally determined molecular polarization P via

$$A_0^{(2)} = (-a + bP)(c - dP)^{-1}, \tag{2}$$

where a, b, c, and d are linear combinations of the products of $\varepsilon(\Omega)$ and $\omega(k, J)$, which can easily be computed. Since the VUV probe laser beam is linearly polarized, only even components of the rotational alignment can be determined, i.e., the quadrupole $A_0^{(2)}$ and the hexadecapole $A_0^{(4)}$ moments in the lowest two orders. The signal-to-noise ratio in this experiment, however, does not permit the determination of $A_0^{(4)}$, which constitutes a correction of only a few percent to the $M_{J''}$ distribution described by $A_0^{(2)}$. A theoretical analysis shows that for a $^1\Sigma$-$^1\Sigma$ electronic transition the alignment is best analyzed via a P-branch excitation, because in this case $A_0^{(2)}$ depends more strongly on the molecular polarization than via the R branch [14].

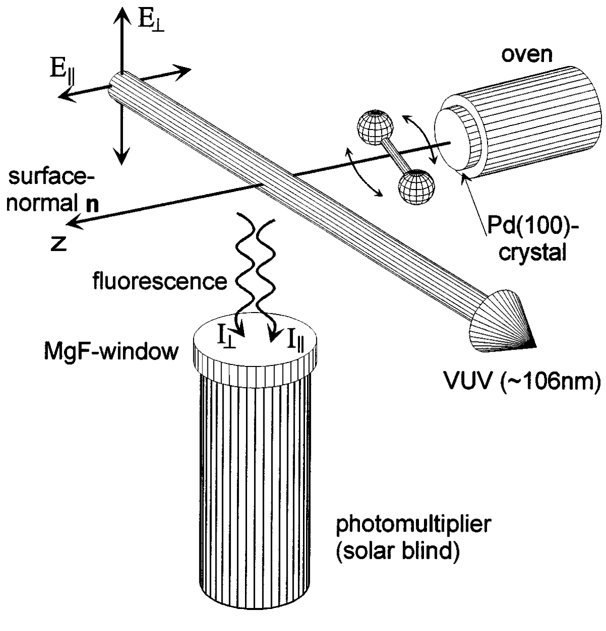

FIG. 1. Schematic diagram of the excitation and detection geometry.

The molecular polarization of D_2 molecules desorbing from Pd(100) in the vibrational ground state has been determined via $P(2)$ to $P(4)$ lines and the $R(5)$ line in the Lyman (4-0) band, the $P(6)$ line in the Lyman (1-0) band, and the $P(7)$ and $P(8)$ lines in the Lyman (2-0) band. The quadrupole alignment factor $A_0^{(2)}$ determined with Eqs. (1) and (2) from these measurements are shown by the filled squares in Fig. 2, upper panel. For $J'' = 2$ no alignment is observed within the experimental error bars. For higher rotational states a significant positive alignment is obtained, with a tendency to larger values for increasing J''. At $J'' = 5$ a value of $A_0^{(2)} = 0.47 \pm 0.18$ is measured. Surprisingly, the alignment disappears for $J'' = 7$ and 8, the highest rotational states which could be detected with sufficient signal-to-noise ratio. Alignment factors for deuterium desorbing in $(v'' = 1)$ are obtained

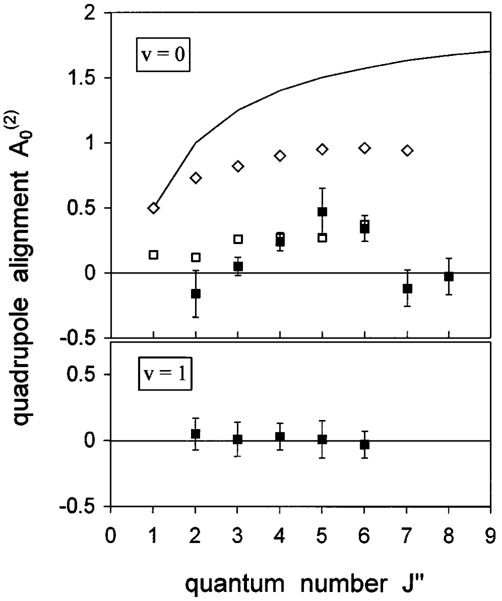

FIG. 2. Quadrupole alignment factor $A_0^{(2)}$ for D_2/Pd(100). (■) denote experimental values for ($v'' = 0$) at $T_s = 690$ K (upper panel) and for ($v'' = 1$) at $T_s = 900$ K (lower panel). Theoretical values are given for H_2/Pd(100) (□, Ref. [13]) and for D_2/Cu(111) (◇, Ref. [19]). The quantum mechanical maximal allowed values of $A_0^{(2)}$ are given as a solid line in the upper panel.

similarly via *P*(2) to *P*(5) lines and the *R*(6) line of the (4-1) Lyman band. The lower panel of Fig. 2 shows the experimental data. Within the statistical uncertainties, a rotational alignment of vibrationally excited molecules is not observed.

The positive alignment for ground state D_2 molecules implies that these molecules preferentially desorb with **J** parallel to the surface normal **n** in the so-called helicopter motion. An alignment value of $A_0^{(2)} = 0.47$ for $J'' = 5$ means that 66% of the molecules desorb with $|M_{J''}| > J''/2$ and 34% with $|M_{J''}| < J''/2$, the probability of desorbing in a helicoptering motion being thus twice as large as that in a cartwheeling motion. The increase of the positive quadrupole alignment up to $J'' = 5$ or 6 suggests a significant rotational-translational coupling for D_2/Pd(100), which mainly affects the cartwheeling motion. A similar selective coupling of the cartwheeling type of rotational motion to the desorption coordinate has been observed earlier by Zare and co-workers [16] for the isothermal desorption of NO from Pt(111). Although this constitutes dynamically a very different desorption process, they also observed an increase of $A_0^{(2)}$ with *J* for rotational states $J'' > 12.5$. A maximum value of $A_0^{(2)} = +(0.17 \pm 0.04)$ at $J'' = 34.5$ was found. The vanishing of the alignment at $J'' = 7$ and 8 for D_2/Pd(100) is certainly not expected. These molecules have 203.46 and 259.96 meV of rotational energy, respectively. The vanishing of the alignment can be understood when the energy exchange from the rotation to the reaction coordinate for *both* rotational motions is sufficiently large so that surmounting a small local barrier poses no hindrance. Alternatively it might be conceivable that these molecules preferentially desorb via nonactivated pathways. The density functional potential energy surface for H_2/Pd(100) shows both, local barriers with a maximal height of about 200 meV, thus lower than the rotational energy in these two states, and nonactivated adsorption paths [12,13].

The experimental results of the present study can be directly compared with the predictions of the six-dimensional quantum mechanical calculation. Gross, Wilke, and Scheffler [13] presented the initial sticking probability for molecules in $M_{J''} = 0$ (cartwheeling rotation) and in $M_{J''} = J''$ (helicopter rotation) states. From these probabilities we derived alignment coefficients, given as open squares in Fig. 2. We arrived at these values by approximating this two-level $M_{J''}$ population for the other $M_{J''}$ states by $\cos^2\theta_{J''}$. These values are close to those obtained by Gross in a preliminary quantum mechanical calculation [17]. Good agreement with the experimental data is obtained considering the fact that only two $M_{J''}$ levels in the calculation, performed for H_2 and a single kinetic energy of 190 meV, have been taken into account. This kinetic energy is significantly higher than the average kinetic energy of about 146 meV of the desorbing molecules in this experiment which follow a Maxwellian velocity distribution [18]. Also shown in Fig. 2 (open diamonds) are results obtained by Brunner and Brenig with a two-dimensional quantum calculation for D_2/Cu(111) [19]. Their alignment factors are generally higher, approaching $A_0^{(2)} = +0.96$ at higher J''. Other calculations performed for the hydrogen/copper system arrived also at high alignment values of $A_0^{(2)} = +1.13$ for $J'' = 4$ [20] and of $A_0^{(2)} = +0.77$ for $J'' = 5$ [21]. Both calculations were performed at an incident kinetic energy of 0.6 eV. The large alignment for this system, also in comparison with the quantum calculation for the Pd(100) surface, may be caused by the much higher adsorption barrier for hydrogen adsorption on copper compared to that on palladium. This conjecture is supported by our finding that D_2 molecules desorbing in ($v'' = 1$) show only isotropic *J* vector distributions. The internal energy in $D_2(v'' = 1)$ due to vibration is about 0.375 eV. Together with the translational energy of about 146 meV the total energy is much higher than the maxima of the energy barrier ($E_b \sim 0.2$ eV) of the hydrogen/palladium potential energy surface. A steric hindrance of the adsorption of such molecules is not to be expected when the efficacy of the vibration to promote sticking is at least 15%, a requirement much lower than what has been observed for H_2/Cu(111) [8]. For the hydrogen/copper system with its much higher barrier a dependence of the rotational alignment on the vibrational state may thus be expected.

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