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Rotational alignment in the UV-laser induced desorption of CO from $Cr_2O_3(0001)$

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Abstract

The rotational alignment of the laser-induced non-thermal desorption of CO adsorbed on an epitaxially grown film of $Cr_2O_3(0001)$ has been studied using 193 nm (6.4 eV) laser light and a $(1 + 1')$-REMPI technique. At low rotational quantum numbers J the molecules desorb like a 'helicopter' (J-vector perpendicular to the surface) while at high J-values a 'cartwheel' like motion is preferred (J-vector parallel to the surface). CO is adsorbed in a flat geometry as a single species. The resulting angular momentum alignment in the laser desorption is interpreted qualitatively as a sum of effects due to corrugation of the surface in the initial state and a change of the adsorption geometry in the intermediate state before desorption.

1. Introduction

As the electronic structure of adsorbate/substrate systems is complex electronically induced photochemical processes on surfaces are very involved. This is a reason why the improvement of the understanding of such processes has been much slower than for isolated molecules in the gas phase. A number of recent review articles and proceedings document the actual status of the field [1–3]. Major contributions for obtaining insight into the elementary processes of photochemical reactions on surfaces have been experiments dealing with the quantum state resolved detection of simple molecules desorbing from well defined single crystal surfaces and related model calculations. More sophisticated calculations for which first examples on a first-principle basis including the excited state have been published [4,5] are still limited to simple systems.

Further insight from the experimental site can be obtained from stereodynamic information such as the angular momentum alignment in space as will be presented in this Letter. The occurrence of such alignment effects is a consequence of the geometry of the ground and intermediate excited states and the shape of the potential energy surfaces involved. In the gas phase stereodynamic studies of photochemical processes have been standard now for over a decade [6–8]. In processes involving solid surfaces similar methods have been used only to a limited extent. The most elaborate studies of angular momentum alignment and orientation in processes at surfaces exist for sophisticated scattering experiments [9–18] which were treated theoretically as

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well [19–22]. The rotational alignment of the thermal associative desorption of D_2/Pd(100) [23] was used to test model calculations on scattering experiments of the H_2/Pd(100) system [22]. Thus it may come as a surprise that in photochemistry on surfaces aspects concerning rotational anisotropy in space have been neglected so far. Only recently has the first successful detection of angular momentum alignment in a photochemical process on a single crystal surface has been reported for the CO/Si(100) system [24]. However, an unambiguous interpretation of these measurements is difficult as there is a lack of information on the initial adsorption geometry for this system. Furthermore, the existence of two species on the surface makes the interpretation of their data more difficult.

In this Letter we shall report the successful detection of an anisotropic spatial distribution of the angular momentum for the CO/Cr_2O_3(0001) system in which only a single species with a flat adsorption geometry exists in the ground state [25]. One of the major motivations for choosing this system is that pronounced effects are expected concerning a helicopter (J-vector normal to the surface) or a cartwheel like desorption (J-vector parallel to the surface) depending on the geometry of the intermediate excited state for a system with such a particular bonding geometry.

2. Experimental

The experiments were carried out in a UHV-chamber of which details are given elsewhere [26]. The preparation chamber was equipped with an X-ray photoelectron spectrometer (XPS), a low-energy electron diffraction facility (LEED), an Auger electron spectrometer (AES) and a quadrupole mass spectrometer for residual gas analysis and thermal desorption spectroscopy (TDS). Neon-sputtering was used to clean the single crystal Cr(110) surface. Heating of the crystal was done via electron bombardment and cooling via a liquid nitrogen reservoir allowing temperatures down to 100 K. The epitaxial film of Cr_2O_3(0001) was grown by oxidizing the Cr(110) sample in an atmosphere of 10^{-6} Torr of oxygen at 500 K and annealing of the film at 1000 K.

CO molecules were desorbed at $\lambda = 193$ nm ($h\nu = 6.4$ eV) with 15 ns pulses of a broad band excimer laser (Lambda Physik EMG 200) impinging normal to the surface with a typical laser fluence of 1 mJ/cm^2 per pulse. Desorbing molecules were detected state selectively after a well defined time delay between desorption and detection using a (1 + 1')-REMPI (resonance enhanced multiphoton ionization) scheme via the $B\,^1\Sigma^+$ state [27]. The detection laser, an excimer laser (XeCl, Lambda Physik LPX 205 i cc) pumped dye laser (Lambda Physik LPD 3002) was run parallel to the surface at a distance of 29 mm. The necessary VUV-laser light for the first excitation step of the REMPI-process at 114.5–115.2 nm was generated via non-linear frequency tripling by focussing the detection laser into a cell filled with 75 Torr of xenon. The photon for the second excitation step corresponded to the fundamental at $\lambda =$ 344–345.5 nm. The emerging VUV light was focussed together with the fundamental via a LiF lens ($f = 50$ mm at 248 nm) into the center of the chamber to excite the desorbing CO. The ionized molecules were detected by a detector consisting of a repeller, a flight tube, a microchannel plate and a phosphor screen.

The original dye laser light as well as the frequency tripled light was already more than 90% planar polarized. 100% of polarization could be obtained with a Glan laser prism. As the prism absorbs a high percentage of the incoming light and as the VUV laser light production is dependent to the third power on the intensity of the fundamental frequency, in experiments with low signal the polarization prism was omitted to optimize the signal to noise ratio. With the aid of a $\lambda/2$ plate the polarization of the laser light could be rotated from vertical to horizontal polarization. The intensity for one setting of laser polarization was measured by averaging over 1000–1500 laser pulses to obtain alignment information. For time of flight measurements averaging over 300 pulses was done per time delay.

The experiments were performed under a steady state coverage of CO in the submonolayer regime by redosing the surface prior to each laser pulse via a background pressure of 2×10^{-7} Torr in most of the experiments. The background signal was subtracted from the desorption signal by running the detection laser with twice the frequency (4 Hz) as the desorption laser (2 Hz) and feeding the signal into a boxcar integrator run in toggle mode.

3. Analysis

The experiments reported here concern the measurement of the alignment of the total angular momentum vector $\boldsymbol{J}$ consisting of nuclear rotation $\boldsymbol{N}$, orbital angular momentum $\boldsymbol{L}$ and electron spin $\boldsymbol{S}$ in relation to the surface normal $\boldsymbol{Z}$. The projection of $\boldsymbol{J}$ onto the space-fixed symmetry axis, the surface normal, is given by the quantum number M_J. A non-uniform distribution within the M_J-values means that the rotation is anisotropic in space. One must distinguish between *orientation* (helicity of the rotation) where the population of the positive M_J values is different from the negative ones and *alignment* where the population of high $|M_J|$ values is different from low values. In the classical limit which is reached for high J values the most probable expectation value of the projection of $\boldsymbol{J}$ onto the surface normal is represented by the quadrupole moment as (like all higher even multipoles) a measure of the rotational alignment. It is defined as twice the expectation value of the second order Legendre polynomial with respect to the projection of the angular momentum vector $\boldsymbol{J}$ on the cylindrical symmetry axis $\boldsymbol{Z}$ [6–8]:

$$\begin{aligned} A_0^{(2)}(J_i) &= 2\langle P_2(\hat{\boldsymbol{J}}\cdot\hat{\boldsymbol{Z}})\rangle \\ &= \langle J_i|3M_J^2 - \boldsymbol{J}^2|J_i\rangle / J_i(J_i+1)\,. \end{aligned} \tag{1}$$

The index i indicates that the quadrupole moment may vary with $\boldsymbol{J}$. If the angular momentum vector is mainly oriented parallel to the surface normal and large values of M_J $(\alpha\, J)$ are populated the quadrupole moment will be positive with a maximum value of $+2$. A negative $A_0^{(2)}$ means that small values of M_J $(\ll J)$ are mainly populated. For the smallest value which is equal to -1 only $M_J = 0$ is populated (= cartwheel motion with $\boldsymbol{J} \perp$ to the surface normal). The number of molecules detected via the $(1+1')$ REMPI method will depend on the polarization of the electric field vector of the linear polarized light of the detection laser relative to the direction of the transition dipole moment of the molecule and thus of the alignment of the total angular momentum. If the distribution is anisotropic in space, a variation of the polarization plane of the detection laser light will lead to an intensity variation of the detected molecules. If the detection scheme implies cylindrical symmetry the population of J and the quadrupole moment $A_0^{(2)}$ can be obtained by measuring the signal for two independent planes of linear polarized light which shows the most pronounced effect for the plane of polarization oriented parallel and perpendicular to the surface normal [θ' (= 0°, 90°)]. The analysis of our data follows the vector approximation developed in the group of Zare in which the eigenstate $|J_i M_J\rangle$ is represented by an angular momentum vector $\boldsymbol{J}$ of length $[J_i(J_i+1)]^{1/2}$ that precesses about the $\boldsymbol{Z}$ axis at an angle γ with a constant projection M_J [6]. A rate model within the limit of a process saturated in the second step is assumed to obtain the final ion intensity [28,29]. From the intensity measurements the so-called polarization R can be calculated in order to extract the quadrupole moment:

$$R = \frac{I_\parallel - I_\perp}{I_\parallel - 2I_\perp}\,, \tag{2}$$

where $I_\parallel$ and $I_\perp$ are the $A_0^{(2)}$ dependent REMPI intensities measured with the probe laser polarization parallel and perpendicular to the surface normal. We approximate the REMPI-intensity of Eq. (2) following the formalism of Jacobs and Zare by

$$\begin{aligned} I_{(\parallel,\perp)} &= \tfrac{1}{2}\int_0^\pi \left[A_0^{(0)} + 2A_0^{(2)} P_2(\cos\gamma)\right] \\ &\quad \times F\left[k_{01}(\theta), k_{12}(\theta), I_L\tau_p\right] \sin\theta\, d\theta\,, \end{aligned} \tag{3}$$

where γ is the angle between the surface normal and molecular axis of rotation which is related via a trigonometric function to the angle between the polarization axis of the detection laser and the surface normal θ' (= 0°, 90°) and the angle between the laser polarization axis and the molecular axis of rotation θ [28]. The term containing k_{01} and k_{12}, the rate constants of the $(1+1')$-REMPI transitions, and $I_L\tau_p$, the intensity and pulse length of the probe laser, depends on the kind of transition (P, R or Q-type transition for example). In our case mainly the rate constant of the first step is relevant for the overall intensity as the second step is saturated. For this reason a dependence of the ionization probabil-

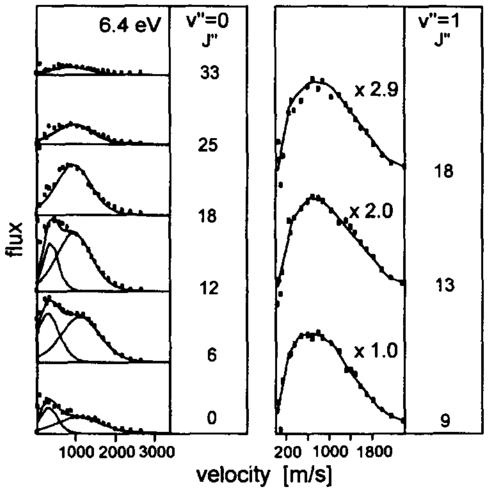

Fig. 1. Velocity flux distributions for $CO/Cr_2O_3(0001)$ for varying rotational quantum numbers, (a) $v'' = 0$, curves fitted with two Gaussian distributions, (b) $v'' = 1$, connecting line: guide for the eye.

ity of the intermediate electronic state on the intermediate M_J-states is also avoided. The quadrupole moment can be extracted from the experimental values by a substitution of the right- = hand term of Eq. (2) by Eq. (3) as described by Jacobs and Zare [28]. The term $(I_{\parallel} + 2I_{\perp})$ only depends on the monopole $A_0^{(0)}$ $(= 1)$ and can be used to extract the relative population of the rotational level J_i [28,29].

4. Results

Before discussing the rotational alignment measurements in more detail some information is necessary concerning the final state distributions, particularly the velocity flux distributions for single rovibrational states. Details of such measurements were already given elsewhere, but for a better understanding we wish to summarize the main results [30–32].

Velocity flux distributions such as shown in Fig. 1 were obtained by fixing the detection laser wavelength to a certain rovibrational transition, measuring the intensity of the desorbing molecules as a function of the time delay between detection and desorption and transforming the time of flight spectra with the help of the distance surface/detection volume into velocity flux distributions. Fig. 1a shows the velocity flux distributions of molecules in the vibrational ground state for different rotational states. Two maxima at 1000 m/s and 300 m/s can be observed which do not shift with rotational excitation. From Boltzmann fits one obtains a rotational temperature of 900 ± 100 K for the fast non thermal channel and of 300 ± 100 K for the slow channel well above the surface temperature of 100 K. The velocity flux distributions of vibrational excited molecules in Fig. 1b for different rotational states only show one maximum at 800 m/s and a rotational temperature of 270 K ± 100 K. The vibrational temperature in relation

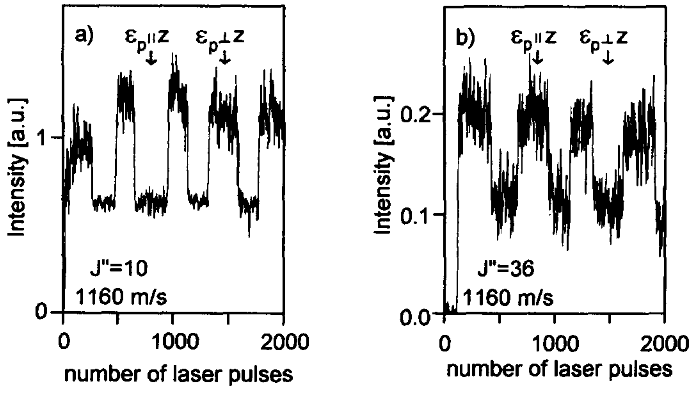

Fig. 2. Intensity change of desorbing CO measured via a (1 + 1')-REMPI method for a variation of the plane of polarization ϵ_p of the detection laser between a polarization, ∥ and ⊥ to the surface normal Z, $v'' = 0$: (a) $J'' = 10$ (transition: $\Delta J = +1$), $v = 1160$ m/s, (b) $J'' = 36$ (transition: $\Delta J = +1$), $v = 1160$ m/s.

to either one of the two channels in $v'' = 0$ is 2000 K. Desorption measurements at 5.0 and 3.5 eV which are published elsewhere [31] show that except for the cross sections the final state distributions are independent of the desorption wavelength and that the non thermal primary excitation step has to take place within the substrate.

Fig. 2 shows the REMPI-intensity in the maximum of a transition measured by varying the laser polarization planes ϵ_p between a polarization parallel and perpendicular to the surface normal Z for molecules of the fast channel ($v = 1160$ m/s) in a low ($J'' = 10$, Fig. 2a) and a high ($J'' = 36$, Fig. 2b) rotational state for the vibrational ground state. The intensities were corrected for variations in laser power when rotating the $\lambda/2$ plate. The change in intensity is quite drastic. For a low rotational quantum number the intensity for a polarization perpendicular to the surface normal is nearly a factor of two higher than for a polarization parallel to the surface normal. The opposite is true for a high rotational quantum number. As we look at R-branch transitions ($\Delta J = +1$) with a transition moment in the plane of rotation, the observed behaviour signifies that molecules with low rotational excitation prefer a helicopter mode while molecules with a large rotational excitation desorb like a cartwheel.

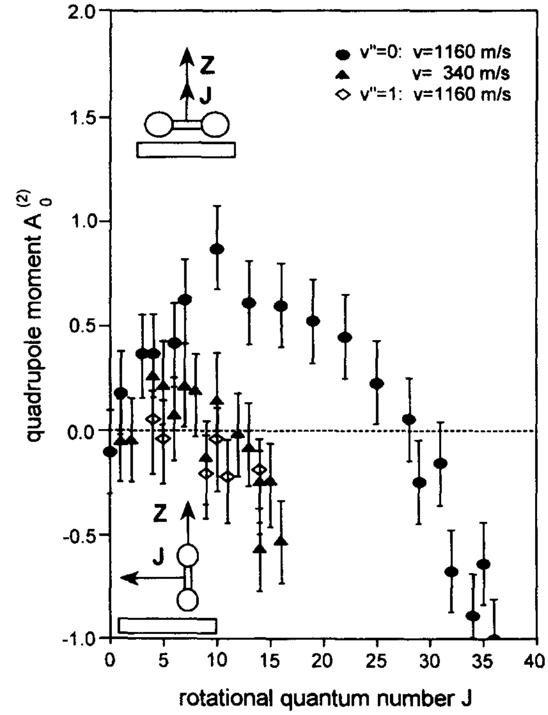

Fig. 3. Quadrupole moments for the desorption of CO from $Cr_2O_3(0001)$ (evaluated in the vector approximation) as a function of rotational excitation, filled dots: $v'' = 0$, $v = 1160$ m/s; filled triangles: $v'' = 0$, $v = 340$ m/s; open rhombuses: $v'' = 1$, $v = 1160$ m/s.

Fig. 3 shows the calculated quadrupole moments $A_0^{(2)}$ as a function of the rotational quantum number for a fast desorption velocity ($v = 1160$ m/s, filled dots) and for a slow velocity ($v = 340$ m/s, filled triangles). The open rhombuses are the quadrupole moments of vibrationally excited CO ($v'' = 1$, $v = 1160$ m/s). The quadrupole moments were calculated as discussed within the vector approximation which is a good approximation for J-values larger than ~ 10 [6]. For lower rotational quantum numbers a full quantum mechanical calculation is necessary and the absolute values will deviate from the ones shown here due to the use of the vector model. However, the statement whether the motion is helicopter or cartwheel like still holds. A hexadecapole moment had to be neglected because the detection uses a Σ–Σ transition. In most cases it is quite small [24]. Its contribution to the rotational alignment is a broadening or narrowing of the alignment described by the quadrupole moment [6]. In our analysis we had to assume a cylinder symmetry of the rotational alignment with respect to the surface normal. This might not necessarily be fulfilled as the threefold symmetry of the surface might lead to a non-cylindric desorption. The consequence could be the appearance of further multipole terms to describe the M_J distribution which would explain the smaller quadrupole moment for the helicopter motion. However, in angular distribution measurements within the axis of the probe laser no unusual distributions deviating from cylindrical symmetry have been observed [32].

Let us first discuss the results for the fast channel (filled dots in Fig. 3). For rotational quantum numbers below $J'' = 20$ the molecules have a quadrupole moment around 0.5. This means that the probability of desorbing with $M_J > J''/2$ (helicopter like motion) is twice as large as with $M_J < J''/2$ (cartwheel like motion) [23]. At higher rotational quantum numbers the rotational alignment starts to change linearly towards a cartwheel motion. With $J'' \geq 30$ the cartwheel motion is dominant and at $J'' \geq 35$ the molecules cartwheel to 100%. Interestingly enough the change from helicopter to cartwheel motion correlates with the disappearance of the slow velocity channel in the velocity flux distributions.

For the slow desorption channel (open triangles in Fig. 3) the change towards cartwheel motion starts at much lower rotational quantum numbers and the helicopter motion at low J is much less pronounced if at all existent. One reason why the alignment is smaller for the slow channel might be a principle one. Due to the resolution of the laser bandwidth one integrates over the total Doppler profile. Therefore, one averages over molecules desorbing under different angles when measuring overall intensity changes as a function of laser polarization. From measurements of the angular distributions we know that the velocity component parallel to the surface has a constant value of 460 m/s for all velocities (most probable value) [32]. The slower molecules thus have broader angular distributions than the fast ones which have a strongly peaked angular distribution along the surface normal. If there is a strong correlation between the translational and the rotational vector the "apparent" alignment concerning the surface normal will be less pronounced for the slow molecules than for the fast ones [7,8].

For vibrationally excited molecules (open rhombuses in Fig. 3) alignment was difficult to measure. The signal to noise ratio is quite small for these transitions as the intensity of the transition itself is already quite weak. The other reason is that in this wavelength region the VUV-laser intensity and thus the detection sensitivity drops strongly. Only intermediate rotational quantum numbers can be clearly distinguished from the vibrational ground state transitions. Due to predissociation transitions including $J' = 18$ or larger rotational states in $v' = 1$ of $B\,^1\Sigma^+$ cannot be observed. In the vibrational ground state the intermediate rotational quantum numbers show the least pronounced alignment relative to the surface normal. One may argue whether any weak alignment can be observed for $v'' = 1$. If at all existent the behaviour is, like the rotational temperature, similar to the one in the slow desorption channel.

5. Summary and discussion

The main experimental findings which need to be explained are (i) a strong cartwheeling (J perpendicular to the surface normal) of highly rotational excited molecules in a translationally fast channel and a spinning within the azimuth of the surface (helicoptering: J parallel to the surface normal) for rotationally colder molecules of the same channel, (ii) a more prominent cartwheeling in a translationally cold as well as a vibrationally excited channel when comparing similar rotational quanta, (iii) the high degree of vibrational excitation and (iv) that both translational channels of $v'' = 0$ and the respective channel in $v'' = 1$ result from the initial surface mediated excitation step as is evident from wavelength dependent desorption measurements [31].

A key for the explanation is first of all the bonding of CO to the surface. Though the mechanism of the bonding of CO on $Cr_2O_3(0001)$ is not yet completely understood, the dominant features are most likely a strong Coulomb attraction caused by the electrostatic interaction of the electric multipole moments of CO in the electrostatic field above the $Cr_2O_3(0001)$ surface and the Pauli repulsion between the fully occupied orbitals of CO and the O^{2-} ions [33]. Experimentally it was deduced that the most favorable adsorption geometry is that of a CO lying flat on the surface with its two lone pair orbitals (4σ and 5σ) being attracted by two Cr^{3+} ions to compensate the strong Pauli repulsion between the 1π orbital of CO and the oxygen band [25]. Although the resulting binding energy of the molecule to the surface is rather small (44 kJ/mol) this geometry seems to be energetically preferable to a bent geometry. One important consequence of this particular bond is that minor deviations from the equilibrium position within the surface plane will most likely destabilize the bonding. As a consequence the potential energy surface of the azimuthal angle coordinate is expected to be corrugated depending on the distribution of Cr ions in the surface layer.

Before speculating about the desorption mechanism one must keep in mind that a helicopter motion initiates from a torsional movement of the flat lying molecule within the azimuthal plane and a cartwheel motion from an out of plane bending movement [6-8]. We now wish to discuss possible excitation mechanisms which can result in torques within these coordinates.

Wavelength dependent measurements indicate that the initial excitation step takes place within the substrate [31]. It is still open whether the relevant excitation step is due to a surface mediated charge transfer or an interatomic, excitonic d–d transition within the strongly localized d band of the chromium ions. The strong vibrational excitation after the desorption of CO indicates the formation of an intermediate CO^- (Antoniewicz type desorption [34]) as one possible desorption channel (for a detailed discussion see Ref. [31]). Whether a possible second desorption channel due to a changed charge distribution within the adsorbate/substrate system alone without a transfer of an electron to the adsorbate exists is still open.

Both excitation steps will have as a consequence a repulsive interaction between one end of CO and the $Cr_2O_3(0001)$ surface. This is either due to an extra electron in a Cr ion at one end of the $CO/Cr_2O_3(0001)$ bond and one of the lone pairs of the neutral CO or due to the Pauli repulsion between the now occupied $2\pi^*$ orbital of CO^- and the O^{2-} ions. In order to minimize the repulsion the molecule will be pushed sideways and upwards with respect to the Cr ion. The overall movement will then be of screwtype with the consequence of a change of bonding geometry from a flat to a bent configuration. When the system then relaxes back to the ground state the molecule is far off its ground state equilibrium geometry within the out-of-plane bending coordinate. With such a bent geometry the molecule senses the surface corrugation much less. The molecule has gained angular momentum within the out-of-plane bending movement as the potential energy surfaces of the initial and intermediate state differ drastically. As a result the molecule will desorb in a cartwheel motion with high rotational excitation. The change from the dominating helicopter to a preferred cartwheel motion could then reflect the barrier within an azimuthal rotation, however for a surface distance different from the molecular ground state position.

Such a helicopter like spinning as a result of a strong change in surface corrugation leading to a rotation within the azimuthal plane was also observed for NH_3 desorbing from Pt(111) in electron stimulated desorption [35]. In scattering experiments for a system like NO/Pt(111) a preferred helicopter motion in a regime where desorption instead of inelastic scattering of NO is dominant was attributed to a higher density of in-plane rotation then hindered out-of-plane rotation [12]. Zimmermann, Houston and Ho attributed the helicopter motion in their laser induced desorption experiments on the CO/Si(100) system to a twisting vibration within the surface plane excited thermally prior to excitation [24].

The explanation of the occurrence of two channels in $v'' = 0$ might be that both excitation mechanisms discussed are present. An alternative explanation is that the molecules of the slow channel might have undergone one or several collisions with the surface before desorption. Such a situation can be compared to scattering experiments as, for example, for the system NO/Pt(111) [12]. In the regime where inelastic scattering is more dominant than desorption a cartwheel motion is observed and explained by a repulsive O end interaction with the surface [21].

The discussion given above tries to explain our observations with a model as simple as possible. The actual process might be more complicated. In any case the alignment measurements indicate a change of geometry during the excitation process in accordance with the high degree of rotational excitation within the fast channel.

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