

## Three-Dimensional *Ab Initio* Quantum Dynamics of the Photodesorption of CO from Cr<sub>2</sub>O<sub>3</sub>(0001): Stereodynamic Effects

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Having performed the first three-dimensional *ab initio* quantum dynamical study of photodesorption from solid surfaces, we gained mechanistic understanding of the rotational alignment observed in the CO/Cr<sub>2</sub>O<sub>3</sub>(0001) system. Our study is based on potential energy surfaces obtained by embedded cluster calculations for both the electronic ground and excited state of the adsorbate substrate complex. Stochastic wave packet calculations demonstrate the importance of the angular degrees of freedom for the microscopic picture of the desorption process in addition to the desorption coordinate.

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The photodesorption of molecules is one of the simplest and most fundamental reactions of adsorbates at surfaces. In this process, an electronically excited state, which is populated by laser irradiation, is involved as a short-lived intermediate and plays the decisive role in the desorption. To understand the basics of DIET (Desorption Induced by Electronic Transitions) processes, two-state models such as the Menzel-Gomer-Redhead (MGR) [1,2] or the Antoniewicz [3] scenarios have been proven to be useful in the past. In those models it is the change in distance of the adsorbed molecule from the surface after laser irradiation, which drives the desorption after the adsorbate-substrate system has relaxed to its ground state. The one-dimensional models account for experimental observables, such as kinetic energy distributions [4].

However, in recent experiments, the phenomenon of rotational alignment was observed for CO molecules desorbing from a Cr<sub>2</sub>O<sub>3</sub>(0001) surface in a quantum state resolved study [5]: In the case of low rotational excitation the CO molecules prefer helicopter motion (*J* vector parallel to the surface normal). Rotationally hot molecules prefer cartwheel motion (*J* vector perpendicular to the surface normal). The description of the motion of the admolecule within its angular degrees of freedom is required to understand this stereodynamic effect. The specific coordinates considered in our study are the center of mass distance *Z* of the molecule from the surface as the desorption coordinate, the azimuthal orientation  $\phi$ , and the polar orientation  $\theta$  of the molecule with respect to the surface normal.

To model the photodesorption event realistically, we need potential energy surfaces based on *ab initio* calculations, since there is no physical intuitive picture to construct a multidimensional potential energy surface (PES)

empirically especially for the electronically excited state. Electronic ground state properties can be calculated using standard electronic structure methods, but the calculation of electronically excited states of adsorbates at surfaces still remains a great challenge. One successful example for the *ab initio* calculation of a two-dimensional PES for an excited state has been reported for the NO/NiO(100)-system [6]. In this Letter, we perform *ab initio* embedded cluster calculations to obtain an excited state PES for CO/Cr<sub>2</sub>O<sub>3</sub>(0001) and to model for the first time alignment effects in photodesorption.

While two-dimensional quantum dynamical studies of photodesorption including the internal molecular vibration are known [4,7–11], a complete three-dimensional study has not been reported so far. Of course high-dimensional quantum dynamical studies exist, for example to treat scattering of hydrogen at surfaces [12]. However, those studies are feasible due to the small number of rotational states the light H<sub>2</sub> molecules occupy and due to the exclusive consideration of the electronic ground state.

The DIET process is treated within a two-state model using a stochastic wave packet approach. The system Hamiltonian

$$\hat{H}_{g,e}(Z, \theta, \phi) = -\frac{1}{2\mu r_e^2} \left( \frac{1}{\sin\theta} \frac{\partial}{\partial\theta} \sin\theta \frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta} \frac{\partial^2}{\partial\phi^2} \right) - \frac{1}{2M} \frac{\partial^2}{\partial Z^2} + \hat{V}_{g,e}(Z, \theta, \phi) \quad (1)$$

has already been applied in [6] for  $\phi$ -independent potentials and includes the calculated *ab initio* PES for the electronic ground state (*g*) and the electronically excited state

(e).  $M$  and  $\mu$  are the total mass and the reduced mass of the CO molecule, respectively, with the internal C-O distance kept frozen at its electronic ground state equilibrium value  $r_e$ . Following the sudden transition model of Gadzuk [13,14], the lowest rovibrational eigenstate  $\Psi(0)$  of the electronic ground state PES is transferred vertically to the excited state PES at time zero. The wave packet is propagated for a specified residence time  $t_n$  before being quenched to the ground state. The individual quantum trajectories are followed up to a final time  $t$ , which is in the order of a picosecond. The final state nuclear wave function then reads  $\Psi(t; t_n) = e^{-i\hat{H}_g(t-t_n)} e^{-i\hat{H}_e t_n} \Psi(0)$  and is the result of an excitation-deexcitation cycle with the finite residence time  $t_n$  on the excited state PES. Asymptotic expectation values  $A(t; t_n)$  are calculated and weighted incoherently with respect to the resonance lifetime  $\tau$  of the exponentially decaying electronically excited state.

To calculate the time evolution, we used the Feit-Fleck split propagator [15]. The numerical results for the observables of interest have been checked and compared carefully versus the Chebychev propagator [16] serving as the accurate reference. The Hamiltonian operation  $\hat{H}(Z, \theta, \phi) \cdot \Psi(Z, \theta, \phi)$  was calculated using fast Fourier-transform techniques and a Gauss-Legendre scheme for the rotational part of the kinetic energy operator [17]. The desorbed part of the wave function, separated by the grid change technique proposed by Heather and Metiu [18], was used to calculate asymptotic observables.

The electronic ground state PES of the adsorbate-substrate system was obtained recently by embedded quantum chemical cluster calculations [19]. We used a  $\text{Cr}_4\text{O}_6$  cluster embedded in a semi-infinite Madelung potential of point charges to simulate the  $\text{Cr}_2\text{O}_3(0001)$  surface. Figure 1 (bottom) shows the angular dependence of this electronic ground state PES as a 2D contour plot at the equilibrium value of the CO center of mass distance ( $Z = 4.5$  bohr). The lowest rovibrational eigenstate of the electronic ground state PES is shown in Fig. 1 (bottom) as well. It is located at the absolute minimum of this PES at  $\theta = 120^\circ$  and  $\phi = 180^\circ$ , which means that the unexcited CO molecule is adsorbed highly tilted with respect to the surface normal and in line with the Cr-Cr axis. The inset in Fig. 1 illustrates this adsorption geometry. The CO molecule does not adsorb on top of a Cr ion, but in the middle of the Cr-Cr connection axis. This is in agreement with experiments, which found evidence for a highly tilted adsorbed species [19,20].

As a representative electronically excited state relevant for laser induced desorption in the CO/ $\text{Cr}_2\text{O}_3(0001)$  system we calculated the  $a^3\Pi$ -like state resulting from an internal CO ( $5\sigma \rightarrow 2\pi^*$ ) electronic excitation. The vertical excitation energy agrees very well with the laser energy of 6.4 eV used in the experiment [5]. A 3D potential energy surface for this state within the relevant degrees of freedom was obtained by complete active space self-consistent field (CASSCF) calculations and fitted to an analytical function.

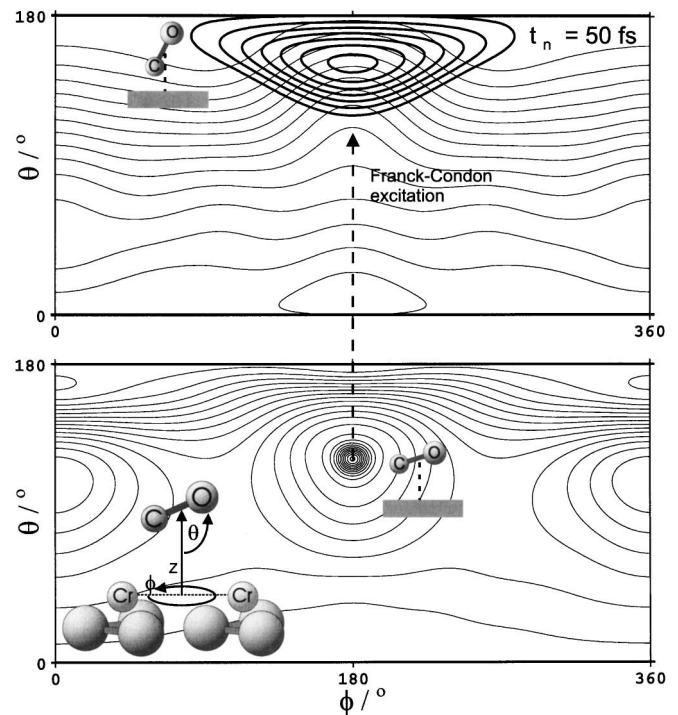


FIG. 1. 2D contour plots of the *ab initio* PES for the CO/ $\text{Cr}_2\text{O}_3(0001)$  system:  $\theta$ - $\phi$  dependences at ground state equilibrium value for the CO distance ( $Z = 4.5$  bohr). Bottom: electronic ground state with the lowest rovibrational nuclear eigenstate. Top: electronically excited  $a^3\Pi$  state with a snapshot of the wave packet after a time evolution of 50 fs. Inset: cluster model, two Cr ions are not shown.

Details of the calculation can be found elsewhere [21]. A two-dimensional  $\theta$ - $\phi$  contour plot of this PES is sketched in Fig. 1 (top) for the ground state equilibrium value for the center of mass distance of the CO molecule from the surface. This is the potential energy surface the CO molecule feels if a sudden vertical transition due to the laser irradiation takes place. In the same figure the vertically excited wave packet is shown after a time evolution of 50 fs on the  $a^3\Pi$ -like state. The CO molecule has left its highly tilted ground state adsorption geometry and has moved towards an upright geometry. This motion is accompanied by slight acceleration with respect to the azimuthal angle  $\phi$ . In a microscopic picture this means that the laser irradiation has excited cartwheel motion (acceleration with respect to  $\theta$ ) and has kicked the CO molecule out of its in line configuration with respect to the Cr-Cr axis.

The experiments reported recently concern the alignment of the total angular momentum vector  $J$  [5] of the desorbing CO molecule. The projection of  $J$  onto the surface normal is given by the quantum number  $M_J$ . The desorbing molecules are aligned if the population of high  $|M_J|$  values is different from the population of low values. The quadrupole moment  $A_0^2$  is a measure of the rotational alignment and is defined as  $A_0^2(J) = \langle J | (3\mathbf{M}_J^2 - \mathbf{J}^2) / \mathbf{J}^2 | J \rangle$  [22]. A value of +2 corresponds to a perfect helicopter molecule ( $J$  vector parallel to the surface normal),

a value of  $-1$  to a perfect cartwheel ( $J$  vector perpendicular to the surface normal). From the topology of our excited state PES cartwheel motion of the desorbing CO molecules is expected to be the dominant feature due to the large gradient towards an upright adsorption geometry after laser irradiation. However, in the experiment (filled circles in Fig. 2), helicopter motion is found for  $J \leq 25$ .

Our results for  $A_0^2$  are shown in Fig. 2 as a function of the rotational quantum number together with the experimental data [5]. The values have been averaged with respect to the CO desorption velocity. An excited state resonance lifetime of  $\tau = 10$  fs results in a desorption probability per excitation event of about 5%, which is in agreement with experiment. In Fig. 2 several cases are studied:

(i) Using our two *ab initio* PES within the excitation-deexcitation cycle we obtain a helicopter motion at medium rotational excitation changing to cartwheel motion with increasing  $J$  in qualitative agreement with the experimental observation. To understand why helicopter motion is observed at all in the experiment, we performed additional calculations in which the azimuthal gradients of the potential energy surfaces were turned on and off. After turning the  $\phi$  gradient off we have the situation of flat, uncorrugated surfaces. From Fig. 2 it is obvious that a helicopter motion of the desorbate is possible only when

the azimuthal corrugation is present in both the electronic ground *and* the excited state.

(ii) A combination of two flat, uncorrugated states within the DIET cycle yields cartwheeling CO molecules in the entire  $J$  range. In this case there is no driving force for helicopter motion in the entire system.

(iii) We do not get any helicopter motion as well if only the excited state  $\phi$  gradient is “switched” off. From a mechanistic point of view this is reasonable, since the CO molecule does not get its “helicopter kick” after laser excitation any more. Apart from spreading, the wave packet rests in its ground state equilibrium position with respect to  $\phi$  during the entire simulation. Acceleration with respect to the polar angle  $\theta$  only can occur and will lead exclusively to cartwheel motion.

(iv) The excited state helicopter kick is not sufficient to explain the desorbate helicopter character on its own, though. Turning off the ground state  $\phi$  gradient and keeping the excited state  $\phi$  corrugation yields cartwheeling CO molecules in the entire  $J$  range as well.

From these cases it follows that it is the combination of the  $\phi$  gradients in the excited state and the ground state which causes the helicopter character of the desorption. The mechanistic picture is such that after laser excitation the CO molecule is forced out of its ground state in-line equilibrium geometry with respect to  $\phi$ . After quenching to the electronic ground state PES the CO molecule feels a  $\phi$  gradient in the opposite direction, which forces the molecule backwards towards its in-line equilibrium geometry. This excitation-deexcitation cycle excites helicopter motion. This detailed mechanistic picture could only be obtained on the basis of our two *ab initio* PES. Especially, the angular topologies could not have been guessed on an empirical basis. At low rotational quantum numbers our results and the experimental data disagree. However, it should be kept in mind that especially for small  $J$  experimental uncertainty exists [23], since the quadrupole moment has been derived from experimental spectra within the classical vector approximation which is only valid in the large  $J$  limit. Therefore, direct comparison of our quantum mechanical results with the experimental data in the low  $J$  regime is by no means straightforward. Of course, also the question of the accuracy of our *ab initio* calculations arises. As shown in Fig. 2, helicopter motion is a result of a delicate interplay of azimuthal forces. However, since our ground state calculation underestimates the adsorption energy by about 0.2 eV [19], we expect an overestimation of the equilibrium distance of the molecule from the surface. Thus, the azimuthal surface corrugation in the electronic ground state could be too small in our *ab initio* calculations. A larger azimuthal gradient within the electronic ground state would promote helicopter motion. Another reason for the difference between theory and experiment might be the restriction of our model to three dimensions or the involvement of another intermediate such as  $\text{CO}^-$ .

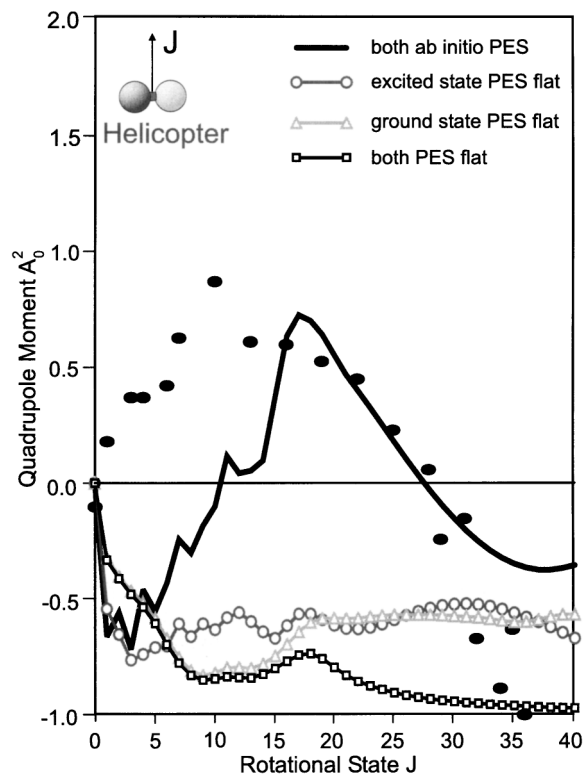


FIG. 2. Quadrupole moment for the desorption of CO from  $\text{Cr}_2\text{O}_3$  as a function of rotational excitation, averaged with respect to the desorption velocity; a resonance lifetime of the  $\text{CO}^*$  intermediate of  $\tau = 10$  fs yields a desorption probability of 5%. Filled circles: experimental data points.

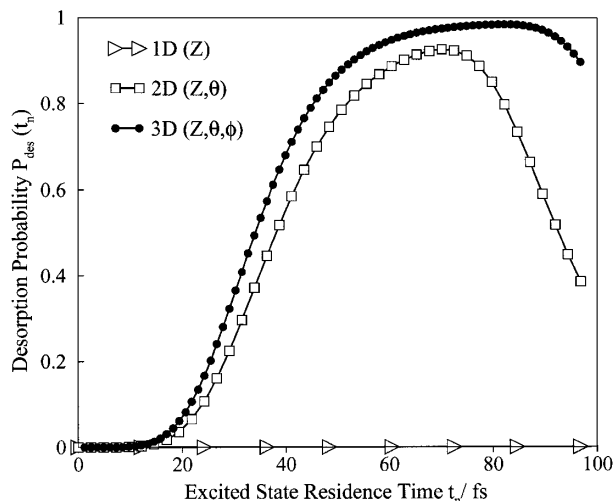


FIG. 3. Asymptotic desorption probability  $P_{\text{des}}(t_n)$ ; open triangles: 1D calculations in  $Z$  with  $\theta$  and  $\phi$  frozen at electronic ground state equilibrium values; open squares: 2D calculation in  $Z$  and  $\theta$  with  $\phi$  frozen; filled circles: 3D calculation in  $Z$ ,  $\theta$ , and  $\phi$ .

Finally, in Fig. 3 we demonstrate the importance of the angular degrees of freedom for the desorption process. In the artificial situation, in which only the center of mass distance  $Z$  was included and the polar and azimuthal angle were frozen at their electronic ground state equilibrium configurations, the desorption probability stays almost zero in this system (independent of the excited state residence time  $t_n$ ). Desorption becomes efficient only when the CO motion towards an upright adsorption geometry is possible. This change in adsorption geometry in the excited state is of crucial importance for the microscopic desorption mechanism. Desorption can occur only after the CO molecule has left its highly tilted ground state equilibrium geometry, because in the electronic ground state the molecule feels a repulsive potential if the polar angle is increased. The azimuthal motion still changes the desorption efficiency, but not as much as the polar angle does. It is the angular degrees of freedom which are responsible for the “success” of the desorption event and not exclusively the dependence of the two PES involved on the desorption coordinate  $Z$ .

In conclusion, we reported the first three-dimensional quantum dynamical study of photodesorption from surfaces based on *ab initio* potential energy surfaces for both the electronic ground and the excited state. With a resonance lifetime of the excited CO molecule of 10 fs we obtain a reasonable agreement with experimental data for rotational alignment, desorption probability, and also the velocity distributions which are not shown in this study. Discrepancies between experiment and theory at low  $J$  have still to be addressed both by experiment and theory. From the wave packet calculations we gained insight

into the microscopic mechanism of the desorption process well beyond the traditional understanding of DIET in terms of the conventional MGR and Antoniewicz models. We demonstrated the importance of a more-dimensional picture for a realistic treatment of a DIET process. We showed that stereodynamic effects depend very sensitively on the topologies of the potential energy surfaces, both for the electronic ground and the excited state. Furthermore, we were able to understand the origin of the helicopter motion observed in experiment.

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