

UV-Laser induced desorption from surfaces: NO/NiO(100)

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Photodesorption of molecules from metal surfaces is a highly unprobable process if we compare its cross-section ($<10^{-20}\text{cm}^2$) with the corresponding cross-sections for semiconductor or insulator surfaces (10^{-17}cm^2). It is our goal to try to understand the desorption dynamics from solid surfaces by investigating the properties of the adsorbed molecule on the surface as well as the properties of the desorbing molecules. This is pursued by applying surface science techniques to study the adsorbate and the methodology of laser gas phase spectroscopy to investigate the energy distribution (translation, rotation, vibration) of the desorbing particles. We present in this paper the results of such experiments for the title system, and try to rationalize the experimental findings on the basis of classical trajectory simulations applying the Menzel-Gomer-Redhead(MGR)/1/ model of electronically stimulated desorption.

The experimental apparatus as well as some of the experimental results have been discussed elsewhere/2-4/. We shall only briefly summarize those results important for the present study:

- the photodesorption cross-sections for NO/NiO(100) has been determined via XPS to be $6 \times 10^{-17}\text{cm}^2/2/$
- the molecules leave the surface with most probable velocities of about 1200 m s^{-1} . The velocities are not distributed according to Maxwellian distributions/5/.
- for increasing rotational energy of the desorbing particle we find increasing translational energy (see Fig.1a)/6/.
- we observe a strong underpopulation of the $^2\pi_{3/2}$ with respect to the $^2\pi_{1/2}$ state of NO for low rotational quanta/6/.

In the following we shall discuss a qualitative, empirical, semiclassical model for the desorption dynamics/7/ that will allow us to understand part of the experimental results, in particular the connection between rotational and translational energy, i.e. c).

The key ingredients of the model are the potentials for the ground and excited states. For the excited state we have assumed a $1/r$ potential as indicated in Fig.2. The ground state potential is more complicated in that it depends on two parameters, namely the distance between the center of gravity of the molecule and the surface, and the angle between the molecular axis and the surface normal as indicated in Fig.3a (inset). Fig.2 only shows the radial dependence of the potential. Its dependence on both parameters is plotted within a polar coordinate system in the θ, r -plane as shown in Fig.3a. The potential is given as a contour diagram where each contour corresponds to a certain distance to the surface and the position on the contour to an angle θ .

The potential for the ground state has been chosen on the basis of our experimental studies of the static adsorption behaviour of NO on NiO(100) for a variety of temperatures/2-4,8/. We have studied this system employing several surface science techniques, and the outcome of these studies relevant to the choice of the potential may be summarized as follows:

- NO is weakly chemisorbed on NiO(100). It desorbs from the surface at 220K which corresponds to an adsorption energy of 0.57eV.

- b) NO shows an electron energy loss spectrum from which we can estimate the curvature of the potential near the minimum.
- c) NO is adsorbed on-top of the Ni sites and its molecular axis is bent by $45^\circ \pm 12^\circ$ with respect to the surface normal.

These experimental findings reflect themselves in the chosen double-well potential in Fig.3. The bending of the molecule surface bond leads to the potential minima in the polar plot at $+45^\circ$ and -45° . By choosing this two parameter θ, r -surface we have neglected that the real system is a surface with fourfold symmetry which offers four equivalent positions for a bent bonded diatomic molecule. For other purposes like angular dependences and a quantitative description of bimodal distributions this fact may have serious consequences but for the present case it is not considered to be important and may be neglected.

The photodesorption process is now imagined to take place in the following way: The system resides in the minimum of the potential well and is considered to behave as a hindered rotor, i.e. the molecular axis is oriented at 45° off normal and performs hindered rotations or bending vibrations ranging from 35° to 55° without vibrational excitation. According to the chosen temperature the energy is distributed over the rotational levels defined by the chosen hindered rotor. At a given time t_0 this system undergoes a Franck-Condon transition onto the excited potential and we assume this transition to be a hindered-free transition, i.e. the molecule behaves as a free rotor in the excited state. The probabilities for the hindered-free transition can be calculated according to Gadzuk and Landman/9/ analytically. The system prepared on the excited potential in this fashion propagates for a given time t_1 , and then undergoes a transition back to the ground state potential. Note that due to the particular functional form of the excited potential the shape of the initially prepared rotational distribution does not change during propagation of the system. The distribution depends on the time t_1 when this distribution is projected back onto the ground state. Therefore, t_1 defines the translational energy the particle has accumulated in the excited state, and thus determines whether the particle has enough energy to escape the ground state after back projection. The whole process is marked with

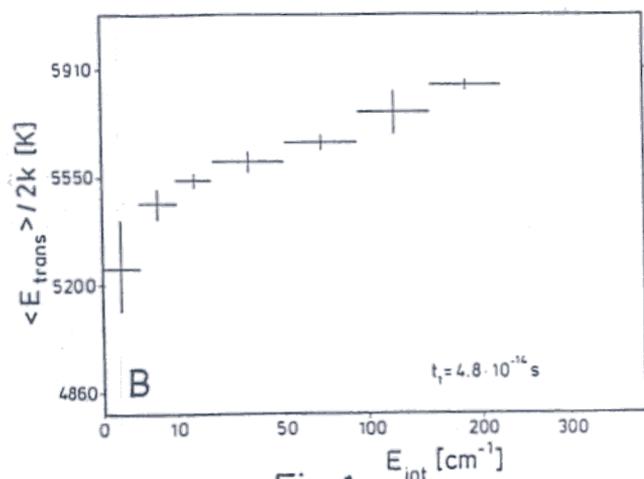
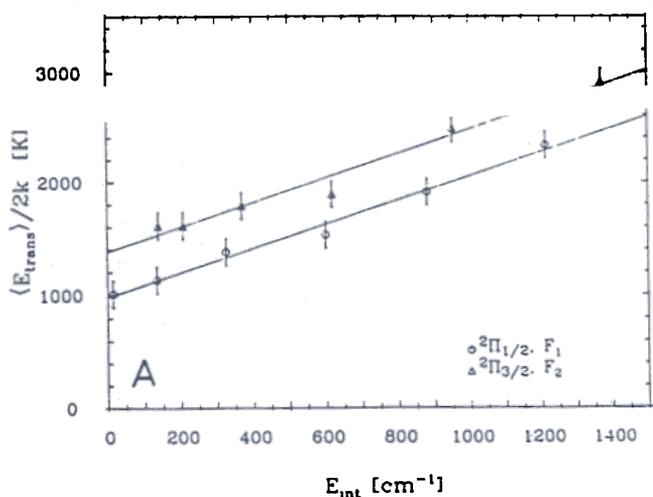


Fig.1

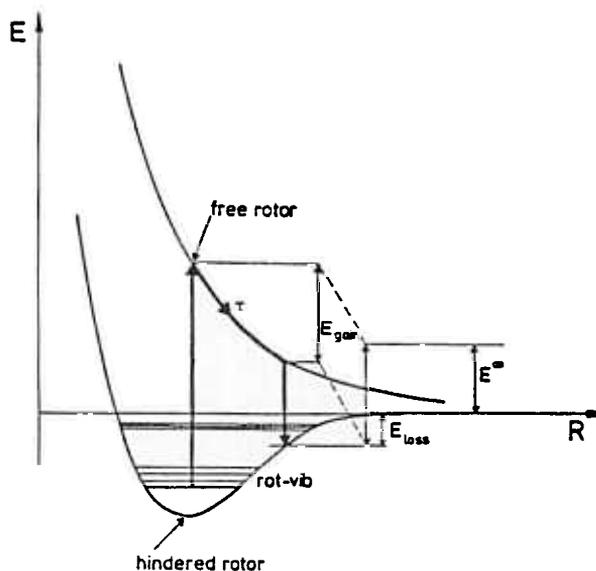
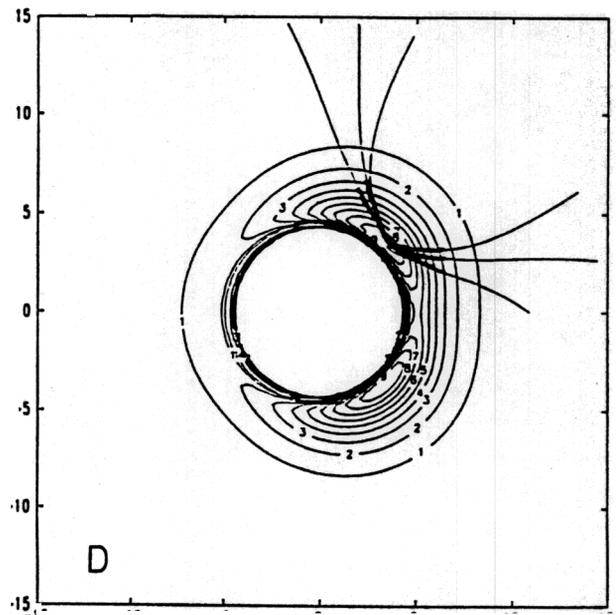
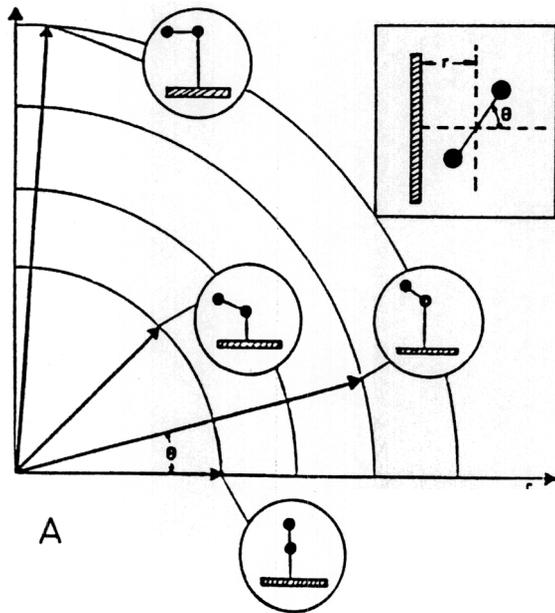
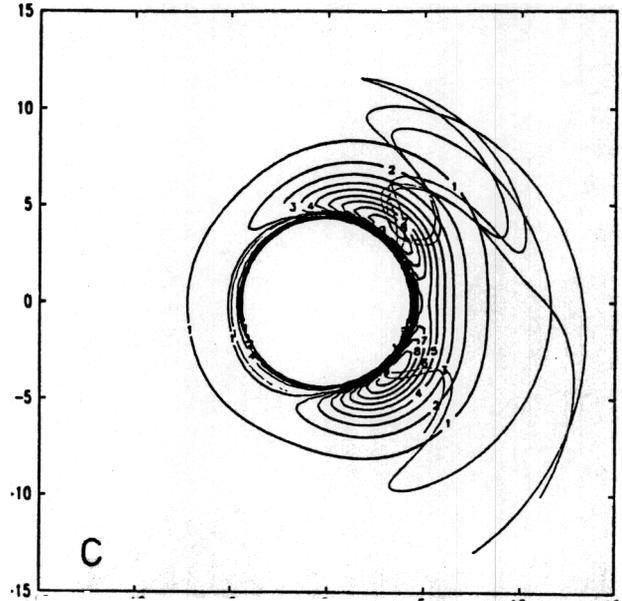
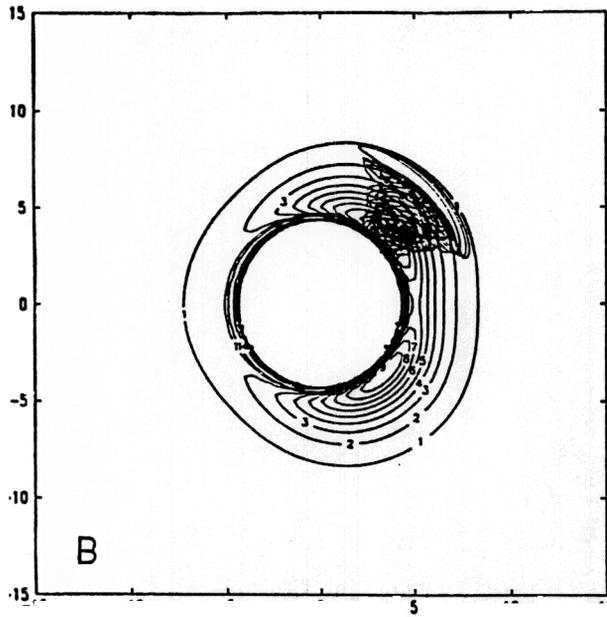


Fig. 2



Fig

arrows in Fig.2. In Fig.3b-d trajectories for three different times t_1 (Fig.3b: 2.4×10^{-14} s, Fig.3c: 2.6×10^{-14} s, Fig.3d: 4.8×10^{-14} s) are plotted. For the shortest time (Fig.3b) the molecules do not escape the ground state, in Fig.3c only a slightly longer time has been chosen such that some molecules start to desorb, and for the longest time t_1 (Fig.3d) every molecule escapes the ground state potential after back projection. We see from curvatures of the trajectories in Fig.3 that the molecules leaving the ground state potential distribute their energy over linear and angular momentum. Note in particular that the rotational motion may lead to a recapturing of the particle leaving one of the minima into the other minimum (Fig.3c).

With these results we are in a position to check how rotational and linear momentum are connected. We have plotted the translational energy as a function of the rotational energy in Fig.1b and may compare the modelled behaviour with the experimentally observed one shown in Fig.1a. Obviously, the observed simultaneous increase of rotational and translational energy can be qualitatively reproduced by the chosen model. In the present case a simple explanation may be deduced from the calculations:

After excitation the molecule is accelerated away from the surface, and after a given time has accumulated a certain energy. While with the return to the ground state potential most of the excitation energy is dumped into the surface, the molecule still carries this accumulated energy. It now depends on the position r on the potential energy curve to which the particle returns, whether the accumulated energy is sufficient to leave the ground state potential. Quantum mechanically this position is connected with a certain rotational quantum. The smaller the rotational quantum the higher the energy needed to leave the ground state r, θ -potential, and the lower the remaining translational energy remaining on the desorbing particle and vice versa.

Summarizing the two main results of our model we may state that:

- a) in a MGR model we may expect a simultaneous increase of translational and rotational energy for desorbing molecules.
- b) the life time of the excited state has to be of the order of 3×10^{-14} sec in order to allow photon stimulated desorption to occur.

It is the future goal to try and understand the interesting spin effect mentioned as experimental result d) above. Alexander et al./10/ already presented a possible clue to solve this problem.

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