Orientation dependence of the sticking probability of NO at Ni(100)

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In a molecular beam experiment we have measured the sticking probability of NO at Ni(100) as a function of coverage and molecular orientation. The NO molecules in the $^2\Pi_{1/2}|\frac{1}{2}, \frac{1}{2}, \frac{1}{2}>$ ground state are state selected by use of an electrostatic hexapole. The orientation was produced by a homogeneous electric field. The initial sticking probability is found to be higher for N-end collisions. The asymmetry of the initial sticking probability was found to depend linearly on the degree of molecular orientation. This effect is of the order of 70 % with respect to the degree of orientation. The orientation dependence of the sticking probability as a function of coverage shows that the asymmetry is nearly constant up to saturation coverage. These results indicate that a simple picture of the adsorption process including only trapping into a 'precursor' state, and neglecting direct chemisorption, cannot explain the adsorption kinetics of NO at Ni(100).

Introduction

In surface physics first studies on steric effects were done by measurements of molecular vector properties after molecule–surface interaction[1–8]. From the well known fact that adsorbed diatomic molecules are most often orientated to the surface to which they are bound Muhlhausen *et al*[9] predicted a strong dependence of the initial sticking probability on the initial orientation of NO at Pt(111) and Ag(111). Using semi-empirical potentials they calculated a higher sticking coefficient for molecules approaching the surface in the favourable bonding configuration, which is given by a perpendicular orientation with the N-end bound to the substrate.

In recent studies[10–16] steric effects in the scattering and adsorption of NO at transition metals were determined. Kleyn and coworkers[10–13] conlcude from their work on direct inelastic scattering and trapping-desorption that, for the case of the weakly physisorbed system NO–Ag(111), the anisotropy of the repulsive part of the interaction potential leads to a higher trapping probability for O-end collisions. We observed a markedly higher initial sticking probability for N-end collisions in the case of NO at Ni(100)[14,15]. This can be explained by the anistropy of the binding energy for the chemisorbed NO–Ni(100) system. Recently, Kuipers *et al*[16] have measured steric effects in the adsorption and scattering of NO at Pt(111), and determined a higher adsorption probability for an initial orientation with the N-end directed towards the surface.

The aim of our work is to bring more insight on the processes which lead to the state where finally all molecules are adsorbed. Therefore, we work at low temperatures where the desorption probability is near zero. In order to observe a strong effect, the sticking coefficient itself should be significantly different from unity or zero. For NO on Ni(100) it is known that the molecules are chemisorbed with the N-end bound to the surface and with perpendicular orientation[17]. Hamza *et al*[18] examined the adsorption kinetics of this system and obtained an initial sticking coefficient of $S_0 = 0.67$ (translational energy: $E_{trans} = 90$ meV, rotational energy: $T_{rot} = 30$ K and surface temperature: $T_s = 140$ K).

Orientation

For our studies, the orientation of a molecule refers to the orientation of the molecular axis (i.e. the dipole moment) in space with respect to the fixed direction of the electric field vector. A free rotating molecule cannot have a fixed orientation in space; however, from quantum mechanics[19] one can easily calculate the probability distribution $P(\cos\phi)$ of the orientation for a given rotational state. Therefore, a molecule in a pure rotational state $|J, \Omega, M_J>$ with $\langle \cos\phi \rangle \neq 0$ is orientated and we have an ensemble of orientated molecules[20] if $\overline{\langle \cos\phi \rangle} \neq 0$. In the case of NO molecules in the $^2\Pi_{1/2}$ electronic ground state with rotational quantum numbers $|J, \Omega, M_J> = |\frac{1}{2}, \frac{1}{2}, \frac{1}{2}>$ the probability distribution is given by[19,21] $P(\cos\phi) = 0.5(1 \pm \cos\phi)$, where ϕ is the angle between the dipole moment P and the electric field E (+ sign refers to the N-end pointing towards the surface). From the orientation probability one calculates the degree of orientation to be $\langle \cos\phi \rangle = (\Omega \cdot M_J / J \cdot (J + 1) = 1/3)$.

Experimental

Orientation of molecules exhibiting a linear Stark-effect can be achieved by use of a combination of electric fields: a hexapole field for focusing and state selection and a subsequent homogeneous orienting field[22]. We use such a configuration in our apparatus, as shown in Figure 1. The NO molecular beam (translational energy: $E_{trans} = 125$ meV; speed-ratio $S = 10$) passes through several stages of differential pumping and is directed into the uhv chamber ($p_b \leq 3 \times 10^{-11}$ mbar; beam off; and $p_b \leq 1 \times 10^{-9}$ mbar; beam on) containing the Ni target. The continuous supersonic beam is generated in the first chamber by expanding NO seeded in Ar(20 %) and He(60 %) through a nozzle ($\phi_N = 0.1$ mm) at a stagnation pressure of $p_0 = 300$ mbar into the vacuum ($p_b = 5 \times 10^{-5}$ mbar). For measurements of the
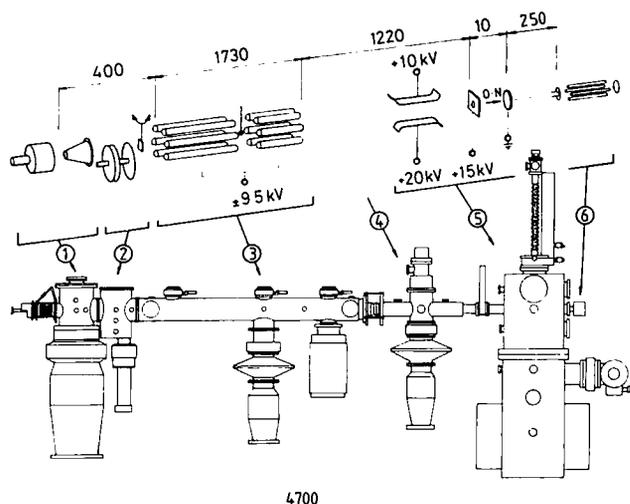
Figure 1. Experimental set-up with typical dimensions (in mm) and typical voltages: (1) Source chamber with nozzle and skimmer, pumped by a 7000 l s^{-1} diffusion-pump backstaged by a 240 m^3 h^{-1} roots-pump followed by a 40 m^3 h^{-1} mechanical pump. The skimmer can be by-passed by opening of a valve. (2) Buffer chamber with velocity selector, chopper and beam shutter, pumped by a 300 l s^{-1} diffusion pump. (3) Hexapole chamber with hexapole and central beam stop, pumped by a 1100 l s^{-1} diffusion pump. A 400 l s^{-1} ion-getter pump is used to hold the hv-part under vacuum if the diffusion pumps are turned off. (4) Buffer chamber pumped by a 1100 l s^{-1} diffusion pump and a 5000 l s^{-1} liquid He cryopump. This chamber is separated from the uhv-chamber by a pneumatic gate valve. (5) uhv-chamber with guiding and orientation field, pumped by a 500 l s^{-1} turbo pump, a 770 l s^{-1} ion getter pump and titanium sublimation pump with lN$_2$ cold trap. In the upper level, this chamber contains the equipment for cleaning of the sample and for surface studies. (6) Quadrupole mass analyser to probe the direct beam (if the sample manipulator is removed) as well as the reflected molecules. (The second analyser used is not shown). All oil diffusion pumps are baffled with lN$_2$ cold traps and can be separated from the chambers by gate valves.

translational energy a slotted-disc velocity selector mounted behind the skimmer ($\phi_s = 1.2$ mm) is used and the beam is modulated with a tuning fork chopper to enable background subtraction by use of a lock-in amplifier. The hexapole is divided into two parts of lengths $l_1 = 1$ m and $l_2 = 0.7$ m. Due to the asymmetric lengths of the hexapoles the beam stop ($\phi_{BS} = 1$ mm) is located at the distance where all molecules have their trajectories parallel to the hexapole axis. Both hexapoles are mounted together at a distance of 10 mm in one adjustable frame with fixed collimators at the entrance ($\phi_{in} = 5$ mm) and the exit ($\phi_{out} = 10$ mm); both located at a separation of 20 mm from the hexapole. The beamstop is mounted adjustable in three directions. Each hexapole is built from six rods of $\phi = 6$ mm mounted on a circle with 12 mm inner diameter. At rod voltages of $U_o = \pm 9.5$ kV the molecules in the $^2\Pi_{1/2}|\frac{1}{2}, \frac{1}{2}, \frac{1}{2}\rangle$ ground state, which show a positive Stark effect ($M_J \cdot \Omega > 0$) are focussed onto the target located 1.20 m behind the exit-collimator of the hexapole. Molecules with $M_J \cdot \Omega < 0$ are defocused from the beam. The focused molecules pass through a guiding field and the diaphragm of the orientation field plate (potential up to ± 15 kV) and impinge at normal incidence on the sample (ground potential). The guiding field is used to hold the molecules at the potential of the orienting field, in order to prevent Majorana flops which may be caused by a field gradient near the orientation plate. The distance sample to field plate can be varied between 10 and 25 mm. At positive voltage at the plate the

molecules impinge on the surface preferentially with the N-end first (upper index N), while a negative voltage reverses the orientation and leads to favoured O-end collisions (upper index O).

To obtain high beam intensities at the target we had to work with a 'large' focus diaphragm ($\phi_f = 6$ mm) and without the beam-stop inside of the hexapole. Therefore molecules not influenced by the hexapole as well as molecules in higher rotational states could also reach the target and the mean degree of orientation is reduced. We have measured the focused intensity as function of the hexapole voltage with beam-stop in and out. From comparison to calculations of the rotational state population at the focus diaphragm, which include the energetical properties of the beam measured and a rotational temperature[18] of $T_{rot} = (30 \pm 5)$ K, we have determined the upper limit of the mean degree of orientation to be $\overline{\langle \cos\phi \rangle} = 0.20 \pm 0.02$.

The Ni(100) single-crystal surface was cleaned as described elsewhere[23] and cooled with liquid nitrogen to temperatures below $T_s \leq 200$ K to avoid dissociation of the molecules.

The sticking probability is determined from the amount of NO molecules which do not stick as measured by means of a quadrupole mass analyser (QMA) shielded from the direct beam. After the opening of a beam shutter, the time dependence of the partial NO pressure is monitored in order to determine the fraction of the incident beam reflected from the surface. This reflector technique was first described by King and Wells[24]. If $p_1(t = 0)$ is the initial rise of NO pressure when the beam flag is opened and $p_2(t = t_{sat})$ is the pressure at a time when the surface is saturated with NO, then the initial and the time dependent sticking probability are given by:

$$S_0 = 1 - (p_1/p_2) \text{ and } S(t) = 1 - (p(t)/p_2).$$

We have taken into account several background corrections[25]. During a run, the background-pressure increases slightly. This increase is determined from a second run at full coverage. Influences from the neighbouring chambers, the response of the vacuum system and from molecules scattered by the focus diaphragm were determined by measuring the background pressures with beam on/off and varying the diaphragm and the beam-stop.

We determine the coverage by time integration of the sticking probability:

$$\Theta(t)_{abs} = I_0 \cdot \int_0^t S(t') \cdot dt'. \tag{1}$$

In general, the incident flux I_o is not well known and therefore the coverage is normalized to the saturation coverage: $\Theta(t) = (\Theta(t)_{abs}/\Theta_{sat})$. From this procedure one derives the sticking probability as function of coverage by a simple transformation. For NO at Ni(100) the saturation coverage is given by $\Theta_{sat} = 0.9 \times 10^{15}$ mol cm^{-2} at low temperatures[18,23].

We have performed the measurements reported here by use of two different mass analysers (Balzers: QMG 511 with cross-beam ionizer and VG Instruments: DX 130 with open uhv-source), used separately and also together during the same runs, since one of them (QMG 511) shows a higher NO signal for positive voltages at the orientation plate, leading to an error in the background correction.

Results and discussion

At a surface temperature of $T_s = 155$ K we have measured the following sticking probabilities (weighted mean values of differ-

ent numbers of runs): With orientation field off: $S_0^U = 0.44 \pm 0.03$; with field at $E = \pm 8\,\text{kV cm}^{-1}$: $S_0^N = 0.45 \pm 0.02$ and $S_0^O = 0.38 \pm 0.01$.

This demonstrates that the mean value $\bar{S}_0 = 0.43 \pm 0.01$ is close to that of unorientated molecules. Therefore we assume $S_0^N + S_0^O = 2 \cdot S_0^U$ and calculate the initial sticking asymmetry A_0^1 from:

$$A_0^1 = \frac{S_0^N - S_0^O}{2 \cdot S_0^U} = \frac{S_0^N - S_0^O}{S_0^N + S_0^O}. \tag{2}$$

From the values obtained we have determined: $A_0^1 = 0.09 \pm 0.01$.

Quantiatively, the asymmetry depends upon the actual degree of orientation and thus upon the field strength. The results of the initial sticking asymmetry vs the orientation field strength are shown in Figure 2 (left). At low field strength state mixing reduces the degree of orientation. This is produced by a second order Stark-effect due to hyperfine-splitting as well as lambda-doubling. We have calculated the degree of orientation as a function of the field strength using the data of the NO Stark-splitting[26,27]. In Figure 2 (left) the measured initial sticking asymmetry A_0^1 is compared to the calculations. From the linear dependence on the degree of orientation (Figure 2 (right)) we have calculated the normalized asymmetry $A_0^1/\langle\cos\phi\rangle$ to be $A = 0.7 \pm 0.1$.

Monte Carlo simulations[28] similar to those described in refs 9, 29 have shown clearly that the asymmetry of the initial sticking probability is affected by the strong anisotropy of the chemisorption potential[9,29,30]. The calculated asymmetry is given by $A = 0.76$ at $E_{\text{trans}} = 125\,\text{meV}$ in the case of NO–Ni(100), in good agreement with the experimental results.

We have also determined the sticking probability as function of coverage, and fitted the experimental data to a Kisliuk model[24,31], where the coverage dependence of the sticking probability is given by:

$$\frac{S(\Theta)}{S_k} = \frac{1}{1 + k \cdot \dfrac{\Theta}{1 - \Theta}}, \tag{3}$$

here, S_k is the initial sticking probability and k describes the slope
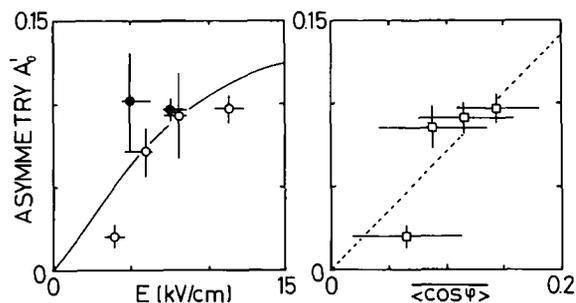
Figure 2. (Left): Measured initial sticking asymmetry A_0^1 as function of orientation field strength as compared to theory (full drawn line). (Open circles measured using DX130, closed circles using QMG511; see text.) **(Right):** Measured initial sticking asymmetry A_0^1 as function of the calculated degree of orientation. The broken line is a least squares fit through the origin. (Open boxes are averages of measured values using both QMA.) The error bars of A_0^1 and E are given by errors in the measurements, those of $\langle\cos\phi\rangle$ are due to the uncertainty of the calculation.
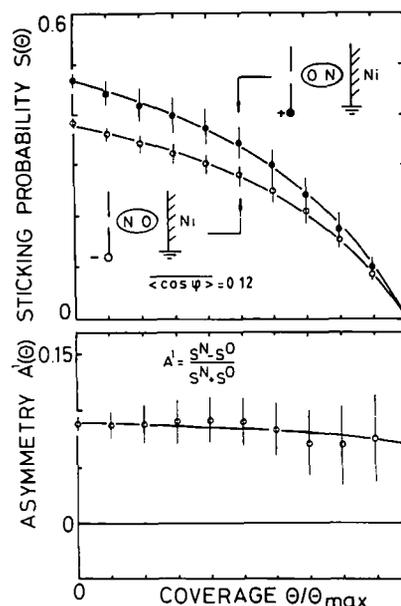
Figure 3. Coverage dependence of the sticking probability $S(\Theta)$ and the sticking asymmetry $A^1(\Theta)$. The values for k are obtained from a weighted orthogonal least square fit and are given by $k^N = 0.38 \pm 0.01$ and $k^O = 0.36 \pm 0.01$. Full drawn lines are calculated with the values of S_k and k from the fit.

at $\Theta = 1$. If p_a and p_d are the probabilities for adsorption and desorption from the 'precursor' above an empty site and p_d' is the desorption probability from the 'precursor' above an occupied site, then $S_k = \alpha \cdot p_a/(p_a + p_d)$ and $k = p_d'/(p_a + p_d)$, where α is the trapping probability to the 'precursor'.

In Figure 3 the results for a field strength of $\pm 8\,\text{kV cm}^{-1}$ ($T_s = 155\,\text{K}$) are shown. The Kisliuk constants calculated to obtain the best fit curves are nearly equal. This leads to an almost constant dependence of the sticking asymmetry on coverage.

Usually one concludes that $k \neq 1$ indicates the existence of a so called 'precursor' state to adsorption. But, if the molecule makes several hops at the surface before being adsorbed, then the adsorption probability may not depend on the orientation. Therefore we conclude that a model describing the coverage dependence of the sticking probability has to include both direct chemisorption and chemisorption through an intermediate physisorbed state.

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