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DEPENDENCE OF THE STICKING PROBABILITY ON INITIAL MOLECULAR ORIENTATION: NO ON Ni(100)

G.H. FECHER, N. BÖWERING, M. VOLKMER, B. PAWLITZKY and U. HEINZMANN

Fakultät für Physik, Universität Bielefeld, D-4800 Bielefeld 1, Fed. Rep. of Germany

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The sticking probability of NO at Ni(100) was examined using a beam of orientated NO molecules. It is found to be higher for N-end collisions. The asymmetry of the sticking probability has been measured to be a linear function of the molecular degree of orientation. It was determined to be $A = 0.7 \pm 0.1$ and nearly independent of coverage when normalized to the degree of orientation. The orientational dependence of the sticking probability as a function of coverage shows that the adsorption of the molecules cannot be described by a precursor model that neglects direct chemisorption.

NO molecules are bond to most surfaces perpendicularly with the nitrogen atom directed towards the surface. The dynamics of the adsorption process should therefore be orientation-dependent due to anisotropic molecule–surface interactions. This leads to the question whether the sticking probability of the molecules can be influenced by a specific orientation of the molecular axis prior to adsorption. In theoretical studies a higher sticking coefficient was calculated for molecules approaching the surface in the favourable bonding configuration for NO/Pt(111) and NO/Ag(111) [1]. Recent experiments were focused on the effects of orientation in scattering and trapping/desorption. Steric effects were observed in scattering experiments of orientated NO from Ag(111) [2] and of oriented CH_3F from graphite [3]. Recently, Kuipers et al. [4] have measured steric effects in scattering and trapping/desorption of NO at Pt(111) from which they determined a higher trapping probability for an initial orientation with the N-end towards the surface. Complementary to these scattering experiments we have examined steric effects in the sticking probability, which probes directly the chemisorption potential. As reported briefly [5], in the case of NO/Ni(100) for molecules with one particular degree of orientation we have observed a higher initial sticking probability when the surface is approached with the N-end first. However, to assess the order of magnitude of the effect measured one has to take into account the actual degree of orientation achieved. Therefore, we present here measurements of the sticking probability of nitric oxide on Ni(100) at different orientation field strengths. In addition, to study the influence of the molecular orientation on the adsorption kinetics we have examined the sticking probability as a function of coverage.

Ni(100) was selected to study asymmetries in the sticking process because it is known that the NO molecules are chemisorbed perpendicularly with the N-end to the Ni surface [6] and have an initial sticking coefficient markedly different from unity and from zero [7]. We work at low target temperatures where the desorption probability from the chemisorbed state has been found to be negligibly small.

Using the electrostatic hexapole technique [8], NO molecules can be state-selected for subsequent orientation in homogeneous electric fields [9] due to their permanent dipole moment. In our experimental apparatus a molecular beam ($E_{\text{trans}} = 125$ meV) is directed into the UHV chamber containing the nickel target. The rotational temperature of the molecules is sufficiently low such that most

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of the NO molecules are in the $^2\Pi_{1/2}\,|\,J, \Omega, m_J\rangle = |1/2, 1/2, 1/2\rangle$ ground state. Molecules with a positive linear Stark effect in the hexapole state selector are focused onto the target, while molecules showing a negative Stark effect are defocused from the beam. The focused molecules pass through a guiding field and approach the Ni(100) target at normal incidence. A high voltage is applied to a plate mounted parallel to the target producing a homogeneous orientation field. At positive voltage, the molecules impinge on the surface preferentially with the N-end first; their orientation can be reversed by changing the polarity of the field (sticking probability S^N and S^O, respectively). The orientational probability distribution of NO in the ground state is given by $P[\cos(\Phi)] = [1 \pm \cos(\Phi)]/2$ (Φ is the angle between the molecular axis pointing from O to N and the electric field vector). To obtain high beam intensities we had to work without a beam-stop inside of the hexapole and with a "large" focus diaphragm. Thus higher rotational states were also focused and the degree of orientation in our experiment was smaller than the theoretical value. Taking into account our hexapole geometry, the rotational temperature ($T_{rot} = 30$ K) of the molecules [7] and the focused intensities (measured as a function of the rod voltage), we have calculated the uppermost limit of the degree of orientation to be $\langle\cos(\Phi)\rangle = 0.20 \pm 0.02$ in our experiment (instead of 1/3 for a pure rotational state), if the nuclear spin is completely decoupled. The Ni(100) single-crystal surface was cleaned by standard procedures. Auger spectroscopy and LEED were used to determine the surface cleanness and geometrical order. The crystal was cooled with liquid nitrogen to temperatures below $T_s = 200$ K to avoid dissociation of the molecules, which was checked by means of workfunction measurements. The sticking probability is determined using the reflector technique by means of a quadrupole mass analyser shielded from the direct beam. This method was first described by King and Wells [10] and later refined [11,12].

The mean value of the initial sticking probability at $T_s = 155$ K measured with the orientation field on ($E = \pm 8$ kV/cm) was found to be $(S_0^N + S_0^O)/2 = 0.43 \pm 0.01$, close to the value of unorientated molecules $S_0^U = 0.44 \pm 0.03$ [13]. Therefore we assume $S_0^N + S_0^O = 2S_0^U$ and we define the sticking asymmetry A^1:

$$A^1 = \frac{S^N - S^O}{2S^U} \approx \frac{S^N - S^O}{S^N + S^O}. \tag{1}$$

The results obtained for the initial sticking asymmetry A_0^1 as a function of the orientation field strength are shown in fig. 1 (left). The full drawn line is calculated from a simple model for the decoupling of the nuclear spin from the rotation of the molecule (using data for the NO Stark splitting from ref. [14]) combined with Monte Carlo simulations [15] of the sticking probability as a function of orientation. In fig. 1 (right) the sticking asymmetry is shown as a function of the calculated molecular orientation. Note that the mean values of $\langle\cos(\Phi)\rangle$ are smaller than the upper limit of 0.2 due to the coupling of the nuclear spin to the rotation, which will produce state mixing especially at low field strengths [14]. The asymmetry measured was found to be proportional to the degree of orientation within the experimental uncertainties. Thus it can be normalized to the degree of orientation yielding: $A = A_0^1/\langle\cos(\Phi)\rangle = 0.7 \pm 0.1$.

We have also determined the sticking probabilities and asymmetry as a function of coverage θ.

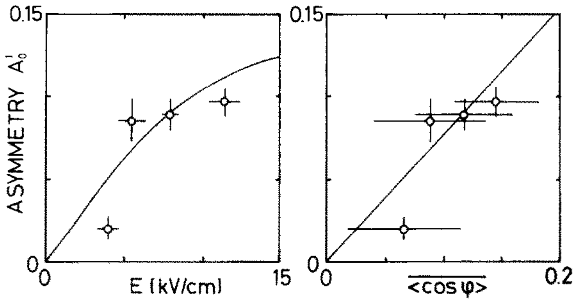

Fig. 1. Left: measured initial sticking asymmetry A_0^1 as a function of orientation field strength E and comparison to theory. Right: measured initial asymmetry A_0^1 as a function of calculated degree of orientation $\langle\cos(\Phi)\rangle$ and comparison to theoretical values. The error bars of A_0^1 and E denote the errors of the measurement, the error bars of $\langle\cos(\Phi)\rangle$ are due to the uncertainty of the calculations. The full drawn lines and the degree of orientation are calculated using a simple model of nuclear spin decoupling combined with Monte Carlo simulations.

As usual, we have fitted the experimental data to a Kisliuk model [16]:

$$S(\theta)=\frac{S_k}{1+k\theta/(1-\theta)},$$

$$S_k=\alpha\frac{p_a}{p_a+p_d},\quad k=\frac{p_d'}{p_a+p_d},\tag{2}$$

where S_k is the initial sticking probability and k is the "Kisliuk" constant; p_a and p_d are the probabilities for adsorption and desorption from the precursor above empty sites and p_d' is the probability of desorption from a state above an occupied site, as defined in ref. [16]. The trapping probability α was introduced to that model by King and Wells [10].

In fig. 2 the results for field strengths of ±8.0 kV/cm ($T_s=155$ K) and ±5.5 kV/cm ($T=135$ K) are shown as a function of coverage for both sticking probability and asymmetry. The sticking probabilities are normalized to the value of the initial sticking probabilities for unorientated molecules. From the best fit curves of the experimental data to the Kisliuk model one finds that the constants are nearly equal ($k=0.35\pm0.02$) for both orientations and field strengths. These values lead to a nearly constant dependence of the asymmetry on coverage, equal to the initial value, but with larger experimental uncertainty when the coverage approaches saturation.

Usually $k\neq1$ indicates the existence of a so-called "precursor" state. But if the molecules were trapped into a physisorbed state before they are chemisorbed, they loose their initial orientation and p_a as well as p_d are not dependent on orientation. Therefore, the trapping probability α is the only orientation-dependent quantity and S_k will depend on the orientation. Hamza et al. [7] have shown in their experiments that the trapping probability to the extrinsic precursor for unorientated NO at NO/Ni(100) is very high (near unity). In this case one does not expect a dependence on orientation because α cannot exceed one. On the other hand, one has to take into account trapping into the intrinsic precursor above empty adsorption sites, with a probability different from that of the extrinsic state. In this case, the Kisliuk model given by the formula above will no longer describe the coverage dependence of the sticking probability.

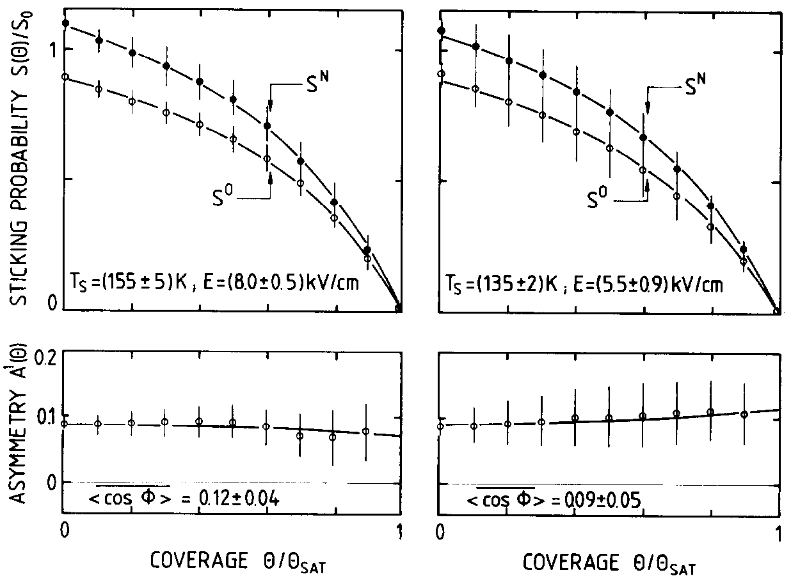

Fig. 2. Normalized sticking probabilities $S(\theta)$ and asymmetries $A^1(\theta)$ as a function of coverage θ at two different degrees of molecular orientation (translational energy $E_{\text{trans}}=125$ meV). Horizontal error bars denoting the uncertainty of the coverage (±10%) are not drawn. The full drawn lines are calculated from a best fit of the experimental data to a Kisliuk model (see text; this is equivalent to using eqs. (3) with $h=0$).

Taking into account direct chemisorption with the probability p_c and neglecting trapping into the intrinsic precursor, we derive the following relations, using a more complex kinetic model given by Cassuto and King [17]:

$$S(\theta) = \frac{S_0 + h\theta}{1 + k\theta(1-\theta)},$$

$$S_0 = p_c,$$

$$h = \left[\alpha p_a - p_c\left(1 - \frac{p_m}{p'_m}\right)\right] \frac{p'_m}{1 - p_m}, \qquad (3)$$

where h is a constant to describe an additional coverage dependence. $p_m = [1 - (p_a + p_d)]$ and $p'_m = 1 - p'_d$ are the probabilities of diffusion from one precursor to the other. These probabilities are connected to the difference in the well-depths of the potentials related to the precursor states. α and p_c are the only orientation-dependent quantities, and the sticking asymmetry as a function of coverage is given by:

$$A^1(\theta) = \frac{S_0^N - S_0^O + (h^N - h^O)\theta}{S_0^N + S_0^O + (h^N + h^O)\theta} \xrightarrow[h \approx 0]{} \frac{p_c^N - p_c^O}{p_c^N + p_c^O}. \qquad (4)$$

If h vanishes which is the case if $p'_m \ll (1 - p_m)$ or if $p_c(1 - p_m/p'_m)$ is nearly equal to αp_a the asymmetry will become independent of coverage even if α is almost equal to one. It is then only given by the asymmetry of the probability for direct chemisorption. Deviations from the constant asymmetry may be detected by varying the surface temperature since this changes the probabilities which occur in the model. As shown in fig. 2 there might be some small influences due to different temperatures at high coverages.

The model outlined above which includes direct chemisorption describes our data. Our measurements of the sticking asymmetry show a strong effect of about 70% with respect to the degree of molecular orientation. The results as a function of coverage show that a simple picture of trapping into a precursor state and neglecting direct chemisorption cannot explain the adsorption of NO at Ni(100).

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[13] The values of the initial sticking probability as well as the initial sticking asymmetry reported in this work are slightly higher than that in our previous work [5], where we had underestimated the background from the molecules scattered at the focus diaphragm. Furthermore, we have now experimental evidence that even small amounts of carbon (C or CO) at Ni(100) lower the initial sticking probability as well as the asymmetry.

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