

molecularly adsorbed on and desorbed from the Pt(111) surface. However, H_2 is dissociatively adsorbed and recombinatively desorbed on the Pd(100) surface. Hence the desorption mechanisms, not to mention the molecule-surface interaction potentials, are quite different for these two systems. The H_2 formed by recombination of atomic hydrogen on the surface is highly excited and experiences a prompt non-thermal desorption. On the other hand, NO is in thermal equilibrium with the Pt(111) surface throughout its residence time and desorption takes place *via* a thermally populated transition state.

Finally, Dr Stolte asked: In addition to the regular torque received by the NO molecule interacting with the surface¹ which you show to be able to induce the rotational alignment of desorbing of inelastically scattered molecules,² the open-shell character of the $^2\Pi$ -electronic ground state of NO allows also for an azimuthal dependence of the interaction Hamiltonian.^{3,4} Can you infer any evidence for the presence of such an interaction from your observations of the NO-Pt(111) system?

1 D. C. Jacobs and R. N. Zare, *J. Chem. Phys.*, submitted.

2 D. C. Jacobs, K. W. Kolanski, R. J. Madix and R. N. Zare, *J. Chem. Soc., Faraday Trans. 2*, 1989, **85**, 000.

3 S. Green and R. N. Zare, *Chem. Phys.*, 1975, **7**, 3218.

4 J. E. Smedley, G. C. Gory and M. H. Alexander, *J. Chem. Phys.*, 1987, **87**, 3218.

Prof. Jacobs replied: In all of our experiments, we observed the same degree of rotational alignment for both Λ -doublet states of NO.¹ If we had observed different rotational populations or alignment within a Λ -doublet pair, we then could infer that the interaction potential for NO/Pt(111) has an azimuthal dependence.

1 D. C. Jacobs, K. W. Kolasinski, S. F. Shane and R. N. Zare, *J. Chem. Phys.*, submitted.

Mr G. Fecher, M. Volkmer, Dr N. Böwering, B. Pawlitzky and Prof. U. Heinzmann (Bielefeld) said: We would like to report our recent measurements of the sticking probability of oriented NO at Ni(100). As described in the paper of Kleyn *et al.*¹ molecules are adsorbed at a surface with preferential orientations. NO is known to bind to most surfaces with the N atom towards the surface and the molecular axis orientated perpendicularly. In theoretical studies^{2a} a strong dependence of the initial sticking probability on the initial orientation for NO at Pt(111) and Ag(111) was predicted.

In order to observe an orientational dependence the sticking probability itself should be significantly different from unity or zero. Therefore, we choose the system NO/Ni(100) where the molecules are known to be chemisorbed with the N end down and with perpendicular orientation.³ Furthermore, the binding energy for this system is *ca.* 1 eV, which is much larger than for the physisorbed NO/Ag(111) system. Hamza *et al.*⁴ have measured an initial sticking probability of 0.67 (at $E_{\text{trans}} = 90$ meV) for this system.

Our molecular-beam apparatus, which is similar to that of Kleyn and co-workers,¹ is shown in fig. 54. We use a continuous supersonic seeded molecular beam (20% NO, 20% Ar, 60% He) with a translational energy of 125 meV (measured by use of a slotted-disc velocity selector). The beam was modulated using a tuning-fork chopper for measurements of the translational energy and the focusing spectra of the electrostatic hexapole state selector. By taking advantage of the linear Stark effect in the hexapole state selector, the NO molecules in the $^2\Pi_{1/2}|J = 1/2, \Omega = 1/2, M_J = 1/2\rangle$ ground state are focused onto a Ni(100) single-crystal target (held at ground potential). The beam is passed through a guiding field and then through a plate parallel to the target which produces a homogeneous orientation field. The molecules approach the Ni surface at normal incidence. By changing the sign of the voltage applied to the plate the preferential orientation of the molecules can be changed. At positive voltage, the molecules impinge

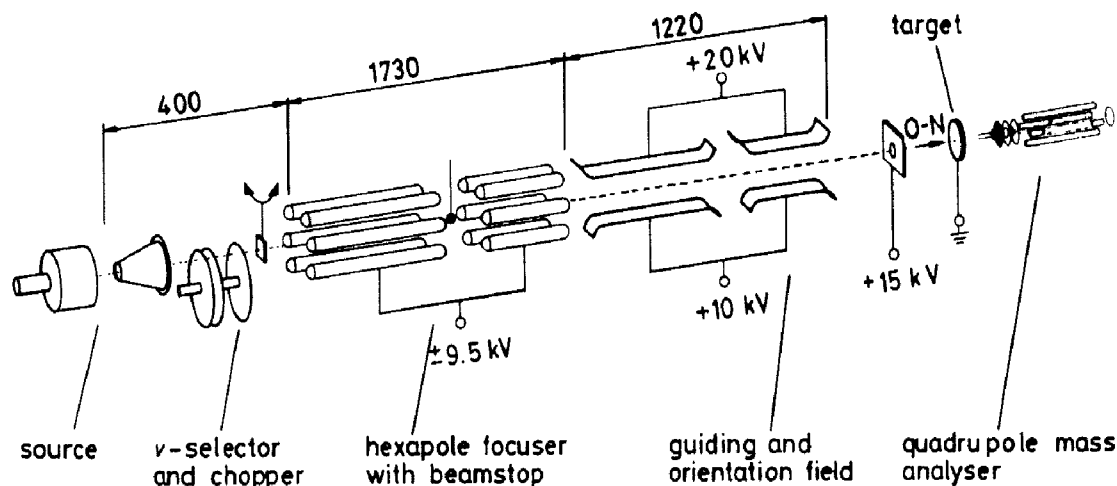


Fig. 54. Schematic view of the experimental arrangement.

on the surface preferentially with the N end first. The orientation probability of NO in the ground state is given by $P(\cos \gamma) = 1/2(1 \pm \cos \gamma)$, where γ is the angle between the dipole moment μ of the molecule and the electric field E . From this distribution a maximum orientation $\langle \cos \gamma \rangle_{\max} = \pm 0.3$ is obtainable (the + sign refers to the N end pointing towards the surface). Taking into account that the molecules from the effusive background and those that are not influenced by the state selector cannot be orientated, the real orientation in our experiment is $\langle \cos \gamma \rangle = \pm 0.26$ for a field strength high enough to decouple the nuclear spin from rotation.

The Ni(100) single crystal is cooled to 135 K to prevent dissociation of the molecules. This was checked by measurement of the change of the electronic workfunction during adsorption.

We use a quadrupole mass analyser (QMA) mounted behind the target to determine the sticking probability. The QMA is shielded from the direct beam and detects all molecules that are *not* adsorbed at the surface. King and Wells⁵ have shown that the sticking probability as function of the time t is given by the ratio of pressures of the initial clean [$P_1(t)$] and fully covered [$P_2(t')$] sample.

$$S(t) = 1 - \frac{P_1(t)}{P_2(t')}$$

In practice $P_2(t')$ is nearly constant with time t , as verified by an additional measurement at t' with full coverage θ_{\max} . The relative coverage is calculated by integrating $I_p S(t)$, where I_p is the incident flux of molecules.

$$\frac{\theta(t)}{\theta_{\max}} = \frac{I_p \int_0^t S(t) dt}{I_p \int_0^{t(S=0)} S(t) dt}$$

Additional LEED and AES studies show a $c(2 \times 2)$ overlayer of NO at $t(S=0)$, which corresponds to one half of a Ni(100) layer and a coverage

$$\theta = 8 \times 10^{14} \text{ cm}^{-2}$$

Fig. 55 shows the results of our experiments on the orientational dependence of the sticking probability. The electric field strength of the orientation field was limited to 5 kV cm^{-1} for these measurements. The emphasis of this work is on the orientational dependence of the initial sticking coefficient $S_0 = S(t=0)$. At large coverage the experimental error bars are larger and the difference for the two orientations is less significant. S_0 is measured to be *ca.* 0.4 with a higher value for the preferential orientation with the

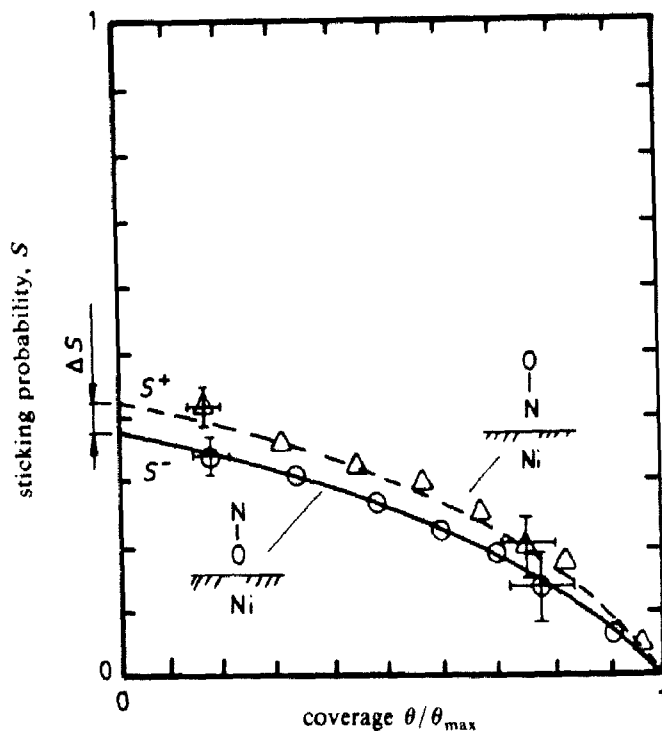


Fig. 55. Experimental results: sticking probability of orientated NO $|1/2, 1/2, 1/2\rangle$ at Ni(100). Δ , Ni-N-O; \circ , Ni-O-N; $E = \pm(5.7 \pm 0.5) \text{ kV cm}^{-1}$; $T_{\text{surf}} = 135 \text{ K}$; $E_{\text{trans}} = 125 \text{ meV}$.

N end pointing to the surface. By dividing the difference of the initial sticking probabilities of the two preferred orientations by the mean value we obtain

$$\frac{\Delta S_0}{S_0} = \frac{2(S_0^+ - S_0^-)}{(S_0^+ + S_0^-)} = 2A = 0.13 \pm 0.03$$

as the experimental result of the sticking asymmetry A for our NO molecular beam with a degree of orientation of 0.26. The mean value of S_0 of ca. 0.4 is smaller than the value measured by Hamza *et al.*⁴ This might be due to the fact that we measure S_0 for a single rotational state, namely $|1/2, 1/2, 1/2\rangle$, in high electric fields. Furthermore, it is conceivable that we have underestimated the effusive background from the hexapole region which is difficult to determine precisely.

In our measurements the sticking probability decreases from the initial value S_0 to zero as function of coverage. We have fitted the experimental points to a Kisliuk model (full curves in fig. 55). The data indicate a deviation from a linear dependence on coverage. This suggests that long-range attraction might also slightly influence the sticking; this influence, however, seems to be small since the deviation from a linear dependence is not large. Thus, we do not think that a so-called precursor state alone can explain our data. For the NO-Ni system, chemisorption dominates. The measured change in the electronic workfunction of 0.8 eV at a coverage $\theta/\theta_{\text{max}} = 1/2$ due to the dipole moment of the molecules indicates that the physisorption potentials as well as the chemisorption potentials must have changed during the adsorption process. The work of Kleyn¹ shows that the trapping into the physisorption potential has an orientational dependence due to the anisotropy in the repulsive part of the interaction potential. We think that this holds also in the case of chemisorption, even if a 'precursor state' is present.

We have also computed the initial sticking probability of orientated NO at Ni by use of one-dimensional classical stochastic trajectory simulations. The features of these calculations are described by Polanyi and Wolf.^{2b} We use an average over one unit

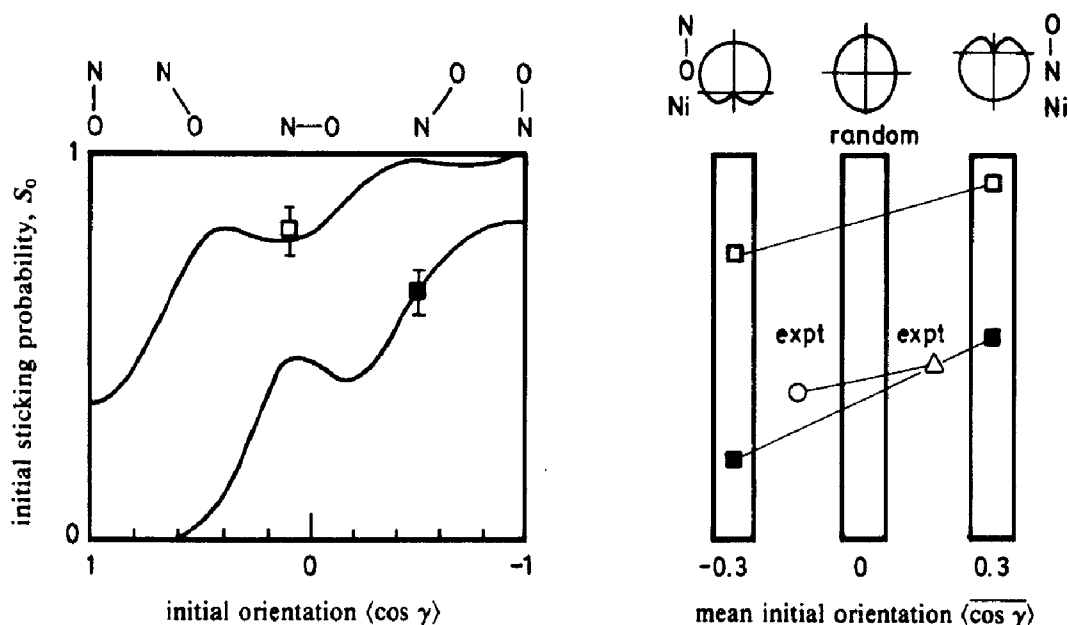


Fig. 56. Left-hand side: calculated orientational dependence of the initial sticking probability ($T_{\text{rot}} = 1.2$ K; $T_{\text{surf}} = 140$ K; \square , $E_{\text{trans}} = 110$ meV; \blacksquare , $E_{\text{trans}} = 250$ meV). The error bars indicate statistical errors of the Monte-Carlo simulation. Right-hand side: comparison between theory and experiment. The experimental values are for $T_{\text{surf}} = 135$ K; $E_{\text{trans}} = 125$ meV.

surface cell of the potential introduced by Muhlhausen *et al.*^{2a} This potential consists of two parts: first, a van der Waals-type physisorption potential and, secondly, a Morse-type chemisorption potential. The latter takes into account that the molecule is strongly bound to the surface by the N end. The results are shown on the left-hand side of fig. 56. To compare these calculations with our experiment, independent runs for each of the two probability distributions of opposite orientations were taken. The comparison is shown in the right-hand side of fig. 56 at the respective mean orientation $\langle \cos \gamma \rangle$. The asymmetry of the sticking calculated for an orientation of ± 0.3 is in the range of $0.08 \leq A \leq 0.3$ (depending on the energy), which is a slightly stronger effect than measured in the experiment. However, as indicated by the higher values of \bar{S}_0 , the calculation uses a binding energy that is too high, caused by an overestimation of the on top-site adsorption.

Summarizing, our experimental studies of NO chemisorption at Ni(100) as well as the corresponding Monte-Carlo calculation have demonstrated a significant sticking asymmetry as function of the orientation of the NO molecule on the order of 25% of the degree of orientation.

- 1 A. W. Kleyn, E. W. Kuipers, M. G. Tenner and S. Stolte, *J. Chem. Soc., Faraday Trans. 2*, 1989, **85**, 000.
- 2 (a) C. W. Muhlhausen, L. R. Williams and J. C. Tully, *J. Chem. Phys.*, 1985, **83**, 2554; (b) J. C. Polanyi and R. J. Wolf, *J. Chem. Phys.*, 1985, **82**, 1555.
- 3 J. Stöhr, K. Baberschke, R. Jaeger, R. Treichler and S. Brennan, *Phys. Rev. Lett.*, 1981, **47**, 381.
- 4 A. V. Hamza, P. M. Ferm, F. Budde and G. Ertl, *Surf. Sci.*, 1988, **199**, 13.
- 5 D. A. King and M. G. Wells, *Surf. Sci.*, 1972, **29**, 454.

Prof. R. D. Levine (Jerusalem) said: In our simulations^{1,2} of rapid laser-induced desorption of diatomic molecules, we observed that the dynamics (and hence, the polarization) of rotational excitation during the exit motion depended also on the strength of binding to the surface. As is only to be expected, stronger, chemical-like binding resulted in more impacts with the surface. In the experiments on different systems, can one correlate the preferred alignment with the nature of the binding?

- 1 T. A. Holme and R. D. Levine, *J. Chem. Soc. Faraday Trans. 2*, 1988, **84**, 1630.
- 2 T. A. Holme and R. D. Levine, *Surf. Sci.*, in press.