molecularly adsorbed on and desorbed from the Pt(111) surface. However, H₂ 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 H₂ 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 ⁰Π₁/₂ 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?


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.


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 studies² 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 Eₜₐₙₙ = 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 ⁰Π₁/₂ J = 1/2, Ω = 1/2, M₁ = 1/2 > 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
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 \( \gamma \) is the angle between
the dipole moment \( \vec{p} \) of the molecule and the electric field \( \vec{E} \). From this distribution a
maximum orientation \( \langle \cos \gamma \rangle_{\text{max}} = \pm 0.3 \) 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 Wells\(^6\) 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 \( \theta_{\text{max}} \). The relative coverage is calculated by integrating \( I_pS(t) \),
where \( I_p \) is the incident flux of molecules.

\[
\frac{\theta(t)}{\theta_{\text{max}}} = \frac{\int_{t'}^{t} I_p S(t) \, dt}{\int_{t'}^{t} I_p S(t) \, dt'}
\]

Additional LEED and AES studies show a \((2 \times 2)\) overlaver 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 $\text{NO}[1/2,1/2,1/2]$ at Ni(100). $\triangle$, Ni-N-O; $\bigcirc$, Ni-O-N; $E = (5.7 \pm 0.5)$ kV cm$^{-1}$; $T_{\text{surf}} = 135$ K; $E_{\text{trans}} = 125$ 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 $1/2, 1/2, 1/2$, 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 Kleyn$^1$ 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.$^{26}$ We use an average over one unit
Fig. 56. Left-hand side: calculated orientational dependence of the initial sticking probability ($T_{\text{rot}} = 1.2 \, \text{K}$; $T_{\text{surf}} = 140 \, \text{K}$; $\square$, $E_{\text{trans}} = 110 \, \text{meV}$; $\blacksquare$, $E_{\text{trans}} = 250 \, \text{meV}$). The error bars indicate statistical errors of the Monte-Carlo simulation. Right-hand side: comparison between theory and experiment. The experimental values are for $T_{\text{surf}} = 135 \, \text{K}$; $E_{\text{trans}} = 125 \, \text{meV}$.

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 $\pm 0.3$ 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 $S_0$, 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.


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?