

# Collision of oriented NO with Ni(100) and with oriented CO on Ni(100)

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The interaction between gas-phase oriented NO molecules with Ni(100) has been investigated by means of pulsed supersonic molecular beam, hexapole and time-of-flight techniques. With TOF we examined the NO molecules leaving the clean Ni(100) surface. A velocity distribution commensurate with the surface temperature was observed. The time-integrated signal of the scattered NO beam shows an orientation asymmetry of  $A_{sc} = 0.38 \pm 0.05$  with respect to the NO and ON initial orientation. An initial sticking probability of 0.27 and 0.30 for preferential O-end and N-end collisions, respectively, at a  $(2 \times 2)$  saturated layer of CO was also obtained. Taking the degree of orientation of the NO molecules into account, this leads to an asymmetry of  $A_{st} = 0.5 \pm 0.1$  independent of coverage. The CO molecules displaced by NO were simultaneously recorded. The CO signal shows an asymmetry with respect to the NO orientation, as well. Two different displacement mechanisms are discussed to explain this behavior.

## 1. Introduction

Coadsorption studies with NO and CO molecules on surfaces have significance in surface physics and in technical applications concerning corrosion or catalysis. If both CO and NO coexist on a surface two processes can occur. Either molecules like  $N_2$  and  $CO_2$  can be produced via a chemical reaction [1,2] or the NO bond prevails and CO is displaced by NO [3]. This second case was found for the Ni(100) surface by Hamza et al. [4]. They examined the displacement by means of a supersonic molecular beam technique at various translational energies (90–1100 meV) and by laser-induced fluorescence. At  $T = 140$  K the NO initial sticking and the CO initial displacement probabilities for the clean Ni(100) surface were found to be about 0.6 for beam energies below 400 meV.

In our experiment NO molecules are oriented electrostatically by means of a hexapole technique [5] and focused onto the target. In front of the Ni(100) surface the direction of the NO orientation is defined by an electrostatic field and

can easily be reversed so that two different configurations can be achieved: preferential N-end or O-end collisions with the surface. Furthermore, the translational energy distribution of the scattered NO molecules is also measured by means of the TOF technique. Orientation-dependent effects on other surfaces were previously observed for direct scattering [6,7] and trapping-desorption [8].

Recently, Fecher et al. [9] measured a higher sticking probability of NO molecules at Ni(100) for N-end collisions than for O-end collisions. We now present results for scattered oriented NO molecules at a clean Ni(100) surface with a substrate temperature of 160 K. At 300 K, work-function measurements proved that NO adsorption at a CO precovered nickel crystal mainly proceeds molecularly [10] in contrast to investigations at clean Ni(100) [11]. Therefore we switched over to the substrate temperature of 300 K for the measurements at the CO precovered target. Both the NO sticking probability and the CO displacement were observed at the same time as a function of coverage and orientation.

## 2. Experimental

The main components of the experimental setup have already been described [9,12,13]. At first, we had to saturate all surfaces of the UHV vessel with NO. After cleaning the nickel crystal (see below) we precovered it with a CO c(2 × 2) superstructure. Finally, the NO and CO signals were recorded by means of two quadrupole mass analyzers to obtain the sticking probability of NO [14] and the CO displacement. Both detectors were shielded from the direct beam. The coadsorption measurements were performed with a continuous beam of NO.

For scattering experiments we replaced the continuous NO beam nozzle with a pulsed nozzle [15]. Consequently, we achieved a decrease of the rotational temperature and an increase of the speed ratio. NO was seeded in 35% He and 45% Ne, which resulted in a translational energy of 125 meV. We used a nozzle on-time of 300 μs. This yielded a high intensity while on the other hand it did not widen our signal too much, because this time was shorter than the thermal spread of  $2\sigma_1 = 420 \mu\text{s}$ . The direct beam signal is shown in fig. 1. As determined by deconvolution, the time of  $2\sigma = 490 \mu\text{s}$  is composed of: 300 μs pulse length of the nozzle, 420 μs time spread of the beam and 120 μs detector response time. The

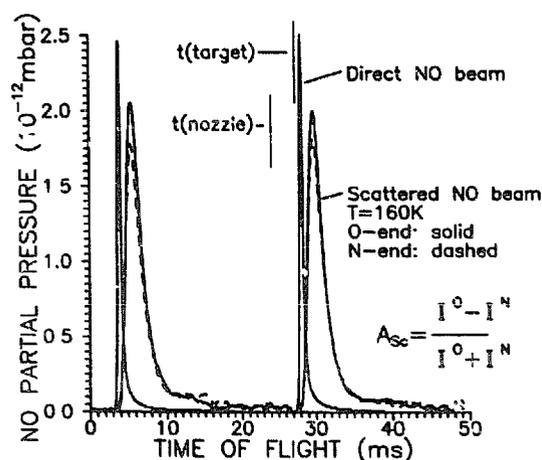


Fig. 1 The direct and the scattered NO beam ( $E_{\text{trans}} = 125$  meV) as a function of time for both NO orientations. The direct signal is scaled down by a factor of 60000.

translational time width corresponds to a speed ratio of  $S = 20$  and  $T_{\text{trans}} = 3.6$  K. A hexapole voltage of 9.5 kV was selected to focus the  $^2\Pi_{1/2} |J, \Omega, m_J\rangle = |\frac{1}{2}, \frac{1}{2}, \frac{1}{2}\rangle$  ground state. With these beam parameters and an orientation field strength in front of the target of 6.4 kV/cm, a degree of orientation of 0.17<sup>#1</sup> results. The scattered beam is detected with a quadrupole mass analyzer mounted inside a differentially pumped chamber (ion getter and liquid N<sub>2</sub> trap). Due to the small signal intensity of the scattered molecules we had to sum over 10000 cycles to increase the signal-to-noise ratio, using a transient recorder PC card [16]. This led to a total run time of about 15 min. In order to avoid saturation of the surface we scanned over the whole area (diameter = 12 mm) in the form of a spiral by means of three steppers. The angles of incidence and scattering were set at  $\Theta_i = \Theta_s = 22.5^\circ$ . The distances nozzle–target and target–detector were 3.38 and 0.49 m, respectively. An aperture with a diameter of 3 mm and at a distance of 90 mm from the surface was used in front of the detector. An NO scattering experiment (as in fig. 1) but on a CO precovered Ni(100) as a function of the CO coverage was not feasible, because the duration of the CO displacement was much shorter than the typical run time to record a TOF spectrum as in fig. 1. In order to characterize the direct NO beam the nickel target was removed.

During the experiment the pressure in the main vessel was below  $3 \times 10^{-10}$  mbar. The crystal was cleaned by cycles of Ar<sup>+</sup>/Ne<sup>+</sup> bombardment ( $10^{-6}$  mbar, 30 min, 5 μA), annealing in O<sub>2</sub> ( $10^{-8}$  mbar, flash, 400°C) and reduction in H<sub>2</sub> ( $2 \times 10^{-8}$  mbar, 2 min). Geometrical structure and cleanness were controlled by LEED and Auger

<sup>#</sup> The sticking experiment described in this contribution has been performed by means of a continuous as well as of a pulsed NO beam. The orientation asymmetry of the sticking coefficient measured has been found to be higher by a factor of 1.7 for the pulsed NO beam than for the continuous beam because of an increase of the degree of orientation from 0.12 [9] to 0.17.

### 3. Results

Fig. 1 shows the results of the scattering experiment at a substrate temperature of 160 K. The two peaks of the direct beam are separated by 24.2 ms which corresponds to the nozzle frequency of 41.3 Hz. The vertical lines indicate when the NO beam leaves the nozzle and when it arrives at the target. The direct beam has a mean velocity of 890 m/s and a time width of 490  $\mu$ s which implies a spread of  $\pm 45$  m/s. Furthermore, fig. 1 also shows the orientation-dependent signal of the scattered beam at a clean Ni(100) surface. An agreement with a Maxwell distribution (160 K) is found for both orientations. Preferential O-end collisions show a higher peak signal (solid line) than those with the N-end directed towards the surface. The integral orientation asymmetry of the scattered beam<sup>#2</sup> has been found to be  $0.064 \pm 0.004$ . Taking the degree of orientation into consideration this leads to a final asymmetry of  $A_{Sc} = 0.38 \pm 0.05$ .

Fig. 2 shows both the NO and the CO signal as a function of time during the displacement measurements with a continuous NO beam at a substrate temperature of 300 K. In the upper part of fig. 2 the precovered nickel target was exposed to the NO beam at  $t = 0$  min. The surface acted like a getter by partial adsorption of the molecules (hatched area). The other part represents the scattered molecules. The entire event took about 10 min which resulted in an NO  $(2 \times 2)$  superstructure. After 15 min the valves were closed again in order to measure the background pressure accurately [13]. In the lower part of fig. 2 the time scale is elongated. Within two minutes almost all the CO molecules were removed, the maximum was reached with a delay of 20 s. No reaction products like  $N_2$  or  $CO_2$  were detected.

The sticking probability and the orientation asymmetry as a function of NO coverage is given in fig. 3. We fitted the experimental data to a Kisliuk model [18] (full curves). Initial sticking probabilities of  $S_0^N = 0.30 \pm 0.01$  and  $S_0^O = 0.27$

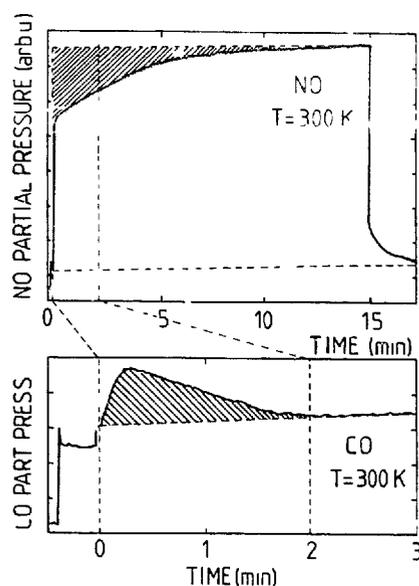


Fig 2 NO and CO partial pressures as a function of time during the displacement measurements with a continuous NO beam. The horizontal dashed lines represent the increasing background pressure. The steps at the beginning and end are due to the opening and closing of valves. The time scale of the CO signal is stretched. The dashed areas represent the contribution of sticking NO and desorbing CO molecules.

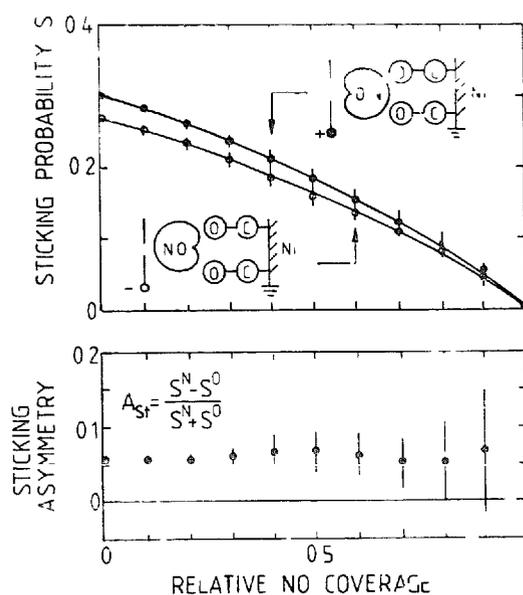


Fig 3 Upper part NO sticking probabilities for both orientations as a function of NO coverage, fitted to the Kisliuk model. Lower part orientation asymmetry of the NO sticking at CO/Ni(100) as a function of NO and CO coverage.

<sup>#2</sup> Note that the definition of the orientation asymmetry of ref [17] is different from our definition (see fig 1).

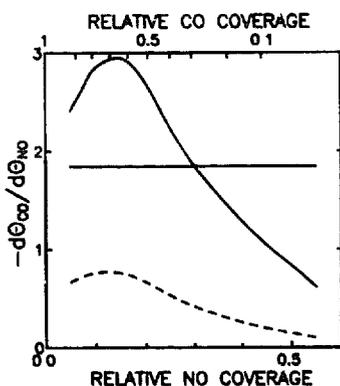


Fig. 4. Number of CO molecules displaced by each sticking NO molecule (full curve) and by each incoming NO molecule (dashed curve, multiplied with the sticking probability) as a function of NO coverage. The horizontal line represents the average displacement for this range of coverage (until the CO signal vanishes)

$\pm 0.01$  for N-end (upper curve) and O-end (lower curve) collisions, respectively, were measured. The Kisliuk constants were found to be  $k^N = 0.66 \pm 0.01$  and  $k^O = 0.67 \pm 0.01$ , respectively. The asymmetry given in the lower part of fig. 3 shows an almost constant behavior as a function of coverage. Normalized to the degree of orientation (0.12) the value of the initial asymmetry is  $A_{st} = 0.5 \pm 0.1$ .

The CO coverage differentiated with respect to the NO coverage is given in fig. 4. An increase at low and a decrease at high NO coverages was measured. The maximum is determined to be 3, i.e., for each sticking molecule 3 CO molecules leave the crystal. An average displacement of almost 2 is given by the horizontal line.

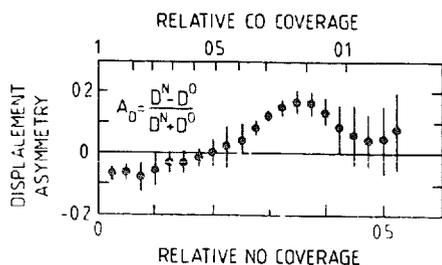


Fig. 5. Orientation asymmetry of the CO displacement as a function of NO coverage and CO coverage. The asymmetry scale refers to each incoming NO molecule

Fig. 5 gives the corresponding asymmetry of the CO displacement. The orientation asymmetry of the displacement shows a change of sign at a relative NO coverage of 0.2; above 0.5 the CO signal is no longer detectable. This behavior refers to the incoming NO molecules. The asymmetry is slightly negative for low NO coverages and shows positive values for higher NO coverages. The highest asymmetry in favour of N-end collisions occurs at a relative NO coverage of 0.35. In order to refer to each sticking NO molecule the vertical scale in fig. 5 would have to be shifted upwards by the constant sticking asymmetry of 0.06 (see fig. 3).

#### 4. Discussion

First, we would like to discuss the scattering results shown in fig. 1. On the one hand ref. [19] established the existence of precursor states and a complete energy accommodation of the beam ( $T_{trans} = T_{rot} = T_{vibr} = T_{electr} = T_{surface}$  [20]). This behavior is valid for low substrate temperatures and low scattering angles (in our case:  $T = 160$  K,  $\Theta_s = 22.5^\circ$ ). If the surface temperature is high, the energy transfer to the precursor state might not be completed [21]. The molecules are very close to the surface and even rotational energy is transferred. This leads to a potential which consists of two parts concerning the cases N-end and O-end pointing towards the surface. On the other hand in ref. [9] the process of the direct chemisorption of NO on Ni(100) and its orientation dependence was studied. A strong orientation asymmetry of 70% for the sticking probability was found. Approaching with the N-end towards the surface the NO molecule sticks with a higher probability. The static orientation at the surface and the choice of adsorption sites as a function of coverage are described in refs. [11,22]. From NEXAFS measurements, adsorption perpendicular to the surface has been found at NO saturation coverage [23,24].

The adsorption system NO on clean Ni(100) shows strong asymmetries both in the scattering and in the sticking investigations. Consequently,

there are two different channels for the NO surface interaction: N-end collisions result in sticking and O-end collisions lead to a precursor state. Due to the direct chemisorption channels the scattering asymmetry for NO on Ni(100) has been found to be higher than for the system NO on Ag(111) [17]. The sticking probability of NO on CO precovered Ni(100) at 300 K is lower than on clean Ni(100) at 160 K which can be understood by the higher potential barrier for NO sticking at a precoverage of CO. The asymmetry measured is independent of coverage as found for the clean crystal [9]. This indicates that a direct chemisorption channel occurs for the coadsorption case, as well. We explain the orientation dependence of the CO displacement at 300 K by the following arguments. A  $c(2 \times 2)$  superstructure of CO has sites left on which molecules can chemisorb directly. Approaching the target with the N-end, NO molecules adsorb onto these sites. For a very short term the coverage of the surface is thus higher than 0.5, the value of the  $c(2 \times 2)$  superstructure coverage. This can be seen in the delay of the maximum CO displacement signal compared to the NO signal (fig. 2). These NO molecules between the CO molecules cause a charge shift in the Ni surface towards the N-atoms [24–26]. The more NO molecules are next to a CO molecule the lower is the d-electron density underneath the CO molecule. The bond becomes weaker and the probability of displacement increases. Hamza et al. [4] found a displacement from the extrinsic precursor above the CO molecules. The probability of this occurrence is proportional to the CO coverage. Ref. [4] used a surface temperature of 140 K and did not find a delay of the CO displacement, because at 140 K the energy barrier is too high to remove CO compared with the 300 K case in our experiment.

The two processes outlined above occur simultaneously. At low NO coverage the displacement mechanism by the molecules in the extrinsic precursor dominates because the CO coverage is high. At high NO coverage the reduction of d-electron density underneath the CO molecules induced by adsorbed NO molecules allows to displace CO easily. Fig. 5 demonstrates the superposition of the two processes. The maximum

is reached when the CO coverage is still high and the NO coverage is sufficient to weaken the CO bond.

In conclusion we have compared different measurements of the NO orientation dependence in collisions with Ni(100) and with oriented CO on Ni(100). Various asymmetries for scattering, sticking and displacement have been discussed.

### Acknowledgement

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