Steric Effects for NO/Pt(111) Adsorption and Scattering

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The adsorption probability for NO/Pt(111) is highest for an initial orientation with the N end of the molecule towards the surface. This steric effect in the adsorption brings about a large averaged steric effect in the direct scattering, which is amplified by the fact that the adsorption probability is very high. In case of direct scattering an N-end collision results in a smaller reflection angle than an O-end collision.

Recently, the first experimental investigations of the vector properties of the initial or final angular momentum J in molecule-surface interactions have been performed. Alignment and orientation of J in the case of diatomic-surface scattering have been demonstrated.[1-5] A preferential orientation of the molecular axis for CHF_3 desorption from Ag(111) has been claimed.[6] For adsorption of NO on Ni(100) a dependence on initial orientation has been observed.[7] In reactive gas-phase collisions orientation and polarization effects are also intensively investigated.[8,9] In our group the influence of initial molecular orientation on direct scattering and on adsorption of NO at Ag(111) have been demonstrated.[10,11] The measured effect in the adsorption was unexpected. One would expect that approaching the surface with the orientation for which the attractive potential is stronger, the N-end towards the surface, would give a higher adsorption probability. This expectation was also confirmed by classical trajectory calculations.[12] But the experiment showed that the approach in the least attracted orientation, the O-end towards the surface, results in the highest adsorption probability. This result could be explained by assuming a strong anisotropic or orientation-dependent repulsion. By means of rotationally mediated adsorption this can lead to the highest adsorption probability for the least attractive orientation.[13] The weaker anisotropy in the attraction eventually causes a trapped molecule to equilibrate with the most attracted end towards the surface.

If the anisotropy in the attraction were larger than NO/Ag(111), it could overrule the effect of the anisotropy in the repulsion in the adsorption dynamics. Therefore, it is interesting to study steric effects for NO adsorption at Pt(111). For this system the binding energy (1.13 eV) is five times larger than for NO/Ag(111).[14,15] The anisotropy in the attraction is likely to be much larger as well. So, in the case of NO/Pt(111) one expects the highest adsorption probability for approach with the most attracted orientation (the N-ends towards the surface).[16]

A steric effect in the adsorption probability can be investigated in two different ways. One possibility is the measurement of the desorption flux as a function of the orientation of the incoming molecules. A second possibility is a measurement of the dependence of the total directly scattered flux on orientation. Since one distinguishes only two ways of reflection, direct scattering and adsorption-desorption, a steric effect in one reflection channel has to be balanced by a steric effect in the other. A steric effect in the adsorption, R_{ads}, gives the relative influence of the initial orientation on the adsorption probability. The steric effect, R, is defined as the relative scattered intensity difference between the O-end and the N-end collision divided by the intensity obtained for a random initial orientation. In the same way R_{di} gives the relative influence of the incoming orientation on the directly scattered flux under a certain reflection angle θ_r. $\langle R_{di} \rangle$ corresponds to the steric effect in the directly scattered flux averaged over θ_r. Since the total reflected flux must be independent of the initial orientation, the relation between both is given by

$$\langle R_{di} \rangle = R_{ads} \frac{P_{ads}}{P_{ads} - 1}, \tag{1}$$

in which P_{ads} is the adsorption probability for a random initial orientation. For NO/Pt(111), $P_{ads} = 0.9$[14,17,18] Therefore, using Eq. (1), $\langle R_{di} \rangle$ must be an order of magnitude larger than R_{ads}. So the adsorption probability acts as a level if it is near unity. This makes a measurement of R_{ads} via direct scattering by far the most sensitive. The only requirement for the steric effect to be measurable is that direct inelastic and adsorption-desorption can be separated experimentally. We present the first experimental observation of R_{ads} determined via the steric effect in direct scattering.

In our experiment a well collimated pulsed molecular beam of NO is state selected by an electrostatic hexapole lens in the $\Pi_{1/2}$ ($J = \frac{1}{2}$, $\Omega = \frac{1}{2}$, $M_J = \frac{1}{2}$) state.[19-21] The
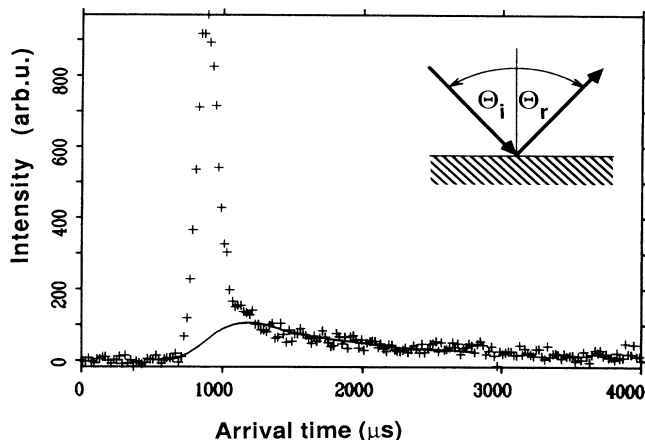
FIG. 1. Time-of-flight distribution of NO scattered Pt(111); $E_i = 180$ meV, $T_S = 573$ K, $\theta_i = 50°$, and $\theta_r = 50°$. The part attributed to desorption is shown by the solid line. Plotted in the inset is the definition of θ_i and θ_r.

FIG. 2. ▲: R_{ads}, measured with $\theta_i = 50°$, $T_S = 673$ K. ■: R_{di}, plotted as a function of θ_r, for $\theta_i = 50°$, $T_S = 573$ K, and $E_i = 180$ meV. R_{di} is defined as the difference in directly scattered signal between an incident orientation with the O-end and with the N-end towards the surface, divided by the intensity for random orientation. □: I_{di}, the angular distribution for the direct scattering of randomly oriented NO from Pt(111); $\theta_i = 50°$, $T_S = 573$ K, and $E_i = 180$ meV.

selected state has a preferential orientational distribution with respect to an electrostatic field given by $P(\cos\gamma_E) = (1 + \cos\gamma_E)/2$, where γ_E is the angle between the molecular axis, pointing from O to N, and the electrostatic field.[22,23] By applying a positive or a negative voltage (± 17 kV) on a rod, which is placed 1 cm in front of the crystal, the molecules are oriented with respectively either the N-end or the O-end preferentially towards the surface. The scattered particles are detected by a differentially pumped quadrupole mass spectrometer, which can rotate around the crystal. At the detector the molecular-beam pulses have a typical spread in arrival time (AT) of 300 μs due to a convolution of the pulse width of the mechanical chopper (200 μs) and the differences in flight time over the 220-cm path length from the chopper to the detector caused by the velocity spread of the beam, $\Delta v/v = 0.08$. Changes in AT due to a different final velocity on the 17-cm path from the surface to the detector are therefore hardly detectable. We can measure residence times at the surface, when these exceed 300 μs.

The crystal is cleaned by 700-eV Ar^+ bombardment and exposure to 30 L [1 L (langmuir) $= 10^{-6}$ Torr s] of O_2 and H_2, respectively, at $T_s = 573$ K. Afterwards, the crystal is flashed to 900 K. During the experiment we maintain an H_2-base pressure of 1×10^{-8} Torr to remove the atomic oxygen deposited at the surface most probably by dissociation of the small amount of NO_2 in the beam.[17] The misalignment of the crystal is smaller than 0.5°. The surface has a reflectivity of 0.4 for specular He scattering, when corrected for Debye-Waller attenuation. Therefore the defect density at the surface must be small and thus practically all NO molecules that hit the surface will impinge on a terrace site. At $T_S = 573$ K the mean residence time of NO adsorbed at a terrace site will be $\tau_{ads} \approx 10$ μs.[14,24] But when the NO
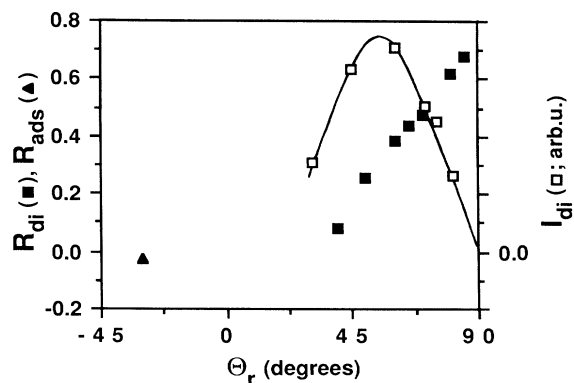
molecules are able to diffuse to an unoccupied defect site, one expects $\tau_{ads} \approx 1$ ms at $T_S = 573$ K.[14,24,25] So the mean residence time will depend on the quality of the crystal. On our crystal sufficient defect sites are available, although the defect density is small. Therefore the mean residence time is long enough (> 300 μs) to be used to discriminate the adsorbed-desorbed from the directly scattered particles by their AT. This is essential in our method.

In Fig. 1 a typical AT profile, measured at $T_S = 573$ K, $E_i = 180$ meV, and specular scattering, is shown. In the inset, the angle of incidence θ_i and the reflection angle θ_r are defined. The profile consists of a narrow peak superimposed on a broader distribution. The broader distribution is caused by desorbing particles. These arrive later due to their residence time at the surface of about 1 ms. In Fig. 1 the part of the signal that has to be attributed to adsorption-desorption is shown by the solid line. The remaining signal is attributed to direct scattering. This assignment has been confirmed in experiments in which T_s and thus τ_{ads} were varied. The direct scattering was recorded as a function of θ_r for the two opposite initial orientational distributions. The measured R_{di} is shown in Fig. 2 as a function of θ_r. R_{di} is linearly increasing with θ_r. For the largest scattering angles a dramatically high steric effect of about 0.7 is observed! For a random orientation we have measured the angular distribution for direct scattering I_{di} accurately. The result is shown in Fig. 2 as well. From this distribution and R_{di} the angular distributions for direct scattering of the oriented beams can be deduced. These are shown in a polar presentation in Fig. 3. Two interesting steric effects can be observed. First, the two distributions are shifted with respect to one another. O-end col-
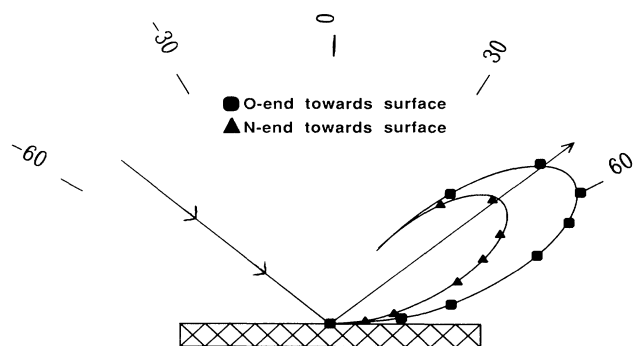
FIG. 3. The angular distributions for direct scattering of preferentially oriented NO and Pt(111), presented in a polar plot; $\theta_i = 50°$, $T_S = 573$ K, and $E_i = 180$ meV. The angular distributions are obtained from the fit to I_{di} and the measured points of R_{di} both shown in Fig. 2. The lines through the angular distributions are drawn to guide the eye. The arrows indicate the angle of incidence and the specular angle. In case of an N-end collision less molecules are directly scattered. Molecules which are directly scattered after an N-end collision come off closer towards the surface normal (maximum I_{di} at $\theta_r = 53°$) than molecules with an O-end collision (maximum I_{di} at $\theta_r = 57°$).

lisions lead to larger θ_r values. This effect will be discussed below. Second, the directly scattered flux in the case of the O-end collisions is much higher. Averaging of R_{di} over the total directly scattered flux yields $\langle R_{di} \rangle = 0.33 \pm 0.05$. This means that NO has a higher adsorption probability when it approaches the surface with the N-end towards the crystal. This is in contrast to the result obtained for NO/Ag(111) adsorption, but in agreement with the generally accepted view.[11] This view is confirmed by he classical trajectory calculations of Jacobs and Zare (JZ).[26]

For a random initial orientation we have integrated the desorption flux over arrival time and the entire solid angle of 2π assuming a $\cos\theta_r$ distribution. Likewise, the directly scattered flux has been integrated assuming an out-of-plane width of $20°$, which is the same as for NO/Ag(111).[27] The proportion of these fluxes gives $P_{ads} = 0.90 \pm 0.05$ at $E_i = 180$ meV and $\theta_i = 50°$, which is equal to the values found in other studies.[14,17,18] Using Eq. (1) we can now deduce that $R_{ads} = -0.035 \pm 0.02$.

As mentioned earlier we can obtain R_{ads} via detection of the desorption flux as well. In principle, the steric effect in the desorption flux could be determined from the signal attributed to desorption under specular angles as shown in Fig. 1. But due to the prominence of direct scattering for this geometry it is better to take a detector setting for which direct scattering is absent, i.e., backward scattering. Therefore, we take $\theta_r = 20° - \theta_i$, which is the smallest reflection angle experimentally accessible. To find the difference in desorption flux for the different

initial orientations, we measured the desorption flux for 3.5 h, while switching the sign of the high voltage on the orientation pole (e.g., the preferential orientation) every 2.5 min. It has been verified that the surface cleanliness does not change appreciably during the experiment. At $T_S = 673$ K a ratio $R_{ads} = -0.025 \pm 0.01$ was measured, independent of θ_i within the experimental error bars. This is in agreement with the value found via direct scattering. Therefore it can be concluded that the large averaged steric effect in direct scattering is due to an amplification of the steric effect in the adsorption by a factor of $P_{ads}/(P_{ads} - 1)$. This is the first observation of such a leverage.

It is found that NO has a higher adsorption probability for an incoming orientation with the N-end towards the surface. This result is qualitatively in agreement with classical trajectory calculations by JZ.[26] But the experimentally found steric effect is much smaller than the calculated one: $R_{ads} = -0.13$. In their potential JZ only assumed an anisotropy in the attraction but the actual presence of an anisotropy in repulsion might partially compensate the effects of the anisotropy in attraction. Moreover, the overall trapping probability calculated by JZ for the $J = \frac{1}{2}$ state amounts to about 0.6, which is clearly too low.

In direct scattering, molecules with an O-end collision come off closer towards the surface than molecules with an N-end collision. This was also observed for direct scattering of NO from Ag(111) and was explained by a difference in rotational excitation.[10,28] For NO/Pt(111), however, this is not likely to be the case. Since for this system an N-end collision results in the highest adsorption probability, on the average in the N-end collision more translational energy must be lost. In this study the surface, as seen by the molecule with low incident energy, is assumed to be flat. Therefore only the normal velocity component can change. Thus for the N-end collision we therefore would expect a larger reflection angle. We observe a steric effect in direct scattering that is just the opposite. This might be explained by corrugation of the surface. When this corrugation is stronger for a molecular orientation with the N-end pointing towards the surface, an N-end collision will cause reflection closer towards the surface normal. Another explanation is that for direct scattering after an N-end collision the molecule will make several hops along the surface before escaping from the deep potential well. This can also result in a scattering closer towards the surface normal.

With this study we showed for the first time experimentally that an anisotropy in the attraction can cause an orientational dependence of the adsorption probability, which is reflected strongly in direct inelastic scattering. NO approaching Pt(111) with the N-end towards the surface results in the highest adsorption probability. The steric effect in the adsorption causes an averaged steric effect in the direct scattering that is a factor

$P_{ads}/(P_{ads}-1)$ larger. The steric effect in direct scattering is θ_r dependent. "Direct scattering" for the N-end collision comes off closer to the surface normal than for the O-end collision.

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