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The influence of the impact site on orientation effects in quantum NO($X^2\Pi$)–Ag(111) scattering

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Abstract. We report a fully quantum analysis of the impact-site dependence of oriented NO collisions with Ag(111). Our simulations are based upon the recent corrected effective-medium potential-energy surfaces of DePristo and Alexander. The main finding is the huge influence of the impact site on both the NO rotational distributions and the steric effect. The global steric effect is found to vary from -8% (centre site) to $+42\%$ (atop site). Yet, calculations with the site-averaged potential surfaces yield a residual steric effect ($+8\%$) in good agreement with the experimental observations of Kleyn, Stolte and co-workers. However, it does not match the site average of the steric results ($+19\%$). This suggests that the detailed topology of the surface should be considered in interpreting the experimental orientation effects and that models based on flat surfaces may be inadequate.

1. Introduction

Collisions of NO molecules with the close-packed Ag(111) surface have been extensively studied both experimentally [1–6] and theoretically [7–20]. One of the reasons for this continued effort is that the surface interaction is weakly destructive and chemisorptive. Therefore, one can focus easily on the direct rotationally inelastic scattering of the NO molecule.

Because the ground $X^2\Pi$ state of the NO molecule has non-zero electronic orbital momentum two potential-energy surfaces (PESS) define the NO–surface interaction and the scattering event has to take place on these two PESS simultaneously, with the occurrence of quantum interference effects [9]. In many theoretical studies of NO–surface collisions this complexity has been neglected and a closed-shell molecule has been assumed with only one average PES. This simplification can be explained in most cases by the lack of information on the true PES, due to the impossibility of obtaining accurate *ab initio* data. Recently, DePristo and Alexander have derived a complete set of PESS within the corrected effective-medium theory [21]. Even though this semiempirical approach may be questionable, it has allowed the first consistent determination of the two PESS of distinct electronic symmetry, characterizing the interaction. Therefore, it gives at least a semiquantitative idea of how the two PESS compare in well depth as well as in anisotropy. In fact, the difference between the two PESS is quite significant since, on average, the well depths are 821 and 1831 cm^{-1} with a much larger anisotropy associated with the deeper well (see figure 8 of [21]). Alexander has demonstrated that a closed-shell treatment based on the average of the two PESS leads to a wrong rotational distribution even when the spin-orbit and Λ -doublet states remain unresolved (see figure 5 of [17]).

When the collider has a non-zero orbital momentum a first-order Stark coupling can be exploited in the preparation of the initial state, to induce a preferential orientation of the NO axis. Owing to this property Kleyn, Stolte and co-workers [2–5] have provided the first experimental evidence of the direct influence of the initial molecular orientation on the spatial and internal distributions of the NO molecule scattered by a surface. In their experiments the $J = M = \Omega = \frac{1}{2}$ ground rotational state of NO is focused by passing a cold ($T_{\text{rot}} = 4$ K) pulsed supersonic beam through an electric hexapole. The state-selected molecules are then oriented in a 15 kV cm^{-1} Stark field normal to the surface. By choosing the polarity of the Stark field, the molecules can be brought into the interaction region with either the N end or the O end preferentially directed towards the surface. This type of experiment provides a much higher sensitivity of the scattered distribution on the PES in comparison to those involving unoriented beams. Indeed, the Stark selection resolves even the quasidegenerate electronic doublet (the Λ doublet in the absence of an electric field) [15]. Hence, a single-state selection, and thereby a greater specificity of the PES sampling, is achieved.

In this work we report numerical results of the scattering of oriented NO molecules on the set of site-dependent PESSs of DePristo and Alexander [21]. We thereby take into account, for the first time, the influence of the impact site on orientation effects. The paper is divided into three sections. Section 2 briefly describes the scattering calculations and presents the results. The conclusions are presented in section 3.

2. Scattering calculations and results

The general treatment is similar to that of [22]. Following our previous theoretical studies of NO–surface collisions [15, 16, 22, 23] and that of Alexander and co-workers [9–11, 17, 19] we assume a flat, rigid surface yet treat fully quantum-mechanically the $^2\Pi$ open-shell character of NO. The inclusion of a Stark Hamiltonian mixing the Λ doublets accounts for the orientation of the molecule initially in its $J = \frac{1}{2}$ rotational state [15, 23]. The intensities of the NO dipole moment and of the Stark field are set to 0.159 D and $\pm 15 \text{ kV cm}^{-1}$, respectively. These give rise to orientational (θ) distributions close to those of the pure-mixing case, given by $P(\cos \theta) = (1 \pm \cos \theta)/2$. The scattering equations are solved within the close-coupled wave-packet approach [16, 24]. As in the work of Alexander the mean collision energy is chosen to be $E_m = 6900 \text{ cm}^{-1}$. The collision-energy range sampled in the calculations (i.e., for which the relative intensity $I/I_m \geq 10^{-4}$) is approximately $5900\text{--}7900 \text{ cm}^{-1}$. At these energies the calculations are facilitated since only direct scattering occurs, as we could check by following the mean positions of the wave packets as a function of propagation time. Indeed, the absence of surface motion precludes multiple-collision events, including chattering [25]. DePristo and Alexander propose four sets of PESS (see figures 5–8 of [21]), three of them describing the interaction of NO lying above a specific site of the Ag(111) surface: atop, bridge, and centre. The last set corresponds to the site-averaged PES appropriate to a formal flat-surface assumption. This set is obtained by $(V_A + 3V_B)/4$ where V_A and V_B characterize, respectively, the atop and bridge sets of PESS [21]. We have performed converged calculations for each set of PESS. The basis-set expansion includes all rotational states up to $J = 90.5$ for the scattering off the atop site, that is, a maximum number of 362 coupled states taking account of spin–orbit and Λ -doublet states.

The results of our simulations are presented in figures 1–3 and include an average over the collision energy range $5900\text{--}7900 \text{ cm}^{-1}$. Figure 1 displays the internal distributions

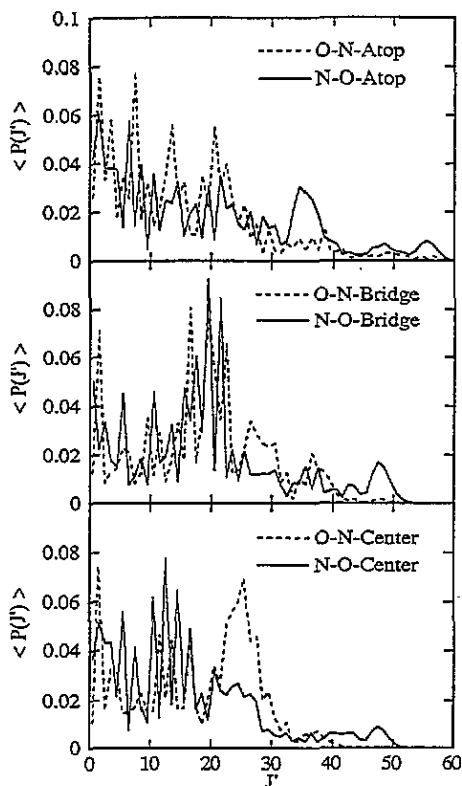


Figure 1. The final rotational transition probabilities ($P(J')$) summed over the spin-orbit manifolds and the Λ doublets. The solid (dashed) curve corresponds to an initial molecular orientation with O (N) pointing towards the surface. The upper, middle, and lower panels refer, respectively, to scattering off the atop, bridge, and centre sites.

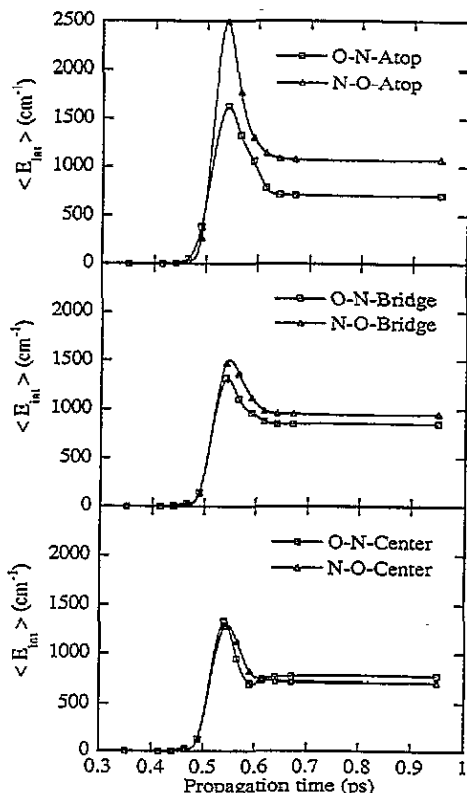


Figure 2. The internal energy (E_{int}) of the molecule, averaged over the rotational-, spin-orbit- and Λ -doublet-state distributions, as a function of propagation time. The triangles (squares) denote an initial molecular orientation with O (N) pointing towards the surface. The upper, middle, and lower panels refer, respectively, to scattering off the atop, bridge, and centre sites.

of oriented NO scattered off the atop, bridge, and centre sites, as a function of the final rotational angular momentum J' . Alexander has provided such a site comparison in the unoriented case (see figure 8 of [17]). Despite the qualitative similarity of the three sets of PESS Alexander has observed considerable variation in the position and magnitude of the rainbow oscillations. As expected, we also observe considerable variations of the oriented NO distributions from one site to another. Furthermore, we note that the distributions oscillate wildly especially for $J' \leq 23.5$. If one takes the average of the two oppositely oriented NO distributions, then one ends up with the corresponding distribution for the unoriented case presented by Alexander [17]. When we plot this average distribution for each site (not shown here) the wild oscillations persist in the low- J' range in contrast to figure 8 of [17]. Alexander [17] has also characterized the scattered distributions with an average over some energy range. He has noticed almost no difference with the results obtained from a calculation at the single energy E_m . Then, the structure damping Alexander obtains must come from the additional averaging over several initial rotational states that he performed to simulate the scattering of a $T_{\text{rot}} \geq 10$ K molecular beam. For example, the weighted Boltzmann distribution of the NO ground electronic state at $T_{\text{rot}} = 10$ K yields

$0.419J = \frac{1}{2}$, $0.403J = \frac{3}{2}$ and $0.178J = \frac{5}{2}$ in the $\Omega = \frac{1}{2}$ manifold [27]. Since there is little difference when the initial rotational temperature is varied from 10 K to 50 K (see figure 3 of [17]), one can conclude that the structure damping becomes very effective as soon as the $J = \frac{3}{2}$ and $\frac{5}{2}$ states are populated in the initial beam. Indeed, we have verified the strong attenuation of the wild $J' \leq 23.5$ oscillations upon comparing unpublished rotational distributions [27] stemming from an initial population consisting of only the two $J = \frac{1}{2}$ Λ doublets, on the one hand, and from $T_{\text{rot}} = 10$ K, on the other hand (not shown here). This slightly long-winded analysis of the structure damping was meant to emphasize the merits of the orientational procedure on producing highly specific scattered distributions. As already stressed this technique is actually capable of selecting a single, non-degenerate state in comparison to at least six states in conventional unoriented-beam experiments. Regarding the steric effect, i.e., the comparison between the two oppositely oriented NO distributions, one can observe that the J' -dependent differences are significant for all sites.

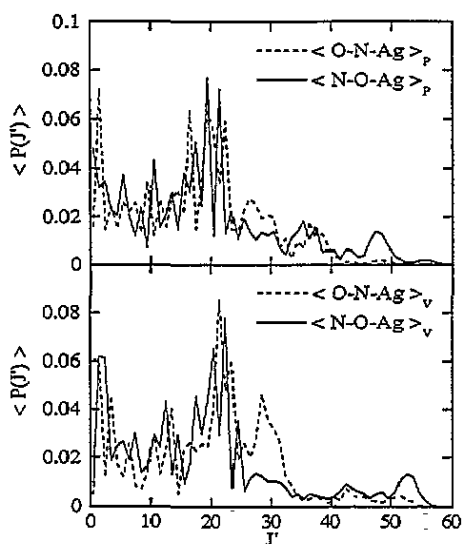


Figure 3. The final rotational transition probabilities ($P(J')$) summed over the spin-orbit manifolds and the Λ doublets. The solid (dashed) curve corresponds to an initial molecular orientation with O (N) pointing towards the surface. The upper panel depicts the site average of the probabilities plotted in figure 1. In comparison, the lower panel displays the probabilities obtained by scattering on the site-averaged PES.

In figure 2 we complement the determination of the asymptotic distributions with a time analysis of the NO internal energy in order to better visualize the site-dependent orientation effects. As expected, for all sites the strong interaction of NO with the repulsive wall of the PES occurs in the time interval associated with the sudden increase of the internal energy up to its maximum. In that interval there exists a more or less apparent crossing between the curves corresponding to the two opposite initial orientational distributions. This thus denotes a reversal of the steric effect, similar to that evidenced in our previous studies on NO-Pt(111) [22, 23]. This is related to the reorientation of the NO axis towards the optimal binding configuration as the molecule approaches the surface [23, 26]. Consequently, this is in contradiction to the Voges and Schinke PES model [7, 23], which supports the commonly accepted hypothesis of the conservation of the initial orientation until NO samples the repulsive wall anisotropy in the interaction with Ag(111). Besides the site-independent reorientation feature the global steric effect is strongly influenced by the impact site, both quantitatively and qualitatively. The atop site induces a steric effect much larger than the two other sites. In addition, there is a second curve crossing as NO scatters off the centre site and recedes into the asymptotic region. This second crossing does not occur in the

atop and bridge cases. Thus, this effects in the reversed asymptotic steric propensity in the scattering off the centre site compared to the other sites. Such an opposite behaviour from one site to another was unexpected in the light of previous stereospecific analyses, which all ignored the role of surface corrugation and hence, of the impact site.

The site dependence of the net results, final internal energies and steric effect, are reported in table 1. The steric effect is found to vary from -8% (centre site) to $+42\%$ (atop site). Yet calculations with the site-averaged PES yield a residual steric effect ($+8\%$) in good agreement with the experimental observations of Kleyn, Stolte and co-workers [2–4]. That is, an initial orientation with the O end directed towards the surface significantly enhances rotational excitation. Because the scattering stereospecificity is dramatically sensitive to the impact site one may wonder whether a flat-surface model is meaningful for obtaining such information. One simple way to address this basic question is to compare the results stemming from the scattering on the site-averaged PES, on the one hand, and from averaging the site-dependent scattered distributions, on the other hand. Consistently with the site averaging of the PES one can define $(P_A + 3P_B)/4$ as the site-averaged transition probabilities, where P_A and P_B pertain, respectively, to the atop and bridge sets [17]. The comparison is displayed in figure 3. There exist similarities between the two curves corresponding to a given initial orientation. However, these similarities are not as high as in the unoriented case (see figure 8 of [17]). This is another manifestation of the increased sensitivity of our results. Significant shifts of rainbow peaks, out-of-phase oscillations, and large variations of orientation effects can be seen upon comparing the two sets of curves in figure 3. A discrepancy persists even in the global steric effect, $+19\%$ instead of $+8\%$ (see table 1). Lastly, when N initially points towards the surface, the final internal energy of NO is predicted to be much larger within the site-averaged PES than in any other case.

Table 1. The steric effect (R) and average internal energy ($\langle E_O \rangle$, $\langle E_N \rangle$) of the molecule scattered off the atop, bridge, and centre sites. R is defined by $2(\langle E_O \rangle - \langle E_N \rangle) / (\langle E_O \rangle + \langle E_N \rangle)$ where $\langle E_O \rangle$ ($\langle E_N \rangle$) corresponds to an initial molecular orientation with O (N) pointing towards the surface. $(P_A + 3P_B)/4$ yields the site average of $\langle E_O \rangle$, $\langle E_N \rangle$, and R . In comparison, $(V_A + 3V_B)/4$ refers to $\langle E_O \rangle$, $\langle E_N \rangle$, and R , as obtained by scattering on the site-averaged PES.

	Atop	Bridge	Centre	$(P_A + 3P_B)/4$	$(V_A + 3V_B)/4$
$\langle E_O \rangle$ (cm^{-1})	1079	952	716	984	1005
$\langle E_N \rangle$ (cm^{-1})	707	852	773	816	963
R	+0.417	+0.110	-0.076	+0.187	+0.079

3. Discussion

This paper was aimed at characterizing the influence of the impact site on orientation effects. Therefore, surface motion and indirect scattering (occurring at a lower collision energy) were not considered although they should play a crucial role [12, 14] in the detailed comparison with the experimental observations of Tenner *et al* [4]. The principal implication of this study is that the flat-surface model does not seem to be satisfactory for two reasons. First, the main, *unexpected* result is that, in addition to large variations in the rotational distributions similar to those observed by Alexander in the unoriented case [17], *opposite* orientation effects are found to occur from one impact site to another. This probes a high sensitivity to the corrugation that is misrepresented in a flat-surface approach. Second, the

results averaged over the sites do not match those obtained with the site-averaged PES. Therefore, the detailed topology of the surface should be considered in interpreting the experimental orientation effects. This is an essential point since the corrugation of the surface has been neglected in all simulations to date of oriented NO scattering. An attempt will be made to precisely assess the significance of a flat-surface model by simulating the NO scattering from the corrugated Ag(111) PES, which can be extracted from the sets provided by DePristo and Alexander [21]. In addition, it would be useful in determining to what degree the quantum oscillations are washed out by the surface corrugation. One may think that the wild oscillations obviously persist as is shown in figure 3. However, one should not forget that the NO molecule has been confined to scatter on 2D PES versus 4D PES. This confinement may result in sharpening of quantum effects. Another question that could be answered concerns the existence of an anticorrelation effect between the rotation and diffraction of NO. That is, if the molecule loses part of its normal momentum to the diffraction will the final NO internal energy be accordingly decreased?

Finally, a second, important result of this study is evidence of the presence of long-range reorientation effects, in contradiction to the commonly accepted hypothesis of the conservation of the initial orientation until NO samples the repulsive wall anisotropy in the interaction with Ag(111). A flux analysis of the degradation of the initial orientation of NO is under way to obtain a measure of the reorientation effect [26].

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