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## Elastic Scattering in a Reactive Environment: NO on Ru(0001)-(1 × 1)H

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Local variations in the reactivity of NO on the Ru(0001)-(1 × 1)H surface have been probed with a supersonic molecular beam. The presence of adsorbed hydrogen atoms creates an elastic scattering channel in the specular direction, concomitant with a suppression of the initial sticking probability. Argon is scattered in a qualitatively similar, but instrumentally limited, specular peak from the same surface. The well characterized position of the hydrogen atoms allows the scattering to be related to collisions at the threefold hollow sites within the surface unit cell. [S0031-9007(97)03398-X]

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One of the recurrent questions in the field of gas-surface dynamics has been the lateral surface site dependence of the reaction probability. It is generally accepted that the reactivity of semiconductor surfaces is dominated by highly localized, dangling bonds. The saturation of these dangling bonds by hydrogen results in the remarkable inertness of silicon surfaces treated with HF. In contrast, on metal surfaces, the electrons are delocalized, suggesting a laterally rather uniform potential energy for a molecule above a surface. However, recent calculations have indicated a considerable lateral dependence of the potential and reactivity of a metal surface [1–3]. In order to investigate the importance of these effects in a reactive environment, we have studied the catalytic NO reduction reaction on Ru(0001), where a number of associative and dissociative adsorption states exist.

Measurements of the sticking probability alone are generally unable to provide information on the position of the adsorption sites within the surface unit cell. The most informative probe of the interaction dynamics is provided by the angle and energy resolved measurement of the directly scattered molecules [4]. In this Letter we report the remarkably elastic, specular scattering of NO from a Ru(0001) surface in which the adsorption channel has been partially closed by the presence of hydrogen atoms in the fcc threefold hollow sites.

The experiments were performed in an ultrahigh vacuum (UHV) scattering chamber equipped with a three stage supersonic molecular beam source [5]. The sample was aligned and polished to within 0.1° of the (0001) crystal face and cleaned by repeated flashing to a surface temperature ( $T_s$ ) of 1500 K in  $2 \times 10^{-8}$  mbar of  $O_{2(g)}$ . A single flash to 1600 K in UHV was found to remove all the remaining oxygen and leave a clean ordered surface, ascertained by a Debye-Waller plot of the thermal helium reflectivity which extrapolated to  $I/I_0 = 1.0$  at 0 K, where  $I_0$  is the incident He beam intensity. The Ru(0001)-(1 × 1)H overlayer was prepared by dosing  $5 \times 10^{-7}$  mbar of  $H_{2(g)}$  for 300 s at  $T_s < 200$  K. Sticking probability experiments were performed using the technique of King and Wells [6]. Angle resolved time-of-flight scattering experiments were

performed with a 0.5% duty cycle chopped beam and the results extrapolated to the zero NO coverage limit. During these measurements the coverage never exceeded a few percent of a monolayer.

The behavior of NO on the Ru(0001) surface is dependent on  $T_s$ . Below 200 K a strongly chemisorbed molecular state is formed ( $E_{\text{ads}} \approx 1.49$  eV), either on top of a ruthenium atom, in a twofold bridging or in a threefold hollow site, depending on the surface coverage [7,8]. Above 200 K, NO can dissociate into  $N_{(\text{ads})}$  and  $O_{(\text{ads})}$  adatoms, given the availability of free sites. Above 450 K, molecular  $NO_{(\text{ads})}$  desorbs from the surface. Finally,  $N_{(\text{ads})}$  and  $O_{(\text{ads})}$  associatively desorb as  $N_2$  and  $O_2$  at  $\sim 500$  and  $\sim 1500$  K, respectively.

The result of scattering NO from Ru(0001), in the zero coverage limit, is shown in Fig. 1. Because of the high chemisorption probability very few molecules are scattered. Those that are form a broad angular distribution [full width at half maximum (FWHM)  $\cong 37^\circ$ ], similar to that observed in the NO-Ag(111) [9] and Pt(111) [10] systems. However, on Ru(0001) it is possible to reduce the surface reactivity by blocking all the fcc threefold hollow sites with hydrogen atoms [11]. Figure 1 shows the final energy and angular distributions of NO molecules scattered directly from the Ru(0001)-(1 × 1)H surface. Strikingly, the angular distribution (top panel) now forms a sharp peak in the specular scattering direction (FWHM =  $8^\circ$ ) and can be approximated by a  $\cos^n(\Theta_f - \Theta_{\text{spec}})$  function where  $n = 380 \pm 170$ , far higher than any previously reported value for a heavy, reactive molecule. Comparison with the direct beam profile reveals a slightly asymmetric broadening towards supraspecular directions, consistent with some rotational excitation at the expense of normal translational energy ( $E_i \cos^2 \Theta_i$ ) [12]. The final energy of the scattered molecules (bottom panel) reveals the surprisingly small energy transfer in the collision.  $E_f/E_i$  increases at more grazing angles of incidence and at lower incidence energies, so that at  $\Theta_i = 60^\circ$ ,  $E_i = 0.34$  eV, and  $\Theta_i = 70^\circ$ ,  $E_i = 2.1$  eV, molecules scatter along the specular direction in a truly elastic collision ( $E_f/E_i = 1.0$ ).

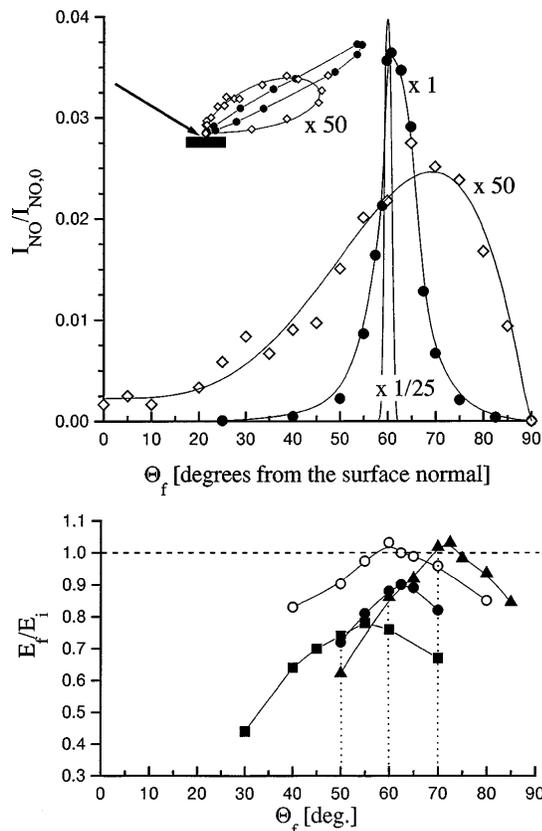


FIG. 1. Top panel: angular distribution of NO molecules scattered from the Ru(0001) (diamonds,  $E_i = 1.56$  eV,  $T_s = 650$  K,  $\Theta_i = 60^\circ$  along the  $\langle 11\bar{2}0 \rangle$  direction) and Ru(0001)-(1  $\times$  1)H (circles,  $E_i = 2.1$  eV,  $T_s = 140$  K,  $\Theta_i = 60^\circ$  along the  $\langle 11\bar{2}0 \rangle$  direction) surfaces, normalized to the direct beam intensity. Direct beam profile is shown for comparison. Bottom panel: final energy distributions of NO scattered from Ru(0001)-(1  $\times$  1)H.  $E_i = 0.34$  eV (open symbols) and 2.1 eV (filled symbols),  $T_s = 140$  K,  $\Theta_i = 50^\circ$  (squares),  $60^\circ$  (circles), and  $70^\circ$  (triangles) along the close packed  $\langle 11\bar{2}0 \rangle$  direction.

In order to measure the effect of  $H_{(ads)}$  on the surface reactivity, the initial sticking probability (zero coverage limit) of NO ( $S_0$ ) was measured on both the clean and hydrogen covered surfaces (Fig. 2). On the clean surface  $S_0$  is high ( $>0.7$ ) at all incidence energies. These data were obtained at a surface temperature of 650 K, where the adsorption of NO is dissociative. However,  $S_0$  was found to be independent of the surface temperature and adsorption into the molecular state at 140 K follows the same curve. The effect of  $H_{(ads)}$  on the Ru(0001)-(1  $\times$  1)H surface is to suppress  $S_0$  but still leaves a significant reaction probability ( $S_0 = 0.17-0.47$ ). Because of the desorption temperature of hydrogen from Ru(0001) (350 K [13]) these data could be measured only at low temperatures, where NO adsorption is entirely molecular.

Figure 3 shows the thermally programmed desorption (TPD) spectra for masses 2 ( $H_2$ ) and 30 (NO) from the Ru(0001)-H + NO overlayer formed by the adsorption of

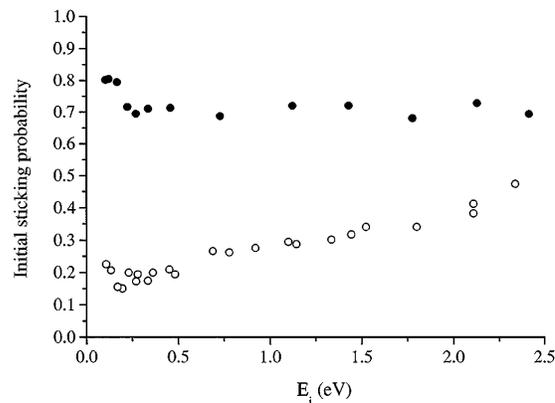


FIG. 2. Initial sticking probability of NO on Ru(0001) ( $T_s = 650$  K, filled circles) and Ru(0001)-(1  $\times$  1)H ( $T_s = 140$  K, open circles) as a function of  $E_i$ .  $\Theta_i = 0^\circ$ .

NO on Ru(0001)-(1  $\times$  1)H. The only other species observed was mass 28 ( $N_2$ ) formed from the well known decomposition of NO on Ru(0001) [8]. The associative desorption of  $H_2$  from the Ru(0001)-(1  $\times$  1)H overlayer and the desorption of NO from the Ru(0001)-(2  $\times$  2)NO overlayer accurately reproduce previously reported spectra [8,13]. When NO is adsorbed on the Ru(0001)-(1  $\times$  1)H surface the  $H_2$  desorption peak narrows and shifts from 350 to 325 K, with a shoulder at higher temperatures, characteristic of compressed Ru(0001)- $n$ H overlayers observed by Jachimowski [13] ( $1.0 < n < 1.4$ ). In contrast, in the presence of  $H_{(ads)}$ , the NO desorption peak remains completely unchanged in both shape and peak position. The area under the desorption peaks remains unchanged for both  $H_2$  and NO, demonstrating that hydrogen is not desorbed during NO adsorption, nor is the number of NO adsorption sites reduced by

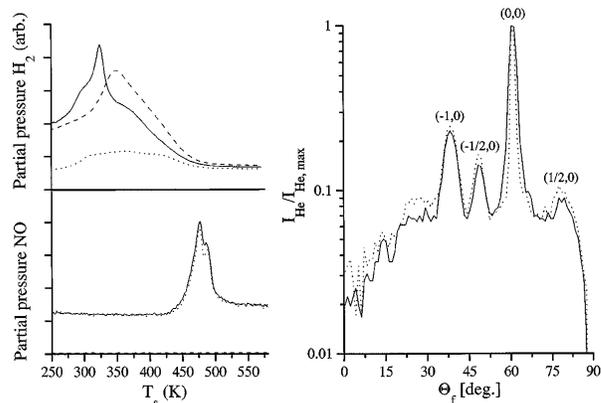


FIG. 3. Left panel: TPD spectra of  $H_2$  and NO from Ru(0001)-(1  $\times$  1)H (dashed lines), Ru(0001)-(2  $\times$  2)NO (dotted lines), and Ru(0001)-(1  $\times$  1)H exposed to an NO beam (solid lines). Heating rate  $5$  K  $s^{-1}$ . Right panel: Normalized scattered helium intensity from Ru(0001)-(2  $\times$  2)NO and Ru(0001)-H + NO,  $E_i = 65$  meV,  $\Theta_i = 60^\circ$  along the close packed  $\langle 11\bar{2}0 \rangle$  direction,  $T_s = 140$  K. Labels show diffraction peak indices.

the presence of hydrogen. These results suggest that in the region exposed to the beam ( $\sim 4$  mm diam), a pure Ru(0001)-(2  $\times$  2)NO phase is created, surrounded by a region of compressed hydrogen adatoms outside the beam area ( $\sim 10$  mm diam).

Figure 3 also shows the diffraction of a helium beam by the Ru(0001)-(2  $\times$  2)NO and Ru(0001)-H + NO surfaces. Both surfaces show almost identical diffraction peaks, indicating that NO adsorbs in the same (2  $\times$  2) structure on the hydrogen precovered surface as on the clean Ru(0001) surface. This conclusion is supported by the observation of a (2  $\times$  2) low energy electron diffraction (LEED) pattern on both surfaces. The long range order of the Ru(0001)-(2  $\times$  2)NO overlayer seen and the high saturation coverage (0.75 monolayers [7,8]) shows that NO adsorption cannot occur only at surface defects.

Our discussion will concentrate on whether the experimental results are consistent with a local site dependence of the molecule-surface interaction. The suppression of  $S_0$  and the increase of direct (single collision) scattering suggest that part of the surface is rendered inert to NO by the presence of  $H_{(ads)}$ . If  $H_{(ads)}$  were to passivate the entire unit cell, then  $\sim 30\%$  of the H sites in the Ru(0001)-(1  $\times$  1)H surface would need to be vacant to account for the remaining sticking probability. This is extremely unlikely on such a well defined surface unit cell. By occupying the Ru bonding orbitals in the fcc threefold hollow sites,  $H_{(ads)}$  seems to create an activation barrier for NO adsorption which is strongly site dependent. At the site occupied by the hydrogen atom this barrier is considerable, creating a local plateau in the potential energy surface, resulting in the narrow specular reflection. Elsewhere in the unit cell a smaller barrier appears to cause the increase of  $S_0$  with energy as observed for the poisoning of palladium by sulfur [14].

Recent theoretical studies on the dissociation of  $H_2$  have shown that where strongly attractive geometries lie close to repulsive ones, the local potential gradient will "steer" the molecule into an adsorption site [15,16]. The result is a tendency for  $S_0$  to approach unity at low energies where the molecule is traveling slowly, and a chaotic scattering of those molecules not adsorbed. For the heavy NO molecule steering reorients the molecule, leading to enhanced sticking on Pt(111) [17]. To what extent steering leads to the remarkably narrow angular distribution requires further study.

In order to compare the behavior of NO with an inert, physisorbed particle, argon was also scattered from the hydrogen covered ruthenium surface and the angle resolved results are shown in Fig. 4 for four different incidence angles. A sharp peak is seen at the specular angle, superimposed on a broad background, similar to observations on the 2H-W(100) surface [18]. The specular peak, which increases in intensity at more grazing angles of incidence, is even sharper than that observed for NO and is essentially limited by the angular

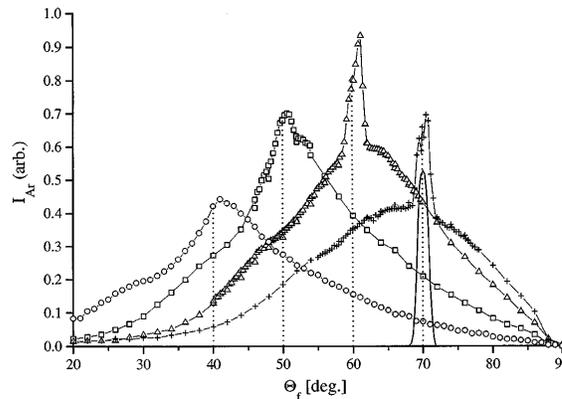


FIG. 4. Angular distribution of Ar scattered from the Ru(0001)-(1  $\times$  1)H surface.  $E_i = 65$  meV,  $T_s = 140$  K,  $\Theta_i = 40^\circ$  (circles),  $50^\circ$  (squares),  $60^\circ$  (triangles), and  $70^\circ$  (crosses) along the close packed  $\langle 11\bar{2}0 \rangle$  direction. Angular profile of the direct beam ( $70^\circ$ ) is shown for comparison.

profile of the direct beam (FWHM =  $2^\circ$ ). Like NO, this is consistent with two distinct scattering regimes. The specular component arises from laterally flat sections of the potential, while the diffuse component originates largely from inelastic collisions on the corrugated sections of the potential, as seen in calculations of Ar on Ag(111) [19]. For NO these inelastic collisions lead to sticking, so scattering from the corrugated section of the potential is not observed.

We will now turn our attention to the most remarkable observation, that the collision of NO with the inert part of the unit cell can be elastic. The simplest model is for the collision of two hard spheres, with no attractive interaction. In this case  $E_f/E_i = 0.74$  for particles of mass 30 (NO) and 101 (Ru). This rises to 0.86 for a surface mass of  $M = 202$ , 0.90 for  $M = 303$ , and 0.94 for  $M = 505$ . Including an attractive molecule-surface interaction in the model would only increase the energy transfer in the collision. Hence, even in the absence of an attractive well,  $E_f/E_i$  can approach unity only when the mass of the surface scatterer becomes extremely large. This model neglects the quantized nature of the surface phonons. However, the phonon energies extend from 0 meV upwards and have been measured on the Ru(0001)-(1  $\times$  1)H surface at only 21 meV [20], easily accessible at the incidence energies used here.

A more likely explanation is related to the stiff binding and high coordination of hydrogen adsorbed in the threefold hollow site with which an NO molecule collides. The high vibrational frequency of  $H_{(ads)}$  perpendicular to the Ru(0001) surface ( $\nu_\perp = 3.4 \times 10^{13}$  Hz [20]) corresponds to a period of 29 fs. In this time the motion of an NO molecule along the surface normal ( $E_i = 0.34$  eV,  $\Theta_i = 60^\circ$ ) will be only 0.22 Å. Hence the H-Ru<sub>3</sub> vibration will adjust adiabatically to the perturbation caused by the NO, leading to the elastic scattering seen in the experiments.

In conclusion, we are able to distinguish two distinct and contrasting interactions of NO within the Ru(0001)-(1 × 1)H unit cell. Directly above H<sub>(ads)</sub>, the NO experiences a weak physisorption well, similar to that of argon. Such an interaction will be smooth and flat leading to the specular, elastic scattering of NO from the hydrogen filled threefold hollow site. Collisions at other impact sites within the unit cell will be inelastic and occur on a more corrugated potential energy surface. This leads to efficient sticking (in the case of NO, where a deep chemisorption well exists) and diffuse scattering (in the case of argon). The adsorption of NO results in a migration of H<sub>(ads)</sub>, forming compressed overlayers of hydrogen adatoms.

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