

Angular Distributions of Neutrals Desorbed by Electron Impact from Chemisorbed and Physisorbed Layers on Metal Surfaces

P. Feulner, W. Riedl, and D. Menzel

Physik Department, Technische Universität München, D-8046 Garching, West Germany

(Received 29 November 1982)

Angular distributions of neutral CO desorbed by electron impact from chemisorbed CO on Ru(001), and of neutral N₂O and N₂ from chemisorbed and physisorbed N₂O on Ru(001), have been measured and compared to angular distributions of desorbing ions. All distributions are peaked around the surface normal. Angular widths of neutrals are generally broader than those of ions, but are much narrower than for thermal desorption, and show large differences. The results are discussed in terms of mechanisms of ionic and neutral desorption.

PACS numbers: 68.45.Da, 79.20.Kz

The most abundant products of desorption induced by electronic excitations—stimulated by electron impact, or photon absorption—in adsorption layers on metal surfaces are neutrals, for all systems investigated so far.¹ Nevertheless, most investigations to date have been concerned with positive ions because of the ease of detection; also, most published theoretical considerations place their main emphasis on mechanisms of ion formation. Specifically, the angular distribution of desorbed ions² has been used to draw conclusions about bond directions in adsorbates. Here we report the first measurements of angular distributions of desorbed *neutrals* for two systems containing chemisorbed as well as physisorbed molecules. We report on rather broad variations of the angular widths and discuss their origin in connection with the probable mechanisms and desorption channels.

The experimental setup consists of a single crystal positioned in front of a small aperture in a glass cap covering a mass-spectrometer (MS) ion source,³ inside a UHV chamber. The crystal is rotatable around an axis in its surface, and an electron gun rotating with it aims at the center of the crystal facing the aperture; the polar distribution of particles leaving the surface can thus be swept over the detector aperture, with constant angle of incidence of electrons. Angular resolution is about 5°. The electron beam is chopped at 20 Hz and the MS output at a certain mass is processed through a lock-in amplifier. Several angular scans are added together, each with a newly prepared adsorption layer for minimal desorption-induced changes (<5%). Detection efficiency is limited by the background of the residual gas and is greatest for particles not abundant there. For the abundant CO, desorbing fluxes corresponding to 10⁻¹⁴ mb were detected

at a background of some 10⁻¹² mb; the use of a capillary doser minimized the latter. Secondary electrons and ions from the surface were kept away by suitable potentials. Because of intensity reasons, electron energies between 200 and 800 eV were used. The ion angular distributions mentioned were obtained in a similar system described in Ref. 4.

So far we have investigated the systems CO/Ru(001)⁵ and N₂O/Ru(001).^{6,7} For CO, a single bonding mode exists throughout the coverage range whose properties are only modified by lateral interactions; at a coverage of $\theta=0.33$ all molecules are equivalent, occupy on-top sites, and are ordered in a $\sqrt{3}$ array up to desorption. In the N₂O system, both chemisorbed and physisorbed species are formed at sufficiently low temperature ($T_s < 90$ K), and coexist in the saturated layer. Stepwise heating to 125 K can be used to isolate the chemisorbed one.

For CO/Ru(001) the only electron-stimulated-desorption (ESD) neutral detected was CO.⁸ Figure 1 shows an angular scan for $\theta=0.33$ and $T_s=200$ K. No dependence on surface temperature (from 140 to 310 K), coverage (checked at $\theta=0.33$ and 0.66), electron energy (from 200 to 800 eV, i.e., below and above the C 1s and O 1s thresholds), or azimuth was observed within the error limits. The half-width is seen to be 55°, i.e., less than half that of a cosine distribution. Angular distributions of ions liberated under roughly the same conditions were much narrower, with about 16° for CO⁺ and 18° for O⁺ (Ref. 9); they do show some dependence on coverage and temperature which will be described elsewhere.

From N₂O layers neutral signals were seen at masses 44 (N₂O), 30 (NO), and 28 (N₂) (Fig. 2). As the N₂O and NO signals varied in parallel and were related as the cracking ratio from gas-

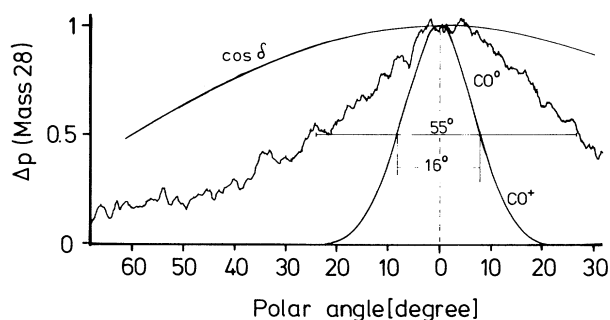


FIG. 1. Angular distributions of ESD neutral CO (CO^0 , $T_s = 140$ K) and CO^+ ($T_s = 120$ K), compared with a cosine distribution. Full half-widths are indicated.

phase N_2O , they are both due to desorbing N_2O . From *chemisorbed* N_2O , the full half-widths for masses 44 and 30 are, at 28° , quite narrow. For comparison, NO^+ and O^+ ions with half-widths of 24° and 13° were seen. A much broader distribution (65°) resulted for neutral N_2 under the same conditions. From *physisorbed* N_2O , the angular width of N_2O was more than twice as large as from the chemisorbed layer; no N_2 or ionic desorption was seen from it. For comparison, pointwise measurements for *thermally* desorbed N_2O from the same layers were compatible with a cosine distribution.

These examples show a rather broad variation of angular widths of induced desorption. As the angular widths are mainly determined by the potential-energy surfaces sampled by the desorbing particle,¹⁰ we expect them to contain information on the channels and possibly even the mechanisms of desorption. One might expect that different—or similar—widths (of the same product from different states, or of corresponding neutral and ion from the same adsorbate) are indicative of different—or similar—desorption channels followed by the respective particles. However, closer scrutiny shows that this is not the case. Since no influence of core excitations has been seen for neutral desorption, both in energy dependences¹¹ and in the angular widths in this work, we use the standard Menzel-Gower-Redhead mechanism^{12,13} of ESD for this discussion and consider only primary valence excitations of one-hole or one-hole-one-particle nature for simplicity (the involvement of two-hole states should not lead to qualitative changes). Neutrals can then desorb either by (direct or indirect) excitation to an antibonding excited neutral state of the adsorbate complex, or by neutralization of an initial ionic excitation; ions will always

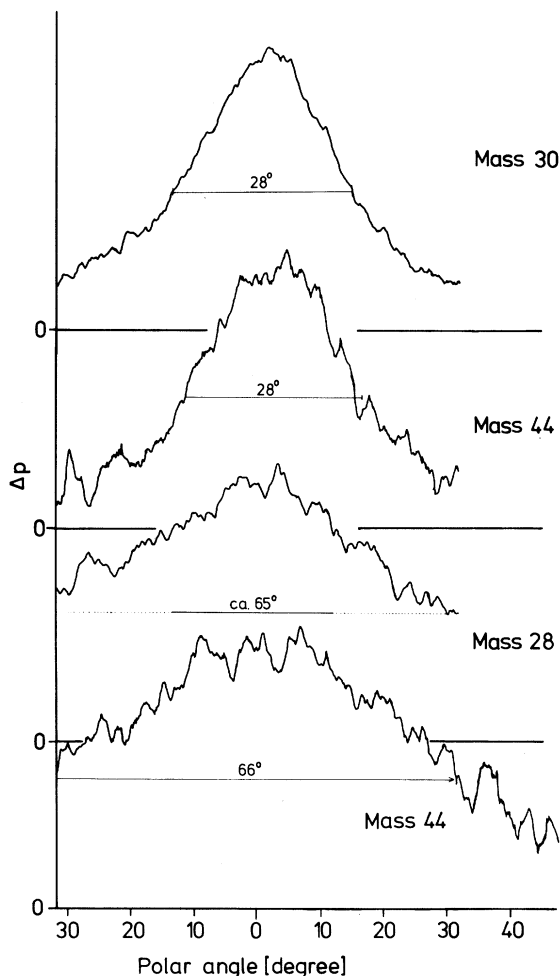


FIG. 2. Angular distributions of ESD neutrals from $\text{N}_2\text{O}/\text{Ru}(001)$. From top: NO , N_2O , N_2 from chemisorbed N_2O ($T_s = 90$ K, after heating to 125 K); bottom: N_2O from physisorbed N_2O ($T_s = 90$ K).

stem from the second type of excitation. In the first case very different potential-energy surfaces are followed by desorbing neutrals and ions, so that their angular widths could be different. While this could possibly explain the width differences between CO^0 and CO^+ , we do not think so. Not only would this contradict our earlier conclusions from threshold measurements¹¹ that neutralization of desorbing CO^+ is an important channel for CO^0 (this could be due to the different electron energies), but a purely repulsive neutral state would be expected to have a rather high slope in the Franck-Condon region and to result in a narrow angular distribution—contrary to observation. On the other hand, desorption of neutrals via ionic excitations comes about by crossing of the ionic and the neutral curve (Fig.

3) at a distance $x > x_c$, where x_c marks the critical distance at which the ion has acquired enough kinetic energy to escape the neutral well after neutralization.¹² Running up the latter, the particle is decelerated and the angular distribution which originally is that of the ion is widened. Most escaping neutrals will stem from neutralization close to x_c (neutralization corresponds roughly to a tunneling event from the metal, so that its probability falls off rapidly with distance from the surface), and have very low final kinetic energies, E^0 , compared with the ion energies, E^+ ; this will lead to strong refraction. An energy ratio E^+/E^0 of 10 would be necessary to give the observed widening (of about a factor of 3 in width), if conservation of parallel momentum is assumed; E^0 would still be considerably above thermal. Further widening could occur by scattering of the outgoing particle in the neutral potential. A realistic calculation is difficult because three-dimensional potential-energy surfaces of excited adsorbate states are not available. But even these rough arguments show that our results on the widths of CO^0 and CO^+ are compatible with both species originating mainly through the same (ionic) channel. Measurements of the kinetic energies of the neutrals which have not been done so far would be very helpful to check this.

The N_2O^0 widths from chemisorbed N_2O , on the other hand, are much narrower than those of

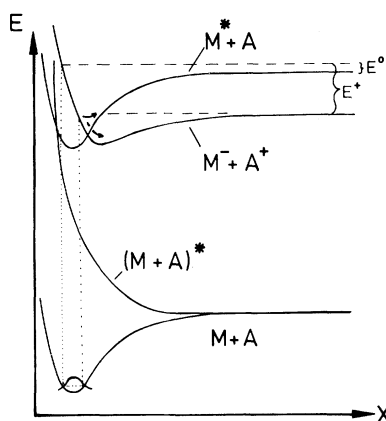


FIG. 3. Simplified one-dimensional potential-energy diagram for ESD of neutrals and ions. $M+A$: ground state; $(M+A)^*$: repulsive excited neutral state; M^-+A^+ : ionic state; M^*+A : adsorbate ground state with excitation energy transferred into the substrate. E^0 (exaggerated) and E^+ are the kinetic energies of neutrals and ions obtained via ionic excitation.

CO^0 and comparable to those of the NO^+ ions from the same system. No N_2O^+ desorption was found, so that a direct comparison with the corresponding molecular ion is not possible. The arguments given in the last paragraph suggest that neutralization should lead to broad distributions; the narrow N_2O^0 width would then be due to its originating from repulsive neutral states. The formation of N_2O^0 , NO^+ , and O^+ , but of no N_2^+ , is compatible with chemisorbed N_2O being adsorbed upright, with the N end bound to the surface.⁷ The observed N_2^0 signal, we believe, is connected to the O^+ signal: Excitations leading to the O^+ fragment leave behind N_2 on the surface, possibly in a repulsive excited state or in the electronic ground state which desorbs thermally under our conditions.¹⁴

The much larger width of N_2O^0 from the physisorbed species as compared with N_2O^0 from chemisorbed N_2O underlines its different bonding mode and is compatible with its lying on the surface.⁷ However, if this species is indeed bound by dispersion forces, then it is an interesting question why there is desorption at all, as any ionization or excitation should lead to stronger bonding. A possible mechanism for neutral desorption of physisorbed atoms has been suggested by Zhang and Gomer¹⁵: In this, primary ionization of the adsorbate leads to its *inward* motion and neutralization *close* to the surface, so that *high-energy* neutrals are obtained; we should then expect again narrow angular distributions. We propose as an alternative for *molecular* adsorption the following mechanism. Electron impact leads to an electronic excitation (or ionization) of the N_2O molecule which is connected to internal vibrational excitation because of the change of internal equilibrium bond lengths. After a certain lifetime the electronic excitation is removed to the substrate, leaving the molecule vibrationally excited, since the nuclei have moved meanwhile. Vibrational coupling can then transfer this excitation energy into the surface bond; as the latter is very weak, this can be sufficient for desorption. This may be partly an analog to the desorption effects observed by direct vibrational excitation¹⁶; it could be termed electronically induced vibrational predissociation. This mechanism would be compatible with the measured width and with the fact that no ionic products are seen to desorb in our case.

In conclusion, we have shown that angular distributions of neutrals desorbed by electron impact on adsorbate-covered surfaces can be measured, that their distributions show a large varia-

tion of angular widths, and that they can give clues as to the mechanisms operative. We argue that neutrals produced via neutralized ionic excitations should have much broader angular distributions than the corresponding ions, while neutrals formed via repulsive neutral states should have narrower widths, and we use these concepts for the assignment of observed processes. For neutral desorption of physisorbed molecules, electronically induced vibrational predissociation is proposed as a possible mechanism.

This work has been supported by the Deutsche Forschungsgemeinschaft through Sonderforschungsbereich 128.

¹See, for instance, T. E. Madey and J. T. Yates, Jr., *J. Vac. Sci. Technol.* **8**, 525 (1971); D. Menzel, *Surf. Sci.* **47**, 370 (1975), and *J. Vac. Sci. Technol.* **20**, 538 (1982).

²T. E. Madey, in *Inelastic Particle-Surface Collisions*, edited by E. Taglauer and W. Heiland (Springer, Berlin, 1981), p. 80, and references therein.

³P. Feulner and D. Menzel, *J. Vac. Sci. Technol.* **17**, 662 (1980).

⁴R. Jaeger and D. Menzel, *Surf. Sci.* **93**, 71 (1980).

⁵H. Pfnür, P. Feulner, H. A. Engelhardt, and D. Menzel, *Chem. Phys. Lett.* **59**, 481 (1978); H. Pfnür and D. Menzel, to be published, and references given therein.

⁶Y. Kim, J. A. Schreifels, and J. M. White, *Surf. Sci.* **114**, 349 (1982); H. Schlichting, P. Feulner, and D. Menzel, to be published.

⁷E. Umbach and D. Menzel, *Chem. Phys. Lett.* **84**, 491 (1981).

⁸No neutral O, which might be expected, was detected. However, this is no proof of its absence as it will stick readily to the detector walls and thus not lead to a detectable partial pressure increase.

⁹T. E. Madey, *Surf. Sci.* **79**, 575 (1979), reported much larger widths [CO^+ : 24 to 32 (± 6) at 90 to 300 K]; he had to correct for acceleration by more than a factor of 2 in width. As we worked essentially field-free between crystal and entrance aperture, and obtained identical results consistently in different machines, we believe our results to be correct.

¹⁰Bending vibrations (Ref. 9) are not governing the angular widths as seen from the large width variations for different systems, and the absence of temperature influences for CO^0 .

¹¹P. Feulner, R. Treichler, and D. Menzel, *Phys. Rev. B* **24**, 7427 (1981).

¹²D. Menzel and R. Gomer, *J. Chem. Phys.* **41**, 3311 (1964).

¹³P. A. Redhead, *Can. J. Phys.* **42**, 886 (1964).

¹⁴P. Feulner and D. Menzel, *Phys. Rev. B* **25**, 4295 (1982).

¹⁵Y.-J. Zhang and R. Gomer, *Surf. Sci.* **109**, 567 (1981).

¹⁶J. Heidberg, H. Stein, E. Riehl, and A. Nestmann, *Z. Phys. Chem.* **121**, 145 (1980), and *Phys. Rev. Lett.* **49**, 666 (1982); T. J. Chuang and H. Seki, *Phys. Rev. Lett.* **49**, 382 (1982).