

Kinetic-Energy Distributions of Neutrals Desorbed by Electron Impact from Adsorbates on Metal Surfaces

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The kinetic energies of neutrals desorbed by electron impact [CO from chemisorbed CO on Ru(001), and N₂O and N₂ from chemisorbed and physisorbed N₂O on Ru(001)] have been measured by a time-of-flight technique. Wide variations are found for peak energies and low-energy behavior. Theoretical calculations are presented for physisorbed N₂O which exclude a desorption mechanism via electronically induced vibrational predissociation of the surface bond, and support desorption from the repulsive region of the ground state which is reached via a strongly bound ionic state.

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Neutrals constitute the neglected majority of the products of desorption induced by electronic transitions (DIET), induced by electron or photon excitation (ESD and PSD, respectively).¹ We have reported measurements of thresholds² and angular distributions³ of neutral ESD products from chemisorbed and physisorbed layers. Their discussion in terms of the acting mechanisms³ led to implications concerning the kinetic-energy distributions, making it desirable to obtain these. Using a time-of-flight method, we have been able for the first time to measure the kinetic energies of ESD neutrals from adsorbate systems. Results are reported for CO from chemisorbed CO on Ru(001), and for N₂O and N₂ from chemisorbed and physisorbed N₂O layers on the same surface. While the results for the chemisorbed species correspond largely to expectations,³ those for the physisorbed layer are more difficult to interpret. Therefore, and as the limited space does not allow extensive discussion of all results, we concentrate on the latter, comparing them to theoretical calculations for several models. As will be shown, the mechanism proposed in Ref. 3 (electronically mediated vibrational predesorption) must be excluded, while an Antoniewicz mechanism leads to excellent agreement of experiment and theory.

The experiments were performed in a UHV chamber with base pressure below 10⁻¹¹ mbar. The time-of-flight setup (path length 32 cm) consisted of a quadrupole mass spectrometer (QMS) in a Cu tube (10 cm diameter) cooled to 77 K, whose inner walls were covered with a freshly sublimated Ti film during measurements; partial pressures of CO and N₂O in the QMS ion source were some

10⁻¹⁴ mbar. Apertures at the entrance of the flight tube and in front of the ion source allowed only particles from the sample to enter the ionizer. A meandered W filament between entrance aperture and sample served as electron source; a negatively biased grid of 99% transparency between filament and sample prevented electrons from entering the flight tube. Application of negative pulses of 250 V and 3–5 μs duration at a repetition rate of 0.5 to 1 kHz to the incandescent filament led to electron pulses of identical shape to the sample. Potentials and current in the ionizer, as well as the QMS field axis potential, were chosen to suppress ESD ions and to avoid degradation of the time resolution by space-charge effects. Events detected by the secondary multiplier of the QMS were processed in a multichannel scaler triggered by the electron pulse to the sample. Total electron doses were limited so as to desorb less than 10% of the layer in one run; about twenty such runs had to be added together to arrive at acceptable signal-to-noise ratios.

The experimental raw data, events in the ionizer as a function of flight time, are converted to energy distributions, at the same time with correction for the fact that the ionizer is a density, not a flux, detector. The $N(E)$ spectra obtained then give the distribution over energy of the particles leaving the surface in a cone of about 2° half-angle around the surface normal. As a result of the mode of measurement, error bars caused by background (residual gas and bremsstrahlung) get larger with decreasing energy (see Fig. 1).

Results for chemisorbed CO and N₂O and for physisorbed N₂O are shown in Fig. 1 (see Ref. 3 for details of preparation of these layers). From chem-

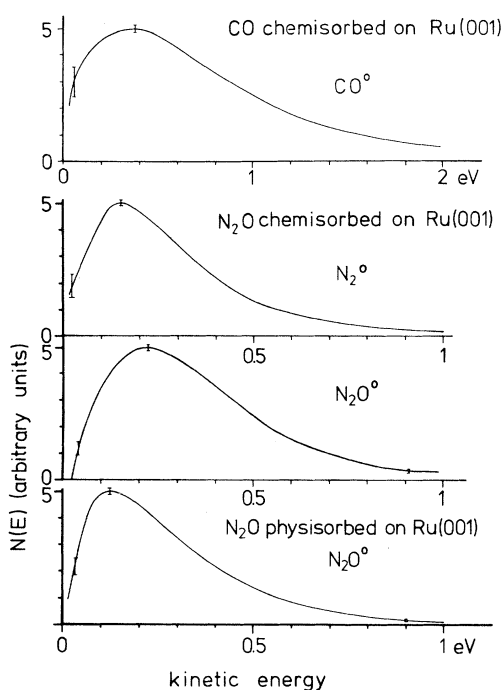


FIG. 1. Kinetic-energy distributions obtained for (from top) neutral CO molecules from CO on Ru(001); neutral N_2 and N_2O from chemisorbed, and neutral N_2O from physisorbed N_2O on Ru(001).

isorbed N_2O , neutral N_2O and N_2 molecules (termed $N_2O_{ch}^0$ and N_2^0 subsequently) are observed; the physisorbed layer only contributes N_2O^0 . From chemisorbed CO, neutral CO^0 and a metastable species (detectable without ionization), which is either CO^* or O^* , are detected.⁴ The energy distribution for N_2O^0 from chemisorbed N_2O and of CO^0 from chemisorbed CO differ in energy (distribution maxima at 0.22 and 0.35 eV, respectively); their shapes are similar but the $N_2O_{ch}^0$ curve shows a definite threshold around 0.02 eV, while the CO^0 curve does not. A similar threshold is observed for the metastable species in the CO system. The low kinetic energies of CO^0 , without a threshold, are consistent with our conjecture drawn from angular distributions³ that the neutrals observed at higher electron energies predominantly stem from reneutralization of CO^+ . Evidence for this is the strong increase of CO^0 yield at the CO^+ threshold² and the broad angular distribution [full width at half-maximum (FWHM) 55° ³] of CO^0 which has been explained by the refraction occurring when kinetic energy is taken mainly out of the perpendicular motion upon reneutralization beyond the critical point of recapture.⁵ Indeed, the kinetic energies of CO^0 found here are consistent with this interpretation.

The higher kinetic energies and clear cutoff at low energies for $N_2O_{ch}^0$ make it likely that in this case desorption proceeds mainly via an antibonding adsorbate state whose asymptote for infinite separation is the ground-state molecule. This also agrees with the much narrower angular width.³ A similar conclusion, albeit at much higher energies, applies to the CO metastable which also exhibits a threshold.

A second neutral ESD signal at mass 28 was observed for chemisorbed N_2O , which must be due to N_2^0 (FWHM 65° ³). $N(E)$ shows a maximum at 0.15 eV and a low-energy cutoff. Previous discussions of the mode of liberation of this particle³ mentioned the possibilities of its desorption being coupled to dissociation (removal of O^+), or following it in a thermally activated fashion. The high kinetic energies observed exclude the latter mechanism, so that N_2^0 formation must be caused by the same electronic event that causes O^+ removal and must immediately follow it (within one vibrational period). No electronic excitation of the Ru- N_2 bond would be necessary for this, because after O^+ removal the residual N_2 finds itself too close to the surface and/or in the wrong site so that it is expelled.

Because of its particular interest, N_2O^0 from physisorbed N_2O on Ru(001) ($N_2O_{ph}^0$) was studied most carefully in this work. Besides at normal emission, its energy distribution was also measured at 15° to the normal, i.e., at about half the half width (FWHM 66° ³); the results were identical (this was not the case for $N_2O_{ch}^0$). As seen in Fig. 1, the maximum occurs at 0.13 eV, and no threshold is found.

In Ref. 3, we discussed two possible mechanisms for the desorption, which at first glance is astonishing since any excitation or ionization of a van der Waals-bound particle should lead to a stronger bond. The first, an application of a proposal of Antoniewicz⁶ to physisorbed species,⁷ assumes an excitation to a more strongly bound ionized state in which, therefore, the particle moves *towards* the surface to be neutralized at a distance corresponding to strong repulsion on the ground-state curve, and thus to desorption. The second is an analogy to laser-induced desorption: An *internal* electronic excitation (e.g., ionization) of the admolecule leads to *internal* vibrational excitation via suitable Franck-Condon factors; when the *electronic* excitation is drained into the substrate by reneutralization, the molecule will normally be left in a vibrationally excited state; the corresponding excitation energy can be fed into the coordinate corresponding to the sur-

face bond by vibrational coupling and, if sufficient, lead to desorption. In Ref. 3 the second mechanism was favored. However, application of the theory of vibrationally stimulated desorption by Gortel and Kreuzer⁸ to the present case, using the parameters appropriate for our system, showed that the range of the rate parameters obtainable lies between 10^6 and 10^{10} sec^{-1} , where the high end is only obtained if the chosen parameters are stretched to somewhat unlikely values. As the actual rate must be much larger to compete with transfer of the vibrational excitation into the metal, we exclude this mechanism as the leading one. We therefore performed calculations for an Antoniewicz mechanism appropriate for our system.

The model is the following: A physisorbed N_2O sitting in the minimum of the surface potential $V_0(z)$ is ionized by electron impact, leading to a sudden transition to a potential curve $V_+(z)$ which differs from $V_0(z)$ by the (attractive) image potential $V_{\text{im}}(z) = e^2/4(z+z_i)$. An overall constant shift amounting to the difference between the ionization energy and the work function is irrelevant. We have treated the dynamics classically and quantum mechanically. In the latter approach the acceleration of the N_2O^+ ion in $V_+(z)$ implies the propaga-

tion of a nonstationary state $\psi(t) = \sum \exp(-i\epsilon_{\tilde{m}}t) \times |\tilde{m}\rangle \langle \tilde{m}|0\rangle$, where $|0\rangle$ is the ground state in $V_0(z)$ and $|\tilde{m}\rangle$ are states in $V_+(z)$. Neutralization after some time t leads to a transition back onto $V_0(z)$. Desorption as a neutral N_2O will take place if the state so reached has positive energy. The probability for this to happen is $P(E,t) = |\langle E|\psi(t)\rangle|^2$. We assume that neutralization, i.e., electron-ion recombination, is exponential in time with the rate constant given by $r = \alpha n_e(z)$, where α is the recombination coefficient and $n_e(z)$ is the electron density which we assume to be decaying exponentially in the region of physisorption, i.e., $n_e(z) = n_0 \times \exp(-\delta z)$, where n_0 is the electron density inside the metal and δ is of the order of 1 \AA^{-1} . Because N_2O and N_2O^+ move more or less classically we can connect the position z with time t via their classical trajectories. The overall probability that N_2O desorbs as a neutral with energy E is then

$$P(E) = \int_0^\infty dt r e^{-rt} P(E,t). \quad (1)$$

To evaluate (1) we must know the wave functions in $V_0(z)$ and $V_+(z)$ and the classical trajectories in these potentials for a similar classical approach. To proceed analytically we set up a one-dimensional model in which

$$V_0(z) = V_0 \{ \exp[-2\gamma_0(z-z_0)] - 2\exp[-\gamma_0(z-z_0)] \}$$

is a Morse potential. $V_0 = 0.43 \text{ eV}$ is the heat of adsorption per N_2O .⁹ γ^{-1} and z_0 are of the order of $1-3 \text{ \AA}$. In the image potential we take $z_i \sim 0.5 \text{ \AA}$ and fit $V_+(z)$ to a Morse potential as well, with respective parameters V_+ , γ_+ , and z_+ . To compare the one-dimensional theory with experiment we have multiplied Eq. (1) by E to account for the difference in the density of states in one and three dimensions.

Figure 2 shows fits to the data (note the logarithmic energy scale). The fits are equally good with the classical or the quantum mechanical theory. Good fits can be obtained with different sets of potential parameters over the range given in the caption. (For $z_0 > 2.5 \text{ \AA}$, V_{im} is too small to cause inward acceleration, and the desorption efficiency of neutrals—experimentally ~ 0.1 —drops sharply. For $z_0 < 1.5 \text{ \AA}$, z_+ is not shifted much from z_0 , and again little ionic acceleration results.) The values of δ and αn_0 are coupled by the requirement imposed by the maximum. The fit favors rate constants around 10^{14} s^{-1} and slow z decay of neutralization (curve b). With an electron density of $n_0 \sim 10^{22} \text{ cm}^{-3}$, a recombination coefficient $\alpha \sim 10^{-8} \text{ cm}^3 \text{ s}^{-1}$ results, a reasonable value for

electrons with the Ru Fermi energy. The influences of changing r and δ on the maximum and the width further corroborate the physical soundness of

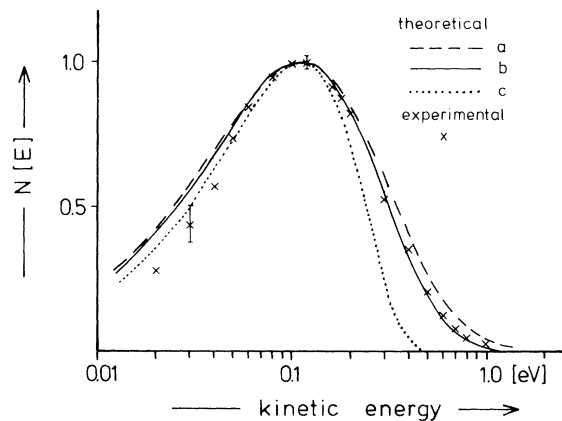


FIG. 2. Comparison of theoretical (curves a, b, c) and experimental (crosses) energy distributions on a logarithmic scale. Potential parameters are as follows: $V_0 = 0.43 \text{ eV}$; $\gamma_0^{-1} = \gamma_+^{-1} = 1.0$ or 1.7 \AA ; $z_0 = 1.5$ or 2.5 \AA ; $z_+ = 0.5$ or 1.2 \AA ; $V_+ = 2.0$ or 2.9 eV . Values for $\delta/\alpha n_0$ are, curve a, $0/(10^{14} \text{ s}^{-1})$; b, $0.5\gamma/(6 \times 10^{13} \text{ s}^{-1})$; c, $5\gamma/(3 \times 10^{12} \text{ s}^{-1})$.

the model, despite the uncertainties of some parameters.

In conclusion, we have succeeded in measuring the energy distributions of ESD neutrals with a method that is applicable to any surface system, to submonolayer coverages, and for doubly differentiated (angle-resolved) measurements. With it, we have obtained the first energy distributions of ESD neutrals from chemisorbed and physisorbed layers. We interpret the results in terms of different mechanisms: reneutralization of ionic desorbates or direct excitation of repulsive neutral states for chemisorbed species; and excitation into a more strongly bound ionic state, with neutralization into a repulsive location on the ground-state curve, for physisorbates. Comparison to model calculations for the latter case, with use of a classical and a quantum mechanical theory, yield good agreement with experiment. The mechanism of vibrationally mediated predesorption favored previously for this last case can be excluded.

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¹See, for instance, *Desorption Induced by Electronic Transition, DIET I*, edited by N. H. Tolk, M. M. Traum, J. C. Tully, and T. E. Madey (Springer, Berlin, 1983), and references given therein.

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