

Thresholds and mechanisms in electron-stimulated desorption of ions and neutrals from covalent adsorbates on metals

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Electron energy dependences of ionic and neutral electron-stimulated-desorption yields have been measured for covalently bonded adsorbates. Valence excitation is shown to be one primary mechanism for all cases. Core ionization with subsequent Auger decay, resulting in multiple-valence ionization, is clearly seen as primary mechanism for ionic desorption only, and only for adsorbate core levels. Neutral desorption has absolute thresholds lower than ions and additional structure at ionic valence thresholds, but not at core thresholds.

In the earlier view of electron-stimulated-desorption (ESD) processes^{1,2} the primary mechanism has been assumed to be a Franck-Condon valence excitation or ionization leading to a repulsive neutral or ionic state, whose disintegration can lead to desorption of a corresponding particle. This view has been corroborated by measurements of absolute thresholds which lie between ~ 3 and 25 eV.^{3,4} A secondary step which is of utmost importance on metal surfaces has been assumed to consist of the possible recapture of the leaving particle by transfer of the excitation energy into the metal. Evidence for this effect comes from the very strong variation of cross sections with adsorbate states, the very high isotope effect, and the preponderance of neutrals over ions in most cases.⁵

Knotek and Feibelman⁶ have shown that on ionic surfaces the ionization of metal (and to a lesser degree of adsorbate) core levels is a primary process for ESD and have assumed that the actual expulsion of a positive ion results from interatomic Auger decay of the metal core hole leading to a reversal of the Madelung potential. Feibelman has postulated⁷ that the occurrence of this process is an indication for the degree of ionicity of the surface bond. For a *covalent* adsorbate [CO on W(100)] we have shown⁸ that *adsorbate* core ionization can be an important primary step for ionic desorption. Adsorbed oxygen on metal surfaces also leads to thresholds at *metal* core states,⁹ but this can be explained by the assumption of local oxidic species on the surface. As these effects exist also in photodesorption¹⁰ they can be used for species-specific surface extended x-ray absorption fine structure (EXAFS).¹¹

The question poses itself, then, as to the applicability of the Menzel-Gomer-Redhead (MGR) and Knotek-Feibelman (KF) mechanisms for covalent adsorbates. The present work was undertaken in order to check whether the nonexistence—seen in one case—of substrate core structure for ESD from covalent adsorbates was universal; whether valence and

core-initiated desorption cross sections are comparable for other systems as well, and whether the ionic and the neutral thresholds are the same. Interesting conclusions about the desorption mechanisms can be derived from the results. We should mention that very recently similar measurements as far as ionic desorption is concerned have also been performed using photoexcitation.¹²

The experiments were done in two UHV systems with base pressures lower than 2×10^{-11} mbar. Both were equipped with electron guns, or filaments for the low-energy range, and quadrupole mass spectrometers in line of site of the sample for the detection of ionic desorption. The system which was used for detection of desorbing neutrals had a glass enclosure around the mass spectrometer ion source similar to that described in Ref. 13. An assembly of a filament between two grids was put in front of the aperture of the glass cap; the sample was positioned about 1 mm in front of this device. Desorbing ions were hindered from entering the mass spectrometer by suitable potentials. The neutral desorption signal was separated from the large background by lock-in detection at 20 Hz. Electron currents were never above 10^{-5} A/cm², so that periodic beam heating was negligible. Continuous thermal desorption by radiation only added to the noise level. By averaging over multiple scans, between which the sample was cleaned and recovered to avoid beam-induced changes, a desorption signal as low as 1/50 of the background (corresponding to some 10^{-13} mbar) in the enclosure could be measured. Even so, considerable noise was encountered which made the direct determination of thresholds difficult. To overcome this difficulty, the integral of the difference of signals with and without adsorbate layer was taken. This procedure effectively removes the noise as seen in Fig. 1.

Results for the systems CO/Ni(111) (desorbing particles: CO⁺, O⁺, O²⁺), NO/Ni(111) (NO⁺, O⁺), CO/Ru(001) (CO, CO⁺, O⁺), N₂/Ru(001) (N⁺, N₂) are shown in Fig. 1 (valence region, ions and neu-

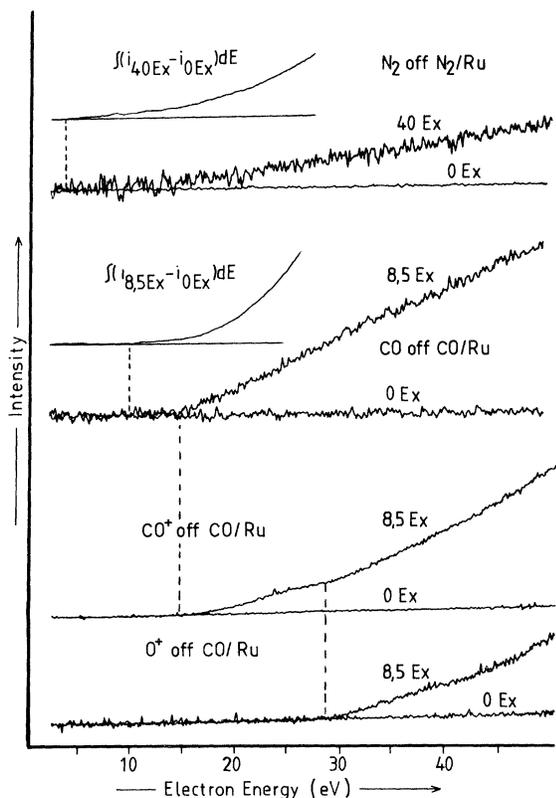


FIG. 1. Electron energy dependencies of CO, CO⁺, and O⁺ yields off CO/Ru(001) and of N₂ off N₂/Ru(001) in the valence region. For the neutral threshold regions, noise suppression by integration is shown in insets. The increased noise for N₂ is due to occurrence of some thermal desorption at the measurement temperature. The vertical lines indicate the correlation between increases of yield for CO (CO⁺) and CO⁺(O⁺) thresholds. $1 \times 10^{14} \text{ cm}^{-2}$ (Ref. 13a).

trals) and Fig. 2 (core region, singly and doubly charged ions; the data⁸ for CO/W are included for comparison).

We note as the main observations:

(1) Figure 1: Absolute, i.e., lowest, thresholds for ions and neutrals are in the valence region. Those for neutrals are considerably lower than for ions and are in fact below the ionization limit. In the case of CO/Ru, the neutral yield is measurable, but very low in the region below the ion (CO⁺) yield, but increases strongly at about the CO⁺ threshold of ≈ 15 eV; this must mean that a new channel for CO desorption opens together with CO⁺ desorption. A similar effect has actually been seen long ago for CO/W in the first work of this kind (Ref. 4; see also Ref. 14). There is also an indication of the opening of a new molecular ion (CO⁺) channel at the fragment ion (O⁺) threshold around 27 eV.

(2) Figure 2: Strong increases of the ionic signals are often seen above adsorbate core excitation, and

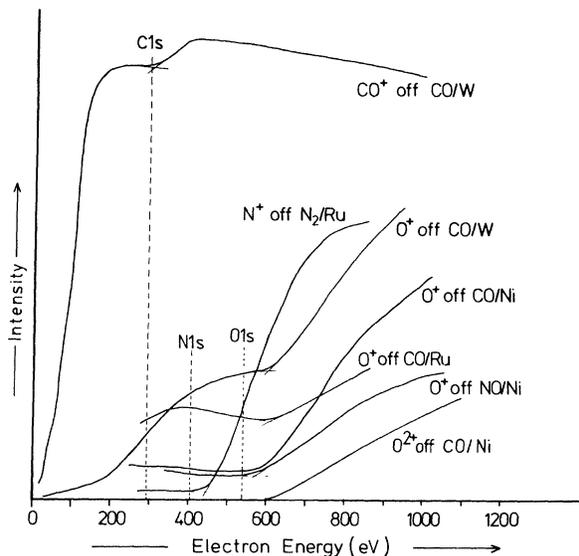


FIG. 2. Ionic yields vs. electron energy for the ions and systems shown, in the core region. [CO⁺ and O⁺ off CO/W(100) after Ref. 8.] Delayed onsets above adsorbate core thresholds are stressed by extrapolation. Doubly ionized fragments (O²⁺) show additional delay.

are strongest for dissociative ionization. The ratio of signals before and after the core threshold can be up to 1:50 [N⁺ off N₂/Ru(001) at about N 1s]. As seen before for CO/W(100),⁸ the yield increases are often delayed relative to the core binding energy by 30 to 60 eV. No substrate-core-related structure has been seen in any case.

(3) Figure 2: A doubly charged fragment ion (O²⁺) has been observed in two cases (CO/W,⁸ and CO/Ni); only for the latter was the intensity sufficient for detailed measurements. Compared to the O⁺ enhancement, there is an additional delay of threshold.

(4) For neutral species [CO and N₂ off Ru(001)] on the other hand, yield measurements in the region up to 1000 eV did not show any recognizable structure around the core energies; smoothly varying curves with very broad maxima around 300 eV were found (not shown). From the signal-to-noise ratio an upper limit of 5 to 10% on possible increases of neutral desorption at core energies can be set which should be compared with the up to 5000% for ions. We shall discuss the results for ions and neutrals separately.

I. IONIC DESORPTION

The existence of absolute thresholds in the valence region shows that a region exists where the MGR mechanism is fully operative as originally suggested,

at least for molecular ions. While the exact identification of the underlying primary excitations is difficult at present because of the uncertainty as to where the two secondary electrons end up energetically, some assignments are possible. The primary threshold for CO^+ formation (at about 14 eV) is most likely due to ionization of the $5\tilde{\sigma}$ orbital; the threshold for O^+ desorption at about 27 eV could be caused by $3\tilde{\sigma}$ ionization. Whether the structure in the CO^+ curve at about the same energy is due to the same process (followed by curve crossing) or some other excitation (e.g., $5\tilde{\sigma} \rightarrow \kappa\tilde{\sigma}$ resonance) cannot be decided at present. Improved insight could be reached by coincidence measurements between ions and loss electrons; such experiments are in preparation.

It is obvious that adsorbate core ionization can also be a very important primary process for ionic desorption. Because of the short life of core holes compared to the desorption time scale, Auger decay will have taken place as suggested in the KF mechanism.⁶ In effect the composite of these two processes is a Franck-Condon transition to doubly or multiply valence-ionized adsorbate states which can evolve corresponding to their potential curve (asymptotic neutral or—singly or doubly—ionized states are possible; even nonrepulsive states can be envisaged if holes are created in non- or antibonding levels) and can underlie recapture. We see that this is in effect an extended MGR or a hybrid of the MGR and the KF mechanisms. There are several puzzling aspects of this view, however, which at present can be only partly resolved.

(1) While direct valence ionization cross sections are expected to be considerably larger than those for core ionization, the increase at the core thresholds shows that total desorption cross sections can be comparable for the two or even much larger for the core path. This can be explained by assuming that the quenching of the two-hole state is much less probable than that of the one-hole state. Arguments in favor of this view have been given by Feibelman.¹⁵ However, recapture should be less important for fragment ion desorption (O^+ and N^+ in our cases), as the molecular orbitals whose ionization breaks the bond should not overlap much with metal states. Indeed, it is these products which show the largest enhancements.

(2) Even though the threshold behavior for electron impact core ionization is not well known in our cases, the delayed onsets of ionic ESD show that by far not all core ionized states can contribute to ESD above the core thresholds. Very recent PSD measurements¹⁶ have corroborated these findings. While excitation close to threshold could lead to many-body interferences, these should be confined to a smaller range and should also show up in Auger yields which is not the case. Most likely core ionization coupled to an additional valence excitation (shakeup) leads to

a drastically increased probability of desorption.¹⁶ Shake-up effects have also been seen in photon-stimulated desorption for the valence region.¹² An analogous explanation should then be valid for the additional delay of O^{2+} . A detailed discussion of these effects will require the understanding of the dynamical nature of screening of the initial and final states of Auger decay.

(3) The nonexistence of thresholds at metal core levels, even for the molecular ions, is surprising at first in view of the mechanism proposed above, as Auger decay of these should lead at least to some ionization of valence states contributing to the surface bond. However, the local density of these orbitals at the metal core is likely to be small; the corresponding small Auger yield of such states will be further reduced by preferential recapture. These questions could also be further clarified by electron-ion coincidence measurements.

II. NEUTRALS

In both systems investigated for neutral desorption the absolute neutral threshold is considerably below the ionization limit (about 10 eV for CO —see the integral curve; about 5 eV for N_2), in qualitative agreement with earlier measurements.^{3,4} This shows that excitations to repulsive neutral states of the adsorbate system are of importance. The most likely candidate is the charge transfer excitation of the $d_\pi - 2\pi$ back-bond prominent in electron loss spectroscopy.^{17,18}

The fact that core structure is at least not prominent in neutral yield curves shows that the contribution of reneutralization without recapture¹ is negligible for core initiated processes. On the other hand the existence of a break in the neutral curve at the absolute ion threshold for CO/Ru (Fig. 1) suggests that such a path does contribute substantially for primary valence excitation. [No such structure is seen in the N_2 yield curve which is in agreement with the finding that no molecular ion (N_2^+) desorption is found in this system.] The explanation for this apparent contradiction is again the strongly decreased reneutralization of multiply valence-ionized species. This means that while neutrals are strongly prevalent in desorption via direct valence excitation, desorption via core excitation leads to essentially ions only. We conclude also that reneutralization without recapture is possible. This is important in connection with a theoretical controversy between Brenig¹⁹ and Bell *et al.*²⁰; it must mean that reneutralization without recapture is a nonadiabatic process.^{19,21}

In conclusion, we have shown that ionic ESD from covalent adsorbates proceeds via direct valence ionization as well as via indirect multiple valence ionization through core ionization plus molecular Auger decay. As both are Franck-Condon-type transitions,

the MGR mechanism can be applied throughout, using a different primary mechanism and modified recapture probability in the latter case. Further refinements are necessary to explain the importance of shake-up processes in the core case, and possibly interference effects close to threshold. No contribution of core initiated processes is seen in neutral desorp-

tion, although direct valence ionization followed by reneutralization without recapture does contribute.

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