Adsorbate Core Ionization as Primary Process in Electron- and Photon-Stimulated Desorption from Metal Surfaces

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It is shown conclusively that electron impact ionization of the C 1*s* and O 1*s* core levels of CO adsorbed on W(100) leads to CO^+ and O^+ desorption, respectively, and that soft–x-ray photons induce the same processes by an intrinsic photoeffect. Disintegration of the adsorption complex which becomes multiply charged by Auger decay of the core hole is assumed as explanation.

In this Letter we show for the first time that soft–x-ray–induced ion desorption from a covalently bound adsorption layer on a metal surface is caused by an intrinsic photoprocess identified as adsorbate core ionization which is followed by Auger decay, as shown by comparison with the corresponding electron-stimulated process. This core-ionization–Auger-decay sequence is different from that postulated recently by Knotek and Feibelman[1] as the main process for O^+ desorption from oxides; it is the surface analog of molecular disintegration processes following deep core ionization[2,3] and the deep-core analog of the intra-atomic processes seen in electron excitation of the oxides with highly reduced probability,[1] and in photon excitation.[4] Implications and applications are briefly discussed.

Electron-stimulated desorption (ESD), the removal of ions and neutrals from an adsorbate layer by electron impact, has been studied extensively in the past, mostly with primary energies up to 150 eV.[5] For metal surfaces, the accepted mechanism has been primary valence excitation followed by secondary recapture processes which can lead to strong variations of the overall cross section.[6] For oxide surfaces, Knotek and Feibelman[1] have shown that primary ionization of high-lying *metal* core levels, followed by *interatomic* Auger processes which lead to removal of electrons from the oxygen and thus to a reversal of the Madelung potential, constitutes important channels for O^+ (as well as OH^+ and F^+) desorption; no secondary recapture processes are to be expected on oxides, of course. These authors also showed in detail that *intra*-atomic Auger decay following O(2*s*) ionization is of much lower probability (by about 10^3); it is better observable with primary excitation by vacuum-ultraviolet photons.[4] The interatomic mechanism appears also to operate for high-coverage adsorbed oxygen on metal surfaces[7] which may be due to a local oxidic nature of these species. Such a mechanism would not be expected to work for covalent adsorbates on metal surfaces. Nevertheless, it is an interesting question whether core-level excitation of the *adsorbate* can be a primary process for ESD in these cases which would result in desorption probabilities comparable to those via valence excitations. Because of the larger spacings between deep core levels which facilitates assignments, and the higher energies available by their decay, we focused our attention on ionization of such levels. In connection with this it is also relevant to ask whether photoexcitation can lead to similar processes, as the energy and species dependences of the ionization cross sections for electrons and photons are very different. Not much is known about photon-stimulated desorption (PSD) from metals,[8] especially at high energies; it is not known with certainty whether the effects reported so far are due to intrinsic photoeffects or to the action of secondary electrons and photoelectrons.[9] Investigating the system CO/W(100) with ESD and PSD, we have been able to answer these questions.

The measurements for both ESD and PSD were done in the same apparatus which was an UHV system (base pressure below 4×10^{-11} Torr) equipped with the necessary provisions to ensure clean starting surfaces and well-defined adlayers, a quadrupole mass spectrometer and electron (5–4000 eV) and photon (Al $K\alpha$) sources (for details see Franchy, Frenkel, and Menzel[10]).

The system CO/W(100) has been investigated with ESD before.[11,12] The molecular adsorption layer formed at low temperature ($T \leq 120$ K) is characterized by ESD of CO^+ and O^+ with the first ion being more abundant by a factor of the order of 10 for the usual electron energies (50–150 eV). In contrast we found that PSD with Al $K\alpha$ photons (1487 eV), which yields the same ions, leads to a reversed ratio of about CO^+:O^+ $\approx$ 1:7. Because of the possible contribution from photoelectrons at high energies, the dependence

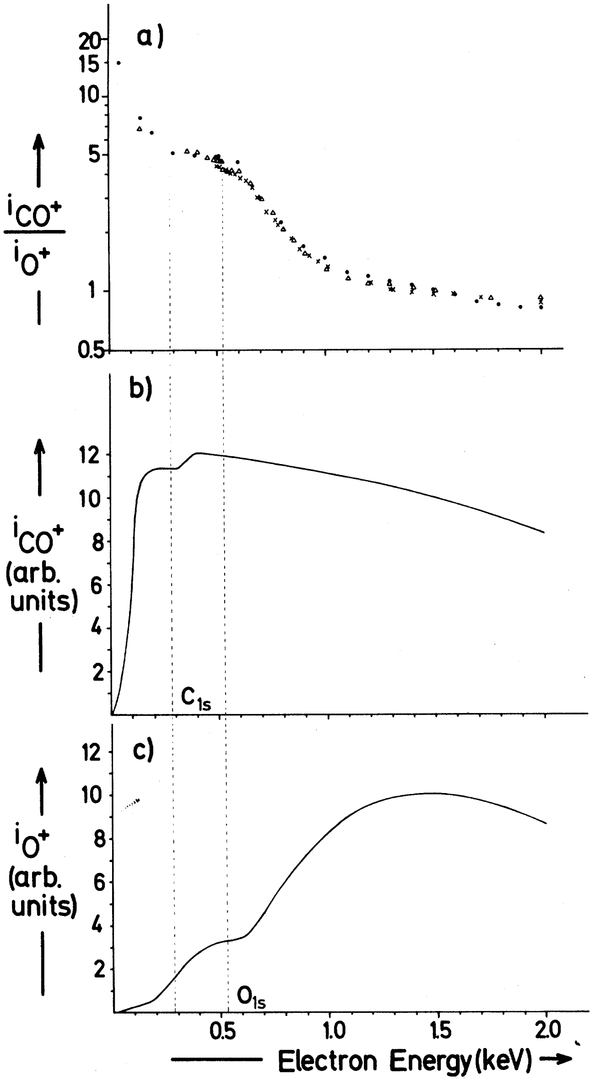

FIG. 1. (a) Dependence of the CO^+/O^+ ratio (on a logarithmic scale) in ESD from CO/W(100) at 120 K, on electron energy. The ratio for PSD at ≈1500 eV is about 0.14. (b), (c) Electron-energy dependences of the relative cross sections for ESD of CO^+ and O^+ for the same system, on linear scales. The threshold energies for C 1*s* and O 1*s* ionization are indicated by vertical dashed lines.

of this ratio on electron energy in ESD was investigated. Care had to be taken to avoid electron-induced changes in the adlayer[10-12] which would complicate the conclusion to be drawn here; electron currents below 10^{-6} A/cm^2 were used therefore. These electron-induced conversions between adsorbate states as well as those induced by heating can provide further information; in the interest of brevity, we shall not discuss these results here, but defer them to a forthcoming publication.[10]

The results for the electron-energy dependence of the CO^+/O^+ ratio in ESD for a 120-K undisturbed layer of CO on W(100) is shown in Fig. 1(a). One conclusion is immediately obvious. As photoelectrons or secondaries emitted under soft-x-ray irradiation must have energies *less* than 1487 eV, but ESD leads to considerably *higher* CO^+/O^+ ratios than PSD even up to 2 keV, the PSD ions must be caused predominantly by an intrinsic primary photoeffect.

Examination of the shape of the curve of Fig. 1(a) suggests that there is structure in the region of the C 1*s* and O 1*s* thresholds. In order to clarify the processes leading to them, the ion yields as functions of electron energy were measured separately; the results are given in Figs. 1(b) and 1(c). They show clearly that C 1*s* ionization leads to enhancement of CO^+ emission, while O 1*s* ionization is a new channel for O^+ desorption only.

As a first explanation, these desorption processes via adsorbate core ionization can be seen as analogous to the effects termed "Coulombic explosion" in molecules[2]: Auger decay, including Auger cascades, of the primary core hole leads to accumulation of positive charge on the originally core-ionized atom and its neighbors which fly apart by Coulomb repulsion. This somewhat crude picture would already suggest that C 1*s* ionization enhances both CO^+ and O^+ desorption (the charge accumulation can act on both sides of the C atom), while O 1*s* ionization yields O^+ only. A more detailed interpretation will have to take account of the decomposition channels of the multiply valence ionized species formed by the Auger processes, as for instance discussed for molecular CO in Ref. 3. That processes similar to those observed there are indeed taking place is borne out by our observation of small amounts of desorbing C^+, CO^{2+}, and O^{2+}, the latter two only above the O 1*s* threshold. The detailed mechanism will have to be investigated more closely, by taking into account the interaction with the metal surface.

The connection of high-energy ESD and PSD to primary core ionization also explains the strong preference of O^+ desorption in PSD: In photoionization at 1500 eV the ratio of the ionization cross sections of O 1*s* and C 1*s* is about 3,[13] while in electron excitation at the same energy it is about 0.4.[14] While an exact comparison of ESD and PSD cross sections with core and valence ionization cross sections is difficult at present, because in both cases a broad distribution of secondary electrons is always active for desorption as well, rough estimates show that ESD and PSD cross sections following core ionization are much closer to the primary ionization cross sections than those following valence excitation.[10] This must mean that secondary recapture processes[5] are much less effective for the particles desorbing after core ionization than after valence excitation. More detailed studies, both theoretically and experimentally, of these conditions should provide appreciable insight in excitation and transfer processes at metal surfaces. It should be stressed, however, that no evidence against the applicability of the Redhead-Menzel-Gomer mechanism[6] for covalent species at *lower* energies has been found.

Two applications come to mind immediately. Angular distributions of ESD ions (ESDIAD)[15] have been used to derive information about adsorbate geometries.[16] The interpretation is made difficult by the fact that for valence excitations three contributions to the angular distributions (the shape of the initial state potential and of both the real and the imaginary parts of the final-state potential) are expected to be effective. If the simple model of "Coulombic explosion" can be carried over, ESDIAD via adsorbate core-level ionization would be mainly determined by the geometry of charge accumulation after Auger decay which will lead to a simpler connection to initial state geometry; in particular, the apparent unimportance of recapture simplifies the analysis. Because photoionization has a much smaller ratio of valence to core cross sections at high energies than electrons,[13,14] the specificity can be enhanced by using PSD instead of ESD. The investigation of PSDIAD (photon-stimulated desorption ion angular distribution) using soft–x-ray photons is therefore proposed.

The second application rests on the finding that a large part of the ion current above the adsorbate core threshold is proportional to the core-ionization cross section. Its energy dependence in PSD will then show extended x-ray–absorption fine structure (EXAFS). This can be used for an extremely surface-sensitive variation of this technique. If the PSD ion current is used as EXAFS monitor, the distance between an adsorbate atom and its neighbors could be determined even with species specificity (ESD efficiencies and even products often differ strongly for different adsorbate binding states[5]; the same is indicated for PSD[10]). A similar proposal has been made by Knotek, Jones, and Rehn[4] using the substrate core levels for their oxidic systems.

In conclusion, it has been shown that photodesorption from metal surfaces by soft–x-ray photons can proceed via an intrinsic primary photoeffect which is identified as adsorbate deep core-level ionization, and that this primary process is also effective in ESD with overall cross sections comparable to or exceeding those for valence excitations. Ion desorption is then due to Auger decay followed by disintegration of the multiply charged adsorbate complex. Recapture processes seem to be less effective under these conditions than for primary valence excitations. The effect promises to have interesting applications for geometry determinations via PSDIAD and adsorbate-sensitive EXAFS.

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