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Reinterpretation of electron-stimulated desorption data from chemisorption systems

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A review of the electron-stimulated-desorption (ESD) literature shows that many of the features of ESD that are difficult to rationalize within the model of Menzel, Gomer, and Redhead can easily be interpreted using the Auger decay model, which has recently been developed to explain ESD from transition-metal oxide surfaces. Specifically, the Auger model helps to explain the charge state of the desorbing species, the high-energy (~ 30–40 eV) onset behavior that is seen, the differences in thresholds for positive and neutral desorbates, ESD cross-section and isotope-effect data, and the high kinetic energies of desorbing particles. The success of the Auger picture for ionically bonded surfaces suggests a number of new applications of ESD, including the deduction of reaction paths in surface chemistry and the study of the evolution of surface oxides.

I. INTRODUCTION

A considerable body of data has been accumulated over the past two decades concerning the electron-stimulated desorption (ESD) of chemisorbed species from a variety of surfaces.[1] However, it has been difficult to draw definitive conclusions concerning surface structure by applying the usual picture of the desorption phenomenon[2–4] to these data. Two recent developments suggest that in the future ESD will be a more powerful surface analytical tool. The first is the observation of angular-desorption patterns which appear to correlate with adsorbate bonding geometry.[1e] The other is the demonstration that new ESD data for a variety of transition-metal oxide surfaces can be explained in terms of a core-hole Auger decay model.[5] This model implies that for ionically bonded surfaces ESD is an easily interpretable, atom-specific, valence-sensitive surface probe.

In this paper we extend the application of the Auger model to ESD from chemisorption systems. We show that the model provides natural interpretations for many important features of published ESD data for ionic chemisorption, including (a) the energies of the major desorption thresholds, (b) the large charge transfers necessary to produce the positively charged ions which are observed, (c) the differences in threshold energies for neutral and positively charged desorbate species, (d) the smallness of ESD cross sections as compared to gas-phase valence-electron ionization cross sections, (e) the absence of an isotope effect in the ESD of neutrals as compared to its presence for positive ions, (f) the differences between various adsorption states (such as the β_1 and β_2 states of O-W),[6] which lead to their vastly different ESD cross sections, and finally, (g) the high kinetic energies (up to ~12 eV) with which ions (such as O^+ off W) are observed to desorb.

Within the previously accepted ESD model, due to Menzel and Gomer[3] and Redhead[2] (henceforth the MGR model), none of these features of the data can be explained in detail.

We begin our discussion of ESD with a brief review of the MGR and Auger decay models including the facts that led to their formulations and some predictions which they make. We then take up the features of ESD data mentioned above and compare their analyses within the MGR and Auger pictures. Finally, assuming the validity of the Auger model for ESD from ionically bonded surfaces, we discuss two classes of phenomena whose understanding might be furthered by ESD studies, surface chemical reactions and the evolution of surface oxides.

II. MGR AND AUGER DECAY MODELS OF ESD

Because the mass of an electron is $\lesssim \frac{1}{2000}$ the mass of any ion, it is clear that desorption induced by a low-energy (<500-eV) electron must be a consequence of an electronic transition and not of a direct kinetic energy transfer from an incident electron to the desorbing species. In the usual picture of ESD, proposed by Menzel and Gomer[3] and by Redhead,[2] it is assumed that the incident electron simply kicks a bonding (valence) electron into a nonbonding or antibonding state. The resulting surface species is then supposed to find itself in a repulsive potential which causes it to desorb.

The attempt to apply this model to the ESD of highly electronegative species in positive charge states (e.g., O^+ and F^+) is beset with difficulties. Perhaps the most important of these is that the MGR model provides no explanation of how the positive ions are generated in the first place. Since an incident electron at 0–100 eV is unlikely to strip a surface atom of more than one electron, one is forced to assume in the MGR picture that surface oxygen atoms, for example, are bonded in equilibrium as O^0's. This assumption violates the chemical wisdom that says because it is so electronegative, oxygen will generally adsorb in a charge state between -1 and -2. (Note that this difficulty does not arise in applying the MGR model to desorption of covalently bonded species, such as H from H_2-W. Accordingly we shall have little new to say about ESD when the surface bonding is covalent.)

The failure of the MGR model to account for the production of O^+ ions in ESD from ionic surfaces, specifically from the maximal-valence transition-metal oxides TiO_2, WO_3, and V_2O_5, was one of two important reasons for the formulation of the Auger decay model of ESD.[5] The other was the inability of the MGR model to explain the fact that the major O^+ desorption threshold for TiO_2, WO_3, and V_2O_5 in each case corresponds to the ionization potential (IP) of the highest-lying metal-atom-core electron.

The reasoning leading to the Auger model of ESD is as follows: TiO_2, WO_3, and V_2O_5 have in common maximal metal-atom valency, i.e., in each oxide the metal atoms are stripped of valence electrons and their highest-lying occupied level is 30–40 eV below the Fermi energy. The main decay channel for a hole in the highest-lying metal-atom-core state is therefore an interatomic Auger transition. If such a transition removes two or three electrons from a surface O, that atom will suddenly find itself in a strongly repulsive Madelung well, and hence will be likely to desorb. Thus the Auger picture of ESD explains both the onset of desorption at the metal-atom-core threshold and the large charge transfer necessary to create an O^+ ion.

For the sake of the discussion to follow, two further aspects of the Auger model are significant:

(i) The O^+ desorption current from a metal oxide is very sensitive to metal-atom valency. In any suboxide, valence electrons do reside on the surface metal atoms. Consequently the Auger decay of the highest metal-atom-core hole is much more likely to be *intra*-atomic than *inter*atomic (because intra-atomic matrix elements are much greater than interatomic ones[7]). However, an intra-atomic decay will make the metal atom more positive and thus will generally increase surface stability. Therefore, as we have verified experimentally for a variety of surfaces (V_2O_3, NiO, Cr_2O_3, sputtered TiO_2, etc.) the Auger model predicts that *no* O^+ desorption threshold should be seen at a metal atom core IP for less than maximally coordinated metal atoms.[5] It is well known that sputtering a TiO_2 surface produces lower valence Ti atoms,[8] and we have confirmed this fact in our own Auger data[9] that shows a Ti $3d$-electron peak for sputtered TiO_2 and no such peak for annealed TiO_2. The fact that high metal-atom valence requires high metal-atom–oxygen coordination means that the observation of O^+ desorption in ESD from oxides has structural implications, within the Auger model. In particular the metal-atom–oxygen coordination in the surface must be essentially that of the bulk oxide. For many oxide surfaces this argument therefore implies that significant surface reconstruction occurs.

(ii) The reason that appreciable desorption of O^+ does not begin at the O-$2s$ threshold from TiO_2, V_2O_5, . . . is that there is little or no phase space available for this process. That is, the ~20 eV associated with the presence of an O-$2s$ hole is simply not enough energy to remove the ~3 electrons necessary to turn a surface $O^{(1+x)-}$ into a desorbing O^+. On the other hand, since the energy difference between an O^0 and O^+ plus an electron at the Fermi level is ~10 eV, the Auger model predicts[5] that there will be sufficient phase space for O^0 desorption at ~20 eV, and thus that the onset of O^0 desorption *should* occur at the O-$2s$ ionization potential.

With these facts in mind we now turn to a discussion of published ESD data for chemisorption systems.

III. ESD THRESHOLDS

To begin our reexamination of ESD data, we focus on desorption thresholds. Despite the great number of papers on ESD in the literature,[1] in fact only a few surface systems have been studied, and little threshold data are available. Most of the work reported has involved the use of W,[3,10] or Mo,[2,11] as an adsorbent, and O_2, CO, H_2O, or H_2 as an adsorbate. In the published work concerning other adsorbents, e.g., Ta,[12] Ir,[13] Si,[14] Ge,[15] C,[16] desorption currents versus primary beam energy E_p, were not reported for the range $25\ \mathrm{eV} < E_p$, which is of particular interest in the Auger model. In other work, e.g., for a variety of oxide surfaces (SrO, BaO, MgO),[17] the beam current was sufficiently high that the desorbed current was not first order in beam current and thermal effects were probably important.[18] Since the Auger mechanism for ESD is primarily of interest in ionically bonded surfaces, attention centers, in what follows, on oxygen as an adsorbate, and thus mainly on the systems O-W and O-Mo.

In considering thresholds for electron stimulated O^+ desorption, an examination of published data suggests that one can distinguish three regions of E_p, namely, (I) $E_p \lesssim 25$ eV, (II) $25 \lesssim E_p \lesssim 50$ eV, and (III) $E_p \gtrsim 50$ eV. What most authors refer to as *the* threshold for O^+ desorption is generally found in region I, i.e., at $E_p \approx 16-25$ eV. However, it is at somewhat higher energies (in region II) that one typically finds the most impressive thresholdlike feature in the desorption curves. At still higher energies (in region III) one sometimes sees structure in the desorption data; but it is generally quite weak.

Given this general description of desorption data, we divide our consideration of O^+ thresholds into three subsections, corresponding to energy regions I, II, and III.

A. Region I, $E_p \lesssim 25$ eV

O^+ desorption thresholds are generally reported to lie in this energy region. However, attempts to interpret the observed threshold energies within the MGR model have not been very satisfactory, as we discuss here.

In both the MGR and the Auger models the event which leads to desorption involves a sudden change in the electron occupation of the states associated with the desorbing species. Thus in both cases, the desorption involves a Franck-Condon-type transition in which the probability of a desorbate being emitted with ~zero kinetic energy may be vanishingly small (see Fig. 1). In order to clarify the analysis it is useful to measure the desorbing ion kinetic energy distribution. One then determines the desorption onset as a function of ion kinetic energy and defines the "minimum ion desorption threshold" as the threshold for emission of ions with the minimum observable kinetic energy (~0 eV for O^+ off Mo,[2] but[10a] ~5 eV for O^+ off W).

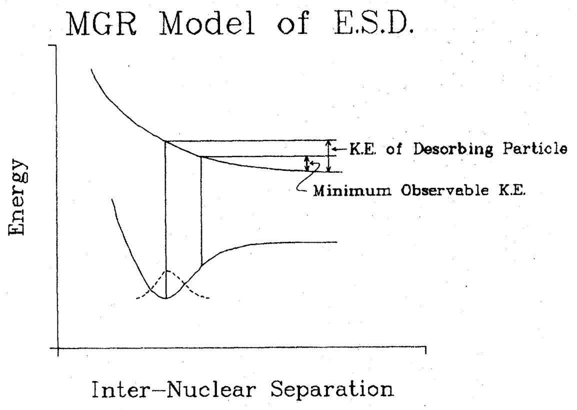

FIG. 1. Franck-Condon diagram illustrating the usual picture of how ESD works. The equilibrium position of the desorbate species is represented by the (dashed) Gaussian distribution in the lower potential. An incident electron causes an electronic transition to a state in which the desorbate feels the upper, purely repulsive potential. Note that when the minimum in the equilibrium well is at sufficiently small R internuclear separation, the probability of desorption with zero kinetic energy is quite small.

It is obvious that ion desorption onset measurements are beset by signal-to-noise problems, insofar as one is attempting to determine where a signal vanishes. Consequently, it is not surprising to see that different groups have obtained O^+ desorption thresholds for the same adsorbent which differ by several eV.[10g] On the assumption that the lowest reported thresholds are the most accurate values (i.e., that they were obtained on instruments with the best dynamic range), we take the minimum thresholds for O off W and Mo, respectively, to be 16.7 eV (reported by Nishijima and Propst[10a]) and 17.6 eV (reported by Redhead[2]), and consider the interpretation of these values within the MGR model.

The minimum O^+ desorption threshold in the MGR model is given by

$$E_{\text{th}}(O^+) = q(O^0) + I(O^0) + T_{\min}(O^+)\,, \qquad (1)$$

where $q(O^0)$ is the binding energy (heat of adsorption) of O^0, $I(O^0)$ is the O^0 ionization potential, and $T_{\min}(O^+)$ is the minimum observable O^+ kinetic energy. However, before applying Eq. (1), it is important to specify the relation between E_{th} and the experimentally applied voltage between cathode and sample at threshold. It is also necessary to specify the final state of the electron removed in ionizing the O^0, before one can quote a value of $I(O^0)$. Regarding the meaning of E_{th}, the onset energies of 16.7 and 17.6 eV quoted above for O^+-W and O^+-Mo are in fact the energy differences between the cathode and sample *vacuum levels* at threshold. That is, in giving these values it is assumed that the incident electrons do not end up *in* the sample (i.e., at the Fermi level) but rather go off into the vacuum. If one makes the more natural assumption that the beam electrons do fall to the Fermi level, then Eq. (1) must be replaced by

$$E_{\text{th}} = V_{\text{ap}}^{\text{th}} + \phi_c = q(O^0) + I(O^0) + T_{\min}(O^+)\,, \qquad (2)$$

where $V_{\text{ap}}^{\text{th}}$ is the voltage difference between the cathode and anode Fermi levels at threshold and ϕ_c is the cathode (i.e., emitter) work function.

Turning to the meaning of $I(O^0)$, one has to face the problem of the electron final state once again, asking if there is any reason to suppose that the electron removed from an O^0 in converting it to an O^+ should not fall to the sample Fermi level. If there is not, then Eq. (2) must be rewritten

$$E_{\text{th}} = V_{\text{ap}}^{\text{th}} + \phi_c = q(O^0) + I_{\text{gas}}(O^0) - \phi_a + T_{\min}(O^+)\,, \qquad (3)$$

where ϕ_a is the sample (or anode) work function.

Unfortunately, Eq. (3) predicts neither of the observed values of $V_{\text{ap}}^{\text{th}}$ for O^+ off W or Mo. For Mo it is found that $q(O^0) + I_{\text{gas}}(O^0) + T_{\min}(O^+)$ is very nearly equal to the "contact-potential corrected" threshold voltage, $V_{\text{ap}}^{\text{th}} + \phi_c - \phi_a$. Thus, Eq. (3) fails to agree with experiment for O^+ off Mo unless one assumes that both the beam and ionized electrons fall only to the vacuum level in their final states, which enables one to drop a term equal to $2\phi_a$(~10 eV) from Eq. (3). For W, agreement between theory and experiment requires one to assume that at threshold the electrons fall to an energy level ~1.7 eV above the Fermi energy.[10a] However, the density of states of W is not believed to rise sharply 1.7 eV above the Fermi level.[19] Thus the agreement between theory and experiment for O^+ thresholds is poor within the MGR model for both the O-W and O-Mo systems.

In the Auger model, the O^+ thresholds seen in energy region I have a very simple meaning; that is, they correspond to the ionization potential of the O $2s$ electron, which typically lies between 20–25 eV, depending on the particular surface in which the oxygen resides. The Auger decay of the $2s$ hole then leads to the formation of an O^+, which desorbs. As far as agreement between theory and experiment is concerned, note that when one makes the natural assumption that the beam electrons fall to the sample Fermi level, one predicts simply that

$$E_{\text{th}} = V_{\text{ap}}^{\text{th}} + \phi_c = I(O(2s)). \qquad (4)$$

Unfortunately, data were not taken for the value of $I(O(2s))$ in the O-W and O-Mo experiments in which the V_{th}'s were measured. But adding the work functions of ~5 eV,[20] and ~6 eV,[10a] for the O-Mo and O-W surfaces to the reported values of V_{th} one is clearly not far removed from agreement with Eq. (4). In many other cases of ESD, such as O^+ from CO-W,[10a] and H^+ from H_2O-W,[10a] and H_2O-TiO_2,[9] etc., one also sees thresholds at energies near 20 eV. These results represent further circumstantial evidence that the Auger mechanism is operative, i.e., that O-$2s$ ionization is the first step in the desorption process.

The explanation of the 20-eV O^+ desorption thresholds via the Auger decay mechanism is not without some difficulties. In order to explain why the O^+ desorption yield from clean TiO_2 is so small at ~22 eV, we have argued[5] that the energy required to convert a surface O^{2-} to an O^+ is sufficiently large that little remains for the kinetic energy of the O^+, and consequently that its desorption is inhibited by lack of phase space. If this argument is valid, however, we need to explain how, e.g., Nishijima and Propst (NP) could have seen 5-eV O^+'s desorbing from O_2-W at a beam energy of ~23 eV.[10a] The most likely explanation is that in NP's sample there were some O^-'s, whereas in our TiO_2 surface there were only O^{2-}'s. Less energy is required to remove two electrons from an O^- than three from an O^{2-}, which would leave more energy over for the desorbing O^+. Precisely this sort of argument has been used[5] to explain why OH^+ will desorb from TiO_2 in large quantities at the O-$2s$ threshold while O^+ will not.

In summary, it appears likely that the Auger model of ESD is responsible for O^+ desorption onsets in energy region I. The unrealistic assumptions concerning electron final states which are necessary to achieve agreement between the MGR model and experiment would appear to eliminate it as a possibility. However, further experiments are necessary to confirm the Auger picture.

B. Region II, $25 \lesssim E_p \lesssim 50$ eV

It is in this region that the most dramatic rise in O^+ desorption current occurs for both the

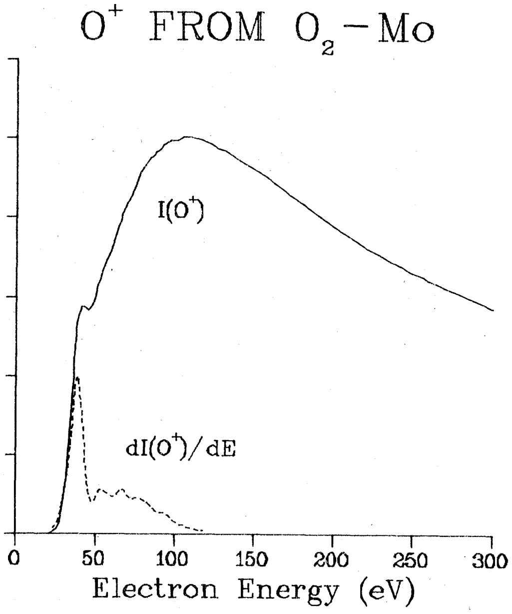

FIG. 2. O^+ desorption current $I(O^+)$ vs electron energy E, after Redhead (Ref. 2, Fig. 4). Also $dI(O^+)/dE$ vs E (after Ref. 2, Fig. 5). Note that the most dramatic rise in $I(O^+)$ begins at ~30 eV, using Redhead's "contact-potential corrected" voltage scale. The higher energy structure in the O^+ desorption current is easily seen in the $dI(O^+)/dE$ curve. Note, however, that this curve, from Redhead's Fig. 5 is not the derivative of the $I(O^+)$ curve which is from his Fig. 4. The negative derivative of the latter at ~ 50 eV, for example, is absent in the former.

chemisorption systems O-W (Ref. 10a) and O-Mo (Ref. 2) as well as for clean, annealed TiO_2, V_2O_5, and WO_3.[5] For example, in Fig. 2 we reproduce Redhead's measured O^+ current versus electron energy for O-Mo.[2] Note that a linear extrapolation of the steeply rising portion of the curve yields an onset of ~30 eV. If we correct this value of beam energy for the anode work function, we see that Redhead's onset measurement falls very close to the Mo-4*p* IP of 35 eV. Similarly, the steeply rising portion of Nishijima and Propst's O^+ versus energy curve begins at a work function corrected energy of ~36 eV, which is within a volt of the W-4*f* and W-5*p* IP's. These results are very similar in nature to those for the clean metal-oxide surfaces which we have discussed previously, and strongly suggest that the Auger mechanism is at work in the O-W and O-Mo chemisorption systems. Within the MGR model there is no obvious reason why a dramatic rise in O^+ current should occur at an energy as high as 30 eV.

C. Region III, $E_p \gtrsim 50$ eV

In this energy region, structure in the O^+ yield versus electron energy has been seen for a number of systems, including O-Mo (cf. Fig. 2),[2] O-W,[10h] TiO_2 (see Fig. 3),[5] etc. At present this structure is poorly understood. Zingerman and Ishchuk have proposed that diffraction effects are responsible for the structure they see for O-W.[10h] However, this structure has not been reproduced by other experimental groups. Phillips[21] has pointed out that the spacing of the structures seen by Redhead in O-Mo is too close in energy to be purely diffractive in origin and has suggested that for this system they may come from ionization losses suffered in an O^+ plasma which is created near the surface in the process of carrying out an ESD experiment. However, this idea requires the observation of an O^+ current, which is quadratic in incident beam intensity, while in both the microamp (beam current) experiments of Redhead, and our own 50-nA experiments on TiO_2 the O^+ current was in fact linear in beam intensity. There is evidence that the structure at 40 eV for TiO_2 is related to surface order (see Fig. 3). However, we are not yet able to distinguish whether the surface order effect on O^+ desorption involves diffraction of the incident beam or the dependence of the electron loss spectrum (i.e., unoccupied density of states) on surface geometry.

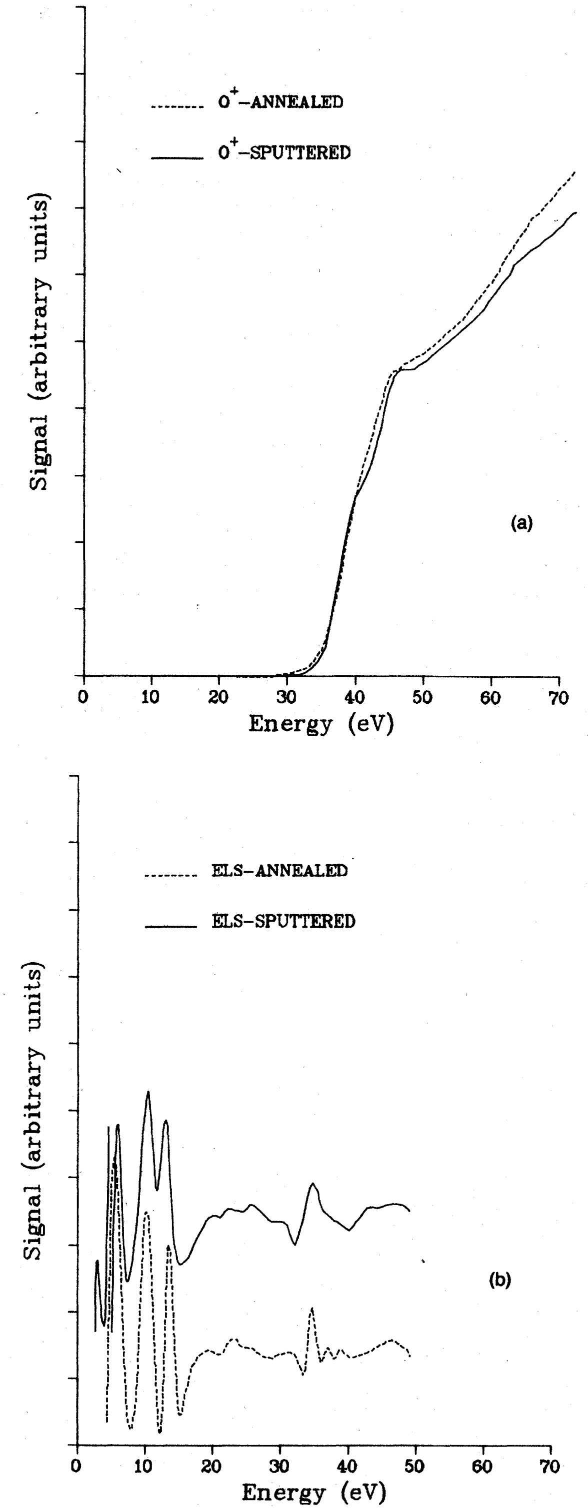

FIG. 3. (a) O^+ desorption currents and (b) electron loss spectra (ELS) for annealed and sputtered TiO_2 surfaces. Note that the structure at ~ 40 eV seen in both the desorption and ELS curves for the annealed surface is much weaker in the sputtered case.

IV. COMPARISON OF O^+ AND O^0 DESORPTION ONSET ENERGIES

Because it is difficult to detect neutral particles, ESD of neutrals has only been studied indirectly, via the observation of the time rate of decrease of ion current at a fixed beam energy.[2] On the assumption that the probability of producing say an O^+ is proportional to the total amount of surface oxygen, the observation of a drop in O^+ current which is faster than that predicted by the total number of O^+'s collected indicates that some desorbing oxygen is escaping detection, and is presumably desorbing in a neutral state.

By this means, Nishijima and Propst[10a] concluded that for O-W, ESD of neutrals is quite probable even when the beam energy is sufficiently close to the O^+ threshold that the O^+ current has dropped considerably (see Fig. 4), and they thereby extrapolated to an O^0 threshold "several eV lower" than that for O^+ desorption.

Within the MGR model, the interpretation of the finding that the O^0 and O^+ onsets occur at different energies is that two different electronic excitation processes are possible, one leads to desorption of neutrals and the other produces ions. However, the nature of electronic processes involved remains unknown.

In the Auger picture, one *expects* different threshold energies for O^0 and O^+ production. The O-2*s* ionization potential is only ~20 eV, which is barely sufficient[5] to remove three electrons from an O^{2-} but is more than adequate for removing two electrons. Consequently, if the surface oxygen is in a doubly negative charge state, one would expect O^0's to desorb at the O-2*s* IP, but because of phase space limitations, only very few O^+'s. Of course, if there are surface O^-'s, these will desorb as O^+'s at the O-2*s* threshold with substantial kinetic energy. Thus we can explain all of NP's O-W data qualitatively by assuming that their surface contained many O^{2-}'s, and a few O^-'s, and that the Auger decay mechanism is operative.

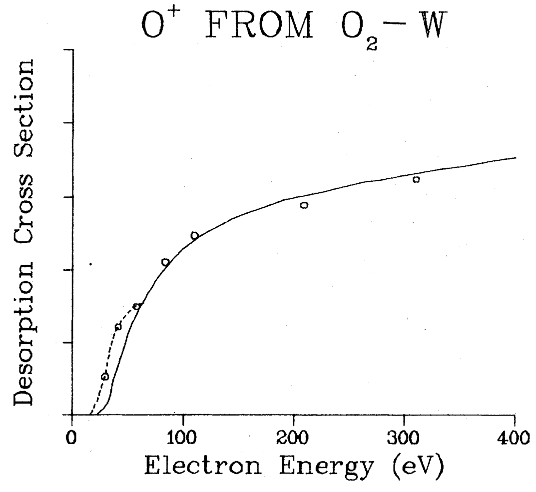

FIG. 4. O^+ desorption (solid curve) and total O desorption (circles connected by dashed curve) current vs energy from O_2-W, after Nishijima and Propst [Ref. 10(a)]. Note that the total desorption threshold appears to be several eV lower than the O^+ threshold. Also note that the major O^+ threshold appears at ~30 eV on this "contact-potential corrected" voltage scale, i.e., just where it should be if the Auger mechanism for the ESD is operative.

V. ISOTOPE EFFECT AND ESD CROSS SECTIONS

One of the main reasons for being interested in whether the O^0 and O^+ thresholds are at the same or different energies has been to learn the extent to which reneutralization of initially produced O^+'s, is an important mechanism for the creation of desorbing O^0's. Clearly, if the *only* mechanism for producing O^0's were the neutralization of O^+'s, then the two species should start to desorb at the same energy. Thus Nishijima and Propst's observation of different thresholds for O^0 and O^+ is important because it implies that it is possible to desorb O directly from W, i.e., without O^+ reneutralization.

Reneutralization has been an important issue in the understanding of ESD because of the observation that ion desorption cross sections, though very difficult to measure accurately, are generally at least three orders of magnitude smaller than gas phase ionization cross sections for the same species. For example at 100 eV the cross section for $e^- + O^0 \rightarrow O^+ + 2e^-$ is[22] $\sim 3\times 10^{-16}$ cm². At the same beam energy Madey and Yates[10d] found the O^+ desorption cross section from O-W (polycrystalline) to be $\geq 3\times 10^{-20}$ cm², while more recently, and illustrating the difficulty of obtaining "hard" numbers for ion cross sections, Leung *et al.*[10i] determined the O^+ cross section for O-W(110) to be $\sim 6\times 10^{-22}$ cm², at beam energies between 40 and 90 eV.

In order to explain the discrepancy between gas phase ionization and ESD cross sections it is generally assumed that following the creation of an ion on a surface there is an appreciable probability that the ion will be reneutralized and then recaptured. In order to verify this idea, isotope effect experiments have been carried out,[10c,10i] based on the fact that since reneutralization is a tunneling process its probability of occurrence should fall off exponentially with the velocity, and thus with the square root of the mass of the desorbing particle. Despite the difficulty of measuring absolute cross sections accurately, the Madey *et al.*[10c] and Leung *et al.*[10i] isotope effect measurements for O-W do agree quite well, the former group reporting a ratio of ~1.5 for the $^{16}O^+$ and $^{18}O^+$ desorption cross sections, while the latter group found a ratio of 1.4. These numbers are consistent with a simple model of reneutralization and correspond to an escape probability for $^{16}O^+$'s of about 10^{-3}. Thus, the isotope effect measurement for O^+ appears to explain the discrepancy of about 10^{-3} between gas phase ionization and ESD cross sections if we accept the Madey *et al.*[10c, 10d] value of the latter, but still leaves the ESD cross section two to three orders of magnitude too small if we assume that the Leung *et al.* value is correct.[10i]

Isotope effect measurements have also been carried out for the total oxygen disappearance cross section. Again both the Madey *et al.*[10c] and the Leung *et al.*[10i] measurements agree, the ratio of ^{16}O to ^{18}O total desorption cross sections turning out to be $\lesssim 1.1$. This ratio leads to an escape probability for neutrals of about 0.2 and to initial neutral oxygen excitation cross sections of $\sim 7 \times 10^{-17}$ cm^2.

Because of the great differences in isotope effect and excitation cross sections for O^0 and O^+, both Madey *et al.*[10c] and Leung *et al.*[10d] propose that O^0 and O^+ desorption arise from different initial electronic excitations, and thus that the O^0 current is *not* simply produced by the neutralization of O^+'s as they leave the W surface.

Let us now ask what help the Auger mechanism is in rationalizing the above results. At the outset, the discrepancy between gas phase and ESD cross sections is reduced in the Auger model because the initial excitation is the ionization of a *core* electron, for which the cross section is only $\sim 10^{-17}$ cm^2 whether the electron is O 2*s*, W 5*p*, or W 4*f*.[23] In order to produce a desorbing O^+, the ionization of a W 4*f* or W 5*p* electron must be followed by an interatomic decay involving a *surface* oxygen atom, since an O under the outer layer would be very unlikely to escape. Additionally since an O^{2-} must be converted to an O^+, three electrons must be removed from the O either via a *double* Auger progress (which in Ne has a relative probability of ~8%)[24] or via an ordinary Auger decay in which one of the O^{2-} electrons is temporarily on a neighboring W. Thus the branching ratio for producing an O^+ which might desorb, following a W-4*f* or W-5*p* ionization, is easily imagined to be between 10^{-1} and 10^{-2}, and the Auger model therefore, appears to favor the Leung *et al.*[10i] value of initial O^+ production cross section of $\sim 1.6 \times 10^{-19}$ cm^2.

As we pointed out in the last section the Auger model is not only consistent with but actually predicts that O^0 desorption should occur via a mechanism other than the reneutralization of O^+'s. Moreover, since O^0's can be produced via the decay of O-2*s* holes while O^+ production via this initial state is impeded by energy conservation, and since the process $O^{2-} \rightarrow O^0 + 2e^-$ requires only a normal Auger decay, while $O^{2-} \rightarrow O^+ + 3e^-$ requires a considerably more improbable event such as a double Auger decay,[24] it is easy to understand why the cross section for direct production of O^0 should be considerably higher than that for O^+. Thus the relative O^0 and O^+ initial excitation cross sections measured by Madey and Yates[10d] and by Leung *et al.*[10i] are easily rationalized within the Auger model of ESD.

VI. SURFACE COORDINATION AND ESD

In this section we turn our attention to the general observation that adsorption in different surface states can correspond to drastically ESD cross sections. For example, the tightly bound β_2 adsorption state of O-W has an ESD cross section more than three orders of magnitude smaller than that of O in the β_1 state.[10d,10f] And this sort of phenomenon has been noted for O on other metal surfaces as well.[2,12]

Within the MGR model it might be presumed that the low cross section state corresponds to adsorption *under* the outer substrate atomic layer. This interpretation would also be possible in the Auger picture. Work function measurements, however are not indicative of any such difference between the β_1 and β_2 states.[25]

Within the Auger picture there is another interpretation of the difference between sites from which ion desorption does and does not occur, which if true is of great importance for future surface studies. Since the metal atom must be stripped of its valence electrons before the interatomic Auger process which leads to O^+ desorption can occur, we predict that no O^+'s will be seen from metal atoms that are not fully coordinated. In the O-W system, for example, O^+'s will only desorb from regions of the surface which are locally WO_3. Thus we propose that the β_1 phase of adsorption involves WO_3-like bonding, whereas the β_2 phase only contains W suboxides. This idea is qualitatively corroborated by Madey and Yates' observation that on a faceted W surface, O desorption begins at the edges, where high W-O coordination is more likely.[1e]

If the correlation between surface coordination and ion desorption is correct it is of particular importance because it will permit the study of the evolution of oxides on a surface. One would for example be able to distinguish just when SiO_2 and not SiO has formed as O is deposited on Si.[26]

VII. ION KINETIC ENERGIES IN ESD

One of the lingering mysteries in ESD data[27] has concerned the mechanism by which ions are produced with kinetic energies (e.g., for O^+ off O-W) up to 12 eV. Although interatomic potentials can be quite repulsive, one doubts that an adsorbate and substrate atom could ever approach one another closely enough to give rise to a strong enough repulsion to produce a 12-eV desorbate species. In the case of ionic adsorption, the source of these high kinetic energies is less mysterious. In equilibrium the Madelung potential at an oxygen site in an oxide surface is typically several tens of eV. If this potential is strongly attractive for an O^{2-}, it will be strongly repulsive when the O^{2-} is suddenly transformed into an O^+.

One piece of evidence in favor of this idea is the spectral data for H^+ from H_2-W versus that for H^+ from H_2O-W given by Nishijima and Propst.[10a] In the former case the bonding is presumably not ionic, there is no clear threshold for H^+ desorption, and the H^+ desorbs with a maximum kinetic energy of 6 eV. In the latter case as one immediately sees from the H^+ desorption versus beam energy curve, which has a threshold at ~20 eV, the H^+ is now mainly desorbing from surface OH^- radicals. Removal of two (bonding) electrons via an Auger decay creates an H ion and a neighboring W-O dipole. Consequently, one would expect a stronger repulsion. This expectation is confirmed by NP's data which show H^+'s desorbing from H_2O-W with as much as 14 eV of kinetic energy.

VIII. DISCUSSION

A review of the chemisorption-ESD literature is not entirely straightforward because certain aspects of the ESD experiment, that would not have been assumed to be important before the development of the Auger model, now appear to be very important. For example, one might wonder whether Madden's reported observation[28] of an O^+ desorption threshold >30 eV in ESD from O_2-Ni contradicts the Auger model's prediction that no O^+ desorption threshold should be seen in this energy range (as well as ESD data from NiO,[5] suggesting that no O^+ should desorb at all), because the Ni atom can never be stripped of valence electrons. The explanation of Madden's data is presumably that in his experiment the Ni sample was mounted on a Mo holder.[29] When the Ni was dosed with O_2, so was the Mo, and since the incident electron beam was not focused on the sample, the O^+ that was seen could easily have desorbed from the sample holder.

The Auger model has a similar problem in explaining the observation of O^+ from O_2-Ir,[13] though in that case the O^+ yield versus primary energy has not been reported, so we do not know whether desorption begins at the O-2*s* threshold or higher, nor is the composition of sample holder mentioned. In future ESD work these aspects of the experiment will have to be considered.

IX. PROSPECTS

A review of the literature concerning ESD from chemisorption systems indicates that when the surface bonding is ionic, the Auger mechanism for desorption is operative. The fact that this mechanism begins with the creation of a core hole suggests important applications of ESD in the analysis of surface reactions. For example, after the adsorption of reactant species on an active substrate one should be able to determine to which surface species the various reactants are bonding, by correlating their desorption thresholds with the core ionization potentials of the surface atoms. If one cools a sample sufficiently to freeze out surface mobility, one can remove reactants from surface atoms with low core IP's, leaving those bonded to the high IP atoms in place. This sort of selective desorption may be extremely important in deducing reaction paths. (We have proven this is feasible, by removing H from Sr while leaving it on Ti, on an $SrTiO_3$ surface.[30])

We also anticipate the use of ESD to study surface corrosion. For example, since the Auger mechanism is only operative for maximal valence metal atoms, one should be able to monitor sensitively the formation of maximal oxides.

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