

Stimulated desorption from surfaces

New techniques for probing the complex electronic excitations that expel atoms and ions from surfaces are putting new demands on our picture of the surface bond.

Michael L. Knotek

After spending years wondering how the surface bond is formed, we are now wondering just as hard how it can be broken. Investigation of the latter problem—possibly the more challenging of the two—is leading to new insight into chemical bonding and the dynamical processes important in chemical kinetics. In this article I discuss a very powerful technique that surface scientists are using in this research: stimulated desorption, the removal of atoms and molecules from surfaces by low-energy ionizing radiation. Concepts from the field of stimulated desorption are already finding their way into other areas. For example, we find that we can offer new insight into the problem of beam damage in electron microscopy and that we can contribute to the very important technological area of plasma processing of surfaces. Insights into chemistry and into the general problem of radiation-induced damage could affect our thinking in areas ranging from radiation treatment in medicine to the interaction of radiation with matter in space.

Newly discovered mechanisms and phenomena have led to desorption

Michael Knotek supervises the surface-physics division at Sandia National Laboratories, in Albuquerque, New Mexico.

techniques that show great potential as analytical probes of the electronic and atomic structures of surfaces. Recent findings raise intriguing questions that challenge our concepts of bonding. These discoveries, together with the promise of a fertile new experimental approach, have stimulated activity in the field.

The new activity is based on recent conceptual advances as well as on the observations.¹ Although physicists had long thought of the excitation that leads to the desorption of an ion as involving a single electron at the bonding levels, work on electron-stimulated desorption at Sandia in 1978 showed that in fact desorption of ions occurs more often from much more complex and interesting multiply ionized and excited states. The dominant mechanism for creating these states is the excitation of core electrons, that is, the generation of core holes in the complex consisting of the surface and the atoms bonded to it. When a core-hole state decays through the emission of an Auger electron, final states containing multiple valence holes are created, and these are much more efficient at inducing desorption than are one-electron excitations. The multiple-valence-hole states are intrinsically localized, contain a large amount of trapped energy

and have lifetimes much longer than those of other surface states. The factors controlling this enhanced lifetime present a new and interesting problem in dynamics.

The number of researchers working on desorption has increased greatly in the last five years. This increase reflects the clear opportunities to make important contributions both experimentally and theoretically. Study of the fundamental processes of bond dissociation has already led to more detailed models of the energetics and dynamics of dissociation.

Whereas early work concentrated on defining the type of excitation that could exhibit the observed thresholds for desorption, we now ask how the initial excited state evolves to yield dissociated fragments. Answers to these questions are coming from more careful work on surface systems (figure 1) and from such work as selective photodissociation of gas-phase systems and studies of photon- or electron-stimulated desorption on condensed molecular species. A significant point about condensed-phase systems is that the dissociation is dominated by surface phenomena. With the local environment and electronic properties of the desorbed species determined by the structure of the adsorbed molecule

Surface analysis chamber used for electron-stimulated desorption measurements. The ultra-high-vacuum chamber contains ESD apparatus (lower left), an electron spectrometer (upper left), a chamber for the preparation and introduction of the sample (right) and other tools for the treatment and characterization of the sample. The photograph on the cover of this issue is a view through the small port at the top of the chamber. (Photograph by Russell Smith, Sandia National Laboratories.) Figure 1



itself, which is easily varied in a controlled manner, condensed-phase systems are ideal to study.

Early work in the field dealt almost exclusively with the desorption of positive ions such as O^+ from substrates such as molybdenum, because of the ease of making those measurements. We now find greater emphasis on the measurement of neutral² and negative ions and in the determination of the internal states of desorbed neutral atoms and molecular fragments. These new techniques involve measurement of luminescence from emitted excited neutrals, and measurement of laser-induced fluorescence and multiphoton ionization of emitted ground-state or excited neutrals.

As an analytical tool, stimulated desorption is finding wide use on many important problems. Studies now in progress are using electron- and photon-stimulated-desorption spectroscopy to analyze stress cracking induced by corrosion. Especially important in this work is the sensitivity of the desorption techniques to hydrogen. Other researchers³ are studying the general problem of hydrogen on metals, and a number of people are looking at atomic and molecular adsorption on metals,

oxides and semiconductors.

Probing specific bonds. We now know that some rather straightforward criteria govern the stability of surfaces in ionizing environments. While it has long been recognized that the stability of a surface depends strongly on the electronic structure of the material, there was little understanding in terms of known electronic properties. For ionic materials we now know many of the critical features that determine relative stability, and we are gradually deriving a similar understanding for covalent materials.

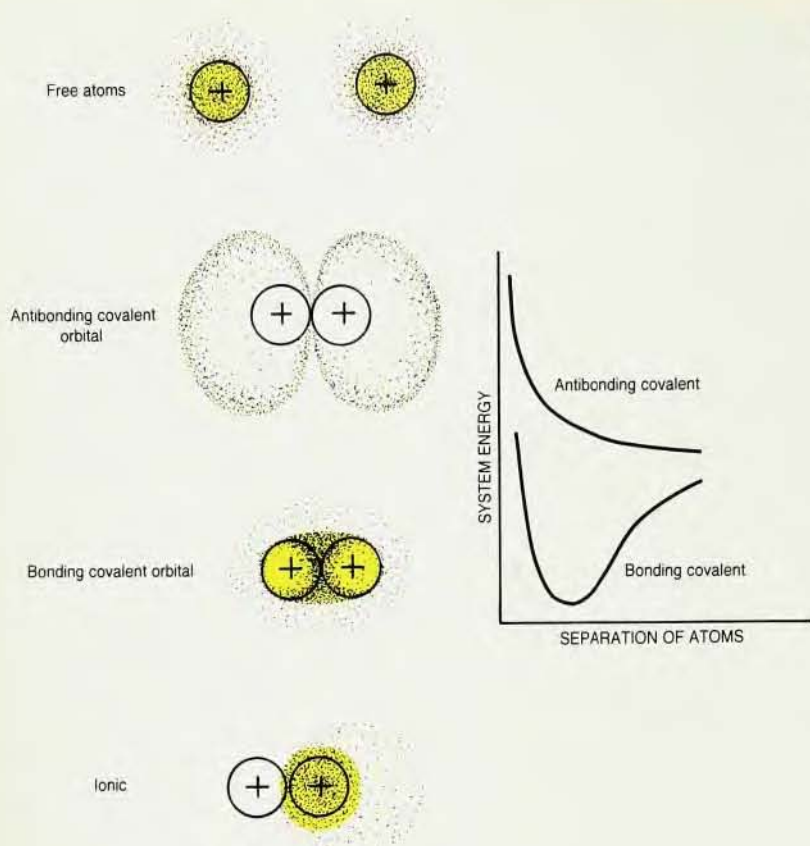
The local nature of the desorption state, and the fact that one can produce it through a characteristic atomic core excitation, give desorption spectroscopy techniques an unprecedented atomic specificity—the power to determine the electronic and geometric structures of specific bonds. The first observation of photon-stimulated desorption, in an experiment using synchrotron radiation, was a result of the unambiguous identification of the core excitation that leads to electron-stimulated desorption. The rich spectral content of photon-stimulated desorption presents new possibilities for the analysis of surfaces and has thereby led to an

important new use for synchrotron radiation.

There have also been significant advances in the analysis of ions or neutral atoms as they leave surfaces. The most exciting observation is that particles are not desorbed isotropically from a surface, but that they leave in well-defined cones along the bond directions. Thus, ion angular distributions give direct information on the configuration of ground-state bonds. One can measure the symmetry of the bonding site and the bond angle relative to the surface normal in an experiment that does not require long-range order in the desorbing layer. In addition to their well-defined angular distributions, desorbing ions have energy distributions that are a signature of the chemical configuration on the surface and give important clues about the nature of the state from which the desorption occurs.

Bonding

A simple picture of the bonds between atoms (figure 2) will help us analyze the effects of radiation on bonding. When atoms come together to form molecules or solids, their equilibrium separations are considerably



Bonds between atoms. This schematic diagram shows the electronic structure of a bond. We can picture a free atom as a positive core surrounded by an electron cloud. The cloud reforms upon atomic interaction to form the bond. Figure 2

smaller than the sum of their free-space radii. The electron clouds around the atoms interpenetrate, exposing the atomic "cores" to one another. In the absence of any electronic rearrangement, the cores would strongly repel each other and the atoms would simply move apart. However, the electrons do rearrange—into three general kinds of covalent orbitals that we can classify according to their effects on the repulsive interaction between the atoms.

► In bonding orbitals, the electrons move between the atoms and screen the repulsion. The electrons gain potential energy and lose kinetic energy.

► In antibonding orbitals, the electrons are removed from the interatomic space. This increases the repulsion and decreases the potential energy of the electrons.

► Nonbonding orbitals, which are not shown in figure 2, have a neutral effect in that the orbital weighting relative to the free atom is not changed in a way to cause either attraction or repulsion. Most chemical systems have an orbital makeup combining all three types. Once we know how the electrons are distributed in the bond, we find the energy by summing the Coulomb interactions of the system. The bond is stable if the energy gained in the

bonding orbitals is greater than that lost in the antibonding orbitals.

If the atoms of the system have differing electronegativities, then in addition to the covalent interaction there will be a charge transfer from the less electronegative to the more electronegative atoms until the chemical potentials of the ions are equal. The ionic bond energy then contains contributions from the Coulomb interactions between the cations and anions and from the chemical potential gain due to the electron transfer.

All heteroatomic systems have contributions from both ionic and covalent bonding. In covalent materials an atom has separate bonds to each of its neighbors, while in ionic materials the bonds to all neighbors are embodied in the one ionic charge. We will see that even though desorption from an ionic bond seems easier to understand than desorption from a covalent bond, the dividing line between ionic and covalent is vague and of very limited significance with respect to desorption.

Breaking the bond

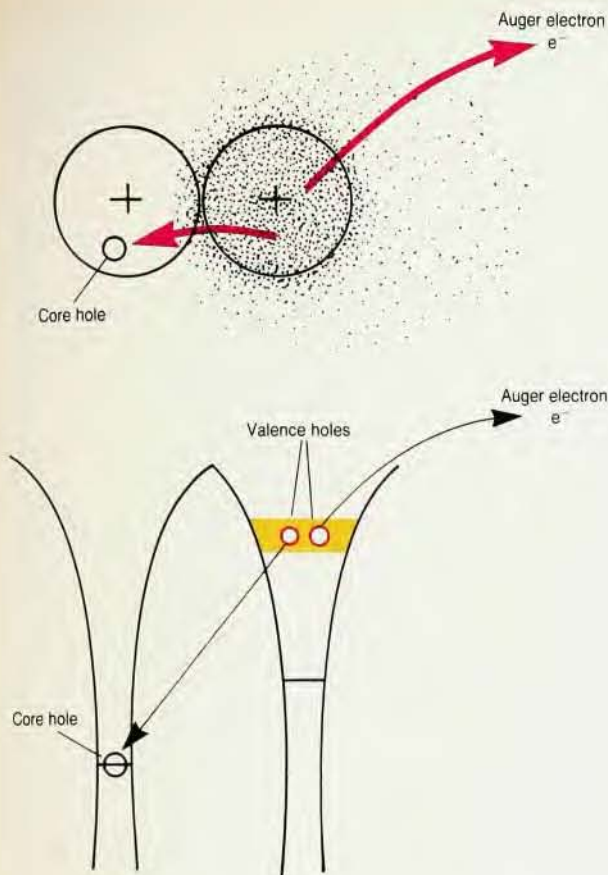
It has long been recognized that desorption of atoms from surfaces is initiated by electronic excitations of the surface bond. The traditional way of envisioning this is the model⁴ of

Dietrich Menzel, Robert Gomer and Paul Redhead, which Gomer summarizes nicely in reference 1. This is an adaptation of the Landau-Zener theory of gas-phase dissociation, in which desorption is the result of excitation from a bonding to an antibonding state. In this model the excitations for gas-phase dissociation and surface desorption are identical, but the surface can recapture or reneutralize an excited atom, which dramatically reduces the overall dissociation yield from surfaces. Typical dissociation cross sections for gas-phase molecules are 10^{-16} cm², whereas from surfaces they range from about 3×10^{-17} to 10^{-25} cm² and lower. Thus, processes that are strong in the gas-phase may be quenched on the surface, leading to a marked difference in the relative importance of competing mechanisms in the two environments.

The cross section σ for desorption is given by

$$\sigma = \sigma_e P$$

Here σ_e is the excitation cross section for the process, equivalent to the gas-phase cross section, and P is the escape probability. The probability P has the general form $\exp(-\beta\tau_c)$, where τ_c is the critical time for desorption and β contains the residence time of the desorbing particle. In practice, the



Auger process in a maximal valency ionic solid. Core holes created on either ion decay to the Fermi level by hole multiplication to selectively strip the anion of charge.

Figure 3

this case means that the titanium is ionized to the noble gas configuration Ti^{4+} , so that titanium ions in the solid have effectively no valence electrons; their highest occupied orbitals are the 3p levels at about 30 eV below the Fermi level. Among other maximal valency materials are Sc_2O_3 , V_2O_5 , WO_3 and NaF.

The important thing about maximal-valency ionic materials is that if a core hole is created on any ion (cation or anion), it will decay toward the Fermi level by single or multiple Auger emission. Because the only electrons near the Fermi level are on anions, these ions are selectively stripped in the process, as figure 3 indicates. Simple Auger events remove a minimum of two electrons, while more complicated Auger cascades can remove as many as four or five electrons. In titanium dioxide, O^{2-} loses one electron by decay into the hole; in about 10% of the events two Auger electrons are emitted, transforming the O^{2-} to an O^+ . We now have neighboring unscreened positive titanium "cores" repelling this O^+ , which leads to its desorption. Thus the Auger emission model explains two observations: that the excitation of core holes leads to desorption, and that the process produces sufficient charge transfer to convert an O^{2-} to an O^+ .

An important prediction of the Auger model is that submaximal-valency compounds, that is, compounds in which the metal atom is not ionized down to the noble gas configuration, should not decompose by desorption. There are two reasons for this. First is the absence of the natural selective stripping of electrons from the anion—the multihole final state is shared between the cation and the anion. Second, the fact that there are electrons on the nearest-neighbor atoms to the anion assures that any positive anion species that is created will be quickly recaptured or reneutralized.

Thus we expect maximal-valency compounds to be unstable in radiation and submaximal compounds to be stable, and experiments have shown this to be true—all of the maximal-valency oxides such as TiO_2 , V_2O_5 , WO_3 and MoO_3 show very high desorption yields, while submaximal valency oxides such as Ti_2O_3 , V_2O_4 , NiO and Cr_2O_3 generally show weak desorption. These findings contribute significantly to our understanding of the stability of materials under ionizing radiation. Peter Williams at Arizona State University and Wayne Rabalais at the University of Houston and their coworkers have shown¹ that ion excitation of surface

escape probability P is proportional to $\exp(-c\sqrt{M})$, where c is a constant for a given physical environment and M is the mass of the desorbing particle. This leads to an isotope effect in which the heavier isotope has a smaller desorption cross section because it spends a longer time in the bonding region where it can be recaptured or reneutralized.

The general features of the model hold for any desorption mechanism. After an electronic excitation there is a competition between electronic deexcitation and desorption. Both actions tend to relieve the high energy of the excited configuration and it is only in situations where the electronic lifetime is sufficiently long that desorption can occur. Thus the question of lifetime is important throughout any discussion of desorption.

Typical lifetimes for one-electron excitations on surfaces are of the order 10^{-16} to 10^{-17} seconds, whereas the lower limit for desorption is thought to be of the order 10^{-14} seconds. Hence, states lending to desorption must have exceptionally long lifetimes for the process to proceed, which helps explain why the cross sections for surface processes are small compared to those for gas-phase processes. W. Brenig and Gomer and their coworkers have con-

sidered¹ important quantum-mechanical corrections to this model.

Something different going on. Experiments beginning in 1978 led to the realization that desorption from surfaces is not a simple extension of the gas-phase bonding-antibonding excitation mediated by the presence of a surface, but is in fact dominated by a different kind of desorption state. The first evidence that there was something quite different going on came in a study of electron-stimulated desorption in titanium dioxide, where Peter Feibelman and I found⁵ that O^+ is desorbed not due to excitation at the valence level, but by excitation of the $Ti(3p)$ core level and to a lesser extent the $O(2s)$ level, both levels having little to do with bonding. Furthermore, the fact that the oxygen is desorbed as O^+ whereas it is nominally an O^{2-} ion on the surface implies a large (three-electron) charge transfer preceding desorption. The Menzel-Gomer-Redhead model, as it was popularly treated, predicted neither of these features, and this conflict led to the formulation of a new model of desorption based on Auger emission.

To understand this, we can picture titanium dioxide as an ionic solid, and more importantly, as a "maximal valency" ionic solid. Maximal valency in

Photon stimulated desorption spectra and corresponding photoelectron spectra. Plot shows the desorption yield of H^+ and F^- from $\alpha\text{-Al}_2\text{O}_3$ and the photoelectric yield from amorphous Al_2O_3 and $\alpha\text{-Al}_2\text{O}_3$ in the vicinity of the L edge of aluminum. The site of the H bond has the signature of a tetrahedral geometry like that of amorphous Al_2O_3 , while the site of the F bond more resembles the octahedral geometry of bulk $\alpha\text{-Al}_2\text{O}_3$. Figure 4

electronic levels induces sputtering phenomena through the same mechanism of desorption. However, as we will see below, desorption is not quite as simple as I have made it sound, even for ionic materials, and it may be quite a bit more interesting and informative in the end. To appreciate the complications, we need to extend the discussion to covalent materials. But first, let us examine the analytical implications of the desorption mechanism as we have developed it so far.

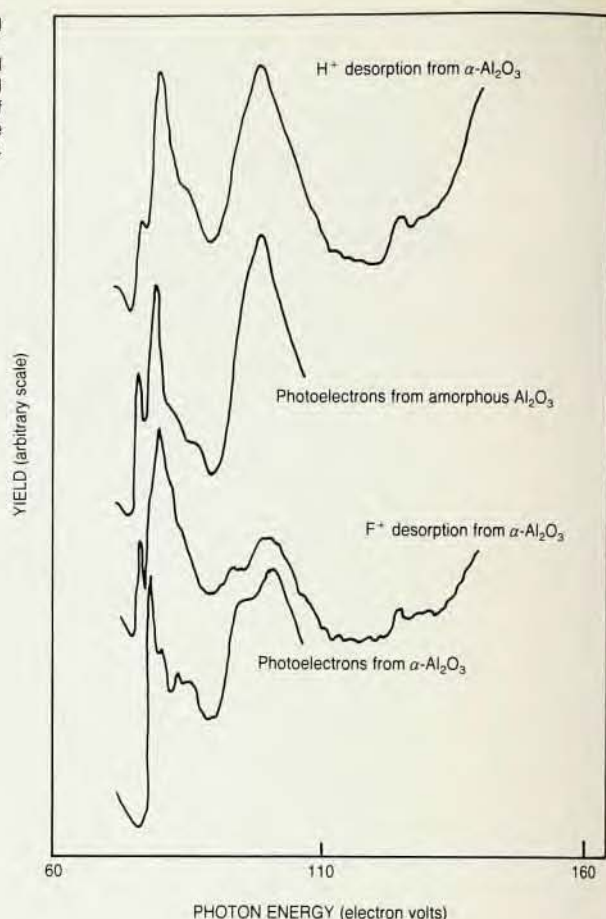
A powerful analytical technique

To desorb an ion we must excite the atom itself or the atom to which it is bonded.⁶⁻¹⁰ In the latter case one sees thresholds at the core levels of the bonding site atom. This tells us the bonding site of the desorbed species, which is important information about a complex surface. Desorption spectra display structure at energies above the excitation threshold for the core level. This structure arises from the interaction of the photoexcited electron with the atoms surrounding the excited atom, and can be used to determine bond lengths and coordination. Within 50 eV of the threshold, the electron scatters from the valence structure in the neighborhood of the atoms,⁶ while at higher energies it scatters from the cores of the neighboring atoms.¹⁰ The structure in the desorption spectra is simply the x-ray or electron absorption structure of the atom being excited. It is important to realize here that by looking at desorbing ions as a probe of the adsorbed atom's x-ray absorption, we are doing spectroscopy specific to the adsorbed atom and its bonding site on the outermost layer of the solid. Thus, on a surface with many bonding sites and adsorbates, we can determine which site-adsorbate combinations are present and study each combination separately, making stimulated desorption a powerful analytical technique. The techniques developed by x-ray spectroscopists to extract electronic and structural information from absorption spectra can now be used to gather the same information on a specific surface site to which a known adsorbate is bonded. An important additional feature of stimulated desorption is that it is extremely sensitive to hydrogen, which most other surface techniques detect indirectly at best.

The analytical usefulness of desorption spectra rests on the extreme localization of the excitation and desorption

phenomena. There is ample evidence that the phenomena are indeed local for a number of oxides and for adsorbates on metals and semiconductors. The degree to which desorption involves nearest neighbors more than second-nearest neighbors is still unknown, but one can certainly distinguish surface bonding sites from bulk sites and one can distinguish the bonding sites for different adsorbates from one another.

Figure 4 gives an example of this, comparing H^+ and F^- desorption from the same $\alpha\text{-Al}_2\text{O}_3$ surface to the photoelectron yields from amorphous Al_2O_3 and $\alpha\text{-Al}_2\text{O}_3$. In amorphous Al_2O_3 the Al atom is tetrahedrally coordinated, whereas in $\alpha\text{-Al}_2\text{O}_3$ it is octahedrally coordinated. The near-edge structure in these spectra is a signature of the local atomic and electronic structures. The hydrogen and fluorine bonding sites clearly differ from each other and from the octahedral bulk $\alpha\text{-Al}_2\text{O}_3$ site. The hydrogen site is obviously tetrahedral, like that of amorphous Al_2O_3 , while the fluorine site has components similar to both tetrahedral and octahedral sites, suggesting a new site or a mixture of two.

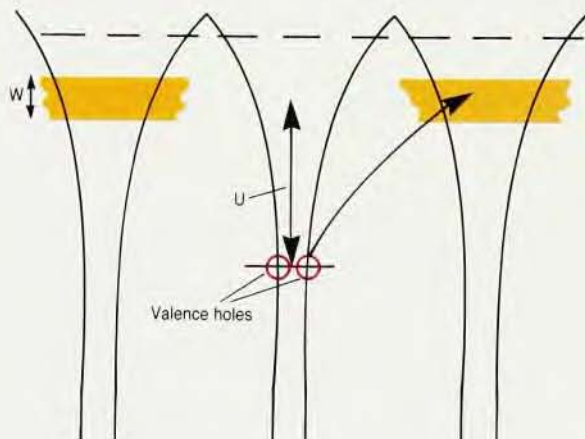
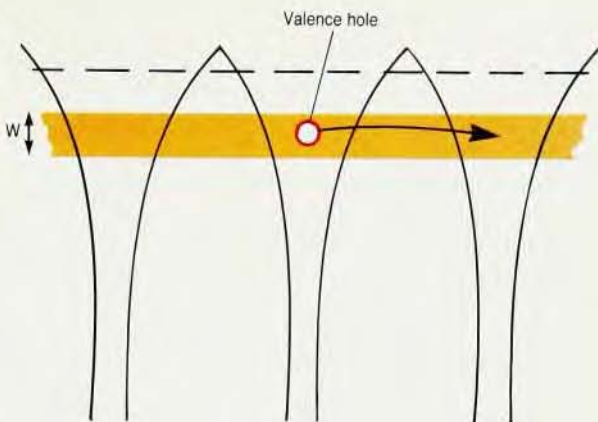


Rolf Jaeger of Exxon and his coworkers carried out¹⁰ the first analysis of extended fine structure in a photon-stimulated-desorption spectrum in their study of O^+ desorption from a molybdenum surface with adsorbed oxygen. Their findings show threshold shifts between the underlying metal and the sites yielding desorption, suggesting desorption from an oxygen environment, possibly maximally valent MoO_3 . The desorption sites have half the coordination that exists in bulk Mo, while the Mo-Mo separation is identical to that in the bulk. An important finding in this and other desorption studies is that the desorption is often dominated by minority species—which is a distinct advantage in some cases, such as when they are the active sites on a catalyst.

The local specificity is sometimes compromised by secondary effects. In photon stimulated desorption from multilayers of condensed NH_3 and H_2O , Jaeger, Dick Rosenberg and their coworkers find¹¹ evidence that secondary electrons from the excitation of bulk atoms can cause ion desorption from the surface, leading to a nonspecific component in the spectrum. We

Localization of the two-hole state. Top: A single hole in the valence band of width W disperses with a characteristic time of order $1/W$. Bottom: Two holes on a single site have an additional repulsion energy U . When this hole-hole repulsion energy U is much greater than the valence band width W , the holes are localized for times much longer than $1/W$.

Figure 5



know this effect must be present to some extent in all systems; why it is so strong in multilayer systems of condensed NH_3 and H_2O is unknown. This problem does point out that one must exercise some care in the choice of systems to study, as in any technique that relies on complicated physical phenomena for information.

Desorption from covalent systems

Now let's return to our discussion of the nature of the desorptive state, that is, the multiple hole configuration. One feels on rather firm ground envisioning ionic materials flying apart from such a state, but what about covalent materials? Menzel and his coworkers in Munich showed⁵ that the same thing occurs for covalent adsorbates on metals. They called the desorption a "Coulomb explosion," using the term coined¹² by Tom A. Carlson and M. O. Krause to describe a similar phenomenon in the gas phase. In a sense we shouldn't be surprised that covalent and ionic materials show similar desorptive behavior, because multiply ionized bonds can be quite similar, whether covalent or ionic. We must realize, however, that in a covalent material there are bonds we could ionize—an antibonding or non-bonding orbital, for example—that wouldn't necessarily lead to desorption.

One difference between covalent and ionic materials that does lead to a dilemma of sorts is that of electronic lifetimes. In ionic materials the valence bands are anion-like, where the anion-anion interaction is relatively weak, so the bands are intrinsically narrow. This makes it easy to think of our 2- or 3-hole states as being localized long enough for the ion to come off.

In covalent materials, on the other hand, the coupling is to nearest neighbors and is inherently strong, leading to the intuitive feeling that any electronic excitation ought to be able to disperse or deexcite in a very short time indeed, especially a state with two strongly repulsive valence holes on the same atom. Typical single-hole lifetimes in covalent systems are of the order of the inverse bandwidth, which is about 5×10^{-16} seconds for a one-volt bandwidth, too short a time to lead to appreciable desorption. So we must ask how desorption works in covalent materials, or in ionic materials for that matter. Observations first made by Peter Feibelman, by Dwight Jennison of Sandia and coworkers and by David

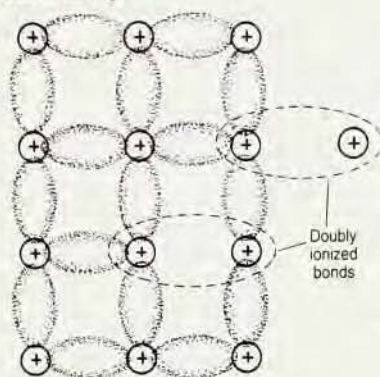
Ramaker of George Washington University and coworkers,¹³ all summarized in reference 1, have helped to carry us through the conceptual dilemma. The answer seems to be that if we make the multiple excitation high enough in energy and complexity, it can be locked on its initial site for times much greater than a normal itinerant electron's hopping time.

Auger spectroscopy gives an important insight into this problem. The primary point the Auger spectroscopists make¹⁴ is that Auger final states are inherently local, so that Auger spectroscopy conveys information about the local density of states of the excited atom. This locality results from the fact that the core hole is strongly localized and the matrix element for Auger decay stresses states with maximum overlap with the core hole. This point is of extreme importance to desorption, because the core hole represents an enormous amount of energy deposited on a single atom and because the local nature of the Auger process keeps the energy localized to that atom's immediate environment.

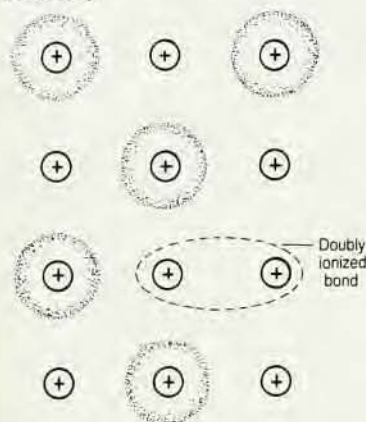
What controls the lifetime of the Auger final state? Figure 5 depicts a

simple system with a valence band of width W . Single holes created in this band will disperse with a characteristic time of order $1/W$. If we create two (or more) holes on a single site, there is an additional hole-hole repulsion energy U . M. Cini and George A. Sawatzky showed¹⁵ that if the additional repulsion energy U is less than the valence bandwidth W , then the holes will separate in a time of order $1/W$. However, if the additional repulsion energy is much greater than the valence bandwidth, then the holes cannot move by resonant processes and they will be localized on the creation site for times much longer than $1/W$. This manifests itself spectroscopically as shifted atomic-like Auger spectra for metals such as copper and nickel, for insulators and for gas-phase organic molecules. Extended lifetimes, which are longer than about 10^{-14} sec, are conducive to desorption, as is the localization of energy.

It may be possible¹⁶ to excite desorption states directly, rather than exciting them via Auger decay. Ramaker suggests¹ that whereas we have added the two-hole excitation to the one-hole excitation described by the Menzel-



Ionic bonding



Covalent and ionic lattices. The two-hole state (dashed oval) has similarities in the two cases. Multiple bonds in a covalent lattice can preclude desorption, while sites of low coordination can facilitate it. In covalent materials, coupling is between nearest neighbors and strong. In ionic materials it is between next-nearest neighbors and is intrinsically weak. Figure 6

Gomer-Redhead model, an even more effective desorption state based on localization might, for example, be one with not only two holes in a bonding orbital but also an electron in a previously empty antibonding orbital. One would obtain such desorption states not only through core-hole decay, but also through "shakeup" excitations, in which departing photoelectrons excite other electrons.

Many paths to desorption. It is becoming increasingly obvious that there is an almost unlimited number of ways one can electronically disrupt a bond, especially if one includes the desorption of neutrals and negative ions, and radiation-induced chemistry. Here the

characteristic times for electronic and nuclear motion are roughly the same. Furthermore, we are forced to consider a system where both the atomic cores and the electrons are affected by the same large force resulting from the multiply ionized state. This is a new dynamical problem that may lead to important insight into the dynamics of bond formation, and it certainly forces us to take a much harder look at our conceptual models of the bond.

Ionic and covalent bonding represent the two extremes of interatomic interaction. Yet, in figure 6 we see that locally the two-hole state in the ionic lattice is much like that in the covalent lattice; what is crucial for desorption is simply a matter of how strongly the state couples to the rest of the system and what other bonds are present. In fact, we need not move very far from the most ionic materials toward covalency before the stronger interatomic interaction affects desorption. In going from NaF to NaCl, for example, Chris Parks and his coworkers observe¹⁷ a significant reduction in Cl^+ yield relative to F^+ yield due to stronger halogen-halogen interactions.

In covalent systems and on metals we find a wide range of desorption behavior. To understand this behavior it is important to realize that the localization we have discussed is only a necessary condition for desorption. The electronic and geometric configuration of the system must also be conducive to desorption; after all, no one has yet seen Cu^+ desorbing from Cu, even though there are clearly localized Auger final states present. Recent experiments¹ by Jeff Kelber and myself on condensed organic molecules suggest that one can maximize desorption by isolating a functional group of atoms, that is, by reducing a group's interaction with its neighbors (see figure 6).

On the other hand, as Cini and Sawatzky first pointed out, the presence of a partially filled orbital on the Auger site provides a ready path for neighboring atoms to transfer electrons to the doubly ionized atom so as to alleviate the hole-hole repulsion. This is dramatically demonstrated by CO and NO on a nickel surface, where the flow of charge from the d band of the metal to the lowest-lying empty antibonding orbital of the adsorbed molecule (its $2\pi^*$ level) leads to a reduction in the repulsion energy U for the carbon "KVV" Auger electron, from 15 eV in the gas phase to zero on the surface. (The carbon "KVV" process begins with a hole created by ionization of a carbon K-level electron. A carbon valence electron decays into the K hole and a second valence electron is emitted.) The reduction in repulsion energy quenches desorption due to simple Auger states, making it necessary to use more complex excitations to give the

system the energy and lifetime necessary for desorption.^{1,18}

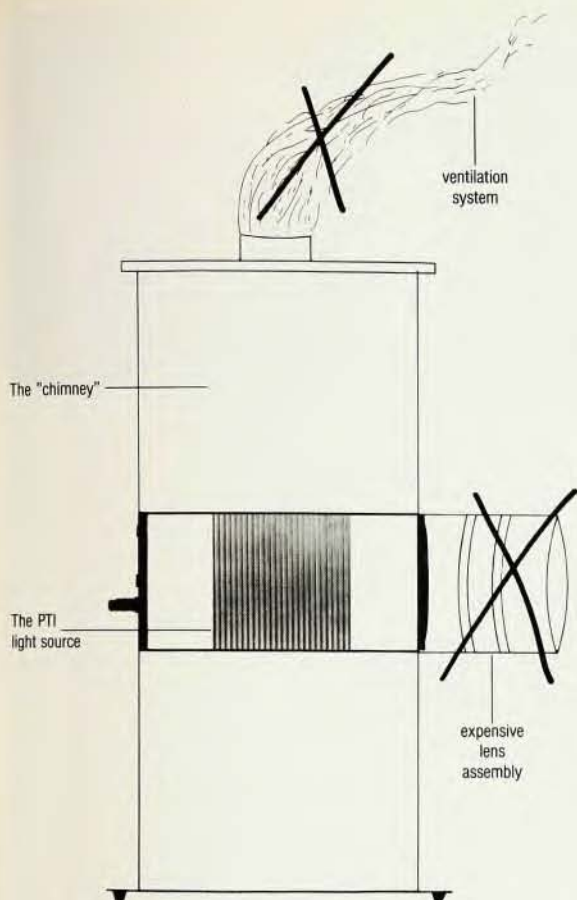
Angle-resolved stimulated desorption

Ted Madey of the National Bureau of Standards and his coworkers were the first to observe^{1,19} that the angular distribution of ions in electron-stimulated desorption is not isotropic, but is in fact a rich source of surface and adsorbate structural information. Angular distribution measurements by Madey and by Horst Niehus²⁰ of the Kernforschungsanlage, in Jülich, West Germany, show that ions are emitted in relatively narrow cones of less than 20° , which project along the nominal ground-state bonding angle. The angular distribution displays an azimuthal pattern that reflects the symmetry of the bonding site and a polar angular distribution that reflects the bonding angle relative to the surface normal.

Thus, angular distribution measurements give the surface bonding geometry directly, in a format that needs little data reduction, although there are complications due to the interaction of ions with their image charges and neighboring ions. Because the technique is a local probe, it requires no long-range order in the measured layer; because desorbed ions are used as the monitor, the technique is specific to those atoms; and because there is no desorption from underlying layers, the technique is specific to the surface. Using the added spectral selectivity of photon-stimulated desorption, it may be possible to measure the angular distributions of ions arising from selected excitations, giving new insight into the desorption process.

Figure 7 shows a striking example of how very direct is the information from angular-distribution measurements of electron-stimulated desorption. This example is from a study^{1,19} of ammonia adsorbed on the (111) surface of nickel. Desorbed H^+ shows an angular distribution consisting of a halo with no apparent substrate symmetry present. This suggested to the investigators that the NH_3 molecule bonds to a nickel surface through the nitrogen atom and is randomly oriented azimuthally. Earlier angle-resolved measurements of ultraviolet photoemission had suggested that the ammonia molecule was oriented relative to the surface. It was not until small quantities of oxygen were preadsorbed on the nickel surface that the angular distribution measurements showed that NH_3 does in fact orient relative to the surface by locking toward the oxygen via a hydrogen bonding interaction. This example shows the directness and simplicity of the technique in pinpointing a subtle interaction.

In an ion angular distribution study²⁰ of the epitaxial growth of $\text{WO}_3(111)$ on $\text{W}(110)$, Niehus settled the



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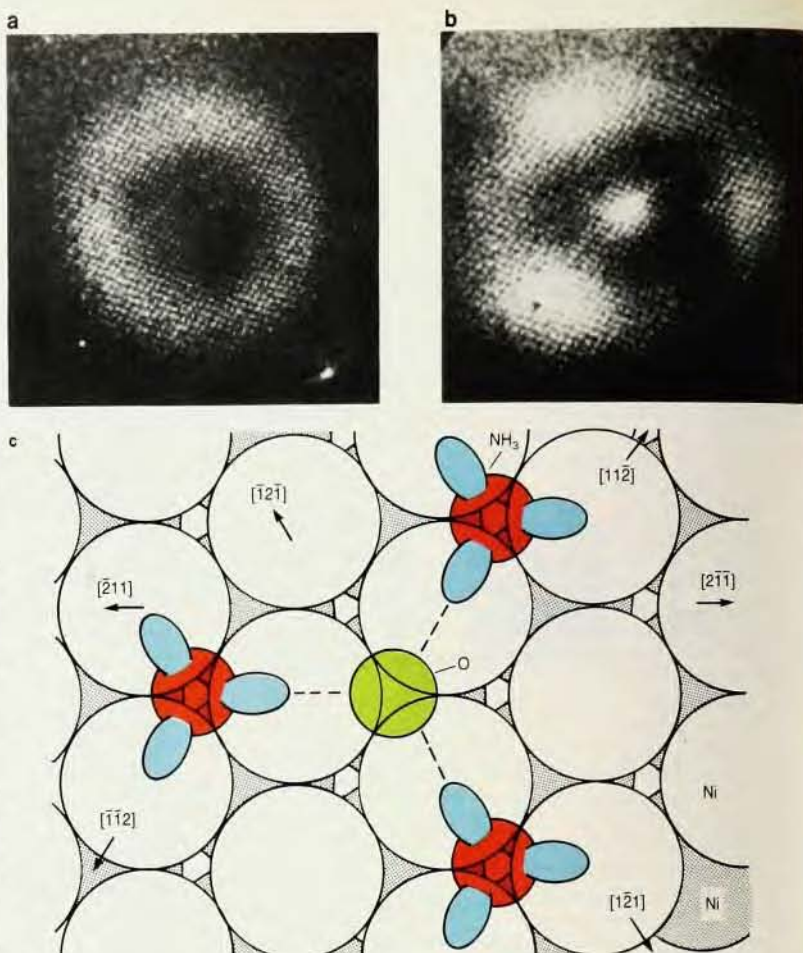
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Data on angles of desorption,^{1,19} indicating bonding angles of ammonia molecules adsorbed on the (111) surface of nickel. The continuous halo of H^+ emission in **a** indicates a random azimuthal orientation for NH_3 molecules on clean Ni(111). The broken H^+ halo in **b** indicates that a fractional monolayer of adsorbed oxygen orients the ammonia molecules. The interaction is through hydrogen bonding and causes the surface structure shown in **c**. Figure 7



question of the orientation of the WO_3 relative to the substrate. Low-energy electron diffraction measurements had been unable to resolve the question but had suggested two possibilities: that one of the $WO_3(100)$ directions is parallel to the $W(111)$, or that there are three pairs of twin domains, each with one of the $WO_3(100)$ axes parallel to the $W(100)$. Under electron-stimulated desorption, the former should have 12 angular distribution maxima, whereas the latter should have only six. Niehus observed six maxima, which supports the latter model.

In a further electron-stimulated-desorption study of the adsorption of oxygen on the (111) surface of tungsten, Niehus observed²⁰ an extremely complex series of angular distribution patterns—and hence bonding structures—as a function of coverage and temperature. The variations in this series of structures with temperature and coverage are so complex that they would be virtually impossible to unravel without the insight provided by the angular distributions.

The uses of desorption are expanding as we develop better ways to acquire and analyze the data. However, I believe the most important impact of the new work in stimulated desorption is the way in which it challenges and gives new insight into our concepts of bonding. The dynamical questions that desorption studies are raising are forcing us to reformulate our picture of the surface bond.

* * *

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