

Photon-stimulated desorption selectively breaks bonds

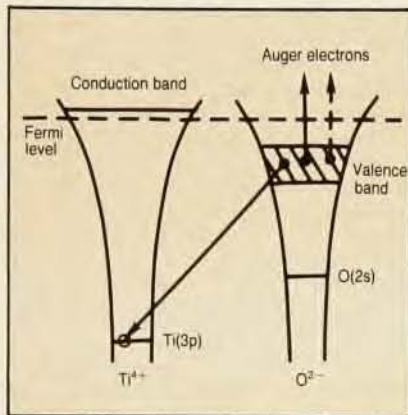
A perennial nuisance to experimenters is electron-stimulated desorption, in which adsorbed atoms leave the surface of a material being struck by electrons. Over the past several years, this widely observed phenomenon has been undergoing development as a tool for studying chemical bonding at single-crystal surfaces between specific kinds of atoms and at defect sites. Last year the existence of photon-stimulated desorption was demonstrated. These techniques can selectively break specific surface bonds and be used to identify bonding sites and bond angles.

Recently a group from the National Bureau of Standards and IBM has produced a two-dimensional display of angle-resolved photon-stimulated desorption from a tungsten (111) surface.

Workers in both electron- and photon-stimulated desorption believe the technique should be valuable in the study of heterogeneous catalysis and a variety of other surface problems.

History. Electron-stimulated desorption was quantitatively characterized in 1964 by Paul Redhead (National Research Council, Canada), who had studied its influence on pressure measurements made with a Bayard-Alpert ionization gauge. Independently in 1964 Dietrich Menzel and Robert Gomer (both then at the University of Chicago) did extensive studies on ESD using field electron emission. That year both Redhead and independently Menzel and Gomer developed a picture of ESD in which the incident beam excites a bonding electron to an antibonding state, causing the effective potential between the surface atom and the solid to become repulsive, so that the atom or ion desorbs (leaves the surface).

For the next decade, considerable effort went into electron-stimulated desorption. Experimenters found that for a given surface, the yield depended on the kind of bonding state. When a molybdenum or tungsten surface was exposed to oxygen, there was a delay time during which no electron-stimulated desorption was observed; eventually the ESD yield would begin, suggesting that only certain specific chemical states yield desorption. It



Energy diagram of TiO₂, a maximal valency oxide. When the electron stolen from the oxygen neutralizes the core hole, more electrons are ejected by Auger decay. The subsequent Coulomb repulsion leads to desorption.

was also found that reneutralization processes are important; for example, in the desorption of hydrogen ions from tungsten, the hydrogen ions were desorbed as much as 100 times more efficiently than deuterium ions, presumably because the lighter ion moves away from the surface faster, thus having less time to be neutralized.

Theodore Madey and John Yates, working at the National Bureau of Standards, speculated that in the angular distribution of emitted ions, there might be relatively small anisotropies because of differences in the surface configuration. In 1974 they and Jerzy Czyzewski (University of Wroclaw, Poland) studied oxygen adsorbed on a tungsten (100) (four-fold symmetry) crystal surface. Their image intensifier screen showed five sharp spots—a central one corresponding to the O⁺ being desorbed normal to the surface, and four arranged in a square around the central spot, corresponding to O⁺ beams emitted at about 45 deg from the normal and 90 deg with respect to each other. When they changed the crystal to a tungsten (111) surface (triangular symmetry), they found the spots arranged in a triangular shape. They found that these complex symmetrical ESDIAD (Electron Stimulated Desorp-

tion Ion Angular Distribution) patterns had the same symmetry as the substrate lattice and that they changed as a function of the oxygen coverage and heat treatment of the surface. The NBS group formulated an intuitive model in which the angle of ion desorption was determined by the orientation of bonds.

Generalizing the NBS model, Joel Gersten, Richard Janow and Narkis Tzoar (City College of the City University of New York) calculated the ion desorption trajectories, averaging the forces over the entire surface. They, like the NBS group, found that the direction at which the adsorbed species is emitted is mainly determined by the atom to which the species is hooked.

A detailed mechanism for the excitation process in electron- or photon-stimulated desorption was proposed¹ in 1978 by Michael L. Knotek and Peter J. Feibelman (Sandia Laboratories). The data underlying their model came from ESD, Auger and low-energy electron-loss spectroscopy done on maximal-valency transition-metal oxide samples such as TiO₂. They found that the energy threshold for desorption of O⁺ ions corresponded to the creation of core holes in the metal ions, that is, creation of vacant inner electron orbitals.

In TiO₂, titanium has a valence of +4; so no Ti electrons can decay into the core hole. They suggested that instead, the electrons are obtained from neighboring oxygen atoms. When the electron stolen from the oxygen neutralizes the core hole, more electrons are ejected by Auger decay. The subsequent Coulomb repulsion, or "Coulomb-explosion," leads to desorption as a neutral or positive ion. This core-hole Auger decay, Knotek and Feibelman argued, explains both the observed thresholds and the large charge transfers involved in ESD of positive ions from maximal valency transition-metal oxides.

It was also found in these early experiments, that an adsorbate could be caused to desorb by excitation of its own core level, followed by an intra-atomic Auger decay (for example OH⁺ and F⁺ from TiO₂).

Knotek notes that their theory is not in disagreement with that of Redhead, Menzel and Gomer. The latter model applies to valence-level electrons whereas the former model applies to core-type excitations. Clear examples of each process are emerging.

Last year, Knotek, Vernon O. Jones (Naval Weapons Center, China Lake, California) and Victor Rehn (China Lake and Stanford Synchrotron Radiation Lab) showed² experimentally that photons also can cause desorption by the core-hole Auger-decay mechanism. By reacting a TiO_2 surface with water, they obtained a high density of OH^+ and H on the surface. Then, using photons from the Stanford Synchrotron Radiation Laboratory 8-deg beam line, they observed photon-stimulated desorption of the H^+ and OH^+ ions. Knotek told us that photo-desorption occurred at the identical threshold (although much sharper) as for ESD and that the ions per core hole created were the same for both PSD and ESD within a factor of two.

In the same year, a Bell Labs group, including Phil Woodruff, Mort Traum, Neville Smith and Helen Farrell and their collaborators, working at the University of Wisconsin Synchrotron Radiation Facility, observed³ photon-stimulated desorption of O^+ and other ions from the metal surface $\text{W}(100)$. Both the Sandia-China Lake² and Bell Labs groups³ reported showing that photons of specific energies selectively knock inner-shell electrons from surface atoms, causing ion desorption, in accordance with the theory of Knotek and Feibelman. Also in 1979 R. Fanchey and Menzel (Technical University of Munich) observed photon-stimulated desorption of O^+ and CO^+ from CO on tungsten.

The recent NBS-IBM experiment⁴ combined the angle-resolved electron-stimulated desorption technique with a two-dimensional display-type spectrometer originally designed by Dean E. Eastman (IBM) primarily for angle-resolved photoemission measurements. The collaboration, consisting of Madey and Roger Stockbauer (NBS), J. F. van der Veen (IBM) and Eastman, used the University of Wisconsin Synchrotron Radiation Facility at Stoughton for photons (8–120 eV). Earlier, Madey and his collaborators had found, with ESD, that the adsorbed layers of oxygen on tungsten single crystals produced three separated ion beams. The NBS-IBM group used the same conditions on a $\text{W}(111)$ surface and found that photon stimulation also produced three ion beams with angular distributions at all photon energies essentially identical to those found with electron (500-eV) stimulation. The NBS-IBM group finds that the direction the atoms or molecules move when re-

leased from a surface by photon stimulation is directly related to the angle of the surface bonds being broken.

In the NBS-IBM experiment, using the two-dimensional detector, desorbing positive ions are reflected and focused by an electrostatic ellipsoidal "mirror," and the signal is amplified by an image intensifier and displayed. From the spot positions, one determines the ion trajectories and thus the angle at which the atoms had been bonded to the surface.

Significance. Other surface-structure measurement techniques such as low-energy electron diffraction generally require long-range order. But both ESD and PSD are sensitive to the local geometry—to the excitation of adsorbed atoms and molecules in individual bonding sites. Both provide electronic structure information on atomic sites on the outermost layer of the surface to which specific adsorbates are bonded. Angle-resolved ESD and PSD promise to give the location and angle of surface bonds directly, with little calculation, even for specimens without long-range order.

Angle-resolved PSD is expected to be useful in the chemical and structural analysis of the surfaces of metal-oxide catalysts. Madey has demonstrated the specific sensitivity of angle-resolved ESD to surface steps and defect sites, which may be of importance in catalysis.

A feature of PSD and ESD with both positive and negative aspects is that ion

yields depend sensitively on the nature of chemical bonding and vary enormously for different species, Eastman told us.

Knotek says ESD is one of the most sensitive techniques available for detecting hydrogen, which is of extreme importance in catalysis. However, until calibration studies have been done, Knotek notes that one cannot tell how many hydrogen atoms are present.

Other groups doing PSD include Joachim Stohr and Rolf Jaeger at the Stanford Synchrotron Radiation Lab, David Shirley and collaborators at Lawrence Berkeley Lab and Stockbauer and Madey at the NBS synchrotron, SURF II. Both the SSRL and Sandia groups are trying to do surface EXAFS with PSD.

Yates, Sylvia Ceyer and Madey at NBS are now coupling angle-resolved ESD with electron-energy loss spectroscopy in the same apparatus to study the structure of surface molecules. —GBL

References

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21-term series yields critical indices

Discoveries in physics often hinge on a disagreement between theory and experiment of a percent or less. Because of such a discrepancy, many workers in statistical mechanics have been concerned about the complete validity of the scaling and renormalization-group theories of critical phenomena. For the three-dimensional Ising model, the experimentally derived values for the critical exponents in fluids have agreed to three significant figures with those predicted by the renormalization group. However, the predictions disagreed by a couple of percent with exponents calculated by series expansions, and the claimed accuracy of these expansion estimates was much less than a percent.

Unfortunately theorists have a finite lifetime; so until this year the best high-temperature series expansion used to determine critical indices had 15 terms, still a backbreaking calculation. Adding even one extra term to the series would have required more than twice as much computer time as calculating all the previous terms.

Now Bernhard Nickel of the University of Guelph (Ontario, Canada) has found a clever way of extending the series to 21 terms, and the discrepancy between the series result and renormalization-group theory seems to have disappeared. (Nickel reported his results at the Cargese Summer Institute in July and the Statphys 14 meeting at Edmonton, Alberta in August.) The general reaction among statistical mechanicians is a collective sigh of relief that the renormalization group-scaling theory is still a beautiful, correct picture of critical phenomena.

Scaling and renormalization group. The magnetic susceptibility, for example, diverges at the critical point as $(T - T_c)^{-\gamma}$, where T_c is the critical temperature and γ is the critical index of the magnetic susceptibility. Other thermodynamic and correlation parameters, such as specific heat and correlation length, each have a singularity at a critical point, all of which can be described by power laws with different critical indices.

Since the pioneering work on scaling