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X-RAY PHOTOEMISSION AND SURFACE STRUCTURE

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ABSTRACT

X-ray photoemission spectroscopy (XPS) is a "semisurface" technique that can be modified to study bulk properties, surfaces, or adsorbed species. As a bulk probe it is capable of yielding band-structure information. It can distinguish amorphous from crystalline materials and is sensitive to magnetic and spatial order. Sensitivity to surface character per se is less pronounced. Relaxation effects are prominent in XPS spectra. Core-level binding energies of adsorbed species yield structural information if relaxation is considered. The same should be true for valence orbitals. Heterogeneous catalysis can be understood in a general sense as arising from the same origins as the relaxation energies in photoemission.
I. INTRODUCTION

X-ray photoemission spectroscopy (XPS), or ESCA, provides an extremely versatile method for studying the electronic structure of atoms, molecules, and solids.¹ For several years the value of this method as a surface tool has been hailed by its practitioners but treated skeptically by other surface scientists. In fact XPS is now generally regarded as in "semi-surface" technique because of the characteristic escape depth of ~15 Å for zero-loss photoelectrons with ~1 keV kinetic energy. One objective of this paper is to examine, in Section II, the surface-sensitivity question and evaluate XPS as a surface tool.

Section III deals with the "standard" applications of XPS to solids. Elemental analysis is considered, as is the study of valence bands. The connection with x-ray emission spectroscopy is noted. Binding-energy considerations then lead naturally to a discussion of relaxation energies in Section IV. Relaxation effects are treated for binding energies and Auger energies in atoms, molecules, and solids. It is shown that Auger and core-level binding-energy shifts in solids are related by final-state (relaxation) effects rather than initial-state charge transfer (chemical shifts).

Sections V and VI deal specifically with relaxation on surfaces. In Section V predictions are made about the relaxation-energy shifts expected when molecules are adsorbed on catalytic surfaces. Specific examples are discussed. In Section VI a model is given in which the essential feature of heterogeneous catalysis—the reduction of the
activation energy—may be understood in terms of screening of separated charges in adsorbed molecular species by valence electrons near the Fermi energy in the substrate. This is the exact analogy of the extra-atomic relaxation energy.

II. X-RAY PHOTOEMISSION AS A SURFACE TECHNIQUE

The energetics of photoemission are governed by the conservation relation

\[ h\nu = E_f - E_i + K \]  \hspace{1cm} (1)

where \( h\nu \) is the incident photon's energy, \( E_i \) and \( E_f \) are the initial and final state energies of the system under study, and \( K \) is the photoelectron's kinetic energy. Equation (1) applies directly to the simplest possible photoemission process, in which the \( j^{th} \) electron in an \( N \)-electron system interacts with the photon's electromagnetic field through the term \( \vec{A} \cdot \vec{p}_j \). The photoelectron is ejected without further energy loss in the sample, and the remanent \( N-1 \) electron system goes into the lowest-energy final state of the proper symmetry (the relaxed state). Under these two conditions the interpretation of XPS spectra is relatively straightforward. In practice it is usually easy to pick out the intense "full energy" peaks in the spectrum that arise from those events that satisfy both conditions. These peaks are, however, each accompanied by spectral structure at lower kinetic energies arising from events in which one or both conditions is violated. The interesting electron-correlation or "shake-up" peaks that arise when the \( N-1 \) electron system goes to a higher-
energy final state lie outside the scope of this paper. Electron-loss mechanisms, which reduce the kinetic energy of the photoelectron, are also not of direct interest, but they play the important role of converting XPS from a bulk to a "semi-surface" technique. To understand this we note that electrons which suffer energy losses are completely removed from the main peak, because the criterion

\[ \Delta E >> \Gamma \]  

is usually satisfied, where \( \Delta E \) is the loss energy (~10 eV) and \( \Gamma \) is the full-energy peak width (~1 eV). Thus the effective sample depth for XPS is \( \lambda^{-1} \), the mean free path of an electron between energy-loss events. To obtain this result we have invoked the fact that the x-ray penetration depth exceeds \( \lambda^{-1} \) by orders of magnitude. The energy dependence of \( \lambda^{-1} \) is shown in the "Universal Curve" for heavy metals, in Fig. 1.

A superficial interpretation of Fig. 1 is that XPS is a "semi-surface" technique, having \( \lambda^{-1} \approx 15 \, \text{Å} \) or five atomic layers, and therefore less valuable as a surface tool than photoemission with lower-energy photons; e.g., ultraviolet photoemission spectroscopy (UPS). It now appears, however, that this interpretation is unduly pessimistic and that XPS may soon emerge as the most powerful electron-spectroscopic method for surface studies, because of two advances discussed below.

The first advance is the enhancement of surface sensitivity by employing low electron-takeoff angles. This approach has been pioneered independently by C. S. Fadley and W. N. Delgass.
The principle is very simple. The sample is tilted to reduce the angle $\theta$ between the sample surface and photoelectrons that are accepted by the spectrometer analyzer. Thus electrons from depth $d$ must traverse an effective sample of thickness $d \csc \theta$ (Fig. 2), and the Universal Curve is effectively lowered by a factor of $\sin \theta$. The work of Fadley and Delgass suggests that values of $\sin \theta$ as low as 0.1 are practical. Thus $\lambda^{-1}$ is effectively reduced from 15 Å to 1.5 Å or less than one atomic layer. Since this is the lowest meaningful effective depth possible, it follows that XPS has a usable surface sensitivity second to none. The possibility of adjusting the effective sampling depth, and thereby the surface/bulk ratio in the spectrum, is a distinct advantage possessed by XPS. It should be feasible, by varying $\theta$, to distinguish between surface and bulk features in a spectrum.

The second advance in XPS is the practical exploitation of the variation of photoelectric cross section $\sigma(E)$ with photon energy. The advantages afforded by comparison of UPS and XPS spectra of free molecule was pointed out earlier by W. C. Price. Variations of UPS spectra with photon energy are well-known, but not always readily interpretable because of final-state effects. By using x-rays of two widely different photon energies, however, it has been shown feasible to observe very different cross-section ratios within a given set of molecular orbitals. Since the energy dependence of $\sigma(E)$ for a given orbital depends on the orbital character, it is a straightforward matter to identify molecular orbitals from $\sigma(E)$ ratios. This
has been demonstrated in molecules, for which ratios obtained with
the YM$_x$ x-ray (132.3 eV)$^5$ and the Mg K$_{a1}$ x-ray (1253.4 eV) are
in good agreement with theory.$^6$ The same arguments should apply
to adsorbed molecules. Thus it should soon be possible to study the
valence-orbital XPS spectrum of molecules adsorbed on a substrate,
varying $\theta$ to establish which spectral features arise from the surface
layer and studying $\sigma(E)$ to determine the molecular-orbital character
of these features.

III. STANDARD APPLICATIONS OF XPS TO SOLIDS

Before discussing relaxation-energy effects it is useful to
build a foundation by reviewing the more mundane subject of bulk-
property studies by XPS. To the extent that the XPS spectrum re-
sembles the initial density-of-states one can safely ignore final-state
effects, and in fact this is the level at which most XPS experiments
are interpreted. It should be noted that, provided only relative ener-
gies are discussed, such an interpretation does not require Koopmans' Theorem$^7$ to apply literally (no relaxation) but only relatively (no
differential relaxation) to the N-1 electron system.

The first important feature of XPS is that it always automat-
ically provides an in-situ semiquantitative elemental analysis of the
effective sample, through intensities of core lines such as C(1s) and
O(1s). This is the salient reason for the term ESCA (Electron Spec-
troscopy for Chemical Analysis). In addition to an elemental analysis,
an XPS spectrum yields, through the position and structure of the core-
level peaks, useful information about oxidation states and number of
chemically inequivalent species of each element. This information is usually strongly indicative, though often not definitive or unique. Experience in the preparation of samples has led us to the opinion that it would be hard to overestimate the value of this analytical (ESCA) capability. Its absence in other kinds of surface electron spectroscopy is a severe handicap.

XPS allows a rather direct determination of the valence-band density of states. The high photon energy assures that the XPS spectrum will not be appreciably distorted by the final-state density available to the photoelectron before it leaves the solid, as is the case in UPS. It does not follow, however, that the photoemission spectral intensity I(E) will directly mirror the valence-band density of states ρ(E). Cross-section modulation may emphasize some bands relative to others. Such an effect was observed in diamond, silicon, and germanium and was explained in terms of atomic orbital relative cross sections.\(^8\) The one-electron component of the photoelectron cross section is given in the dipole approximation by an expression of the form

\[
σ_j(E) \propto |⟨ϕ_j(μ)|r_μ|χ(μ)⟩|^2, \tag{3}
\]

where \(ϕ_j(μ)\) represents electron \(μ\) in its initial state and \(χ(μ)\) is the (photoelectron) continuum final state, an orthogonalized plane wave. The matrix element is qualitatively similar to a Fourier integral of \(ϕ_j(μ)\). Since the de Broglie wavelength of the continuum state is short (\(\sim 0.3\,\text{Å}\)) even compared to atomic dimension, it follows that
The main contributions to the XPS cross sections comes from the high-curvature portions of $\phi_j(\mu)$; i.e., the portions inside the atoms. For this reason XPS is insensitive to the details of the valence-electron wave functions between atoms, but is a good diagnostic tool for determining atomic orbital character in $\phi_j(\mu)$.

XPS can easily detect the difference between crystalline and amorphous materials. In semiconductors and semimetals amorphous character shows up as a loss of splitting in the lowest "s" bands, while in metals it appears as a loss of sharp structure and a decrease in steepness at the Fermi energy. The "s" band structure is also a good index of ionicity and has yielded a new ionicity scale.

Soft x-ray emission spectroscopy (XES) and XPS can be combined in a complementary manner. This is especially true for cases in which the relative cross-sections of different symmetry orbitals are different in XES and XPS. In carbon, for example, the XES ratio $\sigma(2s)/\sigma(2p) = 0$ for K emission, while the XPS ratio is $\sim 20$. Combination of the XES and XPS spectra yields unambiguous orbital character of the valence bands in diamond and graphite.

The foregoing discussion indicated topics in XPS that can be treated considering only initial-state properties. A more sophisticated interpretation requires the inclusion of relaxation effects, discussed in the remaining sections.
IV. RELAXATION ENERGIES IN ATOMS, MOLECULES, AND SOLIDS

Solution of the Hartree-Fock equations for the ground state of an \( N \)-electron system yields a set of one-electron orbital energies \( \epsilon_j \) that correspond to the occupied orbital in the ground state. Koopmans showed\(^7\) that these \( \epsilon_j \) are approximately equal to the one-electron binding energies \( E_B(j) \). In fact the two would be equal in the Hartree-Fock approximation (i.e., neglecting relativistic and correlation effects) if the \( N-1 \) passive electrons remained in invariant, "frozen" orbitals during photoemission. They don't, of course; the \( N-1 \) electron system relaxes to minimize its energy. We can define a relaxation energy \( E_R(j) \) by the equation

\[
E_B(j) = -\epsilon_j - E_R(j)
\]

\[
= |\epsilon_j| - E_R(j),
\]

(4)

where again relativistic and correlation energies are neglected, and the awkwardness with signs is a consequence of different sign conventions for \( E_B(j) \) and \( \epsilon_j \). The relaxation process always acts to reduce the binding energy, so \( E_R(j) \) is always positive, as illustrated in Fig. 3. The size of \( E_R(j) \) can tell us a good deal about the system under study; hence its importance. We now turn our attention to various specific types of system.

In atoms, photoemission from an orbital of quantum number \( n \) is accompanied by relaxation of the passive orbitals toward the attractive hole. The atomic relaxation, \( E_R^a \), may be divided into three parts,
for orbitals with quantum number $n'$ less than, equal to, or greater than $n$. Innershell relaxation ($n' < n$) is always small and may be ignored. Intrashell relaxation ($n' = n$) is of the order of a few eV. Outershell relaxation ($n' > n$) is the largest term if $n$ is a core orbital and several orbitals with $n'>n$ are occupied. The outershell term is intuitively easy to understand; it may be estimated with fairly good accuracy on simple screening models.\textsuperscript{13, 14}

Atomic relaxation effects are also present in Auger transitions.\textsuperscript{15} It might appear that these effects would already be included if one estimated the Auger energy $E(jk\ell)$ from the $j, k,$ and $\ell$ one-electron binding energies (which of course contain $E^a$ terms). In fact, however, additional relaxation is present because in the final two-hole state the charge $2e$ gives four times as much screening energy as would a single charge; i.e., the screening energy varies quadratically with charge.

Thus a relation of the form

$$E(jk\ell) = E^b_B(j) - E^b_B(k) - E^b_B(\ell) - F(k\ell) + R$$

applies, where $R$ is the additional relaxation energy and $F(k\ell)$ is a recoupling energy in the final state (the Asaad-Burhop term\textsuperscript{16}). The energy $R$ can be very large. For KLL transitions the size of $R$ in eV is of the same order as the atomic number.\textsuperscript{15}

Electron binding energies in molecules are affected by extratomic relaxation as well as atomic relaxation, which is still present. We may write

$$E^R_R(j) = E^a_R(j) + E^{ea}_R(j)$$

(6)
for an orbital in a molecule, although the separation into atomic and extra-atomic terms may be quite arbitrary. Physically this separation is quite useful, because it allows us to predict that core-electron binding energies in molecules will be lowered further by the $E_{R}^{ea}$ term, if no competing effects such as chemical shifts are present. Thus the K-orbital binding energy in a homonuclear diatomic molecule is lower than in the neutral atom. For this case the final-state charge distribution is easily understood in terms of screening. The K hole on one atom is screened by a flow of charge is the valence shells until a net charge of approx. + e/2 on each atom is reached. This is the lowest-energy distribution of a total charge of +e between the two atoms. Larger molecules show similar effects: thus in CH$_4$ the carbon K-hole charge is almost exactly shielded by polarization of the C-H bonds, and the final state has charges of approximately + e/4 on each hydrogen. The relaxation energy tends to increase with molecular size because the repulsive effect of the net positive charge decreases. However, the major change in $E_{R}^{ea}$ is realized in rather small molecules, with only small increases as the molecular size is increased further. 17

The extra-atomic relaxation energy is closely related to a chemical effect, the polarization energy. Consider the gas-phase proton attachment reaction

$$\text{ROH} + \text{H}^+ \rightarrow \text{ROH}_2^+.$$  \hspace{1cm} (7)

The heat of this reaction is termed its proton affinity, PA. Now variation in PA with the R group are in large part due to this group's ability to screen the positive point charge (H$^+$) that is added to the OH group.
A similar reaction is photoionization of an oxygen K electron,

\[ \text{ROH} \rightarrow \text{RO}^* \text{H}^+ + \text{e}^-, \]  
\[ (8) \]

where the asterisk denotes a K vacancy. Here again the final state differs from the initial state by the addition of a highly-localized positive charge to the OH group. The heat of this reaction is (minus) the electron binding energy \( E_B(\text{O}1s) \). Variations in PA and \( -E_B(\text{O}1s) \) are essentially identical as the \( R \) group is changed in aliphatic alcohols. Both arise primarily from changes in the extra-atomic relaxation energy.

The \( E_{\text{R}}^{\text{ea}} \) term reaches its saturation value in solids, which can be regarded as very large molecules. An immediate consequence of this is that the work functions for photoionization of solid elements are smaller than the atomic ionization potentials. This arises mainly from an \( E_{\text{R}}^{\text{ea}} \) effect. It is not a consequence of delocalization of the conduction electrons as is widely believed (although they are of course delocalized) but is a many-body relaxation effect. To estimate the size of the \( E_{\text{R}}^{\text{ea}} \) term for core levels in solids it can be calculated for the appropriate molecules and extrapolated to infinite molecular size. This approach has been used for graphite, using benzene, naphthalene, etc., to yield \( E_B(\text{C}1s) = 284.4(3) \) eV for graphite. The experimental value is 284.7(2) eV.

Estimates of \( E_{\text{R}}^{\text{ea}} \) for core levels in metals are more difficult. Two approximate approaches have been suggested. Ley, et al., have assumed that the hole state was completely shielded by forming an exciton, in which an electronic charge fills a state whose character is
essentially that of the next unfilled atomic level, e.g., 2p in carbon, 3d in iron, and 4p in zinc. This leads to the estimate

\[ E_R^{\text{core}} \approx \frac{1}{2} F^0 (\text{core}, b), \]

where \( F^0 \) is the core-vacancy Coulomb integral. This model gives fairly good agreement with the magnitude of \( E_R^{\text{ea}} \) - it yields estimates that are consistently about 3/2 of the experimental value because it exaggerates the exciton localization - and predicts trends well. Another model, due to Citrin and Hamann, focuses on the properties of the lattice rather than the atom being ionized. Its major success is its ability to predict variations in binding energy for a given core level as the atom is placed in different metals.

We finish this section on relaxation with a brief warning about the interpretation of Auger shifts. First we note that shifts in Auger energies or binding energies from solids have absolute meaning only if the energies are referred to a meaningful common reference level - the vacuum level. This is only possible if the work functions are known. However relative shifts in Auger and binding energies may be made directly if the Auger lines are observed in an XPS experiment. This was done for the K, L\(_{23}\), and KLL(\(^1\)D) Auger lines in sodium as NaF, atomic sodium, and as the metal. When the energy scales were shifted to align the L lines the K lines fell into alignment, but the Auger lines did not (Fig. 4). The surprising result is that the Auger lines of NaF and atomic Na fell at about the same energy. This shows that the "chemical" Auger shifts cannot even distinguish between Na and Na\(^+\). By contrast the Auger line of the metal was shifted \(~8\) eV by extra-
atomic relaxation. Thus the Auger chemical shifts may in fact be chemical only in a generic sense.

V. RELAXATION AND SURFACES

In this section the effects of relaxation shifts on binding energies of surface species is treated, with emphasis on adsorbed molecules. This is a fast-growing field and the discussion will be illustrative rather than exhaustive.

First it is useful to compare binding energies in the surface layer of a solid with the bulk values. Naive considerations would suggest large surface/bulk binding energy shifts in ionic solids because of different initial-state Madelung energies. In fact the Madelung energies aren't very different and no such shifts have been observed. In metals the situation is less clear theoretically and controversial experimentally. Although lowered surface binding energies have reported from indirect measurements, careful XPS measurements have not confirmed these results.

When rare-gas molecules are physically adsorbed onto metal surfaces, their core-level binding energies lie between those of the same atoms in the gas phase and embedded in the metals. This is consistent with a reduced relaxation energy for the adsorbed atoms. This is of course expected on simple relaxation arguments. The embedded atoms have about the same extra-atomic relaxation energy as atoms in the bulk, while adsorbed atoms are less effectively screened by the substrate's valence electrons.
From the foregoing discussion we can make several predictions about the expected XPS spectrum of a metal-plus-adsorbate system:

1. The metal peaks should be essentially unshifted. Even for the surface layer of metal atoms we can argue that if core binding energies are unshifted by such a profound change as removing all the metal atoms above the surface plane (the surface to bulk difference), then adsorption of even a layer of adsorbate should not shift the substrate surface-layer energies relative to those of the bulk. Experiment now appears to confirm this expectation, with some early measurements to the contrary apparently being in error.

2. Adsorbate core-level binding energies, referred to the vacuum level, should generally be lower than those of free molecules. The reduction in \( E_B \) should be greatest for core levels, because the molecular equivalent of outershell relaxation is possible. Small molecules should show larger value of \( \Delta E_B(\text{core}) = E_B(\text{gas}) - E_B(\text{adsorbate}) \) than large molecule, because the latter already have a good deal of extra-atomic screening in the gas phase. Experiment again appears to support this prediction. Barber, et al.,\textsuperscript{26} found a binding energy of 532 eV for the 1s electron orbital of atomic oxygen adsorbed on graphite. The work-function correction raises this to a vacuum-referenced value of 537 eV, still \( \sim 9 \) eV lower than the 546 eV expected for atomic
oxygen. The reason for such a large screening energy in oxygen and for carbon itself is that the screening is done by a 2p orbital: hence a large effective value of $e^2/r$. In carbon monoxide adsorbed in various forms on tungsten and molybdenum, oxygen 1s binding energies in the range 537-542 eV (referenced to vacuum) have been reported. This represents some reduction from the value of 542.1 eV for gaseous CO, but the reduction is less than in atomic oxygen.

3. Adsorbate $\sigma$-orbital binding energies should also be lowered relative to gas phase values, but the reduction should be less than in core levels, because the screening charge gives the analogue of intrashell relaxation. Size effects may also be present as before, with smaller molecules having larger reduction. Again, experiment appears to bear this out. Demuth and Eastman found reductions in binding energies of the $\sigma$ orbitals of $C_2H_2$, $C_2H_4$, and $C_6H_6$ adsorbed on Ni(111). The binding energies were reduced by 3.2, 2.1, and 1.7 eV, respectively, confirming the above predictions.

4. Adsorbate $\pi$-orbital binding energies should be in most cases quite strongly affected by adsorption because they are relatively exposed. Particularly in chemisorption, the $\pi$-orbital degeneracy in linear molecules should be removed when these molecules lie on the surface, from symmetry considerations.
Demuth and Eastman interpreted their spectra as showing an increased π-orbital binding energy due to bonding (an initial-state effect). This is an important result because it establishes bonding through the π orbitals as expected, but it requires further elucidation.

5. Finally, molecular orientation should play an important role in adsorbate spectra. A diatomic adsorbate molecule standing up on a surface should show less reduction in core-level binding energy of the upper atom than of the lower atom, relative to gas-phase values. Similar reductions would be observed in a molecule lying down on the surface. Experimental evidence supports this prediction, too. In CO on W, Madey, et al. found an O1s binding energy of 537.2 eV for the strongly bound form, which is believed to lie down. This large reduction in $E_B$, of 4.9 eV from the gas-phase value (542.1 eV) is close to the value of 537 eV for atomic oxygen on graphite, and consistent with CO lying down or even dissociated in the β form. For α-CO on W, these workers found an O1s binding energy of 540.6 eV, only slightly below the gas-phase value and understandable only for CO standing up in the α form with the oxygen away from the surface, as postulated from other evidence. Similar results were reported by Atkinson, et al., for the more complicated case of CO on Mo, and similar conclusions can be drawn. These authors reported a carbon 1s binding
energy of 287 eV (referred to vacuum) for the strongly-bonded \( \beta \) form. This is even lower than the value for graphite, and it strongly supports their conclusion that the \( \beta \) form is dissociated.

Clearly relaxation-energy considerations permit a rather detailed interpretation of the photoemission spectra of adsorbed species. In the future we can expect XPS spectra to be of great diagnostic value in elucidating the molecular mechanisms of adsorption and catalysis.

VI. A RELAXATION MODEL FOR HETEROGENEOUS CATALYSIS

A chemical reaction

\[
A + B \rightarrow C + D
\]  \hspace{1cm} (10)

that is slow in the gas phase will often proceed much faster in the presence of a solid catalyst, because of a change in the interactions between A and B that occurs when they are adsorbed on the catalytic surface. To explain and improve heterogeneous catalysis it is important to understand the nature of this interaction. In this Section we propose a model based on extra-atomic relaxation energies in the formation of the activated complex. We believe that this model can provide a qualitative understanding of the efficiency of heterogeneous catalysis.

The usual model for a reaction's proceeding at a measurable or slow rate, rather than very fast, is that the reactants must form an activated complex,
A + B \rightarrow (AB)^* \quad (11)

which then breaks up to form products

(AB)^* \rightarrow C + D. \quad (12)

The "heat" of reaction (11) is termed the activation energy, $\Delta E^a$. The reaction rate is given by

$$k = (\text{const}) e^{-\Delta E^a/RT}. \quad (13)$$

Now $\Delta E^a$ is a positive quantity forming an energy barrier over which the reactants must pass to form products, as illustrated schematically in Fig. 5. From Eq. (13) we would expect to accelerate the reaction by reducing $\Delta E^a$.

What makes $\Delta E^a$ large? The activated complex can be reached from either side, by continuous distortion of the reactants or products. Since chemical forces are a consequence of electromagnetic interactions, it is a safe bet in most cases that the activation energy arises from some unfavorable form of charge separation in the activated complex. In the gas phase or in most cases even in a dielectric medium little can be done to mitigate this effect. However, on the surface of a metal such as Ni, Pd, or Pt, possessing a very large density of states at the Fermi energy, $\Delta E^a$ for adsorbed molecules is surely reduced. The metal's valence electrons can respond even up to optical frequencies, and they are highly polarizable. Thus they can flow adiabatically either way to screen separated charges in the activated complex. If $(AB)^*$ can be formed only by electron transfer from $A$ to $B,$
for example, the substrate's valence electrons will polarize toward A and away from B, thereby reducing $\Delta E^a$ by a relaxation energy,

$$\Delta E^a (\text{absorbate}) = \Delta E^a (\text{gas}) - E_R,$$

also illustrated in Fig. 5. The magnitude of this relaxation energy should be similar to that of the relaxation energies encountered in photoemission in the earlier sections (the hole state is the analogue of the activated complex); i.e., up to $\sim 5 \text{ eV}$ or $\sim 100 \text{ K cal/mole}$. This is certainly enough to change a reaction rate sufficiently (see Eq. (13)) so that a reaction described as "not going" in the gas phase would "go" on a catalytic surface. We therefore suggest this scheme as a model for studying heterogeneous catalysis.
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5. M. S. Banna and D. A. Shirley, to be published.


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19. These values are referred to the Fermi energy.


24. We have searched for core-peak satellites attributable to surface-layer atoms in several metals, without success. C. S. Fadley has indicated similar results in a private communication.

25. J. T. Yates and N. E. Erickson, Surface Science, to be published.


30. The author is indebted to C. R. Brundle for a discussion of this point. Dr. Brundle also has studied hydrocarbons adsorbed on nickel (private communication).
FIGURE CAPTIONS

Fig. 1. The Universal Curve for electron energy loss in heavy metals, showing the lower surface sensitivity at high energies.

Fig. 2. Increase in surface sensitivity of XPS by the use of a low takeoff angle $\theta$.

Fig. 3. Reduction of core level binding energy below the orbital energy $-\epsilon$ through atomic relaxation in the possible orbitals, and further reduction through extra-atomic relaxation in a solid. The cohesive energy $E_c$ is absorbed in $E_{R}^{ea}$ in this simple picture.

Fig. 4. Relative positions of Na K, Na L$_{23}$, and Auger ($^1$D) peaks in XPS spectra of the metal, NaF, and atomic sodium (indicated by arrows at bottom). Note that atomic Na and NaF are very similar, but the metal Auger peak is strongly shifted.

Fig. 5. Lowering of the activation energy $\Delta E^a$ by screening through valence-electron polarization in heterogeneous catalysis.
Fig. 1

Electron energy (eV)

Attenuation length (Angstroms)
Fig. 2
Frozen orbital "state" ---

Energy

- \( \varepsilon \)

ATOM

Ground state

SOLID

Fig. 3
Fig. 4
Activated complex

\[(AB)^*\]

\[\Delta E^a_{(gas)}\]

\[E_R\]

\[\Delta E^a_{(ads)}\]

A + B
Reactants

C + D
Products

Reaction coordinate

Energy
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