



# Advances in CHEMICAL PHYSICS

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## INTRODUCTION

Few of us can any longer keep up with the flood of scientific literature, even in specialized subfields. Any attempt to do more and be broadly educated with respect to a large domain of science has the appearance of tilting at windmills. Yet the synthesis of ideas drawn from different subjects into new, powerful, general concepts is as valuable as ever, and the desire to remain educated persists in all scientists. This series, *Advances in Chemical Physics*, is devoted to helping the reader obtain general information about a wide variety of topics in chemical physics, which field we interpret very broadly. Our intent is to have experts present comprehensive analyses of subjects of interest and to encourage the expression of individual points of view. We hope that this approach to the presentation of an overview of a subject will both stimulate new research and serve as a personalized learning text for beginners in a field.

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# CONTENTS

CHEMISTRY INDUCED BY CORE ELECTRON EXCITATION <i>By David M. Hanson</i>	1
SYNERGISTIC EFFECTS IN TWO-PHOTON ABSORPTION: THE QUANTUM ELECTRODYNAMICS OF BIMOLECULAR MEAN-FREQUENCY ABSORPTION <i>By David L. Andrews and Kevin P. Hopkins</i>	39
ACCURATE QUANTUM CHEMICAL CALCULATIONS <i>By Charles W. Bauschlicher, Jr., Stephen R. Langhoff, and Peter R. Taylor</i>	103
MOLECULE-SURFACE SCATTERING AND REACTION DYNAMICS <i>By Andrew E. DePristo and Abdelkader Kara</i>	163
PROBING ELECTROCHEMICAL INTERFACES WITH X-RAYS <i>By Héctor D. Abruña</i>	255
PERIODIC SURFACES OF PRESCRIBED MEAN CURVATURE <i>By D. M. Anderson, H. T. Davis, J. C. C. Nitsche, and L. E. Scriven</i>	337
RECENT DEVELOPMENTS IN THE STUDY OF MONOLAYERS AT THE AIR-WATER INTERFACE <i>By Charles M. Knobler</i>	397
RECENT PROGRESS IN THE STATISTICAL MECHANICS OF INTERACTION SITE FLUIDS <i>By P. A. Manson and G. P. Morriss</i>	451
ON THE THEORY OF THE ORIGIN OF SPATIALLY NONUNIFORM STATIONARY STATES (DISSIPATIVE STRUCTURES) IN HETEROGENEOUS CATALYTIC SYSTEMS <i>By Yu E. Volodin, V. N. Zvyagin, A. N. Ivanova, and V. F. Barelko</i>	551
AUTHOR INDEX	607
SUBJECT INDEX	629

# CHEMISTRY INDUCED BY CORE ELECTRON EXCITATION

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## CONTENTS

- I. Introduction
- II. Core Hole Excited States
  - A. Spectroscopic Investigations
  - B. Description of the Resonances
- III. Electronic Relaxation
- IV. Molecular Chemistry
  - A. Ultra-fast Dissociation
  - B. Coulomb Explosion
  - C. Molecular Orbital Depopulation
  - D. Valence Bond Depopulation
  - E. Energy Constraints
  - F. Coincidence Experiments
  - G. Angular Distributions
  - H. Fluorescence Detection
  - I. Electron Impact Excitation and Fragmentation
  - J. Negative Ion Formation
  - K. Transition Stress Theory
- V. Solid State and Surface Chemistry
  - A. Desorption Induced by Electronic Transitions
  - B. Microelectronics Applications
- VI. Concluding Comments
- References

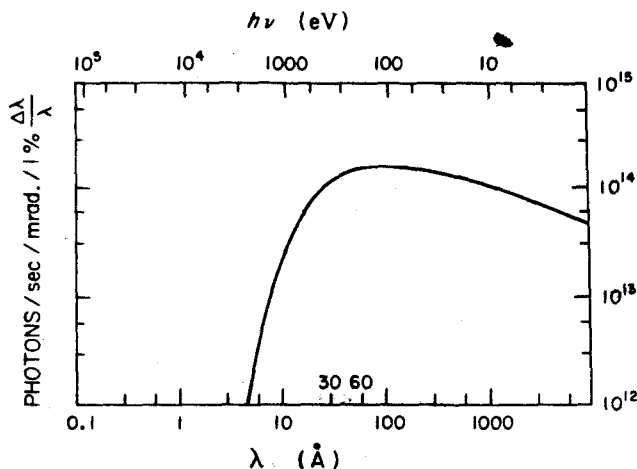
## I. INTRODUCTION

Radiation chemistry generally has been concerned with secondary and tertiary reactions caused by energetic electrons that result from ionization by high-energy radiation or bombardment by high-energy particles. Recently



there has been a surge of interest in the primary steps in radiation chemistry. The term *primary steps* refers to the excitation and relaxation processes of a single molecule exposed to high-energy radiation or particles. This review focuses on steps that begin with the excitation or ionization of a core electron in a molecule. This chemistry is relevant to understanding the effects of radiation on biological systems and on materials used in space, in nuclear reactors, or with the techniques of x-ray and electron lithography and microscopy. X-ray lithography and associated processes of etching and deposition appear to be providing a path into the world of ultra-microelectronics. Core electron spectroscopy and photochemistry also are enhancing our knowledge of surface and interface structure and reactivity.

Many of the unique properties of synchrotron radiation are contributing to this research. These properties include a continuous intensity distribution to very high photon energies, high intensity and brightness, small divergence, polarization, and pulsed time structure. The techniques of electron spectroscopy, mass spectroscopy, and fluorescence spectroscopy are being used with monochromatic radiation for selective excitation to elucidate the processes of interest. Figure 1 shows the spectral distribution for the VUV Ring at the National Synchrotron Light Source. Such a facility clearly opened the region of photon energies up to about 1000 eV for investigation. This energy range matches the binding energies (Ley and Cardona 1979), listed in Table 1, of core electrons associated with the common elements forming molecules of chemical and biological interest.



**Figure 1.** Spectral distribution of the VUV storage ring at the National Synchrotron Light Source, presently operating at 750 MeV with peak beam currents of 900 mA.

TABLE I  
Core Electron Binding Energies

Atom	Orbital	Energy (eV)
C	1s	284
N	1s	410
O	1s	543
F	1s	697
Si	2s	150
	2p	99
P	2s	189
	2p	136
S	2s	231
	2p	163
Cl	2s	270
	2p	201

Existing grating monochromators, designed for the soft x-ray region with resolutions of  $E/\Delta E = 100$  to 1000 or more, can provide a high flux ( $> 10^9/\text{sec mm}^2$ ) of monochromatic photons, which is more than adequate to selectively excite core electrons in molecules in several different ways. It is possible to excite the 1s, 2s, or 2p electrons of one element or another in a molecule by using monochromatic radiation because the differences in binding energies are tens to hundreds of electron volts. Even more interesting is the possibility shown in Fig. 2 of selectively exciting different atoms of the same element that are in different chemical environments of the molecule. Chemical shifts of the binding energy of, say, carbon 1s electrons, are known from ESCA studies (Siegbahn et al. 1969) to be as large as 10 eV. Finally, different final states can be reached in the excitation process with different chemical consequences. These states include configurations with the core electron excited to a valence orbital, a Rydberg orbital, a shape resonance, or the ionization continuum. These various

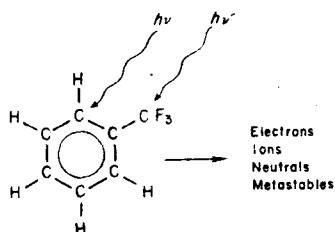


Figure 2. Illustration of atomic site selective excitation by soft x-ray photons.

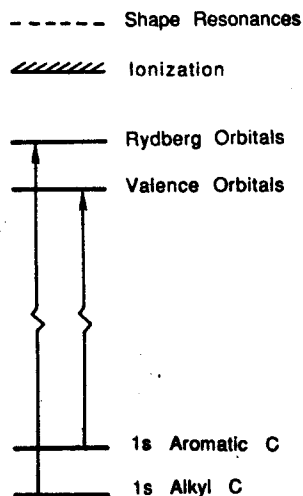


Figure 3. Energy level diagram illustrating chemical shifts of the core levels and different final state configurations that can be reached by core electron excitation.

selective excitation processes are illustrated in Fig. 3. The objective of the research is to determine what happens to molecules following such excitation by using the techniques of electron, mass, and fluorescence spectroscopy to monitor, characterize, and correlate the electrons, ions, neutrals, and metastables that are produced as a consequence.

The following picture is emerging from this research. Core electron excited states have finite lifetimes and unique characters. The electronic and chemical relaxations are coupled and depend upon the atomic and electronic structure of the molecule, the atomic site of the core hole, and the configuration of the core hole excited state. Experiments leading to an understanding of these dependences are just beginning to be done.

## II. CORE HOLE EXCITED STATES

### A. Spectroscopic Investigations

The term *core hole excited state* refers to the situation where a core electron in an atom or molecule has been excited or ionized leaving a vacancy in a core, i.e. nonvalence, orbital. These states have been investigated by x-ray absorption or electron energy loss measurements. Comprehensive reviews of the latter are available (Brion et al. 1982; King and Read 1985; Hitchcock 1989). An x-ray absorption spectrum can be separated into two regions. The EXAFS region (extended x-ray absorption fine structure) extends from about 25 eV to several hundred eV above a core ionization threshold or edge. In this region the dominant excitation process is ionization of the core electron.

The scattering of the outgoing electron wave from surrounding atoms, which generally can be described by a single scattering theory, produces an interference pattern in the absorption spectrum that provides structural information about the atomic site (Teo and Joy 1981; Lee et al. 1981; Prins and Koningsberger 1987). The NEXAFS region (near edge x-ray absorption fine structure), which also is called XANES (x-ray absorption near edge structure), extends approximately 25 eV on either side of the ionization edge. In this region the single-scattering model does not apply. Spectral features

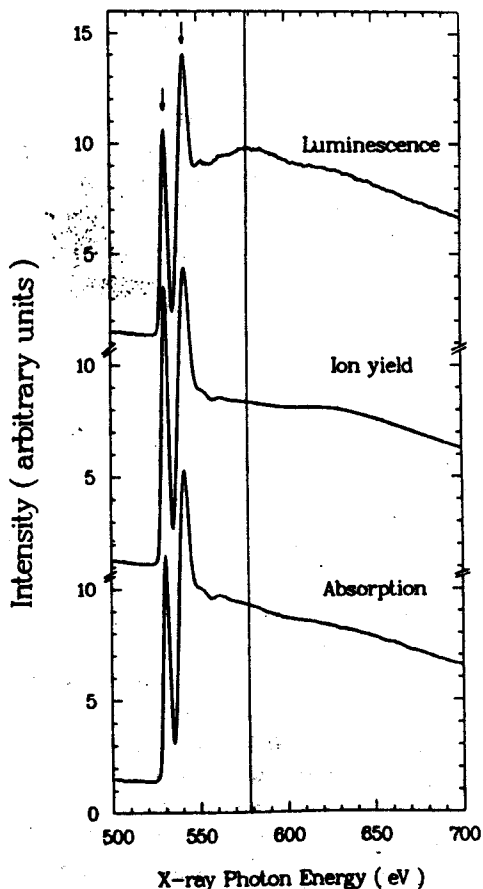


Figure 4. X-ray spectra of molecular oxygen at a pressure of 0.1 torr near the oxygen K-edge. From top to bottom: the total optical luminescence yield, the total ion current, and the absorption coefficient.

are due to resonances that are described by multiple-scattering and molecular orbital theories.

The soft x-ray absorption spectrum of oxygen is shown in Fig. 4 together with the total optical luminescence yield and the total ion yield. Differences between these spectra demonstrate that the relaxation is excitation energy dependent, i.e., the relaxation depends upon the nature of the core hole excited state. The two sharp peaks at 531 and 542 eV below the ionization edge at 543 eV are assigned to core electron transitions to pi and sigma antibonding molecular orbitals. The increase in the luminescence around 580 eV reflects the possibility for shake-up transitions, and the feature around 620 eV has been assigned to an EXAFS oscillation (Yang et al. 1988).

### B. Description of the Resonances

Below the ionization edge, features in the absorption spectra called *discrete resonances* are due predominantly to transitions of the core electron to bound states that result from configurations in which the core electron has been promoted to a valence or Rydberg orbital or an appropriate linear combination. These states are degenerate with the ionization continua of other configurations and therefore can autoionize in an Auger-like process where one electron falls into the core hole and another electron is emitted.

Above the ionization edge, the NEXAFS features are due to transitions to quasi-bound molecular orbitals (also called shape or continuum resonances). In addition, multiple electron excitation processes, in which valence electrons also are excited (shake-up) or ionized (shake-off) can occur. Shape resonances result from the shape of the molecular potential, which temporarily traps the outgoing electron. Two theoretical models have been used to describe the energy position, intensity, spectral lineshape, and other properties of the shape resonances. These other properties include the population of vibrational states, the angular distribution of photoelectrons and Auger electrons, and the dependence of the angular distribution on vibrational state. One model uses a multiple-scattering formalism while the other uses a molecular orbital approach. Both approaches are directed at the same goal, namely the construction of an accurate wavefunction with a large amplitude near the molecule at an energy above the ionization edge (Dehmer et al. 1982; Dehmer 1984; Lynch et al. 1984; Langhoff 1984; Natoli 1983). The dependence of the wavefunction on energy and internuclear separation is critical because the observed characteristics of the shape resonance are a sensitive function of energy and internuclear separation.

The diversity of excitation channels in the NEXAFS region offers many opportunities for research. The near-edge structure, which depends upon geometry, coordination number, and bond order and ionicity, is sensitive to the local bonding environment of the atom. The molecular orbital picture

of the resonances provides insight regarding the potential that NEXAFS has for characterizing bonds around particular atoms. Generally both bonding and antibonding molecular orbitals are associated with a bond. Observation of a resonance assigned to a particular antibonding orbital, e.g. by polarization of the absorption or characteristics of the relaxation, identifies the presence of a particular bond. While the bonding structure of simple molecules is sufficiently well-understood that this identification is not likely to be important, the situation for atoms in complicated or disordered environments or molecular species on surfaces or at interfaces is not so well-defined. NEXAFS reveals the presence of different types of bonds (Stohr et al. 1987; Stohr and Outka 1987a) and can serve to identify chemical reactions occurring on surfaces. A quantitative correlation between the energy of the resonances and bond lengths has been noted (Stohr et al. 1983; Stohr et al. 1984; Hitchcock et al. 1984; Sette et al. 1984; Piancastelli et al. 1987a; Hitchcock and Stohr 1987; Piancastelli et al. 1987b). The coupling between the resonance and the electromagnetic field is anisotropic so the orientation of bonds can be derived from the angular dependence of the absorption with polarized x-rays (Stohr and Outka 1987b).

Since the resonances have distinct characteristics, the relaxation of the core hole excited state and the dissipation of the excitation energy by electron emission, dissociation, luminescence, and the excitation of rotational and vibrational motion will vary from one resonance to another. These relaxation processes are referred to as the photoexcitation or photoionization dynamics, and characterizing the dynamics can aid in identifying and assigning the resonances. For example, it sometimes is difficult to assign bound state resonances to valence or Rydberg orbitals and features above ionization edges to shape resonances or shake-up structure; the characteristics of the electronic relaxation and the subsequent chemistry may serve as an identifying fingerprint. The electronic decay associated with above-threshold features in the 1s absorption spectra of benzene and ethylene recently has been used to identify and assign these features to doubly excited states and shape resonances (Piancastelli et al. 1989).

### III. ELECTRONIC RELAXATION

The decay of a core hole excited state is dominated by autoionization or Auger processes for the light elements of the periodic table. The contribution from x-ray fluorescence is small, amounting to less than 1% for carbon and reaching 10% for argon. For the first series of the periodic table, the lifetime of a core hole excited state is about 10 femtoseconds, corresponding to an Auger transition rate of around  $10^{14}$ /sec. In special cases discussed in Section IV.A, a molecule in a core hole excited state may dissociate prior to

TABLE II  
Core Hole Relaxation Processes

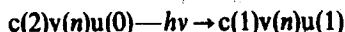
ID	Initial	Final	Charge
PA	$c(1)v(n)u(1)$	$c(2)v(n-1)u(0) + e^-$	+1
SA	$c(1)v(n)u(1)$	$c(2)v(n-2)u(1) + e^-$	+1
PDA	$c(1)v(n)u(1)$	$c(2)v(n-2)u(0) + 2e^-$	+2
SDA	$c(1)v(n)u(1)$	$c(2)v(n-3)u(1) + 2e^-$	+2
CA	$c(2)v(n-2)u(1)$	$c(2)v(n-2)u(0) + e^-$	+2
AD	$c(1)v(n)$	$c(2)v(n-2) + e^-$	+2
ASU	$c(1)v(n)$	$c(2)v(n-3)u(1) + e^-$	+2
DAD	$c(1)v(n)$	$c(2)v(n-3) + 2e^-$	+3
ICD	$c(1)v(n)s(1)$	$c(2)v(n-1)s(0) + e^-$	+1

PA = participant autoionization; SA = spectator autoionization; PDA = participant double autoionization, SDA = spectator double autoionization; CA = cascade autoionization; AD = Auger decay; ASU = Auger decay with shake-up; DAD = double Auger decay, ICD = inter-channel decay.

the electronic relaxation, which then occurs in a fragment particle. The lifetime of the core hole state is known from theoretical calculations (Callan 1961; McGuire 1969; Higashi et al. 1982) and from measurements of linewidths in high resolution spectra. A lifetime of 10 fs is sufficient for vibrational motion to be defined, and vibrational structure is observed in core electron spectra (Gelius et al. 1974; King et al. 1977). The time evolution of the core hole excited state and its effect on vibrational populations and vibronic structure in spectra is a topic of current research (Flores-Riveros et al. 1985; Correia et al. 1985; Carroll and Thomas 1987; Carroll et al. 1987; Poliakoff et al. 1988; Murphy et al. 1988; Carroll and Thomas 1988).

Table II, which is adapted from a previous description (Nenner 1987; Nenner et al. 1988), presents some of the electronic relaxation processes associated with the decay of a core hole. In these equations,  $c$  represents a core orbital,  $v$  an occupied valence orbital,  $u$  an unoccupied valence or Rydberg orbital, and  $s$  represents a shape resonance orbital. The term "orbital" is used simply to mean a one-electron wavefunction. An electron in a continuum orbital free from the influence of the molecular potential is represented as  $e^-$ .

The case of resonance excitation to a bound state is considered first:



Several decay channels are possible. The most important are listed in Table II and are labeled PA (participant autoionization), SA (spectator autoionization), PDA (participant double autoionization), SDA (spectator double autoionization), and CA (cascade autoionization).

In participant autoionization (PA), the core electron excited to the unoccupied orbital is removed in an Auger-like process, and the molecule is left with a missing valence electron in what is called a 1-hole state. In spectator autoionization (SA), which also has been called resonance Auger decay, the electron in the highest energy orbital is not involved. SA leaves the molecule in a 2-hole 1-electron state because two electrons are missing from lower energy orbitals, and one electron is in an excited orbital. Both these autoionization processes leave the molecule with a +1 charge.

The final states in autoionization of a bound state resonance also can be reached by direct photoemission. Since in PA the molecule is left with a single hole in the valence shell, lines in the electron energy spectrum are expected at the energy of the bound state resonance minus the binding energies of the various valence electrons as measured in a standard photoelectron spectrum. In SA the molecule is left with two valence holes and an electron in a higher orbital. These states are reached by shake-up in direct photoemission. The intensities in photoemission and autoionization spectra will be different because the transition matrix elements differ, but matching the transition energies can serve to aid assignments (Eberhardt et al. 1984; Eberhardt et al. 1986c; Freund and Liegener, 1987).

Relaxation involving emission of more than one electron also occurs, e.g., participant double autoionization (PDA) and spectator double autoionization (SDA). These channels leave the molecule with a +2 charge and in 2-hole and 3-hole 1-electron states, respectively. Since relaxation of the core hole may leave the molecule with a deep valence hole or with an electron in a high energy orbital, additional autoionization, called delayed, subsequent or cascade autoionization (CA) can occur. An example is given in Table II.

Shape resonances rapidly decay into the continuum



This diagram represents ionization of a core electron via a shape resonance orbital. In the first step the core electron is excited to an orbital above the ionization threshold that has a large amplitude in the vicinity of the molecule. The second step represents separation of the electron from the molecule. The subsequent relaxation then is identical to the situation where the core electron is ionized directly. These channels, depicted in Table II, are Auger decay (AD), Auger decay with shake-up (ASU), and double Auger decay (DAD). Auger decay also can be followed by cascade autoionization.

For AD the molecule is left in a 2-hole state with a +2 charge, but the +1 ion also can be produced by coupling of the shape resonance to the valence electron ionization continuum. The core hole shape resonance then relaxes by interchannel decay (ICD). AD and ICD can be distinguished by the



ionic products and the electron energies. AD produces the  $+2$  ion and a low-energy photoelectron and a high-energy Auger electron. ICD produces a  $+1$  ion and a high-energy photoelectron (Poliakoff et al. 1989a).

The time between the escape of the electron from the shape resonance, or from the molecule if there is no shape resonance, and Auger decay of the core hole may be sufficiently short to allow the outgoing photoelectron to participate in the Auger process. This participation can be pictured as an interaction between the Auger electron and the photoelectron and is studied under the rubric "post-collision interaction" (Schmidt 1987).

Higher-order processes contribute in both the excitation of the core electron and relaxation of the core hole. These multi-electron processes are significant because of the strong perturbation caused by the creation or the annihilation of a core hole. In these processes, additional electrons are excited (shake-up) or ionized (shake-off). Two electron processes, double autoionization and double Auger decay, were mentioned above. The final states reached in core hole decay may be excited states and also may autoionize. It is clear that excitation of a core electron and the relaxation of the core hole provide many paths leading to multiple-electron excited states. These states have a unique chemistry relative to the single-electron excited states produced by arc lamp, laser, or vacuum ultraviolet (VUV) excitation.

The study of core hole autoionization has been termed deexcitation electron spectroscopy (DES) (Eberhardt et al. 1986b, 1986c). This spectroscopy provides information about the dynamics of excitation and decay and about charge transfer and screening for coordinated molecules (Eberhardt 1986c). Single-electron emission in autoionization, Auger decay, or cascade autoionization can be detected readily by electron spectroscopy since well-defined peaks in an electron energy spectrum are produced by these processes. Double-electron emission events are more difficult to detect because the kinetic energy is shared by the two electrons to produce a broad continuous distribution. Observation of low-energy electrons (threshold electrons) or electron-electron or electron-ion coincidence techniques are needed to pick out the multiple-electron processes (Nenner et al. 1988).

Studies have demonstrated that the electronic relaxation depends upon the location of the core hole site and the configuration of the core hole excited state. The important feature is that the core hole is localized on a specific atom and this localization is projected onto the valence electrons in the decay process. Molecular Auger spectra thus present a view of molecular electronic structure from the perspective of particular atoms in a molecule. The spectra therefore can serve to identify particular molecules and functional groups, to distinguish between localized and delocalized bonding, and to measure orbital atomic populations for various atoms in a molecule (Rye and Houston 1984). This localization and the projection onto the valence