LEGIBILITY NOTICE

A major purpose of the Technical Information Center is to provide the broadest dissemination possible of information contained in DOE's Research and Development Reports to business, industry, the academic community, and federal, state and local governments.

Although a small portion of this report is not reproducible, it is being made available to expedite the availability of information on the research discussed herein.

1

ORNL/M-1028

BC DOESR1.DOC 11/21/89

United States Department of Energy

Workshop on Future Opportunities for Research in Atomic, Molecular, and Optical Sciences

Berkeley, California, November 7, 1989

ORNL/M--1028

DE90 004891

Report of the Panel on

Atomic and Molecular Science with Synchrotron Radiation

Tomas Baer, University of North Carolina

Bernd Crasemann,* University of Oregon

Joseph L. Dehmer, Argonne National Laboratory

Hugh P. Kelly, University of Virginia

Manfred O. Krause, Oak Ridge National Laboratory

Dennis W. Lindle, National Institute of Standards and Technology

*Discussion Leader

Research sponsored by the Division of Chemical Sciences/Office of Basic Energy Sciences, US Department of Energy under contract DE-AC05-84OR21400 with the Martin Marietta Energy Systems, Inc.

Atomic and Molecular Science with Synchrotron Radiation

INTRODUCTION

The electromagnetic radiation emitted by electrons that move at relativistic velocities under transverse acceleration in synchrotrons and storage rings has unique properties (Sokolov and Ternov, 1968; Schwinger, 1946, 1949). Although predicted as early as 1898 and first observed in 1947, the radiation was initially considered but a nuisance factor that limits the capability of circular electron accelerators. Only within the last three decades has the realization grown that synchrotron radiation sources, the only ones known to man that provide a continuous spectrum from the infrared to the hard x-ray and even gamma-ray region, offer powerful and unique opportunitites for research in a vast range of areas of science and technology (see, e.g., Winick and Doniach, 1980).

The potential of synchrotron radiation in atomic physics research was first revealed quite strikingly through a classic experiment conducted by Madden and Codling on the National Bureau of Standards storage ring SURF in 1963; a straightforward absorption measurement led to the discovery of doubly excited, autoionizing states of He, which proved to be of crucial importance for the understanding of electron correlation effects in atoms (Madden and Codling, 1963; Cooper et al., 1963). Since that time, increasing use has been made of synchrotron radiation in investigations of atomic and molecular problems (see, e.g., Crasemann

and Wuilleumier, 1984, 1985; McKoy et al., 1984; Dehmer et al., 1987; Nenner and Beswick, 1987). Nevertheless, applications in this field have lagged behind more widespread use in others, such as surface and solid-state physics, crystallography, and biophysics to name a few. The primary reason for this fact is that atomic and molecular targets must usually be in the gas phase, and their tenuity coupled with the relevant cross sections and branching ratios makes even the imposing flux of synchrotron radiation from bending-magnet sources only barely adequate for some measurements and places the most tantalizingly promising experiments beyond the horizon of attainability.

This situation has changed drastically with the advent of insertion devices---wigglers and undulators---which have recently been coming into increasing use (Brown et al., 1983). These devices, periodic arrays of magnets placed in a straigt section of a storage ring, greatly enhance the intensity of synchrotron radiation and modify its spectral distribution, concentrating the output in the most desirable spectral regions. A new, "third" generation of synchrotron radiation sources, now under construction or on the drawing boards in several countries, will rely primarily on insertion devices for the production of radiation, and is designed ab initio to do so. The first of these new sources expected to come on-line in the United States is the Advanced Light Source in the Lawrence Berkeley Laboratory, to be followed by the Advanced Photon Source in the Argonne National Laboratory. These facilities, in addition to some of those already in existence, will offer opportunities for important new research in atomic and molecular science, a few of which are surveyed in the

present Report. The original scientific case made for atomic and molecular science played a significant part in the decision to build such advanced light sources. In turn, once on line, these light sources will allow us to realize these possibilities.

SCIENTIFIC OPPORTUNITIES

The global frontiers of atomic and molecular science, where knowledge is bounded by lack of experimental information and theoretical understanding, might be crudely characterized as falling into some broad categories which include

* The STRUCTURE of atoms and molecules and the DYNAMICS of their interaction with radiation and matter---especially near energy thresholds,

* MANY-BODY EFFECTS: electron-electron correlations and other phenomena that transcend independent-particle models,

* RELATIVISTIC AND QUANTUM-ELECTRODYNAMIC EFFECTS including those due to the Breit interaction, self energy and vacuum polarization.

In each of these categories, important classes of investigations will become possible with the extraordinary intensity and brightness of synchrotron-radiation beams from the new sources. Some of the most clearly evident topics can be grouped according to experimental research techniques as follows:

* Absorption spectroscopy
  - Absolute cross sections
  - Edge structure
  - X-ray circular dichroism

* X-ray scattering
  - Absolute scattering probabilities
  - Depolarization of resonance fluorescene
  - Angular distributions

* X-ray fluorescence
  - Polarization/angular distributions
  - Chemical shifts
  - Multi-electron effects
* Visible-UV fluorescence
  - Molecular fragmentation
  - Molecular vibration/rotational resolution

* Photoelectron spectroscopy of neutral atoms and molecules, excited atoms, ions and transient species
  - Cross sections
  - Angular and spin distributions
  - Multielectron effects
  - Shape and autoionizing resonances
  - Post-collision interaction
  - Coincidence studies
  - Two-color experiments

* Auger-electron spectrometry
  - Auger yields
  - Energy levels of multiply charged ions
  - Satellites and many-electron effects
  - Time-resolved studies
  - Threshold resonances
  - Cascade effects
  - Post-collision interaction
  - Angular distributions, alignment
  - Spin-resolved spectrometry
  - Coincidence studies

* Ion spectroscopy
  - Molecular fragmentation
  - Multiple ionization
  - Ion coincidence studies
  - Studies of trapped ions
  - Two-color experiments

In the following sections we elaborate on some of these topics, pointing out selected areas of investigation that appear to hold particular promise.

TECHNIQUES AND EXPERIMENTS

Electron Correlation in Atoms

Many-electron processes induced by photon impact epitomize the limitations of the conventional, most tractable models of atomic structure. Because the photon-electron interaction is described in first-order perturbation theory by a one-electron operator, frozen-core central-field models do not predict processes in which more than one electron changes state. The study of such correlation processes consequently is challenging, and relevant to the development of more realistic theory (Becker et al., 1988). Synchrotron-radiation studies of photoelectron and Auger satellites, especially of their dependence on incident x-ray energy near threshold (Fahlman et al., 1984; Becker et al., 1986; Krause and Caldwell, 1987; Wijesundera and Kelly, 1987), have made it possible to differentiate between intrinsic electron correlation effects, treatable in terms of configuration interaction (Heimann et al., 1987), interchannel coupling (Smid and Hansen, 1984), and dynamic correlations produced by the response of the atomic electrons to the changing potential as the ionized atom relaxes (Crasemann, 1987; 1989 and references therein). Near-threshold studies of photoelectron and Auger satellites have indicated that useful insights into these many-body effects can be gained, but have suffered from the intensity limitations of present sources (Armen et al., 1985). The high flux of photons from the new sources will permit significant progress to be made in this field and allow the extension of these studies, that have

emphasized the rare gases, to virtually every element in the periodic table .

Particularly exciting will be the application of threshold time-of-flight photoelectron spectrometry (Baer et al., 1979) to the behavior of deep core levels (Heimann et al., 1987). By this technique, zero-energy electrons are detected, yielding results that are uniquely sensitive to both threshold effects and direct multiple ionization. Such investigations, which will be possible with much greater precision and for deep core levels with the new ultra-short synchrotron-radiation pulses, have revealed the existence of dramatic "correlation-state" structures above and below core-level ionization thresholds, providing a new and unexpected wealth of electronic structural information (Heimann et al., 1986; 1987; Becker et al., 1988). Especially striking are the sensitivity of the method and the importance of high-resolution studies. The latter will be greatly enhanced with insertion-device sources. With sub-natural-linewidth excitation, threshold photoelectron spectrometry has the potential for dramatic improvement in detailed measurements of the behavior of near-threshold cross sections and resonances.

While multielectron effects have heretofore been studied primarily through photoelectron and Auger spectrometry, x-ray emission also exhibits multivacancy effects (Deslattes et al., 1983), and processes at threshold can be studied by analyzing the decay fluorescence of the ion. Very little work has been completed in this area, primarily because of the low signals associated with the fluorescence process, generally two orders of magnitude below photoelectron signals. With stronger sources, one will be

able to employ fluorescence analysis to determine the branching ratios of the excited states of the ions and the alignment of these states. Because of the selectivity of the fluorescence process and its independence of electric fields, the technique is a natural for use at threshold. An example is the fluorescence analysis of the $Cd^+ {}^2D_{5/2}$ ion formed by removal of a d electron at the autoionizing resonances just above threshold (Goodman et al., 1985). This is an energy regime which cannot be explored with photoelectron spectrometry because of difficulties with metal deposition at low levels. While this process can be observed in Cd with success, the same is not true for other atoms. Removal of a d electron from Cd has a large cross section. This is not generally the case, however, especially at threshold. Recent experiments on measurements of alignment in He^+ (Jimenez-Mier et al., 1986) and photoabsorption of NO (Poliakoff et al., 1989) reveal that this technique can deliver a wealth of new information if the low intensity levels can be overcome. With the new sources, fluorescence analysis can be expected to become a standard procedure in both atomic and molecular photoionization.

A related payoff of near-threshold excitation is the ability to "turn off" the multielectron channels, producing x-ray emission spectra free of satellites. These simplified spectra allow determination of relative fluorescence yields, linewidths, and peak shapes in an unambiguous way, and provide a reference for the study of correlation satellites. No other technique can attain this result.

Atomic Inner-Shell Excitation and Decay Mechanisms

Intimately related to the question of electron-electron Coulomb correlations is the issue of the mechanisms that lead from atomic excitation or ionization to the various deexcitation channels (see, e.g., Crasemann, 1985). As discussed in more detail below, photoexcitation and decay can occur as a single quantum process at threshold. At high incident x-ray energies, on the other hand, a two-step process is attained asymptotically: decay is separated and insulated from excitation by a relaxation phase. It has been shown that these two, apparently drastically different dynamical mechanisms are linked by a correlation phenomenon known as post-collision interaction (Tulkki et al., 1987; Armen et al., 1987a), and that the entire evolution of atomic inner-shell dynamics, from threshold to high energy, can be described consistently in terms of resonant scattering theory (Åberg, 1980, 1981; Åberg and Tulkki, 1985). Present sources have made it possible to gain relatively crude information on such post-collision interaction phenomena as the "no-passing effect" (Armen et al., 1987b) and photoelectron recapture (Eberhardt et al., 1988; Tulkki et al., 1990); much more remains to be learned with more intense sources, including the predicted but never yet observed dependence of the post-collision-interaction line shape on the angle between photoelectron and Auger-electron momenta (Armen, 1988).

It was briefly indicated above that, in the vicinity of core-level energy thresholds, atomic photoexcitation and the ensuing x-ray or Auger-electron emission can occur as a single

second-order quantum process, the resonant Raman effect; here the intermediate state is virtual, and there is no relaxation phase. The width of the emitted x-ray or Auger line reflects that of the incident radiation and hence can be much narrower than the natural lifetime of the initial hole state. As one tunes the energy of the incident x rays through a broad core level and observes a characteristic resonant x-ray or Auger line, the energy of the line displays linear dispersion with incident x-ray energy, and the intensity of the line traces out the Lorentzian shape of the core hole state.

With present-day synchrotron-radiation sources, the existence of resonant Raman transitions in atomic inner shells has been demonstrated (Eisenberger et al., 1976; Brown et al., 1980), but signal-to-noise ratios have been so poor as to preclude a thorough investigation of this phenomenon beyond the original pilot study. The next-generation facilities presumably will permit a study of this intriguing phenomenon, both for the crucial role it plays in the evolution of atomic inner-shell dynamics (discussed above) and for applications, such as providing a source of sub-natural-linewidth radiation.

One application of the resonant Raman effect is to determine the "anatomy" of x-ray absorption edges. Absorption cross sections can be decomposed into individual components due to electron excitation to valence or Rydberg states and to ionization to the continuum. This could lead to an explanation of long-standing anomalies in absorption cross sections which have not yet been ascribed to either many-body or solid-state effects.

Another set of possible applications of atomic inner-shell

Raman spectrometry arises from the fact that the envelope of atomic core hole-state energies can be traced, leading to information not only on their exact width but also on their detailed shape. It will be possible to look at deviations from Lorentzian line shapes and to study their origin. The effect of extraatomic influences on widths can be studied. For example, it is well-known that atomic energy-level shifts caused by metallic environments can open intense radiationless channels that grossly alter hole-state widths (Yin et al., 1973); such effects could be studied in detail, especially near thresholds, and traced to modifications of the wave functions in the pertinent Auger matrix elements. It is not inconceivable that resonant Raman spectrometry in the x-ray regime may some day become as useful a tool in atomic physics and materials science as optical Raman techniques now are in biophysics and chemistry.

Timing Experiments

One of the unique characteristics of synchrotron radiation is its time structure which consists of a train of sub-nanosecond pulses separated by times that vary from 2 to >1000 ns, depending on the mode of operation. This time structure is highly suited for a number of time-resolved studies, among them dynamical studies of autoionization, laser-synchrotron double-resonance spectroscopy (mentioned above in the context of molecular physics), and electron time-of-flight analysis.

As one example we consider time-resolved autoionization studies. Autoionization has been investigated for many years by both chemists and physicists. The major experimental approaches

have included the study of absorption, of photoionization spectra, angle-resolved photoelectron spectra as a function of the incident-photon energy, and constant-final-state spectra (final-state excitations spectra). Results have been interpreted in terms of the quantum-defect theory in its various formulations.

An important aspect of the resonance features is their width, which is related to the rate of autoionization. Limited spectral resolution, however, limits width measurements to autoionization lifetimes of less than approximately 10 ps. Longer lifetimes could heretofore only be investigated by either time-resolved measurements or by the use of high-resolution VUV lasers. Synchrotron radiation, however, is ideal for such real-time investigations of long-lived (>30-ps) autoionization processes. Such studies could either be carried out by measuring the arrival-time distribution of electrons, or by a more sophisticated two-color experiment in which a picosecond laser, whose pulse structure is mode-locked to the RF frequency of the synchrotron, is used to probe the autoionizing state as a function of delay time between the synchrotron pump and the laser probe pulse. This type of time-resolved studies would extend the knowledge of autoionization rates by orders of magnitude and allow for the theoretical analysis of weakly coupled systems. Among these are vibrational autoionization states of diatomic molecules in which the nuclear motions are coupled to the electronic motion in a breakdown of the Born-Oppenheimer approximation. There are many sharp autoionization features in atoms as well for which real-time analysis of the rates will be possible. The latter

include autoionizing states that can be created by double excitation through two-color schemes.

Coincidence measurements also fall into the category of timing experiments. For many years coincidence techniques have formed a basic tool in nuclear physics. Their application to atomic and molecular physics has been less widespread, with notable exceptions. In chemistry, coincidence spectrometry has been used quite effectively to study ionic dissociations (Baer et al., 1986), and ion-molecule reactions with state-selected reactants (Baer et al., 1989). Electron-fluorescence coincidence studies have been fruitful (Klapstein and Maier, 1981) and core-excited levels have been investigated by this technique (Larkins et al., 1988). Even some triple coincidences are being measured (Bland, 1987; Stankiewicz et al., 1989). Nevertheless, these experiments are very difficult because of the very low signals associated with coincidence studies. That is unfortunate, because much information about electron correlations can only be elucidated in the coincidence mode. Of the types of coincidences which are important, that between ions and photoelectrons is the most obvious. Coincidences between photoelectrons and Auger electrons or fluorescence photons from the decay of the excited ion, however, also contain valuable information which is lost when the signal from either is averaged. An example is the coincidence between the 11-eV photoelectron and the 2.8-eV Auger electron in Pb following photoionization at 36 eV (Krause et al., 1986). Information about the correlation between these two electrons is invaluable in determining the accuracy of the atomic wave function. With the more intense synchrotron-radiation sources, coin-

cidence studies in atomic and molecular physics should become routine. The high brightness can overcome the weak signals, primarily by an increase of the signal-to-noise ratio and greater efficiency of the coincidence arrangement. Coincidence measurements are essential for angular correlation studies between various ejected particles as well as for the determination of line shapes in post-collision interaction, described above.

X-Ray Scattering

A tunable, monochromatic, high-brightness x-ray source will permit fundamental experiments in x-ray scattering by atoms and molecules. Because x-ray scattering cross sections are even smaller than x-ray emission cross sections, enhanced incident x-ray intensity is even more crucial for these measurements.

In addition to much needed measurements of total scattering probabilities, differential measurements can be performed. Two examples are resonant depolarization of elastic x-ray scattering and angular-distribution measurements of scattered x rays. Initial success in studying resonant depolarization effects in Ar and a few molecules has been achieved recently (P. L. Cowan et al., unpublished), where significant species-dependent effects have been observed. The work provides a basic test of scattering theory as it applies to x-ray resonant processes.

One singular example of the fruitful application of synchrotron radiation to scattering experiments is the recent work on nuclear Bragg diffraction of hard x rays from the PEP storage ring at Stanford (Arthur et al., 1989). Dramatic changes were observed in the time distribution of synchrotron x rays resonantly scattered

from ^{57}Fe nuclei in a crystal. These changes are caused by small shifts in the effective energies of the hyperfine-split nuclear resonances, an effect of dynamical diffraction for the coherently excited nuclei in the crystal. This type of investigation, previously confined to the quantum optics regime, offers promise for new fundamental insights and unique applications.

Properties of Ionized Species

Ion yields from the impact of photons in the various regions of the shell structure remain essentially uncharted---especially in the threshold region---but for a few experiments with classical x-ray sources (Carlson et al., 1966, and references therein) and some exploratory experiments with synchrotron radiation (Short et al., 1986). Basic results on degrees of ionization in atoms and fragmentation of molecules need to be determined to complement x-ray emission and photoelectron spectrometry measurements.

In molecular physics, ion-coincidence studies through which detailed fragmentation patterns for molecules can be determined will be valuable. New observations of ion angular distributions from free molecules (Yagishita et al., 1989) suggest that detailed information on alignment processes following x-ray absorption can be monitored in a unique way. Angle-resolved measurements on ions are much less efficient than integral measurements, thus requiring a much more intense x-ray source. The use of ion time-of-flight analysis can be anticipated, for which the excellent time structure of the new machines will permit improved energy-distribution measurements, as discussed above.

Two thrusts in ion-yield work with molecules are of interest. First, the ansatz of "Coulomb explosion" can be tested for molecules with deep inner-shell holes. Second, the effects of energy redistribution following x-ray absorption can be studied, thereby testing unimolecular models for pre-fragmentation energy transfer.

Photoionization studies of atomic ions are generally beyond the capabilities of the present photon sources and will become an important use of the new sources over the entire available spectral region (Jones et al., 1988). Work in this area is just beginning in Europe (Wuilleumier, 1989). The central difficulty is obtaining sufficient target densities. A wiggler or undulator will be essential for such work, and the high brightness of the new facilities will be crucial, because most ion sources or traps limit the ions to a very small region of space ($<<1$ mm^3). Scientific justification for initiating studies of the interactions of photons with highly charged ions stems from the fact that, except for a few measurements on singly charged species, there is no body of experimental work on ion targets, yet there is undeniable relevance of such work to fundamental atomic science, laboratory and astrophysical plasma behavior, and advanced laser concepts. There are many theoretical calculations, but these need yet to be tested.

The capabilities of ion storage techniques, current and projected, to provide targets for the photoionization of ions with synchrotron radiation has been reviewed recently by Church (1989). Exploratory measurements with bending-magnet radiation

have been performed on the storage of multicharged Ar ions in a Penning trap (Church et al., 1987). Other schemes utilizing electron-beam ion traps (EBIT's) or ion storage rings are under consideration by several groups in the United States and abroad.

Studies of the properties of highly ionized species are of considerable theoretical and practical importance. For example, it was discovered some time ago by Pratt and coworkers (1973) that, in the limit of high photon energy, atomic photoionization cross sections depend only on those parts of the electron wave functions which lie within a Compton wavelength of the origin. Thus, high-energy photoeffect cross sections in a Coulomb potential are expected to vary as the fifth power of the atomic number for s states, and as the seventh power for p states, for instance. Measurements can therefore yield information on the properties of the wave functions at small distances which are relevant, inter alia, to parity non-conservation and hyperfine structure (Church, 1989). Many aspects of the structure of highly charged ions are known only from theory and have never been verified through measurements.

The study of transitions in highly ionized atoms can reveal extremely interesting relativistic and quantum electrodynamic effects (Johnson and Cheng, 1985; Chen, 1985). To give but one example, the high-spin states of three-electron ions tend to be metastable; a major decay channel can be that of Auger transitions made possible only through the Breit interaction, i.e., the lowest-order relativistic correction to Coulomb's law which includes the current-current interaction and retardation (Chen and Crasemann, 1987). Investigations of the structure and transitions

of few-electron ions can thus be of great value for the test of fundamental concepts. In a more practical context, they are important for the understanding of astrophysical and laboratory-made plasmas. One can envision extremely fruitful uses of synchrotron radiation to probe trapped ions for these purposes.

Electronic Properties of Actinide Atoms

Except for the innermost atomic levels and transition energies, the electronic properties of the atoms of the entire actinide series have remained essentially unexplored. This holds true even for such basic information as the electron binding energies of the outer electrons; yet this is the only class of atoms that allow us to study the 5f electrons and 6d electrons. These electrons, which dominate the atomic, chemical, and solid-state properties of the actinides, are expected to display strong correlation effects due to their many-electron environment as well as considerable relativistic and quantum electrodynamic effects. In fact, the various QED contributions are of a similar relative magnitude as for the innermost shells according to initial theoretical calculations (Huang et al., 1976; Chen et al., 1981), amounting to about 50 meV (1 Kcal) for 5f electrons. Using electron and ion spectrometric methods, it will become possible with the advent of the new advanced photon sources to embark into an entirely new endeavor and explore the electronic structure and dynamics of the heaviest elements known to man. Experimental data of the various atomic properties in this frontier region will be invaluable to elucidate the role of many-electron, relativistic and quantum electrodynamic interactions, to provide reference

points for advanced theory, and to extend our predictive powers beyond the presently discovered elements.

Total Photon-Interaction Cross Sections

Accurate x-ray absorption cross sections are needed in many areas of science and technology. Existing survey compilations (e.g., Henke et al., 1982) generally do not include the regions near core-level thresholds, where the most interesting deviations from theoretical predictions occur. Synchrotron-radiation sources can be most useful in filling these information gaps. The fact that atomic absorption spectrometry with such sources can lead to a detailed understanding of the shape of inner-shell absorption edges has already been demonstrated (Breinig et al., 1980). There is an even greater scarcity of x-ray absorption data for molecules, and virtually none are available for ions.

Molecular Physics

High-resolution studies ($\Delta\lambda < 0.1$Å) of the decay dynamics of selectively excited molecular states is becoming possible, probing the interaction of electronic and nuclear motions in molecular fields and lending insight into fundamental mechanisms of molecular physics. The technology is now available to select individual autoionizing states with specified electronic and vibrational quantum numbers and to perform angle-resolved photoelectron spectroscopy on the ejected electrons with sufficient resolution to determine the electronic and vibrational states of the decay products, including bending vibrations in addition to overtone and combination bands. New information can thus be gained that is very important for advancing our basic understan-

ding of molecular photophysics. For ionic state selection, electron-ion coincidence techniques are required that have been used effectively in synchrotron experiments (e.g., Nenner et al., 1980). For neutral molecules, pump (synchrotron radiation in the ultraviolet) and probe (laser) experiments are now becoming possible, but have not yet been performed. Studies of electronic, vibrational, rotational and spin-orbit autoionization phenomena are becoming possible with very high wavelength resolution at Daresbury (West et al., in press), Stoughton (Krause et al., 1989), and soon at the ALS.

Studies of vibronic coupling in excited molecular states hold much promise (Köppel et. al, 1984; Krummacher et al., 1983). Branching ratios and photoelectron asymmetry parameters for individual vibronic components in valence and inner-valence spectra need to be determined. Much of the present understanding of molecular photoelectron spectra is limited by lack of consideration of this mechanism. New insight into the dynamics of excited molecular states is likely to be gained through use of synchrotron radiation to study this active problem.

Fluorescence studies of molecular structure hold great promise; the new facilities will lend themselves to high-resolution x-ray and VUV emission studies of atoms, molecules, and ions that will have substantial impact in this area (Poliakoff et al., 1986). Initial results obtained on a dedicated beam line at the NSLS suggest new opportunitites that can be brought to fruition once significant improvements in incident x-ray intensity are attained. One significant new result is the discovery of strongly

polarized x rays emitted from randomly oriented molecules following selective near-threshold excitation (Lindle et al., 1988). The effect has been found to be sensitive to molecular geometry and molecular-orbital symmetry, for both occupied and unoccupied states. First results were for valence x-ray emission, whereas recent work has shown that even molecular core-to-core x-ray emission can be polarized following selective excitation with synchrotron radiation. This new technique holds promise for several areas of study. One application would be to determine the symmetries of atomic sites in larger, less well characterized molecules, perhaps in aqueous solution. Another potential experiment is to study oriented molecules on crystal surfaces. The intensity and brightness (with a spot size <1 mm^2) of the new sources will be required for this work.

A new direction related to polarized x-ray emission is the measurement of angular distributions of x-ray emission. Such studies can provide complementary information to that obtainable with polarized x-ray emission spectrometry, because x-ray angular distributions also will be sensitive to orientation, geometry, and orbital symmetry. Angular-distribution experiments will be particularly helpful for studying non-dipole effects in gases and orientational effects in solids. These possibilities require a dedicated, very intense source of x rays.

Another new result in x-ray emission made possible by selective, monochromatic excitation is the discovery of chemical shifts specific to individual molecular valence orbitals (Perera et al., 1987). Upon near-threshold excitation, x-ray emission energies are seen to shift appreciably by an amount (1-3 eV) that

depends upon the valence molecular orbital involved, due to differences in electrostatic screening. Measurements so far have been very slow, due to count-rate limitations. The effect is expected to become useful in tests of accurate orbital calculations.

Recent measurements near the N K-shell threshold of N_2 have shown that the molecular ions or fragments left in excited states after decay of the K-shell vacancy emit VUV fluorescence (Poliakoff et al., 1989). Because the fluorescence is emitted subsequent to K-shell relaxation, the natural linewidth of the core hole does not affect the emitted radiation. Vibrational and rotational resoluton can therefore be achieved in monitoring the ions or neutrals produced following core-level absorption. The possibility thus exists of studying photoionization and photofragmentation products in a novel way with unprecedented resolution. Because of the multitude of decay pathways available for deep core-level holes states, a very small fraction of x-ray absorption events will lead to any particular VUV fluorescence process, and a very intense incident-x-ray source is required.

Studies of fragmentation of selectively core-excited molecules are a promising area of research (see, e.g., Nenner and Beswick, 1987; Hanson, in press; Eberhardt et al., 1986, Larkins et al., 1988) that will benefit greatly from brighter sources. The objective is to characterize core-electron excitation and relaxation processes in molecules. Synchrotron radiation offers a unique means for selectively preparing excited complexes, enabling the observation of the decay paths taken under alternative

excitation conditions, e.g., with the excitation localized on different parts of the molecule. This theme will contribute to new insights in fundamental molecular physics and to understanding the selectivity of mechanims of stimulated desorption; it could also contribute to such fields as electron and x-ray microscopy and lithography and to future methods for producing integrated electronic circuit devices.

The greatly enhanced intensity of the next-generation synchrotron light sources will create the opportunity to explore a number of important species that are difficult to study for various reasons. Examples are free radicals, clusters, ions, laser-excited states, and aligned molecules.

The spectroscopy of excited atomic and molecular species through two-color experiments constitutes a vast experimental frontier. Standard photoionization studies are for the most part limited to one-electron excitation states. Two-electron excitations, observed in certain limited regions of the spectrum, are generally weak if they are produced by electron correlations (discussed elsewhere in this Report). Such states can, however, be explored by double-resonance experiments in which synchrotron radiation and laser light (including that from free-electron lasers associated with a synchrotron-radiation source) are used in a pump-probe arrangement. Whether the laser is used to prepare the excited state for synchrotron-radiation interrogation or the synchrotron radiation is used to produce the exicted state for laser interrogation, the greatly enhanced flux and focusability of the future facilities promises much greater flexibility in studying novel circumstances. Pioneering work on doubly excited

states that can be reached systematically through two-color experiments has already been carried out at the Orsay Synchrotron (Bizau et al., 1983, Wuilleumier et al., 1987) and at BESSY in Berlin with cw lasers. The use of picosecond lasers locked to the synchrotron pulse structure can be expected to enhance the signal level considerably and make such experiments a powerful new tool for excited-state studies.

Shape resonances have been studied vigorously over two decades by means of synchrotron radiation as well as other techniques (see, e.g., McKoy et al., 1984; Dehmer et al., 1987; Nenner and Beswick, 1987). Several new concepts in molecular physics have thus emerged, with substantial impact on other fields such as surface science. Yet there are several types of interactions involving shape resonances that require advanced synchrotron-radiation sources for exploration, e.g., the transfer of shape-resonant behavior by continuum-continuum coupling, shape-resonance-induced vibrational effects, and the decay of shape resonances in core-excited systems.

Other techniques of relevance to molecular science that will become increasingly important with the new synchrotron-radiation sources include measurements of the spin polarization of photoelectrons (see, e.g., Heinzmann, 1985); here prospects exist for advances in molecular systems for which new theory has become available. The study of double ionization through electron-electron coincidence studies of angular correlations will be possible with new precision and flexibility. The availability of circularly polarized synchrotron-radiation light will open new

frontiers, such as circular dichroism in the x-ray energy range. The fast time structure of the radiation entails important possibilities, some of which have been discussed in various segments of this Report.

CONCLUSION

The foregoing summary of research opportunities in atomic and molecular science with synchrotron radiation is by no means exhaustive. Without doubt, not all opportunities can be foreseen at this juncture. The Panel hopes that the examples described here may convey an impression of the richness of the field of studies that will become accessible with next-generation sources and of the great importance, for basic science as well as for technology, of the knowledge that is to be gained. These opportunities are being pursued vigorously in other countries, and it is the Panel's sincere hope that scientists in the United States will not be prevented by financial stringencies from contributing their full share to this exciting new phase of investigations.

REFERENCES

Åberg, T., Phys. Scr. 21, 495 (1980) and in Inner-Shell and X-Ray Physics of Atoms and Solids, ed. by D. J. Fabian, H. Kleinpoppen, and L. M. Watson (Plenum, New York, 1981), p. 251; T. Åberg and J. Tulkki, in Atomic Inner-Shell Physics, ed. by B. Crasemann (Plenum, New York, 1985), p. 419.

Armen, C. B., T. Åberg, K. R. Karim, J. C. Levin, B. Crasemann, G. S. Brown, M. H. Chen, and G. E. Ice, Phys. Rev. Lett. 54, 182 (1985).

Armen, G. B., J. Tulkki, T. Åberg, and B. Crasemann, Phys. Rev. A 36, 5606 (1987a).

Armen, G. B., S. L. Sorensen, S. B. Whitfield, G. E. Ice, J. C. Levin, G. S. Brown, and B. Crasemann, Phys. Rev. A 35, 3966 (1987b).

Armen, G. B., Phys. Rev. A 37, 995 (1988).

Arthur, J., G. S. Brown, D. E. Brown, and S. L. Ruby, Phys. Rev. Lett. 63, 1629 (1989).

Baer, T., P. M. Guyon, I. Nenner, A. Tabche-Fouhaille, R. Botter, L. F. A. Ferreira, and T. R. Govers, J. Chem. Phys. 70, 1585 (1979).

Baer, T., Adv. Chem. Phys. 64, 111 (1986).

Baer, T., Ann. Rev. Phys. Chem. 40, 637 (1989).

Becker, U., R. Hölzel, H. G. Kerkhoff, B. Langer, D. Szostak, and R. Wehlitz, Phys. Rev. Lett. 56, 1120 (1986).

Becker, U., E. Langer, H. G. Kerkhoff, M. Kupsch, D. Szostak, R. Wehlitz, P. A. Heimann, S. H. Liu, D. W. Lindle, T. A. Ferrett, and D. A. Shirley, Phys. Rev. Lett. 60, 1490 (1988).

Bizau, J. M., B. Carré, P. Dhez, D. Ederer, P. Gerard, J. C. Keller, P. Koch, J. L. LeGouët, J. L. Picqué, G. Wendin, and F. Wuilleumier, in XIII ICPEAC, Abstracts of Contributed Papers, edited by J. Eichler, W. Fritsch, I. V. Hertel, N. Stolterfoht, and U. Wille, Berlin, 1983, p. 27.

Bland, J. H. D., Mol.Phys. 61, 725 (1987).

Breinig, M., M. H. Chen, G. E. Ice, F. Parente, and B. Crasemann, Phys. Rev. A 22, 520 (1980).

Brion, C. E., private communication (1989).

Brown, G. S., M. H. Chen, B. Crasemann, and G. E. Ice, Phys. Rev. Lett. 45, 1937 (1980).

Brown, G. S., K. Halbach, J. Harris, and H. Winick, Nucl. Instr. Meth. 208, 65 (1983).

Carlson, T. A., W. E. Hunt, and M. O. Krause, Phys. Rev. 151, 41 (1966).

Chen, M. H., B. Crasemann, M. Aoyagi, K.-N. Huang, and H. Mark, At. Data Nucl. Data Tables 26, 561 (1981).

Chen, M. H., in Atomic Inner-Shell Physics, ed. by B. Crasemann (Plenum, New York, 1985), Chap. 2.

Chen, M. H., and B. Crasemann, Phys. Rev. A 35, 4839 (1987).

Church, D. A., S. D. Kravis, I. A. Sellin, C. S. O, J. [illegible]. Levin, R. T. Short, M. Meron, B. M. Johnson, and K. W. Jones, Phys. Rev. A 36, 2487 (1987).

Church, D. A., Nucl. Instr. and Meth. B43, 441 (1989).

Crasemann, B., ed., Atomic Inner-Shell Physics (Plenum, New York, 1985).

Crasemann, B., and F. Wuilleumier, PHYSICS TODAY, June 1984, p. 1, and in Atomic Inner-Shell Physics, ed. by B. Crasemann (Plenum, New York, 1985), Chap. 7.

Crasemann, B., J. Physique C 9, 389 (1987); Comments At. Mol. Phys. 22, 163 (1989).

Dehmer, J. L., A. C. Parr, and S. H. Southworth, in Handbook on Synchrotron Radiation, Vol. 2, ed. by G. V. Marr (North-Holland, Amsterdam, 1987), Chap. 5, p. 241.

Deslattes, R. D., R. E. LaVilla, P. L.Cowan, and A. Henins, Phys. Rev. A 27, 932 (1983).

Eberhardt, W., E. W. Plummer, C. T. Chen, R. Carr, and W. K. Ford, Nucl. Instrum. Meth. A246, 825 (1986).

Eberhardt, W., S. Bernstorff, H. W. Jochims, S. B. Whitfield, and B. Crasemann, Phys. Rev. A 38, 3808 (1988).

Eisenberger, P., P. M. Platzman, and H. Winick, Phys. Rev. Lett. 36, 623 (1976).

Fahlman, A., M. O. Krause, T. A. Carlson, and A. Svensson, Phys. Rev. A 30, 812 (1984).

Goodman, Z. M., C. D. Caldwell, and M. G. White, Phys. Rev. Lett. 54, 1156 (1985).

Hanson, D. M., in Advances in Chemical Physics, ed. by S. A. Rice and I. Prigogine (Wiley/Interscience, New York), in press.

Heimann, P. A., U. Becker, H. G. Kerkhoff, B. Langer, D. Szostak, R. Wehlitz, D. W.Lindle, T. A. Ferrett, and D. A. Shirley, Phys. Rev. A 34, 3782 (1986).

Heimann, P. A., D. W. Lindle, T. A. Ferrett, S. H.Liu, L. J. Medhurst, M. N. Piancastelli, D. A. Shirley, U. Becker, H. G. Kerkhoff, B. Langer, D. Szostak, and R. Wehlitz, J. Phys. B 20, 5005 (1987).

Heinzman, U., in Fundamental Processes in Atomic Collisions, ed. by H. Kleinpoppen, J. S. Briggs, and H. O.Lutz (Plenum, New York, 1985), p. 269.

Henke, B. L., P. Lee, T. J. Tanaka, R. L. Shimabukuro, and B. K. Fujikawa, At. Data Nucl. Data Tables 27, 1 (1982).

Huang, K.-N., M. Aoyagi, M. H. Chen, B. Crasemann, and H. Mark, At. Data Nucl. Data Tables 18, 243 (1976).

Jiménez-Mier, J., C. D. Caldwell, and D. L. Ederer, Phys. Rev. Lett. 57, 2260 (1986).

Johnson, W. R., and K. T. Cheng, in Atomic Inner-Shell Physics, ed. by B. Crasemann (Plenum, New York, 1985), Chap. 1.

Jones, K. W., B. M. Johnson, and M. Meron, in International Symposium on Electron-Beam Ion Sources and their Applications, edited by A. Hershcovitch (American Institute of Physics Conference Proceedings No. 188, New York, 1988), p. 412.

Klapstein, D., and J. P. Maier, Chem. Phys. Lett. 83, 590 (1981).

Köppel, H., W. Domcke, and L. S. Cederbaum, in Advances in Chemical Physics, Vol. 57, ed. by I. Prigogine and S. A. Rice (Wiley/Interscience, New York, 1984), p. 59.

Krause, M. O., P. Gerard, A. Fahlman, T. A. Carlson, and A. Svensson, Phys. Rev. A 33, 3146 (1986).

Krause, M. O., and C. D. Caldwell, Phys. Rev. Lett. 59, 2736 (1987).

Krause, M. O., et al., private communication, 1989.

Krummacher, S., V. Schmidt, F. Wuilleumier, J. M. Bizau, and D. Ederer, J. Phys. B 16, 1733 (1983).

Larkins, F. P., W. Eberhardt, I. W. Lyo, R. Murphy, and E. W. Plummer, J. Chem. Phys. 88, 2948 (1988).

Lindle, D. W., P. L. Cowan, R. E. LaVilla, T. Jach, R. D. Deslattes, B. Karlin, J. A. Sheehy, T. J. Gil, and P. W. Langhoff, Phys. Rev. Lett. 60, 1010 (1988).

Madden, R. P., and K. Codling, Phys. Rev. Lett. 10, 516 (1963); J. W. Cooper, U. Fano, and F. Prats, Phys. Rev. Lett. 10, 518 (1963).

McKoy, V., T. A. Carlson, and R. R. Lucchese, J. Phys. Chem. 88, 3188 (1984).

Nenner, I., P. M. Guyon, and T. Baer, J. Chem. Phys. 72, 6587 (1980).

Nenner, I., and J. A. Beswick, in Handbook on Synchrotron Radiation, Vol. 2, ed. by G. V. Marr (North-Holland, Amsterdam, 1987), Chap. 6, p. 355.

Perera, R. C. C., R. E. LaVilla, P. L. Cowan, T. Jach, and B. Karlin, Phys. Scr. 36, 132 (1987).

Poliakoff, E. D., M. H. Ho, G. E. Leroy, and M. G. White, J. Chem. Phys. 85, 5529 (1986).

Poliakoff, E. D., L. A. Kelly, B. Space, L. M. Duffy, P. Roy, S. H. Southworth, and M. G. White, Proceeding of the Ninth International Conference on Vacuum Ultraviolet Radiation Physics, Phys. Scr. (in press) and Bull. Am. Phys. Soc. 39, 1399 (1989).

Pratt, R. H., A. Ron, and H. K. Tseng, Rev. Mod. Phys. 45, 273 (1973).

Schwinger, J., Phys. Rev. 70, 798 (1946); 75, 1912 (1949).

Short, R. T., C.-S. O, J. C. Levin, I. A. Sellin, L. Liljeby, S. Huldt, S.-E. Johansson, E. Nilsson, and D. A. Church, Phys. Rev. Lett. 56, 2614 (1986).

Smid, H., and J. E. Hansen, Phys. Rev. Lett. 52, 2138 (1984).

Sokolov, A. A., and I. M. Ternov, Synchrotron Radiation (Akademie-Verlag, Berlin, 1968).

Stankiewicz, M., P. A. Hatherly, L. J. Frasinski, K. Codling, and D. M. P. Holland, J. Phys. B 22, 21 (1989).

Tulkki, J., G. B. Armen, T. Åberg, B. Crasemann, and M. H. Chen, Z. Phys. D 5, 241 (1987); G. B. Armen, J. Tulkki, T. Åberg, and B. Crasemann, Phys. Rev. A 36, 5606 (1987).

Tulkki, J., T. Åberg, S. B. Whitfield, and B. Crasemann, Phys. Rev. A 41, 0000 (1990).

West, J. B., M. A. Hayes, A. C. Parr, J. E. Hardis, S. H. Southworth, T. A. Ferrett, J. L. Dehmer, X.-M. Hu, and G. V. Marr, in Proceedings of the Ninth International Conference on Vacuum Ultraviolet Radiation Physics, Phys. Scr., in press.

Wijesundera and H. P. Kelly, Phys. Rev. A 36, 4539 (1987).

Winick, H., and S. Doniach, eds., Synchrotron Radiation Research, (Plenum, New York, 1980).

Wuilleumier, F., D. L. Ederer, and J. L. Picqué, Adv. At. Mol. Phys. 23, 197 (1987).

Wuilleumier, F., in Proceedings of the IV European Physical Society Seminar on International Research Facilities, Zagreb, 17-19 March 1989 (to be published).

Yagishita, A., H. Maezawa, M. Ukai, and E. Shigemasa, Phys. Rev. Lett. 62, 357 (1989).

Yin, L. I, I. Adler, M. H. Chen, and B. Crasemann, Phys. Rev. A 7, 897 (1973).