

Working Group on Atomic, Molecular, and Optical Physics

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1. Introduction

Third-generation synchrotron light sources have opened up research frontiers that may hold the answers to fundamental questions about structure and dynamics in atomic, molecular, and optical (AMO) physics. The advanced spectroscopies being developed at the Advanced Light Source (ALS) give us the ability to control and probe atomic and molecular processes with unprecedented precision. In particular, the spectral resolution, brightness, broad tunability, and polarization control generate novel avenues for the study of tailored states, inner-shell processes, and nonperturbative electron interactions. Driven by the high brightness of the ALS, a whole new world of vacuum-ultraviolet (VUV) and soft x-ray physics is emerging through the development of combined techniques to excite, select, and probe atoms, molecules, and clusters.

Synchrotron-based AMO physics has a long history of producing new advances in our understanding of fundamental physical phenomena. For example, Madden and Codling, in their 1963 experiments using VUV synchrotron radiation, discovered two new series of autoionizing resonances in doubly excited helium. The characterization of these resonances led theoreticians to develop a new classification scheme for doubly excited states that resulted in a new understanding of correlated electron motion. Some of the first experiments at the ALS produced much higher resolution spectra of these same series; these new spectra appear to show signs of the elusive phenomenon of quantum chaos. This work is an example of the surprises and new physics that will be uncovered by using the unique capabilities at the ALS. These new capabilities have already resulted in significant advances and tests of fundamental assumptions in double photoionization and few-body dynamics, in inner-shell photoionization dynamics and sub-natural-linewidth spectroscopy, in doubly and triply excited states, and in the site-specific excitation and characterization of chemical activity in molecules.

In short, AMO physics at the ALS is already a vibrant activity. In less than three years, AMO research at the ALS has resulted in more than 60 refereed articles, including 12 Physical Review Letters that illustrate the breadth and depth of this field. The initial productivity has been remarkable, since it was demonstrated during a period when the relevant beamlines were first being commissioned and sophisticated end stations were still under construction. This fast start reflects the excitement and enthusiasm felt by AMO researchers who now see a wealth of new capabilities engendered by the ALS itself and by state-of-the-art beamlines and detectors.

2. Outstanding Scientific Issues

The scientific motivations in AMO physics fall into two major categories. The first involves the fundamental quest to understand basic phenomena in atomic and molecular systems in their own right. Many of these phenomena remain beyond the realm that can be successfully tackled by present-day theoretical techniques. The second category of motivations concerns atomic, molecular, and optical phenomena that impinge on other areas. Questions in sister fields of science often hinge on a determination of how an atom or molecule will behave in a specific context, often one in which the system is excited to an energy range well above that of typical electronic or chemical binding energies. In this second category, the main goal of the research is to obtain relevant reaction rates or cross sections directly, or to provide critical benchmarks to improve theoretical techniques to the point where cross sections can be calculated to the accuracy desired. In the following we discuss a number of scientific problems on the horizon in AMO science that are driven by at least one of these underlying motivations.

The substantial improvements in sophisticated new spectroscopies, which have only now become possible with the high brightness of the ALS, are already providing new challenges to existing theoretical methods. In some systems, for instance, existing theoretical predictions of three-particle break-up cross sections differ by a factor of two or more. The new high-resolution, multicoincidence experiments that can be performed at the ALS allow the essential components of complex processes to be isolated, which both simplifies and clarifies the comparison with theory. Propensities for final-state energy and momentum sharing can now be explored and unraveled for complex systems. The multidimensionality of the experimental observations also suggests the need to develop new visualization methods for the display and comprehension of complex data sets. New experimental results from the ALS not only provide an important touchstone for such developments but literally drive them. In the following discussions, we present a set of scientific problems whose solutions require the use of state-of-the-art techniques in conjunction with the characteristics of the ALS.

2.1. Photon-Ion Interactions

2.1.1 Positive Ions

More than 99.9% of the matter in the solar system exists in an ionized plasma state. Knowledge of the structure and interactions of ions therefore has both fundamental and practical importance. Because ionization by photons plays a key role in many astrophysical and laboratory plasma environments, accurate VUV and x-ray opacities are critically needed as input data for the plasma modeling. Quantitative studies of ionic photoexcitation and photoionization also serve to test and advance theoretical descriptions of atomic structure, including multichannel resonance phenomena and post-collision interactions. Studies of ions can be conveniently systematized along isoelectronic or isonuclear sequences. Such systematic studies can be used to highlight specific aspects of ionic structure and interaction. For example, as one moves from lighter systems where electron interactions dominate to heavier systems where relativistic effects are more important, the evolution of certain effects as a function of the ionic charge reveals regularities that are often difficult to spot in the spectrum of a single atom or ion. The most definitive tests of quantum electrodynamics (QED) involve transition energies in multiply ionized atomic systems. In addition, photoionization of transition-metal ions is expected to display large qualitative differences from the alkaline-earth atoms, based on hints from measurements with second-generation sources. Measurements of the ratio of multiple- and single-ionization cross sections critically test our understanding of joint electron-electron motions, which are crucial for the very existence of negative ions.

Another type of experiment for molecular ions could measure the correlated center-of-mass motion and energy sharing of the three massive particles H^+ , H^- , H^+ formed in the dissociation of a beam of excited H_3^+ using triple-coincidence techniques. These types of correlation studies can be extended to other massive three-body molecular systems, of course, and are not limited to final states where all particles are charged.

2.1.2 Negative Ions

Photoexcitation and photodetachment processes in negative ions stand out as an extremely sensitive probe and theoretical testbed for the important effects of electron-electron interactions because of the weak coupling between the photons and the target electrons. Numerous studies of outer-shell photodetachment have been conducted using lasers, but no experiment has ever been conducted on inner shells of negative ions using synchrotron radiation because of the very low count rate associated with these experiments. Negative ions present a severe theoretical challenge since the independent-electron model is inadequate for even a qualitative description of their properties. In some instances, the electron-correlation energy contribution to the electron affinity is as large or even larger than the electron affinity itself. With the high flux and brightness of the ALS, detachment resonances associated with excited-state channels well above the first threshold can now be measured for key few-body systems like H^- , He^- , and Li^- .

A permanent multi-user end station is currently being developed by the HRAMO (high-resolution atomic, molecular, and optical) group at the ALS to study photon-ion interactions at ALS Beamline 10.0.1, which is illuminated by a U10 undulator. This facility opens up new and exciting possibilities for studying either negative or positive ions, including multiply charged ions and a variety of triatomic systems. Three-body half collisions can be studied for a variety of prototypical systems as a function of the energy above a dissociation-limit threshold, even (signal permitting) as a function of the orientation of the initial molecular system relative to the polarization state of the initial photon.

This end station, when coupled with the high flux of the ALS, will be the first facility in the world that provides exciting opportunities for pioneering experiments with negative ions (including clusters).

2.2 Inner-Shell Spectroscopy of Atoms and Molecules

Recent improvements in synchrotron-radiation capabilities have generated exciting advances in atomic and molecular core-hole spectroscopy. Excitation selectivity in energy, in momentum, and in spin-polarization has opened the door to a wealth of new information. The following examples highlight some of the diverse possibilities of this broad scientific area.

2.2.1 Spin-Polarized Auger Spectroscopy

During the past two decades, spin polarization of valence photoelectrons excited by circularly polarized light has been studied actively. Owing to the absence of any intense source for circularly polarized VUV or x-ray radiation, the only inner-shell spin-polarized experiments conducted during the past three years were for xenon using the European Synchrotron Radiation Facility (ESRF), the third-generation source in Grenoble, France. When highly differential detection methods are coupled with circularly polarized light from the ALS, the spin-polarization of atomic or molecular Auger electrons in atoms and molecules makes it possible to track down the radiationless decay mechanisms of an inner-shell excitation. In some cases, this spectroscopic method can track the apportionment of both angular momentum and energy among photofragments. Such experiments test the importance of relativistic effects in the atomic or molecular structure, as well as in the photoejection process itself. They also permit a test of models of the angular-momentum coupling for states with two holes. When this experimental tool is applied to transition-metal elements, it can provide an atomic view of properties typically studied in condensed-matter experiments. This can help discern which features observed in condensed-phase experiments are already present in the gas phase; this information could be crucial as physicists attempt to understand surface magnetism, for instance.

2.2.2 Molecular “Structure-Reactivity” Relationships: High-Resolution Core-Level Electron Spectroscopy

Prediction of the chemical properties of molecular systems remains a “holy grail” of chemical physics. Recent advances at the ALS have brought us tantalizingly close to achieving this goal of inferring chemical properties (including reactivity) from high-resolution photoelectron spectroscopy. Inner-shell photoelectron spectroscopy of a molecule probes the ability of a molecule to accept charge at a selected atomic site within that molecule. The shifts in the binding energies of atomic core electrons in different molecular environments, as observed in photoelectron spectra, relate quite directly to properties that control fundamental chemical phenomena, such as acidity, basicity, rates of chemical reactions, and the relative strength of different competing chemical-reaction channels. Studies using high-resolution electron spectroscopy have literally generated a demonstrably deeper understanding of these phenomena. The capabilities of the ALS permit us to explore all implications of this link between spectroscopy and chemical behavior, in previously unimaginable detail.

Broad application of inner-shell electron spectroscopy to extract chemical insights has been frustrated by the fact that much interesting chemistry involves carbon atoms with very different chemical properties but similar ionization energies. An example is propyne (CH_3CCH) in which the range of carbon-1s ionization energies spans less than 2 eV; but remarkably, the reactivities of the three carbon atoms in this molecule differ significantly. Recent experiments at the MAX Lab at the University of Lund in Sweden and the ALS have made a major contribution that was hitherto

impossible: one can now resolve the different roles of the three inequivalent carbons as can be seen in Figure 1 (data taken at the ALS). Analysis of the measured ionization energies has generated a new view of the factors affecting chemical reactivity. A number of further investigations are expected to deeply affect our views of chemical processes at a fundamental level, with many conceivable applications. The ALS with its brightness and resolution in the low-photon-energy range, is presently, the only light source in the world where these experiments can be performed.

2.2.3 Ion- and Electron-Imaging Spectroscopies

Understanding the multibody breakup of a many-component atomic or molecular system when energy and momentum is imparted to the system by a single photon is one of the most basic problems in atomic-collision physics and chemical dynamics. The forces involved are well known, but the manner in which components react to these forces remains inadequately understood. Cold-target recoil-ion momentum spectroscopy (COLTRIMS) unravels the dynamics of a multiparticle ionization and/or dissociation process stimulated by photoionization of an atom or molecule. This method at the ALS has made it practical to construct a comprehensive map of the entire correlated final-momentum space without having to choose *a priori* particular angles or energies of one or more of the particles. The data can of course be presented in any appropriate set of coordinates (e.g., Jacobi or hyperspherical coordinates) that help to emphasize the key interactions or collective motions of components in the system. Finally, advances in visual presentation of the data immediately invite the identification of dominant ionization and dissociation mechanisms. The photon energies required are those that couple to the electronic motion of the target, precisely the UV and soft x-ray regions for which the ALS is optimized. The intensity of the ALS is critical for a successful measurement of these comparatively weak fragmentation channels. Moreover, the momentum resolution of the COLTRIMS imaging technique relies on the small spot sizes permitted by the high brightness of this third-generation light source.

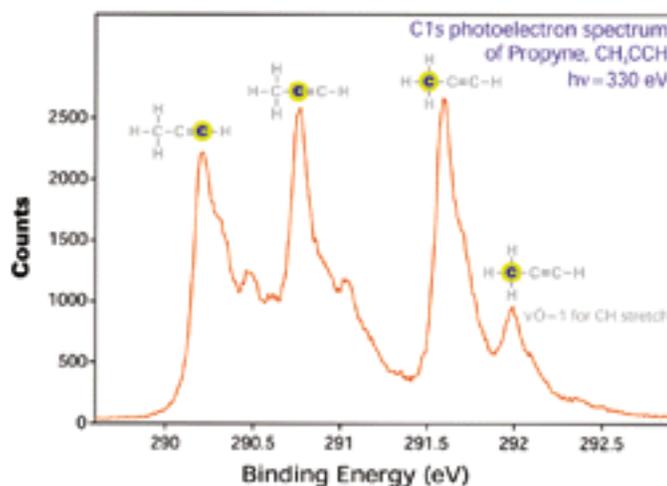


Figure 1. The carbon-1s photoelectron spectrum of propyne, CH_3CCH , measured using 330-eV photons from the Atomic, Molecular, and Optical Physics Beamline (undulator Beamline 9.0.1) at the ALS. Contributions from the three chemically inequivalent carbons in the molecule are well resolved and indicated on the figure. The ability to selectively probe individual carbon atoms within a molecule will lead to a greater understanding of chemical reactivities at the most fundamental level. [Figure courtesy of D. Thomas, Oregon State University, et al.]

Similar imaging techniques used for the energy- and angle-resolved study of photofragmentation of large molecules have provided dynamical information about the fragmentation process, such as bond-specific dissociation. These types of multi-differential studies, limited at second-generation facilities, can provide information on photochemistry induced by inner-shell ionization and multi-charged ion potentials when used at bright sources like the ALS.

2.2.4 Structure and Dynamics of Atoms and Molecules

2.2.4.1 Auger Resonant-Raman Spectroscopy

Understanding Auger decay processes induced by removal of an inner-shell electron in an atom or a molecule is a fundamental scientific issue. The challenge arises because it is generally impossible to resolve all Auger transitions, regardless of experimental resolving power, especially in molecules where vibrational and rotational substructure add complexity. This limitation derives from the fact that natural line widths associated with inner-shell ionization processes can be greater than the separation of subsequent Auger transitions, making them unobservable directly. However, the use of a narrow-bandwidth photon source, such as the ALS, in conjunction with a high-resolution electron-energy analyzer allows this limitation to be bypassed through Auger resonant-Raman measurements (discrete excitation of an inner-shell electron to a specific excited state). In this case, the natural width of the core-excited state does not determine the width of the Auger electron lines; it is controlled by the natural width of the final state alone. Since this can be negligible compared to the width associated with the core hole, Auger resonant-Raman spectroscopy (ARRS) measurements are essentially limited only by experimental factors (photon- and electron-energy resolutions). These types of measurements are thus perfectly matched for the high resolution achievable at the ALS and produce a clearer picture of inner-shell processes with a new level of detail.

For example, the vibrational progressions for molecular Auger decay can be completely resolved and mapped with unprecedented accuracy as can be seen in Figure 2 in the case of the $1s$ excitation of

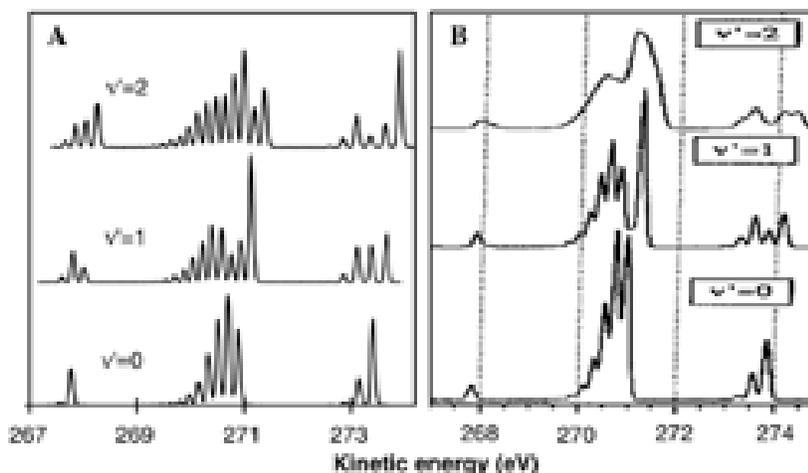


Figure 2. Decay spectra of the carbon $1s \rightarrow \pi^*$ resonance in the CO molecule. A shows spectra recently measured at the ALS. B shows calculated spectra convoluted to match the spectra measured at the National Synchrotron Light Source (NSLS). [Figure A taken from M.N. Piancastelli et al., *J. Phys. B* **30** (1997) 5677; Figure B courtesy of E. Kukk and N. Berrah, Western Michigan University, and J. Bozek, LBNL.]

CO to the molecular π^* orbital (measured recently at the ALS). These results are used to derive accurate shapes for the potential-energy curves. When coupled with imaging measurements, ARRS becomes an excellent tool for studying molecular photodissociation and other dynamic processes where the time scale of the nuclear motion is comparable with the lifetime of the core hole, in addition to discrete excitation to Rydberg series and post-collision interaction effects. It is also possible to adjust this tool by detuning the exciting photon energy from nominal resonance energy, thus decreasing the average decay time of the core-excited state. This experimental method that takes full advantage of high-resolution undulator beamlines of the ALS has the potential to allow the observation of new structure that could be associated with new physics.

2.2.4.2 Soft X-Ray Emission Spectroscopy

Pioneering work at second-generation light sources demonstrated that soft x-ray emission from gas-phase molecules following selective excitation probes their electronic structure and their nuclear geometry sensitively. The difference between selection rules for photon-in/photon-out spectroscopy and photoemission suggests that the two-photon experiments probe electronic structure in a manner complementary to electron spectroscopy. The angular-momentum character of molecular states, for instance, can be easier to discern from soft x-ray emission. In addition, the advantages of sub-natural-linewidth resonant-Raman studies presented above apply equally well to resonant photon emission (resonant inelastic scattering), as has been demonstrated in initial work at the ALS.

Extension to larger molecules, perhaps of biological, chemical synthetic, or pharmacological importance, could be feasible in some cases. The high penetrability of soft x rays in low-Z substances like air and water raises the possibility that species can be studied in realistic (“dirty”) environments. Beyond the immediate AMO scientific interest in sorting out intermolecular interactions in real systems, such studies additionally provide a deeper understanding of soft x-ray emission as a probe. This line of research thereby helps to improve the applicability of this diagnostic to other fields like molecular environmental science and catalysis.

2.2.5 Probing the Limits of Fundamental Approximations in Photoionization

Some of the standard approximations typically adopted for theoretical calculations of atomic and molecular photoprocesses are known to have limitations that require caution. The high flux and brightness available at the ALS permit new tests of these limitations. The most common assumption is the independent-particle approximation (IPA), a picture that neglects electron-electron correlations. While some spectacular failures of the IPA are well-documented in low-energy valence-shell photophysics, the IPA has often been taken for granted in the soft x-ray region, far from all thresholds. The XAMS (x-ray atomic and molecular science) group at the ALS has proven this notion incorrect for ejection of an electron from a non-S-subshell at high energies, which serves as an important warning to theorists.

Also commonly used in photoelectron spectroscopy is the dipole approximation, in which the scalar product of the light wavevector with the electron-position vector is assumed to be much less than unity; equivalently, the relevant electron-nucleus distances are assumed to be far smaller than the wavelength of the ionizing radiation. Measurements of soft x-ray atomic photoemission conducted at the ALS exhibit significant nondipole effects in the electron angular distribution. Even more striking and surprising, results have been observed for molecular species. The limitations of these standard “textbook” approximations deserve further study to delimit the extent of their failures.

2.3 Strongly Correlated Systems

Modern theoretical quandaries in atomic, molecular, and optical physics revolve around systems for which the independent-electron approximation fails qualitatively. In this sense, AMO theory faces many of the same difficulties as other fields, such as high- T_c superconductivity. Even such seemingly simple processes as two-electron photoionization of the lightest atomic species (He, H^-), using VUV photons, have proven to be a formidable challenge, owing to our limited understanding of the three-body continuum states of three charged particles. The “accepted value,” as recently as five years ago, of the peak double-photoionization cross section for helium turned out to overestimate the correct result by more than 25%. A rich variety of two-electron excited-state resonances also exist in helium, in which the electrons move jointly as a correlated pair. The high intensity of the ALS in the VUV and soft x-ray ranges, combined with a detection technique that measures the three-dimensional momentum vectors of all particles after double photoionization, has recently allowed advances in the understanding of the dynamics of this few-body breakup.

An intellectual challenge that remains to be understood for helium is: “Where is the chaos?” The classical dynamics of the helium electrons is chaotic at all energies, yet the low-lying bound and doubly excited autoionizing states exhibit striking regularities that have been the subject of intense study and interpretation dating back to the 1960s. Recent theories have suggested that regimes should exist closer to the double-ionization threshold in which so many resonances overlap that a new spectral regime of “quantum chaos” should emerge. To test these ideas in helium (or the isoelectronic species H^- or Li^+), i.e., to map out the chaos while searching for simplicity and regularity in the spectrum as well, will require the extremely high resolution and brightness of a third-generation source like the ALS. (Note that extensive laser-based experiments have been carried out for other “two-electron systems,” such as barium, but the breaking of the $O(4)$ symmetry in any nonhydrogenic ionic core changes the problem fundamentally, as compared to true two-electron species.)

Another challenge to be overcome for few-body systems is the interpretation of the rich multichannel spectroscopy of triply excited hollow atoms, of which lithium is the prototype. The high spectral resolution achieved at the undulator beamlines of the ALS sparked a very recent breakthrough in which several new hollow states of atomic lithium were measured. These data provided a much-needed confirmation of recent improvements in theoretical methods, as shown in Figure 3. These systems critically challenge theory, which ultimately leads to their quantitative improvement and hones our qualitative understanding. Many intricacies remain to be measured and interpreted.

Progress in these areas is contingent on close cooperation between theory and experiment. The bottom line is that, despite the rapid progress in theory during the past decade, the description of triply and doubly excited states in all light atoms (and negative ions) of the periodic table remains far from routine. Only for energies near the lowest ionization thresholds can the theory be viewed as being basically under control. Experiments at the ALS are perfectly poised to contribute to the improvement of some of the key remaining gaps in theoretical descriptions.

The areas just mentioned relate to problems where our fundamental understanding of the basic processes is still unsatisfactory. Consumers of atomic data (e.g., the plasma modelers) bring a different perspective to these matters, owing to the great number of cross sections needed, which makes it impossible to rely entirely on experiments for every number. Theory must ultimately provide this data, yet, as discussed above, there remains a need for benchmark tests that are sufficiently broad in number and variety to ensure that reliable theoretical methods exist to describe the broad array of photoprocesses that exist in the periodic table.

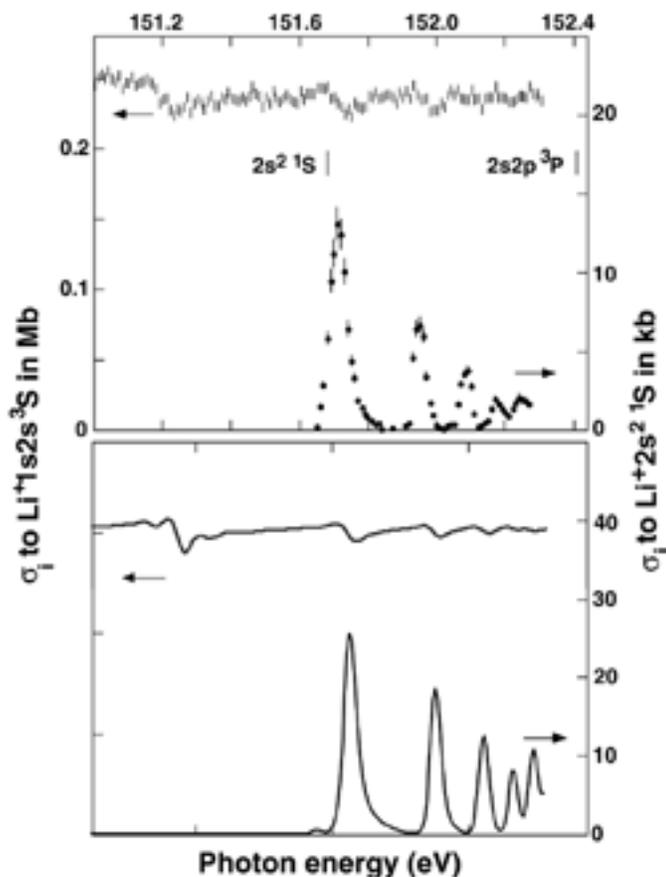


Figure 3. High-resolution spectra over the excitation-energy range of the $[(2s2p^3P)ns]^2P$ Rydberg series. The upper panel shows the measured values of partial cross sections for photoionization of $1s^2 2s^2 S$ lithium atoms into $1s 2s^2 S$ (Li^+ ionic states). The lower panel shows the results of convoluted R-matrix calculations for the same partial cross sections as in the upper panel. [Figure courtesy of François Wuilleumier and Denis Cubaynes, Université de Paris-Sud.]

2.4 Photofragmentation Control: Tailored Excitation and Detection of Atomic and Molecular Systems

A long-standing goal in AMO physics is to achieve maximal control of processes all the way down to the molecular and even atomic levels. The areas described below are directed, in the long run, toward achieving this control and toward extracting the deeper understanding of complicated processes that must be achieved before such control will be feasible.

2.4.1 Laser-Tailored Initial States

The high brightness of the ALS significantly enhances our ability to perform a broad class of experiments in which either the sample or the photofragment detection is tailored in a specific manner. One example is the use of a laser to prepare an oriented or aligned atom by laser-optical pumping,

after which a synchrotron photon ionizes an inner shell of the atom. For example, recent measurements of dichroism in transition-metal atoms have dramatized the inadequacy of the independent-particle model, which is commonly used in condensed-matter calculations, in situations where the core level is split by an effective spin field. Gas-phase atomic studies have demonstrated a strong interaction between the 3p hole and the 3d electrons, which was neglected in past theoretical work. Such studies can pinpoint the role of intra-atomic interactions in spectra of metal surfaces and thin metal films, thereby providing insight into magnetic materials and thin films. The AMO community contributes to our understanding of these problems by disentangling the role of intra-atomic and inter-atomic interactions.

A different use of laser-prepared initial states is exemplified by the planned improvement in resolution through the optical pumping of trapped atoms, which will give a far better measurement of lithium double photoionization, for example. Owing to the tenuous nature of the targets, however, it may be necessary to wait for the arrival of free-electron lasers (FELs) to carry out these experiments.

Although it has not yet been achieved, the prospect of coupling infrared (IR) lasers and synchrotron radiation to study inner-shell excitation of vibrationally excited molecules is extremely appealing. For example, an experiment of this type could be used to probe the dependence of inner-shell processes on the internuclear distance, which translates directly into new insights that bear on the nature of chemical bonding and electron correlation. Another challenge for theory occurs when a molecular target is prepared in a very high vibrational state near the dissociation limit and then photoionized. A key benefit of such experiments is the information they reveal concerning poorly mapped parts of the potential-surface manifolds far away from the ground-state Franck-Condon zone. The simple combination of a cw laser with a synchrotron source permits the photoionization of an electronically excited atom, which exhibits rich and informative spectral dynamics that usually differ qualitatively from ground-state photoionization. Early experiments of this type were performed with second generation sources and, in the case of hollow atomic lithium, were improved in a clear and qualitative manner when reexamined recently at the ALS.

This work lays the foundation for future studies in which laser excitation is used to tailor the atomic or molecular configuration in order to enhance a particular interaction or decay process that is subsequently probed by inner-shell excitation. An immediate extension of these techniques, a pulsed laser that is synchronized with electron bunches (of 40-ps bunch length) in the ALS storage ring opens the possibility of a new class of experiments. In these, the laser labels the species of interest and the synchrotron is used to probe it. Such double-resonance experiments can selectively study a minor component (e.g., a free radical, ion, or size-selected cluster) of a complex mixture, a common desire for many types of samples.

2.4.2 Molecular Studies with Lasers and Synchrotron Radiation: Multicolor Experiments

Although multiphoton spectroscopic techniques are widely used in laboratory laser experiments, the combination with synchrotron radiation brings a new perspective. For example, molecular photon-induced dissociation by two-color experiments (combination of infrared, visible, ultraviolet or soft x-ray photons) can be achieved in a variety of “pump-probe” arrangement where one photon either photodissociates or photoexcites the molecule, while the second photon photoionizes or photoexcites the fragments or the excited target molecule. In addition, pulsed photon sources combined with an appropriate pulsed laser can be employed in time-resolved experiments. Since second-generation

synchrotron-radiation sources could only achieve limited spectral resolution and focusing capabilities, third-generation sources like the ALS will permit significant improvements in several areas, as long as the storage ring operates in few-bunch mode to allow a large dynamical range for the pump-probe delay time.

Photodissociation experiments using double-resonance or pump-probe techniques generally fall into one of two different categories. In the first, molecular photodissociation of suitable precursor molecules is used to provide a clean and efficient source of free radicals (species with unpaired electrons), which can then be characterized by using the full range of VUV and soft x-ray techniques. In this case, the laser is used for the photodissociation step and the synchrotron radiation is used as the probe. In the second category, the photodissociation process is itself the object of study, and the product yields, angular distributions, velocity distributions, etc. are determined as a function of the photodissociation wavelength. In some instances, photoionization mass spectrometry using the synchrotron will be used as a universal detector of the products of photodissociation dynamics initiated by the laser. This scheme will be particularly useful for the detection of radical fragments that are not well characterized spectroscopically. In other instances, laser-based techniques will be used to probe the molecular explosion that often follows inner-shell ionization with the VUV or soft x rays from the synchrotron. Extraction of the dynamical information from this process requires knowledge of the energy content and distribution (electronic, vibrational, and rotational) among the fragments. The large number of competing dissociation channels forces the use of a highly selective and sensitive probe like laser-induced fluorescence. The three-body dissociation of valence-excited molecules poses extraordinary challenges as well, because the dissociation could proceed through a cascade of two-body dissociations or through a concerted three-body process. Analogously, molecular ions (singly or doubly charged) produced by autoionization exhibit peculiar fragmentation signatures, caused in some cases by atomic scrambling (bond breakage and new bond formation).

For time-resolved experiments, synchronization of the two sources is necessary whenever the lifetime of the excited species is less than the temporal separation of the light pulses. High-repetition-rate Q-switched, mode-locked dye lasers are the most suitable. A free-electron laser built in a straight section of a third-generation storage ring can provide tunable light from the IR to the UV, and by harmonic generation to the VUV, with a high peak power that is naturally synchronized with synchrotron radiation produced by the same machine. Some of the scientific questions that can be addressed relate to “chemistry in the time domain,” a topic discussed in the report of the Working Group on Chemical Dynamics.

2.4.3 Propensities for Final-State-Energy and Angular-Momentum Sharing

A fundamental scientific issue having broad interest and significance is the description of how the conserved quantities of energy, angular momentum, and linear momentum are dynamically shared and partitioned among constituent particles in an isolated-multiparticle atomic or molecular system. The quantification of this sharing and partitioning helps to unravel the nature of final-state interactions. These interactions control the extent to which the quantum states of two particles are coupled inseparably; such coupling is frequently denoted generically as a “correlation effect.” In addition to their intrinsic interest as fundamental dynamic processes at the quantum level, the understanding of such correlations is also important in a broad sense because they arise in any quantum-mechanical system having nonseparable degrees of freedom. Such systems can involve so many fragmentation channels that they appear to be theoretically intractable at first sight. This makes the search for propensities and trends for the dominant pathways even more important than in systems that can be treated by *ab-initio* theory with a high probability of success.

As one example, measurements of high-resolution photoelectron spectra and/or photoelectron angular distributions directly provide the predominant resonance-decay pathways. In favorable cases, experiments of this type yield state-to-state propensity rules for the electron-ion collision (or half-collision) process; they can also identify the mechanisms that control the allotment of energy and angular momentum among the myriad photofragment degrees of freedom. In some cases, this information even bears on a question of longstanding chemical importance: how the motion of light electrons can influence the behavior of heavy nuclei. Measurements of anisotropic observables also test theoretical approximation schemes far more critically than studies of total cross sections.

Next on the scale of increasing complexity are circular-dichroism and optical-activity effects in molecular photoionization, which have received little attention and remains poorly understood. Circular dichroism in photoionization has not been observed for molecular targets, although it has received some theoretical attention dating back to the early 1980s. Particularly for chiral molecules, where orientation of the target is not required, such effects have potential importance for biological problems, e.g., the origins of biological homochirality, as well as for the basic physics of photoionization. The photoionization dynamics can be addressed with unprecedented detail if the photoelectrons are also spin-analyzed.

Despite the common conception, atoms and atomic ions are typically *not* spherically symmetrical. The anisotropy of ionic photofragments can now be explored in complex spectral regions characterized by rich resonance physics. Recent measurements at the ALS of interactions between an autoionizing n_s Rydberg electron and an excited Ar^+ photofragment press theory to its current limits, while still showing signs of tantalizing simplicity in some regards. In the future, experiments with circularly polarized light will permit a more complete determination of the angular-momentum distribution in the ionic fragment. If a photoelectron is also detected at a specific ejection angle in coincidence with a fluorescence photon, probability amplitudes of the photoelectron emerge, as well.

2.5 Free Clusters: Site-Specific Inner-Shell Excitation

The domain of free clusters covers aggregates of atoms or molecules in numbers that vary from several to several thousand. One goal is to ascertain how the condensed-matter properties emerge as the number of atoms or molecules increases. Another aim is to search for specific properties of these mesoscopic objects that could be important in related fields, such as new molecules like the fullerenes, nanostructured materials, and specific chemical reactivities.

Pressing technological questions that can be addressed through the study of clusters include the ever-present demand to miniaturize microelectronic circuits, which necessitates a thorough understanding of cluster properties. Metal pads used to join layers of semiconductors are shrinking to the size where only a few thousand atoms of the metal are used. In this regime the metal behaves more like a cluster than a bulk metal. The formation of clusters in deposition processes also requires deeper understanding at the fundamental level in order to prevent contamination of the surface by large clusters, which can cause a device to fail. Two main directions are to be distinguished, one concerning atomic clusters, particularly metallic clusters, and the other concerning molecular clusters.

2.5.1 Atomic Clusters

Even the most refractory materials can now be produced in a very large range of sizes. In divalent metals, for example, it has been possible to observe the transition from an insulator to a metallic structure in which electrons are delocalized and described with a nascent band structure. Collective excitations are signalled by the presence of giant resonances. Photoionization studies (including

partial ion yields, photoelectron spectroscopy, or fragmentation) are fruitful in either the valence or core-level regions. The challenge is to perform such measurements for one size population of free clusters and track one property as a function of size. The low density of single-size-particles, probably in the $10^7/\text{cm}^3$ range, requires an extremely bright and intense photon source like an ALS undulator. Extended x-ray absorption fine structure spectroscopy (EXAFS) is an ideal tool to extract bond distances in amorphous species or nanocrystals.

2.5.2 Molecular Clusters

Homogenous or heterogeneous molecular clusters can mimic a microsolution. Detailed studies help to sort out the extent to which solvation affects the properties of a molecule. One intriguing area is the investigation of geometrical structure of positively or negatively charged clusters above a certain critical size. One problem that complicates the analysis is the coexistence of isomers in the cluster source. Ultimately, double-resonance experiments in which a mass-selected cluster is first labeled, then probed, will eliminate this difficulty. High-resolution pulsed-field-ionization zero-kinetic-energy (ZEKE) spectroscopy can also help to reduce this complexity. Finally, EXAFS near selected core levels is also attractive and, in highly-focused conditions, is the ideal tool to solve such problems.

3. Importance of VUV and Soft X Rays and the Role of the ALS

3.1 Why a VUV/Soft X-Ray Source Is Important for the Proposed Areas of Study

The scientific issues identified in this report require energy in the range for which the ALS is optimized, namely, the VUV and soft x-ray region. The broad and rapid tunability of the ALS in these photon-energy regions enables systematic studies of sequences of atoms and molecules that are inaccessible to even state-of-the-art laser systems. While such systematic studies have always been integral to AMO research, the unprecedented brightness of the ALS combined with the state-of-the-art beamlines and detection methods only now permits the study of large classes of highly rarified species, such as ions, open-shell atoms, and free radicals, and provides a level of detail that was only imagined in the past. Examples of such systematic studies, discussed in the report, include (1) inner-shell excitation; (2) determination of accurate photoabsorption and photoionization cross sections along isoelectronic sequences of atoms and multiply charged ions; (3) use of site-specific, inner-shell excitation to explore chemical reactivity in sequences within different classes of functionalized molecules; and (4) triply differential studies of open-shell elements where wavelength-dependent partial cross sections and angular distributions are measured simultaneously. We emphasize that the *science* is driving the selection of the light source for these experiments, rather than the reverse. Essentially, there are no other methods that are capable of achieving the scientific goals described in Section 2 above.

3.2 What Is the Role of the ALS?

Given the requirement of photons in the VUV/soft x-ray energy range, the question remains whether the proposed scientific programs are contingent upon the advanced capabilities of the ALS. Our answer is emphatically affirmative, as the technical case for this requirement is quite clear. Most of the experiments require *ultrahigh resolution, brightness (small spot size), and very high flux over a broad photon-energy range*. Only a source with the characteristics of the ALS is suitable for such studies. For example, high-resolution inner-shell atomic and molecular experiments using Auger resonant-Raman

or x-ray emission spectroscopy benefit directly from the availability of *bright, narrow-bandwidth, intense excitation*. High-resolution spectrometers, coupled with high-resolution photons, open the door to the investigation of the structure and dynamics of various atoms and molecules with high and revealing precision. These characteristics are also ideal for studies of ionic photoexcitation and photoionization. Although ion beams provide a sparse target for such studies, pioneering experiments have been successfully conducted in Europe and Japan at second-generation synchrotron-radiation facilities, demonstrating their viability and scientific potential. In general, however, these experiments have been limited to species with enormous cross sections. The increased photon flux of the ALS provides a unique opportunity to conduct such studies now with dramatically increased precision, spectral resolution, and variety of ion targets. Such studies have *never* been attempted for negative-ion targets, for example, and offer an exciting opportunity for pioneering experiments.

Another area for which the ALS is uniquely capable is in the area of spin-resolved experiments that require *intense circularly polarized light*. This important resource will be provided by the elliptically polarized undulator (EPU) beamline presently under construction.

3.3 What Tools Are Needed?

In order to measure atomic and molecular processes after photoionization, tools are required for preparing atomic and molecular samples, including ions in specific states, for exciting them, and for detecting the fragments. Two dedicated beamlines (a bend-magnet beamline and an undulator beamline) are being used for AMO research in conjunction with several state-of-the-art end stations that include an ion beamline for study of ion-photon interactions (in construction), high-resolution electron spectrometers (time-of-flight spectrometers, hemispherical analyzers), fluorescence detectors, ion detectors and provisions for a variety of coincidence techniques (e.g., photoelectron photoion coincidence (PEPICO), photoion-photoion coincidence (PIPICO), and COLTRIMS).

Other tools are, however, needed in order to “prepare” and “control” atomic and molecular targets or to otherwise extend experimental capabilities. These are:

- (1) Mott-detectors for spin-polarized detection.
- (2) Pulsed lasers to prepare targets and to synchronize them to the ALS for time-resolved studies.
- (3) Extend the spectral range of the EPU beamline to cover low photon energies. The ALS management has stopped the development of the second undulator (which would have provided low photon energies) on the *only* elliptically polarized beamline of the ALS.
- (4) A branch of an undulator beamline without a monochromator that is capable of running in a “blowtorch mode” in order to provide ultimate intensity for a certain class of experiments that need flux far more desperately than resolution. For example, all experiments that require a high degree of differentiation, such as angle- and/or spin-resolved measurements, electron-electron and electron-ion coincidence measurements, and spectroscopy of polarized targets, are in need of optimum high flux because the count rates are extremely low.
- (5) An undulator beamline that covers the oxygen and nitrogen edges with very high brightness and resolution.
- (6) Timing operation is absolutely necessary for several types of experimental techniques (time-of-flight techniques). The ALS must be committed to serving the AMO community, which depends upon that mode of operation.

(7) UV and IR free-electron lasers are the next-generation sources, and are particularly promising for double-resonance experiments. The ALS management is encouraged to pursue that area of development.

4. Connections to Other Fields

AMO science has a strong track record as an enabling science for other disciplines. The benefits of understanding the underlying atomic and molecular physics occurring in photoexcitation and photoionization have applications in several other fields, including biology, atmospheric physics, astrochemistry, radiation damage of molecules, environmental science, lasers, astrophysics, fusion plasma physics, material and surface sciences, and chemical manufacturing.

Studies of the properties of ions are needed since the production and destruction of negative ions in systems such as dilute plasmas appearing in the outer atmospheres of stars are strongly affected by the characteristics of these ions. The proposed studies of highly charged ions are relevant to the development of novel x-ray laser configurations whose lasing medium is a plasma. Information on ions is also important for the low-energy plasmas used in materials processing, plasma etching, and other industrial applications. Finally, the development of new experimental techniques could lead in the longer term to the manufacture of novel detectors and electronics, as was the case in the past for time-of-flight spectrometers and imaging techniques.

VUV studies are also relevant to questions regarding global climate change. For example, the large-scale industrial consumption of chlorofluorocarbons (CFCs) has attracted a lot of attention because of their destructive effects on atmospheric ozone and global change. Since the Montreal Protocol a decade ago, many industries are attempting to replace traditional CFC-based products (the so-called Annex A and B controlled substances), including refrigerants, aerosol propellants, plasma etchants, etc., with more environment-friendly substitutes, which consist primarily of hydrochlorofluorocarbons (HCFCs), hydrofluorocarbons (HFCs), and their derivatives. The ALS has photon beams well-suited to systematic studies examining the photoexcitation of a series of common substitutes, including HCFCs and HFCs. Comprehensive photoabsorption and photofragmentation cross sections are needed to detail the response of these molecules to photons in the VUV and soft-x-ray regions. Characteristic photoion-photoion coincidence (PIPICO) spectra can not only map out the dynamics of a dissociation process that follows photoexcitation, but it can also provide an element-specific fingerprint of the target of interest by tuning the excitation photon energy to specific ionization edges. This type of photodissociation information could be used ultimately to diagnose unknown waste emission or for other smog analysis.

In addition to potential practical relevance, photoabsorption and photofragmentation measurements of HCFCs and HFCs can provide important insight to shape-resonance phenomena and non-Franck-Condon behavior in relatively large molecules and can aid in critically evaluating photoionization theories and electronic-structure calculations. Experiments feasible at the ALS offer the first comprehensive research on photodissociation of these complex molecules, and they could impact areas such as environmental research, radiation and space sciences, fusion research, aeronomy, and astrophysics.

Absorption spectroscopies using the ALS can provide element-specific and chemical-state-specific detection of trace contaminants in soils, groundwater, and biological materials. The spectroscopy methods can be applied to understand radiation damage in complex biological molecules, since a thorough understanding can only be done through studies of the decay processes after photoionization.

The development of high-resolution, sub-natural linewidth spectroscopies, such as resonant-Raman and resonant-Raman Auger techniques, may ultimately have considerable utility in more applied areas of VUV and soft x-ray physics. For example, traditional near-edge x-ray absorption fine structure (NEXAFS, also known as XANES) spectroscopy has commonly been used to determine the oxidation state of selected elements in environmental and biological samples. For many elements, however, the NEXAFS spectra for different oxidation states are quite similar, and the analysis of samples with mixed oxidation states can be extremely difficult. The increased spectral resolution afforded by resonant-Raman and resonant-Raman Auger spectroscopy promises to improve and simplify such analyses. Ultimately, the development of such new spectroscopies in AMO physics is expected to enable a broad range of new capabilities in the environmental and biological sciences.

5. Conclusions

First- and second-generation synchrotron-radiation sources have been pioneering tools for several areas of atomic and molecular research. They generated new understanding and paved the way to future high-precision and highly differential investigations of the structure and dynamics of atoms and molecules. This future has arrived. Synchrotron-based AMO physics research conducted with the third-generation ALS has already provided a new understanding of basic photon-matter interactions in a number of different systems. These synchrotron research projects provide broad training to large numbers of undergraduate and graduate students, who contribute in turn to other research fields and to industry. First and foremost, however, an enthusiastic community of atomic, molecular, and optical scientists is committed to advancing, with a sense of urgency, the exciting scientific frontiers stimulated by the construction of the ALS.