Jones

Report of Grant No. DE-FG02-96ER14654

SUBMITTED TO

THE US DEPARTMENT OF ENERGY
FUNDAMENTAL INTERACTIONS BRANCH
DIVISION OF CHEMICAL SCIENCES
OFFICE OF BASIC ENERGY SCIENCES

by

Nora Berrah
WESTERN MICHIGAN UNIVERSITY
DEPARTMENT OF PHYSICS
KALAMAZOO, MICHIGAN 49008

For

ATOMIC AND MOLECULAR FACILITY AT THE ADVANCED LIGHT
SOURCE

DOE Patent Clearance Granted
Mark P. Dvorscak 4.16.04
Mark P. Dvorscak
(630) 252-2393
E-mail: mark.dvorscak@ch.doe.gov
Office of Intellectual Property Law
DOE Chicago Operations Office
Date

TABLE OF CONTENTS

	page
Abstract.....	iii
I. Introduction.....	1
II. Report on the Atomic and Molecular Facility.....	4
A. Endstation for Studies of High-Resolution Angle-Resolved Photoelectron Spectroscopy.....	4
1. Introduction.....	4
2. Report on the Angle-Resolved Photoelectron Spectrometer Endstation	5
3. Related Publications and presentations	14
B. Endstation for Electron Spin-Resolved Studies.....	22
1. Introduction.....	22
2. Report on the Electron Spin Polarization Endstation	23
3. Related Publications and Presentations	27
C. Endstation for studies of Photon-Ion Interactions at ALS	28
1. Introduction.....	28
2. Report on the Photon-Ion Endstation	29
3. Related Publications and Presentations	32
D. Quarter-Wave Retarder	33
1. Introduction.....	34
2. Report on the Quarter-Wave Retarder.....	34
3. Related Publications and presentations	36
E. Other Projects.	39
1. Data Acquisition System for a Recoil Ion Spectrometer (COLTRIM).....	39
2. Computer for Collaboration with Theorists.....	39
III. Proposal to Operate the Atomic and Molecular Facility	40
IV. Personnel.....	41
V. Budget.....	42
Current and Pending Support.....	43
Appendix 1- Letter of Support from the ALS	44
Appendix 2- Vitae.....	45

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

I. INTRODUCTION

In September of 1996 we were awarded an instrumental "facilities initiatives" grant of \$900,000 over a three year budget period, to build an Atomic and Molecular Facility (AMF) for research using the Advanced Light Source (ALS) at Lawrence Berkeley National laboratory. This award was supplemented with \$135,000 for the budget period September 1999-August 2000 to allow completion of the projects.

The funds were awarded to develop, build and upgrade state-of-the art end-stations to take advantage of third generation light source attributes such as 1) resolution, better than 10,000 and in some cases 64,000 was achieved (1 meV resolution at 64 eV photon energy for example), 2) circularly polarized light allowing electron spin-resolved experiments, 3) high brightness and high flux allowing precision measurements of tenuous targets such as atomic vapors and ions. These funds were necessary to build new instruments to conduct synchrotron-based research utilizing the ALS since research accomplishments were limited by the experimental apparatus, not the photon source. The AMF, located at the ALS, was built with the intent to be used as a facility for the atomic and molecular community in general. A brochure describing the facility and advertising it to the community is enclosed with this proposal. The facility has been built by the participator research team (PRT) composed of Prof. Duane Jaeks (University of Nebraska, Lincoln), Prof. Ron Phaneuf and collaborators (University of Reno, Nevada), Dr. John Bozek (ALS, Lawrence Berkeley National Laboratory), and myself as their spokesperson. The complete list of scientists involved with the facility initiative proposal can be found in section IV.

All of the undertaken projects are completed and are operational. They consist of 1) a high resolution hemispherical electron analyzer (scientia) housed in a rotatable chamber (to conduct high resolution measurements in atoms and molecules), 2) an electron spin-polarization apparatus to conduct spin resolved experiments 3) an ion-photon collinear beam apparatus to conduct photoionization of positive and negative ions 4) a polarizer device that produces circularly polarized light. Funds were also used to purchase a data acquisition system for a recoil ion spectrometer (COLTRIM end-station, Lew Cocke (Kansas State University)) to conduct e-ion coincidence experiments, and a computer for our theorists collaborators (Chris Grenne (University of Colorado) and Tony Starace (University of Nebraska, Lincoln)).

The choice of the built instruments have been made in order to push forward our fundamental understanding of the many-body problem by conducting photoexcitation and photoionization experiments in atoms, molecules and in the future of clusters. Since no single instrument can measure all the parameters necessary to understand the structure and dynamics of atoms and molecules, we have designed three unique end-stations that are all complementary to each other and which can allow achievement in some cases of the "complete experiments" or allow measurements with unprecedented resolution and details that may give new insight into the many-body problem. For example, the hemispherical analyzer (described in section II. A) allows high resolution measurements of the partial cross-sections and angular distribution parameters in photoionization experiments of molecules and atoms. These measured parameters are then used

with the spin-resolved data measured using the spin-resolved end-stations (described in section II B) to determine all parameters needed to describe entirely a photoionization experiment, ie, a complete experiment is achieved. Thus, these two end-stations are complementary and allow one to extract all the relevant parameters needed to achieve a "complete experiment" on neutral atomic and molecular targets. These two instruments can study any targets, from light to heavy atoms and from small to large molecules, including some clusters. The ion-photon end station (described in section II.C) is also unique, in the sense that it combines an ion and photon beam in a collinear geometry for the study of ions, both positive and negative ions. These three end-stations were proposed to be built to conduct AMO research in the 1996 instrumental facility initiative grant proposal by the PRT. These end stations will allow research that have been specifically mentioned to hold promises in the final report (page 6-7) of the "Atomic Molecular and Optical Physics panel A: Interaction of Atoms and Molecules with Photons-Low Field" chaired by Dan Kleppner in the 1997 DOE workshop held in Chantilly, Virginia and by the Report on "Workshop on Scientific Directions at the ALS" held at ALS, March, 1998 and chaired by Yve Petroff (European Synchrotron Radiation Facility) (page 199-214).

The grant allowed the purchase and manufacture of the above projects as well as the support of two postdocs, located at the ALS since most PRT members do not reside in Berkeley. The postdocs helped with the construction of the projects and are now assisting independent investigators and PRT members with the use of the sophisticated experimental systems.

Studies of absorption of photons by atoms, molecules and ions are not only interesting from a fundamental research point of view but have also connection and important applications in many other areas of science and technology. Understanding of atomic and molecular core excitations and complex decay processes contribute to the development of knowledge and provide data for other disciplines. For example, they may provide solid states effects, element-specific information on trace contaminants in biological materials, and data relevant to radiation damage of molecules, including DNA and proteins, data for astrophysical and fusion plasma research as well as for environmental (global warming), soil and groundwater studies. They will have direct impact on catalysis, atmospheric chemistry and material science and are important for the development of new technologies such as making novel x-ray lasers, and the manufacture of various detectors used in industry and health areas.

From an educational point of view, the use of the AMF by a variety of students will also provide training for students who will graduate with a broad and strong knowledge that prepares them not just for academic careers, which are scarce at present, but also for employment in many other areas that need scientists with broad skills. Thus students with such a training can contribute to the fields of life sciences, protein crystallography and structural biology which are presently experiencing tremendous advances as well as to contribute to laser, micro-chip, nanoscale technologies and other industries that use the ALS for their applied research.

Since this instrumental grant will expire in August of 2000 and since significant investments have already been made, we need to request a modest grant renewal to:

- 1) Operate the facility since beamtime is available year round, 24 hours a day. We request support for at least one postdoc (or research associate) who is necessary to assist independent investigators (I.I.) that submit proposals through the ALS peer review system to use the facility. PRT members can not assist these users most of the time since they reside elsewhere and have other responsibilities. Also, the I. I. cannot use the facility on their own since the experimental systems are complex and delicate.
- 2) Maintain the facility. Material and supply will be needed to replace, fix and maintain the equipments.

Support is therefore requested to pay one postdoc (or research associate) to operate the facility at the ALS and to maintain the facility.

The description of the AMO facility at the ALS and other projects, including initial results and related publications and presentations are given section II. Section III gives a brief proposal to operate the AMO facility. Section IV list the personnel and section V the budget. A letter of support from the director of the ALS is included in Appendix 1.

II. Report on the Atomic and Molecular Facility

A) Endstation for Studies of High-Resolution Angle-Resolved Photoelectron Spectroscopy

T. D. Thomas¹, N. Berrah², K.J. Børve³, J. Bozek⁴, T. X. Carroll⁵, J. Hahne⁵, E. Kukk^{1,4}, and L. J. Sæthre³

¹Department of Chemistry, Oregon State University, Corvallis, OR 97331-4003

²Physics Department, Western Michigan University, Kalamazoo, MI 49008

³Department of Chemistry, University of Bergen, N-5007 Bergen, Norway.

⁴Advanced Light Source, LBNL, University of California, Berkeley, CA 94720

⁵Department of Chemistry, Keuka College, Keuka Park, NY 14478

1) Introduction

The investigation of the structure and dynamics of molecules is benefiting from rapid technological development of high resolution spectrometers and photon sources. Inner-valence photoionization studies exhibit complex photoelectron spectra due to many-electron processes in addition to the main band expected from an independent electron picture. A good description of these spectra generally requires consideration of configuration mixing in the final and initial states. Over the last twenty years, photoelectron spectroscopy (PES) has proven to be one of the most powerful techniques for the study of many-electron processes in atoms and molecules. PES has the unique capacity to study separately the different decay channels that follow photoionization since it can characterize the individual processes contributing to the different ionic yield. Measurements of the partial cross section and of the angular distribution of the emitted electron are necessary to unravel the different processes that occur after absorption of photons.

A challenge for inner-shell photoelectron spectroscopy has been the study of molecules in which the carbon atoms have similar ionization energies even though they are quite distinct chemically. Only recently has it been possible to resolve the contributions from these carbons in the carbon 1s photoelectron spectrum of propyne and to correlate the ionization energies with the reactivity.[1] The very high resolution capabilities of the Advanced Light Source present a long-awaited opportunity to examine inner-shell photoelectron spectra of such molecules and to gain chemical insights that were previously inaccessible. High-resolution inner-shell photoelectron spectra of certain molecules reveal a number of features that relate to the chemistry of the molecule and to the chemical physics and dynamics of the ionization process. Among these are chemical shifts of the ionization energy due to the local environment of the core-ionized atom,

vibrational excitation that occurs during ionization, line broadening that results from the finite lifetime of the core-ionized state, distortion of the line shape that results from interaction of the outgoing photoelectron with the Auger electron (emitted in the deexcitation of the core hole), localization-delocalization effects that can occur in molecules with equivalent atoms (such as HCCH), and, for ionization of levels with $l > 0$, molecular-field splitting, which removes the degeneracy of levels such as $2p_{3/2}$ that are degenerate in the spherical case.

A new endstation for the study of high-resolution differential photoionization experiments in atoms and molecules is described below. In addition, highlights are presented of recent photoionization experiments.

2) Report on the photoelectron Spectrometer endstation

The spectrometer is a commercial Scienta SES-200 hemispherical electron energy analyzer and is optimized for gas-phase studies of atoms and molecules. It is housed in a vacuum chamber, as shown in Fig. 1 a, that maximizes the performance with gaseous samples by using differential pumping stages both in the experimental chamber and in the connection to the beamline.

Fig. 1a) Schematic of the photoelectron spectrometer, the chamber and the stand.

Fig. 1b) Schematic of the hemispherical analyzer.

The analyzer, electron lens, (as shown in Fig. 1b) and experimental chamber are surrounded by μ -metal layers providing magnetic shielding. The number and diameter of access ports has been kept to a minimum in order to reduce the penetration of the magnetic field into the interaction region. The sample gas is fed into a gas cell, which is mounted directly to the lens of the analyzer. The pressure in the cell can be raised to about 10^{-3} torr. Electrodes are placed inside the gas cell at both ends along the photon path to correct for small gradients in the potential and to improve the energy resolution.

A key feature of the system is its ability to record angle-resolved data, which requires the analyzer and experimental chamber to be rotatable around the axis of the photon beam as shown in Fig. 1a. This is a nontrivial mechanical problem because of the high precision required and heavy weight of the analyzer (about 200 kg).

The analyzer is operated in a constant pass energy mode, which can be selected according to the conditions of the experiment. Under the most stringent settings of 5 eV pass energy, an energy resolution better than 5 meV is achieved.

The complete analysis of a molecular spectrum requires an understanding of a number of

factors: the vibrational excitation that occurs during ionization, the line broadening that results from the finite lifetime of the core-ionized state, and the distortion of the line shape that results from interaction of the outgoing photoelectron with the Auger electron (emitted in the de-excitation of the core hole). In addition, it is necessary to understand the instrumental features that affect the spectrum. These include the calibration of the energy scales of the monochromator and electron-energy analyzer, the resolution of the photon beam, the resolution of the electron-energy analyzer, and the variation of the analyzer transmission with electron energy. We included all of these factors in the analysis of the initial results listed below.

Initial Results:

The use of the photoelectron spectrometer has allowed interesting results to be obtained for a number of molecules as can be seen from the publication list. Below is a summary of results in the case of CO, ethyne (HCCH), propyne ($\text{CH}_3\text{C}/\text{CH}$) and methane (CH_4).

Auger Decay of the $\text{C } 1s^{-1} 2\pi^*$ Resonance : Vibrationally and Angularly Resolved Spectra in CO [2]

The Carbon monoxide molecule has evoked considerable experimental and theoretical interest and several calculations related to the Auger decay of the core-hole states have been published. However, no previous experiments measured the full vibrational structure of the final ionic states.

The motivation for this work was to provide precise information used to determine the shape of the potential energy curves by measuring with precision vibrationally resolved Auger electron spectra that decay from the high vibrational levels, $v=0,1,2$, of the $2\pi^*$ and to compare our data with latest theoretical results.

We used Resonant Raman Auger spectroscopy, possible with the above spectrometer and the photon source, to measure spectra linewidths that are limited only by the experimental resolution rather than the lifetime of the core hole. We have measured angle resolved Auger electron spectra from the decay of the $v=0,1$, and 2 levels of the $\text{C } 1s^{-1} 2\pi^*$ bound state resonance at a photon energy of 287 eV with the highest achieved electron and photon energy resolution to date. Our measurements completely resolve the vibrational structure of the final electronic states. The experimental resolution was half the intrinsic width of the $\text{C } 1s$ photoelectron line. This work allowed new information about singly charged states of CO since it revealed new states ($^2\Delta$, $^2\Sigma$) predicted by an ab-initio calculation. Also, the comparison of our data with the calculation is excellent for the low kinetic final ionic states but was only in general agreement with the higher kinetic energy final ionic states. A complete report on this experiment is described in ref [2].

Fig. 2 a) Shows the electron spectra of the $C\ 1s^{-1}$ to $2\pi^*$ excitation in CO in which the Auger decay to various final ionic states are fully vibrationally resolved. b) ab-initio theory.

Carbon 1s Photoelectron Spectrum of Ethyne to Determine the Existence of a Shape

resonance [3]

The motivation for this work is due to fourteen year old predictions [4] that were never verified experimentally.

Namely, is there a shape resonance around 310 eV in the case of core ionization in Ethyne?

When core-ionization takes place in a molecule, there is typically vibrational excitation of the resulting ion, leading to vibrational structure in the photoelectron spectrum. The carbon 1s ionization spectrum of ethyne shows additional structure because there are two closely spaced molecular orbitals

($1\sigma_g$ and $1\sigma_u$) resulting from combination of the equivalent atomic carbon 1s orbitals. This effect,

shown in the spectrum of Fig. 1, has been measured for the first time with our facility. In this spectrum the

principal peak is due to the transition to the vibrational ground state of the ion. The most prominent part of this peak results from ionization of the $1\sigma_g$ orbital and the shoulder at lower ionization energy from the $1\sigma_u$ orbital. The u-g split shoulder on the high-energy side of the peak results from the $v = 1$ excitation of the carbon-carbon stretching mode. It is apparent that the cross section for $1\sigma_u$ ionization is less than that for $1\sigma_g$ ionization.

Since the intensities for these two ionizations are not the same is a direct proof to the existence of a σ_u shape resonance in the photon energy range studied here, and is of special interest because of on-going discussion of the criteria for identifying such shape resonance. In the spectrum shown in Fig.1 the intensity for $1\sigma_g$ ionization is enhanced,

Figure 1. Carbon 1s photoelectron spectrum of HCCH

Figure 2. a. The ratio of the cross sections for ionization of the $1\sigma_u$ and $1\sigma_g$ orbitals in ethyne. b. Cross section for carbon 1s ionization in HCCH. Circles: total single-hole cross section. Triangles: cross section for ionization of $1\sigma_u$ (open) and $1\sigma_g$ (closed). Lines are theoretical cross sections for ionization of $1\sigma_u$ (dashed) and $1\sigma_g$ (solid).

since the transition $1\sigma_g \rightarrow k\sigma_u$ is allowed by dipole selection rules but the transition $1\sigma_u \rightarrow k\sigma_u$ is not. We have mapped out the ionization intensity ratio ($1\sigma_u/1\sigma_g$) as a function of photon energy, and these results are shown in Fig. 2a. Combining these with measurements of the carbon 1s ionization cross section [5], we obtain cross sections for the ionization of the $1\sigma_g$ and $1\sigma_u$ orbitals. These are shown in Fig. 2b, where they are compared with theoretical predictions of the cross sections [6]. Both theory and experiment show a cross section for $1\sigma_u$ ionization that decreases monotonically with increasing photon energy and a cross section for $1\sigma_g$ ionization that has a peak. The theoretical ionization intensity ratio ($1\sigma_u/1\sigma_g$), shown as the solid curve of Fig. 2a, reproduces the trend of the data. Although there is not quantitative agreement between theory and experiment, it is apparent that the theory includes most of the basic physics of the process.

These results are the first unambiguous measurements that support the assignment of a σ_u shape resonance at a photon energy of about 310 eV; they also make clear the importance of having a high resolution spectrometer to measure detailed information for making such an assignment.

Carbon 1s Photoelectron Studies of Methane [7]

Carbon 1s photoelectron spectra have been measured for CH_4 at photon energies of 302, 320, and 330 eV and for CD_4 at 330 eV with an instrumental resolution about half the natural line width for the first time. The spectrum of CH_4 at 330 eV is shown in Fig. 3. The spectra have been analyzed to obtain vibrational spacings, vibrational intensities, and the lifetime of the carbon 1s core hole state. The vibrational intensities vary with photon energy, in agreement with earlier results [8]. At 330 eV, the observed vibrational intensities for both CH_4 and CD_4 can be understood only if anharmonic effects (consistent with the predictions of theory) are included. On the other hand, the vibrational spacings in CH_4 show no evidence for anharmonicity (in contrast with theoretical predictions). In CD_4 the observed anharmonicity in the vibrational energy spacings is about half of the predicted value, but the experimental and theoretical values differ only by an amount comparable to the experimental uncertainty. The measured values of the lifetime show a dependence on photon energy; this is attributed to failure of the theory of post-collision interaction to predict correctly the observed electron spectrum near threshold. At 330 eV, the measured Lorentzian lifetime, 93-95 meV, agrees with predictions of simple theory, but not with the prediction of more complete theory. The measurements also show systematic discrepancies between the observed line shapes and those predicted by the theory of post-collision interaction.

Figure 3. Carbon 1s photoelectron spectrum of CH_4

Carbon 1s Studies of Propyne [9].

In propyne, $\text{CH}_3\text{C}/\text{CH}$, the three carbons are chemically inequivalent. The $\text{CH}/$ unit is the site for electrophilic attack and is the basic end of the molecule. The central carbon, while susceptible to attack is not so reactive as the $\text{CH}/$ carbon. The CH_3 carbon, less reactive than the others, is the acidic end of the molecule. The inner-shell photoelectron spectroscopy of this molecule provides a basis for a better understanding of its chemistry, and, by extension, that of more complex molecules. Such knowledge can enhance our ability to predict properties of molecules and to design molecules with particular properties.

The best previous measurements of the carbon 1s photoelectron spectrum of propyne by Cavell [10] showed only a single asymmetric peak (as shown in the middle panel of Fig. 4). Although he analyzed this in terms of three components, each representing a contribution from one of the carbon atoms, Cavell expressed reservations about both the positions and the assignments of each component. It was, therefore, difficult to draw firm conclusions about the chemistry of the molecule from these measurements.

With the high-resolution capabilities of the spectrometer and the beamline 10.0.1, it has been possible to resolve the contributions from the three inequivalent carbons in propyne. The spectrum for this molecule is shown in Fig. 4, where it is compared with that of ethyne (above) and ethane (below). Shown as a dashed line in the center spectrum is a representation of the earlier spectrum measured by Cavell [10]. The additional structure that is revealed at higher resolution is striking.

Figure 4. carbon 1s photoelectron spectra of ethyne, propyne, and ethane

The three peaks in the propyne spectrum can be assigned to the three carbons by comparison with the model spectra of ethyne and ethane. Comparison with the spectrum of ethane shows a strong resemblance between the peak labeled "c" in propyne and the ethane spectrum, and we are therefore confident in assigning this peak to the CH_3 group in propyne. The vibrational pattern of peaks "a" and "b" are similar to the structure observed for ethyne, allowing us to assign these two peaks to the acetylenic part of the molecule. These assignments are in accord with theoretical calculations of both their shapes and positions, and these calculations allow us to assign peak "a" to the CH carbon and peak "b" to the central carbon of propyne.

The results shown here for propyne indicate that, with the high-resolution capabilities now available, the techniques of x-ray photoelectron spectroscopy can be extended into studies of hydrocarbons. A richness of detail is observed, both in vibrational structure and in the variation in ionization energy. The work on CH_4 provides an important test of ab initio theory and the work on propyne provides insight into a variety of fundamental chemical phenomena.

Molecular-Filed Splitting and Vibrational Structure in the Phosphorus 2p Photoelectron Spectrum of PF_3 [11]

In simplest approximation, the three 2p orbitals of an atom are degenerate. If spin-orbit coupling is important, then this degeneracy is removed, and we have $2p_{1/2}$ and $2p_{3/2}$ orbitals for a spherical atom. In a molecular environment it is possible that the molecular field further splits the degeneracy of the $2p_{3/2}$ orbital into two components corresponding approximately to $\pm 1/2$ and $\pm 3/2$ projections of the angular momentum on the molecular symmetry axis. In addition, for a molecule, there is likely to be vibrational excitation accompanying core ionization, since the equilibrium bond lengths for the core-ionized molecule are usually different from those for the neutral molecule. Both of these features are apparent in the phosphorus 2p photoelectron spectrum of PF_3 , illustrated in Fig. 5. In this figure, the points show the experimental data and the solid line through the points shows a least-squares fit to the data. The unshaded structure to the right shows the fit to the vibrational structure of the $2p_{1/2}$ group. The two shaded structures, which are identical in shape to the $2p_{1/2}$ structure show the fits to the $2p_{3/2, \pm 1/2}$ and $2p_{3/2, \pm 3/2}$ groups. The adjustable parameters in the fit are the positions of the peaks in the $2p_{1/2}$ group, the spin-orbit splitting between the $2p_{1/2}$ group and the centroid of the $2p_{3/2}$ group (881 meV), and the molecular-field splitting between the two components of the $2p_{3/2}$ groups (146 meV).

Figure 5. Phosphorus 2p photoelectron spectrum of PF_3

The pronounced vibrational structure seen in the phosphorus 2p core-ionization of PF₃ indicates that there is a significant bond-length change accompanying ionization. From the measured Franck-Condon factors together with a model that includes the measured anharmonicity, we can infer that the PF bond contracts by 6.0 pm. A simple theoretical model based on the equivalent-cores approximation, which has proven successful for the analysis of vibrational structure in the core ionization of carbon 1s electrons in hydrocarbons [12], predicts a bond contraction of only 4.2 pm, and, therefore, predicts too little vibrational excitation. Modifying this model with a different basis set produces excellent agreement with experiment, but, at this stage, it is impossible to say whether or not this will be a generally useful approach for understanding the vibrational structure seen in the 2p ionization of second-row atoms. An *ab initio* hole-state calculation that has worked quite well for methane [7] gives a predicted bond-length change that is close to the experimental value, but low by 0.8 pm.

The molecular-field splitting of the 2p_{3/2} line in the spectrum, 146 meV, is significant. A simple point-charge, crystal field, model, which would predict a very small splitting, is not adequate to describe this phenomenon. It is necessary to consider the effect of the polarization of the valence electrons because of bonding, and, more important, it is necessary to take account of core-valence correlation in understanding this splitting. [13] When these effects are included, we obtain a predicted value for the molecular-field splitting of 136 meV, in good agreement with the experimental value.

References

1. L. J. Sæthre, O. Sværen, S. Svensson, S. Osborne, T. D. Thomas, J. Jauhiainen, and S. Aksela, Phys. Rev. A **55**, 2748 (1997); L. J. Sæthre, T. D. Thomas, S. Svensson. J. Chem. Soc. Perkin Trans. 2, 749 (1997).
2. E. Kukk, J. D. Bozek, W.-T. Cheng, R. F. Fink, A. A. Wills, and N. Berrah, J. Chem. Phys. **111**, 9642 (1999).
3. T. D. Thomas, N. Berrah, J. Bozek, T. X. Carroll, J. Hahne, T. Karlsen, E. Kukk, and L. J. Sæthre, Phys. Rev. Lett. **82**, 1120 (1999).
4. J. Stohr et al. Phys. Rev. Lett. **53**, 1684 (1984) and references therein.
5. B. Kempgens *et al.*, Phys. Rev. Lett. **79**, 35 (1997); J. Chem. Phys. **107**, 4219 (1997).
6. R. E. Farren, J. A. Sheehy, and P. W. Langhoff, Chem. Phys. Lett. **177**, 307 (1991). R. E. Farren, Ph. D. thesis, Indiana University, Bloomington (1989).
7. T. X. Carroll, N. Berrah, J. Bozek, J. Hahne, E. Kukk, L. J. Sæthre, and T. D. Thomas, Phys. Rev. A **59**, 3386 (1999).
8. H. M. Köppe, B. S. Itchkawitz, A. L. D. Kilcoyne, J. Feldhaus, B. Kempgens, A. Kivimäki, M. Neeb, and A. M. Bradshaw, Phys. Rev. A **53**, 4120 (1996).
9. L. J. Sæthre, N. Berrah, J. D. Bozek, K. J. Børve, T. X. Carroll, E. Kukk, and T. D. Thomas, submitted (to be submitted to J. Chem. Phys.).
10. R. G. Cavell, J. Electr. Spectrosc. and Relat. Phenom. **6**, 281 (1975).
11. K. J. Børve, L. J. Sæthre, J. D. Bozek, J. True, and T. D. Thomas, J. Chem. Phys. **111**, 4472

(1999).

12. T. D. Thomas, L. J. Sæthre, S. L. Sorensen, and S. Svensson, *J. Chem. Phys.* **109**, 1041 (1998).
13. K. J. Børve and T. D. Thomas, *J. Chem. Phys.* **111**, 4478 (1999).

Financial support

This instrumental development was funded by the DOE Facilities Initiative under contract DE-FG02-92ER14299 and by the Office of Basic Energy Sciences, Chemical Sciences Division of the U.S. Department of Energy under contract DE-FG02-96ER14654 with Western Michigan University, by the National Science Foundation under Grant No. CHE-9727471 and by the Research Council of Norway (NFR).

3. Related Publications and Presentations

1. T. X. Carroll, N. Berrah, J. Bozek, J. Hahne, E. Kukk, L. J. Sæthre, and T. D. Thomas, "Carbon 1s photoelectron spectrum of methane: Vibrational excitation and core-hole lifetime," *Phys. Rev. A*, **59**, 3386 (1999).
2. T. X. Carroll, J. Hahne, T. D. Thomas, L. J. Sæthre, N. Berrah, J. Bozek, and E. Kukk, "Carbon 1s core-hole lifetime in CO₂," *Phys. Rev. A*, **61**, xxxx (2000).
3. T. D. Thomas, N. Berrah, J. Bozek, T. X. Carroll, J. Hahne, T. Karlsen, E. Kukk, and L. J. Sæthre, "Photon energy dependence of the $1\sigma_u/1\sigma_g$ intensity ratio in carbon 1s photoelectron spectroscopy of ethyne," *Phys. Rev. Lett.* **82**, 1120 (1999).
4. N. Berrah, B. Langer, A.A. Wills, E. Kukk, J.D. Bozek, A. Farhat, and T.W. Gorczyca: "High-resolution angle-resolved measurements in atoms and molecules using advanced photoelectron spectroscopy at the ALS," *J. Electron Spectrosc. Relat. Phenom.*, v. 101, 1 (1999).
5. G. Snell, E. Kukk, B. Langer and N. Berrah: "Angular distribution measurements of the xenon N_{4,5}O_{2,3}O_{2,3} Auger electrons: determination of alignment and intrinsic parameters," *Phys. Rev. A* v. 61, 42709 (2000).
6. W. T. Cheng, G. Snell, E. Kukk and N. Berrah: "Angular distribution of I 4d photoelectrons from HI molecules," *J. Electron Spectrosc. Relat. Phenom.* (submitted).
7. E. Kukk, J.D. Bozek and N. Berrah: "Photoexcitation and Auger decay of the Renner-Teller split C 1s⁻¹ π^* state in CO₂," *Phys. Rev. A* (submitted).

8. E. Kukk, J.D. Bozek, T.D. Thomas, T.X. Carroll, L.J. Saethre, J.A. Sheehy, P.W. Langhoff and N. Berrah: "New Insights into Molecular Structure and Dynamics Using Soft X-ray Electron Spectroscopy," ICPEAC XXI, AIP Conf. Proceedings 500, edited by Y. Itikawa et al., Melville, New York, 2000
9. J.D. Bozek, N. Berrah, E. Kukk, T.D. Thomas, T.X. Carroll, L.J. Saethre, J.A. Sheehy and P.W. Langhoff: "High-resolution Molecular Inner-Shell Electron Spectroscopies," 18th International Conference on X-ray and Inner-Shell Processes, AIP Conf. Proceedings 506, 188 (2000) edited by R.W. Dunford et al.
10. E. Kukk, J.D. Bozek, N. Berrah, J.A. Sheehy, P.W. Langhoff, "Angular distributions of molecular-field and spin-orbit split core levels of sulfur 2p photoemission in OCS: A sensitive probe of the molecular environment," Journal of Physics B, 33, L51 (2000).
11. E. Kukk, J.D. Bozek, W.-T. Cheng, R.F. Fink, A.A. Wills, N. Berrah, "Auger decay of the C 1s-1 2p^{*} resonance in carbon monoxide: vibrationally and angularly resolved spectra," Journal of Chemical Physics, 111, 9642 (1999).

Invited Talks:

D. Thomas

1. "Chemistry and chemical physics in the inner-shell photoelectron spectroscopy of small molecules," ALS X-ray Science and Technology seminar, 10 Jan 2000
2. "Inner-shell photoelectron spectroscopy of small molecules at high resolution using the ALS," ALS Users Meeting, 19 Oct 1999.
3. "Chemistry and chemical physics in the inner-shell photoelectron spectroscopy of small molecules," Gordon Research Conference on Photoions, Photoionization, and Photodetachment, 19 July 1999.
4. "Core-hole localization as seen by a chemist," Workshop on localization of core hole states, 4 May 1998.

J. D. Bozek

1. "Molecular photoelectron spectroscopy using synchrotron radiation - frontiers of resolution," Physics Colloquium, University of Nevada – Reno, Reno, NV, March 3, 2000.
2. "High resolution inner-shell electron spectroscopies of simple molecules," 18th International Conference on X-ray and Inner-Shell Processes, Chicago, IL, August 23-27, 1999.

3. "Atomic and molecular spectroscopy at the Advanced Light Source," 1998 Canadian Association of Physicists Congress, Waterloo, Ontario, July 14-17, 1998.
4. "Vibrationally resolved core level photoelectron spectroscopy at the Advanced Light Source," 80th CSC CE meeting, Windsor, Ontario, June 4-9, 1997.
5. "Atomic and molecular spectroscopy at the Advanced Light Source," Chemistry Colloquium, Oregon State University, Corvallis, OR, November 13, 1996.

E. Kukk

1. "Fully Vibrationally Resolved Auger Electron Spectra Following the C 1s $\rightarrow \pi^*$ Excitations in CO," APS Centennial Meeting, Atlanta, Georgia USA, March 1999.
2. "Recent Advances in High-Resolution Electron Spectroscopy of Small Molecules," ICPEAC XXI, Sendai, Japan, July 1999.
3. Several seminar talks at the Advanced Light Source (Berkeley) and Oulu University (Finland).

N. Berrah

1. "Recent Progresses in Atoms and Molecules using the ALS," Invited talk at the Sixth European Conference on Atomic and Molecular Physics, ECAMP VI in Siena, Italy, July 14-18, 1998
2. "Angle Resolved 2D Imaging of Electron Emission Processes in Atoms and Molecules using the ALS," Invited talk at the VUV10 International Conference on Vacuum Ultraviolet Radiation Physics, San Francisco, August 3-7, 1998.
3. "Recent Results in Photoelectron Spectroscopy of Atoms and Molecules," Invited talk at the Fifteenth International Conference on the Application of Accelerators in Research and Industry, Denton, Texas; 5-8 November 1998.
4. "High Resolution Photoelectron Spectroscopy in Atoms and Molecules using the ALS," colloquium at the University of Nevada, Reno, November 16, 1998.
5. "High Resolution Photoelectron Spectroscopy in Atoms and Molecules using the ALS," colloquium given at LURE, the Universite d'Orsay, France, Mai 26, 1999
6. "High Resolution Photoelectron Spectroscopy in Atoms and Molecules using the ALS," colloquium given at the physics department of the Royal Technical Institut, Stockholm, Sweden, June 4, 1999

7. "AMO research using the ALS," progress report for the LBNL review of ALS, LBNL, University of CA, June 10, 1999
8. "The AMO Facility at the ALS," colloquium at the physics Dept, Western Michigan University, Sept. 20, 1999
9. "High Resolution Photoelectron Spectroscopy of Molecules," Colloquium at the Chemistry Dept, WMU, Oct. 11, 1999.

Conference Proceedings & Abstracts:

1. E. Kukk, J.D. Bozek, A.A. Wills, W.-T. Cheng, B. Langer, G. Snell, M. Wiedenhöft, O. Nayadin, M. Alsherhi and N. Berrah: "Fully Vibrationally Resolved Auger Electron Spectra Following the C 1s $\rightarrow \pi^*$ Excitations in the CO and CO₂ molecules," The 12th International Conference on Vacuum Ultraviolet Radiation Physics, 3.8 - 7.8.1998 San Francisco, CA USA.
2. E. Kukk, J. Bozek and N. Berrah: "Angular distribution of sulphur 2p photoelectrons in OCS: variations revealed by molecular field splitting," Oct. 1998, Advanced Light Source User's Meeting, Berkeley, USA.
3. T.D. Thomas, N. Berrah, J. Bozek, T.X. Carroll, J. Hahne, E. Kukk and L.J. Saethre: "Carbon 1s Photoelectron Spectroscopy of Ethyne: Unequal Excitation of the $1\sigma_g$ and $1\sigma_u$ States and Evidence for the σ_u Shape Resonance," Oct. 1998, Advanced Light Source User's Meeting, Berkeley, USA.
4. J.D. Bozek, E. Kukk, W.-T. Cheng, N. Berrah: "Resonance Auger spectra of C 1s⁻¹ $2\pi_u$ excited CO₂," APS Centennial Meeting, Atlanta, Georgia USA, March 1999.
5. A.D.O. Bawagan, J. Bozek, E. Kukk, E.R. Davidson: "Peculiar non-adiabatic effects in the photoelectron spectrum of allene (1,2-propadiene)," APS Centennial Meeting, Atlanta, Georgia USA, March 1999.
6. J.D. Bozek, E. Kukk, N. Berrah, J.A. Sheehy, P.W. Langhoff: "Angular distributions in the S 2p photoelectron spectrum of OCS with molecular-field, vibrational and spin-orbit splitting," APS Centennial Meeting, Atlanta, Georgia USA, March 1999.
7. W.T. Cheng, D. Cubaynes, E. Kukk, J. Bozek, G. Snell, S. Diehl, J.-M. Bizau, N. Berrah and F.J. Wuilleumier: "High Spectral-Resolution Photoionization Studies of Lithium Atoms by High Resolution Electron Spectroscopy," ICPEAC XXI, Sendai, Japan, July 1999.
8. B. Langer, E. Kukk, A.A. Wills, A. Farhat, O. Nayandin, M. Alsherhi, N. Berrah, J.D. Bozek,

- D. Cubaynes, R. Hentges and U. Becker: "2-dimensional time-of-flight electron spectrometry: the inner shell excitations in rare gases and small molecules," ICPEAC XXI, Sendai, Japan, July 1999.
9. S. Diehl, W.T. Cheng, E. Kukk, D. Cubaynes, G. Snell, J. Bozek, J.-M. Bizau, N. Berrah and F.J. Wuilleumier: "High-resolution studies of autoionizing states of Li^+ ion," 18th International Conference on X-ray and Inner-Shell Processes, Chicago, USA August 1999.
 10. W.T. Cheng, S. Diehl, E. Kukk, D. Cubaynes, G. Snell, J. Bozek, J.-M. Bizau, N. Berrah and F.J. Wuilleumier: "Term-resolved measurements of the Li^+ satellite photoionization cross-sections in lithium atoms," 18th International Conference on X-ray and Inner-Shell Processes, Chicago, USA August 1999.
 11. E. Kukk, J.D. Bozek, N. Berrah, J.A. Sheehy and P.W. Langhoff: "Angular Distributions of Molecular-Field and Spin-Orbit Split Core Levels of Sulfur 2p Photoemission in OCS: A Sensitive Probe of the Molecular Environment," Compendium of User Abstracts and Technical Reports 1998, ALS, Berkeley 1999.
 12. N. Berrah, K.J. Børve, J. Bozek, T. X. Carroll, J. Hahne, E. Kukk, L. J. Sæthre and T. D. Thomas: "High-Resolution Carbon 1s Photoelectron Spectrum of Small Molecules," Compendium of User Abstracts and Technical Reports 1998, ALS, Berkeley 1999.
 13. E. Kukk, J.D. Bozek, W.-T. Cheng, R.F. Fink, A.A. Wills and N. Berrah: "Auger decay of the $\text{C } 1s^{-1}2\pi^*$ resonance in carbon monoxide: vibrationally and angularly resolved spectra," Compendium of User Abstracts and Technical Reports 1998, ALS, Berkeley 1999.
 14. G. Snell, E. Kukk and N. Berrah: "Angular Distribution Measurements of the Xenon $\text{N}_{4,5} \text{O}_{2,3}$ Auger electrons," Compendium of User Abstracts and Technical Reports 1998, ALS, Berkeley 1999.
 15. W. T. Cheng, G. Snell, E. Kukk and N. Berrah: "Angular distribution of I 4d photoelectrons from HI molecules," Advanced Light Source User's Meeting, Berkeley, USA, Oct. 1999.
 16. T.X. Carroll, J. Hahne, T.D. Thomas, L.J. Saethre, N. Berrah, J. Bozek and E. Kukk: "Carbon 1s core-hole lifetime in CO_2 ," Advanced Light Source User's Meeting, Berkeley, USA, Oct. 1999.
 17. E. Kukk, J.D. Bozek and N. Berrah, "Resonant Auger decay of the $\text{C } 1s^{-1}\pi^*$ core excitations in the CO_2 molecules," Advanced Light Source User's Meeting, Berkeley, USA, Oct. 1999.
 18. E. Kukk, J.D. Bozek and N. Berrah: "Photoexcitation and Auger decay of the Renner-Teller split $\text{C } 1s^{-1}\pi^*$ state in CO_2 ," ALS Compendium of abstracts 1999 (in print).

19. W.-T. Cheng, E. Kukk, D. Cubaynes, J.C. Chang, J.D. Bozek, G. Snell, F. Wulleumier and N. Berrah: "Studies of electron correlations in lithium," ALS Compendium of abstracts 1999 (in print).
20. J.D. Bozek, E. Kukk, N. Berrah, J.A. Sheehy, P.W. Langhoff, "Angular distributions in the S 2p photoelectron spectrum of OCS with molecular-field, vibrational and spin-orbit splitting," 1999 Centennial Meeting of the American Physical Society, March 20-26, Atlanta, GA
21. J.D. Bozek, E. Kukk, W.-T. Cheng, N. Berrah, "Resonance Auger spectra of C 1s⁻¹2π_u excited CO₂," 1999 Centennial Meeting of the American Physical Society, March 20-26, Atlanta, GA
22. E. Kukk, J.D. Bozek, A. Wills, W.-T. Cheng, B. Langer, G. Snell, N. Berrah, "Fully Vibrationally Resolved Auger Electron Spectra Following the C 1s → π Excitations in CO," 1999 Centennial Meeting of the American Physical Society, March 20-26, Atlanta, GA
23. G. Snell, B. Langer, J. Viehhaus, E. Kukk, J. Bozek, N. Berrah, "First spin-resolved gas-phase studies at the ALS," 1999 Centennial Meeting of the American Physical Society, March 20-26, Atlanta, GA
24. A.D.O. Bawagan, J. Bozek, E. Kukk, E.R. Davidson, "Peculiar non-adiabatic effects in the photoelectron spectrum of allene (1,2-propadiene)," 1999 Centennial Meeting of the American Physical Society, March 20-26, Atlanta, GA
25. N. Berrah, A.A. Wills, E. Kukk, B. Langer, J.D. Bozek, O. Nayandin, M. Alshehri, A. Farhat, "Angle-resolved 2D imaging of electron emission processes in atoms and molecules using the ALS," 12th International Conference on Vacuum Ultraviolet Radiation Physics, Aug. 3-7, San Francisco, CA.
26. T.X. Carroll, N. Berrah, J. Bozek, J. Hahne, E. Kukk, L.J. Saethre, T.D. Thomas, "High-resolution carbon 1s photoelectron spectrum of methane: vibrational excitation and core-hole lifetime," 12th International Conference on Vacuum Ultraviolet Radiation Physics, Aug. 3-7, San Francisco, CA.
27. T.D. Thomas, N. Berrah, J. Bozek, T.X. Carroll, J. Hahne, E. Kukk, L.J. Saethre, "High-resolution carbon 1s photoelectron spectrum of HCCH and DCCD: the u-g splitting," 12th International Conference on Vacuum Ultraviolet Radiation Physics, Aug. 3-7, San Francisco, CA.
28. E. Kukk, J.D. Bozek, A. Wills, W.-T. Cheng, B. Langer, G. Snell, M. Wiedenhof, O. Nayadin, M. Alshehri, N. Berrah, "Fully vibrationally resolved auger electron spectra following the C 1s → π* excitations in the CO and CO₂ molecules," 12th International Conference on Vacuum Ultraviolet Radiation Physics, Aug. 3-7, San Francisco, CA.

29. E. Kukk, A.A. Wills, B. Langer, O. Nayandin, M. Alshehri, A. Farhat, D. Cubaynes, J.D. Bozek, N. Berrah, "Angle-resolved 2D imaging of electron emission processes following Cl 2p excitation in HCl," 12th International Conference on Vacuum Ultraviolet Radiation Physics, Aug. 3-7, San Francisco, CA.
30. E. Kukk, A.A. Wills, B. Langer, J.D. Bozek, O. Nayandin, M. Alshehri, A. Farhat, D. Cubaynes, N. Berrah, "Angle-resolved two-dimensional mapping of electron emission following Cl 2p excitation in the HCl molecule," Compendium of user abstracts and technical reports – 1997.
31. J. Bozek, T.X. Carroll, G. Gard, J. Hahne, L.J. Saethre, J. True, T.D. Thomas, "High-resolution carbon 1s photoelectron spectra of small molecules," Compendium of user abstracts and technical reports – 1997.
32. H. Brauning, R. Dorner, J.M. Feagin, C.L. Cocke, T. Osipov, M. Achler, A. Brauning-Demian, O. Jagutzki, V. Mergel, M.H. Prior, J. Bozek, N. Berrah, J. Ullrich, R. Moshhammer, H. Schmidt-Bocking, "Photo double ionization of spatially aligned D₂," Compendium of user abstracts and technical reports – 1997.
33. J.D. Bozek, "Vibrationally resolved core level photoelectron spectroscopy of simple molecules," International Workshop on Photoionization, July 16-21, 1997, Chester, U.K.
34. J. Bozek, T.X. Carroll, J. Hahne, L.J. Saethre, J. True, T.D. Thomas, "High-resolution carbon 1s photoelectron spectrum of ethene, ab initio calculation of vibrational structure," International Conference on Electron Spectroscopy, September 1997, Chiba, Japan
35. J.D. Bozek, T.X. Carroll, J. Hahne, L.J. Saethre, J. True, T.D. Thomas, "Vibrationally resolved inner-shell photoelectron spectroscopy of simple molecules," ALS Users meeting, October 13, 1997, Berkeley, CA
36. H. Brauning, C.L. Cocke, T. Osipov, R. Dorner, V. Mergel, M. Achler, A. Brauning-Demian, O. Jagutzki, H. Schmidt-Bocking, M.H. Prior, J. Bozek and N. Berrah, "Photo double ionization of spatially aligned D₂⁺," 1998 Annual Meeting of the Division of Atomic, Molecular and Optical Physics of the American Physical Society, May 27-30, 1998, Santa Fe, NM
37. N. Berrah, E. Kukk, A.A. Wills, M. Alshehri, A. Farhat, O. Nayandin, B. Langer, D. Cubaynes, J.D. Bozek, "Angle-resolved 2D imaging of electron emission processes following Cl 2p excitation in HCl," 1998 Annual Meeting of the Division of Atomic, Molecular and Optical Physics of the American Physical Society, May 27-30, 1998, Santa Fe, NM
38. A. Aguilar, A.M. Covington, R.A. Phaneuf, N. Berrah, I. Alvarez, C. Cisneros, J. de Urquijo, J. Bozek, I. Dominguez, A.S. Schlachter, M. Lubell, T.J. Morgan, A. Muller, E. Salzborn,

"Development of a collinear apparatus for photon-ion interaction studies," 1998 Annual Meeting of the Division of Atomic, Molecular and Optical Physics of the American Physical Society, May 27-30, 1998, Santa Fe, NM

39. J. Bozek, "Beamline 10.0 - an undulator beamline for high-resolution spectroscopy at the ALS," 1998 Annual Meeting of the Division of Atomic, Molecular and Optical Physics of the American Physical Society, May 27-30, 1998, Santa Fe, NM

B) Endstation for Electron-Spin Polarization Studies.

G. Snell^{1,2}, B. Langer³, S. Canton-Rogan^{1,2} and N. Berrah¹

¹Physics Department, Western Michigan University, Kalamazoo, MI 49008

²Lawrence Berkeley National Laboratory, ALS, Berkeley, CA 94720

³Max-Born Institut, Berlin, Germany

1) Introduction

The so-called "complete experiments" in atomic and molecular photoionization have become possible in recent years due to the development of highly differential experimental methods and elliptical polarized light provided by third generation light sources. An experiment is complete, if in the framework of a given physical model, *all* parameters that describe the process can be determined quantum mechanically.

Most spectroscopy experiments are spin-unresolved, giving partial information on the photoionization and Auger processes. Namely, only the partial cross section and angular distribution can be obtained in differential measurements. Transitions matrix elements and phase shifts between the outgoing waves cannot be determined with these two parameters. Three additional parameters, the three spin-polarization components, are needed. Therefore, measuring spin polarization of photo- and Auger electrons from free atoms and molecules after photoionization by circularly polarized light allows one to conduct *quantum mechanically complete* experiments and to extract the dipole and coulomb matrix elements [1].

The spin polarization of photoelectrons, produced with radiation of any polarization, can occur only if relativistic effects are taken into account, e.g. the spin-orbit split components of the photoion are resolved and/or a strong spin-orbit interaction is present for the electron in the continuum [2]. The hole left behind will be oriented and Auger decay of these holes results in spin polarized Auger electrons [3]. The polarization of the singly charged photoion can be determined both from the properties of the photo- and of the Auger electrons. These measurements allow tests of the validity of the two-step-model of the Auger-decay (in this model the photoionization and Auger decay processes are assumed to proceed independently). Correlations between the outgoing electrons, such as post collision interaction, can be examined and angular momentum coupling models of two-hole states can be tested. A complete characterization of a photoprocess yields the dipole matrix elements of the specific photon-atom interaction. Through the matrix elements information about the most basic quantity of quantum mechanics, the wave functions of the initial (atom) and final (ion) states can be gained and thus different physical models of the atomic structure and photon-atom interaction can be tested. Also the detailed examination of Auger processes by means of spin-resolved electron spectroscopy of free atoms is very important for the understanding of similar phenomena in condensed matter [4]. In the case of experiments on metal vapor, we can extract in addition to fundamental information, the magnetic moments that can be compared to values obtained using solids. The comparison of those values infer solid-state

effects.

Spin-resolved measurements in the gas phase have been pioneered [1, 5, 6] in Europe and researchers have struggled with low counting rates due to the combination of tenuous targets and insufficient photon intensity. Complete photoionization experiments on valence electrons were performed up to about 30 eV photon energy using spin-resolved photoelectron spectroscopy and off-plane synchrotron radiation [7]. Using the same techniques, radiationless decays have been studied on free Ba atoms for excitation energies below 30 eV [8]. Complete innershell photoionization experiments were performed on the Xe 4d subshell at two specific photon energies only, 94 eV and 132 eV, using a photoelectron-Auger electron coincidence technique [5, 9]. At 94 eV also spin-resolved measurements were performed [10] where a Mo/Si multilayer was used to produce circularly polarized light [11]. The first spin-resolved measurements on deep innershell electrons were done at an ionization energy of 834 eV on the Xe 3d photoelectrons and MNN Auger group [4] at the helical undulator beamline of the ESRF.

Due to the lack of an intense source of circularly polarized synchrotron radiation in the energy range of 30-500 eV, no systematic studies of the photoionization and Auger decay of free atoms and molecules could be done in the very important VUV region. However, with the ALS elliptical polarizer undulator (EPU), it is now possible to conduct these types of experiments using circularly polarized beam.

A new endstation for the study of spin-resolved investigation is described below. In addition, highlights are presented of recent photoionization measurements.

2) Report on the Electron Spin-Polarization Endstation

We have built a very efficient experimental system [12], shown in Fig. 1, based on time-of-flight (TOF) electron energy analyzers [13] combined with compact Mott polarimeters [14]. Due to the substantial loss of signal intensity during Mott scattering our experiment benefits considerably from the TOF technique's inherent capability of simultaneous acquisition, and in this case additional spin polarization analysis, of all photolines and Auger electrons in a spectrum with a high signal to noise ratio. A distinctive feature of our system is that it allows the simultaneous measurement of all three components of the spin polarization vector. This has not been achieved yet in any other experimental system.

The Mott polarimeters are of the retarding-field type and follow the Rice University design [14]. We use microsphere plates (MSPs) as electron detectors, to achieve the high timing resolution needed for time-of-flight electron spectroscopy [12]. Briefly, after the gas-phase target interacts with the photons in the interaction region, electrons (photo- and Auger) resulting from photoionization, are detected by an electron TOF spectrometer. The electrons are allowed to drift in the TOF drift tube and are then accelerated to 25 KV to the scattering thorium target. Mott polarimeters take advantage of the left/right scattering asymmetry that results due to the spin-orbit effect when (polarized) electrons scatter quasi-elastically from a high-Z target maintained at a high potential. This asymmetry A is related to the component of electron spin polarization perpendicular to the scattering plane by $P=A/Seff$, where $Seff$ is the effective analyzing power.

The detector signals are treated the same way as any TOF signal, i.e. the time difference between the ionizing light pulse and the arrival of the electrons is measured.

In order to obtain all three polarization components, we have built two Mott-TOF systems. One of the Mott polarimeters is equipped with four MSP detectors and thus can measure the two spin polarization components P_x and P_y , which are perpendicular to the electron propagation direction (transversal components). In order to be able to determine the longitudinal component P_z , i.e. the one parallel to the electron propagation direction, the electron polarization has to be rotated by 90 degrees, before it can be detected in a Mott polarimeter. For this reason, we inserted a Wien filter between the TOF and the Mott in the second spectrometer system. A Wien filter is a device, which can rotate the electron spin polarization by utilizing a crossed electric and magnetic field. Additionally, a standard TOF spectrometer is also part of the apparatus for calibration and setup purposes.

The endstation is separated from the beamline by a differential pumping stage. A similar experimental setup was used in earlier measurements at other synchrotron radiation sources with great success [4]. Our experimental system is greatly improved in comparison, since we will be capable of measuring all components of the spin polarization vector simultaneously.

For these types of experiments, there is a need for high degree of circular polarization and high flux that can be obtained using the EPU beamline 4.01. Since the system is based on TOF electron energy analyzers the experiments are conducted during the double bunch operation of the ALS storage ring that occur twice a year, for two weeks each time.

Fig. 1. Schematic of the spin-resolved apparatus.

Initial Results:

We have already made a proof of principle of the experimental system by carrying-out experiments on rare gases Ar, Kr, and Xe [15] using the EPU without monochromator since it was not ready. For the first time, a complete characterization of the xenon 4d photoionization process over the energy range of 100-300 eV was carried out because the cross section shows an

Fig. 2 Xe $N_{4,5} O_{2,3} O_{2,3}$ Spin-resolved spectra taken with the new endstation and the EPU beamline with circularly polarized light.

interesting behavior over this photon energy range. At 100 eV (approx. 30 eV above threshold) it reaches a broad maximum, a shape resonance, and at 180 eV it runs through a minimum, a Cooper-minimum. Fig.2 shows the spin-resolved Xe $N_{4,5} O_{2,3} O_{2,3}$ Auger spectra taken at photon energy of 141 eV. The bottom curve shows the total intensity of the Auger lines and the top curves show the intensities in the case of the electron spin parallel or anti-parallel to the photon direction. Clearly these spectra show evidence of spin polarization. Also, it is interesting to notice

that although in the total intensity the 3P_1 and 3P_0 are not resolved they are clearly separated in the spin-resolved intensity. The measurement of the spin polarization of the 1S_0 lines of the $N_{4,5}O_{2,3}O_{2,3}$ Auger group allow us to determine the orientation of the singly charged $4d^{-1}$ photoion. These needed results yield additional information about the photoionization process and thus complete the set of the photoionization parameters. The spin polarization of the other lines of the Auger group give information on the Auger-decay itself.

The data is presently being analyzed in detail to extract the orientation and alignment parameters using cross sections and angular distribution parameters already known for this region [16, 17] and some measured by us [18,19]. These parameters are respectively proportional to the magnetic dipole and electric quadrupole moments. Since the EPU's bandwidth was only about 3.5 eV, all we could measure was spin-resolved Auger spectra but not photolines therefore only the Coulomb matrix elements can be obtained. The measurements were also done on the Kr MNN and Ar LMM decay processes in the photon energy range of 130-600 eV. The use of the broadband radiation allowed high efficiency measurements especially around the Cooper minima where the intensity of the lines is weak.

For the first time, our measurements covered a broad photon energy range and in particular the *weak* Cooper minima. Also, for the first time, our measurements allowed us to prove the theoretical expectation of the vanishing of the f component of the outgoing electron wave.[15,19]

Future experiments will be done in vapor targets, metal and transition metal, and in molecules. In the case of metal vapors, from the measurement of the orientation and alignment we can extract the magnetic dipole and electric quadrupole moments that can be compared to the values obtained using solids. The comparison between the values obtained in the gas-phase and the solid state-phase will allow one to infer solid-state effect. In the case of molecules, one is able to study chirality in molecules. These experiments will be hard, since the count rate will be low, but not impossible.

References

1. U. Heinzmann and N. A. Cherepkov, in VUV- and Soft X-ray Photoionization Studies, Eds. U. Becker and D. A. Shirley, p. 521 (Plenum Press, New York, 1996).
2. N. A. Cherepkov, J. Phys. B **12**, 1279 (1979)
3. H. Klar, J. Phys. B **13**, 4741 (1980)
4. M. Landolt and D. Mauri, Phys. Rev. Lett. **49**, 1783 (1982)
5. B. Kämmerling and V. Schmidt, Phys. Rev. Lett. **67**, 1848 (1991)
6. G. Snell, M. Drescher, N. Müller, U. Heinzmann, U. Hergenhahn, J. Viehhaus, F. Heiser, U. Becker and N. Brookes, Phys. Rev. Lett. **76**, 3423 (1996).
7. C. Heckenkamp, F. Schäfers, G. Schönhense and U. Heinzmann, Z. Phys.D **2**, 257 (1986)
8. R. Kuntze, M. Salzmann, N. Böwering and U. Heinzmann, Phys. Rev.Lett. **70**, 3716 (1993)
9. S. J. Schaphorst, Q. Qian, B. Krässig, P. v. Kämpen, N. Scherer and V. Schmidt, J. Phys. B **30**, 4003 (1997)
10. G. Snell, U. Hergenhahn, N. Müller, M. Drescher, J. Viehhaus, U. Becker and U. Heinzmann,

- ICPEAC XX. Book of abstracts, Eds. F. Aumayr and H. Winter, Vienna, Austria, 1997
11. J. B. Kortright, H. Kimura, V. Nikitin, K. Mayama, M. Yamamoto and M. Yanagihara, *Appl. Phys. Lett.* **60**, 2963 (1992)
 12. G. Snell, J. Viehhaus, F. B. Dunning and N. Berrah, *Rev. Sci. Instr.* (Submitted)
 13. N. Berrah, B. Langer, A. A. Wills, E. Kukk, J. D. Bozek, A. Farhat, and T. W. Gorczyca, *J. Electr. Spectr. And relat. Phenom.*, **101**, 1 (1999).
 14. G. C. Burnett, T. J. Monroe and F. B. Dunning, *Rev. Sci. Instrum.* **65**, 1893 (1994).
 15. G. Snell, B. Langer, E. Kukk, and N. Berrah, *Proceedings of the 1999 ICPEAC meeting*, Sendai, Japan.
 16. S. Southworth, U. Becker, C. M. Truesdale, P. H. Kobrin, D. W. Lindle, S. Owaki and D. A. Shirley, *Phys. Rev. A* **28**, 261 (1983).
 17. U. Becker, D. Szostak, H. G. Kerkhoff, M. Kupsch, B. Langer, R. Wehlitz, A. Yagishita and T. Hayaishi, *Phys. Rev. A* **39**, 3902 (1989)
 18. Farhat, M. Humphrey, B. Langer, N. Berrah, J. D. Bozek and D. Cubaynes, *Phys. Rev. A* **56**, 501 (1997).
 19. G. Snell, E. Kukk, B. Langer, and N. Berrah, *Phys. Rev. A* **61**, (2000)

FINANCIAL SUPPORT

This instrumental development was funded by the DOE Facilities Initiative under contract DE-FG02-92ER14299 and by the Office of Basic Energy Sciences, Chemical Sciences Division of the U.S. Department of Energy under contract DE-FG02-96ER14654 with Western Michigan University.

Related Publication and Presentation

1. G. Snell, E. Kukk, B. Langer, and N. Berrah, "Angular distribution measurements of the xenon N_{4,5}O_{2,3}O_{2,3} Auger electrons: determination of alignment and intrinsic parameters," *Phys. Rev. A* **61**, (2000)
2. G. Snell, J. Viehhaus, F. B. Dunning, and N. Berrah, "Microsphere plate detectors used with a compact Mott polarimeter for time of flight studies." *Rev. Sci. Instrum.*, in press (scheduled for June 2000)
3. T. Young, A. Robinson, G. Snell, and N. Berrah, "First results from the ALS Elliptically Polarizing Undulator beamline," *Synchrotron Radiation News* **12**, 31(1999).
4. G. Snell, B. Langer, E. Kukk, and N. Berrah, "Spin- and angle-resolved Auger spectroscopy of xenon," *Proceedings of the 21st International Conference on the Physics of Electronic and Atomic Collisions*, Sendai, Japan, 22-27 July 1999; AIP, New York (2000)

Invited Talks:

"Spin-polarized Auger and photoelectron spectroscopy of Xenon" International Conference on the Physics of Electronic and Atomic Collisions, ICPEAC-XXI, Sendai, Japan, July 22-27 1999.

"Spin-resolved electron spectroscopy on gas-phase targets at the Advanced Light Source" Photon Factory, KEK, Tsukuba, Japan, August 2. 1999.

"Magnetic dipole moment of the Xe 4d-1 and Kr 3d-1 hole states - first measurements with the Elliptical Polarization Undulator", Advanced Light Source User's Meeting, Berkeley, CA, October 18-20 1999.

C) Endstation for Studies of Photon-Ion Interaction

A.M. Covington¹, A. Aguilar¹, I. Alvarez², N. Berrah³, J. Bozek⁴, C. Cisneros², I.R. Covington¹, I. Domínguez⁴, G. Hinojosa¹, M.M. Sant' Anna⁵, A.S. Schlachter⁴, and R.A. Phaneuf¹

¹Department of Physics, University of Nevada, Reno, Reno, NV 89557-0058

²Centro de Ciencias Físicas, UNAM, Apartado Postal 6-96, Cuernavaca, 62131, México

³Physics Department, Western Michigan University, Kalamazoo MI

⁴Lawrence Berkeley Laboratory, Advanced Light Source, Mail Stop 7-100, Berkeley, CA 94720

⁵Conselho Nacional De Pesquisa E Desenvolvimento Brasília D. F., Brazil

1) Introduction

Most of the known matter in the universe exists in the ionized plasma state, and the majority of the information that we have about the distant universe is carried to us by photons. Therefore a quantitative understanding of plasma opacities (the processes by which photons are emitted and reabsorbed by ions) is fundamental to astrophysics. The situation is similar for laser-produced plasmas in both inertial confinement fusion and XUV-photolithography research. A majority of photon opacities are currently based on theoretical calculations, and experimental benchmarks are few. Through the use of well-established accelerator technology, ion beams can be extracted from plasmas under highly controlled laboratory conditions. These ion beams are readily amenable to experimental study. Combining these techniques with emerging synchrotron technologies [1], such as undulator beamline 10.0 at ALS, affords a unique opportunity to study the interactions of photons with atomic and molecular ions found in the plasma state. New measurements may now be carried out that provide high-resolution spectroscopic data, resonance line-shapes, as well as absolute photoionization cross sections. In atomic and molecular physics, such data are needed for isolated ions in order to understand electron-electron interactions in complex, highly correlated systems. A new endstation for the study of ion-photon interactions at ALS is described. In addition, highlights are presented of two recent photoionization measurements; the first a study of metastable states of O⁺, and the second involving measurements on Ne⁺ at high spectral resolution.

2) Report on the Ion-Photon-Beam Endstation

A schematic diagram of the endstation developed for the study of photon-ion interactions is shown in Fig. 1. Singly-charged ions are produced in a hot-filament discharge ion source, and accelerated to ion beam energies ranging from 5-15 keV. Following extraction, the primary ion beam is focused by a series of cylindrical electrostatic einzel lenses. Ionic species are selected using a 60° analyzing magnet with a mass-per-charge resolution of approximately 100. The cross-sectional area of the ion beam is defined by two sets of adjustable beam slits mounted in the plane perpendicular to the ion beam velocity vector. After the ion beam has been selected and collimated, a set of 90° spherical-sector bending-plates merge the ion beam onto the axis of the counter-propagating photon beam from ALS beamline 10.0. The primary ion beam then enters a cylindrical interaction region that can be electrostatically biased to energy label the energy of photo-ions produced therein. In the center of the interaction region, the two-dimensional spatial overlap between the photon and ion beams is measured using a stepping-motor-driven slit scanner. Similarly, rotating-wire beam profile monitors are used at the beginning and end of the interaction region in order to ensure that the beams are well collimated along the entire interaction region. Fine positioning of the ion beam trajectory is achieved by two sets of mutually perpendicular electrostatic steering plates mounted immediately before the merging plates. The photon intensity is monitored using a calibrated Si p-n junction photodiode. A second 45° analyzing magnet demerges the beams and disperses doubly-charged photo-ions produced in the interaction region from singly-charged ions in the primary beam.

Figure 6. Ion-photon-beam (IPB) research endstation installed at ALS undulator beamline 10.0.1

Following dispersion into the vertical plane, the interaction primary beam is collected in a Faraday cup, while the photo-ions pass through a hole in the back of the cup. The primary ion beam current is monitored for normalization of the photo-ion yield. The photo-ion beam enters another set of 90° spherical-sector bending-plates that deflect the beam out of the vertical dispersion plane and help to minimize background counts associated with the collection of the primary ion beam. Thereafter, the photo-ions enter a negatively-biased detection box, wherein the ions impinge upon a stainless steel plate and produce secondary electrons, which are in turn accelerated towards a microspherical plate single-particle detector with a positively-biased anode. It should be noted that doubly charged ions are also produced in collisions between the fast-moving ions in the primary beam and residual gas molecules in the ultra-high vacuum system. Hence, it is necessary to chop the photon beam in order to subtract this background.

Figure 2. Comparison of photo-ion yield measurements and theory for near-threshold photoionization of O^+ , showing the contributions of metastable states.

Figure 3. High-resolution photo-ion yield measurements for photoionization of Ne^+ with $E = 7.5$ meV.

Initial Results

Photoionization measurements on O^+ were made over a broad photon energy range (29-51 eV). A photo-ion yield spectrum taken in the photon energy range near the O^{2+} ionization threshold is shown in Fig. 2. This spectrum was taken with a nominal photon energy resolution of 25 meV. The resonance features below the $O^+(2s^2 2p^3 \ ^4S)$ ground state threshold at 35.12 eV correspond to photoionization from the $O^+(2s^2 2p^3 \ ^2D$ and $^2P)$ long-lived metastable states. O^+ metastable ions are ubiquitous in nature, and account for 60% of the total ion beam current. The metastable fraction was determined by passing the O^+ ion beam through a nitrogen-filled gas cell placed at the output of the ion source. The metastable components of the O^+ beam undergo a resonant charge transfer process with the N_2 gas molecules and are neutralized [2]. In contrast, charge transfer with the 4S ground state is non-resonant. Therefore, it is possible to readily attenuate the metastable ions and to determine their population in the beam. Also shown in Fig. 2 are the results of recent R-matrix calculations of cross sections for photoionization from the 2D and 2P metastable states [3].

Shown in Fig. 3 is a photo-ion yield spectrum for the photoionization of Ne^+ at photon energies just below the $Ne^{2+} (^1D)$ ionization threshold (44.167 eV). At least two Rydberg series are evident in the spectrum, and are assigned to the $Ne^+ 2p^4 (^1D) nP$ autoionizing resonances [4.] The metastable states of Ne^+ all have lifetimes of less than 100 ns, so the beam is comprised of ground state ions only in this case [5]. This spectrum was taken with a nominal photon energy resolution of 7.5 meV, a demonstration of the high-resolution capabilities of the ion-photon-beam endstation at ALS beamline 10.0. Line-widths of several individual resonances have been measured at a nominal resolution of 1 meV. Comparisons with predictions of a recent 28-state R-matrix calculation [6] indicate that spin-orbit coupling may be required to reproduce all of the experimentally observed resonance features. Absolute photoionization cross section measurements have also been completed for both O^+ and Ne^+ .

References

1. Massimo Altarelli, Fred Schlachter and Jane Cross, *Scientific American* **279**, 66-73 (1998).
2. B. G. Lindsay, R. L. Merrill, H. C. Straub, K. A. Smith, and R. F. Stebbings, *Phys. Rev A* **57**, 331 (1998).
3. Sultana Nahar, *Phys. Rev A* **58**, 3766 (1998); Sultana Nahar, Private Communication (1999).
4. C. D. Caldwell and M O Krause, *Phys. Rev A* **53**, 1454 (1996).
5. W. Seim, A. Müller, and E. Salzborn, *Z. Phys. A* **301**, 11 (1981).
6. Brendan M. McLaughlin, Private Communication (1999).

FINANCIAL SUPPORT

This research was supported by the Office of Basic Energy Sciences, Chemical Sciences Division of the U.S. Department of Energy under contract DE-FG03-97ER14787 with the University of Nevada, Reno; by the Nevada DOE-EPSCoR Program in Chemical Physics; by the DOE Facilities Initiative under contract with Western Michigan University; and by CONACyT through the Centro de Ciencias Físicas, Universidad Nacional Autónoma de México, Cuernavaca. The participation of A. Aguilar was supported in part by a scholarship from the Universidad Nacional Autónoma de México through DGAPA.

3) Related Publications and Presentations

Invited talks:

1. "High-Resolution Measurements of Photoionization of O^+ Ions," ALS Users' Association Annual Meeting, October 18-19, 1999.
2. "Energetic Photon and Electron Interactions with Positive Ions," DOE Atomic, Molecular and Optical Physics Workshop, Boulder, CO, October 25-27, 1999.
3. "Studies of Photon-Ion Interactions at the Advanced Light Source," ALS Science Policy Board, Lawrence Berkeley National Laboratory, December 14, 1999.
4. "Atomic, Molecular and Optical Physics at ALS Beamline 10," Basic Energy Sciences Advisory Committee, Lawrence Berkeley National Laboratory, February 5, 2000.
5. "Studies of photon-ion interactions at the Advanced Light Source," R.A. Phaneuf, research seminar, Lawrence Berkeley National Laboratory, July 13, 1998.

Research Presentations at Conferences and Workshops:

XXI International Conference on the Physics of Electronic and Atomic Collisions, Sendai, Japan, July 22-27, 1999: A.M. Covington, A. Aguilar, J.D. Bozek, C. Cisneros, I.R. Covington, I. Dominguez, G. Hinojosa, A.S. Schlachter, C.A. Shirley and R.A. Phaneuf, "Experimental Study of the Photoionization of O^+ ," post-deadline paper.

18th International Conference on X-Ray and Inner-Shell Processes, Chicago, IL, August 23-27, 1999: A.M. Covington, A. Aguilar, I. Alvarez, N. Berrah, J.D. Bozek, C. Cisneros, I.R. Covington, I. Dominguez, G. Hinojosa, A.S. Schlachter, C.A. Shirley and R.A. Phaneuf, "High-Resolution Measurements of Photoionization of O^+ Ions," post-deadline paper.

ALS Users' Association Annual Meeting, Berkeley, CA, October 18-19, 1999: A.M. Covington, A. Aguilar, I. Alvarez, N. Berrah, J.D. Bozek, C. Cisneros, I.R. Covington, I. Dominguez, G. Hinojosa, A.S. Schlachter, C.A. Shirley and R.A. Phaneuf, "High-Resolution Measurements of Photoionization of O^+ Ions," contributed paper.

Annual Meeting of the APS Division of Atomic, Molecular and Optical Physics, Santa Fe, NM, May, 1998: A. Aguilar et al., "Development of a Collinear Apparatus for Photon-Ion Interaction Studies," Bull. Am. Phys. Soc. 43, 1335 (1998).

DOE-BES Workshop on Atomic, Molecular and Optical Physics, Washington, DC, September 21-23 1997: R.A. Phaneuf, "Energetic Photon and Electron Interactions with Positive ions,"

proceedings, page 92.

Advanced Light Source Users' Association Annual Meeting, Berkeley, CA, October 13-14, 1997:
A. Aguilar, R.A. Phaneuf, I. Alvarez, C. Cisneros, J. De Urquijo, N. Berrah, J. Bozek, I. Dominguez, A.S. Schlachter, M. Lubbell, T.J. Morgan, A. Müller and E. Salzbom "Experimental End-Station for Studies of Photon-Ion Interactions."

Related Grant Proposals Submitted

"Energetic Photon and Electron Interactions with Positive Ions," R. A. Phaneuf, U.S. Department of Energy, Office of Basic Energy Sciences, submitted in August, 1996 (\$461,000 awarded, \$150,000 for first year beginning August 1, 1997).

"Energetic Photon and Electron Interactions with Positive Ions," R. A. Phaneuf, U.S. Department of Energy, Office of Basic Energy Sciences. Progress report and continuation application submitted in April 1998 (\$150,000 awarded for second year).

"Energetic Photon and Electron Interactions with Positive Ions," R. A. Phaneuf, U.S. Department of Energy, Office of Basic Energy Sciences. Progress report and continuation application submitted in April 1999 (\$152,313 awarded for third year).

"Nevada DOE/EPSCoR Proposal," U.S. Department of Energy, R.A. Phaneuf, principal investigator, submitted January 1999 to DOE EPSCoR Program (\$750,000 awarded for period September 30, 1999 – September 29, 2000; approximately \$30,000 per year available to ion-photon project since September, 1997).

"Energetic Photon and Electron Interactions with Positive Ions," R.A. Phaneuf, U.S. Department of Energy, Office of Basic Energy Sciences. Three-year progress report and renewal application submitted in January 2000 (\$651,751 requested for three years, beginning August 1, 2000; under review.

D) Quarter Wave Retarder.

O Yenen¹, K.W. McLaughlin², D.H. Jaecks¹, M.M Sant'Anna³, E.A. Seddon⁴,
T.J. Gay¹, B.J. Thaden¹, and D. Calabrese⁵

¹Department of Physics, University of Nebraska-Lincoln, Lincoln NE 68588-0111

²Department of Physics and Engineering, Loras College, Dubuque IA 52004-0178

³Advanced Light Source, Ernest Orlando Lawrence Berkeley National Laboratory,
University of California, Berkeley, California 94720, USA

⁴Daresbury Laboratory, Daresbury, Warrington Cheshire WA4, 4AD, UK

⁵Sierra Community College, Rocklin CA 95677

1) Introduction

We have developed a new paradigm to quantify relativistic electron-electron interactions in multielectron isolated atomic systems using photoionization by circularly polarized vuv radiation. This new paradigm utilizes the property that circularly polarized synchrotron radiation has a specific intrinsic angular momentum and complements the well established methods of using the wave nature of synchrotron radiation to study the details of nanoscale systems. Since the angular momentum is conserved in isolated atomic systems, the one unit of angular momentum of the incident circularly polarized photon is absorbed by the atomic system and transferred to atomic electrons as their orbital and spin angular momenta. After photoionization of the atomic system, we measure the degree of circular polarization of the visible fluorescent radiation from the residual excited ion. In the last step of our algorithm we extract a measure of the relativistic interactions between the electrons using the well-known angular momentum coupling rules.

2) Report on the Quarter Wave Retarder

The quarter wave retarder consists of two set of two parallel gold mirrors, arranged in such a way that the synchrotron beam reflects at grazing incidence, off all four mirrors, yet with no net deflection of the incident beam. Gold has long term stability and also the property that the two electric vector components of linearly polarized light, in and perpendicular to the plane of incidence, suffer a relative phase shift that is photon energy and angle of incidence dependent. The reflection coefficient of the two electric components are also dependent upon the angle of incidence. The angle of incidence of the four mirrors are adjusted so that the relative phase shift between the two components add up to ninety degrees. The mirrors are then rotated axially about the beam axis so that the two components of the emerging radiation have the same amplitude. This axial adjustment takes care of the fact the reflection coefficient is different for the two electric vector components. All of these adjustments are done by computer control of stepper motors that are outside the UHV vacuum chamber. We carried out measurements of the degree of circular polarization using a second analyzer and found it to be 99.7%. So within experimental error, we have pure circularly polarized light.

In April and March of 1999, a four mirror-1/4 wave retarder was successfully installed. This required a precise axial alignment of the UHV chamber that housed the movable gold plated mirrors. The angular position of each mirror was precisely calibrated. The device was tested at several photon energies in the 30-50eV photon energy range. From measurements, the device was found to produced 99.7% circularly polarized radiation of either helicity.

To produce ionizing photons of well-defined angular momentum, we have installed, calibrated and characterized a four-reflection quarter-wave retarder based on earlier suggestions and prototypes.^{1,2} The measurements show the retarder produces better than 99.7% circularly polarized radiation from the linearly polarized VUV radiation from the 10.0.2 beam line in the 35.5 to 37 eV photon energy range typically with 1 % efficiency. Fig. 1 (a) and (b) show polar plots of the intensity of radiation without and with the retardation respectively, as measured by using a 45° gold mirror linear polarization analyzer placed in front of a photodiode.

The degree of circular polarization of the visible fluorescent photons from the excited residual ion is measured in the forward direction with respect to the incident ionizing radiation. In addition, to completely determine the partial wave amplitudes of the emitted photoelectron, when the total angular momentum of the excited ion is larger than $\frac{1}{2}$, the degree of linear polarization of the visible fluorescent radiation is measured in a direction perpendicular to the direction of the incident ionizing photon's helicity. Measurements are obtained for the visible fluorescent radiation from the decay of fine-structure resolved $3p^4 [^3P] 4p \ ^2P_{1/2, 3/2}$, $3p^4 [^3P] 4p \ ^2D_{3/2, 5/2}$, and $3p^4 [^1D] 4p \ ^2F_{7/2}$ excited states of Ar^+ .

The algorithms we have developed give the expectation value of the z-component of a variety of angular momenta associated with the "residual ion + photoelectron" system or its components. These are the total angular momentum, the total orbital and total spin angular momenta, the orbital and spin angular momenta of the $3p^4$ core-electrons, the orbital and spin angular momenta of the $4p$ valence electron, and the spin angular momentum of the photoelectron. In addition, we also obtain the amplitudes of the allowed partial waves of the emitted photoelectron. Although we do not measure the photoelectron, we can deduce from our analysis the total spin polarization of all of the electrons emitted to 4π solid angle.

Figure 1. Polar Plots of the intensity of the radiation as a function of the angle of the 45° Gold mirror linear polarization analyzer.

- (a): The retarder is out of the incident radiation's path, the radiation is linearly polarized;
- (b): The retarder is in the incident radiation's path, the radiation is circularly polarized

Since the absorbed photon cannot change the total spin of the system which is initially zero, any non-zero measurement of the final spin of the "residual ion + photoelectron" system is a

measure of the relativistic interactions during the photoionization. Our measurements show that over the entire energy range studied the relativistic interactions are significant.

Experiments Carried Out to Date.

Using the purely circularly polarized radiation in the 35-38 eV range, we have measured the alignment and orientation parameter of the following satellite states of Ar^{+*} : (all doublets of odd parity) $P(J=1/2)$, $P(J=3/2)$, $D(J=3/2, 5/2)$ and some of $F(J=7/2)$. This is done by measuring the linearly and circularly polarized fluorescence of these states. From the analysis of these parameters, we have determined the degree to which the ionization is influenced by relativistic interactions, we have also determined the probabilities of the partial wave amplitudes in all cases. For the states of $J>1/2$, there are three partial waves. We believe this is the first time that anyone has determined we have also determined that the concept of angular momentum sharing is a viable and important way to characterize the nature of the dynamic photo-process. Two successful experimental runs were carried out in March and again in July-August of 1999. The results of these experiments have led to a new and different interpretation of the photoionization process. Two articles will be submitted to Phys. Rev. Lett; one in early March, 2000 and one in April, 2000.

References

1. P.D. Johnson and N.V. Smith, Nucl. Instr. and Meth. In Phys. Res. **214**, 505 (1983);
N.V. Smith, S.L. Hulbert, P.D. Johnson, and J.L. Erskine, Nucl. Instr. and Meth. In Phys. Res. A **347**, 119 (1994).
2. H. Hochst, R. Patel, and F. Middleton, Nucl. Instr. and Meth. In Phys. Res. A **347**, 107 (1994);
H. Hochst, P. Bulicke, T. Nelson, and F. Middleton, Rev. Sci. Instrum. **66**, 1598 (1995)

FINANCIAL SUPPORT

Funds from the instrumental facility initiative were used to cover part of the cost of the quarter wave plate installed in the beamline. This device can be used by any ALS user that requests the beamline. This research program is supported by the National Science Foundation.

3) Related publications and presentations.

1. O. Yenen, K.W. McLaughlin, and D.H. Jaecks, "High Resolution Polarization Analysis of the

Fluorescence from $\text{Ar}^+ [^3\text{P}]4p\ 2\text{P}^0_{3/2}$ Formed in Photoionization," Phys. Rev. Lett. 79, 5222 (1997).

2. K.W. McLaughlin, O. Yenen, J.A.R. Samson, D.H. Jaecks, A.S. Schlacter, and J. Bozek, "Identification of Weak Autoionizing Resonances Observed Through Fluorescence from the Satellite States of Ar^+ ," Advanced Light Source Compendium of User Abstracts and Technical Reports (Report LBNL-39981, University of California, Berkeley, CA) p. 255 (1997).
3. O. Yenen, K.W. McLaughlin, D.H. Jaecks, A.S. Schlacter, and J. Bozek, "Alignment of the $\text{Ar}^+ [^3\text{P}]4p\ 2\text{P}^0_{3/2}$ Satellite State from the Polarization Analysis of Fluorescent Radiation After Photoionization," Advanced Light Source Compendium of User Abstracts and Technical Reports (Report LBNL-39981, University of California, Berkeley, CA) p. 272 (1997).
4. K.W. McLaughlin, O. Yenen, and D. H. Jaecks, "Production of Purely Spin-Aligned Autoionizing States Which Decay to Orbital Aligned Ionic States," Phys. Rev. Lett. 81, 289 (1998).
5. K. W. McLaughlin, O. Yenen, and D.H. Jaecks, "Production of Purely Spin-Aligned Autoionizing States Which Decay to Orbital-Aligned Ionic States," The 1997-98 ALS Highlights, Published March 1999.

Invited Presentations:

1. D.H. Jaecks, "Experimental Studies of Dynamical Electron Correlation in Ar^+ Satellite State Formation by Measurement of the Intensity and Polarization of Fluorescent Radiations," Two Invited Lectures given at the 2nd School on Synchrotron Radiation, Instituto de Fisica, UNAM, Cuernavaca, Mexico, May 5-9, 1997.
2. O. Yenen and D.H. Jaecks, "The Quadruple Reflection Quarter-Wave Retarder of Hramo Beam Line 10.0.1," presented at the Atomic and Molecular workshop of the Advanced Light Source Users' Meeting, Berkeley National Laboratory, Berkeley, CA, October 15, 1997.
3. D.H. Jaecks, O. Yenen, and K.W. McLaughlin, "Alignment and Magnetic Substate Probabilities of Excited Satellite States of Ar^+ Formed in Photoionization," Ionization Workshop, Lawrence Berkeley Lab, Berkeley, California, Oct. 23, 1996.

Contributed Paper at National and International Meetings:

1. K.W. McLaughlin, O. Yenen, J.A.R. Samson, and D.H. Jaecks, "High Resolution Lineshapes of Weak Autoionizing Resonances Identified Through Fluorescence from the Satellite States of Ar^+ ," Abstracts of the International Workshop of Photoionization (Chester, England), p. 99

(1997).

2. O. Yenen, K.W. McLaughlin, and D.H. Jaecks, "Alignment of $\text{Ar}^+ [^3\text{P}]4p\ 2\text{P}^0_{3/2}$ Satellite State Formed in Photoionization," Abstracts of the International Workshop of Photoionization (Chester, England), p. 100 (1997).
3. D.H. Jaecks, O. Yenen, and K.W. McLaughlin, "Alignment and Magnetic Substate Probabilities of Excited Satellite States of Ar^+ Formed in Photoionization," Ionization Workshop, Lawrence Berkeley Lab, Berkeley, California, Oct. 23, 1996.
4. K.W. McLaughlin, O. Yenen, J.A.R. Samson, and D.H. Jaecks, "High Resolution Lineshapes of Weak Autoionizing Resonances Identified Through Fluorescence from the Satellite States of Ar^+ ," Abstracts of the International Workshop of Photoionization (Chester, England), p. 99 (1997).
5. O. Yenen, K.W. McLaughlin, and D.H. Jaecks, "Alignment of $\text{Ar}^+ [^3\text{P}]4p\ 2\text{P}^0_{3/2}$ Satellite State Formed in Photoionization," Abstracts of the International Workshop of Photoionization (Chester, England), p. 100 (1997).
6. K.W. McLaughlin, O. Yenen, J.A.R. Samson, and D.H. Jaecks, "High Resolution Lineshapes of Autoionizing Resonances Observed Through Fluorescence from the Satellite States of Ar^+ ," Bull. Am. Phys. Soc. 42, 1023 (1997).
7. O. Yenen, K.W. McLaughlin, and D.H. Jaecks, "Alignment of Satellite States of Ar^+ from the Analysis of Measured Polarization of Fluorescent Radiation," Bull. Am. Phys. Soc. 42, 1023 (1997).
8. K. W. McLaughlin, O. Yenen, D. H. Jaecks, "Transfer of Spin-Alignment in Autoionizing Rydberg States to Orbital-Aligned Ionic States," Bull. Am. Phys. Soc. 43, 1336 (1998).
9. K. W. McLaughlin, O. Yenen, D. H. Jaecks, "Alignment in Autoionizing Rydberg States to Orbital-Aligned Ionic States," Bull. Am. Phys. Soc. 43, 1336 (1998).
10. H. Jaecks, O. Yenen, K. W. McLaughlin, "Observation of Spin Aligned Excited Ionic States Produced by Linearly Polarized Radiation," Bull. Am. Phys. Soc. 43, No. 3, 1336 (1998).
11. D. H. Jaecks, O. Yenen, K. W. McLaughlin, "Quantitative Measurements of Dynamic Partitioning of Angular Momentum of Valence Electrons During the Autoionization of Ar^{+**} ," Bull. Am. Phys. Soc. 44, 723 (1999)
12. K. W. McLaughlin, O. Yenen, D. H. Jaecks, "Alignment in Autoionizing Rydberg States to Orbital-Aligned Ionic States," Bull. Am. Phys. Soc. 43, 1336 (1998)
13. D. H. Jaecks, O. Yenen, K. W. McLaughlin, "Quantitative Measurements of Dynamic Partitioning of Angular Momentum of Valence Electrons During the Autoionization of

Ar^{***}," Bull. Am. Phys. Soc. 44, 723 (1999).

E. Report on Other Projects.

1) Data Acquisition System for Recoil Ion Momentum Spectroscopy

We have purchased a fast data acquisition system for a recoil ion spectrometer (COLTRIM) requested by L. Cocke et al. (Kansas State University) in the 1996 instrumental facility initiative proposal. The spectrometer allows simultaneous imaging of ions and electrons momenta in photoionization experiments. The COLTRIM system has been used previously for experiment of double photoionization of He, however, the P.I. (NB) suggested a different and new experiment. The experiment consisted in performing double photoionization in D₂. The team led by L. Cocke and R. Dörner built a new multi-hit detector that allowed the experiment to be a success since it led to a publication printed in Physical Review Letters. Experiments using this apparatus are carried out at other beamlines.

"Double photoionization of spatially aligned D₂," R. Dörner, H. Brauning, O. Jagutzki, V. Mergel, M. Achler, R. Moshhammer, J.M. Feagin, F. Osipov, A. Brauning-Demian, L. Spielberger, J. M. McGuire, M. H. Prior, N. Berrah, J. D. Bozek, L. Cocke, H. Schmidt-Bocking, Physical Review Letters, **81**, 5776 (1998)

2) Computer for collaboration with theorists

A fast computer was purchased for our collaboration with C. Grenne (U. of Colorado) and A. Starace (U. of Nebraska, Lincoln). The computer is located at the University of Colorado/JILA. We have also purchased a terminal to A. Starace so he can access the computer from Lincoln Nebraska.

III. PROPOSAL TO OPERATE THE ATOMIC AND MOLECULAR FACILITY

Since this grant expires in August 1999 I am *concerned* about the operation and maintenance of the AMF facility. In particular I am concerned about the operation of the high resolution electron spectrometer since the operation of the other equipments can be absorbed by the PRT individual grants.

The Independent investigators (II) using the high-resolution spectrometer are numerous. The productivity, as can be seen from section A, has been very high and very good.

The list of II so far that submitted successful proposals through the ALS Proposal Study Panel (PSP) include several national and international research groups: Darrah Thomas (Oregon State University), Francois Wuilleumier (Orsay University, Orsay, France), Andrew Yench (State Univ. N.Y.), George King (University of Manchester, UK), Cristina Lopes (University de Fora, Brazil), Erwin Poliakoff (LSU), K.J. Børve and L. J. Sæthre (University of Bergen, Norway), T. X. Carroll) and J. Hahne (Keuka College, NY. Other users and guests have been S. and H. Aksela (University of Oulu, Finland. Other research group who have used data from the spectrometer but did not come to ALS to collect it (E. Kukk and J.D. Bozek collected the data) are: Paul Morin (LURE, Orsay, France) and Alex Bawagan (Carleton University, Ottawa, Canada). Since these are not my proposals, I can't discuss the nature of the proposed work. However, all of the proposals have been approved by the PSP. They are of the type described in section A and will lead to publishable work.

We request funds to have a postdoc assisting users to operate the instrument. This is in agreement with the February 2000 Basic Energy Science Advisory Committee (BESAC) recommendations (BESAC report, conclusion, section 5). The review team, led by Dr. Petroff, recommended that DOE allocates funds for postdocs for research conducted at the ALS.

We also request funds to maintain and improve the endstation. The experiments are presently limited by the Doppler width, so it is imperative to build a Doppler-free jet and a supersonic jet to increase the resolution capability of the instrument. E. Poliakoff from LSU will collaborate with us to make the necessary improvements.

In the near future, we would like to build a high temperature oven to study transition-metal elements. These studies are interesting because these targets are strongly correlated. They will not only provide a basic understanding of these materials in the gas-phase, but are also extremely relevant to research in material science. We are also trying to attract the laser community to start work on two-photons lasers where one of the photon comes from the synchrotron radiation.

It is very important for the health and growth of the atomic, molecular and chemical dynamics community to have in place resources that can assist scientists. Investments have already been made to build the facility, it is operational and users are eager to use it.

IV. PERSONNEL

The present PRT consist of:

Duane Jaecks, (University of Nebraska, Lincoln)
Ron Phaneuf, (University of Nevada, Reno)
John Bozek, (Lawrence Berkeley National Laboratory), ALS, beamline scientist
Nora Berrah, (Western Michigan Univ)., PRT chair

Posdoc:

Gyorgy Snell, ALS, contract expires August 2000.

The initial team in 1996 consisted of the following scientists. Some of them collaborate presently with the PRT.

J. Berkowitz, ANL
John Bozek, LBNL, Beamline Scientist
C. Cisneros, UNAM, Mexico
Lew Cocke, KSU
Ivan Dominguez, UNAM, Mexico, Postdoc
T. Gorczyca, WMU
C. Greene, UC
Duane Jaecks, UNL
Edwin Kukk, WMU/ALS, Postdoc
M.S. Lubell, CUNY
J. Macek, ORNL
T. Morgan, WU
Ron Phaneuf, UNR
J. Samson, UNL
A. Schlachter, LBNL
A. Starace, UNL
Nora Berrah, WMU, Project Director

Current and Pending Support

This proposal is not submitted to any other agencies. No other support than the one listed in each of the sections (A-D) is available.

No support direct support to operate and maintain the facility is available.

Appendix 1

A letter of support for this proposal is sent directly by Dr. D. Chemla, director of the ALS facility to Dr. E. Rohlring at DOE.