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14. ABSTRACT
An ultrafast x-ray laser system and experimental apparatus have been fully constructed, calibrated and characterized. A titanium sapphire ultrafast laser is tightly focused into a rare gas jet, where high harmonics of the laser are created. A single harmonic can be isolated with a grazing-incidence grating and focused on to a gaseous sample to induce photoionization. Ejected electrons are energy analyzed using a magnetic bottle time-of-flight spectrometer. Harmonics up to the 65th have been generated and photoelectron spectra of helium, krypton, xenon, nitrogen and nitric oxide have been examined. The energy bandwidth has been experimentally determined, and the first time-resolved photoelectron spectra of dissociating states of bromine have been achieved.

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Femtosecond x-ray laser, X-ray photoelectron spectroscopy, Harmonic generation, Photoionization, Energy bandwidths

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Final Report

"Ion and Neutral Dynamics of Ceramic Materials Formation and Atmospheric Chemistry"

AFOSR Grant F49620-98-1-0100

(Grant Period: 15 November 1997 - 14 November 2000)

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Introduction, Recent Publication, Students

With AFOSR support over several grant cycles, we developed new approaches to obtaining detailed information on ion-neutral processes, many of which have atmospheric relevance. To mention a few of the studies, we coupled infrared chemiluminescence[1-3] and laser-induced fluorescence[4-6] detection with flowing afterglow instrumentation for the first time and characterized the energy disposal (product states)[7,8] for a wide variety of ion-molecule reactions. We established rate determinations of reactions[9] and electronic emissions,[10,11] as well as deactivation processes[12,13] and reactions[14,15] of vibrationally state-selected reactant ions. We developed novel experiments to learn about the microscopic basis of mobility and alignment using state selective and frequency-resolved laser Doppler probing of ions in drift tubes.[16-18] We measured the mobilities of many atmospheric cluster ions for the first time.[19-21]

Recently we started a new series of experiments using ultrafast soft x-rays and ultraviolet high order harmonics to probe the photoelectron spectra of chemically interesting neutral species. In the Final Report below, we discuss the highlights of this new ultrafast soft-x-ray project. In the Publications list below, we include all the recent AFOSR sponsored work, from the ongoing ion projects through the new ultrafast soft x-ray project. The students, postdoctoral participants, and visiting facultyu are listed below, as well.

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S. Kato, J. A. de Gouw, C.-D. Lin, V. M. Bierbaum, and S. R. Leone, "Vibrational enhancement of the charge transfer rate constant of N_2^+(v=0-4) with Kr at thermal energies," J. Chem. Phys. **105**, 5455 (1996).

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H. Meyer and S. R. Leone, "Preparation and probing of alignment in molecular ensembles by saturated coherent pulsed laser excitation," J. Chem. Phys. **105**, 5858 (1996).

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E. B. Anthony, W. Schade, M. J. Bastian, V. M. Bierbaum, and S. R. Leone, "Laser probing of velocity-subgroup dependent rotational alignment of N_2^+ drifted in He," J. Chem. Phys. **106,** 5413 (1997).

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M. J. Frost, S. Kato, V. M. Bierbaum, and S. R. Leone, "Reactions of $N_2^+(v)$ with CO and NO," Chem. Phys., Special Issue on New Aspects of Photochemistry and Reaction Dynamics, **231**, 145 (1998).

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J. Li, V. M. Bierbaum, and S. R. Leone, "Laser ionization time-of-flight mass spectrometer detection of methyl radical produced by ion reactions in a flowing-afterglow apparatus," Chem. Phys. Lett. **313**, 76 (1999).

L. Nugent-Glandorf, M. Scheer, M. Krishnamurthy, J. W. Odom, and S. R. Leone, "Photoelectron spectroscopic determination of the energy bandwidths of high harmonics (9th-55th) produced by an ultrafast laser in neon," Phys. Rev. A **62**, 023812-1 (2000).

E. B. Anthony, M. J. Bastian, V. M. Bierbaum, and S. R. Leone, "Laser probing of rotational state-dependent velocity distributions of $N_2^+(v''=0,J)$ drifted in He," J. Chem. Phys. **112**, 10269 (2000).

Student, Postdoctoral, and Faculty Participation, Theses

Eric B. Anthony, Graduate Student, Ph. D. 1998, University of Colorado, "Laser probing of transport properties and rotational alignment of N_2^+ drifted in He," thesis available from the University of Colorado.

L. Nugent-Glandorf, Graduate Student, Ph. D. expected 2001

David Samuels, Graduate Student, 2000-present

Michael Scheer, Posdoctoral Research Associate, 1998-2000

Jian Li, Posdoctoral Research Associate, 1998-2000

M. Krishnamurthy, Posdoctoral Research Associate, 1995-1998

Shuji Kato, Senior Research Associate, University of Colorado, no cost to project, 1997-1999

Joost deGouw, Posdoctoral Research Associate, 1994-1996

Prof. Ed Grant, Department of Chemistry, Purdue University, Visiting Fellow, 1999-2000

Dr. Xueming Yang, Institute for Atomic and Molecular Sciences, Taiwan, Visiting Fellow, 2000

Report

"Ion and Neutral Dynamics of Ceramic Materials Formation and Atmospheric Chemistry"

AFOSR Grant F49620-98-1-0100

(Grant Period: 15 November 1997 - 14 November 2000)

The ultimate goal of this research was to study ultrafast processes and core level spectroscopy in molecular systems relevant to metal-oxidizer chemistry of interest to AFOSR. We developed a powerful new apparatus to provide a productive approach to obtain detailed information about metal reactions and metal halide dissociation processes using pump/probe experiments with ultrafast soft x-rays and tunable vacuum ultraviolet light. The ultrafast x-ray source was fully developed and characterized. It was used for photoelectron spectroscopy studies of stable molecules. The first ultrafast time resolved experiments were performed on the dissociation of stable bromine molecules, to probe the valence photoelectron spectroscopy and x-ray core-level photoelectron spectroscopy of dissociative states during the break-up.

A. Apparatus for Ultrafast Soft X-Rays

Recent developments[22-40] in ultrafast laser generation of high-order harmonics in rare gases now offer excellent opportunities to the experimenter for tabletop soft x-ray investigations. Until recently, these laser sources have been primarily the specialty of groups working on the harmonic generation processes themselves. These tools can now be used to address a large number of intriguing chemical and materials problems of wide interest. The high harmonic sources can now produce up to 460 eV photon energies,[26] with bandwidths comparable to synchrotron sources and photon fluxes of $>10^{10}$ per second, in a reasonably modest laboratory scale apparatus.

The apparatus that we constructed is illustrated in Fig. 1. It consists of a 1000 Hz Ti:sapphire laser that produces 2.5 mJ per pulse at 800 nm with pulses of 70 fs duration, a piezoelectric pulsed valve, also operating at 1000 Hz, to form the jet of high density rare gas that is used as the nonlinear harmonic medium, a vacuum chamber to introduce gaseous samples, and a time-of-flight magnetic bottle electron spectrometer. In addition, the apparatus has frequency doubling and tripling of the Ti:sapphire fundamental pulse in nonlinear crystals to generate a separate photolysis pump pulse, an optical delay line, a grazing incidence grating for wavelength separation to select individual harmonics, a quadrupole mass spectrometer for ion mass detection, and necessary pulse autocorrelation and frequency-resolved optical gating measurement tools.

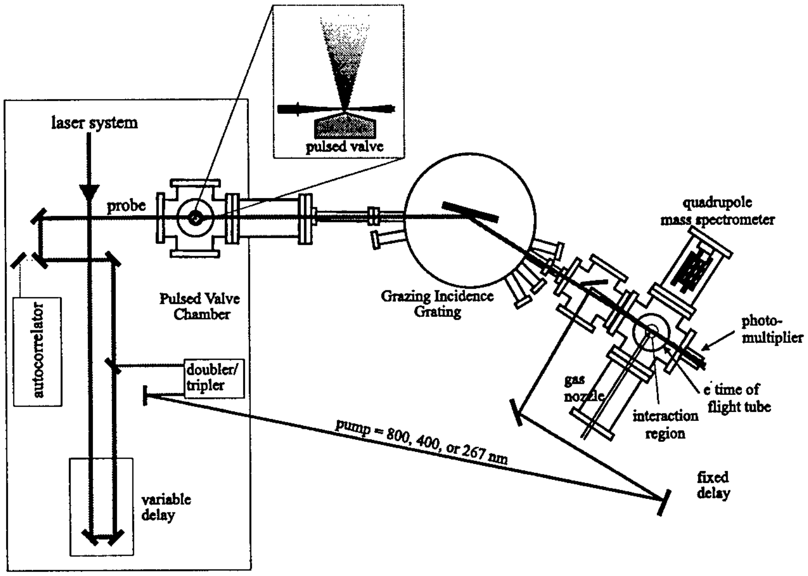

Figure 1. Apparatus for generating high order harmonics and for photoelectron spectroscopy and pump/probe time-resolved studies with x-ray harmonics.

The philosophy in constructing the apparatus was to make a source of femtosecond soft x-rays that would operate at high repetition rate (1000 Hz), not necessarily state-of-the-art in terms of short pulse duration, photon energy (harmonic number), or pulse energy, but very reliable so that it operates dependably on a daily basis. This necessitated a very stable Ti:sapphire laser system consisting of a seed laser, grating pair pulse stretching optics, a regenerative amplifier, a two-pass amplifier, and pulse recompression optics. In order to maintain reasonable spectral bandwidths of the harmonics, a longer pulse of 70 fs was favored, and results are presented below on new measurements of the bandwidths, showing that the x-ray harmonics are indeed sufficiently narrow to perform core level and valence shell photoelectron spectroscopy. We constructed a pulsed valve of our own design that would operate at 1000 Hz, with high pumping speeds and differential gas pumping so that the gas pressure in the harmonic generation region is well-isolated from the time-of-flight electron spectrometer. In addition, since the path of the x-rays cannot be altered once they are formed and only grazing incidence on one grating is used in order to maintain the efficiency of the light production, all the delay line manipulations are carried out before the harmonic generation process (see Fig. 1). With this apparatus, we produce harmonics up to the 65th (≈97 eV) and use them for photoelectron spectroscopy with excellent signal-to-noise (100:1 in minutes).

1. High Harmonic Spectra

The high order harmonic generation process in rare gases has a different mechanism than the usual sum and difference frequency or four wave mixing in nonlinear optics. The laser is focused to 10^{14}-10^{15} W cm^{-2} in a high density of a rare gas (≈10^{18} cm^{-3}) in a pulsed jet. The process qualitatively involves driving an electron away from the ionic core of the rare gas and then, on the opposite cycle of the light, driving the electron back into the core, whereupon the harmonic light can be generated. The light is produced with similar efficiency over a large number of odd harmonics up to some cutoff energy. The fact that only odd harmonics are produced results from momentum matching in an isotropic medium. Figure 2 shows an example of our high harmonic spectra using neon and argon as the medium. These spectra are from photoelectrons generated on a piece of platinum that samples the harmonic light while tilting the grazing incidence grating to scan the harmonics across a slit. The path between the harmonic generation region and the detector is completely evacuated so as not to absorb the light. In neon, the odd harmonics up to the 61st at

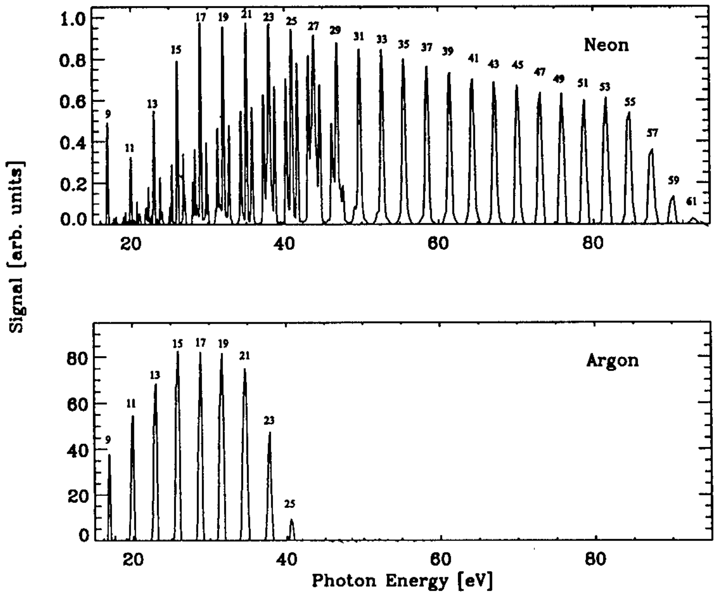

Figure 2. High harmonics generated in neon and argon. Note the lower cutoff in argon and the overlapping orders of the grating in the neon spectrum.

92 eV are observed, followed by an abrupt cutoff; there is some overlapping of higher harmonics in the region of the lower ones that arises from a higher order of the grating. Higher harmonic numbers are achievable with Ne, compared to Ar, because of its higher ionization potential and hence its ability to withstand higher power densities of the ultrafast laser without ionization. However, there is greater efficiency of the harmonic generation process with Ar.

2. Magnetic Bottle Time-of-Flight Electron Spectrometer

The magnetic bottle time-of-flight electron spectrometer[41,42] is based on a design of Neumark and co-workers[43] (Fig. 3), with an additional adaptation to shift the kinetic energies of the electrons from high to low values by a retarding grid system[41,44] to obtain high kinetic energy resolution even for high velocity electrons. The advantages of this system are the ability to collect a large solid angle of the emitted electrons and the elimination of stray electron signals by confining the zone of collection to a very small region around the high field magnets. The intrinsic resolution of our magnetic bottle is measured to be ΔE/E of 4%.

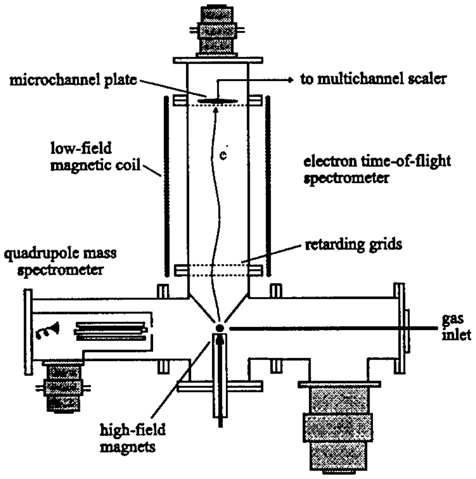

Figure 3. Detail of magnetic bottle time-of-flight electron spectrometer.

With the magnetic bottle spectrometer shown and the range of high harmonics generated by the ultrafast laser, we obtain excellent photoelectron spectra from all the gases introduced thus far. Figure 4 shows an early low resolution example of the typical xenon photoelectron spectra obtained with a variety of single harmonics (43rd to 61st). In these spectra there are transitions that can be assigned to three basic kinds of processes: ejection of core level 4d electrons, ejection of valence shell 5s and 5p electrons, and ejection of Auger electrons. The 4d, 5s and 5p electron energies shift to shorter flight times with increasing photon energy, but the Auger electrons do not.

The Auger processes involve first ejection of a photoelectron, then another electron fills the vacated orbital, followed by ejection of a 3rd electron with the characteristic energy difference between the energy required for ejection of the electron from that orbital and the energy gained by the electron that fills the vacated orbital. We show more detail on this below by tuning the energy of the photon to a Rydberg resonance in the Auger process.

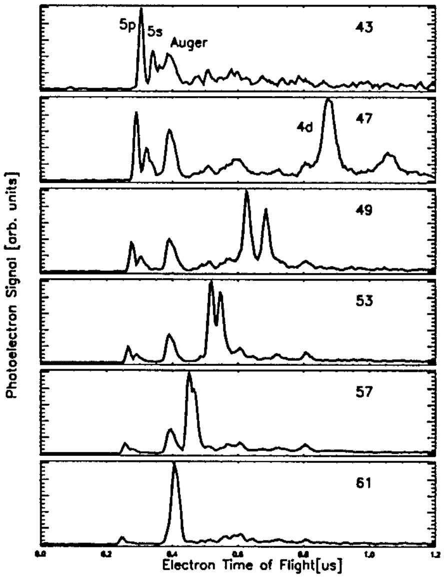

Figure 4. Sample photoelectron spectra vs. arrival time for xenon with selected harmonics, 43rd to 61st, showing the 4d core electron features, the 5s and 5p valence electron peaks, and Auger transitions, which do not shift with photon energy. Acquisition of typical spectra requires only a few minutes of data collection.

3. Chirped Pulse Effect on Harmonics

In addition to characterizing many details about how to generate and optimize the high harmonic process, which are not described here, we also investigated the effect of pulse chirp on the harmonic spectra (chirp is the process where the frequency of the ultrafast pulse sweeps from high to low or low to high over the duration of the pulse). The magnitude of the pulse chirp itself is characterized by frequency-resolved optical gating[45] to determine the amount of chirp. Fig. 5 shows a sequence of ultraviolet photoelectron spectra of NO taken with the 7th harmonic, both chirped and unchirped. It can be seen that the photoelectron energies shift to higher values when the chirp is negative (which means the blue frequencies precede the red) and shifts to lower values when the chirp is positive (red frequencies precede the blue). These frequency shifts are in agreement with theoretical considerations that indicate the harmonics are most likely produced during the leading edge of the femtosecond laser pulse. The shifts are considerable, suggesting that good control over the frequency chirp and tuning of the ultrafast laser is essential.

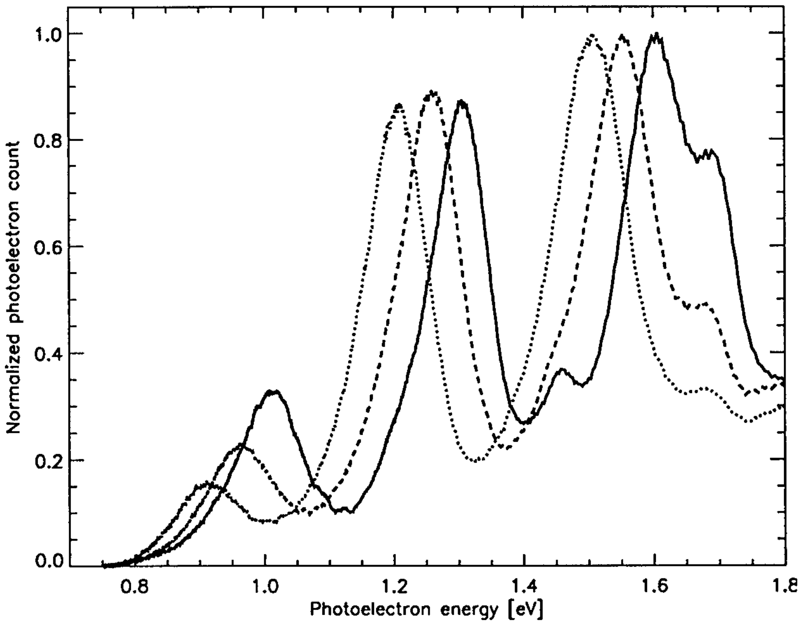

Figure 5. Effect of chirped pulses on the photoelectron spectra of NO with the 7th harmonic. (-----) no chirp, (···) positive chirp, (—) negative chirp.

4. Harmonic Bandwidths from Photoelectron Spectroscopy

For the studies carried out here, it is essential that the energy resolution of the individual high harmonics be as narrow as possible, so that the features in the photoelectron spectra will be well-resolved. There are relatively few studies of the energy bandwidths of individual harmonics, and it is known that the bandwidths depend strongly on the pulse duration and the particular laser. In addition, there is no theoretical treatment for lasers with 70 fs pulse duration or longer. Thus we performed the first comprehensive study of the energy bandwidths.

Fig. 7 shows the photoelectron spectrum of NO taken with the 9th harmonic of a long pulse (5 ns) Nd:YAG laser (tripled in crystals and tripled again by four-wave mixing) and with the 7th harmonic of the ultrafast laser. The linewidth of the long pulse laser contributes almost no bandwidth to the energy resolution; it can be seen in the figure that the features are much narrower with this laser. The long pulse laser establishes the energy resolution of the magnetic bottle time-of-flight electron spectrometer, which is ΔE/E of 4%. The increased energy bandwidth of the electrons ejected with the ultrafast laser from the same transition in NO provides a direct measure of the bandwidth of the high harmonic. The same type of measurement is repeated with many different harmonics. In one type of measurement, only those transitions that give very low kinetic energy electrons were used, and in another set of measurements the retarding grid system in the magnetic bottle spectrometer was used to shift the high electron kinetic energies to lower values to obtain good resolution of the magnetic bottle spectrometer. The results of this latter large series of energy bandwidth measurements are shown in Fig. 7.[46] It can be seen that the bandwidths of the various harmonics are approximately 0.1 eV for the lowest harmonics and increase to as much as 0.4-0.5 eV for the highest harmonics measured. These exciting results show that excellent resolution can be obtained directly from the harmonics of the laser without further need for an additional high resolution monochromator, which would distort the time resolution.

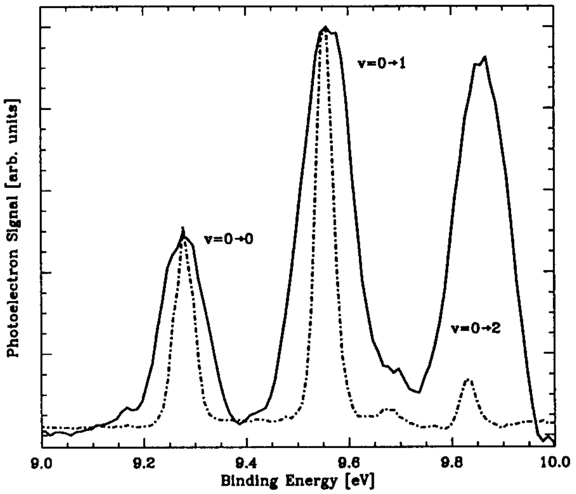

Figure 6. Bandwidth of NO with long pulse YAG (—·—·—) and ultrafast harmonics (—).

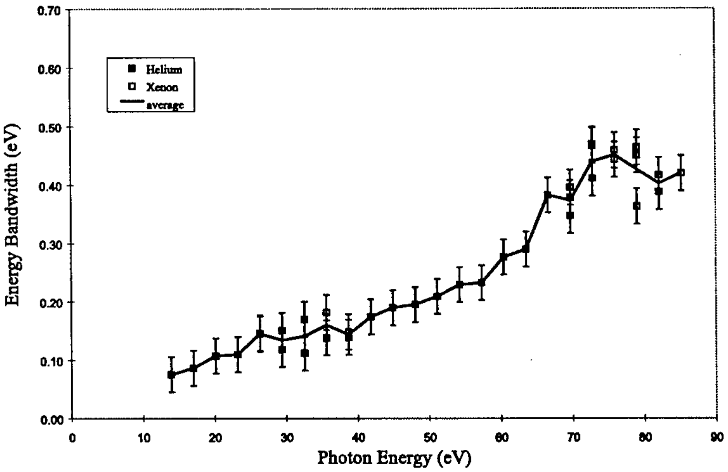

Figure 7. Measured bandwidths of individual harmonics. The symbols represent different species ionized. All experiments utilize the retarding grids.[46]

B. Ultraviolet Photoelectron and X-Ray Photoelectron Spectroscopy of Stable Molecules and Atoms

We embarked on a series of survey measurements of photoelectron spectra of neutral atoms and molecules, as a precursor to setting up the first time-resolved pump/probe experiment.

1. Photoelectron Spectra of Rare Gases and Small Molecules

Surveys of core and valence shell photoelectron spectra were acquired for simple species such as He, Ar, Kr, Xe, N_2, NO, and Br_2. Fig. 8 shows a few examples for Xe and Br_2, taken with low and high harmonics. Note that the spectra are remarkably free of electrons produced by scattered light. The resolution in our Br_2 spectrum is not as good as some of the published ultraviolet photoelectron spectra,[47] since our spectrum was limited by the bandwidth of the laser. However, additional improvements are anticipated, as discussed later. Both valence shell and core levels can be probed, depending on the particular measurements that are carried out. These results contain different information as will be discussed in more detail in the proposal below.

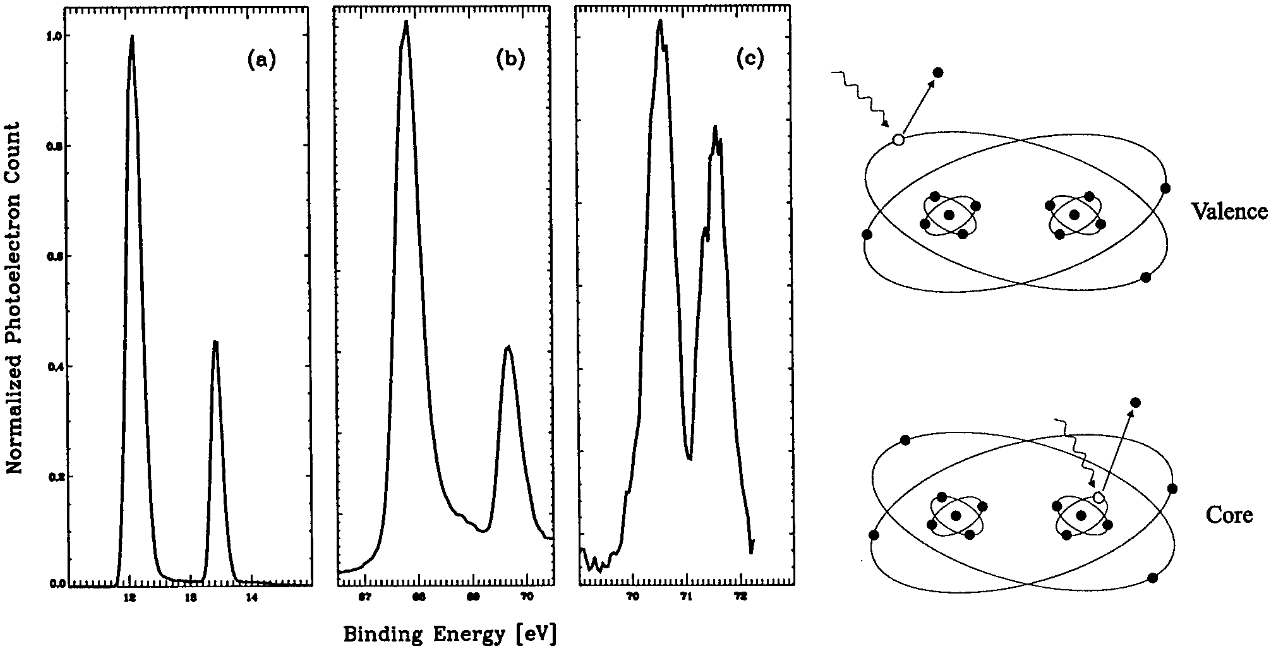

Figure 8. Spectrum of Xe and Br_2 with various harmonics. (a) Xe with the 11th harmonic, (b) Xe with the 47th harmonic, (c) Br_2 with the 49th harmonic. In the panel to the right is shown a schematic of the basic idea that the electrons arise from either valence shells, such as in (a) or inner shells, such as (b) and (c), depending on the photon energy.

More important from the standpoint of the AFOSR experiments to be performed here are results for metal-halogen molecules. Fig. 9 shows the ultraviolet photoelectron spectrum of Al_2Br_6, a bridge-bonded dimer of $AlBr_3$. This group of peaks has an energy consistent with the orbitals of the four terminal Br atoms; at higher photon energies, features from the bridge-bonded Br atoms are expected. In new experiments to be performed, the Al_2Br_6 will be dissociated to measure the changes in the photoelectron and core level spectra of the excited state dissociative potential as a function of time.

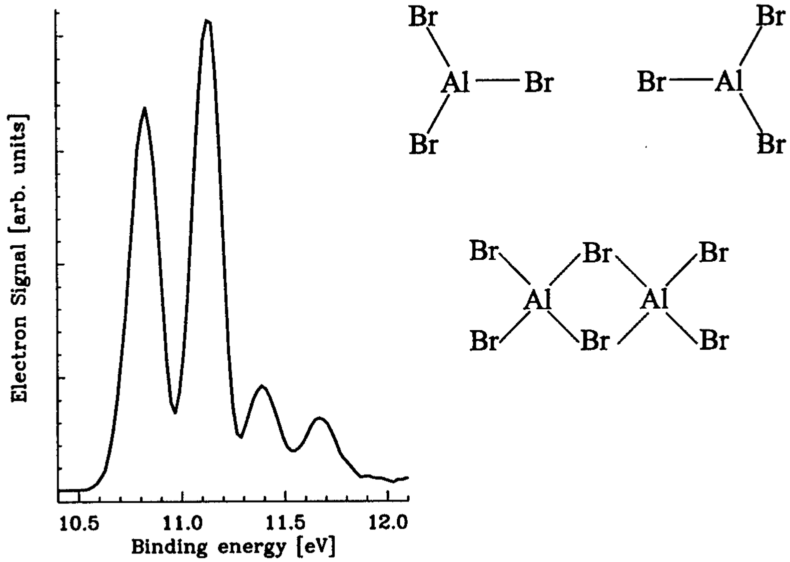

Figure 9. Ultraviolet photoelectron spectrum of Al_2Br_6 taken with the 9th harmonic.

2. Satellite Transitions in He

The photoelectron spectrum of He with fairly energetic photons can produce the He^+ ion in excited states, so-called satellite transitions. The cross sections of these transitions are very small, but well known.[48] Fig. 10 shows a photoelectron spectrum of He taken with the 61st harmonic at 92 eV, in which two satellite transitions are clearly observed. The inset shows that the satellite transitions involve two electrons, where one is removed and the other makes a transition to an excited state of the product ion. From the known density of He, the photoelectron count rates, and the cross sections for these satellite transitions, we estimate the 61st harmonic has 10^5 photons per pulse that reach the small focal volume of the magnetic bottle spectrometer. At 1000 Hz, this means there are 10^8 photons per second. Since this spectrum was taken with a spherical grating used for harmonic separation, the x-ray output is focused to a broad line, rather than a point. In new work, we will soon be using a toroidal grating, which will improve the focus of the harmonic light into a very small spot, and the photon flux is expected to increase by 100-fold.

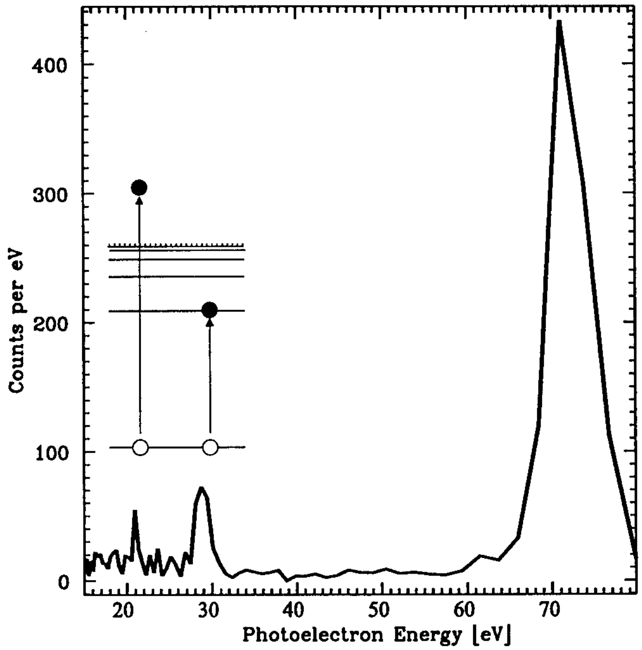

Figure 10. Photoelectron spectrum of He with the 61st harmonic showing the satellite transitions. The retarding grids were not used here.

3. Tuning to Rydberg Resonances in Auger Transitions of Xe

In Xe, as noted above, there are Auger processes that occur, where creation of an inner-shell hole is followed by a rearrangement of the electrons. One of the outer electrons fills the hole, and another outer shell electron is ejected. The kinetic energy of this Auger electron is determined by the energy difference between the inner and outer shell electrons that participate. For photon energies below the threshold for direction ionization, it is known that the precise energy of the photon can induce a resonance to a Rydberg state (instead of direct ejection of the first electron), which is also followed by Auger decay with altered Auger electron energies.[49] This is due to an additional Coulomb interaction between the outgoing Auger electron and the electron in the Rydberg orbital. Fig. 11 shows a result of tuning our high harmonic wavelength to the energy of a Rydberg resonance for an Auger process in Xe by adjusting the fundamental wavelength of the Ti:sapphire laser to 791 nm. The resonant Auger structure appears with the adjustment of this photon energy. Here the tuning from 800 nm to 791 nm for the 43rd harmonic results in a shift of only 0.76 eV in the harmonic energy. If one tunes beyond the Rydberg resonance, the structure of the Auger transitions changes significantly. Work is in progress to explore other aspects of these Rydberg resonances within Auger transitions.

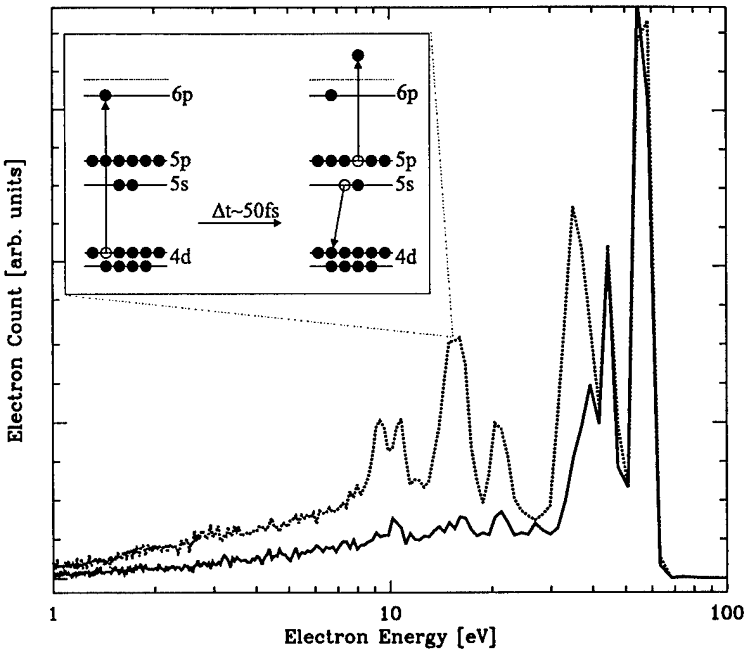

Figure 11. Photoelectron spectrum of Xe with the 43rd harmonic showing effect of tuning the individual harmonic to the Auger resonance transition. (—) 800 nm fundamental, (···) 791 nm fundamental. The inset shows the type of Auger electron transition responsible for one peak in the spectrum.

C. Ultrafast Dissociation of Stable molecules

In recent studies at the end of this project, the first ultrafast dissociation signals were obtained for bromine molecules. In these experiments the bromine is dissociated with 400 nm femtosecond pulses and the photoelectron spectra are probed with the 17th harmonic of the Ti:sapphire laser at 47 nm. Successful cross correlation signals were first obtained in rare gases to determine the spatial and time overlap of the soft x-ray pulses with the 400 nm pump pulses. This is done by the process of above threshold ionization. Then the photoelectron spectra of bromine molecules at several time delays after the laser pulse were obtained (Fig. 12). A clear signature of the bromine atoms appearing is time is observed by two new peaks in the spectra. These first spectra were time broadened by the grating that was used to separate the harmonics. The time broadening of the probe pulse was 450 fs. Therefore the results of these experiments have not yet been interpreted until the time resolution could be improved, since the bromine dissociation is expected to occur in about 100 fs. With a new dual grating technique recently built into the system, the phase fronts of the pulses are presently being recompressed and new experiments will be performed shortly to obtain accurate spectra during the dissociation of the molecule.

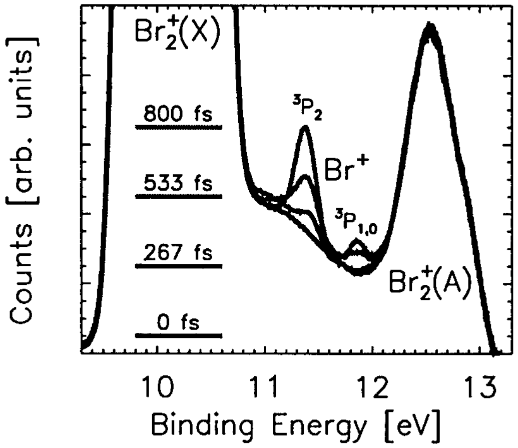

Figure 12 **Time dependent signals of bromine dissociaton. The new peaks are due to Br atoms during the dissociation.**

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