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# MULTIPHOTON IONIZATION AND THIRD-HARMONIC GENERATION IN ATOMS AND MOLECULES

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# MULTIPHOTON IONIZATION AND THIRD-HARMONIC GENERATION IN ATOMS AND MOLECULES*

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The development of tunable dye lasers has totally revolutionized the fields of atomic and molecular physics and chemistry. The very narrow bandwidth and extensive tunability of dye lasers have made a quantum jump in the precision and physical content of spectroscopic data. The high photon flux available from focused, pulsed dye lasers has spawned the entirely new fields of multiphoton spectroscopy and harmonic generation. Nonlinear spectroscopy is one of the most exciting areas of atomic and molecular physics.

The Molecular Physics Group at the Oak Ridge National Laboratory has performed extensive new studies of multiphoton ionization (MPI) and third-harmonic generation (THG) both in beams ($P < 10^{-3}$ torr) and in static pressure cells ($P > 10^{-2}$ torr). Simple cell experiments with proportional counter detectors are used at high pressure and mass spectrometer and photoelectron spectrometers with particle multipliers are employed in the low pressure experiments. The beam from a nitrogen-pumped dye laser on an excimer pumped dye laser is tightly focused to obtain power densities up to $\sim 10^{11}$ W/cm$^2$.

*Resonantly enhanced multiphoton ionization (REMPI) provides a* powerful new method for investigating atomic and molecular energy levels. The method is particularly useful in discovering and characterizing certain optically forbidden transitions. The method is

particularly well suited for studying Rydberg transitions in molecules and is experimentally easier than the traditional use of far ultraviolet radiation in conventional spectroscopy. Specific examples for gaseous benzene, furan, pyrrole, and methyl iodide will be presented. Also, we have shown that the use of two independently tunable dye lasers to produce sequential REMPI spectra has significant advantages in signal intensity, spectral simplification, and the ability to probe different Franck-Condon regions of a molecule.

The addition of mass spectroscopy to studies of MPI of polyatomic molecules has shown that considerable fragmentation can accompany ionization. Data for $NH_3$, $H_2S$, $C_6H_6$, $CH_3I$, and others will be presented. For some molecules the degree of fragmentation is highly dependent upon the wavelength. Our measurements of photoelectron energy distributions (i.e., MPI photoelectron spectroscopy) show unambiguously that the fragmentation results from photodissociation of the initally produced parent ion. We have also measured ion kinetic energies in some cases which provides information about the mechanisms leading to dissociation.

Resonantly enhanced multiphoton ionization photoelectron spectra (MPI-PES) have been recorded for Xe, $I_2$, NO, $NH_3$, $H_2S$, $CH_3I$, and $C_6H_6$. In each case, the resonant intermediate state was a Rydberg state. In a recent study of NO, where fragmentation does not occur, we demonstrated that the distribution of $NO^+$ vibrational levels was determined primarily by the Franck-Condon factors connecting the resonant intermediate ($A^2\Sigma^+$ or $C^2\pi$) state and the ground $X^1\Sigma^+$ ionic state. An intense peak of near zero energy electrons is observed for NO (and several other molecules).

We attribute the peak near zero energy to vibrational autoionization as a result of the admixture of another resonant intermediate state at the third photon energy level.

Multiphoton ionization at high pressures can lead to new and interesting effects. The most significant of our studies concerns the measurement of MPI and THG simultaneously in xenon, krypton, and argon. We find that at low pressures ($10^{-3}$-$10^{-6}$ torr) MPI through three photon resonance enhancement of the 6s state of xenon is intense and dominates the spectrum. However, the ionization signal produced via the 6s state rapidly disappears at pressures above $\sim$0.3 torr. Third-harmonic light in the direction of the pump beam is detected as the ionization disappears. The excitation lineshapes of both the MPI and THG signals are found to shift and broaden asymmetrically to shorter wavelength with comparable, but not identical magnitudes as the pressure is increased. In order to explain such phenomena, it is necessary to include terms involving the coherent effect of the laser light and the third-harmonic field on the excitation of xenon atoms. The inclusion of the cooperative effect of atoms interacting among themselves through the third-harmonic field results in strong suppression of the excitation of the resonance level. Direct confirmation of this phenomenon comes from recent experiments by colleagues at Los Alamos National Laboratory (J. Glownia and R. Sanders) who find the ionization to reappear when the laser light is circularly polarized and counter-propagating. Third-harmonic light cannot result from circularly polarized light.

The third-harmonic light generated in the experiments described above is sufficiently intense to be useful in spectroscopic studies of gaseous species in the near vacuum ultraviolet region (1000-200 nm). The absolute intensity of the third-harmonic light using a nitrogen-pumped dye laser is on the order of $10^7$-$10^8$ photons/pulse depending upon the wavelength. The use of the excimer pump will allow for $\sim$2 orders of of magnitude greater intensity. The bandwidth in angstrom of the THG is smaller than the exciting laser bandwidth by a factor of $3\sqrt{3}$ (without etalons in the laser our vacuum ultraviolet bandwidth is 0.02 Å). We will discuss recent experiments of one-photon absorption and photoionization spectroscopy and photoionization threshold determinations. Two-photon ionization studies of NO, using the vacuum ultraviolet light to probe Rydberg states and the fundamental light to ionize will also be presented.

The potential for use of these new techniques to understand atomic and molecular physics or as analytical techniques is great. Our goal is to use these new techniques to solve old and new problems in radiation chemistry and physics. During the coming year, we hope to study MPI of molecular clusters and to use the THG source for photoionization studies of monomers and molecular clusters. Of particular interest are reactions of the type $h\nu + (H_2O)_n \rightarrow (H_3O^+)(H_2O)_x + OH^- \cdot (H_2O)_y$ where $x + y = n - 2$. These studies will complement our ongoing studies of electron impact ionization of molecular clusters. In addition, we hope to use the electrons generated from MPI as a bright source of monoenergetic, spin polarized electrons for scattering studies. Since the photoelectrons

can be generated in short bursts of duration <10 ns, it is possible to perform ultrahigh resolution electron scattering and time-delay collision experiments for the first time. Such an experiment is under construction in our laboratory and its potential will be discussed.

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Recent Key Publications

1. R. N. Compton, J. C. Miller, A. E. Carter, and P. Kruit, "Resonantly Enhanced Multiphoton Ionization of Xenon: Photoelectron Energy Analysis," *Chem. Phys. Lett.* 71, 87 (1980).

2. John C. Miller, R. N. Compton, M. G. Payne, and W. R. Garrett, "Resonantly Enhanced Multiphoton Ionization and Third-Harmonic Generation in Xenon Gas," *Phys. Rev. Lett.* 45, 114 (1980).

3. John C. Miller and R. N. Compton, "Multiphoton Ionization Photoelectron Spectroscopy of Nitric Oxide," *J. Chem. Phys.* 75, 22 (1981).

4. John C. Miller and R. N. Compton, "Multiphoton Ionization of Iodine and Benzene: Photoelectron and Ion Kinetic Energy Distributions," *J. Chem. Phys.* 75, 2020 (1981).

5. R. N. Compton and John C. Miller, "Multiphoton Ionization and Third-Harmonic Generation in Atoms and Molecules," *Proceedings of International Conference on Lasers '81, New Orleans, Louisiana, December 14-18, 1981.*

6. R. N. Compton and John C. Miller, "Multiphoton Ionization of Atoms and Molecules," *Proceedings of Optical Society of America Topical Meeting on Laser Techniques for Extreme Ultraviolet Spectroscopy, Boulder, Colorado, March 8-10, 1982.*

7. John C. Miller and R. N. Compton, "Vacuum Ultraviolet Spectroscopy of Molecules Using Third-Harmonic Generation in Rare Gases," *Proceedings of Optical Society of America Topical Meeting on Laser Techniques for Extreme Ultraviolet Spectroscopy, Boulder, Colorado, March 8-10, 1982.*