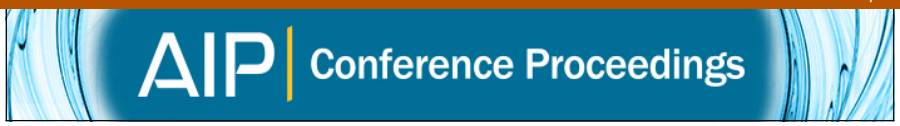

Photoelectron spectroscopy of excited molecular states

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PHOTOELECTRON SPECTROSCOPY OF EXCITED MOLECULAR STATES

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Resonance enhanced multiphoton ionization (REMPI) utilizes the tunable radiation of dye lasers to ionize a molecule by preparing an excited state via absorption of one or more photons and subsequently ionizing that state before it can decay. A remarkable feature of REMPI is that the very narrow bandwidth of laser radiation makes it possible (i) to select a specific rovibrational level in the ground electronic state, (ii) to pump this level up to another specific level of an excited electronic state, and (iii) to subsequently ionize the prepared state via absorption of one or more additional photons. Coupled with high-resolution and angle-resolving photoelectron spectroscopy, REMPI is clearly an important probe of the photoionization dynamics of excited molecular states at a quantum-state specific level. This extreme state-selectivity gives rise to many basic and practical applications of REMPI.

In this talk I will discuss some results of our studies of ion rotational and vibrational distributions for REMPI of small molecules such as H_2, O_2, NO, OH, and CH which illustrate dynamically important features of these processes.[1] Some highlights of these results include (i) non-Franck-Condon ion vibrational distributions arising from the presence of autoionizing and shape resonances in the electronic continuum and from the rapid evolution of the angular momentum composition of resonant orbitals.[2-4] Such non-Franck-Condon ion distributions will be seen in the photoionization of molecular Rydberg states which is generally expected to occur with preservation of vibrational quantum number, i.e., $\Delta v = v^+ - v' = 0$. This behavior introduces serious complications both in the extraction of state populations from REMPI signals and in the use of this technique for state-specific production of ions; (ii) rotational distributions of ions and their associated photoelectron angular distributions.[5,6] These rotationally-resolved studies provide dynamical insight into the angular momentum composition of the photoelectron wave function which is often not evident in rotationally-unresolved spectra.

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