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MOLECULAR PHOTOIONIZATION DYNAMICS

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This program seeks to develop both physical insight and quantitative characterization of molecular photoionization processes. The role of photoionization studies in the more general framework of radiation physics is threefold: (a) many radiation problems involving x-rays, solar radiation, etc., are directly concerned with photoionization; (b) fast charged particles are another important form of radiation, whose interaction with matter is related to photoionization via the Bethe theory; and (c) photoionization represents a precise means for producing specific ionic states with well-defined internal energy, permitting microscopic studies of their subsequent decay.

Several aspects of molecular photoionization are under current investigation by experimental and/or theoretical means: First, in collaboration with co-workers at Boston University and NBS, this project initiated the current widespread study of shape resonances in molecular photoionization. On the theoretical side, this work included the identification of shape resonances in molecular spectra,[1,2] illucidation of their properties,[3-9] and predictions[10,11] of various manifestations such as non-Franck-Condon

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effects in vibrational branching ratios and photoelectron angular distributions. On the experimental side, we have used photoelectron spectrometry in conjunction with synchrotron radiation to confirm[12,13] those predictions and otherwise map shape resonance effects for many molecules. Second, using the same experimental approach referred to above, we have measured[14] vibronic branching ratios and photoelectron angular distributions within autoionizing resonances to test our understanding of molecular photoionization in a multichannel framework. Third, we have performed prototype measurements of polarization of fluorescence from molecular photoions[15] and angular distributions of photofragments[16] to access new information on the relative strengths of degenerate photoelectron channels. Fourth, a new effort in collaboration with P. M. Dehmer (Argonne) is underway to study multicolor, multiphoton ionization of molecules. This program is aimed chiefly at doing requisite research to develop ultrasensitive detection schemes for atmospheric constituents, but is thereby automatically involved with the largely uncharted area of molecular spectroscopy and dynamics in high resolution, high intensity laser fields.

Future work in each of these areas is planned, however special attention will be given to two areas. The main limitation in a major expansion of detailed, triply-differential (incident wavelength, kinetic energy, ejection angle) photoelectron studies within autoionization profiles is the photon resolution and overall sensitivity of the experiment. The ANL-NBS collaboration is in the final stages of assembly of a new instrument from which we expect a factor of 100 greater sensitivity and a factor of two improvements in resolution (to 0.2Å). The multiphoton studies will also receive special

attention as the experimental apparatus has just been completed and preliminary measurements, as well as work in other laboratories, indicate a great scientific potential for this technique in the future.

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