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Multi-Electron and Multi-Ion Coincidence Spectroscopy of Single-Photon Ionization Processes in Molecules

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Abstract

This thesis presents experimental investigations of multi-electron and multi-electron-multi-ion coincidence measurements of samples in the gas phase utilizing a versatile time-of-flight magnetic bottle spectrometer technique. These investigations of multiply ionized atomic and molecular species provide valuable information on, and understanding of, ionization processes and dissociation mechanisms highly relevant to the development of electronic structure theories.

Paper I investigated the double valence photoionization spectra of methyl halides. From this study, the lowest onset and vertical double ionization energies were obtained for CH_3F , CH_3Cl , and CH_3I , and used to test an empirical rule-of-thumb for the double ionization of molecules. The study concluded that the apparent inter-charge distance may be derived by applying the rule-of-thumb on molecules similar to the methyl halide structure group.

Paper II studied the dissociation of D_2O by photoelectron-photoion coincidence measurements. The experiments yielded ion mass-selected photoionization spectra, and dissociation breakdown diagrams, with improved statistics than previous studies of this kind. Minor fragments were detected and modulations in the yield of the fragments were observed of the B^2B_2 state, with the implication that the fragmented system retains memory of the vibrational structure before the dissociation pathway is irreversibly chosen. Measurements of the C^2A_1 state revealed high kinetic energy OD^+ fragments.

Paper III concerned the dissociation mechanisms of ICN upon core site-, and orbital-specific photoionization. The weights of the multiply charged fragmentation channels were obtained from the decay of initial core vacancies, and partial Auger spectra were obtained in coincidence with the doubly charged final products, which revealed the relative extent of the different fragmentation channels in the complete single Auger spectrum of ICN.

Papers IV and V investigated the relative abundance of double Auger decay in molecules upon core vacancy formation. The quantity of double compared to single Auger decay was found to surpass 20% in some of the heavier molecules, which is a significant amount and undoubtedly contradicts the past assumption that such processes are negligible. The amount of double Auger decay follows a linear trend with the number of available valence electrons on the nearest neighbouring atoms. It was also found that the 1s or 2p nature of the initial core vacancy had no significant effect on the amount of double Auger decay. The investigation of multiple Auger decay was expanded in Paper VI towards the amount of triple Auger decay in CO and CO_2 . The quantity of triple compared to single Auger decay in CO and CO_2 upon an initial C 1s core vacancy was determined as 0.82% and 1.44%, respectively, and upon an O 1s vacancy as 0.89% and 1.0%, respectively. The percentage of triple Auger decay also follows a linear trend related to the number of available valence electrons.