

The Effects of Electron Correlation and Nuclear Motion in Core Ionization of Molecular Systems

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Computed cross sections for the core photoionization of small molecular systems will be presented. The photoionization cross sections were computed using correlated initial and final target states obtained with standard ab initio techniques and using a numerical representation of the continuum scattering orbitals. We will examine total cross sections and both molecular frame and laboratory frame photoelectron angular distributions. In a one-electron description, core and valence ionization are very similar, since the one-electron scattering potentials are very similar. When correlation is included in the calculation through interchannel coupling and the inclusion of shake-up and excited ion states, these photoionization energy regimes have very different behavior. Of particular interest are the relative importance of shape-resonance and shake-up features at energies within ~20 eV of the threshold for ionization. Additionally, we find that averaging over the vibrational motion is more important in shape resonances in core ionization than in the corresponding shape resonances in valence ionization. Furthermore, in the photoionization of open shell molecules we find that the spin-coupling scheme that best describes a shape resonant state is also different in the valence and core ionization processes. Examples from the core photoionization of N₂, C₂H₂, NO, CO, and SF₆ will be presented.