Anisotropy in Molecular Inner-Shell Photoexcitation, Photoionization and Subsequent Decay Processes

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Molecular inner-shell photoabsorption processes leading to both discrete and continuum states are intrinsically anisotropic, since an anisotropic orientational distribution of molecules is determined by the orientation of the transition dipole moment relative to the electric vector of the light. This anisotropy is reflected in the angular distribution of the products created either from the initial core hole state or from states following the rapid decay. Processes like photoelectron emission, Auger electron ejection, fluorescence, and photodissociation, all bear the vestige of the symmetry of the initial excited state. Following two recent topics concerning such an anisotropy will be presented.
As is widely recognized, the fragment-ion detection provides a powerful tool for probing the symmetry of the K-shell excited states of linear molecules. Recently a new beamline has been constructed at UVSOR and fragment-ion yield measurements have been applied to the 2p excitation regions where molecular field effects and core-valence exchange interactions are significant, of some simple molecules. Mixing between the perpendicular and parallel transitions, 2p hole dependence of the core-valence exchange interaction, and bond-length dependence of the spin-orbit interaction will be discussed.

The first measurements of the angular distribution of Auger electrons from fixed-in-space molecules have been performed at LURE in the C K-shell ionization region of CO, for both parallel and perpendicular orientation of the molecular axis with respect to the light polarization vector. The angular distributions obtained for a certain Auger final state show dramatic spectral variations, which also depend on the initial ionization channels, σ or π. The result strongly suggests the breakdown of the two-step model in which the Auger decay is treated independently of the initial photoionization process.