ANGULAR DISTRIBUTION OF MOLECULAR K-SHELL AUGER ELECTRONS: SPECTROSCOPY OF PHOTOABSORPTION ANISOTROPY *

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Atomic K-shell vacancies are isotropic, and hence electrons emitted by Auger decay of such vacancies have an isotropic angular distribution.[1-4] Molecules are different, however, for two reasons. First, molecular photoabsorption is highly anisotropic, both in the discrete, because excited states have definite symmetries but generally different energies, and in the continuum, where shape resonances can enhance photoabsorption along characteristic directions of the molecule.[5-9] As a result, molecular photoabsorption produces neutral molecular excited states with definite, characteristic orientations, and shape-resonant photoionization produces molecular ions with energy-dependent orientations characteristic of each resonance. Second, subsequent decay of the K-shell vacancy is a fast process compared to molecular rotation, so that the orientation of the molecular excited state/ion will be reflected in the angular distribution of the emtted Auger electrons. For example, in CO and N_2 there is a very intense discrete absorption of π symmetry about 1 Ry below the K-shell ionization threshold and a broad σ-symmetry shape resonance centered about 1 Ry above threshold.[6,7,10,11] Thus photoabsorption to the π excited states preferentially creates excited molecules perpendicular to the electric vector of the light while photoionization within the σ shape resonance yields molecular ions preferentially parallel. The angular distribution of a particular Auger electron will mirror these alternative orientations produced as one scans through the photoabsorption spectrum. Thus, molecular Auger-electron angular distributions, as a function of photoexcitation energy, provide us with a spectroscopy

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of the anisotropy of molecular photoabsorption spectra, whereby they can be decomposed into their component symmetries.

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