ON THE PHOTOIONIZATION OF STATE-SELECTED ACYL RADICALS: CATION STRUCTURE AND VIBRATIONAL RELAXATION DYNAMICS

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Many open-shell free radicals exhibit complex electronic structure as neutral molecules, but form electronically simple closed-shell cations. As a result, higher excited states often conform with an elementary Rydberg separation. Bound intermediate states commonly found in such systems provide convenient gateways for double-resonant photoionization using ultraviolet and visible laser radiation. Distinctive spectra of photoselected Rydberg series reflect state-to-state electron-ejection dynamics of super-excited neutrals and yield structural information on corresponding cations. We illustrate this principle with new results on formyl radical that characterize anharmonic terms in the vibrational potential of the cation.