PROBING SUPEREXCITED STATE DYNAMICS WITH AN EXTREME-ULTRAVIOLET FREE ELECTRON LASER

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We present the first experimental results obtained with the extreme ultraviolet free electron laser under development at Brookhaven National Laboratory. One experiment probes decay dynamics of superexcited states of methyl fluoride via ion pair imaging spectroscopy. Velocity mapped ion images of the fluoride anion, obtained with excitation via intense, coherent, sub-picosecond pulses of 86-89 nm radiation, reveal low translational energy, implying very high internal excitation in the methyl cation cofragment. Angular distributions show changing anisotropy as the excitation energy is tuned through this region. The dynamics underlying the dissociation are discussed with the aid of theoretical calculations. In a second study, photoelectron imaging of oxygen near threshold has been studied to unravel its complex photoionization dynamics: direct ionization pathways and autoionization via a number of superexcited Rydberg states exist in competition with intense shape resonances. Although there has been a good deal of experimental and theoretical work on these questions, vibrationally resolved photolectron imaging measurements greatly aid in identifying the underlying photoionization mechanisms. A sharp autoionization resonance gives rise to a dramatic change in the O_2^+ vibrational distribution and the photoelectron angular distributions over a change in the photon energy of only 50 meV. A broad underlying shape resonance is responsible for a strongly non-Franck-Condon vibrational distribution as the photon energy is tuned away from the autoionization resonance.