From Freeman Resonances to Resonance-Enhanced ATI: The Role of Vibrational Structure in Strong-Field Molecular Ionization

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Molecules exposed to intense femtosecond laser fields display a complex interplay of multiphoton ionization, resonances, and tunneling dynamics. In particular, the Stark shift effect distorts the potential energy surfaces of molecules by varying both the energy of electronic and rovibrational states and their ionization energies. The Stark shift can then generate resonances between intermediate states and an integer number of laser photons of a given wavelength, which are commonly known as Freeman resonances. Here, the role of molecular and vibrational structure in the strong-field (SF) ionization of polyatomic molecules using 800-nm femtosecond pulses has been investigated by means of photoelectron velocity map imaging. First, SF ionization of a series of linear and branched alkyl iodides is considered. A dominant Freeman resonance is observed, which counter-intuitively appears at the same photoelectron kinetic energy throughout the whole alkyl iodide series. The ionization pathways of this resonance strongly involve the $6p(^2E_{3/2})$ Rydberg state with different degrees of vibrational excitation, revealing an energy compensation effect as the R-chain complexity increases.

Second, the SF ionization of ammonia is studied. This molecule is particularly suited to disentangle resonance-enhanced ionization dynamics in molecular systems since excitation and ionization are characterized by strong bending vibrational motion due to the pyramidal to planar geometrical transformation. A weak Stark-induced Freeman resonance whose ATI replicas are shown to dominate over the parent channel is observed. A pronounced resonance-enhanced above-threshold ionization (REATI) phenomenon is thus demonstrated. The findings presented highlight how the vibrational structure governs strong-field phenomena in complex molecules.