Towards Disentangling High Harmonic Generation: Multiple Active Electrons in Strong Field Ionization of Polyatomic Molecules

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Synopsis We investigate Strong Field Ionization - the first step in High Harmonic Generation - of polyatomic hydrocarbon molecules. By utilizing a novel covariance technique we show that multiple bound electrons respond simultaneously to the strong laser field. The driven sub-cycle ionization process cannot be described within a single continuum approximation.

The process underlying the generation of attosecond light pulses, High Harmonic Generation (HHG) by a strong laser field, is itself one of the most powerful dynamical probes of attosecond timescale dynamics. It is successfully applied to atoms and small molecules based upon a three-step model comprised of adiabatic ionization of a single electron, its acceleration in the laser field and its subsequent radiative recombination. Here we investigate Strong Field Ionization (SFI) - the first step in HHG - of polyatomic molecules and explore how the response of multiple bound electrons to the laser field may affect attosecond timescale measurements.

Strong Field Ionization (SFI) of the four similar hydrocarbon molecules butane, 1-butene, trans-2-butene and 1,4-butadiene have been studied by a novel covariance technique, correlating the kinetic energy of the photoelectron with the mass of the ion. We observe different ionic fragments indicating that the neutral molecule has a probability to ionize into an electronically excited, dissociative cation state. The correlated photoelectron spectra show peaks spaced by the photon energy, the typical pattern linked to Above Threshold Ionization (ATI). Interestingly, photoelectron spectra correlated to different fragmentation channels are shifted in energy depending on the molecule. This implies that: (i) the cation excited state was not prepared post-ionization, and (ii) at least two electronic continua are directly coupled to the sub-cycle SFI of these molecules.

Our results unambiguously demonstrate driven sub-cycle electron dynamics which cannot be described within a single continuum approximation. In principle, these multiple continua can be prepared by both adiabatic (i.e. tunnel ionization of multiple orbitals) and non-adiabatic mechanisms. As Attosecond Science progresses to the more complex world of polyatomic molecules, such multi-electron dynamics driven in the strong laser field will play an increasingly prominent role.

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