

Ultrafast high-harmonic imaging of a chemical reaction

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Synopsis High-harmonic generation in aligned molecules provides information about their electronic structure and ionization continuum within a fraction of a laser cycle. We exploit the ultrahigh time resolution to experimentally observe a chemical reaction of fixed-in-space molecules. We non-adiabatically align Br₂ molecules, launch a photodissociation wave packet and measure the high harmonic yield as a function of time delay and angle between the molecular axis and the polarization of the generating laser field. We develop an interferometric technique to extract the harmonic dipole and phase of the excited state along the photodissociation coordinate. This provides the complete information required for the dynamic tomographic imaging of the chemical reaction.

When a molecule is exposed to a strong laser field, the tunnel-ionized electron wave packet can recombine with the parent ion to emit high-harmonic radiation. The amplitude and phase of the emitted radiation characterizes the electronic structure of the atoms or molecules subjected to this process. This property has been used to image the highest occupied molecular orbital of nitrogen (N₂) using a tomographic procedure [1]. In fact, not only the bound state is characterized by the high-harmonic radiation but also the ionization continuum [2, 3, 4]. This perspective combined with the ultrafast time scale of the process opens exciting perspectives for imaging the electrons in molecules undergoing a chemical reaction [5].

We exploit the ultrahigh time resolution that can be achieved in high harmonic generation to extract high harmonic dipole amplitudes and phases of a molecule undergoing a chemical reaction. Our experiment proceeds in three steps: non-adiabatic alignment, impulsive excitation and high-harmonic generation. We use the photodissociation of Br₂ in a proof-of-principle experiment. The major difficulty is the separation of signals from the dominant ground state population from the excited state. Both coherently related states emit harmonics and interfere on the attosecond time scale. The transient interference of the two states results in a high visibility of the photodissociation process on the fem-

tosecond time scale. The variation of the observed signal with harmonic order provides dynamic information on the attosecond time scale. We develop a homodyne technique that enables us to extract the harmonic amplitude and phase of the excited state undergoing dynamics. Molecular frame information on the evolution of the electronic structure along the dissociation coordinate and the associated ionization continuum is thereby obtained. The results indicate that the coherence of the atomic fragments manifests itself up to very large internuclear separations. These experiments pave the way towards dynamic orbital tomography - a movie of the molecular orbitals undergoing a chemical reaction.

References

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