

TIME-RESOLVED HIGH-HARMONIC SPECTROSCOPY OF CHEMICAL REACTIONS

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The characterization of a chemical reaction on the femtosecond to attosecond timescales requires the understanding of both atomic and electronic motions. Atomic positions can nowadays be precisely measured by diffraction of electrons or X-ray photons but the valence electronic structure of a transient molecule is still difficult to characterize. We employ high-harmonic generation in an intense laser field as a probe of the electronic structure of molecules. The electric field of an infrared laser pulse focused to $\sim 10^{14}$ W/cm² ionizes the molecule, accelerates the electron and allows it to recollide with the parent ion. The recollision can result in photorecombination and the emission of an attosecond pulse¹. The spectrum and phase of the emitted pulse characterize the electronic structure of the parent molecule. Since recollision happens from a direction defined by the laser field and the molecule can be fixed in space, the measurement is performed in the molecular frame. When high-harmonic generation is performed in an ensemble of photoexcited molecules, the signal from the unexcited molecules is time independent and can be used as a reference against which the emission of the evolving excited molecule can be measured². Combining high-harmonic generation with the transient grating allows one to separate spectral amplitudes and phases of the harmonic emission and determine them relative to the unexcited molecules. We illustrate the method by studying the dissociation of Br₂ excited to the C ¹Π_{1u} state³. Minima in the amplitude of the harmonic emission allow us to determine the internuclear separation as a function of time. The variation of the phase with time characterizes the evolution of the vertical ionization potential and the changing electronic structure along the dissociation coordinate. Applied to NO₂, we show that the method is particularly useful for nonadiabatic processes. Following excitation to the \tilde{A} ²B₂ state at 400 nm, we observe femtosecond time scale oscillations in the electronic character of the molecular wave packet as it crosses the conical intersection with the \tilde{X} ²A₁ ground state. On the picosecond time scale, we observe the transition from wave packet motion to statistical dissociation into NO (²II) and O (³P).

¹P. Corkum, *Phys. Rev. Lett.* **71**, 1994 (1993)

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