

# Disentangling structural and dynamical effects via multidimensional high harmonic spectroscopy

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**Abstract:** Extending the dimensionality of high harmonic generation (HHG) measurements has the potential to reconstruct structural features in molecules and resolve multielectron dynamics on attosecond time scales. We demonstrate that structural and dynamical effects in molecules can be unambiguously distinguished using multidimensional HHG techniques.

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## 1. Introduction

HHG spectroscopic techniques provide a general tool for obtaining Angstrom-level structural information about atoms and molecules and for resolving dynamics on the attosecond time scale. However one of the major limitations is the intrinsic coupling between spatial and temporal domains that limits the complete reconstruction of the investigated processes. By increasing the dimensionality of the measurement, in close analogy with the NMR and optical regimes [1], it is possible to unravel structural and dynamical features that are often hidden in HHG spectroscopy.

Past measurements have focused on extracting either structural information, such as tomographic reconstructions [2], or time resolved attosecond dynamics. However, even for a relatively simple molecule such as CO<sub>2</sub>, there is an ongoing debate regarding the interplay between structure and dynamics in the HHG emission. When generating harmonics at 800 nm, there is a multi-orbital contribution to the signal, leading to hole dynamics that are visible in the so-called ‘spectral dynamical minimum’ [3, 4]. However, with mid-IR lasers, the dominant spectral feature is a fixed minimum in the spectrum that was attributed to a structural signature of the CO<sub>2</sub> HOMO [2]. Here, we increase the dimensionality of the measurement by generating harmonics with a two-color mid-IR field. We observed a clear multi-orbital contribution of to the harmonic signal, nearby to- but easily distinguished from the structural minimum.

When generating HHG with a two-color field, composed of the strong generating field and a weak second-harmonic field polarized in the perpendicular direction, the harmonic intensity oscillates as a function of the phase delay between the two components. The delay at which the signal of a given harmonic is maximal is determined by the temporal evolution of the corresponding electron trajectory [3]. When applying this scheme to a signal in which two orbital contributions interfere, the two electron trajectories have slightly different temporal evolution, and the harmonic intensity is peaked at slightly different delays. When the two contributions interfere destructively, the small delay between them can lead to a large phase jump in the position of the maximum of the total signal, as was observed for 800 nm [3].

## 2. Experimental Setup and Results

Powerful mid-IR femtosecond pulses (1.2 mJ, 20 fs, 1.5  $\mu\text{m}$  central wavelength) were generated by an optical parametric amplifier (OPA) pumped by an amplified Ti:S laser system (60 fs, 20 mJ, 800 nm). The molecules were impulsively aligned using a portion of the 800 nm beam. The relative phase delay was controlled with a pair of glass wedges.

The harmonic intensity as a function of the two colour phase delay  $\phi$  was measured for CO<sub>2</sub> molecules aligned at 0 degrees relative to the fundamental field polarization, and for two intensities of the fundamental field. A 2D colour plot of the low intensity measurement is shown in Fig. 1(a) and a clear shift of the maximum HHG signal with respect to  $\phi$  is seen at 70 eV. For the high intensity (2D plot not shown), the shift of the maximum is centered at 75 eV. This is more easily observed by comparing the delay  $\phi$  where the signal maximizes to the calculated delay for a single-orbital contribution (Fig. 1(b)). A large deviation from the single-orbital case is easily observed, and the maximum difference is shifted by about 5 eV between the two intensities.

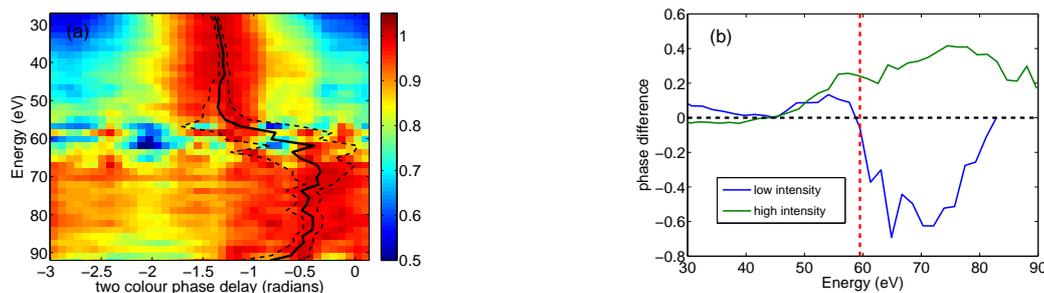


Fig. 1. (a) Normalized 2D colour plot of HHG signal vs phase delay  $\phi$  between the two fields. Bold line: HHG maximum with respect to phase. Dashed lines: error in extracting the maximal phase. (b) Maximum two colour phase delay as a function of HHG energy. The phase differences are shown relative to calculated values for a reference atom (Kr). The intensities in the measurement were  $1.4 \times 10^{14}$  W/cm<sup>2</sup> (high) and  $1.2 \times 10^{14}$  W/cm<sup>2</sup> (low).

Theory predicts that the delay shift should occur at the HHG energies where the relative accumulated phase between electrons ionized from the channels is close to  $\pi$  [3]. The calculated delay shifts are in good agreement with the experiment. The magnitude of the shift depends on the relative signal contributions and contrasts of the two channels, which depends on the laser intensity. The striking difference between the two intensities (both in sign and magnitude) is another strong indication of two-orbital contributions.

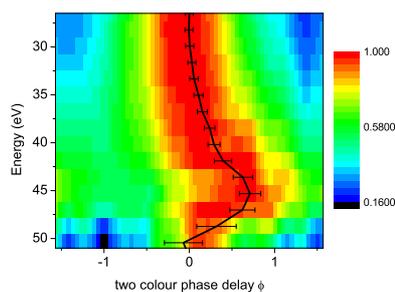


Fig. 2. 2D plot for C<sub>2</sub>H<sub>4</sub> aligned at 0 deg. The signal shows a complex behaviour with respect to  $\phi$ .

We note that the structural minimum in CO<sub>2</sub> is centred at 60 eV and selectively suppresses signal from the HOMO channel over a range of about 15 eV. This structurally-based reduction of the signal from the HOMO relative to the HOMO-2 leads to a more comparable contribution from the two channels and allows the delay shift(s) to be resolvable in a region of the HHG spectrum where the relative contributions of multiple channels is typically obscured [5].

In future work, we are aiming to extend these multidimensional schemes to a wider range of molecular systems. These measurements were also performed in aligned ethylene (C<sub>2</sub>H<sub>4</sub>) molecules (Fig. 2). The harmonic maximum shows a very complex behaviour with respect to  $\phi$ . In CO<sub>2</sub>, the HOMO is a nonbonding molecular orbital and therefore removal of a HOMO electron via tunnel ionization will not affect the bonding structure of the molecule. In contrast, the HOMO in C<sub>2</sub>H<sub>4</sub> is a bonding orbital, and removal of an electron should lead to rapid conformations of the carbon-carbon bond, which is then probed by the recombining electron at later times.

## References

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