

High Harmonic Spectroscopy of Substituted Benzenes at 1.8 micron

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Abstract

We present high harmonic generation spectroscopy of halo- and methy-substituted benzenes using 1.8 μm driving pulses. Compared to that of benzene, the spectra from substituted molecules decay more rapidly at higher orders. The dependence of the effect on the driving laser intensity suggests an origin in the dynamics of the ion rather than the static photorecombination cross section.

The ultrafast rearrangement of atoms and molecules following excitation by an ultrashort laser pulse is of fundamental interest and is pertinent to topical open questions such as the nature of charge migration in biomolecules. High-order harmonic generation (HHG) in a strong laser field is sensitive to electronic [1] and nuclear [2] rearrangement that occurs in the sub-cycle interval between ionization and recombination, and as such enables observation of electronic motion on the few-femtosecond timescale. Most previous studies, using 800 nm driving pulses, have examined molecules with ionization potentials above 10 eV. However many interesting and more complex molecules, such as benzene and its derivatives, have ionization potentials of 8-10 eV, so that ionization saturation prevents the generation of HHG continua at 800 nm. Additionally, dynamics are expected on timescales longer than the 2 fs available at 800 nm.

Here, we present HHG spectroscopy in benzene and its halo- and methyl-substituted derivatives using 1.8 μm pulses. Figure 1(a) shows the harmonic spectrum produced by 60 fs, 500 μJ , 1.8 μm pulses focused with a 50 cm lens into jet of benzene vapour produced by backing a 200 μm hole with 0.3 bar. The molecules, liquids at room

temperature, are delivered by a novel heated delivery system which allows precise pressure control and convenient switching of samples. Figure 1(b) shows the harmonic amplitudes obtained in bromo- and chlorobenzene normalized to those in benzene. There is a reduction in the higher orders, with the effect being stronger in chlorobenzene. Figure 1(c) shows similar behaviour in the doubly methyl-substituted m- and o-xylene.

We probe the origin of these differences by reducing the laser intensity and hence the spectral region sampled by the plateau. Figure 2(a) shows harmonic spectra in bromobenzene at 20 and 30 TW/cm^2 , and Fig. 2(b) shows the harmonic amplitudes normalized to those of benzene under the same conditions. The steeper decline at the lower intensity suggests that the differences from benzene are due to dynamical processes such as nuclear motion or ionic eigenstate evolution which occur during the electron's excursion in the continuum, rather than differences in the static photorecombination cross section which depend on the harmonic frequency only.

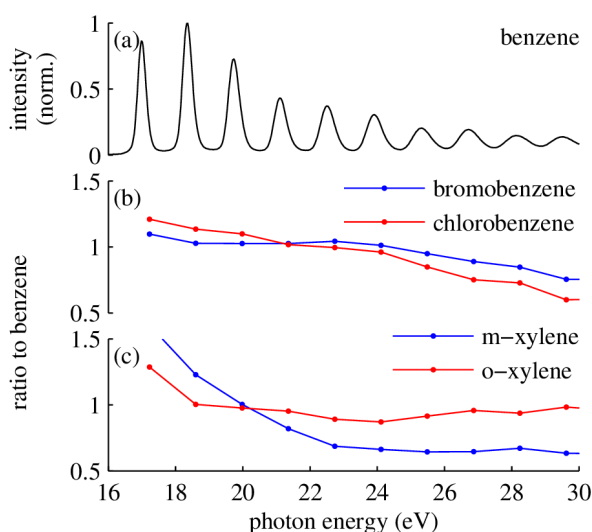


Fig. 1(a) Harmonic spectrum in benzene. (b) Ratios of harmonic intensities in halobenzenes to benzene. (c) As with (b), but for the xylenes.

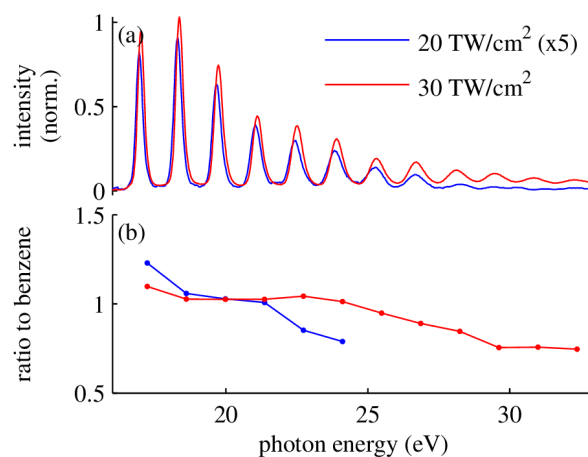


Fig. 2(a) Harmonic spectra in bromobenzene at two intensities. (b) Corresponding ratios of harmonic intensities to those of benzene.

References

- [1] Smirnova et al. *Nature* **460**, 972 (2009).
- [2] S. Baker et al. *Science* **229**, 424 (2006).