Mapping molecular orbitals from high harmonic generation

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Introduction

High-order harmonic generation (HHG) in aligned molecules has received much attention in recent years due to its unique ability to supply information about the molecular structure and the symmetry of the highest occupied molecular orbital (HOMO)[1] with attosecond time resolution. Measurements of harmonic intensity as a function of the angle between the molecular axis and the driving field have been used to tomographically retrieve an image of the HOMO of in N_2[2]. Moreover, the study of the structure of the plateau in harmonic spectra from aligned CO_2 has allowed the identification of two-centre interferences in the harmonic emission, which can be related to the spatial structure of the molecule[3-5]. A recent experiment carried out by our group in Astra TA1[6] has extended the study of harmonic emission in aligned molecules to more complex systems, namely acetylene (HC≡CH), allene ($H_2C=C=CH_2$) and ethylene ($H_2C=CH_2$). This work demonstrated (i) the possibility to align molecules with a variety of structural symmetries to perform angular dependent HHG measurements, and (ii) the ability of HHG to reflect the symmetry of the HOMO in complex polyatomic molecules, even revealing details of their structure[7,8]. This work also exposed some technical limitations to the study of molecular imaging by HHG, in particular the small number of harmonic orders available for molecules with low ionization potential[9].

In recent months a number of criticisms have been raised about the validity of the interpretation of some of the experiments described above. In particular, it has been observed that the position of the two-centre interference in the HHG emission from CO_2 depends on the driving field intensity, challenging its interpretation as a signature of the internuclear distance. Moreover, it has been pointed out that the single active electron approximation used traditionally in the analysis of HHG from molecules is not valid, and that lower-lying orbitals, usually ignored, can have an important influence on the harmonic emission[10].

In order to address these issues, an experiment was arranged to investigate the dependence of HHG in CO_2, N_2, acetylene, ethylene and allene, upon the driving field intensity and ellipticity. The plan for the experiment was: (i) to measure the recombination interference in CO_2 as a function of alignment angle and laser intensity to establish with greater confidence the physical origin of this effect, and (ii) to measure HHG spectra from aligned CO_2, N_2, and organic molecules to test the control of HHG by ellipticity[4,5] and to gain insight into the wave packet spatial distribution in these molecules.

Experimental setup and methodology

The experiment was arranged in a pump – delayed probe configuration, in a similar way to the previous experiment by our group[6]. The main beam from Astra (~15 mJ, 40 fs) was divided by a beam splitter; the pump beam would induce impulsive alignment in the molecular sample whilst the other beam would be compressed by a hollow fibre and chirped mirrors down to ~10 fs and used as a probe generating the high harmonics. The beams were focused by a 40 cm focal length off-axis parabolic mirror into a gas jet. The temperature of the gas in the interaction region was estimated to be a few tens of Kelvin. The harmonics produced in the gas jet were dispersed in a flat field spectrometer and detected with a microchannel plate detector fitted with a phosphor screen. A half-wave plate in the aligning beam was used to control the angle Θ between the aligning and driving fields.

Due to problems encountered during the set up and the lack of availability of stable high-intensity short pulses from the hollow fibre, the experiment was reduced to measuring the harmonic yield in CO_2 as a function of alignment angle using an uncompressed probe pulse (~ 40 fs). The longer pulse had the disadvantage of producing a non-negligible degree of realignment and a higher amount of ionization but the measurements still had the potential to provide useful information.

High harmonics from the 17th to the 39th order where detected with CO_2. The harmonic spectra were recorded for different time delays between the aligning and driving pulses for different alignment angles Θ. In addition, harmonic spectra were measured in unaligned samples in order to obtain a ratio of harmonic intensities.

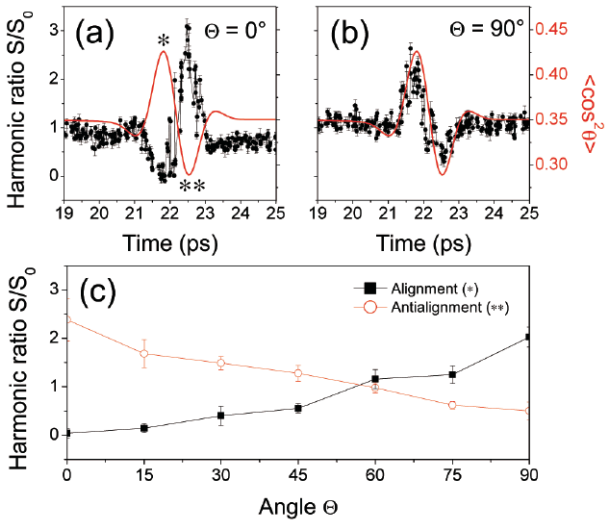

Figure 1. (a) Ratio between intensities of the 27th harmonic in aligned/unaligned samples of CO_2 as a function of the time delay between with the aligning and driving pulses when both fields are parallel; (b) idem with perpendicular fields. The red line shows the calculated evolution of the degree of alignment in CO_2. (c) Ratio between intensities of the 27th harmonic in aligned/unaligned samples of CO_2 as a function of the angle between with the aligning and driving fields at the alignment peak (solid black squares) and antialignment peak (empty red circles).

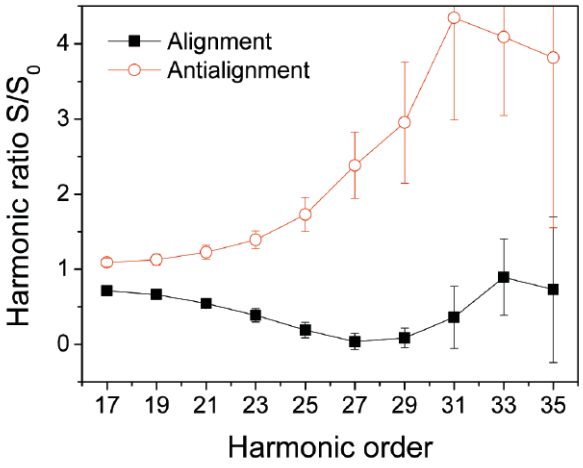

Figure 2. Ratio between harmonic intensities in aligned/unaligned samples as a function of harmonic order in CO_2 for parallel aligning and driving fields at the alignment peak (solid black squares) and antialignment peak (empty red circles).

Results

Figure 1 (a) shows the modulation of the 27th harmonic signal as the probe field scans through a rotational half-revival of CO_2 when the aligning and driving fields are parallel. The red line shows the calculated degree of alignment in terms of $<\cos_2\Theta>$, where Θ is the angle between the molecular axis and the aligning field. It can be seen that the transient alignment peak (marked with an asterisk) causes suppression of the harmonic yield, whereas the antialignment (marked with two asterisks) causes enhancement of the signal. Figure 2 (b) shows the results of a similar measurement when the two fields are perpendicular, hence producing the opposite dependence. Figure 1 (c) shows the variation of the harmonic ratio for the 27th order as the angle Θ between the aligning and driving fields is rotated from 0° to 90°. The effect described above, i.e. signal suppression at Θ = 0° and enhancement at Θ = 90°, as well as the relation between the measurements at the alignment and antialignment peaks is more clearly seen here. It is interesting to point out that the two curves shown in figure 1 (c) cross at an angle Θ ~ 57°, very close to the 54.7° predicted recently by Faisal *et al*[11].

The degree of modulation in the revivals depends on the harmonic order. The harmonic ratio at the alignment and antialignment peaks for different harmonic orders is shown in figure 2. It can be seen that the difference in harmonic ratio between the alignment and antialignment peaks increases up to about the 31st order and seems to decrease at higher orders. In recent measurements of HHG from aligned CO_2 molecules Liu *et al*. have observed a change in the sign of the revivals at high harmonic orders (seen as a crossing between similar curves as the ones plotted in figure 2), also, they have found that this change of sign depends critically on the driving field intensity[12]. For an intensity of 1.9×10^{14} W/cm^2 the crossing occurs around the 25th order, moving towards higher orders as the intensity increases. The estimated intensity of our driving field was 2.6×10^{14} W/cm^2, therefore the fact that we have not observed any inversion in the sign of the revivals is still compatible with the results of Liu *et al*. However, the lack of harmonic orders in our data made it impossible to confirm this point. On the other hand, we could not use lower laser intensities as the number of harmonic orders detected would be further reduced.

Future work

This work is still under development, and there are plans to continue the measurements of HHG in aligned molecules with shorter pulses (to rule out realignment effects), longer wavelengths (to increase the harmonic cutoff in organic molecules) and improved detection efficiency. With a wider range of harmonics available it will be possible to gain more insight into the structural signatures of the organic molecules in the HHG emission and we will be able to address the issues of the intensity dependence of two-centre interference and the variation of harmonic yield with the ellipticity of the driving field.

Acknowledgements

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