

## High harmonic generation from laser aligned organic molecules

N. Kajumba, R. Torres, S. Baker, J. S. Robinson, J. G. W. Tisch, and J. P. Marangos

*Physics Department, Blackett Laboratory, Imperial College of London, London, SW7 2BW, UK*

J. G. Underwood

*Department of Physics and Astronomy, The Open University, Walton Hall, Milton Keynes, MK6 3AQ, UK*

R. de Nalda

*Instituto de Química Física Rocasolano, CSIC, Serrano 119, 28006 Madrid, Spain*

C. Altucci and R. Velotta

*Coherentia-INFN and Dipartimento di Scienze Fisiche, Università di Napoli Federico II, Napoli, Italy*

W. A. Bryan and I. C. E. Turcu

*Central Laser Facility, CCLRC Rutherford Appleton Laboratory, Chilton, Didcot, Oxon., OX11 0QX, UK*

**Main contact email address** nathaniel.kajumba@imperial.ac.uk

### Introduction

High harmonic generation (HHG) in atomic gases with high intensity laser fields has proven to be a fruitful method for the production of coherent XUV beams and attosecond pulses<sup>[1,2]</sup>. In molecules, HHG presents a rich set of new physical phenomena, as both the ionisation and electron recombination steps of HHG are dependent on the particular geometry of the highest occupied molecular orbital (HOMO) and its orientation with respect to the laser field<sup>[3-7]</sup>. This feature can be used as a probe of the molecular orbital<sup>[8]</sup> or as a knob to control the efficiency of the yield of certain harmonics. In either case a detailed knowledge of the effect of the molecular geometry on the processes involved is required.

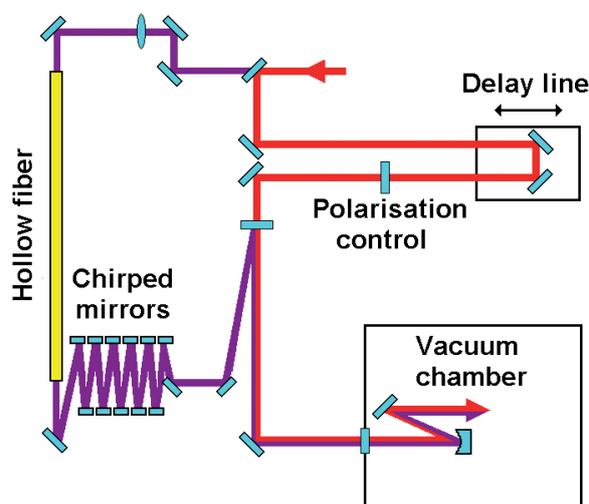
In order to address these problems experimentally it is necessary to fix the molecular axes in the laboratory frame. We use the impulsive alignment technique<sup>[9]</sup> in which a short laser pulse produces a transient distribution of aligned molecules that revives periodically in time. Recent experiments using this technique have measured the angular dependence of the harmonic emission from N<sub>2</sub>, O<sub>2</sub>, and CO<sub>2</sub>, permitting a tomographic reconstruction of the HOMO of N<sub>2</sub><sup>[8]</sup>, and the identification of two-centre interference of electron waves in CO<sub>2</sub><sup>[10,11]</sup>. They have also demonstrated the importance of distinguishing the effects arising from the angular dependence of the ionisation from that of the recombination step in HHG.

Here we extend these studies to the organic molecules acetylene (HC≡CH), ethylene (H<sub>2</sub>C=CH<sub>2</sub>) and allene (H<sub>2</sub>C=C=CH<sub>2</sub>), all of which have bonding  $\pi$  orbitals between the carbon atoms, to investigate the signature of their structure on the HHG spectra. These molecules also have a large anisotropy of the polarisability which ensures a high degree of alignment. Their low ionisation potential requires a sufficiently short driving pulse in order to avoid saturation of the ionisation. These molecules are significantly more complex in their structure than those previously examined by the techniques described above, and so provide a stringent test of the assumptions underlying the interpretation of these experiments, as well as the scalability of the tomographic imaging technique. Furthermore, the complications that arise for molecular axis alignment when one moves from a linear molecule (acetylene) to symmetric top (allene) and asymmetric top (ethylene) molecules are examined in these experiments.

Asymmetric top molecules in particular are challenging to align due to their complex rotational dynamics and irregular energy level spacings.

### Experimental setup

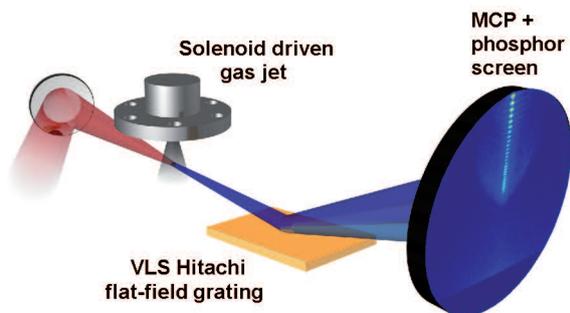
We employed the ASTRA laser system in Target Area 1 which provides laser pulses of  $\sim 10$  fs, 0.5 mJ at 800 nm after a hollow fibre pulse compressor with a repetition rate of 10 Hz. Approximately eighty per cent of the beam energy was split off before the hollow fibre and sent through a delay line in order to produce an aligning pulse correctly synchronized with the HH generating field. Both beams were recombined and propagated collinearly into the interaction chamber (see Figure 1).



**Figure 1. Schematic layout of the experiment.**

The beams were focused by a 40 cm focal length off-axis parabolic mirror into the gas jet. A high degree of rotational cooling is important to ensure a good degree of molecular alignment, and the temperature of the gas in the interaction region was estimated to be a few tens of Kelvin. The HH generating beam had an energy of  $\sim 300$   $\mu$ J and 14 fs duration, providing an on target intensity of  $1.8 \times 10^{14}$  W/cm<sup>2</sup>. The short pulse durations provided in ASTRA-TA1 were required in order to efficiently produce HHG without significantly ionising the sample due to their low ionisation potentials.

The alignment beam had an energy of 200  $\mu\text{J}$  and a pulse duration 90 fs, giving an on target intensity of  $\sim 5 \times 10^{13} \text{ W/cm}^2$ , which was insufficient to cause any detectable HHG. The harmonics produced in the gas jet were dispersed by a flat field spectrometer and detected with a microchannel plate detector fitted with a phosphor screen (Figure 2). A CCD camera was used to image the phosphor screen. A half-wave plate in the aligning beam controlled the angle  $\theta$  between the aligning and HH generating fields.



**Figure 2.** High harmonic generation and detection system.

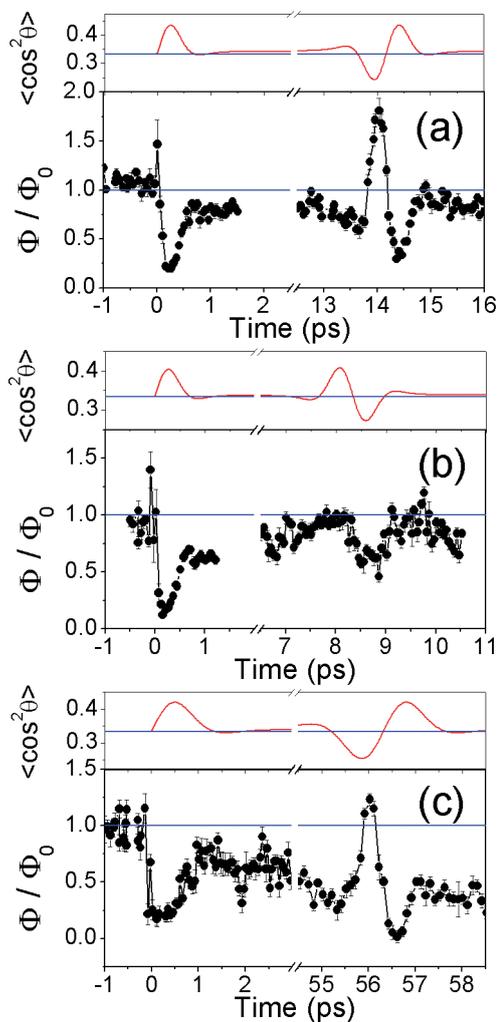
### Results

High harmonics from the 17<sup>th</sup> to the 27<sup>th</sup> order were successfully detected in acetylene, ethylene and allene. The harmonic spectra were recorded for different time delays between the aligning and HH generating pulses while maintaining their parallel polarisations. The integrated signal of each harmonic shows a modulation as a function of the time delay that corresponds to the different degrees of alignment appearing in the molecular ensemble during the rotational revivals. Additionally, the signal was recorded as a function of the angle between aligning and HH generating polarisation directions with the delay set at times corresponding to maximal axis alignment or anti-alignment. Spectra were also recorded in the absence of aligning field to allow the signal ratio between the aligned and isotropic samples to be extracted.

The degree of alignment may be represented by the expectation value  $\langle \cos^2 \vartheta \rangle$ , where  $\vartheta$  is the angle between the molecular axis and the aligning field polarisation. Acetylene and allene, being linear and symmetric top molecules respectively, exhibit regular rotational energy level spacings which results in regular revivals of the molecular axis alignment after the aligning pulse. On the other hand, ethylene is an asymmetric top and possesses irregularly spaced rotational energy levels, and strong axis alignment is only observed immediately after the aligning laser pulse, with no later revivals. The modulation in the HH yield observed in the time delay scans is opposite to the calculated evolution of  $\langle \cos^2 \vartheta \rangle$  for all the molecules and harmonic orders (Figure 3), indicating a suppression in the HH yield when the molecules are aligned with their axes along the HH generating field polarisation. The intensity of the modulation in acetylene increases with the harmonic order. The incoherent alignment (due to non-uniform M-state populations) is also evidenced as a constant signal suppression between the revivals.

The polarisation angle scans taken at the time delays of maximum alignment (prompt and full revival) show that, for all the molecules and harmonic orders, the emission is suppressed when the molecules are aligned parallel to the

HH generating field (Figure 4). In acetylene and ethylene the signal increases steadily with the angle, being maximum when the molecules are perpendicular to the field. Interestingly, the signal suppression is more pronounced than the enhancement and the maximum signal hardly exceeds that of the isotropic case. In allene the polarisation angle scans show some structure, having the maximum signal at  $\theta \sim 70^\circ$ .



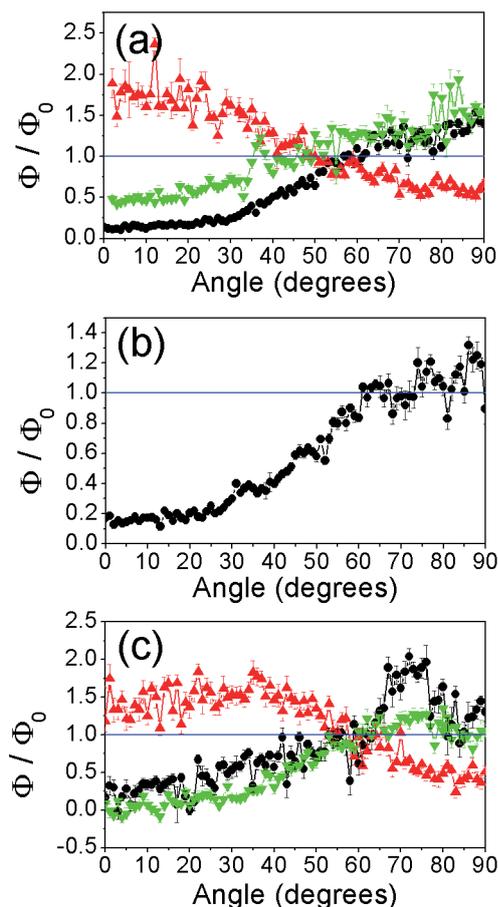
**Figure 3.** Harmonic ratio between aligned and not-aligned molecules as a function of time delay between the aligning and HH generating pulses for: (a) 21st H in acetylene, (b) 17th H in ethylene, and (c) 19th H in allene. The red line in the insets shows the calculated evolution of  $\langle \cos^2 \vartheta \rangle$ .

The polarisation angle scans taken at the point of maximum anti-alignment in acetylene and allene display roughly the opposite behaviour to those taken at the alignment maximum, as expected. However, the differences of modulation measured in the prompt alignment and the full revival shows differences that require further investigation.

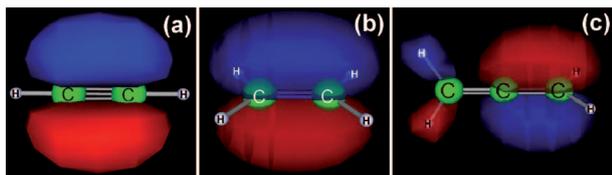
The results are interpreted in terms of the structure of the highest occupied molecular orbital. In acetylene, ethylene and allene, the HOMO has a nodal plane containing the molecular axis, which causes the ionisation, and hence the harmonic generation, to be minimum when the driving field points in that direction (Figure 5). The maximum harmonic signal, on the other hand, corresponds to the

direction of maximum electron density. The fine structure found in the measurements in allene might correspond to the more complex nature of its HOMO though this has to be confirmed by simulations that are currently ongoing.

The results are simulated using the Lewenstein model<sup>[12]</sup> which follows the assumptions of the Strong Field Approximation: in the continuum, the electron is treated as a free particle moving in the electric field without influence of the ionic potential, only the ground state of the molecule is considered, and the depletion of the ground state is neglected.



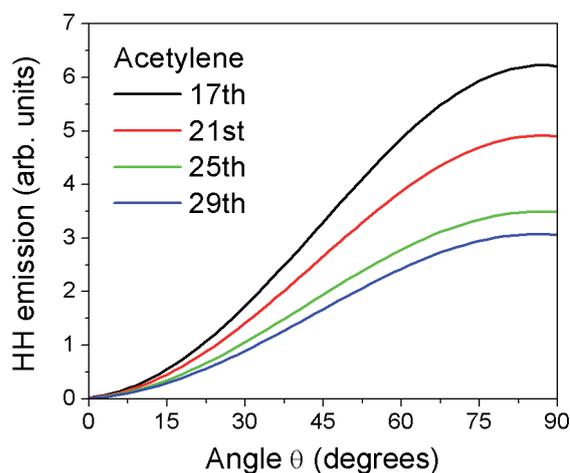
**Figure 4.** Harmonic ratio between aligned and not-aligned molecules as a function of polarisation angle between aligning and HH generating pulses measured at the prompt alignment peak (black dots), antialignment peak (red triangles) and full revival (green triangles), for: (a) 21st H in acetylene, (b) 17th H in ethylene, and (c) 19th H in allene.



**Figure 5.** Representation of the HOMO orbital in: (a) acetylene, (b) ethylene, and (c) allene, calculated with GAMESS-UK.

Using the saddle-point approximation, the time dependent dipole moment can be calculated as a single integral over the return time of the electron that includes the dipole

moments of the bound  $\leftrightarrow$  free transitions, the electric field amplitude, and the phase accumulated by the electron in the continuum. The angle-dependent transition dipole moments are calculated analytically for a two-centre molecular orbital in 2D, and the HOMO orbitals are calculated using the GAMESS-UK package. The angular dependence of the harmonic emission arises from the dependence of the transition dipole moments on the orientation of the orbital with respect to the electric field. The preliminary results agree qualitatively with the observed behaviour.



**Figure 6.** Calculated angular dependence of the harmonic emission from acetylene.

### Conclusions

High harmonic emission has been observed in acetylene, ethylene and allene from the 17th to the 29th orders of the fundamental frequency of the driving field. The molecules have been successfully aligned by the impulsive method, showing clear evidence of prompt alignment and rotational revivals. A suppression of HHG signal with increasing alignment has been observed over a range of harmonics. This shows a behaviour which is characteristic of the bonding  $\pi$  structure in the HOMO orbital of the molecules studied. In general, the emission is suppressed when the electric field points along the nodal plane of the orbital and is enhanced in the perpendicular direction, along the maximum electron density. More detailed structure is also observed in some of the measurements which may provide more detailed information about the molecular orbital composition.

A simple simulation using 2D orbitals successfully reproduces the general features. An improved calculation using 3D orbitals, and taking into account the angular dependence ionisation rate and the angular distribution of the molecular ensemble is currently ongoing.

These results confirm the importance of the HOMO structure in the process of HHG found in previous works<sup>[4-7]</sup>, and illustrate the signature of the molecular  $\pi$  orbitals in the angular dependence of the harmonic signal. These measurements represent a step forward in the generalisation of the tomographic reconstruction technique for the imaging of molecular orbitals to more complex molecules, and test the underlying assumptions of this method.

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