

High harmonic generation in aligned molecules with a mid-infrared laser source

Contact r.torres@imperial.ac.uk

R. Torres, T. Siegel, L. Brugnera and J. P. Marangos

Blackett Laboratory, Imperial College London, Prince Consort Road, London SW7 2BW, UK

I. Procino and J. G. Underwood

Department of Physics and Astronomy, University College London, Gower Street, London WC1E 6BT, UK

C. Altucci and R. Velotta

CNSIM and Dipartimento di Scienze Fisiche, Università di Napoli 'Federico II', Naples, Italy

E. Springate, C. Froud and I. C. E. Turcu

Central Laser Facility, STFC, Rutherford Appleton Laboratory, HSIC, Didcot, Oxon OX11 0QX, UK

Introduction

The interaction of strong laser fields (~ 100 TW/cm²) with molecules has been an extremely prolific area of research over the last few years^[1-7]. The key phenomenon in these interactions is a three-step process consisting on: (i) tunnel ionisation, (ii) acceleration of the electron in the laser field, and (iii) recollision of the high energy electrons with the parent ions^[8]. Upon recollision the electron has some probability of recombining to the initial state, emitting the acquired energy in the form of high order harmonics of the fundamental laser frequency. The recollision event occurs over an extremely short period of time, of the order of 100 attoseconds (1 as = 10^{-18} s)^[9]. It has been demonstrated experimentally that the high harmonic generation (HHG) from molecules exhibits signatures of the molecular structure and the symmetries of the electron orbitals^[10-12]; in fact, by controlling the alignment of the molecules with respect to the recolliding electrons it is possible, in principle, to 'image' the structure of the molecule^[2,13]. Moreover, as the process of harmonic emission is faster than the characteristic timescale of electron dynamics the imaging of molecules by HHG has been proposed as a technique to track molecular reactions with ultrafast time resolution^[4,14].

Some approaches to ultrafast molecular imaging by HHG have been demonstrated in proof-of-principle experiments like the tomographic reconstruction of orbitals of N₂^[2], the measurement of proton dynamics in H₂ and CH₄^[4] with attosecond time resolution, and the observation of a two-centre interference minimum in CO₂ which could be used as an ultrafast probe of the internuclear distances^[3,15]. However, the connection between the molecular structure and the measured harmonic signal is still not entirely clear, and recent advances in harmonic generation from aligned molecules have shown that the physics of strong field interactions with molecules is more complicated than initially thought^[6,7,16]. For example, the tomographic reconstruction of molecular orbitals and the model of two-centre interference assume that a single electron is responsible for the above-mentioned three-step process.

In multielectronic systems, however, the real process may involve non-negligible contributions from electron correlations, exchange, and multiple ionisation channels. Furthermore, the dip in the HHG spectrum of aligned CO₂ has been shown to depend on the laser intensity, challenging its interpretation as a structural interference minimum^[17].

Experimentally, the amount of data available has been limited to a few molecular systems, typically N₂ and CO₂. More recently, the investigation of HHG in aligned molecules has been extended to organic polyatomic molecules: acetylene (C₂H₂), ethylene (C₂H₄) and allene (C₃H₄)^[18,19]. However, the range of harmonics obtained from these molecules was very limited, with maximum photon energies of ~ 40 eV. In order to obtain an comprehensive picture of the molecules in momentum space, quantify the possible effects of electron correlation and ion dynamics in HHG, and gain insight into the connection between molecular structure and harmonic signal, it is desirable to have harmonic spectra as broad as possible.

The maximum photon energy in the harmonic spectrum follows the so-called cut-off law: $E_{\text{MAX}} = I_P + 3.17 U_P$, where I_P is the ionisation potential of the molecule and U_P is the ponderomotive energy given by: $U_P = eE_0^2/4m_e\omega^2$ (e and m_e are the charge and mass of the electron respectively, E_0 is the electric field amplitude and ω is the laser frequency). The maximum photon energy in the harmonic spectra can therefore be extended by increasing the intensity of the laser. However, apart from technical constraints to the laser intensity there is a limitation due to the saturation of the ionisation in the molecular medium that impairs the generation of harmonics. On the other hand, reducing the fundamental laser frequency ω can also extend the harmonic cut-off to higher photon energies, while keeping the laser intensity below the saturation intensity. The drawback of reducing the laser frequency is that, as the electrons spend more time in the continuum, the electronic wavepacket expands more, reducing the probability of recollision. The harmonic signal scales with the laser wavelength as λ^{-5} or λ^{-6} ^[20].

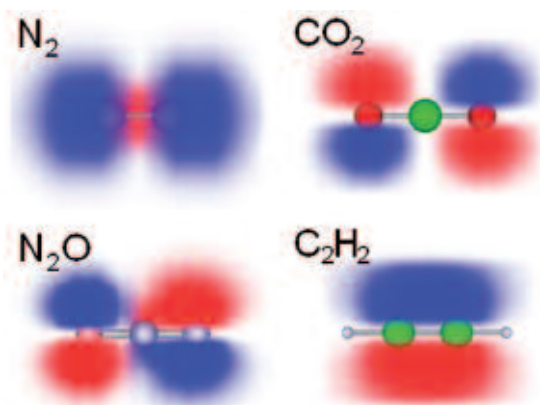


Figure 1. Molecules investigated in the experiment, showing the highest occupied molecular orbital (HOMO).

The 1 kHz laser system available in Artemis is the ideal source for mid-IR high harmonic generation as the high repetition rate allows to average the signal over many laser shots, thus compensating the reduced signal levels with a higher signal to noise ratio.

Experimental procedure and setup

The KML Red Dragon was set to deliver 10 mJ pulses of 80 fs duration at 780 nm with a repetition rate of 1 kHz. Approximately 8 mJ of the beam was reflected off a beam splitter to pump an Optical Parametric Amplifier (Light Conversion HE-TOPAS). The TOPAS was tuned to deliver 1300 nm pulses with an optimum energy output of 1 mJ and 40 fs duration for harmonic generation. The remaining 2 mJ of the 780 nm beam transmitted through the beam splitter was sent through a motorised delay stage and used to induce non-adiabatic molecular alignment. The 1300 nm and 780 nm beams were recombined by a normal incidence dichroic mirror and sent collinearly into the interaction chamber. The chamber was kept under a base pressure of 10^{-6} mbar and housed a 30 cm focal length lens to focus the two beams onto a continuous flow gas jet. The gas jet was produced by expanding the gas with a backing pressure of 2 bar through a 100 microns diameter nozzle. The vertical position of the focus was set at 180 microns below the nozzle. At this position the gas jet temperature is estimated as ~ 90 K, sufficiently cold to obtain a significant degree of molecular alignment, whereas the gas density is $\sim 2.3 \times 10^{18} \text{ cm}^{-3}$, high enough to produce a substantial harmonic signal. The horizontal position of the focus with respect to the gas jet was set to optimise the phase matching of the higher harmonics and the overall signal level. A telescope in the 1300 nm beam was used to compensate the chromatic aberration of the focusing lens, and a set of irises were used to control the energy of both beams in the interaction region. The intensities at the interaction region were typically 10^{14} W/cm^2 for the 1300 nm and $5 \times 10^{13} \text{ W/cm}^2$ for the 780 nm. The latter was set in order to induce a maximum degree of alignment while not generating any harmonics in the detected region. The high harmonic emission generated in the gas jet was spectrally resolved by a 1200 lines/mm curved grating which focussed them onto a microchannel plate detector (MCP) coupled with a phosphor screen. The images of the harmonic spectra were acquired with a CCD camera and transferred to a computer. Each spectrum was averaged over 10^4 laser shots typically.

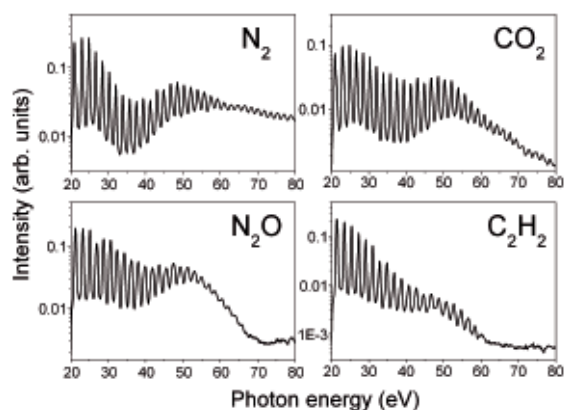


Figure 2. Harmonic spectra obtained from unaligned molecules with the 1300 nm beam.

Results

The molecules investigated were N_2 , CO_2 , N_2O , and C_2H_2 (Fig. 1). The properties of these molecules that are relevant to this experiment are summarised in Table 1.

Harmonic spectra with photon energies up to 60 eV were detected in N_2O , and C_2H_2 , whereas in N_2 and CO_2 the maximum harmonic detected exceeded 80 eV (Fig. 2). This represents a considerable improvement in terms of harmonic range with respect to previous experiments in Astra^[21,22].

The effect of molecular axis alignment was observed as a modulation in the harmonic signal when the delay between the harmonic generating (driving) pulse and the aligning pulse was varied (Fig. 3). These modulations correspond to revivals of the aligned state of the molecules occurring at times multiple of T_{rot} (full revivals) and $T_{\text{rot}}/2$ (half revivals), where T_{rot} is the rotational period of the molecule^[23]. The harmonic signal is normalised to the signal measured in unaligned samples, so a harmonic ratio >1 means signal enhancement, whereas <1 means suppression of harmonic signal upon alignment.

Molecule	Rotational period (ps)	IP (eV)	Internuclear distance (Å)	HOMO symmetry
N_2	8.4	15.6	1.1	σ_g
CO_2	42.7	13.8	2.3 †	π_g
N_2O	39.8	12.9	2.3 ‡	$\sim\pi_g$
C_2H_2	14.2	11.4	1.2 §	π_u

Table 1. Molecular properties relevant to this experiment. († between oxygen atoms; ‡ between the oxygen and the outermost nitrogen atom; § between carbon atoms.)

The degree of alignment is evaluated in terms of $\langle \cos^2\theta \rangle$, where θ is the angle between the aligning field and the molecular axis, and the calculated evolution of $\langle \cos^2\theta \rangle$ is shown as a red line in Fig. 3.

The delay between the driving and aligning pulses was set to the time of maximum alignment and then the angle Θ between the driving field and aligning field polarisations was varied by means of a half-wave plate in order to measure directly the harmonic signal ratio as a function of the alignment angle of the molecules.

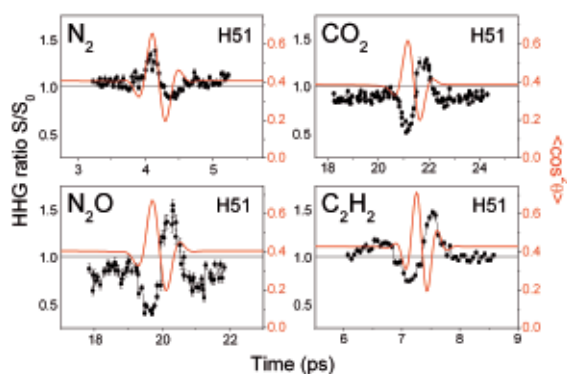


Figure 3. (Black dots) Ratio of 51st harmonic signal between aligned and unaligned molecular samples as a function of the delay between the driving and aligning pulses. (Red line) Calculated degree of alignment.

The dependence of the harmonic emission on the angle between the driving field polarisation and the molecular axis is characteristic of the structure of the molecule and the symmetry of its orbitals. Therefore, these kind of measurements have been used as a probe to image the instantaneous configuration of the molecule with attosecond time resolution.

The results of the angular scans in CO_2 with three different laser intensities are shown in the left column of Fig. 4. The most striking feature is a minimum in the harmonic ratio at $\Theta = 0^\circ$ that turns into a maximum at $\Theta = 90^\circ$, this feature is centred around 55 eV for $I = 0.9 \times 10^{14} \text{ W/cm}^2$, it shifts to 65 eV at $I = 1.2 \times 10^{14} \text{ W/cm}^2$, and then it moves back to 55 eV for $I = 1.6 \times 10^{14} \text{ W/cm}^2$. The dip in the harmonic spectrum of aligned CO_2 has been observed before and has generally been attributed to two-centre interference^[3,15,24]. There was some controversy about the exact position of this dip until it was discovered that it depended on the intensity of the laser. The intensity dependence of the minimum in the harmonic spectrum of aligned CO_2 contradicts its interpretation as a simple structural effect and additional mechanisms have been suggested to explain it^[17,25].

The observation of different angular dependence patterns with different laser intensities may be an indication of the interference between different ionisation channels or, equivalently, a signature of the excited state dynamics of the ion. Therefore, although the information about the internuclear distance is somewhat smeared in these experiments, they can provide potentially more interesting data about the electron dynamics in the ion.

Similar scans were taken in aligned N_2 , N_2O and C_2H_2 (right column of Fig. 4). In N_2 we did not observe any dramatic differences with the laser intensity. The harmonic signal is enhanced when the molecules are aligned parallel to the driving field and suppressed when they are perpendicular. The modulation is stronger for the lower harmonic orders (around 30 eV) and no structural minimum is observed. These observations are in general agreement with previous experiments^[2,3]. In N_2O the angular scan is qualitatively similar to those of CO_2 , reflecting its similar structure. The dip in the harmonic spectrum at $\Theta = 0^\circ$, centred around 57 eV, is compatible with structural interference but, lacking sufficient data for different intensities, we

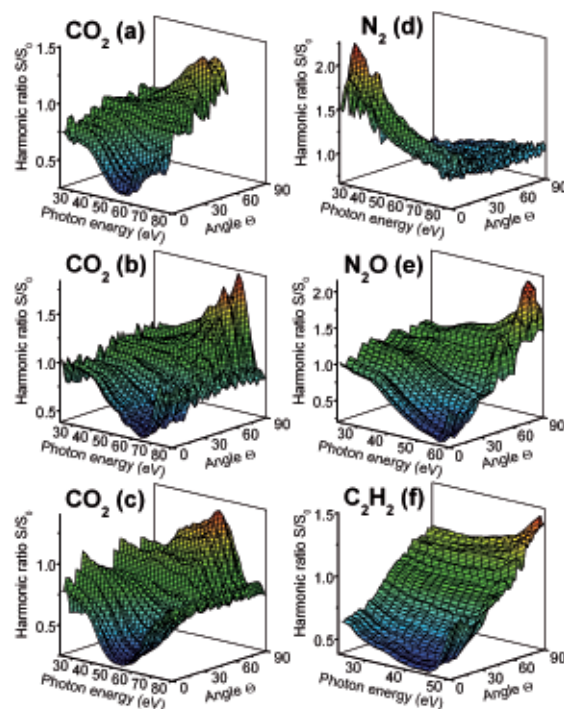


Figure 4. Ratio of harmonic signal between aligned and unaligned molecular samples as a function of photon energy (harmonic order) and alignment angle. The laser intensities are: a) $0.9 \times 10^{14} \text{ W/cm}^2$, b) $1.2 \times 10^{14} \text{ W/cm}^2$, c) $1.6 \times 10^{14} \text{ W/cm}^2$, d) $1.8 \times 10^{14} \text{ W/cm}^2$, e) $1.0 \times 10^{14} \text{ W/cm}^2$, and f) $0.8 \times 10^{14} \text{ W/cm}^2$.

cannot rule out the occurrence of dynamic effects here as in CO_2 . In C_2H_2 we also observe a dip in the spectrum of molecules aligned at $\Theta = 0^\circ$ that is compatible with structural two-centre interference. C_2H_2 has a shorter internuclear distance than CO_2 and N_2O , however it has a bonding HOMO orbital instead of the antibonding HOMO of CO_2 and N_2O and therefore the first destructive interference appears at smaller photon energies (46 eV).

A similar set of measurements was taken setting the delay between the driving and aligning pulses at the time of minimum value of $\langle \cos^2\theta \rangle$ (antialignment peak), where the molecular axes are predominantly delocalised in a plane perpendicular to the aligning field. The angular scans at these points look qualitatively the same as those shown in Fig. 4 but reversed in angle which confirms the results already discussed.

Conclusions

We have generated high-order harmonics from aligned molecules with a mid-infrared (1300 nm) source for the first time. The extension of electron recollision energies, i.e. photon energies, made possible by the long wavelength of the driving field allows us to establish the connection between the molecular structure and the behaviour of the harmonic signal at different alignment angles. We have found new evidence of structural interference in N_2O and C_2H_2 , previously unobserved, and we have verified the variation in the position of the interference dip in the harmonic spectrum of CO_2 with different laser intensities. The observation of changes in the harmonic signal – molecular alignment relation with different laser intensities may offer a unique insight

into the dynamics of the excited states of the ion. Computer simulations are under way to provide a theoretical frame to the experimental results.

Acknowledgements

We thank the CLF staff, and specially Brian Landowski, for the technical support and advice provided throughout the experiment.

References

1. H. Niikura *et al.*, *Nature* **417**, 917 (2002).
2. J. Itatani *et al.*, *Nature* **432**, 867 (2004).
3. T. Kanai *et al.*, *Nature* **435**, 470 (2005).
4. S. Baker *et al.*, *Science* **312**, 424 (2006).
5. W. Boutu *et al.*, *Nature Physics* **4**, 545 (2008).
6. B. K. McFarland *et al.*, *Science* **322**, 1232 (2008).
7. W. Li *et al.*, *Science* **322**, 1207 (2008).
8. P. B. Corkum, *Phys. Rev. Lett.* **71**, 1994 (1993).
9. P. Antoine *et al.*, *Phys. Rev. Lett.* **77**, 1234 (1996).
10. R. de Nalda *et al.*, *Phys. Rev. A* **69**, 031804(R) (2004).
11. B. Shan *et al.*, *Phys. Rev. A* **69**, 021404(R) (2004).
12. X. X. Zhou *et al.*, *Phys. Rev. A* **71**, 061801(R) (2005).
13. M. Lein, *J. Phys. B* **40**, R135–R173 (2007).
14. Van-Hoang Le *et al.*, *Phys. Rev. A* **76**, 013414 (2007).
15. C. Vozzi *et al.*, *Phys. Rev. Lett.* **95**, 153902 (2005).
16. S. Patchkovskii *et al.*, *Phys. Rev. Lett.* **97**, 123003 (2006).
17. P. Liu *et al.*, *Phys. Rev. A* **78**, 015802 (2008).
18. R. Torres *et al.*, *Phys. Rev. Lett.* **98**, 203007 (2007).
19. N. Kajumba *et al.*, *New J. Phys.* **10**, 025008 (2008).
20. B. Shan and Z. Chang, *Phys. Rev. A* **65**, 011804(R) (2001).
21. N. Kajumba *et al.*, Central Laser Facility Ann. Rep., 2005/2006 (Rutherford Appleton Lab., U.K., 2006), p. 80.
22. R. Torres *et al.*, Central Laser Facility Ann. Rep., 2007/2008 (Rutherford Appleton Lab., U.K., 2008), p. 96.
23. R. Torres *et al.*, *Phys. Rev. A* **72**, 023420 (2005).
24. M. Lein *et al.*, *Phys. Rev. Lett.* **88**, 183903 (2002).
25. Anh-Thu Le *et al.*, *Phys. Rev. A* **73**, 041402(R) (2006).