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High-order harmonic generation from organic molecules in ultra-short pulses

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Abstract. We have studied high-order harmonic generation (HHG) from organic molecules irradiated with near-infrared high intensity laser pulses of 70 fs and 240 fs duration. The molecular systems studied were the aromatics benzene and naphthalene and the alkanes cyclopropane and cyclohexane (cyclic) and *n*-hexane (linear). Harmonic intensities were measured both as a function of laser intensity (in the range 5×10^{13}–5×10^{15} W cm^{-2}) and as a function of ellipticity of the laser field polarisation. The results were compared with those from the xenon atom. For 70 fs pulses, harmonic generation from the organic systems was similar to that of xenon, revealing an atom-like behaviour for molecules when the laser pulse duration is shorter than the fragmentation timescale of the molecule. We note significant differences between molecules with respect to HHG efficiencies and the suppression of HHG in larger species. We discuss these differences in the context of the molecular properties, electronic structure and behaviour of ionisation and fragmentation that result in enhancement of field ionisation in larger systems. Study of the polarisation ellipticity dependence of HHG shows that the harmonic yield in molecules is less sensitive to the polarisation than for atoms (xenon). This is consistent with the expected behaviour given the larger recollision cross-section presented by the core in the molecular system compared to the atom. Our results suggest that study of HHG from molecules exposed to ultra-short pulses is potentially a powerful tool for understanding the electron dynamics of molecules exposed to an intense field.

PACS. 42.65.Ky Harmonic generation, frequency conversion – 42.50.Hz Strong-field excitation of optical transitions in quantum systems; multi-photon processes; dynamic Stark shift

1 Introduction

High-order harmonic generation (HHG) from atoms exposed to an intense laser field has been extensively studied to elucidate the basic mechanism of the process [1,2] and to develop as a light source the bright, coherent, XUV radiation that is produced. Recent work has shown how HHG can be used in novel applications requiring a high time-resolution and high brightness source of XUV radiation [3]. Considerable progress has been made in understanding the basic mechanism of HHG in atomic systems. A durable and clear picture for the process has been developed in the strong field limit ($I > 10^{14}$ W cm^{-2}); where field ionisation forms electron wavepackets that are driven in the laser field and re-collide with the atomic core at intervals of half an optical cycle to generate XUV radiation [4,5]. Since it gives an intuitively simple picture, with almost classical behaviour of the laser-driven electron, this model has been called the "Simple-Man's Model". The calculations within this model, however, still must retain a fully quantum treatment of the electrons to successfully predict the harmonic generation observed. This model correctly predicts the cut-off (highest order harmonic in the plateau region) to be at a photon energy of $I_P + 3U_P$ (where I_P is the species ionisation potential and U_P is the ponderomotive energy of the laser field at the saturation fluence for that species).

HHG has also been observed from a variety of molecular systems [6–9]. Most studies have concentrated on diatomic molecules (*e.g.* H_2, N_2, O_2) [6] and a few other small species (N_2O, CO_2, CH_4) [7]. Fraser *et al.* [8] performed the first investigation of HHG in organic molecules. Lyngå *et al.* [7] studied SF_6 and C_3H_8. The characteristics of HHG in small molecules have generally been found to be similar to HHG in atoms. However, Lyngå *et al.* noted a discrepancy using SF_6 and Fraser *et al.* observed some influence of the type of molecular bonding upon HHG. Stronger deviations from atom-like behaviour were observed in benzene and cyclohexane [9]. In part, molecular HHG studies are motivated by the objective of finding molecular systems that can provide harmonic yields higher than in atomic systems. It is well known that, for lower-order non-linear optical processes, certain organic molecules and polymers possess very large

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magnitude non-linear susceptibilities. To what extent, if any, this large non-linear response survives into the non-perturbative regime encountered in strong laser fields is not known.

Due to the additional nuclei and their relative motions, a more sophisticated theoretical picture, going beyond the Simple-Man's Model for atoms, needs to be developed to explain fully the nature of HHG in molecules. In molecules, the electron dynamics will be more complicated than in an isolated atom, with several ionic cores from which the electrons may originate and with which they may recollide. Calculations of HHG from molecules and molecular ions have been reported by a number of authors. These are, however, restricted to simple diatomic and linear chain systems. Due to its relative simplicity the hydrogen molecular ion H_2^+ has been used as the molecular system of many of the calculations reported. 1-dimensional models of H_2^+ have been developed that recognise the importance of the charge resonant (CR) states that give dipole moments much larger than any others in the molecule and thus permit the calculation of HHG as in a simple 2-level system [10,11]. Recent extensions of this work predict that HHG in a series of hydrogen molecular ions (H_2^+, H_3^+, H_3^{2+} etc.) will lead to modified plateaus with cut-offs at $I_P + 6U_P$ in the single electron case and $I_P + 12U_P$ in the 2-electron case [12].

The role of photoionisation and fragmentation in molecular HHG is very important. It is well known that the photoionisation rate in a molecule is strongly dependent upon the dimensions of the molecule and the angle between the laser field polarisation and the molecular axis [13]. Ionisation is significantly enhanced in the case where the molecular axis and laser field polarisation are aligned. This is attributable, in part, simply to the geometry of a typical molecule in a strong static field with a larger potential difference along the (longer) molecular axis in the parallel case than across the molecule in the perpendicular case leading to enhanced field ionisation rates in the former geometry. In the case of parallel alignment, co-operative effects between the distorted double wells have been seen to lead to a critical distance at which ionisation is greatly enhanced [14]. If rapid multiple photoionisation has occurred, this can lead to fast fragmentation of the molecule driven by Coulomb explosion [15]. It has recently been reported that some molecules (*e.g.* benzene), although showing single and double photoionisation, experience strong Coulomb explosion only at relatively high intensities ($> 10^{15}$ W cm^{-2}) [16–20]. In the intensity regime up to 10^{15} W cm^{-2}, the prospects for efficient HHG from the molecule and its ions are good.

Since HHG relies on electron dynamics, it is reasonable to consider the extent to which the properties of the generated harmonics can be used to study the electron dynamics of molecules in an intense field. The experimental study reported here advances this goal by demonstrating that for pulses of sufficiently short duration, the harmonic emission results overwhelmingly from the unfragmented parent molecule (and parent molecular ion). Furthermore, we show that the ellipticity dependence in this limit is significantly different in molecular systems compared to atoms. This ellipticity dependence can be explained at high ellipticity when the electron recollision is more probable in a molecular system than in an atom due to the larger size of the ionic core.

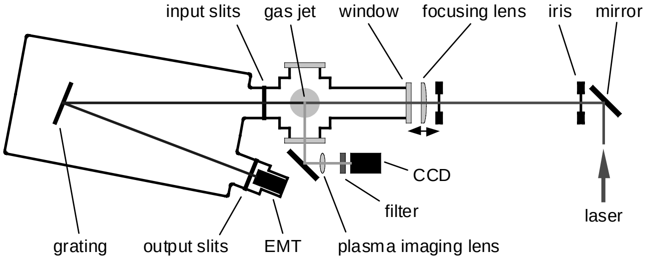


Fig. 1. Experimental setup showing laser, gas jet, interaction chamber and monochromator.

This paper is structured as follows. In Section 2, we describe the experimental apparatus, methodology and the precautions taken to obtain reliable data. In Section 3, we report and discuss the observed harmonic spectra obtained from various molecules. This is followed by results of the scaling of harmonic yield as a function of laser intensity in xenon, benzene and cyclohexane. We show how this is influenced by molecular dissociation and how, if the laser pulse duration is sufficiently short, this effect can be suppressed in most molecules. For naphthalene, however, the behaviour shows a dramatic clamping of harmonic yield at higher laser intensities that we tentatively attribute to the rapid field ionisation of this molecule followed by fast and extensive Coulomb explosion. In Section 4, we present results and a discussion about the ellipticity dependence of HHG in several molecular systems. Finally, our results are summarised and we present our conclusions in Section 5.

2 Experimental

The experimental set-up, shown in Figure 1, was based on a system used for previous experiments in the butane and butadiene molecules [8]. The high-order harmonic generation process was pumped by a Ti:sapphire chirped pulse amplification (CPA) laser system producing a 10-Hz train of near infrared laser pulses with energy up to 40 mJ and full-width at half-maximum duration of either 240 fs or 70 fs. The laser pulses from this system were focused into a small vacuum chamber containing a gas jet produced by a pulsed solenoid valve. The generated harmonic radiation was spectrally resolved by a vacuum ultraviolet (VUV) spectrometer and detected with an electron multiplier.

Two configurations of our Ti:sapphire CPA laser system were used in these experiments. 240 fs, 780 nm pulses were produced by the configuration described in [21]. The system was then adapted to generate 70 fs, 795 nm pulses by installing a new oscillator, pulse stretcher and pulse compressor [22]. In both configurations, the pulse compressor was optimised to minimise pre-pulse on the timescale of the main pulse. A Pockels cell/polariser pair was configured to attenuate pre-pulses on the nanosecond timescale produced by the regenerative amplification stage. The pulse energy was measured by a calibrated photodiode. A second order single-shot autocorrelator measured the pulse duration (assuming a sech^2 pulse shape). After attenuation of the beam, the intensity distribution in the focal spot was measured using a microscope objective mounted on a charge-coupled device (CCD) camera.

For 240 fs pulses, the measurements of pulse energy, pulse duration and focal intensity distribution were used to calculate the peak intensity in the laser focus. We estimate the error in this measurement to be a factor of 5. We reduced the error to a factor of 2 for the experiments using 70 fs pulses by deriving the peak intensity from ion spectroscopic measurements of the pulse energies required to multiply ionise several noble gases. By carefully maintaining a fixed experimental arrangement, for a given pulse duration the relative error in peak intensity between experiments was less than 25%. This was proven by the very good agreement between the results of identical experiments carried out on successive days.

The intensity in the laser focus was varied by an electronically controlled $\lambda/2$ waveplate combined with a fused silica cube polariser which attenuated the pulses at the output of the regenerative amplifier. In this way, the intensity in the focus could be varied over more than two orders of magnitude. Where a constant intensity was required for an experiment the digitised, integrated signal from the diode monitoring the pulse energy at the experiment was passed to the data acquisition computer. This then accepted the corresponding harmonic signal as a valid datum or rejected it depending on whether the energy (intensity) was within a predefined range (typically ±5% of the mean value). This process, termed "energy binning" was essential because of the often highly nonlinear scaling of harmonic signal with laser energy. Where the harmonic signal was examined as a function of intensity, the same technique was used except that many adjacent energy bins (ranges) were defined and the harmonic signal was allocated to the appropriate bin rather than discarded. Typically, the bins were evenly spaced on a logarithmic scale to optimise the signal to noise ratio over a large range of laser intensities.

To study the dependence of HHG upon ellipticity, a zero-order quartz waveplate (CVI, QWPO-800-10-4) was placed in the linearly polarised beam. By rotating the waveplate, the ellipticity was varied continuously from 0 (linear) to 1 (circular) with polarisation purity >99.5%.

The gas jet was produced by a heated pulsed valve mounted on top of a small vacuum chamber connected to a VUV monochromator. The laser pulses were focused by a quartz lens into the molecular jet 3 mm below the nozzle throat, providing an interaction length of ~6 mm. The plasma emission from the interaction region was imaged onto a CCD camera (Pulnix TM500). The heated pulsed solenoid valve described in [9] was used to generate gas jets of cyclopropane (C_3H_6), the room temperature liquids benzene (C_6H_6), cyclohexane (C_6H_{12}) and *n*-hexane (C_6H_{14}) and the room temperature solid naphthalene ($C_{10}H_8$). To compare the efficiencies of the harmonics in the organic compounds with those generated in xenon, we ensured that the target gas density in the interaction region was the same for all the species studied. A gas backing pressure of 220 torr of xenon implied a density of 3×10^{17} atoms cm^{-3} in the laser focus. For all the species studied, the ratio γ of the specific heat capacity at constant pressure to that at constant volume is around 1.6 times lower than that of xenon. Therefore, to produce the same density of molecules in the interaction region, the backing pressure used for both compounds had to be 3 times greater than xenon, *i.e.* 660 torr. A sonic expansion into perfect vacuum with an expansion half-angle of 45° was assumed for the calculation. The density in the gas jet was chosen to avoid defocusing of the fundamental beam in the jet and to minimise the risk of an accidental release of organic vapour to the atmosphere by keeping the required valve backing pressure below atmospheric pressure. The backing pressure of naphthalene was limited to 300 torr by the maximum safe operating temperature of the heated pulsed valve.

The harmonics generated in the laser focus were resolved by a 1 m normal incidence VUV monochromator (GCA McPherson 225) fitted with an aluminium coated 600 lines mm^{-1} grating. The harmonics were detected using an electron multiplier tube (EMT, Thorn EMI 143) operated at 2.5 kV and positioned behind the exit-slit in the image plane of the monochromator. A stepper-motor was fitted to the wavelength selection dial to rotate the grating and select the wavelength. A boxcar gated integrator (Stanford Research SR 250) integrated the signal output from the electron multiplier and from a laser pulse energy monitor diode (Thorlabs DET200). The data were digitised and transferred to a PC *via* an RS-232 serial link. Data acquisition software running on the PC was configured to perform signal averaging and laser energy binning as required. The data acquisition software also controlled the monochromator wavelength *via* a stepper-motor interface.

3 High harmonic spectra and intensity dependences

3.1 High harmonic spectra

Harmonic spectra from order $q = 7$ to 15 were measured for benzene, cyclohexane, cyclopropane, *n*-hexane, naphthalene and xenon irradiated with 70 fs, 795 nm pulses at 1×10^{15} W cm^{-2}. Figure 2 shows the results for all these species except benzene and cyclohexane, which have been published previously [23]. A xenon spectrum was recorded as a reference immediately prior to each of the molecular spectra so that, for a given harmonic order, direct comparisons between the responses of the species could be made. In the case of naphthalene, the density is a factor of two below that of xenon, as higher values could only be achieved by heating the pulsed gas valve to a temperature well above the limit allowed for the device. The data

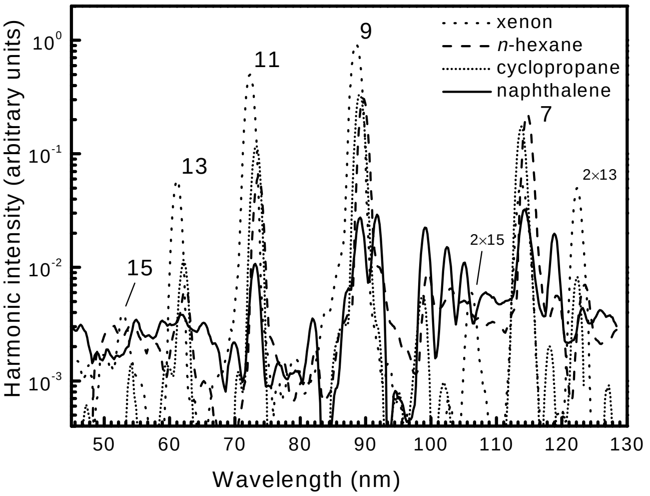


Fig. 2. Harmonic spectra for xenon, *n*-hexane, cyclopropane and naphthalene produced by 70 fs, 795 nm laser pulses focused to a peak intensity of 1×10^{15} W cm^{-2}. The density in the interaction region is $\sim 3 \times 10^{17}$ molecules cm^{-3} except for naphthalene where the density is $\sim 1.5 \times 10^{17}$ molecules cm^{-3}. Harmonics of the 7th to the 15th order are detected. Small peaks from second-order diffraction of the 13th and 15th harmonics can also be seen.

are not corrected for the spectral response of the detection system, so the relative intensities of different order harmonic peaks can not be compared.

Each spectrum consists of 450 points, with each recorded point averaged over 25 laser pulses. Only pulses having energy within ±7% of the chosen energy were permitted to contribute to the mean value. 5-point adjacent average smoothing was applied to all spectra to reduce the noise level. The width of the peaks in the recorded spectra was limited by the instrumental resolution to 1.5 nm.

Peaks corresponding to harmonic order $q = 7$ to 15 are labelled in the spectra. Second order diffraction peaks are also present for $q = 13$ and 15. In addition, there are several peaks present in the molecular spectra from 70 nm to 127 nm which do not correspond to harmonics. We have assigned the extra peaks to plasma recombination emission lines from neutral, singly and double charged hydrogen and carbon atoms. The intensity of these peaks was found to increase with the size of the molecule, with maximum intensity in the case of naphthalene. We measured the dependence of the corresponding signal with laser intensity in the range $1\text{–}5 \times 10^{15}$ W cm^{-2} and found that it follows a cubic dependence.

The 15th harmonic could be detected in xenon and cyclopropane only. The other molecules only yielded detectable harmonics up to the 13th. The intensities of the harmonics generated in the organic molecules are comparable to those of xenon atoms. Table 1 gives a summary of the harmonic intensities relative to the corresponding xenon harmonic. The 7th harmonic generated in all the organic molecules of this study was stronger than the corresponding xenon harmonic, with cyclohexane and *n*-hexane being the most efficient. Higher orders from the organic molecules gave lower yields than from xenon.

Table 1. Harmonic intensity of the organic systems relative to xenon measured at 1×10^{15} W cm^{-2}. The density in the interaction region is $\sim 3 \times 10^{17}$ molecules cm^{-3} except for naphthalene where the density is $\sim 1.5 \times 10^{17}$ molecules cm^{-3}.

Harmonic order $nh\nu$ (eV)	7th 10.91	9th 14.03	11th 17.15	13th 20.27
xenon	1	1	1	1
cyclopropane	3.3	0.38	0.23	0.20
n-hexane	4.5	0.38	0.12	0.13
cyclohexane	4.2	0.06	0.03	0.07
benzene	2.5	0.24	0.18	0.11
naphthalene[(a)]	0.66	0.03	0.02	0.07

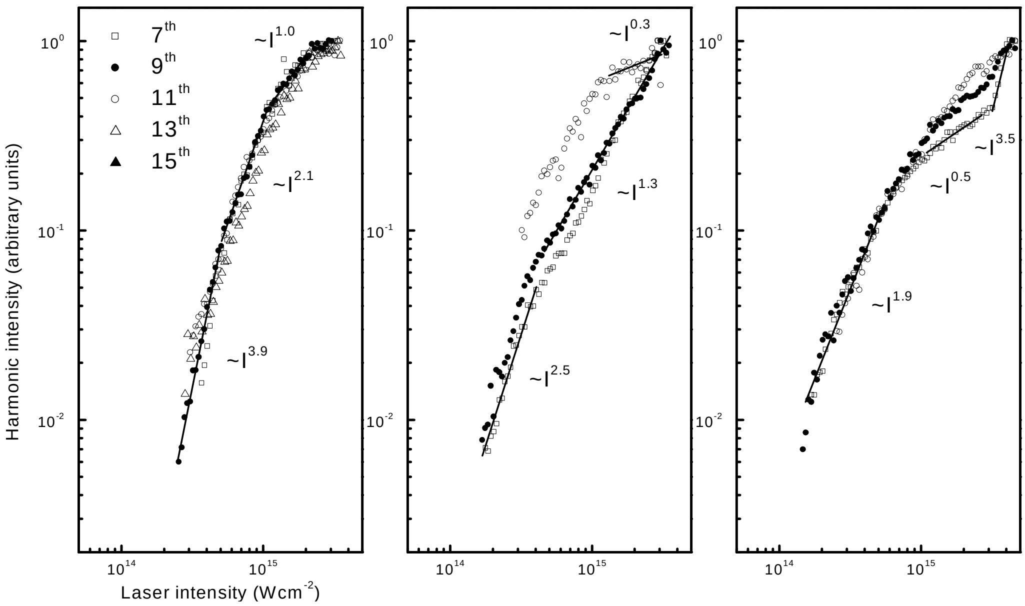
[(a)] Quoted values were obtained for naphthalene pressure a factor of two lower than the one used for the other molecules. For direct comparison with the other organics and with xenon, these values have to be multiplied by a factor of 4 to take into account the quadratic pressure dependence.

3.2 Intensity dependences

We investigated the dependence of HHG in benzene, cyclohexane, *n*-hexane, naphthalene, cyclopropane and xenon upon the intensity of the driving laser. This was done by setting the monochromator to the desired harmonic wavelength and varying the laser energy. Each intensity dependence, consisting of data from around 6 000 laser pulses, was plotted on a log-log graph of harmonic intensity against laser intensity.

As the spectral response of the detection system was not calibrated, the relative yield of the harmonic orders is unknown and so their relative position on the harmonic intensity (vertical) axis is arbitrary. The data of harmonic intensity *versus* laser intensity are scaled for each order by normalising to the maximum harmonic intensity. This facilitates comparison of intensity dependences without resulting in a loss of information about the relative harmonic yields, because this information is contained in the harmonic spectra (see Fig. 2). The observed dependences were fitted by power laws.

Figure 3 shows intensity dependences for harmonics $q = 7$ to 15 in xenon, cyclohexane and benzene using 240 fs and 70 fs pulses. The behaviour observed for the three systems using 240 fs pulses (Figs. 3a–3c) is described in [9] and the comparison with 70 fs pulses is discussed in [23]. The intensity dependences of the xenon harmonics, which are identical across the observed intensity range, show an initial steep rise followed by saturation at intensities greater than $\sim 8 \times 10^{14}$ W cm^{-2}. This behaviour, typical of HHG in atoms, is also observed in benzene and cyclohexane at intensities less than $\sim 5 \times 10^{14}$ W cm^{-2}. However, at intensities above this, the behaviours of the molecules differ markedly from the atomic case. Notably, for some harmonic orders, there is no saturation of harmonic intensity at laser intensity up to 5×10^{15} W cm^{-2}. This anomalous behaviour arises from the ionisation and dissociation occurring during the laser pulse and dynamic resonances between electronic molecular states and harmonics.


(a) Xenon, 240 fs

(b) Cyclohexane, 240 fs

(c) Benzene, 240 fs

(d) Xenon, 70 fs

(e) Cyclohexane, 70 fs

(f) Benzene, 70 fs

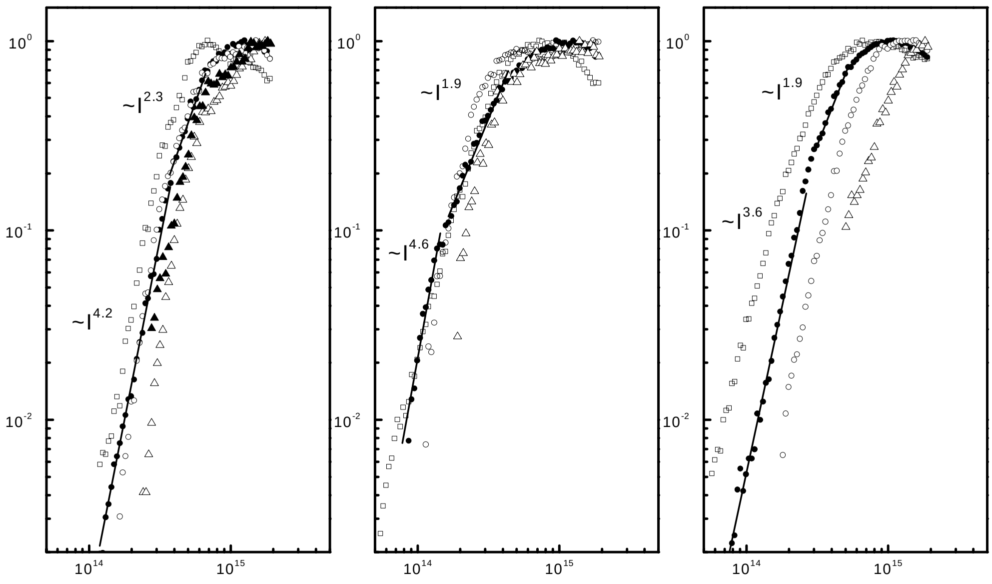


Fig. 3. Harmonic intensity as a function of laser intensity for (a) xenon, (b) cyclohexane and (c) benzene using 240 fs, 780 nm laser pulses in the intensity range 1.5×10^{14}–5×10^{15} W cm^{-2} and for (d) xenon, (e) cyclohexane and (f) benzene using 70 fs, 795 nm laser pulses in the intensity range 5×10^{13}–2×10^{15} W cm^{-2}. Harmonic orders $q = 7$ (□), 9 (●), 11 (○), 13 (△) and 15 (▲) are shown. Power-law fits are shown as solid lines. The density in the interaction region is $\sim 3 \times 10^{17}$ molecules cm^{-3}. Each harmonic has been normalised as described in the text.

Figures 3d–3f depict the normalised dependences of the harmonic intensity upon laser intensity using 70 fs pulses for $q = 7$ to 13. As with 240 fs pulses, the xenon intensity dependences (Fig. 3d) exhibit behaviour characteristic of monatomic HHG. An initial rapid increase with laser intensity in the cut-off regime is followed by a reduced slope as the harmonics enter the plateau and a further reduced slope as ionisation saturates. Cyclohexane and benzene (Figs. 3e and 3f) show similar behaviour.

In contrast to the results obtained using 240 fs pulses, the intensity dependences of benzene and cyclohexane harmonics resemble those of monatomic species when shorter pulses are used. The harmonic intensity steadily saturates as the laser intensity is increased. The additional structure observed using 240 fs duration pulses is no longer present. All harmonic orders saturate. The anomalous behaviour of the molecular systems is no longer observed.

Figure 4 compares the normalised intensity dependences of naphthalene and benzene for harmonic orders $q = 7$ to 11 using pulses with a duration of 70 fs. The number density in the laser focus was $\sim 1 \times 10^{17}$ atoms cm^{-3} and $\sim 3 \times 10^{17}$ atoms cm^{-3} for naphthalene and benzene

Table 2. Properties of the hydrocarbons studied relative to xenon.

	IP$^{(a)}$ (eV)	$\alpha^{(b)}$ ($\times 10^{24}$ cm^3)	Geometry, $L^{(c)}$ ($\times 10^{-10}$ m)
xenon	12.13	4.04	Atom, 1.2
cyclopropane, C_3H_6	10.55$^{(d)}$	5.66	Cyclic, 3.5
n-hexane, C_6H_{14}	10.13	11.9	Linear, 5.6
cyclohexane, C_6H_{12}	9.86	11.0	Cyclic, 4.2
benzene, C_6H_6	9.24	10.0	Cyclic, 5.0
naphthalene, $C_{10}H_8$	8.14	16.5	Cyclic, 6.4

$^{(a)}$ Data taken from [24]. $^{(b)}$ α is the average electric dipole polarisability for ground state molecules. Data taken from [24]. $^{(c)}L$ is the estimated largest dimension in the molecule. Lengths of CC and CH bonds taken from [24]. $^{(d)}$ Data taken from [25].

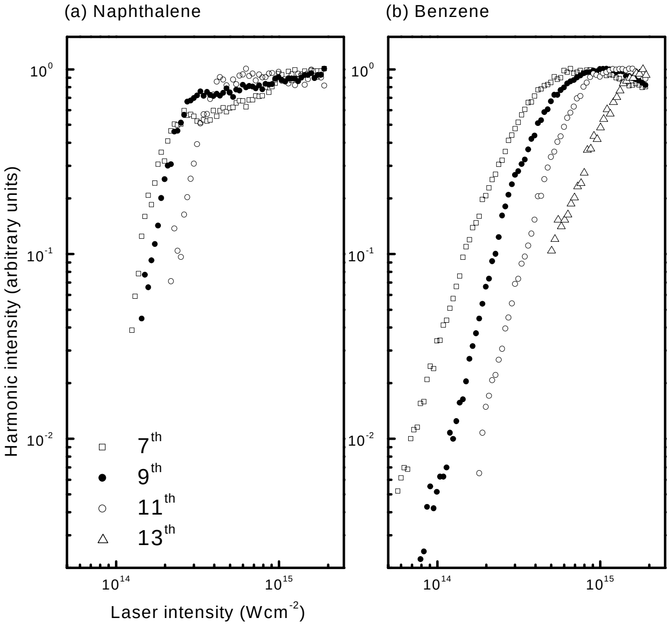


Fig. 4. Harmonic intensity as a function of laser intensity for (a) naphthalene and (b) benzene using 70 fs, 795 nm laser pulses in the intensity range 5×10^{13}–2×10^{15} W cm^{-2}. Harmonic orders $q = 7$ (□), 9 (●), 11 (○) and 13 (△) are shown. The density in the interaction region is $\sim 3 \times 10^{17}$ molecules cm^{-3} for benzene and $\sim 1.5 \times 10^{17}$ molecules cm^{-3} for naphthalene. Each harmonic has been normalised as described in the text.

respectively. The benzene data are the same as those shown in Figure 3. In contrast to benzene and the other smaller organic molecules, the onset of saturation of harmonic intensity with increasing pump intensity is very sudden in naphthalene. After the onset of saturation, the intensity of all three harmonic orders is almost independent of pump intensity up to 2×10^{15} W cm^{-2}.

3.3 Discussion

Differences in efficiencies for harmonic generation between molecules are observed and these can be related to the differences in molecular properties, molecular electronic structure and behaviour regarding ionisation and fragmentation taking place during the interaction with the laser pulse. Table 2 summarises some of the relevant chemical physical properties of the organic compounds used in this study and compares them with the properties of xenon.

Ionisation potential and molecular polarisability are two important factors which influence the laser-molecule interaction. However, several authors have found that they are not the dominant predictors for either ionisation probability [26] or HHG efficiency [6,7] in molecular systems. Table 2 also displays an estimation of the size of the molecules; the values given are in good agreement with the dimensions of the largest electronic molecular orbitals [27–31]. From the properties listed in the table, we note that cyclopropane is the molecular system that displays the highest similarity to xenon atoms.

The electronic molecular structures of the systems studied are significantly different. Benzene and naphthalene are aromatic hydrocarbons with highly conjugated bonding. These give rise to π-π^* transitions on which abundant Rydberg transitions overlap. Photon absorption for these molecules starts at energies above around 5 eV [24,32,33]. The alkanes cyclopropane, cyclohexane and n-hexane have no conjugated orbitals because the molecules consist exclusively of strongly localised σ-bonds. In these molecules, transitions of Rydberg type are greatly suppressed; valence transitions give account of the absorption spectrum that starts in the region of photon energies around 7 eV [34,35]. In previous works [9,23], we have addressed the effect of resonances between harmonic frequencies and molecular energy states on the efficiency for HHG. Resonances are possible from the 3rd harmonic of the fundamental laser frequency for the aromatics and from the 5th for the alkanes.

Several authors [17–20,26–31,36] have studied the photoionisation and dissociation of organic molecules induced by intense laser fields. Relative ionisation probability has been found to increase with the size of the delocalised π molecular orbitals [16,36]. σ-bonded systems, featuring strong electron localisation, ionise less efficiently than the aromatics but present a higher dissociation yield [19,20] which increases exponentially with the number of atoms of the molecule [27]. On the other hand, dissociation is significantly reduced by shortening the duration of the intense laser pulse [19,20].

As discussed in [9], the short wavelength response of our detection system imposes a limit for the experimental determination of the cut-off for harmonic generation in the atom and molecules studied here. This cut-off can be calculated through the $I_P + 3U_P$ rule. However, there is a maximum laser intensity to which a neutral atom may be exposed before it ionises. This maximum intensity is set by the barrier suppression ionisation (BSI) limit [37] which gives a maximum intensity of 9×10^{13} W cm^{-2} for xenon. A xenon atom exposed to this intensity will ionise within a single optical cycle. Harmonics up to $q = 17$ could be generated in xenon at this intensity. Below this value, ionisation can proceed through multiphoton and tunnelling ionisation. The laser intensity that saturates the ionisation in xenon can be calculated considering tunnel ionisation, modelled by the Ammosov, Delone and Krainov (ADK) rates [38]. For 70 fs pulses, the saturation intensity for Xe^+ is $\sim 6 \times 10^{13}$ W cm^{-2}. The corresponding cut-off occurs at $q = 13$. The fact that harmonics up to $q = 15$ are observed at peak intensities up to 5×10^{15} W cm^{-2} is due to emission during the rising edge of the laser pulse before ionisation has saturated and also from the wings of the focus where ionisation does not reach saturation [39]. The highest harmonic observed in cyclopropane is also $q = 15$. With the exception of the 7th harmonic, this molecule also displays a distribution of intensity in the harmonic spectra similar to xenon. Considering the properties listed in Table 1, cyclopropane is, among the organic molecules of this study, the closest to xenon. This could explain the nearly atom-like behaviour of HHG observed in this molecule. DeWitt and Levis [27–31] have developed a model to predict the transition from multiphoton ionisation to tunnel ionisation in large polyatomic molecules. They have found that the transition occurs at much lower laser electric field strengths for molecules with extended electronic orbitals than for atoms of similar ionisation potential. According to this model, saturation of the ionisation in these organic systems will occur at lower laser intensities than for xenon and cyclopropane. This explains the fact that the highest order harmonics observed in the organic systems, other than cyclopropane, are one harmonic order lower. In addition, the cut-off occurred in all cases at lower orders than predicted by the $I_P + 3U_P$ rule, suggesting that the molecules were being ionised before the peak of the pulse was reached.

The generation of high-order harmonics is determined by both the microscopic (single atom or molecule) and macroscopic (propagation) properties of the nonlinear medium. By changing the density of the medium, we vary the propagation properties without altering the single molecule interaction (assuming that the molecules of the medium are non-interacting). If some property of the harmonic radiation remains unchanged as the density is changed, we can conclude that this property is determined solely by the single molecule interaction.

By varying the backing pressure on the pulsed valve in the range 100–1 000 torr, we selected cyclopropane number densities in the laser focus in the range $\sim$0.5–5×10^{17} atoms cm^{-3}. Figures 5a–5c show the dependence of harmonic intensity upon pump intensity for $q = 7$ to 13 in cyclopropane for three different number densities in the laser focus. The intensity dependences in cyclopropane are similar to those observed in the other organic molecules using 70 fs pulses. As in the atomic case, the initially rapid increase in harmonic intensity with pump intensity saturates as the number of harmonic emitters is depleted by ionisation. The intensity dependences are the same for all densities, indicating that the intensity dependences are determined by the microscopic interaction with individual organic molecules and not by propagation of the pump and harmonic radiation through the nonlinear medium.

Although the dependence of the harmonic intensity upon the pump intensity is independent of density, the density affects the absolute intensity of the harmonic radiation because the number of harmonic emitters is proportional to the density. This effect is not observable in Figures 5a–5c because the intensity data is normalised. The intensity of the 7th harmonic in cyclopropane is shown as a function of number density in Figure 5d for constant pump intensity. A least squares fit finds that the harmonic intensity is proportional to number density squared, indicating that phase matching is independent of density and propagation effects can be neglected in our discussion of intensity dependences.

The intensity dependence as a function of pulse duration reveals a strong qualitative difference between the cases of 240 fs and 70 fs pulses. Contributions to dispersion and susceptibility arising from effects such as molecular resonances were suggested to explain the irregularities in the 240 fs results [9] but these are not strongly dependent upon pulse duration and therefore can not satisfactorily explain the change in behaviour at 70 fs. The similarity in the form of the intensity dependence curves for the molecules and xenon using 70 fs pulses is strong evidence that any influence of fragmentation and dissociation on the 240 fs molecular data is significantly suppressed for the shorter pulses. This is consistent with the timescales expected for the dissociation of molecules in a strong field (providing photoionisation is not so severe that Coulomb explosion becomes very rapid compared to the laser pulse duration). Typically, this should be in the 10–200 fs range (depending upon the fragment masses). We infer that for the 240 fs data, extensive fragmentation of the parent molecule has occurred during the laser pulse and a substantial component of the harmonic yield arises from the molecular fragments. This can lead to the lack of a clear roll-off and saturation since the appearance of dissociation products can give rise to a higher yield than from the parent alone. In contrast, for the 70 fs data there is insufficient time for significant fragmentation and the harmonics observed are those arising predominately from the parent molecule [23].

We regard this as an important finding that supports the notion that study of HHG from molecules can yield important information about the electron dynamics in the parent molecule when it is exposed to a strong field. The dissociation of the target molecules should not be ignored and can be very important in some molecular systems or if longer laser pulses are used. In that case, due to the variety of species that might be acting as harmonic emitters in the sample (including the parent molecule, various fragments,

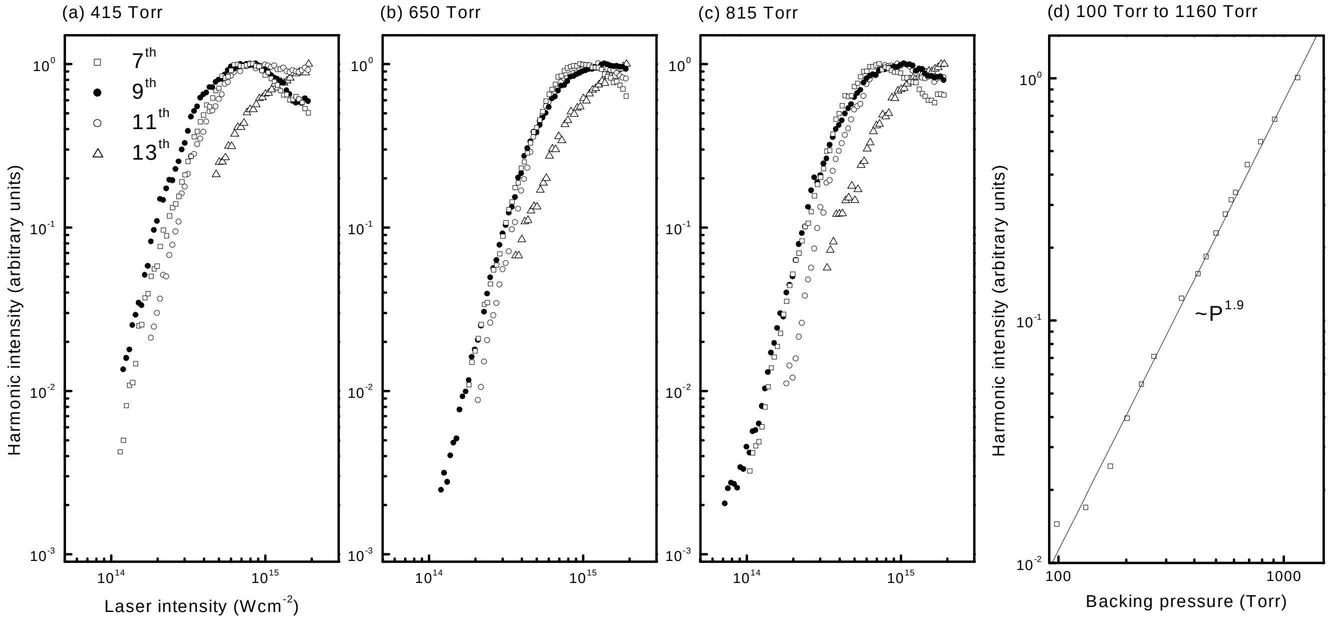


Fig. 5. Intensity of harmonics generated in cyclopropane using 70 fs, 795 nm laser pulses as a function of laser intensity at three pulsed valve backing pressures (a) 415 torr, (b) 650 torr and (c) 815 torr and (d) as a function of backing pressure at a fixed intensity of 1×10^{15} W cm^{-2}. Harmonic orders $q = 7$ (□), 9 (●), 11 (○) and 13 (△) are shown. Each harmonic has been normalised as described in the text.

atoms and ions), the behaviour of the harmonics can provide no clear information about the electron dynamics in a single species. By using an ultra-short pulse, however, the situation where a single species is largely responsible for all the harmonic emission is ensured, and this will permit unambiguous studies to be carried out (see ellipticity dependence discussed in Sect. 4).

Naphthalene showed a significantly different behaviour to the other molecules studied. There is a very strong clamping of the harmonic yield above intensities of 2×10^{14} W cm^{-2}, rather than a smooth roll-over to saturation. This is not in contradiction to the hypothesis presented above (*i.e.* molecules in sufficiently short pulses display similar behaviour to xenon) if the fragmentation time-scale of naphthalene is very fast (<70 fs). It is important to note that because naphthalene is a relatively large molecule, the transition to strong tunnelling ionisation is made at intensities significantly below those for smaller species simply due to the larger potential across the molecule when it is placed in a strong field. As mentioned above, this is invoked to explain the electron spectra results of DeWitt and Levis [16]. We believe that as a result, naphthalene experiences more extensive photoionisation than the smaller molecules studied. The molecule will become highly ionised with more than one electron removed (on average) from each atom and so Coulomb explosion, which will be rapid, will lead to the extensive fragmentation of the molecule into ions. Under these conditions, further harmonic generation will not occur.

4 Ellipticity dependence

HHG is very sensitive to the polarisation of the pump laser beam, showing a rapid decrease in efficiency as ellipticity increases. This is intuitively understood in the context of the recollision model where the probability of rescatter diminishes when the electron wavepacket travels in a trajectory that does not intercept the ion core. Experimentally, this has been observed both in atoms [40] and in molecules [9]. It has been pointed out that due to the relatively weak dependence of phase-matching on field polarisation, the ellipticity dependence of HHG is a sensitive probe of the single-atom (molecule) response to the intense field [40]. In a previous publication [9], we reported a faster drop for higher order harmonics. Here we intend to gain further insight into the effect of ellipticity on HHG by studying its dependence on laser intensity and on the target species. Since our work with 240 fs pulses [9], we have reduced the pulse duration to 70 fs and have improved the signal to noise ratio. We can infer from the results presented in Section 3 that with 70 fs pulses it is the ellipticity dependence of HHG from the parent molecular ion (rather than from fragments) that is being studied.

We have investigated the ellipticity dependence of 9th harmonic generation in xenon, benzene and n-hexane. Experimentally, this work consisted of recording intensity dependences as described above for a range of ellipticity values from linear to circular polarisation. The ellipticity of the laser beam was modified using a $\lambda/4$ waveplate placed in the beam path. As expected, the highest harmonic yield in xenon is produced with the highest intensity, lowest ellipticity laser fields. No striking changes in the ellipticity dependence were detected over an intensity range from 2.5×10^{14} to 2×10^{15} W cm^{-2}.

The main question examined was whether different species show different ellipticity dependences. This was confirmed in the experiments and can be seen in Figure 6, where 9th harmonic generation is plotted as a function

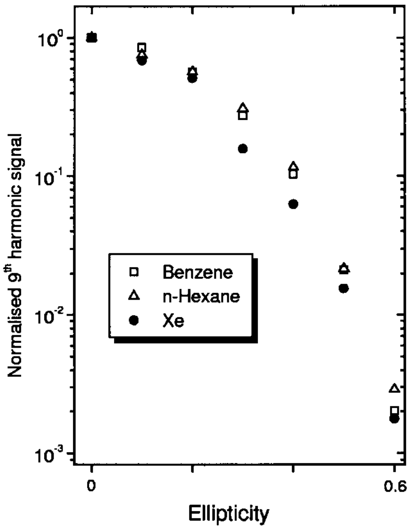


Fig. 6. Dependence of harmonic intensity upon laser polarisation ellipticity for benzene, *n*-hexane and xenon using 70 fs, 795 nm laser pulses. The results are averaged over the intensity range 6×10^{14}–9×10^{14} W cm^{-2}.

of ellipticity for xenon, benzene and *n*-hexane. For clarity of presentation, the 9th harmonic emission signals were normalised so as to make them unity for linear polarisation. Each data point in the graph was calculated as the average of the relative emission for 20 intensities in the range 5.9×10^{14} to 9.3×10^{14} W cm^{-2}. Figure 6 shows clearly that both benzene and *n*-hexane produced a relatively stronger 9th harmonic emission for intermediate values of ellipticity than the noble gas xenon used as a reference. The effect is clear from values of the ellipticity from 0.2 to 0.5 ($I_\perp/I_{||} = 0.04$ to 0.25), since the signal to noise ratio becomes unfavourable for higher values. In that range, the relative emission in the organics approximately doubles that of xenon.

In contrast, earlier measurements with longer pulses [9] revealed that the ellipticity dependence for molecules was similar to atoms, or even that there was less HHG from molecules at higher ellipticity than in the atomic system. The signal to noise ratio of the earlier data was inferior to the present study. The longer pulse duration employed meant that significant fragmentation of the molecule would have taken place, leading to HHG from significantly smaller (even atomic) size fragments being important.

The fact that the two organic molecules favour HHG for relatively high ellipticity when compared to xenon, is an indication that the effective cross-section for rescattering is larger in molecules. Therefore, we tentatively suggest that the phenomenon of electron recollision in molecules is not atom-selective. As we mentioned before, molecules introduce the possibility of an electron recolliding with an ion core other than its parent. For atoms, the spreading of the electron wavepacket as it propagates in the laser field leads to some rescattering probability with the core (and hence harmonic emission) even if the field is elliptically polarised. In a molecular system, a similar degree of wave-packet spreading is anticipated [41]. Thus, we expect the returning electronic wavepacket to have a finite probability of interaction both with its parent atom and with neighbouring atoms even in the case of elliptical polarisation. If the electron recollision with atoms other than the parent leads to final states of the molecule indistinguishable from the initial state then there is a contribution to the harmonic emission. Additional pathways for this to happen can exist in the molecular case, *e.g.* the electron may recombine either with its parent ion or an ionised neighbour. Therefore, in the case of elliptical polarisation extra channels leading to harmonic emission exist in the molecular case compared to the atomic case. Consequently, molecules are expected to show a larger effective rescattering cross-section and be thus less sensitive to deviations from linear polarisation. A detailed theoretical treatment of this system, however, remains to be carried out and we hope that our results stimulate further efforts towards this goal.

Another question concerns the possible anisotropy of the gas target. The initially randomly oriented molecules could suffer an alignment effect because of the torque exerted on them by the polarised laser beam. If this occurred during the laser pulse, we could expect that the orientational distribution of the harmonic generating molecules could be different for linear than for circular polarisation. However, for laser pulses as short as 70 fs, and for relatively heavy molecules, it is generally recognised [42] that the effect upon rotation within the time duration of the pulse would be negligible. Therefore, we can consider that the experiment takes place in a regime where dynamic alignment does not play a role and where the observed emissions corresponds to an average for all possible orientations. We anticipate that results revealing more clearly the dependence of rescatter cross-sections and intensity dependence would be obtained in an experiment where the molecules were first aligned with a laser pulse prior to introducing the pump beam for HHG.

5 Summary and conclusions

We have studied high-order harmonic generation in the organic molecules cyclopropane, cyclohexane, *n*-hexane, benzene and naphthalene pumped by near-infrared laser pulses of 70 fs and 240 fs duration in the intensity range 5×10^{13} W cm^{-2} to 5×10^{15} W cm^{-2}. To investigate the microscopic interaction between single molecules and the laser field, we studied the harmonics generated as a function of the laser pulse duration, laser intensity and ellipticity of the laser polarisation. Varying the molecular number density in the laser interaction region allowed us to examine the influence of propagation effects and confirm that they did not obscure our studies of the single molecule interaction. All of our investigations were also conducted using xenon, to provide a reference and a comparison with harmonic generation in atomic species. Harmonic orders $q = 7$–15 were observed.

We found that for 70 fs pulses, the molecules remain essentially intact during the interaction, leading to atom-like high-order harmonic generation. With 240 fs pulse duration, the laser pulse is longer than the dissociation time of the molecules and so harmonics are additionally produced by the dissociation products. This is observed to increase the total harmonic yield at intensities up to 5×10^{15} W cm^{-2} by preventing the usual saturation of harmonic generation as the parent atoms ionise. An exception to this is the large naphthalene molecule, which undergoes enhanced field ionisation and subsequent Coulomb explosion that is sufficiently rapid to cause dissociation during the shorter, 70 fs laser pulse. The harmonic yield from all of the organic molecules is broadly similar to atomic xenon under identical conditions. Xenon produces consistently higher yields for the 9th to 15th harmonics but the 7th harmonic is up to four times more intense using the organic molecules. The dependence of harmonic intensity upon laser ellipticity using 70 fs pulses showed that the organic molecules were less sensitive than xenon to deviations from linear polarisation. This is consistent with the electron recollision model of high-order harmonic generation if the electron is considered to recollide with the molecule as a whole, which has a larger recollision cross-section than the atom.

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References

1. A. McPherson, G. Gibson, H. Jara, U. Johan, T.S. Luk, J.A. McIntyre, K. Boyer, C.K. Rhodes, J. Opt. Soc. Am. B **45**, 95 (1987).
2. M. Ferray, A. L'Huillier, X.F. Li, L.A. Lompre, G. Mainfray, C. Manus, J. Phys. B **21**, L31 (1988).
3. W. Theobald, R. Häßner, C. Wülker, R. Sauerbre, Phys. Rev. Lett. **77**, 298 (1996).
4. K.C. Kulander, B.W. Shore, Phys. Rev. Lett. **62**, 524 (1989).
5. P.B. Corkum, Phys. Rev. Lett. **71**, 1994 (1993).
6. Y. Liang, S. Augst, S.L. Chin, Y. Beaudoin, M. Chaker, J. Phys. B **27**, 5119 (1994).
7. C. Lyngå, A. L'Huillier, C.-G. Wahlström, J. Phys. B **29**, 3293 (1996).
8. D.J. Fraser, M.H.R. Hutchinson, J.P. Marangos, Y.L. Shao, J.W.G. Tisch, M. Castillejo, J. Phys. B **28**, L739 (1995).
9. N. Hay, M. Castillejo, R. de Nalda, E. Springate, K.J. Mendham, J.P. Marangos, Phys. Rev. A **61**, 053810 (2000).
10. M.Yu. Ivanov, P.B. Corkum, Phys. Rev. A **48**, 580 (1993).
11. T. Zuo, S. Chelkowski, A.D. Bandrauk, Phys. Rev. A **48**, 3837 (1993).
12. A.D. Bandrauk, H. Yu, Phys. Rev. A **59**, 539 (1999).
13. M. Plummer, J.F. McCann, J. Phys. B **30**, L401 (1997).
14. K. Codling, L.J. Fransinski, J. Phys. B **26**, 783 (1993).
15. L.J. Frasinski, K. Codling, P. Hatherly, J. Barr, I.N. Ross, W.T. Toner, Phys. Rev. Lett. **58**, 2424 (1987).
16. M.J. DeWitt, R.J. Levis, Phys. Rev. Lett. **81**, 5101 (1998).
17. K.W.D. Ledingham, D.J. Smith, R.P. Singhal, T. McCanny, P. Graham, H.S. Kilic, W.X. Peng, S.L. Wang, A.J. Langley, P.F. Taday, C. Kosmidis, J. Phys. Chem. A **102**, 3002 (1998).
18. K.W.D. Ledingham, R.P. Singhal, D.J. Smith, T. McCanny, P. Graham, H.S. Kilic, W.X. Peng, A.J. Langley, P.F. Taday, C. Kosmidis, J. Phys. Chem. A **103**, 2952 (1999).
19. M. Castillejo, S. Couris, E. Koudoumas, M. Martin, Chem. Phys. Lett. **289**, 303 (1998).
20. M. Castillejo, S. Couris, E. Koudoumas, M. Martin, Chem. Phys. Lett. **308**, 373 (1999).
21. D.J. Fraser, M.H.R. Hutchinson, J. Mod. Opt. **43**, 1055 (1996).
22. M.B. Mason, Ph.D. thesis, Imperial College, London, 2000 (unpublished).
23. N. Hay, R. de Nalda, T. Halfmann, K.J. Mendham, M.B. Mason, M. Castillejo, J.P. Marangos, Phys. Rev. A **62**, 041803 (2000).
24. *CRC Handbook of Chemistry and Physics* (CRC Press, Boca Raton FL, 1996).
25. M. Gingell, N.J. Mason, I.C. Walker, G. Marston, H. Zhao, M.R.F. Siggel, J. Phys. B **32**, 2729 (1999).
26. M.J. DeWitt, D.W. Peters, R.J. Levis, Chem. Phys. **218**, 211 (1997).
27. M.J. DeWitt, R.J. Levis, J. Chem. Phys. **108**, 7045 (1998).
28. M.J. DeWitt, R.J. Levis, J. Chem. Phys. **110**, 11368 (1999).
29. R.J. Levis, M.J. DeWitt, J. Phys. Chem. A **103**, 6493 (1999).
30. R. Billotto, R.J. Levis, J. Phys. Chem. A **103**, 8160 (1999).
31. B.S. Prall, M.J. DeWitt, R.J. Levis, J. Chem. Phys. **111**, 2865 (1999).
32. M.B. Robin, Can. J. Chem. **63**, 2032 (1985).
33. J.W. Raymonda, W.T. Simson, J. Chem. Phys. **47**, 430 (1967).
34. G. Herzberg, *Electronic spectra of polyatomic molecules* (Van Nostrand, New York, 1966).
35. E.E. Koch, A. Otto, Chem. Phys. Lett. **16**, 131 (1972).
36. M.J. DeWitt, R.J. Levis, J. Chem. Phys. **102**, 8670 (1995).
37. S. Augst, D.D. Meyerhofer, D. Strickland, S.L. Chin, Phys. Rev. Lett. **63**, 2212 (1989).
38. M.V. Ammosov, N.B. Delone, V.P. Krainov, Sov. Phys. JETP **64**, 1191 (1986).
39. J.W.G. Tisch, T. Ditmire, D.J. Fraser, N. Hay, M.B. Mason, E. Springate, J.P. Marangos, M.H.R. Hutchinson, J. Phys. B **30**, L709 (1997).
40. N.H. Burnett, C. Kan, P.B. Corkum, Phys. Rev. A **51**, R3418 (1995).
41. B. Gottlieb, A. Lohr, W. Becker, M. Kleber, Phys. Rev. A **54**, R1022 (1996).
42. S. Banerjee, G. Ravindra Kumar, D. Mathur, J. Phys. B **32**, 4277 (1999).