PHYSICAL REVIEW A, VOLUME 62, 041803(R)

Pulse-length dependence of high-order harmonic generation in dissociating cyclic organic molecules

N. Hay,[1,*] R. de Nalda,[2] T. Halfmann,[1] K. J. Mendham,[1] M. B. Mason,[1] M. Castillejo,[2] and J. P. Marangos[1]
[1]*The Blackett Laboratory, Imperial College of Science, Technology and Medicine, London SW7 2BZ, United Kingdom*
[2]*Instituto de Química Física Rocasolano, CSIC, Serrano 119, 28006 Madrid, Spain*

(Received 12 May 2000; published 18 September 2000)

We compare high-order harmonic generation in gas jets of benzene, cyclohexane, and xenon using ~800-nm laser pulses of 70 fs and 240 fs duration. The harmonic intensities of the 7th to 15th orders are studied as a function of laser intensity in the range 5×10^{13} to $5\times10^{15}\,\mathrm{W\,cm^{-2}}$. Using 240-fs pulses, the dependence of the harmonic intensity on the laser intensity of the organic molecules exhibits significant deviations from the behavior of atoms, and shows strong evidence for harmonic generation from molecular fragments as well as the parent molecule. When the pulse duration is reduced to 70 fs, the intensity dependences of the harmonics are similar to those of xenon. This is attributed to the significant reduction in dissociation occurring during the shorter pulse and suggests that high-order harmonic generation in the ultrafast regime will be important in the understanding of molecular electron dynamics in strong fields.

PACS number(s): 42.65.Ky, 42.50.Hz

I. INTRODUCTION

High-order harmonic generation (HHG) from an intense laser pulse is a widely studied source of short pulse [1], high brightness, coherent [2,3] electromagnetic radiation from the vacuum ultraviolet (VUV) to the x-ray range. The majority of experimental and theoretical studies to date have used monatomic gases as the nonlinear medium [4]. There now exists a good understanding of HHG in these species covering both the microscopic (single-atom) response and the macroscopic (propagation) aspects of the process. An intuitive understanding of HHG in the field ionization limit is provided by the semiclassical wave-packet recollision model [5]. Here, the dynamics are described in terms of an oscillating electron driven in a strong laser field periodically recolliding with the ion core to emit harmonic radiation. This simple model reproduces the maximum harmonic order (cutoff) observed experimentally, the energy of which is given by I_p+3U_p, where I_p is the field-free ionization potential and U_p is the ponderomotive energy.

Several studies of HHG in molecules have also been conducted. These have primarily examined diatomic molecules (e.g., H_2,N_2,O_2) [6,7] and a few other small species (N_2O, CO_2, CH_4) [8]. Very little work has investigated larger molecules. Fraser *et al.* [9] performed the first investigation of HHG in organic molecules. Lyngå *et al.* [8] studied SF_6 and C_3H_8. Theoretical work remains largely limited to diatomic molecules [10–12] and in particular the H_2^+ molecular ion, which is the simplest system to exhibit molecular bonding.

The experimental studies generally find the behavior of small molecules to be similar to that of atoms. However, Lyngå noted a discrepancy when using SF_6 and Fraser *et al.* observed some dependence upon the type of bonding present in the molecular species. Stronger deviations from atomlike behavior were observed in benzene and cyclohexane [13].

Molecules introduce new degrees of freedom to the laser-matter interaction compared with atoms. Vibrational and rotational excitation become possible, and dissociation may occur. In addition, the possibility exists for an electron driven in the laser field to emit a harmonic photon during a collision with an ion core other than its parent. If the electron is delocalized, then the concept of a parent ion becomes increasingly inappropriate as the extent of the delocalization is increased. The consequences of this are poorly understood and the applicability of the recollision model [13] to molecular systems is uncertain.

Ion fragments produced by the interaction of ultrashort pulse, high-intensity lasers with molecules have been studied by time-of-flight spectroscopy. This reveals the final dissociation and ionization channels of the molecules but yields less information about the fragmentation dynamics during the interaction with the laser pulse. The results of these experiments complement and aid interpretation of the HHG results. Again, the majority of the molecular species studied by this technique have been diatomic [14] or triatomic [15]. Recently, however, several groups have investigated a range of organic molecules using laser pulse durations from ~200 to ~50 fs [16–18] in the intensity range $\sim10^{12}$ to $\sim10^{15}\,\mathrm{W\,cm^{-2}}$.

Some organic molecules are remarkably stable under high-intensity irradiation. Benzene, for example, remains essentially intact when irradiated by 50-fs, 800-nm pulses with intensities up to $\sim10^{14}\,\mathrm{W\,cm^{-2}}$ [16]. The duration of the laser pulse is a critical parameter in fragmentation processes, as it has been observed that ionization dominates with respect to dissociation as the pulse duration decreases [19].

In a previous paper, we have reported HHG from cyclic organic molecules using 240-fs pulses [13]. At intensities above $\sim10^{15}\,\mathrm{W\,cm^{-2}}$ the behavior of the organic molecules was markedly different from that of xenon under identical conditions. We also reported some preliminary results using 70-fs pulses. These were limited to intensities below 5

---

[*] Corresponding author. Email address: n.hay@ic.ac.uk

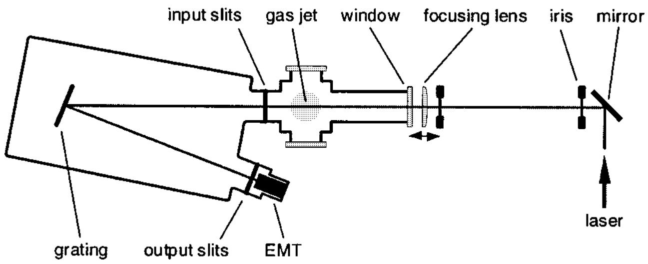

FIG. 1. Experimental setup showing laser, gas jet, interaction chamber, and monochromator.

$\times 10^{14}\,\mathrm{W\,cm^{-2}}$, precluding the investigation of the intensity regime in which the organic molecules exhibited anomalous behavior. A comparison of HHG using different pulse durations is necessary to investigate the influence of molecular dissociation on HHG. In particular, molecular dissociation has been proposed as a possible cause of the anomalous intensity-dependent behavior of HHG in benzene and cyclohexane [13].

We report experimental studies of the dependence of HHG upon the laser pulse duration in gas jets of the cyclic organic molecules benzene (C_6H_6) and cyclohexane (C_6H_{12}). The noble gas xenon was also studied, allowing us to compare our results with the literature concerning HHG in monatomic gases. Pulses of duration 70 and 240 fs in the intensity range 5×10^{13}–$2\times 10^{15}\,\mathrm{W\,cm^{-2}}$ and 1×10^{14}–$5\times 10^{15}\,\mathrm{W\,cm^{-2}}$, respectively, were produced by a Ti:sapphire chirped pulse amplification (CPA) laser system with a central wavelength of ~800 nm [20,21].

II. EXPERIMENT

The experimental setup has been described previously [13] and a short summary is given here (Fig. 1). Pulses from the Ti:sapphire CPA laser system are focused by a planoconvex fused silica lens through a fused silica optical window into a small vacuum chamber. A pulsed gas valve mounted above the laser focus produces a gas jet with which the laser interacts. The center of the laser focus is 3 mm below the nozzle throat, giving an interaction length of ~6 mm. Harmonics produced in the gas jet are detected by a normal incidence vacuum ultraviolet scanning monochromator (GCA McPherson 225).

Two configurations of our Ti:sapphire CPA laser system were used in these experiments. 240-fs full width at half maximum pulses were produced by the configuration described in [13]. The system was then adapted to generate 70-fs pulses by installing a new oscillator, pulse stretcher, and pulse compressor. The pulse duration was measured with a second-order single-shot autocorrelator (a sech^2 pulse shape was assumed). After attenuation of the beam, the intensity distribution in the focal spot was measured using a microscope objective mounted on a charge-coupled-device camera.

For 240-fs pulses, the peak intensity in the laser focus was calculated from measurements of pulse energy, pulse duration, and focal intensity distribution. We estimate the error in this measurement to be a factor of 5. The peak intensity of the 70-fs pulses was derived from ion spectroscopic measurements of the pulse energy thresholds required to multiply ionize several noble gases. We estimate the error in this case to be a factor of 2.

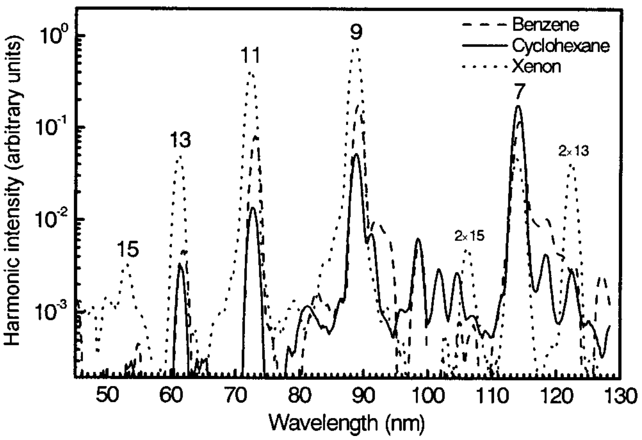

FIG. 2. Harmonic spectra for benzene (— — —), cyclohexane (——) and xenon (···) produced by 70-fs, 795-nm laser pulses focused to a peak intensity of $1\times 10^{15}\,\mathrm{W\,cm^{-2}}$. The density in the interaction region is $\sim 3\times 10^{17}$ molecules $\mathrm{cm^{-3}}$. Harmonics of the 7th to the 15th order are detected. Small peaks from second-order diffraction of the 13th and 15th harmonics can also be seen.

A heated pulsed gas valve system was used to generate gas jets of benzene and cyclohexane, which are liquids at room temperature. Details of this system are given in [13]. To compare the efficiency of harmonic generation in the organic compounds with xenon, we ensured that the target gas density in the interaction region was the same ($\sim 3\times 10^{17}$ atoms $\mathrm{cm^{-3}}$) for all the species studied.

III. RESULTS

Harmonic spectra from order $q=7$ to 15 were recorded for benzene, cyclohexane, and xenon irradiated with 240-fs, 780-nm pulses at $2\times 10^{15}\,\mathrm{W\,cm^{-2}}$ and 70-fs, 795-nm pulses at $1\times 10^{15}\,\mathrm{W\,cm^{-2}}$. The results obtained with 240-fs pulses have been published previously (Fig. 3 in [13]). Figure 2 shows the results obtained from 70-fs pulses. The spectra are not corrected for the spectral response of the detection system, preventing us from comparing the relative intensities of different harmonic orders in the spectra. However, a reference spectrum was recorded in xenon immediately prior to each of the molecular spectra to permit direct comparisons of the harmonic responses of the species. Peaks corresponding to $q=7$ to 15 are labeled. Second-order diffraction peaks are also present for $q=13$ and 15. In addition, there are several unlabeled peaks present in the molecular spectra from 98 to 127 nm. These are due to recombination emission from neutral and singly charged hydrogen and carbon.

The most striking feature of the spectra obtained using 240-fs pulses (Fig. 3 in [13]) is that the intensities of the harmonics generated in the organic molecules are comparable to those from xenon atoms. The 9th and 11th harmonics of the organic compounds are up to 50% as strong as those of xenon, and the 7th harmonic of cyclohexane is up to

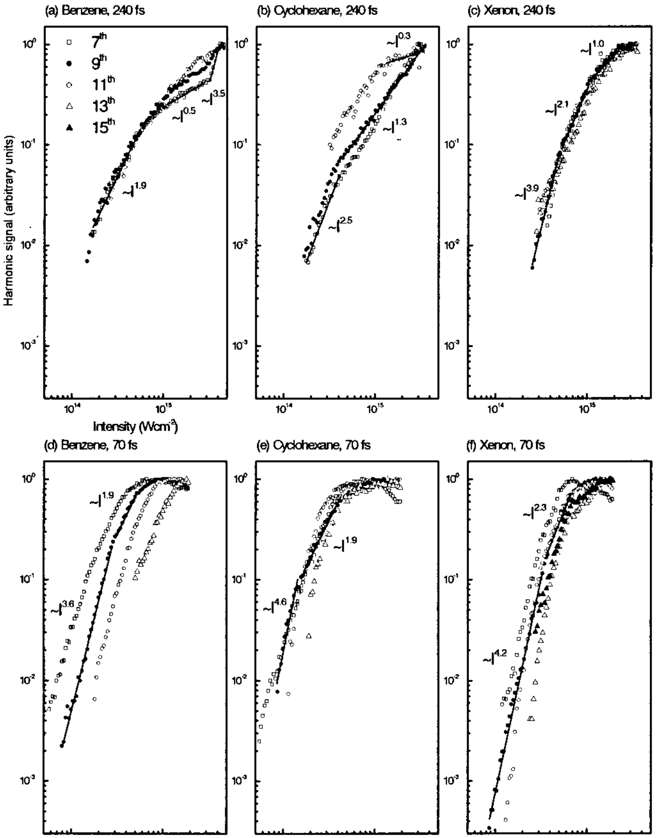

FIG. 3. Harmonic intensity as a function of laser intensity for (a) benzene, (b) cyclohexane, and (c) xenon using 240-fs, 780-nm laser pulses in the intensity range 1.5×10^{14}–$5\times10^{15}\,\mathrm{W\,cm^{-2}}$, and for (d) benzene, (e) cyclohexane, and (f) xenon using 70-fs, 795-nm laser pulses in the intensity range 5×10^{13}–$2\times10^{15}\,\mathrm{W\,cm^{-2}}$. 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 $\sim3\times10^{17}$ molecules $\mathrm{cm^{-3}}$. Each harmonic has been normalized as described in the text.

4 times stronger. No harmonics above $q=11$ are detected from either benzene or cyclohexane.

Similar results are obtained when the pulse duration is reduced to 70 fs (Fig. 2). The 13th harmonic is now detected from both organic molecules and the 15th harmonic is seen from xenon. As with the 240-fs pulse results, the harmonic spectra of benzene and cyclohexane follow a similar trend, having a higher yield for the 7th harmonic than xenon and somewhat lower yields at higher orders. Cyclohexane is generally less efficient than benzene, but again it has an exceptionally high yield at $q=7$, up to 4.5 times higher than the xenon yield. With 240-fs pulses, the harmonics generated in organic molecules were stronger relative to the xenon harmonics because the xenon harmonics had saturated due to ionization, whereas the organics harmonics had not.

We investigated the dependence of HHG in benzene, cyclohexane, and xenon upon the intensity of the driving laser by setting the monochromator to the desired harmonic wavelength and varying the laser energy. Figure 3 shows intensity dependences for harmonics $q=7$ to 15 in xenon, benzene, and cyclohexane using 240-fs and 70-fs pulses. As the detection system was not calibrated, the relative yield of the harmonic orders is unknown, and so their relative position on the vertical axis is arbitrary. The curves of harmonic intensity versus laser intensity are scaled for each order by normalizing 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 (Fig. 2). The observed dependences were fitted by power laws, as shown in Fig. 3.

The behavior observed for the three systems using 240-fs pulses [Figs. 3(a)–3(c)] has been described previously [13]. 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 $\sim8\times10^{14}\,\mathrm{W\,cm^{-2}}$. This behavior, typical of HHG in atoms, is also observed in benzene and cyclohexane at intensities less than $\sim5\times10^{14}\,\mathrm{W\,cm^{-2}}$. However, at intensities above this, the behaviors of the molecules differ markedly from the atomic case. Notably, for some harmonic orders, there is no saturation of harmonic intensity at a laser intensity up to $5\times10^{15}\,\mathrm{W\,cm^{-2}}$.

In contrast to the results obtained using 240-fs pulses, when shorter pulses are used the intensity dependences of benzene and cyclohexane harmonics resemble those of harmonics generated in monatomic species. 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 behavior of the molecular systems is no longer observed.

IV. DISCUSSION AND CONCLUSIONS

The variation of harmonic intensity with laser intensity is sensitive to the dynamical behavior of both the harmonic generation process in individual molecules and propagation of the harmonics and fundamental radiation in the gas jet. Using 240-fs pulses, we found that the dependence upon laser intensity of the harmonics generated in benzene and cyclohexane molecules deviated from the behavior expected of HHG in atoms [Figs. 3(a)–3(c)]. In xenon, typical atomic behavior was observed for all harmonic orders ($q=7-13$) at all intensities from $2\times10^{14}\,\mathrm{W\,cm^{-2}}$ to $4\times10^{15}\,\mathrm{W\,cm^{-2}}$. The harmonic intensity initially increased rapidly with laser intensity but then saturated [Fig. 3(c)].

Saturation of harmonic generation is caused by ionization of the nonlinear medium, which creates free electrons and reduces the number of neutral species available to generate harmonic radiation. Phase matching of the fundamental field with the harmonic field is determined by the dispersion of the neutral medium, the free-electron dispersion, and the Guoy phase shift [22] introduced by the focal geometry. For the medium density and focal conditions discussed here, phase matching is dominated by the Guoy phase shift (for average ionization $\leqslant1$), so the principal effect of ionization and cause of saturation is depletion of the neutral species.

We have previously suggested several effects that may contribute to the behavior observed in the organic molecules using 240-fs pulses [13]. Additional molecular resonances, dynamically modified in the laser field by the ac Stark effect, influence dispersion and susceptibility. Susceptibility may be reduced by ionization to a lesser extent in large organic molecules than in atoms. In addition to ionizing, a molecule can dissociate into neutral or ionic fragments. These fragments will coherently generate further harmonic radiation if they are produced during the laser pulse, potentially increasing the total harmonic yield.

When the laser pulse duration is decreased to 70 fs, the behaviors of benzene and cyclohexane become atomlike. The intensity dependences of the benzene and cyclohexane harmonics show the same general behavior as those of xenon, with initially rapid increases followed by saturation [Figs. 3(d) to 3(f)]. This contrasts with the absence of saturation observed in the case of the organic molecules when 240-fs pulses are used.

A consistent explanation for these observations is that reduced dissociation of the benzene and cyclohexane molecules during the laser pulse is responsible for the changes to HHG observed when the laser pulse duration is reduced from 240 to 70 fs. The contributions to dispersion and susceptibility arising from resonances are not modified appreciably by reducing the laser pulse duration and cannot produce the changes observed in the intensity dependences. However, reducing the pulse duration from ~200 to ~50 fs has been observed to reduce greatly the degree to which benzene and cyclohexane dissociate [19]. With 240-fs pulses, the absence of saturation is predominately due to harmonic generation in the dissociating parent molecule or in neutral or ionized fragments and the presence of additional resonance features in the molecule is less important.

Harmonic radiation is emitted by the interaction with ion cores of oscillating electrons driven by a strong laser field. By interpreting the high-order harmonics generated by a short pulse interacting with a molecular system, we are able to probe the electron dynamics of molecular systems in strong fields. We propose that using pulses short enough to prevent significant dissociation will enable HHG from molecules to offer a clearer picture of electron dynamics in these systems. In particular, these studies will provide insight into the applicability to various molecular systems of the wave-packet recollision model, which has been so successful for single atoms.

ACKNOWLEDGMENTS

We gratefully acknowledge the contributions of J. W. G. Tisch, J. P. Connerade, and M. H. R. Hutchinson and the technical assistance of P. Ruthven and A. Gregory. This work was supported by the UK EPSRC, by a British Council–Ministerio de Educacion y Cultura (MEC, Spain) Acción Integrada, and by EU-IHP (HPRN-CT-1999-000129). R de Nalda acknowledges MEC for financial support.

---

[1] J. W. G. Tisch, D. D. Meyerhofer, T. Ditmire, N. Hay, M. B. Mason, and M. H. R. Hutchinson, Phys. Rev. Lett. **80**, 1204 (1998).
[2] T. Ditmire, E. T. Gumbrell, R. A. Smith, J. W. G. Tisch, D. D. Meyerhofer, and M. H. R. Hutchinson, Phys. Rev. Lett. **77**, 4756 (1996).
[3] L. Le Déroff, P. Salières, B. Carré, D. Joyeux, and D. Phalippou, Phys. Rev. A **61**, 043802 (2000).
[4] A. L'Huillier, L. A. Lompré, G. Mainfray, and C. Manus, in *Atoms in Intense Laser Fields*, edited by M. Gavrila (Academic Press, Boston, 1992), pp. 139–202.
[5] P. B. Corkum, Phys. Rev. Lett. **71**, 1994 (1993).
[6] Y. Liang, S. Augst, S. L. Chin, Y. Beaudoin, and M. Chaker, J. Phys. B **27**, 5119 (1994).
[7] Y. Liang, A. Talebpour, C. Y. Chien, S. Augst, and S. L. Chin, J. Phys. B **30**, 1369 (1997).
[8] C. Lyngå, A. L'Huillier, and C.-G. Wahlström, J. Phys. B **29**, 3293 (1996).
[9] D. J. Fraser, M. H. R. Hutchinson, J. P. Marangos, Y. L. Shao, J. W. G. Tisch, and M. Castillejo, J. Phys. B **28**, L739 (1995).
[10] M. Yu. Ivanov and P. B. Corkum, Phys. Rev. A **48**, 580 (1993).
[11] A. D. Bandrauk, S. Chelkowski, H. Yu, and E. Constant, Phys. Rev. A **56**, R2537 (1997).
[12] R. Kopold, W. Becker, and M. Kleber, Phys. Rev. A **58**, 4022 (1998).
[13] N. Hay, M. Castillejo, R. de Nalda, E. Springate, K. J. Mendham, and J. P. Marangos, Phys. Rev. A **61**, 053810 (2000).
[14] J. H. Posthumus, J. Plumridge, P. F. Taday, J. H. Sanderson, A. J. Langley, K. Codling, and W. A. Bryan, J. Phys. B **32**, L93 (1999).
[15] Ph. Hering and C. Cornaggia, Phys. Rev. A **59**, 2836 (1999).
[16] 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, and C. Kosmidis, J. Phys. Chem. A **102**, 3002 (1998).
[17] R. J. Levis and M. J. DeWitt, J. Phys. Chem. A **103**, 6493 (1999).
[18] M. Castillejo, S. Couris, E. Koudoumas, and M. Martin, Chem. Phys. Lett. **289**, 303 (1998).
[19] M. Castillejo, S. Couris, E. Koudoumas, and M. Martin, Chem. Phys. Lett. **308**, 373 (1999).
[20] D. J. Fraser and M. H. R. Hutchinson, J. Mod. Opt. **43**, 1055 (1996).
[21] M. B. Mason, Ph.D. thesis, Imperial College, London, 2000 (unpublished).
[22] A. E. Siegman, *Lasers* (University Science Books, Mill Valley, CA, 1986), p. 682.