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High-order harmonic generation in molecular gases

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Abstract. We present an experimental study of harmonic generation in molecular gases, using the fundamental (800 nm) and the second harmonic (400 nm) of a 150 fs titanium–sapphire laser at an intensity of $\sim 2 \times 10^{14}$ W cm^{-2}. We compare the conversion efficiency and the maximum energy obtained in different species: rare gases (Ar, Xe), diatomic molecules (N_2, H_2, O_2, CO) and polyatomic molecules (SF_6, N_2O, CO_2, CH_4, C_3H_8). The harmonic spectra from molecular gases are very similar to those obtained in the atomic gases, with a plateau and a cutoff whose location is strongly correlated to the value of the ionization potential. The conversion efficiency is not higher than that of the rare gases.

1. Introduction

High-order harmonic generation in atomic gases has been extensively studied during the past few years, both experimentally and theoretically. The harmonic spectra present a characteristic behaviour: after an initial decrease, the harmonic intensity remains approximately constant up to a rather sharp cutoff, beyond which no further emission is observed. Generation of odd harmonics with orders exceeding 100 has been demonstrated in several laboratories [1, 2]. Besides its fundamental interest, the harmonic radiation presents interesting properties of high brightness, coherence and short pulse duration, which makes it a source of radiation in the extreme ultraviolet (XUV) region useful in a number of applications [3–6].

A recent quasi-classical interpretation of high-order harmonic generation sheds light on the fundamental processes involved [7]. According to this model, the electron first tunnels from the ground state of the atom, through the barrier formed by the Coulomb potential and the laser field, and is subsequently driven away from the atom by the field. When the laser field changes sign, the electron is accelerated in the reverse direction and may be driven back towards the atomic potential, and recombine back to the ground state. This model has been very useful in explaining the location of the cutoff in the harmonic generation spectra [8, 9]. In the single atom response, the cutoff occurs at the energy $I_p + 3.2U_p$, where I_p is the ionization potential and $U_p = E^2/4\omega^2$ is the ponderomotive potential, i.e. the mean kinetic energy acquired by a free electron in a laser field of amplitude E and frequency ω. These predictions are expected to hold in the so-called tunnelling regime for ionization. This regime is usually characterized by the value of the Keldysh parameter $\gamma = \sqrt{I_p/2U_p}$. $\gamma < 1$ denotes the tunnelling regime, while $\gamma > 1$ characterizes the multiphoton regime. The cutoff energy observed experimentally is reduced to approximately $I_p + 2U_p$ owing to propagation effects [9]. The width of the plateau strongly depends on the atomic medium, the laser wavelength and the intensity. It increases with the laser intensity, up to the intensity at which the atom ionizes (saturation intensity). Very high-order harmonics,

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with orders exceeding 100, are generated only in the light rare gases (Ne, He), having high values of I_p. In contrast, the conversion efficiency for the plateau harmonics is low, much lower than that obtained in heavier rare gases (Xe, Ar), with low values of I_p.

Surprisingly, little work has been done so far concerning harmonic generation in molecular systems. Liang *et al* [10] compared the conversion efficiency between Ar and Xe and a few diatomic molecules (H_2, D_2, N_2 and O_2). They showed that for these molecules the conversion efficiency increases with the static polarizability, and gave a theoretical justification to this effect, using a multiphoton type of model [11]. Fraser *et al* investigated harmonic generation in xenon, butane (C_4H_{10}) and butadiene (C_4H_6) [12]. Experimental studies in nitrogen were also performed by Sakai and Miyazaki [13]. The additional complexity introduced by the molecular structure to the already difficult problem of harmonic generation in strong laser fields, has made theoretical studies even sparser. There are, however, several theoretical calculations concerning the molecular ion H_2^+ [14–17].

An important question is: do molecules behave as atoms, or are there additional effects induced by the molecular structure? For relatively low orders, in the plateau, the conversion efficiency for harmonic generation in rare gases increases with the atomic number. In these gases, the polarizability increases, and the ionization energy I_p decreases with the atomic number. If molecules behave in the same way, it might be possible to obtain even higher efficiencies by choosing a suitable molecular species with a low I_p or a high polarizability. This would be of significant importance, when harmonic generation is used as a source of coherent XUV radiation, of not too short wavelength. Another question is whether harmonics are produced in the molecules or in the fragments following dissociation. Also, it has recently been shown [18, 19] that diatomic molecules exposed to very intense laser fields ionize at a critical distance, before dissociating. According to some authors [20], the ionized molecule remains stable with respect to dissociation, until the end of the laser pulse, when it explodes due to the Coulomb repulsion. Could these effects influence, in some way, harmonic generation?

In the present work, we study harmonic generation in several systems: rare gases (Ar, Xe), diatomic molecules (N_2, H_2, O_2, CO) and polyatomic molecules (SF_6, N_2O, CO_2, CH_4, C_3H_8). Our aim is to compare the height (conversion efficiency) and width (maximum energy) of the plateau in these gases. The atomic and molecular species were selected in order to span a very large range of ionization energies, (static) polarizabilities, ionization and dissociation probabilities, and, generally speaking, molecular structures, with or without a permanent dipole moment. We used the fundamental (near infrared, 800 nm) and the second harmonic (near ultraviolet, 400 nm) of a 150 fs titanium–sapphire (Ti:S) laser. Using both 800 nm and 400 nm light, the type of ionization in the experiment changes from tunnelling, at 800 nm ($\gamma < 1$), to multiphoton, at 400 nm ($\gamma > 1$), allowing us to study harmonic generation in different regimes. In section 2, we describe the experimental set-up and method, while the results are presented and discussed in section 3. We conclude in section 4.

2. Experimental set up and method

The experiment was performed using the terawatt laser system of the Lund High-Power Laser Facility [21]. This 10 Hz system is based on chirped-pulse amplification in titanium-doped sapphire. The duration of the recompressed pulse is about 150 fs and the energy can be varied up to 220 mJ at 800 nm. A Type 1 KDP crystal was used for the frequency doubling, required in part of our study, providing a conversion efficiency of approximately

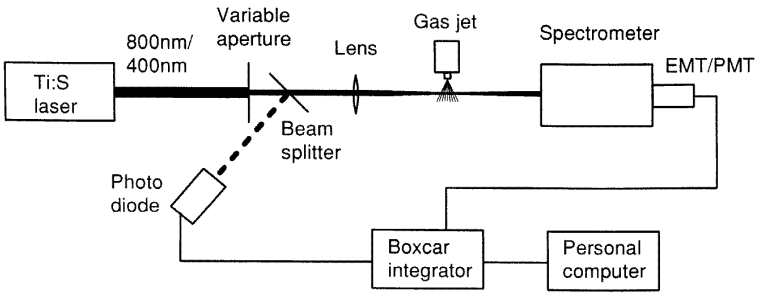

Figure 1. Experimental set-up used for the generation and detection of harmonics.

30%. A schematic outline of the experiment is shown in figure 1. A lens ($f = 50$ cm or $f = 1$ m) focused the beam into a vacuum chamber, where it interacted with free atoms or molecules, in a gas jet from a pulsed nozzle (Lasertechnics, model LPV).

The harmonic radiation was analysed with two different spectrometers. The lowest-order harmonics were studied with a normal-incidence vacuum monochromator (Acton VM- 502, 1200 grooves/mm grating). For the higher harmonics (wavelengths below 60 nm) a grazing incidence spectrometer (Jobin Yvon PGM PGS 200) was used, consisting of a toroidal mirror and a plane, flat-field grating (platinum coated, $\sim$ 450 grooves/mm). We set the entrance slit width to 500 μm and the exit slit width to 100 μm. The entrance slit of the spectrometer was placed at a distance from the jet equal to the focal length of the lens. This was to allow the fundamental beam to expand to its original size, so as not to damage the components of the spectrometer. However, this means that we were collecting only a small part of the generated harmonic radiation. The harmonics with a wavelength below 150 nm were recorded with an electron-multiplier tube (EMT, Hamamatsu R515), while those with a wavelength above 150 nm were detected with a photomultiplier tube (PMT) with a MgF_2 window (Hamamatsu R1220). A boxcar integrator was used in order to integrate the detector signal and to provide a time window for detection, hence increasing the signal-to-noise ratio. The integrated harmonic signal was stored in a personal computer as the spectrometer was scanned in wavelength. Finally, the recorded signal was corrected for the spectral response of the spectrometers and for the spectral sensitivity of the detectors, using data provided by the manufacturers. A thin plate of quartz, placed before the focusing lens, reflected a small fraction of the beam onto a photodiode, enabling accurate monitoring of the energy of each laser pulse. Only pulses within a 10% energy window, centred around a preselected value, were accepted. Each data point was taken as an average of 40 accepted laser shots.

In order to obtain a loose focusing geometry, thus optimising harmonic generation [2], while keeping a low degree of ionization in the medium, the 5 cm-diameter laser beam was reduced by a hard aperture, before it was focused into the vacuum chamber. The diameter of the aperture was optimised with respect to the harmonic signal. An aperture of about 7 mm (14 mm) was found optimal for $f = 50$ cm ($f = 1$ m), resulting in $f\# = 70$. Typically, only a few mJ (5 mJ at 800 nm, and 1 mJ at 400 nm) were used to produce the harmonics. By calculating the far-field diffraction pattern from a circular aperture, we estimate the focused laser intensity, both at 400 nm and 800 nm, to be 2×10^{14} W cm^{-2}, with an uncertainty of about 50%.

The laser focus was positioned at the centre of the gas jet. This position was determined

by recording the harmonic yield as a function of the jet position relative to the laser focus, at very high laser energy (opening the hard aperture). The harmonic signal then exhibits two distinct peaks. The pronounced minimum is essentially due to ionization of the medium, and corresponds to the focus position [2]. At lower energy, i.e. using a much smaller aperture (and thereby increasing the confocal parameter), the harmonic signal remained almost constant over several centimetres when the laser focus was moved with respect to the gas jet, along the beam axis.

The backing pressure of the gas jet was kept constant at 1300 mbar. The pressure in the vacuum chamber was maintained at around 10^{-4} mbar (under jet operation) with a turbomolecular pump. The gas jet released 1 ms pulses of gas, synchronized with the laser pulse. To be able to compare the harmonic efficiency of the different gases, the number of atoms or molecules in the gas jet, interacting with the laser field, must be the same. Due to the different masses of the particles, the velocity with which they emerge from the nozzle varies. The number of particles per pulse, ejected from the nozzle, was determined by measuring the small increase in pressure, due to a given number of pulses of gas, in a closed but evacuated system. The number density in the jet was then calculated, taking into account the different velocities of the atoms or molecules. We found that it is, within experimental errors, independent of the medium, and of the order of 10^{18} atoms/cm^3. Harmonics were produced in eleven different gases; two rare gases and ten molecular gases (including air). To illustrate the reproducibility of our results, we show in figure 2 a spectrum obtained using air, as well as a spectrum obtained by combining our results obtained in O_2 and N_2, multiplied by the percentage of these gases in air. The two spectra are very similar in both intensity and shape. However, the measurements in air were done at a backing pressure of 1000 mbar while the measurements in O_2 and N_2 were done at 1300 mbar. This explains why the signal from air is somewhat lower.

The background signal in our spectra is generally very low. However, for some gases

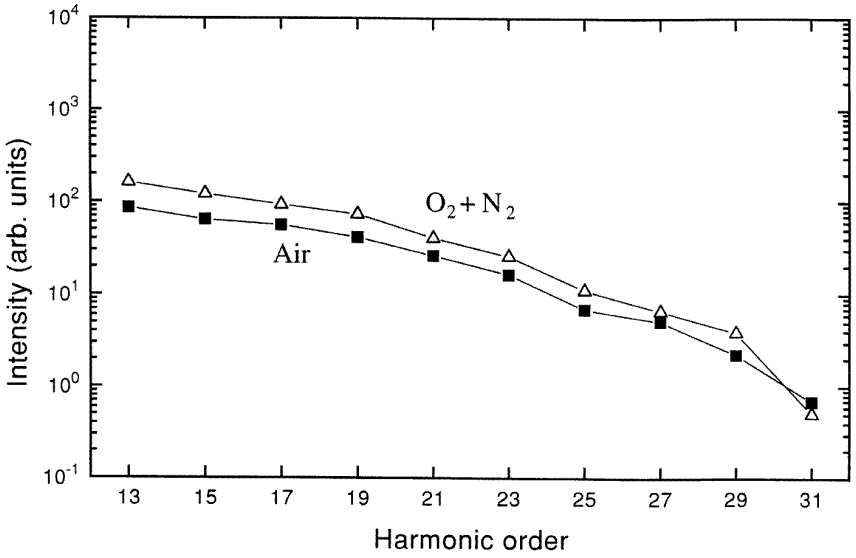

Figure 2. Harmonic spectrum generated in air and a spectrum obtained by combining our measurements in O_2 and N_2. Note that the harmonic spectrum for air is recorded at a slightly lower pressure than the spectrum obtained from O_2 and N_2.

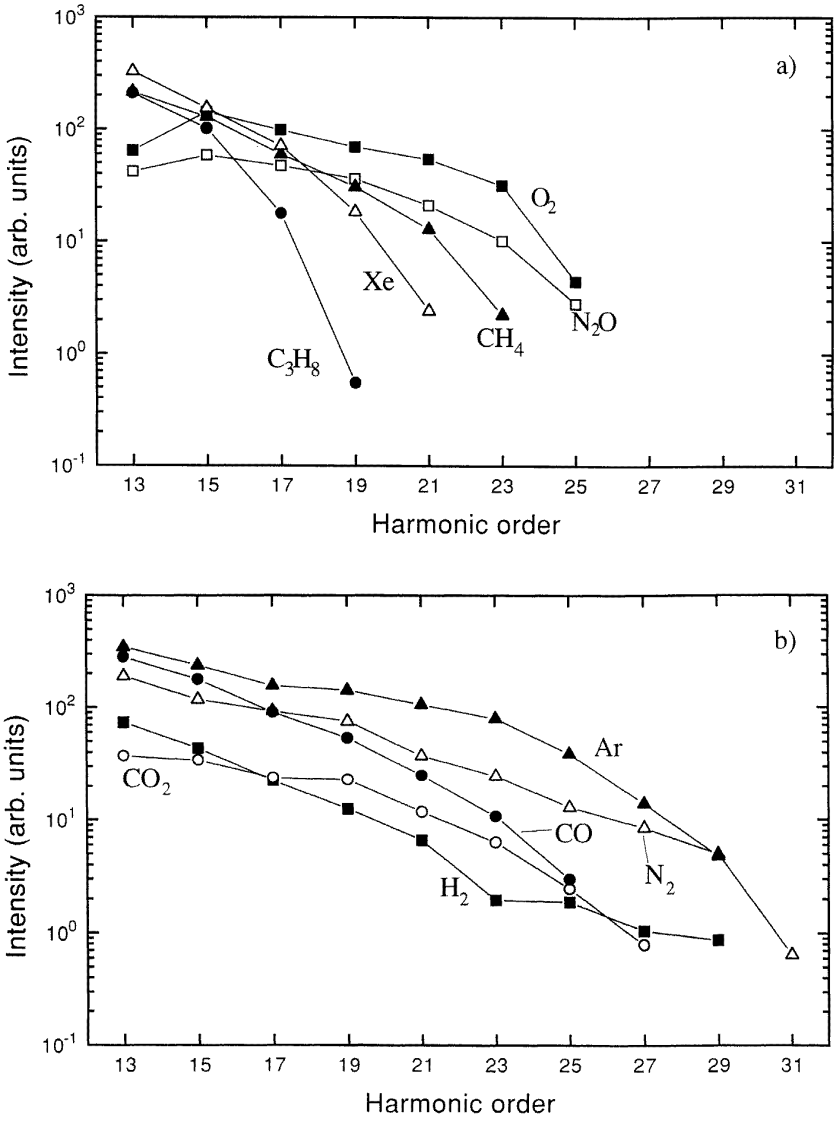

Figure 3. Harmonic spectra generated in gases with an ionization potential from 10.9 eV to 12.9 eV (*a*) and from 13.8 eV to 15.8 eV (*b*).

(Xe, H_2, CO and CH_4) the background noise increases at short wavelengths. We assume that this is due to scattered light from intense lower-order harmonics.

3. Experimental results and discussion

Harmonic spectra obtained with 800 nm laser radiation are shown in figure 3(*a*) and (*b*). The harmonic signal is plotted as a function of harmonic order, starting at the 13th harmonic. All the data points were recorded with the same spectrometer and under the same conditions. Atoms and molecules with a low ionization potential (from 10.9 eV to 12.9 eV) are plotted in

figure 3(*a*) and those with a higher ionization potential (from 13.8 eV to 15.8 eV), in figure 3(*b*). The ionization potentials of the different molecules are listed in table 1, together with their static polarizabilities and existence of a permanent dipole moment. The characteristic plateau and cutoff behaviour is exhibited by both the atomic and the molecular gases. The plateau is wider for the gases with a high ionization potential than for those with a low ionization potential. This shows that the ionization potential is a major factor where the width of the plateau is concerned, not only for free atoms but also for molecules. Note that, according to the cutoff law, I_p influences the value of the cutoff energy, not only because of the I_p term in the expression for the cutoff energy, but also because it determines, to a large extent, the maximum value of the laser intensity (i.e. of U_p) experienced by the neutral molecule before it ionizes. We do not observe any significant difference between the behaviour of diatomic molecules and of more complex ones, nor between those with a permanent dipole moment (C_3H_8, N_2O and CO), and those without.

Table 1. A list of ionization potentials, static average polarizabilities and existence of permanent dipole moment of atoms and molecules relevant for this study.

Atom/molecule	I_p (eV)	Static average polarizability† (10^{-24} cm^3)
C_3H_8	10.9	6.3*
O_2	12.1	1.6
Xe	12.1	4.0
CH_4	12.5	2.6
N_2O	12.9	3.0*
CO_2	13.8	2.9
CO	14.0	1.9*
SF_6	15.3	6.5
H_2	15.4	0.80
N_2	15.6	1.7
Ar	15.8	1.6
S	10.4	2.0
C	11.3	1.8
O	13.6	0.80
H	13.6	0.67
N	14.5	1.1
F	17.4	0.56

† The static average polarizabilities correspond to the ground state atoms and molecules.
* These molecules have a permanent dipole moment.

In the plateau region, the efficiency for harmonic generation in the different species does not vary much. The spread in efficiency between the different gases is about one order of magnitude. To our surprise, the rare gases remain the most efficient. Argon shows the highest efficiency in the spectral range of figure 3, xenon becoming more efficient for harmonic orders below the 13th harmonic. For the diatomic molecules, the efficiency in general increases with the polarizability, with the lowest efficiency for H_2 and the highest for N_2. This is in agreement with the results of Liang *et al* [10]. However, this does not apply to the more complex molecules (see table 1).

In the semiclassical picture of harmonic generation [7, 9], the harmonic emission is interpreted as a recombination process of an electron, liberated through tunnel ionization and accelerated in the laser field. The harmonic spectra should therefore reflect the dependence of the probability for recombination as a function of the photon energy, which is the same

as the one-photon ionization cross section. In most of the gases studied (except for the rare gases and H_2) the one-photon ionization cross section is essentially constant in the spectral range considered (from 20 to 45 eV). It decreases with energy in Xe and H_2, and from 34 eV also in Ar. Dividing the experimental results by the one-photon ionization cross section, we obtained, indeed, curves that are more parallel and practically constant in the plateau region for all the species considered. This is consistent with the semiclassical interpretation.

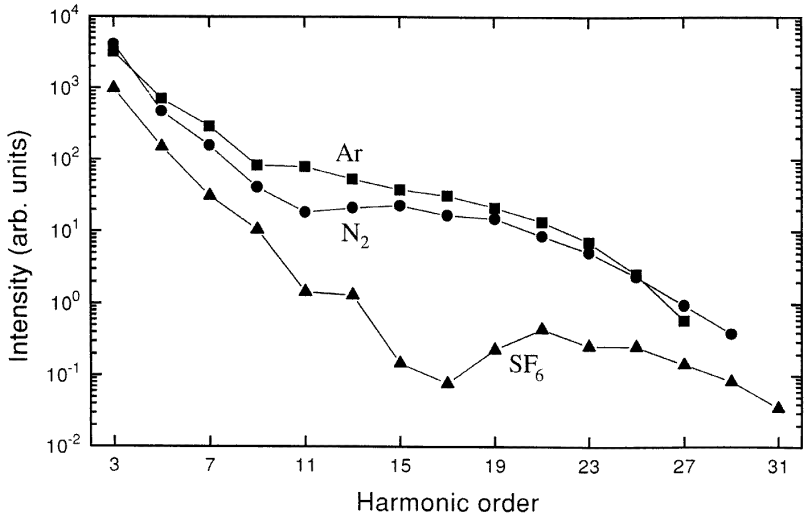

Figure 4. Harmonic spectra from a rare gas (Ar), a diatomic molecule (N_2) and a polyatomic molecule (SF_6).

In figure 4 we present complete spectra obtained from a rare gas (Ar), a diatomic molecule (N_2) and a polyatomic molecule (SF_6). In order to cover the full spectral range, these spectra are based on data acquired with three different set-ups; the normal incidence spectrometer with the PMT, the normal incidence spectrometer with the EMT and the grazing incidence spectrometer with the EMT. All these three gases have approximately the same ionization potential (see table 1). N_2 and Ar exhibit a very similar behaviour, both with respect to the harmonic cutoff and to the height of the plateau. SF_6 does not have the characteristic plateau behaviour. Instead, the intensity of the harmonics decreases continuously until the 17th harmonic. Higher harmonics are produced with a very low efficiency but are present until the 31st harmonic. One possible interpretation of this behaviour is that SF_6 dissociates at low intensity, during the rise time of the laser pulse, and that the harmonics are produced from fragments. To check this, we recorded time-of-flight ion spectra, in similar conditions as in the harmonic generation experiment, but with the pressure reduced to a few 10^{-5} mbar. The time-of-flight spectra show multiple fragments; SF_5^+, SF_4^+, SF_3^+, SF_2^+, SF^+, F^+ and S^+. However, we saw no trace of SF_6^+ ions. This supports the idea that harmonics might be generated not in the SF_6 molecule, but in the atomic or molecular (neutral) fragments. If two fragments, with different I_p, generate harmonics it would lead to two plateaus of different heights and widths. Sulphur and fluorine have very different ionization energies (10.4 eV and 17.4 eV respectively), which could indicate that the high-order harmonics are generated in atomic fluorine. This

behaviour was only found in SF_6 and at low frequency (800 nm). All the other molecules exhibited the single plateau behaviour. However, this does not exclude the possibility that in some cases, in particular for the polyatomic molecules, harmonics could be generated, at least partly, in molecular or atomic fragments. In most of the molecules studied (except SF_6), the constituent atoms have approximately the same I_p as the parent molecule (see table 1), so that we cannot expect to distinguish between harmonic generation from the molecule and from the fragments, on the basis of the behaviour of the harmonic spectra.

We performed systematic measurements also at 400 nm, in order to study the influence of the wavelength on the width and height of the plateau. At the considered intensity (2×10^{14} W cm^{-2}) and for all the species, the regime for ionization, as defined by the Keldysh parameter, changes from tunnelling at 800 nm to multiphoton at 400 nm. However, the results obtained for the different species present the same characteristics as the spectra obtained at 800 nm. The width of the plateau is correlated to the ionization energy, but is shorter than at 800 nm (smaller U_p). The relative harmonic generation efficiencies in the different gases, vary approximately as with 800 nm laser radiation (with a low efficiency for H_2 and the highest efficiency for Ar). In the experimental conditions chosen, the harmonic production was more efficient at 400 nm than at 800 nm, though with a reduced spectral range. As an example, we present in figure 5 spectra in Ar and SF_6, illustrating these results. The data points taken at 400 nm are plotted as a function of the equivalent harmonic orders of the 800 nm radiation. Note that the anomaly in the plateau behaviour observed in SF_6 at 800 nm is not present with 400 nm radiation.

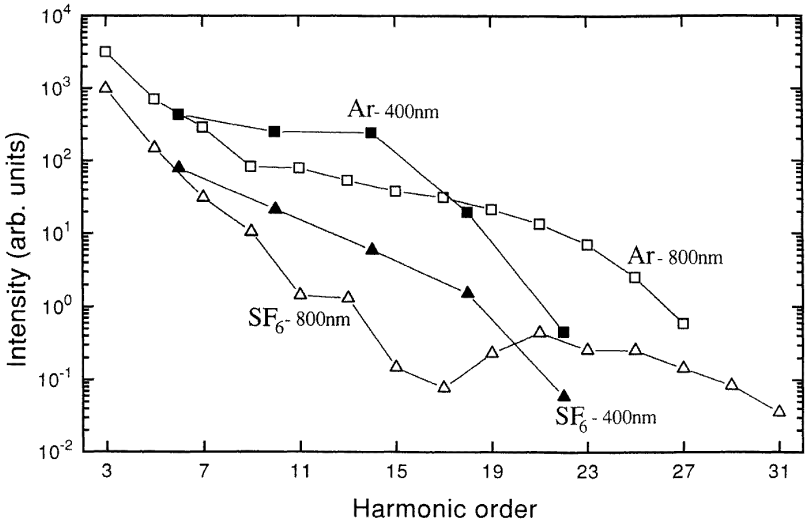

Figure 5. Harmonic spectra in Ar and SF_6 generated with both 800 nm and 400 nm radiation. The data points for harmonics generated with 400 nm radiation are plotted as a function of the equivalent harmonic orders of the 800 nm radiation.

We also studied the harmonic yield as a function of the laser intensity. Some of the results obtained for the 13th and 21st harmonic are shown in figure 6(*a*) and (*b*) respectively. The harmonic signal increases with the laser intensity until the saturation intensity, where the medium ionizes. For argon this is estimated to be about 2.5×10^{14} W/cm^2 [23]. These results show that the relative conversion efficiency obtained in the different molecules depends on the intensity used for the comparison. However, we find

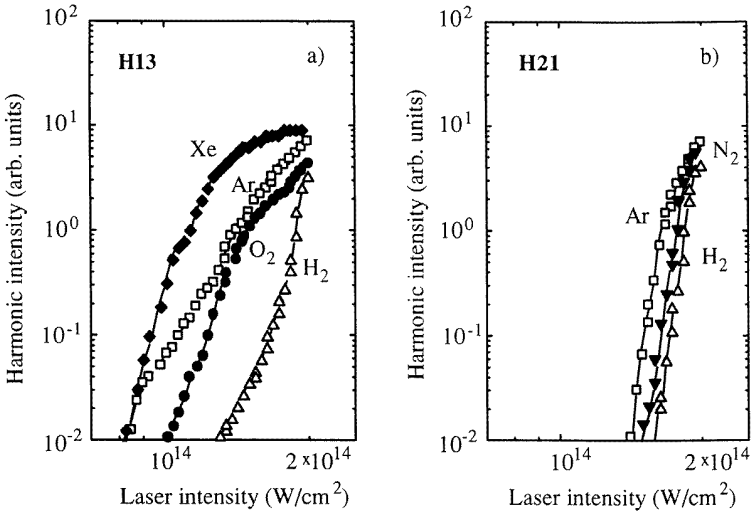

Figure 6. Harmonic yield of the 13th harmonic (*a*) and the 21st harmonic (*b*) as a function of the laser intensity.

that the conclusions drawn previously for the relative conversion efficiencies in the different molecular gases (including the polyatomic), are robust and do not change over the range of intensity ($\leqslant 2 \times 10^{14}$ W cm^{-2}) investigated.

Finally, to complete this study of harmonic generation in molecular gases, we recorded a few spectra in N_2 at higher laser intensities, from 2×10^{14} W cm^{-2}to $\sim 2 \times 10^{15}$W cm^{-2}, in conditions where enhanced ionization [18, 19], and possibly stabilization against fragmentation [20], might occur. According to some theoretical ideas [24] enhanced generation of harmonics might then be expected. Laser up-conversion has also been predicted [25] in similar conditions. With our experimental conditions, however, we did not observe any significant change of the spectra.

4. Conclusion

In summary, we have performed a systematic study of harmonic generation in a number of molecular gases. Our main conclusion is that harmonic spectra in molecular gases are in general very similar to those in the rare gases, with a characteristic plateau/cutoff behaviour. The value of the ionization energy for the different species determines to a large extent the maximum harmonic energy, in accordance with the cutoff law, well established for atoms.

The most efficient gases are the rare gases (argon, xenon), though some of the molecules studied exhibit much higher (static) polarizabilities. For the largest molecules, and in particular SF_6, dissociation might take place at an early stage, leading to neutral molecular or atomic fragments contributing to harmonic generation. More work is, of course, needed to explore this idea.

Acknowledgements

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References

[1] Macklin J J, Kmetec J D and Gordon C L III 1993 *Phys. Rev. Lett.* **70** 766
[2] L'Huillier A and Balcou Ph 1993 *Phys. Rev. Lett.* **70** 774
[3] Haight R and Peale D R 1993 *Phys. Rev. Lett.* **70** 3979; 1994 *Rev. Sci. Instrum.* **65** 1853
Haight R and Seidler P F 1994 *Appl. Phys. Lett.* **65** 517
[4] Balcou Ph, Salières P, Budil K S, Ditmire T, Perry M D and L'Huillier A 1995 *Z. Phys. D.* **34** 107
[5] Larsson J, Mevel E, Zerne R, L'Huillier A, Wahlström C-G and Svanberg S 1995 *J. Phys. B: At. Mol. Opt. Phys.* **28** L53
[6] L'Huillier A *et al* 1995 *J. Nonlinear Opt. Phys. Mater.* **4** 647–65
[7] Corkum P B 1993 *Phys. Rev. Lett.* **73** 1995
Kulander K C, Schafer K J and Krause J L, 1993 *Super-Intense Laser–Atom Physics* (NATO ASI B316) ed B Piraux, A L'Huillier and K Rzążewski (New York: Plenum) p 95
[8] Krause J L Schafer K J, and Kulander K C 1992 *Phys. Rev. Lett.* **68** 3535
[9] L'Huillier A, Lewenstein M, Salières P, Balcou Ph, Ivanov M Yu, Larsson J and Wahlström C-G 1993 *Phys. Rev.* A **48** R3433
[10] Liang Y, Augst S, Chin S L, Beaudoin Y and Chaker M 1994 *J. Phys. B: At. Mol. Opt. Phys.* **27** 5119
[11] Chin S L and Golovinski P A 1995 *J. Phys. B: At. Mol. Opt. Phys.* **28** 55
[12] Fraser D J, Hutchinson M H R, Marangos J P, Shao Y L, Tisch J W G and Castillejo M 1995 *J. Phys. B: At. Mol. Opt. Phys.* **28** L739
[13] Sakai H and Miyazaki K 1995 *Appl. Phys.* B **61** 493
[14] Zuo T, Chelkowski S and Bandrauk A D 1993 *Phys. Rev.* A **48** 3837
[15] Krause J L, Schafer K J and Kulander K C 1991 *Chem. Phys. Lett.* **178** 573
[16] Plummer M and McCann J F 1995 *J. Phys. B: At. Mol. Opt. Phys.* **28** L119
[17] Moiseyev N, Chrysos M, Atabek O and Lefebvre R 1995 *J. Phys. B: At. Mol. Opt. Phys.* **28** 2007
[18] Seideman T, Ivanov M Yu and Corkum P B 1995 *Phys. Rev. Lett.* **75** 2819
[19] Posthumus J H, Frasinski L J, Giles A J and Codling K 1995 *J. Phys. B: At. Mol. Opt. Phys.* **28** L349
[20] Normand D and Schmidt M 1996 *Phys. Rev.* A in press
[21] Svanberg S, Larsson J, Persson A, and Wahlström C-G 1994 *Phys. Scr.* **49** 187
[22] Balcou Ph, Gomes A S L, Cornaggia C, Lompré L A and L'Huillier A 1992 *J. Phys. B: At. Mol. Opt. Phys.* **25** 4467
[23] Wahlström C-G, Larsson J, Persson A, Starczewski T, Svanberg S, Salières P, Balcou Ph and L'Huillier A 1993 *Phys. Rev.* A **48** 4709
[24] Lewenstein M and Seideman T Private communication
[25] Codling K, Frasinski L J and Hatherly P A 1989 *J. Phys. B: At. Mol. Opt. Phys.* **22** L321