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High harmonic generation spectroscopy of hydrocarbons

C. Vozzi,[1] R. Torres,[2] M. Negro,[3] L. Brugnera,[2] T. Siegel,[2] C. Altucci,[4] R. Velotta,[4,a)] F. Frassetto,[5] L. Poletto,[5] P. Villoresi,[6] S. De Silvestri,[3] S. Stagira,[3] and J. P. Marangos[2]
[1]*CNR-IFN, Piazza Leonardo da Vinci 32, 20133 Milan, Italy*
[2]*Blackett Laboratory, Imperial College, Prince Consort Road, London SW7 2BW, United Kingdom*
[3]*Dip. di Fisica-Politecnico di Milano, Piazza Leonardo da Vinci 32, 20133 Milan, Italy*
[4]*CNISM and Università di Napoli "Federico II," Via Cintia 26, 80126 Napoli, Italy*
[5]*CNR-IFN, via Trasea 7, 35131 Padova, Italy*
[6]*DEI, Università di Padova, Via Gradenigo 6a, 35131 Padova, Italy*

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We have demonstrated the ability of few-cycle midinfrared intense laser pulses to produce extended harmonic spectra (≥ 45 eV) suitable for high harmonic spectroscopy in aligned hydrocarbons with ionization potentials in the range 9.07–11.52 eV. Modulations in the spectra measured with different alignment angles show signatures of the molecular structure. These results pave the way for the extension of high harmonic spectroscopy to complex biomolecules. © *2010 American Institute of Physics*. [doi:10.1063/1.3526752]

The study of high harmonic generation (HHG) from molecules has revealed a rich array of phenomena reflecting their structure and internal dynamics. The measured molecular HHG spectra has been used to access, with a uniquely fast temporal resolution, the nuclear[1] and electronic dynamics[2] triggered by the attosecond-timescale field ionization that initiates the HHG process. The HHG channel requires the system to return to its initial state in order to yield the forward scattered harmonic photons that contribute coherently to the observed macroscopic signal from the sample. As a consequence HHG is not affected by all of the myriad channels otherwise opened by the strong field interaction, thus yielding a background-free measurement. This property makes it very suitable for observation of ultrafast structural change even in complex molecules.

Early accomplishments of the technique of HHG spectroscopy have so far been confined to a restricted set of small molecules (H_2, N_2, CO_2, and N_2O).[3–5] A fundamental limit to extending HHG spectroscopy is that while the small molecules studied so far typically have ionization potentials I_p in the range 15–12 eV most molecules have lower I_p (12–8 eV or less). The onset of ionization saturation at a few 10^{13} W cm^{-2} when an 800 nm field is used greatly restricts the extent of the HHG spectrum, and in general these "softer" molecules do not display an extended plateau. The extended plateau is required to confirm that HHG is taking place in the strong field limit, and thus enables the extraction of structural information and temporal mapping. By applying mid-IR radiation (1200–1400 nm) from a source with $\sim$50 fs duration it was earlier shown that HHG generation could be extended to species with lower I_p.[6] This took advantage of the cutoff scaling $I_p+3.17\ U_p$, since U_p is proportional to $I\lambda^2$ (where the intensity I is clamped by the saturation value). HHG spectra from N_2O ($I_p=12.9$ eV) and C_2H_2 ($I_p=11.4$ eV) were generated with cutoffs exceeding 50 eV.

Here we show that by using mid-IR and few-cycle laser pulses extended plateaus can indeed be observed in a range of saturated and unsaturated hydrocarbons with I_p as low as just 9 eV, which opens up the possibility of HHG spectroscopy in a wide range of complex molecules. We have exploited a unique mid-IR few-cycle optical parametric source that produces pulses with duration of just 18 fs in the range 1450–1800 nm.[7] This has the effect of reducing the degree of ionization accumulated by the time the peak of the laser pulse is reached, so leading to an effective raising of the ionization saturation threshold in the molecule. This is ideal for generation of HHG spectra with an extended cutoff. The parametric source is pumped by an amplified Ti:sapphire laser system (60 fs, 800 nm, 10 Hz, 12 mJ). A broadband supercontinuum is generated by filamentation in a krypton-filled gas cell, and a mid-IR seed is then produced by difference frequency of the supercontinuum spectral components in a nonlinear crystal. This seed is then amplified through a two-stage optical parametric amplifier up to 1.6 mJ. The central wavelength of the amplified pulse can be tuned without significantly affecting pulse duration and energy. For the generation of high-order harmonic radiation, the mid-IR driving pulses were focused on a synchronized gas jet operating at 10 Hz. The harmonic spectrum was then detected by means of a soft x-ray spectrometer and a microchannel plate coupled to a phosphor screen and a charge coupled device camera.

In our experiments a portion of the residual 800 nm pump pulse was used to excite a rotational wavepacket in a rotationally cooled sample formed in the supersonic expansion of the molecular gas. Some of the molecular systems have a polarizability anisotropy large enough for impulsive alignment to be achieved. Field-free alignment is thus observed immediately after the laser pulse and, in the case of linear and symmetric top molecules, in the subsequent rotational revivals. A further study measured the delayed spectral effects occurring on a probe pulse propagating inside a filament generated by a pump pulse in the gas of interest to detect alignment of molecules.[8] Whereas in the unsaturated hydrocarbons strong alignment was detected, in the case of the alkanes no alignment was found, confirming an expectation that the small value of polarization anisotropy in these molecules leads to very limited alignment. By varying the relative delay τ or the relative polarization angle θ of the two

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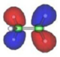
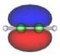
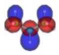
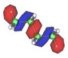
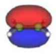
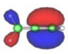
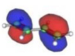
[a)] Electronic mail: rvelotta@unina.it.

TABLE I. Data for molecules examined in the present study. The HOMO orbitals are calculated using the GAMESS-U.K. package (see Ref. 13).

Molecule		Ethane (C_2H_6)	Acetylene (C_2H_2)	Propane (C_3H_8)	Butane (C_4H_{10})	Ethylene (C_2H_4)	Allene (C_3H_4)	1,3-Butadiene (C_4H_6)
I_P (eV)		11.52	11.40	10.94	10.53	10.51	9.69	9.07
Rotational constants (cm^{-1})	A	2.52		0.97	0.78	4.83	4.81	1.40
	B	0.68	1.18	0.28	0.12	1.00	0.30	0.14
	C	0.68		0.25	0.11	0.83	0.30	0.13
$\Delta\alpha$ (A^3)		0.78	2.69	1.92	~1.06	2.02	4.54	6.32
HOMO								

fields it was thus possible to study HHG as a function of the molecular alignment.

We have been able to observe well defined HHG spectra with plateaus extending to cutoffs from 45 to 70 eV for the additional saturated and unsaturated hydrocarbon systems listed in Table I. This includes 1,3 butadiene, a species with an I_p of just 9.1 eV. In Fig. 1 we plot the harmonic spectra as a function of the angle θ between the polarization directions of the aligning and the driving field for the unsaturated hydrocarbons (a) acetylene, (b) ethylene, (c) allene, and (d) butadiene. Harmonics are generated by 1450 nm, 18- s driving pulses with an intensity $\sim 1\times 10^{14}$ W cm^{-2}. In (a) and (c) the data were recorded at the first half revival, although similar data are found at prompt alignment (immediately after the aligning pulse) and full revival, as acetylene and allene are linear and symmetric top, respectively. Ethylene (b) and 1,3 butadiene (d) are asymmetric top molecules and it was necessary to record the alignment data at prompt alignment as they do not produce complete alignment revivals. In the case of all these unsaturated hydrocarbons distinct alignment dependence was observed providing a strong indication that the HHG arises from the intact molecule. For all the molecules, a strong suppression at $\theta=0°$ is observed, likely due to the nodal plane in the highest occupied molecular orbital (HOMO) wave function, which will dominate the spectrum, whereas the cutoff extension dependence on θ is typical of a given molecule, thereby providing an additional signature of the molecular orbital in HHG; for instance, acetylene [Fig. 1(a)] and 1,3 butadiene [Fig. 1(d)] show a maximum in HHG at 40° and 60°, respectively.

In Fig. 2 we plot the harmonic spectra as a function of the aligning field angle θ for ethane, at the time delay where the postpulse alignment should be expected. It was earlier shown that to avoid HHG predominately from molecular fragments of organic molecules it was required to use a short laser pulse[9] and that short pulses also limit the effect of ionization saturation in alkanes.[10,11] Although no evidence of alignment dependence of the harmonic spectrum is found, a very well developed HHG spectrum is observable in ethane (Fig. 2) as well as in propane and butane (data not shown). For all these three alkanes the extension of the plateau scaled with I_p in accordance with the cutoff law, allowing us to deduce that the emission is also from intact molecules for these longer wavelength and short pulses.

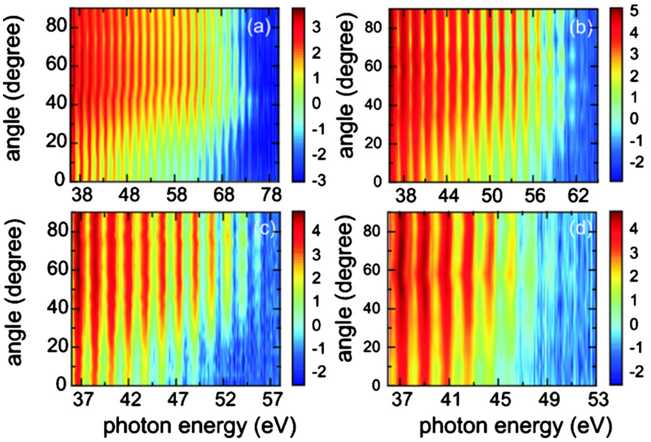


FIG. 1. (Color online) Sequence of harmonic spectra generated in (a) acetylene, (b) ethylene, (c) allene, and (d) 1,3 butadiene as a function of the angle between pump and probe polarizations (log color map).

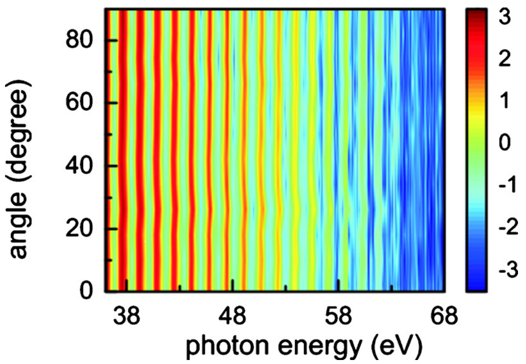


FIG. 2. (Color online) Sequence of harmonic spectra generated in ethane as a function of the angle between pump and probe polarizations (log color map).

In Fig. 3 we plot the experimentally determined ratios between harmonic spectra obtained at an alignment angle of 0° and harmonic spectra without alignment for the unsaturated hydrocarbons. These ratios show a minimum as a function of photon energy likely to arise as a consequence of interferences (two-center, multicenter, or dynamical) that reveal the static structure of the molecules as well as the attosecond dynamics of holes subsequent to ionization. As a first attempt to reproduce our experimental findings, we have worked out the harmonic yields within the strong-field-approximation (SFA) adapted to molecular systems.[5] The results are shown in Fig. 4. Although, under the present experimental conditions, the modal angle of the alignment distribution is $\sim 30°$, a better agreement is achieved for molecules aligned at larger angles, demonstrating the need to go

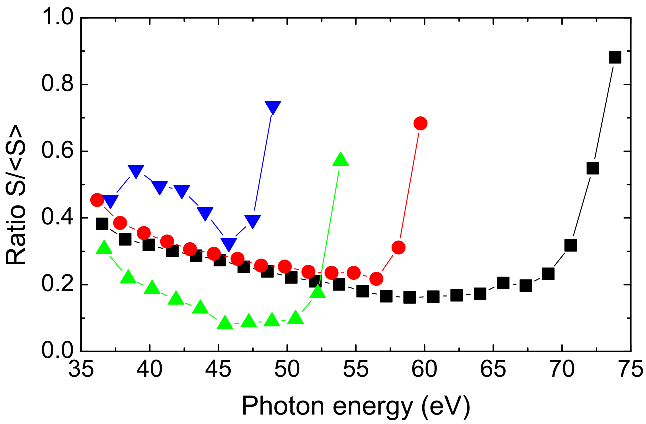


FIG. 3. (Color online) Experimental ratio between harmonic spectra obtained in an aligned distribution at 0° (modal angle ≈30°) and spectra without alignment for acetylene (squares), ethylene (circles), allene (up triangles), and 1,3 butadiene (down triangles).

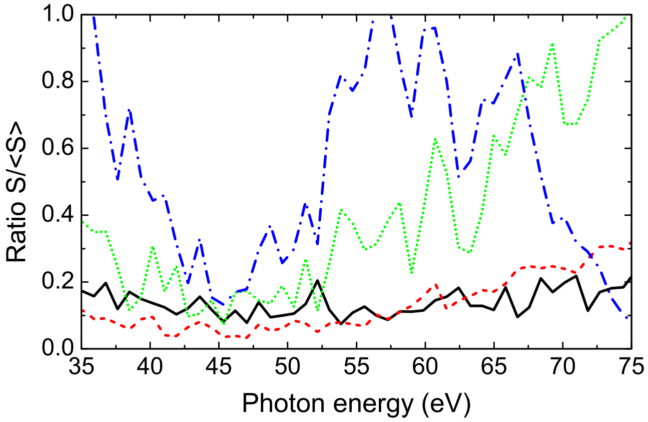


FIG. 4. (Color online) Calculated ratios between perfect alignment at 40° and nonaligned samples, for acetylene (continuous), ethylene (dashed), allene (dotted), and 1,3 butadiene (dashed-dotted).

beyond the SFA for a more accurate description of the electron dynamics in complex molecules.

High order harmonics, with a well defined plateau, have been seen for all the molecules examined even those with $I_p < 10$ eV (for butadiene with an I_p of 9.1 eV, we see HHG up to 45 eV). The extended plateau observed in both the saturated and unsaturated hydrocarbons indicates that we have a strong field condition and so allows us to deduce that (with appropriate trajectory selection) temporal mapping of the harmonic emission should be possible—implying access to any electronic or fast nuclear dynamics of the cation—with a temporal mapping window in the range 2–5 fs.

This work implies that the use of mid-IR radiation will allow HHG spectroscopy to be applied to a wide range of molecules. For instance, chromophores in typical building block biomolecules (dipeptides, arenas, and oligopeptides) have ionization potentials in the range 7.5–9 eV suggesting these systems can indeed be studied using HHG spectroscopy with mid-IR radiation—perhaps working in the range 1.5–2.5 μm. In biomolecules such as peptides, nontrivial charge migration has been predicted,[12] and is thought to play an important role in the photophysics of these molecules as well as providing insight into the mechanisms of ultrafast electron transfer in biochemistry. This means it is likely that HHG spectroscopy, which is exquisitely sensitive to hole motion, can be used to study charge migration in such molecules.

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