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High harmonic generation in ethylene with infrared pulses

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ABSTRACT

We produce harmonics in the molecule ethylene (C_2H_4) with two different wavelengths and three pulse durations. Due to the low ionization potential ($I_p = 10.5$ eV) of C_2H_4, longer wavelengths are needed to extend the maximum photon energy produced. Our results show that regardless of the strong dependence of the efficiency of the harmonic generation process with wavelength, at 1820 nm the cutoff observed is larger than that obtained with 800 nm, 15 fs pulses. We obtain harmonics with energies exceeding 70 eV at 9.0×10^{13} W/cm^2 with a 73 fs 1820 nm pulse. Under these circumstances, the limiting factor for the further extension of the cutoff seems to be the photoionization cross section of the molecule.

1. Introduction

Through the process of high harmonic generation (HHG), new possibilities in chemical physics have arisen. In many aspects, this process can be seen as a new type of atomic and molecular spectroscopy which has lead to the full reconstruction of a molecular orbital [1]. Tomography of molecular orbitals has yet to overcome many hurdles and for this reason alternative approaches has been proposed [2]. However, one aspect which can be improved relatively easy is to increase the spatial resolution by increasing the driving field's wavelength [3]. In the strong field approximation (SFA), the generation of harmonics can be explained in a simple, quasi-classical three step model; Ionization, acceleration under the influence of the electric field, and recombination [4]. Once the electron recombines it emits a photon with energy up to,

$$E_p = I_p + 3.17U_p, \tag{1}$$

with I_p being the ionization potential, and U_p the ponderomotive energy. Thus, the final step in HHG can be seen as the inverse process to photoionization. Therefore, the amplitude of the harmonics obtained in a single shot measurement can contain information about the inverse process; a bound electron absorbing a photon of energy ε and going to the continuum [5,1,6]. This relationship can be exploited to retrieve, in a table top experiment, information about the photoionization cross section of molecules and atoms in the XUV regime. As mentioned above, the main limitation to this approach is the fact that the maximum XUV photon energy is limited by the ponderomotive energy. Since $U_p \propto \lambda^2$, with λ the center wavelength of the driving field, it is expected that by using longer wavelengths the cutoff of the HHG would extend. Furthermore, at high intensities, molecules with low I_p ionize more easily at shorter wavelengths compared to longer wavelengths. The latter has implications for the generation of harmonics due to the fact that, after total ionization, the HHG process in the neutral molecule will cease since there is no interference between the continuum and the ground state and the amplitude of the third step (recombination) is zero. Unfortunately, it was predicted theoretically [7–9] and recently shown experimentally [10] that the efficiency of this process decreases exponentially with wavelength HHG $\propto \lambda^x$ with $x \sim -5$ to -6. This result means that, in principle, one of the more "trivial" ways of extending the cutoff is not a viable one. We should emphasize that this unfavourable dependence of HHG with wavelength is only for a thin jet geometry where phase matching does not play a crucial role. Recent results show that in a waveguide geometry the decrease in XUV brightness with wavelength can be overcome by enhancing phase matching conditions [11].

In the case of molecular imaging, the importance of extending this cutoff lies in that, by expanding the spectrum of the XUV photons, to all possible non-zero values of the dipole moment of the ground state, we can gather enough information to image a molecular orbital [1]. Spatially this means that the photons emitted in the recombination step must have a wavelength small compared to the size of the molecular orbital features. By no means this is the only reason why a higher cutoff is desired and recently some groups have reported on the generation of harmonics with long wavelengths geared towards other applications [11–13]. In this paper, we report of a HHG spectra obtained in the molecule ethylene

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(C_2H_4) that expands to 75 eV, covering an energy range in which the photoionization cross section of C_2H_4 decreases by a factor of 60 [14].

2. Experimental setup

The experiment was conducted at the Advanced Laser Light Source (ALLS) using two laser sources. A schematic of the experiment is shown in Fig. 1. For 800 nm experiments we used a 5 kHz 500 μJ, 35 fs Ti:sapphire laser system. At this wavelength we used pulses of durations 35 fs and 15 fs. Pulse shortening was achieved via spectral broadening in Ar at atmospheric pressure in a 250 μm diameter hollow-core fiber. Subsequent to the capillary, compensation of material dispersion and pulse compression down to 15 fs was achieved by five round trips on chirped mirrors. The same fiber can be used under vacuum, to avoid self-phase modulation and produce spatially filtered 35 fs pulses after compensating for the second order dispersion induced by the chirped mirrors (CM in Fig. 1) with the amplifier grating compressor. Pulse durations at this wavelength were measured with an auto-correlator. For the 1820 nm wavelength experiment, we utilized a 100 Hz, 100 mJ, 45 fs, Ti:sapphire laser system. Laser pulses of 7 mJ at 800 nm were directed to an optical parametric amplifier (HE-TOPAS from Light Conversion) and frequency shifted to 1820 nm idler pulses. The pulse energy and temporal duration were measured to be about 800 μJ and 73 fs. Pulse duration was measured using a second harmonic generation frequency resolved optical gating apparatus. Spatial filtering was performed using a hollow-core fiber (400 μm diameter, 1 m long). As in the case of 800 nm, the fiber was under vacuum to avoid self-phase modulation. We verified that the input and output spectra remained identical.

For both wavelengths we focused into the fiber with a $f = 1000$ mm plano-convex lens. At the output, the laser beam was collimated with an $R = 2000$ mm concave silver mirror. Spatially filtering the beams was crucial in comparing different lasers since it has been observed that it can greatly increase the harmonic efficiency [15–17]. The filtered beam was focused by an $R = 500$ mm concave silver mirror into a thin pulsed gas jet with a 500 μm aperture backed with a pressure of roughly 3 atm. The jet was mounted on a three-axis manipulator for adjustment of its position. The laser energy could be continuously varied using a half-waveplate in front of the fiber, and a Germanium mirror at Brewster's angle acting as a polarizer (P in Fig. 1). The position of the laser focus relative to the center of the jet was determined using the signal of an ion detector, consisting of a mesh biased at

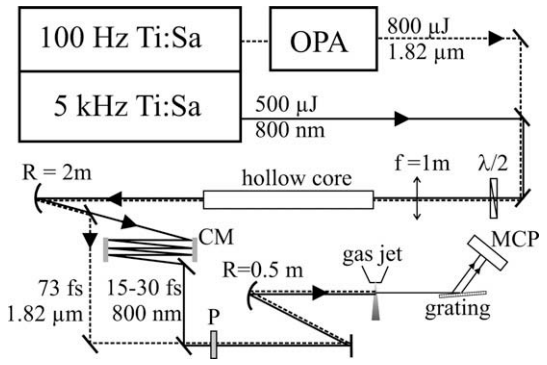

Fig. 1. Optical setup used. Solid line is the 800 nm beam path. The dashed lines show the path for the 1820 nm beam. The diameter of the hollow core fiber was 250 μm for 800 nm and 400 μm for the 1820 nm wavelength. For the longer 800 nm pulse (35 fs), the beam follows the same path (solid line) shown here and the dispersion introduced by the chirped mirrors (CM) was compensated by means of the compressor grating. For curved mirrors we quote the radius of curvature $R = 2 \times f$.

−500 V, a high frequency decoupling circuit and an amplifier connected to a digital oscilloscope. The ion detector assembly was held a few inches below the gas nozzle. The harmonic emission, collimated in the direction of the laser beam was dispersed by a variable groove density concave grating (Hitachi 001-0266) and imaged onto a chevron microchannel plate (MCP) sensitive to wavelengths below 100 nm.

3. Results

Since the focusing conditions vary drastically from 800 nm to 1820 nm, we could not rely on monitoring the energy and pulse durations as a measure of laser intensity. For intensity calibration, we used the space averaged ionization yield with respect to pulse energy in atomic Xe, measured in a separate experiment under the same conditions as C_2H_4. We then fit to this curve an ionization model which gives the intensity for a given pulse energy and duration. This procedure is outlined in [10] and [18]. We used the Yudin–Ivanov nonadiabatic ionization model [19] since it is capable of calculating ionization rates at all regimes, from multiphoton to pure tunnelling. By using an atomic specie for the intensity calibration we avoid many of the complications present in modeling molecular ionization. The intensity calibration for the 800 nm, 15 fs data was done in a different way. We start with the intensity calibration at the same wavelength, 35 fs pulses, using the ionization yield as described above. We then find a pulse energy where the HHG spectra from the 800 nm, 15 fs pulse has the same cutoff as the 15 fs, 800 nm pulse. Since the intensity for the 35 fs case is known and the cutoff does not depend on pulse duration, but only on peak intensity (for the same wavelength and I_p), we then know that the 15 fs pulse has the same peak intensity. This allows to obtain the proportionality factor between energy and intensity which we extrapolate for all energies. The accuracy of this process is then corroborated using Eq. (1) by observing the position of the cutoff at different peak intensities. All the spectra shown in this paper have been corrected by the transformation Jacobian from pixels in the MCP/camera to photon energy $J = \frac{d_{pixel}}{d\varepsilon}$, with ε the photon energy. Since the grating dispersion is almost linear with wavelength, the Jacobian $J(\varepsilon) \approx \frac{1}{\varepsilon^2}$. This correction becomes important for high energies where the resolution of the MCP/eV is lower and different energies *pile up* in a single pixel, thus giving an unrealistic harmonic yield at higher energies. The XUV photon energy is calculated using the grating equation [20]. As the cutoff we used the highest harmonic that is clearly visible above the noise floor.

We produced harmonics in an isotropic sample of C_2H_4. This molecule has $I_p = 10.51$ eV which is a typical value for organic compounds. Harmonics where produced with three different laser pulses. Firstly 800 nm 35 fs, representing a typical pulse out of a commercial Ti:Sa system. Secondly, we used an 800 nm, 15 fs pulse, obtained as explained in the previous section, and finally, we used 1820 nm light from a HE-TOPAS. Fig. 2 shows harmonics produced with 800 nm, 35 fs pulses and intensity $I \approx 9.8 \times 10^{13}$ W/cm^2 focused in C_2H_4. As expected, the cutoff obtained is around 30 eV, confirming that at the focus there is good phase matching. This is achieved by using a 250 μm fiber to spatially filter the otherwise Gaussian beam; a technique that has proven to increase the HHG yield [15–17]. In order to extend the cutoff, another common technique is to use ultrashort short pulses obtained after broadening the spectrum via self-phase modulation in a capillary. The cutoff extension in this case is two fold. Firstly because of the mentioned mode filtering, and secondly because short pulses allow for atoms or molecules to experience higher intensities before ionization saturation occurs. In Fig. 3, we show harmonics obtained with 800 nm, 15 fs pulses in ethylene at the following two intensities $I \approx 9.8 \times 10^{13}$ W/cm^2 (black curve) and