An investigation of harmonic generation in liquid media with a mid-infrared laser

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Abstract: We present a harmonic generation experiment using liquid H_2O and D_2O interrogated by a mid-infrared, 3.66 μm, laser at a maximum intensity of $8\text{x}10^{13}$ W/cm^2. The unique aspects of the experiment include the long wavelength and short (9 cycle-110 fs) pulse duration of the laser as well as the near-resonant excitation of the H_2O and D_2O vibrational modes. We observe up to the 13th harmonic order in H_2O and intensity scaling is consistent with a direct perturbative process up to the 9th harmonic order. Phase matching and resonant absorption are unable to account for the observed differences in harmonic yields between samples.

OCIS codes: (020.2649) Strong field laser physics; (190.2620) Harmonic generation and mixing

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1. Introduction

Harmonic generation (HG) is a particularly interesting manifestation of the interaction of ultrafast laser pulses with matter. While a large fraction of experiments are carried out in noble gas vapors, other media have attracted researchers. For instance, harmonic generation

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up to the 9th harmonic order (H9) of the fundamental was observed from a 1060 nm laser in sodium [1] vapors and up to H7 of a MIR laser was observed in semiconductor ZnSe [2] as well as liquid chloroform [3]. It is well known that the proximity of an electronic resonance [4] can enhance HG in atomic vapors. In addition to this results presented in [3] on a liquid suggest that a vibrational resonance may also offer significant enhancement.

Perturbative harmonic generation is described in terms of nonlinear polarization [5]. In the high-field limit, specifically referred to here as high harmonic generation (HHG), perturbation theory breaks down and the polarization of the medium is understood semi-classically by the three-step or recollision model [6]: (1) tunnel ionization, (2) quiver motion under the Lorentz force (3) recollision and recombination with the core and emission of a harmonic photon. In this model the harmonic high energy cutoff is easily interpreted as the maximum kinetic energy a quivering photoelectron has at the time of recollision. It is well known that both the quiver energy and amplitude scale with the square of the laser wavelength, λ_0 [7]. For example, at an intensity of 1×10^{13} W cm^{-2} the quiver energy and amplitude are 0.6 eV and 0.28 nm at λ_0 = 800 nm and 12.5 eV and 5.8 nm at λ_0 = 3.66 μm respectively. MIR laser sources are thus very effective in extending the harmonic range and conversion efficiency into the water window X Ray region [8]. Moreover, harmonics then occur at visible or near UV frequencies in the systems window of transmission, thus simplifying signal detection and characterization.

Condensed phase media present an attractive domain for HG and HHG because the solid state density promises enhanced efficiencies. However, the applicability of the three-step model is problematic in this case because the average atomic separation (0.1-1.0 nm) is smaller than the quiver amplitude. Although the concept of quiver motion with significant excursion and large kinetic energy may give rise to interesting phenomena not observed at shorter wavelengths or less dense media its relevance towards HG and HHG is questionable. In typical liquids, the electron excursion driven by a MIR laser far exceeds the global maximum, and indeed several subsequent subsidiary maxima, of the pair distribution function. The electron therefore could be perturbed on its return path to the molecule required for HHG. How such situations modify HHG is a question initially best explored experimentally.

The purpose of this work is to address these questions in liquids at the longest MIR wavelength available in our laboratory, 3.66 μm. In this paper we discuss liquid H_2O and D_2O because they are relatively simple fluids with equivalent electronic, but different nuclear structures, thus allowing an assessment of the role of vibrational resonances [3].

2. Experiment

The laser is a mid-infrared optical parametric amplifier utilizing difference frequency generation from femtosecond Ti:Sapphire and picosecond YLF amplifiers, and has been described in detail elsewhere [7]. The laser operates at a repetition rate of 1 kHz with a center wavelength of 3.66 μm, see Fig. 1(b), and generates pulses with more than 600 MW of peak power at a pulse duration of 110fs (9 optical cycles), see Fig. 1(c), full-width at half-maximum (FWHM). The power spectrum, Fig. 1(b), was obtained by measuring the coherence time from a Michelson interferometer with a linear detector placed at the output. The estimated error from this method is ± 1.5% (± 55nm) and corresponds to a ± 200 attosecond (10^{-18} s) per-step residual uncertainty from the delay stage. The error represents a fundamental limitation towards identifying spectral shifting of the harmonics. For example, H5 is located at 732 ± 11 nm while H11 is 282 ± 4.5nm. The peak intensity for these studies is estimated to be between 4×10^{13} W cm^{-2} and 8×10^{13} W cm^{-2} from similar focusing conditions performed to collect photoelectron spectra from xenon gas. We emphasize that this is the vacuum intensity since the dynamics of the condensed phase response are complex and a variety of mechanisms may alter the actual peak intensity from the vacuum intensity. It is the extreme nature of the intense laser field that distinguishes this experiment. Few studies have been performed with fluids in a regime where the material can suffer ionization induced by an ultrafast laser pulse.

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Because these peak intensities can well exceed damage thresholds of many materials we chose to use a liquid source. Our version of the apparatus created by Tauber et al. [9] consists of a 27 cm fluid column constructed from stainless steel tubing, chromatography fittings, custom glassware, and a peristaltic pump to recycle the fluid after the interaction region. At the end of the column is a narrow aperture, 2.7 mm × 0.3 mm, that holds a thin wire loop to provide enough capillarity for the fluid to form a film. Using a fluid source has the advantage of self regeneration and as described in [9] is well suited for kHz spectroscopy. Absorption measurements were performed to determine the thickness of the film at the interaction region. The thickness of the sample was 150 μm and roughly matched the Rayleigh range of the laser focus used here. The average linear velocity of the fluid was 900 μm/ms and corresponds to a Reynold's number of Re = 500. This is well within range of laminar flow (Re<2000). The fluid source remained stable over acquisitions of several hours.

Light generated from the laser-fluid interaction was delivered to a Czerny-Turner spectrometer with an intensified charge-coupled device placed at the output. The spectrometer has a maximum resolution of 1 nm and is energy calibrated from 200 nm - 800 nm within an absolute error of ± 50%. All spectra shown here were acquired over no less than 5,000 laser shots, were verified over several days of acquisition and proved to have excellent reproducibility as a function of laser intensity and fluid source.

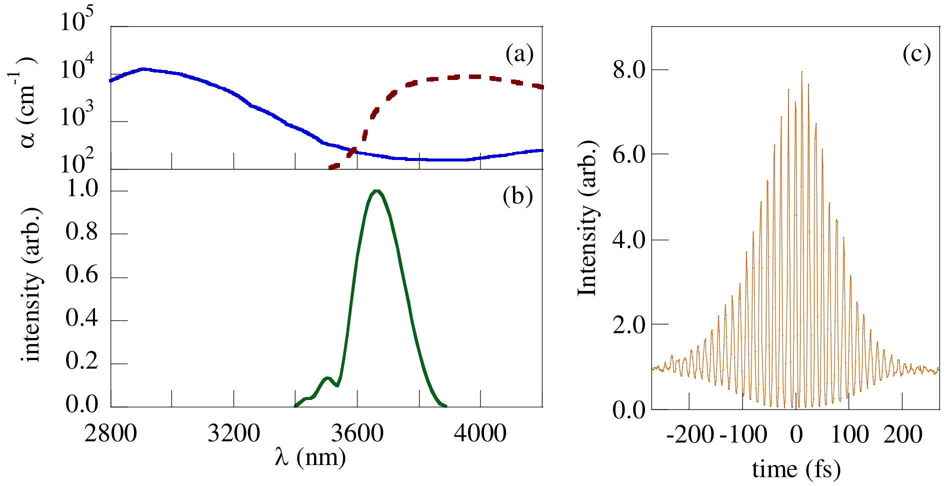

Fig. 1. (a) Absorption profile of H_2O (solid line-blue) and D_2O (dash line-red). α is the linear absorption coefficient that obeys $I = I_0\exp(-\alpha z)$. (b) The MIR power spectrum. (c) Interferometric autocorrelation with a full width-at-half maximum (FWHM) of 110 fs.

3. Results and discussion

H_2O and D_2O were chosen because of their well documented and widely accessible chemical properties and also allow a direct comparison of near resonant OH stretches ~2900 nm and OD stretches ~3900 nm in the two samples. The absorption data for water and heavy water from reference [10] is shown in Fig. 1(a) along with the power spectrum of the MIR laser. Because of the MIR pulse's proximity to resonance, absorption shifts the pulse slightly red in H_2O and strongly blue in D_2O. The calculated absorption loss is 94.7% (98%) for H_2O (D_2O).

3.1 Harmonic spectra

Figure 2(a) illustrates typical HG spectra in H_2O and D_2O at near the maximum pulse power. The highest order harmonic observed (H13 in H_2O and H9 in D_2O) as well as the slow decrease in harmonic intensity with increasing harmonic order in the spectra, suggest a nonperturbative process. However, intensity scaling, discussed below, Fig. 3, demonstrate that this is unlikely. The overall structure of the spectra is likely to be a result of the observed saturation above 270 MW of MIR power. In fact at 100 MW the harmonic intensities of H5, H7 and H9 scale by more than one order of magnitude for each decreasing order. Surprisingly, no evidence of significant spectral broadening of the fundamental or supercontinuum generation (SCG) in the near IR or visible portion of the spectrum is observed. We discuss below possible reasons for the absence of SCG, but first we will consider HG and more specifically the difference in yield, unexpected at first glance, between water and heavy water. The conversion efficiency of all harmonics is 4×10^{-6} for H_2O and 1×10^{-6} for D_2O.

As Fig. 2(a) shows, the HG spectra in H_2O and D_2O do not coincide and are slightly shifted from the values of λ_0/q where λ_0 is the excitation wavelength and q is the order of the harmonic. The other striking observation from Fig. 2(a) is that even though the electronic structure of H_2O and D_2O are identical their efficiency for producing harmonics is not. We believe that at least two distinct physical mechanisms are at play in the harmonic generation. First, there is strong spectral modulation induced on the pulse by resonant absorption from water vibrational modes that manifests as strong absorption of short wavelengths of the laser pulse in water and long wavelengths in heavy water. Phase matching can additionally skew the harmonics. Consider the total bandwidth (180 nm FWHM) of the MIR pulse, Fig. 1(b). Calculations performed in [2] demonstrate that SPM can aid phase matching by adding spectral content to the fundamental pulse. Although SPM is not substantial in our experiment the initial bandwidth is. The phase mismatch in collinear geometry is $\Delta k_q \equiv k_q - qk_0 = 2\pi q/\lambda_0 \left(n(\lambda_q) - n(\lambda_0) \right)$ and the coherence length is $L_c \equiv \pi/\Delta k_q$ [5]. Large values of L_c will result in increased conversion efficiency since destructive interference is minimal. For example, the coherence length for H9 at $\lambda_0 = 3.66$ µm in H_2O is 9.5 µm i.e. short compared to the sample thickness. At $\lambda = 3.57$ µm and $\lambda = 3.75$ µm, the FWHM ends of the spectrum, $L_c = 6.1$ µm and at $L_c = 15.3$ µm respectively. Clearly, the long wavelength side of the laser will phase-match more efficiently in H_2O because of the larger coherence length. In D_2O the corresponding values are $L_c = 0.98$ µm, 1.4 µm and $L_c = 0.9$ µm. Although the coherence length is much shorter in D_2O it is clear that the short wavelength side of the laser is preferred. Thus, absorption of the fundamental will introduce a spectral shift that aids phase matching in both samples yielding a long wavelength shifted spectrum in water and a short wavelength shifted spectrum in heavy water. However, since D_2O absorbs the fundamental more and has a shorter coherence length harmonic production is less efficient.

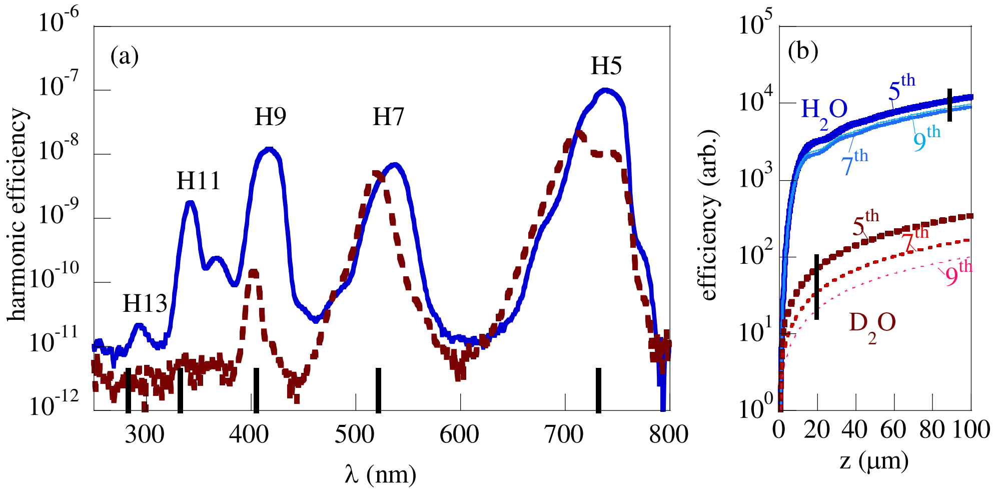

Fig. 2. (a) Heavy water (dash-red) and water (solid-blue) harmonic spectra at approximately 600 MW of MIR. The vertical bars along the wavelength axis are odd multiples of the fundamental field shown in Fig. 1 (b). (b) Efficiencies of water and heavy water considering collinear propagation with phase matching and resonant absorption. The vertical bars are the

I_{max}/10 points within the thickness of the fluid. Shown on top is H_2O (solid lines-blue) and bottom D_2O (dashed lines-red). In both cases H5 is dark, H7 is medium, and H9 is light.

We address the difference in yield in a more quantitative fashion by considering only collinear phase matching and resonant absorption. Averaging α over the entire spectrum of the fundamental and taking Δk_q at λ_0 the HG efficiency parameter, ε(L), is [3,11]

$$\varepsilon(L) = \left(\frac{2\exp\left(-\frac{q\alpha}{2}L\right)}{\left(\left(\frac{q\alpha}{2}\right)^2 + \Delta k_q{}^2\right)} \right) \left(\cosh\left(-\frac{q\alpha}{2}L\right) - \cos\left(\Delta k_q L\right) \right) \tag{1}$$

Where L is the length in the material. Since absorption of the fundamental is different in each sample, we compare propagation lengths where Gaussian focusing geometry and resonant absorption reduce the peak intensity of the field by one order of magnitude assuming the surface of the fluid experiences the peak of the laser focus. The calculated, Fig. 2 (b), (measured) efficiency ratios of H_2O/D_2O are 160 (4), 230 (1.33), and 440 (92) for H5, H7 and H9 respectively. In all three cases this simple calculation largely overestimates the yield ratio between the two samples with the best agreement observed for H9.

The total harmonic yield is determined by Eq. (1) and the medium. According to [3] a nuclear contribution to the nonlinear material polarizability from stretching resonances is responsible for the efficiency enhancement. This may be corroborated by our results since λ_0 = 3.66 μm is much closer to the OD stretches than the OH stretches. Nuclear enhancements would be expected to decrease with increasing harmonic order, according to perturbation theory, which may explain why the simple calculation agrees best with H9. We stress that this is a simplified approach limited by a lack of knowledge of how the laser propagates in the medium. Therefore, the simple treatment presented here is preferred to the more rigorous and accurate coherence mapping approach [12] that may provide better agreement, but is not likely to be the source of the measured discrepancy of one to two orders of magnitude.

3.2 Intensity Scaling

Figure 3 illustrates how the harmonic intensity experimentally scales with laser power. It is found that the harmonic intensity scales as $I_{q\omega_0} \propto I_{\omega_0}^q$ [5]. The results for D_2O (not shown) are comparable. In the perturbative limit, the nonlinear polarization of the material $P^{(q)}(t) = \sum_q \chi^q E^q(t)$ is the source for the radiated field at frequency $q\omega_0$. Each data point is the average of several data points in 10% energy increments. H5, H7, and H9 scale in the perturbative limit as described above with power laws of $I^{4.5}$, $I^{7.1}$, and $I^{8.8}$ respectively. These scaling laws hold over an order of magnitude change in intensity and seven orders in signal, down to the single photon-per-event level. In fact, the yield rates do not change until approximately 270 MW where ionization is assumed to become significant. The presence of ionization is corroborated by white light plasma emission. Further efforts are under way to establish a more robust measurement of the ionization density. The dominant contribution to H11 no longer appears to be a direct 11 photon process as is the case for the lower harmonics observed. Here the power law decreases to a value of $I^{8.1}$ indicating a clear break in the direct perturbative scaling. One possibility is that lower order indirect N-wave mixing process(es) is/are contributing to the total yield. For example, consider fifth harmonic generation from a direct process $\chi^5(5\omega; \omega, \omega, \omega, \omega, \omega)$ and an indirect wave mixing process $\chi^3(5\omega; 3\omega, \omega, \omega)$. The observed rate would then scale as a weighted average from all contributing orders and processes; here we measure $I^{8.1}$. Again the rate holds over the entire measurement up to saturation at approximately 270 MW.

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3.3 Absence of SCG

The absence of SCG is perhaps surprising, but we believe that a simple argument explains why no significant broadening occurs. We emphasize that broadening of the fundamental 3.66 µm laser to the visible would require a spectrum that spans more than two octaves. Therefore, we construct our argument by considering how the efficiency of SCG will scale with wavelength and focusing conditions in the simple limit where self-phase modulation (SPM) is largely responsible for spectral broadening. First, a medium with an intensity dependent refractive index $n = n_0 + n_2 E^2$, electric field strength E, determines a critical power $\mathrm{P}_{crit} = \pi\left(0.61\right)^2 \lambda_0^2 \big/ \left(8 n_0 n_2\right)$ [4] below which self-focusing and significant SPM do not occur. Since the critical power scales as λ_0^2 we observe that at λ_0 = 3.66 µm, P_{crit} is 20 times larger, ~40 MW, than at the Ti:sapphire wavelength of λ_0 = 0.8 µm (neglecting changes in n_2). Second, spectral broadening occurs with the accrual of nonlinear phase given by $\phi = 2\pi n_2 \mathrm{P}_0 L \big/ \left(\lambda_0 \left(Area\right)\right)$ [13] for a pulse with peak power P_0, and propagation length L. If the focusing conditions are such that the Rayleigh range is much larger than L, $\phi \propto \lambda_0^{-3}$, and spectral broadening decreases accordingly. Combining these two arguments with the fact that, even at 800 nm, experiments show minimal spectral broadening in the wings of the pulse representing only a few percent of the total power spectral density, we assert that SPM and SCG will be strongly suppressed for the experiments performed here.

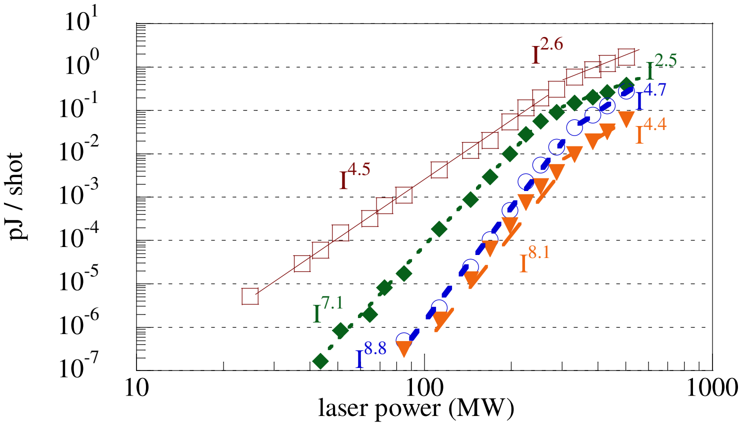

Fig. 3. The intensity of the harmonic yield is given by the peak of the harmonic field averaged to a single laser shot. The harmonic yields measured were the fifth (□-red), seventh (♦-green), ninth (○-blue) and eleventh (▼-orange).

4. Conclusions and outlook

We have observed generation of multiple odd harmonics from H_2O and D_2O irradiated by intense MIR pulses. In accordance with expectations, harmonic spectra are qualitatively very similar in both species, except for a spectral shift due to absorption and phase matching of the fundamental. The harmonic yield scales perturbatively with intensity up to H9 over a large dynamic range. H11 and H13, seen only in the saturation regime, are likely due to indirect wave-mixing processes. An unexpected difference in the harmonic yields between water and heavy water was observed and cannot be explained by absorption and phasematching alone. Tentatively, a nuclear contribution to the polarization may be invoked. The absence of SPM and SCG is, on the other hand, well understood within the conditions of the experiment. The absence of a signature for the 3-step mechanism at the high intensity, long wavelength used might mean that collisions with the surrounding molecules completely quenches this process leaving open the question of the calculation of the corresponding nonlinear susceptibilities.

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We also note that observing recollision harmonics in a condensed phase system may be further obfuscated by the electronic absorption edge of the material that rises sharply at 200 nm or H17. Future studies will explore the role of ionization in condensed phase systems as well as ponderomotive effects of free electrons.

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