

Generation and control of femtosecond pulses by molecular modulation

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(Received 13 April 2004; revision received 18 May 2004)

Abstract. We have demonstrated that coherent molecular modulation can result in the collinear generation of mutually-coherent spectral sidebands that extend in frequency from the infrared to the far ultraviolet. Our technique is based on adiabatic preparation of a highly coherent molecular superpositionstate, which is achieved by using narrow-linewidth lasers slightly detuned from a Raman resonance. The phases of the resultant Stokes and anti-Stokes sidebands are adjusted in order to synthesize desired single-cycle pulse trains at the target. In this article we review recent improvements and developments in this area, including: techniques for increasing the number of generated sidebands; synchronization of the pulse trains with the molecular motion in the given molecular system; laser self-focusing and spatial soliton formation due to the coherent interaction of light with oscillating molecules. In the future, this Raman source may produce sub-cycle optical pulses, and allow synthesis of waveforms where the electric field is a predetermined function of time, not limited to a quasi-sinusoidal oscillation.

1. Introduction

The important role of electronic pulse shaping in the microwave and radio frequency regions of the spectrum is well known. Over the last several years we have developed techniques, which allow pulse shaping in the optical and ultraviolet portions of the electromagnetic spectrum. In particular, we have made a light source that has almost four octaves of optical bandwidth, which extends from $3 \,\mu m$ in the near-infrared to at least 195 nm in the ultraviolet. In recent experiments we have used both manual and electronic techniques to control the phases of a small subset of these sidebands and to thereby make femtosecond pulses with a desired pulse shape.

The prototype system for generating a broad coherent spectrum is shown in figure 1. We apply two lasers, in this case Nd:YAG and Ti:sapphire, whose frequency difference is equal to the fundamental vibrational frequency of molecular deuterium. As explained further below, it is important that the applied

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Figure 1. Experimental set-up and energy level diagram for coherent molecular excitation and collinear Raman generation. The Raman detuning $\Delta \omega$ (positive as shown) is set by the driving laser frequencies (reproduced from [1]).

laser frequencies drive the deuterium transition (2994 cm⁻¹) slightly off resonance. The applied lasers cause the molecules to vibrate in unison. As the molecules stretch, each D₂ molecule looks more like two separate deuterium atoms and the refractive index increases. As the molecules contract, they look more like single helium atoms and the refractive index decreases. Consequently, the refractive index of the medium is modulated at the driving frequency. Light at a frequency ω_0 travelling through the medium experiences a time varying refractive index and is frequency modulated. The large modulation depth allows us to obtain between 10 and 25 sidebands with significant amplitude. By using a technique that we call *multiplicative* the total number of sidebands may exceed several hundred.

2. Background and connections to other work

Our approach to the generation of very broad spectra is an outgrowth of our work on electromagnetically induced transparency (EIT) [2]. EIT, as practiced in three state atoms, usually involves applying two frequencies whose difference is equal to a non-allowed transition of the atom [3]. Both frequencies drive a common upper state $|3\rangle$ with phases such that the population of state $|3\rangle$ is zero. In molecules we also apply two frequencies to drive a Raman transition (figure 1). But now, the equivalent of state $|3\rangle$ is a set of many states which are non-resonant and many electron volts away. A comb of Raman sidebands is produced and cumulatively interacts with the molecular system. The special properties of both the molecular and atomic systems result from the large coherence which is established on the non-allowed transition.

Of particular pertinence to the subject of this paper is the work of Korn and colleagues, who have impulsively excited a vibrational mode of SF_6 and used the resulting time-varying refractive index to produce a sequence of compressed femtosecond pulses [4]. In separate work it was demonstrated that molecular wavepacket revivals can produce frequency chirp, which in turn would allow femtosecond pulse compression by normal dispersion in a thin output window [5]. There has also been significant early work on dynamics of an intense femtosecond

laser pulse in a Raman-active medium, including predictions of 2π pulse formation and attosecond pulse generation [6]. In 1993, Losev and Lutsenko [7] suggested and demonstrated on-resonance two colour pumping, and Yoshikawa and Imasaka [8] suggested the application of multi-component Raman spectra to femtosecond time scale pulses. Rotational Raman spectra extending from the infrared to the ultraviolet have been demonstrated [9]. Hakuta and colleagues have used solid hydrogen for collinear Raman sideband generation [10]. Possible application of Raman sidebands to the synthesis of ultra-broadband solitons have been suggested by Kaplan [11] and by Yavuz *et al.* [12].

3. The role of maximum coherence

The equation governing the propagation of the individual Raman sidebands is

$$\frac{\partial E_q}{\partial z} = -j\eta \hbar \omega_q N \Big(a_q \rho_{aa} E_q + d_q \rho_{bb} E_q + b_q \rho_{ab} E_{q-1} + c_q \rho_{ab}^* E_{q+1} \Big). \tag{1}$$

The quantities ρ_{ij} are the elements of the 2 × 2 density matrix of the effective Hamiltonian. N is the number of molecules per volume and $\eta = (\mu/\epsilon_0)^{1/2}$, and j is imaginary unity; a_q , b_q , c_q , d_q are defined in [2]. The quantities a_q and d_q determine the Stark shift of the molecular states $|a\rangle$ and $|b\rangle$ (figure 1). The drive strength is determined by the coupling constants b_q and its conjugate c_q . The importance of the condition of maximum coherence now becomes clear: since a_q , b_q , c_q , and d_q are of the same order, then, as $|\rho_{ab}|$ approaches its maximum value of 0.5, the driving terms in equation (1) are almost as big as the dispersive terms. Phasematching then plays a negligible role in the generation of the Raman sidebands. By making explicit use of the expressions for the dispersive constants, we obtain conservation conditions for photons and power [2]:

$$\frac{\partial}{\partial z} \left(\sum_{q} \frac{1}{\hbar \omega_{q}} \frac{|E_{q}|^{2}}{2\eta} \right) = 0$$
$$\frac{\partial}{\partial z} \left(\sum_{q} \frac{|E_{q}|^{2}}{2\eta} \right) = -\frac{N\hbar}{2} (\omega_{b} - \omega_{a}) \left[\frac{\partial}{\partial t} (\rho_{bb} - \rho_{aa}) \right]. \tag{2}$$

As noted earlier, the applied lasers are detuned slightly from the Raman transition. This detuning establishes the sign of the molecular coherence relative to the driving beams. When tuned below resonance, as shown in figure 1, the molecular coherence is in phase with the two-photon driving field. When above resonance, the molecular coherence is in anti-phase with this field. To establish a particular molecular eigenstate, one sets the detuning $\Delta \omega$ to be greater than the linewidth of the molecular transition. One then increases the two-photon Rabi frequency until it is large as compared to $\Delta \omega$. When this is the case, the coherence $|\rho_{ab}|$ is, in essence, saturated at its maximum value of 0.5. The dispersive and driving terms in equation (1) are now of the same order. Equivalently, the distance in the cell in which one sideband is converted to another sideband is approximately the same as that distance in which the phase of the sideband would change by π due to refraction. For this reason the role of phasematching, as compared to more traditional nonlinear optics, is greatly reduced. The sidebands are generated much like they would be in a microwave driven LiNbO₃ light modulator. Because



Figure 2. Spectrum generated in the set-up of figure 1 at (a) P = 71 torr and $\Delta \omega = -400$ MHz, (b) P = 71 torr and $\Delta \omega = 100$ MHz, (c) P = 71 torr and $\Delta \omega = 700$ MHz and (d) P = 350 torr and $\Delta \omega = 700$ MHz. We see the two driving infrared fields (on the left) and multiple generated visible and ultraviolet anti-Stokes sidebands. To reduce camera saturation, the driving beam at 807 nm and the first five anti-Stokes beams are attenuated (reproduced from [1]).

these sidebands propagate collinearly, it is possible to disperse them, independently adjust their phases, and then recombine them.

4. Generated spectra

We begin by describing the spectrum obtained with the set-up of figure 1 [1]. In this experiment we drive the vibrational transition of deuterium at 2994 cm⁻¹. The D₂ cell is cooled by liquid nitrogen to T = 77 K, with a length of the cooled region of about 50 cm. Cooling reduces the Doppler line width to 260 MHz and increases the population of the ground rotational state of D_2 to 60%. We use Q-switched injection-seeded lasers with pulse lengths in the 10 to 20 ns range at a repetition rate of 10 Hz. We estimate the laser line widths to be under 50 MHz. The energy of the Nd:YAG laser is about 100 mJ and the energy of the Ti:sapphire laser is about 75 mJ. The laser beams are combined on a dichroic beam splitter and are loosely focused to a nearly diffraction-limited spot in the D_2 cell. When we tune the driving lasers to within 1 GHz of the Raman resonance, we see a bright beam of white light at the output of the D_2 cell. At a D_2 pressure of 50 to 100 torr and a Raman detuning of a few hundred MHz we observe, in addition to the two driving frequencies, up to thirteen anti-Stokes sidebands and two Stokes sidebands. These sidebands range from 2.94 µm to 195 nm in wavelength. The next (fourteenth) anti-Stokes sideband has a wavelength of 184 nm and is absorbed by air. Typical Raman spectra are shown in figure 2.

In general we find that the broadest spectrum with the most power is obtained by tuning below resonance. This detuning establishes a vibration which is in phase with the two-photon excitation of the driving lasers. This broader and more powerful spectrum obtained with the phased state is possibly a result of Raman self-focusing in the medium.

We may also obtain broad spectra by making use of rotational Raman transitions. Figure 3 shows the spectrum produced by the 587 cm⁻¹ rotational transition of H₂ at P = 250 torr [13]. Here we drive the H₂ transition with two Ti:sapphire



driving lasers

Figure 3. The generated rotational spectrum of H₂ (at P = 250 torr) at Raman detuning values of (a) $\Delta \omega = -80$ MHz; (b) $\Delta \omega = 0$; and (c) $\Delta \omega = 280$ MHz. The marked middle portion is attenuated to reduce camera saturation. For below-resonance excitation, we observe generation of twenty-seven anti-Stokes and eight Stokes sidebands in addition to the driving lasers (reproduced from [13])).



Figure 4. (a) Pulse energies for the vibrational spectrum of figure 2 (produced in D_2 at P = 71 torr). The triangles show on-resonance generation ($\Delta \omega = 0$), the circles show generation by phased ($\Delta \omega = 500$ MHz) and the squares by anti-phased ($\Delta \omega = -200$ MHz) states of D_2 (reproduced from [1]). (b) Pulse energies for the rotational spectrum of figure 3(c) produced in H₂ at P = 250 torr (reproduced from [13]).

lasers with energies of about 50 mJ and pulse lengths of about 17 and 14 ns. As in the vibrational case, the broadest spectrum with the most power is obtained at a positive detuning.

Figure 4(*a*) shows the energies of the vibrational Stokes and anti-Stokes sidebands for three different values of the Raman detuning and contrasts the on-resonance generation with generation below and above resonance. Note that we generate hundreds of μ J per pulse and a 10 Hz repetition rate at sidebands far into



Figure 5. Raman self-focusing experiment. (a) Experimental set-up and energy-level schematic. The applied pump and Stokes lasers with opposite circular polarization coherently drive the rotational Raman transition of H₂ (at P = 200 torr). As shown, the detuning $(\Delta \omega)$ is positive, exciting the phased molecular state. (b) Stokes beam defocused $\Delta \omega = -180$ MHz. (c) Stokes beam focused $\Delta \omega = 420$ MHz. These intensity profile images are captured with a CCD camera. Below each image is the vertically averaged beam profile (reproduced from [14]).

the ultraviolet. Figure 4 (b) shows pulse energies as a function of sideband number for the rotational spectrum of figure 3 (c). We obtain over thirty coherent sidebands ranging in wavelength from $1.37 \,\mu\text{m}$ in the infrared to $352 \,\text{nm}$ in the ultraviolet [13].

5. Raman self-focusing

So far we have talked about temporal variation of the refractive index which leads to generation of a broad Raman spectrum. In this section we discuss the refractive index change for individual sidebands due to Raman interaction. Depending on the sign of the Raman detuning, the molecules oscillate either in phase or out of phase with the driving beat note, and the beat note experiences either increased or decreased average refraction. Equivalently, from the frequency domain viewpoint, the applied laser fields (solid arrows in figure 1) form a Λ scheme and interact with molecules in an EIT-like manner [2, 3]. The sign of the Raman detuning determines whether the refractive index seen by the laser fields is reduced or enhanced.

This refractive index change varies over the beam's spatial profile and leads to self-focusing or self-defocusing of the driving lasers. Figure 5 shows the experimental set-up used for demonstrating this effect [14]. We drive a rotational resonance in molecular H₂ with two opposite circularly polarized lasers (termed the pump and the Stokes). The two laser beams are focused to a spot size of \approx 400 µm in the centre of a 50 cm H₂ cell, at a pressure of 200 torr. Due to angular momentum selection rules, no additional sideband generation occurs [15].

We measure the spatial profile of the Stokes beam in the far field with a chargecoupled device (CCD) array. Depending on the sign of the Raman detuning the molecular medium acts either as a positive or a negative lens, altering the beam size. Figures 5 (*b*) and (*c*) show the spatial profile of the Stokes beam for above and below resonance excitations respectively. The intensity profile plots show averages



Figure 6. Calculation of soliton collisions in H_2 at P = 214 torr for three cases. (*a*) Inelastic collision: beams collide and fuse into one soliton. The beams are launched at the collision angle of 0.003 rad. (*b*) Beams collide and disappear; collision angle of 0.006 rad. (*c*) Elastic collision: beams collide, pass through each other and remain as solitons; collision angle of 0.012 rad (reproduced from [17]).

over vertical cross-sections of the images. Here, when it is defocused, the beam is 50% larger than when it is focused.

A natural question to ask is whether the molecular medium can be driven in such a way that diffraction of the driving lasers is exactly compensated by Raman self-focusing. Our analytical and numerical analysis has shown that Raman solitons do exist and are quite stable against perturbations [16, 17]. These solitons are inherently two-colour and require driving lasers with sufficient energy and power. An example of soliton propagation and collisions are shown in figure 5. In these simulations we numerically solve the propagation equations with two transverse dimensions for the pump and the Stokes beams simultaneously with the Schrödinger equation for the molecular system. Figure 6 (*a*) demonstrates an inelastic soliton collision. Two solitons collide and fuse into one stable soliton. In figure 6 (*c*) when the collision angle between two solitons is made large enough, the two solitons pass through each other maintaining their shapes. In figure 6 (*b*), for some critical collision angle the solitons collide and disappear, as the diffraction overcomes self-focusing. The parameters for these simulations are very similar to those used in the experiment of figure 5.

6. Multiplicative technique

As in traditional mode locking, the synthesis of well-formed femtosecond and single-cycle optical pulses will require phase correction of as many sidebands as can be practically obtained. Present liquid-crystal and acoustic techniques [18] allow in excess of 1000 resolvable pixels and it is desirable to have a technique for generating a total number of sidebands which is on this order. It is also desirable that the spacing between synthesized pulses be much larger than the inverse of either the vibrational or the rotational frequency. A schematic of a technique which accomplishes both of these objectives is shown in figure 7 [20].

The essential idea is quite straightforward. Suppose that one had two lithium niobate light modulators driven at two incommensurate frequencies. If the output of the first modulator enters the second modulator then the total number of sidebands produced is the product of the sidebands that each modulator, in its own right, would generate. In figure 7, three lasers are used to drive coherent excitations in D_2 and H_2 .



Figure 7. Schematics of successive molecular modulators. A pair of lasers drives coherent vibrations in molecular D_2 , whereas another pair drives coherent rotations in H_2 . The frequency difference of the driving lasers is slightly detuned from the Raman resonance so as to adiabatically prepare the molecules in a superposition state (reproduced from [19]).

As in the lithium niobate modulator, sidebands are produced at frequencies

$$\omega_{q,r} = \omega_0 + q\omega_\alpha + r\omega_\beta,\tag{3}$$

where q and r are integers and ω_{α} and ω_{β} are the frequencies of the respective Raman transitions. The double Fourier series of equation (3) allows the synthesis of a quasiperiodic time waveform E(t). Formally, quasiperiodicity means that, for every $\epsilon > 0$, there exists a τ such that $|E(t) - E(t - \tau)| < \epsilon$, for all t. The key advantage of the quasiperiodic technique is that the number of sidebands that are produced is equal to the product of the number of sidebands generated by each Raman excitation alone. If the respective cells produce N_{α} and N_{β} sidebands respectively, then the two cells in series produce a total of $N_{\alpha}N_{\beta}$ sidebands with a bandwidth of $N_{\alpha}\omega_{\alpha} + N_{\beta}\omega_{\beta}$.

By adjusting the phases of the respective Fourier components of this spectrum, we may obtain a quasiperiodic waveform with a prescribed temporal shape. At seemingly random times, the prescribed pulse comes close to replicating itself. These replications occur with an average periodicity

$$T = (2\pi) \frac{N_{\alpha} N_{\beta}}{N_{\alpha} \omega_{\alpha} + N_{\beta} \omega_{\beta}}.$$
(4)

This average periodicity may be made quite large. For example, if $\omega_{\alpha} \approx \omega_{\beta}$ and $N_{\alpha} \approx N_{\beta}$, $T \approx \pi N_{\alpha}/\omega_{\alpha}$. For $N_{\alpha} = N_{\beta} = 30$ and $\omega_{\alpha} \approx \omega_{\beta} = 500 \text{ cm}^{-1}$, the average periodicity is 1 ps. Mode locking such a spectrum would produce pulses with a maximum peak power enhancement of about nine hundred. This waveform will have pulses within 80% of maximum enhancement on average once every several picoseconds with smaller amplitude pulses occurring more frequently.

Figure 8 shows the combined ro-vibrational spectrum obtained from the mixture of D_2 (P = 60 torr) and H_2 . (P = 30 torr) [19]. Two hundred sidebands are generated and range in wavelength from $1.06 \,\mu$ m to 195 nm. When the width of the generated rotational spectrum exceeds the width of the vibrational spacing, interleaving sidebands are produced. These interleaving sidebands are shown in part (c) of figure 8.

The multiplicative technique offers increased spectral density and freedom from phase-locking of the driving lasers in exchange for a quasiperiodic waveform.



Figure 8. The combined ro-vibrational spectrum: (a) two hundred sidebands are generated ranging from $1.06 \,\mu\text{m}$ to $195 \,\text{nm}$ in wavelength. The spectrum extends to $3 \,\mu\text{m}$ in the infrared (not captured by the CCD camera). Certain parts of the spectrum are attenuated by neutral density filters to reduce CCD camera saturation. The D₂ pressure is 60 torr and the H₂ pressure is 30 torr. (b) Expansion of the visible portion of the spectrum of part (a). (c) Further dispersion of the vibrational violet sideband shows two interleaving sidebands that result from the quasiperiodic nature of the spectrum (reproduced from [19]).

The quasiperiodicity is a consequence of the limited choice of accessible strong Raman transitions. However, a variation on this technique could generate a precisely periodic waveform by making the ratio of the two modulation frequencies equal to a ratio of small integers, and by generating enough sidebands to produce an equidistant comb of sidebands with comparable amplitudes. Experimentally this could be accomplished, for example, by choosing larger Raman detunings and increasing laser intensities, possibly by using shorter laser pulses of the same total pulse energy.

7. Additive technique

The multiplicative technique, while giving a large increase in the number of generated sidebands, will usually produce quasiperiodic waveforms, as noted above. A simple technique described below will allow synthesis of precisely periodic waveforms (with increased period), as required by many applications that rely on precise field control [21]. This technique relies on molecular modulation by a single modulator (at a single molecular frequency), but assumes that extra laser fields (in addition to the two driving fields that establish the Raman coherence) are applied at the input of the molecular cell, as suggested by Wu and Zeng [22]. We call this technique *additive* because, as opposed to the multiplicative technique, the number of sidebands produced by each of the extra fields simply adds up to that generated by the driving fields.

For experimental convenience, the number of independent tunable lasers can be kept down to two, and additional fields can be obtained by harmonic generation and frequency mixing. The appropriate choice of the fundamental frequencies is crucial and determines the ability to produce a comb of Raman sidebands that is equidistant and, in addition, possibly 'hits zero frequency exactly' (the sideband frequencies are equal to integer multiples of their frequency difference). For the last case, the phase of the carrier under the envelope (as defined in [23], and otherwise known as the absolute phase) will be identical for all pulses in the synthesized train, allowing for a greater control over the laser field.

We model the generation process numerically for a vibrational Raman transition in H₂ ($\omega_m = 4160 \text{ cm}^{-1}$). We solve the propagation equations for laser fields together with density matrix equations for the Raman transition, which is driven



Figure 9. Additive increase in the number of sidebands produced by molecular modulation. Parts (a), (b) and (c) show generation with only two input fields (for comparison). Parts (d), (e) and (f) show sideband generation when five fields with proper frequencies are applied at the input. Parts (a) and (d) show the applied spectrum; parts (b) and (e) show the spectrum at the output of the H₂ cell (20.4 cm long, 250 torr pressure); and parts (c) and (f) show the instantaneous power density versus time after phase correction. The insert in (f) gives $|E(t)|^2$ on a finer time scale, showing an individual single-cycle pulse with a subfemtosecond duration.

by a combination of field pairs such that their frequency sum or difference is equal to the modulation frequency [21]. For comparison, we first model this process with only two input fields (figures 9(a)-(c)). After the phases of these sidebands are made equal, they synthesize a train of single-cycle pulses, with a repetition rate equal to the molecular frequency (figure 9(c)). This result is similar to figure 7 from [24], which considered sideband generation in D₂.

Figures 9(d)-(f) show the results for the same cell length and pressure and five input fields. The fundamental fields are applied at $2.25\omega_{\rm m}$ (1068 nm), $2.75\omega_{\rm m}$ (874 nm), their sum at $5\omega_{\rm m}$ (480 nm) and their second harmonics at $4.5\omega_{\rm m}$ (534 nm) and $5.5\omega_{\rm m}$ (437 nm) respectively. In this simulation we take all the phases of the input fields equal to zero. Figure 9(e) shows roughly four times more spectral sidebands generated at the output (compared to figure 9(b)), resulting from interleaving frequency combs. After the phases of these sidebands are made equal, they synthesize a train of single-cycle pulses (figure 9(f)) with a $4\times$ increased repetition period, and an increased intensity (compared to figure 9(c)). This idea can be easily extended to the case when the desired frequency spacing is one ninth of the molecular modulation frequency $\omega_{\rm m}$, by allowing third-order nonlinear mixing processes to produce more frequencies at the input of the Raman cell [21].

In the present simulation, we allow for arbitrary phases of the generated sidebands, but assume that they are adjusted afterward by a spectral modification apparatus [18] and made equal to zero. Since the laser frequencies are now a multiple of their frequency difference, the absolute phase for a pulse train will



Figure 10. Experimental set-up and energy level diagram for collinear Raman generation, synthesis of FM and AM light, and detection of the modulation (reproduced from [25]).

be fixed. However, this phase will change from shot to shot due to the change of the phases of the two fundamental fields. Depending on the relative value of these phases, one will be able to obtain different waveforms (e.g. sine or cosine type of pulses).

8. Phase control

To demonstrate that the collinearly propagating Raman sidebands are coherent, over their temporal and spatial profiles, we have used these sidebands to generate both amplitude modulated (AM) and frequency modulated (FM) light with a molecular modulation frequency of 2994 cm⁻¹ [25]. The experimental setup is shown in figure 10 where three sidebands are separated out from the Raman comb and propagate through the D₂ cell. The phase of one of the sidebands is varied and all three sidebands are retroreflected through a different region of the cell. We measure the intensity of the generated anti-Stokes sideband as a function of the phase of the returning 650 nm sideband. Since the Raman medium only responds to intensity variations in the driving beam, there will be no anti-Stokes radiation produced when the incident beams have FM phases. Conversely, maximum generation occurs with AM phases. The results of this experiment are shown in figure 11.

In a more ambitious experiment, figure 12, we use the Raman source to demonstrate phase control of multiphoton ionization under conditions where ionization requires eleven photons of the lowest frequency of the spectrum or five photons of the highest frequency of the spectrum [26]. As one test of mutual coherence among the sidebands, we use variable dispersion. We place a cell containing N_2 in the beam path and adjust the sideband phases such that the Xe ion signal maximizes at a N_2 one-atmosphere pressure. As the pressure is changed, the dispersion in the N_2 gas causes the sidebands to dephase and the signal is reduced



Figure 11. Anti-Stokes generation at 544 nm (arbitrary units) as a function of the relative phase φ of the three sidebands (at 1.06 µm, 807 nm and 650 nm). (*a*) Data set 1. (*b*) Data set 2, showing that additional phase retardation does not reduce the contrast. φ_0 is the unknown initial relative phase between sidebands. The solid line is a theoretical fit (reproduced from [25]).



Figure 12. Experimental set-up for multiphoton ionization of Xe with five Raman sidebands (at $1.06 \,\mu$ m, $807 \,n$ m, $650 \,n$ m, $544 \,n$ m and $468 \,n$ m). The mirror M1, which is displaced in the vertical plane, picks off the slightly off-set retroreflected beam. We vary sideband phases independently with tilted glass plates, or by varying dispersion in the N₂ pressure cell (reproduced from [26]).

as shown in figure 13. At higher pressure, the sidebands rephase and the ion signal increases.

It is expected that the five-component spectrum of figure 12, extending over an octave of optical bandwidth from $1.06 \,\mu\text{m}$ to $468 \,\text{nm}$, should correspond to single-cycle pulses which are several femtoseconds long. In figure 14 we show the results of a cross-correlation experiment, which demonstrates that this is the case. Here, we vary the delay of the 544 and 468 nm beams with respect to the 650 nm, 807 nm and $1.06 \,\mu\text{m}$ beams. This is done by tilting a glass plate, which overlaps the 544 and 468 nm beams. From this figure we infer that we are able to synthesize trains of near single-cycle pulses which have a repetition period of 11 fs and a pulse duration of about 2 fs. In the past, single-cycle (and sub-cycle) pulses were available only in the THz spectral region, with a duration of about 0.5 ps [27].



Figure 13. Number of Xe ions produced in the set-up of figure 12, versus pressure in the N₂ cell. For part (*a*) all five sidebands are present. For parts (*b*) and (*c*) we leave only three equidistant sidebands (1.06 µm, 650 nm, 468 nm for part (*b*), and 650 nm, 544 nm, 468 nm for part (*c*)). The solid line is a cubic spline interpolation of the data in part (*a*) and a sinusoidal fit to the data in parts (*b*) and (*c*). The dashed line shows $\int \left[\sum \cos(\omega_m t + \varphi_m)\right]^{12} dt$, where φ_m are determined by N₂ dispersion. For the data in part (*a*), we observe significant saturation for ion signal above 1 rel. units (reproduced from [26]).



Figure 14. Correlation of waveforms, synthesized by subsets of Raman sidebands: Experiment (solid line), time domain calculation: $\int \left[\sum \cos (\omega_m (t + \tau_m))\right]^{1/2} dt$ (dashed line) and perturbative frequency domain calculation (dotted line) (reproduced from [26]).

We have also performed correlation experiments with the multiplicative Raman source described above [19]. The experimental schematic is shown in figure 15. Here, a subset of 15 visible sidebands, which extend in wavelength from 650 to 420 nm are separated with a prism pair, passed through a liquid crystal array, and then recombined by matching prisms. The 15 coherent sidebands used in this experiment are predicted to form a train of pulses with a 3 fs pulse width and a separation of 57 fs. To test this prediction, we performed a cross-correlation



Figure 15. Experimental set-up for the temporal correlation experiment. The spectrum is spatially separated with a prism pair, which allows independent phase control of individual sidebands with the liquid crystal array. Due to the limitations of the liquid crystal, we use fifteen visible sidebands extending from 650 to 420 nm in wavelength. The sidebands are spatially recombined with another prism pair and focused into a NO ionization chamber.



Figure 16. The ion signal as a function of time delay between two pulses (electronically) synthesized by two sets of sidebands. The time delay is achieved electronically by applying a specified phase to each sideband. The solid circles are the data points and the solid line connects these points. The dashed line is a simple time domain calculation (reproduced from [19]).

measurement: initially we optimized sideband phases to give the maximum ion signal thereby synthesizing a single pulse; then starting with the 650 nm sideband and going to 420 nm sideband, we added to every other sideband a phase proportional to its frequency, effectively time delaying those sidebands. In the time domain this corresponds to synthesizing two pulses, one of which is delayed with respect to the other. By varying this time delay and measuring the ion signal, we obtain the cross-correlation which is shown in figure 16.

In these experiments the repetition period of the pulse train is equal to the molecular oscillation period (11 fs for vibrations in D_2 and 57 fs for rotations in H_2). By the very nature of the generation process, these pulses are perfectly synchronized with the molecular motion in the given molecular system, and provide a unique tool for studying molecular and electronic dynamics in that system [28]. We envision producing a coherent molecular oscillation in the target cell, applying

a tightly focused train of perfectly timed pulses and studying electronic properties as a function of molecular coordinates. Possible extensions of this general technique range from studying complicated multi-mode motion of complex molecules, to probing ultra-fast electronic dynamics in atoms.

In the frequency domain, molecular motion corresponds to a coherent superposition of molecular states. The fact that the pulse train can be synchronized with the molecular motion means that there is a possibility for different multiphoton paths, starting from different molecular levels, to interfere constructively or destructively. There is a clear analogy of this technique to EIT [3] (which relies on negation of refraction and absorption by quantum interference and allows unperturbed propagation of resonant laser beams through optically thick media): with appropriate sideband phasing (or rather 'anti-phasing') we can expect an EIT-like molecular stabilization against multiphoton ionization [29].

9. Single pulse compression

We ask a question: can molecular modulation serve to produce single ultrashort pulses with high peak intensity? At present, petawatt powers in focusable beams are obtained by the method of chirped pulse amplification (CPA) of femtosecond pulses [30]. Higher laser powers would open new horizons for fundamental studies (including relativistic nonlinear optics coupled with nuclear physics), as well as allow a number of important applications [31]. Over the last decade, continuous improvements in CPA technology have put it far ahead of other techniques, and an important question is whether molecular modulation can promise further increase in the pulse power, without reducing the beam quality. The answer is probably Yes. As shown in the preceding sections, molecular modulation allows a 100% efficient conversion from the pump beams into the broadband radiation, compressible into few-femtosecond or even subfemtosecond pulses. Moreover, our earlier work has shown that the pulse compression can occur in the same molecular gas, without the need for external phase compensation [2]. Therefore, an intriguing possibility is to combine adiabatic preparation of a large molecular coherence with application of a femtosecond pulse to be compressed.

Figure 17 shows the result of a model simulation (adapted from [32]). In this simulation a single 20 fs laser pulse (figure 17(a)) is compressed into the sub-femtosecond domain (figure 17(b)) by the coherent interaction with the molecular medium (frequency modulation, plus pulse compression by normal dispersion). Such single-pulse compression requires precise timing of the femtosecond pulse with respect to the molecular oscillation. An alternative is to use a femtosecond pulse which is a few times longer than the molecular period. With this method, the probe pulse can be compressed into a doublet or triplet of subfemtosecond pulses, by beating with an adiabatically prepared Raman coherence [33]. A still open question is whether the few-femtosecond and subfemtosecond compression of a single pulse can be combined with sub-cycle field control.

10. Sub-cycle field shaping

Femtosecond pulses, which are now available in many laboratories around the world, consist of few optical cycles and allow synthesis of shaped waveforms with controlled amplitude and frequency. These waveforms are limited to



Figure 17. Single pulse compressed into the subfemtosecond domain by molecular modulation in H_2 . (*a*) Femtosecond pulse (assumed to be properly synchronized with the molecular oscillation) at the input. (*b*) Compressed pulse at the output of the molecular medium (reproduced from [32]).



Figure 18. Non-sinusoidal waveforms synthesized by up to five frequency components, such that $e(t) = \sum_{q} e_q \cos(q\omega_m t + \phi)$, where $\phi = 0$ for parts (*a*) and (*c*), and $\phi = -\pi/2$ for parts (*b*) and (*d*); $e_1 = 0.15$, $e_2 = 0.3$, $e_3 = 0.31$, $e_4 = 0.18$ and $e_5 = 0.05$ for parts (*a*) and (*b*), and $e_1 = 0.66$, $e_2 = 0.24$, $e_3 = 0.08$, $e_4 = 0.02$ and $e_5 = 0$ for parts (*c*) and (*d*).

quasi-sinusoidal pulse shapes, with less than an octave of bandwidth. A bandwidth larger than an octave corresponds to sub-cycle time duration and provides an unprecedented opportunity to control not just the pulse envelope (amplitude and frequency as functions of time), but also the shape of the electric field itself [28].

Figure 18 shows non-sinusoidal waveforms synthesized by up to five frequency components, such that the normalized field amplitude is $e(t) = \sum_{q} e_q \cos(q\omega_m t + \phi)$, where $\phi = 0$ for parts (a) and (c), and $\phi = -\pi/2$ for parts (b) and (d). We have chosen $e_1 = 0.15$, $e_2 = 0.3$, $e_3 = 0.31$, $e_4 = 0.18$ and $e_5 = 0.05$ for parts (a) and (b), and $e_1 = 0.66$, $e_2 = 0.24$, $e_3 = 0.08$, $e_4 = 0.02$ and $e_5 = 0$ for parts (c) and (d).

Most experiments will be done in the focus of a lens or mirror, and special attention will need to be paid to the field-shape evolution throughout the focal region. As noted in [34], when a waveform is focused, the phase of each of the frequency components, and the carrier-envelope phase for the waveform as a whole, changes by $\pi/2$ (due to the Guoy phase shift). Moreover, diffraction-limited focusing enhances spectral field amplitudes by a factor proportional to frequency. This amplitude change, together with the $\pi/2$ change in the carrier-envelope

phase, is equivalent to differentiation of the normalized waveform with respect to time. When a waveform propagates out of the focal (near-field) region, another $\pi/2$ of phase shift is added (while the spectral amplitude change is reversed) and the waveform appears inverted as compared to the far-field region before the focus. Gouy phase shift for few-cycle laser pulses was recently demonstrated by Lindner *et al.* [35].

When an equidistant comb of sidebands, whose frequencies are equal to an integer multiple of their frequency difference, is used for the sub-cycle pulse synthesis, the carrier-envelope phase of the individual pulses will be fixed. However, if no special measures are taken, the carrier-envelope phase will change from shot to shot (even though it will be the same for the pulses within the same train (for a single shot). In order to achieve sub-cycle shape control, one can apply a second harmonic together with the fundamental driving lasers. If laser frequencies are equal to a multiple of their frequency difference, then one of the Raman sidebands will coincide in frequency with the second harmonic. One can then select laser shots based on the interference result (constructive or destructive) of this second harmonic and the corresponding Raman sideband. It can be shown [23] that the interference provides sufficient information for determining the carrier-envelope phase.

In principle, one could stabilize the phases of two laser oscillators, perhaps by locking two external-cavity laser diodes to two longitudinal modes of an optical clock [36], and then using these diodes to injection-seed two Ti:sapphire regenerative amplifiers. If these laser phases are stabilized on the time scale of minutes, one can in principle stabilize the carrier-envelope phase of the waveform synthesized by the Raman sidebands. Alternatively, one can sort shots by the carrier-envelope phase. This sorting will be sufficient for studying absolute phase phenomena and for sub-cycle pulse shaping.

As a first application of this light source, one might look at ion and electron yields in low-pressure gases as functions of the carrier-envelope phase of the synthesized pulse trains. One can study correlations between the ion yield and the type of interference (constructive or destructive) of the second harmonic field with a high-order Raman sideband. Another possibility would be to look at the spatial distribution of photoelectrons as a function of the sub-cycle pulse shape [37]. In the experiments described above we have shown that molecular modulation provides sufficient laser intensities to produce ionization of xenon [26]. In that experiment we used incommensurate laser frequencies; as a result, different multiphoton-order processes lead to different ionized electron energy states and could not interfere with each other. When the sideband frequencies are made equal to a multiple of their frequency difference, different order multiphoton paths will interfere and absolute phase effects will come into play. At increased intensities, electron re-collision processes will become important, and a complex atomic behaviour (revealed by the ion and electron yields), as a function of the subcycle pulse shape, will be expected[†].

The possibility to produce non-sinusoidal waveforms where the electric field is an arbitrary predetermined function of time will also open new opportunities for a

[†]This idea is related to the work on phase control of multiphoton excitations using a second or a third harmonic together with the fundamental laser frequency (for references, see [38]).

direct and precise control of electronic motion in high-order harmonic generation (HHG). Very recently workers in the field of HHG have measured subfemtosecond pulses in the X-ray spectral region [39] and used these pulses to trace the relaxation dynamics of core-excited atoms with subfemtosecond resolution [40]. In a related work, it was suggested that the atomic behaviour could also be studied by an ultra-fast electron wavepacket scattering [41]. In the three-step model for HHG [42], the atomic potential is strongly perturbed by an ultra-strong laser field. A free electron is produced by tunnelling ionization and then moves under the action of the sinusoidal laser field. The electron is driven away from its parent ion and is then accelerated to a high energy as it moves back. The recollision of the electron with the ion results in the production of an attosecond X-ray burst, which in the frequency domain gives the well-known plateau spectrum for high-order harmonics with a cut-off frequency proportional to the electron's pondermotive energy. HHG is a process with a few-femtosecond 'relaxation time', which is a result of a fast spatial spread of the wavefunction for the free electron. This kind of a process is ideal for studying with high-repetition-rate pulse trains.

If in a HHG experiment one is able to adjust the sub-cycle pulse shape, one will have precise control over the electron trajectory, the recollision time and the recollision energy; that will open a range of possibilities for studying fundamental processes in atoms. Subfemtosecond control of electron trajectories was recently demonstrated by using shaped mode-locked laser pulses [43], and also by using femtosecond pulses with controlled absolute phase [44]. It was also shown that a light wave can accelerate or decelerate an electron wave packet when a sub-femtosecond ionizing X-ray pulse is timed to the phase of the light wave [45]. A particularly exciting possibility is to use sub-cycle pulses synchronized with molecular oscillations to study HHG in aligned molecules [46]. There, one will be able to observe structural changes (probed by HHG) as a molecule undergoes large-amplitude motion.

Acknowledgments

This work is supported by the US Air Force Office of Scientific Research, by the US Army Research Office, by the US Office of Naval Research, by the Fanny and John Hertz Foundation, and by the Welch Foundation (Grant #A-1547).

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