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Femtosecond to attosecond light pulses from a molecular modulator

S. Baker[1], I. A. Walmsley[2], J. W. G. Tisch[1]* and J. P. Marangos[1]

Ultrafast science has begun to tackle the measurement of electronic and chemical processes taking place on the few-femtosecond-to-attosecond timescale. This field requires high-power, extremely short-duration laser pulses. Here we review progress towards the generation of such pulses by Raman scattering in a medium whose component molecules oscillate in phase, which modulates the optical polarizability of the medium and generates high-order Raman sidebands on a field propagating through it. This process may occur with high efficiency and thus lead to sufficient bandwidth for supporting few-femtosecond to attosecond pulses. Significant progress has recently been made in the use of this technique to deliver useable ultrashort pulses in the visible to ultraviolet regions of the spectrum.

As we delve deeper into the nanoscopic world, we must understand processes that occur on ever-faster timescales. Many ultrafast molecular processes were first revealed when mode-locked femtosecond lasers reached sufficient temporal resolution, which gave birth to the field of femtochemistry[1]. Generating high-power sub-5-fs pulses in the near-infrared is now possible by utilizing self-phase-modulation in gas-filled hollow-core capillaries[2]. The availability of such short pulses has led to the emergence of the field of attoscience, which harnesses the process of high-harmonic generation to provide attosecond pulses with wavelengths in the extreme ultraviolet (EUV) and soft-X-ray regions of the spectrum[3,4]. The realization of attosecond pulses has made it possible to observe electron dynamics in matter and has provided many new insights into the ultrafast world, such as the real-time observation of electron tunnelling in atoms[5].

The shortest isolated laser pulse generated so far is 80 as (ref. 6). The emergence of such an exquisitely precise temporal probe is an impressive scientific and technical feat. As a consequence of the time–bandwidth product, the generation of attosecond pulses requires the use of radiation covering an extremely large bandwidth (a 1 fs pulse requires a supporting bandwidth of ~500 THz), which remains one of the greatest challenges in optics. Although high-harmonic generation has been a very successful technique for providing the necessary bandwidths at short wavelengths (typically 10–50 nm), attosecond pulses produced through this technique currently have low energy content because the process is relatively inefficient (with an energy conversion efficiency[3] from the laser to the harmonics of $<10^{-6}$), which typically restricts pump–probe experiments for cases when both pulses are of attosecond duration.

The fields of ultrafast time-resolved spectroscopy and attosecond science would be greatly enhanced by the availability of higher power few-femtosecond to attosecond pulses. This need is especially strong where no other sources currently exist; that is, in the visible to UV with pulses of duration from 4 fs to ~0.5 fs — for convenience we refer to these as '~1 fs pulses'. Furthermore, if ~1 fs pulses existed in the UV spectral range, new experiments that exploit electronic resonances in molecules would become feasible, and the range of optical components available at these wavelengths would enable many new measurement strategies, including interferometric methods and nonlinear spectroscopy.

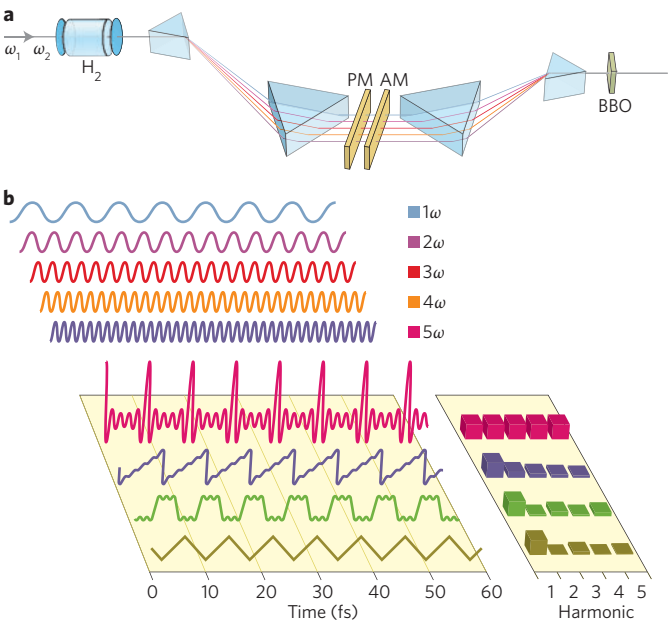

Figure 1 | Schematic of the field synthesis experiments conducted by Chan *et al.*[9] a, Experimental set-up using amplitude modulation (AM) and phase modulation (PM). BBO, β-barium borate. **b**, A schematic of waveform synthesis from five harmonics, including the generation of attosecond pulse trains of stable phase. Figure reproduced with permission from ref. 9, © 2011 AAAS.

Since the late 1990s, a family of schemes for generating ~1 fs pulses using Raman scattering[7,8] has been under development, many of which have the potential to fulfil this role. If brought to experimental fruition, the field of attoscience will be greatly advanced by the resulting range of new coherent light sources. A spectacular realization of this potential was recently demonstrated by Kung and co-workers[9], who used a pair of nanosecond pulses of frequency ω_0 and $2\omega_0$ — tuned in Raman resonance to the vibrational mode of H_2 molecules — to create a modulator that

[1]Blackett Laboratory, Imperial College London, SW7 2AZ, UK. [2]Clarendon Laboratory, University of Oxford, Parks Road, Oxford, OX1 3PU, UK.
*e-mail: john.tisch@imperial.ac.uk

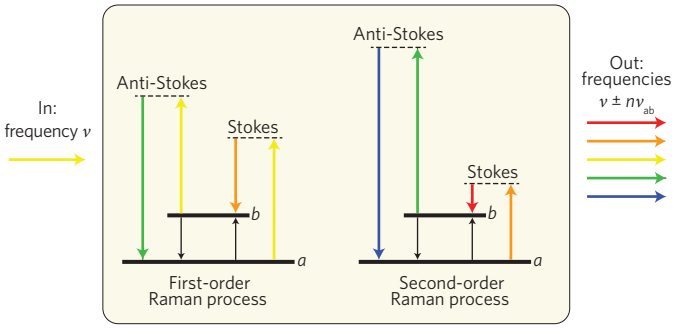

Figure 2 | The process of cascaded Raman scattering. Molecular energy levels separated by energy $h\nu_{ab}$. An input frequency ν (yellow) can cause the spontaneous emission of frequencies $\nu \pm \nu_{ab}$ (known as Stokes (orange) and anti-Stokes (green) frequencies) if the process is accompanied by a molecular transition between states $|a\rangle$ and $|b\rangle$ (black arrows). This initial spontaneous event provides the seed photons necessary for subsequent first-order stimulated Raman scattering (left). The first-order Stokes and anti-Stokes photons can then cause second-order Raman scattering (right) to produce new frequencies $\nu \pm 2\nu_{ab}$ (blue and red) and so on through propagation, resulting in a broadband ladder of frequencies $\nu \pm n\nu_{ab}$.

produced a set of phase-stable sidebands spanning multiple octaves (Fig. 1). The researchers showed that a variety of waveforms could be synthesized from the resulting phase-locked frequency comb, including trains of sawtooth, square and cosine pulses. The temporal width of the field forming the cosine pulses was measured to be less than 850 as.

The principal advantages of molecular modulation schemes are: (1) they can be used to synthesize broadband fields at visible–UV wavelengths; (2) they can be used to synthesize subfemtosecond-duration pulse trains because the pulse phases can be fully controlled; and (3) they have the potential for high-energy subfemtosecond pulse generation and even isolated subfemtosecond pulse generation in the UV, in contrast with the weaker EUV attosecond pulses generated by high-harmonic generation. This Review summarizes the current state of ~1 fs pulse generation by Raman scattering and discusses the possibilities of using this technique to produce high-power isolated attosecond pulses in the visible–UV range in the near future.

The role of coherent material excitations

Raman scattering is a two-photon inelastic scattering process in which the energy difference between the incident and scattered photons is accounted for by a molecular transition. This process can cascade (Fig. 2), leading to the generation of a broadband ladder of frequencies separated by the molecular transition energy[10]. The broadband nature of the resulting spectrum makes cascaded Raman scattering naturally suited to generating trains of ultrashort pulses[11]. Generating ~1 fs pulses by cascaded Raman Scattering becomes feasible if a high-frequency molecular modulator is prepared in the sample in which the Raman scattering will occur. Moreover, it is possible to prepare the molecular modulator using pulses at convenient optical frequencies and then modulate a field at another frequency; for example, preparation at near-infrared frequencies and then modulation of a UV field. The molecules in the modulator are made to oscillate in phase at the molecular transition frequency. Under certain conditions, the two states of the Raman transition will evolve coherently such that their quantum amplitudes possess a well-defined phase for all the molecules in the ensemble. This results in a time-dependent modulation of the vibrational and/or rotational coordinates in the ensemble that leads to an oscillation in the refractive index of the medium. This time-dependent refractive index functions as an incredibly high-frequency (up to 100 THz) modulator[12]. Materials that have large Raman scattering cross-sections (or equivalently large Raman gain coefficients) can undergo a large change in susceptibility, which leads to a high modulation index. This strongly affects the amplitude and phase of Raman scattering[13] and results in bandwidths sufficient for supporting ~1 fs pulses[14].

The relationship between the input (E_{in}) and output (E_{out}) fields passing through a modulator is $E_{out}(t) = M(t; \omega, \eta)E_{in}(t - \tau)$, where ω is the frequency of the molecular transition, η is the phase modulation depth, which depends on the fraction of molecules excited, τ is the delay of the input pulse with respect to the modulator reference, and $M(t; \omega, \eta) = e^{i\eta\sin(\omega t)}$. Two important regimes can be defined. First, when the input pulse is short compared with the modulation period ω^{-1}. In this case, the modulator response can be expanded about the peak of the input pulse $t = \tau$, so that $M(t; \omega, \eta) \approx e^{i\eta\sin(\omega\tau)[1-(\omega t)^2/2] - i\eta\cos(\omega\tau)\omega t}$. Thus, the pulse experiences a quadratic temporal phase modulation if it arrives near a maximum of the molecular motion ($\sin(\omega\tau) \approx 1$), which broadens its spectrum in proportion to the modulation index $\eta\omega^2$. The second regime is when the pulse is longer than the modulation period. In this case, the modulator response may be expanded in terms of harmonics of the molecular frequency:

$$M(t; \omega, \eta) = \sum_{n=-\infty}^{\infty} J_n(\eta)e^{in\omega t}$$

It is clear that the pulse spectrum gains several sidebands at both higher and lower frequencies, with amplitudes that are proportional to the modulation depth.

Preparation of a coherent molecular excitation requires strong two-photon coupling of a Raman transition, typically by fields which are far off-resonant for any single-photon transition (Fig. 3a). The conditions for achieving this can be met in a number of ways. Two extreme cases, known as impulsive and adiabatic, in which the preparation fields are either very short (impulsive) or very long (adiabatic) with respect to the molecular modulation, have both played a key role in the development of molecular modulators.

Impulsive preparation of the modulator, where the laser pulse is shorter in duration than the period of the Raman oscillation (generally 8–100 fs), has successfully been used to generate isolated few-femtosecond pulses in gaseous samples[15]. In this regime, the bandwidth of the applied laser pulse spans across the Raman transition, and hence the two frequencies required to excite the two-photon Raman transition are contained in a single pulse. Impulsive techniques are therefore inherently non-selective and will naturally excite any Raman mode whose frequency lies within the bandwidth of the pump pulse. Impulsive excitation involves the application of a short impulse that starts the molecules vibrating or rotating in phase. This motion then persists until after the pump pulse is no longer present for a coherence lifetime of typically many picoseconds in a gas. The applied pulse is modulated by the resulting time-dependent refractive index to produce a broad bandwidth of Raman sidebands. These sidebands overlap in frequency space to produce a continuous spectrum because each sideband possesses the same broad bandwidth as the pump pulse (Fig. 4a), thus producing an isolated, shortened pulse in the time domain.

Nanosecond pulses have also been used to prepare a very strong modulator in the adiabatic regime[12,16]. Here, the frequencies required for the two-photon coupling of the Raman transition are provided by far-off-resonant narrowband laser fields whose frequencies are precisely tuned with respect to the two-photon resonant condition (Fig. 3a). The eigenstates of the total Hamiltonian are coherent superpositions $|\pm\rangle$ of the two bare states $|a\rangle$ and $|b\rangle$

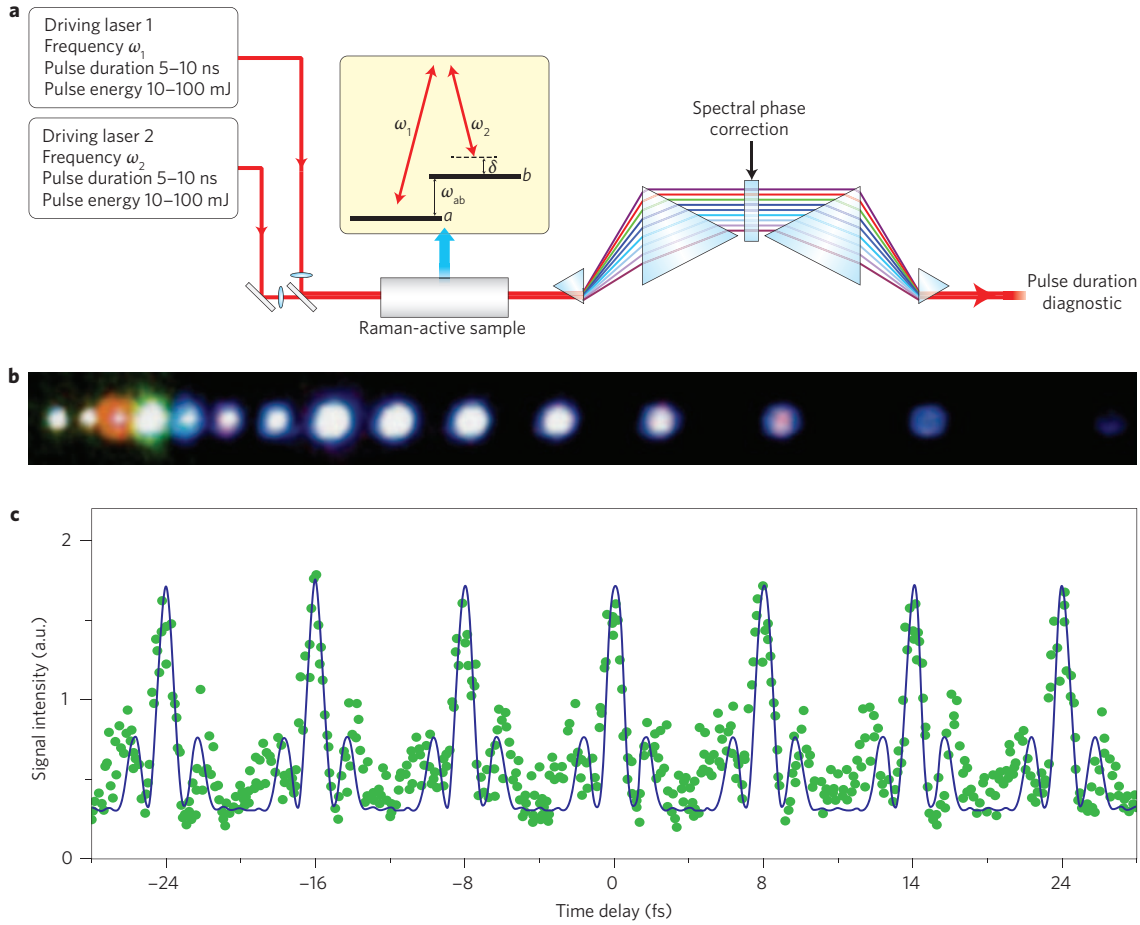

Figure 3 | Adiabatic preparation of a Raman modulator. a, Typical experimental schematic for producing a pulse train through adiabatic preparation of a molecular modulator. Two nanosecond driving fields of frequencies ω_1 and ω_2 two-photon couple a Raman transition (of frequency ω_{ab}) at a detuning of δ. Resulting coherent motion in the Raman medium produces a time-dependent refractive index that frequency-modulates the driving fields. Generated collinear Raman sidebands require spectral phase correction in order to synthesize a long train (repetition rate ω_{ab}) of transform-limited subfemtosecond pulses. **b**, Multiple collinear Raman sidebands covering the UV, visible and near-infrared from a vibrational molecular modulator prepared in D_2 gas using nanosecond driving fields at 1,064 nm and 807 nm. **c**, A train of 1.4 fs pulses with constant carrier–envelope phase offset, generated by modulating nanosecond driving fields at 602 nm and 802 nm, which prepare a coherent vibration in H_2. Figure reproduced with permission from: **b**, ref. 39, © 2002 APS; **c**, ref. 41, © 2008 APS.

involved in the Raman process $|\pm\rangle = \cos(\theta(t))^{(\pm)}|a\rangle + \sin(\theta(t))^{(\pm)}e^{-i\varphi}|b\rangle$, where the mixing angle θ is determined by

$$\tan\theta(t)^{(\pm)} = \frac{2|\Omega_{ab}(t)|}{\Omega_{aa}(t) - \Omega_{bb}(t) + \delta \pm \sqrt{(\Omega_{aa}(t) - \Omega_{bb}(t) + \delta)^2 + 4|\Omega_{ab}(t)|^2}}$$

$\Omega_{aa}(t)$ and $\Omega_{bb}(t)$ are the Stark shifts of levels $|a\rangle$ and $|b\rangle$, $\Omega_{ab}(t) = |\Omega_{ab}(t)|e^{-i\varphi}$ is the two-photon Rabi frequency and δ is the detuning of the applied fields. Expressions for Ω_{aa}, Ω_{bb} and Ω_{ab} can be found in ref. 16. In this regime, the eigenstates of the system smoothly evolve to form a superposition of the two states involved in the Raman process with equal probability amplitudes (a maximally coherent superposition) as the field amplitudes increase ($\tan\theta \to 1$), after which they return to being bare molecular states at the trailing edge of the pulses. Unlike in impulsive schemes, the coherent excitation does not survive after the driving pulses have departed. The strength of a coherent modulator that is close to a near-maximally coherent superposition state with equal populations in both levels is so great that efficient modulation of the driving fields into multiple sidebands occurs within a single coherence length. This process is examined in detail in refs 16–18, and has recently allowed the generation of long trains of few-femtosecond pulses by controlling the carrier–envelope phase offset, φ_{ce} (Fig. 1a)[19,20]. This parameter is important for pulses approaching the single-cycle regime because its variation strongly affects the form of the pulse's electric field, which is given by $E(t) = E_0(t)\cos(\omega t + \varphi_{ce})$.

Isolated femtosecond pulses in the impulsive limit

Impulsive excitation of a coherent modulator requires pulses in the femtosecond regime. Early theoretical and numerical work that examined this regime predicted the generation of ultrabroadband half-cycle pulses[21]. Owing to the extreme brevity of these pulses, it has been necessary to develop simulation approaches that go beyond the usual slowly varying envelope approximation. A pulse whose energy density is sufficient to generate a strong molecular excitation (~100 J cm^{-2}; ref. 22) will have such a high intensity that nonlinear processes such as self-phase-modulation and self-steepening will be induced as it propagates. The back reaction of the sidebands in the generated field incident on the modulator has been identified as an additional spectral broadening mechanism[23]. These effects compete with the Raman process and degrade the efficiency of frequency modulation[24,25]. To circumvent this problem,

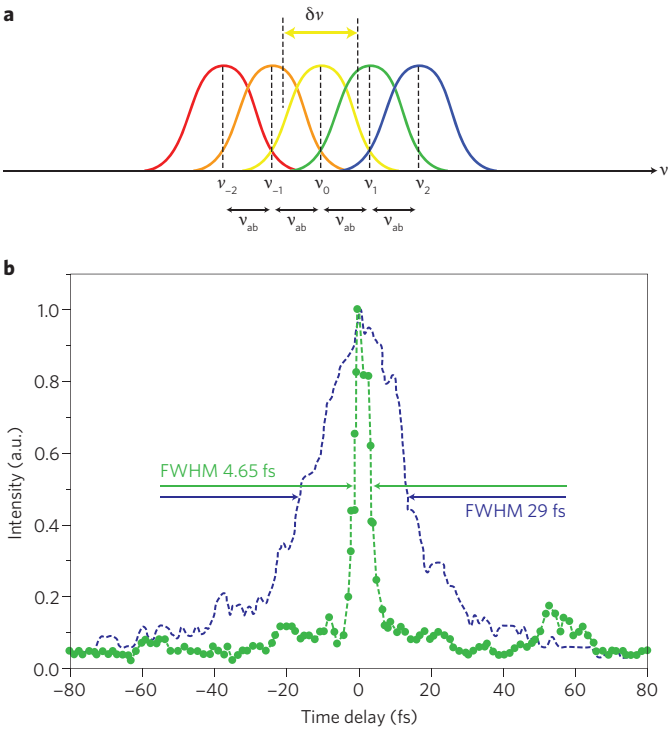

Figure 4 | Impulsive preparation of a Raman modulator. a, Production of a continuous spectrum by impulsive Raman Scattering. Input pulse at frequency ν_0 (yellow) has a bandwidth $\delta\nu$ that is greater than the Raman shift frequency ν_{ab}. As such, Stokes (ν_{-1} (orange) and ν_{-2} (red)) and anti-Stokes (ν_1 (green) and ν_2 (blue)) sidebands overlap in frequency space. **b**, Isolated 3.8 fs pulse generation by impulsive excitation of a coherent vibrational modulator in SF_6 (period of 43 fs). A 30 fs pump pulse of intensity 10 TW cm^{-2} was used. Raman scattering of a time-delayed 15 fs probe pulse in the pre-prepared medium produces the isolated pulse shown. Figure **b** reproduced with permission from ref. 15, © 2002 APS.

a separate, time-delayed weaker probe pulse can be injected into the sample. This may experience efficient Raman scattering by virtue of the molecular excitation that is present following propagation of the pump pulse, without suffering significant nonlinear propagation effects[22,26]. Researchers have predicted that this approach could provide sufficient bandwidth to support a ~1 fs pulse. Moreover, by adjusting the injection time of the probe so it arrives at the optimum phase in the modulator, it is possible to achieve pulse compression[27–29] because the modulator-induced refractive index compensates for dispersion of the ultrahigh-bandwidth pulse.

The impulsive technique has allowed isolated 3.8 fs pulses, centred at around 400 nm, to be generated through excitation of a vibrational mode in SF_6 (Fig. 4b)[15]. Impulsive rotational excitation and subsequent Raman scattering of a probe pulse has also been investigated in H_2 (ref. 30). Impulsive rotational Raman scattering in N_2 was experimentally shown to modulate in the UV, resulting in the high-efficiency production of 23 fs pulses from significantly longer injected pulses at 266 nm (ref. 31). These results have not yet been improved upon in terms of the generation of shorter isolated pulses; further progress will require the generation of a wider spectrum of probe field sidebands. Generating a broader spectrum cannot be achieved simply by increasing the energy content of the probe pulse because of the detrimental nonlinear processes that result; instead, schemes must implement either a higher frequency Raman transition or a stronger molecular modulator. However, in such cases the phase mismatch between the molecular modulation wave and the Stokes and anti-Stokes sideband fields will still limit the efficiency and bandwidth of the generated field. Preparation of a very strong modulation is required to ensure that the full bandwidth of the modulator can be realized in a length that is short enough not to be limited by phase-mismatch effects.

The fundamental vibrational transitions of H_2 or D_2, which have periods of 8 fs and 11 fs, respectively, are the fastest molecular motions available and have been shown to be effective for use in Raman scattering. Impulsive excitation of these transitions therefore offers strong potential for reducing the pulse duration of the pump–probe scheme by generating a wider spectrum of probe field sidebands. However, because the pulse duration required for efficient impulsive excitation is significantly shorter than the period of the Raman transition used[15], excitation of these high-frequency transitions is expected to require pump pulses with durations of 5–8 fs, and has not yet been demonstrated. It was recently shown that the strength of an impulsively excited rotational coherence in H_2 can be amplified without dephasing by applying a high-energy multimode nanosecond pulse to the system before subsequent propagation of the ultrashort probe pulse[32]. This method, which amplifies the strength of the modulator, has the potential to improve the impulsive excitation technique towards the generation of subfemtosecond pulses.

Researchers have also demonstrated the highly efficient frequency modulation of a single 0.1–5 ps pulse to produce bandwidths sufficient for supporting subfemtosecond pulses[25,33,34]. In this case, a small amount of self-phase-modulation spectrally broadens the pulse to produce the Stokes frequency required to drive the molecular motion coherently with a pair of Raman resonant fields. The application of two-colour external fields in Raman resonance has also been used for the excitation of coherent molecular rotations and vibrations using femtosecond pulses longer than the Raman period. This method of producing sufficient bandwidth to support subfemtosecond pulses has been both predicted[23] and demonstrated[35,36]. Although these schemes have led to the realization of very broad bandwidths, the long duration of the pump pulse results in the generation of a train of shortened pulses, rather than an isolated pulse. However, two-colour excitation of a coherent modulator in the femtosecond regime generates coherent motion after the pump pulses have departed, and may be applicable to modulation of a time-delayed probe pulse[37], which, if of a duration shorter than the Raman period, would result in the generation of an isolated ultrashort pulse. The characterization of ~1 fs pulses, both isolated and in pulse trains, still remains a challenge, although methods exist that can in principle provide a solution to this problem[38].

Generation of trains of subfemtosecond pulses

The molecular excitation produced by adiabatic preparation is typically stronger than that achievable through impulsive techniques because the entire laser pulse energy is applied at the appropriate frequency to contribute to the preparation of the coherence. Bandwidth production is also enhanced compared with impulsive techniques because the frequency of the excited Raman transition is not limited by the bandwidth of the pump pulses, and thus it has been possible to access very large Raman shifts to produce bandwidths spanning the entire UV, visible and near-infrared range (Fig. 3b) without needing to employ sub-10-fs pulses[18,39,40]. The generated bandwidth can be extended if the second harmonic of one of the driving fields is also injected into the system[19]. The high degree of molecular coherence that can be produced in the adiabatic limit ensures high gain over a short distance, which significantly overcomes the problem of phase mismatch.

By virtue of the narrowband nanosecond driving fields required for adiabatic preparation, the Raman spectrum produced in this regime is comprised of discrete components. In the time domain, these form long trains of ~10^6 relatively low-energy (nanojoule level) but potentially subfemtosecond pulses. Researchers recently

demonstrated trains of 1.4 fs pulses, in which the comprising pulses had a common (but uncontrolled) carrier–envelope phase offset by coherent preparation of the vibrational transition in H_2 (Fig. 3c; ref. 41). Control over the carrier–envelope phase offset of the pulse train has also been demonstrated[19,20]. However, these studies did not measure the temporal form of the pulses and thus were unable to determine the pulse duration.

In all time-domain demonstrations of near-transform-limited pulse train production from an adiabatically prepared molecular modulator, it has been necessary to implement a form of spectral phase control of the generated sidebands. A common method for external phase control is to employ a liquid-crystal array, which has great flexibility and ease of use. However, the usable wavelength range of a liquid-crystal array is limited to the visible and near-infrared range. Pandiri *et al.*[42] recently demonstrated a compact system for phase control based on pulse propagation through angle-controlled fused silica plates, which can be applied to 48 discrete wavelengths extending into the UV. This system may prove to be an effective method of overcoming the limitations of a liquid-crystal array, thus allowing the pulse duration to be decreased and the energy content of the pulse trains to be increased.

Researchers recently produced a subfemtosecond pulse train controllable using the carrier–envelope phase offset from an H_2 modulator[9]. The drive fields must be commensurate in such a scheme; that is, one frequency must be an integer multiple of the other to ensure that a phase-locked frequency comb is produced. The researchers achieved this by driving the H_2 molecules with transform-limited nanosecond fields at 2,406 nm and its second-harmonic at 1,203 nm, thus ensuring that the frequency difference was situated at the vibrational Raman transition of 4,155 cm^{-1}. The relative phases of the five harmonics (2,406 nm, 1,203 nm, 802 nm, 602 nm and 481 nm) produced in the process were controlled using liquid-crystal pulse shapers located between a prism pair (Fig. 1). The phases were set to the required values using a heterodyne signal generated by frequency-mixing pairs of the harmonics at a $LiNbO_3$ crystal[43]. The synthesized waveforms were then confirmed by using a linear cross-correlation technique between the desired waveform and a small reference waveform of sub-cycle cosine pulses, which was also generated by the pulse shaper. This waveform characterization method and the use of commensurate drive frequencies to ensure phase stability were the key steps in the realization of this first fully controlled ultrafast waveform synthesizer. This technique can now be used to produce subfemtosecond pulse trains.

In studies of ultrafast phenomena, isolated pulses are generally more useful than the very high repetition rate pulse trains produced by adiabatic schemes, as the interval between pulses in the train (for example, 8 fs from a H_2 modulator) does not allow the dynamics under study much time to evolve. However, adiabatic schemes generate a very strong molecular modulator, and thus many studies have discussed the possibilities for exploiting this property for the generation of an isolated subfemtosecond pulse. Researchers have proposed that a weak ultrashort probe pulse injected (while the drive pulses are present) into a molecular modulator prepared in the adiabatic regime will experience enhanced Raman scattering, thereby generating a broad bandwidth of probe field sidebands. If the duration of the probe field is shorter than the period of the Raman transition, the resulting spectrum will be continuous and may form an isolated subfemtosecond pulse in the time domain[23,44–46]. This proposal therefore combines the advantages of both the impulsive and adiabatic schemes for coherent preparation.

These promising approaches have not yet reached experimental fruition. Frequency modulation of a weak broadband (300 cm^{-1}) probe field by an adiabatically prepared coherent molecular vibration in solid H_2 has been demonstrated[47], and the broadband nature of the resulting Raman sidebands has been confirmed. However, in this work the probe field was provided by a free-running laser source and thus was not in the femtosecond regime. Although efficient frequency modulation of a ~130 fs probe laser in a molecular modulator prepared by adiabatic techniques has been observed[48], the temporal form of the pulse formed by the output probe field sidebands was not measured directly.

New hosts for molecular modulation

The development of molecular modulators located in guiding structures is important for decreasing the power requirements of the driving lasers. Gas-filled hollow-core capillaries have been used for some time to increase the interaction length available in Raman scattering experiments[15,35,36,49,50] — a parameter that is limited in free space by diffraction of the laser beams. Hollow-core capillaries also allow group velocity matching between pump and probe pulses of different wavelengths in order to improve modulation of the probe pulse[51]. However, these capillaries (typically 0.2–1 m in length) are subject to coupling and propagation losses and optical damage, which limits the maximum input energy to the few-millijoule level. Sensarn *et al.* compared the performance of a system based on adiabatic excitation of a molecular modulator in a hollow capillary with that under free-space conditions[52]. With optimized focusing, comparable generation of anti-Stokes sidebands were generated in both systems. However, the use of a capillary allowed this level of enhancement to be achieved with only 6 mJ of energy in the driving fields — significantly less than the ~100 mJ required in free-space experiments.

Gas-filled hollow-core photonic crystal fibres (HC-PCFs[53–55]) present further opportunities for significantly increasing the effective field intensity over the interaction length in Raman scattering experiments. In these fibres, light is guided through a hollow core surrounded by a silica cladding that contains an array of holes running down its length. HC-PCFs with tailored optical properties and remarkably low transmission losses can now be reliably manufactured at lengths reaching many tens of metres[56–58]. HC-PCF gas cells can now also be manufactured[59]. The guiding mechanism in an HC-PCF depends on the type of fibre in question. Guiding in the first HC-PCF[53] was due to a photonic bandgap effect[60]. Although efficient Raman Scattering has been demonstrated in such a fibre[61–65], it is not suitable for subfemtosecond pulse generation owing to the limited bandwidth of the photonic bandgap (50–70 THz).

Careful design of the cladding structure has enabled the production of a Kagome lattice HC-PCF whose extended transmission bandwidth supports cascaded Raman scattering[54]. The guidance mechanism in this fibre[66,67] does not occur through the photonic bandgap effect; instead, inhibited coupling between the core and cladding modes, which cannot interact due to the strong transverse-field mismatch between modes, is thought to play an important role[67]. Kagome lattice HC-PCFs also exhibit very low chromatic dispersion[55] — an important property in two-colour Raman scattering experiments that require long interaction lengths. Such fibres have allowed the generation of a multi-octave-spanning spectrum covering 325–2,300 nm using a single pulsed laser of duration 12 ns and remarkably low peak power (40 kW)[68]. The output of such a system in the time domain has yet to be experimentally characterized. In this scheme, achieving a high enough gain to realize cascaded Raman scattering does not require a seed pulse or coherent preparation. Although very high conversion efficiencies have been achieved, the energy content of the output remains low because the pump energy was of the order of a nanojoule. In these experiments, the driving fields used for Raman scattering were around 1 ns in duration[68], thus producing a train of pulses in the time domain. It was recently shown that high-power femtosecond pulses can be guided in short lengths of HC-PCFs without causing damage[69,70]. The use of HC-PCFs therefore has the potential to produce high-energy isolated subfemtosecond pulses, although Raman scattering in the femtosecond regime has yet to be investigated in an HC-PCF.

Coherent preparation in HC-PCFs may allow the generation of very broad spectra. A strong molecular modulator has yet to be prepared in an HC-PCF. Two-colour coherent excitation of a vibrational Raman mode in methane has been demonstrated in a 25-cm-long HC-PCF using a 40 ps chirped pump pulse and a continuous-wave Stokes beam[71]. However, higher-order Raman sidebands were not generated in this work, possibly because only a small fraction of the pump pulse energy was able to prepare the modulator owing to the narrowband nature of the input Stokes pulse.

The strong coupling exhibited by hollow-core photonic fibres was recently used to realize multi-octave-spanning frequency combs through spontaneous creation of stimulated Raman scattering in a hydrogen-filled fibre. This development is important because comb generation is initiated from quantum zero-point fluctuations of the spectral components. These have large phase and energy fluctuations[72], but exhibit strong self- and mutual coherence. This suggests the generation of optical frequency combs with non-classical correlations between comb lines. The recent demonstration of continuous-wave modulation by D_2 molecules in a high-finesse cavity resonant with the pump and Stokes fields also has the potential to advance comb generation to the quasicontinuous limit[73].

A high-density solid-state medium has the potential to ensure a high conversion efficiency over a short distance. Raman-active crystals have recently been investigated as hosts for Raman scattering in the presence of a coherent material excitation by two-colour excitation of a Raman mode (phonon) in the femtosecond regime[74–78]. Application of 50-fs-duration pump and Stokes fields in diamond, which exhibits very large Raman shifts, has allowed the generation of a spectrum capable of supporting a 0.5 fs pulse[77]. The mutual coherence of the sidebands was also experimentally confirmed. Very broad bandwidths — corresponding to the highly efficient generation of high-order anti-Stokes sidebands — have also been generated in $PbWO_4$ (ref. 75) and $KNbO_3$ (ref. 76) by two-colour excitation of Raman modes. Impulsive excitation has been shown to be effective for generating large bandwidths in Raman-active crystals[79]. The use of time-delayed pairs of chirped pulses has also allowed particular selected Raman modes to be excited in these systems[80].

Raman-active crystals have higher Raman gain and a larger number of closely spaced Raman modes than gases. These properties cause the generated spectrum to be partially continuous in nature and thus more suited to synthesizing an isolated attosecond pulse. However, because solids exhibit larger dispersion than gases, phase-matching must be employed to generate Raman-shifted components. This means that the driving fields must be applied in a non-collinear geometry and that the output sidebands emerge at a spread of angles. With careful alignment it is possible to spatially recombine the output to form a temporally compressed waveform. Isolated 13 fs pulses have been generated in this way by two-colour excitation of Raman modes in $KTaO_3$ using 200–300 fs driving pulses[78]. This work indicates that the recombination of spatially separated sidebands covering larger bandwidths than those achieved in ref. 77 may be experimentally feasible. This technique therefore has significant potential for the generation of isolated subfemtosecond pulses in the near future.

Future prospects

Generating trains of carrier–envelope phase-controlled subfemtosecond pulses by modulating fields in a medium that contains a coherent molecular motion prepared by adiabatic processes is now experimentally feasible. It is anticipated that this method can find widespread use in optical waveform synthesis and a range of ultrafast measurements. However, one significant drawback of this technique remains: long trains of low-energy pulses are produced at a very high repetition rate. For many applications in ultrafast science, isolated subfemtosecond pulses are desirable. The strength of modulation prepared adiabatically by these phase-locked techniques is sufficient to efficiently modulate an ultrashort pulse at a different frequency. Modulation of a UV femtosecond probe pulse in a medium that has been pre-prepared with coherent molecular modulation also offers the potential for the synthesis of isolated ultrashort pulses in the mid-UV[15,30,48,81–83]. In principle, it is possible to generate an isolated subfemtosecond pulse using this technique. This will require locking between the phase of the nanosecond fields preparing the modulator and the arrival time of the ultrashort pulse.

Preparing a molecular modulator by impulsive techniques also has the potential for producing isolated subfemtosecond pulses; the broadband nature of the preparation pulse causes the cascading Raman scattering to produce a continuous modulated spectrum, which can be used to synthesize an isolated pulse in the time domain. The shortest pulse generated using this technique is of duration 3.8 fs (ref. 15). A key advance in impulsive schemes would be the preparation of higher frequency modulators. Utilizing the fundamental vibrational transitions in H_2 (125 THz, 8 fs) or D_2 (90 THz, 11 fs) seems to be a promising route[81,82,83], and will require pump pulses of around 5–8 fs in duration. Such pulses can now be produced in the near-infrared regime by employing self-phase-modulation in hollow-core capillaries[2] — a technique shown to be capable of generating sub-4-fs pulses[84]. Over the past decade, the pulse energy provided by the ~30 fs near-infrared pump lasers used in self-phase-modulation has increased greatly, now allowing a single laser source to drive two hollow-core capillaries in parallel. This has allowed the generation of pump and probe pulses, both with durations of around 5 fs for impulsive Raman scattering of high-frequency vibrational transitions, for which the relative timing is not subject to electronic jitter. This is an essential development that ensures the generated output is similar from shot to shot, as the delay of the probe with respect to the pump is controlled to well within the period of the molecular motion.

In the intermediate term, it is likely that the Raman modulation technique will find application in the generation of few-femtosecond pulses in the near- to mid-UV (200–400 nm). In the study of ultrafast chemical processes, these wavelengths are often required to access high-lying molecular states. Currently, the shortest pulses available at wavelengths of <300 nm are in the range 5–15 fs (refs 85–88), and these are of very low energy. Temporal resolution is therefore a current limitation for many studies, including relaxation processes in DNA bases[89], excited-state intramolecular proton transfer[90] and ultrafast 2D spectroscopy[91]. Spectra reaching to wavelengths of <300 nm have been generated by schemes in which Raman scattering is enhanced by a coherent material excitation[25,35,39,50,92,93], thus offering the potential for generating high-energy ultrashort pulses in this spectral region. Excitation of a coherent modulator in the femtosecond regime is perhaps the most promising technique for generating isolated few-femtosecond pulses in the UV.

Raman scattering, enhanced by the presence of a coherent molecular modulator, has significant potential as a much-needed ultrafast tool in diverse fields such as attoscience, femtochemistry and photobiology.

References

1. Zewail, A. Laser femtochemistry. *Science* **242,** 1645–1653 (1988).
2. Nisoli, M., De Silvestri, S. & Svelto, O. Generation of high energy 10 fs pulses by a new pulse compression technique. *Appl. Phys. Lett* **68,** 2793–2795 (1996).
3. Brabec, T. & Krausz, F. Intense few-cycle laser fields: Frontiers of nonlinear optics. *Rev. Mod. Phys.* **72,** 545–591 (2000).
4. Krausz, F. & Ivanov, M. Attosecond Physics. *Rev. Mod. Phys.* **81,** 163–234 (2009).
5. Uiberacker, M. *et al.* Attosecond real-time observation of electron tunneling in atoms. *Nature* **446,** 627–632 (2007).
6. Goulielmakis, E. *et al.* Single-cycle nonlinear optics. *Science* **320,** 1614–1617 (2008).
7. Raman, C. V. & Krishnan, K. S. A new type of secondary radiation. *Nature* **121,** 501–502 (1928).
8. Woodbury, E. J. & Ng, W. K. *Proc. Inst. Radio Eng.* **50,** 2367 (1962).

9. Chan, H.-S. *et al.* Synthesis and measurement of ultrafast waveforms from five discrete optical harmonics. *Science* **331,** 1165–1168 (2011).
10. Garmire, E., Pandarese, F. & Townes, C. H. Coherently driven molecular vibrations and light modulation. *Phys. Rev. Lett.* **11,** 160–163 (1963).
11. Yoshikawa, S. & Imasaka, T. A new approach for the generation of ultrashort optical pulses. *Opt. Commun.* **96,** 94–98 (1993).
12. Harris, S. E. & Sokolov, A. V. Broadband spectral generation with refractive index control. *Phys. Rev. A* **55,** R4019–R4022 (1997).
13. Belsley, M., Smithey, D. T., Wedding, K. & Raymer, M. G. Observation of extreme sensitivity to induced molecular coherence in stimulated Raman scattering. *Phys. Rev. A* **48,** 1514–1525 (1993).
14. Harris, S. E. & Sokolov, A. V. Subfemtosecond pulse generation by molecular modulation. *Phys. Rev. Lett.* **81,** 2894–2897 (1998).
15. Zhavoronkov, N. & Korn, G. Generation of single intense short optical pulses by ultrafast molecular phase modulation. *Phys. Rev. Lett.* **88,** 203901 (2002).
16. Kien, F. L. *et al.* Subfemtosecond pulse generation with molecular coherence control in stimulated Raman scattering. *Phys. Rev. A* **60,** 1562–1571 (1999).
17. Gundry, S. *et al.* Off-resonant preparation of a vibrational coherence for enhanced stimulated Raman scattering. *Phys. Rev. A* **72,** 033824 (2005).
18. Huang, S. W., Chen, W.-J. & Kung, A. H. Vibrational molecular modulation in hydrogen. *Phys. Rev. A* **74,** 063825 (2006).
19. Suzuki, T., Hirai, M. & Katsuragawa, M. Octave-spanning Raman comb with carrier envelope offset control. *Phys. Rev. Lett.* **101,** 243602 (2008).
20. Hsieh, Z.-M. *et al.* Controlling the carrier-envelope phase of Raman-generated periodic waveforms. *Phys. Rev. Lett.* **102,** 213902 (2009).
21. Belenov, E. M., Nazarkin, A. V. & Prokopovich, I. P. Dynamics of an intense femtosecond pulse in a Raman-active medium. *Pisma ZhETF* **55,** 223–227 (1992).
22. Nazarkin, A., Korn, G., Wittman, M. & Elsaesser, T. Generation of multiple phase-locked Stokes and anti-Stokes components in an impulsively excited Raman medium. *Phys. Rev. Lett.* **83,** 2560–2563 (1999).
23. Kalosha, V. P. & Herrmann, J. Phase relations, quasicontinuous spectra and subfemtosecond pulses in high-order stimulated Raman scattering with short-pulse excitation. *Phys. Rev. Lett.* **85,** 1226–1229 (2000).
24. Wang, J. K., Siegal, Y., Lü, C., Mazur, E. & Reintjes, J. Subpicosecond stimulated Raman scattering in high-pressure hydrogen. *J. Opt. Soc. Am. B* **11,** 1031–1037 (1994).
25. Krylov, V. *et al.* Femtosecond stimulated Raman scattering in pressurized gases in the ultraviolet and visible spectral ranges. *J. Opt. Soc. Am. B* **15,** 2910–2916 (1998).
26. Nazarkin, A., Korn, G. & Elsaesser, T. All-linear control of attosecond pulse generation. *Opt. Commun.* **203,** 403–412 (2002).
27. Kalosha, V. P. & Herrmann, J. Pulse compression without chirp control and frequency detuning by high-order coherent Raman scattering in impulsively excited media. *Opt. Lett.* **26,** 456–458 (2001).
28. Kalosha, V. P. & Herrmann, J. Ultrabroadband and phase-amplitude modulation and compression of extremely short UV and VUV pulses by Raman-active modulators. *Phys. Rev. A* **67,** 031801(R) (2003).
29. Kalosha, V., Spanner, M., Herrmann, J. & Ivanov, M. Generation of single dispersion precompensated 1 fs pulses by shaped-pulse optimized high order stimulated Raman scattering. *Phys. Rev. Lett.* **88,** 103901 (2002).
30. Kawano, H., Suda, A. & Midorikawa, K. Control of spectral distribution of Raman sidebands in impulsively stimulated rotational Raman scattering. *Appl. Phys. Lett.* **80,** 894–896 (2002).
31. Noack, F., Steinkellner, O., Tzankov, P., Ritze, H. H. & Herrmann, J. Generation of sub-30 fs ultraviolet pulses by Raman induced phase modulation in nitrogen. *Opt. Express* **13,** 2467–2474 (2005).
32. Bustard, P. J., Sussman, B. J. & Walmsley, I. A. Amplification of impulsively excited molecular rotational coherence. *Phys. Rev. Lett.* **104,** 193902 (2010).
33. Kawano, H., Hirakawa, Y. & Imasaka, T. Generation of more than 40 rotational Raman lines by picosecond and femtosecond Ti:sapphire laser for Fourier synthesis. *Appl. Phys. B* **65,** 1–4 (1997).
34. Kawano, H., Hirakawa, Y. & Imasaka, T. Generation of high-order rotational lines in hydrogen by four-wave Raman mixing in the femtosecond regime. *IEEE J. Quant. Electron.* **34,** 260–268 (1998).
35. Sali, E., Mendham, K. J., Tisch, J. W. G., Halfmann, T. & Marangos, J. P. High-order stimulated Raman scattering in a highly transient regime driven by a pair of ultrashort pulses. *Opt. Lett.* **29,** 495–497 (2004).
36. Turner, F. C., Trottier, A., Strickland, D. & Losev, L. L. Transient multi-frequency Raman generation in SF_6. *Opt. Commun.* **270,** 419–423 (2007).
37. Sali, E. *et al.* Behavior of high-order stimulated Raman scattering in a highly transient regime. *Phys. Rev. A* **72,** 013813 (2005).
38. Walmsley, I. A. & Dorrer, C. Characterization of ultrashort electromagnetic pulses. *Adv. Opt. Photon.* **1,** 308–437 (2009).
39. Sokolov, A. V., Walker, D. R., Yavuz, D. D., Yin, G. Y. & Harris, S. E. Raman generation by phased and antiphased molecular states. *Phys. Rev. Lett.* **85,** 562–565 (2000).
40. Yavuz, D. D., Walker, D. R., Yin, G. Y. & Harris, S. E. Rotational Raman generation with near-unity conversion efficiency. *Opt. Lett.* **27,** 769–771 (2002).
41. Chen, W.-J. *et al.* Sub-single-cycle optical pulse train with constant carrier envelope phase. *Phys. Rev. Lett.* **100,** 163906 (2008).
42. Pandiri, K. R., Suzuki, T., Suda, A., Midorikawa, K. & Katsuragawa, M. Line-by-line control of 10-THz-frequency-spacing Raman sidebands. *Opt. Express* **18,** 732–739 (2010).
43. Hseih, Z.-M. *et al.* Controlling the carrier envelope phase of Raman generated periodic waveforms. *Phys. Rev. Lett.* **102,** 213902 (2009).
44. Kien, F. L., Shon, N. H. & Hakuta, K. Generation of subfemtosecond pulses by beating a femtosecond pulse with a Raman coherence adiabatically prepared in solid hydrogen. *Phys. Rev. A* **64,** 051803(R) (2001).
45. Shon, N. H., Kien, F. L., Hakuta, K. & Sokolov, A. V. Two dimensional model for femtosecond pulse conversion and compression using high-order stimulated Raman scattering in solid hydrogen. *Phys. Rev. A* **65,** 033809 (2002).
46. Kien, F. L., Hakuta, K. & Sokolov, A. V. Pulse compression by parametric beating with a prepared Raman coherence. *Phys. Rev. A* **66,** 023813 (2002).
47. Liang, J. Q., Katsuragawa, M., Kien, F. L. & Hakuta, K. Sideband generation using strongly driven Raman coherence in solid hydrogen. *Phys. Rev. Lett.* **85,** 2474–2477 (2000).
48. Gundry, S. *et al.* Ultrashort-pulse modulation in adiabatically prepared Raman media. *Opt. Lett.* **30,** 180–182 (2005).
49. Burzo, A. M., Chugreev, A. V. & Sokolov, A. V. Optimized control of generation of few cycle pulses by molecular modulation. *Opt. Commun.* **262,** 454–462 (2006).
50. Takahashi, E., Kato, S., Matsumoto, Y. & Losev L. L. Ultra broadband UV generation by stimulated Raman scattering of two-color KrF laser in deuterium confined in a hollow fiber. *Opt. Express* **15,** 2535–2540 (2007).
51. Nazarkin, A., Korn, G., Wittman, M. & Elsaesser, T. Group-velocity-matched interactions in hollow waveguide: Enhanced high-order Raman scattering by impulsively excited molecular vibrations. *Phys. Rev. A* **65,** 041802(R) (2002).
52. Sensarn, S., Goda, S. N., Yin, G. Y. & Harris, S. E. Molecular modulation in a hollow fiber. *Opt. Lett.* **31,** 2836–2838 (2006).
53. Cregan, R. F. *et al.* Single-mode photonic band gap guidance of light in air. *Science* **285,** 1537–1539 (1999).
54. Benabid, F., Knight, J. C., Antonopoulos, G. & Russell, P. St. J. Stimulated Raman scattering in hydrogen-filled hollow-core photonic crystal fiber. *Science* **298,** 399–402 (2002).
55. Couny, F., Benabid, F. & Light, P. S. Large-pitch Kagome-structured hollow-core photonic crystal fiber. *Opt. Lett.* **31,** 3574–3576 (2006).
56. Smith, C. M. *et al.* Low-loss hollow-core silica/air photonic bandgap fibre. *Nature* **424,** 657–659 (2003).
57. Light, P. S. *et al.* Double photonic bandgap hollow-core photonic crystal fiber. *Opt. Express* **17,** 16238 (2009).
58. Beaudou, B. *et al.* Matched cascade of bandgap-shift and frequency-conversion using stimulated Raman scattering in a tapered hollow-core photonic crystal fibre. *Opt. Express* **18,** 12381 (2010).
59. Benabid, F., Couny, F., Knight, J. C., Birks, T. A. & Russell, P. St. J. Compact, stable and efficient all-fibre gas cells using hollow-core photonic crystal fibres. *Nature* **434,** 488–491 (2005).
60. Russell, P. Photonic Crystal Fibers. *Science* **299,** 358–362 (2003).
61. Benabid, F., Bouwmans, G., Knight, J. C., Russell, P. St. J. & Couny, F. Ultrahigh efficiency laser wavelength conversion in a gas-filled hollow core photonic crystal fiber by pure stimulated rotational Raman scattering in molecular hydrogen. *Phys. Rev. Lett.* **93,** 123903 (2004).
62. Benabid, F., Antonopoulos, G., Knight, J. C. & Russell, P. St. J. Stokes amplification regimes in quasi-cw pumped hydrogen-filled hollow-core photonic crystal fiber. *Phys. Rev. Lett.* **95,** 213903 (2005).
63. Couny, F., Carraz, O. & Benabid, F. Control of transient regime of stimulated Raman scattering using hollow-core PCF. *J. Opt. Soc. B* **26,** 1209–1215 (2009).
64. Wang, Y. Y., Couny, F., Light, P. S., Mangan, B. J. & Benabid, F. Compact and portable multiline UV and visible Raman lasers in hydrogen-filled HC-PCF. *Opt. Lett.* **35,** 1127–1129 (2010).
65. Nazarkin, A., Abdolvand, A., Chugreev, A. V. & Russell, P. St. J. Direct observation of self-similarity in evolution of transient stimulated Raman scattering in gas-filled photonic crystal fibers. *Phys. Rev. Lett.* **105,** 173902 (2010).
66. Pearce, G. J., Wiederhecker, G. S., Poulton, C. G., Burger, S. & Russell, P. St. J. Models for guidance in Kagome-structured hollow-core photonic crystal fibres. *Opt. Express* **15,** 12680–12685 (2007).
67. Couny, F. & Benabid, F. Optical frequency comb generation in gas-filled hollow core photonic crystal fibres. *J. Opt. A* **11,** 103002 (2009).
68. Couny, F., Benabid, F., Roberts, P. J., Light, P. S. & Raymer, M. G. Generation and photonic guidance of multi-octave optical-frequency combs. *Science* **318,** 1118–1121 (2007).
69. Schenkel, B., Paschotta, R. & Keller, U. Pulse compression with supercontinuum generation in microstructure fibers. *J. Opt. Soc. Am. B* **22,** 687–693 (2005).

70. Heckl, O. H. *et al.* High harmonic generation in a gas-filled hollow-core photonic crystal fiber. *Appl. Phys. B* **97,** 369–373 (2009).
71. Chugreev, A. V. *et al.* Manipulation of coherent Stokes light by transient stimulated Raman scattering in gas filled hollow-core PCF. *Opt. Express* **17,** 8822–8829 (2009).
72. Wang, Y. Y., Wu, C., Couny, F., Raymer, M. G. & Benabid, F. Quantum-fluctuation-initiated coherence in multi-octave Raman optical frequency combs. *Phys. Rev. Lett.* **105,** 123603 (2010).
73. Green, J. T., Weber, J. J. & Yavuz, D. D. Continuous-wave light modulation at molecular frequencies. *Phys. Rev A* **82,** 011805(R) (2010).
74. Losev, L. L., Song, J., Xia, J. F., Strickland, D. & Brukhanov, V. V. Multifrequency parametric infrared Raman generation in $KGd(WO_4)_2$ crystal with biharmonic ultrashort-pulse pumping. *Opt. Lett.* **27,** 2100–2102 (2002).
75. Zhi, M. & Sokolov, A. V. Broadband coherent light generation in a Raman-active crystal driven by two-color femtosecond laser pulses. *Opt. Lett.* **32,** 2251–2253 (2007).
76. Matsuki, H., Inoue, K. & Hanamura, E. Multiple coherent anti-Stokes scattering due to phonon grating in $KNbO_3$ induced by crossed beams of two-color femtosecond pulses. *Phys. Rev. B* **75,** 024102 (2007).
77. Zhi, M., Wang, X. & Sokolov, A. V. Broadband coherent light generation in diamond driven by femtosecond pulses. *Opt. Express* **16,** 12139 (2008).
78. Matsubara, E., Kawamoto, Y., Sekikawa, T. & Yamashita, M. Generation of ultrashort optical pulses in the 10fs regime using multicolour Raman sidebands in $KTaO_3$. *Opt. Lett.* **34,** 1837–1839 (2009).
79. Matsubara, E., Sekikawa, T. & Yamashita, M. Generation of ultrashort optical pulses using multiple coherent anti-Stokes Raman scattering in a crystal at room temperature. *Appl. Phys. Lett.* **92,** 071104 (2008).
80. Zhi, M. & Sokolov, A. V. Broadband generation in a Raman crystal driven by a pair of time-delayed linearly chirped pulses. *New J. Phys* **10,** 025032 (2008).
81. Kawano, H., Ishikawa, K., Suda, A. & Midorikawa, K. Polarization of multiple rotational Raman sidebands from hydrogen gas by delayed four-wave Raman mixing in the femtosecond regime. *Opt. Lett.* **27,** 1917–1919 (2002).
82. Kida, Y., Kagahara, T., Zaitsu, S., Matsuse, M. & Imasaka, T. Pulse compression based on coherent molecular motion induced by transient stimulated Raman scattering. *Opt. Express* **14,** 3083–3092 (2006).
83. Kida, Y., Zaitsu, S. & Imasaka, T. Generation of intense 11-fs ultraviolet pulses using phase modulation by two types of coherent molecular motions. *Opt. Express* **16,** 13492 (2008).
84. Witting, T. *et al.* Characterisation of high intensity sub 4 fs laser pulses using spatially encoded spectral shearing interferometry. *Opt. Lett.* **36,** 1680–1682 (2011).
85. Durfee III, C. G., Backus, S., Kapteyn, H. C. & Murnane, M. M. Intense 8-fs pulse generation in the deep ultraviolet. *Opt. Lett.* **24,** 697–699 (1999).
86. Baurn, P., Lochbrunner, S. & Riedle, E. Tunable sub-10fs ultraviolet pulses generated by achromatic frequency doubling. *Opt. Lett.* **29,** 1686–1688 (2004).
87. Schriever, C., Lochbrunner, S., Krok, P. & Riedle, E. Tunable pulses from below 300 nm to 970 nm with durations down to 14 fs based on a 2 MHz ytterbium-doped fiber system. *Opt. Lett.* **33,** 192–194 (2008).
88. Kosma, K., Trushin, S. A., Schmid, W. E. & Fuß, W. Vacuum ultraviolet pulses of 11fs from fifth-harmonic generation of a Ti:sapphire laser. *Opt. Lett.* **33,** 723–725 (2008).
89. Satzger, H., Townsend, D., Zgierski, M. Z., Patchkovskii, S. *et al.* Primary processes underlying the photostability of isolated DNA bases: Adenine. *Proc. Natl Acad. Sci. USA* **103,** 10196–10201 (2006).
90. Lochbrunner, S. *et al.* Dynamics of excited-state proton transfer systems via time-resolved photoelectron spectroscopy. *J. Chem. Phys.* **114,** 2519–2522 (2001).
91. Tian, P., Keusters, D., Suzaki, Y. & Warren, W. S. Femtosecond phase-coherent two-dimensional spectroscopy. *Science* **300,** 1553–1555 (2003).
92. Irie, Y. & Imasaka, T. Generation of vibrational and rotational emissions by four-wave Raman mixing using an ultraviolet femtosecond pump beam. *Opt. Lett.* **20,** 2072–2074 (1995).
93. Chen, W.-J. & Kung, A. H. Tunable deep-ultraviolet source generated by scattering off adiabatically prepared Raman coherence in hydrogen gas. *Opt. Lett.* **30,** 2608–2610 (2005).

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