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Review

Review of Multi-Frequency Raman Generation

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To keep pushing the boundaries of ultrafast spectroscopy, high power optical pulses with sub-femtosecond durations must be synthesized. Although pulses with attosecond durations have been generated, the peak power remains low, and the spectral range is in the XUV. The technique of multi-frequency Raman generation shows promise as a simple method to generate visible or UV pulses with single femtosecond duration and sufficient power to drive nonlinear optical processes. In this paper, I review the progress made generating broad spectra by multi-frequency Raman generation and compressing the resulting electric field to generate high power, single femtosecond pulses.

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I. INTRODUCTION

There are a number of different schemes to generate ever shorter, more intense optical pulses for nonlinear optics applications. The shortest pulse duration achieved to date, just 67 attoseconds, has been accomplished using high order harmonic generation (HHG) [1]. The pulses can be very short because HHG produces an extremely broad spectrum that is centered in the VUV. The drawback is that the HHG process is not very efficient (energy conversion efficiency to the harmonic $< 10^{-6}$ [2]) resulting in the intensity of the ultrashort pulse being less than the pump pulse intensity and so is insufficient to drive nonlinear processes. On the other hand the process of multi-frequency Raman generation (MRG) can efficiently generate broad spectral bandwidths centered in the visible to UV. The shortest pulses generated by MRG to date were 1.6 fs in duration [3]. MRG produces many Raman orders spanning from the ultraviolet to the infrared. Trains of short pulses can be generated by properly phasing the coherently generated orders. Because the frequency spacing of Raman orders is significantly smaller than the frequency separation of harmonic orders the temporal separation of the pulses is correspondingly longer making it possible to isolate single pulses with standard nonlinear optics techniques.

HHG proceeds from very different physics than the perturbative nonlinear process of harmonic generation, where a nonlinear material polarization susceptibility $\chi^{(n)}$, of order n, corresponding to the nth harmonic, is driven by a single pump field [4]. At high pump intensities, HHG arises from what is now known as the three-step model [5]. When the laser intensity is high enough and the wavelength is long enough that the electron tunneling time is shorter than the laser period, the atom or molecule undergoes tunnel ionization. The

ejected ion is then accelerated in the oscillating laser field and returns to the atom with high kinetic energy that can be converted back into high-energy photons through recombination with the ion. The resulting spectrum is a large plateau of harmonics. As will be discussed in this paper, the multi-frequency Raman generation process also produces a large number of spectral orders, but, the high order process is still driven by the same $\chi^{(3)}$ Raman process that drives the first anti-Stokes order [6]. The process simply gets stronger as the pump intensity increases. As the Stokes and anti-Stokes orders are generated, they can then re-scatter off the material oscillation and create either higher or lower Raman orders. Once the orders are created they continue to mix with their nearest neighbor to generate Stokes and anti-Stokes in a multi-wave third order nonlinear process. The high order Raman process can start from a single pump pulse. The single pump pulse can generate the first Stokes field efficiently through the linear Stimulated Raman Scattering (SRS) process [6]. Once the two fields are sufficiently strong, they drive the $\chi^{(3)}$ nonlinear Raman process, which generates the first anti-Stokes (AS) order. The MRG process then cascades to higher orders from this initial scattering. The MRG process however gets significantly stronger if two intense pump pulses that have frequencies corresponding to pump and Stokes fields are used to drive the molecular oscillation [7].

As with HHG, for ultrashort pulses to be generated through the MRG process, the material polarization must be coherently driven and the scattering of the electric fields from the oscillation must be coherent. Along with this coherent interaction, the many fields must propagate through the medium requiring the nonlinear medium to have low dispersion. MRG with two-color pumping of the Raman oscillation has been extensively studied in three different temporal regimes. The adiabatic regime uses two equally strong pump pulses that both have durations longer than the coherence time of the Raman transition. It was shown theoretically that not only could you achieve the maximum coherence, that is $|\rho_{ab}| = 0.5$, by adiabatic pumping but that the resulting index of refraction of the nonlinear medium was ~ 1, resulting in the generation of a large number of phased Raman orders [8]. The 1.6 fs pulses have been achieved with adiabatic pumping. However, the ultrashort pulses were separated by 11 fs in a nanosecond long pulse train resulting in a peak power of 1MW [3]. The duration of the pulse train corresponds to the duration of the pump by the Fourier transform of the spectra. The low peak power of the pulses from adiabatic pumping is the drawback of this process. If the goal is to create ultrashort, high-intensity pulses, the pump pulses must be short so that the pulse train has only a few orders. This then leads to the next temporal regime, the transient regime, where the pump pulses have durations of the same order or less than the coherence time. Losev and Lutsenko showed theoretically, that with transient pumping a broader spectrum of Raman orders could be achieved compared to the steady state regime [9]. The total bandwidth could theoretically reach a level of 1.4 times the pump frequency. Unlike the adiabatic case, the Raman orders propagated with a phase mismatch given by the dispersion of the medium, which must be minimized to obtain a broad spectrum. Lastly MRG can be achieved in the impulsive regime, where the two colors are both present within the very large bandwidth of the ultrashort pump pulse [11]. In impulsive pumping, the pulse duration is then shorter that vibrational period of the molecular oscillation [11]. The Raman orders spectrally overlap each other forming a

continuous spectrum that can be compressed to generate single ultrashort pulses. To date, single pulses with 3.8 fs duration have been measured [12]

In this review paper, I will first summarize the work on stimulated Raman scattering, higher order Raman scattering and Coherent Anti-Stokes Raman Scattering (CARS) that led to the development of MRG. I will then describe the MRG studies in the three temporal regimes, where in each case the goal is to maximize both the conversion efficiency and the generated spectral width. I will also discuss the work done to coherently sum the Raman orders to generate ultrashort pulses, high intensity. I will conclude with very recent work on creating ultrashort pulses with stable Carrier Envelope Phase.

II. STIMULATED RAMAN SCATTERING

Although Raman and Krishnan discovered the linear inelastic scattering process back in 1928 [13], it took the discovery of the laser before any nonlinear optical process could be observed and so the nonlinear process of stimulated Raman scattering wasn't observed until 1962 [14]. Jonathan White has written a very extensive review of Stimulated Raman Scattering (SRS) [15]. SRS was first observed by Woodbury and Ng, when they were studying Q-switching of a Ruby laser and detected frequency shifted radiation, but at the time they did not know what caused it [14]. They were using a Kerr cell filled with nitrobenzene and measured an output of $\sim$ 200 mJ at the ruby laser wavelength of 694.3 nm and also 30 to 40 mJ of radiation at 767 nm. The longer wavelength did not appear when the nitrobenzene was not in the cavity. What was striking about the observation was that the secondary emission was almost 20% as energetic as the primary laser radiation, yet linear Raman scattering has an efficiency of just $\sim 10^{-7}$. Later that year, Woodbury and colleagues studied a number of liquids and noted that the shifts corresponded to known Raman shifts and that there was a laser energy threshold to go from an extremely weak signal at the shifted frequency to a signal strength of over 10% of the laser power [16]. One of these colleagues, R. W. Hellwarth then derived a phenomenological theory of SRS that derives the coherent gain of a Stokes field by annihilating a laser photon and creating a photon in the scattered mode, with the excess energy being taken up by a transition from an initial to final state of the medium [17]. In spontaneous Raman scattering the radiation is emitted in a dipole pattern, but in the case of SRS, where the Stokes field exhibits gain, the radiation is predominantly in the forward and backward direction of the driving laser field. Since these initial SRS studies a vast number of vibrational and rotational SRS experiments have been done in various gases, liquids and solids with the main application to generate tunable radiation across the optical spectrum that could not be achieved by lasers alone. References to these experiments can be found in the review by White [15].

Hellwarth pointed out that if there was a population inversion between the two levels of the material transition, then anti-Stokes orders would be generated by the medium giving up the excess energy [17]. Garmire and co-workers developed the theory of coherently driving molecular vibrations with two fields having frequencies separated by the natural molecular vibrational frequency, ω_r [18]. The interaction of the field and the driven molec-

ular oscillation then amplifies the different components of the driving field. If the optical radiation field is comprised of three fields having frequencies of ω_0, $\omega_0 + \omega_r$, $\omega_0 - \omega_r$, where ω_0 is the pump frequency, then under certain phase matching conditions, the Stokes and anti-Stokes frequencies can experience gain through the linear and nonlinear polarization with a susceptibility of the form $\chi = \chi_1 + \chi^{(3)}\mathrm{E}^2$. The authors also point out that the same third order nonlinear process can generate higher order Stokes and anti-Stokes radiation by interaction of fields at ω_0, $\omega_0 - \omega_r$ and $\omega_0 - 2\omega_r$ and $\omega_0 + \omega_r$, $\omega_0 + 2\omega_r$ if sufficient intensity is reached in the first orders. The various Raman orders generated by the third order polarizability would radiate as cones in order to satisfy both energy and momentum matching. For this reason, only Stokes radiation, from the linear polarizability, was seen in the early SRS experiments where the Raman order was generated inside a laser cavity and so only on axis radiation could build up.

III. HIGH-ORDER ANTI-STOKES RADIATION

Shen and Bloembergen in 1965 presented a theory showing that in the forward direction and so ignoring the anti-Stokes radiation, that higher order Stokes radiation was generated in a sequential fashion if the radiation was assumed to be spatially uniform [19]. That is, as the first order Stokes radiation reached equivalent power as the pump, that the pump would therefore decrease and the second order Stokes would then be generated and so on as a function of propagation distance. In 1969, von der Linde, Maier and Kaiser improved on this theory by allowing the spatial profile of the radiation to be Gaussian [20]. In this case, they showed that at the end of the Raman cell a number of Stokes orders can be present and the number of orders increases with input laser intensity. This result was confirmed by their experiments using liquid CS_2 as the Raman medium. Their work also showed that the Raman conversion efficiency was optimum when the pulse duration was on the order of 1 ns so that the competing process of stimulated Brillouin scattering was not significant.

Liquid nonlinear media have higher Raman gain than gases, but they also exhibit much higher dispersion, which limits the generation of high order anti-Stokes (AS). The first SRS experiments in gases were done by Minck, Terhune and Rado, where they observed multiple Raman lines in H_2, D_2 and CH_4 [21]. Because of the low dispersion of the gases, the anti-Stokes radiation was also emitted axially. They observed up to the 4th AS line of the hydrogen vibrational transition at 4155.21 cm^{-1} or 125 THz. By 1978, Wilke and Schmidt were able to cover the spectral range of 189 nm to 2064 nm by generating several Stokes and anti-Stokes orders in hydrogen gas, by pumping with an amplified dye laser having energy of ~ 30 mJ and pulse duration of 9 ns or with the frequency-doubled dye laser [22]. They followed up this experiment in 1979 and reached the shortest wavelength of 175 nm, which was the 5th anti-Stokes order of the frequency-doubled dye laser at 276.5 nm [23]. They generated the 8th anti-Stokes order at 195 nm from the fundamental radiation from the dye laser at 558 nm. The conversion efficiency from the nth to $(n + 1)$st order was always greater than 30% giving an energy of the 8th AS line of ~ 30 μJ. They studied the

pressure dependence on the power of the various AS lines and showed that the dispersion was responsible for optimizing the various orders. The generated total bandwidth of all the orders was greater than the pump frequency.

In 1983, Schomburg, Dobele and Ruckle reported generating up to the 13 AS order at a wavelength of 138 nm [24]. For this work, they built a dye laser that could generate over 100 mJ of energy in a 12 ns duration. The spectral maximum of the tunable dye laser was at 550 nm. They were able to measure the energy of the orders over 8 orders of magnitude to see the 13th AS order. They noted that the efficiency from one order to the next stayed high $\sim 50\%$ until the 8th order, but then drops to 20% for the higher orders because of the dispersion in the VUV.

Baldwin, Marangos and Burgess used an excimer-pumped dye laser to generate radiation further into the UV through high order Raman scattering [25]. The dye laser operated at a wavelength of 360.6 nm with a modest energy of 7.4 mJ in a pulse duration of 4 ns. With this modest energy they still achieved the 11th AS order at a wavelength of 136.2 nm showing that the Raman process is more efficient for higher frequency pumps.

Eimerl, Hargrove and Paisner developed a multi-wave theory for high order Raman generation that is valid when the Raman shift is small in comparison to the pump frequency and so the total generated bandwidth would still be less than the pump frequency [26]. In this theory, all orders, E_n, that oscillate at frequency $\omega_0 + n\Delta\omega$, where is ω_0 is the pump frequency and $\Delta\omega$ is the Raman transition frequency, are mutually coupled to each other through multiple four-wave parametric processes. To describe the interaction of the multiple fields and the material transition, they used Maxwell Bloch equations. In an analogous manner to resonant single field interactions that use a Rabi frequency of $\Omega = \mu E/\hbar$ the authors defined a two-photon Rabi frequency as: $\Omega e^{i\theta} = \sum_r 2\alpha_{12} E_r {E_{r-1}}^*/\hbar$, where α_{12} is the transition polarizability. In the Bloch equations, the time derivative of θ was added to the two-photon detuning of the two fields from the transition frequency. With the assumption of $\omega_r \ll \omega_0$, they could solve the equations exactly and found that the intensity of the nth order at the output was given by $I_n(\xi) = I_0 \xi J_n^2(z|\beta|)$, where ξ is the retarded time in the pulse, I_0 is the pump intensity, J_n is a Bessel function and the $|\beta|$ is the parametric gain parameter. This theory requires two inputs one at the pump frequency and one at the first Stokes. The experimental results to this date were for a single pump and so the second input is considered to come from SRS. The conversion efficiency of this theory agreed reasonably with the experimental results.

The multi-wave theory was improved by Hickman and Bischel in 1986 [27]. It assumes the transient regime where the pump pulse duration is short compared to the relaxation times of the Raman medium. Their theory matches the earlier theory of Eimerl and coworkers in the limit of $\omega_r \ll \omega_0$. The equations have to be solved numerically. They showed that the conversion efficiency to higher orders can be improved by increasing the input power of the Stokes radiation. Using input energies of 8 mJ and 0.8 mJ and pulse durations of 10 ns and 1 ns for the pump laser and first Stokes, respectively, with the Stokes pulse delayed by 5ns from the peak of the pump, which is consistent with the input Raman pulse being generated through SRS and assuming that the relaxation times are infinite, the 8th AS order could be generated with a conversion efficiency of 10^{-3} compared to the

pump energy. This efficiency was improved by using a pump energy of 7.2 mJ and a Stokes energy of 1.6 mJ and thereby keeping the total input energy constant.

Through the 1970's and into the 80's, the work on high order anti-Stokes generation was about generating tunable radiation and extending the range of coherent radiation into the VUV for spectroscopic applications. Yoshikawa and Imasaka realized that in an analogous scheme to laser mode-locking, where ultra-short pulses are produced by phase-locking the spectral orders of the laser cavity, even shorter pulses could be produced by phase controlling the coherently produced multiple Raman orders [28]. They numerically modeled the process by using just 10 rotational lines from ortho-hydrogen and showed that Fourier transform limited pulses of 6.4 fs FWHM could be obtained. The pulses would be separated by 57 fs. They also showed that if it was possible to completely control the phases of 10 vibrational lines of hydrogen that the Fourier transform limited pulses would be just 1.4 fs, but the pulses would be separated by just 7.9 fs.

The advantage of using the rotational lines in H_2 rather than the vibrational lines is that the spectral spacing is closer allowing the temporal pulse spacing to be longer. This has two advantages. First there would be fewer pulses in the pulse train and so the peak power would be higher. Also the longer the time between pulses makes it easier to isolate a single pulse. Kawano, Lin and Imasaka used 100 ps pulses with energies up to 50 mJ at a wavelength of 827 nm from an amplified Ti:sapphire laser and generated up to the 15 AS rotational order [29]. They used elliptical polarization to maximize the rotational excitation. The 7th AS rotational line was stronger than the first AS vibrational line that occurs almost at the same wavelength.

The Imasaka group followed this experiment by measuring the MRG spectrum as a function of pulse duration using a femtosecond amplified Ti:sapphire system [30]. They varied the pulse duration by linearly chirping the pulse and kept the energy constant at 5 mJ. At a pulse duration of 800 fs they observed 40 rotational lines. This was the optimum condition. At longer pulse durations the Raman gain was lower because of the reduced pump intensity and at shorter pulse durations, the competing nonlinearity of self-phase moduation (SPM) caused a spectral continuum to appear and a decrease of Raman orders. These experiments are single pump experiments and so rely on generating the first Stokes radiation to then nonlinear mix to generate the other orders. They discussed that by pumping with a linearly chirped pump pulse that the Raman orders would also be created with a linear chirp. If the 40 rotational orders are to be phased to generate an ultrashort pulse, then the linear chirps on all the orders would also need to be corrected. If this can be done, then the Fourier transform of the total rotational MRG spectra produces sharp pulses of 0.6 fs FWHM surrounded by oscillating wings of 6.4 fs. The pulses would be separated by 57 fs in a pulse train given by the length of the pulse, which in this case was 1.2 ps.

This early work on high order anti-Stokes generation confirmed that the Raman gain increases with pump intensity, and pump frequency and that the generated bandwidth increases with lower dispersion. Recently, high order Raman scattering has been generated in hollow core photonic crystal fibers (HC-PCF). Photonic crystal fibers have the advantages of a very small area so the high intensity can be achieved with relatively low powers and

very low dispersion so the coherence length can be quite long [31]. Since fibers guide the light and the coherence length can be very long, the required Raman gain can be reduced and so further reducing the peak powers. Couny and colleagues used 12 ns long pulses at 1.06μm from a Nd:Yag laser, with just 40 kW peak power to pump a Kagome HC-PCF filled with hydrogen [32]. With linear polarization they observed 5 AS lines and 1 Stokes from vibrational excitation. With circular polarization driving the rotational transition, they generated 45 spectral components covering essentially the same total bandwidth. The group further investigated the transition from the steady state to the transient regime using a laser that generated pulses with a variable pulse duration [33]. They measured the threshold energy for detection of the first Stokes as a function of pulse duration. The plot of the experimental data showed an inflection point around 12 ns between two different linear slopes. The two different slopes matched the theoretical curves for steady state and transient Raman gain. This transition time between the two temporal regimes could be varied between 10 and 30 ns, by varying the gas pressure and the fiber length.

IV. COHERENT ANTI-STOKES RAMAN SCATTERING

So far the experimental work that we have considered used a single input pulse. However, the multi-wave theory assumes two inputs and the numerical modeling showed that increasing the Stokes input would increase the efficiency. Using two inputs was used early on. Maker and Terhune were the first to nonlinearly mix the laser pump and Stokes radiation [34]. They first generated the Stokes radiation in a cell containing a benzene derivative pumped with a Q-switched ruby laser that delivered 100mJ pulses with 30ns FWHM duration. After this cell, the peak powers in the beam were 50 kW at the pump frequency, 10kW at the first stokes, 50 W at the second stokes and less than 10 photons per pulse in the first anti-Stokes. The pump and first Stokes beam were then both focused into a second nonlinear Raman cell. The two beams were focused at the proper phase matching angle to generate the AS line. The generated power of the first AS line was then measured along its phase matching angle. They measured the AS power as a function of cell thickness, L, which showed a $\sin^2(L)$ dependence indicative of the effect phase matching. They measured the AS power for a number of different liquids as the Stokes frequency was tuned by changing the benzene derivative in the first cell. These experiments demonstrated the resonant enhancement of the Raman transitions. The observation of the resonant enhancement led to a new type of spectroscopy, which was coined Coherent Anti-Stokes Raman Scattering (CARS) by Byer's group [35]. Rather than using a weak Stokes signal as the second input frequency, spectroscopists realized that they could measure the Raman levels by using two different laser frequencies, typically provided by a tunable dye laser along with the pump laser radiation. CARS is now a well established spectroscopic technique [36]and more recently is used in microscopy [37]. I will not review this technique as the spectroscopy is concerned with understanding the media rather than generating the Raman orders. However the two techniques are linked because if a Raman medium is pumped by two fields, having a frequency separation given by the Raman transition,

then higher orders are efficiently generated and these orders extend the tunable range used by the spectroscopists. Because two laser fields are input, CARS is carried out at much smaller intensities than the higher order AS generation discussed above. In 1975, Chabay, Klauminzer and Hudson were using two dye lasers with energies less than 500 μJ and 6ns pulse duration operating at wavelengths of 490 nm and 515nm and observed the third Stokes and the second anti-Stokes orders [38]. They dubbed the process higher-order Raman spectral excitation studies (HORSES). The higher orders radiated at angles imposed by phase matching. These pump energies are about three orders of magnitude smaller than in the single pump pulse experiments and so demonstrates the improved efficiency by using two pumps.

Mennicke, Mayer and Sinnott collinearly pumped a Raman cell containing liquid nitrogen with two lasers [39]. They used the 1 MW peak power output of a ruby pumped dye laser at 820 nm and the 10 MW peak power of the ruby laser itself at 694nm. They observed up to the 5th AS order at a wavelength of 384 nm. They not only achieved more orders than Chabay and co-workers with the increased pump power, but the higher AS orders radiated collinearly with the pumps, even though the Raman medium is a liquid and so has significant dispersion. This work shows that collinear AS radiation can be generated if the Raman gain length is shorter than the phase matching coherence length.

In 1989 Imasaka and co-workers generated 40 spectral orders by mistakenly allowing amplified spontaneous emission (ASE) to build up in the laser cavity and thereby provided two strong pumps that strongly drove the molecular polarization oscillation [7]. It was this experiment that made the authors realize that this technique was a candidate for ultrashort pulse generation [28]. They were using an excimer pumped dye laser to generate tunable UV by high order anti-Stokes Raman generation, when they observed that the process was strongly pronounced when the laser was tuned in such a way as to allow a strong amplified spontaneous emission (ASE) pulse. It turned out that the frequency separation between the ASE and the laser pulse was ~ 600 cm^{-1} that corresponded to the frequency difference of the $J = 1$ to $J = 3$ rotational level (588.07 cm^{-1}) of hydrogen. This strong pumping of the rotational levels, with energy between 3 and 9 mJ caused a large number of orders separated by this energy spacing to be produced. Both vibrational stokes and anti-Stokes orders were generated as well as the numerous rotational Stokes and anti-Stokes orders. The orders were all collinear with the pumps.

In 1990, Schulz-von der Gathen and co-workers compared the high order AS generation in liquid nitrogen with and without a second pulse at the first Stokes frequency [40]. They referred to the comparison as SRS versus CARS. They showed an increase in efficiency for the high order generation as the input Stokes field energy was increased for a fixed pump energy of 80 mJ at 532 nm. They also demonstrated a decrease in pump threshold for a fixed Stokes field energy of 2 mJ. With the Stokes field present, they were able to increase the number of AS orders generated and achieved the 14th AS order.

V. MULTI-FREQUENCY RAMAN GENERATION

To achieve a wide band of Raman orders requires large Raman gain and minimal phase mismatch. MRG with two pumps has now been studied extensively in gases in the three temporal regimes. Gases are used because the dispersion is minimal. However large bandwidths have also been observed in solids because of their extremely high Raman gain. The phase matching is accomplished by having the two pump beams cross at a phase matching angle. The Raman orders than radiate at different phase matched angles. I will summarize the MRG work and the ultrashort pulse generation for these four regimes; gas media in the adiabatic, transient and impulsive temporal regimes; and solid media.

VI. ADIABATIC REGIME

The classical physics approach to describe SRS with both a linear and nonlinear susceptibility describes the scattering of the waves off a grating induced by the coupling of the two input waves. To achieve high orders, the nonlinear component must be as large as the linear component and the dispersion must be negligible. Harris and Sokolov showed that the molecular transition can be driven adiabatically to achieve the maximum coherence, that is $|\rho_{ab}| = 0.5$ [8]. A number of Raman sidebands are generated through mixing this coherence with the two driving fields. The most surprising outcome of their theory is that the side bands can be phased in such a way that reduces the material refractive index to near unity. This adiabatic theory of MRG is analogous to electromagnetically induced transparency (EIT) [41]or in the authors' words "a broadening of the EIT theory". Sokolov and Harris then use this theory and solve for the propagation of all the orders. They numerically solved the equations for hydrogen for the cases of phased states where the two pumps have frequencies closer together than the transition frequency, the resonant case when the frequency separation matches the Raman transition and the anti-phased where the detuning has the opposite sign. They showed that more orders were possible with phased states where the detuning corresponded to the AC Stark shift of the transition and all the fields propagate with near unity refractive index.

Huang, Chen and Kung [42]followed up the adiabatic theoretical treatment to include the effects of Doppler broadening, which reduces the maximum coherence and collisions that can reduce the negative effect of Doppler at high pressures. They compared the theory to experimental results of vibrational MRG carried out in room temperature H_2 at pressures ranging from < 1 to 1000 Torr. The agreement was excellent at 200 Torr. There was a discrepancy with the theory at the higher pressure that could not be explained, but both the experiment and theory showed many more orders at the higher pressure.

Le Kien and colleagues theoretically studied adiabatic MRG for high-density hydrogen as a model for solid hydrogen [43]. The solid will have much higher Raman gain but also correspondingly higher dispersion because of the higher molecular density. Their numerical model predicted that the Raman orders would span the spectrum of 864 nm to 188 nm for pumps at 355nm and 416 nm. If the Raman orders are properly phased, they would create

a pulse train of 0.3 fs separated by 7.9 fs.

Sokolov and colleagues experimentally confirmed their adiabatic theory with the experimental demonstration of vibrational Raman generation in molecular D_2, which showed that many more orders were generated when the two pumps were tuned to have phased molecular states [44]. The Stokes field was provided by a Nd:YAG laser at 1.0645 μm with an energy of 100 mJ and pulse duration of 12 ns. The pump laser radiation from a tunable Ti:sapphire laser was tuned through the transition at 807.22 nm with 7 mJ of energy and pulse duration of 16 ns. With the two input fields tuned to be on resonance or further apart, only the 4th AS order was observed, but with the two frequencies tuned to be less than the transition frequency of 89.8 THz by 700 MHz, 13 AS orders were observed. These results are shown in Figure 1.

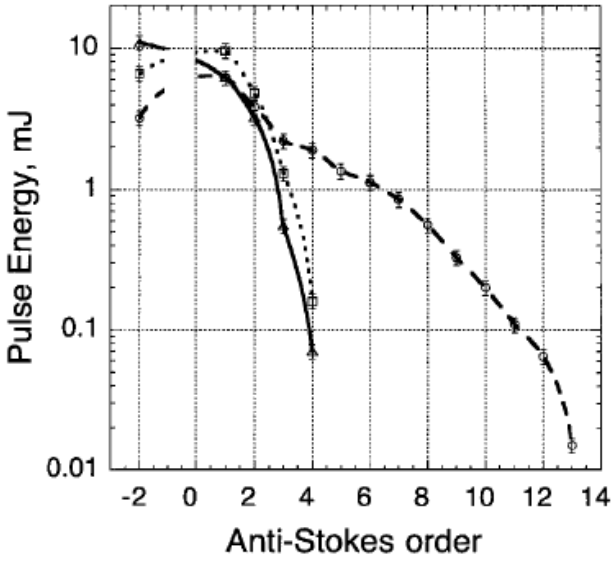

FIG. 1: Pulse energies generated in the setup of (Fig. 1 in ref. 43) at $P = 72$ torr. The triangles show on-resonance generation ($\Delta\omega = 0$), the circles show generation by phased ($\Delta\omega = 500$ MHz) and the squares by anti-phased ($\Delta\omega = -200$ MHz) states of D_2. Figure reproduced with permission from ref. 43 © 2000 APS

The Harris group [45] also studied MRG in the adiabatic regime for a rotational transition in H_2. They found a large number of rotational Raman lines: 27 AS and 8 Stokes when again the two pump frequencies were closer together than the transition frequency corresponding to the phased molecular state. They found that under this condition, the Raman conversion efficiency was near unity with 70% of the pump laser depleted. Both lasers had 60 mJ of energy and transform limited pulse durations of 17 and 14 ns.

Along with demonstrating large bandwidth production by adiabatic pumping, Harris and Sokolov also discussed how the coherence caused the electric field to be frequency modulated [46]. This frequency modulated field could then be compressed by the dispersion

of the medium to create single cycle pulses with envelopes of 0.72 fs duration.

Experimentally the group timed the Raman orders and measured sub-2 fs pulses. In their first experimental work they dispersed just 5 orders in a prism and timed the orders by retro-reflecting them back through the prism [47]. In each beam line glass plates are rotated to correct the phase delay of each field. They performed a correlation measurement using ionization as the nonlinearity and confirmed that the pulses were less than 2 fs. They improved the phase matching apparatus by using a 4-prism delay line with a liquid crystal phase modulator at the center so that each line could be accurately phased [3]. In this arrangement they used 7 lines spanning the spectrum from 1.56 μm to 410 nm and generated 1.6 fs.

Katsuragawa and colleagues used a simple compression set-up comprised of a pair of chirped mirrors with a small movable mirror to generate a stable train of sub-20 fs pulses, with a repetition rate of 10.6 THz. A dual-wavelength, injection locked Ti:sapphire laser adiabatically modulated the rotational Raman transition in liquid nitrogen [48]. The optical axis at the output of the compressor remained fixed as the number of passes of the chirped mirrors was varied by translating the mirror. My varying the compressor, they were able to measure the spectral chirp imposed on the modulated field.

VII. TRANSIENT REGIME

Losev and Lutsenko followed the steady state theory derived by Shen and Bloembergen [19]and numerically solved the equations to determine the maximum bandwidth that could be obtained through multi-frequency Raman generation [49]. For the case of two pumps with equal intensity and a dispersion free Raman medium, they found that a total bandwidth equal to the pump frequency could be theoretically realized. The authors also investigated the role of phase matching on achieving the maximum bandwidth. They calculated the spectrum as a function of the normalized detuning, γ, given by: $\gamma = \Delta k/gI_0(0)$, where $\Delta k = 2k_0 - k_1 - k_{-1}$ is the wave-vector mismatch, I_0 is the total input intensity and g is the steady state gain coefficient. As expected, the broadest spectrum occurs for $\gamma = 0$, with the spectrum shifted to the anti-Stokes side because of the higher gain with increasing frequency. As γ increases the spectrum narrows and becomes more pronounced on the Stokes side. The authors also studied the process experimentally but were not able to have the Stokes signal at the same intensity as the pump laser. They used a hydrogen Raman cell to generate the Stokes radiation and then focused both the pump and Stokes into a second cell. As they increased the intensity of the two pumps the generated spectrum broadened and the anti-Stokes bandwidth grew faster than the Stokes side in agreement with the theory. The maximum energy that they used was 28.1 mJ for the pump at a wavelength of 532 nm and 0.64 mJ for the Stokes with the pump duration of 7 ns. The number of experimental orders did not increase as the Raman growth rate $B = gI_0(0)z$ as the theory predicted.

More recently in 2007, Losev worked with the group of Takahashi, Kato and Matsumoto and carried out a similar experiment but improved both the ratio of the two pump

energies, increased the pump frequency which increases the Raman gain and contained the Raman medium, D_2, in a hollow fiber to eliminate diffraction effects [50]. They first pumped a Raman cell with a KrF excimer laser operating at 248 nm with circular polarization to excite the rotational transition and generated Stokes radiation at 249.1 nm. As this wavelength falls within the gain region of the KrF amplifier both the pump and the Stokes field could be amplified together before being focused into the hollow fiber. 5 mJ of total pump power was focused into the 30 cm long, 124 μm diameter hollow fiber. 34 rotational Raman lines were generated that had power of at least 10% of the output pump pulse. When the D_2 pressure was increased to 60 kPa, a spectrum extending from 220 to 600 nm was achieved. The lines were a combination of vibrational and rotational lines.

Carman and coworkers [51]as well as Akhmanov *et al.* [52] derived the classical theory of SRS in the transient regime where the pulse duration is equal to or shorter than the collisional dephasing time of the Raman transition. It was found that rather than depending on the pump intensity, the transient gain was given by the energy flux and was only weakly dependent on the pulse profile. The Raman power gain in the transient regime is inversely proportional to the dephasing time. May and Sibbett confirmed this theoretical prediction by experimentally investigating transient SRS in hydrogen and methane [53]. As predicted, they found that more AS orders were achieved in the methane which had the much shorter dephasing time. Hickman and Bischel then generalized their multi-wave theory to include phase mismatch between the orders due to dispersion, which becomes important in the transient regime [54]. Their work showed that for low Stokes input energy, the anti-Stokes gain is a minimum for perfect phase matching, which matches the steady state result. However with high power Stokes input signal, where pump depletion occurs, the maximum anti-Stokes gain occurs for perfect phase matching. McDonald and co-workers theoretically modeled multi-frequency Raman generation for transient stimulated rotation Raman scattering in H_2 gas with two pumps having equal intensity [55]. They calculated the maximum generated bandwidth for different pulse durations as a function of dispersion. The amplitude of the grating is increased for short pulses because of the increase in intensity but this increase is balanced by the increased demand on phase matching. They found that the maximum bandwidth occurred for pulse durations equal to the dephasing time or longer. As in the earlier work of Losev and Lutsenko, the anti-Stokes orders dominate when the pulse duration is on the order of or greater than the dephasing time and there is perfect phase matching. The total bandwidth is maximized with a small positive dispersion because this causes an increase in the number of Stokes lines. On the other hand, with short pulses the maximum bandwidth occurs for perfect phase matching.

Losev and Lutsenko followed up this transient theory and found that a larger bandwidth can be generated in the highly transient regime [9]. Where their steady state calculations showed a maximum bandwidth equal to the pump frequency, in the transient regime they found conditions that allowed a bandwidth of 1.4 times the pump frequency. The number of Raman orders scales as the ratio of pulse duration to dephasing time. This theory then points to using a Raman medium with a short dephasing time so that you can maximize the generated spectrum with a short pulse, which will produce the most intense pulses in the shortest pulse train.

Losev collaborated with my group to test this idea using a solid Raman media of $KGd(WO_4)_2$ (KGW) that has a short dephasing time of 1.6 ps and a high Raman gain of ~ 4 cm/GW [56]. The high Raman gain was necessary because of the increased dispersion in a solid. The Raman gain length needs to be shorter than the coherence length. The experiment used two pulses having duration of 150 fs and intensities of 2×10^{12} W/cm^2 in the crystal. At these intensities a large number of Raman orders should have been generated but less than 10 were observed. In fact, with the pulse duration at 150 fs only a few orders were observed over a continuum spectrum. The experiment highlighted that with short pulses the Raman gain is competing with SPM. In order to detect the Raman lines, the pulse duration was increased to 2 ps and so matched the dephasing time, but the intensity was then also reduced by a factor of 10. Most of the Raman lines were Stokes rather than AS indicating that the dispersion was playing a large role. We compared the Raman generating with single pulse pumping where only a single Stokes and AS were generated. The following year, Imasaka's group studied MRG in KGW [57]. They used single pulse excitation with three different pulse durations of 200 ps, 20 ps and 200 fs. They got the most orders for the 20 ps pulses, which were again predominantly on the Stokes side. These experiments in KGW both showed that the high Raman gain was not sufficient to beat the phase mismatch due to dispersion for either single frequency or two frequency collinear pumping.

Sali and co-workers investigated multi-frequency Raman generation in the transient regime in both H_2 and methane in a hollow fiber [58, 59]. They measured the generated spectra for varying gas pressure from 300 mbar to 3 bar. A hollow fiber was used to ensure a long interaction length. The two pulses were from an amplified Ti:sapphire laser at 800 nm and an OPA that could be tuned from 450 to 800 nm. The Stokes pulse from the Ti:sapphire had energy of 500 μJ and the duration was 70 fs, the pump pulse had an energy of just 60 μJ and a pulse duration of 250 fs. The powers of the pump pulses and the gas pressure of the Raman media are both significantly smaller than the previous single pump pulse experiments. With just the single pulse at 800 nm present, no MRG was observed confirming that the MRG process is significantly enhanced with two pumps. In H_2, up to 5 AS orders were generated with energy greater than 10% of the strongest line at a pressure of 0.9 bar. In methane up to 7 AS orders were generated at the optimum pressure of 1.6 bar. Even with both inputs present there was a significant amount of continuum present because of SPM of the strong pumps. To avoid SPM, the short 800 nm pulses were then stretched to 400 fs, and keeping the energy the same as the previous experiment they were able to generate the same number of Raman lines and greatly reduce the continuum background.

Losev collaborated with my group to study transient MRG in Sulphur Hexafluorine, SF_6 gas contained in a hollow fiber [60]. The Raman transition in SF_6 is much smaller than hydrogen or methane. We used two 300 fs pulses from a two-color Ti:sapphire laser system, with a total maximum energy of 6 mJ equally split between the two pumps. We measured the MRG spectrum as a function of pump energy and found that the MRG spectrum increased with energy until a continuum formed under the orders. At higher pump energies, only the continuum spectrum grew. We observed 6 generated Stokes orders and 17 AS orders covering the spectral range of 200 to 700 THz. The AS spectrum in

SF_6 is not as wide as what was observed in hydrogen or methane indicating that the phase mismatch from dispersion limits the bandwidth, not the number of orders. This is also seen in the rotational Raman MRG studies where many more orders are generated but over a similar bandwidth.

Turner and Strickland [61]used a smaller diameter hollow fiber of 129 μm. As will be discussed later in this paper, increased MRG bandwidth had previously been shown in the impulsive regime using the smaller diameter [62]. The geometry-dependent negative GVD of the small diameter fiber can compensate for the positive material GVD of the gas. By balancing the two GVD components the phase matching conditions for MRG can be improved. For these experiments, we stretched the pulses to 600 fs by linearly chirping the pulses and measured the MRG spectrum as a function of pressure. As the dispersion was minimized by reducing the pressure, more orders were generated until a continuum formed under the AS orders, but not under the more intense pump lines and red shifted shoulders appeared on the AS orders. We then studied the MRG spectrum as a function of delay between the two linearly chirped pump pulses [63]. By varying the delay, the instantaneous frequency separation is varied. We could then tune through the Raman transition by varying the time delay. We noted that the frequency separation of the red shifted shoulders varied with time delay, but the separation did not match the separation of the pump frequencies. The appearance of the shoulders is still not understood.

As has been previously discussed the timescale for transient regime in the HC-PCF is 10 to 30 ns. Transient MRG has been carried out with nanosecond pulses from a microchip laser in HC-PCF [64]. The 1064 nm pump pulse was split with10 μJ of pump energy used to efficiently generate a Stokes beam in a hydrogen filled hollow photonic bandgap fiber. The Stokes field was combined with the remaining 90 μJ of pump radiation and launched into a Kagome HF-PCF filled with hydrogen. The Kagome fiber can support a much wider spectrum. 4 AS orders and 5 Stokes orders were generated covering the wavelength range from 800 to 1600 nm. Coherence between the orders was demonstrated by observing the sum-frequency of different Raman components.

A similar experiment was carried out in a photonic crystal fiber (PCF) [65]. The Stokes seed at 1117 nm was a cw signal provided by a diode pump Yb doped fiber. When just the 1064 nm radiation from the pulsed microchip laser is launched into the PCF, 2 Stokes and 4 AS orders are observed. The spectral width of each order is quite large indicating small coherence between the orders. When the narrow band cw Stokes field is added, more Raman lines are observed from the 6th Stokes to the 6th AS and each of the lines has a narrow spectral bandwidth.

VIII. IMPULSIVE REGIME

Kinsler and New developed a single field theory, which was felt to be more appropriate as the pulses get shorter [66]. In this theory the coupling constants oscillate at the Raman frequency and impose the sideband modulation on the propagating field. This single electric field can then no longer have a slowly varying envelope and the authors used a general-

ized few cycle envelope approximation. This theory can then handle broader overlapping spectrum and so could be beneficial in the impulsive regime.

Korn, Duhr and Nazarkin experimentally studied SRS in the impulsive regime [67]. They pumped SF_6 that has a Raman vibrational period of 43 fs with a 40 fs pulse at a wavelength 400 nm, from a frequency doubled Ti:sapphire laser system. The Raman shift is now less than the bandwidth and so a spectrum of discrete orders is not possible. Rather, they observed a broadening of the pump spectrum on the blue side, corresponding to a number of AS orders.

Nazarkin and co-workers [10]generated a discrete multi-order Raman spectrum by scattering a longer pulse from an impulsively excited molecular vibration in SF_6 contained in a hollow fiber. They excited the molecular oscillation with 30 fs pulses from a Ti:sapphire laser system with 500 μJ of energy. Some of the fundamental radiation was frequency doubled in a BBO crystal to be an injection pulse that would be modulated by the molecular oscillation. The frequency of the probe pulse is shifted from the pump so the modulation frequencies are not obscured by the pump radiation. For the probe to generate discrete Raman orders the spectral bandwidth needs to be less than the Raman spectral shift. By tuning the angle of the BBO crystal, the bandwidth could be reduced and produce a longer blue pulse duration of 200 fs. The blue pulse was delayed by $\sim$ 100 fs from the infrared pulse. The sideband generation is investigated as a function of pressure. At first, the MRG spectral width scaled linearly with pressure. The spectrum was symmetric about the pump achieving up to the third Stokes and anti-Stokes orders. At higher pressures, the injection frequency was almost fully converted into side band energy. The authors confirmed that the modulation went away when the pump spectral bandwidth was reduced to below the transition frequency.

Wittman, Nazarkin and Korn, later demonstrated that the spectrally modulated blue field could be compressed to a train of ultrashort pulses [68]. They used chirped mirrors that provided a negative GVD of ~ -300 fs^2. A small variable positive material GVD was introduced by a pair of fused silica wedges. With either a positive or negative net GVD of ~ 100 fs^2, a pulse train of 16 fs pulses separated by the vibrational period of 43 fs was measured using a self-diffraction correlation technique. The peaks of the pulses in the positive GVD case fell exactly in the space between the peaks in the negative GVD case. This clearly showed that the blue probe field had been frequency modulated with sinusoidal character allowing compression with either sign of GVD. Nazarkin and co-workers improved on their earlier MRG results by using a hollow fiber of smaller, 126 μm, diameter [62]. With the GVD minimized they were able to achieve 15 orders symmetrically about the 400nm input.

Zhavoronkov and Korn also generated single 3.8 fs pulses from impulsive molecular modulation in SF_6 [12]. Rather than reducing the spectral bandwidth of the probe pulse they compressed it to 15 fs which is well below the vibrational period. In this way, the probe spectrum experiences a continuous broadening from MRG that gives single pulses rather than a pulse train. This continuous spectral broadening is different than broadening from SPM, which follows the intensity and cannot be easily compressed. The pump pulse experiences SPM, and so a delayed lower power, frequency doubled probe is used. The

pressure of the gas was set to have the pump and probe wavelength phase matched so that the delay remained constant with propagation. The frequency modulation imposed from the impulsive scattering as already demonstrated is sinusoidal and so can be easily compressed with linear GVD supplied by chirped mirrors. The author's showed that the modulation phase changed with delay between the probe and pump pulses and that they had optimum compression resulting in a duration of 3.8 fs for a delay of 242 fs.

Bustard, Sussman and Walmsley demonstrated that the coherence produced by impulsive pumping could be amplified by pumping with a long pulse from a second laser [69]. A linearly polarized beam of 55 fs pulses was split to both impulsively excite the rotational Raman transition in hydrogen and also be a probe pulse. A circularly polarized, frequency doubled, Q-switched Nd:YAG laser was used to pump the coherence. The energy of the first Stokes was measured as a function of pump energy with and without the short seed pulse. More Stokes energy was generated with a seed pulse present. The enhancement saturated at a seed energy of 12 μJ, which would suggest that at this energy the impulsively excited coherence exceeds the spontaneous Raman scattering rate.

IX. ANGLE TUNING IN CRYSTAL MEDIA

For gaseous Raman media, the Raman orders were collinear with the pumps. This was achieved in the adiabatic regime, by the refractive index being controlled by the Raman process itself so that all the orders were phase matched in the forward direction. In the transient and impulsive regimes, the collinear propagation was guided by using hollow fibers. For these cases then, the hollow fiber had to also compensate for the material dispersion so that the orders could be phase matched in the forward direction. The collinear arrangements were chosen so that all the orders could be easily superimposed to give the ultrashort pulses. Crystals have much higher Raman gain but are very dispersive making collinear propagation not possible. The orders tend to phase match by radiating at different angles. In the early SRS experiments with single pumps, the Raman orders radiated at cones with angles given by phase matching. In more recent MRG experiments, it was realized that by crossing two beams at the phase matching angle would cause the higher orders to radiate in single directions, each at their own phase matching angle. The disadvantage of this technique is that the generated Raman orders will have to be both spatially and temporally overlapped.

In 1997, Hakuta and co-workers studied SRS in solid hydrogen placed in a 2 cm long cavity [70]. They observed two Stokes and two anti-stokes orders for pump energy above a threshold of 70 μJ, with 532 nm pulses with duration of 10 ns. They observed that there was AS radiation emitted collinearly with the pump and Stokes showing that the Raman gain was sufficient to overcome the large phase mismatch due to material dispersion. When the Raman cavity is tilted such that the Stokes radiation is no longer collinear with the pump, than the AS line is emitted on the opposite side of the pump for tilt angles of 0 to 45 mrad.

Shon and colleagues numerically modeled adiabatic MRG in solid hydrogen for a tilt angle between the two driving fields [71]. The two driving pulses were long in order to

adiabatically drive the Raman coherence. They studied the sideband generation of a short probe pulse that is input at an angle to the generated Raman coherence. The calculated the generated MRG spectrum as a function of propagation distance and different input angles. They found that they could either optimize the arrangement to have a broad MRG signal or have the energy efficiently driven into a single higher order.

Takashashi, Mano and Yagi [72] experimentally studied impulsive MRG in a 1 mm thick $SrTiO_3$ crystal. The two pumps were from the same 130 fs Ti:sapphire laser system. The laser pulse was split into two pulses and recombined in the crystal at a crossing angle of 1 to 5° between them. Threshold behaviour was observed where a large number of Raman orders were generated when the two beams had intensities greater than 5 GW/cm^2. The higher orders are phase matched by radiating at higher angles from the input Stokes beam. The frequency separation of the lower orders is 340 cm^{-1} and the higher orders are at 230 cm^{-1}. It was also noted that the slope of the curve of output angle versus frequency also changed when the frequency changed, corresponding to different phase matching conditions. The two different frequencies correspond to two different phonon modes of the crystal.

Matsuki, Inoue and Hanamura carried out a similar experiment in the crystal $KNbO_3$, but used the 150 fs signal and idler pulses of an OPA so that the two pumps could have a peak frequency separation that was set to a phonon mode [73]. The two input frequencies were separated by 613 cm^{-1} corresponding to the frequency of the phonon mode of the crystal. The beams crossed at an angle of 4.5°. The crystal was angle tuned such that the inputs were frequency doubled in the crystal. Several Raman orders were scattered at frequency separations of 613 cm^{-1} from the $2\omega_1$ and the $2\omega_2$ frequencies, each radiating at an angle given by phase matching.

Zhi and Sokolov were able to generate up to 20 AS orders and 2 Stokes orders by using a similar approach in lead tungstate [74]. They varied the crossing angle and noted that not only does the MRG efficiency change as you go through the phase matching angle of 4°, but that at angles smaller or larger, the frequency spacing of the orders changes even though the two pump frequencies were held fixed at the Raman separation of 930 cm^{-1}. They also held the angle fixed and changed the frequency separation and noted that the strongest signal occurred at the resonant frequency, but multiple orders occurred even at other frequencies. At other frequencies, the orders are double peaked one at the Raman frequency and one given the four wave mixing signal of the two peak input frequenices. This works shows the importance of phase matching on side band generation. The resonant nature of the Raman process demonstrates that the Raman signal should be much stronger than the non-resonant 4-wave mixing signal if phase matching can be ignored.

Liu, Zhang and Kobayashi used a similar arrangement with a BBO crystal, but one of the input pulses was frequency broadened in a hollow fiber filled with krypton gas so that the one pump had a wavelength span from 660 to 900 nm [75]. Similar to Zhi's and Sokolov's work they showed that if the crossing angle was smaller than the resonant angle the frequency spacing of the orders was closer together and that as the angle increased the frequency spacing increased. Looking at the dependence of output angle as a function of frequency they noted that the slope was 843 cm^{-1}/degree for any of the crossing angles showing that the angular dependence is wavelength dependent and not order dependent

confirming the importance of phase matching.

Zhi and Sokolov generated a broad MRG spectrum by using two linearly chirped pulses [76]. Both pulses were derived from a single, 35 fs pulse that could impulsively drive the Raman transition. However, this spectrally broad pulse was linearly chirped to durations varying between 100fs and 2 ps and then split into two pulses with equal energy. The instantaneous frequency separation of the two pulses can then be tuned through the Raman resonance, by varying the delay between the two pulses. In this way, the Raman transition is driven in the transient regime and it may be optimum to have the stretched duration match the Raman coherence time. They were able to generate up to 40 AS orders of the 325 cm^{-1} Raman order. The highest order is radiated at an angle of 80° to the pump beam. It is not surprising that this Raman order can be driven by a pump pulse, having a bandwidth of 460 cm^{-1} FWHM. However, they were also able to drive the 903 cm^{-1} Raman order, by chirping the pulses with the rate of 620 $cm^{-1}ps^{-1}$ and separating the pulses by 1.43 ps. The Raman coherence was then driven at intensities well below the peak intensity. 19 AS orders were observed. Along with the Raman orders, there were also orders appearing that the authors assume come from the non-resonant 4-wave mixing process. Zhi, Wang and Sokolov used a similar arrangement and achieved broadband coherent radiation in diamond [77]. They observed that the frequency spacing of the orders was more dependent on the phase matching than the Raman resonance. If the crossing angle of the pumps was less than the phase matching angle, the frequency spacing was again less than the Raman frequency and as the angle was tuned through resonance the frequency increased beyond the Raman transition.

The disadvantage of generating the broad spectrum through angled phase matching is that the orders must be recombined both spatially and temporally. Matsubara and colleagues solved this problem by using a pulse compressor comprised of two spherical mirrors and a single prism [78]. The arrangement is depicted in Fig. 2. A $KTaO_3$ crystal was pumped by $\sim$ 200 fs pulses from the signal and idler of an OPA. The Raman spectrum consisted of 6 spectrally broad orders, separated by 692 cm^{-1}. The Raman orders were reflected by a 100 mm focal length, spherical mirror. The spherical mirror imaged the plane of the crystal onto the prism, so that all the beams were focused together onto the prism. The diffracted beam from the prism was collimated with a 500 mm focal length spherical mirror and directed to a SPIDER [79]for pulse characterization. They measured a pulse duration of 13 fs where the transform limited duration of the generated spectrum would be 9.8 fs.

Zhi and co-workers used a similar arrangement but added a combination of glass plates in the different beam lines and a programmable pulse shaper after the prism to better control the phases of Raman lines [80]. They focused the first 5 AS lines generated in diamond onto the prism. They pre-compensated the delays by adding different amounts of glass in each beam line. The programmable pulse shaper was placed in the recombined beam to adjust the phase between the orders. They verified that they could achieve flat spectral phase across the five orders. The phase was measured by a technique developed by the Katsuragawa group [81], which is based on the SPIDER technique [79]. They combine the generated Raman spectrum with the two pump beams in a nonlinear crystal to produce

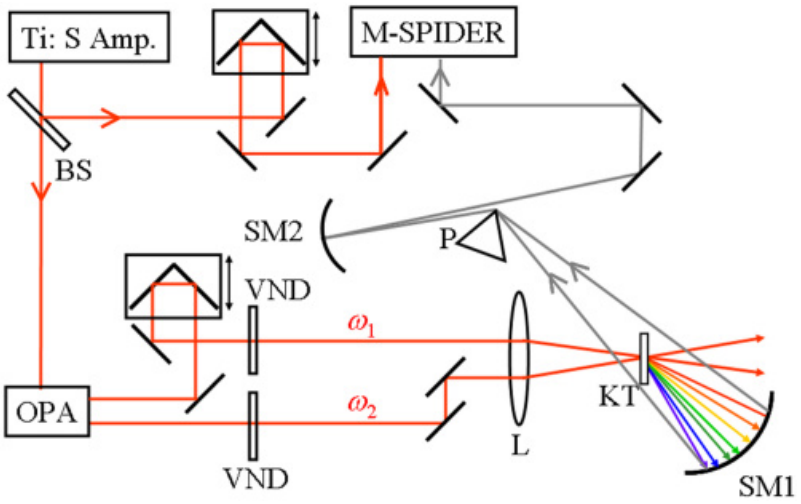

FIG. 2: Experimental setup for ultrashort pulse generation using multiple RN-CARS signals. Figure reproduced with permission from ref. 75 © 2009 OSA

a sum-frequency spectrum. The resulting spectrum is then the addition of two overlapping spectra from the second harmonic of the nth order and from the sum-frequency of the $n-1$ and $n+1$ orders. The interference in the spectrum then gives the spectral phase in the same way as the SPIDER.

X. PHASE STABLE, ULTRASHORT PULSE GENERATION

An excellent review of the field of ultra-short pulse formation created from Raman excitation has been written by Baker and colleagues [82]. I have already described many of the experiments to generate ultra-short pulse that have been carried out in each of the temporal regimes. I want to conclude this review with two recent achievements to generate phase stable trains of ultra-short pulses. In the first Suzuki, Hirai and Katsuragawa have generated a frequency comb with carrier envelope offset (CEO) control [84]. Their experimental arrangement is shown in Fig. 3. The key is that the two pump frequencies are integer multiples of the Raman transition frequency. Because of that a third pulse made from the frequency doubled Stokes line is then also a multiple of the Raman frequency. In this way the third input exactly matches the line generated by MRG. By adding the third input, a very broad frequency comb was generated. In addition to these conditions, the two driving frequencies are generated in a single laser cavity and so they are both integer multiples of the cavity free spectral range (FSR). Therefore with this arrangement the pump frequency is $\Omega_0 = i \times \mathrm{FSR}$, and the Stokes frequency is $\Omega_{-1} = k \times \mathrm{FSR}$, the Raman transition frequency would be given by $\Omega_r = (k-i) \times \mathrm{FSR}$ and the Raman components have frequency $\Omega_n = i \times \mathrm{FSR} + n \times (k-i) \times \mathrm{FSR}$, where i, k and n are all integers. The CEO frequency of the Raman frequency comb is restricted to integer multiples of the cavity

FSR. By setting the pump frequency to also be a multiple of Ω_r, makes the CEO frequency zero.

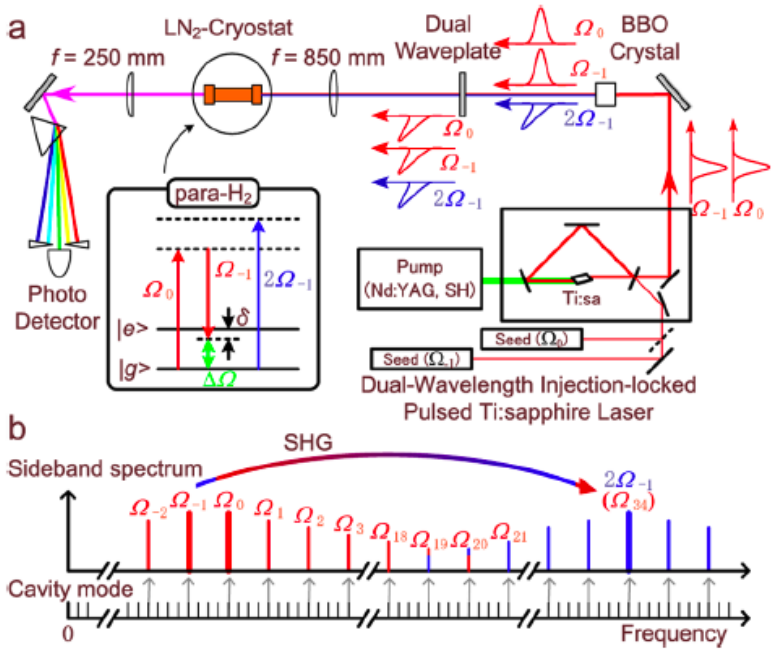

FIG. 3: Generation of octave-spanning Raman comb with control of carrier-envelope-offset frequency. (a) Experimental setup and scheme for Raman comb generation. (b) Ω_0, Ω_{-1}, and $2\Omega_{-1}$ are located at equidistant frequency markers whose spacing is the FSR of the dual-frequency injection-locked Ti:sapphire laser. The expected parametric Raman spectrum is shown, when Ω_0 and Ω_{-1} are set so as to satisfy the zero-CEO frequency condition. Figure reproduced with permission from ref. 80 © 2008 APS

The second approach to CEO phase stabilized frequency comb is MRG that looks like harmonic generation [83]. The Stokes frequency matches the AC Stark shifted vibrational Raman transition frequency of 4155.235 cm^{-1} in hydrogen. To obtain this Stokes frequency, the Kung group difference frequency mixed the transform limited pulses from a dye laser and a Ti:sapphire laser. The pump frequency is then achieved by frequency doubling the Stokes field. The two frequencies are then input to the hydrogen Raman cell. As the lowest possible frequency generated frequency is one of the inputs, only AS orders can be generated. The Raman orders occur at the harmonic frequencies of the input Stokes field. They used a similar phase measurement technique described in [81]but because the orders are harmonic orders of the Stokes, now any order ω_k can be used to heterodyne with the sum frequency of two other order ω_i and ω_j, where $k = i + j$. The authors showed that CEP control of a Raman comb is possible with nanosecond long pumps.

XI. CONCLUSIONS

Broadband MRG spectra have now been generated in all three temporal regions and pulse durations down to 1.6 fs have been achieved. Single pulses with 3.8 fs have been measured and stable pulse trains with CEO control have been achieved. With the new methods of phase controling the broad spectrum MRG should soon be able to produce high intensity, single to sub-femtosecond pulses in the visible to UV ranges that should open up new possibilities in pump-probe spectroscopy or Coulomb explosion spectroscopy.

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