Generation of Multiple Phase-Locked Stokes and Anti-Stokes Components in an Impulsively Excited Raman Medium

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We report on the observation of a highly efficient transformation of laser radiation into higher-order Stokes and anti-Stokes components in impulsively vibrationally excited gaseous SF_6. The specific (Bessel-like) behavior of their intensity with the gas pressure reveals the mutual coherence of the generated frequencies. We propose this new regime of Raman frequency conversion for generation of sub-fs pulses.

The shortest light pulses generated presently by the conventional methods of fs-laser mode-locking and nonlinear pulse compression last for about 5 fs and contain nearly two light wave oscillations [1]. Generation of even shorter laser pulses would provide access to studies of nonlinear-optical interactions on a time scale of only one optical cycle that would be of great significance for both fundamental and applied science. Recently, a considerable interest was concentrated on the alternative approach to sub-fs pulse generation based on the idea of Fourier synthesis of phase synchronized laser fields [2]. In particular, the problem of mode locking of high-order lines of stimulated Raman scattering (SRS) was in the focus of both theoretical [3–5] and experimental [6] studies. Various regimes of Raman mode locking (resonant [3] and quasiresonant [4], mode locking within the Raman soliton [5]) were proposed. Although generation of multiple Raman lines in liquids and gases is presently not a particular problem [6], a serious challenge is to maintain certain phase and amplitude relations between the high-order SRS components during the generation process. On one hand, by increasing the number of SRS components, even shorter pulses can be synthesized. On the other hand, the generation of higher SRS components with comparable amplitudes necessarily leads to higher pump pulse energies. According to the proposed schemes [4,5], energy densities of the order of 10^2 J/cm^2 are required. In these conditions self-focusing and self-phase modulation due to fast electronic response, medium ionization, and other competing processes can make the phase relationships between the components irregular. Note that spectral broadening of Stokes and anti-Stokes frequencies [7], continuum generation in SRS [6], and Kerr-induced shift of the Stokes line [8] were recently reported. In addition, amplitude modulation of the Stokes field (leading to Stokes pulse shortening) was observed even in the first SRS experiments [9].

In this Letter we propose and demonstrate experimentally an alternative approach to the problem of high-order SRS. The idea of the method lies in the fact that the influence of the competing nonlinear processes can be eliminated if SRS occurs in a preliminary vibrationally excited medium. A time-delayed SRS is possible because, once excited, the dipole forbidden Raman transition can radiate only in the presence of the injected field. By exposing the molecule to an intense fs pulse with a duration shorter than the molecular vibrational period T_v, one can prepare the vibrationally excited state "impulsively" (i.e., with only one ultrashort pulse [10,11]). A second, relatively weak, delayed injection pulse propagating in the excited medium in the linear regime experiences scattering due to the modulation of its refractive index by molecular vibrations. This manifests itself in a generation of the Stokes and anti-Stokes sideband frequencies. In essence, in the proposed regime of SRS, the conventional *cascade nonlinear scattering* (i.e., a scattering where the generation of new frequencies results from nonlinear interaction of all the involved fields) is replaced by the *cascade linear scattering* with all the nonlinear-optical effects (medium excitation, nonlinear self-action, ionization, etc.) being confined only within the pumping process.

Based on this new approach, we have realized an efficient (up to 100%) transformation of the injection field into multiple Stokes and anti-Stokes components in an impulsively excited SF_6 gas medium. The picture of the SRS process is found to be qualitatively different from the conventional cascade SRS process [12]. The uniform spectrum of the components, the symmetric character of Stokes and anti-Stokes generation, and their specific dependence on the gas pressure indicate that the components are in certain amplitude-phase relations, and therefore can synthesize an ultrashort pulse sequence.

Practically, the use of the impulsive regime of medium preparation makes the high-order SRS process *completely controllable*. First, pumping with a pulse shorter than the molecular vibrational period enables synchronization of the injection pulse scattering on a time scale less than one vibrational period. Second, the SRS gain of an impulsively pumped medium is determined by the integral characteristic of the pump pulse (full energy) and thus not sensitive to its temporal structure (in contrast to the conventional schemes of SRS [6–9]).

The results also add to the previous observations of impulsive SRS, e.g., continuous down-shift of a fs-excitation

pulse spectrum [13], redshifting and blueshifting of variably delayed fs-probe pulses with a duration $\tau \ll T_v$, propagating after the excitation pulse [11,13]. In fact, the proposed regime can be treated as the opposite limit of the latter scheme where the probe pulse is longer than the vibrational period T_v. The continuous change of the probe pulse spectrum transforms in this case into the discrete Raman line generation.

In our experiments we used a Ti:sapphire chirped pulse amplification laser system at 1 kHz repetition rate. The output pulses at 800 nm (1.5 eV) had an energy up to 500 μJ and a pulse width of 30 fs and could impulsively excite the symmetric vibrational mode A_{1g} of SF_6. A part of the fundamental was frequency doubled with 1-mm-thick type-I BBO (beta-barium-borate) nonlinear crystal. The used output energy at 400 nm was measured to be 3 μJ with a pulse width of 200 fs at full width half maximum (FWHM). By changing the angle between the beam axis of the fundamental and the optical axis of the BBO crystal, we could slightly vary the spectral width (and duration) of the second harmonic signal. The interaction experiments were performed in a gas filled hollow waveguide [13]. This enlarged essentially the effective nonlinear interaction length. The typical value of the pump pulse intensity in the gas filled waveguide (diameter 250 μm, length 1 m) was about 10 TW/cm^2.

Our choice of gaseous SF_6 as a nonlinear medium was motivated by the nonselective character of impulsive pumping. The highly symmetric, spherical top SF_6 molecule exhibits no Raman rotational spectrum. At the same time, the totally symmetric vibrational mode A_{1g} of SF_6 gives rise to a very strong (compared to other two Raman modes) Raman line at 775 cm^{-1} [14]. One can expect therefore that only one Raman active mode of SF_6 (775 cm^{-1}, vibrational period $T_v = 44$ fs) will be effectively excited by the impulsive pumping.

To investigate the discussed regime of high-order SRS, the intense 800 nm pulse was focused on the tip of the waveguide filled with SF_6. The second (injection) pulse at 400 nm with a duration $\approx$200 fs and an energy much lower ($\approx$3 μJ) than that of the pump propagated with a temporal delay of several 100 fs. The pump pulse output spectra showed a typical broadening due to Kerr self-phase modulation [13]. In contrast, the injection pulse dynamics was totally different. Figure 1 shows the output injection pulse spectra for increasing values of pressure $p = 0-470$ mbar. The well-pronounced equidistant character of the lines in Fig. 1 proofs that the scattering of the injection field has been induced by the symmetric vibrational mode (775 cm^{-1}). The generated lines show no spectral broadening and repeat very well the input shape of the injection pulse spectrum [Fig. 1(a)]. This suggests that the regime of scattering is linear.

In the classical picture of cascade SRS, the generation of Stokes components normally dominates over anti-Stokes generation [12]. In the observed regime of SRS the Stokes and anti-Stokes components are generated with
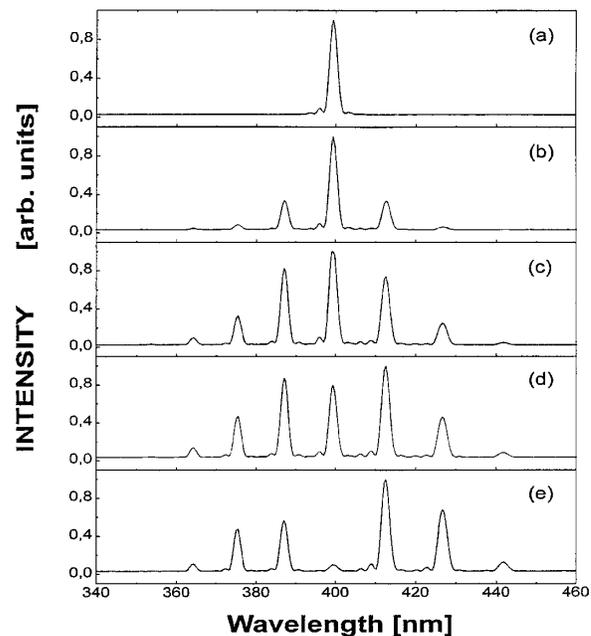
FIG. 1. The measured output Raman spectra of the 400 nm injection pulse for increasing values of SF_6 pressure: (a) $p = 0$; (b) $p = 346$ mbar; (c) $p = 395$ mbar; (d) $p = 410$ mbar; (e) $p = 470$ mbar. The energy of the 800 nm 30 fs-pump pulse is 130 μJ.

nearly equal efficiency [see Figs. 1(a)–1(d)]. Initially, with an increase of gas pressure the number of components increases (up to 3rd order can be seen), and the intensity of the components fall off monotonically with the component order [Figs. 1(a)–1(c)]. But further increase of gas pressure breaks this monotonic distribution. The energy of the central component (at the injection frequency) is seen to be further converted to the sideband frequencies, even though its intensity is getting smaller than the intensity of the sideband components. As a result, a nearly 100% conversion efficiency into the Stokes and anti-Stokes components is realized.

The above behavior was observed only for sufficiently short pump pulses. The impulsive character of the excitation has been checked by changing the bandwidth limited width of the pump pulse. In addition, we did not see any critical dependence of the SRS on the pump intensity (which is characteristic for the usual regime of SRS), and the sideband generation was registered down to very small pump energies (30 μJ) or gas pressures (50 mbar). We also note that with an increase of the injection pulse energy above 20–30 μJ a well-pronounced Kerr broadening of the Raman components was measured.

To give a quantitative explanation of the observed effects, we consider a propagation in the Raman-active medium of an intense pump pulse $\mathcal{E}_p(z,t) = (1/2)E_p \exp(i\omega_p t - k_p z) + \text{c.c.}$ with a duration τ_p much shorter than the molecular vibrational period T_v, and a relatively weak injection pulse $\mathcal{E}_i(z,t) = (1/2)E_i \exp(i\omega_i t - k_i z) + \text{c.c.}$ The molecule normal

vibrational coordinate Q obeys the equation [12]

$$\frac{\partial^2 Q}{\partial t^2} + \frac{2}{T_2}\frac{\partial Q}{\partial t} + \Omega_\nu^2 Q = \frac{1}{2M}\left(\frac{\partial\alpha}{\partial Q}\right)\mathcal{E}^2. \quad (1)$$

Equation (1) represents a linear oscillator with an effective mass M, a natural frequency Ω_ν, and a relaxation time T_2, driven by the force quadratic in the field $\mathcal{E}$. For the totally symmetric vibrational mode ($\Omega_\nu = 775$ cm^{-1}) of SF$_6$ the Raman transition is isotropic [14] and the change of the molecular linear polarizability $\alpha(Q)$ with respect to the vibrational coordinate Q is described by a scalar $(\partial\alpha/\partial Q)$.

Consider the interaction of the molecule with the pump pulse with duration $\tau_p \ll T_\nu = 2\pi/\Omega_\nu$. In this "impulsive" interaction regime, terms $\Omega_\nu^2 Q$ and $(1/T_2)\partial Q/\partial t$ in Eq. (1) can be neglected in comparison to the rapidly changing term $\partial^2 Q/\partial t^2$. By integrating Eq. (1) with the assumption that the pulse appears at the moment $t = 0$ and is nonzero within the time interval $0 < t < \tau_p$, we find that within the interaction time $(0 < t < \tau_p)$ the vibrational velocity $V(t) = \partial Q/\partial t$ and coordinate $Q(t)$ change as

$$V(t) = \frac{1}{2M}\left(\frac{\partial\alpha}{\partial Q}\right)\int_0^t dt'\,\mathcal{E}_p^2(t'),$$
$$Q(t) = \int_0^t V(t')\,dt'. \quad (2)$$

According to Eq. (2), for a δ-short excitation pulse with a finite energy, i.e., in the limit $\tau_p \to 0$ and $\mathcal{E}_p^2\tau_p = $ const, the result of the impulsive pumping is that the molecule acquires some initial vibrational velocity determined by the pulse energy $W_p = (c/8\pi)\int_{-\infty}^{\infty}|E_p(t)|^2\,dt$, whereas its coordinate has no time to change [10]. When the pump field is turned off, e.g., for $t > \tau_p$, the nuclear coordinate exhibits freely damping oscillations

$$Q(t) \approx Q_0 \exp(-t/T_2)\sin(\tilde{\Omega}_\nu t) \quad (3)$$

with $\tilde{\Omega}_\nu^2 = \Omega_\nu^2 - (1/T_2)^2$, and the amplitude $Q_0 = (2\pi/Mc\Omega_\nu)[\partial\alpha(\omega_p)/\partial Q]W_p$ proportional to the pump energy W_p. This integral dependence of $Q(t)$ on the pump pulse parameters is important, because the pump pulse amplitude and phase can change in a complicated and unpredictable way in the course of nonlinear propagation, while its full energy can be easily controlled.

During the propagation, the pump pulse generates a wave of vibrational excitation (3) which moves with the pump pulse group velocity, $Q(z,t) = Q(t - z/\nu_p)$. The dynamics of a weak injection pulse (weak in the sense that it does not change the state of molecular free vibrational motion) can be considered as a scattering in a linear medium with a polarization $P_{\text{Ram}} = N(\partial\alpha/\partial Q)Q(z,t)\mathcal{E}_i$ modulated by the vibrational excitation wave $Q(z,t)$. If the molecular vibrational frequency is much lower than the injection pulse carrier frequency, $\Omega_\nu \ll \omega_i$ (which is the case in the discussed situation), the initial stage of pulse scattering can be treated as a frequency modulation

process. By inserting P_{Ram} in the wave equation and making common approximations, we get the following equation for the injection pulse complex envelope $E_i(z,t)$:

$$\frac{\partial E_i}{\partial z} + \frac{1}{\nu_i}\frac{\partial E_i}{\partial t} = -i\beta_i Q(t - z/\nu_p)Q_0^{-1}E_i. \quad (4)$$

Here $\beta_i = 2\pi\omega_i Nc^{-1}Q_0\alpha'(\omega_i)$, N is the molecule concentration, and $\alpha'(\omega_i) = \partial\alpha(\omega_i)/\partial Q$ is the Raman coupling parameter for the injection field; ν_i is the injection pulse group velocity, and $Q(x)$ is the wave form of vibrational excitation given by Eq. (3). The parameter β_i has the sense of the Raman gain for the injection field. Practically, the vibrational dephasing time T_2 is much longer than both the injection pulse duration τ_i and the molecular oscillation period T_ν. Neglecting the relaxation of $Q(z,t)$ on the time scale of τ_i and using the frame $(z,\tau) \equiv (z, t - z/\nu_i)$ moving with the injection pulse, the solution of Eq. (4) can be written as

$$E_i(z,\tau) = E_i(0,\tau)\exp\Bigg\{-i\beta_i\frac{\sin(\Delta K z)}{\Delta K}$$
$$\times \sin(\Omega_\nu\tau + \Delta K z)\Bigg\}, \quad (5)$$

where $E_i(0,\tau)$ is the input amplitude of the injection pulse, and the parameter $\Delta K = \Omega_\nu[(\nu_i)^{-1} - (\nu_p)^{-1}]/2$ characterizes the group velocity difference between the pump and injection pulse. The physical sense of the solution is immediately evident if one analyzes Eq. (5) in the spectral domain. Assuming the injection pulse duration τ_i to be long compared to the molecular vibrational period $T_\nu = 2\pi/\Omega_\nu$ (narrow spectrum), and making a Fourier transform of Eq. (5), we obtain the following intensity spectrum:

$$|F_i(\Delta\omega)|^2 = \sum_{n=-\infty}^{\infty}|f_i(\Delta\omega - n\Omega_\nu)|^2 J_n^2(\xi)$$
$$\text{with } \xi = \beta_i\frac{\sin(\Delta K z)}{\Delta K}, \quad (6)$$

where $f_i(\Delta\omega) = f_i(\omega - \omega_i)$ is the Fourier spectrum of the input injection pulse $E_i(0,\tau)$. The spectral distribution (6) represents a superposition of uniform equidistant lines spaced by the molecular vibrational frequency Ω_ν. The intensities of the sideband frequencies $\omega_n = \omega_i + n\Omega_\nu$ ($n = 0, \pm1, \ldots$) depend on their arguments as squared Bessel functions $J_n(\xi)$. From the oscillating behavior of the Bessel functions immediately follows that full conversion of the injection field energy into the sideband frequencies is possible. It occurs when $J_0(\xi)$ passes through its zero points. With an increase of the argument, the number of components increases. However, the increase of ξ (and the component number) is limited by the length $L_c = (\pi/2)(\Delta K)^{-1}$. At this length the group delay between the pump and injection pulse is equal to a half of the molecular vibrational period, and the frequency modulation process changes its sign.

In our experiment (Fig. 1), the propagation length z is defined by the hollow waveguide length L_0, and
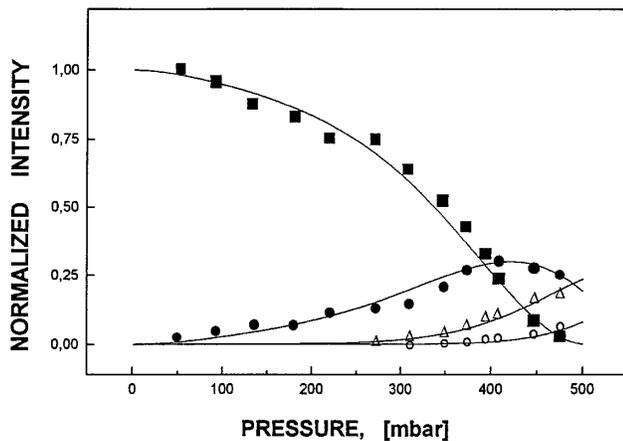
FIG. 2. Dynamics of the intensity of the SRS components with the SF_6 pressure. The filled squares show the measured intensity at the injection frequency (400 nm); the filled circles—at the first anti-Stokes; the triangles—at the second anti-Stokes; and the open circles—at the third anti-Stokes frequency. The full lines show the results of computer modeling of the component generation in SF_6.

FIG. 3. Computer modeling of propagation of a laser pulse ($\lambda \approx 1$ μm) with a spectrum close to the one shown in Fig. 1(e) (two Stokes + two anti-Stokes lines spaced by $\Omega_v = 775$ cm^{-1}) in a normally dispersive medium with a dispersion law $k(\omega) = (\omega/c)(1 + \alpha\omega^2)$, ($\alpha > 0$). The propagation length z is normalized by $z_0 = (k_{\omega\omega}\Omega_v^2)^{-1}$.

therefore the change of ξ is determined by the gas pressure p. The value of ξ increases monotonically with the gas pressure, and the observed full energy transformation at $p_1 = 470$ mbar [Fig. 1(e)] corresponds approximately to the first zero of $J_0(\xi)$ which is realized when $\xi(p_1) = \beta_i \sin[\Delta K L_0]/\Delta K = 2.4048$. The behavior of $J_n(\xi)$ $(n > 0)$ is such that at $\xi = 2.4048$ the values of $J_1(\xi)$ and $J_2(\xi)$ are comparable but $J_3(\xi)$ is still small [see Fig. 1(e)]. By estimating $(\partial\alpha/\partial Q)$ from [14] $(1.5 \times 10^{-16}$ cm$^2)$, the group mismatch from [9], and taking the pump pulse energy ≈ 100 μJ we find that at $p \approx 500$ mbar the argument $\xi(p)$ of $J_0(\xi)$ is, indeed, close to 2.4.

The observed asymmetry of the Stokes and anti-Stokes components [Fig. 1(e)] is explained by the fact that for the Stokes frequencies lying closer to the pump frequency than the anti-Stokes ones, the group velocity mismatch is smaller and therefore conversion is higher. The above considerations are completely supported by the results of computer modeling of the process presented in Fig. 2. (For details of the model see [15].)

The important advantage of the regime of SRS is that the phase modulation $\partial\varphi_i/\partial\tau$ of the injection field in the excited medium changes its sign periodically with the time τ from the leading to the trailing edge [see Eq. (5)]. This remarkable fact suggests that transformation of the phase modulation into an amplitude one can be realized also in a medium with normal dispersion. If, in addition, the injection radiation is tunable, generation of fs pulses and pulse trains in a wide frequency range can be realized. In particular, we have experimental evidence that for an injection pulse in the IR region ($\lambda_i \approx 1$ μm) a component number comparable to that produced with the second harmonic is achievable. In this case the frequency modulated IR-injection pulse would transform, in a normally dispersive medium, into a pulse sequence
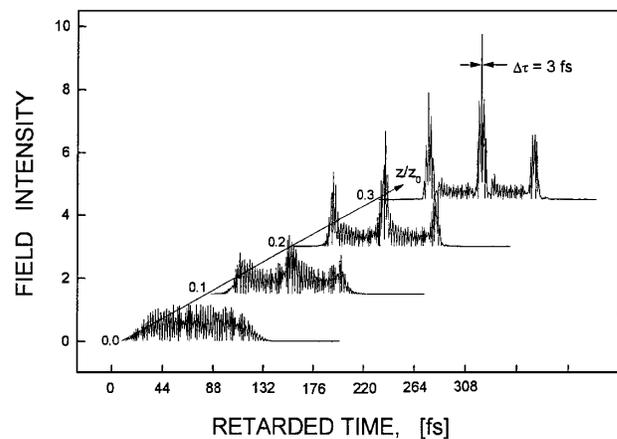
with a duration in each subpulse as short as only one oscillation of the field as shown in Fig. 3.

In conclusion, we have proposed and experimentally demonstrated a new regime of femtosecond SRS which provides efficient generation of multiple Raman components. In this "linear" regime, SRS occurs in a preliminary impulsively excited Raman medium and represents some temporal analogy of wave diffraction by a grating with sinusoidally modulated dielectric index. The specific behavior of the generated components with the gas pressure shows that they are mutually coherent and therefore can be used to synthesize sub-femtosecond pulses.

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