Observation of Raman Self-Conversion of fs-Pulse Frequency due to Impulsive Excitation of Molecular Vibrations

G. Korn, O. Dühr, and A. Nazarkin

Max-Born Institut für Nichtlineare Optik und Kurzzeitspektroskopie, Rudower Chaussee 6, 12489 Berlin, Germany
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We report on the observation of a Raman frequency conversion mechanism different from the usual Stokes (anti-Stokes) stimulated process. A continuous down-shift of laser pulse frequency was measured for sufficiently short (≤ 40 fs) pulses propagating in gaseous SF_6. We attribute this behavior to the extremely nonstationary nuclear response of SF_6 molecules to the light field with a duration shorter than the period of the Raman-active vibration. [S0031-9007(98)06773-8]

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The purpose of this Letter is to present some new experimental and theoretical characteristics of stimulated Raman scattering of light in the region of fs-laser pulse durations. Stimulated Raman scattering (SRS) was extensively studied during the past three decades, and nonlinear properties of this phenomenon are well established in the literature: The effect occurs for laser field intensities exceeding some threshold, and the frequency spectrum of generated coherent radiation generally contains discrete Stokes (anti-Stokes) frequency components whose number increases with an increase of the pump laser intensity and the interaction length [1]. In the ps-pulse regime the physical picture is more complicated, and such factors as nonstationary molecule response, group velocity dispersion, self-phase modulation due to electronic Kerr effect, etc., come into play [2]. Considerable progress in the understanding of short-pulse mechanisms of SRS has been made in nonlinear optics of fibers where SRS is involved in the processes of pulse nonlinear self-action and soliton formation [3].

The transient properties of SRS are usually discussed in the connection with the vibrational dephasing time T_2. For pulses shorter than T_2 the amplitude of resonantly driven molecular vibrations has no time to settle within the interaction time τ_p which gives rise to a number of Raman-type coherent propagation effects observed in gases and liquids. Delayed Stokes generation, shortening of the Stokes pulse, an oscillating structure of the pump, and Stokes field were reported and discussed by many authors [2,4,5]. Despite the different interaction regimes and different parameters of the Raman media used, the main features of the SRS process established in the first experiments are normally observed down to fs-pulse durations.

We draw attention to the fact that a very specific behavior of the SRS process could be expected for laser pulse durations comparable or shorter than the molecular vibrational period:

$$\tau_p < T_v = 2\pi \Omega_v^{-1}. \tag{1}$$

The nature of nonstationarity here originates from the transient character of the buildup of the vibrational response itself. If one remembers that the vibrational frequencies of many Raman-active materials lie in the region of several hundreds of cm^{-1}, it can be seen that the discussed extreme regime of SRS is rather a regular trend for nonlinear optical interactions with pulses of sub-100-fs duration. Within the short time (1), a quantum oscillator has no time to exhibit its vibrational properties, and therefore it cannot be resonantly driven by the laser field. On the other hand, the spectrum of the pulse (1) initially contains frequency components necessary for the SRS process to occur, and thus a sort of nonlinear self-conversion can take place. This raises the questions: What does the process of SRS look like, and what are the characteristics of the Raman frequency conversion in this extremely transient regime compared to the traditional SRS process? Although some aspects of SRS in the condition (1) were discussed [6,7], experimental observation of the Raman frequency conversion with pulses shorter than the molecular vibration period has not yet been reported.

We present here the results of a study of fs-pulse propagation in gaseous SF_6 in the regime of pulse durations comparable to or shorter than the corresponding molecular vibrational period. In contrast to the previous observations of SRS in SF_6 with longer laser pulses, we observed a continuous (pressure-dependent) shift of the pulse central frequency towards lower frequencies. The effect was rather sensitive to the pulse duration and disappeared for longer pulses. By probing the medium response with an additional weak fs-laser pulse following the pump pulse, it was found that the process is associated with the excitation of Raman-active molecular vibrational motion. The results are of great importance for the understanding of the physics of SRS, because they reveal some ultimate characteristics of the Raman effect and seem to be rather general for nonlinear-optical processes involving forbidden quantum transitions (which may possess electronic, vibrational, spin, etc., character).

The discussed mechanism is qualitatively different from that of the soliton self-frequency shift in optical fibers [8]. The latter is quasistationary in nature and occurs because the broad Raman line of fibers extends down to zero detunings, thereby intrapulse Raman scattering

is possible. In the extremely nonstationary regime (1), the scattering process is not sensitive to the Raman line structure. The self-frequency conversion results from the transient process induced by a sudden excitation of nuclear motion and depends on all the laser-molecule interaction history. The regime of molecule excitation (so-called "impulsive SRS" [6]) is of considerable interest due to wide applications of this phenomenon in time-resolved spectroscopy, but until now fs-pulse frequency conversion under the conditions of impulsive excitation has not yet been experimentally investigated.

In our experiments we used a short pulse Ti:sapphire chirped pulse amplification laser system at 1 kHz repetition rate. The output pulses with an energy of 1 mJ and a pulse width of 35 fs at 800 nm (1.5 eV) were frequency doubled with a 100 μm thick type-I beta-barium-borate nonlinear crystal. The output energy at 400 nm was measured to be 300 μJ with a pulse width of 40 fs at full width at half maximum (FWHM), so that we were able to impulsively excite the symmetric vibration of SF_6 with a period of 43 fs using either the fundamental or the second harmonic.

An important element of our setup was a gas-filled hollow waveguide [9]. It enabled us to enlarge the effective nonlinear interaction length. The typical intensity of fs-pulse radiation transmitted by the gas-filled waveguide (diameter: 250 μm; length: 72 cm) was about 5 TW/cm^2.

In Ar, which possess only fast electronic Kerr nonlinearity, the measured spectra at 400 nm showed typical broadening due to self-phase modulation with FWHM up to 70 nm [9]. The physical picture was qualitatively different when a Raman-active medium (SF_6) was used as a nonlinear medium. Figure 1 shows the corresponding output spectra of a 40-fs pulse for increasing values of gas pressures ($p = 0.8$ bar; 1.6 bars). Competing with pulse spectral broadening we observed a well pronounced shift of the pulse central frequency towards lower frequencies that increased nearly proportionally to the gas pressure. In addition, a progressing asymmetry in the shape of the pulse spectrum was observed. With an increase of gas pressure, a noticeable suppression of the high-frequency wing of the spectrum occurred. The features were observed both for the fundamental and for the second harmonic short-pulse radiation, but these appeared only for sufficiently short-pulse durations ($\tau_p \leq 40$ fs). This fact was established by introducing additional glass in the beam path that resulted in longer pulses with the same spectrum.

The mechanism responsible for the observed behavior was examined by measuring the changes in the spectrum of a weak fs-laser pulse delayed in respect to the strong pump pulse. An intense and sufficiently short laser pulse at 800 nm was focused on the tip of the waveguide filled with SF_6. A second frequency doubled pulse generated by an additional self-phase modulation had a duration of 20 fs and an intensity of 4 orders of magnitude lower than that of the pump pulse. In Fig. 2 we display the measured position of the center of the second pulse output spectrum as a function of the time delay between the pulses. The observed oscillation of the center of gravity of the probe pulse spectrum had a period of 43 fs corresponding to the excitation of the symmetric vibrational mode of SF_6. The two observations enabled us to reconstruct the process of fs-pulse nonlinear propagation as follows. The laser pulse experiences a combined action of self-frequency modulation due to the electronic Kerr effect and SRS on the molecular vibrations. For pulses with duration (1) the coherent nuclear response develops very slowly, and that
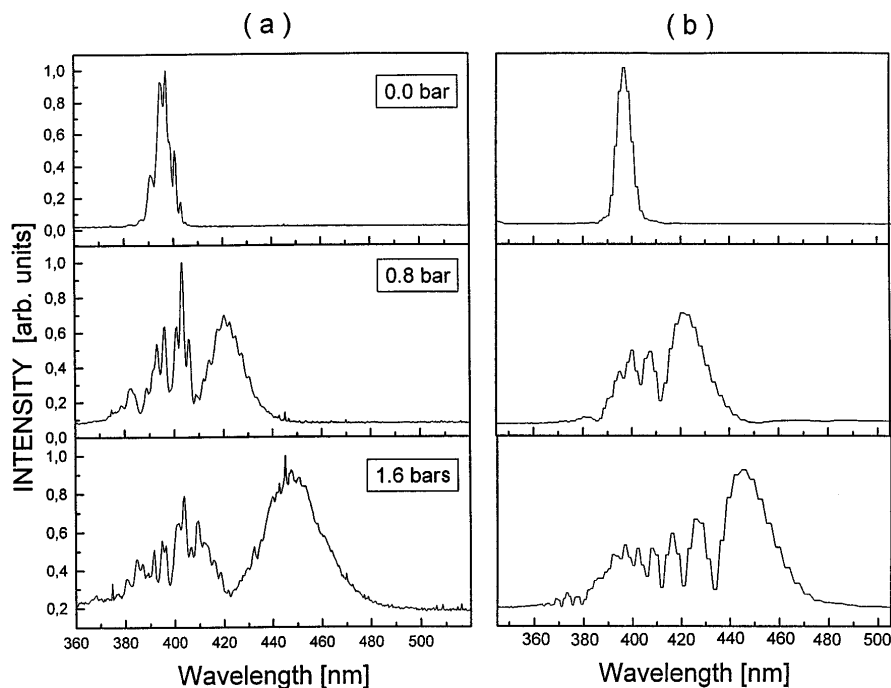

FIG. 1. (a) Spectral broadening and down-shift of the center of the laser pulse spectrum measured at the output of the SF_6-filled hollow waveguide for increasing gas pressures. The intensity of the 40-fs-laser pulse: $I \approx 5$ TW/cm^2. (b) The results of computer modeling of the pulse propagation in SF_6 based on the solution of Eqs. (2) and (3) involving SRS on the symmetric vibration with the period $T_v = 43$ fs.
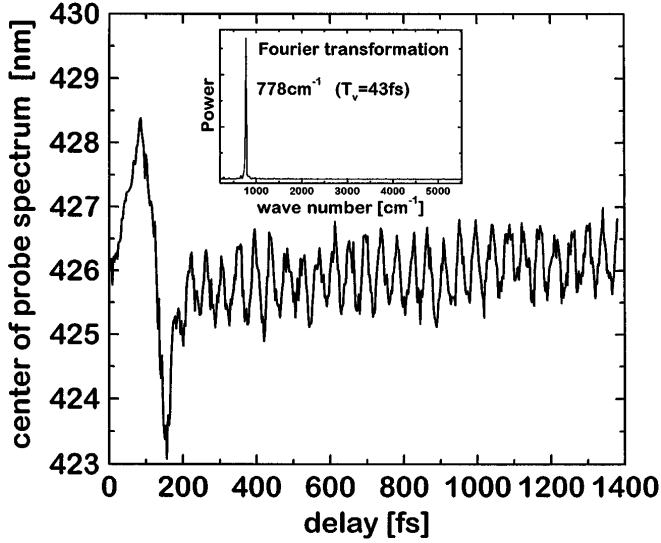
FIG. 2. Measured center of the spectrum of a 20-fs probe pulse as a function of its time delay in respect to the pump pulse. The pump pulse duration: ≈ 40 fs, intensity $I \approx 10$ TW/cm^2. The inset shows the Fourier transform of the depicted probe signal. An excitation of the A_{1g} mode is seen.

leads to an effective negative "chirp" resulting in a downshift of the pulse central frequency. Since the Kerr effect produces the redshift at the leading edge and the blueshift at the trailing edge, the combined action of the processes results in an enhancement of red and suppression of blue spectral components.

We now give a more quantitative explanation of the observed effects. Our choice of SF$_6$ for the study of fs-pulse SRS was motivated by the following reasons. Owing to its high symmetry, this spherical top molecule exhibits no Raman rotational spectrum. The totally symmetric vibrational mode A_{1g} of SF$_6$ gives rise to a very strong (compared to the other two Raman modes) Raman line at 775 cm^{-1}. Because of the small rotational constant of SF$_6$, only one sharp Raman line representing the superposition of all Q lines appears [10]. Since no effects like rotational band Raman excitation [11] or excitation of a superposition of vibrational modes is expected for SF$_6$, to a good approximation, the molecule can be described as a single mode Raman oscillator.

The dynamics of fs-pulse propagation in the medium is generally described by the wave equations for the pulse electromagnetic field $\varepsilon(z,t)$,

$$\frac{\partial^2 \varepsilon}{\partial z^2} - \frac{1}{c^2}\frac{\partial^2 \varepsilon}{\partial t^2} = \frac{4\pi}{c^2}\frac{\partial^2 P}{\partial t^2}, \qquad (2)$$

where the full medium polarization $P = P_{\text{lin}} + P_{\text{electr}} + P_{\text{Raman}}$ contains the linear part P_{lin} (which includes the waveguide linear contribution [9]), the nonlinear part P_{electr} due to the electronic Kerr effect, and the contribution $P_{\text{Raman}} = N(\partial\alpha/\partial Q)Q\varepsilon$ of the molecules of concentration N described by the normal vibrational coordinate Q which obeys the equation [1,2],

$$\frac{\partial^2 Q}{\partial t^2} + \frac{2}{T_2}\frac{\partial Q}{\partial t} + \Omega_v^2 Q = \frac{1}{2M}\left(\frac{\partial\alpha}{\partial Q}\right)\varepsilon^2. \qquad (3)$$

Equation (3) describes a linear oscillator with an effective mass M, a natural frequency Ω_v, a relaxation time T_2, and is driven by a force quadratic in the field ε. For the totally symmetric vibrational mode of SF$_6$ of interest, the Raman transition is isotropic and the tensor $(\partial\alpha/\partial Q)$ which stands for the change of the molecule linear polarizability with respect to the vibrational coordinate Q is reduced to a scalar quantity $(\partial\alpha/\partial Q)$ [10]. If the excited vibrational level population is much less than unity, we arrive at Eq. (3).

The broad spectrum of a laser pulse with duration (1) initially contains frequency components satisfying the conditions of Raman-type resonance. However, the usual treatment in terms of Stokes or anti-Stokes SRS is inapplicable to this situation. For an insight into the physics, we consider the regime where the pulse duration $\tau_p \ll T_v$. In these conditions, terms $\Omega_v^2 Q$ and $(1/T_2)\partial Q/\partial t$ in Eq. (3) can be neglected in comparison to the rapidly changing term $\partial^2 Q/\partial t^2$. Assuming that the laser pulse appears at the moment $t = 0$ and is nonzero within the time interval $0 < t < \tau_p$, we find that during the interaction time $(0 < t < \tau_p)$ the vibrational coordinate changes as

$$Q(t) \approx \frac{1}{2M}\frac{\partial\alpha}{\partial Q}\int_0^t dt' \int_0^{t'} dt'' \, \varepsilon^2(t'') \qquad (4a)$$

and shows a very slow response to the field. After the interaction, e.g., for $t > \tau_p$, the nuclear coordinate exhibits freely damping oscillations,

$$Q(t) \approx Q_0 \exp(-t/T_2)\sin(\tilde{\Omega}_v t), \qquad (4b)$$

with the frequency $\tilde{\Omega}_v^2 = \Omega_v^2 - (1/T_2)^2$, and the amplitude $Q_0(2\pi/Mc\Omega_v)(\partial\alpha/\partial Q)W$ proportional to the pulse full energy $W = (c/4\pi)\int_{-\infty}^{\infty}\varepsilon^2\,dt$.

The initial stage of laser pulse evolution, at which the change of the pulse spectrum is small compared to its carrier frequency, can be treated as a self-frequency modulation process. By passing in the wave equation (2) to the "slow" amplitude $E = |E|\exp(i\varphi)$ and the carrier frequency ω of the field, we find that the change of the pulse instant frequency $\dot{\varphi}(z,\tau)$ with the propagation length z is described by the equation,

$$\frac{d\dot{\varphi}}{dz} = -\frac{2\pi\omega N}{cn}\frac{\partial}{\partial t}\{\chi_{\text{electr}}^{(3)}|E|^2 + (\partial\alpha/\partial Q)Q(E)\}, \qquad (5a)$$

where $\tau = (t - z/v_g)$ is the retarded time coordinate, and $\chi_{\text{electr}}^{(3)}$ is the third-order Kerr electronic susceptibility of SF$_6$. In the regime of ultrashort-pulse-molecule interaction described by the molecule response (4a), the above equation reduces to the following one:

$$\frac{d\dot{\varphi}}{dz} = -\beta_{\text{electr}}\frac{\partial I}{\partial \tau} - \beta_{\text{Raman}}\int_{-\infty}^{\tau} I(\tau')\,d\tau', \qquad (5b)$$

where $\beta_{electr} = 2\pi N \omega \chi^{(3)}_{electr}/cn$, $\beta_{Raman} = 4\pi^2 \times N\omega(\partial\alpha/\partial Q)^2/Mc^2n^2$, and the laser pulse intensity $I = (cn/8\pi)|E|^2$ is introduced. As can be seen, the contribution due to the impulsive vibrational excitation [the second term in Eq. (5b)] appears as an additional redshift which increases monotonically from the leading to the trailing edge in proportion to the laser energy passed through a given cross section. This leads to two features. First, the center of gravity of the pulse spectrum experiences a down-shift with the propagation distance. Second, the combined action of the electronic Kerr effect, which produces the redshift at the leading edge and the blueshift at the trailing edge, and the inertial Raman contribution results in an enhancement of the red and suppression of the blue spectral components. The above considerations are completely supported by the results of a computer modeling of fs-pulse propagation based on the solution of full Eqs. (1) and (2) and showing rather good agreements with the observed spectrum dynamics [Fig. 1(b)].

With the developed model, the results of the pump-probe experiments (Fig. 2) can be readily interpreted. The excitation wave produced by the pump pulse modifies the propagation of the probe pulse at frequency ω_{pr} due to the time-dependent dielectric index: $\tilde{\varepsilon}_{pr}(\tau) = 4\pi N\{\chi^{(3)}(\omega_{pr})|E(\tau)|^2 + [\partial\alpha(\omega_{pr})/\partial Q]Q(\tau)\}$. The first term is the pump pulse-induced change of the electronic index described by the susceptibility $\chi^{(3)}(\omega_{pr}) = \chi^{(3)}(\omega_{pr}, \omega, -\omega, \omega_{pr})$, the second term is due to the vibrational contribution, where $Q(\tau)$ is the nuclear response to the pump field, and $\partial\alpha(\omega_{pr})/\partial Q$ is the value of the coupling parameter at the probe frequency. The frequency modulation of a short probe pulse in the medium depends on its time delay $\Delta\tau$ in respect to the pump pulse and is proportional to $\dot{\varphi}_{pr}(\Delta\tau) \propto -z[\partial\tilde{\varepsilon}_{pr}(\Delta\tau)/\partial\tau]$. For the probe pulse delays within the pump pulse duration τ_p, the measured frequency shift corresponds to the sum of the two terms, while for longer delays $\Delta\tau > \tau_p$ it is characterized by a purely vibrational contribution.

For the center of gravity of the pulse spectrum, $\tilde{\omega} = \int_{-\infty}^{\infty}(\omega + \dot{\varphi})I(\tau)\,d\tau/\int_{-\infty}^{\infty}I(\tau)\,d\tau$, from Eq. (5b) we get the following equation of "motion":

$$d\tilde{\omega}/dz = -\frac{1}{2}\beta_{Raman}W. \qquad (6)$$

The transient character of the SRS process is manifested by the fact that the down-shift (6) is determined by the pulse energy W rather than by its intensity. Another feature is that the shift (6) depends neither on Raman vibration frequency ω_v nor on the gain linewidth $\Gamma = 1/T_2$. Therefore, the observed behavior seems to be some general characteristic of nonlinear dielectric media on the fs-time scale. The shift of a fs-pulse spectrum provides direct information about the value of the coupling parameter $(\partial\alpha/\partial Q)$. From the experimental data we have estimated $(\partial\alpha/\partial Q)$ for the A_{1g} mode of SF_6. For the 400-nm-excitation wavelength its value is 1.5×10^{-16} cm^2,

in reasonable agreement with the available experimental data [10]. We have also estimated that effectively 10% of the SF_6 molecules are excited by the fs pulse to the first vibrational level. This justifies the use of the linear oscillator approximation (3).

The relative change of the pulse spectrum discussed here is not too large compared to the pulse carrier frequency. Our analysis of SRS performed beyond the scope of slowly varying amplitude approximation shows that at higher gas pressures a generation of tunable IR pulses down to pulses with only several cycles of electromagnetic field should be possible [12]. This suggests that the fs-pulse SRS can be interesting from the viewpoint of a generation of IR electromagnetic transients. Unlike the existing techniques of an IR generation in crystals [13], the discussed process requires no phasing matching at all, because there is a self-transformation of the laser pulse spectrum rather than a generation of discrete frequencies.

In conclusion, we have performed an experimental study of SRS in the extremely nonstationary interaction regime with pulses shorter than the period of molecular vibrational motion. We have shown that in this case fs-pulse SRS appears as a continuous self-conversion of the pulse spectrum towards lower frequencies. The discussed self-conversion mechanism is of general nature because many types of matter exhibit Raman activity due to scattering by optical phonons, plasmons, spin, and other elementary excitations.

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