fs-Pulse Synthesis Using Phase Modulation by Impulsively Excited Molecular Vibrations

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We report the temporal characteristics of laser radiation transmitted through impulsively excited SF_6 and exhibiting sideband Raman lines. Even without special dispersion control we observed a sequence of compressed fs pulses following with the period of the excited A_{1g} vibrational mode of SF_6. The use of both negative and positive group velocity dispersion compensation for the temporal compression was found to be as appropriately efficient. The results prove our new concept of the ultrafast molecular phase modulator.

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The development, in the last two decades, of new methods of optical phase control and pulse shaping [1,2] has led to many significant results in nonlinear optics, nonlinear spectroscopy, and diverse fields of laser science [3,4]. For the technique of ultrashort pulse generation, the optical phase control is of fundamental importance. The shortest presently available laser pulses are generated by phasing a very broad, almost white light, spectrum created by the Kerr-self-phase modulation (SPM) [5,6]. In a recently proposed alternative approach, wave forms of sub-fs duration could possibly be synthesized by phase locking of multiple equidistant lines of high-order harmonic generation (HHG) [7] or cascade stimulated Raman scattering (SRS) [8].

In the last few years, the traditional (SPM-based) fs-generation technique has been largely improved [6]. In addition, nonlinear phase locking of optical frequencies has been demonstrated with low-intensity laser sources [9]. At the same time, it has become obvious that direct scaling of the known schemes to the high-intensity regime (necessary for the sub-fs pulse generation) appears to be difficult, because the optical phase behavior becomes much more complicated than that observed in low-order nonlinear processes. In the conditions of fs-pulse compression, deviation of the frequency chirp from linear dependence and higher-order phase distortions in optical elements make complete compensation of the laser phase difficult. Although the generation of multiple equidistant frequencies by HHG or the cascade SRS mechanism is presently not a particular problem, the experiments suggest that the phases of the components are irregular [10] and strongly affected by SPM, self-focusing, and medium ionization [11].

Very recently, we have proposed an alternative approach to the coherence control of fs-pulse generation [12]. Our basic idea was to employ, instead of the nonlinear spectral broadening mechanisms, a linear one, which generally takes place when an electromagnetic wave propagates in an optical medium with temporally modulated dielectric parameters [13]. The temporal modulation can be created, for instance, through a medium excitation. In particular, by preparing coherently a dipole-forbidden atomic (molecular) transition of a frequency Ω, and scattering a second, relatively weak field (of a frequency ω) on the long-living excitation, one will produce sideband frequencies $\omega_n = \omega \pm n\Omega$ $(n = 1, 2, \ldots)$, by analogy with a higher-order wave diffraction on a periodic structure. Because of the temporal separation of the pumping and the scattering processes, the nonlinear effects (excitation, nonlinear self-action, ionization, etc.) are now confined within the pump pulse. A key function of the pumping process is to provide the coherence control of the generated excitation wave. This is achieved by preparing the medium in the impulsive SRS regime [14], e.g., by using an intense nonresonant laser pulse with a duration $\tau_p < T_0 = 2\pi/\Omega$. It is important that in this specific regime the resulting state of the excited transition is nonsensitive to the details of the pump field time structure, which provides "stability" against amplitude-phase distortions. Indeed, for the probability amplitude $a_2(t)$ of a dipole-forbidden transition $E_1 \rightarrow E_2$ exposed to a laser field with a complex envelope $E(t)$ and frequency $\omega \gg \Omega = (E_2 - E_1)/\hbar$, in the second perturbation order [15] we find

$$a_2(t) = (i/2\hbar)\left[r_{12}^{\mathrm{SRS}} \int_{-\infty}^{t} |E(\tau)|^2 e^{i\Omega\tau}\, d\tau + r_{12}^{\mathrm{TPE}} \int_{-\infty}^{t} E^2(\tau) e^{i(\Omega-2\omega)\tau}\, d\tau + r_{12}^{\mathrm{TPA}} \int_{-\infty}^{t} E^{*2}(\tau) e^{i(\Omega+2\omega)\tau}\, d\tau \right]. \quad (1a)$$

In Eq. (1a), the coupling constants r_{12}^{SRS}, r_{12}^{TPE}, and r_{12}^{TPA} are related to the involved SRS, two-photon emission (TPE) and absorption (TPA) processes [16], and $a_2 \ll a_1 \approx 1$ is assumed. The contributions of the nonresonant, fast oscillating TPE and TPA terms are small, while the SRS term leads to an increase of the amplitude a_2 for pulse durations $\tau_p < T_0 = 2\pi/\Omega$. The resulting medium excitation ($\rho_{12} = a_1^* a_2$) produced in the impulsive regime is then given by

$$\rho_{12}(\infty) = (i/2\hbar)\left[r_{12}^{\mathrm{SRS}} \int_{-\infty}^{\infty} |E(\tau)|^2\, d\tau \right] \quad (1b)$$

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and is independent of the field phase (changing rapidly due to Kerr SPM, dispersion, and other propagation effects), but depends only on the pump field integrated intensity.

The possibility of spectral broadening in the "linear" regime was demonstrated in our recent experiments [12], where impulsive vibrational excitation of SF_6 molecules was used to create the temporal modulation wave. The generated multiple Stokes and anti-Stokes Raman components of the delayed field were completely free of the influence of the deteriorating nonlinear effects. The coherence properties of the spectrum were not studied there. But the specific behavior of the component intensity with the gas pressure indicated that phase locking could be achieved.

In this Letter we present results of a study of the temporal characteristics of laser radiation, transmitted through impulsively excited gaseous SF_6 and exhibiting sideband Raman spectra. Even without special dispersion control, we observed a sequence of compressed fs-laser pulses following with the vibrational period of the excited A_{1g} mode of SF_6, with the "envelope" of the sequence repeating well the injection pulse temporal shape. By varying the net group velocity dispersion (GVD) of the output optical elements, we found that the generation of the periodic pulse sequence occurred for both positive and negative GVD compensation.

The results prove experimentally the concept of synthesis of fs pulses by phase locking multiple Raman sideband lines. On the other hand, they establish the coherent origin of the spectra generated by the proposed method, with the coherence time determined completely by the probe radiation. The revealed specific features of the compression dynamics suggest that the mechanism is caused by an ultrafast phase modulation by coherent molecular vibrations. The modulation frequency (23 THz) is at least 3 orders of magnitude higher than that achievable by electro-optical modulation [13].

In our experiments we used a Ti:sapphire chirped pulse amplification laser system with a 1 kHz repetition rate. The output pulses at 800 nm had an energy up to 500 μJ and a pulse width of 25 fs and could impulsively excite the symmetric vibrational mode A_{1g} of SF_6. A frequency doubled part of the fundamental had an energy of $\approx$10 μJ and served as injection radiation. The use of a 100 cm long hollow waveguide enabled us to enlarge the interaction length. The typical value of the pump pulse intensity in the SF_6–filled waveguide was about 10 TW/cm^2.

The highly symmetric, spherical top SF_6 exhibits no rotational Raman spectrum, and its totally symmetric vibrational mode A_{1g} gives rise to a very strong (compared to the other two Raman modes) Raman line [17]. The lowest electronic absorption band of SF_6 (starting at 200 nm) lies far above the pump and probe frequencies [18]. Thus, only one Raman mode ($\Omega = 775$ cm^{-1}, $T_v = 43$ fs) is effectively excited by the nonselective impulsive pumping mechanism, and the laser-molecule interaction can be described by the model of a two-level Raman oscillator [19].

To investigate the temporal characteristics of the output SRS radiation, 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 $\tau_i \approx 160$ fs (FWHM) and intensity $\sim$0, 1 TW/cm^2 was sent with a temporal delay of 200–300 fs much smaller than the vibrational dephasing time T_2 (at 400 mbar it was as long as several ps). T_2 could be estimated by measuring the intensity of the generated Raman spectra as a function of the pump-probe delay. The working pressure of 400 mbar was chosen so that a sufficient number of Raman lines could be generated without noticeable ionization of the medium. The output of the injection radiation (Fig. 1) shows a regular sideband structure spaced by the frequency $\Omega = 775$ cm^{-1} of the excited A_{1g} mode. In contrast to the output pump spectra (strongly broadened by SPM [17]), the generated Raman lines have no spectral broadening at all and repeat very well the input shape of the injection pulse spectrum [Fig. 1(a)]; this suggests that the scattering is linear [12].

The results of self-diffraction correlation measurements [20] of the output radiation are shown in Fig. 2. The measured temporal structure represents a periodical sequence of compressed laser pulses at 400 nm. The pulses follow with a period corresponding to the period (43 fs) of the excited vibration ($\Omega = 775$ cm^{-1}), with the envelope of the sequence close to the input temporal shape of the injection pulse [Fig. 2(a)]. It is interesting that no special GVD compensation in addition to the GVD of the elements in the light pass (exit window of the waveguide chamber and air) was used in the measurements. By estimating the net GVD at 400 nm, we found that the compression occurred in the regime of positive GVD compensation.

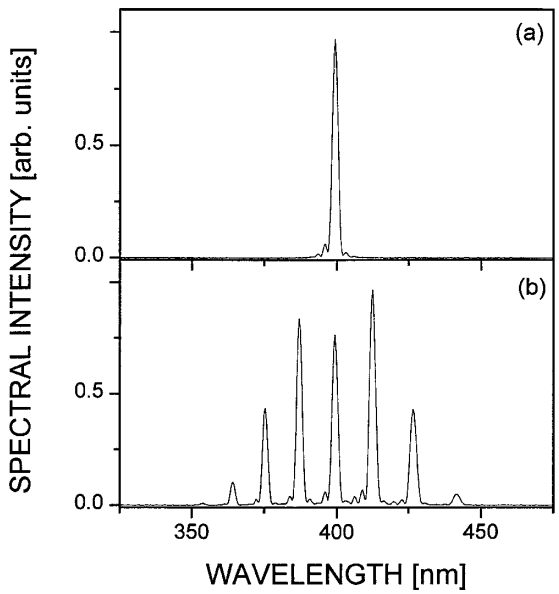

FIG. 1. Output spectra of a delayed injection pulse ($\lambda = 400$ nm) after its passage through a SF_6–filled hollow waveguide ($p = 400$ mbar): (a) without pumping; (b) with preliminary impulsive pumping by a 25 fs pulse at 800 nm.

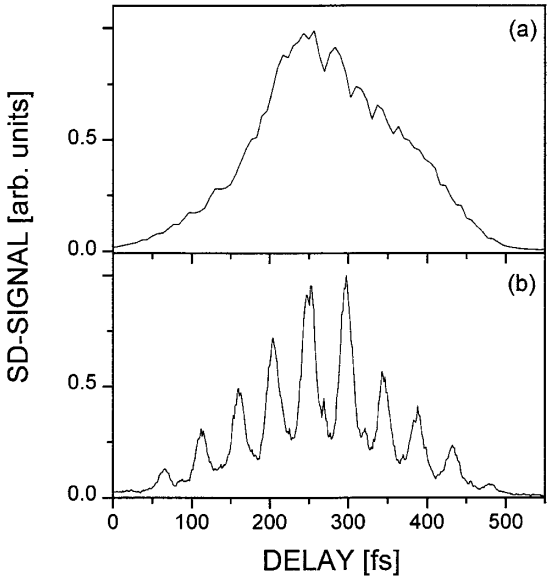

FIG. 2. Temporal structure of the output spectra of Fig. 1 measured by self-diffraction. (a) no changes in the output pulse shape; (b) formation of a train of compressed 16 fs pulses with the period (43 fs) of the A_{1g} mode of SF_6.

To obtain insight into the above behavior, we carried out measurements with adjustable GVD. We used chirped mirrors for 400 nm central wavelength. Eight reflections on the mirrors provided a negative GVD of ≈ -300 fs^2. Two wedges of fused silica were used to introduce additional positive GVD (material dispersion) in the light pass. By moving one of the two wedges perpendicular to the beam, the additional positive GVD could be adjusted. Together with the positive GVD of air and the exit window of the waveguide chamber, the overall dispersion in the light pass could be continuously tuned from negative to positive values.

The main results of the measurements with adjustable GVD compensation are summarized in Fig. 3, where the upper temporal shape [3(a)] corresponds to a positive value of the net GVD, the temporal shape [3(b)] was measured in the vicinity of zero net GVD, and the shape [3(c)] was obtained for negative net GVD. By gradually varying the GVD, from positive to negative values, we established that the compression effect occurs for both negative and positive GVD compensation. One more interesting feature was that the fs sequences generated by both positive and negative GVD compensation were temporally shifted, one from another, nearly by a half repetition period. This is clearly seen in Fig. 3 where the pulses of the upper sequence [3(a)] appear exactly between the pulses of the lower sequence [3(c)]. Since the pump and the injection pulses (generated from the same coherent source) are perfectly synchronized, the temporal structure of the pulse sequences could be measured with sufficient time resolution (<1 fs), which suggested the regular character of the shift.

The observed specific features of the fs-pulse generation can be explained with the following physical model. To a good approximation, the impulsive pumping

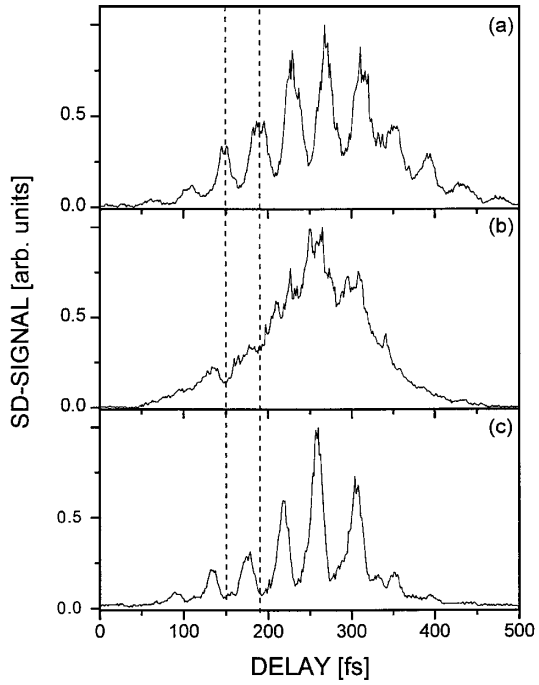

FIG. 3. Compression measurements with adjustable GVD compensation: (a) positive GVD ($\sim +100$ fs^2); (b) GVD close to zero; (c) negative GVD (~ -100 fs^2). The dashed lines indicate the periodical positions of negative chirp due to the sinusoidal molecular phase modulation [see Eq. (5)].

of SF_6 can be treated as the propagation (at the pump pulse velocity v) of a wave of vibrational excitation $\nu = 0 \rightarrow \nu = 1$ of the A_{1g} mode. Let the pump field, $\varepsilon_p(t) = (1/2)E_p(t)\exp(i\omega_p t) + \text{c.c.}$, appear at $t = 0$ and be nonzero within a short interval: $0 < t < \tau_p \ll T_v$. In the time frame $\tau = (t - z/v)$ moving with the pump pulse (z is the propagation coordinate), the excitation wave has the form of freely damping oscillations:

$$\rho_{12}(\tau) = \rho_{12}^{(0)} \exp(-\tau/T_2 - i\tilde{\Omega}\tau) \qquad (\tau > 0), \quad (2)$$

with the initial amplitude $\rho_{12}^{(0)}$ determined by Eq. (1b), the angular frequency $\tilde{\Omega}^2 = \Omega^2 - (1/T_2)^2$, and the dephasing time T_2. A weak injection field $\varepsilon_i(t) = (1/2)E_i(t)\exp(i\omega_i t) + \text{c.c.}$, propagating after the pump pulse, is scattered by the temporal grating given by Eq. (2). For the linear polarization induced by the injection field $\varepsilon_i(\tau)$ we have [15]

$$P(\tau) = 2Nr_{12}^{\text{SRS}}(\omega_i)[\rho_{12}(\tau) + \rho_{12}^{*}(\tau)]\varepsilon_i(\tau), \quad (3)$$

where N is the molecule concentration, and $r_{12}^{\text{SRS}}(\omega_i)$ is given by [16]. By inserting $P(\tau)$ in the wave equation, we come to the following propagation equation for the injection field complex envelope $E_i(z, \tau)$:

$$\frac{\partial E_i}{\partial z} = -iG_i \exp(-\tau/T_2)\sin(\tilde{\Omega}\tau)E_i\,. \quad (4)$$

The coefficient $G_i = 8\pi\omega_i r_{12}^{\text{SRS}}(\omega_i)N|\rho_{12}^{(0)}|/c$ in Eq. (4) has the sense of the Raman gain for the injection field E_i. Since experimentally $T_2 \gg T_v$, τ_i, the relaxation in

Eq. (4) can be neglected, and the solution for the injection field at a distance z takes the form

$$E_i(z,\tau) = E_i(0,\tau)\exp[-iG_i z\sin(\Omega\tau)]. \quad (5)$$

Here $E_i(0,\tau)$ is the input amplitude of the injection field. As can be seen, the field amplitude does not change during the propagation, while the phase shows a temporal modulation with the molecular vibration period $T_v = 2\pi/\Omega$. In our experiments, the injection pulse duration ($\tau_i \approx$ 160 fs) was longer than the vibrational period (43 fs). In the spectral domain, this regime leads to the sideband Stokes and anti-Stokes Raman line generation [12]. For the discussion here it is important that the injection field frequency is getting periodically modulated from the leading to the trailing edge: $\omega_i(\tau) = \omega_i + \Delta\omega_i(\tau)$, with $\Delta\omega_i(\tau) \equiv \partial\varphi_i(\tau)/\partial\tau = -G_i\Omega z\cos(\Omega\tau)$. In a dispersive medium (e.g., in the output optical elements), the frequency modulation is transformed into amplitude modulation, with periodic peaks generated temporally at the time when the frequency sweeping $\partial\Delta\omega_i(\tau)/\partial\tau$ has a local extremum. Because of the sinusoidal character of modulation, both positive and negative GVD are now equally appropriate for the temporal compression. For a negative GVD the corresponding time moments [derived from the conditions $\cos(\Omega\tau) = 0$ and $\partial\Delta\omega_i(\tau)/\partial\tau > 0$] are given by $\tau_m^{(-)} = (\pi/2 + 2\pi m)/\Omega$, while for a positive GVD [assuming $\cos(\Omega\tau) = 0$ and $\partial\Delta\omega_i(\tau)/\partial\tau < 0$] the time moments are determined by $\tau_m^{(+)} = (3\pi/2 + 2\pi m)/\Omega$ ($m = 0, 1, 2, \ldots$). From the above analysis it immediately follows that (1) the compressed pulse trains are formed within the injection pulse envelope, and (2) the trains are shifted, one from the other, by a half vibrational period. This explains the observed features of pulse compression shown in Figs. 2 and 3. The results therefore strongly support the developed physical model of the process treating the sideband Raman line generation as an ultrafast phase modulation by molecular vibrational motion.

In conclusion, we have demonstrated experimentally our new concept of synthesis of fs-pulse trains using modulation of a laser phase by impulsively prepared vibrations. Although several alternative approaches to the phase locking of high-order SRS lines were recently discussed [8], no experimental observations of fs-pulse synthesis have been reported so far. Two constructive moments (distinguishing our approach from the other proposals) should be pointed out. The first one is the idea of a temporal delay between the pumping and the scattering processes which allows the linear regime of spectral broadening. Secondly, with the impulsive regime of excitation, the prepared quantum state is nonsensitive to the pump pulse amplitude-phase variations caused by the deteriorating nonlinear effects. This enables one to completely transmit the coherence properties of the incident field to the generated field.

More generally, the approach offers a practical way of controlling the coherence of laser light generated by a high-order nonlinear process that has recently been the subject of intense discussions [10]. The method seems to be rather general and applicable to various systems. Indeed, using intense 5 fs-laser pulses, one would produce a modulation wave in atoms or ions at a frequency as high as $\sim 2 \times 10^{14}$ Hz (for comparison, SF_6 oscillates at 23 THz). Therefore only two to three sideband lines will be sufficient to realize the sub-fs pulse synthesis. Practically, with the proposed technique of the ultrafast sinusoidal phase modulation, one can choose between both negative and positive GVD for the fs-pulse compression.

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