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Self-compression of a femtosecond pulse due to Raman coherence of molecular rotations

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We have observed self-modulation and self-compression of a femtosecond laser pulse after passing the beam through a Raman-active medium of hydrogen. Femtosecond pulses produce Stokes emissions of ortho-hydrogen and para-hydrogen, depending on the input beam conditions. The shape of the output pulses drastically changed as a function of the intensity of the Stokes emissions and the total width of the spectrum. This is attributed to nonlinear modulation of the wave form induced by coherent rotational motions of hydrogen molecules in the time domain.

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Spectral broadening based on the Raman mixing process has been of considerable concern from the viewpoint of generating an extremely short optical pulse [1–5]. Since high-order stimulated Raman scattering (HSRS) was proposed as a method for the generation of ultrashort pulses with durations of subfemtoseconds [1], octave-band spectrum spreading from the infrared to the extreme ultraviolet has been observed by several research groups [2]. Harris and coworkers reported the generation of a train of pulses with a duration of a few femtoseconds as a result of controlling the relative phase among the sidebands from HSRS [3]. They used multicolor nanosecond lasers to drive the Raman coherence to the maximum level. Therefore, the form of the output pulse inevitably resulted in a pulse train sustained for nanoseconds, i.e., an isolated single pulse could not be obtained in this manner. On the other hand, the excitation of Raman coherence using a femtosecond pulse has also been reported [4,5]. Zhavoronkov and Korn reported phase modulation of a probe pulse due to Raman coherence excited impulsively by a pump pulse with a duration less than the vibrational time of the molecules [4]. This phase modulation caused the generation of phase-locked Raman sidebands, producing a single sub-4-fs pulse after appropriate phase compensation. In addition, the impulsively excited molecular rotational wave packets in CO_2 can produce a spectrally broadened probe pulse with a negative chirp [5]. Phase correction using a silica plate enables the duration of the probe pulse to be compressed by a factor of one-ninth. Both approaches, however, require a linear interaction between the probe pulse and the coherent motion of molecules. Therefore, the input energy is limited to prevent a strong nonlinear interaction that irregularly disturbs the phase of the probe pulse.

Even in a nonlinear propagation region, however, Bartles *et al.* have suggested that the wave equation leads to intensity modulation due to Raman coherence acting as a time-varying refractive index [6]. The equation describing the propagation of an ultrashort laser pulse through a nonlinear optical medium can be written as [7]

$$\left[\left(1+\frac{i}{\omega_0}\frac{\partial}{\partial t}\right)^{-1}\nabla+2ik_0\frac{\partial}{\partial z'}+2k_0D\right]E(r,t) = -\omega_0^2\left(1+\frac{i}{\omega_0}\frac{\partial}{\partial t}\right)p, \quad (1)$$

where $E(r,t)$ and p are the slowly varying amplitude of the electrical field and the polarization in the time domain, respectively. ω_0 is the carrier frequency, k_0 is the linear part of the wave vector at the carrier frequency, and D represents the high-order dispersion term in a power series of the wave vector. The medium response p consists of the contributions from the electronic Kerr effect p_{ele} and the nuclear response p_{ram}, $p=p_{\mathrm{ele}}+p_{\mathrm{ram}}$. In this term, the nuclear response is given by $p_{\mathrm{ram}}=N(\partial\alpha/\partial Q)_0Q(t)E(t)$, where $Q(t)$ is the oscillation amplitude of the nuclear coordinate, N is the number density of Raman-active molecules, and α is the polarizability associated with Raman-active vibrations or rotations. When the Raman frequency shift is expressed as Ω, $Q(t)$ is written as a damping sinusoidal function with a period of $2\pi/\Omega$. The right-hand side of Eq. (1), the nonlinear source term in the wave equation, includes real and imaginary parts, which lead to the modulation of the phase and amplitude of propagating ultrashort pulses, respectively. This imaginary term derived from the contribution of p_{ram} can be described by

$$-\omega_0 i\frac{\partial}{\partial t}p_{\mathrm{ram}} = -\omega_0 iN\left(\frac{\partial\alpha}{\partial Q_0}\right)\frac{\partial}{\partial t}[Q(t)E(t)]. \quad (2)$$

This term results in the intensity modulation that causes the pulse shape to be split into a train with repetition period $2\pi/\Omega$. This means that the reshaping of the laser pulse occurs due to the excited Raman coherence $Q(t)$ while it is propagating in the Raman-active medium. Kalosha and Herrmann analyzed the behavior of ultrashort pulses traveling through a Raman-active medium using the reduced Maxwell equation, expressing the possibility of forming a pulse train and generating a subfemtosecond pulse [8]. Such a pulse compression based on Raman coherence has not been observed experimentally. In the only relevant experimental result, pulse compression caused by phase locking in a four-wave Raman mixing process pumped by a linearly polarized 100-fs laser has been reported [9]. In this report, however, the mechanism of the pulse compression and the role of Raman coherence are not shown in detail.

In this Rapid Communication, we present an observation of the self-modulation and the self-compression of the wave form of a femtosecond optical pulse as a result of interaction with coherent rotational motions of molecular H_2. A femtosecond laser pulse was reshaped into a sinusoidal wave form

due to the rotational Raman coherence of ortho-H_2. The compression of the pulse was achieved by the multiplicative effect from the rotational Raman coherence of both para- and ortho-H_2. In addition, we observed that the output pulse was compressed continuously with increasing intensity of the Stokes emissions and broadening of the spectral width. In this case, the pulse duration was determined by the total width of the spectral region defined by the Raman shift frequency.

In this study, a Ti:sapphire laser regenerative amplifier system (Thales, Concert) was used to generate ultrashort laser pulses at a center wavelength of 785 nm with a 1-kHz repetition rate. The pulse duration was changed from 100 fs (nearly transform limited) to 3 ps by adding either a positive or negative chirp using a stretcher consisting of a pair of gratings. The maximum output energy was 1.5 mJ, attenuated using a polarizer and a rotating wave plate. A Raman cell was filled with H_2 gas consisting of 25% para-H_2 and 75% ortho-H_2 at a pressure of 10 atm. The polarization of the input pulse was varied between linear and circular by rotating a quarter-wave plate placed just before the input window of the Raman cell. In order to prevent unfavorable nonlinear effects induced by the 5-mm-thick silica windows, the length of the Raman cell was varied depending on the focal length of focusing lenses. The output pulses were collimated and measured after cutting off the center part of the output beam with a diameter of 10 mm using an aperture with a diameter of 3 mm. The spectrum was measured with a multichannel spectrometer (Ocean Optics, USB2000), and the pulse shape was estimated from an autocorrelation trace measured with a noncollinear multishot second harmonic autocorrelator (APE, Pulse Check).

The wave form and spectrum of the output pulses strongly depended on the input beam conditions. Figure 1 shows autocorrelation traces and spectra of output laser pulses when we used circularly polarized input beams with a duration of 100 fs under several focusing conditions and input energies. When an input beam with an energy of 1 mJ was tightly focused into the Raman cell by a lens with a focal length of 450 mm, the output spectrum was broadened by self-phase modulation (SPM) on both the red and blue sides, and exhibited newly generated peaks apart from the pump-laser frequency on the red side [Fig. 1(b)]. These two peaks correspond to Stokes emissions of para- and ortho-H_2, which have Raman shift frequencies of 354 and 587 cm^{-1}, respectively. We also observed that the dependence of the generation efficiency of the rotational Raman emissions on the polarization of the input beam agreed with the result derived from the law of conservation of angular momentum [10]. Generally, Stokes emissions resulted from the interaction between a pump laser and a Raman coherence. Therefore, the generation of these peaks indicates that the input pulse certainly excited the Raman coherence. In Fig. 1(a), the output pulse shows the modulated wave form with a split structure probably due to the strong modulation of the wave form by other nonlinear effects, e.g., self-steeping or spatial-temporal coupling. On the other hand, increasing the focal length of the lens to 500 mm and decreasing the input energy to 0.5 mJ resulted in the generation of the intense Stokes emission of ortho-H_2, in addition to the suppression of the effect of the

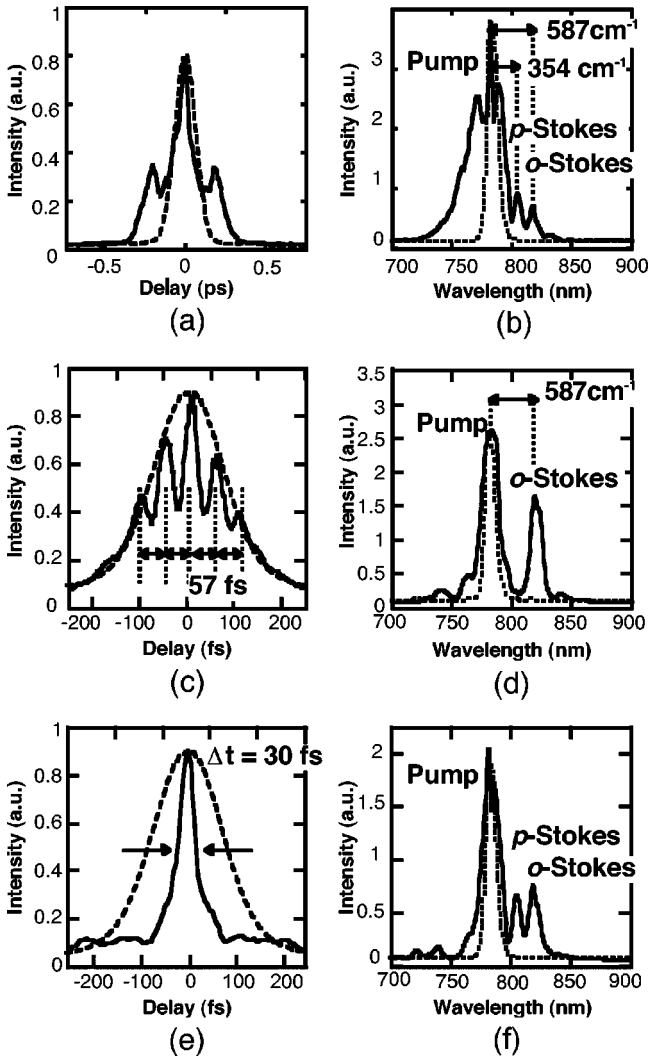

FIG. 1. Autocorrelation traces and spectra of output pulses under several input beam conditions. The dashed curve represents the autocorrelation trace of the input pulse. The dotted curve represents a spectrum of the input pulse. (a) and (b) Input energy: 1 mJ, focal length: 450 mm. (c) and (d) Input energy: 0.5 mJ, focal length: 500 mm. (e) and (f) Input energy: 1 mJ, focal length: 600 mm.

other nonlinear interactions [Fig. 1(d)]. In Fig. 1(c) we can see that the autocorrelation trace has a periodic structure within almost the same envelope as that of the input pulse. The cycle time of the periodic structure was 57 fs; this value was equal to the period derived from the multiplicative inverse of the difference in frequencies between the pump laser and the Stokes emissions of ortho-H_2, i.e., 587 cm^{-1}. This result obviously shows that the intensity modulation of a femtosecond laser pulse in the time domain originating from the term described in Eq. (2) was caused by the coherent motion of ortho-H_2, $Q_o(t)$, that is described by a sinusoidal function with a period of 57 fs. When we interpret this result in the frequency domain, we can regard this periodic structure as the result of a coherent superposition of the pump pulse and the Stokes pulse; the superposition of two waves with a frequency difference $\Delta\nu$ imposes on the envelope a beat pattern with a period of $1/\Delta\nu$ [11]. Figure 1(e) shows an

autocorrelation trace of a pulse whose spectrum includes Stokes emissions of both para- and ortho-H_2 [Fig. 1(f)], which was obtained by means of focusing with a lens of longer focal length (600 nm). In this case, the pulse shape exhibited a single and a compressed wave form without a periodic structure. The full width at half maximum (FWHM) of the trace was 45 fs, which corresponds to 29 fs under the assumption of a sech^2 pulse shape; this value was almost one-third of that of the input pulse. In addition, we observed no loss of energy after the pulse compression. Therefore, the peak intensity of the beam should significantly increase. However, this pulse-compression effect strongly depended on the spatial quality of the input beam. In fact, the inferior spatial distribution resulted in splits or hot spots in the beam profile, preventing the increase of the peak intensity even though the temporal wave form was compressed. This effect may be avoided by use of a hollow core fiber filled with hydrogen as a waveguide to improve the spatial quality of an output beam. In our experiments, under various conditions of input beams, we observed that the pulse compression was always accompanied by Stokes emissions of both para- and ortho-H_2. Therefore, this suggests that the Stokes emission of para-H_2 crucially contributes to differences between the output wave forms in Figs. 1(c) and 1(e). When we consider such pulse compression in the time domain, the pulse should be modulated by the effect of both the rotational Raman coherence of para-H_2 $[Q_p(t)]$ and that of ortho-H_2 $[Q_o(t)]$. The superposition of two coherent rotational motions leads to the modulated sinusoidal change of refractive index. In this case, a large variation of refractive index is provided in the vicinity of a constructive interference point. According to Eqs. (1) and (2), a single compressed wave form with a broad pedestal can be caused by this sharply varying refractive index, whereas just a sinusoidally modulated wave form is caused by only one Raman coherence. This is the reason that two Raman coherent motions led to the pulse compression as shown in Fig. 1(e). However, we believe that quantitative consideration based on the nonlinear propagation equation will be needed for more rigorous discussions.

In an attempt to examine the behavior of this pulse compression, we carried out simultaneous observations of the evolution of the wave forms and spectra of output pulses, while we continuously changed the input laser energy by rotating a wave plate in an attenuator. Figure 2 shows the cooperative behavior of the reshaping of the temporal shape and the broadening of the spectrum. We used negatively chirped 190-fs pulses with circular polarization as input pulses. As the input energy was increased, we observed dynamic acumination of the temporal shape with the growth of the rotational Stokes emissions of para- and ortho-H_2 as shown in Fig. 2(a). Figures 2(b) and 2(c) show details of the evolution of the pulse shape and the relative intensity of the Stokes emissions for the input energy. When the input energy was below 0.52 mJ, the temporal shape of the output pulse exhibited no substantial change compared with that of the input pulse, although the spectrum was slightly broadened in the bottom part. The Stokes emission of para-H_2 began to be generated at an input energy of 0.52 mJ, producing a little bump on the top of the autocorrelation trace. In the limit of input energy from 0.52 to 0.68 mJ [in the shaded areas of

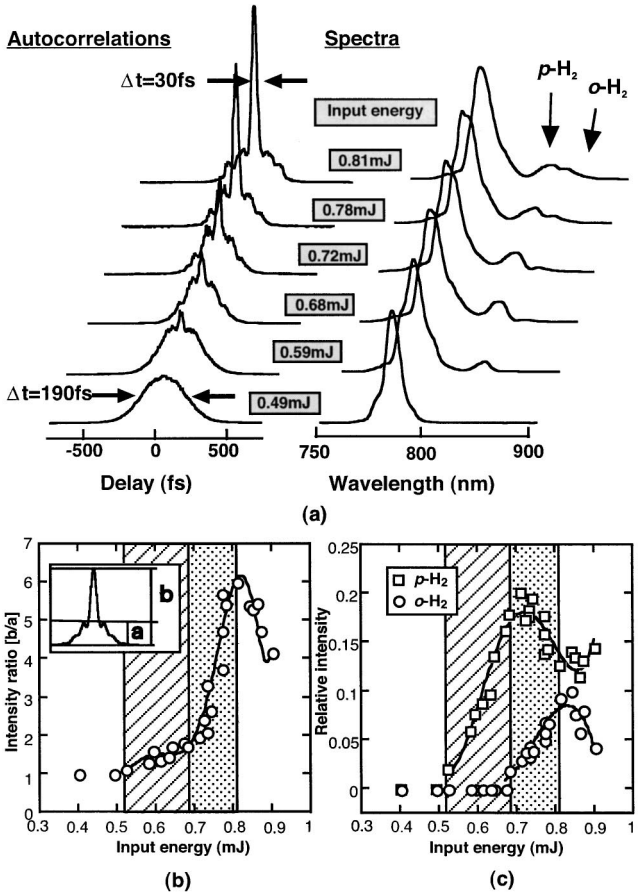

FIG. 2. (a) The behavior of the shape and spectrum of the output pulse as a function of the input beam energy. (b) The ordinate is defined by the ratio of the height of the pulse to that of the pedestal. (c) The circle shows the relative intensity of the Stokes emission of ortho-H_2, and the square shows that of para-H_2.

Figs. 2(b) and 2(c)], the bump gradually became sharpened with an increase in intensity of the Stokes emission of para-H_2. After the Stokes emission of ortho-H_2 appeared at the threshold of 0.68 mJ, the acumination of the pulse shape drastically progressed with an increase in the intensity of the Stokes emissions of ortho-H_2 and a decrease in that of para-H_2 [in the dotted areas of Figs. 2(b) and 2(c)]. When the input energy reached 0.81 mJ, the pulse shape showed the shortest duration with a FWHM of 45 fs. Further increase in input energy to over 0.81 mJ resulted in a broadening of the pulse shape with a decrease in Stokes emission of ortho-H_2; this would be caused by the enhancement of the other nonlinear effects due to the increase in the peak power of the input pulse. These observed results obviously show that the change of spectral shape directly affects the temporal shape of the output pulse. A sech^2 pulse duration of a FWHM of 30 fs needs to have a spectral width of a FWHM of 10.5 THz. The spectrum in Fig. 2(a) apparently did not cover such a spectral range without the Stokes components. In addition, the pulse duration was determined by the total width of the spectrum, i.e., drastic shortening of the pulse duration occurred after the generation of the ortho-H_2 Stokes emission that was 17.6 THz from the pump laser frequency. Therefore,

we conclude that a Raman interaction with the ultrashort pulse brought about not only the spectral broadening with Stokes emissions but also the reshaping of the wave form.

Generally, an ultrashort pump pulse limits the efficiency of excitation of Raman coherence with respect to the steady-state case, because the process becomes highly transient at femtosecond pulse excitations [12]. In order to excite a Raman coherence efficiently in this limit, two-color lasers, with the difference in wavelength tuned to the Raman resonant frequency, are used [13]. This is an application of a conventional concept where two frequency components, pump and Stokes seeding, are needed to excite a molecular motion due to the far off resonance of the pump-laser frequency to the vibrational or rotational frequency of the molecules. The situation, however, is completely different in the case of a pump laser with a spectrum broader than the Raman shift frequency. In this case, the driving force to excite molecular motion depends strongly on the shape of the intensity profile of the pump laser. Even if the pump laser has a sufficient spectrum region, it cannot excite Raman molecular motion without a temporal structure that is equal to or faster than the period of motion of the molecules [6]. If the intensity profile of the pump pulse has a structure that is faster than the rotational period τ_p, or that is a sinusoidal variation with the same period as τ_p, the pump laser is capable of driving the coherence of the rotational motion of the molecules. In particular, a pump pulse with a duration shorter than the motion time of the molecules can cause a self-conversion of the laser spectrum without a threshold. This is called impulsive stimulated Raman scattering [14]. In our experimental results, the Stokes emission of para-H_2 was generated prior to that of ortho-H_2; nevertheless, the concentration of para-H_2 was one-third of that of ortho-H_2. This can be explained by the mechanism shown in the following, which is a quasi-impulsive excitation of Raman coherence, depending on the temporal shape of the pump pulse. In Fig. 2, the shape of the pulse after propagating through the H_2 molecules was gradually sharpened with an increase of input energy. This behavior enables a Raman coherence to be excited after the point where it has a faster structure than the rotational time of the H_2 molecules. At low input energies, the pulse shape has a structure faster than 94 fs, the rotational time of para-H_2, but slower than 54 fs, the rotational time of ortho-H_2. This pulse, therefore, can drive only the rotational motion of para-H_2 and not the rotational motion of ortho-H_2 (in the input energy region from 0.51 to 0.68 mJ in Fig. 2). When the increase of input energy resulted in sufficient excitation of the rotational coherence of para-H_2 $Q_p(t)$, pulse reshaping made further progress because of this strong Raman coherence $Q_p(t)$, producing a pulse shape with a structure faster than 57 fs. As a result, this strongly modulated pulse obtained an ability to excite not only $Q_p(t)$, but also Raman coherence of ortho-H_2. This caused the rapid acceleration of the pulse compression as shown in the input energy region from 0.68 to 0.81 mJ in Fig. 2(b). We also note that this behavior may have the potential to be applied to selective excitation in various molecules by the reshaped femtosecond pulses.

In conclusion, we have shown observations of the self-evolving behavior of an ultrashort pulse as the result of the interaction with a coherent rotational motion of molecular H_2. A femtosecond laser pulse modified by the rotational Raman coherence then exhibited a sinusoidal or compressed structure in the wave form and intense Stokes components in the spectrum. The cooperative behavior of the pulse reshaping and the growth of Stokes emissions suggest that both the rotational Raman coherence of para- and ortho-H_2 contributed to the acumination of the pulse shape in the time domain.

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