Conical three-photon-excited stimulated hyper-Raman scattering

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We investigate the nonlinear interaction of tightly focused femtosecond infrared laser pulses in fused silica and sapphire. For fused silica, emission occurs in the form of a cone with a structured spectrum centered near the third harmonic of the fundamental laser frequency. The emission spectrum evolves with successive laser pulses, suggesting a Raman origin for the emission with laser-induced structural changes of the material. For sapphire, only the third-harmonic component is observed, also in the form of conical emission. The proposed explanation for these observations, three-photon-excited hyper-Raman emission, provides a tool for probing the vibrational and structural properties of solid-state materials.

Raman scattering is a useful tool for studying the vibrational energy levels of a wide array of materials. Typically, this process involves a two-photon transition in which one photon from a pump laser of energy $\hbar\omega_p$ is absorbed and a photon of lower energy $\hbar(\omega_p - \omega_R)$ is emitted [see Fig. 1(a)]. Here $\hbar\omega_R$ is the energy of the material vibrational mode that is excited by this process. A higher-order process known as hyper-Raman scattering (HRS) [1] can occur in which two photons of energy $\hbar\omega_p$ are absorbed and one photon of energy $\hbar(2\omega_p - \omega_{2R})$ is emitted, as illustrated in Fig. 1(b). We designate the energy of the material excitation in this case as $\hbar\omega_{2R}$ to emphasisize that it can be different from $\hbar\omega_R$. In fact, because of the different selection rules involved in these two processes, material properties that cannot be investigated with conventional Raman scattering can be studied with HRS. In particular, HRS is used to study dipole modes in centrosymmetric materials, which are forbidden in conventional Raman scattering. Two-photon-excited HRS has been studied in various glasses [2,3] and HRS was used to study bulk vibrational polaritons and related effects in centrosymmetric media, which are also inaccessible using Raman scattering. In this paper, we present evidence that indicates the production of three-photon-excited HRS. This process is characterized by scattered photons of energy $\hbar(3\omega_p - \omega_{3R})$, and is illustrated in Fig. 1(c).

In our experiments, 40-fs pulses with energies of approximately 10 μJ were generated by an optical parametric amplifier (OPA) operating at a 1-kHz repetition rate, with a central wavelength tunable from 1200 nm to 1800 nm. These pulses were focused onto a fused silica sample using a 0.16 NA aspheric microscope objective. Radiation was found to be generated in the form of a cone with a frequency near that of the third-harmonic of the pump radiation. The generated light was directed to a fiber-coupled spectrometer or photomultiplier tube to measure its spatially integrated spectrum or energy, respectively. The output light generated by linearly polarized input beam retained the same polarization as the input light. The output signal was emitted in the form of a uniform (that is, azimuthally symmetric) cone, which is different from that observed in another recent experiment [4]. We also observed that this process did not occur for circularly polarized light even at significantly greater powers.

The spectra of the generated light near the third-harmonic frequency for three different pump wavelengths are shown in Figs. 2(a)–2(c) for fused silica. These spectra were obtained by integrating the signal for one second, which corresponds to 1000 laser shots. A photograph of the output ring from fused silica is shown in the inset. For comparison, we also show spectra [Figs. 2(d)–2(f)] from a sapphire sample, which were obtained by integrating for several seconds. For the case of sapphire, a single peak centered near the third-harmonic wavelength is observed in each spectrum. This emission also occurs in the forward direction in the form of a cone. The spectra for fused silica have significantly more structure than those of sapphire. We believe that the spectrum for fused silica represents a combination of several different processes, including third-harmonic generation, three-photon-excited stimulated hyper-Raman scattering, and spectral modification due to Raman-induced self-phase modulation. The qualitatively different behavior of these materials can be explained by the fact that the Raman-scattering cross section of sapphire is more than an order of magnitude smaller than that of fused silica [5]. We believe that the presence of the sidepeaks in the spectra from fused silica indicates the occurrence of three-photon-excited hyper-Raman
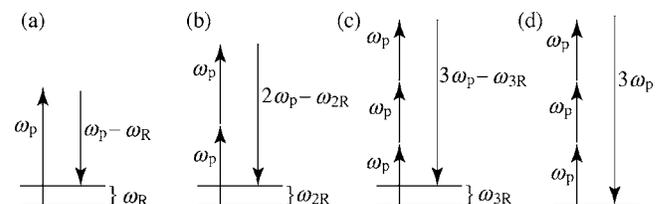

FIG. 1. Energy-level diagrams illustrating the various processes discussed in the text. (a) Raman scattering; (b) two-photon-excited hyper-Raman scattering; (c) three-photon-excited hyper-Raman scattering; (d) third-harmonic generation.
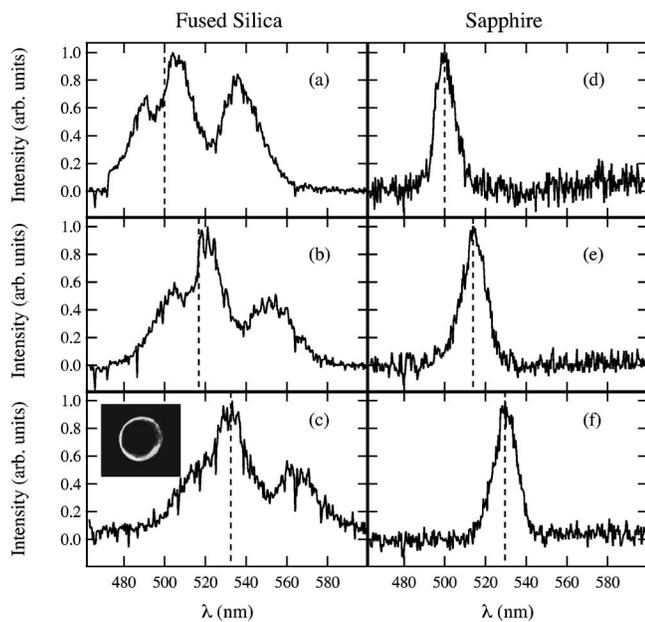
FIG. 2. Spatially integrated spectra for $\lambda_p=1500$, 1550, and 1600 nm, respectively, in (a)–(c) fused silica and (d)–(f) sapphire. The dashed lines mark the positions of the third harmonic of the pump wavelength. The inset is a photograph of the output ring.

scattering. An energy-level description of our proposed explanation is shown in Fig. 3(a). It is similar to that for Stokes-anti-Stokes coupling in normal stimulated Raman scattering except that three photons are absorbed instead of one. In the limiting case in which $\omega_{3R}=0$, six pump photons are converted into two photons of energy ω_p and the angles θ_1 and θ_2 must be equal. For the general case of $\omega_{3R}\neq 0$, the angles θ_1 and θ_2 must be different in order for phase match-
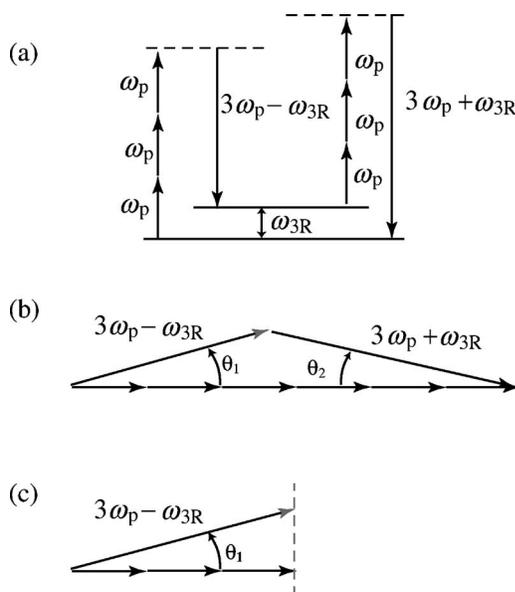

FIG. 3. (a) Energy-level diagram of the eight-wave mixing process leading to Stokes and anti-Stokes emission in three-photon-excited hyper-Raman scattering. (b) Phase-matching diagram of this process. (c) Alternative phase matching diagram in which only the longitudinal components of the interacting fields is conserved.
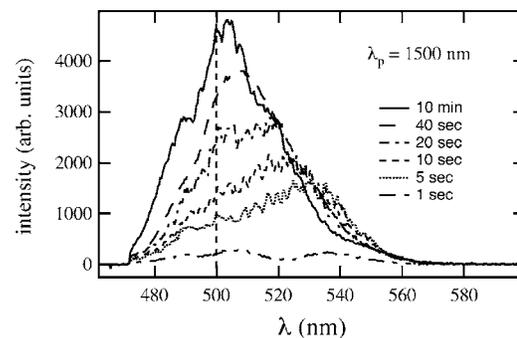

FIG. 4. Spatially integrated output spectra near the third-harmonic frequency of conical emission from fused silica for various exposure times.

ing to be achieved. The theory of this process has been explained in detail elsewhere [6]. It should be noted, however, that contrary to the phase matching picture shown in Fig. 3(b), in which higher energy photons are emitted at small angles, we have observed that the higher energy photons are emitted at slightly larger angles. It is possible that nonlinear refraction effects account for this discrepancy. In particular, in the presence of strong transverse confinement that might result from self-action effects, the phase matching condition can become modified by requiring that only the longitudinal component of the interacting wave vectors be conserved, as shown in Fig. 3(c) [7].

We find that the structure of the emission spectrum for fused silica evolves in time as the sample is exposed to successive laser pulses. In contrast, the spectrum for sapphire remains unchanged with increasing exposure. In Fig. 4 we display the time evolution of the signal strength near the third-harmonic frequency for fused silica. Notice that the spectral signal grows in strength and is gradually blueshifted during exposure and becomes centered near the third-harmonic wavelength. Another difference between the two materials is that the strength of the conical emission in fused silica grows for approximately 10 sec before saturating, whereas the strength of the sapphire signal remains constant. In Fig. 5 we plot the spatially integrated output power for fused silica as a function of time. The initial conversion efficiency (short exposure) to the third harmonic is $\sim 10^{-6}$.

We believe that the qualitatively different behavior for fused silica and sapphire can be explained by the fact that
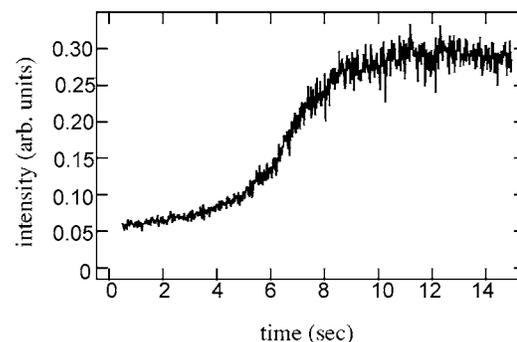

FIG. 5. Intensity of the conical emission near the third-harmonic frequency as a function of time after the turn-on of the laser field.

glasses are much more susceptible than crystals to laser-induced structural morphological changes. It has been observed that over a range of input energies [8–10] infrared pulses tightly focused in glasses can produce a highly localized region of increased refractive index. At higher powers, catastrophic damage can occur resulting in the creation of microscopic voids [11]. In contrast, sapphire is known to have only two regimes: it either is unaffected or catastrophically damaged. Since we have not observed any damage in the sapphire samples in our experiment, we expect that no change in either the spectrum or the signal strength should occur. However in fused silica, waveguides as described in Refs. [8,9] have been created using energies that are an order of magnitude lower than those used in these experiments under the same focusing conditions. We thus infer that in our experiment the microscopic structure of the glass is altered by long exposures.

Ultimately, the emission could be observed with a single incident laser pulse and therefore is not necessarily the result of a cumulative modification of the host material and is indicative of an instantaneous electronic and/or nuclear response. Nevertheless, the photorefractive index change occurring within the glass can lead to an increased number of third harmonic photons to seed the hyper-Raman process. Normally it is not possible to produce phase-matched third-harmonic light within an isotropic medium under strong-focusing conditions because the third-harmonic field produced before the focal point destructively interferes that produced after the focal point [12,13]. However, a gradient in the refractive index breaks the symmetry and allows for the generation of third-harmonic radiation [14]. This effect has been used to obtain precise images of such an index change within a dielectric sample [15]. When the glass is exposed to radiation for a long period of time, the volume of the region in which the photorefractive change occurs increases, which results in the availability of more third-harmonic photons to seed the generation process of Fig. 3(a). According to our model, the third-harmonic signal should increase linearly with the seed intensity [6].

Raman scattering is known to be sensitive to the structure of the material in which it is generated; the temporal variation of our measured spectra can thus be explained by the changing morphology of the glass in the high-intensity portion of the interaction region [16]. Since the extent of the damage within the glass is known to saturate [10], it is expected that the spectrum would evolve to a constant profile for sufficiently long times. This higher-order Raman effect could serve as a sensitive probe of the induced structural changes within glasses by intense laser radiation. One possible concern is that the observed spectra are not perfectly symmetric about the third-harmonic frequency. However, in our experiments, we are using a pulse with a bandwidth of 30 nm (FWHM), in which case many frequency components are available within the pump beam which can lead to a variety of Raman pathways.

In summary, we present experimental results that suggest the presence of three-photon-excited hyper-Raman-scattering in fused-silica glass. We find that the spectrum of the emission varies as a function of time following the turn-on of the laser field, suggesting that structural changes are being induced in the fused silica, which are then reflected in the Raman emission spectrum. This effect could serve as a sensitive probe of structural changes induced within glasses by intense laser radiation.

[1] L. D. Ziegler, J. Raman Spectrosc. **21**, 769 (1990).

[2] V. N. Denisov, B. N. Mavrin, and V. B. Podobedov, Phys. Rep. **151**, 1 (1987).

[3] V. B. Podobedov, J. Raman Spectrosc. **27**, 731 (1996).

[4] P. G. Kazansky, H. Inouye, T. Mitsuyu, J. Qiu, and K. Hirao, *Proceedings of the 2001 Nonlinear Guided Waves Conference* (Optical Society of America, Washington, D.C., 2001), p. 334.

[5] S. Smolorz and F. Wise, Opt. Lett. **23**, 1381 (1998).

[6] K. D. Moll, D. Homoelle, A. L. Gaeta, and R. W. Boyd, Phys. Rev. Lett. **88**, 153901 (2002).

[7] F. Shimizu, U. Bachmann, and B. P. Stoicheff, IEEE J. Quantum Electron. **QE-4**, 425 (1968).

[8] K. Miura, J. Qiu, H. Inouye, T. Mitsuyu, and K. Hirao, Appl. Phys. Lett. **71**, 3329 (1997).

[9] D. Homoelle, S. Wielandy, A. L. Gaeta, N. Borrelli, and C. Smith, Opt. Lett. **24**, 1311 (1998).

[10] C. B. Schaffer, A. Brodeur, and E. Mazur, Meas. Sci. Technol. **12**, 1784 (2001).

[11] E. N. Glezer and E. Mazur, Appl. Phys. Lett. **71**, 882 (1997).

[12] See, for example, R. W. Boyd, *Nonlinear Optics* (Academic Press, New York, 1992).

[13] C. R. Gouy, Acad. Sci., Paris, C. R. **110**, 1251 (1890).

[14] T. Y. F. Tsang, Phys. Rev. A **52**, 4116 (1995).

[15] J. A. Squier, M. Muller, G. J. Brakenhoff, and K. R. Wilson, Opt. Express **3**, 315 (1998).

[16] J. W. Chan, T. Huser, S. Risbud, and D. M. Krol, Opt. Lett. **26**, 1726 (2001).