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Amplified spontaneous emission enhanced forward stimulated Raman scattering in dye solutions

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ABSTRACT We study forward stimulated Raman emission from the weakly fluorescent dye 4'-diethylamino-*N*-methyl-4-stilbazolium tosylate (DEST) in 1,2 dichloroethane solution excited by a 28-ps, 532-nm Nd:YAG laser. Neat 1,2 dichloroethane emits the first Stokes line at 631 nm with a spectral width of 1.6 nm, corresponding to a Raman shift of 2956 cm⁻¹. We observe a reduction of spectral width with the addition of DEST in 1,2 dichloroethane solution. The single-pass conversion efficiency for forward Raman emission is as high as 10% in a 1-cm-path-length sample. The pulse duration of forward stimulated Raman emission, measured by a third-order autocorrelation technique, is 10 ps in neat 1,2 dichloroethane, whereas it is ~ 3 ps for 4 × 10⁻⁵ mol/l of DEST solution.

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1 Introduction

Stimulated Raman scattering (SRS) has been well investigated in a variety of materials [1]. It offers a simple and inexpensive way of extending the wavelength range of a laser system. The stimulated Raman process originates from spontaneous Raman scattering and requires high pump intensities. The overall efficiency of the process is small and, furthermore, at sufficiently high intensities, nonlinear optical effects such as filamentation due to self-focusing start appearing. In ultrashort-pulse interactions, SRS has to compete with continuum generation [2, 3]. Methods such as external seeding, either by way of injection of radiation into the Raman medium at a Stokes-shifted wavelength [4] or by addition of a lasing dye particularly for liquids that fluoresce at the Raman lines of the medium [5], are used to reduce the threshold of the stimulated Raman process. Recently, the stimulated Raman process was observed along with amplified spontaneous emission (ASE) in thin films of conducting polymers at very low excitation intensity [6–10].

The addition of a lasing dye into a neat solvent leads to interesting competition between SRS from the solvent and ASE from the dye, provided there is a spectral overlap between the two processes. Under such conditions, SRS, fluorescence, and

ASE cannot be treated independently as SRS builds up mostly from the dye fluorescence. In absence of the spectral overlap at the Raman-shifted wavelength, SRS builds up from spontaneous Raman scattering. When there is a spectral overlap between the fluorescence and Raman profiles SRS builds up from the fluorescence, which is stronger than spontaneous Raman scattering. In addition, if there is sufficient stimulated emission from the dye, the Raman gain can be substantially boosted. Another important feature of SRS is the shortening of the Stokes pulse width with respect to the width of the input laser pulse. Pulse-compression factors as high as 40 have been observed [11] in backward SRS [12–17]. Such a large compression is possible due to the fact that the backscattered pulse continuously encounters undepleted pump light, giving rise to high amplification and pulse sharpening. On the other hand, a forward-traveling Stokes pulse has access only to the pump energy that is stored in the traveling volume region. In addition, saturation due to pump depletion limits the forward Stokes emission. However, forward SRS has some intrinsic advantages over its backward counterpart in terms of simplicity of the setup and ease of the design. The generated SRS can be easily filtered from the pump beam. There is, therefore, a need to find methods that can enhance forward SRS. The addition of a dye whose fluorescence acts as a seed for SRS is one such option. The availability of population inversion in the dye can further enhance the forward Raman gain dramatically.

Seeding of SRS, albeit in the backward geometry, has been previously reported [5] using highly fluorescent dyes such as rhodamine-6G and DCM. This is a two-stage process where the SRS is initially generated in a cell of hydrogen gas and is then seeded by fluorescence from the dye.

ASE from various dyes have been extensively studied by many groups in the past [18–22]; recently, highly efficient mirror-less lasing using single- and multi-photon absorption in a weakly fluorescent stilbazolium salt of styryl pyridinium cyanine dye (SPCD) or 4'-dimethylamino-*N*-methyl-4-stilbazolium methylsulfate (DMSM) [23, 24] is reported. These belong to a new class of molecules that are weak in fluorescence but having surprisingly high ASE. The high ASE efficiency (40%) has been attributed to large dipole moments associated with charge-transfer transitions in the organic molecular salts. It is therefore interesting to explore the possibility that strong ASE from these molecules

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might enhance SRS efficiencies (particularly for the forward process).

In this paper we investigate forward SRS from solutions of 4'-diethylamino-*N*-methyl-4-stilbazolium tosylate (DEST) in 1,2 dichloroethane. We exploit the strong spectral overlap of the first Stokes line of 1,2 dichloroethane with the ASE of the dye in this solvent. Unlike some previous observations [4, 13], we achieve both seeding and amplification of SRS in a single stage. We also report the spectral evolution of the forward Raman emission at various pump intensities. We demonstrate a three-fold increase in efficiency in comparison to the neat solvent. We achieve a pulse-compression factor of three in the dye solution as compared to that from the neat solvent, giving an overall compression factor of ~ 10 over the pump-pulse duration.

2 Experimental apparatus and method

The step-wise synthesis of DEST [25] is briefly given below. The first step is to reflux equimolar amounts of 4-picoline (0.97 ml) and methyl *p*-toluenesulfonate (1.5 ml) in methanol for 2 h. In the next step 1.49 g of 4-diethylamino-benzaldehyde and 0.2 ml of piperidine are added and further refluxed for 4 h. Finally, the mixture is poured into 200 ml of ether to yield DEST.

Our experiment uses a Nd:YAG laser (Continuum PY61C-10) emitting 28-ps, 532-nm pulses at 10 Hz as the pump source. The laser beam is focused with a lens, of focal length 30 cm, into a 1-cm-path-length cuvette that contains neat 1,2 dichloroethane. The first Stokes Raman signal is detected in the forward direction by using a single-shot spectrometer (Ophir-Wavestar V). In the same setup DEST is added to the neat solvent to detect the generated ASE and Raman signals from the solution.

The pulse duration of the Raman emission is measured as shown in Fig. 1 by third-order autocorrelation, employing two-beam self-diffraction using brilliant green dye (since brilliant green dye has significant absorption at 630 nm). The gel solution is made from standard gelatin for bacteriological purposes (Qualigens) dissolved in distilled water and heated to 55 °C; brilliant green (Exciton) is added to make 6×10^{-5} M/l solution. A microscope cover slide is dipped in the solution; with a doctor's blade the solution is uniformly spread and dried. The film (~ 50 - μm thick) thus formed is clear and transparent. The Raman beam is split into two parts with a beam splitter and the beams are spatially overlapped in the dye film. The angle between the two beams is $< 2^\circ$ and the beams are focused on the film by a lens of focal length 30 cm.

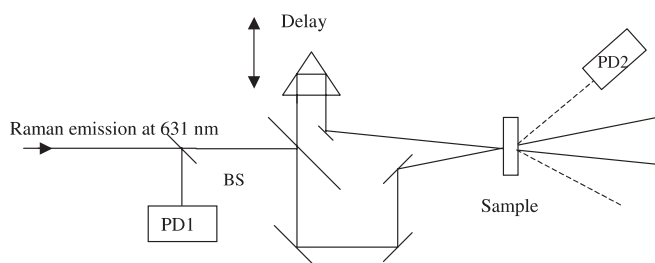


FIGURE 1 Experimental setup to measure the pulse duration

The first-order diffracted signal arises from third-order non-linearity, and is sensitive to the temporal overlap between the beams. The variation of this signal with respect to the temporal separation between the beams is, therefore, a measure of the pulse duration [26, 27]. The first-order diffracted signal is detected by a photodiode PD2 and the fluctuations in the laser energy are monitored by a photodiode PD1. The photodiode signals are acquired using a digital storage oscilloscope (Yokogawa DL 7200). Each data point corresponds to an average of 50 shots.

3 Results and discussion

The chemical structure of DEST is shown in Fig. 2a. A linear absorption spectrum of DEST at low concentration (10^{-6} mol/l) in methanol, shown in Fig. 2b, indicates that the absorption peak is located at around 490 nm and that the absorption cross section at 532 nm is 2.5×10^{-17} cm². Figure 2b also shows an emission spectrum that peaks at around 620 nm and has a width of 70 nm. Further, the fluorescence quantum efficiency is $\sim 0.5\%$ for DEST, which is much lower than that for the well-known laser dye rhodamine6G (R6G). When excited by 532-nm laser light, there is significant narrowing in the emission spectra.

SRS from neat 1,2 dichloroethane has first and second Stokes emission at 631 nm and 776 nm respectively as well as the first anti-Stokes line at 459 nm. Figure 3 shows only the first Stokes signal at 631 nm, having a line width of 1.6 nm at the input energy of 1.1 mJ (peak focused intensity of 800 GW cm⁻²). Note that this line has considerable overlap with the emission spectrum of DEST solution. Figure 4 shows the emission spectrum of DEST in 1,2 dichloroethane at different pump energies. The spectrum shows only ASE with

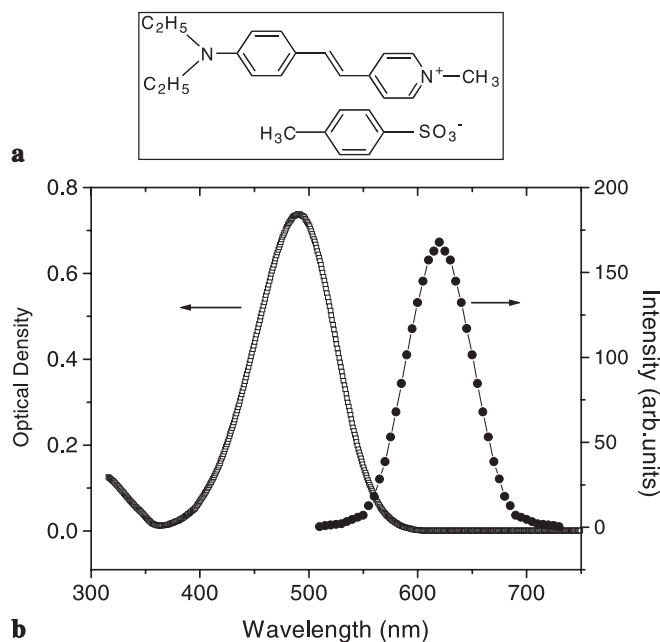


FIGURE 2 **a** Chemical structure of 4'-diethylamino-*N*-methyl-4-stilbazolium tosylate (DEST). **b** Absorption (*open circles*) and emission (*circles and line*) spectra of 4'-diethylamino-*N*-methyl-4-stilbazolium tosylate in methanol when excited by a low-intensity 532-nm laser beam

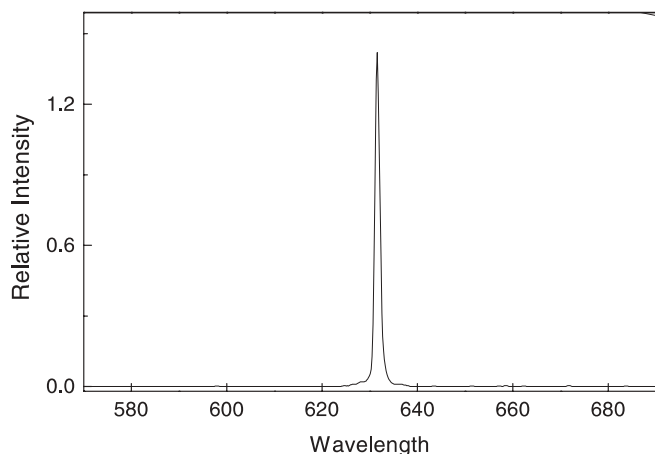


FIGURE 3 Raman emission from 1, 2 dichloroethane at an input energy of 1.3 mJ

a spectral width of 13 nm at 0.3 mJ (Fig. 4a). At the input energy of 0.7 mJ an additional peak, centered at 631 nm, starts appearing (Fig. 4b). This is due to SRS from the solvent along with the ASE. The second Stokes and first anti-Stokes lines observed in the neat solvent are suppressed with the addition of dye. At a higher input energy of 1.1 mJ, the Raman-signal amplitude rapidly increases in relation to the ASE signal, indicating the dominance of the Raman process (Fig. 4c). The ASE peak significantly reduces at 1.3 mJ and the spectrum ex-

hibits dominance of the SRS signal (Fig. 4d). Moreover, the line width of the generated Raman signal (0.8 nm) is reduced compared to that from 1, 2 dichloroethane (1.6 nm). We measured the line width of a He-Ne laser (which is close to the observed Raman line) to be 0.8 nm, which is much higher than the true line width of the laser. Thus, we are limited by spectrometer resolution; the Raman line width that we measure is an upper limit.

Figure 5 depicts the variation of the Raman signal with the input laser energy. Above a pump energy of 0.9 mJ, Raman emission increases rapidly in the case of dye solution in relation to that from neat solvent. The energy of the first Stokes line is measured to be 0.1 mJ at a pump input of 1 mJ, yielding a conversion efficiency of $\sim 10\%$ (with pump corrected for linear absorption in the solution) for 4×10^{-5} mol/l DEST as compared to 8% in neat solvent. This enhancement is clearly due to the overlap between the ASE spectrum of the dye and the Raman emission of 1, 2 dichloroethane. At this concentration, SRS essentially builds up from the ASE of dye, which is stronger than the spontaneous Raman noise, leading to enhancement in the SRS efficiency. Thus, with the addition of a small quantity of dye molecules to the solvent, the efficiency is enhanced. At a higher concentration of 7×10^{-4} mol/l there is a drastic reduction in efficiency, making quantization difficult. This is expected since at higher concentrations the dye (particularly that close to the front surface of the cuvette) absorbs most of the pump energy producing large ASE, thereby

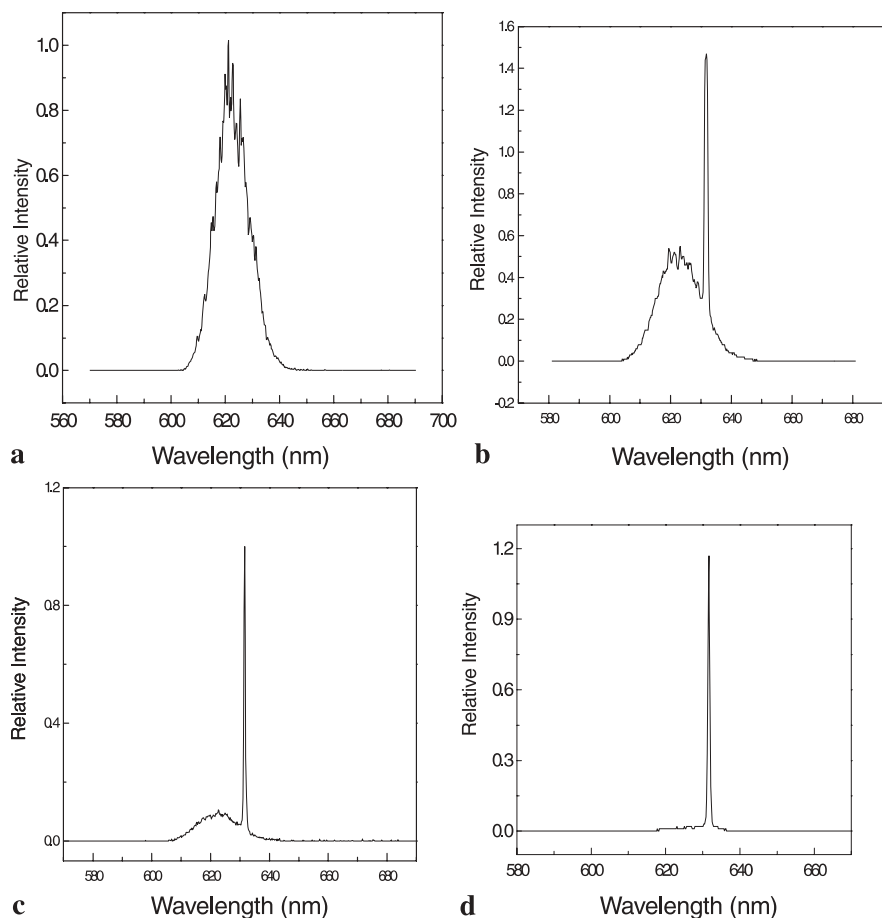


FIGURE 4 Spectral evolution of Raman emission in 4×10^{-5} mol/l DEST at input energies **a** 0.3 mJ, **b** 0.7 mJ, **c** 1.1 mJ, and **d** 1.3 mJ

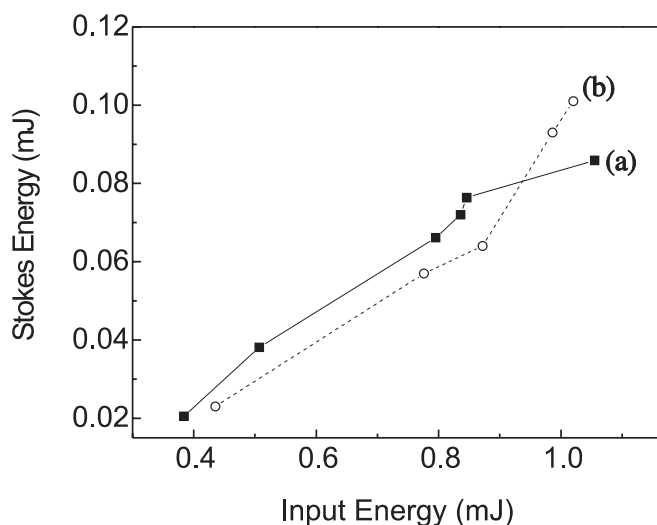


FIGURE 5 Dependence of Raman energy on the pump energy for **a** neat solvent, **b** DEST solution

reducing the energy available for Raman generation. This indicates that there is an optimum concentration for the ASE seeding of SRS.

We can also view this as competition between two different processes: (1) a coherent process (SRS), which has a higher threshold and (2) an incoherent process (ASE) which has a lower threshold. At low laser energies (~ 0.3 mJ), the incoherent process dominates (Fig. 4a). At this intensity, there is a small hump that is seen in the spectrum at 631 nm due to the Raman-shifted emission from the solvent. As the laser energy

increases two distinct peaks appear in the spectra, indicating the presence of both the processes – one broad peak centered at 620 nm due to the ASE from the dye and a narrow peak centered at 631 nm due to the stimulated Raman scattering from the solvent. Thus, at these pumping energies, ASE provides sufficient seeding and amplification for the stimulated Raman process. Moreover, the line width is reduced (to the instrumental limit of 0.8 nm) as compared to 1.6 nm in neat 1,2 dichloroethane at 1.3-mJ input energy. This can be seen as an interesting conversion of incoherent light to a coherent laser beam and offers promise for the design of efficient, coherent light sources with extended wavelength regions. The reduction in the line width on addition of dye molecules to the solvent clearly indicates that the gain is enhanced for the first Stokes line. This can be explained by considering the steady-state pumping conditions, $\tau \gg T_2 = 1/\pi \Delta\nu_R$, where τ is the pump-pulse duration, T_2 is the dephasing (relaxation) time of the SRS-active vibration mode of the solvent, and $\Delta\nu_R$ is the line width of the corresponding Raman-shifted line in the spontaneous Raman-scattering spectrum. An estimate of how large the line width $\Delta\nu_R$ is can be obtained by considering the experimental value for a typical solvent like trichloroethane, which is about 4.6 cm^{-1} [28]. The extra gain provided by the dye results in the spectral narrowing of the SRS spectral width as compared to that in the neat solvent.

We now discuss the effect of the DEST dye on the SRS pulse duration; here we measure the pulse duration by the self-diffraction method [29]. This method is based on the fact that, when two coherent light rays of the same frequency are overlapped in space, interference patterns can be obtained re-

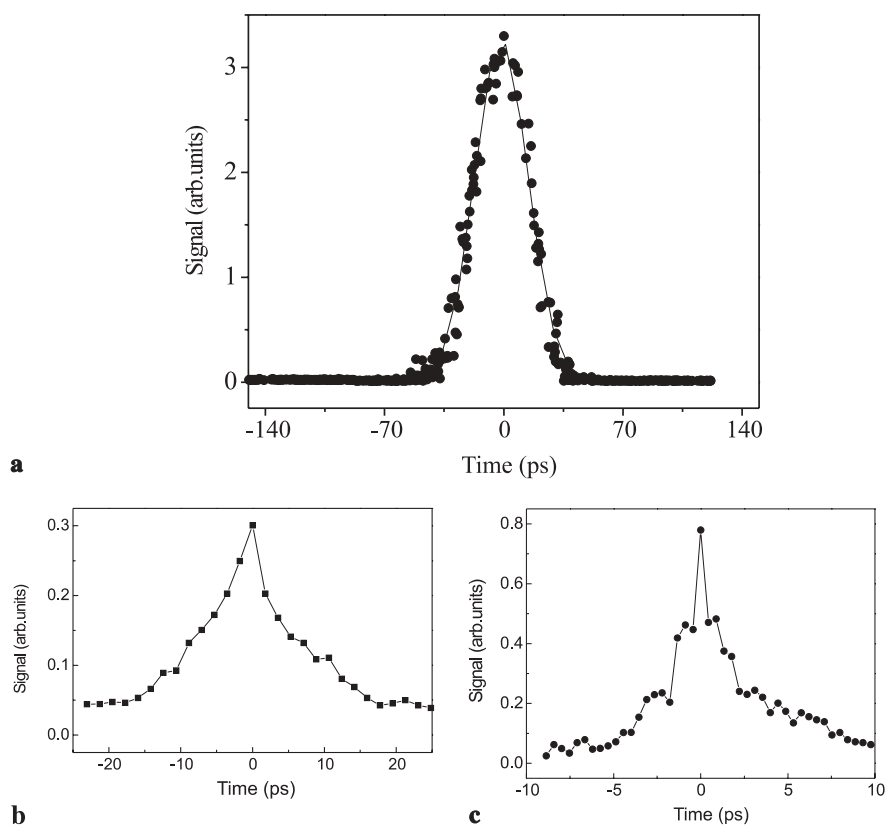


FIGURE 6 Autocorrelation trace of **a** pump laser (532 nm) fitted to a 28-ps-duration Gaussian pulse, **b** SRS emission in neat 1, 2 dichloroethane, and **c** SRS emission in neat 1,2 dichloroethane with 4×10^{-5} mol/l DEST

sulting from the variation of intensity in the region of overlap. By the principle of superposition, the net electric field in a region of space due to two waves with fields

$$E_1(r, t) = E_{10} \exp[i(k_1 \cdot r - \omega t)], \quad \text{and}$$

$$E_2(r, t) = E_{20} \exp[i(k_2 \cdot r - \omega t)] \quad \text{is given as}$$

$$E = E_1 + E_2.$$

The intensity I at the point is $I = EE^*$. Hence, the net intensity is given by

$$I = I_{10} + I_{20} + 2E_{10}E_{20} \cos[(\Delta k) \cdot r],$$

where $\Delta k \cdot r = (k_1 - k_2) \cdot r$ is the phase difference arising from different path lengths.

Thus the net intensity of light at that point in space will depend upon the difference in phases between the rays.

When a medium like a dye is placed at the overlap in space and time of two laser beams, a population-density grating will be formed inside the material due to absorption of light which populates the excited electronic states. In the regions where the intensity is sufficiently high, molecules would be excited, resulting in modulation of refractive index and absorption coefficient. These light-induced gratings can be probed with a third laser beam, or by using either of the beams that produce the gratings. When one of the initial beams acts as a probe beam, the resulting diffraction phenomenon is known as self-diffraction.

Further, the first-order diffraction occurs in the $(2k_1 - k_2)$ direction and arises from the third-order optical non-linearity of the medium. In the case of a transient grating formed by short laser pulses, the diffracted signal is sensitive to the temporal overlap between the beams. Thus, the diffracted beam from a transient grating due to self-diffraction provides a measure of the pulse duration of short laser pulses. We measured the pulse duration of the pump laser (532 nm) by self-diffraction in a 1-mm cell containing CS₂. The autocorrelation trace is shown in Fig. 6a and fitted by a model pulse assumed to have a Gaussian temporal profile. The curve fitting indicated that the pump laser pulse duration is ~ 28 ps. The autocorrelation trace of the pulse duration by the SRS process in a neat 1,2 dichloroethane solution is shown in Fig. 6b; the FWHM is ~ 10 ps. Thus there is nearly three-fold pulse compression as compared to the pump-pulse duration of 28 ps. With the addition of a small quantity of the dye (4×10^{-5} mol/l) the pulse duration further reduces to 3 ps (FWHM) and is shown in Fig. 6c. This is again more than three-fold enhancement over the neat solvent and nearly 10-fold overall compression with respect to the pump-pulse duration. The plausible explanation for pulse compression due to the addition of dye is as follows: the ASE occurs towards the end of the pump pulse, Raman amplification by ASE occurs only where the pump pulse and the ASE seed pulse overlap, and this effective overlap is short compared to the pump-pulse duration.

4 Conclusions

In conclusion, we have reported observations of aided and unaided stimulated Raman emission in neat 1,2 dichloroethane with the addition of the dye DEST. This dye is weakly fluorescent, yet it shows strong ASE. We have observed spectral narrowing of the first Stokes line in DEST solutions. Further, we have demonstrated pulse compression from 28 ps to 3 ps in forward stimulated Raman emission. The single-pass conversion efficiency is 10% in a 1-cm-path-length sample. Such enhanced efficiencies and compression offer tremendous promise for the design of ultra-short coherent light sources with extended spectral coverage.

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