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Effect of a fluorescing impurity on the characteristics of stimulated Raman scattering from acetone

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Abstract. Asymmetry in the intensities between backward and forward stimulated Raman scattered radiations (BSRS and FSRS respectively) in acetone is investigated in the presence of a fluorescing impurity (rhodamine 6G). In the case of pure acetone above a threshold pump power, BSRS becomes more intense than FSRS. On the other hand intensity of BSRS decreases with concentration of the fluorophore in solution, while that of FSRS is found to increase. It is observed that absorption saturation also affects the asymmetry between FSRS and BSRS.

Keywords. Stimulated Raman scattering; phase conjugation; rhodamine 6G.

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Since its accidental discovery in nitrobenzene by Eckhardt *et al* (1962) large amount of work has emerged on the theory and applications of Stimulated Raman Scattering (SRS). The efficiency of SRS is governed by the nonlinear polarization

$$\mathbf{P}_{nl}(\mathbf{r}) = -iG(\nu - \omega, \nu)\mathbf{E}_{\nu}(\mathbf{r})\mathbf{E}_{\nu}(\mathbf{r})\mathbf{E}_{\omega}(\mathbf{r}) \tag{1}$$

where G is the appropriate fourth rank susceptibility tensor, ν is the pump beam frequency and ω is the frequency of scattered beam so that $\nu - \omega$ coincides with one of the vibrational modes of the molecule. Theoretical analysis shows that (Kaiser and Maier 1972) stimulated Raman scattering can be observed above a certain threshold pump power and is confined to backward (BSRS) and forward (FSRS) directions. This narrow beam scattering angle is mainly caused by a geometrical effect, viz. the length of the interacting medium being much larger than the diameter of the pump beam. Since amplification grows exponentially with the interaction length, SRS will be confined to a narrow cone around the laser beam (in the forward as well as backward directions). It may be mentioned here that BSRS in certain organic solvents (eg. CS_2) has been closely associated with wavefront reversal (WFR) or phase conjugation (Sokolovskaya *et al* 1978). Since phase conjugation can be utilized to correct wavefront distortions in an optical beam propagating through aberrating media this technique has attracted considerable attention from an application point of view. The WFR property of SRS can generate BSRS of considerably larger intensities as compared to FSRS (Blekhovskikh *et al* 1978; Hellwarth 1983). This asymmetry can be varied if there is a control parameter. One of such parameters is the absorption loss of pump and Raman radiations. The absorption losses can be

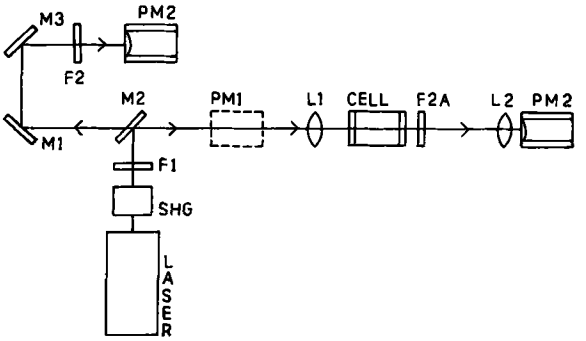

Figure 1. The experimental set up. SHG–Second harmonic generator, F1–Filter to cut 1·06 μm beam, PM1, PM2–Laser energy meters, F2–Laser line filter, F2A–Filter combination to cut scattered laser radiation and dye fluorescence, M2–Dichroic mirror to reflect pump beam and transmit the SRS beam, M1 and M3–Plane mirrors.

continuously varied by adding proper solutes in the solvent at different concentrations. The present paper deals with such studies in acetone in the presence of the fluorescing laser dye rhodamine 6G (Rh6G).

The experimental set-up is shown in figure 1. SRS was excited using the second harmonic (532 nm) of a pulsed Nd:YAG laser (Quanta Ray, DCR-11). The laser was run at a repetition rate of 16 Hz, and the pulse duration was approximately 10 ns. The pump beam was focussed with a lens ($f = 5$ cm) and allowed to pass along the axis of a cylindrical cell of 2 cm diameter and 5 cm length (having plain parallel windows) which contained spectroscopic grade acetone. Above a certain pump threshold intense SRS was observed both in the forward and backward directions. The scattered beam is shifted from the pump frequency by 2921 cm^{-1} corresponding to the C–H streching vibration of acetone. Both FSRS and BSRS were separated from the pump beam using wavelength selective optics. Intensity of both the beams were monitored using a laser power meter (EG & G 460–1A) and the pump power measured on another power meter (Scientech 362). Spectrum of SRS was recorded using a 0·3 meter grating monochromator (McPherson) and PMT unit. The PMT signal was gated and averaged over thirty pulses employing a gated integrator and boxcar averager system (SRS-250), the output of which was fed to a chart recorder. Observations were made at various pump energies and experiments repeated in dilute solutions of Rh6G in acetone. Proper care was taken in optically filtering out the pump and fluorescence frequencies at the detector end.

Figure 2 shows the stimulated Raman spectrum obtained for pure acetone. Intensities were not the same in forward and backward directions (figure 3) even though the threshold intensities did not differ much. Similar to the results of Bret and Denariez (1966) a linear variation of SRS was found in our case also in the range of power levels used (< 7 MW). However, almost from the threshold level itself BSRS begins to grow in intensity in comparison with FSRS. According to Shen and Bloembergen (1965) the gains in the forward and backward directions are expected to be the same at low pump intensities, whereas actually with stronger pump beams a considerable enhancement in BSRS has been observed (Maier *et al* 1966, 1969; Blekhovskikh *et al* 1979). An analysis of this situation can be quite complex because in addition to pump depletion, several nonlinear processes like self-focussing,

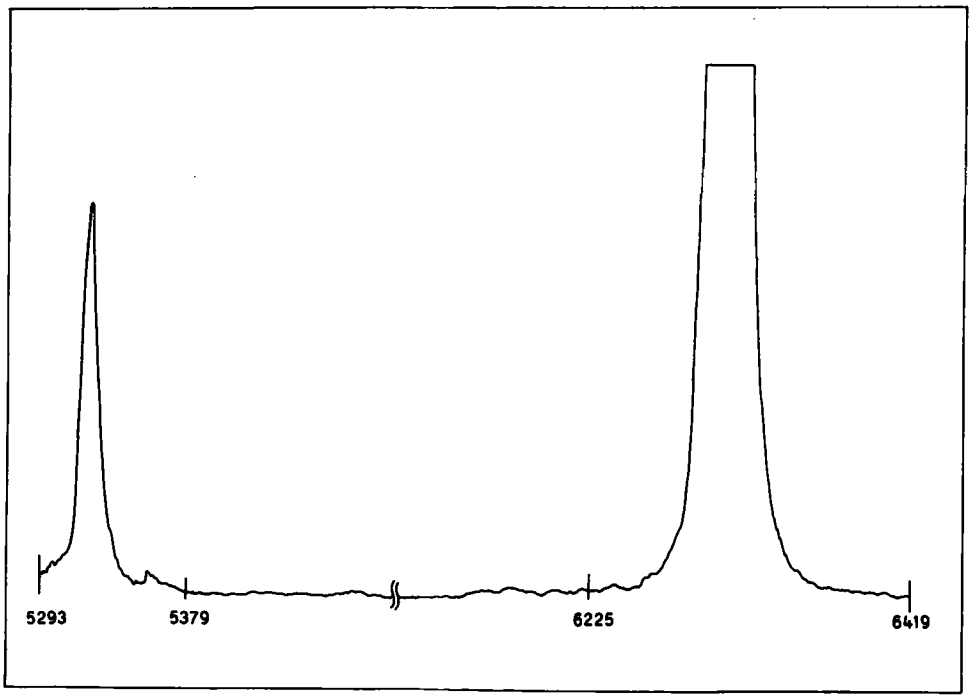

Figure 2. Stimulated Raman spectrum obtained in acetone and dilute solutions of Rh6G in acetone. The smaller peak corresponds to the scattered laser radiation.

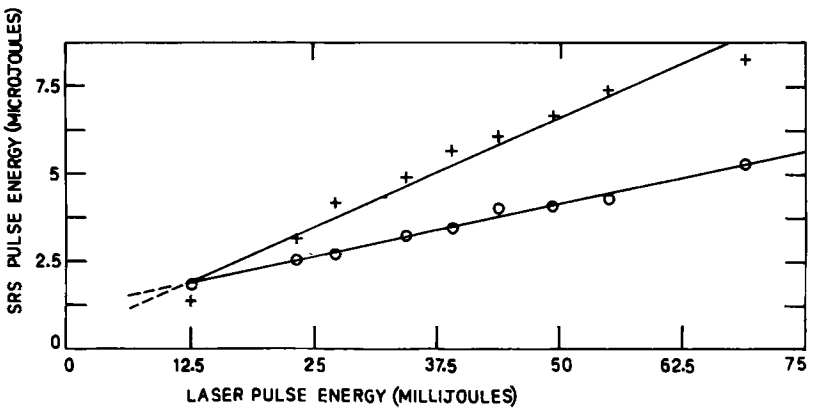

Figure 3. Energy of SRS beam in forward and backward directions, as a function of the pump energy + – BSRS, ○ – FSRS.

stimulated Brillouin scattering (SBS), phase conjugation etc. can also contribute in various degrees to such an enhancement of BSRS (Hellwarth 1983) at higher pump powers. Regarding self-focussing one may note that for ordinary Q-switched laser beam intensities the steady-state refractive index can be written in the form

$$n = n_0 + (n_{2\alpha} + n_{2\rho} + n_{2e})\tfrac{1}{2}|E|^2 \tag{2}$$

where E is the laser field strength and the coefficients $n_{2\alpha}$, $n_{2\rho}$ and n_{2e} are associated with Kerr effect, electrostriction and nonlinear electronic polarizability respectively. In the normal dispersion region, n_{2e} is negligible as compared to $n_{2\rho}$ and $n_{2\alpha}$ for most liquids and with a pump pulse of nanosecond duration, $n_{2\rho}$ also loses its significance in this context. Further, liquids like acetone, hexane, CCl_4 etc. are characterized by low values of Kerr coefficients (Paillette 1966), whereby one is led to think that self-focussing will not take place in acetone under pulsed excitation (Bret and Denariez 1966). However, Shen and Shaham (1967) have shown from their temperature dependence studies of the above effect that SBS can lead to self-focussing phenomenon. The contribution of SBS to self-focussing is thus indeed non-negligible in liquids with relatively small Kerr constants. It is also worth noting that in acetone phase conjugation by SBS also has been already reported (Balkevicius *et al* 1984). Apart from a qualitative description, an estimation of the relative importance of these and other processes taking place in the medium will be quite complicated even though their collective effect is manifested as a significant enhancement in BSRS intensity in the whole range of power levels used here. However, the fact still remains that since in acetone the stimulated Raman cross section is quite high the primary mechanism leading to an enhancement of BSRS is phase conjugation by SRS itself. A detailed theoretical treatment is given in Levenson (1982) and Shen (1984).

SRS from dilute solutions of Rh6G in acetone shows interesting characteristics. Following Kaiser and Maier (1972), we can write the spatial dependence of pump (I_l), FSRS (I_s^f) and BSRS (I_s^b) as

$$\frac{dI_l}{dz} = -g_l[I_l(I_s^f + I_s^b) + \alpha] \tag{3}$$

$$\frac{dI_s^f}{dz} = g_s I_s^f I_l \tag{4}$$

and

$$\frac{dI_s^b}{dz'} = g_s I_s^b I_l \tag{5}$$

where g = gain factor, α = linear optical absorption coefficient for the pump wavelength λ_l and $z' = -z$. For acetone α is negligibly small when excited with 532 nm ($\approx 10^{-4}\,cm^{-1}$) as compared to the dye solution, where $\alpha \approx 10^4\,cm^{-1}$. In Rh6G solution wavelength of I_l (532 nm) lies quite close to the absorption peak indicating large absorption losses resulting in fluorescence emission centred around 570 nm. (Absorption losses of I_s^f and I_s^b are neglected since the Raman emission (631 nm) lies far away from the absorption band of Rh6G). Hence, in the presence of Rh6G the depletion in pump energy along the beam axis in the medium should result in a reduced SRS emission in comparison with that of pure acetone, thereby shifting the threshold pump energy at which BSRS/FSRS = 1 towards a higher value. Our experimental observation of an obvious increase in this threshold value with concentration (figure 4) confirms this assumption. The threshold energy shifts from 25 mJ/pulse at $2{\cdot}9 \times 10^{-8}$ mol/litre to 87·6 mJ/pulse at $3{\cdot}9 \times 10^{-6}$ mol/litre. There is a net reduction in SRS intensity with concentration which is quite understandable since fluorescence excitation in Rh6G increases with concentration. In the range of

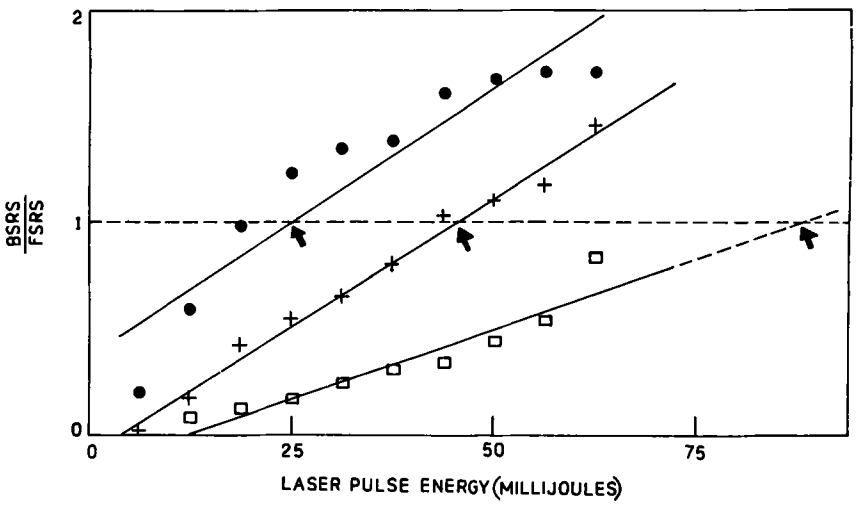

Figure 4. Ratio of BSRS to FSRS in various concentrations, as a function of the pump energy. ● $-2{\cdot}9 \times 10^{-8}$ mol/litre; + $-4{\cdot}3 \times 10^{-7}$ mol/litre. □ $-3{\cdot}9 \times 10^{-6}$ mol/litre.

laser energies studied BSRS is seen to be less intense than FSRS at higher concentrations (figures 5a and 5b). The comparative reduction in BSRS intensity occurs due to the fact that WFR of the pump beam becomes less prominent with concentration, thereby reducing its energy coupling to the BSRS beam. However the intensity of FSRS radiation increases with concentration. If we take the sum of forward and backward intensities and compare it with that in acetone, we find that at low pump energies the total intensity (FSRS + BSRS) decreases with concentration while at higher laser energies it is almost the same as that in pure acetone (figure 6). Rh6G solution has a nonlinear absorption coefficient which depends on the pump intensity as

$$\alpha = \frac{\alpha_0}{1 + I'} \tag{6}$$

where

$$I' = \frac{I_l}{I_{\text{sat.}}} \tag{7}$$

and $I_{\text{sat.}}$ is the saturation intensity with α_0 as the linear absorption coefficient. When $I_l > I_{\text{sat.}}$ we have $\alpha < \alpha_0$ and the transmission characteristics will become more similar to that of the solvent (acetone). Thus, (3) can be modified to give

$$\frac{dI_l}{dz} = -g_l\left[I_l(I_s^f + I_s^b) + \frac{\alpha_0}{1 + I'} \right]. \tag{8}$$

At large I_l, $I' \gg 1$ and (8) reduces to the form of (3) with $\alpha = 0$. This implies that at higher laser energy, the presence of the dye apparently does not affect the total scattered intensity from acetone. However, the anisotropy of scattered intensities in backward and forward directions is modified, which is obvious from figures 5a and 5b.

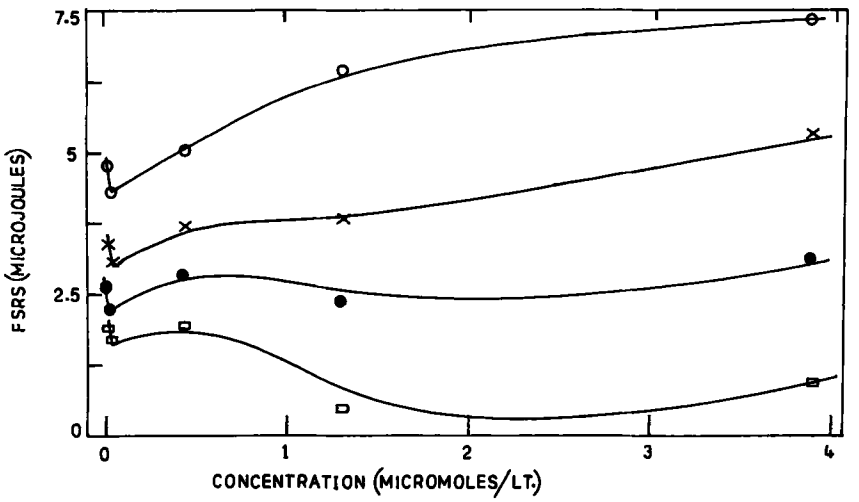

Figure 5a. FSRS intensity with respect to Rh6G concentration, for various pump energies. □ – 12·5 mJ; ● – 25 mJ; × –37·5 mJ; ○ – 62·5 mJ.

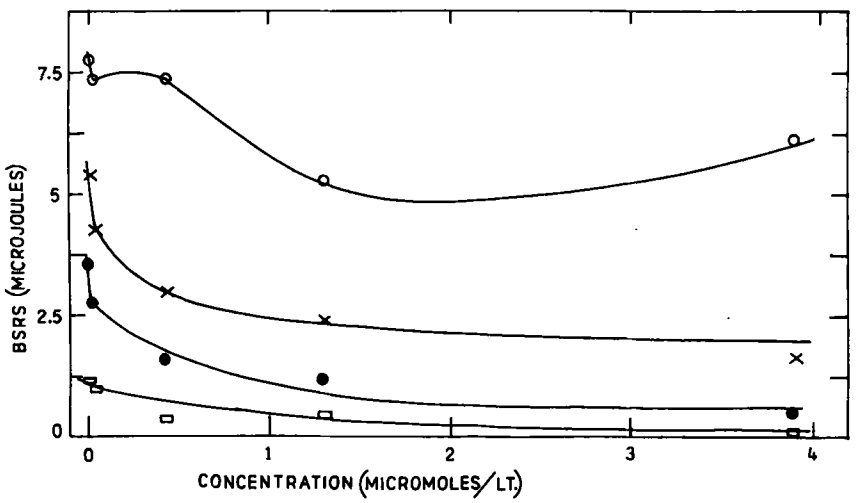

Figure 5b. BSRS intensity with respect to Rh6G concentration, for various pump energies. □ – 12·5 mJ, ● – 25 mJ, × – 37·5 mJ, ○ – 62·5 mJ.

It should, however, be noted that the WFR quality of SBS is better than that of SRS (Mays and Lysiak 1979) and larger Raman frequency shifts always result in a deterioration of the same in the phase conjugate beam (Mays and Lysial 1980) in SRS. In this respect an estimate of pump correlated and uncorrelated parts in the BSRS beam requires detailed phase conjugation experiments. Work in this direction is in progress.

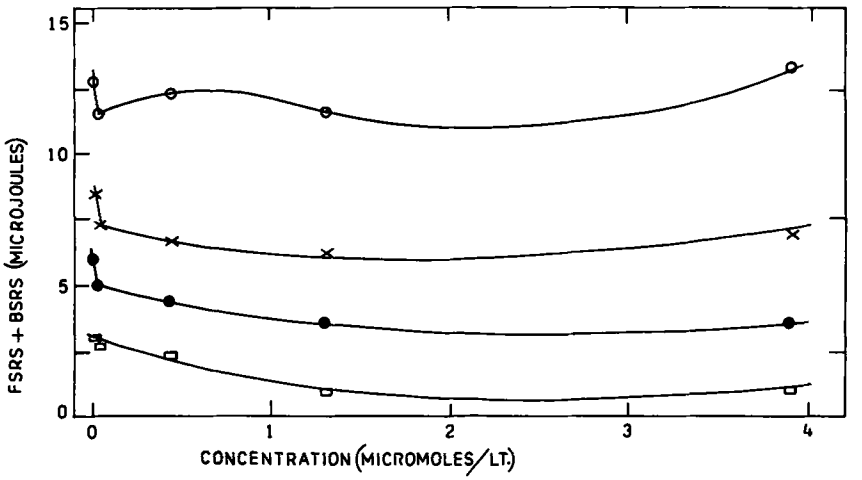

Figure 6. FSRS + BSRS intensity with respect to Rh6G concentration, for various pump energies. □ – 12·5 mJ; ● – 25 mJ; × – 37·5 mJ; ○ – 62·5 mJ.

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References

Balkevicius P I, Dement'ev A, Lukosius J P, Maldutis E K and Tarulis V P 1984 *Bitovskii Fizicheskii Sbornik* **24** 81

Blekhovskikh G L, Kudryavsteva A D and Sokolovskaya A I 1978 *Sov. J. Quant. Electron.* (*Engl. Transl.*) **8** 1028

Blekhovskikh G L, Okladnikov N V and Sokolovskaya A I 1979 *J. Appl. Spectros.* (*Engl. Transl.*) **32** 15

Bret G and Denareiz M 1966 *Appl. Phys. Lett.* **8** 151

Eckhardt G, Hellwarth R W, McClung F J, Schwarz S E, Weiner D and Woodbury E J 1962 *Phys. Rev. Lett.* **9** 455

Hellwarth R W 1983 in *Phase conjugation by stimulated backscattering* in *Optical Phase Conjugation*, (ed.) Robert A Fisher (New York: Academic Press)

Kaiser W and Maier M 1972 in *Stimulated Rayleigh, Brillouin and Raman spectroscopy in Laser Handbook*, vol. 2, (ed.) F T Arecchi (Amsterdam: North Holland)

Levenson M D 1982 *Introduction to nonlinear spectroscopy* (New York: Academic)

Maier M, Kaiser W and Giordmaine J A 1966 *Phys. Rev. Lett.* **17** 1275

Maier M, Kaiser W and Giordmaine J A 1969 *Phys. Rev.* **177** 580

Mays R, Jr and Lysiak R J 1979 *Opt. Commun.* **31** 89

Mays R, Jr and Lysiak R J 1980 *Opt. Commun.* **32** 334

Paillette M 1966 *Compt. Rend.* **262** 264

Shen Y R 1984 *Principles of nonlinear optics* (New York: John Wiley)

Shen Y R and Bloembergen N 1965 *Phys. Rev.* **137** A1786

Shen Y R and Shaham Y J 1967 *Phys. Rev.* **163** 224

Sokolovskaya A I, Brekhovskikh G L and Kudryavtseva A D 1978 *Opt. Commun.* **24** 74