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The Role of Self-Phase Modulation in Stimulated Raman Scattering
from More Than One Mode

by

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Abstract

Stimulated Stokes spectra obtained with picosecond pulses in organic liquids often exhibit transient gain in more than one mode. A theory is developed here to describe the important effect of self-phase modulation on such multiple-component spectra. The nonlinear refractive index generated by a two-component Stokes field produces additional spectral components, separated by the frequency spacing between the two initial components. Calculations indicate that the new components are observable at considerably lower intensities than that necessary to produce noticeable phase modulation of the pulse envelope, and may be an intrinsic part of the excitation process in molecules exhibiting Stokes gain in more than one mode. A comparison between the calculated spectra and experimentally obtained stimulated Raman spectra in methanol confirms the theoretical predictions, and the consequences of the theory with regard to the stimulated Raman spectra of large molecules are discussed.

The exploitation of nonlinear optical effects has played a crucial role in recent investigations of vibrational energy transfer, relaxation, and dephasing^{1,2}. Although transient stimulated Raman scattering (SRS) has proven particularly useful as a means of coherently exciting an ensemble of vibrators whose subsequent time evolution is to be studied, the correct interpretation of the results of such experiments depends upon an accurate knowledge of the initial state of the ensemble as prepared by the excitation laser pulse. Existing theoretical descriptions³⁻⁵ do not treat the case where more than one mode of the molecule exhibits stimulated gain and self-phase modulation is present. In many cases, stimulated Raman spectra obtained from picosecond pulses in organic liquids exhibit complicated spectral broadening characteristic of self-phase modulation. As we will demonstrate, the amount and nature of this modulation depend strongly on the structure of the molecule and the corresponding distribution of intensities in its Raman spectrum, and can be understood when the effect of multiple but well-separated frequency components propagating simultaneously through a nonlinear medium are incorporated into the theory of self-phase modulation⁶⁻¹⁰. This communication extends the theory of phase modulation to include multiple components, and presents experimental verification of that theory.

Beginning with the phenomenological equation^{6,8,9} for the nonlinear index of refraction:

$$n = n_0 + n_2 \left| E(t) \right|^2 \quad (1)$$

where $E(t)$ is the light field upon entry into the nonlinear medium, one can relate the nonlinear index n_2 to changes in phase as:

$$\phi(t) = a_1 \left| E(t) \right|^2 \quad (2)$$

where z is the distance travelled, $a_1 = \omega_1 z n_2 / c$, and ω_1 is the frequency of oscillation of the field. The largest phase shift, ϕ_{peak} , occurs at the peak of the pulse envelope and is the dimensionless product of a_1^2 and the pulse

peak intensity. ϕ_{peak} can be used to characterize the phase modulation for a given choice of $E(t)$. The spectrum of the phase-modulated pulse is given by the Fourier transform of (2):

$$E(\omega) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} dt E(t) \exp(i\omega t + i\phi(t)) \quad (3)$$

Equation (3) has been used to compute the effect of self-phase modulation on a light field of the form:

$$E(t) = E_1(t) \exp(i\omega_1 t) + \text{complex conjugate} \quad (4)$$

When (4) is combined with (2) and (3), the resulting spectrum displays a semi-periodic frequency broadening⁶⁻⁹ which depends upon the intensity of the field and the slope¹⁰ of the pulse envelope $E_1(t)$.

We have investigated the theory when additional frequency components are incorporated into $E(t)$ by setting:

$$E(t) = \sum_j E_j(t) \exp(i\omega_j t) + \text{c.c.} \quad (5)$$

and substituting (5) into (2). This results in the following phase factor:

$$\begin{aligned} \phi(t) = & \sum_i \sum_j a_i a_j E_i(t) E_j(t) \exp(i[\omega_i - \omega_j]t) + \text{c.c.} \\ & + \sum_i \sum_j a_i a_j E_i(t) E_j(t) \exp(i[\omega_i + \omega_j]t) + \text{c.c.} \end{aligned} \quad (6)$$

It should be noted that a term containing a frequency factor $\exp(i[\omega_i - \omega_j]t)$, when substituted into (3), will generate new frequency components separated by exactly $\omega_i - \omega_j$, in addition to the envelope modulation resulting from fields of the form (4).

A series of computer calculations was carried out using equation (3) with various forms for $E(t)$. The effects of varying the pulse envelope, the number and distribution of components, and the intensities of each was systematically investigated. Three different pulse envelopes were used: 1) gaussian, 2) a slightly asymmetric shape (gaussian rise, sech tail) which is known to correspond to the picosecond pulses from a Nd: glass laser, and 3) a Stokes pulse shape calculated numerically by the method of Carman,

et al³, using the Nd:glass pulse shape for the excitation pulse. The results of the calculations are illustrated in Figures 1 and 2, and show that there are two contributions to the modulation. The first is the contribution from the time-dependent pulse envelope, and is present in the single-mode case at moderate intensities (Figure 1a-1d), and in the other cases at relatively high intensities. The second is the contribution from the frequency mixing terms $\exp(i[\omega_i - \omega_j]t)$ in (6), which produce the series of satellite peaks visible at significantly lower intensities than those needed to produce envelope modulation.

These calculations are confirmed by a series of experiments which show that the effect of the multiple components is evident at intensities where the envelope modulation is insignificant. Figure 3 presents a series of observed SRS spectra in methanol, which were obtained by focussing transform-limited, frequency-doubled Nd:glass laser pulses of 10mJ into a cell of methanol, and displaying the resulting Stokes spectra on an optical multichannel analyzer. Both the symmetric and antisymmetric G-II stretch modes of this molecule exhibit stimulated gain¹¹, and by varying the pulse energy and focus a range of phase-modulation effects could be studied. Since the nonlinear constants are not known, and it is difficult to measure the intensity of the Stokes field at the focal point, only a qualitative comparison between theory and experiment is possible. However, it is clear that the calculations explain the observed spectra quite well, particularly with regard to the satellite peaks in Fig. 3b and 3c and the extremely modulated spectra in Fig. 3d and 4. The semiperiodic structure in Fig. 4 and the large broadening in Fig 3d are strong evidence that self-phase modulation of multiple frequency components is the mechanism operating in this system.

Molecules having complicated Raman spectra consisting of numerous close or overlapping bands show even more complex stimulated spectra, as has been observed (but unexplained) by other workers as well¹². The theory presented here makes possible the interpretation of such spectra.

In conclusion, we have extended the theory for self-phase modulation to include the presence of more than one frequency component. Calculations were performed, based on this theory, to describe the spectra of stimulated Stokes pulses as a function of intensity, and excellent qualitative agreement was observed with a series of experimental spectra. The results show that when multiple modes are present, the effects of phase modulation are visible at much lower intensities than in the single-component case. We conclude that self-phase modulation plays an important role in the spectral broadening of transient stimulated Raman pulses, and is an intrinsic part of the excitation process in molecules exhibiting gain in more than one mode.

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Figure Captions

Figure 1: Envelope modulation of single-component pulses. In (a)-(d), a gaussian pulse shape was used; in (e)-(h) a Nd:glass laser exciting pulse propagates with a Stokes pulse, and the Stokes spectrum as a function of laser pulse intensity is plotted. The nonlinear refractive index in (e)-(h) is generated by the laser pulse, and the Stokes spectrum displays the effects of the modulation. ϕ_{peak} values are: (a) 0.0 (b) 0.9 (c) 10.0 (d) 90.0 (e) 0.1 (f) 3.6 (g) 40.0 (h) 250.0. The asymmetry in (e)-(h) results from the asymmetry of the pulse shapes.

Figure 2: These spectra are calculated for the case of a laser pulse and a two-component Stokes pulse. The Stokes spectrum in the absence of phase-modulation is shown in (e). Curves (e)-(h) represent a fixed laser intensity and increasing Stokes intensity; the values of ϕ_{peak} are (e) 0.0 (f) 0.1 (g) 0.4 (h) 2.5. In (a)-(d) the Stokes field of (f), i.e. $\phi_{\text{peak}} = 0.1$, was held fixed as the laser intensity was increased. Values of ϕ_{peak} for the laser field are (a) 0.1 (b) 10.0 (c) 40.0 (d) 250.0. The calculation shows clearly that the sidebands which grow in curves (f)-(h) are related to the presence of two Stokes components. They appear at intensities too low to cause significant modulation of a single peak, and are separated in frequency by the splitting between the two parent Stokes peaks.

Figure 3: Spectrum (a) is the transient stimulated Raman spectrum of methanol in the absence of self-phase modulation, and shows the two peaks corresponding to the two Raman-active C-H stretch modes of this molecule. In (b) and (c) the sidebands resulting from phase-

modulation are shown, as illustrated by the equally spaced arrows. These spectra resemble the calculated spectra Fig. 2(g) and 2(h). In (d) a large amount of broadening is also present, partially obscuring the parent peaks and the periodic sideband structure.

Figure 4: The spectrum on the right was obtained by tight focussing of the pump laser pulse. The arrows indicate the peak positions in the unmodulated methanol spectrum. The calculated spectrum on the left is almost identical to Fig. 1(g); its resemblance to the experimental spectrum indicates the presence of envelope modulation at high light field intensities.

CALCULATED SINGLE COMPONENT PHASE MODULATED SPECTRA

Figure 1

CALCULATED TWO-COMPONENT PHASE MODULATED SPECTRA

Figure 2

STIMULATED STOKES SPECTRUM OF METHANOL

XBL 802-8303

CALCULATED AND EXPERIMENTAL STIMULATED STOKES SPECTRA

XPL 002-0074

Figure 4