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FORWARD PICOSECOND STOKES-PULSE GENERATION IN TRANSIENT STIMULATED RAMAN SCATTERING

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The transient excitation of molecular vibrations by a picosecond laser-pulse train depends critically on the detailed shape of the exciting pulses. Stokes pulses shorter than or equal to the generating laser pulses have been observed in CCl_4. Other aspects of the transient nature include the stimulation of two Stokes lines in methanol and the absence of backward Stokes radiation.

The purpose of this note is to present some new experimental and theoretical characteristics of the transient Raman effect. Several investigations have already demonstrated different Raman gain characteristics under transient excitation.[1-6] The emphasis was, however, mostly on the competition with the Brillouin effect or on transient characteristics of the self-focusing by the quadratic Kerr effect. Here, a quantitative interpretation of picosecond Stokes pulses in terms of transient Raman gain theory[7,8] is given.

The regime of interest here is one in which the laser and/or Stokes pulses have a duration t_p shorter than the dephasing time $\Gamma^{-1}=\tau_v$ of the vibrational-rotational state of the molecules, but the intensity is not large enough to produce significant population changes, which would result in Raman-type 2π pulses of self-induced transparency. More precisely, the condition for transient impact-type excitation of the vibration is $t_p < G_{ss}\tau_v$, where $\exp G_{ss}$, with $G_{ss}=gl$, is the steady-state Raman gain which would obtain in the cell of length l under excitation by a long pulse. The transient gain is given by $\exp G_T$, with $G_T=(4G_{ss}\Gamma t_p)^{1/2}$, in the asymptotic limit of high transient gain which is reached for $G_T>10$

(for $\Gamma t_p = 0.2$, $G_{ss} > 100$). It can be shown[9] that an initially square Stokes pulse of duration t_p would tend to become sharper in time, and consequently broader in the frequency domain. This is in contrast to the frequency narrowing with increasing steady-state Raman gain. The Stokes pulse width at half-intensity for a square pulse excitation is approximately $\Delta t_s = t_p/G_T$. The response is, however, very sensitive to the detailed shape of the exciting pulse. We have extended Wang's theory[7] to take account of the time-varying laser pump intensity. For a Gaussian laser-pulse shape, the Stokes pulse would be narrowed to a considerably lesser extent, $\Delta t_s = t_p/(\ln G_{ss})^{1/2}$. This is a manifestation of important precursor effects. The effect of the exponential rise of the pump intensity in the leading edge of the pulse is counteracted by the increase in gain coefficient, because the perturbation acts over a longer period. Computer solutions[10] indicate that the Stokes intensity reaches its maximum somewhat after the maximum in the laser pulse for the Gaussian. If the laser intensity were to drop off more slowly than Gaussian, the situation would revert more and more to steady-state conditions.

Experiments in CCl_4 were performed with a mode-locked ruby laser[11] yielding a train of pulses each of 5×10^{-12} sec duration. CCl_4 was chosen because of its small dispersion of the group velocities. The delay between laser and Stokes pulse in this fluid is less than 0.03×10^{-12} sec/cm. The spontaneous Raman linewidth Γ_R corresponds to one or two wave numbers for the 459-cm^{-1} line, but is complicated due to chlorine isotope effects.[12] Since the overall Raman gain to reach the observed power levels without feedback is e^{15}, the effect would have a transient nature even for linewidths as large as 30 cm^{-1}.

In a 50-cm-long cell of CCl_4 the energy conversion to Stokes was 10-20% in a collimated beam. Most of the Stokes intensity occurs within 3×10^{-3} rad of the forward direction, while the laser beam has a divergence of 0.5×10^{-3} rad. Most of the Stokes light occurs outside of filaments. Filaments do occur and range in diameter from 10 to 40 μ, somewhat larger than the observations of Brewer and Lee.[13] Anti-Stokes intensity is also observed, both in the forward direction and in a ring pattern.

Precise measurements of forward gain are not possible in an oscillator cell with filamentary structure and must await measurements in a short, picosecond-pulsed amplifier cell. There is no backward-traveling Stokes light. Backward Stokes gain was measured by reflecting 4% of the forward Stokes backward onto itself and looking for amplification. It could be concluded that the backward gain was less than e. If there is a constant-intensity background in the laser pulse train which would allow backward amplification, this intensity must be less than 0.1% of the peak pulse intensity. Otherwise, a backward gain would have been detectable. Our situation is therefore very different from that described in previous work.[2-4]

The efficient forward Stokes conversion made it possible to measure the duration of the Stokes pulses by the two-photon fluorescence technique. Figure 1(a) shows a typical laser and Stokes pulse train. The output Stokes light was separated from the laser light by filters and delayed with respect to the input laser pulses. The drop in Stokes gain toward the end of the pulse train may be caused by an unidentified, competing, slower nonlinear process. Figure 1(b) shows a comparison of the two-photon fluorescence pictures for the laser and Stokes pulses. Microdensitometer traces show that the Stokes pulse duration lies between 0.75 and 1 times the laser duration. The ratio 0.75 would be consistent with a Gaussian pulse shape[14] where $\Gamma_R t_p \approx 0.2$. With more careful measurements, it may be possible to set upper and lower limits on the rate of rise and fall of the laser pulses. Spectral analysis with a 1-m Jarrel-Ash spectrometer was consistent with the spectral width derived from the Fourier transform of the observed pulse dura-

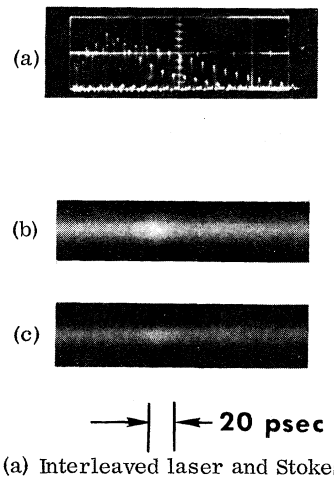

FIG. 1. (a) Interleaved laser and Stokes pulse trains. The Stokes was delayed and corresponds to the second pulse in each pair. The interpulse spacing is 7.5×10^{-9} sec. (b) Two-photon absorption fluorescence track produced by laser pulse train. (c) Two-photon absorption fluorescence track produced by Stokes pulse train.

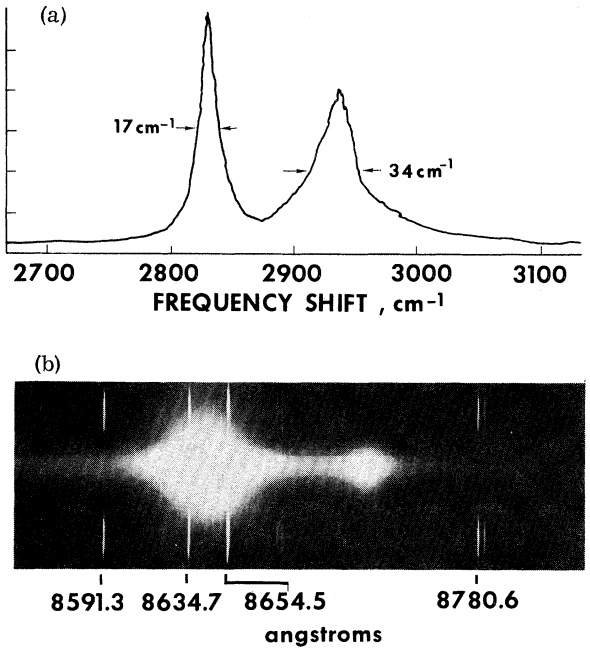

FIG. 2. (a) Spontaneous Raman spectrum of methanol. (b) Picosecond-pulse Raman emission of methanol. The stimulated line at 8726 Å is not seen with longer laser pulses.

tions. It is clear from these results that the stimulated Raman effect has been observed in the extreme transient regime.

The collimated ruby laser beam, consisting of picosecond pulses, has also produced efficient Raman emission in many other liquids. In some of these liquids, Q-switched lasers would reach threshold only with difficulty and only when focused. Examples are methanol, ethanol, acetic acid, dimethyl sulfoxide, and water. In the transient regime, the gain G_T depends only on the total Raman-scattering cross section, while the steady-state gain G_{ss} is inversely proportional to the linewidth. With picosecond pulse excitation, it was possible to observe two Stokes lines in methanol. The spontaneous Raman spectrum is shown in Fig. 2(a), taken with a Spex double monochromator. Line 1 with a Stokes shift of 2837 cm^{-1} has a width of 17 cm^{-1}, while line 2, corresponding to a two-phonon CH_3 breathing mode[15] at 2942 cm^{-1}, has a width of 34 cm^{-1}. The transient gain for line 2 should be larger because of the somewhat larger total cross section. It is likely that at the beginning of each pulse line 2 dominates, but then the intensity of line 1 increases during the peak and trailing edge of the pulse. The integrated intensity for line 1 was approximately 15 times larger than the stimulated emission for line 2, as seen in the microdensitometer scan of the stimulated Raman spectrogram shown in Fig. 2(b). This example of transient competition shows that it may be possible to observe many other broad Stokes lines, especially in gases, provided the higher threshold for transient gain can be reached. Another example of two different stimulated lines has very recently been given for the case of water.[16] Our experiments show that intense picosecond-pulse trains can be made available at many frequencies by using different Stokes shifts.

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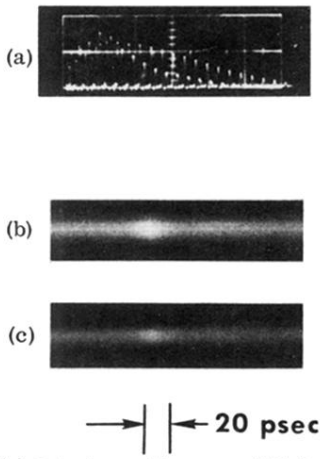

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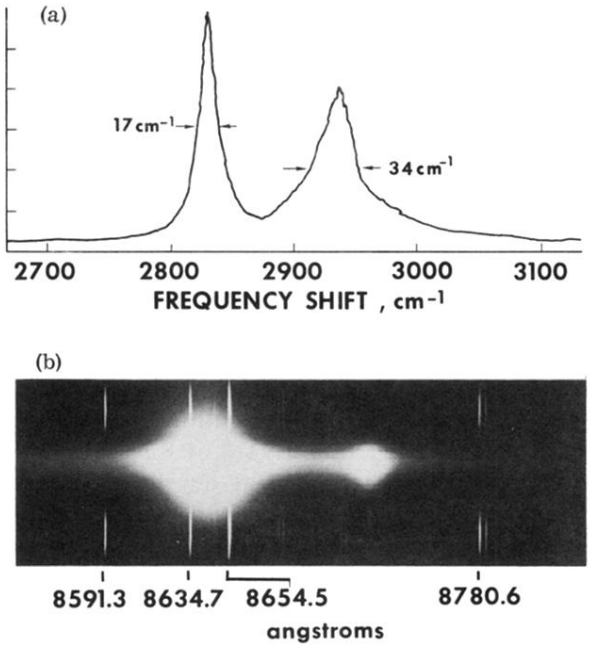

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