Multiorder Stokes Emission from Micrometer-Size Droplets

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The stimulated Raman scattering from a micrometer-size CCl_4 droplet exhibited up to fourteenth-order Stokes peaks and multiorder combination Stokes emission without detectable anti-Stokes emission. Such results are explained qualitatively by the morphology-dependent resonances of a droplet which acts as an optical cavity, providing high optical feedback and supporting enhanced internal fields at the various Stokes shifts.

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Recent reports of nonlinear optical interactions with pure or dyed liquid droplets having dimensions larger than the wavelength include lasing,[1] stimulated Raman scattering (SRS),[2] coherent anti-Stokes Raman scattering (CARS),[3] and coherent Raman mixing (CRM).[3] The micrometer-size droplet behaves like an optical cavity with morphology-dependent resonances (MDR's) at specific wavelengths, which for spherical-shaped droplets can be calculated by the Lorenz-Mie theory.[4] Since the fluorescence or Raman gain profile generally spans several MDR's, the internally generated inelastic radiation at these specific wavelengths experiences high internal reflection, i.e., the liquid-air interface provides large optical feedback which can significantly lower the threshold for lasing and SRS. Particularly noteworthy is the observation of SRS from a water droplet 35 μm in radius at an incident intensity level below the threshold for SRS from water in an 11-cm optical cell.[2] Concurrent with the large optical feedback at MDR's is the buildup of large internal field intensity which, from Lorenz-Mie calculations,[4] is known to be confined near the liquid-air interface.

The large internal field of the first Stokes emission which has achieved SRS threshold can, in principle, act as a pump and provide significant gain for subsequent SRS processes. SRS emissions consisting of multiorder Stokes and anti-Stokes peaks have been reported from meter-long optical fibers.[5–10]

We report the first observation, to our knowledge, of multiorder Stokes emissions for a single CCl_4 liquid droplet ~ 35 μm in radius. Stokes components up to the fourteenth order have been observed in the SRS spectra. The large internal Stokes field associated with one type of CCl_4 vibration could also provide enough Raman gain for SRS emission involving another type of CCl_4 vibration; i.e., multiorder combination Stokes emission could be generated. However, no anti-Stokes components were observed for the droplets. These multiorder SRS observations are qualitatively explained in terms of the large internal field at the nth Stokes wavelength and feedback at the $(n+1)$th Stokes wavelength.

The second-harmonic output (0.532 μm) from a *Q*-switched Nd-doped yttrium aluminum garnet laser (15-ns pulse duration) was focused by a 30-cm focal length spherical lens onto a CCl_4 droplet. A linear stream of droplets ~ 35 μm in radius was produced by a modified vibrating-orifice aerosol generator (TSI model 3050). Although highly distorted in shape near the orifice, the droplets 1.5 to 2 cm downstream are spherical, equally spaced, and nearly equal in radius.[11] Upon irradiation by one incident pulse with less than 1 mJ incident energy, corresponding to an intensity at the focal point of ~ 1 GW/cm^2, the SRS emission from a single droplet is detected by an optical multichannel analyzer (OMA). Two different spectrographs were used for the OMA, a low-dispersion 0.25-m spectrograph containing a 300-lines/mm grating and a higher-dispersion 0.5-m spectrograph containing a 1200-lines/mm grating. The detector was an intensified linear array or a vidicon with a silicon intensified target. In order to suppress further the strong elastic scattering from the droplet at the incident wavelength, color filters were placed in front of the OMA which was set to detect either the Stokes or anti-Stokes range.

Figure 1(a) shows the single-pulse SRS spectrum from one CCl_4 droplet detected by the low-dispersion OMA. The SRS emission from the droplets was nearly isotropic, while the elastic scattering was strongest in the forward direction. The detection angle for the SRS was selected to be 90° relative to the incident beam. Up to fourteenth-order Stokes emission of the ν_1 (459 cm^{-1}) vibrational mode was detected. No anti-Stokes emissions were detected from droplets. The wave-number shift of the nth-order Stokes peak was n times that of ν_1 and each Stokes peak is denoted as $[n00]$ in Fig. 1. Three conclusions can be drawn from this observation: (1) The observed SRS peaks are not higher-order overtones of ν_1, which should exhibit anharmonicity and therefore unequal wave-number shifts between the $(n+1)$th and nth Stokes emissions; (2) the observed multiorder SRS results from successive first-order SRS processes, in which the nth Stokes emission provided the gain for the $(n+1)$th Stokes wave; and (3) the fact that anti-Stokes emis-

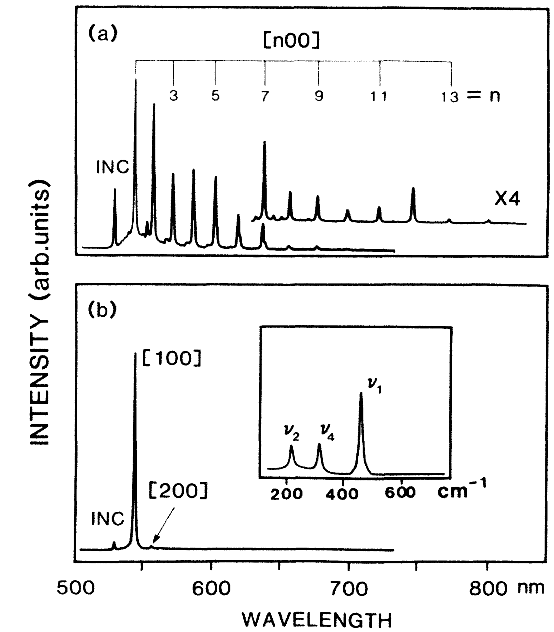

FIG. 1. Single-pulse SRS emissions from (a) a single CCl_4 droplet ~ 35 μm in radius and (b) CCl_4 in an 11-cm cell. Both spectra were detected by an OMA. The inset shows the spontaneous Raman scattering (RS) from CCl_4 in a 1-cm cell. [n00] denotes the nth-order Stokes emission of the ν_1 vibrational model.

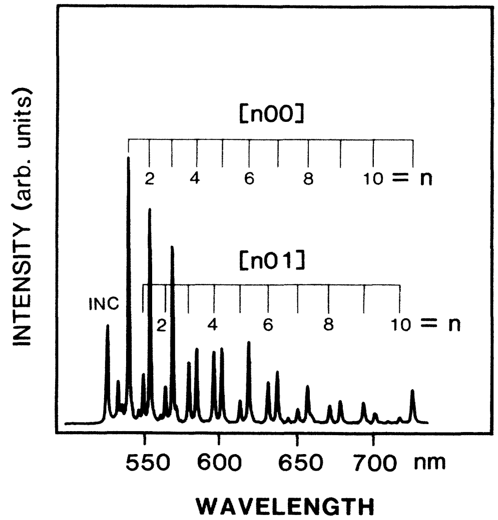

FIG. 2. Single-pulse SRS spectrum from a CCl_4 droplet. Two sets of multiorder Stokes peaks were detected by the OMA. The [n00] peaks have Raman shifts n times that of the ν_1 mode. The [n01] peaks have Raman shifts corresponding to the nth-order ν_1 mode and the first-order ν_4 mode.

sion was not observed implies that the wave-vector mismatching Δk needed for the four-wave mixing process cannot be fulfilled within the droplet. Nevertheless, even when $\Delta k \neq 0$, the four-wave mixing process can provide additional gain to the $(n+1)$th Stokes emission.[3]

While an overall Stokes intensity decrease occurs as the order becomes larger, the intensity of the $(n+1)$th order need not be smaller than that of the nth order. In Fig. 1(a), note in particular the intensity ratio of the third and fourth Stokes emissions and that of the eleventh and twelfth Stokes emissions. Such intensity ratios between successive Stokes orders of droplets differ from those of CCl_4 in an optical cell [see Fig. 1(b)].

Figure 1(b) also shows the SRS spectrum from CCl_4 contained in an 11-cm-long optical cell and irradiated by the same incident intensity. The SRS emission was detected in the forward direction and by the same OMA used in the droplet studies. The second Stokes intensity was at least 50 times weaker than the first Stokes intensity. Multiorder Stokes emission beyond $n=2$ was not detected. The inset of Fig. 1(b) shows the spontaneous Raman spectrum of CCl_4 in a 1-cm optical cell. The Raman shifts of the three strong CCl_4 peaks[12] are $\nu_1 = 459$ cm^{-1}, $\nu_2 = 218$ cm^{-1}, and $\nu_4 = 314$ cm^{-1}.

Some of the SRS spectra from CCl_4 droplets (see Fig. 2), detected under the same conditions, are more complicated than the SRS sepctrum shown in Fig. 1(a). The new set of peaks is red-shifted from the multiorder ν_1 peaks by 314 cm^{-1}, which corresponds to the ν_4 shift of CCl_4. We believe that the Raman gain with ν_4 shift is provided by the incident or nth-order ν_1 Stokes waves. The notation that we have selected to label such multiorder combination SRS peaks is [$n_1 n_2 n_4$], where n_1, n_2, and n_4 are the order numbers of the ν_1, ν_2, and ν_4 modes, respectively. For example, [300] is the third-order ν_1 Stokes emission pumped by the second-order ν_1 Stokes emission. Similarly, [301] has a total Stokes shift of a third-order ν_1 mode plus a first-order ν_4 mode. The [301] radiation is generated by the first-order SRS process of the ν_4 mode pumped by the [300] Stokes emission or of the ν_1 mode pumped by the [201] Stokes emission. This notation should not be construed as the overtone and combination modes resulting from vibrational anharmonicity of CCl_4

By use of the higher-resolution spectrograph with the OMA, the following SRS peaks in Fig. 3 can be resolved: (1) the set labeled [n00] for the nth-order ν_1 modes; (2) a new set labeled [n10] for the first-order SRS process of the ν_2 mode pumped by the [n00] Stokes emission or of the ν_1 mode pumped by [$(n-1)$10] Stokes emission; (3) a peak [001] for the first-order SRS of the ν_4 mode pumped by the incident beam; (4) the set labeled [n01] which was observed in Fig. 2; and (5) a new weak peak labeled [111] for the first-order SRS of the ν_4 mode pumped by [110]

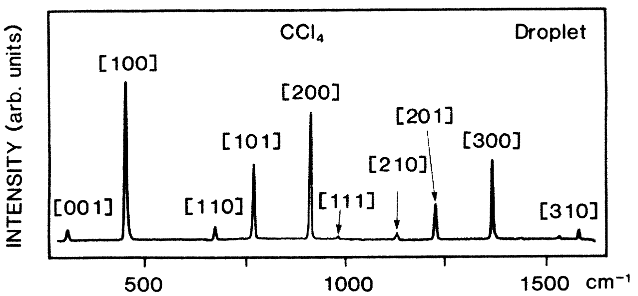

FIG. 3. Single-pulse SRS spectrum detected with higher-spectral-resolution OMA. Weaker multiorder combination Stokes peaks [110], [111], [210], and [310] involving the ν_2 mode of CCl_4 were resolved. (See text for explanation of $[n_1 n_2 n_4]$ notation.)

Stokes emission or of the ν_2 mode pumped by [101] Stokes emission.

Considering the fact that the droplet circumference is some 10^5 times smaller than the typical optical-fiber lengths,[6-10] it is remarkable that multiorder Stokes emission can be achieved from a single droplet. A qualitative comparison between the Raman gain provided by the incident plane wave and the internally generated Stokes wave can be made. The internal field distribution for the incident wave can be calculated by the Lorenz-Mie theory. For the off-MDR case, it is known that the internal field is localized and enhanced at two spots near the front and back areas of the interface and along the diameter which is parallel to the incident beam direction.[13,14] For the on-MDR case, the intensity at these two spots is even more enhanced and there is an increase in the intensity within a region near the droplet interface.[13,14] For both cases, the Raman gain is localized mainly at two spots. Hence the pumping length is only a fraction of the droplet radius.[13,14]

Magnified photographs of SRS droplets clearly confirm that the SRS radiation is uniformly confined near the circumference. Consequently, once SRS oscillation has been achieved, the pumping length of the Stokes field is considerably longer than that of the incident field, i.e., the interaction length is of the order of $2\pi a$ for the Stokes wave versus a fraction of a for the incident wave.

The multiorder SRS emission from droplets can be qualitatively explained by our envisioning the micrometer-size droplets as optical cavities. The MDR's of the droplet at wavelengths corresponding to the various Stokes shifts provide high optical feedback and hence lower the thresholds for multiorder SRS emission. Furthermore, the MDR's enhance the internal Stokes fields to such an extent that these SRS fields become the pump for successive first-order SRS processes.

The probability of the coincidence of the multiorder Stokes and incident laser wavelengths with the MDR's of micrometer-size spherical droplets needs to be examined more quantitatively by the Lorenz-Mie theory.[4] We have shown experimentally[1-3] that for droplets ~ 35 μm in radius the MDR's having the same mode order but different mode number are separated by ~ 50 cm^{-1}. However, the density of MDR's within a wavelength interval greatly increases when different mode orders are considered. MDR's as close together as 2–20 cm^{-1} are possible for droplets having ~ 35-μm radius or size parameters in the 200–500 range. On the basis of our present experimental results, it is somewhat surprising that one or more MDR's always exist within the CCl_4 Stokes bandwidth (~ 10 cm^{-1}) at all the various multiorder SRS wavelengths. However, the coincidence of our incident laser wavelength (0.532 μm with 0.5 cm^{-1} linewidth) with MDR's requires deliberate adjustment of the droplet radius by a change of the orifice driving frequency. For the results reported here, the droplet radius was not tuned to a MDR.

The detected intensity distribution of the multiorder Stokes emission is dependent on several factors: (1) the internal pumping length of the incident or preceding-order Stokes wave; (2) the relative spectral position of the MDR's within the Stokes gain profile; and (3) the MDR mode order and mode number, which affect the optical feedback and hence the amount of Stokes radiation leakage from the droplet. Thus, it is possible that the intensity of the $(n+1)$th-order Stokes peak can be greater than that of the nth-order Stokes peaks, since the OMA detects only the radiated SRS emission and not the internal field strength at each Stokes order.

The optical feedback provided by the droplet at specific MDR's for lasing and SRS processes has previously been reported.[1-3] Multiorder SRS was not examined in our earlier investigations of the SRS of ethanol and water droplets[2,3] because the second- and higher-order SRS from ethanol (with Raman shift of ~ 2900 cm^{-1}) and from water (with Raman shift of ~ 3400 cm^{-1}) exceeded the spectral coverage of our high-dispersion OMA. In this experiment, we used a low-dispersion OMA and CCl_4 which has a small Raman shift (~ 460 cm^{-1}). All fourteenth-order Stokes peaks were therefore within the present OMA spectral coverage. Since the separation between MDR's (with different mode numbers but having the same mode order) is ~ 50 cm^{-1}, the SRS spectra from ethanol and water droplets were noted to consist of a series of equally spaced peaks (~ 50 cm^{-1} apart) within the broad Raman linewidths of ethanol (~ 200 cm^{-1} wide) and of water (~ 450 cm^{-1} wide).[2,3] However, in the case of CCl_4 droplets which have a much narrower Raman linewidth (~ 10 cm^{-1} wide), only one

MDR can exist within the Raman gain profile. We confirmed this by using a high-dispersion OMA and detected only one SRS peak at each of the multiorder Stokes wavelengths.

In conclusion, the SRS spectra of a micrometer-size liquid droplet are remarkably different from those of the same liquid in an 11-cm-long optical cell. The intense multiorder Stokes emission and the undetected anti-Stokes emission from a droplet are analogous to that from meter-long single-mode fibers. The droplet can be envisioned as an optical cavity which enhances the internal fields at the incident and Stokes wavelengths and also provides optical feedback at various Stokes wavelengths. The normal single-pass plane-wave growth equations for the SRS and four-wave mixing processes in an extended medium need to be modified into multipass spherical-wave nonlinear equations more commensurate with the droplet geometry.

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