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Double-resonance stimulated Raman scattering from optically levitated glycerol droplets

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Experimental confirmation of stimulated Raman scattering (SRS) in micrometer-sized droplets supported simultaneously by resonances at the incident (input) laser wavelength and at the emitted (output) SRS wavelength is provided. Identified mode orders of contributing input resonances increase with droplet radii over the size range investigated (~5.4–7.4-μm radius). Measured SRS spectra reveal that the mode order of the input and output resonances coincide in 90% of the cases studied.

Stimulated Raman scattering (SRS) from micrometer-sized transparent liquid droplets irradiated by intense pulsed lasers exhibit spectral,[1-3] temporal,[3-6] and spatial[7,8] characteristics dramatically different from corresponding SRS in bulk liquid. These differences are a consequence of the shape of the droplet-air interface, which provide for electromagnetic resonances,[9] sometimes called structure resonances or morphology-dependent resonances (MDR's) within the droplet. SRS emission in droplets is supported by MDR's within the spontaneous Raman bandwidth of the liquid.

Previous measurements of SRS (Refs. 1–8) have been made for droplets satisfying a resonance condition only at the emitted radiation (output) wavelength, since with the lasers and droplet generation methods used, there was no practical way to tune the incident laser wavelength or droplet size to an input resonance condition. In this paper, we report SRS observations for a double-resonance condition, wherein the considered droplet is in resonance at both incident (input) and emitted (output) wavelengths. SRS emissions for the double-resonance condition occur for incident laser intensities (~0.2 GW/cm^2) that are lower than for single (output) resonance conditions.[7] We further identify, at least tentatively, the resonance mode orders and numbers that support double resonance SRS for ~5–7-μm radius glycerol droplets irradiated by 0.532-μm wavelength radiation from a pulsed Nd:yttrium aluminum garnet (YAG) laser. Our observations suggest that both input and output resonances usually have the same mode order. Further, resonances that support SRS are of lower order than those observed in elastic scattering. Double-resonance emissions have been postulated in fluorescence and Raman spectra,[10,11] and have been observed in fluorescence emission spectra of fibers[12] and fluorescence excitation spectra of droplets.[13] However, to our knowledge, no observation of double-resonance phenomena of nonlinear optical processes in droplets, such as SRS, have been reported before.

We achieve double-resonance conditions using optical levitation[14,15] (Fig. 1). Glycerol droplets trapped in a focused argon-ion laser beam (not shown) slowly evaporate at a rate of ~0.4 nm/sec, allowing droplets to pass through resonance conditions at the incident Nd:YAG wavelength. A position-sensing, split photodiode feedback detector[16] and a Pockel's cell (not shown in Fig. 1) coupled to the argon-laser output permit continuous recorded adjustment of laser power[17] needed to keep the droplet stationary. In addition, scattered argon-laser light is recorded using a photodiode. Monitoring of levitating laser power[17,18] and elastic scattering[19] from the droplet permit determination of drop size to within 0.1% of its radius.

Quasiperiodic bursts of SRS (arising from the 2855-cm^{-1} shift C–H stretching mode) are observed from the droplet only when the combination of droplet size and Nd:YAG wavelength satisfy an input resonance condition. This differs from previous studies where input resonances could not reliably be achieved because of lack of precise

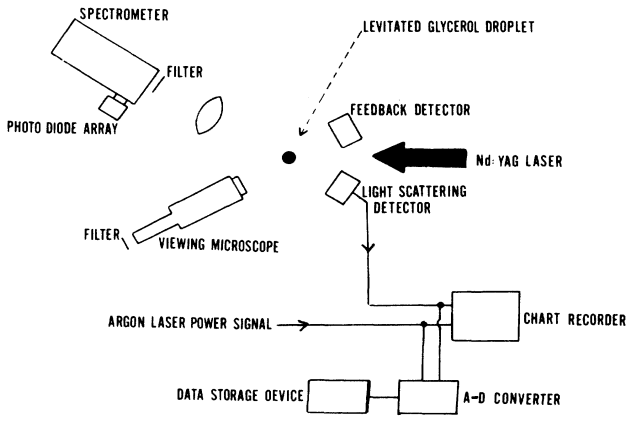

FIG. 1. Schematic top view of experimental arrangement. The levitating argon-laser beam directed normally outward from the plane of the paper and the six-sided glass cell enclosing the droplet are not shown. The feedback-stabilized levitated droplet is positioned at the focus of the Nd:YAG laser. Simultaneous monitoring of argon elastic (light scattering detector), SRS (spectrometer), and viewing of droplet (microscope) are possible using this arrangement.

control of drop size. Spectral content of SRS emission was measured by imaging the droplet onto a spectrometer equipped with a one-dimensional photodiode array detector.

Quasiperiodic bursts of SRS emission, which occur at times when resonance conditions are satisfied, are seen as bright, full, or partial red rings on the droplet rim.[7] The times of occurrence of SRS can be recorded to an accuracy of 1 sec. By comparing levitating laser power with theoretical radiation pressure calculations,[18] droplet radius and hence size parameter ($X_i = 2\pi r_i/\lambda$, where r_i is the radius and λ is the incident Nd:YAG wavelength) evolution can be precisely determined. A comparison of measured X_i with resonant size parameters calculated from Mie theory[20] allow an identification of input resonances. Known droplet radii together with measured SRS wavelengths allow identification of the corresponding output resonances.

Uncertainties in levitating and pump-laser linewidths and in evaporation rates produce an accuracy of < 1 nm in estimating droplet radii. However, our observations exhibit larger deviations; we arbitrarily impose an upper limit of ± 5 nm for acceptable matches between measured and theoretical radii. The larger errors may be partly due to small deviations in refractive index from the handbook values used in the calculations.

Figures 2(a) and 2(c) show chart recorder traces for a typical evaporating droplet; Fig. 2(a) shows the monitored laser power and 2(c) the scattered argon-laser light from the droplet. Figure 2(b) is the computed radiation pressure[18] (Q_{pr}) where TE_n^1 (TM_n^1) designate a transverse-electric (magnetic) resonance with mode number n and mode order 1.[9] Figure 2(d) is the computed[20] scattering efficiency (Q_{SCA}) appropriately averaged over angle and polarization to account for the finite acceptance angle of the detector and its orientation. Comparison of Figs. 2(a) and 2(c) with 2(b) and 2(d) enable unique determination of droplet size shown on the abscissa. The vertical arrows along the abscissa correspond to radii at which SRS is observed. Figure 2(e) shows the computed Q_{pr} for the same size but at the incident Nd:YAG wavelength, and here it appears that the occurrences of SRS correspond to fourth-order input resonances. However, an analysis of the measurement errors reveals that in some cases both third- and fourth-order input resonances may contribute to SRS. We note that third-order resonances do not appear in the elastic scattering [Fig. 2(a)].

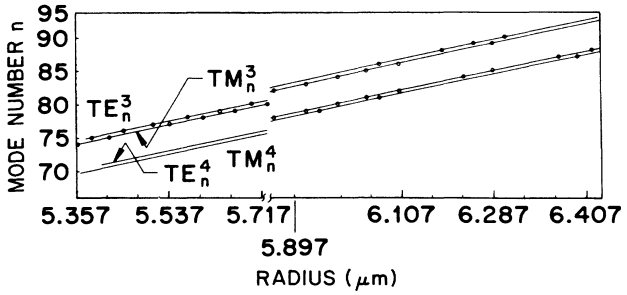

FIG. 3. Measured (points) and Mie theory predicted (straight lines) variation of droplet radius with mode number (n) for TE and TM third- and fourth-order resonances.

Figure 3 identifies input resonances for droplet radii ranging from ~ 5.4 to 6.4 μm. The straight lines represent theoretically predicted variations of radius versus mode number for the third- and fourth-order transverse electric and transverse magnetic resonances. The points indicate radii at which SRS is observed. This plot reveals that for droplet radii (5.4–5.7 μm) only third-order input resonances occur, whereas for radii (5.8–6.4 μm) both third- and/or fourth-order resonances are seen, and for ra-

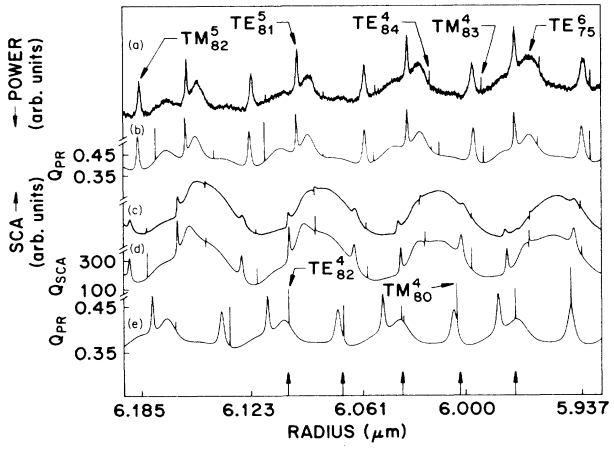

FIG. 2. (a) Measured argon-laser power (radiation pressure) and (c) measured scattered argon-laser light (SCA). (b),(d) Calculated radiation pressure (Q_{pr}) and scattering efficiency (Q_{SCA}) at the argon-laser wavelength (514.5 nm). (e) Calculated Q_{pr} for Nd:YAG laser wavelength (532.0 nm). Vertical arrows show the radii at which double-resonance SRS is observed.

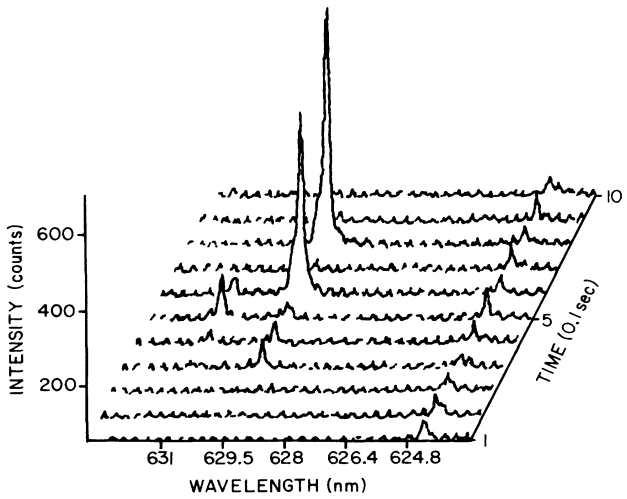

FIG. 4. A burst of SRS spectra for an Nd:YAG laser irradiated evaporating glycerol droplet. The 624.3-nm peak from the argon-laser plasma line serves as a fiducial. Two SRS peaks, 629.4 and 630.9 nm, occur over a sequence of laser shots.

TABLE I. Identification of input and output resonances for double-resonance SRS.

Observed radius (μm)	Input resonance	% error	Q_0	SRS wavelength (μm)	Output resonance	% error	Q_0
5.5131	TE^{3}_{77}	0.1	3.3×10^{6}	0.6284	TM^{3}_{63}	0.08	4.6×10^{4}
5.6038	TM^{3}_{78}	0.03	2.5×10^{6}	0.6306	TM^{3}_{64}	0.09	6.0×10^{4}
5.9190	TM^{3}_{83}	0.07	1.1×10^{7}	0.6285	TE^{3}_{69}	0.02	3.7×10^{5}
	TE^{4}_{79}	0.09	1.3×10^{5}	0.6288			
6.1067	TE^{4}_{82}	0.07	2.7×10^{5}	0.6302	TE^{4}_{67}	0.02	9.8×10^{3}
6.2335	TE^{4}_{84}	0.09	4.3×10^{5}	0.6282	TE^{4}_{69}	0.09	1.5×10^{4}
6.2532	TE^{3}_{89}	0.09	3.3×10^{6}	0.6284	TM^{3}_{73}	0.08	4.6×10^{4}
	TM^{4}_{84}	0.10	2.6×10^{5}	0.6303	TE^{4}_{69}	0.10	1.5×10^{4}
6.8281	TM^{4}_{93}	0.08	2.5×10^{6}	0.6319	TM^{4}_{76}	0.20	3.7×10^{4}
6.8890	TM^{4}_{94}	0.06	3.3×10^{6}	0.6285	TM^{4}_{77}	0.14	4.6×10^{4}
7.1957	TM^{4}_{99}	0.00	1.2×10^{7}	0.6309	TM^{4}_{81}	0.07	1.2×10^{5}
	TE^{5}_{95}	0.08	2.2×10^{5}	0.6294	TM^{5}_{77}	0.14	3.3×10^{3}
7.2771	TM^{5}_{96}	0.09	1.6×10^{5}	0.6340	TE^{5}_{78}	0.11	7.3×10^{3}
7.2917	TE^{4}_{101}	0.10	3.4×10^{7}	0.6312	TM^{4}_{82}	0.18	1.5×10^{5}

dii beyond $\sim$6.3 μm a transition to fourth-order resonances occurs. A region ($\sim$6.5–7.4 μm) (not shown in Fig. 3) contains both fourth- and fifth-order input resonances.

We note that in the region where only third-order input resonances support SRS the observed elastic scattering exhibits fourth- and fifth-order resonances. In the region where fourth-order elastic resonances are suppressed, $\sim$6-μm [see Fig. 2(a)] SRS input resonances are a mix of third and fourth orders. From $\sim$6.3–7.2 μm, where fifth- and sixth-order elastic resonances are observed, contributing SRS input resonances are fourth and fifth order. Similarly when fifth-order elastic resonances are suppressed ($\sim$7.14–7.29 μm) we still observe fourth- and fifth-order input resonances.

Previous observations of fluorescence emission spectra from fibers[12] show a third-order fluorescence input resonance while fourth- and fifth-order resonances appear in elastic scattering. These observations are similar to ours in that the input resonance mode order is one or two lower than the lowest mode order observed in elastic scattering.

Spectra for only 40% of observed SRS events are spectrally recorded due to our primitive method of manually triggering the photodiode array upon visual observation of the initial SRS burst. Figure 4 shows one such burst of SRS. The peak at 624.30 nm is an argon-laser plasma line reflected into the spectrometer by the droplet; its continuous presence serves as a droplet fiducial. Two SRS peaks are observed, at 630.9 and 629.4 nm. The spacing between these peaks[18] suggests different mode orders, contrary to previous output resonance SRS spectra[1,3] where the occurrence of only one mode order was inferred from the spacing of the peaks. In this case two input resonances TM^{4}_{99} and TE^{5}_{95} are consistent with the measured droplet radius (7.1957 μm). Computation of X_{SRS} reveals that the peak at 630.9 nm corresponds to a TM^{4}_{81} output resonance, and the 629.4-nm peak corresponds to a TM^{5}_{77} resonance. This suggests that the droplet can support two input resonances simultaneously, each contributing to a corresponding mode-order output resonance. Furthermore the temporal duration of the peaks provides an estimate of ΔX_i of the input resonances. Estimated ΔX_i's of 9.6×10^{-4} and 2.6×10^{-3} are obtained for the fourth- and fifth-order input resonances, compared to theoretical (zero absorption) linewidths (ΔX_i's) of 7.0×10^{-6} and 3.8×10^{-4}, suggesting that theoretical bare Q's are not realized, presumably due to droplet imperfections[21] and nonzero absorption.

A summary of input and output resonances deduced from measured SRS spectra is provided in Table I. In $>90\%$ of the cases, the mode orders of input and output resonances match. This suggests that spatial overlap of the internal electromagnetic field distributions[22] for input and SRS, as dictated by mode-order matching, is an important criterion for SRS emission. Table I also gives percentage errors and bare Q values for the resonances.

Delays of 5–7 nsec in the initiation of output resonance SRS have been reported.[3,5,6] For input resonance conditions, measured initiation delays vary over a wider range of <2–14 nsec.

In conclusion we have confirmed double-resonance SRS from levitated droplets. The identification of the input resonances reveals that the mode order increases with droplet size. Mode orders of input and output resonances match with few exceptions. Future investigations are planned to determine laser-energy thresholds and the temporal behavior of input-resonance SRS.

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