Two-photon-pumped lasing in microdroplets

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Lasing is observed in laser-dye-doped ethanol droplets after two-photon absorption by the dye molecules. The two-photon-pumped lasing emission by the droplets is at a higher frequency than the input laser. Competitive nonlinear-optical effects that occur at high input-laser intensity are discussed.

Various third-order nonlinear-optical effects have been observed in micrometer-size droplets. The front surface of a droplet acts as a thick lens to enhance the internal intensity of the input-laser radiation, and the spherical shape of the droplet acts as an optical cavity to provide feedback at specific wavelengths corresponding to morphology-dependent resonances (MDR's). These two effects together greatly reduce the input-laser intensity required to observe various nonlinear-optical effects.

Lasing can occur in droplets of laser-dye solutions that are pumped by either a cw or a pulsed laser. It has been shown that the lasing threshold is further decreased because of the gain enhancement through cavity QED effects. In all the previous observations of lasing in microdroplets, the upper lasing transition is pumped by one-photon absorption (OPA) to the first excited band of the dye molecule. Upconversion of semiconductor diode lasers has been studied recently for their potential applicability as an all-solid-state source with a wavelength range from the ultraviolet to the red.

In this Letter we report the observation of lasing when the dye molecules are pumped by two-photon absorption (TPA) in various Coumarin and Rhodamine 6G (R6G) dyes. We compare the characteristics of TPA-induced lasing by pumping to the first or the second excited bands of R6G, and we discuss some of the potential problems encountered at the high pump-laser intensity required for two-photon-pumped lasing.

In our experiments, a modified Berglund–Liu vibrating-orifice droplet generator is used to produce a stream of monodispersed ethanol droplets (with radius \( a \approx 50 \mu m \)) containing fluorescent dyes of various concentrations. The various lasers used to pump the droplets by TPA are synchronously triggered by the frequency generator that drives the droplet generator orifice at \( f = 50 \) kHz. The TPA-induced lasing emission from the dye-doped ethanol droplets is collected at 90° to the incident laser beam and is imaged onto the entrance slit of a spectrograph (Spex Singlemate Model 1870). At the exit plane of the spectrograph, a CCD detector is used for the Coumarin-doped droplet measurements, whereas a red-enhanced intensified linear photodiode array detector is used for the R6G-doped droplet measurements.

Two-photon pumping of Coumarin-doped ethanol droplets is studied with the Stokes-shifted emission (at 629.6 nm) of a methane-gas Raman cell, which is pumped by the second harmonic (532 nm) of a Q-switched Nd:YAG laser. To our knowledge, there are no detailed TPA studies in Coumarin dyes. TPA of the 629.6-nm photons causes an electronic transition to the tail of the first excited electronic band that is usually reached by OPA. Figure 1 shows a lasing spectrum (integrated over 100 laser shots) of \( 10^{-2} \) M Coumarin 460 droplets that are pumped by input radiation at 629.6 nm and with an intensity of 1 GW/cm². The lasing emission in the 455–460-nm region exhibits a distinct set of MDR's (with nearly equal wavelength spacing). Another set of MDR's (with weaker intensity), corresponding to MDR's of a different mode order, can occasionally be observed in the Coumarin 460 lasing spectrum. The high dye concentration used can cause dimer formation and subsequent fluorescence quenching. However, when
Two-photon pumping of electrons into the $S_1$ band of R6G dissolved in ethanol [see Fig. 2(c)] is achieved with a Q-switched multimode Nd:YAG laser with emission wavelength $\lambda_m = 1064$ nm. Figure 3 shows the TPA-induced emission spectrum from ethanol droplets (with $\alpha = 50$ $\mu$m) containing $2.5 \times 10^{-4}$ M R6G at several input-laser intensities ($I_{in}$). Because the laser-induced breakdown (LIB) threshold is higher in the near infrared than in the visible, higher input-laser intensities at 1064 nm can be used to irradiate the droplets without total LIB-related droplet destruction. At $I_{in} = 5$ GW/cm², only fluorescence is detected. At $I_{in} = 9$ GW/cm², the MDR-related peaks and a sharp increase in the output intensity are indicative of the onset of lasing. Even though the plasma continuum is not so evident, the LIB-generated plasma can introduce both absorption and scattering losses.

With R6G in an optical cell, lasing from the $S_1$ band has been observed with two-photon excitation into the $S_2$ band by the radiation from a Q-switched ruby laser (at 694.3 nm). Although the TPA is to the $S_2$ band, rapid nonradiative decay occurs, and the radiative transition is from the $S_1$ band. In our study, an excimer-pumped dye laser (operating at 697 nm with Exciton dye LDS 698) is used to study two-photon pumping into the $S_2$ band of R6G in ethanol droplets [see Fig. 2(d)]. Figure 4 shows the lasing spectrum of $10^{-3}$ M R6G-doped ethanol droplets ($\alpha = 50$ $\mu$m) that are illuminated at $\lambda_m = 697$ nm with $I_{in} = 1$ GW/cm². This input intensity is just below the LIB threshold for $\lambda_m = 697$ nm. The lasing spectrum in Fig. 4 contains a set of well-defined MDR-related peaks. Because of the increase in absorption due to the higher dye concentration used (compared with Fig. 3), the lasing spectrum is red shifted. The R6G emission signal is weak, and the spectrum shown in Fig. 4 is obtained with an integration of 170 laser shots with a laser repetition rate of 15 Hz. The MDR-related peaks in the lasing spectrum can be broadened by the variation in the droplet size and possible LIB-generated plasma. During the experiment, the droplets were viewed through a microscope as they were irradiated by the laser. We observed bright arcs around the rim of the droplet. These arcs are a characteristic feature of lasing droplets. When the R6G concentration is the dye concentration is reduced to below $10^{-2}$ M (e.g., $10^{-3}$ M), lasing cannot be detected.

There have been extensive TPA studies of R6G in bulk solutions. The OPA molar absorption coefficient into the $S_1$ band is approximately $10^9$ M⁻¹ cm⁻¹. A R6G concentration of $10^{-4}$ to $10^{-3}$ M, with an absorption coefficient $\alpha = 1$–$10$ cm⁻¹, provides enough gain for lasing with OPA pumping. The OPA spectrum of R6G also has a weaker absorption peak at 350 nm that is associated with the second-excited singlet band [labeled as $S_2$ in Fig. 2(a)]. The OPA molar absorption coefficient into the $S_2$ band is approximately $10^4$ M⁻¹ cm⁻¹. After excitation into the $S_2$ band, the electrons rapidly decay nonradiatively to the $S_1$ band. Radiative decay from the $S_1$ band to the ground state has nearly unity quantum efficiency. TPA from the ground state into the $S_1$ or $S_2$ band [see Figs. 2(c) and 2(d)] has also been well studied, and it has been found that the TPA coefficient of the $S_2$ band is 30 times that of the $S_1$ band.
further reduced to $10^{-4}$ M, no lasing spectrum can be detected at $I_{in}$ below the LIB threshold of the droplets. Even though the droplet morphology provides increased internal input-laser intensity, optical feedback, and cavity QED gain enhancement, the input-laser intensity needed to invert the electron population with TPA pumping can cause other competing nonlinear-optical effects. Stimulated Raman scattering (SRS) is a phase-matched third-order nonlinear-optical process that is readily observable in ethanol droplets. The Raman gain coefficient for ethanol at 694.3 nm is $g = 1.3$ cm/GW and is larger than the degenerate TPA absorption coefficient $\beta = 0.0075$ cm/GW (for $10^{-3}$ M R6G in ethanol) that involves two input-laser photons at 694.3 nm. In the case of one-photon-pumped lasing excitation of $10^{-4}$ M R6G in ethanol droplets with $I_{in} = 0.1$ GW/cm$^2$, the Raman gain $G = gl_{in}$ (at the internal high-intensity spot) is small and, consequently, the SRS signal is much weaker than the lasing signal. However, in the case of two-photon-pumped lasing excitation, which requires that $I_{in} \approx 1$ GW/cm$^2$, the Raman gain (at the internal high-intensity spot) is large. With a red-enhanced intensified linear array, we observed that the SRS output from ethanol at 875 nm (2928 cm$^{-1}$, Stokes-shifted from $\lambda_{in} = 697$ nm) is 2 to 3 orders of magnitude larger than the lasing signal. At $I_{in} = 1$ GW/cm$^2$, because the Raman gain is larger than the lasing gain that is induced by TPA, the growth of SRS occurs sooner than the growth of the lasing. Consequently the intense SRS can deplete the input-laser intensity. When $\lambda_{in} = 1064$ nm, competition from SRS is not so severe, because the O–H vibrational overtones of water and ethanol molecules absorb the first-order Stokes SRS and prevent the growth of SRS further in the near infrared. Therefore the TPA-induced lasing signal can be observed with a concentration of only $2.5 \times 10^{-4}$ M R6G at $\lambda_{in} = 1064$ nm [see Fig. 2(c), although the TPA coefficient of the $S_1$ band is smaller than that of the $S_2$ band since there is no SRS competition. As a confirmation, we were not able to observe third-harmonic generation or third-order sum-frequency generation involving the SRS of ethanol and water droplets with $\lambda_{in} = 1064$ nm, which indicates that SRS is either too weak or not generated at all in these droplets. However, third-harmonic generation and third-order sum-frequency generation were readily observed in D$_2$O droplets because the O–D vibrational overtones are further in the near infrared and the stimulated Raman scattering intensity can thus be intense.

There can be other deteriorative factors working against the buildup of lasing intensity at $\approx 610$ nm in R6G-doped ethanol droplets. The first factor is stimulated emission by the input laser at 697 nm. The R6G fluorescence spectrum has a long tail that extends beyond 700 nm, corresponding to transitions from the bottom of the $S_1$ band to the higher vibrational levels of the ground state. Previous research has shown that the input-laser beam at 697 nm can induce stimulated emission from the $S_1$ band and thus deplete the upper lasing level. Since lasing with R6G–ethanol droplets with TPA of 697-nm photons is observed, this loss by stimulated emission of the input laser is not too deteriorative. The second factor is excited-state absorption. Excited-state absorption induced by input-laser photons at 697 nm or fluorescent photons at 610 nm can also occur and can potentially prevent the lasing at 610 nm by depleting the upper lasing level. Since we are able to observe lasing, excited-state absorption is not prominent. The third factor, nondegenerate TPA involving an input lasing photon at 697 nm and a fluorescent photon at 610 nm, can also prevent lasing at 610 nm from building up. However, such nondegenerate TPA is not within any electronic bands of R6G and therefore not important in our experiment.

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