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Lasing Spectral Blue Shifts of Fluorescent Saturable Absorbing Dye in Microdroplets

I-Ju Yu and Wen-Feng Hsieh*
Institute of Electra-Optical Engineering, National Chiao Tung University,
Hsin Chu, Taiwan 300, R.O. C.

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We report blue shifts of emission spectra of microdroplet lasers containing fluorescent saturable absorbing dye as compared with those of conventional dye lasers. The results cannot be simply explained by matching the lasing peaks to the minima of threshold condition without taking into account cavity enhancement. We find that the microdroplet lasers have quality factors of 10^4 with a *3X* cavity enhancement and their lasing peaks at fixed concentration are independent of the incident pump power.

PACS. 42.60.Da – Resonators, cavities, amplifiers, arrays, and rings.

I. Introduction

Micrometer-sized liquid droplets are extremely high quality factor optical cavities. The quality factors or Q values of confined whisper-gallery or morphology dependent resonance (MDR) [1] modes are as high as 10^6-10^8 and can be obtained from photon lifetime measurements [2-4]. Due to their high Q, the observed lasing spectra of microdroplets are red shifted as compared with the conventional dye lasers [3-5]. This can be realized by the threshold condition [6,7]

$$\gamma(\lambda) = \frac{n_2(\lambda)}{n_T} = \frac{\dfrac{2\pi m}{n_T\lambda Q} + \dfrac{\alpha_{abs}}{n_T} + \sigma_a(\lambda)}{\sigma_a(\lambda) + \sigma_e(\lambda)}, \tag{1}$$

where n_2 is the population density of the upper state of a four-level laser system, n_T the total dye concentration, m the relative refractive index of the liquid, Q the quality factor of the corresponding MDR lasing, α_{abs} is the absorption loss of the absorber, σ_a and σ_e are the stimulated absorption and emission cross sections, respectively. The larger the quality factor and the higher dye concentration is the lower the threshold. The lasing peak tends to locate at the lowest threshold spectral region of the gain curve where there is less absorption overlap. Thus, in general, the lasing peaks of microdroplets are located at longer wavelengths than those of the conventional dye lasers (Q $\approx 10^4 - 10^5$) with the same concentration. In addition, the effects of both internal scattering and absorption on elastic scattering and lasing MDR spectra [8-11] indicate that higher-Q MDR's gradually disappear as absorption or scattering increases. Thus, a blue shift of lasing spectra in microdroplets when an absorber is added and a red shift in the lasing spectra as the fluorescence dye concentration is increased [6].

In this paper we report blue shifts of emission spectra from microdroplets containing fluorescence dye which is also a saturable absorbing dye as compared with the conventional lasers with the same concentration. The spectral shifts can not be explained by matching the experimental lasing peaks to the minima of threshold condition without taking into account cavity enhancement effects which have been observed in our previous works, that 100X spontaneous emission enhancement for 35 μm radius microdroplet lasers [4] and 3X Raman cross section enhancement of the same size droplets [12]. We find that the quality factors of the fluorescent saturable absorbing microdroplet lasers are about 4 x 10^4 for concentration of 10^{-5} to 10^{-3} M and a 3X enhancement of emission cross sections is required to match the experimental results to the simulated results of threshold equation. Furthermore, extra higher Q MDR modes are observed with low concentration droplets (10^{-5} M) and the lasing peaks from a fixed concentration droplets are independent of the incident pump power.

II. Experimental

We first dissolved the fluorescent saturable absorbing dye IR-125 in ethanol (IR-125/EtOH) and measured its absorption and fluorescence spectra by using an 1 mm thick optical cell. In order to prevent the reabsorption of the radiation emitted from the excited state dye molecules by the ambient ground state molecules while it passes through, one uses 10^{-7} M concentration in the fluorescence measurement. A homemade cw Ti:sapphire laser pumped by all-line Argon ion laser to generate wavelength 793 nm radiation was used as the excitation source. Whereas, a linear stream of monodispersed IR-125/EtOH droplets with 35 μm radius is produced from a modified Berglund-Liu vibrating orifice droplet generator. The lasing droplets pumped by cw Ti:sapphire laser is imaged onto the entrance slit of a spectrometer equiped with 1200 grooves/mm grating, a photomultiplier, and a x-y recorder.

III. Results and discussion

Fig. 1 shows three lasing spectra of IR-125/EtOH droplets of various concentrations. Besides the broad spectral lines located at 793 nm are the elastic scattering of the pump laser, we found that (1) The lasing peaks are located at 809, 824, and 832 nm for concentration of 10^{-5},10^{-4}, and 10^{-3} M, respectively; (2) The spectra become narrawer and blue-shifted as the concentration decreases and all the spectra are blue shifted as compared with the conventional dye lasers of the same concentrations in which the wavelengths of lasing maxima are longer than 845 nm; (3) More spectral feature from low concentration lasing droplets indicates that the higher Q MDR modes may appear when the dye concentration is as low as 10^{-5} M; (4) The blue shifted lasing spectra have even extended to the region where the wavelengths are shorter than that of the excitation laser.

The observed broad lasing spectra rather than sharp ones are resulting from the spectra are taken by integrated more than 100 droplets as well as spectrally homogeneous but spatially inhomogeneous nature of the droplet lasers with many MDR's [6]. By expanding the emission spectra of 10^{-3} and 10^{-5} M, we plotted the spectra with wavelength range from 840 to 860 nm in Fig. 2. We found that besides the same order (the same Q values)

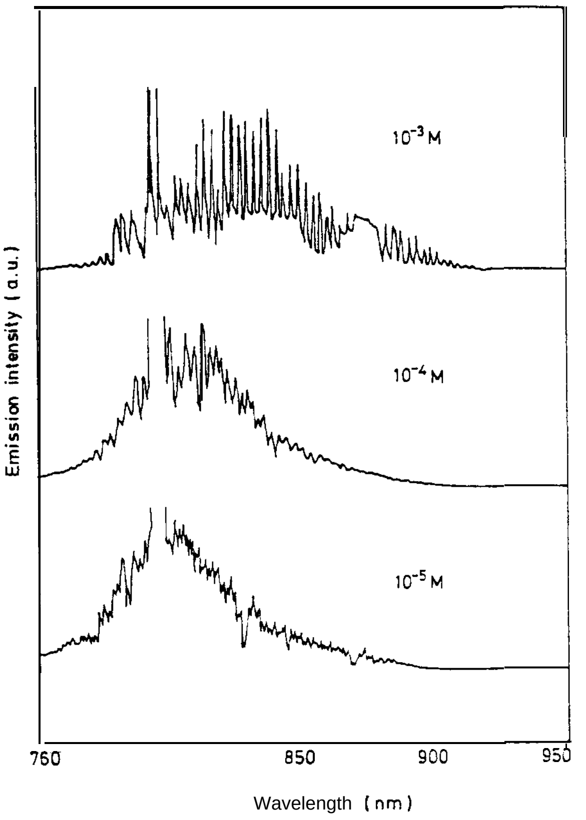

FIG. 1. Lasing spectra of microdroplet fluorescent saturable absorbing dye with concentrations of 10^{-3},10^{-4} and 10^{-5} M.

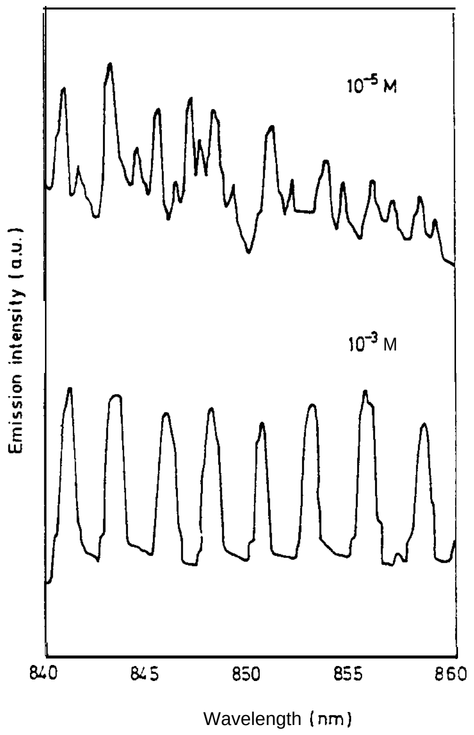

FIG. 2. Extended lasing spectra of dye droplets with concentrations of 10^{-3} and 10^{-5} M.

MDR modes as in 10^{-3} M emission spectra, there are an extra group of higher Q MDR modes appearing in 10^{-5} M spectrum. Since the less concentrate solutions have less internal absorption [11] to sustain higher Q MDR's, and thus the more spectral feature were observed in lower concentration droplets. Meanwhile, the dye molecules may be pumped by the incident laser to high-lying upper singlet states before they decay to the ground states, when the dye molecules make transition from the upper singlet states to the lower high-lying singlet states by emitting stimulated photons. Therefore, the re-emitted photons will have higher photon energy than that of the excitation laser as shown in Fig. 1 there are lasing peaks located at wavelengths shorter than the pump one.

In Ref. (6), Mazumder *et al.* have found that the lasing spectral peaks are not only blue shifted with higher absorber concentration as compared with that of without absorber, but red shifted if one increases the fluorescent dye concentration and keep the concentration of absorber constant or no absorber at all. In our experiment, however, the IR-125 dye is both fluorescence and saturable absorber dye, both gain and absorption α_{abs} of Eq. (1) increase as increasing dye concentration. In order to understand this phenomena as mentioned above, we modified the threshold equation by replacing α_{abs} of saturable absorber by $n_T\sigma_T$ due to triplet-state absorption in IR-125 to evaluate the positions of lasing peaks. Again where n_T is the dye concentration and σ_T is triplet-state absorption cross section of IR-125 dye. Thus the threshold condition can be rewritten as

$$\gamma(\lambda) = \frac{n_2(\lambda)}{n_T} = \frac{\dfrac{2\pi m}{n_T \lambda Q} + \sigma_T + \sigma_a(\lambda)}{\sigma_a(\lambda) + \sigma_e(\lambda)}. \tag{2}$$

We found that the relative lasing peak positions are mostly determined by product of n_T and Q, meanwhile the amount of blue shift is governed by σ_T. By using the measured absorption and fluorescence spectra (see Fig. 3 with constant triplet cascade absorption) with the corresponding peak absorption cross section, σ_a is $5 \times 10^{-16}\,\mathrm{cm}^2$ at 778 nm (c.f., $\sigma_a = 3 \times 10^{-16}\,\mathrm{cm}^2$ in DMSO, maximum at 795 nm) [5] and the maximum emission cross section, σ_e is $3 \times 10^{-16}\,\mathrm{cm}^2$ at 808 nm of the fluorescence spectrum. To best fit the lasing maxima (corresponding to minima of threshold) of three different dye concentrations (see Fig. 4), the Q value and σ_T are chosen to be $Q \approx 4 \times 10^4$ and $\sigma_T \approx 0.6 \times 10^{-16}\,\mathrm{cm}^2$. Unfortunately, we obtained not only an unreasonable result which has lasing threshold greater than 1 for the same order MDR's with $Q \approx 4 \times 10^4$ for 10^{-5} M dye droplet but also the simulated spectral widths can not match with the emission spectra. By adjusting σ_e to best-match all the lasing spectral widths, as shown in Fig. 4, we found that an enhancement factor of 2.7X which corresponds to $\sigma_e = 8 \times 10^{-16}\,\mathrm{cm}^2$ is necessary to resolve this unreasonable result. The enhancement factor agrees with that of the study on multiple order Raman scattering [12] which has 3X enhancement and is far less than 100X enhancement in lasing droplets without saturable absorber which has $Q \approx 10^6$. Since the lasing threshold is mainly determined by the small signal gain and the total cavity loss in the very early stage far before the laser oscillation reaches its steady state. By using two pumping power we also found that the lasing spectra of 10^{-3} M dye droplets are independent of the incident pump powers as shown in Fig. 5 with 40 and 400 mW pump powers.

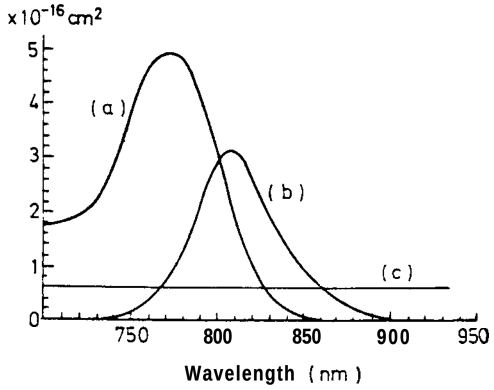

FIG. 3. The absorption [curve (a)], emission [curve (b)], and cascade triplet state absorption [curve (c)] cross sections.

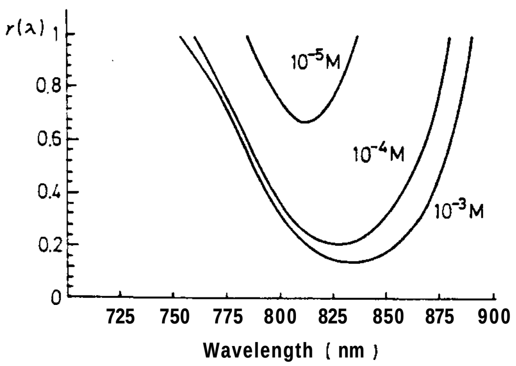

FIG. 4. The simulated curves of threshold condition for 10^{-3}, 10^{-4}, and 10^{-5} M.

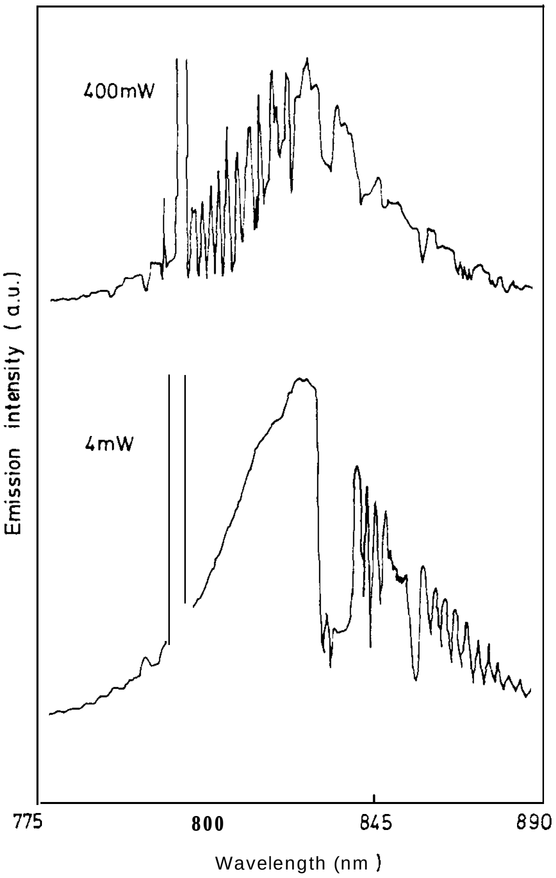

Fig. 5. Lasing spectra with power depedent pumping.

IV. Conclusions

We have observed blue shifts of emission spectra of microdroplet lasers containing fluorescent saturable absorbing dye as compared with those of conventional dye lasers. It can not be explained by matching the lasing peaks to the threshold condition without taking into account cavity enhancement. By best fitting to the peaks of lasing spectra of three different dye concentration, we find that the microdroplet lasers have quality factors of 10^4 with about 3X cavity enhancement of stimulated emission cross section and their lasing peaks at fixed concentration are independent of the pumping power. Unfortunately, there are lack of σ_e and σ_T data for comparison at this moment, if one is able to calculate mode volume of given Q modes of the certain microdroplet cavities, then the cavity enhancement factors can be calculated accordingly, then the adjusting parameters Q and σ_T can be obtained. Furthermore, if one can measure the cavity quality factor independently, this experiment could provide a simple method for measuring emission cross section and cascade triplet-state absorption cross section σ_T without using complicated pump-probe nonlinear laser spectroscopy.

Acknowledgments

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References

[1] H.-M. Tzeng, K. F. Wall, M. B. Long, and R. K. Chang, Opt. Lett. 9, 499 (1984).
[2] J.-Z. Zhang, D. H. Leach, and R. K. Chang, Opt. Lett. 13, 270 (1988).
[3] S. Arnald and L. M. Folan, Opt. Lett. 14, 387 (1989).
[4] K.-H. Lin and W.-F. Hsieh, Opt. Lett. **16**(20), 1608 (1991).
[5] For example, "*Exciton **Laser Dyes,***" Catalog Exciton, Inc. (1992), and references therein.
[6] Md. M. Mazumder, G. Chen, and R. K. Chang, Opt. Lett. **20**(8), 378 (1995).
[7] F. P. Schafer, in ***Dye lasers,*** 2nd revised ed. (Springer-Verlag, New York, 1977), pp. 32-37.
[8] P. Chylek, D. Ngo, and R. G. Pinnick, J. Opt. Soc. Am. **A9**, 775 (1992).
[9] P. Chylek, H.-B. Lin, J. D. Eversole, and A. J. Campillo, Opt. Lett. 16, 1723 (1991).
[10] D. Ngo and R. G. Pinnick, J. Opt. Soc. Am. **All, 1352** (1994).
[11] R. L. Armstrong, J.-G. Xie, T. E. Ruekgauer, and J. Gu, Opt. Lett. 18, 119 (1993).
[12] A. Serpenguzel, G. Chen, R. K. Chang, and Wen-Feng Hsieh, JOSA **B9**(6), 871 (1992).