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Stimulated Emission Observed from an Organic Dye, Chloro-aluminum Phthalocyanine*

We have observed that when a specific phthalocyanine solution (chloro-aluminum phthalocyanine dissolved in ethyl alcohol) is irradiated by a sufficiently powerful beam from a giant-pulse ruby laser, there occurs intense stimulated emission from the phthalocyanine molecules. The wavelength of this stimulated emission is centered at approximately 0.755 μ. Its spectral half-width was observed to be some 5 cm^{-1}.

The apparatus with which the effect was observed is diagrammed in Fig. 1. A giant-pulse ruby laser (Korad K-2QP) was positioned so that its unfocussed output was incident upon the cylindrical surface of a standard absorption cell (length 1 in., diameter 1 in.) containing the phthalocyanine solution. Mirrors A and B are flat, multiple dielectric mirrors having reflectivities of 92% and 97%, respectively, at ≈0.76 μ. The mirrors were made parallel by optical alignment carried out with the absorption cell in place just before the ruby laser was fired. During alignment the cell contained only ethyl alcohol, the dye being added later in concentrations[1] ranging from 5×10^{16} to 2×10^{17} molecules/cm^3. A Bausch and Lomb dual-grating spectrograph received the phthalocyanine beam through mirror A. The beam was not focused in the spectrograph slit for a single shot was sufficient to produce severe blackening of a type 1-N plate through a 1 mm slit. The phthalocyanine beam transmitted through mirror B was projected across the room to a target where it formed a brilliantly visible spot. The angular divergence was estimated to be about 3 milliradians (half-angle).

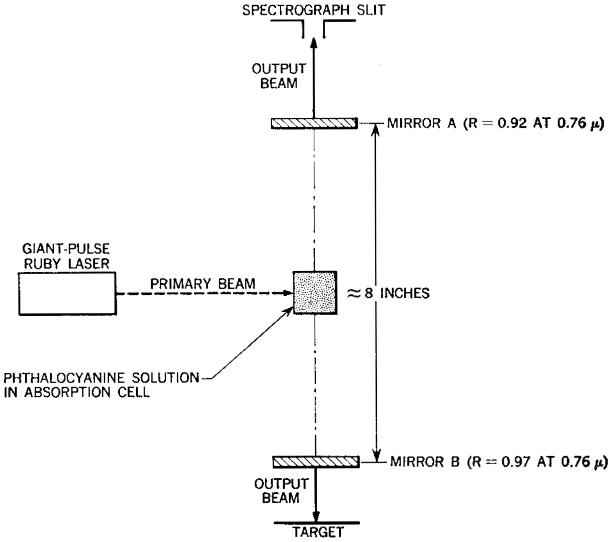

Figure 1 Diagram of the experimental apparatus.

The stimulated emission was seen to have a quantifiable threshold, but accurate measurements of this parameter have not been taken. The intensity of the primary beam from the ruby laser was estimated to be on the order of 100 MW/cm^2. Stimulated emission was not observed from the phthalocyanine when the ruby laser was operated in the normal mode, i.e., was not Q-switched.

Our present evaluation of the phenomenon is as follows. The output wavelength of the coherently generated phthalocyanine beam exactly coincides with the peak of the longest wavelength fluorescence band, Fig. 2. This band represents transitions from the lowest vibrational state of the first excited singlet state to an excited vibrational level of the ground singlet state. The emitting state is directly and efficiently populated by the action of the primary ruby laser beam.[2] The lifetime of the emitting state is short, of the order of several nanoseconds, and the phthalocyanine stimulated emission thus should show approximately the same temporal variation as that for the ruby laser giant pulse.

An estimate of the inversion density required for oscillation is easily computed from well known formulae. For a Lorentzian line shape the appropriate expression is

$$\frac{N_{\mathrm{th}}}{V} = \frac{8\pi^2 \tau \Delta\nu (1 - R) n_r^2}{\lambda^2 l \phi}, \qquad (1)$$

in which l represents the active region length; ϕ, the fractional fluorescence in the (lasing) band; $\Delta\nu$, the half

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* This work was supported by the Army Research Office—Durham, under Contract No. DA31-124-ARO-D-205.

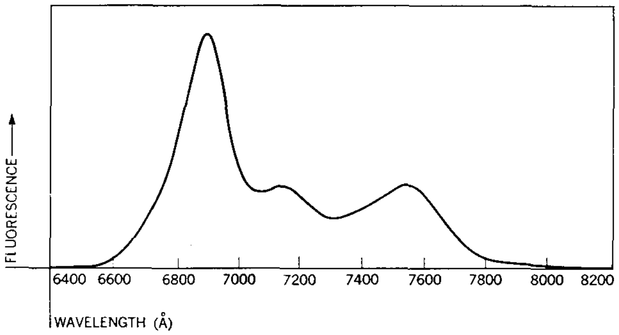

Figure 2 Fluorescence of chloro-aluminum phthalocyanine in ethyl alcohol. The shortest wavelength peak corresponds to the resonance line but is severely attenuated and shifted (to longer wavelengths) by the effects of self-absorption.

width of the (lasing) band; τ, the observed lifetime of the fluorescence; n_r, the index of refraction; and R, the reflectivity of the end mirrors. Equation (1) assumes that every photon absorbed will decay via a fluorescent channel and for phthalocyanines with light, diamagnetic central ions that assumption is probably valid to within an order of magnitude. (We note, for instance, that the quantum efficiency of Mg-phthalocyanine is known[3] to be about 80% at 300°K.) Now, choosing the values $\phi = 1/10$, $l = 2.5$ cm, $\Delta\nu = 200\ \mathrm{cm}^{-1}$, $\tau = 7.9 \times 10^{-9}$ sec (a value quoted in the literature[4] for Mg-phthalocyanine), and $R = 0.95$, one finds $N_{\mathrm{th}}/V \approx 3.2 \times 10^{14}/\mathrm{cm}^3$. To maintain this inversion requires a minimum absorbed pumping power of $\approx 100\ \mathrm{kW/cm}^3$. While this requirement is easily met by a giant pulse ruby laser, it is great enough to make it clear why no laser action was observed when the ruby laser was not Q-switched.

Although this optically pumped laser and a Raman laser show similarities, it is unlikely that stimulated Raman scattering (SRS) by the phthalocyanine molecules allows an acceptable explanation. There are at least three reasons:

First, there is no evidence of darkening on the spectrograph plates at positions that would correspond to higher order Stokes or anti-Stokes lines.

Second, the phthalocyanine molecular densities that are involved appear to be too small by a factor of ten or so when compared with an estimate, made below, of the Raman scattering cross-section that should obtain as a consequence of the *resonance Raman effect.* (The importance of the resonance Raman effect here stems from the fact that the ruby frequency is only $\approx 500\ \mathrm{cm}^{-1}$ away from the peak of the phthalocyanine resonance line, which has a half width $\approx 170\ \mathrm{cm}^{-1}$ and an oscillator strength ≈ 1). We begin the estimate we require by observing that the oscillator strengths of the two other main absorption sidebands (mirror images of the two longest wavelength fluorescent sidebands) are both approximately 0.1. Taking the resonance Raman cross-section as *proportional* to the product of the f number of the resonance line and that of either of the two main sidebands, and *inversely proportional* to the square of the energy separation between the ruby frequency and the peak of the resonance line, and *inversely proportional* to the square of the resonance line frequency leads to this prediction: The Raman scattering cross-section for the phthalocyanine molecule at 6943 Å should be some 10^3 to 10^4 times greater than the cross section (at 6943 Å) for a molecule whose first excited singlet state is some 35 000 cm^{-1} above the ground state, and for which the analogous f number products are taken, respectively, to be ~ 1 and ~ 0.1. Now, the phthalocyanine molecular densities in our experiments were, on the other hand, less than concentrated organic solvent densities by a factor of 10^4 to 10^5. In order for SRS to occur, one would expect that the product of the phthalocyanine molecular density, n_{phthal}, and its Raman cross-section, σ_R, would have to be comparable to the corresponding quantity in the case of concentrated organic solvents, the Raman linewidths being assumed equal in each case. Hence we draw the implication (although not a strong one) that the product $n_{\mathrm{phthal}}\, \sigma_R$ is not great enough for SRS to occur in phthalocyanine.

The third and last argument against the involvement of SRS is closely related to the preceding argument but is perhaps more convincing; it is that the deduced Raman frequency does not correspond to any of the vibrational frequencies computed from the separation of the various absorption and fluorescence components from the 0-0 resonance line which peaks at $\lambda \approx 6{,}700$ Å.

We are continuing to study this effect. As far as is known to us, it provides the only reported case in which stimulated emission has been obtained from a fluorescent liquid wherein the lasing transition is an allowed singlet-singlet transition.

References and footnotes

1. Chloro-aluminum phthalocyanine, unlike most other metal phthalocyanines, is fairly soluble in ethyl alcohol.
2. P. P. Sorokin, J. J. Luzzi, J. R. Lankard, and G. D. Pettit, "Ruby Laser Q-Switching Elements Using Phthalocyanine Molecules in Solution," *IBM J. Res. and Dev.* **8**, 182–184 (1964).
3. G. P. Gurinovitch, A. N. Sevchenko, and K. N. Solov'ev, *Soviet Phys. Usp.* **6**, No. 1, 67 (1963).
4. *Ibid.*

Received February 15, 1966