LASER PROPERTIES OF SOME PHTHALOCYANINES*

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The lasing behavior of solutions of the phthalocyanines of aluminum, gallium, magnesium, and zinc was studied with nitrogen laser optical pumping. Aluminum phthalocyanine chloride showed simultaneous lasing at two wavelengths separated by approximately 70 nm. Gallium, magnesium, and zinc phthalocyanine each lased at only one wavelength. This behavior is explained in terms of some of the intrinsic physical properties of these phthalocyanines.

1. Introduction

The first demonstration of laser action in an organic dye was made by Sorokin and Lankard [1], using a giant pulse ruby laser to induce stimulated emission in an ethyl alcohol solution of chloro-aluminum phthalocyanine. Laser output was observed at approximately 755 nm. More recently, laser output from this molecule has been observed at 690 nm when pumped by a nitrogen laser [2].

The luminescence properties of the phthalocyanines are of interest because of their structural similarities to the porphorins and chlorophylls. In the course of studies on the behavior of chlorophylls and related compounds as laser dyes, we have made some further studies on the phthalocyanines. In this communication, we report conditions for the observation of simultaneous lasing at two wavelengths for chloro-aluminum phthalocyanine and the first observations of lasing from solutions of magnesium, zinc and gallium phthalocyanines when pumped by a nitrogen laser.

2. Experimental

Population inversions were effected by direct optical pumping with the pulsed ultraviolet output from an N_2 laser at 3371 Å (FWHM = 8 ns, P_{peak} = 1 MW). The N_2 laser beam was focussed by means of a quartz cylindrical lens to a thin horizontal line ($< 100 \mu$); the dye solutions contained in 1 cm quartz cuvettes were placed at the focus of this ultraviolet output and pumped transversely. The laser cavity was usually formed by the two opposite uncoated surfaces of the quartz cuvette adjacent to the surface excited by the nitrogen laser, although sometimes a grating (1200 line/mm) was used as one of the reflectors to achieve some degree of tunability. The optical detection system and signal averaging electronics have been described previously [3].

The phthalocyanine samples were obtained from Eastman Organic Chemicals and were used without further purification. The absorption spectra of the phthalocyanine solutions were run on a Cary 14 spectrophotometer.

3. Results

Table 1 shows the lasing characteristics of the phthalocyanines which were observed under direct N_2 laser pumping. Note that the solutions of aluminum phthalocyanine chloride (AlPcCl) lased simul-

Table 1

Lasing characteristics of phthalocyanine solutions with an N_2 laser optical pump at 337.1 nm

Compound	Concentration solvent [a]	Lasing wavelength λ_{ϱ} (nm)	$\Delta\lambda_{\varrho}$ FWHM [b] (nm)	Threshold
Aluminum phthalocyanine chloride (AlPcCl)	1×10^{-3} M EtOH	753.3	1.5	–
		685.7	1.6	–
	1×10^{-3} M py	761.6	1.4	7.7
		692.6	4.4	–
	2.5×10^{-4} M py	690.1	2.8	2.5
Gallium phthalocyanine chloride (GaPcCl)	2.8×10^{-4} M py	694.0	1.8	20
Magnesium phthalocyanine (MgPc)	1.2×10^{-3} M py	688.2	4.0	3.1
	5×10^{-4} M DMF	682.5	3.0	–
Zinc phthalocyanine (ZnPc)	5×10^{-4} M py	686.0	2.7	31
	1.4×10^{-4} M py	684.9	2.4	10

[a] EtOH: ethyl alcohol; py: pyridine; DMF: N,N-dimethylformamide.

[b] FWHM: full width at half maximum of untuned lasing output.

taneously in two wavelength regions separated by approximately 70 nm. Gallium phthalocyanine chloride (GaPcCl), magnesium phthalocyanine (MgPc) and zinc phthalocyanine (ZnPc) on the other hand each lased in only one wavelength region below 700 nm. Stimulated emission has been previously observed from MgPc in quinoline at 759.0 nm when pumped by a ruby laser [4] and from AlPcCl in ethanol at 755 nm [1], in DMSO at 762 nm [5], and in chloronaphthalene at 708 nm [6] when pumped by a ruby laser, and from AlPcCl in methanol at 690 nm when pumped by a nitrogen laser [2].

Table 2 shows the relative quantum yields of the lasing solutions of AlPcCl, GaPcCl, MgPc, and ZnPc in pyridine. The solutions were excited with the nitrogen laser at 337 nm at ~ 1 MW/cm^2 and the fluorescence from the front faces of the cells was recorded using the Hilger-Engis 1-m scanning monochromator. The resulting fluorescence curves were integrated and the relative quantum yields were calculated from

Table 2

Relative fluorescence quantum yields for pyridine solutions of AlPcCl, GaPcCl, MgPc, and ZnPc.

Compound/Concentration	ϕ_F/ϕ_F (AlPcCl)
AlPcCl/0.25 mM	1.00
GaPcCl/0.28 mM	0.33
MgPc/1.0 mM	1.11
ZnPc/0.14 mM	0.59

these integrals. The lower observed fluorescence yields in GaPcCl and ZnPc are presumably due to higher triplet yields in these compounds as a result of enhanced spin orbit coupling.

The two wavelength lasing observed from AlPcCl solutions is an interesting although not unprecedented phenomenon. Similar effects have previously been observed in the lasing behavior of solutions of pheophytin *a* and methyl pheophorbide *a* [3] as well as in the lasing behavior of some other laser dyes [7]. Each of the lasing maxima in AlPcCl is centered within one of its fluorescence bands as is illustrated in fig. 1. The short and long wavelength lasing bands correspond to electronic transitions to the ground and a vibrationally excited level of the ground state, respectively. The relative intensities of the two lasing bands are a sensitive function of the concentration with the long wavelength band favored at higher concentrations. For example AlPcCl in pyridine at 0.5 mM lases at 691.8 nm only but at 2.0 mM it lases at 762.6 and 692.0 nm with an intensity ratio of $\sim 3:1$. This behavior indicates that at low concentrations the gain is higher at 692 nm than at 762 nm primarily due to the higher fluorescence yield. At higher concentration, however, the 692 nm lasing is quenched by self absorption because of its overlap with the 0—0 absorption band, and consequently the gain at 692 decreases relative to that at 762.

Since the absorption and fluorescence spectra of GaPcCl, MgPc, and ZnPc are similar to the correspond-
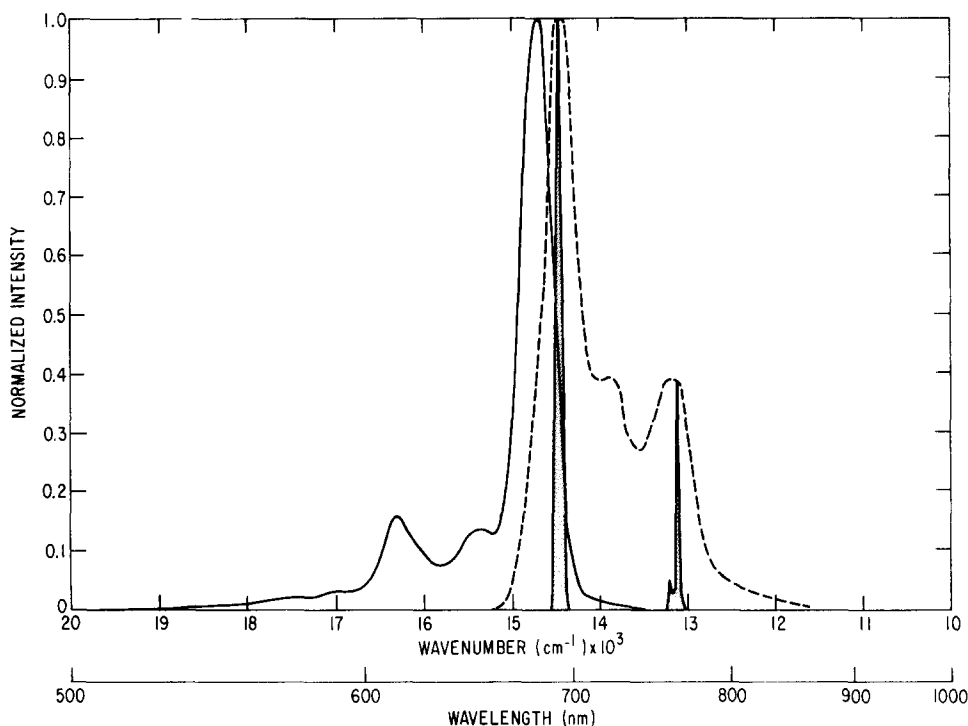
Fig. 1. Normalized absorption ——, fluorescence — — —, and lasing (shaded area) spectra of AlPcCl, 10^{-3} M in pyridine.

ing spectra of AlPcCl, one might expect to see similar two wavelength lasing behavior in these compounds. However, lasing was observed only in the short wavelength (0–0) fluorescence bands in GaPcCl, MgPc, and ZnPc (table 1). That GaPcCl did not lase in the long wavelength fluorescence band may be due to its lower solubility and lower conversion efficiency. The highest concentration of GaPcCl achieved was 2.8 × 10^{-4} M after refluxing in pyridine for 72 hr. At this concentration AlPcCl also lases only in its short wavelength fluorescence band. MgPc and ZnPc, on the other hand, are quite soluble in pyridine up to concentrations of at least 1 × 10^{-3} M. Solutions of ZnPc did not lase at all at this higher concentration. As these solutions of ZnPc were diluted, lasing began to appear in the short wavelength fluorescence band with a relatively high threshold. This behavior manifests the low fluorescence quantum yield of ZnPc. With its resulting low gain, lasing in ZnPc is more easily quenched by absorptive losses whether they be from the ground state or from excited states. Similar arguments apply to the relatively high lasing threshold observed in GaPcCl.

MgPc, however, has a relatively high fluorescence quantum yield as shown in table 2, and a low threshold for lasing in its short wavelength fluorescence band. The absorption, fluorescence and lasing spectra of MgPc are shown in fig. 2. Stimulated emission was not observed in its long wavelength band even at MgPc concentrations as high as 6.0 × 10^{-3} M. The reason for the failure to observe long wavelength lasing in MgPc lies in the fact that its absorption cross section at the red maximum is nearly a factor of 3 less than that for AlPcCl as shown in table 3. This has a dual effect on the wavelength dependence of gain. First, the gain in the long wavelength band of MgPc is reduced relative to that of AlPcCl because of a lower overall stimulated emission cross section in the former. Secondly, the gain in the short wavelength 0–0 band of MgPc is increased relative to that of AlPcCl because of the lower absorption cross section at the fluorescence maximum in the case of MgPc. The net result of these two effects is that it should be easier to shift lasing to the long wavelength fluorescence band in AlPcCl than in MgPc. An illustration of these arguments is given in fig. 3 which shows the
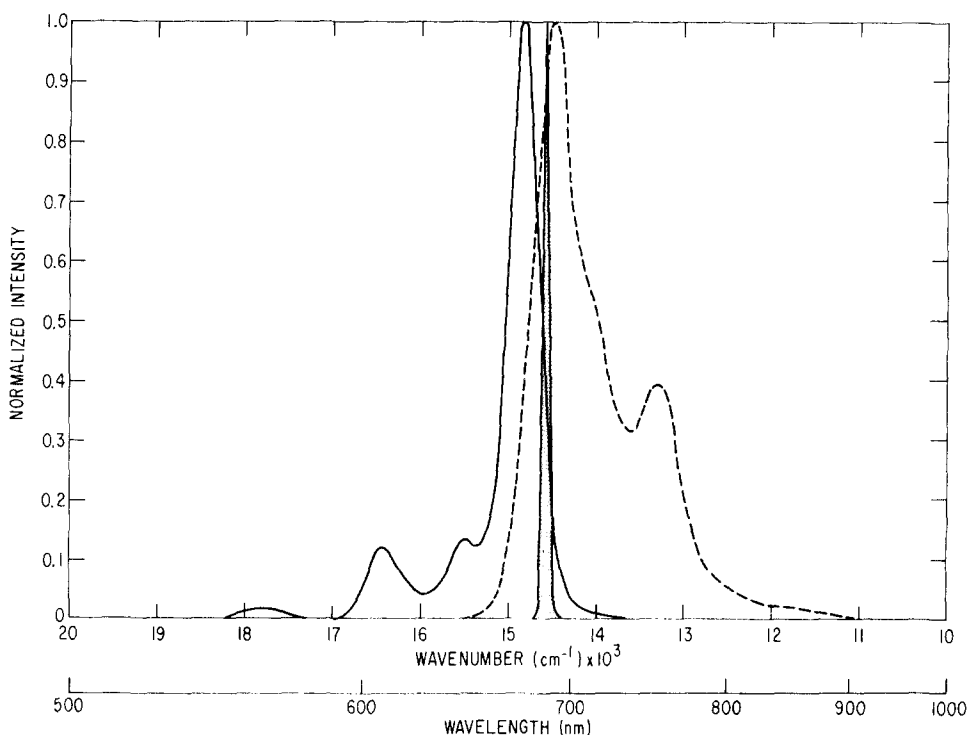
Fig. 2. Normalized absorption ——, fluorescence — — —, and lasing (shaded area) spectra of MgPc, 10^{-3} M in pyridine.

minimum population inversion necessary for lasing as a function of wavenumber for MgPc and AlPcCl. At threshold, lasing should occur near minima in these curves. Since the long wavelength minimum is deeper for AlPcCl than for MgPc, a lower population inversion and hence a lower threshold is necessary to induce lasing of AlPcCl in this region.

Recently, it has been suggested that various types of solution equilibria such as dimerization can affect the lasing properties of the phthalocyanines [8].

While this is certainly true, we believe that in our solutions no significant dimerization occurred. The dimer of AlPcCl has been previously characterized [9]. Its absorption spectrum contains two broad over-lapping bands at 826 and 592 nm. The dimer is formed when AlPcCl is dissolved in any chlorinated hydrocarbon solvent. Whereas only monomer is formed when AlPcCl is dissolved in alcohols, ketones, or amines [9]. In our experiments, the solvents used include ethanol, pyridine, and DMF, and no absorption

Table 3

Absorption coefficients and cross sections of pyridine solutions of AlPcCl, GaPcCl, MgPc, and ZnPc

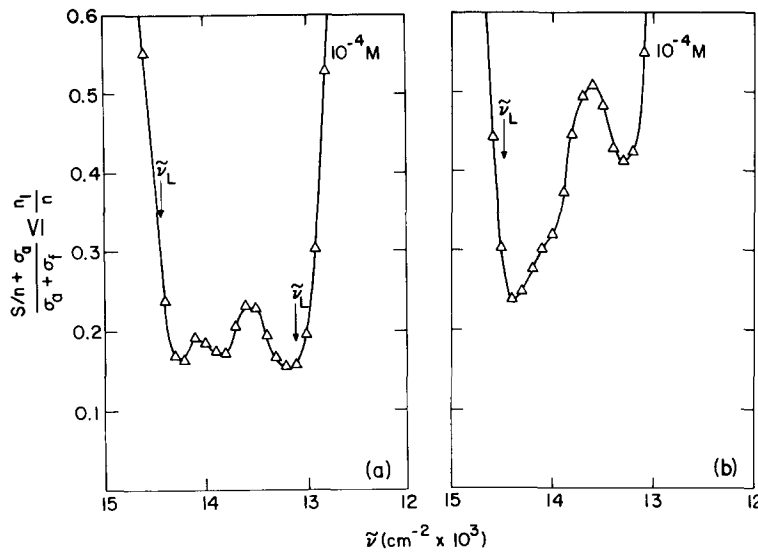| Compound	λ_{max} (nm)	$\epsilon_{max} \times 10^{-4}$ (M^{-1} cm^{-1})	$\sigma_{a\ max} \times 10^{16}$ (cm^2)	$\epsilon_{337} \times 10^{-4}$ (M^{-1} cm^{-1})	$\sigma_{a\ 337} \times 10^{16}$ (cm^2)
AlPcCl	681	23 [a]	8.8	5.6	2.1
GaPcCl	684	13 [a]	5.0	2.0	0.76
MgPc	674	8.7 [b]	3.3	1.9	0.73
ZnPc	674	28 [b]	10.7	6.3	2.4

[a] Present work.
[b] Ref. [10].

Fig. 3. Plot of the calculated minimum inversions $[N_1/N \geqslant (S/N + \sigma_a)/(\sigma_f + \sigma_a)]$ versus wavenumber for (a) 10^{-3} M AlPcCl in pyridine and (b) 10^{-3} M MgPc in pyridine. N_1 is the number density in the upper laser level, N is the total number density, S is the loss factor, σ_a is the absorption cross section, σ_f is the stimulated emission cross section.

bands attributable to the dimer were observed in any of these cases. It should also be noted that from our results one cannot rule out excimer formation in these systems. However, since the lasing behavior can be explained strictly on the basis of monomeric phthalocyanines, there is no need to invoke any new species.

We have by this study been able to correlate the lasing behavior of some laser dyes with some of their intrinsic physical properties i.e., solubility, aggregation, fluorescence quantum yield, absorption and emission cross sections. This correlation is important since it provides a useful tool to probe the molecular properties of fluorescent materials.

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