Short Communication

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Ruby Laser Q-Switching Elements Using Phthalocyanine Molecules in Solution*

Following the original suggestion of R. W. Hellwarth,[1] many investigators have succeeded in obtaining coherent light from optically pumped solid state lasers in the form of intense, sharp, single pulses. These pulses are commonly referred to as "giant" pulses, in recognition of the fact that their peak intensity far exceeds that of any of the several pulses ("spikes") which are normally emitted in several-hundred-microsecond bursts when a laser is pumped beyond threshold. The duration of a giant pulse is usually only a few tens of nanoseconds. In contrast, the duration of each spike in the output of a normally operated laser is several hundred nanoseconds.

The basic technique employed in all giant pulse generating schemes consists of keeping Q for the cavity at an abnormally low value while a large population inversion is being built up. Just before instability can occur, the cavity Q is suddenly switched to a high value. Stimulated emission then occurs at a very high rate. Q-switching is commonly implemented with Kerr cells or with rotating reflecting prisms. Thin foils of gold inserted between a laser crystal and a high-reflectivity end-plate have also been used to generate giant pulses.[2] Recently it has been reported[3,4] that initial laser action can produce sufficient (irreversible) transparency in thin films of organic dyes deposited on glass plates to permit such units to be employed satisfactorily as "single shot" Q-switching elements. Still more recently a group of investigators has been able to produce giant pulses by inserting uranium glass elements into the primary cavity.[5] This last experiment truly involves the saturation of a spectral transition; however, it is required that a metastable state in the order of 20,000 cm^{-1} above the ground state be heavily populated, which means that the uranium glass element must be excited by a strong flashlamp for each shot.

In this paper we note that some of the *metal phthalocyanines* (including the free base) dissolved in ordinary liquid organic solvents show enough bleachable absorber action at $\lambda = 6943$A to serve quite satisfactorily as repeatable Q-switching elements for ruby lasers. No prior pumping of the element is required. The bleaching process is based upon saturation of a singlet-singlet spectral transition, although there remains the possibility that population of a triplet state having a relatively low absorption is involved to some extent.

The absorption spectrum for a metal phthalocyanine in solution is characterized by intense band groups in the red and near-uv regions of the electromagnetic spectrum. (In Fig. 1 the red group is shown.) These band groups correspond to highly allowed electronic (singlet-singlet) transitions of the phthalocyanine ring. The main absorption band occurring in the red portion of the visible spectrum is particularly intense and narrow. This absorptio results from transitions occurring between the lowes vibrational level of the ground state S and the lowes vibrational level of the first excited singlet state S' (Fig. 2) The oscillator strength f of this band alone is nearly unity The molar absorptivity at the peak of the band reache values as high as $\epsilon = 300\,000$ for many of the meta phthalocyanines.

The metal ion occupying the center of the molecul influences the basic absorption and fluorescence spectrur in two important ways. First, it affects the exact locatio of the absorption peaks.[6] (We find, for example, that th main peak of dilithium phthalocyanine diluted in aceton occurs at about 6560 A, and that of chloro-aluminur phthalocyanine diluted in chloronaphthalene occurs a about 6935 A (Fig. 1). Vanadium phthalocyanine in th latter solvent peaks at about 6980 A, but in nitrobenzen it peaks at 6955 A. Our determinations of the locations c these peaks are somewhat at variance with the data pre sented in Ref. 6.) Second, as the other main effect, th central metal ion influences $k_{S'S}/k_{S'T}$, the ratio of *th*

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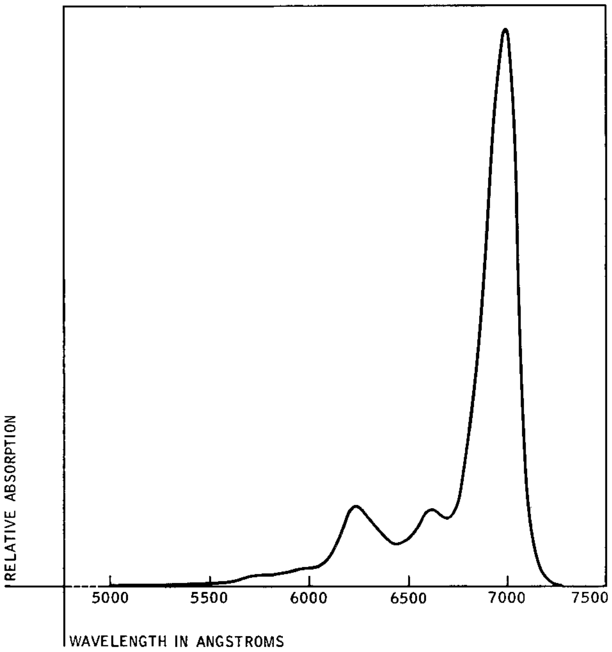


Figure 1 **Absorption vs wavelength for a solution of chloro-aluminum phthalocyanine in chloronaphthalene.**

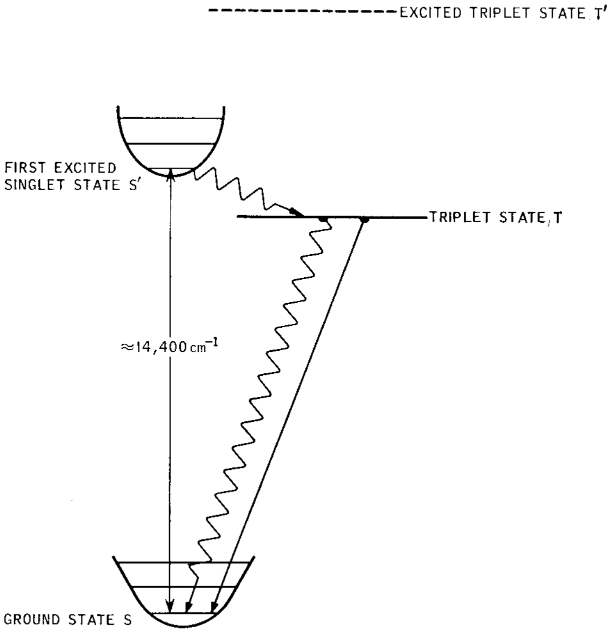
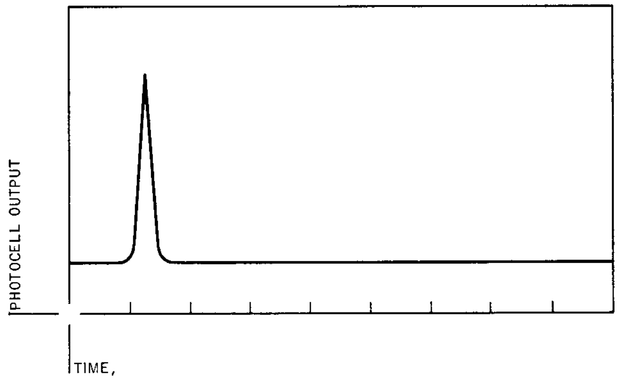


Figure 2 **Energy level diagram for phthalocyanine molecules in solution.**

rate constant for fluorescent decay from the excited singlet state to the ground state to the *rate constant for nonradiative decay to the metastable triplet state T* that is assumed to exist a few thousand wavenumbers below state *S′*. Emission data taken in the case of related metalloporphyrin compounds[7] is generally thought to provide an indication of the trend that should hold for the phthalocyanines. Presumably, with increasing atomic number of the central metal ion there is represented an increased interaction of this ion with the ring system, resulting in greater probability for the essentially forbidden singlet-to-triplet transition to occur. Simple visual inspection on our part revealed brighter fluorescence, in general, from the compounds having lighter central metal ions. No one appears to have actually seen phosphorescence, i.e., emission from the triplet state, in any of the phthalocyanines.

Figure 3 **Oscilloscope trace recording of the giant pulse, as detected by a vacuum photocell (RCA 925).** *Each division represents 100 nsec.*



In our experiments a cell either 5 cm or 3 cm long (containing either the free base, chloro-aluminum or vanadium phthalocyanines diluted in either chloronaphthalene or nitrobenzene) was placed between an uncoated ruby laser crystal (polished with a totally-internally-reflecting rooftop on one end) and a multiple dielectric mirror reflecting 99% at 6943 A. The concentrations of the phthalocyanine solutions (in the order of 10^{-6} M) were adjusted to transmit 50% at 6943 A at low levels in a single pass through the cell. The ruby laser was then pumped to the point where it should normally have started to lase. Instead, a giant pulse occurred (Fig. 3). This appeared to have no more than a 20-nanosecond width in the cases of the chloro-aluminum and vanadium solutions. It appeared wider and less sharp in the case of the free base solution. In all cases the giant pulses were as intense as any we have obtained using rotating prisms for Q-switchers. With very heavy pumping a series of giant pulses could be produced, with spacings varying from times on the order of 100 microseconds to lesser values as the ruby pumping rate was increased. The chloronaphthalene solutions showed some tendency to decompose on accidental exposure to intense uv light. The nitrobenzene solutions were completely free from this defect.

It is most probable that the bleaching which occurs during the first giant pulse mainly represents saturation of the singlet-singlet transition. In the case of Mg phthalocyanine,[8] there exists the estimate $k_{S'T} \approx 1.3 \times 10^7$ sec^{-1}. Taking this value, one easily computes that immediately after a 20-nanosecond giant pulse roughly 13% of all the phthalocyanine molecules should be in the triplet state. Thus it is likely that the role played by triplet state absorption is only fractionally important whenever only one giant pulse is produced, at least in the case of the lighter metal phthalocyanines. For Mg phthalocyanine, absorption in the triplet state has actually been measured[9,10] and is at least an order of magnitude lower than the absorption in the ground singlet state at $\lambda = 6750$ A, the peak absorption wavelength for this particular compound in pyridine. Also measured, again in the case of a solution of Mg phthalocyanine in pyridine, was the lifetime at room temperature of the bleached state corresponding to a large fraction of molecules being in the triplet state.[10] This had the value 0.8×10^{-3} sec. Thus it is likely that triplet states were important in our experiments involving multiple giant pulses.

Acknowledgments

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Note added in proof

Since submitting this Communication it has come to our attention that definite Q-switching effects have recently been observed by a group of investigators working with chlorophyll, methylene blue, and Victoria Blue B solutions. See J. I. Masters, P. Kafalas, and E. M. E. Murray, *Report No. TO-B64-15*, prepared for the Office of Naval Research under Contract No. Nonr-4126(00), January 31, 1964.