

STUDY OF ANTHRACENE FLUORESCENCE EXCITED BY THE RUBY GIANT-PULSE LASER

J. L. Hall

Joint Institute for Laboratory Astrophysics, Boulder, Colorado

and

D. A. Jennings and R. M. McClintock

Boulder Laboratories, National Bureau of Standards, Boulder, Colorado

(Received 18 September 1963)

This paper is concerned with a study of the blue fluorescence of single anthracene crystals when excited by the ruby "giant-pulse" laser.^{1,2} Recently Peticolas *et al.*³ have reported two-photon absorption as the mechanism for exciting the fluorescence. However, Kepler *et al.*,⁴ attribute the fluorescence to the creation of triplet excitons and their bimolecular recombination. The experiments performed by the authors using the ruby giant-pulse excitation of the fluorescence in single crystals of anthracene show that both mechanisms are present and are easily separated by observing the time dependence of the fluorescence.

The unfocused beam of a 3-megawatt giant-pulse ruby laser Q switched by a 25 000-rpm rotating prism was incident on the anthracene parallel to its [100] direction. Reorientation around the [100] direction of the polarized laser electric field produced no observable effect. A fraction of the laser light, highly attenuated, was monitored by an S-1 photocell operated for linearity at 720 volts. The output was fed into a 30-Mc/sec dual-beam scope through 180-ohm cable terminated at both ends. An integrated output was also available to calibrate the photocell against a copper sulfate liquid-cell calorimeter. The blue fluorescence was monitored with a 1P28 photomultiplier feeding 90-ohm cable terminated at both ends. A Wratten No. 47 and two Corning 4-76 blue-pass filters reduced the contribution of the scattered red light to the observed photocurrent to less than 1 part in 10⁴. Neutral density filters of up to ND4.6 were used to stay well in the linear region. The absolute measurements were normalized with S-5 photocells using the published cathode sensitivity. The time resolution of the blue photomultiplier was separately measured to be less than 3 nanoseconds. However, the blue fluorescence exhibited a detectably slower decay than the red laser pulse, which was nearly symmetric and 30 nsec wide at half power. We attribute this slower decay to the 26-nsec lifetime of the excited singlet fluorescent level.⁵

In the study of the power dependence of the nonlinear fluorescence, the laser was operated under

fixed conditions to minimize the change of coherence properties from pulse to pulse. The laser beam was attenuated with dielectric mirrors used and calibrated at 45°. Figure 1 shows on a logarithmic plot the dependence of the normal blue fluorescence power on the red intensity. Our data can be summarized by the relation

$$P_{\text{blue}} = \delta (I_{\text{red}})^m,$$

where P_{blue} is the fluorescent power in photons/sec-cm³ of illuminated crystal, I_{red} is the inci-

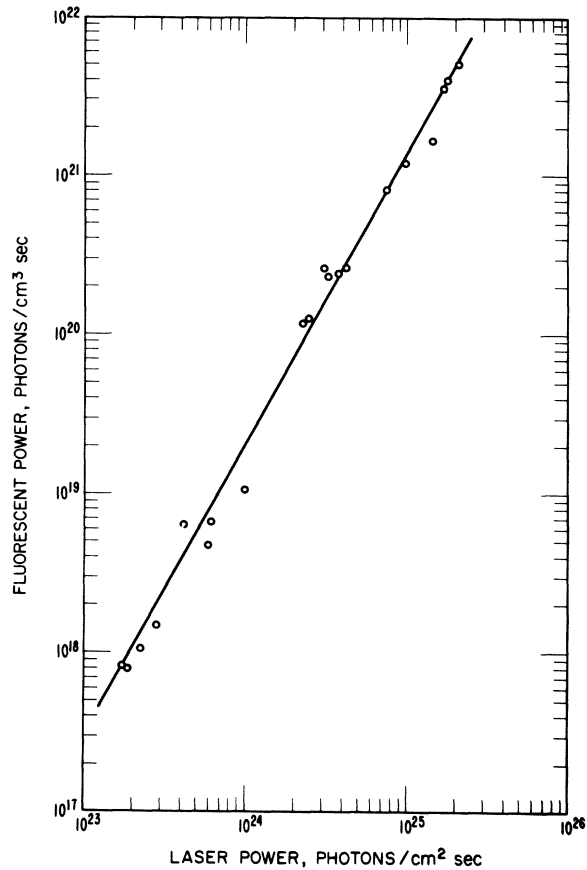


FIG. 1. Log-log plot of normal singlet fluorescence versus peak laser intensity. The observed slope of 1.85 ± 0.15 is satisfactorily close to the integer 2 expected for a two-photon process.

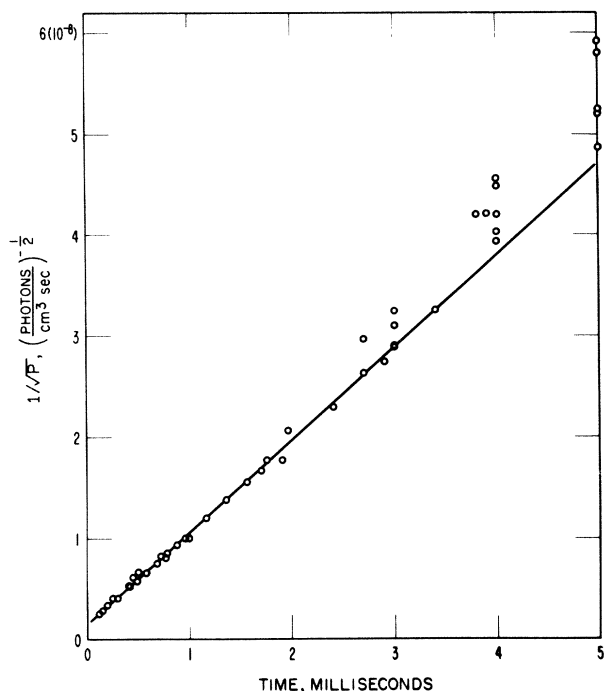


FIG. 2. Plot of reciprocal of square root of delayed blue fluorescence power versus time. A straight line at short times is expected for a bimolecular recombination mechanism.

dent intensity in photons/sec-cm, and $\delta = 1.26 \times 10^{-29}$ cm sec/photon. The observed slope, $m = 1.85 \pm 0.15$, is satisfactorily close to the in-

teger 2 to show that the two-photon process postulated by Peticolas is operative. The possibility of second-harmonic generation⁶ followed by reabsorption and subsequent blue fluorescence is eliminated by the following experiment. A neodymium glass laser rod was Q-switched in the same apparatus to produce about 20 megawatts. The second-harmonic wavelength of the neodymium, in the green at 5300 Å, is not short enough to excite the blue fluorescence. We directly measured the second-harmonic output from anthracene and found that less than 1 photon in 5000 of the ruby-induced fluorescence is attributable to second-harmonic generation and reabsorption.

The delayed fluorescence of the anthracene crystal was observed by the same apparatus as was used to observe the normal fluorescence except that the blue photomultiplier tube was gated on 10 μsec after the intense normal singlet fluorescence to prevent saturation. We were able to observe the delayed fluorescence for times as short as 50 microseconds and as long as 70 milliseconds after the giant pulse. As discussed by Kepler *et al.*,⁵ the delayed fluorescence is attributed to bimolecular annihilation of the triplet excitons generated by the ruby light. Figure 2 shows the signal decaying as $1/t^2$ for short times, while Fig. 3 shows the exponential decay for later times. This behavior is consistent with the bimolecular decay mechanism as shown by Kepler

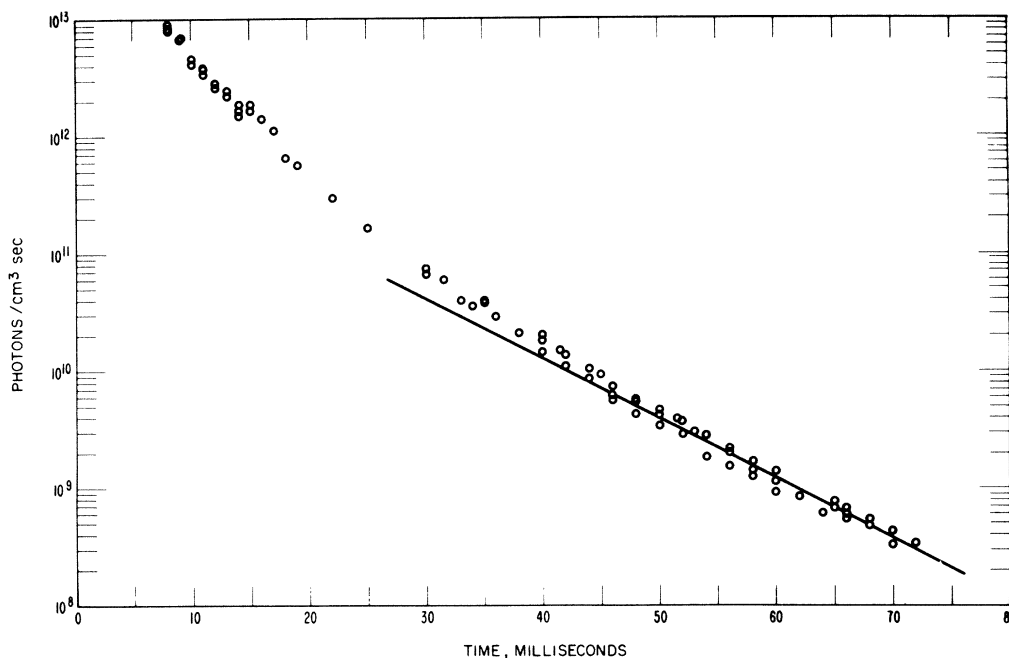


FIG. 3. Semilog plot of delayed fluorescence power versus time. The observed exciton lifetime is 17.2 milliseconds.

et al. The density of triplet excitons n is described by the equation

$$dn/dt = \alpha I - \beta n - \gamma n^2,$$

where αI represents the generation of excitons by the laser light, β is the reciprocal lifetime of the triplet exciton, and γ is the bimolecular interaction rate constant. From our data we find with an uncertainty of 50% the following values:

$$\alpha = 8.6 \times 10^{-6} \text{ cm}^{-1},$$

$$\beta = 58 \text{ sec}^{-1},$$

$$\gamma = 5.5 \times 10^{-11} \text{ cm}^3 \text{ sec}^{-1}.$$

Measurements of α and δ as a function of integrated laser power showed these quantities to be independent of the incident laser power up to approximately 500 kW cm^{-2} .⁷ This would indicate that the creation of excitons is a first-order process, whereas the decay is via bimolecular recombination.

The Raman-shifted ruby line from nitrobenzene at 7670 \AA ⁸ was used to determine the wavelength dependence of both processes. The power at 7670 \AA was 500 kW . It was found that to within 50%, δ was independent of λ at 6943 \AA and 7670 \AA , and that

$$\alpha(\lambda = 6943 \text{ \AA}) = 5.1\alpha(\lambda = 7670 \text{ \AA}).$$

This further suggests that the generation of triplet excitons is a resonant process.

The experiments performed by Peticolas et al., Kepler et al., and the authors lead one to the following conclusions:

(1) The ruby laser can excite 2-photon processes

and triplet excitons in the anthracene crystal leading to normal and delayed fluorescence, respectively.

(2) The ratio of the number of blue photons emitted by normal and by delayed fluorescence is proportional to the number of photons per square centimeter per second of the laser and independent of the total number of photons in each pulse. We believe this is the origin for the different conclusions reached in references 3 and 4.

(3) As expected on the basis of the crystal symmetry, anthracene is a very inefficient generator of optical second harmonics.

The authors would like to thank J. E. Drumheller for his help during the initial stages of the investigation.

¹R. W. Hellwarth, *Advances in Quantum Electronics*, edited by J. Singer (Columbia University Press, New York, 1961), 2nd ed., pp. 334-341.

²F. J. McClung and R. W. Hellwarth, *Bull. Am. Phys. Soc.* **6**, 414 (1961); *J. Appl. Phys.* **33**, 838 (1962).

³W. L. Peticolas, J. P. Goldsborough, and K. E. Rieckhoff, *Phys. Rev. Letters* **10**, 43 (1963); W. L. Peticolas and K. E. Rieckhoff, *J. Chem. Phys.* **39**, 1347 (1963).

⁴R. G. Kepler, J. C. Caris, P. Avakian, and E. Abramson, *Phys. Rev. Letters* **10**, 400 (1963).

⁵J. B. Birks, T. A. King, and I. H. Munro, *Proc. Phys. Soc. (London)* **80**, 355 (1962).

⁶P. A. Franken, A. E. Hill, C. W. Peters, and G. Weinreich, *Phys. Rev. Letters* **7**, 118 (1961).

⁷The interesting increase in α and associated decrease in δ at the higher intensities is presently being studied.

⁸Gisela Eckhardt, R. W. Hellwarth, F. J. McClung, S. E. Schwarz, and D. Weiner, *Phys. Rev. Letters* **9**, 455 (1962).

INFRARED QUANTUM COUNTER ACTION IN Pr-DOPED FLUORIDE LATTICES

M. R. Brown

Ministry of Aviation, Signals Research and Development Establishment, Christchurch, Hampshire, England

and

W. A. Shand*

Department of Natural Philosophy, University of Aberdeen, Aberdeen, Scotland

(Received 20 September 1963)

The principle of the solid-state infrared quantum counter as proposed by Bloembergen,¹ that is, the excitation of fluorescence radiation by the simultaneous absorption of two photons, was demonstrated by Porter² using Pr^{3+} doped 1% in LaCl_3 at liquid helium temperature. This Letter reports infrared quantum counter action in Pr^{3+}

doped 0.5% in LaF_3 , SrF_2 , CaF_2 , and 2.5% in BaF_2 at both room and liquid nitrogen temperatures. The results show that the action has application both in spectroscopic measurements and as a narrow-band infrared detector sensitive to more than one infrared frequency.

The fluoride single crystals used in these ex-