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TWO PHOTON EXCITATION IN
PHENANTHRENE:ANTHRACENE

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ABSTRACT

The intense beam of optical radiation from a ruby laser has been used to excite a two photon absorption in crystals of phenanthrene containing 0.1% anthracene. The spectral analysis and intensity measurements indicate a two photon absorption. The results are compared with the existing theory.

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The intense source of monochromatic radiation, which is obtained from optical masers,[1,2] makes it possible to observe and study two photon processes. We have observed the generation of blue phosphorescent light around λ = 4300Å by illuminating a crystal of phenanthrene containing 0.1% anthracene with red light λ = 6943Å obtained from a ruby optical maser. Our experiments are very similar to those of Kaiser and Garrett,[3] who observed a similar effect in $CaF_2:Eu^{2+}$ crystals. The anthracene has a strong absorption around λ = 4000 - 3500Å.[4] The fluorescence of anthracene is in the blue region of the spectrum at λ = 4500 - 4000Å.[5,6] The observation of the blue fluorescence when the sample is irradiated with the ruby laser light indicates a two photon absorption.

The crystals of phenanthrene with 0.1% anthracene were grown from the melt. A block diagram of the laser and optical apparatus is shown in Figure 1. A crystal of phenanthrene:anthracene 1 mm thick was mounted at the entrance slit of a constant deviation photographing spectrometer. The spectrometer covered the range 7000Å to 3800Å. The photographic plates had a sensitivity of 0.035 erg/cm^2. The light beam of the ruby laser (~ 2.5 joules) was focused onto the crystal. Three Wratten #25 red filters with transmission values totalling $T < 10^{-9}$ for λ < 6000Å and T ~ 0.75 for λ = 7000Å were placed between the laser

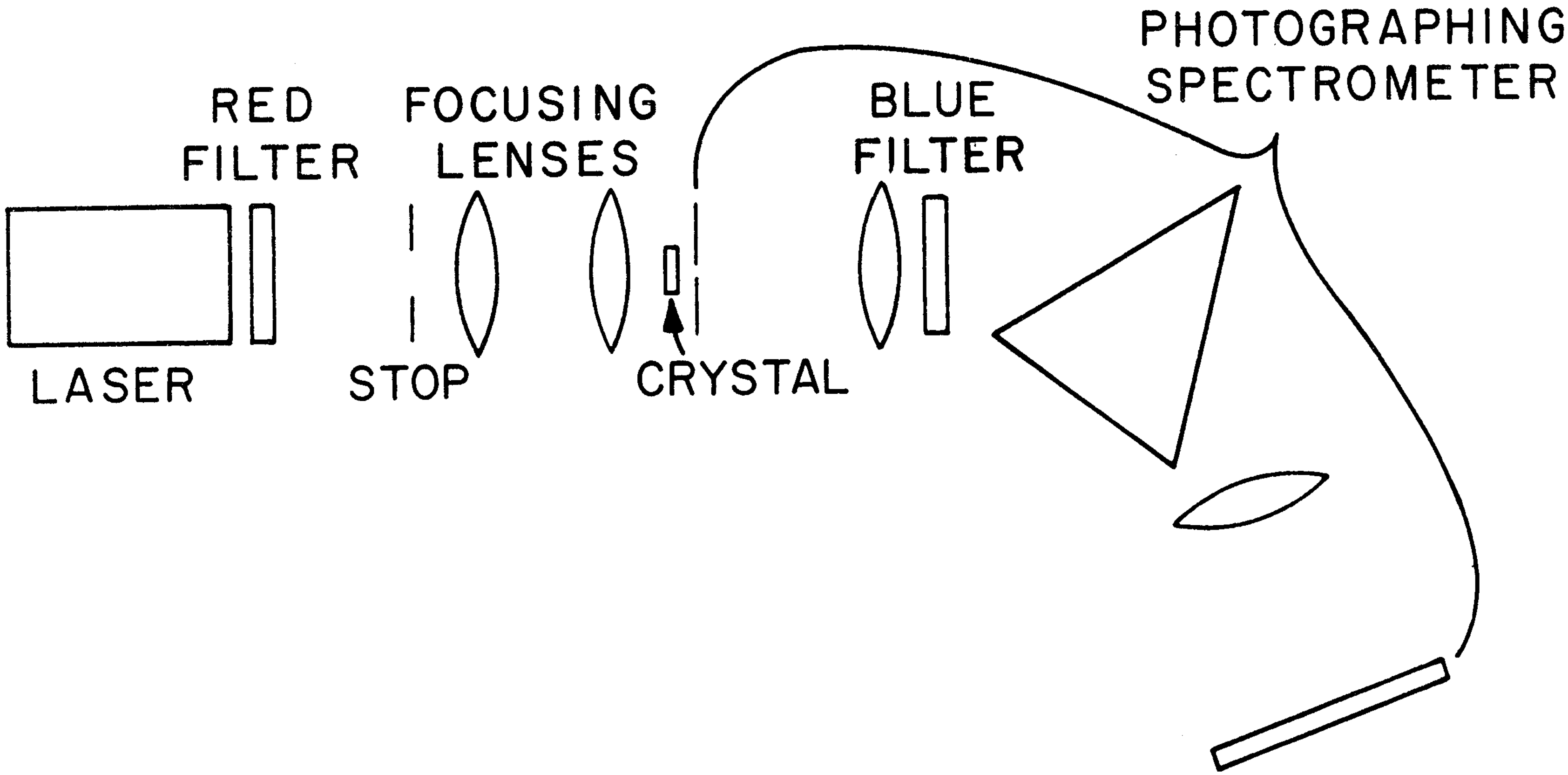

Figure 1   A block diagram of the experimental equipment.

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and sample so that blue and ultraviolet radiation from the flash lamp would not reach the sample. A blue filter Wratten #47 with $T \sim 0.50$ at $\lambda = 5000 - 4000$Å and $T < 10^{-3}$ at $\lambda = 7000$Å was placed between the spectrometer slit and the prism in order to avoid excessive blacking of the photographic plate. A picture of the output spectrum which was obtained by a single flash (~ 500 μsec) of the ruby laser is shown in Figure 2. The overexposed spot near $\lambda = 7000$Å is, of course, the radiation from the ruby laser. The exposed region near $\lambda = 5000 - 4000$Å shows clearly the three band character of the anthracene fluorescence. A second spectrum of the same experiment in which phenanthrene:anthracene has been replaced by $CaF_2:Eu^{2+}$ is shown for comparison.

In another experiment, two photomultiplier tubes were used to observe the intensity of the blue light relative to that of the red light. The outputs of the photomultiplier tubes were displayed on a dual beam scope and photographed. The integrated intensity of the blue light was then plotted against that of the red light. These data are shown in Figure 3. The point of interest here is the relationship

$$I_B \sim I_R^2$$

which is indicated by the slope of two.

The theory of a two photon absorption was first treated by Goeppert-Mayer[7] in 1931 and recently by Kleinman.[8] From Kleiman's work, assuming a quantum efficiency of one for the fluorescence of anthracene, we have the following expression for the number of fluorescent photons emitted per unit volume of the sample per second.

$$P_B = \left(\frac{e^2}{mc^2}\right)^2 \left(\frac{c^2}{n_c^2 \nu_R^2 \Delta\nu}\right) N \; F_R^2 \quad ,$$

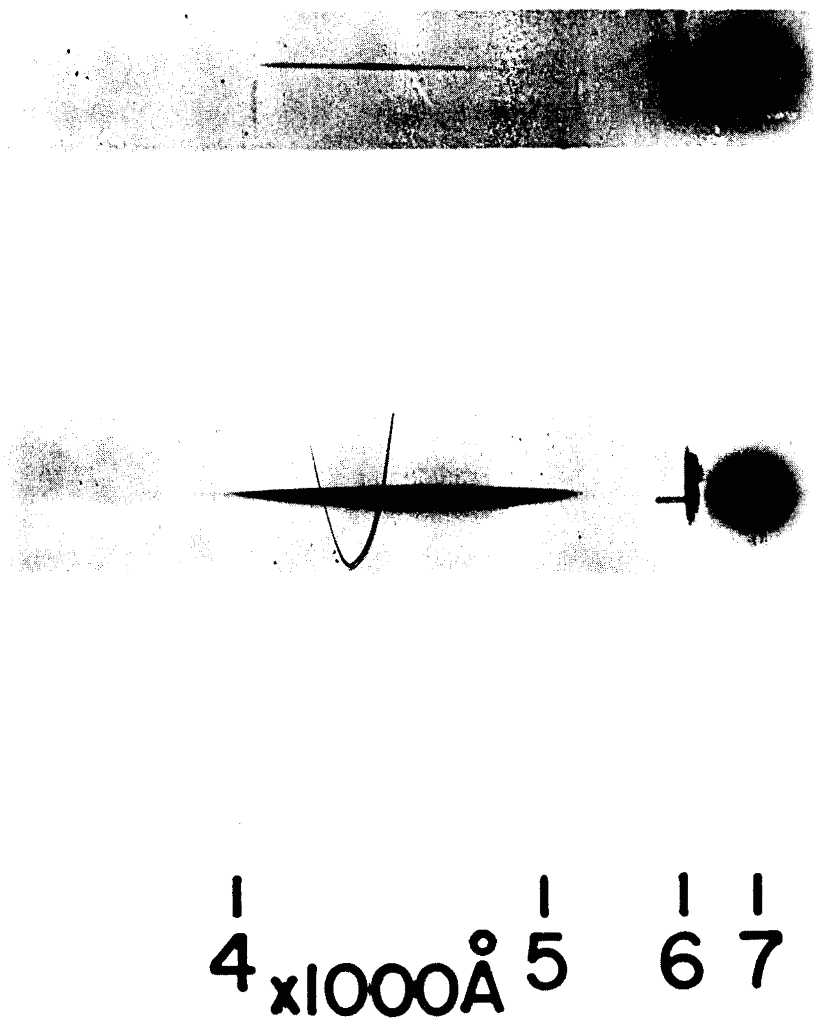

Figure 2 The two photon excitation in phenanthrene:anthracene (top) and $CaF_2:Eu^{++}$ (bottom).

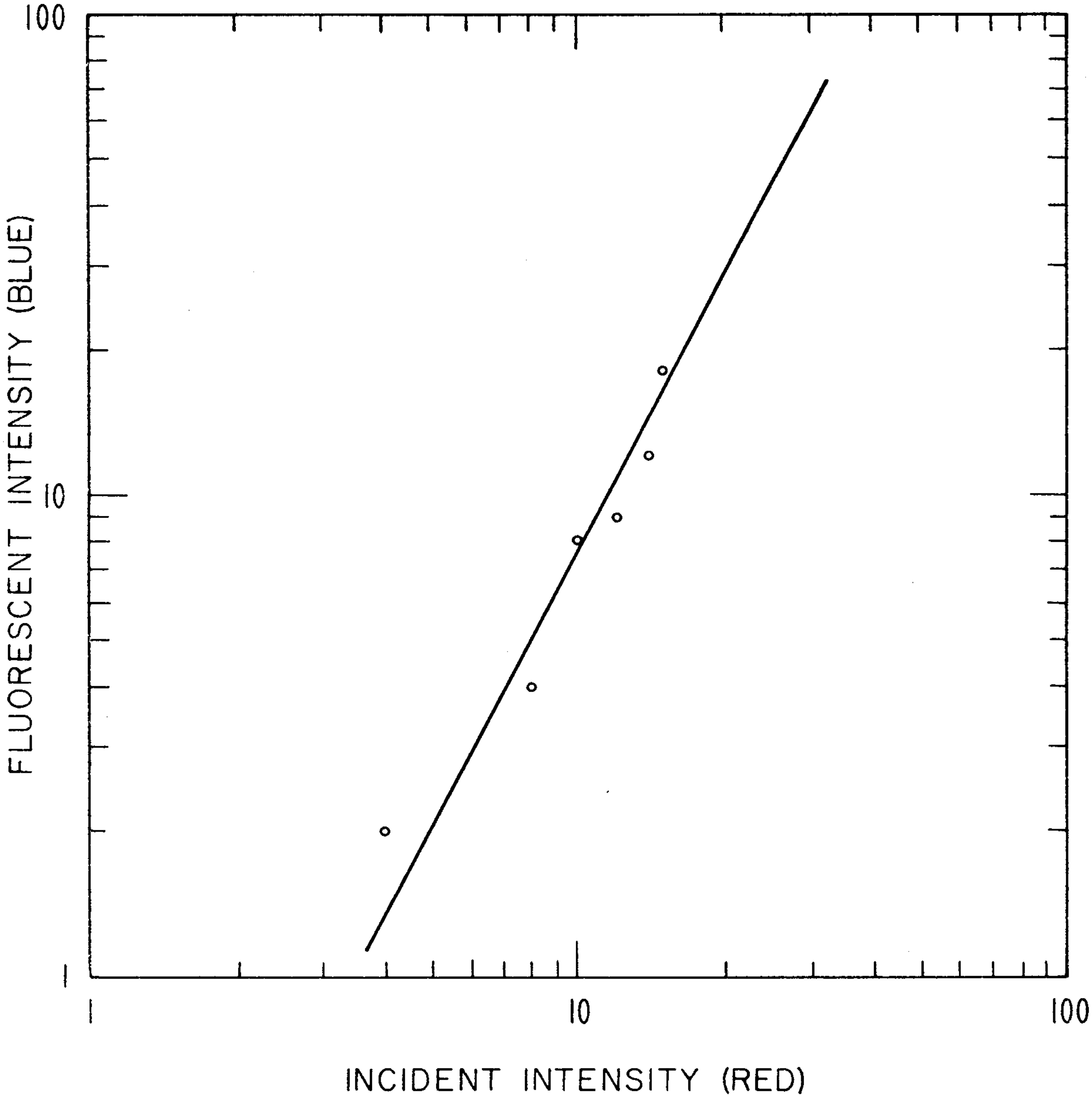

Figure 3 A log-log plot of the relative intensity measurements showing the square law dependence of the blue intensity on the red intensity.

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where e^2/mc^2 is the classical radius of the electron, c is the velocity of light, n_c is the index of refraction of the sample, ν_R is the ruby laser frequency, $\Delta\nu$ is the width of the absorption band of the crystal at $2\nu_R$, N is the number of absorbing centers per unit volume, and F_R is the incident photon flux from the ruby laser. In estimating P_B, the following data were used:

$$\frac{e^2}{mc^2} = 2.8 \times 10^{-13} \text{ cm},$$

$$c = 3 \times 10^{10} \text{ cm/sec}$$

$$n_c = 1.7,$$

$$\nu_R = 7 \times 10^{-5} \text{ cm},$$

$$\Delta\nu = 1.2 \times 10^{14} \text{ sec}^{-1},$$

$$N = 2.3 \times 10^{18} \text{ mol/cm}^3,$$

and

$$F_R \simeq 7 \times 10^{25} \text{ photons/cm}^2\text{sec}.$$

Then, the number of fluorescent photons to be expected is $P_B \simeq 10^{22}$ photons/cm^3/sec. The active volume of sample is 10^{-5} cm^3 so that in a single flash (500 μsec) one would expect 10^{12} fluorescent photons. However, one must consider the solid angle subtended by the spectrometer slit and the losses in the filter which are estimated to decrease the number of blue photons by a factor of 10^3. We estimate that there are approximately 10^9 blue photons at the exit of the spectrometer. This is in agreement with the number that we observe with the photomultiplier tube and from the blackening of the photographic plate by the anthracene fluorescence.

We believe that the observed anthracene fluorescence is an indication that anthracene has been excited by a two photon process. The observed $I_B \sim I_R^2$ dependence also is an indication that one is observing a two photon process. It is possible that the excitation we observe is through the phenanthrene since the phenanthrene crystal exhibits absorption in the spectral region $\lambda = 3500 - 3000\text{Å}$[6] and is fluorescent in the absorption region of anthracene $\lambda = 4000 - 3500\text{Å}$. However, we feel that this does not affect our interpretation of the results to any great degree.

The low symmetry of the phenanthrene crystal (monoclinic) might lead one to expect harmonic generation from the laser beam similar to that reported by Franken, et al.,[9] in quartz. The second harmonic of the laser beam generated by the crystal would also be effective in exciting the fluorescence of anthracene and would give the observed intensity dependence. Franken reports 10^{11} second harmonic photons per laser flash (3 joule, 500 μsec) from quartz and it would seem reasonable to expect that the harmonic generation efficiency in phenanthrene is no greater than that in quartz and very likely somewhat less. Since we have observed $\sim 10^{12}$ fluorescent photons per laser flash (2.5 joule, 500 μsec) we think that the two photon process is the more likely excitation mechanism.

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