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FLUORESCENCE OF CERTAIN ORGANIC DYES
EXCITED BY HELIUM-NEON LASER

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ABSTRACT

Fluorescence from several organic dyes (methyl violet, neutral red, thymol blue, cresol red, methyl orange, and orcein) has been observed upon irradiation with the red line from a continuous wave helium-neon laser. The process appears to involve two-photon absorption as the excitation step.

INTRODUCTION

Two-photon excitation of anthracene fluorescence has been recently observed.^{1,2,3} This communication serves to report preliminary results on apparent two-photon excitation of the fluorescence of several organic dyes in solution at room temperature. Possible analytical significance for this type of luminescence excitation is discussed with regard to the variation of fluorescence signal with concentration of the luminescing species.

EXPERIMENTAL

A Brice-Phoenix Universal Light-Scattering Photometer equipped with an RCA 1P28 Multiplier phototube was modified in the following manner. The lamp and its housing were removed and an 8 mW Perkin-Elmer helium-neon continuous wave laser was optically aligned for

sample excitation. A sharp-cut filter (Corning CS-2-63) was placed in the excitation path to block radiation below 580 nm. A sample tube holder was constructed from aluminum block and was sprayed with optically black paint. At ninety degrees from the laser excitation path a broad band pass optical filter (Corning CS-7-54) was used to isolate fluorescence emission. Excitation and emission path polarizers were employed to reduce scatter background signals. Corning 9741 glass tubing was used for the sample cell material (cells were approximately $3 \times 3/8$ inches). The high voltage power supply and electrometer of the Brice-Phoenix instrument and an American Instrument Company Solid State Microphotometer were used for signal measurement. A Heath EUW 20A strip chart recorder was employed for signal-to-noise ratio measurements.

Nineteen organic dyes were selected for study. Stock solutions of these dyes (0.1 mg./ml.) were prepared in aqueous or ethanolic 0.1 M HCl solutions depending upon solubility. Successive dilutions of the stock solutions were prepared by addition of the aqueous or ethanolic HCl solution.

RESULTS AND DISCUSSION

Of the nineteen dyes studied only six displayed significant and reproducible variation of signal with concentration. These six are: methyl violet, neutral red, thymol blue, orcein, cresol red, and methyl orange. The nature of the concentration variation of signal is demonstrated in Figure 1; in all cases the log of the square of the signal reading from the recorder is plotted against the log of the dye concentration. Two of the dyes showed only small fluorescence signals. The curves in Figure 1 are very nearly linear over a wide concentration range. Using the 8mW laser, detection limits

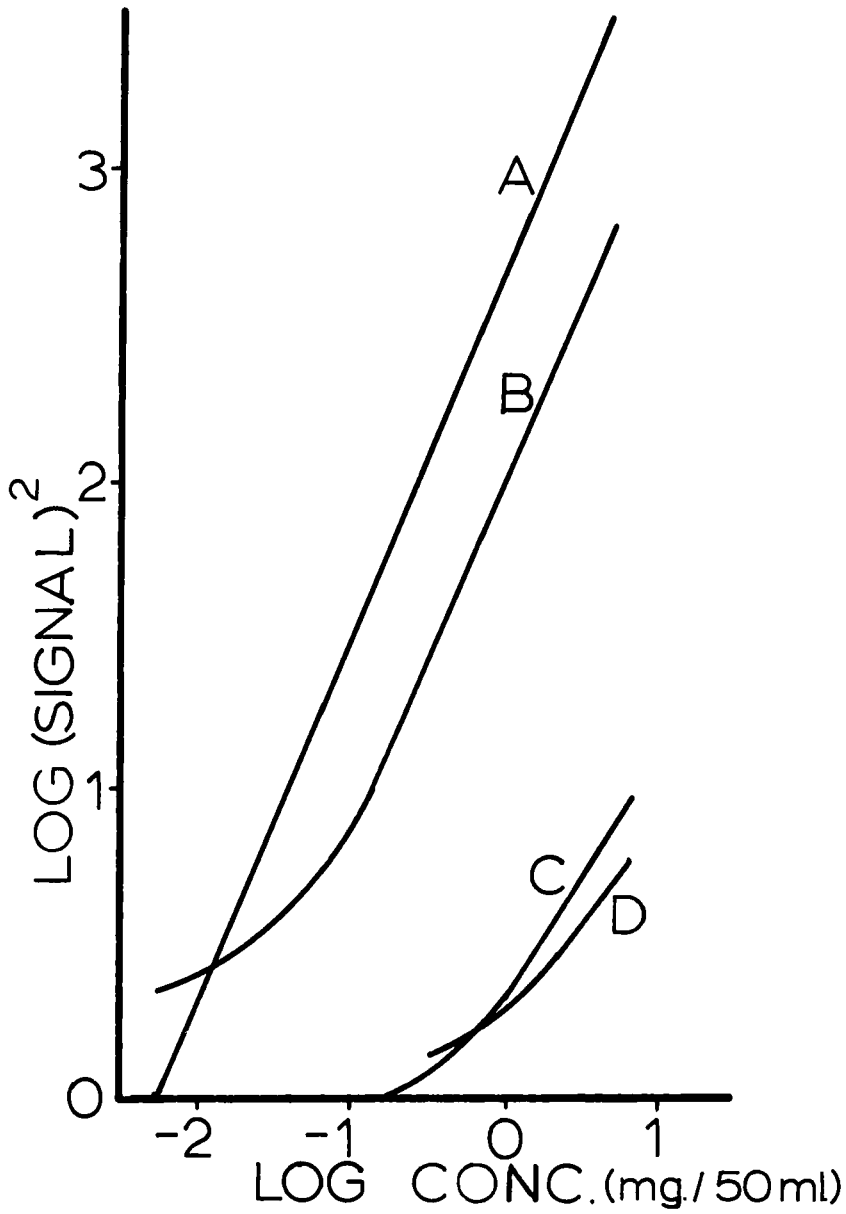


FIG. 1

Analytical curves for: A - neutral red; B - methyl violet;
C - thymol blue; and D - orcein.

for the four dyes showing intense laser excited fluorescence are listed in Table 1.

Table 1
Detection Limits of Dyes by Laser Excited Fluorescence

Compound	Detection Limit (mg./50 ml.)	Linearity Range (decades)
Methyl violet	0.005	2
Neutral red	0.005	3
Thymol blue	0.15	1
Orcein	0.31	1

Detection limits should easily be reduced by increasing laser power. In addition, the reduction of scattered background by suitable zero suppression and/or improvement on optical arrangement should lead to much lower limits of detection. Work is currently being carried out in this laboratory with these improvements in mind. It appears, also, that the mechanism for the production of this fluorescence is indeed, two-photon excitation. The plots in Figure 1 support this assumption. Further mechanistic interpretation is being performed in the laboratory. Other classes of compounds are currently being studied in order to determine the generality of this phenomenon.

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