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Fluorescence Studies of Electron-Beam Pumped POPOP Dye Vapor*

G. Marowsky and *F. P. Schäfer*

Max-Planck-Institut für Biophysikalische Chemie,
D-3400 Göttingen, Fed. Rep. Germany

*J. W. Keto** and *F. K. Tittel*

Departments of Physics and Electrical Engineering,
Rice University, Houston, TX 77001, USA

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Abstract. Fluorescence studies on electron-beam excited mixtures of POPOP dye vapor and various buffer gases are reported. Xenon has been found to be a promising candidate as a buffer gas for efficient energy deposition of the electron-beam and energy transfer to the POPOP dye vapor. These experiments may be an important step towards realization of an electrically excited dye vapor laser.

Organic lasers have become a very useful tool for a broad field of applications on account of their wavelength tunability, wide spectral coverage, and simplicity. Their usefulness could be considerably improved, if the overall efficiency, presently limited to the 1% range for flashlamp and even less for laser pumped systems, could be enhanced. This may be accomplished by direct electrical excitation which requires operation of the dyes in the vapor phase. Successful laser operation of a N_2-laser pumped solvent-free gaseous phase dye has been reported recently [1–3]. Various scintillator dyes show tunable laser emission in the UV spectral range [4], especially POPOP [*p*-phenylen-bis(5.-phenyl-2.-oxazol)], with a tuning range of 25 nm from 380 nm to 405 nm [5]. The excited singlet state manifold of the dyes in the vapor phase undergoes rapid thermalization, indicating that fast intramolecular relaxation processes occur even in the absence of an interacting solvent. The optimum performance characteristics are obtained under operating conditions similar to those of lasers using organic dye solutions. In order to achieve the necessary concentration of about 10^{-3} mole/l in the vapor phase, temperatures between 300 °C and 400 °C are required.

Experiment

The purpose of this paper is to describe experimental results on POPOP fluorescence under intense electron-beam excitation, which may be considered as a further step towards direct electrical excitation of organic dyes. For the first time strong fluorescence of POPOP vapor has been observed under bombardement with relativistic electrons from a Physics International Pulserad 110 electron-beam accelerator. This fluorescence could be considerably enhanced by adding various buffer gases. A schematic diagram of the experimental apparatus is shown in Fig. 1. A compact stainless steel cell was placed directly behind the field emission cathode-anode assembly of the accelerator. This cell had provisions for electrical heating, sapphire and quartz windows for optical access and gas hand-

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** Present address: Physics Department, The University of Texas at Austin, Austin, Texas, USA.

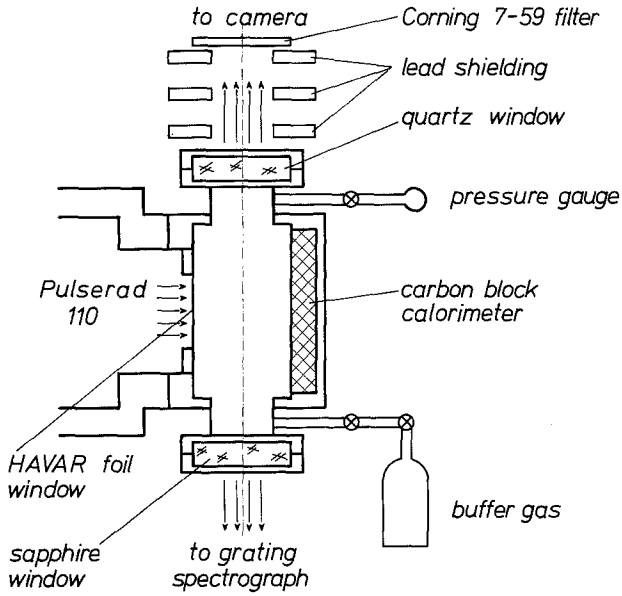

Fig. 1. Schematic of experimental apparatus

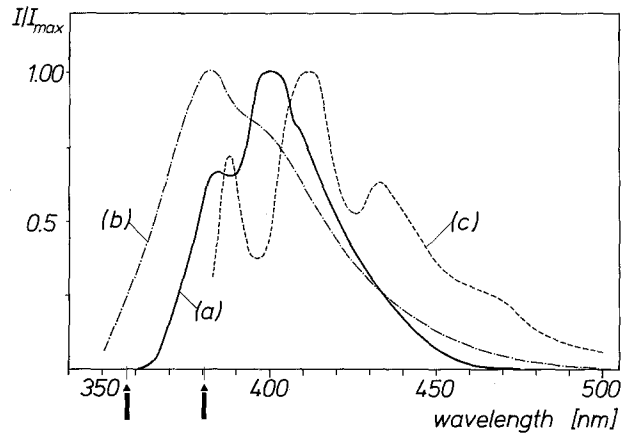

Fig. 2a—c. Normalized electron-beam excited fluorescence of POPOP dye vapor with xenon buffer gas (a) as a function of wavelength. Dashed curves from [4] depict optically excited POPOP fluorescence in the vapor phase (b) and in a $2.75 \cdot 10^{-5}$ molar liquid solution of POPOP in cyclohexane (c). Ar–N_2 laser lines at 357.7 nm and 380.5 nm used for calibration are indicated

ling connections for the introduction of buffer gases. The electron beam was injected into the chamber transverse to the optical axis. Energy measurements were performed with conventional carbon block calorimetry, indicating an energy input to the gas cell of up to 130 joules, as compared to approximately 200 joules (1 MeV, 20 KA, e-beam discharge of 10 ns duration), available from the electron beam accelerator before passage through a HAVAR [6] foil anode window of 25 μm thickness. This foil was used to cover a rectangular window (8 cm × 0.7 cm) which defined the electron-beam cross-sectional area. The construction of the gas cell allowed successful operation up to 400 °C at a total pressure of up to 3 atm. The optical emission of the POPOP vapor was monitored by a camera, suitably shielded with lead sheets against X-rays. In addition, an optical filter with transmission in the POPOP fluorescence region was placed in front of the camera. A grating spectrograph, calibrated by the Ar–N_2-laser lines at 357.7 nm and 380.5 nm [7, 8] was used to analyze the time integrated UV spectrum of the dye vapor.

Results

Figure 2 shows the electron-beam excited fluorescence spectrum of POPOP dye vapor taken at 260 °C with xenon buffer gas and two optically excited fluorescence spectra of POPOP in the gaseous and liquid phase. The electron-beam excited fluorescence was obtained by densitometric evaluation of the output of the grating spectrograph, as recorded on Polaroid film. The shape of the fluorescence in the presence of the buffer gas shows vibrational structures and a spectral position of the fluorescence maximum, intermediate between that of POPOP in the pure gaseous phase and in liquid solution. Optical pumping of POPOP vapor with the strong laser lines at 357.7 nm and 380.5 nm of an electron-beam pumped Ar–N_2-mixture was tried. However, even small amounts of POPOP vapor completely quenched the onset of superradiant laser emission. This quenching effect may be utilized to detect extremely small concentrations of POPOP vapor of the order of 10 ppb.

In order to exploit the efficient electron-beam energy deposition in pressurized gas mixtures systems reported in several recent publications [9, 10], we have studied the influence of different buffer gases (He, Ar, Xe, N_2, and SF_6) on the fluorescence characteristics of POPOP dye vapor. In the case of the rare gases the electron-beam energy can be efficiently and rapidly deposited and stored in excited atomic and molecular states of these gases and subsequently transferred to specific excited states of another potential laser material. This concept led to the de-

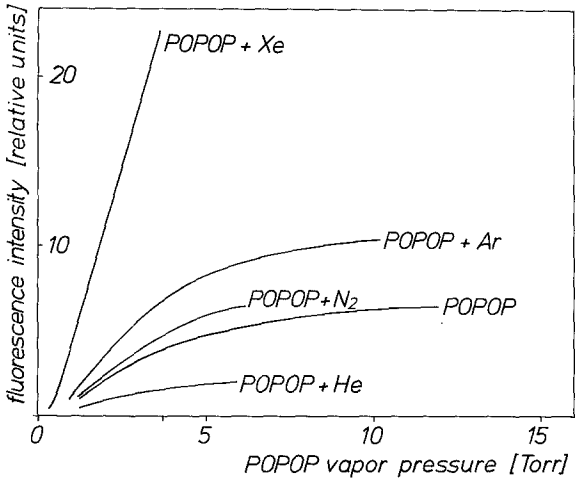

Fig. 3. Fluorescence intensity versus vapor pressure of POPOP dye vapor and several POPOP dye vapor—buffer gas mixtures. Buffer gases added at 100 °C at a constant pressure of 0.5 atm

velopment of the already mentioned Ar–N_2-laser [7, 8] and the highly efficient high power He–N_2-laser [9]. From Fig. 3 it is apparent that the addition of a rare gas buffer considerably changes the fluorescence intensity of POPOP vapor. The addition of buffer gases (Ar, He, N_2) resulted in a saturation of the POPOP fluorescence at higher pressures, similar to the behavior of pure POPOP vapor. One explanation of this saturation effect for the cases of Ar, He, and H_2 is that the energy stored by the electron beam in excited states of these gases is nearly totally removed at intermediate POPOP densities; then an increase in POPOP density produces little additional fluorescence. However, this does not explain saturation for pure POPOP as only a small fraction of the electron energy is removed from the electron beam by the dye. A possible explanation for all cases is the presence of a quenching state whose density is proportional to the POPOP density. This state may be a POPOP fragment generated by dissociation of the POPOP molecule by electron impact or energy transfer from excited buffer gas states. The density of the fragments and the rate of quenching would then be proportional to the POPOP density as observed. In the case of helium, the energy absorbed by the helium must preferentially result in the production of fragments rather than excitation of the dye. These fragments prevent the fluorescence of dye states excited by electron impact thus decreasing the overall intensity from that of pure POPOP. The effect cannot be explained by direct quenching by ground state helium atoms as [4] shows that the addition of He results in a negligible decrease of the fluorescence with optical excitation. In contrast to this behavior, the addition of xenon results in an increase in intensity by a factor of six over the fluorescent intensity of pure POPOP vapor; and the fluorescence rises linearly with vapor pressure as far as experimentally observed. This linearity suggests that energy transfer from excited states or ions does not result in dissociation of the POPOP molecule. The increased enhancement of the dye fluorescence with xenon over that of argon is greater than expected from the increased stopping power of xenon [11], suggesting that, in addition to reducing fragmentation, xenon may be more efficient in transferring energy to the dye vapor. Both the reduction of fragmentation and the more favorable energy transfer may possibly be due to better matching of excited states energy to the singlet-singlet transition of the dye. The deexcitation energy of He, Ar, and Xe molecules is 15, 9.9, and 7.2 eV, respectively [12], as compared to the required energy of 3.6 eV for population of the first excited singlet state of POPOP. The use of SF_6 as a buffer gas led to complete suppression of the dye vapor fluorescence. Although SF_6 should be a good candidate as a buffer gas in terms of its stopping power, either its large cross-section for cooling of secondary electrons or a small charge transfer or excitation transfer cross-section may prevent the significant production of radiating dye molecules.

Conclusion

In conclusion, intense fluorescence from electron-beam pumped POPOP dye vapor has been observed for the first time. These studies, including the influence of various buffer gases, are an important step towards achieving laser action in an electron-beam pumped dye vapor. Such a laser system would be an efficient source of tunable radiation capable of high power operation due to high energy storage capacity of the electron-beam pumped buffer gas and the absence of thermal schlieren effects created by heat absorption of the liquid solvent. Important problems that remain to be investigated before realizing electron-beam pumped dye laser action include studies of spin selectivity of the excitation transfer process and kinetic modeling of the various energy transfer mechanisms, particularly those leading to efficient resonant excitation.

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