

Intense electron-beam excitation of organic dye vapors

G. Marowsky

Max-Planck-Institut für biophysikalische Chemie, Abteilung Laserphysik, D-3400 Göttingen, Federal Republic Germany

F. K. Tittel and W. L. Wilson

Department of Electrical Engineering and Rice Quantum Institute, Rice University, Houston, Texas 77001

(Received 24 July 1980; accepted for publication 4 September 1980)

Experimental studies of electron-beam excitation of organic dye vapors of *p*-phenylene-bis-(5-phenyl-2-oxazole) POPOP and *p*-quaterphenyl have demonstrated short-duration high-gain and super-radiant laser behavior accompanied by severe fluorescence quenching due to dye fragmentation. This has been analyzed quantitatively by evaluation of the nitrogen fluorescence, originating from the complete breakdown of the POPOP structure.

PACS numbers: 42.55.Mv

INTRODUCTION

Electron-beam excitation of binary mixtures of organic dye vapors and rare-gas buffers has resulted in intense fluorescence output and optical gain as high as 0.2 cm^{-1} for short durations.¹⁻⁵ The purpose of our most recent research effort has been to determine why these mixtures do not exhibit resonator enhanced laser action in spite of the observed high-gain values. Our experiments have been conducted using the apparatus described in Ref. 6 in conjunction with time integrated, wavelength resolved optical multichannel analyzer (OMA) measurements and simultaneous recording of wavelength integrated time resolved (photodiode) measurements. In particular, the effect of an optical resonator on the dye-vapor emission characteristics and the influence of electron-beam pump excitation energy (i.e., 100-J excitation with a Pulserad 110 as compared to 500-J excitation from an Apex S³ machine) have been explored. Such studies have shown that the stimulated emission induced by a resonator lowered the degree of dye decomposition due to pronounced repopulation of the S_0 groundstate and hence a reduction of excited-state absorption.

EXPERIMENT

Figure 1 shows details of the high-temperature, high-pressure vapor cell with both electron beam and optical access which has been described in detail.⁶ The present cell design maintains good vacuum and pressure integrity for temperatures as high as 450 °C and pressure as high as 15 atm. High temperatures are necessary to produce dye-vapor pressures between 1 and 100 Torr. Absorption measurements with a 325-nm HeCd laser probe beam were used to verify equilibrium dye concentrations within the reaction cell. Careful thermal design of both the cell as well as the heating apparatus allows us to maintain a ± 1 °C profile across the cell. Wide-angle, high-pressure quartz or sapphire windows permit optical access to the interaction region. Both prealigned quartz resonators and externally adjustable intracell resonators were used. The Pulserad 110 accelerator delivered 1-MeV electron-beam pulses of 10-nsec duration full width at half maximum (FWHM) with an input energy of $\sim 100\text{J}$, resulting in current densities of up to 1 kA/cm^2 across an area of 10 cm^2 close to the anode foil. The electron-

beam pulses of the Apex S³ accelerator with a total energy of 500J had longer pulse duration (25 nsec) and higher current densities of 1-MeV electrons. Typically 80% of the incoming energy could be detected behind the titanium foil window and only a few percent of this energy was actually deposited in the active resonator volume close to the foil window at rare-gas pressures between 2 and 6 atm.

RESULTS

Registration of time integrated fluorescence spectra of e-beam excited dye vapors in the presence of a rare-gas buffer enabled us for the first time to observe a high degree of spectral narrowing that occurs with increasing gas pressures. Figure 2 shows a sequence of POPOP spectra taken at approximately 3 Torr of POPOP dye vapor pressure with in-

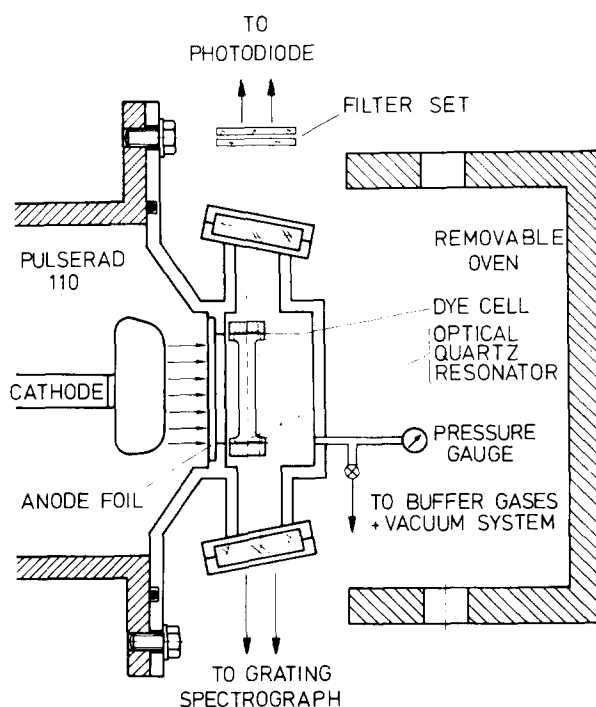


FIG. 1. Experimental setup showing Pulserad 110 e-beam accelerator diode, reaction cell (including prealigned quartz-resonator), and removable oven. (Further details cf. Ref. 6.)

POPOP + ARGON
(100 j excitation)

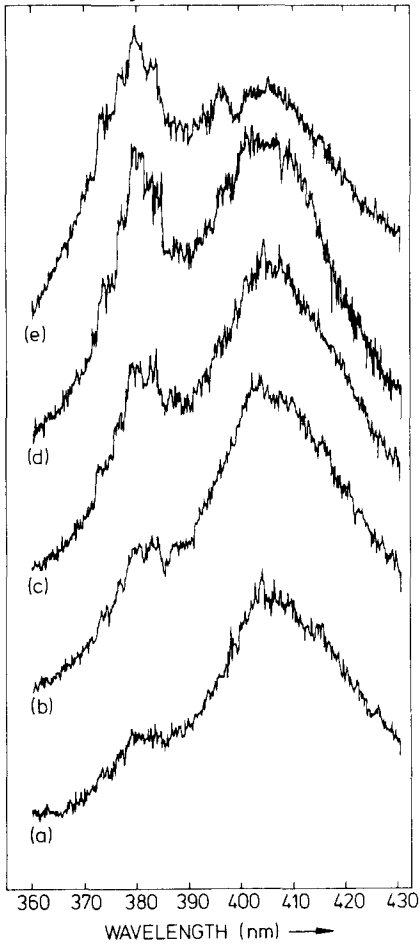


FIG. 2. e-beam excited POPOP fluorescence spectra in the presence of (a) 1-atm, (b) 2-atm, (c) 3-atm, (d) 4-atm, (e) 5-atm argon as buffer gas. Spectra have not been corrected for a factor-of-10 drop in spectral sensitivity between 410 and 380 nm of the OMA1 recording system.

creasing argon pressures from 1 to 5 atm. These spectra were not corrected for the spectral response of the OMA vidicon, which is flat below 380 nm and increases by one order of magnitude from 380 to 410 nm. The corrected fluorescence spectra exhibit the well-known characteristics of POPOP vapor with its main peak at 380 nm.^{7,8}

The spectra shown in Fig. 2 indicate cavity enhanced absorption features, which may be due to absorption of dye breakdown products or a consequence of the surrounding buffer gas. Figure 3 shows a comparison of POPOP spectra in the presence of elevated argon and neon pressures together with a preliminary assignment of potential breakdown products based on published spectral data. Only those absorption lines were identified that occurred consistently for consecutive excitation pulses, thereby ruling out spurious noise signals. It is evident from these data that neon is more effective in enhancing the fluorescence output at 7-atm buffer gas pressure compared to argon, whereas the degree of spectral narrowing is lower in both cases compared to 5-atm argon pressure (cf. Fig. 2). It is also evident that the cavity enhanced absorption peaks are more or less buffer-gas independent and appear to be due to POPOP fragments. If the chemical structure of POPOP is considered (see Fig. 4), the C-O bond is probably the most fragile bond, giving rise to breakdown of the structure and the subsequent release of such radicals as [CN],[CH], ..., [C₂], [H₂] listed in Fig. 4. A more stable organic dye-vapor laser candidate, *p*-quaterphenyl (*p*-QTP) was also studied for which only [C₂]-breakdown complexes were identified in its fluorescence spectrum (Fig. 5). This greater structural stability of *p*-QTP under intense e-beam excitation is in agreement with previous observations of Zuev *et al.*,⁹ who had already shown that optical UV excitation at 266 nm leads to a reduced quantum efficiency of POPOP as compared to the more stable *p*-QTP.

Use of the Apex S³ electron-beam accelerator allowed

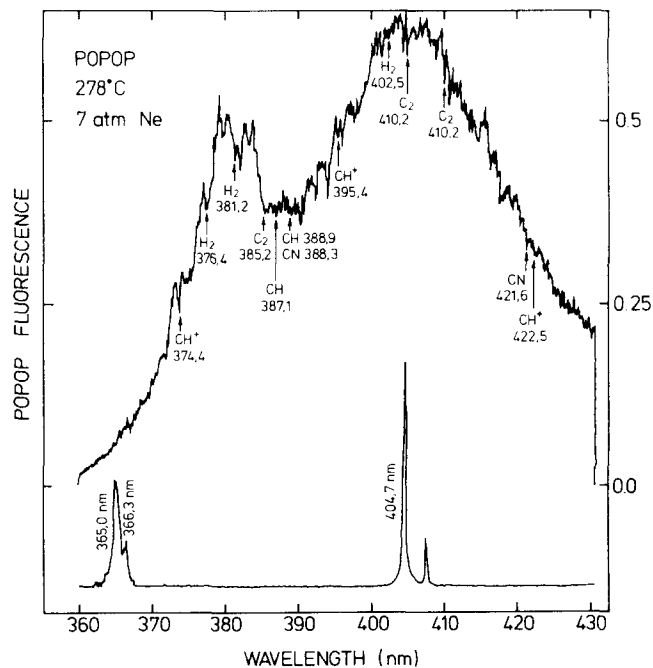
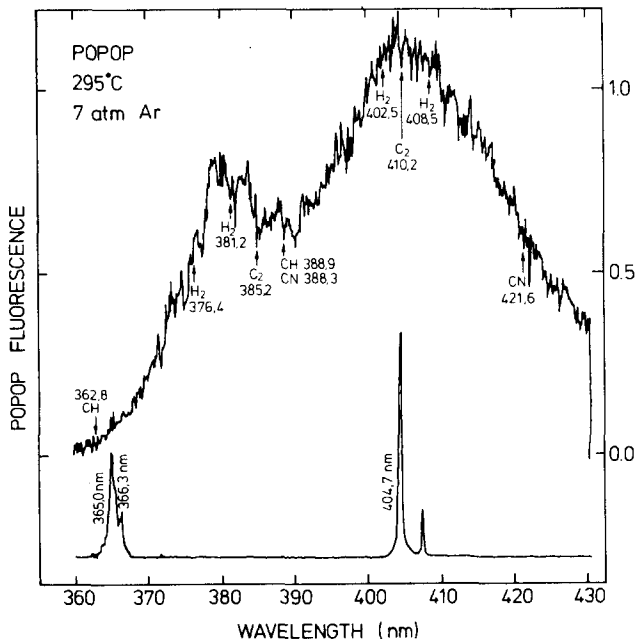


FIG. 3. Comparison of Ar- and Ne-buffered POPOP fluorescence identifying potential breakdown products. Hg spectral lines are indicated for wavelength calibration.

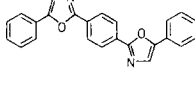
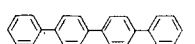
Dye Vapor	Breakdown Products
POPOP 	[H ₂], [N ₂], [C ₂], [CN], [CH], [CO]
p-Quaterphenyl 	[C ₂],

FIG. 4. Chemical structure and breakdown products of POPOP [*p*-phenylenebis(5-phenyl-2-oxazole) and *p*-quaterphenyl].

the study of high-energy (500 J) excitation of organic dye vapors. In addition to decomposition as a result of high-energy excitation, the dye fragmentation products were themselves so heavily excited that they exhibited fluorescence. The 500-J excitation leads to the appearance of N₂ fluorescence lines at 337.1, 357.7, 380.5, and 405.9 nm for a 6-atm argon buffered POPOP mixture (3-Torr POPOP partial pressure) in the presence of an optical resonator. This was usually not the case for low-energy 100-J excitation. However, upon removal of the resonator the OMA spectra taken with a high-resolution grating revealed the presence of several N₂ lines. Identification of N₂ lines in the POPOP fluorescence indicates complete dye fragmentation upon e-beam excitation. Quantitative measurement was possible by identification of several N₂ transitions from the N₂(C)-N₂(B) scheme shown in Fig. 6. Figure 7 shows a sequence of POPOP fluorescence spectra taken first in the absence of any additive N₂, then with the addition of 3 Torr and finally with 15 Torr of N₂. The short wavelength N₂ lines at 337.1 and 357.7 nm are absorbed by the dye vapor and do not aid optical pumping since buildup of N₂ radiation is too slow.³ A quantitative analysis of the N₂ fluorescence contribution (for appropriate reduction of POPOP background) at a selected spectral position of 405.9 nm from spectra shown in Fig. 7 yields the plot shown in Fig. 8. The observed N₂ lines result

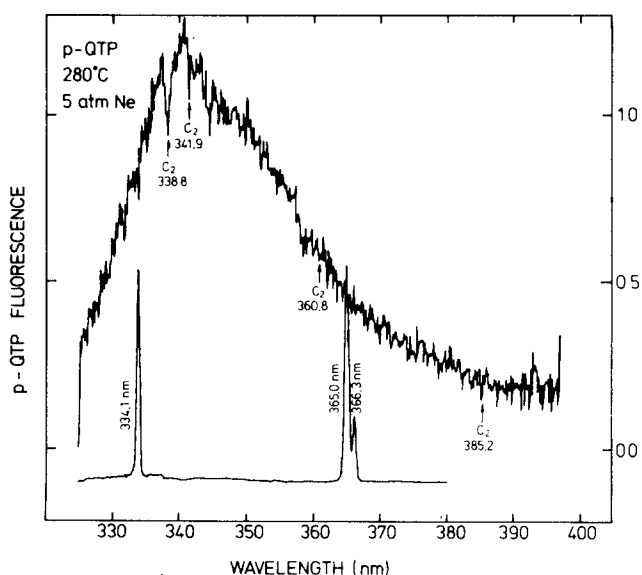


FIG. 5. *p*-Quaterphenyl fluorescence spectrum showing C₂ absorption features. An Hg spectrum is shown for wavelength calibration.

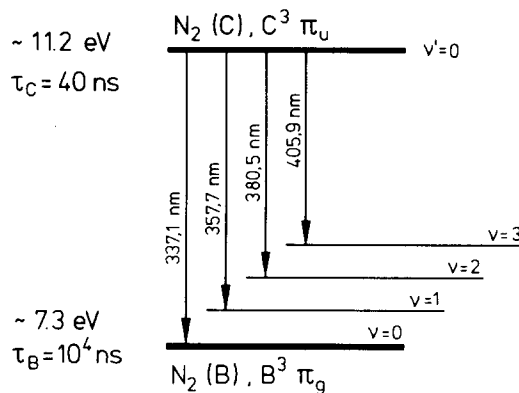


FIG. 6. N₂(C)-N₂(B) transitions (details cf. Ref. 10).

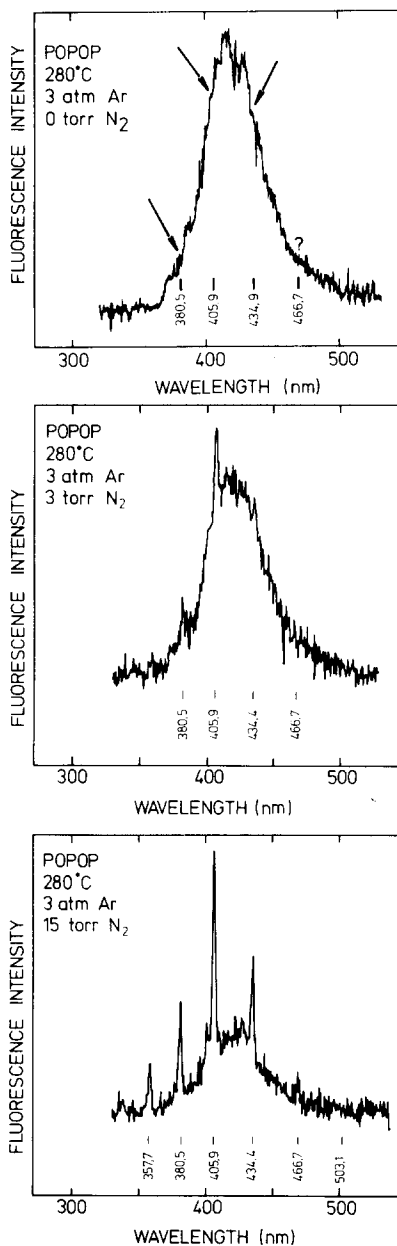


FIG. 7. Ar-buffered POPOP fluorescence with addition of 0-, 3-, and 15-Torr nitrogen.

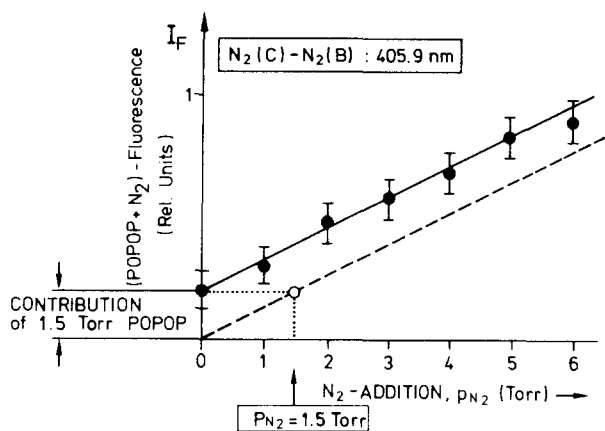


FIG. 8. Evolution of POPOP- N_2 fluorescence data taken from 405.9-nm transition of nitrogen to show contribution of nitrogen from breakdown of POPOP structure.

from the breakdown of an equivalent amount of POPOP dye. Similar plots can be obtained for the other N_2 lines shown in Fig. 7. On the other hand, the p -QTP spectrum (Fig. 5) indicates the absence of any N_2 contamination due to impurities, since no N_2 lines appear as in the case of e-beam excited POPOP mixtures.

CONCLUSION

So far, p -quaterphenyl has come the closest to resonator enhanced laser action on account of its higher structural stability under e-beam excitation. A comparison of two typical resonator enhanced laser shots ($R_1 = 100\%$, $r_1 = \infty$; $R_2 = 96\%$, $r_2 = 1m$) of p -QTP at 280 °C and 7-atm Ne as buffer is shown in Fig. 9 for a misaligned and an aligned resonator. From these two spectra an increase in intensity by one order of magnitude and a reduction in bandwidth by a

factor of 2 for the aligned resonator is apparent. Both spectra have mercury lines superimposed for calibration purposes and indicate absorption features by e-beam induced breakdown products. In particular, absorption of the C_2 complexes at 338 nm is apparent that has already been identified in Fig. 5.

Based on the above presented data it is possible to explain the fact that no reliable laser cavity operation has been achieved for e-beam excited organic dye vapors despite high-optical gain and significant spectral and temporal narrowing of the dye emission. As discussed in earlier publications² the e-beam excited fluorescence prevails only for approximately half of the time of the available excitation source (i.e., e-beam current, Ar metastables, as well as secondary products, such as delayed low-energy electrons). Therefore our present conclusion is that the leading edge of the excitation pulse excites the available dye vapor which results in optical gain. Deposition of the major portion of available pulse energy leads to complete fragmentation of the dye molecules, and as soon as this occurs the dye emission ceases. This is an immediate consequence of the high-electron energy of up to 45 eV (produced by decay of up to 3-Ar metastables) in the neighborhood of one dye molecule. Reduction of the pump excitation pulse length may reduce this effect. The rare-gas buffer is needed for stabilization of the fragile dye structure since both fluorescence and gain increase with buffer pressure. Hence we shall explore buffer gas systems (e.g., pentane) that are more effective in electron energy cooling to resonant energies as low as 3–4 eV, corresponding to the S_1 energy level, and also search for dyes with longer excited singlet lifetimes. Such dyes would allow better storage of the available buffer energy and no quasi-instantaneous decay as in the case of POPOP, although the possibility of harmful excited-state absorption effects that increase with S_1 lifetime cannot be ruled out.

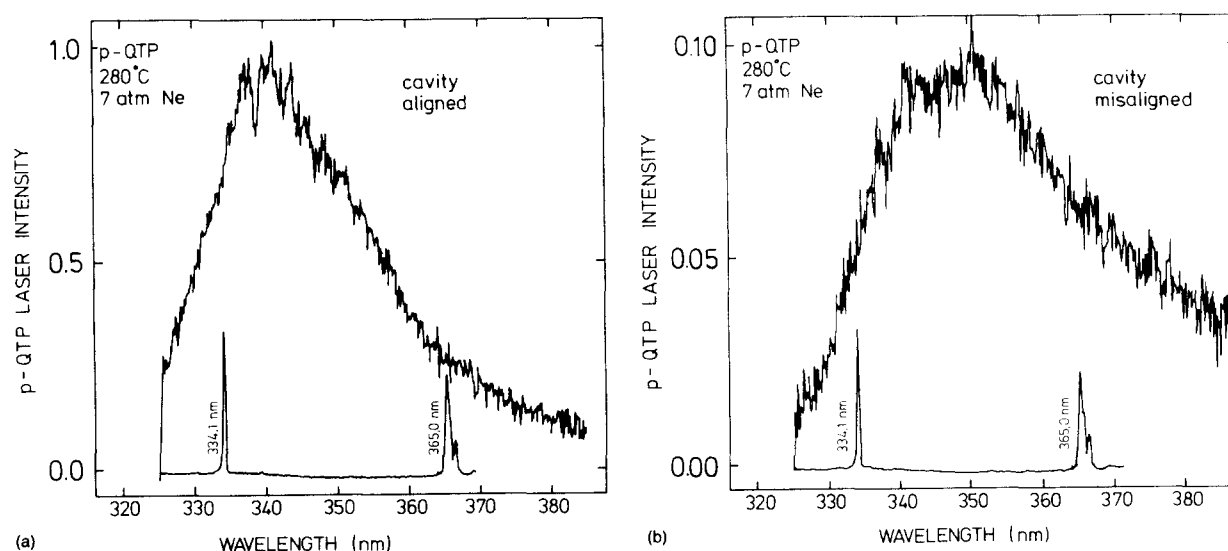


FIG. 9. Fluorescence and laser output of p -quaterphenyl (p -QTP) at (a) 280 °C and (b) 7-atm Ne buffer gas. Resonator consisted of a 100% reflector ($r = \infty$) and 96% output coupler ($r = 1m$) separated by 6 cm.

ACKNOWLEDGMENTS

Financial support by the Office of Naval Research, National Science Foundation, and the Robert A. Welch Foundation is gratefully acknowledged.

¹G. Marowsky, F. P. Schafer, J. W. Keto, and F. K. Tittel, *Appl. Phys.* **9**, 143 (1976).

²G. Marowsky, R. Cordray, F. K. Tittel, and W. L. Wilson, *Appl. Phys. Lett.* **32**, 561 (1978).

³G. Marowsky, R. Cordray, F. K. Tittel, W. L. Wilson, and C. B. Collins,

Appl. Phys. Lett. **33**, 59 (1978).

⁴G. Marowsky, G. P. Glass, F. K. Tittel, and W. L. Wilson, *Chem. Phys. Lett.* **67**, 243 (1979).

⁵G. Marowsky, *IEEE J. Quantum Electron.* **OE-16**, 49 (1980).

⁶G. Marowsky, R. Cordray, F. K. Tittel, and W. L. Wilson, *Appl. Opt.* **17**, 3491 (1978).

⁷B. Steyer and F. P. Schafer, *Appl. Phys.* **7**, 113 (1975).

⁸G. Marowsky, F. K. Tittel, W. L. Wilson, and E. Frenkel, *Appl. Opt.* **19**, 138 (1980).

⁹V. S. Zuev, O. A. Logunov, Yu. V. Saninov, A. V. Startsev, and Yu. Yu. Stoilov, *Appl. Phys.* **17**, 321 (1978).

¹⁰R. M. Hill, R. H. Gutcheck, D. L. Huestis, D. Mukherjee, and D. C. Lorents, Stanford Research Institute Report No. MP74-39 (1974).