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Electroluminescence of Liquid Dye Solutions in a Waveguide Cell

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Abstract. Luminescence from dye molecules is observed when a liquid dye solution is subjected to a high electric field. The structure and geometry of the electrodes and the refractive index of the dye solution make the cell a waveguide. The radiation pattern of the electroluminescence and the spectral dispersion of the emission are explained.

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Luminescence from fluorescent molecules has been observed when a liquid solution is subjected to a high electric field [1–3]. The mechanism of the formation of the excited state of the dye molecule could be one or more of the following: field excitation, ionisation-recombination, and secondary processes following the breakdown of the solvent. Although the dielectric breakdown of organic liquids has been studied extensively [4, 5], the mechanism that leads to the breakdown is not clear yet. In view of the many uncertain effects of high electric field in liquids an electrically pumped liquid dye laser, analogous to the vapour-phase dye laser [6], has not been realised. In this communication, we report the electroluminescence of dye solutions in a waveguide cell. Spectrally narrow dye emission apparently observed under some conditions is not due to amplified spontaneous emission, but due to dispersion effects in the waveguide cell.

A platinum plate was fused in glass (Schott AR 8418, $n_D = 1.516$) and polished to expose a cross section, 10 mm × 0.5 mm, of the platinum plate which acts as the electrode (Fig. 1A). The schematic cross section of the cell is shown in Fig. 1B. The spacing between the two electrodes was maintained at 20 µm by means of quartz fiber spacers. The electrodes were sealed after aligning them for maximum capacitance (10–15 pF with toluene as the dielectric medium). The mechanical arrangements which facilitate the rotation of one electrode and the clamping of the two electrodes are not shown in the figure. The dye solution flows through a hole in one of the glass parts of the electrode assembly into the cell gap and then out. Degassing of ~100 ml dye solution by argon gas bubbling was carried out outside the cell before the solution was flown in through a microfilter (pore size: 5 µm). POPOP (Lambdy-Physik laser grade), 9,10-diphenylanthracene (DPA, Aldrich Chemical, gold label, vacuum sublimed) and spectrograde solvents were used in the experiments. The high voltage pulse (up to 10 kV) was generated in a circuit similar to the one described in [7], but using a thyratron (HY 1102) as the switching device. The width of the high voltage pulse was ~30 ns.

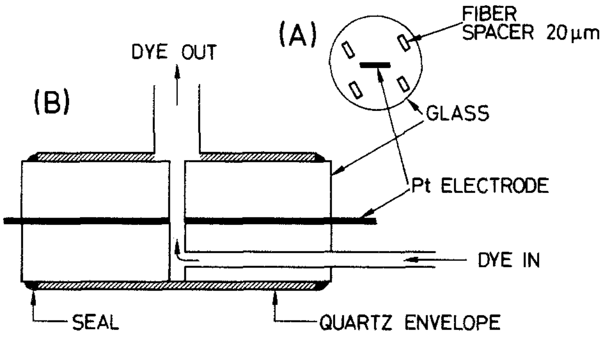

Fig. 1. Schematic cross sections of the electrode (A) and the cell (B)

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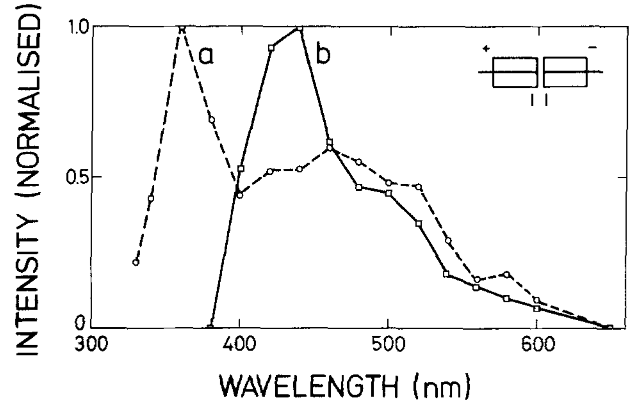

Fig. 2. The electroluminescence spectra of chlorobenzene (a) and POPOP (1×10^{-3} M) in chlorobenzene (b). Peak voltage: 4 kV, pulse width: 30 ns and electrode separation: 20 µm

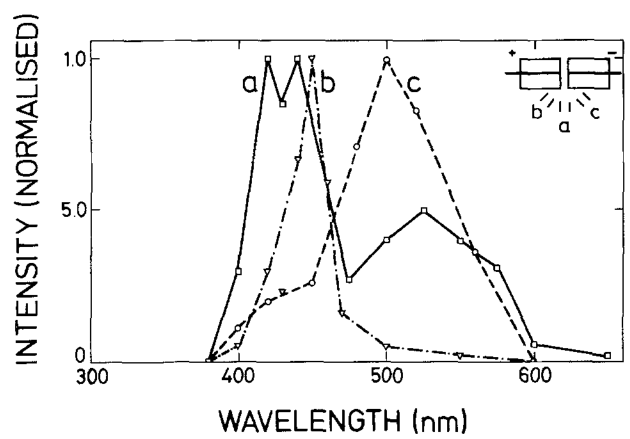

Fig. 3. The electroluminescence spectrum (see details in text) of POPOP (1×10^{-3} M) in toluene. Peak voltage: 5 kV, pulse width: 30 ns and electrode separation: 20 µm

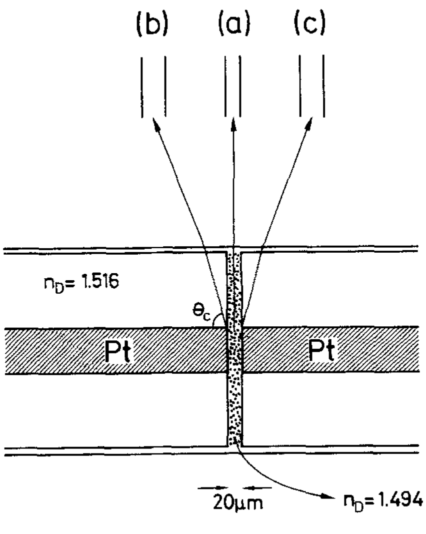

Fig. 4. The radiation pattern of electroluminescence in the hollow waveguide cell

When the electrodes and the solutions were fresh the threshold for electroluminescence was ~3–5 kV, corresponding to a peak electric field of 1.5 to 2.5×10^6 V/cm. After a few hundred pulses the threshold is lowered to $\sim 0.5 \times 10^6$ V/cm due to the deterioration of the electrode and the dye solution. The initial threshold is comparable to the dielectric breakdown of many hydrocarbon liquids [4, 5, 8]. The experimental data were obtained in the near-threshold region.

With chlorobenzene as the solvent, the solution filled cell gap acts as a waveguide since the refractive index of chlorobenzene ($n_D = 1.523$) is higher than that of glass ($n_D = 1.516$). The radiation pattern of the emission consists of an intense line centered at the cell gap. The electroluminescence spectra of chlorobenzene alone and that of POPOP (1×10^{-3} M) in chlorobenzene are shown in Fig. 2. The electroluminescence spectrum of chlorobenzene (Curve a) shows a band at 360 nm and a broad emission in the visible region. In the presence of POPOP the band at 360 nm is absent and POPOP luminescence is observed at 400–460 nm. The total luminescence intensities, with and without POPOP, are nearly identical. In view of the negligible influence of POPOP on the threshold electric field, the above results indicate that excited states of POPOP are formed essentially through secondary routes, namely, absorption of uv photons and energy transfer from excited species originating from chlorobenzene.

With toluene as the solvent, the solution filled cell gap acts as a hollow waveguide since the refractive index of toluene ($n_D = 1.494$) is lower than that of glass ($n_D = 1.516$). The radiation pattern of the electroluminescence of toluene or POPOP (1×10^{-3} M) in toluene showed a weak line at the centre and two intense bands on either side of the central line. The emission spectra of the three emission bands were obtained by using a slit (1 mm) to isolate the band, a lens to focus the emission onto the monochromator slit and a photomultiplier. The normalised spectra of the three bands are shown in Fig. 3. The emission band at the centre (a) shows the luminescence due to POPOP (400–460 nm) and a broad emission (480–600 nm) due to other species originating from toluene. The emission bands (b) and (c) show spectral features which are different from that of the central band (a). It is interesting to note that the spectral width of the emission band (b) is considerably small and overlaps with the luminescence spectrum of POPOP. However, the spectral maximum and the spectral width are sensitive to the angle of observation, thus indicating spectral dispersion in the radiation pattern.

The emission bands (b) and (c) emerge from the cell as shown in Fig. 4. The divergence of these two bands is ~27° and ray tracing indicates that these bands emerge at the critical angle θ_c as shown. The variation of the refractive index of toluene (1.493 at 656 nm to 1.518 at 434 nm) and that of glass (1.514 at 656 nm to 1.528 at 434 nm) implies that θ_c varies from 83.4° at 434 nm to 80.3° at 656 nm. This dispersion would account for the observed spectral narrowness and angular dependence. The radiation at critical angle could arise mainly due to two reasons: 1) The light incident at grazing angle near the edge of the electrode and 2) surface plasmons which may be created at the edge of the electrode which radiate into the high index medium (glass at $\cong \theta_c$).

The electroluminescence of DPA (1×10^{-3} M) in toluene was more intense than that of toluene alone. The radiation pattern was similar to that of POPOP in toluene. The increase in intensity in the presence of DPA is probably due to an additional route in which excited states of DPA are formed; namely, the creation of ions, DPA^+ and DPA^- and their recombination. The lower ionisation potential and higher electron affinity and, more importantly, the chemical stability of the ions [9] are more favourable for ionisation-recombination of DPA compared to POPOP.

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