

Artifacts and Trivial Effects in the Measurement of Delayed Fluorescence

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A spurious delayed fluorescence from perylene solutions is reported, and the experimental pitfall is discussed in relation to previous observations of delayed fluorescence.

IN contrast to the weak delayed fluorescence produced by exciting solutions of perylene at room temperature with light of wavelength 436 nm,¹ we observed a relatively much stronger delayed fluorescence when the same solutions were excited by light of wavelength 250 nm. However, the following observations showed that this emission was not *P*-type delayed fluorescence. First, the intensity of the delayed emission was proportional to the first power of the rate of light absorption. Secondly, aeration of the solution reduced the intensity by only the same small amount as it reduced the intensity of the prompt fluorescence. Thirdly, the intensity was dependent on the material of the container and the geometrical arrangement used for illumination and viewing; with containers of phosphorescent fused quartz the intensity was greater than with containers of the less phosphorescent synthetic silica. Frontal illumination, in which the liquid near the illuminated cell face was viewed, gave a greater intensity of perylene delayed fluorescence than right-angle illumination in which the observations were made on liquid further removed from the illuminated cell faces. We therefore conclude that most of this delayed fluorescence was an artifact, *i.e.*, it was in reality prompt fluorescence excited by absorption of the phosphorescence emitted by the material of the cell, and that the triplet formation efficiency of perylene with short-wavelength excitation is probably as small as with long-wavelength excitation. The absorption band of perylene is favourably situated for the production of this artifact because the main phosphorescence of fused quartz is emitted in the region 370–430 nm. Anthracene, which absorbs little at wavelengths longer than 380 nm, gave much less delayed emission than perylene in aerated solution.

The causes of such spurious delayed fluorescence are not restricted to phosphorescence of containers. If the delayed emission from one component of the solution itself is situated in a spectral region absorbed by a second component, it will excite prompt fluorescence of the latter (a "trivial effect"), and this prompt fluorescence will decay at a rate identical with that of the delayed emission of the first component. We have therefore scrutinised all cases of delayed fluorescence previously reported by us to determine whether the trivial effect or the artifact could have been responsible. We can eliminate their occurrence in all those experiments with solutions containing a single fluorescent component excited in its first absorption band, since any phosphorescence of the container would not then be absorbed

by the solution. Similarly, most cases of sensitised delayed fluorescence can be exonerated because, with concentrations of acceptor sufficient to absorb an appreciable proportion of the donor emission, the latter was completely quenched. The dependence of the rate of decay of the two emissions on the acceptor concentration was also quite different. There is one kind of delayed fluorescence reported by us which is suspect, namely, that produced by mutual sensitisation.² We have reinvestigated the case of proflavine hydrochloride and have found that, although the trivial effect is appreciable in some solutions, it does not account for more than a small proportion of the sensitised delayed fluorescence of proflavine hydrochloride.

The fact that the triplet formation efficiency of perylene is small in fluid solution suggests that it may also be small in rigid solution at 77° K. It might then be necessary to find an alternative explanation for the delayed fluorescence observed by Stevens and Walker.³ We have attempted to repeat their experiments using a liquid paraffin solution in a synthetic silica cell, and excited by light of wavelength 250 or 297–302 nm. Although the liquid paraffin had been passed over alumina, it still gave rise to a broad band of phosphorescence emission extending from 380 nm to longer wavelengths. This showed a non-exponential decay similar to that of the perylene delayed fluorescence. Solutions of perylene in ethanol at 77° K gave a much weaker phosphorescence from impurities, and the delayed fluorescence of the perylene was also 30–100 times weaker. Measurements of the delayed emission from the same ethanolic solution at 77° K in a fused quartz vessel showed phosphorescence in the 400 nm region greater than in the synthetic silica vessel, and the delayed emission from the perylene was also 2–3 times greater. These results suggest that most of the delayed fluorescence was due either to the artifact (with the ethanolic solution in the fused quartz vessel) or to the trivial effect (with liquid paraffin in the synthetic silica vessel).

The artifact and the trivial effect may also be expected to occur in the measurement of other forms of luminescence, for example, in the measurement of thermoluminescence spectra.

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¹ C. A. Parker and T. A. Joyce, *Chem. Comm.*, 1966, 108.

² C. A. Parker, C. G. Hatchard, and T. A. Joyce, *Nature*, 1965, **205**, 1282.

³ B. Stevens and M. S. Walker, *Chem. Comm.*, 1965, 8.