

PRESSURE EFFECTS ON THE TRIPLET EXCIMER EMISSION IN PYRENE

O.L.J. GIJZEMAN, J. LANGELAAR and J.D.W. VAN VOORST

*Laboratory for Physical Chemistry, University of Amsterdam,
Amsterdam, The Netherlands*

Received 1 September 1971

Application of pressure to powdered pyrene is found to induce broad triplet excimer emission originating from lattice defects. Another type of defect is also created, giving rise to structured monomer emission.

1. Introduction

The triplet excimer emission from pyrene single crystal flakes has been found to possess a broad and a structured component [1] with a vibrational progression also observed in the phosphorescence of isolated pyrene molecules. In general several conditions can determine the lineshape. Firstly, in the crystal the geometrical structure of the excimer pair may differ from one to another excimer, giving rise to a spread in transition energy and thus to an inhomogeneous line broadening. A similar effect is expected for the triplet excimer emission in fluid solution, although in this case the repulsive situation in the ground state, which is connected to a continuum of translational levels may contribute to a diffuse lineshape. On the other hand a slackening of a vibrational progression can also originate from a large excimer interaction, giving rise to a homogeneous line broadening.

In an earlier report [1] the broad triplet excimer emission in pyrene single crystal flakes was attributed to excimers formed on lattice defects. More evidence for this assignment is given by the enhanced emission of previously compressed powders.

2. Results

The following results have been obtained:

(a) In an uncompressed powder at room tempera-

ture no broad excimer emission at 13800 cm^{-1} could be detected.

(b) However, when before the measurement the powder was treated with pressures up to 15 ton/cm^2 the broad emission could be detected also at room temperature.

(c) After a pressure treatment also a very weak structured emission (quantum yield $\approx 10^{-6}$) can be detected on the tail of the delayed excimer fluorescence (see fig. 1). The progression as well as the position of the individual bands coincides with those of

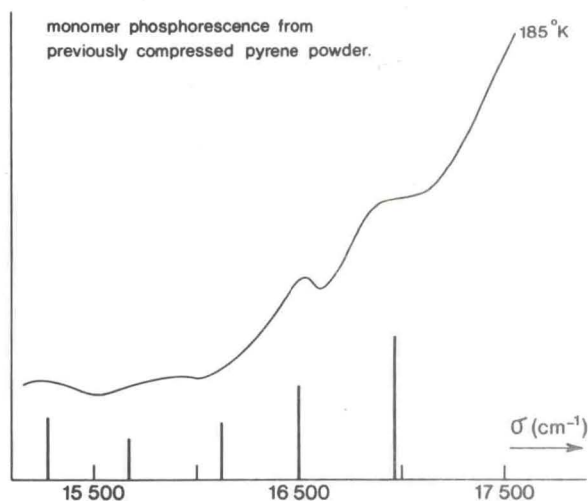


Fig. 1. Monomer phosphorescence from previously compressed pyrene powder. The solution spectrum is indicated by vertical bars to show the agreement in band position.

the monomer phosphorescence as obtained in rigid glass or fluid solution [2]. At lower temperatures this emission disappears in the red shifted delayed excimer fluorescence which is much more intense than the monomer phosphorescence.

(d) Below 200°K previously compressed powders also show structured triplet excimer phosphorescence with a similar quantum yield as uncompressed powders.

(e) It has been verified that the delayed excimer fluorescence intensity depends almost quadratically upon the exciting light intensity (see table 1).

3. Discussion

The observation of the broad emission at room temperature and the increase in the broad emission after a pressure treatment of a powder sample shows clearly that the broad emission cannot be due to impurities.

Since it is known [3] that the application of pressure on the powder of an aromatic crystal results in the creation of lattice defects, this supports our previous assignment of this emission to a triplet excimer trapped on a lattice defect.

Of particular interest is the appearance of monomer phosphorescence in the crystalline state. Since this has the same location and progression as in liquid and solid solutions the created defect is to be attributed to a pyrene molecule without sandwich partner. The location of the monomer phosphorescence is also in complete agreement with the $S_0 \rightarrow T_1$ absorption spectrum reported by Avakian and Abramson [4]. Additionally the observation of monomer phos-



Table 1
Values of the exponent c , relating emission and exciting light intensity according to $I_{em} \propto I_{exc}^c$

T (°K)	power dependence of exciting light
300	1.75
203	1.67
133	1.54
90	1.78
77	1.72
4.2	1.63

phorescence supports the assignment of the structured emission with 0-0 band at $15\,200\text{ cm}^{-1}$ to an excimer emission.

Acknowledgement

The investigations were supported in part by the Netherlands Foundation for Chemical Research (SON) with financial aid from the Netherlands Organisation for the Advancement of Pure Research (ZWO).

References

- [1] O.L.J. Gijzeman, J. Langelaar and J.D.W. van Voorst, *Chem. Phys. Letters* 5 (1970) 269.
- [2] J. Langelaar, R.P.H. Rettschnick and G.J. Hoytink, *J. Chem. Phys.* 54 (1971) 1.
- [3] S. Arnold, W.B. Whitten and A.C. Damask, *J. Chem. Phys.* 53 (1970) 2878.
- [4] P. Avakian and E. Abramson, *J. Chem. Phys.* 43 (1965) 821.