

## PHOSPHORESCENCE OF ORTHO-BROMOBENZOPHENONE FROM 1.6 K TO MELTING

M. A. STRZHEMECHNY, A. A. AVDEENKO, O. S. PYSHKIN, and L. M. BURAVTSEVA, *Verkin Institute for Low Temperature Physics & Engineering, Kharkov 61103, Ukraine.*

The basic mechanisms of the triplet exciton phosphorescence and transport in organic molecular solids, both in their crystalline and vitreous forms, are well known. They include resonance jumps (in crystals) or random walks (in glasses) from molecule to molecule with subsequent inherent and trap-promoted emission. The tacitly implied important factor is insignificance of the excitation-promoted conformational changes, which is actually true in most cases, for example, in solid unsubstituted benzophenone, an ideal model system in this field. It is interesting to understand whether large enough excitation-related conformational changes are able to modify the basics of triplet exciton emission and transport.

Ortho-bromobenzophenone (2Br-BP), which drastically changes its molecular shape upon electronic excitation<sup>a</sup>, is very suitable for this purpose. Like unsubstituted benzophenone, it can be easily vitrified, allowing a comparative study of phosphorescence and, on the basis thereof, triplet exciton transport in the crystal and glass phases. In this report we present results related only to part of the problem, namely, phosphorescence in both morphologic states of 2Br-BP.

At low temperatures up to 10 K, the phosphorescence spectrum of 2Br-BP glass exhibits a single, evidently monomeric vibronic progression of 4-5 bands separated by the carbonyl stretch frequency of about  $1700\text{ cm}^{-1}$ . In the crystal, *two* similar series appear, one of which, barely discernable, roughly coincides with that in the glass while the other, much stronger band is considerably (by about  $1100\text{ cm}^{-1}$ ) blue shifted. As the temperature increases, the weaker series intensifies while the high-energy one grows dimmer to disappear at around 60 K. Concurrently, at temperatures above 50 K the crystal spectrum reveals two red-shifted very broad bands, which persist up to room temperatures, the monomeric emission disappearing at around 180 K. Structure data and special time-resolved and varying-excitation-intensity experiments allowed us to conclude that this emission is due to a single-photon-excited bimolecular triplet excimer. Similar, somewhat modified excimer features are observed in the glass as well.

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<sup>a</sup>A. A. Avdeenko, O. S. Pyshkin, V. V. Eremenko, M. A. Strzhemechny, L. M. Buravtseva, and R. V. Romashkin, *Low Temp. Phys.* 32, 1028 (2006).