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To cite this version:
H. Wolf. EXCITONS IN ORGANIC MOLECULAR CRYSTALS. Journal de Physique Colloques, 1967, 28 (C3), pp.C3-127-C3-128. <10.1051/jphyscol:1967326>. <jpa-00213277>

HAL Id: jpa-00213277
https://hal.archives-ouvertes.fr/jpa-00213277
Submitted on 1 Jan 1967

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EXCITONS IN ORGANIC MOLECULAR CRYSTALS

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1. Introduction. — Excitons in organic crystals are perhaps better understood than in any other substance. There are many similarities with excitons in other types of crystals, for instance Cu2O, CdS, alkalai halides. Excitons in organic crystals are the extreme case of molecular excitons, this means very small excitons. Therefore they are of interest not only for specialists in organic crystal spectroscopy but also for other branches of solid state physics.

Since the author has given several recent review articles on excitons in organic crystals [1, 2, 3] the reader is referred to these articles. The following is only a brief summary on experiments showing the mobility of excitons.

2. The Davydov-splitting. — The Davydov-splitting in absorption and emission spectra is directly proportional to the rate of energy exchange between two neighbour molecules [1]. The magnitude of the Davydov-splitting can be calculated for singlet states using dipole or multipole interaction. In triplet states the Davydov splitting is determined by exchange interaction. Using ESR-spectroscopy one is able to measure the rate of energy exchange within one unit cell of the crystal directly. The measured value for naphthalene is 5 cm−1 [4].

3. Structure of the exciton band. — In many cases exciton lines are resonance lines in absorption and emission. This shows that \( k = 0 \) is in the minimum of the exciton band.

The temperature dependence of line width and line shape is very characteristic. Free exciton emission lines without phonon or vibronic interaction are symmetric; they are determined by the \( k \)-selection rule. The minimum line width at lowest temperature is in principle a measure for the region of coherence of the exciton. But due to crystal imperfections the lines are broadened [1]. Vibronic exciton emission lines are not limited to transitions from \( k = 0 \). Therefore the line shape of these lines reflects the energy distribution within the exciton band. It can be shown that a Maxwellian velocity distribution of excitons in the band is a good first approximation [5, 6].

Emission lines which are due to localised excitons, for instance impurity molecules or disturbed exciton states, have a very characteristic structure at lowest temperature. An extremely sharp zero phonon line is accompanied by a nicely structured one-phonon wing. This structure can be used to measure the phonon spectrum of the host crystal [6].

4. The structure of absorption and emission spectra. — One has to distinguish between exciton series of the pure crystal and disturbed exciton series [1] due to chemical or crystallographical imperfections. These disturbed exciton series are the analog to the \( \beta \)-bands in the alkalai halides. They are very characteristic for organic crystals. Measuring temperature dependence of intensities, the spectroscopic and thermal energy gaps can be compared. For singlet states [7] and triplet states [8] one finds excellent agreement. Disturbed triplet exciton states play an important role in the process of low temperature delayed fluorescence by triplet triplet annihilation [8].

5. Energy transfer. — Energy transfer can be studied by direct measurement of exciton diffusion [9] or by sensitized fluorescence [3]. Hopping model and band model are competing to give an appropriate theoretical analysis. Still more accurate measurements of the temperature dependence of sensitized fluorescence have to be done in order to answer the question which is the energy transfer mechanism.

6. Characteristic experimental values. — For excitons in crystals like naphthalene or anthracene the following numerical values are representative:

<table>
<thead>
<tr>
<th></th>
<th>Singlet excitons</th>
<th>Triplet excitons</th>
</tr>
</thead>
<tbody>
<tr>
<td>Davydov-splitting</td>
<td>200 cm⁻¹</td>
<td>10 cm⁻¹</td>
</tr>
<tr>
<td>Hopping time of energy</td>
<td>10⁻¹³ s</td>
<td>10⁻¹¹-10⁻¹² s</td>
</tr>
<tr>
<td>between two neighbours</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Number of hops per lifetime</td>
<td>10⁴-10⁶</td>
<td>10⁰-10¹²</td>
</tr>
<tr>
<td>Diffusion coefficient</td>
<td>10⁻⁻²-10⁻⁵ cm² s⁻¹</td>
<td>10⁻⁻²-10⁻⁶ cm² s⁻¹</td>
</tr>
<tr>
<td>Diffusion length</td>
<td>10⁻⁻²-10⁻⁵ cm</td>
<td>10⁻⁻³-10⁻⁴ cm</td>
</tr>
</tbody>
</table>
References

[6] HAMMER (A.) and WOLF (H. C.), to be published.


DISCUSSION

I. BROSER. — What are the essential differences between the excited states called by you «local excitons» or «disturbed excitons»?

H. C. WOLF. — Localized excitons show in their fluorescence vibronic states of the guest molecules. Disturbed excitons have vibronic transitions characteristic for the host.