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Luminescence and ODMR studies of X-traps for triplet excitons in organic crystals

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The excited triplet states of shallow X-traps in neat single crystals of 4,4′-dichlorobenzophenone were studied at liquid helium temperature by liminescence spectroscopy and magnetic resonance with optical detection. The vibrational phosphorescence bands, the polarization of phosphorescence spectra, and the triplet zero-field splitting parameters of these traps have been analyzed. A specific model of the structure defect (a molecule is turned by 180° on its long axis) has been considered in organic crystals of benzophenone type which consist of molecules whose dipole moments compensate each other in a unit cell. The calculated depth of such a dipole X-trap for triplet excitons in 4,4′-dichlorobenzophenone crystals at the account of a defect molecule relaxation upon its slewing was found to be comparable with the experimental one.

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1. Introduction

The electron excitation energy transfer by excitons in real organic crystals can be interrupted because of the existence of trapping centers. Those centers are formed by the structure defects and impurities [1,2]. In pure crystals the trapping centers, the so-called X-traps, are mainly attributable to the lattice imperfections [3]. Of great interest is to study the nature of X-traps. In organic crystals consisting of molecules with a large dipole moment the structure defects can induce the appearance of so-called dipole traps [4].

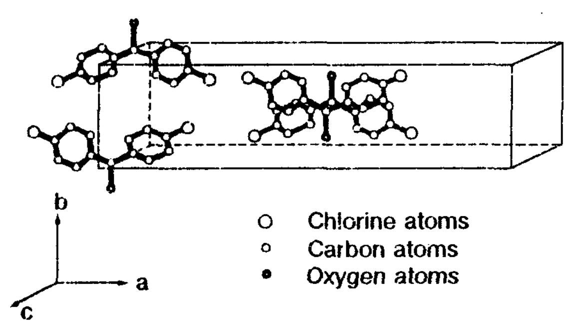

Fig. 1. The arrangement of 4,4′-dichlorobenzophenone molecules in a crystal unit cell C_{2h}^6.

In the present paper we will examine the nature of X-traps of a 4,4′-dichlorobenzophenone (DCBP) molecular crystal (the molecular and crystal structures [5,6] are shown in Fig. 1) by luminescence spectroscopy and magnetic resonance with optical detection (ODMR). We studied the low-temperature phosphorescence spectra and their polarization, as well as microwave transitions between spin sublevels of the excited triplet states of X-traps in a zero magnetic field. A particular model of the structure defect is studied in organic crystals which consist of molecules with a dipole moment. The electronic levels of the corresponding X-traps are calculated.

2. Experimental

4,4′-dichlorobenzophenone was recrystallized and zone refined. Single crystals were grown by the Bridgman method. Plates about 1 mm thick were cleaved along the bc-plane for measurements. Measurements were carried out in a liquid-helium cryostat at 1.4 and 4.2 K. The crystals were excited with the emission of a 500-W mercury-discharge lamp which was filtered at 366 nm. The phosphorescence was monitored at right angles to the excitation path with a double-grating, 0.8-m DFS-12 scanning spectrometer.

The spectral slit widths of the spectrometer were $0.5\ cm^{-1}$. Signals were detected by a cooled FEU-79 (S-6) photomultiplier in a standard photon-counting scheme with long signal averaging. Similar optical scheme was used to record the magnetic resonance spectra with optical detection (ODMR) in the zero field. The crystals were placed in a helix which was connected to a microwave sweep oscillator operated at 1–6 GHz, 5 mW, via a coaxial line. The positions of resonance frequencies were determined within accuracy of 3 MHz. For polarization measurements the phosphorescence was analyzed with a film polarizer and a depolarizer was placed in front of the spectrometer entrance slit.

3. Results and discussion

Phosphorescence spectra

The DCBP crystal phosphorescence spectra at 1.4 and 4.2 K are shown in Fig. 2. The spectral position of the 0—0 band of the triplet exciton emission is [7] $\nu = 24\,245\ cm^{-1}$ (where ν is wavenumber). The exciton origin of the band is confirmed by the temperature measurements: in contrast with the exciton emission, the emission of shallow *A*-traps is absent at 4.2 K due to detrapping to the exciton band (the inset in Fig. 2). The same vibronic structures of the exciton phosphorescence and of the traps (Fig. 3) serve as the most convincing evidence which confirms that the radiating traps for triplet excitons are the *X*-traps [1]. In each case the vibronic mode at $1\,670\ cm^{-1}$, which is characteristic of the carbonyl groups [8], gives rise to the progression. Since the triplet emission is strictly polarized along the carbonyl axis and along the crystal *b*-axis [9], the polarization of triplet emission

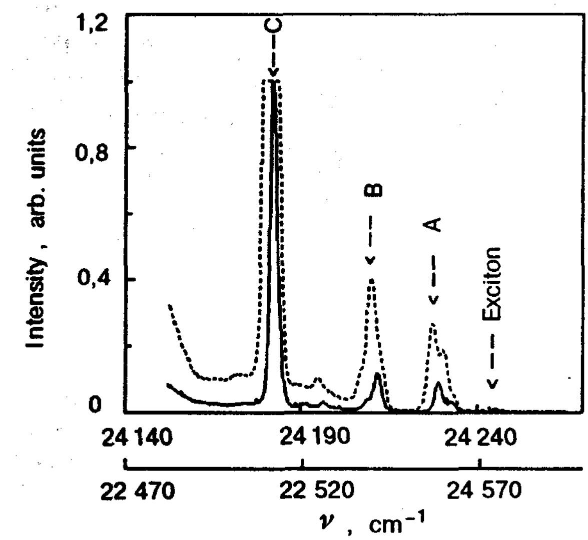

Fig. 3. Phosphorescence spectra of a 4,4'-dichlorobenzophenone single crystal at 1.4 K : 0—0 bands (solid curve, top axis of the abscissa); 0—1 bands (dashed curve, bottom axis of the abscissa).

bands of *X*-traps were studied in order to define possible deviation of the carbonyl axis of defect molecules from the crystal *b*-axis. A thorough study shows that while measuring the polarization within the accuracy of 3° the defect molecule dipoles are directed along the crystallographic *b*-axis.

ODMR spectra in the zero field of excited triplet states of X-traps at 1.4 K

Absolute values of the triplet zero-field splitting (ZFS) parameters *D* and *E* [8] for different traps (Table 1) were defined using the experimental resonance microwave frequencies (Fig. 4). It can be shown that because of the way in which the molecules

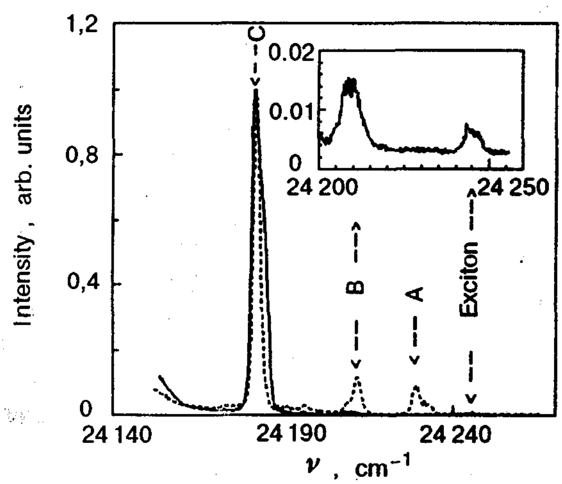

Fig. 2. Phosphorescence spectra of a 4,4'-dichlorobenzophenone single crystal at 4.2 (solid curve) and at 1.4 K (dashed curve). The inset scale up the phosphorescence spectrum at 4.2 K in close vicinity to the 0—0 band of triplet exciton emission.

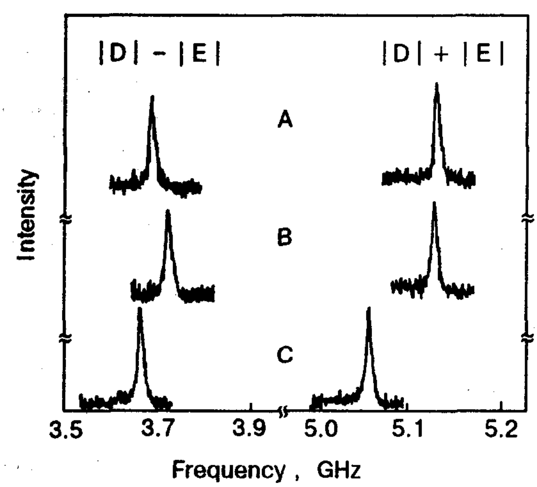

Fig. 4. ODMR signals in the excited triplet states of different *X*-traps in a 4,4'-dichlorobenzophenone single crystal at 1.4 K: $|D|-|E|$ and $|D|+|E|$ microwave transitions for *A*, *B*, and *C* traps, where *D* and *E* are the ZFS parameters.

are packed in the DCBP crystal lattice, the triplet exciton ZFS parameters nearly coincide with the molecular parameters. Our resonance frequencies for traps are close to those for excitons [10]. As is well known [8], splitting of the excited triplet in the zero field reflects the electron density distribution over a molecule and therefore is an individual feature of a molecule. As can be seen from Table 1, the ZFS parameters for different radiation centers are similar. It can therefore be stated that shallow trapping centers in the crystal under study are X-traps. It was shown earlier that ZFS parameters are fairly sensitive to the distortion of the shape of such nonrigid molecules as benzophenones [11]. On the basis of our data it can therefore be inferred that rotation and displacement of a molecule in a crystal are responsible for the structure defects which lead to the appearance of X-traps.

Table I

Resonance microwave frequencies (ν_1, ν_2) and ZFS parameters ($|D|$ and $|E|$) in the excited triplet states of 4,4'-dichlorobensophenone single crystal X-traps (Δ — trap depth).

X-trap	ν_1	ν_2	$\|D\|$	$\|E\|$	Δ
	GHz		cm^{-1}		
A	3.687	5.129	0.14843	0.02447	16
B	3.722	5.127	0.14897	0.02365	37
C	3.662	5.060	0.14683	0.02353	65

Model of the dipole X-trap

The dipole moments of individual molecules in a DCBP crystal are directed along the carbonyl axes. They are compensated for a unit cell (Fig. 1), and the dipole moment of a unit cell is zero.

Let us consider a simple model of a structure defect: a nondefect molecule is turned on the carbonyl axis by 180° and is then reflected in the plane that passes through the centers of molecules phenyl rings and normal to the crystallographic b-axis. Thus, the dipole moment of a defect molecule is fixed opposite to that of a nondefect molecule. The reorientation of the defect molecule dipole leads to a change of the interaction energy with the remaining crystal molecules. As a result, X-traps for an exciton appear. The structure defects of the above type were detected experimentally in dibenzfuran crystals [12]. The trap depth was calculated in accordance with the theory developed in Ref. 4, taking into account the defect molecule relaxation.

Let us consider the traps for triplet excitons. Bands for such excitations are quite narrow (e.g., the width of one of the triplet exciton bands in a DCBP crystal is [13] 8 cm^{-1}. It can therefore be assumed that the electronic excitation is localized at a separate molecule. Since a DCBP molecule has a dipole moment in the ground state and since the dispersion interaction energy decreases with the distance much faster than the dipole-dipole interaction energy, it is expected that the main contribution to the trap depth is from a change in the energy of the dipole-dipole interaction of a defect molecule with the remaining crystal molecules upon excitation.

Let us label the molecules in a crystal by $n\alpha$, where n is the number of the unit cell, and α is the number of the molecule in the cell. Let us label the defect molecule by $0\alpha^\circ$ ($n = 0$, $\alpha = \alpha^\circ$).

The trap depth due to the electrostatic interaction can be calculated as

$$E^{\mathrm{dip}}_{0\alpha^\circ} = D_{0\alpha^\circ} - D^{\mathrm{dip}} \,, \tag{1}$$

where $D_{0\alpha^\circ}$ is a change in the energy of the dipole-dipole interaction of a defect molecule with the remaining molecules following electronic excitation, and D^{dip} is a similar value for a nondefect molecule. In the calculation we took into account that the dipole moment is localized at the carbonyl C = O bond and that at the reorientation the dipole position characterized by the vector $\mathbf{r}_{0\alpha^\circ}$ changes to the vector $\vec{\rho}_{\alpha^\circ}$. We can then write

$$D^{\mathrm{dip}} = \sum_{m\beta \neq 0\alpha^\circ} V(\Delta\mathbf{P}_{\alpha^\circ}, \mathbf{r}_{0\alpha^\circ}; \mathbf{P}_\beta, \mathbf{r}_{m\beta}) \,, \tag{2}$$

$$D_{0\alpha^\circ} = \sum_{m\beta \neq 0\alpha^\circ} V(-\Delta\mathbf{P}_{\alpha^\circ}, \mathbf{r}_{0\alpha^\circ} + \vec{\rho}_{0\alpha^\circ}; \mathbf{P}_\beta, \mathbf{r}_{0\alpha^\circ}; \mathbf{P}_\beta, \mathbf{r}_{m\beta}), \tag{3}$$

where

$$V(\mathbf{P}_1, \mathbf{r}_1; \mathbf{P}_2\mathbf{r}_2) = \frac{1}{\varepsilon}\left[\frac{(\mathbf{P}_1\mathbf{P}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|^3} - \frac{3(\mathbf{P}_1[\mathbf{r}_1 - \mathbf{r}_2])(\mathbf{P}_2[\mathbf{r}_1 - \mathbf{r}_2])}{|\mathbf{r}_1 - \mathbf{r}_2|^5}\right] . \tag{4}$$

Here $\Delta\mathbf{P}_\alpha$ is an additional dipole moment which a molecule with a number α gains at the transition to the excited state, ε is the crystal static dielectric constant, and the vector $\mathbf{r}_{m\beta}$ passes through the dipole centers of all the nondefect molecules. The coordinates of nondefect molecules are taken from data of the known crystal structure of DCBP [5,6].

It can be shown that the calculated values of trap depths are strongly dependent on the relaxation position of a defect molecule. The relaxation position was determined by the atom-atom potentials. To determine the minimum energy, the defect molecule is moved in three directions along the crystallographic a, b, and c-directions and is rotated about the carbonyl axis of the C = O bond. The surrounding molecules are regarded as fixed molecules. In the relaxation position a defect molecule is displaced by the vector **R** with the coordinates $0.1647a$, $0.0647b$, $0.2721c$, where a, b, and c are the lattice constants, and the molecule is rotated about the carbonyl axis by about 3° with respect to the initial position. It was used for the calculations of the distribution of charge for a benzophenone molecule [14].

Tne dipole sums (2) and (3) were calculated by the Evald–Kornfeld point dipole lattice summation [15]. Taking into account the relaxation of a defect molecule in a crystal and the specific parameters of the DCBP crystal [16,17] ($|\mathbf{P}_\alpha| = 2.7D$, $|\Delta\mathbf{P}_\alpha| = 0.8D$, the direction of the vector $\Delta\mathbf{P}_\alpha$ is opposite to $\mathbf{P}_\alpha$, and $\varepsilon = 3$), the calculated depth of a dipole trap is 93 cm^{-1}, which is comparable to that of a pronounced X-trap (65 cm^{-1}) (Fig. 2, trap C).

The accuracy of calculation of the dipole trap depth can be improved by taking into account the contribution from the interaction between dipoles, which are located along the C–Cl bonds (the dipole moment of this bond is [18] $1.7D$) of a defect molecule, and the remaining molecules of a crystal.

Because the disturbance of the crystal molecules nearest to a defect is weak, the energy spectrum exhibits a set of levels connected with these molecules [19,20]. An energy funnel is therefore formed [19,20]. This energy funnel induces trapping of a triplet exciton by a defect molecule after nonradiative relaxation through the local levels.

The A and B shallow X-traps in the DCBP crystal phosphorescence spectra (Fig. 2) therefore do not seem to be associated with the traps induced by the C trap. This assumption is confirmed by the fact that the intensity ratios of different trap bands in the phosphorescence spectra change from one sample to another. It can be assumed that these traps are also the dipole traps. In this case however, a defect is formed due to the rotation of crystal molecules about the carbonyl axis. This leads to a change in the interaction between the dipoles of the C–Cl bond. We plan to continue studies of the nature of shallow X-traps.

In conclusion, measurements of the low-temperature phosphorescence spectra, of their polarization, and of the ODMR spectra in zero field in the excited triplet states made it possible to infer that in a 4,4′-dichlorobenzophenone crystal shallow traps are X-traps. A particular model of the structure defect, i.e., a model of the dipole trap, is proposed.

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