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Energy transfer in ethane-bisporphyrin dimers studied by fluorescence line narrowing and spectral hole burning

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Abstract

The quasi-line fluorescence excitation spectrum of 1,2-bis(2,3,7,8,12,13,17,18-octaethyl-21*H*,23 *H*-porphino) ethane at 4.8 K consists of two subbands with the splitting mean value of $51 \mathrm{cm}^{-1}$, that are ascribed to the donor and the acceptor half of the homodimer. The donor's fluorescence is quenched by an efficient energy transfer to the acceptor. The energy transfer rate of $10^{11} \mathrm{s}^{-1}$, determined by spectral hole burning, has been compared with the calculated value and a conclusion of nonconsistency with the Forster energy transfer mechanism has been drawn.

1. Introduction

Chemical dimers of porphyrins are suitable objects for studying various problems in molecular spectroscopy [1–4] and serve as good models for the energy and charge transfer processes taking place in photosynthetic systems [5–7]. In numerous papers, dealing with porphyrin dimers, the regularities of the electronic excitation energy transfer (ET) have been studied mainly at room temperatures [8] and the limits of different theoretical models describing this phenomenon have been evaluated [9]. At the same time ET at low temperatures including liquid helium range is strongly influenced by the arising of zero phonon lines and phonon side bands [10], but these effects on ET in dimers have almost not been studied yet.

The shape of the absorption and fluorescence 0–0 bands of molecular systems at low temperatures is basically determined by inhomogeneous broadening. The methods of fluorescence line narrowing (FLN) and spectral hole burning (SHB) make possible overcoming the inhomogeneity and revealing the underlying sharp-line homogeneous spectra. High spectral resolution makes these methods very informative for studying the behavior of systems of various complexity [10, 11]. For instance, SHB experiments have been used to measure the dynamics of initial photoprocesses of energy and electron transfer in native photosynthetic systems [12]. However, due to the complexity of such natural samples a detailed analysis of real spectral features has been difficult. Chemical dimers of porphyrins occupy an intermediate position between monomeric systems and associated complexes in vivo and the spectroscopic data on dimers may be used in the analysis of pair interaction of linked

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macrocycles in living organisms in the presence of spectral inhomogeneity.

This paper presents the results of FLN and SHB experiments for homo- and heterodimers of porphyrins (ethane-bisporphyrins) and the corresponding monomer of a meso-substituted porphyrin in the temperature range of 1.8–50 K. The spectral peculiarities and the specificity of interaction of homodimer fragments are discussed and the estimation of kinetic and energetic parameters of ET within the dimer have been carried out.

2. Experimental

A homodimer, 1,2-bis(2,3,7,8,12,13,17,18-octaethyl-21*H*,23*H*- porphino) ethane ($(OEP)_2$), a heterodimer, free-base OEP linked by 10,20′-ethylene to its copper(II) complex (OEP + CuOEP), as well as a representative monomer, 1-monomethyl-OEP (m-OEP), have been synthesized and identified by NMR and mass-spectroscopy [13]. The structural features of the dimers (Fig. 1) and their main spectral and kinetic parameters at 77–293 K have been given in Ref. [14]. A mixture of tetrahydrofuran and toluene (3: 1) has been used as a host matrix. It should be noted that below 77 K the glassy matrix becomes opaque; no Shpolskii effect has been observed down to 1.8 K.

Fluorescence spectra were recorded on a DFS-24 0.8 m double spectrometer by a cooled RCA C31034-A02 photomultiplier under a broadband excitation in the Soret band. Excitation and low-resolution SHB spectra were obtained by using a tunable broadband (0.3 cm^{-1}) CR-490 dye laser and fluorescence detection through a 650 nm cut-on filter. Fluorescence line narrowing was obtained by replacing the cut-on filter to the double monochromator. To avoid the effect of photochemical bleaching on the selective laser excitation an additional non-selective excitation (441.6 nm, Cd-laser of 10 mW) through a chopper working in the opposite phase with respect to the detection chopper, was used.

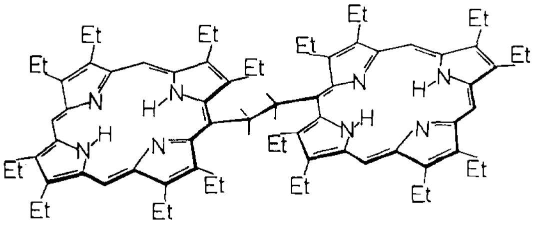

Fig. 1. Schematic representation of the fully-staggered $(OEP)_2$ dimer. The centre-to-centre distance is 1.05 nm [14].

Narrow spectral holes were burnt with a single-frequency dye laser CR-699-29 (frequency jitter of 2 MHz). The power density at the sample was 0.01–1.0 mW/cm^2 for the burning times between 10 and 300 s. To probe the holes the fluorescence excitation spectra were measured by using the same laser at an intensity reduced by a factor of 100. The fluorescence signal from the sample was detected at the angle of 45° to the excitation beam direction by a photomultiplier (EMI D341B/350) through the cut-on filter.

3. Results and discussion

3.1. *Fluorescence line narrowing*

Non-selective excitation in the Soret band of homodimer $(OEP)_2$ results in a fluorescence spectrum similar to that of the heterodimer OEP + CuOEP as well of the monomer m-OEP (except 6.5 nm red shift, cf. the spectral curves in Figs. 2 and 3). However, the half-width of the homodimer 0–0 fluorescence band (FWHM = 120 cm^{-1}) is 1.5 times narrower than that of the corresponding excitation band (FWHM = 175 cm^{-1}). The latter is close to the half-width (FWHM = 180 cm^{-1}) of the 0–0 excitation and fluorescence bands of m-OEP (cf. Figs. 2 and 3) and OEP + CuOEP. To interpret these findings FLN experiments have been carried out.

Well-resolved vibronic fluorescence spectra under monochromatic excitation at the ‘red’ side of the homodimer 0–0 absorption band have been observed (Fig. 4). Similar spectra have been obtained for the monomer (Fig. 5) and the heterodimer, where the FLN is observable over the entire *Q*(0, 0)-band (for the heterodimer the absorption into the free-base half is assumed). Thus vibrational frequencies could be measured for a homodimer,

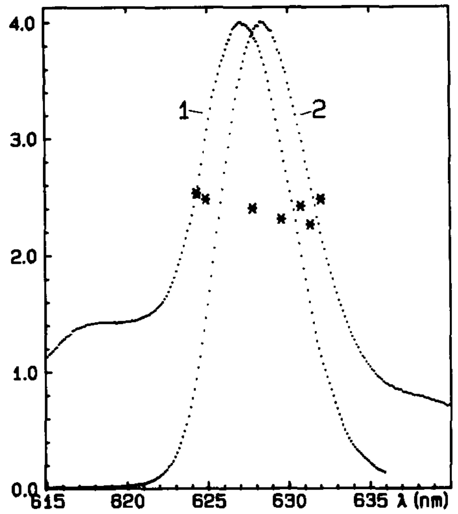

Fig. 2. Widths (asterisks) of spectral holes burnt at different wavelengths in the fluorescence excitation spectrum (1) of m-OEP. The complementary non-selective fluorescence spectrum (2) of m-OEP is also depicted for comparison.

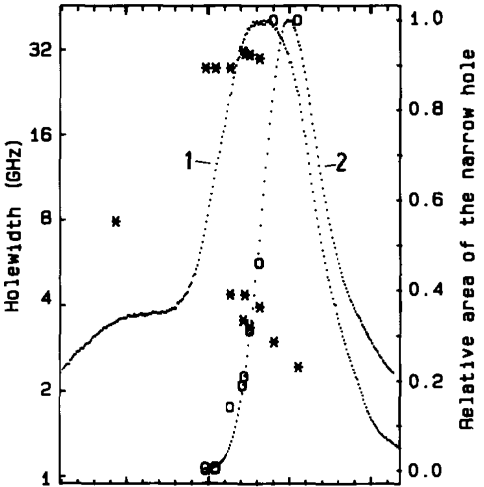

Fig. 3. Widths (asterisks, in logarithmic scale) and the relative area of the narrower component (circles) of the two-Lorentzian spectral holes burnt at different wavelengths in the fluorescence excitation spectrum (1) of $(OEP)_2$. Also, the complementary non-selective fluorescence spectrum (2) of $(OEP)_2$ homodimer is shown.

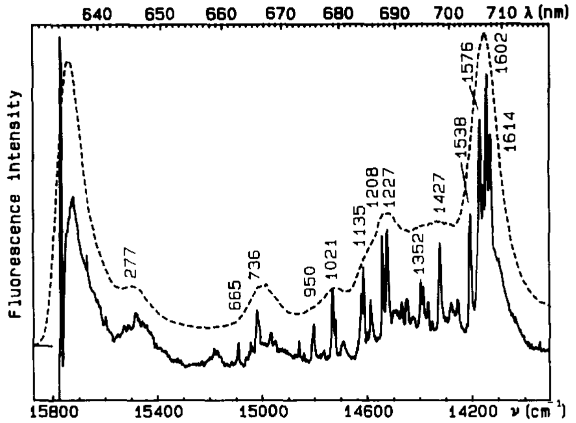

Fig. 4. Fluorescence spectra of $(OEP)_2$ under selective excitation (1) into the 0–0 absorption band and non-selective excitation (2) in the Soret band.

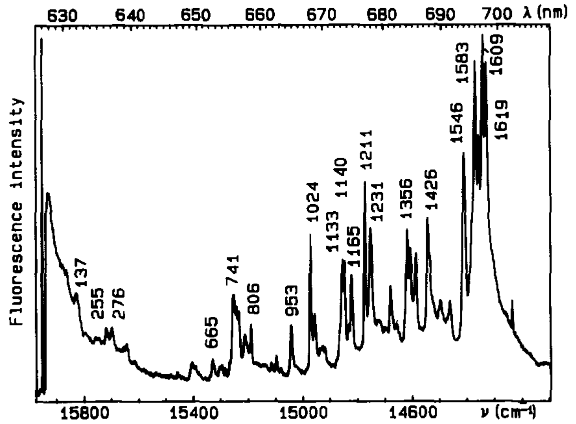

Fig. 5. Fluorescence spectrum of m-OEP at 4.8 K under selective excitation in the 0–0 absorption band.

the results being listed in Table 1 along with the values for m-OEP. These vibronic spectra are typical of porphyrins in terms of frequencies and intensities [15]. It means that mutual influence of π-conjugated macrocycles in the present dimers is weak and does not change the character of the vibronic interactions determining the shape of the visible electronic spectra. We believe that this situation reflects a large spatial separation of porphyrin macrocycles (the intercenter distance of 1.05 nm is typical of a fully staggered dimer conformation [14]).

In contrast to red excitation, excitation at the blue side of the $Q(0, 0)$ band of the homodimer gives no FLN effect and the fluorescence spectrum resembles the one in the case of excitation in the Soret band. Similar facts are known from the FLN

Table 1
Comparison of vibrational frequences (in cm^{-1}) in the quasi-line fluorescence spectra of mesomethyloctaethylporphyrin (m-OEP) and ethane-bis(octaethyl porphyrin) ((OEP)$_2$)

m-OEP	(OEP)$_2$	m-OEP	(OEP)$_2$
137	–	1024	1021
	165	1036	1030
–	232	1055	–
255	248	1064	1062
276	277	1072	–
–	301		
322	–	1133	1127
334	–	1140	1135
		1153	1163
531	527		
–	577	1211	1208
587	587	1231	1227
601	–	1260	1256
–	640	1273	1280
665	665	1299	1299
691	–		
699	–	1321	1322
		1356	1352
712	712	1365	1362
727	–	1385	1381
741	736	–	1396
745	–		
754	–	1426	1427
762	–	1469	1467
784	787	1501	1491
806	806	1546	1538
882	–	1574	1566
898	895	1583	1576
		1596	1589
914	912		
953	950	1609	1602
–	989	1619	1614

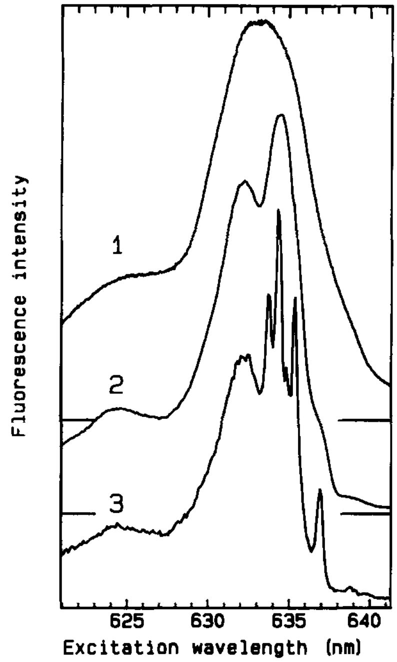

Fig. 6. Fluorescence line narrowing in the fluorescence excitation spectra of (OEP)$_2$: fluorescence recording through 650 nm cut-on filter (1) and through a monochromator with slits of 1.1 (2) and 0.23 nm (3).

experiments on concentrated dye solutions [10] and light harvesting antenna chlorophyll complexes [12] where a directed ET takes place. The disappearance of the quasi-line structure was attributed to a non-resonance energy transfer through phonon wings [16]. Taking into consideration this possibility we carried out some additional experiments to clarify the situation. In Fig. 6 the 0–0 transition of the excitation spectra of (OEP)$_2$ at different detection resolutions is shown. The first effect of FLN is the manifestation of two components: D (donor, FWHM = 100 cm^{-1}) and A (acceptor, FWHM = 120 cm^{-1}) subbands. The mean value of the splitting between the maxima of D and A subbands is 52 cm^{-1}. It is noteworthy that no such kind of splitting could be observed for m-OEP and OEP + CuOEP under the same conditions. Secondly, at a higher detection resolution the A subband displays a quasi-line structure where the lines correspond to the vibrations of the excited S$_1$ state (four prominent vibrations 1628, 1612, 1588, 1549 cm^{-1} can be seen), contrary to the D subband which remains non-structural. The presence of vibrational frequencies in the A subband of the dimer excitation spectra close to the monomer frequencies (1620, 1610, 1582, 1546 cm^{-1}) indicates the realization of a quasi-monomeric situation in (OEP)$_2$. The A subband corresponds to the absorption and the fluorescence process taking place in the acceptor component of the dimer without any ET between the halves of (OEP)$_2$.

For porphyrins the dependence of such quasi-line excitation spectra on the detection wavelength has been widely investigated [16, 17]. It is well known that for monomers the positions ν_e of excitation vibronic quasilines follow the frequency ν_d of monochromatic detection: $\nu_e = \alpha\nu_d + \Omega$ with $\alpha = 1$ and Ω being the vibrational quantum that is almost independent of the 0–0 transition frequency ν_d [17]. Apparently the situation characteristic of the A subband is similar to the monomeric case, i.e., the factor α is also equal to 1 (Fig. 7). On the other hand, the variation of the maximum of non-structural D subband, when moving the fluorescence detection within the region of 0–0 transitions, gives the α value of 0.52, i.e. the shift of the excitation peak is almost twice as small as that of detection. In addition, the halfwidth of the D subband is reduced when shifting the detection to shorter wavelengths, which indicates that a simple Gaussian model breaks down.

The above-mentioned experimental data could be explained by ET between the two halves of the homodimer. The fact that the 0–0 fluorescence band is 30% narrower than the complementary excitation band indicates the presence of effective ET which quenches the donor fluorescence. (Effects of reabsorption, which could also squeeze the fluorescence band, are excluded due to the small optical density of the samples). The structureless D subband in the excitation spectra of the homodimer, which has not been observed for the monomer and the heterodimer, shows that there is no exact correlation between the energies of 0–0 transitions of the dimer components, i.e. the donor–acceptor energy splitting is not constant. In an extreme case, if this splitting were a stochastic quantity with the mean value of 52 cm^{-1} not depending on the 0–0 transition frequency, the maximum of the D subband in the excitation spectra would have to follow the fluorescence detection frequency with the α factor of 1. However, as indicated above, the experimentally determined value is half of that. It means that between the splitting and 0–0 transition frequencies there exists anticorrelation.

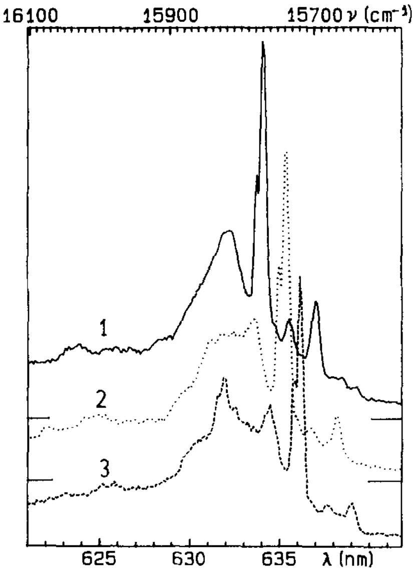

Fig. 7. The effect of correlation in the quasi-line fluorescence excitation spectra of $(OEP)_2$ on selective detection of fluorescence at the wavelengths of 678.2 (1), 679.6 (2), and 680.6 nm (3).

3.2. Spectral hole burning

Additional information about the peculiarities of donor–acceptor interactions in chemical dimers at temperatures lower than 5 K can be obtained by SHB experiments. It is well known that in the case of free-base porphyrins the hole-burning mechanism at low temperature is the photoinduced *NH*-tautomerism [18]. The tetrahydrofuran and toluene mixture is a good low-temperature matrice for SHB, as it yields a high Debye–Waller factor (e.g. 0.7 for $(OEP)_2$ when burning in the acceptor band). This indicates that the electron–phonon coupling is rather weak and it is possible to burn deep (up to 70% of the initial value) holes in absorption bands. An intense SHB results in a saturated zero-phonon line (with laser-limited and power-broadened half-width) and a pseudo-phonon wing (FWHM = 31 cm^{-1}) shifted from the line to the red by 22 cm^{-1} (Fig. 8). The shape of the hole was similar for all the systems investigated. The absorption of the photoproduct manifests itself at shorter wavelengths.

To determine the real homogeneous width of zero-phonon lines a non-saturating SHB was carried out. In the case of m-OEP both the efficiency of hole burning and the halfwidth of the holes (2.4 GHz) were almost the same over the whole $Q(0, 0)$ band (see Fig. 2). The shape of the spectral holes could well be approximated by a Lorentzian, which

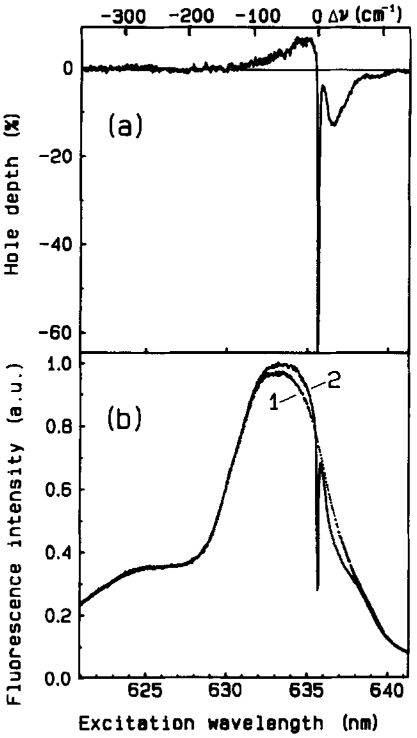

Fig. 8. Excitation spectra of $(OEP)_2$ at 4.8 K before (1) and after (2) a saturated burning at 635.7 nm (b) and the corresponding difference spectrum (a).

indicates their homogeneous nature. The hole-width was essentially determined by the phase relaxation caused by the scattering of matrix phonons at dopant molecules (For m-OEP the lifetime limited hole-width is 20 MHz). In glasses the homogeneous spectral width is additionally influenced by the existence of two-level systems and relaxation is not frozen out even at temperature of 1.8 K.

The SHB experiments on heterodimer, OEP + CuOEP, show a similar spectral behavior when the excitation takes place in the 0–0 absorption band of porphyrin free base. This indicates a weak mutual influence of π-conjugated macrocycles on the hole burning parameters. The coupling between electronic transitions of the dimer components is reduced due to a poor resonance condition ($\Delta E \approx 1500\,\mathrm{cm}^{-1}$) and a very high probability of singlet–triplet interstystem crossing in the copper containing half ($r = 4 \times 10^{13}\,\mathrm{s}^{-1}$) of the heterodimer [19].

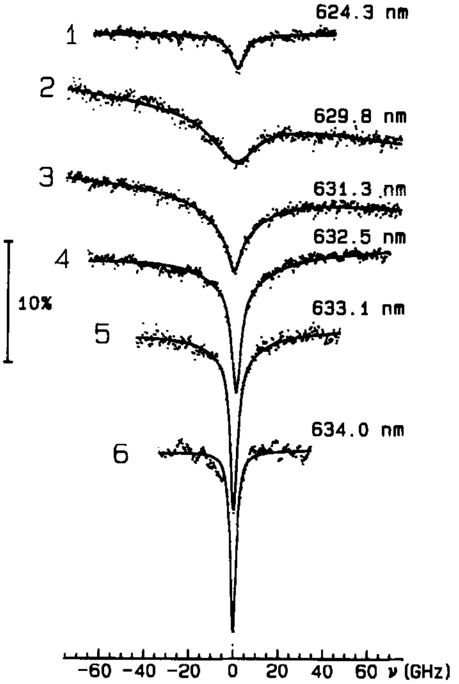

Fig. 9. Spectral holes at different wavelengths in the $(OEP)_2$ fluorescence excitation spectrum at 1.8 K. Solid curves are the least-squares fits by the sum of one (1, 2, 6), two (3, 4, 5) Lorentzian functions and a linear background.

The homodimer, $(OEP)_2$, revealed no additional peculiarities of SHB compared to the above-mentioned results for m-OEP or OEP + CuOEP, when burning is performed at the red side of the $Q(0, 0)$ band (e.g. $\lambda \geqq 636$ nm, see Fig. 8). However, the tuning of laser excitation to the blue side led to the decrease of the burning efficiency by more than an order of magnitude and a noticeable broadening of holes. Moreover, now the contour of the zero-phonon line could be approximated by two Lorentzian components with rather different half-widths of 2.4 and 30 GHz (Figs. 3 and 9), but for the blue edge of the band ($\lambda < 631$nm) one-Lorentzian approximation with the broader half-width of 30 GHz was characteristic. It is noteworthy that the spectral dependence of the relative area contribution of the narrow Lorentzian component follows the short-wavelength edge of the 0–0 fluorescence band of the dimer (see Fig. 3, empty circles). It proves the real physical background for the separation of spectral holes: the narrower component can be assigned to electronic excitation in the acceptor half of the dimer (recall that fluorescence is emitted only by this half of the dimer), while the broad component is connected with hole burning into the donor band where the excited state S_1 lifetime is shortened due to ET from D- to A-halves of $(OEP)_2$. The donor half's lifetime τ_1 can be estimated from the well-known formula for the spectral hole-width [12]:

$$\delta_{\text{Hole}} = \frac{1}{\pi}\left(\frac{1}{\tau_1} + \frac{2}{\tau^*{}_2}\right) [\text{Hz}].$$

It gives $\tau_1 = 10^{-11}$ s if we take into account that in our case $\tau_1 \ll \tau_2^*$, where τ_2^* is a pure dephasing time. The corresponding effective ET probability is $F^{\text{ET}} = 10^{11}\,\text{s}^{-1}$. The hole width of the narrower component is determined by phase relaxation, similar to the case of m-OEP.

The Forster ET mechanism predicts the F^{ET} values for fully-staggered conformation of $(OEP)_2$ in the following ranges: (2–20) $\times 10^9\,\text{s}^{-1}$ at 293 K and (0.5–11) $\times 10^9\,\text{s}^{-1}$ at 77 K [20]. These estimates are by an order of magnitude lower than the F^{ET} obtained from the present SHB experiments. This difference cannot be explained by the temperature dependence of the Forster ET mechanism, as commonly the non-radiative energy migration probability drops on the lowering of temperature due to the decrease of the spectral overlap integral [21].

Additionally, it is necessary to take into consideration different spectral broadening effects at room and liquid helium temperature. In the first case the absorption and fluorescence spectra are mainly homogeneously broadened and the Forster theory can directly be applied to the calculation of the spectral overlap integral and the ET rate. At 4.8 K the inhomogeneous broadening prevails and the calculation of the spectral overlap must be carried out for the 'elementary spectra' of the donor–acceptor pairs combined in the dimer. Afterwards these values should be averaged over all such pairs to obtain the effective ET probability. Our measurements showed that even at 50 K distinguishable holes ($\delta = 750$ GHz $= 25\,\text{cm}^{-1}$) can be burnt in the $Q(0, 0)$ band of $(OEP)_2$. This holewidth reflects the homogeneous width of the 0–0 transition, which is considerably narrower than the halfwidth of the whole band ($213\,\text{cm}^{-1}$). Obviously, even at 77 K the absorption and fluorescence spectra of the homodimer are to be considered as inhomogeneous ones. This means that for the systems under investigation at low temperatures the calculation of overlap integrals in [20] by using the inhomogeneous contours of the bands is incorrect.

Let us discuss some of the above-mentioned experimental facts. First, the full quenching of the donor fluorescence in $(OEP)_2$ (Fig. 2) and the diminishing of the narrower Lorentzian component contribution at the blue edge of absorption band can be explained by high ET probability for all inhomogeneously broadened D–A pairs. When calculating the overlap integral for a nonresonant ET, we have to consider both, the mutual overlap of the phonon wings and the overlap of the donor's zero-phonon line with the acceptor's phonon wing and vice versa. Due to the high Debye–Waller factor (0.7) the first term is four times lower than the second one (0.3×0.3 and ($0.7 \times 0.3 + 0.3 \times 0.7$), respectively), and the most favourable D–A spectral splitting for the maximal overlap integral would be $21\,\text{cm}^{-1}$, when the line coincides with the counterpart's wing maximum. Recall that the mean value for splitting, determined experimentally, is $52\,\text{cm}^{-1}$. Thus, we can conclude that resonance conditions for individual dimer molecules are not optimal in terms of Forster ET efficiency.

Second, the anticorrelation between the donor–acceptor splitting and 0–0 transition frequency results in different values of the fluorescence-absorption overlap integrals. This is in contradiction with the experimental fact that the ET rate is independent of the dimer's spectral position. A conclusion can be drawn that the Forster ET mechanism is of minor importance in the covalently linked dimer and an alternative interaction is important. An exact answer to this problem would be possible after a comparison of the experimental data with the quantum mechanical calculations of ET probability.

4. Summary

The present work has demonstrated the productivity of the technique of high-resolution laser spectroscopy in the investigation of energy transfer in complex systems. Naturally, the application of this method assumes the presence of zero-phonon lines in the spectra. These can be revealed in low-temperature optical spectra in case electron–phonon interaction is weak enough.

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