Host-Guest Energy Transfer Via Dipole-Dipole Interaction in Doped Fluorene Crystals

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Z. Naturforsch. **36a**, 697–704 (1981); received May 16, 1981

Fluorene mixed crystals have been investigated by sensitized fluorescence measurements in order to prove the importance of dipole-dipole interactions for singlet energy transfer.

Fluorene: dibenzofuran (F:DBF) and fluorene:benz[f]indan (F:BI) are used. In these systems the optical transition dipole moments of host and guest molecules are perpendicular and parallel to one another, respectively. For these systems the host-guest energy transfer rate has been determined as a function of the guest concentration from the quantum ratio of guest and host emission (F:BI) and from fluorescence decay time measurements (F:DBF). The latter verified the particularly low transfer rate in F:DBF found in previous steady state investigations.

The measured transfer rates at 1.3 K could be explained quantitatively taking into account the relative orientations of the host and guest transition dipoles and the oscillator strengths of the optical transitions. An increase of the transfer rate with increasing temperature between 1.3 K and 100 K in the system F:BI could be related to a change from energy transfer within perturbed states to excitonic band states of the fluorene crystal.

1. Introduction

The measurement of sensitized fluorescence in doped organic molecular crystals provides information about singlet excitonic energy transfer. The host-guest transfer process often is described in the hopping model [1, 2]: Excitation energy is hopping from host molecule to host molecule until becoming trapped at a guest molecule (Figure 1). The quantum flux of sensitized guest fluorescence Q_G relative to host fluorescence Q_H is an appropriate measure for the singlet energy transfer efficiency. Usually the ratio Q_G/Q_H is found to be several orders of magnitude higher than the guest concentration.

Due to its statistical nature the hopping model does not specify the transfer mechanism. The mechanism of energy transfer between two molecules in the singlet excited state has been described theoretically by dipole-dipole interaction, for solutions [3] as well as for molecular crystals [4].

In a previous paper [5] the first experimental evidence of the influence of dipole orientation on energy transfer has been found for fluorene doped with dibenzofuran (F:DBF). A drastic reduction of the transfer rate has tentatively been attributed to the perpendicular orientation of the optical transition dipole moments of host and guest molecules in this mixed crystal system.

In this paper a quantitative comparison of the energy transfer rates of F:DFB and a second mixed crystal system, fluorene doped with benz(f)indan (F:BI), is performed applying the dipole model. The latter system is known to exhibit the other extreme, in which the transition dipole moments of host and guest molecules are parallel [6, 7]. Using the same host for both systems, the difference in the energy transfer rates can be correlated with the different

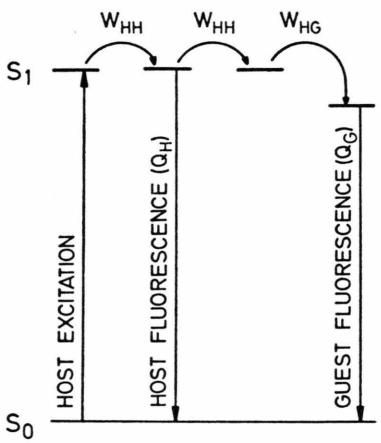

Fig. 1. Hopping model of the energy transfer in the first excited singlet state S_1 schematic.

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probabilities of the last single step of host-guest transfer (independently of the host-host transfer contribution).

The energy transfer rate of F:BI is determined from the concentration dependent quantum ratio Q_G/Q_H of guest and host fluorescence, which is measured as a function of temperature between 1.3 K and 100 K. The transfer rate of F:DBF obtained previously [5] from Q_G/Q_H at 1.3 K is confirmed in complementary measurements of the decay time of host fluorescence as a function of the DBF guest concentration. In the quantitative comparison of the host-guest transfer probabilities in the two mixed systems the relative oscillator strengths and the different dipole orientations of host and guest molecules are included. Further aims of this work are to distinguish the single steps of host-guest and host-host energy transfer and to determine the transfer efficiency within the host system separately and as a function of temperature.

2. Kinetic Equations and Experimental Methods

2.1. Kinetic Equations of the Hopping Model

The energy transfer in doped organic crystals strongly depends on the guest concentration c_G. In the hopping model it can be described by an overall rate constant k_{HG} [1]:

$$k_{HG}(c_G) = k^0_{HG}\, c_G^P, \tag{1}$$

where p is an empirical exponent (typically $0.7 \lesssim p \lesssim 1$), and k^0_{HG} the concentration independent rate as an appropriate measure for the energy transfer efficiency. k^0_{HG} is determined in the present investigations in the low temperature limit, where thermal deactivation of the guest traps can be excluded.

k^0_{HG} can be determined from the quantum ratio of guest and host fluorescence Q_G/Q_H after stationary excitation of the host, using the equation [2]:

$$Q_G/Q_H = \tau^0_H(\eta_G/\eta_H)\, k^0_{HG}\, c_G^P. \tag{2}$$

Q_G/Q_H is measured as a function of the guest concentration. The lifetime τ^0_H of the undoped host and the quantum yield ratio η_G/η_H of guest and host fluorescence must be determined separately. The transfer rate can also be deduced from the concentration dependent decay time τ_H of the host fluorescence in the doped crystal after short pulse excitation, according to the equation [8]

$$Q_H(t) = Q_H(0) \exp\{-[k^0_H + k_{HG}(c_G)]t\}. \tag{3}$$

$Q_H(t)$ describes the time dependent quantum flux of host emission, k^0_H the reciprocal decay time $(\tau^0_H)^{-1}$ of the undoped and $[k^0_H + k_{HG}(c_G)]$ the reciprocal host decay time $(\tau_H)^{-1}$ of the doped crystal. From the concentration dependence of k_{HG} the energy transfer rate k^0_{HG} can be determined according to Equation (1).

2.2. Experimental

Stationary fluorescence spectra of the mixed crystals F:BI have been measured as a function of the guest concentration and at different temperatures between 1.3 K and 100 K. As a reference the temperature dependent spectra of undoped fluorene have been studied. After narrow-band excitation with a xenon high pressure arc (XBO 450) and a 0.25 m Jarrell Ash monochromator the fluorescence spectra were recorded photoelectrically using a 2 m Jarrell Ash spectrometer (operated at a spectral resolution of 0.8 Å).

The relative quantum flux of guest and host fluorescence Q_G/Q_H in F:BI was determined after selective host excitation (at 33280 cm^{-1}; $\Delta\tilde{\nu} =$ 90 cm^{-1}) with light polarized parallel to the crystal c-axis. The selectivity had been justified for the mixed crystal system from fluorescence excitation spectra described in [9]. In order to determine the ratio of guest and host quantum yields η_G/η_H separate measurements were performed comparing the quantum flux after host excitation (at 33280 cm^{-1}; $\Delta\tilde{\nu} = 27$ cm^{-1}) with the quantum flux after direct guest excitation (at 32785 cm^{-1}; $\Delta\tilde{\nu} =$ 27 cm^{-1}). The relative guest and host quantum flux has been obtained from the integral guest and host intensity after correction of the wavelength and polarization dependent sensitivity of spectrometer and photomultiplier.

Fluorescence decay time measurements have been performed in order to determine τ^0_H of the undoped host that is used in Eq. (2) and of the concentration dependent host decay time τ_H of F:DBF from which k^0_{HG} can be calculated applying Eqs. (3) and (1). Furthermore, from a comparison of host and guest decay rates their relative oscillator strengths can be obtained.

A pulsed excitation source was provided by a frequency doubled dye laser which was pumped by

a nitrogen laser (pulse duration 1 ns). The fluorescence lines were selected by a 0.25 m Jarrell-Ash monochromator (operated at a resolution of 1.6 Å) and detected by a fast photomultiplier (rise time 1.8 ns), a Sampling oscilloscope (time resolution 0.2 ns) and a Signal averager (CAT). The deconvolution of the fluorescence signal and the photomultiplier response was performed by complex Fourier transformation on the computer (HP 2100 S). The same computer was used for a fit of the decay curves.

All measurements have been performed in a temperature range between 1.3 K and 100 K. For the stationary fluorescence measurements a bath cryostat was used, where temperatures down to 1.3 K were controlled by the vapour pressure above the helium bath. Temperatures above 4.2 K were obtained by heating the helium gas flowing in the cryostat. For the time-resolved investigations a continuous flow cryostat Oxford Instruments CF 204 with electronic temperature control for $T \geqq 5$ K was used.

2.3. *Crystal Samples*

The starting materials fluorene (F) and benzindan (BI) have been synthesized, sublimed and zone-refined in the Stuttgarter Kristallabor (DBF was obtained from Schuchardt in München). Mixed crystal series of fluorene doped with DBF (F:DBF) and fluorene doped with BI (F:BI) have been grown by the Bridgman method.

The guest concentration has been determined for each sample of F:DBF by gas-chromatography, and for each sample of F:BI by absorption in ethanol solution at 100 K. Within the limits of error a homogeneous guest destribution was found in the samples investigated. For F:DBF there is experimental evidence [10, 11] that the guest molecules replace the host molecules substitutionally. A substitutional arrangement has also been assumed for F:BI, since the BI molecule has the same size and a very similar structure as the fluorene molecule.

The molecular structures of fluorene, DBF and BI are shown in Fig. 2, as well as a projection of the unit cell of the fluorene crystal. The crystal structure [12] is orthorhombic with four molecules per unit cell, all of which are oriented with their long axis parallel to the crystal c-axis, and with their short axis perpendicular to c. The optical transition

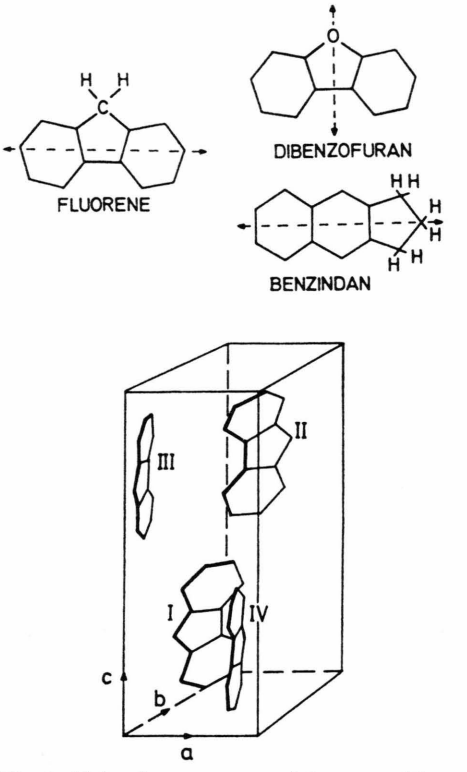

Fig. 2. Molecular structure of fluorene, dibenzofuran and benzindan (the directions of the $S_1 \leftrightarrows S_0$ transition dipoles are indicated); crystal structure of fluorene.

dipoles of host and guest molecules [6, 7, 13], which are also indicated in Fig. 1, are in the case of F:BI parallel, in the case of F:DBF perpendicular to each other.

The surface of all Bridgman samples (typical size $5 \times 5 \times 1$ mm^3) contained the crystal *c*-axis, since they had been cut perpendicular to the ab cleavage plane.

3. Results

3.1. *Fluorescence Spectra of Mixed Crystals F:BI*

In Fig. 3 the fluorescence spectrum of fluorene doped with 0.03% benzindan at 1.3 K is shown as an example and in comparison with the spectrum of the undoped fluorene crystal. The fluorescence of the guest BI is shifted far to the red. The guest 0.0 transition at 31153 ± 3 cm^{-1} and the vibrational intervals given in Fig. 3 are found in agreement with the literature [7]. The relative intensity of the guest BI as compared to the fluorene host is considerably higher than that of the guest DBF at the

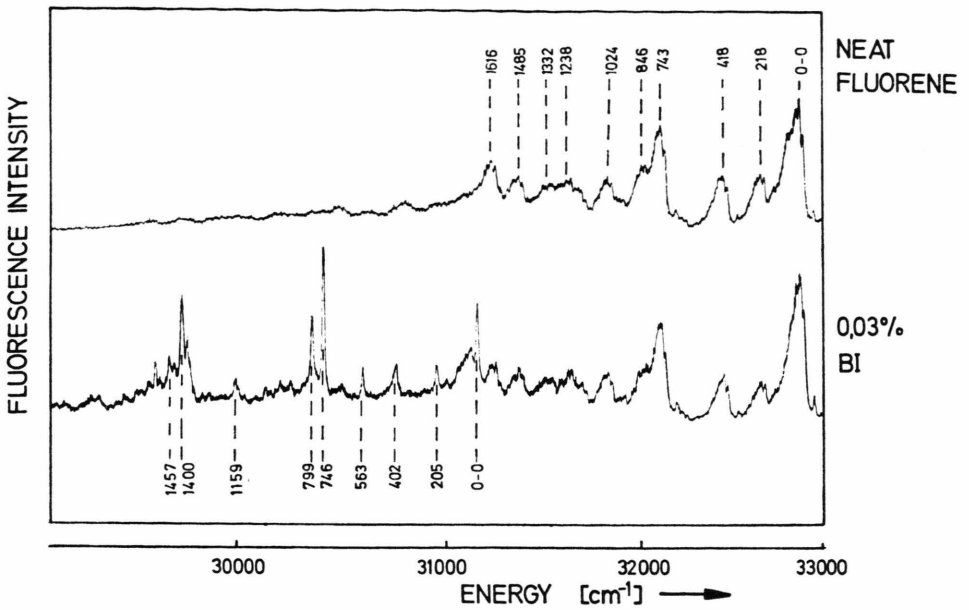

Fig. 3. Fluorescence spectra of undoped fluorene and fluorene doped with 0.03% BI at 1.3 K. The vibrational analysis is given for the host in the upper curve and for the guest in the lower curve.

same guest concentration ($c_G = 0.03\%$; see Fig. 2 in [5]). The relative guest contribution to the mixed crystal spectrum of F:BI increases monotonically with c_G.

The trap depth of the guest BI is 1670 cm^{-1} and much larger than that of the guest DBF (40 cm^{-1} [5]). In contrast to the DBF trap, which becomes thermally deactivated above 40 K [9], BI is acting as a deep trap at all temperatures investigated. With increasing temperature the fluorescence spectra of F:BI reveal a strong increase of the guest intensity relative to the host intensity (Figure 4). This increase is observed above 30 K and is most obvious between 40 K and 60 K. In the same temperature range a change within the host spectrum occurs, which in detail is studied on the undoped fluorene crystal (Section 3.2).

From the mixed crystal spectra of F:BI the quantum ratio of guest and host fluorescence Q_G/Q_H is calculated and plotted as a function of the guest concentration at 1.3 K, 50 K and 100 K, Figure 5. For the plot in double logarithmic scale a linear relationship between Q_G/Q_H and c_G is found for all the temperatures, in accord with Equation (2). The absolute values of Q_G/Q_H at a given concentration increase with increasing temperature. The values at 1.3 K are about an order of magnitude larger than the corresponding values in the mixed system F:DBF [5].

The ratio of guest and host fluorescence quantum yields η_G/η_H is determined for F:BI from measurements on a medium guest concentration ($c_G = 0.03\%$). A value of $\eta_G/\eta_H = (0.9 \pm 0.2)$ is obtained

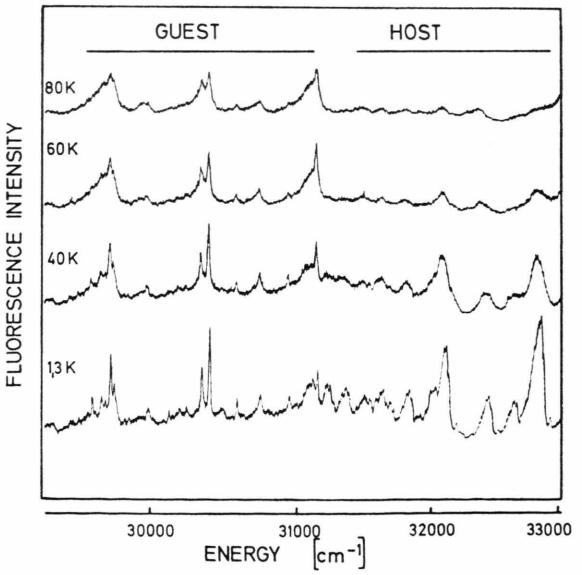

Fig. 4. Temperature dependence of F:BI mixed crystal fluorescence.

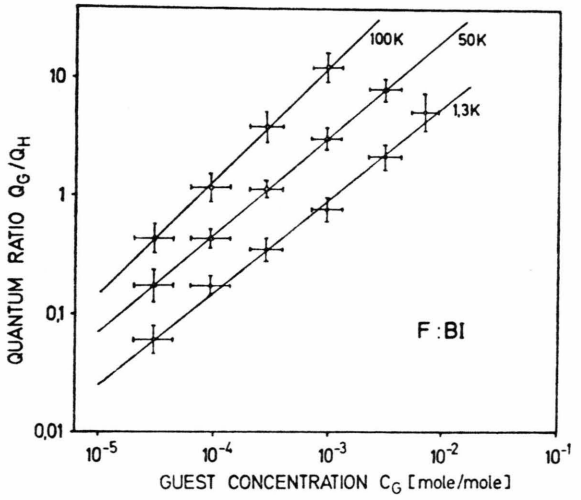

Fig. 5. Quantum ratio of guest and host fluorescence of F:BI as a function of guest concentration at 1.3 K, 50 K and 100 K.

at 1.3 K. This value is the same as for F:DBF [5] within the limits of error.

The quantum yield ratio η_G/η_H increases with temperature up to (1.4 ± 0.4) at 50 K and (3 ± 1) at 100 K. This increase is smaller, however, than the relative increase of the quantum ratio Q_G/Q_H between 1.3 K and 100 K. That indicates according to Eq. (2) a concomitant increase of the energy transfer rate with increasing temperature (anticipating the result of Sect. 3.3, that τ_H^0 is temperature independent).

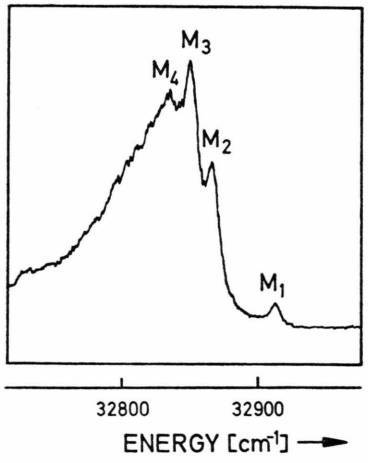

Fig. 6. Fluorescence 0.0 transition of fluorene at 1.3 K. The multiplet components M_1, M_2, M_3 and M_4 are centered at 32922 cm^{-1}, 32865 cm^{-1}, 32845 cm^{-1} and 32825 cm^{-1}, respectively.

3.2. *Fluorescence Spectra of Undoped Fluorene*

The low temperature fluorescence spectra ($T \lesssim 20$ K) of undoped fluorene crystals reveal the same substructure which has been observed in the host spectrum of F:DBF [5] and F:BI mixed crystals. The fluorene spectra are composed of four subspectra (labelled M_1, M_2, M_3, M_4; see Fig. 6 for the 0.0 transition). Their spectral positions and relative intensities are independent of the crystal material and are not affected if the crystal is doped with BI or DBF. The multiplet structure M_i obviously has to be explained as an intrinsic property of the fluorene crystal.

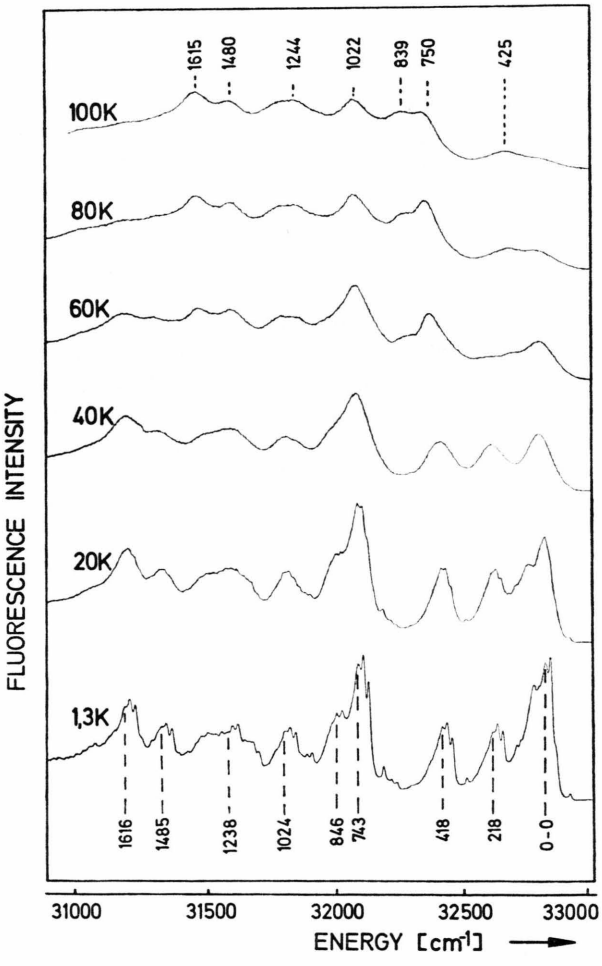

Fig. 7. Temperature dependent fluorescence spectra of undoped fluorene. The vibrational analysis is given for the multiplet component M_4 (which corresponds to the centre of gravity of the multiplets in the spectrum at 1.3 K) and for the thermally activated line series in the spectrum at 100 K.

With increasing temperature the lines broaden and the multiplet structure is smeared out (Figure 7). Below 40 K the spectral distribution is maintained. Above 40 K, however, a new line series appears that becomes dominant above 60 K (Figure 7). This series shows the same vibronic intervals but the lines are shifted to higher energies, by 250 cm^{-1} relative to the most intensive multiplet component M_3. Due to reabsorption the corresponding 0.0 transition cannot be detected [9].

3.3. Fluorescence Decay Times

The fluorescence decay of undoped fluorene and F:DBF and F:BI mixed crystals (host and guest) is monoexponential, to a good approximation, at all temperatures investigated. The decay time of undoped fluorene τ_H^0 has been measured, spectrally resolved, for the 0.0 transition and individual vibronic lines. The value $\tau_H^0 = 1/k_H^0 = (6 \pm 0.5)$ ns does not depend on temperature ($5\,K \leqq T \leqq 100\,K$).

In doped crystals of both F:DBF and F:BI it has been observed qualitatively that the decay time τ_H of the host fluorescence is monotonically reduced with increasing guest concentration. Quantitatively $\tau_H(c_G)$ has been measured for F:DBF at 5 K (0.0 transition). Using Eq. (3) the overall rate constant k_{HG} has been calculated and plotted in Fig. 8 as a function of the guest concentration in double logarithmic scale. A linear relationship has been found, as is expected from Equation (1).

The experimental decay times τ_G of the guest fluorescence of both DBF and BI in fluorene are independent of the guest concentration. Values of $\tau_G = (7 \pm 0.5)$ ns for DBF at 5 K and $\tau_G = (55 \pm 5)$ ns for BI at 5 K, 50 K and 100 K have been obtained.

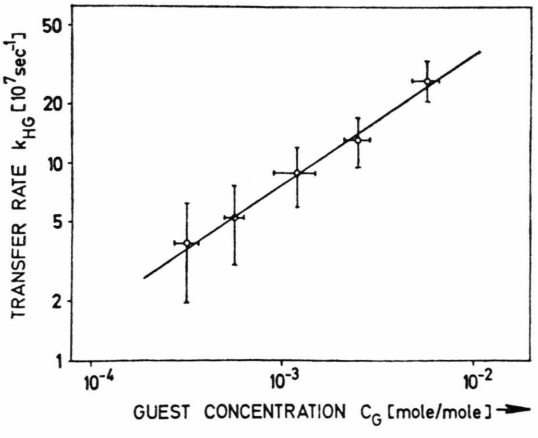

Fig. 8. Concentration dependence of the overall rate constant k_{HG} of F:DBF, as calculated from fluorescence decay time measurements ($T = 5$ K).

The experimental values of τ_G and τ_H^0 together with the quantum yield ratio η_G/η_H (Sect. 3.1) can be used to deduce the relative oscillator strengths of the guest (f_G) and host (f_H) transitions. These are proportional to the radiative decay rates k_G^* and k_H^* given by: $k_G^* = \eta_G(\tau_G)^{-1}$ and $k_H^* = \eta_H(\tau_H)^{-1}$. Using the experimental values for η_G/η_H (Sect. 3.1) the ratios f_G/f_H at 5 K are obtained:

$$(f_G)_{DBF}/f_H = 0.75; \quad (f_G)_{BI}/f_H = 0.1;$$
$$(f_G)_{DBF}/(f_G)_{BI} = 8 \pm 2.$$

The latter value confirms the result $(f_G)_{DBF}/(f_G)_{BI} = 6 \pm 2$ which was obtained from absorption measurements [9].

For F:BI at 100 K the experiment gives $(f_G)_{BI}/f_H = 0.3$.

4. Discussion

The energy transfer rates k_{HG}^0 of F:DBF and F:BI, as determined from the concentration dependent quantum ratio and from the fluorescence decay time measurements (Sects. 3.1 and 3.3), are listed in Table 1. Pronounced differences in the values of k_{HG}^0 are found between the two mixed crystal systems at helium temperature and also for F:BI between the low and high temperature limit (1.3 K and 100 K). These differences are the subject of the following discussion.

On the basis of the results on F:DBF [5] it already has been noted, that the transfer rate k_{HG}^0 of this system at 1.3 K was found to be about two orders of magnitude smaller than the transfer rates of other mixed crystal systems. An interrelationship was suggested between the reduction of energy transfer efficiency and the perpendicular orientation of fluorene host and DBF guest transi-

Table 1. Energy transfer rates k_{HG}^0.

Crystal system	k_{HG}^0 [s^{-1}]	T [K]	Measurement
F:DBF	$(1.6 \pm 0.8) \cdot 10^{10}$	1.3	Quantum ratio [5]
F:DBF	$(1.4 \pm 1) \cdot 10^{10}$	5	Decay times
F:BI	$(6 \pm 3) \cdot 10^{10}$	1.3	Quantum ratio
F:BI	$(1.6 \pm 0.8) \cdot 10^{11}$	50	Quantum ratio
F:BI	$(6 \pm 3) \cdot 10^{11}$	100	Quantum ratio

tion dipoles. The comparison with F:BI, the other extreme with parallel orientation of host and guest transition dipoles reveals for F:**BI** a larger value of k^0_{HG} (Table 1). The experimental difference of a factor of about four, however, is less than one would expect qualitatively from the different relative dipole orientation.

The quantitative application of the dipole model as given in the next sections shows the importance of both dipole orientation and oscillator strength. The discussion treats the individual steps of host-guest and host-host transfer separately.

Table 1 shows an increase of k^0_{HG} in F:BI between 1.3 K and 100 K which is in contrast to theoretical predictions [1, 8]. Exciton-phonon interaction generally reduces the energy transfer at higher temperatures. The increase of energy transfer efficiency in this case can be explained by a change of the transport properties of the fluorene host system.

4.1. Quantitative Evaluation of the Host-guest and Host-host Transfer Probabilities in the Dipole Model

The probability of a quantum mechanical transition is proportional to the square of the interaction energy. For the probability w_{HG} of direct energy transfer from a host (H) to a guest (G) molecule via dipole-dipole interaction one obtains:

$$w_{HG} \sim \frac{|p_{nm}|^2 |q_{mn}|^2}{r^6} x^2, \tag{4}$$

where p_{nm} and q_{nm} are the transition dipole moments of host and guest molecules, r the intermolecular distance (between the centers of gravity) and x an orientation factor

$$x = \cos\varphi_{HG} - 3\cos\varphi_H \cos\varphi_G . \tag{5}$$

In Eq. (5) φ_{HG} is the angle between the dipole moments of host and guest in the crystal, whereas φ_H and φ_G are the angles between the direction of energy transfer and the dipole moments of host and guest molecules, respectively.

Since the excitation energy can be transferred to the guest molecule from various neighbouring host molecules N, the total probability of a single step host-guest transfer is the sum over the probabilities of different host-guest configurations

$$W_{HG} = \sum_N w_{HG} \sim |p_{nm}|^2 |q_{mn}|^2 \sum_N x_N^2 / r_N^6 . \tag{6}$$

According to Eq. (6) the total host-guest transfer probability contains two contributions, the oscillator strengths of host and guest transitions ($|p_{nm}|^2$ and $|q_{mn}|^2$ are proportional to f_H and f_G, resp.) and the dipole orientation factor $\sum_N x_N^2/r_N^6$. In the following comparison of the host-guest transfer probability of F:DBF and F:BI these two contributions are compared separately.

Taking into account the nearest 30 host molecules for each guest molecule, the calculation yields for the parallel and perpendicular transition dipoles:

$$(\sum x_N^2/r_N^6)_\parallel / (\sum x_N^2/r_N^6)_\perp = 30 .$$

The average value for the ratio of guest oscillator strengths determined by two experimental methods (Sect. 3.3) is:

$$|q_{mn}|^2_{DBF} / |q_{mn}|^2_{BI} = (f_G)_{DBF}/(f_G)_{BI} = 7 .$$

With these values the ratio of the total host-guest transfer probabilities in the two systems is calculated:

$$(W_{HG})_{F:BI}/(W_{HG})_{F:DBF} = 4.3 .$$

This value is in agreement with the experimental ratio of the overall energy transfer rates (at 1.3 K):

$$(k^0_{HG})_{F:BI}/(k^0_{HG})_{F:DBF} = 4 .$$

Thus the ratio of host-guest single step transfer probabilities of F:DBF and F:BI reproduces the ratio of the transfer rates k^0_{HG} of these mixed crystal systems.

So far the probabilities of the last step of energy transfer from host to guest molecules have been compared for F:DBF and F:BI. In the following these probabilities are related to the preceding steps of transfer between host molecules.

For the single step probability of host-host transfer W_{HH} a relationship analogous to Eq. (6) holds with $|p_{nm}| = |q_{mn}|$. Taking into account the parallel dipole orientation of the host molecules and the ratio of host and guest oscillator strengths from Sect. 3.3 one obtains (at helium temperature):

$$(W_{HG})_{F:DBF}/W_{HH} = 1/40 ,$$
$$(W_{HG})_{F:BI}/W_{HH} = 1/10 .$$

According to these values in both mixed crystal systems the probability of the last step of host-guest energy transfer is considerably reduced as compared to the steps of host-host transfer.

For this reduction, however, there are different reasons in the two systems. In F:DBF it is caused mainly by the perpendicular orientation of host

and guest transition dipoles, in F:BI by the low oscillator strength of the BI guest molecules relative to that of the fluorene host molecules.

4.2. Temperature Dependent Host-host Transfer

The explanation of the observed increase of the energy transfer rate k^0_{HG} in the F:BI mixed crystals with increasing temperature is based on the following experimental results:

(i) The quantum flux of the guest fluorescence relative to the host fluorescence increases with temperature (Figure 5). This increase is especially pronounced between 40 K and 60 K.

(ii) In the same temperature range a spectral change occurs within the host spectrum (Figure 7). The multiplet states are thermally deactivated, and the fluorescence from an energetically higher fluorene level becomes dominant. Obviously there exists an interrelationship between the reduced energy transfer efficiency at low temperature and the multiplet states.

The multiplet components have already been identified as an intrinsic property of the fluorene crystal (Section 3.2). Their thermal deactivation and their recently observed [9, 14] relatively low optical densities in absorption spectra characterize them as fluorene X-traps.

The essential role of these X-traps for the energy transfer is verified in additional fluorescence measurements with selective excitation of the multiplet components M_1, M_2 and M_3 [9]. It turns out that at 1.3 K the host-guest transfer efficiency after selective M_i excitation is the same as after excitation of energetically higher fluorene levels. Apparently at low temperature energy transfer occurs within the multiplet system. These X-traps act as perturbed exciton bands.

Energy transfer in perturbed bands has been observed previously, e.g. in doped naphthalene crystals [15—17]. There the direct energy transfer via guest molecules becomes dominant at guest concentrations above 10^{-3}.

In the fluorene crystal the energy transfer above 40 K involves the thermally activated fluorene level and most probably can be attributed to excitonic transfer. A comparison of the transfer efficiencies within the multiplet system and the thermally activated level can be given, using the relationship $k^0_{HG} = k^0_{HH} \cdot W_{HG}/W_{HH}$, and the values W_{HG}/W_{HH}, as determined in Section 4.1. The host transfer rate k^0_{HH} within the perturbed bands of the multiplet-system is calculated from k^0_{HG} at 1.3 K:

$$k^0_{HH} = 6 \cdot 10^{11}\ s^{-1}.$$

The host transfer rate $k^{0'}_{HH}$ within the higher excitonic level is determined from k^0_{HG} of F:BI at 100 K using the experimental ratio $W_{HG}/W_{HH} = 0.3$:

$$k^{0'}_{HH} = 2 \cdot 10^{12}\ s^{-1}.$$

The actual ratio of the transfer efficiency of perturbed and excitonic host states is thus only about 3—4.

Acknowledgement

The authors are grateful to the Stuttgarter Kristallabor in particular W. Tuffentsammer for providing the mixed crystals and G. Pampel for the gas chromatography measurements. They acknowledge the assistance of A. Braun with the lifetime measurements. H. Zimmermann (Heidelberg) kindly supplied some material of F:DBF to be used for comparison purposes. This work has been supported by the Deutsche Forschungsgemeinschaft (SFB 67).

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