

# Triplet States in Isotopically Mixed Naphthalene Crystals: High Resolution Optical Spectroscopy

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The triplet 0.0 transitions ( $T_1 \leftrightarrow S_0$ ) of guest and host in various isotopically mixed naphthalene crystals, with guest states below and above the host exciton band, are investigated applying both laser excitation spectroscopy and phosphorescence emission spectroscopy.

Guest monomer and aggregate spectra are analyzed at helium temperatures (1.6–4.2 K) with regard to line positions, splittings, polarizations and intensities. Shift and broadening of the host Davydov components are studied as a function of the guest concentration (at 1.6 K). In particular, the analysis provides precise values for the individual isotopic shifts  $U_0$  and the exciton band structure parameters including the critical isotopic shift. Site splitting is spectrally resolved for several monomers and also for the AB-dimer of 1,4-Nd<sub>2</sub> in Nd<sub>8</sub>.

## 1. Introduction

The triplet excited state in organic molecular crystals has been investigated extensively. The present paper contributes to the research on spectroscopic properties of substitutionally disordered crystals [1–4] and the triplet exciton line shape problem [5–8]. It is concerned with host-guest and guest-guest nearest neighbour interaction, the impurity band energy transfer and the impurity-induced exciton line shift and broadening.

The experimental data are obtained from photoexcitation and phosphorescence emission spectra of a variety of naphthalene isotopically mixed crystals, at higher spectral resolution than in previous studies [9–12]. In particular the paper discusses the detailed substructure within the guest spectra, its dependence on isotopic composition and guest concentration. Mixed crystals with guest levels below and above the exciton band are investigated. Due to the high sensitivity achieved also intrinsic impurities in natural abundance, <sup>13</sup>C and deuterium substituted naphthalenes, can be characterized spectroscopically. (The spectroscopic identification of the various <sup>13</sup>C isomers of naphthalene is reported separately in a comparison with anthracene [13]).

Similar spectroscopic studies have been performed previously on isotopically mixed anthracene [7] and phenazine [14].

## 2. Experimental

The experimental results reported in this work were obtained by triplet excitation and phosphorescence emission spectroscopy.

The photoexcitation spectra were obtained using a tunable cw dye laser (Coherent Mod. 699) in broad and narrow band version, at bandwidth of 0.5 cm<sup>-1</sup> and 0.001 cm<sup>-1</sup>, resp. The triplet absorption was monitored by the integrated delayed fluorescence intensity in its regime of linear dependence on the absorption coefficient. The delayed fluorescence was separated from the excitation light by a filter Corning C.S. 7-37.

The absolute wavenumber calibration of the host and guest line positions was performed with a wave-meter. Relative line shifts of the lower host Davydov component as function of the guest concentration (Sect. 3.2) were measured using an undoped sample in a second cryostat as reference. The phosphorescence emission spectra were measured at the Physikalisches Institut, Bayreuth university, in collaboration with H. Eichele using a 1.5 m spectrometer (Mod. THR, Jobin Yvon) with a photon counting system. The triplet state was populated indirectly by lamp excitation (HBO 200) into the singlet manifold. (The direct laser excitation into the triplet exciton band turned out to be less efficient).

Crystal samples have been grown by sublimation and by the Bridgman method. The starting material has been zone refined extensively in the Stuttgarter Kristalllabor. Some of the partially deuterated

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compounds kindly have been provided by R. Kopelman. Apart from increased inhomogeneous line broadening the excitation spectra obtained from Bridgman samples were equal to those of thin sublimation flakes. The weak phosphorescence emission was detectable at high spectral resolution only with thick Bridgman samples.

The samples were held strainfree between paper masks. They were immersed in liquid helium in standard helium bath cryostats and irradiated perpendicular to the crystal ab-plane.

The following labels for the various deuterium or hydrogen substituted naphthalene guest molecules are adopted instead of the complete notation given in brackets: 1-Nd<sub>1</sub> (1-Nd<sub>1</sub>h<sub>7</sub>), 2-Nd<sub>1</sub> (2-Nd<sub>1</sub>h<sub>7</sub>), N-d<sub>2</sub> (1,4-Nd<sub>2</sub>h<sub>6</sub>), Nd<sub>3</sub> (1,4,5-Nd<sub>3</sub>h<sub>5</sub>), Nd<sub>4</sub> (1,4,5,8-Nd<sub>4</sub>h<sub>4</sub>), Nd<sub>5</sub> (1,2,4,5,8-Nd<sub>5</sub>h<sub>3</sub>), 1-Nh<sub>1</sub> (1-Nd<sub>7</sub>h<sub>1</sub>), 2-Nh<sub>1</sub> (2-Nd<sub>7</sub>h<sub>1</sub>).

### 3. Experimental Results

#### 3.1. Excitation spectra of partially deuterated naphthalenes in Nd<sub>8</sub>

Figure 1 shows excitation spectra of the guest-host systems of partially deuterated naphthalenes in perdeuterated naphthalene, analyzed in the following, in comparison with undoped Nd<sub>8</sub> and undoped Nh<sub>8</sub>. The spectra are measured at 1.6 K with light polarized parallel to the a-crystal axis and with spectral resolution of 0.4 cm<sup>-1</sup>.

The subspectra of Fig. 1 are normalized to equal height of the a-polarized upper Davydov components (*H<sub>a</sub>*) of the host Nd<sub>8</sub> at 21 307.4 cm<sup>-1</sup> and of Nh<sub>8</sub> at 21 211.4 cm<sup>-1</sup>, resp.\*. Since the lower Davydov components (*H<sub>b</sub>*) at 21 299 cm<sup>-1</sup> in Nd<sub>8</sub> and at 21 202.2 cm<sup>-1</sup> in Nh<sub>8</sub> are predominantly b-polarized, they carry only weak intensity in the spectra of Figure 1. The guest spectral regions are recorded at higher sensitivity (×20 or ×10) than the Davydov components. The guest lines at 21 272.7 cm<sup>-1</sup>, 21 240.5 cm<sup>-1</sup> and 21 208.7 cm<sup>-1</sup> which belong to the dopants Nd<sub>4</sub>, Nd<sub>2</sub> and Nh<sub>8</sub>, resp., are marked by arrows. These lines increase linearly in intensity relative to the host lines with increasing guest concentration. They are referred to as the main monomers in the following.

\* The upper Davydov components of both Nd<sub>8</sub> and Nh<sub>8</sub> exhibit a high energetic substructure, only partially resolved in Fig. 1, which has been explained in detail elsewhere [8].

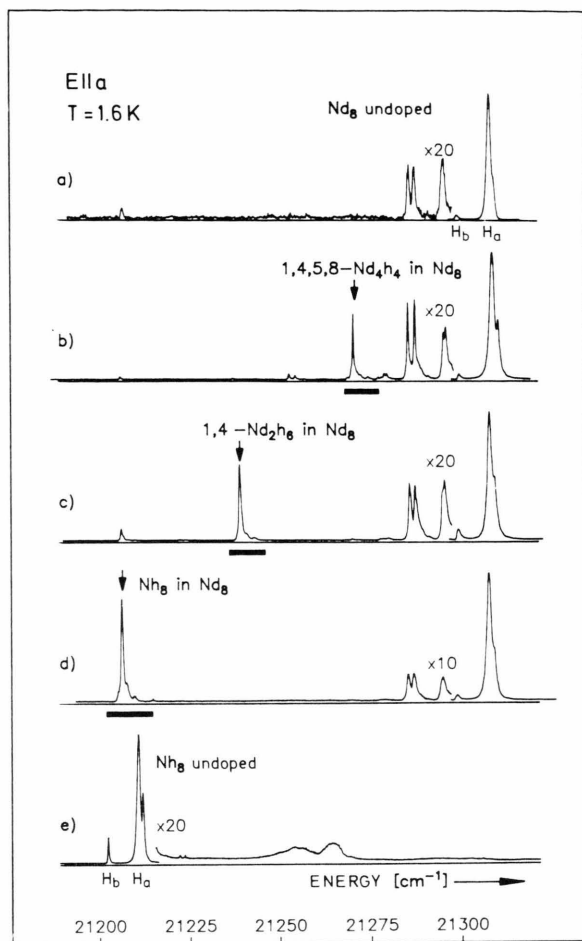


Fig. 1. Polarized excitation spectra ( $E \parallel a$ ) at 1.6 K of undoped Nd<sub>8</sub> (a), of Nd<sub>8</sub> doped with Nd<sub>4</sub> (b), with Nd<sub>2</sub> (c), with Nh<sub>8</sub> (d) and of undoped Nh<sub>8</sub> (e). The subspectra are normalized to equal height of the upper host Davydov components *H<sub>a</sub>*. The guest spectral regions are recorded at increased sensitivity (20 or 10 times, resp.).

The spectrum of Fig. 1a is observed for an undoped Nd<sub>8</sub> reference crystal. In addition to the Davydov components it reveals several lines at lower energy, which belong to isotopic impurities of partially deuterated naphthalenes always present in the Nd<sub>8</sub> starting material (at a total amount of about 10% according to mass spectroscopy). Since the same starting material was used for growing the mixed crystals, these lines appear in the subspectra of Figs. 1b...1d as well. (As compared to Fig. 1a, however, in these figures the relative intensity of some of the impurity lines is increased due to the fact, that the dopant material, too, contains partially

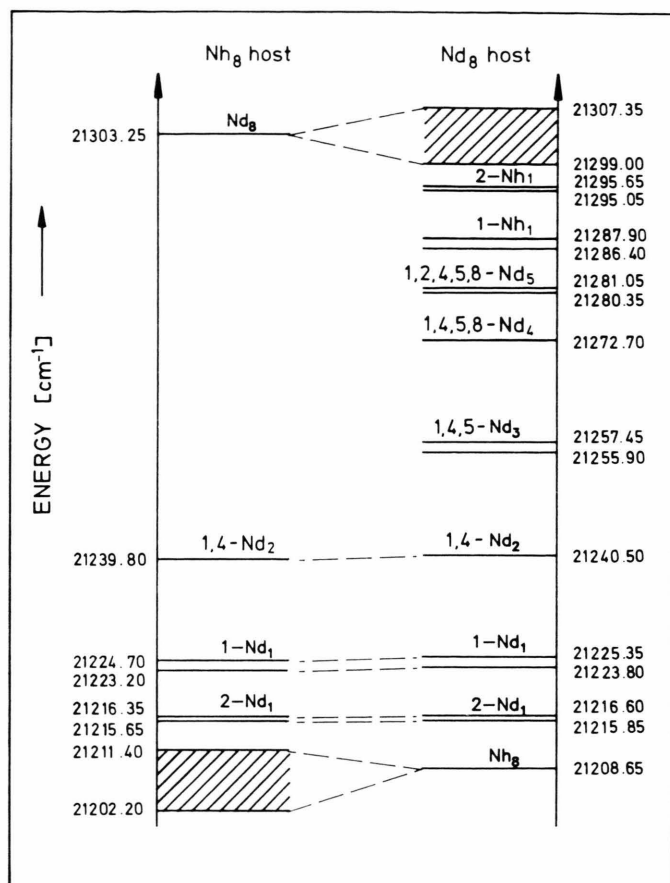


Fig. 2. Triplet energy level scheme (purely electronic region of  $T_1$ ) of the naphthalene mixed systems investigated in this paper. The host excitation bands are represented by their  $k = 0$  levels (Davydov components). *Left:*  $Nh_8$ . *Right:* host  $Nd_8$ .

deuterated compounds as impurities.) The spectrum of Fig. 1e is observed for the undoped  $Nh_8$  reference crystal. At their high energy side the  $Nh_8$  Davydov components are accompanied by weak lines due to naturally abundant  $Nd_1$  impurities (see also Sect. 3.2) and phonon sidebands [15] with broad maxima at 21 250  $cm^{-1}$  and 21 270  $cm^{-1}$ .

The absolute energetic positions of host, guest and impurity lines were determined at high spectral resolution by use of a direct reading wavemeter. They are summarized in the energy level scheme of Figure 2. (The scheme includes several impurities which do not appear in the spectra of Fig. 1 due to their low relative intensities.)

In  $Nd_8$  the lines of 1- $Nd_1$ ,  $Nd_3$ , 1- $Nh_1$  on the one hand and 2- $Nd_1$ ,  $Nd_5$ , 2- $Nh_1$  on the other hand are found split into two components of equal intensity, with splittings of 1.5  $cm^{-1}$  and 0.7  $cm^{-1}$ , resp. The

$Nd_1$  impurity lines in  $Nh_8$  show the corresponding splittings but are slightly shifted to lower energies (see Sects. 3.2 and 4.1.1). The  $Nd_2$  and  $Nd_4$  lines are not split (within 0.05  $cm^{-1}$ ).

The polarization ratios  $I_{||b}/I_{||a}$  of the guest and impurity lines in  $Nd_8$  monotonically increase with decreasing trap depth (see Fig. 2) from 0.37 for the deep trap  $Nh_8$  to 4.0 for the shallow trap 2- $Nh_1$ . This behaviour is known as Rashba effect [16]. The experimental intensity ratios are plotted in Fig. 3 versus  $(E_a - E_G)/(E_b - E_G)$  together with the theoretical curve (see Section 4.1.3).

The guest main monomer lines in Fig. 1, as discussed so far, are accompanied by a weak satellite substructure. This is studied in the following at high spectral resolution as a function of the guest concentration for the system  $Nh_8$  in  $Nd_8$  and compared with  $Nd_2$  in  $Nd_8$  and  $Nd_4$  in  $Nd_8$ .

Nh<sub>8</sub> in Nd<sub>8</sub>

Figure 4 shows the polarized excitation spectra of the Nh<sub>8</sub> guest region for various guest concentrations. The energetic positions of the lines are independent

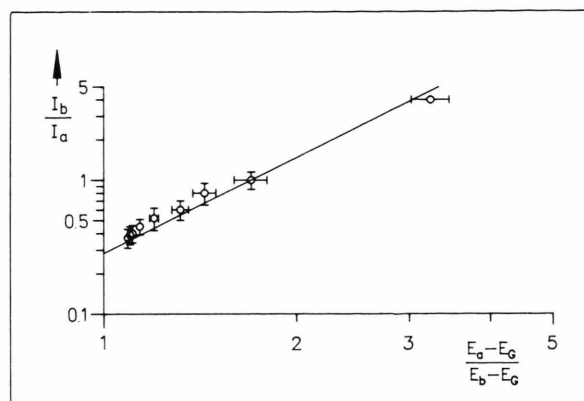


Fig. 3. Experimental monomer guest polarization ratios  $I_b/I_a$  plotted versus  $(E_a - E_G)/(E_b - E_G)$ . ( $E_a$ ,  $E_b$ ,  $E_G$  are the energetic positions of host  $a$ - and  $b$ -Davydov components and guest monomer, resp.). The straight line represents the fit to the Rashba formula (see Sect. 4.1.3).

of the concentration. The total linewidth is about  $0.25 \text{ cm}^{-1}$  and only slightly increases with concentration. All spectra are normalized to the respective main monomer intensity (the spectra polarized  $\parallel b$  therefore are reproduced with 2.7 times increased sensitivity as compared to the corresponding  $\parallel a$  spectra, see above). The normalization allows to distinguish guest aggregate lines, which gain intensity with increasing concentration, from further monomeric lines. The three monomer satellites at the high energy side of the main line (at  $+1.7 \text{ cm}^{-1}$ ,  $+2.1 \text{ cm}^{-1}$  and  $+3.5 \text{ cm}^{-1}$ ) correspond to the one-fold  $^{13}\text{C}$ -substituted naphthalene isomers ( $\beta$ ,  $\gamma$  and  $\alpha$  substitution positions are indicated in Fig. 4 schematically), which act as intrinsic impurities of the guest system in natural abundance of 4%, 2% and 4%, resp. Details about the identification of the different isomers were published separately in a comparative study with anthracene [13].

In the representation of Fig. 4 the pair line intensities depend linearly on guest concentration. Clearly three dominant pair lines are distinguished.

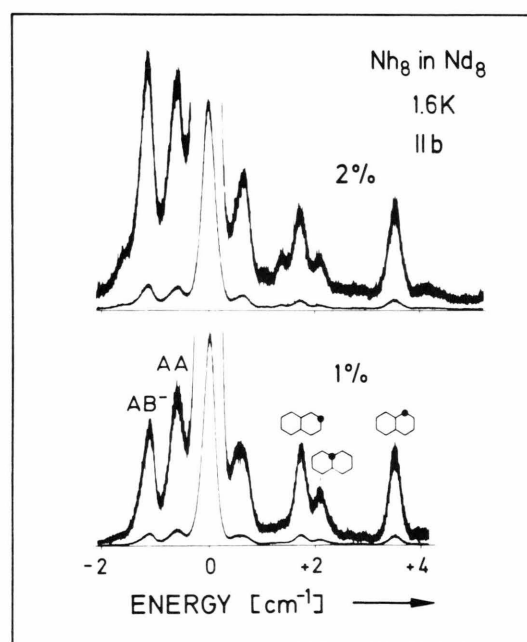
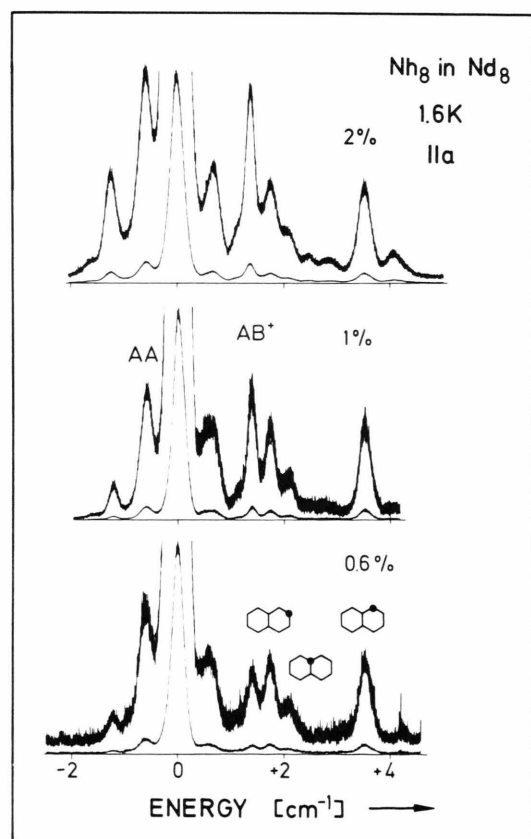


Fig. 4. Nh<sub>8</sub> in Nd<sub>8</sub> guest excitation spectra at different concentrations in  $\parallel a$ - and  $\parallel b$ -polarized light (left and right figure, resp.). The AA and AB dimer lines and the  $^{13}\text{C}$  monomer satellites are labelled. The spectra are normalized to the main monomer at  $21\,208.7 \text{ cm}^{-1}$ .



The two lines AB(+) and AB(−), at  $+1.35\text{ cm}^{-1}$  and  $-1.10\text{ cm}^{-1}$ , belong to the interchange group states of one translationally inequivalent guest pair. They are equally polarized as the Davydov components of the host (Figure 1). The line AA at  $-0.60\text{ cm}^{-1}$  corresponds to the optically active component of a translationally equivalent guest pair. The AA-pair line is equally polarized as the guest monomer line and therefore appears with equal intensity in the normalized  $\parallel a$ - and  $\parallel b$ -subspectra of Figure 4.

Trimer lines, whose intensity (in the normalized representation of Fig. 4) depends quadratically on the guest concentration, are observed at the low energy side of the AB(−) pair line.

Additional monomer satellites at about  $+0.6\text{ cm}^{-1}$  and at  $-0.5\text{ cm}^{-1}$ , underlying the AA-line, are not clearly identified so far. They resemble the ones observed in the anthracene guest spectrum [7]. Tentatively they are attributed to  $\text{Nh}_8$  monomers neighbouring one of the isotopic impurity molecules of the host and sensing a different solvent shift as compared to the  $\text{Nh}_8$  monomers in an undisturbed  $\text{Nd}_8$  environment.

#### $\text{Nd}_2$ in $\text{Nd}_8$ and $\text{Nd}_4$ in $\text{Nd}_8$

Examples for the polarized excitation spectra of the other two guest systems are given in Figs. 5

Table 1. Line positions and splitting of  $\text{Nh}_8$ ,  $\text{Nd}_2$ ,  $\text{Nd}_4$  guest dimers in the host  $\text{Nd}_8$ , given in  $\text{cm}^{-1}$  (relative to the respective main monomer; for the split dimer lines of  $\text{Nd}_2$  the average positions are given).

Guest	$\text{Nh}_8$	$\text{Nd}_2$	$\text{Nd}_4$
$U_0$	96	64	32
AB(−)	−1.10	−1.15	−1.30
AA	−0.60	−0.60	−0.55
AB(+)	1.35	1.30	1.20
AB-splitting	2.45	2.45	2.50

and 6 at guest concentrations of 1%. The spectra exhibit the same overall substructure as the  $\text{Nh}_8$  guest spectra.

As an additional feature of the  $\text{Nd}_2$  guest spectrum, however, both high and low energy AB pair satellites are split into two components, Figure 5. The splitting amounts to about  $0.3\text{ cm}^{-1}$ .

Slight systematic shifts (relative to the main monomer) are found for the pair lines in going from  $\text{Nh}_8$  to  $\text{Nd}_2$  and  $\text{Nd}_4$ , see Table 1 (for  $\text{Nd}_2$  in  $\text{Nd}_8$  the average AB positions are given).

The energetic shifts of the  $^{13}\text{C}$  monomer lines relative to the main ( $^{12}\text{C}$ ) monomer line are found identical in the three guest systems within an experimental error of  $\pm 0.05\text{ cm}^{-1}$ .

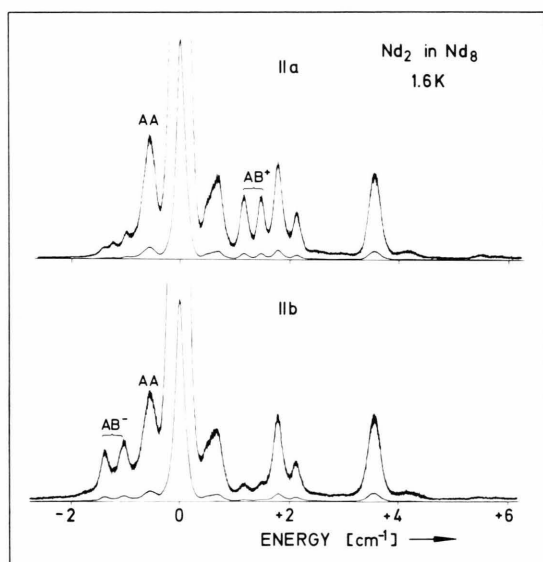


Fig. 5. Guest excitation spectra of 1%  $\text{Nd}_2$  in  $\text{Nd}_8$  in  $\parallel a$ - and  $\parallel b$ -polarized light (upper and lower trace, resp.). The spectra are normalized to the main monomer at  $21\,240.5\text{ cm}^{-1}$ .

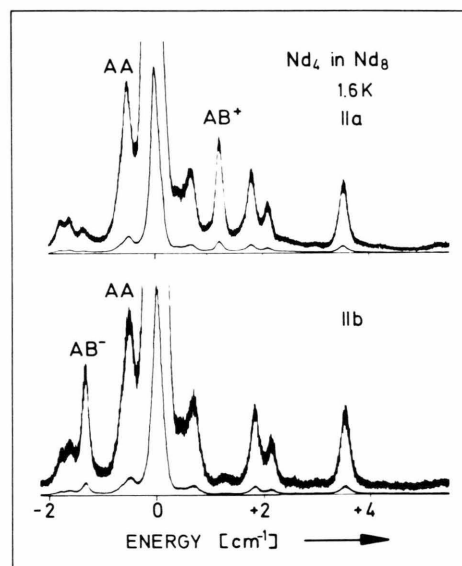


Fig. 6. Guest excitation spectra of 1%  $\text{Nd}_4$  in  $\text{Nd}_8$  in  $\parallel a$ - and  $\parallel b$ -polarized light (upper and lower trace, resp.). The spectra are normalized to the main monomer at  $21\,272.7\text{ cm}^{-1}$ .

### 3.2. Excitation spectra of partially deuterated naphthalenes in $Nh_8$

#### Guest monomer lines

In Fig. 7 the excitation spectra of isotopically mixed naphthalene systems are shown, in which the guest energy levels are lying *above* the  $Nh_8$  host exciton band. The spectra (similarly as in Fig. 1) are measured at 1.6 K with  $\parallel$  a-polarized excitation and normalized to equal height of the a-polarized upper Davydov component of the host  $Nh_8$  at  $21\,211.4\text{ cm}^{-1}$ . The guest spectral regions are recorded at 10 times increased sensitivity. The guest monomer lines are marked by arrows. The guest lines of 1- $Nd_1$  (at  $21\,223.2\text{ cm}^{-1}$  and  $21\,224.7\text{ cm}^{-1}$ ) and 2- $Nd_1$  (at

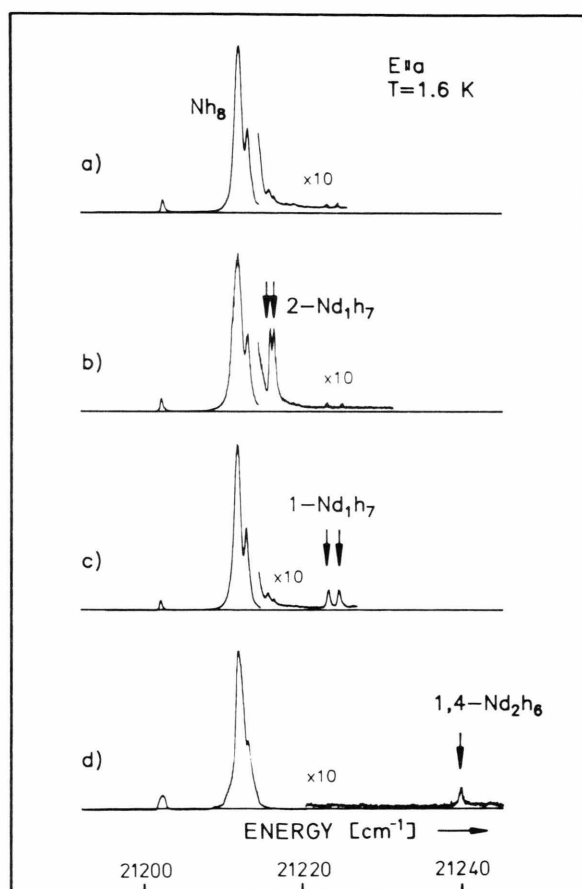


Fig. 7. Polarized excitation spectra ( $E \parallel a$ ) at 1.6 K of undoped  $Nh_8$  (a) and of  $Nh_8$  doped with 2- $Nd_1$  (b), with 1- $Nd_1$  (c) and with  $Nd_2$  (d), resp. The subspectra are normalized to the upper host Davydov component. The guest spectral regions are recorded at 10 times increased sensitivity.

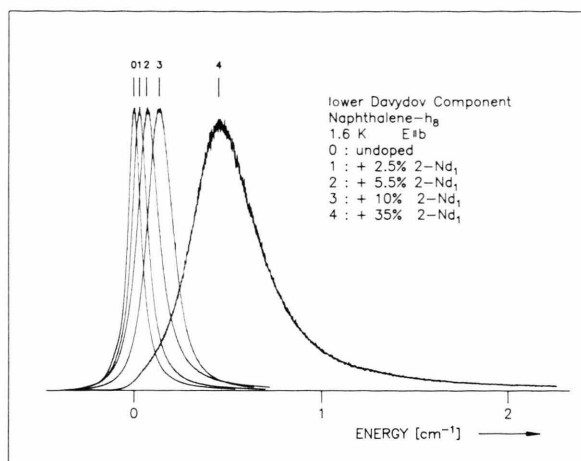


Fig. 8. Excitation spectra of the lower Davydov component of the host  $Nh_8$  at different 2- $Nd_1$  guest concentrations ( $E \parallel b$ ,  $T = 1.6\text{ K}$ ).

$21\,215.7\text{ cm}^{-1}$  and  $21\,216.4\text{ cm}^{-1}$ ) exhibit the same splitting as the corresponding guest lines in the  $Nd_8$  host. The weak relative intensity of these lines in the undoped  $Nh_8$  (Fig. 7a) is due to the low natural abundance of these isotopic naphthalene molecules (about 0.06%). For the  $Nd_2$  line (at  $21\,239.8\text{ cm}^{-1}$ ) as in  $Nd_8$  no splitting is observed. The absolute line positions are slightly shifted to lower energies as compared to those obtained in Sect. 3.1 (see the complete energy scheme of Figure 2).

#### Host line position and line width

The isotopic guests influence position, width and shape of the host excitation lines (Davydov components). A systematic study is performed for the lower Davydov component in the system 2- $Nd_1$  in  $Nh_8$ .

Figure 8 shows the concentration dependence of the lower Davydov component of the  $Nh_8$  host in extended energy scale. In the undoped  $Nh_8$  crystal this line is as narrow as  $0.08\text{ cm}^{-1}$  [8]. In the doped crystal the line monotonically shifts to higher energies and broadens drastically. At 35% the line shift is about  $0.45\text{ cm}^{-1}$  and the linewidth is increased to  $0.35\text{ cm}^{-1}$ . Quantitatively a linear concentration dependence is found for the lineshift (line maximum position), Fig. 9a, and a rough square root concentration dependence for the line width (FWHM), Figure 9b.

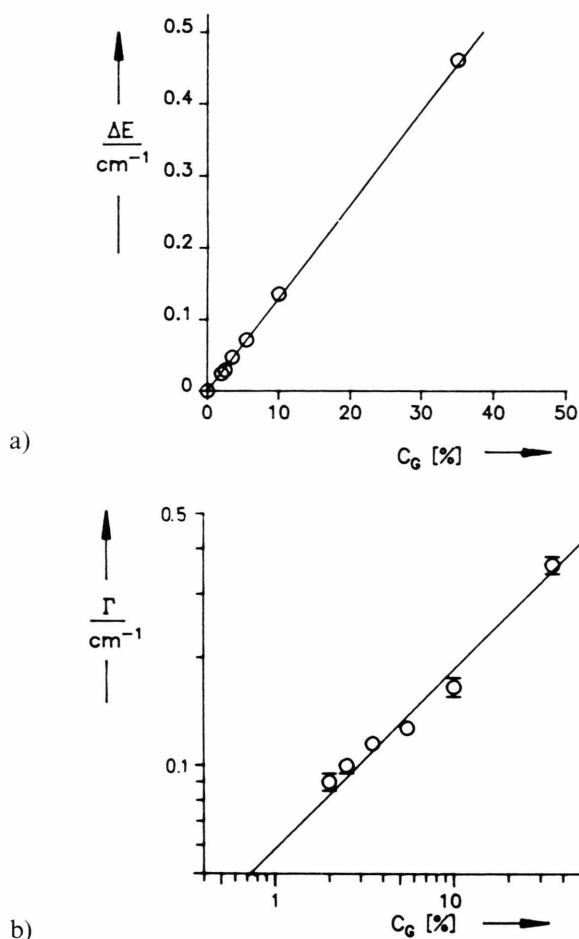


Fig. 9. Energetic position, upper plot (a), and linewidth (FWHM), lower plot (b), of the lower host Davydov component as a function of guest concentration in the system 2-Nd<sub>1</sub> in Nh<sub>8</sub> ( $T = 1.6$  K).

### 3.3. Phosphorescence emission spectra of Nh<sub>8</sub> in Nd<sub>8</sub>

The guest phosphorescence emission spectra are measured for the system Nh<sub>8</sub> in Nd<sub>8</sub> at concentrations between 0.1% and 15% Nh<sub>8</sub>. As emphasized already in Sect. 2 relatively thick Bridgman grown samples have to be used for to observe the weak phosphorescence still at high spectral resolution.

The spectra presented in the following are normalized, similarly as the excitation spectra, to the main Nh<sub>8</sub> monomer at  $21\,208.6\text{ cm}^{-1}$ . The main monomer is the dominant line in the guest spectrum up to 6% and is not shifted with increasing concentration. Its linewidth slightly increases from about  $0.25\text{ cm}^{-1}$  below 0.5% to about  $0.35\text{ cm}^{-1}$  at 6%.

At guest concentrations up to 3% the guest spectra exhibit the same substructure as the excitation spectra described in Sect. 3.1. In the low concentration limit only the three  $^{13}\text{C}$  monomer lines appear as high energy satellites in the spectrum (Figure 10). At 3% the AB and AA pair lines appear stronger in intensity than the  $^{13}\text{C}$ -lines (Figure 11). The relative

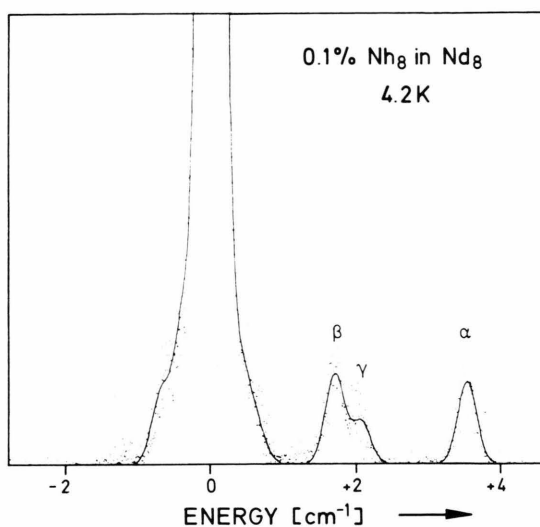


Fig. 10. Guest phosphorescence emission of 0.1% Nh<sub>8</sub> in Nd<sub>8</sub> at 4.2 K; experimental plot (dotted) and computer fit (full line).

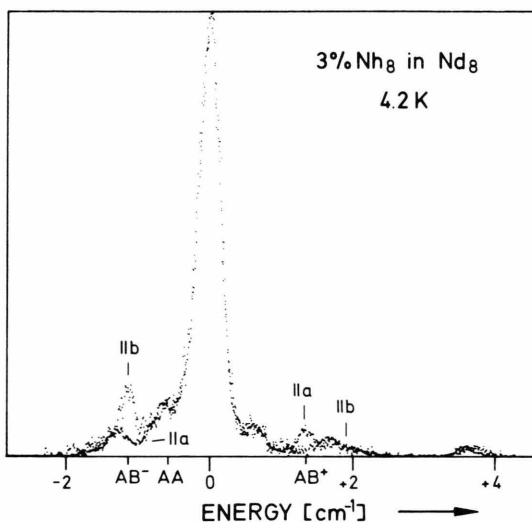


Fig. 11. Guest phosphorescence spectra of 3% Nh<sub>8</sub> in Nd<sub>8</sub> at 4.2 K in  $\parallel a$ - and  $\parallel b$ -polarized light. "AA" and "AB" indicate the positions of the dimer lines. The subspectra are normalized to the main monomer line at  $21\,208.7\text{ cm}^{-1}$ .

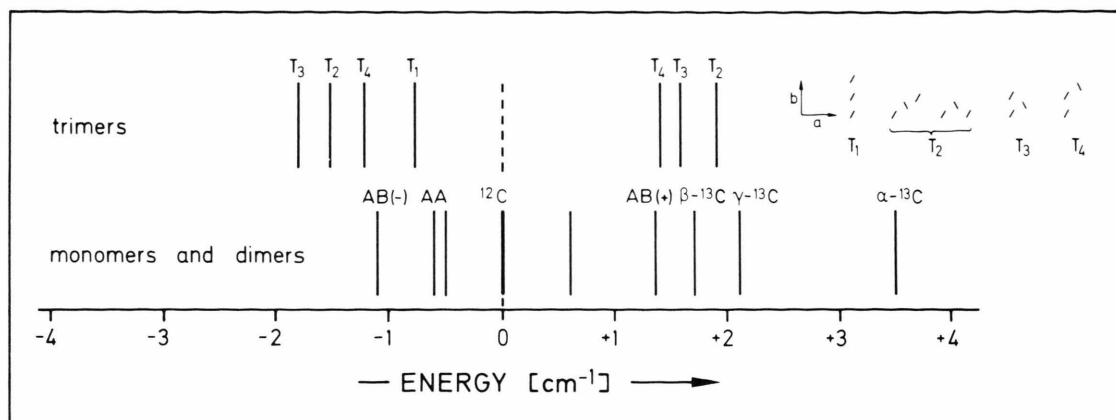


Fig. 12. Guest aggregate level scheme of the  $\text{Nh}_8$  in  $\text{Nd}_8$  mixed system. The main ( $^{12}\text{C}$ ) monomer line position is taken as origin for the energy scale. The dimer lines are attributed to the configurations  $T_1 \dots T_4$  schematically shown in the insert.

pair line intensities in the emission spectrum do not correspond to those observed in the excitation spectra. As expected, the relative intensities of the AB lines reflect the Boltzmann population difference (at 4.2 K) for the  $\text{AB}(+)$  and  $\text{AB}(-)$  pair levels being about  $2.4 \text{ cm}^{-1}$  apart. In addition the trimer lines are more intense than expected at this concentration.

In the level scheme of Fig. 12 are summarized the guest monomer, dimer and trimer levels obtained from the complete analysis of both excitation and emission spectra of  $\text{Nh}_8$  in  $\text{Nd}_8$ . (For the attribution of the trimer lines to the configurations  $T_1 \dots T_4$  given in the insert see Section 4.1.)

At higher guest concentrations the intensity distribution within the guest spectra changes drastically and also becomes strongly temperature dependent. In Fig. 13 as an example the polarized spectra at 1.5 K and at 4.2 K are given for a 6% crystal.

Comparing Figs. 13 qualitatively with each other and with Fig. 11 two features are remarkable: At first, the relative intensity of the aggregate spectral contributions at the low energy side of the main monomer strongly increases upon lowering the temperature from 4.2 K to 1.5 K. In both polarizations this increase is much more than can be accounted for by the respective Boltzmann factors. Secondly, the high energy  $^{13}\text{C}$  monomer satellites at 1.5 K (Fig. 13) no longer are observed in the spectrum. At concentrations above 6% the intensities of higher aggregates increase rapidly, details of the substructure are smeared out and the center of gravity shifts to lower energy (Figure 14).

## 4. Discussion

The discussion of the experimental results is divided in three subsections. It starts with the analysis of the guest monomer and aggregate spectra with respect to line positions, splittings and intensities. From the experimentally determined resonance pair interactions the triplet exciton band structure is calculated. Finally the effects of isotopic doping on the host exciton lines are compared with theoretical predictions.

### 4.1. Guest spectra

The guest spectra of isotopically mixed crystals generally as zero order approach are described applying the concept of the "ideal mixed crystal" (IMC) [17]. This implies several assumptions: The guest molecules are perfectly substituted in the host lattice. Guest and host only differ in their site excitation energies (isotopic shift  $U_0$ ); both static and dynamic interactions (solvent shift  $D$  and pair resonance interactions  $J$ ) are invariant to isotopic substitution. Nonresonant interactions between guest and host molecules can be neglected, as long as  $U_0$  is large as compared to the width of the host exciton band ("deep trap limit"). In the IMC-approximation guest dimer lines are split symmetrically with respect to the monomer line. The splitting is given by two times the resonance interaction  $J$ .

In actual cases, however, "quasiresonance" effects are expected to occur, which originate in non-

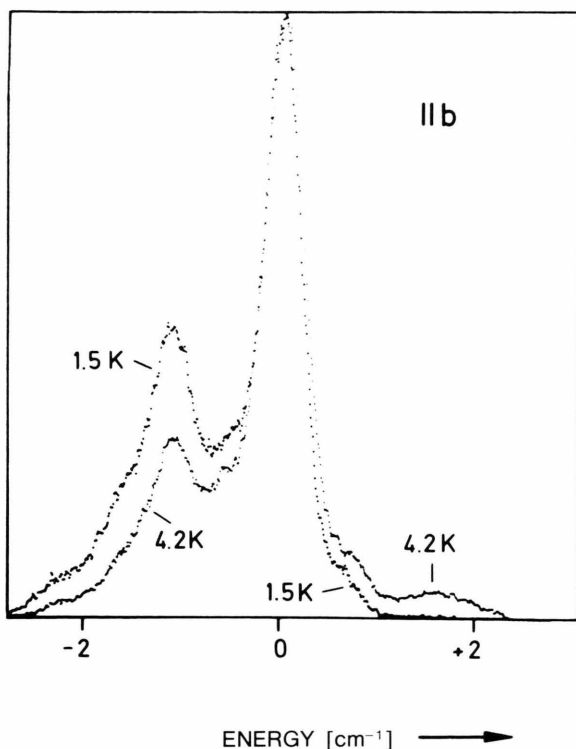
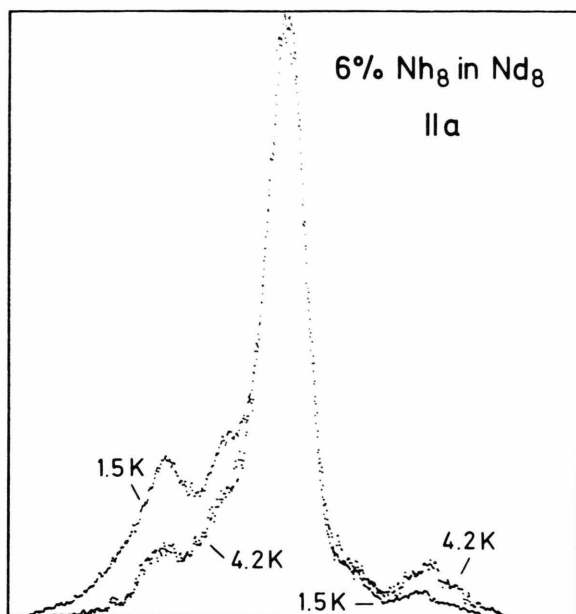


Fig. 13. Guest phosphorescence spectra of 6%  $\text{Nh}_8$  in  $\text{Nd}_8$ , at 1.5 K and 4.2 K, in  $\parallel a$ - and  $\parallel b$ -polarized light, upper and lower plots, resp.

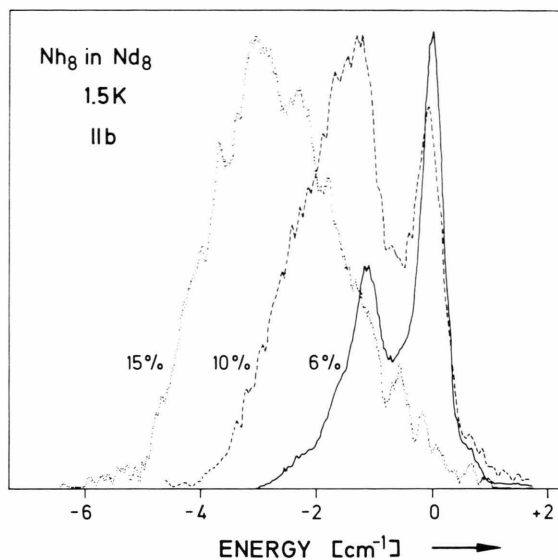


Fig. 14. Guest phosphorescence spectra at concentrations of 6%, 10% and 15%  $\text{Nh}_8$  in  $\text{Nd}_8$  at 1.5 K ( $E \parallel b$ ).

resonant guest-host interactions [17, 18]. These lead to shifts of both monomer and dimer lines and changes in the polarization properties of the guest lines relative to the IMC case. The following analysis does include the corrections for quasiresonance and accounts for differences in guest and host solvent shifts.

#### 4.1.1. Monomer line positions

The guest spectra of partially deuterated naphthalenes in host matrices of both  $\text{Nh}_8$  and  $\text{Nd}_8$  are studied. By comparison of the energetic line positions given in the energy scheme of Fig. 2, the relevance of quasiresonance and solvent shift corrections can be found out and the true isotopic shifts  $U_0$  can be determined.

At first the relative energetic positions of the guest main monomers and the host Davydov components of the complementary mixed systems  $\text{Nh}_8$  in  $\text{Nd}_8$  and  $\text{Nd}_8$  in  $\text{Nh}_8$  are compared. Keeping within the IMC-model the energetic differences between the  $\text{Nh}_8$  and  $\text{Nd}_8$  guest monomer levels on the one hand and the average positions of the Davydov components of the hosts on the other hand are expected to be equal. (The quasiresonance shifts of the  $\text{Nh}_8$  and  $\text{Nd}_8$  monomer levels are small,



about  $0.05\text{ cm}^{-1}$ , and can be neglected.) Instead the experiment yields  $94.6\text{ cm}^{-1}$  and  $96.4\text{ cm}^{-1}$  for the respective differences. Obviously, and similarly as in other crystals (benzene [19], anthracene [7] and phenazine [14]) the static solvent shifts  $D$  of the molecules in the undeuterated and perdeuterated naphthalene matrices are different. The solvent shift in  $\text{Nh}_8$  is larger than in  $\text{Nd}_8$ ,  $\Delta D = D^h - D^d = 0.9\text{ cm}^{-1}$ . This means that the actual isotopic shift  $U_0$  between  $\text{Nh}_8$  and  $\text{Nd}_8$  should be  $95.5\text{ cm}^{-1}$ .

These conclusions can be tested applying the energy scheme of Fig. 15 in which a further correlation is made plausible. The energy difference between the average position of the  $\text{Nd}_8$  Davydov components and the  $\text{Nh}_8$  guest monomer level on the one hand and the  $\text{Nd}_8$  guest monomer level and the average position of the  $\text{Nh}_8$  Davydov components on the other hand are given by  $U_0 - L_{11}^h$  and  $U_0 + L_{11}^d$ , resp., where  $L_{11}$  is the translational shift (i.e. the sum over the resonance interactions  $J$  of a molecule with its translationally equivalent neighbours). The experimental values for the differences are  $94.55\text{ cm}^{-1}$  and  $96.45\text{ cm}^{-1}$ , i.e. the translational shift is the same and about  $1\text{ cm}^{-1}$  in both mixed crystal systems. This finding is in good agreement with the results deduced from the guest dimer spectra (next section):  $J$  isotope-independent and  $L_{11} = 2J_b = 1.14\text{ cm}^{-1}$ .

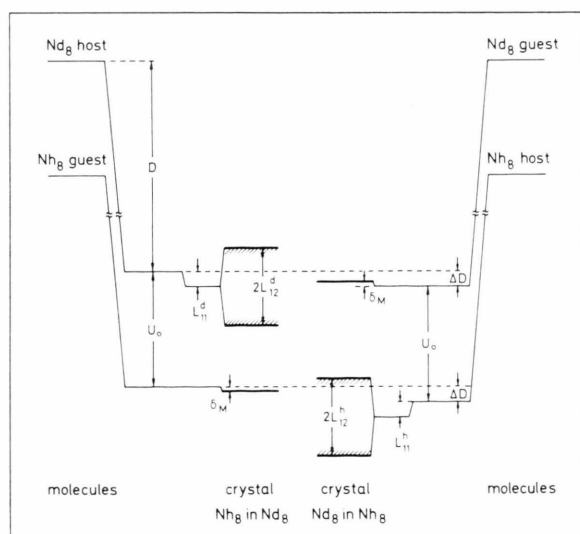


Fig. 15. Energy level scheme of the reversed mixed systems  $\text{Nh}_8$  in  $\text{Nd}_8$  and  $\text{Nd}_8$  in  $\text{Nh}_8$ , comparison of molecular and crystal levels (see text).

Table 2. Isotopic shifts  $U_0$  and orientational splittings of the various guests with respect to the host  $\text{Nd}_8$ , given in  $\text{cm}^{-1}$  (both values are corrected for quasiresonance, for the split levels the average  $U_0$  is tabulated).

Guest	$U_0$	splitting
$\text{Nh}_8$	95.5	—
2- $\text{Nd}_1$	87.9	0.75
1- $\text{Nd}_1$	79.5	1.55
1,4- $\text{Nd}_2$	63.9	—
1,4,5- $\text{Nd}_3$	47.4	1.55
1,4,5,8- $\text{Nd}_4$	31.8	—
1,2,4,5,8- $\text{Nd}_5$	23.5	0.7
1- $\text{Nh}_1$	16.2	1.5
2- $\text{Nh}_1$	7.8	0.65

According to Fig. 2 the absolute energetic positions of the guest monomers 1- $\text{Nd}_1$ , 2- $\text{Nd}_1$  and  $\text{Nd}_2$  are redshifted in the  $\text{Nh}_8$  host as compared to the  $\text{Nd}_8$  host. These shifts are understood quantitatively when the opposite effects of quasiresonance and the solvent shift difference  $\Delta D$  determined above are superimposed. The true isotopic shifts  $U_0$  of the guests (with respect to the  $\text{Nd}_8$  matrix) are listed in Table 2.

The comparison of the energetic positions of the 1- $\text{Nd}_1$ , 2- $\text{Nd}_1$ ,  $\text{Nd}_2$ ,  $\text{Nd}_3$ ,  $\text{Nd}_4$  and  $\text{Nd}_5$  guest monomers (Fig. 2) shows that the isotopic shifts of the multiple  $\alpha$ - or/and  $\beta$ -deuterium naphthalenes are given by the sum of the individual shifts (within  $\pm 0.5\text{ cm}^{-1}$ ). Since the energetic shifts of the  $^{13}\text{C}$  satellite lines in the various guest spectra are found to be equal, it is concluded that the additivity also holds for mixed deuterium and  $^{13}\text{C}$  substitution. Both conclusions previously have been verified also for the anthracene triplet state [7, 13].

The observed splittings of certain monomer levels are understood as orientational splitting of the non-inversion symmetric isotopic molecules in the matrix of  $\text{C}_{2h}^b$  symmetry. From the experimental findings in Sects. 3.1 and 3.2 (see Table 2) it is evident that splittings of  $1.5\text{ cm}^{-1}$  and  $0.7\text{ cm}^{-1}$  (within  $\pm 0.05\text{ cm}^{-1}$ ) result, if the molecular inversion symmetry is removed by substitution in the  $\alpha$ - and  $\beta$ -position, resp.\*. (In contradiction to this general statement no splitting is observed for the 1,4- $\text{Nd}_2$  monomer line. This seems to indicate that the  $\alpha$ -orientational splitting is essentially caused by

\* Measured under low resolution conditions a splitting of about  $0.7\text{ cm}^{-1}$  for the  $\alpha$ -substituted 1- $\text{Nd}_1$  guest line in  $\text{Nd}_8$  previously has been reported [11].

the asymmetry with respect to the long molecular axis.)

#### 4.1.2. Dimers and trimers

##### Dimers

From the guest spectra of  $\text{Nh}_8$ ,  $\text{Nd}_2$  and  $\text{Nd}_4$  in  $\text{Nd}_8$  two dimers AB and AA are identified from the concentration dependence and polarization behaviour of the satellite lines. The high energy AB(+) and the low energy AB(−) component of the translationally inequivalent AB-pair are equally polarized as the Davydov components of the naphthalene crystal, predominantly  $\parallel a$  and  $\parallel b$ , resp. (The attribution of the Davydov components to the (+) and (−) factor group components of the  $C_{2h}^h$  symmetry group of the naphthalene crystal has been given in [20]. The ordering is reversed as compared to the anthracene triplet state [7].)

The dimer splittings in the three guest systems analyzed are found to be almost equal (Table 2). The slight increase of the AB-splitting between  $\text{Nh}_8$  and  $\text{Nd}_4$  is due to quasiresonance shifts of the dimer levels. It is understood quantitatively from Fig. 16, where the calculated quasiresonance shifts  $\delta$  for monomers and dimers (using the Green's function formalism [21, 18]) are plotted as a function of the isotopic shift  $U_0$ .

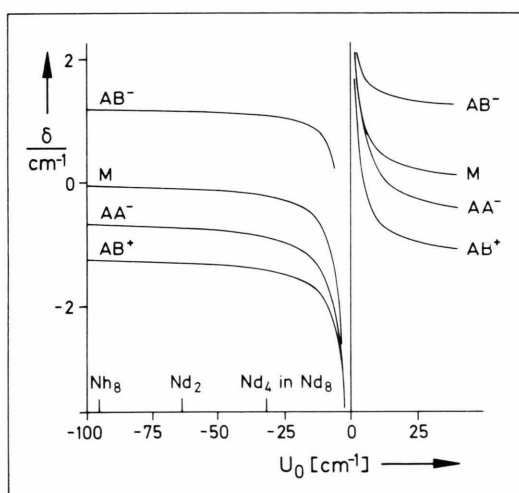


Fig. 16. Calculated quasiresonance shifts  $\delta$  for isotopically mixed naphthalene host-guest systems as a function of the respective isotopic shift  $U_0$  (monomer level "M", pair levels "AB" and "AA").

From the energetic positions  $E_{AB}$ ,  $E_{AA}$  and  $E_M$  of the dimer and monomer lines measured for  $\text{Nh}_8$  in  $\text{Nd}_8$  the resonance interactions  $J$  can be evaluated:  $2J_{AB} = E_{AB(+)} - E_{AB(-)}$  and  $J_{AA} = E_{AA} - E_M$ . (Here-with the usual convention is applied for the sign of  $J$ .) After quasiresonance correction the following values are obtained:

$$J_{AB} = +1.20 \text{ cm}^{-1} \pm 0.05 \text{ cm}^{-1},$$

$$J_{AA} = -0.57 \text{ cm}^{-1} \pm 0.05 \text{ cm}^{-1}.$$

There is no doubt about the attribution of the dimers and  $J$  values to the pair configurations  $0/\frac{1}{2}(a+b)$  and  $0/b$  since these are distinguished by their small intermolecular distances as compared to the other configurations. The  $J$  values also are within the limits of error of literature values which have been conjectured previously from theory [22] and experiment [9, 10, 12, 23, 24]\*.

Since the quasiresonance-corrected dimer splittings of the different guest systems analyzed are identical it follows, that the resonance interactions are isotope-independent. (This is not in contradiction to the finding that the Davydov splitting of the 0.0 transition in  $\text{Nd}_8$  is smaller than in  $\text{Nh}_8$ , see [8].)

An asymmetry of the AB dimer lines with respect to the monomer is observed in the present experiments, about  $0.1 \text{ cm}^{-1}$  for  $\text{Nh}_8$  in  $\text{Nd}_8$ . It does not influence the evaluation of  $J_{AB}$ , but is larger than expected from the calculated quasiresonance shifts of the monomer and AB levels (Figure 16). A similar asymmetry has been observed for the anthracene triplet AB dimer [7]. It is supposed to be correlated to the differing solvent shifts in the  $\text{Nh}_8$  and  $\text{Nd}_8$  environments (see Sect. 4.1.1).

The observed splitting of the AB dimer components in the spectra of  $\text{Nd}_2$  in  $\text{Nd}_8$  can be understood as a site splitting related to the asymmetry of the  $\text{Nd}_2$  molecule, in contrast to the symmetric  $\text{Nh}_8$  and  $\text{Nd}_8$  guests.

##### Trimers

For the  $\text{Nh}_8$  in  $\text{Nd}_8$  guest spectra the analysis has been extended to higher guest concentrations. This requires the consideration of guest trimers and higher aggregates.

\*  $\text{N-h}_8$  guest AB-dimers as well as ABA trimers (see below) have been identified originally by ESR in high magnetic field [25].

If the two dominant resonance interactions  $J_{AB}$  in the  $\frac{1}{2}(a+b)$ -direction and  $J_{AA}$  in the  $b$ -direction are considered, four trimer configurations  $T_1 \dots T_4$  have to be distinguished (see the insert in Figure 12). In IMC-approximation the corresponding trimer energy levels can easily be calculated, using the experimental  $J$ -values. The comparison with the experimental trimer lines in Sect. 3 leads to the attribution given in Figure 12. The experimentally determined line positions of the trimers slightly differ from the calculated ones, presumably because of similar additional solvent shift effects (of the trimer partner molecules in their heterogeneous  $Nh_8$  guest/ $Nd_8$  host environment) as discussed for the AB dimer.

In the excitation spectra the relative intensities of the guest monomer, dimer and trimer lines are determined by the respective statistical probabilities and dipole matrix elements. However, in the phosphorescence emission spectra of  $Nh_8$  in  $Nd_8$  deviations from the statistical intensity distribution are observed already at guest concentrations  $c_G \geq 3\%$ . The observed concentration and temperature dependencies are understood as result of population transfer within the guest system via the (most abundant) monomer traps, which is effective *without* thermal activation to the host exciton band. In the spectral features with increasing concentration no abrupt change is observed, which would be indicative for a threshold between localized and extended states [26–28]. The present experimental results are not yet as complete as to allow for conclusions about the kinetics of the guest-guest energy transfer. Further considerations also must take into account the competing effect of long range guest-guest triplet-triplet annihilation, which presumably is responsible for the temperature-independent part of the delayed fluorescence in  $Nh_8/Nd_8$  mixed crystals [29]. (Possibly in this context also long range dipole-dipole interactions have to be taken into account for the triplet state [30].)

#### 4.1.3. Guest polarization behaviour

The experimental polarization ratios  $I_{\parallel b}/I_{\parallel a}$  of the guest monomer lines of the various isotopic guests in  $Nd_8$  (Fig. 3) exhibit the “Rashba effect” [16], i.e. they are becoming larger as the guest levels approach the host exciton band. This behaviour is

caused by the concomitant increased delocalization of the guest excitation on neighbouring host molecules. As a consequence, the optical transitions to the guest states partially adopt the polarization behaviour of the energetically nearest  $k=0$  level of the host band (i.e. the almost exclusively b-polarized lower Davydov component).

According to the theory the following expression should be valid:

$$\frac{I_{\parallel b}}{I_{\parallel a}} = \left( \frac{E_a - E_G}{E_b - E_G} \right)^2 \left( \frac{\mu_b}{\mu_a} \right)^2.$$

$E_a$ ,  $E_b$ ,  $E_G$  are the energetic positions of the  $\parallel a$  and  $\parallel b$  polarized Davydov components of the host exciton band and of the guest monomer line, resp.  $(\mu_b/\mu_a)^2$  is the “oriented gas” polarization ratio [20, 31], i.e. the ratio of the squared projections of the molecular transition dipole onto the crystal axes  $b$  and  $a$ . The straight line in Fig. 3 represents the theoretical dependence using for  $(\mu_b/\mu_a)^2$  the value 0.28, which is obtained for a transition  $T_1 \leftarrow S_0$  polarized perpendicular to the molecular plane [31]. This value is also found for the integral polarization ratio of the b- and a-polarized naphthalene host Davydov components.

#### 4.2. Exciton band structure

Within the restricted Davydov-Frenkel limit the exciton band dispersion is determined by only nearest neighbour interactions [32]. For the  $T_1$  exciton band in naphthalene it is given in good approximation by:

$$\varepsilon(\mathbf{k}) = 2J_{AA} \cos(\mathbf{k} \cdot \mathbf{b}) \pm 2J_{AB} \{ \cos[\mathbf{k} \cdot \tfrac{1}{2}(\mathbf{a} + \mathbf{b})] + \cos[\mathbf{k} \cdot \tfrac{1}{2}(\mathbf{a} - \mathbf{b})] \}.$$

Using the experimental  $J$ -values  $\varepsilon(\mathbf{k})$  is calculated explicitly and plotted in Fig. 17 for the three reciprocal lattice directions  $a^{-1}$ ,  $b^{-1}$  and  $c^{-1}$ .

The calculated band structure is two-dimensional. The exciton dispersion in the third dimension, however, is not negligible as can be inferred from the experimental results discussed in Section 4.3. According to theoretical predictions the most probable out-of-plane contribution should be due to resonance pair interaction of the AB-configuration  $0/\frac{1}{2}(a+b)+c$  [33]. Such an additional AB-interaction in the order of  $0.05 \text{ cm}^{-1}$  (and with opposite sign) would also explain the slight difference between the experimentally observed Davydov splitting  $\Delta_h = 9.2 \text{ cm}^{-1}$

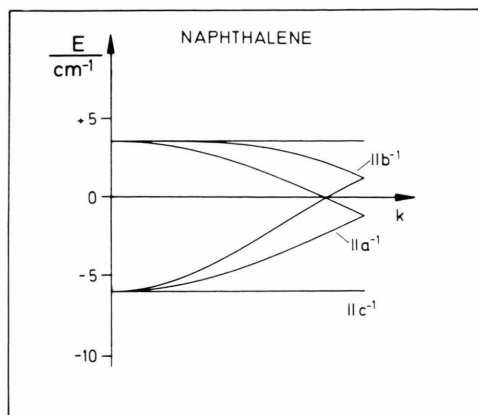


Fig. 17. Calculated exciton band structure of the naphthalene  $T_1$  state for the reciprocal lattice directions  $a^{-1}$ ,  $b^{-1}$  and  $c^{-1}$ . The experimentally determined values of the triplet resonance interactions have been used.

[8] and the expected value ( $\Delta_h = 2 \sum_i J_{AB}^i \cong 8 J_{AB} = 9.6 \text{ cm}^{-1}$ ). From the pair spectra an upper limit for additional resonance interactions of about  $\pm 0.1 \text{ cm}^{-1}$  can be estimated.

Similarly as for anthracene and phenazine the lower  $k=0$  level is situated at the bottom of the exciton band. This causes the much narrower line-width of the lower Davydov component as compared to the upper one, observed in the excitation spectra of these crystals [14, 15, 8].

#### 4.3. Host lines

Shift and broadening of the host Davydov components are observed upon doping with isotopic guests.

The concentration dependence of the *shift* can be described by a theory deduced by Lifshitz [34]. The theory predicts a linear shift  $\Delta E$  of the lower edge of the host band, i.e. (Fig. 17) the lower Davydov component, as a function of the guest concentration  $c_G$ :

$$\Delta E = c_G U_0 U_{cr} / (U_0 + U_{cr}).$$

$U_{cr}$  is the critical value of the isotopic shift  $U_0$  for which a guest term just splits off the host band and forms a bound state (actually there exist two parameters  $U_{cr}^+$  and  $U_{cr}^-$  for guest levels at higher or lower energy from the host band center, resp.).

In the experiments on  $\text{Nh}_8$  doped with 2- $\text{Nd}_1$  the linear dependence of the shift on  $c_G$  is actually found (Figure 9a). The fit to the Lifshitz formula (solid curve in Fig. 9a) yields  $U_{cr}^+ = 1.6 \pm 0.2 \text{ cm}^{-1}$

for the naphthalene  $T_1$  excitation band (since the 2- $\text{Nd}_1$  guest lines are split into two components with  $U_0 = 7.2 \text{ cm}^{-1}$  and  $U_0 = 8.0 \text{ cm}^{-1}$ , the average value  $U_0 = 7.6 \text{ cm}^{-1}$  has been used in the calculation). From the corresponding shifts in the 1- $\text{Nd}_1$  in  $\text{Nh}_8$  mixed system ( $U_0 = 16 \text{ cm}^{-1}$ ) within the experimental error ( $\pm 0.2 \text{ cm}^{-1}$ ) the same value for  $U_{cr}^+$  is obtained.

The existence of a critical isotopic shift makes evident, that the triplet  $T_1$  exciton band in naphthalene is effectively three-dimensional. Idealized one- and two-dimensional bands lead to  $U_{cr}^\pm = 0$  [18]. Since  $U_{cr}^+$  is smaller than the  $^{13}\text{C}$  isotopic shifts in the naphthalene  $T_1$  state (Sect. 3.1 and [13]), all impurity levels of naturally abundant  $^{13}\text{C}$ -substituted molecules in the undoped naphthalene crystal split off the ( $^{12}\text{C}$ ) exciton band. They cause the complex substructure of the upper Davydov component of undoped  $\text{Nh}_8$  and  $\text{Nd}_8$  [15, 8]. (In the low resolution spectra of Figs. 1 and 6 only the predominant  $\alpha$ - $^{13}\text{C}$  subcomponent is resolved in the high energy tail of the upper Davydov component.)

For the host line *broadening* experimentally roughly a square root dependence on the guest concentration is obtained. This is in agreement with predictions of the theory of substitutionally disordered solids [1] for low concentrations. The proportionality factor, however, is smaller than expected by about a factor of five.

#### 5. Conclusion

From high resolution optical investigations new experimental data are obtained on the guest and host triplet  $T_1$  state of a variety of naphthalene isotopically mixed crystals. Guest monomer and aggregate spectra are analyzed with regard to line positions, splittings, polarizations and intensities. Information is deduced about guest-guest interactions and energy transfer on a microscopic scale, which should prove useful for a more detailed understanding of impurity band transfer in the naphthalene crystal.

The mutual dynamic guest-host interaction manifests itself not only in the properties of the guest lines but also in shift and broadening of the host exciton lines. The derived critical isotopic shift together with the exciton band structure are essential for the interpretation of exciton line shape data of undoped naphthalenes.

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