INVESTIGATION OF THERMAL DETRAPPING IN A NAPHTHALENE CRYSTAL

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We investigated thermal detrapping for a series of naphthalene X-traps. The difference in the pre-exponential factor of the detrapping rate for the series studied is related to the difference in optical electron–phonon coupling.

Triplet excitons in organic crystals can be immobilised on trap sites, thus creating localized excited triplet states. Because this trapping and its reverse, the detrapping, greatly affect the energy migration in the crystal, several attempts were made to understand these processes. Fayer and Harris [1] developed a model for the detrapping process, where an excited trap state plus a phonon form an intermediate, which decays into the exciton band. In this model the detrapping rate k_s varies with temperature via an Arrhenius-type law

$$k_s = k_s^0 \exp(-\Delta E_s/kT) \, ,$$

where ΔE_s is the depth of the excited trap state (here referred to as "shallow trap t_s") below the energy of the exciton band. If there is an additional deeper trap t_d, coupled to the shallow trap via the exciton band, one can determine the temperature independent detrapping rate k_s^0 of the shallow trap from a logarithmic plot of the intensity ratio I_s/I_d of the trap emissions versus the reciprocal temperature [2]. Experiments of this kind have been done mainly on shallow traps 1,2,4,5-tetrachlorobenzene [2–4].

In this letter we present a study of detrapping of the lowest triplet state of a series of naphthalene X-traps. These X-traps were created by doping a naphthalene crystal with a small amount of β-halonaphthalene (10^{-3} mol/mol). We refer to these X-traps as the "shallow traps". Additionally to the β-halonaphthalenes the crystal was doped with a second impurity (also 10^{-3} mol/mol) to which we refer as the "deep trap". The molecules used as deep traps are indicated in fig. 1. The phosphorescence spectra of the X-traps have been published elsewhere [5]. Their trap depths increase from ≈ 250 cm^{-1} for the Cl X-trap [*] to 470 cm^{-1} for the I X-trap. We attribute this to the increasing charge-transfer character of the perturber–trap system with increasing halogen mass. This CT enhancement leads to remarkable changes in the electron–phonon coupling [5] and triplet decay dynamics [6]. In contrast, the relative orientation of the trap molecules in the crystal seems to be little affected by the perturber [7].

Fig. 1 shows the temperature dependence of the phosphorescence intensity ratio I_s/I_d of the system studied. From its high-temperature onset the emission intensity ratio increases exponentially with decreasing temperature until it reaches its constant low-temperature value. The pre-exponential detrapping rates k_s^0 calculated from the data of fig. 1 are displayed in fig. 2. They are $\approx 10^{11}$ s^{-1} and exhibit a notable increase of a factor of six between the Cl and the I X-trap.

To explain these results we keep in mind that the detrapping rate is governed by both the electronic and nuclear overlap integrals. As to the former, we assume

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[*] Cl X-trap is a short notation for a naphthalene X-trap created by doping the naphthalene crystal with a small amount of β-chloronaphthalene.
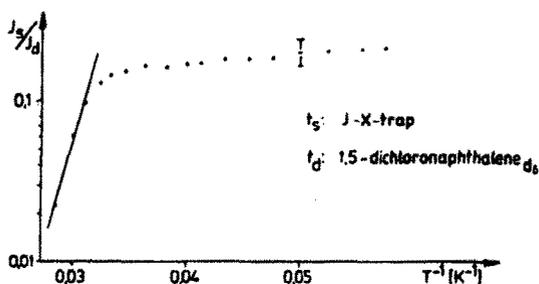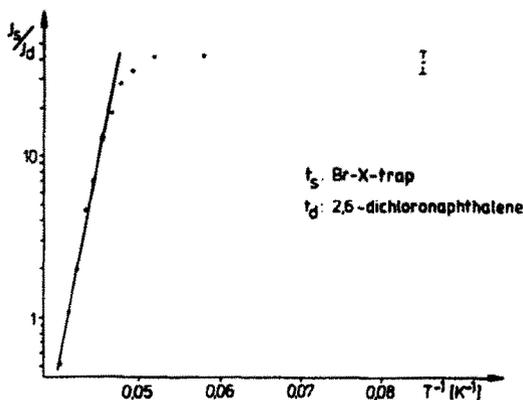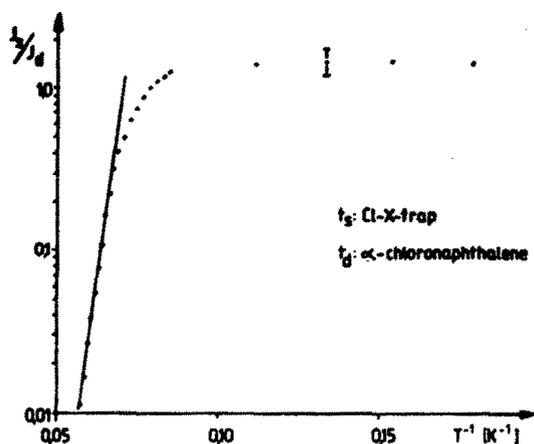
Fig. 1. Temperature dependence of the phosphorescence intensity ratio I_s/I_d of a shallow trap t_s (X-trap) and a deep trap t_d (chemical impurity).
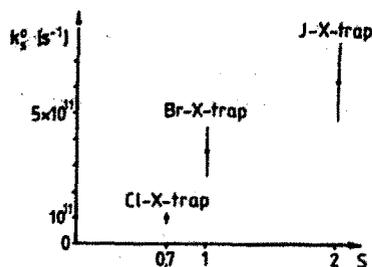

Fig. 2. Pre-exponential detrapping rates k_s^0 and electron—phonon coupling parameters S for the various X-traps. The S values were taken from ref. [5].

that they remain essentially unchanged throughout the series of X-traps, because we are looking always to the same molecule which changes only slightly its relative orientation to the host in the various situations. Thus we concentrate our considerations on the nuclear overlap integrals.

Due to its delocalized nature the electron—phonon coupling of an excitonic state in an organic crystal is commonly very small. Accordingly, there are no major changes in the geometry of the lattice when the excitonic state is excited. On the other hand, the electron—phonon coupling for the phosphorescence transition of the X-traps is considerably stronger, depending on the heavy-atom perturber [5]. Hence, we conclude that in the linear coupling regime (for example see ref. [8]), the electron—phonon coupling parameters S and associated nuclear overlap integrals should be approximately of the same size for the thermal trap-to-band and the optical trap-to-ground-state transitions. Therefore, the various S values for the trap-to-band transitions of the series studied, to which we attribute the observed differences in the detrapping rates, may be estimated from the optical transitions. These values were determined in a recent paper [5]. Fig. 2 shows the dependence of the pre-exponential detrapping rate as a function of the optical S value. Since this value increases with the halogen mass, the pre-exponential detrapping rate is also expected to show an increase with the halogen mass. This is clearly demonstrated by fig. 2.

The assumption of linear coupling, i.e. of negligible distortion of the potential surface in the excited trap state, is corroborated by a measured hot phonon of the I X-trap phosphorescence, the frequency of which

is the same as for the ground-state phonon within the experimental uncertainty [9]. Summarizing, the observed increase of the pre-exponential detrapping rate of the series of naphthalene X-traps investigated, is attributed to an increase in electron–phonon coupling. As has been discussed in ref. [5], this increased electron–phonon coupling is brought about by a heavy-atom-induced enhancement of the charge-transfer character in the lowest triplet trap state.

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