

## SINGLE-MODE ELECTRON-PHONON COUPLING AND OPTICAL LINESHAPE ANALYSIS ON A NAPHTHALENE X TRAP SYSTEM

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We measured the temperature dependence of the Debye-Waller factor for the phosphorescence of a special naphthalene X trap and performed a lineshape calculation of the phonon sideband based on a Morse oscillator. The experimental, as well as the theoretical, results agree with the assumption of a pseudo-localized mode.

### 1. Introduction

The influence of temperature on the electron-phonon coupling is described by the relation [1]

$$\alpha(T) = \exp \left[ - \int d\omega \rho(\omega) s(\omega) \coth(\hbar\omega/2kT) \right]. \quad (1)$$

$\alpha$  is the Debye-Waller factor and represents the relative intensity in the zero-phonon line. The integral in eq. (1) is determined by the spectral distribution of the Huang-Rhys factor  $s(\omega)$ . If the density of phonon modes  $\rho(\omega)$  may be approximated by a Debye spectrum, it was shown by Silsbee [2] that, in this case,  $s(\omega)$  can be represented by

$$s(\omega) = \bar{s} \omega^{-1}.$$

Then, an evaluation of the integral yields

$$\alpha(T) \approx \exp \left\{ -\bar{s} \left[ 1 + \frac{2}{3} \pi^2 (T/\Theta)^2 \right] \right\}. \quad (2)$$

This relation is usually used to describe the temperature-dependent intensity distribution in excited states of impurity centers (for example, see refs. [3,4]). It holds for temperatures well below the Debye temperature  $\Theta$  and may be used to determine  $\Theta$  from spectroscopic measurements.

This paper is concerned with a study of the electron-

phonon coupling in the phosphorescence emission from a naphthalene X-trap system. The X traps were created by doping the naphthalene crystal with a  $10^{-3}$  mole fraction of  $\beta$ -I-naphthalene [5-7]. In an earlier paper [5] we attributed the rather intense and structured phonon sideband to multiphonon transitions of a single pseudo-local mode coupled to the electronic transition by a CT interaction between the X trap and the neighboring halogen-substituted perturber molecule.

With the present study we want to support the model of a single-mode coupling by investigating the temperature dependence of the Debye-Waller factor, which differs in the case of a single mode from eq. (2). Further, we calculate the spectral lineshape of the trap emission on the basis of a single displaced Morse oscillator and show that it is possible to fit the experimental data.

### 2. Single-mode electron-phonon coupling

In case the electron-phonon coupling is dominated by a single mode, the Huang-Rhys factor may be written as

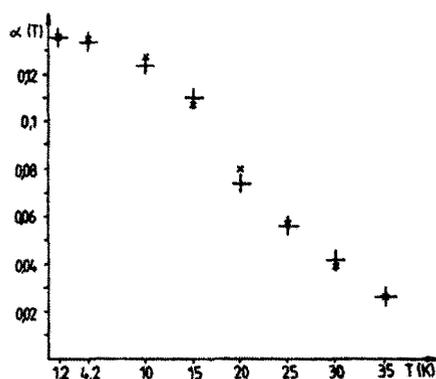


Fig. 1. Debye-Waller factor of the phosphorescence emission of the I X trap (see footnote) as a function of temperature. + Experimental values, x values calculated according to eq. (3).

$$S(\omega) = \bar{s} \delta(\omega - \omega_{\sigma})$$

with the single-mode frequency  $\omega_{\sigma}$ . Inserting this distribution in eq. (1), we get, instead of eq. (2),

$$\alpha(T) = \exp[-\bar{s} \coth(\hbar\omega_{\sigma}/2kT)] . \quad (3)$$

This expression is independent of the Debye temperature  $\Theta$ . Hence, its validity is not limited to a temperature range well below  $\Theta$ . Since  $\bar{s}$  as well as  $\omega_{\sigma}$  can be determined experimentally from the low-temperature limit of the Debye-Waller factor and from the resolved multiphonon structure respectively, it is possible to calculate  $\alpha(T)$  without adapting any parameter. Fig. 1 shows the result. The calculation was done with  $\bar{s} = 2$  and  $\hbar\omega_{\sigma} = 15 \text{ cm}^{-1}$  [5]. The agreement with the experimental values is fairly good.

### 3. Calculation of the lineshape function

To support further the model of a single-mode electron-phonon coupling in the phosphorescence emission of the I X trap<sup>†</sup>, we performed a lineshape calculation based on multiphonon excitations of a single mode. Usually, within the linear coupling regime and the harmonic approximation, multiphonon transitions are described by a Poisson distribution [8] according to

<sup>†</sup> We use the notation I X trap to characterize a naphthalene X trap, created by doping a naphthalene crystal with a small amount of  $\beta$ -I-naphthalene.

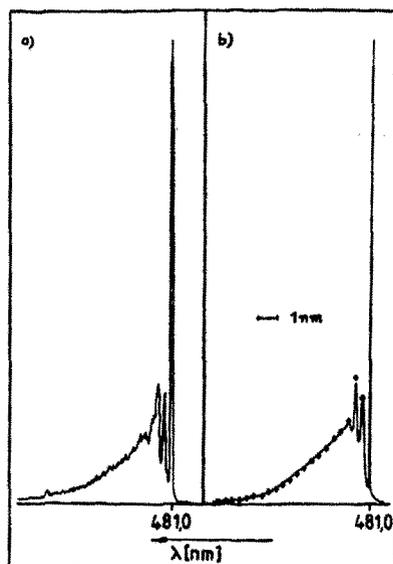


Fig. 2. (a) Zero-phonon line and phonon sideband spectrum of the phosphorescence of the I X trap. (b) Theoretical lineshape based on a single-mode Morse oscillator. Calculation was carried according to eq. (7). The points represent the experimental values.

$$P(E) = \sum_n e^{-s} (s^n/n!) \delta(E - E^T - n\hbar\omega_{\sigma}) . \quad (4)$$

$E^T$  is the energy of the trap state. However, the Poisson distribution accounts only for the basic features of the lineshape of an electron-phonon band. For example, it is conceivable that the harmonic approximation breaks down in case of high quantum excitations. As a matter of fact it was impossible to fit the phonon sideband (fig. 2a) with the harmonic overlap integrals of eq. (4) for the long-wavelength tail of the band. Hence, we used a Morse function [9] for the oscillator potential

$$V = D \{1 - \exp[-\alpha(q - q_0^*)]\}^2$$

with the dissociation energy  $D$  and the anharmonicity parameter  $\alpha$ . Both quantities are related by

$$D = m_{\sigma} \omega_{\sigma}^2 / 2\alpha^2 .$$

$m_{\sigma}$  is the reduced mass and  $\omega_{\sigma}$  the oscillator frequency.  $q_0^*$  is the displacement of the equilibrium position induced by the electronic excitation ( $q_0 = 0$  in the electronic ground state). The eigenvalues  $E_n$  of a Morse oscillator are well known and are given by [9]

$$E_n = \hbar\omega_\sigma(n + \frac{1}{2}) - \chi(n + \frac{1}{2})^2, \quad (5)$$

$$\chi = (\hbar\omega_\sigma)^2/4D. \quad (6)$$

As to the overlap integrals of a displaced Morse oscillator, they can be calculated in an analytic fashion, as first shown by Makshantsev and Perstnev [10]. The basic difference between the harmonic overlap integrals [eq. (4)] and those of a Morse function is their asymmetry concerning the sign of the displacement. If this sign is negative the decay of the Morse overlap integrals is monotonic in energy with increasing number of vibrational quanta and is much slower as compared to the harmonic case [11].

Apart from the breakdown of the harmonic approximation, the intensity distribution in the phonon sideband is strongly influenced by the energy dependence of the linewidth of the multiphonon transitions. To account for this fact we substituted the  $\delta$  functions in the lineshape eq. (4) by lorentzians with an energy-dependent width.

As to this energy dependence of the linewidth of the phonon transitions, one would expect a quadratic increase with excess energy above the zero-phonon line, since the number of phonon states which may accept the relaxing energy increases quadratically within the Debye approximation. However, not all the lattice phonons may couple uniformly to the multiphonon transitions. In fact, the best fit to the experimental spectrum was obtained with a linear dependence of the linewidth on the oscillator energy:

$$\Gamma_n(\text{cm}^{-1}) = 0.4 n \hbar\omega_\sigma.$$

The increasing linewidth of the phonon states leads to a smoothing of the sideband spectrum, so that the multiphonon structure vanishes for  $n > 3$ . This is clearly seen in fig. 2a.

Hence, the lineshape function we used to fit the electron-phonon transition depicted in fig. 2a, was of the form

$$L(E) = -\pi^{-1} \sum_n |\langle \Psi_0^M(q - q_0^*) | \Psi_n^M(q) \rangle|^2 \times \frac{1}{2} \Gamma_n / [(E - E_n)^2 + \frac{1}{4} \Gamma_n^2] \quad (7)$$

with the Morse overlap integral  $\langle \Psi_n^M(q - q_0^*) | \Psi_0^M(q) \rangle$ .

For the fit procedure the linewidth of the first four transitions were kept fixed, to account for the right

Table 1  
Calculational parameters

$q_0^* = -2.00$	$\Gamma(E_0) = 0.2 \text{ cm}^{-1}$
$\alpha = 0.31$	$\Gamma(E_1) = 9.0 \text{ cm}^{-1}$
$\chi = 0.49 \text{ cm}^{-1}$	$\Gamma(E_2) = 10.0 \text{ cm}^{-1}$
	$\Gamma(E_3) = 18.0 \text{ cm}^{-1}$

intensity ratio between the zero-phonon line and phonon sideband. All the parameters used are listed in table 1.

Fig. 2b shows that it is possible to fit the phonon sideband spectrum assuming a coupling to a single-mode Morse oscillator. From eq. (4) we calculate the dissociation energy  $D$  to be  $\approx 112 \text{ cm}^{-1}$ . In the model used  $D$  is the same in the ground and excited states.

As to the displacement  $q_0^*$  of the excited-state Morse oscillator, we note that it is negative. A negative displacement is indicative of an attractive force between the excited trap molecule and the adjacent lattice points in the excited state. This fits well with our earlier interpretation [5], which related the rather strong electron-phonon coupling in the I X trap to an excited state CT interaction between the X trap and the neighbouring halogen atom.

Summarizing, we can say that the temperature dependence of the Debye-Waller factor as well as the lineshape analysis support the idea of a single-mode electron-phonon coupling in the special naphthalene X trap system studied.

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