

## SITE SELECTIVE IMPURITY PHONON COUPLING IN GLASSY SOLUTIONS

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It is shown that the impurity phonon coupling strength in glassy solutions at 4 K varies continuously with site energy.

### 1. Introduction

The optical transitions of aromatic molecules dissolved in organic glasses are known to be inhomogeneously broadened [1-5]. This is due to a quasi-continuous site splitting. Thus, selecting a special site, say in the region of the 00 transition, by means of narrow band width excitation, a remarkable narrowing of the emission line is possible. Moreover, the shape of a thus narrowed band reveals the characteristic features known from the emission properties of organic molecules in crystals: the band shows a so-called intense narrow zero phonon line and a broad phonon wing. The shape of the phonon wing is strongly related to the coupling strength between the impurity molecule and the phonon bath of the medium [6,7]. This paper shows how the impurity phonon coupling strength and the optical band shape depend on the energy of the emitting site.

### 2. Experimental

We investigated solutions of anthracene in 2-methyltetrahydrofuran with various concentrations between  $2 \times 10^{-2}$  and  $10^{-4}$  M.

The solutions were sealed in small quartz tubes and immersed in liquid He. The excitation source consists of a high pressure Xe lamp (450 W) followed by a prism double monochromator. The band width used was  $12 \text{ cm}^{-1}$ . The fluorescence signal was detected by a grating monochromator (Chromatix CT 103), a pho-

tomultiplier (RCA 7265) and a heterodyne lock-in amplifier (Ithaco). The bandpass of the detecting system was about  $15 \text{ cm}^{-1}$ . Excitation was carried out in the region of the 00 transition between 26000 and  $26400 \text{ cm}^{-1}$ . The various positions of excitation differ by  $100 \text{ cm}^{-1}$ . Detection was made on the first quantum of the  $1400 \text{ cm}^{-1}$  vibration.

### 3. Results

The experimental results are shown in figs. 1 and 2: The following points summarize some noteworthy features:

(1) There is a remarkable change of the band shape with increasing site energy. Exciting a low site one gets a rather narrow phonon wing, a maximum of which outside the zero phonon band is not clearly detectable. With increasing site energy the phonon wing is continuously broadened and shows a maximum (fig. 1).

(2) The distance of the maximum of the phonon wing from the zero phonon line increases stronger than linear with site energy (fig. 2).

(3) Though, within the experimental limitations, the line width of the zero phonon band does not change with the site, the intensity distribution within the band, however, changes significantly with the site. In the low sites a large amount of the total intensity of the band is in the zero phonon line, while in the high energy sites most of the intensity goes into the phonon wing.

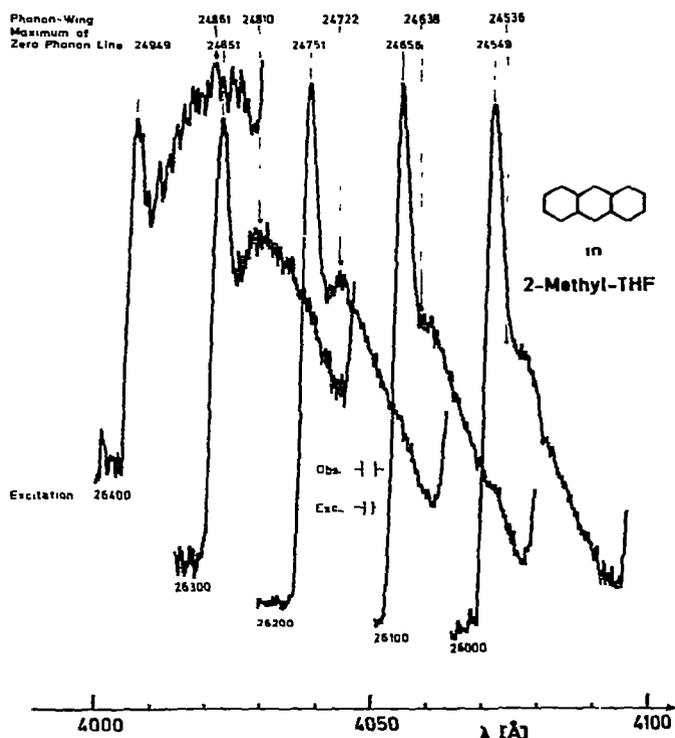


Fig. 1. The emission line shape at 4.2 K of the first quantum of the  $1400\text{ cm}^{-1}$  vibration as a function of the site energy. Excitation was carried out in the region of the 00 transition. The band width used for excitation and detection are shown.

#### 4. Discussion

Optical bandshapes of impurities in a crystal were treated by several authors, e.g. refs. [6,7]. The emission shape of a special molecule is determined by the temperature of the system and the coupling strength between the molecule and the medium. In our case we may confine the situation to the zero temperature limit because the width of the sites ( $12\text{ cm}^{-1}$ ) by far exceed the width due to temperature broadening ( $3\text{ cm}^{-1}$ ). In the linear coupling case [6] the line shape function for a special normal lattice mode  $q_k$  with frequency  $\omega_k$  is given by

$$G(E) = \sum_{n=0}^{\infty} \exp\left(-\frac{1}{2}g_k^2\right) \left(\frac{1}{2}g_k\right)^n (n!)^{-1} \times \delta(E_1 - n\hbar\omega_k - \hbar\omega_0 - E) \quad (1)$$

$E_1$  is the energy of the excited electronic state.  $\omega_0$  is

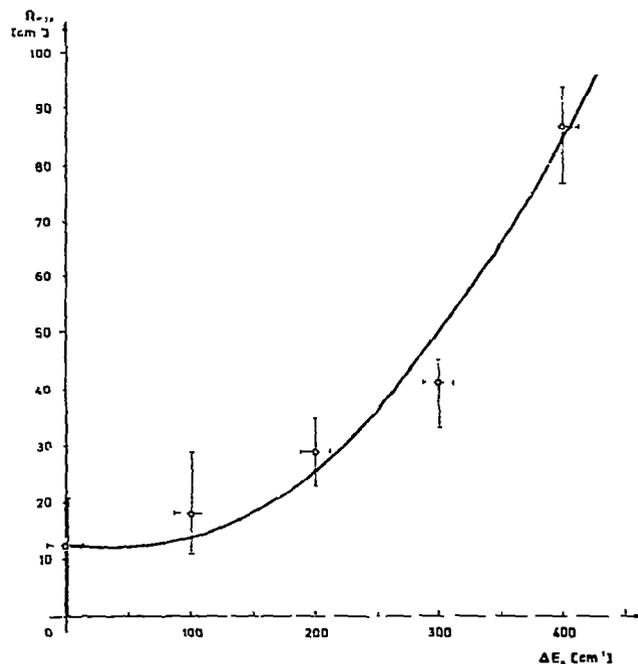


Fig. 2. The distance of the maximum of the phonon wing from the zero phonon line as a function of the difference in the site energy  $\Delta E_s$ . The solid line is a quadratic fit to the experimental points.

the frequency of the impurity vibration ( $1400\text{ cm}^{-1}$ ), the phonon wing of which we investigate.

The shape function  $G(E)$  reaches a maximum, the distance of which from the zero phonon line is determined by

$$n_{\max} \hbar\omega_k = \frac{1}{2}g_k^2 \hbar\omega_k \equiv \hbar\Omega_{k,\max} \quad (2)$$

$g_k$  is a dimensionless coupling constant which is related to the displacement  $\Delta q_k$  of the lattice mode  $q_k$  by

$$g_k = (m_k \omega_k / \hbar)^{1/2} \Delta q_k \quad .$$

$m_k$  is the reduced mass.  $\Delta q_k$  denotes the equilibrium position which the lattice mode will assume, when the impurity molecule is promoted to an excited state.

The experimental outcomes show that  $\Omega_{k,\max}$  increases with site energy (fig. 1). As a consequence of eq. (2) the coupling constant  $g_k$  has to increase with site energy, too. To explain this fact, we remind that inhomogeneous broadening in the excited state is caused by an attractive interaction  $-W(\theta, \{q_i\})$  between the impurity and the solvent cage, e.g. a dipole-dipole or a dispersion interaction

$$-W(\theta, \{q_j\}) = u(\theta) v(\{q_j\}).$$

$u(\theta)$  accounts for the fact that in an amorphous medium the impurity molecules may assume all possible orientations with respect to the resulting dipole moment of the solvent cage. The consequence is a quasi-continuous site splitting.  $\{q_j\}$  denote the normal model of the solvent cage with respect to the impurity molecule.

If the impurity molecule is promoted to an excited state  $|1\rangle$ , its geometry and its charge distribution is altered. The lattice molecules, therefore, assume a new equilibrium position with respect to the ground state at  $\{\Delta q'_j\}$  (fig. 3).

Considering one active mode  $q_k$ , the lattice hamiltonian in the excited state is given by

$$H_{1,k}^{(1)} = \hbar\omega_k (b_k^+ b_k + \frac{1}{2}) - 2^{-1/2} \hbar\omega_k g'_k (b_k^+ + b_k) + \frac{1}{2} \hbar\omega_k (g'_k)^2 + E_1. \quad (3)$$

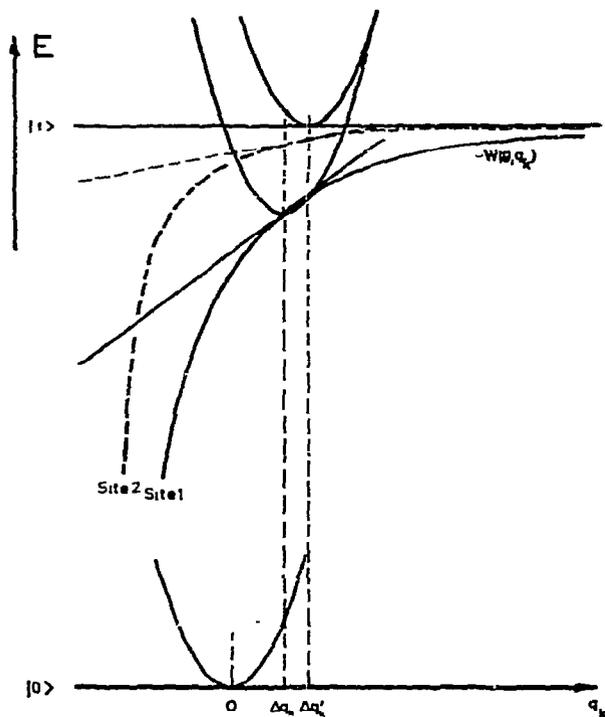


Fig. 3. Dependence of the impurity phonon coupling on the energy of the site. The attractive interaction  $-W(\theta, q_k)$  in the excited state and its linear approximation is shown for two sites. The shift in the equilibrium position is much larger in the low site (site 1) than in the high site (site 2).

$b_k^+$ ,  $b_k$  denote the phonon creation and destruction operators in the mode  $q_k$ . Taking now into account the attractive interaction  $-W(\theta, \{q_j\})$  which we approximate by a linear expansion around  $\{\Delta q_j\}$

$$-W(\theta, \{q_j\}) = u(\theta) \left[ v(\Delta q'_j) + \sum_j (\partial v / \partial q_j)_{\Delta q'_j} (q_j - \Delta q'_j) \right], \quad (4)$$

the lattice hamiltonian (3) changes to

$$H_{1,k}^{(1)} = \hbar\omega_k (b_k^+ b_k + \frac{1}{2}) - [2^{-1/2} \hbar\omega_k g'_k - (\hbar/2m_k\omega_k)^{1/2} u(\theta)(\partial v / \partial q_k)_{\Delta q'_k}] (b_k^+ + b_k) - u(\theta)(\partial v / \partial q_k)_{\Delta q'_k} (\hbar/m_k\omega_k)^{1/2} g'_k + \frac{1}{2} \hbar\omega_k (g'_k)^2 + u(\theta)v(\Delta q'_k) + E_1.$$

Because the equilibrium position of the active mode  $q_k$  has changed from  $\Delta q'_k$  to  $\Delta q_k$  (fig. 3), we obtain a new coupling constant  $g_k$ , given by

$$g_k = g'_k - (\hbar m_k \omega_k^3)^{-1/2} u(\theta)(\partial v / \partial q_k)_{\Delta q'_k}. \quad (5)$$

$g'_k$  is the coupling constant which belongs to the hamiltonian (3). From eq. (5) we conclude that in a low site, where  $u(\theta)$  is large,  $g'_k$  is diminished by a considerable amount and, therefore, we have a small coupling constant  $g_k$ . On the other hand, in a high site  $u(\theta)$  is small. Therefore  $g_k \approx g'_k$  and  $g_k$  is large, respectively. Comparing these results with (2) it is clear that the maximum of the phonon wing shifts apart from the zero phonon line as the site energy increases (fig. 1).

The model presented concerning the interaction between the impurity molecule and the solvent cage as a function of the site energy is based on the assumption that the characteristic features of the active mode, e.g. the frequency, the reduced mass and the parameter  $g'_k$ , do not depend on the site. These assumptions imply some ordered structure of the solvent cages in the various sites, at least concerning the active mode.

Within the model considered it follows from (4) and (5) that a change in the site energy  $dE_s$  is linearly related to a change in the coupling constant  $dg_k$

$$dg_k = [1/v(\Delta q'_k)] (\partial v / \partial q_k)_{\Delta q'_k} (\hbar m_k \omega_k^3)^{-1/2} dE_s \equiv a dE_s. \quad (6)$$

Inserting this result in eq. (2) we obtain a relation between the distance of the maximum of the phonon wing from the zero phonon line and the difference in the energy of the excited sites  $\Delta E_s$ :

$$\Omega_{k,\max} - \Omega_{k,\max}^0 = \frac{1}{2} \omega_k a^2 [(\Delta E_s + g_k^0/a)^2 - (g_k^0/a)^2] .$$

$\Omega_{k,\max}^0$  is the distance of the maximum at the starting point ( $26000 \text{ cm}^{-1}$ ,  $\Delta E_s = 0$ ). From fig. 2 we see that  $\Omega_{k,\max}^0$  is about  $12 \text{ cm}^{-1}$ .  $g_k^0$  is the corresponding coupling constant. The result above shows that  $\Omega_{k,\max}$  increases quadratically with the change in the site energy  $\Delta E_s$ . This is just the situation we observe.

In the zero temperature limit it follows from eq. (1) that the relative amount of intensity in the zero phonon line  $G_k(0)$  due to the mode  $q_k$  is given by

$$G_k(0)/G = \exp(-\frac{1}{2}g_k^2) , \quad (7)$$

where  $G$  is the total intensity of the band. From (6) and (7) it is clear that by changing  $g_k$  to higher values with increasing site energy, we obtain an exponential decrease in the relative intensity of the zero phonon line (fig. 1):

$$G_k(0)/G = \exp[-\frac{1}{2}(g_k^0 + a \Delta E_s)^2] .$$

## 5. Concluding remarks

In this paper we showed that the optical band shape of anthracene as an impurity molecule in a glassy medium depends strongly on the energy of the emitting site. The experimental outcomings were related to a continuous increase of the coupling strength with increasing site energy. In a low site the phonon wing shows no maximum outside the zero phonon

line, that is  $g_k \leq 1$ . In a high site the maximum of the wing shifts strongly apart from the zero phonon line, that is  $g_k > 1$ . Therefore, changing the energy of the emitting site we go from the weak coupling limit ( $g_k \leq 1$ ) to the strong coupling limit ( $g_k > 1$ ). As a consequence not only the optical band shape, but also the dynamic properties of the impurity may vary in a systematic way with the energy of the site [10].

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