

HEAVY-ATOM EFFECT IN THE ELECTRON-PHONON COUPLING OF NAPHTHALENE X-TRAPS

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We investigated electron-phonon coupling in phosphorescence from X-traps of a naphthalene crystal at 1.2 K. X-traps were created by doping the crystal with β -halonaphthalenes. The results show that the electron-phonon coupling increases with increasing mass of the heavy atom. In the iodine X-trap, multiphonon structure is detectable. The results are interpreted as a charge-transfer interaction with the adjacent heavy atom.

It is well known that a heavy atom interacting with a probe molecule may enhance dramatically the dynamic processes into and from the lowest triplet state [1]. In this letter we report on another feature of the external heavy-atom effect, namely its influence on the electron-phonon coupling of the probe molecule. We discuss our experiments in terms of a model which links the influence of the heavy atom on the electron-phonon coupling to its influence on the dynamics of spin-forbidden processes.

The system studied is a naphthalene crystal doped with low concentrations of β -halonaphthalenes. The perturbation of the halonaphthalenes on the crystal lattice results in the formation of X-traps in the immediate neighbourhood of the heavy-atom-containing perturber [2]. The phosphorescence from these X-traps is a sensitive probe for the external heavy-atom effect.

Fig. 1 shows the zero-phonon origins of the phosphorescence from the various X-traps investigated, together with their accompanying phonon wings. The experiments were carried out at 1.2 K. This series of spectra clearly shows that the Debye-Waller factor α , defined as the intensity ratio of the zero-phonon line and the total band, increases as the mass of the heavy atom increases. α is related in a simple way to the Huang-Rhys factor S [3], which carries all the information about the interaction of the probe molecule with the phonons

$$\alpha \equiv J_z/J_{\text{tot}} = e^{-S} \quad (1)$$

The α and S values obtained from a band integration according to eq. (1) are shown in figs. 1 and 2. The evaluation was based on the fact that the zero-phonon line is sharp compared to the band pass of the spectrometer which, in turn, is sharp compared to the phonon part of the band. In this case, the experimental band pass used does not affect the determination of the Debye-Waller factor.

Fig. 2 shows that the F, Cl and Br X-trap are characterized by $S \leq 1$, and are thus in the weak electron-phonon coupling limit, while the I X-trap is in the intermediate to strong coupling limit. The phosphorescence from the I X-trap exhibits a well-resolved multiphonon structure (fig. 3), similar to those observed for charge-transfer crystals [4,5]. The frequency ω_p of the phonon observed is $\approx 15 \text{ cm}^{-1}$. The first two quanta are clearly resolved while the third and the fourth appear only as shoulders. This is obviously due to the fact that the width of the multiphonon transitions increases with increasing number n of excited quanta. The phonon tail peaks at $n = 2$. Using the theory of linear electron-phonon coupling in the zero-temperature limit [6], we can calculate the S value from the ground-state relaxation energy δ (i.e. the energy shift of the phonon maximum from the zero-phonon line)

$$\delta \equiv n_{\text{max}} \hbar \omega_p = S \hbar \omega_p \quad (2)$$

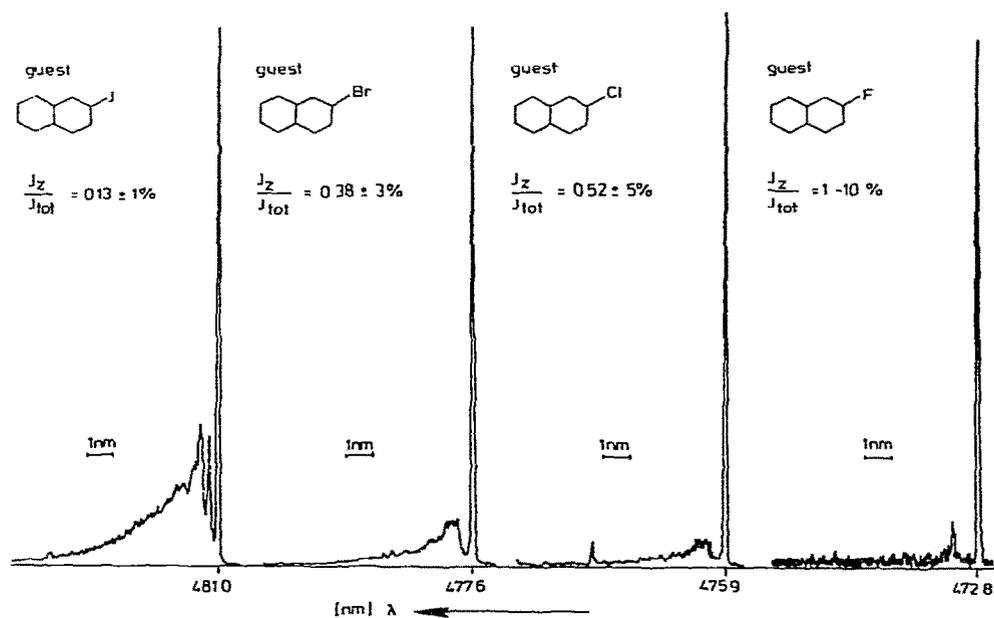


Fig. 1 Zero-phonon origins of the phosphorescence from naphthalene X-traps. The guest molecules are shown. Temperature 1.2 K, resolution 5 cm^{-1} , concentration 0.1% (wt/wt).

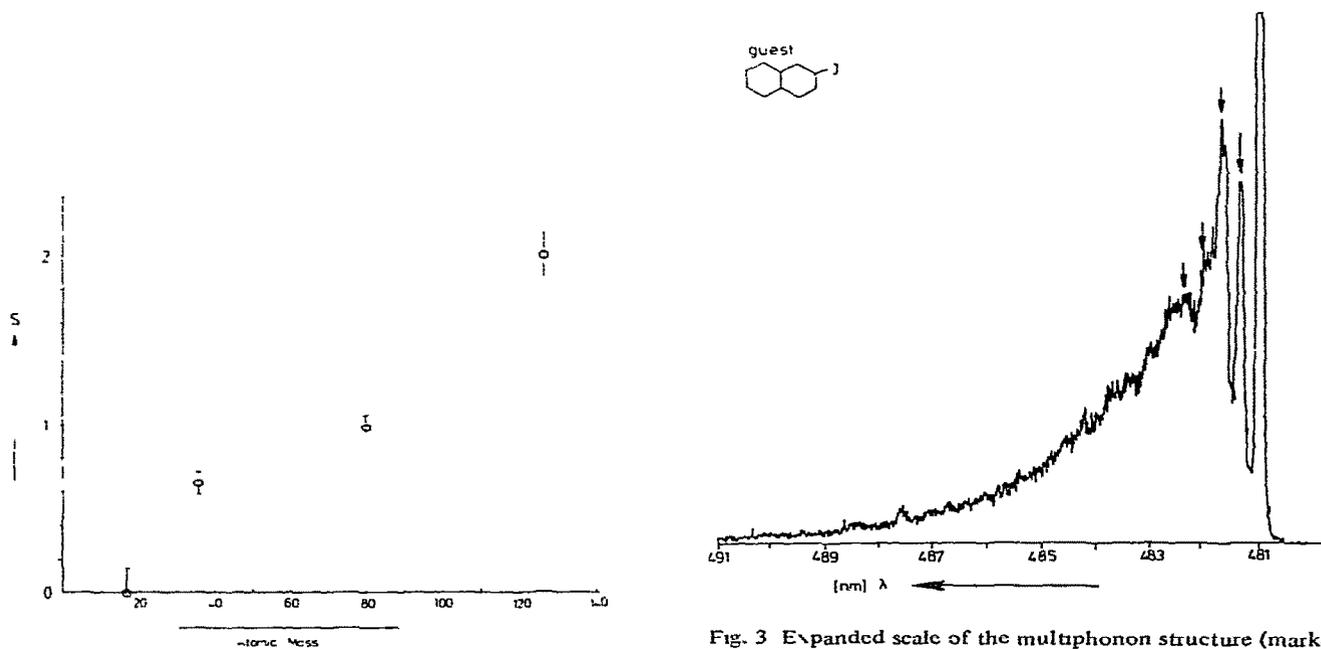


Fig. 2 Huang-Rhys factor as a function of the mass of the external heavy atom.

Fig. 3 Expanded scale of the multiphonon structure (marked by arrows) of the I X-trap. The frequency of the phonon is 15 cm^{-1} . Temperature 1.2 K, resolution 5 cm^{-1} , concentration 0.1% (wt/wt).

From eq. (2) we obtain $S = 2$, in complete agreement with the determination via the band integration.

The strength of the electron-phonon coupling is related to the relative change of the equilibrium geometry of the lattice in the excited state. Usually a strong distortion of the excited state occurs when its polarity differs markedly from that in the ground state. This is the reason for the strong electron-phonon coupling in charge-transfer crystals [7].

From fig. 2 it is obvious that the heavier the perturber the stronger the excited-state distortion of the lattice. We interpret these results on the basis of the model developed for electron-phonon coupling in charge-transfer crystals [7]. We thereby assume that the lowest triplet state of the X-trap gets an admixture of a charge-transfer state, where the charge is transferred between the X-trap and the heavy atom. This CT-state admixture increases the excited-state polarity and hence leads to a distortion of the equilibrium geometry, which results in the rather strong electron-phonon coupling observed.

As to the heavy-atom effect on the dynamics of the spin-forbidden processes of a probe molecule, it is well known that the leading contributions are the one-center spin-orbit integrals at the heavy center [1,8,9]. However, one-center contributions at the heavy center occur only if the unpaired electrons of the probe molecule are delocalized to some degree onto the heavy atom. That is, a charge transfer has to occur to get effective spin-orbit coupling. In the internal heavy-atom effect in monohalophthalenes, Pratt and co-workers (for a review see ref. [10]) were able to determine the most effective CT configurations in the lowest triplet state by analyzing the quadrupole and hyperfine interactions. They are of the type where an electron is transferred from the fully occupied non-bonding p_π orbital of the halogen to an orbital of the aromatic frame. If we adopt this result for our situation, we see immediately that the CT contribution to the triplet state is lowest for the F X-trap because the high electronegativity of the F atom inhibits an electron transfer. On the other hand, the CT contribution is highest for the I X-trap due to the reduced electronegativity and the larger overlap of the orbitals involved.

It was shown by Haarer [7] that the Huang-Rhys factor depends strongly on the degree q of charge transfer and on the frequency of the active phonon,

$S \propto q^4 / \omega_p^3$. Hence, a small increase in the CT character results in a large increase in S . On the basis of this model, we can qualitatively explain the influence of a halogen atom on the electron-phonon coupling as demonstrated by our experimental results. We can further link this influence on electron-phonon coupling to the influence on external spin-orbit coupling. From this discussion it is also obvious that the multiphonon structure observed must be due to a local lattice vibration involving the perturber and the trap molecule.

Because of the localized nature of the multiphonon transition in the phosphorescence of the I X-trap, we can calculate the excited-state equilibrium shift from the measured phonon frequency and S value

$$\Delta Q = (2Sh/m^*\omega_p)^{1/2} = 0.32 \text{ \AA}$$

m^* is the reduced mass of the X-trap and the perturber molecule. We have assumed that the 15 cm^{-1} phonon corresponds to a stretching vibration of the two molecules involved. Employing proper mass weighting, we find that the shift of the X-trap in the excited state is $\approx 0.21 \text{ \AA}$ while that of the β -I-naphthalene is 0.11 \AA .

Finally, we point out that the observation of a heavy-atom effect in the electron-phonon coupling is not unique to the X-trap system studied. It has also been observed in different systems [11,12]. Using photochemical hole-burning, we found very recently [13] that bromoethane dissolved in an organic glass has a large influence on the electron-phonon coupling of dihydroxyanthraquinone in its first-excited singlet state.

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