INVESTIGATION OF INHOMOGENEOUS LINE BROADENING OF ODMR TRANSITIONS IN DOPED ORGANIC GLASSES

G. GRADL and J. FRIEDRICH

Physikalisches Institut der Universität Bayreuth, Postfach 3008, D-8580 Bayreuth, Federal Republic of Germany

We investigated the influence of internal and external heavy-atom-induced spin—orbit coupling on the inhomogeneous broadening of ODMR transitions. From the very small heavy-atom effect observed, we conclude that the leading mechanism is not spin—orbit interaction but an electrostatic coupling between probe molecule and solvent

1. Introduction

As is well known, the magnetic transitions within the sublevels of excited triplet states of organic molecules in amorphous hosts are inhomogeneously broadened like the optical transitions. In both cases the relative magnitude of the line broadening $\Delta\omega/\omega$ is of the same order of magnitude. However, as yet, the question as to the origin of the magnetic line broadening and its relation to the optical states involved, has not been solved. This question was first addressed by van Egmond, Kohler and Chan [1]. These authors found that the solvent-induced shift of the optical frequency is linearly related to a shift in the microwave frequency. The model they employed to explain their results was based on a solvent-induced mixing of molecular triplet states.

Later, Lemaistre and Zewail [2] developed a model in which the magnetic inhomogeneity was directly related to the optical inhomogeneity via the intramolecular spin—orbit coupling.

There is a third model by Clark and Tinti [3] based on a microscopic description of the inhomogeneous broadening via a linear Stark coupling between the molecular states and the random electric fields of the solvent. This model is of first order in the molecule—solvent coupling and of second order in the intramolecular spin—orbit coupling, and is thus in some respects very similar to the model by Lemaistre and Zewail.

All these models are, in principle, capable of explaining the observed facts such as, for example, the linear variation of the ODMR frequency and width with the optical excitation frequency [4,5], in a qualitative way. In order to get an idea as to what the leading mechanism is, we investigated the influence of internal and external heavy atoms on the inhomogeneous line broadening of the magnetic transitions. If magnetic and optical inhomogeneity are related via a spin—orbit coupling mechanism, a strong heavy-atom-induced inhomogeneous broadening is expected.

2. Experimental

The concentration of the probe molecules (naphthalene, 1,5-dichloronaphthalene, 1-bromonaphthalene) was, in each case, 10^{-3} M. The solvent used was 3-methylpentane. The samples were immersed in liquid He at a temperature of 1.3 K. The microwave source was a HP 8620A sweep generator followed by a TWT amplifier. Maximal power output was 1 W.

The inhomogeneous ODMR profiles were probed by sweeping the microwave through a small frequency interval (roughly 1/10 of the inhomogeneous width) and detecting the corresponding MIDP signal [6]. In the case of 3-methylpentane doped with bromoethane this technique yielded too noisy signals. Hence, we determined the inhomogeneous width by deconvoluting the signal of a sweep over the whole band [7].

Table 1
Inhomogeneous widths (measured at 1 3 K) and high-temperature lifetimes (77 K) of naphthalene (N), 1,5-dichloronaphthalene (DCIN), and 1-bromonaphthalene (BrN) in 3-methylpentane. x is chosen as the out-of-plane axis

	Δ^{xz} (MHz)	Δ^{xy} (MHz)	Δ^{yz} (MHz)	K (77 K) (s^{-1})
N	25 ± 2	—	17 ± 3	0.39 ± 0.03
DCIN	30 ± 2	17 ± 2	28 ± 3	5.3 ± 0.4
BrN	79 ± 4	42 ± 3	60 ± 5	70 ± 5

The samples were excited with a high-pressure Hg lamp (100 W). Detection was performed at the phosphorescence 00 transition. The resolution varied within 8 and 23 cm^{-1}.

3. Results

The results of our experiments are the following

(a) There is indeed a heavy-atom effect in the inhomogeneous broadening of the ODMR transitions. However, its magnitude is very small compared to the heavy-atom effect in the triplet lifetime (table 1).

(b) The magnitude of the inhomogeneous broadening is different for the different types of transitions. However, there is no uniform behavior (table 1).
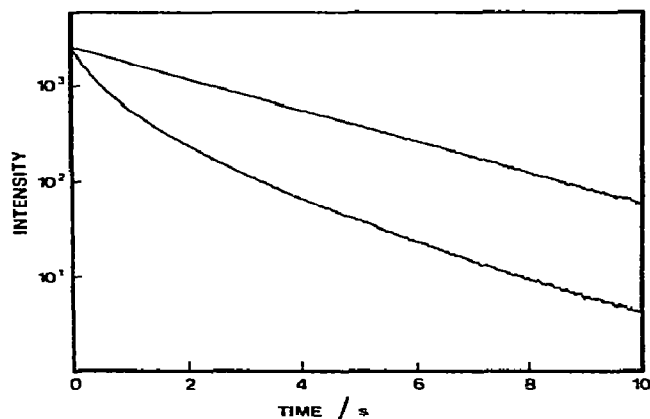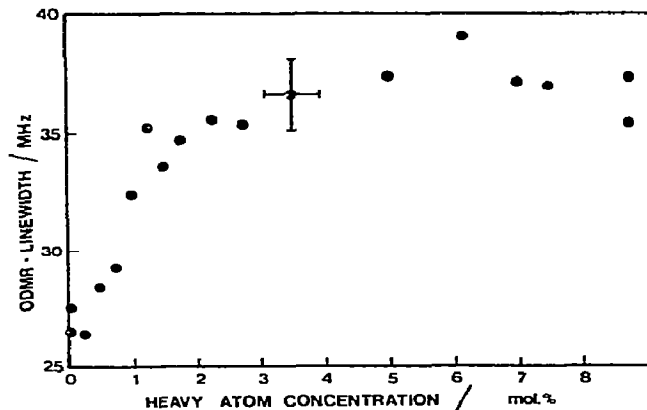

Fig. 2 Inhomogeneous width of the $D + E$ transition of naphthalene as a function of heavy-atom concentration. Solvent. 3-methylpentane/bromoethane. Temperature· 1.3 K.

(c) The influence of an external heavy atom on the inhomogeneous width of the magnetic transition is also rather weak as compared to the lifetime. In the concentration range investigated, the latter increases by a factor of roughly ten and becomes strongly non-exponential (fig. 1). The inhomogeneous width, on the other hand, increases by only about 40%. We stress that the relative increase of the width of the microwave transition scales exactly with the relative increase of the optical width (figs. 2 and 3).

Fig 1. Decay of the T_1 state of naphthalene in 3-methylpentane (upper trace) and in 3-methylpentane doped with bromoethane (7 mol%)
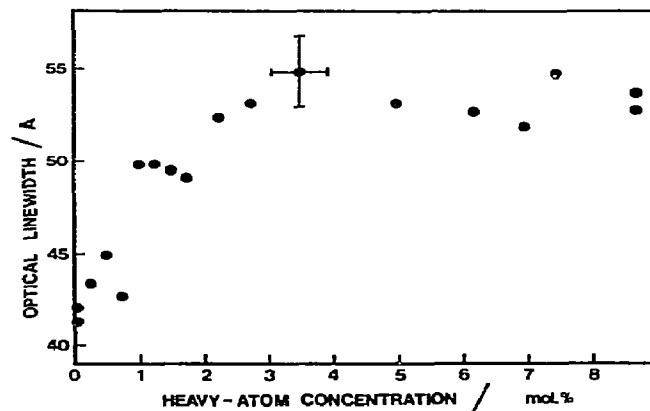

Fig. 3. Inhomogeneous width of the 00 transition of the naphthalene phosphorescence as a function of heavy-atom concentration. Solvent: 3-methylpentane/bromoethane. Temperature: 1.3 K.

4. Discussion

Our results show a definite heavy-atom effect in the inhomogeneous broadening of the ODMR transition, and, hence, follow qualitatively the predictions of the Lemaistre–Zewail model. We now examine whether this model can be used to interpret the results on a more quantitative level. For example, is it possible to understand the small heavy-atom effect in the width as compared to the lifetime, or the exact scaling of the ODMR width with the optical width in case of the external heavy-atom effect?

According to this model the ODMR transition frequency is given by

$$\hbar\omega^{mn} = \hbar\omega_0^{mn} + \sigma$$

$$+ \left(\sum_k \frac{|\langle T_1^m|H_{so}|\psi_k\rangle|^2}{\Delta_{1k}^2} - \sum_j \frac{|\langle T_1^n|H_{so}|\psi_j\rangle|^2}{\Delta_{1j}^2} \right)\delta_1$$

$$+ \sum_j \frac{|\langle T_1^n|H_{so}|\psi_j\rangle|^2}{\Delta_{1j}^2}\delta_j - \sum_k \frac{|\langle T_1^m|H_{so}|\psi_k\rangle|^2}{\Delta_{1k}^2}\delta_k . \quad (1)$$

σ denotes a shift of the band center induced by the spin–orbit coupling. The intermediate states ψ_k and ψ_j can be either of singlet or triplet type. $\delta_1, \delta_j, \delta_k$ are the solvent-induced fluctuations in the electronic energies of T_1, ψ_j and ψ_k, respectively. The Δ_{ij} denote the corresponding zero-order electronic energy differences. The inhomogeneous width follows from (1) by calculating the root mean square

$$\Delta^{mn} \equiv \langle(\hbar\omega^{mn} - \hbar\omega_0^{mn} - \sigma)^2\rangle^{1/2} . \quad (2)$$

We see two possibilities to explain the small influence of the heavy atom on the inhomogeneous width: (i) the heavy-atom-induced spin–orbit coupling terms in eq. (1) are almost completely cancelled or (ii) there is a contribution to the ODMR width which does not depend on the spin–orbit coupling, and which is large compared to this interaction. Let us examine the possibility of cancellation of the spin–orbit terms: Since Δ^{mn} is determined by the root mean square of eq. (1), a partial cancellation is expected only in the term $\propto\delta_1$. The terms $\propto\delta_j$ and $\propto\delta_k$ can destructively interfere only when the mth and the nth substate couple to the same intermediates. Such a coupling is, however, strongly restricted by symmetry rules [8–10]. Even if one takes into account further

perturbative corrections like the spin–orbit–vibronic coupling, it is unlikely that all one-center spin–orbit contributions at the heavy atom should cancel almost completely. We further stress, that if strong cancellation occurs one would expect the width of the $2E$ (yz) transitions to be smaller than the widths of the $D + E$ and $D - E$ transitions because in the $2E$ transition the spin–orbit coupling of the states involved is of similar magnitude. As the results show, this holds only in the case of naphthalene but not in the case of the halonaphthalenes.

Hence, we favour the second possibility, i.e. that the dominating term in the line-broadening mechanism is given by an electrostatic interaction H_{MS} between the probe molecule and the solvent, and that the spin–orbit interaction is a rather small correction to this type of coupling.

The electrostatic interaction H_{MS} is, of course, also responsible for the inhomogeneous optical width of the states ψ_j. Up to second order in H_{MS} one gets

$$E_j^m = [E_0]_j + \epsilon_j^m + \delta_j^m , \quad (3)$$

where ϵ_j^m is the zero-field shift for the mth substate and δ_j^m is given by

$$\delta_j^m = \langle\psi_j|H_{MS}|\psi_j\rangle + \sum_k \frac{|\langle\psi_j^m|H_{MS}|\psi_k^m\rangle|^2}{\Delta_{jk} + \epsilon_j^m - \epsilon_k^m} . \quad (4)$$

From (3) and (4) one calculates the ODMR transition frequency as

$$[\hbar\omega^{mn}]_1 = [\hbar\omega_0^{mn}]_1$$

$$- \sum_k \frac{|\langle T_1^m|H_{MS}|T_k^m\rangle|^2}{\Delta_{1k}^2}([\hbar\omega_0^{mn}]_1 - [\hbar\omega_0^{mn}]_k). \quad (5)$$

$\hbar\omega^{mn}$ scales with the difference of the microwave frequencies in the states T_1 and T_k, respectively [1]. Within the model used, this difference is responsible for the fact that the various transitions have different widths. In the case where solvent and probe molecules are non-polar, the diagonal term in eq. (4) may be small and, hence,

$$[\hbar\omega^{mn}]_1 = [\hbar\omega_0^{mn}]_1 - \delta_1 \frac{[\hbar\omega_0^{mn}]_1 - [\hbar\omega_0^{mn}]_k}{\Delta_{1k}} . \quad (6)$$

Here we have assumed that the coupling occurs preferentially only to one state T_k. Within these approxi-

mations the inhomogeneous ODMR width scales with the optical width of the lowest triplet state. This is exactly what is observed in case of the external heavy-atom perturber (figs. 2 and 3). From (6) we get

$$\Delta^{mn} = \Gamma_1 \frac{|[\hbar\omega_0^{mn}]_1 - [\hbar\omega_0^{mn}]_k|}{|\Delta_{1k}|} \qquad (7)$$

and, consequently,

$$\Delta^{mn}/\Delta^0 = \Gamma_1/\Gamma^0 ,$$

where Δ^0 and Γ^0 denote the respective widths at zero concentration. Since the frequency factor $[\hbar\omega_0^{mn}]_1 - [\hbar\omega_0^{mn}]_k$ is expected to scale roughly with $[\hbar\omega_0^{mn}]_1$, one gets the order of magnitude result that the ratio between width and energy of a transition is roughly constant. This result is rather general and does not depend on the type of transition [11,12]. This generality is of course based on the fact that the above formalism can be applied equally well to other types of transitions, e.g. vibrational transitions. In case of a dominating spin—orbit interaction, the situation would be different. Since in our case the probe molecule is naphthalene, which has a center of inversion, we expect that the diagonal term in (4) is small and, hence, the approximations leading to eq. (6) are well founded.

5. Summary

We have investigated the influence of heavy-atom-induced spin—orbit coupling on the inhomogeneous linewidth of the magnetic transitions in the lowest triplet state. The experiments show that this influence is very small compared to the heavy-atom effect in the decay dynamics. From this result we conclude that the leading term in the inhomogeneous broaden-ing is, as a rule, the electrostatic interaction between the probe molecule and the solvent, as suggested by van Egmond et al. [1]. Only in molecules with very strong spin—orbit coupling, like bromonaphthalene, are both contributions of the same order of magnitude. Within the frame of the electrostatic coupling mechanism, we can explain the features of the influence of external perturbers on the inhomogeneous ODMR width.

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