Deuterium Isotope Effect in the Radiative Triplet Decay of Heavy Atom Substituted Aromatic Molecules

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We studied the effect of deuteration on the radiative decay of the triplet sublevels of naphthalene and some halogenated derivatives. We found that the influence of deuteration is much more pronounced in the heavy atom substituted than in the parent hydrocarbons. The strongest change upon deuteration is in the radiative decay of the out-of-plane polarized spin state T^x. These findings are consistently related to a second order Herzberg-Teller (HT) spin-orbit coupling. Though we found only a small influence of deuteration on the total radiative rate in naphthalene, a significantly larger effect is observed in the rate of the 00-transition of the phosphorescence. This result is discussed in terms of a change of the overlap integral of the vibrational groundstates of T_1 and S_0 upon deuteration.

I. Introduction

Deuterium (d) substitution has proved to be a powerful tool in the investigation of the decay mechanisms of excited states[1]. The change in lifetime on deuteration provides information on the electronic relaxation processes in large molecules. Much work has been done concerning the nonradiative decay. In 1972 Johnson and Ziegler[2] found that in the case of benzene, deuteration likewise affects the radiative decay rate. This radiative d-isotope effect was interpreted in terms of vibronic interaction in the orbitally forbidden T_1-S_0-transition of benzene. Later on, Lim and coworkers[3, 4] represented a quantitative study of the luminescence of aromatic hydrocarbons in an organic glass matrix. They found that the radiative d-isotope effect is a common feature in aromatic molecules, and that it may arise even in cases where the phosphorescence transition is not orbitally forbidden. Fischer and Lim interpreted those observations in terms of a non-adiabatic coupling[5].

In a recent study of the influence of a heavy atom on the various triplet decay mechanisms, Friedrich, Metz and Dörr proposed a connection between the heavy atom effect and the d-isotope effect via a second order HT-coupling mechanism[6, 7]. By observing the polarization of the phosphorescence 00-transition of haloaromatics, they found that the presence of a halogene tends to destroy the selective spin-orbit coupling of the individual triplet sublevels, which is originally present in the parent hydrocarbon. If the interpretation via higher order HT-coupling is correct, then a heavy atom must have a great influence on the radiative d-isotope effect. Besides this, deuteration must strongly affect the 00-rate of the phosphorescence. Moreover, the polarized phosphorescence excitation and emission spectra are expected to be sensitive to d-substitution.

It is the aim of this paper to investigate the influence of d-substitution on the radiative rates of the triplet sublevels of naphthalene in the presence of heavy atoms in order to obtain further insight into the various decay mechanisms of the lowest triplet state in aromatic molecules.

II. Experimental

The experimental setup for measuring the degree of polarization was described elsewhere[6]. The bandpasses used were about 50 cm^{-1} in the emission region (in the case of naphthalene 100 cm^{-1}) and about 100 cm^{-1} (naphthalene 200 cm^{-1}) in the absorption region.

To determine the quantum yield, the spectral response of the detector side of the spectrometer was corrected by use of a tungsten band lamp (Osram). The spectral emissivity of tungsten was taken from reference[8]. To produce corrected emission spectra automatically, a procedure was used originally employed by Grüneis et al.[9]: The output of the lock-in amplifier (PAR mod 129) at a particular wave number was multiplied by the corresponding cor-

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rection factor by use of PROM's (Programmable Read Only Memories). The fluorescence quantum yield, Φ_F was obtained from the corrected emission spectra using well established methods[10]. As a reference standard we used diphenylanthracene in EPA solution, the quantum yield of which is very near to unity[11, 11a].

The phosphorescence quantum yield, Φ_P, was determined assuming that internal conversion from the first excited singlet state is negligible. Because of the high energy gap, this approximation should hold very well in the case of the molecules considered.

The quantum yield of the 00-transition, $\Phi_P{}^0$, was determined by taking the ratio of the area of the 00-band and the area of the total phosphorescence spectrum. To be sure that the results were not influenced by reabsorption (we used concentrations of about 10^{-3} m) we measured the quantum yield of a very dilute solution (10^{-5} m) of diphenylanthracene versus a 10^{-3} m solution. The results agree within the error limit of the experiment.

The total radiative rate k and the 00-rate k^0 from the lowest triplet state were obtained from the equations

$$k_r = \Phi_P/(1-\Phi_F)\,\tau\,; \quad k_r{}^0 = \Phi_P{}^0/(1-\Phi_F)\,\tau\,.$$

The triplet lifetime τ was measured by using a phase modulation technique. The exciting beam was chopped at a suitable frequency and the phase shift of the emitted light was determined with the lock-in amplifier. For those molecules which had a lifetime longer than the reciprocal cut-off frequency of the lock-in amplifier (5 cps) we used a shutter and a xy-recorder (HP 7045 A).

All results were obtained in an ethanol matrix at 77 K. The dihalonaphthalenes investigated were synthesized from the corresponding diaminonaphthalenes[12, 12a]. The substances were carefully purified by means of column chromatography and repeated sublimation. The Br- and I-derivatives were deuterated by an exchange reaction with perdeuterobenzene as a deuterium source[13]. In the case of 1,4-dichloronaphthalene, deuteration was achieved by starting the synthesis with perdeuteronaphthalene (Merck). Thus, in this case, the isotopic purity should exceed 98%. In the case of the I- and Br-derivatives, the degree of deuteration was determined from the NMR spectra to be at least 90%.

Table 1. Quantum yields and rate constants of naphthalene and its derivatives. PG$(0,\nu_{La})$ and PG$(0,\nu_{Lb})$ represent the degree of polarization in the L_a and L_b-transition respectively, taken with respect to the 00-band of the phosphorescence. $k_r{}^{0,ip}$ and $k_r{}^{0,op}$ denote the in-plane (ip) and the out-of-plane (op) polarized radiative rate constants of the lowest triplet to the vibrationless ground state of S_0. The errors in the various rates of naphthalene are somewhat larger due to the uncertainty in the determination of $\varnothing_{ISC}$.

	1,4-dichloronaphthalene		2,7-dibromonaphthalene		2,7-diiodonaphthalene		naphthalene	
	h_6	d_6	h_6	d_6	h_6	d_6	h_8	d_8
$\varnothing_F$ (±10%)	0.04	0.04	0.0009	0.0008	10^{-4}	10^{-4}	0.45	0.41
$\varnothing_{ISO}=1\text{-}\varnothing_F$ (±0.1%)	0.96	0.96	1	1	1	1	0.55 (±5%)	0.59 (±4%)
$\varnothing_P$ (10%)	0.25	0.85	0.51	1	0.64	1	0.039 (±11%)	0.34 (±11%)
$\frac{\varnothing_P{}^0}{\varnothing_P}$ (±10%)	0.05	0.05	0.04	0.04	0.045	0.05	0.08 (±11%)	0.07 (±11%)
PG$(0,\nu_{La})$ (±2%)	−0.2	−0.2	−0.31	−0.315	−0.29	−0.29	−0.32	−0.32
PG$(0,\nu_{Lb})$ (±2%)	−0.175	−0.205	−0.17	−0.2	−0.13	−0.16	−0.29	−0.29
$k=\tau^{-1}$ [sec^{-1}] (±3%)	9.1	1.8	200	59	1560	555	0.43	0.049
k_r [sec^{-1}] (±10%)	2.4	1.6	102	59	1000	555	3.05×10^{-2} (±12%)	2.9×10^{-2} (±12%)
$k_r{}^0$ [sec^{-1}] (±10%)	0.12	0.08	4.1	2.36	45	28	2.54×10^{-3} (±12%)	2.14×10^{-3} (±12%)
$k_r{}^{0,op}$ [sec^{-1}] (±11%)	1.8×10^{-2}	0.96×10^{-2}	8.1×10^{-1}	3.4×10^{-1}	10.6	5.75	1.3×10^{-4} (±12%)	1.1×10^{-4} (±12%)
$k_r{}^{0,op}$ [sec^{-1}] (±11%)	0.1	0.07	3.3	2.0	34.4	23.3	2.4×10^{-3} (±12%)	2.03×10^{-3} (±12%)

III. Results

In this section we summarize the principle findings from our results (see Tables 1 and 2).

Table 2. Ratios of rate constants of the protonated and deuterated compounds.

	1,4-dichloro-naphthalene	2,7-dibromo-naphthalene	2,7-diiodo-naphthalene	naphthalene
$\frac{k(\mathrm{H})}{k(\mathrm{D})}$ (±4%)	5	3.4	2.8	8.8
$\frac{k_\mathrm{r}(\mathrm{H})}{k_\mathrm{r}(\mathrm{D})}$ (±14%)	1.5	1.7	1.8	1.05 (±17%)
$\frac{k_\mathrm{r}^\mathrm{o}(\mathrm{H})}{k_\mathrm{r}^\mathrm{o}(\mathrm{D})}$ (±14%)	1.5	1.75	1.6	1.2 (±17%)
$\frac{k_\mathrm{r}^{\mathrm{o,ip}}(\mathrm{H})}{k_\mathrm{r}^{\mathrm{o,ip}}(\mathrm{D})}$ (±15%)	1.88	2.44	1.9	1.2 (±17%)
$\frac{k_\mathrm{r}^{\mathrm{o,op}}(\mathrm{H})}{k_\mathrm{r}^{\mathrm{o,op}}(\mathrm{D})}$ (±15%)	1.45	1.63	1.48	1.2 (±17%)

a) The total decay rate of the lowest triplet state is much less influenced by deuteration in the case of the haloaromatics than in naphthalene itself.

b) The radiative rate, however, is much more affected in the heavy atom containing molecules than in the parent hydrocarbon. In naphthalene the ratio $k_\mathrm{r}(\mathrm{H})/k_\mathrm{r}(\mathrm{D})$ deviates little from unity (about 5%), whereas, for example, in 2,7-I-naphthalene, we have a change in this ratio upon deuteration by about 80%. That is, in the presence of a heavy atom, the d-isotope effect in the total radiative rate increases.

c) The 00-rate changes in the same way upon deuteration as does the total radiative rate in the case of the halogen substituted molecules. However, even in naphthalene itself we observe a remarkable influence of deuteration on the 00-rate (nearly 20%). This is a large enhancement as compared with a change of 5% in the total radiative rate.

Looking now to Fig. 5 we see that deuteration indeed causes a significant change in the polarization of the phosphorescence. From the change in the degree of polarization we can determine the influence of d-substitution on the in-plane- and on the out-of-plane polarized rate using the photoselection equation [14]. Since the different directions of polarization originate from the radiative decay of different triplet sublevels we can determine from the degree of polarization the influence of deuteration on the individual radiative rates from T^x and T^y or T^z (see Fig. 6). A few facts are obvious:

a) In naphthalene-d_8 and -h_8 there is no difference in the degree of polarization when excited either in the L_b- or L_a-state. From this observation it follows that there is no different deuterium effect in the in-plane and in the out-of-plane polarized rates.

b) In the halonaphthalenes, especially in the case of the Br- and I-compounds, however, there is indeed a significant change in the degree of polarization upon deuteration with respect to L_b-excitation (see Figure 5).

On the other hand, L_a-excitation produces no significant difference in the polarization of the phosphorescence 00-transitions of the protonated and deuterated species respectively.

From this behaviour we conclude that there is a much more pronounced d-effect in the in-plane than in the out-of-plane rate.

How can we explain the influence of deuteration on the radiative decay of the triplet substates in heavy atom substituted aromatic molecules?

IV. Discussion

1. Sources of the radiative d-isotope effect

There are several interactions which may influence the decay of the lowest triplet state and which depend on d-isotope substitution. To arrive at an explanation of the experimental facts, we consider these interactions and discuss their relative magnitudes.

The hyperfine interaction (HFI)

As early as the influence of deuteration on triplet lifetimes was discovered, the HFI was considered to be a possible explanation of the observed facts [15]. Though it is nowadays well understood that the main influence of d-substitution is via the Franck-Condon (FC)-factor which governs the radiationless rate, it is nevertheless true, that the coupling between the electronic and nuclear spin may in principle change the rates from the triplet sublevels. There is a twofold influence of the HFI on the triplet state: On the one hand it mixes the zero field wavefunctions, thus changing the properties of an individual substate; on the other hand, it can mix singlets and triplets.

However, there are several reasons which allow us to rule out the HFI as a possible source of the radiative isotope effect: From ODMR-spectroscopy we know the HFI splitting to be in the MHz-region while the spin orbit splitting is in the GHz region. Thus HFI can not successfully compete with SOC. This result is also confirmed by calculations of Colpa et al. and Stehlik et al.[16, 17].

Moreover HFI fails to explain the overall trend in our experiment: since it does not depend on the nuclear charge this interaction can not account for the observed influence of the heavy atoms on the d-effect.

The non-adiabatic interaction

The non-adiabatic interaction was in the past often considered to be responsible for vibronic spin-orbit coupling and therefore to govern the population and the decay of the lowest triplet state in aromatic molecules. Though this mechanism is indeed strongly dependent on isotope substitution, there is in the meantime much theoretical[18, 19] and experimental[20] evidence available which indicates that this mechanism is of minor importance in triplet decay. Another argument against non-adiabatic spin-orbit coupling arises from our own experimental results: From the polarized excitation spectra (Figs. 1 – 5) and from Table 2 we see that there is a correlation between heavy atom and deuterium isotope-effect in the 00-rate of the phosphorescence. As already stated in Sect. III it is the T^x-rate which is predominantly influenced by deuteration. From symmetry arguments, however, it follows that the T^x-rate in the 00-transition (in-plane polarized) cannot be affected by non-adiabatic spin-orbit interaction via one center integrals at the heavy center. Thus we are left with the HT-interaction to explain our results.

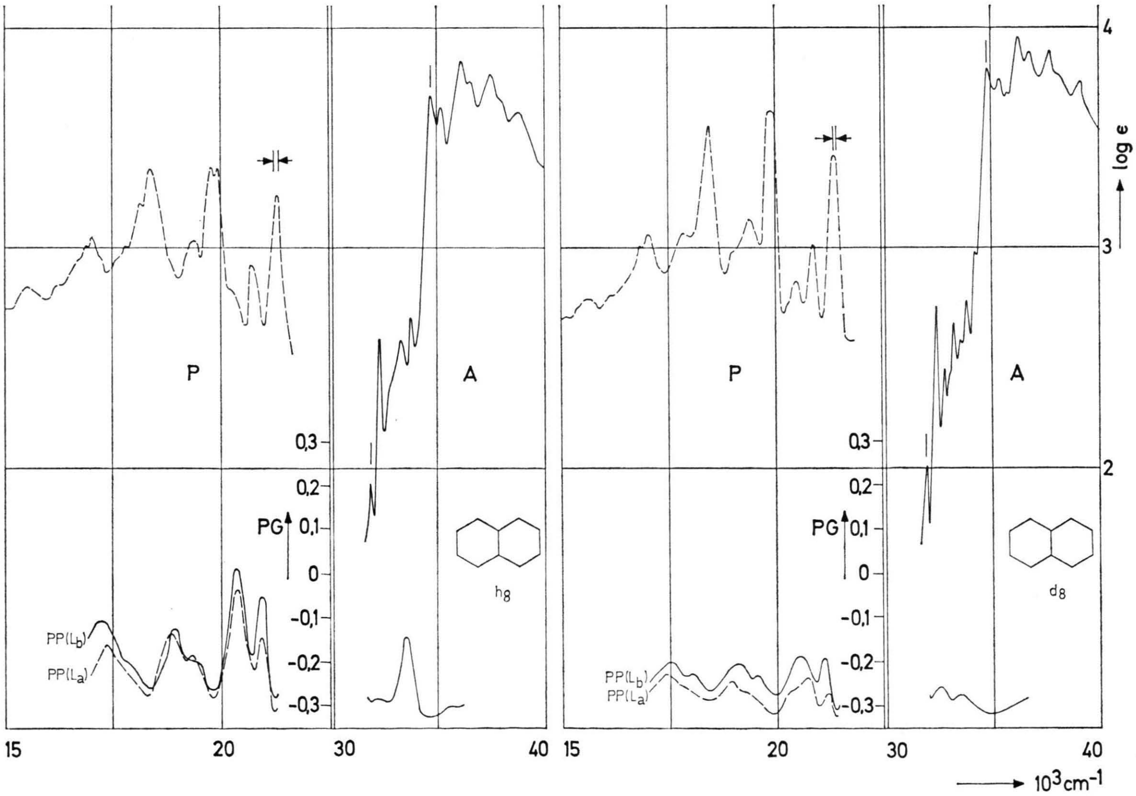

Fig. 1. Phosphorescence P and absorption spectra A with the corresponding degree of polarization of naphthalene-h_8 and -d_8 in an EtOH-glass matrix at 77 K. The band passes used are shown in the figure.

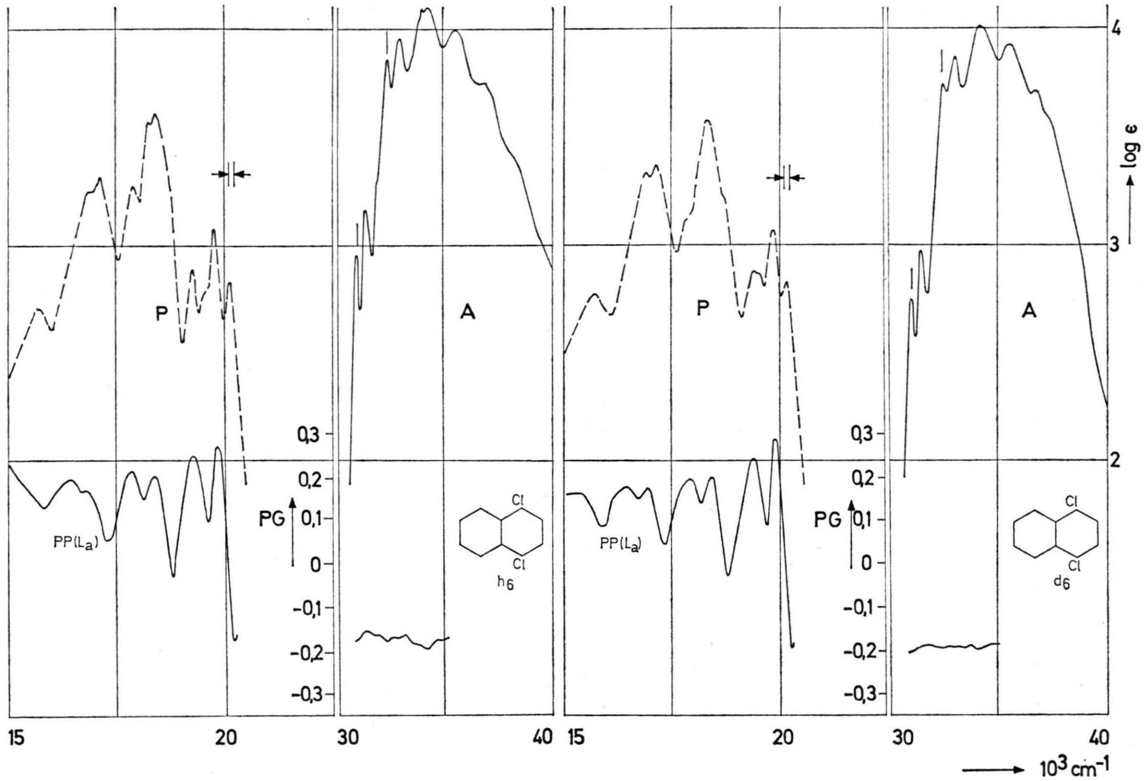

Fig. 2. Phosphorescence P and absorption spectra A with the corresponding degree of polarization of 1,4-dichloronaphthalene-h_6 and -d_6 in an EtOH-glass matrix at 77 K. The band passes used are shown in the figure.

The HT-Interaction

The α-component ($\alpha = x, y, z$) of the transition moment of a sublevel T_1^τ is given by

$$M^{\tau,\alpha}_{S_0T_1}(\{Q\}) = \sum_j \left[\frac{\langle S_0|H_{SO}|T_j^\tau \times T_j^\tau|r_\alpha|T_1^\tau\rangle}{\varepsilon_{S_0}-\varepsilon_{T_j}} + \frac{\langle S_0|r_\alpha|S_j \times S_j|H_{SO}|T_1^\tau\rangle}{\varepsilon_{T_1}-\varepsilon_{S_j}}\right]; \qquad (4)$$

ε_{S_0} is the energy surface in the ground state S_0, H_{SO} is the operator for spin-orbit coupling. The influence of the normal vibrations on the transition moment are taken into account by an expansion around the equilibrium position $\{Q\} = 0$ of the molecule:

$$M^{\tau,\alpha}_{S_0T_1}(\{Q\}) = M^{\tau,\alpha}_{S_0T_1}(\{0\}) + \sum_P \left[\frac{\partial}{\partial Q_p} M^{\tau,\alpha}_{S_0T_1}\right]_{Q_p=0} \cdot Q_p + \sum_{p,p'} \left[\frac{1}{2}\frac{\partial^2}{\partial Q_p\,\partial Q_{p'}} M^{\tau,\alpha}_{S_0T_1}\right]_{Q_p,Q_{p'}=0} Q_p Q_{p'} + \dots \qquad (5)$$

In this expansion we only took into account the variation with the out-of-plane promoting modes $\{Q_p\}$ which yield one center spin-orbit terms.

The contribution due to the totally symmetric modes are of minor importance compared with the zero order term (ca. 10%). We therefore neglect their contribution to the isotope effect.

It seems possible to probe the various vibronic spin-orbit mechanisms in heavy atom containing hydrocarbons by means of deuterium substitution:

The equilibrium term $M^{\tau,\alpha}_{S_0T_1}(\{0\})$ is insensitive to deuteration. The second term can essentially affect only the overall radiative rate, the influence on the 00-rate being very weak. The question is, whether or not the promoting modes in the first order mechanism are CH-vibrations, which would lead to a d-isotope effect. We try to answer this question by looking at the polarized phosphorescence emission spectra. There is a large difference in the polarization of the vibronic bands in the case of naphthalene and naphthalene-d_8, but there is only a very small difference in the case of the corresponding halogenated derivatives (see Figs. 1 – 4). That is, in naphthalene itself there is a considerable

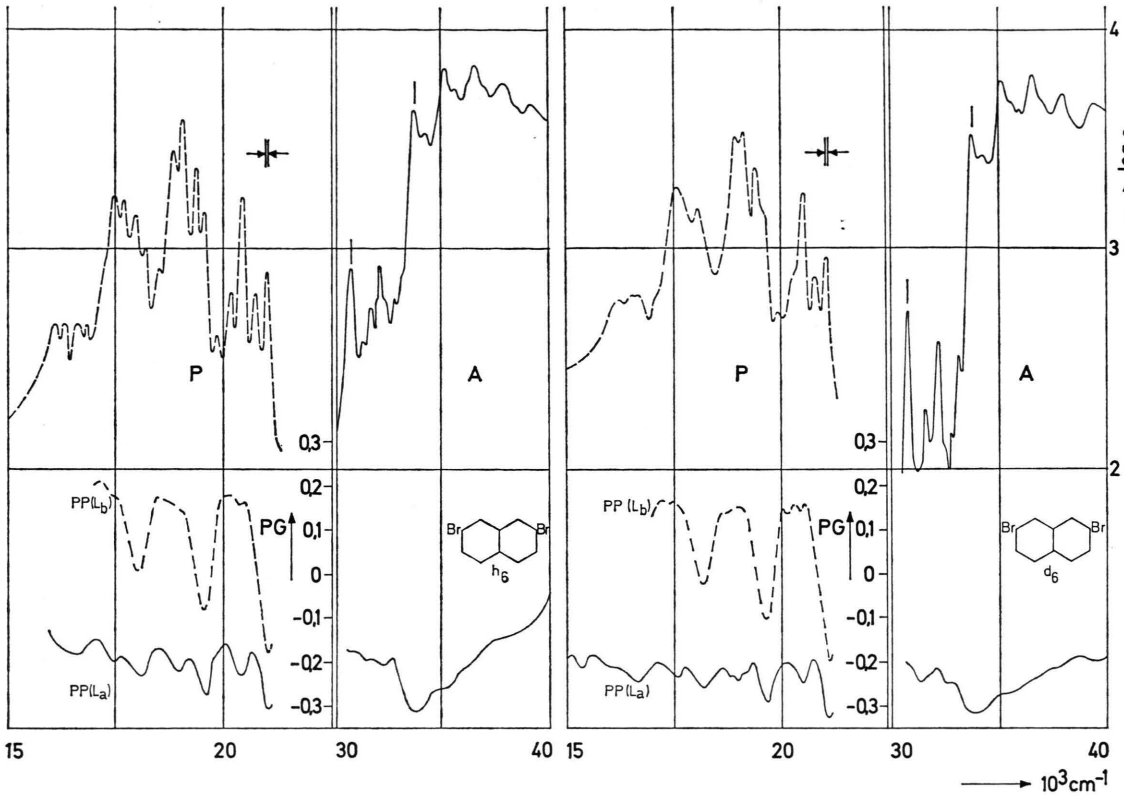

Fig. 3. Phosphorescence P and absorption spectra A with the corresponding degree of polarization of 2,7-dibromonaphthalene-h_6 and -d_6 in an EtOH-glass matrix at 77 K. The band passes used are shown in the figure.

amount of CH-modes in the 1st-order HT-mechanism, but in the heavy atom containing molecules, there is only a very small influence of CH-vibrations in the 1st-order HT-coupling. This observation is consistent with theoretical results [6]: It is an out-of-plane vibration of that C-atom which is the nearest neighbour to the heavy substituent, which accounts for the most important contribution.

Thus the 2nd-order HT-interaction remains as the only explanation for the radiative d-isotope effect in the case of heavy atom substituted aromatic molecules.

There are many terms such as

$$\langle \frac{\partial}{\partial Q_p} \psi_S | H_{SO} | \frac{\partial}{\partial Q_p} \psi_T \rangle \langle \psi_T | r_a | \psi_T' \rangle ,$$

$$\langle \frac{\partial}{\partial Q_p} \psi_S | H_{SO} | \psi_T \rangle \frac{\partial}{\partial Q_p} \langle \psi_T | r_a | \psi_T' \rangle ,$$

$$\langle \psi_S | H_{SO} | \psi_T \rangle \frac{\partial^2}{\partial Q_p^2} \langle \psi_T | r_a | \psi_T' \rangle .$$

Since in the spectra we observe a large activity of the in-plane-polarized component with increasing nuclear charge at the heavy center, we only take into account those terms which lead to a one center spin-orbit contribution at the halogen. The only term with this property is of the type *

$$\langle \frac{\partial}{\partial Q_p} \psi_S | H_{SO} | \frac{\partial}{\partial Q_p} \psi_T \rangle \langle \psi_T | r_a | \psi_T' \rangle ;$$

The change of the vibrational ground state overlap integral on deuteration

Though there is no influence of deuteration via the vibrational overlap integrals in the total radia-

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* Very recently there appeared a paper by Kanamaru and Lim [21] on the d-isotope effect in pyrazine in which they considered the derivative of the matrix elements of the dipole operator to be the dominant source. Though this mechanism may be effective in the singlet-singlet absorption and in the radiative triplet decay in the case of nearby $n\pi^*$ and $\pi\pi^*$-states in N-heterocyclics, it seems to fail in explaining our results. The reason ist that a term like $\langle H_{SO} \rangle \partial^2 / \partial Q_p^2 \langle r_a \rangle$ cannot provide one center spin-orbit-terms if the intermediate states are of $\pi\pi^*$-type.

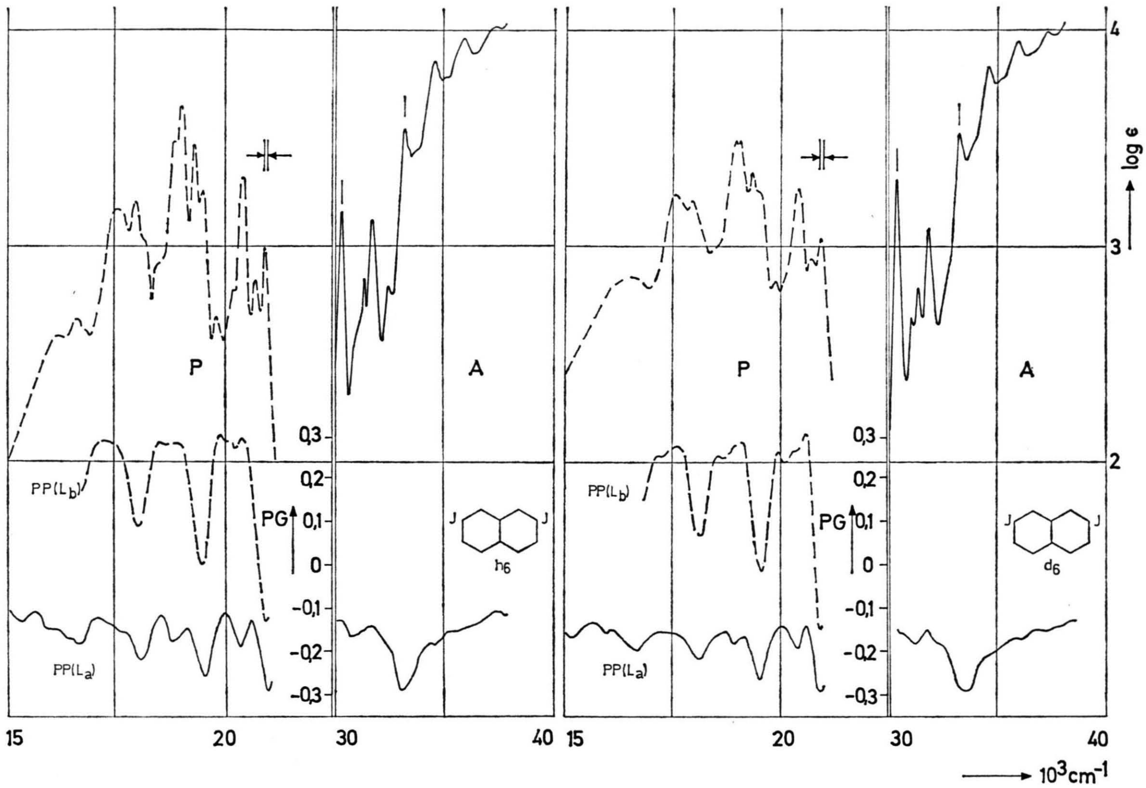

Fig. 4. Phosphorescence P and absorption spectra A with the corresponding degree of polarization of 2,7-diiodonaphthalene-h$_6$ and -d$_6$ in an EtOH-glass matrix at 77 K. The polarization spectra are taken with respect to the marked (|) transitions. The band passes used are shown in the figure.

tive rate, there may arise such an influence in the 00-rate.

The rate in the 00-transition of the phosphorescence is given by

$$k_r^0 \sim \sum_{\tau,\alpha} |\langle \chi_{S_0} | M^{\tau,\alpha}_{S_0T_1} | \chi_{T_1} \rangle|^2 .$$

Since we expand $M^{\tau,\alpha}_{S_0T_1}$ only in terms of the promoting modes $\{Q_p\}$, and assume that the dependence of $M^{\tau,\alpha}_{S_0T_1}$ on the totally symmetric modes is very weak, we get

$$k_r^0 \sim \sum_{\tau,\alpha} | M^{\tau,\alpha}_{S_0T_1}(\{Q_p\})|^2 \, |\prod_t \langle O^t_{S_0} | O^t_{T_1} \rangle|^2 .$$

$\langle O^t_{S_0} | O^t_{T_1} \rangle$ is the overlap integral between the t'th totally symmetric zero point vibration in the triplet state T_1 and in the ground state S_0, respectively. The point is, whether there may indeed be an observable change in the overlap integral of the zero point vibrations upon deuteration.

If we assume that there is no strong distortion of the energy surfaces in the T_1-state, the integral is given by [22]

$$\langle O^t_{S_0} | O^t_{T_1} \rangle = e^{-\frac{1}{2} g_t^2}$$

where g_t is a parameter depending on the equilibrium shift of the modes t:

$$g_t^2 = \frac{K_t}{\omega_t} \Delta_t^2 .$$

K_t, ω_t and Δ_t are the force constant, the frequency and the shift of the equilibrium position of the mode t, respectively. Thus one has

$$|\prod_t \langle O^t_{S_0} | O^t_{T_1} \rangle|^2 = \exp\{-\sum_t g_t^2\} .$$

Making the simplifying assumption that the electronic matrix element is not influenced by deuteration, one finds that the variation in the 00-rate due to an overlap change is given by

$$\frac{k_r^0(\mathrm{D})}{k_r^0(\mathrm{H})} = \exp\left[\sum_t \{g_t^2(\mathrm{H}) - g_t^2(\mathrm{D})\}\right] .$$

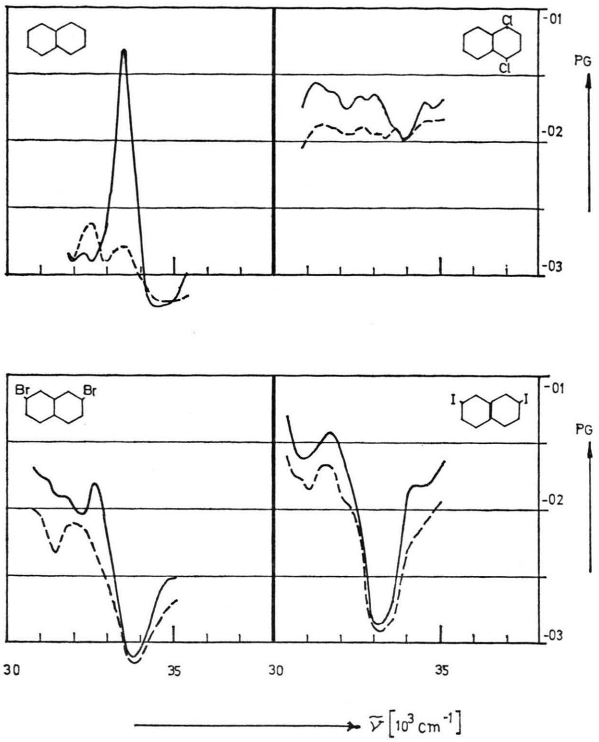

Fig. 5. The polarized excitations spectra of the protonated (———) compared to the deuterated (– – –) compounds.

2. *The radiative isotope effect in naphthalene*

From experimental work [23] we know that about 90% of the total radiative rate comes from the T^y-substate (see Fig. 6) due to one-center spin-orbit coupling between the $\pi\pi^*$ and $\sigma\pi^*$ states. That is, in the parent hydrocarbon, the matrix elements at the equilibrium position of the molecule [Eq. (5)] are large compared with the vibronic spin-orbit coupling mechanisms. The weak in-plane polarized component is partly due to the decay of the T^x-state via three-center spin-orbit integrals, and partly due to the vibrational influence on the transition matrix element. Because the total in-plane component is small, we expect upon deuteration only a small change ($<10\%$) in the total radiative rate. Looking at Table 2, we see that this is indeed the case; the rate decreases by 5% upon deuteration. Discussing the 00-rate, however, we find a significantly larger d-effect than in the total radiative rate. Since, as argued, vibronic interaction (i. e. the 2nd-order HT-spin-orbit coupling) is very small, the d-effect must arise from the difference in the overlap integral between the vibrational ground-states. Assuming no frequency change in the excited state, and taking the parameters g_t^2 from [24], we find a ratio

$$k_r^0(\mathrm{D})/k_r^0(\mathrm{H}) \approx 0.6\,.$$

Though this result does not agree with our experiment very well, it shows nevertheless that the change in the overlap integral may indeed provide a large contribution to the radiative isotope effect in the 00-transition.

Let us now consider the polarized excitation spectra. There is no difference in the degree of polarization between the protonated and the deuterated species in the 00-transitions when excited into either the L_b or the L_a-band. The wavefunction of the L_a-state transforms like B_{1u} and thus the corresponding transition is z-polarized. From Fig. 6 we see that there is no z-polarized component in the phosphorescence which could be changed upon deuteration. This situation prevails in both the protonated and the deuterated species.

On the other hand the L_b-transition (B_{2u}) has a parallel polarized component in the phosphorescence emission (from T^x). Though this is small, it may in principle be influenced by deuteration via 2nd-order HT-coupling. Because, however, the polarization does not change, we conclude that the radiative T^x-decay in the phosphorescence 00-band is mainly governed by three center spin-orbit integrals which are not sensitive to deuteration, and (or) by vibronic spin-orbit interaction due to C-C-vibrations. Therefore we relate the d-isotope-effect in the 00-band of the T_1-S_0-emission to a change in the overlap factor. In this case it is clear that there is no different isotope influence in the in-plane and out-of-plane rate.

3. *Radiative deuterium effect and heavy atom effect*

The situation is quite different in the case of the halonaphthalenes.

In the first place, there is a great difference of the d-isotope-effect in the triplet lifetimes. From experimental and theoretical work (for a review see [1]) we know that the main influence of deuteration in aromatic hydrocarbons is upon the radiationless rate via the FC-factor. Since there is no reason to assume that the electronic matrix elements in the radiationless decay are changed less efficiently by the heavy atom than the matrix elements in the radiative decay, we argue that the FC-factor decreases upon halogen substitution. Thus in the halonaphthalenes the non-radiative processes are diminished compared with the radiative processes and the quantum yield becomes larger. As a consequence the d-effect on the triplet lifetime is much smaller than in naphthalene itself. The situation is quite different, if we consider the radiative rates.

There is a very large influence of deuteration in the presence of a heavy atom. While there is only a 5% change in the radiative rate of naphthalene, we get, for example in 2,7-iodonaphthalene a change of 80%. Nearly the same situation holds for the 00-rate. From this fact we conclude that the isotope effect in the 00-transition is mainly due to a vibronic coupling mechanism and not to a change in the overlap integral. Moreover we see that even in the total radiative rate this mechanism must be the 2nd-order HT-coupling since deuteration has no different effect on the 00-rate and on the total radiative rate. This statement is consistent with the argument we used in Sect. IV 1, concerning the magnitude of the first order HT-coupling.

Let us now compare the deuterium effect in the in-plane (T^x) and in the out-of-plane rates (T^y or T^z). We see that in the Br- and I-derivative the ratio $k_r^{0,\mathrm{ip}}(\mathrm{H})/k_r^{0,\mathrm{ip}}(\mathrm{D})$ is considerably larger than $k_r^{0,\mathrm{op}}(\mathrm{H})/k_r^{0,\mathrm{op}}(\mathrm{D})$. To explain this fact, we remember that the out-of-plane polarized decay from the T^y- or T^z-substate is governed by large matrix elements at the equilibrium position of the molecule. Higher order HT-coupling surely is of minor importance, though possible. Thus the isotope effect in the T^y (or T^z) decay should be due to both a relatively small influence of second order HT-spin-orbit coupling and to a change in the zero point overlap integrals.

However, the in-plane polarized decay at $\{Q\}=0$ is governed only by very small three-center spin-orbit integrals in which there is no influence of the heavy atom because the nuclear charge is shielded to a high degree. Therefore these equilibrium terms are dominated to a high degree by vibronic spin-orbit mechanisms which are sensitive to heavy atom substitution[6]. An immediate experimental consequence of these conclusions is that there should be a change in the degree of polarization upon deuteration, if the promoting modes are CH-vibrations.

Looking at the polarized excitation spectra (all are taken with respect to the phosphorescence 00-transition), we see that the degree of polarization with respect to L$_b$-excitation of the deuterated species is always less than that of the protonated species. This is because the 2nd-order HT-spin-orbit coupling is reduced by deuteration, thus the relative extent of the out-of-plane polarization which is less sensitive to deuteration, increases.

On the other hand, there is no difference in the 00-transition of the L$_a$-band of the protonated and the corresponding deuterated molecules. This is due to the fact that the L$_a$-transition obviously has no parallel component in the phosphorescence (the corresponding transition is forbidden, as is shown in Fig. 6). Thus no vibronic coupling mechanism can influence the relative direction between the L$_a$ band and the 00-transition of the phosphorescence.

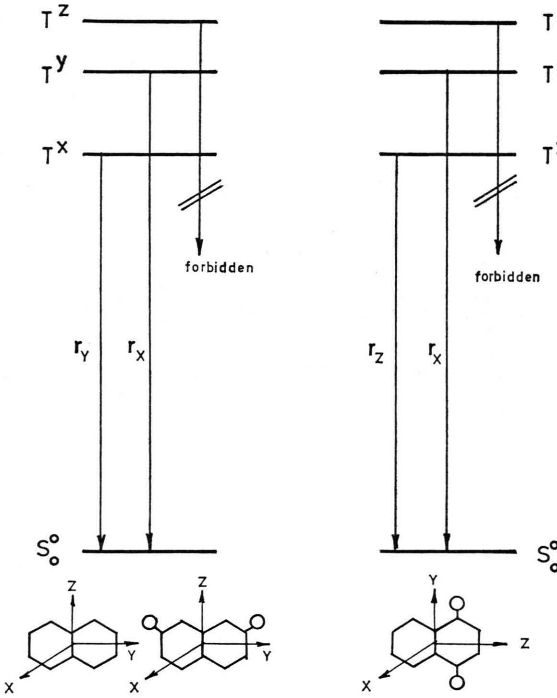

Fig. 6. Schematic level diagram and choice of axes.

V. Summary

In this paper we investigated the influence of deuteration upon the radiative decay of the T$_1$-substates in naphthalene and some halogenated derivatives.

The relation between deuterium isotope and heavy atom effects we found is consistently related to a second order HT-spin-orbit coupling. The isotope effect in the phosphorescence 00-transition of naphthalene, in which vibronic spin-orbit coupling is small, is interpreted in terms of a change of the overlap integral of the zero point vibrations upon deuteration. There are a few outstanding points concerning the d-isotope-effect in heavy atom substituted aromatic molecules: We find

1. A large deuterium effect in the 00-transition of the phosphorescence.
2. A very strong influence of deuteration on the radiative decay of the out-of-plane polarized spin substate T^x.
3. A clear dependence of the polarization of the phosphorescence upon deuteration.

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