POSITION-DEPENDENT HEAVY ATOM EFFECT IN THE SUBRATES OF THE LOWEST TRIPLET STATE OF DICHLORONAPHTHALENES

G. FLATSCHER and J. FRIEDRICH

Institut für Physikalische und Theoretische Chemie der Technischen Universität München.
D-8046 Garching, Germany

By means of the microwave-induced delayed phosphorescence (MIDP) technique, the dynamics of the lowest triplet state T_0 of several dichloronaphthalenes in naphthalene and durene are investigated. It is shown that the position dependence is very selective in the nonradiative decay of the spin-sublevels: The out-of-plane spin state is nearly not affected, while the in-plane states are strongly affected. The radiative rates, on the other hand, are not selectively influenced by the position of substitution. Besides, the results show that the dynamics of the lowest triplet state is determined by the type of substitution, rather than by the symmetry of the molecule. The spin—orbit coupling of the in-plane states seems to profit from some distortion the guest molecule experiences in the naphthalene host lattice.

1. Introduction

In his early work on the influence of a heavy substituent on the spin—orbit coupling of aromatic hydrocarbons, McClure had already noted that the triplet lifetimes depend on the position of the heavy atom within the aromatic ring [1]. In the following years, many authors observed an influence of the position of a heavy atom on various, different spectral properties of the lowest triplet state (T_0) [2]. However, the most direct relation of the position-dependent heavy atom effect is to the dynamic features of T_0. In his thesis, the first systematic investigation in this field, Miller [3] measured the influence of the position of substitution on the triplet lifetimes of various halonaphthalenes and -phenanthrenes [3]. He tried to relate the changes in the decay time (at 77 K) to the MO coefficient at the position of substitution, since it is commonly assumed that this coefficient governs the feedback of the strong atomic spin—orbit coupling into the aromatic frame. However, there are different spin—orbit coupling mechanisms for the different sublevels which may differ in their dependence on the position of the heavy atom(s) [4]. Furthermore, the radiationless and the radiative channel may also show a different behavior, since they are usually dominated by different types of spin—orbit coupling matrix ele-

ments. Therefore, the influence of the position of the heavy atom on the dynamics of the isolated substates is expected to be totally different from the influence on the average triplet lifetime.

To test these ideas we investigated a series of dichloronaphthalenes (DCIN) in a naphthalene host by means of microwave-induced delayed phosphorescence (MIDP) [5]. The advantage of this technique is that the relative decay rates of the substates are independent of the Franck—Condon (FC) factor, because the three sublevels have almost the same energy gap to the ground state. Changing the position of substitution may change the energy of T_0 up to several hundred wave numbers. This, in turn, may influence the FC factor.

The dichloronaphthalenes were chosen, because their parent molecule is one of the best known aromatic compounds. A series of papers deal with the influence of halogenes on spin—orbit coupling in naphthalene [3,4,6,7]. The position-dependent heavy atom effect on the triplet lifetime in the case of α- and β-monochloronaphthalene is known to be very small (10%) [3] and seems to be in no way related to the MO coefficients. The reason for this behavior is not known. Since the monochloronaphthalenes cannot be compared by the MIDP technique neither in a durene nor in a naphthalene matrix

[8], we chose the dichloronaphthalenes to investigate the position-dependence of the heavy atom effect on the dynamics of the lowest triplet state.

2. Experimental

2.1. Spectrometer

The sample, placed inside a slow wave helix, which is attached to a stainless steel semirigid coaxial cable, is immersed in liquid helium. For the dynamic experiments the temperature was kept constant at about 1.2 K by pumping on the He bath. To measure the zero field transitions, a proper temperature was chosen somewhere between 4.2 and 12 K. Temperature leveling and control was achieved by a commercial temperature control loop (E3; Leybold), the accuracy of which was 0.2 K below and 1 K above 4.2 K. Excitation of the sample was carried out by use of a high-pressure Hg lamp (200 W; Oriel), the light of which was filtered by a solution of $NiSO_4$ and $CoSO_4$ in water (100 + 100 mg per 1 H_2O; path length 10 cm). The emission from the crystal was dispersed by a grating monochromator (CT103; Chromatix), and detected by a cooled photomultiplier (R649; Hamamatsu). The photon pulses are fed into a single photon counter (5 Cl; Brookdeal/Ortec). The output of the counter is either displayed on an xy recorder (7045A; Hewlett—Packard), or, for time-resolved measurements, is fed into a multichannel averager (1072, SW77B + SD77B; Nicolet). During the measuring cycle, the various components of the experiment are controlled by a home-made digital device.

The microwave source consists of a solid state sweep oscillator (8620A; Hewlett—Packard) and a series of TWT-amplifiers (1401H; Hughes; 489A + 497C; Hewlett—Packard), with a maximum output of 1 W. Microwave frequency and power are controlled by a Hewlett—Packard counter (5340A) and power meter (432A), coupled to a thermistor mount (8478B).

Two pin diodes (DM186BH; General Microwave) control the transmitted microwave power during sweep-up and -down. They also modulate the microwave power transmitted to the slow wave helix during stationary ODMR (optical detection of magnetic resonance). The modulation voltage from a signal generator (3311A; Hewlett—Packard) is fed into the reference input of a vector lock-in amplifier (Dynatrac 3; Ithaco). The modulation frequency used was 4 Hz.

In most cases the optical bandpass of the instrument was set to about 5 cm^{-1} (at 5000 Å) for recording the phosphorescence spectra. The relative radiative rates and the zero field spectra were detected at the 00 transition with a bandpass of 100 cm^{-1}.

2.2. Sample preparation

The host material, purchased from Merck, was recrystallized three times from ethanol and then filled into glass tubes (9 mm inner diameter). The tubes were sealed off under vacuum and then zone-refined by about 120 passes (7 cm/d). Materials under investigation (DClN) were also recrystallized three times from ethanol and then doped into zone-refined naphthalene with a concentration of about 2×10^{-3} m/m. The mixed crystals were grown from the melt under vacuum in a standard Bridgman furnace, then cleaved with a razor blade to a size of about $10 \times 4 \times 2$ mm and placed in the slow wave helix. Several independent measurements were made with fresh crystals. Spectra were exactly reproducible, total rates to about ±5% and relative radiative rates within ±20%.

3. Results

3.1. Spectra and zero field parameters

The molecules investigated differ not only with respect to the position of substitution, but also with respect to their molecular symmetry (C_{2v} for 1,4- and 2,3-DClN and C_{2h} for 1,5- and 2,6-DClN). However, the optical and microwave spectra (figs. 1—4) suggest that it is the type of substitution (α or β) and not the symmetry of the molecule which determines the properties of T_0: The energy is lower up to several hundred wave numbers for the α-substituted molecules as compared to the β-substituted (table 1). The D-values are all very similar. They differ from each other within 3% for the same type of molecules (e.g., α-derivatives) and within 6% for different types of
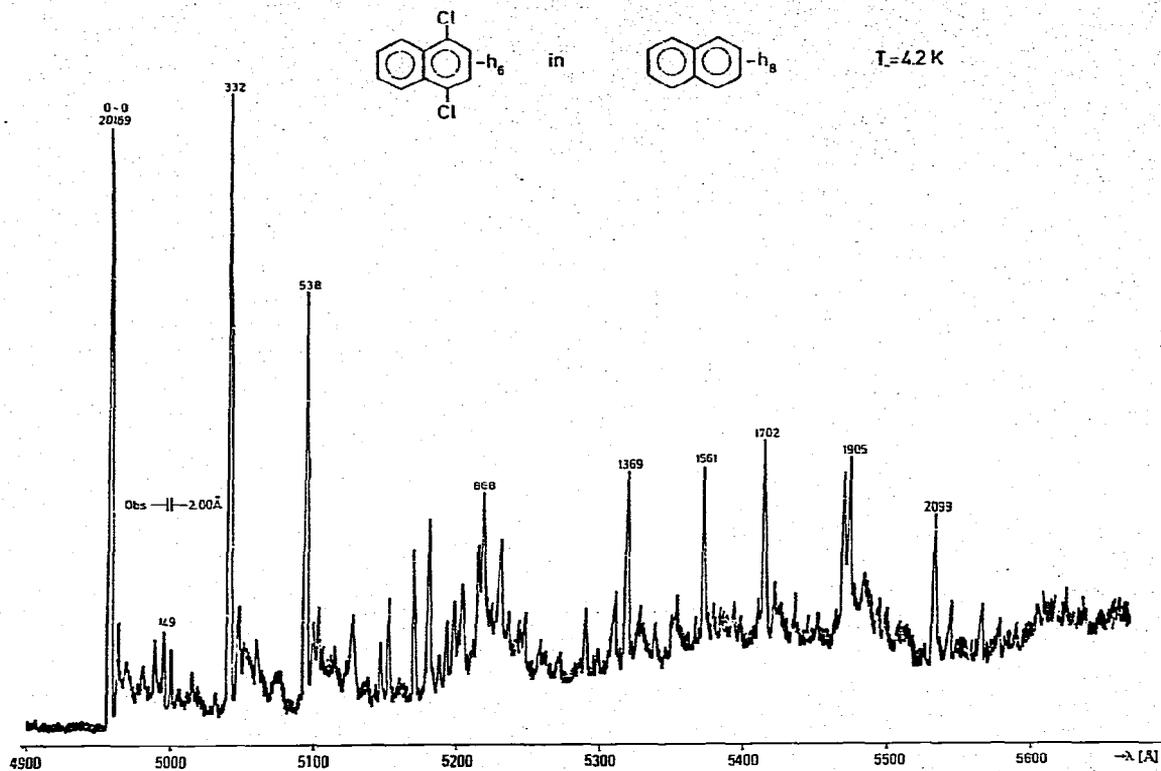
Fig. 1. Phosphorescence spectrum of 1,4-DClN in naphthalene at $T = 4.2$ K. Numbers are in wavenumbers relative to 0,0.

molecules. The same holds for the E values (except for 2,6-DClN, where it deviates up to 100 MHz from the others). The chlorine atoms seem to be weak perturbers with respect to the stationary properties of the triplet wavefunction. Thus we infer that:

(1) all the molecules investigated have the same type of orbital wavefunction, namely ^3L_a, as one gets it by symmetry reduction from the parent D_{2h} group, and

(2) there occurs no rotation of the spin axes by going from molecules with C_{2v}- to molecules with C_{2h}-symmetry.
This latter point is also strongly corroborated by the dynamical measurements. For instance, 2,3-DClN shows the same lifetime pattern as 2,6-DClN (table 1). The same is true for 1,4- and 1,5-DClN. On the other hand, the lifetime pattern of 1,4- and 2,3-DClN is different.

Most of the optical spectra exhibit more or less the same intensity distribution between zero-phonon lines and phonon wings. However, 1,4-DClN is an exception (fig. 1). There is a considerable amount of diffuse background. The FC envelope of the spectrum is also very much different. In fact, the phosphorescence intensity of this compound was too low to measure any zero field spectrum. It seems that 1,4-DClN does not fit as well as the others in the host lattice.

3.2 Dynamic features

The influence of a heavy atom substituent is most directly related to the change in the dynamics of T_0. Table 1 shows the results: The position-dependence of the heavy atom effect in the high-temperature rates amounts to less than 45%. This is somewhat
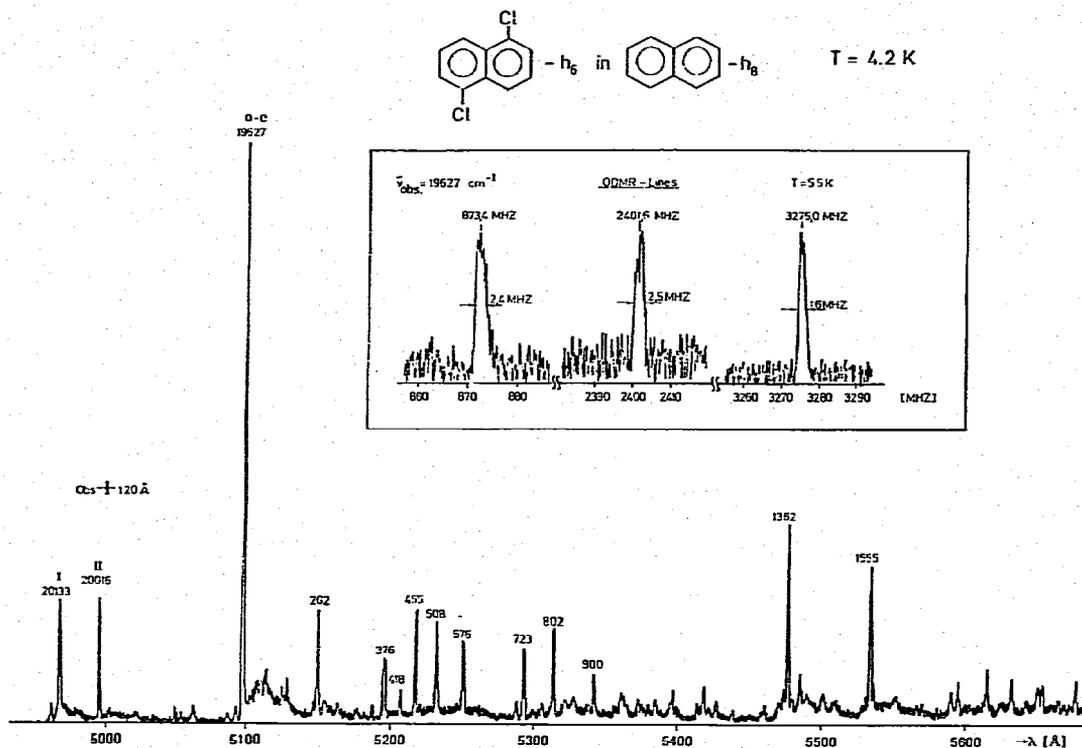
Fig. 2. Phosphorescence spectrum at $T = 4.2$ K and ODMR lines at $T = 5.5$ K of 1,5-DClN in naphthalene. Numbers are in wave-numbers relative to 0,0. I and II may be due to impurity-emission.

higher than in the monochloronaphthalenes (10% [3]). The results on the subrates, however, turn out to be very different: First, we see that for the β-substituted derivatives the fastest level is sandwiched, while for the α-substituted, the fastest level is on the top.

Second, the position-dependence is very selective concerning the sublevels. While there is nearly no influence on the K_x rate, we observe a change by a factor of 2 to 4 in the K_z rate. This statement also holds for the relative rates, which do not depend on the FC factor and energy gap: We have a very pronounced effect in the ratio K_z/K_x, while the influence on K_y/K_x is by far smaller. Again we want to stress that these results do not seem to be influenced by the molecular symmetry, because we have both symmetry groups (C_{2v} and C_{2h}) in the α- as well as in the β-derivatives. The radiative rates, on the other

hand, do not exhibit any pronounced specificity concerning the influence of the position on the individual sublevels. Therefore, we conclude that the position-dependence mainly enters into the nonradiative transitions.

3.3. Host—guest interaction

In a molecule with C_{2v}-symmetry radiation from the T_y level into the 00 transition is forbidden. Though we did our MIDP experiments on the 00 transition, we observed a rather high amount of radiation from this forbidden state (table 1). As a consequence, we conclude that the molecules must be distorted. This distortion could be intrinsic for 2,3-DClN because of the neighborhood of the chlorine atoms, but it is certainly not intrinsic for the 1,4-derivative. Therefore, this distortion must be due to
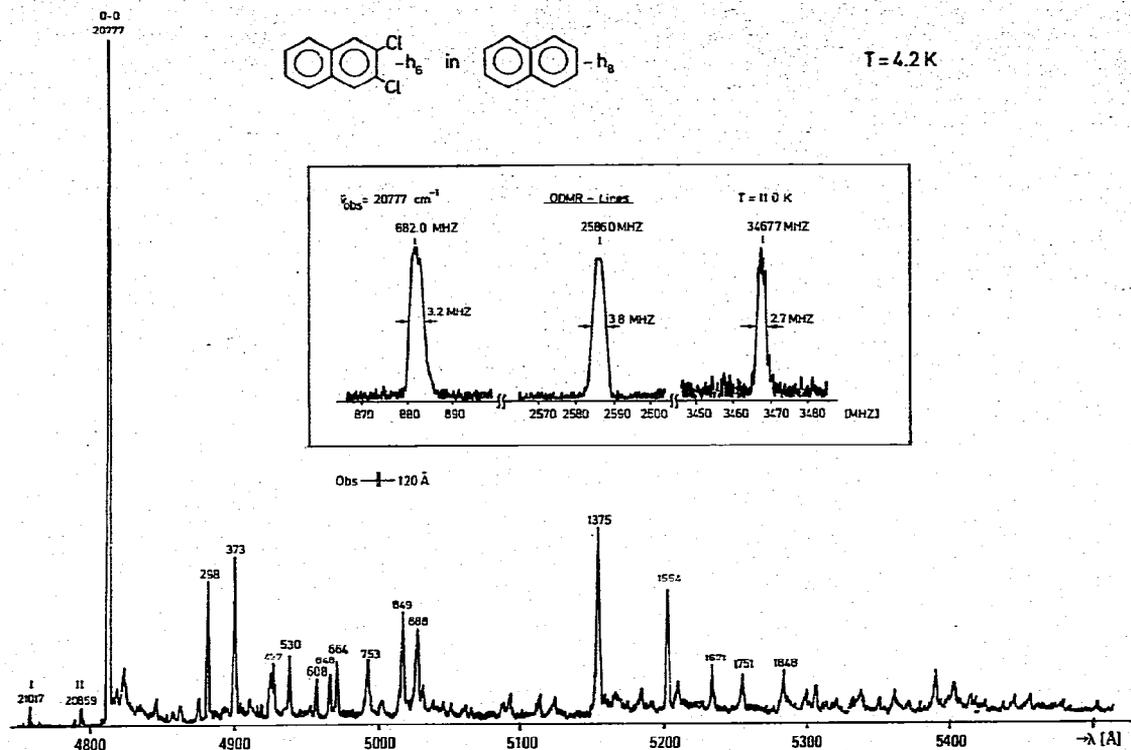
Fig. 3. Phosphorescence spectrum at $T = 4.2$ K and ODMR lines at $T = 11$ K of 2,3-DClN in napththalene. Numbers are in wavenumbers relative to 0,0. I and II may be due to impurity emission.

some host—guest interaction, which clearly influences not only the C_{2v}, but also the C_{2h} molecules.

To get a feeling of how large the guest—host interaction is and how strongly it may influence the molecular properties, we tried to investigate the series of guest molecules in a durene host, too. However, only the 1,5-DClN showed a reasonable phosphorescence intensity in durene. In all the other cases, naphthalene included, there appeared a strong impurity emission. Table 1 shows the results of the experiments on 1,5-DClN in durene. We see that the main features do not change: The zero-field parameters remain constant within 3%. The same holds for the energy of the 00 transition. The T_z level remains the fastest; the T_y level again is the medium one. On the other hand, however, the differences are clearly seen: The overall rate decreases by about 25%, K_y decreases by about 35%, and K_x increases by about 64%. The influence of the matrix turns out to be

specific for each substate. The most dramatic change, however, occurs in the relative radiative rates of the 00 transition: K_y^r decreases from 32% to 9%, while K_z^r increases from 67% to 87%. Since in the parent molecule K_y^r is zero by symmetry, it should also be low in 1,5-DClN, because the chlorine atoms act as weak perturbers. Therefore we draw the conclusion that in a naphthalene host the guest molecules are much more distorted than in durene. This distortion affects the rates, but does not seem to influence the spin axes, because the D and E values do not change.

These results are consistent with the crystal structure of durene, the unit cell of which is much more voluminous than that of naphthalene [9].

4. Discussion

In the case of a lowest triplet state of $\pi\pi^*$ type, it was shown [4] that an expansion up to second order
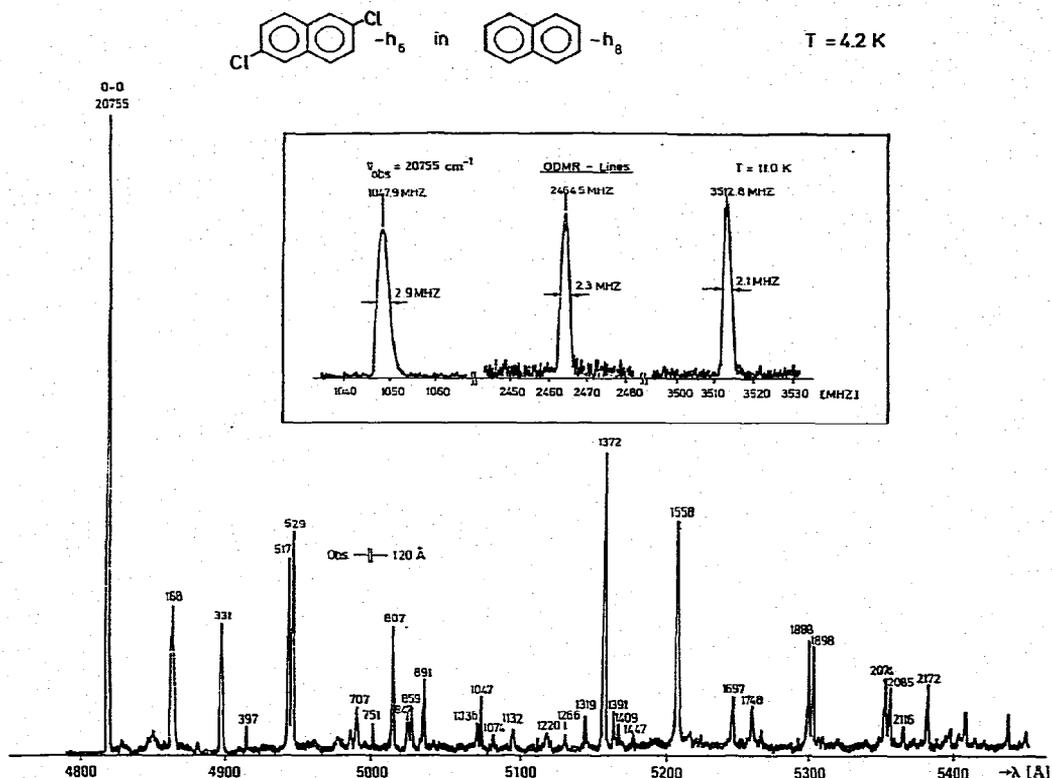
Fig. 4. Phosphorescence spectrum at $T = 4.2$ K and ODMR lines at $T = 11$ K of 2,6-DCIN in naphthalene. Numbers are in wave-numbers relative to 0,0.

in the normal coordinates is necessary to describe the influence of geometry on the matrix element of spin—orbit coupling (SOC):

$$\langle H_{SO}(\{Q\})\rangle$$

$$= \langle H_{SO}(0)\rangle + \sum_{p} \frac{\partial}{\partial Q_p} \langle H_{SO}(\{Q\})\rangle \Big|_{\{Q\}=0} Q_p$$

$$+ \frac{1}{2} \sum_{p,p'} \frac{\partial^2}{\partial Q_p \partial Q_{p'}} \langle H_{SO}(\{Q\})\rangle \Big|_{\{Q\}=0} Q_p Q_{p'} + \dots .$$

We may confine the index p to the out-of-plane modes, which were shown to provide the largest contributions. $\langle H_{SO}(0)\rangle$ represents the matrix element of SOC at the equilibrium position of the molecule. It is called *direct SOC*. In case of radiationless decay to the ground state, the direct term couples only the T_x-state to the singlet manifold. As is well-known,

the corresponding coupling matrix elements depend solely on the three center integrals. We had earlier shown that these do not depend on the nuclear charge [4]. Therefore, the position of the heavy atom substitution is not distinguished. Hence, we do not expect very much position-dependence in these coupling terms.

The second term, the first order Herzberg—Teller (HT) contribution, describes the SOC within a slightly distorted equilibrium geometry. In our case we have to distinguish between the dynamical contribution due to the molecular promoting modes and those contributions due to stationary distortion within the host lattice. These latter terms are important as is seen from the change in the forbidden character of the radiative transition from the T_y level in the C_{2v} molecules. The main difference between the

Table 1

Triplet-energies (00), zero field parameters (D) and (E), total rates K_i high temperature rates K_{HT}, and relative radiative rates K_i^r of 1,4-DClN, 1,5-DClN, 2,3-DClN, 2,6-DClN in *naphthalene*. Dynamic parameters are measured at $T = 1.2$ K. Also shown are the corresponding rates of 1,5-DClN in a durene matrix. Numbers in parentheses represent relative rate constant normalized to the decay of the out-of-plane spin state

0-0	[Å]	4958	5095	4812	4818	5031
	[cm⁻¹]	20169	19627	20781	20755	19877
zero field par.	|D|[MHZ]	2911	2838	3027	2989	2911
	|E|[MHZ]	428	437	441	524	428
total rates	K_z[sec⁻¹]	18.30 (33)	13.87 (36)	4.19 (8)	6.53 (14)	10.94 (17)
	K_y[sec⁻¹]	9.05 (16)	10.52 (27)	14.82 (29)	12.97 (27)	6.87 (11)
	K_x[sec⁻¹]	0.56 (1)	0.39 (1)	0.51 (1)	0.48 (1)	0.64 (1)
$K_{HT}=\Sigma K_i /3$ [sec⁻¹]		9.30	8.26	6.51	6.66	6.15
rel. radiative rates	K_z^R [%]	73 (20)	65 (24)	67 (19)	67 (18)	87 (22)
	K_y^R [%]	23 (6)	32 (12)	29 (8)	29 (6)	9 (2)
	K_x^R [%]	4 (1)	3 (1)	4 (1)	4 (1)	4 (1)

Matrix: (naphthalene)-h_8 Matrix: (durene structure)

static and dynamic first order interaction is the shift in equilibrium positions for out-of-plane vibrations. The first order term couples the T_y and the T_z level to the singlet intermediates.

The second order HT interaction was shown to have the same symmetry properties as the direct term, i.e., it couples the T_x level to the singlet manifold [4]. However, the one-center terms do appear in this second order term. Therefore, it is considered to be more important than the direct term. Concerning the position-dependence of the HT terms, we have to consider two different factors, namely the elements of the reciprocal overlap matrix [4] and the MO coefficients. Since we assume the strongest vibra-

tional interaction with the protons in the immediate neighborhood of the heavy atom, we consider only the overlap to these protons. In the case of the second order coupling, the various spin—orbit terms for α- and β-substitution do not differ very much from each other. Besides, in the case of chlorine substitution, the position-independent three-center terms are of the same order of magnitude. Therefore, we expect the decay from the T_x level to be nearly independent of the position of substitution. This is clearly demonstrated by our experimental results (table 1). To rule out the possibility of mutual compensation of the FC factor and the electronic matrix element, we want to stress that the matrix elements

in the β-sbustituted compounds are in no way larger than in the α-substituted compounds due to the somewhat reduced overlap integrals to the neighboring protons. Thus, if there were a compensation, we would have to conclude that the FC factor in the β-substituted compounds should be larger. This, however, is opposed to the energy gap law [10]. Thus, we infer that the matrix element for the direct process as well as the FC factor are roughly the same for both types of molecules. This view is also corroborated by our experiments on the deuterated compounds [11].

We are left with the first order HT coupling to interpret the position-dependence in the T_y and T_z level. The most striking influence of position-dependence occurs in the T_z decay. The rate is lower by a factor of 2 to 4 for the β-derivatives. To explain this sublevel specific influence of the position of substitution, we note that our results demonstrate that the halogen lone pair orbital $|1_y\rangle = 2^{-1/2}(|S\rangle - |P_y\rangle)$ dominates the spin–orbit coupling in 1,4- and 1,5-DClN. Assuming that this orbital does not lose very much from its efficiency in the β-substituted compounds (in this case $|1_y\rangle \Rightarrow |1_{yz}\rangle = 2^{-1/2}(|S\rangle - \cos\frac{1}{3}\pi|P_y\rangle - \sin\frac{1}{3}\pi|P_z\rangle)$) its contribution to the matrix element in the T_z rate is reduced by a factor of $\cos\frac{1}{3}\pi$, while to the matrix elements of the T_y rate, it adds a contribution proportional to $\sin\frac{1}{3}\pi$. Thus, the dependence of the radiationless rate of the in-plane spin states on the position of a heavy atom is strongly determined by the projection of the most effective orbital on the spin axes. It is somewhat surprising that the 1_y orbital shows such an activity in spin–orbit coupling. In the free molecule one would expect the T_y level to be the fastest, due to the fact that the lone pair orbital $|p_z\rangle$ overlaps with the adjacent protons (especially with H_8) much more than the $|1_y\rangle$ orbital. However, as discussed above, the data show that the dichloronaphthalenes experience a large distortion in the naphthalene host. If this distortion is an out-of-plane distortion of the centers around the heavy atom, the situation may change. The overlap of the $|1_y\rangle$ orbital with the neighboring protons increases. Depending on the amount of distortion, the spin–orbit coupling via $H_{SO}^{\bar{z}}$ may even become dominant as in 1,4-DClN and (to a lesser extent) in 1,5-DClN.

In the case of radiative transitions, the situation is different. Radiation from the T_z level is allowed via first order spin–orbit coupling (direct coupling

between $^3\pi\pi^*$- and $^1\sigma\pi^*$-states). We argue that the absence of any selective influence of the position of substitution might be due to the fact that, in first order, the lone pair orbitals $|1_y\rangle$ and $|1_z\rangle$ are equally effective in spin–orbit coupling. Hence, no net gain or loss occurs in the radiative dynamics of T_y and T_z.

We want to stress, however, that our experiment measures only the relative radiative rates. The absolute rates may change considerably by changing the position of substitution.

5. Summary

Our microwave optical double resonance experiments on some dichloronaphthalenes in a naphthalene matrix have shown that, in the nonradiative rate, there indeed exists a selective position-dependence of the heavy atom effect. The influence of the position-dependence has proven to be much more pronounced in the T_x and T_y sublevels than in the overall decay rates, due to the Herzberg–Teller terms, the spin–orbit coupling of which is very specific for the individual substate. According to the theory, the out-of-plane spin state is not affected. Further, radiative and total rates show a different behavior. The simple picture that the feedback of SOC of a heavy atom center to the aromatic ligand depends solely on the MO coefficient may only hold in the case of radiative transitions from the T_y or the T_z level via direct spin–orbit interaction.

In general, one has to take into account at least two factors, namely the MO coefficient and the elements of the reciprocal overlap matrix between the heavy atom and the adjacent protons. The protons are the most active centers in vibronic spin–orbit coupling, due to their large vibronic amplitudes. In the systems investigated here, there are also large contributions from local distortions. Finally, one has to be sure that there is no mutual compensation between position-dependent spin–orbit matrix elements and FC factors.

References

[1] D.S. McClure, J. Chem. Phys. 17 (1949) 905.
[2] S.P. McGlynn, T. Azumi and M. Kinoshita, Molecular spectroscopy of the triplet state (Prentice-Hall, New York, 1969).
[3] J.C. Miller, Thesis, University of Colorado (1975).
[4] J. Friedrich, F. Metz and F. Dörr, Mol. Phys. 30 (1975) 289.
[5] J. Schmidt, Thesis, University of Leiden (1971).
[6] T. Pavlopoulos and M.A. El-Sayed, J. Chem. Phys. 41 (1964) 1082;
N.K. Chaudhuri and M.A. El-Sayed, J. Chem. Phys. 47 (1967) 2566.
[7] J. Friedrich, J. Vogel, W. Windhager and F. Dörr, Z. Naturforsch. 31 (1976) 61.
[8] H. Auweter, D. Schmid and H.C. Wolf, Chem. Phys. 5 (1974) 382.
[9] J.M. Robertson, Proc. Roy. Soc. A141 (1933) 594.
[10] E.W. Schlag, S. Schneider and S.F. Fischer, Ann. Rev. Phys. Chem. 22 (1977) 465.
[11] G. Flatscher and J. Friedrich, in preparation.