SELECTIVE EXTERNAL HEAVY ATOM EFFECT ON THE DYNAMICS OF THE ISOLATED TRIPLET SUBLEVELS OF NAPHTHALENE X-TRAPS

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We investigated the external heavy atom effect on the dynamics of the isolated sublevels of naphthalene X-traps. The rate constants of the T^x (out of plane) and the T^y (short axis) states are selectively influenced. The heavy atom nearly exclusively affects the radiative decay. Certain symmetry restrictions may affect the external spin–orbit coupling.

1. Introduction

Since the discovery of external spin–orbit coupling by Kasha [1], this field has lost nothing of its attraction to spectroscopists and photochemists. The main effort of numerous investigations was concentrated on the problem of how the spin of the probe molecule is coupled to the external heavy atom [2–7]. It seems well established that the heavy atom effect is exclusively governed by one-center spin–orbit integrals, regardless of whether the coupling is internal or external, since the many-center type contributions are small and do not show any dependence on the nuclear charge [8]. The main difference between the internal and external heavy atom effect is the loss of symmetry which is inherent to the problem if the heavy atom is covalently bound to the aromatic probe molecule. Indeed, we showed, using photoselection techniques, that in an organic glass, there is no selective influence of the external heavy atom effect on the individual triplet sublevels [9]. However, several groups reported a selective influence of an external heavy atom on the dynamics of the lowest triplet state [10–13]. Both crystal and glass matrices were used as host materials. There are certain symmetry restrictions concerning the influence of the external heavy atom on the dynamics of the probe molecule, forced onto the system by a definite relative geometry.

In this paper we present an investigation of the dynamics of the individual sublevels of the lowest triplet state T_0 of naphthalene X-traps which were isolated at 1.2 K. The various X-traps were created by doping a naphthalene crystal with a small fraction (10^{-3} mol/mol) of β-halonaphthalenes (F, Cl, Br) [14]. We confirm for this series of X-traps a strong selective influence of the external heavy atom effect on the T^x (out of plane) and the T^y (short axis) substate. We also show that interaction with the nearby external heavy atom leads to a destruction of optical selection rules which prevail in the unperturbed molecule. We discuss our results in terms of symmetry constraints on the intermolecular overlap integrals and show that there exist certain positions at which the external heavy atom effect selectively prevails in one (or two) of the three substates.

2. Experimental

Naphthalene was recrystallized from EtOH and zone refined. The halonaphthalenes were purified by recrystallization from EtOH. Crystals were grown by the Bridgman technique.

The samples, immersed in superfluid He, were excited by a Xe high-pressure lamp (450 W) followed by several filters. The optical spectra have been published [15]. The ODMR signals (optically detected magnetic resonance) were sampled at the 0–0 transition with a bandwidth of ≈150 cm^{-1}. MIDP (microwave-induced delayed phosphorescence [16]) as well as fast-passage

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techniques [17] were used to determine the rate constants. In the case of the I X-trap, the dynamic processes were too fast to be detected accurately.

The microwave absorption was measured by slowly sweeping through the resonances and averaging the observed change in the optical signal on a Nicolet 1072 data processing system.

The apparatus is described in more detail in ref. [18].

3. Results and discussion

The results are displayed in fig. 1 and table 1. Fig. 1 shows that the originally least-active zero-field level T^x experiences a very strong influence from the nearby heavy atom. In the case of the Br X-trap it is almost as active as the T^y level. The external heavy atom effect on the originally most-active level T^z is much less.

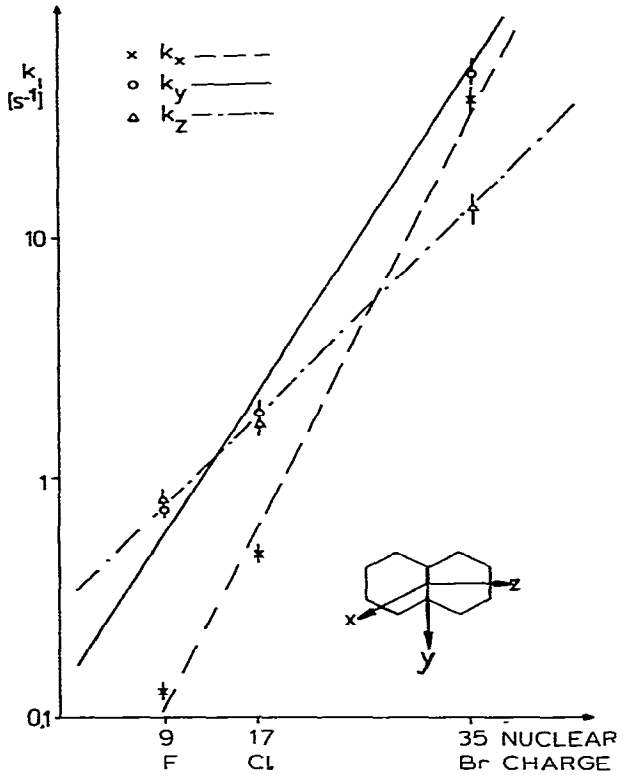


Fig. 1. Semilogarithmic representation of the total decay rates of naphthalene X-traps as a function of the nuclear charge of the external heavy atom.

Table 1 shows another interesting result: In the unperturbed molecule, radiation from the T^y level into the vibrationless level of the ground state is forbidden by symmetry. This selection rule is still reflected in the relative radiative constants of the F X-trap. With increasing nuclear charge in the external halogen the radiative rate constant of this forbidden state increases very fast. In the Br X-trap it is the most active one.

The dynamics of the lowest triplet state is governed by the matrix elements of the spin–orbit operator H_{so}, which are different for the radiative and the radiationless decay. For the radiative decay the matrix element is given by

$$M^{\tau,\alpha}_{S_0T_0} \approx \sum_j \left[\frac{\langle S_0|H_{so}|T_j^\tau\rangle\langle T_j^\tau|r_\alpha|T_0^\tau\rangle}{E_{S_0} - E_j} + \frac{\langle S_0|r_\alpha|S_j\rangle\langle S_j|H_{so}|T_0^\tau\rangle}{E_{T_0} - E_j} \right], \quad (1)$$

whereas for the radiationless decay

$$V^\tau_{S_0T_0} \approx \langle S_0|H_{so}|T_0^\tau\rangle . \quad (2)$$

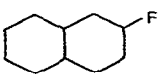
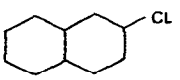
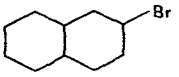
Here we do not consider any influence of intramolecular vibrations on these matrix elements, because the interaction with an external heavy atom reduces the symmetry restrictions of spin–orbit coupling in the unperturbed molecule. Moreover, it was often stated in the literature (e.g. refs. [3,6]) that the external heavy atom effect is purely electronic in nature ‡. A further consequence of this reduction in symmetry is that we can confine our considerations of external spin–orbit coupling to the interaction of the heavy atom with the π electrons of the probe molecule. They show spin–orbit coupling via one-center interaction at the heavy atom. Moreover, the overlap integrals (see below) with the π electrons are considered to be much larger than the corresponding ones with the σ electrons. Then, reducing the spin–orbit part of the transition matrix elements in the usual way to integrals over MOs, we see that the radiative decay is governed by integrals of the type

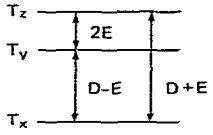
$$\langle \pi_S|H_{so}|\pi_{T_0}\rangle ,$$

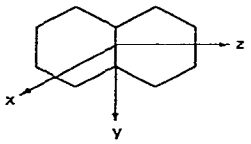
where π_{T_0} refers to the MOs of the lowest triplet state T_0, and π_S to those of the singlet intermediates.

‡ We showed that there is a very strong phononon influence on the external heavy atom effect [15].

Table 1
Triplet energies, zero-field parameters, total decay rates and relative radiative rates of naphthalene X-traps

	Guest		
			
$\lambda_{0,0}^{(X)}$ (nm)	472.8	475.9	477 6
D (MHz)	2977.8	2961.6	2950 8
E (MHz)	459.8	454.8	451.8
k_z (s^{-1})	0.82	1.74	13.44
k_y (s^{-1})	0.74	1.91	49.35
k_x (s^{-1})	0.13	0.48	36.86
$k = \frac{1}{3}\Sigma k_i$ (s^{-1})	0 56	1 38	33.22
k_z^r (rel.)	50	0.9	0.2
k_y^r (rel.)	0.7	<0.9	1 4
k_x^r (rel.)	1	1	1





The radiationless decay to the ground state is governed by an integral of the type

$\langle \pi_{T_0} | H_{so} | \pi'_{T_0} \rangle$.

Projecting the MOs onto an atomic basis set [9] which includes the orbitals of the external heavy atom, we get (for the decay of the T^x state)

$$\langle \pi_S | H_{so}^x | \pi'_{T_0} \rangle \approx \langle u_{p_z} | H_{so}^x(R_h) | u_{p_y} \rangle \times (S_{u^{T_0},p_z}^{-1} S_{u^{T_0},p_y}^{-1} - S_{u^{T_0},p_y}^{-1} S_{u^{T_0},p_z}^{-1}) , \quad (3)$$

$$\langle \pi_{T_0} | H_{so}^x | \pi'_{T_0} \rangle \approx \langle u_{p_z} | H_{so}^x(R_h) | u_{p_y} \rangle \times (S_{u^{T_0},p_z}^{-1} S_{u'^{T_0},p_y}^{-1} - S_{u^{T_0},p_y}^{-1} S_{u'^{T_0},p_z}^{-1}) . \quad (4)$$

$\langle u_{p_z} | H_{so}^x(R_h) | u_{p_y} \rangle$ is the one-center spin–orbit integral at the heavy atom (which is located at R_h), $S_{u^{T_0},p_z}^{-1}$ the reciprocal overlap integral between one of the atomic orbitals u^{T_0}, which describe the MO π_{T_0}, and the p_z orbital of the heavy atom. A cyclic permutation of x, y and z yields the contributions to the T^y and T^z substates.

The one-center spin–orbit integral is a constant for each sublevel. Hence any symmetry restriction to the above matrix elements must occur in the overlap integrals. Of course we do not know the exact mutual orientation of the perturber and the probe molecule, but we show that there exist certain configurations for which the external heavy atom couples selectively to one or two of the three spin states.

In the axis system chosen here (fig. 1) the orbital part of T_0 transforms like B_{2u}. The corresponding π orbitals are of a_u and b_{2g} symmetry. Both orbitals are depicted in fig. 2. Also shown is the heavy atom in a position with high symmetry. In this position there is no contribution at all to the non-radiative decay becasue the overlap factor in eq. (4) is totally cancelled. The same argument holds if we shift the heavy atom along the short axis. However, moving the heavy atom along the long axis, we get contributions via the x and z components of H_{so}. The decay from the T^y level is still forbidden.

As to the radiative transitions, the situation is somewhat different. We firstly consider the mixing of

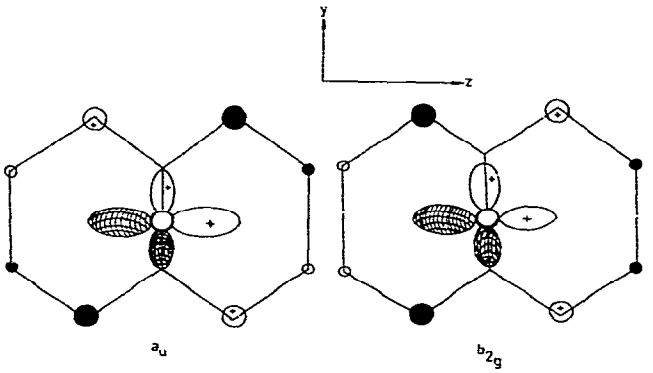


Fig. 2. Schematic representation of the π orbitals of the lowest triplet state of naphthalene together with the p orbitals of the external heavy atom in a highly symmetric position.

the lowest triplet state with singlet intermediates [second term of eq. (1)]. Only states of L_b type contribute, since L_a is of the same symmetry as T_0 and hence the spin–orbit matrix element vanishes. For all the other $\pi\pi$ intermediates the dipole matrix element vanishes.

At the central position (fig. 2) there is only a contribution from the x component of H_{so}. Radiation from the T^y and the T^z spin substate is zero because the S factor in eq. (3) vanishes. Moving the heavy atom along the short axis, we get radiation from T^x as well as T^y. Radiation from T^z is still forbidden. If the heavy atom is in the xz plane, radiation is allowed from the T^x and the T^z substates, but forbidden from T^y.

These considerations show that the radiative process from the out-of-plane spin state is affected by the external heavy atom regardless of the mutual orientation, but radiation from the in-plane states is subject to the relative geometry. This explains the strong influence of external spin–orbit coupling on the out-of-plane spin state which is, as a rule, observed in crystal systems.

Our data further show that radiation from the T^y state is dramatically enhanced, though forbidden in the unperturbed molecule and still very small in the F X-trap. On the other hand, radiation from the T^z level is much less affected. This situation is met by a configuration with the heavy atom close to the xy plane. Such a configuration only allows a small rate constant for the radiationless transition, because, as stated above, the corresponding matrix element is zero. This is strongly supported by our results (table 1), because the ratio of the total rates is very close to the ratio of the radiative rates. Hence we conclude (in agreement with other groups) that the influence of the external heavy atom is mainly on the radiative processes.

Having narrowed down the problem to symmetry restrictions in the radiative processes, we may ask why the radiation from T^y is more intense than from T^x. We keep in mind that the non-bonding p electrons of the heavy center allow for two types of overlap integrals with the π electrons of the aromatic probe molecule: The overlap integrals $S^{-1}_{u\pi,p_x}$ with the p_x electron of the heavy atom are considered to be larger than the overlap with the p_y and p_z electrons ($S^{-1}_{u\pi,p_y}$ and $S^{-1}_{u\pi,p_z}$) because the overlapping electrons are directed along the same axis (x). Now the T^y level decays via spin–orbit interaction of H^y_{so}, which involves the p_x orbital in two of the four overlap integrals of eq. (3). On the other hand, spin–orbit interaction via H^x_{so}, which leads to the decay of the out-of-plane spin state T^x, allows only for the other (smaller) type of overlap factors. This might explain the stronger radiation from T^y as compared to T^x.

Finally, we comment on the different slope of the T^y and T^x decay in fig. 1. This is probably brought about by the fact that the intramolecular contributions to the matrix elements play an important role for the decay from the T^y state of the F and Cl X-trap. In the case of the originally very weak decay from the T^x state, the intramolecular contributions are negligible compared to the contributions of the heavy atom, even for the F and Cl X-trap. That is, T^x decay is totally dominated by the external heavy atom for the whole series, while for T^y decay this is true only for the Br X-trap.

4. Summary and conclusions

We investigated the influence of an external heavy atom on the individual sublevels of T_0 of naphthalene X-traps. The experiment shows that the influence is selective. We interpreted the results in terms of symmetry restrictions which enter the spin–orbit matrix elements via overlap integrals between the π electrons of the probe molecule and the orbitals of the heavy atom. Within this model, it is clear that the selectivity in the T^x and T^y state, as measured by our experiment, is no general feature, but depends on the mutual sym-

metry of the perturber and probe molecules. In a glass matrix, these symmetry restrictions average out, so that there is no selectivity except when the probe and the perturber form a charge-transfer complex with definite mutual orientation, as observed by Anderson and Maki [13].

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