

WHAT IS THE LEADING MECHANISM FOR THE NONRADIATIVE DECAY OF THE LOWEST TRIPLET STATE OF AROMATIC HYDROCARBONS?

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Received 27 June 1972

It is shown that in aromatic hydrocarbons the ISC rate constants ($T_1^\alpha \rightarrow S_0$) are governed by HT vibronic coupling. Some established rules for deciding between different coupling mechanisms are proved to be invalid. Application to naphthalene yields excellent agreement with experimental results.

1. Introduction

The detailed understanding of the processes which lead to the deactivation of the lowest triplet state of an excited molecule has rapidly progressed during the last few years. For a review see [1]. Different mechanisms for this deactivation have been discussed in the literature. In this paper we will show that the most important of these mechanisms are not those which, at present, are widely accepted as the leading ones.

2. Theory

The rate constant for the nonradiative transition $T_1^\alpha \rightarrow S_0$ is given by

$$k^\alpha = (2\pi/\hbar) |\langle T_1^\alpha | R | S_0 \rangle|^2 \text{FC} , \quad (1)$$

where R is the level shift operator [2], FC the Franck-Condon factor, and α denotes the different sublevels of T_1 .

If S_0 and T_1 are chosen to be adiabatic pure spin states [$T_1 = T_1(r, Q)$, $S_0 = S_0(r, Q)$] the following perturbation has to be considered for the evaluation of R :

$$H' = H_{SO}(r, Q) + H_{NBO} ; \quad (2)$$

$$H_{SO} = \sum_i L_i \cdot S_i ,$$

$$L_i = \frac{1}{2} \alpha^2 \sum_\mu (r_i - r_\mu) \times p_i / |r_i - r_\mu|^3 ,$$

$$H_{NBO} = H_0 - H_{BO} .$$

Expansion to the second order of H' yields

$$\begin{aligned} \langle T_1^\alpha | R | S_0 \rangle &\approx \langle T_1^\alpha | (r, Q) | H_{SO}(r, Q) | S_0(r, Q) \rangle \\ &+ \sum_j \langle T_1^\alpha | H_{NBO} | T_j^\alpha \rangle \langle T_j^\alpha | H_{SO} | S_0 \rangle (E_{T_j} - E_{T_1})^{-1} \\ &+ \sum_j \langle T_1^\alpha | H_{SO} | S_j \rangle \langle S_j | H_{NBO} | S_0 \rangle (E_{S_j} - E_{S_0})^{-1} \\ &= R_{10}^\alpha + R_{10}'^\alpha . \end{aligned} \quad (3)$$

With (3), the total rate constant k^α can be written as:

$$k^\alpha = k_1^\alpha + k_2^\alpha + k_3^\alpha + \dots + k_3'^\alpha + \dots , \quad (4)$$

where

$$k_1^\alpha = (2\pi/\hbar) |\langle T_1^\alpha | H_{SO} | S_0 \rangle|^2 \text{FC} , \quad (4a)$$

$$k_2^\alpha = (2\pi/\hbar) \sum_p |\partial \langle T_1^\alpha | H_{SO} | S_0 \rangle / \partial Q_p|^2 FC \frac{\hbar}{2\mu_p \omega_p}, \quad (4b)$$

$$k_3^\alpha = \frac{2\pi}{\hbar} \sum_{p,p'} \left| \frac{1}{2} \frac{\partial^2 \langle T_1^\alpha | H_{SO} | S_0 \rangle}{\partial Q_p \partial Q_{p'}} \right|^2 FC \frac{\hbar}{2\mu_p \omega_p} \frac{\hbar}{2\mu_{p'} \omega_{p'}}, \quad (4c)$$

$$k'_3^\alpha = \frac{2\pi}{\hbar} \sum_p \left| \sum_j \left[\frac{\langle T_1^\alpha | H_{SO} | S_j \rangle \langle S_j | \partial / \partial Q_p | S_0 \rangle}{E_{S_j} - E_{S_0}} + \frac{\langle T_1^\alpha | \partial / \partial Q_p | T_j \rangle \langle T_j | H_{SO} | S_0 \rangle}{E_{T_j} - E_{T_1}} \right] \right|^2 FC \frac{\hbar^3 \omega_p}{2\mu_p}. \quad (4d)$$

k_1, k_2 and k_3 originate from R_{10} , whereas k'_3 originates from R'_{10} .

Due to the different matrix elements which appear in the expressions for these k 's, it is common to speak of different mechanisms responsible for triplet deactivation. The main question is, however, which is the most important one?

Let us first consider mechanism (4a). Due to symmetry, neither k_1^x nor k_1^y can contribute to k of planar hydrocarbons if the triplet T_1 is of $\pi\pi^*$ -type. This symmetry argument does not hold for the rate constant k_1^z , and it is often claimed [1, 3] that k_1^z is dominant if the transition $T_1^z \rightarrow S_0$ is orbitally allowed. At this point, however, we have to remember the fact that by symmetry arguments we can only state that a term is zero or not. To estimate the magnitude of k_1^z we must take into account that matrix elements of the spin-orbit operator are mainly governed by one-center integrals (OCSOI). As we will show in a further publication [4], multi-center integrals of spin-orbit coupling do not exceed 1% of the OCSOI. Thus rate constants that are derived from matrix elements containing no OCSOI's are burdened with a factor 10^{-4} . We therefore conclude that k_1^z cannot contribute essentially to the total rate constant in planar aromatic hydrocarbons, because no OCSOI's appear in the corresponding matrix elements as was shown by McClure [5].

The same argument holds for the constant k_2^z , where the promoting mode (pm) has to be an in-plane vibration (ipv), that does not cause any OCSOI's to appear in the electronic matrix elements. Therefore the contribution from k_2^z should be even less important than the contribution from k_1^z . Consequently, we do not believe k_2^z to be the dominant term in (4) as it is assumed by other authors [6, 7].

If we now consider k_2^x and k_2^y we first have to refer to the work of Siebrand and coworkers. In a well-known series of papers these authors came to the following conclusion: k_2^x and k_2^y are negligible; the leading terms in (4) are k'_3^x and k'_3^y . This statement is based on a selection rule [8] which causes no contribution from OCSOI's to all the k 's, which originate from R_{10} . As far as this selection rule is based on symmetry arguments, it is only valid for k_2^z . Later on, however, Siebrand and Orlandi [9] claimed to have proved that all the OCSOI's which do in fact appear cancel each other in the case of k_2^x and k_2^y .

To check this proof we have to take into account the influence of the nuclear motion on the total electronic wavefunction: because of the out-of-plane vibrations, the molecular plane is only an approximate element of symmetry. This results in a perturbation of the $\sigma\pi^*$ -separation. Therefore small contributions of $\sigma\pi^*$ - and $\pi\sigma^*$ -states are added to the $\pi\pi^*$ -states. To include this effect we use the following expansion:

$$\begin{aligned} \partial R_{10}^\alpha / \partial Q_p = & \sum_j [- \langle T_1^\alpha | \partial / \partial Q_p | T_j^\alpha \rangle \langle T_j^\alpha | H_{SO} | S_0 \rangle \\ & + \langle T_1^\alpha | H_{SO} | S_j \rangle \langle S_j | \partial / \partial Q_p | S_0 \rangle] \\ & + \langle T_1^\alpha | \partial H_{SO} / \partial Q_p | S_0 \rangle. \end{aligned} \quad (5)$$

There is a contribution of OCSOI's, if the promoting mode is an out-of-plane vibration. In this case the intermediate states are of $\sigma\pi^*$ - and $\pi\sigma^*$ -type. It is also seen from (5) that the symmetry argument for the selection rule does not hold for $\alpha = x, y$ because the operators L_x and L_y are antisymmetric with respect to the molecular plane. Reduction of (5) into integrals over MO's yields

$$\begin{aligned} \partial R_{10}^x / \partial Q_p = & \sum_\sigma - [\langle \pi^* | \partial / \partial Q_p | \sigma \rangle \langle \sigma | L^x | \pi \rangle \\ & + \langle \pi^* | L^x | \sigma \rangle \langle \partial \sigma / \partial Q_p | \pi \rangle] + \langle \pi^* | \partial L^x / \partial Q_p | \pi \rangle. \end{aligned} \quad (6)$$

We consider the case $\alpha = x$ and $T_1 = T_1(\pi\pi^*)$. Neglecting all multi-center spin-orbit integrals further

reduction to AO's leads to

$$\begin{aligned} \partial R_{10}^x / \partial Q_p = & - \sum_{ij,k} (c_{\pi_j^*} c_{\pi_i} - c_{\pi_j} c_{\pi_i^*}) \langle 2p_{z_j} | \partial / \partial Q_p | \sigma_k \rangle \\ & \times S_{\sigma_k, 2p_{y_i}}^{-1} \langle 2p_{y_i} | L_i^x | 2p_{z_j} \rangle + \langle \pi^* | \partial L^x / \partial Q_p | \pi \rangle. \end{aligned} \quad (7)$$

A similar equation is obtained for $\alpha = y$.

Expression (7) corresponds to formula (17) of [9] where the identity

$$S_{\sigma_k, \sigma_j}^{-1} = \sum_{\sigma} c_{\sigma, \sigma_k}^* c_{\sigma, \sigma_j}$$

is used.

If all the contributions of OCSOI should cancel each other as claimed by Siebrand and Orlandi the following condition has to be fulfilled for all i and j :

$$[c_{\pi_j^*} c_{\pi_i} - c_{\pi_j} c_{\pi_i^*}] = 0. \quad (8)$$

Condition (8) holds for $i = j$ as shown in [9]. For alternant hydrocarbons it also holds if both, i and j , belong to the set of starred or unstarred atoms. But (8) is normally not valid if i and j are adjacent atoms. It can be seen from (7) that in such a case there are contributions for which one of the two terms

$$\langle 2p_{z_j} | \partial / \partial Q_p | \sigma_k \rangle \quad \text{and} \quad S_{\sigma_k, 2p_{y_i}}^{-1}$$

is a one-center and the other a two-center integral. If we further recall that two-center integrals of this type are not small but may reach 50% of the one-center contribution then there is no reason to neglect k_2^x and k_2^y .

Moreover if we take into account the factor

$$|\hbar\omega_p/(E_{S_j} - E_{S_0})|^2 \approx |\hbar\omega_p/(E_{T_j} - E_{T_1})|^2 \approx 10^{-4}$$

appearing in k'_3 we can estimate k_2^x and k_2^y to be 1000 times greater than k'_3^x and k'_3^y . Therefore we come to the result that k_2^x and k_2^y are the leading terms in (4) which means that the most important mechanism for the nonradiative deactivation of T_1 is Herzberg-Teller vibronic coupling.

There is an additional advantage, if we can use (7) for the calculation of decay rates. Due to the appear-

ance of S^{-1} , no assumption about hybridization is necessary. Such an assumption, though widely used [10-12], introduces an additional approximation into the evaluation of electronic matrix elements.

3. Application to naphthalene

In order to calculate k_2^x and k_2^y for naphthalene, we used the following data: Hückel orbitals for the π - and π^* -MO's; Slater orbitals ($\zeta_C = 1.625, \zeta_H = 1.0$) for the AO basis set; a value of 32 cm^{-1} for the OCSOI $\langle 2p_{y_i} | L_i^x | 2p_{z_j} \rangle$. The vibrational constants were taken from Luther and Drewitz [13]. The full details of the calculation will be given in a further publication together with results for some other aromatic hydrocarbons. Here we only want to show the main results. These are as follows.

3.1. The transitions $T_1^x \rightarrow S_0$ and $T_1^y \rightarrow S_0$

(i) The CH-vibration γ_3 ($b_{1u}, \omega = 955 \text{ cm}^{-1}$) contributes 90% to the rate constant $k_2^x = 0.200 \text{ FC} [\text{cm}^{-2}]$.

(ii) The calculation of k_2^y shows that the spin vibronic term $\langle \pi^* | \partial H_{SO} / \partial Q_p | \pi \rangle$ cannot be neglected. It provides a remarkable contribution of about 40%. The calculated value of the rate constant is $k_2^y = 0.081 \text{ FC} [\text{cm}^{-2}]$. The transition $T_1^y \rightarrow S_0$ gets 80% of its intensity from the skeleton vibration $\Gamma_2(a_u, \omega = 285 \text{ cm}^{-1})$ and 20% from the CH-vibration $\gamma_1(a_u, \omega = 965 \text{ cm}^{-1})$. If the spin-vibronic term is neglected, the contribution to the rate constant which originates from Γ_2 is lowered by a factor 1/2.

(iii) The total rate constant $k_2^x + k_2^y = 0.28 \text{ FC} [\text{cm}^{-2}]$ is about 3 orders of magnitude greater, than that obtained by Siebrand ($k'_3^x + k'_3^y = 6 \times 10^{-4} \text{ FC} [\text{cm}^{-2}]$ [10]). One may, however, argue that — due to the uncertainty of the Franck-Condon factor — the total rate constant is of little use for a comparison with experimental data. We therefore look at the ratio k_2^x/k_2^y . Since the three sublevels of T_1 are nearly degenerated, the ratio of two rate constants should only depend on the electronic matrix elements. For the ratio k_2^x/k_2^y we obtained a value of 2.5, which is in much better agreement with the experimental result of Sixl and Schwoerer [17] ($k^x/k^y \approx 2$) than the value obtained by Siebrand ($k'_3^x/k'_3^y = 4$) [10].

(iv) Because of the different promoting modes, one

gets a considerably stronger deuterium effect on the electronic matrix element of the transition $T_1^x \rightarrow S_0$, than on $T_1^y \rightarrow S_0$, where the deuterium substitution should be effective only via the FC-factor.

(v) k_2^x and k_2^y show a position dependent deuterium effect originating from the electronic matrix element. This is in contradiction to Siebrand and Orlandi. According to these authors one should not be able to explain the local deuterium effect measured by [14], if the rate constant is governed by R_{10} . The values of k_2^x and k_2^y were calculated for different partially deuterated naphthalenes and are given in table 1.

Table 1

	Obs. a)	Calc. b)	Calc. c)
$k(1)/k(2)$ d)	0.94	0.94	0.88
$k(1,4)/k(2,3)$	0.84	0.89	0.76
$k(1,4)/k(1,5)$	0.99	1.00	1.00
$k(1,5)/k(1,8)$	1.00	1.00	1.00
$k(2,3)/k(2,7)$	1.00	1.00	1.00
$k(1,4,5,8)/k(2,3,6,7)$	0.87	0.85	0.56
$k(1,3-8)/k(2-8)$	0.79	0.96	0.85

a) Experimental results taken from [14, 15] and corrected for radiative decay.

b) Calculated values taken from this work.

c) Calculated values taken from the work of Henry and Siebrand [3].

d) The numbers in parentheses indicate the centers of deuteration according to [3].

We, like Siebrand et al., are unable to explain the last value in terms of only the electronic matrix element. But for the remaining values of the rate constants, we obtain considerably better agreement with experiment than Siebrand.

3.2. The transition $T_1^z \rightarrow S_0$

In naphthalene this transition is orbitally forbidden. Therefore $k_1^z = 0$. k_2^z can only contribute via an ipv, which does not cause any one- or two-center integrals in spin-orbit coupling. Our calculation shows that the values of the three-center integrals given by Hameka [16] are much too high. So we conclude that the transition $T_1^z \rightarrow S_0$ is governed by k_3^z .

If we expand the corresponding matrix element

$$\sum_{p,p'} \frac{1}{2} \partial^2 \langle T_1^z | H_{SO} | S_0 \rangle / \partial Q_p \partial Q_{p'} \quad (9)$$

in a similar way as we did in (5), the only term which contains OCSOI is given by

$$-\frac{1}{2} \sum_{p,p'} \sum_{j,k} \langle T_1^z | \partial / \partial Q_p | T_j^z \rangle \langle T_j^z | H_{SO} | S_k \rangle \langle S_k | \partial / \partial Q_{p'} | S_0 \rangle, \quad (10)$$

where both Q_p and $Q_{p'}$ are opv.
Reduction to AO's yields

$$\sum_{i,j,k,k'} \sum_{p>p'} (c_{\pi_j}^* c_{\pi_i} - c_{\pi_j} c_{\pi_i}^*)$$

$$\begin{aligned} & \times \langle 2p_{z_j} | \partial / \partial Q_p | \sigma_k \rangle \langle \partial \sigma_{k'} / \partial Q_{p'} | 2p_{z_i} \rangle \\ & \times [S_{\sigma_k, 2p_{y_i}}^{-1} \langle 2p_{y_i} | L^z | 2p_{x_i} \rangle S_{2p_{x_i}, \sigma_{k'}}^{-1} \\ & + S_{\sigma_k, 2p_{x_i}}^{-1} \langle 2p_{x_i} | L^z | 2p_{y_i} \rangle S_{2p_{y_i}, \sigma_{k'}}^{-1}] . \end{aligned} \quad (11)$$

If we evaluate this contribution for naphthalene we obtain the following results.

(i) The main contribution (90%) to $k_3^z = 0.013$ FC [cm^{-2}] arises from combinations of CH-bending out-of-plane vibrations with skeleton opv's. The remaining 10% are caused by combinations of skeleton opv's. Combinations of CH out-of-plane vibrations yield nearly no contribution.

(ii) With $k^z \approx k_3^z$ we obtain the following result for the total rate constant:

$$k \approx k_2^x + k_2^y + k_3^z \approx 0.30 \text{ FC} [\text{cm}^{-2}] .$$

The different ratios

$$(k^x/k, k^y/k, k^z/k) = (0.69, 0.27, 0.05)$$

agree rather well with the experimental results of Sixl [17] ($0.59 \pm 0.08, 0.33 \pm 0.08, 0.08 \pm 0.04$). If we compare the calculated value for the total rate constant with the measured lifetime $\tau_{\text{exp}} = 2.6$ sec we obtain a Franck-Condon factor $FC = 6$. This estimation neglects, however, the contribution of the radiative decay.

(iii) According to the considered mechanism

$k^z = k_3^z$ there should be a remarkable deuterium effect on k^z . This result is contrary to the assumption, usually made in the literature, where k^z is believed to be governed by k_1^z or k_2^z (in combination with skeleton ipv) and therefore should show no deuterium effect.

4. Conclusions

For naphthalene we have shown, that much better agreement with experiment is obtained for the transition $T_1^\alpha \rightarrow S_0$, if the rate constants k_2^x , k_2^y and k_3^z are considered instead of the rate constants k'_3^x , k'_3^y and k_2^z . The leading position of k_2^α is not, however, restricted to a special molecule. From these results for naphthalene and some other compounds, we expect the following orders of magnitude for all aromatic hydrocarbons:

$$k_2^x + k_2^y \approx (10-30) k_3^z \approx (50-500) k_1^z \text{ (if not forbidden),}$$

$$k_2^x + k_2^y \approx 10^3 (k'_3^x + k'_3^y).$$

In linear polyacenes the following relation should hold:

$$k_2^x \approx (2-5) k_2^y.$$

k_2^x is governed by CH-bending modes, k_2^y mainly by CC-bending modes.

If k_2^α is mainly induced by the CC-bending modes, it seems to be necessary to include the spin-vibronic term $\partial H_{SO} / \partial Q_p$.

Since the total rate constant is not dominated by k_3^α , the different rules for the deuterium effect in aromatic hydrocarbons as stated by Siebrand [8], lose their validity and must be revised. Due to the fact, that the electronic matrix elements which appear in k_2^x and k_2^y show a deuterium effect too, it is impossible to establish a special mechanism from an experimental deuterium effect. The deuterium effect only provides some hints on the type of promoting mode (CC or CH), which induces the decay of the considered sublevel.

In naphthalene we calculated the ratios

$$k^x/k^x(d) \approx 1.3 \quad k^z/k^z(d);$$

$$k^x/k^x(d) \approx 1.8 \quad k^y/k^y(d).$$

There is no experimental value for naphthalene. But similar results are expected for all the linear polyacenes. In anthracene Sixl et al. [18] found

$$k^x/k^x(d) = 5.2; \quad k^y/k^y(d) = 2.4; \quad k^z/k^z(d) = 3.$$

However, the value of k^z is within the limits of experimental error. This result is in line with our predictions that k^x is mainly governed by CH-, k^y by CC-vibrations, and k^z by CH- and CC-vibrations.

Our consideration holds also for the $S_1 \rightarrow T_1$ non-radiative transition, where the corresponding rate constant k_2^α should not be a priori neglected. We will investigate this problem in a future publication [19].

Acknowledgement

We wish to thank the Deutsche Forschungsgemeinschaft for financial support; the Leibnitz Rechenzentrum of the Bavarian Academy of Sciences for computer time; and Mr. Willis E. Howard for his help in preparing the manuscript.

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