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DESCRIPTION OF THE RADIATIVE PROPERTIES OF UNSATURATED MOLECULES CONTAINING A TRIPLE BOND BASED ON A QUASI π-MODEL

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In this paper we provide a model for the theoretical calculation of radiative triplet properties of aromatic molecules containing a triple bond. Such molecules have special low-lying electronic states with the symmetry properties of a $\sigma\pi^*$-state. These states are caused by electron promotion from an "in-plane π-system" (quasi π-system), which is highly localized at the triple bond, to the aromatic π-system and vice versa. It is shown that these states lead to one-center spin–orbit integrals and therefore are highly active in radiative triplet decay. Theoretical and spectroscopic investigations of ethynylbenzene show that the radiative properties of the lowest triplet state, such as phosphorescence yield, emission spectrum and degree of polarization can be explained not only qualitatively but also quantitatively by restriction to these states (quasi π-model). The theoretical evaluation of the radiative rate was done with respect to individual promoting modes. It is shown that the first order rate (at the equilibrium position of the molecule), though allowed by symmetry, has nearly no influence on the radiative lifetime. As a consequence the first transition in the phosphorescence emission cannot be assigned as the 0–0 transition.

1. Introduction

The dynamic properties of the lowest triplet state of molecular systems have been studied with great effort in theory and experiment during the last few years [1,2]. The aromatic hydrocarbons have been the main objects of these studies. Theoretical models have been developed which successfully explain the dependence of the rate of the radiationless decay on parameters like energy gap, variations in geometry and special vibrations.

Contrary to the radiationless decay, the theoretical treatment of radiative transitions from the lowest triplet state has been known formally for many years. However, quantitative calculations do in general not succeed in explaining the observed phosphorescence yield and triplet lifetime. This is mainly due to a lack of exact information on the rate determining $\sigma\pi^*$– or $\pi\sigma^*$–states. Only if the radiative rate is mainly governed by one or a few such states, on which more detailed information is available, are we in a better situation. For example, Veeman and van der Waals [3], and earlier Goodman [4] obtained relatively good results in the case of aza-aromatic systems, where the rate is determined mainly by $n\pi^*$– states.

We now wish to show, that there exists another group of molecules for which a very accurate theoretical description of the radiative properties of the lowest triplet state can be achieved: unsaturated molecules containing a conjugated triple bond.

As a first example, we present results for ethynylbenzene. This molecule has a very useful symmetry and there is also a lot of experimental information available.

2. Basic theory

The fundamental equation for the radiative triplet decay is given by the expression (atomic units)

$$\tau_{\mathrm{rad}}^{-1} = k_{\mathrm{rad}} = \tfrac{4}{9}\,\omega\alpha^3 \sum_{\nu} |\langle\chi^{\nu}_{S_0}|P_{S_0T_1}(Q)|\chi^{0}_{T_1}\rangle|^2 . \quad (1)$$

The sum ν runs over all the vibrational states $\chi^{g}_{S_0}$ of the electronic ground state. $P_{S_0T_1}$ is the electronic transition matrix element

$$P_{S_0T_1}(Q) = -\sum_j \left[\frac{\langle S_0|H_{so}|T_j\rangle \langle T_j|p|T_1\rangle}{E_{T_j}(Q) - E_{S_0}(Q)} + \frac{\langle S_0|p|S_j\rangle \langle S_j|H_{so}|T_1\rangle}{E_{S_j}(Q) - E_{T_1}(Q)} \right] . \tag{2}$$

p is the momentum operator, which one has to use in evaluating matrix elements of forbidden transitions [5]. The zero-order states are chosen to be pure adiabatic spin states.

Since $P_{S_0T_1}(Q)$ is a slowly varying function in Q, expansion to the first order of a power series around the equilibrium position $Q = 0$ of the molecule in the ground state S_0, should be sufficient.

$$P_{S_0T_1}(Q) = P_{S_0T_1}(0) + \sum_{p'} \left[\frac{\partial P_{S_0T_1}(Q)}{\partial Q_{p'}} \right]_{Q_{p'}=0} Q_{p'} . \tag{3}$$

The spin–orbit operator H_{so} is used in the one-particle approximation (μ denotes the atomic center):

$$H_{so}^{\tau} = \tfrac{1}{2}\alpha^2 \sum_\mu \frac{Z_\mu \{[r - r_\mu] \times p\}^\tau s^\tau}{|r - r_\mu|^3} = \sum_\mu \xi_\mu l_\mu^\tau s^\tau = \sum_\mu h_{so_\mu}^\tau s^\tau ;\ \tau = x, y, z , \tag{4}$$

where Z_μ has the meaning of an effective core charge. If the matrix elements of H_{so} are reduced to integrals over molecular orbitals,

$$\langle S_0|H_{so}|T_j^\tau\rangle \to \int d^3r\, \phi_i(r)\, h_{so_\mu}^\tau\, \phi_k(r)$$

and the MO's ϕ_i and ϕ_k are represented in an LCAO basis set, one gets one- , two- and three-center integrals. Numerical evaluation of these integrals with Slater-type orbitals (STO's) shows, that there is an unequivocal order in their size [6]: one-center spin–orbit integrals (OCSOI's) exceed the more-center integrals by at least one order of magnitude. Therefore the possible coupling mechanisms are nearly exclusively governed by OCSOI's. Consequently, from all the intermediate states only those have to be taken into account which yield a contribution via OCSOI's (one-center approximation).

From

$$h_{so}^x(r_\mu)|2p_y(r_\mu)\rangle = -\xi(r_\mu)|2p_z(r_\mu)\rangle;\ x,y,z \text{ cyclic}, \tag{5}$$

it is easily verified, that OCSOI's will appear only if the atomic orbitals are geometrically orthogonal. This condition implies, that one of the MO's ϕ_i, ϕ_k has to be symmetric to the molecular plane, if the other is a π-orbital. Therefore the intermediate states have to be of $\sigma\pi^*$-type if T_1 is a $\pi\pi^*$-triplet.

The restriction to the one-center approach is common in the case of an orbitally allowed $T_1 \to S_0$ transition [3, 4, 7, 8]. However, these rules have been recently shown to be valid, even if the transition via OCSOI's is forbidden by symmetry in first order, but allowed in second order via promoting modes [9].

3. The quasi π-model

If a triple bond is conjugated to a planar aromatic hydrocarbon one of the two π-systems of the triple bond becomes a σ-system with respect to the overall symmetry of the substituted hydrocarbon. However, the interaction of these σ-orbitals with those of the aromatic ring is expected to be small, due to a large difference in orbital energies. Therefore, it seems to be a very reasonable approximation to regard these orbitals as completely localized in the region of the triple bond. Due to their behaviour with respect to the local symmetry of the substituted group we call these orbitals "quasi π-orbitals" (q-orbitals).

The separation of highly localized "quasi π-orbitals" from ordinary σ-orbitals is justified by the photoelectron spectra of a series of ethynyl-substituted aromatic hydrocarbons [10]: if we inspect, for example, the photoelectron spectrum of ethynylbenzene (fig. 1), we find two bands (between 10 and 11.5 eV), which undoubtedly originate from the triple bond. Compared to acetylene [17], one of these bands is shifted to higher energies by interaction with the π-orbitals of the ring. This band shows a vibrational pattern, which is completely different from that observed in the free acetylene molecule. The vibrational quantum observed originates from the ν_8 (a_1) (ν_{C-CCH})-mode (in King's notation [11]). This fact clearly shows, that the orbital in question extends over the whole molecule.

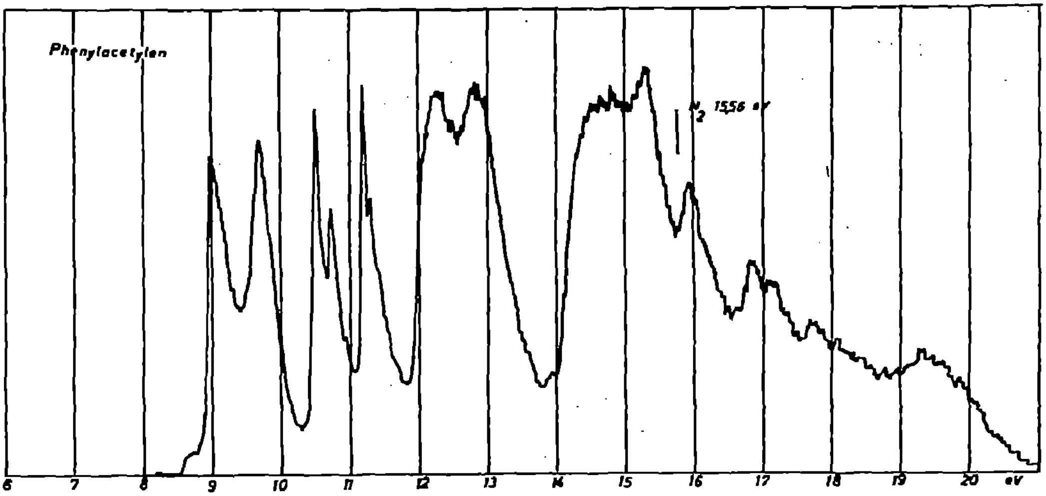

Fig. 1. Photoelectron spectrum of ethynylbenzene.

The other band appears at somewhat lower energies than in acetylene. However, since one does not observe any mode which would indicate a delocalization of the quasi π-system into the phenyl σ-system, we conclude that the quasi π-orbitals must be strongly localized at the triple bond. Therefore the observed shift is nearly exclusively due to an inductive perturbation. We further assume that there exist excited states which are mainly caused by electron promotion from the q-orbital to the π^*-orbitals or vice versa. Such states, we call $q\pi^*$-states. As pointed out in the foregoing section it is easy to verify that $q\pi$-states can lead to one-center contributions in spin–orbit coupling. Besides, these states are expected to be lower in energy than ordinary $\sigma\pi$-states. Therefore, they should be highly active in spin–orbit coupling and radiative triplet decay.

In the next sections we take ethynylbenzene as an example and show that one is able to describe the radiative properties of the lowest triplet state by restriction to these special states only (quasi π-model). Moreover, since the $q\pi$-states can be easily handled within the framework of semi-empirical calculations, the theoretical results should be fairly accurate compared to calculations using ordinary $\sigma\pi$-intermediate-states.

4. Application to ethynylbenzene

To evaluate the radiative properties of ethynylbenzene on the basis of the quasi π-model, we need an approximate knowledge of the $\pi\pi^*$ as well as of the $q\pi$-states. To obtain this information, we used a modified PPP treatment in which, in addition to the normal π-system, the quasi π-system was taken into account explicitly.

The choice of axes together with the numbering of the atomic centers is given in fig. 2.

The γ-parameters, which appear in addition to the conventional PPP treatment, and also the β-parameters $\beta_{7x,8x} = \beta_{7y,8y}$ for the very short triple bond have not been used as adjustable parameters but were calculated

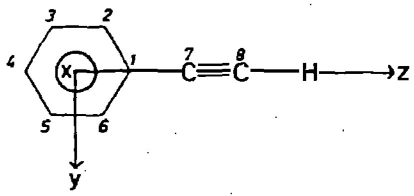

Fig. 2. Numbering of centers and choice of axes for ethynylbenzene.

Table 1
PPP parameter [eV]; $\gamma_{i_x j_y} = \gamma_{i_x j_x}$, if $r > 2$ A

	Atomic center	1	2	3	4	5	6	7_x	8_x	7_y	8_y
	1	10.96	6.89	5.66	4.90	5.66	6.89	6.89	5.25	6.5	5.25
γ	7_x								7.45	9.40	6.95
	8_x									6.95	9.40
β	$\beta = 1.45\,\beta_0 = \beta_{7_x 8_x} = \beta_{7_y 8_y}$; $\beta_0 = -2.37$										

Table 2
MO coefficients

Atomic – center	π_4 (b_1)	π_3 (b_1)	π_2 (a_2)	π_1 (b_1)	q (b_2)	q* (b_2)	π_1^* (b_1)	π_2^* (a_2)	π_3^* (b_1)	π_4^* (b_1)
1	−0.5	0.11	0	0.49	0	0	−0.49	0	−0.11	0.5
2	−0.36	−0.14	0.5	0.31	0	0	0.31	0.5	−0.14	−0.36
3	−0.29	−0.35	0.5	−0.21	0	0	0.21	−0.5	0.35	0.29
4	−0.26	−0.44	0	−0.48	0	0	−0.48	0	−0.44	−0.25
7	−0.41	0.52	0	−0.25	0.71	0.71	−0.25	0	0.52	−0.41
8	−0.29	0.49	0	−0.41	0.71	−0.71	0.41	0	−0.49	0.29

Table 3
Symmetry, energy and CI coefficients of some states. Note: there exists a state $[S_q^{\pi^*}]_i$ degenerate with $[S_\pi^{q^*}]_i$ with exactly the same CI coefficients

State	Symmetry	Energy [kK]	CI coefficients
$[T_\pi^{\pi^*}]_1$	A_1	24.0	$0.78\,|{}^{\pi_1^*}_{\pi_1}\rangle - 0.54\,|{}^{\pi_2^*}_{\pi_2}\rangle + 0.22\,|{}^{\pi_3^*}_{\pi_3}\rangle$
$[S_\pi^{q^*}]_1$	A_2	45.8	$0.8\,|{}^{q^*}_{\pi_1}\rangle - 0.56\,|{}^{q^*}_{\pi_3}\rangle + 0.21\,|{}^{q^*}_{\pi_4}\rangle$
$[S_\pi^{q^*}]_2$	B_1	69.7	$|{}^{q^*}_{\pi_2}\rangle$
$[S_\pi^{q^*}]_3$	A_2	70.6	$0.57\,|{}^{q^*}_{\pi_1}\rangle + 0.6\,|{}^{q^*}_{\pi_3}\rangle - 0.55\,|{}^{q^*}_{\pi_4}\rangle$
$[S_\pi^{q^*}]_4$	A_2	96.0	$0.18\,|{}^{q^*}_{\pi_1}\rangle + 0.56\,|{}^{q^*}_{\pi_3}\rangle + 0.81\,|{}^{q^*}_{\pi_4}\rangle$

by a procedure described in ref. [12]. The numerical values of all the parameters used in the calculation of ethynylbenzene are given in table 1. Parts of the result are listed in tables 2 and 3. The experimental spectra are shown in fig. 3.

Within the approximations of this modified PPP-treatment, the qπ-triplet states are degenerated with the corresponding singlet states since the exchange integrals, which cause the splitting, vanish.

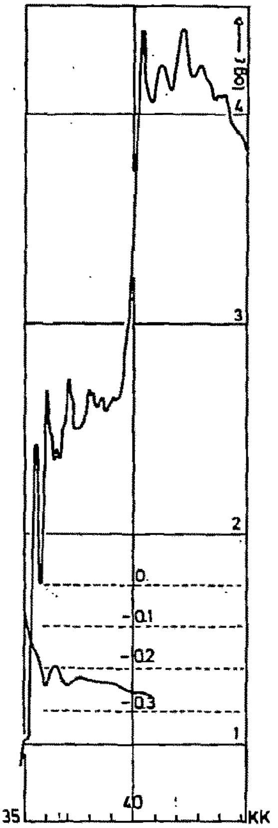

Fig. 3. Absorption spectrum and polarized excitation spectrum of ethynylbenzene.

5. Evaluation of the zero-order term

In a first step, we try to evaluate the contribution to the transition matrix element (2), which originates from the zero-order term $P_{S_0T_1}$ (0). Since the lowest triplet state is of A_1-symmetry, there are two possible coupling mechanisms

$$\begin{tikzcd}
& S_j(B_2)\rangle \arrow[dr, "y"] & \\
|T_1\rangle \arrow[ur, squiggly, "H^x_{so}"] \arrow[dr, "y"'] & & S_0\rangle, \\
& |T_j(B_2)\rangle \arrow[ur, squiggly, "H^x_{so}"'] &
\end{tikzcd} \qquad (I)$$

$$\begin{tikzcd}
& S_j(B_1)\rangle \arrow[dr, "x"] & \\
|T_1\rangle \arrow[ur, squiggly, "H^y_{so}"] \arrow[dr, "x"'] & & S_0\rangle. \\
& |T_j(B_1)\rangle \arrow[ur, squiggly, "H^y_{so}"'] &
\end{tikzcd} \qquad (II)$$

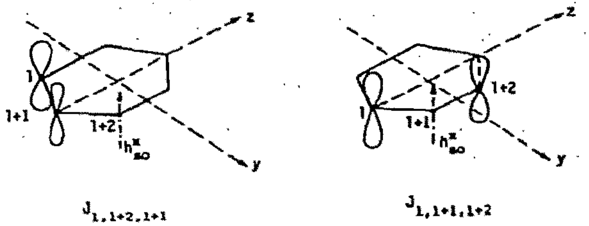

Fig. 4. Types of three-center integrals considered.

Mechanism I yields a component in the phosphorescence emission polarized in plane (y). The corresponding intermediate states have to be of $\pi\pi^*$-type. Therefore, the only non-vanishing spin–orbit integrals are of three-center-type, defined by

$$J_{klm} = \tfrac{1}{2}\, \alpha^2 Z_l \int d^3r\, \theta_k(r)\, \frac{[(r-r_l)\times\nabla]_x}{|r-r_l|^3}\, \theta_m(r).$$

Among these, the largest are those between nearest neighbours, as illustrated in fig. 4. All the contributions from the integrals $J_{l,l+1,l+2}$ cancel each other exactly because of the properties of an alternant hydrocarbon. The contributions from the integrals $J_{l,l+2,l+1}$ compensate each other, too, but only in part.

If we take, as usual [13] a value of 0.33 cm^{-1} for the three-center integrals $J_{l,l+2,l+1}$ and take into account all the 25 singly-excited configurations of our modified PPP calculation, we obtain a rate constant according to mechanism I

$$k^y_{\text{rad}} = 6 \times 10^{-4}\ \text{sec}^{-1}.$$

Mechanism II yields an out-of-plane component in the phosphorescence emission. The intermediate states are of $\sigma\pi$-symmetry type.

Due to the poor experimental and theoretical knowledge of ordinary $\sigma\pi$-states, it is nearly impossible to obtain any reliable theoretical estimation of the contribution to the rate constant originating from these states. Some authors [3, 7, 8] have tried to estimate these contributions by constructing the σ-orbitals from AO's with fixed combination of STO's for all centers μ. In a further approximation the $\sigma\pi^*$ and $\pi\sigma^*$-states are grouped together to $\sigma_C\pi^*$-, $\sigma_H\pi^*$, $\pi\sigma_C^*$ - and $\pi\sigma_H^*$ -states, with the assumption that the energies of these states are well described by mean values $E_{\sigma_C\pi^*}$, $E_{\sigma_H\pi^*}$, $E_{\pi\sigma_C^*}$ and $E_{\pi\sigma_H^*}$

Since there is a strong cancellation of the individual terms, k_{rad} depends strongly on the values of the hybridization coefficient and on the averaged values $E_{\sigma_{\mathrm{C}}\pi^*} - E_{\pi\sigma_{\mathrm{C}}^*}$ and $E_{\sigma_{\mathrm{H}}^*\pi} - E_{\pi\sigma_{\mathrm{H}}^*}$.

Because of these crude approximations, one cannot expect to obtain more than an estimation within one order of magnitude even in favourable cases.

On the other hand, a calculation of the rate according to mechanism II by restriction to the qπ-states does not succeed either because symmetry allows only those of B_1-representation to couple. However, these states are very ineffective in spin–orbit coupling, since all the one-center integrals vanish. This statement results from the fact that the corresponding a_2 MO has zero coefficients at the centers of the quasi π-orbitals.

As a consequence of these considerations we cannot obtain any reliable theoretical estimate of k_{rad}^x from the zero-order term. Therefore, we have to use experimental information: we start the analysis of the experimental data with the assumption that the absorption in the region of the second band (40200 cm^{-1}) is nearly completely z-polarized (fig. 3). From the degree of polarization of the phosphorescence with respect to the 40.2 kk band (PP_2) (see fig. 5), we find that there is only a small z-polarized component in the phosphorescence emission. From the equation [16]

$$\frac{2\,\mathrm{PG}}{3-\mathrm{PG}} = \tfrac{1}{5}\left[\,3\,(s_x r_x + s_y r_y + s_z r_z) - 1\right], \qquad (6)$$

where PG denotes the degree of polarization, s_x the fraction of the emission at the wavenumber $\bar{\nu}_e$, polarized in x, r_x the fraction of the absorption at $\bar{\nu}_a$, polarized in x, it follows that the z-polarized component does not exceed 6%, except within the gap around 24900 cm^{-1} following the short-wavelength band.

For further discussion we have to know the polarization of the absorption in the region of the first band. The corresponding 0–0 transition is allowed by symmetry but very weak since it is an L_b-type transition. King and So [11], who carefully investigated the vibrational structure of this "forbidden" band, found that it gains the main part of its intensity (75%) by b_2-vibrations inducing a z-polarized component.

To obtain an estimate of the x- and y-polarized components in the phosphorescence we first assume the absorption in the region around 35500 cm^{-1} to be completely y-polarized. Then it follows from PP_1 that about 62% of the triplet emission must be x-polarized.

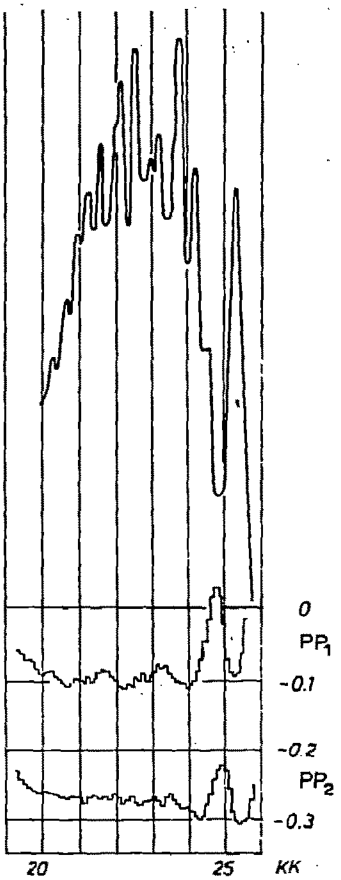

Fig. 5. Phosphorescence emission with the corresponding degree of polarization of ethynylbenzene.

On the other hand, if one assumes as a lower limit that only 25% of the intensity around 35500 cm^{-1} is y-polarized, one finds from eq. (6) that the x-polarized component amounts to 30%. From these considerations we find that the ratio s_x/s_y certainly does not exceed 3.

If we use this experimental result together with the decay rate calculated from mechanism I, we find an upper limit of the total radiative rate of about 3×10^{-3} sec^{-1}. To compare this value with experiment we measured the phosphorescence yield ϕ^{P} by comparing the relative intensities of ethynylbenzene and 1,9-diphenylanthracene. The latter molecule has its emission in the same energy region as ethynylbenzene and its quantum yield was determined by Lim to be close to unity [14]. From this we find for ethynylbenzene: $\phi^{\mathrm{P}} = 0.3 \pm 0.2$.

The high uncertainty is due to the fact, that we did not correct the polarization effects appearing in our experimental setup.

From fluorescence decay measurement we know the intersystem-crossing yield ϕ_{ISC} to be close to unity.

Using the relation

$$k_{rad} = \phi^P / (\tau^P \phi_{ISC})$$

and taking τ^P from ref. [15], we obtain as a lower limit $k_{rad} = 0.04\ \mathrm{sec}^{-1}$, a value which exceeds the calculated one by at least one order of magnitude.

From this result it seems to be very likely that the phosphorescence of ethynylbenzene is nearly completely vibrationally induced. We therefore have to evaluate the second term of eq. (3).

6. Vibrationally induced processes

To evaluate the second part of eq. (3) we first restrict ourselves to the contributions originating from the quasi π, π^* – intermediate states (quasi π-model). As already stated, the evaluation of the corresponding terms should be fairly accurate, because these states may be well described by our semi-empirical calculation. Moreover, this restriction seems to be justified due to the favourable energy denominator appearing in eq. (2).

Within the quasi π-model the variation of $P_{S_0T_1}$ with the normal coordinates Q is limited to the variation of the matrix element of the momentum operator with Q. Then, using the abbreviation

$$\langle S_0|\nabla|S_j\rangle^{p'} = [\partial \langle S_0|\nabla|S_j\rangle/\partial Q_{p'}]_{Q_{p'}=0},$$

the second-order contribution [eq. (3)] from the quasi π-states is given by

$$\sum_{p'}\sum_{j} \frac{1}{i}\left[\frac{\langle S_0|\nabla|S_j\rangle^{p'} \langle S_j|H_{so}|T_1\rangle}{E_{S_j} - E_{T_1}} + \frac{\langle S_0|H_{so}|T_j\rangle \langle T_j|\nabla|T_1\rangle^{p'}}{E_{T_j} - E_{S_0}}\right]. \tag{7}$$

From symmetry arguments it follows that only $q\pi$-states $|T_j\rangle$ and $|S_j\rangle$ with symmetry A_2 can contribute an essential part, because only the corresponding b_1 (π) orbitals have nonvanishing coefficients at the centers of the quasi π-MO's and therefore can produce OCSOI's in the matrix elements of H_{so}. This consideration implies that only promoting modes of symmetry b_1 and b_2 can successfully induce the transition. Because of this fact, the emission must be polarized in y- and x-directions, respectively. Reduction of the matrix elements to integrals over MO's yields expressions of the following type:

$$\langle q^*|\nabla|\pi^*\rangle^{p'} \langle \pi|h^z_{so}|q^*\rangle, \quad \langle q^*|h^z_{so}|\pi^*\rangle \langle \pi|\nabla|q^*\rangle^{p'},$$

$$\langle \pi|h^z_{so}|q\rangle \langle q|\nabla|\pi^*\rangle^{p'}, \quad \langle \pi|\nabla|q\rangle^{p'} \langle q|h^z_{so}|\pi^*\rangle.$$

To calculate the derivatives, we assume that the quasi π-system is conserved during the change of the nuclear coordinates as illustrated in fig. 6.

The leading contribution to the integrals $\langle q|\nabla|\pi^*\rangle^{p'}$ is found to result from the electronic interaction between centers 1 and 7. Therefore,

$$\langle q|\nabla|\pi^*\rangle^{p'} \approx c_q(7) c_{\pi^*}(1) \langle 2p_y(7)|\nabla|2p_x(1)\rangle^{p'}.$$

The mean derivation at the equilibrium position of the center i in the vibrational ground state of T_1 is defined by

$$(2\,\omega_{p'})^{-1/2}\,\partial/\partial Q_{p'}(i) = (R_i^{p'} - R_i^0)(2\,M_i\,\omega_{p'})^{-1/2}\,\partial/\partial R_i,$$

where the factor $(2\,\omega_{p'})^{-1/2}$ results from the relation

$$\langle \chi^0_{T_1}|Q^2_{p'}|\chi^0_{T_1}\rangle = 1/2\,\omega_{p'},$$

where M_i denotes the mass of the i'th-atom and $Q_{p'}(i)$ is the value of the mass-weighted normal coordinate at center i. $R_i = (X_i, Y_i, Z_i)$ denotes the position vector of center i. The out-of-plane normal coordinates we deter-

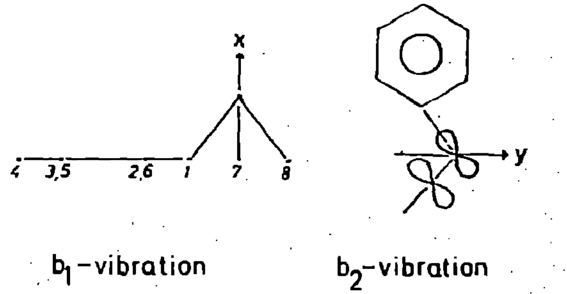

Fig. 6. Schematic representation of the most efficient in-plane and out-of-plane promoting modes.

Table 4

Promoting mode p' (b_1)			$\frac{(R_i^{p'} - R_i^0)}{(2M_C\omega_{p'})^{1/2}} \times 10^4$ [au]			$K_{rad}^y \times 10^2$
$\bar{\nu}_{cal}$ [cm^{-1}]	$\bar{\nu}_{exp}$ [cm^{-1}]	type	$i = 1$	$i = 7$	$i = 8$	[sec^{-1}]
130	162	γ (C–C≡C)	835	398	−1011	0.13
320	349	γ (C–CCH)	900	43	− 235	0.51
492	530	(ϕ_{C-C})	614	−360	58	0.66
656	613	γ (CC–H)	15	−160	392	0.02
690	689	ϕ_{C-C}	153	44	− 39	0.01
732	756	γ(C–H)	408	− 80	10	0.17
895	915	γ (C–H)	141	− 40	4	0.02
964	985	γ (C–H)	18	3	0	0.00

mined from the force constants of the free molecules, benzene and acetylene. The theoretical frequencies together with the assignment and the assumed corresponding experimental values are listed in table 4.

For out of plane vibrations of symmetry b_1 we finally obtain (see appendix)

$$\langle 2p_y(7)|\nabla_y|2p_x(1)\rangle^{p'} = \frac{X_1^{p'} - X_7^{p'}}{R_{17}} \langle 2p_\pi(7)|\nabla_\pi|2p_\sigma(1)\rangle .$$

Application of the relation (see appendix)

$$\langle 2p_\pi(7)|\nabla_\pi|2p_\sigma(1)\rangle$$

$$= R_{17}^{-1}\,[\langle 2p_\sigma(7)|2p_\sigma(1)\rangle - \langle 2p_\pi(7)|2p_\pi(1)\rangle ,$$

together with the values

$R_{17}' = 1.45$ Å, $\xi_C = 1.625$, $\langle 2p_\pi(1)|2p_\pi(7)\rangle = 0.22$,

$\langle 2p_\sigma(1)|2p_\sigma(7)\rangle = 0.33$

yields

$\langle 2p_\pi(7)|\nabla_\pi|2p_\sigma(1)\rangle = 0.21$ au.

Taking the values of the MO and CI coefficients and the energies listed in tables 2 and 3 as well as the mean deviation of the equilibrium position at centers 1, 7 and 8 given in table 4, we obtain a radiative transition rate for y-polarized emission of

$k_{rad}^y = 0.015$ sec^{-1}.

From table 4 it follows that about 80% of k_{rad}^y is caused by the b_1-vibrations γ (C–CCH) and ϕ_{C-C} with $\bar{\nu} = 350$ cm^{-1} and $\bar{\nu} = 530$ cm^{-1}, respectively.

For the b_2 in-plane vibration β (C–CCH) which is degenerated with γ (C–CCH) ($\bar{\nu} = 350$ cm^{-1}) one obtains a similar expression

$$\langle 2p_y(7)|\nabla_x|2p_x(1)\rangle^{p'}$$

$$= \left[\frac{Y_7^{p'} - Y_1^{p'}}{R_{17}} + \frac{Y_7^{p'} - Y_8^{p'}}{R_{78}}\right] \frac{\langle 2p_\pi|\nabla_\pi|2p_\sigma\rangle}{(2M_C\,\omega_{p'})^{1/2}} ,$$

which yields a radiative transition rate for the out-of-plane polarized component of the emission of

$k_{rad}^x = 0.025$ sec^{-1}.

There might be a contribution to k_{rad}^x from some other b_2 in-plane vibrations too, but if the mechanism discussed here is really the most important one, these contributions should be small and enhancement of k_{rad}^x should be less than a factor 2. The ratio

$k_{rad}^x / k_{rad}^y \approx 2$

is in very good agreement with the data we obtained from the experimental spectra.

If one does not restrict oneself to the qπ-states, those contributions must be taken into account which originate from ordinary $\sigma\pi$ intermediate states. Because of the arguments stated above, however, no accurate theoretical estimate of these terms is possible. Moreover, there appears an additional part to eq. (7) which is not taken into account within the quasi π-model. It originates from the variation of the matrix element of the spin–orbit operator with Q:

$$\sum_{p'} \sum_{j} \frac{1}{\mathrm{i}} \left[\frac{\langle \mathrm{S}_0 | \nabla | \mathrm{S}_j \rangle \langle \mathrm{S}_j | H_{\mathrm{so}} | \mathrm{T}_1 \rangle^{p'}}{E_{\mathrm{S}_j} - E_{\mathrm{T}_1}} + \frac{\langle \mathrm{S}_0 | H_{\mathrm{so}} | \mathrm{T}_j \rangle^{p'} \langle \mathrm{T}_j | \nabla | \mathrm{T}_1 \rangle}{E_{\mathrm{T}_j} - E_{\mathrm{S}_0}} \right]. \tag{7a}$$

Two mechanisms will contribute to (7a): the first one leads to an out-of-plane polarized emission and is caused by in-plane vibrations. The corresponding intermediate states have to be of $\sigma\pi$-type. The second one yields in-plane emission and is caused by out-of-plane vibrations. The corresponding intermediate states have to be of $\pi\pi^*$-type. In the former case the matrix element of the momentum operator is expected to be much smaller than in the latter case. Therefore we only have to consider the contribution in (7a) induced by out-of-plane promoting modes.

To evaluate these terms we used a method developed in an earlier paper [9]. We took into account all the singly-excited $\pi\pi^*$-states of our PPP calculation. Using the relation

$$\langle \mathrm{S}_0 | p | \mathrm{S}_j \rangle = -\mathrm{i}\, E_{\mathrm{S}_j} \langle \mathrm{S}_0 | r | \mathrm{S}_j \rangle,$$

we obtained the values of the matrix elements p_{0j} and p_{j1} of the momentum operator from the oscillator strength calculated in the usual way from the PPP results.

The contribution from (7a) to the y-polarized component of the triplet emission, obtained in this way, amounts to only a few percent. There appears, however, a considerable contribution to a z-polarized component originating from highly excited intermediate states of $^3\pi\pi^*$-type. Contrary to the low-lying excited states which are known to be well described by semiempirical SCF CI methods we know nothing of the physical reality of the higher excited states calculated in this way. We therefore have to regard with doubt the result originating from our evaluation of (7a). However, if this result is actually true, the contribution of (7a), which would lead to a z-polarized component in the emission, must be nearly cancelled by a similar contribution of (7) originating from ordinary $\sigma\pi$-intermediate states. Otherwise we would find a substantial z-polarized component in the experimental spectrum.

Altogether we find that the main properties of the triplet emission of ethynylbenzene are well described by using the quasi π-model: The total rate for the radiative decay $k_{\mathrm{rad}} = k_{\mathrm{rad}}^{x} + k_{\mathrm{rad}}^{y} = 0.04\ \mathrm{sec}^{-1}$, as well as the ratio $k_{\mathrm{rad}}^{x}/k_{\mathrm{rad}}^{y} \approx 2$, is in very good agreement with the values we derived from the experimental results. Moreover, there appeares to be another feature in the phosphorescence spectrum which confirms our model contrary to most aromatic hydrocarbons, the degree of polarization of the phosphorescence of ethynylbenzene (fig. 5) exhibits nearly no vibronic structure. The only deviation from a nearly constant degree of polarization appears in PP_1 as well as in PP_2 around 24900 cm^{-1} where the intensity of the emission is very weak. This structural feature is well understood on the basis of our results: the promoting modes γ (C–CCH) and β (C–CCH) which yield the largest contribution to the total intensity are degenerate and therefore the ratio s_x/s_y should stay nearly constant. The positive deviations in PP_1 and PP_2 can be due to the weak z-component in the emission or to completely polarized scattered light both of which should gain some dominance in this region because of the deep gap in the emission.

Finally, we have to discuss an outstanding consequence of our results: if our interpretation is correct, the phosphorescence emission of ethynylbenzene is nearly completely vibrationally induced and the short wavelength band at 25300 cm^{-1} cannot be the 0–0 transition, as assigned by Laposa [15]. Instead, this band must be due to the first excitation of the degenerate promoting modes γ (C–CCH) and β (C–CCH). The 0–0 transition should appear at about 25650 cm^{-1} but, because of its low intensity, it is hidden in the short-wavelength tail of the emission.

The assignment given here is further confirmed by the appearance of the deep gap following the 25300 cm^{-1} band: since the corresponding transition is induced by the first excitation of unsymmetrical in-plane and out-of-plane promoting modes having nearly parallel potential surfaces in the ground and in the excited states, transitions which are accompanied by higher excitations of these vibrations must be nearly forbidden. The following transitions are combined excitations of the promoting modes ($\bar{\nu} \approx 350\ \mathrm{cm}^{-1}$) with totally symmetric ring vibrations, such as the 1100 cm^{-1} or the 1500 cm^{-1} mode, and the acetylenic stretching mode (2200 cm^{-1}).

7. Conclusion

Using theoretical and experimental arguments, we have shown in this paper that the spectral features of the lowest triplet state of ethynylbenzene, such as lifetime, quantum yield, emission spectrum and degree of polarization can be clearly understood on the basis of a quasi π-model. In addition, ethynylbenzene provides an example where, for a radiative process, second-order spin–orbit coupling dominates the first order, though the latter is not forbidden by symmetry. As a consequence, the 0–0 band of the phosphorescence is not observed in the experimental spectrum.

We have also gathered experimental and theoretical evidence that the quasi π-model is not limited to ethynylbenzene, but can be used to explain the triplet properties of a series of aromatic compounds containing a triple bond, such as phenyl-substituted poly-acetylenes and nitriles. We will discuss these results in a further publication.

Note added in proof

Experimental work by E.C. Lim [18] does not provide evidence for a "hidden" 0–0-transition in unsymmetric benzonitriles. Since this result is of some importance for the applicability of the quasi π-model to ethynylbenzene, we hope to clear up this discrepancy by spectroscopic investigation of *o*-di-ethynylbenzene. This experiment, which is in preparation, should provide a crucial test for our assignment.

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Appendix

We want to show that

$$\text{(i)}\ \partial\langle 2p_y(7)|\nabla_y|2p_x(1)\rangle/\partial x_7 = R_{17}^{-1}\langle 2p_y(7)|\nabla_y|2p_z(1)\rangle$$

and

$$\text{(ii)}\ \langle 2p_y(7)|\nabla_y|2p_z(1)\rangle = R_{17}^{-1}\,[\langle 2p_z(7)|2p_z(1)\rangle - \langle 2p_y(7)|2p_y(1)\rangle]\,.$$

We introduce the hermitian operators

$$L_y^1 = \mathrm{i}^{-1}\,[(z-z_1)\nabla_x - x\nabla_z]\,,$$

$$L_x^7 = \mathrm{i}^{-1}\,[y\nabla_z - (z-z_7)\nabla_y]\,,$$

which correspond to rotations around the y- and z-axis at center 1 and 7, respectively.
From

$$\langle 2p_y(7)|L_y^1\,\nabla_y|2p_x(1)\rangle = \mathrm{i}^{-1}\langle 2p_y(7)|\nabla_y|2p_z(1)\rangle$$

$$= -\mathrm{i}^{-1}[(z_1-z_7)\langle\nabla_x\,2p_y(7)|\nabla_y|2p_x(1)\rangle]$$

$$= \mathrm{i}^{-1}\,[R_{17}\,\partial\langle 2p_y(7)|\nabla_y|2p_x(1)\rangle/\partial x_7]$$

(i) follows.
From

$$\langle 2p_y(7)|L_x^7|2p_z(1)\rangle = \mathrm{i}^{-1}\,[\langle 2p_y(7)|y\nabla_z|2p_z(1)\rangle$$

$$-\langle 2p_y(7)|(z-z_7)\nabla_y|2p_z(1)\rangle]$$

$$= \mathrm{i}^{-1}\,[\langle 2p_y(7)|2p_y(1)\rangle - (z_7-z_1)\langle 2p_y(7)|\nabla_y|2p_z(1)\rangle]$$

$$= -\mathrm{i}^{-1}\,[-\langle 2p_z(7)|2p_z(1)\rangle]$$

(ii) follows.

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