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TRIPLET-TRIPLET ABSORPTION IN BENZENE

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Abstract—Triplet-triplet absorption in benzene has been calculated semiempirically by considering all single excitations and a limited number of double excitations. The numerical results show several allowed $3_{B_u} \rightarrow 3_{E_{2g}}$ transitions of varying intensity.

INTRODUCTION

SINCE the earlier work on the lower excited singlet levels of benzene,[1] most of these calculations have involved either non-empirical[1–7] or semiempirical[8–17] methods with π-electron approximation and have considered only the singlet excited levels. Although the experimental evidence[18–20] shows the existence of lower energy triplet-triplet states in benzene, until the recent work of Porter *et al.*[21] the spectral observation has never been successful. Pariser[17] predicted an intense triplet-triplet absorption in benzene in terms of only singly excited states. But the description of the triplet-triplet absorption should take not only singly excited states but also at least double excited states into consideration because they have first order configuration interaction with the former. The effect of doubly excited states on the singlet levels has been emphasized by many workers,[11–16] but none has extended the calculation to the triplet states in benzene. Donath,[16] however, has calculated the tiplet-triplet transition in benzene by a PP-like method considering CI up to and including double excited configurations, but has not examined the intensity of such transition. Recently Orloff[22] has calculated the triplet-triplet transition in several alternant hydrocarbons by a PPP-like semi-empirical SCF MO theory and has shown his method to be capable of accounting for the observed most intense triplet-triplet transition with great accuracy in these molecules. He has, however, not included benzene in his calculation.

The purpose of the present paper is to calculate the triplet-triplet transition in benzene by considering all single excitations and double excitations only from highest filled MO's to lowest unfilled MO's by a method where all the molecular integrals are treated as parameters determinable empirically from the observed spectra of the molecule. Another purpose is to see the effect of inclusion of nearest neighbour atomic orbital overlap into the molecular core integrals on the energy levels and intensity of such transition in benzene. Zero differential overlap approximation has been assumed in the construction of MO's and in the electron repulsion integrals.

Mathematical formalism

The benzene molecule belongs to the point group D_{6h}. Due to high symmetry, the

MO's are completely determined by the LCAO approximation. Denoting the six atomic $2p_z$ orbitals on C atoms as x_k ($k = 1, 2, 3 \ldots 6$), one can form six MO's given by the general expression:

$$\phi_l = \frac{1}{\sqrt{6}} \sum_{k=1}^{6} \exp 2\pi\, ilk/6)x_k$$

where $l = 0, \pm 1, \pm 2$ and 3 denotes the number of nodes in the corresponding MO or the component of total angular momentum along z-axis. Total Hamiltonian is given by:

$$H = \sum_{\mu=1}^{6} H^{\text{core}}(\mu) + \frac{1}{2} \sum_{\mu,\nu=1}^{6} 1/r_{\mu\nu}$$

where μ, ν etc number the electrons. Under zero differential overlap approximation four electron repulsion integrals (J-Coulomb, K_1, K_2 and K_3-exchange integrals) will appear in the energy calculation. These integrals have the following definition.

$$J = \int \phi^*_{l(1)} \phi_{m(2)} \frac{1}{r_{12}} \phi_{l(1)} \phi^*_{m(2)} \mathrm{d}V$$

where $l^* + m = l + m^* = 0$.

$$K_1 = \int \phi^*_{l(1)} \phi_{m(1)} \frac{1}{r_{12}} \phi_{l(2)} \phi^*_{m(2)} \mathrm{d}V$$

where $l^* + m = \pm 1$ and $l + m^* = \mp 1$ in the sense of modulo 6.

Similar is the case with K_2 and K_3.

The core integral I_{lm} is defined as

$$I_{lm} = \int \phi^*_l(\mu) H^{\text{core}}_{(\mu)} \phi_m(\mu) \mathrm{d}V$$

Four core integrals will appear which are I_{00}, I_{11} or I_{-1-1}, I_{22} or I_{-2-2} and I_{33} denoted respectively by I_0, I_1, I_2 and I_3. Keeping overlap S for the nearest neighbour atomic orbitals, we can express them as follows.

$$I_0 = \frac{\alpha + 2\beta}{1 + 2S}$$

$$I_1 = \frac{\alpha + \beta}{1 + S}$$

$$I_2 = \frac{\alpha - \beta}{1 - S}$$

$$I_3 = \frac{\alpha - 2\beta}{1 - 2S} \quad \text{where } \alpha_{pp} = \int x^*_p(\mu) H^{\text{core}}_{(\mu)} x_p(\mu) \mathrm{d}V$$

$$\text{and} \quad \beta_{pq} = \int x^*_p(\mu) H^{\text{core}}_{(o)} x_q(\mu) \mathrm{d}V$$

When the energy of the excited states is expressed with respect to the ground state, the following four differences in the core integrals will appear. Difining $\gamma = \beta - S\alpha$ and putting $S = 1/4$, we can express them as follows in three sets of approximation.

$$\begin{aligned} I_2 - I_1 &= -2\gamma = \Delta\,(\text{Say}) \\ I_3 - I_1 &= -3\gamma = 1{\cdot}5\Delta \\ I_2 - I_0 &= -3\gamma = 1{\cdot}5\Delta \\ I_3 - I_0 &= -4\gamma = 2\Delta \end{aligned} \qquad \begin{aligned} &\text{Set (a).} \\ &S = 0 \text{ and } S^2 = 0. \end{aligned}$$

$$\begin{aligned} I_2 - I_1 &= -2\gamma = \Delta \\ I_3 - I_1 &= -4\gamma = 2\Delta \\ I_2 - I_0 &= -2{\cdot}4\gamma = 1{\cdot}2\Delta \\ I_3 - I_0 &= -4\gamma = 2\Delta \end{aligned} \qquad \begin{aligned} &\text{Set (b).} \\ &S \neq 0, S^2 = 0. \end{aligned}$$

$$\begin{aligned} I_2 - I_1 &= -32/15\gamma = \Delta \\ I_3 - I_1 &= -48/10\gamma = 9/4\Delta \\ I_2 - I_0 &= -8/3\gamma = 5/4\Delta \\ I_3 - I_0 &= -16/3\gamma = 10/4\Delta \end{aligned} \qquad \begin{aligned} &\text{Set (c).} \\ &S \neq 0, S^2 \neq 0. \end{aligned}$$

Configurations belonging to different symmetry species

The ground state of benzene has the configuration $(0\bar{0}1\bar{1} - 1 - \bar{1})$ with total angular momentum Λ_2 along z − axis = 0. The excited configurations have $\Lambda_z = 0$, ± 1, ± 2 and ± 3 in the sense of modulo 6. The symmetry of the different configurations can be very easily determined in this case from their Λ_z values. Thus configurations with $\Lambda_z = 0$ belong to A_{1g} and A_{2g} states. A_{1g} and A_{2g} arise from ± combinations of some configurations with $\Lambda_z = 0$. Configurations with $\Lambda_z = \pm 1$ and ± 2 belong respectively to degenerate E_{1u} and E_{2g} states and ± combinations of ± 3 give rise to B_{1u} and B_{2u} states respectively. Transition from $0 \rightarrow 3$ belongs to B_{1u} state. The excited configurations in different state of multiplicity ($S = 0$, 1 and 2) along with their diagonal energies are summarised in Table I where the notations employed by Murrel and McEwen[11] have been used.

Determination of the parameters and results

The four observed levels of benzene[23] are at 6·76 ev ($^1E_{1u}$), 5·96 ev ($^1B_{1u}$), 4·71 ev ($^1B_{2u}$) and 3·59 ev ($^3B_{1u}$) with respect to the ground state. None of these states will have any configuration interaction with any of the doubly excited configurations arising from $\pm 1 \rightarrow \pm 2$ transition. Moreover, B_{1u} state arising from $0 \rightarrow 3$ transition is energetically so much higher than that arising from $1 \rightarrow -2$ and $-1 \rightarrow 2$ transitions, that we can neglect their interaction in forming the expressions for the determination of our integrals. If we represent by δ, the ground state stabilisation owing to CI among the A_{1g} states, we can write down the following four energy expressions for the observed levels with respect to the ground state.

$$\begin{aligned} (^1E_{1u})\,6{\cdot}76\,\text{ev} &= \Delta + 2K_1 - K_3 + \delta \\ (^1B_{1u})\,5{\cdot}96\,\text{ev} &= \Delta + 3K_2 - K_3 + \delta \\ (^1B_{2u})\,4{\cdot}71\,\text{ev} &= \Delta + K_2 - K_3 + \delta \\ (^3B_{1u})\,3{\cdot}59\,\text{ev} &= \Delta - K_2 - K_3 + \delta \end{aligned}$$

TABLE 1. EXCITED CONFIGURATIONS WITH THEIR DIAGONAL ENERGIES

Configuration		Λ_z	S	Diagonal energy	
0^21^4	$0^21^2 - 1^2$	0	0	w_0	0
0^21^32	$0^21^2 - 1\,2$	-3	1	w_1	$I_2 - I_1 - K_3$
			0	$w_1 + 2K_3$	$I_2 - I_1 + K_3$
	$0^21 - 1^2 - 2$		1	w_1	$I_2 - I_1 - K_3$
			0	$w_1 + 2K_3$	$I_2 - I_1 + K_3$
	$0^21 - 1^2\,2$	± 1	1	w_1	$I_2 - I_1 - K_3$
	$0^21^2 - 1 - 2$		0	$w_1 + 2K_1$	$I_2 - I_1 + 2K_1 - K_3$
0^21^33	$0^21^2 - 1\,3$	± 2	1	w_2	$I_3 - I_1 - K_1 - K_2 - K_3$
	$0^2 - 1^21\,3$		0	$w_2 + 2K_2$	$I_3 - I_1 + K_1 + K_2 - K_3$
01^42	$01^2 - 1^2\,2$	± 2	1	w_3	$I_2 - I_0 + K_1 - K_2 - K_3$
	$01^2 - 1^2 - 2$		0	$w_3 + 2K_2$	$I_2 - I_0 + K_1 + K_2 - K_3$
01^43	$01^2 - 1^23$	$+3$	1	w_4	$I_3 - I_1 + 2K_1 - 2K_2 - K_3$
			0	$w_4 + 2K_3$	$I_3 - I_1 + 2K_1 - 2K_2 + K_3$
$0^21^22^2$	$0^21^22^2$	0	0	$w_5 + 2K_2 + 2K_3$	$2(I_2 - I_1) = A$ (say)
	$0^2 - 1^2 - 2^2$	0	0	$w_5 + 2K_2 + 2K_3$	A
	$0^21 - 1 - 2^2$	± 2	1	$w_5 + K_1 + K_2 + K_3$	$A + K_1 - K_2 - K_3$
	$0^21 - 1\,2^2$		0	$w_5 + K_1 + 3K_2 + K_3$	$A + K_1 + K_2 - K_3$
	$0^21^22 - 2$	± 2	1	$w_5 + K_1 + K_2 + K_3$	$A + K_1 - K_2 - K_3$
	$0^2 - 1^22 - 2$		0	$w_5 + K_1 + 3K_2 + K_3$	$A + K_1 + K_2 - K_3$
	$0^2 - 1^22^2$ $0^21^2 - 2^2$	± 2	0	$w_5 + 2K_1 + 2K_2$	$A + 2K_1 - 2K_3$
	$0^21 - 1\;\;2 - 2$	0	2	w_5	$A - 2K_2 - 2K_3$
			1(a)	$w_5 + 2K_1 + 2K_3$	$A + 2K_1 - 2K_2$
			1(b)	$w_5 + 2K_2 + 2K_3$	A
			1(c)	$w_5 + 2K_1 + 2K_2$	$A + 2K_1 + 2K_3$
			0(a)	$w_5 + K_1 + 4K_2 + K_3$	$A + K_1 + 2K_2 - K_3$
			0(b)	$w_5 + 3K_1 + 3K_3$	$A + 2K_1 - 2K_2 + K_3$

Definitions in Table 1

The states with lower case letters in the parentheses arise owing to different arrangement of the spin-orbitals in these cases.

$w_0 = 2I_0 + 4I_1 + 15J - 2K_2 - 4K_1$

$w_1 = 2I_0 + 3I_1 + I_2 + 15J - 4K_1 - 2K_2 - K_3 = w_0 + I_2 - I_1 - K_3$

$w_2 = 2I_0 + 3I_1 + I_3 + 15J - 3K_1 - 3K_2 - K_3 = w_0 + I_3 - I_1 + K_1 - K_2 - K_3$

$w_3 = I_0 + 4I_1 + I_2 + 15J - 3K_1 - 3K_2 - K_3 = w_0 + I_2 - I_0 + K_1 - K_2 - K_3$

$w_4 = I_0 + 4I_1 + I_3 + 15J - 24_1 - 4K_2 - K_3 = w_0 + I_3 - I_0 + 2K_1 - 2K_3$

$w_5 = 2I_0 + 2I_1 + 2I_2 + 15J - 4K_1 - 4K_2 - 2K_3 = w_0 + 2(I_2 - I_1) - 2K_2 - 2K_3$

Solving these equations we get K_1 = 1·30 ev, K_2 = 0·56 ev, K_3 = 0·59 ev and δ = (4·74 − Δ) ev. Substituting these values of K_1, K_2 and K_3 in the matrix elements of the secular determinant of A_{1g} state, we can expand the determinant in terms of E and Δ. Now $-\delta$ will be the lowest root of this polynomial and so substituting for $E = -\delta = \Delta - 4{\cdot}74$, we find out Δ to be 4·19 ev and δ = 0·55 ev, the ground state stabilisation. With this set of parameters (K_1 = 1·30 ev, K_2 = 0·56 ev, K_3 = 0·59 ev, Δ = 4·19 ev) we perform the rest of the configuration interactions and determine all the energy levels. The results are summarized in Table 2. After CI, the B_{1u} levels have undergone slight change. But this change is not large enough (as we assumed earlier) to alter our parameters to any significant extent.

TABLE 2. ENERGY LEVELS (ev) OF THE EXCITED STATES OF BENZENE ACCORDING TO THREE SETS OF CALCULATION

Symmetry species	Singlets (a)	Singlets (b)	Singlets (c)	Triplets (a)	Triplets (b)	Triplets (c)	Quintet (a)	Quintet (b)	Quintet (c)
A_{1g}	−0·55			8·38			6·08	Same as in (a)	
	8·0228	Same as in (a)		9·80	Same as in (a)				
	9·6594			9·86					
	13·2077								
A_{2g}	8·38	Same as in (a)		—			—		
B_{2u}	4·16	Same as in (a)		4·16	Same as in (a)		—		
B_{1u}	5·394	5·394	5·396	2·93	2·93	2·957	—		
	10·456	10·456	12·548	9·38	9·38	11·447			
E_{1u}	6·21	Same as in (a)		3·60	Same as in (a)		—		
E_{2g}	5·635	5·109	5·285	4·626	4·291	4·549	—		
	6·866	7·764	8·271	6·955	7·538	7·805			
	9·244	9·254	9·267	8·45	8·644	8·829			
	10·689	10·684	10·738	9·90	10·293	10·841			
	11·776	12·224	12·737						

Next we have calculated the oscillator strength "f" of the triplet-triplet transitions occurring from $^3B_{1u}$ to $^3E_{2g}$ (these are only symmetrically allowed) states with the help of the following expression.[24]

$$f = 2{\cdot}170 \times 10^{-5} \bar{\nu} \mu^2$$

where $\bar{\nu}$ is the transition energy in cm^{-1} and μ is the dipole length for the corresponding transition in A°. The results are summarised in Table 3 along with the results of some previous calculations.

TABLE 3. TRIPLET ENERGY LEVELS (ev) IN BENZENE AND INTENSITY OF TRIPLET-TRIPLET TRANSITION

	Pariser[x]		Donath[y]		(a)	Present work*	(b)		(c)		Observed[z]	
	Energy	f	Energy		Energy	f	Energy	f	Energy	f	Energy	f
$^3B_{1u}{}^+$	3·59	ref.	4·19	$^3B_{1u}$	0	ref.	0	ref.	0	ref.		
$^3E_{1u}{}^+$	4·149	0	4·65	$^3E_{2g}$	1·696	0	1·361	0·0113	1·592	0·0397		4·89
					4·025	0·0227	4·668	$1·86 \times 10^{-5}$	4·848	0·0034		$\varepsilon \approx 1300$
$^3B_{2u}{}^-$	4·71	0	5·58									
$^3E_{2g}{}^+$	5·961	0	6·71		5·517	0	5·714	0·1039	5·872	0·283		
$^3E_{2g}{}^-$	8·359	0·807	8·82		6·970	1·9100	7·363	1·8640	7·884	1·849		
$^3B_{1u}{}^+$	10·170	0	9·88	$(^3A_{1g})$								

[x]—Ref. 17

[y]—Ref. 16

[z]—Ref. 21

* Other T → T transitions are symmetrically forbidden and, therefore, are not included in this Table. However, their magnitudes can be known from Table 2

TABLE 4. COMPARISON OF THE PARAMETERS (ev) USED IN THE PRESENT AND PREVIOUS WORK

	Pariser Parr[a]	Pariser and Semiempirical[b]	Anno and Sado[c]	Donath[d]	Mataga[e]	Theoretical[f]	Present work
$-\beta$ or $\frac{1}{2}\Delta$	2·390	2·370	2·733	2·48	2·388	2·734	2·095
K_1	1·245	1·300	1·348		1·463	2·688	1·300
K_2	0·445	0·560	0·498	Same as (a)	0·865	1·333	0·560
K_3	0·325	0·590	0·365		0·741	1·007	0·590

[a] Ref. 8

[b] Refs 7 and 22

[c] Ref. 12

[d] Ref. 13

[e] N. Mataga and K. Nishimoto, *Z. Physik-chem, Frankfurt* **13**, 140 (1957)

[f] Ref. 5

DISCUSSION

Semiempirical calculations[8–17] on PPP scheme including singly excited configurations give quite good results for the lower excited states of benzene. To get equally good result after inclusion of higher excited states by semiempirical method one is forced to increase the value of β[12–15] (here $-\frac{1}{2}\Delta$). This is because the electron repulsion integrals are given fixed values and only β is kept as a parameter which is adjusted to reproduce one of the observed levels. Our method of parametrisation, however, is completely different from those employed in the previous calculations.[8–17] We have employed all the four observed levels to determine the molecular integrals and have got a lower value of β owing to the inclusion of limited number of configurations which have kept the lower observed levels unperturbed. The three other integrals K_1, K_2 and K_3 are also slightly different in the present case from others (Table 4). In fact, the semiempirical calculation of this type where all the molecular integrals have been determined empirically can be applied in general to benzene-like molecules for the determination of their higher excited states and the spectra of their ions. But one drawback with such method is that in most of the molecules, the molecular integrals to be determined are generally more in number than the observed levels and this causes difficulty in their evaluation.

From Table 3 one can see that the inclusion of atomic orbital overlap in the molecular core integrals has a pronounced effect on the intensities and transition energies of the triplet-triplet transition. However, these changes in transition energy and oscillator strength are not at all regular with respect to the inclusion of different degrees of overlap and no definite conclusion can be made regarding this effect. It is difficult to compare at this moment our result with that observed by Porter *et al.*[21] The oscillator strength of the observed triplet-triplet transition is not known but the reported value[21] of extinction coefficient ($\varepsilon \approx 1300$) suggests the observed transition to be fairly strong. From our results one can see that we have predicted some very intense transitions which are not observed. So in the present situation, we may ascribe the band observed by Porter *et al.* to be our second excited E_{2g} triplet. It will be interesting to see the results of such calculations after inclusion of configurations higher than the doubly excited ones.

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REFERENCES

[1] M. Geoppert-Mayer and A. L. Sklar, *J. Chem. Phys.* **6**, 645 (1938)
[2] A. L. Sklar, *Ibid.* 7, 984 (1939)
[3] C. C. J. Roothaan and R. G. Parr, *Ibid.* 17, 1001 (1949)
[4] K. Nira, *J. Phys. Soc. Japan* **8**, 630 (1953)
[5] R. Parr, D. P. Craig and I. Ross, *J. Chem. Phys.* **18**, 1561 (1950)
[6] [a] R. Pauncz, J. de Heer and P. O. Lowdin, *Ibid.* **36**, 2247 (1962)
[b] *Ibid.* **37**, 2739 (1962)
[c] J. de Heer, *Ibid.* **66**, 2288 (1962)
[7] J. W. Moskowitz and M. P. Barnett, *Ibid.* **39**, 1557 (1963)

[8] R. Pariser and R. G. Parr, *Ibid.* **21**, 466, 767 (1953)

[9] J. A. Pople, *Trans. Farad. Soc.* **49**, 1375 (1953)

[10] H. Kon, *Bull. Chem. Soc. Japan* **28**, 274 (1955)

[11] J. N. Murrel and K. L. McEwen, *J. Chem. Phys.* **25**, 1143 (1956)

[12] T. Anno and A. Sado, *Ibid.* **39**, 2293 (1963)

[13] W. E. Donath, *Ibid.* **40**, 77 (1964)

[14] J. Koutecky, J. Cizek, J. Dulsky and K. Hlaraty *Theor. Chim. Acta, Berlin* **2**, 462 (1964)

[15] J. Koutecky, J. Cizek and K. Hlaraty *Ibid.* **3**, 341 (1965)

[16] W. E. Donath, *J. Chem. Phys.* **42**, 118 (1965)

[17] R. Pariser, *Ibid.* **24**, 250 (1956)

[18] G. Porter and M. W. Windsor, *Proc. Roy. Soc.* **A245**, 238 (1958)

[19] W. A. Gibbon, G. Porter and M. I. Saradatti, *Nature, Lond.* **206**, 1355 (1965)

[20] W. A. Noyes, Jr., and I. Unger, *Adv. in Photochem.* **4**, 49 (1966)

[21] T. S. Godfrey and G. Porter, *Trans. Farad. Soc.* **62**, 7 (1966)

[22] M. K. Orloff, *J. Chem. Phys.* **47**, 235 (1967)

[23] R. G. Parr, *Quantum Theory of Molecular Electronic Structure*, p. 62. Benjamin (1963)

[24] L. Salem, *Molecular orbital theory of conjugated system*, p. 358. Benjamin (1966)