THE NEAR ULTRAVIOLET SPECTRA OF BENZENE, PART II

A COMPARATIVE STUDY OF THE ABSORPTION, EMISSION AND FLUORESCENCE BANDS

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ABSTRACT. A comparative study is made of the ultraviolet benzene bands recorded in absorption, emission and fluorescence, as regards the distribution of intensity and the development of vibrational levels. It is found that the intensity distribution in the emission spectrum is substantially different from that in the absorption spectrum at room temperature and appears to be governed by the Boltzmann factor in the excited state and the Franck-Condon principle. The intensity distribution also differs from that of fluorescence bands in which the distribution is generally governed by the conditions of excitation. The emission spectrum gives data for a more complete picture of the state of the molecule and the selection rules governing the transition to which all the three spectra are due.

The region of the near ultraviolet absorption spectrum of benzene is between 2765Å and 2218Å and the corresponding emission spectrum lies in the region 2536Å to 3180Å. Hence there is a considerable stretch of region which is common to both the spectra.* The first bands of the *E* series lie outside this region whereas the first bands of the series *A*, *B*, *C*, *D*, *G*, *H*, α and β lie in this region. Among them B^0_0, B^0_1 and B^0_2 with their associated 160 quanta and A^0_{-1}, A^0_{-2}, C^0_0 and G^0_0 are common to both spectra. In *D* system D^0_0, D^0_1, D^1_2 are common with the associated 160 progressions as also α^0_0 and β^0_0 (*cf*. Table I).

The most prominent bands involving e^+_g vibration which are absent in the emission spectrum are A^n_0 ($n = 0, 1, 2 \ldots$). These bands are very strong in absorption, A^0_0 being the strongest. Similarly in C^n_0 series, C^0_0 is present and is very weak in emission but the higher members are absent. In the B^n_2 series the members higher than B^1_2 and in G^n_0 series members other than G^1_0 and also the members of the *E* series lying in this region are absent in emission although they are present in absorption. The band corresponding to the excitation of 1178 e^+_g vibration is found in absorption but not in emission. The bands corresponding to 1 – 1 transition of 849 vibration which are prominent in absorption in this region are not present in emission. The bands which are present in emission but are not observed in absorption are

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* The analysis of emission bands is given in Part I. The results of analysis of absorption bands proposed by Sponer *et al* and Radle and Beck, extended by Garforth and Ingold with which our own analysis agrees are utilised in this part.

TABLE I

Development of Different Band Systems in Various Near Ultraviolet Electronic Spectra of Benzene (Comparative Study)

Absorption (Radle and Beck)	Emission (present investigations)	Fluorescence (Ingold Wilson)	Emission (Austin and Black)
$A^0_0-A^4_0$		$A^0_0-A^7_0$	
$A^0_1-A^5_1$ $A^0_{-1}-A^3_{-1}$	$A^0_{-1}-A^3_{-1}$	$A^0_{-1}-A^6_{-1}$	
$A^0_2-A^5_2$	$A^0_{-2}-A^2_{-2}$	$A^0_{-2}-A^6_{-2}$	
$A^0_3-A^5_3$		$A^0_{-3}-A^3_{-3}$	
$A^0_4-A^3_4$		$A^0_{-4}-A^3_{-4}$	
$A^0_5-A^2_5$		$A^0_{-5}-A^3_{-4}$	
A^0_6			
$A^0_{1-1}-A^3_{1-1}$			
$A^0_{2-1}-A^4_{2-1}$			
$A^0_{3-1}-A^3_{3-1}$			
$A^0_{4-1}-A^2_{4-1}$			
$A^0_{1-2}-A^1_{1-2}$			
$A^0_{2-2}-$			
$A^0_{3-2}-A^3_{3-..}$			
$B^0_0-B^4_0$	$B^0_0-B^5_0$	$B^0_0-B^6_0$	$B^0_0-B^4_0$
$B^0_1-B^3_1$	$B^0_1-B^4_1$	$B^0_1-B^7_1$	$B^0_1-B^2_1$
$B^0_2-B^4_2$	$B^0_2-B^1_2$		$B^0_2-B^1_2$
$B^0_3-B^2_3$			
$B^0_4-B^2_4$			
$B^0_{2-1}-B^2_{2-1}$		$B^0_{2-1}-B^3_{2\ 1}$	
		$B^0_{2-2}-B^3_{2-2}$	
		$B^0_{2-3}-B^2_{2-3}$	
$C^0_0-C^4_0$	C^0_0	$C^0_0-C^6_0$	
$C^0_1-C^4_1$ $C^0_{-1}-C^3_{-1}$	$C^0_{-1}-C^2_{-1}$	$C^0_{-1}-C^6_{-1}$	C^0_{-1}
$C^0_2-C^3_2$ C^0_{-2}	$C^0_{-2}-C^3_{-2}$	$C^0_{-2}-C^6_{-2}$	C^0_{-2}
$C^0_3-C^3_3$	$C^0_{-3}-C^2_{-3}$	$C^0_{-3}-C^1_{-3}$	$C^0_{-3}-C^2_{-3}$
	$C^0_{-4}-C^2_{-4}$	$C^0_{-4}-C^4_{-4}$	
$C^0_{1-1}-C^4_{1-1}$	$C^1_{1-1}-C^5_{1\ 1}$		
$C^0_{1-2}-C^1_{1-2}$			
$C^0_{2-1}-C^2_{2-1}$			

TABLE I (*contd.*)

Absorption (Radle and Beck)	Emission (present investigations)	Fluorescence (Ingold Wilson)	Emission (Austin and Black)
$C^0_{3-1}-C^4_{3-1}$			
$D^0_0-D^2_0$	$D^0_0-D^4_0$	$D^0_0-D^4_0$	$D^0_0-D^3_0$
$D^0_1-D^3_1$ D^0_{-1}	$D^0_1-D^4_1$ $D^0_{-1}-D^3_{-1}$	$D^0_{-1}-D^5_{-1}$	$D^0_1-D^4_1$ $D^0_{-1}-D^1_{-1}$
$D^0_2-D^3_2$	D^0_2 $D^0_{-2}-D^2_{-2}$	D^0_{-2}	D^0_2 $D^0_{-2}-D^1_{-2}$
$D^0_3-D^2_3$	$D^0_{-3}-D^2_{-3}$		$D^0_{-3}-D^1_{-3}$
D^0_4	$D^0_{-4}-D^2_{-4}$		
$D^0_{1-1}-D^1_{1-1}$	$D^0_{1-1}-D^3_{1-1}$		
$D^0_{2-1}-D^1_{2-1}$			
D^0_{3-1}			
$D^0_{4-1}-D^3_{4-1}$			
$E^0_0-E^3_0$			
$E^0_1-E^1_1$ E^0_{-1}			
E^0_3			
$E^0_{2-1}-E^1_{2-1}$			
$\alpha^0_0-\alpha^1_0$	$\alpha^0_0-\alpha^5_0$	$\alpha^0_0-\alpha^5_0$	$\alpha^0_0-\alpha^3_0$
	α^0_2 $\alpha^0_{-1}-\alpha^4_{-1}$	$\alpha^0_{-1}-\alpha^5_{-1}$	$\alpha^0_{-1}-\alpha^2_{-1}$
	α^0_2 $\alpha^0_{-2}-\alpha^2_{-2}$	$\alpha^0_{-2}-\alpha^2_{-2}$	$\alpha^0_{-2}-\alpha^2_{-2}$
	$\alpha^0_{1-1}-\alpha^1_{1-1}$		$\alpha^0_{1-1}-\alpha^1_{1-1}$
	$\alpha^0_{1-2}-\alpha^1_{1-2}$		$\alpha^0_{1-2}-\alpha^1_{1-2}$
α^0_{2-1}			
α^0_{2-2}			
β^0_0	$\beta^0_0-\beta^5_0$	$\beta^0_0-\beta^5_0$	$\beta^0_0-\beta^4_0$
$\beta^0_1-\beta^3_1$	$\beta^0_{-1}-\beta^3_{-1}$	$\beta^0_{-1}-\beta^5_{-1}$	$\beta^0_{-1}-\beta^2_{-1}$
	$\beta^0_{-2}-\beta^3_{-2}$	$\beta^0_{-2}-\beta^4_{-2}$	$\beta^0_{-2}-\beta^2_{-2}$
	$\beta^0_{-3}-\beta^2_{-3}$		$\beta^0_{-3}-\beta^2_{-3}$
	$\beta^0_{-4}-\beta^2_{-4}$		$\beta^0_{-4}-\beta^1_{-4}$
	$\beta^0_{1-1}-\beta^2_{1-1}$		$\beta^0_{1-1}-\beta^1_{1-1}$
	$\beta^0_{1-2}-\beta^1_{1-2}$		$\beta^0_{1-2}-\beta^1_{1-2}$
	$\beta^0_{1-3}-\beta^2_{1-3}$		

TABLE I (*contd.*)

Absorption (Radle and Beck)	Emission (present investigation)	Fluorescence (Ingold Wilson)	Emission (Austin and Black)
	$\beta^0_{2-1} - \beta^3_{2-1}$		
$G^0_0 - G^2_0$	G^0_0		
$G^0_1 - G^2_1$			
$G^0_2 - G^2_2$			
$G^0_3 - G^1_3$			
G^0_{1-2}			
$H^0_0 - H^3_0$	H^0_0	$H^0_0 - H^2_0$	
$H^0_1 - H^1_1$		$H^0_{-1} - H^2{}_1$	
$H^0_2 - H^1_2$			
$H^0_3 - H^1_3$			
$A'_0{}^0 - A'_0{}^1$	$A'_0{}^0 - A'_0{}^4$		
$A'_1{}^0 - A'_1{}^1$	$A'_{-1}{}^0 - A'_{-1}{}^2$		
$A'_2{}^0$			
$B'_0{}^0$	$B'_0{}^0 - B'_0{}^2$		
$B'_1{}^0$ $B'_{-1}{}^0$	$B'_1{}^0 - B'_1{}^1$		
$B'_2{}^0$			
$C'_0{}^0$			
$C'_1{}^0$			
$D'_0{}^0$	$D'_0{}^0 - D'_0{}^2$		
$D'_1{}^0$			
	$\alpha'_0{}^0 - \alpha'_0{}^3$		
	$\alpha'_1{}^0 - \alpha'_1{}^2$ $\alpha'_{-1}{}^0 - \alpha'_{-1}{}^2$		
	$\alpha'_2{}^0 - \alpha'_2{}^3$		
	α'^0_{1-1}		
	$\alpha'^0_{2-1} - \alpha'^2_{2-1}$		
	$\beta'_0{}^0 - \beta'_0{}^2$		
$I^0_0 - I^2_0$			
$I^0_1 - I^3_1$ $I^0_{-1} - I^3_{-1}$			
$I^0_2 - I^2_2$ $I^0_{-2} - I^3_{-2}$			
$I^0_{1-1} - I^2_{1-1}$			
	$K^0_0 - K^2_0$		$K^0_0 - K^2_0$
	$K^0_1 - K^1_1$ $K^0_{-1} - K^0_{-1}$		$K^0_{-1} - K^2_{-1}$
	$K^0_{-2} - K^1_{-2}$		

TABLE I (*contd.*)

Absorption (Radle and Beck)	Emission (present investigations)	Fluorescence (Ingold Wilson)	Emission (Austin and Black)
	(530−671 a_2^u)		
520+2 × 513	−606−2×671		
,, ,, +923			
1045+2 × 513 (2)*	−1178+2 × 513,		
3047+2 × 513	1045−2×671		
	(1001−1010 b_{1u})		
	+520−2 × 1010		
- 606 + 2 × 1001			
	−1596−2 × 1010		
-1596+2 × 1001 (2)*			
-1178+2 × 1001			
	−3047−2 × 1010		
	(774−983 b_{2g})		
	520−2 × 985		
520+2 × 774 (2)*			
,, ,, 923			
	−1596+2 × 774		
1476+2 × 774			
,, ,, 923			
-1596+2 × 774			
,, ,, 923			
1045+2 × 774 (2)*			
,, ,, 923			
	−3047+2 × 774		
	(364−703b_{2g})		
− 606+2 × 364	−606−2 × 703		
	+520+2 × 364,		
−1596+2 × 364	+520−2 × 703		
1476+2 × 364	1596−2 × 703		
−1178+2 × 364			
+1045−703+364 (2)*			
	+3047+2 × 364		

* These denoted the number of hands in the 160 progression.

TABLE I (*contd*).

Absorption (Radle and Beck)	Emission (present investigation)	Fluorescence (Ingold Wilson)	Emission (Austin and Black)
	(?$-1648\ b_{2u}$)		
	$+520-2\times1648$		
	$-606-2\times1648$		
	$1045-2\times1648$		
	(?$-1110\ b_{2u}$)		
	$-606-2\times1110$		
	$-1596-2\times1110$		
	$-3047-2\times1110$		
	(?$-1326\ a_{2g}$)		
	$+520-2\times1326$		
	$-606-2\times1326$		
	(non-totally symm degenerate vibrations)		
$-849+586$ (2)*	$-849+586$	-2×849 (5)*	
		$-2\times849-992$	
-2×586 (3)*		$-849+586$	
$-2\times586+923$ (3)*		$-606-264$	
$-2\times586+2\times923$		,, -992	
$-606+2\times586$			
$+520+2\times586$			
,, ,, $+923$			
,, ,, $+2\times923$			
	$0+2\times240$ $0-2\times404$	$0+2\times240$	
	$0-2\times3080$		

$0-2\times404$ corresponding to $\Delta V = 2$ of the e_u^+ frequency, the $\alpha^0_0+2\times240$ and $\beta''_0+2\times240$ bands and the 160 progression of the α^0_0 and β^0_0 series (*cf.* Table I).

This shows that the intensity distribution in the two spectra is not the same. This can be clearly seen from the study of the relative intensities of the prominent bands of different series which are common to both the spectra. The relevant data are given in Table II. The intensities marked are only

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* These denote the number of bands in the 160 progression.

useful for the study of the relative intensities of different band groups and of the relative intensity distribution amongst the bands in the group. The intensities in the present experiments have been visually estimated and the values given are, therefore, very rough. The intensities marked by Radle and Beck seem to be more reliable since their method of estimation is more accurate.

TABLE II

Series	I absorption	I emission	Series	I absorption	I emission	Series	I absorption	I emission	Series	I absorption	I emission	Series	I absorption	I emission	Series	I absorption	I emission
A^0_0	7500	abs	B^0_0	420	10	C^0_0	650	0	D^0_0	55	6	α^0_0	4	8	β^0_0	3	8
			B^0_1	550	8.5	C^0_1	675		D^0_1	130	5	α^0_1	abs.	0	β^0_1	7	abs.
			B^0_2	350	4				D^0_2	40	2						
A^0_1	85	3				$C^0{}_{-1}$	4	2	$D^0{}_{-1}$	0	5						
A^0_2	3	2.5				$C^0{}_2$	1	3.5									

The intensities (I) given for bands in absorption spectrum are from Radle and Beck. (1940). They have given intensity 7500 to the strongest band A_0^0.

The intensities (I) given for bands in emission spectrum are those observed in the present experiments (Asundi and Padhye, 1949) the intensities being relative to the B^0_0 the strongest band being 10.

Making due allowance for these facts certain conclusions can be drawn from this Table. Thus,

(1) In absorption A^0_0 and C^0_0 bands are stronger than B^0_0 and D^0_0 whereas in emission B^0_0 and D^0_0 are definitely more intense than A^0_0 and C^0_0.

(2) $A^0{}_{-1}$ and $C^0{}_{-1}$ decrease in intensity in absorption whereas they increase in intensity in emission. The positive members of these series do not lie in the spectral region of the emission spectrum.

(3) Taking either α^0_0 or β^0_0 as $B^0{}_{-1}$ (since it is due to Fermi degeneracy between 1596 and 606+992=1598, $B^0{}_{-1}$), it is seen that $D^0{}_{-1}$ and $B^0{}_{-1}$ decrease in intensity more rapidly in absorption than in emission.

(4) B^0_1 and D^0_1 have greater intensity than B^0_0 and D^0_0 in absorption but are slightly weaker than B^0_0 and D^0_0 in emission.

(5) For B^0_2 and D^0_2 the intensity falls both in absorption and emission compared to B^0_1 and D^0_1.

(6) The band involving 1596 (either α^0_0 or β^0_0) is relatively stronger in emission than in absorption.

The bands B^0_0, D^0_0, α^0_0 and β^0_0 lie to the long wave-length limit of the absorption spectrum and bands A^0_0 and C^0_0, to the short wavelength limit of the emission spectrum. This cannot be a sufficient argument for the weakness of the bands in the corresponding spectra more so in the emission spectrum because the bands $B^0{}_2$, $D^0{}_2$ and $B^1{}_2$ which are still to the shorter weavelength side than $A^0{}_0$ and $C^0{}_0$ bands come out with appreciable density.

In the *A* series the 520 frequency in the upper state is excited and transition takes place between this and the zero level of the ground state. In *C* series the fundamental transition is 606 (ground)—2 × 520 (excited), ni *B*, 606—0 and in *D*, 2 × 606—520. It is found that transition involving high frequencies of excited state and of low ground state are stronger in absorption than in emission (*vide* Table II). This is to be expected on the basis of the Boltzmann factor. Similarly transitions involving frequencies of low excited states and high ground state are stronger in emission than absorption. This fact seems to agree well with Sponer's (1939) hypothesis that in flourescence (hence also in emission) the 1-0 and 0-1 transitions of the $e_{g}{}^{+}$ vibration should occur with inverted intensities corresponding to the Boltzmann distribution in the upper state. The relative intensities of the groups on this basis should decrease in the following order *B*, *α*, *β*, *D*, *A*, *C*. This is also generally borne out by the data. An interesting observation is that *D* which involves two quanta of 606 in the ground state is stronger than *A* which involves no ground state frequency, although both contain one quantum of 520 in the excited state. This illustrates the operation of the Franck-Condon principle in addition to the Boltzmann equilibrium in the excited state. This inversion of intensity may be even perhaps due partly to self-absorption although in the present experiments such a possibility is rather remote.

With the superposition of the 992 frequency in the ground state, the intensity of all the four *A*, *B*, *C*, and *D* series decreases in absorption. But in emission the intensity increases in *A* and *C* series for the first quantum of 992 and decreases for the second quantum ; while it decreases uniformly for *B* and *D* the decrease is not so rapid as in absorption. The superposition of the 923 quantum in the upper state raises the intensity of the $D^0{}_0$, $B^0{}_0$ and $C_0{}^0$ bands in absorption for the first quantum after which it falls. In emision it falls uniformly, This seems to agree with another observation by Sponer *et. al.* (1939) that in absorption the second member of the 923 progression is the strongest while in emission it should be the second member of the 992 progression which should be by far the most outstanding in intensity. The agreement is not strictly complete since the intensities of B^0_{-1} and D^0_{-1} are slightly less than of $B_0{}^0$ and $D_0{}^0$ in emission. In absorption, however, the agreement is uniformly satisfactory.

Turning to fluorescence spectrum in relation to emission spectrum, we find that the region of both the spectra is the same.* The flourscence

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* The data of Ingold *et al* are used to analyse these bands along the lines adopted for absorption and emission. The general trend of analysis is indicated by Sponer *et al*, a detailed analysis agrees with that of Garforth and Ingold.

spectrum gives a large number of bands belonging to A series while the emission spectrum does not. On the other hand, the D series is more prominent in emission than in fluorscence. The emission spectrum also shows two intense parallel systems of bands due to Fermi resonance extending to high quanta of vibrations in the ground state whereas in fluorescence they are limited to two quanta. Similarly the 3062 a_{1g} (the value of which has been found to be 3054 in present experiments) which is expected to be present in fluorescence is not unambiguously found. In the case of emission all the bands belonging to (') series are due to the excitation of this frequency in the ground state. In emission a number of non-totally sýmmetrical degenerate and nondegenerate frequeneies are excited. Such is not the case in fluorescence.*

The intensity distribution in the fluorescence spectrum is rather irregular. This has been already pointed out by Sponer *et al* and they say "The explanation of the relative intensities of the different band groups in the fluorescence spectrum is somewhat complicated. This is due to the fact that the bands are a result of mechanism of excitation, subsequent collision, and reabsorption. As we should expect B^0_0 series is the strongest in the spectrum." Furthermore, the scale of intensity adopted by Ingold and Wilson (1936) seems to be different from that of Wilson (1936) and since for a comparison of intensities in the emission and fluorescence spectra it will be necessary to consider all the fluorescence bands, it is not possible or profitable to discuss the relative intensity distribution in the two spectra. However, it appears that the course of intensity-decrease in fluorescence follows the order B, α β, C, A, and D while in emission bands the order is B, α β, D, A and C, α β being Fermi doublets practical of equally intensity and represent vibration mixtures.

Thus experimentally it is found that the emission spectrum obtained and discussed in Part I of this series (Asundi and Padhye, 1949) shows a great advantage over the high pressure fluorescence in the matter of excitation of the numerous ground level frequencies. It also gives a picture of intensity distribution since it is neither influenced by selection rules nor by self-absorption to a very great extent. The latter can be eliminated by the proper adjustment of the experimental conditions. The electrical method of excitation develops also the weaker bands which are not found in fluorescence and thus it gives a more complete picture of the state of the molecule and the selection rules governing such a transition.

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* It may be noted that even though the same dispersion and resolution was used in both the cases, the bands in fluorescence naturally show a very open structure while in the present case they are far from being resolved.

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