

THE NEAR ULTRA-VIOLET SPECTRA OF TOLUENE PART I. THE ABSORPTION BANDS WITH PARTI- CULAR REFERENCE TO THE NEW BANDS OBSERVED.

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Plate XIV

ABSTRACT. The absorption spectrum of toluene has been studied between the temperatures 0°C and 250°C and different initial vapour pressures. It was only after the investigations were being undertaken that a paper by Ginsberg, Matsen and Robertson appeared. These authors have recorded and analysed a large number of bands. In addition to these bands, about twenty new bands on the longer wavelength side are also recorded on our plates. These bands have been tabulated and analysed. The main results of the work are as follows:

- (1) The bands involve a combination of two or more quanta of vibrations in the ground state.
- (2) The intensity consideration leads to the classification of the band at 35202 cm^{-1} as due to the excitation of a single quantum of vibration with frequency 2273. Thus a new vibration frequency is proposed.
- (3) Some bands are classified as due to the excitation of the non-totally symmetrical frequencies not included in the analysis of the previous workers.
- (4) Incidentally a complete analysis of the already known absorption bands is also given and the results are discussed.

INTRODUCTION

The absorption spectrum of toluene recorded by Savard (1929) was first suggestively analysed by Sponer (1942) who gave also a theoretical discussion. The analysis comprises only a few bands. Sometime after an experimental investigation on these bands was undertaken by us, a paper dealing with the same subject was published by Ginsberg, Matsen and Robertson (1946). They have recorded a large number of absorption bands of toluene. They also give a detailed analysis of the bands observed by them which confirms the first suggestive analysis by Sponer. The wavelength data recorded by them go up to 2760 \AA . In our experiments we have obtained the data extended on the longer wavelength side up to 2891 \AA at higher temperatures thus recording 20 new bands. As they were thought likely to yield more informations regarding the vibrational levels in the ground state of the molecule, they are measured and reported here. The bands observed by Ginsberg and others are also recorded on our plates but they have not been measured.

EXPERIMENTAL

An all-quartz absorption cell of 10 cms. length was used. A few drops of the liquid were put in the cell which was then evacuated and sealed off.

For the development of the bands on the longer wavelength side, the cell was sealed off when there was a small amount of liquid still left in it at room temperature (28°C). It was not possible to estimate the exact pressure of the vapour in the cell but no bands on the longer wavelength side of the already known bands were recorded at room temperature. The cell was then enclosed in an electric furnace. When the temperature of the cell was in the range of 90°C–150°C the band-system developed new bands towards the longer waves. At still higher temperatures, continuous absorption sets in. Toluene supplied by the Fine Chemicals Section of this University was used without further purification. A Hilger medium quartz spectrograph was the recording instrument and Eastman III-O and Kodak Special Rapid plates were employed.

The source of continuous radiation was a locally prepared π type hydrogen discharge tube run on a transformer delivering about 6,000 volts.

Two suitable plates were measured on a Hilger comparator (least count .0001 cm.), one of them twice, and the data presented in Table I are the mean of the three values thus obtained for each band. The intensity data are those visually estimated relatively on the basis of the 0,0 band at 37475^{cm} taken as 10. From the average difference in wavenumbers found in the three readings, it is estimated that the values of wavenumbers recorded are correct to within ± 3 .

THEORY OF THE SPECTRUM

Due to the substitution of CH_3 in place of one of the H atoms of benzene, the symmetry D_{6h} is reduced to C_{2v} . This group has three elements of symmetry namely the two-fold axis and a plane of reflection perpendicular to the molecular plane. There can be only four different kinds of vibrations possible; one, a_1 , being totally symmetrical and the others a_2 , b_1 and b_2 being non-totally symmetrical. All the vibrations are non-degenerate. The transition $A_{1g} - B_{2u}$ of benzene in this symmetry becomes $A_1 - B_1$ and is allowed, as also the transitions involving a_1 vibrations which have the transition moment lying in the plane of the ring in a direction perpendicular to the C- CH_3 bond. The direct product Table shows that transitions involving b_1 and a_2 types of vibrations are also allowed since the direct product transforms like a translation but the moments in this case lie in the other two perpendicular directions and hence these transitions give rise to weak bands. The symmetry considerations show that the transitions involving single excitation of b_2 vibration should be forbidden since the transition integral is not invariant for any of the three moments.

Since this point group has no degenerate vibrations, most of the degenerate vibrations of benzene are split up into one totally symmetrical a_1 and one non-totally symmetrical vibrations. As in benzene, it can be expected that these large number of a_1 vibrations will give rise to intense bands due

* Positions of bands are given in units of cm^{-1} in this paper.

to 1-0 or 0-1 transition and also the combinations of these vibrations. Theoretically we can expect to find weaker bands due to non-totally symmetrical vibrations of the type a_2 and b_1 . An interesting feature of this part of the spectrum is that there is comparatively a strong band corresponding to the frequency of 620.* This vibration has been classified as the b_1 part of the split 606 e_g^+ vibration of benzene. In most of the mono-substituted benzenes so far studied, this is the only non-totally symmetrical vibration which has been found to be prominently excited. The other totally symmetrical frequencies are superposed on this. This part of the spectrum is quite analogous to that of benzene and the intensity of this transition shows the extent to which the substitution has brought about perturbation in the six-fold symmetry of the ring. This also shows that some of the characteristics of the benzene spectrum are still carried in the spectra of its mono-substituents.

REMARKS ON THE ANALYSIS OF THE ABSORPTION BANDS OF TOLUENE

Pitzer and Scott (1943) classified the fundamental frequencies of toluene, as obtained from investigations of infra-red and Raman spectra, according to the various symmetry classes appropriate to the structure of the molecule and have compared the frequencies with corresponding ones of benzene. From the analysis of its absorption spectrum, Ginsberg *et al* (1946) have proposed values for the frequencies in the excited state of the molecule. They find that of the ground state frequencies, six a_1 vibrations are given by the absorption spectrum and in the excited state five of these are obtained. These five ground state vibrations which can also be recognised in the excited state with altered frequencies are 514, 785, 1003, 1012 and 1212. The 1176 vibration does not seem to have its excited frequency represented in the absorption spectrum.

Among the non-totally symmetrical vibrations in the ground state, a frequency of 620, classified as corresponding to e_g^+ 606 frequency of benzene, is found to be very prominent. Its value in the excited state as identified by Ginsberg is 528. Superimposed on the 0-1 and 1-0 transitions of this vibration appear the already mentioned totally symmetrical vibrations. The analysis of the absorption spectrum shows that some more non-totally symmetrical frequencies are also probably excited. Ginsberg found that the frequencies 845, 988 a_2 and 1062 b_1 were detectable in the spectrum. But since the bands involving these frequencies also afford a possible analysis in terms of totally symmetrical vibrations, the latter classification is preferred by them.

Ginsberg (1936) and others have classified some bands as due to intercombination of these frequencies. They also note that the stronger bands are

* Frequencies are given in cm^{-1} units.

accompanied towards the longer wavelengths, by fairly intense bands at spacings of 59 and 178. These are suggested to be due to difference frequencies. The high intensity of the bands involving these difference frequencies probably indicates that the bands arise in low frequency vibration. They have thus classified a large number of bands measured by them. Still some intense bands are left over and in an attempt to classify them we find that some of them involve as high as four quanta of different a_1 vibrations. It is also possible to account for some more bands on the assumption that they involve other non-totally symmetric vibrations. Such new assignments for the recorded bands of Ginsberg are included in Table II.

The excitation of the totally symmetric part of the e_g^+ frequency 514 whose value in the excited state falls to 456 shows some characteristic differences from other substituted benzene spectra (Sponer and Wollman, 1941; and Wollman, 1946). In the case of halogen derivatives it is found that the $0-1$ transition is very weak. But in the case of toluene as also aniline and phenol it is found that $0-1$ and even $0-2$ transitions are fairly intense. Similarly the halogen derivatives the $0-1$ transition corresponding to b_1 frequency 620 is weaker than $0-2$ transition but in toluene reverse is true. Sponer (1941) has explained these characteristics of the halogen derivatives on theoretical grounds.

NEW BANDS AND THEIR CLASSIFICATION

Twenty new bands have been measured on our spectrograms which were not recorded by Ginsberg *et al* (1946). The wavenumbers, intensity and the possible assignment is given in Table I. As the bands can only be observed at higher temperatures, it is probable that the higher ground level frequencies may be involved in these bands. Analysis indeed shows that in some cases the ground level has to be loaded with four quanta of different vibration frequencies to account for the bands.

In the present experiments the band at 35202 is the strongest in this part of the spectrum. It is possible to classify it as due to the excitation of 1062 b_1 together with 1212 a_1 vibration in the ground state. An alternative classification can be, excitation of two quanta of 620 b_1 with two quanta of 514 a_1 . Its high intensity is, however, incompatible with any of these classifications since both involve the excitation of non-totally symmetric frequencies b_1 which ought to be weak. In the second alternative two quanta of non-totally symmetrical vibrations are excited and the intensity of such a transition is expected to be weak since the non-totally symmetrical vibrations have their minima one above the other. Hence we are inclined to regard the band as due to a fundamental frequency of 2273 in the ground state. The band at 36160 and 36050 can then be classified as due to superposition of 932 and 964 a_1 frequencies in the excited state over this transition.

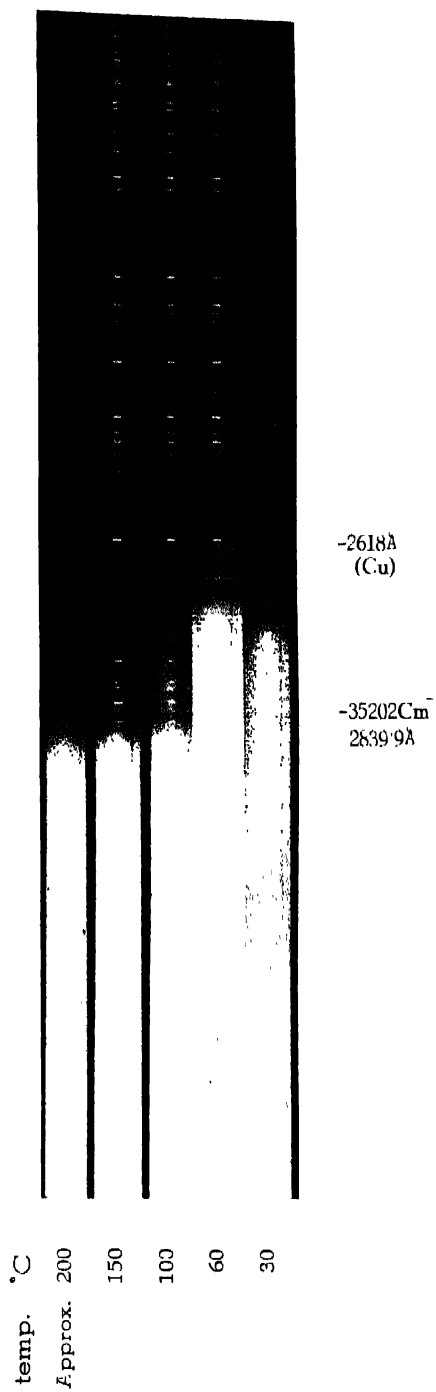


Fig. 1.

The bands next in intensity are 35087 and 35604. The one at 35087 involves an excitation of 1176 and 1212 a_1 in the ground state. There are also bands corresponding to further loading of 620 b_1 and 514 a_1 on this transition. The band at 35604 which is 1871 wavenumbers distant from the 0,0 band is also one which does not afford a convincing classification. It can be due to excitation of three quanta of 620 b_1 frequency but intensity considerations do not support such a classification. The alternative is the excitation of 1178 a_1 and 1212 a_1 in the ground state with 528 in the excited state. The discrepancy between the observed and calculated values in this case is, however, large.

The band at 35496 is in a similar category. It can be regarded as due to excitation of two quanta of 998 a_2 vibration but its fairly high intensity suggests the alternative classification of two quanta of 1212 a_1 in ground state with 456 in the excited state. Here also the numerical agreement is not satisfactory.

In considering the intensity distribution in this part of the spectrum, it must be borne in mind that this part of the spectrum is developed only at higher temperatures. The intensity, therefore, corresponds to this temperature.

There are also a number of bands due to combination of 514 a_1 with 620 b_1 frequencies and also with other totally symmetric vibrations. The complete analysis is shown in Table I.

TABLE I
New Bands in the Absorption Spectrum of Toluene

ν_{vac} cm^{-1}	Int.	Assignment proposed	Alternative assignments
34574	0	-1176-1212-514	
34658	1	-1176-1012-620	
34764	2	-1176-1012-514	
34876	1,2	-2 × 1212 + 456 - 620	-2 × 988 - 620
34983	3	-2 × 1212 + 456 - 514	-2 × 988 - 514
35087	5	-1176-1212	-2 × 1176 - 785 + 751
35202	8	-2273	-1062 - 1212 -2 × 620 - 2 × 514
35288	4	-1176-1012	
35409	2	-2 × 1003 - 1012 + 964	-2 × 1030
35496	2,5	-2 × 1212 + 456	-2 × 988
35604	5	-1176-1212+528	-2 × 620
35687	0	-1003-785	
35720	1	-514-2 × 620	
35756	1,5	-1212-514	
35827	0	-620-2 × 514	
35893	0	-1586 (b_1)	
36012	1,5	-1176-1212+932	
36050	3	-1176-1212+664	
36160	3	-2273+964	-1062-1212+964 -2 × 620 - 2 × 514 + 964
36568	0	-785-2 × 59	

TABLE II

Extended analysis of the Absorption Bands of Toluene

* Bands already analysed by Ginsberg

$\nu_{\text{obs}} \text{ cm}^{-1}$	Int.	Assignments	$\nu_{\text{calc}} \text{ cm}^{-1}$	Int.	Assignments
36268 ⁺	<i>vw</i>	-1212	37329	<i>vw</i>	-620+528-59
36301 ⁺	"	-1176, -1003-178	43	<i>vvw</i>	+932-1062
36415 ⁺	"	-1003-59	56 ⁺	<i>w</i> }	-2 × 59
65 ⁺	<i>vvwBD</i>	-1012	60	<i>w</i> }	
74 ⁺	"	-1003	81 ⁺	<i>w</i> }	-620+528
93	"	-988	84	<i>w</i> }	
36517 ⁺	"	-785-178	93	<i>vvw</i>	+932-1012
71	"	-785-2 × 59	37418 ⁺	<i>ms</i> }	-59
36631 ⁺	<i>vvw</i>	-785-59	21	<i>ms</i> }	
76 ⁺	"	-620-178	32 ⁺	<i>vvw</i>	-1003+964
92 ⁺	<i>w</i>	-785	66 ⁺	<i>s</i> }	-9
36729 ⁺	<i>vvw</i>	-1212+456	70	<i>s</i> }	
35	"	-620-2 × 59	37477 ⁺	<i>vvs</i> }	(0-0)
63	"	-2 × 620+528	37480	<i>s</i> }	+528-514
84 ⁺	<i>vw</i>	-514-178	95	<i>vw</i>	+528-2 × 178,
96 ⁺	"	-620-59	37649	"	-1189-1012
36857 ⁺	<i>w</i>	-620	37706 ⁺	<i>vvw</i>	-620+964-2 × 59
72	<i>vvwB</i>	-1062+456	60 ⁺	<i>vw</i>	+456-178
36903 ⁺	<i>vvw</i>	-514-59	85 ⁺	<i>vvwBD</i>	-620+932
63 ⁺	<i>w</i>	-514	37823 ⁺	<i>w</i>	-620+964
37121 [±]	<i>vvw</i>	-2 × 178	28 ⁺	<i>w</i> }	+520-178
51 ⁺	"	-456-785	31	<i>w</i> }	
37191	<i>vvw</i>	+932-1212	50	<i>vvwBD</i>	-2 × 1003-2 × 1189
37206	"	-620+528-178	59	<i>vw</i>	
45 ⁺	<i>vw</i>	-178-59	72	<i>vw</i>	+456-59
37299 } ⁺	<i>ms</i>	-178	75 ⁺	"	+1189-785
37302 }			37913	<i>mBD</i>	-620+2 × 528
37304 ⁺	<i>vw</i>	-3 × 59	24 ⁺	"	-514+964
15	"	-620+456	33 ⁺	<i>s</i> }	+456
25	"	-1212+2 × 528	36 ⁺	<i>m</i> }	
			48 ⁺	<i>w</i> }	+528-59
			53	<i>m</i> }	
			93 ⁺	<i>s</i> }	+528-9
			98	<i>s</i> }	

TABLE II (contd.)

$\nu_{\text{vac}} \text{ cm}^{-1}$	Int.	Assignments	$\nu_{\text{vac}} \text{ cm}^{-1}$	Int.	Assignments
38005 ⁺	$\left. \begin{array}{l} vs \\ vs \\ vs \end{array} \right\}$	0+528	38738	m'	
08			49 ⁺	wBD	+751+528-9
10			57 ⁺	$\left. \begin{array}{l} m \\ m \end{array} \right\}$	+751+528
80	$vwBD$	+932-334	59		
38173 ⁺	vw	+751-59	94	vw'	+964+528-178
38212	wD	+2×456-178	38805	$vwvBD$	+456+932-59, +2×751-178
28 ⁺	$\left. \begin{array}{l} m \\ m \end{array} \right\}$	+751	40	m	+3×456
31			38869 ⁺	m'	+456+932
33 ⁺	m'	+932-178	81	w	+932+528-59
59 ⁺	$\left. \begin{array}{l} w \\ w \end{array} \right\}$	+964-178	38932 ⁺	w'	+932+528-9
63			41 ⁺	s	+932+528
82	vw	+528+456-178	60 ⁺	wBD	+964+528-9
93 ⁺	"	+932-2×59	72 ⁺	s'	+964+528
38317 ⁺	vwv	+3×456-3×178	84 ⁺	w	+751+932-178, 2×751
21	"	+964-2×59	39065 ⁺	vwv	+456+1189-59, +3×528
38342	vwD	-1003+2×932	99	vw	+751+932-59,
51 ⁺	$\left. \begin{array}{l} m \\ w \end{array} \right\}$	+932-59	39124 ⁺	wBD	+456+1189
54			44 ⁺	$\left. \begin{array}{l} vw \\ vw \end{array} \right\}$	+2×456+751, +456+528+751-59
82 ⁺	mBD	+964-59	47		
91 ⁺	vw	+2×456	62 ⁺	m	+751+932
38402 ⁺	mBD	+932-9	39204 ⁺	s	+1189+528
09 ⁺	$\left. \begin{array}{l} vs \\ vs \end{array} \right\}$	+932	39335 ⁺	vw'	+456+3×528-178, +456+932+528-59
11			41 ⁺	$\left. \begin{array}{l} m \\ m \end{array} \right\}$	+2×932
31 ⁺	mBD	+964-9	43		
41 ⁺	$\left. \begin{array}{l} s \\ m \end{array} \right\}$	+964	67 ⁺	mBD	+932+964-9
44			75 ⁺	$\left. \begin{array}{l} msD \\ w \end{array} \right\}$	+932+964
56	$vwBD$	456+528	77		
86	"	+1189-178, +3×456-2×178	91	wD	+456+528+932
38539 ⁺	vwv	+2×528	39406 ⁺	m'	+2×964
17 ⁺	$vwvBD$	+1189-2×59	52	vw	964+1189-178
77	"	+528+751-178	39513 ⁺	$vwBD$	+2×751+528, +456+3×528
38601 ⁺	$\left. \begin{array}{l} wBD \\ wBD \end{array} \right\}$	+1189-59			
10					
66 ⁺	$\left. \begin{array}{l} s' \\ ms \end{array} \right\}$	+1189			
72					

TABLE II (contd.)

$\nu_{\text{vac}} \text{ cm}^{-1}$	Int.	Assignments	$\nu_{\text{vac}} \text{ cm}^{-1}$	Int.	Assignments
39543	<i>vw</i>	+932+1189-59	39903 ⁺	<i>s'</i>	+932+964+528
39602 ⁺	<i>ms'</i>	+932+1189	30 ⁺	<i>wD</i>	+2×964+528
39636 ⁺	<i>s'</i>	+964+1189	45 ⁺	<i>vwBD</i>	+2×751+964, +751+1189+528
62	<i>vw</i>	+751+964+528-59	40135 ⁺	<i>w'</i>	+932+1189+528
72	<i>vwBD</i>	+3×751-59	66 ⁺	<i>w'</i>	+2×751+1189
39692 ⁺	<i>m'</i>	+751+932+528	40306 ⁺	<i>wBD</i>	+2×932+964
37735 ⁺	<i>w</i>	+3×751, +528+751+964	22	<i>wD</i>	+2×1189+528-59
82	<i>vw</i>	+3×456+932	37 ⁺	<i>wBD</i>	+2×964+932
39800 ⁺	<i>w'</i>	+2×932+456	49 ⁺	<i>vwBD</i>	+751+932+1189
11 ⁺	<i>wD</i>	+456+751+1189-59	84 ⁺	,	+2×1189+528
35 ⁺	<i>w'</i>	+751+932+964	40555	<i>s'</i>	
53 ⁺	<i>wD</i>	+2×1189	65 ⁺	<i>vw</i>	+932+964+1189
72 ⁺	<i>m'</i>	+456+751+1189, +528+2×932	40816	<i>vw</i>	+2×1189+964
			41030	<i>vwv</i>	+3×1189

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