

# THE NEAR ULTRAVIOLET EMISSION SPECTRUM OF TETRALIN (TETRAHYDRONAPHTHALENE)

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## ABSTRACT

An emission spectrum of tetralin (tetrahydronaphthalene) in the near ultraviolet excited by a transformer discharge through flowing vapour has been studied and about twenty-nine bands in emission have been photographed and measured on suitable instruments. Vibrational analysis of the bands in terms of the fundamental frequencies of the molecule is proposed and is compared with those obtained in the corresponding absorption spectrum of tetrahydronaphthalene studied by the author.<sup>2</sup> The results afford further confirmation of the correctness of the analysis and particularly the assignment of the (0, 0) band proposed in the absorption spectrum of the molecule.

## INTRODUCTION

THE ultraviolet absorption spectrum of tetralin in solution has been reported by Weinstock and Boekelheide.<sup>5</sup> Its absorption spectrum in the vapour state has been reported by the author.<sup>2</sup> So far no work on emission spectrum of tetralin appears to have been reported. The present work deals with its emission spectrum excited by an uncondensed transformer discharge through the flowing vapour of the substance. The ground state vibration frequencies of tetralin are known from its infra-red and Raman spectra.<sup>4</sup> It was observed that in vapour absorption the ground state frequencies could not be identified with those found in Raman and infra-red spectra and hence the work on emission spectrum was undertaken. These investigations explain some of the peculiarities observed in the spectrum of vapour absorption.

Tetralin can be considered essentially as an *o*-dialkyl substituted benzene since the nonplanar saturated six membered ring is not expected to make any profound difference in the spectrum. The emission spectrum is hence compared with the emission spectra of *o*-xylene<sup>1</sup> and *o*-cresol<sup>3</sup> obtained by other workers.

## EXPERIMENTAL

The emission spectrum of tetralin was obtained by means of an uncondensed transformer discharge. The discharge tube was of pyrex glass and had the conventional  $\pi$ -form. It was about 80 cm. in length and about 1.5 cm. in diameter. One end of the discharge tube was sealed off while a quartz window was attached at the other end with sealing wax. As the sealing wax is attacked by the substance it was necessary to seal the quartz window repeatedly after about every six hours. The electrodes consist of hollow aluminium cylinders about 1 cm. in diameter and were about 75 cm. apart. Vertically below the electrodes, tubes of about 6 inches in length were sealed to the discharge tube to collect the liquid which is formed during the discharge. The discharge brings about a deposit of a dark reddish-brown thick liquid. The quartz window was about 3 cm. away from the nearest electrode. The substance to be investigated was contained in a side bulb attached to the discharge tube near the quartz window. The tube was evacuated by a Cenco hvac pump which was connected suitably to the other end of the discharge tube. A trap immersed in ice was also included between the discharge tube and the pump to reduce the amount of the substance escaping to the pump. The pump was kept continuously running during the period of exposure. The excitation source consisted of a variac and a 0.25 Kilowatt Hilger transformer. The discharge was maintained throughout the present investigations by applying the minimum voltage necessary. This was found to be about 2,000 volts under the continuous flow of vapour when a faint greenish glow could be seen in the discharge. Under higher voltage the discharge glow becomes brighter and there is decomposition of the substance. The emission spectrum was recorded on a Hilger medium quartz spectrograph, the exposure time needed being about 72 hours.

## RESULTS

The spectrum consists of twenty-nine fairly sharp bands in the region 2695–2895 Å, superposed by a continuum beginning at about 2700 Å and extending to beyond 2900 Å (Fig. 2). All the spectra taken were centrally superposed by the spectrum of an iron arc taking about two amperes on 220 volts D.C. This served as a source of standard lines for measuring the plates. Plates were measured on a Hilger Comparator whose least count is 0.0001 cm. Three plates were measured and the mean of the three wavelengths was taken and converted to wave numbers in vacuo using Kayser's tables. The values are correct to about  $\pm 4 \text{ cm.}^{-1}$  in the case of strong bands and about  $\pm 8 \text{ cm.}^{-1}$  in the case of weak bands. The results are recorded

in Table I. In Fig. 1, the emission spectrum obtained with present investigation and the vapour absorption spectrum obtained at room temperature with a 2 meter column are shown. The corresponding bands have been made to coincide.

TABLE I

*Near ultraviolet emission bands of tetralin (tetrahydronaphthalene)*

(Intensity visual estimation in terms of 10)

$\lambda$ in A in air	$\nu$ cm. <sup>-1</sup> in vacuo	Intensity (visual) <sub>1</sub>	Separation from (0, 0), i.e., from 36791 cm. <sup>-1</sup>	Assignment
2695.2	37092	1	301	0+301
2699.9	37027	0	236	0+236
2703.5	36978	0	187	0+187
2708.0	36916	0	125	0+125
2711.1	36874	2	83	0+92
2714.3	36831	1	40	0+45
2717.2	36791	5	0	(0, 0)
2721.0	36740	1	51	0-51
2724.2	36697	1	-94	0-94
2728.7	36636	1	-155	0-155
2731.9	36593	0	-198	0-198
2744.0	36432	0	-359	0-359
2753.3	36309	1	-482	
2762.5	36188	0	-603	
2765.9	36143	00	-648	
2772.0	36064	10	-727	0-727
2776.3	36008	1	-783	0-727-51
2779.4	35968	00	-823	0-727-94
2783.6	35914	00	-877	0-727-155
2796.5	35748	8	-1043	0-1043
2800.4	35698	1	-1093	0-1043-51
2803.7	35656	0	-1135	0-1043-94
2809.2	35586	7	-1205	0-1205
2816.7	35492	0	-1299	0-1205-94
2821.2	35435	0	-1356	0-1205-155
2854.2	35025	2	-1766	0-1043-727
2866.8	34871	2	-1920	0-1205-727
2880.4	34707	2	-2084	0-1043-1043
2893.7	34547	2	-2244	0-1043-1205

## DISCUSSION

Tetralin can be essentially considered as an *o*-dialkyl substituted benzene since even though the two ortho-positions are bridged by a nonplanar saturated six-membered ring the latter is not expected to disturb the electronic spectrum profoundly. The near ultraviolet vapour absorption spectrum reported earlier demonstrates the validity of such a deduction. In fact it is shown that the absorption spectrum shows a great similarity not only with *o*-xylene but also with other *o*-disubstituted benzenes as far as the vibrational structure of the spectrum is concerned. It was however observed that the bands involving ground state frequencies specially those on the longer wavelength side of the 0-0 band did not give the correct frequency intervals as found in Raman and infra-red spectra. This was attributed to an impurity of naphthalene in the sample of tetralin. This however, left the assignment of the 0-0 band rather tentative as also the molecular species responsible for absorption.

The near ultraviolet emission spectrum of tetralin starts with a fairly strong band at  $36791\text{ cm.}^{-1}$ . This coincides with the strongest band in absorption at  $36790\text{ cm.}^{-1}$  which is taken as the 0-0 band. Figure 1 also shows that all the bands in this group are common to emission and absorption. The emission spectrum also shows a band on shorter wavelength side of the  $36791\text{ cm.}^{-1}$  band which has a corresponding band in absorption. This shows that the emission spectrum obtained corresponds to the absorption spectrum reported. Thus the band at  $36791\text{ cm.}^{-1}$  in emission is taken as the 0-0 band in common with absorption. The medium intensity of this band in emission as compared to some of the stronger bands on the longer wavelength can be understood as due to self-absorption. The vibrational analysis further confirms the choice of the 0-0 band as would be seen presently. Thus the emission spectrum confirms unambiguously the choice of the 0-0 band.

The most intense bands on the longer wavelength side of the 0-0 band at  $36064$ ,  $35748$  and  $35586\text{ cm.}^{-1}$  are separated from the 0-0 band by  $727$ ,  $1043$  and  $1205\text{ cm.}^{-1}$ . Comparison of the data from Raman spectrum shows that these frequency intervals correspond to the frequencies of three intense Raman lines and hence represent ground state fundamentals possibly of the totally symmetric type. The bands corresponding to these ground state frequencies however are not observed in the absorption spectrum as has already been mentioned. This was explained as being probably due to the impurity of naphthalene found in the sample of tetralin employed. In the emission spectrum there are bands involving combinations of these frequencies and a few overtones. The frequencies principally involved

in the emission spectrum of tetralin and other two *o*-disubstituted benzenes which have been investigated are compared in Table II. It is observed that there is a close correspondence between the spectra. The corresponding frequencies involved in the spectra of these three compounds can be possibly correlated to the similar frequencies of the parent compound namely benzene. The above analogy thus shows that the emitter in the present case is the tetralin molecule. This also lends support to the view that the difficulty of observing ground state frequencies in absorption due to naphthalene impurity arises out of some type of interaction between these molecules.

The emission spectrum thus shows the excitation of three ground state frequencies namely 727, 1043 and 1205. The absorption spectrum principally involved the excited state frequencies 682, 951 and 1185  $\text{cm}^{-1}$  and hence these are correlated to the ground state frequencies as shown in Table III in the previous work.<sup>2</sup> Apart from these, there may be a still smaller frequency analogous to 260  $\text{cm}^{-1}$  in *o*-xylene or 278 and 192  $\text{cm}^{-1}$  of *o*-Cresol. But since the combinations of these frequencies with other frequencies are not observed it is not possible to assign them unambiguously. The Raman and Infra-red data are rather insufficient in this range and only record a frequency 263 in Raman effect. The emission spectrum however does not show any ground state frequency of that order.

It is significant to find that some of the split components corresponding to 606  $e_g^+$  frequency of benzene is involved in emission. In *o*-Cresol emission the 524  $\text{cm}^{-1}$  gives a strong band and there is also the corresponding band in *o*-xylene emission. In the emission of tetralin there are weak bands separated from 0-0 band at 482, 603 and 648  $\text{cm}^{-1}$  but none of these corresponds to Raman frequencies. They do not also give any combination band with other strong frequencies. This seems to be a unique case where none of the components corresponding to 606  $e_g^+$  frequency of benzene is excited. There are bands separated from strong bands involving the ground state frequencies 51 and 94  $\text{cm}^{-1}$  on the longer wavelength side. These small frequencies are classified as due to *v-v* transitions. The values corresponding to these in absorption were found to be 46 and 86. It is found that the difference between the ground state frequency of 727  $\text{cm}^{-1}$  and its excited state frequency of 682  $\text{cm}^{-1}$  is 45 and the corresponding difference between 1043 and 951 is 92. But it is unlikely that such high frequencies are involved in *v-v* transitions. The coincidence may be purely accidental.

TABLE II

Ortho-cresol			Ortho-xylene			Tetralin		
Ground state frequencies	Excited state frequencies	Excited state frequencies	Ground state frequencies	Excited state frequencies	Ground state frequencies	Excited state frequencies	Ground state frequencies	Excited state frequencies
Raman	U.V. emission	U.V. absorption	Raman	U.V. emission	U.V. absorption	Raman	U.V. emission	U.V. absorption
190	192	124	256	260				
274	278	202						
526	524	360	505	505	375			
584	590		582	580	505			
748	744	702 719	733	733	692	725	727	682
1044	1040	944	1052	1054	940	1039	1043	951
1154	1163	955						
1254	1261	1251	1223	1230	1195	1203	1205	1185
			1380	1365				
			1584	1600				

All frequencies are expressed as wavenumbers (cm.<sup>-1</sup>).

## SUMMARY

The near Ultraviolet emission spectrum is studied in the present investigation. The spectrum consists of sharp bands. Vibrational frequencies in the ground state have values 727, 1043 and 1205  $\text{cm}^{-1}$  and combinations and overtones of these are found to be present as discussed and mentioned in the analysis. These frequencies have been correlated with the Raman frequencies and the infra-red frequencies of the molecule. The frequencies in the emission spectra of *o*-xylene and *o*-cresol are compared with those of tetralin and similarity between them is pointed out. The results confirm the correctness of the assignment of the (0, 0) band in the absorption spectrum of tetralin.

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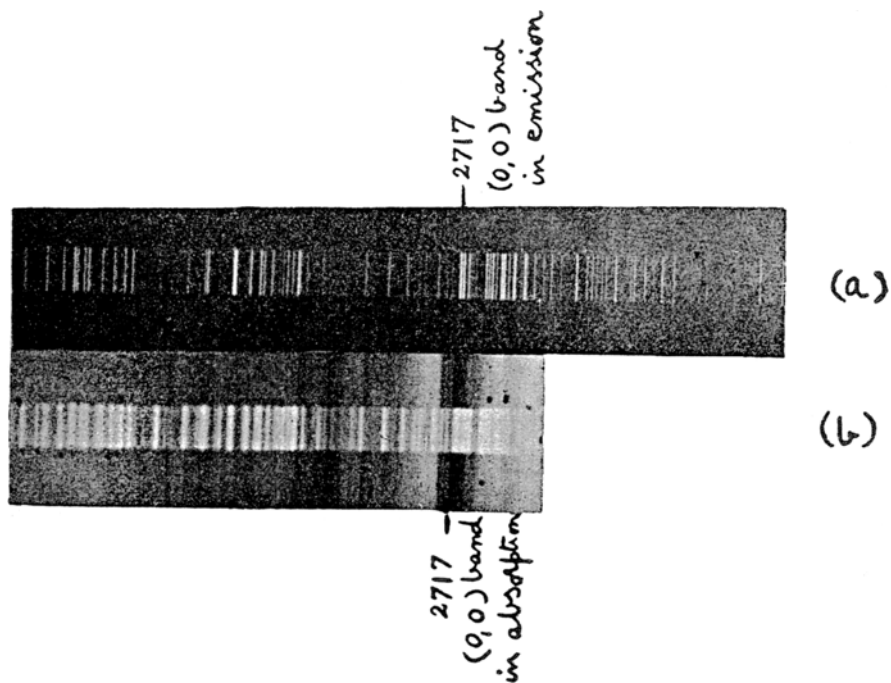


FIG. 1. (a) (0, 0) band in emission at 2717 Å.  
(b) (0, 0) band in absorption at 2717 Å in Tetralin.

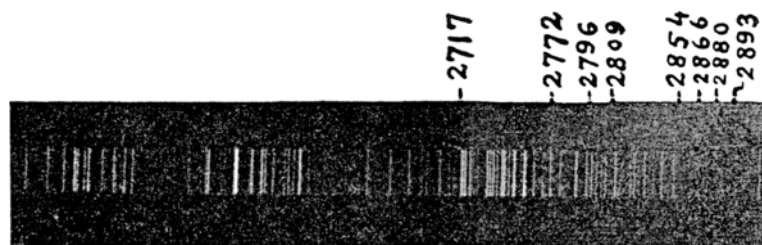


FIG. 2. Emission spectrum of Tetralin.