

THE NEAR ULTRAVIOLET ABSORPTION SPECTRUM OF TETRAHYDRO-NAPHTHALENE

BY R. N. BAPAT

(Physics Department, College of Science, Nagpur)

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ABSTRACT

The near ultraviolet absorption spectrum of tetrahydronaphthalene commonly known as tetralin consists of sharp bands in the region from 2800 to 2500 Å. The spectrum consists of about sixty bands. The maximum number of bands is obtained by using a path length of 200 cm. at room temperature which was nearly 30° C. Several of these very sharp bands have to be assigned to ν - ν transitions. The 0, 0 band is chosen to be at 36790 cm.⁻¹ Vibrational frequencies in the excited state have values 1185, 951 and 682 and combinations and overtones of these are present. Assignments of the different frequencies are discussed.

INTRODUCTION

WORK on the ultraviolet absorption spectrum of tetralin in solution has been reported by Joseph Weinstock and V. Bockcheide,¹⁵ R. A. Morton and A. J. A. de Gouveia,⁷ C. S. Marvel, Ralph Mozingo and E. C. Kirkpatrick.⁶ The absorption spectrum of tetralin in solution shows a peak at about 2740 Å with log E value nearly 2.8. So far no work on an absorption spectrum of tetralin in the vapour state appears to have been reported. The present work deals with this subject. The effects of temperature and increase in path length on the absorption in the vapour state have also been studied. With the help of the infra-red and Raman data¹² frequency assignments have been made and discussed.

EXPERIMENTAL

Tetralin is a colourless liquid with boiling point 207.2° C. The liquid was distilled and the fraction of the distillate before the boiling point was reached was discarded while the liquid distilling at the temperature corresponding to the boiling point only was taken for the experimental work. Absorption path lengths used were from 40 cm. to 200 cm. The liquid was filled in a bulb attached to the absorption tube and quartz windows were attached to both the open ends of the tube by sealing wax to carry out the experiment at room temperature. For higher temperatures varying from

30° C. to 100° C. two tubes one of 40 cm. length and the other of 160 cm. length were used. These tubes were made of pyrex glass and nichrome wire was wound over the tube. The tube could be heated to various temperatures by controlling the current by means of a variac. No windows were used and ends of the tube were open to atmosphere. There were dents provided in the tube so that the liquid could be introduced through these dents from time to time. The liquid was introduced every ten minutes and the temperature of the tube was maintained constant. The hydrogen tube prepared in this laboratory was made use of as the source for the continuum. Hilger's medium quartz and small quartz spectrographs were used to photograph the spectra with Ilford special rapid plates. Exposures of about two hours were given using Hydrogen discharge lamp and 200 cm. path length for absorption. The bands were measured by means of a Hilger comparator, copper or iron lines being used as standard lines. The wavelengths of the bands were calculated by Hartman's dispersion formula. The wavelengths of bands given in Table II represent the means obtained on five different plates and are expected to be correct to $\pm 3 \text{ cm.}^{-1}$ in the case of sharp bands and $\pm 6 \text{ cm.}^{-1}$ in the case of weak bands.

RESULTS

Tetralin absorbs in the region of 2800 to 2500 Å in solution phase. In the vapour absorption about sixty bands were obtained between 2750 to 2500 Å. At room temperature (25° C.) with a 40 cm. tube only two bands at 2717 Å and 2648 Å have been recorded (Fig. 1 *a*). As the temperature is increased to 50° C. and 70° C. the band at 2717 gets broadened while there is continuous absorption from 2717 to 2500 Å (Figs. 1 *b* and *c*). On increasing the temperature to nearly 90° C. the continuous absorption extends up to the band at 2717 towards longer wavelengths (Fig. 1 *d*). Hence a tube of 200 cm. length with sealed on windows was employed to record the spectrum at room temperature (25° C.). A side bulb attached to the tube contained a few drops of the liquid even after the tube was evacuated and sealed, the vapour pressure inside thus corresponding to the saturated vapour pressure of tetralin at 25° C. These were conditions which were favourable to bring out the maximum number of bands. A reproduction of these is given in Fig. 1 *e*. At a temperature of 70° C. and an absorption tube of 160 cm. it is observed that continuous absorption extends up to 2900 Å and that very faint bands appear on the longer wavelength side (Fig. 2). The possibility of these bands being due to an impurity suggests itself strongly on other grounds. Indeed a comparison of the wavelengths of these bands with those of naphthalene shows that within experimental

errors the values agree (Table I). It is thus very probable that the faint bands might be due to a trace impurity of naphthalene. A few of these bands are also observable in Fig. 1 e. The data on the observed bands together with the proposed assignments are given in Table II. The analysis is discussed below.

TABLE I
Absorption spectrum of naphthalene in vapour state

| (Seshan ¹¹) | | Here | |
|-------------------------|----------------------------|----------------|----------------------------|
| λ in Å | ν in cm.^{-1} | λ in Å | ν in cm.^{-1} |
| 3190 | 31320 | | |
| 3145 | 31780 | | |
| 3120 | 32020 | | |
| 3085 | 32390 | 3086.6 | 32388 |
| | | 3082.5 | 32431 |
| 3055 | 32730 | | |
| 3035 | 32930 | 3037.3 | 32914 |
| 3015 | 33150 | 3017.1 | 33134 |
| 2990 | 33440 | 2989.5 | 33440 |
| 2975 | 33640 | 2971.5 | 33643 |
| 2935 | 34060 | | |
| 2910 | 34350 | 2911 | 34342 |
| 2875 | 34750 | | |
| 2850 | 35100 | | |
| 2820 | 35410 | | |
| 2790 | 35830 | | |
| 2755 | 36280 | | |
| 2720 | 36750 | | |
| 2690 | 37160 | | |

* Probably misprint.

| (Sponer and Cooper ¹¹) | ν cm.^{-1} |
|------------------------------------|-------------------------|
| 35780 | 35781 |
| 35845 | 35841 |
| 35920 | 35924 |
| 36000 | 35990 |
| 36395 | 36396 |
| 36525 | 36515 |

TABLE II

Tetralin bands 2800 Å system

| λ in air A | Wave number <i>in vacuo</i> ν cm. ⁻¹ | Intensity (Visual) | Separation from (0, 0) <i>i.e.</i> , 36790 cm. ⁻¹ | Assignment |
|-----------------------|---|-----------------------|---|------------|
| 2793·3 | 35781 | v.w. | -1009 | |
| 2789·3 | 35841 | v.w. | -949 | |
| 2782·8 | 35924 | 3 | -866 | |
| 2777·7 | 35990 | 1 | -800 | |
| 2746·7 | 36396 | v.w. | -394 | |
| 2737·8 | 36515 | v.w. | -275 | |
| 2730·4 | 36614 | 1 | -176 | 0-176 |
| 2727·4 | 36654 | 2 | -136 | 0-136 |
| 2723·7 | 36704 | 3 | -86 | 0-86 |
| 2720·7 | 36744 | 4 | -46 | 0-46 |
| 2717·3 | 36790 | 10 | 0 | (0, 0) |
| 2714·0 | 36835 | 2 | 45 | 0+45 |
| 2710·5 | 36882 | 5 | 92 | 0+92 |
| 2703·5 | 36978 | v.w. | 188 | |
| 2699·6 | 37031 | w | 239 | 0+424-185 |
| 2696·0 | 37081 | w | 291 | 0+424-133 |
| 2692·6 | 37128 | w | 338 | 0+424-86 |
| 2689·8 | 37166 | w | 376 | 0+424-48 |
| 2686·3 | 37214 | 4 | 424 | 0+424 |
| 2682·8 | 37263 | w | 473 | 0+424+49 |
| 2679·9 | 37303 | 3 | 513 | 0+424+89 |
| 2673·6 | 37392 | w | 602 | 0+682-80 |
| 2670·8 | 37430 | 2 | 640 | 0+682-42 |
| 2667·8 | 37472 | 5 | 682 | 0+682 |
| 2664·6 | 37517 | 1 | 727 | 0+682+45 |
| 2661·2 | 37565 | 2 | 775 | 0+682+93 |
| 2657·9 | 37612 | 1 | 882 | 0+951-129 |

TABLE II—(Contd.)

| λ in air A | Wave number in <i>vacuo</i> ν cm. ⁻¹ | Intensity (Visual) | Separation from (0, 0) <i>i.e.</i> , 36790 cm. ⁻¹ | Assignment |
|-----------------------|---|-----------------------|---|---------------|
| 2654.9 | 37655 | 2 | 865 | 0+951-86 |
| 2651.9 | 37697 | 1 | 907 | 0+951-44 |
| 2648.8 | 37741 | 6 | 951 | 0+951 |
| 2645.2 | 37793 | 1 | 1003 | 0+951+52 |
| 2642.3 | 37834 | 3 | 1044 | 0+951+93 |
| 2638.4 | 37890 | w | 1100 | 0+1185-85 |
| 2635.4 | 37934 | w | 1144 | 0+1185-41 |
| 2632.5 | 37975 | 4 | 1185 | 0+1185 |
| 2629.0 | 38026 | w | 1236 | 0+1185+51 |
| 2625.9 | 38070 | 2 | 1280 | 0+1185+95 |
| 2622.2 | 38125 | w | 1331 | 0+1185+146 |
| 2620.2 | 38154 | 1 | 1364 | 0+1185+179 |
| 2610.2 | 38299 | 1 | 1509 | 0+951+682-124 |
| 2607.5 | 38339 | w | 1549 | 0+951+682-84 |
| 2604.5 | 38383 | w | 1593 | 0+951+682-40 |
| 2601.8 | 38423 | 2 | 1633 | 0+951+682 |
| 2598.8 | 38468 | w | 1678 | 0+951+682+45 |
| 2595.5 | 38516 | 1 | 1726 | 0+951+682+93 |
| 2589.2 | 38610 | 1 | 1820 | 0+951+951-82 |
| 2586.3 | 38653 | 1 | 1863 | 0+951+951-40 |
| 2583.7 | 38693 | 2 | 1903 | 0+951+951 |
| 2580.7 | 38737 | w | 1947 | 0+951+951+45 |
| 2577.6 | 38784 | w | 1994 | 0+951+951+92 |
| 2573.8 | 38841 | w | 2051 | 0+951+1185-85 |
| 2571.0 | 38884 | w | 2094 | 0+951+1185-42 |
| 2568.2 | 38926 | 2 | 2136 | 0+951+1185 |
| 2565.1 | 38973 | w | 2183 | 0+951+1185+47 |
| 2561.9 | 39021 | 2 | 2231 | 0+951+1185+95 |

TABLE II—(Contd.)

| λ in air A | Wave number <i>in vacuo</i> ν cm. ⁻¹ | Intensity (Visual) | Separation from (0, 0) <i>i.e.</i> , 36790 cm. ⁻¹ | Assignment |
|-----------------------|---|-----------------------|---|-------------------|
| 2550.7 | 39193 | w | 2403 | 0+2×951+682-180 |
| 2546.9 | 39251 | w | 2461 | 0+2×951+682-122 |
| 2544.3 | 39291 | 1 | 2501 | 0+2×951+682-82 |
| 2541.7 | 39331 | w | 2541 | 0+2×951+682-42 |
| 2539.0 | 39373 | 1 | 2583 | 0+2×951+682 |
| 2536.1 | 39418 | v.w. | 2628 | 0+2×951+682+45 |
| 2533.8 | 39454 | w | 2664 | 0+2×951+682+87 |
| 2524.1 | 39606 | 1 | 2816 | 0+951+1185+682 |
| 2521.2 | 39651 | v.w. | 2861 | 0+951+1185+682+45 |
| 2518.4 | 39696 | w | 2906 | 0+951+1185+682+90 |
| 2507.3 | 39871 | 1 | 3081 | 0+951+1185+951 |
| 2501.8 | 39959 | v.w. | 3169 | 0+951+1185+951+88 |
| 2492.6 | 40106 | w | 3316 | 0+951+1185+1185 |

DISCUSSIONS

Tetralin (Text-Fig. 1) resembles O-Xylene in structure except that the two methyl groups in the *ortho*-position of the benzene ring are replaced by a saturated ring structure. It is observed that O-Xylene might be regarded as belonging to the group C_{2v} with two methyl groups treated as point substituents coplanar with the ring. In the case of tetralin, three more bonds



TEXT-FIG. 1



TEXT-FIG. 2

forming the ring are no longer coplanar. There is evidence to show that this saturated part of the ring is either in puckered form or the half boat form.^{1,8} Thus the molecule may not be considered even to a first approximation as belonging to C_{2v} group. It may, however, be noted that the π

electron skeleton with the substituents as shown in Text-Fig. 2 essentially has a C_{2v} symmetry. Hence from the point of view of electronic structure and energy levels the molecule may be taken to belong to C_{2v} symmetry with levels suitably modified by strain in the non-planar part of the saturated ring. The near ultraviolet spectrum in the region 2750 to 2500 Å corresponds to the 2550 Å band system of benzene and is attributed to transition A_1-B_1 under the reduced C_{2v} symmetry as in all other *ortho*-disubstituted benzenes. The transition is hence allowed and should show the characteristics of an allowed transition. Such a transition is expected to show a strong (0, 0) band with long progressions of totally symmetric vibrations in the excited state, the non-totally symmetric vibrations appearing mainly as $\nu-\nu$ transitions. In substituted benzenes, however, this latter rule has to be slightly modified because as is generally observed the non-totally symmetric component of the 606 cm^{-1} degenerate frequency of benzene is involved more prominently than is usually expected. This feature is what many workers (Sponer and others) call the forbidden part of the allowed transition. This has been attributed to the fact that, though under reduced symmetry, substituted benzenes remember some of the characteristics of the benzene spectrum.

The near ultraviolet spectra of different *O*-disubstituted benzenes generally show a close similarity as far as vibrational structure is concerned. Table III records the vibrations superposed on the pure electronic transition both in the ground and the excited state of some of such molecules.

The position of the (0, 0) band is, however, determined by the general substitution effect. The spectrum of tetralin consists of sharp bands and the group of bands near 36790 to 36882 is the strongest in the spectrum. It, therefore, shows the position of the 0-0 band. It consists of a group of three sharp bands at 36790, 36835, and 36882 cm^{-1} of which the first is the strongest and the second is quite weak. Similar groups of bands are found on the shorter wavelength side separated from this group by about 424, 682, 951, 1185 cm^{-1} and combinations and multiples of these. Each of these groups consists of three bands separated by about 45 cm^{-1} . A similar situation exists in the case of the near ultraviolet spectrum of *O*-Xylene⁴ where a group of the three bands repeats itself separated from the 0-0 group at 37308 by 76 cm^{-1} . The choice of the 0-0 band has obviously to be between bands at 36790 and 36882 cm^{-1} in tetralin or 37232 and about 37308 cm^{-1} in *O*-Xylene. In the case of *O*-Xylene the 37308 band has been chosen as the 0-0 band and the bands preceding it is due to $\nu-\nu$ transitions. In the case of tetralin a similar choice would lead to band 36882 as the zero band and to an explanation of the two preceding bands as due to $\nu-\nu$ transitions

TABLE III
*Ultraviolet absorption spectra table showing the frequencies in the ground
 and excited state of certain O-disubstituted benzenes*

| O-Cresol ⁹ | O-Dichloro benzene ² | O-Fluorochloro benzene ⁵ | O-Xylene ⁴ | O-Chloro Anisole ³ | O-Cl Toluene ¹⁴ | O-Fluoro Toluene ³ | Tetralin | |
|--|--|---|--|--|---|-------------------------------|--|-------|
| Ground Excited | Ground Excited | Ground Excited | Ground Excited | Ground Excited | Ground Excited | Ground Excited | Ground Excited | |
| 1261 (1264)R 1163 (1164)R 1040 (1044)R 744 (748)R 524 (526)R 278 (274)R 192 (190) | 1134 (1139)R 1037 (1039)R 662 (610 640) 503 437 307 (428) 226 (240) v-v 24 59 | 1246 (1237)R 1103 (1127)R 1031 (1029)R 830 (826)R 685 (680)R 556 (554)R 489 367 (375)R 170 (167)R v-v 35 69 126 | 1233 (1222)R 1054 (1052)R 736 (733)R 582 (582)R v-v 56 60 72 76 126 | 948 767 641 690 (685)R 565 (576)R 418 (410)R 279 270 | 1084 1005 915 813 530 249 (247) 161 (163) | 1230? 924 707 | 1185 (1205)R 951 (1039)R 682 (725)R 45 92 | 36790 |
| 0, 0 band 36418 in cm. ⁻¹ | 36232 | 37035 | 37308 | 36760 | 36638 Swamy | 37576 | | |

separated by 45 and 92 cm^{-1} on the shorter wavelength side. But this choice has the following difficulty. It is observed that the short wavelength band, in each of the groups of three bands, is the weakest one and the longest wavelength band is the strongest. Thus in the analysis the 0-0 band would be found to be weaker than 0-2 ($\nu-\nu$) band at 36790 cm^{-1} . This will also be true of subsequent groups involving 0- ν' transitions of various vibrations. Such an intensity distribution is not theoretically justifiable and therefore in the case of tetralin 36790 cm^{-1} band is chosen as the 0, 0 band. The two bands following this band at 36835 and 36882 cm^{-1} are analysed as due to transition 0-45 and 0-92. The origin of these small frequencies specially on short wavelength side of the 0-0 band is however not very clear. A similar choice of 0, 0 band could be made in O-Xylene but in this case authors always put the shortest wavelength band as stronger than that on the short wavelength side. It is significant to note that the choice of the 0-0 band does not affect the subsequent analysis since exactly a similar group repeats separated by excited state frequencies and hence the corresponding band in each group can be chosen as the first band in the group. There are two ways in which the choice of the 0-0 band can be confirmed. Firstly the bands on the longer wavelength side involving ground state frequencies are likely to decide the choice by comparison of the ground state frequencies from ν,ν data, with those of strong and polarized lines in Raman spectrum. Secondly the emission spectrum and the intensity distribution bands therein may decide the choice of the 0-0 band. In the present case no bands involving the ground state frequencies have been observed which can be definitely assigned to excitation of fundamentals. In the case of O-Xylene the bands specially involving ground state frequencies 1054, 1122 and 1373 support the choice of earlier workers. Having fixed the 0-0 band as the one at 36790 cm^{-1} the rest of the analysis is straightforward. On the shorter wavelength, side as has been mentioned before, there are bands separated from the 0, 0 band by 424, 682, 951, 1185 cm^{-1} and their combinations. These probably involve the excited state frequencies corresponding to the ground state frequencies 508, 725, 1039 and 1205 cm^{-1} as given by Raman spectrum. All these except the one at 508 cm^{-1} are strong bands in the Raman spectrum and possibly arise out of totally symmetric vibrations. The case of 424 cm^{-1} in the excited state will be subsequently discussed. Apart from the excited state frequency of 424 cm^{-1} , the other frequencies show a behaviour very much alike other similar molecules as shown in Table II. All the *ortho*-disubstituted benzenes seem to involve the corresponding frequencies and it is interesting to note that the same trend is maintained in tetralin in spite of the ring strain.

It is interesting to note that the spectra of various O-disubstituted benzenes have one of the excited state frequency near 510 cm.^{-1} . There are, however, two exceptions, namely, O-dichloro benzene and tetralin. Both these compounds give bands involving a frequency of the order of 430 cm.^{-1} , instead of about 510 cm.^{-1} . The excited state frequency 510 cm.^{-1} has been assigned to correspond to the ground state frequency of about 580 cm.^{-1} which is the totally symmetric α_1 component of the split $606 e_g^+$ degenerate frequency of benzene under the reduced symmetry. The other component is expected to be of the smaller frequency and Anno *et al.*² have assigned the 437 cm.^{-1} excited state frequency as corresponding to 409 cm.^{-1} Raman frequency which represents the β_1 component of the same $606 e_g^+$ benzene vibration. In the case of tetralin the excited state frequency 424 cm.^{-1} may be similarly assigned. The corresponding ground state frequency cannot be definitely identified, since no bands on long wavelength side in the region of 500 cm.^{-1} from the 0-0 band could be recorded. This characteristic excitation of the α_1 component or the β_1 component of e_g^+ benzene vibration is rather significant and it may be tentatively assigned to the ring strain either by electronic forces as in O-dichloro benzene or due to steric factors as in tetralin. It may also be observed that it is likely that both may be present in the spectrum of O-fluoro-chloro-benzene⁵ though the actual assignment is not very certain. This behaviour may be further studied with increasing strain as in indene, etc., where less than six-membered rings are fused to phenyl.

A few bands have been observed on the longer wavelength side of the 0-0 band. These bands, however, show a different type of appearance and are more broad and diffuse. The analysis of these bands showed that the ground state frequencies involved did not correspond to any Raman frequency. Comparison with the naphthalene spectrum shows that the strong band at 35924 cm.^{-1} agrees closely with the 0-0 band of the $2500\text{--}2900\text{ \AA}$ system of naphthalene. It is, hence, thought that the long wavelength bands may be due to naphthalene impurity. This observation is corroborated by the fact that at higher temperatures and under very long paths even the 3100 \AA band system of naphthalene weakly appears on the plates. It is rather significant to note that hot bands belonging to tetralin do not develop even at sufficiently high temperatures and long columns. It is very likely that the presence of naphthalene has a part to play in this behaviour.

SUMMARY

The near ultraviolet absorption spectrum of tetrahydro-naphthalene has been studied in the present investigation. The spectrum consists of sharp bands. Vibrational frequencies in excited state have values 1185, 951 and

682 and combination and overtones of these are found to be present as discussed in the analysis. The spectrum appears to be similar to that of O-Xylene and the frequencies in the ground and excited state of certain O-disubstituted benzenes have been compared with those obtained in tetralin.

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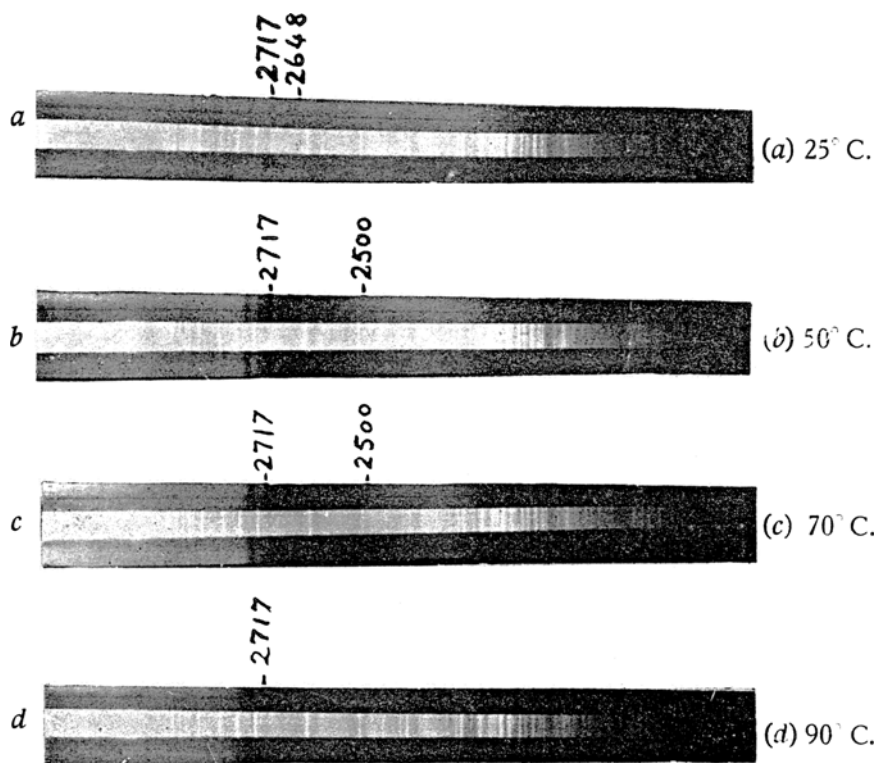


FIG. 1. Absorption Spectrum of Tetralin 40 cm. tube.

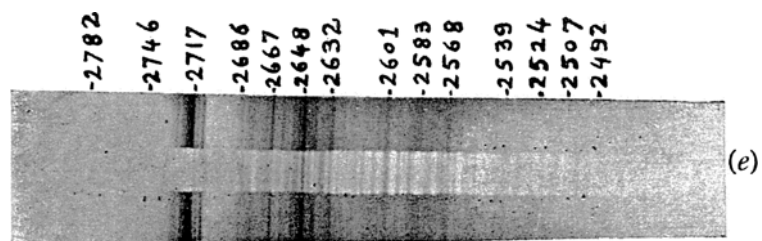


FIG. 1 (e). Absorption Spectrum of Tetralin 200 cm. tube.

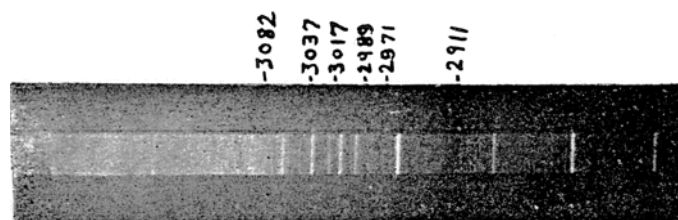


FIG. 2