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THE EMISSION SPECTRUM OF BENZENE IN THE REGION 2500–3000A

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Abstract

The ultra-violet emission band spectrum of benzene vapor has been observed with a Tesla discharge as a means of excitation. The wave-lengths of over 100 bands lying between 2400 and 3000A have been measured with an accuracy of ±0.5A. It is found that the measurements are in general in agreement with those of McVicker, Marsh and Stewart. All the bands except the fainest and most diffuse ones may be represented by the following equations:

$1/\lambda = 37485 + 924m - 161n$ $\quad 1/\lambda = 37425 - 986m - 162n$

$1/\lambda = 37398 + 924m - 162n$ $\quad 1/\lambda = 36479 - 991m - 162n$

$1/\lambda = 37485 - 986m - 162n$ $\quad 1/\lambda = 36412 - 991m - 162n$

where m and n are integers.

The evidence supporting the conclusion that the bands are due to benzene and not to some decomposition product is summarized. The applicability of the data to spectroscopic analysis is also discussed.

Introduction

THE general features of the spectra obtained from the vapor of benzene and its simple derivatives under the excitation of the Tesla discharge have been described by McVicker, Marsh and Stewart,[1] who have designated them as Tesla luminescence spectra to distinguish them from the absorption and fluorescence spectra. The present research was undertaken as an extension of their work; it was hoped, on the purely chemical side, to develop the suggestion made by them that a means of ascertaining the identity and quantity of any impurity present could be elaborated. In this regard it has been shown that such a method would be unwieldy in practice, except perhaps for routine work on a large number of samples; moreover, the number of likely impurities which yield satisfactory spectra under these conditions is rather small. On the other hand, it was felt that more comprehensive data on the Tesla luminescence spectra, particularly on the spectrum of benzene which is noteworthy for the sharpness of its bands and the absence of any continuous background, might be obtained, which with the increased accuracy would lead to some theoretical interpretation of the observed regularities. In this object some success has been achieved and the present work describes the results for benzene; the results for the simple derivatives will be published in the near future.

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* From a dissertation presented by J. B. Austin to the Graduate School of Yale University, June 1928, in candidacy for the degree of Doctor of Philosophy.

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[1] McVicker, Marsh and Stewart, J. Chem. Soc. **123**, 642 (1923).

EXPERIMENTAL METHOD

The methods employed differed from those of McVicker, Marsh, and Stewart in many ways, the most significant difference being the use of much lower pressures of the vapor. They used benzene vapor at pressures as high as 65 mm of Hg and were forced to use a steam jacket to prevent condensation; in the present work the pressures ranged from 0.01 to 0.10 mm which yielded satisfactory results at room temperature. In its final form our apparatus was fitted with internal electrodes whereas the previous practice used external ones. The general scheme for producing and maintaining these low pressures was to place the liquid benzene in a side limb of the discharge tube, to immerse it in liquid air to freeze the liquid to a solid cake, and then to seal the side limb and evacuate the system with a mercury diffusion pump until the residual air was so attenuated that a discharge could not be produced. The liquid air bath was then partially removed to allow the frozen benzene to warm slightly so that its vapor at low pressure could continuously diffuse through the discharge tube to a liquid air trap where it was condensed. In this manner equilibrium between speed of pumping and rate of sublimation was soon established and could be modified to give pressures between the limits of 0.01 and 0.10 mm. This method of maintaining a constant flow of vapor in the tube helped to remove any decomposition products as soon as they were formed and in conjunction with the low kinetic energy, and consequent small molecular disruptive power of the Tesla discharge gave some assurance that the spectrum originated in the benzene molecule. As a further precaution against contamination a new tube and liquid air trap were used for each exposure.

The first attempt to obtain the desired spectrum was made with the so-called "electrodeless" discharge, produced by placing the discharge tube in a helix of stout brass rod through which the current from a 1 KW Thordarson transformer was passed. A few trials sufficed to show that the spectrum obtained under these conditions was not that of the undecomposed molecule, but was due apparently to molecular fragments. Moreover, this discharge was very sensitive to slight fluctuations in pressure; with the pressure above a certain limiting value the free electrons and ions did not seem to attain a velocity sufficiently high to excite the rest of the vapor; with pressures too low the intensity of the glow suffered appreciably. At times this discharge showed a tendency to form a shell adjacent to the inside wall of the tube which electrically shielded the interior and caused a luminescent cylinder to form; the dark core of this cylinder rendered the discharge quite unsuitable for photographing.

It is interesting to note that the exciting coil and discharge tube grew quite warm during the passage of the current through the former; at the end of a run the latter invariably cracked, the cracks following the helix around the tube; whether the rupture of the glass was caused by thermal or electrical strain was not determined.

The next attempt was made with electrodes of lead foil wrapped around a Pyrex tube. This set-up yielded a satisfactory spectrum but endless trouble was experienced with the breakdown of the glass along the surface between the electrodes. The presence of air streaks in the glass made trouble certain.

Finally it was decided to install internal electrodes, a procedure which had hitherto been regarded as hazardous because of the possibility of excessive decomposition of the vapor. Such electrodes, however, proved the most satisfactory of all the arrangements tried and in most cases caused no greater decomposition than the other types. This system was used to obtain all the results herein reported. Fig. 1 shows the discharge tube which consisted of a cylinder of Pyrex, *P*, with a quartz window, *W*, sealed on at one end with de Khotinsky cement; the other end was connected to a vacuum system and a mercury diffusion pump. The electrodes, *T*, were cylinders of aluminum attached to tungsten seals; a side bulb, *S*, held the benzene.

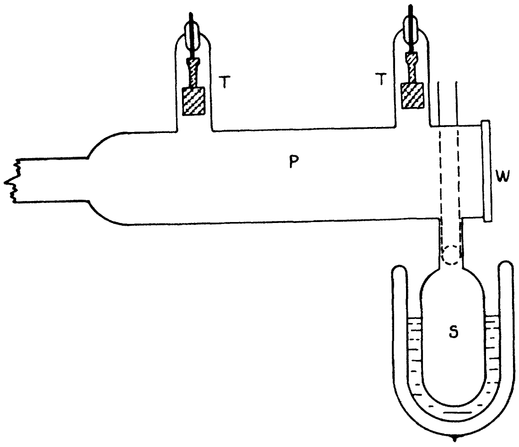

Fig. 1. Discharge tube.

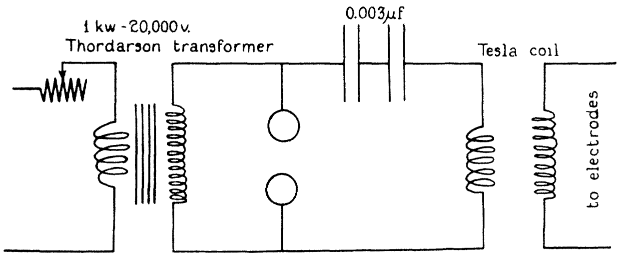

Fig. 2. Electrical connections.

The electrical system is shown in Fig. 2. When properly tuned this circuit gave a potential of about 120,000 volts as estimated from the spark produced between metal points.

SPECTROSCOPIC AND PHOTOGRAPHIC METHODS

In this work two spectrographs were employed:

(a) A Hilger size C quartz spectrograph, giving a photograph 200 mm in length for the range 2100A to 7000A. On this instrument exposures ranging from 3 to 12 hours were made; a plate exposed for 12 hours was used for the final measurements. For comparison, the spectrum of a mercury arc was superposed on the middle of the benzene spectrum with the aid of a reducing stop on the slit.

(b) A Hilger E_1 quartz spectrograph (Littrow mounting) giving a spectrum 140 mm in length for the region 2500A to 3000A. The spectrum of the mercury arc was superposed on these plates as on the others.

All photographs were taken on Eastman 33 plates of a special thin glass so that they could conform to the curvature of the plate holder without danger of breaking. In the earlier stages of the work Nujol and transformer oil were tried as sensitizers but were later discarded since they did not appreciably enhance the intensities of the ultra violet lines and were not deemed of sufficient value to warrant the extra trouble.

The spectra obtained with the smaller instrument extended almost 150A farther into the ultra-violet than those from the larger one; on the latter no bands were measured beyond 2600A while on the former they were recorded as far as 2471A. This difference is probably due to the greater absorption of the thicker quartz prism in the big spectrograph. On the other hand the large Hilger resolved some of the bands and permitted greater accuracy in measurement; hence, to obtain a complete spectrum of considerable accuracy the data obtained with the two instruments have been combined.

WAVE-LENGTH MEASUREMENTS

All plates were measured on a Société Genevoise ruling engine whose ruling mechanism had been replaced by a plate holder and a fixed telescope with cross hair attachment. The screw head was graduated in divisions of 0.005 mm with a vernier which allowed readings to be made to 0.001 mm. Tests on the accuracy of the screw showed that any deviations or flaws in it were negligible compared to other errors. The wave-lengths of the unknown lines were calculated by means of the parabolic interpolation formula:

$$\lambda_i=\lambda_0+as_i+bs_i^2$$

where λ_0, a and b are constants determined from the mercury lines[2] and s_i is the reading of the measuring engine corresponding to the i^{th} line. This formula proved to be as accurate as the observations for ranges of 200A in the lower visible and ultra-violet and involved much less labor than the Hartmann formula. The whole spectrum was covered in overlapping sections of 200A.

Each plate was measured in the center of the spectrum to avoid any error due to curvature of the lines. The further precaution was taken of having

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[2] Kayser, Tabelle der Hauptlinien der Linienspektra J. Springer, Berlin 1926.

TABLE I.

λ in A A & B	$1/\lambda$ in cm^{-1} A & B	$1/\lambda$ in mm^{-1} McV., M. & S.
2471.1*	40456	
2483.0*	40262	
2528.5*	39537	
2541.5*	39335	
2547.3*	39245	
2551.6*	39179	
2562.5*	39013	
2571.9*	38870	
2585.1*	38672	
2589.0*	38613	
2595.0*	38524	
2599.9*	38452	
2602.6	38411	
2608.7	38321	
2613.6	38250	
2619.8	38159	
2624.8	38086	
2629.8*	38014	
2631.1*	37996	
2641.7*	37843	
2647.8*	37776	
2649.0*	37739	
2657.5	37618	3765
2663.6	37532	3752
2667.4	37478	
2667.9	37472	
2668.4	37465	
2669.1	37455	
2673.5	37393	3741
2678.6	37321	
2684.6	37233	
2685.6	37224	3725
2689.2*	37175	3717
2690.2	37061	
2696.2	37078	3708
2701.7	37002	3703
2702.2	36995	
2705.1*	36956	
2707.7*	36921	3693
2714.0*	36835	3686
2718.6*	36773	
2727.8	36648	3666
2729.6	36624	
2734.6	36557	
2736.5	36532	
2739.1	36497	3652
2740.5	36478	
2743.7	36436	
2745.4	36413	3642
2747.3	36388	3636
2751.2	36337	
2752.7	36317	
2755.9	36275	
2757.7	36251	3625
2759.6	36239	
2763.4	36176	
2764.9	36157	3611
2771.7	36068	
2775.4	36020	3602
2777.2	35996	
2789.4	35839	3586
2800.2	35701	3570
2810.6	35569	
2812.3	35535	3554
2815.2	35511	
2817.2	35485	
2820.0	35450	
2822.6	35417	3542
2824.7	35391	3537
2828.1	35349	
2830.2	35322	
2832.9	35289	3528
2834.5	35269	
2835.7	35254	
2837.9	35227	3521
2841.0	35188	
2848.6	35094	3512
2852.9	35041	3504
2854.4	35023	
2857.5	34985	3498
2866.5	34875	
2895.5	34526	3454
2898.1	34496	
2900.6	34465	3445
2903.7	34428	
2909.1	34364	3438
2911.9	34331	
2914.5	34301	
2917.6	34264	3428
2920.5	34230	3422
2922.8	34203	
2925.5	34172	
2930.4	34115	3411
2932.9	34086	
2937.0	34038	3405
2951.0	33876	3390
2961.0	33763	3376
2980.6	33540	3357
2983.5	33507	
2985.9	33481	
2989.5	33440	
2995.1	33378	3339
2998.5	33340	
3003.4*	33286	
3009.5	33218	3322
3012.8*	33182	
3018.6*	33118	3308
3052.7*	32748	
3060.6*	32664	
3068.3*	32582	3257
3074.2	32519	
3075.5*	32506	
3080.1	32457	3242
3085.6	32399	
3090.4*	32349	
3095.1*	32300	
3102.0*	32228	3229
3158.1	31654	

each of us independently measure each plate twice, once when it was run along the measuring engine forward and once backward; in this way each line was approached from both sides. The agreement obtained in these sets of observations was most satisfactory, the difference rarely exceeding ±0.5A and in most cases being less than ±0.25A. The four measurements of each line have been averaged and converted to wave numbers in vacuo.

PREPARATION OF BENZENE

Merck's product was shaken six times with concentrated sulfuric acid; at the end of this treatment no color was imparted to fresh acid. The benzene was then washed successively with concentrated sodium hydroxide, dilute sodium hydroxide, and distilled water, until the final wash water was neutral to litmus. The resulting product was dried over sodium for 25 hours and redistilled from the same. A large fraction came over at a constant temperature and this was taken for use. B. P. 80.0°C at 760 mm Hg pressure.

RESULTS

The general scheme of the bands is shown in the photograph, Fig. 3. The following table gives the average results obtained from the two spectrographs. Lines observed only on the smaller spectrograph are marked with an asterisk. The results of McVicker, Marsh, and Stewart are given for comparison.

While a rough notion of the relative intensities of the bands may be gathered from Fig. 3, a more exact measure for the most prominent band groups is given in the microphotograph, Fig. 4. This was made on a Koch-Goos microphotometer from a plate taken on the large spectrograph. The ratio of length on this curve to length on the plate is 2 : 1.

It was found that all the principal bands could be accounted for with an accuracy of $\pm 3\ \mathrm{cm}^{-1}$ by the following equations:

$$1/\lambda = 37485 + 924m - 161n \qquad 1/\lambda = 37425 - 986m - 162n$$

$$1/\lambda = 37398 + 924m - 161n \qquad 1/\lambda = 36479 - 991m - 162n$$

$$1/\lambda = 37485 - 986m - 162n \qquad 1/\lambda = 36412 - 991m - 162n$$

where m and n are assigned integral values. In one band (2667.4) some of the fine structure was observed, the wave-length difference being about ±0.5A. This agrees with the value reported by Henri[3] in the absorption spectrum. It is interesting to note in this connection that the wave-number differences 991 and 162 cm^{-1} appearing in these equations are found also in the Raman spectrum of benzene. It is hoped that before long some definite significance can be attached to these values.

It may be well to review the evidence supporting the assumption that this spectrum originates in the benzene molecule for in spite of all precautions some decomposition did occur. At the end of the 12 hour runs the surfaces of

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[3] Henri, Structure des Molecules, Paris, 1925, p. 109.

the aluminum electrodes were found to be covered with a layer of carbon and the discharge tube showed a very thin film of a shellac-like substance adhering to the walls. However, despite the appearance of these products there is little doubt that the spectrum observed is actually that of benzene. Apart

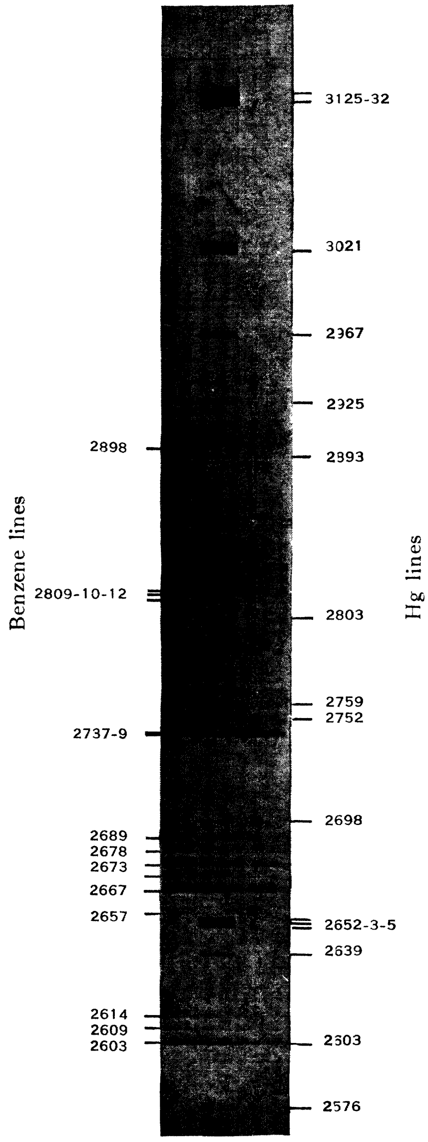

Fig. 3.

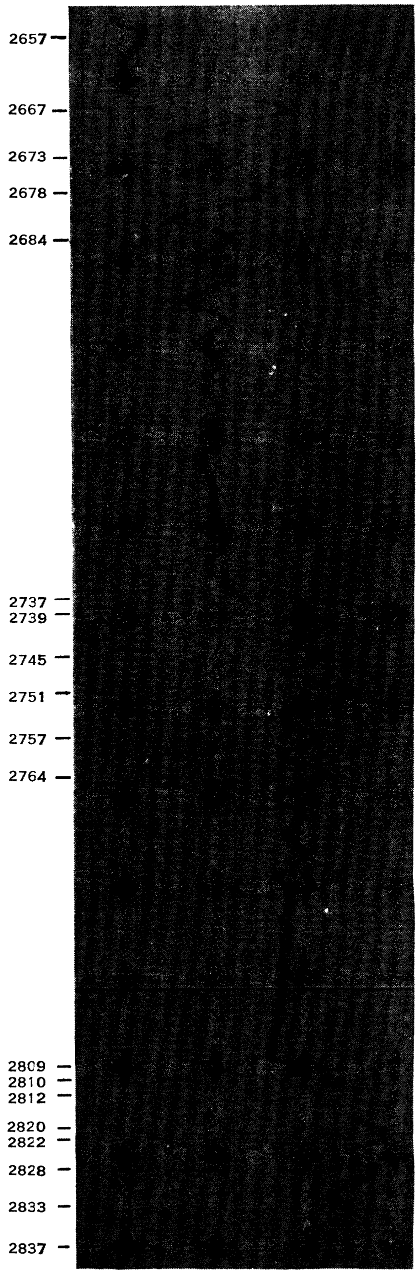

Fig. 4.

from the fact that the decomposition products seem non volatile, the following considerations point to the same conclusion.

First, it was observed that conditions which produced the greatest visible decomposition gave spectra of low intensity. Thus, for example, as the pressure is lowered decomposition is decreased while the intensity of the glow is increased. This is just what is to be expected since, for a given energy input, the larger the amount of energy used in molecular rearrangements, the smaller will be the fraction of the total energy as light.

Second, the regularity exhibited by the spectrum seems to militate against any decomposition hypothesis, for this regularity implies a uniformity in the system which produces it; if this system is a benzenoid molecule, its symmetry is easily understood, but if it is produced by some dissociation or rearrangement under the stress of the discharge then it is necessary to postulate an absolute uniformity of decomposition which would be hard to concede from a theoretical view point and would certainly not account for the fact that several decomposition products are actually found.

Aside from these considerations, which involve only the emission spectra, the results can be checked with the spectra in solution. For instance, Dickson[4] has observed the fluorescence spectrum of benzene in alcohol solution. It is well known that a solvent shifts the spectrum of a substance in solution but this shift is generally a translation of the system as a whole so that the relative positions of the bands remain unchanged. It is found that if 19 units of wave-number are added to the values given by Dickson the broad bands of his spectrum coincide with the principal emission bands which we have observed.

Even more convincing is the agreement between the absorption and emission spectra of the vapor, which prove to have identical band arrangements. The emission spectrum should include the bands found in absorption but the far ultra-violet part of the former is lacking due to the absorption by unexcited benzene molecules in the discharge tube. However, it is found that the most refrangible emission band group coincides with the bands of the red end of the absorption spectrum as determined by Henri.[5] This arrangement is shown in the following table.

TABLE II.

Absorption Bands of benzene vapor after Henri λ	Emission Bands of benzene vapor (A & B) λ	Absorption Bands of benzene vapor after Henri λ	Emission Bands of benzene vapor (A & B) λ
2528.6	2528.6	2599.9	2599.7
2541.7	2541.5	2603.0	2602.6
2552.5	2551.7	2610.2	2610.1
2589.0	2588.7	2613.9	2613.5
2595.2	2595.2		

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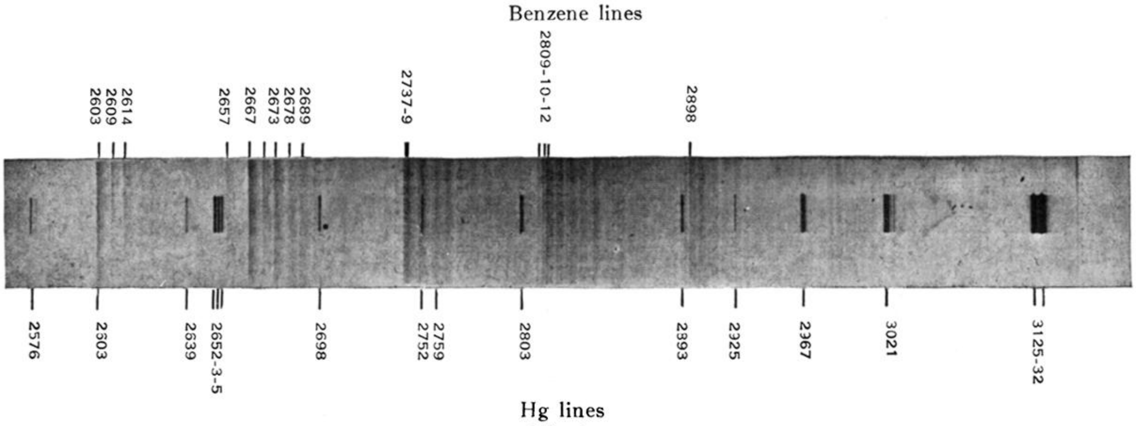
[4] Dickson, Zeit. Wiss. Photo. **10,** 166 (1912).

[5] Henri, J. de Phys. et Rad. **3,** 181 (1922).

This check is sufficient to establish the fact that the carrying structure is the the same, and, since no decomposition is to be expected, nor indeed is any found, in the absorption work, it follows that both spectra are due to undecomposed benzene.

The foregoing considerations, in addition to demonstrating that the benzene molecule is the carrier of the spectrum, also indicate a very satisfactory agreement between our work and the known absorption and fluorescence spectra. It may be of interest to conclude with a comparison of our results with those of McVicker, Marsh and Stewart. Taking the results from both spectrographs we have recorded the wave-length of about 110 bands and in addition to more than doubling the known number of emission bands have given evidence of two new band systems in the far ultra-violet. We do not claim to have measured all the bands in the spectrum, however, for in many cases bands could be seen on the plates with the naked eye which were not susceptible of measurement under the microscope. We have also shown that many of the lines reported by McVicker, Marsh, and Stewart are really doublets. A number of our measurements when expressed in wave numbers seem to be about 30 units smaller than those of the corresponding lines in the work of McVicker, Marsh, and Stewart. This is interesting on account of the fact that in the comparison made between their results and Hartley's values for the absorption of benzene approximately 20 units were added to the latter in order to make the regularities coincide.

In conclusion the authors wish to express their thanks to Dr. John Johnston at whose suggestion the work was undertaken, to Dr. A. E. Ruark who gave valuable assistance with the experimental work, to Professor Uhler for much help in the spectroscopic and photographic work and for suggesting the methods of measurement and calculation, to Professor McKeehan who kindly placed the resources of the Sloane Physics Laboratory at our disposal. The authors wish also to thank the Commonwealth Fund for the fellowship which one of them held and without which he would have been unable to undertake this research.


Benzene lines
2603
2609
2614
2657
2667
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2689
2737-9
2809-10-12
2898
2576
2603
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2652-3-5
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2803
2893
2925
2967
3021
3125-32
Hg lines

Fig. 3.

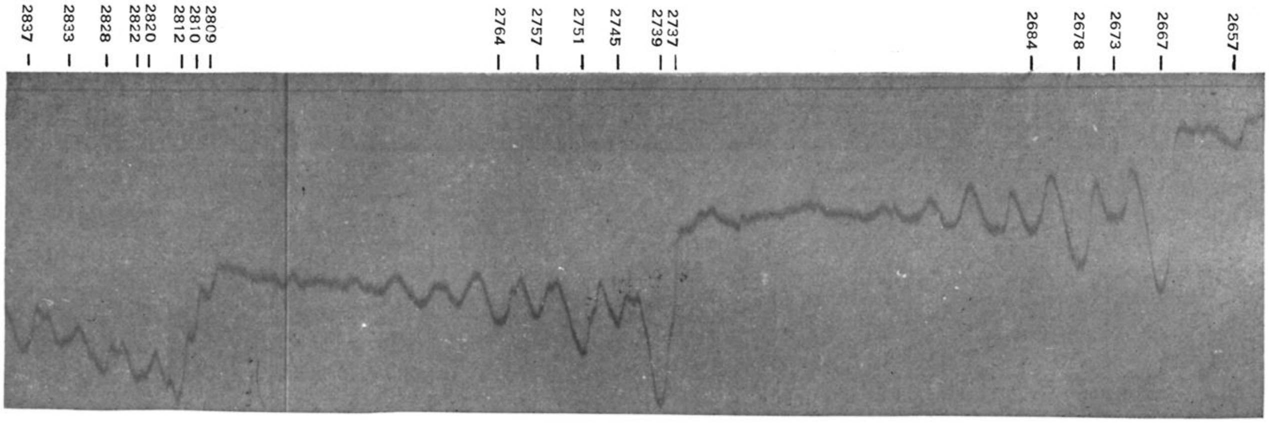
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Fig. 4.