THE EFFECT OF TEMPERATURE UPON THE ULTRA-VIOLET BAND SPECTRUM OF OZONE AND THE STRUCTURE OF THIS SPECTRUM

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Abstract

The ultraviolet absorption of ozone in the region 3400 − 2300A consists of a large number of bands appearing against a background of continuous absorption. The effect of temperature upon this spectrum has been studied over the range −78° to 250°C. A definite though small effect has been observed. Grossly it manifests itself as an increase in contrast with decreasing temperature. Photometric results show this to be a decrease in absorption between the bands, all of the bands appearing to come from normal vibrational levels of very low if not the lowest energy. Though somewhat diffuse, the bands tend to degrade to the red. The observed influence of temperature can be explained as a decrease of intensity in the continuous background, and also in the higher rotational absorption of the bands, with decreasing temperature. Discontinuities in the intensity relations and the regular spacing of certain of the bands have led to a partial vibrational analysis indicating two active vibrational degrees of freedom in the excited electronic state. The observed change in the absorption with temperature may affect somewhat the estimates which have been made of the amount of ozone existing in the upper atmosphere, and may possibly afford a method of estimating the temperature of the upper atmosphere.

F OLLOWING plans mentioned in an earlier report upon the visible absorption spectrum of ozone[1] the authors have made a study of the influence of temperature upon the ozone spectrum working with the absorption which lies in the ultraviolet. The ultraviolet absorption of ozone consists of a large number of rather diffuse bands appearing against a background of continuous absorption.[2] It is not one of the most promising spectra for the study of triatomic molecules, but it is an important spectrum because of the several fields in which the ozone molecule is of interest. The limitation of the solar and stellar spectra in the ultraviolet is due to the ozone of the upper atmosphere, and the determination of the amount and variation in amount of this atmospheric ozone has, to the present, been done chiefly through a study of its ultraviolet absorption spectrum as it shows on the short wave-length edge of the solar spectrum. Furthermore, the reversion of ozone to oxygen is a chemi-

[1] Wulf, Proc. Nat. Acad. Sci. 16, 507 (1930).

[2] Hartley, Jour. Chem. Soc. 39, 57 (1881); Huggins, Proc. Roy. Soc. 48, 216 (1890); Meyer, Ann. d. Physik 12, 849 (1903); Ladenburg and Lehmann, Ibid. 21, 305 (1906); Krüger and Moeller, Physik. Zeits. 13, 729 (1912); Fabry and Buisson, Jour. de physique et le radium 3, 196 (1913); Fowler and Strutt, Proc. Roy. Soc. 93, 729 (1917); Shaver, Proc. Roy. Soc. Canada 15, Sec. III, 5 (1921); Lambert, Dejardin and Chalonge, Compt. rend. 183, 800 (1926); Lauchli, Zeits. f. Physik 53, 92 (1929); Lambry and Chalonge, Gerland's Beiträge z. Geophysik 24, 42 (1929); Dutheil and Dutheil, Jour. de physique et le radium 7, 414 (1926).

cal reaction which has received a great deal of attention in both thermal and photochemical kinetics, making important a knowledge of the energy levels and processes of dissociation of the molecule. The molecule is probably a result of the combination of the normal reactive $^3\Sigma$ state of oxygen molecule with the normal ^3P state of oxygen atom, the two sets of unpaired electrons pairing, leaving the normal state of ozone diamagnetic.[3]

The infrared data for ozone[4] indicates vibrational states[1] which might lead to an appreciable temperature effect in its electronic absorption at ordinary temperatures. If such did occur in ozone it would be important[5] for it might alter somewhat the estimation of the amount of ozone present in the upper atmosphere, and part of the apparent variation in the amount of this ozone might be simply a variation in the temperature of the atmosphere at the height of the ozone layer. It might, furthermore, lead to a direct method of estimating the temperature at this altitude. And any knowledge of the influence of temperature on the spectrum should aid in understanding its structure.

We have studied the effect of temperature upon this absorption over the region 3400–2300A. The region 3400–2900A has been studied from about −78°C to room temperature, while in the region of stronger absorption, i.e., 2550A, it has been photographed as high as 250°C. The former region has, however, been studied in most detail.

A definite influence of temperature has been observed though it is small and hence difficult to measure. Grossly it manifests itself as an increase in contrast with decreasing temperature, perceivable with the eye alone on the original plates. The work has been done on two Hilger spectrographs, one the familiar E2, the other of the Féry design. The continuous spectrum of hydrogen was used as a background, and the absorption of ozone, produced in a silent discharge ozonizer and of a wide variation of concentrations, was photographed in quartz and pyrex cells at the temperature of solid carbon dioxide and at a series of higher temperatures. In the work at the low temperature the cells were packed in crushed solid carbon dioxide, being fitted in most cases with projecting auxiliary cells at both ends containing dry air and phosphorus pentoxide to prevent frosting at the windows. In the case of the bands at the extreme red a two meter cell was used, its windows projecting from the cold pack and being kept at room temperature, thus nearly all but not strictly all of the path of gas being at the low temperature in this case.

A photometric study of the plates has been made against a series of exposures of the same source weakened by calibrated screens.[6] In this study,

[3] Lewis, Valence and the Structure of Atoms and Molecules, Chem. Cat. Co., 1923, pp. 130, 147 et seq; Chem. Rev. **1**, 234 (1924); Wulf, Proc. Nat. Acad. Sci. **13**, 744 (1927); Vaidyanathan, Indian Journ. Phys. **2**, 422 (1928).

[4] E. Ladenburg and E. Lehmann, Ann. d. Physik (4), **21**, 305 (1906); Verh. d. deutsch. Phys. Ges. **8**, 125 (1906).

[5] R. Ladenburg, Gerlands Beiträge z. Geophysik **24**, 40 (1929); Ruedy, ibid. **24**, 49 (1929); See also Ref. (1).

[6] The authors are indebted to Dr. F. S. Brackett for the use of the recording microphotometer of the Smithsonian Institution.

constant exposure time was used and the series of comparison exposures using the screens were made on the same plate as the exposures of the absorption of ozone. From the calibration exposures, density was plotted against the logarithm of the transmission, and the transmission of the ozone in the experimental exposures under any particular conditions was read from this, the density being determined from direct measurements on the photometer curves. The results over the region 3400A to 2900A show that the bands all behave the same within the accuracy of measurement, exhibiting a strengthening in the maxima with decreasing temperature and a weakening of absorption in the space between the bands. The temperature effect appears to be essentially the same whether carried out at constant total gas density (closed absorption cell) or at constant pressure (cell open to atmosphere), in both cases the same number of ozone molecules in the path. A blank run showed no appreciable photochemical ozone decomposition over the time of an experiment. The continuous background, which builds up strongly as one goes from 3400A to 2900A, decreases in strength with decreasing temperature. At 3100A the bands are almost negligible compared to the background and the absorption here shows a decrease over this temperature range of about 10 percent. Passing to longer wave-lengths, where the bands come more in evidence, the maxima tend to increase against the background with decreasing temperature while in the space between bands the absorption falls away more strongly. This is shown in Table I which contains the results of the most re-

TABLE I. *Temperature effect in band maxima and minima.*

Band	Wave-length A	$\dfrac{\alpha_{195°K}}{\alpha_{295°K}}$	Band	Wave-length A	$\dfrac{\alpha_{195°K}}{\alpha_{295°K}}$
6:7	3058	0.90	5:4	3155	0.95
7:5	3066	0.91			0.81
		0.89	4:5	3169	0.96
6:6	3081	0.90	5:3	3175	0.99
7:4	3088	0.90			0.84
		0.86	4:4	3194	0.97
6:5	3102	0.88	5:2	3199	0.98
7:3	3113	0.91			0.85
		0.89	4:3	3220	1.11
5:5	3135	0.96	5:1	3226	1.09
		0.82			0.91

liable measurements. The figures in the third and sixth columns are the ratios of the absolute values of the absorption coefficient at the two temperatures, 195°K and 295°K at the points of band maxima and minima. The bands are designated by the number of the group to which they appear to belong and their number in that group, this numbering being further explained later on. Thus it appears that all of the bands that have been studied come from vibrational states of very low if not the lowest energy. Bands from a vibrational level of as high as 400 cm^{-1} would show a change of a few fold in intensity over this range of temperature, and of course much more from a level as high as 1000 cm^{-1}.[1] A general picture of the whole absorption is given in Fig. 1.

The bands, though somewhat diffuse with no rotational structure re-solved,[7] tend to degrade to the red in the near ultraviolet region. This can be seen best by a careful study of the photometer curves given in Fig. 2. Thus
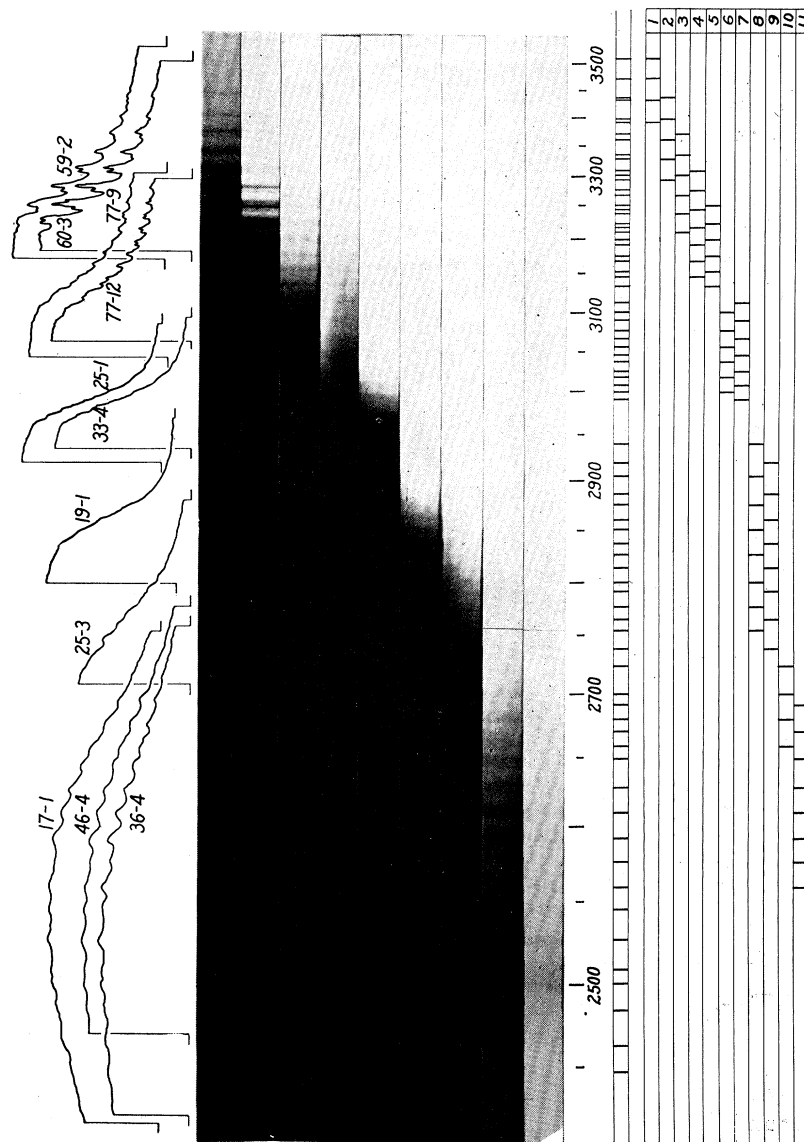

Fig. 1. Scale of wave-lengths in Angstroms. Above are tracings of photometer curves; where two are given the lower is at 195°K and the upper at 295°K. In the 2500A region the third and upper curve is at approximately 525°K. Below is diagram illustrating the tendency toward regularity in certain groups of the bands. A scratch on plate shows at about 2750A in the two lowest exposures.

[7] Fowler and Strutt, Proc. Roy. Soc. **93**, 582 (1917).

the absorption between two bands is apparently due partially to the rotational structure of the bands lying just to shorter wave-lengths, chiefly of course to that of the adjacent band. Partially it appears to be due also to the overlying continuous absorption, and in an amount which increases with decreasing wave-length. The observed change of absorption with temperature can thus be explained as a decrease in the absorption of the continuous background, and a decrease in the higher rotational absorption of the bands with decreasing temperature.

Certain groups of the bands show a decided tendency toward regular spacing;[8] also several discontinuities occur in the intensity change from band to band within such groups, appearing to identify a series of partial progressions. We have used this fact to afford a numbering for the bands, each band being designated by two numbers, the first its partial progression number and the second (starting with zero) its position in the progression. These groups with the wave-lengths of the bands as we have observed them are given in Table

TABLE II. Band groups.

Band Number	Partial Progression Number
	1	2	3	4	5	6	7	8	9	10	11
0	3513	3439	3371	3310	3254			2945	2930	2724	2666
1	3473	3401	3337	3278	3226			2907	2890	2700	2646
2	3432	3362	3302	3247	3199			2876	2862	2678	2629
3	3394	3333	3270	3220	3175		3113	2852	2837	2658	2611
4			3240	3194	3155		3088	2827	2814		2594
5			3213	3169	3135	3102	3066	2801	2789		2579
6				3145		3081	3045	2778	2766		2560
7						3058	3025	2753	2738		
8						3039	3008				
9						3020	2990				
10						3000					

II. At the beginning of the absorption in the near ultraviolet the bands comprise five groups having a band separation within the groups of the order of 300 cm^{-1} and a displacement between the groups of the order of 600 cm.$^{-1}$ These are shown in Fig. 2 with two photometer curves above them, the upper at the high and the lower at the low temperature. Consistent intensity relations between the bands within the partial progressions lend further support for this grouping. Somewhat further in the ultraviolet are two more groups that have fairly closely the same band separation and may belong with these. The first members of these may not have been observed because of their low intensity and the lack of contrasty plates in this region of strong continuous background. It is to be noted that while the absolute numbering of these partial progressions is arbitrary, the relative numbering and especially the absolute

[8] Kondratjew, Zeit. f. physik. Chem. B, 7, 70 (1930), has taken six of the bands as measured by Fowler and Strutt as representing a series. As will be seen later the last five of these are members of our partial progression 4, while the first we have not observed, the nearest to this being band 2 of partial progression 3. Partial progression 5 shows a close resemblance to 4, but 2 and 3 are not so evidently similar. Within the low accuracy of placing such poorly defined bands it does not seem possible to go much further with the extrapolation of the progressions.

numbering of the bands within these progressions is not. The latter depends on the intensity discontinuities at the start of each partial progression, the next band to the red being absent. This is best seen in progressions 3, 4, and 5. All these bands appear to exhibit the same behavior with respect to tem-
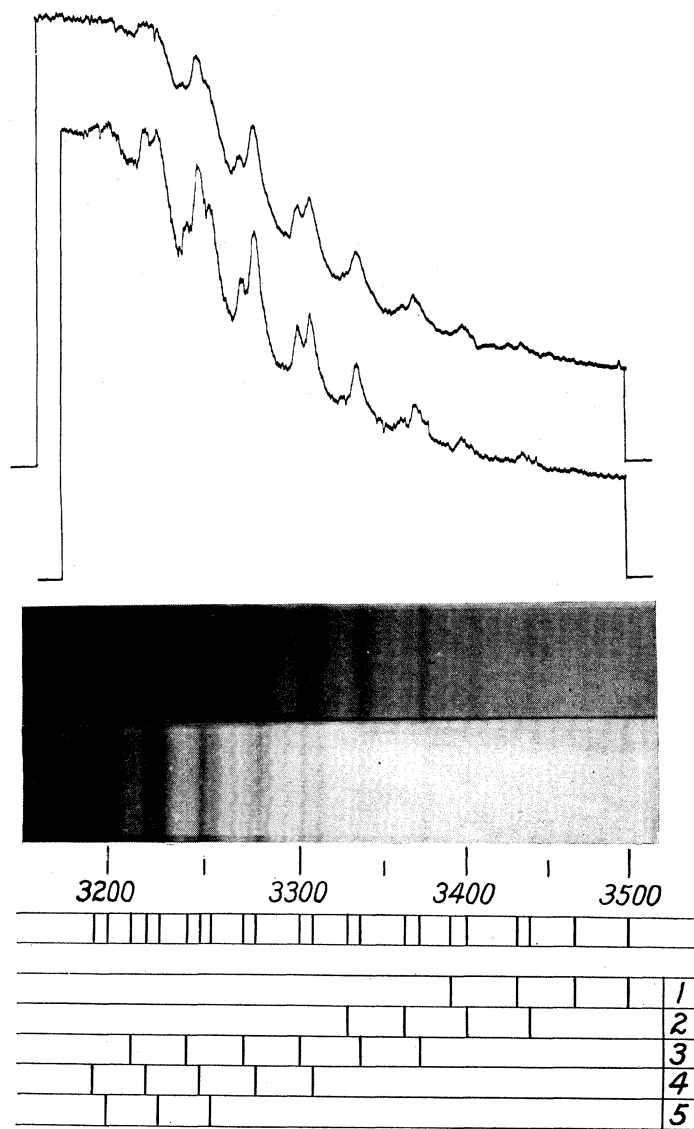

Fig. 2. Beginning of the bands in the near ultraviolet. Original photometer curves showing change in contrast, the lower at 195°K, the upper at 295°K. Note that these are not records of the illustrative exposures shown below which are of different times and both at the low temperature.

perature. Considerably further in the ultraviolet are a number of bands which, while they show some tendency toward regular spacing, may not be con-

nected with the others. These bands appear to exhibit a similar behavior with respect to temperature, though this is not certain. It seems possible that the ultraviolet absorption of ozone may consist of two electronic transitions overlaying one another. The bands in the near ultraviolet appear to establish two vibrational degrees of freedom in one excited electronic state, the transitions, as stated above, being from normal vibrational levels of very low if not the lowest energy, probably the latter.

This situation seems to offer a possible explanation for the abnormally high absorption coefficient of ozone. Its value[9] is $\alpha = 1/x \log_{10} I_0/I = 123$ at the maximum where x is in cm of pure ozone at n.t.p., while for bromine[10], for instance, a very colored gas, it is but 7. For every one transition from the lower state to one of the upper vibrational levels of a diatomic molecule there is the possibility of a series of transitions to one of the upper vibrational levels of one degree of freedom in the triatomic case and to a number of upper vibrational levels in the other degree of freedom. These bands and the continuous beyond them will overlap closely the similar sets built on the other vibrational levels of the first degree of freedom due to the small energy separation of the vibrational levels, leading, it would seem, to the possibility of a very much higher over all absorption coefficient than would be expected for a similar transition in a diatomic molecule.

This influence of temperature upon the ozone spectrum may affect somewhat the estimation of the amount of ozone in the upper atmosphere which depends upon the values of absorption coefficients measured in the laboratory. While the effect is not large it may be of importance, especially in the method of estimation which uses the difference in intensity of solar radiation at two wave-lengths at one time. The effect would be greatest if these wave-lengths happened to be located one in a band edge and the other well in a minimum of absorption between bands. The measurements indicate at present that this might be as great as a variation of ten percent in the ratio of $\log I_1/I_2$ for the range from room temperature down to $-78°C$. If such a variation in temperature occurs in the ozone layer this effect could account for a part of the apparent variations in the amount of ozone from day to day. It might also account in part for any differences found to exist in the values determined for a series of wave-lengths on any one day from a number of photographs. Depending of course upon the actual variations in temperature of the upper atmosphere the effect might be correspondingly greater or less than that estimated above for a temperature range of 100° in the neighborhood of 0°C.

It should be pointed out particularly that only the temperature effect has been considered here and that if there is also an effect of pressure upon the absorption this would further complicate the matter. (See Ladenburg, ref. 2.)

In conclusion, it does not seem hopeless to attempt to obtain some idea of the temperature of the atmospheric ozone from a study of the intensity distribution in the ozone bands at the edge of solar or stellar spectra. The change

[9] Fabry and Buisson, ref. 2.
[10] Ribaud, Ann. de phys. **12,** 107 (1919).

in contrast shows sufficiently on the laboratory plates to judge, for example, whether the ozone used in a particular exposure was at a temperature considerably below zero centigrade or considerably above.[11] Thus, unless the presence of the Fraunhofer lines and some further factor such as a pressure effect complicates the procedure too much, it should be possible to gain a rough idea of the temperature at the height of the ozone layer from a careful comparison of the ozone bands on solar plates with those taken under known conditions of temperature in the laboratory.

[11] An observation of Fowler and Strutt is of interest in this connection. They state "The bands as a whole are more diffuse in the photograph of Sirius than in the laboratory spectra, · · · " (Proc. Roy. Soc. **93,** 584 (1917)). Thus, barring other complications, this might be taken as indicating a temperature greater than room temperature in the ozone layer at some 50 km altitude. This is, of course, an observation made at night.
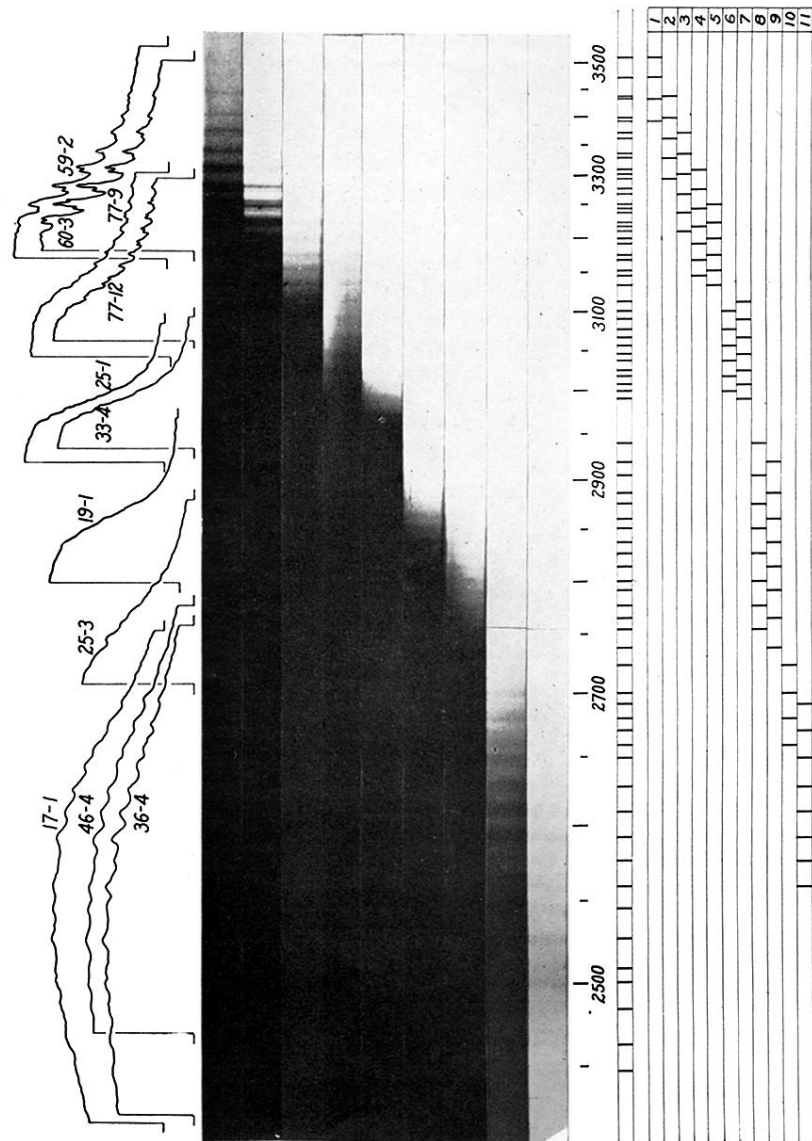
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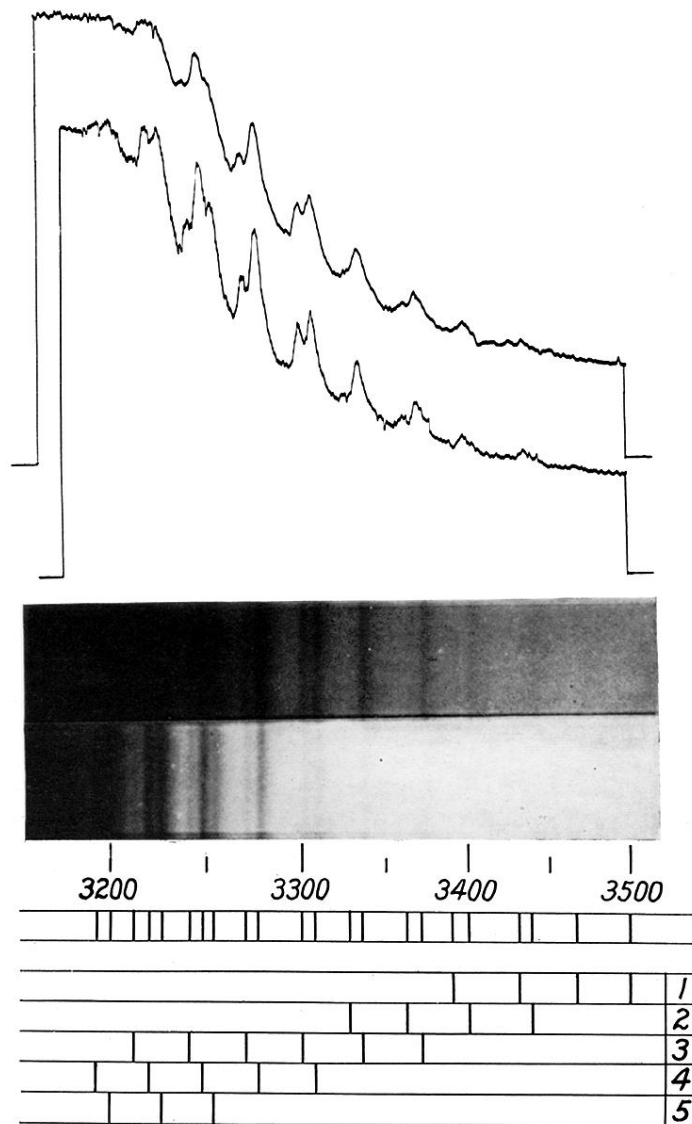
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