THE RAMAN EFFECT IN TOPAZ AND ITS RELATION TO THE LUMINESCENCE SPECTRUM

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1. Introduction

The Raman spectrum of topaz was first photographed by K. S. Krishnan (1929) who reported only a single feeble Raman line with a frequency shift of 1053 cm.$^{-1}$ Nisi (1929) working with a clear crystal of topaz recorded two Raman lines. In a subsequent investigation, Nisi (1932) observed no less than 11 Raman lines including one with a large frequency shift, *viz.*, 3647 cm.$^{-1}$ He further showed that interchanging the direction of observation and illumination did not affect the relative intensities of the Raman lines which were generally influenced by both directions. Kopcewicz (1937) studied the influence of temperature on the Raman lines of topaz over the range from 20° C. to 500° C. Even by giving exposures of the order of 100 hours, Kopcewicz recorded only five Raman lines. He noticed that with increase of temperature the low frequency lines shifted towards the exciting line proportionately much more than the high frequency lines.

Judging from the complicated structure of topaz, $(AlF, OH)_2SiO_4$, it appeared that the results obtained by the above-mentioned authors are obviously incomplete. This is due to the feeble scattering power of topaz and also to the fact that the earlier workers used the λ 4046 and λ 4358 radiations of the mercury arc for exciting the Raman spectrum. It appeared likely that the use of the intense λ 2536·5 mercury resonance radiation as exciter would yield a more satisfactory Raman spectrum for the substance. This hope has been realised and the results obtained are presented in this paper together with a satisfactory explanation of the luminescence of topaz.

2. Results

While examining different specimens of topaz, it was found that only colourless samples are transparent to the λ 2536·5 radiation. A colourless specimen of topaz from a large collection of Ceylon gems presented to Sir C. V. Raman by Mrs. Jayawardane, was available for the present investigation. It was in the form of a prolate spheroid about 1″ long and $\frac{1}{2}$″ thick. The edges were flattened and polished. Both the Hilger medium and

large quartz spectrographs were employed for photographing the spectrum. In order to determine the frequency shifts of the lines an iron arc comparison spectrum was taken in all cases, partially overlapping the Raman spectrum.

TABLE I

Raman Spectrum of Topaz

Serial No.	Author (1947)		Nisi (1932)	Kopcewicz (1937)	Infra-red frequencies $cm.^{-1}$
	Frequency shift in $cm.^{-1}$	Intensity			
1	156	4			
2	167	2			
3	190	1		189	
4	241	8	241 (1)	232	
5	269	9	268 (4)	270	
6	287	7	285 (4)		
7	317	2			
8	335	4	336 (2)		
9	362	2			
10	374	2			
11	405	4	393 (2)		398
12	441	1			
13	459	4			*458*
14	490	2			*477*
15	520	5			510
16	550	2			550
17	558	4	560 (0)		
18	650	2			*652*
19	705	1			
20	770	1			
21	850	4	857 (4)		
22	874	1			
23	898	3			*897*
24	920	8	925 (4)	920	
25	934	10			932
26	940	2			*958*
27	985	6	983 (1)		1010
28	1162	4	1165 (0)		
29	1235–1280	0			
30	1355–1435	0			
31	3636	2			
32	3649	7	3647 (1)		3600

Photographs of the Raman spectrum of topaz taken with the medium and large quartz spectrographs are reproduced in Figs. 1 (*b*) and 2 (*b*) respectively. Using a fairly fine slit (0·05 mm.), exposures of the order of 36 hours were given when working with the medium spectrograph, while exposures of the order of 6 days were necessary for the bigger instrument. Figs. 1 (*a*) and 2 (*a*) represent the photographs of the mercury arc spectrum. The Raman spectrum of topaz exhibits 30 lines and 2 bands the frequency shifts of which together with the relative intensities are tabulated in Table I.

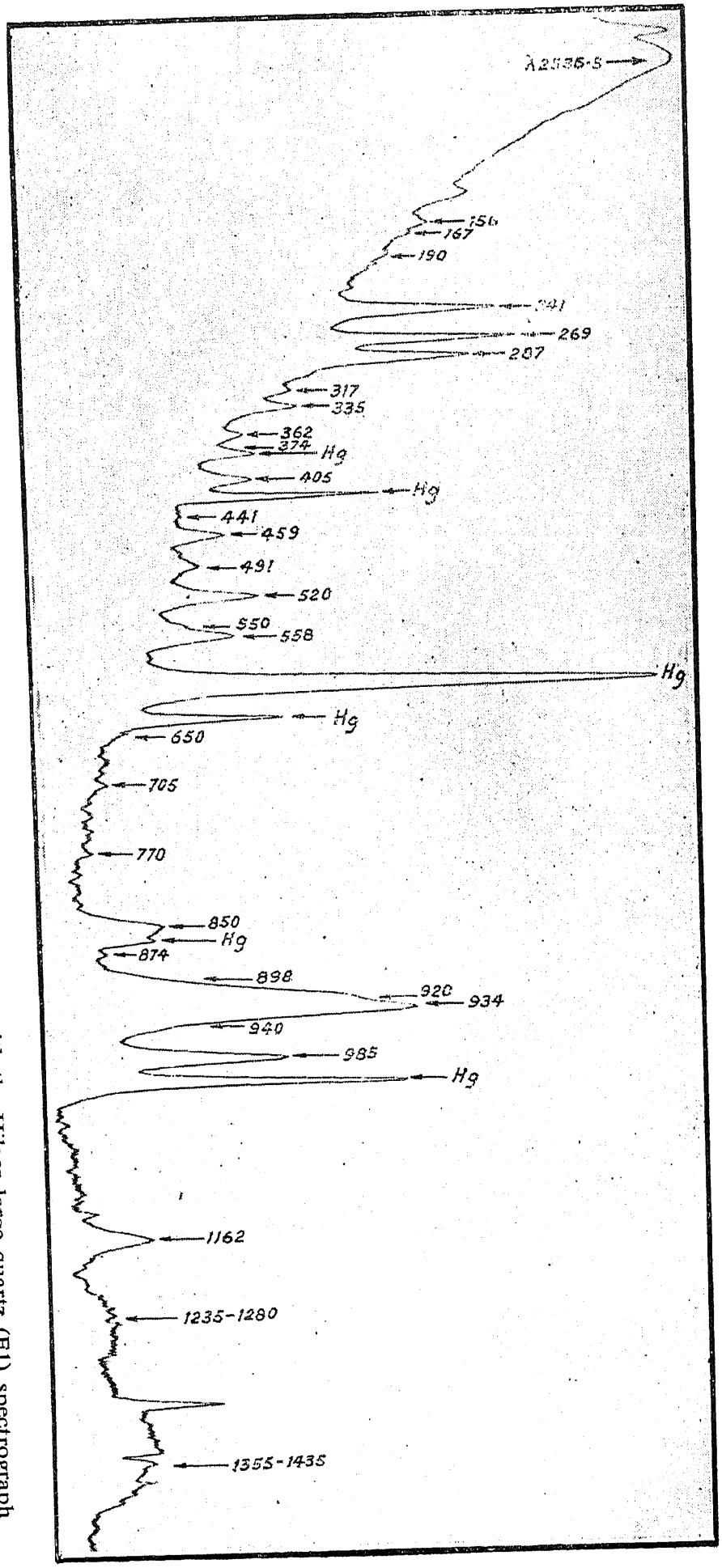

FIG. 3. The microphotometer record of the Raman Spectrum of topaz taken with the Hilger large quartz (E1) spectrograph

Note.—The fogging very near the exciting line is due to inefficient filtering.

The frequency shifts of the Raman lines reported by Nisi (1932) and by Kopcewicz (1937) are also included. About twenty Raman shifts have been recorded for the first time. The positions of the lines are marked in the figures. Some lines form closely spaced doublets. They are not easily discernible as distinct lines in the reproduced photographs. They are, however, more clearly identified in the microphotometer record reproduced in Fig. 3 above. The line with the frequency shift 934 cm.$^{-1}$ is the most intense one in the whole spectrum. The 3649 cm.$^{-1}$ line which was first reported by Nisi is extremely sharp and is followed by a weak companion on the shorter wave-length side. The low frequency lines are in general sharper than the lines in the high frequency shift region. This generalisation is not applicable to the lines 3636 and 3649 cm.$^{-1}$ The existence of a feeble line at about 1056 cm.$^{-1}$ reported by K. S. Krishnan and Kopcewicz has not been confirmed in the present investigation and consequently it is omitted from Table I.

3. Infra-Red Spectrum

The infra-red spectrum of topaz was first investigated by Coblentz (1908) who reported the appearance of three reflection maxima at 9·9 μ, 10·45 μ and 11·0 μ respectively. Schæfer, Matossi and Wirtz (1934) studied the infra-red reflection spectra of several silicates including that of topaz. They reported the existence of thirteen reflection maxima the corresponding wavelengths being 9·9, 10·44, 10·75, 11·15, (15·00), 15·35, (15·60), 17·10, 18·20, 18·96, 21·0, 21·8 and 25·2 μ. Those given in brackets are doubtful. The frequencies in wavenumbers of the ten reflection maxima are entered in column 6 of Table I. Those shown in italics correspond to the more prominent reflection maxima. It is interesting to note that those frequencies which appear strongly in infra-red absorption are recorded only with feeble intensity in the Raman spectrum. The agreement between the observed Raman and infra-red frequencies can be taken to be satisfactory in view of the fact that the infra-red frequencies have been evaluated from positions of reflection maxima. Matossi and Brouder (1938) investigated the infra-red absorption spectra of several silicates including topaz in the short wave-length region. They have recorded 23 absorption maxima in topaz in the region from 7·4 μ to 1·45 μ. All the infra-red frequencies appearing in this region except those corresponding to the sharp maxima at 2·9 μ (3405 cm.$^{-1}$), 2·7 μ (3600 cm.$^{-1}$) and 2·6 μ (3850 cm.$^{-1}$) have been assigned as combinations and octaves of the fundamental infra-red frequencies obtained by Schæfer, Matossi and Wirtz (1934) and entered in column 6 of Table I. The strong absorptions at 2·94 μ, 2·78 μ and 2·6 μ

have been explained by them as arising from OH bands appearing with great intensity. The frequency shift of the middle OH band, namely 2·78 μ (3600 cm.$^{-1}$) coincides roughly with that of the Raman line at 3649 cm.$^{-1}$ Consequently the value is also entered in column 6 of Table I.

4. Discussion of Results

The crystal structure of topaz has been analysed using the X-ray method by Leonhardt (1924), Pauling (1928) and Alston and West (1928). Topaz is regarded as dialuminyl difluoro-silicate $(AlF)_2SiO_4$. The structure belongs to the orthorhombic class. X-ray investigations reveal that there are 4 molecules of $(AlF)_2SiO_4$ in each elementary parallelopiped. The structure is based upon a closest packing of oxygen atoms, though it is not one of the simple forms but a combination of the cubic and hexagonal closest packing. It is composed of linked octahedral groups around silicon as in other alumino-silicates. According to Bragg (1937), each alumina atom is surrounded by six atoms of which four belong to the SiO_4 group and the rest are fluorine atoms. It is suggested that in some specimens the F may be partly replaced by OH to form $(AlF,OH)_2\,SiO_4$.

It is clear from the above analysis that topaz possesses very low symmetry and that each unit cell contains a large number of atoms. Consequently, nearly all the numerous possible modes of atomic vibration should be active in the Raman effect and also in infra-red absorption. The experimental results fully support the above conclusion. The line at 3649 cm.$^{-1}$ is a genuine Raman shift as it is observed both with λ 4046 and λ 2536·5 excitations. This line should be attributed to the OH oscillation and its appearance in the Raman spectrum of topaz clearly suggests that the molecular structure is $(AlF, OH)_2SiO_4$ and not $(AlF)_2SiO_4$. The recorded spectrum of topaz should exhibit the frequencies corresponding to all the nine characteristic modes of oscillation of the SiO_4 group which may not behave as a tetrahedrally symmetric group inside the crystal. A more complete and satisfactory interpretation of the Raman spectrum of topaz is not possible at present for want of full data on the Raman spectra of other complex silicates.

5. Raman Effect and its Relation to Luminescence

The foregoing results on the Raman spectrum of topaz are of interest in relation to the luminescence exhibited by certain varieties of topaz. Deutschbein (1932 *a*) examined the emission spectrum of topaz containing chromium phosphors both at room temperature and at liquid-air temperature ($-$ 195° C.). The spectrograms taken by him have been schema-

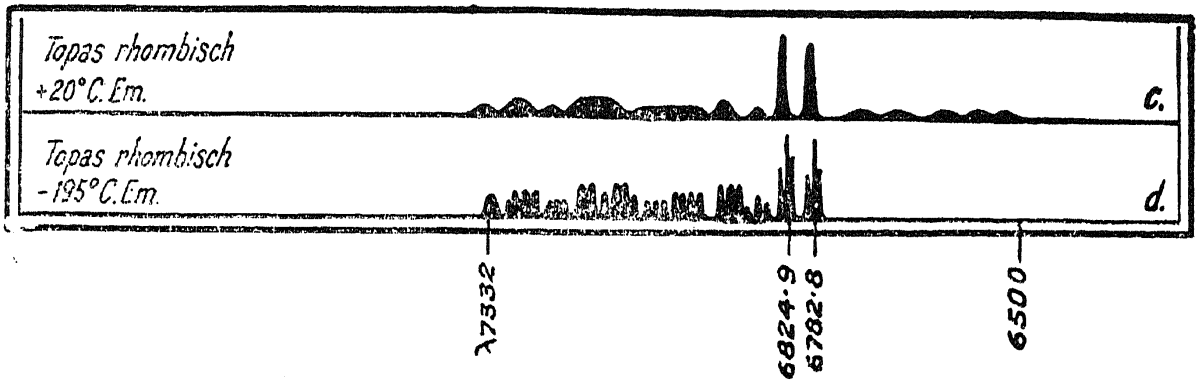

FIG. 4. Chart showing the luminescence spectrum of ptoaz reproduced from Deutschbein's paper

tically represented in the accompanying chart (Fig. 4). At 20° C., the luminescence spectrum consists of two broad and intense lines λ 6791·7 and λ 6832·7, accompanied by five broad bands on the shorter wave-length side and seven bands of varying width and intensity on the longer wave-length side of the principal doublet. At − 195° C. the principal doublet sharpens and each of its components is accompanied by two secondary lines which are absent in the spectrum taken at 20° C. At these low temperatures the bands on the shorter wave-length side of the principal doublet disappear completely from the fluorescence spectrum, while those on the longer wave-length side become sharp and exhibit some structure. Deutschbein identified 23 lines, each one of them being fairly broad. Their wave-lengths and frequencies as reported by Deutschbein are entered in Table II below. In a subsequent paper, Deutschbein (1932 *b*) explained the appearance of the principal doublet as due to the electronic transitions of the chromium ions present as impurity in the crystal. The 4 faint secondary lines accompanying the principal doublet on either side which are omitted from Table II have been ascribed by Deutschbein to an intra-molecular Stark effect. The principal electronic lines of Cr^{+++} are shifted towards shorter wave-length side by about 100 A.U. compared to those in ruby. Since the Stokes law was obeyed by the diffuse bands, Deutschbein suggested that they might arise from the superposition of the vibration frequencies of the ground material on the electronic transitions of the Cr^{+++} ions. On this basis, he showed that the frequency shifts of the bands λ 7271 and λ 6917 from the principal line R_1 were of the same order of magnitude as the two Raman shifts 911 and 260 cm.$^{-1}$ observed by Nisi (1929), which were the only ones known to exist at that time.

As more complete data on the Raman spectrum of topaz are made available by the present investigation, it is possible to give satisfactory assignments for all the vibrational bands observed by Deutschbein. These are

TABLE II

Emission Spectrum of Topaz at — 195° C.

Serial No.	Wavelength in A.U.	Wavenumber in cm.$^{-1}$	Intensity	Width in cm.$^{-1}$	Shift in cm.$^{-1}$ from R_1	Shift in cm.$^{-1}$ from R_2	Raman frequency
	6782·8	14739	9	10	Principal Line R_2		
	6824·9	14648	10	10	Principal Line R_1		
1	6860	14573	2	20		166	167
2	6873	14545	3	20		194	190
3	6893	14504	1	20		246	241
4	6903	14483	4	20	165		167
5	6917	14454	4	20	194		190
6	6936	14414	4	20	234		241
7	6970	14344	3	15		395	405
8	6985	14313	3	15	335		335
9	7000	14282	3	15	362		362
10	7012	14257	3	15	391		405
11	7032	14217	2	15	431		441
12	7045	14191	2	15	457		459
13	7059	14163	2	15	485		490
14	7080	14120	3	25	528		520
15	7102	14076	4	40	572		558
16	7131	14020	3	25		719	705
17	7162	13958	4	45	690		705
18	7215	13857	2	40	791		770
19	7255	13779	3	22	869		874
20	7271	13750	3	22	898		898
21	7288	13718	4	22	930		934
22	7299	13696	2	22	952		940
23	7332	13635	3	40	1013		985

4 Secondary electronic lines appearing in the neighbourhood of the principal doublet have been left out from the table.

indicated in Table II. As in the case of ruby, in topaz also, the most intense line of the principal doublet, *e.g.*, λ 6824·9, is mainly operative in producing the vibrational bands. Taking into consideration the finite width of the bands, the agreement between their frequency shifts from the principal doublet and the observed Raman shifts of topaz can be considered as very good. The loading of the lattice by the chromium ions must give rise to a perturbation of the vibrational modes and this would explain the fact that in luminescence, lattice vibrations appear as diffuse bands and not as sharp lines. The broadening might also be due to the fact that the principal electronic transitions themselves are broad to the extent of about 10 cm.$^{-1}$ and that the bands arising from the modulation of the principal line R_1 by certain lattice frequencies fall adjacent to those arising from the modulation of the principal line R_2 by other lattice frequencies.

It may be remarked that in luminescence and in the Raman effect, the vibrations of the crystal lattice are excited by entirely different mechanisms, and yet, as we have seen, there is complete correspondence between the frequency shifts of the vibrational bands appearing in luminescence and the Raman shifts of topaz. This result is very significant and has far-reaching consequences. According to the Born lattice dynamics, the appearance of sharp lines in the first order Raman spectrum of any crystal is explained as due to some kind of a selection rule which picks out only certain frequencies from the continuous vibration spectrum of the lattice. There is no reason to suppose that the same type of selection rule should be operative in luminescence also. In fact, the entire vibration spectrum should appear as a continuous band in emission without showing any fine structure of the kind actually observed. It follows therefore that what is actually recorded in luminescence and in Raman effect indicates the real nature of the vibration spectrum, namely that it consists of a set of discrete frequencies.

The author is grateful to Professor Sir C. V. Raman for the loan of the crystal of topaz and also for his kind interest in the work.

6. Summary

The Raman effect in topaz has been investigated using the 2536·5 mercury resonance radiation as exciter. The spectrum exhibits 32 Raman shifts of which no less than 21 have been recorded for the first time. The results obtained are discussed with special reference to the infra-red absorption and luminescence spectra of topaz. The significance of the complete correspondence noticed between the Raman shifts and the frequency shifts of the vibrational bands in luminescence is pointed out.

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Description of Plate

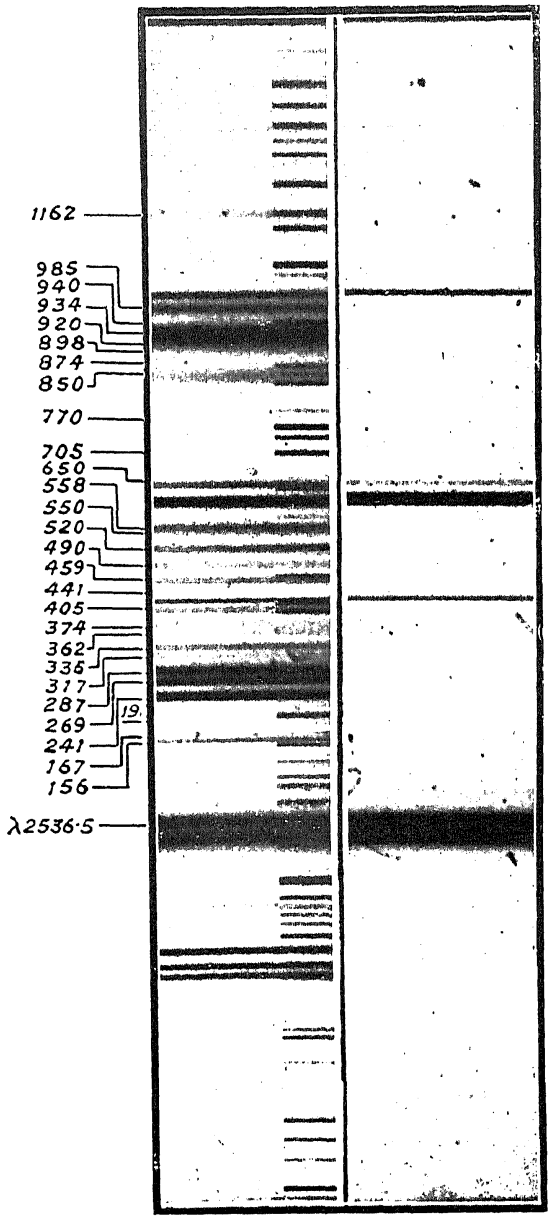
Plate XXI

Fig. 1. (*a*) Mercury spectrum taken with the medium quartz E 3 spectrograph.

(*b*) Raman spectrum of topaz taken with the same instrument.

Fig. 2. (*a*) Mercury spectrum taken with the large quartz E 1 spectrograph.

(*b*) Raman spectrum of topaz taken with the same instrument. Fogging very near the exciting line is due to inefficient filtering.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λ2536·5
b
a

FIG. 1

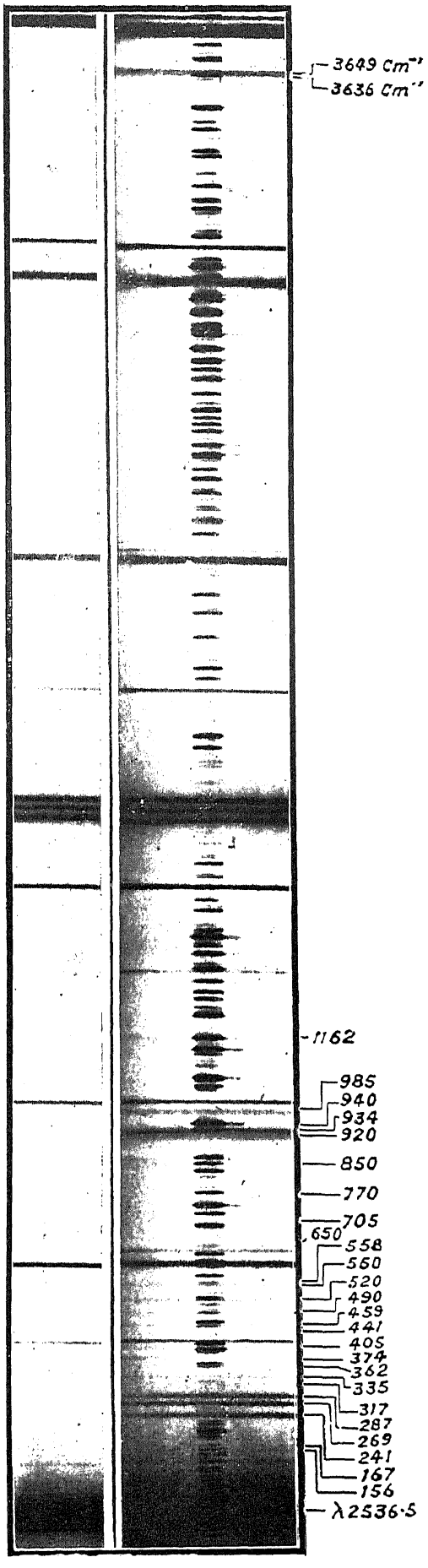
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FIG. 2