

RAMAN SPECTRUM OF AMMONIUM BROMIDE AND ITS VARIATION WITH TEMPERATURE

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1. INTRODUCTION

As was pointed out in a recent paper which appeared in these *Proceedings* (Krishnan, 1947) a study of the effect of temperature on the Raman spectra of ammonium halides offers a means of settling two fundamental issues connected with these solids, namely (1) the behaviour of the NH_4 ions in the neighbourhood of the transition temperature and (2) the nature of the lattice spectrum in which the NH_4 ions oscillate as single units. Accordingly, the author undertook a thorough investigation of the Raman effect in ammonium halides in the form of single crystals and its variation with temperature using the λ 2536.5 mercury resonance radiation as exciter. The results obtained with ammonium chloride which have already been reported in the paper referred to above, indicated that Pauling's hypothesis that there was onset of free rotation of the NH_4 ions immediately above the transition temperature was not correct. They also confirmed the discrete character of the vibration spectrum of the ammonium chloride structure (which is of the caesium chloride type), as demanded by the new crystal dynamics. These investigations have now been extended to the case of ammonium bromide and the results are presented in this paper.

2. EARLIER WORK

Studies on the Raman effect in crystalline ammonium bromide are very scanty. Its spectrum was first photographed by Kastler (1932) who reported the existence of three lines with frequency shifts 2810, 3030 and 3130 cm^{-1} . Subsequently, Menzies and Mills (1935) identified five Raman lines with frequency shifts, 1380, 1420, 1689, 3032 and 3140 cm^{-1} in the spectrum of ammonium bromide taken at room temperature. They further investigated the effect of temperature on the Raman spectrum in the range from 25° C. to -150° C. With decrease of temperature of the crystal, the spectrum sharpened considerably, while there was no change in the relative intensities of the lines. Unlike in the case of ammonium chloride, Menzies and Mills failed to observe any low frequency Raman lines in the spectrum of ammonium bromide taken below the transition temperature, *i.e.*, 235° T. (-38° C).

Using the technique of complementary filters for crystal powders, Anantakrishnan (1937) photographed the Raman spectrum of ammonium bromide. Besides confirming the results obtained by Menzies and Mills, Anantakrishnan reported the existence of two additional Raman lines with frequency shifts 2000 and 2800 cm.^{-1}

None of the investigators mentioned above has recorded any low frequency line in the Raman spectrum of ammonium bromide. Even as regards the internal frequencies of oscillation of the NH_4 ion, their studies appear to be far from being complete. This fact may be attributed to the use by the earlier workers of the λ 4046 and λ 4358 radiations of the mercury arc as exciter. Ammonium bromide being transparent to the ultra-violet, the λ 2536.5 mercury resonance radiation could be profitably used to obtain more satisfactory spectrograms.

3. DETAILS OF THE EXPERIMENT

Transparent crystals of ammonium bromide were prepared by the method of slow evaporation from aqueous solutions of the salt. In order to facilitate the growth of crystals in the form of cubes a small quantity of urea was added to the solution. The largest single crystal grown by this method had the dimensions of $1 \times 1 \times 0.5$ cm. The specimens were slightly coloured yellow.

The experimental technique employed by the author for photographing the Raman spectrum at different temperatures has already been described in one of the earlier papers (Krishnan, 1947). Using the Hilger E 3 quartz spectrograph, photographs of the Raman spectrum of ammonium bromide were taken with the crystal maintained successively at 85° T., 173° T., 308° T. and 398° T. Exposures of the order of twelve hours were given for the low temperature photographs, as the optical arrangement was not very efficient due to the necessity for the use of windows for the demountable Dewar flask. Four hours were sufficient to get reasonably intense spectrograms at room temperature. At 398° T., the crystal became translucent and consequently satisfactory photographs could not be taken at this temperature.

4. RESULTS

Photographs of the Raman spectrum of ammonium bromide taken at 308° T., 173° T. and 85° T. are reproduced in Figs. 1 to 3. The corresponding microphotometer records are also included in the Figures. In Fig. 4 are reproduced photographs of the Raman spectrum of ammonium bromide taken at four different temperatures together with two photographs of the Raman spectrum of ammonium chloride taken at room temperature and

at liquid-air temperature. The positions of the Raman lines together with their frequency shifts in wave-numbers from the exciting line are marked in Figs. 1 to 3. The most striking feature of the Raman spectrum of ammonium bromide which has not been noticed before is the appearance of a lattice spectrum consisting of a series of sharply defined lines with frequency shifts varying from about 50 cm.^{-1} to about 600 cm.^{-1} . In the high frequency shift region also, the photographs taken by the author exhibit many more Raman lines than those reported by the earlier workers. The Raman shifts of ammonium bromide are classified under two heads, namely (1) low frequency or lattice spectrum and (2) the spectrum of the NH_4 group.

The lattice spectrum.—Microphotometer records of the lattice spectrum of ammonium bromide taken at different temperatures are reproduced in Fig. 5. The frequency shifts of the lattice lines together with visual estimates (figures given in brackets) of the relative intensities of the lines are entered in Table I.

TABLE I
Lattice spectrum of crystalline NH_4Br

Sl. No.	Group	85° T.	173° T.	308° T.	398° T.
1	I	69 (15)	63 (15)	56 (12)	51 (12)
2		77 (6)	75 (8)	75 (3)	70 (4)
3		136 (10)	133 (8)	128 (6)	124 (5)
4		158 (0)	156 (2)	136 (6)	134 (5)
5		182 (12)	178 (8)	155 (4)	150 (5)
	II			175 (2)	171 (2)
6		260 (1)	258 (2)	256 (1)	
7		315 (1)			
8		335 (5)	328 (3)	325 (0)	
9	III	490 (3)	490 (1)	450 (1)	
10		626 (4)			
11		660 (2)			

The spectrum consists of a series of discrete frequency shifts of which the one nearest to the exciting line is the most intense. At liquid-air temperature (*i.e.*, 85° T.) the lines are extremely sharp. As the temperature of the crystal is slowly raised, the lines become less sharp and exhibit progressive shift in their positions. The discrete character of the spectrum persists even at 398° T. , *i.e.*, about 163 degrees above the transition temperature. See the microphotometer records reproduced in Fig. 5 (*d*). At this temperature some of the lines especially those lying in the region of frequency shifts $100\text{--}200 \text{ cm.}^{-1}$ are so broad that they run into one another. It should be remarked that unlike in the case of ammonium chloride, the lattice

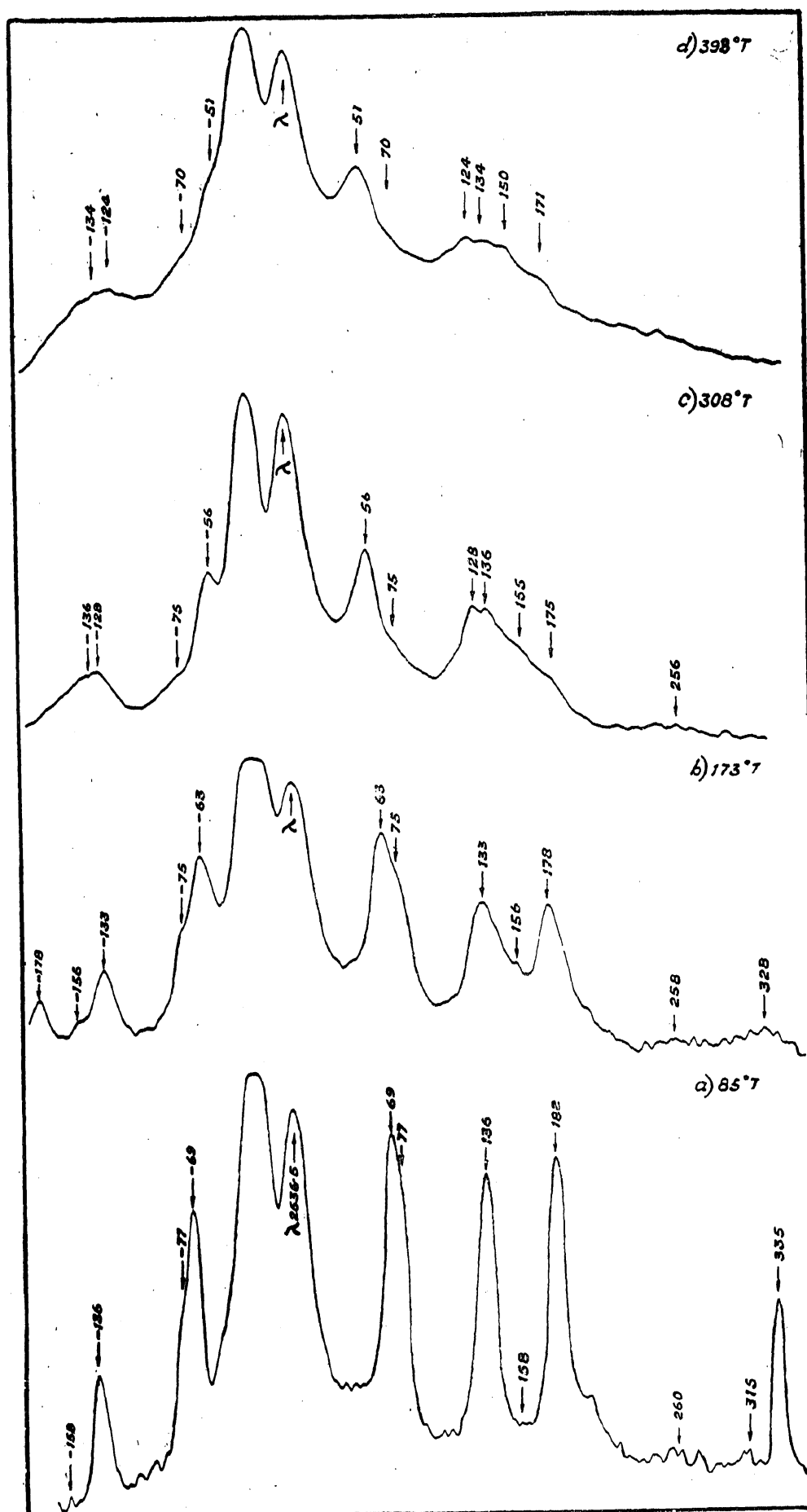


FIG. 5. Microphotometer records of the lattice spectrum of ammonium bromide taken at different temperatures.

spectrum of ammonium bromide does not exhibit any striking change in its structure when the temperature of the crystal is lowered from room temperature to that of liquid air.

At liquid-air temperature the lattice spectrum consists of eleven lines. They can be classified under three groups depending on their frequency shifts. The first group comprises of the lines falling in the region of frequency shifts 0–200 cm.^{-1} , the 2nd those falling in the region 200–400 cm.^{-1} and the 3rd those falling in the region 400–700 cm.^{-1} . The first group contains the most prominent lines. In the spectrum taken at 85° T., the line with the frequency shift 77 cm.^{-1} falls very close to the intense line at 69 cm.^{-1} . Nevertheless, it can be seen clearly resolved from the latter on the anti-Stokes side of the photograph (Fig. 3 c) or in the microphotometer record reproduced in Fig. 5 (a). The lines with frequency shifts 620 and 660 cm.^{-1} coming under the third group fall adjacent to the mercury lines $\lambda 2576.3$ and $\lambda 2578.4$ respectively. They are, however, easily discernible in the photograph reproduced in Fig. 3 (c).

As the temperature of the crystal is raised, the general intensity of the lines coming under the first group undergoes very little change. The 2nd, 3rd and 5th lattice lines progressively decrease in intensity, while the 4th line increases in intensity. At 308° T. and above, the 3rd line is split up into components. The proportionate shift with variation of temperature is different for different lines.

The three lattice lines falling in the second group become progressively weaker in intensity with increase of temperature. At 85° T. the third line with a frequency shift of 335 cm.^{-1} is sharp and fairly intense. When the temperature is raised to 173° T. this line shows an abrupt fall in intensity. See Figs. 5 (a) and (b). The spectrum taken at 398° T. exhibits a feeble continuum extending from about 200 to 400 cm.^{-1} and exhibiting some structure. The intensity of the continuum decreases with increasing frequency shift. In the spectrograms taken at 173° T. and above, no lines are recorded corresponding to the 626 and 660 lines observed at 85° T.

The spectrum of the NH_4 ion.—The lines with frequency shifts greater than 1390 cm.^{-1} appearing in the Raman spectrum of ammonium bromide are catalogued in Table II. Visual estimates of the relative peak intensities have been made and the values are given in brackets. The frequency shifts of the Raman lines of ammonium bromide recorded earlier by Menzies and Mills (1935) at 123° T. and those obtained by them and by Ananthakrishnan (1937) for room temperature are also entered in Table II.

TABLE II

Raman lines due to internal oscillations in NH₄Br

Group	Low Temperature			Room Temperature		
	Menzies and Mills 123° T.	Krishnan 85° T.	Krishnan 173°	Krishnan	Menzies and Mills	Anantha-krishnan
IV	1456	1401 (3s) 1420 (2s) 1435 (1s)	1399 (2s) 1416 (1s) 1432 (1s)	1398 (4s) 1429 (2s)	1380 1420	1395
VIII		1491 (2s)	1480 (1s)	1472 (1b)		
II	1694	1693 (20s)	1690 (20s)	1686 (25s)	1689	1690
VIII		1979 (6s) 1986 (6s)	1976 (5b)	1960 (3bd)		2000
V		2794 (1s) 2816 (10s) 2836 (6s) 2886 (1s) 2970 (5b)	2814 (10b) 2885 (1) 2987 (6b)	2806 (8b)		2800
I	3035	3038 (30s) 3080 (10s)	3037 (30s) 3078 (8s)	3037 (30b)	3032	3025
III	3118	3122 (25s)	3122 (25s)	3121 (25b)	3140	3126
VI		3202 (8s) 3254 (5s) 3289 (6s) 3306 (4s) 3346 (4s) 3392 (1s) 3470 (1b)	3208 (10b) 3276 (6b) 3338 (4s) 3454 (1b)	3211 (10b) 3267 (8b) 3323 (5) 3368 (4) 3450 (1)		

The spectrum at room temperature exhibits no less than 13 Raman shifts as against six reported by Ananthakrishnan. The lines are of varying width. At 173° T., 16 Raman lines have been identified, whereas at 85° T. no less than 22 Raman lines could be seen as against 4 reported by Menzies and Mills. See Figs. 2 and 3. The observed Raman frequencies have been classified under eight groups as shown in Table II. In the spectrum taken at room temperature the Raman lines are in general broad and diffuse. The line at $\sim 1960 \text{ cm.}^{-1}$ has the maximum width which is of the order of 60 cm.^{-1} . As the crystal is cooled down, the lines sharpen considerably. Besides, some lines split up into components. This is particularly noticeable in the case of the lines ~ 1960 and $\sim 2806 \text{ cm.}^{-1}$. These changes appear to take place gradually and not abruptly very near the so-called λ -point transition (235° T.).

5. DISCUSSION

Before discussing the significance of the results described in the last section, it is useful to recall some of the known properties of ammonium bromide and their variations as one passes through the transition temperature. X-Ray studies carried out by Bartlett and Langmuir (1921), Ketelaar (1934) and by Weigle and Saini (1936) indicate that ammonium bromide exists in three modifications. The α - NH_4Br which is stable above 138°C . possesses the sodium chloride structure (face-centred cube). The β - NH_4Br which is stable between -40°C . and 138°C . has the caesium chloride structure (body-centred cube); each nitrogen atom is surrounded by 4 hydrogen atoms tetrahedrally and by 8 chlorine atoms at the corners of a cube. Below -40°C . the cubic form undergoes slight deformation into the tetragonal form, γ - NH_4Br . Ketelaar observed extra X-ray reflections with NH_4Br at -100°C . They reveal the occurrence of a superlattice in the crystal structure of the low temperature modification. From this Ketelaar concluded that γ - NH_4Br belongs to the space group $D_{4h}^{7/2}$, each unit cell containing two molecules of NH_4Br . According to Weigle and Saini, the change from the cubic to the tetragonal form may be regarded as a contraction by two of the cubic axes by 3 parts in 1000 and by 2% displacement by the bromine ions along a 3rd axis in alternatively a positive and negative direction with respect to the two shortened axes. This result fits in with the observation made by Simon and Bergmann (1930) on the thermal expansion of ammonium bromide. The coefficient of thermal expansion assumes a negative value just at the transition temperature, while above and below the transition temperature it has a positive value. This observation of Simon and Bergmann has been confirmed by Weigle by the X-ray method. Ruhemann (1927) measured the specific heat of ammonium bromide above and below the transition temperature. While passing through the transition temperature the specific heat at constant pressure increases rapidly and falls again to the normal value. Unlike cold ammonium chloride, ammonium bromide is not piezo-electric both above and below the transition temperature (Hettich and Schleede, 1928). According to the observations of Hettich (1934), ammonium bromide exhibits double refraction below the transition temperature showing thereby that its crystal structure does not possess cubic symmetry. As it is also non piezo-electric, the correct space group of the cold bromide should be $D_{4h}^{7/2}$.

As in the case of ammonium chloride, the anomalous behaviour of ammonium bromide near the transition temperature has been attributed by Pauling (1930) to the existence of free rotation of the NH_4 ion in the lattice above the transition temperature. Frenkel (1935), on the other hand,

favoured the view that both above and below the transition temperature, the NH_4 ion executes rotational oscillations the only difference being that above the transition temperature the orientations are irregularly distributed. The appearance of a lattice spectrum with discrete frequency shifts and with great intensity in crystalline ammonium bromide at temperatures far above the transition point as revealed by the present study does not support Pauling's hypothesis. If the NH_4 ion is capable of free rotation above the transition temperature as suggested by Pauling, and in consequence possesses spherical symmetry, none of the atomic vibrations in which NH_4 moves as a unit should appear as fundamentals in the Raman effect due to the similarity of its structure to that of caesium chloride. The very appearance of a lattice spectrum with discrete frequency shifts at ordinary temperatures and its persistence without any striking change below the transition temperature support Frenkel's explanation, namely, that both above and below the transition temperature the NH_4 ion executes rotational oscillations and that only a reorientation of the NH_4 tetrahedra takes place in the lattice at the transition temperature.

The activity of the lattice vibrations of ammonium bromide in the first order Raman effect enables one to observe directly the discrete nature of the vibration spectrum of the caesium chloride type of structure and thus to confirm the validity of Raman dynamics. K. G. Ramanathan (1947) has given expressions for the frequencies of the fundamental modes of oscillation of the caesium chloride structure. The respective modes and the formulæ for the frequencies are enumerated in Table III. With the help of these formulæ, it is possible to give tentative assignments to the lattice lines appearing in the spectrum of ammonium bromide taken above the transition temperature. In order to do this, it is necessary to know whether all the observed low frequency lines given in Table I belong to the first order spectrum or not. In the case of NH_4Cl the first order lattice spectrum is confined to a region of frequency shifts, $0\text{--}200\text{ cm.}^{-1}$. It follows therefore that the first order lattice spectrum of NH_4Br should not extend beyond 200 cm.^{-1} . On this basis, one can assign the lattice lines coming under Group I (see Table I) to the first order spectrum while those coming under Group II to the second order spectrum.

To a first approximation, the eleven modes of oscillation characteristic of the caesium chloride structure have only seven distinct frequencies, ν_1 to ν_7 , as given in Table III. Of these, ν_7 should be very weak. The six lattice lines appearing in the spectrum taken at 308° T. may be identified with ν_1 to ν_6 . The corresponding frequency shifts are entered in column 7 of Table III. Because of the high refractivity and the heavy mass of the

Vibration spectrum of the NH_4Br lattice above the transition temperature

Sl. No.	Oscillating planes	Nature and direction of oscillation	Degeneracy	Formula $4\pi^2\nu^2c^2$		Frequency in cm.^{-1} observed at 308°C.
I	Dodecahedral	NH_4, Br in phase ; normally along $[\bar{1}\bar{1}0]$ NH_4, Br out of phase ; tangentially $[110]$	6	$\frac{P-2T}{m_1} + \frac{P'-2T'}{m_2} + \frac{4(T+T')}{m_1+m_2}$	ν_1	175
II	Two Lattices	NH_4 against Br , arbitrary	3	$\frac{P+2T}{m_1} + \frac{P'+2T'}{m_2}$	ν_2	136
III	Cubic	NH_4 alone oscillating normally along $[100]$	3	$\frac{P-2T}{m_1}$	ν_3	155
IV	Octahedral	NH_4 alone oscillating along any three orthogonal directions	3	$\frac{P-2T}{m_1}$		
V	Cubic	NH_4 alone oscillating tangentially along $[010]$ or $[001]$	6	$\frac{P+2T}{m_1}$	ν_4	128
VI	Dodecahedral	NH_4 tangentially along $[100]$ contained in the $[110]$ plane	3	$\frac{P+2T}{m_1}$		
VII	Cubic	Br alone oscillating along $[100]$ normally	3	$\frac{P'-2T'}{m_2}$	ν_5	75
VIII	Octahedral	Br alone oscillating in any three orthogonal directions	3	$\frac{P'-2T'}{m_2}$		
IX	Cubic	Br alone oscillating tangentially along $[010]$ or $[001]$	6	$\frac{P'+2T'}{m_2}$	ν_6	56
X	Dodecahedral	Br tangentially along $[100]$ contained in the $[110]$ plane	3	$\frac{P'+2T'}{m_2}$		
XI	Dodecahedral	NH_4, Br in phase, tangentially along $[110]$ NH_4, Br out of phase ; normally along $[110]$	6	$-\frac{4(T+T')}{m_1+m_2}$	ν_7	

P and P' represent the force on any atom proportional to its own displacement and T and T' represent the force on any atom proportional to the displacement of the next nearest neighbours. The undashed quantities refer to the NH_4 ion and the dashed ones to Br ion. m_1 and m_2 are the respective masses of NH_4 and Br ions.

bromine ions, those oscillations in which the bromine ions alone move may be expected to appear with great intensity and should have the lowest frequencies. The most intense line at 56 cm.^{-1} is therefore assigned to ν_6 and the next line at 75 cm.^{-1} to ν_5 . Since $P \approx P'$, and $T \approx T'$, ν_3/ν_5 and ν_4/ν_6 should be nearly equal to $\sqrt{\frac{m_2}{m_1}}$. The pairs of lines $56\text{--}128 \text{ cm.}^{-1}$ and $75\text{--}155 \text{ cm.}^{-1}$ satisfy the above relationship. Therefore, the lines 128 cm.^{-1} and 155 cm.^{-1} have been assigned respectively to ν_4 and ν_3 . The remaining two lines 175 and 136 have been assigned to ν_1 and ν_2 respectively as they roughly satisfy the relationships:— $\nu_1^2 \approx \nu_3^2 + \nu_5^2$ and $\nu_2^2 \approx \nu_4^2 + \nu_6^2$. At 308° T . the lattice lines are rather broad and most of them run into one another. The frequency shifts given in Table I correspond to the positions of maxima as judged from the microphotometer record (Fig. 5 c). In view of this, no attempt has been made to evaluate the force constants P , P' , T and T' from the observed frequencies.

Below the transition temperature, the crystal structure belongs to the tetragonal class. The expressions for the frequencies of oscillations for this type of structure have not been worked out on the basis of the new crystal dynamics. Therefore no quantitative comparison of the experimental results with theory is possible at present; but certain features of the spectrum may be mentioned. At 173° T ., the first order lattice spectrum exhibits 5 lines. The frequency shifts of the 1st and 2nd lines are related to the shifts of the 3rd and 4th lines in the inverse ratio of the square roots of the masses of bromine and ammonium ions. It follows therefore that the first two lines arise from the oscillations of the bromine ions alone, while the next two lines are due to the oscillations of the NH_4 ions.

The Spectrum of the NH_4 ion.—The observed frequency shifts in crystalline ammonium bromide lying in the neighbourhood of 3000, 1700, 3100 and 1400 and classified under Groups I, II, III and IV in Table II, represent the fundamental frequencies of internal oscillation of the NH_4 ion. In the crystalline state, the degeneracies of the four characteristic frequencies of the free NH_4 ion appear to have been partly removed as indicated in Table IV.

The corresponding frequency shifts observed in the spectrum of NH_4Cl are also included in Table IV for purposes of comparison. In crystalline NH_4Br , only the degeneracy of ν_4 is removed, whereas corresponding to ν_2 and ν_3 of the free ion, only single lines are recorded both at 308° T . and at 85° T . In the case of NH_4Cl , on the other hand, the degeneracies of ν_2 , ν_3 and ν_4 are completely removed at 85° T . It follows therefore that

TABLE IV
Raman frequencies of the NH_4 ion

State		ν_1 (1)	ν_2 (2)	ν_3 (3)	ν_4 (3)
Free	ion	3033	1685	3134	1397
NH_4Br Crystal	308° T.	3037	1686	3121	1398, 1429
	85° T.	3038	1693	3122	1401, 1420, 1435
NH_4Cl crystal	308° T.	3041	1710, 1765	3146	1400, 1418, 1440
	85° T.	3048	1716, 1790	3121, 3138, 3162	1401, 1420 ?

(Figures given in brackets represent the respective degeneracies.)

the force fields surrounding the vibrating NH_4 ion are more symmetrical in crystalline NH_4Br than in crystalline NH_4Cl . This is true both at room temperature and at the temperature of liquid air.

In the photographs taken at 173° T. and 85° T, the most intense line corresponding to the totally symmetric oscillation of the NH_4 ion has a weak companion at about 3080 cm.^{-1} . This may be assigned as a combinational line ($\nu_2 + \nu_4$) which appears with some appreciable intensity due to its proximity to the most intense line at $\approx 3038 \text{ cm.}^{-1}$. See Table IV.

As in the case of ammonium chloride, the spectrograms taken with ammonium bromide exhibit four groups of bands (V, VI, VII and VIII of Table II) with frequency shifts lying in the neighbourhood of 2800, 3200–3470, 1980 and 1490 cm.^{-1} , some of which are fairly intense. They have been observed for the first time. Table V gives the frequency shifts of the groups of extra bands observed in the Raman spectra of ammonium chloride and bromide. The frequency shifts of the intense bands are shown in heavy type. There is complete correspondence between the bands appearing in the bromide spectrum and those appearing in the chloride spectrum except for the following. The frequency shifts in the case of the bromide are generally less than those in the chloride. The bands in the chloride are broader than the corresponding ones in the bromide. The chloride exhibits an intense band at $\approx 1800 \text{ cm.}^{-1}$, whereas there is no such band in the bromide spectrum. The latter shows a weak line at about 1490 cm.^{-1} which is absent in the chloride spectrum. The significance of these results will be discussed in a later paper.

TABLE V

	Liquid air temperature		Room temperature	
	NH ₄ Cl	NH ₄ Br	NH ₄ Cl	NH ₄ Br
VIII	1810	1491	1780	1462
VII	2025 2025	1979 1986	2010	1960
V	2829 2876	2794 2816 2836 2886 2970	2828	2806
VI	3215 3235 3285 3310 3365 3395 3420 3515 3535	3202 3254 3289 3306 3346 3392 3470	3231 3308 3380 3518	3211 3267 3323 3450

6. INFRA-RED SPECTRUM

The absorption and reflection spectra of crystalline ammonium bromide in the infra-red region were examined by Reinkober (1921) who recorded five maxima corresponding to some of the frequencies of oscillation of the NH₄ ions in the crystal. Pohlmann (1932) made a detailed investigation of the infra-red absorption spectrum of thin layers of ammonium bromide at room temperature and at -80°C . (193°T). From the absorption curves reproduced in his paper, the author was able to identify 20 maxima for the room temperature and 23 maxima for -80°C . The frequency shifts corresponding to these maxima have been evaluated and entered in Table VI. Those given in heavy types correspond to positions of intense absorption. The Raman shifts recorded in the spectra of ammonium bromide taken at 308°T . and 173°T . are also given in the same table. The internal oscillations of the NH₄ ion are active both in Raman effect and in infra-red absorption.

Beck (1944) has investigated the fine structure of the infra-red absorption band of ammonium bromide lying in the region $5-6\mu$ at four different temperatures, namely 27°C ., -20°C ., -45°C . and -60°C . He recorded eleven peaks in the region $1602-1750\text{cm}^{-1}$ with an average separation of

TABLE VI

Raman and infra-red frequencies characteristic of the NH₄ ion in NH₄Br

Low Temperature		Room Temperature	
Raman 173° T.	Infra-red 193° T.	Raman	Infra-red
	1359		1360
1399	1382		1369
1416	1417		1374
1432	1443	1398	1410
	1467	1429	1437
1480	1483	1462	1468
	1648		1483
	1662	1686	1680
	1673		1697
1690	1698		1717
	1740		1728
1976			1739
2814	2830		1757
2885			1768
2987	2963	1960	
	2990	2806	2830
3037	3009	3037	3055
3076	3060	3121	3162
3122	3150	3211	
3208	3202	3267	
	3240	3323	3313
3276	3271	3368	3362
3338	3305	3450	3460
	3372		
3454	3486		

14.8 cm.⁻¹ between two consecutive peaks. The fine structure appeared practically unaltered at 27° C. and - 20° C. Between - 20° C. and - 45° C. there was a noticeable change in the fine structure which persisted down to at least - 60° C. The fine structure appeared at the same wavelengths but with decreased intensity at lower temperatures. The absorption curve for the bromide showed more irregularity than that for the chloride. The appearance of the fine structure below the transition temperature should be attributed to the torsional oscillations of the NH₄ ions.

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7. SUMMARY

Using the λ 2536.5 mercury resonance radiation as exciter, the Raman spectrum of crystalline ammonium bromide has been photographed with the crystal maintained successively at four different temperatures, namely, 398°, 308°, 173° and 85° T. The following facts emerge from this study:—

(1) In the region of temperatures investigated, the Raman spectrum of ammonium bromide exhibits a series of low frequency or lattice lines a fact which has been noticed for the first time. The frequency shifts, intensities and widths of the lines are found to vary with temperature. The lines observed in the spectrum taken above the transition temperature (235° T.) have been identified as the fundamental modes of vibration of the caesium chloride structure in which the NH_4 ions oscillate as units as demanded by the new crystal dynamics.

(2) The lattice spectrum exhibits discrete frequency shifts even at 398° T., *i.e.*, 163° above the transition temperature. This does not support Pauling's hypothesis that there is onset of free rotation of the NH_4 ions above the transition temperature.

(3) The spectrum characteristic of the NH_4 ions exhibits 5 distinct Raman lines at room temperature and 6 lines at liquid-air temperature. From this it is concluded that the oscillating NH_4 ions do not possess the full tetrahedral symmetry. A comparison of the spectrum of NH_4Br with that of NH_4Cl reveals that the oscillating NH_4 ions in NH_4Br possess a higher order of symmetry than those in NH_4Cl .

(4) The spectra recorded at all temperatures reveal the presence of a large number of bands of which those lying in the region ≈ 2800 and 3200 – 3500 are the most prominent.

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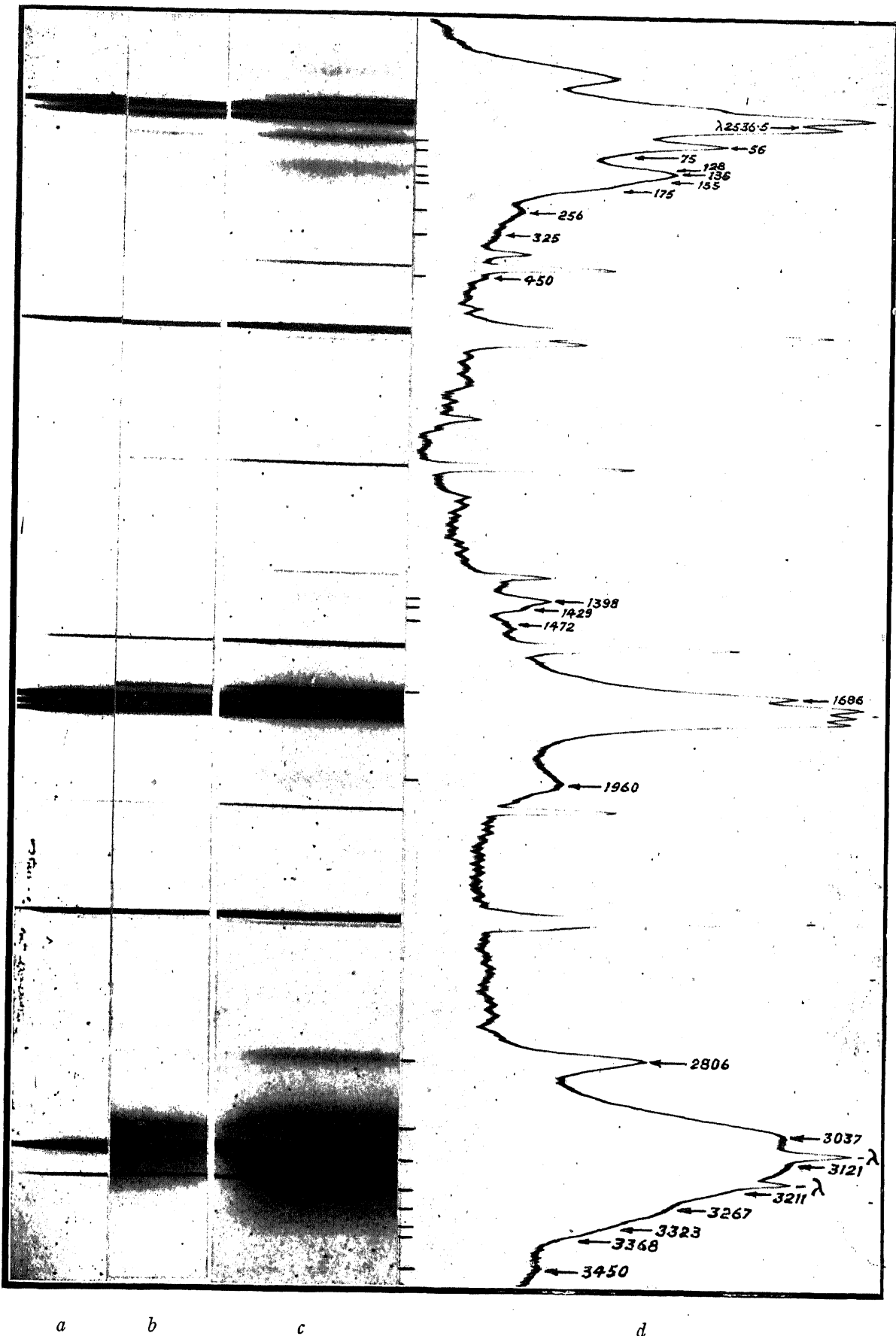
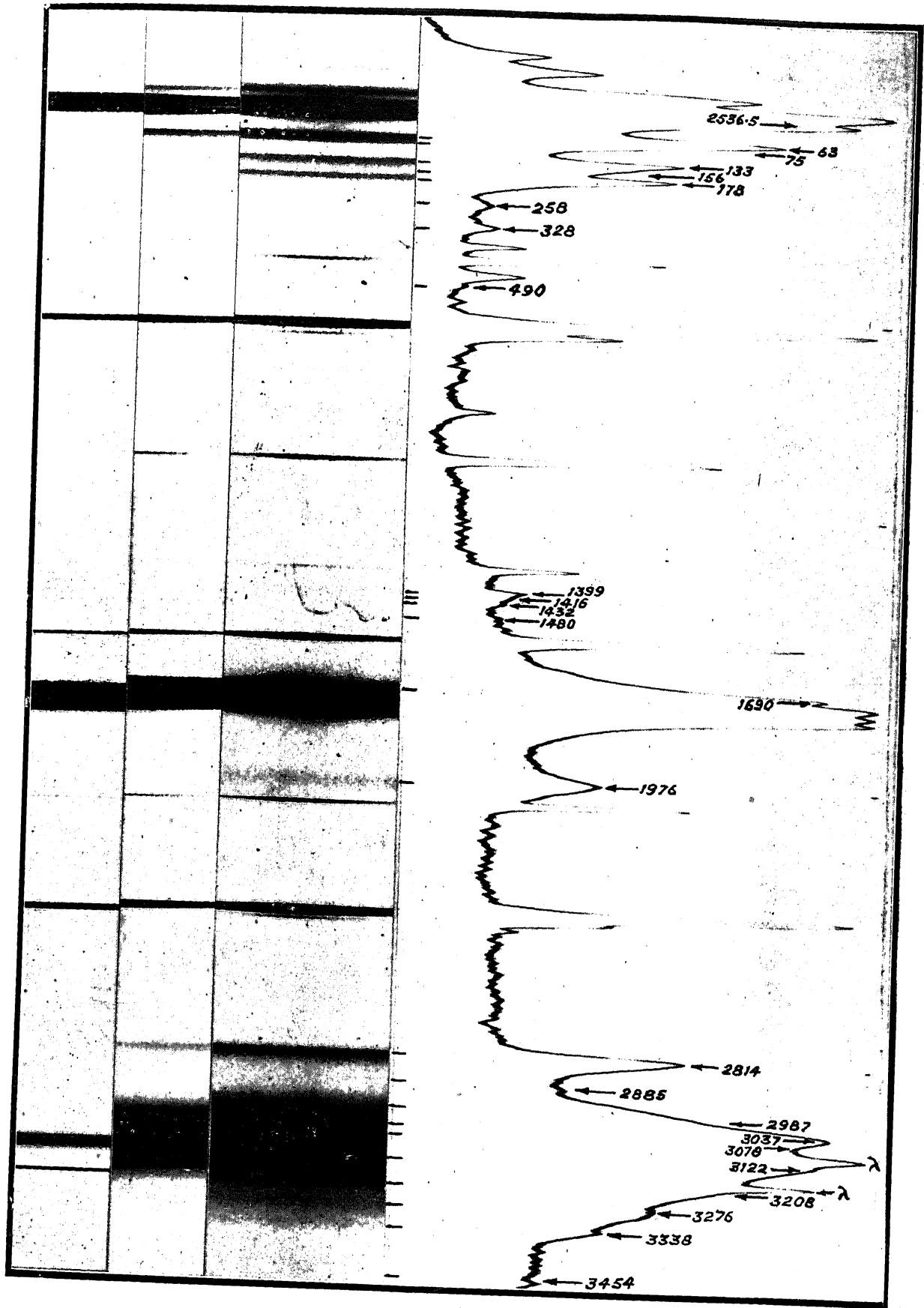


FIG. 1



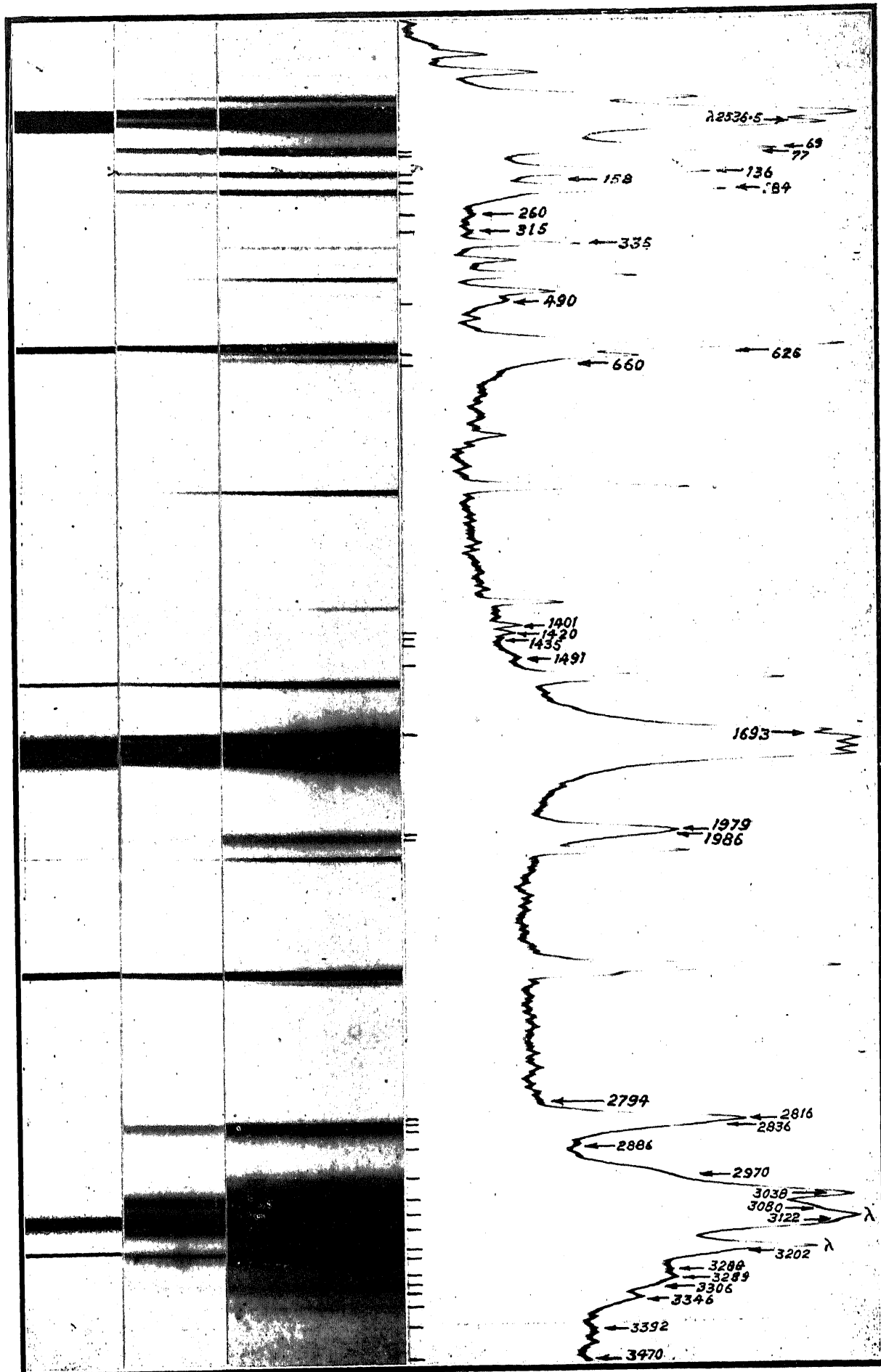
a

b

c

FIG. 2

d



λ 2536.5

λ 2576.3

λ 2652.0

λ 2698.9

λ 2759.8

I₄Cl

308°T.(f)

I₄Cl

85°T.(e)

I₄Br

85°T.(d)

Br

173°T.(c)

Br

308°T.(b)

Br

398°T.(a)

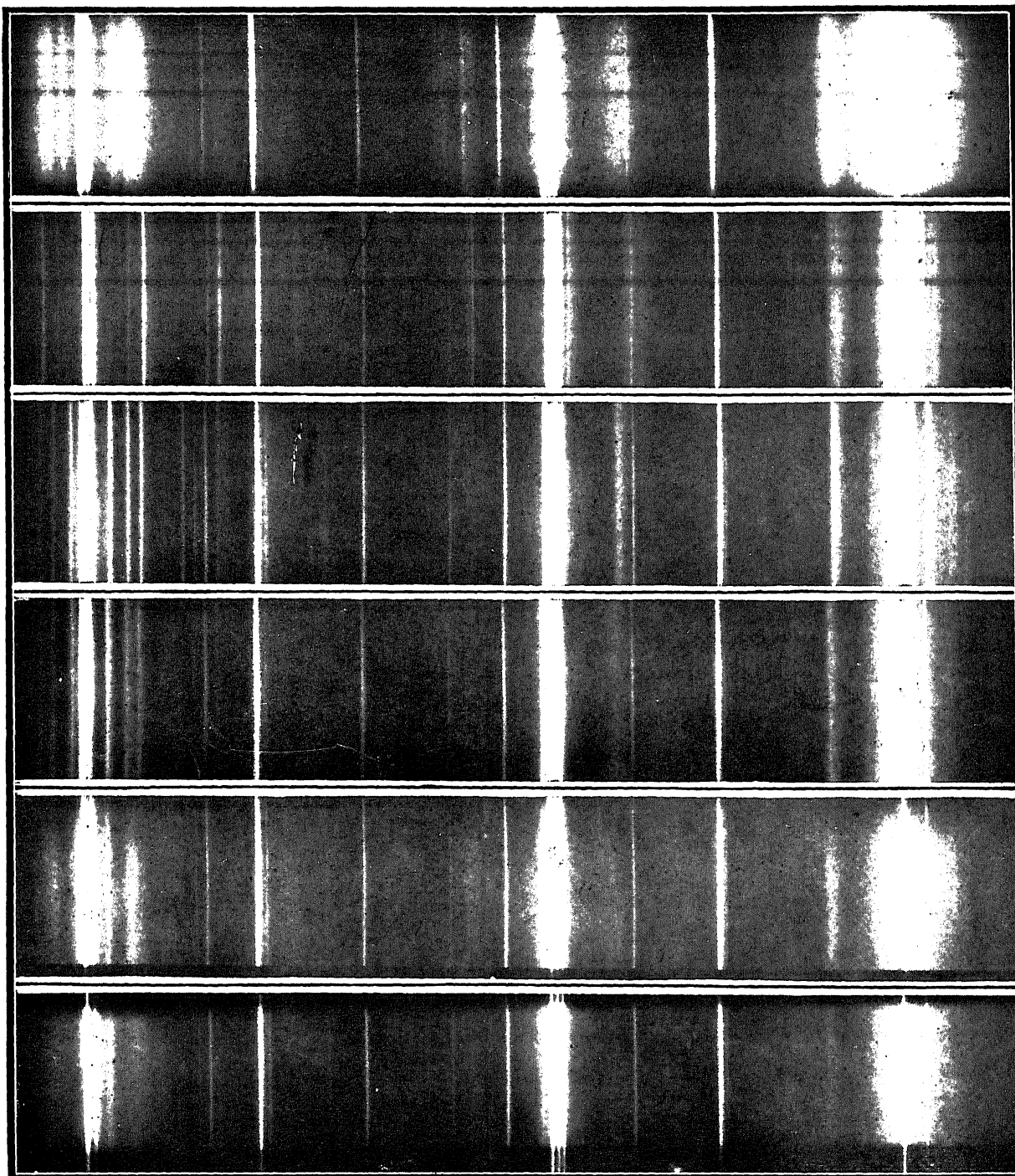


FIG. 4

DESCRIPTION OF PLATES

PLATE V

- FIG. 1. (a) Mercury spectrum taken with a Hilger medium quartz spectrograph,
(b) and (c) Prints of different depths enlarged from the same negative showing the
Raman spectrum of ammonium bromide taken at 308° T.,
(d) its microphotometer record.

PLATE VI

- FIG. 2. (a) Mercury spectrum.
(b) and (c) Raman spectrum of ammonium bromide taken at 173° T.,
(d) its microphotometer record.

PLATE VII

- FIG. 3. (a) Mercury spectrum,
(b) and (c) Raman spectrum of ammonium bromide taken at 85° T.,
(d) its microphotometer record.

PLATE VIII

- FIG. 4. (a) to (d) Raman spectrum of ammonium bromide taken at four different temperatures.
(e) and (f) Raman spectrum of ammonium chloride taken at two different
temperatures.