RAMAN SPECTRUM OF AMMONIUM CHLORIDE AND ITS VARIATION WITH TEMPERATURE

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1. Introduction

A study of the Raman spectrum of crystalline ammonium chloride and its variation with temperature is of great theoretical interest from two points of view. Firstly, as is well known, ammonium chloride crystal possesses a λ-point transition ($=242 \cdot 8°$ T.) at or in the vicinity of which its various physical properties exhibit anomalous behaviour. Pauling (1930) has suggested that the NH_4 ion is capable of free rotation above the transition temperature and the rotation changes to oscillation below that temperature and that the observed phenomena are just those expected to accompany the transition from rotation to oscillation of the NH_4 ion. Frenkel (1935), on the other hand, favoured the view that the NH_4 ion executed only torsional oscillations both above and below the transition temperature. A study of the Raman spectrum of ammonium chloride at different temperatures should throw some light on the behaviour of the NH_4 ion in the neighbourhood of the transition temperature.

Secondly, ammonium chloride crystallises in the cubic system, its structure being similar to that of cæsium chloride below 450° T. On the basis of the new crystal dynamics, a structure of the cæsium chloride type should have 11 fundamental frequencies of oscillation, none of which would be active as fundamentals in light-scattering. This would also be the case with ammonium chloride crystal if the NH_4 ion is capable of free rotation and in consequence possesses spherical symmetry. If, however, this condition be not satisfied because of the specific orientation of the tetrahedral NH_4 ion in the lattice, some of the 11 modes of oscillation in which the ion moves as a unit may be active as fundamentals in light-scattering. This actually proves to be the case, as we shall see and the study of the Raman spectrum of NH_4Cl, therefore, enables us directly to confirm the discrete nature of the vibration spectrum of the cæsium chloride structure.

2. Earlier Work

The Raman effect in ammonium chloride in the crystalline state has attracted a good deal of attention. The earlier investigators, namely,

Schæfer, Matossi and Aderhold (1930), Kastler (1932), Silveira, (1932), Holmes (1932) and Rao and Rao (1933, 1934) reported the existence of only a few lines in the spectrum of ammonium chloride. More detailed investigations were carried out by Menzies and Mills (1935), Holmes (1936) and Ananthakrishnan (1936, 1937). Menzies and Mills recorded spectrograms with the crystal powder maintained at the room temperature, $-24°$ C., $-28°$ C., $-32°$ C., $-65°$ C. and at $-150°$ C. respectively. The most interesting observation reported by them is the appearance of a lattice line with frequency shift 183 cm.$^{-1}$ when the temperature of the crystal is lowered below about $-30°$ C. For the NH_4 group, the same authors reported five diffuse lines at room temperature and seven sharp lines at $-150°$ C. Holmes worked with a single crystal of ammonium chloride and studied its Raman spectrum in the range from room temperature to well above $510°$ T. at which the crystal has the NaCl structure. Although he succeeded in recording the complete spectrum of the NH_4 group, *i.e.*, nine Raman lines, he failed to record any Raman line with a frequency shift less than 1400 cm.$^{-1}$ Employing the technique of complementary filters for crystal powders, Ananthakrishnan examined the Raman spectrum of ammonium chloride and confirmed the existence of eight of the nine NH_4 lines reported by Holmes. He also failed to record any low frequency line.

From what has been said above, it is clear that the results of the earlier workers on the Raman spectrum of ammonium chloride are incomplete, presumably because of the difficulty experienced by them in obtaining good photographs. Most of them used the $\lambda 4046$ and the $\lambda 4358$ radiations of the mercury arc as exciter. Single crystals of ammonium chloride being transparent to the ultra-violet, the use of the $\lambda 2536 \cdot 5$ mercury resonance radiation as exciter suggests itself as a marked improvement in the technique of study, especially when one is interested in recording low frequency or lattice lines on a clear background. Accordingly, the author undertook a detailed investigation of the Raman spectrum of ammonium chloride in the form of a single crystal and its temperature variation, using the $\lambda 2536 \cdot 5$ excitation.

3. Details of the Experiment

Single transparent crystals of ammonium chloride with well-developed faces were prepared by the method of slow evaporation from aqueous solutions of the salt to which a small quantity of urea was added.* The latter acts as a catalyst and facilitates the growth of the crystal. Kahlbaum's

purest chemicals were used. The biggest grown crystal had the dimensions $2 \cdot 5 \times 2 \cdot 5 \times 1 \cdot 5$ cm. The specimens used in the present investigation were usually of the size $1 \times 1 \times 0 \cdot 5$ cm. Refractive index measurements were made with the ammonium chloride crystals. The measured value was the same as that of the pure salt indicating thereby that the crystals were not contaminated with urea. This conclusion was further supported by the fact that the Raman spectrum did not exhibit the characteristic urea lines even faintly.

The experimental technique employed for photographing the Raman spectrum using the $\lambda 2536 \cdot 5$ excitation was the same as in the recent investigations of the author with various other crystals. For experiments below room temperature, a demountable Dewar flask was used. The crystal of ammonium chloride was firmly fixed to a copper block which was in turn screwed on to the lower end of the inner tube of the Dewar flask. The latter was provided with two quartz windows for illumination and observation. Liquid air, solid carbon dioxide in alcohol, solid carbon dioxide in acetone and salted ice were successively used as refrigerants. At very low temperatures the crystal acquired a fugitive yellow colouration on irradiation by ultra-violet light. For work above room temperature, a specially designed heater described in detail in one of the earlier papers of the author (Krishnan, 1946) was used.

A series of spectrograms was taken with the crystal held at seven different temperatures from $395°$ T. down to that of liquid air, *i.e.*, $85°$ T. A Hilger medium quartz spectrograph was used. With a slit-width of $0 \cdot 04$ mm., exposures of the order of 15 hours were given to get reasonably intense spectrograms at liquid-air temperature, whereas exposures of 3 hours sufficed for the room temperature photograph. Ilford special rapid plates were used. The negatives were measured with the aid of a Hilger cross-slide micrometer.

4. RESULTS

Photographs of the Raman spectrum of ammonium chloride taken at $308°$ T. and $85°$ T. are reproduced in Figs. 1 (b) and 2 (b) respectively. The corresponding microphotometer records are shown in Figs. 1 (c) and 2 (c). Figs. 1 (a) and 2 (a) represent the spectrum of the mercury arc for purposes of comparison. The spectrograms taken by the author and reproduced in Figs. 1 and 2 exhibit many more Raman lines both in the low and high frequency shift regions than any recorded by the earlier workers. The positions and the frequency shifts of the Raman lines and bands are marked in the Figures. In order to get a very heavily exposed spectrogram at liquid-air temperature, crystalline quartz windows were used for the demountable
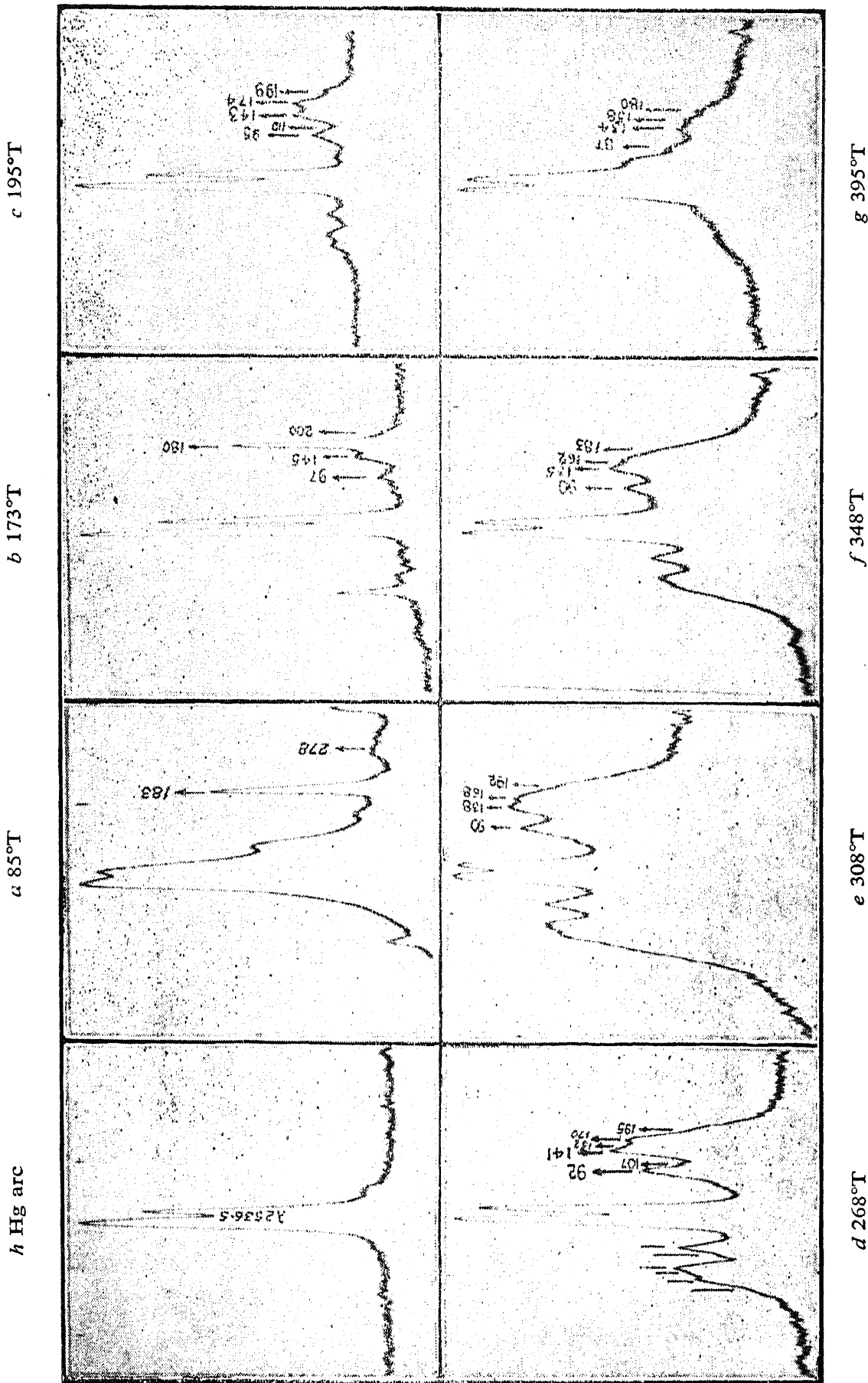
FIG. 4. (*a*) to (*g*) Microphotometer records of the lattice spectrum of ammonium chloride taken at different temperatures. (*h*) Microphotometer record of the mercury spectrum.

Dewar flask. With this arrangement some of the Raman lines of quartz appeared feebly in the spectrogram (see Fig. 2). The quartz lines are marked as "Q" in the microphotometer record. The Raman shifts of ammonium chloride are classified under two heads, namely, (1) low frequency or lattice lines and (2) lines due to the internal oscillation of the NH_4 group, and are described separately.

Lattice lines.—The series of spectra reproduced in Figs. 3 (a) to (g) represents the lattice spectrum of ammonium chloride taken at different temperatures. The corresponding microphotometer records are reproduced in Figs. 4 (a) to (g). As the photographs reproduced in Fig. 3 with the exception of the one at 195° T., were taken with fused quartz discs as windows for the Dewar flask and for the heater, the low frequency lines appearing in the spectra are not quartz lines, but genuine lattice lines of ammonium chloride. Even in the spectrogram taken at 195° T., only the most intense Raman line of quartz is recorded feebly. The photographs reproduced here, while confirming Menzies and Mills' results for very low temperature, reveal numerous other interesting facts. The lattice spectrum becomes diffuse and faint when the crystal is heated above room temperature. At the highest temperature investigated, namely 395° T., the crystal began to sublime slowly and thereby became translucent. Consequently, it was not possible to get any heavily exposed photograph at this temperature. Careful examination of Figs. 3 (g) and 4 (g) indicates that even at this high temperature, four Raman lines could be easily identified in the lattice spectrum. As the crystal is cooled down, the spectrum brightens and also sharpens considerably, exhibiting even above the so-called λ-transition (242·8° T.) a group of three fairly well-defined Raman lines with indications of three fainter ones. Of the latter, the one with the highest frequency shift is rather broad and can be clearly seen in all the photographs except the one taken at liquid-air temperature. The other two are fairly sharp and are just discernible in the photograph taken at 268° T. They are more clearly seen in the corresponding microphotometer record both on the Stokes and the anti-Stokes sides. At other temperatures they are partially masked by the presence of the intense lines in the neighbourhood. The features of the spectrum persist far below the λ-point transition, becoming at the same time quite sharp and showing progressive shift in their positions with falling temperature. A remarkable change in their intensities also occurs at the same time. At liquid-air temperature, all the lines disappear except the very intense one with the frequency shift 183 cm.$^{-1}$ A new line with frequency shift 278 cm.$^{-1}$ unmistakably makes its appearance. This is quite sharp but faint. See Figs. 3 (a) and 4 (a). The microphotometer record reproduced

in Fig. 2 (c) exhibits another faint line with a frequency shift of 91 cm.$^{-1}$ which is not one of the characteristic lines of quartz. In Fig. 4 (a) the existence of this line is not so clearly discernible as in Fig. 2 (a), probably due to the overexposure of the coma accompanying the exciting line. The frequency shifts of the lattice lines at different temperatures are entered in Table I. The photograph taken at room temperature shows the existence

TABLE I

Lattice Spectrum of NH$_4$Cl

Temperature °T	Frequency shifts in wave numbers							
85	91					183		278
173		97		145		180	200	
195		95	110	143		174	199	
268		92	107	141	152	170	195	
308		90		138		168	192	
348		90		135		162	183	
395		87		134		158	180	
Assignment	$2\nu_7$	ν_6	ν_5	ν_4	ν_3	ν_2	ν_1	$2\nu_4$

of a weak continuum starting from about 200 cm.$^{-1}$ and extending up to 380 cm.$^{-1}$ at which the intensity drops down to almost nothing.

The spectrum of the NH$_4$ group.—All the Raman lines with frequency shifts greater than 1400 cm.$^{-1}$ have been attributed to the internal oscillations of the NH$_4$ group. The spectrum at room temperature exhibits no less than 14 Raman shifts, some of which are sharp, some broad and the rest broad and diffuse. In the spectrogram taken at liquid-air temperature, no less than 23 Raman shifts could be identified as due to the NH$_4$ group. The frequency shifts of these are entered in Table II. Rough estimates of the relative peak intensities have been made and the values are given in Table II along with the description of the lines: *b*, *d*, and *s* represent broad, diffuse and sharp. The values of the frequency shifts of ammonium chloride recorded earlier by Menzies and Mills (1935) at 123° T. (— 150° C.) and those obtained by Holmes (1936) and by Ananthakrishnan (1937) for room temperature are also included in Table II for purposes of comparison. Menzies and Mills' data are far from being complete, while Holmes and Ananthakrishnan recorded all the important lines of the NH$_4$ ion exhibited at room temperature.

The general nature of the change which the spectrum undergoes as the temperature is progressively lowered, is best described by stating the appearance of the lines themselves. The Raman shifts entered in Table II have

R. S. Krishnan

TABLE II

Raman Spectrum of the NH₄ Group in Ammonium Chloride

Group	Low Temperature			Room Temperature			
	Menzies and Mills (1935) 123°T	Author (1947) 85°T	Relative peak Intensity	Holmes (1936)	Anantha-krishnan (1937)	Author (1947)	Relative peak Intensity
IV	1403	1401	5s	1407 unresolved doublet	1398	1400	15s
	1464	1420	10s		1424	1418	10b
						1440	8b
II	1712	1716		1709	1700	1710	
	1770	1790	15s	1768	1750	1765	
		1810	10b			1780	8b
VII		2025	8b	2010	2009	2010	10d
		2075	5b				
V		2829	10b	2824	2813	2828	20b
	2870	2876	8b				
I	3043	3048	50s	3041	3040	3041	50b
		3072	15s				
III	3123	3121	30s	3146	3142	3146	35b
		3138	26s				
		3162	28s				
VI		3215	10b }	3232		3231	20b
		3235	10b }				
		3285	6b }	3300		3308	15b
		3310	4b }				
		3365	2b }				
		3395	2b }			3380	8b
		3420	1b }				
		3515	1d }			3518	2d
		3535	1d }				

been classified into seven groups. The most intense Raman line appearing in the spectrum at room temperature has the frequency shift of 3041 cm.⁻¹ (Group I) and is rather broad. At liquid-air temperature this line becomes sharp and is followed by a feeble companion with a frequency shift of 3072 cm.⁻¹ The two lines with frequency shifts lying between 1700 and 1760 cm.⁻¹ which were reported by Holmes and Ananthakrishnan cannot be identified in the author's spectrogram as they fall on the top of the mercury triplet $\lambda 2652 \cdot 0$, $\lambda 2653 \cdot 7$ and $\lambda 2655 \cdot 1$. An examination of the spectrograms and the microphotometer record reproduced in Fig. 1 reveals that the outer components of the triplet which are separated from $\lambda 2536 \cdot 5$ by 1716 and 1760 cm.⁻¹, appear to have bulged out in the scattered spectrum due to the superposition of the Raman lines. Their frequency shifts have

therefore been tentatively taken as 1710 and 1765 cm.$^{-1}$ The room temperature photograph exhibits an additional broad line with a mean shift of 1780 cm.$^{-1}$ At liquid-air temperature, two lines with frequency shifts 1790 and 1810 cm.$^{-1}$ are seen clearly separated from the triplet. One Raman line with frequency shift 1716 cm.$^{-1}$ has been included in Table II. Its existence is inferred from the appearance of the mercury line λ 2652·0 on which it falls, and also from the fact that Menzies and Mills have reported a fairly intense line with a shift of 1712 cm.$^{-1}$ The intense and broad Raman line appearing in the spectrum at room temperature with a frequency shift of 3146 cm.$^{-1}$ splits up into a triplet with shifts 3121, 3138 and 3162 cm.$^{-1}$ at liquid-air temperature, the first one being the most intense. One of the three fairly sharp lines which appear at room temperature with shifts 1400, 1418 and 1440 cm.$^{-1}$, is absent in the spectrogram taken at liquid-air temperature. The relative intensities of the other two lines are reversed. Two broad bands lying at $\approx$ 2010 and 2828 cm.$^{-1}$ in the spectrum at room temperature sharpen as the temperature is lowered. At liquid-air temperature each one of them has a companion band on the high frequency shift side. The photograph reproduced in Fig. 1 exhibits a group of four Raman bands with frequency shifts greater than 3200 cm.$^{-1}$, the intensity of the band decreasing with increasing frequency shift. Two bands $\approx$ 3232 and 3300 cm.$^{-1}$ have already been reported by Holmes (1936). The four bands recorded in the present investigation split up into nine components with frequency shifts $\approx$ 3215, 3235, 3285, 3310, 3365, 3395, 3420, 3515 and 3535 cm.$^{-1}$ when the temperature of the crystal is lowered to that of liquid air. These components may be seen only with some difficulty in the reproduced photograph, but they can be more easily identified in the microphotometer record (Fig. 2 c).

Besides the Raman shifts listed above, the spectrogram taken at room temperature exhibits four broad and diffuse bands 460–540, 670–780, 1065–1145 and 1280–1335 cm.$^{-1}$ respectively. They are marked as B_1, B_2, B_3 and B_4 in Fig. 1 (a). These bands cannot be attributed to the internal oscillations of the NH_4 ion. The intensity distribution in each band is asymmetrical, the low frequency shift end being more intense than the other. See Fig. 1. In the spectrogram taken at liquid-air temperature, one notices only two fairly sharp lines with frequency shifts 560 and 750 cm.$^{-1}$ See Fig. 2.

It should be remarked that as the temperature is lowered, the changes in relative intensity, width and number of the Raman shifts take place progressively. See the series of photographs of the complete spectrum of NH_4Cl reproduced in Fig. 5. The characteristic features of the liquid-air photograph begin to appear in the spectrum taken at 173° T. It will be seen from

the photographs (Fig. 5) that the intensity of the $\lambda 2536 \cdot 5$ line relative to that of its companion ($\lambda 2534 \cdot 8$) increases with increase in temperature. This can be explained as due to the fact that the unmodified scattered radiation is mostly made up of thermal scattering (Brillouin components) which is not absorbed by mercury vapour filter and whose intensity is directly proportional to the absolute temperature.

5. DISCUSSION

Before discussing the significance of the results presented in the last section, it is useful to review the conclusions arrived at regarding the behaviour of the NH_4 ion from other investigations. It is known from X-ray studies (Bartlett and Langmuir, 1921; Wyckoff, 1922) that ammonium chloride possesses the cæsium chloride structure (body-centered cube); each nitrogen atom is surrounded by 4 hydrogen atoms tetrahedrally and by 8 chlorine atoms at the corners of a cube. Many physical properties of the crystal are found to vary sharply but continuously with temperature in the neighbourhood of the so-called λ-point transition (242·8° T.). As the temperature is raised through an interval of only a few degrees, the specific heat at constant pressure (Simon, 1922; and others, 1927; Ruhemann, 1927; Crenshaw and Ritter, 1932) and the coefficient of thermal expansion (Simon and Bergmann, 1930; Smits and MacGillavry, 1933; Adenstedt, 1936) increase many times in value and then decrease. Similar behaviour is also exhibited by the dielectric constant and dielectric absorption of ammonium chloride (Weigle, 1935). The crystal becomes strongly piezoelectric below the transition temperature (Hettich and Schleede, 1928; Hettich, 1934; Bahrs and Engl, 1937). From this observation Hettich concluded that the crystal has no centre of symmetry at low temperatures and therefore belongs to the class T_d, while at ordinary temperatures it belongs to the class O_h. X-ray studies carried out by Simon and von Simson (1926), Smits and MacGillavry (1933) and Ketelaar (1934) showed that the crystal structure remained unaffected as the temperature was lowered below the λ-point. The transition temperature is accompanied by a small volume change less than 1%. These investigators therefore concluded that the transition point should be associated in some manner with the behaviour of the hydrogen tetrahedra, since the light hydrogen atoms alone would not give any trace of their presence in the X-ray method.

In order to explain the observed anomalous behaviour exhibited by ammonium chloride crystal, Pauling (1930) put forward the hypothesis that at temperatures above the transition point, there would be free rotation of the NH_4 ion in the lattice. The failure to observe any lattice lines in the

Raman spectrum of ammonium chloride above the λ-point by Menzies and Mills (1935) is explained by them as due to the presence of free rotation of the NH_4 ion. Frenkel (1935), on the other hand, is opposed to the idea that free rotation starts just at the transition temperature, as there is no supporting evidence so far for the implied weakening of the interatomic binding force in the neighbourhood of the λ-point. He favours the view that both above and below the transition temperature, the NH_4 ion executes rotational oscillations. In the former case, there exists some order in the orientation of the axes about which oscillations occur, whereas above the transition temperature the orientations are irregularly distributed throughout the lattice. Lawson (1940) has calculated the temperature variation of the specific heat under constant volume from measurements on the temperature variations of adiabatic and isothermal Young's and rigidity moduli and the coefficient of thermal expansion, and has come to the conclusion that the transition is not associated with the occurrence of almost free rotation as suggested by Pauling. Lawson favours Frenkel's explanation, namely, that only a reorientation of the NH_4 ion takes place in the lattice at the transition temperature.

Let us now examine the spectroscopic behaviour of ammonium chloride in the light of what has been said above. The appearance of low frequency Raman lines constituting the lattice spectrum with great intensity in crystalline ammonium chloride at temperatures above the λ-point transition supports Frenkel's hypothesis rather than Pauling's. If the NH_4 ion is capable of free rotation and in consequence possesses spherical symmetry, none of the atomic vibrations of ammonium chloride in which NH_4 moves as a unit should appear as fundamentals in Raman effect due to the similarity of its structure to that of cæsium chloride. In fact, the Raman spectrum of ammonium chloride exhibits lattice lines with discrete frequency shifts even at as high a temperature as 395° T., showing thereby that the NH_4 ion is not capable of free rotation at this temperature.

At liquid-air temperature only one intense Raman line appears in the lattice spectrum with frequency shift $183\ cm.^{-1}$ which agrees with the reststrahlen frequency of ammonium chloride (Rubens and Wartenberg, 1914). This line therefore represents the mutual oscillations of the NH_4 and Cl lattices against each other. The appearance of the fundamental vibration both in the scattering of light and in the infra-red absorption supports Hettich's suggestion that at very low temperatures the crystal does not possess any centre of symmetry and therefore belongs to T_d class. It follows therefore that there is a common preferred orientation for all the

hydrogen tetrahedra which have ceased to oscillate and are at rest in the crystal. Menzies and Mills (1935) are of the opinion that the orientations of hydrogen tetrahedra are such that a symmetry axis of the tetrahedron lies parallel to the diagonal axis of the cube. As the temperature is raised above 170° T., the full lattice spectrum of ammonium chloride makes its appearance in the Raman effect, indicating thereby that a definite change has taken place in the relative orientation of the hydrogen tetrahedra. The effect can be visualised as follows:—As the temperature is raised, the NH_4 ion begins to oscillate and the preferred orientation of the hydrogen tetrahedra gets disturbed. The slight mis-setting of the hydrogen tetrahedra during torsional oscillations makes all the lattice vibrations of the structure in which NH_4 moves as a unit, active in the Raman effect. This enables us to observe directly the discrete nature of the vibration spectrum of the cæsium chloride type of structure. As long as the torsional oscillations are of small amplitudes, the lattice lines should be sharp. As the temperature is still further increased, the oscillations become more violent and the orientations of the hydrogen tetrahedra tend to be more irregularly distributed resulting in a broadening of the lattice lines. This is what is observed experimentally. Thus, the spectroscopic data strongly indicate the correctness of Frenkel's picture regarding the behaviour of the NH_4 ion above and below the transition temperature.

Identification of the fundamental frequencies of the lattice.—The fact that the lattice spectrum of ammonium chloride consists of a finite number of discrete frequencies is a direct confirmation of the validity of the Raman dynamics. On the basis of the new dynamics, cæsium chloride structure has eleven fundamental modes of oscillation. They are enumerated in Table III for the case of the ammonium chloride structure. The expressions for the frequencies have been worked out by K. G. Ramanathan (1947) in a paper appearing elsewhere in these *Proceedings*. The approximate formula involving only four force-constants are given in column 5 of Table III. The frequencies of the 11 modes are in the descending order of magnitude. 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 Cl ion. m_1 and m_2 are the respective masses of NH_4 and Cl ions. To a first approximation the 11 modes have only 7 distinct frequencies, ν_1 to ν_7. Since $P \approx P'$ and $T \approx T'$, in order to evaluate the frequencies, we are justified in putting $P = P'$ and $T = T'$. If two of the lattice lines are identified, the remaining frequencies can be calculated using the formulæ given in Table III. The spectrum taken at

TABLE III

Vibration Spectrum of the NH₄Cl Lattice

Sl. No.	Oscillating planes	Nature and direction of Oscillation	Degeneracy	Formula $4\pi^2\nu^2C^2$		Frequency in cm.⁻¹ calculated	Frequency in cm.⁻¹ observed at 268°
I	Dodecahedral	NH₄, Cl in phase; normally along [1̄10] NH₄, Cl out of phase; tangentially along [110]	6	$\dfrac{P-2T}{m_1} + \dfrac{P'-2T'}{m_2} + \dfrac{4(T+T')}{m_1+m_2}$	ν_1	179	195
II	Two Lattices	NH₄ against Cl, arbitrary	3	$\dfrac{P+2T}{m_1} + \dfrac{P'+2I'}{m_2}$	ν_2	170	170
III	Cubic	NH₄ alone oscillating normally along [100]	3	$\dfrac{P-2T}{m_1}$	ν_3	150	152
IV	Octahedral	NH₄ alone oscillating along any three orthogonal directions	3	$\dfrac{P-2T}{m_1}$			
V	Cubic	NH₄ alone oscillating tangentially along [010] or [001]	6	$\dfrac{P+2T}{m_1}$	ν_4	139	141
VI	Dodecahedral	NH₄ tangentially along [100] contained in the [110] plane	3	$\dfrac{P+2T}{m_1}$			
VII	Cubic	Cl alone oscillating along [100] normally	3	$\dfrac{P'-2T'}{m_2}$	ν_5	107	107
VIII	Octahedral	Cl alone oscillating in any three orthogonal directions	3	$\dfrac{P'-2T'}{m_2}$			
IX	Cubic	Cl alone oscillating tangentially along [010] or [001]	6	$\dfrac{P'+2T'}{m_2}$	ν_6	98	92
X	Dodecahedral	Cl tangentially along [100] contained in the [110] plane	3	$\dfrac{P'+2T'}{m_2}$			
XI	Dodecahedral	NH₄, Cl in phase; tangentially along [110] NH₄, Cl out of phase; normally along [1̄10]	6	$-\dfrac{4(T+T')}{m_1+m_2}$	ν_7	42	

268° T. exhibts the maximum number of lattice lines. From a comparative study of the figures given in Table I, it is seen that the mode in which the NH_4 and Cl lattices vibrate against each other has a frequency of 183 cm.$^{-1}$ at 85° T. which decreases to a value 170 cm.$^{-1}$ at 268° T. Therefore ν_2 can be taken as equal to 170 cm.$^{-1}$ The eleventh mode given in Table III should have a very low frequency. At 268° T. no line with frequency shift less than 90 cm.$^{-1}$ has been recorded. At liquid-air temperature two feeble lines with frequency shifts 91 and 278 cm.$^{-1}$ are recorded which should be assigned as octaves from intensity considerations. It is quite reasonable to assign the 91 line as the octave of ν_7. The corresponding fundamental will have a frequency of 45 cm.$^{-1}$ at 85° T. and 42 cm.$^{-1}$ at 268° T. Therefore ν_7 at 268° T. is taken as equal to 42 cm.$^{-1}$ Putting these values of ν_2 and ν_7 in the expression for frequencies, the values of P and T have been calculated:—

$$P = P' = 2 \cdot 176 \times 10^4 \text{ dynes/cm.}$$

$$T = T' = -0 \cdot 07 \times 10^4 \text{ dynes/cm.}$$

The force-constants in ammonium chloride are of the same order of magnitude as in sodium chloride. Taking the above values of the force-constants, the remaining five frequencies have been evaluated and are entered in column 7 of Table III. The measured values of the frequency shifts of the lines appearing in the spectrum at 268° T. are given in the last column of the same table. Considering the approximations made in the calculations, the agreement between the theoretical and observed values is satisfactory. It is important to point out that ν_2 is the most intense line below 180° T., while above that temperature ν_4 is the most intense one. The identification of the frequency shifts entered in Table I is shown in the last row of the same table.

The spectrum of the NH_4 ion.—Because of its tetrahedral symmetry, NH_4 ion in the free state should have only four distinct modes of oscillation of which ν_1 is single, ν_2 is doubly degenerate and ν_3 and ν_4 are triply degenerate. The corresponding Raman shifts are 3033, 1685, 3134 and 1397 cm.$^{-1}$ The observed frequency shifts in crystalline ammonium chloride lying in the neighbourhood of 3000, 1700, 3100 and 1400 cm.$^{-1}$ 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 frequencies of the free NH_4 ion appear to have been removed as indicated in Table IV. It will be evident from a comparative study of the figures given in this table that the degeneracy of ν_3 is removed only at very low temperature, *i.e.*, below 180° T. At liquid-air temperature only 8 lines due to the NH_4 ion are recorded. The

TABLE IV

Raman Frequencies of the NH_4 Ion

State	ν_1	ν_2	ν_3	ν_4
Free ..	3033	1685	3134	1397
NH_4Cl crystal at 308°T ..	3041	1710, 1765	3146	1400, 1418, 1440
,, at 85°T ..	3048	1716, 1790	3121, 3138, 3162	1401, 1420, ?

ninth one may be too feeble to be recorded. The appearance of nearly all the frequencies characteristic of a penta-atomic group in the spectrum of ammonium chloride suggests that in the crystal lattice the vibrating NH_4 ion possesses lower symmetry evidently due to the presence of potential fields of the neighbouring ions, although the NH_4 ion has the full tetrahedral symmetry when the atoms are at rest.

At liquid-air temperature, the intense Raman line with frequency shift 3048 cm.$^{-1}$ corresponding to the totally symmetric oscillation of the NH_4 ion has a weak companion at 3072 cm.$^{-1}$ The origin of this line and also of the band $\approx$ 1780 cm.$^{-1}$ recorded at room temperature and the one $\approx$ 1810 cm.$^{-1}$ at liquid-air temperature is not yet understood.

The spectrograms taken both at liquid-air temperature and at room temperature exhibit three groups of bands (V, VI and VII of Table II) with frequency shifts lying in the neighbourhood of 2800, 3200–3500 and 2000 cm.$^{-1}$ respectively, some of which are fairly intense. Holmes (1936) and Ananthakrishnan (1937) suggested that the band at $\approx$ 2828 cm.$^{-1}$ might be the octave of the 1400 line. This suggestion is untenable since the 2828 band is more intense than the 1400 line. A comparison of the frequency shifts of the bands lying at $\approx$ 2800 and 3200–3500 cm.$^{-1}$ with the characteristic frequency shifts of HCl and NH_3 observed in liquids and solutions shows that there is complete correspondence regarding the frequency shifts and relative intensity. It does not necessarily follow that there are free HCl and NH_3 molecules present in crystalline ammonium chloride at all temperatures. The significance of this result will, however, be discussed in a forthcoming paper by the author on the Raman spectrum of ammonium bromide and its temperature variation.

The reason for the appearance of a group of three diffuse bands between 450 and 1350 cm.$^{-1}$ in the spectrogram taken at room temperature and the line 560 cm.$^{-1}$ in the spectrogram at liquid-air temperature is at present not clear. The broad band 670–780 cm.$^{-1}$ (B_2) appearing at room temperature

and the sharp line at 760 cm.$^{-1}$ appearing at liquid-air temperature may be assigned as the intense 3041 band excited by λ 2399·4.

6. Infra-Red Spectrum

Infra-red absorption and reflection spectra of crystalline ammonium chloride have been studied by various workers, most of whom examined the 2–7 μ region. Rubens and Wartenberg (1914) were the only workers who studied the long wavelength region. They reported the existence of a strong reststrahlen frequency at 183 cm.$^{-1}$ corresponding to the principal oscillation of the ammonium chloride structure. Reinkober (1921) examined the infra-red spectrum of ammonium chloride by absorption and by reflection and recorded three maxima corresponding to some of the principal internal oscillations of the NH$_4$ ion. Hettner and Simon (1928) who investigated the influence of the transition temperature on the absorption of ammonium chloride in the 2–8 μ region, found that the absorption maxima at 1770 cm.$^{-1}$ in the warm chloride sharpened considerably and moved to 1800 cm.$^{-1}$ as the temperature was lowered. A similar behaviour is exhibited by the Raman lines at 1710 and 1765 cm.$^{-1}$ Wilberg (1930) subsequently reported the existence of nine absorption maxima with frequencies varying from 1400 to 3100 cm.$^{-1}$ Pohlmann (1932) has made a detailed investigation of the infra-red absorption spectrum of thin layers of ammonium chloride at room temperature and at − 80° C. No less than 26 maxima at room temperature and 17 maxima at − 80° C. could be identified from absorption curves reproduced by Pohlmann. These lie in the region of frequencies in wavenumbers from 1380 to 3385. The frequencies of the various maxima have been estimated and those which correspond to the observed Raman shifts are entered in Table V. Those which are shown in italics appear prominently in the Raman spectrum and in the infra-red absorption spectrum. It is interesting to note that the totally symmetric oscillation of the NH$_4$ ion which appears very strongly in the Raman effect is recorded only as a weak maximum in infra-red absorption. The activity of all the frequencies of internal oscillation both in Raman effect and in infra-red absorption indicates that the vibrating NH$_4$ ion has not the full tetrahedral symmetry. According to Pohlmann's data the 1400 and the 1700 cm.$^{-1}$ bands exhibit fine structure at room temperature which is absent at 193° T.

The fine structure in the 5–6 μ vibrational band of ammonium chloride appearing in the infra-red absorption has been resolved and studied in detail by Beck (1944). He recorded eleven peaks in the region 1608–1760 cm.$^{-1}$ with an average separation of 15 cm.$^{-1}$ between any two neighbouring peaks.

TABLE V

Low temperature		Room temperature	
Raman (Author) 85°T	Infra-red (Pohlmann) 193°T	Raman (Author)	Infra-red (Pohlmann)
3395	3400	3380	3385
3310	3335		
3285	3280		
3235	3247		
3131	3146	3146	3160
3072	3080		
3048	3025	3041	3065
2829	2860	2828	2854
1790	1800	1780	1804
		1765	1777
1716	1728	1710	1707
		1440	1443
1420	1426	1419	1426
1401	1409	1400	1412

The fine structure was attributed by Beck to the rotation of the NH_4 group in the molecule. The fine structure appeared practically unaltered at temperatures down to $-20°$ C. There was a change between $-20°$ C. and $-45°$ C. and the altered fine structure persisted down to at least $-60°$ C. The observed fine structure should be attributed to torsional oscillations of the NH_4 ion rather than to free rotation. As the Raman shifts lying in the ≈ 1700 region fall on the intense mercury triplet in the spectrum taken with 2536·5 excitation, it has not been possible to confirm or deny the existence of the fine structure in Raman effect similar to the one reported by Beck in infra-red absorption.

In conclusion, the author wishes to express his grateful thanks to Prof. Sir C. V. Raman for his kind interest in the work.

7. SUMMARY

Using the λ 2536·5 mercury resonance radiation as exciter, the Raman spectrum of ammonium chloride has been investigated in detail over the range of temperature from 85° T. to 395° T. The recorded spectra at all temperatures exhibit many more frequency shifts than those obtained by the previous workers. The present study reveals the following facts:

(1) The Raman spectrum in the region of frequency shifts 90–200 cm.$^{-1}$ exhibits seven lattice lines, the frequency shifts and intensities of which show marked variations with temperature. These lines have been identified as the fundamental modes of vibration of the cæsium chloride structure, in

which the NH$_4$ ions oscillate as units, as demanded by the new crystal dynamics.

(2) The lattice spectrum persists far above the transition temperature. This fact indicates that Pauling's hypothesis that there is onset of free rotation of the NH$_4$ ions immediately above the transition temperature is not correct.

(3) The internal oscillations of the NH$_4$ ions exhibit nine distinct Raman shifts, showing thereby that these oscillations are not those of a freely vibrating tetrahedrally symmetric group.

(4) The spectra recorded at all temperatures reveal the presence of Raman shifts characteristic of HCl and NH$_3$ molecules.

REFERENCES

1. Adenstedt, H.   .. *Ann. d. Physik*, 1936, **26**, 69.
2. Ananthakrishnan, R.   .. *Nature*, 1936. **138**, 803.
                              .. *Proc. Ind. Acad. Sci.* A, 1937, **5**, 76 & 175.
3. Bahrs, S., and Engl, J.   .. *Zeit. f. Physik*, 1937, **105**, 470.
4. Bartlett and Langmuir   .. *Journ. Amer. Chem. Soc.*, 1921, **43**, 84.
5. Beck, C.   .. *Journ. Chem. Phys.*, 1944, **12**, 71.
6. Crenshaw and Ritter   .. *Zeit. Phys. Chemie*, B, 1932, **16**, 143.
7. Frenkel, J.   .. *Acta Physicochemica*, 1935, **3**, 23.
8. Hettich   .. *Zeit. Phys. Chemie*, A, 1934, **168**, 353.
9. ———— and Schleede   .. *Zeit. f. Physik*, 1928, **50**, 249.
10. Hettner and Simon   .. *Zeit. Phys. Chemie*, B, 1928, **1**, 293.
11. Holmes, F. T.   .. *Phys. Rev.*, 1932, **41**, 389.
                              .. *Journ. Chem. Phys.*, 1936, **4**, 88.
12. Kastler, A.   .. *Bull. Soc. Chim. France*, 1932, **51**, 728.
13. Ketelaar   .. *Nature*, 1934, **134**, 250.
14. Krishnan, R. S.   .. *Proc. Ind. Acad. Sci.* A, 1946, **24**, 45.
15. Lawson   .. *Phys. Rev.*, 1940, **57**, 417.
16. Menzies and Mills   .. *Proc. Roy. Soc.* A, 1935, **148**, 407.
17. Pauling, L.   .. *Phys. Rev.*, 1930, **36**, 430.
18. Pohlmann   .. *Zeit. f. Physik*, 1932, **79**, 394.
19. Ramanathan, K. G.   .. *Proc. Ind. Acad. Sci.* A, 1947, **26**, 500.
20. Rao, I. R., and Rao, C. S. .. *Cur. Sci.*, 1933, **2**, 209.
                              .. *Zeit. f. Phys.*, 1934, **88**, 127.
21. Rubens and von Wartenberg .. *Ber. deuts. Chem. Ges.*, 1914, p. 69.
22. Reinkober, O.   .. *Zeit. f. Physik*, 1920, **3**, 1; 1921, **5**, 192.
23. Ruhemann   .. *Zeit. Phys. Chemie*, A, 1927, **129**, 339.
24. Schæfer, Matossi and Aderhold *Zeit. f. Physik*, 1930, **65**, 289.
25. Silveira   .. *Comp. Rend.*, 1932, **195**, 521.
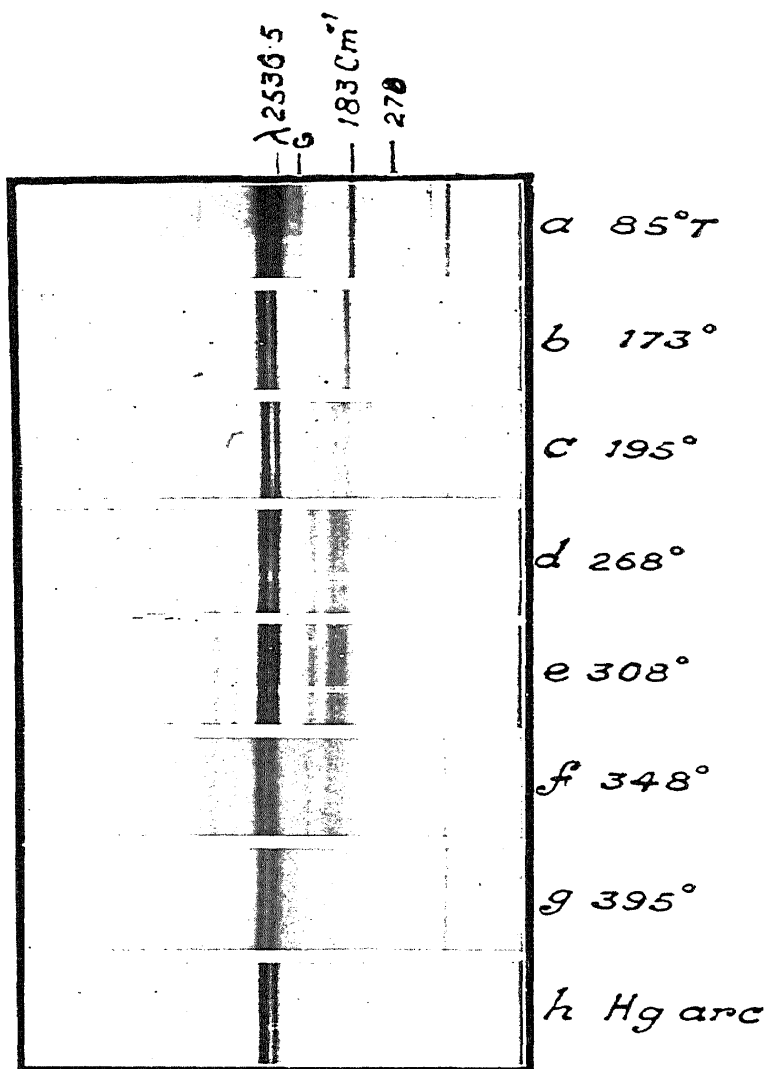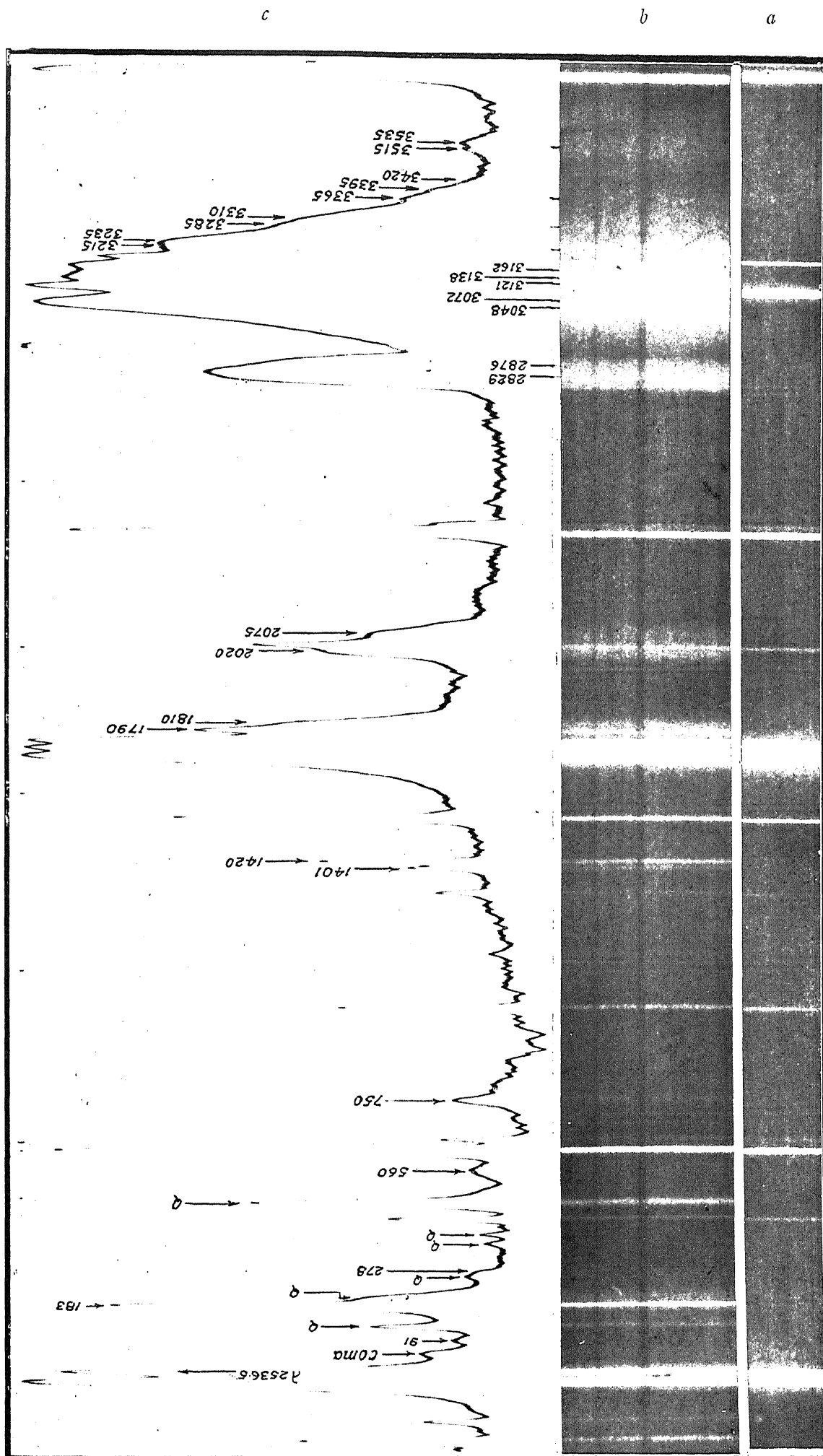
—λ2536·5
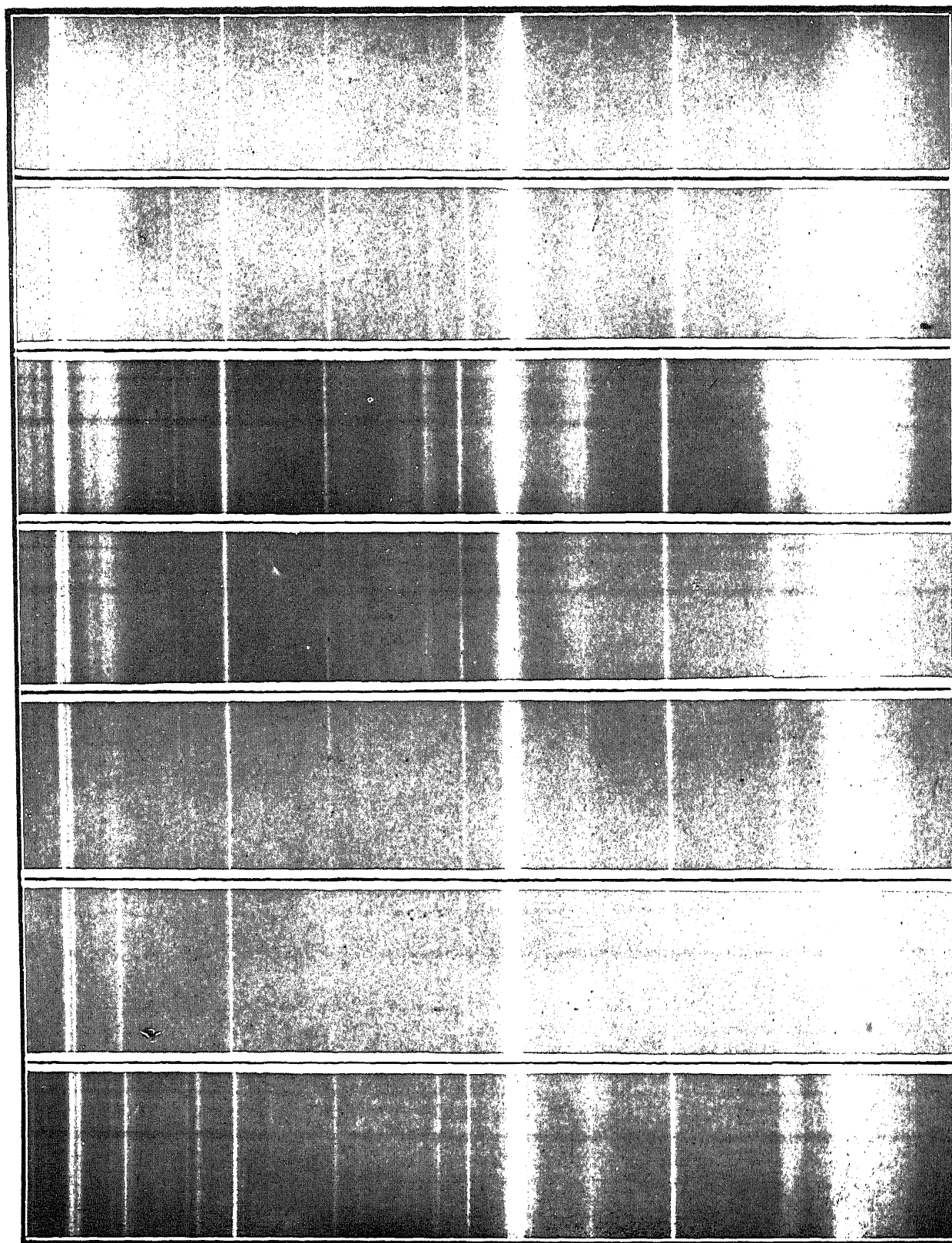
395°T

348°

308°

268°

195°

173°

85°

26. Simon, F.   .. *Ann. d. Physik*, 1922, **68**, 263.

27. —— and von Simson, C. .. *Naturwiss.*, 1926, **38**, 880.

28. —— — and Ruhemann, R... *Z. f. Phys. Chemie*, A, 1927, **129**, 339.

29. Simon, F.   .. *Ber. deuts. Chem. Ges.*, 1926, **33**, 477.

30. Simon and Bergmann   .. *Zeit. Phys. Chemie*, B, 1930, **8**, 255.

31. Smits and MacGillavry   .. *Ibid.*, A, 1933, **166**, 97.

32. Weigle   .. (1935) Referred to in Menzies and Mills' paper.

33. Wilberg, L.   .. *Zeit. f. Physik*, 1930, **64**, 304.

34. Wyckoff   .. *Amer. Journ. Sci.*, 1922, **3**, 177; **4**, 193.

DESCRIPTION OF PLATES

PLATE XV

FIG. 1. (*a*) Spectrum of the mercury arc taken with a Hilger medium quartz spectrograph.

(*b*) Raman spectrum of ammonium chloride taken at 308° T.

(*c*) Its microphotometer record.

PLATE XVI

FIG. 3. (*a*) to (*g*) Lattice spectrum of ammonium chloride.

(*h*) Comparison spectrum of the mercury arc.

PLATE XVII

FIG. 2. (*a*) Spectrum of the mercury arc.

(*b*) Raman spectrum of ammonium chloride taken at 85° T.

(*c*) Its microphotometer record.

PLATE XVIII

FIG. 5. Complete Raman spectrum of ammonium chloride taken with the medium quartz spectrograph.