THE RAMAN SPECTRA OF CRYSTAL POWDERS.

I. The Halides and Sulphate of Ammonium.

BY R. ANANTHAKRISHNAN.

(From the Department of Physics, Indian Institute of Science, Bangalore.)

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1. Introduction.

In a recent communication to these Proceedings¹ the author gave a preliminary account of the Raman spectra of a few compounds belonging to the nitrogen group. The obvious incompleteness of the data reported therein for some of these substances—these are crystalline solids under ordinary conditions—as well as the importance of a detailed elucidation of their spectra from the standpoint of the electronic theory of valency was realised and emphasised in the same paper. In the meanwhile, a new technique has been developed by the author which has rendered it possible for the first time to photograph the complete Raman spectra of crystal powders, and even of amorphous substances with as much facility and elegance as in the case of liquids by the well-known method due to Prof. R. W. Wood. Although a brief report of the new technique and also of some of the results obtained have already appeared,² a short description of the exact experimental arrangement employed by the author and of certain improvements that have been effected subsequent to the publication of the notes referred to above are added in the next section. The present paper which is the first of a series deals with the results obtained in the case of NH₄F, NH₄Cl, NH₄Br, NH₄I, and (NH₄)₂SO₄ all of which have been studied in the solid state. All the chemicals excepting NH₄I were Kahlbaum's purest reagents; ammonium iodide was prepared from NH₄ and HI.

2. Experimental: Technique of Complementary Filters.

Although the powder technique for photographing the Raman spectra of crystalline solids originated by Menzies³ and Bär⁴ has been applied to the

study of a variety of crystals, it is well known that at best only the strongest Raman lines can be recorded by this method. This is because of the powerful continuous spectrum that extends over the entire plate and obliterates all the fainter lines even when the duration of exposure is comparatively short. The origin of this continuous spectrum has been very often attributed to the continuous spectrum present in the mercury arc light itself, but attempts to get rid of it have hitherto been entirely futile. After some preliminary work, the present author soon realised that the continuous spectrum was actually due to the intense illumination in the interior of the spectrograph caused by the powerful light of the mercury arc reflected by the crystal faces. The difficulty was therefore successfully overcome by the selective absorption of the exciting line from the scattered light before the latter was admitted into the spectrograph.

The experimental technique will be sufficiently clear from Figs. 1a and 1b. Mercury arc light filtered by a moderately strong solution of iodine in CCl₄ falls on the crystal powder contained in the inner of the two concentric tubes A. The transversely scattered light is collected by the lens L and is focussed on the slit S of the spectrograph after it has passed through a glass cell B which contains a solution of NaNO₂ of suitable strength. Filter A, provided it be of sufficient strength and thickness (these can be easily adjusted) transmits freely λ 4046 of the mercury arc, which therefore serves as the exciting line while it practically absorbs the entire mercury spectrum to the longer wave-length side. Filter B, the concentration and thickness of which can also be varied, transmits the spectral regions to the longer wave-length side of λ 4046, while it has got a fairly sharp cut off to the shorter wave-length side starting from very near λ 4046. The exciting line is thus considerably weakened if not completely absorbed before the scattered light enters the spectrograph, and this procedure results in a vast improvement.
in the technique of the photography of the Raman spectra of crystal powders. Indeed, exposures of duration comparable to that in the case of liquids are rendered possible, and the photographs so obtained reveal a corresponding wealth of detail and information in the case of every one of the crystal powders which the author has so far examined.

The above technique, however, fails to reveal the presence (if any) of Raman lines between $\Delta \nu = 1650$ and $\Delta \nu = 1760$ cm$^{-1}$ because of the presence of the $\lambda 4358$ group of mercury lines in this region, which, although considerably enfeebled by the iodine filter are nevertheless recorded on the plate. A simple modification of the technique has been found to overcome this difficulty. A very dilute solution of iodine in $CCl_4$ is employed in place of the original strong solution. This freely transmits the mercury lines $\lambda 4046$ and $\lambda 4358$ which therefore function as the exciting lines, while this filter has got the remarkable property of absorbing practically completely the $\lambda 4916$ group of feeble mercury lines as well as the powerful green line $\lambda 5461$. The necessity and importance of cleaning up the $\lambda 4916$ region, particularly in working with crystal powders using $\lambda 4358$ excitation is only too well known, and although various filters have been suggested for this purpose, it appears that the above filter is the ideal one. When employing this filter, a very dilute solution of $KCrO_4$ serves as the filter B in front of the slit of the spectrograph.* Its concentration and thickness are so adjusted, that it absorbs the violet end of the spectrum up to $\lambda 4358$, suitably weakens the exciting line $\lambda 4358$ itself, and transmits freely the spectrum to the longer wave-length side of $\lambda 4358$. Thus two photographs taken first with a concentrated and then with a dilute solution of iodine in $CCl_4$ to filter off the exciting light with the corresponding complementary filters give the complete spectral details of the substance under investigation.†

The remarkable stability of the iodine filter apart from its other properties mentioned above renders it extremely useful in powder work as an efficient filter for the incident light. The solution of $NaNO_2$ has got a sharp and steep absorption edge near $\lambda 4046$ and so forms an efficient combination with the iodine filter. The absorption edge of the $KCrO_4$ solution is, however, not so sharp, but extends over a few hundred wave numbers; it is therefore unsatisfactory for investigating Raman lines which fall close to the exciting line $\lambda 4358$.

* The absorption band of $KCrO_4$ solution as given in the absorption chart in Prof. R. W. Wood's *Physical Optics*, 1934, p. 16, seems to be incorrect. Even for a dilute solution, the absorption extends beyond $\lambda 4358$.

† The technique ought to be extended to the green and yellow lines of the mercury arc so as to enable the investigation of coloured solids.
Unlike liquids and gases, increasing the depth of the illuminated column does not give a corresponding increase in intensity of the scattered light when working with crystal powders, and in practice, it is unnecessary to employ a depth exceeding a centimetre or two. Increased intensity of the scattered light can only be secured by increasing the illumination of this short column, and this is realised by the use of a circular arc of the type shown in Fig. 1b and placing the Raman tube containing the crystal powder at its centre. Such an arc is easily made out of a tube of pyrex glass about a centimetre in diameter, and works continuously for any length of time when cooled by a stream of air from a fan which serves at the same time to prevent the filter A as well as the crystal powder from getting unduly heated.

3. Results.

Photographs of the Raman spectra obtained by the new technique are reproduced in Fig. 2. The following table gives the frequency shifts, relative intensities (visual) and nature of the observed Raman lines or bands for the substances studied in the present paper:

\[ s = \text{sharp} \quad k = \lambda \text{4046} \]
\[ b = \text{broad} \quad i = \lambda \text{4078} \quad \text{Exciting lines.} \]
\[ d = \text{diffuse} \quad e = \lambda \text{4358} \]

**TABLE I.**

<table>
<thead>
<tr>
<th></th>
<th>NH₄F</th>
<th>NH₄Cl</th>
<th>NH₄Br</th>
<th>NH₄I</th>
<th>(NH₄)₂SO₄</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>?</td>
<td>1398 (k) 1s</td>
<td>1395 (k) 1</td>
<td>?</td>
<td>(984) (k) Od</td>
</tr>
<tr>
<td>?</td>
<td>1424 (k) 0d</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>?</td>
<td>1700 (e) 3s</td>
<td>1690 (e) 6s</td>
<td>1665 (k) 0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2262 (k) 1bd</td>
<td>2000 (k, e) 1bd</td>
<td>2000 (k) 0d</td>
<td>2780 (k) 0d</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2820 (k) 3bd</td>
<td>2813 (k, e) 3bd</td>
<td>2800 (k, e) 3d</td>
<td>2780 (k) 0d</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2870 (incompletely resolved)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3088 (k) 2bd</td>
<td>3040 (k, e) 8bd</td>
<td>3025 (k, e) 8bd</td>
<td>3100 (k, e) 1bd</td>
<td>3160 (k) 3bd</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3142 (k, e) 5bd</td>
<td>3126 (k, e) 6bd</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

4. Discussion of Results.

The Raman spectra of the ammonium salts are of great interest because apart from the question of the constitution of the ammonium ion which is a
problem of interest and importance, one might, perhaps, expect to gain some
insight into the nature of the rotational motion of molecules in crystals, the
existence of which has been predicted by Pauling\textsuperscript{5} from theoretical consider-
ations. Thus, in the case of the ammonium salts, the $[\text{NH}_4]^+$ ion is supposed
to be executing free rotation at ordinary temperatures, the rotational motion
gradually subsiding and giving place to angular oscillations of diminishing
amplitude as the temperature is progressively lowered.

The Raman\textsuperscript{6} and infra-red absorption\textsuperscript{7} spectra of the ammonium salts in
the crystalline state have attracted a good deal of attention. The results of
the earlier workers on the Raman spectra are incomplete, presumably because
of the difficulty experienced by them in obtaining good photographs. Recently,
Holmes\textsuperscript{6} has succeeded in recording the complete Raman spectrum of $\text{NH}_4\text{Cl}$
by working with a single crystal of the substance the preparation of which
appears to have taken him nearly a month. While Menzies and Mills\textsuperscript{6} came
to the conclusion that many of the observed facts relating to crystalline
$\text{NH}_4\text{Cl}$ and $\text{NH}_4\text{Br}$ could be explained by assuming a tetrahedral structure for
the $[\text{NH}_4]^+$ ion, Holmes concluded that his results tended to show that the
symmetry of the $[\text{NH}_4]^+$ ion in crystalline $\text{NH}_4\text{Cl}$ departs from the usually
assumed tetrahedral structure. The object of the present investigation was
to make a detailed comparative study of the Raman spectra of all the four
ammonium halides at room temperature. Such an investigation is lacking
and is obviously necessary before any definite conclusions can be drawn.

(1) $\text{NH}_4\text{Cl}$ and $\text{NH}_4\text{Br}$.—We shall consider the Raman spectra of these
salts together because, it is known from X-ray work\textsuperscript{8} that at room temperature
both ammonium chloride and ammonium bromide possess the caesium-
chloride structure, (body centred cube) each ammonium ion being surrounded
by eight halogen ions at the corners of a cube. The following tables give a
comparison between the Raman and infra-red absorption frequencies of these
two substances at room temperature.

\textsuperscript{5} L. Pauling, \textit{Phys. Rev.}, 1930, 36, 430.
\textsuperscript{7} O. Reinkober, \textit{Z. f. Phys.}, 1921, 5, 192.
L. Wilberg, \textit{Z. f. Phys.}, 1930, 64, 304.
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### Table II. NH₄Cl.

<table>
<thead>
<tr>
<th>Raman</th>
<th>Infra-red</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Menzies and Mills (1935)</strong></td>
<td><strong>Holmes (1936)</strong></td>
</tr>
<tr>
<td>1400</td>
<td>1407 (2)</td>
</tr>
<tr>
<td></td>
<td>(unresolved doublet)</td>
</tr>
<tr>
<td>1712</td>
<td>1769 (5)</td>
</tr>
<tr>
<td>1758</td>
<td>1768 (2)</td>
</tr>
<tr>
<td></td>
<td>2010 (2)</td>
</tr>
<tr>
<td></td>
<td>2824 (7)</td>
</tr>
<tr>
<td>3040</td>
<td>3041 (20)</td>
</tr>
<tr>
<td>3163</td>
<td>3146 (15)</td>
</tr>
<tr>
<td></td>
<td>(3232)</td>
</tr>
</tbody>
</table>

### Table III. NH₄Br.

<table>
<thead>
<tr>
<th>Raman</th>
<th>Infra-red</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Kastler (1932)</strong></td>
<td><strong>Menzies &amp; Mills (1935)</strong></td>
</tr>
<tr>
<td>1380</td>
<td>1395 (1)</td>
</tr>
<tr>
<td>1420</td>
<td></td>
</tr>
<tr>
<td>1689</td>
<td>1690 (6s)</td>
</tr>
<tr>
<td></td>
<td>2000 (?) (00d)</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>2810</td>
<td>2800 (3d)</td>
</tr>
<tr>
<td>3030</td>
<td>3032</td>
</tr>
<tr>
<td>3130</td>
<td>3140</td>
</tr>
</tbody>
</table>

*The relative intensities of infra-red absorption given in this column are visual estimates from the absorption curves given by Pohlman.

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If, as it appears justifiable to conclude, it is assumed that all the Raman frequencies observed in the case of these two ammonium halides are due to the \([\text{HN}_4]^+\) ion, then one has to identify nearly six distinct frequencies as those appertaining to this ion in these crystals. These lie in the neighbourhood of 1400, 1700, 2000, 2800, 3000 and 3100 cm\(^{-1}\) respectively. The 1400 frequency is faint but sharp in the chloride and is accompanied by a diffuse companion. The corresponding frequency is faint but somewhat more diffuse in the bromide. The 1700 frequency is strikingly different in the two cases, a feature which has not been noticed before. It is sharp and very intense in the bromide, but is less intense and is split up into two components in the chloride. There is no such difference in the case of the corresponding infra-red absorption. The frequency \(\Delta \nu \sim 2000\) is a diffuse band in the case of \(\text{NH}_4\text{Cl}\); the presence of the corresponding band in the spectrum of the bromide is uncertain. It might be noted that the Raman spectrum of the hydrazinium ion \([\text{N}_2\text{H}_6]^{++}\) in crystalline \(\text{N}_2\text{H}_6\cdot2\text{HCl}\) shows a band in exactly the same position. The remaining three frequencies are all diffuse bands and present more or less a similar appearance in the two cases. Of these three, the one at 2800 shows an asymmetric structure. It has got a fairly sharp edge towards the side of the exciting line, but is diffuse towards the other side. It is also less intense than the other two bands which are the most intense in the whole spectrum. Of these two, the band of lesser shift is more intense than the other, the difference in intensity being more conspicuous in the chloride than in the bromide. It might be of interest to mention that when employing the technique of complimentary filters, these two bands can be seen very clearly with the naked eye as soon as the complementary filter \(B\) is brought in front of the slit of the spectrograph, but when it is removed, the bands are lost in the general illumination.

Holmes has given for \(\text{NH}_4\text{Cl}\) two other frequencies 3232 and 3300 which he calls subsidiary frequencies of the \([\text{NH}_4]^+\) ion. When employing \(\lambda 4046\) excitation, the author has observed on his plates two faint bands following the two intense ones mentioned above. Careful measurement and intensity considerations show that these can be regarded as the corresponding \(\lambda 4078\) excitation, so that the author is unable to confirm the reality of these bands.

(2) \(\text{NH}_4\text{I}\).—The crystal structure of this substance at room temperature is of the rocksalt type, each ammonium ion being surrounded by six equidistant halogen atoms. At low temperatures, the ammonium iodide lattice changes over to the caesium chloride structure so that it becomes isomorphous with the chloride and the bromide. At higher temperatures, the chloride and the bromide are transformed to the rocksalt structure. Thus the three ammonium halides exhibit polymorphism.
Ammonium iodide prepared from NH₃ and HI was coloured pale yellow but the crystals became perfectly colourless on repeated washing with acetone as recommended by Menzies and Mills. Two separate photographs were obtained in the manner explained in Section 2, but the spectrum in either case was weaker than that of the chloride or of the bromide. However, since the background was quite clear, the corresponding frequencies even if only faintly present could not have escaped notice.

As can be seen from Table I, the Raman spectrum of NH₄I at room temperature is very different from the spectra of the other two halides considered above. While the chloride and the bromide show two strong bands in the 3000 region, the spectrum of the iodide shows only a single diffuse band in this region. Its position (3100 cm⁻¹) is somewhat midway between the above two bands. The band near 2800 appears to be present in the iodide, although its relative intensity has gone down considerably. The frequency near 1700 is doubtful, and in any case is very much less intense than the corresponding frequency for the chloride or the bromide. The band near 2000 is absent; the frequency near 1400 is probably too feeble to be recorded.

The infra-red frequencies of NH₄I at room temperature observed by Reinkober are 3106 (strong), 2342 (weak), 2000 (doubtful), 1667 (doubtful) and 1398 (strong). Menzies and Mills have observed two frequencies 3091 (strong) and 1662 in the Raman spectrum of NH₄I at -50°C, when its crystal structure is of the caesium chloride type.

(3) NH₄F.—Crystals of NH₄F belong to the hexagonal system (wurtzite type) and do not exhibit polymorphism as the crystals of the other three halides. The substance investigated was Kahlbaum's analytical reagent and contained as per specification 5% of the double salt NH₄F·HF. It attacks glass, but there was no difficulty in photographing the spectrum in the usual manner. Only λ 4046 excitation was employed and the spectrum thus obtained was much less intense than in the case of the other halides in spite of comparable conditions of illumination and exposure. Comparison with the infra-red frequencies observed by Reinkober is given below:

<table>
<thead>
<tr>
<th>Raman</th>
<th>3088 (2bd) 2870 (3bd) 2820 (4d) 2262</th>
<th>?</th>
<th>?</th>
</tr>
</thead>
<tbody>
<tr>
<td>Infra-red</td>
<td>2857 2222 2000 1667 (?) 1495</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

(4) (NH₄)₂SO₄.—The crystal structure of ammonium sulphate is orthorhombic. The Raman spectrum of the ammonium ion was extremely feeble
in this case. Barring the totally symmetric vibration frequency of the \( \text{SO}_4^{2-} \) ion, which was strongly recorded, the plate showed only a very diffuse band with a frequency shift of approximately 3160 cm\(^{-1}\). We see that the anion in this case has a profound influence on the vibrations of the ammonium ion. Pohlman's infra-red measurements also reveal a similar influence.

5. Conclusion.

From the preceding section it is clear that the Raman spectrum of the ammonium ion in the case of crystalline ammonium salts is dependent intimately upon the crystal structure as well as upon the nature of the anion. It follows therefore that a satisfactory and unique interpretation of the observed results can only be obtained if we consider the vibrations of the ammonium ion in its crystalline environment. The chloride, the bromide and the iodide are from this standpoint the simplest because of the comparatively simple crystal structure of the salts and also because the anion being monatomic cannot give rise to vibrational frequencies of its own. But even in these cases, the spectral facts do not admit of a simple interpretation.

Taking first the chloride and the bromide, we see that in spite of the strong resemblance between their spectra, there are at the same time differences which cannot be ignored. Judging merely from the number of frequencies, one might conclude, as Holmes did in the case of \( \text{NH}_4\text{Cl} \), that the \([\text{NH}_4]^+\) ion in these crystals has not got the symmetry of a regular tetrahedral molecule such as \( \text{CH}_4 \). Indeed, there is very little comparison between the spectra of these crystals and the Raman spectrum of methane.

Holmes investigated the Raman spectrum of \( \text{NH}_4\text{Cl} \) at high temperature when its crystal structure is of the rocksalt type. He found that in place of the two bands in the 3000 region observed in the spectrum at ordinary temperatures, there was only a single broad and very intense band, the frequency shift of which was found to be 3102 cm\(^{-1}\). Practically all the other Raman frequencies observed in the spectrum at ordinary temperature were also present in the spectrum of the high temperature modification of the chloride, but his results show a distinct fall of intensity for the 1700 and 2800 Raman shifts. These facts suggest a broad resemblance between the Raman spectrum of \( \text{NH}_4\text{I} \) at room temperature and that of \( \text{NH}_4\text{Cl} \) at high temperatures when they both possess the same crystal structure.

Menzies and Mills have tried to give an explanation of their results on the Raman spectra at room temperature as well as at low temperatures, as also of many peculiar and interesting properties such as anomalous heat capacity, piezo-electric behaviour (\( \text{NH}_4\text{Cl} \)), double refraction (\( \text{NH}_4\text{Br} \)), etc., shown by crystalline \( \text{NH}_4\text{Cl} \) and \( \text{NH}_4\text{Br} \) at low temperatures by basing
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themselves on the tetrahedral model of the ammonium ion—as suggested by the crystal structure of these halides—and by adopting the view put forth by Pauling that above a certain transition temperature (about \(-30^\circ C\)) rotation of the \([\text{NH}_4]^+\) ion sets in in the crystal lattice of these salts. Thus, according to these authors, the following comparison can be drawn between the fundamental vibrational frequencies of \([\text{NH}_4]^+\) and \(\text{CH}_4\).

<table>
<thead>
<tr>
<th></th>
<th>Single (v_1)</th>
<th>Doubly degenerate (v_2)</th>
<th>Triply degenerate (v_3)</th>
<th>(v_4)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{CH}_4)</td>
<td>2915</td>
<td>1520</td>
<td>3022</td>
<td>1304</td>
</tr>
<tr>
<td>([\text{NH}_4]^+)</td>
<td>3043</td>
<td>1712</td>
<td>3123</td>
<td>1403</td>
</tr>
</tbody>
</table>

One important feature of the spectra of crystalline \(\text{NH}_4\text{Cl}\) and \(\text{NH}_4\text{Br}\) which has not received adequate emphasis by the previous workers might be pointed out in this connection. We see from Tables II and III that practically all the Raman frequencies of these two substances have their analogues in the corresponding infra-red absorption spectra. This seems to be true also for the fluoride and the iodide although the infra-red spectra of these two substances have not been so thoroughly investigated as those of the other two halides. This result is indeed very significant because it is entirely at variance with what we should expect for a regular tetrahedral molecule. Whether this result indicates an actual departure of the \([\text{NH}_4]^+\) ion from the symmetry of a regular tetrahedron can only be decided after the influence of the electric field of the surrounding halogen ions on the vibrations of the \([\text{NH}_4]^+\) ion has been carefully considered.

Some other points that come out of the present investigation might also be mentioned. The Raman band near 2800 occurs in the spectra of all the four halides. It might be the octave of the 1400 Raman frequency, but if this were so we have the somewhat strange and interesting result that the octave in all cases is very much stronger than the fundamental. It is also not improbable that at least in the chloride and the bromide of ammonium at room temperature, there is an accidental degeneracy \((1400 + 1700 \approx 3100)\) which causes the splitting of the 3100 frequency into the two observed components. A more comprehensive study of the Raman spectra of all the ammonium halides covering a wide range of temperature is perhaps necessary before any definite conclusions can be drawn on the constitution of the ammonium ion. There is, however, little doubt that the crystalline
field has a large influence on its vibrations and presumably also on its actual configuration in the crystal lattice.

The author's respectful thanks are due to Professor Sir C. V. Raman for his kind interest and suggestions in the course of the present work.

Summary.

The paper describes a new technique which has been developed by the author for photographing the Raman spectra of crystal powders. It consists essentially in employing a fairly monochromatic beam for excitation, and absorbing the exciting line from the scattered light before the latter enters the spectrograph, and involves thus the use of a pair of complementary filters. The new technique enables for the first time to obtain Raman spectrograms of crystal powders which are as elegant and rich in detail as those of liquids. The Raman spectra of NH₄F, NH₄Cl, NH₄Br, NH₄I and (NH₄)₂SO₄ in the crystalline state at room temperature have been examined by this method. The Raman spectrum of the ammonium ion shows a pronounced dependence upon the crystal structure of the salt as well as upon the nature of anion. The spectra of crystalline NH₄Cl and NH₄Br at room temperature are particularly intense, and comprise about six distinct frequencies. These crystals are isomorphous at this temperature and there is a striking general resemblance between their spectra in spite of individual differences. All the Raman frequencies of the ammonium ion in these two substances have their analogues in the infra-red absorption spectra. This result is very significant and although it suggests a priori the lack of tetrahedral symmetry for the [NH₄]⁺ ion, it is pointed out that the influence of the crystalline environment on the vibrations of the ion has to be carefully considered before any definite conclusions are drawn. The spectra of NH₄I and NH₄F are weaker than and differ from those of the other two halides. This might be due partly to the fact that their crystal structure at room temperature is different from that of the other two halides. The Raman spectrum of the ammonium ion is extremely feeble in the case of (NH₄)₂SO₄ which shows the enormous influence of the complex anion on the vibrations of [NH₄]⁺.
FIG. 2. Raman spectra of crystalline ammonium halides.