RAMAN SPECTRUM OF LITHIUM AMMONIUM TARTRATE MONOHYDRATE

BY C. SHANTA KUMARI
(From the Department of Physics, Indian Institute of Science, Bangalore)

Received January 25, 1951
(Communicated by Prof. R. S. Krishnan, F.A.S.C.)

1. INTRODUCTION

Padmanabhan (1948, 1950) has made a detailed investigation of the Raman spectra of a series of six crystalline tartrates which included Rochelle salt and sodium ammonium tartrate. Crystalline lithium ammonium tartrate whose electrical properties have been extensively studied, is found to be transparent to the ultraviolet and hence its Raman spectrum has been investigated using the A2537 mercury resonance radiation as exciter. The results obtained are described in this paper.

The specimen of lithium ammonium tartrate used for the present study was in the form of a thin rectangular plate of dimensions $16 \times 12 \times 3$ mm. Light from the mercury arc was incident on the broad face of the crystal and the scattered light was taken through the edge. Using a slit width of 0.035 mm. and a Hilger medium quartz spectrograph, an exposure of thirty-six hours was found to be necessary to get a picture with reasonable intensity. Another spectrogram was taken with a different orientation of the crystal in which the light was incident on the broad face while the scattered light was taken through the edge which is perpendicular to the former one. The frequency shifts of the lines were accurately estimated by comparison with a standard iron arc spectrum which was partially superposed over the Raman spectrum.

2. RESULTS AND DISCUSSION

An enlarged photograph of the Raman spectrum of lithium ammonium tartrate and its microphotometric record are reproduced in Fig. 1. The mercury lines are indicated in the figure by the symbol $\lambda$. The recorded spectrum exhibits thirty-seven Raman lines. In Table I are listed the frequency shifts along with those of ammonium tartrate observed by Padmanabhan (1950). The figures given in brackets represent visual estimates of the relative intensities of the lines. Almost all the lines appear quite sharp in the spectrum.
Like Rochelle salt, lithium ammonium tartrate also belongs to the orthorhombic class of crystals. Further details regarding its crystal structure are not available.

**Lattice spectrum.**—There is a close correspondence between the lattice spectrum of lithium ammonium tartrate and that of ammonium tartrate. As is to be expected, because of the lower mass of the lithium ion, the frequency shifts in the case of the former are slightly higher than the corresponding ones of the latter. Of the eight lattice lines with frequency shifts 50, 67, 82, 104, 126, 149, 170 and 192, the more intense ones, namely 82, 104, 126 and 149 are almost equally spaced. The other four lines are rather feeble, but they are easily discernible in the microphotometric record.

**The tartrate spectrum.**—The twenty-seven Raman lines with frequency shifts lying in the range from 245 to 3005 cm.\(^{-1}\) are due to the internal oscillations of the tartrate ion. The most important feature of the spectrum which is not found in the Raman spectra of other crystalline tartrates so far studied is the appearance of a group of six lines with frequency shifts 2836, 2878, 2921, 2944, 2978 and 3005 cm.\(^{-1}\) due to the C-H oscillations. It is
interesting to note that the spectra of aqueous solutions of tartrates and of crystalline potassium tartrate exhibit only one Raman line characteristic of the C–H oscillation. When the atomic mass of the cation is lowered, the line due to the C–H oscillation gets split up giving rise to two lines in the case of sodium and ammonium tartrates and their mixed salts and six in the case of lithium ammonium tartrate. The presence of six lines in the latter case may be due to the greater influence of the lighter lithium ion on the C–H oscillation.

The frequency shifts of the Raman lines due to carboxyl, C–OH and C–C group oscillations show a general correspondence with those of other tartrates. In the spectrum of lithium ammonium tartrate the lines at 245, 469 and 522 cm\(^{-1}\) arising from the deformation oscillations of the C–C chain are very weak as compared with those appearing in the spectrum of Rochelle salt.

Oscillations due to the water molecule.—Lithium ammonium tartrate contains one molecule of water of crystallisation. Unlike in the case of other tartrates, its spectrum exhibits only a single sharp line at 3413 cm\(^{-1}\). This frequency shift agrees well with that due to the symmetric O–H oscillation in water.

Spectrum of the NH\(_4\) ion.—It is interesting to note that the characteristic frequencies of the NH\(_4\) ion are very much suppressed in the spectrum of this double salt. In fact the only Raman line which can be attributed with certainty as due to the internal oscillations of the NH\(_4\) ion is the one at 3029 cm\(^{-1}\) which appears very weak in the spectrum. Similar behaviour is exhibited by sodium ammonium tartrate.

3. Effect of Crystal Orientation

Two different spectrograms of the crystal were taken with the light incident on the broad face (16 × 12 mm.) of the crystal and the scattered light taken normally from the

1. Perpendicular to the edge 16 × 3 mm. and
2. Perpendicular to the edge 12 × 3 mm. respectively.

Since the structure of the crystal is not known, the orientations of the crystal with respect to the actual crystallographic axes could not be specified. In the two spectra the Raman lines with frequency shifts 50, 88, 104, 522, 988, 1109, 1378, 1421, 2944 and 2978 cm\(^{-1}\) are found to undergo marked variation in intensity. A correspondence is noticeable between these Raman lines and those in the case of Rochelle salt and sodium tartrate (Padmanabhan,
Raman Spectrum of Lithium Ammonium Tartrate Monohydrate

1949) which also showed similar variation in intensity. These lines can be tentatively assigned as due to symmetric oscillations.

I am extremely thankful to Professor R. S. Krishnan for his suggestions and encouragement in the present work. The specimen of lithium ammonium tartrate used in the investigation was the one presented by Dr. W. P. Mason of the Bell Telephone Laboratories to whom the author's thanks are due.

SUMMARY

Using λ2537 resonance radiation as exciter, the Raman spectrum of a single crystal of lithium ammonium tartrate has been recorded for the first time. The spectrum exhibits thirty-seven Raman lines. The observed frequency shifts are compared with those of other tartrates. The frequencies due to the NH₄ ion are seen to be very much suppressed in the spectrum of this crystal.

A few of the Raman lines show marked variations in intensity with orientation of the crystal.

REFERENCES

3. . . Unpublished work.