

RAMAN SPECTRA OF SINGLE CRYSTALS OF ZINC AND LITHIUM ACETATES DIHYDRATES

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1. INTRODUCTION

THE Raman spectra of aqueous solution of the acetate ion and the infra-red spectra of solid metal acetate have been studied by many workers and reliable assignment of the fundamental frequencies of the acetate ion have been made (Ito and Bernstein, 1956). In a communication which appeared in these *Proceedings*, Padmanabhan (1953) reported the Raman spectra of crystalline barium, sodium and magnesium acetates. The Raman spectra of crystal powders of many acetates including lithium and zinc acetates were recorded by Theimer and Theimer (1950). They have reported only the C—C and C—O stretching frequencies in these cases.

The crystal structures of zinc acetate dihydrate and lithium acetate dihydrate have been recently solved (Van Niekerk, Schoening and Talbot, 1953; Amirthalingam and Padmanabhan, 1958). These two acetates are easily crystallised from aqueous solutions and it was felt desirable to investigate their spectra in single crystal form. Being transparent to ultra-violet, their Raman spectra were recorded using $\lambda 2537$ excitation. Interesting results are obtained which are presented here.

2. EXPERIMENTAL DETAILS

Single crystals of zinc acetate dihydrate and lithium acetate dihydrate were grown from aqueous solutions of the pure substances by the method of slow evaporation. The biggest crystals of these two substances measured respectively $10 \times 10 \times 3$ mm. and $20 \times 20 \times 5$ mm. The crystals were free from inclusions. Employing a medium quartz spectrograph and a slit width of 0.025 mm. fairly intense photographs were obtained with exposures of the order of six hours.

3. RESULTS

Enlarged photographs of the Raman spectra of zinc and lithium acetates dihydrates are reproduced in Figs. 1 and 2 on Plates VI and VII. Their respective

microphotometer records are also included. The observed frequency shifts in wave-numbers have been marked in figures. They have also been listed in Table I. The figures given in brackets represent the relative intensities of the Raman lines estimated visually. For the sake of comparison the frequencies observed in the spectra of magnesium acetate tetrahydrate, sodium and barium acetates trihydrates by Padmanabhan (1953) are also included in Table I. In column 6 are given the frequencies of the free acetate

TABLE I

| Padmanabhan | | | Author | | Ito and Bernstein | Assignment |
|----------------------------|---------------------------------|----------------------------|----------------------------|-------------------------|-------------------|--|
| Sodium acetate tri-hydrate | Magnesium acetate tetra-hydrate | Barium acetate tri-hydrate | Lithium acetate di-hydrate | Zinc acetate di-hydrate | Free acetate ion | |
| 46 | | | | 25 (5) | | Lattice frequencies, hydrogen bond vibrations and internal frequencies of the arrangement of water molecules and oxygens around the metal ions |
| | 52 | | | 50 (f) | | |
| | 60 | 61 | 60 | 65 (8) | 67 (10) | |
| | 81 | 79 | | | 80 (12) | |
| | | | | | 91 (12) | |
| | 109 | 114 | 102 | 101 (15) | 109 (12) | |
| | 126 | | 130 | 129 (1) | | |
| | | 140 | 142 | 147 (1) | 158 (f) | |
| | 165 | 169 | | 169 (2) | | |
| | 196 | 196 | 197 | | | |
| | 218 | 218 | 215 | 212 (4) | 230 (4) | |
| | 254 | | | 237 (1) | | |
| 306 | | | | 266 (8) | | |
| | 306 | | | 288 (f) | *310 (-) | |
| | 340 | | 332 | | *420 (-) | |
| | | | | | | |
| 480 | | 498 | 427 (-) 456 (f) | 476 (1) | 471 (f) | 2×212 $\nu_{11} (b_1)$ COO rocking (in plane) |
| | | | | 509 (f) | | 266 + 230 |
| 538 | 540 | | | | 621 (f) | $\nu_{15} (b_2)$ COO rocking (out of plane) |

TABLE I (*Contd.*)

| Padmanabhan | | | Author | | Ito and Bernstein | |
|---------------------------|--------------------------------|---------------------------|---------------------------|------------------------|-------------------|--|
| Sodium acetate trihydrate | Magnesium acetate tetrahydrate | Barium acetate trihydrate | Lithium acetate dihydrate | Zinc acetate dihydrate | Free acetate ion | Assignment |
| | 668 | 656 | 670 (8) | 695 (2) | 650 (3) | $\nu_5 (a_1)$ COO deformation |
| 910 | 920 | 909 | 940 (20) | 954 (20) | 926 (5) | $\nu_4 (a_1)$ C—C stretching |
| | 930 | 918 | | | 1020 (f) | $\nu_{10} (b_1)$ CH ₃ rocking |
| | | | | 1062 (f) | 1052 (?) | $\nu_{14} (b_2)$ CH ₃ rocking |
| | | | 1267 (f) | 1248 (f) | | $\nu_2 - 101$ $\nu_2 - 109$ |
| | | | | 1311 (f) | | 3223—2 ν_4 |
| 1350 | 1350 | 1344 | 1356 (10) | 1360 (4) | 1344 (4) | $\nu_2 (a_1)$ CH ₃ deformation |
| 1416 | 1429 | 1434 | | | 1413 (8) | $\nu_3 (a_1)$ C—O stretching |
| | | | 1445 (15) | 1456 (15) | | ν_3 and ν_{13} |
| | | | | | 1429 (1) | $\nu_9 (b_1)$ CH ₃ deformation |
| 1450 | 1458 | | | | 1456 (9) | $\nu_{13} (b_2)$ CH ₃ deformation |
| | | | | | 1556 (f) | $\nu_8 (b_1)$ C—O stretching |
| | | | 2696 (1) | 2709 (2) | | $2 \nu_2$ $2 \nu_2$ |
| | | | 2720 (f) | | | $2\nu_3 - 169$ |
| | | | 2758 (1) | | | $3248 - \nu_5$ |
| | | | 2779 (1) | | | $2\nu_3 - 101$ |

TABLE I (Contd.)

| Padmanabhan | | | Author | | Ito and Bernstein | Assignment |
|----------------------------|---------------------------------|----------------------------|----------------------------------|-----------------------------|---|--|
| Sodium acetate tri-hydrate | Magnesium acetate tetra-hydrate | Barium acetate tri-hydrate | Lithium acetate di-hydrate | Zinc acetate di-hydrate | Free acetate ion | |
| | | | | 2800 (1) | $\nu_3 + \nu_2$ | |
| | | | 2809 (1) | | $\nu_3 + \nu_2$ | |
| | | | | 2838 (1) | $\begin{cases} \nu_1 - 91 \\ \nu_1 - 109 \end{cases}$ | |
| 2939 | 2938 | 2939 | 2863 (2) 2949 (10) | 2937 (15) | 2935 (10) | $2\nu_3$ $\nu_1 (a_1) C-H$ stretching |
| 2980 | 2982 | 2989 | 2979 (1) | 2977 (1) | 2981 (3) | $\nu_7 (b_1) C-H$ stretching |
| 3030 | 3032 | 3019 | 3049 (2) | 3038 (1) | 3010 (4) | $\nu_{12} (b_2) C-H$ stretching |
| 3406 | 3543 | 3470 | 3165 (-) 3342 (8) 3428 (4) | 3223 (4) 3337 (4) | | $\nu_1 + 212$ |
| | | | Continuum from 2983-3541 | Continuum from 2872-3518 | | Water bands |

f = feeble; * Measured from antistokes side.

ion. The assignments are given in the last column. The assignments closely follow those given by Ito and Bernstein (1956) for the free acetate ion.

4. STRUCTURE DATA

Magnesium, sodium and barium acetates crystallise in monoclinic class. Their space groups and number of molecules in the unit cell are indicated against their formulæ below: $Mg(CH_3COO)_2 \cdot 4 H_2O$ (C_{2h}^2 , 2); $NaCH_3COO \cdot 3 H_2O$ (C_{2h}^3 , 8) and $Ba(CH_3COO)_2 \cdot 3 H_2O$ (C_{2h}^5 , 2). Details of the crystal structure for these three acetates are not available (Padmanabhan, 1948, 1952, 1953, 1954).

Zinc acetate dihydrate $[Zn(CH_3COO)_2 \cdot 2 H_2O]$ crystallises in the monoclinic class space group C_{2h}^6 with four molecules in the unit cell, with the following unit cell dimensions: $a = 14.50 \text{ \AA}$, $b = 5.32 \text{ \AA}$, $c = 11.02 \text{ \AA}$ and $\beta = 100^\circ$. The six nearest neighbours of a zinc atom are four oxygen atoms and two water molecules which form a badly distorted octahedron around the zinc atom. The following are the distances reported: $Zn-O_{(1)}$

$= 2 \cdot 18$, $\text{Zn} - \text{O}_{(2)} = 2 \cdot 17$ and $\text{Zn} - \text{H}_2\text{O} = 2 \cdot 14 \text{ \AA}$. The formula units form extended columns parallel to the b -axis. Along such columns the units comprising them are firmly linked by hydrogen bonds of lengths $2 \cdot 49 \text{ \AA}$. Such bonds exist between the two water molecules of one unit which are bonded respectively to the two oxygen atoms of the unit immediately above. Along the c -direction such bonds have lengths equal to $2 \cdot 74 \text{ \AA}$.

Lithium acetate dihydrate $[\text{LiCH}_3\text{COO} \cdot 2 \text{ H}_2\text{O}]$ crystallises in orthorhombic class space group C_{2v}^{11} with four formula units in the unit cell with the following unit cell dimensions: $a = 6 \cdot 86 \text{ \AA}$, $b = 11 \cdot 49 \text{ \AA}$ and $c = 6 \cdot 59 \text{ \AA}$. The acetate ions are linked by weak hydrogen bonds to the water molecules having lengths $3 \cdot 08 \text{ \AA}$ and $3 \cdot 14 \text{ \AA}$ along the a -axis and along c by the c -spacing. Along b the nearest distance is $3 \cdot 68 \text{ \AA}$ and along c $3 \cdot 87 \text{ \AA}$. Lithium is surrounded by six oxygens four of which belong to the acetate ions and the two other to the water molecules. The $\text{Li} - \text{O}$ and $\text{Li} - \text{H}_2\text{O}$ linkages are reported to be $2 \cdot 27 \text{ \AA}$ and $2 \cdot 57 \text{ \AA}$ long.

5. DISCUSSION

Low Frequencies.—The low frequency spectra of these two acetates are quite complicated by the fact that lattice vibrations, low frequency vibrations of the hydrogen bonds and fundamental modes of the octahedral arrangements of oxygens and water molecules around the metal ions, all will be crowded in this region (0 – 500 cm^{-1}) and overlap with one another.

The vibration spectrum of the hydrogen bonded $\text{O} - \text{O}$ linkage has been investigated both theoretically and experimentally by many workers. Gross and his co-workers (1957) have identified in the Raman spectra of simple substances like light and heavy ice, formic acid crystals, etc., frequencies of the hydrogen bond in the ~ 150 – 300 cm^{-1} region. Reid (1959) had considered the stretching motions of $\text{O} - \text{H} \cdots \text{O}$ bonds as a function of the bonded distances. The theoretically calculated frequencies vary from 850 cm^{-1} for $\text{O} - \text{H} \cdots \text{O}$ distance of $2 \cdot 43 \text{ \AA}$ to about 110 cm^{-1} for a distance of $2 \cdot 74 \text{ \AA}$. In zinc acetate dihydrate hydrogen bonds of lengths $2 \cdot 49 \text{ \AA}$ and $2 \cdot 74 \text{ \AA}$ are reported to be present, whereas very much weaker hydrogen bonds are present in lithium acetate dihydrate crystal. It is likely that the two intense diffuse lines at 80 and 91 cm^{-1} in zinc acetate dihydrate are due to the hydrogen bond vibrations. Gross (1957) had observed that when the $\text{O} - \text{H}$ vibrator is not excited, the vibrations of the hydrogen bond are defined by means of the potential curve with a very strong anharmonicity. The consideration of the vibrational energy levels of the hydrogen bond helps

in explaining the presence of more than one hydrogen bond frequency. It is significant that there are no corresponding frequencies in the spectrum of lithium acetate dihydrate. However, frequencies in this region are present in the spectra of the other three acetates. In these cases data concerning the length of the hydrogen-bonded linkages are not available.

The vibrational spectra of the octahedral MO_6 type complexes (M = metal atom) have been investigated by many workers (Eucken and Sauter, 1934; Lafont, 1959; Ananthanarayanan, 1961, 1962, 1962). These complexes belong to the point group O_h and have six normal vibrations designated as below: ν_1 (A_{1g} —totally symmetric), ν_2 (E_g —doubly degenerate) and ν_3 (F_{2g} —triply degenerate) active in Raman effect only; ν_4 (F_{2u}), ν_5 , ν_6 (F_{1u}) triply degenerate vibrations active in infra-red absorption only. The theoretical method of calculating the mean vibrational frequencies of such groups in crystals have been already dealt in the references quoted above and will not be repeated here. In the case of many magnesium and zinc sulphates where such octahedral $\text{M}(\text{OH}_2)_6$ ions are present the fundamental frequencies of these groups have been calculated and identified, where possible, experimentally (Lafont, 1959; Ananthanarayanan, 1962). The average values in wave numbers are for ZnO_6 [393, 200, 276, 147, 275 and 378] and MgO_6 [370, 205, 251, 133, 268, 499]. It is interesting to note that excepting sodium acetate trihydrate the low frequency spectra extend considerably further up to $\sim 300\text{--}400 \text{ cm.}^{-1}$ in all the other acetates. The 420 cm.^{-1} line in zinc acetate dihydrate may be assigned to the totally symmetric ν_1 mode. The slight enhancement from the usual value of 393 cm.^{-1} may be due to the differing crystalline field in the acetate compared to that found in the sulphates. The lines at 266 and 310 cm.^{-1} are the split components of the triply degenerate mode and that at 230 cm.^{-1} the doubly degenerate mode. However polarisation studies may be useful in confirming these assignments. Details about the arrangement of water molecules and oxygens around the metal atoms in magnesium and barium acetates are not available. It is obvious that the frequencies in the $\sim 200\text{--}340 \text{ cm.}^{-1}$ in these two cases are due to the groups formed by oxygens and water molecules around the metal ions. In lithium acetate dihydrate the line at 237 cm.^{-1} may be assigned to the totally symmetric mode. This view is supported by an estimation of this frequency from the Badger's rule (1935) using the average of the reported $\text{Li}-\text{O}$ and $\text{Li}-\text{H}_2\text{O}$ distances. It was also estimated by assuming $\nu_1 = 237 \text{ cm.}^{-1}$ and employing the Eucken and Sauter's force field (1934) that the other two Raman active modes ν_2 and ν_3 will occur near ~ 100 and $\sim 180 \text{ cm.}^{-1}$. Since these will overlap with the lattice modes no attempt was made to identify them.

Group theoretical analyses of the lattice spectra of zinc and lithium acetates have been worked out and are given in Tables II and III. Six translatory and six rotatory type of external modes in the former and nine translatory and twelve rotatory type modes of the latter are allowed by selection rules to appear in the Raman effect. The molecule is treated as one unit for these calculations. Only a much smaller number of external modes have been experimentally observed in all cases. There are common lattice lines with practically the same frequency shifts at ~ 63 and $\sim 107 \text{ cm}^{-1}$ which are very intense. These may be attributed to the rotatory type of external oscillations of the acetate ion. Polarisation studies are essential to make definite assignments.

TABLE II

| C_{2h}^5 | E | C_2 | i | σ_h | T | T' | R' | Selection Rules | |
|--------------------|----|-------|----|------------|---|----|----|-----------------|-----------|
| | | | | | | | | Raman | Infra-red |
| A_1 | 1 | 1 | 1 | 1 | 0 | 3 | 3 | p | f |
| A_2 | 1 | -1 | 1 | -1 | 0 | 3 | 3 | p | f |
| B_1 | 1 | 1 | -1 | -1 | 1 | 2 | 3 | f | p |
| B_2 | 1 | -1 | -1 | 1 | 2 | 1 | 3 | f | p |
| U_R (S) | 4 | 0 | 0 | 0 | | | | | |
| U_R ($S - v$) | 4 | 0 | 0 | 0 | | | | | |
| $h_p \chi_p' (T)$ | 3 | -1 | -3 | 1 | | | | | |
| $h_p \chi_p' (T')$ | 9 | 1 | 3 | -1 | | | | | |
| $h_p \chi_p' (R')$ | 12 | 0 | 0 | 0 | | | | | |

p = permitted; f = forbidden.

Internal Frequencies.—The fundamental vibrations of the acetate ion are distributed under the different symmetry types as below: $5a_1 + 1a_2 + 5b_1 + 4b_2$. The torsional vibration about C—C bond (ν_6) belonging to a_2 type is forbidden by selection rules to appear in the vibrational spectrum. All the remaining vibrations are active in both Raman effect and infra-red absorption.

TABLE III

| C_{2v}^{11} | E | C_2 | σ_v | σ'_v | T | T' | R' | Selection Rules | |
|-------------------------|----|-------|------------|-------------|---|----|----|-----------------|-----------|
| | | | | | | | | Raman | Infra-red |
| A_1 | 1 | 1 | 1 | 1 | 1 | 2 | 3 | p | p |
| A_2 | 1 | 1 | -1 | -1 | 0 | 3 | 3 | p | f |
| B_1 | 1 | -1 | 1 | -1 | 1 | 2 | 3 | p | p |
| B_2 | 1 | -1 | -1 | 1 | 1 | 2 | 3 | p | p |
| U_x (S) | 4 | 0 | 0 | 0 | | | | | |
| U_x ($S - v$) | 4 | 0 | 0 | 0 | | | | | |
| $h_p \chi_{\rho}'$ (T) | 3 | -1 | 1 | 1 | | | | | |
| $h_p \chi_{\rho}'$ (T') | 9 | 1 | -1 | -1 | | | | | |
| $h_p \chi_{\rho}'$ (R') | 12 | 0 | 0 | 0 | | | | | |

p = permitted; f = forbidden.

It is noted that some of the fundamental modes of the free acetate ion are absent in the spectra of all these acetates. It is likely that the ν_{15} mode falls over either of the two mercury lines at 2576.3 Å and 2578.4 Å and escaped detection. Similarly the ν_{10} and ν_8 modes might have been masked respectively by the mercury lines at 2603.2 Å and 2639.9 Å. All these lines are too feeble to be recorded in the antistokes side.

The C—C distances are reported to be 1.55 Å in $\text{LiCH}_3\text{COO} \cdot 2 \text{H}_2\text{O}$ and 1.48 Å in $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2 \text{H}_2\text{O}$. It is interesting to note that the C—C stretching frequency is comparatively lowered in lithium acetate dihydrate which is to be expected on theoretical grounds. There are two sets of C—O distances in these acetates being 1.22 Å and 1.33 Å long in lithium acetate and 1.33 Å and 1.38 Å long in zinc acetate. The ν_3 (C—O stretching) and ν_{13} (CH_3 deformation) frequencies of the free acetate ion are equally strong and occur close to one another (1413 and 1456 cm.⁻¹). In both these acetates a very intense and broad band at ~ 1450 cm.⁻¹ alone is observed in this region. It is likely that these two modes merge together into the broad band at ~ 1450 cm.⁻¹. These two modes are however clearly resolved in the spectra of magnesium and barium acetates.

There are a number of extremely feeble lines in the spectra of these two acetates at 427, 527, ~ 1250 –1310, and ~ 2700 –2870 cm. $^{-1}$ which have been explained as overtones and combination frequencies (see Table I).

The lowering of the hydrogenic stretching frequency by hydrogen bond formation is well known and correlation table connecting O—H...O distances and O—H frequencies is available (Nakamoto, Margoshes and Rundle, 1955). The considerably larger lowering of the O—H frequencies in zinc acetate dihydrate is indicative of the presence of stronger hydrogen bonds. There is appreciable lowering of O—H frequencies in the spectra of sodium and barium acetates.

6. SUMMARY

The Raman spectra of single crystals of zinc acetate dihydrate and lithium acetate dihydrate have been recorded for the first time. $\lambda 2537$ excitation has been used. Twenty-eight Raman frequency shifts in the spectrum of the former and twenty-seven in the latter have been recorded. Group theoretical analyses of the external modes of these acetates have been made and from intensity considerations the lines at ~ 63 and 107 cm. $^{-1}$ have been identified as the rotatory type of external oscillations of the acetate ion. The low frequency spectra which extend up to ~ 400 cm. $^{-1}$ have been divided into three parts: external oscillations, low frequency hydrogen bond oscillations and vibrational frequencies of the octahedral arrangements of oxygens and water molecules around the metal ions. The internal frequencies are made up of acetate ion frequencies and water bands. Appropriate assignments have been given for all these observed Raman lines. Besides these a series of extremely feeble lines are present which have been explained as the octaves and combinations involving mainly the acetate frequencies and low frequency vibrations. A comparative study of the spectra of these two acetates with those of barium, magnesium and sodium acetates has also been made.

7. ACKNOWLEDGEMENTS

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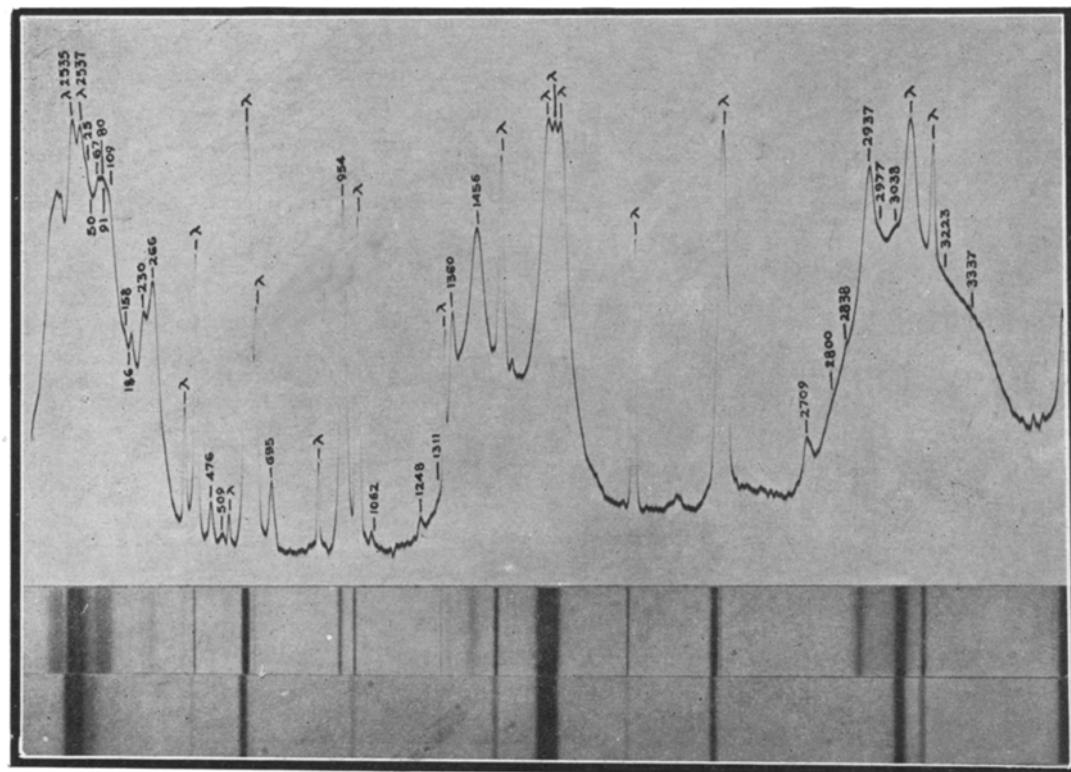


FIG. 1. (a) Microphotometer tracing of the Raman spectrum of zinc acetate dihydrate.
(b) Raman spectrum. (c) Mercury spectrum.

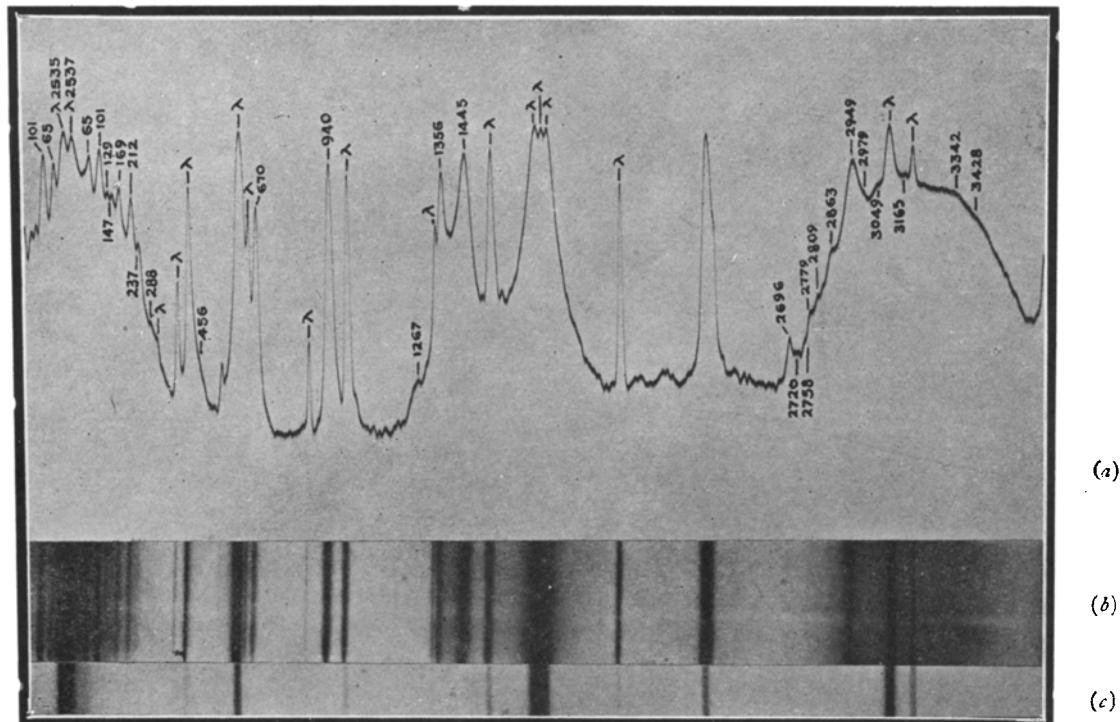


FIG. 2. (a) Microphotometer tracing of the Raman spectrum of lithium acetate dihydrate.
(b) Raman spectrum. (c) Mercury spectrum.