RAMAN SPECTRA OF CRYSTALLINE ACETATES
(SODIUM, MAGNESIUM AND BARIUM)

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INTRODUCTION

ALTHOUGH the Raman spectra of acetic acid, its salts and esters in the liquid state have been studied in great detail (Hibben, 1939), very little work has been done on their spectra in the crystalline state. Only sodium acetate has been recently investigated by Marignan (1948). He used the method of complementary filters and confined himself to the region of frequency shifts from 2,900 to 3,500 cm\(^{-1}\). As the crystals, though small in size, can easily be grown from aqueous solutions by the method of slow evaporation and as they are transparent to the ultraviolet, it was considered desirable to investigate their Raman spectra. The results obtained in the case of sodium, magnesium and barium acetates are reported here.

RESULTS AND DISCUSSION

The experimental details are the same as those described by the author in the previous papers (Padmanabhan, 1948, 1950). Using \(\lambda 2536\) as the exciting radiation and a medium quartz spectrograph exposures of the order of 10 hours were found to be sufficient to obtain spectra of reasonable intensity.

In Fig. 1 (on Plate XX) the Raman spectra of the three crystals are reproduced along with the mercury arc spectrum. The recorded spectra exhibit as many as 15 lines with sodium acetate, 23 with magnesium acetate and 23 with barium acetate. The frequency shifts are listed in Table I.

The broad line at about 3500 cm\(^{-1}\) due to the O–H oscillation is very weak in barium acetate, while the corresponding line in magnesium and in sodium acetate is more intense. The low frequency lines can be clearly seen in the three spectra, those of magnesium acetate being the most intense among them. Most of the lines in this region have been recorded for the first time. The lines 46, 60 and 109, 126 in sodium acetate form close doublets, of which the former is more intense than any other lattice line.
Similarly there are two doublets in the lattice spectrum of barium acetate also with frequency shifts 91, 102 and 122, 131 cm\(^{-1}\)

All the three acetates crystallise in the monoclinic class. Magnesium acetate \([\text{Mg} (\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}]\) tetrahydrate belongs to the space group \(C^2\) with two molecules in the unit cell while sodium acetate trihydrate \((\text{CH}_3\text{COONa} \cdot 3\text{H}_2\text{O})\) belongs to \(C^2\) with 8 molecules in the unit cell (Padmanabhan, 1952). The space group of barium acetate trihydrate has not yet been determined.
The observed frequency shifts in all the three cases can be roughly classified into three groups—lattice frequencies, frequencies due to the acetate ion and water bands.

**Lattice Oscillations.**—The lattice frequencies are indicated in Table I by the letter L within brackets, along with the frequency shifts. From symmetry considerations it can be shown that for magnesium acetate, 12 lattice lines are theoretically allowed in Raman effect (6 translatory and 6 rotatory) of which only 8 have been recorded. Polarisation studies show that the lines 61 and 140 are symmetric while the other lines are antisymmetric. Among the low frequency lines, since those with frequency shifts 61, 169 and 196 cm$^{-1}$ appear in all the spectra without much shift, they may be attributed to the oscillations of the acetate ion. However, complete polarisation studies for all the three crystals are necessary for a more detailed analysis of the lattice spectra.

**Internal Frequencies Due to the Acetate Ion.**—Following Engler (1937) and treating methyl groups as a unit, the rest of the acetate ion may be visualised as of the type $\text{C} - \text{A} \leftarrow \text{B}$. The fundamental vibrations of a group of type $\text{A} - \text{B} - \text{C}$ are six in number ($\nu_1$ to $\nu_6$) of which three will give rise to polarised Raman lines. The methyl group may be considered as having a pyramidal structure with four characteristic frequencies ($\nu_1'$ to $\nu_4'$) of which two will be polarised and the other two depolarised. In Table I, the types of oscillation and polarisation of the frequencies due to the acetate ion are indicated. The Raman lines corresponding to $\nu_1 (\sim 1650)$ and $\nu_4 (\sim 1100)$ have not been observed showing thereby that even if present they are of negligible intensity. The state of polarisation of the lines 668 and 3032 could not be judged properly. Some of the lines such as 910 and 1416 cm$^{-1}$ which appear single in the spectrum of sodium acetate split up into two or three lines in the spectra of magnesium and barium acetates. This might be due to the presence of more than one acetate ion in the molecule.

**Water Bands.**—The broad line with a frequency shift of 3406 cm$^{-1}$ in sodium acetate is due to the O—H oscillation, while the corresponding lines in magnesium and barium acetates are those at 3543 and 3470 cm$^{-1}$ respectively.

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**Summary**

Using $\lambda$ 2536 as exciter, the Raman spectra of single crystals of sodium, magnesium and barium acetates have been investigated. The spectra of
magnesium and barium acetates and the lattice spectrum of sodium acetate have been reported for the first time. The recorded spectra exhibit as many as 15 lines with sodium acetate, 23 with magnesium acetate and 23 with barium acetate. Tentative assignments have been made for some of the lines observed.

REFERENCES

Hibben .. The Raman Effect and its Chemical Applications. 1939.
Kaman Spectra of Crystalline Acetates

(a) Sodium Acetate  (b) Magnesium Acetate  (c) Barium Acetate  (d) Comparison Hg Spectrum