RAMAN SPECTRUM OF CRYSTALLINE CADMIUM ACETATE DIHYDRATE

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1. INTRODUCTION

RAMAN spectra of crystal powders of many acetates were recorded by Theimer and Theimer (1950) and those of single crystals of barium, sodium and magnesium acetates by Padmanabhan (1954) and zinc and lithium acetates by Ananthanarayanan (1962). Reliable assignments of the fundamental frequencies of the acetate ion have been made by Ito and Bernstein (1956), from a study of the Raman spectra of aqueous solutions, of the acetate ion together with the infra-red data on the solid metal acetates studied by early workers. The Raman spectrum of single crystal of cadmium acetate has not been reported so far. As this salt can be easily crystallised from aqueous solutions, it was felt desirable to investigate its spectrum in single crystal form.

2. EXPERIMENTAL

Single crystals of dimensions $2 \times 2 \times 1$ mm. were used in the investigation. With the Hilger medium quartz spectrograph and Ilford Zenith Astronomical plates, exposures of the order of two days had to be given to record intense spectra. As the crystal faces got frosted due to the heat of the arc, light was condensed on the crystal by a short focus-condensing lens. A slit width of 0.02 mm. was used.

3. RESULTS

An enlarged photograph of the Raman spectrum of cadmium acetate is reproduced in Fig. 1 together with its microphotometer record. The observed frequency shifts in wave numbers have been marked in the figure. 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 wave numbers observed in the spectrum of zinc acetate dihydrate by Ananthanarayanan (1962) are also included in Table I. The

TABLE I

Sl. No.	Cadmium acetate	Zinc acetate	Free ion	Assignments
	Author	Ananthanarayanan	Ito and Bernstein	
1	30 (2)	25 (5)	..	Lattice
2	52 (3)	50 (<i>f</i>)	..	„
3	62 (1)	67 (10)	..	„
4	80 (1)	80 (12)	..	„
5	95 (10)	91 (12)	..	OH...O
6	122 (10)	109 (12)	..	„
7	145 (1)	..	..	Lattice
8	155 (1)	158 (<i>f</i>)	..	„
9	190 (0)	..	..	„
10	210 (5)	230 (4)	..	„
11	243 (1)	266 (8)	..	„
12	308 (4)	310 (—)	..	Cd-O ₆
		420 (—)	..	..
13	461 (3)	476 (1)	471 (<i>f</i>)	$\nu_{11} (b_1)$ COO inplane rocking
14	496 (2)	509 (<i>f</i>)	..	..
15	685 (3)	695 (2)	650 (3)	$\nu_5 (a_1)$ COO deformation
16	951 (20)	954 (20)	926 (5)	$\nu_4 (a_1)$ C—C stretching
		1062 (<i>f</i>)	1052 (?)	..
		1248 (<i>f</i>)	..	..
		1311 (<i>f</i>)	..	..
17	1349 (5)	1360 (4)	1344 (4)	$\nu_2 (a_1)$ CH ₃ deformation
18	1445 (15)	1456 (15)	..	$\nu_3 (a_1)$ and $\nu_{13} (b_2)$
		2709 (2)	..	..
		2800 (1)	..	..
		2838 (1)	..	..
19	2898 (1)	..	..	..
20	2947 (15)	2937 (15)	2935 (10)	$\nu_1 (a_1)$ C—H stretching
21	2997 (1)	2977 (1)	2981 (3)	$\nu_7 (b_1)$ C—H stretching
22	3041 (1)	3038 (1)	3010 (4)	$\nu_{12} (b_2)$ C—H stretching
23	Continuum up to 3560	Continuum	..	Water bands

f, feeble.

frequencies of the free acetate ion and their assignments as given by Ito and Bernstein (1956) are given separately in Table II.

TABLE II
Vibrational assignment of the acetate ion

Species		Description	Observed wave numbers in cm^{-1}
a_1	ν_1	C-H stretching	2935
	ν_2	CH_3 deformation	1344
	ν_3	C-O stretching	1413
	ν_4	C-C stretching	926
	ν_5	COO deformation	650
a_2	ν_6	Torsion	..
b_1	ν_7	C-H stretching	3010 or 2981
	ν_8	C-O stretching	1556
	ν_9	CH_3 deformation	1429
	ν_{10}	CH_3 rocking	1020
	ν_{11}	COO rocking (inplane)	471
b_2	ν_{12}	C-H stretching	2981 or 3010
	ν_{13}	CH_3 deformation	1456
	ν_{14}	CH_3 rocking	1052
	ν_{15}	COO rocking (out of plane)	621

4. DISCUSSION

Crystallographic data.—According to Groth (1910), cadmium acetate dihydrate crystallises in the monoclinic prismatic class with $a:b:c = 2.6076 : 1 : 2.1473$, $\beta = 101^\circ 25\frac{1}{2}'$ and the hydrated cadmium and zinc acetates show similar crystal forms. Complete crystal structure analysis of this salt does not seem to have been carried out so far, while that of the zinc salt has been

reported recently by Van Niekck, Schoening and Talbot (1953). Their structural data indicate the space group of the zinc acetate dihydrate to be C_{2h} with four molecules in the unit cell and an octahedral arrangement of the oxygens of the acetate ion and those of water molecules around the metal ion. A similar structure may be expected for the cadmium salt also even though there is no crystallographic information to support this at present.

Low frequencies.—The low-frequency spectra of acetates are expected to be quite complicated by the fact that lattice vibrations, low frequency vibrations of the hydrogen bonds and the fundamental modes of the octahedral arrangements of oxygens and water molecules around the metal ions all will be crowded in this region and overlap with each other.

There is in general a close similarity in the wave number shifts of the lattice lines in the spectra of the two acetates of Cd and Zn. But the distribution of their intensities is in general different. The fairly intense lines at 30, 52, 210 cm^{-1} can be attributed to rotatory types of lattice oscillations of the molecules in the unit cell. Since the crystal appears to be isomorphous with zinc acetate, we can expect six translatory and six rotatory type of lattice oscillations active in Raman effect. The two broad and intense low-frequency lines at 95 and 122 cm^{-1} appear to indicate the presence of O—H...O hydrogen bonding in this crystal. Gross and his co-workers (1959) have identified in the Raman spectra of simple substances like light and heavy ice, formic acid crystals frequencies of the hydrogen bond in the $\sim 150\text{--}300\text{ cm}^{-1}$ region. Reid (1959) has considered the stretching motions of the O—H...O bonds as a function of the bonded distances. The theoretically calculated frequencies vary from 850 cm^{-1} for O—H...O distance of 2.43 Å to about 110 cm^{-1} for a distance of 2.74 Å. In particular, the bonded distances 2.64–2.74 Å can be expected to give lines in the region 120–100 cm^{-1} . It appears therefore that such bonds are present in this crystal also. In the absence of exact structure of the crystal, this conclusion cannot be confirmed. The 308 cm^{-1} line has been attributed to the Cd—O₆ fundamental vibration as such lines are expected in this region.

Internal frequencies.—The fundamental frequencies of the acetate ion are distributed under the different symmetry types as follows: $5a_1 + a_2 + 5b_1 + 4b_2$. The torsional vibration about the C—C bond ν_6 belonging to the 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. A description of these fundamental modes of the acetate ion together with their frequencies observed by Ito and Bernstein

(*loc. cit.*) is given in Table II. The modes corresponding to ν_{10} , ν_8 , and ν_6 might have escaped detection as they overlap with the mercury lines at $\lambda 2603.20$, $\lambda 2639.93$ and $\lambda 2578.4 \text{ \AA}$.

The water band extends from 3250 to 3560 cm^{-1} and the lowering of its stretching frequency is thus an indication of the presence of hydrogen bonding (Nakamoto, Margoshes and Rundle, 1955).

5. SUMMARY

The Raman spectrum of a single crystal of cadmium acetate dihydrate has been recorded for the first time using $\lambda 2537$ excitation. Twenty-three lines have been observed out of which ten have been attributed to the internal oscillations of the acetate ion, nine to the lattice modes, two to low-frequency hydrogen bond vibrations. A line at 308 cm^{-1} and the continuum 3250 – 3560 cm^{-1} have been assigned to the Cd—O_6 and internal vibrations of the water molecules.

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FIG. 1 (a) Mercury spectrum.
(b) Raman spectrum of cadmium acetate dihydrate.
(c) Microphotometer record.