RAMAN SPECTRUM OF CRYSTALLINE CADMIUM SULPHATE

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1. Introduction

Cadmium sulphate ($3CdSO_4 \cdot 8H_2O$) differs from most other crystalline sulphates containing water of crystallisation in that the proportion of water is very much less and the crystal structure analysis (Lipson, 1936) shows that the forces between the cadmium and SO_4 ions are so large that to a first approximation one can regard the structure as composed of Cd and SO_4 groups in which the water molecules occupy the interstices. Although the spectrum of its water of crystallisation has been studied and compared with those of other crystals containing water of crystallisation (Hibben, 1937; P. G. N. Nayar, 1938) its Raman spectrum has not been so far investigated in any great detail. Its Raman spectrum recorded by Hibben and reproduced in his book ' Raman Effect and its Chemical Applications " (1939) does not show much detail and Hibben limited himself to pointing out the splitting in the crystalline state of the triply degenerate oscillation (1106 cm.$^{-1}$) of the free SO_4 ion and no further study of the spectrum was made by him. Besides these, the strongest Raman line 1003 cm.$^{-1}$ alone was recorded by Embirikos (1930) and compared with those of other sulphates. An investigation of its Raman spectrum made by us recently revealed such an abundance of detail due to the use of spectrographs of large dispersion, improved Rasetti technique and more efficient filtering of the exciting radiation that it was felt desirable to report the results given below.

2. Experimental Details

The crystals used were prepared from the aqueous solution of the salt by the method of slow evaporation and were about 1 cm. × 5 mm. × 5 mm. in size with well-developed faces. Besides those grown in our laboratory, one other fine specimen also grown from solution by the same method was made available to us through the kindness of Prof. J. P. Mathieu to whom our sincere thanks are due.

The resonance radiation of mercury (λ 2537) from a specially designed water-cooled quartz arc placed in the field of an electromagnet was used to excite the Raman spectrum. Using the medium quartz spectrograph and slit width of ·025 mm. exposures of the order of 2 hours were found to be sufficient to record the complete spectrum. It is worth mentioning here that though the experimental arrangement was found to be adequate to record the symmetric oscillation (1006 cm.$^{-1}$) of the SO_4 ion and the waterbands in a couple of minutes, even exposures of the order of 2 days failed to bring out the second order lines. In order to study the lattice spectrum in more detail a large quartz spectrograph with a dispersion of about 40 cm.$^{-1}$ per mm. in the λ 2537 region was employed. With this instrument using a slit width of ·05 mm. an exposure of the order of a day was enough to record the complete Raman spectrum.

3. RESULTS AND DISCUSSION

The Raman spectrum of cadmium sulphate $3CdSO_4 \cdot 8H_2O$ consists of 23 frequency shifts all of which except the waterbands are marked in Fig. 1 *b* of Plate XIII. Fig. 1 (*a*) is the spectrum taken with the large quartz spectrograph and enlarged to the same extent as its microphotometer record shown in Fig. 1 (*b*). The waterbands as well as the other Raman lines could also be easily identified in Fig. 2 *a* which is an enlargement of the spectrogram taken with the smaller instrument while Fig. 2 *b* shows the direct mercury spectrum. The observed frequency shifts are 45 (2), 56 (7), 64 (7), 75 (2), 89 (2), 104 (5), 124 (4), 138 (5), 170 (2), 190 (3), 219 (5), 261 (1), 331 (3), 456 (6), 462 (5), 626 (2), 1006 (30), 1077 (3), 1101 (9), 1115 (10), 1157 (3), 3347 (7) and 3428 (15) cm.$^{-1}$ the figures within brackets representing the visually estimated relative intensities. The values of the frequency shifts of all the lines except those of the waterbands were determined from measurements made on the spectrogram taken with the El (large) spectrograph and may therefore be regarded as accurate. We will now consider the observed spectrum in relation to the known crystal structure.

The crystal structure of $3CdSO_4.8H_2O$ has been determined by Lipson (1936) and reveals certain interesting features. Unlike most other sulphates with water of crystallisation, like alum, $KAl(SO_4)_2 12 \cdot H_2O$ or Epsom salt $MgSO_4 \cdot 7H_2O$ where the water is known to form an essential part of the structure, in cadmium sulphate eight-third hydrate the main structure is governed by the forces between the metal atoms and the SO_4 groups and the water molecules just fill up the interstices. The crystal belongs to the monoclinic space group I 2/*h* (C^6_{2h}) and contains four molecules of $3CdSO_4 \cdot 8H_2O$ in the unit cell. In the crystal, only 4 Cd and 4 SO_4 occupy special positions and are located on the two-fold axis and all the remaining atoms are in general positions. The local symmetry of even the special SO_4 group in the crystal is only C_i and as such it is only reasonable to suppose that on account of this and also the known multiplicity of ions in the unit cell, the degeneracies of the frequencies belonging to tetrahedral SO_4 ion are removed. Actually one observes only 8 frequencies which could be attributed to the internal oscillations of the SO_4 ion as shown below.

RAMAN FREQUENCIES OF THE SO_4 ION IN $cm.^{-1}$

In the free state→	454		622	983	1106			
In $3CdSO_4.8H_2O$→	456	462	626	1006	1076,	1101,	1115,	1157

The Raman line 1076 $cm.^{-1}$ has been explained by Hibben as a combination of the frequencies 450 and 626 $cm.^{-1}$; this appears to be erroneous since in the crystal the line 1076 $cm.^{-1}$ is very intense while the fundamental 626 $cm.^{-1}$ itself is very weak. While the degeneracy of the oscillation (1106 $cm.^{-1}$) of the free SO_4 ion is seen to be removed completely and splitting is evident, one notices, however, a different behaviour of the other two degenerate oscillations. In the crystal the Raman lines due to the splitting of the doubly degenerate oscillation are neither well resolved nor sharp as for example in gypsum which also belongs to the monoclinic class and is known to contain loosely-bound water of crystallisation (Wooster, 1936). Also in the present study only a very weak line corresponding to the triply degenerate oscillation of the free ion is observed at 626 $cm.^{-1}$ while in gypsum three fairly sharp lines (618, 622 and 672 $cm.^{-1}$) have been recorded by R. S. Krishnan (1945) in the same region. Further the spectrum of the water of crystallisation is comparatively simple and consists of only two bands the frequency shifts of which agree well with those reported by Hibben (1937) and by P. G. N. Nayar (1938). These observed features of the lines due to the internal oscillations of the SO_4 ions and of the water of crystallisation suggest that in the crystalline state while the influence of the additional forces due to the neighbouring ions is by no means negligible, it does not lead to any major distortion of the disposition of the bonds from their idealized nature as expected by Lipson (*loc. cit.*).

Besides the 8 Raman lines due to the internal oscillations of the SO_4 groups and the two waterbands, the Raman spectrum contains 13 low frequency shift lines which arise from lattice oscillations. Neglecting the water molecules, a simple group theoretical calculation shows that the number of translatory type of oscillations permitted in Raman effect is 36, of which

16 are of type A_{1g} and the remaining 20 of type B_{1g}. However, we find that even under the high dispersion of the large quartz spectrograph the crystal exhibits only 13 Raman lines which are attributable to the translatory type of lattice oscillations. Since it is known that for this crystal only the vibrations of type A_{1g} will show a variation of intensity with orientation an attempt was made to study the variation of the intensity with orientation with incident unpolarised light. The observations indicate that the lines 219, 104, 138 cm.$^{-1}$ may tentatively be assigned to type A_{1g} and those with frequency shifts 170, 190, 331 cm.$^{-1}$ to the type B_{1g}. It was also observed that among the Raman lines due to the SO_4 ions and the waterbands those at 462 and 3347 are of type A_{1g}.

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SUMMARY

The Raman spectrum of a single crystal of cadmium sulphate ($3CdSO_4.8H_2O$) has been investigated using the resonance radiation of mercury as exciter. The recorded spectrum reveals 23 Raman lines and of these 8 have been attributed to the internal oscillations of the SO_4 ion and 2 to the oscillations of the water molecules. While the number of translatory type of lattice oscillations permitted by the selection rules is 36, only 13 are observed experimentally. A tentative assignment for some of these vibrations has been made from a study of the variation of intensity of the lines with orientation.

REFERENCES

1. Embirikos, N. .. *Zeit. Phys.*, 1930, **65**, 266.
2. Hibben, J. H. .. *Journ. Chem. Phys.*, 1937, **5**, 166.
3. ———— .. *The Raman Effect and its Chemical Applications*, 1939, 332, 399.
4. Krishnan, R. S. .. *Proc. Ind. Acad. Sci.*, 1945, **22A**, 274.
5. Lipson, H. .. *Proc. Roy. Soc.*, London, 1936, **156A**, 462.
6. Nayar, P. G. N. .. *Proc. Ind. Acad. Sci.*, 1938, **8A**, 419.
7. Wooster, W. A. .. *Zeits. f. Krist.*, 1936, **94**, 376.

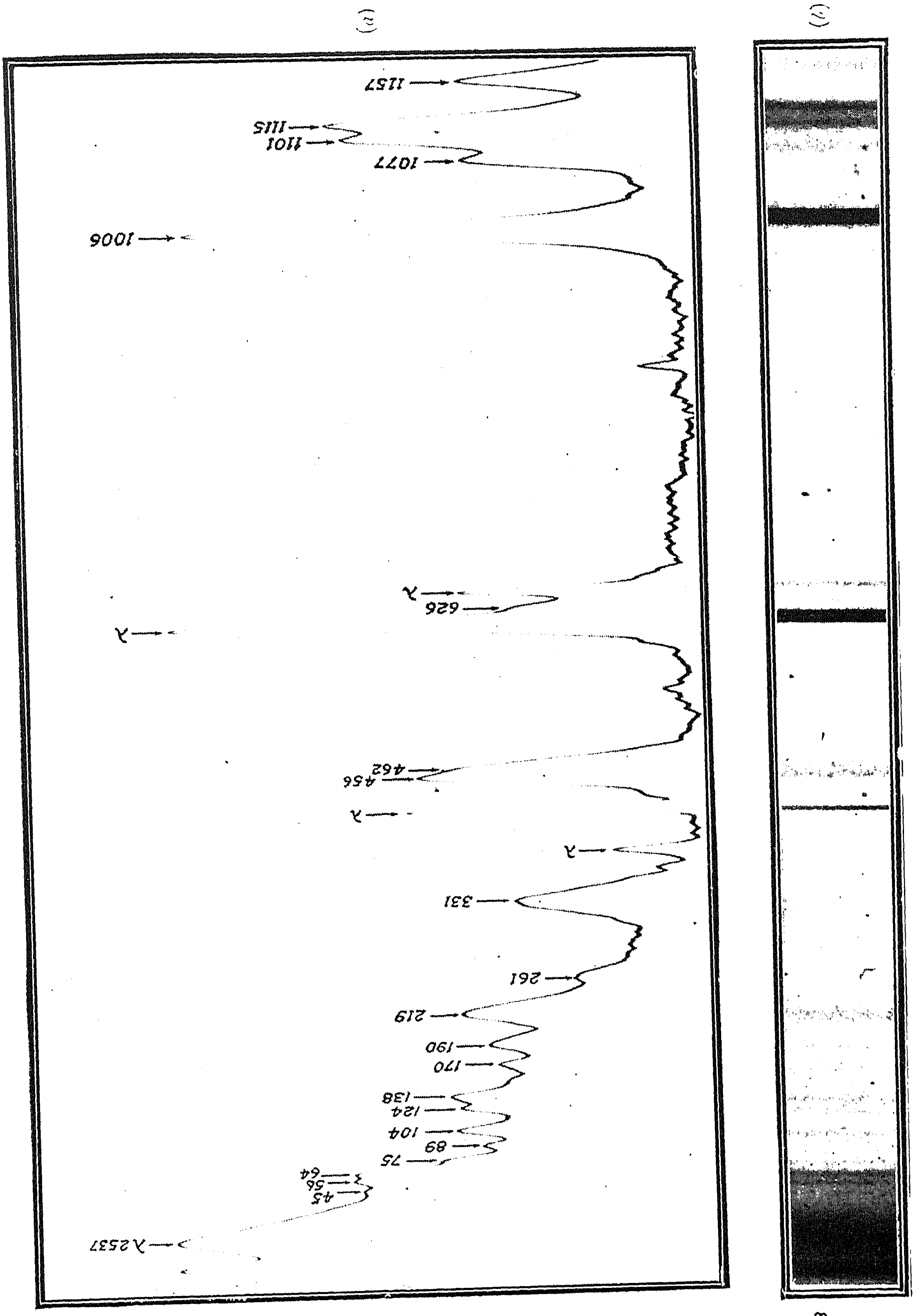

FIG. 1. (a) Raman spectrum of crystalline cadmium sulphate taken with a large quartz spectrograph
(b) Its microphotometer record

FIG. 2. (a) Raman spectrum of crystalline cadmium sulphate taken with the medium quartz spectrograph.
(b) Direct Mercury Spectrum.