

RAMAN SPECTRA OF BORAX, KERNITE AND COLEMANITE

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1. INTRODUCTION

THE Raman effect in boric acid and its derivatives and the glasses associated with them has been studied by several investigators. A brief summary of the results appears in Hibben's treatise on "The Raman Effect and its Chemical Applications". The Raman spectrum of borax ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$) has been observed by Nielsen (*vide* Hibben's treatise, p. 433) and has been found to consist of seven frequencies at 578 (1), 853 (1), 891 (1), 942 (1), 3340 (1), 3455 (1) and 3574 (1) cm^{-1} . Kernite ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 4\text{H}_2\text{O}$) was investigated by Hibben (1937) who reports ten frequencies at 500 (2), 575 (0), 735 (3), 850 (0), 934 (6), 1100 (?), 3269 (2), 3343 (3), 3425 (2) and 3552 (10) cm^{-1} . Gross and Vuks have reported in borax glass diffuse bands in the regions 430–535 (0), 950–1000 (0), 1077–1127 (0), and 1310–1520 (0) and a strong line at 760 (5) cm^{-1} . It is rather surprising that Nielsen did not notice any shift corresponding to 760 cm^{-1} in borax. The Raman spectrum of colemanite ($\text{Ca}_2\text{B}_6\text{O}_{11} \cdot 5\text{H}_2\text{O}$) has not so far been investigated. In view of the interest attached to these substances and the fact that the low frequency spectra of these have not so far been reported, it appeared to be desirable to investigate the spectra of these substances. The paper reports the findings from the study.

2. EXPERIMENTAL DETAILS

The Raman spectra were recorded with a Hilger medium quartz spectrograph having a dispersion of 140 cm^{-1} per mm. in the λ 2536.5 region. A quartz mercury arc of the sealed type with mercury pools as electrodes was immersed in a trough of running water and an electromagnet was used to deflect the discharge towards the top wall of the arc. With a current of 3 amperes this arrangement constituted to give an intense source of λ 2536.5. The crystals were kept quite close to the arc and the scattered radiations from the crystal were focussed on the slit of the spectrograph with a quartz condenser. Two mercury dishes were placed inside the spectrograph one at the collimator side and the other at the plate-holder side. The mercury

vapour inside the spectrograph was sufficient to effectively suppress the exciting λ 2536.5 radiation so that in the spectrograms obtained, it appeared much feebler than its satellite λ 2534.8.

The crystals of borax which were rather small were efflorescent and as such fresh crystals had to be used periodically. A large specimen of kernite in the form of a thick plate was available and it was possible to record in this case a very intense spectrum. The specimen of colemanite which was somewhat smaller in size had well-developed faces forming a pyramid, but was intensely luminescent under near ultraviolet radiations. Kernite was also slightly luminescent. This fact coupled with the feeble scattering in these crystals made it impossible to record their Raman spectra with λ 4358 in the visible. In the ultraviolet region on the other hand, because of the large scattering power of the λ 2536.5 radiations the luminescence did not overpower the scattering. With a slit width of 0.045 mm. and an exposure of the order of 16 hours it was possible to obtain reasonably intense spectrograms. The complete spectrum of borax could not be obtained since the crystals grown by the method of slow evaporation were small.

3. RESULTS

Figures 1 (b), 1 (c), 1 (d) in the accompanying plate reproduce the Raman spectra of borax, kernite and colemanite respectively while Figs. 1 (a), and 1 (e) reproduce the spectrum of the mercury arc for comparison. In some cases the lines were rather weak and diffuse or else were partially overlapping on a mercury line and the frequency shifts of these were estimated by comparison with the position of the iron arc lines.

Borax exhibits seven lines at 159 (*w*), 349 (*w*), 458 (*m*), 572 (*m*), 753 (*w*), 847 (*v. w*), and 944 (*s*) cm^{-1} and four bands due to water at 3325, 3444, 3500 and 3577 cm^{-1} . Of these the frequency at 3577 cm^{-1} is very intense and comparatively sharp. Nielsen has not reported the faint band at 3500 cm^{-1} . The line reported at 891 cm^{-1} by Nielsen has not been recorded and only a trace of a line could be noticed at about 847 cm^{-1} .

Table I presents the data in the case of kernite and colemanite and the general correspondence between the two spectra can be noticed. In the case of colemanite, the intense frequency shift at 940 cm^{-1} observed in kernite and borax has not been recorded.

The spectrum due to water shows striking variations in its structure and in particular the frequency shift of the sharp and intense band corresponding to the hydroxyl group changes from 3552 cm^{-1} in kernite to 3577 cm^{-1} in borax and to 3605 cm^{-1} in colemanite,

TABLE I
Frequency Shifts

Kernite cm. ⁻¹	Colemanite cm. ⁻¹	Kernite cm. ⁻¹	Colemanite cm. ⁻¹
55 s.	..	806 m.	786 w.
82 v.s.	..	846 m.	~ 870 w.
104 s.	95 v.s.	932 v.s.	..
127 s.	..	951 v.w.	~ 982 v.w.
152 w.	148 m.	~ 1028 m.	..
184 s.	181 s.	1087 s.	1078 m.
~ 215 v.w.	223 m.	1135 m.	~ 1150 w.
258 s.	251 m.	1321 s	~ 1252 w.
		1375 v.w.	~ 1310 w.
315 w.	318 s.	1448 w.	..
346 w.	..	~ 1480 v.w.	..
371 ~ 391 b.m.	..	~ 3000 s.	..
426 v.w.	..	3248 s.	~ 3310 s.
459 m.	~ 450 v.w.	~ 3305 s.	..
498 v.s.	~ 490 v.w.	~ 3360 s.	..
541 ? v.w.	538 s.	~ 3425 s.	..
562 w.	565 s.	3548 v.s.	~ 3520 s.
..	670 s.	..	3605 v.s.
739 v.s.	745 v.s.	..	

s. strong; w. weak; m. moderate; v.s. very strong; v.w. very weak; b. broad. ~ value of frequencies estimated by comparison with position of adjacent iron arc lines.

4. DISCUSSION

Borax, kernite and colemanite crystallize in the holohedral class of the monoclinic system and have been assigned to the space groups C2/c, P2/c and P2₁/a respectively [*Structure Reports*, Vol. 11, pp. 428-31 and Christ, Clark and Evans (1954)]. The existence of a centre of symmetry in all these cases precludes the possibility of observing any of these lines in infra-red absorption also. Reference to the literature has revealed that no infra-red absorption studies have so far been made with borax and kernite. However, the infra-red spectrum of metallic orthoborates have been studied by Sen and Sen Gupta (1935) in the near infra-red by transmission, by Parodi (1937) in the far infra-red both by reflection and transmission, and lately extensively by Lecomte and Duval (1952) in the near infra-red by transmission. For calcium borate [Ca₃(BO₃)₂] they observe maxima at 676, 734, 784, 814, 876, 922, 1000, 1100, 1168, 1340 and 1412 cm.⁻¹ Parodi reports in the far infra-red for calcium borate frequencies at 365, 325, 250 and 192 cm.⁻¹

Lecomte and Duval have discussed in detail the origin of such a large number of frequencies since an ordinary planar BO_3 group should possess only four vibration frequencies. They attribute the large number of frequencies to the coupling of BO_3 groups and they calculate that two such groups coupled would give rise to eighteen vibration frequencies, the totally symmetric valence vibration frequency being in the region $909\text{--}934\text{ cm.}^{-1}$. The structure of borax is reported to consist of BO_3 triangles sharing common vertices and forming an infinite chain along the c -axis consisting of B_4O_7 rings. Kernite on the other hand, is supposed to be made up of B_3O_6 rings formed by three BO_3 triangles sharing vertices, coupled together by B_2O_3 groups from two BO_3 triangles, thus forming an infinite B_4O_7 zig-zag chain along the b -axis. The vibrations of such a structure consisting of coupled BO_3 triangles would give rise to a large number of frequencies and it is possible here to identify only the frequency at 932 cm.^{-1} in kernite and at 944 cm.^{-1} in borax as due to the valence oscillation of the borons and oxygens.

The structure of colemanite recently determined by Christ, Clark and Evans (1954) is reported to consist of infinite boron-oxygen chains running parallel to the a -axis, the chain element being constituted by a BO_3 triangle and two BO_4 tetrahedra forming a ring, the chain element having the composition $[\text{B}_3\text{O}_4(\text{OH})_3]^{-2}$. It has also been found by them that the B—O bond lengths in the tetrahedra are larger than the bond lengths in the triangles. Again, since colemanite also possesses a centre of symmetry no correspondence could be normally expected between the data from Raman and infra-red spectra. But the studies of Coblenz (1906) on the infra-red reflection spectrum of colemanite reveal the existence of frequencies at $1370, 1316(?)$, $1064, 943$ and 893 cm.^{-1} , which have nearly corresponding frequencies at $1310, 1078, 982$ and 870 cm.^{-1} in Raman effect. It is rather surprising that there is no Raman frequency in colemanite corresponding to the 940 cm.^{-1} shift in borax and kernite. If the vibrating structure in colemanite consists of BO_3 triangles coupled to BO_4 tetrahedra having different bond lengths, as has been suggested by Christ, Clark and Evans, the principal vibration frequency of this system might be different from what has been observed in kernite and borax.

The existence of the O—H group in the chain element of colemanite is consistent with the observation in Raman effect of an intense and sharp band at 3605 cm.^{-1} and corresponding to the hydroxyl group frequency. Though the reported structures of kernite and borax do not contemplate the existence of the hydroxyl group in them, the observation of sharp and intense bands at 3548 and 3577 cm.^{-1} in their respective Raman spectra indicate the existence

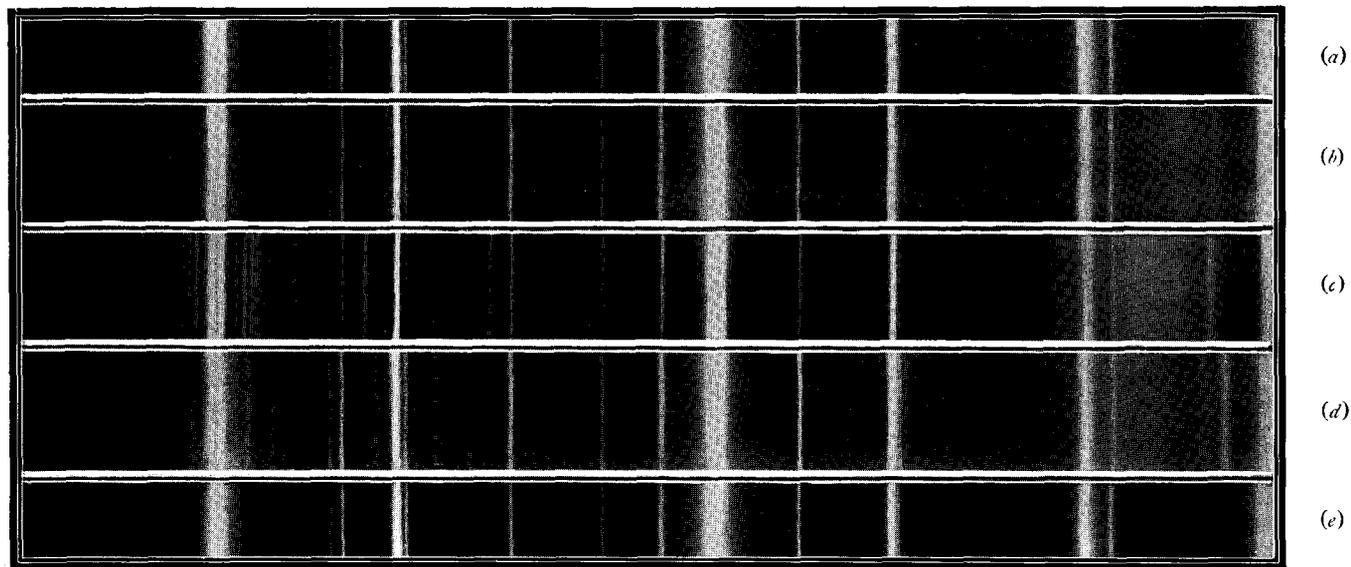


FIG. 1. Raman Spectra of Borax, Kernite and Colemanite
(a) Mercury arc. (b) Borax. (c) Kernite. (d) Colemanite. (e) Mercury arc.

of such groups in their structures. It is hoped that polarisation and orientation studies would help towards a more detailed analysis of the observed spectra of these chain structures.

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SUMMARY

The Raman spectra of borax, ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$), kernite ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 4\text{H}_2\text{O}$) and colemanite ($\text{Ca}_2\text{B}_6\text{O}_{11} \cdot 5\text{H}_2\text{O}$) have been investigated using $\lambda 2536.5$ as exciting radiation. The spectrum of colemanite is reported for the first time. Many additional lines hitherto unreported have been found in the case of kernite and borax. The spectrum of borax exhibits seven lines, besides four bands due to water of crystallisation while the spectrum of kernite is found to consist of twenty-eight lines and six water bands. Colemanite exhibits nineteen Raman lines, and three bands due to water of crystallization. The observed spectra are discussed in relation to the known structures of the substances.

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