

RAMAN SPECTRUM OF CRYSTALLINE SODIUM CITRATE

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SUMMARY

Using the λ 2537 radiation of a mercury arc as exciter, the Raman spectrum of a single crystal of trisodium citrate ($\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot 5\text{H}_2\text{O}$) has been photographed. Of the 28 Raman lines observed, five lines have been assigned to lattice oscillations, twenty lines to internal oscillations and the remaining three lines to the oscillations of the water molecule.

1. INTRODUCTION

The Raman spectrum of a solution of sodium citrate was studied by Edsali (1937) using the λ 4358 radiation as exciter. More recently Marignan (1948) has investigated the Raman spectrum of sodium citrate ($2 \text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot 11\text{H}_2\text{O}$) utilising the powder technique and the method of complementary filters ; but he confined himself to the region of frequency shifts from 2900 to 3500 cm^{-1} . As such, the author has investigated the Raman spectrum of sodium citrate more thoroughly using a single crystal of the same and the results are presented here.

2. RESULTS AND DISCUSSION

Crystals of sodium citrate with well-developed faces were grown from an aqueous solution by the method of slow evaporation. The biggest crystal grown had the dimensions $2\frac{1}{2} \times 1\frac{1}{2} \times 1$ cm. But owing to the presence of inclusions within the crystal, it had to be cut and polished to get a clear and suitable specimen. The spectrum was excited by the λ 2537 radiation from a water-cooled, magnet controlled quartz mercury arc and a Hilger medium quartz spectrograph was used to record the spectrum. The crystal was found to lose its water of crystallisation and the side through which it was illuminated became opaque in the course of the exposure partly due to the heat and partly due to the ultraviolet radiation of the arc and it was therefore necessary to polish this face of the crystal often. An exposure of the order of 24 hours was found to be sufficient to obtain a fairly intense spectrogram. An enlarged photograph of the Raman spectrum of sodium citrate and a microphotometer record of the same are reproduced in

Plate (XIII) in which frequency shifts of the Raman lines have also been marked. The observed spectral shifts have been tabulated along with those reported by Edsall (1937) in the case of solution (see Table I). The figures within brackets represent the intensity estimated visually.

TABLE I
Raman Spectrum of Sodium Citrate

Author	Edsall	Author	Edsall
60 (7)		1140 (2)	1100
93 (1)		1206 (4)	1210
111 (1)		1267 (.5)	
139 (2)		1299 (2)	1302
187 (3)		1408 (10)	
233 (.5)	233	1430 (6)	1415
	317		
405 (1)	409	1476 (.5)	
	583		
842 (2)	845	1589 (1)	1580
898 (.5)		1625 (1)	
945 (.5)	956	2920 (6)	2929
968 (4)		2935 (8)	
1069 (1)	1045	2961 (7)	2982
1084 (2)		3435 (4)	
		3511 (2)	
		3550 (1)	

Frequency shifts in cm.^{-1}

The observed spectrum consists of 28 Raman lines the first five low frequency shifts being unambiguously due to the lattice oscillations. A more detailed study of the lattice spectrum could not be made for want of crystal structure data; in fact while according to "Groth" sodium citrate crystallises in the rhombic bisphenoidal class and shows pyroelectricity (Skritzký, 1900), it is definitely known that sodium citrate is not piezoelectric (Gilbert, Greenwood, 1935; A. Hettich and A. Schleede, 1928). It is probable that sodium citrate belongs to the point group V_h and the observed pyroelectricity, as with topaz, is not a true one. Of the other twenty-three Raman lines, those of frequency shifts 2920, 2935 and 2961 cm.^{-1} may be attributed to C-H oscillations. While Marignan has recorded all the three lines with almost the same frequency shifts, Edsall was able to observe only two (2929 and 2982 cm.^{-1}) in solution.

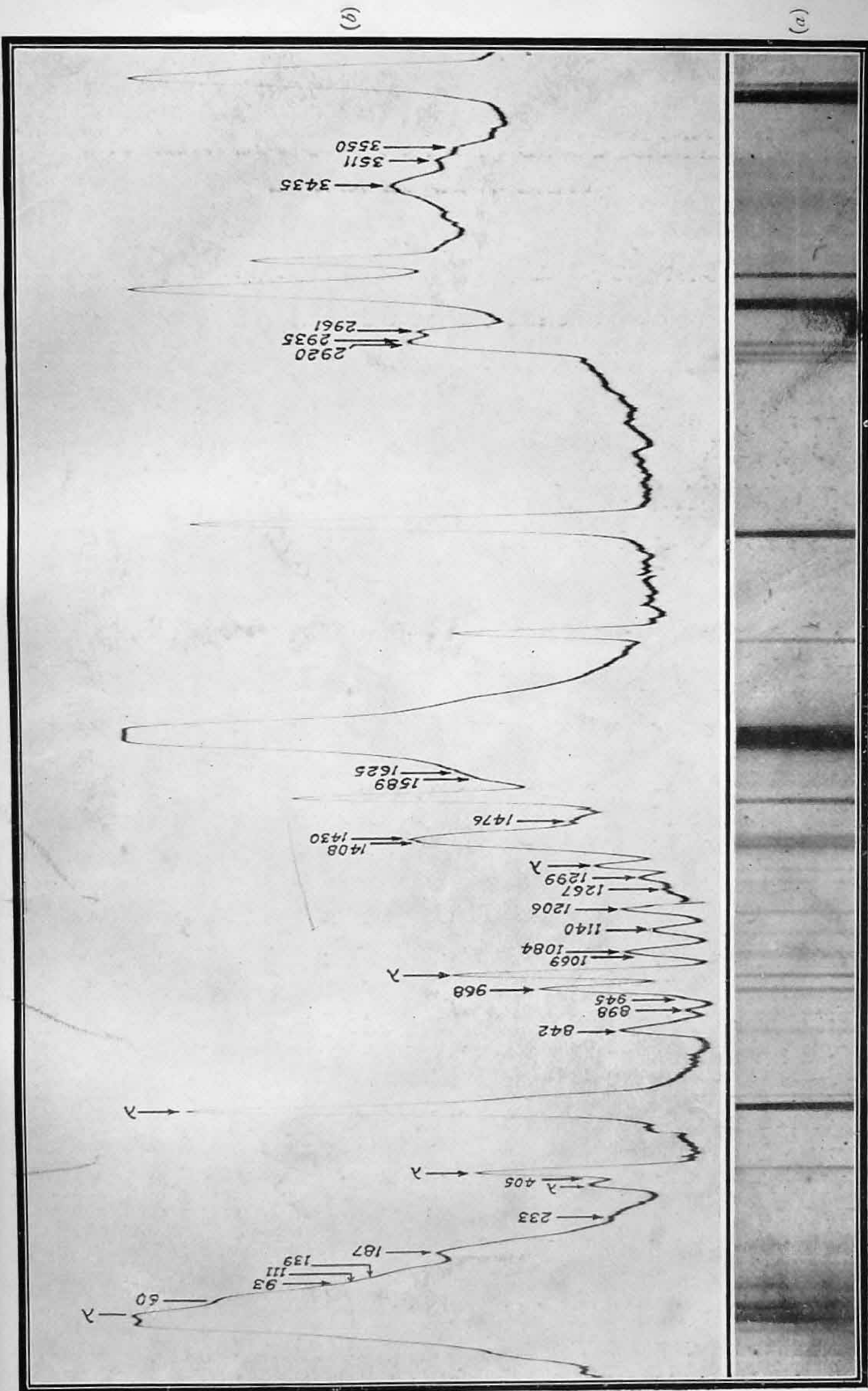
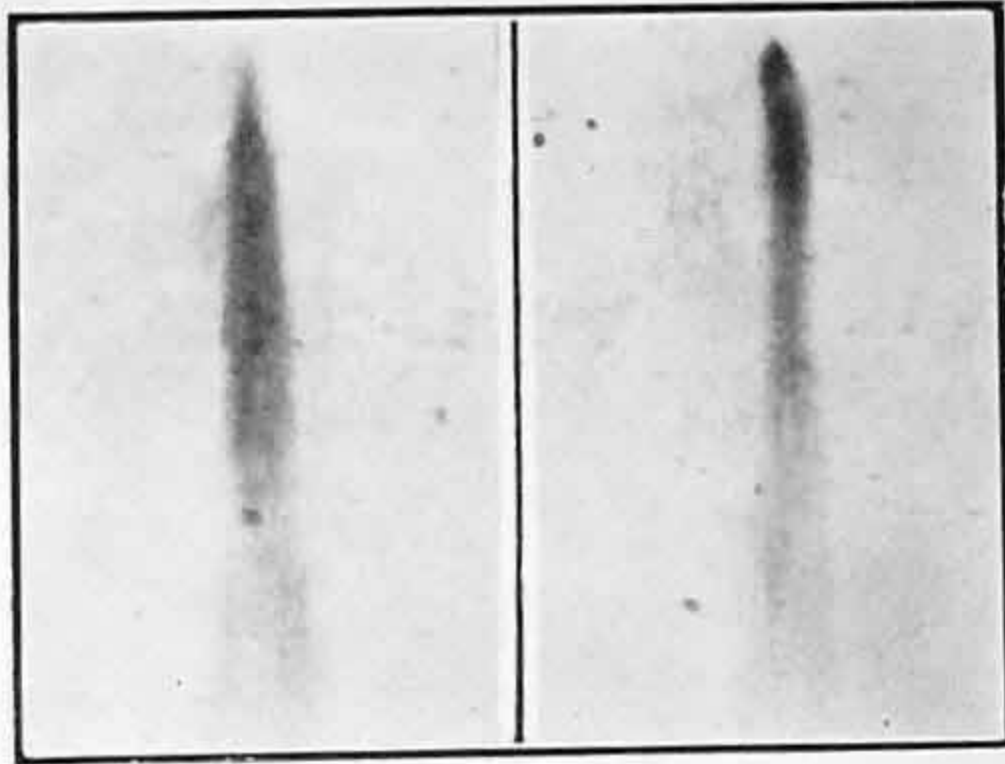


FIG. 1. (a) Raman spectrum of sodium citrate taken with a medium quartz spectrograph
(b) Microphotometer record of the above



(a)

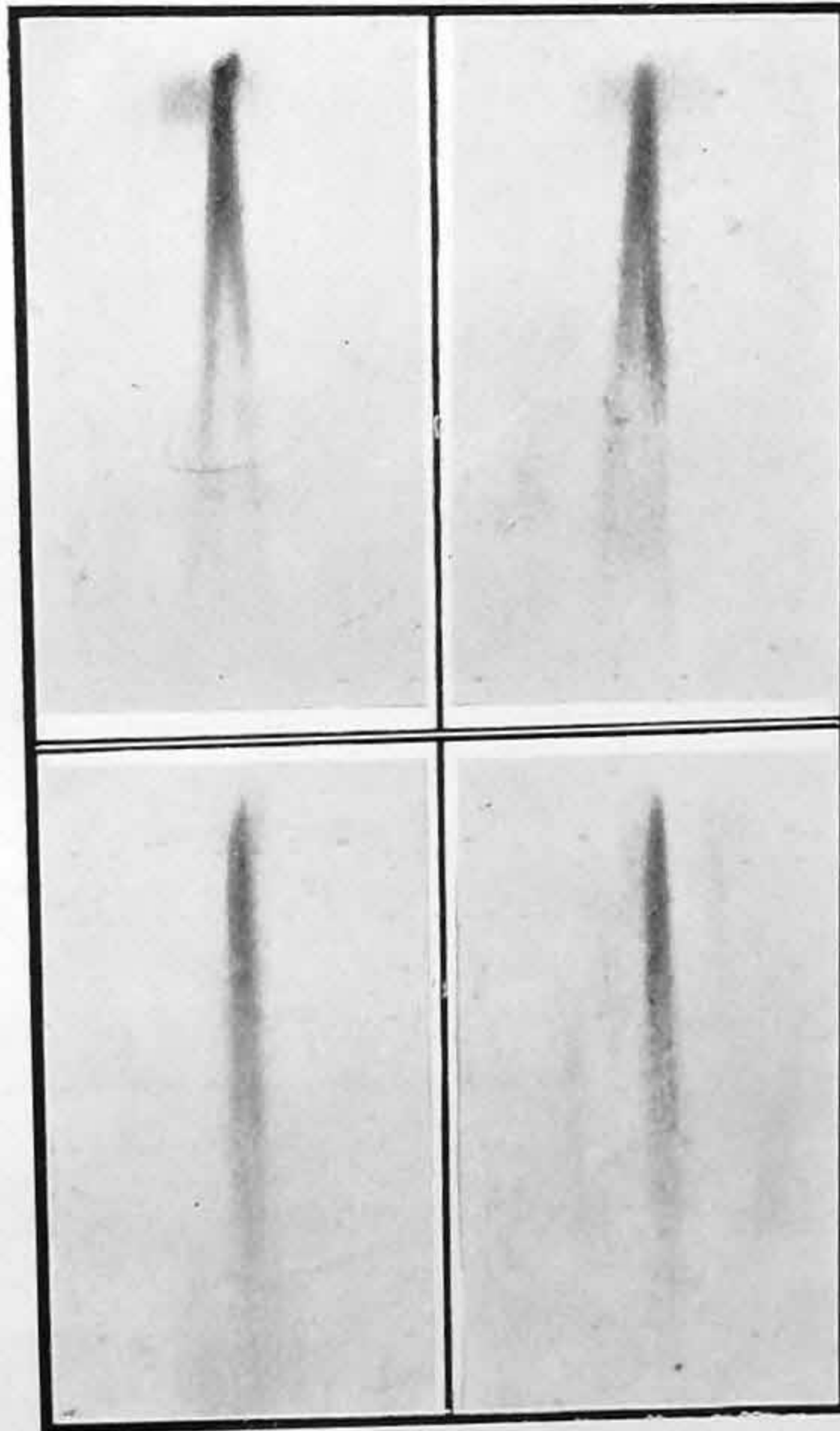
(b)

FIG. 2

Internal reflection in (a) NaCl crystal
(b) LiF crystal

(a)

(b)



(c)

(d)

FIG. 3

Internal reflection of (a) etched MgO crystal; (b) chilled MgO crystal
(c) etched KCl crystal; (d) chilled KCl crystal

The spectrum of the water of crystallisation is found to comprise of three lines of frequency shifts 3435, 3511 and 3550 cm^{-1} of which the first one is comparatively broad and diffuse. The Raman lines 3150 and 3310 reported by Marignan could not be observed even in heavily exposed spectra. This might, however, be due to the difference in the amount of water of crystallisation.

Although the crystal structure is not known, an attempt was made by the author to infer the character of the vibrations from orientation studies. Spectra were taken with the incident light along the a -axis and the scattered light along the b and c axes respectively. In the two spectra the Raman lines with frequency shifts 1069, 1084, 2920, 2935 and 2961 cm^{-1} were found to undergo slight variations in intensity. It is known that in crystals belonging to the orthorhombic class, only the totally symmetric vibrations show a variation in intensity with orientation and as such the five Raman lines mentioned are of symmetry type A_{ig} .

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