

# THE INFRA-RED ABSORPTION SPECTRUM OF POTASSIUM CHLORATE CRYSTALS: PART I

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## 1. INTRODUCTION

THE infra-red spectrum of potassium chlorate was first investigated by Schæfer and Schubert (1921) using pressed powder and employing the restrahlen method. They reported two reflection maxima at  $10.12 \mu$  ( $988 \text{ cm.}^{-1}$ ) and  $16.12 \mu$  ( $620 \text{ cm.}^{-1}$ ) respectively. Subsequently, several studies have been published of the Raman effect in the substance in solution, as crystal powder and also as a single crystal. It is proposed in this paper to report the results of the investigation of the infra-red absorption spectrum of thin single crystals of potassium chlorate, made by the transmission method, using a Beckman infra-red spectrophotometer (Model IR 2) in the range between  $1 \mu$  to  $15 \mu$  provided by a dispersing prism of potassium bromide.

Single crystals of potassium chlorate were obtained from a solution of the pure substance in water by slow evaporation. The crystals are formed as plates parallel to the 001 plane. Three crystals were examined. One of them (about  $5 \times 5 \times 1 \text{ mm.}$  size) was studied in detail, readings being taken at intervals of  $0.25 \mu$ , and at still closer intervals near the absorption maxima. The other two plates were examined less closely, readings being taken at intervals of  $0.5 \mu$ . But as these specimens were thinner than that examined in greater detail, they exhibit a clearer resolution of some of the broad absorption bands. The crystal was interposed with its flat face perpendicular to the infra-red radiation, the percentage transmission being read off directly with the instrument.

Figs. 1 and 2 exhibit the percentage cut-off for the different wavelengths investigated. Fig. 1 gives the results with the specimen examined in detail, while Fig. 2 gives the results obtained with a thinner specimen.

Table I gives the position of the absorption bands observed in this investigation. For comparison with the same, the reflexion maxima reported by Schæfer and Schubert, the results of Shantakumari on the Raman effect

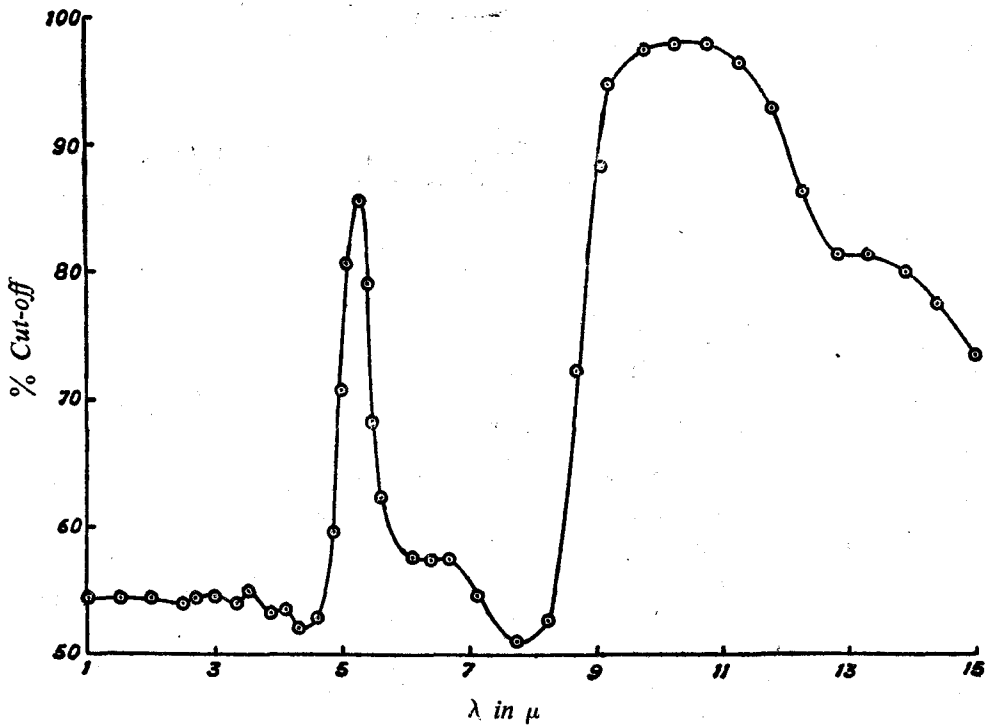


FIG. 1. Infra-red absorption spectrum of single crystal of potassium chlorate (thickness about 1 mm.)

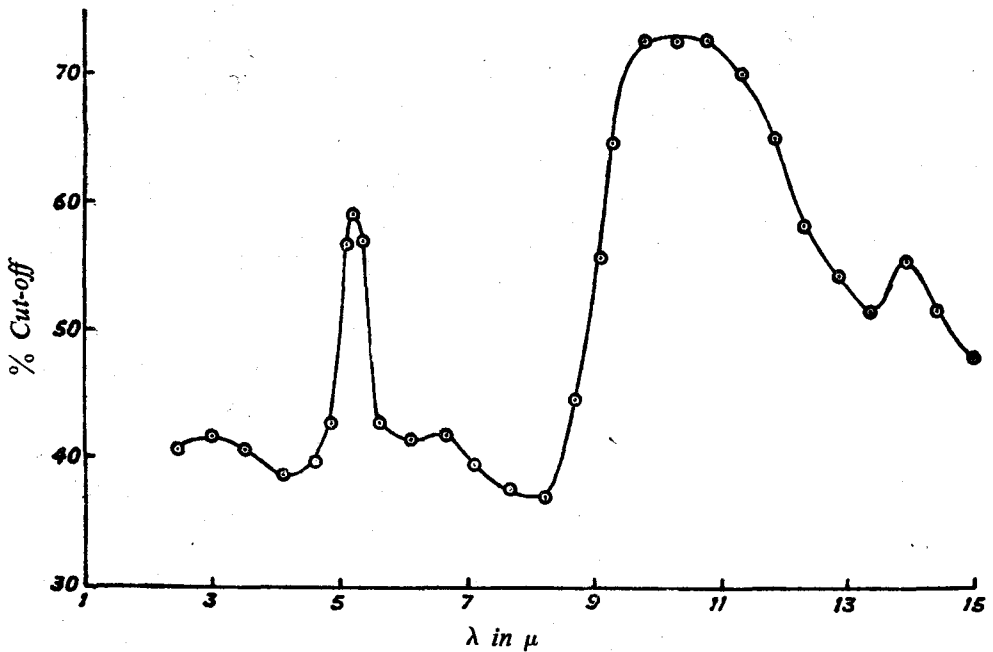


FIG. 2. Infra-red absorption spectrum of single crystal of potassium chlorate (thickness < 1 mm.)

in single crystals of potassium chlorate and of Venkateswaran on the Raman effect in solution are also tabulated.

TABLE I  
*Infra-red and Raman Spectra of KClO<sub>3</sub>*

Infra-red Absorption Bands (a)			Infra-red Reststrahlen (b)		Raman effect single crystal (c)		Raman effect in solution (d)			
$\mu$	cm. <sup>-1</sup>	Description	$\mu$	cm. <sup>-1</sup>	$\mu$	cm. <sup>-1</sup>	$\mu$	cm. <sup>-1</sup>		
2.85	3509	Weak								
3.5	2857									
4.1	2439									
5.3	1887	Strong and sharp								
6.7	1493	Weak								
9.2	1087	Strong, broad	10.12	988	10.26	975(7)	10.24	977(1)		
↓	↓				10.75	930(10)			10.75	930(10)
12.0	833				10.87	920(1)				
12.8	781	Weak								
↓	↓									
13.6	735									
			16.12	620	16.12	620	?			
					20.58	486(6)	20.92	478(4)		
					73.53	136(4)				
					102.0	98(5)				
					122.0	82(3)				
					185.2	54(3)				

a—Author, b—Schæfer-Schubert (1921), c—Shantakumari (1950), d—Venkateswaran (1938).

It will be noticed from the figures that a well-defined infra-red absorption band is observed with its maximum located at 5.3  $\mu$ , while on the other hand there is a very broad band covering the region between 9.2  $\mu$  to 12  $\mu$ . Other and less prominent features are also noticeable, viz., a subsidiary absorption band with its maximum at about 6.7  $\mu$  and another at about 13.5  $\mu$ .

## 2. DISCUSSION OF THE RESULTS

The experimental data for the Raman effect in potassium chlorate crystal and in solution exhibit the characteristic frequencies of the ClO<sub>3</sub> group in nearly the same positions; the relative intensities of the lines, however, show differences. We shall come to this point a little later. It is well established that the chlorate ion in the free state has a pyramidal structure with chlorine at the apex, with the symmetry of the point group C<sub>3v</sub>.

Accordingly, the free ion possesses two totally symmetric ( $A_1$ ) vibrational modes and two doubly degenerate ones (E). All the modes are permitted both in infra-red and Raman effect. The totally symmetric vibrations should give polarised Raman lines ( $\rho < \frac{6}{7}$ ) while the doubly degenerate lines are depolarised ( $\rho = \frac{6}{7}$ ). By polarisation studies of the Raman lines of the chlorate ion Shen, Yao and Wu (1937) have classified them as follows:

TABLE II

*Classification of the Raman Lines of the  $\text{ClO}_3^-$  Ion*

	cm. <sup>-1</sup>	$\mu$	$\rho$	Class
$\nu_1$	930	10.75	0.35	$A_1$
$\nu_2$	975	10.26	6/7	E
$\nu_3$	620	16.12	0.56	$A_1$
$\nu_4$	486	20.58	6/7	E

The selection rules allow the combinations and the overtones of all the fundamental oscillations in Raman effect and infra-red.

In addition to the high frequency internal oscillations of the  $\text{ClO}_3^-$  ion as modified by the interactions of the surrounding  $\text{K}^+$  ions, low frequency lattice oscillations will occur in the crystal of potassium chlorate. The crystal belongs to the monoclinic prismatic class, and contains two molecules per unit cell, its space group being  $C_{2h}^2$ . The group-theoretical analysis shows that there should be nine Raman-active lattice oscillations and six infra-red-active oscillations, the two sets being mutually exclusive. Shantakumari has recorded five lattice oscillations in Raman effect.

The lattice oscillations are of low frequencies and lie outside the range of the spectrophotometer used in this work. The frequencies  $\nu_3$  and  $\nu_4$  also lie out of the range investigated. But the combinations and overtones of these internal frequencies will occur within the experimental range. Similarly, one may expect to find difference as well as combination lines between the lattice and internal vibrations. In the light of these remarks, one may interpret the experimentally observed absorption bands as shown in Table III.

Besides the principal absorption frequencies  $\nu_1$  and  $\nu_2$ , the various combinations  $\nu_1 \pm L$ ,  $\nu_2 \pm L$ , where L represents a lattice vibration frequency are also possible, and the presence of such combinational absorptions may

TABLE III

Observed absorption maxima		Assignment	Calculated	
$\lambda\mu$	$\text{cm.}^{-1}$		$\lambda\mu$	$\text{cm.}^{-1}$
5.3	1887	$2\nu_1$	5.38	1860
		$\nu_1 + \nu_2$	5.25	1905
		$2\nu_2$	5.13	1950
6.7	1493	$\nu_1 + \nu_3$	6.45	1550
		$\nu_2 + \nu_4$	6.84	1461
9.2	1087	$\nu_2$	10.26	975
↓	↓	$2\nu_4$	10.29	972
12	833	$\nu_1$	10.75	930

partly or wholly be responsible for the notable width of the band covering the range between  $9\mu$  and  $12\mu$ .

As remarked earlier, the internal frequencies of  $\text{KClO}_3$  show remarkable changes of intensity in the Raman effect as we pass from liquid to crystalline state. For example, the frequencies:  $\nu_2$ , 977 (1), and  $\nu_1$ , 930 (10) in solution become  $\nu_2$ , 975 (7) and  $\nu_1$ , 930 (10) in the single crystal. In the infra-red restrahlen of the pressed powder as observed by Schæfer and Schubert,  $975\text{ cm.}^{-1}$  comes out much stronger than  $930\text{ cm.}^{-1}$ . In the present work, both the frequencies  $\nu_1$  and  $\nu_2$  seem to have come out with more or less equal intensities, as fundamentals and also as octaves.

The behaviour of sodium chlorate affords some interesting comparisons with potassium chlorate. In Raman effect in  $\text{NaClO}_3$  solution studied by Venkateswaran (1938),  $\nu_1$ , 927 (10) appears much stronger than  $\nu_2$ , 971 (2). Even in the Raman effect in a single crystal of  $\text{NaClO}_3$  as studied by Chandrasekharan (1950) in different settings, the lines 933-36 are very much stronger than the 966-84 lines. On the other hand, in the restrahlen studies with  $\text{NaClO}_3$  crystal made by Schæfer and Schubert, 966-84 lines appear more strong than 933-36 lines, the latter being noticeable as a weak wing.

Potassium chlorate has a highly anisotropic structure and the specific orientations of the crystal may therefore be expected to influence its behaviour. It appears therefore not unlikely that the manifestation of  $\nu_1$  and  $\nu_2$  with nearly equal intensity, both in this investigation as well as in the Raman effect study with a single crystal of  $\text{KClO}_3$  by Shantakumari, is a consequence of the particular orientation of the crystal with which these studies

were made. Further studies are, however, needed to establish whether this is the actual explanation of the striking differences in the relative intensity of  $\nu_1$  and  $\nu_2$  as between the chlorates of sodium and potassium observed in respect of both infra-red and Raman activities.

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### 3. SUMMARY

The infra-red transmission through the 001 face of a single crystal of potassium chlorate reveals, besides a broad absorption band in the range  $9.2\mu$  to  $12\mu$ , a second and narrower band with its maximum at  $5.3\mu$ . The former band can be explained as due to the infra-red activity of the vibration frequencies  $\nu_1$  ( $930\text{ cm.}^{-1}$ ) and  $\nu_2$  ( $975\text{ cm.}^{-1}$ ) of the crystal also observed in the Raman effect, and their combinations with the low frequency lattice oscillations. The band at  $5.3\mu$  may likewise be explained as due to the infra-red activity of the octaves of  $\nu_1$  and  $\nu_2$  and of their summational frequency.

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