THE INFRA-RED ABSORPTION SPECTRUM OF POTASSIUM CHLORATE CRYSTALS—Part II

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1. Introduction

In Part I, the author published the results of a study on the infra-red absorption by a single crystal of potassium chlorate in the range $1\,\mu$ to $15\,\mu$, by means of a Beckmann infra-red spectrophotometer (model I R2). In the present investigation the work has been extended upto $22\,\mu$ using thinner crystals than formerly. The instrument itself had meanwhile been overhauled and its sensitiveness improved. The results now reported are therefore superior to those presented in Part I.

The crystals were studied, as before, with the flat face (001) perpendicular to the infra-red radiation, percentage transmission being read off directly with the instrument. Readings were taken at $0\cdot1\,\mu$ intervals and at still closer intervals near absorption maxima. The percentage cut-off curves of two of them which show the absorption maxima most clearly have been reproduced in Fig. 1. Curve III represents the % cut-off of the specimen of thickness $0\cdot15$ mm. and Curve I of specimen of thickness $0\cdot06$ mm.

The following features are shown by the curves:

I. A sharply defined, strong absorption band with its maximum at $5\cdot3\,\mu$ (1887 cm.$^{-1}$).

II. Two well-defined absorption maxima at $6\cdot3\,\mu$ (1587 cm.$^{-1}$) and $6\cdot9\,\mu$ (1449 cm.$^{-1}$) which are weak in comparison with the $5\cdot3\,\mu$ band. In Part I of the paper, this doublet was not resolved and a rather broad band with its maximum at $6\cdot7\,\mu$ was recorded. Coblentz (1906), to whom no reference was made in the previous paper through oversight, had noticed these bands as also the one at $5\cdot3\,\mu$.

III. A very strong absorption band with a flat top, extending from $10\,\mu$ to $10\cdot8\,\mu$ (1000 cm.$^{-1}$ to 926 cm.$^{-1}$).

IV. A medium strong absorption band at $13\cdot5\,\mu$ (741 cm.$^{-1}$).

V. A strong and sharply defined absorption maximum at $16 \cdot 2 \mu$ (617 cm.$^{-1}$).

VI. In the slope of the absorption maximum at $16 \cdot 2 \mu$, we notice inflexions at $17 \cdot 25 \mu$ (580 cm.$^{-1}$), 18μ (556 cm.$^{-1}$), and $18 \cdot 75 \mu$ (533 cm.$^{-1}$).

VII. A strong and sharply defined absorption maximum at $20 \cdot 3 \mu$ (493 cm.$^{-1}$). This band shows indications of structure.

Schæfer and Schubert (1921) in their reststrahlen studies with pressed powder of $KClO_3$ found reflexion maxima at $10 \cdot 12 \mu$ and $16 \cdot 12 \mu$ which evidently are related to the absorptions referred to in III and V above.
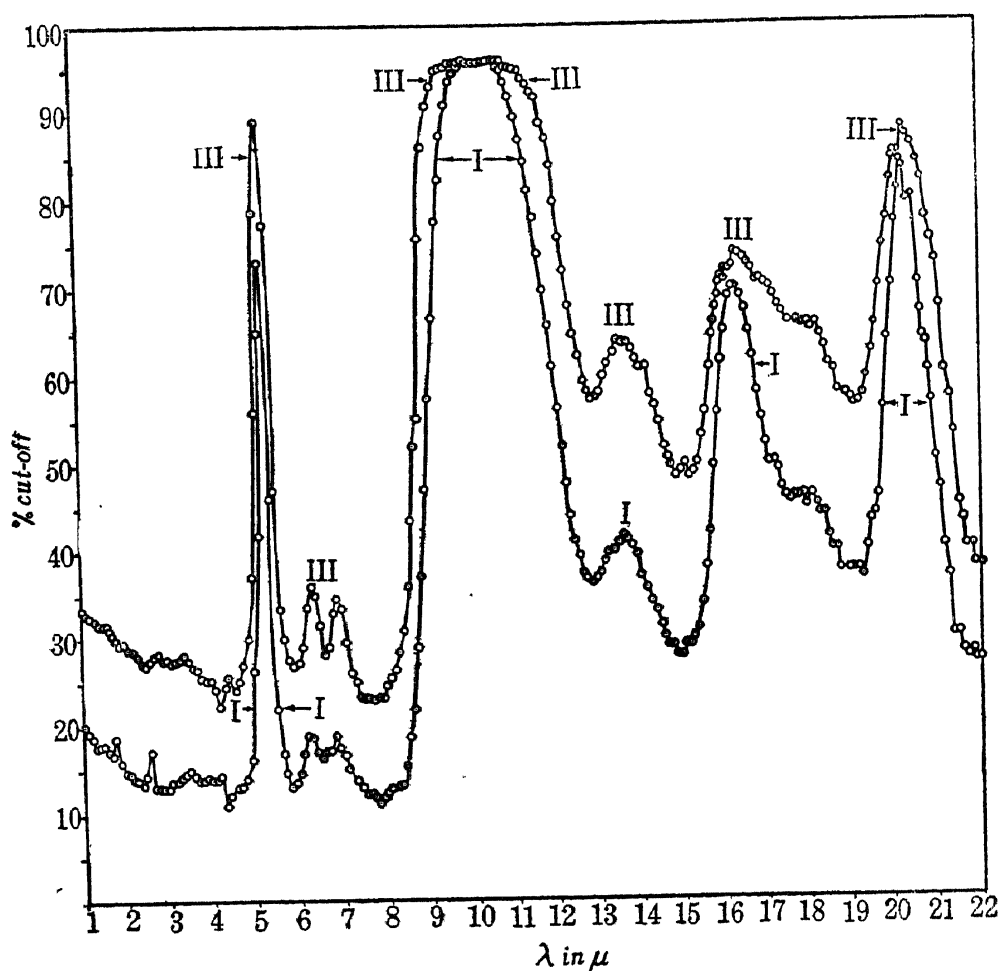

FIG. 1. Infra-red absorption spectra of single crystals of potassium chlorate.

2. INFRA-RED ACTIVE FUNDAMENTALS

In Part I, the absorption maxima in the infra-red were explained in a general way in terms of the characteristic frequencies of the chlorate ion in the free state, viz., ν_1 (930 cm.$^{-1}$) and ν_3 (620 cm.$^{-1}$) belonging to the totally

symmetric class A_1; ν_2 (975 cm.$^{-1}$) and ν_4 (486 cm.$^{-1}$) belonging to the doubly degenerate class E. But in the transformation from a free ion to a crystal, the number of internal vibrations increases because there are two molecules in each unit cell and the symmetry of the crystal structure ($C_{2h}{}^2$) removes the degeneracy of modes of the E class. The group analysis gives the number of internal vibrations and the selection rules as shown, in Table I.

TABLE I

Class	Number	Raman effect	Infra-red
A_1	4	Active	Inactive
A_2	2	Active	Inactive
B_1	2	Inactive	Active
B_2	4	Inactive	Active

i.e., there are six Raman active internal vibrations and six infra-red active, the two sets being mutually exclusive because of the presence of a centre of symmetry. We can picture the change in internal frequencies from a free ion to crystal as follows:

TABLE II

Free ion	Crystal	
Raman active and Infra-red active	Raman active	Infra-red active
ν_1 (A_1)	ν_1 (A_1)	ω_1 (B_2)
ν_3 (A_1)	ν_3 (A_1)	ω_3 (B_2)
ν_2 (E)	ν_2 (A_1), $\nu_2{}'$ (A_2)	ω_2 (B_2), $\omega_2{}'$ (B_1)
ν_4 (E)	ν_4 (A_1), $\nu_4{}'$ (A_2)	ω_4 (B_2), $\omega_4{}'$ (B_1)

Thus the infra-red and Raman frequencies would, strictly spreaking, be different.

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The Raman effect in the powdered crystals has been studied by Krishna-murthi (1930) and Venkateswaran (1938), and by Shantakumari (1950) in a single crystal. Their results have been given in Table III.

TABLE III

Krishnamurthi (Powder)	Venkateswaran (Powder)	Shantakumari (Single crystal)	ClO_3^- ion
	915 (1)	920 (1)	
934·8	929 (10)	930 (10)	930
971*	977 (4)	975 (7)	975
..	615 (1)	620 (1)	615
482	478 (3)	486 (6)	480
	493 (0)		

* With two faint companions.

We notice that the Raman frequencies which have been reported fall into four main groups which approximate respectively to the four fundamental frequencies of the ClO_3^- ion. The results of the different authors are somewhat divergent, which may in part be ascribable to their having recorded the spectra in different circumstances. For our present purpose, we may ignore the splitting of the fundamental frequencies in the crystal shown in Table II and base our interpretation of the infra-red absorption data on four fundamental frequencies denoted as ω_1, ω_2, ω_3, ω_4 respectively, for which we assume the values 930, 975, 620 and 486 cm.$^{-1}$, these being the same as those observed in the Raman effect by Shantakumari.

3. INTERPRETATION OF RESULTS

On the assumptions made above, the following interpretations of the observed bands are put forward as the most probable (Table IV).

The bands IV and VI have been interpreted as combinations of the internal and lattice frequencies of the crystal. There are actually nine Raman active and six infra-red active lattice frequencies, the two sets being mutually exclusive. The selection rules permit combinations between infra-red active internal frequencies and Raman active lattice frequencies and vice versa. The infra-red active lattice oscillations are unknown. Shantakumari has recorded five lattice lines in Raman effect which we may denote

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TABLE IV

Serial No.	Observed Absorption Maxima		Assignment	Calculated	
	$\lambda\mu$	cm.$^{-1}$		$\lambda\mu$	cm.$^{-1}$
I	5·3	1887	$\omega_1+\omega_2$	5·25	1905
II	6·3	1587	$\omega_2+\omega_3$	6·27	1595
	6·9	1449	$\omega_2+\omega_4$	6·84	1461
III	10–10·8	1000–926	ω_2	10·26	975
			ω_1	10·75	930
IV	13·5	741	ω_3+L_4	13·4	747
V	16·2	617	ω_3	16·13	620
VI	18·0	556	ω_3-L_1	17·7	566
	18·75	533	ω_4+L_1	18·5	540
VII	20·3	493	ω_4	20·58	486

as L_1 (54 cm.$^{-1}$), L_2 (82 cm.$^{-1}$), L_3 (98 cm.$^{-1}$), L_4 (127 cm.$^{-1}$) and L_5 (145 cm.$^{-1}$). Since the data regarding the lattice oscillations are incomplete, the assignments shown against IV and VI are necessarily somewhat conjectural.

Some interesting features are noticed as regards the relative intensities of the internal vibrations in Raman effect and infra-red. In Raman effect, all the workers have got 620 cm.$^{-1}$ line very weak. In fact, Krishnamurthi in his study of Raman effect in $KClO_3$ crystal powder and Venkateswaran in Raman effect in solution of $KClO_3$ failed to observe this line. On the other hand, corresponding to that line we notice a strong and sharp absorption in infra-red. The 486 cm.$^{-1}$ line which is strong in Raman effect is also strong in infra-red absorption. As regards 930 cm.$^{-1}$ and 975 cm.$^{-1}$, the indications are that the latter is more strongly active than the former in absorption, while in Raman effect, 930 cm.$^{-1}$ is stronger than 975 cm.$^{-1}$, though it has a comparable intensity.

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4. SUMMARY

Crystals of potassium chlorate exhibit strong absorption bands in the infra-red at $10\,\mu$–$10\cdot8\,\mu$, and at $16\cdot2\,\mu$ and $20\cdot3\,\mu$. These are identified with the active fundamentals at ω_1 (930 cm.$^{-1}$, $10\cdot75\,\mu$), ω_2 (975 cm.$^{-1}$, $10\cdot26\,\mu$), ω_3 (620 cm.$^{-1}$, $16\cdot13\,\mu$) and ω_4 (486 cm.$^{-1}$, $20\cdot58\,\mu$). It is noticed that ω_3 is quite strong, while the corresponding Raman frequency comes out very weakly. The vibration ω_1 is more strongly Raman-active than ω_2, while the reverse appears to be the case in the infra-red. Absorptions are also observed at $5\cdot3\,\mu$, $6\cdot3\,\mu$ and $6\cdot9\,\mu$ which are interpreted as first-order combinations among these four fundamental frequencies, while other bands at $13\cdot5\,\mu$, $18\,\mu$ and $18\cdot75\,\mu$ appear to be combinations of internal frequencies with low frequency lattice vibrations.

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