THE INFRA-RED ABSORPTION SPECTRA OF SODIUM CHLORATE AND POTASSIUM CHLORATE CRYSTALS

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1. INTRODUCTION

THE infra-red reflexion spectrum of sodium chlorate was examined by Schæfer and Schubert[1] in short wavelengths ($\lambda\mu < 20$) and observed maxima at $10\cdot04\,\mu$ and $16\cdot04\,\mu$, while Laski[2] who investigated the spectrum in the range $20\,\mu$ to $120\,\mu$ by the reststrahlen method noticed maxima at $25\cdot0\,\mu$, $60\cdot0\,\mu$ and $83\cdot0\,\mu$. The present author has studied the infra-red transmission spectrum of sodium chlorate crystals in the range $1\,\mu$ to $22\,\mu$ using a Beckman infra-red spectrometer (Model IR 2). The author has also studied the transmission spectrum of a thick specimen of potassium chlorate crystal, and observed a few more absorption bands than reported in the previous papers.[3] It is proposed to present these experimental observations in this paper and discuss them in the light of the Raman effect data for these two crystals.

Two crystals of sodium chlorate were studied (sp. I $= 2\cdot1$ mm., and sp. II $= 1$ mm. thick). The potassium chlorate crystal was studied as previously in the 001 plane (sp V $= 1$ mm. thick). The Fig. 1 gives the percentage cut-off *vs.* wavelength for sodium chlorate (sp. II) and Fig. 2 for potassium chlorate.

The following absorption maxima are noticed in Fig. 1 (sodium chlorate:

(1) Weak absorption maxima at $2\cdot6\,\mu$, $3\cdot5\,\mu$, $4\cdot0\,\mu$, $4\cdot1\,\mu$ and $4\cdot3\,\mu$. Of these the $3\cdot5\,\mu$ absorption maximum is the strongest.

(2) A very intense absorption band extending from $5\cdot1\,\mu$ to $5\cdot4\,\mu$.

(3) Two well-defined absorption bands at $6\cdot3\,\mu$ and $6\cdot95\,\mu$, of medium intensity.

(4) Very strong and very broad maxima between $9\,\mu$ to $13\cdot4\,\mu$; from $15\,\mu$ to $17\cdot8\,\mu$; and from $19\cdot9\,\mu$ to $20\cdot7\,\mu$.

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In Fig. 2, (potassium chlorate) in addition to the absorption maxima reported in the previous papers, *viz.*, $5 \cdot 3 \mu$ (sharply defined and strong); $6 \cdot 3 \mu$ and $6 \cdot 9 \mu$ (well-defined and medium); 10μ to $10 \cdot 8 \mu$ (very strong with a flat top); $13 \cdot 5 \mu$ (medium); $16 \cdot 2 \mu$ (strong and sharply defined); $17 \cdot 25 \mu$, 18μ, and $18 \cdot 75 \mu$ (inflexions in the slope of the $16 \cdot 2 \mu$ band); and $20 \cdot 3 \mu$ (strong, sharply defined, with indications of structure)—we notice the following additional bands: (1) $2 \cdot 85 \mu$ (very weak); (2) $3 \cdot 5 \mu$ (well defined); (3) $4 \cdot 1 \mu$ (very weak); (4) $4 \cdot 3 \mu$ (very weak); (5) the $20 \cdot 3 \mu$ band definitely shows a structure and maxima at $20 \cdot 1 \mu$ and $20 \cdot 4 \mu$ can be easily recognised.

2. DISCUSSION OF THE RESULTS

(i) *Sodium chlorate.*—Sodium chlorate belongs to the space group T^4, and contains four molecules per unit cell. The vibrations of this crystal class are classified as: A (totally symmetric); E (symmetric with respect to the three two-fold axes and doubly degenerate with respect to the four
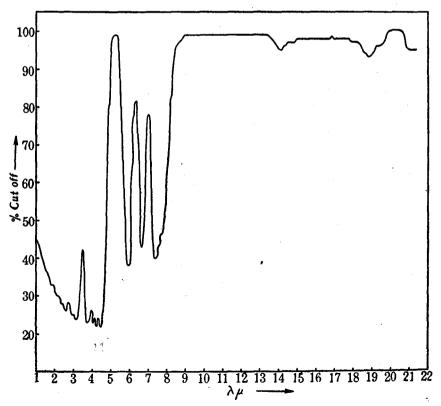

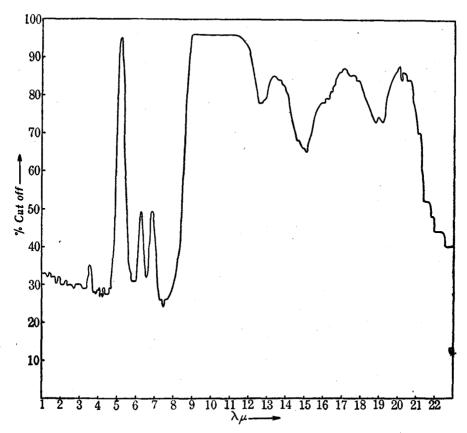FIG. 1.   Infra-red absorption spectrum of sodium chlorate (Specimen II)

FIG. 2. Infra-red absorption spectrum of potassium chlorate (Specimen V)

three-fold axes); and F (triply degenerate with respect to the three two-fold axes). Further, selection rules permit all these vibrations to appear as fundamentals in the Raman effect but *only* those belonging to the F-class to appear in the infra-red.

The Raman spectrum of single crystal of sodium chlorate has been very thoroughly studied (Couture, L. and Mathieu, J. P.[4]; Chandrasekharan[5]) and with the exception of two, all the Raman lines observed have been classified according to their polarisation characteristics. In Table I we give all the Raman lines observed, with their symmetry types.

Corresponding to each of the F-type oscillation in the high frequency region (*i.e.*, the internal frequencies) there are broad absorption bands, *viz.*, from $9 \cdot 0 \mu$ to $13 \cdot 4 \mu$ corresponding to $10 \cdot 72 \mu$ (933 cm.$^{-1}$), $10 \cdot 33 \mu$ (968 cm.$^{-1}$), $10 \cdot 16$ (984 cm.$^{-1}$); from 15μ to $17 \cdot 8 \mu$ corresponding to $16 \cdot 0 \mu$ (625 cm.$^{-1}$); and from $19 \cdot 9 \mu$ to $20 \cdot 7 \mu$ corresponding to $20 \cdot 53 \mu$ (487 cm.$^{-1}$). It is possible

TABLE I

Vibration	cm.$^{-1}$	Type	Vibration	cm.$^{-1}$	Type
ν_1'	933	F	L_1	66·5	E
ν_1''	936	A	L_2	92·5	F?
ν_2'	963	E	L_3	122·5	F
ν_2''	968	F	L_4	130·0	E
ν_2'''	984	F	L_5	179·0	E
ν_3'	617	A			
ν_3''	625	F			
ν_4'	480	E			
ν_4''	487	F			
ν_2''''	1026	?			

to give a reasonable interpretation of the higher harmonics in terms of the observed Raman lines following the selection rules which permit: F^2; $F \times F$; $E \times F$; $A \times F$; F^3; $A^2 \times F$; $A \times F \times F$; $A \times F^2$; $A \times E \times F$; $F \times F \times F$; $F \times F^2$; etc.

As regards the low frequency oscillations, they naturally lie beyond the range investigated. Laski, however, has observed reflexion maxima at $60\,\mu$ (167 cm.$^{-1}$) and $83\,\mu$ ($120·5$ cm.$^{-1}$). The latter can be attributed to the F-type lattice oscillation L_3 ($122·5$ cm.$^{-1}$). There is no F-type Raman line corresponding to 167 cm.$^{-1}$ Combination and difference bands of the type $\nu \pm L$, *i.e.*, between internal and lattice oscillations can however occur in the range under investigation when allowed by the selection rules. This no doubt contributes to the notable breadth of the fundamental absorption bands. An examination of the infra-red absorption bands using crystals much thinner than those used in the present investigation is necessary.

In Table II we give the assignments of the observed absorption maxima.

(ii) *Potassium chlorate.*—Potassium chlorate belongs to the space group C_{2h}^2, and contains two molecules per unit cell. Due to the coupling between these two molecules and due to the removal of degeneracy of vibrations of chlorate ion in the free state, the internal vibrations of the chlorate ion in the crystal increase in number as shown in a previous paper (see Table III), *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. This difference and splitting was ignored in the previous papers

TABLE II

Observed λμ	Observed cm.$^{-1}$	Assignment	Calculated cm.$^{-1}$
2·6	3846	$3\nu_2''+\nu_1''$	3840
3·5	2857	$\nu_1'+\nu_2'+\nu_2''$	2864,
		$\nu_1+\nu_1''+\nu_2'''$	2853
4·0	2500	$2\nu_1'+\nu_3''$	2491
4·1	2439	$\nu_2''+\nu_2'''+\nu_4''$	2439
4·3	2326		——
5·1	1961	$2\nu_2'''$	1968
↓	↓	$\nu_2''+\nu_2'''$	1952
		$\nu_2'+\nu_2'''$	1947
5·4	1852	$2\nu_2''$	1936
		$\nu_2'+\nu_2''$	•1931
		$\nu_1''+\nu_2'''$	1920
		$\nu_2'''+\nu_1'$	1917
		$\nu_1''+\nu_2''$	1904
		$\nu_1'+\nu_2''$	1901
		$\nu_2'+\nu_1'$	1896
		$\nu_1''+\nu_1'$	1869
		$2\nu_1'$	1866
6·3	1587	$\nu_2''+\nu_3'$	1585
6·95	1440	$\nu_2''+\nu_4'$	1448
9·0	1111	ν_2'''	984
↓	↓	ν_2''	968
13·4	746	ν_1'	933
15·0	667		
↓	↓	ν_3''	625
17·8	562		
19·9	502·5		
↓	↓	ν_4''	487
20·7	483		

TABLE III

Free ion	Crystal	
Raman 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$_1$), ν_2' (A$_2$)	ω_2 (B$_2$), ω_2' (B$_1$)
ν_4 (E)	ν_4 (A$_1$), ν_4' (A$_2$)	ω_4 (B$_2$), ω_4' (B$_1$)

in giving the assignments of the observed absorption bands. But actually it is possible to recognise the difference in the corresponding infra-red active

and Raman active fundamentals. In Table IV we give the Raman active
vibrations observed by Shantakumari[6] and infra-red active fundamentals
observed in the present work.

<div align="center">TABLE IV</div>

Raman effect	Infra-red
ν_1 $(A_1) = 930$ cm.$^{-1}$	ω_1 $(B_2) = 910$ cm.$^{-1}$
ν_3 $(A_1) = 620$,.	ω_3 $(B_2) = 617$,,
ν_2 (A_1), ν_2' $(A_2) = 975$,,	ω_2 (B_2), ω_2' $(B_1) = 960$,,
ν_4 (A_1), ν_4' $(A_2) = 486$,,	ω_4 (B_2), ω_4' $(B_1) = 493$,,

The frequencies ω_1 and ω_2 (ω_2') are chosen so as to represent the data best.
The crystal structure of potassium chlorate is almost uniaxial (pseudo-hexa-
gonal) and hence the splitting due to removal of degeneracy may not be
significant. However, in the present work the $20 \cdot 3\,\mu$ (493 cm.$^{-1}$) band does
show recognisable structure with maxima at $20 \cdot 1\,\mu$ (497·5 cm.$^{-1}$) and $20 \cdot 4\,\mu$
(490 cm.$^{-1}$) and similarly Venkateswaran[7] working with crystal powder did
notice Raman lines at 478 cm.$^{-1}$ and 493 cm.$^{-1}$. This point requires further
investigation.

The selection rules permit the following combinations to appear in infra-
red: $A_1 \times B_1$; $A_1 \times B_2$; $A_2 \times B_1$; $A_2 \times B_2$; $A_1{}^2 \times B_1$; $A_1{}^2 \times B_2$;
$A_2{}^2 \times B_1$; $A_2{}^2 \times B_2$; $B_1{}^3$; $B_2{}^3$; $A_1 \times B_1{}^3$; $A_1 \times B_2{}^3$; $A_2 \times B_1{}^3$; $A_2 \times B_2{}^3$;
$A_1{}^3 \times B_1$; $A_1{}^3 \times B_2$; $A_2{}^3 \times B_1$; $A_2{}^3 \times B_2$. etc. In Table V we give the
assignments of the observed absorption maxima on this basis.

From Table V it is seen that most of the bands are very satisfactorily
explained on the basis indicated above.

The bands 9, 11, 12 and 13 are interpreted as combinations between
internal and external vibrations. The combinations allowed to appear in
infra-red are $\omega \pm$ Raman active L, and $\nu \pm$ infra-red active L. The observed
Raman lines are 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.$^{-1}$). With this data only the absorption maximum at $13 \cdot 5\,\mu$
(741 cm.$^{-1}$) can be explained. Since the data regarding the lattice oscillations,
especially the infra-red active, are incomplete no interpretation can be given
at present to the remaining bands at $17 \cdot 25\,\mu$, $18 \cdot 0\,\mu$ and $18 \cdot 75\,\mu$.

TABLE V

Observed			Assignment	Calculated
No.	$\lambda\mu$	cm.$^{-1}$		cm.$^{-1}$
1	2·85	3509	$3\omega_2 + \nu_3$	3500
2	3·5	2857	$\omega_1 + 2\nu_2$	2860
3	4·1	2439	$\omega_4 + 2\nu_2$	2443
4	4·3	2326	$\omega_1 + \nu_1 + \nu_4$	2326
5	5·3	1887	$\omega_2 + \nu_1$	1890
6	6·3	1587	$\omega_2 + \nu_3$	1580
7	6·9	1449	$\omega_2 + \nu_4$	1446
8	10–10·8	1000–926	$\omega_4 + \nu_4,$	979,
			$\omega_2,$	960,
			ω_1	910
9	13·5	741	$\omega_3 + L_4$	744
10	16·2	617	ω_3	617
11	17·25	581·5	$\nu_4 + L$	—
12	18·0	556·0	$\nu_4 + L$	—
13	18·75	533·0	$\nu_4 + L$	—
14	20·3	493	ω_4	49

3. SUMMARY

The infra-red absorption spectrum in the range $1\,\mu$ to $22\,\mu$ of sodium chlorate crystals shows besides intense regions of absorption maxima between $9\,\mu$ and $13\cdot4\,\mu$, $15\,\mu$ and $18\cdot7\,\mu$, $19\cdot9\,\mu$ and $20\cdot7\,\mu$, numerous absorption bands, *viz.*, at $3\cdot5$, $4\cdot0$, $4\cdot1$, and $4\cdot3\,\mu$; from $5\cdot1$ to $5\cdot4\,\mu$; and at $6\cdot3$ and $6\cdot95\,\mu$. All these are satisfactorily interpreted in terms of the Raman lines, following selection rules appropriate to the space group T^4 to which sodium chlorate belongs. By using a fairly thick crystal of potassium chlorate, some additional bands not previously noticed are observed, *viz.*, at $2\cdot85$, $3\cdot5$, $4\cdot1$ and $4\cdot3\,\mu$. By recognising the difference between the infra-red active fundamentals and Raman active fundamentals in the crystal of potassium chlorate, it is possible to give a satisfactory explanation of all the absorption maxima.

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