

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

BY A. K. RAMDAS

(From the Raman Research Institute, Bangalore)

Received March 12, 1952

(Communicated by Sir C. V. Raman, F.R.S., N.L.)

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 10.12μ (988 cm.^{-1}) and 16.12μ (620 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 1μ to 15μ 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 0.25μ , and at still closer intervals near the absorption maxima. The other two plates were examined less closely, readings being taken at intervals of 0.5μ . 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 Schæfar and Schubert, the results of Shantakumari on the Raman effect

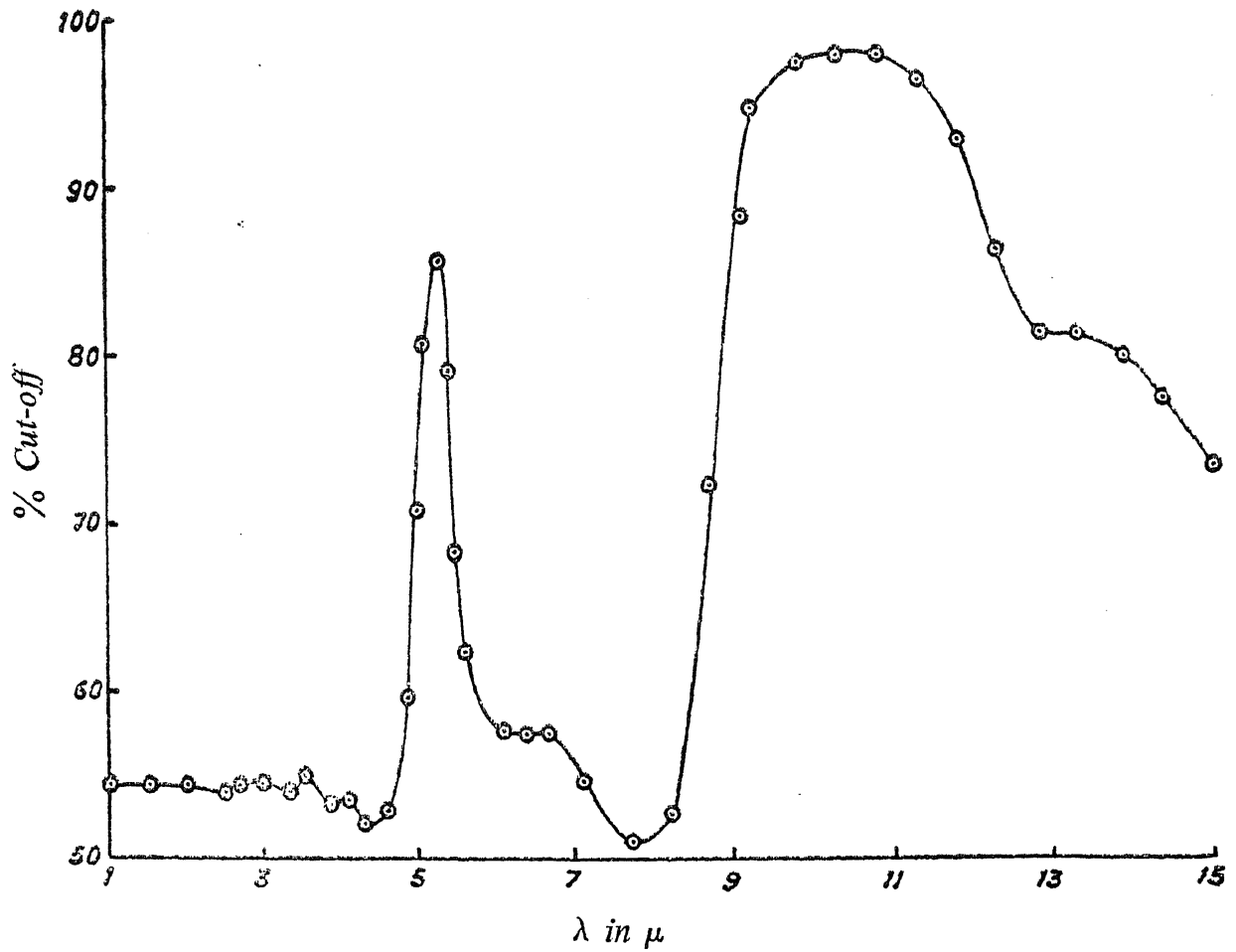


FIG. 1. Infra-red absorption spectrum of single crystal of potassium chlorate (thickness about 1 mm.)

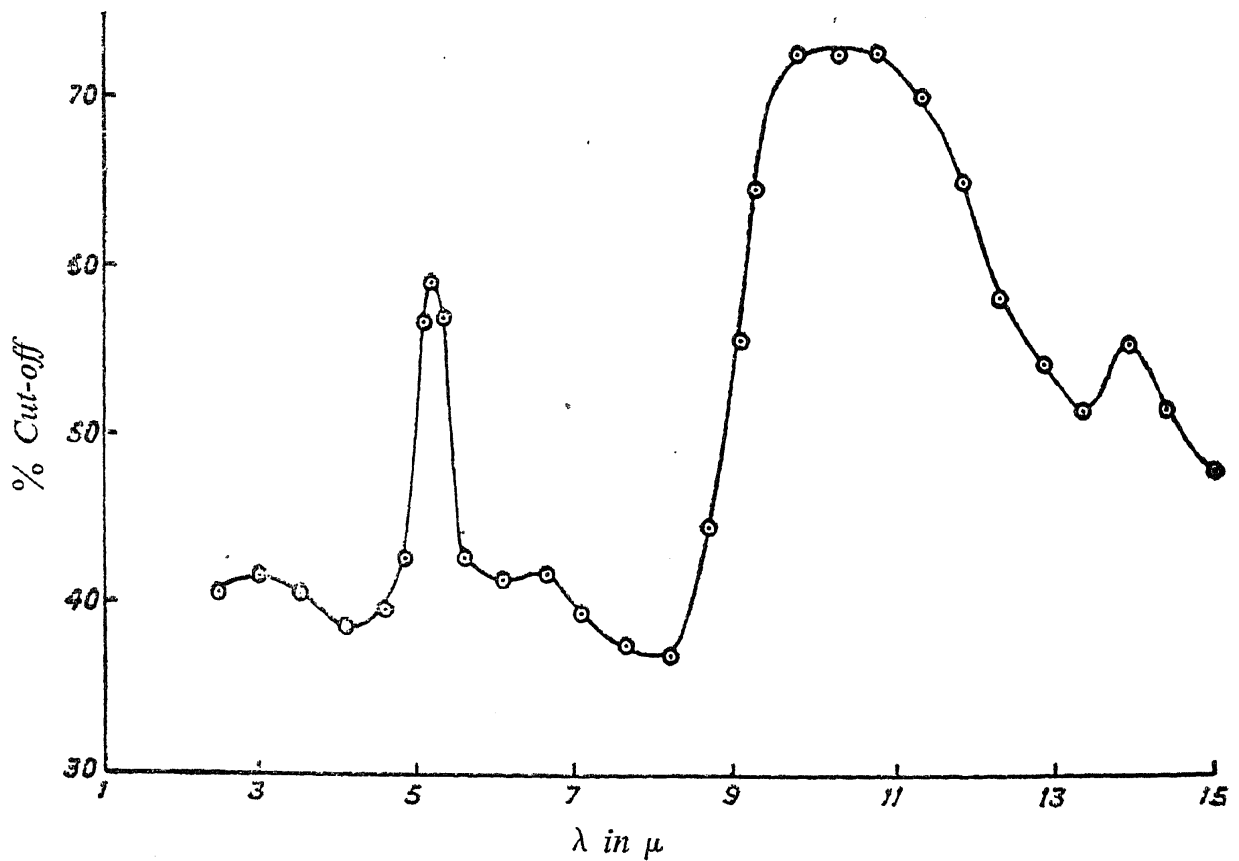


FIG. 2. Infra-red absorption spectrum of single crystal of potassium chlorate (thickness < 1 mm.)

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 KClO₃

| Infra-red Absorption Bands (a) | | | Infra-red Reststrahlen (b) | | Raman effect single crystal (c) | | Raman effect in solution (d) | | | |
|--------------------------------|-------------------|------------------|----------------------------|-------------------|---------------------------------|-------------------|------------------------------|-------------------|-------|---------|
| μ | cm. ⁻¹ | Description | μ | cm. ⁻¹ | μ | cm. ⁻¹ | μ | cm. ⁻¹ | | |
| 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—Schäfer-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 μ , while on the other hand there is a very broad band covering the region between 9.2 μ to 12 μ . Other and less prominent features are also noticeable, viz., a subsidiary absorption band with its maximum at about 6.7 μ and another at about 13.5 μ .

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 ClO₃⁻ 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_{3v}.

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 ClO_3^- Ion

| | cm. ⁻¹ | μ | ρ | Class |
|---------|-------------------|-------|--------|-------|
| ν_1 | 930 | 10.75 | 0.35 | A_1 |
| ν_2 | 975 | 10.26 | 6/7 | E |
| ν_3 | 620 | 16.12 | 0.56 | A_1 |
| ν_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 ClO_3^- ion as modified by the interactions of the surrounding 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 ν_3 and ν_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 ν_1 and ν_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 | |
|----------------------------|-------------------|-----------------|--------------|-------------------|
| $\lambda\mu$ | cm.^{-1} | | $\lambda\mu$ | 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 | ν_2 | 10.26 | 975 |
| ↓ | ↓ | $2\nu_4$ | 10.29 | 972 |
| 12 | 833 | ν_1 | 10.75 | 930 |

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

As remarked earlier, the internal frequencies of KClO_3 show remarkable changes of intensity in the Raman effect as we pass from liquid to crystalline state. For example, the frequencies ν_2 , 977 (1), and ν_1 , 930 (10) in solution become ν_2 , 975 (7) and ν_1 , 930 (10) in the single crystal. In the infra-red restrahlen of the pressed powder as observed by Schæfer and Schubert, 975 cm.^{-1} comes out much stronger than 930 cm.^{-1} . In the present work, both the frequencies ν_1 and ν_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 NaClO_3 solution studied by Venkateswaran (1938), ν_1 , 927 (10) appears much stronger than ν_2 , 971 (2). Even in the Raman effect in a single crystal of 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 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 ν_1 and ν_2 with nearly equal intensity, both in this investigation as well as in the Raman effect study with a single crystal of 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 ν_1 and ν_2 as between the chlorates of sodium and potassium observed in respect of both infra-red and Raman activities.

The author's sincerest thanks are due to Professor Sir C. V. Raman, F.R.S., N.L., for his kind encouragement and guidance. The author also wishes to express his indebtedness to Mr. A. U. Momin of the C.S.I.R. Radiation Scheme at the Meteorological Office, Poona, for his kind help in recording the infra-red spectra.

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 9.2μ to 12μ , a second and narrower band with its maximum at 5.3μ . The former band can be explained as due to the infra-red activity of the vibration frequencies ν_1 (930 cm.^{-1}) and ν_2 (975 cm.^{-1}) of the crystal also observed in the Raman effect, and their combinations with the low frequency lattice oscillations. The band at 5.3μ may likewise be explained as due to the infra-red activity of the octaves of ν_1 and ν_2 and of their summational frequency.

REFERENCES

1. Chandrasekharan, V. .. *Proc. Ind. Acad. Sci.* 1950, 32 A, 374.
2. Schæfer and Schubert .. *Z. fur Physik.*, 1921, 7, 309.
3. Shantakumari, C. .. *Proc. Ind. Acad. Sci.*, 1950, 32 A, 177.
4. Sheu, Yao and Wu .. *Phy. Rev.*, 1937, 51, 235.
5. Venkateswaran, C. S. .. *Proc. Ind. Acad. Sci.*, 1938, 7 A, 144.