

# THE INFLUENCE OF OPTICAL ACTIVITY ON LIGHT SCATTERING IN CRYSTALS

## Part II. Sodium Chlorate

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### 1. INTRODUCTION

IN a paper which appeared in these *Proceedings* (and which will be referred to as Part I), the author (Chandrasekharan, 1948) indicated for the first time that the optical activity of quartz could be successfully made use of for verifying the selection rules of Raman lines for polarised light traversing the crystal along the optic axis. The incident light vector, as it traverses the crystal, becomes alternately parallel and perpendicular to the plane of scattering. In the spectrogram of the light scattered in the transverse direction, both the Brillouin components and the Raman lines exhibit a banded structure. From the nature of the bands, it is possible to distinguish between Raman lines coming under symmetric class and those coming under degenerate class. These investigations have now been extended to the case of sodium chlorate crystal and the results are presented here.

In the case of optically active cubic crystals like sodium chlorate, the rotatory power is the same in all directions and is not masked by birefringence. Therefore, unlike in the case of quartz, the selection rules for the Raman lines of sodium chlorate which have already been worked out by Couture and Mathieu (1948) could be verified for more than one orientation of the crystal with reference to the directions of incidence and of observation. However, the smaller rotatory power of sodium chlorate which is nearly a tenth of that of quartz for  $\lambda$  2537 would necessitate the use of a larger crystal. Besides, the Raman spectrum of sodium chlorate exhibits a few closely spaced doublets. In view of this, a spectrograph having a higher dispersion than the one used for studying quartz had to be employed.

### 2. THEORETICAL CONSIDERATIONS

Before describing the experimental results, it is considered desirable to describe briefly the selection rules for Raman lines in cubic crystals. According to the theory of the Raman effect, there are three classes of oscillations

possible which are usually designated by A—(totally symmetric), E—(symmetric with respect to the three 2-fold axes and doubly degenerate with respect to the four 3-fold axes of symmetry) and F—(triply degenerate with respect to the three 2-fold axes). Let us consider the case of transverse scattering. The intensity and the state of polarisation of the Raman lines belonging to Class A should remain unaffected for different orientations of the crystal since the tensor associated with each oscillation has spherical symmetry. In the case of degenerate oscillations coming under Classes E and F, on the other hand, the intensity and the state of polarisation should vary with orientation. For seven important settings of the crystal, the relative intensities as obtained theoretically are given in Table I. The method of evaluation is given in the paper by Couture and Mathieu (1948).

TABLE I

Setting	Incident light along	Scattered light along	Symmetry Class	Intensity of scattering in the transverse direction when the incident electric vector is		$\rho'$	Total intensity	Nature of banding
				$\perp$ to plane of scattering	$\parallel$ to plane of scattering			
All			A	$a$	0	0	$a$	normal perfect
1	[100]	[010]	E	$4e$	0	0	$4e$	normal perfect
	"	"	F	$f$	$2f$	2	$3f$	reverse imperfect
2a	[100]	[011]	E	$e$	$3e$	3	$4e$	reverse imperfect
	"	"	F	$2f$	$f$	$1/2$	$3f$	normal imperfect
2b	[011]	[100]	E	$4e$	0	0	$4e$	normal perfect
	"	"	F	$f$	$2f$	2	$3f$	reverse imperfect
2c	[011]	[01 $\bar{1}$ ]	E	$4e$	$3e$	$3/4$	$7e$	normal imperfect
	"	"	F	$f$	$f$	1	$2f$	—
3a	[111]	..	E	$3e$	$3e$	1	$6e$	—
	"	..	F	$3/4f$	$f$	$4/3$	$7/3f$	normal imperfect
3b	..	[111]	E	$2e$	$4e$	2	$6e$	reverse imperfect
	..	"	F	$5/3f$	$2/3f$	$2/5$	$7/3f$	normal imperfect
3c	Plane of scattering } (111)		E	$2e$	$3e$	$3/2$	$5e$	reverse imperfect
			F	$5/3f$	$f$	$3/5$	$8/3f$	normal imperfect

The intensities of the Raman lines belonging to each class for incident unpolarised light are given in column 8. The intensities of the Raman lines for incident light polarised with electric vector perpendicular and parallel to the plane of scattering are given in columns 5 and 6 respectively.  $a$ ,  $e$  and  $f$  are arbitrary quantities.  $\rho'$  represents the ratio of the intensity of any Raman line for incident light polarised with the electric vector parallel

to the plane of scattering to that of the same Raman line for incident polarised light with electric vector perpendicular to the plane of scattering, *i.e.*, the ratio of the value given in column 6 to that given in column 5. The values of  $\rho_{\nu}'$  are entered in column 7. The last column describes the appearance of the Raman lines coming under the different classes and for different settings when a beam of monochromatic light is passed through the crystal and the entire track inside the crystal is focussed on to and parallel to the slit of a spectrograph. The Raman lines, in general, exhibit fluctuations of intensity or banding throughout the length of the track. The banding is defined as "normal" when the intensity of scattering is maximum for incident electric vector perpendicular to the plane of scattering and minimum when the incident electric vector is parallel to it. If the reverse is true, the banding is termed as "reverse". Normal and reverse bandings are completely out of phase. Perfect banding is one in which the minimum is of zero intensity, while imperfect banding corresponds to the case when the minimum has a finite intensity.

In order to assign the Raman lines to the three different classes, it is sufficient if the experiment is carried out for two orientations of the sodium chlorate crystal corresponding to settings 1 and 2 (*a*). In the former setting, A and E lines behave in the same way, while F lines behave differently and consequently can be distinguished. In the latter setting, A and F lines behave nearly in the same way, while E lines exhibit reverse and imperfect banding and can therefore be identified. In the experiment to be described in the next section, only these two settings have been investigated.

### 3. EXPERIMENTAL DETAILS

The specimen of sodium chlorate used in the present study was a synthetic crystal with well-developed cubic faces kindly presented by Dr. F. W. Mason of the Bell Telephone Laboratories, New Jersey. It had the following dimensions: 5.7 cm.  $\times$  5 cm.  $\times$  4.2 cm. Although there were some inclusions in the centre of the specimen, the portions near the edges were nearly free from flaws and defects of any kind. One of the edges was ground and polished normal to the dodecahedral direction for studying setting 2 (*a*) described in Table I.

The resonance radiation from a specially designed quartz mercury arc after polarisation with the aid of a nicol was focussed on the crystal in a vertical direction. The vertical track of the beam inside the specimen was focussed on the slit of a medium quartz spectrograph. As the condensing lens was not achromatic, its position was adjusted by trial to give the best focus in the region between  $\lambda$  2537 and  $\lambda$  2600. Exposures of the order of five days

had to be given. A mercury vapour filter was kept in the path of the scattered light as usual to absorb the resonance radiation. This enabled the Brillouin components due to the exciting radiation to be recorded on a clear background.

#### 4. RESULTS AND DISCUSSION

Figs. 1 (a) and 1 (b) in Plate (XVIII) represent the spectrograms obtained for the two different settings of the crystal with reference to the directions of incidence and observation. The banding for different lines is clearly visible in the photographs. Due to the presence of parasitic illumination, the mercury lines recorded do not exhibit as perfect a banding as the Raman lines. The length of the crystal is 5.7 cm. and nearly five bands were visible. In the figure reproduced in the Plate, only two bands are shown. The length of the bands was 11.9 mm. This agrees well with the value of 12.1 mm. calculated from the known rotatory power of sodium chlorate for  $\lambda$  2537. As is to be expected, the band width for the exciting line ( $\lambda$  2537) is the same as that for the different Raman lines.

The Raman lines are marked in the figures. The Brillouin components exhibit perfect and normal banding. See Fig. 1 (a). For the second setting, the filtering was not very efficient. The Brillouin components are perfectly polarised irrespective of the orientation of the crystal. Unlike in the case of quartz, these components appear to be less intense than the symmetric oscillation (936) of sodium chlorate.

Comparing the behaviour of the individual Raman lines in the two settings investigated with that to be expected theoretically (Table I), the 15 Raman lines have been assigned as follows: 70 (E), 83 (F), 103 (F), 123 (F), 131 (A), 179 (E), 480 (E), 487 (F), 627 (A + F), 933 (F), 936 (A), 959 (E), 966 (F), 984 (F), 1026 (?). The author's assignments except for the 131 line are in general agreement with the conclusions arrived at by Couture and Mathieu (1948) from a study of the polarisation of the Raman lines in the usual way. The line  $131 \text{ cm.}^{-1}$  has been classified by them as belonging to Class E. The fact that this line exhibits normal banding for the two settings (Fig. 1 a and 1 b) indicates clearly that it belongs to Class A. In place of the two lattice lines  $83 \text{ (F)}$  and  $103 \text{ (F) cm.}^{-1}$  Couture and Mathieu reported the appearance of a single line at  $92.5 \text{ cm.}^{-1} \text{ (F ?)}$ .

When a closely spaced doublet is formed of an E-F or A-F combination the resulting group for setting No. 1 shows a "zig-zag" course. This is because one component exhibits minimum intensity, when the second component has maximum intensity. See the doublets 123-31, 482-87 and 933-36 in Fig. 1 (a). Contrary to theoretical expectation, the line 936

*belonging to Class A does not exhibit perfect banding, i.e., the depolarisation factor  $\rho_{\nu}$  is not equal to zero and its value varies with orientation.*

In agreement with the observation of Couture and Mathieu, the  $1026\text{ cm.}^{-1}$  line cannot be classified properly. Its origin itself has not been satisfactorily explained till now.

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#### SUMMARY

As in the case of quartz (Chandrasekharan, 1948), using the property of optical activity, the selection rules for Raman lines of sodium chlorate have been experimentally verified using  $\lambda 2537$  excitation for two different orientations of the crystal. Its 15 Raman lines have been classified as follows into the various symmetry classes possible for a cubic crystal:— 70 (E), 83 (F), 103 (F), 123 (F), 131 (A), 179 (E), 482 (E), 487 (F), 627 (A+F), 933 (F), 936 (A), 959 (E), 966 (F), 984 (F),  $1026 (-)$ . The results agree with earlier ones of Couture and Mathieu (1948) except for the Raman line  $131\text{ cm.}^{-1}$  which they classify as belonging to Class E.

The Brillouin components are well polarised and weaker than the symmetric Raman line  $936\text{ cm.}^{-1}$

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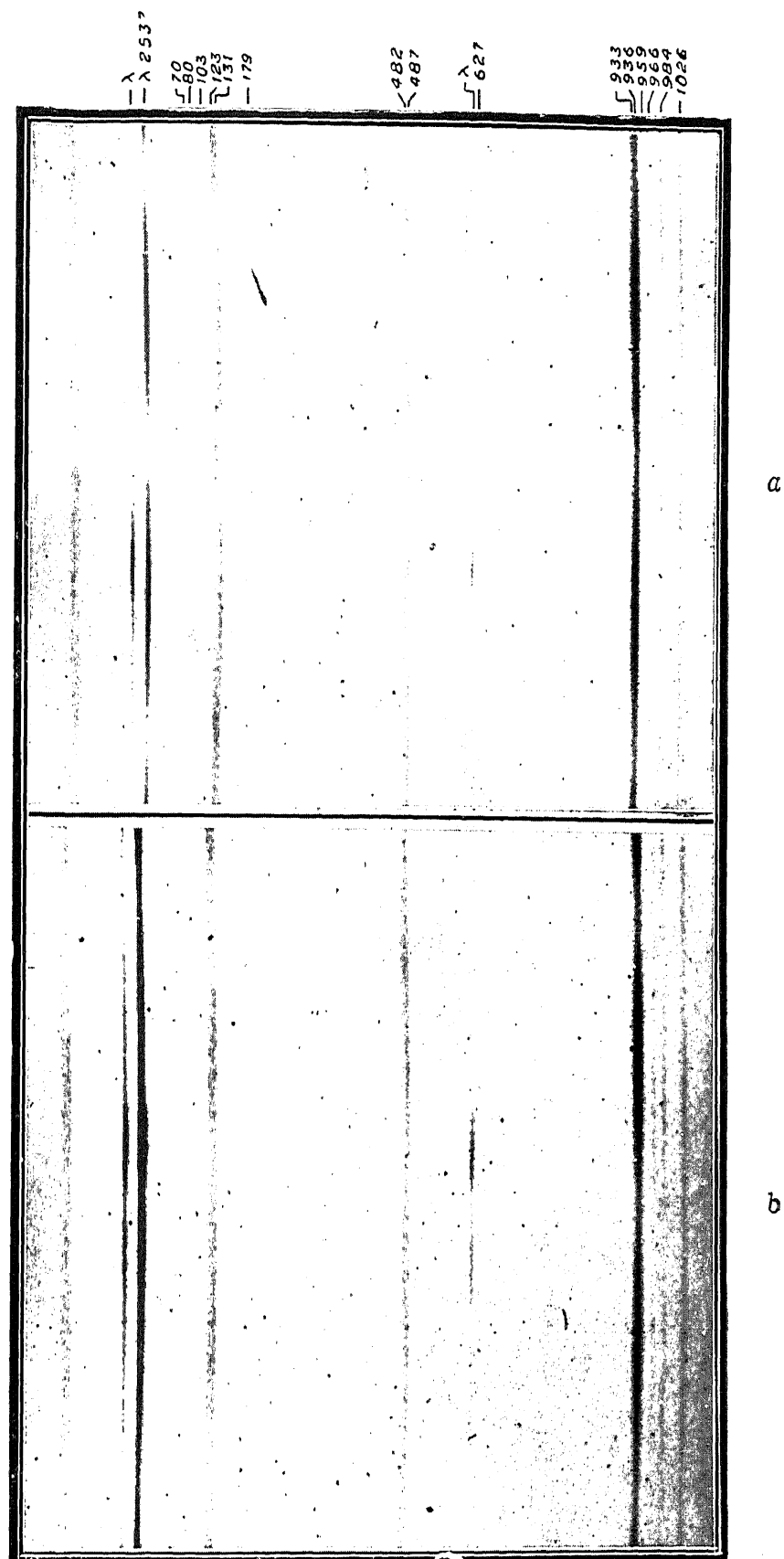


FIG. 1. Raman spectrum of sodium chlorate for two different orientations.

(a) Incident along [100]; Scattered along [010]

(b) Incident along [100]; Scattered along [011]