RAMAN SPECTRUM OF CESIUM BROMIDE

By P. S. Narayanan

(Department of Physics, Indian Institute of Science, Bangalore-3)

1. Introduction

The Raman spectra of a few alkali halides have in recent years been examined in detail by a number of investigators [Menzies, A. C. and Skinner, J. (1948 a, b), Krishnan, R. S. (1947), Krishnan and Narayanan, P. S. (1948) and Welsh et al. (1949)] in view of their importance for a proper understanding of the nature of the vibration spectra of these alkali halides in particular and that of crystals in general. Yet all these have been of the NaCl lattice type and so far no crystal of the body centred lattice type, i.e., CsCl structure* has been experimentally investigated and any new data on such crystals are all the more valuable because of the opposing views which prevail concerning the vibration spectra of crystals. Some preliminary observations on the Raman spectrum of cesium bromide are therefore presented here.

2. Experimental Details

Cesium bromide which crystallises with CsCl structure is being grown synthetically by a few companies and in the present study two specimens were employed, one of which was supplied by Messrs. Harshaw Chemical Co., U.S.A., and the other was presented to Prof. R. S. Krishnan by Dr. Menzies, Research Director of Adam Hilger Ltd. The specimen from Harshaw Chemical Co. was of size 3 cm. × 2 cm. × ·5 cm. while the one from Hilger was about 5 cm. × 3 cm. × 2 cm. and clearer and more transparent than the former.

The spectra were recorded using as exciter the λ 2537 radiation from a quartz arc designed for this purpose. The experimental arrangement was such that the crystal could be placed close to the arc without the former getting heated and its polish getting spoiled. As in the case of the earlier studies on the spectra of alkali halides carried out in this laboratory, cesium bromide also was studied employing two spectrographs, viz., the medium quartz spectrograph with a dispersion of about 140 cm.$^{-1}$ in the λ 2537 region and a large Littrow quartz spectrograph (E1) with a dispersion of 40 cm.$^{-1}$

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* Although NH_4Cl and NH_4Br have CsCl structure, as the lattice points are occupied by NH_4 group rather than a single ion, they are not taken into consideration for this statement.

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in the same region. With the smaller instrument and using a slit width of ·03 mm. it was found possible to obtain satisfactory spectra in about an hour while with the E 1 spectrograph and the same slit width an exposure of the order of 2 days was necessary. The spectra were measured with a cross-slide micrometer having an accuracy of ·0001 cm. and it was possible to measure the frequency shifts of the intense lines with an accuracy of 2 cm.[1]

An attempt was made to study the polarisation of the Raman spectrum using a collimated beam of unpolarised incident radiation but owing to the feebleness of the spectrum it was not possible to obtain any result even with an exposure of 5 days. Consequently the arc was kept close to the crystal and the condensing system dispensed with. Although the incident beam had now a wide angle of convergence determined only by the critical angle, it can easily be seen that even in spectra obtained in this manner it should be possible to identify lines with depolarisation less than 0·2 or 0·3 (Menzies and Skinner, loc. cit.). Yet no line could be definitely stated to be polarised to this extent and all the observed Raman lines were depolarised. Consequently a more accurate experimental measurement with collimated incident beam is being tried again with some improvements.

3. RESULTS AND DISCUSSION

The observed spectrum, as is to be expected because of the large masses of the constituent atoms, is restricted to the region of very small frequency shifts and as such a prerequisite to any satisfactory observation of either the frequency shift and the intensity distribution is efficient filtering of the exciting radiation from the scattered light. Figures 1 and 3 on Plate XIII show the spectrum of cesium bromide taken with the large and the medium spectrographs respectively, while Figs. 2 and 4 on the same plate represent the corresponding microphotometer records. One can easily identify five Raman lines in the recorded spectrum in spite of their being slightly broad and diffuse and the observed frequency shifts are given in Table I. The frequency shifts have also been marked in the figures. As will be seen in more detail later, the reason for the apparent diffuseness is a crowding together of a large number of lines which differ in frequency from one another by only very small amounts.

The figures within brackets by the side of the frequency shifts indicate roughly the relative intensity of the Raman lines. In the most intense spectrograms taken, there are indications of the existence of a spectrum in the region beyond $190 \, cm.^{-1}$ up to $220 \, cm.^{-1}$ although it is extremely weak. There is evidence also for the presence of lines in the spectrum in the region of 30 to $50 \, cm.^{-1}$ but owing to the halation caused by $\lambda \, 2537$ and the spurious

TABLE I

Raman spectrum of cesium bromide

Observed frequency shift in cm.⁻¹	Assignment	Calculated frequency in cm.⁻¹
79 (5)	$\nu_2, \nu_5 + \nu_7$	80
86		86
107 (4)	$2\nu_5$	108
135 (10)	$2\nu_3$	136
155 (1)	$2\nu_2$	156
190 (1)	$2\nu_1$	190

band in this region it was not possible to measure these. An accurate measurement of the intensity distribution in the entire spectrum is being carried out.

So far the only theoretical consideration of the frequencies of vibration of CsCl structure on the basis of the Born model is that of Krishnan and Roy (1952); even they have calculated explicitly only that of one mode, *viz.*, that in which the cesium lattice oscillates as a whole against that of bromine. On the other hand, according to Prof. Raman (1943, 1947), the cesium chloride structure which consists of two simple cubic lattices interpenetrating in such a manner that the atoms of one lattice are located at the body centres of the cubic lattice formed by the other has only 11 distinct normal modes of vibration (Chelam, 1943) all of which are inactive as fundamentals in light scattering. Exact expressions for these 11 discrete normal vibrations have also been worked out (K. G. Ramanathan, 1947) in terms of 12 force constants which take account of the influence of the 26 nearest neighbours of every atom. A considerable reduction in the number of force constants can be effected once certain simplyfying assumptions are made. But they lead to a reduction of the number of distinct frequencies also from 11 to 7 and simplified formulæ for these 7 frequencies have also been given in terms of 4 independent constants only which are again connected by an additional relation. Consequently it is possible to evaluate roughly the frequencies of the various modes if one can identify in the spectrum three frequency shifts. For this it will be advantageous to consider first the activity of the different modes in second order scattering along lines dealt with in detail by Prof. Raman (1947 *a*, *b*). Since the two

TABLE II

Sl. No.	Degeneracy	Description of mode	Direction of oscillation	$4\pi^2\nu^2c^2$	Frequency	Frequency in cm.$^{-1}$ calculated	Theoretical 2nd order activity
I	6	(011) Plane	(011) or (0ĪĪ)	$\dfrac{P-2T}{m_1} + \dfrac{P'-2T'}{m_2} + \dfrac{4(T+T')}{m_1+m_2}$	ν_1	82	Very weak
II	3	Two lattices	Arbitrary	$\dfrac{P+2T}{m_1} + \dfrac{P'+2T'}{m_2}$	ν_2	78	Weak
III	3	(III) Br ions	,,	$(P'-2T')/m_2$	ν_3	68	Very strong
IV	3	,,	Normal	,,	ν_3		Weak
V	3	,,	(100)	$(P'+2T')/m_2$	ν_4	58	Weak
VI	6	,,	Tangential	,,	ν_4		Weak
VII	3	(III) Cs ions	Arbitrary	$(P-2T)/m_1$	ν_5	54	Strong
VIII	3	(100) Cs ions	Normal	,,	ν_5		Weak
IX	3	(011) ,,	(100)	$(P+2T)/m_1$	ν_6	45	Weak
X	6	(100) ,,	Tangential	,,	ν_6		Weak
XI	6	(011) Plane	(011) or (0ĪĪ)	$-\dfrac{4(T+T')}{m_1+m_2}$	ν_7	26	Very weak

interpenetrating lattices in the structure of cesium bromide consist of dissimilar particles, their oscillation against each other (mode II in Table II) is necessarily active in infra-red absorption and as has been done by Krishnan and Roy (*loc. cit.*) can be identified with the infra-red absorption at $134\,\mu$ (Barnes, 1932). Therefore, the observed frequency shift of 155 cm.$^{-1}$ in the second order Raman spectrum obviously corresponds to the octave of mode II. Of the remaining modes, modes III and VII involve appreciable changes in the relative distances of the Cs and Br ions, and the octaves of these are therefore to be expected to appear with considerable intensity, that involving a movement of the Br ions only being stronger because of the larger refractivity. Further ratio of the frequencies of these two modes should be roughly proportional to the square root of inverse ratio of the masses of the ions. Therefore, one can take the observed second order lines 135 cm.$^{-1}$ and 107 cm.$^{-1}$ to represent the octaves of modes III and VII respectively.

The force constants P, P', T, and T' are now easily calculated using for ν_3, ν_5 and ν_7 the values 78, 68, 54 cm.$^{-1}$ in formulæ given in Table II and utilising the relation $P + 2T = P' + 2T'$. They are given by

$$P = 2.02 \times 10^4 \text{ dynes/cm.} \quad P' = 1.97 \times 10^4 \text{ dynes/cm.}$$

$$T = 1.2 \times 10^4 \text{ dynes/cm.} \quad T' = .09 \times 10^4 \text{ dynes/cm.}$$

and the other frequencies calculated using these force constants are also included in Table II. The rough theoretical second order activity to be expected is also indicated in the same Table II. As mentioned earlier the approximations made in the calculation lead to a reduction in the number of distinct frequencies and even these are very close to each other. While these themselves are adequate to explain in a satisfactory manner the observed features of the second order spectrum, a more rigorous calculation of all the 11 frequencies will give a better account of the width and intensity of the second order lines. A very striking feature of the spectrum is the high intensity of the Raman line at 79 cm.$^{-1}$ which has been attributed to the combination of modes VII and IX, *i.e.*, the frequency $\nu_6 + \nu_7$. A possible reason for this is that it is very nearly equal to the frequency of mode II and consequently results in an appreciable activity of both due to this accidental coincidence. The extremely faint line at 190 cm.$^{-1}$ is probably the octave of ν_1. The assignment of the observed Raman lines on the basis of the frequencies given in Table II is also indicated in Table I. However, it will be evident that though only a few of the theoretically allowed octaves and combinations which comprise the second order spectrum have been found essential to explain the prominent frequency shifts it is necessary to consider in detail

all of them and their activity in second order Raman effect for a quantitative explanation.

In conclusion the author wishes to express his grateful thanks to Prof. R. S. Krishnan for his kind interest and constant encouragement.

SUMMARY

The Raman spectrum of cesium bromide, which crystallises with CsCl structure, has been studied using the resonance radiation of mercury as exciter. It consists of a number of lines very close to the exciting line of which five prominent frequency shifts are 79, 107, 135, 155 and 190 cm.$^{-1}$ A calculation of the 7 distinct frequencies of CsBr using the approximate formulæ worked out by K. G. Ramanathan on the basis of Raman's theory has been carried out and an attempt made to explain the prominent features of the observed spectrum.

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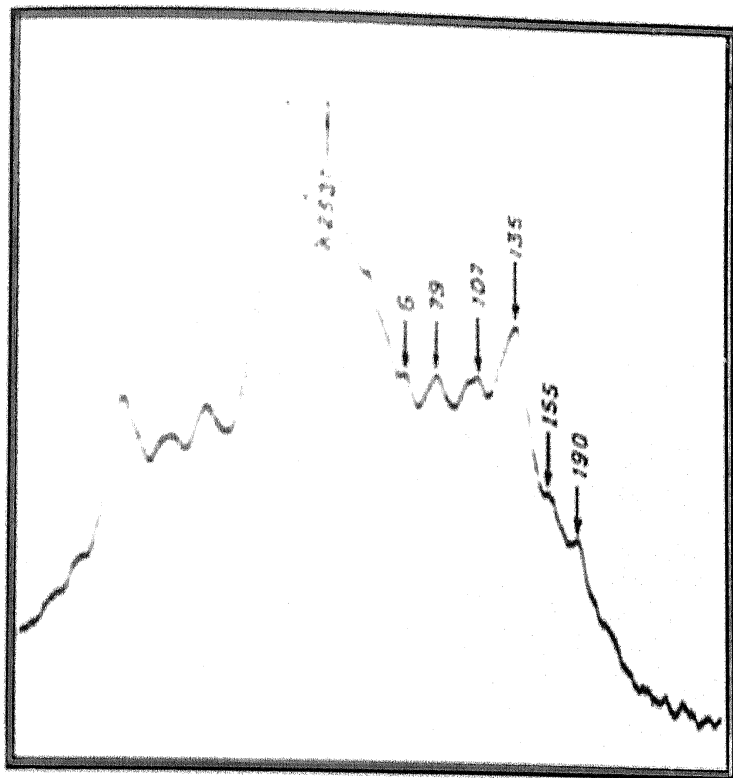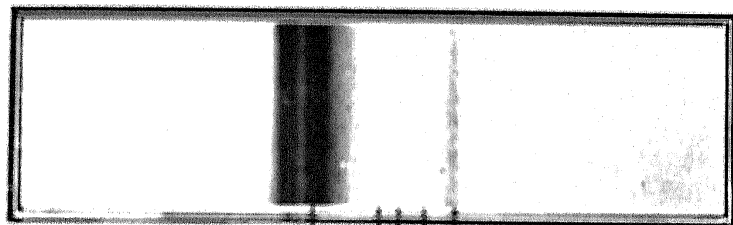|	
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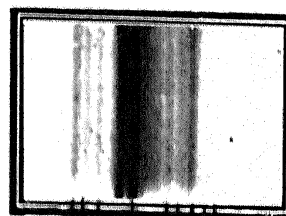
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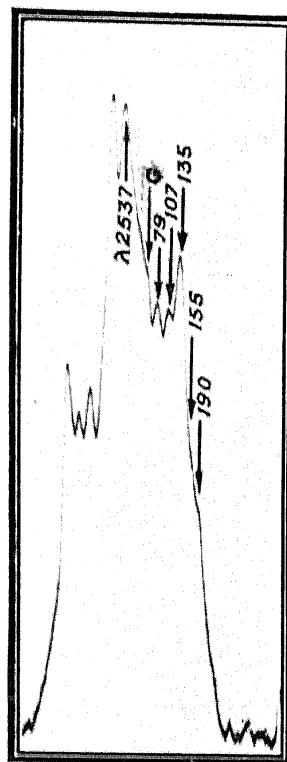
Proc. Ind. Acad. Sci., A, Vol. XLII, Pl. XIII

FIG. 2

FIG. 4

FIG. 1

FIG. 3

FIG. 1. Microphotometer record of Spectrum taken with E.1 Quartz Spectrograph.

FIG. 2. Microphotometer record of Spectrum taken with E.1.

FIG. 3. Raman Spectrum of Cæsium Bromide taken with medium Quartz Spectrograph.

FIG. 4. Microphotometer record of picture recorded with the medium Spectrograph.