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RAMAN SPECTRA OF ALKALI HALIDES

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ABSTRACT

The Raman spectrum of potassium iodide has been recorded recently by using the 2536 excitation. The results obtained have been compared with the spectra of sodium chloride, potassium bromide and cæsium bromide. The details of the spectra of these four halides have been critically examined in the light of the existing theories of crystal dynamics.

1. INTRODUCTION

The alkali halides NaCl, KCl, KBr, etc., form the most important group of crystals that have been studied in great detail experimentally mainly because of the simplicity of their structure and high symmetry and also because of the ease with which the results obtained with these crystals could be compared with those to be expected theoretically. Among the several physical properties their vibration spectra naturally play a significant role and it is therefore not surprising that the basic ideas of the crystal dynamics were worked out by Born and von Karman (1912) long before experimental facts regarding the spectra of alkali halides were available from spectroscopic studies. Further on account of their cubic symmetry the first order Raman spectra of the alkali halides are forbidden and our knowledge is therefore restricted by what can be deduced from their second order spectra which arise through the anharmonicity of the vibrations either mechanical or electrical or both. Recently, using the Born model, it has been shown that in the case of the alkali halides, electrical anharmonicity alone is important (K. S. Krishnan and S. K. Roy, 1951, 1952).

Rasetti (1929) was the first to succeed in recording the second order Raman spectrum of the alkali halide, NaCl, using the resonance radiation of mercury as exciter. Utilising the fact that the parent radiation can be almost completely eliminated from the scattered light he was able to obtain spectrograms free from halation and fogging and in the case of NaCl the observed spectrum was interpreted as a continuous band with small peaks, one of them being so sharp as to have a line like character. But it was soon realised by Rasetti and Fermi (1930) that the "very peculiar structure" of the spectrum of rock salt needed special assumptions regarding the influence of the polarisability of the crystal atoms by elastic displacements. Subsequently, using the Rasetti technique and taking precautions for eliminating spurious effects, the Raman spectra of NaCl, KBr and KCl were studied in detail by R. S. Krishnan (1943, 1945, 1946, 1947 unpublished) and R. S. Krishnan and P. S. Narayanan (1948, 1949) and it was found that the experimental facts were in the nature of a discrete line spectrum overlaying which was a weak continuous background intensity arising chiefly from thermal and other causes.

Menzies and Skinner (1948, *a*, *b*) in addition to studying the spectra of NaCl, KBr, KCl, KBr and RbBr have examined also the polarisation of the Raman lines using incident unpolarised light. The general features of the spectra have been explained by these authors on the basis of the mass ratios of the cation and the anion and their influence on the frequency-phase diagram. In the case of NaCl and KBr it was found that the spectra were polarised except for the peaks at 232 and 127 cm.$^{-1}$ respectively. The Russian workers Stekhanov and Petrova (1949, 1950) have studied KCl, NaBr and KI mainly to verify the law governing the temperature dependence of the intensity of the second order spectra. They are inclined to favour the continuum theory; it should be mentioned however that heating up the specimen as has been done by them, will lead only to a broadening of the lines and obliterate the details of the spectrum. In fact to observe the features better, the crystal should have been cooled down; such studies on the Raman spectra of alkali halides at liquid-air temperatures are in progress in this laboratory and the results will be dealt with later. Welsh, Crawford and Staple (1949) made an accurate investigation of the intensity distribution in the Raman spectrum of NaCl using an instrument having a dispersion of 27 cm.$^{-1}$ per mm. as compared to a dispersion of 40 cm.$^{-1}$ per mm. of the Hilger Large Quartz spectrograph used by R. S. Krishnan (1947). The observed intensity distribution was according to them in conformity with the predictions of Born's theory. However, these authors have not stated if the specimen used by them was completely free from fluorescence in the region 2400–2600 A. It is well known that crystals of NaCl usually exhibit fluorescence in this region (Krishnan, 1946). If these authors had given the intensity distribution on the anti-stokes side also it would have been helpful in judging whether there was any fluorescence.

From among the large number of alkali halides that are available many are yet to be studied experimentally, in fact none of the body-centred type (ammonium halides excluded) has been studied by Raman effect. Recently the Raman spectra of CsBr and KI have been recorded in this laboratory. It is therefore proposed to give here the results of the four alkali halides namely, NaCl, KBr, CsBr and KI, which have been studied in detail in this laboratory and to discuss them critically in relation to the theories proposed.

2. RESULTS AND DISCUSSION

The second order Raman spectra of the alkali halides, which are very weak and the frequency shifts of which are very small, are best studied only with the Rasetti technique. It is therefore to be anticipated that the present study like those of others was made with the resonance radiation of mercury as exciter and with the help of techniques adequately described elsewhere (R. S. Krishnan, 1947; R. S. Krishnan and P. S. Narayanan, 1948). Both CsBr and KI samples were free from coloration and fluorescence. The experimental technique, etc., were the same as that employed in the earlier study on NaCl and KBr. It was found possible with the medium quartz spectrograph to obtain satisfactory spectra in about 10 minutes with KI and about one hour with CsBr. Polarisation studies on the Raman spectra of NaCl, KBr, KI and CsBr were also carried out by a method similar to that of Menzies and Skinner. In CsBr all the lines were found to be depolarised while in NaCl, KBr, KI except for the strongest line in each, *viz.*, 235, 126 and 89 cm.$^{-1}$ all the others were found to be polarised. KI was so intensely scattering that it was possible to use a collimated beam of incident light for polarisation study and the spectrogram along with those of NaCl, KBr, and CsBr can be seen in Fig. 1. In view of the high intensity of scattering in KI, it was considered also a good case for an experimental study at liquid-air temperature. The Raman spectrum of KI was therefore recorded at liquid-air temperature by a technique which has been fully described elsewhere (R. S. Krishnan, 1947). Even with a continuous exposure of 36 hours only one line at 93 cm.$^{-1}$ was observed with reasonable intensity. The width of this line at liquid-air temperature was about 10 cm.$^{-1}$

Before we proceed to discuss the observations in NaCl, KBr, KI and CsBr with theoretical predictions it is but proper that we briefly outline the implication of the theories. NaCl, KBr, and KI all have the same structure and the vibration spectrum of this structure has been generally treated on the basis of Born's theory. But in particular specific calculations have been made only for NaCl (Kellerman, 1940; Born and Bradburn, 1947). However, recently Krishnan and Roy (1951, 1952) have in connection with their study of the anharmonicity of vibrations of the alkali halides considered the vibration spectra of the NaCl as well as CsBr type of structure. Even they have calculated explicitly only that of one mode, *viz.*, that in which the Na or Cs lattice oscillates as a whole against the Cl or Br lattice. The calculated values of this mode which is infra red active, are in good agreement with the frequency shifts observed in second order Raman effect (Table I). According to Born and Bradburn (1947) the second order Raman spectrum of NaCl is a continuous one derived from combinations of frequencies belonging to the three optical and three acoustic branches of NaCl structure. This second order spectrum has been calculated for rock-salt with the help of the tables of the lattice frequencies published by Kellermann. It is found to consist of 36 peaks each belonging to a combination frequency and from these they have derived a curve to explain the position of the maxima in the microphotometer curve published by R. S. Krishnan. However, to account quantitatively for the observed intensities also, three coupling constants have been employed.

But the recorded spectrum of NaCl consists of a series of distinct Raman lines of which at least 6 can be distinguished without any difficulty while accurate measurements enable one to identify no less than 19 lines and 5 other comparatively weaker ones. The observed frequency shifts are included in Table I along with the assignment to be dealt with below. A comparison of these experimental facts with the predictions of Born's theory leads to discrepancies. Firstly the observed lines are not merely peaks on a continuous background but have the character of discrete monochromatic frequencies overlaying which is a small amount of continuous background whose origin appears to be due to the thermal broadening, crowding together of the frequencies in a narrow region and consequent perturbation, etc. In the low frequency region Born's theory indicates two bands of frequency shift less than 60 cm.$^{-1}$ Investigations definitely show that there are no bands in this region (R. S. Krishnan. 1947) and the band in the spectrogram reproduced by Rasetti is evidently due to optical coma in the instrument used by him. Similarly on the high frequency side also, the Raman spectrum shows an abrupt fall in intensity after the 350 line. However, by a careful scrutiny one can identify 5 weak lines in this region and their extreme feebleness is a significant point because it indicates that they represent the third order spectrum of rock-salt.

If we now consider the observations in the light of the lattice dynamics due to Sir C. V. Raman we can expect for the NaCl structure with two non-equivalent atoms in the unit cell a total of 45 degrees of freedom lead only to 9 distinct frequencies. While all the 9 are inactive in the first order, we may hope to record them as octaves and the 36 possible combinations also in the second order Raman spectrum. Exact expressions have been worked out in a very general manner by K. G. Ramanathan (1947) and the activity and intensities of the combinations have been indicated by Sir C. V. Raman (1947). Using these it has been possible to account satisfactorily the observed features of the spectrum and the agreement between the calculated and observed values is good (see Table I). It may be added that, if one puts down all the 9 octaves and 36 combinations possible no fewer than 20 of them are bunched together in the region from 260 cm.$^{-1}$ to 350 cm.$^{-1}$ This would account for the strong unresolved continuum appearing in this region.

Potassium bromide has a crystal structure of the NaCl type but as the ions in KBr are heavier the observed Raman shifts are smaller and is confined to the region from 46 cm.$^{-1}$ to 280 cm.$^{-1}$ The second order spectrum of KBr exhibits a series of lines of which 11 could be easily identified. These are also included in Table I along with their relative intensities. In spite of the smaller values of the frequency shifts in KBr the lines do not appear bunched up as in sodium chloride but are evenly distributed over the entire spectrum. Here also as in NaCl it has

TABLE I

Observed Frequency in cm.$^{-1}$	NaCl		Observed Frequency in cm.$^{-1}$	KBr		Observed Frequency in cm.$^{-1}$	KI	
	Intensity	Assignment		Intensity	Assignment		Intensity	Assignment
85	1	$2\nu_9$	46	5	$2\nu_9$	63	8	$2\nu_8$
125	1	$2\nu_8$	84	6	$2\nu_8$	89*	10	$2\nu_9$
140	..	$\nu_7+\nu_9$	126*	10	$2\nu_7$	101	8	$2\nu_6$
162	..	$\nu_6+\nu_9$	145	9	$2\nu_6$	102	6	$\nu_5+\nu_6$
184	4	$\nu_6+\nu_7$	170	5	$\nu_4+\nu_7$	175	3	..
199	..	$\nu_5+\nu_8$	186	3	$2\nu_5$	210	1	..
292	3	$2\nu_7$	216	5	$2\nu_4$	252	2	..
220	..	$\nu_6+\nu_7$	228	2	$2\nu_3$			
235*	10	$2\nu_6$	232	2	$2\nu_2$			
258	6	$2\nu_5$	242	2	$2\nu_1$			
270	..	$\nu_4+\nu_5$						
276	10	$\nu_2+\nu_6$						
285	10	$2\nu_4$						
300	8	$2\nu_3$						
314	9	$2\nu_9$						
320	..	$\nu_1+\nu_4$						
326	..	$\nu_2+\nu_3$						
343	7	$2\nu_1$						
350	8							
I.R. Frequency in †Absorption		61·1 μ (164 cm.$^{-1}$)		88·3 μ (113 cm.$^{-1}$)			102·0 μ (98 cm.$^{-1}$)	

* Strongly depolarised; remaining lines polarised.

† Infra-red absorption maxima; Barnes, R. B. (1932).

been found possible to explain 9 frequencies calculated from the formulæ referred to above (Table I) (R. S. Krishnan and P. S. Narayanan, 1948, 1949). It is interesting to note that in all the cases studied *i.e.*, NaCl, KBr, KI, the vibrations most active in second order Raman effect are those in which the halogen ions lying in the octahedral layers alone move either normally or tangentially and this is in agreement with the known higher refractivity of the halogen ions. Also it is the most intense line in NaCl, KBr, KI that is depolarised, all the other lines being polarised. A more detailed analysis study of the polarisation characteristics is in progress.

Though the disparity between the masses of the constituent ions is the largest in the case of KI and its second order spectrum is not split up, it serves better to assess the true nature of the vibration spectra of alkali halides. The observed spectrum does not show any line of frequency shift less than 60 cm.$^{-1}$ and the frequency shifts of the 7 lines which could be easily identified are given in Table I. The agreement with the values reported by Stekhanov and Petrova (1949) is good. As in KBr and NaCl, the observed second order lines of KI are explained as combinations and octaves and the assignment is shown in Table I. Detailed calculations on the spectrum of KI on the Born model have not yet been published although such a study is reported to be in progress.

Before we proceed to consider the case of a body centred type of structure like CsBr, a few observations on the analysis of the spectra of the NaCl type may be made. Firstly, in all the three cases considered here we find in the recorded spectra a few weak lines of frequency shifts larger than $2\nu_1$ and which have been attributed to the third order. KI in particular exhibits 2 lines 210 and 252 whose intensity is roughly 1/20 of the strongest line 89 cm.$^{-1}$ For a quantitative comparison it is therefore essential to calculate the intensity of the allowed third order frequencies also. Further, the present investigation shows that the lines 235, 126 and 89 cm.$^{-1}$ in NaCl, KBr, KI respectively besides being sharply defined are the only lines depolarised the rest being polarised (101 cm.$^{-1}$ line KI also appears to be depolarised though a study with the higher dispersion instrument is necessary before it is taken for certain). Though one would normally expect these frequencies to be of the same assignment in all the three cases, one finds that in NaCl it has to be attributed $2\nu_6$ while, in the others to $2\nu_7$. This discrepancy arose mainly because it was found that if one attributed the lines 126 cm.$^{-1}$ and 89 cm.$^{-1}$ to $2\nu_6$, the agreement between observed and calculated values on the Raman theory were far from satisfactory and also the frequencies of ν_1, ν_2 and ν_3 modes were considerably enhanced. One can explain in a qualitative manner the observed depolarisation and intense character of this line by assigning it to one of the oscillations of halogen ions alone in the octahedral planes. But this leads to another difficulty. Purely from symmetric considerations the oscillations of alkali ions in the octahedral plane should also exhibit the same polarisation characteristics as the halogen ions. The available data do not indicate the existence of any other depolarised line.

Cæsium bromide is the first crystal of the cubic body-centred type whose second order Raman spectrum has been studied. In spite of the large masses and consequently the small frequency shifts involved, it has been possible to identify five Raman lines (see Fig. 1) although they are slightly broad and diffuse. The frequency shifts are indicated in Table II. 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.$^{-1}$ upto 220 cm.$^{-1}$ although it is extremely weak.

There is some 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 λ2537 and the spurious band, in this region it was not possible to measure these.

TABLE II

Raman Spectrum of Cæsium Bromide

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

So far the only theoretical consideration of the frequencies of vibration of CsCl structure on the basis of the Born model is that of K. S. Krishnan and S. K. Roy (1951, 1952); even they have calculated explicitly only that of one mode *viz.*, that in which the cæsium lattice oscillates as a whole against that of bromine. On the other hand according to Sir C. V. Raman (1943, 1947) the cæsium 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. With some approximations it is possible to reduce the number of constants to 4. Also as the two interpenetrating lattices in the structure of cæsium bromide consist of dissimilar particles, their oscillation against each other is necessarily active in infra-red absorption and as has been done by K. S. Krishnan and S. K. Roy (1951) can be identified with the infra-red absorption at 134 μ (Barnes, 1932). Making the assumption that $\nu_2 = 78$ and $\nu_5 = 54$, besides $\nu_3 = 68$ cm.$^{-1}$ it has been found possible to calculate the 7 frequencies given by simplified formulæ and explain the observed Raman lines as overtones and combinations (See Table II). The notation of the frequencies is as given by K. G. Ramanathan (*loc. cit.*). A striking feature of the spectrum is the high intensity of the Raman line at 79 cm.$^{-1}$ which has been attributed to the combination $\nu_5 + \nu_7$. A possible reason for this is that it is very nearly equal to the frequency ν_2 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. 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.

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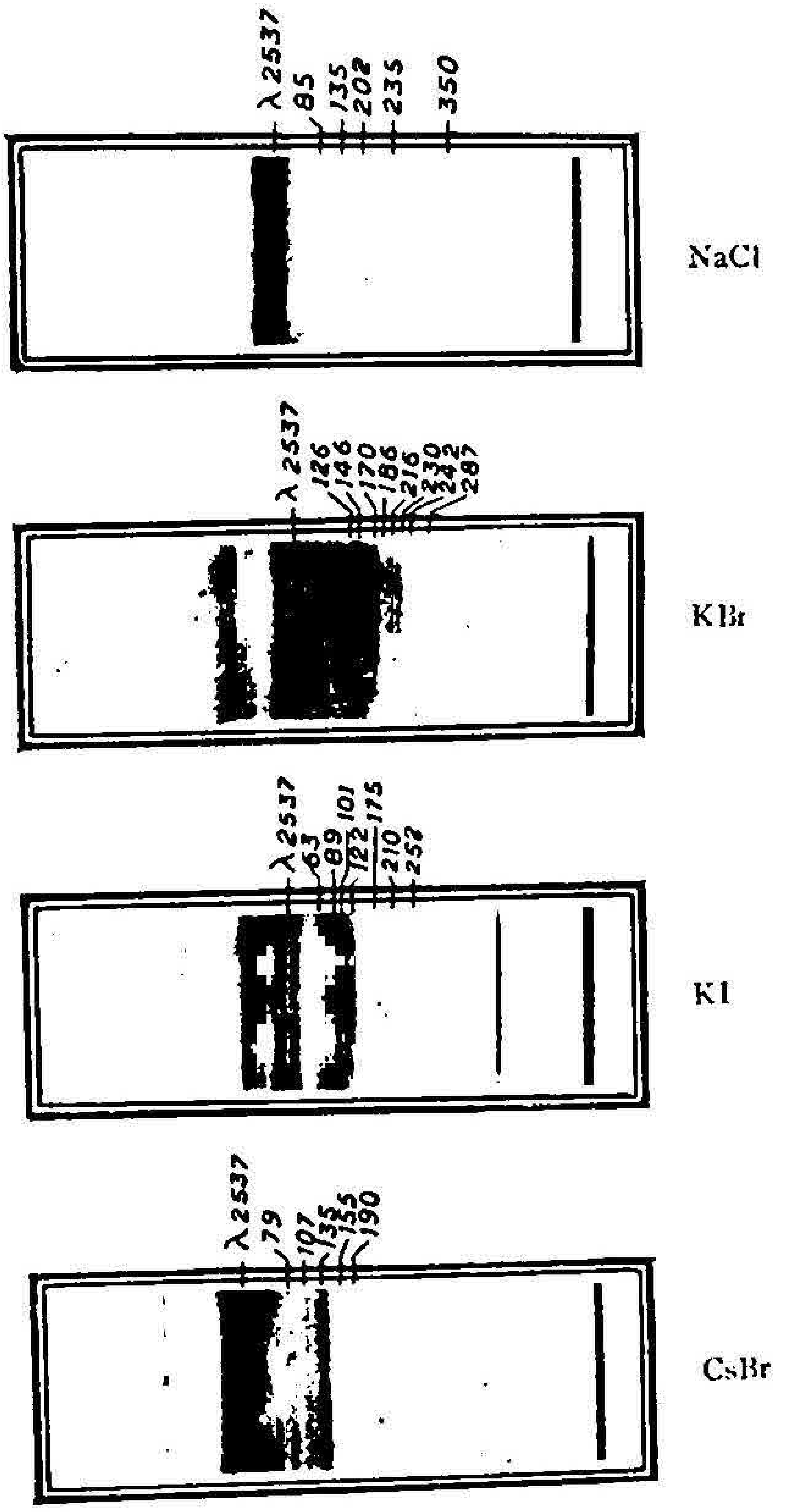

FIG. 1. Raman Spectra of Alkali Halides taken with the Medium Quartz Spectrograph