

THE VIBRATION SPECTRA OF THE ALKALI HALIDES

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1. INTRODUCTION

THE scattering of light in crystals comprises two different phenomena, the thermal scattering and the Raman effect. The former is due to the optical stratifications in the crystal associated with thermally excited stationary vibrations of the elastic type. The latter arises from the excitation of the vibrations of the atoms in a crystal by the radiations traversing it and is closely linked up with its vibration spectrum. Theoretical considerations and facts of observation alike indicate that we are here concerned, not with a coherent reflection as in the case of the thermal scattering, but with an incoherent scattering in which the process involved is the transfer of energy in discrete quanta between the radiation field and the individual volume elements of molecular dimensions in the crystal. This view of the phenomenon is indicated in the first place by the obvious points of similarity between the effects exhibited by crystals and those observed in the Raman scattering by gases and liquids. In the case of ionic or molecular crystals, vibrational frequency shifts appear as sharp lines and have nearly the same values as those observed with the same substance in the fluid state. In fact, the lines are generally sharper in the case of the crystal than in the liquid because of the more precise character of the force-fields in the crystalline medium. Overtones and summations of the fundamental frequencies are also recorded as sharp lines with observable intensities in the well-exposed spectrograms of numerous crystals like calcite, quartz, gypsum, barite, etc. (Krishnan, 1945 *a*, 1946 *a*). This is an indication that the amplitudes of the excited vibrations are not negligibly small in comparison with inter-atomic distances and that in consequence, the optical anharmonicity or lack of proportionality between the atomic displacements and the resulting variations of optical polarisabilities becomes operative. For this to be possible with an oscillator of which the energy is quantised and hence determinate, its dimensions should be of molecular order of magnitude.

In view of the situation stated above, it becomes evident that we are concerned with the evaluation of the normal modes of vibration of the

structural units of which the crystal is composed. This is the problem which has been considered and solved by Sir C. V. Raman (1943, 1947) in two theoretical papers in these *Proceedings*. If there are p atoms in the unit cell of the crystal structure, one might think that there would be only $3p$ normal modes characteristic of the individual unit cells. But this is not actually the case because the influence of the neighbouring units on the oscillation of any particular unit cell has to be taken into consideration. Since the crystal consists of sets of equivalent atoms ordered in such a manner that each atom in a set is geometrically and physically related to its environment in exactly the same way as every other atom of the same set, the oscillations of the atoms in adjacent cells of the structure have to be alike in every respect except that the phases may be either the same or opposite along each axis of the lattice. Combining the three pairs of these alternative possibilities gives eight possibilities and therefore, eight times $3p$ or $24p$ modes of vibration as has been shown by Sir C. V. Raman. In $(3p-3)$ of these modes, equivalent atoms in adjacent cells have the same amplitudes and the same phase of vibration, while in the remaining $21p$ modes, they have the same amplitude but alternately opposite phases in successive cells along one, two, or all three axes of the space lattice. In relation to the entire crystal, the $(24p-3)$ oscillation frequencies are highly degenerate, being the characteristic frequencies of the group of $8p$ atoms in a volume element having twice the linear dimensions and eight times the volume of the lattice cells. The three excluded modes are the simple translations of such a volume element. Thus, if we approach the problem from the atomistic standpoint, the $(24p-3)$ modes are the only ones possible and they describe the vibration spectrum of the structure completely. In any actual case, the number of distinct frequencies would necessarily be less than $(24p-3)$ if the crystal possesses additional elements of symmetry. In the first order Raman effect, only the fundamentals of not more than $(3p-3)$ of these modes are active, while all the $(24p-3)$ modes can appear as overtones and summations in the second order Raman effect, thus yielding highly complex spectra which are necessarily of low intensity.*

A verification of the foregoing ideas is already forthcoming in the case of diamond from the results of a variety of studies on different aspects, namely, light-scattering, infra-red absorption, luminescence, ultra-violet absorption, etc. The considerations mentioned in the last paragraph are

* The basic principles of lattice dynamics have been critically examined by Bhagavantam and Venkatarayudu in their book on *Group Theory and Its Application to Physical Problems*, Bangalore Press, 1948, Chapters X and XI, to which the reader may be referred.

perfectly general and should be applicable to all crystals alike in such simple cases as the alkali halides and to complex ones such as quartz, topaz, organic crystals, etc. Detailed investigations on the Raman spectra of rock-salt, ammonium chloride and ammonium bromide carried out by one of us (R. S. Krishnan, 1945 *b*, 1946 *b*, 1947 *a*, 1948) have clearly established the discrete character of their vibration spectra, thus confirming the correctness of the theoretical ideas presented earlier in this section. The Raman spectrum of potassium bromide has now been studied by us and the results are presented in this paper.

2. EXPERIMENTAL DETAILS

Because of the ionic nature of the binding forces, and the heavy atomic weights of the ions in alkali halides, their vibration spectra are spread over a narrow range and the actual frequencies have low values. The large number of frequency shifts belonging to the second order Raman spectrum therefore appear crowded together. The spectrum exhibiting these frequency shifts is weak and is recorded near the exciting radiation which, unless it is completely eliminated, results with prolonged exposures in recording various spurious effects in its vicinity even with the best of instruments. Further, the fact that the vibration frequencies are low has the consequence that the vibrations will be thermally excited to an appreciable extent, giving rise to a broadening of the lines. If all these factors are taken into consideration, the resulting spectrum could easily be mistaken for a continuous one. In order to find the real nature of the spectrum, it may be necessary to use the highest possible dispersive and resolving powers. In spite of these difficulties, the very first photograph of the Raman spectrum of rock-salt taken by Rasetti with a medium quartz spectrograph showed the presence of a line at 235 cm.^{-1} to the sharpness of which Rasetti drew special attention. Since then, detailed studies of the Raman spectrum of rock-salt under more favourable conditions of dispersion and resolution have not only confirmed Rasetti's observation but also shown the discrete character of the rock-salt spectrum unambiguously.

Potassium bromide has a crystal structure similar to that of rock-salt, but as the ions in the former are heavier, the Raman frequency shifts are smaller and hence less easy to record in a satisfactory manner. Menzies and Skinner (1948 *a*, *b*) who first photographed the spectrum of potassium bromide observed some details in the spectrum. In the present investigation, the authors have made considerable improvements in the experimental technique. By effecting a very perfect elimination of the diffuse continuum of instrumental origin and by using a large quartz spectrograph, the details of the KBr spectrum have been clearly brought out in the photograph.

Three specimens of synthetic potassium bromide were made available to us for the present study by the kindness of Dr. A. C. Menzies to whom the authors' thanks are due. One of them which had a slight yellowish tinge was found to be only partially transparent to the λ 2537 radiation and as such it had to be rejected. The second one was extremely clear and free from any colour. This had the following dimensions ($2'' \times 1\frac{1}{2}'' \times 1''$). Using this specimen and a medium quartz spectrograph with a fine slit (0.025 mm.) an exposure of about 4 hours was sufficient to record all the features of the spectrum. However, longer exposures of the order of 24 hours were given to get intense photographs. The experiment was repeated with a Hilger large quartz spectrograph. Due to prolonged exposure to the rays from the mercury arc, this crystal acquired a distinct colouration and a diminished transparency and the spectrum was, therefore, not recorded with the full intensity hoped for even after an exposure of 15 days. The third specimen ($4'' \times 2'' \times 1\frac{1}{2}''$) which was not as clear as the second one was also found to be partially opaque in thick layers to the λ 2537 radiations. Using this, moderately intense spectrograms were taken with the large quartz spectrograph with a moderate slit width and an exposure of ten days. The negatives were measured with the aid of a Hilger cross slide micrometer.

3. RESULTS

The spectrogram taken with the medium quartz spectrograph having a slit width of 0.025 mm. and an exposure of 24 hours is reproduced together with the microphotometer record of a lighter negative as Figs. 1 (a) and (b) respectively in the Plate. As is evident from the reproduced photograph, the spectrum of potassium bromide is confined to a region of frequency shifts from 46 cm.^{-1} to about 290 cm.^{-1} . It consists of a series of distinct Raman lines with frequency shifts 46 (5), 84 (6), 126 (10), 146 (9), 170 (5), 186 (3), 216 (5), 228 (2), 232 (2), 242 (2) and $287 (1) \text{ cm.}^{-1}$. They can be easily distinguished in the photograph. Their positions have been marked in the microphotometer record. The figures given in brackets represent visual estimates of the relative intensities of the lines. Menzies and Skinner (1948 b) were able to identify only seven frequency shifts in the spectrogram taken by them. The values agree reasonably well with those reported by them. Our photographs show greater detail than the ones taken by Menzies and Skinner* evidently due to better technique of experimentation and more efficient filtering of the exciting radiation.

* Dr. Menzies informs us that they have recently succeeded in getting good photographs showing as many details as those taken by us.

The most conspicuous feature in the spectrum of potassium bromide is the extreme sharpness of the lines 84, 126, 146, 170 and 216 cm^{-1} . The corresponding anti-Stokes lines are also clearly visible in the spectrogram. The line 126 cm^{-1} is most intense. The line at 46 cm^{-1} is also fairly intense and sharp. Unfortunately, it falls adjacent to a ghost line at about 60 cm^{-1} . In spite of this, it can be seen as a separate kink in the microphotometer record. The high frequency shift lines at 242 and 287 cm^{-1} are rather broad, the latter being less intense and more diffuse having a width of about 50 cm^{-1} . Beyond this broad line the intensity falls off abruptly.

Figs. 2 (a) and 2 (b) represent photographs enlarged to the same extent of the spectrograms taken with the large and medium quartz spectrographs respectively. In spite of the fact that a fairly wide slit had to be used with the larger instrument to get the spectrograms within a reasonable time of exposure, the details of the bromide spectrum are more clearly seen in

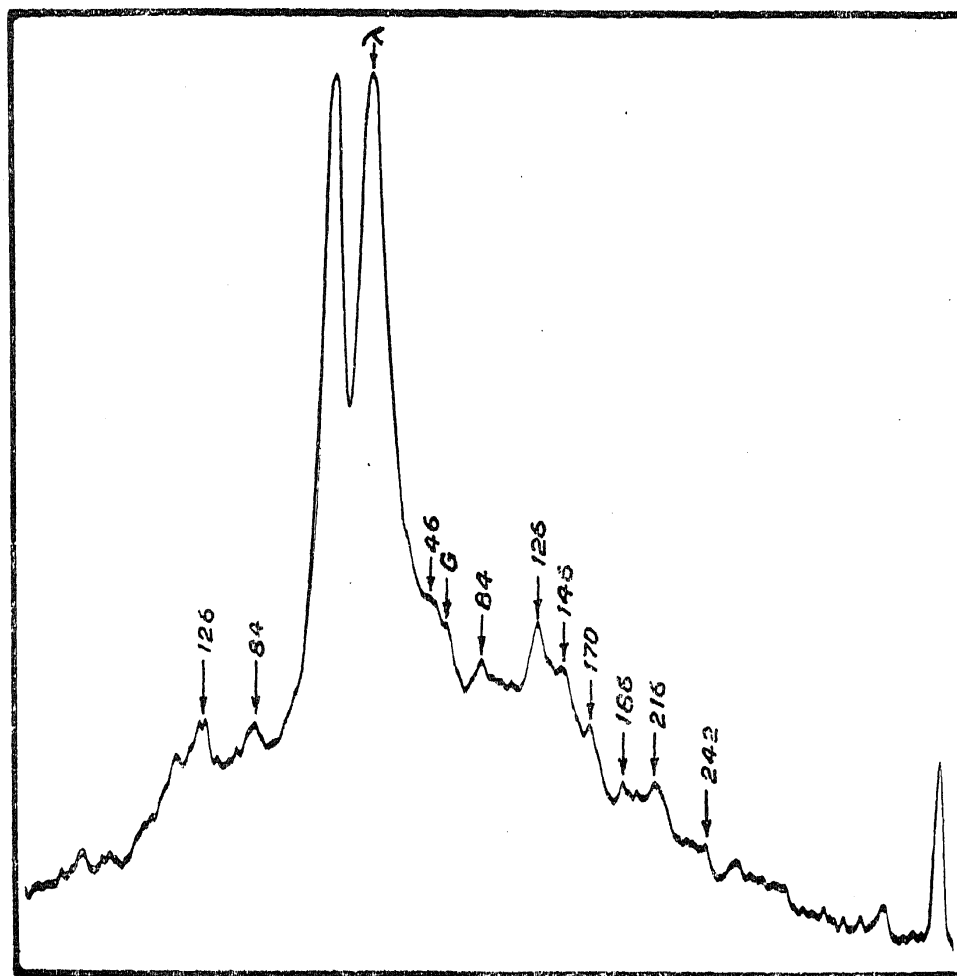


FIG. 3. Microphotometer record of the Raman spectrum of potassium bromide taken with the large quartz spectrograph.

Fig. 2 (a), evidently due to the higher dispersion and resolution of the larger spectrograph. The sharpness and discrete character of some of the Raman

lines are also evident from a scrutiny of the microphotometer record of the spectrogram taken with the large quartz spectrograph reproduced in Fig. 3.

The lines 228 and 232 cm.^{-1} appear as a single line with a mean shift of 230 cm.^{-1} in the photograph taken with the medium quartz spectrograph. In the microphotometer record of the spectrogram taken with the larger quartz spectrograph (Fig. 3) the doublet nature could be easily identified. The width of the line at 186 cm.^{-1} is partly due to presence of a mercury line separated from $\lambda 2536.5$ radiation by about 184 cm.^{-1}

Fig. 2 (c) represents the spectrum of rock-salt taken with the large quartz spectrograph and a fine slit and enlarged to the same extent as Fig. 2 (a). It is interesting to note that the discrete character of the second-order spectrum is more clearly evident in the case of potassium bromide than in the case of rock-salt. In the case of the latter, only one line at 235 cm.^{-1} stands out very prominently while in the case of the former, no less than five lines, *viz.*, 84, 126, 146, 170 and 216 cm.^{-1} appear conspicuously. In spite of the smaller values of the frequency shifts in potassium bromide, the lines do not appear bunched up as in sodium chloride, but are evenly distributed over the entire spectrum. Photographs of the Raman spectra of NaCl and KBr taken under comparable conditions with the aid of the medium quartz spectrograph suggested that the scattering power of KBr is greater than that of NaCl.

4. DISCUSSION

Crystal structures of the rock-salt type contain two interpenetrating face-centred cubic lattices. The unit cell is a rhombohedron with one metallic ion and one halogen ion contained in it. According to the new lattice dynamics, of the 48 degrees of freedom, 45 will appear as the atomic frequencies. These 45 frequencies would be reduced by degeneracy to 9 modes with distinct frequencies ν_1 to ν_9 . The detailed description of these modes are given in Table I. The expressions for the frequencies of these modes as worked out by K. G. Ramanathan (1947) using only four force constants P, P', T, T' are also included in the table. P and P' represent the forces arising from unit displacements respectively of the two types of atoms in the structure from their positions of equilibrium, while T and T' represent the forces on a given atom due to a unit displacement of a neighbouring atom of the same kind. The undashed quantities refer to the ions of mass m_1 and dashed ones to ions of mass m_2 ; $P + 8T = P' + 8T'$. The descriptions of the modes given in Table I are determined only by the crystal structure and are independent of the masses of constituent ions and of the nature of the forces in the crystalline medium. If m_1 and m_2 are the masses of the

TABLE I
The Eigenvibrations of the Rock-salt Structure

Descending Sequence of Frequency	Symbol	Degen.	Oscillating unit	Direction of motion	$4\pi^2\nu^2c^2$	Detailed description
I	ν_1	3	Cubic planes	Normal	$\frac{P-8T}{m_1} + \frac{P'+8T'}{m_2} + \frac{16(T+T')}{m_1+m_2}$	K and Br ions moving in the same phase
II	ν_2	6	Cubic planes	Tangential	$\frac{P}{m_1} + \frac{P'}{m_2} + \frac{8(T+T')}{m_1+m_2}$	K and Br ions moving in opposite phases
III	ν_3	3	Two lattices	Arbitrary	$\frac{P+8T}{m_1} + \frac{P'+8T'}{m_2}$	K and Br ions moving in opposite phases
IV	ν_4	4	Octahedral planes	Normal	$\frac{P-8T}{m_1}$	K ions moving and the Br ions at rest
V	ν_5	8	Octahedral planes	Tangential	$\frac{P+4T}{m_1}$	K ions moving and Br ions at rest
VI	ν_6	4	Octahedral planes	Normal	$\frac{P'+8T'}{m_2}$	K ions at rest and Br ions moving
VII	ν_7	8	Octahedral planes	Tangential	$\frac{P'+4T'}{m_2}$	K ions at rest and Br ions moving
VIII	ν_8	3	Cubic planes	Normal	$-\frac{16(T+T')}{m_1+m_2}$	K and Br ions in opposite phases
IX	ν_9	6	Cubic planes	Tangential	$-\frac{8(T+T')}{m_1+m_2}$	K and Br ions in the same phases

lighter and heavier ions respectively and $P, P' \gg T, T'$, Sir C. V. Raman (1947) has shown that the nine eigenvibrations arrange themselves in descending sequence of frequency in the order indicated in Table I. Before considering the case of potassium bromide in detail, it is useful to discuss the general features of the spectra of different alkali halides possessing the rock-salt structure.

Because of the high symmetry of the structure, all the nine modes will be inactive in the first order Raman effect. In the second-order Raman spectrum, the 9 octaves and 36 combinations of the primary vibration frequencies are allowed to appear. In any particular case, only the octaves and a few combinations may be expected to appear in the spectrum with any appreciable intensity. The actual magnitude of the frequency shifts and their distribution in the spectrum will be determined by the absolute and relative values of the masses of the two kinds of ions. As is to be expected, if the ions are of low atomic weight as in LiF , the frequencies will be high and conversely if the ions are heavy the frequencies will be low. If the ratio of the masses of the cation and the anion is large, the frequencies of nine modes will be such that in the resulting second-order spectrum the Raman lines would be more evenly distributed, thus enabling the discrete character of

the spectrum to be exhibited quite clearly. As the ratio of the masses is progressively decreased, the majority of the modes will have frequencies slightly different from one another and the Raman lines appear bunched together over a narrow region of frequency shifts. These conclusions are fully substantiated by the results obtained with KBr and NaCl. As the ratio of the masses of K and Br ions is greater than the ratio of Na and Cl ions, the details of the spectrum are more clearly evident in the case of KBr than in the case of NaCl [see Figs 2 (a) and 2 (c)]. If the ratio of the masses is nearly unity, *i.e.*, if $m_1 \sim m_2$ as in NaF, KCl and RbBr, the frequencies of some of the pairs of modes become identical, resulting in a perturbation of the vibrational modes. The resulting spectrum will be a complicated one. This aspect of the problem will be discussed in greater detail in a forthcoming paper on the Raman spectrum of potassium chloride.

5. CASE OF POTASSIUM BROMIDE

The nine eigenfrequencies of potassium bromide can be calculated to a first approximation with two assumed force constants only. $P = P'$ and $T = T'$. For the alkali halides P is nearly fifty times T . The force constants, for KBr may be expected to be smaller than those for NaCl and KCl (C. V. Raman, 1947). Taking $P = 2.2 \times 10^4$ dynes/cm. and $T = -0.034 \times 10^4$ dynes/cm., the frequencies have been evaluated and the values are given in Table II.

TABLE II

Eigenfrequencies of KBr

Mode	$4\pi^2\nu^2c^2$	Calculated frequency cm. ⁻¹	Observed frequency cm. ⁻¹
ν_1	$\frac{P-8T}{\mu} + \frac{32T}{m_1+m_2}$	121	121
ν_2	$\frac{P}{\mu} + \frac{16T}{m_1+m_2}$	117	116
ν_3	$\frac{P+8T}{\mu}$	112	114
ν_4	$\frac{P-8T}{m_1}$	104	108
ν_5	$\frac{P+4T}{m_1}$	95	93
ν_6	$\frac{P-8T}{m_2}$	73	73
ν_7	$\frac{P+4T}{m_2}$	67	63
ν_9	$-\frac{32T}{(m_1+m_2)}$	40	42
ν_8	$-\frac{16T}{(m_1+m_2)}$	28	23

As already indicated above, the nine eigenvibrations are inactive in the Raman effect to a first approximation. The frequency shifts recorded in the spectrum should therefore be identified as the octaves and some of the combinations of the eigenvibrations. The octaves are generally more intense than the combinations. Taking this as well as the relationships between ν_4 and ν_6 , ν_5 and ν_7 and ν_8 and ν_9 (see Table I), into consideration, the observed frequency shifts 242, 232, 228, 216, 186, 146, 126, 84 and 46 cm.^{-1} have been assigned as octaves of ν_1 , ν_2 , ν_3 , ν_4 , ν_5 , ν_6 , ν_7 , ν_8 and ν_9 . The observed values for the eigenfrequencies are entered in the last column of Table II. The agreement between the observed and calculated frequencies is satisfactory. The line at 170 cm.^{-1} may be identified as a combination of ν_4 and ν_7 . The diffuse and faint band at 287 cm.^{-1} may belong to the third-order spectrum.

The modes ν_4 and ν_5 represent oscillations of the K ions only lying in the octahedral planes, while modes ν_6 and ν_7 represent similar oscillations of the Br ions only. In the normal modes, ν_4 and ν_6 , six ions of one kind simultaneously approach or recede from an ion of the other kind, while in the tangential modes, *viz.*, ν_5 and ν_7 , two ions of one kind approach, two recede and two others remain at the same distance. Hence the changes of polarisability should be much larger in the normal modes ν_4 and ν_6 than in the tangential modes ν_5 and ν_7 . It follows, therefore, that ν_4 and ν_6 should show much stronger activity in the second-order Raman effect than ν_5 and ν_7 respectively. Experimentally it is found that octave of ν_4 (216 cm.^{-1}) is more intense than the octave of ν_5 (186 cm.^{-1}), while the octave of ν_6 (146 cm.^{-1}) is less intense than that of ν_7 (126 cm.^{-1}). The abnormally high intensity of the 126 cm.^{-1} line may be attributed to the fact that the combination of ν_4 and ν_9 falls roughly on the octave of ν_7 . Since the refractivity of the Br ions is very much larger than that of the K ions, the octaves of modes ν_6 and ν_7 may be expected to appear with greater intensity than the octaves of the corresponding modes ν_4 and ν_5 . Indeed, the octaves of ν_6 and ν_7 , *viz.*, 146 and 126 cm.^{-1} , would be the most intense lines in the spectrum. This is what is actually observed. See Fig. 1.

In modes ν_1 , ν_2 and ν_3 , the movements of the K and Br ions are similar, the two Br ions on each side of a K ion along the cube axis respectively approaching and receding from it, while the two K ions on each side of a Br ion behave similarly with respect to the latter. Each pair of neighbouring K and Br ions at the phase of their nearest approach would have polarisability greater than the value averaged over the whole period, thus giving rise to scattered radiations of double frequency. Therefore, modes ν_1 , ν_2

and ν_3 would be active more or less to the same extent and their octaves would have nearly the same intensity. This conclusion is also supported by facts.

6. THE INFRA-RED ABSORPTION SPECTRUM

The infra-red absorption spectrum of thin films of potassium bromide has been investigated by Barnes (1932). The principal absorption peak was located at $88.3 \pm 0.5 \mu$ (113 wavenumbers). Besides this, the existence of one other subsidiary maximum at about 82μ (122 wavenumbers) has been established.

Since the two interpenetrating lattices in the structure of potassium bromide consist of dissimilar particles, their oscillation against each other, *viz.*, mode ν_3 in Table I is necessarily active in infra-red absorption. The frequency of the principal infra-red absorption maximum agrees very well with the calculated value for ν_3 (see Table II). In all the other eight eigenvibrations, the phase of the motion is reversed at each successive layer, and hence if they are regarded as independent normal vibrations of the structure they should be inactive in respect of infra-red absorption. But, as has been shown by Sir C. V. Raman, owing to the anharmonicity and the finite amplitudes of oscillation, there would be sufficient coupling between the different modes to make some of the fundamentals or combinations having frequencies near about the frequency of ν_3 active in infra-red absorption. This would explain the broad character of the principal infra-red absorption maximum at 88.3μ (113 cm.^{-1}) and also the appearance of a subsidiary infra-red maximum at about 82μ (122 cm.^{-1}) corresponding to the intense Raman line at 126 cm.^{-1}

7. SUMMARY

The physical basis for the derivation of the result that any crystal has only $24p-3$ normal modes of atomic vibration, p being the number of non-equivalent atoms in the unit cell, has been briefly reviewed. The difficulties connected with the successful recording and interpretation of the spectra of the alkali halides have been pointed out. The Raman spectrum of potassium bromide excited by $\lambda 2536.5$ radiation has been recorded, using both moderate and high dispersion spectrographs. It exhibits a series of sharp Raman lines, eleven of which could be easily identified. The five most intense lines which stand out prominently in the spectrum on account of their extreme sharpness have frequency shifts 84, 126, 146, 170 and 216 cm.^{-1} . The numerical evaluation of the nine eigenfrequencies for KBr on the basis of the new lattice dynamics leads to results in good agreement with observational data. Their activities in light-scattering and infra-red absorption

are also discussed. The vibrations which are most active in Raman effect are those in which the Br ions lying in the octahedral layers alone move. This result is in general agreement with the observed facts.

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