Spectroscopic evaluation of the specific heats of potassium bromide

SIR C V RAMAN

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1. Introduction

KBr occupies a position of considerable importance amongst the alkali halides, as it is the material of the dispersing prisms commonly used for the range of wavelengths in the infra-red spectrum lying beyond the reach of rock-salt prisms. NaCl optics carries us up to $15\,\mu$, while KBr optics covers the range between 13 and $24\,\mu$ satisfactorily. The lower limit of $13\,\mu$ is set by the fact that the dispersive power becomes too small at lesser wavelengths, while the upper limit of $24\,\mu$ is determined by the fact that the loss of energy by absorption in the material of the prism becomes much too large at greater wavelengths. As has been shown in part VIII of the author's memoir on the alkali halides (reference 1), the absorption due to the infra-red activity of the principal mode of highest frequency in their structures passes successively from the first to the second, third and higher orders as we move towards shorter wavelengths, the strength of such absorption becoming rapidly weaker with increase of order. Hence, by noting the stepwise diminution in absorption with diminishing wavelength, it is possible to make a reliable estimate of the characteristic wavelength corresponding to the highest frequency of vibration of the structure.

Figure 1 shows the transmission percentages in the region of wavelengths between 17 and $24\,\mu$ of a rectangular block of KBr of the highest purity supplied by the firm of Karl Korth of Kiel, West Germany. The block was 40 mm long and 20 mm wide, and the two curves in the figure refer respectively to these two thicknesses. It will be noticed that the absorption is extremely weak at $17\,\mu$ and remains weak at $20\,\mu$, while beyond $21\,\mu$ it increases rapidly. The graphs thus indicate that the absorptions effective at 17 and $21\,\mu$ are of different orders of magnitude. If we assume that the absorption effective at $21\,\mu$ is of the fourth order, the characteristic wavelength of KBr comes out as $84\,\mu$ and its characteristic frequency expressed in wave-numbers as $119\,\mathrm{cm}^{-1}$. The reliability of this procedure is confirmed by the fact that in the case of NaCl, a similar study of the spectrophotometric records enables us correctly to locate the wavelengths corresponding to the successive orders of absorption (reference 2).
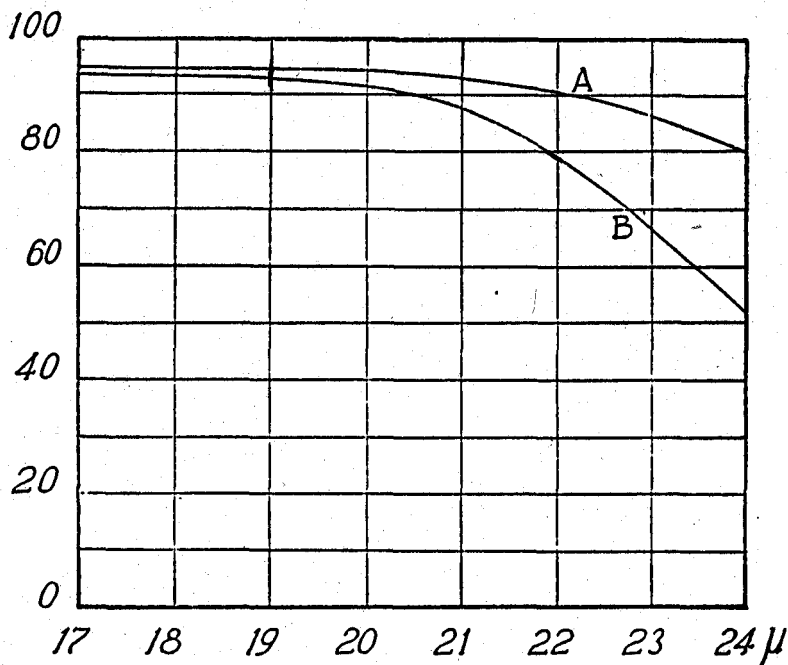
Figure 1. Infra-red transmission percentages of potassium bromide, (A) 20 mm path, (B) 40 mm path.

2. The spectrum of free vibrations

It is unnecessary here to traverse in detail, the derivation of the modes of free vibration of the structure of the alkali halides given in the memoir already quoted (reference 1). We shall therefore merely list the nine modes with their respective degeneracies as below.

Table 1 shows the four modes of coupled oscillation of the cubic layers arranged in diminishing order of frequency as indicated by the dynamical theory. The four modes of oscillation of the octahedral layers have like-wise been shown in the table arranged in the descending order of frequency amongst themselves. Obviously, however, it would be very helpful to arrange all the nine modes in a consolidated list in descending order of frequency. Part VI of the memoir already cited (reference 1) contains the theoretical considerations and numerical computations which enable this to be done. We reproduce here the computed frequencies of the nine modes arranged in descending order of frequency.

The degeneracies listed in table 2 and the description of the modes given in table 1 enable us to identify them individually. It has to be emphasised that the

Table 1

	Degeneracy
I. Oscillation of the potassium and bromine atoms in opposite phases	3
II. Coupled oscillations of the potassium and bromine atoms in the cubic planes:	
(a) Tangential to the planes in opposite phases	6
(b) Normal to the planes in the same phase	3
(c) Normal to the planes in opposite phases	3
(d) Tangential to the planes in the same phase	6
III. Oscillations of the atoms appearing in the octahedral layers:	
(a) Potassium atoms normal to the planes	4
(b) Potassium atoms tangential to the planes	8
(c) Bromine atoms normal to the planes	4
(d) Bromine atoms tangential to the planes	8
IV. Translations of all atoms in the same phase	3
Total	48

Table 2. KBr: Computed frequencies of free vibration (cm^{-1})

Degeneracy	3	6	3	4	8	4	8	3	6
Frequency	105	96	88	86	86	60	60	58	43

Table 3. KBr: Amended table of computed frequencies (cm^{-1})

Degeneracy	3	6	3	4	8	4	8	3	6
Frequency	119	108	99	97	97	68	68	66	49

computations of the frequencies as shown in table 2 do not claim any great accuracy. They have been made on the basis that only two force-constants α and β are taken into account and that those two force-constants are very simply related respectively to the bulk-modulus and to the rigidity modulus of the crystal. The neglect of all the force-constants except α and β results in making the frequencies of vibration having the degeneracies 4 and 8 which appear side by side in table 2 equal to each other, instead of the former being distinctly greater as is to be expected. In spite of these defects, the figures shown in table 2 serve as useful guides in the interpretation of the observed spectra. It has been remarked earlier

that the most strongly active mode of highest frequency has a frequency of $119\,\mathrm{cm}^{-1}$ as is indicated by the spectrophotometer records. In the light of this finding, we have to correct the frequencies listed in table 2. This may be done by increasing all the frequencies in the same proportion. The figures as thus amended are shown in table 3.

We shall presently see how the computed frequencies listed in table 3 can be made use of in the final evaluation of the spectroscopic data.

3. Activity of the modes

In part VIII of the memoir already cited (reference 1), the infra-red activities of all the nine normal modes of vibration have been discussed in detail. From the considerations there advanced, it emerges that when the electrical and mechanical anharmonicities of the vibrations are ignored, only the mode of vibration of the highest frequency can manifest itself in the absorption of infra-red radiation, while all the other eight modes are inactive. When, however, the finiteness of the amplitudes of vibration in the structural elements of the crystal is considered in conjunction with electrical anharmonicity, it emerges that the four coupled modes of vibration of the cubic layers of the crystal can be active in the absorptions of higher order, including especially that of the second-order in which they appear in the spectrum with doubled frequencies. The four modes of vibration of the octahedral layers, on the other hand, cannot exhibit such activity, for the movements involved are those of the potassium atoms only or of the bromine atoms only, normal to the layers in the modes of degeneracy 4 and tangential to them in the modes of degeneracy 8. The atomic layers of one species move symmetrically with respect to the layer of the other species of atoms located midway between them. Such symmetry results in cancelling out the electrical charge displacements even for finite amplitudes of vibration. Hence, provided the mechanical anharmonicity of the vibrations is ignored, the four octahedral modes would not display any activity as absorbers of infra-red radiation. The mechanical anharmonicity would result in certain modifications of these conclusions. These, however, do not concern us here.

In part IX of the memoir already cited (reference 1), the activity of the nine free modes of vibration of the alkali halides in the scattering of light with altered frequencies was discussed in considerable detail. It emerged that by reason of the symmetry properties of the structure, none of the nine modes can manifest itself as a frequency shift in the scattering of monochromatic light traversing the crystal. On the other hand, it was shown that all the nine modes could manifest themselves with *doubled* frequency, thus opening the way to the complete determination of the frequency spectrum from the spectrum of light scattering.

It is, however, important to remark that we cannot expect all the nine doubled frequency shifts corresponding to the different free modes of vibration to be

recorded with equal intensities in the spectrum of the scattered light. There are several considerations to be borne in mind in this connection. Firstly, we have to take note of the degeneracies of the respective modes. Apart from all other factors, the greater the degeneracy, in other words, the larger the number of distinct modes having the same frequency, the greater the intensity with which the modes would be recorded as a shift with doubled frequencies. In consequence, we may expect the two modes of degeneracy 8 to record themselves with notable intensities and the two modes of degeneracy 6 to follow them next in order, while the two modes of degeneracy 4 and the three modes of degeneracy 3 would have lesser intensities.

A second factor of importance in determining the strength with which particular frequency shifts would be recorded is the symmetry of the modes of vibration concerned. As has already been remarked, the four modes of vibration of the octahedral layers are of symmetric type, two layers of one atomic species moving in opposite phases and the intermediate layer of atoms of the other species remaining at rest. It is because of such symmetry that these modes do not display any infra-red activity even when the vibrations are of finite amplitude. It is well known that, in general, symmetric modes of vibration which do not exhibit infra-red activity are those which record themselves most strongly as frequency shifts in light-scattering and *per contra*, antisymmetric modes which exhibit strong infra-red activity fail to manifest themselves as frequency shifts in the light-scattering. On general grounds, therefore, we shall be justified in expecting that there would be a marked difference between the octahedral symmetric modes and the cubic antisymmetric modes in respect of their recorded intensities as doubled frequency shifts, the former being recorded more strongly than the latter.

Thirdly, we have also to consider the nature of the individual modes. Since we are concerned with the second-order scattering of double frequency, movements which involve a closer approach to each other of neighbouring atoms, in other words, involve a greater measure of optical inharmonicity, would give rise to greater intensity of light-scattering than the modes in which the approaches are less close. The two modes in which adjacent potassium and bromine atoms move together in the same phase and hence approach each other less closely would, therefore, manifest themselves more weakly than the two other modes in which they oscillate in opposite phases.

Finally, we have also to take note of the great difference in the refractivity of the two species of atoms with which we are concerned. The bromine atoms have a greater refractivity than the potassium atoms. Hence the two modes in which the former alone approach or recede from each other may be expected to record themselves as frequency shifts more strongly than the corresponding modes in which the potassium atoms alone oscillate with respect to each other.

We may sum up the foregoing remarks by the following statements. The observed frequency shifts would divide themselves into two groups differing in their intensities, the six having degeneracies of 8, 6 or 4 being of greater intensity

and the three others with degeneracy 3 of a smaller intensity. In the first group, the modes of degeneracy 8 would appear more strongly than those of degeneracy of 4, and amongst these again, the modes in which the bromine atoms alone oscillate would be recorded more strongly than those in which the potassium atoms alone oscillate. In the second group of riply degenerate oscillations, that having the lowest frequency would appear much more feebly than the other two.

4. The spectrum of light scattering

As has already been explained in part IX of the memoir already cited (reference 1), the fact that the frequency shifts in light scattering recorded with the alkali halides are only those of the second-order gives rise to special difficulties in experiment-ation. These can only be overcome by use of material of the highest quality and guarding against the several pitfalls which await the unwary experimenter. For this reason and the importance of obtaining complete data which could be absolutely relied upon, it appeared necessary to undertake a fresh and independent investigation at this Institute of the case of potassium bromide. This was made with the block of perfectly pure KBr supplied by Karl Korth mentioned earlier.

The well known technique was employed in which a water-cooled magnet-controlled mercury arc in quartz illuminates the crystal. A filter of mercury vapour put inside the spectrograph prevents the photographic plate being fogged by the intense resonance radiation entering the instrument. The crystal block was placed as close as possible to the quartz tube containing the arc, the latter being kept pressed against the side of the tube nearest the crystal by the action of the magnetic field. An excessive heating of the crystal was avoided by a current of air kept blowing on it throughout the exposure. To obtain a well-exposed picture with KBr, an exposure of eight hours was found to be necessary, using the medium-size quartz spectrograph.

It should be emphasised that the filter of mercury vapour inside the instrument cuts out only the core of the resonance radiation. In the spectrum recorded with an eight-hour exposure, the rest of the radiation emitted by the mercury vapour and entering the spectrograph in whatever fashion would necessarily appear. Its intensities would naturally be greatest in the spectral regions not far removed from the position of the resonance radiation. As a matter of actual experience, the resulting continuum appears more conspicuously in the region of greater wavelengths and therefore of lower frequencies than the resonance radiation. The failure to recognise the presence and actual origin of this continuum is one of the pitfalls awaiting the experimenter in this field. It should be noted that Rasetti who devised the technique employed fell into the same error and made the mistake of identifying the continuum as part of the effect under study by him in the case of rock-salt.

Since the frequency shifts in the cases of KBr are substantially smaller than in the case of NaCl, the overlap with the continuous radiation of the mercury arc might have had serious consequences. Fortunately, however, the refractive index of KBr is higher than that of NaCl and hence its scattering power is much greater. Thus, the presence of the continuous background does not actually interfere with the possibility of recognising the significant features in the recorded spectrum of KBr.

5. The recorded spectral shifts

The spectrum of KBr recorded with the arrangements described above and an eight-hour exposure is reproduced as figure 1 in plate I. The observed frequency shifts have been marked in figure 2 in plate II. Both positive and negative frequency shifts appear in the recorded spectra, thus affording a welcome confirmation of their reality and enabling them to be identified without any possibility of error. The spectrum of the arc is reproduced alongside that KBr in plate I for comparison with it. The continuum referred to above can be recognised in it.

A visual examination of the recorded spectrum shows three sharply defined lines which are clearly resolved from each other, their frequency shifts being respectively 122, 142 and $169 \, \text{cm}^{-1}$ respectively. Of these, the first is the most intense and is accordingly identified as arising from the eight-fold degenerate oscillation of the bromine atoms. The second has likewise been identified as arising also from the oscillation of the bromine atoms with a degeneracy 4. The third line is ascribable to the eightfold degenerate oscillations of the potassium atoms.

The two other features which appear conspicuously in the spectrum as well-defined lines exhibit frequency shifts of 85 and $215 \, \text{cm}^{-1}$ respectively. The latter is clearly ascribable to the sixfold degenerate coupled oscillations of the potassium and bromine atoms in the cubic layers. The frequency shifts of $\pm \, 85 \, \text{cm}^{-1}$ are also sharp and clear, the positive shift which is less disturbed by the overlapping continuum being especially sharp and clear. This is recognized as the mode of oscillation with degeneracy 6 having the lowest frequency. The shift of $240 \, \text{cm}^{-1}$ recorded in the spectrum is distinctly diffuse and therefore rather weak. It has been identified as the mode of oscillation with degeneracy three and having the highest frequency. Adjacent to the frequency shift of $215 \, \text{cm}^{-1}$ appears a diffuse band which is clearly a superposition of two frequency shifts. These have been identified as due to the oscillation of degeneracy 4 with a frequency shift of $196 \, \text{cm}^{-1}$ and an oscillation of degeneracy 3 with a frequency shift of $184 \, \text{cm}^{-1}$.

Finally, between the sharply defined lines at $85 \, \text{cm}^{-1}$ and $122 \, \text{cm}^{-1}$, there appears a weak line recorded with frequency shifts of $\pm \, 140 \, \text{cm}^{-1}$. This has been

identified as the triply degenerate oscillation of the potassium and bromine in the cubic layers.

All these features can also be recognized in the reproduced spectra. They have been entered below in table 4.

Table 4. Observed frequency shifts and their identification (cm^{-1})

Degeneracy	3	6	3	4	8	4	8	3	6
Observed shifts	240	215	184	196	169	142	122	104	85
Halved values	120	108	92	98	85	71	61	52	42
Computed values (table 3)	119	108	99	97	97	68	68	66	49

6. Computation of the specific heats

It will be seen from table 4 that there is a satisfactory general agreement between the spectroscopically determined frequencies and those dynamically computed a priori and shown in table 3. The identifications of the spectroscopically determined frequencies with the different modes of known degeneracies have not been arbitrarily made, but are based on considerations of both frequency and intensity as set out earlier. We can, therefore, confidently proceed to an evaluation of the specific heats of KBr as a function of the temperature on the basis of the spectroscopically determined frequencies.

Table 5 shows the details of the computation which follows the same lines as those adopted in numerous cases in the later chapters of the memoir already cited (reference 1). It is, therefore, unnecessary to explain the procedure here in detail. A comparison between the observed and computed specific heats is made at the foot of table 5. The general trend of the temperature dependence of the specific heat is clearly indicated by the theoretical computations. Quantitatively, however, the agreement can by no means be considered satisfactory. The reason for this is not far to seek. In the actual recording of the spectrum of the light scattered by the crystal, the latter was distinctly warmed up by the heat emanating from the mercury arc and its temperature was about 350° K. On the other hand, the experimentally determined specific heats cover the temperature range between 10 and 200° K, the most rapid variation being in the temperature range 20 and 60° K. Hence, to obtain a satisfactory representation of the specific heat data on the basis of the spectroscopically determined frequencies, the latter should have been recorded with the crystal held at about 40° K instead of at 350° K as was actually the case. It can by no means be supposed that the spectrum of free vibrations of the lattice would remain unaltered as between such widely different temperatures.

Table 5. Comparison of the computed and observed values of the atomic heats of potassium bromide

	10° K	15° K	20° K	40° K	60° K	80° K	100° K	150° K	200° K
3E(120)	—	0·0004	0·0045	0·0918	0·1913	0·2534	0·2903	0·3324	0·3491
6E(108)	—	0·0023	0·0175	0·2339	0·4312	0·5443	0·6073	0·6805	0·7071
4E(98)	0·0001	0·0033	0·0200	0·1887	0·3161	0·3827	0·4198	0·4606	0·4761
3E(92)	0·0001	0·0039	0·0205	0·1567	0·2491	0·2958	0·3213	0·3486	0·3587
8E(85)	0·0006	0·0174	0·0777	0·4713	0·7031	0·8158	0·8738	0·9377	0·9616
4E(71)	0·0017	0·0237	0·0758	0·2920	0·3891	0·4330	0·4544	0·4772	0·4854
8E(61)	0·0108	0·0934	0·2353	0·6689	0·8299	0·8964	0·9297	0·9646	0·9770
3E(52)	0·0108	0·0613	0·1265	0·2780	0·3265	0·3455	0·3549	0·3644	0·3680
6E(43)	0·0556	0·2053	0·3472	0·6088	0·6805	0·7080	0·7204	0·7339	0·7398
3D(43)	0·0905	0·1775	0·2381	0·3302	0·3525	0·3612	0·3650	0·3690	0·3705
Calculated C_v	0·1702	0·5885	1·1613	3·3203	4·4693	5·0361	5·3369	5·6689	5·7933
Experimental C_v	0·116	0·390	0·802	2·650	3·934	4·663	5·076	5·572	5·771

Experimental values from Berg, W T and Morrison, J A, *Proc. R. Soc. (Lond.)* **A242**, 471 (1957).

Table 6 shows a fresh computation of the specific heats of potassium bromide in which all the observed spectral frequencies have been increased uniformly by 10 per cent of their values. An increase of this magnitude is justifiable in view of what is known regarding the temperature changes of the low-lying lattice frequencies of various crystals, such as calcite and quartz, which have been determined by studies on light-scattering with the crystals held at liquid air and at room temperatures respectively. The increase of 10 per cent made also appears fully justified in view of our knowledge of the great increases in the elastic constants of the alkali halides and especially of their bulk moduli which occur when they are cooled down to very low temperatures.

Table 6. Comparison of the computed and observed values of the atomic heats of potassium bromide

	10° K	15° K	20° K	40° K	60° K	80° K	100° K	150° K	200° K
3E(132)	—	0·0002	0·0023	0·0713	0·1681	0·2345	0·2755	0·3253	0·3449
6E(119)	—	0·0009	0·0095	0·1879	0·3875	0·5103	0·5821	0·6662	0·6993
4E(108)	—	0·0015	0·0117	0·1560	0·2874	0·3629	0·4049	0·4537	0·4714
3E(101)	—	0·0019	0·0128	0·1339	0·2301	0·2830	0·3119	0·3439	0·3558
8E(94)	0·0002	0·0089	0·0491	0·4040	0·6530	0·7825	0·8512	0·9269	0·9544
4E(78)	0·0007	0·0144	0·0547	0·2639	0·3707	0·4208	0·4462	0·4732	0·4832
8E(67)	0·0053	0·0623	0·1813	0·6183	0·7994	0·8770	0·9170	0·9585	0·9733
3E(57)	0·0063	0·0453	0·1038	0·2628	0·3178	0·3408	0·3516	0·3630	0·3669
6E(47)	0·0368	0·1645	0·3030	0·5869	0·6693	0·7003	0·7158	0·7316	0·7382
3D(47)	0·0744	0·1575	0·2204	0·3231	0·3491	0·3588	0·3636	0·3683	0·3701
Calculated C_v	0·1237	0·4574	0·9486	3·0081	4·2324	4·8709	5·2198	5·6106	5·7575
Experimental C_v	0·116	0·390	0·802	2·650	3·934	4·663	5·076	5·572	5·771

Experimental values from Berg, W T and Morrison, J A, *Proc. R. Soc. (Lond.)* **A242**, 471 (1957).

A satisfactory agreement between the computed and observed values of specific heat emerges from the figures shown at foot of table 6. There is thus little doubt that the discrepancies noticed in table 5 have the origin indicated above.

Summary

The spectrum of free vibrations of the structure of potassium bromide is determined spectroscopically from the scattering within the crystal of the resonance radiation of the mercury arc. The modes are recorded with doubled frequency shifts. The identification of these shifts as arising from the various modes of vibration is made on the basis of the frequencies as computed a priori from the dynamic theory and from a consideration of their observed spectral intensities. From these spectral frequencies, the specific heat of the crystal can be evaluated as a function of the temperature. When the variations with temperature of the vibration frequencies are taken into account, a satisfactory agreement emerges between the theoretically computed and experimentally observed specific heat data.

References

1. Memoirs of the Raman Research Institute No. 131 and *Proc. Indian Acad. Sci.* **A56** 1 (1962).
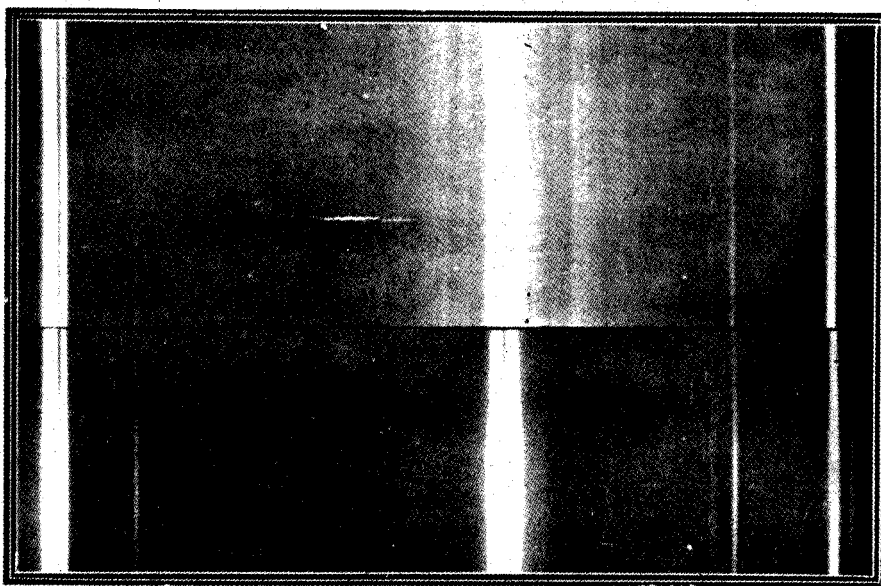2. Memoirs of the Raman Research Institute No. 128 and *ibid* **A54** 253 (1961).

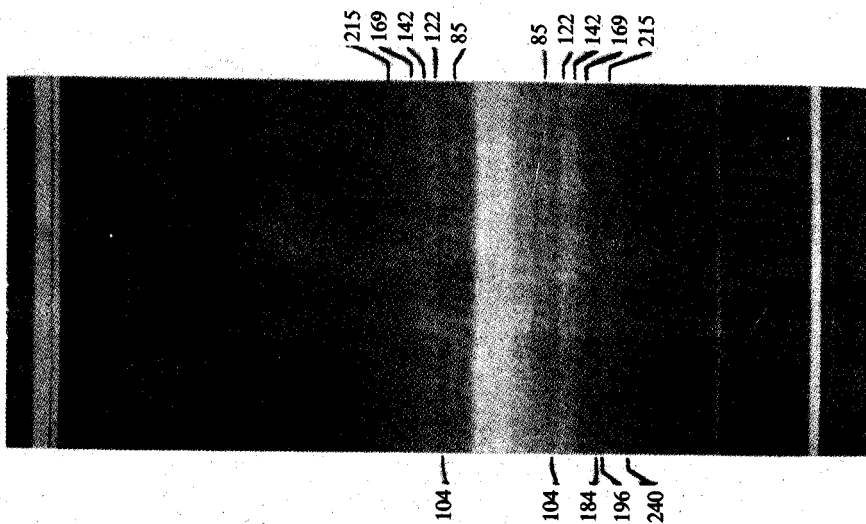**Figure 1.** KBr: Frequency shifts in light scattering.

Plate I

Figure 2. KBr: Frequency shifts in light scattering.

Plate II