

# THE SPECIFIC HEATS OF THE ALKALI HALIDES AND THEIR SPECTROSCOPIC BEHAVIOUR

## Part VI. The Atomic Vibration Spectra

BY SIR C. V. RAMAN

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THE preceding parts of this memoir have been devoted to a development of the theory of the vibration spectra of the alkali halides. We have considered the geometry of the free modes of atomic vibration, as also the degeneracies arising from the symmetry of the crystal and shown how the frequencies of vibration may be expressed in terms of certain force-constants and the latter again determined from the elastic moduli of the crystal. The success of the theory was illustrated by reference to the particular case of rock-salt, the behaviour of which is known experimentally. We proceed to consider the cases of all the alkali halides comprehensively, following the same procedures.

The expressions for the frequency of atomic vibration as simplified and tabulated in Part V of the memoir contain four quantities which differ from halide to halide, *viz.*, the atomic weights  $m_1$  and  $m_2$  of the metal and halogen atoms respectively and the force-constants  $\alpha$  and  $\beta$ . The latter are measures of the restoring forces arising respectively from a longitudinal and a transverse displacement of adjacent metal and halogen atoms in the crystal relatively to each other. As has been shown in the preceding part of the memoir, these force-constants can be equated to the product of the bulk-modulus and the shear-modulus respectively with the distance  $d$  between the adjoining metal and halogen atoms in the crystal. The quantity  $m_1 m_2 / (m_1 + m_2)$  designated as  $\mu$  or the reduced mass appears in several of the frequency expressions. Accordingly in Table I, these five quantities, *viz.*,  $m_1$ ,  $m_2$ ,  $\mu$ ,  $\alpha$ ,  $\beta$  have been entered in the successive columns of the Table for all the sixteen halides.

The following remarks may be made regarding the entries appearing in the Table. The reduced mass  $\mu$  is necessarily smaller than either  $m_1$  or  $m_2$ . When  $m_1$  and  $m_2$  differ greatly,  $\mu$  approximates pretty closely to whichever of them is the smaller. This is the case for all the lithium halides, as also for the bromide and iodide of sodium and for rubidium fluoride.

TABLE I  
*Atomic Weights and Force-Constants*

Substance	$m_1$	$m_2$	$\frac{m_1 m_2}{m_1 + m_2}$	$\alpha$ (dynes/cm.)	$\beta$ (dynes/cm.)
LiF ..	6.94	19.0	5.08	$1.399 \times 10^4$	$1.270 \times 10^4$
LiCl ..	6.94	35.5	5.80	$0.811 \times 10^4$	$0.640 \times 10^4$
LiBr ..	6.94	79.9	6.39	$0.704 \times 10^4$	$0.524 \times 10^4$
LiI ..	6.94	127.0	6.58	$0.566 \times 10^4$	$0.405 \times 10^4$
NaF ..	23.0	19.0	10.40	$1.121 \times 10^4$	$0.647 \times 10^4$
NaCl ..	23.0	35.5	13.95	$0.709 \times 10^4$	$0.359 \times 10^4$
NaBr ..	23.0	79.9	17.86	$0.625 \times 10^4$	$0.294 \times 10^4$
NaI ..	23.0	127.0	19.47	$0.520 \times 10^4$	$0.233 \times 10^4$
KF ..	39.1	19.0	12.79	$0.849 \times 10^4$	$0.341 \times 10^4$
KCl ..	39.1	35.5	18.59	$0.571 \times 10^4$	$0.199 \times 10^4$
KBr ..	39.1	79.9	26.25	$0.510 \times 10^4$	$0.168 \times 10^4$
KI ..	39.1	127.0	29.90	$0.437 \times 10^4$	$0.134 \times 10^4$
RbF ..	85.5	19.0	15.55	$0.769 \times 10^4$	$0.256 \times 10^4$
RbCl ..	85.5	35.5	25.07	$0.533 \times 10^4$	$0.156 \times 10^4$
RbBr ..	85.5	79.9	41.30	$0.474 \times 10^4$	$0.132 \times 10^4$
RbI ..	85.5	127.0	51.09	$0.407 \times 10^4$	$0.103 \times 10^4$

The magnitudes of both the force-constants  $\alpha$  and  $\beta$  diminish progressively in the sequence of increased atomic weight of the alkali metal as well as of the halogen. For any particular alkali metal, the force-constants for the fluoride are conspicuously the highest, the differences between the other halides being considerably smaller. A similar situation was remarked for the elastic moduli, but the differences are rather less conspicuous for the force-constants, since the elastic moduli now appear multiplied by the length  $d$  which increases progressively in either of the two sequences,

When we compare the variation of the two force-constants  $\alpha$  and  $\beta$  from halide to halide, it is seen that  $\beta$  changes more rapidly than  $\alpha$ . Indeed, while  $\alpha$  and  $\beta$  are of the same order of magnitude for lithium fluoride,  $\beta$  becomes rapidly the smaller of the two as we go down the Table. While  $\beta$  is roughly about one-half of  $\alpha$  for sodium chloride, it is only about one-fourth for rubidium iodide.

The results of the calculation of the nine frequencies for all the alkali halides are listed in Table II. The degeneracies entered at the top of the

TABLE II  
*Calculated Wave-Numbers of the Normal Modes (in  $\text{cm}^{-1}$ )*

De- gene- racies	3	6	3	4	8	4	8	3	6
LiF ..	514	454	450	440	440	266	266	249	241
LiCl ..	350	326	322	320	320	142	142	137	128
LiBr ..	305	295	293	293	293	86	86	84	78
LiI ..	267	261	260	260	260	61	61	60	55
NaF ..	281	241	210	208	208	189	189	187	144
NaCl ..	187	164	146	146	146	117	117	117	91
NaBr ..	152	140	134	134	134	72	72	72	59
NaI ..	131	124	121	121	121	51	51	51	42
KF ..	202	182	167	166	166	116	116	114	87
KCl ..	133	119	102	96	96	92	92	85	60
KBr ..	105	96	88	86	86	60	60	58	43
KI ..	90	84	80	79	79	44	44	42	32
RbF ..	167	158	152	151	151	71	71	69	55
RbCl ..	103	95	89	87	87	56	56	53	39
RbBr ..	78	71	63	56	56	54	54	47	33
RbI ..	64	59	53	49	49	40	40	36	26

Table enable us to identify the different modes. The first entry is that of the triply degenerate oscillation of the metal and halogen atoms against each other in opposite phases. In the case of the other frequencies, a degeneracy of six indicates a coupled oscillation of atoms in the cubic planes tangential to those planes, one of them having the second highest frequency and the other being the lowest. A degeneracy of three indicates a coupled oscillation of the atoms in the cubic planes normal to those planes. It will be noticed that of the two frequencies with this degeneracy, one is much greater than the other. A degeneracy of four indicates the frequency of the oscillations of the atoms in the octahedral layers normal to those layers, while a degeneracy of eight represents the frequency of an oscillation tangential to those layers. These two frequencies for these atoms which have the lower atomic weight are shown first. They are followed by the two frequencies of the atoms with the higher atomic weight.

The very high frequencies of atomic vibration for lithium fluoride are a striking feature of the results of calculation exhibited in Table II. They are a consequence, partly of the low atomic weights of both metal and halogen, and partly of the great strength of the binding between them in this compound. The spectroscopic behaviour of lithium fluoride formed the subject of a recent investigation by the present author (Reference 1). The experimental results showed the highest frequency of vibration of the structure to be  $508 \text{ cm.}^{-1}$  which is in gratifyingly close agreement with the theoretically calculated value of  $514 \text{ cm.}^{-1}$  shown in Table II. The nine frequencies of lithium fluoride as then found and as now calculated are exhibited in Table III. The calculated values, being based on the simplified formulæ, necessarily differ from the observed values for those modes in which the neglected force-constants  $\phi$  and  $\psi$  play a significant role.

TABLE III  
*Frequencies of Lithium Fluoride (in  $\text{cm.}^{-1}$ )*

Degeneracies	3	6	3	4	8	4	8	3	6
Calculated ..	514	454	450	440	440	266	266	249	241
Observed ..	508	417	384	435*	435*	263*	263*	210	210

\* Calculated from the observed highest frequency of  $508 \text{ cm.}^{-1}$

A scrutiny of the frequencies for all the halides as calculated and listed in Table II shows a significant but not unexpected feature, viz., that when the

atomic weights of metal and halogen differ greatly, the five highest frequencies form a group which do not differ much from each other and stand apart from the other four frequencies which are much lower. The reason is that the three highest frequencies are those of coupled modes of vibration. When the masses of metal and halogen are very different, the lighter atoms oscillate in the mode of higher frequency while the heavier atoms remain nearly at rest: in the mode of lower frequency, the situation is reversed. Thus, the first five modes listed in the Table would have a frequency determined principally or solely by the mass of the lighter atom, while the other four modes would have a frequency determined principally or solely by the mass of the heavier atom. As Table II shows, such a situation arises in the cases of all the lithium halides, sodium bromide, sodium and potassium iodides and rubidium fluoride.

Cases of special interest are those in which the metal and halogen atoms have nearly equal atomic weights, *viz.*, potassium chloride and rubidium bromide. On the basis of the simplified formulæ, the oscillations of both species of atoms appearing in the octahedral layers, either normal or tangential to those layers, would have nearly the same frequencies. This situation would be altered when the force-constants  $\phi$  and  $\psi$  are taken into account in the calculations. We should nevertheless expect all the four frequencies to approximate to each other and stand apart from those of the modes of higher and lower frequencies.

Finally, we have the cases in which the atomic weights of metal and halogen are neither very close to each other, nor yet very different. The frequencies would then be distributed more or less uniformly over the spectrum instead of being clustered together into groups. Sodium chloride, potassium fluoride and potassium bromide are such cases.

#### SUMMARY

The frequencies of the nine normal modes of atomic vibration have been tabulated for all the sixteen alkali halides. The results of the calculation are in striking accord with the results of the spectroscopic studies in the two leading cases of lithium fluoride and sodium chloride respectively. The manner in which the structure of the vibration spectra varies with the relative weights of the atoms of metal and halogen is described and discussed.

#### REFERENCE

1. Raman, C. V. .. *Proc. Ind. Acad. Sci.*, 1962, **55 A**, 131-52.