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The specific heats of the alkali halides and their spectroscopic behaviour—Part IV. The equations of motion

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The number and nature of the normal modes of atomic vibration have been discussed in part II of this memoir, while it has been shown in part III that the forces of atomic interaction coming into play during such vibrations may be expressed in terms of five constants, viz., α, β, γ, ϕ and ψ, which between them take account of the interactions between each atom and its twenty-six nearest neighbours in the crystal. Reasons were stated indicating that the most important of them are α and β which express the magnitude of the forces arising when adjacent metal and halogen atoms are displaced with respect to each other respectively along and transverse to the line of their join.

It is now possible to write down and solve the equations of motion for each of the nine normal modes of vibration. It is to be noted that in these modes, the displacements of equivalent atoms appearing in the equations are the same, only their phases being either the same or opposite, and that in each unit cell of the crystal there are only two non-equivalent atoms. The movements of the two species of atoms are coupled with each other in the triply-degenerate principal mode of vibration and also in the four modes of vibration of the atoms appearing in the cubic layers of the structure. Hence, in their cases, we have only two equations of motion which have simultaneously to be solved. But in the four modes of vibration of the octahedral layers, either only the metal atoms or only the halogen atoms oscillate and hence we have only one equation to be written down and solved for each of these four modes. It may also be remarked that in all cases, the *relative* displacements of equivalent atoms are either zero or double their actual displacements according as their phases of vibration are the same or opposite. An important consequence of this is that the frequency of the principal mode of vibration in which the atoms of each species oscillate together is determined only by the three constants α, β and γ, the other two constants, viz., ϕ and ψ not appearing in the equations of motion.

We may denote the masses of the metal and halogen atoms respectively by m_1 and m_2 and the components of their displacements along the three cubic axes respectively by ξ_1, ξ_2 and η_1, η_2, and ζ_1, ζ_2. The equations of motions for the principal mode of vibration are accordingly

$$\frac{m_1 d^2\xi_1}{dt^2} = (2\alpha + 4\beta + 8\gamma)[\xi_2 - \xi_1]$$

$$\frac{m_2 d^2\xi_2}{dt^2} = (2\alpha + 4\beta + 8\gamma)[\xi_1 - \xi_2]$$

with similar but independent equations for the other two pairs of components. We assume ξ_1 and ξ_2 to be time-periodic and proportional to $\sin \omega_1 t$. Solving the equations, we find that the frequency of the vibration is given by the formula

$$\omega_1^2 = \frac{F}{\mu},$$

where F is an abbreviation for $(2\alpha + 4\beta + 8\gamma)$, and μ is the reduced mass given by the formula

$$\frac{1}{\mu} = \frac{1}{m_1} + \frac{1}{m_2}.$$

Considering next the oscillations of the metal atoms in the octahedral layers *normally* to those layers and alternating in phase from layer to layer, the relevant equation of motion is

$$\frac{m_1 d^2\xi_1}{dt^2} = -(F + 16\phi)\xi_1$$

with two similar equations for the displacements η_1 and ζ_1 which appear simultaneously. Accordingly, the frequency of this mode is given by

$$\omega_2^2 = \frac{(F + 16\phi)}{m_1}.$$

The equations for an oscillation of the metal atoms in the octahedral layers in any direction *tangential* to those layers may similarly be written down and solved. The frequency ω_3 of the oscillation is given by the formula

$$\omega_3^2 = \frac{(F + 4\phi)}{m_1}.$$

As is to be expected, the formulae indicate that the vibrations normal to the octahedral layers have the higher frequency. Proceeding similarly, we obtain for the frequencies ω_4 and ω_5 of the oscillations of the halogen atoms in the octahedral layers in directions respectively normal and tangential to those layers, the expressions

$$\omega_4^2 = \frac{(\mathrm{F} + 16\psi)}{m_2}$$

$$\omega_5^2 = \frac{(\mathrm{F} + 4\psi)}{m_2}.$$

It will be noticed that the frequencies ω_2 and ω_3 and likewise also ω_4 and ω_5 differ from each other solely by reason of the fact that in these modes, the atoms of the same species oscillate in opposite phases in the successive layers of the structure and hence interact with each other. If the force-constants ϕ and ψ are left out from the expressions for the frequencies, the normal and tangential modes would have identical frequencies and would also be very simply related to each other in the following manner:

$$\omega_1 = \frac{\mathrm{F}}{\mu}, \quad \omega_2 = \omega_3 = \frac{\mathrm{F}}{m_1}, \quad \omega_4 = \omega_5 = \frac{\mathrm{F}}{m_2}.$$

We have next to consider the coupled oscillations of the metal and halogen atoms appearing in the cubic layers of the structure *tangentially* to those layers, the phases alternating from layer to layer. The equations of motion which have simultaneously to be satisfied are

$$\frac{m_1 d^2\eta_1}{dt^2} = -(\mathrm{F} + 8\phi)\eta_1 + (\mathrm{F} - 4\beta - 16\gamma)\eta_2$$

$$\frac{m_2 d^2\eta_2}{dt^2} = (\mathrm{F} - 4\beta - 16\gamma)\eta_1 - (\mathrm{F} + 8\psi)\eta_2.$$

The frequencies of vibration are given by the pair of roots of the equation obtained by assuming η_1 and η_2 to be time-periodic and eliminating them from the equations. The formula thus obtained is

$$\omega^4 - \omega^2\Omega_1^2 + \pi_1 = 0$$

where

$$\Omega_1^2 = \left[\frac{(\mathrm{F} + 8\phi)}{m_1} + \frac{(\mathrm{F} + 8\psi)}{m_2}\right]$$

and

$$\pi_1 = \left[\frac{(\mathrm{F} + 8\phi)(\mathrm{F} + 8\psi) - (\mathrm{F} - 4\beta - 16\gamma)^2}{m_1 m_2}\right].$$

The two roots of this equation are

$$\omega_6^2 = \tfrac{1}{2}\Omega_1^2 + (\tfrac{1}{4}\Omega_1^4 - \pi_1)^{1/2}$$

$$\omega_7^2 = \tfrac{1}{2}\Omega_1^2 - (\tfrac{1}{4}\Omega_1^4 - \pi_1)^{1/2}.$$

It is evident that ω_6 would be the higher of the two frequencies. It corresponds to the case in which the metal and halogen atoms in any one cubic layer oscillate in opposite phases; ω_7, on the other hand, would be the frequency of the vibration in which they oscillate in the same phase, and the restoring forces brought into play are therefore quite small.

Finally, we consider the coupled oscillations of the metal and halogen atoms *normal* to the cubic layers with phases alternating from layer to layer. The equations of motion simultaneously to be satisfied are

$$\frac{m_1 d^2\xi_1}{dt^2} = -(\mathrm{F}+16\phi)\xi_1 - (\mathrm{F}-8\beta)\xi_2$$

$$\frac{m_2 d^2\xi_2}{dt^2} = -(\mathrm{F}-8\beta)\xi_1 - (\mathrm{F}+16\psi)\xi_2.$$

Assuming ξ_1 and ξ_2 to be time-periodic and eliminating them from the equations, we obtain the formula

$$\omega^4 - \omega^2\Omega_2^2 + \pi_2 = 0$$

where

$$\Omega_2^2 = \left[\frac{(\mathrm{F}+16\phi)}{m_1} + \frac{(\mathrm{F}+16\psi)}{m_2}\right]$$

and

$$\pi_2 = \left[\frac{(\mathrm{F}+16\phi)(\mathrm{F}+16\psi) - (\mathrm{F}-8\beta)^2}{m_1 m_2}\right].$$

The two roots of this equation are

$$\omega_8^2 = \tfrac{1}{2}\Omega_2^2 + [\tfrac{1}{4}\Omega_2^4 - \pi_2]^{1/2}$$
$$\omega_9^2 = \tfrac{1}{2}\Omega_2^2 - [\tfrac{1}{4}\Omega_2^4 - \pi_2]^{1/2}.$$

It is evident that ω_8 would be greater than ω_9. The former gives the frequency of the vibration in which the metal and halogen atoms in any cubic layer oscillate in the same phase, while ω_9 is the frequency of a similar vibration in which they oscillate in *opposite* phases. The restoring forces in these modes arise principally from the interactions of the metal and halogen atoms appearing in the adjacent layers.

Comparing the formulae for the four frequencies ω_6, ω_7, ω_8, ω_9, it is evident that π_2 is greater than π_1. Hence, these four frequencies when arranged in a descending order of magnitude would appear on the sequence $\omega_6 > \omega_8 > \omega_9 > \omega_7$. This is the order in which the four modes were listed in part II of the memoir.

Summary

Explicit formulae are obtained for the frequencies of the nine normal modes of vibration in terms of the five force-constants α, β, γ, ϕ and ψ. The formulae show that the principal mode in which the metal and halogen atoms oscillate with opposite phases has also the highest frequency of vibration. The formulae also enable the four octahedral modes and the four cubic modes to be arranged amongst themselves in a descending order of frequency.