

The dynamics of the fluorite structure and its infra-red behaviour—Part III. Activity of the normal modes

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In the preceding part of the memoir it has been shown that the fluorite structure has fourteen different monochromatic frequencies of vibration. Two of these may be designated as the principal frequencies, since the vibrational modes repeat themselves in adjoining cells of the structure without change of phase. The remaining twelve may be referred to as the subsidiary frequencies, since in these vibrations, the phase of the vibration is reversed as we pass from cell to cell along one, two, or all three axes of the structure. For an evaluation of the thermal energy of the crystal as a function of the temperature, as also for a complete determination of its spectroscopic behaviour, a knowledge of all the fourteen frequencies is necessary. For the theoretical evaluation of these frequencies to be possible, the force-constants which determine the magnitude of the interactions between neighbouring atoms arising from their relative displacements should be known. Since, however, our immediate purpose is the interpretation of the observed spectroscopic behaviour of the crystal, the problem of evaluating the frequencies will be deferred for later consideration and we shall proceed to discuss the activities of the fourteen different normal modes, in other words, the possibility of their revealing themselves in various methods of spectroscopic study.

It is evident that the principal mode of vibration pictured in figure 1 of the second part of this memoir would play the major role in the infra-red activity of the crystal. For, in that mode, the calcium atoms move together in one phase and the fluorine atoms move together in the opposite phase and the movement repeats itself from cell to cell of the structure. These movements of the calcium and fluorine atoms would disturb the distribution of the negative electric charge in the cells of the structure and result in a periodic displacement of negative charge which does not vanish when summed over the volume of each unit cell, and therefore also over any small volume-element of the crystal. This movement of electric charge would enable the electric field of the infra-red radiation incident on the crystal to react with it and transfer energy to it, the energy-quanta of the incident radiation being taken over by the crystal as one, two, three or more

quanta of vibrational energy. Hence, the mode of vibration referred to would result in an absorption of the incident radiation in its spectral region corresponding to its fundamental frequency and also to multiples of that frequency; the absorption would thereby manifest itself in a succession of regions whose wavelengths form a harmonic progression. The possibility of the overtones of the fundamental frequency thus manifesting themselves in absorption arises by reason of the finiteness of the amplitudes of the vibration in the unit cells of the structure excited by the incident radiation. It is, therefore, to be expected that the absorption would fall off rapidly in strength as we go up the series of overtones to higher frequencies and thus towards smaller wavelengths in the spectrum.

We proceed to consider the second principal mode of vibration which is an oscillation of the two lattices of fluorine atoms against each other in opposite phases, the calcium atoms remaining at rest. It is evident that such an oscillation, considered as an independent mode of vibration, would be totally inactive in the absorption of infra-red radiation. For, the displacements of electric charge on either side of every calcium atom resulting from the movements of the fluorine atoms belonging to the two lattices would be in opposite senses and would therefore cancel out when summed up. Such cancellation would be effective not only as a first approximation but also in the higher approximations.

The possibility of the frequencies of vibration corresponding to the two principal modes appearing as frequency shifts in the scattering of monochromatic light may be next considered. Such frequency shifts owe their origin to the periodic variations in the optical polarisability of the structural units of the crystal associated with their internal vibrations. It is clear that in this respect, the roles of the two principal modes of vibration would be quite different. The mode which is active in the absorption of infra-red radiation would be inactive in respect of the scattering of light with altered frequency. Vice versa, the mode which is inactive as an absorber of infra-red radiation would be active in light-scattering and would give rise to a frequency shift equal to its own frequency. It should be noted, however, that since the refractive index of fluorite and therefore also the optical polarisability is very low, the variations resulting from the internal vibrations would also be small. Hence, the intensity with which the active mode is recorded as a frequency shift would be low. In the second approximation, in other words, when the effect of the finite amplitudes of vibration is taken into account, both of the principal modes of vibration should be active in light-scattering and give rise to shifts of frequency which are double their natural frequencies. But in view of what has been stated above regarding the low scattering power of the fluorite structure, this possibility is not of much practical significance.

We may here content ourselves with a few remarks regarding the activities of the twelve subsidiary modes of vibration. These modes of vibration involve a reversal of phase from cell to cell of the structure along one, or two or all three axes of the structure. This excludes the possibility of their manifesting themselves either in the absorption of infra-red radiation or in the scattering of light in the

first approximation. In the second approximation, infra-red activity is allowed in respect of some of the modes and not permitted in respect of the others, the considerations which determine the appearance or non-appearance being the symmetry characters of the respective modes. Theoretically also, the twelve subsidiary modes can appear in the scattering of light with doubled frequency shifts and with intensities depending on the actual nature of the modes. But for the reasons already explained, this possibility is not of much practical significance.

Summary

It is shown that the first of the two principal modes of vibration is strongly active in the absorption of infra-red absorption both as a fundamental and as a series of overtones and that the other mode would be wholly inactive. The position is reversed in the scattering of light with shifts of frequency; the first mode is not allowed, but the second is permitted.