

The specific heats of the alkali halides and their spectroscopic behaviour—Part VIII. Their infra-red activity

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The alkali halides play a highly important role in infra-red spectroscopy. Dispersing prisms of large size fashioned from synthetically prepared crystals of optical quality are made use in the recording infra-red spectrophotometers currently in use. The dispersive power of the materials in the spectral regions of free transmission, the absorption which they exhibit further out in the infra-red and the intense surface reflections by them observable at still greater wavelengths are thus matters of particular interest and importance. We shall proceed to consider these topics in relation to the subject-matter of the earlier parts of the memoir, viz., the free modes of atomic vibration possessing discrete frequencies in the region of the infra-red.

We may begin with some comments on the general nature of the relationship which we shall consider presently in greater detail. The specific heats of crystals and their infra-red activity deal with matters which may at first sight seem wholly unrelated to each other. The heat energy of a crystal is identifiable with the mechanical energy of vibration of the massive nuclei of the atoms carrying positive charges about their positions of equilibrium. The infra-red activity of a crystal, on the other hand, is ascribable to the movements of the negatively charged electronic clouds induced by the field of the incident radiation. That there is a connection between these subjects is a consequence of the fact that the atomic nuclei in a crystal are held in their places by the negatively charged electronic clouds and vice versa. In appropriate circumstances, but not necessarily in every case, an oscillation of the atomic nuclei may be accompanied by periodic displacements of the negatively charged electronic clouds, and vice versa.

Infra-red activity implies the possibility of a transference of the energy of the incident radiation to the crystal. If such transference actually occurs, the incident radiation is absorbed, the quanta of its energy being taken over and transformed into one, two or more quanta of vibrational energy in the crystal. If, on the other hand, the transference is only virtual, the velocity of propagation of the electromagnetic waves is influenced and we have free transmission but with an

altered velocity. In appropriate circumstances also, the response of the crystal to the field may be so great that the incident energy is returned to the external medium, in which case we observe a powerful reflection.

The part which the positively-charged massive atomic nuclei and the negatively charged electrons respectively play in the infra-red activity of crystals may next be considered. As has been shown in the preceding parts of the memoir, the discrete frequencies of atomic vibration are determined by the specific modes of such vibration, by the masses of the atomic nuclei, and by the interatomic forces. The latter arise by virtue of the metal and halogen atoms being held together by the bonding electrons. The displacements of electric charge which are responsible for the absorption, dispersion and reflection of infra-red radiation are solely due to the movements of the negatively charged electrons, the movements of the positive charges represented by the atomic nuclei making no contribution to it. To make this point obvious, we have only to recall the infra-red behaviour of crystals such as quartz and rock-salt. In these crystals, the nuclear masses bear to each other the same ratio as the positive charges which they carry. Since in every one of the modes of atomic vibration, the centres of inertia of the oscillating units remain at rest, the centres of positive charge also remain undisturbed in any such oscillation.

If each of the atomic nuclei has around it a spherically symmetrical distribution of negative charge equal and opposite to the positive charge of the nucleus and if further, this situation is not sensibly altered by a movement of the nuclei, there could evidently be no infra-red activity. Actually, the alkali halides display a powerful infra-red activity. It is also well known that their dielectric constants as determined with periodically varying electric fields of low frequency are notably higher than the square of their refractive indices in the visible region of the spectrum. The data for all the sixteen halides are exhibited in table 1.

Table 1. Dielectric constants of the alkali halides*

	Fluoride	Chloride	Bromide	Iodide
Lithium	9.27	11.05	12.1	11.03
Sodium	6.00	5.62	5.99	6.60
Potassium	6.05	4.64	4.78	4.94
Rubidium	5.91	5.0	5.0	5.0

*From table in *American Institute of Physics Handbook*, 1957.

The dielectric behaviour of the alkali halides as set out in table 1 exhibits some significant features. It is obviously unrelated to the strength of the binding between the metal and halogen atoms. The latter exhibits large variations as is indicated by the elastic moduli and the frequencies of atomic vibration of the various halides. The variations of dielectric behaviour are altogether of a different

character. The dielectric constant is highest when the metal and halogen atoms differ greatly in their sizes. It is low when the two sets of atoms are of comparable dimensions. The former situation is exemplified by the lithium halides and the latter by potassium chloride. These show respectively the highest and lowest dielectric constants listed in table 1.

An explanation of the facts which suggests itself is that an external electric field produces a displacement of the negatively charged electronic cloud located between each pair of metal and halogen atoms in the crystal. Such a displacement may be expected to be comparatively small when the metal and halogen atoms are nearly of the same dimensions and distinctly large when they are very different. A similar explanation would account for the infra-red activity exhibited by the alkali halides. Indeed, such activity could only be explained on the basis that the field of the incident radiation induces a periodic displacement of the negatively charged cloud of electrons in the crystal.

On the basis of the ideas set forth above, one can proceed to draw inferences regarding the infra-red activity of the nine characteristic modes of vibration of the alkali halides. A periodic displacement of negative electric charge which does not vanish when summed up over the volume of the oscillating unit is essential for any particular mode of vibration to exhibit activity. The magnitude of the displacement of charge is also a measure of the strength of such activity. It follows that the mode of vibration of the highest frequency in which the metal and halogen atoms oscillate against each other in opposite phases would be powerfully active. For, the phases of the oscillation being the same in successive cells of the structure, their effects would add up.

Altogether different would be the behaviour of the oscillations of the atoms located in the octahedral layers of the structure. There are four modes of this kind, *only* the metal atoms oscillating in two of them and *only* the halogen atoms in the two others, the movements being respectively normal and tangential to those layers. Since in each of the modes the phase of the oscillation is reversed as we pass from layer to layer, the displacements of negative charge resulting therefrom would cancel each other completely. In other words, these four modes would be totally inactive.

The coupled oscillations of the metal and halogen atoms appearing in the cubic layers may next be considered. Since adjacent metal and halogen atoms in the structure alternately approach and recede from each other, there would be a resulting displacement of negative charge. But since the phases are reversed in the successive layers of the structure, they would cancel out when summed up over the volume of the oscillating unit. But in the second approximation when the amplitudes of vibration are not infinitesimal, the cancellation would not be complete, and there would be a surviving component of charge displacement which has a doubled frequency. In other words, these four modes which are inactive in the first approximation would be active as overtones, the radiation being absorbed when it has twice the frequency of the mode. It should be

remarked that the four modes would display such activity with very different strengths. The two having the higher frequencies should, for fairly obvious reasons, be much more strongly active than the two others.

As was remarked earlier, when the radiation is absorbed, its energy quanta are taken up and transformed into one, two or more quanta of vibrational energy in the crystal. The frequency of the absorbed radiation would then be a multiple of the frequency of vibration of the structure. The circumstances in which such absorption may be expected to occur are of importance. It is clear that the absorption of radiation with frequencies which are overtones of the frequencies of atomic vibration would only be possible when the oscillations are of large amplitude and there is an appreciable anharmonicity, a situation that could only arise when the oscillating unit is itself not of any large dimensions.

The mode of vibration having the highest frequency is also the most strongly active, viz., that in which the metal and halogen atoms oscillate in opposite phases. It is, therefore, to be expected that this mode would exhibit the absorptions of higher orders in which the frequency of the absorbed radiation is a multiple of its own frequency. Their strength would naturally fall off rapidly with the increasing order of absorption. Hence, the absorption paths necessary to exhibit them would progressively become greater. Experimental studies with MgO, rock-salt and lithium fluoride¹⁻³ completely substantiate this inference.

The absorptions of higher order determine the upper limit of wavelength beyond which the alkali halides are not sufficiently transparent for use as dispersing prisms. This limit is about 15 microns for NaCl, 21 microns for KCl, 27 microns for KBr and 31 microns for KI. These figures may be compared with the infra-red wavelengths which correspond to the highest atomic vibration frequencies. For the four halides mentioned, they are respectively 53 microns, 75 microns, 95 microns and 111 microns; in each case, these wavelengths are between three and four times greater than the limits mentioned. It is clear that the third-order absorption by the alkali halides is of considerable strength and that not until it has disappeared and given place to the much weaker fourth-order absorption is the material sufficiently transparent for use as a dispersing prism.

The possession of an adequate dispersive power is essential for the satisfactory performance of its functions by a dispersing prism. All the four halides mentioned, viz., NaCl, KCl, KBr and KI have very small dispersive powers in the near infra-red, in other words in the wavelength range between one micron and five microns. In this range, therefore, prisms of the materials mentioned cannot be usefully employed. The dispersive power of NaCl reaches satisfactory values beyond 8 microns, that of KCl beyond 10 microns, that of KBr beyond 15 microns and that of KI beyond 20 microns. The experimental data exhibit a significant parallelism between the increases of the absorption coefficient and of the dispersive powers with increasing wavelength. The useful range is thus set at one end by the dispersive power being too small and at the other end by the absorption being too great.

The mechanism of infra-red activity discussed in the foregoing pages lends itself to a very simple explanation of the well known phenomenon of the surface reflections exhibited by the alkali halides. The incidence of radiation on the crystal would result in a periodic displacement of negative electric charge in each unit cell of the structure. Since the displacements in all the cells have a coherent phase-relationship, their effects would be additive and hence could give rise to a reflected wave-front, the strength of such reflection being proportional to the strength of the electric displacements induced by the field. An effect of this nature would *not* necessarily be limited to the particular cases in which the incident radiation has the same or nearly the same frequency as the most strongly active mode of atomic vibration. It should also be observable in other circumstances and especially when the frequency of the incident radiation approximates to that of the other modes of free atomic vibration and/or their overtones.

Lithium fluoride furnishes a very striking illustration of the foregoing remarks. The manner in which the intensity of the surface reflections by that crystal varies with the wavelength of the incident radiation has been described and discussed in the memoir dealing with it. Magnesium oxide and rock-salt also show distinctive features in their reflection spectra. These have been described and adequately discussed in the memoirs dealing with those materials. There is, therefore, no need to traverse the same ground here again in detail.

Summary

The dispersion, absorption and reflection of infra-red radiation by the alkali halides receive a satisfactory explanation as consequences of the electric field of the incident radiation inducing a periodic displacement of the negative electric charges located between each pair of metal and halogen atoms in the crystal. The dielectric behaviour also receives an acceptable interpretation on the same basis. The appearance of infra-red absorption at wavelengths corresponding to the overtones of the frequencies of atomic vibration indicates that the oscillating units in the crystal have dimensions comparable with those of the unit cells.

References

1. Raman C V *Proc. Indian Acad. Sci.* **A54** 205-25 (1961).
2. Raman C V *ibid.* **A54** 253-304 (1961).
3. Raman C V *ibid.* **A55** 131-52 (1961).