

THE SPECIFIC HEATS OF THE ALKALI HALIDES AND THEIR SPECTROSCOPIC BEHAVIOUR

Part IX. Spectral Shifts in Light Scattering

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THE dynamical theory which enabled the evaluation of the thermal energy of the alkali halides was also the basis for the discussion of their infra-red activity contained in the preceding part of the memoir. But there is a great difference between the two problems; whereas all the nine modes of vibration are excited by the thermal agitation to extents determined by their frequencies and the temperature, the infra-red activities of the different modes are determined by totally different considerations. Some are wholly inactive and some others are active only in the higher orders. In consequence, rather elaborate studies with absorption paths ranging from large down to the smallest values in the different spectral ranges are necessary to enable any useful conclusions to be drawn regarding the character of the vibration spectrum in each particular case. Further, the characteristic frequencies for most of the alkali halides lie in the remote infra-red far beyond the range of the recording spectrographs provided with NaCl and KBr optics.

From the foregoing remarks, it is evident that for a complete determination of the modes and frequencies of atomic vibration in the alkali halides, we have of necessity to rely upon methods of observation other than those of infra-red spectroscopy. Since the alkali halides are transparent both in the visible and in the ultra-violet regions of the spectrum, one naturally turns to the application of the methods based on the spectroscopic examination of the radiations scattered in the crystal when traversed by a powerful beam of monochromatic light. Actually, however, the earlier attempts made with rock-salt to record the spectral shifts of frequency usually noticeable in such circumstances did not prove successful. The reason for this failure is not far to seek. It is to be found in the nature of the modes of atomic vibration when considered in relation to the structure of the crystal. We shall comment on these matters in some detail as this will lead us to

a clearer understanding of the circumstances in which positive results can be expected as well as the nature of such results.

The nine possible modes of vibration of the structure of the alkali halides differ from each other both in the geometry of the movements and in their frequencies. But they exhibit certain features in common arising from the cubic symmetry of the structure. The principal mode of vibration of the highest frequency and the four modes of vibration of the atoms appearing in the cubic layers may all be described as an approach of each atom of one species towards an atom of the other species on one side of it and a recession from a similar atom on the other side, these movements being reversed in the successive half-periods of the oscillation. The four octahedral modes in which only the atoms of one species oscillate and the atoms of the other species remain at rest are of a different character. Each moving atom of one species approaches a group of atoms of the second species on one side of it and recedes from a similar group lying on the other side, and these movements are reversed in the successive half-periods of the oscillation. The group of stationary atoms consists of three atoms for the perpendicular modes and of two atoms for the tangential ones.

The spectral shifts of frequency recorded in the scattering of light are a consequence of the periodic changes in the optical polarisability of the oscillating groups of atoms resulting from their internal vibrations. These changes are a summation of the changes produced by the approaches and recessions of the individual atoms during their movements. From the description of the modes of vibration given above, it is evident that in all the nine cases, the result of the summations would be zero in the first approximation but finite in the second approximation, the magnitude of the resultant being naturally very different for the different modes. The vanishing result of the summation in the first approximation is a consequence of the effects produced by the approaches on one side being cancelled out by the effects due to the recessions on the other side; since the movements are of equal amplitude, the effects arising therefrom may be assumed to be equal in magnitude but opposite in sign. The assumption is a reasonable one provided the movements are of infinitesimal amplitude. But it ceases to be valid if the amplitudes are not small, and hence in the second approximation, the summation would give a finite result and this would evidently be periodic with twice the frequency of the oscillation.

Thus we arrive at the result that spectral shifts of the first order, in other words, changes of frequency identical with those of the modes of vibration would fail to manifest themselves when a beam of monochromatic light

traverses a crystal of the alkali halides and the scattered radiation is examined spectroscopically. The possibility of spectral shifts of doubled frequency is however indicated by the argument. For such shifts to be observable, there are two prerequisites. In the first place, the optical polarisabilities should themselves be of sufficient magnitude so that any changes thereof could produce sensible effects. Secondly, the amplitudes of vibration of the oscillating units should be sufficiently large so that the second-order effects due to optical anharmonicity may be observable. Since the energy of mechanical vibration is quantised and therefore determined by the frequency and not by the dimensions of the oscillators, amplitudes of oscillation of a magnitude comparable with the dimensions of the individual atoms are only possible if the oscillator is itself not of very large dimensions, in other words, is a group of atoms comparable in its size with the dimensions of the unit cell of the crystal. Thus, the observability of spectral shifts with doubled frequency may be regarded as a demonstration that the oscillators in the crystal are sufficiently small to exhibit the effects of optical anharmonicity.

The spectral shifts of doubled frequency would be both positive and negative, in other words, would appear on both sides of the exciting radiation in the spectrum, the ratio of their intensities being the ratio of the numbers of the thermally excited to the non-excited vibrational states. This ratio also figures in specific heat theory. Thus, the observable features in the spectra of light scattering of the alkali halides all stand in the closest relationship to the dynamical theory developed in the earlier parts of the memoir. All the nine modes of atomic vibration would appear with doubled frequency shifts though necessarily with very different intensities, thereby making it possible to obtain a complete observational proof of the theory on which the evaluation of the specific heats was based.

We now turn to a consideration of the circumstances which would favour the spectral shifts of doubled frequency being recorded with observable intensities. It is obvious that the light beam traversing the crystal should be of great intensity. This, however, may result in various spurious effects of instrumental origin. Thus, unless the crystal is itself highly transparent and non-luminescent, a successful recording of the second-order spectrum could scarcely be hoped for.

As can be seen from the tabulated values in the first part of this memoir, the fluorides of all the alkali metals have very low refractive indices. Hence, one could scarcely hope to record the second-order spectra successfully with them. The refractive indices of the chlorides, bromides and iodides of all

the alkali metals are much greater, particularly those of the iodides. They are, therefore, much more promising material for the studies.

The spectral shifts of frequency would be greatest in the case of the lithium compounds and smaller for those of the other alkali metals. The shifts in each case would be smaller for the bromides and iodides than for the chlorides. The smaller frequency shifts would be recorded in closer proximity to the exciting radiation in the spectrum. In the vicinity of the latter, various spurious effects are inevitable, *e.g.*, ghosts and continuous spectrum. Unless the presence of such spurious effects is recognised and allowed for, erroneous interpretations of the observed results are possible.

For the interpretation and evaluation of the recorded spectra, a comparison with the theoretically expected frequency shifts and especially their relative intensities should obviously be helpful. These intensities are determined by two considerations, *viz.*, the geometry of the vibrational modes and their degeneracies. Those modes of vibration in which adjoining metal and halogen atoms do not approach each other closely and hence cannot strongly influence each other's optical polarisabilities could only be recorded very feebly. This is illustrated by the two modes of vibration of the lowest frequencies of the atoms appearing in the cubic layers. These modes are necessarily also the modes exhibiting the lowest recorded intensities in the spectra.

It was remarked in the preceding part of the memoir that the four modes of vibration of the octahedral layers of atoms are totally inactive in the absorption of infra-red radiation. It is, therefore, a particularly valuable feature of the spectra of light scattering that all these four modes can appear in them with doubled frequency shifts. In particular, the two tangential modes of vibration of the octahedral layers may be expected to appear with high intensities by reason of their degeneracy being eightfold. Indeed, they might well be the most conspicuous features in the spectra in all cases.

The support which the results of studies of light scattering in the alkali halides give to the theory of their specific heats set out in the present memoir is strikingly illustrated by the case of rock-salt. In the memoir dealing with the spectroscopic behaviour of this crystal¹ the microphotometer record of the spectrum of light scattering in it obtained by Rasetti with the special technique developed by him was reproduced. It was shown that the record exhibits a highly satisfactory agreement with the consequences of the theory. All the nine frequency shifts expected on the basis of the theory appear in the positions and with the relative intensities indicated by it.

We may conclude this part of the memoir with some comments on the spectroscopic behaviour of the alkali halides as manifested respectively in light-scattering and infra-red absorption. The alkali halides are extremely powerful absorbers of infra-red radiation in the appropriate wavelength ranges. Far from this being a helpful circumstance, it is actually an embarrassing feature. The absorption arises from the movements of the negative charges in the crystal set up by the electromagnetic field of the incident radiation. These movements react with the field and result in the observed absorption. The moving charges are the bonding electrons located between the metal and halogen atoms in the crystal. The atomic nuclei and the electrons surrounding them are also disturbed in consequence, but the role played by their movements is a purely subordinate one. It is not to be expected in these circumstances that infra-red absorption studies could fully reveal the real characters of the atomic vibration spectrum.

On the other hand, the scattering of light is a feeble effect and this is a helpful feature, since the various complications which arise in the infra-red investigations are thereby excluded. The spectral shifts of frequency in the scattering of light are a consequence of the localised periodic variations of optical polarisability in the structure due to its vibrations. All the electrons surrounding each atomic nucleus contribute to the optical polarisability of the structure. Hence the movements of the atomic nuclei control the magnitude and character of the variations of optical polarisability. Accordingly, we would be justified in expecting that the spectrum of light scattering would be a more or less faithful representation of the atomic vibration spectrum and would enable the real character of the latter as a set of discrete frequencies to be recognised.

SUMMARY

The spectral shifts of doubled frequencies observed in the scattering of light by the alkali halides—rock-salt for example—are discussed and explained and it is shown that they demonstrate the validity of the approach to the theory of their specific heats developed in the present memoir.

REFERENCE

1. Raman, C. V. .. *Proc. Ind. Acad. Sci.*, 1961, **54 A**, 253-304.