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The dynamics of the fluorite structure and its infra-red behaviour—Part IV. The spectrophotometer records

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In the present part of the memoir, we shall reproduce and discuss a series of spectrophotometer records of the infra-red transmission by plates of fluorite, their thicknesses ranging from a maximum of 37 millimetres down to less than a tenth of a millimetre, the greatest absorption path being thus some 400 times smaller. An enormous range of absorptive powers is thus covered and displayed by the records.

Synthetically prepared fluorite of optical quality which is commercially available has been employed for obtaining the spectrophotometer records reproduced in this memoir. As is well known, such fluorite is prepared by melting chemically pure CaF_2 in a platinum crucible having a conical vertex and allowing it to solidify slowly. The material thus obtained is perfectly colourless and its transparency extends far into the ultra-violet. Specimens of natural fluorite have, however, also been investigated. With material of the best quality which is colourless, transparent and free from inclusions, the results do not differ noticeably from those recorded with the synthetic specimens.

Three specimens of synthetic fluorite from different sources were available for the studies. The first was a block of dimensions 37 mm × 37 mm × 9 mm supplied by a well known British firm. The second specimen was a fluorite window 25 mm × 25 mm × 1·52 mm gifted to the author by Dr E K Plyler of the National Bureau of Standards at Washington. The third specimen was a small plate 1·7 mm thick sent by Prof. R Mecke from his Institute at Freiburg. All records reproduced in the present memoir were made with the material of British origin, the plates of the requisite thickness being obtained by cutting, grinding and polishing. The specimens of American and German origin give records similar to those recorded with the British material and hence they have not been reproduced.

In all, some fifty records were made with twenty different absorption paths. With a plate thickness of a millimetre or more, there is a complete cut-off beginning at 13 μ and extending towards greater wavelengths. Hence with such plates the KBr optics is ineffective and only the NaCl optics could be used. The range between 13 μ and 15 μ is common to both the NaCl and the KBr optics.

Though there was a fair agreement between the results they recorded, the KBr results were clearly the more trustworthy. Hence the records made with the NaCl optics reproduced in the memoir exhibit only the transmission curves up to 13 μ, while at 13 μ and greater wavelengths, only the records made with the KBr optics are shown. All the latter refer to absorption paths which are less than a millimetre.

An inspection of the nine figures reproduced in the text indicates that we are dealing with absorptions of an altogether different order of magnitude in the three wavelength ranges, 7 μ to 8 μ, 9·5 μ to 10·5 μ and 13 μ to 17 μ. We shall remark upon these separately.

7 μ to 8 μ.—There is a readily observable absorption in this region with the largest thickness employed, viz., 37 mm (figure 1). It has sensibly weakened when the path is reduced to 29 mm (figure 2); it is very weak with an absorption path of 11 mm (record not reproduced) and still weaker with a thickness of 9 mm (figure 3). It is nearly unobservable with a 4 mm path (figure 4).

9·5 μ to 10·5 μ.—A complete or nearly complete cut-off is exhibited in this region in figure 1 and figure 2, the absorption path being in these cases a few centimetres. When the thickness is reduced to about a centimetre, the wavelength of cut-off moves to 13 μ beyond which there is a complete opacity. The transmission between 9·5 μ and 10·5 μ then rapidly increases as the thickness is reduced. This is shown very clearly in the series of records, figure 3, figure 4 and figure 5. Finally, when the thickness is reduced to a fraction of a millimetre, the absorption between 9·5 μ and 10·5 μ becomes very weak or unobservable.

13 μ to 17 μ.—Nine different absorption paths ranging from 9 mm down to 0·09 mm were investigated. They exhibit a progressive increase in transmission between the wavelengths of 13 μ and 17 μ commencing from complete opacity at a thickness of one millimetre. Two very significant features are noticeable in the records. The transmission curve exhibits a dip at 14 μ which is conspicuous and well-defined. Its position remains unaltered as the thickness is progressively reduced to the smallest possible value determined by the fragility of the material. At the same time, the actual transmission at 14 μ increases progressively upto about 75%. It is thus clear that 14 μ is a characteristic wavelength for fluorite. The other feature is noticeable in the records for the two smallest thicknesses reproduced as figure 8 and figure 9 respectively. It will be seen that the transmission curve descends steeply beyond 14 μ and then takes a sharp turn after which it slopes down less steeply. The location of this turning point is quite definite, viz., 15·6 μ and remains unaltered as the thickness is diminished to the limit. Thus, we are led to recognize 14 μ and 15·6 μ as two characteristic wavelengths in the infra-red absorption spectrum of fluorite.

The facts of observation set forth above are readily understood when considered in the light of the theoretical ideas developed in the two preceding parts of the memoir. It was shown that the principal mode of vibration of the structure in which the calcium atoms and the fluorine atoms oscillate in opposite phases would be strongly active in the absorption of infra-red radiation, not only

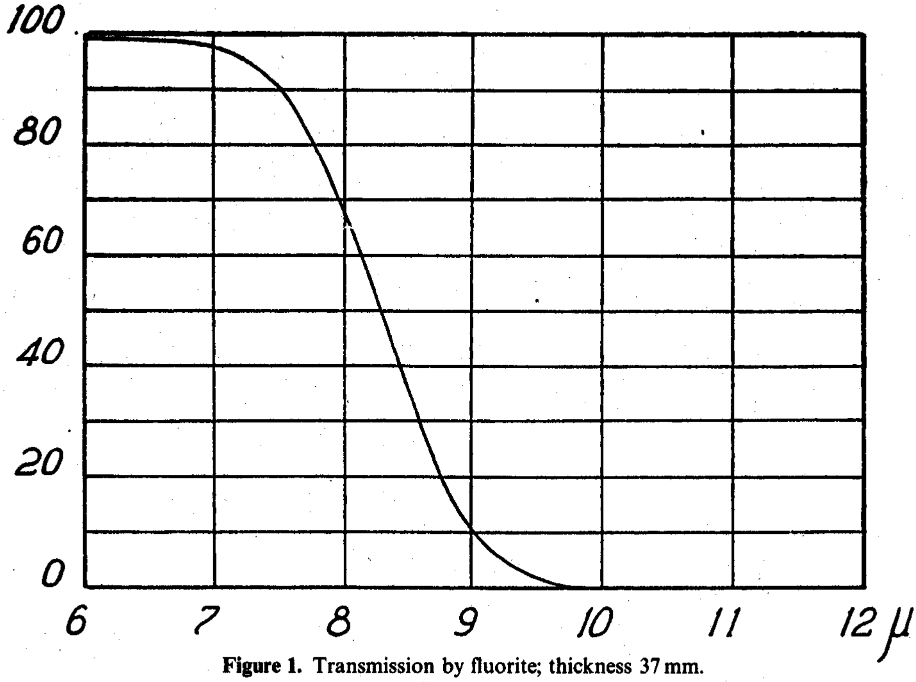

Figure 1. Transmission by fluorite; thickness 37 mm.

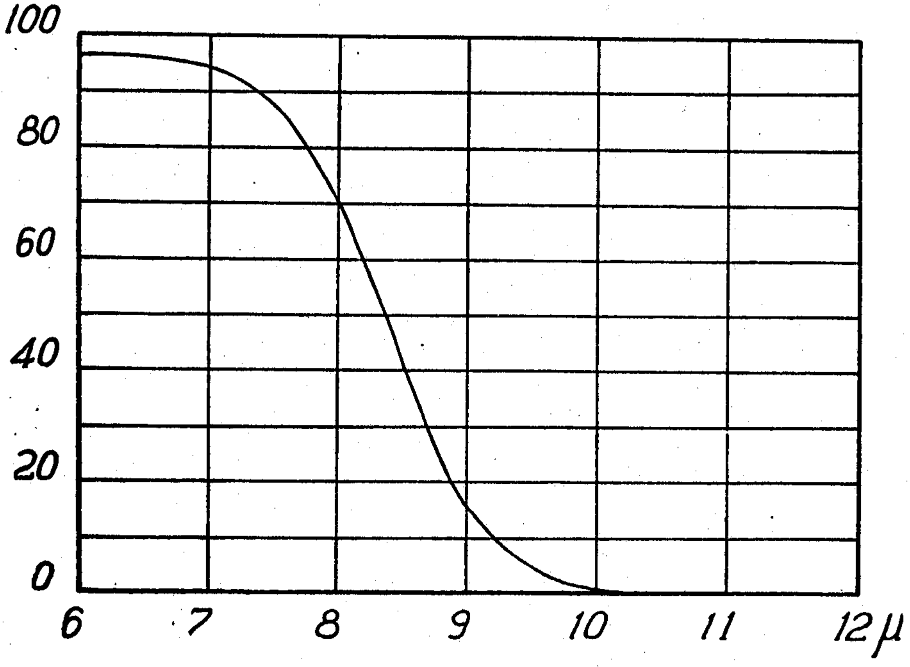

Figure 2. Transmission by fluorite; thickness 29 mm.

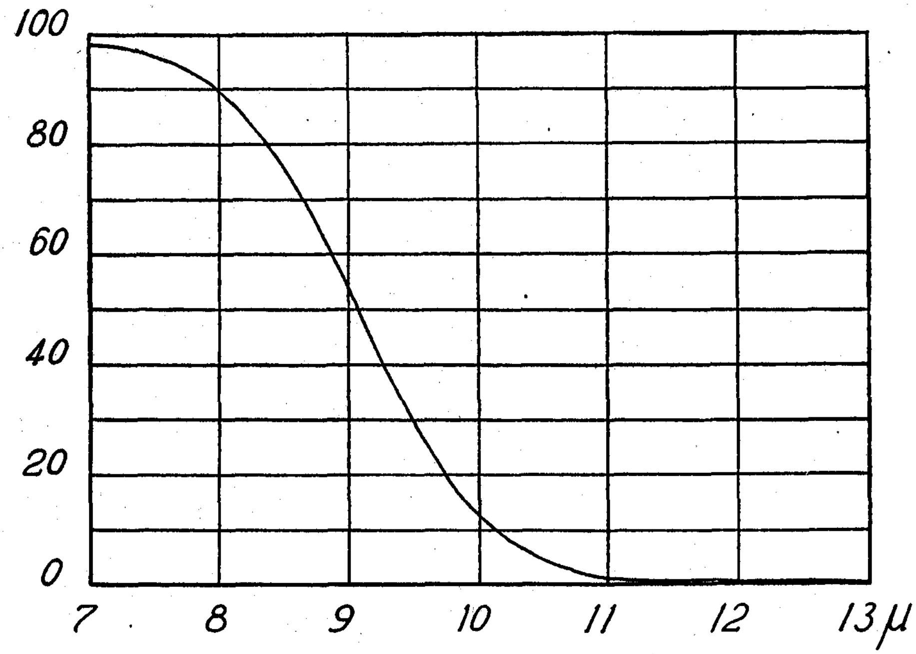

Figure 3. Transmission by fluorite; thickness 9 mm.

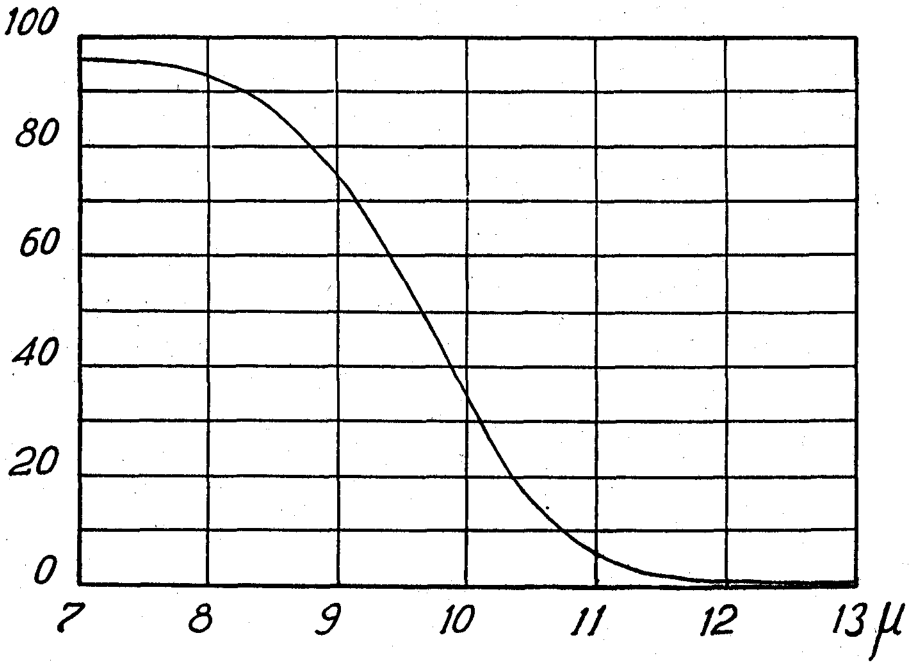

Figure 4. Transmission by fluorite; thickness 4 mm.

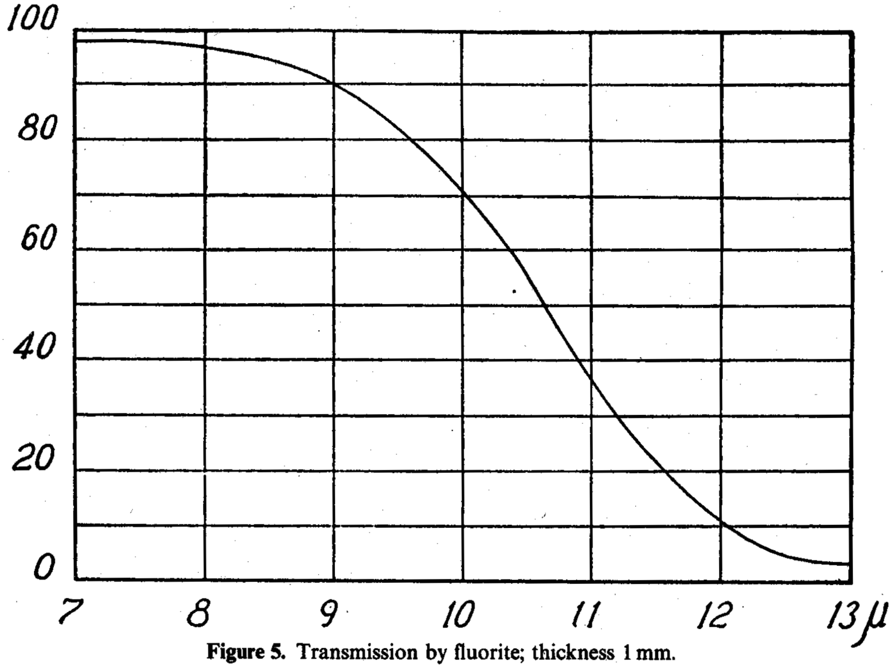

Figure 5. Transmission by fluorite; thickness 1 mm.

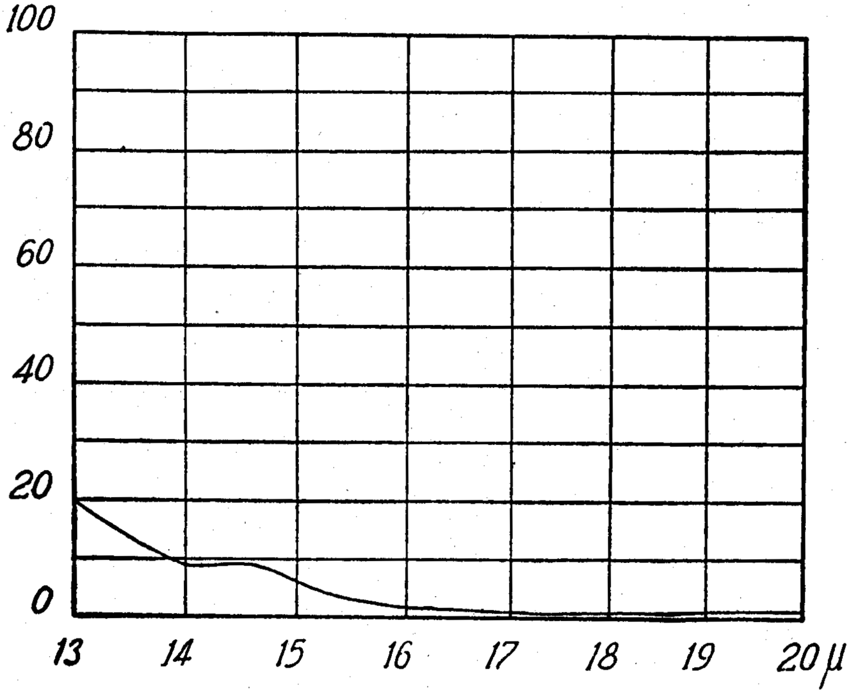

Figure 6. Transmission by fluorite; thickness 0·38 mm.

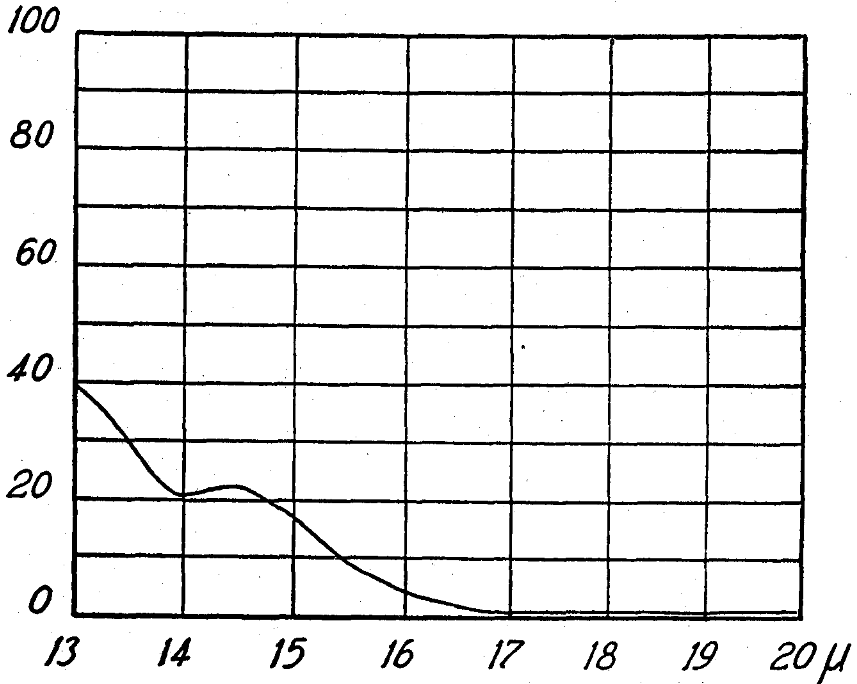

Figure 7. Transmission by fluorite; thickness 0·3 mm.

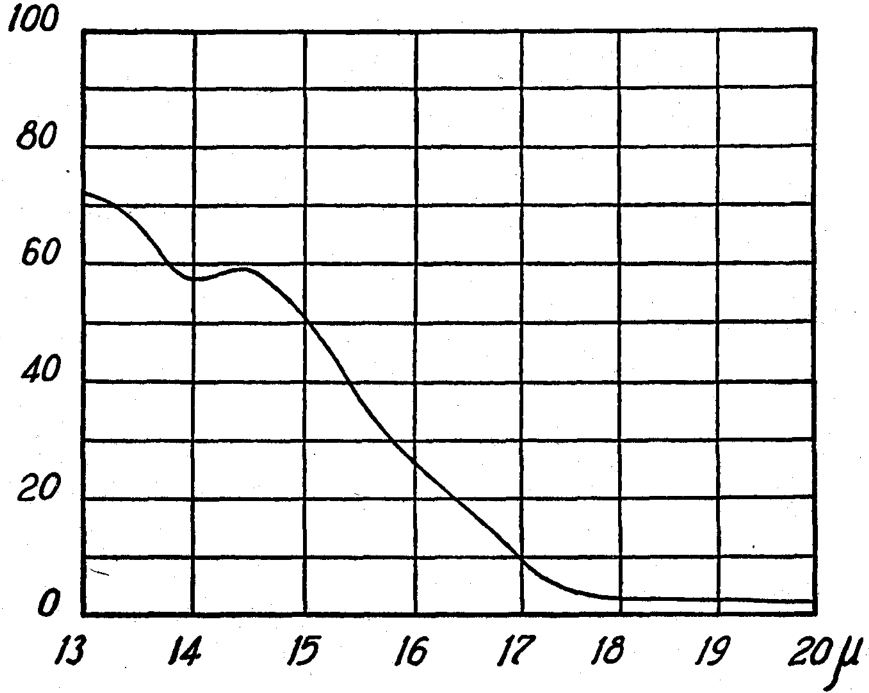

Figure 8. Transmission by fluorite; thickness 0·11 mm.

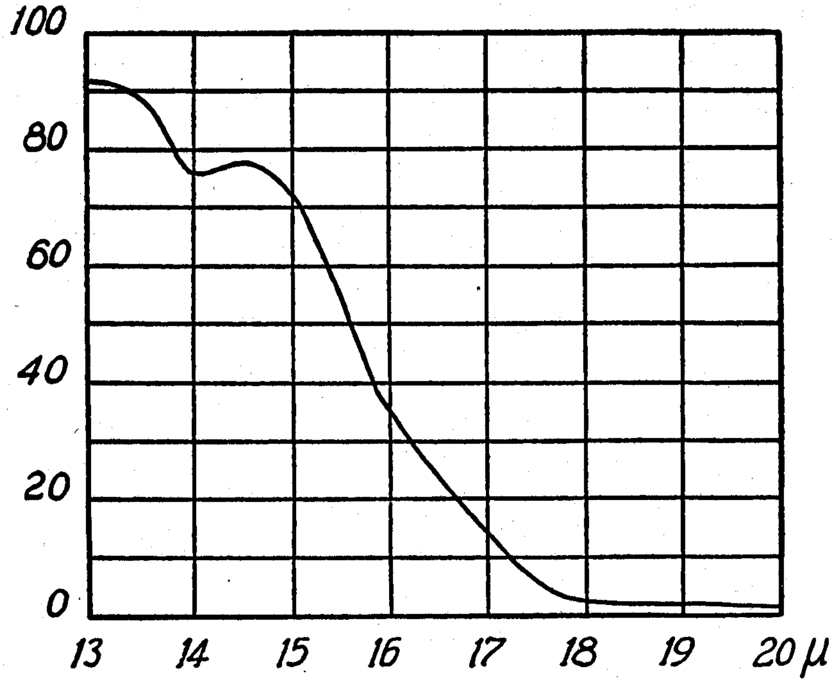

Figure 9. Transmission by fluorite; thickness 0·09 mm.

as a fundamental but as a series of overtones. Taking 28 μ as the characteristic infra-red wavelength and hence 357 cm^{-1} as the frequency of that oscillation expressed as a wave-number, the octave of the fundamental would manifest itself in the absorption spectrum at 14 μ, the third harmonic at 9·3 μ and the fourth harmonic at 7 μ, these absorptions rapidly decreasing in strength. The appearance of absorptions of very different orders of magnitude at and near these wavelengths evident from the spectrophotometer records is thus satisfactorily explained. We accordingly recognise 28 μ as the wavelength corresponding to the fundamental mode of vibration referred to above and the dip at 14 μ in the transmission curve as due to the octave of that mode.

The appearance of a turning point or inflexion in the transmission curve at 15·6 μ is also readily explained. Expressed as a wave-number, the spectral frequency corresponding to that wavelength is 641 cm^{-1} which is just double the frequency shift of 321 cm^{-1} recorded as a sharply defined line in the scattering of monochromatic light by fluorite. This shift was first noticed by Rasetti who used the intense resonance radiation of a water-cooled and magnet-controlled mercury arc in his experiments. It has been confirmed using the same technique and excellent spectrograms showing the frequency shifts ± 321 cm^{-1} have been obtained at this Institute. They are clearly ascribable to the second principal mode of vibration of the fluorite structure in which the two lattices of fluorine atoms oscillate against each other in opposite phases. Considered as an independent normal mode, this vibration should be totally inactive in the infra-red both as a fundamental and as its overtones. Its contiguity in frequency to the principal mode of wave-number of 357 cm^{-1} which is strongly active both as a fundamental and as overtones would, however, influence its behaviour noticeably. We may indeed expect the mode of wave-number 321 cm^{-1} to exhibit a kind of induced infra-red activity both as a fundamental and as its various overtones. The form of the transmission curve actually seen in figure 8 and figure 9 thus receives a satisfactory elucidation.

Summary

The spectrophotometer records enable us to determine 28 μ as the characteristic wavelength and 357 cm^{-1} as the characteristic wave-number of the infra-red active mode of oscillation of the calcium and fluorine atoms against each other in opposite phases. This mode is active also as its overtones, the octave in particular appearing as a conspicuous and well-defined dip at 14 μ in the transmission curve. By reason of its contiguity in frequency with the strongly active mode, the vibration of the two fluorine lattices against each other which gives rise to an observable frequency shift in the scattering of monochromatic light also displays an induced infra-red activity and is recorded in the transmission curve as a sharp inflexion located at 15·6 μ. The corresponding wave-number 641 cm^{-1} is just double the frequency shift of 321 cm^{-1} observed in light-scattering.