

## The infra-red behaviour of sodium fluoride

SIR C V RAMAN

Memoir No. 132 of the Raman Research Institute, Bangalore-6

Received October 26, 1962

Sodium fluoride has the distinction of possessing the lowest refractive index of any crystalline solid, being about the same as that of water which is 1.333. It has the same crystal structure as rock-salt. But its infra-red reflection maximum appears at a much smaller wavelength, viz.,  $36 \mu$ , than that of rock-salt which is at  $54 \mu$ . Hence, the infra-red behaviour of NaF is more readily accessible to investigation than that of NaCl.

Synthetically prepared crystals of NaF of excellent optical quality are available. A rectangular block of NaF  $40 \text{ mm} \times 21 \text{ mm} \times 21 \text{ mm}$  in size was procured from Dr Karl Korth of Kiel, West Germany. The material had a perfect cleavage parallel to the faces of the block, making it possible to obtain plates of various thicknesses for a detailed study of its infra-red absorption. The aim of the investigation was to establish the relationship between the absorption spectra of the material and the activities of the various modes of free vibration of the structure set out and discussed in a recently published memoir<sup>1</sup> by the present author.

In the memoir under reference, the principles of classical mechanics were employed to deduce the normal modes of free vibration of the atoms in crystals having the rock-salt structure. It emerged that the vibrational mode of highest frequency is that in which the atoms of metal and halogen oscillate against each other in opposite phases. Eight other modes of free vibration are also possible. They may be described simply in terms of the crystal structure; four of the modes are oscillations of the cubic layers, while the other four modes are oscillations of the octahedral layers of the structure, the movement alternating in phase from layer to layer, and being either normal or tangential to those layers. Since the oscillations of the metal and halogen atoms may be either in the same phase or in opposite phases, we have four modes for the cubic layers and four modes for the octahedral layers and hence eight in all. The oscillations of the metal and halogen atoms in the cubic layers would be coupled with each other, since both sets of atoms appear interspersed in these layers. But the oscillations of the metal and halogen atoms in the octahedral planes would appear independently since they are located in distinct and alternating layers in these planes.

It was further shown in the memoir that approximate expressions for the frequencies of the free modes of vibration could be obtained in terms of *two* force-constants only. The first force-constant  $\alpha$  expresses the resistance to a longitudinal movement of the neighbouring metal and halogen atoms in the structure with respect to each other. The second constant  $\beta$  is the force which expresses the resistance to a transverse relative displacement of these atoms.  $\alpha$  and  $\beta$  were numerically evaluated from the relations  $\alpha = k \times d$  and  $\beta = c_{44} \times d$  where  $d$  is the spacing of the cubic layers,  $k$  is the bulk modulus and  $c_{44}$  is the shear-elasticity of the crystal. The frequencies thus calculated were tabulated in the memoir.

In table 1 below, the fundamental frequencies thus computed of the mode of highest frequency and of the four modes of coupled oscillation of atoms in the cubic layers for NaF have been shown converted into infra-red wavelengths to facilitate comparison with the observational data. The four modes of oscillation of the atoms in the octahedral layers have not shown, as they are totally inactive. Besides the wavelengths corresponding to the fundamental frequencies, the wavelengths corresponding to the overtones up to the fourth have also been listed.

Table 1. Wavelengths in microns

Modes	I	II	III	IV	V
Fundamentals	35.6	41.5	47.6	53.5	69.4
First overtones	17.8	20.8	23.8	26.7	34.7
Second overtones	11.9	13.8	15.8	17.8	23.1
Third overtones	8.9	10.4	11.9	13.8	17.4
Fourth overtones	7.1	8.3	9.5	10.7	13.5

The infra-red activity with which we are principally concerned is that of the principal mode of highest frequency, both as a fundamental and as its various overtones. Its fundamental wavelength lies outside the ranges covered by the NaCl and KBr optics of the recording spectrophotometer. Its first, second, third and fourth overtones, however, fall within the range of these instruments. Hence, it should be possible to find evidence of the absorptions due to them at or near the wavelengths (using round figures)  $18 \mu$ ,  $12 \mu$ ,  $9 \mu$  and  $7 \mu$  respectively. The strength of these absorptions would naturally diminish rapidly with their increasing order. Hence, greater and greater absorption paths would be needed to exhibit the absorptions of higher orders. We cannot altogether ignore the absorptions of the second and higher orders due to the four other modes of free vibration listed in table 1. The superposition of their effects on those due to the overtones of the fundamental of highest frequency would tend to smooth out the step-like character of the falls in absorption to be expected at the wavelengths  $18 \mu$ ,  $12 \mu$ ,  $9 \mu$  and  $7 \mu$ . These falls should nevertheless appear clearly enough to be recognized in the spectrophotometer records.

The foregoing remarks prepare the ground for an understanding of the features noticeable in the series of spectrophotometer records reproduced as figures 1 to 12 in the text. The largest absorption path is 21 mm and the smallest is 0.18 mm, one being more than a hundred times greater than the other. The very great differences in the magnitudes of the specific absorptions recorded with these thicknesses will thus be evident.

The most significant result revealed by the investigation is the sharply-defined peak of absorption at  $18.2 \mu$  seen in figures 10, 11 and 12 which are the records obtained with the three thinnest plates of the series. These three figures show a large and steep fall in transmission in the range of wavelengths immediately preceding the minimum of transmission at  $18.2 \mu$ . In figures 7, 8 and 9 recorded in the KBr range with plates of thicknesses 2 mm, 1 mm and 0.65 mm respectively, the transmission also falls in the same range of wavelengths but it ends in a cut-off at  $18 \mu$  beyond which there is no transmission. These features make it clear that the wavelength  $18 \mu$  represents the boundary between the regions in which the third and second-order absorptions due to the fundamental mode of highest frequency are respectively effective, and that the sharply-defined peak of absorption at  $18.2 \mu$  gives us the precise frequency of the octave of that mode;

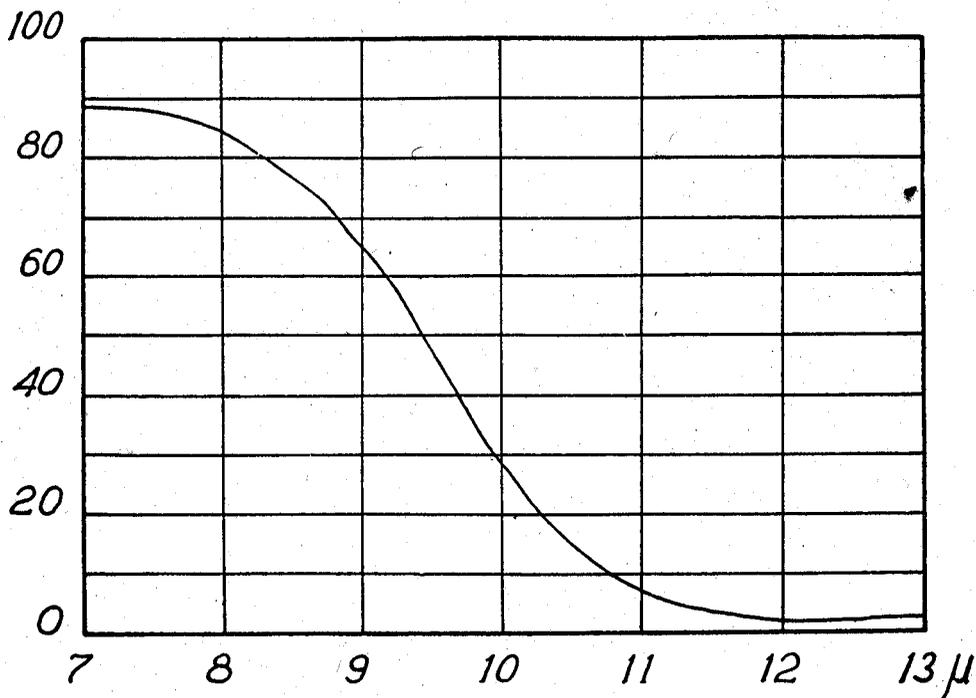


Figure 1. Absorption by NaF; plate thickness: 21 mm.

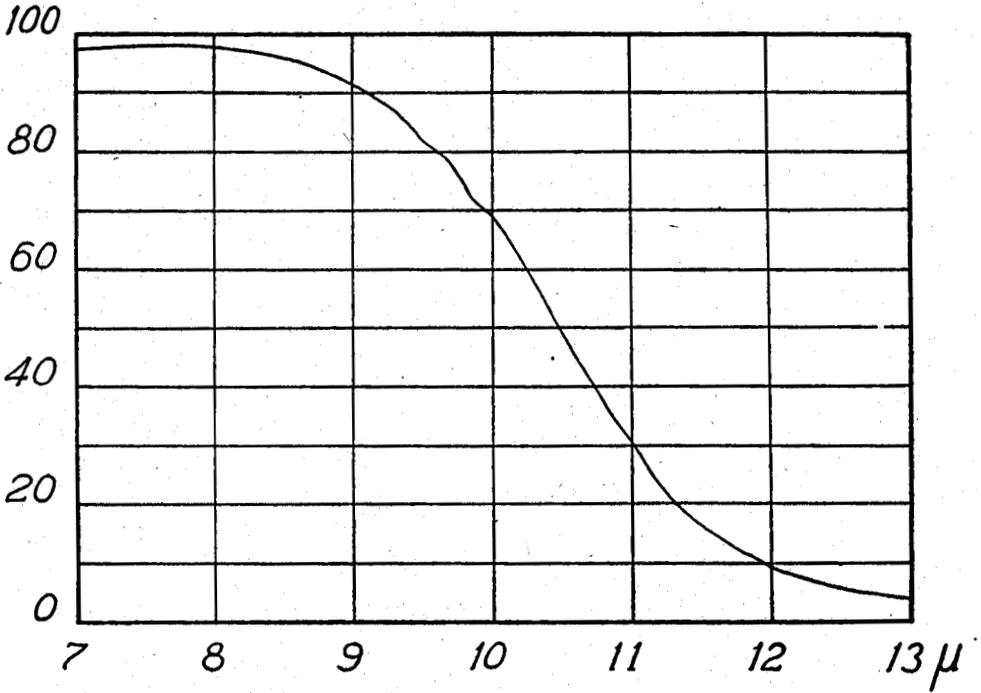


Figure 2. Absorption by NaF; plate thickness: 8 mm.

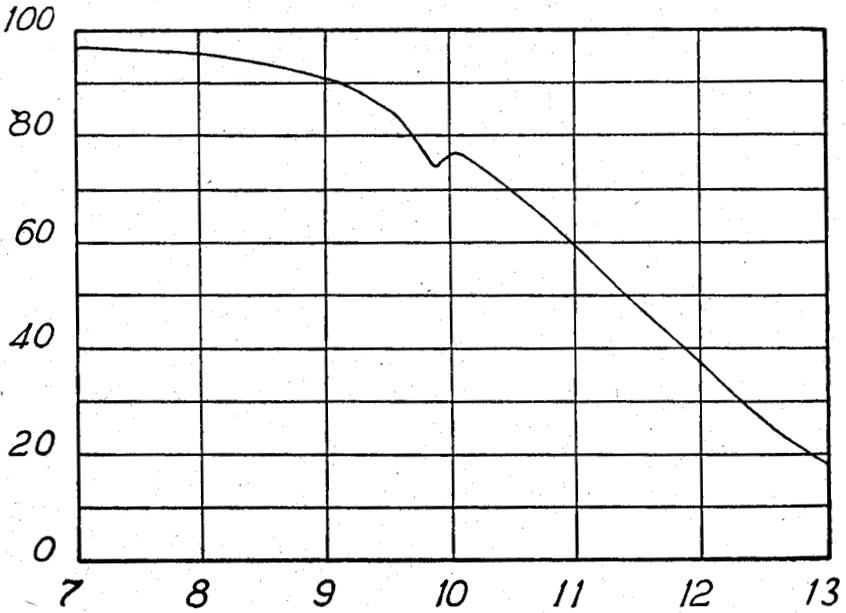


Figure 3. Absorption by NaF; plate thickness: 3 mm.

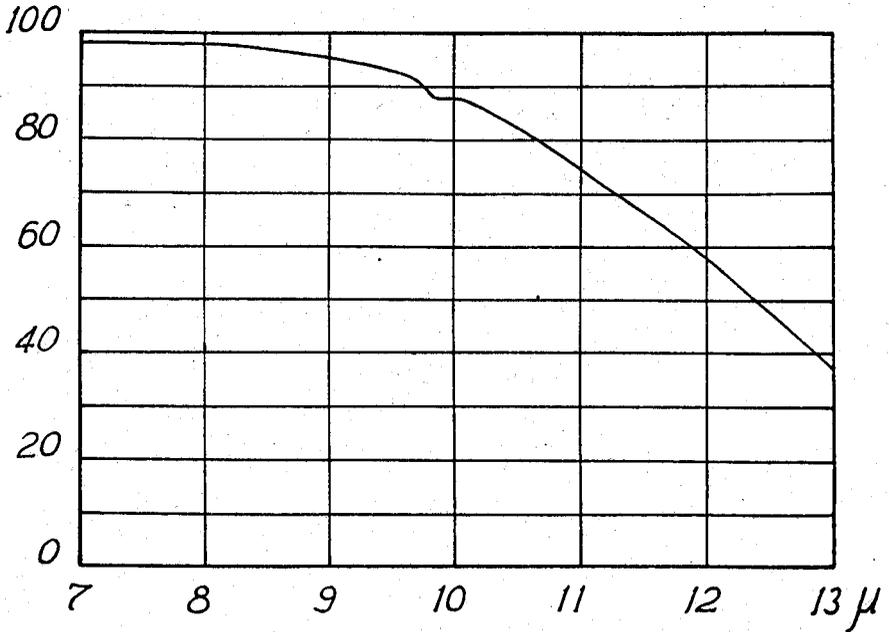


Figure 4. Absorption by NaF; plate thickness: 2 mm.

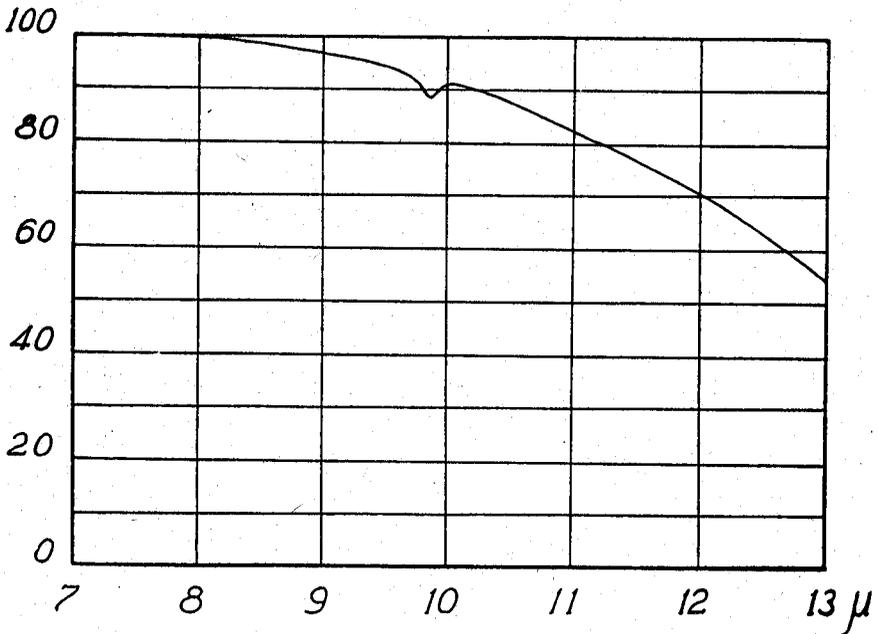


Figure 5. Absorption by NaF; plate thickness: 1 mm.

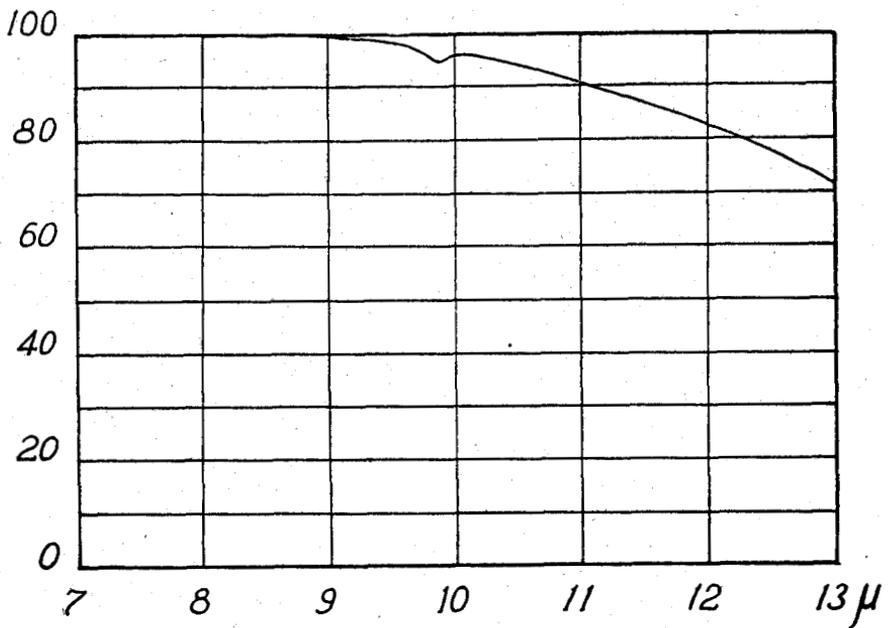


Figure 6. Absorption by NaF; plate thickness: 0.65 mm.

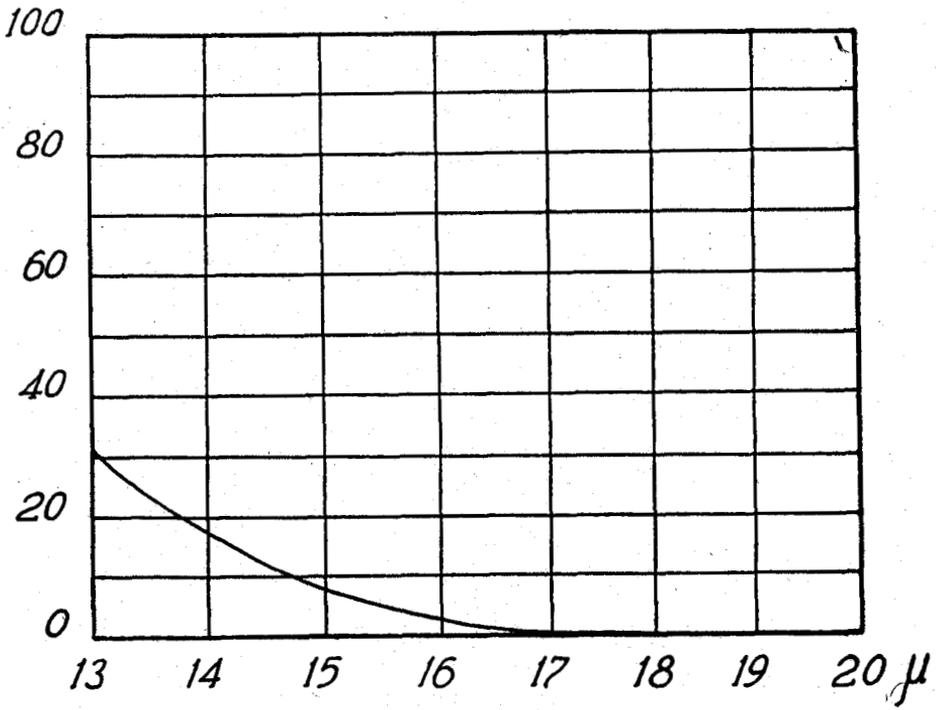


Figure 7. Absorption by NaF; plate thickness: 2 mm.

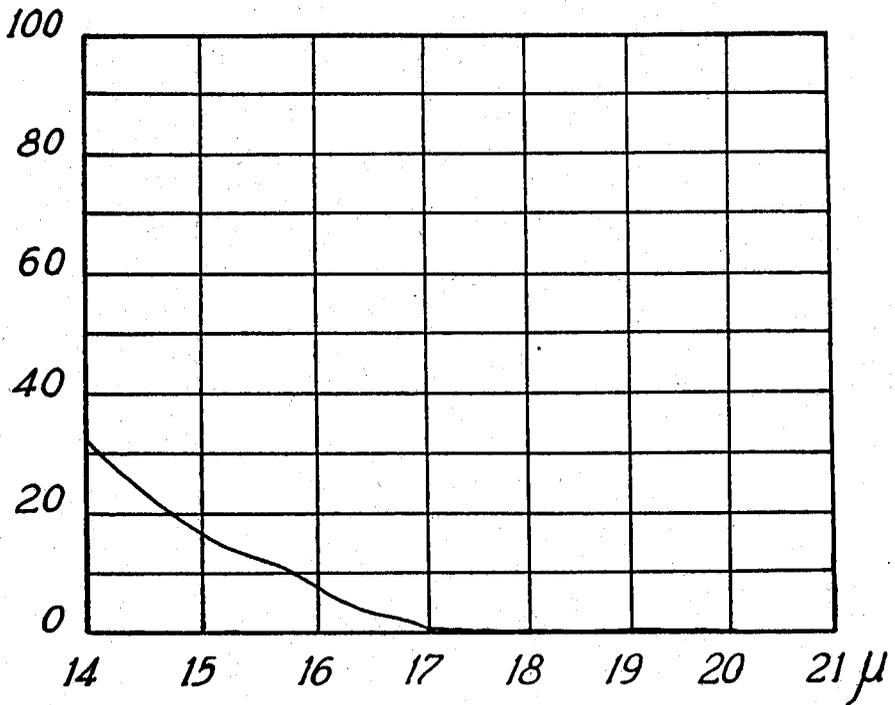


Figure 8. Absorption by NaF; plate thickness: 1 mm.

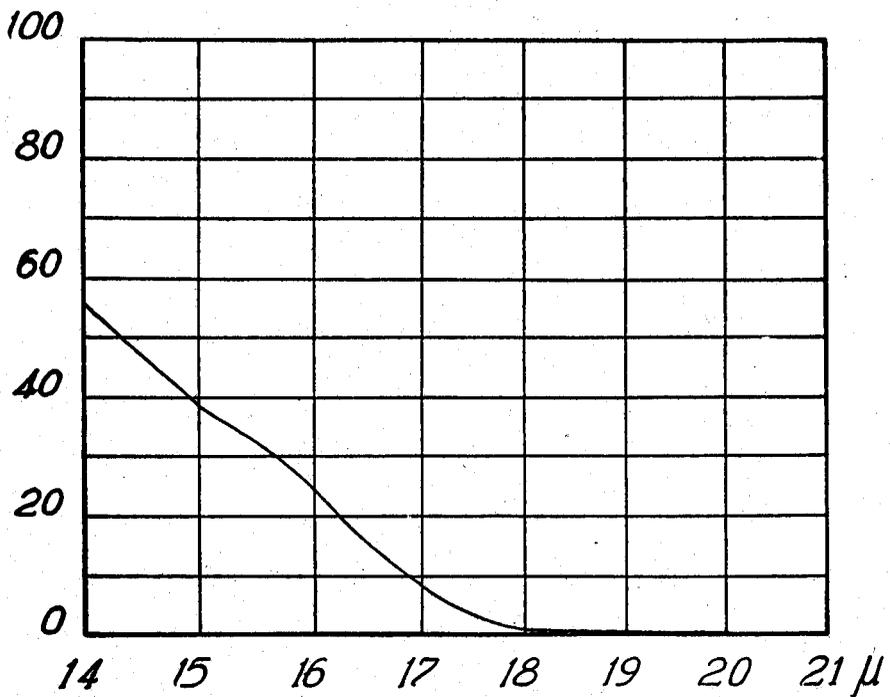


Figure 9. Absorption by NaF; plate thickness: 0.65 mm.

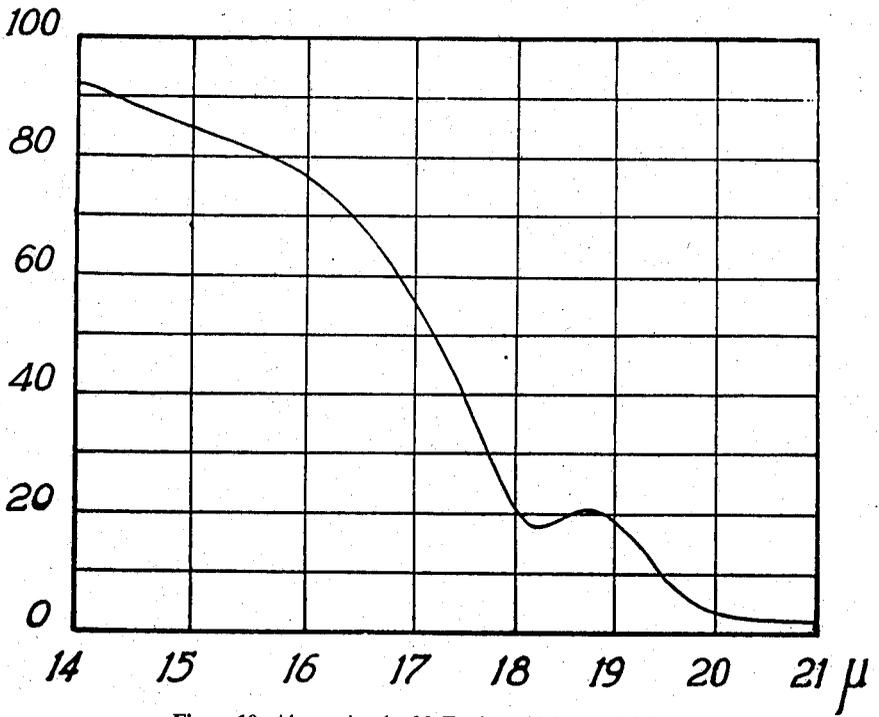


Figure 10. Absorption by NaF; plate thickness: 0.36 mm.

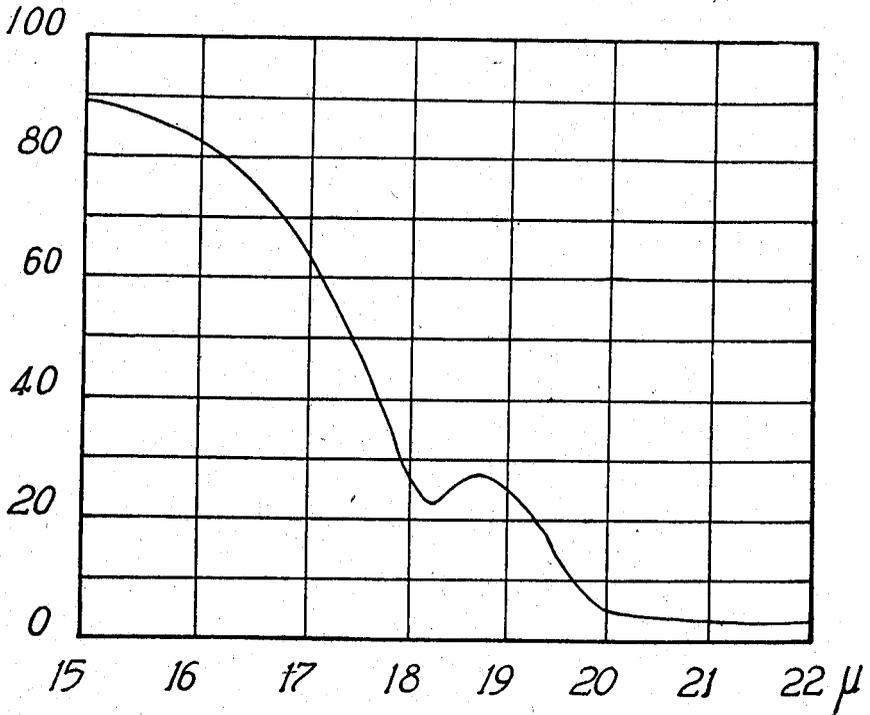


Figure 11. Absorption by NaF; plate thickness: 0.25 mm.

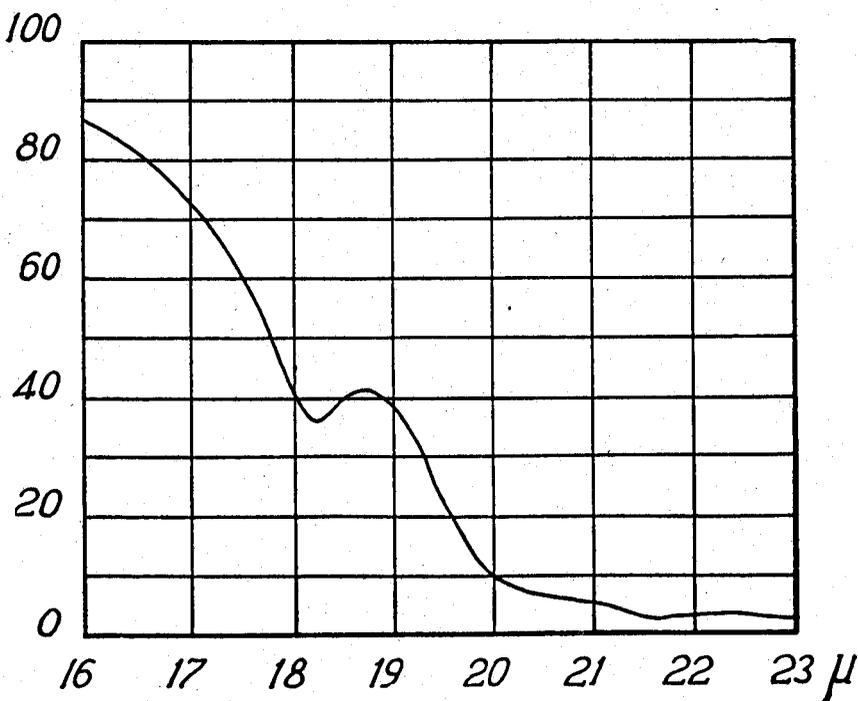


Figure 12. Absorption by NaF; plate thickness: 0.18 mm.

expressed as a wavelength, the fundamental is  $36.4 \mu$  and as a wave-number it is  $275 \text{ cm}^{-1}$ .

Not much need be said regarding the records covering the range between  $7 \mu$  and  $13 \mu$  obtained with the comparatively thicker plates and reproduced as figures 1 to 6 in the text. The features exhibited by them will be readily understood in the light of the remarks made earlier. At  $7 \mu$ , the absorption is that principally of the fifth-order due to the fundamental mode of highest frequency. This is readily observed in the record with the thickest plate (figure 1, 21 mm) but ceases to be noticeable with the smaller thicknesses. The absorption at  $9 \mu$  which is of the fourth-order is quite evident in figures 1 and 2, is weak in figure 3, and ceases to be noticeable in the later figures of the series. The transmission between  $9 \mu$  and  $12 \mu$  becomes progressively more complete with diminishing thickness, as can be seen from figures 3, 4, 5 and 6. In the region between  $12 \mu$  and  $18 \mu$ , we observe another significant series of changes. The cut-off at  $12 \mu$  due to the third-order absorption seen in figure 1 has disappeared in figure 2. It has, in fact, shifted to  $18 \mu$  as can be seen from figures 7, 8 and 9. As the result of the increasing transmission at  $12 \mu$  and the cut-off at  $18 \mu$ , the drop in transmission between  $12 \mu$  and  $18 \mu$  becomes progressively steeper with diminishing absorption path. This is apparent in

figures 7, 8 and 9. In these figures, there is also a perceptible dip in the transmission curve in the wavelength range between  $14\ \mu$  and  $16\ \mu$ . This may be identified as the effect of the second overtones of modes II and III listed in table 1. There are also indications of the absorption due to the first overtones of the same two modes in the wavelength range between  $20\ \mu$  and  $23\ \mu$  in figure 12.

### Summary

Twelve spectrophotometer records of the absorption by NaF plates are reproduced covering the wavelength range between  $7\ \mu$  and  $23\ \mu$  for absorption paths ranging from 21 mm down to 0.18 mm. The octave of the fundamental mode of highest frequency records itself as a sharply-defined absorption at  $18.2\ \mu$ . This gives  $275\ \text{cm}^{-1}$  as the fundamental frequency, in fair agreement with the theoretically computed value of  $281\ \text{cm}^{-1}$ . It also fits in with the observed infrared reflection maximum at  $36\ \mu$ .

### Reference

1. Raman C V "The specific heats of the alkali halides and their spectroscopic behaviour" *Memoir No. 131 of the Raman Research Institute and Proc. Indian Acad. Sci. A56* (1962).