

COMBINATION FREQUENCIES OF THE INFRA-RED BANDS
OF QUARTZ

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ABSTRACT

Many observers have studied the infra-red absorption bands of quartz and have found regions of intense absorption at 9μ , 12.5μ , 20μ and 26μ . These regions of absorption are assumed to be the fundamental frequencies of quartz. By combining these assumed fundamental frequencies six bands in the region from 3μ to 9μ are accounted for. Also the writer has experimentally located two bands at 2.72μ and 3.18μ which have not been previously observed. The frequencies of these two bands agree with two combinations of the fundamental frequencies. This gives a total of eleven absorption bands for the ordinary ray of quartz, extending from 2.72μ to 26μ whose frequencies agree, with only small differences, with the calculated values.

INTRODUCTION

THE infra-red absorption of quartz has been studied by several investigators. There have been found bands due to the absorption of the ordinary ray and the extraordinary ray but only bands due to the ordinary ray have been considered in this work. Schaefer, Bormuth and Matossi¹ have shown that there exists many combination bands in CaCO_3 and in other carbonates. In the present work the same method has been applied to the infra-red bands of quartz. Four intense bands of quartz are assumed to be the fundamental bands and other bands are calculated by simple combinations of the fundamental frequencies. A comparison is then made between the wave-lengths of the calculated bands and observed bands. Some simple combinations of the fundamental frequencies indicated that there might be several bands, yet unobserved, in the near infra-red and the writer has made a study of this region to see if they were present.

EXPERIMENTAL PROCEDURE IN PRESENT WORK

A Hilger quartz spectrometer for the infra-red was used as the resolving instrument. The high resolution was an advantage, but the absorption by the prism in the region from 2.9μ to 3.10μ caused the deflections of the galvanometer to be small. The new bands which were found did not fall in this region so that this did not prove a disadvantage. Globar was used for the light source and it was found that the deflections of the galvanometer were about three times as great as for a Nernst glower. The detecting system was made up of a Hilger thermopile and a galvanometer of a sensitivity of 10 mm per microvolt.

The thermopile was well wrapped and isolated and the galvanometer was placed on a pier not connected to the floor. At times the galvanometer showed some unsteadiness which at first was attributed to its high sensitivity. However, upon investigation it was found that the galvanometer was steady

¹ Matossi, Zeits. f. Physik **39**, 648 (1926).

when placed in a closed circuit with the same resistance as the thermopile resistance. The unsteadiness of the galvanometer when connected with the thermopile was due to small adiabatic changes in the air of the room. By suddenly opening a door in that part of the building a deflection was obtained in one direction and closing the door would give a deflection of the galvanometer in the opposite direction. On using a flourite window over the thermopile slit and making all openings to the thermopile chamber air tight, the fluctuations of the galvanometer ceased.

RESULTS OF PRESENT EXPERIMENTAL WORK

The absorption for a piece of quartz cut at right angles to the optic axis is shown in Fig. 1. The specimen was 3 mm thick. The readings were made at intervals of 0.01μ and the slit width of thermopile included about 0.015μ in this region. An absorption band was found at 2.72μ which is probably a part of the more intense band at 2.96μ . The band at 2.96μ is complex and has been studied by Dreische² who found three maxima at 2.91μ , 2.97μ and 3.02μ . Another band of small intensity has been observed by the writer at 3.18μ .

SUMMARY OF WORK OF PREVIOUS INVESTIGATORS

The bands at 2.72μ , 2.96μ and 3.18μ as found by the writer will now be used in connection with the work of Rubens,³ Nichols⁴ and Coblenz⁵ to study the frequency combinations of the infra-red bands of quartz. Coblenz has studied the region from 2μ to 6μ and found that at 3.5μ the absorption began increasing rapidly. A band was observed at 4.35μ which is shown in Fig. 2, curve A. Merritt⁶ has also studied the infra-red absorption of quartz for this region and he found small bands at 3.75μ and 4.10μ . Dreisch has recently studied the absorption of quartz and observed a band at 3.75μ .

In Fig. 2, curve B, the absorption bands of quartz for the ordinary ray are shown as observed by Nichols. The absorption of quartz is large in the region from 4.5μ to 8μ and it was necessary to use a very thin section.

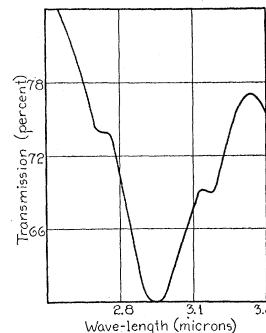


Fig. 1. The infra-red absorption of quartz for a section 3 mm thick cut perpendicular to the optic axis.

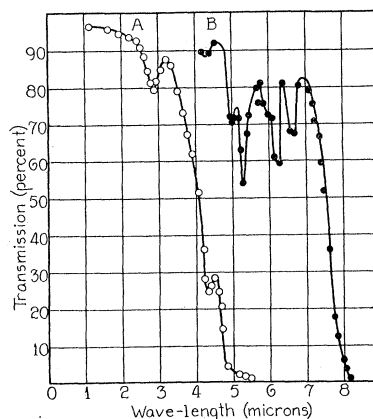


Fig. 2. Curve A, the absorption spectrum of quartz as observed by Coblenz. Curve B, the absorption spectrum of quartz to 8μ as observed by Nichols.

² Dreisch, Zeits. f. Physik **42**, 426 (1927).

³ Rubens, Preuss. Akad. Wiss., Berlin **16**, 198 (1919).

⁴ Nichols, Phys. Rev. **4**, 297 (1897).

⁵ Coblenz, Investigations of Infra-Red Spectra, Part 3, p. 21.

⁶ Merritt, Phys. Rev. **2**, 424 (1894).

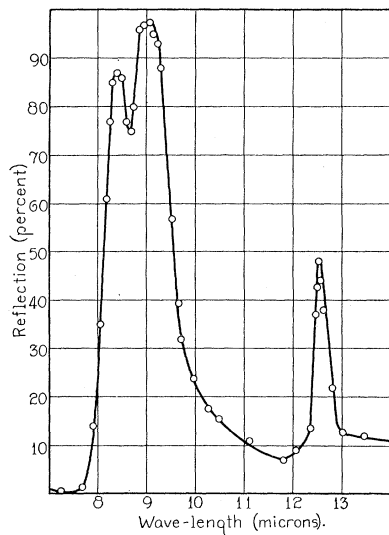


Fig. 3. The reflection spectrum of quartz observed by Coblenz.

In Fig. 3 are shown the reflection spectra of quartz from 8μ to 14μ as observed by Coblenz. Nichols found that although the thickness of his specimen was only 0.18 mm, he was not able to obtain any transmission beyond 8μ .

Bands were observed at 8.40μ , 9.00μ and 12.5μ . Rubens has found that two selective bands of quartz are located at 20.5μ and 26μ .

INTERPRETATION OF OBSERVED BANDS

Eleven bands have been observed in the infra-red spectra of quartz for the ordinary ray. The four bands at 9.00μ , 12.5μ , 20μ and 26μ are assumed to be fundamental bands. This assumption is made on the basis of the great intensity of the bands and their position in the spectrum.

By the theory of band spectra each band observed must be a fundamental, a harmonic or a combination band. The intensity relations, which are very helpful in the study of combinations, have not been studied closely. This was not possible as all of the fundamental bands have been observed by reflection. The existence of other bands of small intensity agreeing with other combinations of the fundamental frequencies is likely, but the intensity is probably small and in some cases is concealed by some of the stronger bands. In many cases several combinations would agree with an observed band to within the limits of error, but the simplest combination was always chosen as it was thought this would be the most intense.

In Table I are given the wave-lengths of the observed and the calculated bands and the combination which is thought to have produced the bands. Also the frequencies of the calculated bands are given.

The band at 9μ , which is assumed to be one of the fundamental bands, and is designated ν_1 , has a weaker component at 8.40μ . When there is a band which may be identified with a combination including ν_1 there should be two components of the band. Some of the combination bands including ν_1 have two components, but others do not. For example, only one component of the band, which is identified with the combination $2\nu_1 + \nu_2$, has been observed. The other component of $2\nu_1 + \nu_2$ should probably be less intense and is probably overlapped by the stronger band at 2.96μ .

Other combinations, which have not been included in Table I, point to the existence of many bands of small intensity. The reason that they do not appear is likely because these bands may be concealed in the stronger bands observed or the combination may have zero intensity. In addition to experimental errors there are other factors which should be considered

TABLE I. Observed and calculated absorption bands of quartz.

Obs. Band	Cal. Band	Combination	Wave-Number	Obs. Band	Cal. Band	Combination	Wave-Number
2.72 μ	2.80 μ	$3\nu_1$	3570 cm^{-1}	6.00	5.96	$\nu_1 + \nu_3$	1678
2.96	3.00		3333	6.26	6.26		1599
3.18	3.14	$2\nu_1 + \nu_2$	3180		6.25	$2\nu_2$	1600
	3.33		3022				
	3.55	$2\nu_1 + \nu_3$	2868		6.35	$\nu_1 + \nu_4$	1575
	3.69		2710	6.65	6.68		1496
3.75	3.62	$2\nu_1 + \nu_4$	2765	8.40	8.40	ν_1	1190
	3.84		2607	9.00	9.00		1111
4.10	4.20	$2\nu_1$	2380	12.5	12.5	ν_2	800
4.35	4.50		2222				
5.02	5.02	$\nu_1 + \nu_2$	1994	20.5	20.5	ν_3	488
5.30	5.23		1911	26	26	ν_4	385

in giving the reason for the variation of the observed and calculated bands. In the first place the wave-lengths of all the assumed fundamental bands have been observed by reflection and the wave-lengths of the combination bands and harmonics have been observed by absorption. Secondly, the calculated values of $2\nu_1$ and $3\nu_1$ and all combinations including $2\nu_1$ should have a correction factor. Kratzer⁷ has shown that the ratio of the frequencies of the fundamental and successive overtones should be

$$\nu_0(1-x) : 2\nu_0(1-2x) : 3\nu_0(1-3x)$$

This correction has not been made because it would probably not be accurate due to the large errors in the observed value of ν_1 . We would expect to find differences between the observed and calculated bands.

UNIVERSITY OF NORTH CAROLINA,
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⁷ Kratzer, Zeits. f. Physik 3, 289 (1920).