JANUARY 1, 1932 PHYSICAL REVIEW VOLUME 39

CONCERNING THE ABSORPTION AND REFLECTION SPECTRA OF CALCITE IN THE INFRARED

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(Received October 30, 1931)

Abstract

The reflection and absorption bands of calcite at 6.6–7.4μ have been studied with an echelette grating spectrometer of high resolving power, employing the resonance radiometer. A great deal of hitherto unobserved fine structure has been detected. It is to be noted: (1) that the maxima of the envelopes of the absorption and reflection bands differ widely in wave-length, as has been previously reported in the literature; (2) that within the bands, there is good agreement as to wave-length between the absorption and reflection lines. Possible explanations of this fine structure are offered, including that of combinations of reststrahlen and near infrared frequencies.

THE infrared absorption and reflection spectra of the carbonates have been studied over a long period of years. They are fairly easy to obtain in suitable form and are to be found in several interesting crystalline types. It was felt, after a previous paper[1] on the fine structure of quartz, that it would prove of value to study calcite more carefully, in view of its importance in optics, which is perhaps second only to quartz, among the uniaxial group.

The spectra of the carbonates, especially those of the uniaxial group such as calcite, have been found to be rather simple; and considerable work has been done in the exploration of their structure. Thus far there has been very good agreement between theory and experiment in depicting the form of the CO_3^{--} ion. X-ray evidence points to a plane structure for the CO_3 group, in which the oxygen-centers form the vertices of an equilateral triangle with the carbon situated at the centroid. Theoretical reasoning by Kornfeld,[2] Brester,[3] and others[4] predicts for such a model three active vibrations. The first of these lies at 7μ, and is due to a motion of the carbon in the plane of the group, either along or perpendicular to one of the medians; the relative positions of the oxygens remain fixed, or nearly so. The second vibration is to be found at 11μ, and is due to a vibrating membrane type of motion of the carbon perpendicular to the plane of the group. The third active vibration to be expected is at 15μ; it is due to a motion of an oxygen along a meridian, with an accompanying distortion of the remaining oxygen members. These predictions are well borne out, for in fact, in the near infrared there are three general regions of absorption and reflection: at 7μ, 11μ and 15μ. Moreover, the 7μ and 15μ bands are actually due solely to the ordinary ray, and the 11μ band is found only in the spectrum of the extraordinary ray.

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[1] Hardy and Silverman, Phys. Rev. **37**, 176 (1931).

[2] Kornfeld, Zeits. f. Physik **26**, 205 (1924).

[3] Brester, Zeits. f. Physik **24**, 324 (1924).

[4] A full discussion, with complete references, is to be found in Schaefer and Matossi, "Das Ultrarote Spektrum," (Springer 1930) and in Rawlins and Taylor "Infrared Analysis of Molecular Structure" (Cambridge Univ. Press 1928).

Of these absorption bands, that at 7μ is very broad and deep, and it has defied complete resolution. The 11μ band is rather weak, and that at 15μ is sharper but not as strong as the band at 7μ. The reflection band at 7μ is sharp and narrow compared to the absorption at this wave-length; that at 11μ is much weaker than its predecessor, and the last band at 15μ is quite faint in comparison.

There are two outstanding features concerning the relationship between the absorption and reflection spectra. The first is the relative ease with which resolution of the reflection spectrum is obtained as compared to the absorption spectrum; the second is that the wave-lengths of the 7μ and 15μ reflection bands are shorter than the corresponding absorption wave-lengths, whilst the reflection at 11μ lies to the long wave side of the absorption band.

Now, a recent investigation of the reflection spectrum of quartz,[1] in which an unsuspected amount of fine structure was revealed, caused some doubt as to the simplicity of the reflection spectra of solids in this region. It was felt that this question and the question of disparity of wave-length between absorption and reflection ought to be reinvestigated with an instrument of high sensitivity and resolving power. The 7μ band was chosen for the first study because of its great strength, and because it is generally assumed to be the first eigenfrequency of the CO_3 group.

For this exploration, the spectrometer and resonance radiometer used by J. D. Hardy[1,5] and the author earlier this year in a similar investigation of quartz, proved to be adequate. The set-up was very much the same as that described in this paper. The same grating was employed with a different mounting so that its "blaze," or concentration of maximum energy, was cast into the region to be studied. Improvements in the resonance radiometer itself were made so that the sensitivity was doubled, and a mechanical adjustment of the grids was provided to compensate zero-drifts caused by rising temperatures in the room.

Magnesium oxide was found to be quite a good filter to eliminate the higher orders of radiations of shorter wave-lengths, when prepared under the proper conditions. As reported by Pfund,[6] this oxide is an excellent filter for wave-lengths of 6μ and longer. It was found that one could fume the powder at varying particle sizes simply by burning the metal at different distances from the mirror which was being coated; since the particle size is a function of the time of growth, which varies directly with the distance through which the particle rises. After a little experimentation, a filter was prepared (by the method of trial and error) which permitted only 10 percent contamination at 6.5μ. This filter was then mounted and made a permanent part of the apparatus.

The calibration of the instrument was made by observing the higher orders of the 5461 and the 5790 lines of the mercury arc. This calibration was then compared to the wave-lengths of prominent atmospheric absorption lines.[7]

[5] J. D. Hardy, Rev. Sci. Inst. **1**, 429 (1930).

[6] A. H. Pfund, Phys. Rev. **36**, 71 (1930).

[7] Plyler and Sleator, Phys. Rev. **37**, 1493 (1931).

The two methods checked very well, the average discrepancy being less than 10A. The slits were 0.10 mm wide, which gave an effective slit-width of 20A.

For the reflection spectrum, a large calcite crystal was cut and polished to produce a mirror-surface of 5×5 cm. The final polish was as good as plate glass, and the sheet produced an image completely free of distortion; this latter is an item of considerable importance, as it is necessary to be able to reproduce the image of the filament identically. The absorption spectrum was taken in the following manner. A piece of calcite was rubbed down against a wet piece of ground glass. The fine milky powder which resulted upon drying was collected and dispersed with water to the proper degree of pastiness. This was then painted with a soft brush on a polished slab of rock-salt. Upon drying, the powder formed a thin, uniform white crust which appeared a golden brown against a bright background. In light of the previous paper, the transmission spectrum should yield, for such a powder, true absorption lines, as there is no contamination by reflection from these particles, which are small compared with the wave-length of light. The "cell" was so mounted that it could be removed from the path of the incident radiation without disturbing the calcite-coated surface. This film was thin enough to be some 14 percent transparent in the region of maximum absorption (a solid sheet 0.03–0.04 mm thick is about 2–3 percent transparent at this point). Because of the very strong and irregular atmospheric absorption in this region, it was necessary to take all readings with cell in and cell out in immediate succession. In the case of reflection, the calcite mirror was replaced by its gold counterpart for each new setting of the grating.

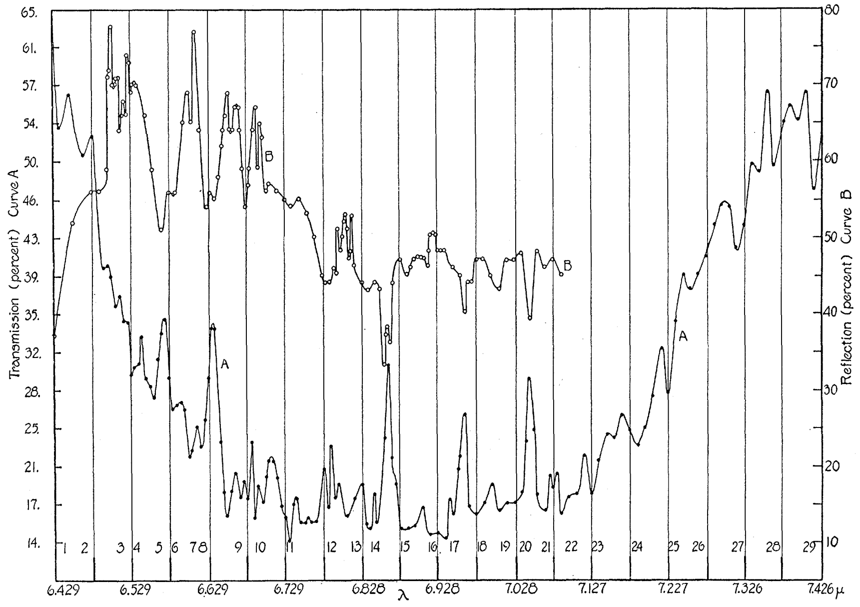

Fig. 1. *A*, Transmission of powdered calcite; *B*, Reflection from cleavage plane of calcite.

RESULTS

The spectra are plotted in Fig. 1. The envelopes of the absorption and reflection curves are seen to be quite dissimilar, with the minimum of transmission lying to the longer wave-length side of the reflection maximum, in complete accord with the literature.[4] It is further seen that there is remarkably good correspondence between the wave-lengths of the absorption and reflection lines; as is shown in Table I.

TABLE I.

Wave-lengths of Reflection Maxima			Wave-lengths of Absorption Maxima (Transmission Minima)	
Line number	λ	$\tilde{\nu}$	λ	$\tilde{\nu}$
1			6.439	1551.6 ± 0.3
2			6.467 ± 0.0015μ	1546.3
3	6.507 ± 0.0015μ	1536.8 ± 0.3	6.505	1537.3
	6.512	1535.6		
	6.522	1533.3		
4	6.527	1532.1	6.529	1531.6
	6.537	1529.8		
5			6.559	1524.6
6			6.584	1518.8
7	6.604	1514.2	6.404	1514.2
8	6.614	1511.9	6.616	1511.4
	6.657	1502.2	6.655	1502.7
9	6.662	1501.0		
	6.669	1499.4	6.669	1499.4
			6.679	1497.1
10	6.691	1494.5	6.689	1494.8
	6.696	1493.4	6.699	1492.6
11			6.734	1484.9
12			6.783	1474.4
	6.798	1471.0	6.793	1472.1
13	6.808	1468.9	6.808	1468.9
	6.816	1467.1		
14			6.838	1462.4
	6.848	1460.3	6.848	1460.3
15	6.878	1453.9	6.878	1453.9
16	6.923	1444.4	6.928	1443.3
17			6.948	1439.2
18	6.986	1431.4	6.984	1430.9
19			7.008	1426.6
20	7.038	1420.9		
21	7.063	1415.8	7.068	1414.8
22			7.088	1410.8
23	observations not carried further		7.127	1403.1
24			7.187	1391.4
25			7.227	1383.7
26			7.257	1378.0
27			7.317	1366.7
28			7.366	1357.6
29			7.416	1348.4

It will be noted that a similar correspondence in wave-lengths of absorption and reflection lines is to be found in the case of ammonium chloride, although the agreement is not as striking as that presented here.

DISCUSSION

A brief summary of the literature calls for a region of absorption and reflection at 7μ, Schaefer,[4] in a rather comprehensive treatment of the subject concludes that there is a double absorption band at 7.14μ and 7.40μ respectively, corresponding to the double reflection maxima found at 6.68μ and 6.98μ. Recent results of Plyler[8] confirm the position and apparent doubling of the reflection band. In this present paper, it will be noticed that the envelopes of both the absorption and reflection bands agree admirably with the results of Plyler and Schaefer. In addition, however, a maze of fine structure, both in the absorption and reflection spectrum appears, which entirely escaped detection of less sensitive instruments. It is also to be remarked that there is actual identity in wave-length between many reflection and absorption lines, although the intensities are such as to preserve the general contours of the earlier bands. In light of the previous paper (A.H.P. and S.S.)[9] this indicates true coincidence of reflection and absorption; this means then, that it is possible to study the frequencies of crystals by either method. The theoretical side of this problem offers interesting ground, and it is hoped that such calculations will throw light upon this question.

There are two alternatives in explaining this fine structure, which in complexity rivals that of a gas. First, one might assume that there are crystal irregularities which greatly multiply the number of possible vibrations without disturbing the macroscopic symmetry of the crystal. Such an explanation has been previously offered to account for the "doubling" of this band. Secondly, one might assume that this fine structure is caused by a combination of far infrared frequencies with frequencies in the near infrared, similar to the combination of vibration and rotation frequencies in gaseous spectra. In support of this last assumption, it was noticed that there are 29 strong lines, or centers of absorption, in the band. Now, if we investigate the sequence of lines 1–16, 2–17, 3–18, · · · , 14–29, we find that these transitions are all very close to 107 wave-numbers, with an average of $107.5\bar{\nu}$. This agrees fairly well with the frequency of the far infrared reststrahlen of calcite which is at 106 wave-numbers. There are also other possible combinations to be located. For example, the set of lines 1–9, 9–15, 15–23, 23–29 are separated by approximately 50 wave-numbers. This explanation is so far only tentative, for these sets are merely the best in agreement out of several possibilities; in addition, it appears evident that complete resolution has not yet been reached. This has been acknowledged in the grouping of these lines in which two or three weak lines clustering a strong line have been merged as one frequency. However, in spite of this arbitrariness, the coincidence of these recurring frequencies is so striking that it is not possible entirely to neglect it. As a check, it is planned to pursue a similar investigation of the harmonics of this band, as well as the corresponding bands of the other carbonates of similar crystallographic structure.

The author wishes to acknowledge a Grant-in-Aid of the National Research Council which has materially aided this work. He also wishes to express his thanks to Professors Pfund and Herzfeld of this laboratory, with whom he has discussed this experiment in detail.

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[8] E. K. Plyler, Phys. Rev. **33**, 948 (1929).

[9] A. H. Pfund and S. Silverman, Phys. Rev. **39**, 64 (1932).