THE ABSORPTION OF INFRARED RADIATION BY SMALL PARTICLES

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ABSTRACT

The absorption of infrared radiation by small particles of quartz, calcite and ammonium chloride has been studied. For this purpose a special radiometer was constructed, with its vanes coated with the material to be studied. Evidence is brought forth to show that the crystals, when sufficiently finely divided, do not reflect well in their regions of metallic reflection. This offers a simple method of studying the absorption spectra in these regions. In addition, a new type of selective filter employing a radiometer seems possible, with preliminary experiments in accord with expectations.

A N INVESTIGATION by one of us (S.S.)[1] on the fine structure reflection spectrum of polished calcite revealed a number of narrow reflection maxima whose positions agreed precisely with those of narrow transmission minima revealed by thin layers of powdered calcite. The question arose as to whether these minima were true absorption bands or whether they owed their existence to selective reflection, in virtue of which less energy would enter the powder film, thus decreasing the intensity of the transmitted radiation. To decide this matter, a study of the absorbing and reflecting properties of particles whose linear dimensions are small in comparison to the wave-length of radiation was undertaken.

The question might have been settled by using a hemispherical, silvered mirror of the Paschen[2] type. Such a mirror not being available it was decided to attack the problem by a method long used by one of us (A.H.P.). This procedure involves coating the receiving area of a thermopile or radiometer with a thin film of the powdered material to be studied. True absorption would cause an increased heating of the receiver while selective reflection would cause decreased heating.

For this work the radiometer was chosen in preference to the thermopile. The reason was that, since the sensitivity of the radiometer is primarily dependent upon the temperature difference between front and back of the vane, it was anticipated that, because of the high extinction coefficients of calcite, quartz, etc. in the regions of selective reflection, intense surface heating would be produced in case the powder particles acted as absorbers.[3] Two additional reasons which prompted the choice of the radiometer were: (1) ease of application of thin powder-films, (2) possibility of developing a "selective" radiometer, i.e., one which responds largely to a limited region of the spectrum.

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[1] To be published shortly.

[2] W. W. Coblentz, Bur. Stan. Jour. Res. 9, 283 (1913).

[3] A detailed description dealing with the construction of radiometer vanes will appear shortly. A. H. P.

Apparatus and Method of Procedure

For such an investigation, on which slight demands are placed upon resolving power and sensitivity, it was found advisable to use a rock-salt prism spectrometer with an ordinary Wadsworth mounting. A single prism was used with mirrors of 30 cm focal length with slit-widths of approximately 0.5 mm. A Nernst glower, run at 0.2 amperes and 220 volts, was used as the source of radiation. The radiometer was very robust; the vanes were 1×7 mm and were mounted upon a quartz fiber of a length which gave a period of about 1 sec. The vanes were prepared by mounting lens-paper on thin films of nitrocellulose, and combined extreme lightness with great sturdiness. The vanes were mounted in pairs in the usual fashion; one was given an additional coat of gold-leaf which was then sooted with camphor-black, and the other was coated with the material to be studied. It was found that the precaution of adding gold-leaf enormously facilitated the deposition of an adequate layer of soot. The radiometer behaved admirably. It was very stable, being practically free of drifts and stray vibrations which render a lighter system of long period so difficult to operate; and it was possible to take all readings during the daytime.

The method of procedure was to mount the radiometer in place with a large bottle of some three liters capacity, containing some phosphorous pentoxide, placed in series with the tube; the system was then evacuated by means of an ordinary oil-pump. The large capacity served to prevent pressure fluctuations when the pump was shut off, and the pentoxide prevented water vapor from curling the vanes when the outfit was at atmospheric pressure. The system was evacuated until the radiometer became slightly ballistic; this is the optimum point obtainable as it provides good sensitivity with high speed of response and accuracy of readings. The radiometer at these pressures is an extremely good pressure gauge, so that it was rather easy to ascertain that the sensitivity of the radiometer remained constant throughout a run. In practice it was found that the sensitivity did not suffer any measurable change within 48 hours after turning off the pump. The radiometer gave readings of about 5–20 cm at a scale distance of 2 meters. The spectral runs covered a region from 3μ to about 11μ, at intervals of about 0.1μ. Readings were taken first with the blackened vane in place and immediately afterward a second run was taken with the powdered vane in position. The relative radiometric powers follow by simple ratios, for, with identical air-paths, atmospheric absorption is equal for both runs. Following this, a set of readings was taken to yield the transmission spectra of the various salts on nitrocellulose; the cellulose itself was so thin that it showed first order Newton's colors, and hence was almost perfectly transparent to the entire region covered. Inasmuch as NH_4Cl sublimes very readily, it was more feasible to fume the salt than to "paint" it. Powdered calcite and quartz were obtained in a state of fine subdivision and were mixed with water and a minute amount of gum arabic. These mixtures were well dispersed, and spread uniformly over the surface of nitrocellulose. The films were laid down to such a thickness that a bright tungsten filament could not be seen through them. The radiometer vanes, it might be

added, were coated in a similar fashion, except that the films were very much thinner, giving a smooth chalky surface which was gray against its dark background.

The reflection data for quartz and calcite were easily obtained from previous investigations.[4,5,6] However, for NH_4Cl, the best curve obtainable was that of Reinkober[7] which was taken on a plate of highly compressed powder. Although such a plate should approximate a smooth massive crystal, it was thought best to use a single slab of the salt, if possible. Fortunately a large crystal possessing a good surface of about 3×4 cm was found in a laboratory supply jar. The crystal was fairly clear and when ground and polished, it yielded a very creditable surface.
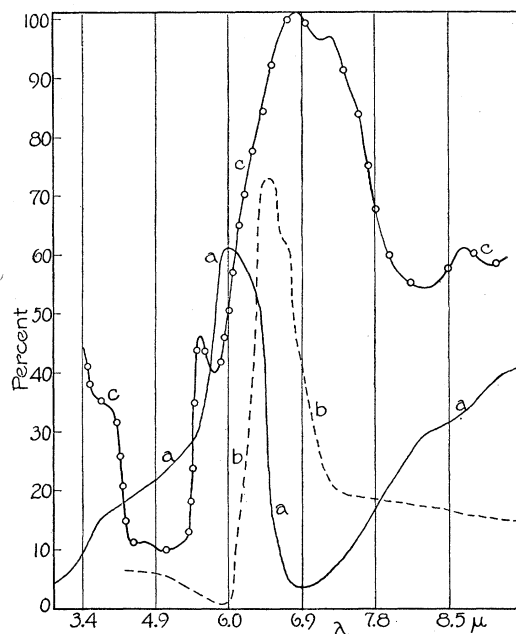

Fig. 1. Calcite (a, c powder, b, plate) a, transmission; b, reflection: c, radiometer.

RESULTS

The reflection spectrum of calcite, Fig. 1b shows a strong maximum at $6.5 - 6.6\mu$ rising very sharply on the short wave side, and falling off less rapidly on the long wave side. The transmission of the thin powder, Fig. 1a, shows strong opacity at 2.9μ with a sharp rise in transparency, broken slightly at 3.5μ, to a maximum at 5.9μ of 60 percent. This is followed by a region of strong absorption whose center lies at about 6.8μ. The calcite again becomes transparent but never reaches a value much higher than 40 percent on the long wave side of this band. The radiometric curve Fig. 1c shows calcite to be

[4] Lecomte, "Le Spectra Infrarouge."
[5] Schaefer and Matossi, "Das Ultrarote Spektrum."
[6] Hardy and Silverman, Phys. Rev. 37, 176 (1930).
[7] Reinkober, Zeits. f. Physik 3, 1 (1920).

about 40 percent as good as soot at 3.5μ. This then falls with increasing wavelength to a minimum of 10 percent in the region of 5μ. Following this is a sharp, steady increase in radiometric power broken only by a small dip at 5.8μ. The curve rises again, increasing through the successive regions of strong reflection and absorption to a maximum value of nearly 100 percent between 6.7μ and 7.3μ. The curve then falls off to a fairly steady value of 60 percent as far out as 9.2μ. It might be pertinent to remark at this point that it is quite essential to provide a heavily sooted vane for comparison work of this sort. The first sooted vane which was used was prepared simply by depositing the soot directly on the paper vane; the second vane was prepared, as mentioned above, by depositing the black on goldleaf. It was found that at 10μ the second vane was nearly four times as sensitive as the first.
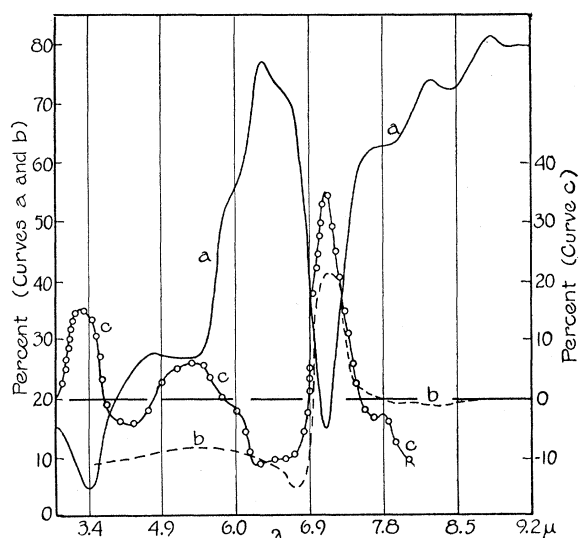

Fig. 2. Ammonium chloride (a, c, fumed; b, plate); a, transmission; b, reflection; c, radiometer.

Fig. 2b shows the reflection curve for NH_4Cl; the data taken for the large polished crystal were found to coincide very nicely with the results of Rein-kober on a compressed plate of the same salt. There is relatively a strong maximum at 7.1μ, and a very weak one at 3.4μ. The transmission of the sublimed film is shown in Fig. 3, curve a. There is a minimum at 3.4μ and indications (which are not very pronounced) of another minium at 5.2μ; there follows a sharp maximum at 6.2μ with a precipitious minimum at 7.1μ. The absorption then falls off, and the material becomes increasingly transparent toward longer waves with slight fluctuations in percentage of transmission. The radiometric power (curve c) yields a trace which is a fine counterpart of the reflection and absorption curves; at 3.4μ and 5.2μ there are maxima, followed by a minimum at 6.2μ and a strong maximum at 7.1μ. Beyond this wave-length there is a sharp decrease. It will be noted here that there are recorded negative percentages, which correspond to a radiometer throw in the negative direction. Their significance is that at the wave-lengths where these

negative throws occur, the NH_4Cl is so transparent that the radiation pene-
trates to the back of the vane, which is in this case charred paper. This ma-
terial is sufficiently black to create, upon heating, a "back radiometric"
effect; and in these regions it is from this side of the vane that the radiometric
action takes place; so that in this way a complete reversal of the direction of
deflection may occur. Quite obviously this difficulty can be readily avoided by
depositing a sufficiently heavy film of salt, or by employing some transparent
material for the back of the vane.

Fig. 3, curve b, illustrates the reflection spectrum of quartz. It possesses a
strong double maximum at 8.5 and 9μ as reported by previous investiga-
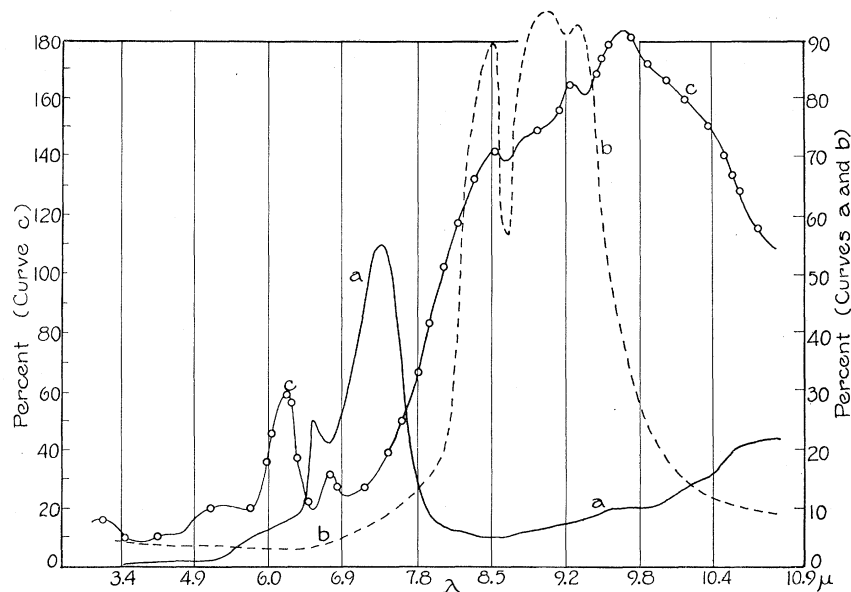tors[4,5,6] Curve a of the same diagram represents the transmission spectrum of

Fig. 3. Quartz (a, c powder; b, plate); a, transmission; b, reflection; c, radiometer.

the powdered crystal. There are maxima at 6.7 and 7.5μ and a minimum at
6.9μ; following the strong maximum at 7.5μ there is a region of opacity from
8.3μ to 10.4μ. Curve c is the radiometric curve. It shows small maxima at 6.2
and 6.9μ, rising to a high peak at about 9.5μ, where it is nearly twice as effec-
tive as soot; following, the radiometric power subsides with increasing wave-
length to an efficiency of about 100 percent at 10.8μ.

DISCUSSION

In all cases studied, it is to be noted that a strong radiometric effect is
found both in the regions of selective absorption and selective reflection. In
the case of calcite at 6.6μ where the reflection is over 70 percent and the trans-
mission is about 25 percent, the radiometric effect is close to 100 percent.
Again for NH_4Cl, at 7.1μ the reflection is 45 percent, the transmission is 15
percent and the radiometric effect is 35 percent. (It is to be noted here that

this is one of the few instances where the wave-lengths of the absorption and reflection bands have been reported to be identical. This question will be discussed later in connection with similar results obtained in connection with a study, by one of the writers,[8] of the 6.7μ band of calcite). In the case of quartz, ˙ ave a reflecting power of about 90 — 95 percent around 9μ, with a low transmission of only 10 percent. The radiometric power, despite the extremely high reflecting power, is better than that of soot. This may partly be due to the poor absorption of soot. Inasmuch as the greater portion of the radiometric effect is due to the heating in the superficial surface layer, the powdered salts are remarkably well adapted for use as radiometer coatings; since their absorption coefficients are high, most of the absorption will take place near the surface, which is advantageous for the production of a large radiometer effect. This means then, that in the study of the strong absorption or reflection bands of a particular solid, that the receiving device should be coated with the same material, when possible.
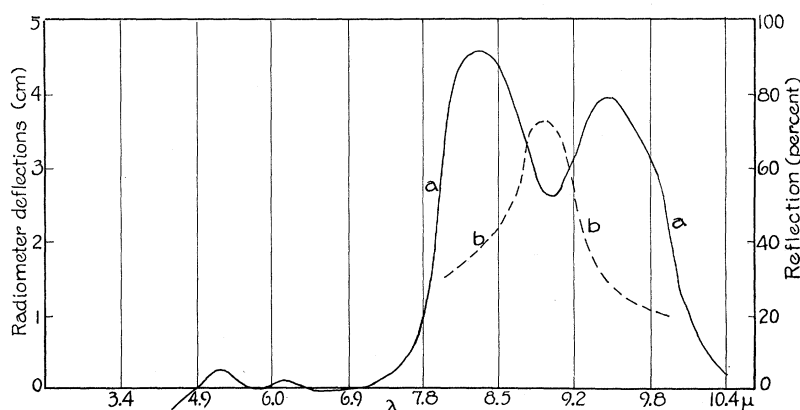

Fig. 4. a, Radiometric curve, fused quartz flake; b, Reflection spectrum, fused quartz plate.

Since the radiometric effect requires the phenomenon of absorption, these thin powders cannot reflect directly in their regions of selective reflection, for the possibility of such high reflection does not hold with the observed high radiometric power. This is illustrated in Fig. 4, curve a, which represents the energy curve for a vane made of a quartz film several μ thick. A strong minimum is perceived in the region of high reflection, (curve b). Since scattering is, for the same reason, not possible to any great extent, unless it leads to multiple reflections among the discreet particles within the powder, with ultimate absorption due to trapping, one is lead to the conclusion that the particles are too small to behave as reflectors, and absorb directly.

The particles are very fine: the quartz and calcite particles measure between 2.0 — 3.0μ and the ammonium chloride particles are considerably smaller, appearing reddish in transmitted light. This minuteness of particle and film seem to preclude possibility of trapping, and it appears that the logical explanation lies in a true absorption. This thesis has some support in a prob-

[8] S. Silverman, in print.

lem in the far infrared spectra of the carbonates which has been discussed briefly by Wood.[9] He arrives at the conclusion that particles, when too small to behave as resonators for reststrahlen, are unable to reflect, but absorb these radiations. It is quite likely that herein lies the explanation of the intense absorbing power of metallic substances such as bismuth black.

Use of the Radiometer as a Filtering Device

From an entirely different view-point, these results introduce interesting possibilities. In the ever important question of filters, it has always been desired to find a material which is transparent to the region to be studied and which is opaque to the shorter waves that lead to the contamination of higher orders in grating spectrometers. One of the writers has recently described one
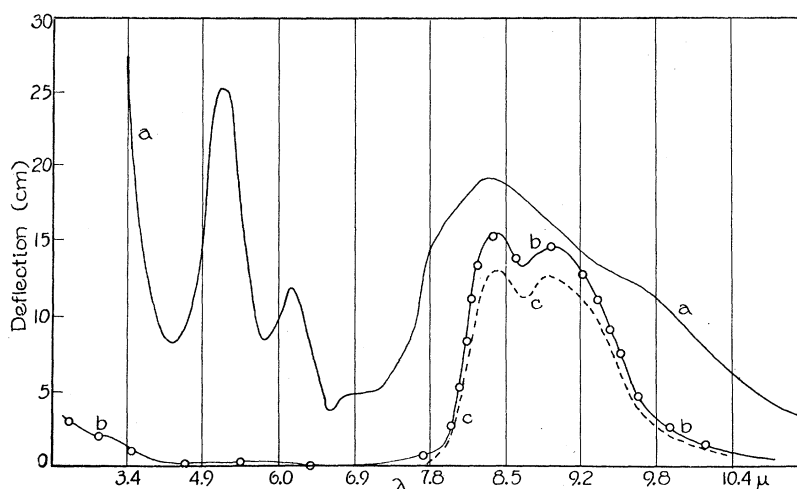

Fig. 5. Energy curves. a, Quartz coated vane: b, Quartz coated vane; radiation reflected from quartz mirror: c, Quartz coated vane with quartz mirror and MgO filter.

method by which this goal may be approached by using such powders as zinc oxide and magnesium oxide.[10] The reverse problem is much simpler: it is relatively easy to find a material which is opaque to a given region and which is transparent to shorter waves. A radiometer coated with a substance which fulfills these conditions should show a small sensitivity to the waves to which its coating is transparent, and a relatively large sensitivity to those radiations to which its coating is opaque. There is a possibility that such a filter might be very useful in the far infrared, where this difficulty has been very pronounced. For example, a vane covered with a thin film of one of the alkali-halides should be quite opaque to radiations longer than about 30μ, and shorter waves, due to the transparency of these halides in this region, should have a relatively small radiometric effect. Such a vane used with a transmission filter of quartz to deaden the enormously powerful region of 1.5μ might

[9] R. W. Wood, Physical Optics, p. 632 (Macmillan).

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

offer interesting possibilities in the long-wave region beyond 50μ where quartz again becomes transparent. Furthermore, by proper combinations, one could obtain a group of powders opaque to almost any given region. It is planned to attempt such an experiment in this laboratory in the near future. A preliminary attempt to construct a filter for the 9μ region is shown in Fig. 5. By a succession of combinations of a quartz-coated vane, a quartz mirror, and a film of magnesium oxide, a filter is produced which is opaque to radiations shorter than 8μ, and which is fairly transparent out to 9.5μ.

CONCLUSION

These investigations show that finely divided powders act as absorbers in the region of metallic reflection, and do not reflect. In a subsequent paper this is brought out to indicate that the coincidence of reflection maxima and transmission minima in calcite represents a true agreement between absorpton and reflection lines. This offers an extremely simple method of studying absorption spectra in regions of high reflection without having to allow for the loss of energy by reflection. The advantages of the radiometer over the thermocouple for this work are manifold. In addition to its superiority in speed and durability—a single suspension lasted throughout the entire experiment despite the many changes in vanes—it offers possibilities in filtering out radiations of lower wave-lengths. A preliminary combination has produced a radiometer vane and filter which is quite good for the region of 8μ to 9.5μ The general usefulness of such a filter is limited only by its transparency to shorter waves, and by the width and depth of its region of opacity. Since it has been shown that these finely divided materials become intensely black within the region of selective reflection and absorption, it is proposed to study the temperature emission of thin layers of such substances. It is anticipated that intense selective emission will occur within the region of great absorption.