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THE INFRA-RED ABSORPTION OF BRUCITE AND SOME SULPHATES; ISOTOPIC EFFECT*

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ABSTRACT

By means of an infra-red spectrometer the structure of the absorption band of brucite [$Mg(OH)_2$] was studied. The region of greatest absorption was found to be at 2.48μ. Besides this maximum there were small maxima of absorption located at 2.40μ, 2.30μ, 2.14μ. The maxima at 2.48μ, 240μ, and 2.30μ correspond approximately in position and absorption to the isotopes of Mg^{24}, Mg^{25}, and Mg^{26} as found by Aston. The small band at 2.14μ, corresponds in position to Mg^{28}. However, this isotope is not given. The work of Coblentz has been examined for the isotopic effect. In the reflection spectrum of nickel sulphate in solution there are two maxima located at 9.15μ and 9.50μ. The second is more intense. These maxima are probably due to Ni^{58} and Ni^{60}. In the spectrum of potassium sulphate there are two maxima, one at 9.00μ and the other at 9.40μ. The maxima at 9.40μ is much more intense. These two maxima are probably due to K^{39+41} and K^{39} taken twice. Other sulphates in solution showed only one maximum. The sulphates of barium, strontium, and magnesium in the solid state also had complex maxima. As the light was unpolarized, these maxima might be due to pleochroism.

INTRODUCTION

SINCE Aston first found the existence of isotopes in some elements by means of the mass spectrograph, many attempts have been made to find a difference between the spectra of materials obtained from different places. In line spectra the displacement due to the different isotopes is very small and thus it is difficult to detect them. However, in band spectra the mass of the atoms composing the molecule considerably influences the position of the maxima. Kratzer[1] and Loomis[2] first showed the relation between mass of atoms and location of bands. Kratzer has extended the theory of band spectra more recently. It is shown that in band spectra there exists a band for each isotope. For example, in the case of hydrogen chloride there exists a set of bands for HCl^{35} and HCl^{37}. The intensity of these are about in the ratio of the abundance of the two isotopes. Sometimes the fine structure of the two bands overlap and makes it difficult to separate them. In like manner we should expect every absorption band which was caused by molecules that contained isotopic atoms to have as many maxima of absorption as there were

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[1] Kratzer, Zeit. Phys. **3,** 460(1920).

[2] Loomis, Astrophys. J. **52,** 248(1920).

different isotopes. By examination of many absorption and reflection spectra in the infra-red, there are not found the separate maxima due to the isotopes. This should not be interpreted to mean that the isotopic effect does not exist, but rather that it has not been observed. There are probably two reasons for this: first, the resolution of a prism spectrometer is not sufficient in some band spectra to separate the maxima; second, the investigators have been more interested in the position and percent absorption of the maxima of the bands than in the study of the fine structure of bands. Readings were made at intervals of .10μ; so we should expect to find the isotopic effect only in a few cases. Further on an example of this is given.

It should be remarked that the theory of band spectra and its application to the isotopic effect has been built up on the basis of a diatomic molecule of a gas. For a more complex molecule the results would be different. We would still find the isotopic effect but it would be more difficult to calculate the relative displacements. In the case of a liquid there would be some interaction between the different molecules. Yet we should expect to observe the isotopic effect.

In the case of solids it cannot be seen that it is an isolated molecular rotation. However, the absorption in solids is in general similar to that in liquids, and the isotopic effect should also appear in the bands of solids.

In order to see if the isotopic effect was of the same nature in solids as in gases, cleavage sections of brucite, $Mg(OH)_2$, were prepared. Brucite was selected because the optic axis is perpendicular to the cleavage planes. That made it certain that other maxima were not found due to the radiation having a path not parallel to the optic axis.

Apparatus and Experimental Procedure

An infra-red spectrometer with rock salt prism was used to disperse the radiation. The collimator and telescopic slits were each .25 mm. A Nernst glower was used for the source. For regions below 3μ a 20 ampere tungsten lamp was used. The detecting system consisted of a linear thermopile and a low resistance galvanometer of high sensitivity (10 mm per microvolt). The deflections were read by means of a telescope two meters from the galvanometer. The deflections were approximated to .1 mm. Very little error was present in taking readings for the least deflection obtained in the region of greatest absorption was over 4 cm. At each setting of the instrument four deflections were obtained; two when the specimen was in the beam and two for the source.

RESULTS

A. BRUCITE

In Fig. 1 is shown the absorption curve for brucite for a thickness of .30 mm. The points are not put on this curve as they come so close together. From 2μ to 2.60μ readings were made at intervals of .02μ. From 2.60μ to 4μ readings were made at intervals of .05μ. Maxima of absorption were found at 2.48μ, 2.40μ, 2.30μ, and 2.14μ. At the most absorbing region there was about 19 percent of the energy transmitted. Since the coefficient of absorption was not desired in this work, no correction was made for reflection. The transmission curve shown here corresponds in general with that obtained by Coblentz.[3] However, the writer also found a band at about 1.30μ. The true shape of this band could not be obtained because of small rough places on the surface. This causes a greater percent of diffuse reflection for short wave lengths than for longer ones. The region from 2μ to 2.60μ was studied five times and two different specimens were used. There existed slight differences due to experimental error, but the four bands appeared for each trial. As can be seen from the curve, it is difficult to find the exact location of the maxima. The readings at 2.12μ and 2.14μ were the same. Since the

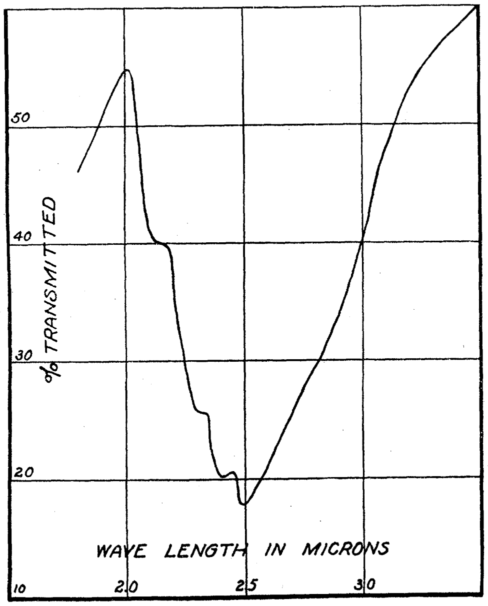

Fig. 1. Brucite.

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[3] Coblentz, Investigations of Infra-red Spectra, Part 1 and 2.

settings were made at intervals of .02μ, any of the maxima might be in error by that amount.

These maxima are of especial importance as they correspond to the maxima for the isotopes of magnesium. The atomic weight of magnesium is 24.32. Aston[4] gives the isotopes Mg^{24}, Mg^{25}, and Mg^{26}. The separation between the bands can be found approximately by considering Mg as one center of mass and $(OH)_2$ as the other. The equation for a diatomic molecule can then be used. In Table I is given the observed and calculated values for the isotopes. All the calculations are made on the basis of the more abundant isotope Mg^{24} having its maxima at 2.48μ.

TABLE I

Isotope	Observed Band	Calculated Band
Mg^{24}	2.48μ	2.48μ
Mg^{25}	2.40	2.39
Mg^{26}	2.30	2.30
Mg^{27}	——	2.21
Mg^{28}	2.14	2.13

It can be seen from the above table that the observed bands are located at the proper positions. Fig. 1 also shows that the intensity is of the right magnitude. When the percent absorption increases so rapidly with change in wave length, errors are more likely to occur. However, the small band at 2.14μ appeared each time. This band could be due to impurities in the brucite. The material was transparent and of a silvery white color. No band was formed which corresponded to Mg^{27}. There is a slight inflection of the curve at 2.20μ, but this is probably due to experimental errors. Watson[5] has recently studied magnesium hydride and finds the isotopes for Mg^{24}, Mg^{25}, Mg^{26} but no lines due to Mg^{28}. This would cause us to think that the small band at 2.14μ might be due to some other cause.

B. SULPHATES

The writer also desired to find the isotopic effect for some liquids. Kindred materials such as the different sulphates would be suitable because they all have absorption bands of nearly the same type. Coblentz[6] has already shown that all sulphates have bands of reflection in the region of 9μ. Thus we should expect any differences in the bands to be caused by the combining element rather than by the SO_4 radical.

All of these spectra were obtained by reflection. A solution of the different materials was made. As water does not have any strong bands at 9μ, it is not likely that the reflection spectra were modified by the water.

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[4] Aston, Isotopes, London.

[5] Watson, Astrophys. J. **63**, 20 (1926).

[6] Coblentz, Investigations of Infra-red Spectra, Part 3 and 4.

However, the percent reflection is much less for the solution than for the solid state of the substance. Coblentz also measured the reflection from nickel sulphate in the solid state and finds a double maxima as in the case of the solution. The band in solution is shifted to greater wavelengths. Pfund[7] has measured the reflection spectra of the sulphates in the solid state. His values give maxima for all the sulphates at around 9μ. So it seems reasonable to assume that all these maxima are due to the sulphates and that they are little influenced by water.

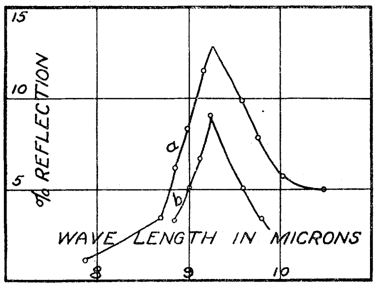

Fig. 2. (a) Cadmium sulphate, (b) dilute solution.

By examination of these reflection spectra the isotopic effect was observed. In Fig. 2 is shown the reflection spectra for cadmium sulphate. It can be seen that a rather sharp band is found. In this reflection band as well as in the others represented the readings were made at intervals of about .10μ. So in some cases there might be a complex structure which is not brought out by the observations.

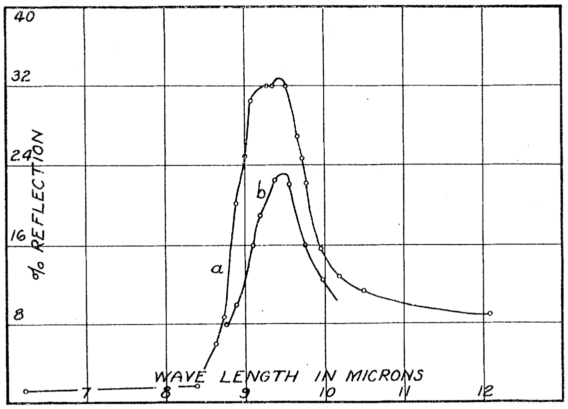

Fig. 3. (a) Nickel sulphate, (b) dilute solution.

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[7] Pfund, Astrophys. J. **24,** 19 (1906).

Curve *a* represents a concentrated solution and curve *b* represents a more dilute solution. Only one maxima is present and it occurs at 9.2μ.

In Fig. 3 are shown the reflection spectra of nickel sulphate. Curve *a* is for a concentrated solution and curve *b* for a solution of 50 percent strength. The reflection band is complex. There are two maxima located at 9.15μ and 9.5μ. As the readings were made at intervals of .1μ, these values cannot be considered to have a greater accuracy than that amount. These two maxima are probably due to Ni^{58} and Ni^{60}. The atomic weight of nickel is 58.68; so the intensity of the maximum due to Ni^{58} should be about twice that of Ni^{60}. Also the maximum of reflection due to the lighter isotope should have a greater wave-length.

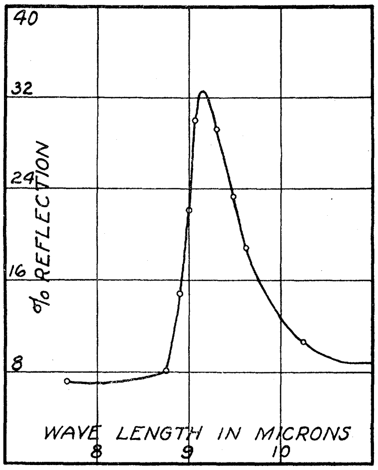

Fig. 4. Zinc sulphate.

In Fig. 4 is shown the reflection spectrum of zinc sulphate. Four isotopes have been found for zinc: Zn^{64}, Zn^{66}, Zn^{68}, and Zn^{70}. Only one maximum was found by Coblentz. However, from examination of the curve it can be seen that the head of the band was not studied. Other maxima could be located between the points studied. The writer plans to determine the reflection band of zinc sulphate to see if the isotopic effect is present.

In Fig. 5, curve *b*, is given the reflection band as obtained from potassium sulphate. Two maxima appear at 9.1μ and 9.4μ. The atomic weight of potassium is 39.10 and the two isotopes are K^{39} and K^{41}. That means that there is 19 times as much K^{39} as K^{41}. Since two atoms of potassium combine with the SO$_4$ to form the potassium sulphate, we would expect to find molecules with $K^{39}{}_2SO_4$, $K^{41}{}_2SO_4$, and $K^{39}K^{41}SO_4$. Since there are 19 K^{39} atoms for each K^{41}, the ratio of the three kinds of molecules will be 1 : 1/400 : 1/9. So the two bands represent $K^{39}_2SO_4$ and $K^{39}K^{41}SO_4$. The $K^{41}_2SO_4$ would have only 1/400 the intensity of the greatest intensity and so was not observed.

Coblentz[6] also measured the reflection spectra of barium sulphate, strontium sulphate, and magnesium sulphate from the crystals. All of these sulphates had reflection bands near 9μ. They also had complex bands, showing two or three maxima. It is likely that the different maxima are caused by the isotopes of barium, strontium, and magnesium. The different maxima could be caused by reflection bands due to the different optical directions through the crystals. Since polarized light was not used, it is not correct to attribute these maxima to the isotopes. Also there is no way of obtaining the true intensity as it would vary considerably with the plane of polarization of the incident light.

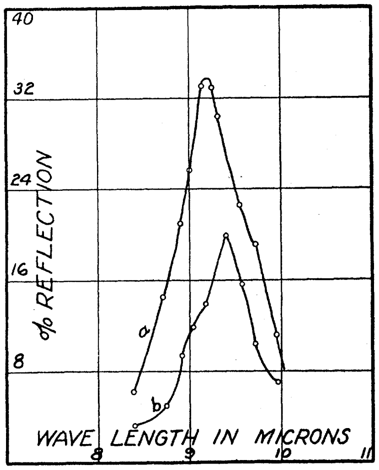

Fig. 5. (a) Copper sulphate, (b) potassium sulphate.

The writer is at present investigating these materials by the use of definite directions in the crystals. Then the isotopic effect can be observed. This method will show whether the isotopes are distributed at random in the crystals or have certain positions.

University of North Carolina,
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