

COMPARISON OF THE OPTICAL PROPERTIES OF SEA WATER  
WITH THOSE OF PURE WATER

by 6408

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## CHAPTER 1

### INTRODUCTION

If the sun is considered to be a black body radiating at a temperature of  $5780^{\circ}$  Kelvin<sup>1</sup>, the power per unit area  $P$  emitted by the sun equals  $\sigma T^4$ , where  $\sigma$  is the Boltzmann constant and  $T$  is the temperature of the body. It is usually assumed that the earth absorbs incoming solar radiation, most of which is in the visible region of the spectrum, at the rate<sup>1</sup> of  $1.966 \text{ cal cm}^{-2} \text{ min}^{-1}$ , and re-radiates this energy received from the sun as a gray body at a temperature of  $285^{\circ}$  Kelvin<sup>2</sup> with maximum intensity in the infrared region of the spectrum. Actually, the radiant power emitted by the earth is given by the equation  $P = \int_0^{\infty} \epsilon(\nu) \cdot B(\nu) d\nu$ ; where  $P$  is the total radiant power per unit area;  $\epsilon(\nu)$  is the emissivity of the earth at frequency  $\nu$ ; and,  $B(\nu)$  is the radiated power per unit area in a unit frequency range at frequency  $\nu$  for a black body at the same temperature as the earth. The emissivity of any body is characteristic of the surface of the material composing the body. Since the surface of the earth is composed of many different materials, an approximation must be made.

Because approximately eighty percent of the earth's surface is covered by sea water, the earth may be crudely approximated as a sea-water-covered sphere. With this approximation, the emissivity function for sea water can be used for the entire earth's surface. Although the emissivity as a function of frequency for sea water is not known, the emissivity of pure water can be expressed in terms of the real and imaginary parts of the index of refraction,  $n_r$  and  $n_i$ . These values throughout the infrared region from  $5000 \text{ cm}^{-1}$  to  $300 \text{ cm}^{-1}$  have been determined in recent studies by Irvine and Pollack<sup>3</sup>, Pontier and Dechambenoy<sup>4</sup>, Query, Curnutte, and Williams<sup>5</sup>, Zolotarev, Mikhailov, Aperovich, and Popov<sup>6</sup>, and Rusk, Williams, and Query<sup>7</sup>.

The normal-incidence reflectance  $R_0$  is given by the Cauchy relation:

$$R_0 = \frac{(n_r - 1)^2 + n_i^2}{(n_r + 1)^2 + n_i^2} \quad (1)$$

The imaginary part of the index of refraction can be determined from measurements of fractional transmittance  $T$  for samples of known thickness  $x$ , according to Lambert's law:  $T = (1-\rho) e^{-kx}$ , where  $\rho$  is the fraction of incident radiant flux reflected at the cell window and  $k$  is the absorption coefficient which is related to  $n_i$  by the expression:

$$n_i = \frac{k \lambda}{4 \pi} \quad (2)$$

With measured values of  $n_i$  and  $R_0$ , the real part of the refractive index can be determined from Eq. (1). The value of  $R_0$  for pure water can be regarded as well known in the infrared region from  $5000 \text{ cm}^{-1}$  to  $300 \text{ cm}^{-1}$  from published values of  $n_r$  and  $n_i$  for pure water.

The purpose of the present work was to compare the optical properties of sea water with those of pure water in the infrared region of the spectrum. Comparison of the spectral reflectance of sea water at normal incidence with that of pure water was chosen as a method of comparison. The experimental part of the study involved measurement of the ratio of  $R_0$  for sea water with Rusk's recent direct measurements of  $R_0$  for pure water.<sup>8</sup>

## CHAPTER 2

## THE SPECTRAL PROPERTIES OF WATER AND AQUEOUS SOLUTIONS

Before beginning a discussion of the details of the present study, a review of the known spectral properties of water and of aqueous solutions in the infrared will be given. In discussions of the general spectral characteristics of water and of aqueous solutions, a distinction must be made between spectral absorption and spectral reflection. We shall first discuss the spectral absorption of water, followed by the spectral reflection of water, the properties of the absorption spectra of some aqueous solutions, and the spectral reflectance of some aqueous solutions.

## A. Absorption Spectrum of Water

In the vapor phase, the water molecule has three normal modes of vibration in the near infrared. The three normal modes<sup>9</sup> are (1) a weakly infrared-active symmetric valence vibration  $\nu_1$  associated with a fundamental absorption band at  $3651.7 \text{ cm}^{-1}$ , (2) a scissors-type bending mode  $\nu_2$  associated with a fundamental band at  $1595 \text{ cm}^{-1}$ , and (3) an asymmetric valence vibration  $\nu_3$  associated with a fundamental absorption band at  $3755.8 \text{ cm}^{-1}$ . The last two normal modes are found<sup>10</sup> to combine to give an absorption band attributed to  $\nu_2 + \nu_3$  centered at  $5332.0 \text{ cm}^{-1}$  and also higher overtones such as  $2\nu_2$  centered at  $3151.4 \text{ cm}^{-1}$ . In addition to the absorption bands associated with the normal modes of vibration, the water vapor absorption spectrum also contains many absorption lines in the far infrared due to transitions between rotational levels; these pure-rotational lines are found in the spectral region between  $1000 \text{ cm}^{-1}$  and  $1 \text{ cm}^{-1}$ .

In the liquid phase, the near-infrared spectrum of water is characterized

by strong absorption bands, three of which can be attributed directly to the normal vibrational modes of the water molecule. A broad intense absorption band is centered at  $3430\text{ cm}^{-1}$  and can be attributed to the  $2\nu_2$ ,  $\nu_1$ , and  $\nu_3$  vibrational modes. A narrow band is centered at  $1630\text{ cm}^{-1}$  and is attributed to  $\nu_2$ . The third band is a broad, less intense band centered at  $5140\text{ cm}^{-1}$  and attributed to  $\nu_2 + \nu_3$ .<sup>11</sup>

In the far infrared, liquid water has two absorption bands:  $\nu_L$  at  $685\text{ cm}^{-1}$ , attributed to hindered rotations or librations, and  $\nu_T$  at  $170\text{ cm}^{-1}$ , attributed to hindered translations of the molecule in the field of its neighbors.<sup>12</sup>

Liquid water also has three weak associational absorption bands located at  $2130\text{ cm}^{-1}$ ,  $3950\text{ cm}^{-1}$ , and  $5600\text{ cm}^{-1}$ . The strongest of these bands is the one observed at  $2130\text{ cm}^{-1}$  and has been attributed to  $\nu_2 + \nu_L - \nu_T$ .<sup>11</sup>

## B. Reflection Spectrum of Liquid Water

The normal-incidence reflection spectrum of liquid water in the region from  $5000\text{ cm}^{-1}$  to  $100\text{ cm}^{-1}$  is dominated by three major features as indicated in Fig. 1. (1) The first feature is a minimum in reflectance values located near  $3650\text{ cm}^{-1}$  followed by a maximum in reflectance values at  $3200\text{ cm}^{-1}$ ; this feature is associated with the water absorption band centered at  $3430\text{ cm}^{-1}$ . The reflectance minimum has a value of 0.0052 and the maximum a value of 0.0416. Reflectance values decrease from the maximum at  $3200\text{ cm}^{-1}$  until the second major feature of the water reflectance spectrum is reached. (2) The second feature consists of a minimum at  $1700\text{ cm}^{-1}$  with a reflectance value of 0.0117, followed by a maximum at  $1610\text{ cm}^{-1}$  of 0.0236; this feature is associated with the  $\nu_2$  absorption band of the water molecule. (3) The third major feature of the reflectance spectrum is associated with the  $\nu_L$  absorption band. This

feature consists of a minimum at  $910\text{ cm}^{-1}$  and a maximum at  $420\text{ cm}^{-1}$ , with reflectance values of 0.0075 and 0.0667, respectively.<sup>8</sup> It should be noted in Fig. 1 that the values of reflectance generally are greater following (at lower frequencies) one of these major features than before the feature at higher frequencies.

### C. Influence of Solutes on the Absorption Spectrum of Water

In the spectral region from  $5000\text{ cm}^{-1}$  to  $100\text{ cm}^{-1}$ , the major features of the absorption spectra of aqueous solutions of electrolytes consisting of monatomic ions are, in general, similar to the major features of the liquid-water absorption spectrum. However, the absorption bands of water are shifted slightly in frequency when solutes are added. Williams and Millett<sup>13</sup> studied the shifts of the water absorption bands in the region between  $7000\text{ cm}^{-1}$  and  $1600\text{ cm}^{-1}$  produced by the addition of alkali halides and alkaline-earth halides to water. It was found that, in general, the presence of large ions such as  $\text{I}^-$  produced shifts in the frequencies of the water absorption bands that are similar to the shifts produced by the increase of the water temperature. Increasing the water temperature causes the absorption bands centered at  $1630\text{ cm}^{-1}$  and  $2130\text{ cm}^{-1}$  to shift slightly to lower frequencies, and the absorption bands centered at  $3430\text{ cm}^{-1}$  and  $5140\text{ cm}^{-1}$  to shift slightly to higher frequencies. Draegert and Williams<sup>14</sup> in their far-infrared studies obtained similar results for the water absorption band  $\nu_L$ . In general, the frequency shifts observed increased with increasing concentration. Most of the absorption bands of water broaden with increasing concentration of the alkali halides.

The absorption spectra of solutions containing electrolytes yielding polyatomic ions show additional absorption bands, which are associated with charac-

teristic vibrations of the polyatomic ions. The  $\text{ClO}_3^-$  ion has a characteristic absorption band centered near  $625 \text{ cm}^{-1}$ ; in solution this band was found to increase in intensity with increasing ion concentration.<sup>14</sup> The polyatomic ions  $\text{SO}_4^{--}$  and  $\text{HCO}_3^-$  also have characteristic absorption bands. The sulfate ion has an absorption band near  $1100 \text{ cm}^{-1}$ , as does the bicarbonate ion near  $1300 \text{ cm}^{-1}$ ; the absorption bands of both of these ions can be associated with an asymmetric stretching of the ion.<sup>15</sup>

#### D. Influence of Solutes on the Reflection Spectrum of Water

The reflectance spectra of aqueous solutions is also dependent upon the nature of the solutes. Rhine<sup>16</sup> studied the normal-incidence reflectances of various aqueous solutions of alkali halides as a function of concentration. He reported no major spectral features other than those characteristic of the water reflectance spectrum itself. However, the major features of the water reflectance spectrum were shifted slightly in frequency and slightly changed in shape. He also observed that in spectral regions remote from the three major features of the water reflectance spectrum, reflectance values generally increased with increasing concentration of the solute.

It would be expected that reflection spectra of aqueous solutions of electrolytes yielding polyatomic ions that have strong absorption bands should also exhibit additional reflectance features other than those characteristic of the water reflectance spectrum itself. Variations in reflectance values of these expected additional features with ion concentration might also be anticipated. Sea water contains the polyatomic ions  $\text{SO}_4^{--}$  and  $\text{HCO}_3^-$  which might be expected to produce reflectance features not present in pure water.



### CHAPTER 3

#### EXPERIMENTAL METHODS

Since the purpose of this study was the comparison of the optical properties of sea water with pure water, the composition of sea water will be discussed before the explanation of the experimental methods that were used.

Sea water contains ninety-two elements ranging in concentration from oxygen, with an average concentration of 857 grams per liter of sea water, to radon, with an average concentration of  $0.6 \times 10^{-18}$  grams per liter of sea water, with traces of other elements of an even smaller concentration. However, only 14 elements (O, H, Cl, Na, Mg, S, Ca, K, Br, C, Sr, B, Si, and F) have concentrations greater than one part per million.<sup>17</sup> Since we are concerned with a comparison of the reflectance spectrum of sea water with the reflectance spectrum of pure water, the concentration of various ions in sea water is an important factor. Table I lists the major ion constituents and their molarity as found in a representative sample of sea water. The chloride ion has the greatest concentration, 0.56 molar, with the sodium ion having the second highest concentration of 0.48 molar. Other constituents have concentrations less than 0.03 molar.

As a result of these small concentrations, identification of features in the reflectance spectrum of sea water prove difficult. Therefore, reflectance spectra of major ion constituents of sea water were investigated at concentrations greater than those found in sea water, thus enabling any spectral features characteristic of a sea-water constituent to be easily identified. By successively reducing the concentration of a sea-water constituent until its actual concentration as found in sea water is reached, it is possible to attribute any additional features observed in the sea water reflectance spectrum

other than those characteristic features of the pure water reflectance spectrum to the correct constituent of sea water.

#### A. Choice of Solutes and Concentrations

Although the sodium and chloride ions have larger concentrations than any other major constituent ions in sea water, aqueous solutions of sodium chloride were not investigated. In solution, sodium chloride yields sodium and chloride ions which are both monatomic and are not expected to produce any additional spectral features in the water reflectance spectrum. Also, Millett and Williams<sup>13</sup> observed only a very slight frequency shift in the water absorption bands centered at  $1600\text{ cm}^{-1}$  and  $3430\text{ cm}^{-1}$  when NaCl was added to water.

It was decided to investigate first the reflectance spectra of aqueous solutions of  $\text{MgCl}_2$ . This electrolyte in water yields  $\text{Mg}^{++}$  ions and  $\text{Cl}^-$  ions. Since both anion and cation of this electrolyte are monatomic, no additional features were expected to be observed in the reflectance spectrum of water.

The reflectance spectra of aqueous solutions of  $\text{KHCO}_3$  were chosen for study next. In solution,  $\text{KHCO}_3$  yields a monatomic  $\text{K}^+$  ion and a polyatomic  $\text{HCO}_3^-$  ion. It has been shown<sup>16</sup> that the  $\text{K}^+$  ion will add no major features to the water reflectance spectrum. However, the bicarbonate ion may add some features to the water reflectance spectrum because of its strong absorption band centered near  $1300\text{ cm}^{-1}$ . It is conceivable that  $\text{KHCO}_3$  in solution might yield a  $\text{K}^+$  ion and a polyatomic  $\text{CO}_3^{--}$  ion, with the  $\text{H}^+$  ion bonding to a water molecule forming  $\text{H}_3\text{O}^+$ . It has been found, however, that in sea water, the  $\text{HCO}_3^-$  ion has a concentration ten times greater than the  $\text{CO}_3^{--}$  ion, and that 69% of the  $\text{HCO}_3^-$  ions in sea water are free ions, while only 9% of the  $\text{CO}_3^{--}$  ions are free.<sup>17</sup> In either case, the  $\text{CO}_3^{--}$  ion has a strong absorption band<sup>15</sup>

centered near  $1450\text{ cm}^{-1}$  so that any additional features arising in the reflectance spectra of  $\text{KHCO}_3$  solutions in the region from  $1450\text{ cm}^{-1}$  to  $1300\text{ cm}^{-1}$  could be attributed to either the  $\text{HCO}_3^-$  ion or the  $\text{CO}_3^{--}$  ion, but most probably the  $\text{HCO}_3^-$  ion.

Since the magnesium ion and the sulfate ion are the third and fourth most abundant ions in sea water, reflectance spectra of aqueous solutions of  $\text{MgSO}_4$  were also chosen for study. Again, any additional features observed in the reflectance spectra of  $\text{MgSO}_4$  solutions other than those characteristic features of the water reflectance spectrum would be attributed to the polyatomic  $\text{SO}_4^{--}$  ion. Should reflectance features characteristic of the sulfate ion occur, they should be observed near  $1100\text{ cm}^{-1}$  where the sulfate ion has a strong absorption band.

Finally, it was decided to investigate the reflectance spectra of aqueous solutions of  $\text{K}_2\text{SO}_4$ . This would provide a verification of any characteristic features of the sulfate ion observed in the reflectance studies of  $\text{MgSO}_4$  solutions.

It was decided to investigate first the reflectance spectrum of each sea-water constituent at its near maximum concentration. Therefore, any additional features in the sea-water constituent's spectrum would be clearly evident. Then, if the concentration of the sea-water constituent were halved and the reflectance spectrum observed, any additional reflectance features other than those characteristic to the water reflectance spectrum could be studied as a function of concentration. By successively halving the concentration of the sea-water constituent until its concentration reaches the value as found in sea water, any additional spectral features observed could be identified with corresponding spectral features observed in the reflectance spectrum of real sea water.

## B. Experimental Apparatus

The reflectometer used in this study is shown schematically in Fig. 2. Radiant flux from globar A is directed by plane mirror B and spherical mirror C to the water or sea-water-constituent sample at D. The reflected flux is then directed by spherical mirror E and plane mirror F to the spectrometer entrance slit G. This arrangement allowed near-normal incidence, as the central ray of the incident flux reaching D was incident at an angle of approximately 4 degrees.

The spectrometer employed was a Perkin-Elmer Model 112 single-beam, double-pass instrument with a Reeder thermocouple employing a CsBr window as a detector. A NaCl prism was employed and calibrated in terms of the atmospheric absorption by water vapor and carbon dioxide, and by ammonia vapor. A calibration curve was used similar to Rhine's calibration curve<sup>16</sup> which employed 33 H<sub>2</sub>O and CO<sub>2</sub> vapor absorption lines in the region from 3900 cm<sup>-1</sup> to 1350 cm<sup>-1</sup> and 20 ammonia vapor absorption lines in the region from 1230 cm<sup>-1</sup> to 780 cm<sup>-1</sup>. A calibration check was made periodically by checking atmospheric H<sub>2</sub>O and CO<sub>2</sub> vapor absorption lines at 3881 cm<sup>-1</sup>, 3740 cm<sup>-1</sup>, and 3619 cm<sup>-1</sup> to insure constant calibration.

## C. Sample Preparation and Experimental Procedures

The sea-water-constituent samples were prepared by diluting a measured weight of standard reagent grade chemicals with distilled, de-ionized water to a measured volume of solution, thus giving a solution of a known molarity. After experimentation with a sea-water-constituent sample, the volume of the sample was doubled by the addition of water, thus halving the molarity.

Pure sea-water samples were collected from four locations: Panama City,

Florida; St. Marks, Florida; Woods Hole, Massachusetts; and San Simeon Beach, California. All samples were collected within one-half mile of shore, except for one sample from St. Marks, Florida, which was collected four miles from shore. Care was taken to collect sea-water samples as relatively free of organic matter and insoluble material as possible.

Since the reflected flux from the surface of the pure water or sea-water-constituent sample was small compared to the flux incident on the surface of the sample, a relatively high amplifier gain was used. To compensate for the increased noise caused by high amplifier gain, relatively wide spectrometer slit widths were employed. The region of the spectrum studied was from  $4100\text{ cm}^{-1}$  to  $780\text{ cm}^{-1}$ . This region was divided into seven sub-regions or intervals. Over the first interval from  $4100\text{ cm}^{-1}$  to  $1900\text{ cm}^{-1}$ , a spectral slit width varying from  $85.3\text{ cm}^{-1}$  at  $4100\text{ cm}^{-1}$  to  $14.2\text{ cm}^{-1}$  at  $1900\text{ cm}^{-1}$  was employed. However, over the last interval studied from  $832\text{ cm}^{-1}$  to  $780\text{ cm}^{-1}$ , a spectral slit width that varied from  $11.9\text{ cm}^{-1}$  at  $832\text{ cm}^{-1}$  to  $9.6\text{ cm}^{-1}$  at  $780\text{ cm}^{-1}$  was employed. The decreasing spectral flux and the increasing dispersion of the prism as the spectrum was scanned from  $4100\text{ cm}^{-1}$  to  $780\text{ cm}^{-1}$  necessitated the increase of amplifier gain for each successive interval observed in order to obtain a satisfactory spectral tracing on the recorder chart.

The data were obtained for the sea-water-constituent samples in the following manner. (1) Distilled, de-ionized water was poured into a 200-ml beaker to a marked depth of approximately 2-cm, which was an adequate depth to eliminate spurious reflection from the bottom of the beaker, and placed in position D in Fig. 2. (2) The reflectance spectral trace of the pure water sample was recorded over an interval of the spectrum. (3) The incident beam was blocked by placing a metal plate between the globar source and the first plane mirror located at B in Fig. 2, and the spectral trace of the zero-level radiation was

recorded with the water sample still in place at D. (4) The pure water sample was then replaced by the sea-water-constituent sample at D, and the reflectance spectral trace was recorded again over the same interval. (5) Again the incident beam was blocked as before in step (3) and a zero-level was recorded over the same interval with the sea-water-constituent sample in place at D. All four reflectance traces were recorded on the same chart paper with the spectrometer prism positions coinciding on all four traces; amplifier gain and spectrometer slit widths were the same for all four traces recorded on that interval.

The same procedure was used when reflectance data were obtained for real sea-water samples. For each sea-water-constituent sample and sea-water sample, reflectance data were recorded over the region from  $4100\text{ cm}^{-1}$  to  $780\text{ cm}^{-1}$  at least twice.

#### D. Data Reduction

A representative sample of raw data for an interval of the region of the spectrum studied is shown in Fig. 3. The reflectance trace AA gives the chart deflection obtained from a sea-water-constituent sample or sea-water sample during step (3) of the preceding section. The trace A'A' shows the chart deflection for the zero-level for the same sea-water-constituent or sea-water sample as described in step (4). The trace BB in Fig. 3 shows the chart deflection for the pure water sample when it is placed at D in Fig. 2 as described in step (1) of the preceding section, and the trace B'B' shows the zero-level chart deflection for pure water obtained as in step (2).

The points P, Q, P', and Q' in Fig. 3 are, respectively, the intersection points for the reflectance traces AA and BB and the zero-level traces A'A'

and B'B', with the line  $L_2$ . The spectrometer prism was in the same position for each trace at the intersection points along  $L_2$ . Also, along the line  $L_1$ , the intersection of line  $L_1$  with the traces AA, BB, A'A', and B'B', respectively, at the points S, T, T', and S' occur at the same spectrometer prism positioning. A correlation between the prism position at line  $L_1$  or  $L_2$  and the frequency of the radiant flux causing the chart deflection at  $L_1$  or  $L_2$  can be obtained from a calibration curve. The calibration curve for the NaCl prism used in this study was constructed by observing known chart deflections at the known frequencies of atmospheric water vapor and carbon dioxide and of ammonia vapor, and correlating these known deflections with prism position. Along line  $L_2$ , the frequency of the radiant flux causing each of the four traces at points intersecting  $L_2$  is  $\nu_{L2}$ ; and also along  $L_1$ , the frequency of the radiant flux causing each of the four traces at points intersecting  $L_1$  is  $\nu_{L1}$ , where the correlation of prism positions at  $L_1$  and  $L_2$  with the frequencies  $\nu_{L1}$  and  $\nu_{L2}$  were obtained from the calibration curve for the NaCl prism.

The distance QQ' along  $L_2$  in Fig. 3 is a measure of the magnitude of the reflected flux from the surface of the pure water sample at frequency  $\nu_{L2}$ . In like manner, the distance PP' is a measure of the magnitude of the reflected flux from the sea-water-constituent sample or sea-water sample at frequency  $\nu_{L2}$ . By taking the ratio of the distances QQ' to PP', we can obtain  $\rho(\nu_{L2})$ , the reflectance of the sea-water-constituent sample or sea-water sample at frequency  $\nu_{L2}$  relative to water from the equation

$$\rho(\nu_{L2}) = (PP') / (QQ'). \quad (3)$$

The reflectance  $R_0(\nu)$  of pure water at frequency  $\nu_{L2}$  can be obtained from Rusk's tabulated values of  $R_0(\nu)$ .<sup>8</sup> The reflectance  $R(\nu_{L2})$  of the sea-water-constituent sample or of the sea-water sample at this frequency can now be



calculated from the equation

$$R(\nu) = \rho(\nu) \cdot R_0(\nu). \quad (4)$$

As indicated in Fig. 3,  $R(\nu)$  may have values larger, smaller, or equal to  $R_0(\nu)$ . Thus at  $L_2$ , the ratio  $\rho(\nu_{L2})$  has a value greater than unity, which yields by means of Eq. (4),  $R(\nu_{L2}) > R_0(\nu_{L2})$ . Along  $L_1$ ,  $\rho(\nu_{L1})$  has a value less than unity, which yields  $R(\nu_{L1}) < R_0(\nu_{L1})$ . At some frequency  $\nu$ , located in the frequency range between  $\nu_{L1}$  and  $\nu_{L2}$ , the sea-water-constituent sample and the pure water sample reflect the same fraction of the incident flux. Therefore, the ratio  $\rho(\nu)$  is unity, yielding the experimental result  $R(\nu) = R_0(\nu)$ .

By measuring the ratio  $\rho(\nu)$  at closely-spaced points in Fig. 3, and multiplying this ratio by the tabulated value of  $R_0(\nu)$ , the reflectance  $R(\nu)$  of either a sea-water-constituent sample or a real sea-water sample may be plotted versus frequency over the whole spectral region studied.

In this study, the experimental uncertainty in the determination of the fractional reflectance  $R(\nu)$  was estimated to be  $\pm 5\%$ ; the limitations in determining  $R(\nu)$  were imposed by uncertainties in amplifier noise, reproducibility of prism setting, and possible errors in data reduction. Therefore, any values of  $R(\nu)$  for the sea-water or sea-water-constituent samples which were found to be within  $\pm 5\%$  of  $R_0(\nu)$  were considered to be indistinguishable from  $R_0(\nu)$ .



## CHAPTER 4

### EXPERIMENTAL RESULTS

#### A. Sea-Water-Constituent Samples

Figure 4 shows the spectral reflectance  $R(\nu)$  for 3.90 and 1.95 molar solutions of  $\text{MgCl}_2$  and of pure water for the spectral region observed; the spectral reflectance  $R(\nu)$  is plotted versus frequency  $\nu$ . From the reflectance studies of aqueous solutions of  $\text{MgCl}_2$  it was found that no additional features, other than the three characteristic features of the water reflectance spectrum, were observed. Reflectance values of the  $\text{MgCl}_2$  solutions are greater than the reflectance values of pure water over the spectral region from  $4100\text{ cm}^{-1}$  to  $840\text{ cm}^{-1}$ , and less than the water reflectance values from  $840\text{ cm}^{-1}$  to  $780\text{ cm}^{-1}$ . In general, the greater the concentration of the  $\text{MgCl}_2$  solution, the greater the reflectance values.

There are two regions where major features in reflectance spectra of the  $\text{MgCl}_2$  solutions are shifted in frequency with respect to the major features of the water reflectance spectrum. The most noticeable shift occurs in the region near  $900\text{ cm}^{-1}$ . The minimum value of the 3.90 molar reflectance spectrum in this region is shifted  $75\text{ cm}^{-1}$  to lower frequencies with respect to the minimum value of the water reflectance spectrum near  $900\text{ cm}^{-1}$ . The 1.95 molar  $\text{MgCl}_2$  solution has a frequency shift of  $20\text{ cm}^{-1}$  with respect to the water reflectance spectrum. The second spectral region where a frequency shift occurs is near  $3200\text{ cm}^{-1}$ . The maximum value of the 3.90 molar solution's reflectance spectrum is shifted  $20\text{ cm}^{-1}$  to lower frequencies, and the reflectance spectrum of the 1.85 molar solution is shifted  $10\text{ cm}^{-1}$  to lower frequencies with respect to the maximum value of the water reflectance spectrum.

Since no additional features other than the three major features were

observed in the water reflectance spectrum when  $\text{MgCl}_2$  was added, it is anticipated that neither the  $\text{Mg}^{++}$  ions or the  $\text{Cl}^-$  ions will cause any additional features in the infrared reflectance spectrum of real sea water.

Figure 5 shows the reflectance plotted versus frequency for 1.85 and 0.985 molar solutions of  $\text{KHCO}_3$  and for pure water. No additional features are observed in the reflectance spectra of the  $\text{KHCO}_3$  solutions over the interval from  $4100\text{ cm}^{-1}$  to  $1500\text{ cm}^{-1}$ . From  $4100\text{ cm}^{-1}$  to  $3640\text{ cm}^{-1}$ , the reflectivity of the  $\text{KHCO}_3$  solutions is greater than the reflectivity of water, with the solution of greater concentration having the greater reflectivity. The  $\text{KHCO}_3$  solutions and water have approximately the same reflectance values from  $3640\text{ cm}^{-1}$  to  $3440\text{ cm}^{-1}$ . From  $3440\text{ cm}^{-1}$  to  $3000\text{ cm}^{-1}$ , the water has greater reflectance values than the  $\text{KHCO}_3$  solutions, with the solution of greater concentration having the smaller reflectance values. Over the spectral region from  $3000\text{ cm}^{-1}$  to  $1820\text{ cm}^{-1}$ , the  $\text{KHCO}_3$  solutions again have greater reflectance values than water, while the minimum at  $1700\text{ cm}^{-1}$  is reversed, with water having the largest reflectance value and the 1.85 molar  $\text{KHCO}_3$  solution having the smallest reflectance value. At the reflectance maximum at  $1610\text{ cm}^{-1}$ , the  $\text{KHCO}_3$  solutions have greater reflectance values than water, with the greater concentration having the greater reflectance value. Over the spectral region from  $1610\text{ cm}^{-1}$  to  $1500\text{ cm}^{-1}$ , the  $\text{KHCO}_3$  reflectance spectra, in general, resemble the water reflectance spectrum. There are no additional features added to the water reflectance spectrum and no frequency shifts are observed at the maxima or minima of the reflectance spectra of the  $\text{KHCO}_3$  solutions with respect to the major features of the water reflectance spectrum over this spectral region from  $1610\text{ cm}^{-1}$  to  $1500\text{ cm}^{-1}$ .

However, between  $1500\text{ cm}^{-1}$  and  $900\text{ cm}^{-1}$ , an additional feature is observed in the water reflectance spectrum when  $\text{KHCO}_3$  is added. This additional feature

consists of a minimum in reflectance values at  $1400\text{ cm}^{-1}$  followed by a maximum at  $1320\text{ cm}^{-1}$ . The greater the concentration of the  $\text{KHCO}_3$  solution, the greater the value of reflectance at the maximum and the smaller the value of reflectance at the minimum. If it is assumed that aqueous solution of  $\text{KHCO}_3$  yield  $\text{K}^+$  ions and  $\text{HCO}_3^-$  ions, this additional feature of the  $\text{KHCO}_3$  reflectance spectrum can be attributed to the  $\text{HCO}_3^-$  ion which has a strong absorption band near  $1300\text{ cm}^{-1}$ .

In sea water, the concentration of the  $\text{HCO}_3^-$  ion is 0.00238 molar. However, it was observed in this study that the magnitude of this additional feature in the  $\text{KHCO}_3$  spectrum had reduced to within  $\pm 5\%$  of the reflectance values of pure water when a 0.25 molar solution of  $\text{KHCO}_3$  was studied. Therefore, it was not anticipated that the  $\text{HCO}_3^-$  ion would cause any additional features to be observed in the reflectance spectrum of sea water.

Figure 6 shows the reflectance spectra of 1.98 and 0.995 molar solutions of  $\text{MgSO}_4$  and of pure water. Over the spectral region from  $4100\text{ cm}^{-1}$  to  $1400\text{ cm}^{-1}$ , the reflectance spectra of solutions of  $\text{MgSO}_4$  resemble the reflectance spectra of the  $\text{MgCl}_2$  solutions shown in Fig. 4, as the reflectance spectra of the  $\text{MgSO}_4$  solutions also have the same characteristic features as the water reflectance spectrum in this spectral region. The  $\text{MgSO}_4$  solutions have reflectance values greater than the reflectance values of water in this region, with the more concentrated solutions of  $\text{MgSO}_4$  having the greater reflectance values. In this spectral region from  $4100\text{ cm}^{-1}$  to  $1400\text{ cm}^{-1}$ , there are no frequency shifts observed of the maximum or minimum reflectance values of the  $\text{MgSO}_4$  solutions when compared with the corresponding maximum or minimum of the water reflectance spectrum.

There is, however, a very sharp additional feature occurring in the  $\text{MgSO}_4$  reflectance spectrum which does not correlate with any major feature of the

water reflectance spectrum. This additional feature, located in the spectral region between  $1400\text{ cm}^{-1}$  and  $900\text{ cm}^{-1}$ , consists of a minimum in reflectance values of the  $\text{MgSO}_4$  solutions at  $1150\text{ cm}^{-1}$  followed by a maximum in reflectance values at  $1080\text{ cm}^{-1}$ . Since the  $\text{SO}_4^{--}$  ion has a strong absorption band centered near  $1100\text{ cm}^{-1}$  caused by asymmetric stretching of the  $\text{SO}_4^{--}$  ion, this additional feature of the  $\text{MgSO}_4$  reflectance spectra can be associated with this strong absorption band. It was observed that the magnitude of the maximum and minimum of this feature decreased with decreasing concentration of the  $\text{MgSO}_4$  solutions. However, it was observed that when the molarity of the  $\text{MgSO}_4$  solutions was successively halved and the reflectance spectrum investigated, reflectance values of this feature were still appreciably different from pure water reflectance values in this region until the concentration of the  $\text{MgSO}_4$  solution was reduced to 0.031 molar. This concentration is near the value listed in Table I for the actual sulfate ion concentration as found in real sea water. Therefore, if any additional features are found in the sea water reflectance spectrum in the spectral region near  $1100\text{ cm}^{-1}$ , this feature might be attributed to the  $\text{SO}_4^{--}$  ion.

For verification, a 0.5 molar solution of  $\text{K}_2\text{SO}_4$  was investigated. The reflectance spectrum of this solution matched the reflectance spectrum observed for the 0.5 molar solution of  $\text{MgSO}_4$ . This adds further evidence to the assumption that the characteristic feature of the reflectance spectra of the  $\text{MgSO}_4$  solutions observed near  $1100\text{ cm}^{-1}$  can be attributed to the  $\text{SO}_4^{--}$  ion absorption band centered at  $1100\text{ cm}^{-1}$ .

## B. Sea-Water Samples

The reflectance spectra for three different sea-water samples is shown in Fig. 7. Over the spectral region from  $4100\text{ cm}^{-1}$  to  $1100\text{ cm}^{-1}$ , the reflectance spectra of all sea-water samples observed was found to be identical to the pure water reflectance spectrum within the experimental error of  $\pm 5\%$  in  $R(\nu)$ . From  $1100\text{ cm}^{-1}$  to  $780\text{ cm}^{-1}$ , a deviation of the reflectance spectra of the three sea-water samples from the water reflectance spectrum is observed. This deviation is largest near  $1100\text{ cm}^{-1}$  and could be attributed to the  $\text{SO}_4^{--}$  absorption band centered near  $1100\text{ cm}^{-1}$ .

The reflectance spectrum of the sea-water sample collected at San Simeon Beach, California was identical to the pure water reflectance spectrum, within experimental error, over the whole spectral region observed from  $4100\text{ cm}^{-1}$  to  $780\text{ cm}^{-1}$ .

Because of the slight deviation observed in the sea water reflectance spectra from the pure water reflectance spectrum, the modification to the reflectance spectrum of water by replacing pure water with sea water may be considered a marginal modification.

## CHAPTER 5

### DISCUSSION OF RESULTS

In this study, the optical properties of sea water were to be compared with the optical properties of pure water by using the near-normal reflectance spectrum as the method of comparison. It was observed that only aqueous solutions containing  $\text{HCO}_3^-$  or  $\text{SO}_4^{--}$  ions produced any features other than those observed in the water reflectance spectrum. The feature near  $1100\text{ cm}^{-1}$  observed in the reflectance spectra of solutions containing the  $\text{SO}_4^{--}$  ion was observed to be much stronger than the feature near  $1400\text{ cm}^{-1}$  observed in the reflectance spectra of solutions containing the  $\text{HCO}_3^-$  ion. Since the magnitude of both of these features decreased with decreasing concentration of the ion assumed to cause these features, it was observed that the reflectance spectra of only solutions containing the  $\text{SO}_4^{--}$  ion deviated appreciably from the water reflectance spectrum at concentrations near those found in sea water. Therefore, it was assumed that the deviation of the reflectance spectrum of sea water from the reflectance spectrum of pure water near  $1100\text{ cm}^{-1}$  could be attributed to the  $\text{SO}_4^{--}$  ion in sea water. This agrees with the conclusion reached by Plyler and Griff<sup>19</sup> by absorption studies.

However, this deviation of the reflectance spectrum of sea water from pure water is slight. Because of this slight deviation, the sea water reflectance spectrum may be approximated by the pure water reflectance spectrum. It is therefore possible to use pure water values of  $n_i$  and  $n_r$  for sea water to a good approximation in computing the emissivity of sea water.



#### TABLE I

This table lists the eleven most concentrated constituent ions found in sea water and lists their concentration as found in an average sample of sea water.



TABLE I<sup>17</sup>

## Constituent Ions in Sea Water

Constituent	gm./kg. of water of salinity of 35 <sup>0</sup> /oo	Molarity
Chloride	19.353	0.56
Sodium	10.76	0.48
Sulphate	2.712	0.0278
Magnesium	1.294	0.0546
Calcium	0.413	0.0105
Potassium	0.387	0.0102
Bicarbonate	0.142	0.00238
Bromide	0.067	
Strontium	0.008	
Boron	0.004	
Fluoride	0.001	

NOTE: Riley and Skirrow only give values for grams of constituent per kilogram of water of salinity of 35 parts per thousand, which is an average salinity for sea water. Molarity was calculated using an average density of sea water of 1.025 grams per cubic centimeter. (18)

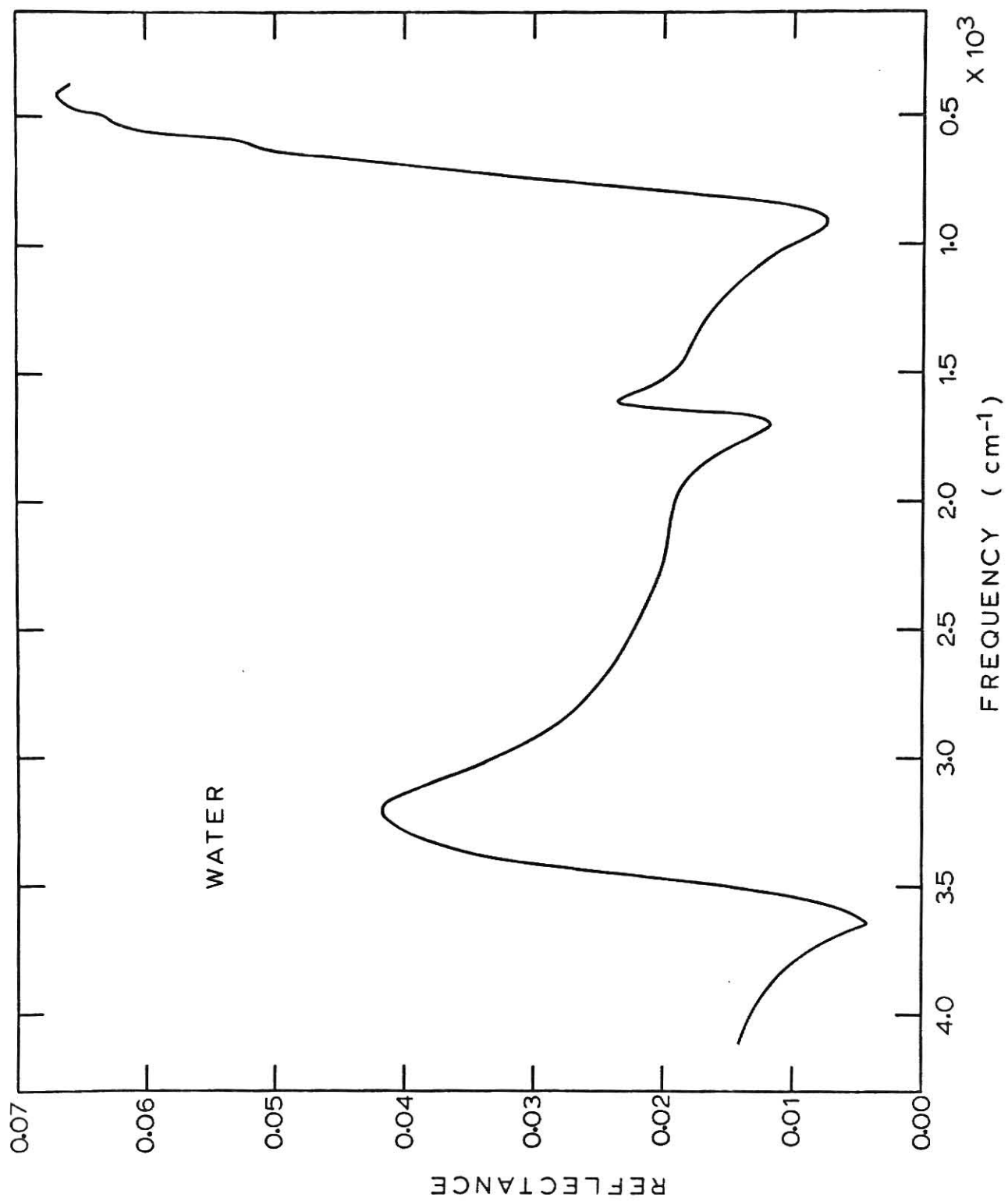


FIGURE 1

The reflection spectra of pure water

**THIS BOOK  
CONTAINS  
NUMEROUS PAGES  
WITH DIAGRAMS  
THAT ARE CROOKED  
COMPARED TO THE  
REST OF THE  
INFORMATION ON  
THE PAGE.**

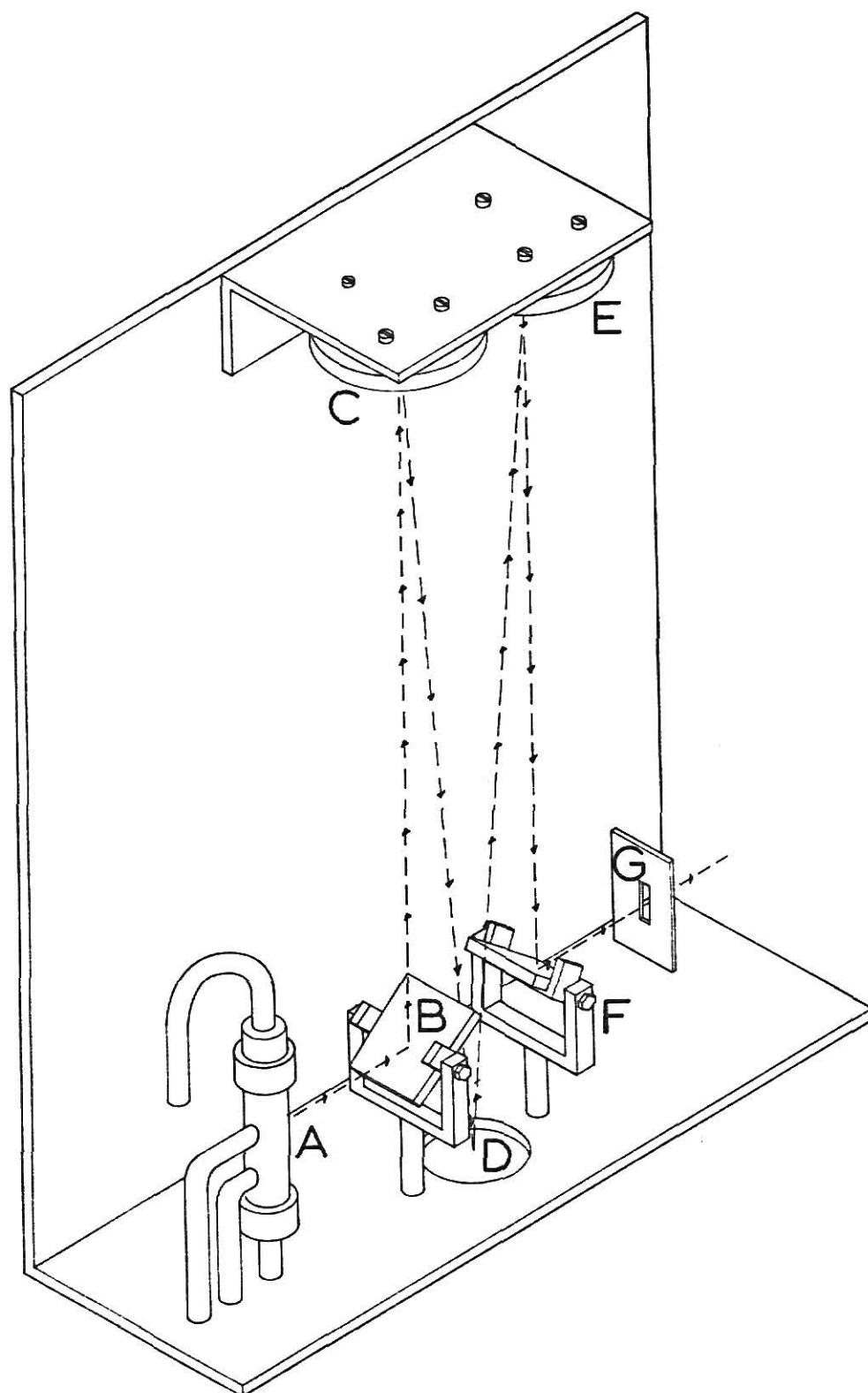
**THIS IS AS  
RECEIVED FROM  
CUSTOMER.**





**FIGURE 2**

**A schematical diagram of the reflectometer  
employed in this study**







**FIGURE 3**

**This figure is a representative set of raw data for an interval of the spectrum observed in this study.**

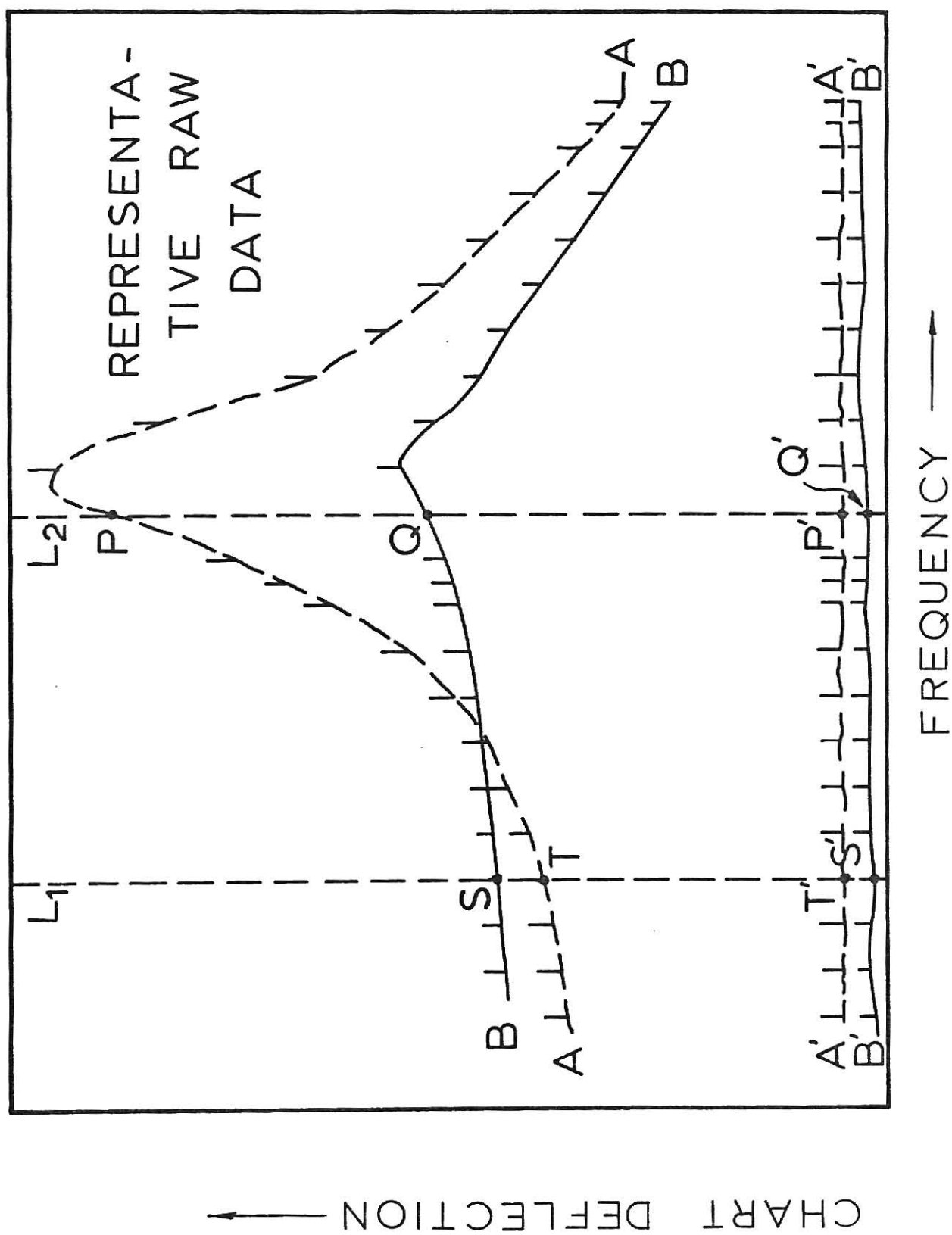




FIGURE 4

The spectral reflectance of 3.90 and 1.95  
molar solutions of  $\text{MgCl}_2$  and of water

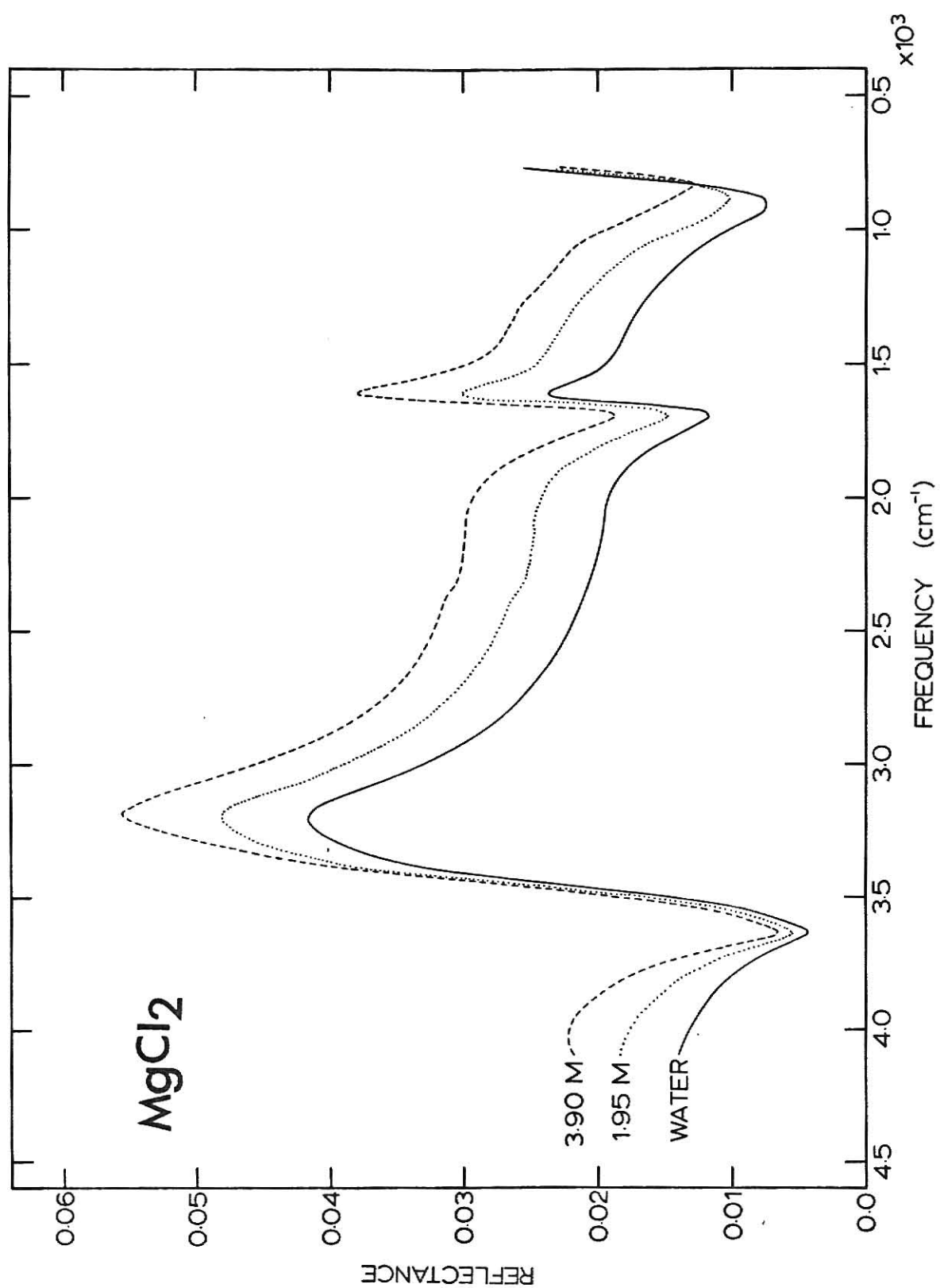




FIGURE 5

The spectral reflectance of 1.85 and 0.985  
molar solutions of  $\text{KHCO}_3$  and of water



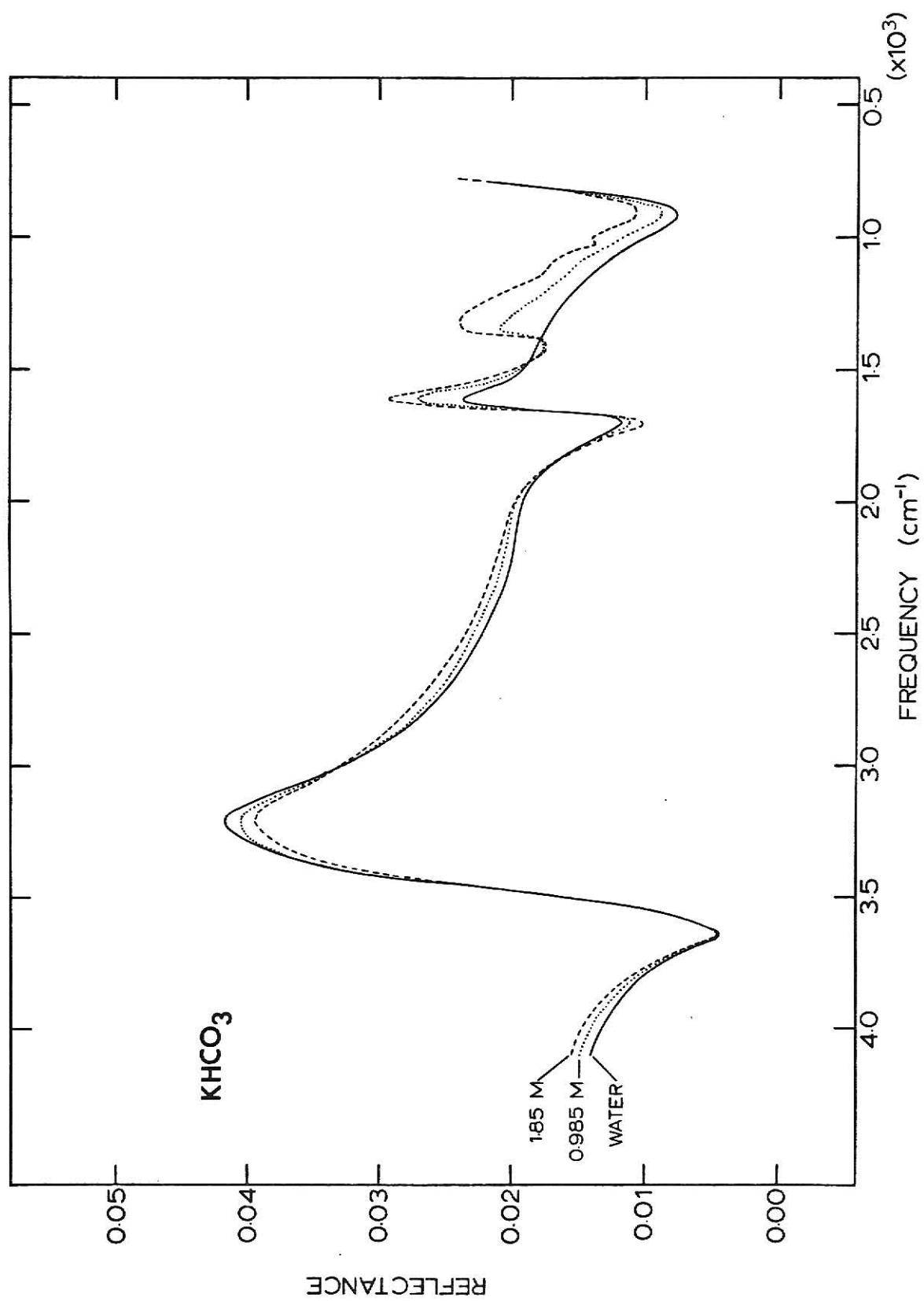




FIGURE 6

The spectral reflectance of 1.98 and 0.995 molar solutions of  $\text{MgSO}_4$  and of pure water

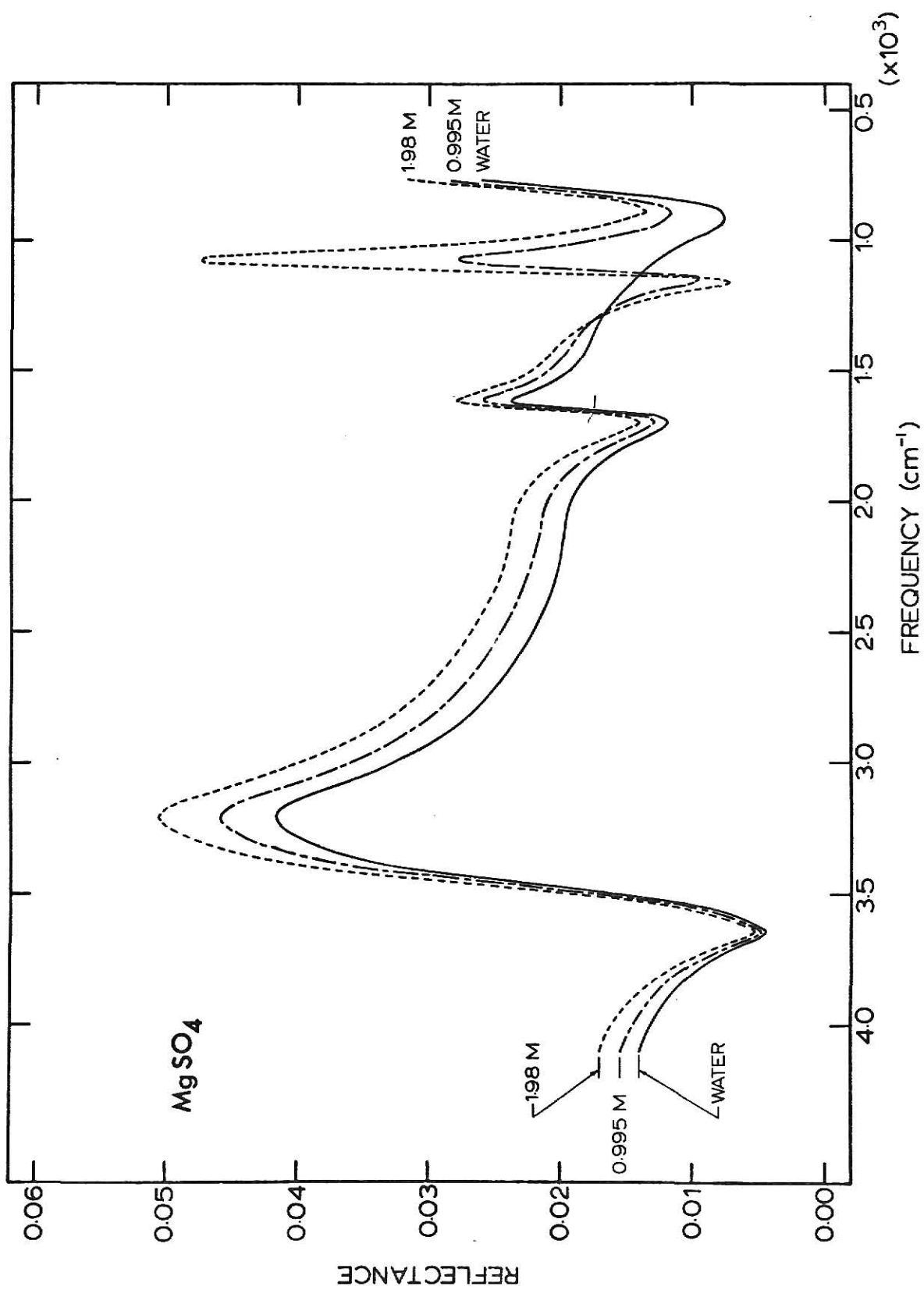
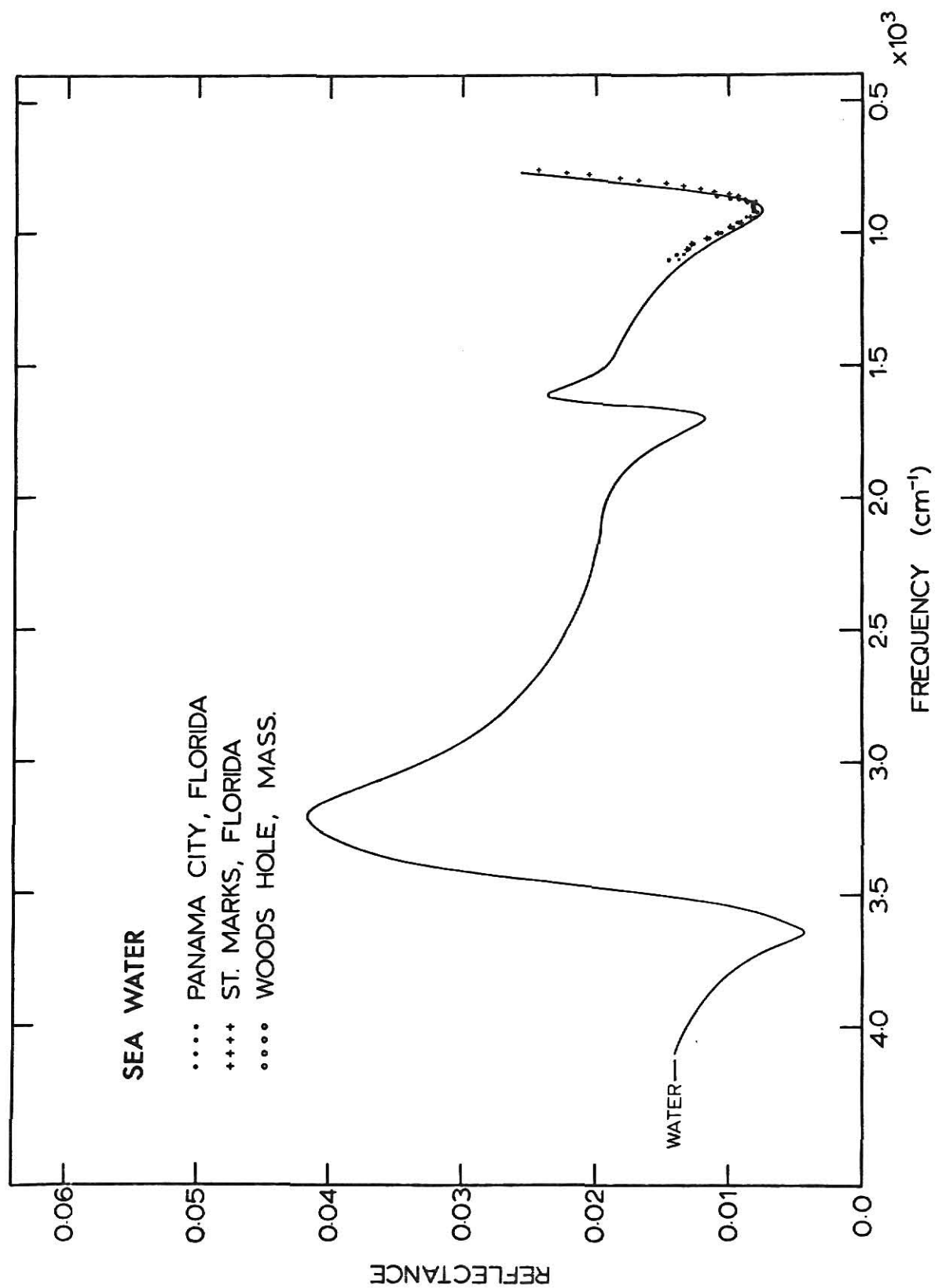




FIGURE 7

The spectral reflectance of three sea-water  
samples and of pure water



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COMPARISON OF THE OPTICAL PROPERTIES OF SEA WATER  
WITH THOSE OF PURE WATER

by

DANA ELWOOD HOBSON, JR.

B. S., Baker University, 1969

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AN ABSTRACT OF A MASTER'S THESIS

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Manhattan, Kansas

1971

The purpose of this study was to compare the optical properties of sea water with those of pure water in the infrared region of the spectrum. Comparison of the spectral reflectance of sea water with that of pure water was chosen as the method of comparison, as the spectral reflectance of pure water was considered to be known.

Sea water is composed of 92 elements, but only aqueous solutions of those elements forming polyatomic ions produced any additional features in the water reflectance spectrum. The reflectance spectra of aqueous solutions of  $\text{MgCl}_2$ ,  $\text{KHCO}_3$ ,  $\text{K}_2\text{SO}_4$ , and  $\text{MgSO}_4$  were studied, and it was observed that only those solutions containing the  $\text{HCO}_3^-$  ion or the  $\text{SO}_4^{--}$  ion caused additional features to be observed in the water reflectance spectrum. It was also observed that the magnitude of these additional features decreased with decreasing concentration of the ion causing the feature.

The fractional reflectance of sea-water samples collected from the Atlantic, Pacific, and Gulf of Mexico was observed to be identical, within an uncertainty of  $\pm 5\%$ , to the pure water reflectance values over the spectral region from  $4100\text{ cm}^{-1}$  to  $1100\text{ cm}^{-1}$ . From  $1100\text{ cm}^{-1}$  to  $780\text{ cm}^{-1}$ , the sea-water samples were observed to have reflectance values differing by more than  $\pm 5\%$  from the pure water values, with maximum deviation from the pure water reflectance values occurring at  $1100\text{ cm}^{-1}$ . This was the same spectral region that a strong additional feature was observed in the reflectance spectra of aqueous solutions containing the  $\text{SO}_4^{--}$  ion. However, because of the small concentration of the  $\text{SO}_4^{--}$  ion in sea water, this feature was reduced to a small deviation from the pure water reflectance values near  $1100\text{ cm}^{-1}$ .

It was therefore concluded that the sea water reflectance spectrum may be approximated by the pure water reflectance spectrum. This allows the use of pure water optical constants in calculations of the emissivity of sea water.