PERMITTIVITY OF SEA WATER AT MILLIMETER WAVELENGTHS

FINAL REPORT

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ABSTRACT

Measurements of reflectivity of sea water and ice at 100 GHz, 140 GHz, and 180 GHz are reported. Measurements on water covered the temperature range 0°C to 50°C. No anomalies in the dielectric properties of water due to the presence of either salts or organic matter were found. The reflectivity of water and its temperature dependence are consistent with recent dielectric property models derived from data at other wavelengths. The index of refraction of ice is constant at 1.78 throughout this region.
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I. INTRODUCTION

Only within the last dozen years has an extensive effort been made to measure physical properties of materials and to otherwise explore the spectral region lying between 50 GHz and 1000 GHz. The reasons are due largely to the lack of readily available hardware and to the experimental difficulties. In the microwave region, previous investigators have used cavity resonators or a length of waveguide as a means of defining the configuration of the electromagnetic field with the precision needed for accurate determination of dielectric properties. In the millimeter wave region, such techniques become increasingly difficult to apply. The problems include the difficulty of accurate matching of specimens and cavities, air gaps between sample and cavity wall, and the problem of surface tension and accurate sample shape for liquid dielectrics.

On the other hand, the extension of optical techniques using lenses and prisms to the short millimeter region encounters problems due to low source radiance, poor detector sensitivity, and a lack of available components.

The result has been the use of closed and open resonators at wavelengths greater than one millimeter, with free-space quasi-optical techniques employed at shorter wavelengths. Typically the quasi-optical and open resonator techniques give information about the index of refraction directly, while techniques employed in the microwave region usually give dielectric constant information.

Liquids are a special case, for the range of sample geometries is limited compared to solids. The dielectric properties of seawater have been measured to high accuracy from dc to the microwave region, and in the optical and infrared region of the spectrum. Measurements in the millimeter region are few and of limited accuracy. The work described here was undertaken for the purpose of providing better defined properties for sea water and ice in the short millimeter region.
After an initial look at open resonator techniques for these measurements, a reflectivity method was deemed most suitable for several reasons. Previous measurements of the dielectric properties of water and ice at longer wavelengths provide a base for extrapolating these properties through the millimeter wavelength region. Unless additional sources of dispersion occur, as eventually occur in the submillimeter region, these extrapolations should be approximately correct. A means of substantiating the extrapolated values or improving them if necessary is desired.

The use of reflectivity data provides such a method for the technique, as used in this program, yields reproducible data with a minimum of measured quantities and corrections. It can be quickly implemented and is adaptable to a wide range of wavelengths.

Briefly, reflectivity at normal incidence is measured. The result is used to obtain the index of refraction \( n = n - ik \). Both reflectivity and phase information are required for an unambiguous determination. Phase information requires a more complex experimental arrangement with a concomitant reduction in accuracy. To avoid this problem, we make use of the frequency and temperature dependence of \( n \) as determined by extrapolation from longer wavelengths. Small corrections are sufficient to fit normal reflectivity. To check our assignment of \( n - ik \) values, we then measure reflectivity at oblique incidence. The quantities \( n \) and \( k \) contribute to reflectivity in varying amounts depending on the angle of incidence. If calculated reflectivity tracks experiment for oblique incidence, we have a set of refractive indices which agree with experiment. Normal incidence measurements have the highest accuracy, and are always used as the basis for adjusting \( n \) and \( k \).

In practice we find the measured reflectivity agrees quite well in absolute value and temperature dependence with values calculated using a modified Debye equation described in Section III. The experimental technique is described in detail in Section II.
II. EXPERIMENTAL PROCEDURE

Reflectivity measurements compare power reflected from a water surface with power reflected from a surface of liquid mercury. A schematic of the arrangement used for normal incidence measurements at 100 GHz is shown in Figure 1. The actual geometry had the source and receiver horns at 2.25 degrees off normal incidence. The horns had dimensions of 2.85 cm x 3.40 cm at the output and were 8.5 cm in length. Various lens configurations were used, but caused undesirable coupling between source and receiver horns. Best results were obtained using absorber panels to define the illuminated area and to eliminate stray reflections. Similar arrangements were used for measurements at oblique incidence.

A typical experiment consists of exchanging dishes of water and mercury, each filled to the same height, while measuring the energy reflected from each surface. Surface height is adjusted to match a reference level and a further small adjustment may be made to maximize reflected power if possible.

For measurements at temperatures away from room temperature, the experimental procedure was changed.

As the depth of mercury on the sample dish is only a few millimeters, a matching sample of water has low heat capacity and large surface area permitting temperature drift at an excessive rate. To avoid this problem, reflectivity at other temperatures was referenced to water at room temperature, and samples containing larger volumes of liquid were used.

The data were corrected for a small amount of horn-horn coupling which was occasionally present. Other experimental problems were drift and short term fluctuations in klystron power.

At 140 GHz, these fluctuations forced use of a metal plate which could be quickly interposed between source and sample. A comparison between plate and sample could be made quickly, much faster than the usual interchange of liquid samples. The reflectivity of the plate was a constant for a set of measurements.
Figure 1. Experimental Arrangement for Normal Incidence Reflectivity Measurements at 100 GHz.
The sample surface reflectivity is determined by the properties of the first few µm of water. Any temperature gradient caused, for example, by evaporation will result in an error no larger than the variation of reflectivity between wet and dry bulb temperatures. Because the variation of measurements of reflectivity was small and typically less than the standard deviation within one data set, we believe errors from all sources are no greater than the standard deviation.

In contrast to water, ice has quite low absorption at millimeter wavelengths and modifications to our technique were required. The bottom of the ice container was covered with absorber and oriented so as to eliminate any contribution from reflected energy. Errors due to surface irregularities and tilted surfaces reduce reflected power while free water on the surface increases reflected power.

Ice temperature for reflectivity measurements was determined by using a thermistor frozen 1/4 inch deep three inches from the center of the dish. The radiation source produced a spot about three inches in diameter. Liquid nitrogen was used to keep the water frozen. The ice surface tended to have irregularities which were smoothed and polished with a damp cloth. The dish containing the ice was leveled with a spirit level to an accuracy of 1/8 degree. Care was taken to raise the surface of the reference mercury to the same position as the ice surface for the reference measurement.

An ice prism was also used. The deviation of the incident radiation by the prism is related to the prism angle and the index of refraction. At 140 GHz and 180 GHz with an unstable klystron, this technique was particularly useful.

We have considered the potential magnitude of the error arising from the no-signal power coupled and reflected into the receiver horn from the signal source and surroundings. We have taken precautions to minimize the magnitude of this stray radiation, but is has not always been possible to completely eliminate it. It is a limitation most noticeable in situations where the reflectivity is very small. A good example is the case where absorber materials are being measured.
In Table I we show a typical set of readings taken from a set of data obtained during this study. Our usual procedure is to subtract the coupling voltage from the signal voltage, correct this difference for any increase or decrease of the reference power, and record the ratio. In this case, the ratio is 1.82/4.51.

### Table I

Typical Values From Measurement Of Reflectivity
On 0.1 mV Scale, DVM

<table>
<thead>
<tr>
<th>Item</th>
<th>Coupling Voltage</th>
<th>Signal Voltage</th>
<th>Phase Degrees</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reference Power</td>
<td>-</td>
<td>4.2</td>
<td>181.1</td>
</tr>
<tr>
<td>Hg</td>
<td>0.01</td>
<td>4.52</td>
<td>0.87</td>
</tr>
<tr>
<td>H₂O</td>
<td>0.01</td>
<td>1.83</td>
<td>0.84</td>
</tr>
</tbody>
</table>

The measured signal power, \([A']^2\), consists of the sum of the true reflected power, \(A^2\), and the no-signal power, \(a^2\), where the amplitudes \(A\) and \(a\) have a phase difference \(\phi\). The measured power is then

\[
[A']^2 = A^2 + 2aA \cos \phi + a^2
\]  

[1]

The quantity used in our reflectivity calculations is the measured power less the no-signal power. This quantity is given by

\[
[A'']^2 = A^2 + 2aA \cos \phi
\]  

[2]
The no-signal power does not depend on the position of objects beyond the immediate neighborhood of the source and receiver horns. It appears to be constant or nearly so during the course of an experimental run, independent of the reflectivity of the surface being measured. If we assume that $\alpha$ and $\phi$ do not change between sample and reference, we can write an expression identical to equation [2] for the reference power to be used in calculations,

$$[B'']^2 = B^2 + 2 \alpha B \cos \phi$$

[3]

The power reflectivity is given by the ratio of the corrected power measurements which is

$$\frac{[A'']^2}{[B'']^2} = \frac{[A^2/B^2]}{[1 + 2 \alpha \cos \phi (1/A - 1/B)]}$$

[4]

The error involved in using this technique is given by the term $2 \alpha \cos \phi (1/A - 1/B)$. If we assume that $\cos \phi$ is close to one, the error for the data in Table I using this technique turns out to be 0.0066, or 2/3 percent. We believe this error to be smaller than that which arises from klystron power drift and temperature drift. We have been able to reproduce values of reflectivity using a similar experimental arrangement in two different locations. Our results suggest that most of the no-signal power is due to horn-horn coupling from transmitter to receiver and does not represent energy reflected indirectly to the receiver off the sample surface or off other nearby surfaces. Thus terms not included in this analysis such as phase shifts of the no-signal power between sample and reference measurements are believed to be insignificant.

The technique described here for compensating measured power for the no-signal power has the advantage of simplicity and ease of calculation. The error incurred with this technique can be severe if the ratio $\alpha/A$ becomes sizeable.
An alternative technique which is preferable, particularly where drift in temperature and power are small, is to subtract the square-root of the no-signal power reading from the square root of the reflected power reading. In this case the ratio of the power measurements becomes, in analogy to equation [4],

\[
\frac{[A'']^2}{[B'']^2} = \frac{[A^2/B^2]}{[1 - 2 \alpha (1 - \cos \phi)(1/A - 1/B)]}
\]

The error is given by the term \(2 \alpha (1 - \cos \phi)(1/A - 1/B)\) which can be expected to be smaller than the corresponding term in equation [4]. As the value of \(\phi\) is very close to the phase of the reference and sample for measurements on water, the magnitude of the error could be reduced by a considerable factor. The technique of subtracting square-roots of measured powers should be particularly useful for cases where no-signal power cannot be reduced to negligible proportions and power fluctuations and drift are not major limitations.
III. ANALYSIS TECHNIQUES

The reflective properties of a plane surface of material are completely determined by the dielectric properties. These properties are described either by the complex index of refraction, \( n - ik \), or the complex dielectric constant, \( \varepsilon' - i\varepsilon'' \). For reflection at angles of incidence other than normal incidence, the reflection coefficient depends on the polarization of the electric field relative to the surface. The relationships between \( \varepsilon \) and \( n \), and expressions for the power reflectivity are given in Table II.

The dielectric constant of pure water has no significant frequency dependence from dc up to beyond \( 10^8 \) Hz. Over 30 determinations of the static field dielectric constant have been reported in the literature between 0°C and 100°C. These measurements are quite accurate.

At sufficiently high frequencies, the real part of the dielectric constant falls to a value of approximately the square of the optical index of refraction while the imaginary part displays a broad absorption band.

An expression describing this behavior is due to Debye [1]. It may be written as

\[
\varepsilon = \varepsilon_\infty + \left( (\varepsilon_s - \varepsilon_\infty) / (1 + i\omega\tau) \right)
\]

where \( \varepsilon_s \) is the static or low frequency value of the dielectric constant and \( \varepsilon_\infty \) is the residual value of the dielectric constant at frequencies much higher than that of the dielectric relaxation process. The relaxation time \( \tau \) for the process of dipole orientation is a measure of the frequency at which the broad band absorption appropriate to this process reaches its peak.

These equations may be rationalized yielding

\[
\varepsilon' = \varepsilon_\infty + \left( (\varepsilon_s - \varepsilon_\infty) / (1 + \omega^2 \tau^2) \right)
\]

\[
\varepsilon'' = (\varepsilon_s - \varepsilon_\infty) \omega \tau / (1 + \omega^2 \tau^2)
\]
TABLE II

RELATIONSHIPS BETWEEN REFRACTIVITY AND REFRACTIVE INDEX

The refractive index \( n = n - i k \) and the dielectric constant \( \varepsilon = \varepsilon' - i\varepsilon'' \) are related by \( \varepsilon = n^2 \)

\[
\varepsilon' = n^2 - k^2
\]

\[
\varepsilon'' = 2nk
\]

\[
n = \left( \varepsilon'/2 \right)^{1/2} \left\{ \left[ 1 + \left( \frac{\varepsilon''}{\varepsilon'} \right)^2 \right]^{1/2} + 1 \right\}^{1/2}
\]

\[
k = \left( \varepsilon'/2 \right)^{1/2} \left\{ \left[ 1 + \left( \frac{\varepsilon''}{\varepsilon'} \right)^2 \right]^{1/2} - 1 \right\}^{1/2}
\]

for normal incidence, the reflectivity is given by

\[
R = \left[ \frac{(n - 1)^2 + k^2}{(n + 1)^2 + k^2} \right]
\]

At angle of incidence \( \theta \), the reflectivity for radiation polarized parallel to the plane of incidence, \( R_p(\theta) \), and perpendicular to the plane of incidence, \( R_s(\theta) \), is given by

\[
R_p(\theta) = \left| \frac{(n^2 - \sin^2 \theta)^{1/2} - n^2 \cos \theta}{(n^2 - \sin^2 \theta)^{1/2} + n^2 \cos \theta} \right|^2
\]

\[
R_s(\theta) = \left| \frac{(n^2 - \sin^2 \theta)^{1/2} - \cos \theta}{(n^2 - \sin^2 \theta)^{1/2} + \cos \theta} \right|^2
\]

Both expressions reduce to the normal incidence case at \( \theta = 0 \). The above formulas refer to a dielectric-air interface.
These relations, the "Debye equations", have been subjected to many alterations and embellishments. Among these, the equations of Cole and Cole [2] are quite useful here. The equations are,

\[
\varepsilon' = \varepsilon_\infty + \frac{(\varepsilon_s - \varepsilon_\infty) [1 + (\lambda_s/\lambda)^{1/2} - \alpha \sin(\alpha \pi/2)]}{1 + 2(\lambda_s/\lambda)^{1/2} - \alpha \sin(\alpha \pi/2) + (\lambda_s/\lambda)^2(1 - \alpha)}
\]

\[
\varepsilon'' = \frac{(\varepsilon_s - \varepsilon_\infty)(\lambda_s/\lambda)^{1/2} - \alpha \cos(\alpha \pi/2)}{1 + 2(\lambda_s/\lambda)^{1/2} - \alpha \sin(\alpha \pi/2) + (\lambda_s/\lambda)^2(1 - \alpha)} + \frac{\sigma \lambda}{18.85 \times 10^{10}}
\]

where for pure water \(\sigma = 12.57 \times 10^8\) esu.

Here \(\lambda\) is the wavelength of the exciting radiation and \(\lambda_s\) is the relaxation wavelength corresponding to \(\tau\). The quantity \(\alpha\) corresponds to a small variation in relaxation time. A small conductivity term is added in equation 10 to account for the effect of the conductivity of water to the dielectric properties.

As will be seen, the effect of this conductivity for sea water as well as pure water on the dielectric properties is too small to be observed at the frequencies of interest to this work.

Recent reviews using these equations to fit data concerning the dielectric properties of water over the spectrum from dc to the optical region are by Ray [3] and by Mason, Hasted, and Moore [4]. The results of the measurements to be described will be compared with the predictions of these reviews.

Finally, let us consider the reflectivity of the mercury used as a reference surface. The bulk power reflectivity of a metal varies with the conductivity and is given by,

\[
R = 1 - (8\varepsilon_\omega/\sigma)^{1/2}
\]

where \(\varepsilon = \varepsilon_0 \varepsilon' = (8.854 \times 10^{-12} \text{ f/m}) \varepsilon'\)

and \(\sigma = \text{conductivity in mhos/m.}\)
Data on optical properties of metals in this region are relatively rare. For silver at 50 GHz, $\sigma = 6.139 \times 10^7$ mhos/m at 20°C and $\varepsilon'$ is near 2. For these values, $R = 0.9996$.

Using a value of the dc conductivity of mercury at 20°C, $\sigma = 10^6$ mho/m and a value of 2 for $\varepsilon'$ leads to an expected minimum value of $R = 0.991$.

The reflectivity of a clean mercury surface in the millimeter wavelength region should be higher than this value and its value has been taken as 1 in the calculations described in the following sections. Any errors associated with this assumption should be much less than one percent.
IV. MEASUREMENTS AT 100 GHz

Measurements near 100 GHz include measurements at normal incidence over the temperature range 0°C to 50°C, measurements at oblique incidence, measurements on saline solutions, plankton solutions, sea water, and measurements on ice.

The results for normal reflectivity are shown in Figure 2 for the temperature range 0°C to 50°C. The three curves were calculated from equations [7] to [10] and the relations in Table II using the parameters given by Mason, Hasted, and Moore [4] and Ray [3]. The Deby model (D) and the Cole-Cole model (C-C) are within a half percent of each other in this frequency region and it is not possible to distinguish between them. The curve calculated using the parameters by Ray (R) has a slightly greater temperature dependence than the other two models and does not agree as well with experiment.

The experimental value of reflectivity at 103.8 GHz at 20°C is 0.392 ± 0.014 and represents the average of 122 measurements. The slope at 20°C is taken to be 0.0037°C.

The appropriate dielectric constant for water at 103.8 GHz at 20°C is

\[ \varepsilon' - i\varepsilon'' = 7.16 - i 11.825. \]

The related index of refraction at 20°C is

\[ n - ik = 3.24 - i 1.825. \]

Values obtained at 6.3°C and 47°C represent averages for 10 and 12 measurements respectively.

Measurements of reflectivity at oblique incidence were made with polarization perpendicular and parallel to the reflecting surface. The results for two different angles of incidence are compared in Table III to values calculated from the parameters given by Ray. These measurements were taken over temperatures between 0°C and 50°C. As
Figure 2. Reflectivity of water at normal incidence as a function of frequency. The measurements were performed at 103.8 GHz. The value obtained at 20°C represents an average of 12 measurements. The experimental results are compared with the theoretical models. Small circles represent measurements, and the line represents the theoretical model calculated from the Cole-Cole (C-C) model. The slope of the line at 20°C is 0.0044/°C.

At 20°C, R = 0.391.

Reflectance of water at normal incidence, at 103.8 GHz.
TABLE III
REFLECTIVITY AT OBLIQUE INCIDENCE

A. Measurements Near 46° Incident Angle

<table>
<thead>
<tr>
<th>Measurement</th>
<th>Angle</th>
<th>Temperature</th>
<th>Experimental Value</th>
<th>Calculated Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_s$</td>
<td>46.2°</td>
<td>18.8°C</td>
<td>0.557</td>
<td>0.528</td>
</tr>
<tr>
<td>$R_p$</td>
<td>46.2°</td>
<td>19.7°C</td>
<td>0.271</td>
<td>0.268</td>
</tr>
</tbody>
</table>

B. Measurements Near 31° Incident Angle

<table>
<thead>
<tr>
<th>Measurement</th>
<th>Angle</th>
<th>Temperature</th>
<th>Experimental Value</th>
<th>Calculated Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_s$</td>
<td>31.0°</td>
<td>19.0°C</td>
<td>0.478</td>
<td>0.454</td>
</tr>
<tr>
<td>$R_p$</td>
<td>31.0°</td>
<td>17.6°C</td>
<td>0.452</td>
<td>0.449</td>
</tr>
</tbody>
</table>

C. Reflectivity Ratios for Different Temperatures

<table>
<thead>
<tr>
<th>Measurement</th>
<th>Angle</th>
<th>$T_1$</th>
<th>$T_2$</th>
<th>Experimental Value</th>
<th>Calculated Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_s(T_1)/R_s(T_2)$</td>
<td>47.2°</td>
<td>19.7°C</td>
<td>5.3°C</td>
<td>1.106</td>
<td>1.123</td>
</tr>
<tr>
<td></td>
<td>47.2°</td>
<td>19.2°C</td>
<td>4.5°C</td>
<td>1.098</td>
<td>1.153</td>
</tr>
<tr>
<td></td>
<td>47.2°</td>
<td>39.6°C</td>
<td>20.1°C</td>
<td>1.093</td>
<td>1.1201</td>
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<tr>
<td></td>
<td>47.2°</td>
<td>40.5°C</td>
<td>19.6°C</td>
<td>1.084</td>
<td>1.127</td>
</tr>
<tr>
<td></td>
<td>31.0°</td>
<td>17.7°C</td>
<td>3.9°C</td>
<td>1.133</td>
<td>1.176</td>
</tr>
<tr>
<td></td>
<td>31.4°</td>
<td>16.8°C</td>
<td>3.9°C</td>
<td>1.096</td>
<td>1.160</td>
</tr>
<tr>
<td></td>
<td>31.0°</td>
<td>39.9°C</td>
<td>17.7°C</td>
<td>1.159</td>
<td>1.239</td>
</tr>
<tr>
<td></td>
<td>31.4°</td>
<td>39.7°C</td>
<td>17.9°C</td>
<td>1.150</td>
<td>1.163</td>
</tr>
</tbody>
</table>
previously discussed, reflectivity ratios were obtained for measurements above and below room temperature. The ratio of the sample reflectivity to the reflectivity of a water sample at room temperature was measured. Each of the experimental values listed in Table III represents an average of approximately 16 readings. These measurements had a larger standard deviation than measurements made at normal incidence. Coupling between transmitter and receiver horns was quite small. The results provide a check on the reduction of normal reflectivity measurements into real and imaginary dielectric constants or indices of refraction.

The results discussed thus far have been obtained using tap water. Sea water contains salts and organic matter. In order to verify that these data are representative of sea water, two solutions were prepared. One contained NaCl to approximate the ionic content of sea water, and the other contained plankton to simulate the organic content. Sea water samples were also measured.

A 0.7N solution of NaCl was used. This corresponds to 4.1% salinity, equivalent to a very saline region of the ocean. The ratio of reflectivity at normal incidence of the salt solution to the reflectivity of fresh water was measured at room temperature. The result was $\frac{R(\text{salt water})}{R(\text{fresh water})} = 1.006 \pm 0.010$. The deviation of the ratio from unity is less than the standard deviation. Therefore there is no measurable difference between the reflectivity of fresh water and a 0.7N solution of NaCl at 97.75 GHz.

This result may be anticipated from the frequency dependence of the ionic conductivity of salt water. The imaginary part of the dielectric constant can be considered to comprise an effective conductivity arising from the orientation of the polar water molecules and a real conductivity arising from the mobile ions. The ionic conductivity has a frequency dependence given by

$$\sigma_1(\omega) = \sigma_0 \left(1 + \frac{\omega^2 \tau^2}{\epsilon_0}\right)^{-\frac{1}{2}}$$

[12]
The imaginary part of the dielectric constant may then be written as

\[ \varepsilon'' = \varepsilon_0'' + 2\sigma_I(\omega)/f \]

where \( f \) is the radiation frequency.

The conductivity of sea water is discussed by Halley [5]. Typical values of dc conductivity are in the range \( 35 - 45 \times 10^9 \text{ sec}^{-1} \) (esu units) and relaxation times near \( 1.1 \times 10^{-10} \text{ sec} \). At a frequency of 100 GHz, the conductivity will be \( 0.45 - 0.7 \times 10^9 \text{ sec}^{-1} \) using equation [12]. At a frequency of 100 GHz, the ionic contribution to \( \varepsilon'' \) using equation [13] will be no larger than 0.014. The value of \( \varepsilon'' \) at this frequency is close to 11. The effect of the added conductivity, near one part per thousand, is less than the sensitivity of our measurements.

Samples of sea water from the Gulf of Mexico were compared with fresh water with the result \( R(\text{sea water})/R(\text{fresh water}) = 0.9996 \pm 0.0040 \). Again the deviation of the ratio from unity is less than the standard deviation. There was no measurable difference between the reflectivity of this sea water sample and fresh water at 20°C.

The organic component of sea water contains both dissolved matter and particulate matter. From estimates of the total amount of living cells [6], we can estimate the concentration of particulate matter for most ocean areas to be in the range of 150-300 g/m³.

For these measurements, we prepared a solution containing 580 g/m³. This concentration would correspond to a heavy concentration of organic matter representing fertile coastal waters during the spring and summer.

The reflectivity of this solution was compared to the reflectivity of fresh water. The result was \( R(\text{plankton})/R(\text{fresh water}) = 0.999 \pm 0.014 \), and the deviation from unity was less than the standard deviation. We conclude that the presence of plankton in water does not alter its reflectivity at 100 GHz.
We have used our equipment to measure the normal reflectivity of ice at a frequency of 99 GHz. As mentioned previously, the sample holder was modified for this measurement. The bottom of the dish was lined with absorber material. Water was frozen in the dish in a wedge shape. Energy reflecting from the bottom of the dish will follow a different path than energy reflected from the surface.

Temperature was determined with a thermistor frozen 1/4 inch deep in the ice surface three inches from the center of the dish. The radiation was focused to a spot diameter of about eight centimeters. Liquid nitrogen was used to keep the water frozen. The ice surface tended to develop irregularities which were smoothed and polished with a damp cloth. The dish containing the ice was leveled with a spirit level to an accuracy of 1/8 degree. Care was taken to raise the surface of the reference mercury to the same position as the ice surface for the reference measurement.

The result for ice at 99 GHz is

\[ R(\text{ice}) = 0.0785 \pm 0.0112 \]

where no temperature dependence was observed in the temperature region -5°C to -20°C. Assuming negligible absorption, the index of refraction and dielectric constant for ice are

\[ n = 1.78 \pm 0.08 \]

\[ \varepsilon = 3.17 \pm 0.27 \]

The results of Cumming [7] at a wavelength of 3.2 cm give a value of 1.78 for the index of refraction of ice. The literature indicates no absorption bands and no dispersion in the millimeter-centimeter wavelength region. Thus the result quoted here near 3 mm is in excellent agreement with the measurement at 3.2 cm. Furthermore, the result should be independent of temperature in agreement with these observations.
As an independent check on the measurements reported here using the apparatus developed for water, we also determined the index of refraction of ice by sending radiation through an ice prism. The klystron energy, entering normal to the back face, was deflected 27° upon emerging from the front face of the prism with a prism angle of 28°. The index of refraction, by Snell's law, is given by

\[ n = \frac{\sin(28° + 27°)}{\sin(28°)}. \]

This gives a value of \( n = 1.745 \) for ice at 99 GHz. The result agrees well with the value, obtained from reflectivity, of 1.78. The results substantiate the expected result, a dielectric constant that is frequency and temperature independent in the millimeter-centimeter wavelength region. Measurements on ice at higher frequencies, as discussed in the following sections, are consistent with this interpretation.
V. MEASUREMENTS AT 140 GHz

Measurements near 140 GHz include reflectivity measurements at normal incidence over the temperature range from 0°C to 50°C and measurements on ice.

The results of normal incidence reflectivity measurements at a frequency of 135.6 GHz are shown in Figure 3. As before, the data are compared to reflectivity calculated from three current models for the dielectric properties of water. For these measurements, an OKI klystron was used as a source, and a GaAs point contact detector was used to detect the reflected energy. In other respects the procedures were nearly identical with those used at 100 GHz.

The result of 115 measurements averaged at 20°C for a frequency of 135.6 GHz is a value for reflectivity at normal incidence of 0.341 ± 0.002. The slope at 20°C is found to be 0.0042/°C. This corresponds to a dielectric constant of

\[ \varepsilon' - i\varepsilon'' = 6.33 - i 8.96. \]

The related index of refraction at 20°C is

\[ n - ik = 2.94 - i 1.52. \]

Measurements of the reflectivity of ice were scattered and irreproducible. This may have been the result of the particular geometry used at this frequency. A slight variation in elevation or angle from horizontal of the ice surface seemed to produce extremely large variations in reflected power. Coupling between source and receiver horns at this wavelength was very small. The coupled power was at least a factor of 10^4 smaller than the reflected energy, and was not a factor in these measurements.

To circumvent these problems, we returned to measurements on an ice prism used briefly at 100 GHz as a check on reflectivity measurements. A prism with an angle of 28.4° was cast. The results of three
Measurements were represented by small circles. The curves were calculated from Cole-Cole (C-C) and Dewey models (4) and the model by Ray (R) [3]. Individually, 49 measurements, while the value at 48°C represents 79 measurements. The value obtained at 29°C represents an average of 135.6 GHz. The value obtained at 29°C represents an average of the measurements at normal incidence at a frequency of Figure 3. Reflectivity of Water at Normal Incidence at a Frequency of
separate measurements give the value $n = 1.78 \pm 0.02$. This value is the same as that obtained at 100 GHz and agrees with measurements in the centimeter wavelength region [7].

No measurements were made as a function of temperature. The ice prism was maintained below its melting temperature by periodic applications of liquid nitrogen. The temperature of the measurement was in the vicinity of -10°C.
VI. MEASUREMENTS AT 180 GHz

Measurements at 180 GHz used a varactor doubler to double the frequency of a klystron operating near 90 GHz. The actual output frequency was 183.3 GHz. The output power was considerably less than was available at 100 GHz and 140 GHz. At no time was the power greater than 4 mW, and most measurements were obtained at lower power. At 100 GHz and 140 GHz power levels closer to 20 mW were typical.

The resulting signal-to-noise ratio was lower than for measurements at lower frequencies. The power output of the varactor was less stable than was typical for the klystrons used at lower frequencies. These problems combined to make accurate reflectivity measurements more of a problem than in previous measurements.

It was found that use of a strip chart recorder provided a means of accommodating the drift and variations in output power. The ratio of reflectivities of mercury or water to a metal plate could be obtained quickly and reproducibly from the strip chart record. Coupling between source and receiver horns was so low as to be into the noise level. As always, careful adjustment of the liquid level was necessary to tune the system to the point of maximum signal.

Figure 4 shows the result of this measurement. At 20°C and at a frequency of 183.3 GHz, we find the reflectivity of water to be 0.301 ± 0.009. This corresponds to a dielectric constant of

\[
\varepsilon' - i\varepsilon'' = 5.85 - i 7.13.
\]

The corresponding index of refraction is

\[
n - ik = 2.74 - i 1.30.
\]

At this point measurement of the temperature variation of the reflectivity was initiated. This series of measurements was barely underway when two equipment failures occurred. The klystron, which
Figure 4: Reflectance of Water at Normal Incidence at 183.3 GHz Compared to Calculated Reflectivity Based on Cole-Cole and Debye Models [3, 14].
had been used extensively prior to these measurements, began to fail
with a radical loss of power and a large increase in beam current.
In addition, the lock-in amplifier lost its lock-in ability in the
synchronous detector section.

We were able to complete measurements of the index of refraction
of ice at this frequency by substituting another tube and using the
preamplifier section of the lock-in amplifier in conjunction with
another tuned amplifier. These measurements completed the tasks ex-
pected during this grant. Additional measurements would have been
desirable to be consistent with the data taken at lower frequencies.

Sufficient signal-to-noise for additional measurements will not
be available until the lock-in amplifier is repaired. In the meantime,
the funds and time available for this task are expended.

Measurements on ice again used a prism with an angle of 28.4°.
The prism was cooled by occasional drenching with liquid nitrogen. The
result of three separate measurements was

\[ n = 1.79 \pm 0.03. \]

This result is in good agreement with our measurements at lower
frequencies and is consistent with the results of Cumming [7].
VII. AUXILIARY MEASUREMENTS

During the course of this research program, the facility we have developed has been used to measure the reflectivities of several materials of interest to on-going NASA programs. A set of measurements was made on absorber materials of concern to our parallel program "Research In Millimeter Wave Techniques", NASA Grant No. NSG-5012. Values ranged from 20% for Devcon plastic to 0.15% for a grooved Rexolite absorber panel. A grooved carbon surface, to be used in a chopper, had a reflectivity less than the system noise level. The noise was typically 35 dB or more below the signal from a mercury reference surface. These measurements were made at 100 GHz.

Samples of radiation absorbing sheet material from Rantec Division of Emerson Electric Company, Calabasas, California were measured using the OKI klystron at 140 GHz. The materials were designated EP-5 and EHP-8.

The absorber materials were so effective at 140 GHz that a definitive measurement was beyond the capabilities of this experimental arrangement. Absorption was greater than 40 dB and the reflected energy was below the system noise level for both absorber types. The increased sensitivity at 140 GHz compared to 100 GHz was due to the use of a new tube with increased power. The results were as follows,

\[
\begin{align*}
\text{EHP-5} & \quad \text{Absorption} > 41.5 \text{ dB} \\
\text{EHP-8} & \quad \text{Absorption} > 43 \text{ dB}
\end{align*}
\]

The reflected energy for both absorber materials was in the $10^{-5}$ range or smaller. This result is consistent with the general result that most absorber materials become increasingly effective as wavelength decreases into the short millimeter region.
VIII. SUMMARY

Dielectric properties of water and ice in the short millimeter wavelength region have been studied by measuring reflectivity at normal incidence and oblique incidence. Measurements were made at frequencies of 103.8 GHz, 135.6 GHz and 183.3 GHz. Measurements on water covered the temperature range between 0°C and 50°C. A search for possible anomalies in the dielectric properties of water due to the presence of either salts or organic matter was made. No effect on reflectivity was observed within the accuracy of our measurements.

The reflectivity at normal incidence of water at 20°C at the three frequencies used in this study is shown in Table IV. Results for the index of refraction of ice at three frequencies are given in Table V. The frequencies near 100 GHz differ for the water and ice measurements because the frequency of the klystron was shifting as it approached the end of its useful life.

The experimental reflectivities were compared with reflectivities calculated from three recent models [3] [4]. The Cole-Cole model parameters by Mason, Hasted, and Moore [4] are in good agreement with experiment at all frequencies and temperatures. Parameters for the Debye model [4] are also within experimental error and are somewhat easier to apply. These models are discussed in more detail in the next section.
TABLE IV. REFLECTIVITY OF WATER AT SHORT MILLIMETER WAVELENGTHS

<table>
<thead>
<tr>
<th>Frequency (GHz)</th>
<th>Reflectivity at Normal Incidence Measurements at 20°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>103.8</td>
<td>0.392 ± 0.014</td>
</tr>
<tr>
<td>135.6</td>
<td>0.341 ± 0.002</td>
</tr>
<tr>
<td>183.3</td>
<td>0.301 ± 0.009</td>
</tr>
<tr>
<td>Frequency (GHz)</td>
<td>Refractive Index</td>
</tr>
<tr>
<td>----------------</td>
<td>-----------------</td>
</tr>
<tr>
<td>99</td>
<td>1.78 ± 0.08</td>
</tr>
<tr>
<td>135.6</td>
<td>1.78 ± 0.02</td>
</tr>
<tr>
<td>183.3</td>
<td>1.79 ± 0.03</td>
</tr>
</tbody>
</table>

TABLE V. INDEX OF REFRACTION OF THE Ih PHASE OF ICE AT SHORT MILLIMETER WAVELENGTHS
IX. DISCUSSION

The measurements reported here agree well with the models for dielectric properties of water given by Mason, Hasted, and Moore [4]. Parameters for the Debye and Cole-Cole models were given. A major difference between these models and the model by Ray [3] is the temperature variation of the high frequency dielectric constant \( \varepsilon_\infty \). In Figure 5, the parameter \( \varepsilon_\infty \) is presented for the three models. The larger temperature variation used in the model by Ray (R) is the major source of the larger temperature dependence of reflectivity as shown in Figures 2, 3 and 4.

Work at lower frequencies plus some data in the submillimeter wavelength region makes it a near statistical certainty that there is some spread of relaxation times in water in this temperature range [4]. We conclude that the Cole-Cole model with the parameters of [4] gives the most satisfactory fit to the dielectric properties of water in the millimeter wavelength region.

The Debye and Cole-Cole equations discussed in Section III are respectively:

\[
\varepsilon = \varepsilon' - i\varepsilon'' = \varepsilon_\infty + [\varepsilon_s - \varepsilon_\infty]/[1 + i\omega \tau] \tag{6}
\]

\[
\varepsilon = \varepsilon' - i\varepsilon'' = \varepsilon_\infty + [\varepsilon_s - \varepsilon_\infty]/[1 + (i\omega \tau)^{1-\alpha}] \tag{14}
\]

The modification of the Debye equation by including the spread parameter \( \alpha \) has the following significance. Equation (14) is appropriate for a dielectric with a distribution of relaxation times about a most probable value \( \tau_0 \) [4]. The full width of the distribution at half height is about \( 400 \alpha \tau_0 \). The form of the distribution is similar to a Gaussian, but the frequency variation of the dielectric constant is not sensitive to the form of the distribution function for relaxation times.
Figure 5: Temperature dependence of the high frequency dielectric constant $\varepsilon_\infty$ for various electric models. In References [3] and [4], $\varepsilon_\infty$ is used in the three models.
Water is an example of several liquids believed to possess a distribution of relaxation times for dipole orientation. An essentially single relaxation time implies that the dipole orientation process is unique. That is, the reorienting dipoles have essentially identical surroundings. A small spread of relaxation times suggests a distribution of environments. Both bond-bending and bond-breaking may occur during reorientation. Bond-breaking is thought to dominate and can account for the principal relaxation.

Water is considered to be a statistical assembly of molecules bonded to 0, 1, 2, 3, 4 neighbors with the fraction of bonds of a given type varying with temperature. Three-bonded molecules require for reorientation the breakage of two hydrogen bonds, two-bonded molecules require the breakage of one hydrogen bond, while one- and zero-bonded molecules are free to rotate without bond breakage.

If all types of bonds are present, the faster, low energy processes dominate and make the slower high energy processes rare even though the three- and four-bonded species may be present in large proportions. In water, the principal reorientation process appears to be due mainly to two-bonded molecules as the necessary activation energy for breakage of a hydrogen bond matches the activation energy of the principal reorientation process.

The zero- and one-bonded molecules may well contribute to a higher-frequency process, but there are so few of these that this process contributes only slightly to the static dielectric constant.

Haggis, et. al. [8] have proposed that symmetric and asymmetric two-bonded cases exist with the asymmetric molecules dominating. It appears that the asymmetric types can orient more easily. A calculation of \( \tau \) based on the rate of formation of molecules in the two-bonded state when compared with experiment yields a value for the activation energy somewhat lower than the bond energy of the OH...O bond. The result supports the idea that the asymmetrically two-bonded molecules can rotate with less energy than the OH...O bond energy.
The symmetrically and asymmetrically two-bonded species can be expected to have different relaxation times. With both species expected to coexist, two relaxation times should be observed. This model can explain the small observed value of the spread parameter $\alpha (\alpha = 0.015)$. The experimental result is consistent with equal populations with relaxation times of $0.8\tau$ and $1.2\tau$ where $\tau$ is the average value for equation [14].

Studies related to the dielectric properties of water continue, and recent work has changed the interpretation of the origin of the polarization in the submillimeter wavelength region [9]. Bearing in mind the likelihood that further refinements are certain to be forthcoming, the parameters used to calculate reflectivity with the Cole-Cole model in Figures 2, 3 and 4 are listed in Table VI. These parameters with equations [9], [10], and [14] represent an excellent fit to the data obtained in these measurements on water in the short millimeter region. The effect of salt and organic components in sea water may be neglected.

For ice, the index of refraction $n = 1.78$ through this region. The absorptive part of the index of refraction is very small, and is believed to be less than $10^{-3}$ at millimeter wavelengths. No measurements have been published.
TABLE VI
PARAMETERS DERIVED FROM THE COLE-COLE EQUATION
FOR WATER [4]
90% Confidence Intervals Are Listed.

<table>
<thead>
<tr>
<th>T(°C)</th>
<th>( \varepsilon_0 )</th>
<th>( \varepsilon_\infty )</th>
<th>T((10^{-9}s))</th>
<th>( \alpha )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>88.26 ± 0.81</td>
<td>4.46 ± 1.60</td>
<td>17.90 ± 0.60</td>
<td>0.014 ± 0.023</td>
</tr>
<tr>
<td>10</td>
<td>84.04 ± 0.40</td>
<td>4.10 ± 1.16</td>
<td>12.61 ± 0.29</td>
<td>0.014 ± 0.012</td>
</tr>
<tr>
<td>20</td>
<td>80.35 ± 0.22</td>
<td>4.23 ± 0.14</td>
<td>9.31 ± 0.079</td>
<td>0.013 ± 0.005</td>
</tr>
<tr>
<td>30</td>
<td>76.75 ± 0.30</td>
<td>4.20 ± 0.20</td>
<td>7.21 ± 0.097</td>
<td>0.012 ± 0.008</td>
</tr>
<tr>
<td>40</td>
<td>73.18 ± 0.28</td>
<td>4.16 ± 0.19</td>
<td>5.83 ± 0.089</td>
<td>0.009 ± 0.009</td>
</tr>
<tr>
<td>50</td>
<td>69.90 ± 0.31</td>
<td>4.13 ± 0.22</td>
<td>4.76 ± 0.088</td>
<td>0.013 ± 0.009</td>
</tr>
<tr>
<td>60</td>
<td>66.62 ± 0.36</td>
<td>4.21 ± 0.28</td>
<td>3.95 ± 0.131</td>
<td>0.011 ± 0.013</td>
</tr>
</tbody>
</table>
BIBLIOGRAPHY


8. G. H. Haggis, J. B. Hasted and T. J. Buchanan