GEORGIA INSTITUTE OF TECHNOLOGY ENGINEERING EXPERIMENT STATION

PROJECT INITIATION

Date: December 2, 1975

Tost in

Project Title: Permittivity of Sea Water at Millimeter Wavelengths

Project No.: A-1784

Project Director: Dr. M. D. Blue

Sponsor: NASA - Goddard Space Flight Center

Agreement Period: From 10/1/75 Until 6/30/76 (Grant Period)

Type Agreement: Grant No. NSG-5082

Amount: \$31,971 NASA + \$1,608 GIT = \$33,579 Total

Reports Required: Semiannual Status, Final Technical

Sponsor Contact Person:

Technical Matters Hr. J. L. King - Code 952 Communications & Navigation Div. Applications Directorate Goddard Space Flight Center Greenbelt, Maryland 20771 (301) 982-5702 Administrative Matters (Ihru GIRI) Ms. Genevieve F. Wiseman Grants Officer Office of the Director - Code 100 Goddard Space Flight Center Greenbelt, Maryland 20771 (301) 982-4511

TORESPECTOR SCHOOL SCHO

Electromagnetics Laboratory

Assigned to:

COPIES TO: Project Director Director, EES Assistant Director Division Chief EES Accounting Patent Coordinator

RA-3 (8-75)

EES Supply Services Security-Reports-Property Office General Office Services Library, Technical Reports Section Office of Computing Services Project File Other Sue Corbin; Bonnee Wettlaufer

GEORGIA INSTITUTE OF TECHNOLOGY OFFICE OF CONTRACT ADMINISTRATION

SPONSORED PROJECT TERMINATION

July 19, 1978 Date:

10/1

Project Title:

Permittivity of Sea Water at Millimeter Wavelengths

Project No:

Project Director:

A-1784

Sponsor: NASA - Goddard Space Flight Center

Dr. M. D. Blue

5/15/78 (Grant Expiration) Effective Termination Date:

Clearance of Accounting Charges: by 5/31/78

Grant/Contract Closeout Actions Remaining:

Final Invoice and Closing Documents

X Final Fiscal Report (NASA Form 1031, etc.)

X Final Report of Inventions

X Govt. Property Inventory & Related Certificate

Classified Material Certificate

Other

Electromagnetics Laboratory (School/Laboratory) Assigned to:

COPIES TO:

Project Director Division Chief (EES) School/Laboratory Director **Dean/Director-EES** Accounting Office Procurement Office Security Coordinator (OCA) Reports Coordinator (OCA) V

Library, Technical Reports Section Office of Computing Services **Director**, Physical Plant **EES Information Office** Project File (OCA) Project Code (GTRI) Other

PERMITTIVITY OF WATER AT MILLIMETER WAVELENGTHS

Semi-Annual Report for the Period October, 1975 - March, 1976

NASA Grant No. NSG-5082 GT/EES Project Number A-1784

Project Director: M. D. Blue Project Monitor: J. L. King

Engineering Experiment Station Electromagnetics Laboratory Georgia Institute of Technology Atlanta, Georgia 30332

FOREWORD

This is the first status report on NASA Grant NSG-5082. The grant covers the period from October 1, 1975 to June 30, 1976. The grant amount is \$31,971 in NASA funds and \$1,608 in Georgia Tech cost-sharing funds for a total of \$33,579. During the course of the program, three letter-type reports on progress have been written and sent to the NASA/GSFC technical monitor, J. Larry King, for the purpose of providing information regarding technical progress on a current basis, and to provide a better opportunity to direct the program so as to maximize its value to the government. Copies of these reports are attached as an Appendix.

The Principal Investigator at the Georgia Tech Engineering Experiment Station is Dr. M. D. Blue. The internal project number is A-1784. The matching funds in the amount of \$1,608 have been assigned the internal project number E240-805. Major contributions to the work reported here have been made by J. Barry McManus, student assistant.

I. Introduction

This report covers the first six months work on the permittivity of seawater. Measurements have been made over the temperature range 0°C to 50°C at a frequency of 97.75 GHz.

II. Permittivity Measurement Techniques

Only within the last ten 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 depend largely on the lack of readily available hardware and on the experimental difficulties. In the microwave region, previous investigators have used cavity resonators or a length of waveguide as a means of defining 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 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.

An open resonator technique was briefly studied for this program. The details are described in the Appendix in the report covering the period 1 October - 31 December 1975. It was found that the dissipative component of the dielectric constant of water was too high to permit the open resonator technique to be used. The method involves measurement of the resonance frequency and cavity Q with the empty cavity and with a thin layer of speciment inserted.

A reflectivity method was selected for these measurements for several reasons. From previous measurements of the dielectric properties of water, the dielectric properties may be extrapolated through the millimeter/submillimeter region yielding approximate values. A method of improving the accuracy of these values 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, normal incidence reflectivity is measured. The result is used to obtain the index of refraction $\underline{n} = n - ik$. 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 \underline{n} as determined by extrapolation. Small corrections are sufficient to fit normal reflectivity. To check our assignment of n - ikvalues, 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 Table I, we have collected several expressions relating the relative dielectric constant $\varepsilon = \varepsilon' - i\varepsilon''$ to the index of refraction, and expressions for reflectivity for radiation polarized parallel or perpendicular to the plane of incidence.

TABLE 1

RELATIONSHIPS BETWEEN REFLECTIVITY AND REFRACTIVE INDEX

The refractive index $\underline{n} = n - ik$ and the dielectric constant $\varepsilon = \varepsilon' - i\varepsilon''$ are related by $\underline{\varepsilon} = \underline{n}^2$

 $\varepsilon' = n^2 - k^2$

 $\varepsilon^{"} = 2nk$

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

for normal incidence, the reflectivity is given by

$$R = (n - 1)^{2} + k^{2} / (n + 1)^{2} + k^{2}$$

At an angle of incidence Θ , the reflectivity for radiation polarized parallel to the plane of incidence, $R_p(\Theta)$, and perpendicular to the plane of incidence, $R_q(\Theta)$, is given by

$$R_{p}(\Theta) = \left| \frac{\left(\underline{n}^{2} - \sin^{2}\Theta\right)^{1/2} - \underline{n}^{2} \cos\Theta}{\left(\underline{n}^{2} - \sin^{2}\Theta\right)^{1/2} + \underline{n}^{2} \cos\Theta} \right|$$

$$R_{s}(\theta) = \left| \frac{\left(\frac{n^{2} - \sin^{2}\theta}{\theta}\right)^{1/2} - \cos\theta}{\left(\frac{n^{2} - \sin^{2}\theta}{\theta}\right)^{1/2} + \cos\theta} \right|^{2}$$

Both expressions reduce to the normal incidence case at $\theta = 0$. The above formulas refer to a dielectric-air interface.

Figure 1 shows the experimental arrangement for reflectivity measurements. The horns had dimensions of 2.85 cm x 3.40 cm at the output and were 8.5 cm in length. The plastic lens served to focus the energy to a 12 cm diameter circle at the sample surface. With the high attenuation of water, only the wave reflected from the surface is received. The use of absorber panels eliminates possible contributions from stray reflections. A similar arrangement was used for measurements made at oblique incidence.

Transmitter and receiver were separated and absorber panels served to define the geometry of the received energy.

For the case of normal incidence, reflectivity at a fixed temperature was reproducible to better than one percent.

III. Experimental Results

Measurements of reflectivity at normal incidence was made relative to liquid mercury whose reflectivity was taken to be unity. A typical experiment consists of exchanging dishes of water and mercury, each filled to the same height, while measuring the reflected energy for each surface. Surface height is adjusted to match a reference level and a further small adjustment is made to maximize reflected power if possible. For water at 20°C, we find

 $R = 0.433 \pm 0.006$



where the stated error is the standard deviation. The frequency of the klystron was determined to be 97.75 GHz.

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

As the depth of mercury in the sample dish is only a few millimeters, a matching sample of water has low heat capacity with large surface area and will drift in temperature 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. Other experimental problems were instrument drift and drift in klystron power. As reflectivity is determined by the properties of the first few hundred um of water surface, any temperature gradient near the surface 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 between different runs was small and less than the standard deviation, we believe errors from all sources are no greater than the standard deviation.

The results for normal reflectivity are shown in Figure 2 which covers the temperature range 0°C to 50°C. The solid line below the experimental curve is taken from an extrapolation by Peter S. Ray^[1]. The diamond at 20°C represents reflectivity calculated from data supplied by NASA/GSFC^[2]. At 20°C, the extrapolations lead to reflectivity approximately 3.5 percent low, the error increasing as the temperature decreases to 5 percent at 0°C. The data represent over 50 measurements. If each point in Figure 2 is given equal weight, the standard deviation from the line is 0.0025. Near room temperature, the absolute value of reflectivity was repeatedly measured. Measurements were corrected to 20°C. The mean for 30 values with the associated standard deviation is shown at 20°C in Figure 2. The result is

 $R(20^{\circ}C) = 0.433 + 0.006.$

The slope at 20°C is taken to be R = 0.0035/°C. A consistent index of refraction at 20°C is



Figure 2.

$n(20^{\circ}C) = 3.539 - 1 2.089.$

As outlined previously, values of $\underline{n} = n - ik$ to fit the data for Figure 2 were obtained using previous extrapolations as a starting point. The values of n and k shown in Figure 3 fit the reflectivity versus temperature curve of Figure 2 to \pm 0.001 or better.

The curves of Figure 3 were used to compute expected values of reflectivity for specified values of (1) temperature, (2) angle of incidence, and (3) polarization. Experimental values of reflectivity at 97.75 GHz for two different angles of incidence are compared with experiment in Table 2. Absolute values of reflectivity were measured at room temperature using liquid Mercury as a reference. For temperatures above and below room temperature, the ratio of the sample reflectivity to a water sample at room temperature was measured. Each of the experimental values listed in Table 2 represents an average of approximately 16 readings. These measurements had a larger standard deviation than the measurements made at normal incidence. For example, in Table 2B, two independent measurements of reflectivity for perpendicular polarization are reported. These measurements should give nearly identical results as indicated by the calculated values, whereas the experimental values differ by 0.025. We find calculated values, using the equations of Table 1, agree to within experimental error with reflectivity at oblique angles of incidence. This result is a check on the values of n and k of Figure 3.

The results discussed thus far have been obtained using pure water. Two solutions were prepared, one containing NaCl and the other containing plankton, to simulate the ionic content and the organic content of seawater.

A 0.7N solution of NaCl was prepared. This corresponds to 4.1% of 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 $R(salt water)/R(fresh water) = 1.0056 \pm 0.010$. 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.



TABLE 2

REFLECTIVITY AT OBLIQUE INCIDENCE

A. Measurements Near 46° Incident Angle

MAA		Townserstand		Experimen	tal	Calculated	
neasurement	Augue	temperature		Varue		value	
R	46.2°	18.8°C	:	0.557		0.557	
R	46.2°	19.7°C		0.271		0.297	

B. Measurements Near 31° Incident Angle

Measurement	Angle	Temperaturé	Experimental Value	Calculated Value	
R	31.0°	19.0°	0.478	0.485	
Rs	31.0°	17.6°	0.452	0.481	

C. Reflectivity Ratios

Measurement	Angle	т ₁	т ₂	Experimental	Calculated
$R_{s}(T_{1})/R_{s}(T_{2})$	47.2°	19.7°C	5.3°C	1.106	1.093
$R_s(T_1)/R_s(T_2)$	47.2	19.2°C	4.5°C	1.098	1.093
$R_s(T_1)/R_s(T_2)$	47.2	39.6°C	20.1°C	1.093	1.081
$R_s(T_1)/R_s(T_2)$	47.2	40.5°C	19.6°C	1.084	1.086
$R_{s}(T_{1})/R_{s}(T_{2})$	31.0°	17.7°C	3.9°C	1,133	1.117
$R_s(T_1)/R_s(T_2)$	31.4°	16.8°C	3.9°C	1,096	1.105
$R_s(T_1)/R_s(T_2)$	31.0°	39.9°C	17.7°C	1.159	1.122
$R_s(T_1)/R_s(T_2)$	31.4°	39.7°C	17.9°C	1,150	1.120

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 solutions. The ionic conductivity has a frequency dependence given by

$$\sigma_{T}(\omega) = \sigma_{O}(1 + \omega^{2}\tau^{2})^{-1/2}.$$
 (1)

(2)

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

$$\varepsilon'' = \varepsilon'' + 2\sigma_{T}(\omega)/f$$

where f is the radiation frequency.

The conductivity of seawater is discussed by Halley^[3]. Typical values of dc conductivity are in the range $30-45\times10^9$ sec⁻¹ (ESU units) and relaxation times near 1.1×10^{-10} sec. At a frequency of 98 GHz, the conductivity will be $0.45 - 0.7 \times 10^9$ sec⁻¹ using equation (1). At a frequency of 98 GHz, the ionic contribution to $\varepsilon^{"}$ using equation (2) 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.

The organic component of seawater contains both dissolved matter and particulate matter of from estimates of the total amount of living cells^[4], 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 $R(plankton)/R(freshwater) = 0.999 \pm 0.014$. Again, 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 97.75 GHz.

III. Future Work

Recent discussions with NASA/GSFC personnel have indicated the desirability of extending the reflectivity measurements to include ice. We shall measure normal reflectivity of ice during the next month of this contract. Ice should have a very small temperature dependence of reflectivity. The real part of the index of refraction should be near a value of 1.78 with an imaginary component near 10⁻⁴. Thus the real part of the index of refraction determines reflectivity.

We will not be able to determine an imaginary index component as small as 10^{-4} using our present techniques. A different experimental arrangement will be required. However most properties of interest are determined by the real component which will be determined.

We will also obtain a sample of seawater for reflectivity measurements. Although the conductivity of sea water should not be observable through the dielectric properties (and should not produce a noticable effect on the reflectivity of ice), we believe such measurements will be useful to provide assurance that unexpected effects do not occur.

Following these measurements, work at 98 GHz will be complete. We plan to repeat the previous measurements at 140 GHz. The source will be doubled 70 GHz klystron.

We also have a 300 GHz carcinotron which can be used for reflectivity measurements. Measurements over this extended frequency range will be desirable for the following reason.

A desirable end product for this study would be a set of equations for the index of refraction of seawater including the effects of temperature, frequency, salinity, etc. A desirable set of equations would be the modification of Debye's equation by Cole and Cole $\begin{bmatrix} 5 \\ 1 \end{bmatrix}$. In order to produce a fit to the accuracy of the measurements reported here, similar data for other frequencies in the millimeter region are necessary.

Conversations with J. L. King, NASA/GSFC, have resulted in consideration of techniques for dielectric measurements of structural materials of interest for use in the millimeter wave region. Examples of materials of current interest

are fiberglass, Rexolite, Kevlar, and Teflon. In the past, measurements at Georgia Tech have provided some of the few dielectric measurements in this region. We shall review and summerize relevant information from previous studies and suggest appropriate measures to obtain dielectric properties of interest to current NASA/GSFC programs.

REFERENCES

- 1. Peter S. Ray, Applied Optics 11, 1836 (1972).
- 2. J. L. King, NASA/GSFC, personal communication.
- 3. P. Halley, "Introduction to the Electromagnetism of the Sea," Optics of the Sea (Interface and In-Water Transmission and Imaging), Advisory Group for Aerospace Research and Development, Neuilly sur Seine, France, AGARD LS-61, (1973), NASA-TTF-15658.
- 4. J. P. Riley and R. L. Chester, "Introduction to Marine Chemistry," Academic Press, New York, p. 263 (1971).

5. Kenneth S. Cole and Robert H. Cole, J. Chem. Phys. 9, 341 (1941).

PERMITTIVITY OF WATER AT MILLIMETER WAVELENGTHS

Final Report for the Period

October, 1975 - August, 1976

NASA Grant No. NSG-5082 GT/EES Project Number A-1784

Project Director: M. D. Blue Project Monitor: J. L. King

Engineering Experiment Station Electromagnetics Laboratory Georgia Institute of Technology Atlanta, Georgia 30332

FOREWORD

This is the final report for work performed on NASA Grant NSG-5082. The grant covered the period from October 1, 1975 to August 15, 1976. The amount of the grant was \$31,971 in NASA funds and \$1608 in Georgia Tech cost-sharing funds for a total of \$33,579. During the course of this program, a semi-annual report covering the period October 1, 1976 to March 31, 1976 was prepared. In addition, six letter-type reports on progress have been written and sent to the NASA/GSFC technical monitor, J. Larry King, for the purpose of providing current information on the technical status of the program, and to provide a better opportunity to direct the program so as to maximize its value to the government. Copies of the six monthly letters covering the period 1 April 1976 to 30 June 1976 are attached to this report as an Appendix.

I. Introduction

This report covers work performed on the permittivity of seawater and ice at 100 GHz. Measurements on water covered the temperature range 0°C to 50°C. The measurements on ice were taken at temperatures near -10°C. In addition, a small number of measurements were made on reflectivity of absorber materials used in the program "Research in Millimeter Wave Techniques", NASA Grant No. NSG-5012.

II. Permittivity Measurement Techniques

Only within the last ten 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 depend largely on the lack of readily available hardware and on the experimental difficulties. In the microwave region, previous investigators have used cavity resonators or a length of waveguide as a means of defining 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 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.

An open resonator technique was briefly studied for this program. The details were described in the report covering the period 1 October - 31 December 1975. This report is attached in the Appendix. It was found that the dissipative component of the dielectric constant of water was too high to permit the open resonator technique to be used. The method involves measurement of the resonance frequency and cavity Q with the empty cavity and with a thin layer of specimen inserted.

A reflectivity method was selected for these measurements for several reasons. From previous measurements of the dielectric properties of water, the dielectric properties may be extrapolated through the millimeter/submillimeter region yielding approximate values. A method of improving the accuracy of these values 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, normal incidence reflectivity is measured. The result is used to obtain the index of refraction $\underline{n} = n - ik$. 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 \underline{n} as determined by extrapolation. 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 Table I, we have collected several expressions relating the relative dielectric constant $\varepsilon = \varepsilon' - i\varepsilon''$ to the index of refraction, and expressions

for power reflectivity for radiation polarized parallel or perpendicular to the plane of incidence.

TABLE I

RELATIONSHIPS BETWEEN POWER REFLECTIVITY AND REFRACTIVE INDEX

The refractive index $\underline{n} = n - ik$ and the dielectric constant $\varepsilon = \varepsilon' - i\varepsilon''$ are related by $\underline{\varepsilon} = \underline{n}^2$

$$\varepsilon' = n^2 - k^2$$

$$\varepsilon$$
" = 2nk

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

for normal incidence, the reflectivity is given by

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

At an angle of incidence 0, the reflectivity for radiation polarized parallel to the plane of incidence, $R_p(0)$, and perpendicular to the plane of incidence, $R_s(0)$, is given by

$$R_{p}(\Theta) = \left| \frac{\left(\underline{n}^{2} - \sin^{2}\Theta\right)^{1/2} - \underline{n}^{2} \cos\Theta}{\left(\underline{n}^{2} - \sin^{2}\Theta\right)^{1/2} + \underline{n}^{2} \cos\Theta} \right|^{2}$$

$$R_{s}(\Theta) = \left| \frac{\left(\underline{n}^{2} - \sin^{2}\Theta\right)^{1/2} - \cos\Theta}{\left(\underline{n}^{2} - \sin^{2}\Theta\right)^{1/2} + \cos\Theta} \right|^{2}$$

Both expressions reduce to the normal incidence case at $\Theta = 0$. The above formulas refer to a dielectric-air interface.

Figure 1 shows the experimental arrangement for reflectivity measurements. The horns had dimensions of 2.85 cm x 3.40 cm at the output and were 8.5 cm in length. The absorbers and the transmission horn served to limit the radiation to a 12 cm diameter at the liquid surface. With the high attenuation of water, only the wave reflected from the surface is received. The use of absorber panels eliminates possible contributions from stray reflections. A similar arrangement was used for measurements made at oblique incidence.

Transmitter and receiver were separated and absorber panels served to define the geometry of the received energy.

For the case of normal incidence, reflectivity at a fixed temperature was reproducible to one percent for values near forty percent. For reflectivity measurements of ice, the lack of attenuation leads to reflection from the back surface of the sample. This complication was circumvented by using a wedge shaped sample and freezing the water in a container lined with absorber material.

III. Experimental Results

Measurements of reflectivity at normal incidence were made relative to liquid mercury whose reflectivity was taken to be unity. A typical experiment consists of exchanging dishes of water and mercury, each filled to the same height, while measuring the reflected energy for each surface. Surface height is adjusted to match a reference level and a further small adjustment is made to maximize reflected power if possible. For water at 20°C, we find

R = 0.392 + 0.014

where the stated error is the standard deviation. The frequency of the klystron was determined to be 103.8 GHz.

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

As the depth of mercury in the sample dish is only a few millimeters, a matching sample of water has low heat capacity with large surface area and will drift in temperature at an excessive rate. To avoid this problem, re-flectivity 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. Other experiment problems were instrument drift and drift in klystron power. As



REFERENCE SURFACE

Figure 1. Experimental Arrangement for Normal Incidence Reflectivity Measurements at 100 GHz. reflectivity is determined by the properties of the first few hundred µm of water surface, any temperature gradient near the surface 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 between different runs was small and less than the standard deviation, we believe errors from all sources are no greater than the standard deviation.

The results for normal reflectivity are shown in Figure 2 over the temperature range 0°C to 50°C. The dashed line lying above the experimental curve at temperatures greater than room temperature is the extrapolation given by Peter S. Ray [1]. This extrapolation is within our experimental error up to 30°C, thus covering the temperature range of interest to most earth observation measurements. The diamond at 20°C represents reflectivity calculated from data supplied by NASA/GSFC [2]. These data, at 20°C, lead to a reflectivity approximately seven per cent low.

The experimental value for reflectivity at 103.8 GHz, 0.392 ± 0.014 , represents the average of 122 measurements. The slope at 20°C is taken to be R = 0.0036/°C. A consistant index of refraction at 20°C is

n - ik = 3.24 - 1 1.825.

Appropriate dielectric constants for water at 103.8 GHz and 20°C are

 $e^* - i e^* = 7.16 - 1 11.825.$

As this program progressed, the klystron became less stable, and its output shifted to higher frequencies. Originally oscillating at a frequency near 96 GHz, the frequency shifted during the course of the program to a value near 104 GHz. The shift was accompanied by less signal, increased noise, and reduced power stability. The main effect on data has been an increase in the standard deviation. We find that with increasing numbers of measurements at temperatures near 20°C, the average value of reflectivity is not altered and the standard deviation does not decrease. Difficulties with the lock-in amplifier, as described in the Appendix in the report covering the period June 1 to June 30, have been overcome by a modification of the experimental procedure.

As a result, we obtain a reproducible value for room temperature reflectivity which agrees with the extrapolation of Ray [1] in this frequency region.



Diamond at 20°C is the Result Predicted from NASA Data [2].

We have used Ray's extrapolation to calculate values of reflectivity for specified values of (1) temperature, (2) angle of incidence, and (3) polarization. The calculated values are compared with experimental measurements of reflectivity for two different angles of incidence in Table 2. Absolute values of reflectivity measured at room temperature used liquid mercury as a reference. For temperatures above and below room temperature, the ratio of the sample reflectivity to a water sample at room temperature was measured. Each of the experimental values listed in Table 2 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 very 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.

A 0.7N solution of NaCl was used. This corresponds to 4.1% of 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 R(salt water) / R(fresh water) =1.0056 ± 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.

Measurements were also made on sea water samples from the Gulf of Mexico near Panama City, Florida. The ratio of reflectivity at normal incidence of sea water to the reflectivity of tap water was R(sea water)/R(fresh water) = 1.004 ± 0.008 . Again, in the 100 GHz frequency region, there is nothing in this sample of sea water to cause an anomaly in permittivity.

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

. 7

TABLE 2

REFLECTIVITY AT OBLIQUE INCIDENCE

A. Measurements Near 46° Incident Angle

Measurement	Angle	Temperature	Experimental Value	Calculate Value	d
Rs	46.2°	18.8°C	0.557	0.528	
R	46.2°	19.7°C	0.271	0.268	

B. Measurements Near 31° Incident Angle

Measurement Angle		Temperature	Experimental Value	Value	
R	31.0	19.0°C	0.478	0.454	
R	31.0	17.6°C	0.452	0.449	

C. Reflectivity Ratios for Different Temperatures

Measurement	Angle	T ₁	r ₂	Experimental	Value	Value
$R_{g}(T_{1})/R_{g}(T_{2})$	47.20	19.7°C	5.3°C	1.106		1.125
11	47.2°	19.2°C	4.5°C	1.098		1.153
**	47.2	39.6°C	20.1°C	1.093		1.1201
¥ B	47.2	40.5°C	19.6°C	1.084		1.127
3 8	31.0°	17.7°C	3.9°C	1.133		1.176
11	31.4°	16.8°C	3.9°C	1.096		1.160
	31.0°	39.9°C	17:7°C	1.159		1.239
	31.4°	39.7°C	17.9°C	1.150		1.163

$$\sigma_{I}(\omega) = \sigma_{0}(1 + \omega^{2}\tau^{2})^{-1/2}$$

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

$$\varepsilon^{n} = \varepsilon_{0}^{n} + 2\sigma_{T}(\omega)/f$$
 (2)

(1)

where f is the radiation frequency.

The conductivity of seawater is discussed by Halley [3]. Typical values of dc conductivity are in the range $35-45 \times 10^9 \text{ sec}^{-1}$ (ESU units) and relaxation times near 1.1×10^{-10} sec. At a frequency of 98 GHz, the conductivity will be $0.45 - 0.7 \times 10^9 \text{ sec}^{-1}$ using equation (1). At a frequency of 98 GHz, the ionic contribution to ε'' using equation (2) will be no larger than 0.014. The value of ε'' 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.

The organic component of seawater contains both dissolved matter and particulate matter. From estimates of the total amount of living cells [4], 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/m^3 . 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 $R(plankton)/R(freshwater) = 0.999 \pm 0.014$. Again 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 97.75 GHz.

IV. Dielectric Properties of Ice

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(ice) = 0.0785 + 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 [5] 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

 $n = \sin(28^\circ + 27^\circ)/\sin(28^\circ).$

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.

V. Auxiliary Measurements

We have been preparing our 300 GHz carcinotron for use on this program. A diode detector and frequency measuring cavity were assembled and used with the unit. In our work to date, the tube has fluctuated in power output and we have not been able to obtain reproducible measurements.

An additional set of measurements similar to those reported here but at a higher frequency well removed from 100 GHz is desired to provide a check on a suitable expression for permittivity. The desired expression will be frequency and temperature dependent. In the event that the carcinotron cannot be stabilized sufficiently to permit useful measurements of reflectivity to be made, it would be desirable to proceed directly with measurements using frequency doubled klystrons at 140 GHz or 180 GHz. The objective is the development of a model for the complex index of refraction of sea water and ice over the millimeter wavelength region and over temperatures from -10° C to 50° C.

Additional measurements have been made on absorber materials to be used in the program "Research In Millimeter Wave Techniques," NASA Grant No. NSG-5012. Measured reflectivities have ranged from near 20% for Devcon plastic to 0.15% for a grooved Rexolite absorber panel. We anticipate using this facility for measurements on absorber and on window materials in the future.

VI. Summary

Our results indicate a power reflectivity for water at a frequency of 103.8 GHz and a temperature of 20°C of

R(water) = 0.392 + 0.014.

We find that the salt content and the organic content of sea water do not effect reflectivity at this frequency. No difference between the reflectivity of tap water, sea water, and solutions of NaCl and solutions containing plankton could be found.

Measurements on reflectivity of ice at 99 GHz gave a value of

R(ice) = 0.0785 + 0.0112.

Our measurements are consistent with the expectation that the reflectivity of ice should be frequency and temperature independent in this region.

From these experiments, we determine the index of refraction of water and ice to be

> for water (103.6 GHz, 20°C) $\underline{n} = (3.24) - i (1.1825)$ for ice (99 GHz, -10°C) $\underline{n} = 1.78$

The result for ice agrees with the extrapolation of Peter S. Ray [1]. The result for water is in agreement with Ray's expression below 30°C. At higher temperatures, the experimental results fall below the value given by the extrapolation.

REFERENCES

1. Peter S. Ray, Applied Optics, 11, 1836 (1972).

2. J. L. King, NASA/GSFC, personal communication.

3. P. Halley, "Introduction to the Electromagnetism of the Sea," Optics of the Sea (Interface and In-Water Transmission and Imaging), Advisory Group for Aerospace Research and Development, Neuilly sur Seine, France, AGARD LS-61, (1973), NASA-TTF-15658.

4. J. P. Riley and R. L. Chester, "Introduction to Marine Chemistry," Academic Press, New York, p. 263 (1971).

5. W. A. Cumming, "The Dielectric Properties of Ice and Snow at 3.2 Centimeter," J. Applied Physics, 23, 768 (1952).

PERMITTIVITY OF WATER AT MILLIMETER WAVELENGTHS

PROGRESS REPORT FOR THE PERIOD 1 October 1975 to 31 December 1975

> NASA Grant No. NSG-5082 GT/EES Project Number A-1784

Project Director: M. D. Blue Project Monitor: J. L. King

Engineering Experiment Station Electromagnetics Laboratory Georgia Institute of Technology Atlanta, Georgia 30332

PERMITTIVITY OF SEAWATER AT MILLIMETER WAVELENGTHS Grant No. NSG-5082

Report for the Period 1 October - 31 December 1975

SUMMARY OF WORK

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 and submillimeter regions are lacking. The present program addresses this region.

Previous investigators have used a cavity resonator or a length of waveguide as a means of defining the configuration of the electromagnetic field with the high precision needed for accurate determination of dielectric properties. These methods have worked well, but they become increasingly difficult to apply as the wavelength decreases to the millimeter region and below. This difficulty arises from the difficulty of accurate machining of specimen and cavity, the problem of air gaps between specimen and cavity wall in the case of solid dielectrics, and the problem of surface tension and accurate sample shape for liquid dielectrics.

The extension of optical techniques using lenses and prisms encounters difficulties at longer wavelengths due to low source radiance, poor detector sensitivity, and a lack of available components.

As a result of these problems, techniques for dielectric measurements in the millimeter/submillimeter region have tended to employ closed and open resonators at wavelengths greater than one millimeter with free-space quasioptical techniques employed at shorter wavelengths. Longer wavelength techniques usually give dielectric constant data directly, while the quasioptical techniques yield the index of refraction.

Cullen and Yu [1] (Proc. Roy. Soc. 325 A, 493 (1971)) have described a method for the measurement of permittivity at microwave frequencies using an open resonator. This method was of interest to the program because it does not involve small cavities, and all quantities involved in the equations may be accurately determined. Moreover, a suitable resonator was available to the program.

Equations were derived for a semi-confocal cavity configuration based on the work of Cullen and Yu. The real part of the index of refraction is obtained from the frequency shift in cavity resonance produced when a thin film of water is added to the plane mirror. The loss tangent (and therefore the imaginary component of the index of refraction) is determined from the drop in cavity Q factor after the water film is added.

During the month of October, the semiconfocal cavity was modified for use with liquid samples. A 95 GHz klystron was used as the radiation source. Diode detectors were used to monitor source power and signal power. A PAR lock-in amplifier was used to improve signal-to-noise ratio.

For the empty cavity, the resonance could be followed as source power was reduced 50 dB. The presence of a small amount of water attenuated the signal more than 50 dB, and no signal could be observed with a partial film of water in the cavity. We also checked the signal with a wet paper towel. No signal was observed. A slightly damp paper tower caused a drop of 40 dB to 50 dB in the signal.

The absorption coefficient of water can be estimated from permittivity data taken at longer wavelengths. The review by Hogg and Chu [2] (David C. Hogg and Ta-Shing Chu, Proc. IEEE 63, 1308 (1975)) indicates a value near 40 dB/mm for the absorption coefficient of water. Chamberlain [3] (John Chamberlain, "High Frequency Dielectric Measurement," IPC Science and Technology Press Ltd., Guildford, Surrey, England, p. 104 (1973)) indicates a value closer to 5 dB/mm. For values near 5 dB/mm, the cavity resonance scheme should be satisfactory. Values near 40 dB/mm will be too high. After spending several days attempting to follow the cavity resonance with small amounts of water added to the cavity, it was concluded that water was too lossy for the cavity method to be used with success, and the scheme was reluctantly abandoned. The measurements indicated that the attenuation coefficient of water was in the 40 dB/mm range, or at least above 24 dB/mm.

Several alternative methods for permittivity measurements were considered and discarded. The reflectivity method was selected on the basis of simplicity, and availability of necessary components. This method is currently being pursued. The relevant equations are the following:

The complex dielectric constant is given by

$$\varepsilon = \varepsilon' - i\varepsilon''$$

and the index of refraction by

$$n = n - ik,$$

These quantities are related by

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

The reflectivity for normal incidence is

$$R(0) = \frac{(n-1)^2 + k^2}{(n+1)^2 + k^2}$$

For other than normal incidence, the radiation components with the E-vector parallel and perpendicular to the plane of incidence take different values. For the perpendicular case, the reflectivity for an angle of incidence θ will be

$$R_{\perp}(\theta) = \left| \frac{\left(\underline{n}^2 - \sin^2 \theta\right)^{1/2} - \cos \theta}{\left(\underline{n}^2 - \sin^2 \theta\right)^{1/2} + \cos \theta} \right|^2$$

Our plan is to measure reflectivity at three angles near 0°, 30°, and 45°. These measurements will be sufficient to determine n and k. The measurements will include pure water and seawater, and will cover an extended temperature range.

During the last half of November and the month of December, reflectivity measurements were made on water, aluminum plates, and an aluminum coated front
surface mirror. Measurements were referenced to the mirror. Various horn and lens combinations were tried in order to focus the radiation to as small a spot as possible, and to minimize reflections. Measurements were reproducible to about 3% for the best horn lens arrangement.

A critical survey of the literature on the refractive index of water was performed by Peter S. Ray [4] (Peter S. Ray, Applied Optics <u>11</u>, 1836 (1972)). The data were fit to equations by Cole and Cole [5] (Kenneth S. Cole and Robert H. Cole, J. Chem. Phys. <u>9</u>, 341 (1941)) which were extensions of the Debye theory. The equations have parameters ε_{s} , ε_{∞} , λ_{s} , and α . In the equations, σ is the conductivity and λ is the wavelength of the radiation. The equations are,

$$\varepsilon' = \varepsilon_{\infty} + \frac{(\varepsilon_{s} - \varepsilon_{\infty}) \left[1 + (\lambda_{s}/\lambda)^{1 - \alpha} \sin(\alpha \pi/2)\right]}{1 + 2(\lambda_{s}/\lambda)^{1 - \alpha} \sin(\alpha \pi/2) + (\lambda_{s}/\lambda)^{2(1 - \alpha)}}$$

$$\varepsilon^{\prime\prime} = \frac{(\varepsilon_{s} - \varepsilon_{\infty})(\lambda_{s}/\lambda)^{1 - \alpha}\cos(\alpha\pi/2)}{1 + 2(\lambda_{s}/\lambda)^{1 - \alpha}\sin(\alpha\pi/2) + (\lambda_{s}/\lambda)^{2(1 - \alpha)}} + \frac{\sigma\lambda}{18.85 \times 10^{10}}$$

where for pure water $\sigma = 12.57 \times 10^8$.

The quantities ε_s , ε_{∞} , α , and λ_s are temperature dependent. The result implies an increase in reflectivity of 60% between 0°C and 50°C for pure water at 95 GHz. Our preliminary measurements tend to confirm this trend.

Also, our measurements indicate a value of reflectivity near 40% for water at 17°C at a frequency of 95 GHz. This is above the value obtained from Ray's equations but still reasonable. The attenuation coefficient, based on our preliminary work, appears to be near 31 dB/mm.

WORK PLANNED FOR NEXT MONTH

The first three months of the program have been used to verify that cavity resonance methods cannot be used because of the high attenuation coefficient

of water, and that reflectivity measurements will be satisfactory. The next month will be used for measuring the radiation pattern of the horn and lens combination that has proven to be most useful. An absolute standard is also needed for our reflectivity measurements which are now referenced to the aluminum coated mirror. We plan to use mercury for this purpose.

When we have optimized the horn/lens arrangement for normal incidence, substitution of water for mercury, leaving the experimental arrangement otherwise unchanged, should provide the desired absolute reflectivity. A clean mercury surface will be considered to have 100% reflectivity at 95 GRz.

Measurements of reflectivity at temperatures between 0°C and 50°C and measurements at various salinity values will be completed for normal incidence. At that time, we will begin measurements at 30° and 45° incidence.

5

MISIS

PERHITTIVITY OF WATER AT MILLIMETER WAVELENGTHS

PROGRESS REPORT FOR THE PERIOD 1 January 1976 to 31 January 1976

NASA Grant No. NSG-5082

GT/EES Project Number A-1784

Project Director: M. D. Blue Project Monitor: J. L. King

Grant No. NSG-5082 Report for the Period 1 January - 31 January 1976

SUMMARY OF WORK

During the month, activity was directed toward establishing an accurate value for the reflectivity of water at room temperature for radiation at 95 GHz. Previous measurements using a mirror as a reference surface were consistent within a given day's data, but not sufficiently reproducible on later runs. The source of this deviation was believed to be the difficulty of matching surface height and maintaining the mirror surface level.

During the month, a fixture was constructed to hold a pyrex dish with provision for adjusting its height. Three pounds of mercury were purchased for use as a reference liquid. A typical experiment consists in exchanging dishes of water and mercury in the sample fixture and measuring reflected energy for each sample. Surface level is adjusted after each substitution to match a reference level, and a further slight adjustment is made if necessary to maximize reflected power.

The measurements have given us internal consistency. We find for water at 20°C,

R = 0.4343 + 0.0065

where the stated error is the standard deviation. The stated reflectivity is the result of 22 independent measurements corrected to 20°C. The slope of reflectivity at room temperature was taken to be 0.0038/°C. The reflectivity of a clean mercury surface at 95 GHz is taken to be 100%.

Following these measurements, the reflectivity was measured at temperatures between 0°C and 50°C. The experimental procedure was changed slightly from the previous set of measurements near room temperature. Because three pounds of mercury is already a bit heavy for easy handling, we do not wish to fill the sample dish to a higher level. The mercury depth is only a few millimeters. The matching water dish should also be filled to the same depth for ease in matching surface levels. However, with a volume of water sufficient to fill the dish to a few millimeters, temperature drift is a problem at temperatures away from room temperature. These difficulties were resolved by referencing high and low temperature measurements to a sample at room temperature using large volumes of water to reduce temperature drift. The room temperature data could then be referenced to the mercury surface.

All data were corrected for a small amount of horn-horn coupling, drift in klystron power, and instrument drift. The results of reflectivity measurements between 0°C and 50°C are shown in the attached figure. The point at 20°C has error bars indicating standard deviation. Also shown is the approximation by Ray [Peter S. Ray, Applied Optics, <u>11</u>, 1836 (1972)] for this frequency. The value of reflectivity at 20°C is consistent with a refractive index of

n = 3.548; k = 2.098.

The standard deviation of 0.0065 is equivalent to an error in molecular temperature of 1.7°C. This error can be reduced as our experimental statistics improve.

WORK PLANNED FOR NEXT MONTH

The next month will be used to complete measurements at normal incidence. We will measure reflectivity of solutions of various salinity values, and mixtures containing plankton to simulate the organic component of seawater.



PROGRESS REPORT FOR THE PERIOD 1 February 1976 to 29 February 1976

> NASA Grant No. NSG-5082 GT/EES Project Number A-1784

Project Director: M. D. Blue Project Monitor: J. L. King

Grant No. NSG-5082

Report for the Period 1 February 1976 - 29 February 1976

SUMMARY OF WORK

During February, we have added additional data to our measurements of reflectivity of water at normal incidence. The best value at 20° C has changed slightly, and the best value for the refractive index has been adjusted accordingly. The room temperature reflectivity is reproducible to better than one percent. Additional data at higher temperatures have increased our confidence in reflectivity values in this region of the reflectivity-temperature curve. These results are shown in the attached figure. The value of reflectivity at 20° C shows the standard deviation.

Also shown in this figure is the normal reflectivity calculated from data supplied by J. L. King, GSFC and indicated by the diamond at 20° C. These data represent an extrapolation through the millimeter-centimeter wavelength region based on the limited amount of permittivity data on water for this wavelength region in the published literature. As might be expected, the extrapolation agrees well with that of P. S. Ray over the same region. However, both extrapolations lead to a reflectivity three percent low at 20° C, increasing to five percent low near 0° C in comparison to experiment.

We have calibrated the klystron used in this program using a Hitachi W2210 frequency meter. At the reflector voltage used in these measurements, the frequency was 97.75 GHz.

The polarization of the wave has also been checked in preparation for measurements of reflection at oblique angles of incidence where polarizations parallel and perpendicular to the plane of incidence have differing reflection coefficients. We find better than 25 dB difference between power received with the horns oriented for maximum power and the power received with the horns crossed. This result indicates a negligible amount of cross-polarized component in the wave. As an approximation to sea water, we have measured the reflectivity at room temperature of a NaCl solution. The dielectric properties of sea water will be close to those of a 0.62 N solution of NaCl which corresponds to a salinity of 3.6%. The composition of sea water varies with season, location, depth and latitude, the southern hemisphere being somewhat more saline than the northern hemisphere.¹ An average figure is 3.5% salinity, or 0.6 N. Our measurements used a 0.7 N solution of NaCl which would be an approximation to a very saline ocean corresponding to 4.1% salinity. The <u>ratio</u> of the reflectivities of the salt solution to fresh water differed by less than 0.6%. The measured ratio was 1.0056 ± 0.010 . The deviation from unity is less than the standard deviation for the ratio. Thus, we conclude that within the accuracy of our measurements, there is no difference between the reflectivity of fresh water and a 0.7 N NaCl solution at 97.75 GHz.

This result is consistant with out expectations. The contribution of the then added conductivity of the salt to the relative permittivity of water increases the imaginary (lossy) component. The relation is²

$$\varepsilon^{11} = \varepsilon_1 + \sigma(\omega) \lambda / 18.85 \ge 10^{10}$$

where ε_1 is the imaginary component of the dielectric constant in the absence of a conductivity contribution. λ is the wavelength in cm, and $\sigma(\omega)$ is the conductivity in Gaussian units at the angular frequency ω as given by

$$\sigma(\omega) = \sigma_{0}(1 + \omega^{2}\tau^{2})^{-1/2}$$

where τ is the relaxation time for the conductivity. The conductivity of ocean water is discussed by Halley.³ Values of dc conductivity are in the range

- 1 Dorsey, N. E. "Properties of Ordinary Water Substance," Reinhold Publishing Corp., New York (1940).
- 2 Peter S. Ray, Applied Optics <u>11</u>, 1836 (1972) "Broadband Complex Refractive Indices of Ice and Water."
- 3 P. Halley, "Introduction to the Electromagnetism of the Sea," Optics of the Sea (Interface and In-Water Transmission and Imaging), Advisory Group for Aerospace Research & Development, Neuilly sur Seine, France, AGARD LS-61, 1973, NASA-TTF-15658.

 $30 - 45 \times 10^9 \text{ sec}^{-1}$ with a relaxation time of 1.08×10^{-10} sec. The conductivity at 97.75 GHz will then be $0.45 - 0.7 \times 10^9 \text{ sec}^{-1}$.

The contribution to the imaginary part of the dielectric constant is then approximately 0.001. Thus

$$\varepsilon^{11} = \varepsilon_1 + .001 \ge 11.001.$$

The effect of the conductivity at 3 mm wavelength is an increase of one part in 10^4 . This change is too small to be observed, in agreement with our measurements.

We have approximated the organic component of sea water by using a solution of freeze dried plankton⁴ in fresh water. Organic matter in the sea includes particulate matter plus dissolved matter. From estimates of the total amount of living cells⁵, we can estimate a value of 150-300 g/m³ of particulate material for most ocean areas.

Our solution had a concentration of 580 g/m³ which would correspond to a heavy concentration of organic matter such as might be found in fertile coasted waters during the spring and summer.

Reflectivity at normal incidence was compared to the reflectivity of fresh water. The measured ratio of reflectivities [R (plankton)/R (fresh water)] was 0.999 ± 0.014 . The deviation from unity was less than the standard deviation. Thus we conclude that the addition of plankton to the water does not alter its normal reflectivity at 97.75 GHz.

WORK PLANNED FOR NEXT MONTH

During March we shall measure reflectivity at two different angles of incidence and at various temperatures. These data will serve to substantiate our semiempirical assignment of n and k from reflectance at normal incidence.

4 Freeze dried plankton containing 69% protein was obtained from Breedmore Aquarium Products Ltd., Shohola, Pa. 18458.

5 J. P. Riley and R. L. Chester, "Introduction to Marine Chemistry," Academic Press, New York, p. 263 (1971). We will also obtain a sample of sea water for measurement. Our salt soulution measurements tell us that the conductivity of the salt is not observable through the dielectric properties. However, sea water measurements will be necessary to provide assurance that unexpected effects do not arise.

We expect to complete work at 97.75 GHz with a graph of n and k over the measured temperature range. A set of equations giving n and k as functions of frequency and temperature can also be derived. However, additional data at other frequencies will be required as these measurements have already shown that data in this frequency region are not consistant.

Following completion of measurements at 97.75 GHz, we plan to move to 145 GHz using the second harmonic of a 70 GHz klystron as the source.

PROGRESS REPORT FOR THE PERIOD 1 April 1976 to 30 April 1976

NASA Grant No. NSG-5082

GT/EES Project Number A-1784

Project Director: M. D. Blue Project Monitor: J. L. King

Grant No. NSG-5082

Report for the Period 1 April - 30 April 1976

Summary of Work

During the month of April we obtained salt water samples from the Gulf of Mexico hear Panama City, Florida. These samples were used for a reflectivity comparison with fresh water. No difference was detected. The standard deviation of a set of readings of reflected power is 0.4 percent to 0.8 percent with our present apparatus. The reflected power from salt water and fresh water agreed to within 0.04 percent, less than a standard deviation. The result indicates that there is nothing in this ocean water sample to cause an anomaly in permittivity in the 100 GHz frequency region.

Our measurement apparatus has been moved to a new location and the new arrangement is somewhat more versatile. Considerable effort was spent determining sources of coupling voltage between source and receiver. Some of the coupling signal was found to be pickup between cables. Additional coupling reduction was obtained by tilting all surfaces such as the lens and absorber panels with respect to horizontal; in effect spoiling resonances in the cavity-like arrangement. Finally, the coupling was reduced effectively to zero by removing the lens and separating the horns to give an angle of incidence of 3.6°. For this arrangement, the output signal from a mercury surface is 5.3 mV, while the coupling signal is less than 0.01 mV.

We have measured the normal reflectivity of ice at 99 GHz using different configurations of the apparatus. Temperature was determined with a thermister frozen 1/4 inch deep in the ice surface three inches from the center of the dish. The spot size has a radius of about 1.5 inches. 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. Errors due to surface irregularities and tilted surfaces should cause a lower reflected power. We find values near 16 percent, which is larger than expected. The results of $Cumming^{[1]}$ at a wavelength of 3.2 cm give a value of 1.78 for the index of refraction of ice. As there should be no absorption bands and no dispersion in the millimeter-centimeter wavelength region, we would expect the index of refraction to be near 1.78 in the millimeter region. The expected reflectivity would be 7.9 percent.

We have tried various configurations in our apparatus and searched for possible means of reconciling the difference without success. For example, the bottom of the ice container is covered with absorber. Any reflection from this surface will increase the apparent reflectivity. We have determined that any contribution from this source is critically dependent on the orientation of the container. The maximum error is less than one percent, and in practice is probably much less.

Another possibility is the presence of a thin layer of liquid water on parts of the surface. The reflectivity of water is near 36 percent so it can greatly change the apparent reflectivity of ice. These measurements will continue.

We have also begun to set up the 300 GHz Carcinotron tube for measurements at this frequency. The tube has five power supplies including power for the electromagnet, and three water cooling systems.

 W. A. Cumming, "The Dielectric Properties of Ice and Snow at 3.2 Centimeter," J. Applied Physics, 23, 768 (1952).

PROGRESS REPORT FOR THE PERIOD 1 May 1976 to 31 May 1976

NASA Grant No. NSG-5082

GT/EES Project Number A-1784

Project Director: M. D. Blue

Project Monitor: J. L. King

Grant No. NSG-5082

Report for the Period 1 May - 31 May 1976

Summary of Work

During the month of April we were concerned with determining reflectivity of ice near 100 GHz. Our previous measurements gave a reflectivity larger than expected, and we were concerned with the reason for the larger value. This month we found two sources of error effecting these measurements. First, the expansion of the water upon freezing caused the surface of the ice to become slightly concave and thus gave rise to a focusing effect at the receiver horn. This effect was eliminated by repeated surface remelting and refreezing until the surface was level to 1/4 degree over the entire dish.

The second problem was the PAR model 124 lock-in amplifier. The amplifier was found to couple the two input channels. Thus, the reflectivity signal was mixed with the reference power measurement signal. In addition, the more sensitive gain positions had gradually become unstable and tended to oscillate.

The stability problem was solved by cleaning the contents of a rotary switch, but the coupling problem appears to be caused by a special dual transistor at the input. We circumvent this problem by shorting one input and connecting one signal at a time to the other input. Because the reflectivity of ice is small, the signal corresponding to the reflected energy is small. To minimize corrections to this signal we have eliminated the focusing lens and use separate transmitter and receiver horns. The hornhorn coupling signal is about 2% of the reflected energy signal.

As a result of these modifications, the most recent result for the reflectivity of ice is

R(ice) = 0.0785 + 0.0112

at a frequency of 99 GHz. The frequency of the klystron has been increasing, a result of its increasing age. Our previous measurements were at 97.75 GHz.

As an independent check on these measurements we determined the index of refraction of ice by sending the 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 $n = \sin (28° + 27°)/\sin (28°)$. This gives a value of n = 1.745 for ice at 99 GHz. This result is in excellent agreement with the value, obtained from reflectivity, of 1.78 ± 0.08 . These results are also in excellent agreement with expected results from the literature as discussed last month.

It is worth mentioning that use of an ice prism must be accomplished quickly. As moisture accumulates on the surface, absorption rises rapidly. The experiment described here provides a convenient check on reflectivity data, but would require considerable effort to develop into a high accuracy technique. It is also unsuitable for water.

We are currently rechecking measurements on reflectivity of water. It is possible that the reflected signal was enhanced by coupling to the reference power signal as in the case of ice. The effect on the measured reflectivity should be less for water because the reflected power signal is stronger, but may still be significant. We shall continue to use the separated horn arrangement which gives a transmitter-receiver coupling signal of about 1% of the reflected energy. A disadvantage is that the received power is greatly reduced without the concentrating effect of the lens.

We have continued work with the 300 GHz carcinotron and have obtained oscillation. The power supply has been a source of problems and will require some further work to operate correctly. However, this does not appear to be a time consuming task.

Future Work

We shall recheck reflectivity versus temperature for water at 100 GHz, and duplicate these measurements at 300 GHz. The results will be compared with data

and extrapolations in the millimeter wavelength region available in the published

literature.

PROGRESS REPORT FOR THE PERIOD 1 June - 30 June 1976

NASA Grant Nó. NSG-5082 GT/EES Project Number A-1784

Project Director: M. D. Blue Project Monitor: J. L. King

Grant No. NSG-5082

Report for the Period 1 June - 30 June 1976

Summary of Work

During June, an extension was granted moving the termination date for this Grant to August 15. The final technical report will be due on September 15. This is a no-cost extension. Program completion has been delayed because of our occasional use of the facilities and personnel from this program to supplement other ongoing programs for Goddard Space Flight Center on a temporary basis. We expect to complete this program on or before August 15.

During the month of June our major effort was spent working with the system components: klystron, detectors, lock-in amplifier. We have mentioned these problems in our previous monthly letter. The primary problem at this time appears to be the klystron.

As the klystron has shifted to higher frequencies, it has lost power and become less stable. As a result we have less signal, increased noise, and reduced power stability; all of which have made verification of our previous data difficult. Recently it appears that we can bring these problems under control and obtain reproducible data.

Our recent results at 103.6 GHz adjusted to a temperature of 20° C give a value of normal reflectivity of R = 0.393 + 0.015. This value is in excellent agreement with the value obtained from Ray's approximation as described in previous monthly reports.

We continue to use the PAR 124 lock-in amplifier using only one input channel at a time. The unused channel has its input shorted. The amplifier couples signals between the two channels to about 1%. The magnitude of the coupling depends on the resistance of the input, being highest for high resistance input networks. The coupling also causes a high frequency oscillation to appear at the inputs when the unused channel is not shorted.

Future Work

We shall complete a set of reflectivity versus temperature data at frequencies near 100 GHz for water. We will then obtain a similar set of data at 300 GHz using our carcinotron.

A-1784

Semi-Annual Report for the Period

August 15, 1976 - February 15, 1977

NASA Grant No. NSG-5082 (Supplement No. 1)

GT/EES Project Number A-1784

Project Director: M. D. Blue Project Monitor: J. L. King

FOREWARD

This is the first report on work performed on NASA Grant NSG-5082 (Supplement No. 1). The grant covers the period from August 15, 1976 to August 15, 1977. The amount of the grant 1s \$30,000 in NASA funds and \$1,446 in Georgia Tech cost sharing funds for a total of \$31,446. This report discusses work performed under this contract for the period of August 15, 1976 to February 15, 1977. The project director at Georgia Tech is Dr. M. D. Blue, and the technical monitor at NASA/GSFC is J. Larry King.

I. Introduction

The objectives of the 1975-1977 supplement to this program are to extend the previous measurements of the reflection coefficient of water and ice at 100 GHz to 140 GHz and 180 GHz. The measurements will be made over the temperature range -10° C to 50° C.

In addition, reflectivity measurements in the same frequency range will be made on structural and window materials of interest to current NASA programs.

II. Progress During This Report Period

Laboratory measurements during this period have been plagued by equipment malfunctions and tube degradation. As a result of these problems we have suspended further measurements until the difficulties can be overcome. Some problems with the 100 GHz tube were noted during the previous phase of this program. The loss of power and mode instability were becoming much worse as we began measurements under this contract supplement. After some initial measurements, it was decided to suspend further work and await the availability of a more satisfactory tube. The press of other NASA/GSFC programs at EES in this same frequency range has been such as to keep our tubes in use, and we now expect to wait until summer before being able to resume the measurements.

Our PAR lock-in amplifier had several problems and we have used the delay in measurements to provide the time to send the unit to the factory for repair. The lock-in has now been returned and is in use in our other ongoing NASA/GSFC programs. In this report we shall summarize the measurements that have been made, and present a discussion of errors arising from radiation reflected into the receiver from surfaces other than the surface being measured. We then present a discussion of the physical significance of the dielectric constant of water and its temperature dependance.

Radiation Absorber Measurements

Samples of radiation absorbing materials were received from Rantec Division of Emerson Electric Company, Calabasas, California. The two types of absorber material were designated EHP-5 and EHP-8. Measurements of the reflectivity of the EHP-5 type absorber used a Varian VC 710D klystron operating at 103 GHz. The material caused no measurable phase shift in the reflected signal. The small amount of reflected power combined with a noisy and weak klystron source made measurements extremely difficult. Two series of measurements gave values of -37 dB and -40 dB for the reflection coefficient of the EHP-5 absorber. These values vary by a factor of two, significantly worse than our usual accuracy of a few per cent. At this stage, further measurements were discontinued.

Scattered Radiation

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 it has not 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. Typical reflectivity measurements comprise a series of reflected power measurements, alternating a mercury reference surface with a liquid water surface, all measurements at the same temperature. We must also correct for the slow drift of source power.

In Table I we show a typical set of readings taken from a set of data obtained under the previous grant. 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

Item	Coupling Voltage	Signal <u>Voltage</u>	Phase Degrees
Reference	Pwr	4.2	181.1
ng	0.01	4.52	0.87
H ₂ 0	0.01	1.83	0.84

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 <u>A</u> and <u>a</u> have a phase difference ϕ . The measured power is then

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

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

 $[A^n]^2 = A^2 + 2 \alpha A \cos \phi$

[2]

[1]

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 α and ϕ 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

$$[A^{"}]^{2}/[B^{"}]^{2} = [A^{2}/B^{2}] [1 + 2\alpha \cos \phi (1/A - 1/B)] [4]$$

The error involved in using this technique is given by the term 2 α cos ϕ (1/A - 1/B). If we assume that cos ϕ 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 α/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],

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

The error is then 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 ϕ 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 useful when we resume experiments. We expect to have the use of newer tubes with more stable output. As a result, the standard deviation of the experimental values of reflectivity may be improved.

The Dielectric Constant

Water is typical of several liquids believed to possess a distribution of relaxation times for dipole orientation. As discussed in previous reports, the dielectric constant for such a material corresponds to the equation:

$$\varepsilon = \varepsilon_{\alpha} + \{(\varepsilon_{\alpha} - \varepsilon_{\alpha})/[1 + (j \omega \tau)^{(1 - \alpha)}]\}$$

[6]

151

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 higherfrequency process, but there are so few of these that this process contributes only slightly to the static dielectric constant.

Haggis, et. al.² have proposed that symmetric and asymmetric twobonded cases exist with the asymmetric molecules dominating. It appears that the asymmetric types can orient more easily. A calculation of T 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 α ($\alpha \approx 0.015$). The experimental result is consistant with equal populations with relaxation times of 0.8t and 1.2t where τ is the average value for equation [6].

G. H. Haggis, J.B. Hasted, and T.J. Buchanan, J. Chem. Phys. <u>20</u>, 1452 (1952).

Our measurements at 100 GHz gave good agreement with a dielectric constant extrapolated from lower frequencies using equation [6] from 0° C up to about 30° C. At higher temperatures, the change in properties with temperature was not as great as predicted by the extrapolation. An interpretation of this result using the hydrogen-bond disruption model sketched briefly here would be that the mole fraction of two-bonded molecules is not increasing with temperature as rapidly as implied by low frequency behavior. The effect is small but gives rise to a few percent difference in reflectivity at 50° C.

Measurements at a higher frequency such as 180 GHz will be especially valuable. The effect noted here should also be observed at 180 GHz, and some additional contribution from the submillimeter absorption bands may be observable. We hope to resume experimental measurements in a few months to obtain these data.

III. Future Work

As soon as a strong tube near 90 GHz and a doubler are available, we shall measure reflectivity of the water surface between 0^oC and 50^oC. We shall also measure the reflectivity of ice at the same frequency. Further, we shall complete measurements of the attenuation of the sheet absorber discussed earlier.

Semi-Annual

Report for the Period

February 16, 1977 - August 16, 1977

NASA Grant No. NSG-5082

(Supplement No. 1)

GT/EES Project Number: A-1784

Project Director: M. D. Blue Project Monitor: J. L. King

FOREWORD

This is the second report on work performed on NASA Grant NSG-5082 (Supplement No. 1). The grant covers the period from February 16, 1977 to August 16, 1977. The amount of the grant is \$30,000 in NASA funds and \$1,446 in Georgia Tech cost sharing funds for a total of \$31,446. This report discusses work performed under this contract for the period of February 16, 1977 to August 16, 1977. The project director at Georgia Tech is Dr. M. D. Blue, and the technical monitor at NASA/GSFC is J. Larry King.

I. Introduction

The objectives of the 1976-1977 supplement to this program are to extend the previous measurements of the reflection coefficient of water and ice at 100 GHz to 140 GHz and 180 GHz. The measurements will be made over the temperature range -10° C to 50° C.

In addition, reflectivity measurements in the same frequency range will be made on structural and window materials of interest to current NASA programs.

II. Progress During This Period

As discussed in the last report, the klystron tube operating at 100 GHz has reached the end of its useful life. As other klystrons in our laboratory have been in continual use, an OKI klystron at 140 GHz has been ordered.

Until this tube arrives, we have suspended further measurements on reflectivity of H_2O and other dielectric materials.

III. Future Work

With the arrival of the new tube, we shall measure the reflectivity of water between 0°C and 50°C. We shall also measure the reflectivity of ice at the same frequency. Further, we shall complete measurements of the attenuation of several samples of dielectric sheet absorber.

The results of measurements of reflectivity of water will be discussed in relation to several models for the dielectric constant of water which have appeared in the literature in recent years. The models, based on measurements at lower frequencies, provide an estimate for measurements in the short millimeter region.

- 1 -

Semi-Annual

Report for the Period August 15, 1977 - February 15, 1978

> NASA Grant No. NSG-5082 (Supplement No. 1)

GT/EES Project Number: A-1784

Project Director: M. D. Blue Project Monitor: J. L. King

Georgia Institute of Technology Engineering Experiment Station Electromagnetics Laboratory Atlanta, Georgia 30332

FOREWORD

This is the third report on work performed on NASA Grant NSG-5082 (Supplement No. 1). The grant covers the period from February 16, 1977 to February 15, 1978. The amount of the grant is \$30,000 in NASA funds and \$1,446 in Georgia Tech cost sharing funds for a total of \$31,446. This report discusses work performed under this contract for the period of August 16, 1977 to February 15, 1978. The project director at Georgia Tech is Dr. M. D. Blue, and the technical monitor at NASA/GSFC is J. Larry King.

I. INTRODUCTION

The objectives of the 1976-1977 supplement to this program are to extend the previous measurements of the reflection coefficient of water and ice at 100 GHz at 140 GHz and 180 GHz. The measurements will be made over the temperature range -10° C to 50° C.

In addition, reflectivity measurements in the same frequency range will be made on structural and window materials of interest to current NASA programs.

II. PROGRESS DURING THIS REPORT PERIOD

Radiation Absorber Measurements at 140 GHz

Samples of radiation absorbing sheet from Rantee Division of Emerson Electric Company, Calabasas, California, designated EHP-5 and EHP-8 were measured using a new 140 GHz Oki klystron.

The absorber materials were so effective at 140 GHz that a definitive measurement was beyond the capabilities of our experimental arrangement. Absorption was greater than 40 dB and the reflected energy was below the system noise level for both absorber types. Our results were as follows:

EHP-5	Absorption	×	41,	.5 dE	
EHP-8	Absorption	>	43	dI	3

Thus, reflected energy for normal incidence was in the 10^{-5} range or smaller for these materials at 140 GHz.

Reflectivity of Water at 140 GHz

The Oki 140 GHz klystron arrived in December permitting measurements of reflectivity of water to resume. A new set of millimeter wave waveguide plumbing was assembled with a GaAs point contact detector. The new tube provides ample power but the power output has not been stable. Fluctuations in output power over periods of a few seconds as well as periods of several minutes increase the difficulty of obtaining accurate reflectivity readings. These problems have been circumvented in part by measuring the ratio of reflectivity of water and the mercury standard t a metal plate. With the water or mercury in place, the metal can be interposed in the beam and removed in a reproducible manner. s way, a series of readings comparing sample reflectivity with plate reflectivity can be obtained quickly, minimizing effects of term fluctuations and drift.

In extensive amount of data has been obtained during the past several . These data have not been completely analyzed. Measurements at remperature have given a value for the reflectivity of water at normal ence at 20°C of $34.1 \pm 0.4\%$ at 140 GHz. This value is an average of eparate measurements.

The attached graph shows the room temperature reflectivity value with several other measured points. Additional data will be evaluated dded later. Also shown are three curves of reflectivity versus rature obtained from three variations of the Debye model. These are odel by Ray [1] used in previous reports (designated R), and the Debye Cole-Cole models (designated D and C-C respectively) with parameters by 1, Hasted, and Moore [2].

Differences between these models are about one percent or less over of the temperature range, but reach two percent near 50°C. A prenary conclusion is that the Cole-Cole model looks best at this time. eems clear that there are no surprises at the two measurement frequencies so far, and the data are quite close to expected values. Also attached to this report is a copy of an extended abstract of this

which has been accepted for presentation at the Third International erence on Submillimeter Waves which will be held in Guildford, England March 29, 1978 to April 1, 1978. A copy of a letter to Ms. Wiseman lesting permission to attend this conference is also attached.

Ray, P. S., Appl. Optics, <u>11</u>, 1836 (1972). Mason, P. R., Hasted, J. B., and Moore, L., Adv. In Molecular Relaxation Processes, 6, 217 (1974).
III. FUTURE WORK

Immediate measurements at 140 GHz include calibration of the operating frequency, measurements on ice, and additional measurements near 50°C if needed. Further experimental measurements will use the doubled 90 GHz source.

Funds from this Grant are available, but additional time is needed. A three month no-cost extension has been requested to complete the work described above. While attending the conference in Guildford, we shall take advantage of the opportunity to discuss both measurements and techniques with colleagues and in particular discuss work in the U. K. on dielectric properties of water in the extreme infrared. The U. K. work has provided the improved parameters for the Cole-Cole model which fits our data well.

Reflectivity of Water Normal Incidence 5 at 140 GHz 10/0 2-4-78 35 40 Reflectivity, D CC Sm R At 20°C R1= 34.1 = 0.4 % slope = 0.420 %/°C 25 20 25 30 3 Temperature, (°C) 40 45 0 5 10 15 35 50

GEORGIA TECH RESEARCH INSTITUTE ADMINISTRATION BUILDING GEORGIA INSTITUTE OF TECHNOLOGY ATLANTA, GEORGIA 30332

January 17, 1978

Refer to: AAC/A-1784

NASA-Goddard Space Flight Center ATTN: Ms. Genevieve Wiseman, Code 100 Greenbelt, Md. 20771

Subject: Grant No. NSG-5082; Approval of Foreign Travel.

Dear Ms. Wiseman:

As required by the General Provisions of the subject grant, NASA approval is requested for the Principal Investigator, Dr. M. D. Blue, to attend the Third International Conference on Submillimeter Waves And Their Applications, to be held in Guildford, England from March 29, 1978 to April 1, 1978. No additional funding will be required since travel funds were originally provided for in the project budget.

Attendance at this conference by Dr. Blue will clearly be a benefit to the research program under this grant since his work has been accepted for presentation at the conference. Researchers in several locations in Britain have been pursuing programs in dielectric measurements and properties in the millimeter and submillimeter wavelength regions. Therefore, Dr. Blue will be afforded the opportunity to exchange ideas on measurement techniques and physical phenomena of interest to his program with an international group of specialists, both at the meetings and through visits at one or more laboratories in the area. Comments he receives on the work performed under this grant, and the techniques employed, will be of interest and value.

The estimated total cost of this trip is outlined as follows:

Airfare (Atlanta to London and return)	\$480.00
Lodging and Subsistence (7 days)	280.00
Local Travel (Atlanta and London)	100.00
Pees and Registration	100.00
Total	\$960.00

Please note that this grant has a current expiration date of February 15, 1978, and that it may be necessary to extend the completion date to permit the above requested travel. If that is the case, please NASA-Goddard Space Flight Center January 17, 1978 Page 2

consider this a formal request to extend the grant through about May 15, 1978. We understand that the possible extension, and the proposed foreign travel, has been discussed with the NASA Technical Officer, Mr. J. L. King, and has his concurrence. We trust that the above, together with Mr. King's knowledge of the situation, will provide you with sufficient information. If anything additional is required, please phone the writer at (404)894-4819.

Very truly yours,

Alfred A. Camp Sr. Contracting Officer

mas

Addressee: In duplicate.

cc: Mr. J. L. King, Code 952 Dr. M. D. Blue V

REFLECTANCE OF WATER AT 100 GHz and 140 GHz

M. D. Blue

Georgia Institute of Technology, Atlanta, Georgia 30332

The dielectric properties of liquid water have been the subject of extensive investigation for several decades. Measurements of static properties as well as measurements in the radio-frequency, microwave, and infrared regions have been reported. The measurements presented here lie in the short millimeter region, a region of increasing importance to radiometry but relatively unexplored experimentally. The measurements were designed to assess the suitability of current modifications and extensions of the Debye equations for both water and ice in this region. In addition, the possibility that certain constituents of sea water may affect dielectric properties was considered.

The experimental technique selected was measurement of reflected power for reasons of simplicity and suitability. Both normal incidence and oblique incidence geometries were used. Mercury was used as a reference liquid. Varian and Oki klystrons were used as sources with point contact diode detectors. Appropriate source and receiver horns as well as absorber panels served to define the geometry of the system.

Sea water contains both salts and organic matter. A search for possible anomalies in dielectric properties from these constituents was made. For both sea water samples and a 0.7 N solution of NaCl (equivalent to 4.1% salinity) no effect on reflectivity was observed at 100 GHz. A solution containing 580 g/m^3 of plankton was prepared which would correspond to a heavy concentration of organic matter representative of fertile coastal waters during the spring and summer. Again, no effect on reflectivity was observed within the accuracy of our measurements.

Measurements of reflectance of water at normal incidence over the temperature range $0^{\circ}C - 50^{\circ}C$ are shown in Figure 1. These data are taken at 103.8 GHz. Error bars indicate standard deviation for three points shown in the figure. The point at 20°C represents an average of 122 readings. Small circles indicate typical individual measurements above and below room temperature.

The experimental results at 103.8 GHz are compared with three expressions for normal reflectance obtained from Debye and Cole-Cole models. Parameters for these models obtained from Mason, Hasted, and Moore [1] produce nearly parallel curves with the Cole-Cole model indicating a reflectance less than one percent higher than that indicated by the Debye model. A set of parameters for the Cole-Cole model by Ray [2] gives rise to a steeper temperature dependence. A major difference in this latter set of parameters is the temperature dependence of the high frequency dielectric constant. The data are in better agreement with a slower rise of reflectance with increasing temperature.

At 103.8 GHz, the average value of 122 measurements adjusted to 20° C is, $R = 0.392 \pm 0.014$. Similarly, measurements of reflectance of ice at 103.6 GHz and -11° C give $R = 0.079 \pm 0.011$. This value is in good agreement with measurements at lower frequencies. As there are no strong absorption bands in the microwave region, reflectivity should be constant over the microwave spectrum. At 140 GHz, the situation is similar to our results described above at 100 GHz. Reflectance values lie about 10% lower, and the model by Ray again has a slightly larger temperature dependence.



Figure 1. Reflectance of water at 103.8 GHz between 0°C and 50°C. Calculated reflectances are from the Cole-Cole (C-C) and Debye (D) models [1], and the Cole-Cole (C-C) model of Ray (R) [2]. Small circles represent typical individual measurements

REFERENCES

- Mason, P.R., Hasted, J.B., and Moore, L., Adv. in Molecular Relaxation Processes, 6, 217 (1974).
- 2. Ray, P.S., Appl. Optics, 11, 1836 (1972).

This work was supported by a grant from the NASA Goddard Space Flight Center.

PERMITTIVITY OF SEA WATER AT MILLIMETER WAVELENGTHS

A-1784

FINAL REPORT

NASA Grant No. NSG-5082 (Supplement No. 1) GT/EES Project Number A-1784

Project Director: M. D. Blue Project Monitor: J. L. King

Georgia Institute of Technology Engineering Experiment Station Electromagnetics Laboratory Atlanta, Georgia 30332

May 15, 1978

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.

TABLE OF CONTENTS

	I.	INTRODUCTION	*	•	*	×		٠		*	٠	•	* •	•	•	*	•	٠	*
•	II.	EXPERIMENTAL PROCEDURE .	•	•	*	•	*		•	•	*		• •	•		•	*	•	•
	III.	ANALYSIS TECHNIQUES	÷			•	•		•	•	*	•	• •	٠	٠	•		•	•
	IV.	MEASUREMENTS AT 100 GHz	*		•	*	*	•	٠	•		•		•	•	•	•	•	
	۷.	MEASUREMENTS AT 140 GHz		*	٠			•	•	•	٠	•		•	•		٠	•	٠
	VI.	MEASUREMENTS AT 180 GHz	٠	•		•	*	•	*	•	•	•		*	*	•	*	•	*
	VII.	AUXILIARY MEASUREMENTS	•	•	•	•	•	•	•	•		•	• •		•	•.	•		•
	VIII.	SUMMARY	•	•		•	•	•	•	•		•	• •	•	•	•	*	•.	•
	IX.	DISCUSSION			•		•		•	•				,		*			•

PAGE

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 quasioptical 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 $\underline{n} = n - ik$. 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 \underline{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 proceedure 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 μ m 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 O.1 mV Scale, DVM

Item	Coupling Voltage	Signal Voltage	Phase Degrees
Reference Power		4.2	181.1
Hg	0.01	4.52	0.87
H ₂ 0	0.01	1.83	0.84

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

 $[A^{*}]^{2} = A^{2} + 2 \alpha A \cos \phi + \alpha^{2}$

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

6

 $[A^{n}]^{2} = A^{2} + 2 \alpha A \cos \phi \qquad [2]$

[1]

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 α and ϕ 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,

[3]

[4]

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

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

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

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 α/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].

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

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 ϕ 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.

8

[5]

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 ε 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

$$\varepsilon = \varepsilon_m + [(\varepsilon_c - \varepsilon_m)/(1 + i\omega \tau)]$$

where ε_s is the static or low frequency value of the dielectric constant and ε_{∞} is the residual value of the dielectric constant at frequencies much higher than that of the dielectric relaxation process. The relaxation time τ 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

$$\varepsilon' = \varepsilon_{\infty} + [(\varepsilon_{s} - \varepsilon_{\infty})/(1 + \omega^{2} \tau^{2})]$$
$$\varepsilon'' = (\varepsilon_{s} - \varepsilon_{\infty}) \omega \tau / (1 + \omega^{2} \tau^{2})]$$

[6]

[7]

[8]

TABLE II

RELATIONSHIPS BETWEEN REFLECTIVITY AND REFRACTIVE INDEX

The refractive index $\underline{n} = n - ik$ and the dielectric constant $\varepsilon = \varepsilon' - i\varepsilon''$ are related by $\underline{\varepsilon} = \underline{n}^2$

 $\epsilon' = n^2 - k^2$

$\varepsilon'' = 2nk$

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

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

for normal incidence, the reflectivity is given by

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

At angle of incidence 0, the reflectivity for radiation polarized parallel to the plane of incidence, $R_p(\Theta)$, and perpendicular to the plane of incidence, R_s (Θ), is given by

$$R_{p}(\theta) = \left| \frac{(\underline{n}^{2} - \sin^{2}\theta)^{1/2} - \underline{n}^{2} \cos\theta}{(\underline{n}^{2} - \sin^{2}\theta)^{1/2} + \underline{n}^{2} \cos\theta} \right|^{2}$$
$$R_{s}(\theta) = \left| \frac{(\underline{n}^{2} - \sin^{2}\theta)^{1/2} - \cos\theta}{(\underline{n}^{2} - \sin^{2}\theta)^{1/2} + \cos\theta} \right|^{2}$$

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,

$$\varepsilon' = \varepsilon_{\infty} + \frac{(\varepsilon_{s} - \varepsilon_{\infty}) \left[1 + (\lambda_{s}/\lambda)^{1 - \alpha} \sin(\alpha \pi/2)\right]}{1 + 2(\lambda_{s}/\lambda)^{1 - \alpha} \sin(\alpha \pi/2) + (\lambda_{s}/\lambda)^{2(1 - \alpha)}}$$

[9]

[11]

$$\varepsilon'' = \frac{(\varepsilon_{\rm s} - \varepsilon_{\rm s})(\lambda_{\rm s}/\lambda)^{1 - \alpha}\cos(\alpha\pi/2)}{1 + 2(\lambda_{\rm s}/\lambda)^{1 - \alpha}\sin(\alpha\pi/2) + (\lambda_{\rm s}/\lambda)^{2(1 - \alpha)}} + \frac{\sigma\lambda}{18.85 \times 10^{10}}$$
[10]

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

Here λ is the wavelength of the exciting radiation and λ_s is the relaxation wavelength corresponding to τ . The quantity α 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,

> $R = 1 - (8\varepsilon\omega/\sigma)^{\frac{1}{2}}$ where $\varepsilon = \varepsilon_0 \varepsilon^{i} = (8.854 \times 10^{-12} \text{ f/m})\varepsilon^{i}$ 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 ε ' 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 ε' 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

 $\epsilon' - i\epsilon'' = 7.16 - i 11.825.$

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



TABLE III

REFLECTIVITY AT OBLIQUE INCIDENCE

A. Measurements Near 46° Incident Angle

leasurement	Angle	Temperature	Expe	rimental V	alue	Value
R	46.2°	18.8°C		0.557		0.528
R	46.2°	19.7°C		0.271		0.268

B. Measurements Near 31° Incident Angle

Angle	Temperature	Experimental Value	Value
31.0	19.0°C	0.478	0.454
31.0	17.6°C	0.452	0.449
	Angle 31.0 31.0	Angle Temperature 31.0 19.0°C 31.0 17.6°C	Angle Temperature Experimental Value 31.0 19.0°C 0.478 31.0 17.6°C 0.452

C. Reflectivity Ratios for Different Temperatures

Neasurement	Angle	T ₁	T ₂	Experimental Value	Value
$R_{e}(T_{1})/R_{e}(T_{2})$	47.2°	19.7°C	5.3°C	1.106	1.125
31	47.2°	19.2°C	4.5°C	1.098	1.153
8 3	47.2	39.6°C	20.1°C	1.093	1.1201
33	47.2	40.5°C	19.6°C	1.084	1.127
. \$3	31.0°	17.7°C	3.9°C	1.133	1.176
\$\$	31.4°	16.8°C	3.9°C	1.096	1.160
\$\$	31.0°	39.9°C	17.7°C	1.159	1.239
**	31.4°	39.7°C	17.9°C	1.150	1.163

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 $R(salt water)/R(fresh water) = 1.006 \pm 0.010$. 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

[12]

$$\sigma_{1}(\omega) = \sigma_{0}(1 + \omega^{2}\tau^{2})^{-\frac{1}{2}}$$

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

$$z^{*} = \varepsilon_{0}^{*} + 2\sigma_{T}(\omega)/f$$

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 (sea water)/R (fresh water) = 0.9996 ± 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/m^3 . 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 $R(plankton)/R(fresh water) = 0.999 \pm$ 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. [13]

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(ice) = 0.0785 + 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

 $n = 1.78 \pm 0.08$ $\epsilon = 3.17 \pm 0.27$

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

$n = sin(28^{\circ} + 27^{\circ})/sin(28^{\circ}).$

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 proceedures 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 \pm 0.002. The slope at 20°C is found to be 0.0042/°C. This corresponds to a dielectric constant of

 $\epsilon' - i\epsilon'' = 6.33 - i 8.96.$

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



Figure ŵ ments. The C Debye Models 49 Measurements, Reflectivity of 135.6 GHz. The Measurements The Curves were are 4 value Obtained at 200 , While the Value at or rves were Calculated fi Water and the Mode Represented by at Normal by Ray Small Incidence at a Frequency of 20°C Represents t 48°C Represents l from Cole-Cole (C Ray (R) [3]. Indi nall Circles. Individua an Average of ts 79 Measure-(c-c)and

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 accomodating 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

 $\epsilon^{*} - i\epsilon^{*} = 5.85 - i 7.13.$

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.

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 expected 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 + 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 EHP-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,

EHP-5	Absorption	>	41.5 dB
EHP-8	Absorption	>	43 dB

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

Frequency	Reflectivity at Normal Incidence
GHz	Measurements at 20°C
103.8	0.392 <u>+</u> 0.014
135.6	0.341 ± 0.002
183.3	0.301 ± 0.009

TABLE V. INDEX OF REFRACTION OF THE IN PHASE OF ICE AT SHORT MILLIMETER WAVELENGTHS

Frequency	(GHz)	Refractive Index
99		1.78 ± 0.08
135.6		1.78 <u>+</u> 0.02
183.3		1.79 + 0.03

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 ε_{∞} . In Figure 5, the parameter ε_{∞} 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:

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

The modification of the Debye equation by including the spread parameter α has the following significance. Equation [14] is appropriate for a dielectric with a distribution of relaxation times about a most probable value τ_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.

30





ŝ

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 oneand 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 higherfrequency 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 τ 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. . .0 bond. The result supports the idea that the asymmetrically two-bonded molecules can rotate with less energy than the OH. . .0 bond energy.

32

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 α ($\alpha \approx 0.015$). The experimental result is consistent with equal populations with relaxation times of 0.8τ and 1.2τ where τ 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.

33

TABLE VI

PARAMETERS DERIVED FROM THE COLE-COLE EQUATION FOR WATER [4]

T(OC)	ε _o	ε _∞	T(10 ⁻⁹ s)	œ
0	88.26 ± 0.81	4.46 ± 1.60	17.90 ± 0.60	0.014 ± 0.023
10	84.04 ± 0.40	4.10 ± 1.16	12.61 ± 0.29	0.014 ± 0.012
20	80.35 ± 0.22	4.23 ± 0.14	9.31 ± 0.079	0.013 ± 0.005
30	76.75 ± 0.30	4.20 ± 0.20	7.21 ± 0.097	0.012 ± 0.008
.40	73.18 ± 0.28	4.16 ± 0.19	5.83 ± 0.089	0.009 ± 0.009
50	69.90 ± 0.31	4.13 ± 0.22	4.76 ± 0.088	0.013 ± 0.009
60	66.62 ± 0.36	4.21 ± 0.28	3.95 ± 0.131	0.011 ± 0.013

90% Confidence Intervals Are Listed

BIBLIOGRAPHY

- P. Debye, "Polar Molecules," The Chemical Catalog Co., Inc., New York, 1929.
- Kenneth S. Cole and Robert H. Cole, "Dispersion and Absorption In Dielectrics," J. Chem. Phys., 9, p. 341, 1941.
- 3. P. S. Ray, "Broadband Refractive Indices of Ice and Water," Appl. Optics, 11, p. 1836, 1972.
- 4. P. R. Mason, J. B. Hasted and L. Moore, "The Use of Statistical Theory in Fitting Equations to Dielectric Dispersion Data," Adv. in Molecular Relaxation Processes, 6, p. 217, 1974.
- 5. P. Halley, "Introduction to the Electromagnetism of the Sea," Optics of the Sea (Interface and In-Water Transmission and Imaging), Advisory Group for Aerospace Research and Development, Neuilly sur Seine, France, AGARD LS-61, NASA-TTF-15658, 1973.
- 6. J. P. Riley and R. L. Chester, "Introduction to Marine Chemistry," Academic Press, New York, p. 263, 1971.
- W. A. Cumming, "The Dielectric Properties of Ice and Snow at 3.2 Centimeter," J. Applied Physics, 23, p. 768, 1952.
- 8. G. H. Haggis, J. B. Hasted and T. J. Buchanan
- 9. M. N. Afsar and J. B. Hasted, "Measurements of the Optical Constants of Liquid H₂O and D₂O Between 6 and 450 cm⁻¹," J. Opt. Soc. Am., 67, p. 902, 1977.