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ELECTRONIC PROPERTIES OF LIQUID WATER IN THE VACUUM ULTRAVIOLET*

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Reflectance of liquid water has been measured between 1050 and 3000 Å by two methods, one with the water in an open dish in equilibrium with its vapor and one with a CaF_2 or quartz cell. Real and imaginary parts of the index of refraction and dielectric constant, deduced from the data and Fresnel's equations, suggest an exciton transition at 8.3 eV, an interband transition at 9.6 eV, and a band gap of 9 eV.

The importance of the study of the interaction of radiation with water has been pointed out by Platzman[1]: Liquid water is perhaps the most important inorganic chemical substance and certainly the fundamental biological material. Therefore, the study of the passage of electromagnetic radiation through water is of critical importance to biology. The measurement of the optical properties of water gives information also about the interaction of charged particles with water since these two processes are related. Previous measurements of the optical properties of water have only extended down to 1700 Å because of formidable experimental difficulties in the short wavelength region of the spectrum.

We have obtained the real and imaginary parts of the complex index of refraction of water, $\tilde{n} = n + ik$, in the spectral region 1050-3000 Å.

In order to determine the optical properties of water in the vacuum ultraviolet two general methods were used. In the first the reflectance of water in equilibrium with its vapor at 1°C was measured in the spectral region 1050-3000 Å for three angles of incidence. Light from a Seya-Namioka monochromator was reflected from a gold mirror onto either the water surface or a gold reference surface at the various angles and reflected specularly onto a coronene-coated photomultiplier. The optical constants were then obtained from a solution of Fresnel's equations. This method gave reliable values of n, but the reflectances measured in this way were not accurate enough to give good values of k. These values of n are labeled "free surface" in Fig. 1.

The second method involved placing water against the plane surface of a transparent semicylinder which formed one side of a sealed cell. Light is incident normally on the curved surface, reflects from the water-semicylinder interface, and exits, again normally. A quartz semicylinder was used down to 1680 Å, where it becomes opaque, and a CaF_2 semicylinder from 1680 down to 1250 Å. The reflectance was measured as a function of angle of incidence for angles between 13° and 87°, using an angle-doubling scanning device.[2] From 1250 to 1720 Å the optical constants n and k were determined from a least-squares fit

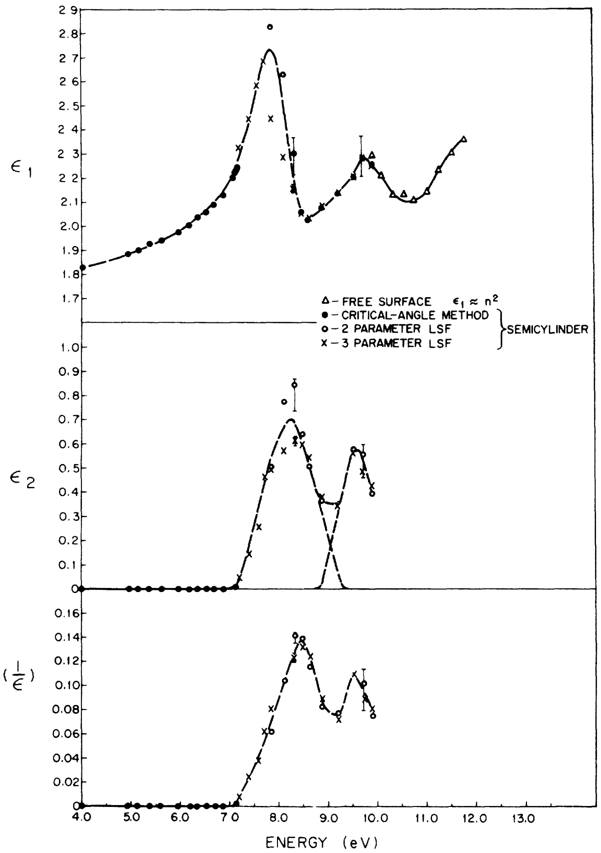

FIG. 1. Optical constants n and k of liquid water.

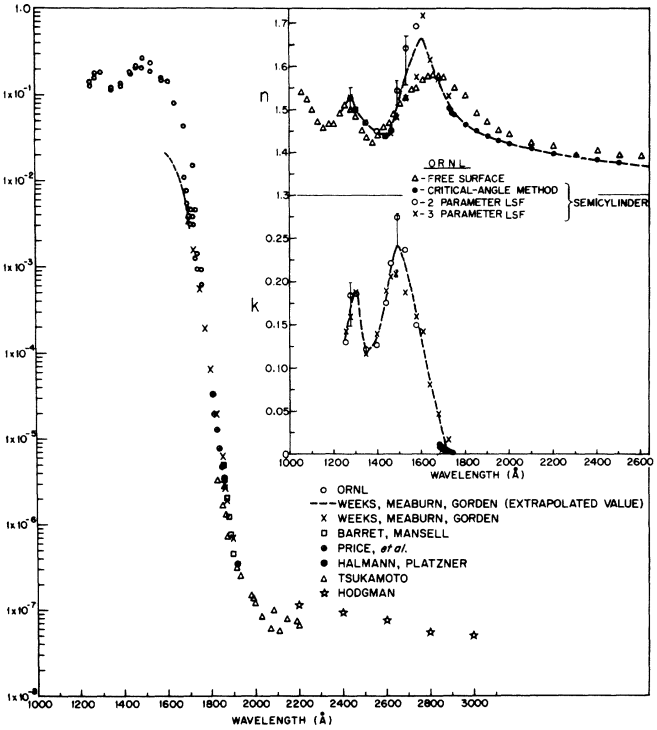

FIG. 2. Real and imaginary parts of the complex dielectric constant and energy-loss function of liquid water.

of the measured reflectances to Fresnel's equations. Above 1720 Å the absorption of water becomes weak and a critical angle may be measured from which the index of refraction n was determined. Values of k were determined from the shape of the reflectance curve just above the critical angle, since the reflectance in this region is very sensitive to k.[3] This method of determining k was applicable for k values between about 0.02 and 0.0005. The optical constants as determined using a semicylinder are relative to the index of refraction of the semicylinder and must be multiplied by the semicylinder index to be compared with vacuum-water constants.

The values obtained by the various experimental methods in the present work are shown in Fig. 1. Values of k obtained elsewhere using an absorption cell[4-9] are also shown. The Oak Ridge National Laboratory values are in good agreement with those of Weeks, Meaburn, and Gordon[4] in the region of overlap from 1700 to 1750 Å. The long-wavelength values of n are consistent with dispersion measurements.[10-12]

Figure 2 shows the real and imaginary parts of the complex dielectric constant $\epsilon = (\tilde{n})^2 = \epsilon_1 + i\epsilon_2$, where $\epsilon_1 = n^2 - k^2$ and $\epsilon_2 = 2nk$, and the energy-loss function $-\mathrm{Im}(1/\epsilon)$ for volume plasmons.[13]

Unambiguous identification of the ultraviolet spectrum would require a knowledge of the "band" structure of liquid water. The positions of the two peaks in k for the liquid state are not the same as in the vapor,[14,15] suggesting that either the same absorption processes are occurring at different energies in the liquid and vapor, or possibly that other processes are involved in the condensed state. Structure in the ultraviolet spectra of insulators in the solid state has been interpreted primarily in terms of exciton transitions, interband transitions, and volume plasma resonances.[16,17] Although the shape alone does not permit positive identification of the process, one possible interpretation is that the sharp oscillatorlike structure in the dielectric constants near 8.3 eV is due to an exciton transition, while the structure at 9.6 eV is due to an interband transition. According to this interpretation, the exciton transition obscures the position of the absorption edge for band-to-band transitions, estimated to be at approximately 9 eV (see Fig. 2).

Attempts are being made to extend the measurements to the spectral region below 1050 Å, where absorption in the water vapor surrounding the sample is more intense.

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EXCITONIC INSULATOR IN GaAs JUNCTIONS

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In this paper a case will be given for the existence of an excitonic insulating region in semiconductor junctions (either metal-semiconductor or *p-n* semiconductor).

Recently, quite a theoretical interest has been developed in the possibility of a many-body excitonic state[1] analogous to the superconducting state. Jerome, Rice, and Kohn[1] have shown that a Bose condensation of excitons (electron-hole pairs) can occur if in the two-band approximation the gap E between the bands becomes less than the binding energy of the electron-hole pair. As long as the electron-electron and hole-hole screening is small, this state will exist even when there is band overlap $E<0$. The excitonic condensation will have a ground state at the Fermi level of the material and an energy gap Δ before single particles can be excited from the ground state. Since the ground state has zero charge, the state will have infinite dc resistance at $T=0$. A resistive transition will occur around $2\Delta \approx 3.5kT_c$, where T_c is the condensation temperature for the state.[2] There may or may not be magnetic interactions with this state depending on whether the triplet ($S=1$) or the singlet spin ($S=0$) pairing is preferred. Finally, the excitonic insulator will have a first-order phase transition because there is diagonal rather than off-diagonal long-range order.[1]

For the purposes of our experiment the author wishes to extend this argument for the excitonic insulator to the case of electron-hole pairing in junctions. This can be done quite well by using the model of Cohen and Douglass for superconducting sandwiches.[3] In fact, the argument works much better for the excitonic insulator because of the diagonal long-range ordering. The pairing of the electron on one side and hole on the other side of the junction comes about directly from the Coulomb interaction, reduced by the dielectric constant. The range of the interaction in real space is limited by the junction width including the skin depths on either side. The lifetime energies of the state Γ (in energy units) is determined by a number of terms, the junction width, the Fermi momentum of the electrons and holes, and the thickness of the material on either side of the junction. For the case in point the lifetime is sufficiently short that the excitonic insulator is gapless. The density of states will then have the form analogous to gapless superconductivity,[4] with an excitation spectrum from the ground-state energy.

The principal evidence for the existence of an