The Journal of Chemical Physics

The Infrared Absorption of Water from 2.5μ to 6.5μ

E. K. Plyler and C. J. Craven

Citation: The Journal of Chemical Physics **2**, 303 (1934); doi: 10.1063/1.1749477
View online: http://dx.doi.org/10.1063/1.1749477
View Table of Contents: http://scitation.aip.org/content/aip/journal/jcp/2/6?ver=pdfcov
Published by the AIP Publishing

THE JOURNAL OF CHEMICAL PHYSICS

VOLUME 2 JUNE, 1934 NUMBER 6

The Infrared Absorption of Water from 2.5μ to 6.5μ

E. K. PLYLER AND C. J. CRAVEN, *Department of Physics, University of North Carolina*
(Received February 26, 1934)

A study has been made of the infrared absorption bands of water from 2.5μ to 6.5μ and new bands have been found at 3.30μ, 5.56μ and 5.83μ. The band at 4.7μ showed an irregular envelope and may contain several components. The 3μ band showed a shift with thickness and is probably made up of four components. The change in position of the maximum in the 3μ region with thickness is explained as due to difference in sharpness of the components which constitute the band. The band at 6.15μ did not show the corresponding shift with thickness.

MANY studies have been made on the absorption of water, but only in recent years have studies been made with instruments of moderate or high resolution. Practically all of the recent work[1, 2] has been concentrated in the near infrared and has not included the bands at 3μ, 4.7μ and 6.1μ. All the absorption bands of water were once thought to be harmonics of the intense band at 6.1μ, but newly discovered bands at 1.74μ, 1.79μ, 2.79μ, 2.90μ and 3.14μ indicate that the absorption of water is more complex.

The present work was undertaken to extend the study of water through the strong band in the region of 6.1μ. In starting a study of solutions in this region it was found of importance to know the position and percent absorption of the bands of water.

A Hilger infrared spectrometer with a fluorite prism was used as the resolving instrument and a thermocouple made by Dr. J. D. Hardy was used to detect the radiation. The spectrometer and other equipment were the same as used in previous work. Cells with fluorite windows were used to hold the water, and the water layer varied in thickness from 0.1 mm to 0.001 mm. The cells were made by putting a drop of water between the plates and pressing to the desired thickness. The plates were sealed around the edges with wax which prevented vaporization and also held the cell to a constant thickness.

The 3μ region was studied at the outset and it was found that the region of maximum absorption was a function of the cell thickness. Then the series of absorption curves which are shown in Fig. 1 was obtained by using cells of different thicknesses. It is seen that the position of maximum absorption occurs at 3.18μ for the thickest cell which transmitted only 5 percent of the radiant energy, and at about 2.94μ for the thinnest cell which transmitted 80 percent of the radiant energy. With still thinner cells this maximum probably would be around 2.91μ, which is the position given by Raman spectra.[3] In Fig. 2 are shown more accurate results obtained when 0.1 mm slits were used and the readings were taken at intervals of 0.02μ. The third curve shows bands at 3.18μ and 3.30μ.

[1] J. R. Collins, Phys. Rev. **20**, 486 (1922).
[2] J. W. Ellis, Phys. Rev. **38**, 693 (1931).
[3] E. L. Kinsey, Phys. Rev. **34**, 541 (1929).

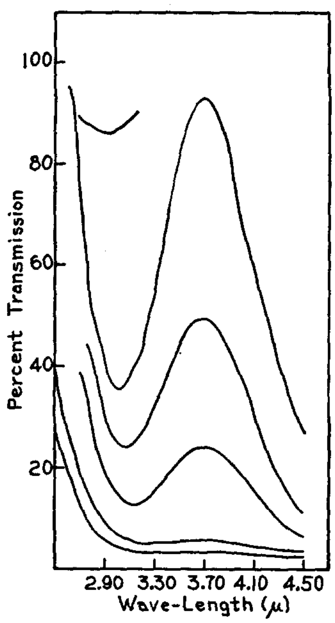

FIG. 1. The variation in transmission of water in the 3μ region due to change in thickness.

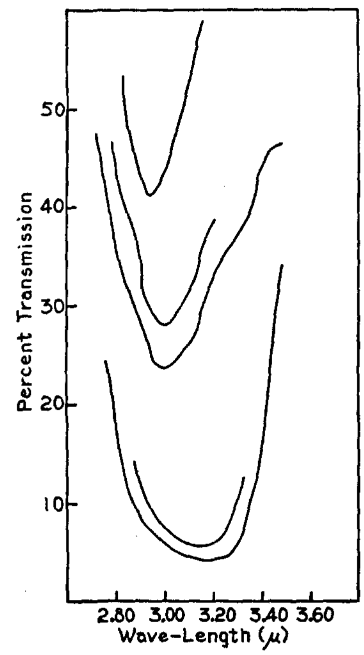

FIG. 2. The variation in transmission of water in the 3μ region due to change in thickness, with higher resolution.

The band at 3.14μ in Raman spectra may be the one shown here at 3.18μ, but the one at 3.30μ has not been previously observed.

The shift in the maximum of absorption of a band is found to be caused by temperature changes, and a change in position due to thickness is found when a weak band is located close by an intense band. The shift of the 3μ water band is not due to either of these effects, but may be the result of its complex nature. From the work of Kinsey[3] bands have been found at 2.79μ, 2.90μ and 3.14μ, and in the present work bands have been observed at 3.18μ and 3.30μ. These four overlapping bands produced the absorption which is called the 3μ water band. The intensity of the maximum absorption in a sharp band will increase more rapidly than in a broad one. If we assume that the bands which overlap in the 3μ region vary in sharpness, which seems probable as they arise from different types of vibration, the position of maximum absorption in the resultant band will be a function of cell thickness. Collins[4] has observed that the near infrared bands of water shift in position and intensity as the temperature is changed. He interpreted these changes as due to a change in the number of di-, and trihydrol molecules. While this effect may be due to the change in the groupings of water molecules, yet the same effect could be produced if these bands are made up of two or more components of different sharpness which vary in intensity with the temperature. According to the classification of Ellis[2] the bands at 1.96μ, 1.45μ, 1.18μ and 0.98μ are all double, and a shift (may be) produced by a change in thickness or temperature.

When cells with thicknesses from 0.01 mm to 0.001 mm are used, no bands appear in the region from 3.5μ to 6μ. With a cell of about 0.06 mm thickness bands were observed as shown in Fig. 3. Besides the band at 4.70μ, two other bands, which previously have not been observed, have been found at 5.56μ and 5.83μ. In thick cells the band at 5.5μ appears more intense, but with cells of decreasing thickness the 5.83μ band becomes more intense. It was also noticed that the positions of these bands varied with cell thickness. These effects are probably due to these weak bands being on the side on an intense band. The wave-lengths given for these bands are taken from the upper curve. These bands have low intensity in comparison to that

[4] J. R. Collins, Phys. Rev. **26**, 771 (1925).

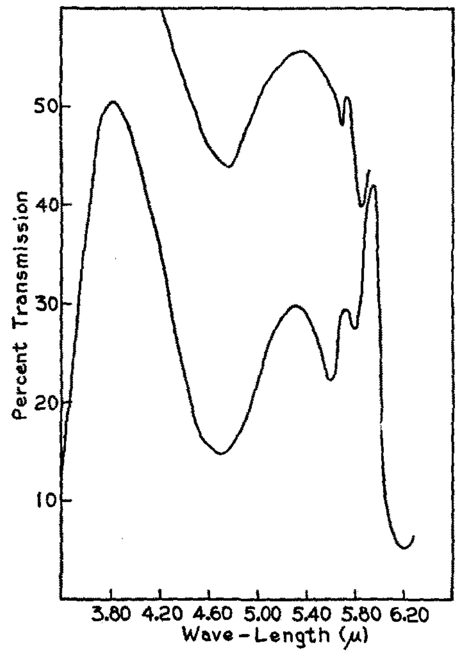

FIG. 3. The transmission of water from 3.40μ to 6.20μ for two cell thicknesses.

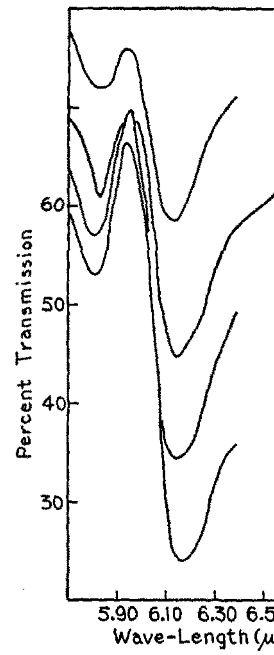

FIG. 4. The transmission of water from 5.70μ to 6.50μ for four cell thicknesses.

in the 6μ region and may arise due to differences in other frequencies or, at least, one of them may be a second harmonic of a long wave-length band. Such a band has been proposed by Ellis to account for the presence of certain short wave-length bands. The 4.7μ band seems to become irregular with thin cells and to be made up of several bands. The different maxima could never be clearly found but it will be noticed in the upper curve of Fig. 3 that there is a slight shift of the band and that an irregularity appears on the side of the band.

The absorption in the region of 6μ was studied as a function of the cell thickness, but no appreciable shift in the band was observed. In Fig. 4 are shown the results obtained with cells from 0.001 to 0.1 mm in thickness. The lowest curve in Fig. 3 or in Fig. 4 shows the maxima at 6.18μ, while all other curves give 6.15μ. This makes it seem probable that the absorption in the 6.15μ region of water is due to a single band.

It is expected to continue this work into the longer wave-length region. It can then be seen if there exists another fundamental band for water in the region from 16μ to 20μ. Until the longer wave-length region is studied, it is impossible to make a complete classification of the vibrational bands in water.