INFORMATION TO USERS

This manuscript has been reproduced from the microfilm master. UMI films the text directly from the original or copy submitted. Thus, some thesis and dissertation copies are in typewriter face, while others may be from any type of computer printer.

The quality of this reproduction is dependent upon the quality of the copy submitted. Broken or indistinct print, colored or poor quality illustrations and photographs, print bleedthrough, substandard margins, and improper alignment can adversely affect reproduction.

In the unlikely event that the author did not send UMI a complete manuscript and there are missing pages, these will be noted. Also, if unauthorized copyright material had to be removed, a note will indicate the deletion.

Oversize materials (e.g., maps, drawings, charts) are reproduced by sectioning the original, beginning at the upper left-hand corner and continuing from left to right in equal sections with small overlaps.

ProQuest Information and Learning
300 North Zeeb Road, Ann Arbor, MI 48106-1346 USA
800-521-0600

UNIVERSITY OF CINCINNATI

6 June, 19 34

I hereby recommend that the thesis prepared under my supervision by ARTHUR LOUIS CASSELMAN

entitled THE INFRARED SPECTRA OF LIQUID WATER CONTAINING HYDROGEN AND DEUTERIUM.

be accepted as fulfilling this part of the requirements for the degree of DOCTOR OF PHILOSOPHY.

Approved by:

R. C. Gourley

L. T. Jones

Form 668—G. S. and Ed.—1M—7-31

THE INFRARED SPECTRA OF LIQUID WATER CONTAINING HYDROGEN AND DEUTERIUM.

A dissertation submitted to the
Graduate School
of the University of Cincinnati
in partial fulfillment of the
requirements for the degree of
Doctor of Philosophy
1934

Arthur Louis Casselman

A. B., Louisiana College, 1925
B. S., Georgia Institute of Technology, 1928
M. S., University of Cincinnati, 1930

TABLE OF CONTENTS

The Infrared Spectra of Liquid Water Containing Hydrogen and Deuterium.

A. L. Casselman,* University of Cincinnati

Summary

The infrared absorption spectra of HDO and D_2O were compared with the spectrum of H_2O with the view of learning the difference between them, if any, and to determine which pair of atoms in the molecule is responsible for each particular band. By using water of 57 o/o D content and a second sample of water of 99+ o/o D content, it is reasonably shown that the bands occurring at 3.17μ, 4.2μ, 4.4μ, and 6.9μ are due, respectively, to the combinations H-H, H-D, D-D, and H-D. Absorption due to similar atoms in a molecule is much greater than that due to dissimilar atoms.

Introduction

The spectra distribution of the absorption bands of ordinary liquid water was determined by Aschkinass(1) in 1895. His investigations took in the wavelength range from 0.45 to 8.5 and the thickness of the absorber varied from 0.001 cm. for the longer wavelength region to 100 cm. for the shorter wavelength region. The bands obtained by him

---

*Laws Fellow in Physics
(1) Ann. d. Phys., 55, 401, 1894.

are located at the wavelengths 0.77μ, 1μ, 1.25μ, 1.5μ, 1.94μ, 3.02μ, 4.7μ, and 6.09μ.

The work previously done on the infrared absorption of water did not give any direct evidence of the origin of the bands, but the discovery of Deuterium, the heavy isotope of hydrogen, by Urey, Brickwedde, and Murphy[2] in 1932, suggested the possibility that the spectrum of Deuterium oxide (heavy water) might, by comparison with that of ordinary water, indicate the mechanism by which the absorption is produced. With this end in view, the present investigation was made. The absorption spectra of ordinary water and of two samples of heavy water have been obtained in the region 1.1μ to 7.9μ.

Apparatus

The Leiss prism spectrometer, used and described by Schaffert[3], was used in this investigation of the water absorption bands. No changes were made except that the D lines of sodium (5893) were used in the calibration instead of the (5461) green line of mercury.

The angle of the rocksalt prism, determined by the usual method with a Gaussian eyepiece, was found to be 60° 4' 40". The prism was very clear but contained several bubbles.

The two spectrometer slits were set at 0.2 mm. and were left there throughout the experiments.

---

(2) Phys. Rev. 39, 164, 1932.
(3) Journ. of Chem. Phys. July, 1933, 507.

The absorption cells used in this work were constructed as shown in Fig. 1. The framework is of brass.

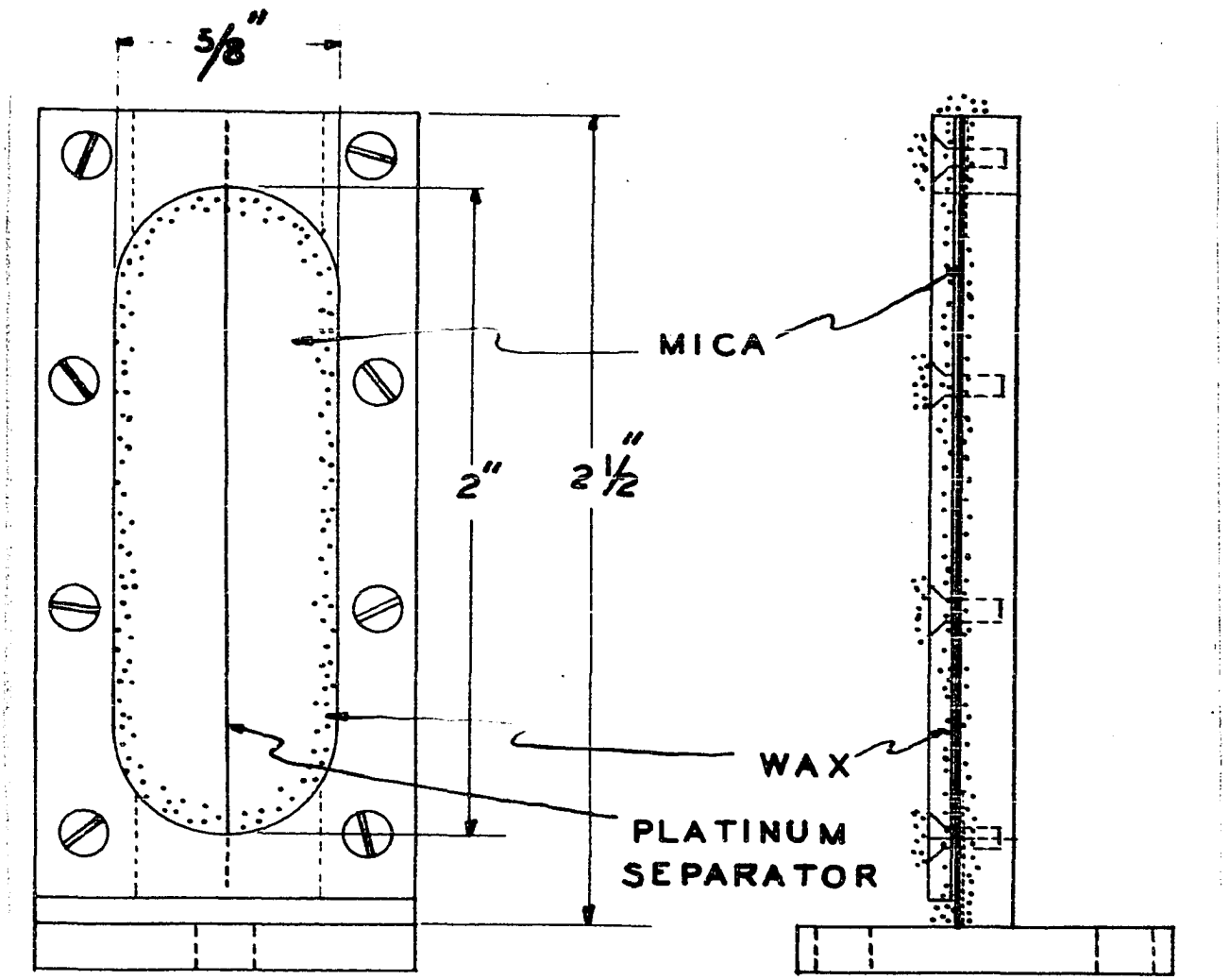

Fig 1. Type of cell used in this investigation.

A small portion of the heavy vertical piece is machined out slightly to permit the introduction of water at the top and to allow the escape of air below. The liquid is introduced by means of a fine eyedropper. Surface tension between the clean mica plates causes the water to spread over the surfaces very readily.

Two pieces of mica 1 1/8" x 2 1/2" and about 0.005 cm. thick are separated along the sides by mica strips of the thickness desired for the absorbing layer. Straight down the centre, and between the mica plates is inserted a narrow piece of rolled platinum wire of the desired thickness. The final thickness of platinum separator used in this work was about 0.0035 cm. The screwholes in the 1/8" piece are countersunk so that the flathead screws might be covered with wax. At the edges where the mica is flush with the metal, and around the edges of the windows on both sides of the cell, molten wax is made to run. After the liquid has been introduced, the top and bottom of the cell are sealed. In this way, the water could be kept in the cell for several days. If the mica plates are made much thinner than 0.004 cm. they tend to crack easily. This occurred several times during runs. Even though cracking does not take place, the water will disappear very quickly. Plates of 0.0055 cm. thickness held the water for as long as a week. Less than 0.2 c.c. of water was sufficient to fill the cell.

To make the presence of the platinum wire separator effective it is essential that the mica plates tend to form a double concave cell when the wire separator has not yet been inserted. After introducing a heavier wire to press the two plates apart, the separator is inserted and the heavier wire is withdrawn. The cell thickness at the region of the image of the glower will then be approximately the thickness of the measured platinum separator.

The cell is placed in the light path at a point where the image of the glower from the first reflecting mirror is smallest. Near it is placed a similarly constructed "dummy" cell, with the same thickness of mica plates and separators. These two could then be alternately thrown in and out of the light path.

Experimental Data

Readings were taken for every 30 seconds of arc, corresponding to 0.086μ steps in wavelength near the 2μ region and 0.045μ steps near the 6μ region, covering a wavelength range from about 1μ to 7.8μ. A sufficient number of sets of readings were taken to indicate reproducible results for each of the following cases.

1. (a) Distilled water (0.008 cm. cell)
   (b) Distilled water (0.0035 cm. cell)
2. Heavy water of Deuterium content 56+ o/o
   (Manufacturer's value) (0.0035 cm. cell)
3. Heavy water of Deuterium content 99+ o/o.[4]
   (0.0035 cm. cell)

The Absorption Spectra of H_2O, HDO, and D_2O.

The results of these three experiments are shown in Fig. 2. The curves for ordinary water are marked H_2O.

---

(4) Professor Taylor of Princeton Chemistry Department presented a gram of the heavy water to Dr. Gowdy of the University of Cincinnati Physics Department. We here wish to express our thanks to Professor Taylor for the water sample.

for the 57 o/o sample HDO, (indicating the approximate average composition), and for the high concentration, D_2O.

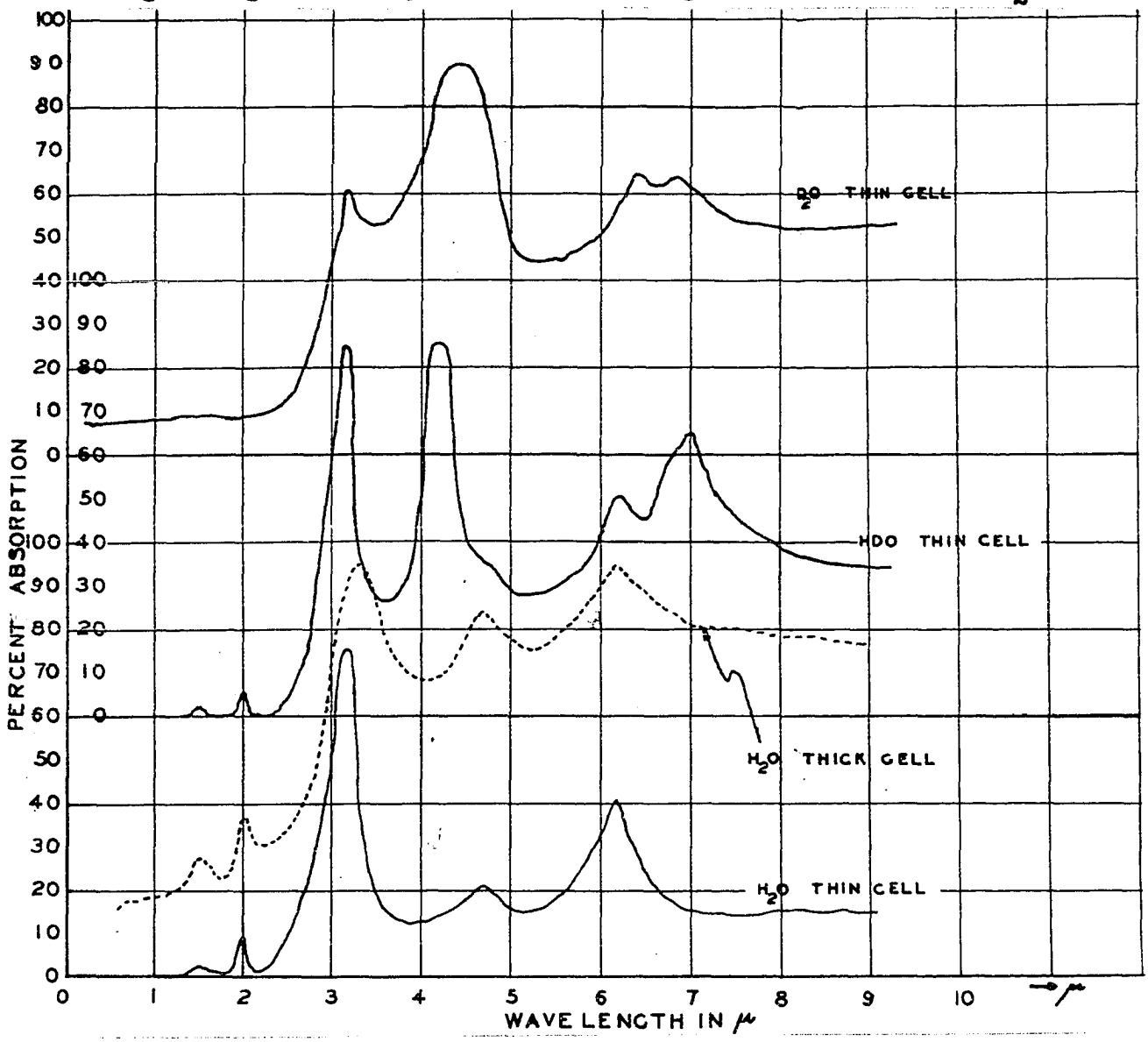

Fig 2. Absorption bands obtained for the various water samples.

The bands of H_2O at 1.5μ, 2μ, 3.17μ, 4.7μ, and 6.1μ were found with the thin cell as expected, but the bands at 0.77μ, 1μ, and 1.25μ were not evident due to insufficient thickness of absorber. With the thicker cell (about 0.008 cm.), the entire absorption increased somewhat but particularly did

the 4.7μ band increase, and the 3.17μ band shifted to 3.34μ. This latter effect has been discussed by Ellis[5] but no satisfactory explanation of it has been suggested.

For the sample containing about half Deuterium, new bands are shown at about 4.2μ and 6.9μ. Both these bands are strong. The contour of the band at 6.9μ indicates an additional band at about 6.76μ not clearly resolved. It is also to be seen that all the H_2O bands are present, since nearly half of the light atoms were hydrogen.

In the Phys. Rev., Feb. 1, 1934, preliminary results on this investigation were published by me in the "Letters to the Editor" columns. The absence of the 4.7μ band noted at that time was evidently due to the thinness of the cell then used. Subsequent work with a thicker cell has shown definitely the existence of this band, although it is weak.

For the sample containing high Deuterium concentration there is a very strong band at 4.4μ, and the 3.17μ band practically disappears. The band at 6.16μ and the band at 6.92μ are reduced in intensity (especially the latter), and appear to be shifted towards each other to the approximate points 6.4μ and 6.86μ respectively. The experimental values of the wavelength positions of the bands are given in Table I.

---

(5) Ellis - Journ. Opt. Soc. of Amer., Jan., 1924, 1.

Table I

Bands obtained with cell (Experimental)

Substance	Cell Thickness (cm.)	Position of bands					
H_2O	0.008		3.34 μ		4.7 μ	6.16 μ	
H_2O	0.0035	3.17 μ			4.7 μ	6.16 μ	
HDO	0.0035	3.17 μ	4.21 μ		4.7 μ	6.16 μ	6.92 μ
D_2O	0.0035			4.4 μ		6.4 μ	6.86 μ

Discussion of the Absorption Bands Obtained

The arrangement of the atoms in the water molecule is a disputed question. The most generally accepted configuration is triangular in form. Debye[6] gives arguments from electric moment considerations that the angle made by the lines joining the hydrogens to the oxygen is acute. It can be seen that, in the case of an acute angle, when vibrations take place between the hydrogens, the vibrations between hydrogen and oxygen are very little affected, and vice versa, the two motions taking place in nearly normal directions. If the angle were obtuse these vibrations would have a decided effect on each other.

It is generally considered that the bands existing between the individual atoms of a molecule are comparable to the action of a mechanical weightless spring of some force constant, K. Kettering, Shutts, and Andrews[7] have illustrated

(6) Polar Molecules, p. 73.
(7) Phys. Rev., vol. 36, Aug., 1930.

the agreement of the frequency of mechanical models for nonpolar molecules with data from Raman Spectra. They conclude that the molecular forces are directed along the lines associated with the chemical bands and that, mechanically, they are analogous to helical springs. Under these conditions, then, the relationship, $\nu = \frac{1}{2\pi}\sqrt{\frac{K}{\eta}}$ where $\eta = \frac{m_1 m_2}{m_1 + m_2}$ is the reduced mass, should apply. Stating this in terms of wavelengths, $\lambda \propto \sqrt{\eta}$

Since the 3.17μ and the 6.16μ bands of H_2O are always strong, let us consider them as the fundamental references. Table II provides a comparison of observed values with those computed according to this mechanical model.

Table II

Combination	η	$\sqrt{\eta}$	$\frac{\sqrt{\eta}}{.707}$	λ Observed	λ Computed. base $\lambda = 3.17\mu$	λ Observed	λ Computed. base $\lambda = 6.16\mu$
H-H	0.5	0.707	1	3.17μ	3.17μ	6.16μ	6.16μ
H-D	0.667	0.816	1.155	4.2μ	3.66μ	6.92μ	7.1μ
D-D	1.00	1.00	1.414	4.4μ	4.48μ		

The relation $\lambda \propto \sqrt{\eta}$ shows that the H-D band should be near 3.7μ and the D-D band near 4.4μ. The D-D band showed where expected but the H-D band occurred at a wavelength greater than the computed value. This may be explained by the fact that the HDO used contained nearly 57 o/o D concentration. Hence we have a gradual approach towards 4.4μ as the D concentration is increased.

Considering the 6.16μ band of H_2O as a reference, we find by experiment a new band at 6.9μ for HDO. From the relation $\lambda \propto \sqrt{\eta}$ it should be due to an H-D combination and fall near 7.1μ. For D_2O this peak nearly disappears, since there was only about one percent of H present in the absorber.

According to these results, any absorptions due to O-H or O-D combinations are extremely weak, and any vibrations between similar atoms produce very strong absorption bands.

Comparison of the curves shows that the band at 3.17μ decreases rapidly in intensity with the reduction in H content. A new band at 4.2μ appears when D is present and moves to 4.4μ at high concentrations of D. The band at 6.16μ, like the band at 3.17μ, decreases in intensity with decrease in H content. A new band appears at approximately 7μ when D is present but decreases in intensity when the concentration of D is high and that of H is low.

These observations indicate that it may reasonably be assumed that the bands at 3.17μ and at 6.16μ are due to the oscillations of an H-H combination. Similarly, the band at 4.4μ is due to a D-D combination. The behavior of the band in the neighborhood of 7μ indicates that it is due to an H-D combination.

I wish here to express my sincere thanks to Dr. R. C. Gowdy, for his suggestions, help, and encouragement during the time this investigation was under way. I wish also to express my appreciation to other members of the staff of the Department of Physics for their interest shown in this work.