

# Intensity Measurements of Some Fundamental Absorption Bands of H<sub>2</sub>O, D<sub>2</sub>O, and CS<sub>2</sub>

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Heavy water						
Infrared spectroscopy						
Infrared spectrophotometers						
Integrated intensity						
Interference fringes						
Reflectance						
Vacuum deposition (metals)						
Water						

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# Intensity Measurements of Some Fundamental Absorption Bands of Liquid H<sub>2</sub>O, D<sub>2</sub>O, and CS<sub>2</sub>

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Techniques for fabricating and calibrating liquid absorption cells having path lengths of about  $1\mu$  were developed. The thin spacers required for such cells were formed by the vacuum deposition of aluminum directly onto the cell windows. The path lengths of the assembled cells were determined by the well known interference fringe method. However, in order to produce discernible fringes in the visible and near-ultraviolet spectral regions, it was necessary to polish the internal surfaces of the cell windows to a high degree of flatness.

Using such cells, several very intense bands of H<sub>2</sub>O (3410 and 1645 cm<sup>-1</sup>), D<sub>2</sub>O (2510 cm<sup>-1</sup>), and CS<sub>2</sub> (1510 cm<sup>-1</sup>) were measured. The absorptivity values obtained for H<sub>2</sub>O and D<sub>2</sub>O appear to be significantly higher than those reported previously, while the integrated intensity of the  $\nu_3$  band of CS<sub>2</sub> is somewhat less than that calculated from dispersion and reflectance data. Distortion of the cell by the liquid sample and photometric accuracy of the spectrometer are briefly discussed as possible sources of systematic error.

## INTRODUCTION

During the past several years, there has been a revival of interest in the structure of liquid water. In particular, the relationship between the degree and kind of hydrogen bonding and the infrared absorption spectrum of water has been the subject of a number of papers (1-6). The structure of water and its thermodynamic properties are discussed in several theoretical papers (7,8). However, as Stevenson (5) has pointed out, there seem to be serious discrepancies between theoretical and experimental results, particularly with regard to the monomer concentration in liquid water.

Perhaps even more disconcerting than the disagreement between theory and experiment is the disagreement between various experimental results. Consider, for example, the peak absorptivity of the band that occurs at approximately 3400 cm<sup>-1</sup> in liquid water. Stevenson (5) reports a value of 78 liter-mole<sup>-1</sup>-cm<sup>-1</sup>, Adams and Katz (9) a value of 61 liter-mole<sup>-1</sup>-cm<sup>-1</sup>, and Greinacher *et al.* (10) a value of 55 liter-mole<sup>-1</sup>-cm<sup>-1</sup>. This disparity can almost certainly be attributed to the extreme intensity of this band, which requires the use of very small path lengths. Uncertainty in

the thickness ( $t$ ) of these extremely thin cells (about 1 to  $4\mu$ ) seems to be the major source of experimental error. This work was undertaken in an effort to develop improved methods for constructing and calibrating extremely thin absorption cells and thereby improve the reliability of absorption measurements of intense bands.

## EXPERIMENTAL METHOD

Constructing and calibrating absorption cells of  $1\mu$  thickness presents a real challenge to the experimentalist. There are many examples of absorption spectra of very thin samples in the literature, but virtually all of these are accompanied by the notation, "thin films of unknown thickness." In other cases, path lengths have been determined indirectly by comparing the absorption of weaker bands with that obtained with a cell whose thickness is large enough to be measured directly. This approach has been used by Adams and Katz (9) and Plyler and Acquista (11).

There are two basic problems in constructing an absorption cell having a spacing in the  $1\mu$  range. First, a means of maintaining separation of the two cell windows at a constant distance of  $1\mu$  must be devised. In addition the two inner surfaces must be parallel to each other. The use of conventional metal or Teflon spacers is not too promising, since it is extremely difficult to

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manipulate foils or films of this thickness (assuming that they are available). Second, assuming that a thin cell has been successfully fabricated, the problem of measuring its separation still remains. The most obvious approach is to use the technique of interference fringes.

### Construction of Cell Spacers

The first method of constructing cell spacers that was attempted is a logical extension of the conventional use of thin metal foils as spacers. In order to achieve the desired cell length, it was necessary to use a suitably thin foil. Attempts to fabricate a normally shaped spacer from very thin domestic silver leaf such as is used for lettering on glass failed because of its extreme fragility. However, it was possible, with considerable difficulty, to place four separate strips of this foil around the perimeter of the cell window. Quite obviously, such an arrangement does not give a vacuum-tight seal. Using this approach, a cell having a thickness of  $1.4\mu$  was constructed.

In view of the difficulties of using silver leaf as a cell spacer, alternate approaches were considered. One possibility is the technique that has been used successfully in constructing cells of variable spacing; namely, elimination of the spacer entirely. Adams and Katz (9) have already described the construction of such a cell. However, they were unable to observe interference fringes at thicknesses less than about  $4\mu$ . This would seem to indicate that it is difficult to maintain window parallelism at small separations in such a cell.

An eminently satisfactory solution was to simply form the metal spacer *in situ* by vacuum evaporation. The two windows were placed in the vacuum system with their optically figured surfaces exposed to the deposition source. A suitably shaped mask restricted deposition of the metal to the desired area. The two figured surfaces were coated with aluminum to a thickness of approximately  $0.5\mu$ . The  $\text{CaF}_2$  windows, one of which was drilled to permit filling of the cell cavity, were mounted in a conventional liquid-absorption cell body. The retaining screws were tightened in such a manner that a uniform interference color under fluorescent light was produced over the clear aperture of the cell, thereby rendering the two inner surfaces parallel.

### Determination of Path Lengths of Cells

If two plane, parallel, partially reflecting surfaces are separated by a distance  $t$ , their transmission spectrum will show a series of interference fringes. The positions of the maxima of these fringes are given by  $2t \cos \theta = N\lambda$ , where  $N$  is the order of interference,  $\lambda$  the wavelength of the maximum, and  $\theta$  the angle of incidence. Coincidentally, the positions of the interference minima are given by  $2t \cos \theta = [N + (1/2)] \lambda$ . Assuming  $t = 1\mu$  and  $\cos \theta = 1$ , maxima are observed at the following wavelengths:  $\lambda_1 = 2\mu$ ,  $\lambda_2 = 1\mu$ ,  $\lambda_3 = 666.7\text{m}\mu$ ,  $\lambda_4 = 500\text{m}\mu$ ,  $\lambda_5 = 400\text{m}\mu$ ,  $\lambda_6 = 333.3\text{m}\mu$ , etc., where the subscript of each  $\lambda$  denotes the order of interference. Thus, the interference fringe system for a  $1\mu$  cell lies mainly in the visible and near-ultraviolet region. This location places more stringent requirements on the optical quality of the two reflecting surfaces than are usually needed in the infrared region. For example, plates having a flatness of  $0.5\mu$  would give well defined fringes in the  $10\mu$  region but not in the visible region. Therefore, a window material that can be polished to the required degree of flatness and that also possesses sufficient mechanical and chemical stability to maintain this flatness over a period of time must be used. These requirements eliminate the use of window materials such as NaCl, KBr, CsBr, AgCl, and KRS-5.

Windows for the absorption cell used in this study were fabricated from  $\text{CaF}_2$ , which possesses satisfactory chemical, mechanical, and optical properties, particularly in the visible and near-ultraviolet regions. One distinct disadvantage is that its use in the infrared is limited to the region below about  $8\mu$ . The  $\text{CaF}_2$  plates were rectangular, having dimensions of 37 by 25 by 7 mm. The transmission aperture of the assembled cell was limited to a central zone of 10 by 20 mm. One surface of each window was figured to a flatness of better than  $\lambda/10$  (at the wavelength of the yellow lines of sodium) over the aperture zone. This flatness was adequate to produce fringes throughout the visible and ultraviolet regions.

Infrared absorption measurements were made with a Beckman IR-12 grating spectrophotometer, and the interference fringe measurements were made with a Perkin-Elmer Model 350 spectrophotometer. Sample temperature during the absorption measurements was about  $30^\circ\text{C}$ .

Materials investigated were distilled H<sub>2</sub>O, a commercial (Bio-Rad Laboratory) sample of D<sub>2</sub>O (99.84 mole-%), and reagent grade CS<sub>2</sub>.

## RESULTS AND DISCUSSION

Infrared spectroscopists have been using the interference method for cell thickness measurements for more than twenty years (12,13), and the details of the method are well known. This application differs from most previous ones in that the extremely thin cells used produce interference fringes in the visible and ultraviolet regions of the spectrum rather than in the infrared region. An example of such a fringe system is shown in Fig. 1. Since fringes can be observed down to a wavelength of 200m $\mu$ , it is apparent that high degrees of planarity and flatness have been achieved.

These high degrees of planarity and flatness are further supported by analysis of the data. Since relatively low orders of interference were used, determination of the absolute order of interference is straightforward. Knowing the absolute order of interference enables a thickness value to be calculated from the position of each maximum or minimum by applying the equations  $2t = N\lambda$  or  $2t = [N + (1/2)] \lambda$ , respectively. The results of one such analysis are given in Table 1.

TABLE 1  
Cell Thicknesses ( $t$ ) Calculated  
from Interference Orders

$N$	$\lambda_{max}(m\mu)$	$N + 1/2$	$\lambda_{min}(m\mu)$	$t (m\mu)$
2	915			915.0
		2.5	736	920.0
3	610			915.0
		3.5	525	918.7
4	456			912.0
		4.5	404	909.0
5	367			917.5
		5.5	336	924.0
6	306			918.0
		6.5	281	913.2
7	263			920.5
		7.5	243	911.2
8	231			924.0
		8.5	217	922.5
9	205			922.5

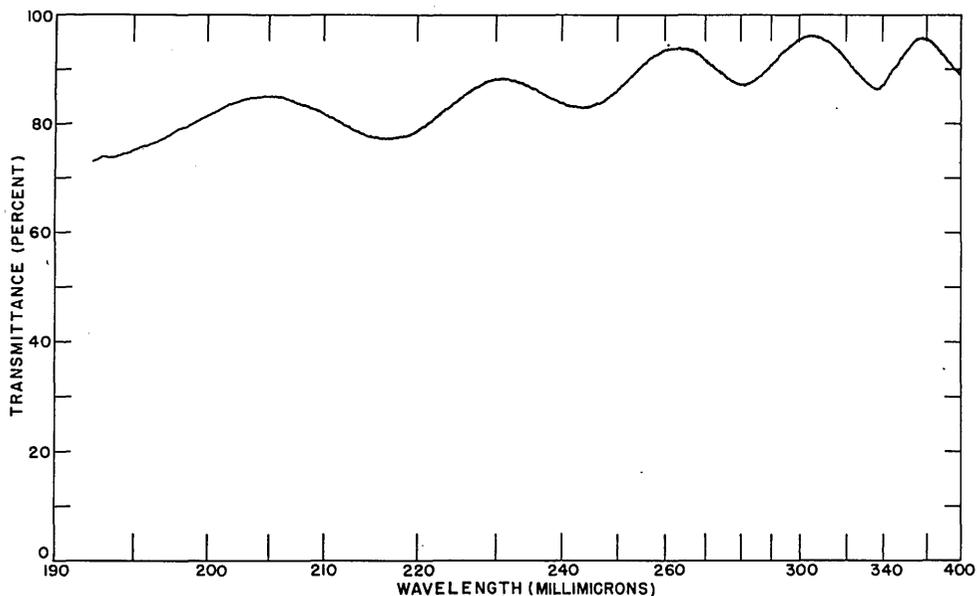


Fig. 1 - Transmission spectrum of the empty absorption cell in the near-ultraviolet region,  $t \approx 0.9\mu$

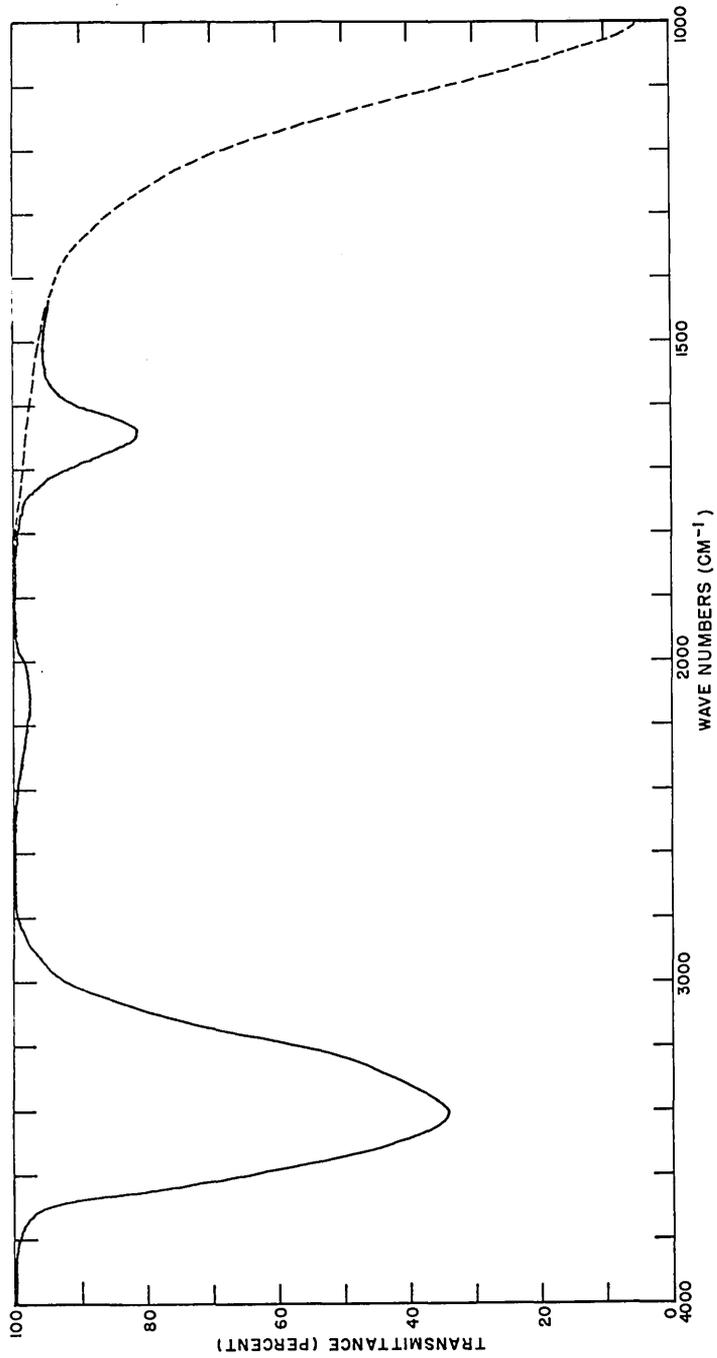


Fig. 2 - Absorption spectrum of liquid H<sub>2</sub>O, using a path length  $\approx 0.9\mu$ . The dashed line indicates absorption due to the cell windows.

The observed positions of the maxima and minima are given in the second and fourth columns, respectively, and the corresponding calculated cell thicknesses,  $t$ , in the fifth column. Statistical analysis of the data gave an average value of  $917\text{m}\mu$  for the thickness, with a probable error of  $\pm 3\text{m}\mu$ .

The above cell was filled with water and the absorption spectrum in the region from  $4000$  to  $1400\text{ cm}^{-1}$  was observed (Fig. 2). Removal of water was accomplished by placing the entire cell under a vacuum for several hours. The thickness was again determined and was found to be  $901\text{m}\mu$ . This difference of  $16\text{m}\mu$  is somewhat greater than that which would have been predicted from the statistical probable errors but still represents only a 2% uncertainty in the thickness. Similar measurements were carried out for  $\text{D}_2\text{O}$ , and the observed spectrum is shown in Fig. 3. Unfortunately, the  $1210\text{-cm}^{-1}$  bending vibration of  $\text{D}_2\text{O}$  falls too close to the absorption cutoff of  $\text{CaF}_2$  to permit reliable determination of its intensity. Table 2 summarizes the molar absorptivity values obtained in this study, and some previously reported values are given for comparison.

To avoid confusion or uncertainty, it seems desirable to state the form and units of the well known Beer-Lambert Law used in making these calculations:

$$A = \log_{10} \frac{1}{T} = \alpha ct, \quad (1)$$

where  $A$  is the absorbance,  $T$  the transmittance,  $c$  the concentration in moles/liter,  $t$  the cell thickness in cm, and  $\alpha$  the molar absorptivity in liter-mole $^{-1}$ -cm $^{-1}$ . When previously published data were expressed in different units, the appropriate conversion factors were applied.

As can be seen from Table 2, the molar absorptivity values determined in this investigation show a reasonably high degree of internal consistency. However, these values do not agree with any of the previously reported values, with the possible exception of those for the  $1645\text{-cm}^{-1}$  band of  $\text{H}_2\text{O}$ . It would be informative, therefore, to be able to compare the directly determined absorptivity values with those based on indirect methods, such as dispersion or reflectance measurements.

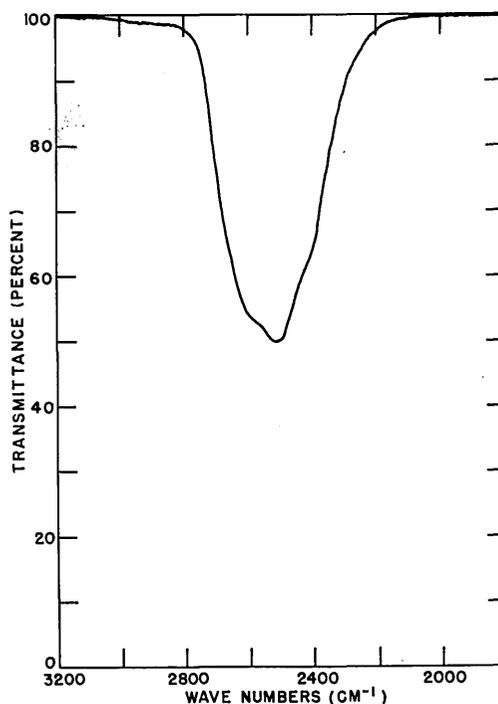


Fig. 3 - Absorption spectrum of liquid  $\text{D}_2\text{O}$ , using a path length  $\approx 0.9\mu$

In making such a comparison, it is convenient to determine the integrated intensity,  $B$ , of the absorption bands, defined by

$$B = \int_{\text{band}} \alpha_\nu d\nu = \frac{1}{ct} \int_{\text{band}} \log_e \frac{1}{T} d\nu, \quad (2)$$

where  $c$  is the concentration in moles/liter,  $t$  the path length in cm, and  $T$  the transmittance at wave number  $\nu$ , expressed in  $\text{cm}^{-1}$ . Under this definition,  $A$  is expressed in liter-mole $^{-1}$ -cm $^{-2}$ . This combination of units is commonly referred to as a dark.

Integrated intensities have been determined for the bands of  $\text{H}_2\text{O}$  and  $\text{D}_2\text{O}$  under consideration, and the observed values are given in Table 3. Greinacher *et al.* (10) have also made a direct measurement of the integrated intensity of the  $3410\text{-cm}^{-1}$  band of  $\text{H}_2\text{O}$ , and report a value of  $2.36 \times 10^4$  darks. In view of the marked discrepancy between this value and those given in Table 3, it is possible that their integration was performed using the quantity  $\log_{10} (1/T)$  rather than  $\log_e (1/T)$ . However, applying the factor 2.303 increases this value to  $5.4 \times 10^4$ , which still differs considerably from the values in Table 3.

TABLE 2  
Summary of Molar Absorptivity Values for H<sub>2</sub>O and D<sub>2</sub>O

Methods	Molar Absorptivity (liter-mole <sup>-1</sup> -cm <sup>-1</sup> )		
	H <sub>2</sub> O		D <sub>2</sub> O
	3410-cm <sup>-1</sup> band	1645-cm <sup>-1</sup> band	2510-cm <sup>-1</sup> band
This work ( $t \approx 9 \times 10^{-5}$ cm)	93.1, 91.3*	15.8, 16.0*	59.5
This work ( $t \approx 8 \times 10^{-4}$ cm)	—	18.8	—
This work ( $t \approx 1.5 \times 10^{-4}$ cm)	95.4	17.0	64.8
This work (average value)	93 ± 2	17 ± 2	62 ± 3
Adams and Katz (9)	60.8	15.2	50.0
Stevenson (5)	≈78	—	—
Greinacher, <i>et al.</i> (10)	≈55	—	—
Plyler and Acquista (11)	—	≈30	—

\*Two independent determinations.

TABLE 3  
Summary of Integrated Intensity Measurements

Cell Thickness	Integrated Intensity (liter-mole <sup>-1</sup> -cm <sup>-2</sup> )		
	H <sub>2</sub> O		D <sub>2</sub> O
	3410-cm <sup>-1</sup> band	1645-cm <sup>-1</sup> band	2510-cm <sup>-1</sup> band
9 × 10 <sup>-5</sup> cm	8.3 × 10 <sup>4</sup> , 8.4 × 10 <sup>4</sup> *	3.1 × 10 <sup>3</sup> , 3.0 × 10 <sup>3</sup> *	4.2 × 10 <sup>4</sup>
1.5 × 10 <sup>-4</sup> cm	8.2 × 10 <sup>4</sup>	—	4.7 × 10 <sup>4</sup>

\*Two independent determinations.

As previously mentioned, absolute integrated intensities can be calculated from dispersion data. Refractive index data in the infrared region for H<sub>2</sub>O have been reported by Centeno (14), and similar data are available for D<sub>2</sub>O\*. Efforts were made to fit these data into an equation of the form

$$n(\nu) - n_e(\nu) = \frac{c}{2\pi^2} \sum_i \frac{B_i}{\nu_i^2 - \nu^2}, \quad (3)$$

the derivation of which has been given by Maeda and Schatz (16). However, all such efforts failed to give reliable values for the integrated intensities

\*Unpublished data obtained in this Laboratory using the interferometric method of Kagarse and Mayfield (15).

$B_i$ . Whether this situation resulted from inadequacies in the experimental data, limitations in Eq. (3), or a combination of both cannot be stated firmly at this time. In any event, it has not been possible to compare the direct intensity measurements on H<sub>2</sub>O and D<sub>2</sub>O with indirect values based on dispersion data.

Since the absolute intensity of the  $\nu_3$  fundamental of CS<sub>2</sub>, which occurs at 1510 cm<sup>-1</sup> in the liquid, had been calculated from refractive index (17,18) and reflectance (19,20) data, it seemed worthwhile to attempt to determine the absolute intensity of this band directly, employing the same cell used in the H<sub>2</sub>O and D<sub>2</sub>O measurements. This attempt was successful, and the observed absorption band is shown in Fig. 4. While this band

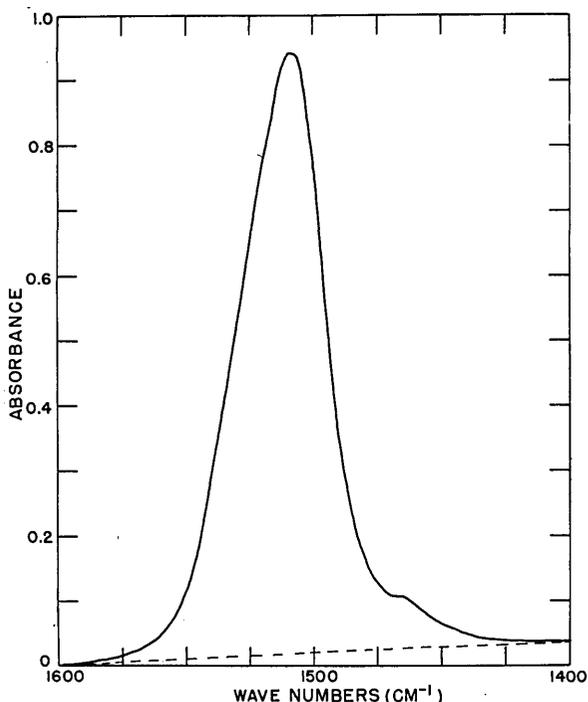


Fig. 4 — Absorption due to the  $\nu_3$  fundamental of liquid  $\text{CS}_2$ , using a path length  $\approx 0.9\mu$ . The dashed line indicates absorption due to the cell windows.

is somewhat strong for maximum quantitative accuracy, it appears to be adequate for the purpose at hand. The absolute intensity of this band was found to be  $(62.0 \pm 3) \times 10^3$  darks, which overlaps (within estimated uncertainty limits) the values of  $(71.2 \pm 5) \times 10^3$  and  $(69.8 \pm 8) \times 10^3$  darks obtained from dispersion (18) and reflectance (20) data, respectively. In addition, absolute intensities have been reported (18) for the  $\nu_3$  band of  $\text{CS}_2$  in solutions of  $\text{CCl}_4$  and  $\text{C}_2\text{Cl}_4$ , these values being  $54.6 \times 10^3$  and  $55.6 \times 10^3$  darks, respectively. These values are in fair agreement with that for the pure liquid as measured directly, but seem to be significantly lower than those obtained from dispersion and reflectance data. Whether this is due to solvent effects or systematic errors cannot be stated definitely.

On the basis of the results obtained for  $\text{CS}_2$ , it seems reasonable to conclude that it is possible to measure intensities of strong bands directly with an accuracy of better than  $\pm 15\%$ . The internal consistency of these measurements is considerably greater, being about  $\pm 4\%$ , but on

the basis of existing data the possibility of systematic errors cannot be ruled out. Applying this liberal uncertainty to the observed absorptivity for the  $3410\text{-cm}^{-1}$  band of  $\text{H}_2\text{O}$ , a value of  $93 \pm 14$  liter-mole $^{-1}$ -cm $^{-1}$  is obtained. This value is still significantly higher than previously reported values, with the possible exception of the  $78$  liter-mole $^{-1}$ -cm $^{-1}$  found by Stevenson.

Because of the serious discrepancies among the reported absorptivity values for the  $3410\text{-cm}^{-1}$  band of  $\text{H}_2\text{O}$ , some discussion of possible sources of systematic errors seems in order. As previously demonstrated, the thickness of a given cell can be determined with an accuracy of about  $\pm 0.3\%$  using the interferometric method. If this cell is filled with a liquid, emptied, and the path length redetermined, the two values agree within  $\pm 2\%$ . However, the very fact that the path length changes suggests one possible source of systematic error, namely, a distortion of the cell by the liquid sample. In view of the many factors involved, it is difficult to predict either the direction or magnitude of the forces resulting from the introduction of the sample into the cell cavity. However, it is possible to observe any gross effects experimentally. As previously mentioned, the empty cell exhibits a uniform interference color when viewed under fluorescent light. Any drastic change in either the parallelism or separation of the reflecting surfaces would perceptibly alter this color. However, no such changes were observed as the cell was filled; the area in front of the advancing liquid exhibited the same uniform color as did the empty cell. For the cell studied, a change in thickness of  $0.1\mu$  (about  $10\%$ ) would have shifted the visible interference color by  $50\text{m}\mu$ , which should have been discernible visually.

The photometric accuracy of the spectrometer is a second potential source of a systematic error. However, modern spectrometers are generally capable of measuring transmittance with less than  $1\%$  error, so this does not appear to be a serious source of error.

## SUMMARY

The main problem in the direct measurement of intense absorption bands is the fabrication of very thin absorption cells of known path lengths.

This has been solved by using vacuum-deposited metal films as spacers. In addition, it appears possible to determine the path lengths of such cells quite accurately by the well known interference fringe method. However, cell windows with a high degree of optical flatness are necessary for successful application of this technique. This flatness cannot be attained with many commonly used window materials, such as NaCl, KBr, CsBr, CsI, KRS-5, and AgCl, because of their softness and/or chemical instability. However, materials such as CaF<sub>2</sub>, LiF, BaF<sub>2</sub>, sapphire, and certain of the synthetic infrared glasses appear to possess the requisite optical properties.

The absorptivity values for H<sub>2</sub>O and D<sub>2</sub>O obtained in this investigation seem to be significantly higher than those reported by previous workers, particularly for the 3410-cm<sup>-1</sup> band of H<sub>2</sub>O. In view of the high internal consistency of the present measurements ( $\pm 4\%$ ), it must either be concluded that the previous measurements are incorrect or that the present values are subject to systematic errors of unknown origin. In an effort to differentiate between these two possibilities, an attempt was made to calculate the integrated intensity of the 3410-cm<sup>-1</sup> band of H<sub>2</sub>O from refractive index data. However, this approach failed, probably because of inaccuracies in the dispersion data.

Similar studies of the  $\nu_3$  band of CS<sub>2</sub> were more successful but far from conclusive. The integrated intensity determined from the absorption data was about 15% less than that calculated from dispersion and reflectance data. However, the probable errors in the latter two cases were too

large to firmly establish the presence of a systematic error in the absorption measurement. It is apparent, therefore, that additional studies, both experimental and theoretical, will be required to determine the absolute accuracy of integrated intensity values, regardless of whether they are based on absorption, dispersion, or reflectance measurements.

## REFERENCES

1. Buijs, K., and Choppin, G.R., *J. Chem. Phys.* **39**:2035 (1963)
2. Choppin, G.R., and Buijs, K., *J. Chem. Phys.* **39**:2042 (1963)
3. Hornig, D.F., *J. Chem. Phys.* **40**:3119 (1964)
4. Buijs, K., and Choppin, G.R., *J. Chem. Phys.* **40**:3120 (1964)
5. Stevenson, D.P., *J. Phys. Chem.* **69**:2145 (1965)
6. Thomas, M.R., Scheraga, H.A., and Schrier, E.E., *J. Phys. Chem.* **69**:3722 (1965)
7. Némethy, G., and Scheraga, H.A., *J. Chem. Phys.* **36**:3382 (1962)
8. Marchi, R.P., and Eyring, H., *J. Phys. Chem.* **68**:221 (1964)
9. Adams, R.M., and Katz, J.J., *J. Opt. Soc. Am.* **46**:895 (1956)
10. Greinacher, E., Lüttke, W., and Mecke, R., *Z. Elektrochem.* **59**:23 (1955)
11. Plyler, E.K., and Acquista, N., *J. Opt. Soc. Am.* **44**:505 (1954)
12. Smith, D.C., and Miller, E.C., *J. Opt. Soc. Am.* **34**:130 (1944)
13. Sutherland, G.B.B.M., and Willis, H.A., *Trans. Faraday Soc.* **41**:182 (1945)
14. Centeno, M.V., *J. Opt. Soc. Am.* **31**:244 (1941)
15. Kagarise, R.E., and Mayfield, J.W., *J. Opt. Soc. Am.* **48**:430 (1958)
16. Maeda, S., and Schatz, P.N., *J. Chem. Phys.* **36**:571 (1962)
17. Schatz, P.N., *J. Chem. Phys.* **29**:959 (1958); **31**:1146 (1959)
18. Ferguson, E.E., and Kagarise, R.E., *J. Chem. Phys.* **31**:236 (1959)
19. Schatz, P.N., Maeda, S., Hollenberg, J.L., and Dows, D.A., *J. Chem. Phys.* **34**:175 (1961)
20. Barnes, D.W., and Schatz, P.N., *J. Chem. Phys.* **38**:2662 (1963)