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Infrared Intensities of Liquids IV: Recent Measurements of Infrared Optical Constants and Absolute Infrared Absorption Intensities of Liquids by Multiple Attenuated Total Reflectance

by

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Recent refinements are described to the CIRCLE, multiple attenuated total reflection method for measuring infrared optical and dielectric constants, absolute integrated intensities and, hence, molecular dipole derivatives. Attention is focussed on the accuracy of the method, which is estimated from measurements on H_2O (l) and D_2O (l). The real and imaginary optical constants agree with literature values to $< 1.5\%$ and about 6%, respectively, which is about the agreement of the literature values. The integrated areas agree with literature values to $< 2\%$, and OH and OD bond dipole derivatives for H_2O and D_2O agree to $< 1\%$.

pATR, refractive index, dielectric constant, and absorption cross section spectra are reported from 8000 to 350 cm^{-1} for 2-butanol, and integrated absolute absorption intensities and bond dipole derivatives are presented for 2-butanol, 2-hexanol, and 2-octanol and compared with those for primary alcohols and water.

I. INTRODUCTION

The method that has been described[1] for the measurement of infrared optical and dielectric constants, and, hence, absolute infrared absorption intensities of liquids, has been refined and applied to some secondary alcohols. The intensities of the hydrogen-bonded O—H stretching bands are compared with those of some primary alcohols studied previously.[2,3]

The method has been refined with attention on improving the accuracy. To determine the accuracy, the optical constants and intensities of liquid water have been remeasured, because they have been reported many times in the literature as is summarised in references 4 to 7. The optical constants and intensities of liquid heavy water have also been measured and compared with the limited literature.[6,8] They have also been compared with those of water, to provide further evidence about the method's accuracy.

The method is not particularly satisfactory from the purist's viewpoint because the reflection geometry is not well defined. However it is fairly quick and easy to use and the evidence presented in this paper shows that it can yield optical constants and integrated absolute intensities that are accurate to a few percent. Further the samples are isolated from the atmosphere during the measurement, thus enabling compounds with labile deuterium atoms to be examined without exchange with hydrogen.

The method is briefly outlined in the next section, and is followed by brief descriptions of the recent refinements, the study of H_2O (l) and D_2O (l), and the study of the secondary alcohols 2-butanol, 2-hexanol, and 2-octanol. Because of production difficulties, in this paper the symbol ν is used for the wavenumber of the radiation in vacuum.

II. METHOD

Spectra were recorded with a Bruker IFS 113V FT-IR spectrometer. The optical bench was kept evacuated. Samples were contained in the CIRCLE cell (Figure 1) which is manufactured by Spectra Tech Inc. of Stamford, CT., U.S.A.. The cell was filled from hypodermic syringes via 0.75 mm i. d. teflon tubing, and the sample was sealed against the vacuum by teflon O-rings. Intensity spectra were recorded with the cell containing first the sample liquid, $I_s(\nu)$, and then nitrogen gas, $I_N(\nu)$.

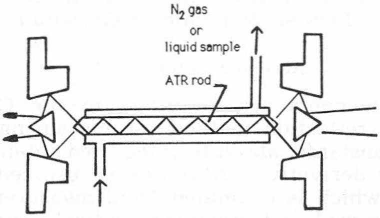

Figure 1. The essential features of the CIRCLE cell.

These intensity spectra are converted to a pATR[9] spectrum via

$$\mathrm{pATR}(\nu) = -\log_{10}\{I_S(\nu)/I_N(\nu)\}.$$

Some smoothing and some straightening of the baseline above 4000 cm^{-1} can be done during this process if needed. The pATR spectra of 2-butanol, H_2O, and D_2O are shown in Figure 2.

By the following steps, the pATR spectrum is converted to the infrared real and imaginary refractive index spectra, $n(\nu)$ *vs.* ν and $k(\nu)$ *vs.* ν, where the complex refractive index, $n_c(\nu)$, is $n_c(\nu) = n(\nu) + i\,k(\nu)$, where i is $\sqrt{(-1)}$.

1) In zeroth approximation, the pATR spectrum is treated as an absorbance spectrum and $k_{app}(\nu)$ is calculated via

$$\alpha(\nu) = 4\pi\,\nu\,k_{app}(\nu). \qquad \text{where } \alpha(\nu) = -L^{-1}\ln\{I_S(\nu)/I_N(\nu)\}.$$

For ATR, the effective absorption path length at each reflection is $2d(\nu)$, where $d(\nu)$ is the (wavenumber-dependent) penetration depth into the less-optically-dense medium. In the CIRCLE cell there are m reflections, so $L = 2md(\nu)$ and

$$k_{app}(\nu) = 2.303 \cdot \mathrm{pATR}(\nu)/\{[4\pi\nu]\,[2md(\nu)]\}.$$

The zeroth approximation assumes the liquid is non-absorbing, whence[10]

$$d(\nu) = \lambda_{vac}/\{2\pi n_r\sqrt{\{\sin^2\Theta - (n^2/n_r^2)\}}.$$

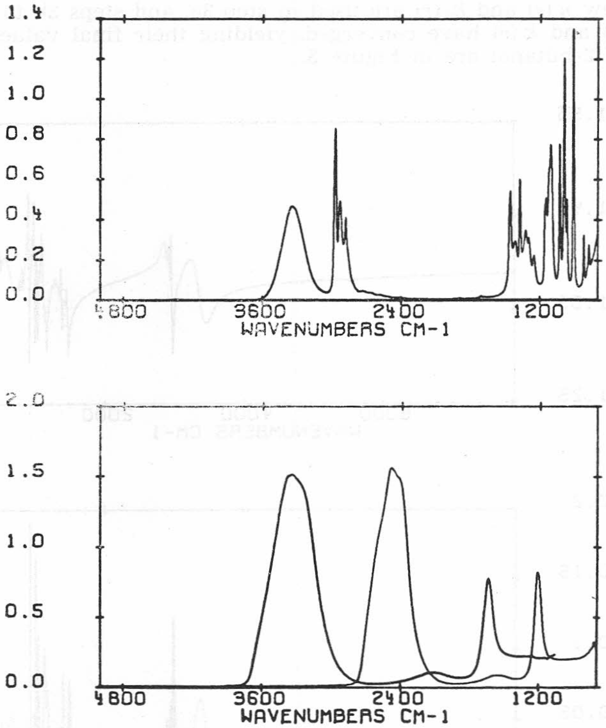

Figure 2. pATR spectra with a ZnSe rod of: (top) 2-butanol (l); (bottom) H_2O (l) and D_2O (l).

n and n_r are the refractive indices of the sample and rod and λ_{vac} is $1/\nu$, the vacuum wavelength of the radiation. The angle of incidence, Θ, is nominally 45° in our experiments. The approximate number of reflections, m, was determined to be 6 from the known$^{11-13}$ optical constants of benzene, CH_2Cl_2 and toluene. Also it is found empirically to be helpful to calculate the starting value of k, k_1, via

$$k_1 = k_{app}\,(1 + \sqrt{k_{app}}).$$

2) $k_1(\nu)$ is used to calculate starting values, $n_1(\nu)$, of $n(\nu)$ via Kramers-Kronig transformation. This is a Hilbert transformation, and is done as two successive integer fast Fourier transforms. n_∞, the real refractive index at the highest wavenumber in the $k_1(\nu)$ spectrum, must be supplied.

3) $k(\nu)$ is refined by the following iterative procedure.

3a) $k_1(\nu)$, $n_1(\nu)$, and Fresnel's equations are used to calculate the pATR spectrum for R reflections. R here is determined precisely and independently from the pATR spectrum of a liquid of known optical constants, usually benzene.

3b) For each wavenumber, the ratio, F, is determined of the observed pATR value to that calculated, and this ratio is used to adjust k via

$$k_{new} = k_{old}\,[1 + \mathrm{DMP}\,(\mathrm{F}\text{-}1)]. \qquad \text{DMP is usually set to 1.}$$

3c) $k_{new}(\nu)$ is used as $k_1(\nu)$ in 3a, and 3a and 3b are repeated to convergence to yield $k_c(\nu)$. $n_1(\nu)$ is unchanged as yet.

3d) The converged k values, $k_c(\nu)$, are put back into step 2 to calculate a new $n(\nu)$.

3e) The new $n(\nu)$ and $k_c(\nu)$ are used in step 3a, and steps 3b to 3e are repeated until both $n(\nu)$ and $k(\nu)$ have converged, yielding their final values. The $k(\nu)$ and $n(\nu)$ spectra of 2-butanol are in Figure 3.

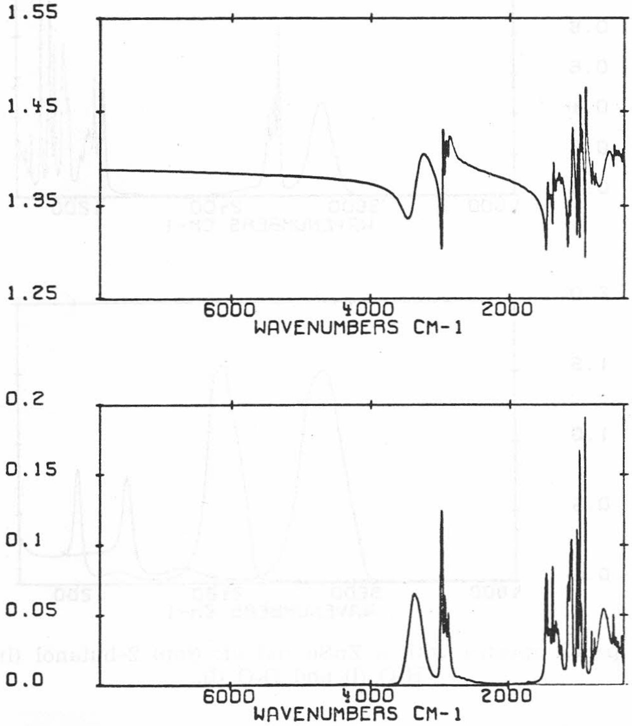

Figure 3. Infrared refractive indices of 2-butanol: (top) $n(\nu)$; (bottom) $k(\nu)$.

The calculations in this procedure are done via programs written for Bruker's Aspect 2000 computer in PASCAL and the Aspect's assembler language, MACRO. Steps 1, 2, and 3 are done by the programs CIRCLEP, AHILBERT, and REFLECT, respectively, where AHILBERT is based on the Bruker program HILBERT. These programs are described more fully in reference 1 and, to some extent, later.

Once the infrared $n(\nu)$ and $k(\nu)$ spectra have been calculated, they are converted to the infrared real and imaginary dielectric constant spectra, $\varepsilon'(\nu)$ and $\varepsilon''(\nu)$. The complex dielectric constants is $\varepsilon(\nu) = \varepsilon'(\nu) + i\,\varepsilon''(\nu)$, and equals the square of $n_c(\nu)$. Hence $\varepsilon'(\nu) = n^2(\nu) - k^2(\nu)$ and $\varepsilon''(\nu) = 2\,n(\nu)\,k(\nu)$.

The $\varepsilon'(\nu)$ and $\varepsilon''(\nu)$ spectra of 2-butanol are in Figure 4.

The infrared refractive indices and dielectric constants are basic physical properties of materials and are of value for their own sakes. They are required for the correct analysis of spectra, including conventional transmission spectra but particularly scattered spectra as from aerosols, and they determine the response of materials to sub-picosecond changes in electric fields.

III OBTAINING MOLECULAR INFORMATION

Molecular information is obtained from the dielectric constants via the classical damped harmonic oscillator model.[10,14,15] For a liquid, this theory shows that the area under a band in the conductivity spectrum, $\nu\varepsilon''(\nu)$ *vs.* ν, is given by

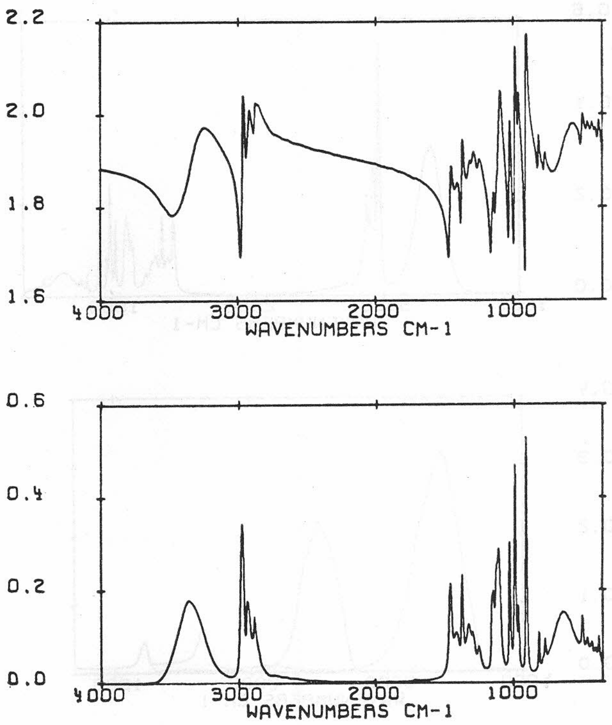

Figure 4. Infrared dielectric constants of 2-butanol: (top) $\varepsilon'(\nu)$; (bottom) $\varepsilon''(\nu)$.

$$\int \nu\varepsilon''\,\mathrm{d}\nu = (N/6\,c^2)\,g_j\,(\partial\mu/\partial Q_j)^2\,[(\mathbf{n}^2+2)/3]^2.$$

The Lorentz local field has been used to obtain the latter term, **n** is the real refractive index at band *j* due to all absorption other than in band *j*, and *N* is the number density of molecules.

We define the spectrum $\{V_m\,\nu\varepsilon''(\nu)/[\mathbf{n}^2+2)/3]^2\}$ *vs.* ν, where V_m is the molar volume, as the absorption cross-section (CS) spectrum. The CS spectra of 2-butanol, H_2O, and D_2O are in Figure 5. The area, B_j, under the *j*th band in the CS spectrum is

$$B_j = (N_a/6\,c^2)\,g_j\,(\partial\mu/\partial Q_j)^2,$$

where N_a is Avogadro's number. The area under a CS bands is in km/mole. If multiplied by 0.1487 or 9.96×10^{-14} it yields $(\partial\mu/\partial Q_j)^2$ in the units (Debye Å^{-1} amu$^{-1/2}$)^2 or the S. I. units, C^2/kg.

The area of a band in the CS spectrum is not a commonly used measure of absorption intensity, although we believe it to be the one that is always correct for condensed phases. It is frequently not necessary to use it, however, and it is desirable to relate it to other measures of absorption intensities. To do this, we define for band j,

$$A_{Nj} = V_m \int \alpha(\nu)\,\mathrm{d}\nu,$$

where *N* indicates use of the napierian logarithm and $\alpha(\nu)$ is defined in section II. We use A_{Dj} if $\log_{10}$ is used. If $n(\nu) = 1$, as for gases, $A_{Nj} = (N_a\,\pi/3c^2)\,g_j\,(\partial\mu/\partial Q_j)^2$. $\alpha(\nu)$ has been used also for condensed phases, for which

$$A_{Nj} = (1/\mathbf{n})\cdot\{N_a\,\pi/(3\,c^2)\}\,g_j\,(\partial\mu/\partial Q_j)^2\cdot[(\mathbf{n}^2+2)/3]^2$$

is approximately correct.

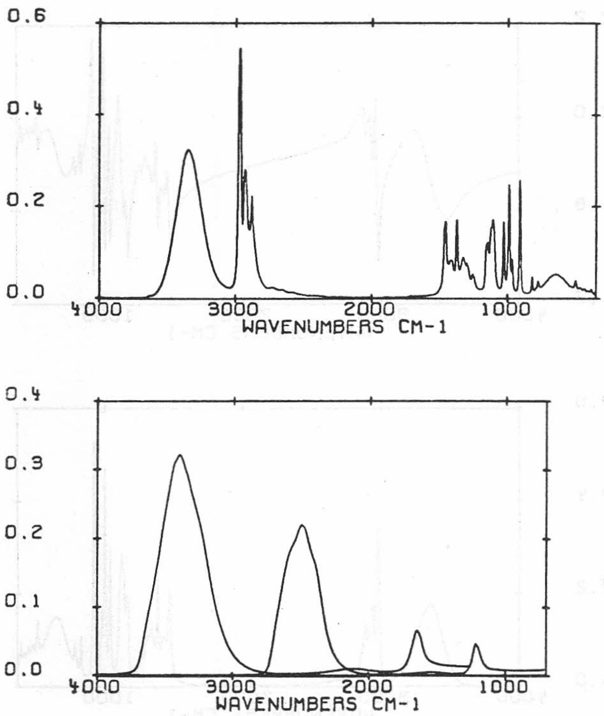

Figure 5. Absorption cross-section spectra. The ordinate units are 10 cm^2/mole: (top) 2-butanol (l) ($V_m = 91.8\ \text{cm}^3$, $\mathbf{n} = n_{7900} = 1{,}389$); (bottom) H_2O (l) ($V_m = 18.02\ \text{cm}^3$, $\mathbf{n} = n_{9000} = 1.325$) and D_2O (l) ($V_m = 18.09\ \text{cm}^3$, $\mathbf{n} = n_{8500} = 1.325$).

Thus $B_j = A_{Nj} \cdot \mathbf{n}/\{2\pi\,[(\mathbf{n}^2 + 2)/3]^2\}$, which allows our intensities measured from the CS spectrum to be related to those deduced from transmission measurements with liquid samples.

IV. RECENT REFINEMENTS

We have obtained a large amount of data on the liquid primary alcohols up to C_{10} which is clearly precise. Before we put it into the literature, we wanted to obtain a better estimate of its accuracy[16], and to tidy up a few details of the procedure which reduced the accuracy. Our recent work described below has been directed towards this end.

We have considerably improved the programs we use for this work.

The programs were originally written in the Bruker implementation of p-type PASCAL, with the repetitive mathematical procedures written in Bruker's Aspect-2000 assembler language, MACRO, for improved speed. The major disadvantage of this, apart from the non-transferability of the programs to computers other than the Aspect-2000, was a severe limitation on the number of data points that could be processed at one time. Thus the Kramers-Kronig transform program, AHILBERT, could only be used with 4096 points at a time, and the refinement program, REFLECT, could only handle 2048 points at a time. This was inconvenient, but a more serious problem was the significant limitation on the accuracy of the transformation of the $k(\nu)$ spectrum to the $n(\nu)$ spectrum when only a 4000 cm^{-1} range could be transformed at one time.

The release of the PASCOM compiler by Bruker enabled these problems to be solved. The PASCOM compiler translates PASCAL code into the assembler language MACRO, which is the compiled and linked to the repetitive mathematical procedures like any other assembler language program with the help of appropriate libraries. The executable files produced run faster than p-type PASCAL files and the limitations on the data size are much relaxed. We can now refine and Hilbert-transform over an 8000 cm^{-1} range (8192 points) which improves the accuracy, and convenience, considerably.

We have made the calibration of the number of reflections, R, in the CIRCLE cell more routine and reliable.

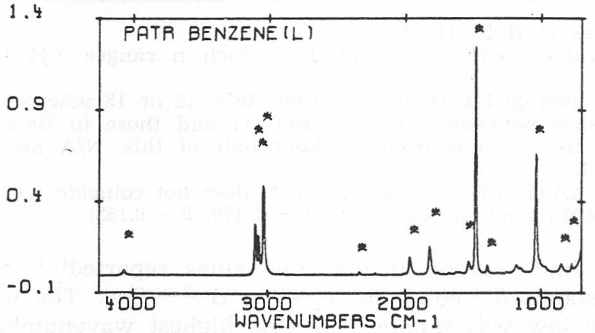

Figure 6. pATR spectrum of benzene (ZnSe rod) with the bands used to calibrate the CIRCLE cell starred.

The cell is now calibrated with the 13 bands of liquid benzene that are starred on the benzene pATR spectrum in Figure 6. Table I shows for each band the peak pATR value with a ZnSe rod, the values of n and k of benzene, and the percentage agreement between the peak $k(\nu)$ values measured by calibrated dispersive infrared spectroscopy[11] and by uncalibrated FT-IR spectroscopy.[12,13,16] To calibrate the cell, a pATR spectrum of benzene is measured and is read by a program which also calculates peak pATR values from Fresnel's equations, the known $n(\nu)$ and $k(\nu)$ values for liquid benzene and the known $n(\nu)$ values for the rod material. This is done for various values of the number of reflections, NRF. and for each NRF the Root-Mean--Squared Percent Deviation is calculated. The lowest RMSPD is typically about 3%, which is consistent with the accuracy of the calibration data, which is indicated by the Δk values in Table I. The value of NRF that gives the lowest RMSPD is taken as the number of reflections in the cell. It has been shown to be reproducible, and to be unaffected by change of beamsplitter, as should be the case.

We have improved the selection of the n_∞ which is required input to the Kramers-Kronig transform.

The value of n_∞ at the sodium-D line was used previously,[1] except for water. In fact the value at the high-wavenumber end of the data should be

TABLE I

Data for Benzene Used to Calibrate the CIRCLE Cell

Band[a]	ν/cm^{-1}	pATR[b]	n[c]	k[d]	% Δk[e]
3	4056.5	0.034	1.476	0.00337	3
16	3090.4	0.289	1.467	0.0304	2
17	3071.1	0.226	1.473	0.0231	3
19	3036.4	0.502	1.477	0.0531	4
36	2324.8	0.023	1.475	0.00230	0
41	1960.3	0.102	1.473	0.01007	3
43	1815.7	0.154	1.473	0.01535	5
49	1528.3	0.073	1.464	0.00734	N/A
50	1478.2	1.31	1.516	0.139[f]	1.5
51	1393.3	0.056	1.478	0.00528	0
56	1035.6	0.672	1.464	0.0714	1
60	849.5	0.060	1.454	0.00575	2
61	774.3	0.061	1.430	0.00618	N/A

[a] Band number as in Refs. 11—13.

[b] Approximate values with ZnSe rod, for which n ranges 2.44 to 2.39.

[c] From Ref. 11.

[d] From Ref. 11, averaged with values from Refs. 12 or 13 where possible.

[e] Percent difference between values in Ref. 11 and those in Refs. 12 or 13. The uncertainty in the k value used is about half of this. N/A means no value is in Refs. 12 or 13.

[f] The maximum pATR value is calculated. It does not coincide with the maximum k value (ν = 1479.1 cm^{-1}, pATR = 1.24, n = 1.470, k = 0.153).

used. We now find this by fitting the values reported[17,18] for the visible region to the standard[19] equation $n^2 = \mathrm{A} + \mathrm{B}\,\nu^2 + \mathrm{C}\,\nu^4$. The equation allows extrapolation to low wavenumber, to the highest wavenumber of the data which is usually 7800 to 9000 cm^{-1}. As can be seen in Figure 7 for water,

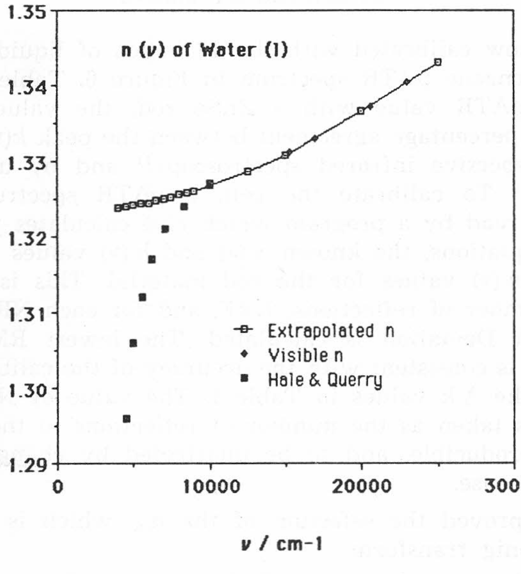

Figure 7. The real refractive index of H_2O (l), showing the experimental data in the visible[17] ◆ and infrared[5] ■ regions, and the extrapolation of the former □.

the reported[5] infrared refractive index curve coincides with the extrapolated visible refractive index values to ≤ 0.004, *i. e.* 0.3%, at these wavenumbers. For other liquids, like alcohols, which have weaker absorption than water near 3000 cm^{-1}, the agreement is expected to be as good or better.

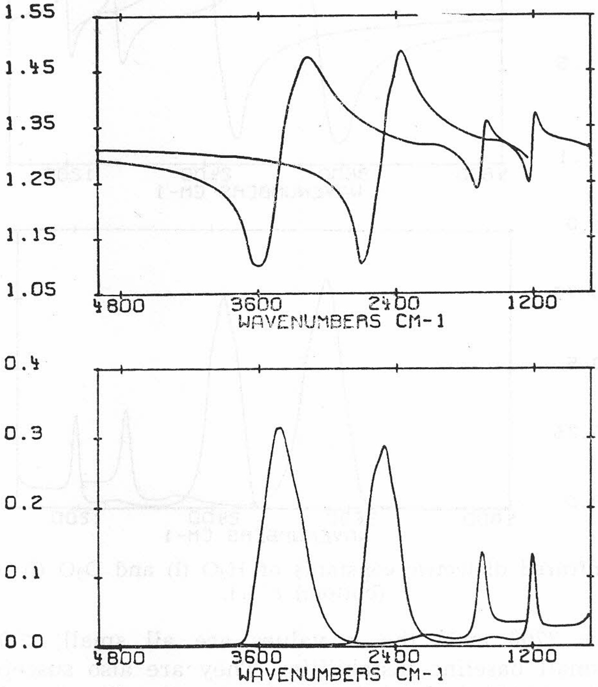

Figure 8. Infrared refractive indices of H_2O (l) and D_2O (l): (top) $n(\nu)$; (bottom) $k(\nu)$.

V. REPRODUCIBILITY AND ACCURACY: H_2O (l) AND D_2O (l)

To obtain an indication of the accuracy of the current method we have restudied[1] H_2O (l), and have studied D_2O (l).

For each liquid a ZnSe rod was used. pATR spectra were recorded with a KBr beamsplitter and globar source, a CaF_2 beamsplitter and globar source, and a CaF_2 beamsplitter and a tungsten source. The pATR spectra superimposed where their wavenumbers overlapped, so they were merged to a single pATR spectrum from 9000 to 1250 cm^{-1}. This was processed to $n(\nu)$ and $k(\nu)$, $\varepsilon'(\nu)$ and $\varepsilon''(\nu)$, and the cross-section spectrum. n_∞ was taken as n_{9000}, 1.325 from Figure 7. These spectra are shown in Figures 8, 9, and 5.

Reproducibility

The reproducibility of $k(\nu)$ was judged in two ways. The short-term reproducibility is shown to be excellent, ~2% or better, by the fact that pATR spectra taken with the same or different beamsplitters superimposed.

The long-term reproducibility was judged by comparing the new results for H_2O with those measured in 1984 and reported[1] in 1985. For the imaginary refractive index, $k(\nu)$, this comparison revealed three distinct regions.

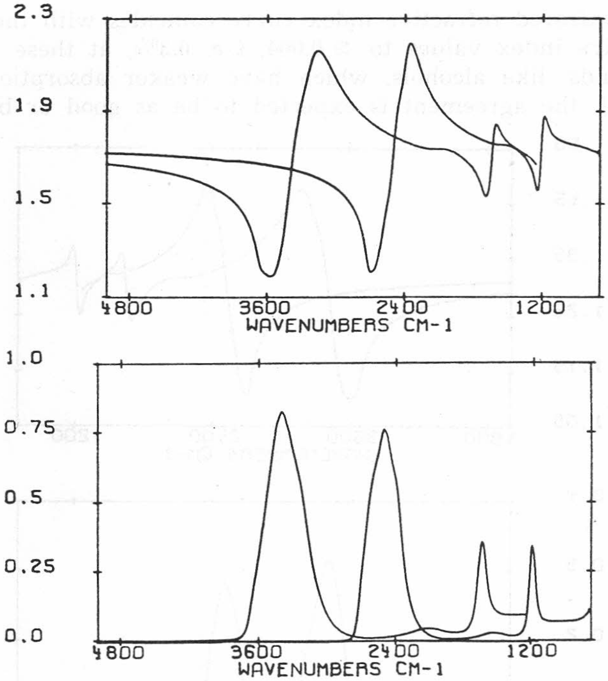

Figure 9. Infrared dielectric constants of H_2O (l) and D_2O (l): (top) $\varepsilon'(\nu)$; (bottom) $\varepsilon''(\nu)$.

First, above 3700 cm^{-1} the k values are all small, ≤ 0.009, and are susceptible to small baseline instabilities. They are also susceptible to noise, which was about 0.0004 in $k(\nu)$. In this region the k values >0.001 agreed to about $15 \pm 5\%$ while k values <0.001 differed by factors up to 2. Our method does not yield accurate data for the very weak bands in this region, but it gives good qualitative indications for $k < 0.009$ and would give good quantitative results for any stronger bands that lie above 3700 cm^{-1}.

The second region is the main one, from the low wavenumber limit, 1050 cm^{-1}, to 3300 cm^{-1}. The k values range from 0.25 to 0.003 and the two sets agreed to better than 2%. In this region, our long-term reproducibility is very good.

The third region is from 3300 cm^{-1} to 3700 cm^{-1}, and covers the peak and high-wavenumber side of the OH stretching band. Here the new data were consistently 6 to 7% higher than the old. The onset of the greater differences occurred rather sharply, between 3320 and 3380 cm^{-1}. It might be significant that a very similar effect exists in the literature data. Figure 10 shows, on a reversed wavenumber scale, that the results of Downing and Williams[4] agree with Zolotarev's[6] up to 3300 cm^{-1} and fall below them from 3300 to 3700 cm^{-1}. Thus it is not clear to us that the discrepancy in this region must be taken as inaccuracy of our method. The sample may be involved.

Accuracy of k(ν)

Figure 10 also indicates the accuracy of our imaginary refractive indices of H_2O, because it contains data (joined by a line) from our new k spectrum

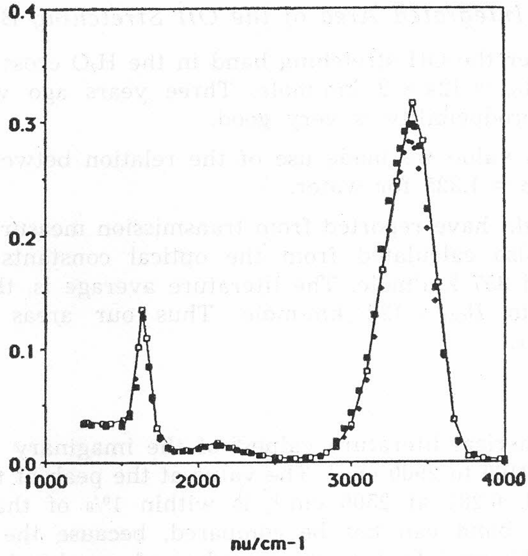

Figure 10. Imaginary refractive indices of water. Our new data □ (points joined by a line), and the data of Downing and Williams (Ref. 4) ◆, and of Zolotarev and Demin (Ref. 5) ■.

as well as the most recent results from the groups of Williams and Zolotarev. It is clear that our values tend to be high but, in general, agree with the literature as well as the agreement found in the literature. The region 3300 to 3700 cm^{-1} is clearly a problem; it has been alluded to in the literature[4,6] but not resolved.

Zolotarev has published two major sets of optical constants for water.[6,20] The latest set[6] is in Figure 10. Large (25 to 50%) differences exist between the two sets of k values, largely because of an apparent shift of the OH stretching band by ~25 cm^{-1} to low wavenumber in the most recent.[6] Accordingly we compared only with the region below 2800 cm^{-1}, where we agree on average to 7% and tend to be higher, and the top of the OH stretching band where we are higher by 6%. Zolotarev claimed about 3% to 5% accuracy, and agreed with the k values of Williams[4] to 5% on average.

Further, we used two sets[4,21] of k values from Williams and coworkers, which agreed on average to 3% and had estimated accuracies of 5%. The latest sets[4] are in Figure 10. Between 3380 cm^{-1} and 1050 cm^{-1} our recent k values agree to 4% on average, with our values tending to be high. At the top of the OH stretching band our values are higher by 10% and, because of the variation in the band shape noted above, differences of 25% occur in the high-wavenumber side of the band.

Accuracy of n(ν)

Our recent n values for H_2O agree with those of Zolotarev[6] and Williams[4] to $\leq 1.5\%$, except near 3500 cm^{-1} where our stronger OH stretching band causes our $n(\nu)$ to be lower by up to 5%.

Accuracy of the Integrated Area of the OH Stretching Band

The area under the OH stretching band in the H_2O cross section spectrum in Figure 5 is $B_{OH} = 124 \pm 2$ km/mole. Three years ago we measured 124 km/mole. The reproducibility is very good.

To check this value we made use of the relation between B_j and A_{Nj} in section III, with $\mathbf{n} = 1.325$ for water.

Motojima *et al.*[7] have reported from transmission measurements, $A_{OH} = 899$ km/mole. They also calculated from the optical constants in Refs. 4 and 20, $A_{OH} = 962$ and 857 km/mole. The literature average is, thus, 906 km/mole which converts to $B_{OH} = 122$ km/mole. Thus our areas agree with the literature to $\leq 2\%$.

D_2O (l)

The only numerical literature values[6] of the imaginary refractive indices of D_2O (l) are for 2100 to 2900 cm^{-1}. The value at the peak of the OD stretching band in Figure 8, 0.287 at 2500 cm^{-1}, is within 1% of that reported.[6] The remainedr of the band can not be compared, because the literature band[6] is shifted about 25 cm^{-1} to low wavenumber of our band and is about 15 cm^{-1} narrower than our band. The area under the OD stretching peak in the cross-section spectrum (Figure 5) is $B_{OD} = 66.7$ km/mole.

TABLE II

Integrated Cross-Section Areas and Dipole Moment Derivatives for OH Stretching Bands

Pure liquids	B_{OH} km/mol	$\partial\mu/\partial Q_{OH}$ D/{Å √ amu}	$\partial\mu/\partial r_{OH}$ D/Å
H_2O	124		2.95
D_2O	66.7		2.97
2-C_4H_9OH	76.7	3.38	3.29
2-$C_6H_{13}OH$	73.0	3.36	3.27
2-$C_8H_{17}OH$	74.8	3.34	3.25
CH_3OH	79.6	3.44	3.35
C_2H_5OH	78.9	3.43	3.34
n-C_3H_7OH	80.1	3.45	3.36
n-C_4H_9OH	76.2	3.37	3.28
n-$C_7H_{15}OH$	79.7	3.44	3.35
t-C_4H_9OH	67.2	3.16	3.08
Dilute Solutions in CCl_4			
CH_3OH	7.56	1.06	1.03
C_2H_5OH	7.66	1.06	1.04
n-C_3H_7OH	9.69	1.20	1.17
H_2O(g)			0.67

To relate the OD and OH areas for D_2O and H_2O, we calculated bond dipole derivatives for the OH and OD bonds in liquid water. To do this correctly, we must know the correct molecular force field. We do not know this and probably can not know it because of the variation between molecules in the liquid. Thus we made the simplest approximation, that the force field is diagonal and the bending vibration can be neglected. Under this approximation, $\Sigma (\partial\mu/\partial Q_j)^2$, which is $(\partial\mu/\partial Q_j)^2$ summed over ν_1 and ν_3, is simply $(\partial\mu/\partial r)^2$ times 1.126 $(\text{amu})^{-1}$ for D_2O or times 2.115 $(\text{amu})^{-1}$ for H_2O.

From the areas, $\Sigma (\partial\mu/\partial Q_j)^2$ is 18.4 ± 0.3 $\{D/Å \sqrt{\text{amu}}\}^2$ for H_2O and 9.92 ± 0.14 for D_2O, from which $\partial\mu/\partial r_{OH}$ is 2.95 ± 0.02 Debye/Å and $\partial\mu/\partial r_{OD}$ is 2.97 ± 0.02 D/Å. In S. I. units, 8.84 and 8.90×10^{19} C, respectively. Theoretically, these two quantities should not be exactly the same but they should be very similar.

It is clear from the results for H_2O and D_2O that the accuracy available is enough to justify measurements of the relative intensities of hydrogen and deuterium bonded systems.

VI. SECONDARY ALCOHOLS

The same methods as were used for water yielded $n(\nu)$ and $k(\nu)$ from 8000 to 700 cm^{-1} for 2-butanol, 2-hexanol, and 2-octanol. A KRS-5 rod was used to extend the range to 350 cm^{-1} and the k spectra were merged to get $k(\nu)$ from 8000 to 350 cm^{-1}. The $n(\nu)$ spectrum was recalculated by Kramers-Kronig transformation over the entire range, and the $k(\nu)$ and $n(\nu)$ values were re-refined to fit the ZnSe pATR spectrum. The resulting k values are believed accurate to $\sim 5\%$ throughout, and the n values to $\leq 1.5\%$. The pATR, refractive index, dielectric constant and absorption cross section spectra of 2-butanol are in Figures 2 to 5.

The cross-section areas, B_{OH}, for the OH stretching bands were measured, and $\partial\mu/\partial r_{OH}$ values were calculated under the assumption of isolated OH oscillators. These results are compared with those for primary alcohols and water in Table II. The intensities and dipole moment derivatives of the secondary alcohols appear to be marginally lower than those of the primary alcohols and significantly higher than that of *t*-butanol. Further details of these results will be published.

CONCLUSION

The CIRCLE multiple attenuated total reflection method is a relatively quick and easy way to get absolute integrated absorption intensities of rather strongly absorbing liquids with an accuracy of a few percent. The real and imaginary optical constants appear to be accurate on average to about 1.5% and $5 \pm 3\%$, respectively, below 3300 cm^{-1} and perhaps below 4000 cm^{-1}. The method is inferior to specular reflection spectroscopy for very strong bands ($k > \sim 0.6$) and inferior to transmission spectroscopy for very weak bands. It appears to be particularly well suited for bands typically seen in spectra of hydrogen-bonded liquids, and results are reported for OH stretching bands of water and several primary and secondary alcohols.

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SAŽETAK

Infracrveni intenziteti u tekućinama IV: Novija mjerenja infracrvenih optičkih konstanti i apsolutni infracrveni intenziteti u tekućinama s višekratnom prigušenom totalnom refleksijom

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Opisana su novija poboljšanja za CIRCLE, metodom višekratne prigušene totalne refleksije za mjerenje infracrvenih optičkih i dielektričkih konstanti, apsolutnih integriranih intenziteta, te prema tome i derivata molekulskog dipola. Pažnja je usmjerena na točnost metode, koja se procjenjuje prema mjerenjima na H_2O (l) i D_2O (l). Realne i imaginarne optičke konstante slažu se s literaturnim vrijednostima na $<1,5\%$, odnosno 6%, što je otprilike i slaganje vrijednosti u literaturi. Integrirane površine slažu se s literaturnim vrijednostima na $<2\%$, a derivati dipola za veze OH i OD za H_2O i D_2O slažu se na $<1\%$.

pATR, indeks loma, dielektrična konstanta i apsorpcijsko presjecište dani su za spektre u području od 8000 do 350 cm^{-1} za 2-butanol, a integrirani apsolutni apsorpcijski intenziteti i derivati dipola veza prikazani su za 2-butanol, 2-heksanol i 2-oktanol, te uspoređeni s vrijednostima za primarne alkohole i vodu.