M.Sc.

TEMPERATURE DEPENDENCE OF THE 2125 CM<sup>-1</sup> AND 1555 CM<sup>-1</sup> INFRARED ABSORPTION BANDS IN LIQUID H<sub>2</sub>O AND D<sub>2</sub>O

R. Oder

#### ABSTRACT

The thermal dependence of peak height, frequency, extinction coefficient, and half width of the 2125 cm<sup>-1</sup> infrared absorption band in liquid  $H_2O$  and the corresponding 1555 cm<sup>-1</sup> band in liquid  $D_2O$  was determined. In most cases, sigmoidal behaviour was exhibited by the parameters, with an inflection temperature between 30 and 40°C. Superposition of spectra recorded between 5 and 70°C revealed the presence of a diffuse isosbestic point on the low frequency side of this band in both isotopes of water. These results have been discussed in terms of liquid water structure, based on a mixture model in which rotation of unstructured molecules is possible at higher temperatures.

Band contour analysis of the frequency range investigated (1000 to 2700 cm<sup>-1</sup>) was also carried out, by fitting Cauchy-Gauss product functions to the absorptions contained within this frequency interval. Temperature-dependent shape changes, specific for a particular vibrational mode, were observed and interpreted in terms of water structure.

A previously unreported infrared absorption band was discovered and assigned to the first overtone of the far infrared librational band.

## TEMPERATURE DEPENDENCE OF THE INFRARED

## ABSORPTION OF LIQUID WATER

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by Reet Oder

A thesis submitted to the Faculty of Graduate Studies and Research in partial fulfilment of the requirements for the degree of Master of Science

Department of Chemistry McGill University Montreal

July 1969

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A previously unreported infrared absorption band was discovered and assigned to the first overtone of the far infrared librational band.

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### FOREWORD

The main topic of this thesis is an investigation of the effects of temperature on the intermolecular absorption band at 2125 cm<sup>-1</sup> and at 1555 cm<sup>-1</sup> in the infrared spectrum of liquid  $H_2O$  and liquid  $D_2O$  respectively.

The thesis starts with a General Introduction in which the topics pertinent to the investigation are reviewed briefly. Then follows the main portion of the thesis which is divided into four Parts, each in the form of a scientific paper suitable for publication with little revision. The first of these deals with the temperature dependences of the conventional infrared parameters of intensity, position and width for the intermolecular band. In the next section, the origin of a diffuse isosbestic point observed with the intermolecular band is discussed. The third Part contains a detailed analysis of band shape as carried out with the help of computer programmes recently developed by Dr. R.N. Jones of the National Research Council. The fourth section of the Thesis is a short note describing the discovery and assignment of a previously unreported absorption maximum in the infrared spectrum of both isotopes of liquid water. Experimental or analytical methods have been included in each of the sections where appropriate.

The main text ends with concluding remarks and suggestions for future investigations. Claims to original

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research are then noted.

Finally several appendices are listed, containing details of experimental techniques, data, and computer programmes used during the investigation.

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## GLOSSARY OF PRINCIPAL SYMBOLS

A	absorbance
К	proportionality constant in absorption band area calculations
М	number of symmetric absorption peaks fitted with mathematical function
NP	number of data points taken along experimental contours
Р	infrared parameter
S	spectral slit width
S	shape ratio
t	cell thickness
т	temperature
т	transmittance
x <sub>l</sub>	variable parameter in curve fitting programme, corresponding to peak height
x <sub>2</sub>	variable parameter in curve fitting programme, corresponding to frequency of maximum absorption
x <sub>3</sub>	variable parameter in curve fitting programme, corresponding to Cauchy half-width
x <sub>4</sub>	variable parameter in curve fitting programme, corresponding to Gaussian half-width
α	variable parameter in curve fitting programme, corresponding to base-line transmittance
ε	coefficient of molecular absorption
<sup>€</sup> max	maximum molecular extinction coefficient
η	viscosity
∆T <sub>m</sub>	peak height, in percent transmittance units

معنقة	ν	frequency, in wavenumbers
	vo	frequency of maximum absorption
	<sup>Δν</sup> 1/2	band half-width
	<sup>(∆v</sup> 1/2 <sup>)</sup> c	Cauchy band half-width
	<sup>(Δν</sup> 1/2 <sup>)</sup> G	Gaussian band half-width
	ν <sub>2</sub>	deformation band
	<sup>v</sup> 2+L	combination band
	<sup>2</sup> vL	overtone of librational band

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GENERAL INTRODUCTION

### 1. LIQUID WATER STRUCTURE

Structurally what is known about liquid water is that it is an associated liquid with great numbers of hydrogen bonds giving rise to short range order of molecular positions on a time scale of about  $10^{-10}$  seconds. It is in the details of extent of bonding, size and configuration of resultant aggregates, and types of motions possible that differences of opinion arise.

In Table G-1, the pertinent features of several of the major water-structure theories are listed. The theories fit into one of two broad categories: those presenting water on the basis of a continuum model (column 1), and those assuming a mixture model (columns 2 to 5).

In continuum models, water is pictured as forming an essentially hydrogen-bonded network in the liquid as well as in ice, with increase of temperature causing an increase in the amount of bond bending and stretching possible. The main experimental support for a continuum model has been the seeming lack of evidence for the existence of non-hydrogenbonded molecules in certain spectroscopic investigations (12). From studies of the HDO fundamental stretching vibrations in Raman (13) and infrared absorptions (14-16), several workers have concluded on the basis of the smooth shapes of the absorption envelopes that a continuum model for water was indicated. It has since been shown, however, that smoothness of band profiles is not necessarily indicative of the existence \_\_\_\_....



#### TABLE G-1

#### Comparison of Water Structure Theories

	Pople (1), Bernal 6	Pauling	Marchi and Eyring	Nemethy and Scheraga	Walrafen	Sparnaay
	Fowler (2)	(3)	(4)	(5-7)	(8-10)	(11)
Model	Continuum	Clathrate	Cage	Cluster	Cluster	Continuum + Cluster
Species	<sup>H</sup> 2 <sup>O</sup>	<sup>н</sup> 2 <sup>0</sup>	<sup>н</sup> 20	н <sub>2</sub> о, D <sub>2</sub> о	H <sub>2</sub> 0, D <sub>2</sub> 0	<sup>H</sup> 2 <sup>O</sup>
Bonding	Tetrahedral		Tetrahedral	Tetrahedral, co-op process	Tetrahedral, co-op process	Tetrahedral
Bonded Species	All molecules	20- and 24- molecule polyhedra	Ice-III like	Plickering ice- like clusters. 1,2,3, and 4 bonded	C <sub>2V</sub> structure for doubly bonded	Nemethy- Scheraga type con- figurations
Unbonded Molecules	None (0-100°C). Lack of spectral evidence	Inside clathrates	<pre>Few % at 0°C. Occupy inter- stitial sites and fluidized cavities</pre>	24% at 0°C. Between clusters. Spectral evidence	0° singly bonded (0°C). Non-bonded first above 25°C. Spec- tral evidence	None at 0°C
Bond Bending	Yes	-	No	No (but mention possibility)	Yes	Freely bending between O<0<0
Librations	About bonds	-	Very highly restricted rotations for bonded molecules	All species	Only structured C <sub>2V</sub> species	Occur with angle 0
Rotations	No	Free for unbonded	Free for unbonded inside cavities	Free about dipole axis for unbonded. Free about bond for singly bonded	-	Freer rotations above θ'
Effect of Temperature Increase	Inc. amount of bond stretch and bend	-	Inc. occupancy of interstitial sites. Inc. creation of fluidized cavities	Dec. in cluster size. Inc. in cluster conc. Inc. in monomer conc.	Inc. conc. of unstructured (singly and non-bonded)	Inc. size of angle θ
Anomaly at 30-40°C	-	-	Unspecified rearrangement of ice-III like structure on inc. monomer conc.	Mention, but not explained	No mention, but non- bonded mole- cules occur at temp. >25°C	No mention, but angle 0 dependent on temp. & determines motion

of only one type of absorbing species (17,18).

Basic to mixture models of liquid water is the assumption that at least two species of molecules are present - hydrogen-bonded molecules forming the main structural units and unstructured molecules not bound by normal covalent hydrogen bonds. Mixture models however are divisible into two further categories depending on the geometric form envisaged for the hydrogen-bonded associates and the corresponding locations of unstructured molecules. In one class, bonded molecules form either clathrate (column 2) or cage-like (column 3) structures; in the other, bonded molecules associate into geometrically less specified clusters (columns 4 and 5).

The major difference between liquid  $H_2O$  and liquid  $D_2O$  is that bond strengths in deuterated water are stronger although bond lengths are essentially the same (19,20). A comparison of physical and chemical properties of the two isotopic waters is given by Kohn (12), Scatchard (22) and Nemethy and Scheraga (6). Most properties are almost identical with a few important exceptions. Structurally,  $D_2O$  is thought to be almost identical to  $H_2O$  (6,7,23-25).

During the present investigation, the two theories found to be most relevant were of the cluster type, as developed by Nemethy and Scheraga, and by Walrafen. Hence these are given in more detail in the following subsections of the General Introduction.

#### 2. THEORY OF NEMETHY AND SCHERAGA

Nemethy and Scheraga's flickering cluster model of liquid water structure is the most comprehensive to date, applicable to the pure liquid (5,7), to  $D_2O$  (6,7), and to solutions (26). In their model, five types of molecules, dependent on the bonding, are distinguishable. Molecules in interiors of clusters are assumed to have all four hydrogen bonds unbroken while molecules on the surface have three, two, and one hydrogen bonds. The fifth category is the unbonded molecules in the unstructured regions. In the structured regions, an ice-like tridymite arrangement of tetrahedrally bonded molecules is assumed to occur because of the large number of hydrogen bonds it offers per cluster. Occupying the spaces between clusters are molecules with all four bonds broken, participating in dipole-dipole and London interactions. Bond making and bond breaking is assumed to be a stepwise process.

On passing from the solid to the liquid, Nemethy and Scheraga postulate that approximately 50% of hydrogen bonds are broken. At 0°C adjacent clusters are assumed to contain on the average 90  $H_2^{0}$  molecules, and to be separated by only one or two layers of unbonded molecules. Increase of temperature causes a rapid initial decrease in cluster size together with an increase in cluster concentration and a slower increase in total number of unbonded molecules.

No hydrogen bond bending of clustered molecules is

Fig. 5. Schematic representation of the model of liquid water, showing hydrogen-bonded clusters and unbonded molecules. The molecules in the interior of the clusters are tetracoordinated, but not drawn as such in this two-dimensional diagram.



## FIGURE G-1. Nemethy and Scheraga's model of liquid water, from reference (5).

permitted in the model, although the possibility of there being such motion is mentioned. Free rotation about the dipole axis, not involving changes in dipole interaction with the instantaneous field, is assumed for unbonded molecules. Free rotation of the singly bonded molecule about its hydrogen-bond axis is assumed also, with a frequency close to that of the unbonded molecule. About the two axes perpen-



FIGURE G-2. Diagrammatic model of water, showing principal axes and H-bond axis. Large circles, O atoms; small circles, H atoms; molecule is in AB plane.

dicular to the dipole moment, unbonded molecules are assumed to be librating, free rotation being prevented by the strong dipole field of the environment. For the two, three and fourbonded molecules, librational motion is also allowed.

In liquid D<sub>2</sub>O, Nemethy and Scheraga (7) have been successful in reproducing experimental thermodynamic properties

with calculated values based on a model of heavy water identical to that of  $H_2O$ , with the additional assumption of stronger bonds and a higher degree of bonding. The higher degree of bonding they associate with greater structural order in the form of larger but fewer clusters. At the melting point, the average cluster size is calculated to be 115  $D_2O$  molecules. Decrease in cluster size and increase in cluster concentration are postulated as being quicker in  $D_2O$  on temperature increase than in  $H_2O$ . The rate of increase of unbonded molecules is about the same for both isotopes. The overall effect is that structural breakdown with temperature is more pronounced in  $D_2O$ , yet  $D_2O$  is more highly structured than  $H_2O$  over the entire temperature range for which the theory is valid (~0-70°C).

A weak point of Nemethy and Scheraga's theory is that it does not account for the approximate constancy of heat capacity between 0 and 100°C, nor for the transitional behaviour of water between 30 and 40°C. In addition, their theory does not give correct assignments to low frequency infrared and Raman absorption bands (6). Band assignments are discussed in detail in subsection 5 of the General Introduction.

#### 3. THEORY OF WAFRAFEN

A more recent model for liquid water, and one which is successful in some of the areas where Nemethy and Scheraga's falls short, is the one presently being developed by Walrafen (8-10). This model, as Nemethy and Scheraga's, consists of an intermolecular structure involving ice-like tetrahedral hydrogen bonding. However, in this theory - as in Buijs and Choppin's - only three types of molecules are differentiable - those with two hydrogen bonds, with one bond, and with no bonds. The doubly bonded molecules form structured water of C<sub>2V</sub> symmetry. Stepwise breakage of hydrogen bonds is envisaged, forming the singly bonded and non-bonded water molecules, assumed to have surpassed the  $C_{2V}$  potential barrier of fully bonded molecules. The species are in temperature-dependent equilibrium, with increase of temperature favouring formation of unstructured water molecules, presumed to be the singly bonded and unbonded molecules. At 0°C, all molecules are postulated as being at least partially bonded, with nonbonded molecules first appearing at temperatures higher than 25°C.

A comparison of the mole fractions of structured and unstructured species in liquid H<sub>2</sub>O as a function of temperature calculated from Nemethy and Scheraga's, and Walrafen's theories, is given in Fig. G-3. A substantial portion of the obvious discrepancy is due to the different degrees of bonding



FIGURE G-3. Comparison of temperature dependence of mole fractions of structured and unstructured molecules in liquid H<sub>2</sub>O, according to Nemethy and Scheraga's, and Walrafen's theories.

assumed for 0°C, and to the fact that Nemethy and Scheraga consider partially bonded species as belonging to the bonded (structured) category, whereas Walrafen designates singly bonded molecules together with non-bonded molecules as the unstructured species.

**(** 

Although only pure liquid  $H_2^0$  has been considered by Walrafen to date, studies involving isotopic, electrolytic and non-electrolytic solutions are in progress or contemplated for the future. Qualitative agreements between calculated and measured values of entropies and heat capacities between 0 and 100°C have been obtained for  $H_2^0$ . No mention of transitional behaviour is made, but the appearance of nonbonded molecules first at 25°C might be relevant in this context. Clear evidence for broken hydrogen bonds is claimed from Raman spectra of intramolecular vibrations.

Absorption band assignment is particularly good by Walrafen's approach to liquid water structure. Essentially, it is as given in Table G-2.

#### 4. TEMPERATURE-INDUCED TRANSITIONS IN LIQUID WATER

From investigations of temperature effects on the Raman spectrum of liquid water, Magat (12) in 1937 concluded that higher order transitions were occurring in the properties of water at about 40°C. The concept of thermallyinduced transitions in water has been challenged ever since (14,27,28). The importance of this behaviour to the understanding of liquid water is apparent from the previous discussion on structure. Its possible biological significance has been pointed out by Oppenheimer and Drost-Hansen (29), Davey and Miller (30), and Ives and Lemon (31).

The most convincing evidence for transitions between about 30° and 40°C in liquid water comes from Raman (12) and infrared (32-34) spectral investigations. For the maximum infrared absorption of  $H_2O$  near  $1.15\mu$  (8700 cm<sup>-1</sup>), Luck (33) found that the displacement of the frequency with rising temperature was an order of magnitude greater between 36° and 38°C than anywhere else on the temperature scale. Salama and Goring (34) obtained a well-defined inflection at 32°C in the temperature dependence of the peak height of the 2125 cm<sup>-1</sup> absorption in  $H_2O$ . However, acceptance of the spectroscopic evidence for transitions in water is not universal: Falk and Kell (14), for example, believe that the discontinuities reported with near-infrared overtone bands are artefacts, arising from underestimation of experimental errors.

Transitional behaviour is not as evident in the bulk properties of pure water (14,27,28), but seems to be considerably sharpened in aqueous solutions of systems having a large interface with water (35-38). The transition is generally attributed to the onset of rotation of water molecules about their dipole axis (12,34). Hence it would not be expected to be as evident in investigations of bulk properties as it is in spectroscopic analyses carried out on the molecular level. That some of the discontinuities reported from near-infrared studies are, in truth, questionable may be due to the fact that optimum absorption bands were not selected for the investigation. Since the origin of the transition is thought to reside in rotational motion, investigations of the temperature dependence of infrared and Raman absorptions due to librations might be the most sensitive methods of detecting such transitions.

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#### 5. INFRARED AND RAMAN SPECTRA OF LIQUID WATER

In the vapour, where separations between molecules are large and interactions weak, water molecules move independently of one another. Nine essentially independent types of motion are possible for each molecule, namely translations in each of the three perpendicular directions, rotations about the three principal axes of inertia, and three vibrations symmetric and asymmetric stretching vibrations and a symmetric bending vibration. None of the translations nor rotation about the dipole axis involves change in dipole moment: hence these are infrared inactive modes. The remaining five modes give rise to fundamental infrared absorptions. The two rotations occur at low frequency, in the microwave region of the spectrum. The vibrations are of higher frequency, with absorptions at 1595 cm<sup>-1</sup> for the bending mode and at 3657 cm<sup>-1</sup> and 3756 cm<sup>-1</sup> for the symmetric and asymmetric stretching vibrations (39). In all the vapour absorptions a welldefined rotational fine structure is present.

Increasing molecular density by progressively increasing pressure broadens the rotational lines so, that at densities higher than 30 times that of water vapour at normal boiling conditions, the rotational fine structure is no longer observable (16).

In condensed water at normal pressures, absorption is continuous from at least 30 cm<sup>-1</sup> to over 4000 cm<sup>-1</sup>. No rotational fine structure is observable, and all bands are smooth and broad (39). Each of the three intramolecular vibrations of the vapour gives rise to an absorption band, but all are substantially shifted from their value with monomeric molecules. In ice at 0°C, the absorptions are at 1655  $\text{cm}^{-1}$  for the deformation (bending) mode and at 3370  $cm^{-1}$  and at 3270  $cm^{-1}$  for the fundamental stretching vibrations (40) while in liquid H<sub>2</sub>O absorption peaks at 1645 cm<sup>-1</sup> and between 3250 to 3630 cm<sup>-1</sup> are found at 25°C (41,42). With all these vibrations the ratio of  $H_2O$ frequency to D<sub>2</sub>O frequency is approximately 1.35, as expected from considerations of mass differences of hydrogen and deuterium atoms. Owing to the close proximity of neighbouring molecules and the presence of strong intermolecular forces, free rotations of monomeric molecules corresponding to those of the vapour are absent from the condensed state spectra. Instead, intermolecular modes which are absent from the vapour now give rise to absorptions, centered at 840 cm<sup>-1</sup> and at 229 cm<sup>-1</sup> in the infrared spectrum of ice (40), and at 685 cm<sup>-1</sup> and at 170 cm<sup>-1</sup> in the liquid (43). Deuteration causes a drop in frequency by a factor of 1.35 in the higher frequency band but hardly affects the lower (40,43): on this basis the former band has been assigned to restricted rotations (librations) and the latter to translations or lattice vibrations.

In ice, where there is long-range order of molecular position, the frequency spectrum can be interpreted, at least

theoretically, on fundamental principles of lattice dynamics and normal vibrations. Whalley has discussed the infrared spectrum of ice in detail in these terms (39). In contrast, the liquid state is completely disordered on a long time scale (microseconds). Yet, it is subject to strong intermolecular forces. Neither an "H<sub>2</sub>O molecule" nor a crystal lattice concept is entirely appropriate in describing it. The best classification of observed liquid frequencies is in terms of a tetrahedral group of C<sub>2V</sub> symmetry, X<sub>2</sub>YZ<sub>2</sub> type, on which Walrafen based his assignment (8,9). In Walrafen's model (8), the central H<sub>2</sub>O molecule is represented by Y, the outer H<sub>2</sub>O molecules, attached to Y by hydrogen bonds, by X and Z. The latter are assumed distinguishable on the basis of their orientation to Y. The model encompasses structures of  $C_{2V}$ ,  $C_2$  and  $C_1$  symmetry, which differ by rotations of the outer  $H_2O$  molecules about the O-H···O units of identical length. A slightly different version of a  $C_{2V}$  model, also of  $X_2YZ_2$ symmetry for tetrahedrally bonded water, and one which is simpler to correlate to normal vibrations, is shown in Fig. G-4. This model differs from Walrafen's in that orientation of outer molecules does not affect the symmetry. Y now represents the central oxygen atom, X the hydrogen bonds attached to it to form a normal water molecule, and Z the two protons hydrogen bonded to Y.

There are nine possible fundamental modes of vibration possible for a species of  $X_2YZ_2$  symmetry. Three correspond

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# FIGURE G-4. C<sub>2V</sub> model of X<sub>2</sub>YZ<sub>2</sub> symmetry for structured liquid water molecule.

essentially to symmetric and asymmetric stretching and symmetric bending vibrations of the  $X_2Y$  portion (O-H bonds), three to similar vibrations of the  $YZ_2$  portion (O···H bonds), and the remaining three to oscillations about the three principal axes, of which torsion about B, or the dipole axis, is infrared forbidden.

In Table G-2, observed infrared and Raman absorption


## TABLE G-2

Absorption Band Assignment for Liquid  $H_2O$  and  $D_2O$ 

$(cm^{-1})$ H <sub>2</sub> O					(cm <sup>-1</sup> ) D <sub>2</sub> O	
IR		<b>Polarization</b>	Species	Vibration	IR	R
3625 <sup>(1)</sup>	3622 (4)	pol	u	asym str	2680 <sup>(5)</sup>	2662 (6)
	3535 (4)	pol	u	sym str		
3410 <sup>(1)</sup>	3435 (4)	pol	S	O-H asym str	2515 <sup>(5)</sup>	2515 <sup>(6)</sup>
3250 (1)	3247 <sup>(4)</sup>	pol	S	O-H sym str	2360 (5)	2363 (6)
2125 (2)	2130 <sup>(5)</sup>	-	S		1555 (2)	1600 <sup>(6)</sup>
1645 <sup>(2)</sup>	1645 <sup>(4)</sup>	depol	S	H-O-H bend	1215 (2)	1235 <sup>(6)</sup>
(3)	722 (4)	depol	s	torsion		550 <sup>(7)</sup>
685 (**	475 <sup>550 (4)</sup>	depol	S	torsion	505 <sup>(3)</sup>	375 <sup>(7)</sup>
	450		S	torsion about B (IR forbid)		
170 <sup>(3)</sup>	166 <sup>(4)</sup>	pol	S	H-bond str	165 (3)	175 <sup>(7)</sup>
	60 <sup>(4)</sup>		S	H-bond bend		60 (7)

(1) ref. 42; (2) ref. 41: (3) ref. 43: (4) ref. 9: (5) ref. 39: (6) ref. 44: (7) ref. 8.

U = unstructured; s = structured.

frequencies of liquid water are listed, together with assignments based on this  $C_{2V}$  model for structured water. Raman polarization ratios, also given in the table, agree with the assignments. The Raman spectrum of liquid  $D_2$ 0 has not yet been analyzed in the same detail as that of  $H_20$ , and band positions in it are in some cases tentative.

Based on the observations that their intensity increases on temperature increase in both the infrared and Raman for liquid H<sub>2</sub>O, the highest frequency stretching bands have been assigned to non-bonded species by Walrafen. Hence these maxima correspond closest to absorptions by vapour-type of molecules. All other vibrations listed are due to structured water molecules. The stretching bands below 3460  $\rm cm^{-1}$ in H<sub>2</sub>O decrease in intensity on temperature increase, as expected for decreasing concentration of bonded species on temperature elevation. The deformation band at 1645  $\rm cm^{-1}$  in  $H_2O$  and at 1215 cm<sup>-1</sup> in  $D_2O$  has the most straightforward assignment. In the region of restricted rotations between about 200 to 800 cm<sup>-1</sup>, one absorption maximum is evident in the infrared spectrum and two in the Raman. However, the lower, 475 cm<sup>-1</sup>, Raman band in  $H_0$  has been successfully resolved by Walrafen into two components, the more intense at about 450  $cm^{-1}$  and the weaker at 550  $cm^{-1}$ . Experimental resolution of low frequency D20 bands has not been attempted, but the similarity of absorption contours in both isotopes of water strongly suggests that the 375  $\text{cm}^{-1}$  Raman band in  $\text{D}_2\text{O}$  is also

(8)

a composite band. Rough analysis showed that components at 450 cm<sup>-1</sup> (weak) and at 350 cm<sup>-1</sup> (stronger) could be expected from it. Together with the 722 cm<sup>-1</sup> absorption (550 cm<sup>-1</sup> in  $D_2O$ ), the three librational modes expected for liquid water from a  $C_{2V}$  model are thus present in the Raman spectrum. In the infrared spectrum, only one absorption maximum at 685 cm<sup>-1</sup> in  $H_2O$  and at 505 cm<sup>-1</sup> in  $D_2O$  is observed. This band has not been resolved into components, but it is decidedly asymmetric (45) and very likely corresponds to the 550 and 722 cm<sup>-1</sup> Raman absorptions (450 and 550 cm<sup>-1</sup> in  $D_2O$ ), to which it is intermediate. The Raman component at 450 cm<sup>-1</sup> (350 cm<sup>-1</sup> in  $D_2O$ ), corresponding to librations about the dipole axis, appears to be absent from the infrared as required by  $C_{2V}$  symmetry.

The lowest frequency bands absorb at the same frequency in both  $H_2O$  and in  $D_2O$ . The one at about 170 cm<sup>-1</sup> has been assigned to hydrogen bond stretching vibrations. No absorption at 60 cm<sup>-1</sup> has been reported in the infrared, whereas a band in this region has been observed in both Raman and neutron scatter experiments (10), leaving little doubt of its reality. It has been assigned to a hydrogen bond bending vibration.

The reasonably complete interpretation of the spectroscopic frequency data by the  $C_{2V}$  model may be compared with the limited success in this respect of the treatment by Nemethy and Scheraga. Their assignment of low frequency absorp-

tions combined frequency data obtained from both the solid and liquid states, and from both the Raman and infrared spectra. It is reproduced in Table G-3.

Considering the highly accessible region of the spectrum at which the band at 2125 cm<sup>-1</sup> (1555 cm<sup>-1</sup> in  $D_2O$ ) absorbs, and its relatively large separation from neighbouring absorptions, the little that has been investigated about this band is somewhat surprising. It is an intermolecular band, being absent from the vapour spectrum. It is also highly sensitive to changes in temperature. Generally it has been considered a combination band, involving the deformation mode with a librational mode. The absence of a librational absorption of the necessary frequency in the infrared spectrum has led some to speculate on its being a fundamental mode (43) and others to account for it as a sum and difference band (46). Still others suggest for its origin the second overtone of the observed far infrared libration. With the latter assignment, a discrepancy is evident on comparing the Raman and infrared spectra: whereas the frequency of maximum absorption of this band is almost identical in the Raman and infrared, the observed librational regions differ markedly in the two. However, the band might be a combination involving the deformation mode and the libration about the dipole axis, now resolved at 450 cm<sup>-1</sup> in H<sub>2</sub>O and expected at about 350 cm<sup>-1</sup> in D<sub>2</sub>O. Since forbidden fundamentals can give rise to active overtone and

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## TABLE G-3

Low Frequency Band Assignment According to

Nemethy and Scheraga (6)

	<sup>H</sup> 2 <sup>O</sup>	D <sub>2</sub> O	Species*	State
rotations	800	600		
	650	460	4,3	
	500	360		
	450	320	2	
	60	42	1	
	175	130	1 0 11	liquid
	145	105	1,2,0	liquid
translations	160	150	1,2	solid and liquid
	210	200	3,4	solid and liquid

\*Numbers in column refer to number of hydrogen bonds.

 $U \equiv$  unbonded molecules.

combination bands, the band's presence in the infrared spectrum is accounted for. The frequencies expected for it with such an assignment are 2095 cm<sup>-1</sup> in  $H_2^0$  and 1565 cm<sup>-1</sup> in  $D_2^0$ , quite close to the observed values of 2125 cm<sup>-1</sup> and 1555 cm<sup>-1</sup>.

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With the above assignment, onset of rotational motion about the dipole axis of a water molecule could be expected to have noticeable effects on this band, equalled only by effects on the 450 cm<sup>-1</sup> (350 cm<sup>-1</sup> in  $D_2$ O) Raman band. The latter has not been investigated: in the present work the former is examined.

## 6. BAND SHAPE ANALYSIS

The interpretation of infrared spectroscopic information is almost always based on the correlation of absorptions in a spectrum to particular vibrating groups undergoing particular vibrations. This aspect of the liquid water spectrum was dealt with in the preceding subsection. However, in recent years it has been recognized that shapes of liquid-phase absorption bands are related to the environment and nature of the motion of the absorbing molecules, and more attention is being paid to this aspect of spectroscopy. A considerable amount of theoretical work on spectral densities has been done by Shimizu (47), Gordon (48), and Voorhof and Pollak (49). A more experimentally-oriented approach to the problem has been followed by Jones (50,51), Crawford (52), and Waggener (53,54).

Finite line widths of infrared absorptions in the vapour are due principally to (a) radiation damping, (b) Doppler broadening, and (c) perturbations by neighbouring molecules. General discussions of these effects have been given by Seshadri and Jones (50) and others (55); hence the present discussion will be limited to a consideration of their effects on band shape.

Radiation damping leads to a Cauchy-shaped profile<sup>1</sup>, given by

$$y_{(C)} = \frac{a}{b^2 + x^2}$$
 (1)

<sup>1</sup>Often also called a "Lorentz" profile; see however p.1023, ref. (50).

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where 2b is the band width at half maximum height and  $a/b^2$  is the peak height, with x measured from the band centre. The Doppler effect, resulting from the thermal motion of molecules, has a Gauss form

$$y_{(G)} = \frac{a}{b^2} \exp\left(-\frac{x^2(ln2)}{b^2}\right)$$
 (2)

The two contours are compared in Fig. G-5 for equal heights and widths. The widths associated with these effects are less than  $10^{-3}$  cm<sup>-1</sup>, however, and too narrow to account for the 5 to 550 cm<sup>-1</sup> wide bands observable in condensed (liquid) systems. Thus perturbation by neighbouring molecules has been considered the major contributor to band widths, hence shapes, of these systems. If a statistical distribution of perturbation is assumed - i.e., a homogeneous, isotropic environment for the absorbing molecule - the shape of the broadened band may be represented by a Cauchy profile (equation 1). For non-interacting systems, conforming to the above conditions, the agreement obtained by fitting Cauchy curves to experimental curves is good, as shown by the results of Waggener et al. (54) for infrared overtone bands of liquid CO<sub>2</sub>, given in Fig. G-6.

Where more specific interactions occur between molecules, as in the case of solute-solvent interactions or with polar liquids, the resultant distribution is no longer adequately described by a pure Cauchy equation. Under such circumstances, Jones (50,56) has suggested a Gaussian com-



FIGURE G-5. Comparison of profiles of Cauchy and Gauss curves of equal peak height and half-width.

ponent would be present in the contour. Band envelopes intermediate to Cauchy and Gaussian have been obtained by Baker, Kerlinger and Shulgin (57), for example, for liquid phenols perturbed by the solvent.

Rotational motion of molecules or molecular groups also affects the shapes of liquid-phase absorption bands, causing deviations from a Cauchy contour (48,50,52,56). For



FIGURE G-6. Comparison of Cauchy curves and experimental curves for overtone bands of liquid CO<sub>2</sub> (from Waggener, Weinberger and Stoughton (54)).

a solution of methyl bromide in carbon tetrachloride, Jones and Sheppard (58) have demonstrated that observed widening of some bands is suggestive of the methyl group rotating about the C-Br bond. Investigators using a harmonic oscillator model to derive analytical expressions for contours of absorption bands have obtained a Gaussian function (49,59).



Hence, an analysis of band shapes might lead to information about both interactions and rotations of molecules in the liquid state.

This method of obtaining structural information about water has been almost totally ignored to date. Only in the recent investigation reported by Waggener, Weinberger and Stoughton (53) for near-infrared absorption bands of liquid water has contour shape analysis been carried out. In two other investigations, pure Gauss contours were used. In one by Luck (17) of liquid HDO overtone bands, comparison of experimental and calculated curves was not made. The other, by Ikawa and Maeda (59), involved libration bands of ice. In the latter, fits to experimental data were not too good. In neither was any significance placed on the actual mathematical function of the theoretical band profile.

For band shape analysis on liquid water, the intermolecular combination band is well suited. Its wide, smooth, Contour minimizes the accuracy to which spectral indices must be obtained, thus simplifying the experimental aspect of the band-fit procedure. From previous determinations of its frequency and peak height temperature dependencies (34,43), it is known to be sensitive to changes in environmental conditions. Its origin is related to (restricted) rotational motion, very likely to rotations about the dipole axis of the molecule as discussed in subsection 5. Hence, any effects on band shape due to environmental changes or advent of rotation **~**0



about the dipole axis should be evident from examining the temperature dependence of the combination band contour.

#### 7. SCOPE OF THE PRESENT INVESTIGATION

In the present work the temperature dependence of the 2125 cm<sup>-1</sup> and 1555 cm<sup>-1</sup> infrared absorption bands of liquid  $H_2O$  and  $D_2O$  respectively have been studied and findings are reported in Parts I to IV of the thesis. Part I deals with qualitative and quantitative shifts with temperature of the infrared parameters of peak height, frequency and halfwidth for these bands. Polynomial curves have been fitted to the data, and evidence for transitional behaviour is examined.

In Part II, effects of temperature on the intermolecular combination band and the intramolecular deformation band of  $H_2O$  and  $D_2O$  are compared with effects of hydrogenbond formation on restricted rotation and bending modes in general. Overlap of varying proportions of two synthetic Cauchy contours, with relative infrared parameters simulating quantities for bonded and unbonded species undergoing restricted rotations, is compared with observed effects of superimposing the combination band contours at different temperatures. The nature of the isosbestic obtained with this band is discussed in qualitative terms.

Part III deals with analysis of the shapes of the combination and deformation bands as carried out with the help of computer programmes recently developed by Dr. R.N. Jones of the National Research Council. Cauchy-Gauss product functions are fitted to digitized experimental data, and results are interpreted qualitatively using prevailing theories of condensed system absorption contours and of liquid water structure.

In Part IV spectral support for an absorption occurring between the librational and deformation bands in both  $H_2O$  and  $D_2O$  is presented. Temperature effects on the  $H_2O$  band are given and an assignment of the band is made.

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PART I Temperature Dependence of the 2125 cm<sup>-1</sup> and 1555 cm<sup>-1</sup> Infrared Absorption Bands in Liquid  $H_2O$  and  $D_2O$ : Thermally Induced Transitions.

#### ABSTRACT

The temperature dependence curves of the peak height, frequency and half-width of the infrared intermolecular combination bands absorbing at 2125 cm<sup>-1</sup> (25°C) in liquid  $H_20$  and at 1555 cm<sup>-1</sup> in liquid  $D_20$  have been observed to behave sigmoidally between 5° and 70°C, and have been best fitted by calculated polynomials of  $3^{rd}$ degree. No convincing evidence of sharp discontinuities has been obtained but transitional behaviour in the rather broad temperature interval of about 30° to 40°C is supported. Results are discussed in terms of structural changes occurring in the liquid.

#### 1. INTRODUCTION

In an earlier infrared study of the intermolecular  $2125 \text{ cm}^{-1}$  absorption band in liquid water (1), a well defined inflection point at 32°C was obtained on plotting the peak height versus temperature. There was no clear evidence for a similar effect in the temperature dependence of the frequency, but the data indicated the possibility of an inflection between 30 and 40°C.

Whether there is acceptable evidence for the existence of higher order transitions in liquid water has been a subject of controversy for some time. Numerous authors have reported the presence of anomalies in the temperature dependence of certain properties of water (1-9): however, there are others claiming all such effects are artefacts and that no discontinuities beyond the experimental error are evident (10-13). Nevertheless, the persistence of reports of anomalous behaviour especially between 30 and  $40^{\circ}$ C from spectral, volume, viscosity and other types of studies lends some validity to the concept of a transition in liquid H<sub>2</sub>O.

The purpose of the present work was to re-investigate the effects of temperature on the peak height and the frequency of the 2125 cm<sup>-1</sup> IR absorption band of liquid  $H_2O$ , and to obtain the thermal dependences of its intensity and half-width. In addition, measurements were made on the corresponding band in liquid  $D_2O$  absorbing at 1555 cm<sup>-1</sup>. Spectra were recorded between 5 and 70°C and at least one deformation band contour was included at each temperature.

2. EXPERIMENTAL

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#### 2.1 Infrared Measurements

Infrared spectra were recorded linearly in percent transmission and wavenumber with a Unicam SP-100G double beam vacuum grating spectrophotometer. During runs, the sample and reference cell wells were purged with dry nitrogen. All spectra were recorded with an empty reference cell well, and a sample cell with CaF<sub>2</sub> windows. Lead shims used as spacers were amalgamated with mercury to make tightly sealed liquid cells. Path lengths, chosen to give combination band peaks of about 50 to 60% transmission, were measured by the interference pattern method (14) and checked frequently but found to remain unchanged for the duration of the experimental work. With H<sub>2</sub>0 the sample thickness was  $0.00116 \pm 2 \times 10^{-5}$  cm. and with D<sub>2</sub>0 it was  $0.00160 \pm 2 \times 10^{-5}$  cm. One cell was used throughout for studies on H<sub>2</sub>0, another for D<sub>2</sub>0.

For temperature control, the CaF<sub>2</sub> cell was placed in a tightly fitting water jacket through which circulated a dilute water-glycol solution from a control bath. The sample temperature was measured with a copper-constantan thermocouple calibrated before use, one end of which was dipped into an oilfilled cone-shaped hole in one window of the cell, the other into an oil-filled test tube placed into an ice-bath. The thermocouple tip was approximately  $1/8^{th}$  inch from the liquid sample. The temperature of the sample as read on a millivolt-meter could be determined to + 0.3°C.

The samples were double-distilled  $H_2O$  passed through a Rexyn I-300 (HOH) ion exchange column and 99.7%  $D_2O$  from Merck, Sharp and Dohme. The  $D_2O$  samples were checked for HDO content by measuring the HDO absorption at 3400 cm<sup>-1</sup>. Calculations showed that HDO content was never greater than 1.0%. The air-tightness of the cells was verified by observing only a 1% decrease in transmission in the 3400 cm<sup>-1</sup> absorption band in a  $D_2O$  sample over a period of 26 hours (15). This corresponded to a change in concentration of less than 0.1% HDO.

The liquid cells were filled by injecting the sample quickly from a needleless sterile syringe that fitted tightly into the filling port of the cell. With this method, no air bubbles were found in the cell and no loss of sample due to evaporation occurred at elevated temperatures.

The number of spectra taken of the combination band region at each temperature averaged four. For the deformation region one or two spectra only were recorded. Scan times used were from 50 to 80 cm<sup>-1</sup> per minute. Spectra of  $CaF_2$  windows were recorded at varying temperatures but no trends with temperature were noted: thus the effects due to window materials were assumed to remain constant. Losses due to scattering and reflection amounted to about 10%T.

(2)

The infrared spectrophotometer was calibrated with water vapour absorption lines and liquid indene. Frequency calibrations are accurate to  $\pm$  1.0 cm<sup>-1</sup>. Reproducibility was checked by taking standard spectra of a polystyrene film.

The instrument was operated with automatic slit programming resulting in spectral slit widths of 2.0 to 5.5 cm<sup>-1</sup> (15). The effect of finite slit widths on recorded absorption spectra was investigated for it is known that observed infrared band contours are dependent on spectral slit widths (16). For the deformation bands

$$s/\Delta v_{1/2}^{a} \simeq 1/25$$

and for combination bands

$$s/\Delta v_{1/2}^{a} = 1/80$$
 ,

where s is the spectral slit width and  $\Delta v_{1/2}^{a}$  the apparent or observed band half-width, both measured in wavenumbers. According to calculations based on the tables of Ramsay (17) and of Roesler (18) these ratios were too small to have any observable effects on band contours. This was demonstrated experimentally by recording spectra using manual slit controls set at openings narrower and wider than those of the automatic programme. Hence no corrections for finite slit widths have been made in this investigation.

Due to the nature of the Unicam SP-100G, a change in controls is necessary at 2150  $\text{cm}^{-1}$ , resulting in a discontinuity in recorded spectrum at this point. For the range 41

(1)

650 to 2150 cm<sup>-1</sup> the instrument operates with a NaCl prism and a grating of 1500 lines per inch used in the first order and blazed at 1250 cm<sup>-1</sup>. For the range 2150 to 3650 cm<sup>-1</sup> a NaCl prism and a grating of 3000 lines per inch used in second order and blazed at 3000 cm<sup>-1</sup> is used. The maximum difference in observed transmittance at 2150 cm<sup>-1</sup> was 0.5%T with an average difference of less than 0.1%T.

#### 2.2 Analytical Methods

(33)

The major features of liquid water transmittance curves in the frequency range investigated (900-2700 cm<sup>-1</sup>) are shown in Fig. I-1. The sharp intense band,  $v_2$ , centred at 1645 cm<sup>-1</sup> in  $H_2O$  (1215 cm<sup>-1</sup> in  $D_2O$ ) arises from the fundamental intramolecular deformation mode (19). The less intense broad band overlapping the high frequency wing of the deformation band and with maximum absorption at 2125  $\text{cm}^{-1}$  (1555  $\text{cm}^{-1}$ in  $D_2O$ ) is due to intermolecular restricted rotation. It is most generally assigned to a combination of the deformation mode with a lower frequency librational mode (19,20), and is designated  $v_{2+1}$ . Incomplete double beam cancellation leads to CO<sub>2</sub> absorption at approximately 2400 cm<sup>-1</sup>: this region is shown with a dotted line in Fig. I-1. Also shown is the background curve arising from CaF, cell windows. The liquid water spectra after correction for window effects are shown by the In all measurements window effects have been dashed lines. taken into account.



FIGURE I-1. Infrared absorption curves of liquid  $H_2^0$  and liquid  $D_2^0$  showing effect of correction for  $CaF_2$  windows.

The frequency of maximum absorption of the broad combination band was determined by the method illustrated in Fig. I-2. A tracing of the recorded band contour was inverted and superimposed on the original spectrum with maximum overlap of the two curves. A base-line PQ was drawn between the two minima and a perpendicular drawn from its midpoint R to



FIGURE 1-2. Schematics of  $v_0$  determination for the combination band.

intersect the original spectrum at S. The frequency at S was then measured in wavenumbers and called  $v_0$ . For the much sharper deformation mode,  $v_0$  was read directly from the recorded spectrum.

In determining both the extinction coefficient and the half-width of the bands, the minimum on the high frequency side of the combination band was taken as base-line transmittance,  $T_0$ . The molecular extinction coefficient at maximum absorption,  $\varepsilon_{max}$ , was derived from (21)

$$\varepsilon_{\max} = \frac{1}{ct} \log_{10} \left( \frac{T_o}{T} \right)_{v_o}$$
(2)

where T is the transmittance at frequency  $v = v_0$ , t is the thickness of the absorbing layer and c is the concentration of the absorbing species: c has a value of 55.34 moles/l for H<sub>2</sub>O and 55.14 moles/l for D<sub>2</sub>O (22).

In determining half-widths of H<sub>2</sub>O spectra recorded above 57°C, the low frequency side of the combination band was extended to compensate for overlap with the deformation band. Deformation band half-widths were measured only at ambient temperature.

The peak height,  $\Delta T_m$ , of the combination band of liquid H<sub>2</sub>O was determined previously (1) from the interval between the minimum and the maximum transmittance of the band on its low frequency side, without compensation for window effects. This measurement is affected in both waters by the increasing degree of overlap of the combination and deformation bands on increasing temperature, and in D<sub>2</sub>O by the curved base-line resulting from significant CaF<sub>2</sub> absorption in the vicinity of its combination band. In the present work,  $\Delta T_m$ corresponded to the difference in transmittance between the minimum and the maximum on the high frequency side of the combination band, after correction for window effects.

The experimental standard deviations of the various infrared parameters determined for the combination band are given in Table I-1. The greater experimental error in the extinction coefficient and half-width of  $H_2O$  over that of  $D_2O$  is due to the changes in operating conditions required at 2150 cm<sup>-1</sup> in the Unicam SP-100G. The experimental standard deviation of  $v_O$  for the deformation band was  $\pm 1.0$  cm<sup>-1</sup>.

#### 3. RESULTS

The temperature dependence of the peak height obtained for liquid  $H_2O$  and  $D_2O$  is shown in Fig. I-3. For comparison, the data of Salama and Goring (1) are also plotted in the figure. The close similarity in the peak height behaviour of the two isotopes of water is apparent. Both showed a marked decrease with increase of temperature and a change of slope near the middle of the temperature range.

Observed frequencies of maximum absorption in light and heavy water are shown in Fig. I-4 together with values taken from the literature for which temperatures have been cited. Qualitatively, the large decrease in frequency with increasing temperature is well documented. Quantitatively, between 5 and 70°C we calculated an overall shift of about  $-1.0 \text{ cm}^{-1}/\text{C}^{\circ}$  for liquid H<sub>2</sub>O, in good agreement with the magnitude obtained from Salama and Goring's (1) data, and by Draegert et al. (20) who calculated a shift of about  $-0.9 \text{ cm}^{-1}/\text{C}^{\circ}$  for H<sub>2</sub>O between 5 and 75°C. For heavy water, Draegert was

	]	Parameter	Exp. Std. Dev.	Calc. η = 1	Std. η = 2	Dev. η = 3	Deg. of Best-fit Polynomial	Calc. Inflection Temp. (°C)
<sup>н</sup> 2 <sup>0</sup>	∆T*m	(%T)	0.15 <sup>†</sup>	0.49	0.51	0.35	3	40
	∆T <sub>m</sub>	(%T)	0.2	0.25	0.16	0.15	3	55
	νο	(cm <sup>-1</sup> )	1.5	3.8	3.7	2.1	3	39
	€ max	(l.mole <sup>-1</sup> cm <sup>-1</sup> )	0.025	0.04	0.03	0.03	2	-
	<sup>Δν</sup> 1/2	(cm <sup>-1</sup> )	5.0	4.6	4.6	4.4	3	42
<sup>D</sup> 2 <sup>O</sup>	∆T <sub>m</sub>	(%T)	0.2	0.25	0.24	0.19	3	38
	vo	(cm <sup>-1</sup> )	1.5	3.1	2.3	0.5	3	26
	<sup>€</sup> max	(1.mole <sup>-1</sup> cm <sup>-1</sup> )	0.01	0.02	0.02	0.01	3	38
	<sup>Δν</sup> 1/2	(cm <sup>-1</sup> )	2.5	2.9	2.4	2.2	3	31

### TABLE I-1

Experimental Errors and Characteristics of the Polynomials Best Fitting the Temperature Dependent Infrared Parameters of the Liquid Water Combination Band

\* Salama and Goring's data points (1).

t mean standard deviation.



FIGURE I-3. Peak heights versus temperature for the combination band of liquid H<sub>2</sub>O and D<sub>2</sub>O. The data of Salama and Goring (1) measured on the low frequency side of the band are included for comparison. The curves are the calculated best fit polynomials.

unable to obtain a value because of overlap of the  $D_2O$  combination band with the strongly absorbing HDO deformation band at 1460 cm<sup>-1</sup>. The air-tightness of the present cells eliminated



FIGURE I-4. Frequency versus temperature for the combination band of liquid H<sub>2</sub>O and D<sub>2</sub>O. The curves are the calculated best fit polynomials. The numbered crosses are from the literature as follows: 1. Fox and Martin<sup>23</sup> 2. Bayly, Kartha and Stevens<sup>22</sup> 3. Draegert, Stone, Curnette and Williams<sup>20</sup> 4. Salama and Goring<sup>1</sup>

interference by HDO, and an overall frequency shift of about  $-0.8 \text{ cm}^{-1}/^{\circ}\text{C}$  was obtained for liquid  $D_2O$ .

In Fig. I-5 the temperature dependence found for the extinction coefficients of the combination bands are given. As would be expected, the behaviour of  $\varepsilon_{\rm max}$  is similar to that of peak height in that a marked decrease accompanied temperature elevation. In contrast to the other infrared parameters measured, the half-width of the combination band increased on temperature elevation for both H<sub>2</sub>O and D<sub>2</sub>O, as shown by Fig. I-6.

Since the half-width is increasing with temperature, the decrease in  $\varepsilon_{max}$  shown in Fig. I-5 does not necessarily mean a decrease in absorption intensity. An approximate evaluation of the intensity of the absorption could be obtained by calculating the band area from

Area = 
$$K \cdot \epsilon_{max} \cdot \Delta v 1/2$$
 (ref. 24) (3)

in which the proportionality factor K has a value of 1.57 for a pure Cauchy (Lorentz) absorption profile and 1.06 for a pure Gaussian profile (24). For the intermolecular combination band of both isotopes of water, the actual shape of the band contour was found to be temperature dependent (25). However, it was possible to characterize the extent to which each absorption band profile was Cauchy or Gaussian in character and thus to determine at each temperature a K value (15) from which the band area could be calculated by equation 3. In this manner, it was found that the combination band intensity decreased non-linearly



FIGURE I-5. Maximum molecular extinction coefficient versus temperature for the combination band of liquid  $H_2O$  and  $D_2O$ . The curves are the calculated bestfit polynomials.

with rising temperature, by about 20% in liquid  $H_2O$  and 30% in liquid  $D_2O$  between 5 and 70°C.

The infrared parameters of the deformation bands absorbing at 1645 cm<sup>-1</sup> and 1215 cm<sup>-1</sup> in  $H_2O$  and  $D_2O$  respectively were found, in agreement with previous reports (26), to be



FIGURE I-6. Half-width versus temperature for the combination band of liquid  $H_2O$  and  $D_2O$ . The curves are the calculated best-fit polynomials.

but slightly affected by temperature. Observed frequency trends are shown in Fig. I-7 together with values taken from the literature. The magnitude of the shift was about -0.1  $cm^{-1}/C^{\circ}$  for both isotopes, in good agreement with Draegert et al. (20). With increasing temperature the maximum extinction coefficient was observed to increase slightly.



FIGURE I-7. Frequency versus temperature for the deformation band of liquid H<sub>2</sub>O and D<sub>2</sub>O. The numbered crosses are from the literature as follows: 1. Fox and Martin<sup>23</sup> 2. Bayly, Kartha and Stevens<sup>22</sup> 3. Draegert, Stone, Curnette and Stevens<sup>20</sup> 4. Salama and Goring<sup>1</sup> 5. Falk and Ford<sup>27</sup>


Ratios of the measured infrared parameters in  $D_2^0$  to those of  $H_2^0$  at 25°C are given in Table I-2. These agree fairly well with similar ratios obtained from the data of Bayly, Kartha and Stevens (22). Thus the generally good agreement between our results and the literature data shown in Figs. I-4 and I-7 and in Table I-2 supports the validity of the recording and analytical techniques used in the present investigation.

#### 4. DISCUSSION

#### 4.1 Transitional Behaviour

The first question to be discussed is whether or not the data collected indicate the presence of a transition in liquid water. Analysis of the fine structure of the temperature dependence of the combination band parameters reveals sigmoidal behaviour in all but one of the nine trends shown in Figs. I-3 to I-6. The sigmoidal effect is particularly evident with peak height and frequency (cf. Figs. I-3 and I-4). It is absent from the  $\varepsilon_{max}$  versus temperature curve for liquid H<sub>2</sub>0. However, instrumental errors arising from the necessity of changing gratings at 2150 cm<sup>-1</sup> would be expected to have a marked effect on this parameter and might be obscuring the inflection.

Sigmoidal behaviour was not apparent in the frequency versus temperature plots shown in Fig. I-7 for the deformation band. Here the total shift in frequency between 5 and 70°C is **J**4

## TABLE I-2

	Combinat:	ion Band	Deformation Band		
Parameter	Present Work	Bayly et al. (22)	Present Work	Bayly et al. (22)	
v <sub>0</sub> <sup>D2O</sup> H2O v <sub>0</sub> /v <sub>0</sub>	738	738	748	74୫	
D20 H20 emax emax	55%	54%	66%	77%	
	74%	648*	-	-	

Effect of Deuteration on the Infrared Parameters of Liquid Water, at 25°C

\*  $\Delta v_{1/2}$  measurement approximate only.

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only 1/10<sup>th</sup> that of the combination band and thus any similar effects could be expected to be too minute for detection.

A quantitative characterization of the temperaturedependence curves of the combination band was obtained on an IBM 360/50-360/75 computer by fitting polynomials of the form

$$P = A_0 + A_1 T + A_2 T^2 + \dots A_n T^n$$
 (4)

to the experimental data points by the method of least squares. In equation 4, P represents the infrared parameter under investigation,  $A_0$ ,  $A_1$ ,  $A_2$ ,  $A_n$  are the coefficients, T is the temperature in °C, and n is the degree of the polynomial. Goodness of fit was tested for by comparing the estimated variance about a polynomial of degree n with that of the n+1 degree polynomial: whichever n value gave the smallest variance was taken as the degree of the polynomial giving the best approximation of experimental data. An estimation of the standard deviation of the computed curve from the experimental points was obtained by calculating the square root of this variance.

The best fitting polynomial curves thus obtained are drawn in the appropriate Figs. I-3 to I-6 and their coefficients listed in Table I-3. The calculated "standard deviations" for polynomials of degree one to three are given in columns 3 to 5 of Table I-1. For all but one of the nine parameters of the combination bands ( $\varepsilon_{max}$  versus temperature for H<sub>2</sub>O) the analysis showed that best fit was achieved with

## TABLE I-3

Coefficients of Best-fit Polynomials, in the Expression P =  $A_0 + A_1T + A_2T^2 + A_3T^3$ 

	. <u></u>	P	A	A_1	$\frac{A_2 \times 10^2}{2}$	$A_3 \times 10^4$
<sup>н</sup> 2 <sup>0</sup>	∆T*m	(%T)	19.1	-0.28	0.52	-0.44
	∆T <sub>m</sub>	(%T)	30.6	-0.15	0.17	-0.10
	vo	(cm <sup>-1</sup> )	2163.3	-2.80	6.14	-5.25
	€ max	$(1.moles^{-1}cm^{-1})$	2.66	-0.0126	0.0057	-
	<sup>∆v</sup> 1/2	(cm <sup>-1</sup> )	312.7	1.87	-3.45	2.77
<sup>D</sup> 2 <sup>O</sup>	∆T <sub>m</sub>	(%T)	24.9	-0.18	0.30	-0.26
	vo	(cm <sup>-1</sup> )	1575.3	-1.43	3.46	-3.86
	ε <sub>max</sub>	(l.moles <sup>-1</sup> cm <sup>-1</sup> )	1.57	-0.012	0.0193	-0.017
	<sup>Δν</sup> 1/2	(cm <sup>-1</sup> )	222.8	1.71	-2.64	2.03

\* Salama and Goring's data points (1).

a third degree polynomial. On going to a fourth degree polynomial the fit again became poorer. The temperatures calculated from the coefficients of the third degree polynomial curves for their points of inflection are given in the last column of Table I-1. In six cases these fell between 31° and 42°C. Only two were outside this range, one low at 26°C and the other high at 55°C.

It must be admitted that the validity of any individual temperature-dependence trend shown in Figs. I-3 to I-6 is somewhat open to question. However, the combined observations for almost all the infrared parameters of

1) sigmoidal behaviour with temperature,

2) best fit to experimental points by a third degree equation, and 3) a calculated inflection temperature close to the 30° tc 40°C temperature region suggests that transitional behaviour is manifest in both light and heavy liquid water.

It is important to note that the shapes of the temperature-dependence curves show that the transition taking place is a gradual one. As Falk and Kell (11) noted, there is no convincing evidence for sharp kinks or sudden discontinuities over a narrow temperature range in the pure liquid. Rather, the data show the first derivative to be changing slowly with temperature to give a broad minimum in a temperature range covering at least  $100^{\circ 1}$ . It is interesting to note that broad

It is possible that in systems which have a large interface with water the inflection is sharpened considerably to give fairly sudden changes over a much narrower temperature range. The prevalence of such transitional behaviour in interface water has been suggested recently by Drost-Hansen (29,30)

inflection regions in plots of infrared transmission versus temperature have recently been shown to be associated with glass transition behaviour in amorphous polymers (28).

## 4.2 Interpretation of Trends

At this stage it is possible to attempt a qualitative explanation of the trends observed in terms of the "mixture" concept of liquid water. Walrafen (34,35) has given a good description of the two major species in a mixture model. The structured component consists of an assembly of water molecules of C<sub>2v</sub> symmetry held in regular array by tetrahedral hydrogen bonding and resembling ice on a local scale. These are in equilibrium with an unstructured component in which molecules are not bound by the directional covalent interactions usually associated with hydrogen bonding but by other forces. The equilibrium is readily shifted in the direction of unstructured molecules by increase of temperature. For all the lower frequency intermolecular absorption bands of water he has investigated by Raman spectroscopy, Walrafen (37) has found a large intensity decrease with temperature increase, which he has attributed to a decrease in the concentration of structured component. A similarly large decrease was observed in intensity on raising temperature for the intermolecular combination bands of  $H_2O$  and  $D_2O$ , and, as shown elsewhere (36), and may account for the transitions observed in carbohydrate-

water systems (31,32), and in dilute acid solutions (33).

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has been accounted for by a decrease in structured species with a simultaneous increase in unstructured species, in agreement with Walrafen's interpretation.

In Walrafen's model, increase of temperature causes 'melting' of the structured component which is initially the more rapid but slows down somewhat at higher temperatures (37). A similar qualitative picture of structure disruption by temperature elevation in liquid water is obtained from numerous other mixture models, for example from the cluster models of Nemethy and Scheraga (38) or of Buijs and Choppin (39). This type of behaviour would be expected to give a monotonic decrease in the first derivative of a species-dependent parameter with increase of temperature. In the present work, the temperature-dependence curves of the infrared parameters of the combination band show that up to about 30° or 40°C the slopes are indeed gradually decreasing. However, above 40°C the first derivative starts to increase again. Something new must be taking place in the liquid water systems to account for this resurgence of slope change. A possibility is that, as the structured component melts to give more and more unstructured water on temperature increase, the nature of the unstructured component changes from that of a pure librator to a mixture of librating and rotating molecules. The postulate implies that at lower temperature complete rotation of water molecules is inhibited in both structured and unstructured regions but that between about

30° or 40°C rotation of unstructured molecules begins to occur. Magat (2) first suggested onset of rotation as an explanation for observed anomalous behaviour of liquid water in this temperature range. He based his conclusion on calculations of the energies involved in the rotation of an individual molecule about its three principal axes: at low temperatures he found rotations about all of the axes to be negligible but at temperatures above 40°C rotation of a molecule about its to be energetically possible.

Further experimental evidence for the possibility of onset of rotation of water molecules in the transition temperature region is obtained from examining the half-width behaviour of the infrared absorption bands. Fig. I-8 shows the smoothed half-widths of the combination band, obtained from the best-fit polynomials in Fig. I-6, plotted against the inverse of viscosity for both  $H_2O$  and  $D_2O$ . Rakov (40) noted that for infrared absorption bands of molecules undergoing reorientation, a plot of band half-width versus the inverse of viscosity is linear. From Fig. I-8 it can be seen that at lowest temperatures (smallest  $1/\eta$  values) a definite curvature is present but that at higher temperatures the relationship between  $\Delta v_{1/2}$  and  $1/\eta$  becomes linear for the combination band. It is extremely tempting to take the linearity at higher temperatures as indicative of rotation of water molecules occurring in this region. Carrying the analysis further and equating the temperature at which the



FIGURE I-8. Half-width versus the inverse of viscosity for the combination band of liquid  $H_2O$  and  $D_2O$ .  $\Delta v_{1/2}$  values are from the smoothed polynomials of Fig. I-6: viscosity data from ref. (41).

straight-line relationship begins as the temperature of onset of rotation, a value of about 30°C is obtained for both  $H_2O$  and  $D_2O$  for the transition temperature. In addition, a preferential direction of reorientation of water molecules about the dipole axis is indicated by Rakov's theory (40,42)

on considering the reported temperature invariance of the deformation band half-width (26). The same conclusion as proposed by Magat for the temperature and nature of the transition in liquid water thus is reached from the half-width behaviour of the absorption bands; namely, that at about 30° to 40°C, rotation of water molecules, which is restricted at lower temperature, sets in about the dipole axis.

In conclusion, it should be emphasized that the observed sigmoidal effect in the temperature dependence curves is slight. The differences in the fits of the various degrees of polynomials as given in Table I-1, though not insignificant, are small. This suggests that the main trends are governed by equilibrium between the structured and unstructured components and that the equilibrium between librators and rotators in the unstructured species represents a minor perturbation only. As such, more clear-cut evidence for the existence of two major species should be obtainable. It is, from observed isosbestic behaviour of water absorption bands, a phenomenon best explained by assuming the presence of two absorbing species in equilibrium (43). The presence and nature of isosbestics found with the intermolecular combination bands are discussed in detail in Part II.

**b**3

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PART II Temperature Dependence of the 2125 cm<sup>-1</sup> and 1555 cm<sup>-1</sup> Infrared Absorption Bands in Liquid  $H_2O$  and  $D_2O$ : Isosbestic Behaviour.

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#### ABSTRACT

An isosbestic point has been observed on the low frequency side of the 2125 cm<sup>-1</sup> and 1555 cm<sup>-1</sup> infrared intermolecular absorption bands in liquid  $H_2O$  and liquid  $D_2O$  respectively on superposition of spectra recorded between temperatures of 5 and 70°C. Both the isosbestic behaviour and the temperature dependence of the infrared parameters of the band have been accounted for by assuming that an equilibrium exists between structured and unstructured species and that the concentration of the latter increases with increase in temperature.

#### 1. INTRODUCTION

Because of strong intermolecular interactions in condensed water, certain infrared absorption bands appear in the liquid that are absent from the vapour. Such is the weak 2125  $\text{cm}^{-1}$  intermolecular combination band in H<sub>2</sub>O (1555  $cm^{-1}$  in D<sub>2</sub>O) generally assigned to a librational type of motion in combination with the deformation absorption at  $1645 \text{ cm}^{-1}$  (1215 cm<sup>-1</sup> in D<sub>2</sub>O) (1,2). Its intensity and position show the same marked temperature dependence (3) as do the libration bands absorbing at 685  $\text{cm}^{-1}$  (505  $\text{cm}^{-1}$  in  $D_2O$ ) in the infrared (2) and at 475 cm<sup>-1</sup> and 710 cm<sup>-1</sup> (375  $cm^{-1}$  and 550  $cm^{-1}$  in D<sub>2</sub>O) in the Raman (4,5). The temperature sensitivity of the combination band is indicative of its sensitivity to molecular environment and motion - i.e. to the structure of liquid water. Hence a careful examination of this band should provide a useful probe in looking for mixtures of species in the liquid.

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If there are two absorbing species present with a large separation in central frequency, a shoulder will appear on the composite band envelope. However, a superficially simple contour may also be the result of two or more component bands (6,7). Luck and Ditter (8) have shown that certain intramolecular bands of liquid HDO can be interpreted in terms of an equilibrium of different species despite the smooth contours of the curves.

If the component bands correspond to species which

are in equilibrium, so that changes in conditions such as temperature favour formation of one at the expense of the other, then curves corresponding to different temperatures will often display the isosbestic phenomenon, with or without overt shoulders evident in the individual envelopes.

The infrared spectra of the intermolecular combination bands of liquid  $H_2O$  and liquid  $D_2O$  were recorded between 5 and 70°C for Part I. These curves are now examined for evidence of isosbestic behaviour.

#### 2. EXPERIMENTAL

The samples used were ion-free double-distilled liquid  $H_2O$  and 99.7% pure  $D_2O$  from Merck, Sharp and Dohme. Spectra were recorded with a Unicam SP-100G double-beam vacuum spectrometer using  $CaF_2$  plates for the liquid cell windows. The recorded curves were corrected for window effects. Details of the spectroscopic techniques are given in Part I of the thesis.

## 3. RESULTS AND DISCUSSION

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In Figs. II-1 and II-2 respectively the experimentally observed effects of temperature increase on the combination bands of liquid  $H_2O$  and liquid  $D_2O$  are shown. The band intensity decreases, width increases and frequency of maximum absorption shifts to lower wavenumbers. The presence of a diffuse isosbestic point at 2075  $\pm$  25 cm<sup>-1</sup> in  $H_2O$  and at 1500





 $\pm$  20 cm<sup>-1</sup> in D<sub>2</sub>O is clearly evident.

The observed behaviour may be elucidated by comparing the effects of hydrogen bond formation on infrared parameters of condensed systems in general (9-13) with the effects of temperature on the infrared parameters of liquid water (3,11). As shown in Table II-1, lowering the temperature in water produces effects similar to those due



FIGURE II-2. Temperature dependence of the 1555 cm<sup>-1</sup> IR combination band of liquid  $D_2O$ .

to H-bond formation, on the plausible assumption that  $v_2$  in water corresponds to the bending mode and that the combination band designated  $v_{2+L}$  can be equated to a torsional mode. The only discrepancy is in the observed decrease in the half-width of the combination band with the reported band-broadening of torsional modes on H-bond formation. Torsional bands of certain alcohols however have been observed to decrease in  $\Delta v_{1/2}$ 

## TABLE II-1

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## Effects of H-bond Formation and Temperature

## on Infrared Parameters

System	Effect	Mode	<u>vo</u>	<sup>ε</sup> max	$\frac{\Delta v_{1/2}}{2}$	Magnitude	Reference	
Condensed Systems	ondensed H-bond ystems Formation		dec	inc	inc	large	10,11,12	
		ν <sub>b</sub>	inc	same or dec	same or inc	small	10,11,12	
		ν <sub>t</sub>	inc	inc	inc*	large	11	
Liquid	Lowering	<sup>v</sup> 2	inc	dec	~	small	3,11	
<sup>n</sup> 2 <sup>0</sup>	remp.	<sup>V</sup> 2+L	inc	inc	dec	large	3	
Liquid D <sub>2</sub> O	Lowering	<sup>v</sup> 2	inc	dec	~	small	3,11	
	2 Cp 1	<sup>v</sup> 2+L	inc	inc	dec	large	3	
ν <sub>s</sub> stretching vibration								
	$v_{b}$ in plane deformation (bending)							
$v_t$ out of plane deformation (torsion or libra $v_2$ deformation mode in liquid water							or libration)	
<u> </u>	v <sub>2+L</sub> comb	inati	on b	and i	n liqu	id water		

\* dec.; ref. 10.

on bond formation (10).

The anomalous temperature dependence of the halfwidths and the appearance of isosbestic points in the combination bands of liquid  $H_2O$  and liquid  $D_2O$  can be accounted for qualitatively in terms of a mixture model for liquid water. The properties of the model may be described in the following terms:

- (i) Water consists of a mixture of structured and unstructured species in equilibrium at a given temperature.
- (ii) Water molecules in the structured regions are hydrogenbonded much like ice. Librational modes of such molecules are infrared absorbing:  $v_0$ ,  $\varepsilon_{max}$  and  $\Delta v_{1/2}$  of libration bands of structured species are assumed to be invariant with temperature.
- (iii) In the unstructured regions, intermolecular bonds do not have the directional, partly covalent character usually associated with hydrogen bonds. However, the strong dipolar forces between adjacent molecules restrict rotational motion to librations, which are infrared absorbing. The frequency, intensity and half-width of the librational bands of unstructured water are assumed to be less than for structured water, thereby conforming to the trends in Table II-1 which show increase in all these parameters on H-bonding for torsional modes. As with the structured water are assumed

to be invariant with temperature.

- (iv) Increase in temperature favours the formation of unstructured regions and the depletion of structured regions.
- (v) The combination band is predominantly librational in character (14).

Curves S and U of Fig. II-3 are drawn for two Cauchy (Lorentz) distributions<sup>1</sup> bearing the relationship to one another expected on the basis of Table II-1 of librational bands due to completely structured and to completely unstructured species respectively. Nominal values for the IR parameters of these curves are given in Table II-2. Curve S thus corresponds to the structured species and curve U to the unstructured molecules. In addition, three curves are drawn corresponding to the mixture of structured and unstructured species shown in Table II-2.

<sup>1</sup>For a Cauchy distribution, the molecular extinction coefficient as a function of frequency,  $\varepsilon_{ij}$ , is given by

$$\varepsilon_{v} = \varepsilon_{\max} \left[ 1 + 4 \left[ \frac{v_{o} - v}{\Delta v_{1/2}} \right]^{2} \right]^{-1}$$
 (15).

That the noted shape changes in the band envelope are not dependent on the form of the distribution function chosen to represent the experimental IR absorption curves was shown by the fact that similar trends were obtained with two Gaussian functions. For a Gaussian distribution

$$\varepsilon_{v} = \varepsilon_{\max} \exp\left(-4\ln 2\left(\frac{v_{o}-v}{\Delta v_{1/2}}\right)^{2}\right) \qquad (15)$$

Cauchy curves were chosen in the present investigation since analysis of the shapes of the combination bands showed them to more closely resemble Cauchy than Gaussian profiles. The actual contours of these bands are intermediate to the two mathematical functions (16).



FIGURE II-3. Calculated overlap of two Cauchy curves simulating relationships expected between torsional absorption bands of structured and unstructured water molecules.

# TABLE II-2

Curve	C <sub>s</sub>	с <sub>U</sub>	<u>vo</u>	<sup>E</sup> max	<u>Δν1/2</u>
S (Structured)	1.0	0.0	150	6.0	400
Ml	0.9	0.1	140	5.6	415
<sup>M</sup> 2	0.8	0.2	135	5.2	430
м <sub>3</sub>	0.7	0.3	120	4.7	438
U (Unstructured)	0.0	1.0	0	5.0	200
$C_{c} + C_{tt} = Constant:$	: C <sub>c</sub> = 0	Concentrat	ion of st	ructured s	species.

Parameters of Calculated Cauchy Curves

 $S + C_U = Constant: C_S = Concentration of structured species.$  $C_U = Concentration of unstructured species.$ 

It can be seen that as the proportion of curve U increases the composite band envelope maximum shifts to lower frequency, the apparent  $\varepsilon_{max}$  value decreases and an isosbestic point is created on the low frequency side of the band. Moreover, the total half-width increases as the proportion of curve U is raised from 0 to 30% despite the fact that the composite band is progressing towards higher concentration of the species having the narrower band width. These changes in composite band envelope with increase in proportion of unstructured species parallel precisely the actually observed changes of the combination band in liquid water with increasing temperature.

It is important to recognize that the curves of Fig. II-3 are representative and valid only in giving qualitative directions of changes expected on changing equilibrium concentrations of structured and unstructured water molecules. In comparison to the sharp point of intersection given by the model system the observed isosbestics in both light and heavy water are blurred as shown in Figs. II-1 and II-2. Several effects could be contributing to the spread of the isosbestic region. Almost all infrared absorption bands of liquids show some sensitivity to temperature and thus the assumption of temperature invariance in the IR parameters of the librational bands of structured and unstructured species is likely to be invalid (6,8). Also, it is probable that more than two types of species are present

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in the liquid water systems (17-24). Indeed, at least three distinct types of molecules are to be expected, if a mixture model of liquid water is applicable: these are a) molecules completely within the structured regions, b) molecules completely within the unstructured regions, and c) molecules intermediate to (a) and (b) forming the instantaneous boundaries to structural aggregates. Cluster models of the Nemethy-Scheraga (25-27) and Buijs-Choppin (28,29) types are built up on the supposition that equilibrium between such species exists. Molecules within structured regions would be librators, incapable of rotation: complete rotation of molecules in the other regions would be possible at temperatures above which intermolecular forces were sufficiently weak to permit this. As discussed in Part I of the thesis, rotational motion above about 30 to 40°C is conceivable in which case rotational effects would also be expected to be contributing to the nature of the observed isosbestic.

A careful examination of the isosbestic region reveals that rather than a uniform displacement of the frequency at which individual absorption lines cross one another, two more or less distinct crossover points are evident, the higher frequency one sharper and involving spectra recorded below about 30°C.  $H_2O$  and  $D_2O$  behave identically in this respect. The advent of rotational motion causing a decrease in total concentration of librating species and an additional

though not necessarily infrared absorbing equilibrium component would be expected to have just such an effect on librational bands.

The water model used in much like that of Walrafen (4,5,24,30,31). Walrafen however assumes that structured molecules are all associated with the  $C_{2V}$  tetrahedral structure of fully hydrogen-bonded ice-like molecules and that unstructured molecules have surmounted the Con potential barrier, are unbonded, and do not contribute significantly to intermolecular absorption band intensities. The proximity of liquid water molecules makes discussions of structure in terms of hydrogen-bonded versus unbonded molecules unfeasible: whether or not normal H-bonds are present, strong intermolecular forces are still to be expected between molecules in the liquid at all temperatures. Theoretically molecules of symmetry lower than  $C_{2V}$  such as  $C_2$  would still be active and absorbing for intermolecular modes in both the Raman and infrared spectra. The presence of the isosbestic point on superposition of the intermolecular combination band curves for different temperatures strongly suggests equilibrium between species contributing to this band's intensity. Thus there is every indication that librations of unstructured molecules are occurring and are absorbing infrared radiation close to the frequency of the ice-like component. As has been shown in the present analysis, the observed temperature effects on the combination band can be accounted

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for very well in terms of changing equilibrium concentrations of structured and unstructured molecules with the properties given in assumptions (i) to (v) and Table II-1.

Isosbestic behaviour of absorption bands has been observed by others both in Raman and infrared spectra, for liquid water (5,7,8,33-37), water solutions (33,34), and alcohols (7,8,38,39). Not always has it been commented on (33,35,40), but in each case where the isosbestic point has been reported (8,34,36), its presence has been taken as indicative of equilibrium between different species. For the fundamental stretching vibrations of liquid water, a simple analysis analogous to that carried out in the present investigation shows that an isosbestic point would be expected on the high frequency side of the band: this is precisely where it has been observed (5,33,37). In some HDO overtone bands the centres of absorption of the bands due to structured and to unstructured water are sufficiently separated that, on temperature increase, a decrease in the intensity of the former is accompanied by an increase in intensity of the latter (8).

On examination of published spectra showing isosbestic behaviour in water absorption, one more feature is noteworthy. The curves for liquid water at various temperatures and for ice and vapour do not cross at the same point but rather the solid and vapour curves are shifted substantially in opposite directions from the isosbestic point of

the liquid (8,41). This is the expected behaviour, indicating that molecules inside the structured regions in liquid water are not identical to those in ice and that unstructured molecules in the liquid differ from the unbonded non-interacting molecules of the vapour.

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# PART III

The temperature dependence of infrared absorption band contours of liquid  $H_2O$  and  $D_2O$  in the 1000-2700 cm<sup>-1</sup> region

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#### ABSTRACT

Cauchy-Gauss product functions have been fitted to infrared absorption band envelopes of liquid  $H_2O$  and liquid  $D_2O$  in the frequency range 1000 to 2700 cm<sup>-1</sup>. Systematic shape changes with temperature have been obtained between 5 and 70°C: the intermolecular combination band at 2125 cm<sup>-1</sup> (1555 cm<sup>-1</sup> in  $D_2O$ ) rapidly became more Gaussian on temperature increase whereas the intramolecular deformation band at 1645 cm<sup>-1</sup> (1215 cm<sup>-1</sup> in  $D_2O$ ) changed only slightly and became more Cauchy in character. The results are interpreted in terms of present theories of condensed system absorption band profiles and of liquid water structure.

#### 1. INTRODUCTION

That the frequency and intensity of certain absorption bands in the infrared spectrum of liquid water vary markedly with temperature is well known (1-14). These effects are related to temperature-induced changes in the hydrogen bonding between molecules, to which the infrared spectrum is known to be sensitive (2,15-19). Recently it has been recognized that shapes of absorption contours also are related to the environment and motion of absorbing molecules in condensed systems (20-25). Temperature could thus be expected to have an effect on band shapes, as well as on the more conventional infrared band parameters, especially in liquids where strong intermolecular interactions are present. Accordingly, it seemed profitable to investigate in detail the thermal dependence of band shape in liquid H<sub>2</sub>O for the highly temperature sensitive intermolecular combination band absorption at 2125 cm<sup>-1</sup> (25°C) (1,3,11,13,14) and its neighbouring intramolecular band at 1645 cm<sup>-1</sup>. Also investigated is the corresponding spectral region in liquid  $D_2^0$ , where the absorption maxima occur at 1555  $\text{cm}^{-1}$  and at 1215  $\text{cm}^{-1}$  for the combination and deformation vibrations respectively.

Few data on the temperature dependence of the shapes of infrared absorption bands are available. Waggener, Weinberger and Stoughton (26) found the profiles of liquid CO<sub>2</sub> bands to be invariant with temperature. Likewise, Baker, Kerlinger and Shulgin (27) could detect no changes with temperature in the shapes of OH stretching vibrations of substituted phenols. Only in a recent investigation by Waggener and co-workers (28) on near-infrared absorptions of liquid water has a temperature dependence of profiles been reported.

The mathematical expressions most often used to fit experimentally observed infrared contours of condensed system absorptions are distribution functions of either a Cauchy<sup>1</sup> (20,26,29-33) or a Gaussian (10,34-37) form. Preliminary analysis of the water bands indicated they were intermediate to the two. Combining the functions either as a convolution (20,38,39), a sum (20,23,40), or a product (20, 23,36) gives an intermediate contour and also enables the proportion of Cauchy or Gaussian character for a profile to be determined. A convolution function is theoretically justified only if the origins of the two component functions are independent of one another, such as in calculations of instrumental distortions on true sample absorption profiles, for which the convolution has been used with good success (38,41,42). This approach was not considered appropriate in the present work since the effect of sample temperature change on the performance of the spectrometer was negligible.

<sup>1</sup>The term "Cauchy" refers to a mathematical function only. The often synonymously used term "Lorentz function" has connotations of a physical process as well (p. 1023, ref. 20).

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Computer techniques for fitting Cauchy-Gauss sum and product functions to digitized spectral curves have recently been developed by R.N. Jones and co-workers (43-46). Using their methods, it was found that best fit necessitating least number of input variables could be obtained with a product function. Cauchy-Gauss product functions have therefore been applied throughout the present analysis.

#### BAND CONTOUR ANALYSIS 2.

In terms of the common parameters of an infrared absorption band, a Cauchy profile is given by

$$A(v)_{C} = \ln \left( \frac{T_{O}}{T} \right)_{v_{O}} \left( \frac{1}{1+4 \left( \frac{v - v_{O}}{\Delta v_{1/2}} \right)^{2}} \right)$$
(1)

where

 $A(v)_{C}$  = the absorbance at frequency v

 $\ln\left(\frac{T_{O}}{T}\right)_{V}$  = the peak height v = the frequency, in wavenumbers  $v_{o}$  = the frequency at maximum absorption  $\Delta v_{1/2}$  = the band width at half maximum height, in wavenumbers.

For a Gaussian function

$$A(v)_{G} = ln \left( \frac{T_{o}}{T} \right)_{v_{o}} exp \left( -4ln2 \left( \frac{v - v_{o}}{\Delta v_{1/2}} \right)^{2} \right)$$
(2)

In order to incorporate these functions into a computer programme, Pitha and Jones (23,43) transformed to
generalized variables  $x_1$ ,  $x_2$ ,  $x_3$  and  $x_4$ , with

 $x_{1} = \ln \left( \frac{T_{0}}{T} \right)_{v_{0}}$   $x_{2} = v_{0}$   $x_{3} = 2/(\Delta v_{1/2})_{C}$   $x_{4} = 2\sqrt{\ln 2}/(\Delta v_{1/2})_{G}$ (3)

 $(\Delta v_{1/2})_{\rm C}$  refers to the half-width of the Cauchy component and  $(\Delta v_{1/2})_{\rm G}$  to the half-width of the Gauss component: these are equal to the half-width of the composite curve only at the limits of a pure Cauchy or a pure Gauss function respectively.

Using the transformations given in equation 3, equation 1 becomes

$$A(v)_{C} = x_{1}(1 + x_{3}^{2}(v - x_{2})^{2})^{-1}$$
(4)

and equation 2 becomes

$$A(v)_{G} = x_{1} \exp(-x_{4}^{2}(v-x_{2})^{2}).$$
 (5)

The product function is given by

$$A(v)_{p} = x_{1}(1 + x_{3}^{2}(v-x_{2})^{2})^{-1}exp(-x_{4}^{2}(v-x_{2})^{2})$$
(6)

and a shape ratio is defined for the product function by

SHAPE RATIO = 
$$\frac{x_3}{x_3 + x_4}$$
 (7)

For a pure Cauchy contour,  $x_4$  is zero and for a pure Gaussian contour  $x_3$  is zero. Thus the shape ratio has a value of unity for a Cauchy curve and zero for a Gaussian curve.

Writing absorbance, A(v), as equal to  $ln\left(\frac{T_o}{T}\right)$  and equating  $lnT_o$  to  $\alpha$  or the "base-line displacement" of Jones (43), equation 6 rewritten in terms of measurable transmittance units becomes

$$T(v)_{p} = \exp\left(\alpha - x_{1}(1 + x_{3}^{2}(v - x_{2})^{2})^{-1}\exp\left(-x_{4}^{2}(v - x_{2})^{2}\right)$$
(8)

Equation 8 gives the actual working curve, the function with which experimentally observed liquid water band contours were fitted. For any one absorption band one set of  $x_1...x_4$ is required. For a frequency range including M bands, M sets of  $x_1...x_4$  are needed. Thus the minimum number of variables necessary to describe the envelope generated by M bands is 4M+1, the additional one arising from inclusion of the parameter  $\alpha$ , i.e. from freeing the base-line from zero absorbance. Programme IRCURFIT\*, the central one in this investigation, simultaneously optimizes the 4M+1 variable parameters of M symmetric curves by a non-linear least squares approximation. Agreement between observed and calculated band envelopes is given by

$$\phi = \sum_{i=1}^{NP} f_i^2$$
(9)

\*Programme X(PC-116), (46)

where  $f_i = T_i (obs) - T_i (calc)$ , the difference between observed and calculated transmittance, and NP is the number of transmittance measurements taken on the experimental curve. Optimum fit is achieved when  $\emptyset \leq S^2 \cdot NP$  in which S is the standard deviation of transmittance measurements. To avoid excessive use of computer time the programme terminates after completion of a preset number of cycles or when  $\emptyset \leq S^2 \cdot NP$ , whichever condition is met first. Complete details of the programme are given in the papers of Jones et al. (41-46).

## 3. EXPERIMENTAL

# 3.1 Data

The infrared absorption spectra were recorded with a Unicam SP-100G double-beam vacuum spectrophotometer for temperatures between 5 and 70°C.  $CaF_2$  plates were used exclusively for sample cell windows. Spectral slit widths ranged from 2.4 to 5.5 cm<sup>-1</sup> in the frequency intervals involved but observed band widths were about 25 to 80 times greater: instrumental band shape distortion due to finite slit widths was thus negligible. Experimental details are given in an earlier section of the thesis (13).

Percent transmittance readings were taken at 20 cm<sup>-1</sup> intervals from 2700 cm<sup>-1</sup> to 1000 cm<sup>-1</sup> for  $H_2O$  and from 2000 cm<sup>-1</sup> to 1000 cm<sup>-1</sup> for  $D_2O$  and averaged for 4 separate runs at each temperature. Percent transmittance readings of CaF<sub>2</sub> window spectra were averaged for a number of temperatures

at the same frequency intervals. The 95% confidence level for the standard deviation in experimental %T determinations was 0.2, 0.7 and 0.8%T for  $H_2O$  in the frequency intervals 2660-1960 cm<sup>-1</sup>, 1960-1600 cm<sup>-1</sup> and 1600-1160 cm<sup>-1</sup> respectively and 0.3, 1.0 and 0.9%T for  $D_2O$  in the frequency intervals 1960-1400 cm<sup>-1</sup>, 1400-1160 cm<sup>-1</sup> and 1160-1000 cm<sup>-1</sup>. The values are higher for  $D_2O$  because of a slightly higher noise level while recording its spectra.

Band contours corrected for window effects are shown in Fig. III-1. For curve fitting purposes the minimum on the high frequency side of the combination band was taken as the upper limit of frequency. The scanned regions were treated as a one-band, two-band and three-band system (M=1, M=2 and M=3, respectively) in both  $H_2O$  and  $D_2O$ . The frequency ranges fitted by the calculated curves, the number of variable parameters required to describe each system, and the number of experimental data points taken along the experimental contours are tabulated in Table III-1. Thus the frequency ranges fitted corresponded to the following:

one-band system = most of the combination band two-band system = all of the combination band plus most of the deformation band

three-band system = all of the combination and deformation bands as well as an irregular absorption maximum on the low frequency side of the deformation band.



FIGURE III-1. Example of infrared absorption spectra of liquid H<sub>2</sub>O and D<sub>2</sub>O showing the frequency intervals for the one-band, two-band and three-band systems.

# 3.2 Input Parameters

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In addition to the infrared absorption data of observed band indices it was necessary to select a starting set of input variable parameters. Clearly it was desirable to start with values reasonably close to the optimized ones.

# TABLE III-1

Input Data for Curve Fitting

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	M	$\Delta v (cm^{-1})$	4M + 1	NP
н <sub>2</sub> 0	l	2660-1940	5	37
	2	2660-1600	9	54
	3	2660-1160	13	76
D <sub>2</sub> 0	l	1960-1400	5	29
	2	1960-1160	9	41
	3	1960-1000	13	49

M number of experimental bands fitted.

 $\Delta v$  frequency interval fitted.

4M+1 number of variable input parameters.

NP number of input data points (band indices).

For liquid  $H_2^0$  the selected starting value of  $\alpha$  corresponded to 90.8%T, the average minimum at 2660 cm<sup>-1</sup> after removal of CaF<sub>2</sub> window effects. For liquid D<sub>2</sub>0 the average minimum at 1960 cm<sup>-1</sup> by coincidence was also 90.8%T.

 $x_1$  was obtained by converting equation 3 from natural logarithms to Naperian logarithms and calculating  $\log_{10}T$ , with  $\log_{10}T_0 = \alpha$ .

 $x_2$  was determined by measuring  $\nu_{O}^{}$  directly from the recorded spectrum in wavenumbers and converting to a scale given by

$$x_{2} = (v_{0} - 1000)/40 \text{ for } H_{2}O$$

$$x_{2} = (v_{0} - 500)/40 \text{ for } D_{2}O$$
(10)

and

(3)

The effect of the transformation was to shift and contract the scale, making it easier for the programme to handle the data. It had no other effect on the analysis.

As shown by equation 3,  $x_3$  and  $x_4$  are related to the half-widths of the Cauchy and Gaussian component curves respectively which in turn are dependent on the total or observed band width,  $(\Delta v_{1/2})_{obs}$ , and on the shape ratio. Of these, only the total band width corresponds to an experimentally measurable quantity. Although the interrelationship between the four quantities cannot be expressed simply in the form of an equation, it can be represented graphically for a product function. From the tables of band parameters for product functions of various total widths and shape ratios as

calculated by Pitha and Jones (44,45) it is readily demonstrated that for any particular product shape ratio,  $x_3(\Delta v_{1/2})_{obs}$  is a constant as also is  $x_4(\Delta v_{1/2})_{obs}$ : the variation of these quantities with shape ratio is shown in Fig. III-2 for shape ratios >0.5. From a starting value of the shape ratio and the experimentally determined halfwidths, suitable input values for  $x_3$  and  $x_4$  were determined from Fig. III-2. However it was still necessary to choose arbitrarily an initial shape ratio. From preliminary investigations of liquid water spectra it was found that both the combination and deformation bands were more highly Cauchy than Gaussian, and that initially chosen shape ratios between 0.7 and 0.9 all converged to the same final value. Thus it seemed expedient to select a highly Cauchy shape ratio as an input value. For consistency, the same ratio of 0.8 was chosen in all cases. The same scale conversion as with  $x_2$  was used in expressing  $x_3$  and  $x_4$  values.

## 3.3 Computer Programmes

Fig. III-3 indicates schematically how the data were treated. The recorded percent transmittance and wavenumber readings (band indices) of the water spectra at any one temperature and of the  $CaF_2$  cell formed the input to Computer Programme IRCELL (47). The output of this programme gave the indices of the water band less  $CaF_2$  absorption in units of %T and cm<sup>-1</sup>/40 and is termed the "observed band". These indices,



FIGURE III-2. Total half-band width versus Shape Ratio for Cauchy-Gauss product functions:  $x_i$  on the ordinate represents  $x_3$  or  $x_4$ .

together with the appropriate variable parameters  $x_i$  (i = 1 to 4) determined separately at each temperature for each of the M bands (M = 1 to 3) and  $\alpha$ , formed the input to the central Computer Programme IRCURFIT (47). This programme was modified slightly from the original to give calculated product function shape ratios as well. The optimum calculated

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FIGURE III-3. Schematics of data treatment. Note that PLOTS programme output reverses frequency axis.

output parameters of IRCURFIT were fed into CALCBAND (Programme XIV (PC-122) (46)) which calculated the indices corresponding to the best fit computed parameters. These indices define the "calculated band". Finally the observed and calculated band indices formed the input to Computer Programme PLOTS (47). This programme gave a point-by-point

plot of the observed and calculated contours at 20 cm<sup>-1</sup> intervals and enabled a visual comparison of the fit achieved between experimental and computed curve shapes.

All computations were performed on McGill University's 360/50-360/75 computer. During computations, 10 iterative cycles were permitted.

4. RESULTS

4.1 Curve Fit

The fits achieved between mathematically computed Cauchy-Gauss product functions and experimental curves for liquid H<sub>2</sub>O treated as one, two and three-band systems are shown in Fig. III-4. For one-band systems the largest discrepancy between computed and experimental transmittance values was 1.3%T: at all temperatures the maximum difference occurred near the high frequency limit, where the observed band is starting to curve upwards owing to absorption by stretching vibrations at about 3400 cm<sup>-1</sup>. In two-band systems of H<sub>2</sub>O the largest f; value amounted to 2.2%T and came on the steep shoulder of the bending mode where small errors in read frequency values would lead to large differences in input %T values. The biggest discrepancy in three-band systems occurred either on the side of the bending mode or close to the low frequency limit where accuracy in observed T readings is least because of the necessity of subtracting strong CaF, window absorption. Here maximum difference in



FIGURE III-4. A comparison of the experimental points and the calculated curves of liquid H<sub>2</sub>O at 30°C for one, two, and three-band systems.

transmittance was 3.3%T. The average root mean square deviations between calculated and observed spectra were 0.4, 0.6 and 1.1%T for the one, two and three-band systems of  $H_2O$  respectively. Similar trends were found for liquid  $D_2O$ : as with the  $H_2O$  spectra, the largest discrepancies between computed and experimental transmittance values





occurred near the high frequency minimum in one-band systems, on the steep side of the bending mode in two-band systems, and in the region below 1100 cm<sup>-1</sup> in the three-band systems. The maximum  $f_1$  values in the  $D_2O$  systems were 1.2, 5.2 and 3.8%T respectively, with average root mean square deviations of 0.4, 1.3 and 1.0%T. With neither  $H_2O$  nor  $D_2O$  did the

quality of the fit show a trend with temperature. This is illustrated by curves in Fig. III-5 for the  $H_2O$  three-band systems and in Fig. III-6 for  $D_2O$  two-band systems near the upper and lower limits of the temperature range studied.

The results indicate that a Cauchy-Gauss product function approximates quite well the infrared band envelopes of liquid  $H_2O$  and  $D_2O$  over the frequency range investigated, for all temperatures between 5 and 70°C. Furthermore, fit is achieved whether experimental points for either only a part of a curve contour or for complete contours of more than one absorption peak are used. The absolute values of calculated band indices and output parameters differed slightly depending on whether the data were treated as a one, two or three-band system, but the relative trends with temperature were the same. The detailed data are available elsewhere (47).

## 4.2 Temperature Trends

The effect of temperature on the calculated combination band contour of liquid  $D_2O$  is shown in Fig. III-7: a similar figure can be drawn for  $H_2O$ . Qualitatively it closely resembles the experimental curves (14) in that a temperature increase from 4 to 66°C causes the band intensity to weaken and its profile to become wider and more rounded. The present investigation indicates that the actual shape of the band is changing with temperature as well.





Fig. III-8 is a plot of computed shape ratio,  $\frac{x_3}{x_3+x_4}$ , versus temperature for the intermolecular combination band at 2125 cm<sup>-1</sup> and the intramolecular deformation band at 1645 cm<sup>-1</sup> of liquid H<sub>2</sub>O. The ratios given for the combination band are averages calculated from one and two-band systems. For the deformation band, the averaged values of two and three-



FIGURE III-7. Temperature dependence of calculated product function curves for liquid D<sub>2</sub>O, one-band systems. Shape Ratios for the 4°, 30°, and 66°C curves are 0.84, 0.63 and 0.34 respectively.

band systems are plotted. The corresponding results for liquid  $D_2O$  are shown in Fig. III-9.

It is clear from Figs. III-8 and III-9 that a definite temperature dependence of the shape ratio is present and

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FIGURE III-8. Thermal dependence of Shape Ratios of the combination  $(v_{2+L})$  and deformation  $(v_2)$  bands of liquid H<sub>2</sub>O. Mean deviations of averaged values are  $\pm 0.045$  and  $\pm 0.050$  respectively.

that it is far more pronounced in the combination band than in the deformation band. Furthermore, the trends are in opposite directions, the combination band becoming more Gaussian as temperature is increased whereas the deformation

(2)



FIGURE III-9. Thermal dependence of Shape Ratios of the combination  $(v_{2+L})$  and deformation  $(v_2)$  bands of liquid D<sub>2</sub>O. Mean deviations of averaged values are  $\pm 0.08$  and  $\pm 0.02$  respectively.

becomes slightly more Cauchy at higher temperatures. The difference in sensitivity to temperature change of the shape profiles of these two infrared absorption bands parallels the difference in degree of temperature dependence of their other infrared parameters (14).

From the calculations using the three-band system, it was possible to derive the temperature dependence of the infrared parameters of the "third band". In the experimentally observed spectra this is not a well-defined absorption but rather an irregularity in the minimum on the low frequency side of the deformation band (Fig. III-1). However, the evidence suggests that there is indeed an absorption band in liquid water at about 1360 cm<sup>-1</sup> in  $H_2O$  and 1010 cm<sup>-1</sup> in  $D_2O$  and, as shown in a later section (48), the temperature dependences of the infrared parameters calculated for the third band closely resemble those of the intermolecular combination band.

# 5. DISCUSSION

From theoretical considerations (20,22,25,29), it has been found that in a homogeneous environment where perturbations are statistically distributed, an infrared absorption band of a condensed system has a Cauchy profile. In liquids such a situation is most likely to occur where molecular interactions are very weak (26,29,32). However, Shimizu (22) has shown that where intermolecular interactions are very strong, line shape may also be Cauchy if there is no appreciable distribution in the local potential at molecules. Non-Cauchy characteristics have been interpreted as being due either to instrumental factors or to deviations of the environment of the absorbing species from the two extremes

of weak or strong intermolecular interactions (20,22,25, 31,38).

Distortions of true band profiles by the optical and electrical components of an infrared spectrophotometer will always be present (20). Of the various distorting factors involved only the optical element is directly related to a parameter which changes with temperature in the liquid water absorption bands. The extent of distortion can be estimated from the relative value of spectral slit width to observed band width and is negligible for ratios less than about 1/10 (27,41). With the very wide bands of this investigation the possibility of instrumental factors causing the observed band shape changes on temperature variation can safely be discarded.

On temperature increase, the possibility of intensity contribution to absorption bands from spontaneous thermal emission by the sample should be considered (20,49, 51). Previous calculations (11) showed that errors in Tdeterminations from this cause are insignificant in the frequency range of interest, although they might be important below about 1000 cm<sup>-1</sup>. Errors due to the temperature differential between various parts of the spectrophotometer on measuring spectra at temperatures that depart appreciably from the ambient were also found to be negligible. Thus all observed temperature dependent changes must be intrinsic to changes in the liquid water medium itself.

From Figs. III-8 and III-9, it is seen that both the combination and deformation bands of liquid water are highly Cauchy at low temperatures. Thus the low temperature infrared band shapes of water are consistent with a model which represents liquid water close to the freezing point as an essentially completely tetrahedrally bonded network in which hydrogen bonds are arranged homogeneously. In terms of water structure both large-cluster (7,52) and continuum (8,53) models of liquid water are acceptable for this interpretation.

The frequency, intensity and width of the intramolecular deformation band are affected but little by temperature (1,2,10,13): the shape ratio of this band also changes but slightly. The fact that the  $v_2$  mode becomes more Cauchy as temperature is raised seems to indicate that perturbing influences on this intramolecular vibrational mode are decreasing with temperature. Since hydrogenbonding is known to weaken on temperature elevation (2), the interpretation is valid. Similarly, the observed greater Gaussian nature of the D<sub>2</sub>O bands compared to the H<sub>2</sub>O bands at any one temperature may be related to the greater strength of deuterium bonds compared with hydrogen bonds (54,55). The opposite and much larger temperature effects on the combination band contour indicate that factors other than a decrease in bond strengths are affecting its shape ratio. Nonstatistically distributed perturbations could be one cause of

deviations from a Cauchy contour (22). Physically, such perturbations could arise as a result of tetrahedrally bonded groups of water molecules, forming clusters interspersed with unstructured liquid, and leading to increased inhomogeneity in the medium.

That band contours are dependent on the homogeneity of the environment is substantiated by results of a recent investigation by Ikawa and Maeda (35) of the infrared librational bands of cubic and vitreous ice. Pure Gaussian functions were fitted to both forms of ice: with vitreous ice the fit was good whereas with cubic ice, it seems from their data that a partly Cauchy contour would have given better agreement. Cubic ice has long range order of molecular position and forms a homogeneous network of tetrahedrally bonded water molecules. In contrast vitreous ice, deposited from the vapour before molecules have time to rearrange themselves favourably, has a structure consisting of randomly distributed regions of strongly bonded molecules: lacking the mobility of liquid water, the arrangement is permanent. The differences in the molecular arrangements in cubic and vitreous ice may be somewhat analogous to the structural changes occurring in liquid water as temperature is raised. Nemethy and Scheraga (7,52) have calculated that, on temperature increase, the average size of a cluster diminishes but that the total number of clusters increases. This would give rise to increased inhomogeneity in the environment of

water molecules on temperature elevation. The average life-time of a cluster is about 100 times longer than the duration of absorption of infrared radiation: thus despite the greater mobility of liquid water molecules over those of the solid ice, in both, associations would have a finite life-time during infrared measurements.

A Cauchy profile corresponds to a model in which only a single rotational diffusion constant is involved. If there is some departure from this model, the correlation function will be caused to deviate from its normal form (22, 25,34). For example, were rotational motion around different molecular axes characterized by different rotational diffusion constants, then bands would be expected to show differences in their shape parameters (25). The possibility of molecular rotation about the dipole axis in liquid water was suggested some time ago by Magat (56) and has been discussed in a previous report (13,14), in which it was proposed that such motion might be occurring at temperatures above the transition region of 30 to 40°C. This thermally-induced change in the rotational state of the molecule could give rise to the increasing Gaussian character of the combination band profile at higher temperatures.

Another possible cause of Gaussian characteristics in band envelopes of condensed systems is the presence of a series of different polymeric species, giving rise to absorption bands only slightly displaced from one another (20). Spectral evidence for a mixture of species in liquid  $H_2^0$  and liquid  $D_2^0$  has been obtained from the isosbestic behaviour of their absorption bands (14,34,57). The presence of an isosbestic is generally regarded as convincing evidence of a temperature dependent equilibrium between absorbing species (58), so that it is conceivable that the combination band envelope of liquid water does consist of more than one absorption band.

Thus the causes of the temperature-induced loss of Cauchy character of the intermolecular combination band could be a combination of the following effects occurring on temperature elevation:

- Structural "melting" producing inhomogeneities in the medium.
- 2. Development of rotational motion about the dipole axis.
- 3. A series of associated species replacing the continuum of liquid water at lower temperatures.

All of these transformations can be accounted for by a mixture model of liquid water. With the interpretations given to Gaussian characteristics, it is difficult to account for observed temperature effects in terms of a continuum model. It is interesting to note that on the basis of a mixture model, structural breakdown with temperature has been postulated as being more rapid in liquid  $D_2O$  than in  $H_2O$  (7). In the light of the present interpretation of band contours, this is confirmed by the considerably larger decrease with increasing

temperature observed in the shape ratio of the combination band of liquid  $D_0O$  over that of  $H_0O$ .

### 6. CONCLUDING REMARKS

This work demonstrates that changes in shapes of infrared band envelopes with temperature are taking place, can be measured, and are dependent on the vibrational mode involved. Thus shape may be just as much a parameter of an infrared absorption band as the more conventional ones of frequency, intensity and half-width.

The quantitative determination of shape changes is highly dependent on the accuracy with which band indices can be recorded. Here, improvement may be realized by automatic encoding of spectral data in digital form in the manner described by Jones (59).

A factor inherently important to the successful application and interpretation of the method is the precision with which mathematical functions correspond to experimental contours. Functions other than Cauchy or Gauss have been suggested for absorption curve fitting (30, p.280, 39). However, use of Cauchy and Gauss functions does allow a meaningful theoretical interpretation, and it is unlikely that much will be gained at this stage of band analysis from the investigation of other mathematical forms. The validity of combining these functions as a sum or a product is more difficult to justify. In the present study, a product function was used as

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a means of determining changes in absorption contour character. A sum function more closely resembles the behaviour of correlation functions of Gordon (21), and thus may have more of a theoretical justification. A new sum function computer fitting programme, removing one of the arbitrary constraints of the previous one, has been developed by Jones and Young (60), and may be useful in further applications.

In the foregoing, interpretation has been based not on actual shapes but on magnitudes of Gaussian deviations from a Cauchy profile, and on the factors considered to cause such trends. This approach, though having limitations, does seem to be a useful method of acquiring information about the motion of molecules in the liquid. With the development of even more sophisticated methods of band shape analysis it should be possible to secure definite answers to some of the controversial questions concerning the structure of liquid water.

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PART IV

An Overtone of the Infrared Librational

Absorption in Liquid Water

### ABSTRACT

A previously unreported absorption maximum in the infrared spectrum of liquid water at about 1360  $cm^{-1}$  in H<sub>2</sub>O and at 1010  $cm^{-1}$  in D<sub>2</sub>O has been obtained. The dependence of the peak height, frequency and shape of the H<sub>2</sub>O band has been obtained. The band has been assigned to the first overtone of the far-infrared librational band.

### 1. INTRODUCTION

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During the investigations of temperature effects on the infrared combination and deformation bands of liquid water, described in Parts I to III,  $CaF_2$  window absorptions were subtracted from the observed spectra. After doing so, a slight increase in absorption was evident between 1000 and 1500 cm<sup>-1</sup> in H<sub>2</sub>O, indicating the presence of an infrared absorption band in this region.

A literature search revealed that few published spectra for liquid water show the absorption region between the strong librational band at approximately 685 cm<sup>-1</sup> and the deformation band at 1645 cm<sup>-1</sup> (1). However, a bump in this region is seen in the infrared spectra of Blout and Lenormant (2) for liquid  $H_2O$  and of Giguère and Harvey (3) for ice. Walrafen (4) notices a shoulder on the low frequency side of the deformation band in his Raman spectra but attributes it to failure of the optical filter in removing exciting radiations. Busing and Hornig (5) do not show their original Raman spectra of the deformation region but do show an assumed shape of the mercury exciting line with a shoulder at approximately 1500 cm<sup>-1</sup>.

In the previous work it was found that the correction for the  $CaF_2$  windows was rather large below a frequency of about 1400 cm<sup>-1</sup> and therefore some doubt existed as to the interpretation of the effect observed. It was therefore decided to re-investigate the infrared absorption of liquid H<sub>2</sub>O and

liquid D<sub>2</sub>O on the low frequency side of the deformation band using windows with negligible absorption in this region.

# 2. EXPERIMENTAL

Infrared spectra were taken at ambient temperature on a Unicam SP-100G double-beam vacuum spectrophotometer as described in Part I. With  $H_2O$ , windows of  $BaF_2$  were used for the liquid cell while KRS-5 windows were used with  $D_2O$ . With the conventional, parallel-window cell, the high refractive index of KRS-5 led to an intense interference pattern which distorted the observed spectrum for the sample. This difficulty was overcome effectively by use of a wedge-shaped spacer.

### 3. RESULTS AND DISCUSSION

As shown in Fig. IV-1, the spectrum confirmed the presence of an absorption band at approximately 1360 cm<sup>-1</sup> in liquid  $H_2O$ . Were there no absorption maximum between 685 and 1645 cm<sup>-1</sup>, the recorded tracing would show a smoothed minimum such as the one near 1900 cm<sup>-1</sup>. The corresponding spectral region between the librational band at 505 cm<sup>-1</sup> and the deformation band at 1215 cm<sup>-1</sup> in liquid  $D_2O$  at room temperature is also shown in Fig. IV-1. Here, the minimum flattens out in a manner that cannot be accounted for by mere superposition of the two neighbouring absorption bands, and a previously unreported absorption maximum at approximately



FIGURE IV-1. IR absorption of liquid  $H_2O$  in 0.0012 cm  $BaF_2$ cell and of liquid  $D_2O$  in wedge-shaped KRS-5 cell, 30°C.

1010 cm<sup>-1</sup> is indicated.

From its position at about 1360 cm<sup>-1</sup> in  $H_2O$  (almost exactly 2 x 685 cm<sup>-1</sup>), a tentative assignment of this new band to the first overtone of the librational band at 685 cm<sup>-1</sup> is proposed. The  $D_2O$  band at 1010 cm<sup>-1</sup> supports this assignment: its position is at twice the librational band frequency of 505 cm<sup>-1</sup>. Moreover, the  $H_2O/D_2O$  frequency ratio of 1.35 is the isotope effect expected for a vibrational involving hydrogen atoms replaced by deuterium.

It is now interesting to examine the temperature dependence of the infrared parameters of the band in this region as predicted for H<sub>2</sub>0 by the three-band system computer analysis described in Part III. As shown in Fig. IV-2, the peak height, central frequency and Cauchy character of the band in H<sub>2</sub>O decreased with increasing temperature. These trends are closely parallel to the behaviour observed with librational absorption bands. The intensity and frequency of the combination band at approximately 2125  $\text{cm}^{-1}$  in H<sub>2</sub>O believed to be predominantly librational in character - and of the librational band at 685 cm<sup>-1</sup> are known to decrease rapidly with temperature (1,6): a loss in Cauchy character has been observed for the combination band on temperature elevation (7). Thus the assignment of the new band to the first overtone of the librational mode is supported by the temperature dependence of its infrared parameters as well as by its position in both liquid  $H_2O$  and  $D_2O$ .



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FIGURE IV-2. Temperature dependence of 1360 cm<sup>-1</sup> IR absorption band parameters of liquid H<sub>2</sub>O. Shape ratio is 1.0 for a pure Cauchy curve and 0.0 for a pure Gauss curve.
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#### CONCLUSIONS AND SUGGESTIONS FOR FUTURE WORK

Almost all of the infrared parameters investigated for the combination band of both liquid  $H_2O$  and liquid  $D_2O$ were found to behave sigmoidally with temperature, with an inflection region between 25° and 42°C. This transition should be observable from spectral analysis of the librational region as well, and should be most evident with the Raman band originating from librational motion about the dipole axis of a water molecule. Transitional behaviour would not be expected to be as evident in examination of either intramolecular absorption bands, or of bulk properties of liquid water. The present investigation confirms both the reality and the structural origin of a transition in liquid water at about 30° to 40°C.

The variation with temperature of the 2125 cm<sup>-1</sup> and 1555 cm<sup>-1</sup> infrared absorption band parameters of pure liquid  $H_2O$  and 99.7%  $D_2O$  respectively have now been characterized thoroughly. It would thus be possible to use either as a standard in determining effects of other substances on water structure. Band shape behaviours might prove the most informative in such an analysis and continued research in this direction is highly recommended. Dilute solutions of "structure making" hydrophobic substances could be expected to increase the Cauchy nature of the combination band profile, with hydrophilic "structure breakers" conversely enhancing the

(3)

Gaussian nature of this band.

Analysis of the temperature sensitivity of the shapes of other intermolecular absorption bands of liquid water, in particular of the far infrared and Raman librational bands, would be desirable. The composite origin of the spectra in this region would have to be taken into account. However, the overall band envelope shape dependence on temperature in the librational region could be expected to be similar to that observed with the combination band. Experimental and theoretical investigations of condensed system absorption band shapes in general should be continued.

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In the Raman effect, a weak librational overtone band at about 1560-1440 cm<sup>-1</sup> in liquid  $H_2O$  and 1120-1080 cm<sup>-1</sup> in liquid  $D_2O$  should be observable, corresponding to the 1360 cm<sup>-1</sup> and 1010 cm<sup>-1</sup> infrared absorptions.

#### ORIGINAL RESEARCH

1. Making and using a wedge-shaped spacer with KRS-5 plates to obtain a liquid cell suitable for far infrared analysis that eliminated the strong interference pattern of the window material.

2. Obtaining quantitative frequency shifts with temperature for the  $D_2O$  infrared combination band at 1555 cm<sup>-1</sup>.

3. Obtaining a thermal transition in 99.7% pure liquid  $D_2O$ , and the temperature of the transition (25°-42°C).

4. Using Cauchy-Gauss product functions to fit observed infrared absorption contours of liquid water.

5. Obtaining qualitative half-width, intensity, and band shape ratio changes with temperature for the infrared combination band at 2125 cm<sup>-1</sup> and 1555 cm<sup>-1</sup> in  $H_2O$  and  $D_2O$  respectively.

6. Obtaining and interpreting an isosbestic point with the combination band of liquid  $H_2O$  and  $D_2O$ .

7.

Obtaining shape ratio changes with temperature for



the infrared deformation band at 1645  $\text{cm}^{-1}$  and 1215  $\text{cm}^{-1}$  in  $\text{H}_2\text{O}$  and  $\text{D}_2\text{O}$  respectively.

8. Interpreting infrared band shape changes in terms of structural changes of the liquid sample.

9. Observing an absorption maximum at about 1360 cm<sup>-1</sup> in the infrared spectrum of liquid  $H_2O$  and at 1010 cm<sup>-1</sup> in liquid  $D_2O$ , and obtaining the temperature dependence of the infrared parameters of the former.



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APPENDICES

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## APPENDIX I

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The appendices in this section supplement the experimental details given in the previous sections (Parts I to IV) of the Thesis.

#### APPENDIX I-a: SPECTROMETER PERFORMANCE

The performance of the SP-100G spectrophotometer used in recording the infrared spectra of liquid water was checked prior and during the analysis, using as a basis the specifications suggested by the Coblentz Society Board of Managers (1).

#### FREQUENCY

In the SP-100G spectrophotometer, frequency is indicated by fiduciary marks recorded on either side of the chart paper simultaneously with the transmittance spectrum. Frequency was calibrated with standard water vapour (2) and liquid indene (2) absorption lines in the range investigated (1000 to 2700 cm<sup>-1</sup>). The correction term,  $\delta v$ , to be added to the frequency as read from the chart paper, v, is given graphically in Fig. A-1.

#### RESOLVING POWER

The resolving power,  $\nu/\Delta\nu$ , where  $\nu$  is the frequency and  $\Delta\nu$  the observed frequency separation of peaks, as measured from the water vapour spectrum, was better than 600 at the scanning speeds used (50 and 80 cm<sup>-1</sup>/min).

### NOISE LEVEL

The average peak-to-peak noise was about 0.4% during investigations on liquid  $H_2O$  and about 1% in liquid



FIGURE A-1. Frequency calibration curve. Correction factor  $\delta v$  to be added to frequency read, v.

 $D_2O$ . The increase in noise level in  $D_2O$  had no connection with the nature of the sample under analysis, but was due to internal, instrumental causes.

#### TRANSMITTANCE

Before spectra recording, the transmittance scale was carefully adjusted each time. Special care was taken to

ensure no pen drift with both beams blocked.

# REPRODUCIBILITY

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Reproducibility of the instrument was checked by recording a standard polystyrene spectrum at frequent intervals. APPENDIX I-b: SPECTRAL SLIT WIDTH

In any infrared spectrophotometer, the radiation of all wavelengths emitted by the source passes first through the sample, is subsequently resolved by the monochromator, and finally reaches the detector and recording parts of the instrument. The monochromator portion consists of two parallel slits with a variable width between them, an optical system composed primarily of mirrors for directing the radiation, and a method of resolution, consisting of prisms and diffraction gratings in the SP-100G. The slit width determines the amount of radiant energy which enters a monochromator and is called the "mechanical slit width". It is the corresponding "spectral slit width" that is of importance in determining instrumental effects on recorded spectra. The spectral slit width depends on properties of the optical system and on means of resolution as well as on the mechanical slit width. We were able to estimate the spectral slit width fairly accurately for the frequency range  $650-3650 \text{ cm}^{-1}$  by using the following procedure: (1) The mechanical slit widths were calibrated by setting up a microscope with measuring graticule vertically, and focussing it on the slit via a mirror held at 45° to the horizontal. The slit width was then varied manually and meter readings versus measured slit opening readings taken (Fig. A-2). (2) Operating the SP-100G under normal conditions with automatic slit programming, meter reading versus frequency data

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FIGURE A-2. Mechanical slit width calibration curve: meter reading versus mechanical slit width.

were obtained for Cam 1 (650-2150 cm<sup>-1</sup>) and Cam 2 (2150-3650 cm<sup>-1</sup>). (3) From steps 1 and 2 above, mechanical slit width versus frequency data were obtained (Figs. A-3 and A-4). (4) Spectral slit width is approximately given by

$$\Delta v \simeq Q \cdot s \tag{1}$$

where  $\Delta v$  is the spectral slit width in cm<sup>-1</sup>.



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FIGURE A-3. Slit width calibration curves for Cam 1 (650-2150 cm<sup>-1</sup>), automatic slit programme 5, slit width selector 11.



FIGURE A-4. Slit width calibration curves for Cam 2 (2150-3650 cm<sup>-1</sup>), automatic slit programme 6, slit width selector 10.

Q, dependent on the optics of the system, is in  $cm^{-1}/mm$  and s is the mechanical slit width in mm.

Q versus frequency data for the 1500 lines/inch grating used with Cam 1 and the 3000 lines/inch grating used with Cam 2 were obtained from Unicam Instruments Ltd. (3) and are given in Table A-1. Fig. A-5 shows the dependence of spectral slit width on frequency calculated from equation 1.



FIGURE A-5. Spectral slit width versus frequency, 650-3650 cm<sup>-1</sup>, for automatic slit programming.

### TABLE A-1

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### Prism/Grating Data

# NaCl/1500 lines per inch

ν	Q	ν	<u> </u>	ν	Q
<u>cm<sup>-1</sup></u>	cm <sup>-1</sup> /mm	<u>cm<sup>-1</sup></u>	cm <sup>-1</sup> /mm		cm <sup>-1</sup> /mm
650	1.84	1150	7.68	1650	18.55
700	2.23	1200	8.89	1700	19.96
750	2.76	1250	9.61	1750	21.45
800	3.24	1300	10.58	1800	22.84
850	3.78	1350	11.53	1850	24.20
900	4.31	1400	12.68	1900	25.50
950	4.91	1450	13.72	1950	26.95
1000	5.51	1500	14.86	2000	28.30
1050	6.37	1550	15.95	2050	29.75
1100	7.07	1600	17.20	2100	31.40
				2150	32.45

### NaCl/3000 lines per inch

2150	8.70	2650	14.27	3150	21.15
2200	9.24	2700	14.95	3200	21.50
2250	9.71	2750	15.51	3250	22.46
2300	10.20	2800	16.19	3300	23.3
2350	10.75	2850	16.90	3350	24.1
2400 2450 2500 2550 2600	11.33 11.85 12.45 13.00 13.63	2900 2950 3000 3050 3100	17.55 18.22 18.90 19.56 20.13	3400 3450 3500 3550 3600 3650	24.7 25.7 26.4 27.2 27.8 28.7

#### APPENDIX I-c: THERMOCOUPLE CALIBRATION

A copper-constantan thermocouple was made up from stock wires, and its emf at various temperatures spanning the temperature interval investigated measured (4) with the circuit shown in Fig. A-6. The cold end  $(T_1)$  was placed inside a small test tube containing oil which was immersed in a container of crushed ice (distilled water):  $T_2$ , the "hot end", was similarly placed in a test tube that was immersed in a controlled bath, the temperature of which was determined with a National Bureau of Standards calibrated thermometer, after stem correction. A second thermocouple had to be made prior to investigation of liquid  $D_2O$ . Emf versus temperature calibration charts of both are given in Fig. A-7. By this method, temperature could be determined to + 0.3°C.



FIGURE A-6. Circuit used to calibrate Cu-constantan thermocouple.



FIGURE A-7. Cu-constantan thermocouple calibration curves; (1) used with  $H_2O$ , (2) with  $D_2O$ .

#### APPENDIX I-d: MEASUREMENT OF PATH LENGTH

The path length as measured from the interference pattern obtained with an empty cell (5) is

$$t = \frac{n}{2\Delta\nu}$$
(2)

where t is the path length in cm

n is the number of fringes

and  $\Delta v$  is the frequency interval in cm<sup>-1</sup>. Interference patterns obtained with the CaF<sub>2</sub> liquid cells of this investigation are shown in Fig. A-8 (curves a and b) from which a path length of 0.00116  $\pm 2 \times 10^{-5}$  cm was calculated for the cell used with H<sub>2</sub>O, and 0.00160  $\pm 2 \times 10^{-5}$ 

cm for  $D_2O$ .

# EFFECT OF TEMPERATURE ON CaF, WINDOW ABSORPTION

Curve c of Fig. A-8, drawn on expanded frequency scale, indicates the negligible effect changes of temperature had on the CaF<sub>2</sub> window spectrum.



FIGURE A-8. Interference patterns of empty CaF<sub>2</sub> cells: curve (a), cell used with H<sub>2</sub>O; curve (b), cell used with D<sub>2</sub>O; curve (c), superposition of empty CaF<sub>2</sub> cell transmittance patterns obtained at 33.4°, 45.4°, and 52.6°C. Frequency scale of curve (c) expanded 1-1/2 times.

APPENDIX I-e: HDO CONTENT OF D<sub>2</sub>O SAMPLE

Since at high concentrations of  $D_2^0$  the  $H_2^0$  content of a sample is negligible, and since  $D_2^0$  itself does not absorb at 3400 cm<sup>-1</sup>, it was possible to estimate the HDO content of the  $D_2^0$  sample (6) from this absorption and the equation

$$c = \frac{1}{\varepsilon_{\max} \cdot t} \log_{10} \left( \frac{T_o}{T} \right)_{v_o}$$
(3)

using the following values.

$$\varepsilon_{max} = \text{maximum molecular extinction coefficient} of HDO at 3400 cm-1 (25°C)= 62.5 & mole-1cm-1 (7)t = path length = 0.0016 cmTo = base line transmittance = 90.8%TT1 = minimum transmittance at 3400 cm-1= 81.0%Tc1 = concentration of HDO in the D2O sample,in moles  $\ell^{-1}$   
c<sub>0</sub> = concentration of "pure" HDO = 55.24  
moles  $\ell^{-1}$  (7).$$

The calculated  $c_1$  value was 0.496 moles  $\ell^{-1}$ . Hence the HDO content =  $\frac{c_1}{c_0} = \frac{0.496}{55.24} = 0.9$ % HDO.

The decrease in transmittance at 3400 cm<sup>-1</sup> for a heavy water sample retained in the liquid cell over a period of 26 hours was 1.0%T. The concentration of HDO after 26 hours,  $c_2$ , calculated from equation 3 with  $T_2 = 80.0$ %T was 0.550 moles  $\ell^{-1}$ . This corresponds to an HDO content of 1.0%,





FIGURE A-9. Spectra showing the HDO absorption at 3400 cm<sup>-1</sup> and the  $D_2^{O}$  combination band at 1555 cm<sup>-1</sup>, for sample retained in cell over a period of 26 hours.

or a total increase of HDO amounting to 0.1%. Fig. A-9 shows spectra recorded of the 3400 cm<sup>-1</sup> and 1555 cm<sup>-1</sup> regions of liquid  $D_2O$  at 25°C, from times immediately after filling the cell up to 26 hours later.

#### APPENDIX I-f: BAND OVERLAP IN CHOSEN SETS OF

### CAUCHY AND GAUSS PROFILES

The indices of the mathematical curves, S and U, used to obtain envelopes of overlapped bands (Part II, Fig. II-3) were obtained from the expression

$$\varepsilon(v) = \varepsilon_{\max} \left[ 1 + 4 \left( \frac{v - v_0}{\Delta v_{1/2}} \right)^2 \right]^{-1}$$
(4)

for Cauchy contours, and are listed in Table A-2. On letting  $C_S$  and  $C_U$  correspond to concentration of curve S and curve U respectively, with  $C_S + C_U = 1.00$ , indices of combined curves  $M_i$  (i = 1,2,3) were obtained by calculating  $\varepsilon(v)_{M_i}$  as a function of v from

$$\varepsilon(v)_{M_{i}} = C_{S_{i}} \cdot \varepsilon(v)_{S} + C_{U_{i}} \varepsilon(v)_{U}$$
(5)

with

$$C_{s_1} = 0.9 \text{ for } M_1$$
  
 $C_{s_2} = 0.8 \text{ for } M_2$ 

and

$$C_{S_3} = 0.7 \text{ for } M_3.$$

For a Gaussian contour, molar extinction coefficient as a function of frequency is given by

$$\varepsilon(v) = \varepsilon_{\max} \cdot \exp\left[-4\ln 2\left(\frac{v-v_o}{\Delta v_{1/2}}\right)^2\right]$$
 (6)

Indices of two Gaussian curves,  $S_{G}$  and  $U_{G}$ , with the properties given in Table A-3, are also listed in Table A-2. Envelopes of combined curves,  $G_{1}$  and  $G_{2}$ , corresponding to  $C_{S_{1}} = 0.8$  and

# TABLE A-2

V	ε(ν) C	auchy	ε(ν) (	Jauss
	S	U	S <sub>G</sub>	U <sub>G</sub>
-200	1.475	1.00	0.376	0.315
-150	1.850	1.54	0.798	1.05
-100	2.340	2.50	1.26	2.50
- 75	2.65	3.20		
- 50	3.00	4.00	2.028	4.20
- 25	3.395	4.70		
0	3.84	5.00	3.00	5.00
25	4.32	4.70		
50	4.80	4.00	4.08	4.20
75	5.26	3.20		
100	5.64	2.50	5.04	2.50
125	5.91	1.95		
150	6.00	1.54	5.76	1.05
175	5.91	1.23		
200	5.64	1.00	6.00	0.315
225	5.26	0.825		
250	4.80	0.69	5.76	0.065
300	3.84	0.50	5.04	0.010
350	3.00	0.38	4.08	0.001
400	2.34	0.29	3.00	0
450	1.85	0.24	2.028	
500	1.475	0.19	1.260	
550	1.20	0.16	0.798	
600	0.99	0.13	0.376	
650	0.83	0.11	0.183	
700	0.70	0.10	0.080	
<u> </u>				
vo	150	, 0	200	0
ε <sub>max</sub>	6.00	5.00	6.00	5.00
<sup>Δν</sup> 1/2	400	200	400	200

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# Indices of Cauchy and Gauss Calculated Curves

### TABLE A-3

Curve	C <sub>S</sub>	CU_	vo	<sup>e</sup> max	$\frac{\Delta v_{1/2}}{2}$
s <sub>G</sub>	1.0	0.0	200	6.0	400
G <sub>1</sub>	0.8	0.2	175	4.9	440
G2	0.6	0.4	50	4.1	465
U <sub>G</sub>	0.0	1.0	0	5.0	200

Parameters of Gauss Curves

 $C_{S} + C_{U} = 1.00$ 

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 $C_{S_2} = 0.6$  respectively, were calculated from

$$\varepsilon(v)_{G_{i}} = C_{S} \cdot \varepsilon(v) S_{G} + C_{U} \cdot \varepsilon(v) U_{G}$$
(i = 1,2)
(7)

The Gaussian contours obtained are shown in Fig. A-10. The decrease in observed peak height, increase in width and shift to lower frequency that occurs on passing from curve  $S_{G}$  through  $G_{1}$  to  $G_{2}$  is apparent. Thus the same trends are obtained with Gaussian contours as with Cauchy.



FIGURE A-10. Calculated Gauss overlap curves. Parameters of curves given in Table A-3.



The integrated absorption intensity (B) of a band is the area beneath its absorption curve. For band shapes corresponding to a Cauchy contour, integration yields (8)

$$B_{C} = \int_{-\infty}^{+\infty} A(v)_{C} dv = \int_{-\infty}^{+\infty} \varepsilon_{max} \left( \frac{1}{1+4 \left[ \frac{v - v_{o}}{\Delta v_{1/2}} \right]^{2}} \right) dv$$

$$= 1.57 \varepsilon_{\max}^{\Delta v} \frac{1}{2}$$
(8)

and for a Gaussian shaped curve (8)

$$B_{G} = \int_{-\infty}^{+\infty} A(v)_{G} dv = \int_{-\infty}^{+\infty} \exp\left(-4\ln 2\left(\frac{v-v_{O}}{\Delta v_{1/2}}\right)^{2}\right) dv$$

$$= 1.06\varepsilon_{\max} \Delta v_{1/2} \tag{9}$$

That is, for either shape the integrated absorption intensity is given by the general expression

$$B = K \cdot \varepsilon_{\max} \cdot \Delta v_{1/2} \tag{10}$$

in which K equals either 1.57 or 1.06, as required.

To determine the integrated intensity of a band with shape conforming to a Cauchy-Gauss product function, the required integration is

$$B_{p} = \int_{-\infty}^{+\infty} \varepsilon_{max} \cdot \left(1 + X_{3}^{2} (v - v_{o})^{2}\right)^{-1} \cdot \exp\left(-X_{4}^{2} (v - v_{o})^{2}\right) dv$$
(11)

in which the Cauchy half-width  $(\Delta v_{1/2})_{\rm C}$  and the Gaussian half-width  $(\Delta v_{1/2})_{\rm G}$  have been replaced by

$$(\Delta v_{1/2})_{\rm C} = 2 \cdot (x_3)^{-1}$$
 (12)

and

$$(\Delta v_{1/2})_{\rm G} = 2\sqrt{\ln 2} \cdot (x_4)^{-1}$$

Equation (11) cannot be calculated directly. The proportionality between the Cauchy and Gauss characteristics of the profile, however, is obtainable, from the shape ratio (S) of the product function, where

$$S = \frac{x_3}{x_3 + x_4} = \begin{cases} 1.0 \text{ (pure Cauchy curve)} \\ 0.0 \text{ (pure Gaussian curve)} \end{cases}$$
(13)

Assuming that equation (10) is still applicable in the case of a product function, the problem now resolves into determining the correct value of K to incorporate in the expression. This was accomplished by introducing the shape ratio factor into the calculation of K:

$$K = S \cdot 1.57 + (1 - S) \cdot 1.06$$
 (14)

With the liquid water bands investigated, S was calculated in Part III and found to be temperature dependent. Hence K is also dependent on temperature.

The values used to obtain K and band area, B, of the combination band  $(v_{2+L})$  of liquid  $H_2O$  and  $D_2O$  are tabulated in Table A-4. In Table A-5, data for calculating K of the deformation band  $(v_2)$  are given. B was not calculated for  $v_2$  because of lack of accurate half-width temperature

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### TABLE A-4

Data for Calculating K and B for  $\nu_{2+L}$  for  $\text{H}_2\text{O}$  and  $\text{D}_2\text{O}$ 

Temp. (°C)	S*	K=S·1.57 +(1-S)·1.06	<sup>e</sup> max <sup>†</sup> <u>l mol<sup>-1</sup>cm<sup>-1</sup></u>	$\frac{\Delta v_{1/2}}{cm^{-1}}$	$\frac{B=K\cdot\varepsilon_{\max}\cdot\Delta\nu}{1/2}$
5.4	.97	1.55	2.59	322	1295
8.1	.98	1.56	2.56	326	1300
12.2	.94	1.54	2.51	331	1280
14.7	.91	1.52	2.48	334	1260
20.C	.93	1.53	2.425	339	1257
29.7	.825	1.48	2.33	345	1190
33.0	.78	1.46	2.30	347	1162
38.0	.806	1.47	2.26	349	1156
40.2	.70	1.41	2.24	350	1104
41.7	.75	1.44	2.23	351	1125
45.0	.74	1.44	2.20	352	1112
53.4	.71	1.42	2.14	356	1082
57.4	.68	· 1.41	2.12	359	1070
63.7	.66	1.40	2.08	364	1058
67.1	.64	1.39	2.06	367	1050
67.5	.66	1.40	2.06	367	1060
			D <sub>2</sub> 0		
4.2	.84	1.49	1.52	230	518
6.8	.90	1.52	1.49	233	527
10.2	.84	1.49	1.46	238	510
13.6	.725	1.43	1.43	242	494
19.7	.70	1.41	1.39	248	486
27.2	.61	1.34	1.34	254	457
30.6	.63	1.35	1.325	256	457
34.0	.63	1.35	1.31	259	457
38.0	.60	1.34	1.29	261	451
46.2	.55	1.31	1.25	266	435
48.4	.54	1.31	1.24	267	432
52.6	.52	1.30	1.21	269	423
62.3	.47	1.28	1.145	276	405
66.0	.34	1.22	1.11	279	380

<sup>н</sup>2<sup>0</sup>

\* Averages calculated from 1 and 2 Band Systems.

<sup>†</sup> Obtained from smoothed best-fit polynomial curves.

### TABLE A-5

Data for Calculating K for  $\nu_2$  of  ${\rm H_2O}$  and  ${\rm D_2O}$ 

H <sub>2</sub> O	
<u></u>	K=S•1.57+(1-S)•1.06
.765	1.45
.776	1.46
.782	1.46
.797	1.47
.807	1.47
.817	1.48
.827	1.48
.838	1.49
D <sub>2</sub> 0	
.695	1.41
:702	1.42
.724	1.43
.741	1.44
.760	1.45
.780	1.46
.798	1.47
.808	1.47
	$H_2O$ <u>s*</u> .765 .776 .782 .797 .807 .817 .827 .838 $D_2O$ .695 :702 .724 .741 .760 .780 .780 .798 .808

\* Obtained from straight line curve fitted to averaged 2 and 3 band system calculated values.



FIGURE A-11. Calculated temperature dependence of K, for combination  $(v_{2+L})$  and deformation  $(v_2)$  bands of liquid H<sub>2</sub>O and D<sub>2</sub>O.

data for it. In Fig. A-11 the temperature dependence of K obtained for these two bands is given.

# APPENDIX II

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In this section, input data required for the curve analysis described in Part III of the Thesis are tabulated. APPENDIX II: INPUT DATA FOR COMPUTER PROGRAMME IRCURFIT

The input data required during the Cauchy-Gauss product function curve fitting procedure were:

 $\alpha$  - the base line absorbance

- x<sub>1</sub> to x<sub>4</sub> four variable parameters for each of M bands fitted
  - and, band indices i.e. cm<sup>-1</sup> and %T values at specified frequency intervals.

 $\alpha$  equalled 0.0419, corresponding to 90.8%T.

In Appendix II-a, the parameters forming the input to programme IRCURFIT are tabulated. Appendix II-b gives the indices of the CaF<sub>2</sub> cell window subtracted from the observed water spectra and Appendix II-c lists the indices of the water spectra after correction for window effects.



The variable input parameters for  $H_2O$  are listed in Table A-6 and for  $D_2O$  in Table A-7. At each temperature, the first value refers to the combination band, the second to the deformation band and the third to the new, overtone band. The values listed can be converted easily to actually measured quantities as follows:

> $\underline{X}_{1}$ , peak height:  $\underline{X}_{min} = \operatorname{antilog}_{10} - (x_{1} + \alpha)$

 $\underline{X}_2$ , frequency of maximum absorption:

 $v_{o}(cm^{-1}) = \frac{40X_{2} + 1000 (H_{2}O)}{40X_{2} + 500 (D_{2}O)}$ 

 $\frac{X_3 \text{ and } X_4, \text{ band width}}{\Delta v_{1/2} (\text{cm}^{-1})} = \frac{76.00}{X_3}$ or  $\Delta v_{1/2} (\text{cm}^{-1}) = \frac{18.640}{X_4}$ 

$$\frac{\alpha, \text{ base line}}{T_{0}(%)} = \text{antilog}_{10}(-\alpha)$$

# TABLE A-6

Variable Input Data for  $H_2O$ 

Temp. (°C)	x	x	X	X_4
5.4	0.1718	28.825	0.2336	0.0572
	1.2022	16.250	0.752	0.184
	0.2483	9.400	0.147	0.036
8.1	0.1702	28.525	0.2300	0.0564
	1.1947	16.125	0.752	0.184
	0.2509	9.375	0.147	0.036
12.2	0.1692	28.450	0.2336	0.0572
	1.1910	16.050	0.752	0.184
	0.2432	9.375	0.147	0.036
14.7	0.1649	28.275	0.2228	0.0544
	1.2679	16.050	0.752	0.184
	0.2365	9.375	0.147	0.036
20.0	0.1611	28.250	0.2264	0.0558
	1.1877	15.925	0.752	0.184
	0.2365	9.375	0.147	0.036
29.7	0.1559	28.012	0.2214	0.0542
	1.3203	16.000	0.752	0.184
	0.2246	9.375	0.147	0.036
33.0	0.1515	28.075	0.2140	0.0524
	1.3340	16.000	0.752	0.184
	0.2210	9.375	0.147	0.036
38.0	0.1493	27.900	0.2140	0.0524
	1.3001	16.050	0.752	0.184
	0.2226	9.375	0.147	0.036
40.2	0.1500	27.950	0.2164	0.0542
	1.3675	16.175	0.752	0.184
	0.2210	9.375	0.147	0.036
41.7	0.1471	27.775	0.2164	0.0542
	1.3675	16.075	0.752	0.184
	0.2210	9.375	0.147	0.036
45.0	0.1486	27.900	0.2164	0.0532
	1.3146	16.000	0.752	0.184
	0.2210	9.375	0.147	0.036

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(cont'd.)

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# Table A-6 (cont'd.)

Temp. (°C)	X	2	X	X
50.2	0.1449	27.838	0.2152	0.0538
	1.3207	16.125	0.752	0.184
	0.2210	9.375	0.147	0.036
53.4	0.1435	27.650	0.2140	0.0524
	1.2610	16.075	0.752	0.184
	0.2210	9.375	0.147	0.036
57.4	0.1420	27.650	0.2068	0.0504
	1.2620	16.050	0.752	0.184
	0.2210	9.375	0.147	0.036
57.4	0.1428	27.650	0.2104	0.0516
63.7	0.1392	27.475	0.2104	0.0516
	1.2803	16.000	0.752	0.184
	0.2210	9.375	0.147	0.036
67.1	0.1370	27.350	0.2080	0.0508
	1.2903	16.000	0.752	0.184
	0.2210	9.375	0.147	0.036
67.5	0.1365	27.325	0.2052	0.0500
	1.2903	16.000	0.752	0.184
	0.2210	9.375	0.147	0.036

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Variable Input Data for  $D_2O$ 

Temp. (°C)	X	X	X	X
4.2	0.1325	26.750	0.3300	0.0808
	1.0149	17.875	1.086	0.266
	0.0897	13.850	0.095	0.027
6.8	0.1325	26.675	0.3220	0.0792
	1.0649	17.925	1.086	0.266
	0.1106	13.850	0.095	0.027
9.8	0.1301	26.625	0.3220	0.0792
	1.0881	17.875	1.086	0.266
	0.1231	13.700	0.095	0.027
10.2	0.1318	26.625	0.3220	0.0792
	1.0984	17.900	1.086	0.266
	0.1231	13.750	0.095	0.027
13.6	0.1272	26.500	0.3160	0.0772
	1.0793	17.875	1.086	0.266
	0.1231	13.250	0.095	0.027
13.7	0.1272	26.500	0.3160	0.0772
	1.0507	17.800	1.086	0.266
	0.1168	14.000	0.095	0.027
19.7	0.1226	26.438	0.3030	0.0744
	1.1062	17.875	1.086	0.266
	0.1326	13.500	0.095	0.027
27.2	0.1170	26.375	0.2970	0.0728
	1.0777	17.750	1.086	0.266
	0.1046	13.200	0.095	0.027
30.6	0.1155	26.325	0.2970	0.0728
	1.0970	17.775	1.086	0.266
	0.1231	13.500	0.095	0.027
34.0	0.1145	26.250	0.2920	0.0716
	1.1157	17.775	1.086	0.266
38.0	0.1135	26.250	0.2920	0.0716
	1.1595	17.750	1.086	0.266
	0.1231	13.500	0.095	0.027



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#### Table A-7 (cont'd.)

Temp. (°C)		×2	×3	×4
46.2	0.1108	26.125	0.2890	0.0708
	1.1746	17.750	1.086	0.266
48.4	0.1095	26.050	0.2810	0.0688
	1.1812	17.750	1.086	0.266
	0.2049	13.500	0.095	0.027
52.6	0.1060	25.975	0.2810	0.0688
	1.1812	17.750	1.086	0.266
	0.1962	13.500	0.095	0.027
62.3	0.0995	25.700	0.2760	0.0676
	1.1812	17.750	1.086	0.266
62.3	0.1030	25.725	0.2920	0.0716
66.0	0.0985	25.500	0.2710	0.0664
	1.0426	17.800	1.086	0.266



APPENDIX II-b: CaF<sub>2</sub> CELL INDICES

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In Table A-8 the  $CaF_2$  cell transmittance values at 20 cm<sup>-1</sup> intervals subtracted from the recorded liquid water spectra by computer programme IRCELL are listed.

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CaF2	Cell	Input	Indices
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cm <sup>-1</sup>	%т (н <sub>2</sub> 0)	%T (D <sub>2</sub> O)	cm <sup>-1</sup>	%T (H <sub>2</sub> O)	%T (D <sub>2</sub> O)
2700	92.4	_	1360	87.0	85.1
		-	1340	86.1	83.2
2000	92.4	91.6	1320	84.3	81.1
			1300	82.4	78.7
1660	92.4	91.6	1280	80.3	76.3
1640	92.4	91.6	1260	77.5	73.5
1620	92.3	91.5	1240	74.2	70.3
1600	92.2	91.3	1220	70.2	67.0
1580	92.0	91.1	1200	66.1	63.1
1560	91.8	90.9	1180	61.1	58.8
1540	91.5	90.7	1160	55.6	54.0
1520	91.2	90.5	1140	49.3	48.6
1500	90.8	90.2	1120	42.7	42.6
1480	90.4	89.8	1100	36.1	36.0
1460	90.0	89.4	1080	29.4	29.3
1440	89.6	89.1	1060	22.4	22.6
1420	89.1	88.5	1040	16.4	16.8
1400	88.4	87.6	1020	11.0	-
1380	87.8	86.5	1000	6.0	-

APPENDIX II-c: Water Band Indices Input Data

Band indices input data for  $H_2^0$  are listed in Table A-9. Frequency decreases across the table. The first series of numbers in each of the nine columns refers to frequency, in "new units" of  $\frac{1}{4}(\nu(cm^{-1}) - 1000)$ : the second set of numbers gives percent transmittance after correction for CaF<sub>2</sub> windows.

Table A-10 lists band indices input data for  $D_2^0$  spectra. Frequency is in "new units" of  $\frac{1}{4}(v(cm^{-1}) - 500)$  in this case.

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Band Indices Input Data for  $H_2^{0}$ 

Frequency in "New Units"

Transmittance in percent

H<sub>2</sub>O TEMP. 5.4°C

425	89.50	420	90.26	415	90.69	410	90.80	405	91.02	400	90.80	395	90.37	390	89.83	385	29.07
380	88-20	375	87.12	370	86.15	365	85.00	360	83.77	355	82.47	350	81.28	345	79.98	340	78.57
335	76.73	330	75.65	325	73.70	320	71.64	315	69.91	310	67.86	305	65.80	300	63.85	295	02.55
290	61.58	285	61.26	280	61.80	275	62.88	270	64.50	265	66.34	260	68.72	255	71.54	250	73.48
245	75.65	240	77.27	235	78.35	230	79.11	225	79.33	220	79.33	215	78.90	210	77.92	205	76.41
200	73.70	195	69.70	190	63.74	185	55.09	180	41.02	175	22.62	170	12.34	165	7.79	160	7.25
155	12.35	150	22.13	145	31.41	140	35.84	135	40.97	130	43.20	125	46.15	120	47.79	115	48.44
110	49.78	105	50.39	100	50.85	95	51.48	90	52.07	35	52.61	80	53.62	75	54.49	70	55.17
65	56.00	60	57.14	55	58.26	50	58.85	45	60.39	40	60.97	35	62.68	30	63.00	25	63.43
20	64.29	15	64.29	10	67.68	5	67.27	Ũ	90.00								
		н <sub>2</sub> о т	remp. 8	.l°C													
125	00.00	( 20	00.15	( ) 5	00 / 0	( ) 0	00.01	105		(00)	00 00	205	00 / 8	300		204	<b>00 07</b>
420	89.39	420	90.15	415	90.69	410	90.91	405	90.91	400	90.80	375	90.48	390	89.83	305	59.01 79.70
330	88.20	315	87.12	310	86.15	305	85.00	560	83.87	300	62.00	350	51.28	340	80-19	340	10.19
335	11.38	230	15.81	325	13.92	320	11.86	315	69.81	310	01.15	305	66.02	300	04.10	295	72 0/
290	61.69	285	61.30	280	61.60	215	02.00	270	54.29	200	20.11	260	08.29	200	77 01	250	72.94
245	75.11	240	70.04	235	18.03	230	18.90	225	19.11	220	19.11	215	10.01	210	7 ( 0	205	7 03
200	13.00	195	70.24	140	64.29	185	55.30	180	41.77	175	25.00	170	12.55	105	1.00	160	1.03
155	11.48	150	20.12	145	30.54	140	37.15	135	41.04	130	44.72	125	40.79	120	45.01	115	49.11
110	49.78	105	50.39	100	50.96	95	51.48	90	51.95	85	52.20	80	22.14	15	24.00	70	24.92
65	55.01	60	56.41	55	57.83	50	59.15	45	59.90	40	61.33	35	62.07	30	63.41	25	63.99
20	64.97	15	65.18	10	10.13	5	73.64	0	93.33								
		н <sub>2</sub> о л	TEMP. 1	2.2°C													
425	89.39	420	90.37	415	91.02	410	91.13	405	91.02	400	90.80	395	90,48	390	89,93	385	89.07
380	88.10	375	87.45	370	86.47	365	85.39	360	84.20	355	83.01	350	81.60	345	80.19	340	78.90
335	77.71	330	76.08	325	74.24	320	72.40	315	70.24	310	68.18	305	66.34	300	64-61	295	63.20
290	62.34	285	61.90	230	62.12	275	63.20	270	64.61	265	66.34	260	68-51	255	71.00	250	73.16
245	75.22	240	77.05	235	78.25	230	79.11	225	79.33	220	79.33	215	78.90	210	78-14	205	76.84
200	74.57	195	70.67	190	65.04	185	50.06	180	42.53	175	24.68	170	12.23	165	7.14	160	6.71
155	11.70	150	20.93	145	30.65	140	37.36	135	42.40	130	45.29	125	47.14	120	48.45	115	49.67
110	50.11	105	50.73	100	51,41	95	52.05	90	52.64	5-0 55	52.96	80	53.74	75	54.73	70	55.17
65	56.26	60	55.65		57.55	50	58.70	45	60.23	40	60.79	35	61.46	30	62.76	25	64.54
20	63.95	15	68.30	10	65.85	5	70.91	0	88.33	. •				20			
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#### TABLE A-9 (cont'd.)

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	H_O TEMP. 14.	.7°C	Į.			٠,	•	
	2							385 89.07
425 88.10	420 85.07	415 85.83	410 90.37	405 90.69	400 90+80	195 90.75	345 90.43	340 79.44
380 88.31	375 87.34	370 26.59	365 85.61	360 84.31	355 83.01	179 8107t	300 65.15	295 63 64
335 78-25	220 76.41	325 74.68	320 72+73	315 70.67	310 69.61	11.3 CC0 77	255 73.24	250 72-51
290 62.55	285 62.12	2-0 62-12	275 62.00	270 64.07	265 65.10	215 79 70	210 78.03	205 76.84
245 74.35	240 76.30	235 77.49	230 78.68	225 79-11	720 79.11	170 17 55	165 6.93	160 5.52
200 74.57	195 71.21	190 65,80	185 56.73	120 45.02	1/5 20.02	100 120 33	120 42.45	115 49.56
155 9.86	150 19.63	145 30.00	140 36.60	135 41.09	130 45.07	123 47014	75 53.64	70 54,30
110 50.11	105 50.51	100 50.96	95 51.37	97 51.84	45 57.00	75 61.05	30 62.30	25 62.67
65 54.97	60 55.80	55 56.84	50 58.40	45 59.08	40 27+23	22 01-02	7.5 O. O. S	
20 63.27	15 62.95	10 61.59	5 64.55	0 80.00				
	HO TEMP. 20	.0°C				•		
	2						200 80 87	285 86.29
105 00 04	420 85.83	415 50.37	410 90.69	405 90.80	400 90.58	395 00.15	350 290 74	343 79.55
300 99 63	375 67.45	370 86.47	365 85.39	260 84.42	355 93+23	350 82.75	345 604 64	205 43 05
225 78.03	330 75. 57	325 74.44	320 73.05	315 71.32	310 65.16	343 Chett	755 69-68	250 71.97
200 62.99	285 62.34	280 62.23	275 52.99	270 64.18	265 65.58	2012 01+44	210 77.60	205 76.30
245 74.03	240 75.76	275 77.27	230 78.14	225 78.20	SS0 18+46	170 12 12	145 6 39	160. 5.09
200 74.35	195 70.78	190 64.94	1,85 55+95	180 42.42	1/5 26+19	170 12012	120 49.89	115 50.00
155 9.43	150 19.20	145 30.65	140 37.25	135 42.30	130 45+18	123 41+30	75 54 13	79 54.79
110 50.33	105 50.73	100 51.30	95 52.05	90 52 <b>.</b> 76	85 53.08	21, 234 /4	30 61-36	25 51.50
65 55-61	60 55.53	55 56.84	50 57.79	45 58.43	40 58-81	22 23023	30 01030	
20 60.20	15 58.93	10.64.63	5 59.09	0 78.33				
	H <sub>2</sub> O TEMP. 29	.7°C						
	· •			( 05 00 01	400 00 80	305 00 58	300 90.15	385 89.61
425 89.29	420 89.94	415 90.58	410 90.91	403 90.91	255 84 09	350 82.90	345 81.60	340 80.30
380 88.85	375 87.77	370 87.34	303 80+20	300 03.20	310 70 74	305 68.72	300 66.77	295 65 37
335 78.90	330 77.49	325 15.65	320 13492	313 12+17	265 65-69	260 67-10	255 69.37	250 71.43
290 64.07	285 63-31	280 62.99	213 03.31	270 04427	220 78.14	215 77.81	210 77.27	205 76.08
245 13.21		233 10.32	195 56.82	180 44-05	175 26-52	170 11.80	165 5.52	150 4.11
200 /4.24	195 70.89	146 20 02	140 37-04	135 42.84	130 45.94	125 47.80	120 49.23	115 50-22
175 8.13	105 51 40	145 27.02	95 57-16	90 52-41	85 52.50	80 53-14	75 53.64	70 53.80
110 51.00	60 54 95	55 55 84	50 56-28	45 56.79	40 57.01	35 57.20	30 57.85	25 57-34
20 55.10	15 54.46	10 56.10	5 51.82	0 61.67				
	н <sub>2</sub> 0 темр. 33	.0°C			•			
· ·· •·		(15 00 3/	410 00 FP	405 90-80	400 90-80	395 90.58	390 90.37	385 89.72
425 88.96	420 89.72	415 90.20	372 87 37 410 30*30	360 85.61	355 84.52	350 83.44	345 82.36	340 81.28
380 89.07	375 88.20	310 81.47	220 76 22	315 73.27	310 71.64	305 69.91	300 68.18	295 66.45
335 79.98	330 78.57	325 11.00	320 13.22	270 64.94	265 66.13	250 57.64	255 69.48	250 71.43
290 65.26	285 64.50	200 04+01	212 07027	225 78.25	220 78.57	215 78.46	210 78.03	205 76.95
245 73.16	Z40 /5.11	233 10.32	125 59,85	180 47.40	175 31.17	170 16.56	165 8.98	160 6.06
200 75.11	145 12.08	146 20 12	140 37.36	135 43.06	130 46.38	125 49.01	120 50.66	115 51.67
155 8.99	150 17-14	143 29.13	140 21120		05 67 60	80 55 16	75 55.34	70 55.54
110 52.12	105 53 44	100 53 11	95 53,53	90 54.14	CJ J4.J3		15 22 22	
	105 52.64	100 53.11	95 53.53 50 58-25	90 54.14 45 59.25	40 59.89	33 61.26	30 62.06	25 62.60
65 56.13	105 52.64	100 53.11 55 57.55 10 68.29	95 53.53 50 58.25 5 73.64	90 54.14 45 59.25 0 96.57	40 59.89	33 61.26	30 62.06	25 62.60

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TABLE A-9 (cont'd.)

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H<sub>2</sub>O TEMP. 38.0°C

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425 88.74 380 88.85 335 80.09 290 66.02 245 73.81 200 74.78 155 9.75 110 52.79 65 56.13 20 57.82	420 89.29 375 88.20 330 78.46 285 64.83 240 75.22 195 71.43 150 20.07 105 53.31 60 55.93 15 60.27	415 89.83 370 87.23 325 77.16 280 64.29 235 76.62 190 65.48 145 32.07 100 53.79 55 56.98 10 60.98	410 90.48 365 86.58 320 75.76 275 64.61 230 77.81 185 56.82 140 38.13 95 54.33 50 56.73 5 62.73	405       90.91         360       85.71         315       73.92         270       65.37         225       78.25         180       44.91         135       44.26         90       54.60         45       58.10         0       83.33	400 90.80 355 84.52 310 72.19 265 66.23 220 78.57 175 28.68 130 47.15 85 54.59 40 58.45	395       90.58         350       83.33         305       70.35         260       67.86         215       77.27         170       12.45         125       49.56         80       55.16         35       58.82	390       90.26         345       82.36         300       68.29         255       69.70         210       77.81         165       6.49         120       50.77         75       55.46         30       59.72	385 89.61 340 81.17 295 66.88 250 71.54 205 76.84 160 5.09 115 52.00 70 55.67 25 59.56
	H <sub>2</sub> O TEMP. 40	.2°C						
425 88.74 380 89.29 335 80.09 290 65.69 245 72.84 200 74.68 155 _ 8.88 110 52.46 65 55.10 20 59.52	420 89.61 375 88.42 330 78.68 285 64.72 240 74.68 195 71.97 150 18.55 105 52.97 60 55.80 15 59.38	415 90.15 370 87.77 325 77.27 280 64.29 235 76.08 190 67.32 	410 90.58 365 86.90 320 75.54 275 64.39 230 77.38 185 59.20 140 37.80 95 53.87 50 57.79 5 67.27	405 90.69 360 85.93 315 73.92 270 64.94 225 77.92 180 47.29 135 43.39 90 54.37 45 58.43 0 86.67	400 90.30 355 84.85 310 72.08 265 66.02 220 78.25 175 31.06 130 47.37 85 54.24 40 58.81	395       90.69         350       83.87         305       70.24         260       67.32         215       78.14         170       14.83         125       49.78         80       54.69         35       60.24	390       90.37         345       82.47         300       67.32         255       69.05         210       77.71         165       8.01         120       51.00         75       54.85         30       59.48	385 89.94 340 81.39 295 66.88 250 71.00 205 76.52 160 5.74 115 52.11 70 54.79 25 60.11
	H <sub>2</sub> O TEMP. 41	•7°C						
425 88.42 380 89.18 335 80.74 290 66.13 245 73.38 200 75.22 155 8.78 110 51.79 65 54.58 20 58.16	420 89.29 375 88.42 330 79.33 285 65.37 240 75.11 195 72.19 150 18.00 105 52.08 60 54.72 15 58.48	415 89.94 370 87.66 325 78.03 280 64.94 235 76.52 190 67.21 145 29.46 100 52.43 55 54.99 10 60.37	410 90.37 365 86.90 320 76.30 275 64.94 230 77.60 185 59.63 140 37.69 95 52.73 50 56.88 5 61.82	405 90.69 360 86.04 315 74.24 270 65.48 225 78.79 180 47.19 135 43.83 90 53.10 45 57.45 0 71.67	400 90.80 355 82.90 310 72.84 265 66.45 220 78.57 175 30.41 130 47.81 85 53.31 40 57.73	395 90.69 350 83.98 305 71.21 260 67.86 215 78.57 170 14.72 125 50.00 80 53.62 35 58.01	390       90.26         345       82.90         300       69.05         255       69.48         210       78.14         165       7.36         120       51.44         75       53.88         30       58.78	385 89.83 340 81.71 295 67.21 250 71.54 205 76.95 160 5.09 115 51.44 70 54.05 25 58.45
	н <sub>2</sub> 0 темр. 45	.0°C						
425 87.45 380 89.18 335 90.63 290 66.22 245 73.16 200 74.35 155 8.68 115 8.68 115 5.48	420 85.18 375 88.31 320 79.11 285 85.15 240 74.85 195 71.10 150 19.74 105 55.76	415 P5.54 370 P7.66 325 77.25 280 64.72 235 76.08 190 62.45 145 30.65 100 52.50 55 55.94	410 90.48 365 86.80 370 76.19 275 64.94 230 77.37 105 57.59 140 37.90 95 54.21 50 55.52	405 90.80 360 85.93 315 74.24 270 65.37 225 77.81 180 44.59 135 43.93 50 54.48 45 55.97	400 90.80 355 84.96 310 72.51 765 66.34 770 78.03 175 28.35 130 47.70 85 54.47 40 56.12	365 90.58 360 93.77 305 70.78 760 67.75 315 78.03 170 12.12 175 46.89 80 54.57 35 56.19	390 90.26 345 82.90 300 69.16 355 69.59 310 77.69 165 6.879 125 51.44 35 54.35 30 58.67	385 89.72 340 81.82 295 57.53 250 71.43 160 4.65 115 52.56 70 55.29 25 55.96

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TABLE A-9 (cont'd.)

H<sub>2</sub>O TEMP. 50.2°C

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421 91.29	415 90.04	410 90.49	435 93.PU	400 90.69	395 90.58	390 90.37	385 89.94
375 39.53	370 87.66	365 36.90	360 86.04	355 84.96	350 33.57	345 32.79	340 81.82
331 71.22	325 77-61	320 76.19	315 74.24	310 72.51	305 71.10	300 59.16	295 67.36
265 65 59	220 55.15	275 55.04	270 65.48	265 65.45	250 57.42	255 69.05	250 71.00
243 74 35	235 75.97	230 75.30	225 77.49	220 77.81	215 77.92	210 77.33	205 75.19
195 71.00	190 65.69	165 57.36	190 43.61	175 25.76	170 11.15	155 6.25	150 4.65
15.1 20.93	145 37.93	140 39.54	135 44.55	130 48.03	125 50.22	120 51.38	115 52.67
105 53.31	110 53.55	95 53.75	90 53 79	85 53.77	30 54.45	75 54.51	. 70 54.42
60 54-58	55 55.27	50 54.92	45 55.32	40 55.4)	35 55.38	30 54.57	25 53.46
15 57.45	10 52.44	5 50.00	0 63.33				
	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	420 $99.29$ $415$ $90.04$ $410$ $90.49$ $435$ $90.90$ $375$ $38.53$ $370$ $87.66$ $365$ $36.90$ $360$ $86.04$ $330$ $71.22$ $325$ $77.51$ $320$ $76.19$ $315$ $74.24$ $285$ $55.59$ $290$ $55.15$ $275$ $65.04$ $270$ $65.48$ $240$ $74.35$ $235$ $75.97$ $230$ $76.30$ $225$ $77.49$ $195$ $71.40$ $190$ $65.69$ $105$ $57.36$ $180$ $43.61$ $150$ $20.93$ $145$ $32.73$ $140$ $39.54$ $135$ $44.55$ $105$ $53.31$ $100$ $53.56$ $95$ $53.76$ $90$ $53.79$ $4$ $54.53$ $55$ $55.27$ $50$ $54.92$ $45$ $55.32$ $15$ $50.45$ $10$ $52.44$ $5$ $50.00$ $0$ $63.33$	420 $99.29$ $415$ $90.04$ $410$ $90.49$ $405$ $90.90$ $400$ $90.69$ $375$ $38.53$ $370$ $87.66$ $365$ $36.90$ $360$ $36.04$ $355$ $84.96$ $330$ $71.22$ $325$ $77.51$ $320$ $76.19$ $315$ $74.24$ $310$ $72.51$ $285$ $65.59$ $290$ $65.15$ $275$ $65.04$ $270$ $65.47$ $265$ $66.45$ $240$ $74.35$ $235$ $75.97$ $230$ $76.30$ $225$ $77.49$ $220$ $77.81$ $195$ $71.50$ $190$ $65.69$ $165$ $57.36$ $190$ $43.61$ $175$ $25.76$ $150$ $20.93$ $145$ $32.73$ $140$ $39.54$ $135$ $44.55$ $130$ $48.03$ $105$ $53.31$ $100$ $53.56$ $95$ $53.76$ $90$ $53.79$ $95$ $53.77$ $4)$ $54.58$ $55$ $55.27$ $50$ $54.92$ $45$ $55.32$ $40$ $55.43$ $15$ $57.45$ $10$ $52.44$ $5$ $50.00$ $0$ $63.33$	42099.2941590.0441090.4940590.8040090.6939590.5837538.5337087.6636536.9036036.0435584.9635083.6733070.2232577.5132076.1931574.2431072.5130571.1028565.5929065.1527565.0427065.4826566.4526067.4224074.3523575.9723076.3022577.4922077.8121577.9219571.0019065.6916557.3618043.6117525.7617011.1515020.9314532.9314039.5413544.5513048.0312550.2210553.3110053.569553.769053.799553.773054.454054.535555.275054.924555.324055.403555.381550.451052.44550.00063.333555.403555.33	42099.2941590.9441090.4940590.9040090.6939590.5839090.3737538.5337087.6636536.9036036.0435584.9635033.6734532.7933070.2232577.6132076.1931574.2431072.5130571.1030069.1626565.5929065.1527565.0427065.4826565.45526067.4225569.1524074.3523575.9723076.3022577.4922077.8121577.9221077.3819571.0019065.6416557.3619043.6117525.7617011.151556.2515020.9314532.9314039.5413544.5513048.0312550.2212051.5810553.3110553.569553.769053.773054.457554.514054.535555.275054.924555.324055.403555.383054.571550.4551052.44550.00063.333555.403555.403555.403555.40

H<sub>2</sub>O TEMP. 53.4°C

425	88.85	420	89.72	415	90.26	410	90.48	405	90.69	400	90.80	395	90.58	390	90.37	385	89.94
380	39.39	375	89.85	370	87.88	365	86.69	360	86.15	355	85.28	350	84.31	345	83.33	340	32.25
335	91.06	330	79.75	325	78.25	320	76.73	315	75.11	310	73.05	305	71.64	300	70.02	295	oð.51
290	66.99	285	66.13	280	65.48	275	65.26	270	65.58	265	66.45	260	67.53	255	69.16	250	.70.89
245	72.51	240	74.03	235	75.43	230	76.73	225	77.27	220	77.38	215	77.49	210	77.06	205	76.05
200	74.35	195	71.10	190	60.45	185	58.87	180	45.89	175	29.11	170	13.42	165	5.84	160	4.55
155	9.10	150	19.96	145	31.96	140	39.65	135	44.70	130	48.68	125	50.55	120	52.10	115	53.11
110	53.46	105	53.87	100	54.69	95	55.13	90	55.40	85	55.05	80	54.92	75	54.73	70	54.42
65	54.71	60	55.12		54.70	50	55.07	45	54.65	40	54.68	35	54.56	30	54.80	25	53.74
20	52.38	15	50.89	10	54.27	5	50.91	0	65.00								

H<sub>2</sub>O TEMP. 57.4°C

A25 82 20	420 89.14	415 89.72	410 90.37	405 90.69	400 90.80	395 90.69	390 90.48	385 90.04
	775 00 05	370 89 20	365 87.23	360 86-58	355 85.71	350 84.63	345 83.00	340 82.68
380 84.34	313 00.03	310 88.20	300 77 00	316 76 43	310 73 70	305 71 97	300 70.45	295 68.83
335 81.49	330 80.41	325 18.68	320 11.00	313 13.43	310 13.10			260 70 73
290 67.32	285 66.13	280 65.48	275 65.37	270 65.80	265 66.45	260 67.64	255 68.94	250 10.18
245 72.40	240 73.81	235 75.22	230 76.30	225 76.95	220. 77.16	215 77.16	210 76.73	205 75.54
200 73.92	195 70-67	190 65.48	185 58.44	180 44.91	175 28.68	170 12.45	165 5.95	160 4.44
155 9.21	150 20.61	145 32.07	140 39.76	135 45.36	130 48.79	125 50.99	120 52.21	115 53.00
120 52 25	105 53 65	100 53.90	95 54.10	90 54.37	85 54.12	80 54.33	75 54.25	70.54.17
45 54 10	60 56 58	55 54 84	50 54.46	45 54.83	40 53.96	35 53.75	30 52.69	25 51-25
	16 44 97	10 45 73	5 45 45	0 58.33				1
20 49.32	12 40.01	10 47412	2 4 2 4 4 2	• • • • • • • •				

H<sub>2</sub>O TEMP. 57.4°C

425 88.64	420 89.50	415 90.15	410 90.48	405 90.69	400 90.80	395 90.69	390 90.26	385 89.72
380 89.07	375 88.53	370 87.77	365 87.12	360 86.26	355 85.39	350 84.31	345 83.55	340 82.58
335 81.28	330 79.78	325 78.46	320 76.84	315 75.43	310 73.48	305 71.75	300 70-24	295 68.12
290 67.10	285 66.34	280 65.58	275 65.37	270 65.69	265 66.45	260 67.42	255 69-05	
245 72.29	240 73.92 195 70.67	235 75.11	230 76.52	225 77.16	220 77.60	215 11.49	210 76.95	203 13.03

**D**JT

TABLE A-9 (cont'd.)

### H<sub>2</sub>O TEMP. 63.7°C

425 88.85	420 FC. 25	415 50.04	410 00.37	405 60.90	400 90.80	366 60°46	340 69.37	285 QA 24
380 99.50	375 86.55	370 88.31	365 87.45	PA 48 035	355 35.82	350 54.95	365 93. 97	340 37,70
335 91.71	230 EC.E?	225 74 <b>.1</b> 1	77.45	315 75.87	210 74.46	205 72.62	300 70.79	205 40 42
290 59.19	285 66.55	280 66.34	775 66.13	270 66.23	265 66.77	240 67.44	255 63,05	251 70,67
245 72.10	240 72.70	275 75.22	230 76.20	775 77 <b>.</b> 06	220 77.28	215 77.49	213 77.16	205 76 19
200 74.46	195 71.43	100 44.00	195 50.31	109 40.27	175 32.03	170 15.80	1 45 4.71	167 4,22
155 7.37	150 17.46	145 71.05	140 20.97	135 45.44	130 49.45	175 51 77	170 57 89	115 53 79
110 54.35	105 54.99	100 55.37	95 55,58	90 55 63	95 55.28	80 65 98	75 54 09	70 54 67
65 55.10	60 54.72	55 F4 QC	50 55.07	45 54.99	40 53 96	25 54.77	30 54 22	75 54 70
20 51.26	1 <u>5</u> 4ç, F <u></u>	10 49.79	5 57, 54	7 66.67			-	•

# H<sub>2</sub>O TEMP. 67.1°C

425	88.64	420	89.39	415	90.15	410	90.48	405	90.69	400	90.80	395	90.80	390	90.58	385	90.15
380	89.61	375	89.07	370	88,53	365	87.66	360	87.01	355	86.15	350	85.17	345	84.09	340	83.12
335	81.93	330	80.84	325	79.44	320	77.81	315	76.30	310	74.78	305	73.16	300	71.43	295	70.02
290	68.51	285	67.64	280	66.67	275	66.45	270	66.45	265	66.38	260	67.97	255	69.16	250	70.56
245	71.86	240	73.48	235	74.89	230	76.19	225	76.84	220	77.38	215	77.38	210	77.16	205	76.19
200	74.68	195	71.75	190	66.99	185	59.85	180	48.48	175	33.33	170	16.02	165	7.36	160	4.44
155	7.37	150	17.57	145	31.30	140	39.54	135	45.14	130	49.67	125	51.98	120	53.32	115	54.67
110	55.36	105	55.89	100	56.38	95	56.61	90	56.21	85	55.75	80	55.52	75	55.22	70	54.55
65	55.23	60	54.99	55	55.27	50	54.92	45	54.50	40	54.50	35	54.36	30	54.57	25	53.46
20	50.34	15	48.21	10	50.61	5	50.00	0	66.67								

### H<sub>2</sub>O TEMP. 67.5°C

425	88.64	420	89.39	415	89.93	410	90.48	405	90.80	400	90.80	395	90.69	390	90.58	385	90.04
380	89.39	375	88.74	370	88.10	365	87.55	360	86.58	355	85.82	350	84.85	345	83.87	340	82.68
335	81.49	330	80.30	325	79.11	320	77.71	315	75.87	310.	74.57	305	72.73	300	71.32	295	69.59
290	68.40	285	67.10	280	66.56	275	66.23	270	66.23	265	66.67	260	67.42	255	68.61	250	70.13
245	71.97	240	73.27	235	74.46	230	75.76	225	76.30	220	76.95	215	76.95	210	76.52	205	75.76
200	74.13	195	71.21	190	66.67	185	58.98	180	47.29	175	29.98	170	14.39	165	5.84	160	3.90
155	7.04	150	18.44	145	31.52	140	39.43	135	45.79	130	49.23	125	51.43	120	53.10	115	54.11
110	54.69	105	55.22	100	55.71	95	55.92	90	55.75	85	55.52	80	54.92	75	54.25	70	53.92
65	54.32	60	53.77	55	54.42	50	54.01	45	54.01	40	53.60	35	53.35	30	52.69	25	52.08
20	50.34	15	49.11	10	46.95	5	48.18	0	65.00								

#### TABLE A-10

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Band Indices Input Data for D20

Frequency in "New Units"

Transmittance in percent

D<sub>2</sub>O TEMP. 4.2°C

	-							· 7/
		_		255 02 23	350 90.72	345 90.28	34] 99.63	337 27.15
375 97 99	370 89.30	365 90.17	360 91.51	333 40.03		710 70 15	235 77.29	290 74.39
313 81.00		220 25 15	315 33.24	310 82.31	305 80-79	330 19.13		3/5 75 30
330 87.66	325 85.40	320 03.12	272 (7 20	265 67 11	260 69.47	255 70.61	250 72.95	240 (2.009
285 72.60	280 70.38	275 63.46	210 51.29		215 23 31	21.1 82 69	205 30.39	200 75.73
2.0 12.00	225 70 90	230 81.24	225 32.42	220 83.12	210 33.31	213 52.00		155 54 34
240 11.53	233 19.50		100 6 57	175 10.62	170 25.85	165 42.04	15) 50.32	100-04
195 67.10	190 43.81	185 14.51	150 0.01	119 19002	126 7/ 22	120 27 45	115 12.50	110 17.39
	1/2 43 97	140 67.25	135 55.67	130 68.33	125 14+32	125 21.42		
150 60.28	143 93.02	140 010:00	• • •					
105 20.00	100 20.00							

D<sub>2</sub>O TEMP. 6.8°C

	-					+45 31.25	340 99.52	735 22.45
375 67.99 330 67.55 235 72.93 240 77.40 195 65.40 150 59.44 105 75.00	370 89.30 325 86.35 230 70.71 235 79.45 190 42.04 145 61.09 100 75.00	305 90.17 320.35.15 275 07.07 230 51.29 175 14.00 140 63.72	360 90.61 315 83.75 270 87.15 225 82.42 160 4.15 135 01.90	355 70.83 310 42.01 265 97.70 220 53.12 175 9.35 130 61.67	353 73.72 365 80.90 267 6-25 215 83.76 170 26.19 125 59.40	303 79-26 303 79-26 255 70-50 217 82-7 155 40-7 120 47-05	295 77.51 250 72.75 205 85.27 160 49.59 115 95.57	29, 75.33 245 75.23 220 76.11 155 55.44 110 65.23

D<sub>2</sub>O TEMP. 9.8°C

375       87.77         330       87.55         235       73.03         240       76.73         195       65.92         150       59.17         105       15.00	370 89.19 325 86.46 280 70.93 235 78.79 190 42.59 145 £0.75 100 15.00	365 89.96 320 85.15 275 69.00 230 80.50 135 14.65 140 63.27	360 90.50 315 83.62 270 87.82 225 81.62 180 5.22 135 54.52	365 90.83 310 82.31 265 67.44 220 82.31 175 9.19 130 60.33	350 90.72 305 50.90 200 68.58 215 32.49 170 25.17 125 50.31	345 90.23 300 70.37 255 70.17 210 51.67 165 40.37 125 45.15	340 89.63 295 77.51 250 72.28 205 79.53 150 50.00 115 9.34	335 58.65 290 75.33 245 74.61 200 75.22 155 55.40 110 13.04
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# D<sub>2</sub>O TEMP. 10.2°C

375       87.88         330       87.55         285       73.14         240       77.18         195       65.01         150       57.22         105       5.30	370 89.0h 325 mo.24 280 70.32 235 79.01 190 42.99 145 60.07 100 5.00	365 29.96 321 05.20 275 50.67 239 80.90 135 13.60 140 62.34	360 +0.50 315 83.95 270 67.20 225 02.00 130 4.75 135 00.12	555 90.72 310 32.53 265 07.11 220 33.01 175 2.17 130 59.17	350 90.72 303 -1.0 200 04.0 210 03.2 170 23.2 170 23.2 120 02.10	345 02.17 361 79.54 255 72.59 213 32.21 155 49.12 122 41.12	345 49.32 295 77.51 209 72.51 205 79.41 107 49.33 115 3.13	335 42.55 240 75.33 245 74.72 200 74.21 155 54.05 113 4.35
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TABLE A-10 (cont'd.)

D<sub>2</sub>0 TEMP. 13.6°C

375 87.66	370 85.97	305 89.85	360 90.39	355 90.72	350 90.43	345 9).39	340 P9.74	335 80.25
330 87.77	325 85.74	320 85.59	315 24.17	310 32.64	305 81.22	300 79.54	295 77.84	29) 75.65
235 73.47	280 71.25	275 69.44	270 65.00	265 97.77	260 66.47	255 70.34	250 72.51	245 74.72
240 76.96	235 78.30	230 30.08	225 61.74	223 42.43	215 82.73	210 82.21	205 79.73	201 75.35
195 65.92	190 42.57	185 14.65	160 5.67 •	175 3.40	170 27.72	165 41.30	160 50.01	155 54.64
150 57.78	145 59.04	140 61.00	135 61.31	130 26.57	125 62.15	120 45.10	115 9.33	115 13.34

D<sub>2</sub>O TEMP. 13.7°C

375 87.55 330 87.77 285 73.69	370 88.36 325 86.99 280 71.37	355 89.77 320 35.43 275 69.55	300 50.35 315 44.30 270 03.17 225 01.05	355 90572 310 52175 255 67177 225 82177	350 90.72 305 41.44 209 60.59 215 33.03	345 591.25 362 74.89 255 79.39 215 52.33	3-0-49.63 245-76.00 240-72.57 245-57.02	535 (***9* 535 (***9*) 249 (***5 533 (***5
175 66.71 150 60.33 105 20.00	190 45.44 145 61.09 100 20.00	1=5 10.22 140 03.72	180 5.47 135 64.40	175 8.55 136 65.3	170 25.34 125 72.97	165 41.47 120 56.28	100 53.07 115 43.75	155 - 56.35 110 - 17.57

D<sub>2</sub>O TEMP. 19.7°C

375 87.56 330 38.10 285 74.45 240 75.62 195 66.45 150 58.06	370 49.30 325 37.01 230 72.30 235 74.34 190 43.31 145 58.70	305 90.07 320 55.01 275 70.54 230 40.11 105 14.70 140 58.41	200 90.00 315 84.50 270 89.24 225 31.62 190 9.52 135 57.74	365 40.72 310 42.14 245 65.43 229 42.43 175 4.35 124 55.43	350 70.33 515 81.17 252 89.32 215 93.45 170 25.70 125 55.70	3.6 - 7.5 ) 3.0 - 7.5 13 255 77.39 215 - 1.67 105 - 42.64 123 - 7.55	3+, 13+5 245 73+4 245 73+3 245 73+3 245 23+3 168 23+1 115 4+2 115 4+2	235 - 44.00 141 70.31 245 74.50 200 74.50 200 75.41 155 95.47 110 - 77
105 10.00	100 10.00							

D<sub>2</sub>O TEMP. 27.2°C

375 87.00 330 88.21 285 75.22 240 75.95 195 67.10 150 58.89 105 10.00	370 58.97 325 87.55 280 73.44 235 77.89 190 47.21 145 62.12 100 10.69	365 87.65 520 66.46 275 71.52 230 79.85 155 20.20 140 62.85	540 90.50 515 55.20 270 70.14 225 51.51 140 5.27 135 63.71	355 90.72 310 33.54 255 85.53 220 62.31 175 7.77 130 80.30	3530933.83 305322.53 250653.69 21562.49 17522.49 17522.49 17562.22	345 -).e1 303 -).40 299 70.01 213 51.73 185 41.11 123 52.94	343 99.46 295 79.15 255 77.23 265 23.02 133 53.62 115 5.25	335 + 49,30 27) 76,495 245 74,05 201 75,59 155 55,57 115 5,57
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D<sub>2</sub>O TEMP. 30.6°C

375 87.66 330 88.65 285 75.65 240 76.06 195 67.76 150 59.44 105 5.00	370 67.55 325 67.45 260 73.4 235 77.49 190 4(.57 145 52.12 100 7.2	365 89.25 320 86.45 275 71.60 230 79.85 145 22.53 140 92.73	360 40.37 315 39.37 270 70.55 225 51.52 135 54.57 135 54.57	855 90.72 510 -4.17 265 90.75 220 2.77 175 7.45 150 50.00	351 40.55 355 83.35 200 63.74 215 58.35 175 58.35 175 58.35 175 83.51	345 - 0.01 319 - 1.50 255 - 70.03 219 - 70.03 105 - 90.13 105 - 90.13	340 50.37 235 73.54 235 73.54 235 72.35 235 3.23 150 7.41 115 5.25	335 29.41 200 77.73 245 73.94 200 78.11 105 55.87 110 5.73
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TABLE A-10 (cont'd.)

D<sub>2</sub>O TEMP. 34.0°C

375       37.66         330       88.43         285       75.98         240       75.84         195       67.10         150       57.50         105       65.00	370 88.76 325 87.66 230 74.10 235 77.44 199 47.44 145 57.68 100 65.00	365 89.85 320 86.57 275 72.29 230 79.43 185 13.80 140 58.41	360 90.39 315 85.26 27C 70.80 225 81.16 180 5.22 135 54.76	355 90.72 310 84.06 265 69.97 220 82.20 175 7.13 130 55.83	350 90.83 305 82.36 260 69.79 215 92.26 170 23.30 125 63.51	345 90.50 300 81.44 255 70.72 210 91.73 165 40.19 120 50.98	340 89.96 295 79.69 250 72.17 205 79.53 16C -9.79 115 31.25	335 89.30 290 77.73 245 73.83 200 75.35 155 54.46 110 56.52
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# D<sub>2</sub>O TEMP. 38.0°C

375 87.66 330 98.76 235 76.42 240 75.06 195 69.46 150 56.94 105 30.00	370 88.00 325 87.33 280 74.54 235 76.93 190 50.34 145 58.02 100 80.00	305 89.25 320 80.49 275 72.73 230 78.32 185 22.95 140 59.73	500 40.39 315 55.70 270 71.13 225 51.05 180 5.22 135 57.52	355 92.72 310 84.39 255 70.30 220 92.31 175 5.36 130 5F.33	350 90.33 305 53.30 260 89.90 215 32.49 170 23.41 125 54.35	345 93.61 303 41.55 255 73.61 213 41.67 165 33.89 120 43.02	340 40.17 295 > 3.24 250 71.14 205 80.02 160 49.31 115 31.25	335 Pr.52 295 Pr.17 295 Pr.17 295 Pr.18 200 Pf.29 155 P4.63 115 Pf.57
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D<sub>2</sub>O TEMP, 46.2°C

375       37.66         330       89.08         245       75.96         240       74.33         195       55.40         150       52.50         105       5.00	370 40.30 325 26.21 280 74.97 235 76.00 193 46.12 145 52.56 100 5.00	365 09.74 320 57.12 275 73.33 230 75.53 185 19.00 140 50.44	360 96.28 315 88.14 270 71.79 225 80.37 180 3.56 135 47.02	355 9C.72 310 84.83 265 70.74 220 81.50 175 4.23 130 40.83	350 90 3 305 - 3. 73 265 70.34 215 81.57 170 20.24 125 32.43	345 99.51 303 -2.21 255 70.73 210 -31.21 165 37.79 120 - 7.94	340 90.23 235 80.01 250 71.35 205 79.10 160 46.53 115 31.25	335 244.74 249:74.22 245 73.27 239:74.34 155 51.17 110 4.35
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### D20 TEMP. 48.4°C

375 87.88 330 88.86 285 76.86 240 75.06 195 64.35 150 53.06 105 45.00	370 89.08 325 87.88 280 74.97 235 70.06 190 44.76 145 52.22 100 45.00	365 89.96 320 87.01 275 73.38 230 78.64 135 17.50 140 50.86	360 90.28 315 86.03 270 71.90 225 80.37 180 3.13 135 47.62	355 90.72 310 34.72 265 70.96 220 81.27 175 0.66 130 44.17	350,90,83 305 33.73 260 70.56 215 91.03 170 23.13 125 40.54	345 90.50 300 52.10 255 71.05 210 80.17 165 40.55 120 25.49	343 43.17 245 63.57 256 72.28 235 72.33 169 47.94 115 9.36	335 34.63 2910 78.60 245 73.39 200 73.57 155 51.88 110 52.17
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#### D<sub>2</sub>O TEMP. 52.6°C

375       87.77         330       89.30         285       77.73         240       74.72         195       65.45	370 88.97 325 80.54 280 75.90 235 75.32 190 48.10 195 54 27	365 89.85 323 87.34 275 74.15 230 78.31 135 20.44 140 52.60	360 90.54 315 45.25 270 72.56 225 80.02 130 4.45 135 45.41	355 40.61 310 55.15 154 71.51 20 30.92 175 5.35 130 47.50	35) 90.63 375 23.06 200 71.11 215 91.78 170 24.15 125 44.55	345 90.72 300 72.75 255 71.16 210 71.29 165 71.19 120 37.25	343 40.60 245 81.33 253 71.99 255 74.99 255 74.30 155 74.13 155 29.13	335 89.96 200 70.49 246 73.15 200 74.21 156 52.56 110 13.04
150 53.39 105 70.00	145 54.27	149 52.00	133 4:1	190 01190		•••		

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TABLE A-10 (cont'd.)

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D<sub>2</sub>O TEMP. 62.3°C

375 87.38	370 Ho.76	305 39.03	360 90.07	355 90.39	250 40.72	345 41. 3	340 90.01	335 20.28
330 89.52	325 34.54	320 87.71	315 85.90	310 35.59	3.75 84.39	300 23.30	245 - 1.94	299 22.45
285 78.71	250 77.16	272 75.30	270 73.98	255 72.94	253 72.11	255 72.27	253 72.24	245 13.72
240 75.05	235 76.43	230 78.31	225 79.91	220 80.45	215 20.61	210 -0.17	200 74.15	233 74.04
195 64.48	190 45.99	185 16.21						

# D<sub>2</sub>O TEMP. 62.3°C

375 87.99	370 88.30	305 89.03	369 69-26	355 90.61	350 70.43	245 20.01	347 42.50	335 -1.17
330 89.52	325 30.65	320 E7.Er	315 ot.40	313 35.73	305 .4.50	323 33.34	206 P1.05	2-1-5.35
285 78.60	280 77.00	275 75.57	270 73.37	205 72.00	250 72.37	200 72.3:	25 / 72.04	245 13.72
240 75.06	235 76.54	230 78.42	225 80.02	220 20.69	215 51.04	210 03.53	212 74.51	1 1 1 1 4 . 74
195 56.06	190 51.15	185 23.04	180 7.31	175 7.61	170 25.03	100 +1.4-	140 49.74	100 04.45
150 55.56	145 56.60	149 50.64	135 55.35					

### D<sub>2</sub>O TEMP. 66.0°Ç

375 28.10	370 83.97	305 89.74	366 90.17	355 90.50	350 - 03	345 34.72	341 63.30	N35 10.07
330 29.41	325 33.65	320 s7.cc	315 86.79	310 35.73	365 4.72	5 ··· 1	235 81.49	241 - 0.35
265 78.71	220 77.05	275 75.57	270 74.04	205 73.15	263 72.44	255 72.35	200 73.17	245 73.61
240 74.83	235 70.43	230 78.05	225 79.57	225 h0.12	215 80.20	213 79.59	205 77.oF	20) 73.52
195 54.35	190 45.09	135 20.34	120 6.27	175 5.12	170 22.37	165 41.55	100 49.1:	155 51.41
150 53.06	145 51.54	140 50.00	135 45.31	130 42.50				

APPENDIX III

Programme IRCURFIT computed variable parameter output data and curve fitting data are listed in this section.

APPENDIX III-a: CALCULATED OUTPUT VARIABLE PARAMETERS

Variable parameter output data as calculated by computer programme IRCURFIT are given in Tables A-11 to A-16 for  $H_2O$  and Tables A-17 to A-22 for  $D_2O$ .

M = 1 refers to curve fitting of the frequency range including only the combination band  $(v_{2+L})$ , M = 2 includes the combination and deformation  $(v_2)$  bands, and M = 3 covers the entire frequency range recorded, thus including the librational overtone band  $(2v_L)$  discussed in Part IV of the Thesis.

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TABLE	A-11
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Temp. (°C)	x	×2	×3	×4	%T min	∨ <sub>o</sub> (cm <sup>-⊥</sup> )	S	α(٩
5.4	0.194	-28.696	0.210	0.007	61.7	2147.8	0.969	96
8.1	0.194	28.612	0.208	0.006	61.7	2144.5	0.973	90
12.2	0.191	28.599	0.207	0.008	62.1	2143.9	0.961	9
14.7	0.185	28.441	0.208	0.030	62.2	2137.6	0.874	9
20.0	0.186	28.362	0.202	0.023	62.4	2134.5	0.899	9
29.7	0.170	28.049	0.195	0.055	63.5	2122.0	0.781	9
33.0	0.162	27.964	0.194	0.064	64.2	2118.6	0.752	9
38.0	0.161	27.944	0.197	0.057	64.6	2117.8	0.777	9
40.2	0.157	27.883	0.184	0.084	64.4	2115.3	0.686	9
41.7	0.156	27.721	0.194	0.073	64.6	2108.8	0.724	9
45.0	0.154	27.830	0.190	0.074	64.9	2113.2	0.719	9
50.2	0.151	27.754	0.180	0.082	65.1	2110.2	0.686	9
53.4	0.150	27.621	0.180	0.080	65.5	2104.8	0.694	9
57.4	0.146	27.540	0.177	0.093	65.6	2101.6	0.655	9
57.4	0.149	27.548	0.181	0.079	65.5	2101.9	0.695	9
63.7	0.142	27.431	0.171	0.092	66.2	2097.3	0.650	9
67.1	0.139	27.336	0.164	0.098	66.6	2093.4	0.627	9
67.5	0.142	27.331	0.167	0.090	66.3	2093.2	0.650	9

 $H_2O$  M = 2  $v_{2+L}$ 

Temp. (°C)	×1	×2	×3	×4	%T min	ν <sub>o</sub> (cm <sup>-1</sup> )	S	a (%T)
5.4	0.193	28.708	0.211	0.004	61.7	2148.3	0.983	96.3
8.1	0.195	28.625	0.216	0.001	61.7	2145.0	0.995	96.5
12.2	0.190	28.606	0.207	0.018	62.2	2144.2	0.921	96.2
14.7	0.187	28.458	0.209	0.013	62.3	2138.3	0.942	95.7
20.0	0.188	28.378	0.203	0.009	62.4	2135.1	0.959	96.2
29.7	0.176	28.066	0.198	0.030	63.5	2122.6	0.869	95.4
33.0	0.167	27.960	0.196	0.047	64.3	2118.4	0.809	94.4
38.0	0.165	27.964	0.200	0.040	64.6	2118.5	0.835	94.4
40.2	0.159	27.895	0.189	0.074	64.4	2115.8	0.720	92.9
41.7	0.158	27.849	0.198	0.057	65.0	2114.0	0.776	93.4
45.0	0.156	27.881	0.196	0.065	64.9	2115.2	0.751	93.0
50.2	0.152	27.733	0.179	0.076	65.3	2109.3	0.702	92.7
53.4	0.151	27.645	0.184	0.073	65.5	2105.8	0.717	92.8
57.4	0.146	27,584	0.182	0.087	65.7	2103.3	0.676	92.0
63.7	0.143	27.475	0.176	0.086	66.2	2099.0	0.672	92.1
67.1	0.140	27.380	0.169	0.093	66.6	2095.2	0.646	91.9
67.5	0.143	27.354	0.169	0.086	66.4	2094.2	0.664	92.1

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 $H_2O$  M = 2  $v_2$ 

Temp. (°C)		×2	×3	×4	<sup>%T</sup> min	ν <sub>o</sub> (cm <sup>-1</sup> )	S 
5.4	1.213	16.201	0.807	0.188	5.9	1648.1	0.811
8.1	1.223	16.158	0.815	0.186	5.8	1646.3	0.814
12.2	1.260	16.165	0.837	0.191	5.3	1646.6	0.815
14.7	1.333	16.116	0.887	0.187	4.5	1644.7	0.826
20.0	1.348	16.124	0.870	0.192	4.3	1644.9	0.820
29.7	1.368	16.044	0.914	0.183	4.2	1641.8	0.833
33.0	1.239	15.993	0.838	0.197	5.4	1639.7	0.809
38.0	1.351	16.116	0.914	0.185	4.2	1644.6	0.831
40.2	1.306	16.041	0.899	0.184	4.6	1641.6	0.830
41.7	1.338	16.042	0.904	0.195	4.3	1641.7	0.823
45.0	1.396	16.110	0.930	0.171	3.8	1644.4	0.844
50.2	1.399	16.160	0.927	0.200	3.7	1646.4	0.823
53.4	1.423	16.102	0.973	0.178	3.5	1644.1	0.845
57.4	1.435	16.122	0.985	0.164	3.4	1644.9	0.857
63.7	1.416	16.016	0.968	0.171	3.5	1640.6	0.850
67.1	1.390	16.005	0.961	0.173	3.7	1640.2	0.847
67.5	1.493	16.056	1.002	0.177	3.0	1642.2	0.850

	TABLE 2	A-14	
	<sup>H</sup> 2 <sup>O</sup> M =	3 v <sub>2+L</sub>	
×3	X_4	<sup>%T</sup> min 	ν <sub>o</sub> (cm <sup>-1</sup> )

Temp. (°C)	x	x2	x <sub>3</sub>	x4	<sup>%T</sup> min	ν <sub>o</sub> (cm <sup>-1</sup> )	S	a (%T)
5.4	0.169	28.860	0.190	0.114	61.9	2154.4	0.625	91.3
8.1	0.170	28.774	0.193	0.107	61.9	2151.0	0.644	91.5
12.2	0.167	28.770	0.190	0.110	62.3	2150.8	0.632	91.5
14.7	0.163	28.620	0.185	0.117	62.5	2144.8	0.612	90.9
20.0	0.162	28.565	0.175	0.121	62.7	2142.6	0.592	90.9
29.7	0.155	28.272	0.173	0.119	63.8	2130.9	0.592	91.0
33.0	0.149	28.186	0.173	0.120	64.5	2127.4	0.591	91.0
38.0	0.145	28.193	0.169	0.126	64.9	2127.7	0.574	90.7
40.2	0.148	28.113	0.164	0.126	64.7	2124.5	0.566	90.9
41.7	0.144	28.083	0.179	0.118	65.2	2123.2	0.603	90.8
45.0	0.142	28.106	0.162	0.132	65.3	2124.2	0.551	90.6
50.2	0.140	28.053	0.148	0.137	65.6	2122.1	0.519	90.6
53.4	0.138	27.938	0.150	0.136	65.9	2117.5	0.524	90.6
57.4	0.137	27.859	0.153	0.138	66.1	2114.3	0.527	90.5
63.7	0.133	27.765	0.145	0.139	66.6	2110.6	0.511	90.5
67.1	0.131	27.683	0.134	0.144	67.0	2107.3	0.483	90.6
67.5	0.132	27.688	0.138	0.139	66.8	2107.5	0.500	90.5

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TABLE A-15

 $H_2^0 M = 3 v_2$ 

Temp. (°C)	x <sub>1</sub>	×2	×3	×4	*Tmin	ν <sub>o</sub> (cm <sup>-1</sup> )	S
5.4	1.022	16.178	0.788	0.260	8.7	1647.1	0.752
8.1	1.042	16.148	0.798	0.270	8.3	1645.9	0.747
12.2	1.072	16.150	0.815	0.275	7.8	1646.0	0.748
14.7	1.135	16.092	0.858	0.269	6.7	1643.7	0.761
20.0	1.181	16.114	0.880	0.256	6.0	1644.6	0.775
29.7	1.178	16.015	0.885	0.266	6.3	1640.6	0.768
33.0	1.080	15.982	0.830	0.272	7.6	1639.3	0.753
38.0	1.192	16.093	0.919	0.240	5.8	1643.7	0.793
40.2	1.130	16.013	0.869	0.265	6.7	1640.5	0.766
41.7	1.157	16.022	0.868	0.285	6.3	1640.9	0.753
45.0	1.226	16.077	0.922	0.227	5.4	1643.1	0.803
50.2	1.228	16.138	0.923	0.261	5.4	1645.5	0.780
53.4	1.260	16.072	0.972	0.232	5.0	1642.9	0.807
57.4	1.268	16.098	0.980	0.240	4.9	1643.9	0.804
63.7	1.291	16.002	0.998	0.223	4.6	1640.1	0.817
67.1	1.259	15.983	0.978	0.218	5.0	1639.3	0.817
67.5	1.344	16.029	1.011	0.225	4.1	1641.2	0.818

TABLE A-16

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 $H_2OM = 3 2v_L$ 

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Temp. (°C)		×2	×3	×4	<sup>%T</sup> min	ν <sub>o</sub> (cm <sup>-1</sup> )	S
5.4	0.260	9.710	0.009	0.128	50.1	1388.4	0.068
8.1	0.260	9.641	0.015	0.127	50.2	1385.6	0.103
12.2	0.257	9.544	0.011	0.126	50.7	1381.7	0.078
14.7	0.257	9.399	0.010	0.126	50.3	1376.0	0.072
20.0	0.252	9.229	0.005	0.124	50.9	1362.2	0.040
29.7	0.246	9.048	0.009	0.121	51.6	1359.4	0.071
33.0	0.238	9.052	0.012	0.121	52.6	1362.1	0.091
38.0	0.234	8.747	0.003	0.119	52.9	1349.9	0.027
40.2	0.238	8.817	0.007	0.119	52.5	1352.7	0.053
41.7	0.246	8.738	0.008	0.118	51.6	1349.5	0.061
45.0	0.233	8.223	0.003	0.114	52.9	1328.9	0.028
50.2	0.240	8.309	0.005	0.112	52.2	1332.4	0.044
53.4	0.233	7.868	0.003	0.110	53.0	1314.7	0.030
57.4	0.236	7.915	0.002	0.108	52.5	1316.6	0.019
63.7	0.228	7.478	0.001	0.107	53.5	1299.1	0.011
67.1	0.225	7.191	0.000	0.106	53.9	1287.6	0.000
67.5	0.231	7.206	0.002	0.105	53.1	1288.2	0.016

 $D_2 O M = 1 v_{2+L}$ 

Temp. (°C)	x <sub>1</sub>	×2	×3	×4	%T min	ν <sub>o</sub> (cm <sup>-1</sup> )	S	α(%T) 
1 2	0 143	26 791	0 294	0 052	67 5	1571.6	0 850	93.8
68	0.146	26.747	0.298	0.010	67.5	1569.9	0.967	94.3
9.8	0.138	26.672	0.278	0.073	67.8	1566.9	0.792	93.2
10.2	0.144	26.699	0.295	0.024	67.5	1567.9	0.924	94.2
13.6	0.132	26.640	0.274	0.100	68.2	1565.6	0.732	92.3
13.7	0.132	26.607	0.280	0.088	68.2	1564.3	0.760	92.5
19.7	0.127	26.504	0.263	0.104	68.9	1560.2	0.717	92.3
27.2	0.117	26.363	0.230	0.143	69.7	1554.5	0.616	91.3
30.6	0.116	26.288	0.242	0.137	69.9	1551.5	0.639	91.3
34.0	0.115	26.228	0.234	0.135	70.1	1549.1	0.634	91.4
38.0	0.114	26.110	0.223	0.147	70.2	1544.4	0.603	91.2
46.2	0.110	25.988	0.207	0.158	70.6	1539.5	0.567	91.0
48.4	0.109	26.009	0.205	0.153	70.9	1540.3	0.572	91.1
52.6	0.107	25.839	0.198	0.161	71.2	1533.6	0.552	91.0
62.3	0.099	25.697	0.174	0.173	72.4	1527.9	0.501	90.8
62.3	0.098	25.707	0.174	0.173	72.4	1528.3	0.501	90.8
66.0	0.097	25.662	0.150	0.183	72.6	1526.5	0.451	90.7

Temp. (°C)	×1	×2	×3	×4	%T min	ν <sub>o</sub> (cm <sup>-1</sup> )	S	α(%T) 
4.2 6.8 9.8 10.2 13.6 13.7 19.7 27.2	0.139 0.139 0.134 0.135 0.127 0.129 0.126 0.116	26.751 26.716 26.632 26.681 26.613 26.580 26.472 26.335 26.335	0.290 0.294 0.270 0.286 0.260 0.273 0.252 0.252	0.063 0.063 0.087 0.090 0.121 0.102 0.119 0.147	67.6 67.5 68.0 67.6 68.3 68.3 69.0 69.8	1570.0 1568.6 1563.3 1567.3 1564.5 1563.2 1558.9 1553.4	0.822 0.823 0.756 0.761 0.682 0.728 0.680 0.680	93.2 93.0 92.5 92.2 91.5 91.9 91.7 91.2
30.6 34.0 38.0 46.2 48.4 52.6 62.3 66.0	0.115 0.114 0.113 0.109 0.107 0.105 0.096 0.095	26.276 26.183 26.082 25.980 26.013 25.852 25.728 25.679	0.234 0.226 0.221 0.194 0.186 0.173 0.132 0.065	0.144 0.137 0.145 0.168 0.171 0.182 0.201 0.223	70.0 70.2 70.7 71.0 71.3 72.5 72.7	1551.0 1547.3 1543.3 1539.2 1540.5 1534.1 1529.1 1527.2	$\begin{array}{c} 0.619 \\ 0.622 \\ 0.604 \\ 0.537 \\ 0.521 \\ 0.487 \\ 0.398 \\ 0.226 \end{array}$	91.1 91.2 91.1 90.8 90.8 90.7 90.5 90.4

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TABLE A-18

 $D_2O M = 2 v_{2+L}$ 

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 $D_2O M = 2 v_2$ 

Temp. (°C)		×2	×3	×4	<sup>%T</sup> min 	ν <sub>o</sub> (cm <sup>-1</sup> )	S 
4.2	1.155	17.781	1.039	0.456	6.5	1211.2	0.695
6.8	1.231	17.788	1.081	0.446	5.5	1211.5	0.708
9.8	1,219	17.774	1.088	0.432	5.6	1211.0	0.716
10.2	1.264	17.776	1.136	0.408	5.0	1211.0	0.736
13.6	1.223	17.792	1.139	0.413	5.5	1211.7	0.734
13.7	1.214	17.761	1.134	0.424	5.6	1210.4	0.728
19.7	1.206	17.786	1.103	0.443	5.7	1211.4	0.714
27.2	1.205	17.725	1.182	0.390	5.7	1209.0	0.752
30.6	1.221	17.700	1.211	0.384	5.5	1208.0	0.759
34.0	1.351	17.745	1.210	0.431	4.1	1209.8	0.737
38.0	1.327	17.670	1.252	0.409	4.3	1206.8	0.754
46.2	1.446	17.700	1.305	0.370	3.3	1208.0	0.779
48.4	1.396	17.749	1.324	0.344	3.6	1210.0	0.794
52.6	1.342	17.717	1.346	0.334	4.1	1208.7	0.801
62.3	1.177	17.706	1.275	0.331	6.0	1208.2	0.794
66.0	1.153	17.753	1.211	0.335	6.4	1210.1	0.783

Temp. (°C)	×1	x <sub>2</sub>	×3	×4	%T 	ν <sub>o</sub> (cm <sup>-1</sup> )	S 	α(%T) 
4.2	0.133	26.843	0.282	0.124	67.5	1573.7	0.694	91.6
6.8	0.132	26.787	0.277	0.126	67.6	1571.5	0.688	91.6
9.8	0.131	26.716	0.266	0.119	67.9	1568.7	0.691	91.8
10.2	0.133	26.739	0.283	0.114	67.6	1569.6	0.713	91.7
13.6	0.127	26.683	0.261	0.133	68.2	1567.3	0.663	91.4
13.7	0.129	26.639	0.278	0.109	68.2	1565.5	0.718	91.8
19.7	0.121	26.567	0.236	0.152	69.0	1562.7	0.609	91.2
27.2	0.115	26.402	0.220	0.159	69.8	1556.1	0.580	91.0
30.6	0.114	26.329	0.227	0.159	70.0	1553.2	0.589	91.0
38.0	0.111	26.192	0.192	0.184	70.3	1547.7	0.511	90.7
48.4	0.106	26.145	0.185	0.186	71.0	1545.8	0.501	90.7
52.6	0.104	25.972	0.174	0.192	71.3	1538.9	0.476	90.6

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 $D_2 O M = 3 v_{2+L}$ 

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 $D_2 O M = 3 v_2$ 

Temp. (°C)		×2	×3		%T 	ν <sub>o</sub> (cm <sup>-1</sup> )	S
4.2	1.080	17.874	1.120	0.646	7.6	1215.0	0.634
6.8	1.242	17.854	1.313	0.476	5.2	1214.2	0.734
9.8	1.195	17.842	1.258	0.507	5.9	1213.7	0.713
10.2	1.260	17.851	1.345	0.481	5.0	1214.1	0.737
13.6	1.223	17.873	1.359	0.506	5.5	1214.9	0.729
13.7	1.157	17.848	1.261	0.590	6.4	1213.9	0.681
19.7	1.199	17.860	1.301	0.520	5.8	1214.4	0.714
27.2	1.165	17.791	1.340	0.483	6.2	1211.6	0.735
30.6	1.197	17.757	1.383	0.437	5.8	1210.3	0.760
38.0	1.311	17.720	1.436	0.459	4.4	1208.8	0.758
48.4	1.413	17.811	1.548	0.412	3.5	1212.4	0.790
52.6	1.356	17.778	1.581	0.406	4.0	1211.1	0.796

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TABLE A-22

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 $D_2O M = 3 2v_L$ 

Temp. (°C)	×1	×2	×3	×4	tr min	ν <sub>o</sub> (cm <sup>-1</sup> )	S 
4.2	0.190	15.588	0.182	0.226	59.2	1123.5	0.445
6.8	0.184	14.071	-0.0	0.233	60.0	1062.8	0.001
9.8	0.188	14.125	-0.003	0.227	59.5	1065.0	0.012
10.2	0.193	14.321	-0.015	0.238	58.8	1072.9	0.061
13.6	0.198	14.352	-0.006	0.236	57.9	1074.1	0.025
13.7	0.188	15.327	0.071	0.262	59.5	1113.1	0.212
19.7	0.208	13.691	0.193	0.219	56.4	1047.6	0.081
27.2	0.179	14.424	0.033	0.238	60.3	1077.0	0.121
30.6	0.177	13.980	0.017	0.236	60.5	1059.2	0.065
38.0	0.202	13.297	0.012	0.213	56.9	1031.9	0.051
48.4	0.362	10.745	0.073	0.156	39.4	929.8	0.319
52.6	0.304	11.483	0.045	0.173	45.0	959.3	0.205

APPENDIX III-b: CURVE FITTING DATA

Curve fitting data are given in the following six tables (A-23 to A-28).

NIT+1 = Number of iterations performed: maximum allowed = 10
FM = Maximum discrepancy in experimental and calculated
%T values

a,b : GL = a + 10<sup>-b</sup>  
= 
$$\sum_{i=1}^{N_{p}} (T_{calc} - T_{obs})$$
, in %

DIS = Root mean square of residuals in %T. Averaged over all temperatures, DIS gives the estimated deviation of calculated curves from experimental points.

- WFM = Frequency of maximum discrepancy in experimental and calculated %T value, in cm<sup>-1</sup>
- NP = Number of experimental data points used to fit calculated contours
- V = Comments column
- C : Not converging
- N : Negative  $X_3$  or  $X_4$
- P : Trouble with P matrix

<sup>H</sup> 2 <sup>O</sup>	1	Band	Product	NP	=	37

Temp. (°C)	NIT	a	b	DIS	FM(%T)	WFM (cm <sup>-1</sup> )
5.4	9	0.14	3	0.48	0.80	2420
8.1	7	0.69	4	0.41	0.81	2400
12.2	5	0.32	4	0.39	0.75	2380
14.7	9	0.40	3	0.44	1.33	2660
20.0	9	0.45	3	0.37	0.92	2660
29.7	4	0.96	5	0.32	0.90	2660
33.0	4	0.91	5	0.33	1.00	2660
38.0	3	0.20	4	0.41	1.38	2660
40.2	4	0.39	4	0.36	1.01	2660
41.7	4	0.55	5	1.02	5.29	2020
45.0	4	0.21	5	0.35	1.22	2660
50.2	4	0.28	4	0.33	1.11	2660
53.4	4	0.11	4	0.87	0.87	2660
57.4	4	0.28	4	0.35	1.26	2660
57.4	4	0.18	4	0.27	0.88	2660
63.7	5	0.59	5	0.31	1.05	2660
67.1	5	0.61	5	0.28	0.88	2660
67.5	5	0.52	5	0.32	1.16	2660

<sup>н</sup> 2 <sup>0</sup>	2	Band	Product	NP	=	54
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Temp. (°C)	NIT	a	b	DIS	FM (%T)	WFM (cm-l)	v
5.4	9	0.16	3	0.83	3.09	1700	c
8.1	9	0.20	0	0.81	2.05	1700	С
12.2	9	0.16	2	0.74	2.17	1700	С
14.7	9	0.38	3	0.70	1.85	1700	Ρ
20.0	9	0.27	3	0.57	1.27	1740	
29.7	8	0.82	5	0.58	1.37	1700	
33.0	5	0.29	4	0.59	1.66	1740	
38.0	7	0.31	4	0.60	1.90	1680	
40.2	4	0.29	4	0.62	2.02	1680	
41.7	3	0.90	4	0.61	1.61	1680	
45.0	3	0.43	4	0.62	1.97	1760	
50.2	4	0.92	5	0.65	1.78	1740	
53.4	3	0.58	4	0.53	1.60	1740	
57.4	4	0.24	4	0.56	1.82	1740	
63.7	4	0.25	4	0.44	1.11	1680	
67.1	4	0.19	4	0.42	1.58	1680	
67.5	4	0.37	4	0.48	1.22	1700	

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 $H_2O$  3 Band Product NP = 76

Temp.	NIT	a	b	DIS	FM	WFM	v
<u>(°C)</u>					<u>(%T)</u>	$(cm^{-1})$	-
5.4	9	0.39	2	1.40	3.95	1700	
8.1	9	0.43	2	1.14	2.79	1520	
12.2	9	0.35	2	1.24	2.90	1160	
14.7	9	0.34	<b>2</b> :	1.20	3.18	1160	
20.0	9	0.32	2	1.19	3.35	1160	
29.7	9	0.41	2	1.15	3.26	1160	
33.0	9	0.32	2	1.06	2.66	1520	
38.0	9	0.23	2	1.24	3.17	1680	
40.2	9	0.40	2	1.06	3.12	1680	С
41.7	9	1.50	2	1.00	2.53	1680	С
45.0	9	0.26	2	1.20	3.27	1680	
50.2	9	Q.38	2	1.26	3.16	1160	
53.4	9	0.97	2	1.25	3.14	1160	С
57.4	9	0.31	2	1.13	3.38	1160	С
63.7	9	0.63	2	1.07	3.27	1160	С
67.1	9	0.85	2	1.06	2.79	1680	
67.5	9	0.91	2	1.13	2.86	1500	

TABLE	A-2	6
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D<sub>2</sub>0 l Band Produc

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coduct	NP	=	29
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Temp.	NIT	a	b	DIS	FM	WFM	V
(°C)		<del></del>			(%T)	$(cm^{-1})$	_
1 2	6	0 43	4	0 42	1 00	1960	
4.2	U	0.43	7	0.42	1.00	1900	
6.8	3	0.36	4	0.46	0.90	1960	
9.8	4	0.15	5	0.44	1.11	1960	Ρ
10.2	3	0.69	4	0.42	1.05	1960	
13.6	2	0.23	4	0.45	1.19	1960	
13.7	2	0.24	4	0.42	1.21	1960	
19.7	3	0.48	4	0.39	0.98	1960	
27.2	5	0.43	5	0.33	1.06	1960	
30.6	5	0.47	5	0.34	1.04	1960	
34.0	5	0.53	5	0.33	1.04	1960	
38.0	5	0.34	5	0.32	1.01	1960	
46.2	5	0.11	4	0.33	1.04	1960	
48.4	5	0.40	5	0.28	0.80	1960	
52.6	5	0.27	5	0.32	0.99	1960	
62.3	5	0.21	4	0.37	1.03	1960	
62.3	5	0.22	4	0.34	1.08	1960	
66.0	4	0.38	4	0.29	0.92	1960	

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#### TABLE A-27

 $D_2O$  2 Band Product NP = 41

Temp. (°C)	NIT	a	b —	DIS	FM(%T)	WFM (cm <sup>-1</sup> )
4.2	6	0.68	4	1.52	4.91	1420
6.8	6	0.96	4	1.55	4.93	1160
9.8	9	0.11	3.	1.48	4.37	1160
10.2	5	0.32	4	1.48	4.58	1420
13.6	5	0.69	4	1.56	5.24	1160
13.7	5	0.44	4	1.35	4.04	1160
19.7	5	0.86	4	1.48	4.65	1160
27.2	4	0.77	4	1.07	3.42	1180
30.6	4	0.46	4	1.05	3.59	1180
34.0	5	0.43	4	1.56	5.61	1420
38.0	4	0.68	4	1.06	3.27	1180
46.2	5	0.29	4	0.97	3.69	1180
48.4	5	0.87	5	1.07	3.62	1160
52.6	6	0.72	5	1.18	4.19	1160
62.3	8	0.37	4	1.13	3.91	1160
66.0	9	0.16	2	1.12	4.10	1160

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 $D_2O$  3 Band Product NP = 49

Temp. (°C)	NIT 	a 	b —	DIS	FM (%T)	WFM (cm <sup>-1</sup> )	V 
4.2	9	0.85	3	1.10	3.11	1060	
6.8	9	0.13	2	1.42	4.03	1060	N
9.8	9	0.25	2	1.23	4.07	1060	N
10.2	9	0.89	2	1.18	3.83	1060	N
13.6	9	0.45	2	1.24	3.82	1020	N
13.7	9	0.76	2	0.89	2.71	1020	
19.7	9	0.57	2	1.07	3.16	1080	Р
27.2	9	0.11	1	0.93	3.07	1020	с
30.6	9	0.35	2	0.90	2.77	1060	
38.0	9	0.38	2	1.10	3.49	1000	Р
48.4	9	0.12	1	0.81	2.68	1080	
52.6	9	0.21	1	0.86	2.91	1080	

#### APPENDIX IV

Computer programmes used during the investigation are presented in the following section.
APPENDIX IV-a: Programme LEASTSQR

The Polynomial Curve Fitting Programme

This programme is now available as subroutine

"CURVFT" at McGill Computing Centre, suitable for a 360/75 computer.

APPENDIX IV-b: Programme IRCELL

The Window Cancellation Programme

<u>Cards 1 and 2</u> are heading cards, containing any desired information. They must be included.

Card 3 carries four fixed point instructions, NP, NDATA,

IDECK and NEXP, in format 6110.

NP is the number of experimental data points.

- NDATA Use NDATA = 1 to process a single data deck or the last deck of a series and use NDATA = 2 to process consecutive data decks.
- IDECK Use IDECK = 1 for printed output only and use IDECK = 2 for both printed and punched output.
- NEXP Use NEXP = 1 with the  $H_2O$  data and use NEXP = 2 with the  $D_2O$  data.
- <u>Card 4</u> carries the input value of DELTA, in format F5.1. Delta is a small correction value, to be added to all the input transmittance values of the first input data deck, if necessary. The card must be included.
- <u>Card Deck 5</u> carries the NP experimental frequency data points in 13(I5,1X) format.
- <u>Card Deck 6</u> carries the NP experimentally observed transmittance data points, of sample plus cell, in format 13(F5.1,1X).

Card Deck 7 carries the NP experimental cell transmittance

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points to be subtracted at each frequency (Card Deck 5) from the values on Card Deck 6, in format 13(F5.1,1X).

<u>Card 8</u> is the terminating card and carries the base line transmittance,  $\alpha$ , in F15.5 format.

OUTPUT DATA

The punched output data cards of this programme are in a format suitable for direct input to programme IRCURFIT (Card Deck 6), or to programme PLOTS (Card Deck 3).



С 01 С 02 WINDUW ABSORPTION CANCELLATION С \* 03 С 04 С 05 С 06 С MAY 16, 1968 С PROGRAM I R. ODER 07 С 08 С THIS PROGRAM CONVERTS TWO TRANSMISSION INPUTS TO NATURAL LOGS 09 С THEN SUBTRACTS THE ABSORPTION OF ONE FROM THE OTHER, AND PRINTS 10 С THE CORRECTED TRANSMISSION VALUES WITH THEIR CORRESPONDING 11 С WAVENUMBERS . 12 С 13 С \* 14 С 15 С 'NEW' UNITS. FREQUENCY IN ( CM-1 - 1000)/40 FOR H20 С AND IN ( CM-1 - 500)/40 FOR D20 С С NP IS THE NUMBER OF DATA POINTS 16 С NDATA = 1 PROCESSES A SINGLE DATA DECK OR THE LAST DECK OF A 17 С SERIES AND NDATA = 2 PROCESSES CONSECUTIVE DATA DECKS 18 С 19 С IDECK = 1 GIVES PRINTED OUTPUT ONLY 20 С IDECK = 2 GIVES BUTH PRINTED AND PUNCHED DUTPUT 21 С 22 С USE NEXP = 1 FOR H20 AND USE NEXP = 2 FOR D20 29 C. С 23 С ORDER OF DATA INPUT 24 С 1. FREQUENCY 25 С 2. OBSERVED TRANSMITTANCE 26 С 3. CAF2 TRANSMITTANCE 27 С 28 С DELTA IS THE VALUE TO BE ADDED TO MEASURED TRANSMITTANCE VALUES С С С С 30 С \*\*\*\*\* 23 ſ 24

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0001		DIMENSION IX(100), LY(100), Y(100), Z(100), A(100), YNEW(100), HEAD1(20)	
		1,HEAD2(20),YI(100)	- <b>-</b>
0002		IRD=5	21
0003		IPCH=7	28
0004		IPRNT=6	29
0005	10	WRITE (IPRNT,400)	30
0006		READ (IRD,401) HEADI	31
0007		READ (IRD,401) HEAD2	32
0008		READ (IRD,402) NP,NDATA, IDECK, NEXP	
0009		IF (IDECK.EQ.1) GO TO 12	
0010		WRITE (IPCH,401) HEAD2	
0011	12	WRITE (IPRNT,410) HEAD1	
0012		WRITE (IPRNT,410) HEAD2	35
	ſ		36
0013	C	READ (IRD.415) DELTA	
0014		READ (IRD, 411) (IX(I), I=1, NP)	
0014		$READ (IRD \cdot 412) (Y(I) \cdot I = I \cdot NP)$	
0015		(IRD.404) (7(1).I=1.NP)	38
0010		READ (IRD.408) ALPHA	39
0018		WRITE (IPRNT.409) ALPHA.DELTA	
0010	C		41
0019	•	$DO_{36}I = 1 \cdot NP$	
0020		Y(I) = Y(I)	•
0021		IE (DELTA .GE. 0.0) GO TO 34	
0022		IF ( Y(I) LE.ABS(DELTA)) GO TO 35	
0023	34	Y(I) = Y(I) + DELTA	
0024		GO TO 36	
0025	35	Y(I) = Y(I)	
0025	36	CONTINUE	
0027		DO 30 I=1.NP	42
0028		A(1) = A(OG(Y(1)/Z(1)))	43
0029	3(	$\Delta(1) = \Delta(1) + \Delta I P H \Delta$	44
0030		$DO_{32}$ I=1.NP	45
0031		$YNEW(I) = EXP(\Delta(I))$	46
0032		IE (YNEW(1)   IE 0.0010) GO TO 31	47
0033		IE (YNEW(1), IT, 10, 0) GD TO 32	48
0034		YNEW(1) = 10.0	49
0035		GO TO 32	50
0036	21	YNEW(T) = 0.0	51
0030	23	> VNEW(T)=VNEW(T)+10.0	52
0031	26		_

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		5 <b>3</b>
	L 140 TTE (100 NT - 405)	54
0038	WRITE (IFRNI) + 4007	
0039	WRITE (IPRNI) $(1)$ (I)	
0040	WRITE (TERNITYTO) (TATTYTO) TO	55
0041		
0042		
0043	$IY(I) = YNEW(I) * IU \cdot U$	
0044	$Y_{1}(1) = 1Y_{1}(1)/10.0$	
0045	IF ((YNEW(I)-YI(I)).LI.0.037 GU TU 33	
0046	IY(I) = IY(I) + I	
0047	33 CONTINUE	
0048	IF (NEXP .EQ. 1) GU TU 16	
0049	IF (NP .GE. 51) GO TO 17	
0050	IF (NP . GE. 43) GO TO 18	
0051	IF (NP .GE. 31) GU TO 19	
0052	IF (NP .LT. 31) GO TO II	
0053	17 WRITE (IPCH, 407) (IX(I), $IY(I)$ , $I=3+51$ )	
0054	18 WRITE (IPCH, 407) (IX(I), $IY(I)$ , $I=3,43$ )	
0055	19 WRITE (IPCH,407) (IX(I),IY(I),[=3,31)	
0056	GO TO 11	
0057	16 IF (NP.GE.78) GO TO 13	
0058	IF (NP.GE.56) GU TO 14	
0059	IF (NP.GE.39) GO TO 15	
0060	IF (NP.LT.39) GO TO 11	
0061	13 WRITE (IPCH, 407) (IX(I), $IY(I)$ , $I=3,78$ )	
0062	14 WRITE (IPCH,407) (IX(I),IY(I),I=3,56)	
0063	15 WRITE (IPCH,407) (IX(I),IY(I),I=3,39)	
0064	11 WRITE (IPRNT,414)	
0065	WRITE (IPRNT, 406) (IX(I), YNEW(I), I=1, NP)	
0066	TE (NUATA-EQ-1) GU TO 40	58
0000	$G_{0}$ TO 10	59
0068	40 CALL EXIT	60
0000	400 FORMAT ('IR ODER REMOVAL OF CAF2 WINDOW ABSORPTION FROM OBSERVED B	61
0007	$1 \text{ AND } \text{ENVEL}(\text{PE}^{1})$	62
0070	401  EURMAT (2044)	63
0070	402 FORMAT (6110)	64
0072	403 EDRMAT (8115-E4-1-1X))	65
0012	404  FURMAT (13(F5.2.1X))	66
0074	405 FORMAT ("OORDINATES IN TRANSMITTANCE UNITS"/)	67
0014	$406 = 608MAT (9(1) \times 15 \cdot 1 \times 15 \cdot 2 \cdot 2 \times 1)$	68
0015	TOO TOURAT TYTERTYTERT YEART TO TOUR TOUR TOUR TOUR TOUR TOUR TOUR	

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0076	407 FORMAT (8(I5,I4,1X))	
0077	408 FORMAT (4F15.5)	70
0078	409 FORMAT (4X,6HALPHA=,F8.5,17X,6HDELTA=,F8.5/)	
0079	410 FORMAT (2X,20A4)	72
0800	411 FORMAT (13(15,1X))	
0081	412 FORMAT (13(F5.1,1X))	
0082	413 FORMAT ('OOBSERVED BAND ENVELOPE. NEW UNITS AND PERCENT TRANSMITTA	
	1NCE. */)	
0083	414 FORMAT ("OBAND ENVELOPE ON REMOVAL OF CAF2 ABSORPTION"/)	
0084	415 FORMAT (F5.1)	
0085	END	73

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TOTAL MEMORY REQUIREMENTS 00168C BYTES

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APPENDIX IV-c: Programme IRCURFIT (9)

The Basic Band Fitting Programme

The printed version of PROGRAM X (PC-116) in NRC Bulletin No. 12 (9) is slightly different from the version used in the investigation. The version used did not contain the following lines:

> 0466A to 0466E 0467A to 04673 0469A to 0469B 0470A 0560A to 0560F.

To use the programme on McGill University's IBM 360/50-360/75 computer (FORTRAN IV, level G) the following changes were necessary:

(1)	line	from	to
	0035 0036 0037	IRD = 1 $IPCH = 2$ $TDPNT = 3$	IRD = 5 $IPCH = 6$ $IPRNT = 7$

(2) internal timing instructions, contained on lines 0121 to 0126, 0255 to 0257, and 0469, were removed, and "ISEC" deleted from the WRITE statement on line 0260.

(3) deleted from line 0517

,4x,54ISECS,15

In addition, the following changes were made to the programme:

(4) ,L was added to end of READ statement,

line 0045, with the comments use L = 1 for frequency in cm<sup>-1</sup> use L = 2 for frequency in  $(cm^{-1}-1000)/40$  (H<sub>2</sub>O) use L = 3 for frequency in  $(cm^{-1}-500)/40$  (D<sub>2</sub>O).

(5) Line 0475 changed to

WRITE (IPRNT,436)

```
(6) Between lines 0480 and 0481, inserted
```

RATIO = ABS(X(K)) / ((ABS(X(K)) + ABS(X(L))))

(7) Line 0483 changed to

319 WRITE(IPRNT, 406)X(I), X(J), X(L), X(L), RATIO

(8) Line 0488 changed to

GO TO 700

(9) Inserted between lines 0503 and 0504

```
700 WRITE(IPRNT,437)
DO 701 I = 1, M
J = I+M
X(I) = X(I)+X(N)
X(I) = EXP(-2.30259*X(I))
IF (L.EQ.1) GO TO 701
IF (L.EQ.2) GO TO 702
IF (L.EQ.3) GO TO 802
702 X(J) = X(J)*40.0)+1000.0
GO TO 701
802 X(J) = (X(J)*40.0)+500.0
701 WRITE(IPRNT,438)X(I),X(J)
X(N) = EXP(-2.30259*X(N))
WRITE(IPRNT,439)X(N)
```

(10) Line 0512 changed to

403 FORMAT (11 I 5)

(11) Inserted between lines 0529 and 0530 the following

436 FORMAT ('0',15x,4HX(1),17X,4HX(2),17X, 4HX(3),17X,4HX(4),17X,5HRATIO) 437 FORMAT('0',12X,7HX(1) T,17X,9HX(1)CM-1) 438 FORMAT(1X,2(6X,F15.6)) 439 FORMAT(6X,7HALPHA=F8.5)



APPENDIX IV-d: Programme CALCBAND (10)

Calculation of the Ordinates of the Composite Band Envelope

The printed version of Program XIV (PC-122)

in NRC Bulletin No. 12 (10) differed from the one used in that the latter

- (1) did not include line 93A
- (2) line 94 read

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21 IW(II) = W\*10.0

In addition, the following changes were necessary:

line	from	to
29	IRD = 1	IRD = 5
30	IPCH = 2	IPCH = 6
31	IPRNT = 3	IPRNT = 7

APPENDIX IV-e: Programme PLOTS

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Graphic Comparison of Calculated and Experimental Data Points

This programme is now available as McGill subroutine "MULTPLT", suitable for the 360/75 computer, at McGill Computing Centre.

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