

THE USE OF LOW TEMPERATURE
INFRA RED SPECTROSCOPY
IN THE STUDY OF
IONIC SOLVATION

A Thesis presented for the degree of
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by
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S T A T E M E N T

This thesis is based upon experimental work conducted by the author in the laboratories of the Department of Chemistry of the University of Leicester mainly during the period between October 1973 and September 1976.

The work recorded in this thesis is original unless otherwise acknowledged in the text or by references. None of the work has been submitted, in whole or in part, for any other degree.

Signed

A handwritten signature in black ink, appearing to read 'I. M. Strauss', with a long horizontal flourish extending to the right.

I. M. STRAUSS

January 1981

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I would like to express my gratitude to Professor M. C. R. Symons for suggesting the field of study and his guidance, encouragement and continued interest throughout the duration of this investigation.

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I. M. Strauss

Leicester, 1981

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SUMMARY

The introductory chapter deals with general theoretical aspects of vibrational spectroscopy leading on to a discussion of the infra red spectrum of water and electrolyte solutions. Reviews of existing literature concerning the absorption bands in the far, near and fundamental infra red regions of electrolyte solutions suggested that isotopically dilute solutions of HOD in D_2O would produce the least complicated and most informative absorption bands to study in the fundamental O-H stretching region. In view of the similarity in structure and functional groups between methanol and water, the study of methanolic solutions was chosen to provide a sound base from which the more complicated problem of aqueous solutions could be tackled. The chapter ends with a review of the major theoretical models of water and a comparison of the continuum and mixture models. An alternative approach to the understanding of the structure of liquid water is also suggested.

A description of the three infra red spectrometers and the liquid cells is found in chapter two together with details of the variable temperature control system. Details are given here of the experimental procedures undertaken to obtain low temperature data.

The first part of chapter three deals with ambient temperature infra red spectral data of methanolic solutions and the effect of inorganic salts upon the fundamental O-H stretching band. From this systematic investigation certain trends regarding solvent-solute interactions were noted. A significant decrease in band width was observed when the pure solvent was cooled to liquid nitrogen temperatures. This formed the basis of an investigation of methanolic electrolyte solutions at low temperatures. A series of interesting fundamental infra red spectra with many resolvable features in the O-H stretching region were studied over a salt concentration range which led to band assignments that have only previously been speculated. Previously deduced relative band strengthening properties of the cations Mg^{2+} , Na^+ and Li^+ were confirmed. The low temperature study of perchlorate and other polyatomic ion solutions produced further evidence that the high frequency band absorbing at 3530 cm^{-1} could be

associated with weakly bonded anions rather than the formation of non-banded O-H groups. The final section of this chapter deals with a general discussion of anion solvation where the important role of the secondary methanol molecules in determining the wave number for the primary solvent shell, and hence the way they knit into the solvent structure, is detailed.

The role of water in solvating ionic species is the subject of investigations in chapter four. Here the O-H stretching band in the infra red spectrum of HOD in liquid D₂O was first studied as a function of the concentration of electrolytes at room temperature. These results, together with data collected from the literature, were systematically recorded so that information on the different solvent species could be extracted. The low temperature spectral data of these salt solutions and their corresponding salt hydrate data were considered together to assign the well defined absorption bands. These results enabled infra red stretching frequencies to be used to determine hydrogen bond strengths. Polyatomic anion solutions were investigated at room and liquid nitrogen temperatures where experimental evidence suggested that the (O-H) free groups are not caused by "structure breaking" by the polyatomic ions, but by the imbalance of (O-H) free and free lone pair groups. Electrostatic forces in polyatomic anion hydrates provide a possible explanation of the anion sequence NO₃⁻, ClO₃⁻, SO₄²⁻, ClO₄⁻ and PF₆⁻ which absorb at increasing frequencies. An anion solvation model based on a liquid possessing normal dibasic and diacidic properties is proposed for liquid water where the secondary solvation, however, is involved in the bulk solvent structure, rather than being an area of disorder.

Chapter five deals with the infra red studies of the tetrahydroborate anion in various pure solvents and binary aqueous mixtures in the fundamental O-D stretching region and at the asymmetric B-H stretching band for the BH₄⁻ ion. Results from both investigations suggest an interaction between BH₄⁻ and water protons which have the spectroscopic characteristics of hydrogen bonding.

Vibrational studies of methanolic tetraalkylammonium halide solutions

in inert and bulk solvent solutions were the topic considered in the final chapter. The anion-solvent interactions were first investigated at both room and low temperatures in an inert media to identify the monosolvate bands. Concentrated methanolic salt solutions were then studied which, at low temperatures, produced a range of anion solvates where both primary and secondary solvation could be observed. These interesting results provided a marked contrast to the alkali metal salt solution studies where the solvent shared ion pairs were dominant.

CHAPTER ONE

INTRODUCTION

The nature of the structure of liquid water has been a matter of scientific interest since before the beginning of this century. However, from 1933, the suggestion¹ that the structure of water was due to the hydrogen bonding between molecules has been the basis of all structural models. This thesis contains a discussion of some of the evidence that has been provided by the study of the vibrational spectra of liquid water and its electrolyte solutions in conjunction with some corresponding methanolic solution data. These ideas have provided a useful platform to tackle the new line of investigating the low temperature methanolic and aqueous electrolyte solutions in the infra-red region of the spectrum for further information in the study of the structure of water in aqueous solutions.

Although there are many experimental procedures designed to provide information on the role of the solvent in the neighbourhood of the solute particles, we have focussed our attention on the fundamental O—H stretching region of the infra-red spectrum. This is just one way of characterising the structural changes in the solvent as the solute-solvent interactions modify the vibrational spectra of the solvent.

Vibrational spectroscopy is only one aspect of molecular spectroscopy which can be generally said to be the study of the interaction of electromagnetic waves and matter. A molecule in space can have many sorts of energy such as rotational energy by virtue of bodily rotation about its centre of gravity, vibrational energy which is due to periodic displacement of its atoms from their equilibrium positions and electronic energy. These energies are quantised with a particular molecule existing in a variety of energy levels. When an appropriate amount of energy in the form of a beam of monochromatic radiation is directed onto the molecule, energy can be absorbed from the beam and a transition between one level and another is achieved. As a result of this interaction with the molecule, the intensity of the beam containing a wide range of frequencies is decreased at this one

frequency, producing an absorption spectrum. When a molecule in a higher energy level reverts to a lower level with a consequent emission of radiation a complementary spectrum called an emission spectrum is produced.

If a molecule is to absorb infra-red radiation, the radiation must be of the correct frequency to cause a quantum jump in its vibrational energy. A vibrating molecule will interact with electromagnetic radiation if an oscillating dipole moment accompanies the vibration. A change in dipole moment occurs for a molecule whenever a change in position of the centres of positive and negative charge resulting from atomic motion occurs.

A diatomic molecule has repulsion between the positively charged nuclei and the negative electron clouds and attraction between the nucleus of one atom and the electrons of the other. The two atoms do, however, settle at a mean internuclear distance, r_e , which is referred to as the bond length. Under these conditions, all the forces are balanced and hence for the whole system, energy is at a minimum. The bond length can be distorted by the input of energy to the molecule which compresses and extends the bond in a similar manner to the behaviour of a spring where the vibrational characteristics are dependent on the mass of the particle and the nature of the spring. The behaviour of a spring follows a simple harmonic oscillator model which can be expressed more conveniently in terms of the potential energy, U , of the vibrating molecule. The potential energy at r_e is taken as zero and the displacement of the particle from a position, x , to position dx , requires a force to be exerted to overcome that of the spring. The work done, all of which is stored in the system and is therefore potential energy, is equal to this applied force times the distance dx through which it acts.

$$\begin{aligned} dU &= (\text{applied force}) \, dx \\ &= -f \, dx \end{aligned}$$

For a spring, Hookes law states that

$$f = -kx$$

where k is the force constant

$$\Rightarrow dU = kx dx$$

By integration we find that

$$U = \frac{1}{2} kx^2$$

which produces a potential energy curve that rises parabolically on either side of the equilibrium distance, r_e .

This potential function for motion can be substituted in the Schrödinger equation and the allowed vibrational energies can be calculated as:

$$E_v = (v + \frac{1}{2}) \bar{W}_{osc} \text{ joules } (v = 0, 1, 2, \dots)$$

where v is the vibrational quantum number and \bar{W}_{osc} is the wavenumber of the radiation emitted or absorbed by the oscillator.

Also obtained from the Schrödinger equation was the selection rule for the harmonic oscillator undergoing vibrational changes of $\Delta V = \pm 1$ which gives rise to the spectral line absorbed or emitted at $\bar{W}_{osc} \text{ cm}^{-1}$ as shown in Figure 1.1.

However, real molecules do not exactly obey the law of simple harmonic motion and instead of a simple harmonic parabola, a Morse energy curve as shown in Figure 1.2 is a better approximation for a diatomic molecule. The allowed energy levels obtained from the Schrödinger equation are then:

$$E_v = (v + \frac{1}{2})\bar{W}_e - (v + \frac{1}{2})^2 \bar{W}_e x_e \text{ cm}^{-1} (v = 0, 1, 2, \dots)$$

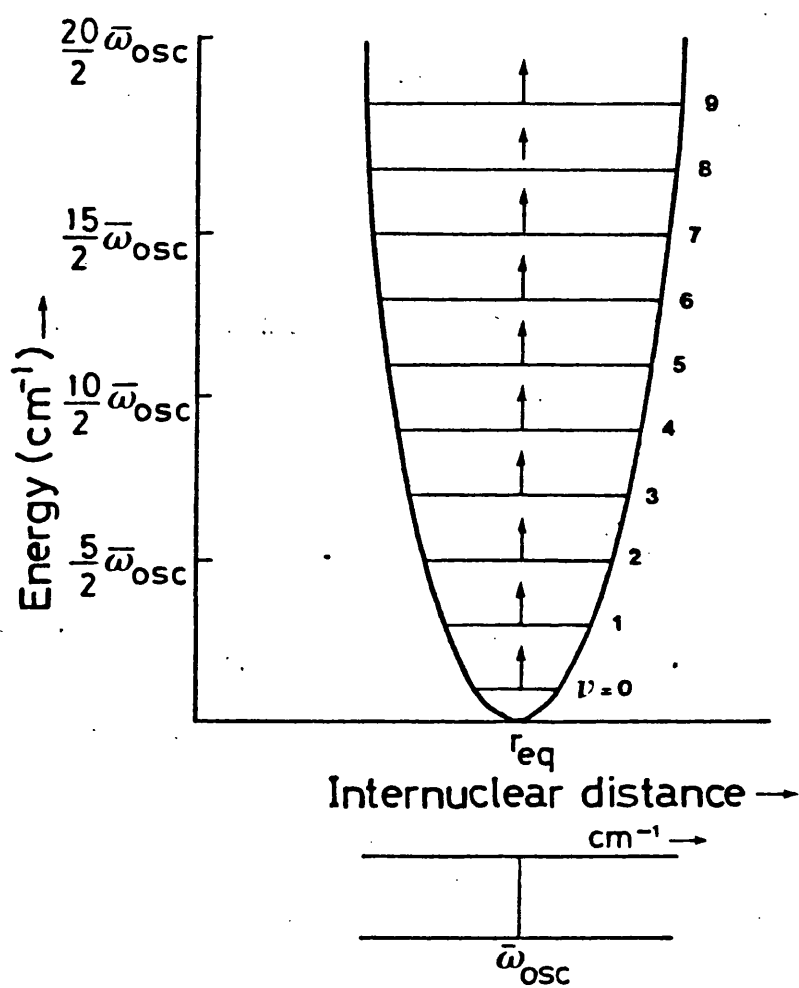
where \bar{W}_e is an oscillation frequency and x_e the anharmonicity constant.

The selection rules for the anharmonic oscillator are:

$$\Delta V = \pm 1, \pm 2, \pm 3, \dots$$

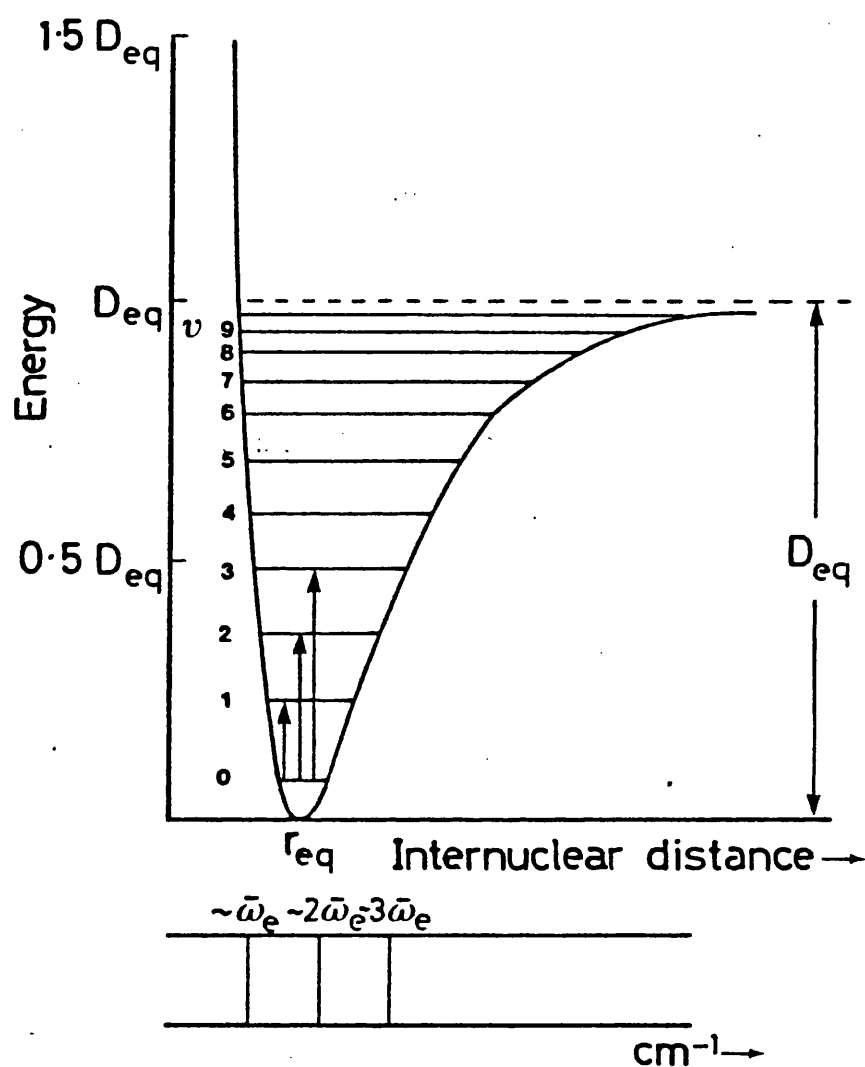
However, only lines associated with transitions of $\Delta V = \pm 1, \pm 2, \pm 3$ have observable intensity. Due to the anharmonicity term introduced the separation between successive vibrational levels are not constant and decrease with increasing values of v so the wavenumber of the first overtone is not precisely double that of the fundamental absorption value. Taking into consideration the Boltzmann distribution calculation that states that less than 1% of the ground state population is situated at the $v = 1$ level,

FIG. 1.1



The allowed vibrational energy levels and transitions between them for a diatomic molecule undergoing simple harmonic motion.

FIG.1.2



The allowed vibrational energy levels and some transitions between them for a diatomic molecule undergoing anharmonic oscillations.

to a good approximation only three transitions can be observed:

Strong $v = 0 \longrightarrow v = 1$ fundamental absorption

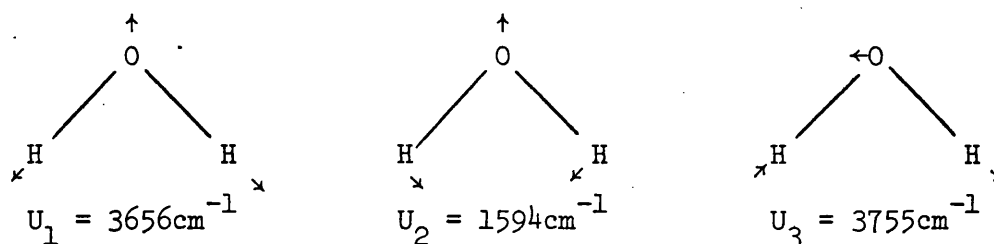
Weak $v = 0 \longrightarrow v = 2$ first overtone

Very weak $v = 0 \longrightarrow v = 3$ second overtone.

Although no Raman spectroscopy of the aqueous system discussed has been attempted in this work, reference is made to Raman work that has been found in the literature. Hence, a description of how Raman lines are obtained is included.

In the Raman experiment, light of energy large compared with the vibrational energy spacings is passed through the system. This large energy quantum of radiation can interact with the sample molecules and give up some energy to the vibrating molecules or even withdraw some of the vibrational energy and release the remaining energy as light of a different frequency. This is called the Raman effect. It does not obey the usual rule that the quantum must fit the energy gap. This difference in frequency of the incident light and of the scattered light therefore corresponds to a rotational or vibrational frequency. In order for a vibrational frequency to appear in the Raman spectrum, it is necessary for the particular vibration to change the polarisability of the molecule.

Vibrations can be described by a limited number of basic vibrations known as normal modes which are stationary wave functions. The water molecule has three normal modes as shown below² and every possible vibration can be described as a superposition of these three modes



The bonds are represented by the full lines and the arrows show the relative directions and displacements of the nuclei during a given vibration.

A typical infra-red spectrum of water is shown in Figure 1.3 where the three fundamental modes are assigned. As can be seen from this diagram the most prominent band is the broad band in the 3400cm^{-1} region which is associated with the O—H stretching vibrations of the molecule. As the motion of the nuclei in the symmetric and asymmetric vibrations is along the direction of the O—H bond, these modes are often referred to as O—H stretching vibrations. Within this broad absorption band a contribution from the first overtone of the bending mode is observed. The band near 1650cm^{-1} arises from the bending mode of the molecule and a very broad but weak band with its maximum in the 2100cm^{-1} region has been denoted to an association band which may comprise overtones of intermolecular modes with or without the bending mode. The assignment that it is due to $U_2 + U_2 + U_T$ has been proposed³.

Bands found at lower frequencies probably arise from intermolecular vibrations and rotations. The most intense band in this region has its maximum at 700cm^{-1} and has been described as a libration mode, U_L . A band with its maximum near 190cm^{-1} appears as a prominent shoulder on the 700cm^{-1} band and is assigned to the hindered translations, U_T , of the molecule.

Bands found at higher frequencies are displayed in Figure 1.4 where there are a number of overtone and combination bands. Except for the sharper feature at 7100cm^{-1} which has been denoted to (O—H) free groups, assignments are not clear cut, but will be discussed later in this chapter.

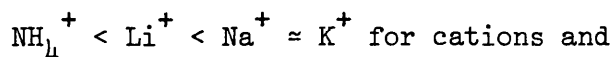
Far Infra-Red Review

The far infra-red absorption of pure water is produced by rotational and translational motions of molecules restrained by intermolecular forces exerted by neighbouring water molecules. X-ray studies^{4,5,6} of ice and to a lesser extent water, have shown that the four nearest neighbours are at the corners of a tetrahedron. Motions of a given molecule are restricted chiefly by the hydrogen bonds linking it to its nearest neighbours and the displacement from its equilibrium orientation and position gives rise to

restoring forces. A given molecule would have three modes of hindered rotation about the principle axis of the molecule. Two of these modes would be strongly infra-red active, since they involve changes in the direction of the molecular dipole moment. Rotation about the symmetry axis would produce absorption by an indirect process involving changes in molecular polarizations.

However, because the water structure does not have the regularity of a true crystal, broad absorption bands are obtained due to hindered rotations. Although some have reported evidence of the existence of more than one component^{7,8}, in the librational band in the infra-red and Raman spectra, no conclusive evidence can be drawn as no resolved points of maximum absorption can be located. Even the addition of ions does not produce any new features although a pronounced effect upon the librational band in liquid water is observed^{9,10,11}. The qualitative conclusions drawn were that the anions produced the greatest effect on the librational band in the order below $\text{NO}_3^- < \text{ClO}_3^- < \text{ClO}_4^- < \text{Cl}^- < \text{Br}^- < \text{I}^-$. However, the librational frequencies were independent of the molality of salt probably because the water molecules in the immediate solvation shell were tightly held. With no integrated absorption intensities available because of difficulty in measurement, no further insight into the relative strengths of the ion-water hydrate bands in comparison to the pure water bands can be made.

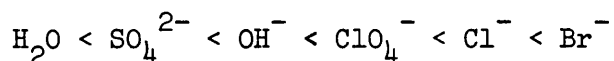
The low intensity intermolecular bands in the Raman spectrum have been investigated in detail^{12,13,14}, with the three librational bands centred at 450, 550 and 720cm^{-1} and the hydrogen bond stretching and bending centred at 170 and 60cm^{-1} respectively. The addition of salts causes perturbations in this spectral region, ~~but~~ No study of individual components has been attempted, but molar intensity enhancements increase in the order:



$\text{NO}_3^- < \text{Cl}^- < \text{Br}^-$ for anions. It has also been observed that the increase of temperature results in a diminution of intensity of these intermolecular absorption bands which has been attributed to the reduction in

concentration of the four hydrogen-bonded units.

Effects of added electrolytes on the 175cm^{-1} band have been studied⁸, with the resulting conclusion being that there is no marked cation effect but the pronounced anionic effects ~~are~~ in the order



This order was explained by implying that the bromide ion destroys the four hydrogen bonded water units more than the chloride ion etc to give fewer O—H---O bonds with the conclusion that the fall in intensity of this band can be directly attributed to the breaking of the O—H---O bonds by the added electrolytes.

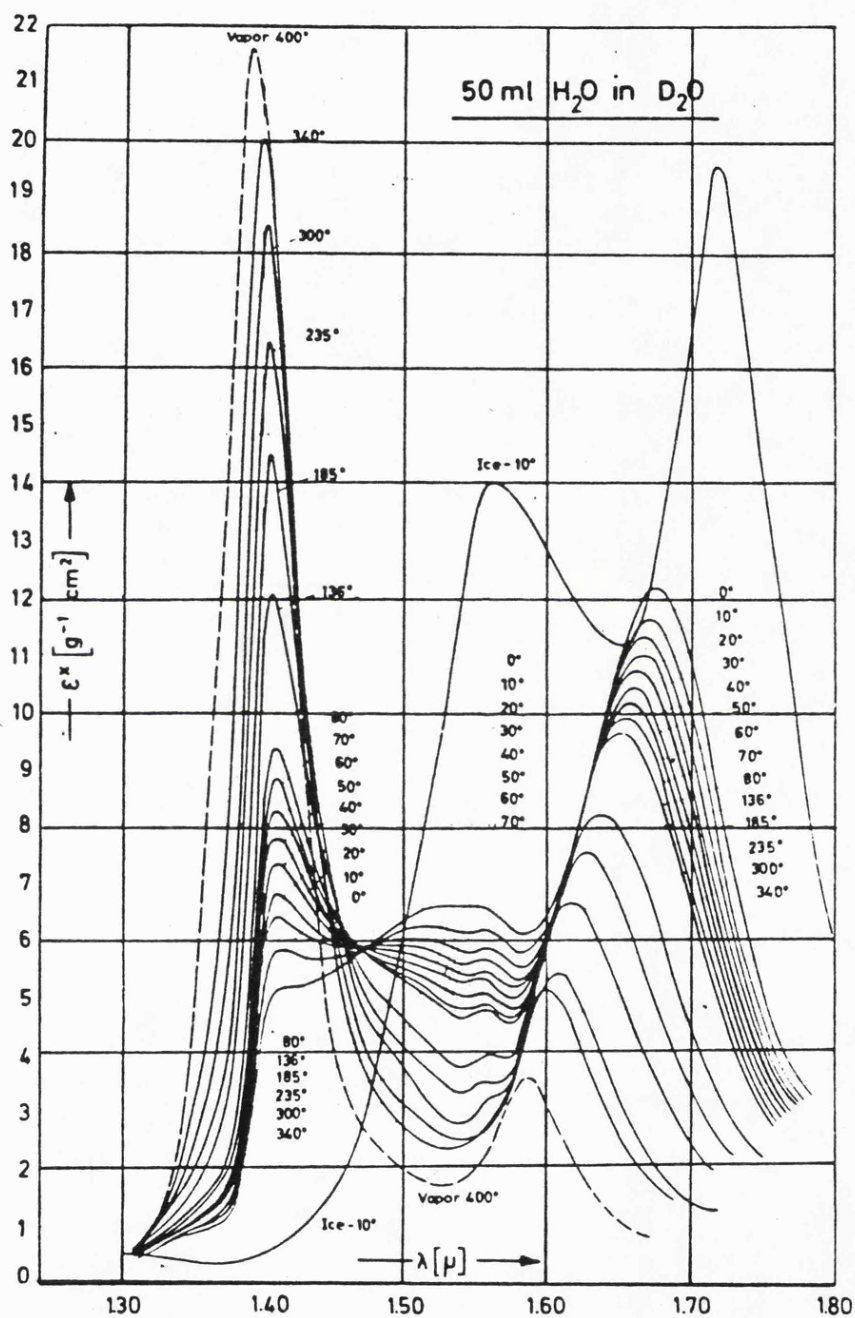
Although these low frequency studies certainly give an indication of the effects of electrolytes in solution, precise and detailed interpretation of solvation is hindered by the large widths and low intensities of the bands.

Near Infra-red Review

The effect of ions on the near infra-red spectrum of water is primarily concerned with qualitative changes as there is uncertainty governing the assignment of a number of bands in this region which have been summarised by Bayly¹⁵ before the introduction of isotopic mixtures¹⁶. Detailed investigations in this region have been undertaken by many workers^{17,18,19}, since, with many of the earlier qualitative studies centred around temperature and dissolved salt effects. These produced very little shift as regards band positions but certain distinctive changes in the intensity of the bands as shown in Figure 1.4 where temperature changes of an HOD in D_2O solution are well illustrated. The assignment of the sharp band in the 7100cm^{-1} region to the first overtone of the (OH)free band or the non hydrogen bonded O—H stretching vibration has been accepted but the remaining bands are best said to be due to different hydrogen bonded species.

Therefore the only way to study this area of the spectrum would be to monitor the intensity of the (OH)free band from HOD in D_2O solutions in the 7100cm^{-1} region. Salt effects on this band have been recorded²⁰ with the

FIG.1.4



Temperature-dependence of the HOD spectrum.
 50ml. H_2O / D_2O liquid plastic under saturation
 conditions.

conclusion that some salts are called "structure makers" while others are "structure breakers", depending on whether there is a decrease or increase in the (O—H)free band intensity respectively.

A suggestion²¹ that this terminology has lead to some incorrect conclusions because ~~no~~^{the} presence of free "lone pairs", (LP)free, has ever been mentioned in this context has been made. So the situation when the water structure is broken by say heating is that the increase in the number of (OH)free groups is equal to the number of (LP)free groups, but no evidence ~~or an attempt to find~~^{for} the latter species has been observed or made. This concept can be used further to explain salt effects as cations scavenge(LP)free groups and anions(OH)free groups. The net effect of either a gain or loss of (OH)free groups can conveniently be monitored in the near-infra-red region. This point is well illustrated by the results obtained from reference 20 where a decrease in the (OH)free band intensity was observed on the addition of tetrabutylammonium bromide and an increase when sodium tetraphenylboron was added. In the former case only the anions solvate producing the decrease in the (O—H)free band while in the latter case the sodium ions solvate to the lone pairs of the solvent thus generating an excess of (OH)free groups.

Recently, near infra-red difference spectra of aqueous alkali halide solutions have been resolved and interpreted quantitatively^{22,23}, in an attempt to evaluate a number of parameters and relate these to the hydration of the ionic species in aqueous solutions. The negative difference spectrum obtained from having a salt solution in the sample beam and pure solvent in the reference beam was associated with the excluded volume of the salt which was then resolved into two components, one representing the hydration of the solute and the other the volume of the hydrated solute. By subtracting this curve from the normalized water spectrum which represented the minimum net contribution by the water in the reference cell, a hydration spectrum was obtained. Studies of different spectra obtained by varying the sample cell temperature with the reference sample being kept constant, revealed

strong support for the mixture model concept for water as did results obtained from sodium perchlorate solutions. However, the result that the sharp peaks obtained from the temperature studies and from the perchlorate studies do not absorb at the same wavelength seems to suggest that the high frequency band from the perchlorate solutions might not be the (OH)free band but the anion solvate band or a band containing both the (OH)free species and a perchlorate solvate absorbing at lower wavelengths than the 7067cm^{-1} reported²², but not resolved as two separate bands.

Fundamental Region

The stretching bands in pure water in the $3200 - 3600\text{cm}^{-1}$ region have been studied thoroughly, but because of the great breadth of this band, dilute solutions of HOD in either H_2O or D_2O were used. The breadth of the pure solvent band arises from several sources. The proximity of the frequencies at which the two O—H stretching vibrations, ν_1 and ν_3 , and that of the first overtone of the bending vibration, $2\nu_2$, absorb, could be responsible. Each of these vibrations may couple with the vibrations of neighbouring molecules, causing a splitting of each band. Since the band frequencies are closely spaced, the split bands overlap one another adding to the breadth of the overall band. It is believed that the overlapping ν_1 and $2\nu_2$ modes may be in Fermi resonance with each other which means that the $2\nu_2$ band borrows intensity from ν_1 .

However, the shapes of the stretching bands of pure H_2O have led to several proposals as explanations. Walrafen¹⁴ describing the Raman stretching band claims a presence of water molecules forming different numbers of hydrogen bonds on the basis of his temperature data. Walrafen splits the absorption in this region into four Gaussian components which he assigns to two intramolecular stretching modes of non hydrogen bonded molecules which increase in intensity on the increase of temperature and two vibrations of hydrogen bonded molecules which decrease in intensity and absorb at the lower frequencies.

Another interpretation²⁴ of this band shape proposed that collisions of molecules in the liquid gave rise to a range of ν_1 and ν_3 vibrational frequencies with their appropriate mean frequencies near 3400 and 3600cm^{-1} respectively. The overtone of ν_2 near 3200cm^{-1} overlaps the ν_1 vibration and thereby gains intensity through Fermi resonance. The change of band shape on heating was explained by the mean frequencies of ν_1 and ν_3 increasing which diminishes the Fermi resonance between ν_1 and $2\nu_2$ and thus decreasing the band intensity in the 3200cm^{-1} region.

The isotopically dilute solutions of HOD in either H_2O or D_2O produce much simpler absorption bands in the stretching band region because the HOD molecules are only weakly coupled to the vibrations of neighbouring molecules and also because of the absence of Fermi resonance with the overtone of ν_2 . This means that the shape of the bands can be interpreted in terms of local environments of water molecules.

When oscillations of weakly connected vibrators have nearly the same characteristic frequency, one vibrator produces forces in the other vibrator and the system is said to be coupled. The frequency changes produced by connecting two very different vibrators are small and hence are called uncoupled vibrators. In this way the O—H bond in a particular water molecule is strongly coupled with the other O—H bonds in the liquid, but if all the neighbouring protons were replaced by deuterons, then the particular O—H bond is said to be uncoupled.

Returning again to the water molecule where both protons are subject to nearby equivalent force fields, either both unbonded or both hydrogen bonded equally, the two O—H stretching modes are coupled and split to yield an upper frequency antisymmetric stretch, ν_3 , and a lower frequency symmetric stretch, ν_1 . However, when only one proton forms a hydrogen bond, the two stretching modes remain uncoupled and behave as independent group vibrations or in the case of the HOD species, nearly pure O—H and O—D elongations are observed.

Infra-red studies²⁵, of dissolved water showed displacements to lower frequencies and an increase in bandwidth of the stretching bands with increased hydrogen bonding to the solvent. The band frequencies of ν_3 and ν_1 for water solutions in 24 solvents are given in reference 26 and the linear correlation which exists between the values of ν_3 and ν_1 is displayed.

Some data²⁶ is given from the decoupled O—H stretching modes of the water molecules that arise from unequal hydrogen bonding of the two protons with the solvent. Here the bands are due to either an unbonded or strongly bonded species. Details of the change from the 2:1 complex (A---HOH---A) to the 1:1 complex (A---HOH) was demonstrated²⁷ using a dilute solution of water in an inert solvent, CCl_4 , and then adding pyridine. This produced a decoupling of the two stretching modes. Another example²⁸ of decoupled bands was produced when a series of organic bases and solutions containing halide ions were added to the $\text{H}_2\text{O} - \text{CCl}_4$ system. For all the bases studied at concentrations around 0.2M, the 1:1 complex was obtained with the higher frequency band lying slightly shifted from the position of the asymmetric, ν_3 , stretching mode of free water and the lower frequency band characterising the association species. However, further addition of the base led to the disappearance of the high frequency band and the appearance of two broader bands at lower frequencies which is due to the 2:1 complex.

From all the data available from the references mentioned, a detailed plot as shown in Figure 1.5 was constructed. As can be seen from this diagram, ice and many crystal hydrate data fit onto the line for the 2:1 complex. For the symmetrical 2:1 species, as stated earlier, as the polarity of the solvent increased, the two bands moved towards lower frequencies and became broader as well as moving closer together which results in a loss of resolution and the appearance of a single broad band. It was claimed³¹ that because of the linearity of the relationship that similar association effects occur in other solvents and so crystal hydrate data with narrow bandwidths was utilised to provide further evidence. This

diagram can therefore be used to predict the environment of any given water molecule whose symmetric and asymmetric stretching frequencies can be obtained. The evidence that the perchlorate hydrates lie on this curve provides further evidence that a perchlorate-water interaction occurs.

Absorption Band Shapes

As molecules are thought to consist of relatively wide ranging bond lengths and angles whose distribution normally shows continuity and passes through a single maximum, a distribution in the form of a symmetrical Gaussian or Lorentzian curve would be expected. However, because of the occurrence of changes in dipole separation and therefore oscillator strengths, asymmetric absorption curves are observed as illustrated in Figure 1.6.

In the fundamental infra-red spectrum, the bands are more intense in the lower frequency region which produces an asymmetric absorption band with the peak maximum shifting to lower frequencies. This is due to the charge centres of the O—H oscillator being further apart and hence having a larger dipole moment which increases the oscillator strength and therefore the intensity of the band. The argument is reversed for the O—H oscillators engaged by weak hydrogen bonding because of the oscillator strengths being reduced as the charge centres are closer together thus producing small dipole moments. However, the distribution of such weak bonds are not as common and therefore only a weak shoulder in the high frequency region is observed.

For the Raman spectra, such band asymmetries are not observed to such an extent because the dipole moment does not play such a dominating role, hence a smaller band intensity effect on decreasing the band frequency is observed. The actual band shape obtained is close to the distribution curve drawn in Figure 1.6 with the high frequency shoulder also present.

In the overtone infra-red region the band intensities are all greatly reduced because the bands are due to forbidden transitions but the relative oscillator strengths have changed. The oscillator strengths are now greatest for the weaker O—H oscillators and so the spectrum obtained in

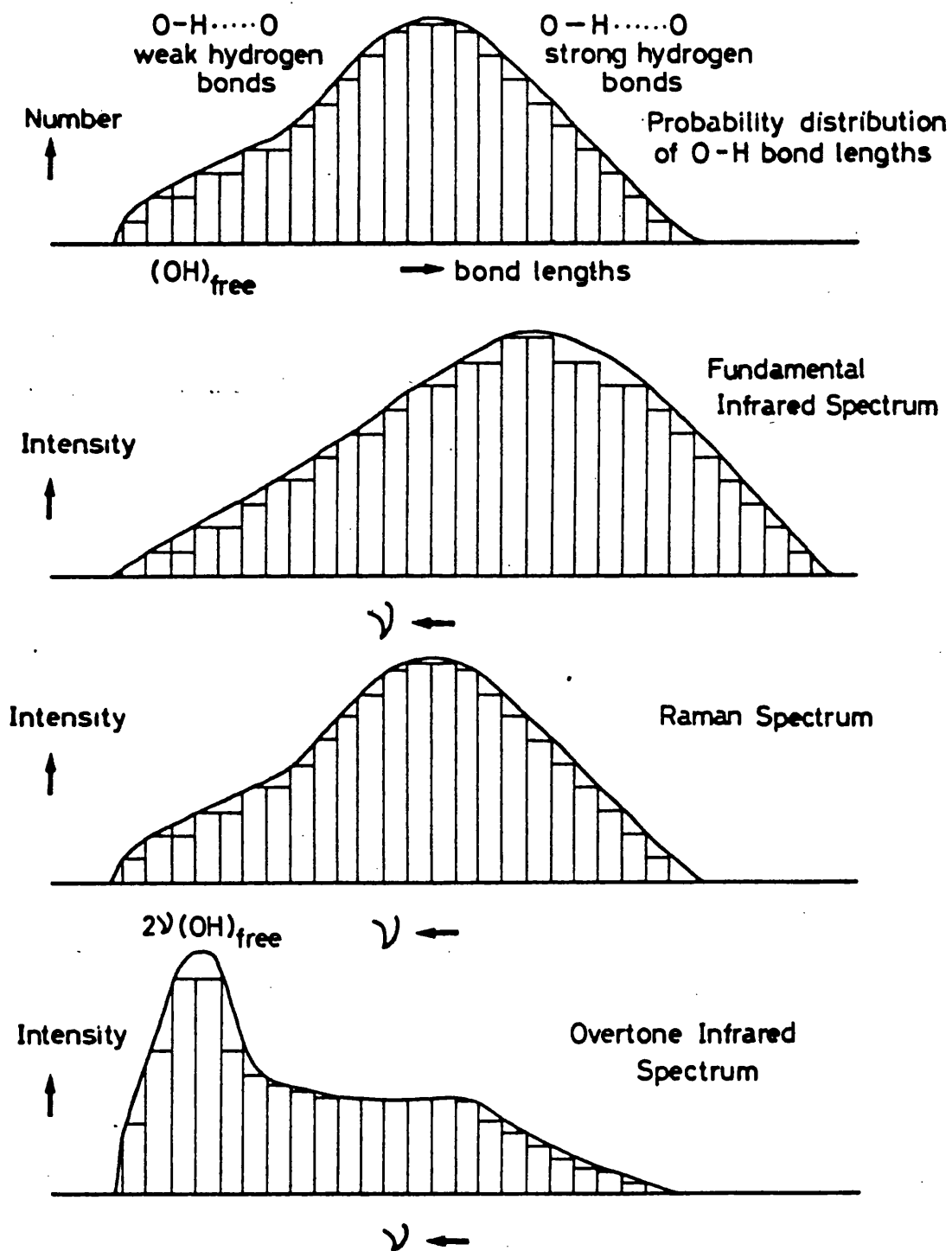


FIG. 1.6 A comparison of the fundamental and overtone infrared and Raman absorption band shapes with the probability distribution of O-H bond lengths.

this overtone region produces a band maximum in the (O—H)free region and a much weaker broad band in the (O—H)bonded region as illustrated in Figure 1.6.

Solvation Models

Solvation models not only concern themselves with interactions between the solute molecules and the solvent molecules, but also with molecules in their immediate vicinity and with all the rest of the solvent structure.

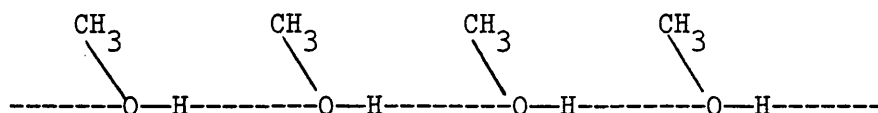
To explain or provide a solvation model, it is beneficial to understand the solvent structure based on the properties of the individual molecules and then to propose changes in solvent structure on replacing solvent molecules by ions. As both methanol and water have been used as solvents in the following chapters, a brief description of the liquid structures of both solvents are discussed.

Methanol

Methanolic solutions were investigated because monohydric alcohols can be regarded as being derived from water by replacement of one hydrogen atom by an alkyl group. This produces a much simpler solvation picture as one of the two donor sites have been replaced by a more inert alkyl group, leaving two acceptor and only one donor bonding sites for the methanol molecule as compared with the more complex two donor and two acceptor sites for the tetrahedral water molecule.

A linear, open-chained liquid structure for methanol is most likely on two accounts.

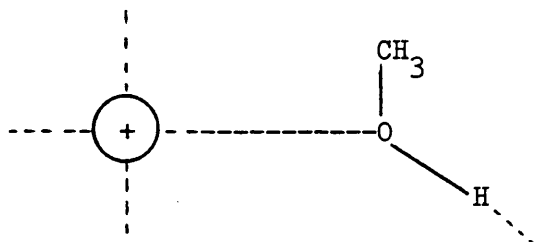
Firstly, the crystal structure of the solid methanol^{32,33}, suggests a linear arrangement of methanol molecules as illustrated below:



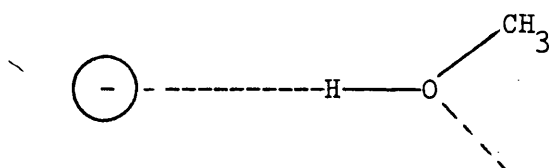
Secondly, the infra-red spectrum of liquid methanol displays no absorption band in the (O—H)free region which implies that all the hydroxyl groups must be hydrogen bonded in some way.

In cation solvation, a solvent molecule has been replaced by a cation which modifies the solvent structure in such a way to obtain a

configuration of minimum energy. This would produce a situation where the O—H bond would point outwards ensuring that the two centres of negative charge on the oxygen atom were oriented towards the cation, forming a linkage which is essentially different in character from the hydrogen bond. The cation and the oxygen and hydrogen atoms are coplanar. Cations are of widely differing sizes which lead to differing configurations that adapt themselves to the surrounding methanol structure.



Anions tend to have the proton of the methanol molecule directed towards themselves as they attract the centres of positive charge. In this position the negatively charged oxygen atom is also satisfied as it is the furthest distance away from the anion.



In other words just simply forming a hydrogen bond.

Water

To discuss the structure of liquid water, it is very useful to consider the relationship between the structure of water and ice. Long ago³⁴ suggestions had been made that as there were different phases of ice, there should be many different "kinds" of water. Bernal and Fowler¹ were able with the help of the structure of ice I to recognise the important role of hydrogen bonding in the structure and properties of water as the basic structural relationship that exists between the two phases is just primarily a loss of crystalline long range order accompanied by a great increase in molecular mobility.

All ice structures where each water molecule is hydrogen bonded to four others in nearly perfect tetrahedral co-ordination, serve as a basis for the concept of liquid water where the hydrogen bond is formed by

electrostatic attraction between the proton of one molecule and an unshared electron pair of another.

However, liquid water properties indicate a substantial amount of hydrogen bond breakage in the structure. This could be due in some cases to local imbalances in availability of the needed donor protons and acceptor electron pairs or from large distortions from the tetrahedral co-ordination which every individual water molecule likes to be in, so that some protons and acceptors are left dangling, out of range of any possible hydrogen bonding interactions.

With no universal agreement and many theories regarding the structure of water, the only way to review these models is to separate them into two classes (a) continuum models and (b) mixture models.

(a) Continuum Models

Here water is viewed as being completely hydrogen bonded or nearly so at normal temperatures but the lengths and angles of the hydrogen bonds between the molecules are distorted continuously over a relatively wide range of values. As the temperature of water is increased, so the hydrogen bond strengths become progressively weaker as a result of increased distortion and elongation of the hydrogen bonds. There could be in liquid water a wide variety of possible structures all of which would contain a distribution of hydrogen bonds. Based on their hydrogen bonding, the net result is that the different structural groups would be essentially indistinguishable at normal temperatures. The whole water sample could thus be viewed as a single entity with temperature effects related to the changes in the distribution of hydrogen bond lengths and angles.

(b) Mixture Model

In the mixture models the two or three different structural species in liquid water would absorb at slightly different frequencies. The experimental absorption maximum is a result of the overlap of two or more component bands related to the different species. In the simplest type model, the bands would be composed of two components, one at a lower frequency associated

with hydrogen bonded molecules and the other at a higher frequency associated with non hydrogen bonded species. As conditions are altered, the relative numbers of the two types of molecules and, therefore, the contribution of their component sub-bands to the total band would result in a shift in the position in the peak absorption.

Bernal and Fowler¹, initiated a change of view in water structure models by introducing an extensive hydrogen bonding model that did not account for the fluidity of water because of its rigid crystalline like structure that produced undue bending strain in the systems.

This then led onto several mixture models such as the 'network'³⁵ and 'gas hydrate'³⁶ models. The 'network' model is a two state model where one state is the framework which consists of hydrogen bonded molecules and the other of 'monomeric' interstitial molecules which allow molecular translatory motion. The 'gas hydrate' model suggests water-clathrate structures which may be empty or be occupied by non-hydrogen bonded water molecules. Hence the state of the water molecules differ just in the number of hydrogen bonds which are assumed to be short-lived and interchange roles. The non-hydrogen bonded species in these models are taken to be more mobile than the rigid hydrogen bonded species.

Developments based on the ideas of Frank and Wen^{37,38}, about the covalent, directional and co-operative nature of the hydrogen bond, produced a further mixture model. Here hydrogen bonds were only approximately linear bonds while 'bent' hydrogen bonds were terms as non-associated molecules. The non-hydrogen bonded oxygen of an associated molecule is more basic and the non-hydrogen bonded hydrogen atom more acidic than the corresponding atoms of a non-associated water molecule. Consequently, hydrogen bonding in water was postulated to be mainly a co-operative phenomenon, so that the formation of a 'cluster' of hydrogen bonded molecules and the breaking of one hydrogen bond will be followed by the 'dissolution' of a whole cluster. So water was described as a mixture of clusters and a surrounding liquid of monomer molecules.

Nemethy and Schéraga³⁹ just added that the clusters should contain a maximum of probably four co-ordinated hydrogen bonds to any molecule and be compact.

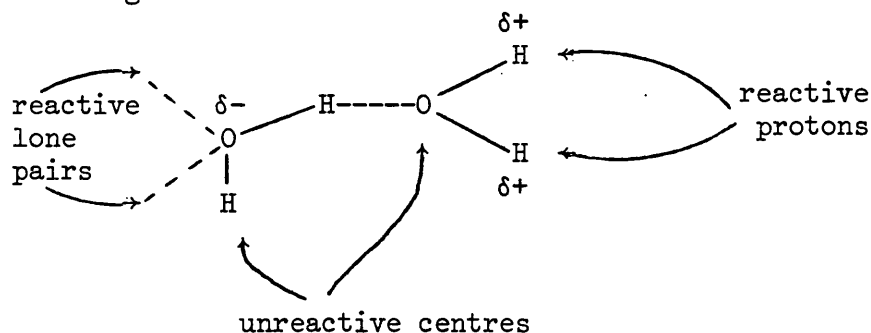
H. S. Franks and F. Franks⁴⁰ produced another two-state model where water was considered to be an equilibrium mixture of distinguishable species, which fall into categories designed as bulky and dense respectively where the bulky state consists of a structured solute in a quasiclathrate, while the dense state is the normal liquid.

Pople and Lennard-Jones^{41,42} offered a theory in which the liquid water was not described in terms of a crystalline structure nor having many hydrogen bonds broken, but just having distorted hydrogen bonds.

An alternative way⁴³ of approaching the problem of understanding the structure of liquid water is by basing the model on the structure of the well documented monomer molecule⁴⁴. Good quantum mechanical calculations on water monomer, dimer and oligomers⁴⁵⁻⁴⁸ reinforce the near tetrahedral array of two hydrogen atoms and two 'lone pairs' of electrons in a water molecule. This tetrafunctional molecule with an equal number of acidic and basic groups is an ideal unit for three dimensional growth to produce a single macromolecule, ordered in the solid state, but haphazard in the liquid state. The major difference between water and a tightly cross-linked polymer is that the bonds are weak and are therefore constantly breaking and reforming on a time scale in the region of 10^{-11} s.

The acid-base properties of water vary in donor and acceptor strengths depending on its environment. For example, if the acidic and basic reactivities of the monomer molecule are considered to be the norm, in the dimer case the hydrogen bonded proton will influence the other proton on the same molecule to be less acidic than the norm. Similarly, the effect produced when the lone pair of the oxygen atom on a molecule has bonded produces a less reactive remaining lone pair. However, such a bond involving a lone pair will make the protons of the same molecule more acidic in

comparison with the monomer protons. These effects are well demonstrated in the diagram below:



These reactive protons and lone pairs will tend to scavenge any monomer molecules thus forming water aggregates that increase in size until two reactive protons and two reactive lone pairs form bonds to produce a cyclic structure which occurs frequently and have relatively long lives.

These centres of reactivity occur at terminal water molecules which provide an ordered growth pathway until cyclisation occurs. Further developments in the way of multiple ring growth would happen on the breaking of some bond that would provide reactivity centres and only be satisfied by monomer or other chains of molecules. These rings could be of any size and be placed haphazardly which is unlike the rigid ice structure and be mismatched producing temporary free protons and lone pairs. Of course momentarily in between these two extremes of free groups and linearly hydrogen bonded groups, there will be a range of bent and stretched bonds due to the constraints of the surrounding structures.

This concept seems to fit the results that non-bonded water molecules are not observed with the vast majority of water molecules forming four tetrahedrally arranged hydrogen bonds that vary considerably in length and direction. This produces the observed broad infra-red spectrum in the fundamental region instead of the narrow bands observed for ice where the structure is very rigid.

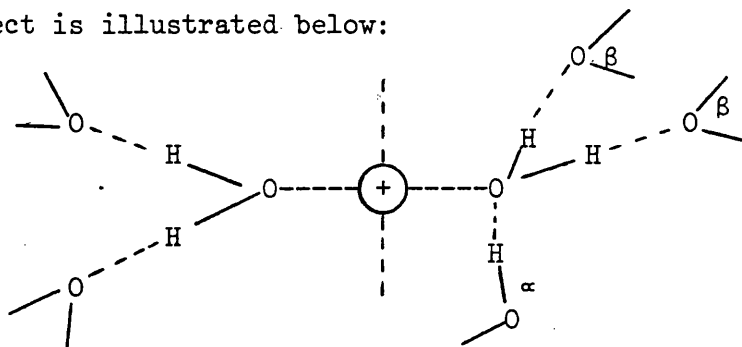
Cations and anions modify water structure in various ways depending on the bonds they form to other molecules and the way these solvent molecules are bonded to each other.

Cations are electrophiles and tend to co-ordinate to water molecules via lone pairs of electrons as is proven by X-ray studies of salt hydrates.

However, the difference between the fluid and solid states is that in the fluid state a competition for lone pairs exists which is not the case in the structured salt hydrates. Therefore, if the co-ordinating power of the cation were to fall sufficiently, these lone pairs might well be scavenged preferentially by water molecules in such a way that the ion would be enclathrated in the water structure.

Anions form hydrogen bonds to water molecules which are in competition with solvent lone pairs. With both these competitions taking place, the overall picture produced is of similar numbers of (O—H)free and (LP)free groups that probably interact with each other if at all possible. This would mean very few (O—H)free and (LP)free groups would remain. The 'structure breaking' model differs from the model above in that these 'free' groups are thought not to recombine.

Approaching ion solvation by understanding all the bonding to the solvated water molecule might be a more advantageous method of approaching the topic than using the ion as the centre point of interest as the number of bonds that a particular water molecule might form to other water molecules affects the strength of interaction between the ion and the water molecule. This effect is illustrated below:



Here strong bonding to (H₂O)_α would weaken the bond to the metal ion but strengthen the hydrogen bonds to (H₂O)_β. Strong bonding to (H₂O)_β will strengthen the bonding to the cation. In the absence of (H₂O)_α, the cation-water interaction will be strengthened and this may be the preferred

method of solvation for some cations. This would of course weaken the hydrogen bonds to $(\text{H}_2\text{O})_6$.

Many hypotheses about the structure of water have been put forward and numerous experiments been conducted to provide information on the properties of liquid water. The following quotation by Kae⁴⁹, assesses the value of the various models:

"Models are, for the most part, caricatures of reality, but if they are good, then, like good caricatures, they portray, though perhaps in distorted manner, some of the features of the real world."

The following description of the low temperature infra-red study of aqueous and methanolic solutions was an attempt to provide another piece of the jigsaw puzzle.

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CHAPTER TWO

INSTRUMENTATION AND EXPERIMENTAL DETAILS

2.1 INTRODUCTION

Vibrational spectra of aqueous and methanolic solutions were recorded using either the UNICAM SP200G for quick, routine room temperature work or the UNICAM SP100 for low temperature investigations in the fundamental infra-red region ($600 - 4000\text{cm}^{-1}$). For the near-infra red region ($6000 - 8000\text{cm}^{-1}$), the UNICAM SP700 spectrophotometer was used.

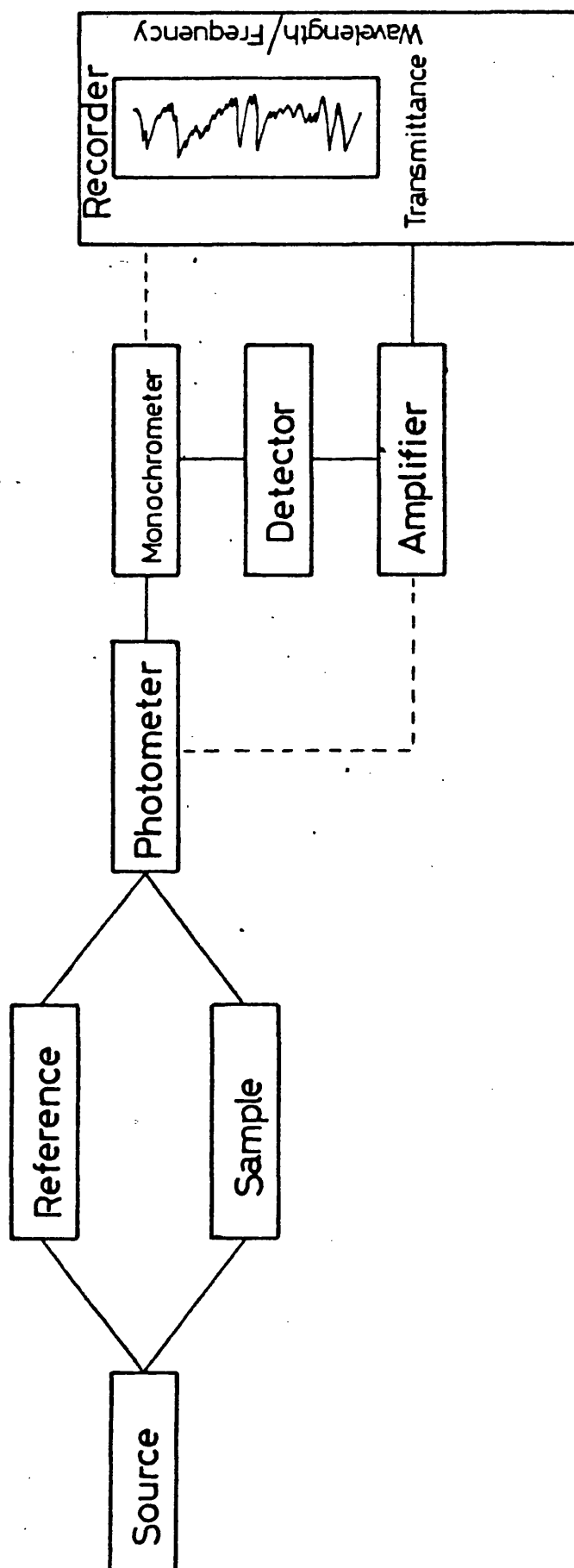
2.2 INFRA-RED INSTRUMENTS

(1) UNICAM SP100 Infra-Red Spectrophotometer

The The SP100 spectrophotometer has been designed with the aim of recording transmittance spectra over the region 375 to 8000cm^{-1} for routine investigations as well as high resolution spectra in atmospheric absorption regions due to the evacuable optical path and prism-grating double monochromator. The instrument comprises an infra-red source, the photometer unit, the monochromator, the detector, amplifier and servo-operated drum recorder linked to the double beam photometer. (Figure 2.1)

An absorption spectrophotometer needs a continuous source of radiation without sharp discontinuities created by emission lines or self-absorption bands. In the SP100, the source which radiates energy over the entire band of spectral interest, is a Nernst filament which is fitted together with its starting heaters, on a mounting which may be inserted into a water cooled housing. The Nernst filament, because of its large negative temperature coefficient of resistance, has so high a resistance at room temperature that it is not feasible to heat it by passing current through it. Hence the filament is indirectly heated to a dull red temperature by switching on the Nernst source and the Nernst heaters, and then by direct means to reach the required temperature. This latter action is physically achieved by switching on the Nernst brightness switch on the preset Control panel as are the other two switches previously mentioned. Usually the initial indirect heating procedure is not necessary, as the instrument is left on a low standby current when not in use. This current is sufficiently

FIG. 2.1 Block diagram of a double-beam spectrophotometer.



low so as not to deteriorate the life of the source.

The photometer in the SP100 is a double beam null-balancing unit which established the spectral variation of energy transmitted through the sample and relates it to a reference. It is an electro-optical servosystem which continually attenuates the energy in the reference beam, so that there is no net signal difference between the reference and sample beams.

From the diagram of the SP100 optics (Figure 2.3), it can be seen that light from the source is reflected by mirrors M1 and M2 to M3, which, along with M4*, is a rotating beam switch. The beam switch allows light to pass through the reference or sample cell well and rejoin the beams later. If the light from the source is reflected through the reference cell well and focussed at the beam attenuator starwheel by M3, it is then reflected by mirror M4 through the second sector disc of the beam switch. However, if the beam from the source passes through the first sector disc (M3), it is reflected by M3* through the beam balancing starwheel, which is connected to the 100% transmission adjustment control, and brought to focus in the sample cell compartment, and then reflected by M4* to rejoin the reference beam. Both beams are refocussed to form an image at the entrance slit to the monochromator by mirrors M5 and M6. The beam attenuator starwheel is driven by the servo-system to maintain a null energy balance between the reference and sample beams, and is connected to the recorder pen carriage, hence indicating the transmission of the sample relative to the reference at the wavelength set.

The monochromator disperses the energy from the photometer, so that only a narrow spectral region is transmitted to the detector at any one time. This part of the instrument determines both the resolution through its angular dispersion characteristics and the spectral range by virtue of its inherent physical properties.

The monochromator in the SP100 consists of a prism-grating system. Light from the photometer is reflected by mirror M7 through the magnetically operated slits onto M8 which is a parabolic mirror reflecting a parallel beam of light onto the selected grating or, when the gratings are not in use, onto

plan mirror M9. The light is dispersed by the grating and travels back along a similar path to strike mirror M10. This mirror reflects the light through the selected prism onto a Littrow mirror M11, which then reflects back the beam through the prism a second time, hence involving four instead of two reflections of the light beam. The frequency scan in the monochromator is provided by rotating the Littrow mirror M11. Once through the prism a second time, the beam of light follows a similar path and passes via the slits to M12, from where it enters the Pfund condensing system, which involves mirrors M13 and M14. Mirror M13 reflects the diverging light from the exit slit of the monochromator onto a spherical mirror M14 which condenses it onto the Golay detector with a demagnification of 5:1. The Golay detector is of the thermal, pneumatic variety and has the function to convert the infra-red radiation into an electrical signal.

The amplifier operates on the signal from the detector so as to present the sample-to-reference comparison from the photometer on the ordinate of the recorder. For the recorder to plot this information as a function of position in the spectrum, the abscissa of the recorder is coupled to the monochromator.

There were many small disadvantages in using the SP100 spectrophotometer such as the age of the instrument (installed 1961), the inability to obtain the required replacement parts when initially the machine broke down several times, after being restored to use after a couple of years disuse, the complexity and slowness of the instrument, and last but not least, the hazardous prism, grating, cam and filter interchange.

Nevertheless, there were two main advantages of using the SP100 spectrophotometer. One was the high resolution obtainable because of the prism-grating monochromator, although this advantage mattered more in the low temperature spectra when many narrow absorption bands were observed, than for the broad room temperature spectra. The other was the various modes of operation for the optical system, which were either completely evacuated, or used as a sealed system at atmospheric pressure, or finally flushed with

dry gas. The latter advantage was very useful as the two regions that were most commonly used ($3000 - 3650\text{cm}^{-1}$ and $2000 - 2800\text{cm}^{-1}$) both contained atmospheric absorption bands such as water vapour in the $3500 - 3650\text{cm}^{-1}$ region and carbon dioxide in the 2350cm^{-1} region.

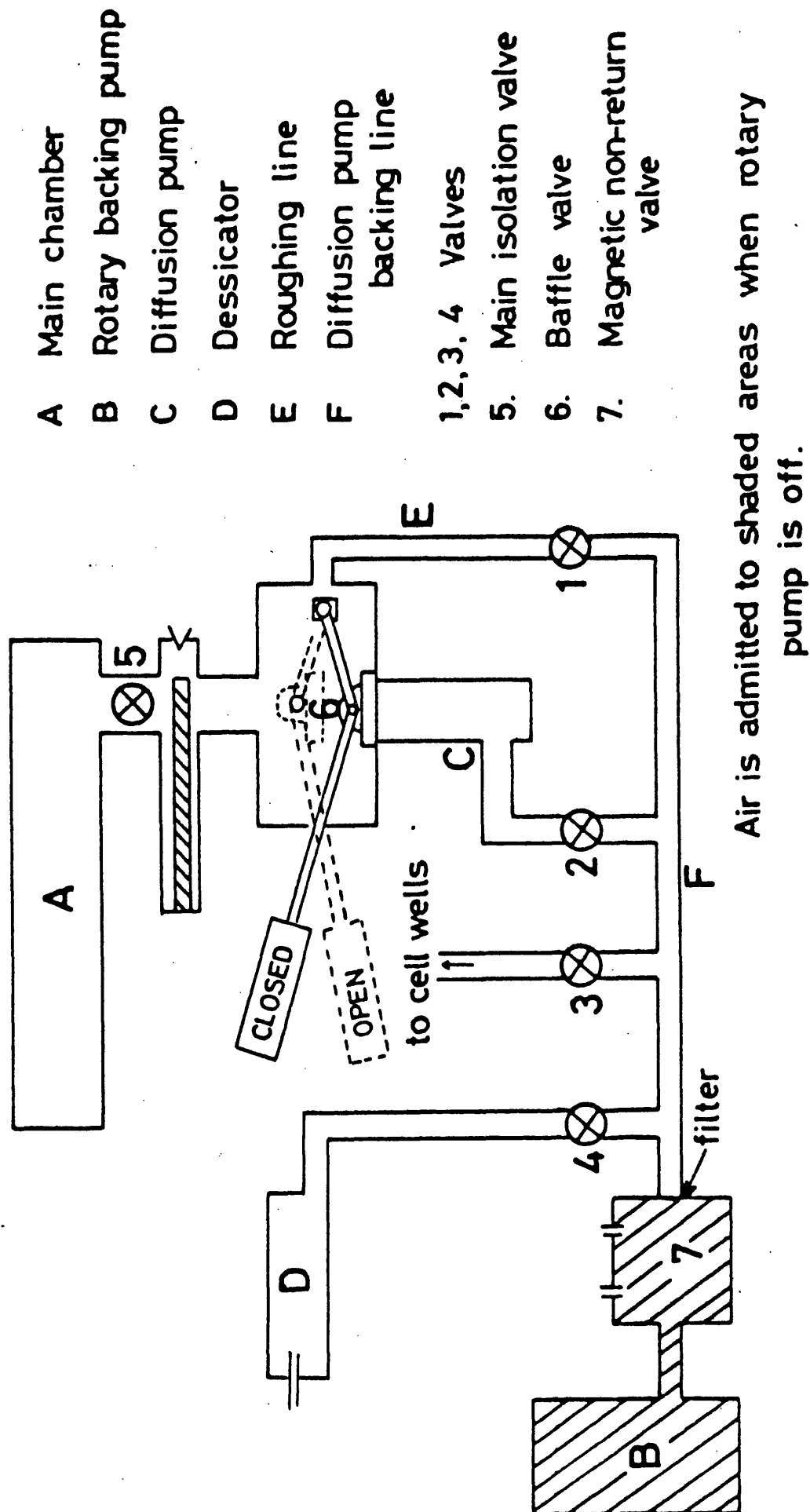
When the SP100 was used, the optical system was first evacuated and then dry nitrogen gas was readmitted into the system. This was achieved by switching on the rotary backing pump with all four valves closed as well as the baffle valve. Valve No 2 was then opened for a short while and then closed in order to evacuate the gap between the baffle valve and valve No 2. Then the main isolating valve and No 1 valve were opened for a couple of hours, so that the main chamber could be evacuated. The diffusion pump heater was then switched on for a quarter of an hour after which No 1 valve was closed and No 2 valve and baffle valve opened for an hour. This then has evacuated all the optical system with the added advantage of protecting the rocksalt prism and windows from humidity. The next step was to flush the instrument with dry nitrogen gas by closing all the valves and switching off the rotary backing pump, then fixing the bordon gauge to valve No 2, then opening valves Nos 1, 2 and 4, and finally opening the main isolation valve. The gas must be let in very slowly so as not to disturb the optics, and when the operation has been completed, all the valves are closed and the instrument was ready for use. (Figure 2.2)

(ii) UNICAM SP200G Infra-Red Spectrophotometer

The SP200G spectrophotometer records transmittance spectra over the range of 650 to 4000cm^{-1} . The simplicity and speed of its operation makes it an ideal instrument for routine work.

The optics and the fundamental set up of the SP200G spectrophotometer are very similar to the SP100 instrument as they both have a Nernst source, a double beam optical null photometer, a Golay detector with a Pfund condensing system and amplifier. The instruments differ in monochromator because the SP200G has a filter-grating monochromator and in recorder where the SP200G

FIG. 2.2 Block diagram of the SP100 Vacuum System.



The diagram illustrates the optical layout of a double monochromator spectrophotometer. The light path begins at the **Source** (bottom right), which directs light through mirror **M2** and prism **M1** into **Star Wheel No. 1**. This wheel contains a **Transmittance** aperture and a **Reference Cell Well**. Light from the transmittance aperture passes through mirror **M4** and prism **M4*** into **Star Wheel No. 2**, which also features a **Sample Cell Well**. Light from the sample cell well passes through mirror **M6** and prism **M6*** into the **Photometer Bridge**, which includes mirror **M5**. Light from the reference cell well passes through mirror **M3** and prism **M3*** into the **Sample Cell Well**. The light path then enters the **Monochromator Bridge**, which contains mirrors **M8**, **M9**, **M12**, and **M13**, and gratings **G1** and **G2**. The light is then directed through mirrors **M10** and **M11** into a series of prisms **P1**, **P2**, **P3**, and **P4**. The light path continues through mirrors **M7** and **M14** into the **Golay Detector**. The diagram also shows **Magnetic Slits** and a **Beam Switch** mechanism. The entire system is designed to measure the transmittance of a sample by comparing it to a reference.

has a flat-bed type recorder. After passing through an appropriate interference filter in order to remove all unwanted orders, light from the photometer is focussed on the entrance slit of the monochromator, and then reflected by a plane mirror onto an off-axis paraboloid mirror, which produces a parallel beam to fall onto and be dispersed by a grating. This beam then returns along a similar path to the exit slit and into the Pfund condenser as in the SP100.

(iii) UNICAM SP700 Spectrophotometer

The Unicam SP700 Spectrophotometer automatically recorded the transmittance of the sample cell relative to the reference cell and this was plotted on a linear wavenumber scale. As the region of interest was the near infrared region, radiation from the tungsten filament lamp was used and directed onto the entrance slit of the monochromator. It was dispersed by a prism, or in the 3600cm^{-1} region by a diffraction grating, so that a narrow band of wavenumbers could be selected from the dispersed beam by the exit slit, with filters removing unwanted orders of light as the grating was used. The beam then fell on the beam splitter mirror and after reflection by two identical concave mirrors was brought to focus inside the cell compartments. However a chopping disc was situated in front of the compartments to allow light to pass through the sample and reference compartments alternately. The two beams are rejoined by two mirrors and directed onto the lead sulphide detector in the near infrared region. The output of the detector was amplified, rectified, filtered and passed to the recorder.

In the infrared region 1cm or 1mm silica cells, similar to those employed in U.V. spectrophotometry, were used. These were maintained at the desired temperature by either water circulated through the cell mounting block from a thermostatically controlled bath or electrically heated, aluminium alloy attachment block. A thermistor was in contact with the block heaters which were in good contact with the optical cells and formed one arm of a D.C. Wheatstone bridge. The bridge was balanced using an external variable

resistance. The off-balance current drove an on-off relay controlling the heaters.

2.3 TEMPERATURE CONTROL SYSTEM

The variable temperature control system that was used for all the low temperature data basically consisted of a vacuum jacket, a cell holder and an automatic temperature control unit. The vacuum jacket and cell holder with refrigerant chamber are drawn in Figures 2.4 and 2.5.

The vital parts of the vacuum jacket were the vacuum tight jacket, two sodium chloride windows and a mounting plate. A special aluminium mounting plate was made to fit the cell wells of the SP100 Spectrophotometer and this was secured parallel to the jacket by a retaining ring. The jacket contained an adaptor which has a locating pin on its rim and could be rotated. The top plate of the cell holder, because of this locating pin, was secured in position, and could be aligned square to the optical beam by rotating the adaptor to a position of maximum transmission. To provide a good seal between these two units, a rubber 'O' ring was placed on top of the adaptor, which contained a shallow groove for this purpose. However great care was needed to remove all foreign matter from the three touching surfaces to provide as good a vacuum seal as possible. A light smear of silicone grease on each surface in this case and many others, where a good vacuum seal was needed, proved to be a very useful procedure. The sodium chloride windows were kept in position by milled retaining rings, which when sufficiently tightened, enabled the arrangement of teflon gasket, window and silicone elastomer seal to form a vacuum tight seal. The windows were heated by the temperature control unit, which kept them at a constant temperature of 313°K , to avoid frosting when low temperature measurements were made.

The sample cell holder was connected directly to the base of the stainless steel refrigerant chamber with all the electrical leads and the vacuum pump connection on the top plate of this chamber. The cell heater

FIG. 2.4

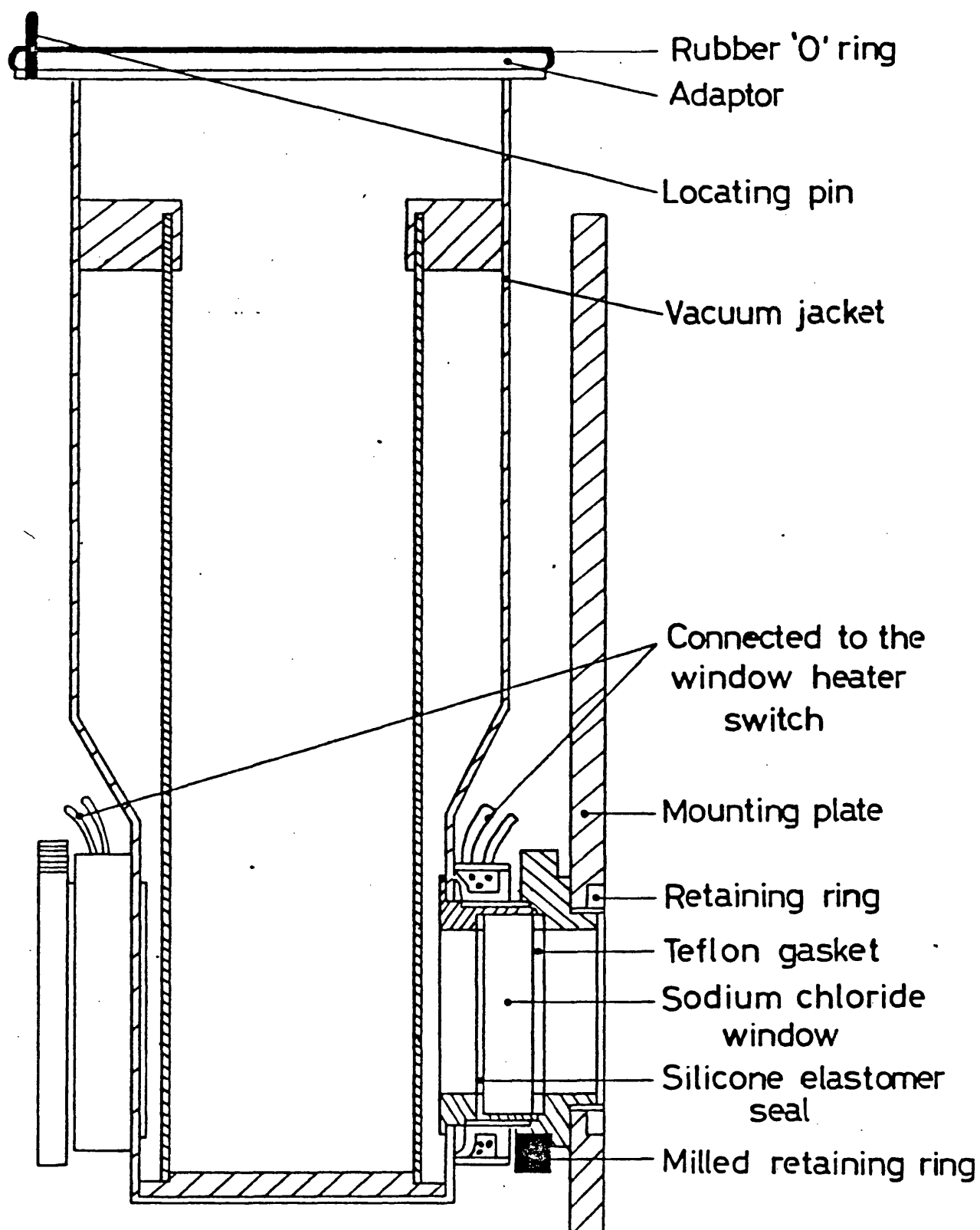
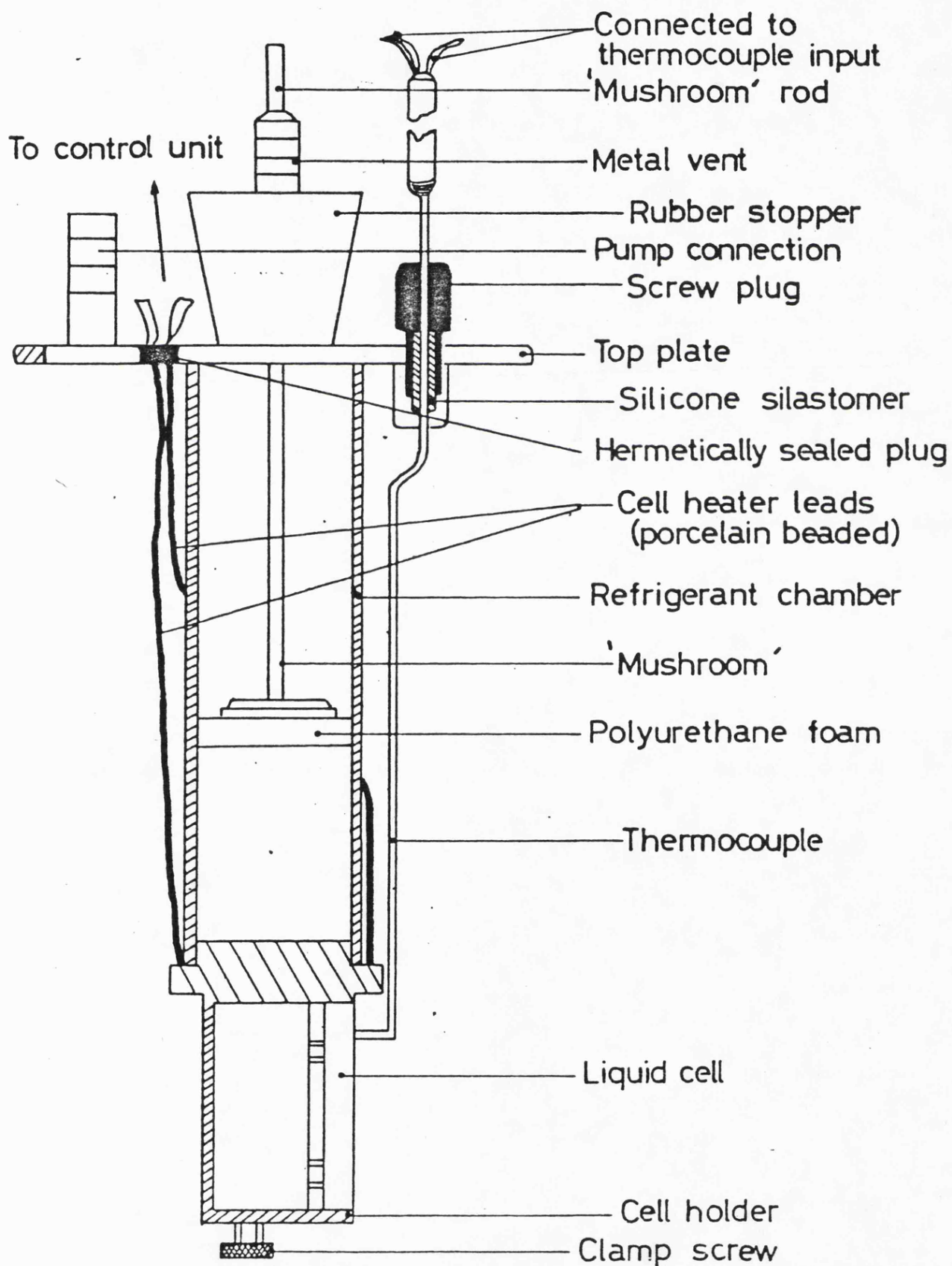
Variable Temperature Control Unit - Vacuum Jacket

FIG.2.5

Variable Temperature Control Unit - Sample Cell Holder and Refrigerant Chamber



leads passed through a five way hermetically sealed plug on the top plate and then were connected to the temperature controller unit. The other three ports were not used and were plugged with silicone silastomer sealed solid stainless steel rods and a screw plug. However great care was taken not to overtighten any of these screw plugs as they damaged the seals and formed a vacuum leak which proved very time consuming to locate.

The thermocouple was a copper-constantan junction, the junction end of which was fitted into the small drilled hole in the liquid cell (Figure 2.6) and the other end accommodated into the temperature control unit via the thermocouple input connection. The thermocouple, like the unused parts, passed through a silicone silastomer seal and a screw plug, which ensured a vacuum seal for the thermocouple porthole in the top plate of the cell holder.

The automatic temperature control unit accommodated the thermocouple and supplied the power to the cell holder and vacuum jacket window heaters. The unit recorded the actual temperature of the sample cell by means of a moving red pointer above the temperature scale and a temperature setter dial below the scale which was connected to the cell heater. So if a higher temperature was required than the sample temperature, the bottom pointer was set at the required temperature and the cell heater would raise the sample temperature to the required one. Other controlling factors are discussed in the next paragraph. However to first complete the set up, the description of the evacuating system is all that is required. A mercury pressure gauge, tap and a glass bulb, to accommodate any oil suck back from the pump and hence preventing the oil from reaching the sample area, were connected by pressure rubber tubing in between the vacuum port on the top plate of the cell holder and the vacuum pump. The unit was evacuated to a pressure of 0.1mm of mercury.

Two component parts that helped a great deal to control the temperature were a rubber stopper, which was vented with a metal tube,

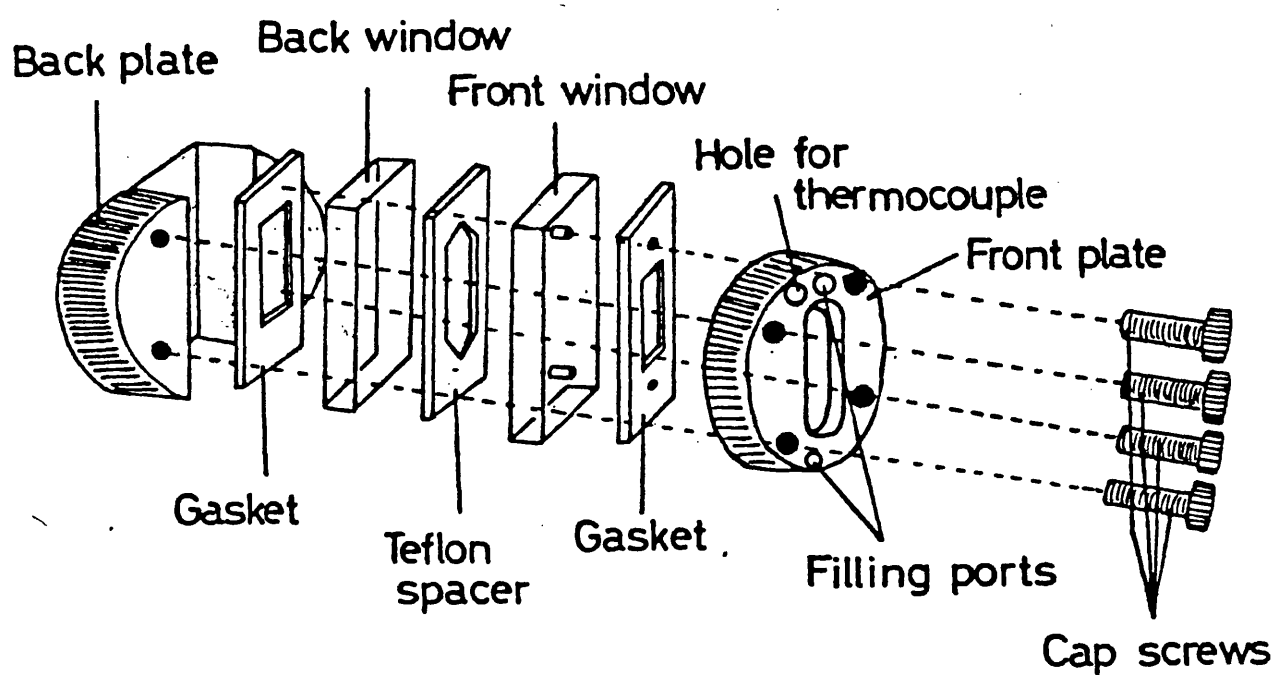


FIG. 2.6

Demountable liquid cell and its component parts.

connected to a long piece of rubber tubing to remove the boiling off refrigerant vapour from the instrument and a 'Piston like' object called a 'mushroom'. This vented stopper prevented air of room temperature from heating the lower temperature refrigerant in the chamber. The two sized 'mushrooms' had bases of polyurethane foam, which acted as a partial thermal barrier between the refrigerant and the sample cell holder as well as reducing the consumption of refrigerant. As most of the low temperature spectra were recorded at either 173°K or 148°K, the smaller 'mushroom' and liquid nitrogen as the refrigerant were used. The larger 'mushroom' was used for intermediate temperatures between room temperature and 173°K.

The actual procedure of recording a series of low temperature spectra on the SP100 spectrophotometer can now be described. The sample cell, which will be discussed in the next section, was fitted into the cell holder and secured in position by tightening the clamp screw below the holder. The cell holder was then inserted into the jacket and a room temperature spectrum recorded. The complete unit was then evacuated to a pressure of 0.1mm of mercury by switching on the vacuum pump, closing the tap and checking the pressure using the gauge. The small 'mushroom' was inserted into the refrigerant chamber, the liquid nitrogen poured in and the rubber stopper replaced. When the temperature of the cell holder had fallen below the required temperature, the temperature controller dial was set at the required temperature and the cell heater switched on. Meanwhile the chamber must be kept filled with liquid nitrogen. When the actual temperature of the cell holder had come to rest at the required temperature about a quarter of an hour was allowed for the sample temperature to equilibrate and then a spectrum could be recorded. Further increases in temperature could be obtained by just resetting the dial and waiting for thermal equilibrium. When the required temperature was in the larger 'mushroom' range (303°K to 173°K), the 'mushrooms' were exchanged. The temperature was kept constant to $\pm 1^\circ\text{K}$ with the error coming in the reading of the temperature on the temperature controller as the markers were divided by 5°K .

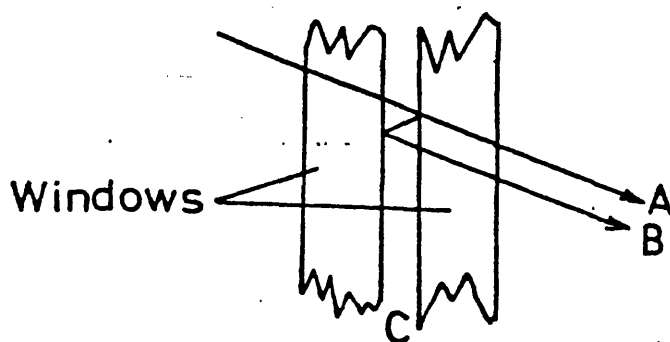
2.4 THE LIQUID CELL

Vacuum tight heated liquid cells supplied by Beckman R.I.I.C. (Type FH-01) were used for all the data obtained from the SP200G and SP100 spectrophotometers. The cells were of the demountable sealed variety as can be seen from Figure 2.6. These cells essentially comprised of two rectangular windows screwed together with teflon spacers of various sizes sandwiched between them. One window was drilled to provide an inlet and outlet to the enclosed space, so that the cell could be filled after being completely assembled. The separation of the windows or the sample thickness was therefore known or could be determined by making use of the interference fringes produced by internal reflection between the window surfaces as represented in Figure 2.7. The path length (L) was determined by counting the number of complete fringes (n) between two frequencies (ν_1 and ν_2) at which a transmittance maximum or minimum was observed and using the below equation:

$$L = \frac{n}{2(\nu_2 - \nu_1)} \quad \text{cm}$$

The teflon spacers formed a good seal when the windows were screwed down firmly, although great care was taken to avoid the cracking of the windows by gently tightening diagonally opposite screws and then repeating this procedure to clamp them more securely.

After the cell had been assembled, the inlet screw was removed and the outlet screw loosened. A hypodermic needle was fitted to a syringe and sufficient liquid to fill the cell taken up. The needle was then removed and a Luer - lock holder was fitted into the vacant inlet plug. The syringe was then placed into this lock and, with the cell slightly inclined from an horizontal position to avoid any air locks, the sample was injected through the lower plug until the aperture was filled, and the liquid was starting to appear through the partially unscrewed plug. After the removal of the Luer - lock holder and syringe, the plugs were screwed down tightly.



B – internally reflected
beam

C – distance between
windows

FIG. 2.7 Interference fringes

Although the liquid sample could be recovered by the reverse procedure to filling the cell, the next vital step was to clean the cell. This could be achieved using two different methods, one was to keep the cell assembled and flushing the sample area with a low boiling point solvent and then using air to remove the solvent, the other which was most commonly used was to take the whole cell apart and wipe all the surfaces and teflon spacer with medical wipes.

As most of the samples were aqueous or methanolic solutions, it was not possible to utilise the cheap sodium chloride and so calcium fluoride windows were used as they were useful for high pressure work and had excellent transmission over the required range. Although these windows could be fractured by thermal shock, it was found that by minimising the rate of temperature change, they did not frequently fracture, and so were used for the low temperature aqueous solution work. For the methanolic solutions I_{rtran_2} windows were used as these were extremely durable and withstood thermal shock. However great care was taken to clamp down these windows as the fractures were more likely connected with this rather than cooling down to low temperatures for the I_{rtran_2} windows.

The pathlength of the cell used depended on the intensity of the band observed but was most commonly either 0.012mm or 0.025mm. Sometimes just a capillary film of liquid with no teflon spacer between the windows was employed just to obtain qualitative but not quantitative results. On the other hand when very dilute solutions of methanol in an organic solvent were studied, a pathlength of 1mm was not uncommon.

2.5 EXPERIMENTAL DETAILS

(i) Materials used

Deuterium oxide (99.8%) was obtained from Nuclear Magnetic Resonance Limited and used as received.

Methanol- d_1 was bought from Koch-Light Limited and used directly.

Deionised water was doubly distilled from alkaline potassium permanganate in a still under an atmosphere of nitrogen.

Analytical grade methanol obtained from B.D.H. was refluxed with magnesium turnings and resublimed iodine and then distilled over to give dry methanol.

All other solvents were of an analytical grade and were dried over molecular sieve and then checked by recording their infrared spectra for the absence of water absorption bands in the appropriate regions.

All salts were dried in a vacuum oven for at least 24 hours before use at temperatures that depended on the nature of the salt. A mull of the ground salt in nujol was then investigated in the appropriate regions of the infrared spectrum to see if the region was clear of water absorption bands and other impurities.

Glassware, syringes and needles were cleaned using a dilute solution of potassium permanganate in concentrated sulphuric acid and then rinsed many times with water and then dry acetone.

(ii) Preparation of solutions

Most of the electrolyte solutions were prepared by volume and by weight so that both molarities and molalities could be calculated. However with two solvent systems mole fractions were used.

In the room temperature work, the electrolyte solutions were made up by volume. The procedure was to make up concentrated solutions of electrolyte in D_2O and H_2O in D_2O . Two equal aliquots of the electrolyte solution were pipetted into two graduated flasks, followed by an aliquot of H_2O in D_2O into the sample flask. Both graduated flasks were then filled to the mark with D_2O . In this case equal amounts of electrolyte were in each flask. However this method is limited by the solubility of the electrolyte. When more concentrated solutions were required equal amounts of electrolyte were weighed out in each flask with one made up to the mark with a stock solution of 2% H_2O in D_2O and the reference sample with D_2O .

Most of the solutions were prepared in a dry box although the liquid cells were filled outside the dry box near the infrared instruments.

(iii) Band parameters

A typical room temperature infrared absorption band of uncoupled HOD was drawn in Figure 2.8. This band was a broad, smooth and Gaussian in shape as it fitted the Gaussian curve on the Dupont curve analyser.

The most important parameter was the actual wavenumber of the maximum absorption (ν_{\max}). This was obtained by a line joining the mid points of the absorption band at various percentage transmissions. The point at which this line disects the absorption band was taken as the wavenumber at which maximum absorption occurred. The band height was taken as the difference between the transmittance at ν_{\max} and the baseline at the same wavenumber. The baseline was taken as the line joining the two shoulders of the band. However if the band had only one shoulder then the baseline was drawn parallel to the 100% transmission through the shoulder. If the band height which was measured in transmittance units from the spectra obtained needed to be converted to absorbance units, then the calculation used was:-

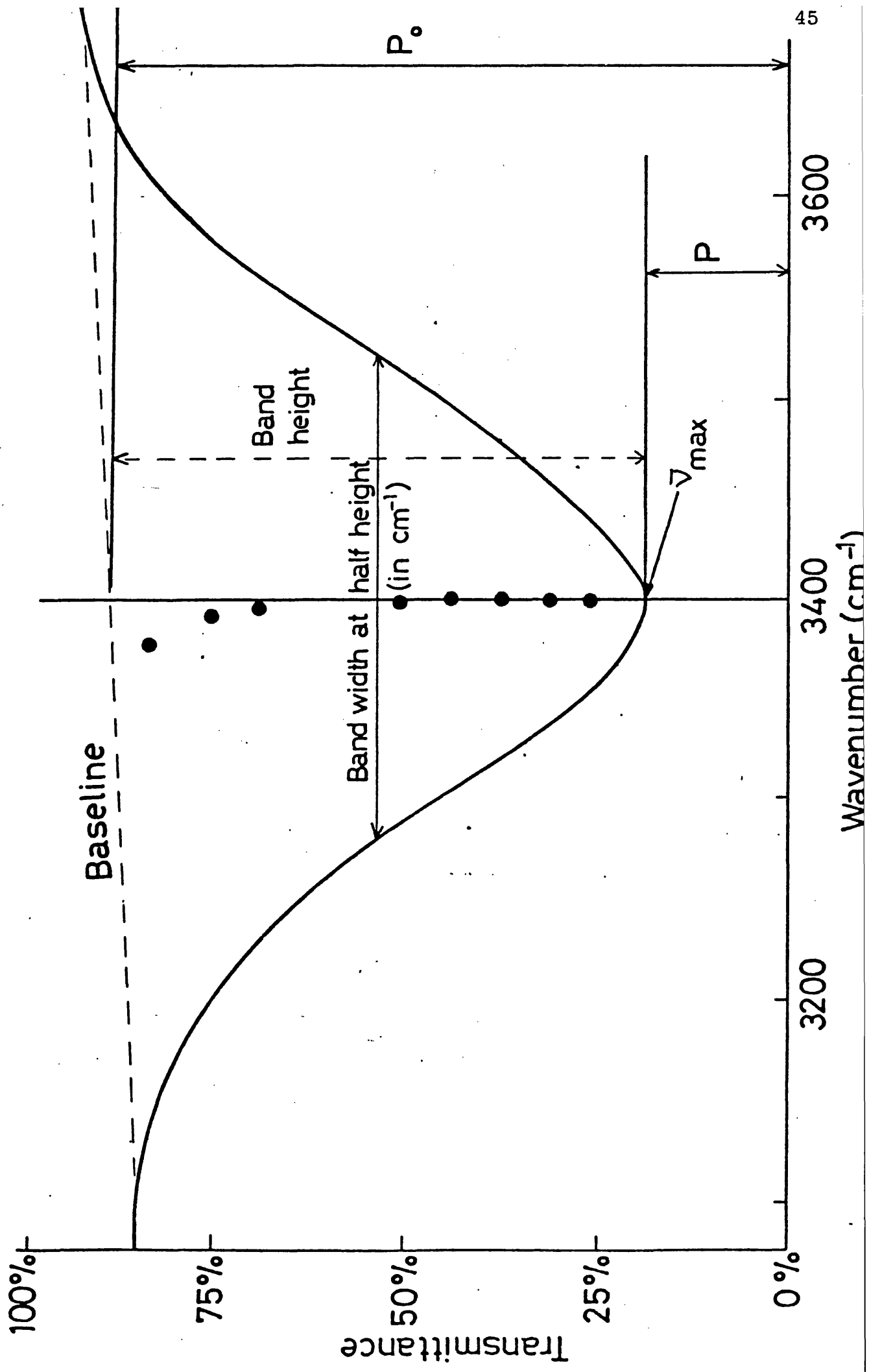
$$A = \log (P_0/P)$$

where P_0 is the transmittance of the background and

P is the transmittance of the peak maximum as indicated in Figure 2.8.

The halfwidth ($\Delta\nu_{\frac{1}{2}}$) which was measured in cm^{-1} was obtained by finding the width of the absorption band at the midpoint of the band height.

FIG. 2.8 Typical infrared absorption band and parameters used.



CHAPTER THREE

VIBRATIONAL SPECTRA OF METHANOLIC ELECTROLYTE SOLUTIONS

3.1 INTRODUCTION

The aim of the work described in this chapter was to collect all the ambient temperature infra-red spectral data on methanolic solutions together so that a detailed analysis and discussion of the results could be attempted for the fundamental O-H stretching region of the spectrum. After arriving at several points of interest, low temperature data of the same solutions were obtained and correlated with the ambient temperature data, to produce an insight into ionic solvation.

The effect of solutes on solvents, or putting this another way, how the solvent was modified by the various different solutes, has been of great interest and has led to many theoretical, thermodynamic and spectroscopic investigations. However no systematic investigation in the fundamental infra-red region of methanolic electrolyte solutions has seemed to have been undertaken. The great similarity in structure and functional groups between methanol and water molecules and the advantage of a greater liquid range of temperatures and the greater tendency to glassify, made the study of methanolic solutions advantageous as an initial project to provide a sound base from which the more complicated problem of aqueous solutions could be tackled.

At room temperature methanol and other lower alcohols produced very broad absorption bands in the fundamental O-H stretching region of their infra-red spectra. Although the methanolic solutions do not have the problem of the overtone bending mode absorbing at similar frequencies to the O-H stretching mode as is the case for water, coupling of neighbouring molecules does occur and produces a broadening of the absorption band in this region. However isotopically dilute solutions of CH_3OH in CH_3OD were used to narrow the band, but this still remained broad and hence not very informative. These isotopically dilute solutions produce O-H oscillators in a mostly O-D environment and because these different oscillators absorb at very different frequencies almost pure O-H stretching modes

or uncoupled oscillators are produced. However when oscillations of weakly connected vibrators have nearly the same characteristic frequency and are coupled, there are frequency changes in the system which produce shifts and hence give a broader absorption band than the uncoupled system.

The addition of different electrolytes to isotopically dilute solutions of CH_3OH in CH_3OD might reveal changes in the solvent hydrogen bonding in the proximity of the dissolved solute molecules and so provide some useful information about the solvent structure. However these changes were only observable when large salt concentrations were used so that the interactions around the neighbouring ionic particles became significant.

The vibrational spectra of the solvent in the O-H stretching region can be modified in a number of ways on the addition of solutes, for example, in the integrated intensity, in the maximum frequency and in the bandwidth. The integrated absorption intensity reflects the strength of the intermolecular interaction and is the most difficult of the three parameters to measure accurately. This property is consistently being demonstrated by the difference in room and low temperature results where the stronger interactions occur at low temperatures producing greater integrated intensity at low temperatures.

The bandwidths of absorption bands are functions of the type of environment in which the solvent molecules find themselves. This can be illustrated by the large difference in bandwidth between the structurally disordered liquid state (where $4\nu_{\frac{1}{2}} = 225\text{cm}^{-1}$) and the highly structured crystal hydrates ($\Delta\nu_{\frac{1}{2}}$ a few wavenumbers). Bandwidths can be interpreted to be due to the intensity distribution of bond lengths of the intermolecular vibrations. So that in gas phase spectra no significant perturbations of the isolated molecule by neighbouring molecules are present while in a crystal lattice only a small number of neighbouring configurations occur. Liquids, however, have intermolecular distances and orientations that are distributed statistically with weak, strong and bent bonds.

The frequency shift can be described as the measure of strength of the ion-methanol interaction and was the parameter most utilised in the discussion.

When electrolytes were added to the isotopically dilute solutions of CH_3OH in CH_3OD , these three parameters are only slightly altered, as has been demonstrated for many aqueous solution surveys,^{1,2,3}. However, no such corresponding data is available for methanolic electrolyte solutions. These minor changes in band parameters were analysed and some insight into the structure of these solutions was obtained although the lack of any precise bands with the exception of some polyatomic salts has meant that many chemical models have been developed. These can be split up into two general categories as the continuum and mixture models.

The latter model describes the structure of methanol as composed of relatively small numbers of distinguishable species with an increase of temperature resulting in an increase in the number of hydrogen bonds broken. Walrafen⁴, in particular, has used this model to explain the high frequency band obtained in the fundamental O-H stretching region of the Raman spectra of aqueous perchlorate solutions. The explanation used is that the anion acts as a "structure breaker" which produces this high frequency band that is therefore classified as due to free O-H oscillators, (O-H) free.

However, a different concept favoured by several workers^{5,6,7,8,9} attributed this high frequency band to anions weakly bonded to solvent molecules and is described as the continuum model. This concept uses the basic assumption that methanol is completely hydrogen bonded at room temperature. However, the lengths and angles of the hydrogen bonds between the molecules are distributed continuously over a relatively wide range of values. As the temperature is increased, the hydrogen bond strengths on average become progressively weaker as a result of increased distortion and elongation. Thus, for methanol, there could be a wide variety of possible structures containing a wide distribution of hydrogen

bonds, but being indistinguishable in the recorded spectra. This produces the broadest interpretation of the continuum model possible as the whole methanol network is viewed as a single entity with temperature effects related to the changes in the distribution of hydrogen bond lengths and angles.

The low temperature study of methanolic systems was undertaken after the decrease in bandwidth was obtained for just the pure solvent on cooling to liquid nitrogen temperatures. The thought behind the cooling of methanolic electrolyte solutions was to narrow the broad room temperature bands to obtain some resolvable features that could be studied in relation to concentration changes thus producing some band assignments.

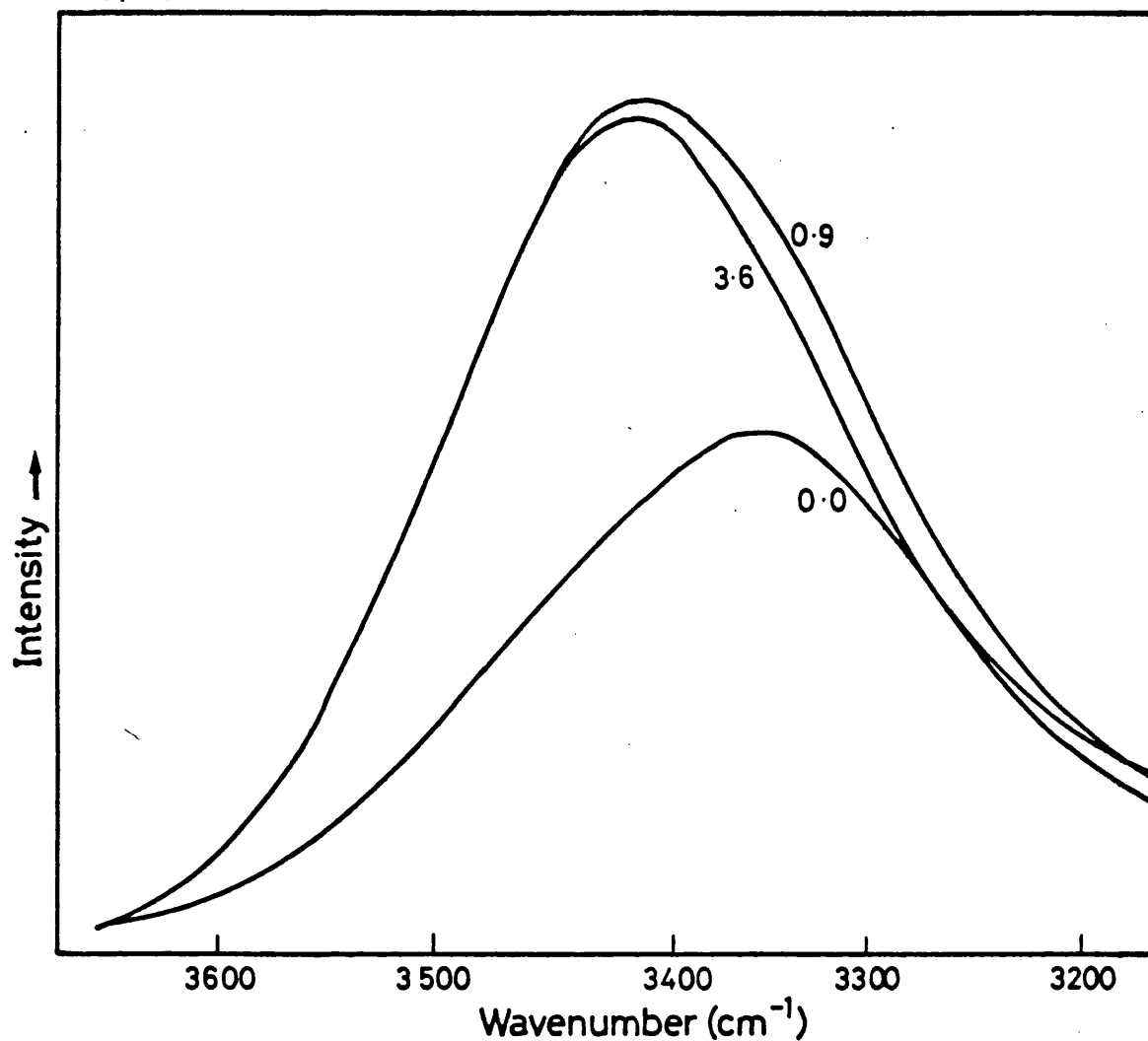
However, a most important factor to consider in this low temperature work was to ensure the absence of significant phase separation. Solutions that did phase separate often produced a break in smooth shifts and developments in bands and usually occurred in conjunction with a large scattering background. Other tests for phase effects had been developed in conjunction with radiation processes¹⁰ which corresponded well with the infra-red method. Many of the solutions were recorded several times to ensure the data was reproducible with all the phase separated data being ignored.

3.2 ROOM TEMPERATURE DATA AND DISCUSSION

The room temperature data on methanolic electrolyte solutions has been best summarised and represented on a diagram that plots the shift of the absorption band maximum against the molality of the salt. The shift is measured as the difference in wavenumber ($\Delta\nu$) between the bulk solvent band and the methanolic electrolyte solution band. A high frequency shift is denoted as a positive $\Delta\nu$ and a low frequency shift is denoted as a negative $\Delta\nu$.

For an example of a band maximum shift, sodium iodide in isotopically dilute methanol at several molalities is shown in Figure 3-1.

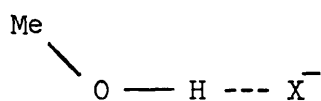
FIG.3.1



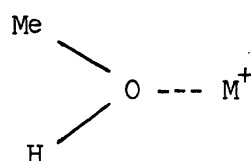
Infrared absorption spectra of CH_3OH in CH_3OD in the O-H stretching region containing sodium iodide at several molalities (0, 0.9, and 3.6 mol Kg⁻¹) at 303K.

The principle of this systematic analysis is described in more detail in Chapter 4, but in essence consists of a shift v molality plot which reaches a saturation point when no further frequency shift is obtained with an increase in the molality of the salt. At this point anion solvation in the case of the tetraalkylammonium salts or solvent shared ion pairs when electrolyte solutions were studied have become the dominant bands.

At lower molalities solvate bands such as



(i)

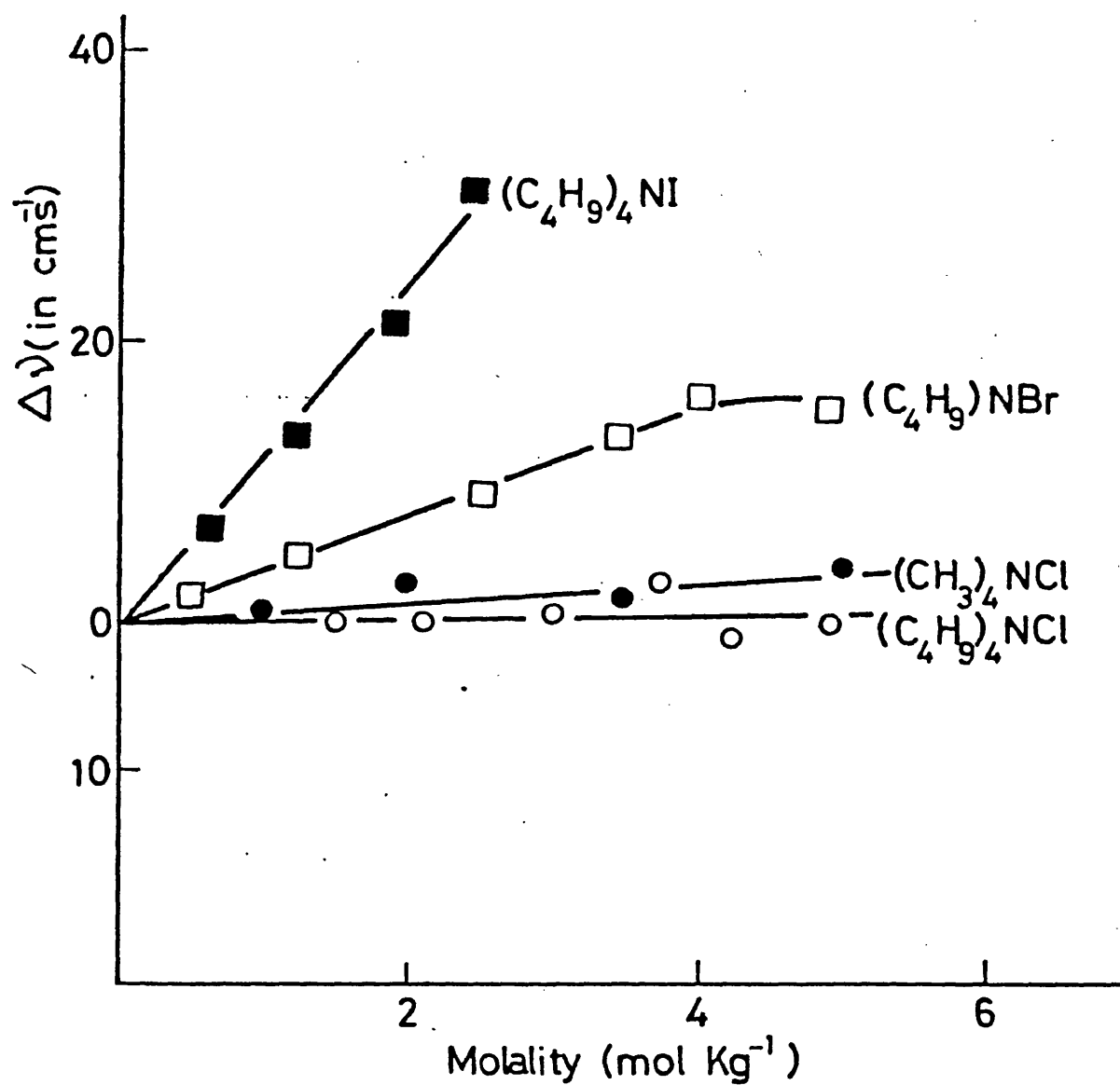


(ii)

These two species (i) and (ii) are in direct competition with the bulk solvent band at 3350cm^{-1} . This saturation point has been used to give some frequency values for certain bands that are dominant and extended to provide an overall picture of the solvate bands mentioned above.

Alkylammonium salts produce only an anion effect as the cation does not modify the solvent structure when the solvent is methanol. There is evidence that these salts do modify the structure of aqueous solutions¹¹, but no such effects have been observed for methanolic solutions. So by using the data obtained, an attempt to pinpoint the chloride and bromide solvate bands has been made. As shown in Figure 3-2, the graph demonstrates that the methanol-chloride anion interaction for both the tetramethyl- and tetrabutyl- ammonium salts shows only a small high frequency shift from the bulk solvent band at 3350cm^{-1} . The bulk solvent value is in good agreement with literature values¹². The lack of apparent shift suggests that the average strength of the $\text{O} \text{ --- } \text{H} \text{ --- } \text{Cl}$ bond is of the same strength as the $\text{O} \text{ --- } \text{H} \text{ --- } \text{O}$ bond found in the bulk solvent. We suggest that the anion solvate band in this case absorbs at 3352cm^{-1} .

FIG.3.2



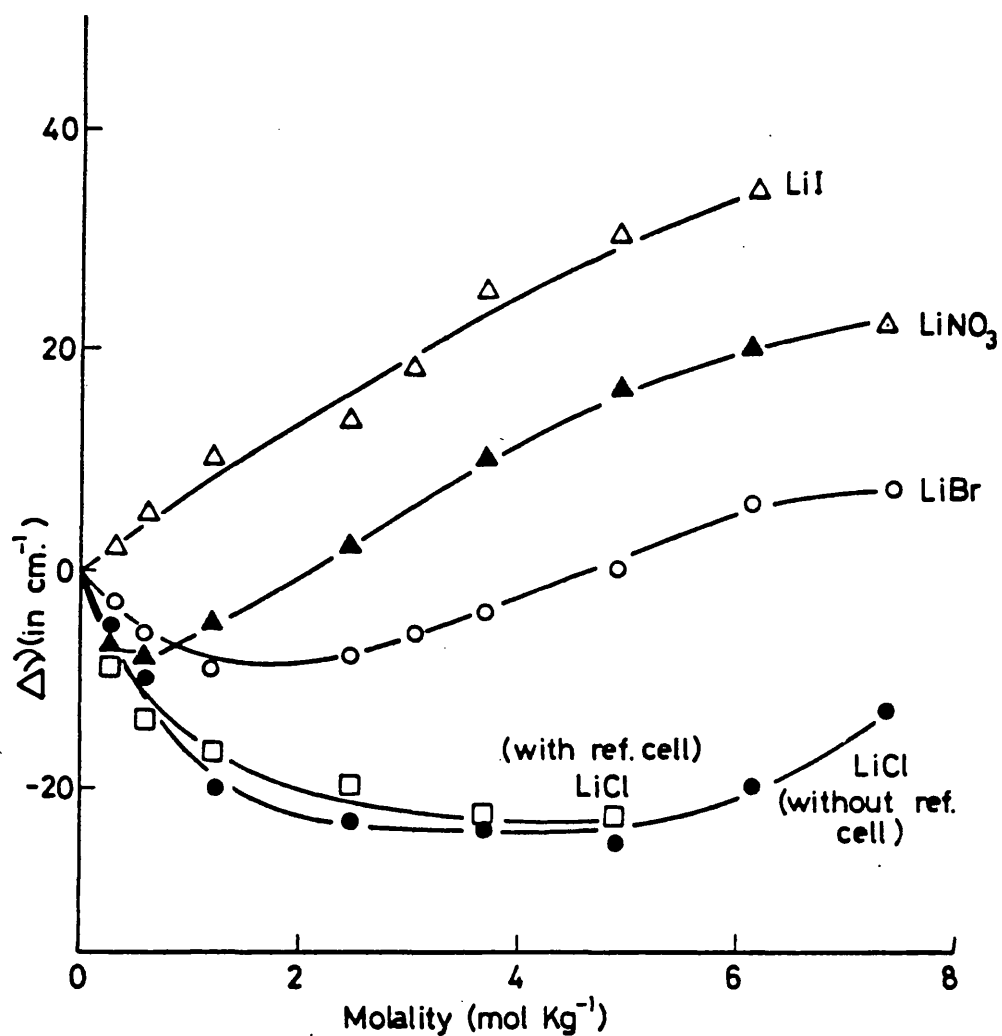
Dependence of frequency maximum on concentration (mol Kg) of added salt in $\text{CH}_3\text{OH}/\text{CH}_3\text{OD}$ solutions at 303K .(Infrared Spectra).

The results from the *t*-butylammonium bromide solutions show a gradual high frequency shift which levels out at a wavelength of 3365cm^{-1} . This implies that the $\text{O} \text{ --- } \text{H} \text{ --- } \text{Br}$ bond is on average weaker than the chloride-methanol bond and so this solvate band was pinpointed to absorb at 3365cm^{-1} and hence produce a $\Delta\nu = +15\text{cm}^{-1}$. Unfortunately the iodide salt in this series does not dissolve to such a great extent as the other two halide salts, but even the dilute solutions unmistakably prove that the iodide solvate band would absorb at higher frequency than both the chloride and bromide solvate bands. With no saturation point where no further shift is observed, no specific value for the iodide solvate can be estimated.

Having established the relative hydrogen bond strengths for the anion-methanol interaction, attention was turned to some methanolic alkali-metal salt solutions. The initial problem of solubility played a large part in the salts extensively studied, because salts of potassium and, to a certain degree, sodium, were unsuitable. This meant that the bulk of this chapter concentrates on methanolic lithium salt solutions which are illustrated in Figure 3-3.

With the chloride solvate being denoted to absorb in the same frequency region as the bulk solvent from the tetraalkylammonium salt results, we believe that any frequency shift observed from lithium chloride solutions must be due to the cation solvate band. As can be seen from the diagram 3-3, lithium chloride solutions produce a gradual low frequency shift which appears to level out or reach a steady frequency value in the 3327cm^{-1} . This would infer that when the lithium ion co-ordinates to the oxygen atom of the methanol molecule, it strengthens the $\text{O} \text{ --- } \text{H}$ bond as compared with the bulk solvent bonds. One important point that has just been demonstrated for these chloride solutions, but has not been investigated for other salts is the use of a reference sample. This consists of lithium chloride at the same molality as the actual sample in a solution of pure CH_3OD , so that any absorption in the $\text{O} \text{ --- } \text{H}$ stretching region is due to the

FIG. 3.3



Dependence of frequency maximum on concentration (mol Kg^{-1}) of added salt in $\text{CH}_3\text{OH}/\text{CH}_3\text{OD}$ solutions at 303K. (Infrared Spectra).

uncoupled CH_3OH molecule and not to any other irregularities in the solutions. Indeed, judging from the results obtained, no great difference in the plot as shown in Figure 3-3 can be observed.

The molality v frequency shift plot for methanolic lithium bromide solutions produced a small low frequency shift at low molalities (less than 1 molal) and then a gradual much larger high frequency shift to the point where the graph levelled off in the 3360cm^{-1} region. To explain this result, the fact that the band maxima are weighted means of several bands have to be accepted. These bands with differing positions and intensities influence these gradual shifts, but with unknown oscillator strengths, just tentative assignments have been attempted. At low molalities, bulk solvent, anion-methanol and cation-methanol interactions should be in competition and hence influence the band maxima, but at higher molalities a new band associated with the solvent shared ion pair will complicate the picture further until at the highest molalities this band should dominate the envelope completely. We have used these values at the point where no further frequency shifts are noted as representing the latter solvate band. The explanation for the lithium bromide solution curve could be that the initial low frequency shift is due to the domination of the lithium solvate band in the overall envelope of the band. At higher molalities the bromide solvate band begins to influence the band maxima by producing this gradual high frequency shift until the saturation point where just the solvent shared ion pair dominates.

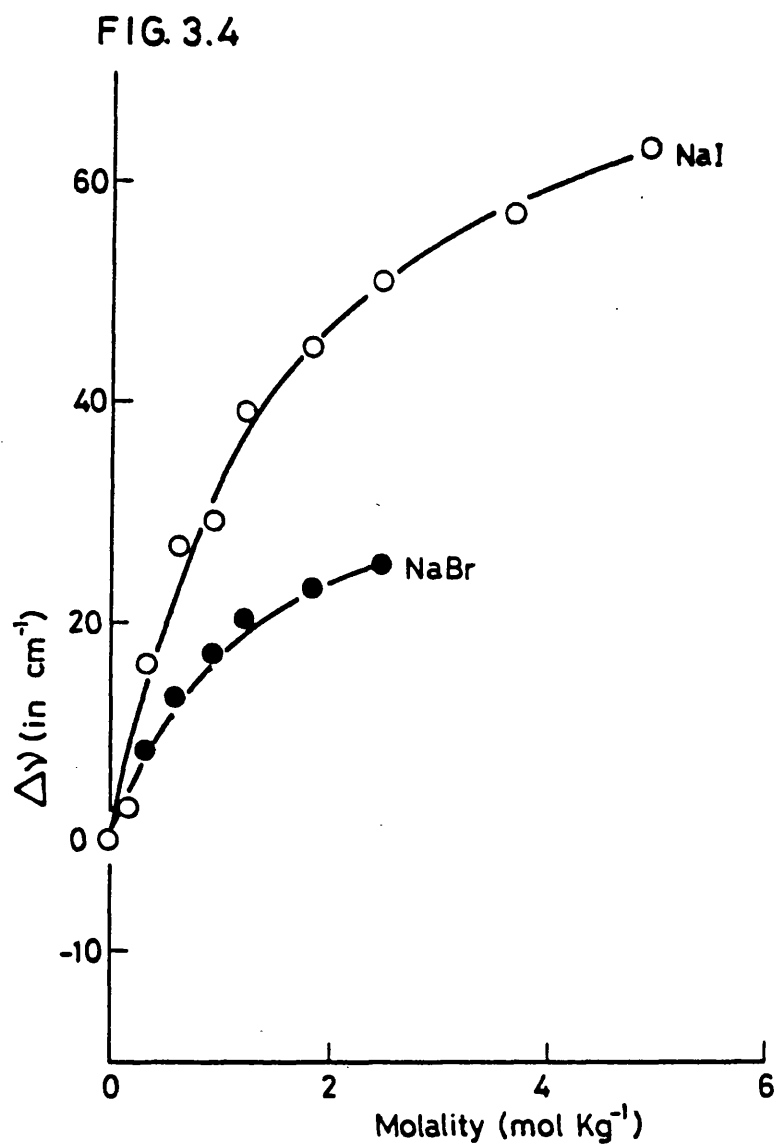
A similar explanation is applicable for lithium nitrate solutions. The only difference is the high frequency shift begins at lower molalities for the nitrate solutions compared with the bromide solutions. This can be explained by the nitrate anion band absorbing at a higher frequency than the bromide band hence affecting the overall envelope at lower molalities. Lithium iodide solutions produce a graph that gives a gradual high frequency shift that levels out in the 3390cm^{-1} region. These results just reinforce the anion bond strength order with the chloride-methanol interaction being

the strongest and the iodide-methanol interaction the weakest.

The attention was then turned to the two soluble sodium salts. The bromide was only soluble to 2.5 molal while the iodide dissolved to 5 molal. Sodium bromide solutions produced a gradual high frequency shift which began to level out at the saturation molality in the $3375\text{--}3380\text{cm}^{-1}$ region. The sodium iodide results produced a similar picture but a much greater high frequency shift than for the bromide solutions which is illustrated in Figure 3-4.

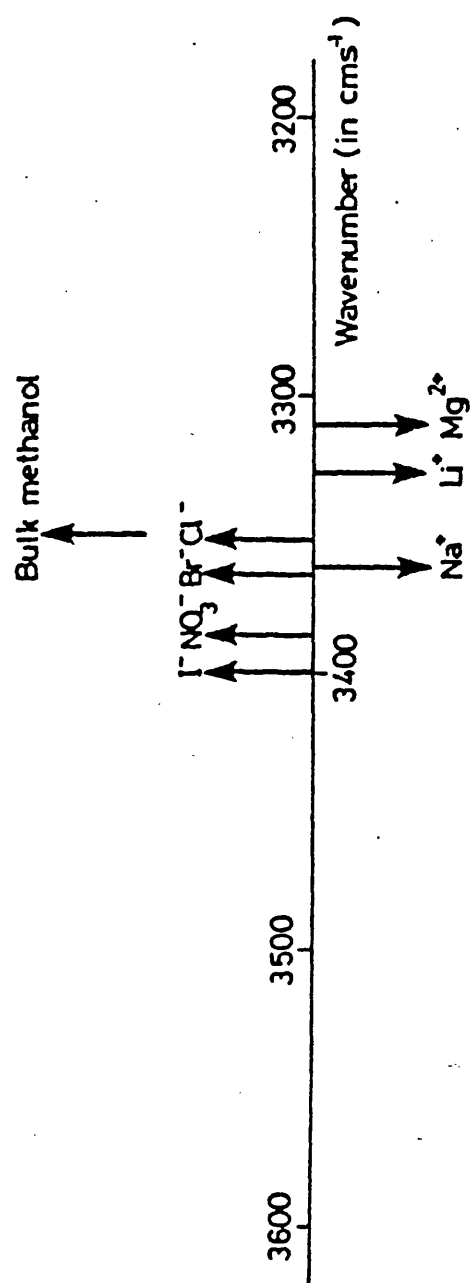
From the data reported so far, the chloride and bromide solvate bands have been pinpointed at 3352 and 3365cm^{-1} respectively. From the lithium chloride solution data, the lithium solvate band absorbs at 3327cm^{-1} . This produces the initial low frequency shift observed for the lithium salts and the low frequency shift at high molalities when compared with tetraalkylammonium anion shifts of the solvent shared ion pair band. The latter shift is in the order of 15cm^{-1} , so accepting that a similar situation occurs for the lithium nitrate and iodide solutions, the argument can be reversed by implying that the anion solvate bands for these two salts must absorb at a 15cm^{-1} higher frequency value than the documented solvent shared ion pair bands which are seen in Figure 3-3. This would pinpoint the nitrate solvate band to absorb at 3387cm^{-1} and the iodide solvate band to absorb at 3400cm^{-1} . These band positions are summarised in diagram 3-5.

When attention was turned to the two sodium salts, the bromide solution data produced a figure as shown in Figure 3-4 that has a gradual high frequency shift which starts to tail off at saturation molality in the 3375 to 3380cm^{-1} region. With the bromide solvate band placed to absorb at 3365cm^{-1} , this further high frequency shift must be due to the sodium effect on the anion-methanol interaction. The shift is a positive one of 12cm^{-1} which would pinpoint the sodium solvate band to absorb at 3362cm^{-1} . The sodium iodide solution results give a greater high frequency shift than the bromide solutions with the levelling of the frequency values



Dependence of frequency maximum on concentration (mol Kg^{-1}) of added salt in $\text{CH}_3\text{OH}/\text{CH}_3\text{OD}$ solutions at 303K. (Infrared Spectra).

FIG. 3.5



Location of major component bands observed in the infrared spectra of electrolytes
in $\text{CH}_3\text{OH}/\text{CH}_3\text{OO}$ at 303K.

occurring at 3413cm^{-1} . This would imply that the sodium effect on the iodide-methanol interaction is again to weaken the bond which produces the high frequency shift of 13cm^{-1} which is in good agreement with the only other sodium salt solution studied.

These cation solvate band positions are double checked by comparing the same anion salts at the same molality and obtaining consistent results that should be similar to the difference in wave-number of the lithium and sodium solvate bands 3327 and 3362cm^{-1} which is 35cm^{-1} . A few examples of testing this check are displayed below:-

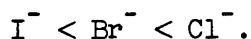
Salt	Molality (in mol Kg ⁻¹)	Band maximum (in cm ⁻¹)	Difference in wave number (in cm ⁻¹)
LiBr	2.5	3343	33
NaBr	2.5	3376	
LiI	2.5	3366	35
NaI	2.5	3401	
LiI	5.0	3380	33
NaI	5.0	3413	

The only other salts investigated were magnesium chloride and bromide solutions. Both molality v frequency shift plots produced a similar pattern with a gradual low frequency shift levelling out for the bromide salt at 3325cm^{-1} and the chloride solution in the 3310cm^{-1} region. These results suggest that the cation shift is in the region of 40cm^{-1} which implies that the magnesium solvate band can be placed to absorb at 3310cm^{-1} . The interesting point that the difference between the bromide and chloride is 15cm^{-1} again is in good agreement with previous data and these bands are shown in Figure 3-5.

The other parameter investigated at room temperature was the band-width. As the molality of the salts was increased, there seemed to be a general trend of a decrease in bandwidth which suggests that a slightly more ordered solvent structure or statistically more anion-methanol bonds are

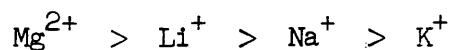
absorbing at the band maximum frequency. A concept of the role of the anion on the solvent is discussed after the low temperature data in full detail.

Summarising the achievements of the room temperature study, we have the halide ion order of increasing hydrogen bond strengths in solution of



This order is certainly not novel but the actual frequency at which these solvate bands absorb has not been recorded before. Many other salt solutions were studied, but because solubilities were low no really extensive study was possible. The cation order for the induced bond strengths have been mentioned before in both nuclear magnetic resonance^{13,14} and infra-red spectroscopy¹⁵.

In the latter reference a correlation of the two spectroscopic methods was reported which used the data from references 13 and 14 and the infra-red study of the O - H stretching mode of the HOD molecules solvating the perchlorate ions. This band is clearly resolved and so the remaining bulk band was analysed to give values for the O — H absorption for the cation solvation shell. Generally, the frequency shift of this lower frequency band levelled off in the 2-4 molal region. These limiting shifts were tabulated and displayed in a plot of the shift against the charge to radius ratio¹⁵ with the result that the below order induced bond strengths was again reinforced.



3.3 LOW TEMPERATURE RESULTS AND DISCUSSION

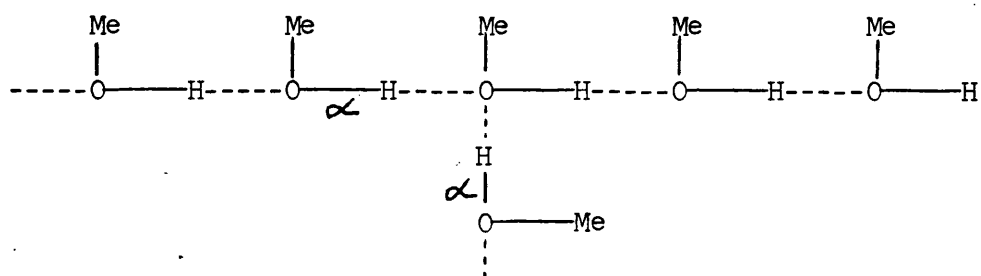
The low temperature work was approached in a similar manner to the room temperature procedure. Initially solutions of salts that contained tetraalkylammonium salts and tetraphenyl-boron salts were investigated because of the belief that O — H groups will prefer to remain bonded to solvent molecules rather than form very weak and ill-defined hydrogen bonds to the phenyl groups of the BPh_4^- ions or to the butyl groups of the $(\text{C}_4\text{H}_9)_4\text{N}^+$

ions which would then provide us with just cation or anion effects individually.

(1) Sodium tetraphenyl boron

A typical spectrum of the room temperature sodium tetraphenylboron solution is shown in Figure 3-6. This shows a broad band centred in the 3360cm^{-1} region and a high frequency band at 3540cm^{-1} . On cooling, this high frequency band shifts to lower frequencies linearly as illustrated in Figure 3-7, and so the position of this band can be obtained at any temperature. The broad low frequency band, on cooling, does not narrow as the pure solvent band, but remains broad and moves slightly to a lower frequency.

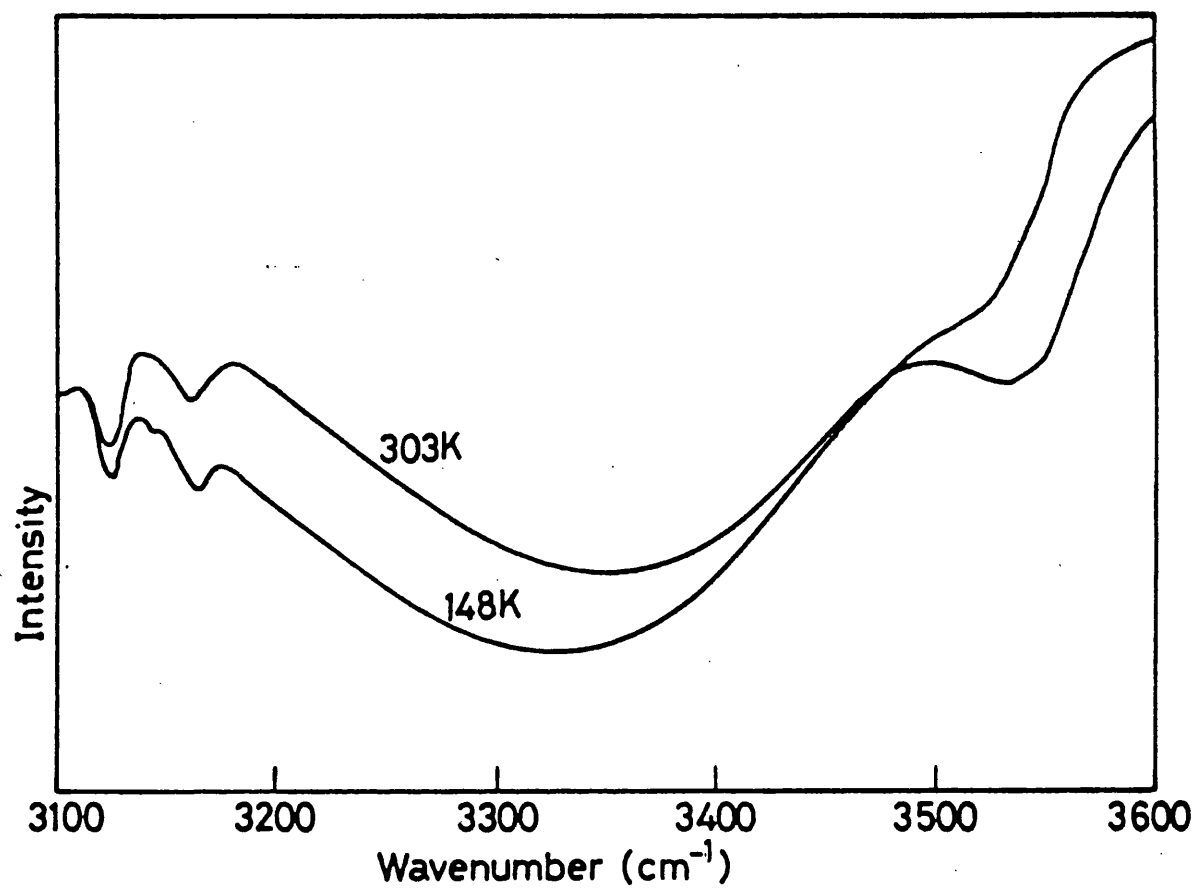
If the non-bonding phenyl groups of the BPh_4^- ion is the correct concept, then it seems logical to claim that since the sodium ion will weakly solvate to the second set of lone pairs of the methanol molecules, there should be an excess of $(\text{O} - \text{H})$ free groups. However, since no such groups are detected in cold bulk methanol, whatever the additive, and the band at high frequencies is temperature dependent and not in the $(\text{O} - \text{H})$ free region, we postulate that the methanol accommodates such groups by forming weak hydrogen-bonds to the second set of lone pairs of electrons that are not usually involved in bonding to produce a cross-linking structure as shown below:



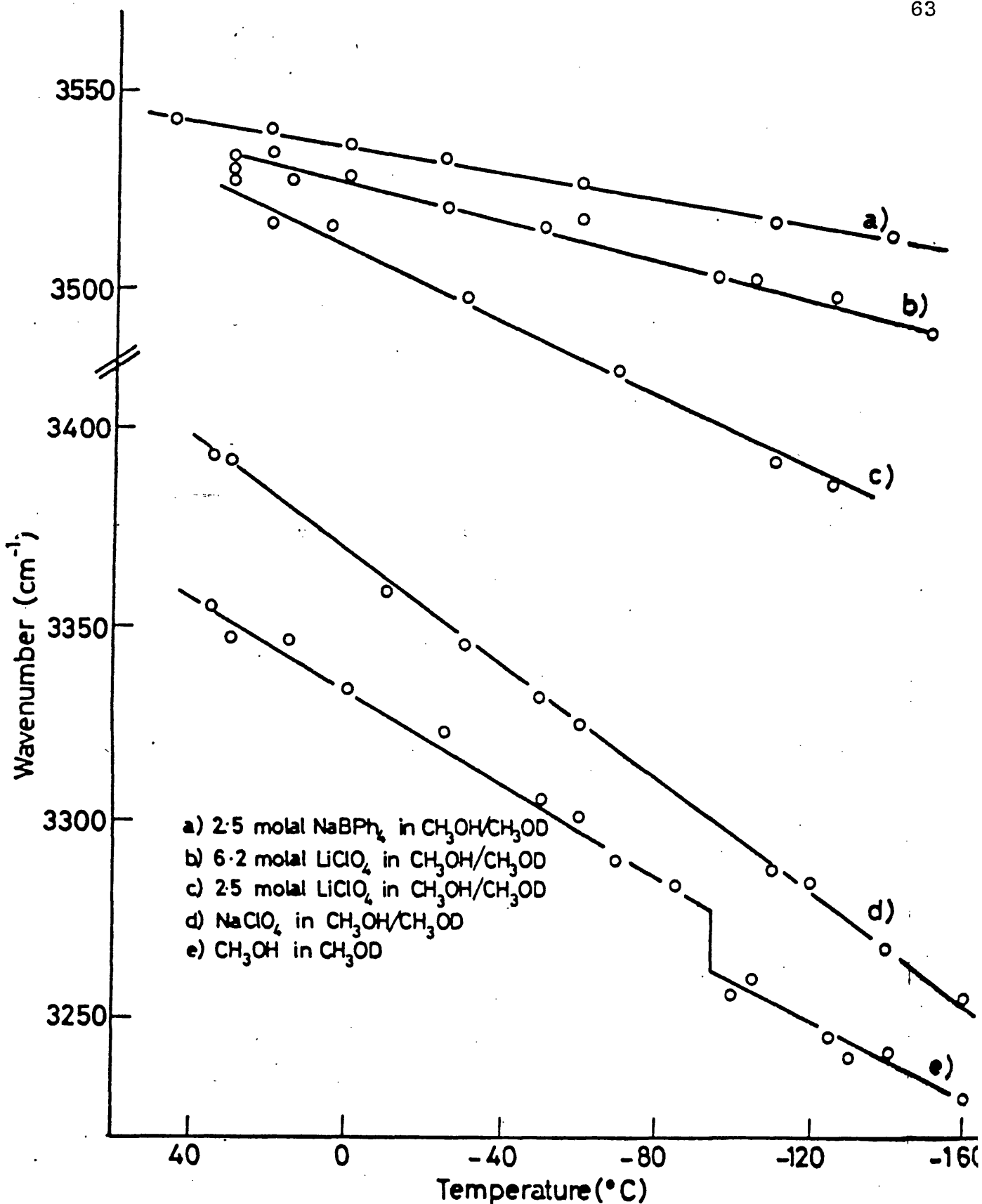
So the high frequency band at 3520cm^{-1} at low temperatures and 3540cm^{-1} at higher temperatures is due to the $\text{O} - \text{H}$ groups marked α in the above structure and for convenience they are described as $(\text{O} - \text{H})'$ free groups.

The broad band centred at 3330cm^{-1} conceals the bulk solvent band and the cation solvate band as the former should absorb in the 3240cm^{-1} region.

FIG.3.6

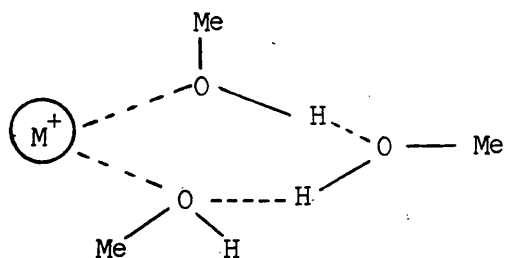


Infrared absorption spectrum of CH_3OH in CH_3OD in the O-H stretching region containing sodium tetraphenylboron (25 molal) at two temperatures 303K and 148K.



Dependence of the frequency maximum upon temperature of the Infrared Spectra.

The belief that the absorption in the 3370cm^{-1} region could be related in some way to the dilution effect of the large BPh_4^- anions could be very real because such an effect in dilute methanol-inert solvent systems has been observed. These methanol-methylene chloride solutions gave a prominent band halfway between the (O — H) free and normal bulk methanol bands. Obviously the structures in those solutions and the ones obtained from sodium tetraphenyl-boron solutions cannot be identical because of the sodium ions. Hence to satisfy both systems a cyclic structure that incorporates sodium ions could be the correct assignment and the possible configuration is represented below:-

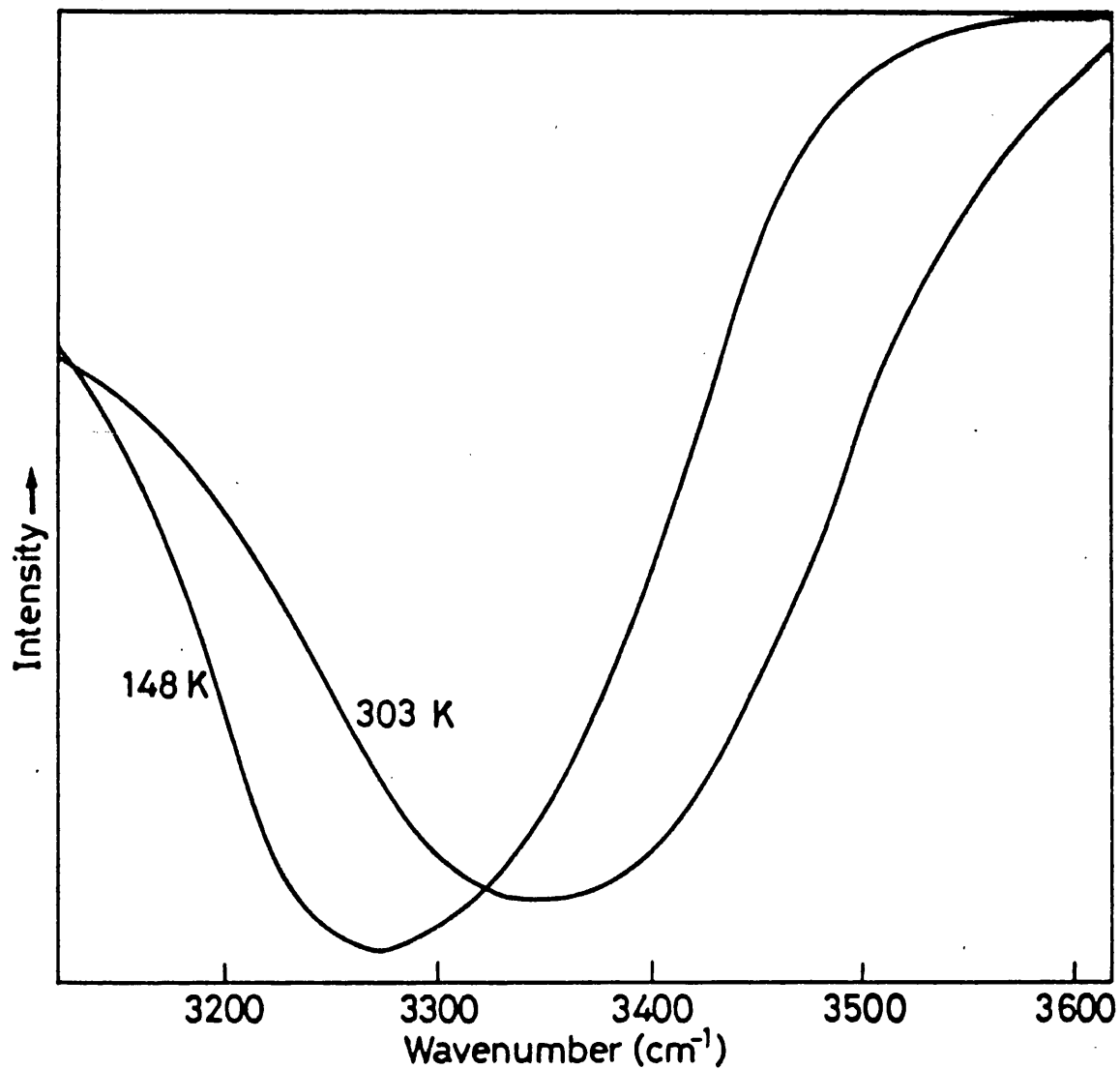


This structure also gives an O — H oscillator of the (O — H)' free type which produce the high frequency band at 3540cm^{-1} . These structures contain bent hydrogen bonds which produce weak O — H oscillators and so absorb at a higher frequency than the bulk solvent band but because they are hydrogen bonded, however weakly, they absorb at a lower frequency than the (O — H) free band at 3640cm^{-1} .

(ii) Tetraalkylammonium halides

On cooling dilute solutions of tetrabutylammonium chloride and bromide in isotopically dilute methanol to 148K, the infra-red spectrum in the O — H fundamental stretching region gave a broad band in the 3250 region and a shoulder at 3350cm^{-1} for the chloride and 3370cm^{-1} for the bromide solutions. The former is illustrated in Figure 3-8. These high frequency shoulders became more prominent as the concentration of the salt was increased. As the $(\text{C}_4\text{H}_9)_4\text{N}^+$ part of the salt has negligible effect on the solvent structure, the bands at 3350 and 3370cm^{-1} have been assigned to the chloride and bromide solvates respectively. At molalities greater than

FIG. 3.8



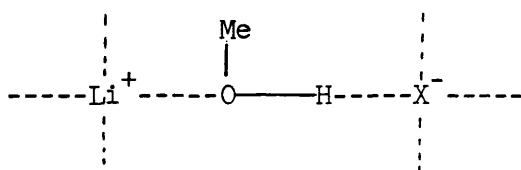
Infrared absorption spectra of CH_3OH in CH_3OD in the O-H stretching region containing \bullet butylammonium chloride (1.24 molal) at two temperatures 303 K and 148 K.

2.5mol Kg⁻¹ solutions of tetrabutylammonium chloride and bromide produce a multiband spectra on cooling, a discussion of which will appear in a later chapter.

(iii) Lithium salts

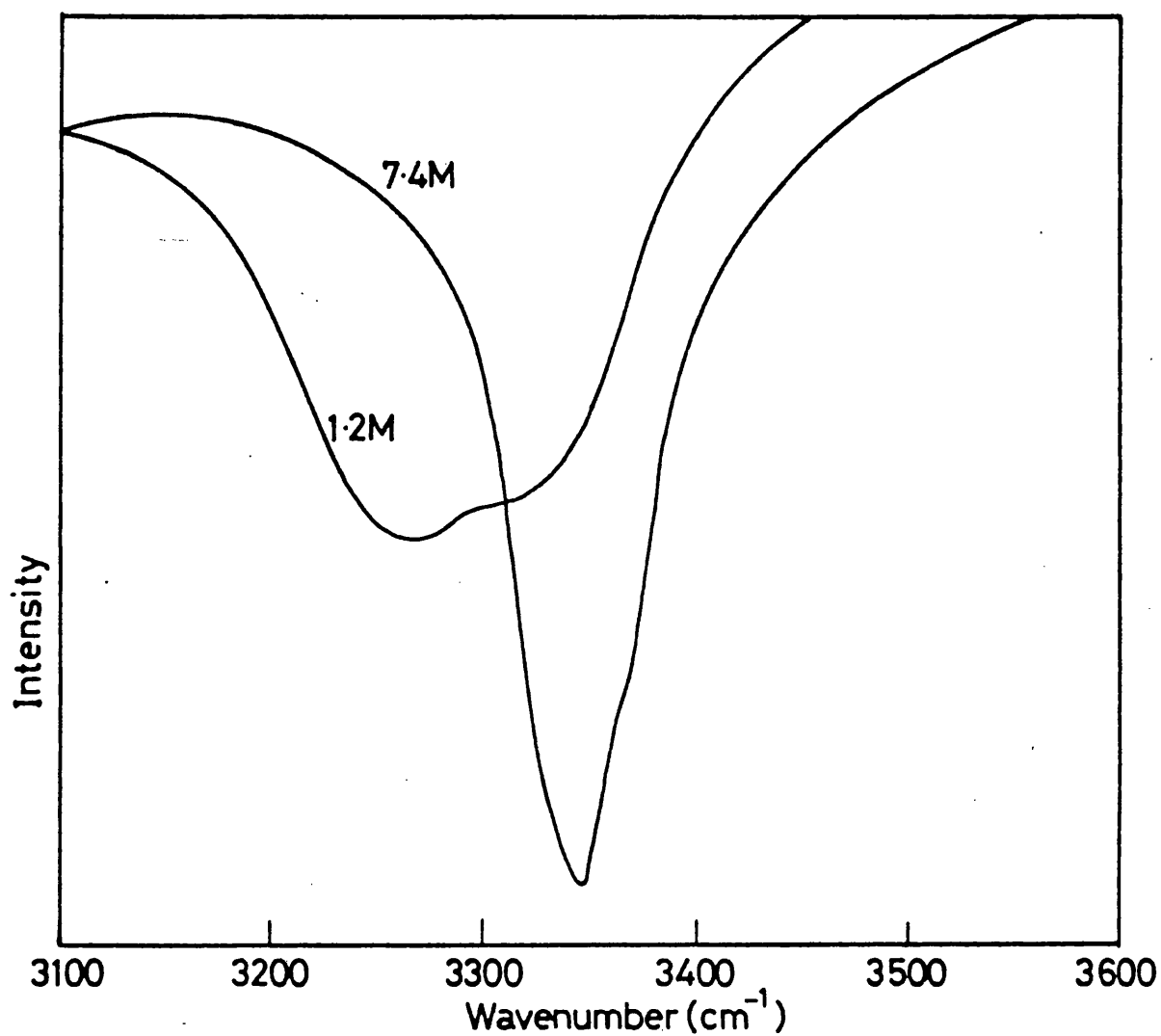
Since lithium salts were much more soluble than the other alkali metal halides, they were the salts studied extensively. On cooling dilute lithium chloride solutions produced an anion solvate band at 3340cm⁻¹ and a bulk solvent band in the 3250cm⁻¹ region. On increasing the molality of the salt under the same conditions the bulk methanol band decreased in intensity and the anion solvate band increased in intensity. However for concentrations greater than 3.5 molal a new band on the high frequency side of the anion band appeared and gradually increased in intensity as the concentration of lithium chloride was increased. These three bands are shown in Figure 3-9. The bulk methanol band shifted to slightly higher frequencies when the concentration of the salt was in the intermediate range and this shift was attributed to lithium ions and so classified as the cation solvate. The band at 3340cm⁻¹ was attributed to the anion solvate as they absorbed in the same region as those for the alkylammonium salt. The new high frequency band 20cm⁻¹ further than the anion solvate band has been assigned to solvent shared ion pairs¹⁶. This is consistent with the fact that the cation solvate has been denoted to absorb 20cm⁻¹ to the high frequency side of the bulk methanol band.

The solvent shared ion pair unit is illustrated below:-



The net effect on the O — H stretching frequency for the solvent shared ion pair molecule is simply the sum of the effects of the cation and anion individually and so the eventual band absorption at 3365cm⁻¹ would be quite feasible for the lithium chloride/methanol system. Accurate determination of the band positions can be obtained because of the relative narrowness of

FIG. 3.9



Infrared absorption spectra of CH_3OD (OH) in the O-H stretching region containing lithium chloride at several molalities (1.2 and 7.4 mol Kg^{-1}) at 148 K.

the bands despite the proximity of them. There seems to be a general trend that the cation solvates are the broadest of the bands studied with the anion bands being in the order of two narrower, while the solvent shared ion pair bands are less than half the width of the anion solvate bands. In the case of tetrabutylammonium salts, no such species can be formed, so as described in a later chapter different methods of economising in the solvent are required.

Methanolic lithium bromide solutions at 148K produced a very similar picture to the above described solutions. Dilute solutions gave bulk methanol bands that shifted to 3270cm^{-1} because of the cation effect, anion solvate bands at 3365cm^{-1} , which is in good agreement with the alkyl-ammonium salt data and a high frequency band at 3380cm^{-1} which is assigned to the solvent shared ion pair band.

At 148K dilute lithium iodide solutions gave spectra that contained two broad bands centred at 3250cm^{-1} and 3395cm^{-1} . The former is the bulk solvent band that shifts to slightly higher frequencies in the region of 3265cm^{-1} with increasing salt molalities due to the cation solvation effect while the latter is due to the anion solvate band. More concentrated solutions gave in addition a high frequency band at 3405cm^{-1} which was assigned to the solvent shared ion pair band. All these species are well illustrated in Figure 3-10.

However, as can be seen from this figure, concentrated solutions of lithium iodide and also the bromide salt display a new narrow band at 3495cm^{-1} . This is certainly not due to (O — H) free groups nor to fortuitously long O — H bonds formed under the geometric constraints of a crystalline solvate since they are clearly present in the fluid solutions at -60°C . One possible unit that could have such weak bonds is given below:-

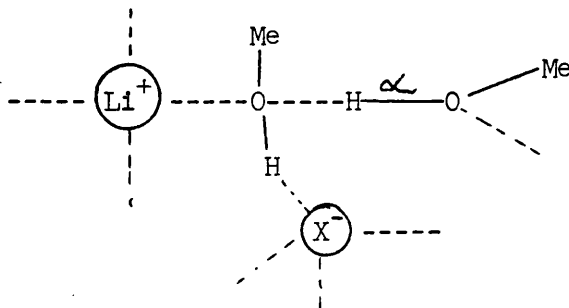
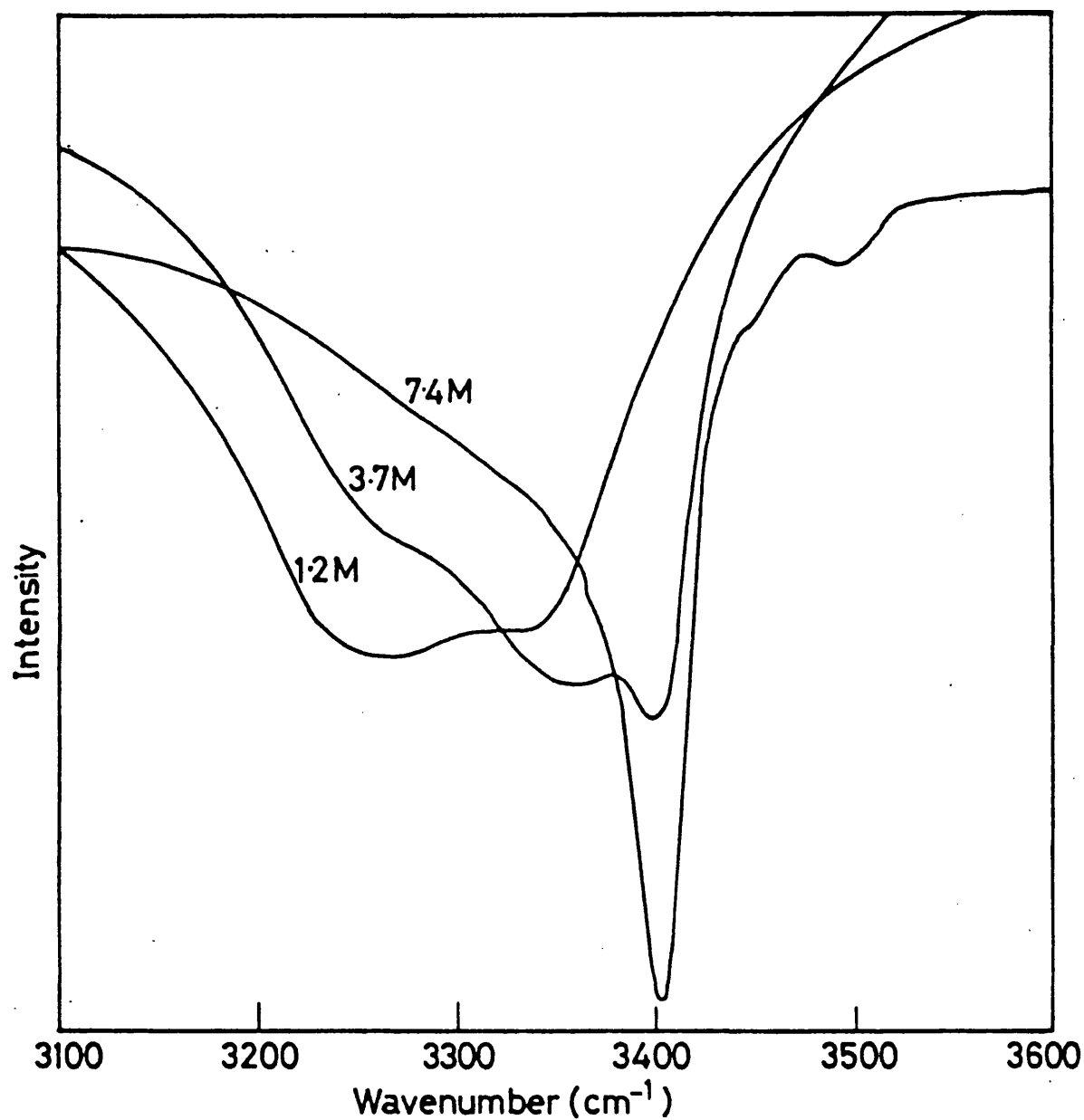


FIG. 3.10



Infrared absorption spectra of $\text{CH}_3\text{OD} (\text{OH})$ in the O-H stretching region containing lithium iodide at several molalities (1.2, 3.7 and 7.4 mol Kg^{-1}) at 148 K.

This structure in effect is a combination of the solvent shared ion pair structure and the solvent network described when methanolic sodium tetraphenylboron solutions were investigated. The high frequency oscillator which is marked α in the diagram above is the bond that absorbs at 3495cm^{-1} .

Dilute lithium nitrate in solutions of CH_3OH in CH_3OD in the $\text{O} - \text{H}$ stretching region of the fundamental infra-red spectrum displayed at low temperatures an anion solvate band in the 3330cm^{-1} region and a bulk methanol band at the usual frequency. At higher concentrations a broad band at 3360cm^{-1} is observed and assigned to the solvent shared ion pair as shown in Figure 3-11(a).

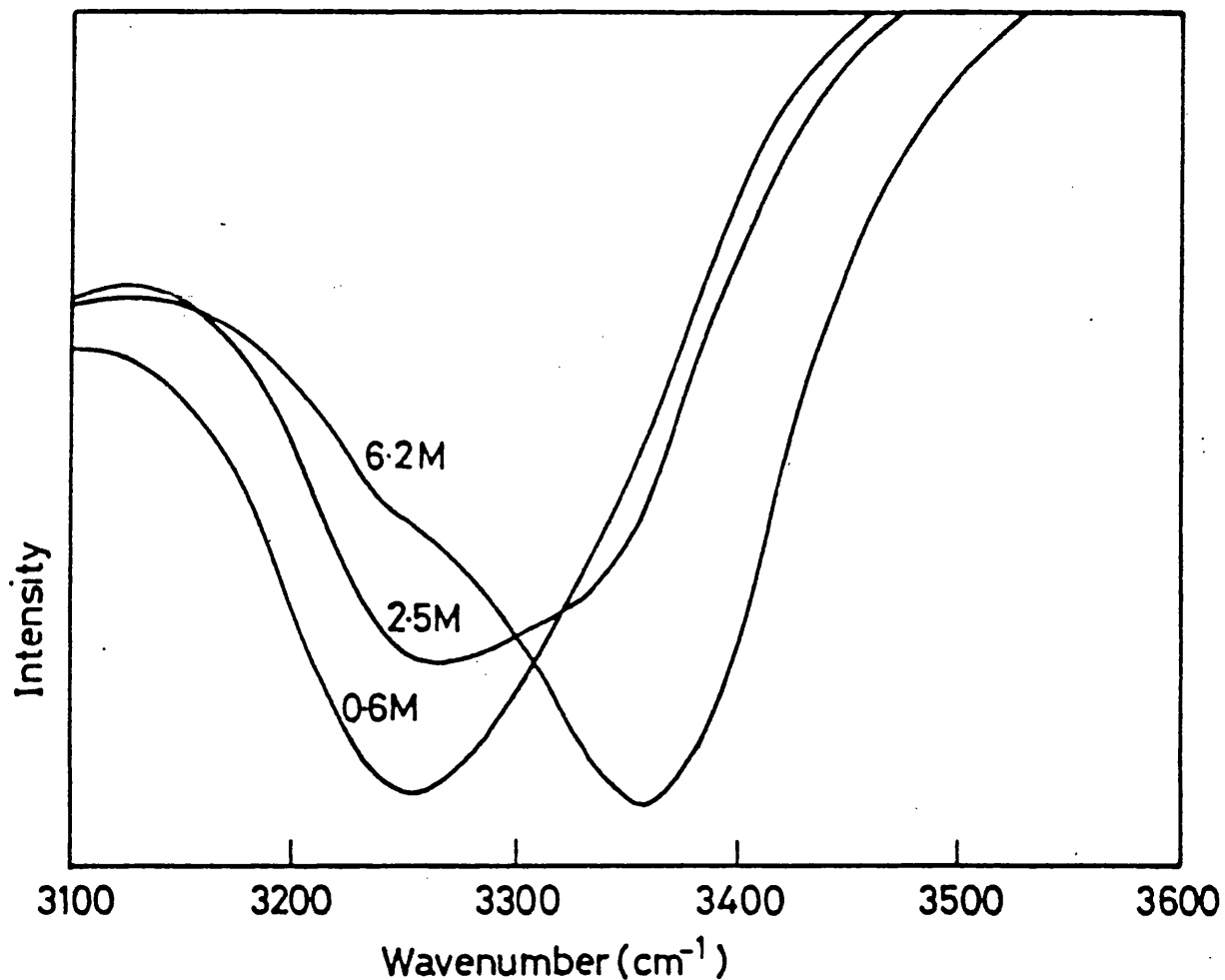
(iv) Sodium salts

Sodium salts have not provided much additional information because of their solubility properties, but the data obtained just reinforced the previous band assignments. The chloride salt was insoluble, but the bromide salt solution produced a typical dilute solution spectra that contained the bulk methanol band at 3350cm^{-1} which shifted to higher frequency but because of the low solubility no exact value for the cation effect could be determined while the anion solvate band absorbed at the typical bromide value of 3370cm^{-1} . The iodide solutions gave the same type of absorption bands as for the bromide solutions with the iodide solvate band coming at 3395cm^{-1} . The nitrate salt was insoluble as far as the other salt concentrations used were concerned.

(v) Caesium salts

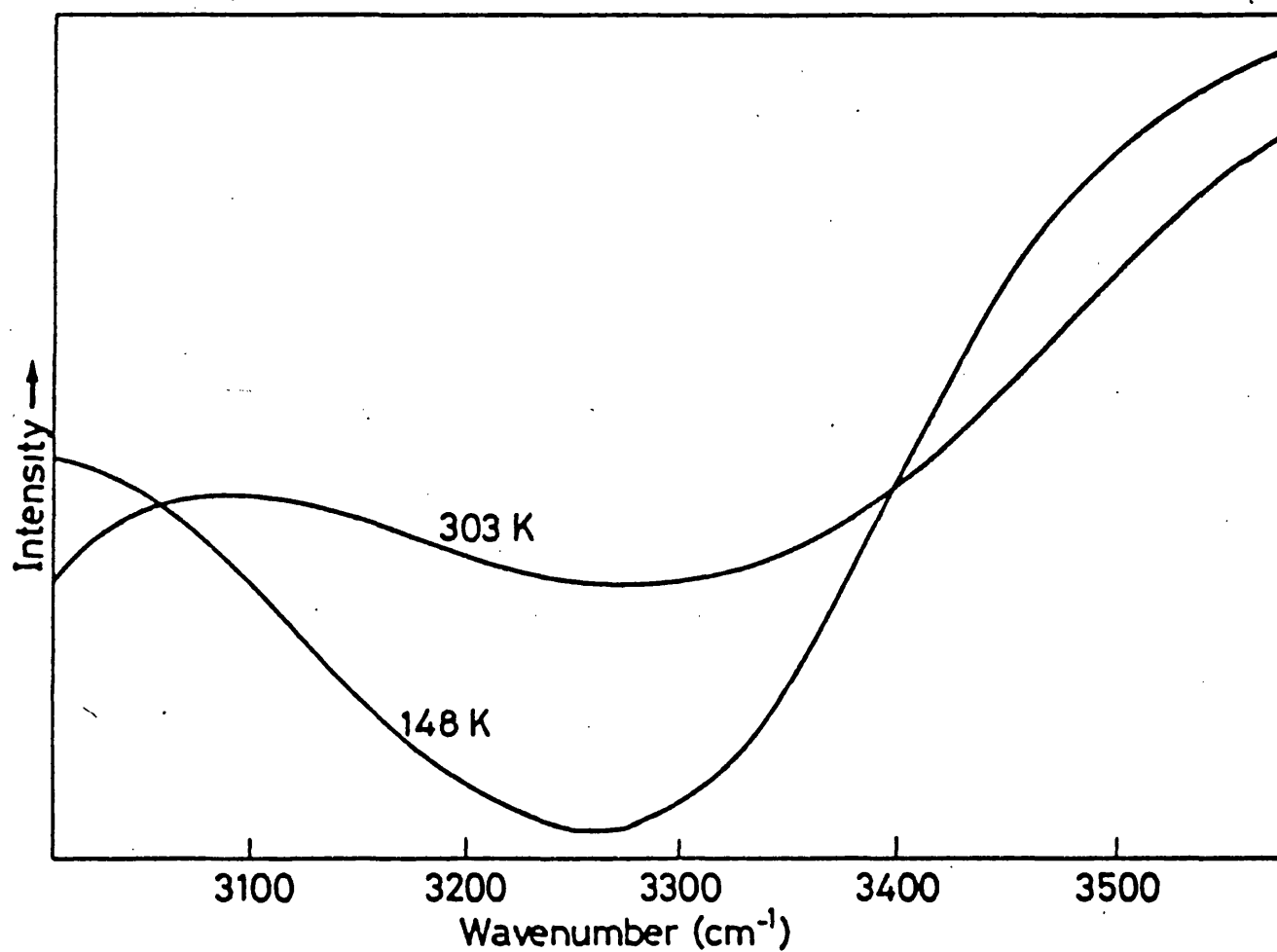
Although the majority of the caesium salts were too insoluble for good low temperature spectra to be developed, caesium fluoride solutions produced a broad shoulder on the low frequency side of the bulk methanol band. Unfortunately the band was too broad for a precise estimate of the band maximum, but it absorbs in the region of 3100cm^{-1} . This band has been attributed to the fluoride solvate. A good value for the caesium ion solvate band has not been obtained but a shoulder in the 3370cm^{-1} region is in evidence as shown in Figure 3-11(b).

FIG. 3.11a)



Infrared absorption spectra of $\text{CH}_3\text{OD}(\text{OH})$ in the O-H stretching region containing lithium nitrate at several molalities (0.6, 2.5 and 6.2 mol Kg^{-1}) at 148K.

FIG. 3.11b)



Infrared absorption spectra of CH_3OH in CH_3OD in the O-H stretching region containing caesium fluoride (5.4 molal) at two temperatures, 303K and 148 K.

(vi) Magnesium halides

Magnesium chloride and bromide solutions produced bands in the normal regions of the infra-red spectra for solvated chloride and bromide ions together with the normal bulk methanol band and a shoulder in the 3140cm^{-1} region. This is well illustrated in Figure 3-12. The low frequency shoulder became more prominent with the increase in molality of the salt and so this band has been assigned to the magnesium ion solvate.

3.4 DISCUSSION OF CATION SHIFTS

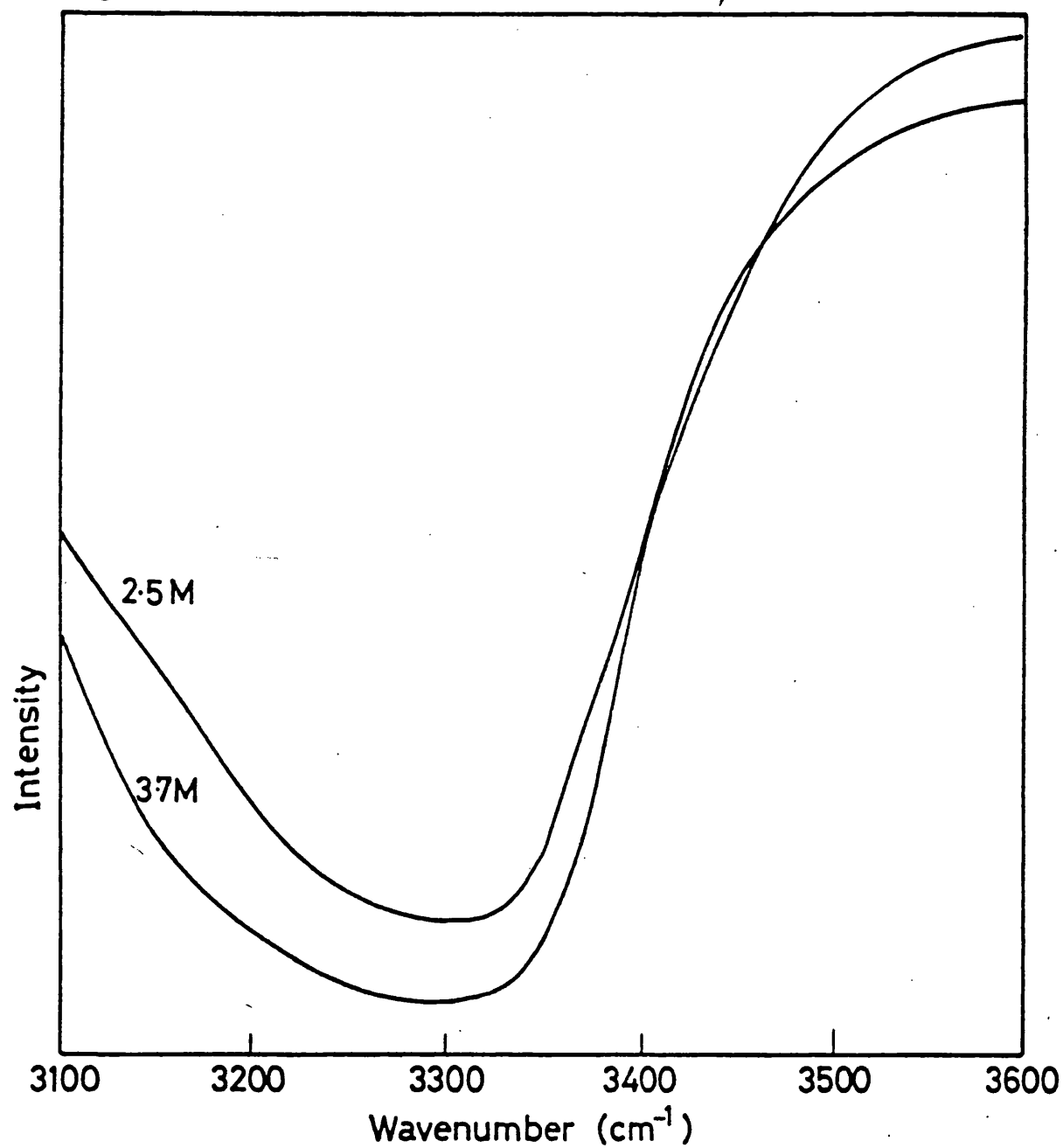
The relative order of $\text{Mg}^{2+} > \text{Li}^+ > \text{Na}^+$ with reference to the bond strengthening properties of the cations is comparable with those previously deduced from solutions at room temperature and are in good agreement with the cation induced proton resonance shifts for methanol^{13,14}.

However, the lack of data on the caesium solvate except in the case of caesium fluoride solutions which still do not give resolvable spectra has prevented the correlation with the nuclear magnetic resonance result being extended to the caesium ion. This ion produced a smaller upfield hydroxy-proton shift than the sodium ion. This was interpreted as a tendency to non solvate or in other words, the weak solvation caused the upfield shift for a reduced number of solvent molecules. This would be represented in the infra-red spectra by a larger high frequency shift than that obtained for the sodium solvate. In fact a shoulder on the high frequency side of the main methanol bulk band in the 3370cm^{-1} region was observed. If this band was due in some way to caesium ions bonded to solvent molecules, then the bonding must be very weak which would correlate with the n.m.r. results. This could be the true explanation but with no other caesium salt data possible, no conclusive assignment can be made.

3.5 PERCHLORATE AND OTHER POLYATOMIC ION SOLUTIONS

One of the most interesting developments in the fundamental infra-red room and low temperature studies has been the effects of these anions on the O — H stretching band which has provided several noteworthy points.

FIG. 3.12



Infrared absorption spectra of $\text{CH}_3\text{OD (OH)}$ in the O-H stretching region containing magnesium chloride at several molalities (2.5 and 3.7 mol Kg^{-1}) at 148 K.

Firstly a shoulder on the high frequency side of the bulk methanol band in the 3530cm^{-1} region appeared at low salt concentrations and increased in intensity to become a well-defined peak at higher concentrations. While this band increased with the molality of salt, the bulk methanol band at 3340cm^{-1} decreased in intensity with an existence of an isosbestic point¹⁷. The high frequency band is narrower than the bulk methanol band by a factor of two and shows a slight dependence upon the cationic species at high concentrations. The bulk methanol band also varies in position with a change in concentration.

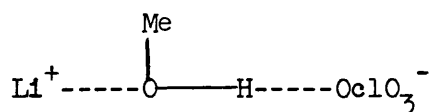
This high frequency band has been the centre of many arguments as one set of workers choose to believe that its cause is the formation of 'free' non bonded O — H groups. The same effect, it is stated, occurs when the temperature of a solution is increased and so the explanation of a high frequency shoulder is free O — H groups. The other argument is that the band is due to the formation of weakly bonded perchlorate ions. The fact that tetrafluoroborate solutions produced a similar picture but the high frequency band absorbs at 16cm^{-1} higher in frequency, both wavenumbers not being at 3640cm^{-1} which is where the (O — H) free band absorbs, but in a region of 100cm^{-1} lower frequency, seems to suggest the latter concept is the more reasonable.

Now if the perchlorate ion was able to induce the formation of 'free' O — H groups, then the intensity of the free O — H band of the methanol molecule in the inert solutions of methylene chloride at 3640cm^{-1} should increase in intensity. However, this does not happen. In fact a band is formed that has shifted from that of the monomeric methanol. The shift is much less than the average value for bulk methanol, which would indicate that the perchlorate ion is a somewhat weaker proton acceptor than the oxygen atom of the methanol.

In the hope of distinguishing between the two concepts mentioned above, the study of the infra-red spectra of dilute solutions of CH_3OH in

CH_3OD containing sodium, lithium and magnesium perchlorates in a range of concentrations was undertaken at low temperatures.

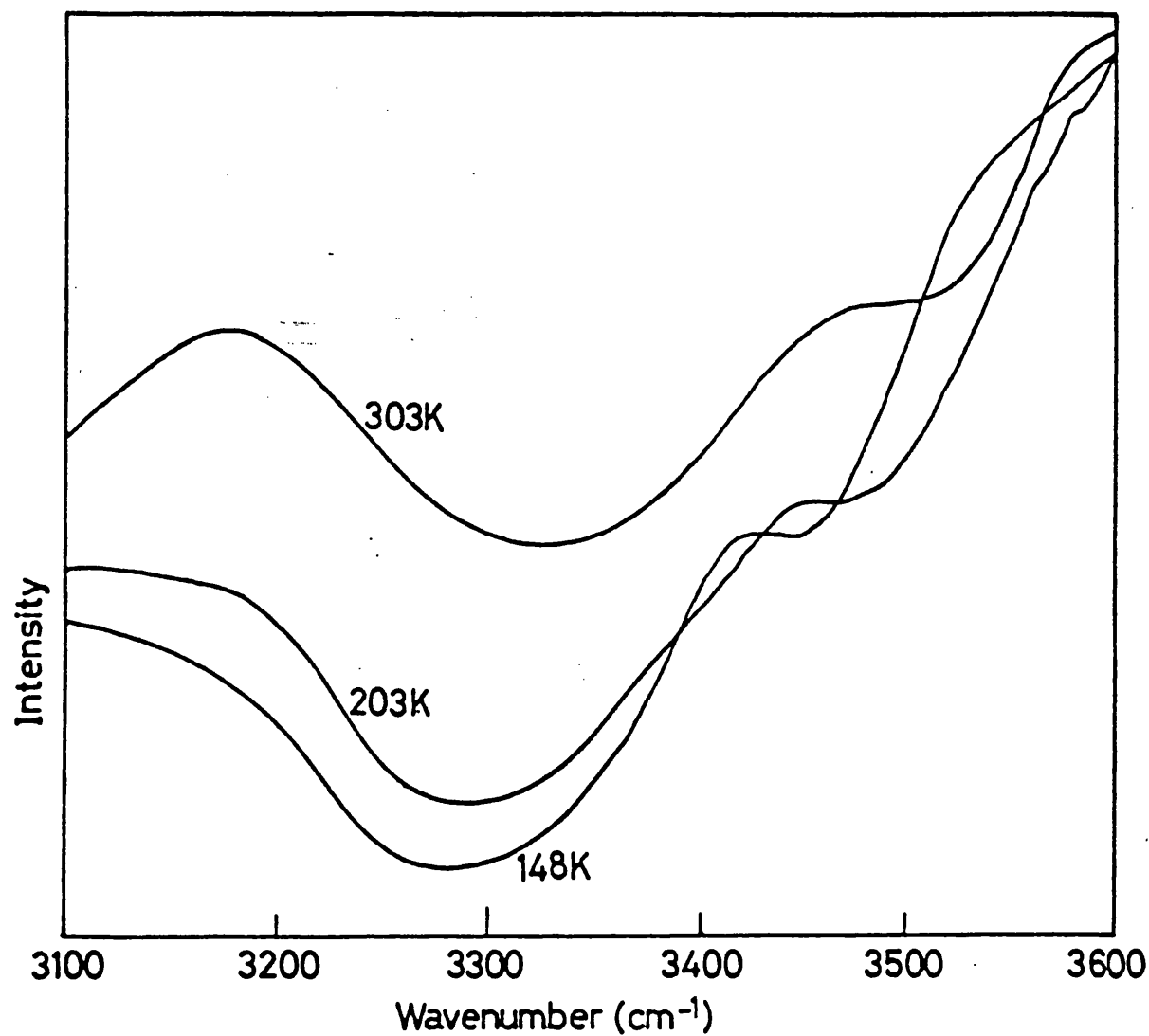
Room temperature results show that the high frequency band for all the dilute perchlorate solutions studied absorbed at 3530cm^{-1} . However, with concentrated solutions this band absorbs at 3550cm^{-1} for the lithium salt as this is the only salt that dissolves in large quantities. With a lithium shift of $+20\text{cm}^{-1}$ reported for the halide solutions, the band at 3550cm^{-1} was assigned to the solvent shared ion pair of the type



The broad bulk methanol bands at room temperature for the three perchlorates studied show a definite peak maximum difference with the lithium perchlorate band at 3340cm^{-1} , the sodium perchlorate band at 3390cm^{-1} and the magnesium perchlorate band at 3250cm^{-1} . This is well-illustrated when the room temperature spectra in Figures 3-13, 3-14 and 3-15 are compared. This effect has been attributed to cation-methanol interactions. The shifts produced from the bulk methanol band are in very good agreement with other aqueous and methanolic salt solution room temperature data.

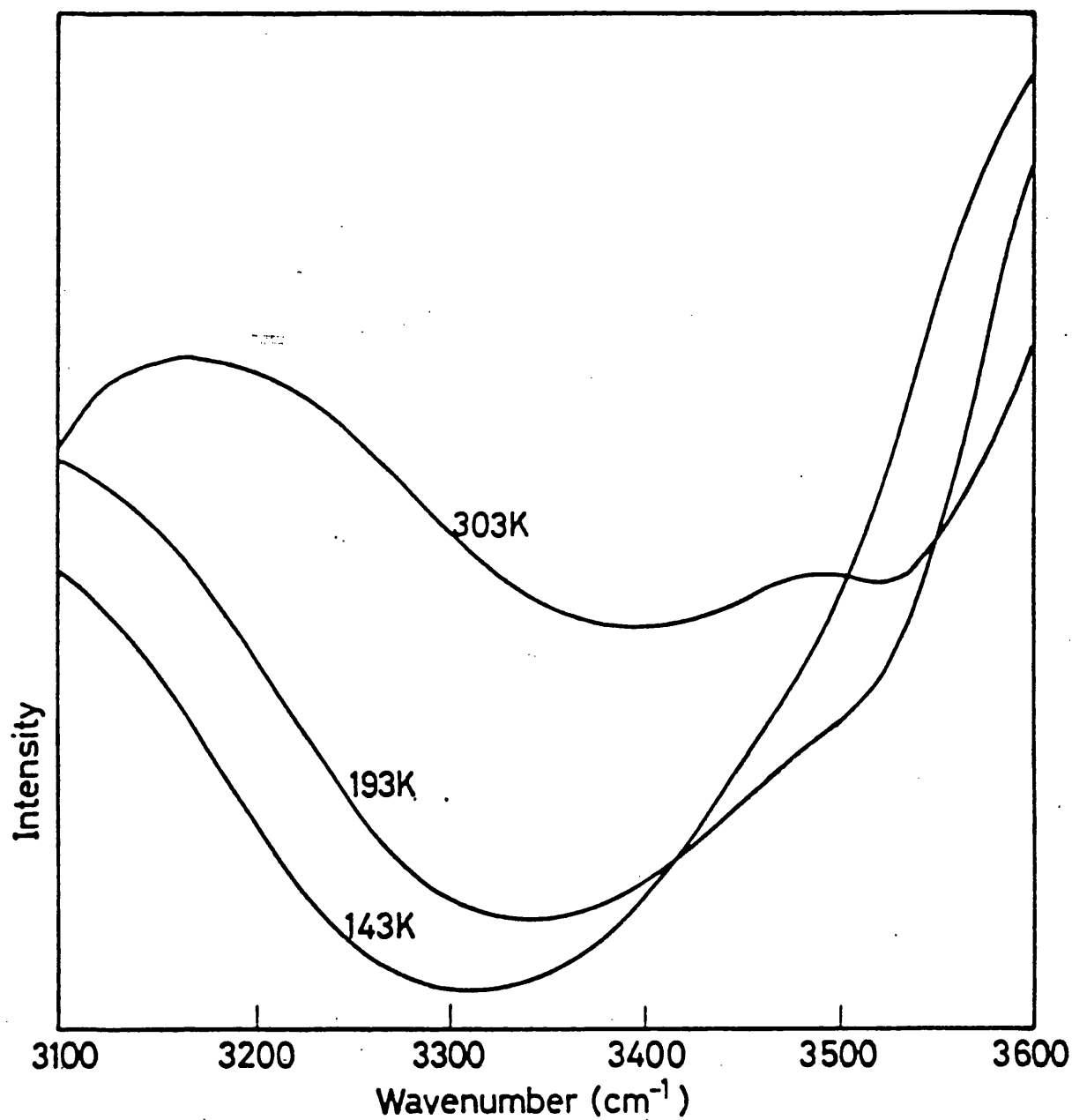
On cooling these dilute perchlorate solutions to 148K , the high frequency band at 3530cm^{-1} was found to steadily shift to lower frequencies. At these low temperatures there was no sign of the band in the 3530cm^{-1} region and so the conclusion that this band could not be due to $(\text{O}=\text{H})$ free groups was arrived at. This steady shift is shown in Figure 3-7 and shows that the weakly solvated perchlorate band at low temperatures absorbs at 3450cm^{-1} . The broad bulk methanol bands in all three sets of spectra as shown in Figures 3-13, 3-14 and 3-15, also shift to lower frequencies with the maxima at 3260 , 3295 and 3150cm^{-1} for the respective lithium, sodium and magnesium perchlorate solutions. This is in good agreement with the order of cations at room temperature. In the spectrum obtained from

FIG. 3.13



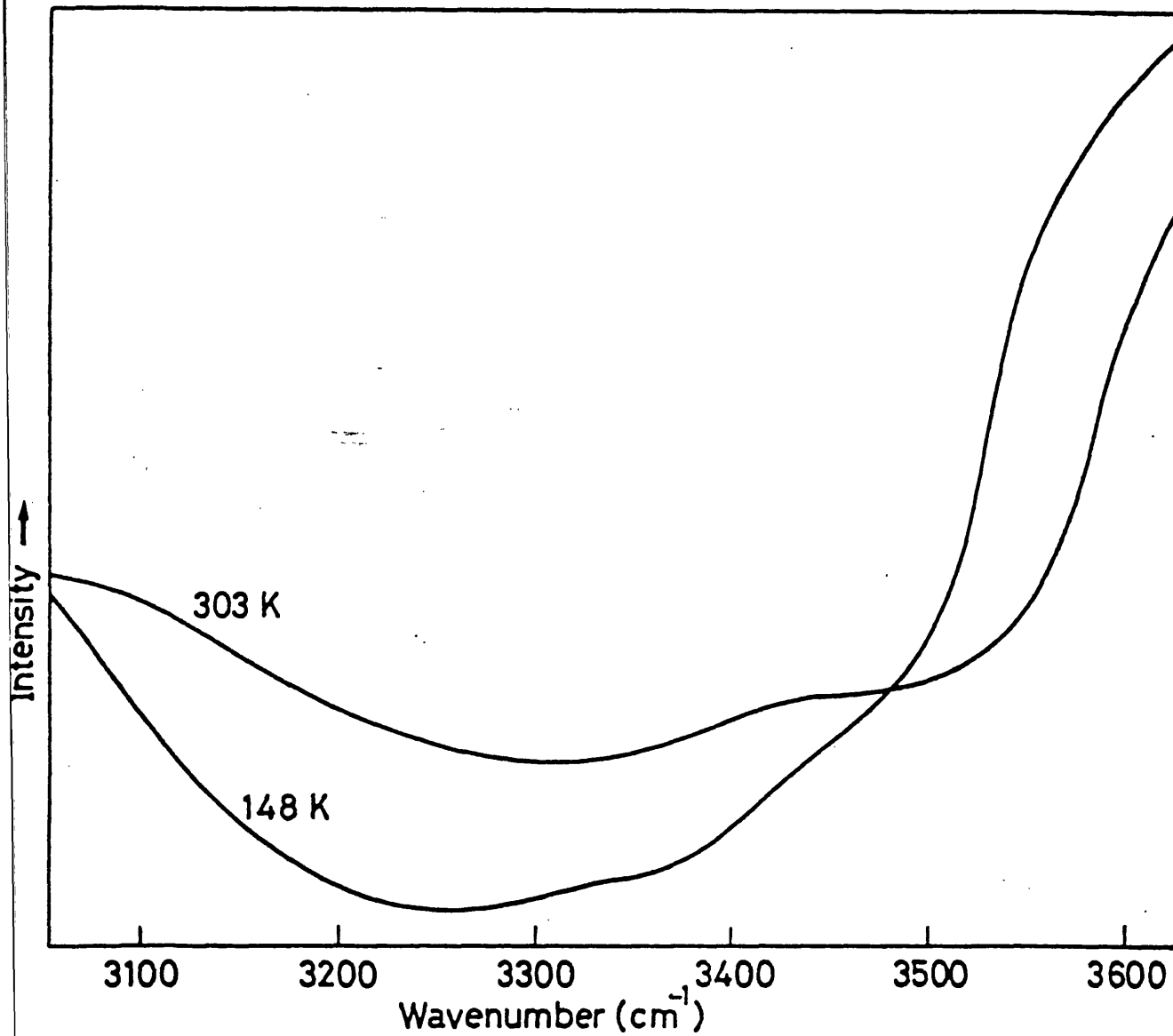
Infrared absorption spectra of CH_3OH in CH_3OD in the O-H stretching region containing lithium perchlorate (2.5 molal) at three temperatures 303K, 203K, and 148K.

FIG. 3.14



Infrared absorption spectrum of CH_3OH in CH_3OD in the O-H stretching region, containing sodium perchlorate (2.5 molal) at three temperatures, 303K, 193K and 143K.

FIG. 3.15



Infrared absorption spectra of CH_3OH in CH_3OD in the O-H stretching region containing magnesium perchlorate (2.5 molal) at two temperatures 303 K and 148 K.

methanolic magnesium perchlorate solutions an additional band at 3370cm^{-1} was observed. If the shared solvent molecule in a solvent shared ion pair situation has an O—H stretching frequency that is the net effect of the cation and anion solvate effects separately, then the band at 3370cm^{-1} could well be attributed to the solvent shared ion pairs.

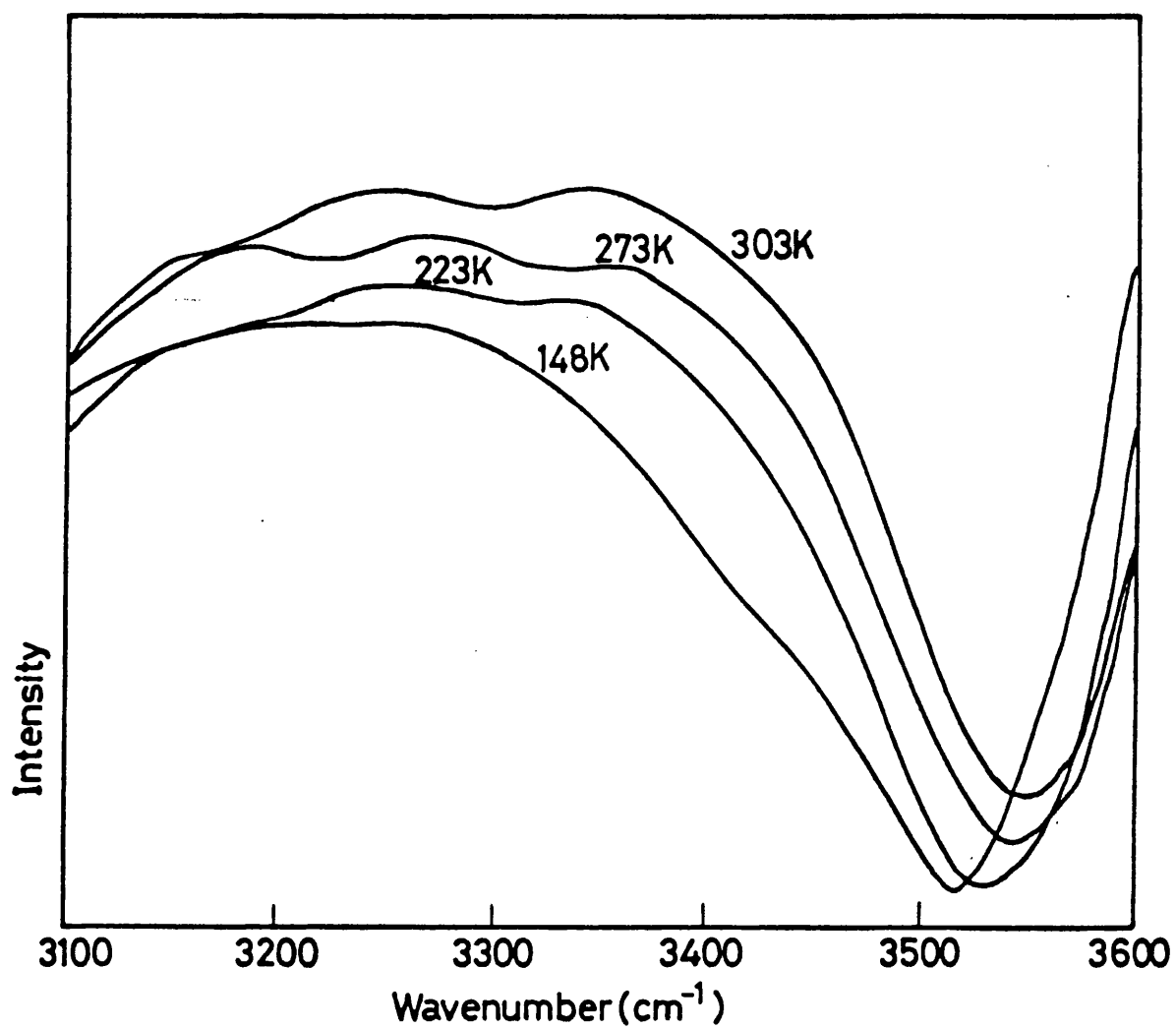
From Figure 3-16 of the concentrated lithium perchlorate solutions, the low frequency shift of the high frequency band is not so pronounced as for the dilute solutions as shown in Figure 3-7. This can be explained by the fact that the solvent shared ion pair molecule has a more rigid structure than the weakly bound perchlorate ion to the solvent and so the effect of the temperature to shorten and strengthen the O—H oscillators in the shared system is not so great as for the weakly bound ion type solvent molecule so the large effect between the two bands at 3450 and 3510cm^{-1} is not the cation shift but a temperature effect.

This section shows that the perchlorate ion does not possess unique qualities for "structure breaking" as some say to explain the high frequency band, but can be explained in a perfectly normal manner as other anions producing solvate bands of varying bond strengths.

3.6 DISCUSSION OF ANION SOLVATION

All the bands associated with anion solvates absorbed on the high frequency side of the bulk methanol band with the possible exception of the fluoride ion. In general terms this result reinforces the concept that anion solvation is simply a specific manifestation of solvent-solute hydrogen bonding which on average was weaker than solvent-solvent bonding. This again brings into light the factor that concerns the competitive nature of both the anion and the solvent molecule for another methanol molecule. However, as stated below the fact that several hydrogen bonds are formed to the anion with the remaining molecules taking up the normal solvent sites seems the probable conclusion which is based upon infra-red and nuclear magnetic resonance data ^{11, 13, 14}.

FIG. 3.16



Infrared absorption spectra of CH_3OH in CH_3OD in the O-H stretching region containing lithium perchlorate (6.2 molal) at four temperatures 303K, 273K, 223K and 148K.

This difference in solvation number between the anions and the methanol molecule is substantial because an average methanol molecule has only one O — H group attached while a chloride ion probably has four or even six solvent O — H groups surrounding it. When the higher solvation number for the anion is compared with the solvent molecule association and analysed in conjunction with the fact that both solvate bands absorb at very similar frequencies, and corresponding monosolvate situations are compared, the anion-methanol monosolvate should absorb at much lower frequencies than the bulk methanol band at 3240cm^{-1} . This is indeed the case for the chloride ion as is demonstrated in the final point of this discussion. This gives the precedent that the higher the solvation number the weaker the hydrogen bonding. This concept is further reinforced when a solvent molecule instead of the usual situation of having one O — H group attached has two such groups hydrogen bonded to the oxygen via the lone pairs. This type of bonding was in evidence in sodium tetraphenylboron solutions. The additional hydroxyproton produces a drastic fall in the strength of these two bonds and shifts the O — H oscillator frequency from the bulk solvent band at 3240cm^{-1} to even higher values than those found for anions which includes the weakly bonded perchlorate anion. This species produced a band at a considerably lower frequency than the (O — H) free group at 3640cm^{-1} .

The order of frequencies for the anion solvates is $\text{F}^- < \text{Cl}^- < \text{NO}_3^- < \text{Br}^- < \text{I}^- < \text{ClO}_4^-$, but the results for the chloride, nitrate, bromide and iodide anions absorb within a scan of 50cm^{-1} . For Cl^- , Br^- and I^- the apparent lack of large difference in frequency can be explained in terms of the above idea that six solvent molecules were bonded in the chloride solvate with approximately the same strength as four solvent molecules in the bromide solvate case.

The difference between the nitrate and perchlorate solvates is probably due to the difference in the polarisability of the ions. The

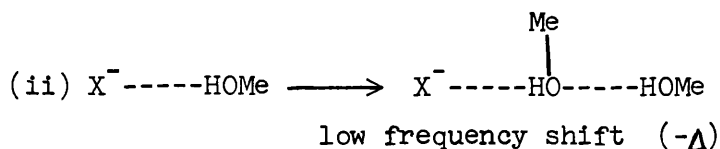
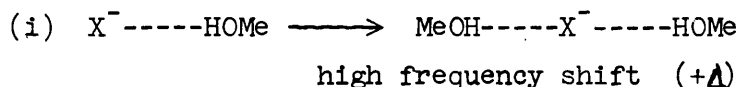
perchlorate ion is very weakly hydrogen bonded to each oxygen because the negative charge is evenly dispersed through the ion. A hydration number of four has been calculated for aqueous perchlorate ions from infra-red spectra of metal perchlorate solutions⁹. However, the nitrate ion is clearly asymmetrically solvated in methanol¹⁸, with one or two relatively strong hydrogen bonds. This effect which is in contrast to the solvated perchlorate ion can be explained in terms of the ions high polarisability with the strongly bonded oxygen ligands pulling the negative charge away from the remaining ligand. These stronger hydrogen bonds are the reason behind the nitrate solvate bands absorbing at lower frequencies than the perchlorate solvate band.

Another worthwhile point to note is the apparent lack of any appreciable shift in frequency of the anion solvates with changes of temperature when ambient and low temperature data are compared, but a large shift in frequency of 100cm^{-1} when bulk solvent and cation solvate bands were studied. This phenomena has been explained in the following manner. The solvent manifestation contains many long and bent hydrogen bonds which produce the broad continuum band at room temperature. On cooling these distorted weak bonds become shorter and hence stronger and the whole structure becomes more ordered. This was shown to be true by the decrease in bandwidth of the bands at the different temperatures but was in no way as dramatic as that obtained from aqueous solutions.

This apparent lack of frequency shift in the same order for the anion solvates could be explained by the concept that the O — H oscillators of the methanol molecules that are hydrogen bonded to the anion all form straight bonds. The reasoning behind this is that the negative charges on the anion and the oxygen atom of the methanol molecules would prefer to be as far away from each other as possible. On cooling these bonds only slightly shorten and so only a small frequency shift was obtained. A fuller explanation with more detail is described for aqueous systems in the next chapter.

A final worthwhile point emerged when the bulk solvent bands were compared with the 1:1 complexes, $X^- \cdots \cdots HOCH_3$, which are formed in dilute solutions of the tetraalkylammonium salts in methanol in inert media like carbon tetrachloride or methylene dichloride^{7,19,20}. The differences in wavenumber between the two systems are tabulated at the end of this chapter. There is a small shift to low frequencies on cooling for the monosolvate systems and these results have been extrapolated to 148K.

In attempting to explain these differences (Δ) in wavenumber of the two solvate bands, two factors have been taken into account. Firstly, when an anion has an increased solvation number, a fall in the bond strength was expected and hence a shift to high frequency should be observed. Secondly, when the second solvent molecule prefers to bond to the solvated methanol molecule to give type (ii) in the diagram below, an increase in the strength of the hydrogen bond formed to the anion was expected and hence a low frequency shift should be observed:



These explanations were also used to explain the multi-line spectra obtained from low temperature solutions of methanolic tetraalkylammonium halide solutions which are discussed in Chapter 6. Although the exact amount of each effect will differ from one ion to the next and the net effect of the two interactions when combined together will not be precise, a qualitative interpretation of the solvation properties of the ions can be drawn. So for the chloride ion the former effect (i) which is due to the high solvation number must be responsible for the positive shift on going from the monosolvate to the anion solvates in the bulk methanol. The smaller positive shift for the bromide ion can be interpreted in terms of a smaller solvation number which would mean that the latter effect would begin

to play a significant part, while the low frequency shift for the iodide ion seems to suggest that the latter effect now is dominant.

The nitrate ion with, as postulated ¹⁸, just one or possibly two of the oxygen ligands involved in solvation should and does have the latter effect dominating. However, for the perchlorate ion the lower polarisability of the anion means that there is little change in the wavenumber on going from a monosolvate situation to a tetrasolvate system provided that the four solvent molecules are bonded to the four oxygen ligands. This produced the latter effect to be dominant. The great difference in wavenumber for the perchlorate shift than the nitrate shift suggests that the solvation number for nitrate is greater than one.

This produces a detailed picture of anion solvation showing especially the major role of the secondary methanol molecules in determining the wavenumber for the primary solvent shell. These secondary solvent molecules simply are knitted into the solvent structure and bonded to the anions, which produces a commonsense model with no region of disorder that is so frequently postulated while in other cases denoted as being improbable²¹.

In principal oscillator strengths of the component bands of these solutions should be able to be assigned and this would lead to some idea of the solvation numbers for the anions studied. Our attempts to resolve the bands using a DuPont curve analyser have given us some relatively consistent results which are plotted in Figure 3-17. This diagram shows that the solvation number for chloride is greater than that for the other anions studied with the iodide solvation number the smallest. The order of the anions being:

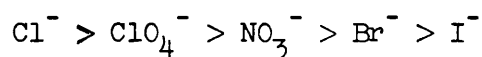


FIG. 3.17

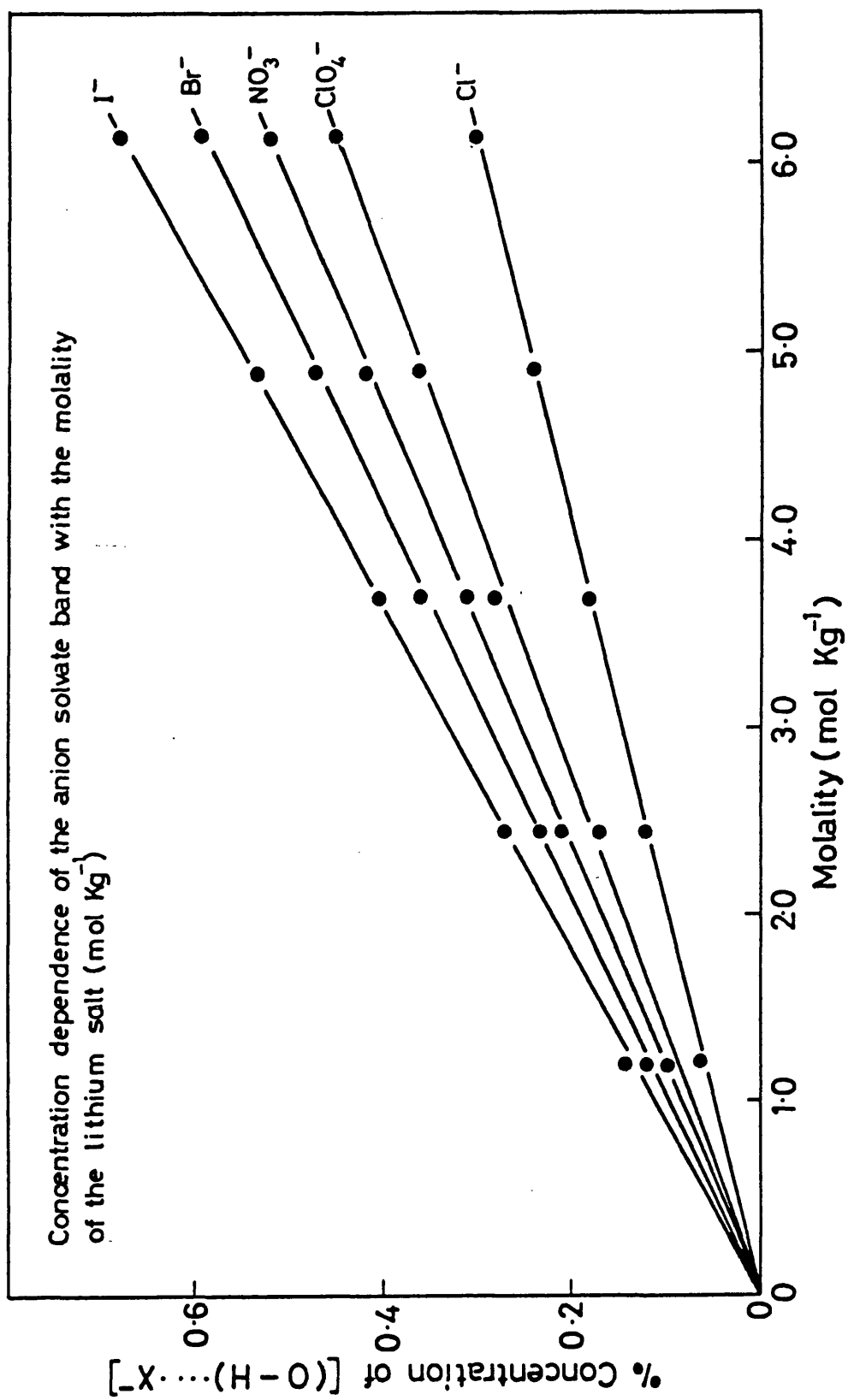


TABLE 1

Anion	Wavenumber 1:1 complexes (cm ⁻¹)	Wavenumber Bulk solvent bands (cm ⁻¹)	Difference in wavenumber of the two solvate bands Δ (cm ⁻¹)
Cl ⁻	3275	3340	+ 75
Br ⁻	3339	3365	+ 26
I ⁻	3390	3395	+ 5
ClO ₄ ⁻	3540	3450	- 90

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CHAPTER FOUR

VIBRATIONAL SPECTRA OF WATER AND AQUEOUS ELECTROLYTE SOLUTIONS

4.1 INTRODUCTION

The aim of this chapter was to collect information concerning interactions between water molecules and ions that have been studied by infra-red spectroscopy in the O — H stretching region only at room and low temperatures and arrive at some consistent conclusions. Pure water displays a very broad and complicated absorption band in the fundamental stretching region of the infra-red spectrum. This width is due to three factors:

- (i) Overlap of ν_1 and ν_3 fundamental stretching vibrations.
- (ii) Fermi resonance with $2\nu_2$
- (iii) Intramolecular coupling of the OH stretching vibrations with neighbouring molecules^{1,2}.

These three problems are eliminated by the use of dilute isotopic solutions of HOD in D₂O, which display narrower but still relatively uninformative infra-red absorption bands. These bands have no high frequency features that could be attributed to (OH)free species, but this could be due to the dominating intensity of the (OH)bound absorption band. This intensity is gained on the formation of hydrogen bonds^{3,4}.

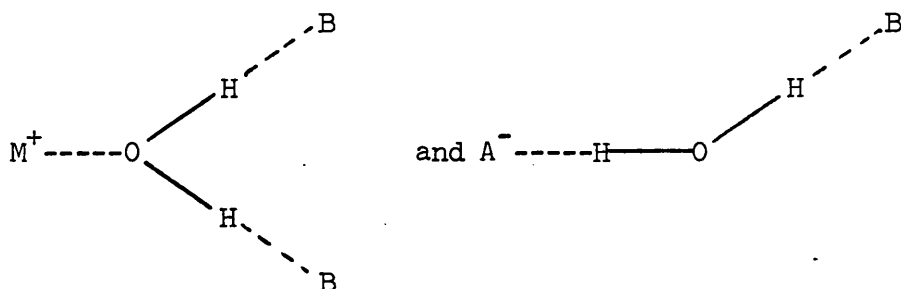
However, a weak shoulder on the high frequency side of the main band has been observed in the Roman spectrum which has been assigned to non hydrogen bonded water molecules by Walrafen⁵.

The most informative region for the study of free OH oscillators is in the near infra-red region of the spectrum, since the loss of intensity for bound O — H is far greater than that for free OH^{6,7}.

Returning to the fundamental region and using the O — H stretching modes of water to study the interactions between water molecules and ions, three different approaches can be made. Firstly, studies of water-anion complexes in an almost completely inert medium such as CCl₄ were used to investigate the hydrogen bonding between anions and monomeric water molecules⁸.

Secondly, an aprotic basic solvent such as CH₃CN was employed⁹ which made it possible to study alkali metal salts in addition to the quaternary

ammonium salts and so obtain information about cation-water interactions. However, the situation is more complicated because on the one hand the basic solvent co-ordinates to the cations and added water enters in the competition equilibrium, and on the other, the water forms hydrogen bonds to the basic solvent molecules, and anions compete with this bonding. However weakly solvated perchlorate ions may not be able to do this appreciably. Nevertheless the infra-red bands are quite narrow and a considerable range of solvates can be studied under these conditions. Another difference of importance when compared with the inert conditions in the first approach is that the basic units studied are no longer just the ions bonded to monomeric water, but rather, the species



Where B is a basic solvent molecule.

The third system which is the one studied herein, is the widely studied solutions of electrolytes in bulk water. Generally even HOD solutions of electrolytes gave broad single peaked bands that displayed only small changes in band widths and peak positions compared with the pure solvent band^{10,11}. However, perchlorates, tetrafluoroborates and hexafluorophosphates produce a shoulder on the high frequency side of the $O-H$ band at low salt concentrations, which increase to a well-defined peak at higher concentrations. These resolved bands have been the centre of controversy. On the one hand, Walrafen¹² has favoured the concept that perchlorates are not solvated, but induce the formation of free $O-H$ oscillators, $(OH)_{free}$, and so act as "structure breakers". On the other hand, a variety of workers^{13,14,15,16,17} have preferred to assign the high frequency bands as $O-H$ oscillators weakly bonded to the large anions. Whatever the correct assignment might be,

the generalisation that the anion effect is entirely located in the high frequency area, and any residual shifts caused by the salt to the bulk water must stem from the effect of the cations can be made. The study described below was undertaken to explore the possible advantages of recording low temperature infra-red spectra of aqueous electrolyte solutions.

4.2 GENERAL DISCUSSION

For direct information about liquid phase solutions, the most imperative factor to avoid was extensive phase separation. When this was achieved, the rigid glasses obtained resembled their fluid solutions and so their infra-red spectral features could be directly related. Hence the most important factor in analysing the spectra obtained was to ensure that samples had glassified. A glass is a liquid which has been cooled to a rigid condition without crystallising. The appearance of a broad diffuse diffraction ring for glasses in contrast to the sharp line spectra of crystalline solids shows a lack of long range order in glasses¹⁸. However, the fact that both phases absorb in the same region of the infra-red spectrum, shows that the interatomic forces in both phases are very similar.

As shown in the previous chapter, phase separation in methanolic solutions results in a break in smooth shifts and the development of bands, together with the appearance of a large scattering background¹⁹. A variety of tests were applied to the aqueous systems to determine whether or not phase separation had occurred. For water we used the following criteria:

(i) The appearance of a narrow absorption band at 3280cm^{-1} with a band halfwidth of 50cm^{-1} which was assigned to ice crystals. Such features are very similar to those for pure HOD in D_2O at 173K ²⁰.

(ii) Very often dilute electrolyte solutions gave very similar results to that for the pure solvent, but more concentrated solutions gave narrow multiband spectra which we have attributed to various crystal hydrates, some of which closely resembled those already published, but others seem to be novel.

(iii) If there was a large discrepancy in transmission between the room temperature and low temperature spectra (greater than 50% transmission), the spectra were ignored. This scattering arises from the presence of small crystallites of different phases.

(iv) In several instances, other tests for phase effects have been developed in connection with studies of radiation processes²¹. Using nitroxide radicals or manganese ions as probes, sharp multiline esr signals indicated a glassy state while a broad single signal was assigned to a multiphase sample.

In order to prevent phase separations, traces of t-butanol or glycerol were sometimes added to the aqueous solutions. Generally this resulted in better glassification. Reproducibility of the spectra independent of phase was fair.

Before specific electrolyte solutions are discussed, some generalizations have been noted and explanations given.

The first noteworthy feature that arose in many cases was that the resolved bands were obtained between the limiting values of the ice band at 3280cm^{-1} and the "(OH)free" band in the $3550\text{--}3600\text{cm}^{-1}$ region.

There are two reasons why these bands were only resolved at low temperatures. One was that on cooling the absorption bands narrow and the other is that the bulk water band shifts to low frequencies more rapidly than those assigned to certain solvates as shown in Figure 4.1.

These bands that became resolved on the high frequency side of the 3280cm^{-1} band have been assigned to the anion hydrates rather than the cation hydrates on the strength of the tetra-alkylammonium salt data and the crystal structure data. The observation that these bands were initially independent of the nature of the cations seemed to reinforce the assignment. The third and most satisfying point was the good agreement with the corresponding results obtained for the anion solvates for methanolic solutions which is displayed in Figure 4.2.

All these anions gave high frequency shifts which increased in

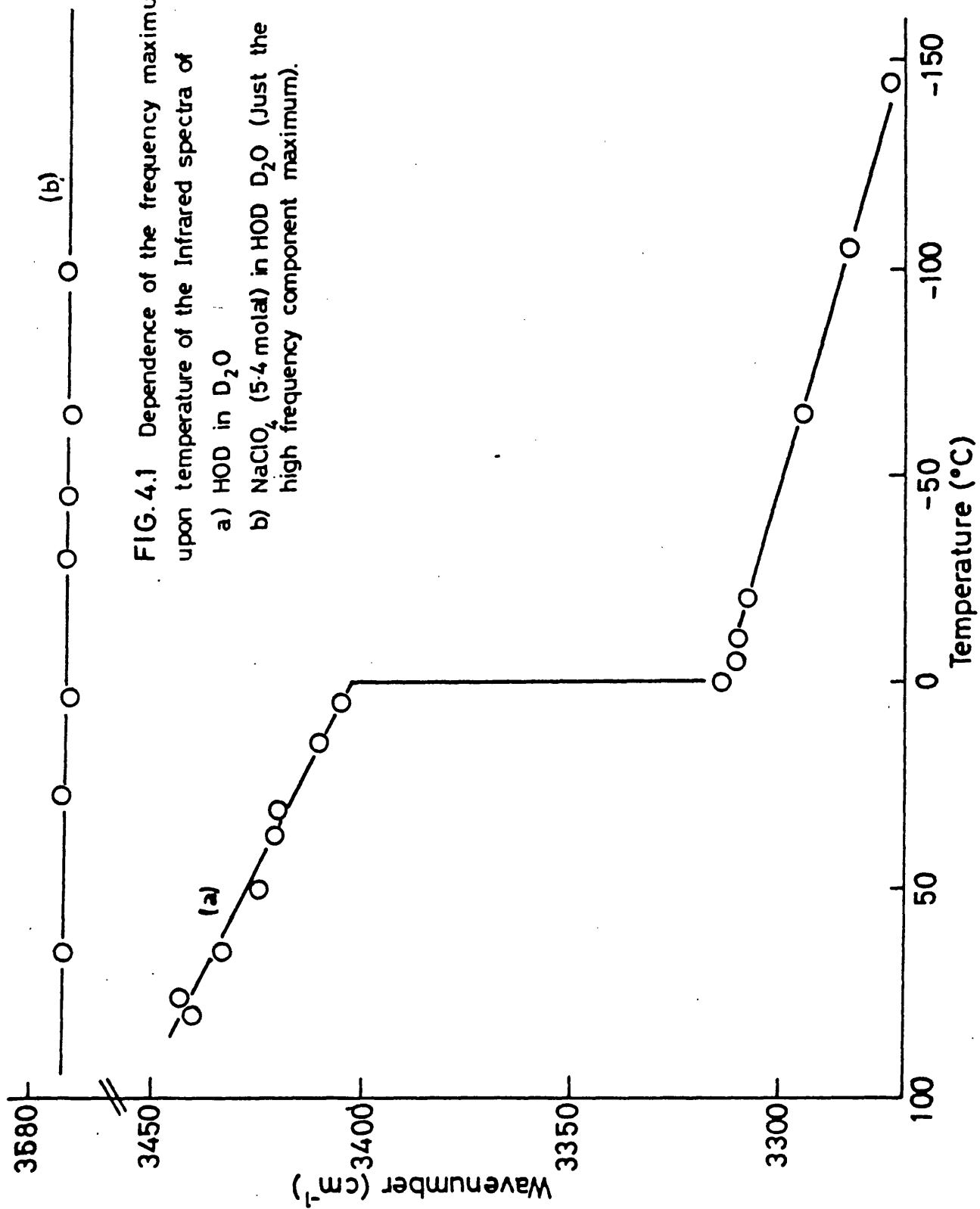
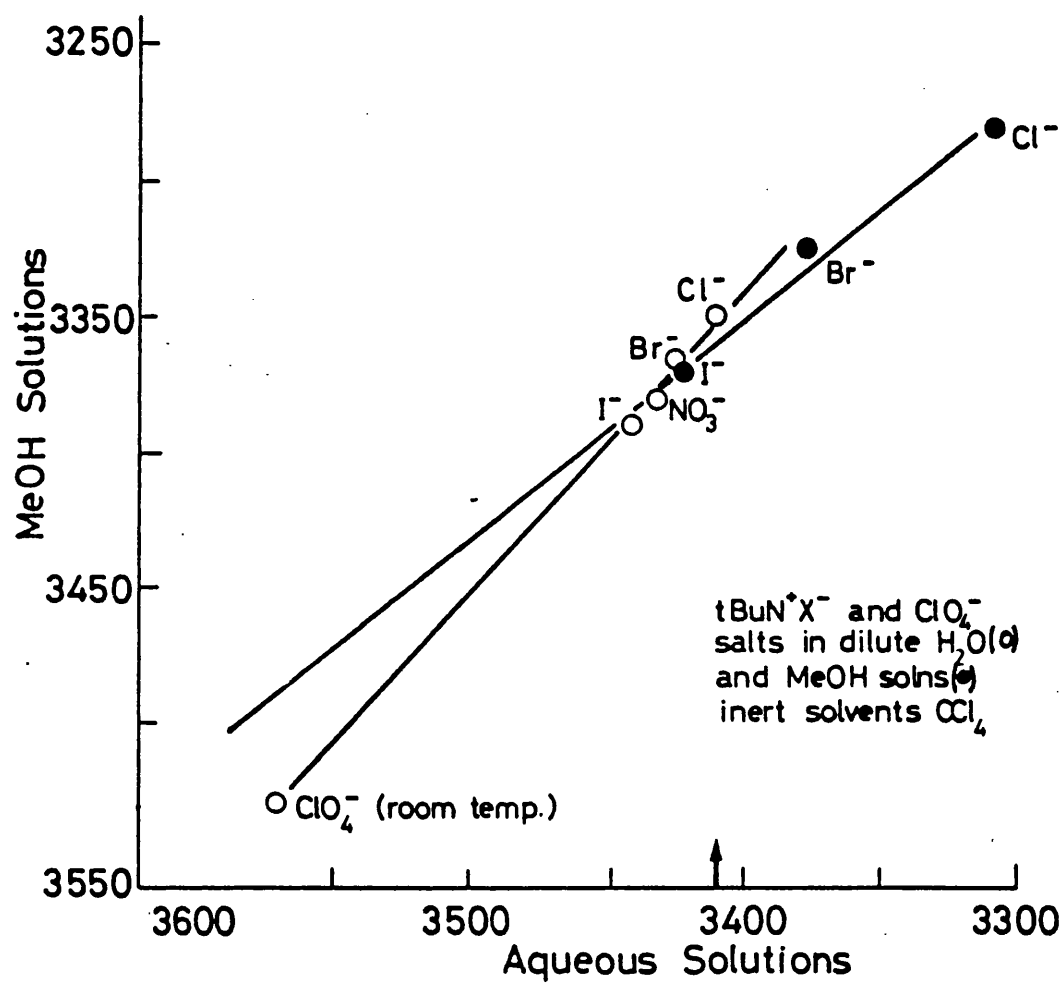


FIG. 4.2

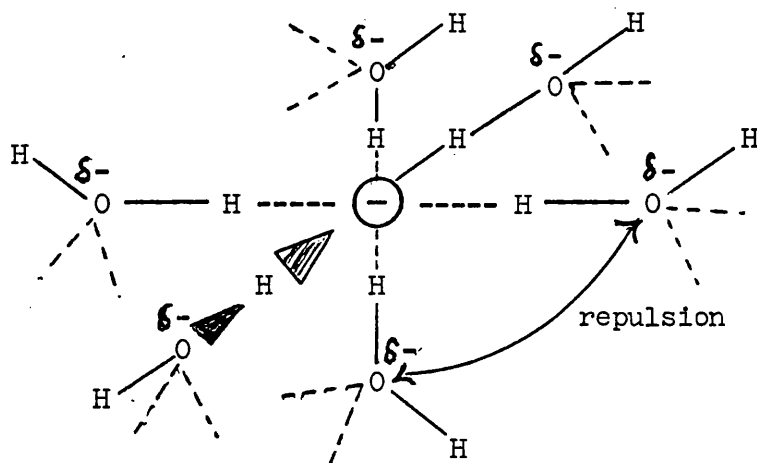


Correlation of the band frequency maxima obtained in aqueous and methanolic solutions at 298K.

general with the increase in ionic radius. These high-frequency shifts indicate weaker hydrogen bonding between water-anion interactions than water-water bonds.

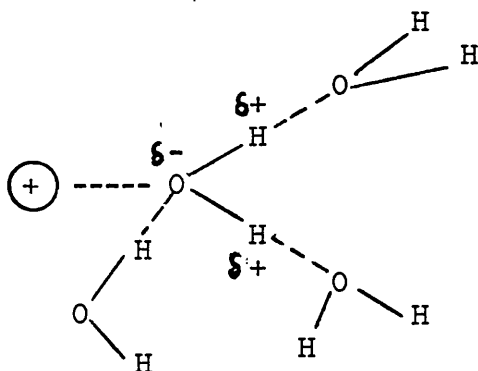
Another common property was that the resolved anion hydrate bands are relatively narrow and temperature insensitive while the cation solvates did not produce resolved bands and only the divalent and trivalent cations produced evidence of a cation solvate band by producing long low frequency tails. However from the shifts observed in the bulk water band at room temperature, the low frequency tails and the production of solvent shared ion pairs¹⁹ for methanolic solutions, the conclusion that alkali metal cations induced small high frequency shifts with the shift increasing with cation size and divalent cations induced small low frequency shift seemed valid. Even in concentrated solutions, widths were comparable with or broader than those for bulk water bands in glassy solutions and there was no indication of band narrowing such as that observed for the anion solvates.

These generalisations can be explained satisfactorily in terms of the following model. The hydrogen bonds formed in the water-anion interaction are weaker than those in water-water interactions because each anion forms more than the two bonds formed by water molecules. For example, from neutron and X-ray diffraction data²², for lithium chloride solutions, it has been deduced that each chloride ion forms six such bonds. Because of the powerful negative field around the ion, the negatively charged oxygen atoms of water molecules are constrained away from the anions. In addition to these forces, repulsion between the six co-ordinated molecules also occurs which forces the hydrogen bonds to the anion to remain linear and equivalent.



This ordering of the anion solvates explains the small widths of the absorption bands obtained and also the temperature insensitivity of the bands, provided that the solvation number of the anion does not alter. The reverse argument can also be applied stating that the band insensitivity infers a temperature independent solvation number.

In contrast, the hydrogen bonds for the cations are made to secondary solvent molecules that are themselves part of the bulk solvent structure. Hence variations in the strength of the cation-water bonds have only a secondary effect upon the O — H stretching frequencies.



This suggests that the span of available frequencies on the high frequency side of the bulk water band for the cations is far smaller than that for anions since even if the metal-water bond was infinitely weak, the O — H protons will generally remain bonded to neighbouring water molecules.

This would explain the smaller shifts observed for cation solvate bands and also the absence of any band narrowing and the temperature sensitivity remaining close to that for bulk water. These properties arise

because the O — H protons are directly bonded to bulk water and hence subject to the same influences such as hydrogen bond stretching and bending, and indeed, breaking.

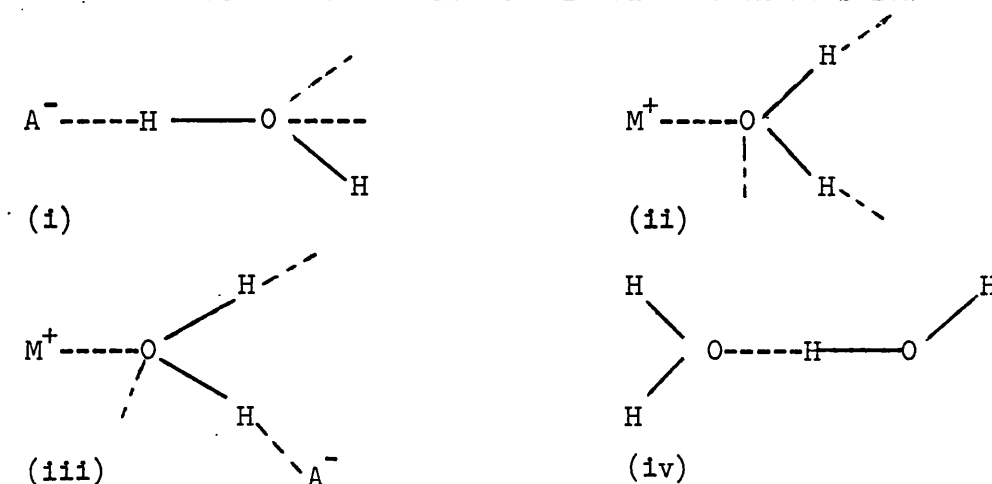
Steric crowding makes it difficult for the secondary solvent molecules in some cases to form good hydrogen bonds, so the probable increase in band-width relative to bulk water could be for this reason. Although quantitative data was difficult to obtain because no separate bands for bulk solvent and cation solvates were resolved, after deconvolution of the bands, the results seemed to confirm the above statement.

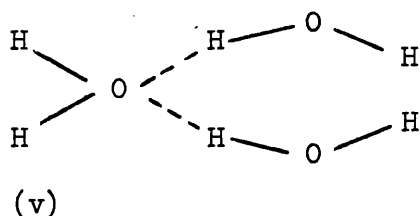
4.3 ROOM TEMPERATURE DATA AND DISCUSSION

Before attempting to analyse the low temperature results, room temperature data was collected from the literature which in some cases needed extending and in others repeating because the data obtained was in the O — D stretching region and so could not be used directly in conjunction with results in the O — H stretching region.

The O — H stretching band in the infra-red spectrum of HOD in liquid D₂O has been studied as a function of concentration of some electrolytes at room temperature. Although a lot of work has been done in this area,^{10,11,23} an extensive systematic survey was attempted to extract as much information as possible concerning different solvate species.

For liquids, the intermolecular distances and orientations are well distributed because of the different species present, which provides a spectrum containing absorption bands for solvent molecules bonded to cations and anions as well as other solvent molecules as shown below





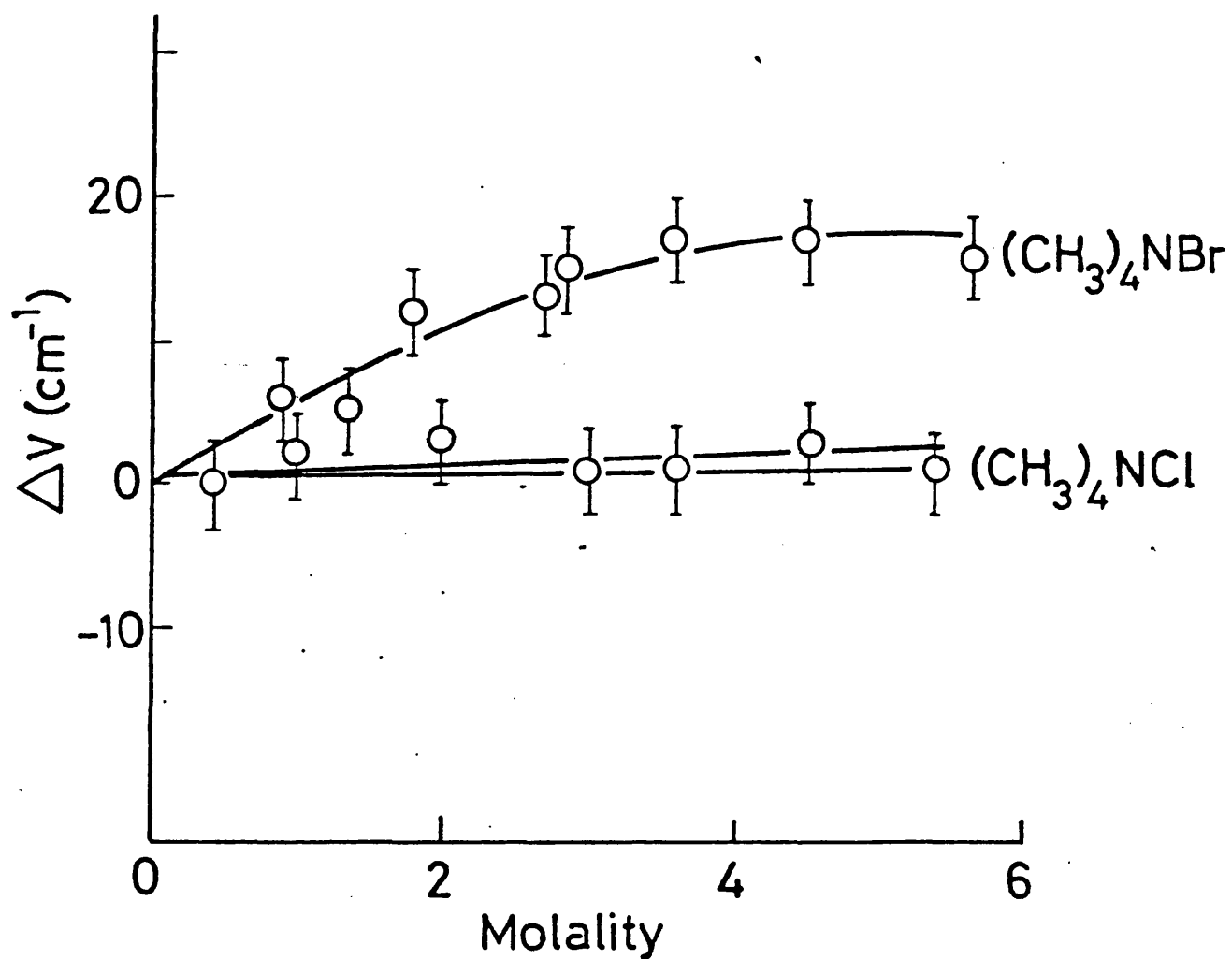
When the $\nu(\text{O} - \text{H})$ bands of HOD molecules in D_2O solutions containing electrolytes were recorded, changes in the frequency of the band maxima and band shapes were observed as the solute concentration was varied.

The band maximum of the $\text{O} - \text{H}$ stretching frequency of the pure HOD in pure D_2O at 298K occurred at $3410 \pm 3\text{cm}^{-1}$ which is in good agreement with previous results¹¹. This value was subtracted from the frequency the electrolyte solutions absorbed at to give a $\Delta\nu$ value that was then plotted against the molal concentration of the salt studied.

The first set of results plotted in this manner were the tetramethylammonium halide solution results shown in Figure 4.3. From this diagram, the point of interest was the limiting shift value which we tentatively suggest pinpoints the chloride solvate band at 3412cm^{-1} which would show that the chloride-water and the water-water interactions are very similar in strength. The bromide salt solution results, however, produced a gradual high frequency shift with the increase in solute concentration until a concentration of 4 molal had been reached, whereupon the band frequency value gradually tailed off to produce a steady value of 3427cm^{-1} . This limiting shift value has been taken as indicative of a bromide shift and occurs 15cm^{-1} to the high frequency side of the chloride solvate band. (These assignments require that the N^+ ion has a negligible effect upon the spectra.)

After establishing these two anion solvate bands, attention was turned towards results obtained from aqueous electrolyte solutions. The first set of salts studied were the lithium halides. The picture here becomes more complicated because of the competition between the anion, cation and water-water solvate bands at low concentrations with the

FIG. 4.3



Dependence of frequency maximum on concentration
(mol Kg^{-1}) of added salt in HOD/ D_2O solutions.
(Infrared Spectra)

addition of a fourth band due to a solvent shared ion pair to add further complications at high concentrations.

A brief explanation showing the difference between a real frequency shift and one that shows an overall effect because of two or more bands might be of use. An example of the former is the frequency shift ν temperature graph as shown in Figure 4.1 where there is a linear relationship between the two observed properties.

However in the latter case where two components overlap through an isosbestic point, a straight line plot was not obtained as shown in Figure 4.4. Gradual slopes are obtained when either of the two species predominate at the frequencies the bands would absorb at individually. These slopes are joined by a rapid change of frequency in the intermediate region when neither species predominates around the isosbestic point frequency.

The lithium salt data can be best represented by a diagram (Figure 4.5). From the tetramethyl ammonium chloride result, the anion solvate has been pinpointed to absorb at 4312cm^{-1} . Lithium chloride solutions produce a graph that initially (below 2 molal) gives no frequency shift, in the intermediate concentration region there is a small high frequency shift, and this tails off at higher concentrations to give a stable frequency value of 3422cm^{-1} . At these concentrations of over 4 molal, the solvent shared ion pair must be affecting the band, and so this high frequency shift of 10cm^{-1} has been attributed to the lithium solvate as the anion has only a very small effect. Having obtained this information, the other anion/solvate bands have been assigned to absorb at the following frequencies: Br^- at $+15\text{cm}^{-1}$, I^- at $+30\text{cm}^{-1}$ and NO_3^- at $+20\text{cm}^{-1}$.

Using the above arguments, we have been able to produce a diagram (Figure 4.8) that summarises the obtained data (Figures 4.6 and 4.7) and produces relative anion and cation solvate bond strengths. The solvate band shifts are checked and counterchecked as was described in the previous chapter

FIG. 4.4

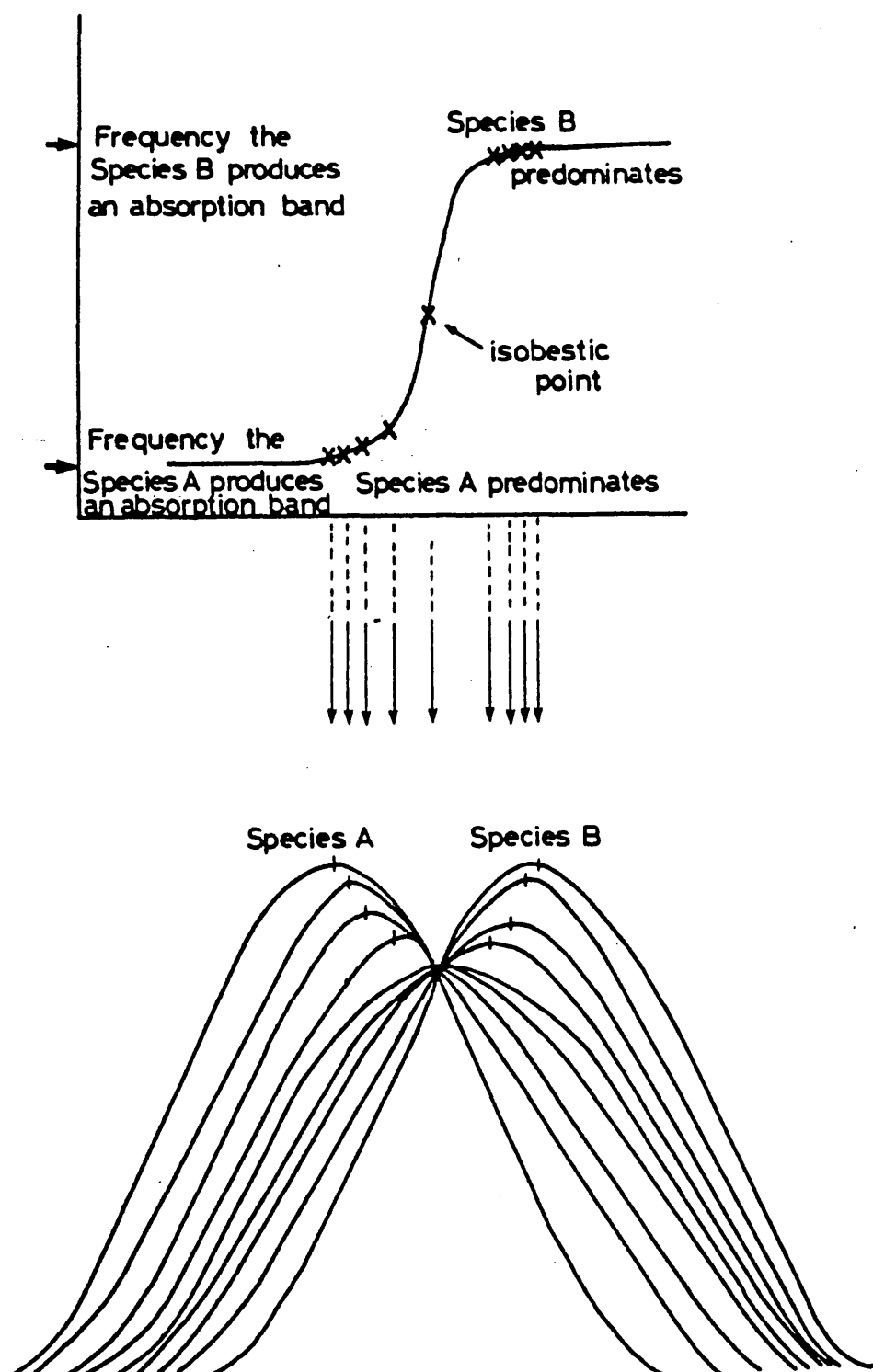
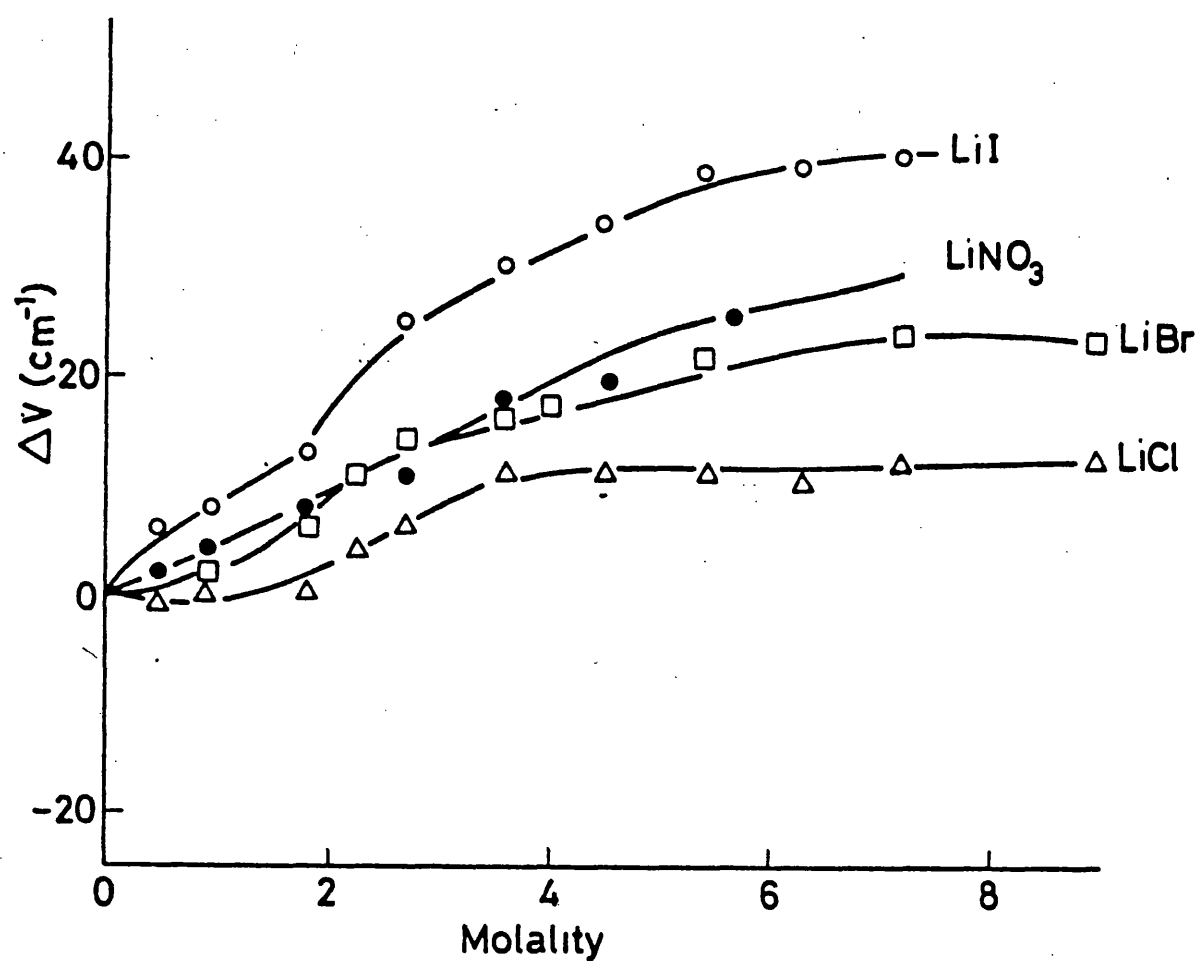
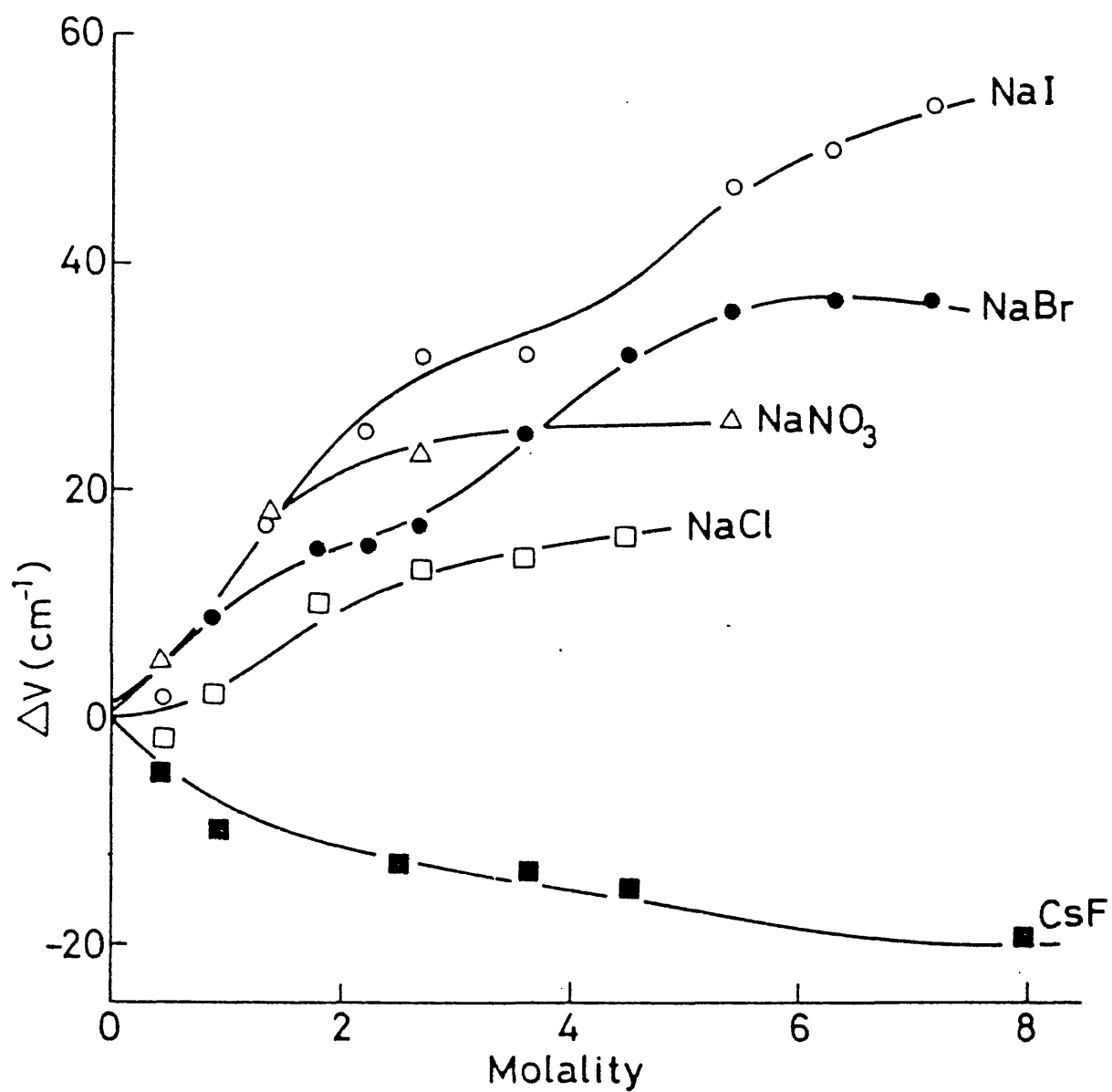


FIG. 4.5



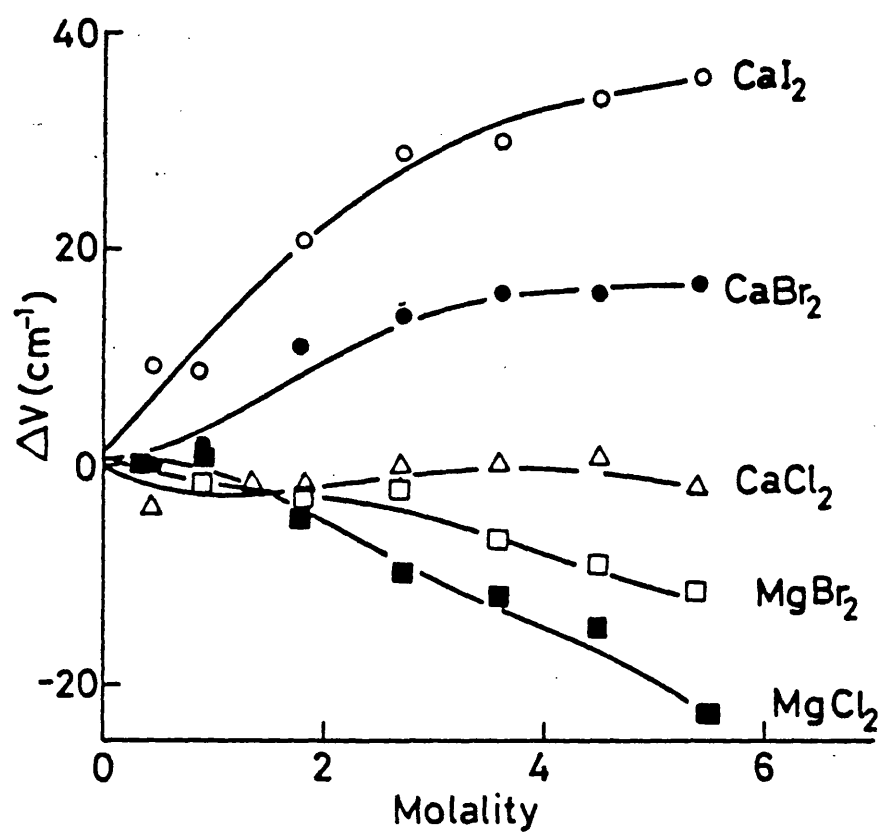
Dependence of frequency maximum on concentration (mol Kg⁻¹) of added salt in HOD/D₂O solutions, (Infrared Spectra) at room temperature.

FIG. 4.6



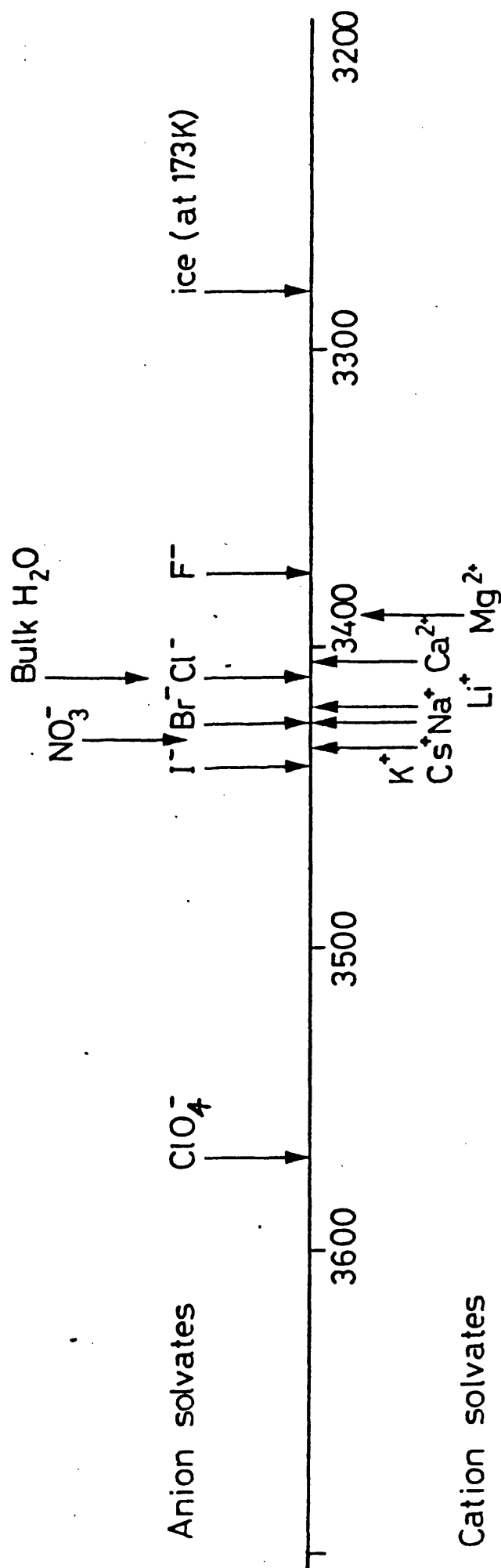
Dependence of frequency maximum on concentration (mol Kg^{-1}) of added salt in HOD/ D_2O solutions, (Infrared Spectra) at room temperature.

FIG. 4.7



Dependence of frequency maximum on concentration (mol Kg^{-1}) of added salt in $\text{HOD}/\text{O}_2\text{O}$ solutions at room temperature. (Infrared Spectra)

FIG. 4.8



Location of major component bands observed in the infrared spectra of electrolytes in HOD/D₂O at 298K.

for methanolic solutions. The anion series order of increasing average bond strength in solution is $\text{ClO}_4^- < \text{I}^- < \text{NO}_3^- < \text{Br}^- < \text{Cl}^- < \text{F}^-$ with the cation series being $\text{Cs}^+ = \text{K}^+ < \text{Na}^+ < \text{Li}^+ < \text{Ca}^{2+} < \text{Mg}^{2+}$.

4.4 LOW TEMPERATURE RESULTS AND DISCUSSION

The aim of obtaining the low temperature data was to resolve out bands that were contained in the broad envelope at room temperature and so further justify our assignments that have been made in the last section. The procedure used to discuss the data is to consider each salt individually and draw some conclusions at the end of the chapter.

(1) Sodium Tetrphenylboron

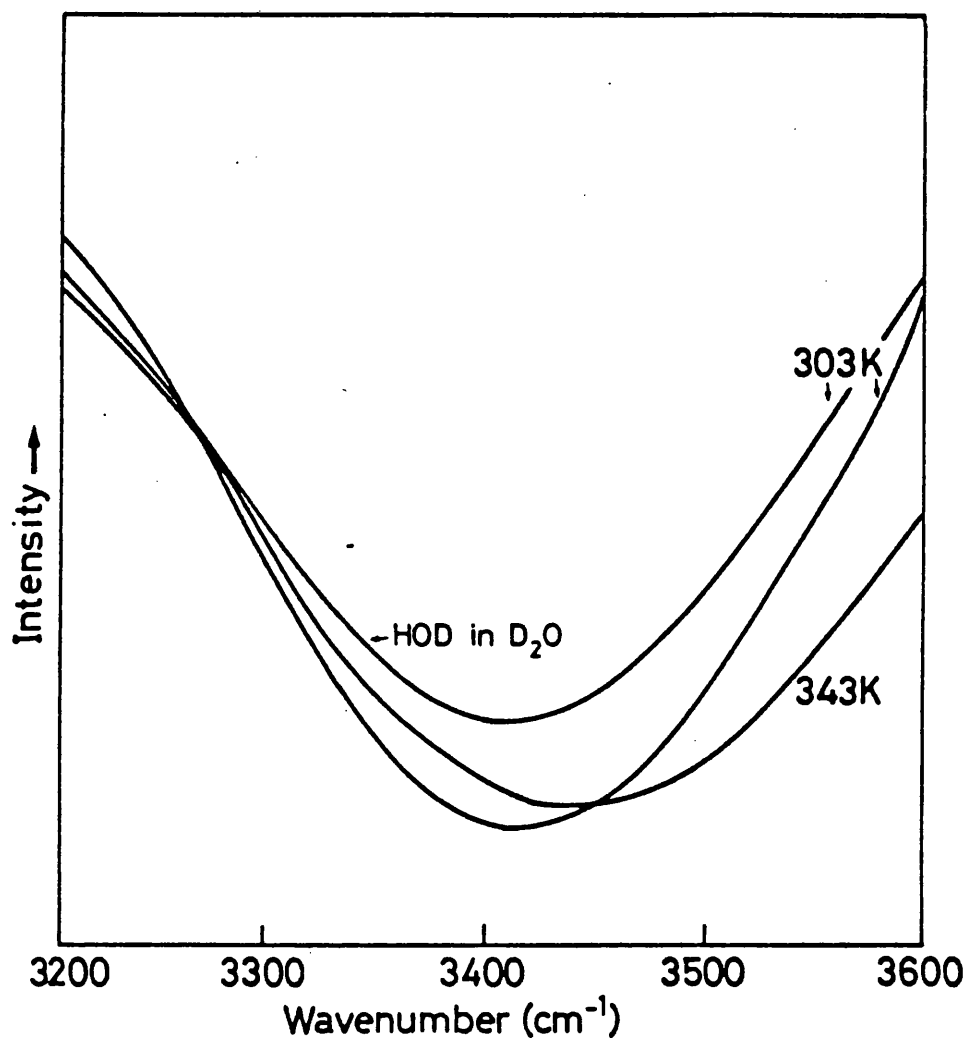
The low temperature spectra of aqueous solutions of sodium tetraphenylboron unfortunately were not as informative as the methanolic solutions¹⁹ because of two factors. The first was that the solubility of the salt in methanol was more than twice that in water, and the second factor was that the aqueous solution phase separated on cooling below ca 250K. Some information was obtained when saturated aqueous solutions of the salt were heated to temperatures ca 340K.

The Raman^{5,24} and infra-red spectra²⁵ of the uncoupled O — H stretching band of pure water showed only slight asymmetry on heating to ca 340K. However, a saturated solution of sodium tetraphenyl boron in isotopically diluted water gave a typically broad O — H stretching band with a high frequency shoulder appearing at 3550cm^{-1} at room temperature. This increased in intensity and became more pronounced as the temperature was raised as shown in Figure 4.9.

We denote the 3550cm^{-1} absorption band to (O — H)free groups because an increase in the concentration of sodium tetraphenylboron results in a large increase in the 7120cm^{-1} absorption band which has been attributed to (O — H)free groups⁷.

This can be explained by accepting that O — H groups will preferentially remain bonded to water molecules rather than form very weak

FIG. 4.9



Infrared absorption spectra of HOD in D₂O in O-H stretching region at 303K and of a saturated solution of sodium tetraphenyl boron in HOD in D₂O at 303K and 343K.

and ill-defined hydrogen bonds to the phenyl groups of the BPh_4^- ions. The sodium ion forms bonds with the oxygen lone pairs of the solvent molecules which leaves an excess of (O — H) free groups. For methanolic solutions we suggest these groups form weak hydrogen bonds to the second set of lone pairs of electrons, but for water there are no such extra lone-pairs, and so these OH groups remain effectively "free".

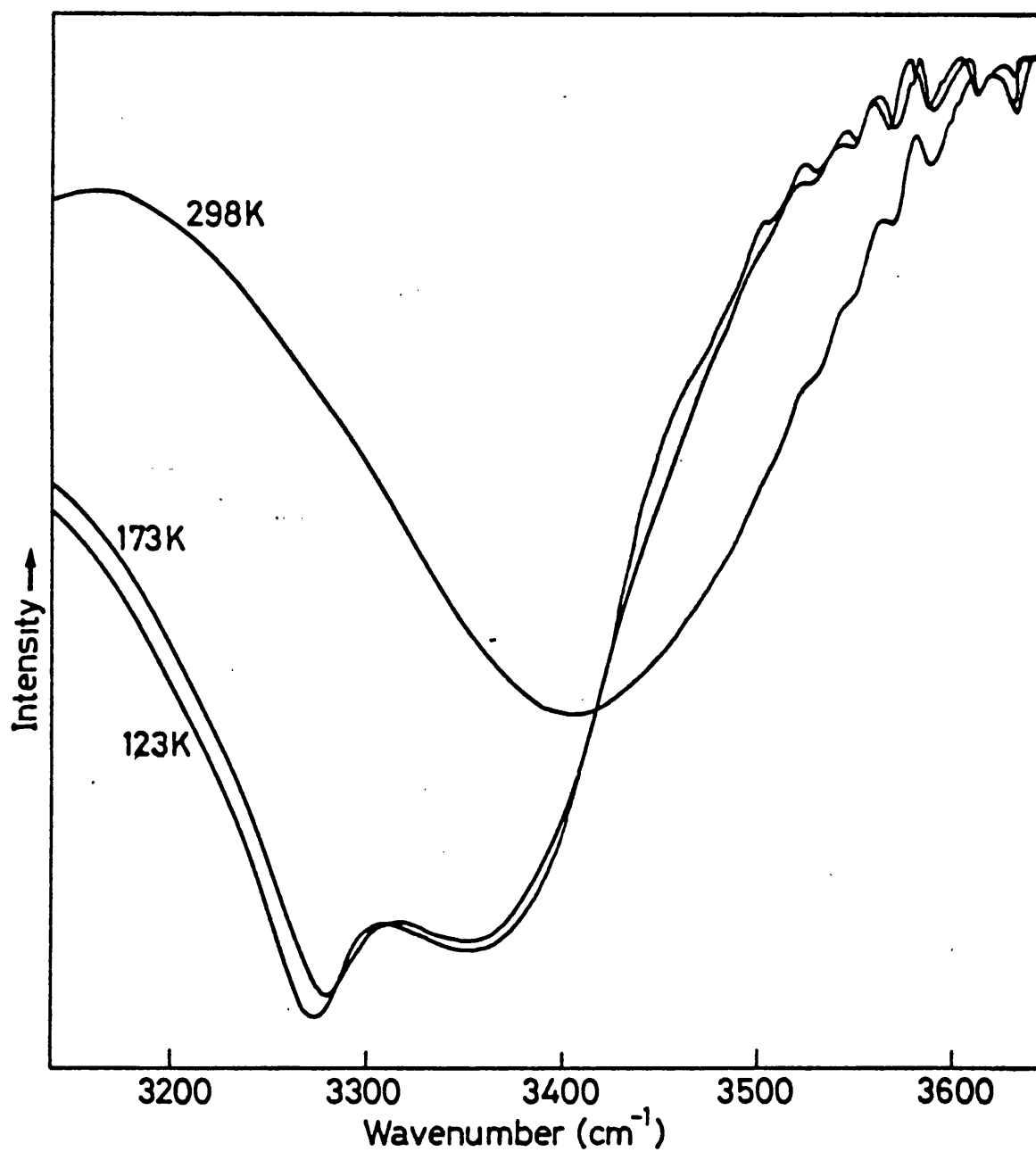
(11) Tetra alkyl ammonium Halides

On cooling to ca 170K dilute tetramethyl ammonium chloride and bromide solutions (< 2 molal) produced infra-red spectra with just the normal ice line at 3280cm^{-1} indicating phase-separation. More concentrated chloride solutions produced a broad absorption band centred at 3370cm^{-1} that increased in intensity with an increase in concentration of salt whilst the sharp ice feature diminished, (Figure 4.10). We assign the 3370cm^{-1} band to the chloride solvate, it has a half-width of ca 100cm^{-1} . At concentrations above 3 molal solutions of tetramethyl ammonium bromide produced spectra containing an ice peak and a narrow band at 3440cm^{-1} having a band width of ca 40cm^{-1} at low temperatures. We attribute this higher frequency band to water molecules associated with the bromide anion in a crystal hydrate structure.

The low temperature spectra obtained from aqueous tetrabutyl ammonium chloride and bromide displayed three peaks: a sharp ice-like peak at 3280cm^{-1} , a broader strong absorption band at 3340cm^{-1} and a less intense broad band in the chloride case at ca 3420cm^{-1} (as shown in Figure 4.11), and for the bromide salt at ca 3430cm^{-1} . For dilute solutions only the ice band was prominent but on increasing the concentration of the salts the pattern that emerged from the spectra was the gradual disappearance of the ice band, the growth of the broad band in the 3340cm^{-1} region and the appearance of a shoulder in the 3420cm^{-1} region.

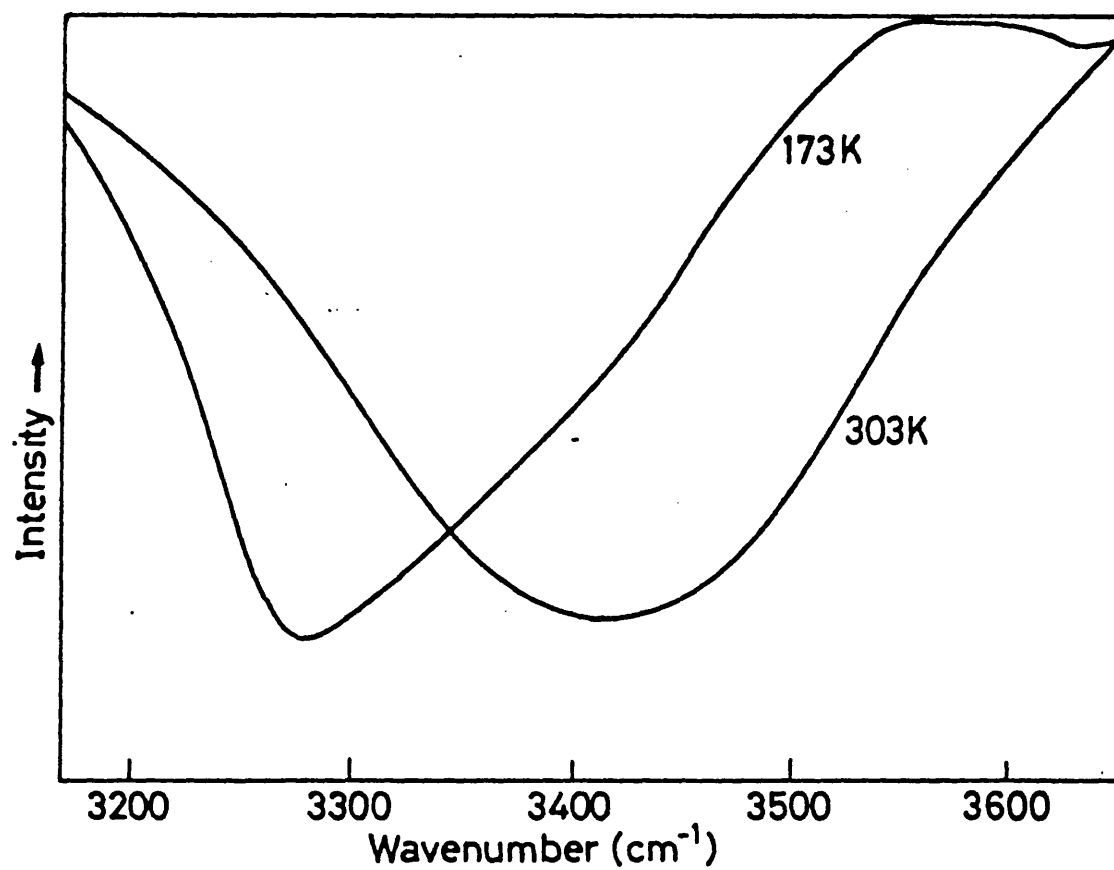
As each water molecule is hydrogen bonded to its four nearest neighbours in both clathrate hydrates and ices, we believe that the more

FIG. 4.10



Infrared absorption spectra of HOD in D₂O in the region containing (CH₃)₄NCl (9 molal) at three temperatures 298K, 173K and 123K.

FIG. 4.11



Infrared absorption spectra of HOD in D₂O in O-H region containing (C₄H₉) NBr (1.25 molal) at 303K and 173K.

concentrated tetrabutyl ammonium halide solutions tend to form clathrate hydrates. The fact that O — O bond lengths only exceed those in hexagonal ice (2.76\AA) by 1% makes them comparable with most forms of ice and is consistent with the correlation between hydrogen bond lengths and the frequency at which the bond absorbs²⁶. This correlation will be discussed later. We believe that the ca 3340cm^{-1} absorption band is due to water molecules forming clathrate hydrate cages around the tetrabutyl ammonium ions with the halide anions replacing some water molecules in the cage structure to produce a distorted cage which broadens the absorption band considerably as compared with the structured ice band and weakens the hydrogen bonded structure. This explains the high frequency shift of this band when compared with the structured ice band.

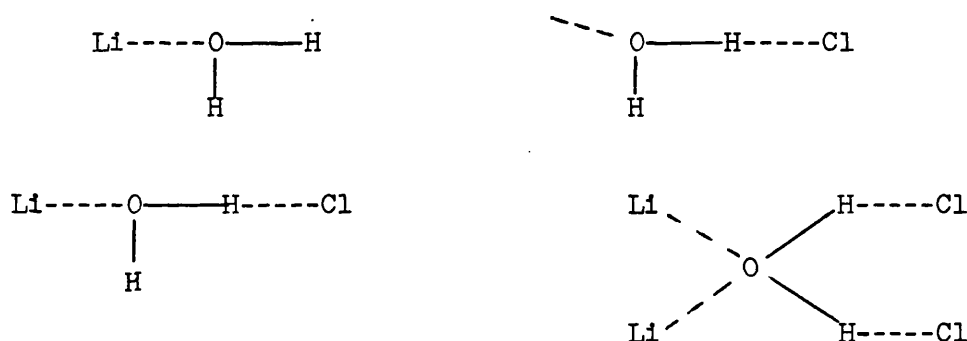
Room temperature chloride and bromide solutions of many electrolytes absorb in the 3420cm^{-1} region. When these solutions are cooled to ca 170K, sharp hydrate features in this same 3440 to 3420cm^{-1} region are observed. With these two points in mind it seems reasonable to attribute the 3420 and 3430cm^{-1} absorption bands to water molecules associated with the halide ions which have replaced water molecules in the clathrate hydrate structure.

Low temperature solutions of tetra ethyl ammonium fluoride in isotopically dilute water produced similar spectra, with bands at 3240cm^{-1} and 3380cm^{-1} as well as the ice band at 3280cm^{-1} . As the hydrogen bond strength for the halide ions increases in the order $\text{F}^- > \text{Cl}^- > \text{Br}^- > \text{I}^-$ 11 we have attributed the 3380cm^{-1} shoulder to water molecules hydrogen bonded to the fluoride ion in the actual cage structure. The 3240cm^{-1} band is attributed to the other water molecules engaged in the hydrate structure. The low frequency shift of this band, as compared with the tetrabutylammonium halides is probably due to the small fluoride ionic radius compared with the chloride and bromide radii which ensures no distortion in the clathrate hydrate cage because the radii of oxygen and fluoride ions are very similar. As fluoride ions form stronger hydrogen bonds the difference in band frequency

of the ion band and the 3240cm^{-1} band could be attributed to strengthening the hydrate cage structure by the fluoride ion in addition to the tetraethyl ammonium ion being a more ideal guest ion.

(iii) Lithium Salts

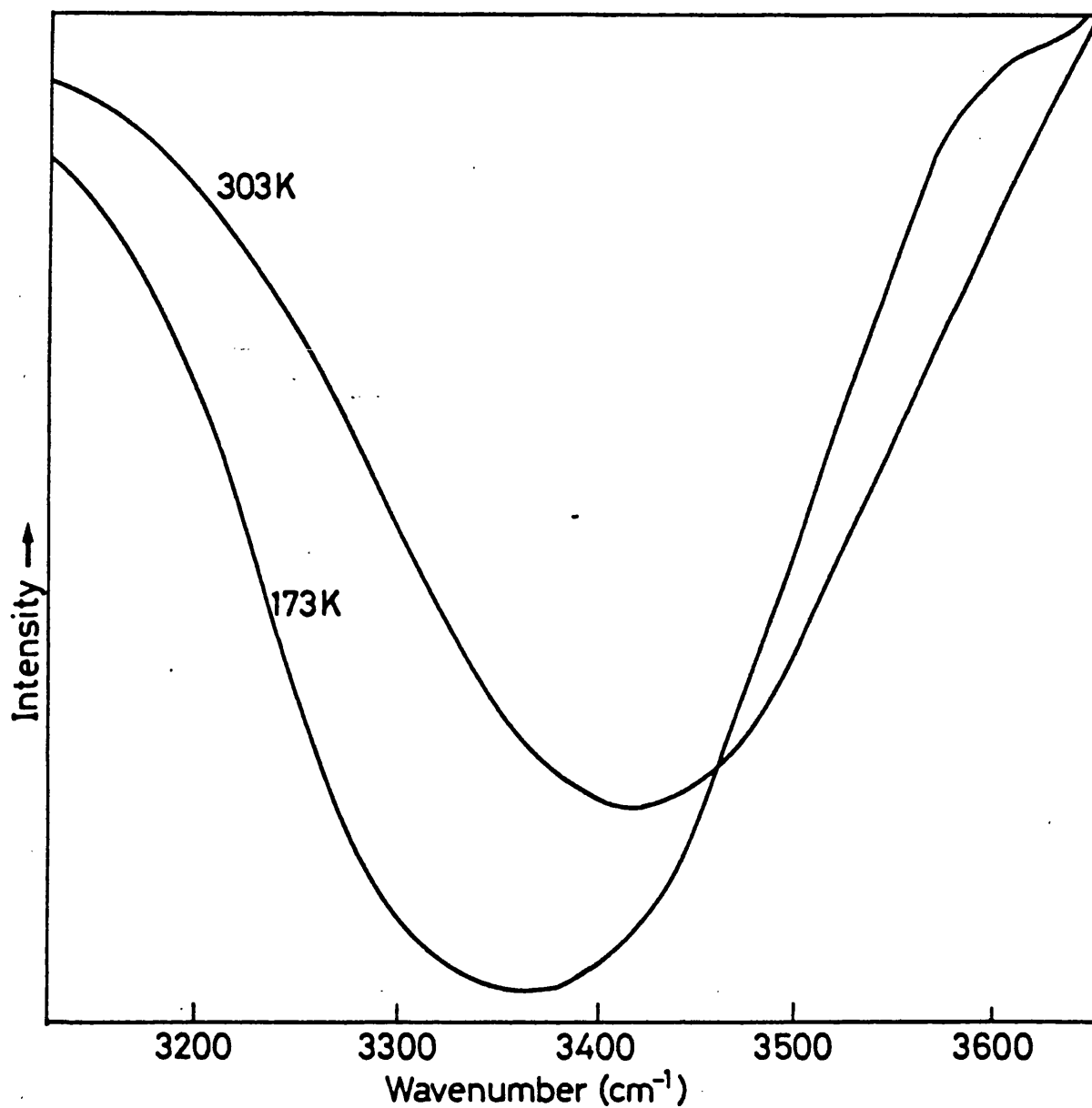
On cooling aqueous lithium bromide and chloride solutions to ca 170K, the infra-red spectra obtained displayed very similar characteristics for both salts. For low concentrations of salt (< 2.5 molal) only the distinctive ice band with a long high frequency tail was observed. On curve analysis, this tail was split into two broad absorption bands centred at 3310 and 3430cm^{-1} . The interpretation we have given this spectral data is that the majority of the water molecules form ice, but the remaining water molecules are either associated with anions and cations or surrounded by both ions in a solvent shared situation.



With increasing molality of salt, a broad absorption band in the 3370cm^{-1} region became increasingly prominent until, for very high concentrations (> 7 molal), this broad band becomes the only feature. This band occurs at 3360cm^{-1} for lithium chloride solutions and 3375cm^{-1} for the lithium bromide solutions. All the spectra were recorded at 170K. This difference of 15cm^{-1} we have attributed to the relative bond strengths of $\text{O}—\text{H}—\text{Cl}$ and $\text{O}—\text{H}—\text{Br}$ as the cation in both cases was lithium. This broad envelope overlaps the 3310 and 3430cm^{-1} bands observed in dilute solutions and is very similar to the liquid phase band at room temperature. (Figure 4.12)

From previous work recorded by others²⁷, lithium chloride is a glass former, and so we have attributed this broad liquid-like band to the lithium

FIG. 4.12



Infrared absorption spectra of HOD in D₂O in the O-H stretching region containing lithium chloride (9 molal) at two temperatures 303K and 173K.

chloride glass. Accepting the properties of glasses, which were discussed earlier, a broad envelope shifted down to lower wave number by 60cm^{-1} and increased in intensity is the expected outcome of glassification, but unfortunately is not as informative as narrow hydrate lines obtained from other salts investigated.

Low temperature spectra of dilute aqueous lithium sulphate solutions gave a broad "ice" peak with a high frequency tail in the usual wavenumber region. The "ice" peak was twice the width of the pure isotopically diluted ice band. This broadening was due to an underlying broad absorption band centred at 3310cm^{-1} . On increasing the concentration of salt to its saturation point, the high frequency tail developed into a broad absorption envelope which overlapped the 3280cm^{-1} band and the tail absorption. On curve analysing the dilute solution spectra a minimum of three bands were needed, centred at 3280, 3310 and 3470cm^{-1} . The 3310cm^{-1} band we have attributed to water molecules associated with the cation as this band also appears in low temperature results of lithium halides. The 3470cm^{-1} band has been assigned to anion solvation which is in good agreement with the bond length²⁸ and the band position correlation which will be discussed later and the infra-red data on the lithium sulphate monohydrate²⁹.

In complete contrast to the other lithium salt solutions, lithium nitrate solutions at low temperatures produced spectra containing four distinct, narrow absorption bands at 3280, 3380, 3475 and 3533cm^{-1} . These peaks were produced even at low concentration of salt and the only observable difference in spectra between a 1.8 and 9.0 molal solution at 170K was the slight increase in intensity of the three high frequency bands and a decrease in the ice band intensity. These narrow features are attributed to separated crystallites of a cell defined hydrate whose crystal structure has not been determined.

(iv) Caesium Salts

Dilute and concentrated aqueous solutions of caesium chloride and

bromide at 170K produced very similar infra-red spectra to that of HOD in D_2O in the OH stretching region. Caesium nitrate, although not very soluble in water, appeared to modify the shape of the ice band by broadening the peak and decreasing its intensity.

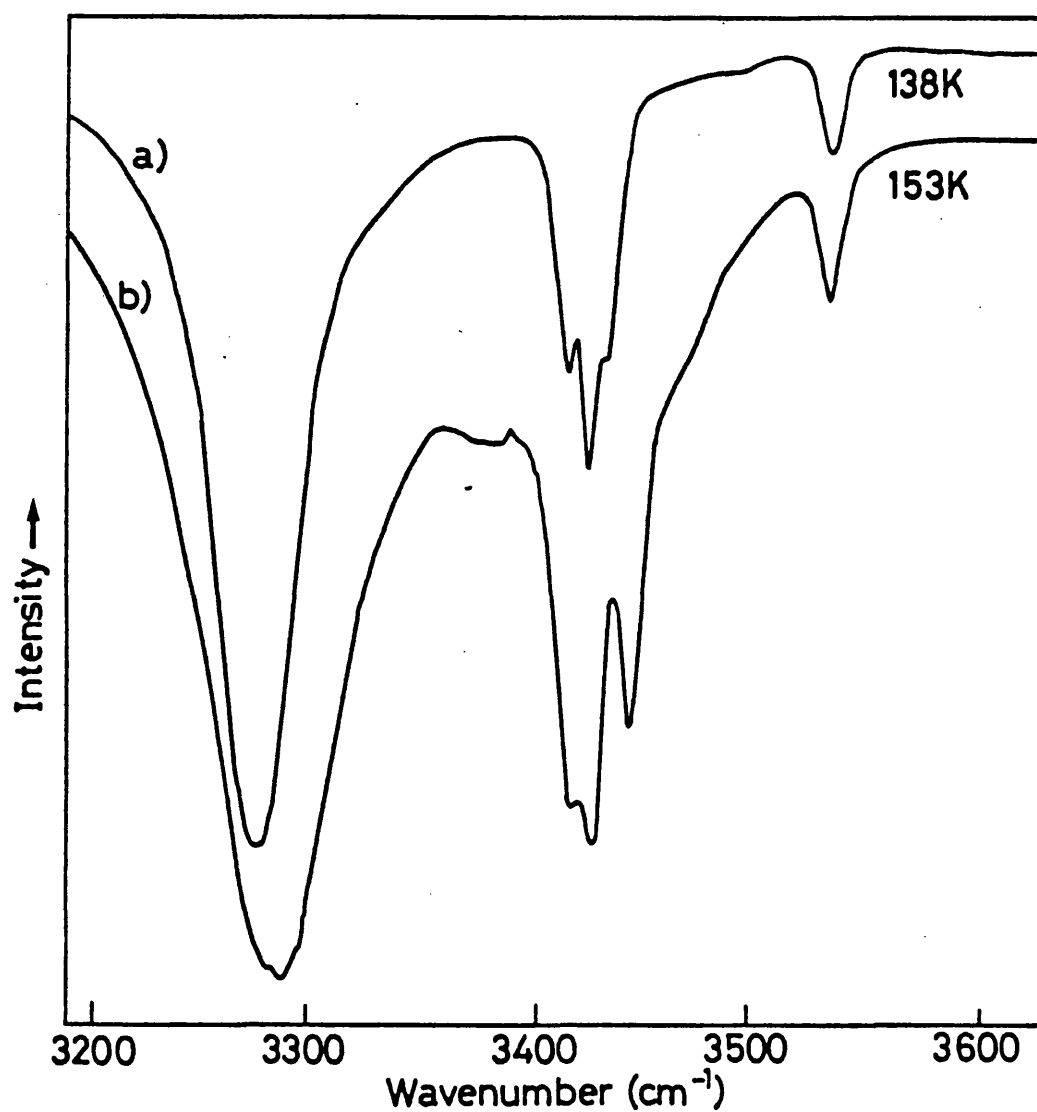
Caesium fluoride at low concentrations in aqueous solutions produced a broad ice band at 3280cm^{-1} with a high frequency tail at 170K. When the concentrations of the salt was increased to over 10 molal, a broad envelope centred at 3340cm^{-1} was obtained. For intermediate concentrations, an intermediate spectral picture was obtained, containing both the ice band at 3280cm^{-1} and a high frequency band in the 3380cm^{-1} region. Only tentative assignments can be offered as explanations. From the tetraethyl ammonium fluoride results, we have assigned the 3380cm^{-1} band as the anion solvation band. The broad envelope of the cooled down concentrated solutions is due to the glassy state. However, this broad envelope seems to contain stronger bonds than lithium chloride and bromide as it absorbs at a lower frequency than either of the two lithium halides inferring that we have $I^- < Br^- < Cl^- < F^-$ for the order of increasing average hydrogen bond strength in solution and also glasses.

(v) Sodium Salts

Most of the sodium salt solutions when cooled to ca 170K gave narrow multiline spectra with the exception of sodium chlorate, sodium hydroxide and salts that split the O — H stretching band like sodium hexafluorophosphate and perchlorate. The latter group of salts will be discussed in a different section later in this chapter.

Saturated aqueous sodium chloride solutions produced an ice band at 3280cm^{-1} , an apparent triplet of bands at 3415, 3425 and 3435cm^{-1} and a high frequency band at 3535cm^{-1} (see Figure 4.13). This infra-red data is in good agreement with the dihydrate results obtained by Schiffer³⁰ and Ford and Falk³¹. From neutron diffraction data³², we have acquired the bond lengths in the dihydrate. The infra-red spectrum inferred the existence

FIG. 4.13



Infrared absorption spectra of HOD in D_2O in the O-H stretching region containing a) sodium chloride (4 molal) at 138K and b) sodium bromide (10 molal) at 153K.

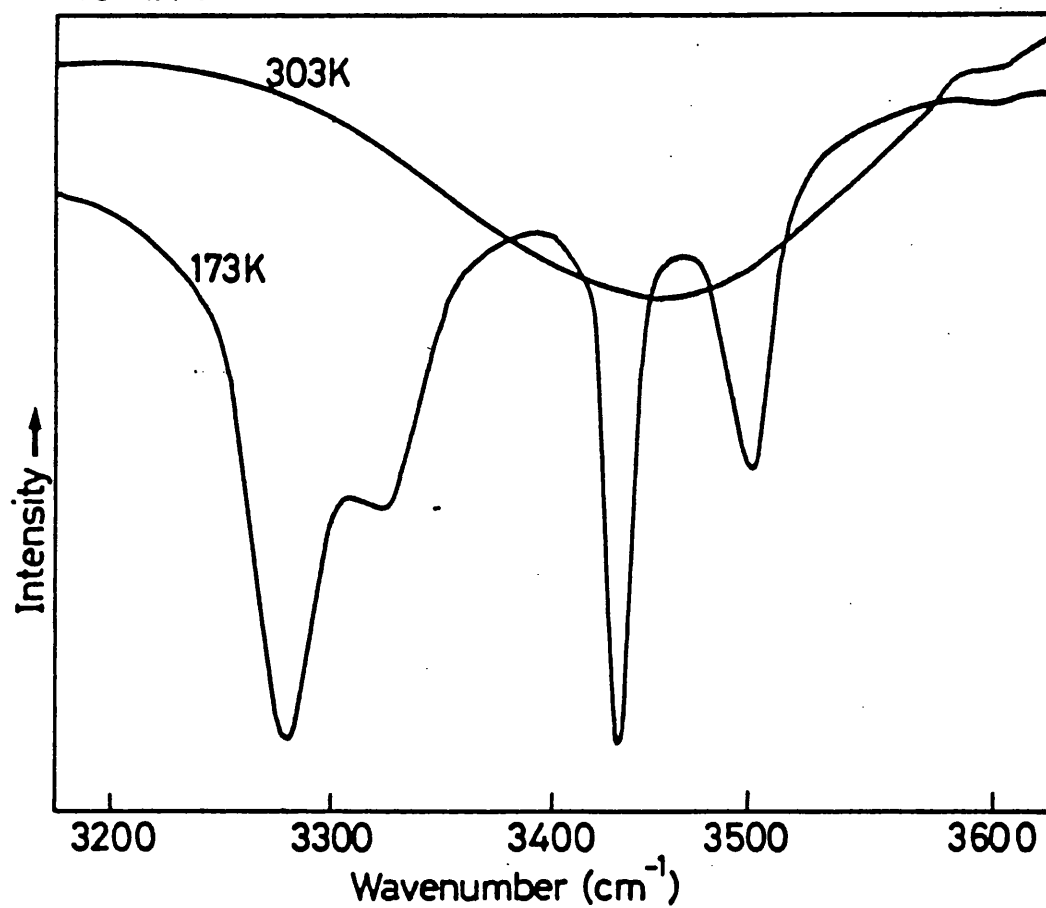
of three O — H groups with hydrogen bonds of nearly identical strength, and a fourth O — H group more weakly hydrogen bonded and in fact the O—H---Cl bond lengths of 3.223, 3.199, 3.196 and 3.364Å backed up this information. Around each cation we have four oxygen atoms from four water molecules and two chlorine atoms in cis positions in an octahedral configuration. Each chloride ion is surrounded by four protons from water molecules and two sodium ions in cis positions. Each tetrahedrally orientated water molecule has two chloride ions hydrogen bonded and two sodium ions co-ordinated by the lone-pair orbitals of the molecule. The reason behind the weak band at 3535cm^{-1} is due to some restrictive property of the crystal enforcing this hydrogen bond to be longer and more highly bent than the other three O—H bonds associated with chloride ions. And so the spectra obtained from aqueous sodium chloride solutions is that of sodium chloride dihydrate and ice.

Dilute aqueous solutions of sodium bromide (<4.5 molal) on cooling produced samples that gave unresolvable spectra in the 10-20% transmission range because of scattered radiation by the opaque material formed. However, the addition of a small amount of t-butanol prevented the formation of this opaque material and produced spectra that contained the usual but broader ice line and two broad, weak absorption bands at 3420 and 3470cm^{-1} . The amount of t-butanol used was too small to have a significant effect on the spectra as this was checked beforehand.

In the concentration range 5 to 7.5 molal we have obtained spectra containing narrow absorption bands at 3280, 3330, 3430 and 3490cm^{-1} (as shown in Figure 4.14). However, for salt concentrations greater than 8 molal, a different set of narrow bands are produced at the following wavenumbers: 3280, 3420, 3425, 3445 and 3535cm^{-1} .

From other infra-red dihydrate results published³⁰, we have attributed the latter set of peaks to water molecules in the sodium bromide dihydrate. From the structural data of the dihydrate³³, we find as in the case for sodium chloride dihydrate, three very similar O—H---Br bond lengths

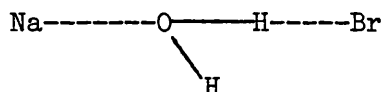
FIG. 4.14



Infrared absorption spectra of HOD in D₂O in the O-H stretching region containing sodium bromide (7.2 molal) at two temperatures, 303K and 173K.

and one much longer. In both cases the narrow bands show that the water molecules must be fully ordered in their hydrates. The explanation of the spectra obtained is identical to the sodium chloride dihydrate case. The slight shift of all the bands to higher frequency in the bromide salt case can be explained in the comparative hydrogen bond strengths of the chloride and bromide anions.

The explanation for the results obtained in the intermediate range of concentrations is not so clear. However, we have assigned the 3330cm^{-1} band to the cation solvate. The shift of 50cm^{-1} from the pure solvent band of the cation solvate band to higher frequency is in good agreement with the similar cation shift observed in the low temperature methanolic solutions. The 3430cm^{-1} band has been attributed to water molecules associated with the anion. This correlates well with the dihydrate and room temperature data. The high frequency band at 3490cm^{-1} could be due to the solvent shared ion pair, as

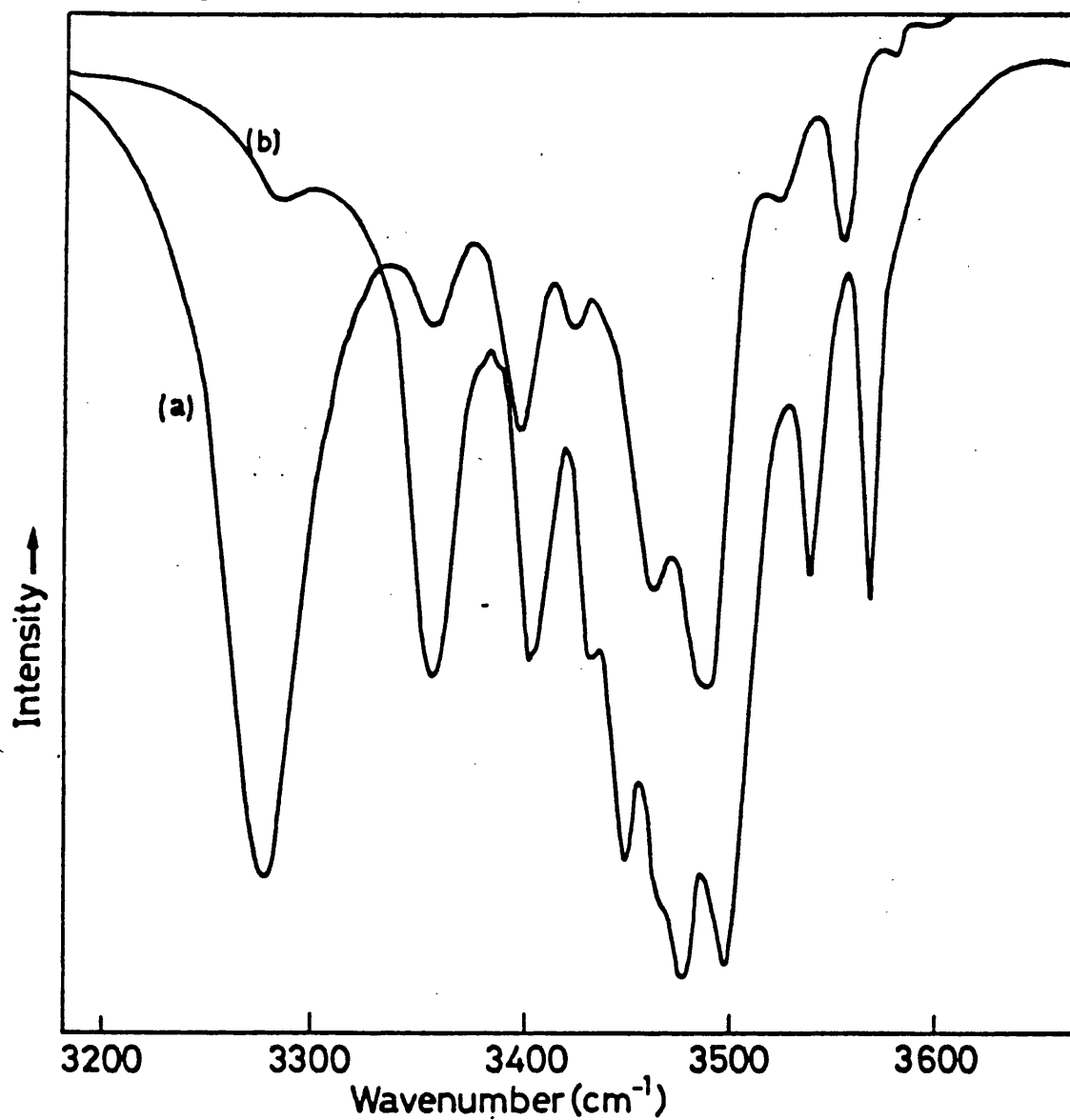


the difference between the anion band and this band is ca 60cm^{-1} , ⁵⁰, so this could be a satisfactory explanation.

Cooled down sodium iodide solutions produced an even more complicated picture with a spectrum that contained nine narrow peaks which appeared at all concentrations above five molal, and with a trace of t-butanol were obtained at concentrations down to 3.5 molal. These bands can be seen in Figure 4.15. At lower molalities just the normal ice band at 3280cm^{-1} with a high frequency tail was obtained. This ice band, however, decreased in intensity with increasing molality until at 11 molal only a weak absorption band occurred.

From the most direct techniques for structural information on solutions such as X-ray and neutron scattering^{34,35}, the information obtained has led to the conclusion that most water molecules are tetrahedrally

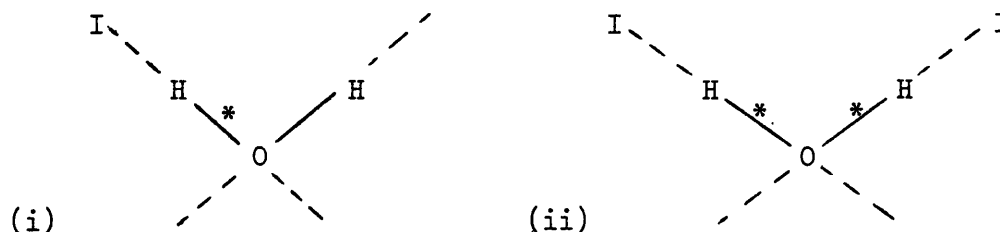
FIG. 4.15



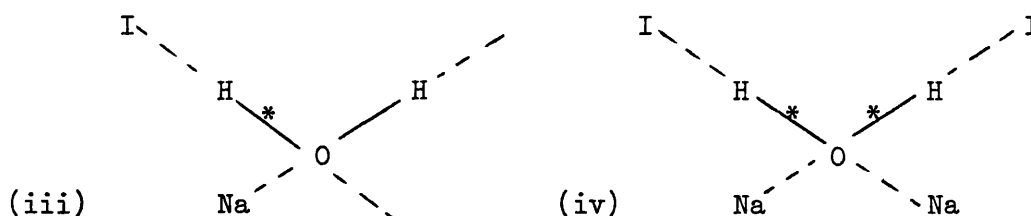
Infrared absorption spectra of HOD in D_2O in the O-H stretching region containing sodium iodide at several molalities (5.4 and 10.8 mol Kg^{-1}) at 173K.

co-ordinated, but with no long range order.

Room temperature data denotes the anion solvate absorption band to be in the 3370cm^{-1} region, and so we have assigned the 3365cm^{-1} and 3390cm^{-1} bands to the corresponding species below:

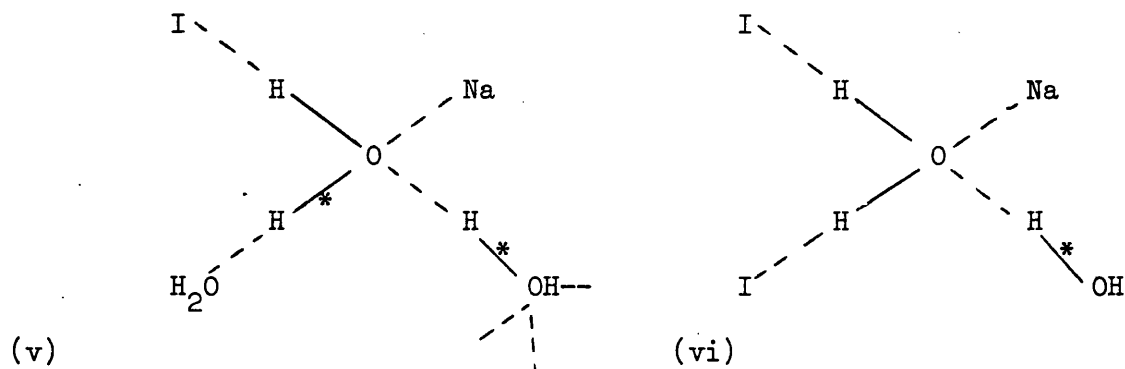


Replacing the water molecules that are bonded through the lone-pair orbitals of the water molecule in question with sodium ions to give the following entities:



should weaken the hydrogen bonding to the anion and hence absorb at a higher frequency. This is indeed the case if the assignments are correct with absorption bands occurring at 3525 and 3555cm^{-1} . This shift of 60cm^{-1} is consistent with previous data^{10,19}.

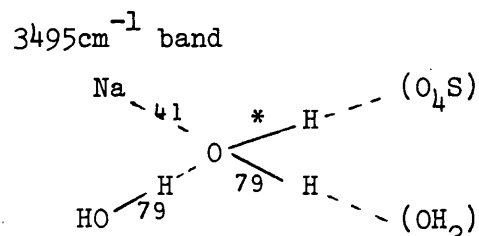
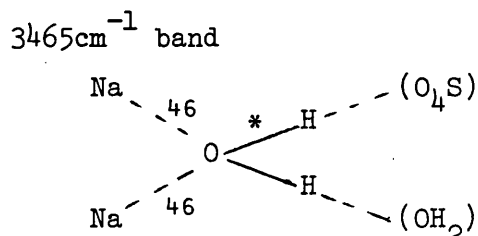
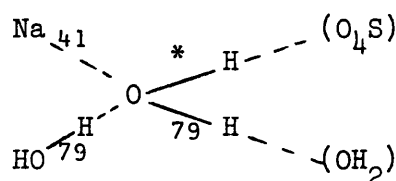
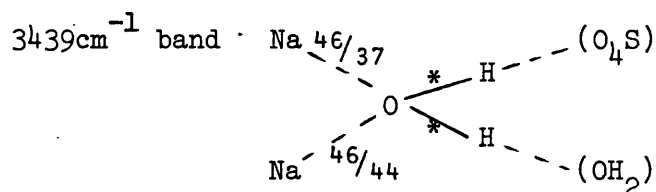
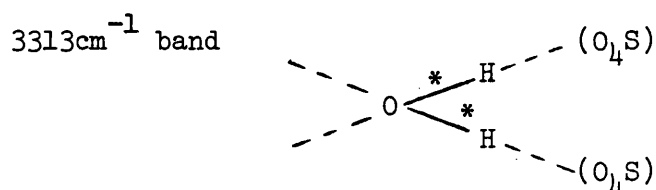
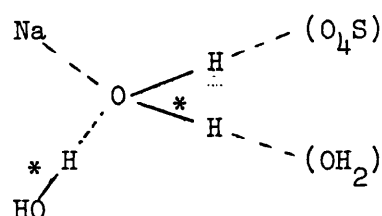
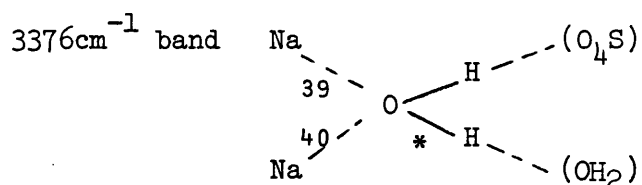
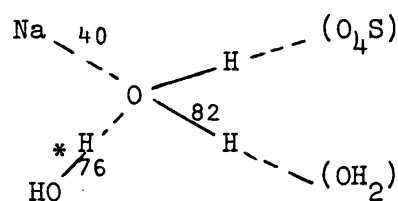
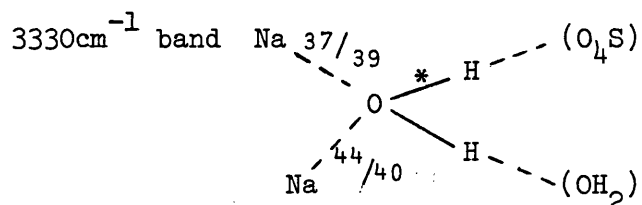
The bands at the lower frequencies of 3360 and 3403cm^{-1} we believe are due to water-water interactions of the following types:



The other peaks occur at 3435 , 3445 and 3498cm^{-1} , but only become prominent in spectra of very concentrated salt solutions. The infra-red spectrum of sodium iodide dihydrate³⁰ in the O—H stretching region produces

peaks at 3439 , 3445 and 3494cm^{-1} at 81K . Taking into consideration the difference of temperature which produces a small low frequency shift, the results obtained correlate well with the literature values and so those bands at 3435 , 3445 and 3498cm^{-1} have been attributed to sodium iodide dihydrate.

Aqueous solution of sodium sulphate recorded at 170K gave a multi-line infra-red spectrum with absorption bands occurring at 3280 , 3330 , 3375 , 3440 , 3465 and 3495cm^{-1} suggesting the formation of a crystal hydrate in this case the decahydrate whose crystal structure has been determined by X-ray crystallography³⁶. From this determination we have proposed the following assignments to explain our infra-red data. The absorption band at 3280cm^{-1} was again the usual pure solvent ice band

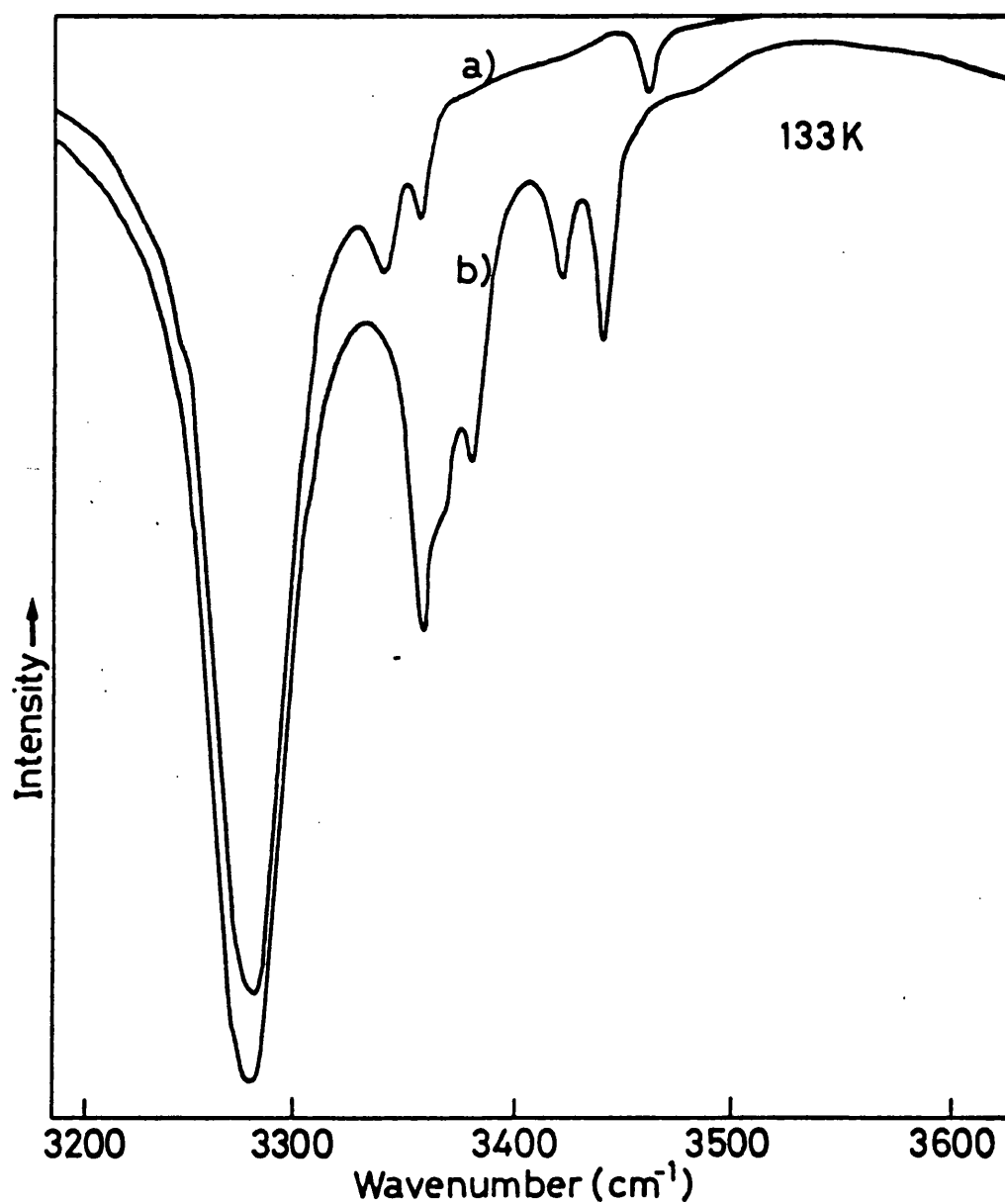


From the above data the point of interest surrounds the cation-oxygen interatomic distances and their effect on the anion-water hydrogen bonding, ie $O \overset{*}{\text{---}} H \text{---} X^-$ bond where X is the anion or a solvent molecule. It is generally true for the sodium sulphate decahydrate that the stronger the cation interaction is with the lone pair orbitals of the water molecule, the stronger the corresponding anion interaction or the shorter the hydrogen bond between the water oxygen and the anion. The converse is also true. So we find that all the weakly hydrogen bonded sulphate ions absorb at high frequencies, ie 3439, 3465 and 3495cm^{-1} , strongly bonded sulphate ions absorb in the 3330cm^{-1} region, while sulphate ions associated with water molecules unaffected by cations absorb in the 3413cm^{-1} region. The latter observation is in agreement with the room temperature data.

The cation interaction with the water molecule could also be responsible for the three nearly identical hydrogen bonds that provide the triplet peak in the sodium bromide and chloride dihydrate case and the one much more weakly hydrogen bonded anion that produces the individual absorption band at higher frequencies. From the interatomic distances given we find that for sodium chloride and bromide dihydrates, one of the sodium-oxygen bonds is substantially longer than the other three distances which could be an explanation of the 100cm^{-1} difference in peak position of the triplet and singlet bands. In the corresponding iodide dihydrate the difference in inter-atomic distances between the cation and the oxygen atom has three bonds of similar length, but the difference between the fourth bond and the others is only half that for the other two halide dihydrates, and so the 50cm^{-1} difference between the triplet and singlet bands for iodide is the expected outcome.

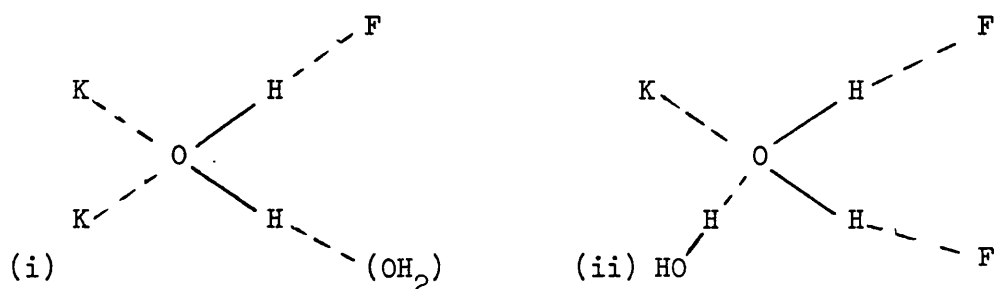
Although sodium fluoride was only soluble up to 1 molal, the low temperature spectrum of such an aqueous solution produced the typical solvent ice band and small sharp peaks at 3339, 3355 and 3460cm^{-1} as shown in Figure 4.16.

FIG. 4.16



Infrared absorption spectra of HOD in D_2O in the O-H stretching region containing a) sodium fluoride (1 molal) at 133K and b) potassium fluoride (3.6 molal) at 133K.

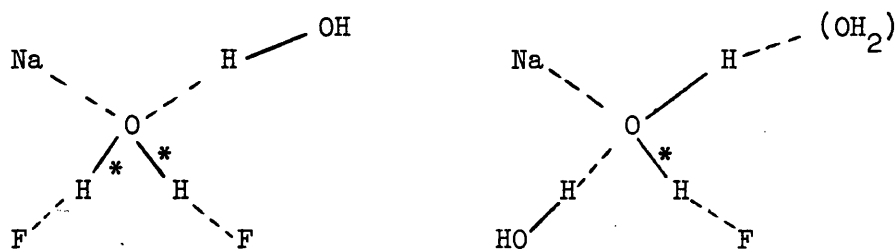
However the solubility range for potassium fluoride in isotopically dilute water stretched up to 9 molal and so obviously was a more suitable salt solution to study. These aqueous potassium fluoride solutions produced multi-line spectra that contained narrow absorption bands at 3280, 3359, 3370, 3382, 3420 and 3440cm^{-1} . From the crystal structure data³⁷ of the low temperature stable tetrahydrate, each potassium ion and fluoride ion is surrounded by six water molecules in an octahedral co-ordination, while each water molecule has a tetrahedral co-ordination but two different environments. One environment has two fluoride ions, one potassium ion and a water molecule, while the other has two potassium ions, one fluoride ion and a water molecule as shown in the diagram below:



The interesting point to note was that in the two cation species (i) both cation-oxygen distances are longer than the singly co-ordinated cation. These weaker cation interactions seem to produce weaker hydrogen bonding to the anion or the water molecule, while the two fluoride ions and the water molecule that are co-ordinated to the strongly bonded cation have shorter bond lengths than the former case. This produces two different bond lengths for the water-water interaction which in turn provides two absorption bands in the spectra at 3420 and 3440cm^{-1} .

From the interatomic distances reported, the two fluoride anions in species (ii) are the most strongly bound and so the 3359cm^{-1} band has been assigned to these O—H oscillators. The 3370 and 3382cm^{-1} bands in the observed spectra have been attributed to the O—H---F oscillators in species (i) with two different bond lengths. As the environments are the same, the explanation here could be due to some crystal structure constraint.

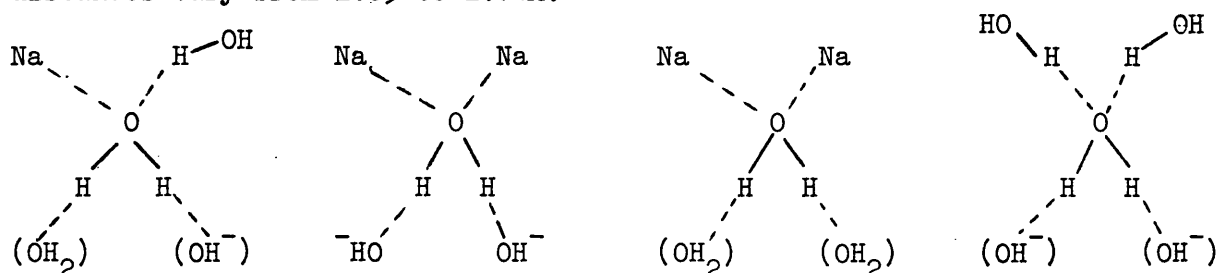
No crystal structure has been determined for any of the sodium fluoride hydrates, but from the information on the potassium counterpart we have attributed the 3339 and 3355cm^{-1} peaks as due to the anion-water interactions and the 3460cm^{-1} to water-water bonds. If this assignment was correct, a network structure of infinite size very similar to the lithium sulphate monohydrate structure could be the explanation. The specific anion-water interactions that produced the two different oscillators could be



the asterisked oscillators, with all the water-water interactions being the same strength.

As potassium salts have already been introduced into this section, the aqueous potassium and sodium hydroxide solutions shall be discussed together as both provide identical results. At low concentration of salt (< 4 molal), the low temperature infra-red spectra produced gave a broad ice band centred at the usual wavenumber. On increasing the salt concentration to 6.5 molal for the sodium salt and 10 molal for the potassium salt, a broad liquid-like absorption band centred at 3345cm^{-1} was obtained with the complete loss of the sharp ice band.

The width of the band is probably due to the many different O—H oscillators in the solution and the glass. These below are no doubt some of the species that occur in the glass as well as being detected by X-ray crystallography of the salt tetrahydrate³⁸, whose oxygen-oxygen interatomic distances vary from 2.65 to 2.84\AA .



The final sodium salt that was investigated was sodium chlorate. This provided a similar picture to the lithium halide solutions with the production at high concentrations (5 molal) of a broad band at 3460cm^{-1} along with the ice band at 3280cm^{-1} as shown in Figure 4.17. This high frequency band which, because of the larger separation of the peaks was better resolved than the corresponding high frequency band for the halides, was attributed as the anion solvate band. In relation to their relative hydrogen bond strengths, the chlorate ion is very similar to the sulphate ion.

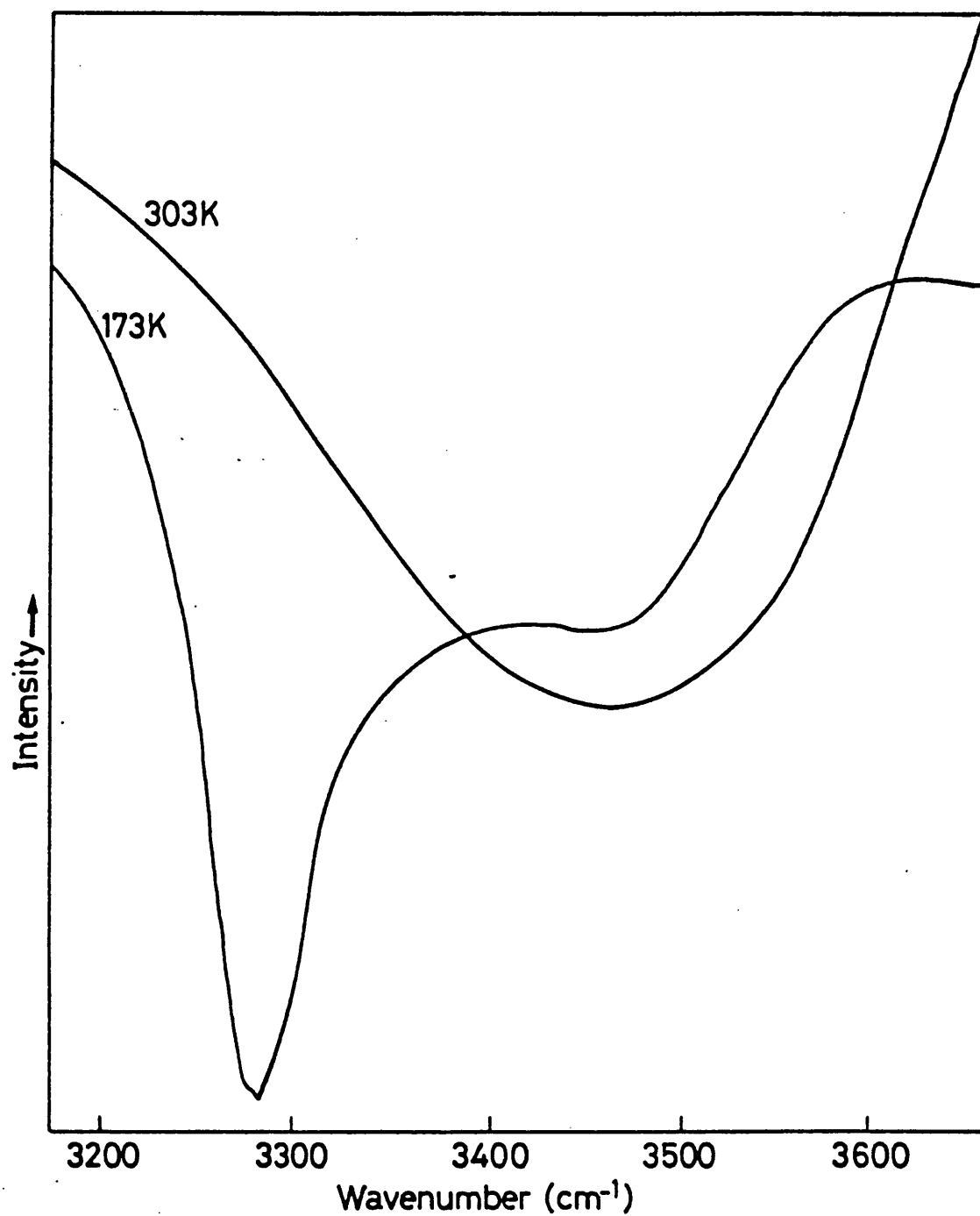
(vi) Magnesium Salts

When attention was turned to the divalent cations, the results obtained were again varied. Concentrated magnesium chloride solutions, when cooled to 170K, produced multi-line infra-red spectra that began to develop in the 2 molal concentration range. Even at 1 molal the only band that was resolved out was the usual ice band at 3280cm^{-1} . However, even that peak was appreciably broader than the pure solvent peak at 170K, with the addition of a high frequency tail and some obvious absorption in the 3410cm^{-1} region. The narrow multi-bands occurred at above 2.5 molal at the following wavenumbers 3265, 3295, 3378, 3395, 3415, 3455 and 3490cm^{-1} .

Magnesium chloride forms five hydrates with the stable hydrate at temperatures below 259.4K being the duodecahydrate³⁹. The crystal structure has been determined and from this information we have assigned various infra-red absorption bands to particular species.

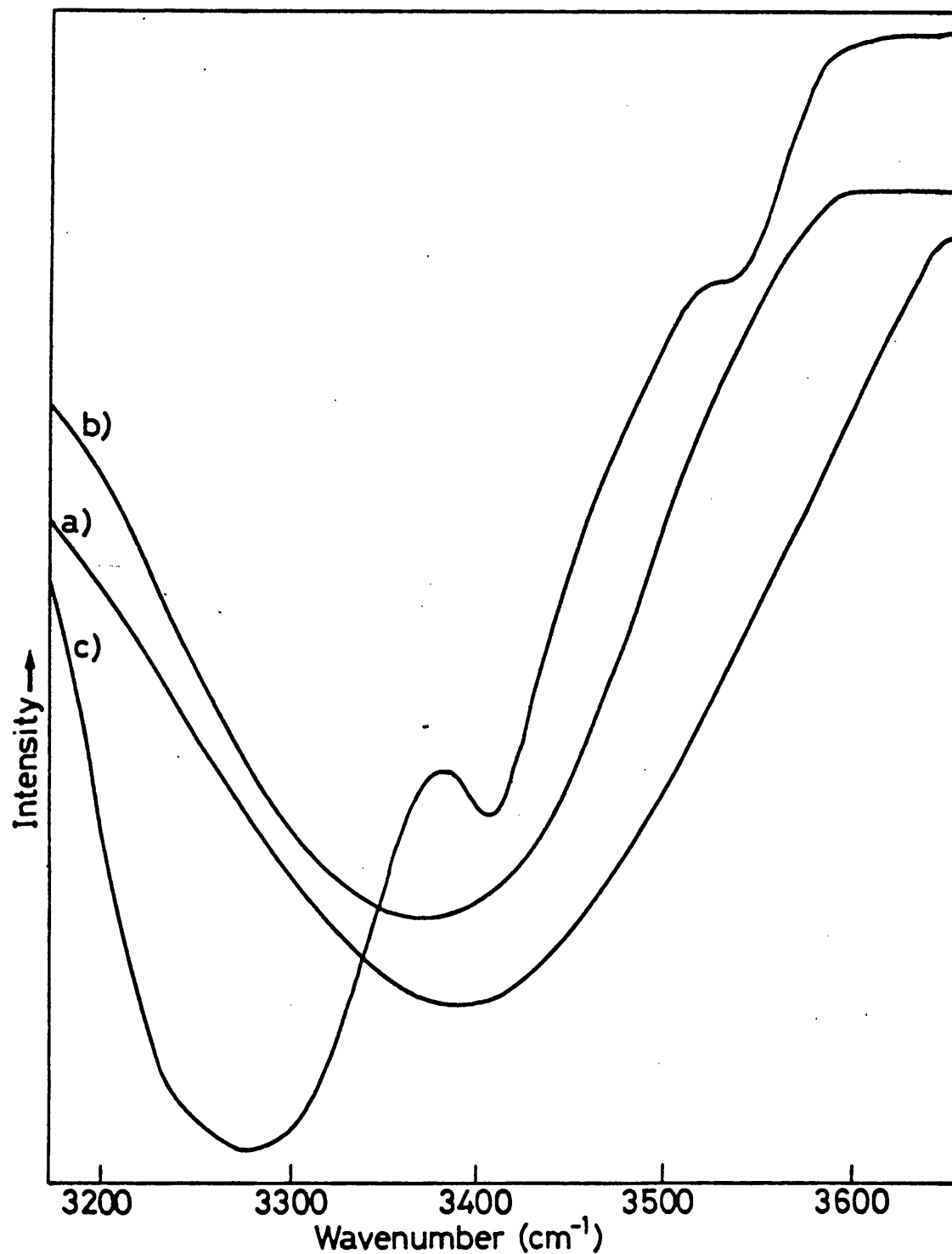
The magnesium hydration polyhedra are within experimental error perfect octahedra, while the chloride ion hydration co-ordination occurs in a distorted octahedral environment. Each water molecule forms two hydrogen bonds towards either an anion or another water molecule in a tetrahedral environment. However, only one magnesium ion is co-ordinated to any one

FIG. 4.17



Infrared absorption spectra of HOD in D₂O in the O-H stretching region containing sodium chlorate (3.6 molal) at two temperatures 303K and 173K.

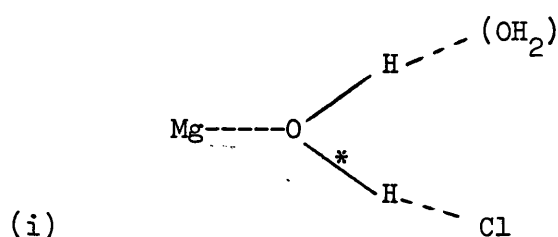
FIG. 4.18



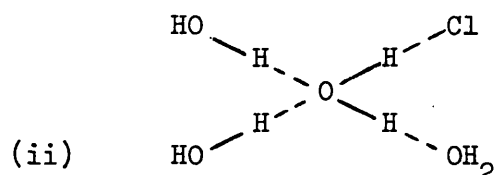
Infrared absorption spectra of HOD in D_2O in the O-H stretching region containing a) magnesium chloride (3.6 molal) b) magnesium bromide (3.6 molal) and c) magnesium nitrate (3.6 molal). All spectra recorded at 133K.

water molecule in this hydrate and this interaction tends to be along the bisector of the lone-pair orbitals. From the magnesium-oxygen interatomic distances, all the cations are co-ordinated with equal strength and so differences in anion-water and water-water bond lengths cannot be attributed to the cation-water interactions.

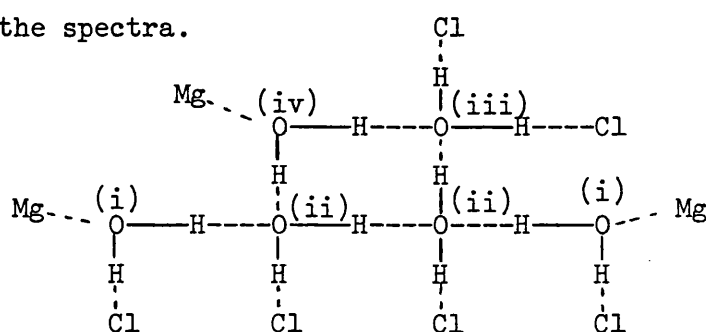
The two longest anion-water bonds occur in the below species for two different water molecules and we have attributed the 3455 and 3490cm^{-1} absorption bands to the asterisked oscillator.



The unasterisked O—H oscillator between the two water molecules in the above species also has two different frequencies which we have pencilled in at 3265 and 3415cm^{-1} . Some water molecules are tetrahedrally co-ordinated to three other water molecules and a chloride ion as shown below:

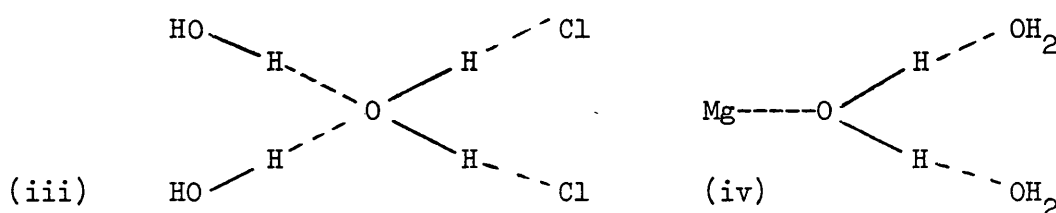


There are two different bond lengths for the anion-water distance which should produce two distinct infra-red bands. One of these bonds is the shortest and hence the strongest which we have assigned to the 3260cm^{-1} region, the other appears as the 3415cm^{-1} band. One of the three water-water interactions concerns the same bond as for species (i) as these are bonded together in the following manner and have been attributed the 3265 and 3415cm^{-1} bands in the spectra.



For the molecule that contains the O—H oscillator that absorbs at 3265cm^{-1} , the other two O—H oscillators have similar bond lengths to ice and so should absorb in that same region. For the water molecule containing the oscillator that has been denoted to absorb in the 3415cm^{-1} region, the other two O—H oscillators are of different bond lengths to produce bands at 3280cm^{-1} and 3415cm^{-1} .

That just leaves two other species (iii) and (iv) to consider, which are water molecules with either two anions or a cation, and two water molecules tetrahedrally co-ordinated.



Species (iii) provides the final two anion solvate bands with one of these being the strongest of all the O—H oscillators in this hydrate which we have denoted to absorb in the 3240cm^{-1} region and the other absorbing in the 3400 region judging from its interatomic distance. The two water-water bonds in species (iv) are of different strengths, but taking into consideration of all the other band lengths, we believe these O—H oscillators to absorb in the 3380 and 3415cm^{-1} regions.

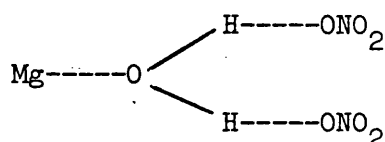
For concentrations between 2 and 4.5 molal we obtained the peaks mentioned at the beginning of this section, but for concentrations greater than 4.5 molal we obtain a similar multi-line spectrum but not so well resolved. It would seem that a broad liquid-line envelope was dominating the spectrum, but small weak bands occurred at the usual frequencies given above on top of this envelope. The four strong absorption bands at 3265 , 3378 , 3455 and 3490cm^{-1} seemed to have decreased in intensity for concentrated solutions. These bands seem to be associated with species (i) and (iv) which both are co-ordinated by cations.

Cooled down aqueous magnesium bromide solutions produced a liquid-like absorption band centred at 3375cm^{-1} , as shown in Figure 4.13. This is

in good agreement with other such glassified solutions and occurs at the same wavelength as lithium bromide solution bands.

Cooled down magnesium nitrate solutions produced infra-red spectra in the O—H stretching region which contained a broad band at the usual ice peak wavenumber with a shoulder in the 3250cm^{-1} region and two weak broad bands at 3410 and 3530cm^{-1} (see Figure 4.18).

From the structural data⁴⁰ available, all the water molecules are co-ordinated identically to a magnesium ion and two nitrate ions through the two hydrogen bonds.



However, each hydrogen bond is of a different strength. Three of the bond lengths from three water molecules are longer than the rest. From a wavenumber - bond length correlation discussed later, the three bond lengths should absorb in the 3550cm^{-1} region, so we have attributed the 3530cm^{-1} band to these oscillators. Two of the other bond lengths are of very similar length to bond lengths found in ice and so should absorb in the 3280cm^{-1} region which could explain the width of the band in this region.

Finally, the remaining bond length corresponds to a band in the 3400cm^{-1} region which is indeed what was obtained in the spectra. Therefore, it would seem that the spectra produced at low temperatures provides hydrate data. At low concentrations of salt that 3280cm^{-1} band was still very broad and this could very reasonably be due to the magnesium solvate as the two high frequency bands are not very pronounced.

(vii) Barium Salts

At 170K a saturated barium chloride solution was uninformative producing an infra-red spectrum of a broad ice band at 3280cm^{-1} and some absorption on the high frequency side of this band which in fact is a very similar picture to dilute magnesium chloride solutions. The barium solvation band we feel is responsible for the breadth of the ice band as this band

seems to absorb in the 3260cm^{-1} region.

From the structure⁴¹ and infra-red data⁴² of the dihydrate, we find that three of the four hydrogen atoms are hydrogen bonded to chloride ions, the fourth is only loosely shared between two chloride ions. This bond is called a bifurcated bond. It is stated that the principal factor which determines the orientation of the water molecules in a crystal is the proximity of the cations. The attraction of these ions for the unshared electron pairs of the water oxygen atoms results in the hydrogen atoms and cations being distributed approximately tetrahedrally about the oxygen atom. This arrangement permits hydrogen bonding of only three of the four hydrogens to the chloride ions.

Bauer⁴³ has shown that the positions of hydrogens in crystalline hydrates are determined by that orientation of the water molecule in the lattice which results in the lowest electrostatic energy. So it may happen that even though hydrogen bonds are geometrically possible in a particular lattice, non-bonded O—H groups will result because of strong cation-oxygen interactions.

The recorded wavenumbers for the dihydrate O—H oscillators were at 3300, 3316, 3352 and 3452cm^{-1} , but because of its low solubility we were unable to obtain any resolved out bands at low temperatures, although absorption in the high frequency region was observed.

Dilute barium bromide solutions (1.8 molal) produced a very similar result as the barium chloride solutions at low temperatures with the addition however of a weak but well resolved band at 3385cm^{-1} .

For an aqueous saturated solution of the bromide salt at 170K, the broad sharp peaked ice band has developed into a flat topped broad absorption band centred at 3270cm^{-1} . This development has been attributed to water molecules associated with the cation. At these higher molalities of salt three higher frequency bands are observed at 3385, 3430 and 3520cm^{-1} .

The barium bromide dihydrate is isomorphous with its chloride which

has led us to assign the 3520cm^{-1} band to the weak bifurcated hydrogen bond and the other bands to bromide solvates.

It is interesting to note the lower O—H frequencies in $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ compared with $\text{NaCl} \cdot 2\text{H}_2\text{O}$. This could well be due to the stronger oxygen-cation bonds in the barium compound. This would cause greater electron withdrawal from the O—H groups, and consequently result in longer and weaker O—H bonds and stronger O—H—Cl bonds resulting in the lower frequencies of these groups. This property has been noted for previous salts and seems consistently true.

(viii) Calcium Salts

Dilute aqueous calcium chloride solutions at 170K produced infra-red spectra that contained the ice peak and a weak absorption region in the 3410cm^{-1} region that produced this long high frequency tail phenomena. On increasing the concentration of salt, the sharp band at 3285cm^{-1} decreased in intensity and two bands began to develop at 3390 and 3425cm^{-1} with shoulders developing in the 3480 and 3350cm^{-1} regions. These bands are probably due to various anion-water interactions, but with no crystal hydrate structure data, no definite assignments can be made.

Calcium bromide solutions behaved very similarly to lithium and magnesium bromide solutions at 170K. They produced a broad liquid-like absorption band at 3420cm^{-1} at high concentrations of salt (> 5 molal). A decrease of the broad band and the appearance of the normal ice band was the result obtained when the molality of the salt was decreased to dilute proportions. This result would seem to imply that the calcium ion produces a weaker O—H oscillator than lithium and magnesium.

Calcium iodide solutions produced infra-red spectra very similar to results obtained from lithium sulphate spectra. Two very broad bands centred at 3280 and 3440cm^{-1} were obtained with the latter band increasing in intensity as the concentration of salt was increased and the former band just becoming broader. It is most likely that the higher frequency band at

3440cm^{-1} is due to anion-water interactions and the breadth of the ice band due to some cation-water interaction or bulk solvent. The absorption between these two band centres shows the many different bond strengths that occur in cation, anion and solvent shared ion pair interactions.

4.5 DISCUSSION

Water molecules in crystalline hydrates play an important role in their structures because they participate in hydrogen bonds to anion groups and are satisfactory ligands for cations through their lone pair orbitals. The presence of the water is essential for the stability of the structure because the compound may not be formed in the absence of water and the removal of the water from a hydrate nearly always results in a collapse of the structure and the formation of a new anhydrous one.

Under usual conditions a water molecule in a crystalline hydrate will assume a structure having two proton acceptors and co-ordinated cations along the two lone pair orbitals or, if only one cation is co-ordinated, along the C_{2v} axis. The replacement of the cations by other water molecules does not seem to affect the O—H oscillators a great deal in the tetrahedral environment in the hydrate. This buffering effect could be explained by the flexibility of the water geometry and of its environment in a crystal structure and enabling the whole structural group to act as a strain absorber. However, the replacement of cations by water molecules should produce an unbalanced distribution of bond strengths which would produce local strain in the structure which in order to minimise its energy will assume a packing with local distortions. Hence the production of many different strength hydrogen bonds which in turn provide the many multi-line infra-red spectra of many different salts in aqueous solutions could stem from the flexibility of the water molecule probably distributing itself randomly over a wide range of structures. This could be achieved by the hydrogen atom moving towards the underbonded oxygen atom to compensate the difference in bond strengths between donor and acceptor.

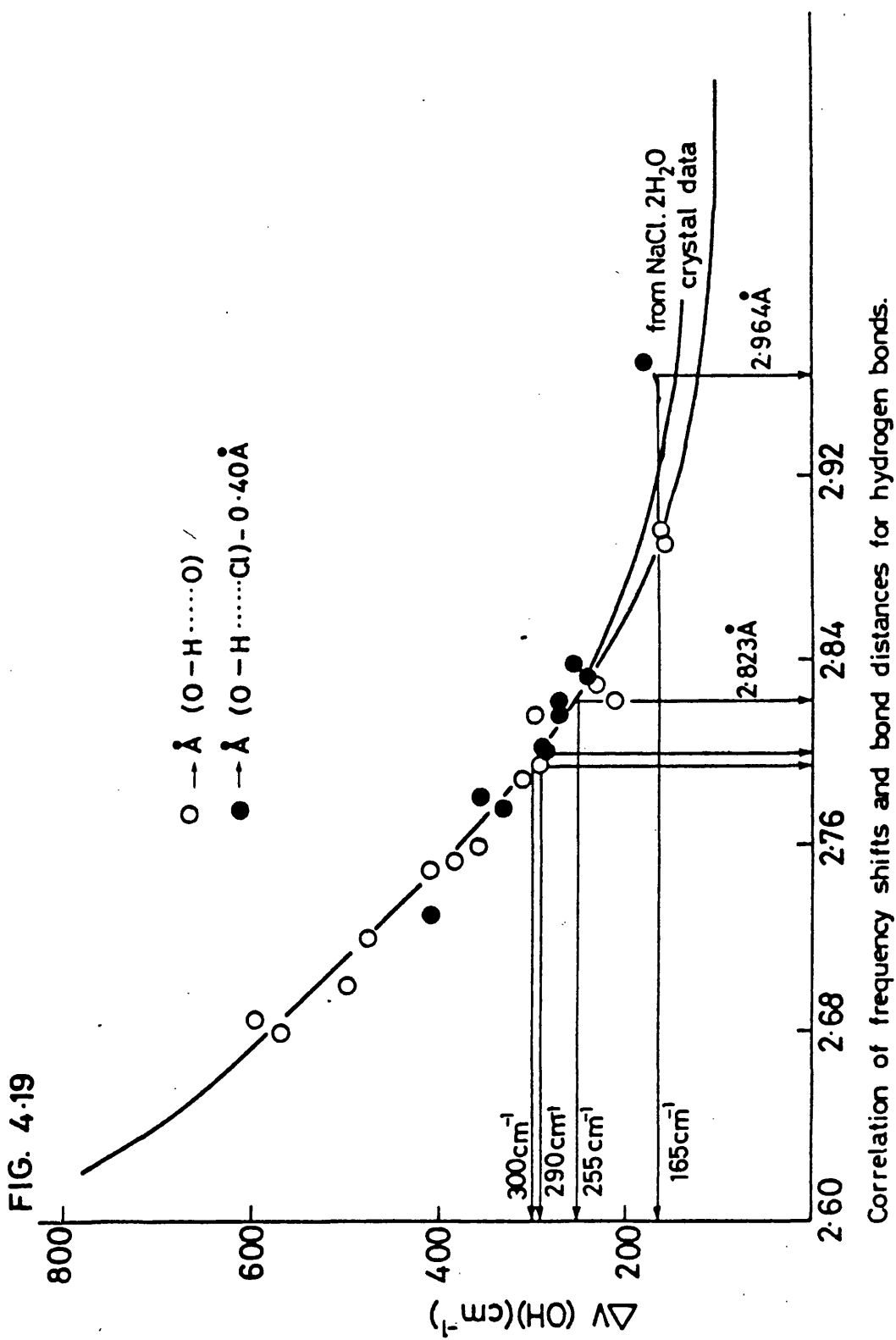
The second point of interest has been the use of stretching frequencies to determine hydrogen bond distances and strengths^{25,44}.

The formation of hydrogen bonds produces the well-known effect of lowering the O—H stretching frequency. The above references have established the relationship between the frequency shift of the O—H...O hydrogen bonds and the O—H...O distance and stated it is nearly a linear relationship for straight hydrogen bonds. However, bent and bifurcated hydrogen bonds deviate a great deal from this linear relationship.

Using two salts whose crystal structures have been determined by neutron or X-ray diffraction, and the above mentioned relationship, we have tried to assign different types of bands obtained in the infra-red spectra to appropriate hydrogen bonded species and then checking the assignments with other infra-red data obtained to validate this method. From the data presented in reference 26, we have found that by subtracting the difference in ionic radii between the oxygen and chlorine ions from the known O—H...Cl distance, the two independent curves for O—H...O and O—H...Cl in the frequency versus distance plots can be treated as the same as most of the points on the O—H...Cl curve can be translated to the O—H...O curve where the majority of points have been recorded. We have used this same criterion for other anions besides chloride anion subtracting the corresponding value of the ionic radius in question. This is demonstrated in Figure 4.19.

For an example we show the aqueous sodium chloride results. We found from our infra-red data that the hydrate peaks occurred at 3416, 3424, 3431 and 3535 cm^{-1} . Crystal structure studies show that the O—H...Cl bond lengths of the dihydrate are 3.199, 3.196, 3.223 and 3.364 \AA . By subtracting the difference in ionic radii, we obtained bond lengths of 2.799, 2.796, 2.823 and 2.964 \AA . Now using the correlation curves^{26,44}, these bond lengths correspond to frequencies of 3417, 3407, 3452 and 3542 cm^{-1} which correspond to the infra-red data obtained within experimental error.

Considering the crudity of the method, we feel it is a useful tool in assigning



appropriate crystal hydrate bands.

4.6 POLYATOMIC ANION SOLUTIONS

As mentioned before, the O—H stretching vibrations of HOD in aqueous solutions of electrolytes generally give rise to broad single peaked bands which resemble the bands of HOD in D_2O . However many workers^{9,10,45,46,47} have noted that aqueous perchlorate and fluoroborate solutions display two distinct bands with a new high frequency component in the O—H stretching region of the infra-red or Raman spectra.

From the room temperature results of sodium, lithium and magnesium perchlorate solutions, the high frequency shoulders appeared at low salt concentrations (about 1 molal) and increased in intensity to become a well defined peak as the solute concentration was increased. The position of this band was independent of perchlorate concentration, but showed a slight dependence upon the cationic species. However, its bandwidth appeared to be independent of the salt concentration and the cation. This observation was further reinforced when aqueous solutions of calcium, zinc, aluminium and silver perchlorates were investigated. Unfortunately due to the insolubility of potassium and caesium perchlorates in water, no data were obtainable from these salts to provide the whole spectrum of cation effects as obtained for the NMR molal cation shifts for water protons^{48,49}. This dependence of the perchlorate band on the cation could be explained by the formation of solvent shared ion pairs which would make the frequency of the band dependent of the cation, but remain independent of the perchlorate concentration for any particular cation.

There are frequency shifts between the high frequency bands for sodium perchlorate, fluoroborate and hexafluorophosphate solutions and a similar splitting of the bands for methanolic solutions of perchlorates¹⁹, which would seem to suggest that this band is due to weakly bonded perchlorate ions.

Another piece of information that backs up the existence of weak

bonds rather than (O—H)free groups is that a new band was formed on the addition of tetraethylammonium perchlorate to dilute solutions of methanol in an inert solvent which in this case was dichloromethane²³. From previous studies on other anions in similar systems⁵⁰, the anion was found to be solvated by the methanol. If the formation of (O—H)free groups was due to the perchlorate ion, the (O—H)free band in methanol at 3640cm^{-1} should increase in intensity as the concentration of perchlorate was increased, but instead a new band at lower frequency was produced between the bulk solvent band and the monomeric methanol value, indicating the weaker solvating power of the perchlorate ion as compared with the oxygen atom of the methanol. Since the aqueous solution results resemble those obtained for methanol and are backed up by nuclear magnetic resonance studies⁴⁹, the high frequency band has been assigned to weakly solvated perchlorate ions.

These perchlorate solutions were cooled down to 170K to extend the temperature range and see whether the low temperature would be consistent with higher temperature results that have been thoroughly analysed. The high frequency perchlorate band remained stationary as regards temperature changes. This characteristic along with the relatively narrow bandwidth have been stated to be the properties of O—H groups that interact weakly with their environment⁵¹. This result appears to be in good agreement with observations that state the frequency of the perchlorate band in aqueous solutions is almost identical to the stretching frequencies of HOD in the corresponding crystalline hydrates. The water molecules in these compounds participate in $\text{OH} \cdots \text{ClO}_4^-$ hydrogen bonds and are well documented¹⁶.

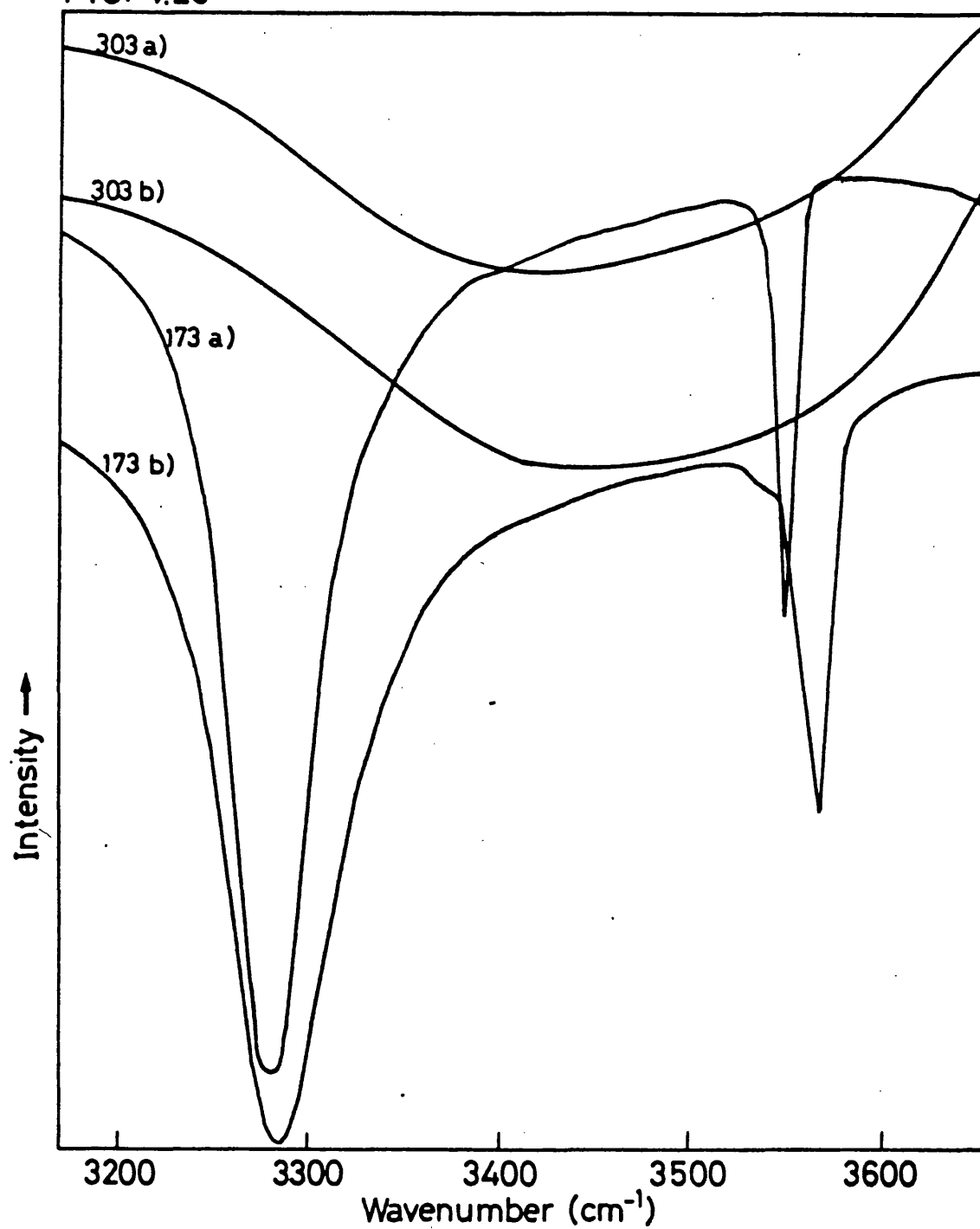
In room temperature data, the low frequency band which often is called the solvent band, corresponds to all the remaining O—H groups of varying bond strengths. This accounts for the breadth of the band. The average bond strength of this group is stronger than the weak anion interaction and so absorbs at lower frequencies. However, the frequency of this band is dependent on the temperature and the concentration of salt. The

temperature shift of the solvent band was very similar to that observed for the corresponding pure solvent band of HOD in D_2O . The frequency shift of the solvent band varied with the salt concentration. Increasing the concentration of the sodium salt led to a high frequency shift, while the lithium and silver perchlorates do not seem to shift the solvent band at all. The magnesium, zinc and aluminium perchlorates shift the band to lower frequencies. In addition to the solvent band shift, an extra band at lower frequency was needed by the DuPont curve analysis for the latter set of salts. These bands have been attributed to cation solvates. Although a general increase in band width has been mentioned, we have had no evidence for this. The difference of magnesium and sodium ions as regards the solvent band is probably due to the greater water co-ordinating ability of the magnesium ion, which causes a small net strengthening of water-water hydrogen bonds.

To add further evidence and information to this controversy of whether the high frequency band is due to solvated ions or $(O-H)$ free groups, low temperature infra-red studies were undertaken on the above mentioned perchlorates. The results were divided into two categories, the first being salts that produced similar spectra at low temperature to the room temperature ones.

We shall firstly deal with alkali metal perchlorate solutions. Only data obtained from solutions that exhibited no phase separation on solidification were used. As potassium and caesium perchlorates were practically insoluble in water, our results were obtained using sodium and lithium perchlorates. These salt solutions produced intense, relatively narrow bands in the same region (3280cm^{-1}) as that for pure water together with narrow bands in the 3570 and 3550cm^{-1} region for the sodium and lithium solutions respectively as shown in Figure 4.20. These high frequency bands increased in intensity linearly with concentration and at high concentrations of sodium perchlorate (7.2 molal), two satellite lines one on either side of the 3570cm^{-1} band at 3540 and 3590cm^{-1} developed. We have assigned these

FIG. 4.20



Infrared absorption spectra of HOD in D₂O in the O-H stretching region containing a) lithium perchlorate (1.8 molal) and b) sodium perchlorate (3.6 molal) at two temperatures, 303K and 173K.

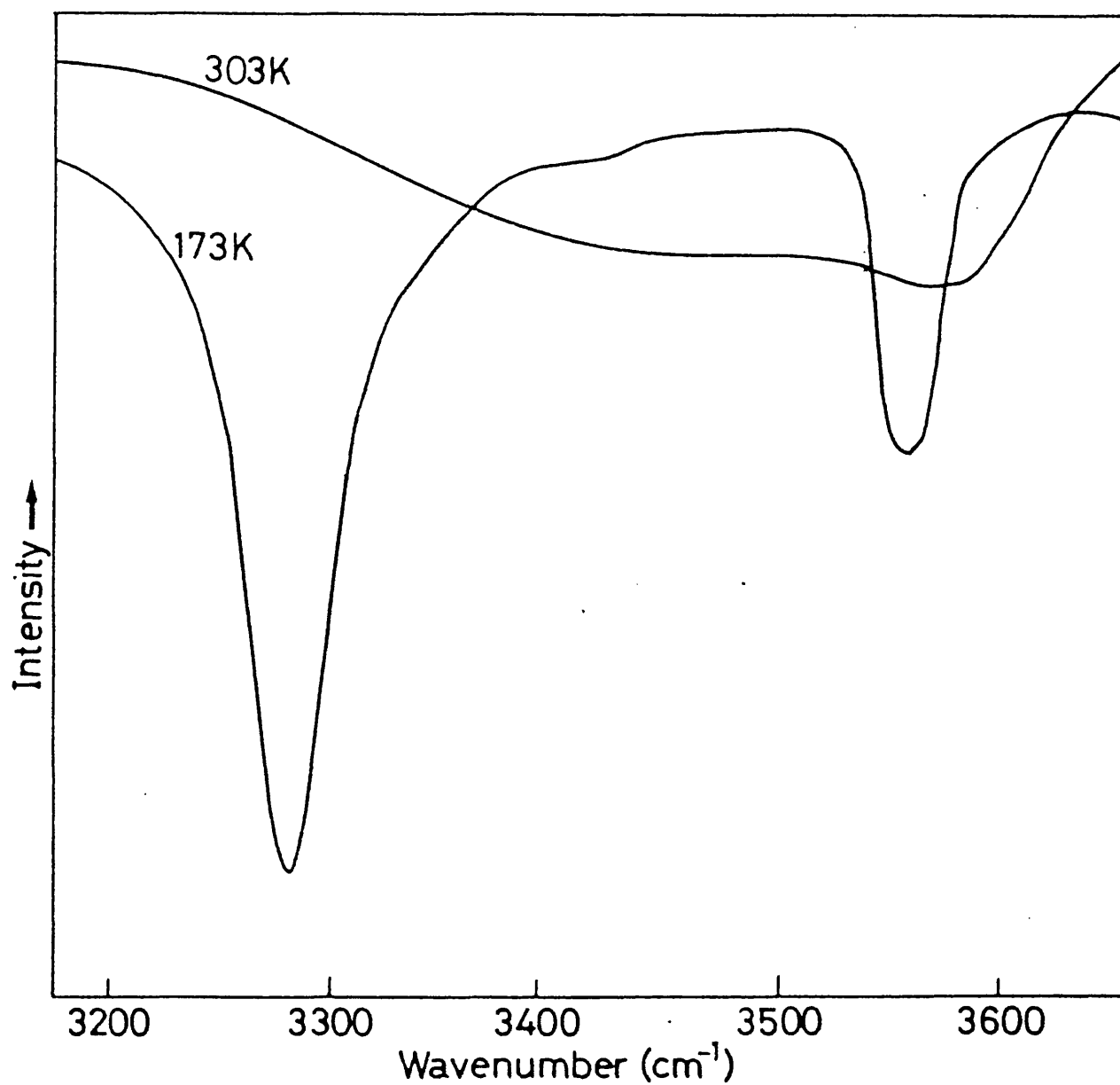
lines to the monohydrate, $\text{NaClO}_4 \cdot \text{HOD}$ as these have been reported in the literature¹⁶. The two individual high frequency lines from the sodium and lithium perchlorate solutions are two separate species as both lines are resolved out at low temperature when a mixture of the two perchlorates was analysed. On the addition of small amounts of t-butanol, both sharp bands at 3550 and 3570cm^{-1} were observed as seen in Figure 4.21. These points would seem to imply that there was a certain cation dependence of this band.

Although the bandwidth was decreased by fivefold on cooling the solutions down to 120K , there was very little frequency shift. Even so the crystal hydrate powder corresponding bands were still a great deal narrower than the above observed bands. The fact that in the monohydrate each hydrogen atom is shared by two O—H bands that are not crystallographically equivalent should provide two different O—H stretching bands. However, the appearance of only one seems to provide enough evidence that the sharp high frequency band was not a hydrate feature.

There seems to be no temperature dependence of these bands at 3550 and 3570cm^{-1} which is in good agreement with the anion solvate bands that occurred in methanolic electrolyte solutions which is unlike the ice band at 3280cm^{-1} that shifts linearly with temperature. The bandwidth at half height of the ice band also varies linearly with temperature except for an abrupt narrowing at glassification point. The apparent lack of shift of the perchlorate band could be explained by the frequency ν hydrogen bond length plot⁴³. This plot shows that a large change in bond length for a weakly bonded hydrogen bond will only produce a small frequency shift, while a large change in bond length for a strongly bound bond would produce a greater frequency shift. This could be the explanation behind the apparent dependence of the ice band and the independence of the weakly solvated perchlorate band with temperature.

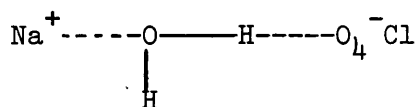
With all these points in mind we have come to the conclusion that at room temperature the high frequency band has contributions from water

FIG. 4.21



Infrared absorption spectra of HOD in D_2O in the O-H stretching region containing both sodium perchlorate (3.6 molal) and lithium perchlorate (1.8 molal) at 303K and 173K.

solvating perchlorate ions together with (OH)free groups. On cooling the sharp feature at high frequencies is due to (O—H) groups that are still associated with the cation and anion.



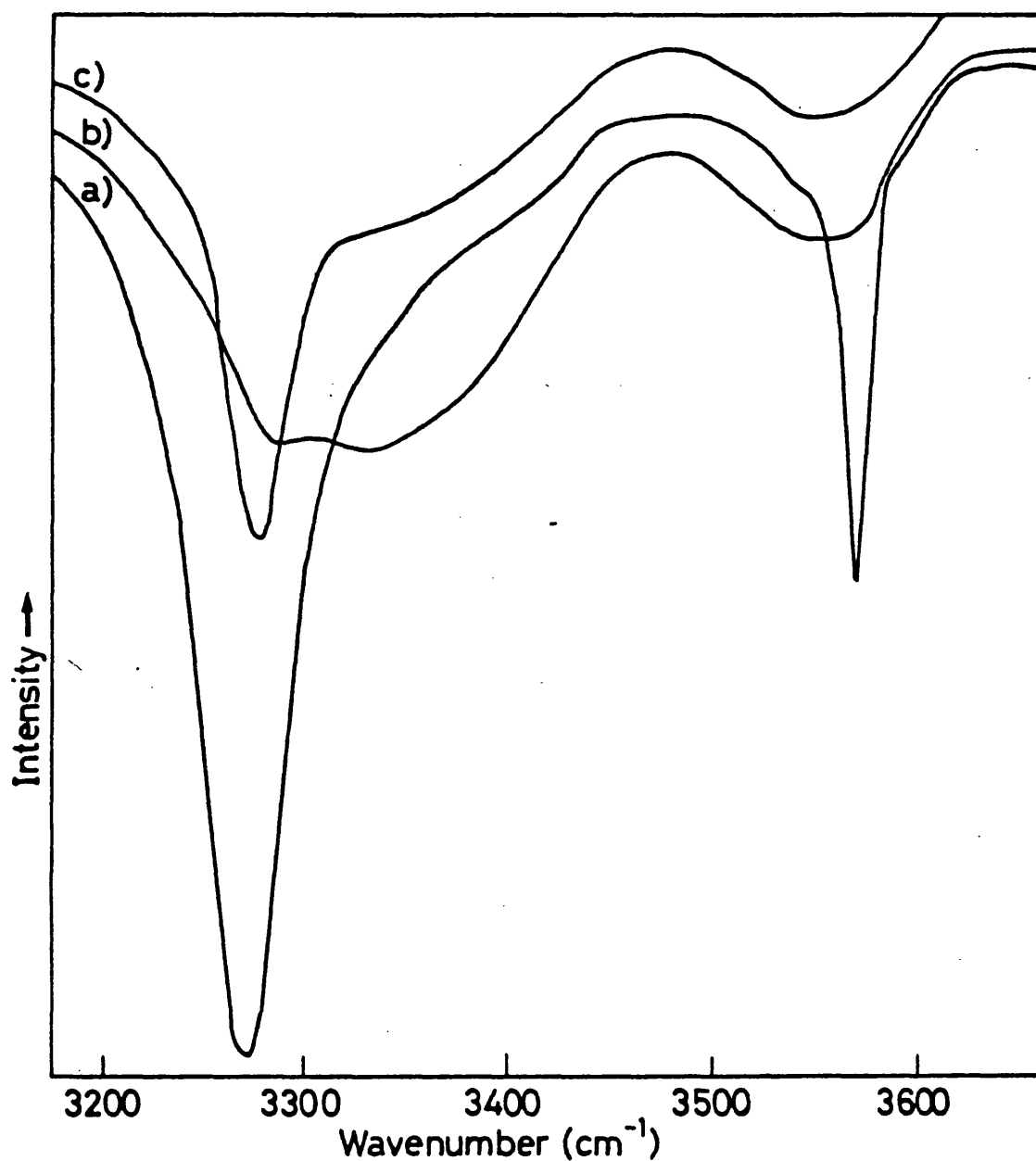
However this band occurs at the same frequency as a broad band centred at 3550cm^{-1} .

This ties in with the concept that the (O—H)free groups are not caused by "structure breaking" by the perchlorate ions, but due rather to the imbalance of (O—H)free and free lone pair groups, (LP)free. In other words, on the hypothetical argument of the addition of only cations, the lone pair orbitals are utilised for bonding, but this generates more (O—H)free groups than the initial equilibrium state where we have equal numbers of (O—H)free and (LP)free groups. On the addition of perchlorate ions some (O—H)free groups are scavenged, but provided the average effective solvation number of the cation is greater than that of the perchlorate ion, there will be an excess of (O—H)free groups even on cooling. This could be the situation for sodium and lithium perchlorate solutions.

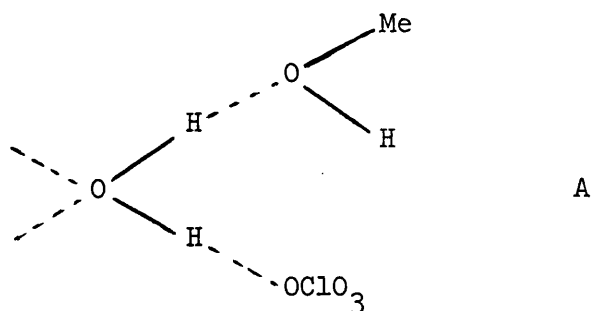
This assignment can also explain the results obtained when concentrated sodium perchlorate solutions were cooled to 170K, containing small amounts of organic solvents such as methanol, dimethyl sulphoxide and t-butanol. On the addition of methanol to these perchlorate solutions the results obtained were that the sharp feature at 3570cm^{-1} gradually lost intensity with increasing methanol concentration, leaving just a broad band in the 3550cm^{-1} region, the ice band gradually decreased intensity and a new broad band in the 3340cm^{-1} region developed (see Figure 4.22).

The loss of the sharp 3570cm^{-1} feature we have attributed to the scavenging effect of the (O—H)free groups by its two lone pair orbitals. The broad band centred at 3550cm^{-1} is due to the perchlorate solvate groups forming the below species:

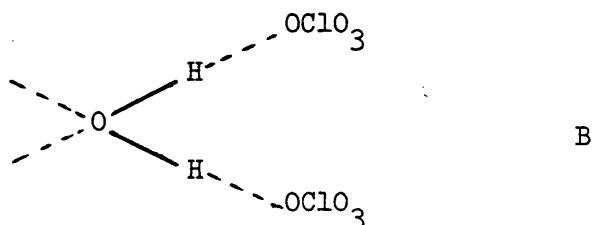
FIG. 4.22



Infrared spectra of HOD in D_2O in the O-H stretching region containing sodium perchlorate (7.2 molal) plus a) CH_3OD (0.018 mole fraction), b) CH_3OD (0.055 mole fraction) and c) dimethyl sulphoxide (DMSO) (0.015 mole fraction). -All spectra recorded at 133K.



The bond between the water and methanol is a strong bond which makes the hydrogen bond to the perchlorate ion weaker. The breadth of this band could be due to a species as shown below that would produce slightly stronger perchlorate bonds, although both bonds are still very weak.

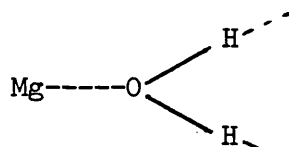


For a situation that had an excess of cations because of the larger solvation numbers over perchlorates, situation A would dominate. However, as described later, if the reverse situation arose and the perchlorate ion was in excess, then situation B would dominate. This seems to be a reasonable explanation for the slight difference in shift between sodium and magnesium perchlorates at low temperature as the latter salt produces a broad band centred at 3530cm^{-1} . The two organic solvents (MeOH and DMSO) produce a similar pattern with the only difference being the position of the bands, 3340cm^{-1} for methanol and 3370cm^{-1} for dimethyl sulphoxide. These bands we have assigned to (O—H) oscillators associated with water-methanol and water-dimethyl sulphoxide interactions. The difference in band position we have attributed to the difference in interaction strengths of the water-organic solvent. The variety of interactions is responsible for the breadth of the band.

The results for magnesium, zinc, calcium and aluminium perchlorates are very similar. At low concentrations and low temperatures, magnesium perchlorate solutions produce an ice band and a broad, weak 3530cm^{-1} band in the O—H stretching region of the infra-red spectrum. On increasing the

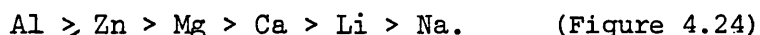
concentration to 3.5 molal the ice band gradually lost intensity and a broad band in the 3330cm^{-1} region with a low frequency tail developed. The 3530cm^{-1} band increased in intensity but was never as narrow as the sodium and lithium high frequency bands, although a slight narrowing was evident on cooling when compared with the room temperature spectra. This perchlorate band only slightly shifted to lower frequencies as predicted by the frequency ν bond distance plot. (Figure 4.23)

The long low frequency tail became more prominent as the salt concentration was increased which we have attributed to magnesium ion solvate.



For the broad band at 3330cm^{-1} , we have denoted the usual bulk solvent band with some solvent shared ion pairing producing the broadening of the band and being centred in the 3350cm^{-1} region.

When the spectra of other metal perchlorate solutions were analysed, the only change to the explanation given for magnesium perchlorate solutions was the position of the long low frequency tail. After curve analysis on the DuPont curve analyser, the order in increasing O—H bond strengthening properties of the cations was



The lack of sharp (O—H)free features can be explained by implying that with these divalent cations there would be an excess of perchlorate ions which would scavenge all the (O—H)free groups.

The two other polyatomic anions investigated were the hexafluorophosphate and the tetrafluoroborate. At room temperature these salt solutions produced a bulk solvent band ca 3400cm^{-1} region and high frequency bands at 3620 and 3590cm^{-1} respectively. These bands are due to weakly bonded anion solvates giving the sequence:

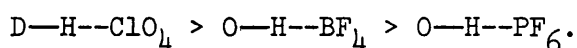
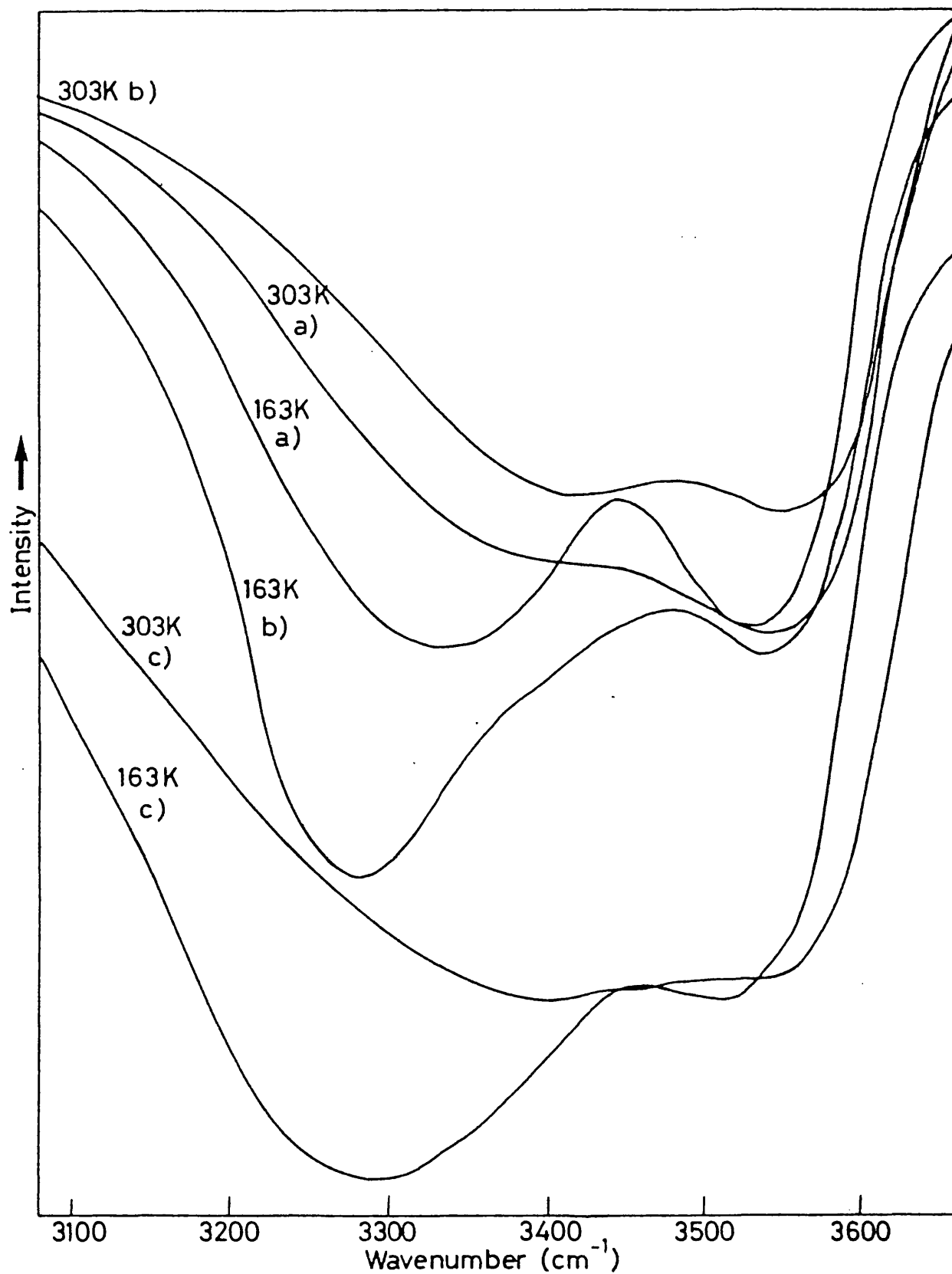


FIG. 4.23

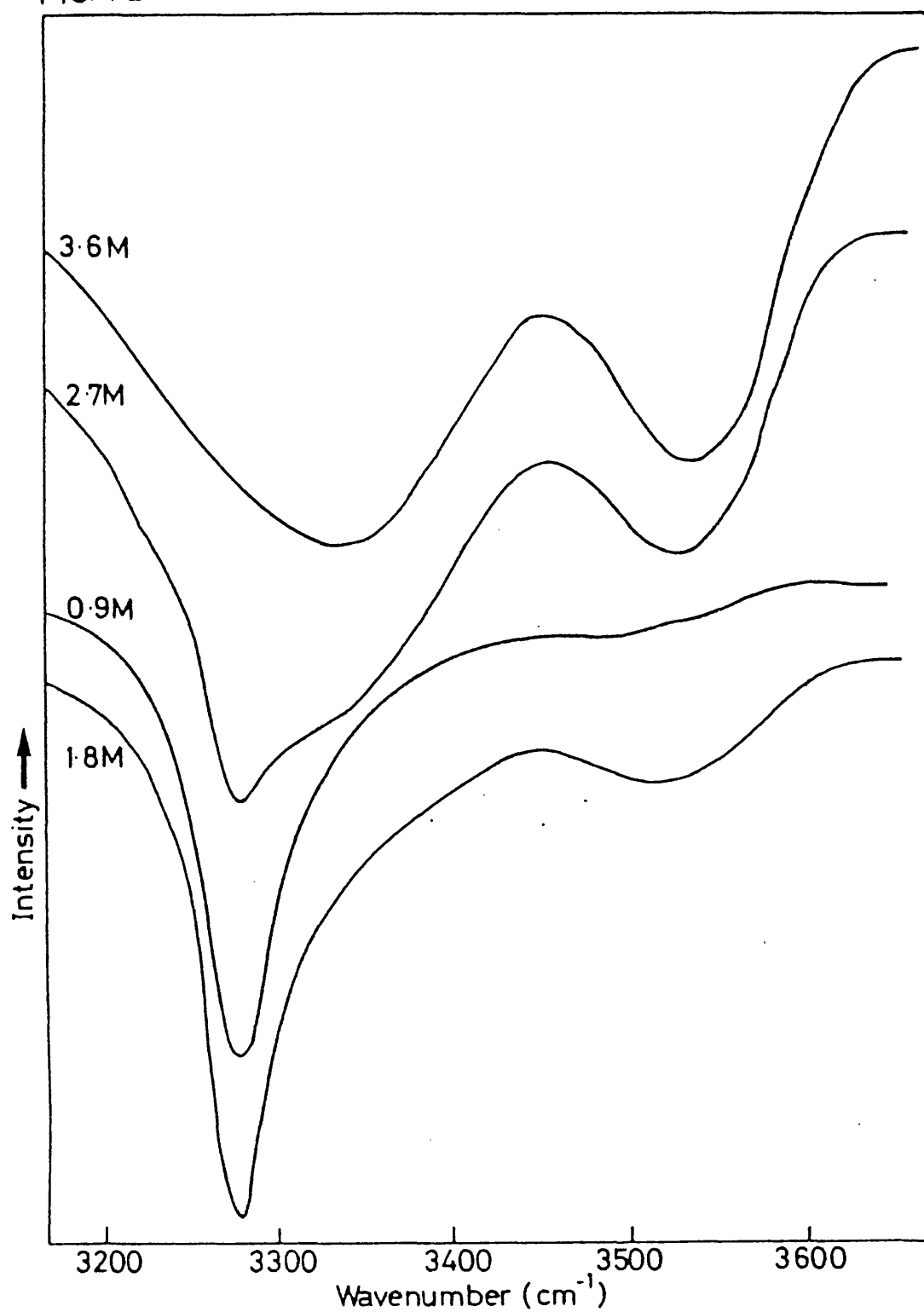


Infrared absorption spectra of HOD in D₂O in the O-H stretching region containing saturated inorganic salts at 163K & 303K.

(a) Magnesium perchlorate

(b) Calcium perchlorate

(c) Aluminium perchlorate



Infrared absorption spectra of HOD in D₂O in the O-H stretching region containing magnesium perchlorate at several molalities (0.9, 1.8, 2.7 & 3.6 mol Kg⁻¹) at 143K.

with the perchlorate forming the strongest of the weak bonds that produce a splitting of the O—H stretching bands (see Figure 4.25).

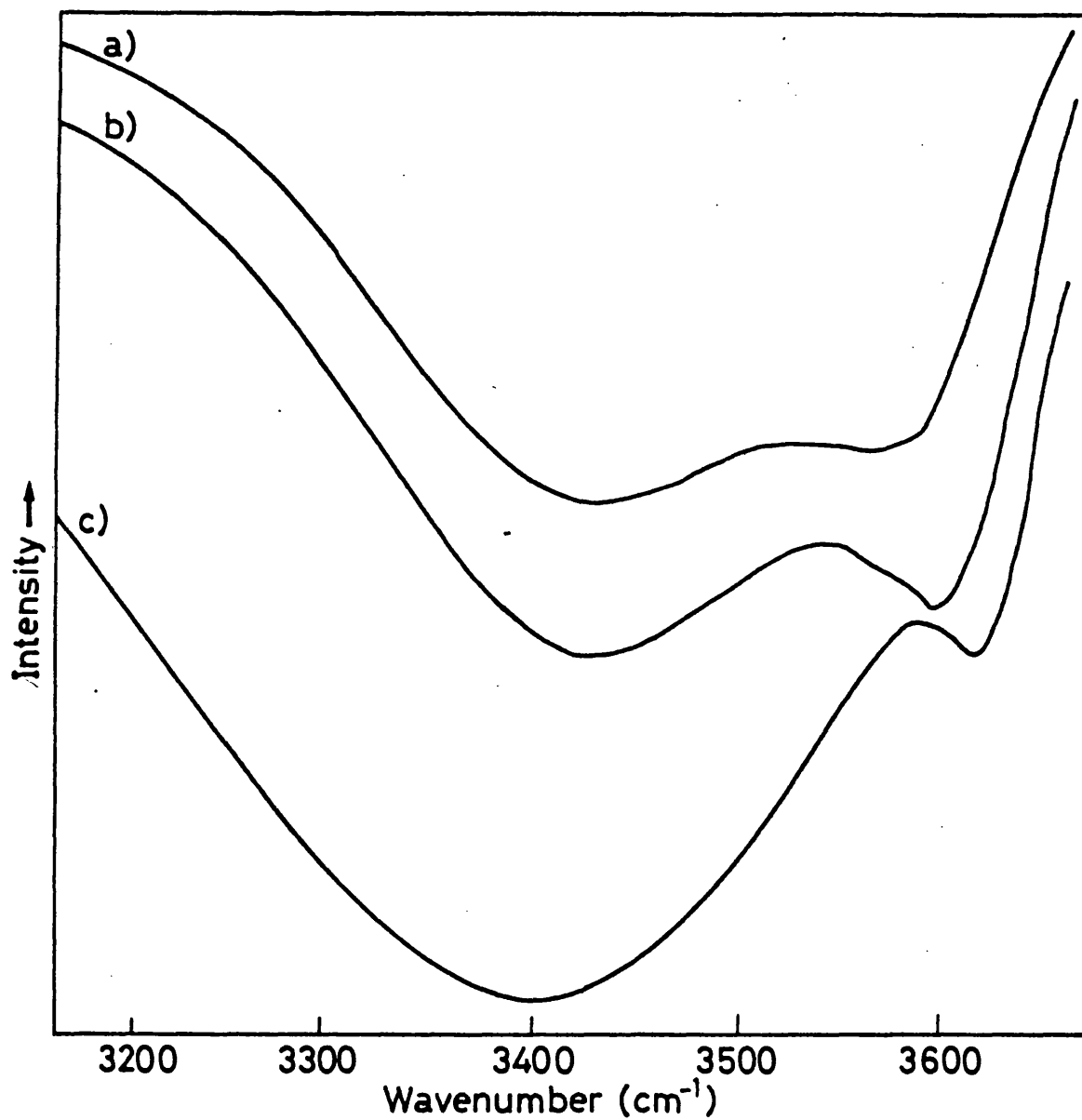
Unfortunately on cooling just the ice band at the usual wavenumber was observed for tetrafluoroborates solutions which could be due to phase separation. However, concentrated hexafluorophosphate solutions at 170K produced a very broad ice band at the usual frequency and a long high frequency tail leading to a weak band at ca 3600cm^{-1} .

4.7 CONCLUSION

In Figures 4.26 and 4.27, all the available data has been summarised to give all the crystal hydrate information in one diagram and all the remaining broad absorption band data in another diagram which are due to glassified samples. All the crystal hydrate results were interesting as regards the varying bond strengths and hydrogen bond orientations including severely bent, bifurcated bonds and even hydrogen atoms of a water molecule that do not participate in hydrogen bonds at all that were observed in the infra-red spectra. Some new hydrates that were formed are analysed by comparison with the available data.

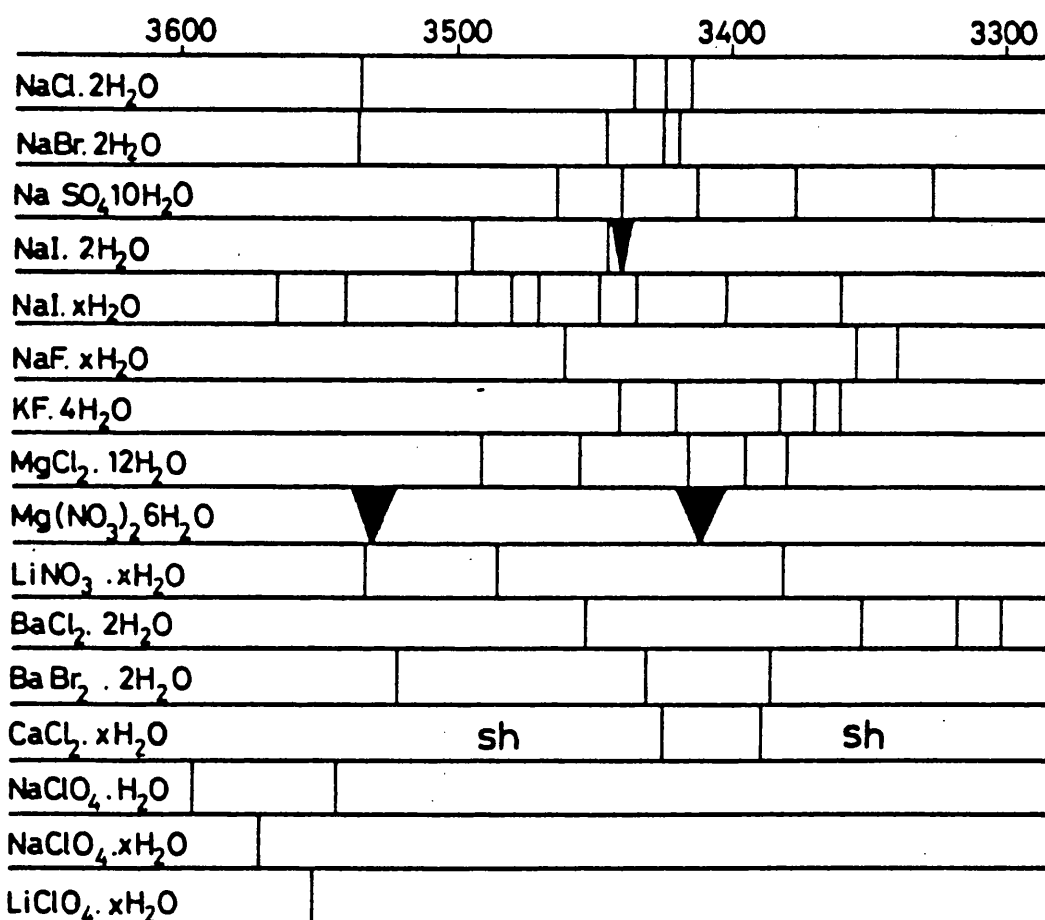
As electrostatic forces must play a part in these hydrates with some workers even predicting the position of hydrogen atoms in crystalline hydrates by an electrostatic theory^{43, 52}, it is interesting to note from Figure 4.27 the sequence of NO_3^- , ClO_3^- , SO_4^{2-} , ClO_4^- and PF_6^- absorbing at higher and higher frequencies at low temperature. This sequence seems to suggest or reinforce that stronger hydrogen bonds are formed with anions of higher surface charge density. We know that the nitrate ion is assymmetrically solvated⁵³ and so one or two strongly hydrogen bonded ligands are pulling the negative charge away from the remaining ligands giving a charge away from the region of one or a half. We believe that the perchlorate ion is weakly hydrogen bonded through each oxygen with the negative charge evenly dispersed throughout the ion giving a negative charge of around a quarter each. Now the chlorate ion which is not so polarisable would have a charge of about a

FIG. 4.25



Infrared absorption spectra of HOD in D_2O in the O-H stretching region containing a) sodium perchlorate (3.6 molal), b) sodium fluoro-borate (3.6 molal) and c) sodium hexafluorophosphate (5.3 molal) at 298 K.

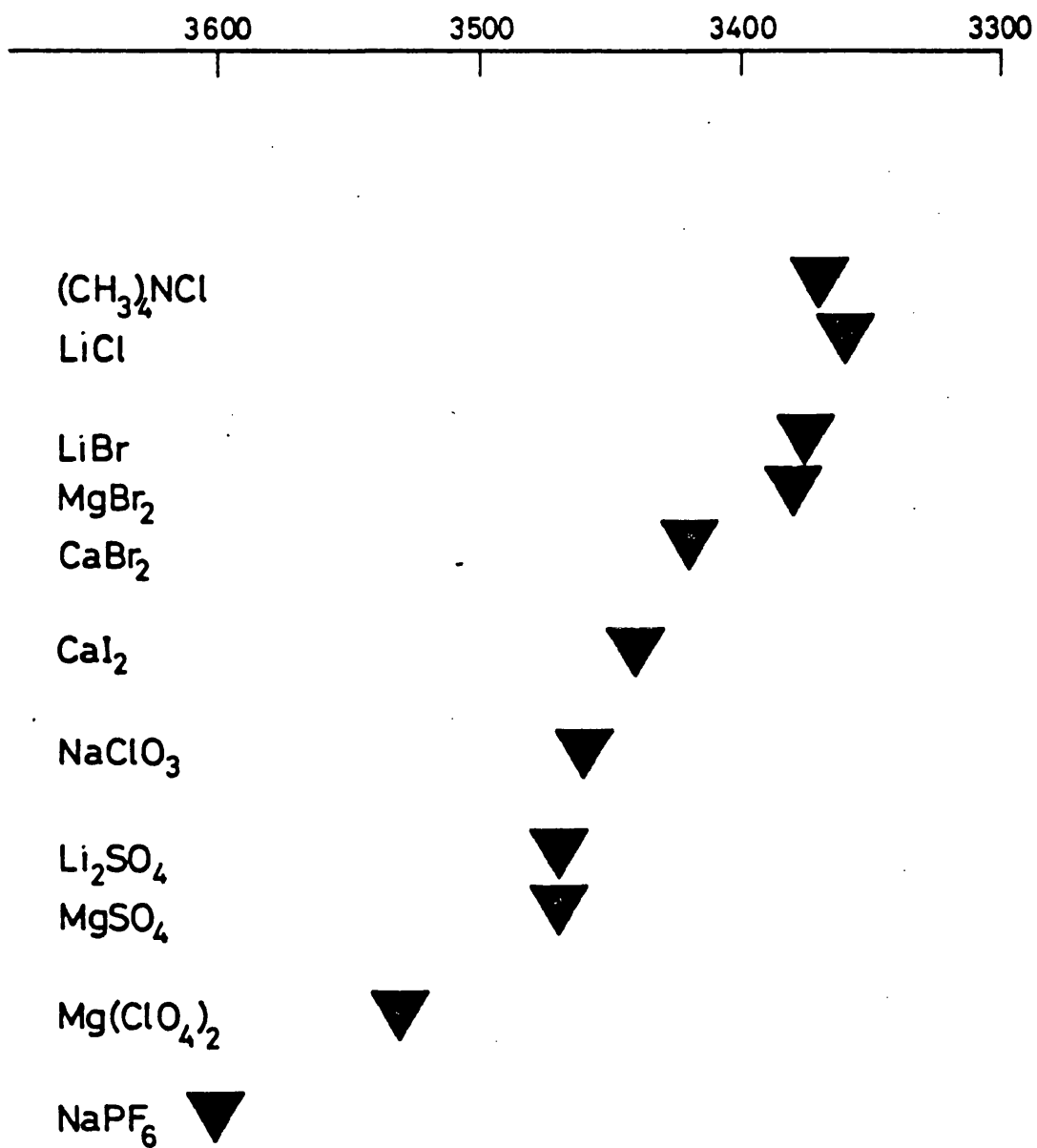
FIG. 4.26



sh—shoulder, ▼ broad band, | narrow band.

Location of absorption bands observed in the infrared spectra of aqueous electrolyte solutions at 173K.

FIG. 4.27



Location of major bands observed in the infrared spectra of electrolytes in $\text{HOD}/\text{D}_2\text{O}$ at 173K.

third if the same argument as above was applied. This should in theory mean that the chlorate solvate band should absorb in the intermediate region between the nitrate and perchlorate solvate bands which is exactly what is produced.

With the hexafluorophosphate and tetrafluoroborate solvate band difference, the same reasoning could apply with the sixth of a charge on each fluorine atom for the PF_6^- ion being more weakly solvated than the BF_4^- ion which would have a quarter charge on each peripheral atom.

A final point of interest appears when bulk water-anion interaction data are compared with the 1:1 complexes such as $\text{X}^- \cdots \text{HOH}$ which are formed in dilute solutions of tetra-alkylammonium salts in inert media⁸. This comparison produced interesting differences between the two systems¹⁹.

For the chloride solvate the difference in wavenumber was positive which was interpreted as the effect of going from a $\text{X}^- \cdots \text{HOME}$ species to a $\text{MeOH} \cdots \text{X}^- \cdots \text{HOME}$ species. However, the iodide solvate produced a negative difference in values which was attributed to the factor of going from a $\text{X}^- \cdots \text{HOME}$ species to a $\text{X}^- \cdots \text{HO}(\text{Me})_2$ species.

When a similar approach was repeated for the water systems, it was found that the differences in wavenumber between the monosolvates and the bulk solvates were all positive with differences of 102, 49 and 18cm^{-1} for the chloride, bromide and iodide solvates respectively. These positive differences suggest that the species $\text{X}^-(\text{HOH})_n$ is the more dominant factor in anion solvation than the $\text{X}^- \cdots \text{HO}(\text{H})_2$ species especially for the chloride ion, although the latter type of solvation does play a significant role for the iodide ion and to a lesser extent the bromide ion. However, in all three halide cases, the former effect predominates.

This again produces a detailed picture of anion solvation and emphasises the point that water simply possesses the properties of a normal dibasic and diacidic liquid with the normal secondary solvation however involved in the normal bulk solvent structure rather than being an area of disorder.

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CHAPTER FIVE

VIBRATIONAL STUDIES OF THE TETRAHYDROBORATE ANION IN VARIOUS PURE SOLVENTS AND BINARY AQUEOUS MIXTURES

5.1 INTRODUCTION

In this chapter a different approach with the same aim to study ionic solvation was employed. Whereas in the previous systems studied the O—H stretching mode has been the mode of interest, attention here was turned to the fundamental O—D stretching vibration of HOD in H_2O and the asymmetric B—H stretching band for the BH_4^- ion in the infra-red spectrum.

As described in the previous chapters, useful information concerning ionic solvation has been obtained from infra-red and Raman spectroscopy of aqueous and methanolic solutions particularly for solutions of some polyatomic molecules that display a second resolved feature in the O—H stretching region. Although some assign this feature to (O—H)free groups¹, which are water molecules that have up to three hydrogen bonds associated to neighbours but one hydrogen atom not involved in hydrogen bonding, others have preferred the concept that the anions are weakly hydrogen bonded to solvent molecules^{2,3}. Whatever be the correct interpretation, it seems reasonable that if no such high frequency band was present, the anions must be relatively strongly solvated by hydrogen bonds or not bonded at all. However, for aqueous solutions containing sodium or potassium tetrahydroborate, the O—D stretching profile exhibited is indicative of relatively strong hydrogen bonding to the anion, comparable with that for chloride ions⁴. Secondly the asymmetric B—H stretching band shifted strongly to lower frequencies as basic aprotic solvents were added. Both these points seem to suggest hydrogen bonding to the anion by the solvent molecules.

Proton magnetic resonance studies of a range of various solvent protons has enabled values for separate ionic molal shifts to be determined^{5,6,7} and accepted^{8,9}. The proton resonance for water shifts linearly on the addition of borohydride salts and from this shift and previously estimated cation shifts, a molal shift for the anion that falls between the shifts induced by chloride and bromide ions was observed¹⁰. These results for the anions correlate well with the acidities of their conjugate acids^{5,6} which is taken to support the hydrogen bonding model for the solvation of anions in protic media.

Similar infra-red and Raman methods as have been used here have been employed to study other polyatomic anions such as the nitrate ion^{11,13}, and the bisulphate ion¹², where the $\bar{\nu}_3$ band splits from a singlet into aprotic solvents to a doublet in protic solvents, indicating asymmetric solvation and the O—D stretching profile shows a small high frequency shift indicating the anion-water interaction to be slightly weaker than the solvent-solvent bond.

Infra-red and Raman spectra of BH_4^- in various salts have been reported^{14,15}, and an extensive study has been made of lithium tetrahydroborate in liquid ammonia¹⁶. An extensive Raman study of tetrahydroborate ions in a range of solvents has been undertaken¹⁷, but the conclusion that was reached gave no support for the concept of hydrogen bonding to the BH_4^- ions.

So the aim of this study was to extend the general spectroscopic studies of ionic solvation and investigate the particular question of hydrogen bonding to the BH_4^- ions. The idea of hydrogen bonds between hydrogen atoms of different molecules has been discussed^{18,19}, but experimental evidence is sparse. However, there is kinetic evidence for the participation of protonated BH_4^- (BH_5) in the acid catalysed hydrolysis of tetrahydroborates²⁰. The result of isotopic exchange suggests that the structure of this adduct should be written as $\text{H}_2\text{B H}_3$ as there are only two equivalent exchangeable protons. There have been several theoretical studies of the isostructural CH_5^- species,^{21,22} but the important point here is that the excess proton is thought to be bonded to the boron atom rather than to one of the hydrogens.

5.2 RESULTS AND DISCUSSION

As the rate of hydrolysis of metal borohydrides is increased with the presence of acid and decreased with the presence of alkali, the tetrahydroborate solutions were stabilised by the addition of 0.5 molar sodium or potassium hydroxide. N.m.r. spectra were checked periodically for evidence of any hydrolysis products and if any were detected, the solutions were rejected. This addition of alkali only slightly decreased the absorption

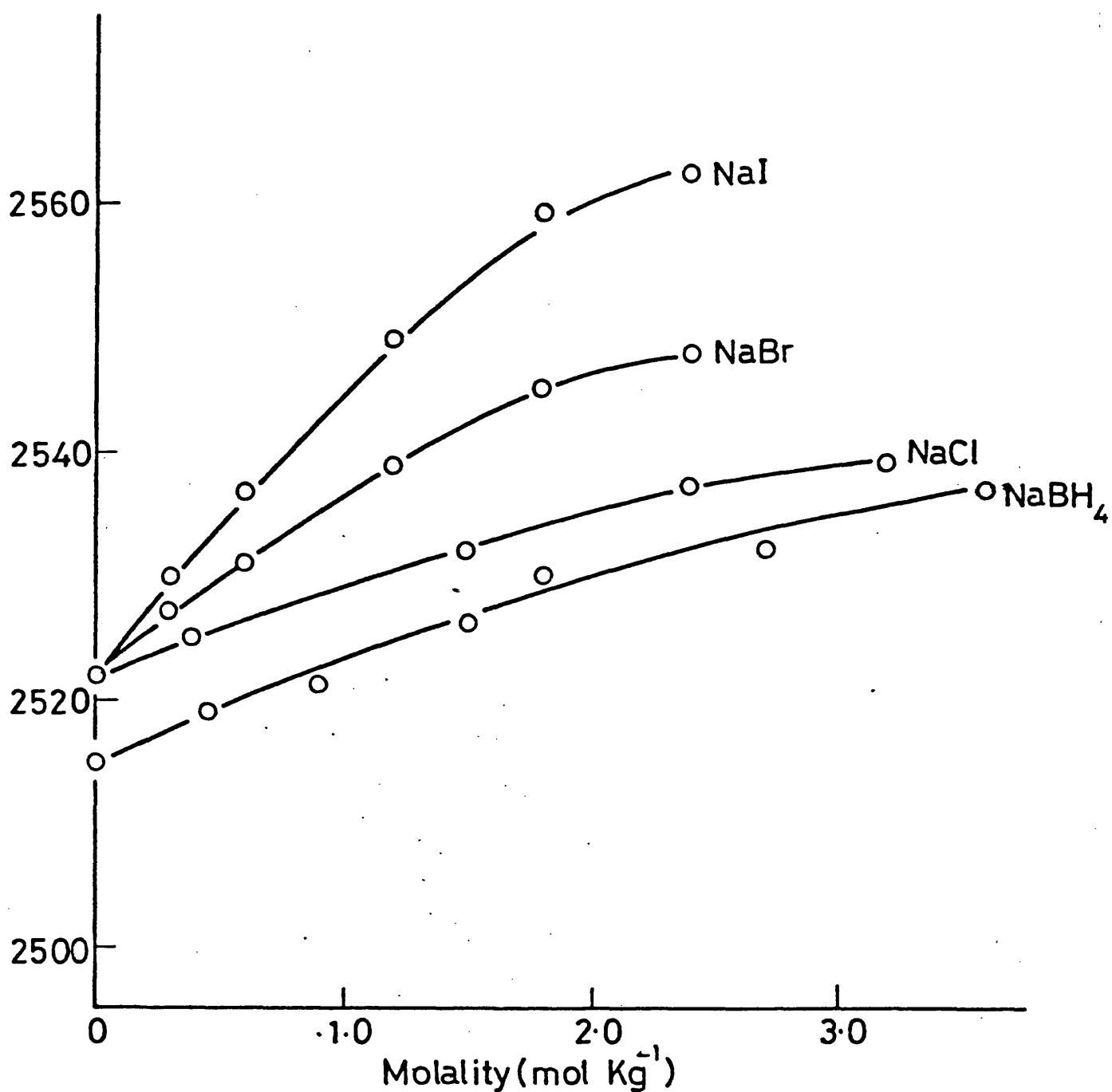
of the B—H stretching band and no change of peak position was observed.

A 10% D₂O (by volume) in the H₂O solution was used for these studies of the O—D stretching mode of HOD. The band maxima of these tetrahydroborate solutions shifted to higher frequencies on increasing the salt concentration, in a manner closely resembling the shift found for aqueous chloride solutions as shown in Figure 5.1. The sodium ions are known to induce a small high energy shift²³ and so the observed shift has been assigned to be largely due to the BH₄⁻ ion as the cation is the same in all the plots as shown in diagram 5.1. With no sign of a band in the high frequency region (ca 2645cm⁻¹) of the type found for BF₄⁻ in conjunction with the observed shift just mentioned, this seems to suggest that the BH₄⁻ ions are strongly solvated to water molecules despite the fact that only the former ions have lone-pairs of electrons on the ligands.

The next point to follow up was the involvement, if any, of the protons of the solvent. This investigation was centred around the asymmetric 2270cm⁻¹ band which seems to be cation independent¹⁵ and in good agreement with other crystal data^{14,24}. However, this band was greatly influenced by hydrogen bonding by such solvents as dimethylsulphoxide and hexamethylphosphoramide as well as protic solvents as can be seen in Figures 5.2 and 5.3. A detailed study of the effect of the two aprotic solvents in a binary system with water within the full range of mole fractions is shown in diagram 5.4. The only solvent that produced a broad spectrum of the B—H stretching band with no specific resolved bands to give data was dimethoxyethane (glyme). This could be due to ion pair formation, in which case the value recorded does not relate to the normal ion.

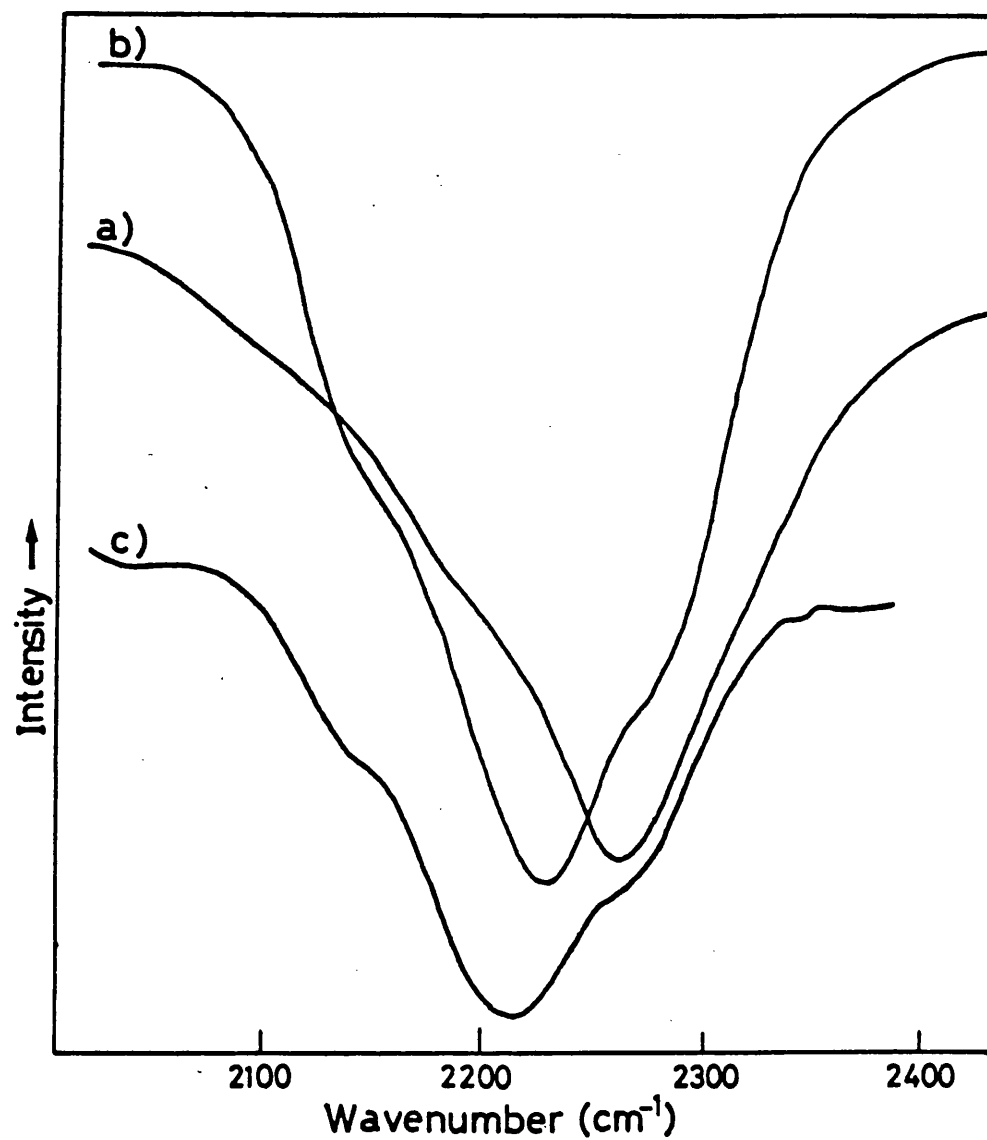
From Figure 5.2, the data suggests that water has induced a high frequency shift in the B—H stretching frequency. This seems to be the case for other "acidic" solvents. There is no noticeable splitting of this band, so the solvation is probably symmetrical. However, for mixed protic-aperotic solvents (Figure 5.5), the band became appreciably broader in the

FIG. 5.1

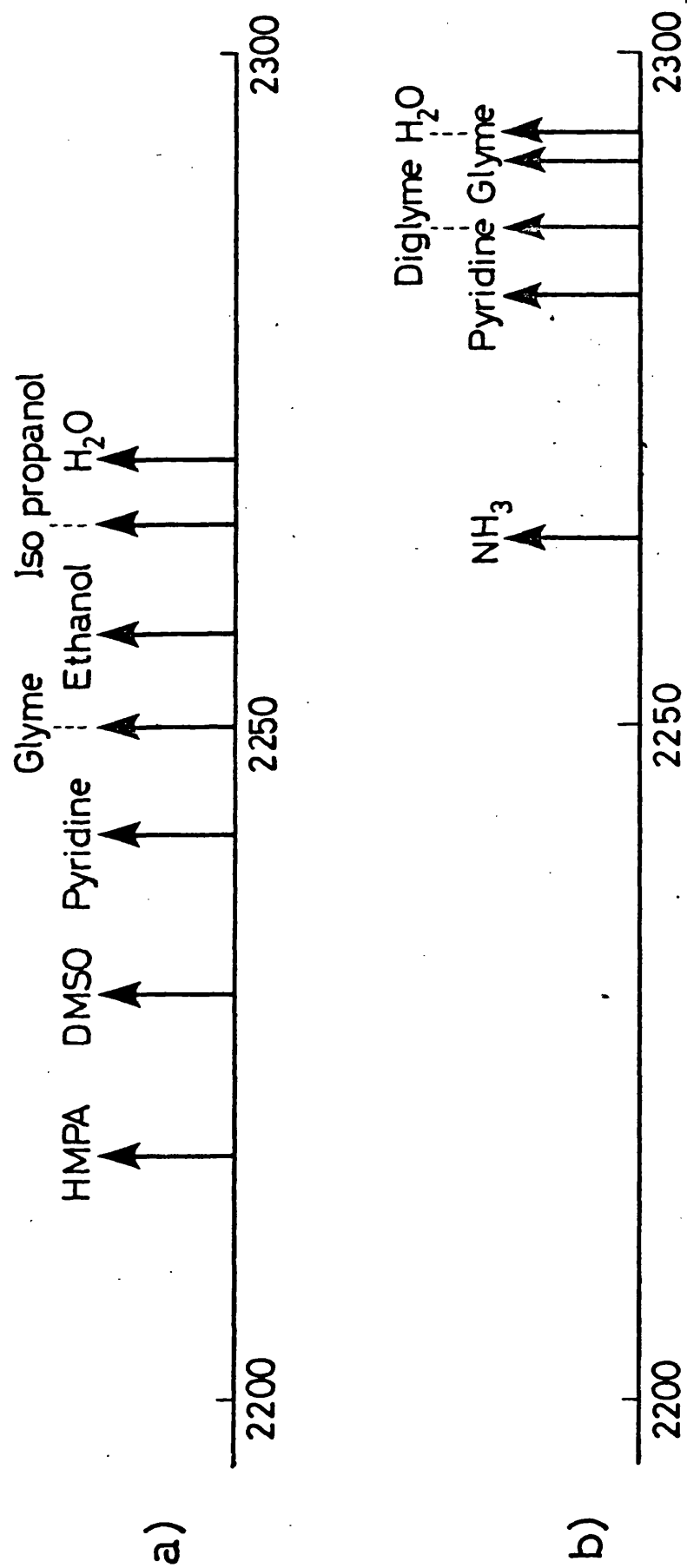


Band energy for the O-D stretching frequency of HOD in D_2O containing various salts as a function of salt molality at ambient temperature.

FIG.5.2



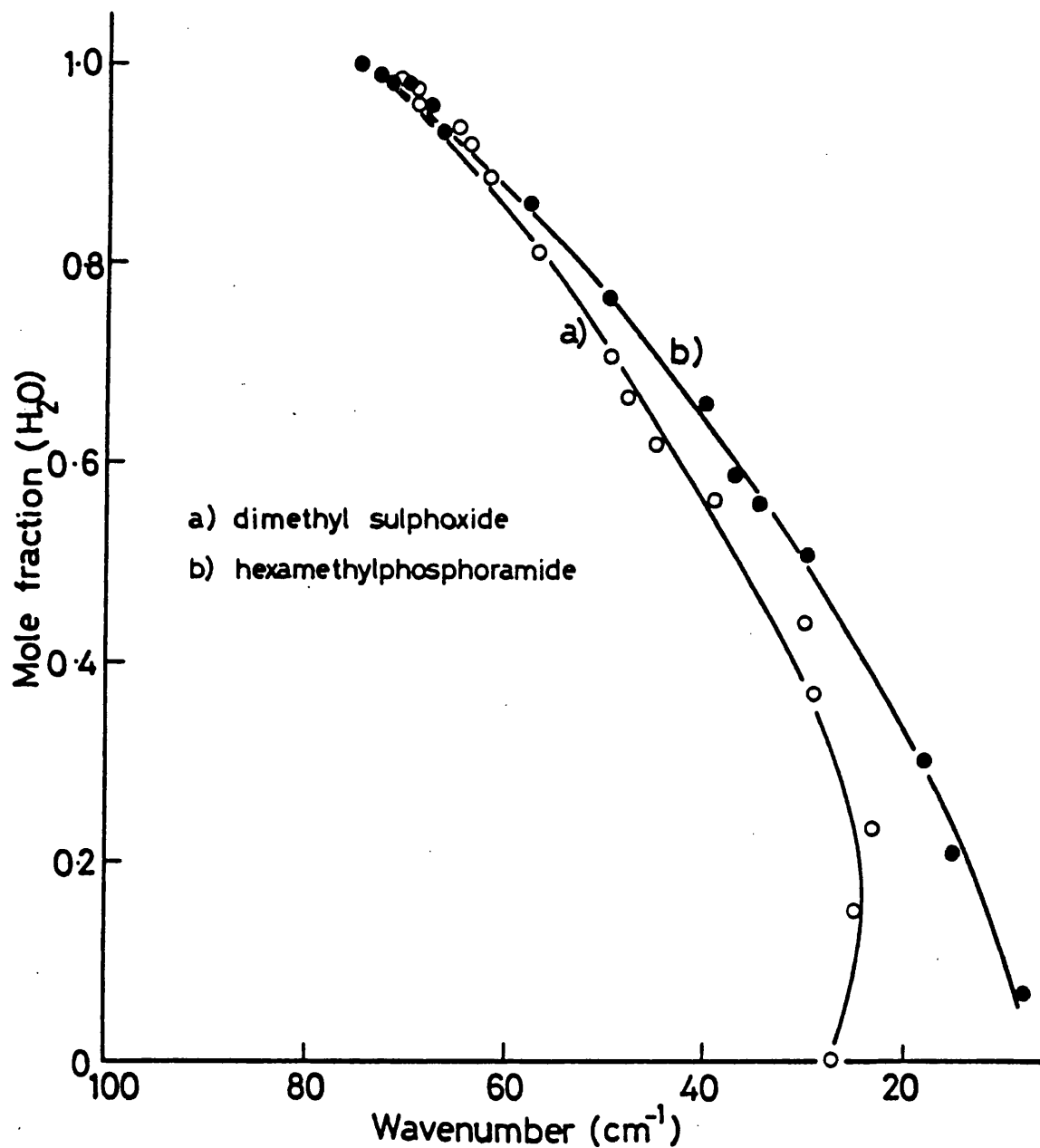
Infrared absorption spectra for the $\bar{\nu}_3$ asymmetric B-H stretch for BH_4^- ions of sodium tetrahydroborate (0.25 mol Kg) in a) H_2O , b) DMSO, c) HMPA.



Band maxima a) for the $\bar{\nu}_3$ asymmetric B-H stretch for BH_4^- ions in various solvents, together with Raman shifts for $\bar{\nu}_1$ taken from ref. 17, at ambient temperature.

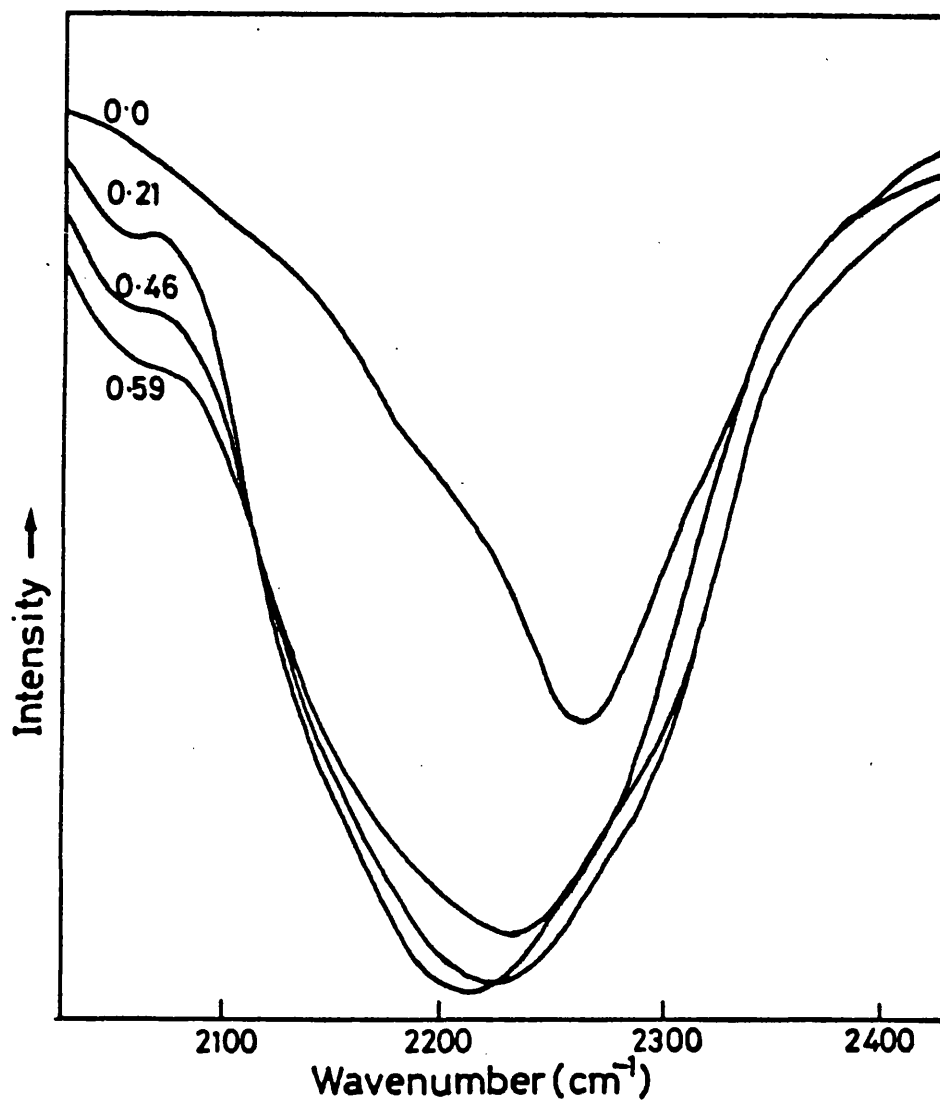
FIG. 5.3

FIG.5.4



Band maxima for the $\bar{\nu}_3$ band of BH_4^- in mixed aqueous solvents,
at ambient temperature.

FIG.5.5

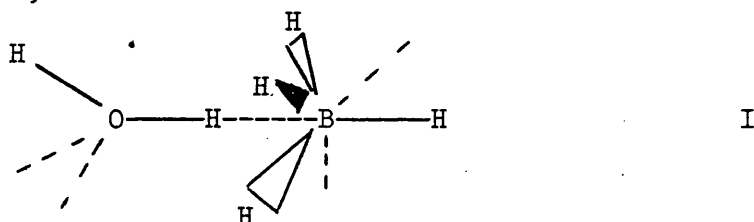


Infrared absorption spectra of HOD in H₂O in the O-D stretching region containing sodium tetrahydroborate (0.9 mol Kg⁻¹) and HMPA at several mole fractions (0.0, 0.21, 0.46 and 0.59) at 298 K.

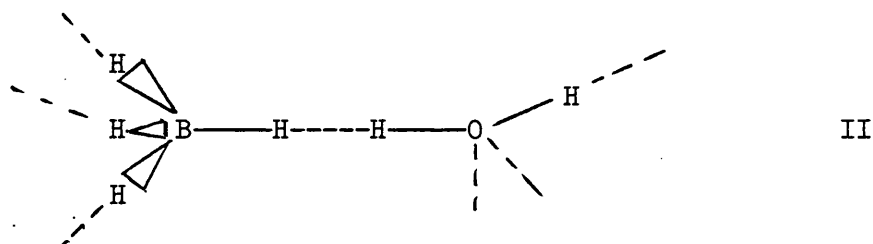
region of rapid shift, relative to the results for the pure solvents. This may have two contributing factors. One is that, as BH_4^- loses bound water molecules, a series of discrete spectra should be detected, in contrast with the averaged shift observed by n.m.r. spectroscopy. The other is that these intermediate spectra will have low symmetry and this might result in some band splitting. The net result was just simply a marked broadening, with no clear isobestic point.

5.3 CONCLUSIONS

All these results seem to point towards an interaction between BH_4^- and water protons which have the spectroscopic characteristics of hydrogen bonding. This conclusion is the opposite to that drawn by Shirk and Shrivar in their less extensive Raman spectroscopic study¹⁷. We suggest that the solvation is tetrahedral, so that the ion can fit into water structural units. However, the solvation of the ion probably takes the form shown below with the protons pointing towards the faces of the BH_4^- tetrahedron,



rather than the structure below:



Structure I results in electron donation from BH_4^- into the hydrogen bond with a consequent deshielding of the BH_4^- protons. This donation of electrons from the B—H bond on the formation of hydrogen bonds produces a subsequent strengthening of the B—H bonds which could result in a high frequency shift for $\bar{\nu}_3$. The B—H bonds are strongly polarised with a large δ^- charge on the protons. On the formation of structure I this polarisation would be partially reversed and so an increase in bond strength could be envisaged.

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CHAPTER SIX

VIBRATIONAL STUDIES OF
METHANOLIC TETRA-ALKYLAMMONIUM
HALIDE SOLUTIONS

6.1 INTRODUCTION

This final chapter is concerned with approaching the solvation problem from a different angle. In the previous chapters, solvation data have been obtained by the study of the effect of ions on the bulk solvent by means of infra-red absorption band parameter changes in the O—H or O—D stretching region. In the case of the borohydride anion study, additional information from the anion stretching modes was obtained.

The approach in this chapter was slightly different because the anion-solvent interactions were investigated in inert media with which there is no appreciable formation of hydrogen bonds with methanol molecules. These results are discussed in conjunction with results for tetra-alkylammonium salts in methanolic solutions which provided a range of anion solvates where both primary and secondary solvation can be observed. It was hoped that the inert media systems would produce an explanatory picture as such systems have provided more detailed spectral data in the past at ambient temperatures than the bulk solvent systems. The low temperature technique as described in previous chapters was employed in the hope of obtaining more precise resolved bands than was possible at ambient temperatures.

Various studies^{1,2,3} of similar aqueous and methanolic solutions at ambient temperatures have been reported. These inert solvent studies have established the O—H stretching frequency and oscillator strength of monomeric methanol and other alcohols which have provided a measure of the unbound alcohol concentration. Further addition of tetra-alkylammonium salts to such solutions produces anion-alcohol complexes with absorption bands at lower frequencies than the (O—H)free band, the relative shifts corresponding to the anion-solvent hydrogen bond strengths.

Anion-alcohol interactions in chloroform have been investigated and found to establish a similar spectral pattern⁴, while studies using benzene⁵ and tert -butyl alcohol⁶, have been discussed in terms of solvent aggregations rather than hydrogen bonding to the anion.

Some dispute concerning the strength of the hydrogen bonding to the fluoride ion in relation to the other halide solvates has arisen, but the increasing order of bond strengths $\text{O—H---F} > \text{O—H---Cl} > \text{O—H---Br} > \text{O—H---I}^{2,3,7,8}$ has now been established, contrary to the results obtained by Allerhand and Schleyer¹.

6.2 RESULTS AND DISCUSSION

(i) Methanolic Solutions in Dichloromethane

Dilute methanol solutions in dichloromethane produced a sharp (O—H)free peak at 3620cm^{-1} with no absorption in the 3300cm^{-1} region. On addition of more methanol a band in the 3550cm^{-1} region was observed. This band was obscured by a newly formed even broader band at lower frequencies when the methanol concentration was increased further. These peaks are well illustrated in Figure 6.1 and are assigned to unbound, dimerised and bound methanol molecules.

On cooling, the spectra obtained from these solutions revert back to their typically broad lower frequency bulk methanol profile that is obtained at ambient temperatures with the narrow high frequency O—H feature decreasing in intensity and the (O—H)bound region gaining in absorption. This phenomenon can be explained by the fact that oscillator strengths of different bands, in general, increase as a function of hydrogen bond strength. In this case the decrease in temperature will strengthen the hydrogen bonds and the solution structure and hence decrease the number of unbound bonds, (O—H)free, but this in turn will increase the intensity of the band envelope at the lower frequency.

This leads to a number of general considerations that have to be taken into account when the numerous proceeding bands are assigned. Firstly, the lower the frequency of the band, the stronger the average hydrogen bond. However, only changes in band frequencies can be considered as oscillator strengths or extinction coefficients are unobtainable and so concentrations of species cannot be determined. There is a great disparity in oscillator strengths between weakly and strongly hydrogen bonded units.

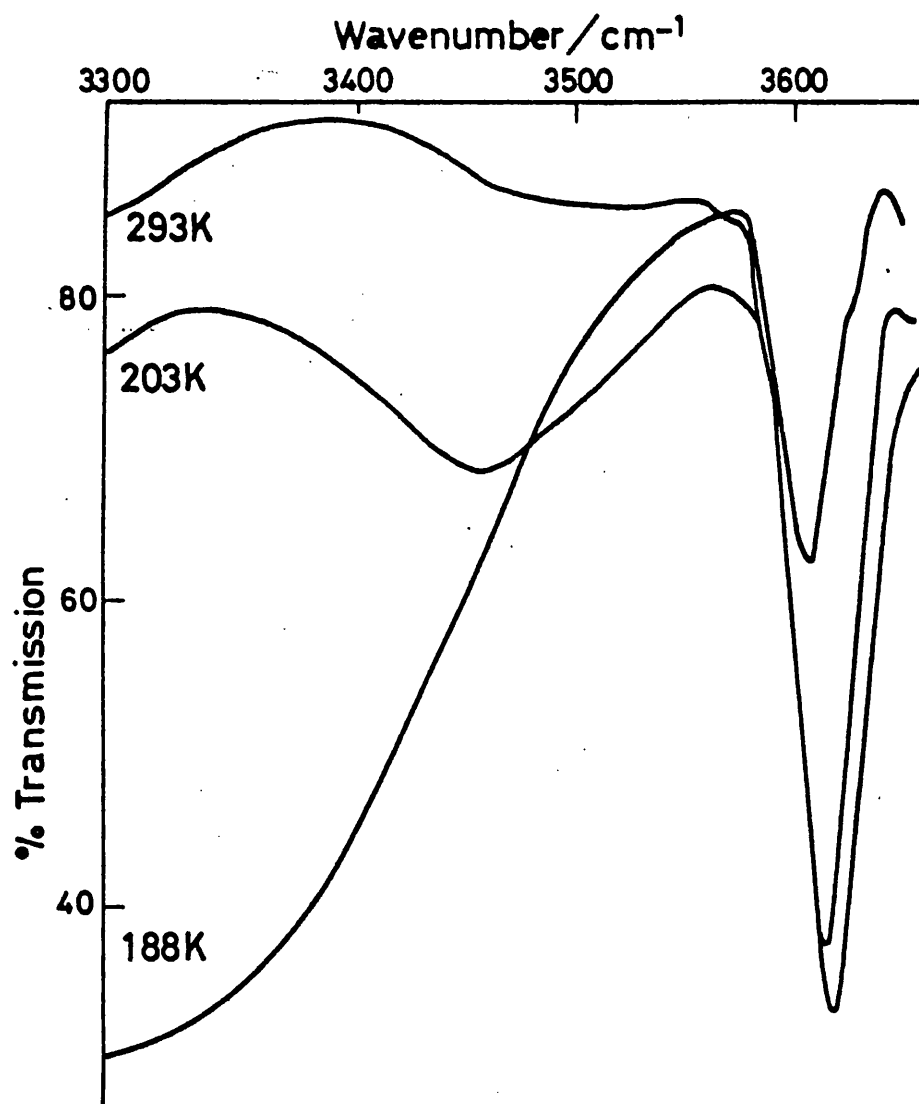


FIG. 6.1 Infrared absorption spectra of dilute CH_3OH in CH_2Cl_2 in the O-H stretching region at three temperatures 293K, 203K and 188K.

So for bands of comparable width, the intensity increases on going to low frequencies or in other words, as the strength of the bond increases, the oscillator strength of the band increases. This explains the large increase in the low frequency band area when the dilute solution of methanol in dichloromethane was cooled down to liquid nitrogen temperatures and the much less noticeable decrease in band area of the (O—H)free band.

(ii) Salt Solutions in Dichloromethane

Dilute methanolic solutions of tetra-alkylammonium salts in dichloromethane or some other inert solvents like carbon tetrachloride all produce a pattern that entails the loss of the (O—H)free band and an increase of intensity at differing frequencies which depend on the nature of the anion when the salt concentration was increased. These bands seem to be independent of the tetra-alkylammonium cations which are thought to play no significant role as regards the hydroxyl group bonding.

Solutions of small amounts of methanol in dichloromethane that contained sufficiently high salt concentrations to produce just the lower frequency absorption band were studied in the lower temperature range. The tetrabutylammonium chloride solutions at room temperature gave a broad band which on cooling shifted by 30cm^{-1} to a lower frequency. However, the low frequency shoulders on the main band which were observed at ambient temperature were obscured by the cooled down, broad, shifted band, and so no further study of these weak absorptions could be attempted. However, additional high frequency bands at 3380cm^{-1} and 3450cm^{-1} were resolved out on cooling as shown in Figure 6.2.

All the band assignments that are made, are discussed in terms of shift from the anion solvate band (for $\text{A}^{-}\text{---HOMe}$) detected in dilute solutions. These anions probably have maximum primary solvation numbers between four and six. These primary molecules (S_1) will be directly bonded to the bulk solvent (S_2 , S_3 etc) as shown below:

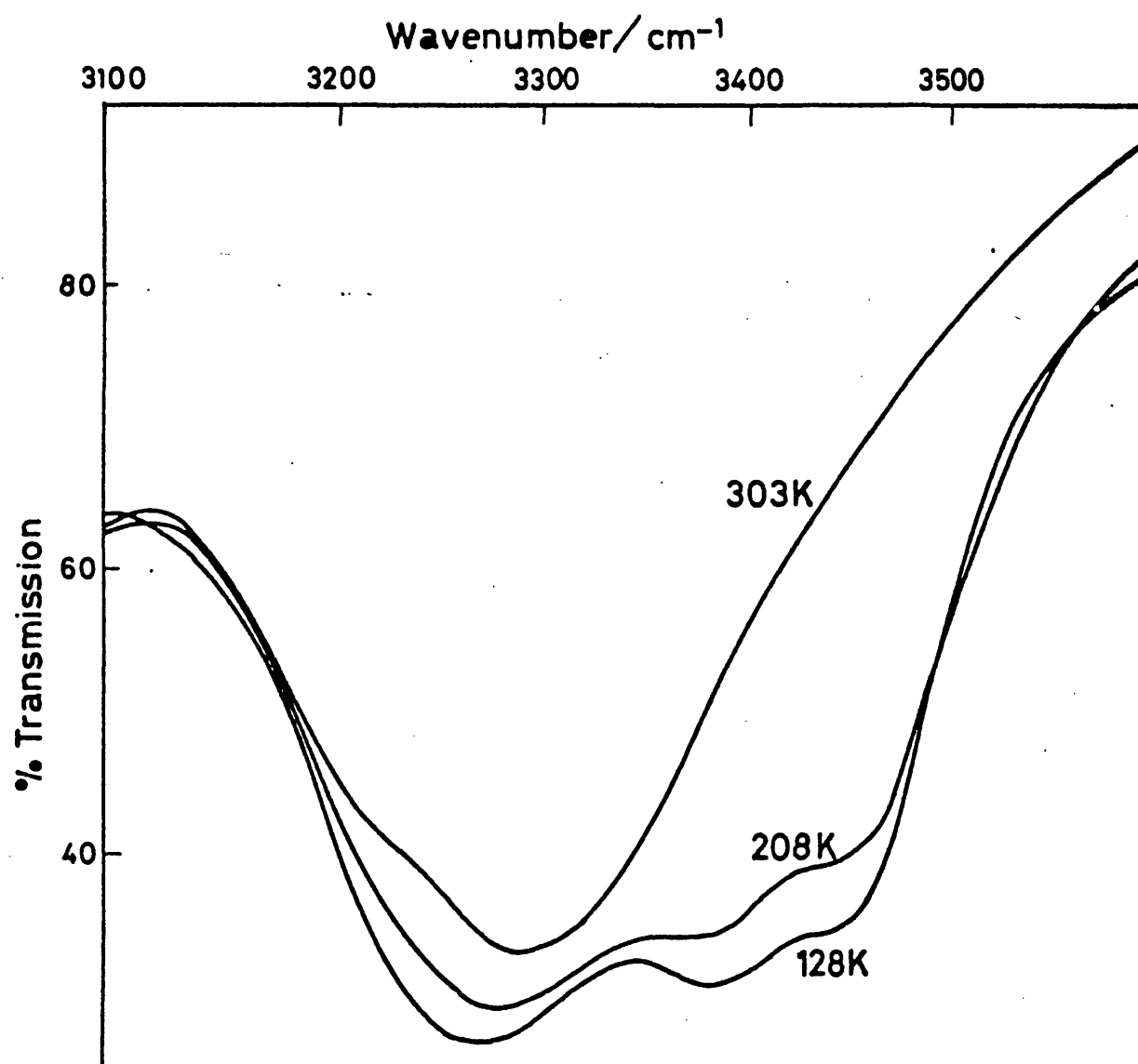
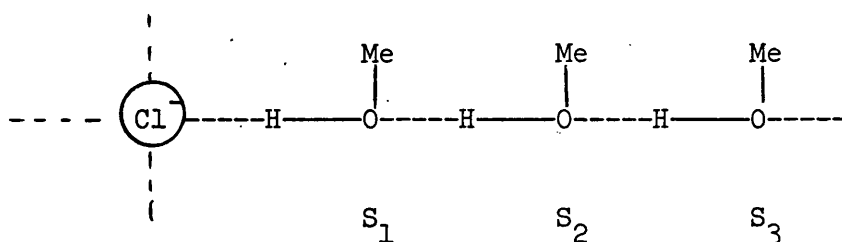


Fig. 6.2 Infrared absorption spectra of $\text{Bu}_4\text{N}^+\text{Cl}^-$ in methanol (1% v.v) / dichloromethane at various temperatures (303K, 208K and 128K).



When the salt concentration is increased, the anions will compete with the methanol solvent molecules and could remove the methanol molecules from the S_1 ----- S_2 ----- S_3 ----- unit and shorten the solvent chain structure. These units will always terminate in a methanol molecule (St) that only forms one hydrogen bond which can be identified with the (lone pair)free or (LP)free unit that has been frequently invoked to explain properties of aqueous solutions¹⁰. Although previously no spectroscopic evidence for their existence had been put forward, there is a strong case that one or both of the high frequency bands could be assigned to St molecules. This will be discussed in the next section dealing with concentrated salt solutions. Addition of inert solvent molecules is expected to lead to loss of S_3 , leading to units having only primary (S_1) and secondary (S_2) solvation. On cooling, aggregation of cations and anions could inhibit primary solvation and force primary methanol molecules into secondary sites.



The width of the low frequency band hides the details that are obtained from pure methanolic solutions (see (iii) below) but the long low frequency tails probably do include some units of a more varied range of species that do not necessarily involve anions.

(iii) Concentrated Methanolic Solutions

Attention is centred on the typical infra-red spectrum for tetrabutylammonium chloride in methanol which is demonstrated in Figure 6.3, where the six bands are labelled (i) to (vi) from the low frequency end.

As described in the previous chapter, methanolic solutions of electrolytes cooled down to temperatures just above and below their glass points, produced two narrower resolved bands instead of the very broad O—H stretching band. For dilute solutions, the narrow high frequency band which

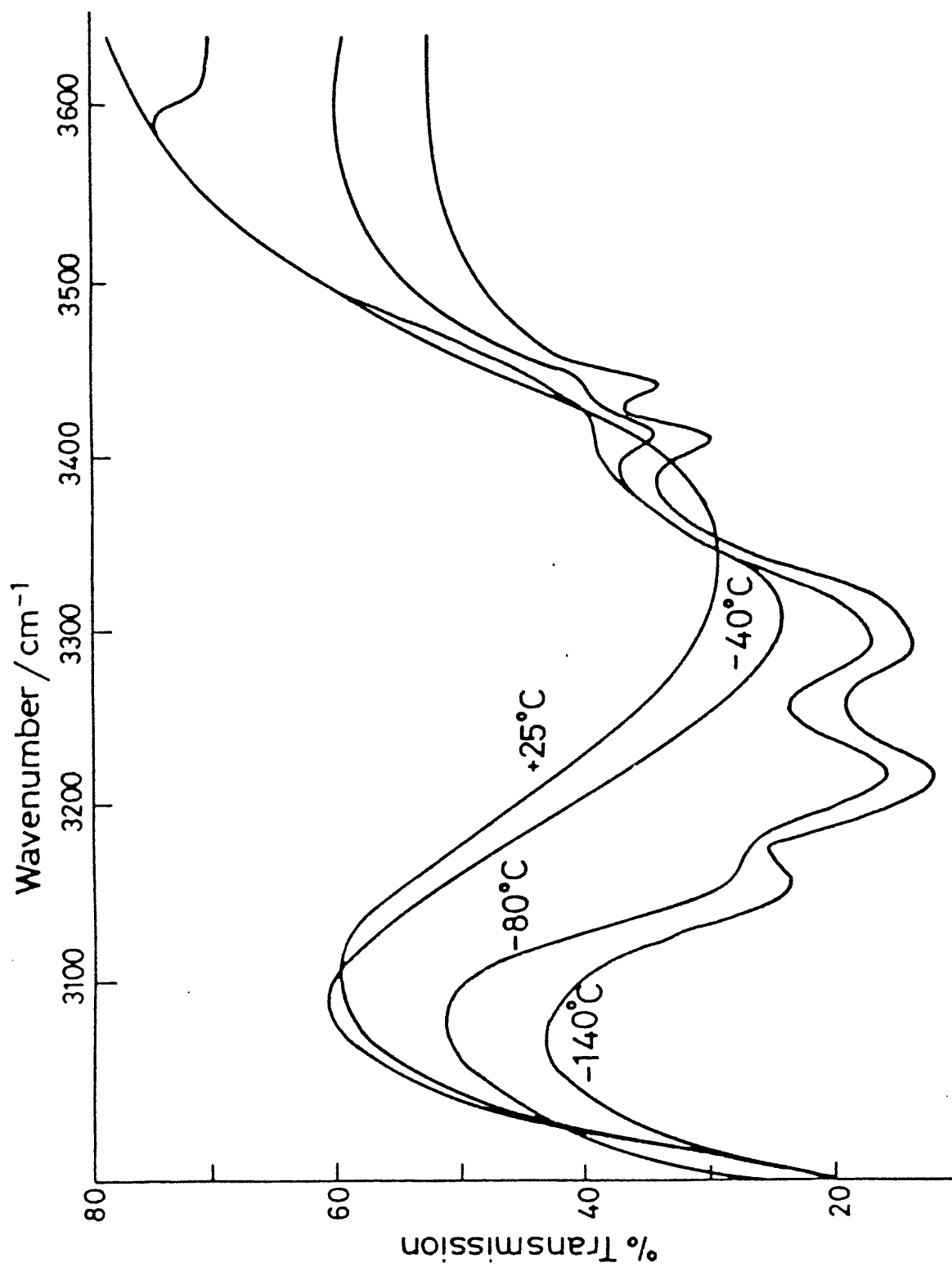


Fig. 6.3 Infrared absorption spectra of $\text{Bu}_4\text{N}^+\text{Cl}^-$ in methanol (CH_3OD) at various temperatures.

was strongly anion dependent, was assigned to primary (S_1) solvent molecules hydrogen bonded to the anion with the broader low frequency band being assigned to residual solvent molecules and to cation solvates. These results showed anion solvation to be precise, but such an extensive process that the hydrogen bonds are weaker than those formed between methanol molecules.

The intense bands (iii) and (iv) in the multiband spectra of concentrated solutions of tetrabutylammonium chloride in methanol are assigned to S_1 molecules for ions having a reduced primary solvation number. It might be argued that the loss of the primary solvent would not occur until all the secondary and tertiary solvent molecules had been lost. This would lead to high frequency shifts for S_1 molecules since the loss, especially S_2 molecules, will weaken the hydrogen bonds to the anions. However, loss of S_1 molecules will cause a strengthening of the remaining S_1 -anion bonds and hence lead to the low frequency shift observed. It is probable that the loss of S_3 also occurs, but not a loss of S_2 prior to the loss of S_1 . Hence band (iii) has been assigned to anions having a solvation number of four while the higher frequency band (iv) has been assigned to a similar arrangement but having a solvation number of five.

The low frequency bands (i) and (ii) at 3150 and 3220cm^{-1} are at much lower frequencies than those obtained for the monosolvate Cl^- ---HOME in dilute solutions of methanol in dichloromethane¹¹ or carbon tetrachloride³. From the statements above, this must mean that S_2 molecules are present as they increase the strength of the S_1 -anion band and also that there are far less S_1 molecules around the anion than that for a fully solvated anion. The difference in the two bands has been attributed to S_1 molecules attached to ion pairs having two or three (S_1 --- S_2 ---) solvent chains which seems to be supported by the observation that band (i) is favoured over band (ii) as the salt concentration is increased.

This reduction in primary solvation could arise from the fact that

in these concentrated solutions contact ion pairs are formed in contrast to the solvent shared ion pairs that are formed in electrolyte methanolic solutions. Here the large quaternary ammonium cations strongly screen the anions so the solvent molecules are physically unable to hydrogen bond to the anion to fully solvate the anion.



The two high frequency bands have both been attributed to St molecules. This suggestion is strongly supported by the fact that bromide salt solutions display an intense band in this region and accords well with studies on solutions of basic aprotic solvents in methanol which also generate LP free groups. Further evidence of this assignment is discussed in the results obtained on the addition of water to these concentrated methanolic solutions. The difference in the two bands associated with St molecules is assigned to different types of terminal methanol molecules where the lower frequency band (vi) could be when the terminal methanol molecule is in the secondary solvation shell while band (v) could arise when the terminal molecule is in the ternary solvation area.

When the spectra of tetrabutylammonium bromide solutions were investigated, a very similar picture to the one described above emerged as shown in Figure 6.4, with the bands at 3280 and 3330cm^{-1} being attributed to non ion-paired anions of different solvation numbers and the bands at 3450 and 3230cm^{-1} to St molecules and molecules attached to ion pairs respectively. The lack of a band in the 3150cm^{-1} region for the bromide solution spectra could be explained by the fact that the bromide ion is of a greater diameter than the chloride ion, and hence more solvent chains, say three $(S_1\text{---}S_2\text{---})_3$ could stereochemically be attached to the bromide ion while for the smaller chloride ion only two solvent chains to the ion-paired chloride ion are possible.

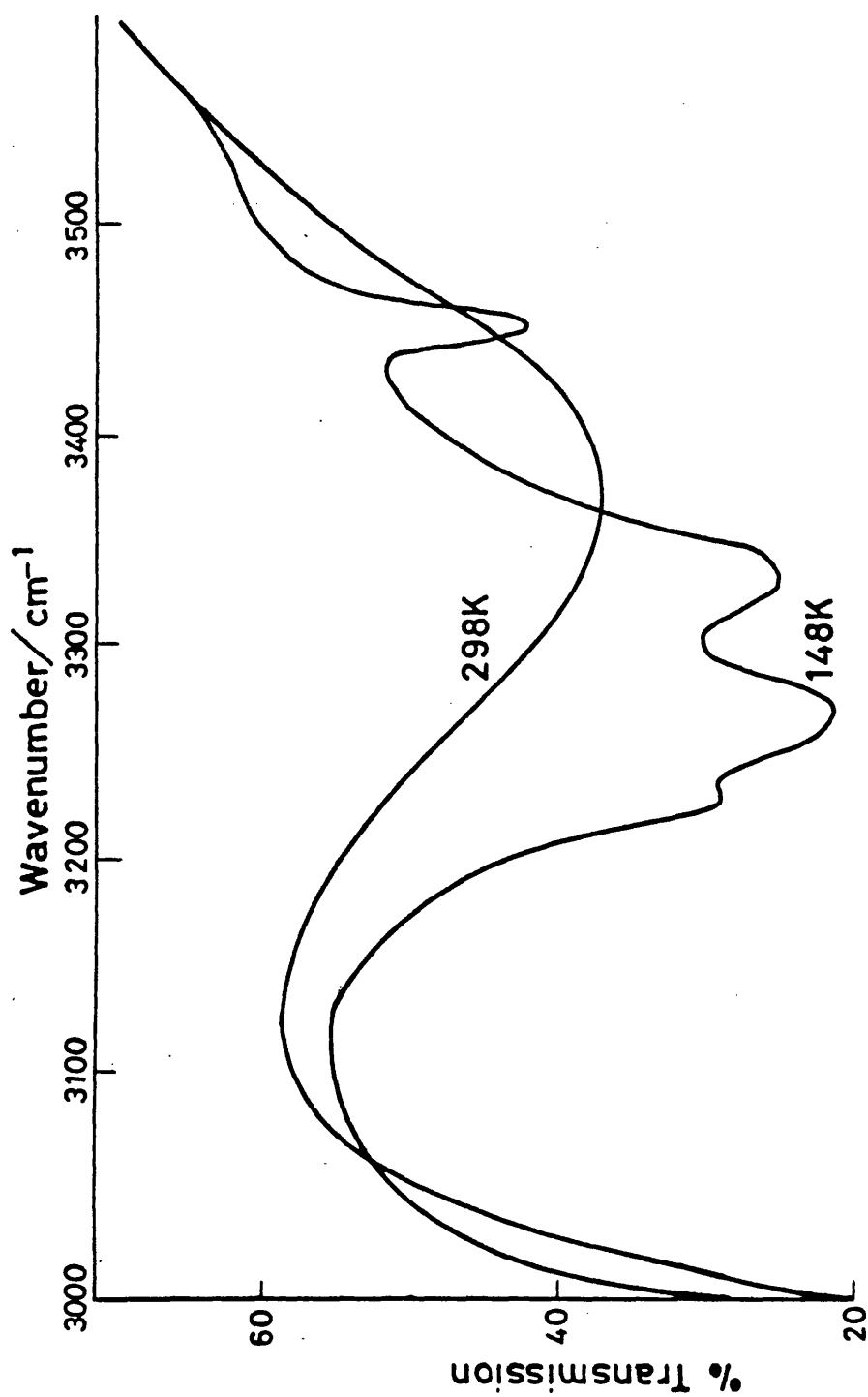


Fig. 6.4 Infrared absorption spectra of $\text{Bu}_4\text{N}^+\text{Br}^-$ (3.6 molar) in methanol (CH_3OH in CH_3OD) at various temperatures (298K and 148K).

The lack of the 3400cm^{-1} band for the concentrated bromide solutions could arise if all the terminal molecules are in the secondary solvation shell, while a much more even distribution of both secondary and ternary terminal molecules occurs for the chloride ion. With more solvent molecules around the bromide ion pair in the primary solvation shell as mentioned above, but approximately equal methanol molecules in both halide solutions, it would seem a reasonable situation that the chloride ion would have longer but fewer solvent chains surrounding it rather than the shorter solvent chains solvated to the bromide ion-pair. Hence, the terminal solvent molecules for the bromide ion-pair are in the secondary solvation shell while the terminal solvent molecules for the chloride ion pair exist in both secondary and ternary solvation shells.

(iv) Addition of Water to Concentrated Tetrabutylammonium Halide

Solutions in Methanol

Trace amounts of water in deuterium oxide (HOD in D_2O) were added to concentrated salt solutions in methanol and the solutions analysed by low temperature infra-red spectroscopy. Trace quantities of water (HOD in D_2O) had no appreciable effect on the spectra, but as the water concentration was increased, the high frequency band at 3450cm^{-1} was lost and a new band at 3410cm^{-1} appeared for the chloride solutions. The high frequency band for the bromide solutions was also lost and only a shoulder in the same frequency range was observed. The central bands at 3280 and 3320cm^{-1} increased in intensity but merged into a single broad feature centred at 3290cm^{-1} . The lowest frequency band was also lost but the other ion-paired solvation band was retained for both halide solutions. These spectral changes were all observed in the water mole fraction range of 0.01 to 0.1 and are well-illustrated in Figure 6.5.

The loss of the high frequency band seems to suggest the removal of the primary and/or secondary solvation shell while the fact that only high solvation numbers exist around the ion-paired chloride ion seems to explain the loss of the low frequency band.

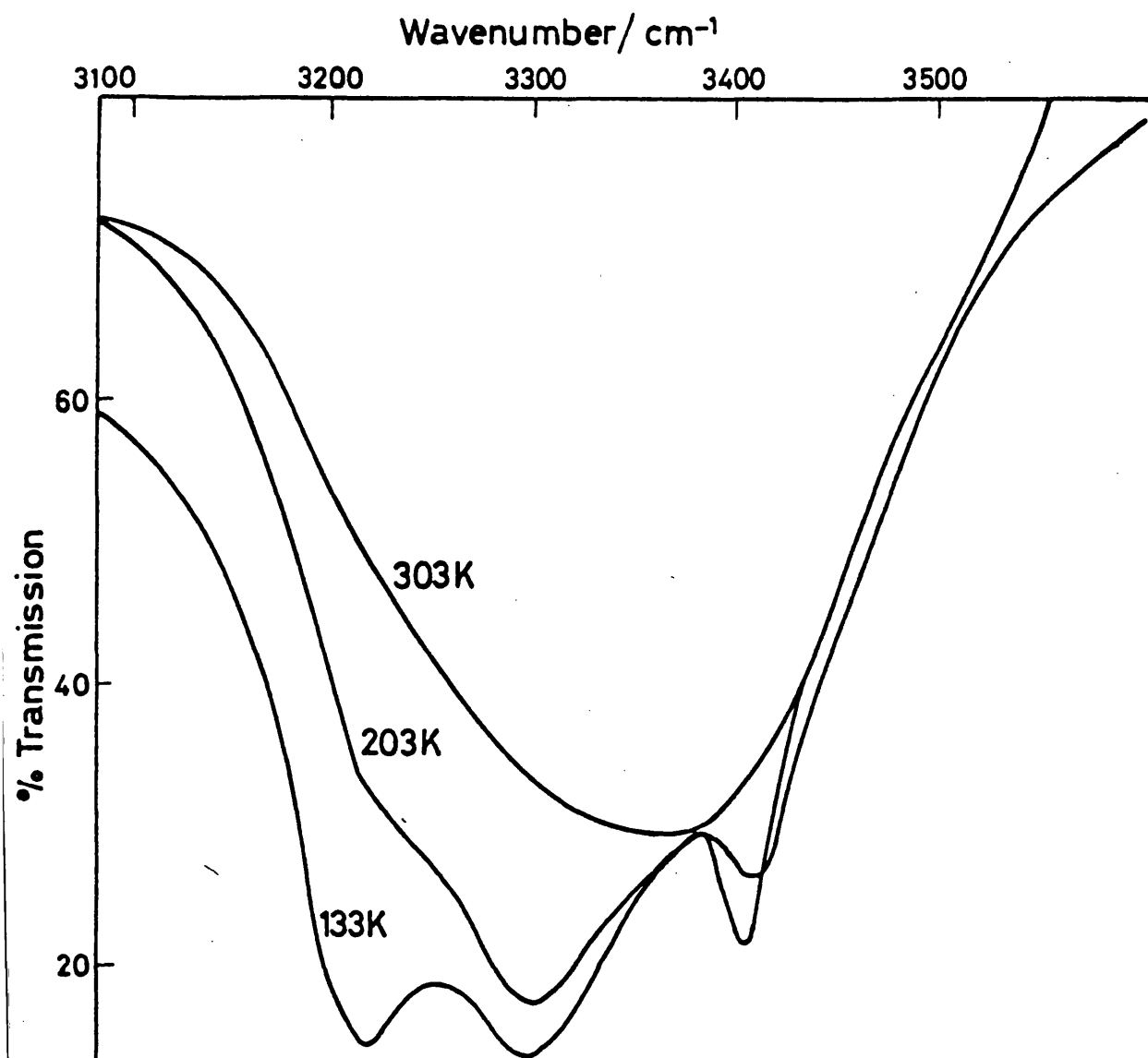
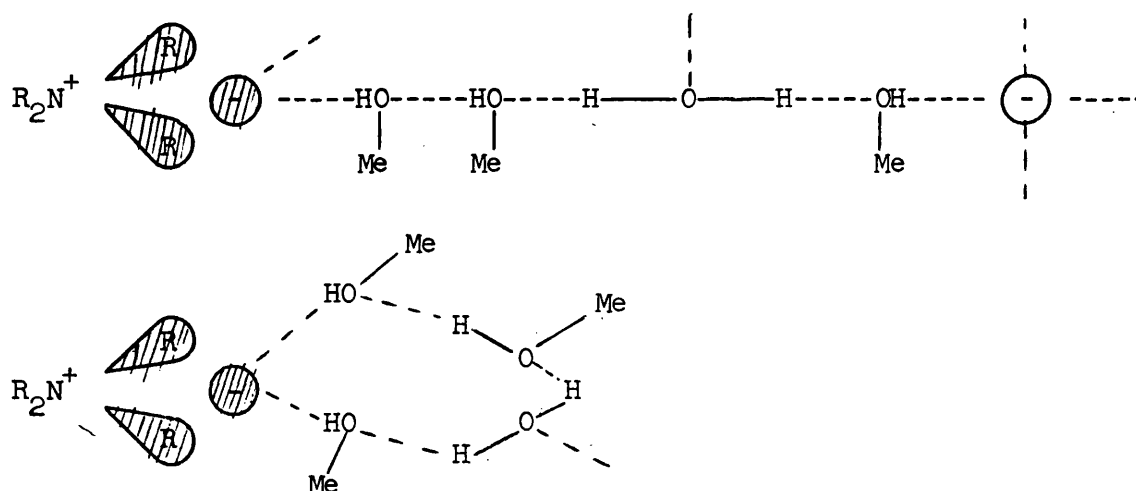


Fig. 6.5 Infrared absorption spectra of $\text{Bu}_4\text{N}^+\text{Cl}^-$ (5.4 molal) in methanol (CH_3OH in CH_3OD) containing 0.01 mole fraction water (HOD in D_2O) at various temperatures (303K, 203K and 103K).

This latter phenomenon could be explained by some water molecules tending to bind to the chloride ion that is already bonded to two solvent chains. This becomes feasible as the hydrogen atom on the water is of much smaller diameter than the methyl group on the methanol and hence can fit in between the large cation and the attached solvent chains and hydrogen bond to the anion while for another methanol molecule to do likewise is physically more difficult.

The loss of the 3450cm^{-1} band could be explained by the formation of a wide variety of chain units or cyclic units as shown below:



This would fit the fact that there is a relatively low concentration of water in the solutions. However, it is important to note that at least one of the water "lone pairs" has to be hydrogen bonded to a methanol molecule otherwise hydrogen bonds formed by water would be very weak and hence give rise to a high frequency band that was not observed in the spectra.

Another possible explanation of the 3410cm^{-1} band could be the O—H stretching mode of the water (HOD in D₂O). However, here again such a molecule would be expected to absorb at much high frequencies. However, addition of methanol molecules to the water oxygen atoms would strengthen these hydrogen bonds and could make the water molecule resemble a modified St molecule which could quite conceivably absorb in the 3410cm^{-1} region.

Nevertheless, a more favoured explanation for the loss of both the high and low frequency bands for the concentrated chloride methanolic

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ABSTRACT

This thesis is concerned with the theoretical and experimental aspects of low temperature infra red spectroscopic studies of ionic solvation.

Isotopically dilute methanolic and aqueous solutions were investigated in the fundamental infra red region, particularly in the O-H stretching region of the spectrum. Systematic room temperature investigations were undertaken for aqueous and methanolic electrolyte solutions as a function of the salt concentrations. These results provided certain trends regarding solvent-solute interactions which the low temperature experiments on the same solutions confirmed so that cation and anion solvation models could be put forward.

Particular attention was given to the study of methanolic and aqueous polyatomic ion solutions to provide further evidence as to whether these anions cause the formation of free or weakly bonded O-H groups.

Infra red studies of the tetrahydroborate anion in various pure solvents and binary mixtures suggested an interaction between BH_4^- ion and water protons which had spectroscopic characteristics of hydrogen bonding.

Finally vibrational studies of methanolic tetraalkylammonium halide solutions in inert and bulk solvent solutions produced a range of anion solvates where both primary and secondary solvation could be observed.