A STUDY OF THE POLARIZATION OF WATER AND METHANOL BY VARIOUS DIAMAGNETIC IONS IN AN APROTIC SOLVENT

Thesis by

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ABSTRACT

Part I. Proton Magnetic Resonance Studies on the Polarization of Water and Methanol by $NaClO_4$, $LiClO_4$, $Mg(ClO_4)_2$, Et_4NClO_4, Bu_4NI, Et_4NBr, and Et_4NCl in an Aprotic Solvent.

The polarization of water by $NaClO_4$, $LiClO_4$, $Mg(ClO_4)_2$, Et_4NClO_4, Bu_4NI, Et_4NBr, and Et_4NCl in acetone and acetonitrile has been investigated by studying the variation in the chemical shift of the water protons as a function of the salt and water concentration. The effects of cation solvation were obtained from the perchlorate salts since Et_4NClO_4 showed no effect on the water resonance. The effects of anion polarization were obtained from the tetra-alkylammonium salts.

The chemical shifts at low salt and low water concentration are analyzed. Information on solvation constants and the chemical shifts of the solvated ion-water complex are reported and discussed. The results indicate the expected dependence on ion size and charge as well as on the solvent.

Similar studies on the methanol molecule were made using acetonitrile as solvent. These studies have indicated that only one proton of the water molecules is complexed in the anion-water complex.

The experimentally-determined polarization shifts of the OH proton in the various ion complexes of water and methanol are discussed in terms of the electric field and neighbor magnetic anisotropy effect.

Part II. Infrared Spectroscopic Studies on the Influence of $NaClO_4$, $LiClO_4$, $Mg(ClO_4)_2$, Et_4NClO_4, Bu_4NI, Et_4NBr, and Et_4NCl on the OH Stretching Frequency of Water and Methanol in Acetonitrile.

The effects of $NaClO_4$, $LiClO_4$, $Mg(ClO_4)_2$, Et_4NClO_4, Bu_4NI, Et_4NBr, and Et_4NCl on the OH stretching frequency for H_2O and CH_3OH and on the OD stretching frequency of D_2O and CH_3OD in acetonitrile have been investigated. This work was undertaken to supplement the proton magnetic resonance studies reported in Part I. The various complex bands attributed to the various solvated complexes have been assigned and interpreted in terms of the symmetry and the structure of the solvated ion complex.

Part III. Infrared and Proton Magnetic Resonance Studies on the Polarization of Water and Methanol by NaI, LiI, and LiBr in an Aprotic Solvent.

In Parts I and II, a study of the polarization of water and methanol in an aprotic solvent by various diamagnetic salts was reported for the case where the polarization is dominated by one ion. In the more general case, the polarization of water or methanol by diamagnetic salts can be effected by both cation and anion. In this part, the results of some infrared and proton magnetic resonance studies on the polarization of water and methanol by NaI, LiI, and LiBr in an aprotic solvent are reported.

The infrared spectrum of the OH stretching and OD stretching vibration for the various ion complexes of water and methanol is characterized by the appearance of several bands. An attempt has been made towards the assignment and interpretation of the complex bands. The proton chem-

ical shifts for the water resonance are also discussed and analyzed in terms of several possible ion water or methanol complexes.

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PART I

PROTON MAGNETIC RESONANCE STUDIES ON THE POLARIZATION OF WATER AND METHANOL

BY

$NaClO_4$, $LiClO_4$, $Mg(ClO_4)_2$, Et_4NClO_4, Et_4NBr,
Bu_4NI, and Et_4NCl IN AN APROTIC SOLVENT

A. INTRODUCTION

The nature of ions in solution is a problem which has been subjected to considerable investigation and review (1-5). The general aim of work in this area is the understanding of the specific interaction between ions and between ion and solvent molecules.

The large bulk of the work in this area has been concerned with aqueous electrolyte solutions due to the great importance of water in chemical and biological systems. Despite the enormous amount of work that has already been done in the area of aqueous electrolytic solutions, there still remains a considerable amount of conflicting viewpoints even over very fundamental points concerning the details.

Our present state of understanding of electrolytic solutions at the molecular level is definitely limited. This is, in part, due to the inherent complexity of the system and also due to the fact that many investigations have not been designed in such a manner that definitive and quantitative results can be obtained. It is not to be inferred from this statement, however, that experiments which yield qualitative information are of lesser importance. In fact, these studies have provided the basis of our present knowledge of these systems.

Numerous methods of investigation have been used in the past to study electrolytic solutions. Of these, the spectroscopic methods (U. V., visible, IR, NMR, EPR, etc.) have indicated a distinct advantage over other methods, such as those involving the measurement of properties such as vapor pressure, osmotic pressure, electrical conductance, etc. (1,2). The method of magnetic resonance is particularly promising by virtue of the sensitivity of the method to small changes in electronic environment of the chemical species under investigation.

The effects of various diamagnetic salts on the proton magnetic resonance of bulk water, for example, have already received considerable attention (6-11). The original data were interpreted by Shoolery and Alder (6) in terms of the combined effect of a low field shift (chemical shifts measured at constant RF frequency) due to the electrostatic polarization of the molecules together with a high field shift due to the breakdown of the hydrogen-bonded structure of water upon ion solvation. Since the two effects are of comparable orders of magnitude, the observed shifts are consequently rather small. Shifts both to high and low magnetic fields were observed depending upon ion size and charge. Moreover, any perturbation of the water molecules is attenuated because of the small salt-to-water concentration ratio in aqueous solutions. In aqueous electrolytic solutions, the maximum salt-to-water concentration ratio is typically 1/10 to 1/5. Since the water resonance is averaged over all the molecules, any perturbation is attenuated by this factor. Typical relative molar shifts of the proton resonance for various ions are only a few tenths of a part per million (ppm) (6).

The theoretical interpretation of these shifts has been a difficult problem since the shielding is not dominated by one effect alone. The quantitative partitioning of the observed shift in terms of the structure-breaking and polarization effects is by no means trivial. Factors entering into the separate ion contributions were considered by Hindman (9), and an attempt was made to evaluate in a quantitative manner the magnitude of these factors. The results, however, are subject to considerable uncertainty since the effects of structure-breaking and the effects due to the polarization of molecules, such as water, on the chemical shift are still not understood quantitatively.

In view of the general importance of understanding such specific interactions as the polarization of water molecules by various ions, we have made a proton magnetic resonance study of the chemical shift of the O-H proton in water and methanol at low concentrations in the presence of various diamagnetic ions in acetone and in acetonitrile. Nonaqueous salt solutions containing small amounts of water still represent a complicated situation. It is, however, a better defined system than the bulk water case in so far as polarization studies are concerned.

In dilute solutions of water in acetone or acetonitrile, or methanol in acetonitrile, the strong hydrogen-bonded structure between water molecules or between methanol molecules is essentially broken down and replaced by a weaker hydrogen-bonded structure between water and solvent. This is indicated by the fact that the observed shift of the water or methanol O-H resonance moves upfield upon dilution in these solvents. Infrared spectroscopic studies concerning the O-H stretching frequency and band width (12,13) have also indicated that water and methyl alcohol at concentrations less than 0.4 moles/kgm of solvent is essentially monomeric (hydrogen-bonded to the solvent) in solvents such as acetone, acetonitrile, etc.

The subsequent dissolution of salts to these solutions results in a breakdown of the solvent structure and also in the solvent-water (or solvent-methanol) structure upon specific complex formation of the ions to the water or methanol molecules. In the latter case, a change in the polarization of the water (or methanol) results, causing the proton resonance to shift downfield, in some cases by several ppm. Considerably larger shifts are expected here due to the fact that, in comparison to the bulk water case, the salt-to-water concentration ratio is greater. At higher water concentrations where water dimers and trimers exist, the water-water structure is also altered upon salt dissolution. The same applies to methanol in acetonitrile.

In salts where there is a large difference between the size of its ions, only the small ion was found to produce a chemical shift in the O-H proton resonance. It was, therefore, possible to study individual cation and anion effects separately by a suitable choice of a large counter ion, such as the perchlorate or tetraalkylammonium ion. This possibility does not exist in the bulk water case because of the large structure-breaking effect of these large counter ions.

Analysis of the experimental results leads to a determination of the complex formation constants for the various ion-water or ion-methanol complexes as well as their chemical shifts in these solvent systems. In this work, data will be presented for water in acetone and in acetonitrile and for methanol in acetonitrile.

The theoretical interpretation of the polarization shifts for various ions complexed to water in aqueous solutions has received prior attention (9,13). In these cases, it was assumed that the shifts brought about by the polarization of the water molecule could be interpreted in terms of a model which involves the calculation of electric fields effected by the ion and solvent molecules.

The results of such an approach have often been considered to be inadequate and non-representative of the actual problem being considered. This has been a well-recognized fact, but little experimental evidence has been available which defined the polarization problem in a definitive manner so that treatments based on static electric field models could be tested. Furthermore, it is generally felt that such models, although perhaps physically unrealistic, might predict with a fair degree of accuracy chemical shifts involving molecules polarized by ions (9,14).

For molecules in an electric and magnetic field, the nuclear magnetic shielding constant is, to a first approximation, dependent upon both a linear and quadratic electric field dependence. From the experimentally determined polarization shifts obtained in this work, it is possible to make calculations based on the electric field approach to obtain information concerning the polarization phenomena.

The applicability of the electric field approach as well as the results of the calculations are discussed.

B. EXPERIMENTAL

The proton magnetic resonance spectra were recorded on a Varian A-60 NMR spectrometer operating at a temperature of 35°C. Frequency calibrations were made at certain intervals of the measurements using the standard side band techniques. Most of the shifts reported in this work were obtained by measuring directly the difference between the reference signal (internal tetramethyl silane) and that of water or methanol. Accuracy was estimated to be about ± 0.02 ppm.

Since the effect of salt perturbation on the chemical shift of the C-H resonance of tetramethyl silane is negligible, the use of tetramethyl silane as an internal standard eliminates corrections in the observed shift which arise from changes in the volume diamagnetic susceptibility of the sample.

For very dilute solutions of water or methanol in these solutions, a computer of average transients was used in order to obtain a detectable signal.

Spectrograde acetone and acetonitrile were distilled over molecular sieve No. 4A obtained from Union Carbide to reduce the amount of water content in these solvents. Residual water was approximately 0.005%. The solvents were obtained from Matheson, Coleman and Bell.

Triple-distilled water was used throughout this work and was obtained from Professor Anson's laboratory. Spectrograde methanol was obtained from Matheson, Coleman, and Bell.

All of the salts used in this study were of reagent grade and were redried in a vacuum apparatus (Figure 1) at appropriate temperatures ($NaClO_4$ and $LiClO_4$ at 115°C; Et_4NBr and Et_4NCl at 35°C) for a period of 12 to 15 hours before use.

Solutions were prepared by adding anhydrous acetone or acetonitrile to the dry salt followed by the addition of methanol or water.

Anhydrous $Mg(ClO_4)_2$ was obtained from the hexahydrate after recrystallization from a mixture of acetone and carbon tetrachloride. This salt was dried in a vacuum at 215°C for 24 hours. Et_4NCl and Et_4NBr were recrystallized from a mixture of carbon tetrachloride and acetonitrile. The remaining salts were dried without recrystallization.

The salts used in this study were obtained from the following sources: $LiClO_4$, $NaClO_4$, and $Mg(ClO_4)_2 \cdot 6H_2O$ from G. Frederick Smith Chemical Company, and Et_4NBr, Et_4NCl, Et_4NClO_4, and Bu_4NI from Eastman Kodak Chemical Company.

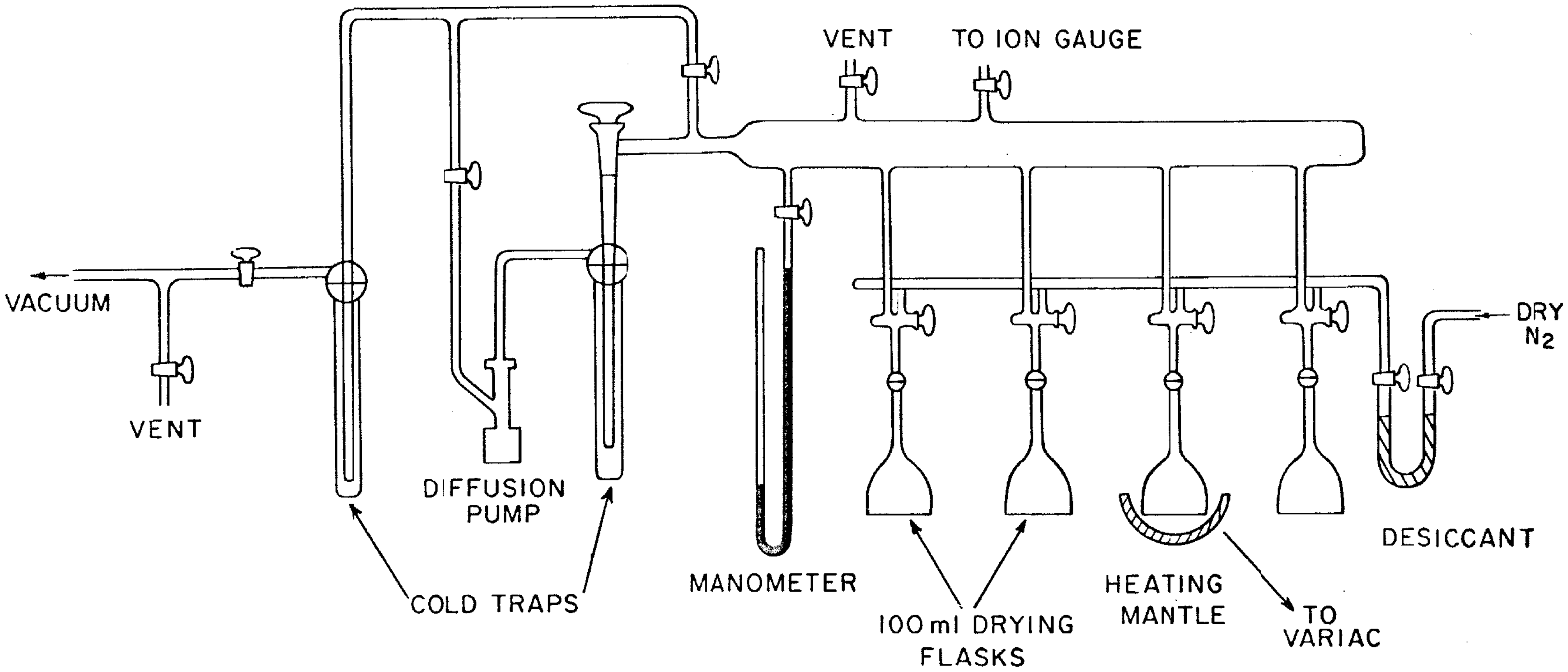

Figure 1. Vacuum Apparatus

C. RESULTS

1. Infinite Dilution Shifts for Water in Acetone and in Acetonitrile and for Methanol in Acetonitrile

The study of the complexation of various ions to molecules, such as water in an aprotic solvent, necessitates some knowledge of the hydrogen bond between water and solvent since the solvent molecule as well as ions are involved in the complex. For this reason, it is imperative to know the chemical shift of monomeric water or methanol (hydrogen-bonded to the solvent) relative to some standard. For reasons which will be discussed later, this reference state has been chosen to be gaseous water.

The chemical shifts at infinite dilution of water in acetone, dioxane, tetrahydrofuran, and pyridine were originally investigated by Mavel (15) at 22°C. Additional studies concerning infinite dilution shifts for water in acetonitrile and other organic solvents were made by Holmes, Kivelson, and Drinkard (16) at 25°C. We report here the essential features pertinent to the present work.

a. Infinite Dilution Shifts for Water in Acetone and in Acetonitrile

The proton resonance of bulk water consists of a single resonance at -5.77 ppm (-4.26 ppm corrected for bulk-susceptibility effects) relative to gaseous water at 35°C. This value was obtained by comparison of the position for the bulk water resonance relative to a sample of gaseous ethane at 20 atm. The position of gaseous water relative to gaseous ethane was reported earlier by Schneider, Bernstein, and Pople (17). The shift for H_2O (gas) relative to C_2H_6 (gas) is + 0.15 ppm, where (+) denotes an upfield shift.

In acetone or acetonitrile, the water resonance shifts to higher field in agreement with the expected breakage of water-water hydrogen bonds. In Figure 2, the observed chemical shifts for the water resonance are reported as a function of the water (or methanol) concentration expressed in mole fraction units for water in acetone and acetonitrile and for methanol in acetonitrile. The shifts are reported relative to internal tetramethyl silane.

It appears that the chemical shift dependence on water concentration is linear within experimental error for water mole fractions less than 1/10. Extrapolation of the data to zero water concentration yields the following infinite dilution shifts for water in acetone (-2.75 ppm) and for water in acetonitrile (-2.24ppm) relative to internal tetramethyl silane.

The infinite dilution shifts relative to gaseous water and corrected for bulk-susceptibility effects are -2.15 ppm for water in acetone and -1.62 ppm for water in acetonitrile at 35° C. A summary of infinite dilution shifts for water and methanol in various solvents is presented in Table 1.

The infinite dilution shifts reported at 35° C are representative shifts for the water molecule hydrogen-bonded to the solvent. This shift is not temperature in-

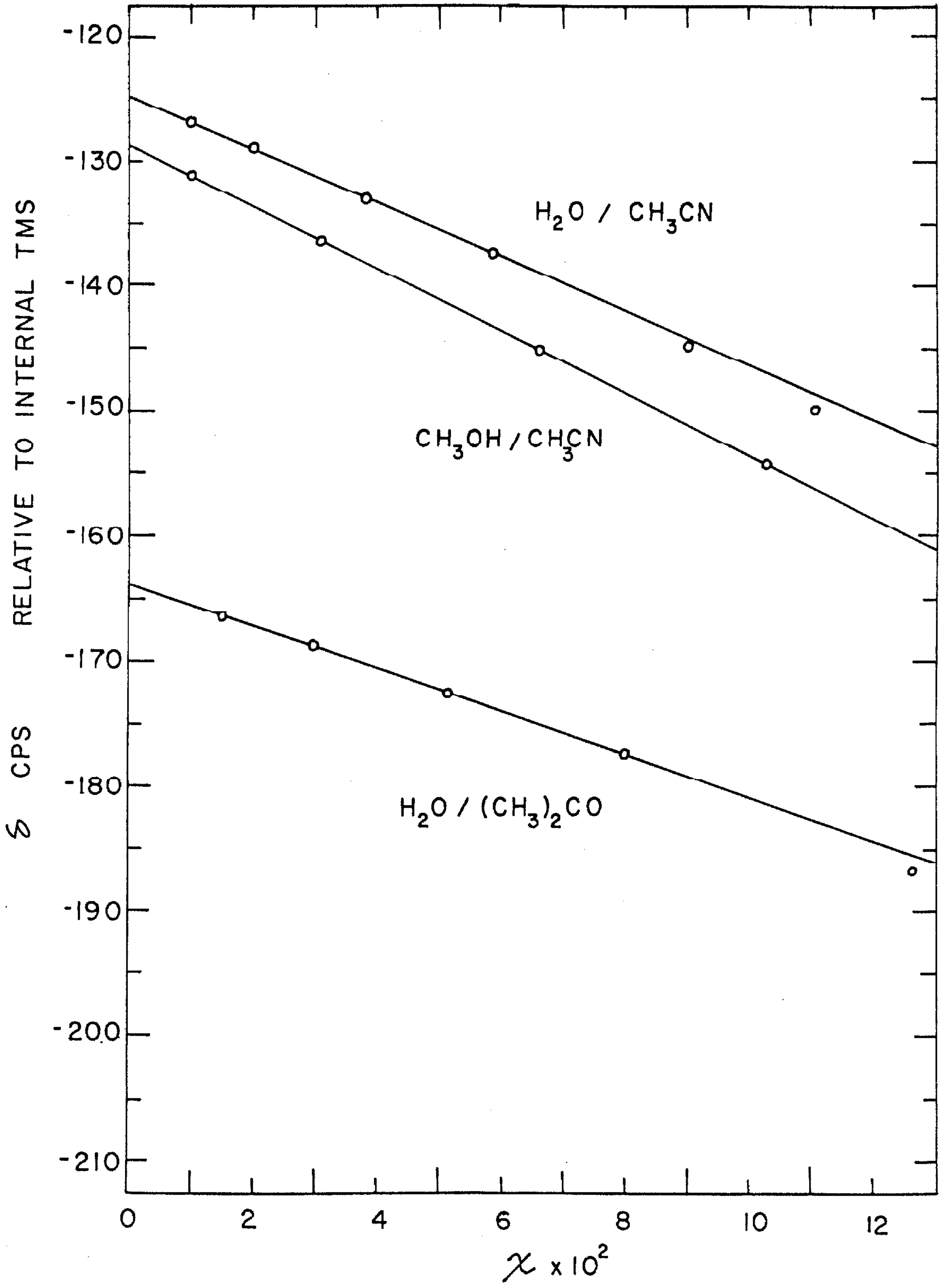

Figure 2. OH Proton Chemical Shifts for Water in Acetone and Acetonitrile and for Methanol in Acetonitrile

TABLE 1

A. Infinite Dilution Shifts for Water in Various Solvents

Solvent	$\delta_H$ppm	T°C	Reference
Water (gas)	0.00	180	17
Ethane (gas)	-0.15	180,35	17,19
Carbon tetrachloride	-0.82	29	18
Benzene	-0.26	29	18
Nitromethane	-1.91	25	16
Acetonitrile	-1.62	35	19
Acetone	-2.15	35	19
Tetrahydrofuran	-2.41	25	16
p-Dioxane	-2.37	25	16
Dimethylsulfoxide	-3.31	25	16
Triethylamine	-3.11	25	16
Pyridine	-4.10	25	16
Water (liquid)	-4.57	25	16

B. Infinite Dilution Shifts for Methyl Alcohol (OH) in Various Solvents

Solvent	$\delta_H$ppm	T°C	Reference
Methanol (gas)	0.00	125	19
Ethane (gas)	-0.65	125,35	19
Carbon tetrachloride	-0.51	35	20
Acetonitrile	-2.16	35	19
Acetone	-3.07	35	19

dependent, but the variation is small amounting to about 5 cps over a range from 25°C to 45°C which is due to the formation of free (non-hydrogen-bonded) monomers.

b. Infinite Dilution Shifts for Methyl Alcohol in Acetonitrile

The proton magnetic resonance spectrum of methyl alcohol in acetonitrile consists of a CH_3 doublet and an O-H quartet (AB_3, J_{AB} = 5.0 cps). The infinite dilution shifts relative to gaseous methanol and corrected for bulk-susceptibility effects is -2.16 ppm for methanol in acetonitrile at 35°C. The observed chemical shifts for the methanol (OH) resonance as a function of the methanol concentration are summarized in Figure 2.

The O-H shift for gaseous methanol relative to gaseous ethane is + 0.65 ppm and -2.64 ppm for the methyl resonance of methanol. The measurements were made with a 100 Mc/s JEOLCO NMR spectrometer. The spectrum of a sample consisting of a mixture of methanol and ethane was recorded at 125°C at an internal pressure of about 7 atm.

c. Polymerization of Water and Methanol in Acetone and in Acetonitrile

To a certain extent, information concerning the polymerization of water in nonaqueous solvents can be obtained from chemical shift measurements (15, 16). The following approximate molal dimerization constants were obtained: 1.9 (moles/kgm acetone)$^{-1}$ for water in acetone and 2.1 (moles/kgm acetonitrile)$^{-1}$ for water in acetonitrile at 35° C.

Approximate trimer equilibrium constants were obtained by Mavel (15) and were considered by Holmes, Kivelson, and Drinkard (16). For water concentrations less than 1 mole/kgm of solvent, the trimer concentration was estimated to be less than 2% (16). The situation for methyl alcohol is expected to be similar.

2. Electrolyte Shifts

The effects of various diamagnetic salts on the proton magnetic resonance of water or methanol can be studied in a number of ways. In the present work, electrolyte shifts (shifts resulting from the addition of electrolyte), were studied as a function of the water or methanol concentration up to approximately 1 mole/kgm of solvent (acetone or acetonitrile) at various salt concentrations. This procedure permits the convenient extrapolation of the chemical shift data to infinite dilution of water where the effects of higher order water-water aggregates on the chemical shift can be neglected.

The experimental data concerning the electrolyte shifts for the various salts studied in this work are summarized in Appendix A (Table I) for water in acetone and acetonitrile and for methanol in acetonitrile.

Representative electrolyte shifts for $LiClO_4$, $Mg(ClO_4)_2$, and Et_4NCl for water in acetonitrile are summarized in Figures 3, 4, and 5. The shifts are reported

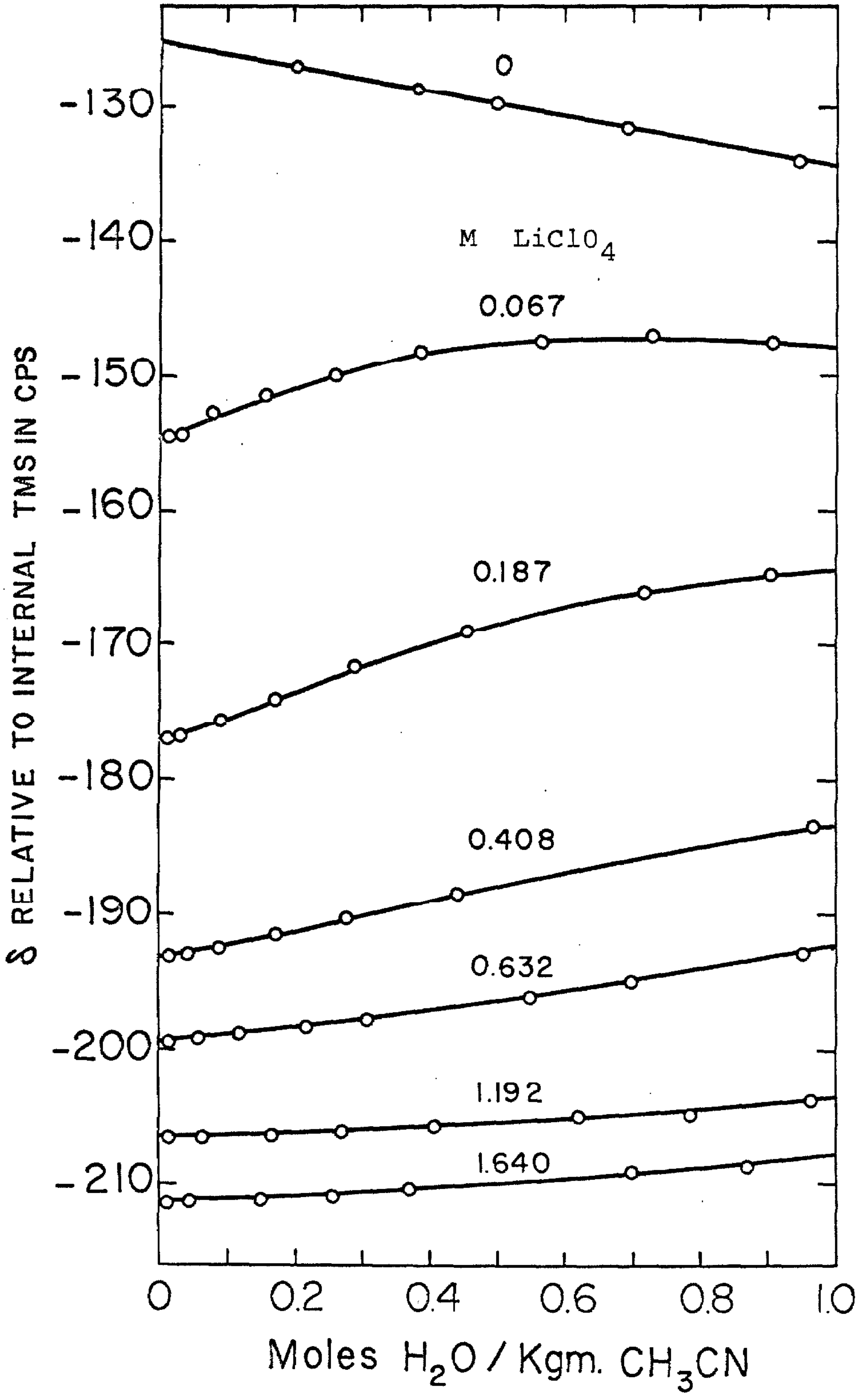

Figure 3. Electrolyte Shifts for $H_2O/LiClO_4/CH_3CN$ System

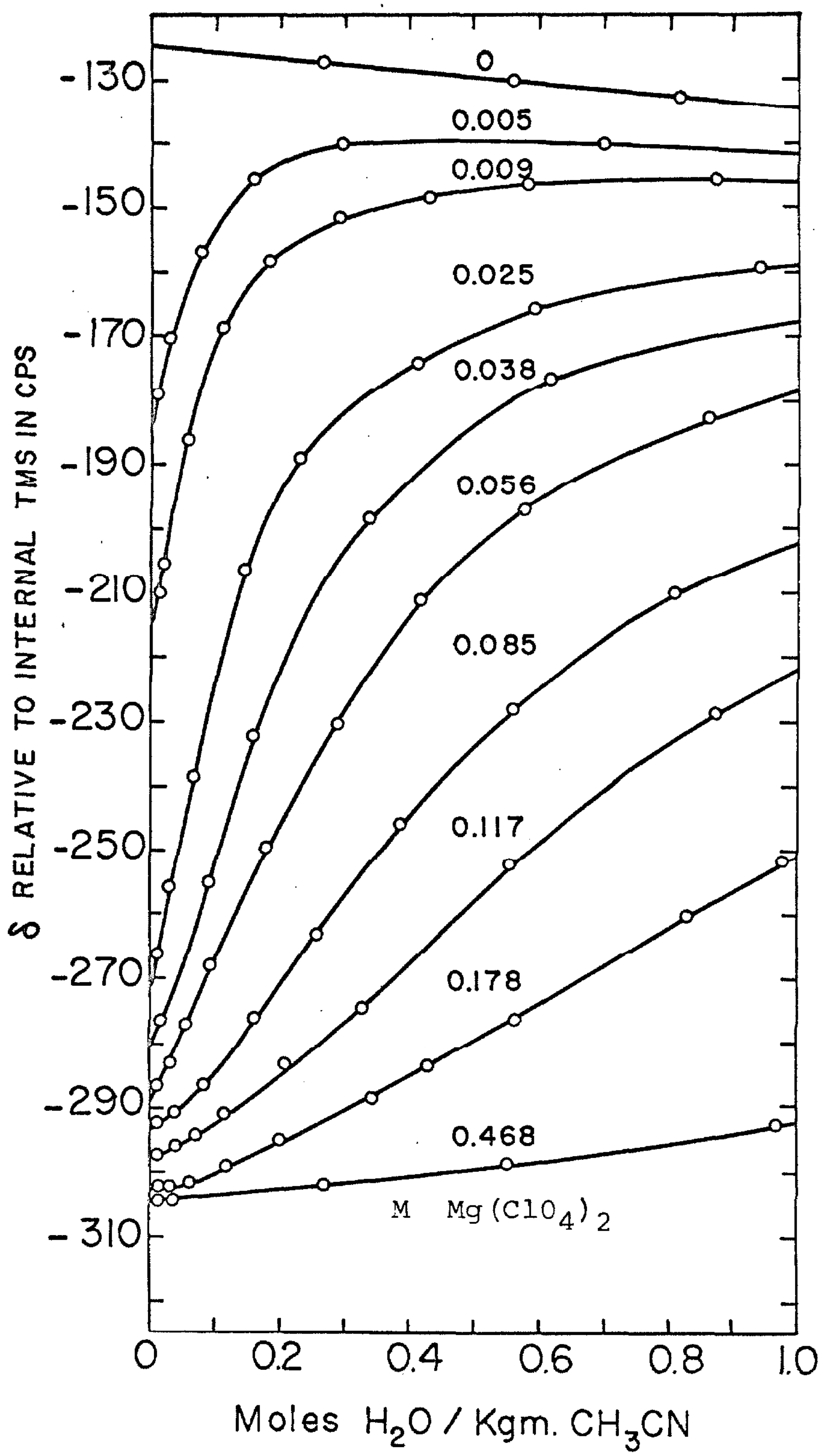

Figure 4. Electrolyte Shifts for $H_2O/Mg(ClO_4)_2/CH_3CN$ System

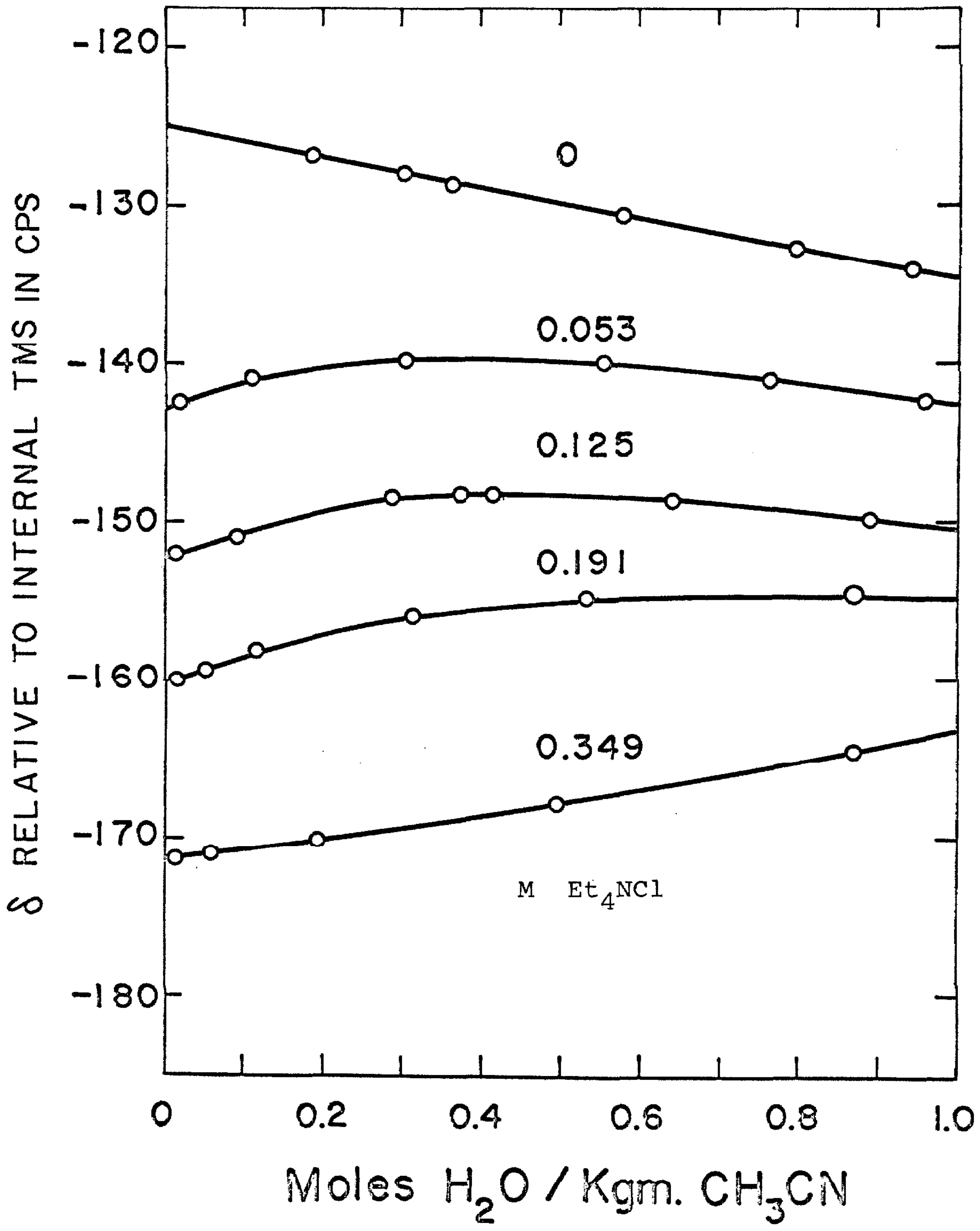

Figure 5. Electrolyte Shifts for $H_2O/Et_4NCl/CH_3CN$ System

in cps relative to internal tetramethyl silane at a RF frequency of 60 Mc/sec. (temperature 35° C).

Since Et_4ClO_4 has been shown to have no effect on the proton resonance of water or methanol in these solutions even at very high concentrations (2 molal), the corresponding perchlorate or tetraalkylammonium salts were used to study the effects of anion or cation polarization of water and methanol.

D. ANALYSIS

1. Polarization Shifts for Water in Acetone and in Acetonitrile and Methyl Alcohol in Acetonitrile

The electrolyte shifts reported in the preceding section represent a comprehensive study of the variations in the chemical shift of water as a function of both water and salt concentration. These shifts represent an average over all the various complexes of water (water-ion complexes, water-solvent monomers, water-water dimers, higher order ion-water solvated complexes, etc.). As the water concentration is increased, all of the electrolyte curves approach the dilution curve for water in the absence of salt since the fraction of complex water molecules decreases for any given salt concentration.

The separation of the individual contributions to the chemical shift due to the various complex species of water is an important but difficult problem.

One aspect of this complex problem concerns the polarization of individual water monomers (hydrogen-bonded to the solvent) by various ions. Information concerning this part of the problem can be obtained by extrapolation of the electrolyte shifts to infinite dilution of water. In this state, the activity coefficient for the hydrogen-bonded monomer will be close to unity. This, in effect, allows us to neglect the possible state of aggregation of water (methanol) molecules as water-water dimers, etc. which occurs even at very low (0.5 molal) water or methanol concentrations.

The extrapolated data illustrating the effects of cation polarization of water by Na^+, Li^+, and Mg^{++} in acetone and in acetonitrile are summarized in Figures 6, 7, and 8.

The magnitude of these shifts is in the expected order of ion size and charge. In addition to the effect of ion size and charge, it can be seen that the limiting slopes for these salts are nearly the same in the two solvents for a particular ion. At high salt concentration, however, there is a noticeable difference in the shifts between the two solvents. This observation suggests that either the state of aggregation of ions, such as ion pairs, ion quadrupoles, etc. is greater in acetonitrile than it is in acetone or possibly that the fraction of water-salt complex is lower in acetonitrile due to stronger ion solvation in acetonitrile.

It is not possible at the present time to decide definitively one way or the other which factor is more important. Both effects are probably involved. Further studies concerning the electrical conductance of these solutions are required before this point can be settled.

Although no shift was seen for the perchlorate or iodide ion this is not the case for the bromide or chloride ion. The effects of anion polarization of water by bromide and chloride using the tetraalkylammonium ion as counter ion are summarized in Figure 9, for acetonitrile.

Due to the low solubility of these salts in acetone, it was not possible to obtain electrolyte shifts in this solvent.

Figure 10 summarizes the polarization data for methyl alcohol polarized by Na^+, Li^+, and Mg^{++}. The shifts are in

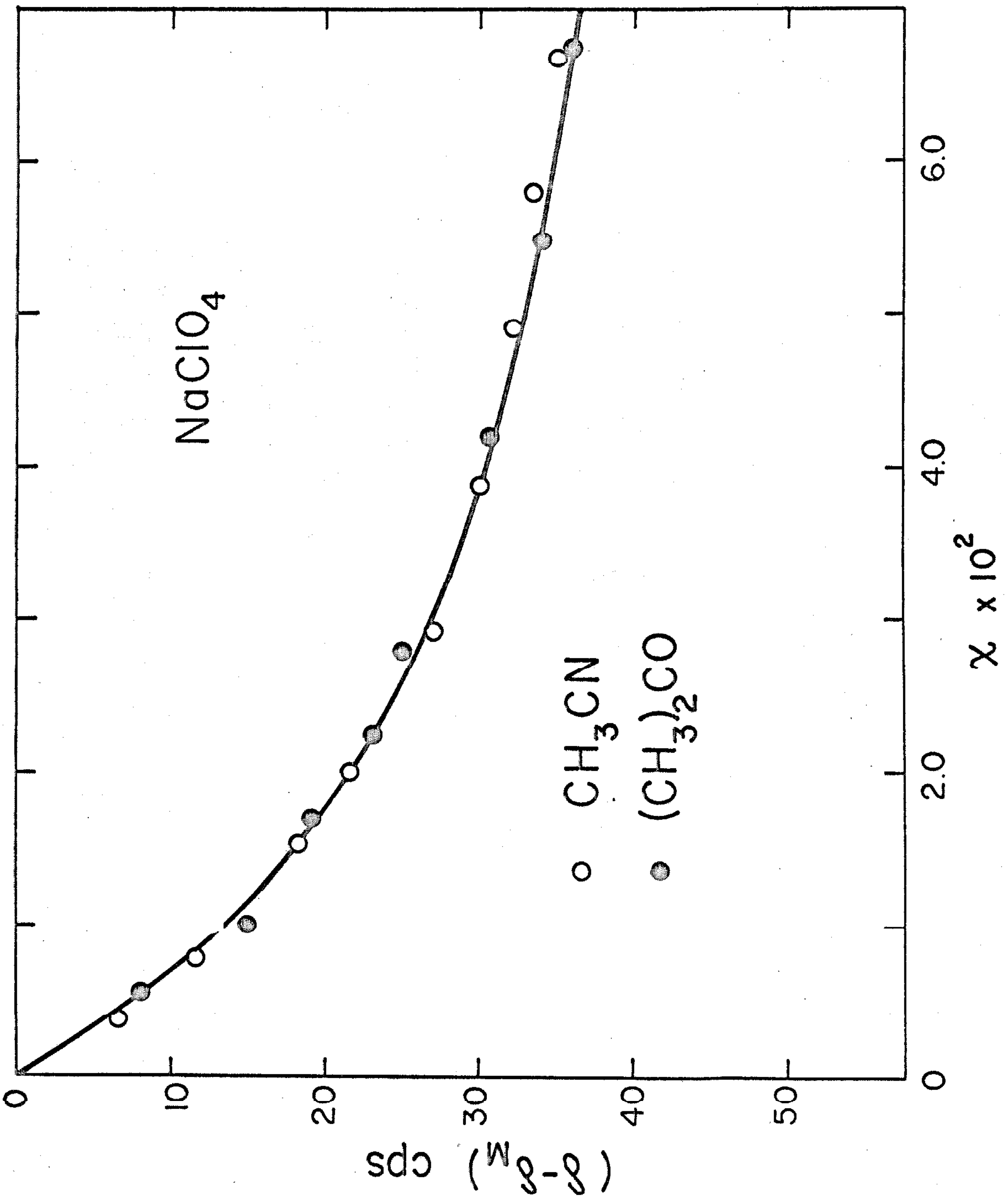

Figure 6. Extrapolated infinite dilution shifts for H_2O in acetone and acetonitrile as a function of $NaClO_4$ mole fraction. The solid curve represents calculated shifts; circles represent experimental data.

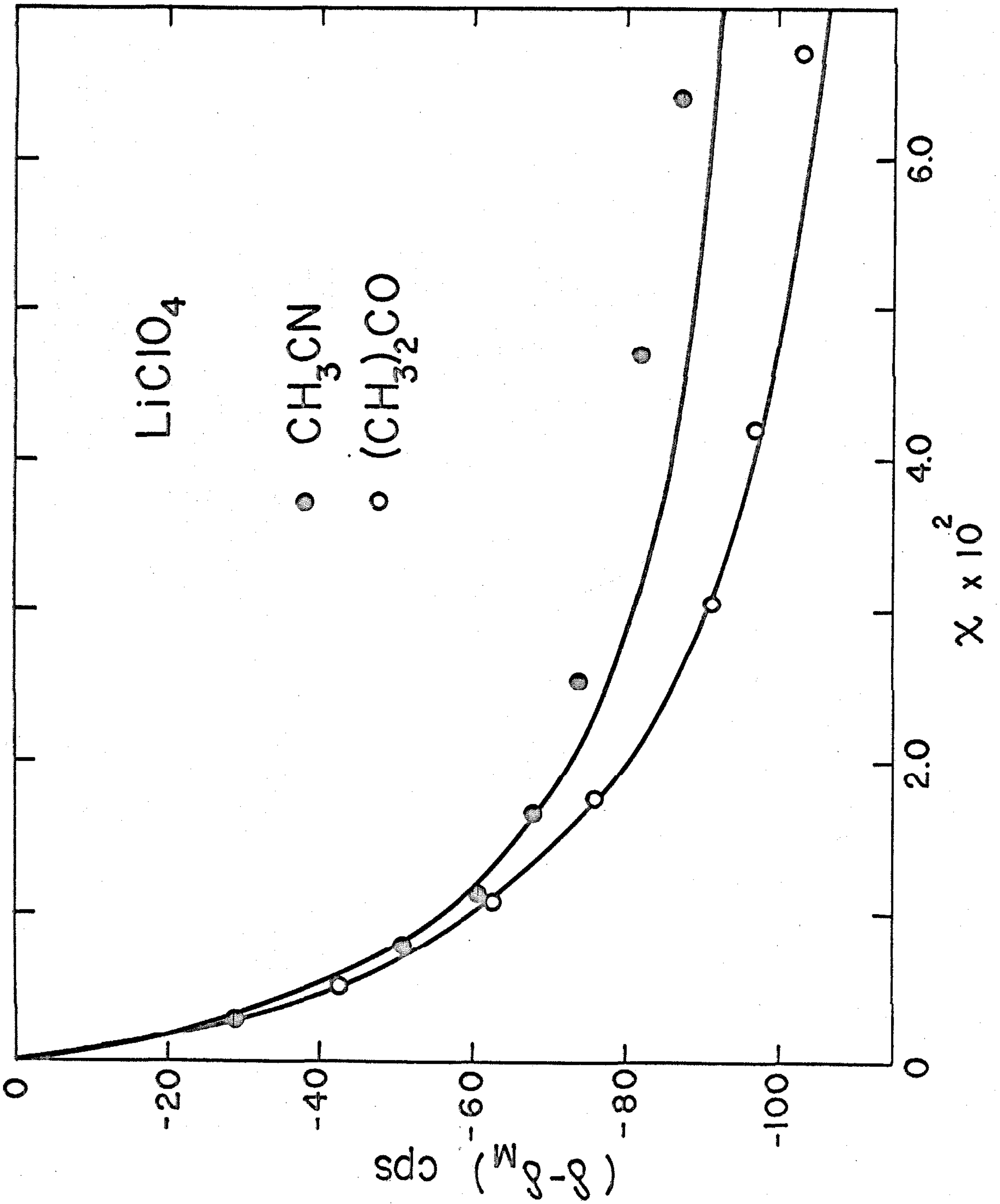

Figure 7. Extrapolated infinite dilution shifts for H_2O in acetone and acetonitrile as a function of $LiClO_4$ mole fraction. The solid curve represents calculated shifts; circles represent experimental data.

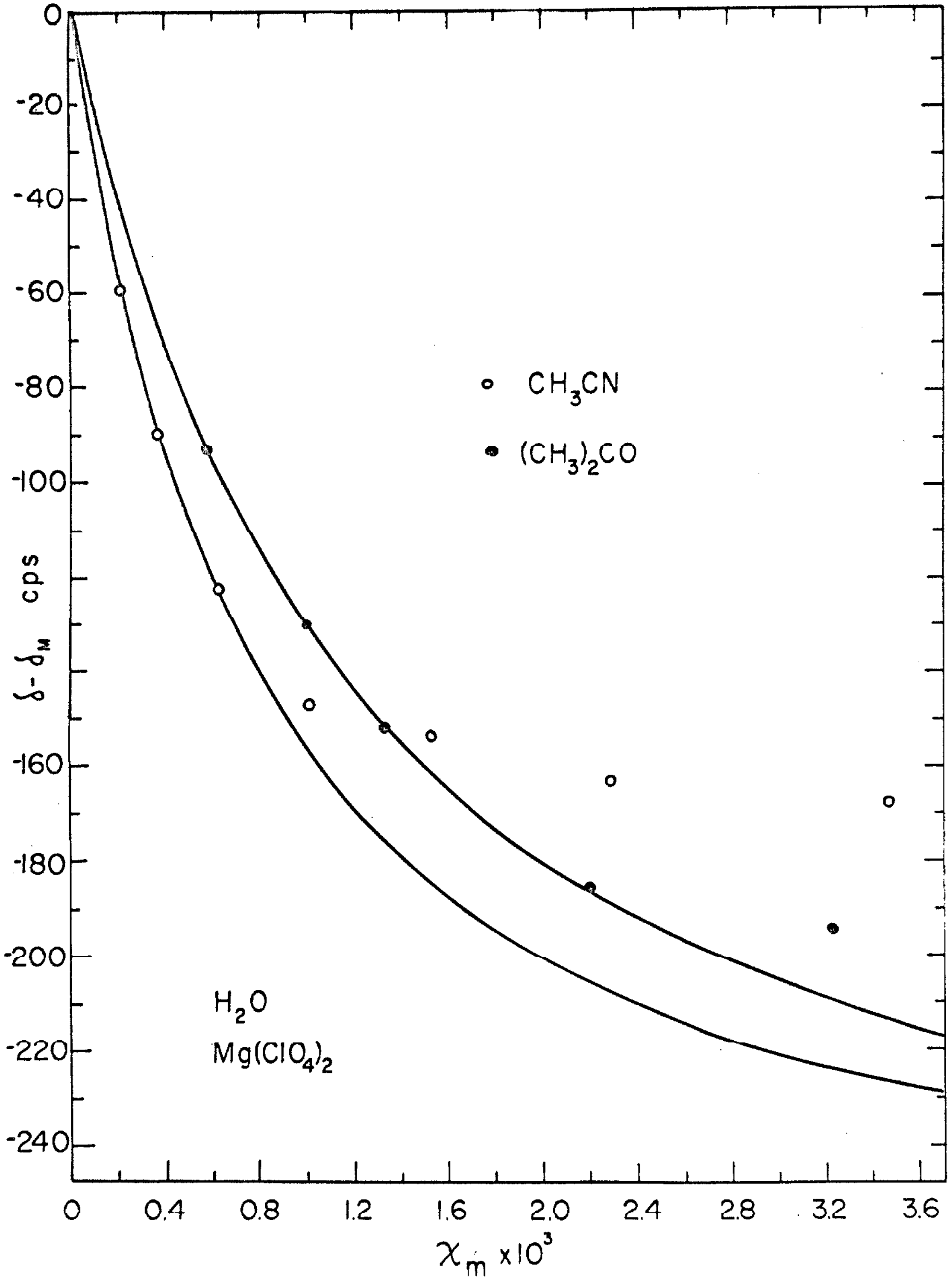

Figure 8. Extrapolated infinite dilution shifts for H_2O in acetone and acetonitrile as a function of $Mg(ClO_4)_2$ mole fraction. The solid curve represents calculated shifts; circles represent experimental data.

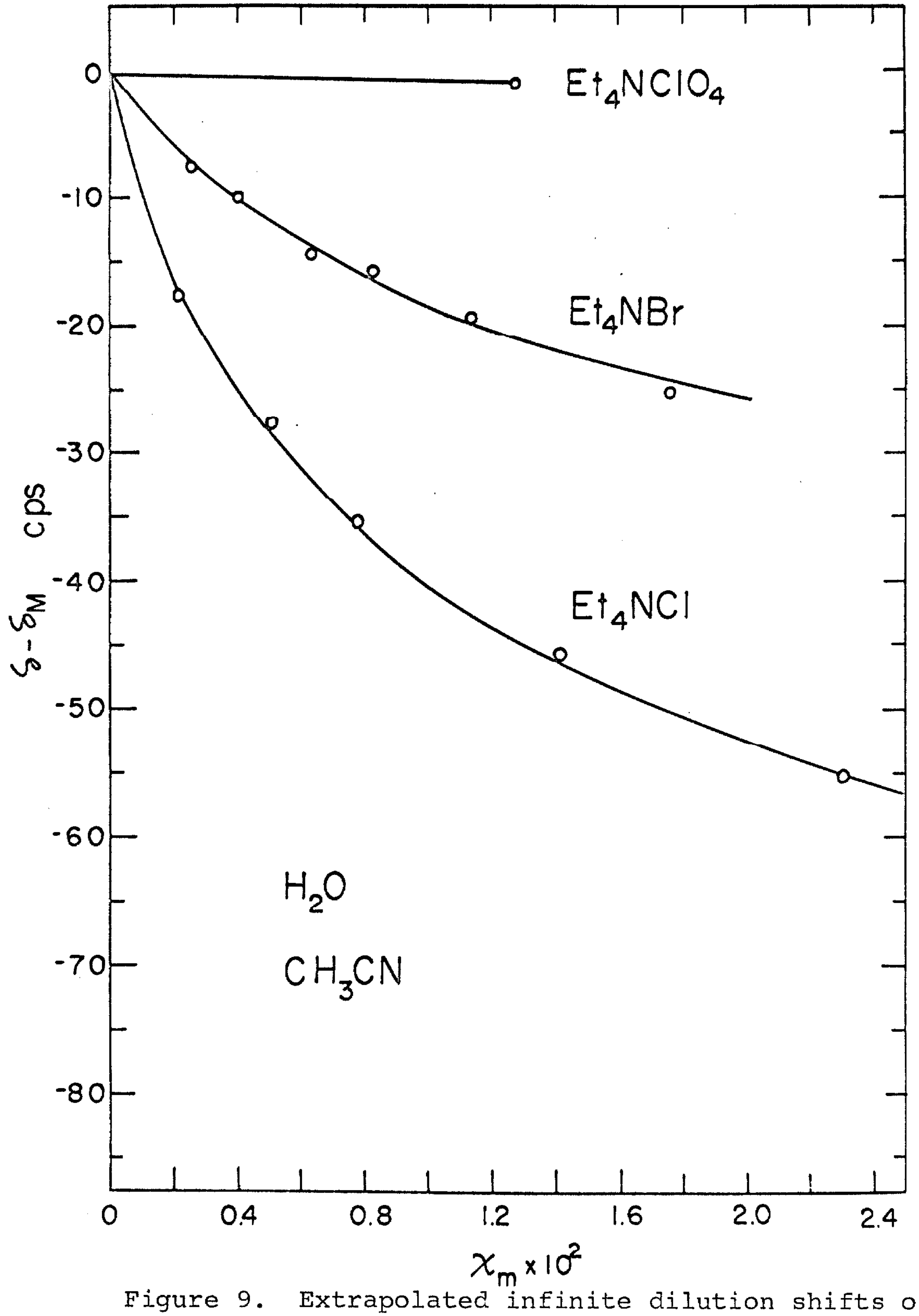

Figure 9. Extrapolated infinite dilution shifts of H_2O in acetonitrile for Et_4NClO_4, Et_4NBr, and Et_4NCl. The solid curve represents calculated shifts; circles represent experimental data.

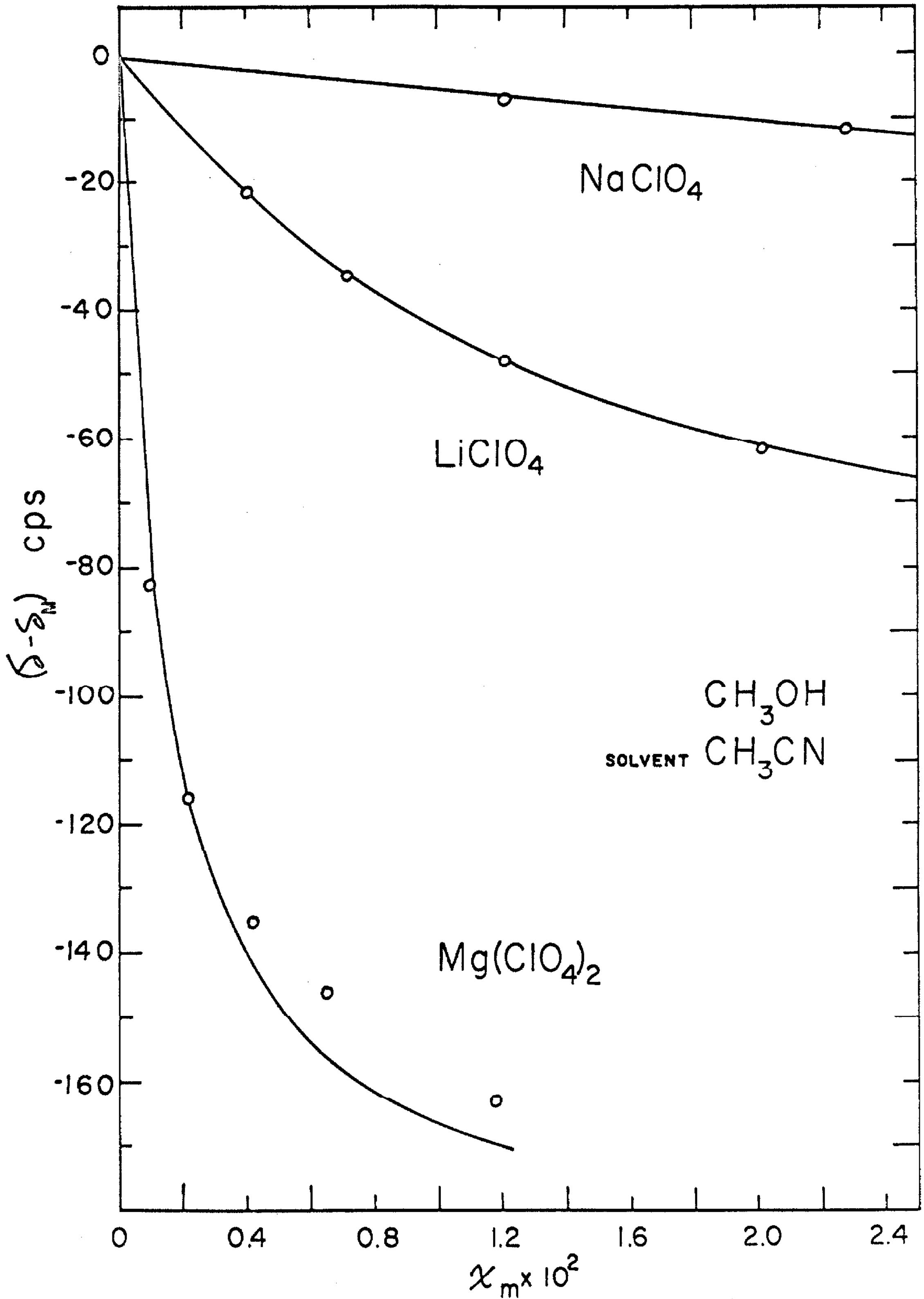

Figure 10. Extrapolated infinite dilution shifts for CH_3OH in acetonitrile for $NaClO_4$, $LiClO_4$, and $Mg(ClO_4)_2$. The solid curve represents calculated shifts; circles represent experimental data.

agreement with those obtained for water in acetonitrile in so far as orders of magnitudes are concerned.

Because of complications due to catalysis of acetal formation by metal ions, similar studies for methanol in acetone will not be reported.

Finally, Figure 11 summarizes the data for methanol polarized by Br^- and Cl^-.

In the case of the addition of Bu_4NI to dilute solutions of methanol or water in acetonitrile, no shift was observed even at 2 molal. This result is not surprising since the polarization effected by iodide and the fraction of complexed iodide water or methanol complexes is expected to be much smaller than for Br^- or Cl^-.

It is immediately apparent that the anion polarization shifts for water are approximately half as large as those for methanol. This can be rationalized by assuming that the ion replaces a solvent molecule attached to one proton leaving the solvent interaction with the other proton of the water molecule essentially unperturbed. Recent studies by Barrow _et_. _al_. (21) on anion water complexes in carbon tetrachloride solutions also indicate the preferential attack of only one proton of water to the anion.

2. Limiting Slopes, Ion Pair Shifts, and Complex Formation Constants

The fact that the polarization shifts are very nearly linear at low salt concentrations suggests that the polarization shifts characteristic of water or methanol polarized by cation or anion can be calculated from the

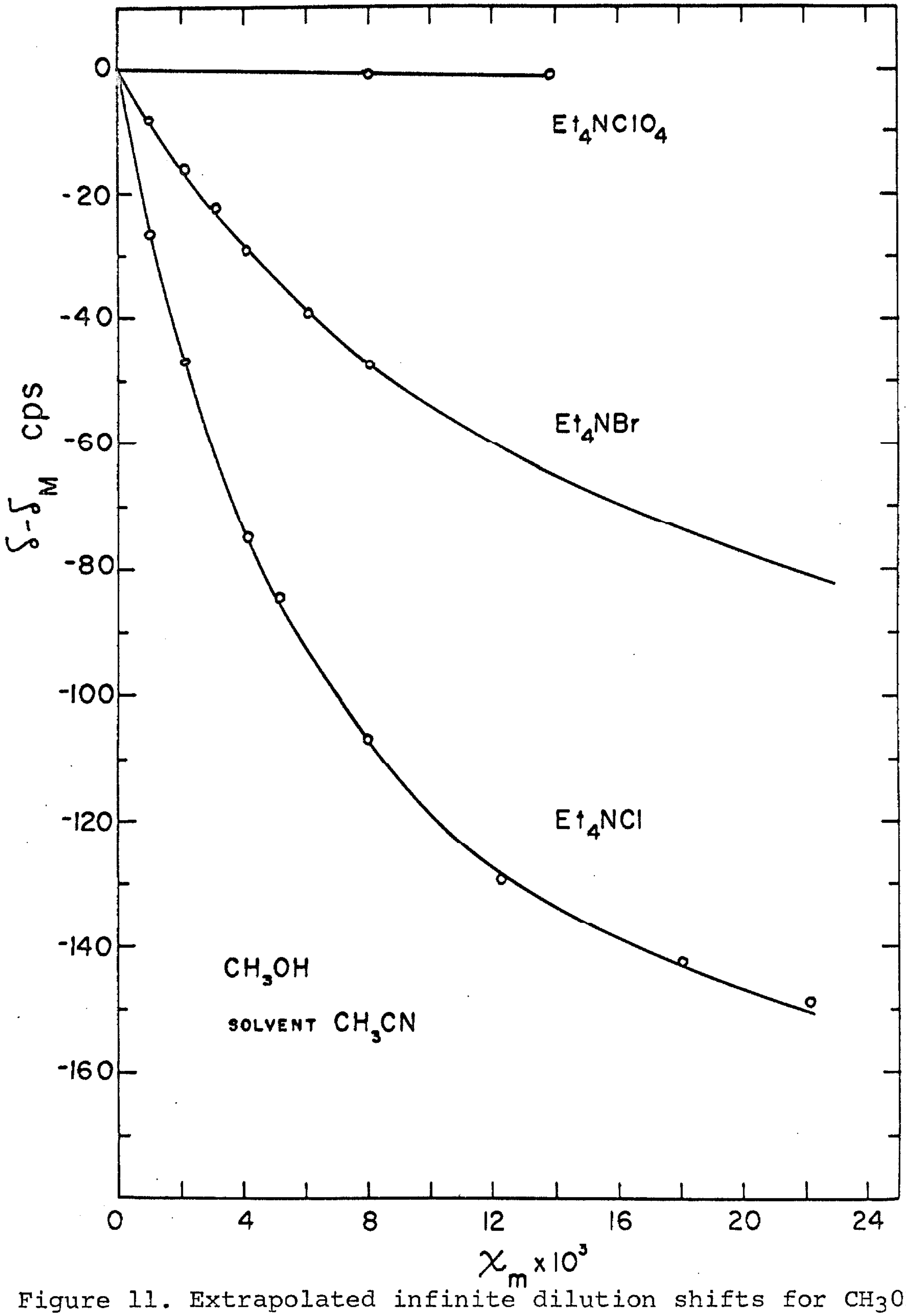

Figure 11. Extrapolated infinite dilution shifts for CH_3OH in acetonitrile for Et_4NClO_4, Et_4NBr, and Et_4NCl. The solid curve represents calculated shifts; circles represent experimental data.

limiting slopes at infinite dilution of salt. In actuality, the polarization shifts are not linear even at low salt concentrations. An appropriate plot can be made, however, so that the shifts at low salt concentrations can be analyzed.

Studies concerning the infrared absorption of water in the presence of these salts in acetone and in acetonitrile indicate that the complexed species involved is a contact ion pair (19). The polarization shifts are, therefore, not cation or anion shifts in the true sense. Since the effects of counter ion on the chemical shift are expected to be small, the shifts can be taken to be representative ion shifts.

For both cation and anion complex formation, we shall consider the following equilibrium:

$$M + S \overset{K}{\rightleftharpoons} C \quad \text{(in solvent)} \qquad (1)$$

where M is the water monomer hydrogen-bonded to the solvent, S, the solvated cation or anion-ion pair; and C, the solvated ion pair salt water or methanol complex.

In terms of the observed salt mole fraction, χ_m; the observed water concentration, χ_w; and the equilibrium constant, K, it is easily shown that the chemical shift relative to the water monomer in solvent is given by:

$$\delta_{obs.} = \frac{K \chi_m \delta_c}{1 + K\chi_m + K\chi_w} \qquad (2)$$

where K is mole fraction complex formation constant. δ_c

is the chemical shift of the salt-water or methanol complex relative to the hydrogen-bonded monomer.

In the limiting case of low water concentrations we obtain:

$$\lim_{W \to 0} \delta_{obs.} = \frac{K \chi_m \delta_c}{1 + K \chi_m} \qquad (3)$$

rearranging terms, equation 3 can be written as

$$\frac{\chi_m}{\delta_{obs.}} = \frac{1}{K \delta_c} + \frac{\chi_m}{\delta_c} \qquad (4)$$

values for the mole fraction equilibrium constant K and the shift δ_c , can therefore be obtained by extrapolation of a plot of χ_m / δ_{obs} vs. χ_m to $\chi_m = 0$.

The results concerning the variation in $\chi_m / \delta_{obs.}$ as a function of χ_m are summarized in Figures 12-17, for the various ion complexes of methanol and water in acetonitrile and acetone.

The results for the mole fraction equilibrium constant K, the shift δ_c, and the polarization shift $\delta_p = \delta_c + \delta_H$ for water in acetonitrile and in acetone and for methanol in acetonitrile are summarized in Table 2.

These values have since been used to calculate the observed shift as a function of the salt concentration for the various ions. The calculated shifts are represented by the solid lines in Figures 6, 7, 8, 9, 10, and 11; the extrapolated infinite dilution shifts relative to the hydrogen-bonded monomer are represented by open circles.

The results concerning methanol polarized by magnesium are subject to considerable uncertainty since the

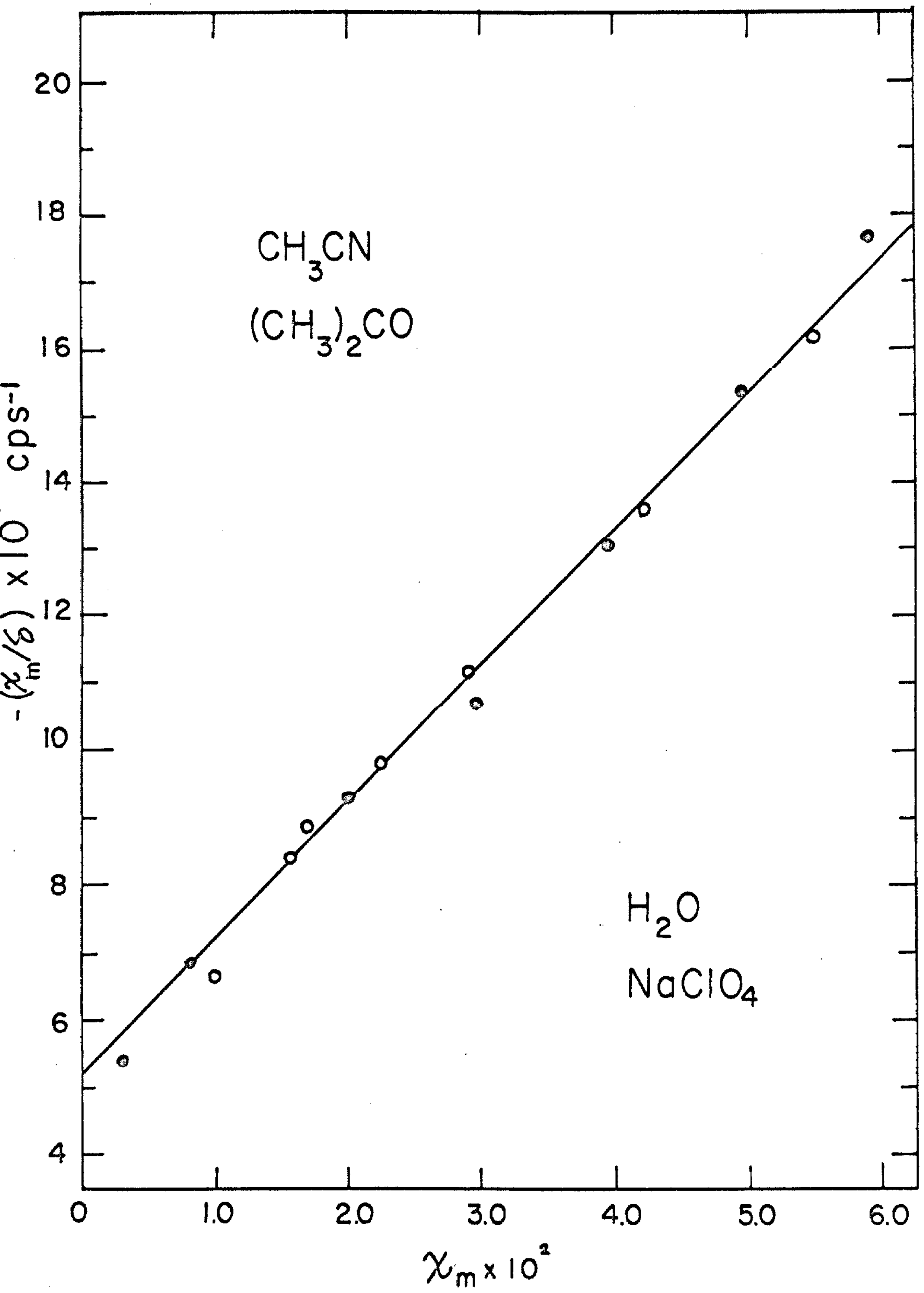

Figure 12. Extrapolation Plot for $NaClO_4/H_2O/CH_3CN$ and $NaClO_4/H_2O/(CH_3)_2CO$

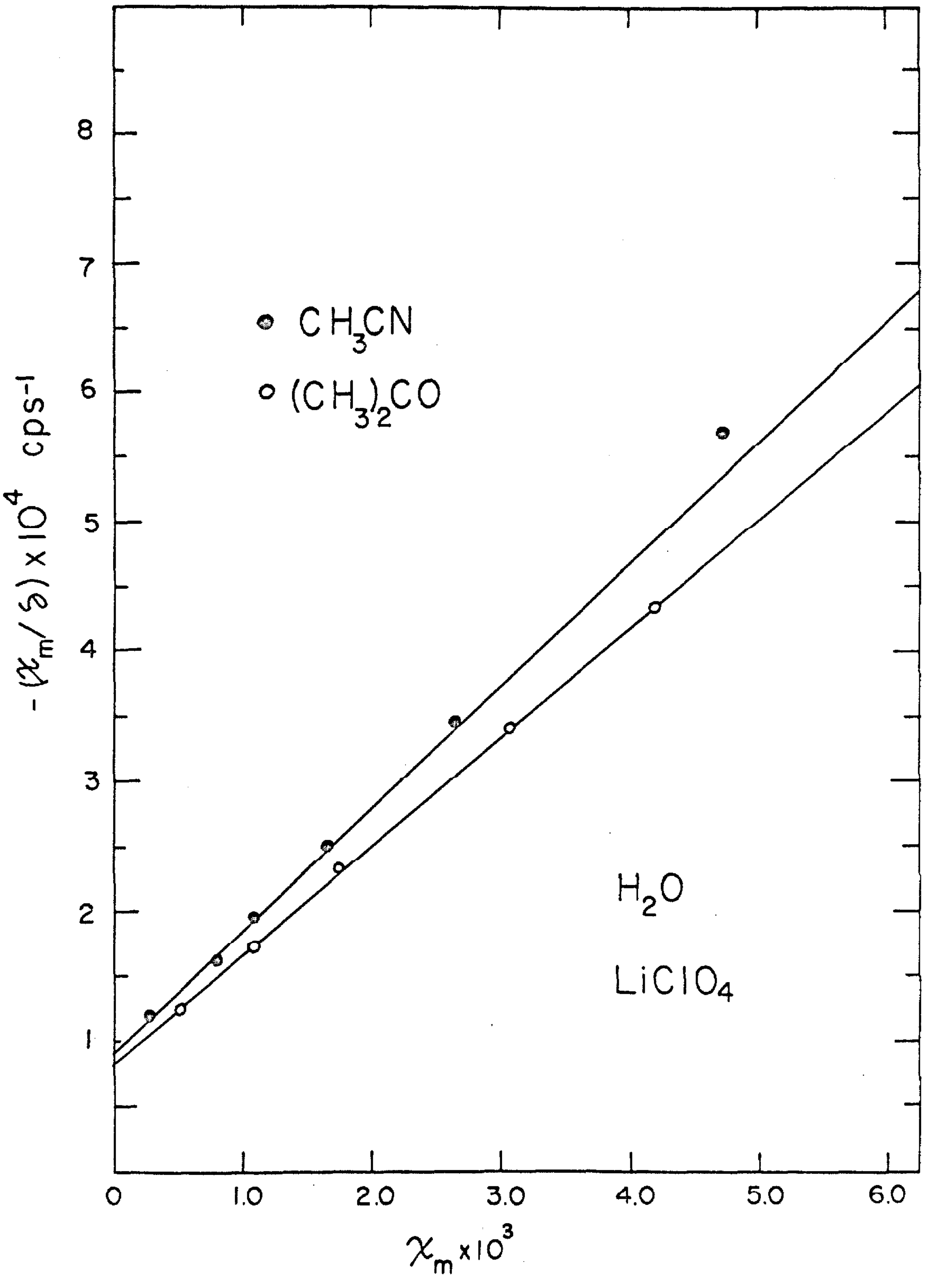

Figure 13. Extrapolation Plot for $LiClO_4/H_2O/CH_3CN$ and $LiClO_4/H_2O/(CH_3)_2CO$

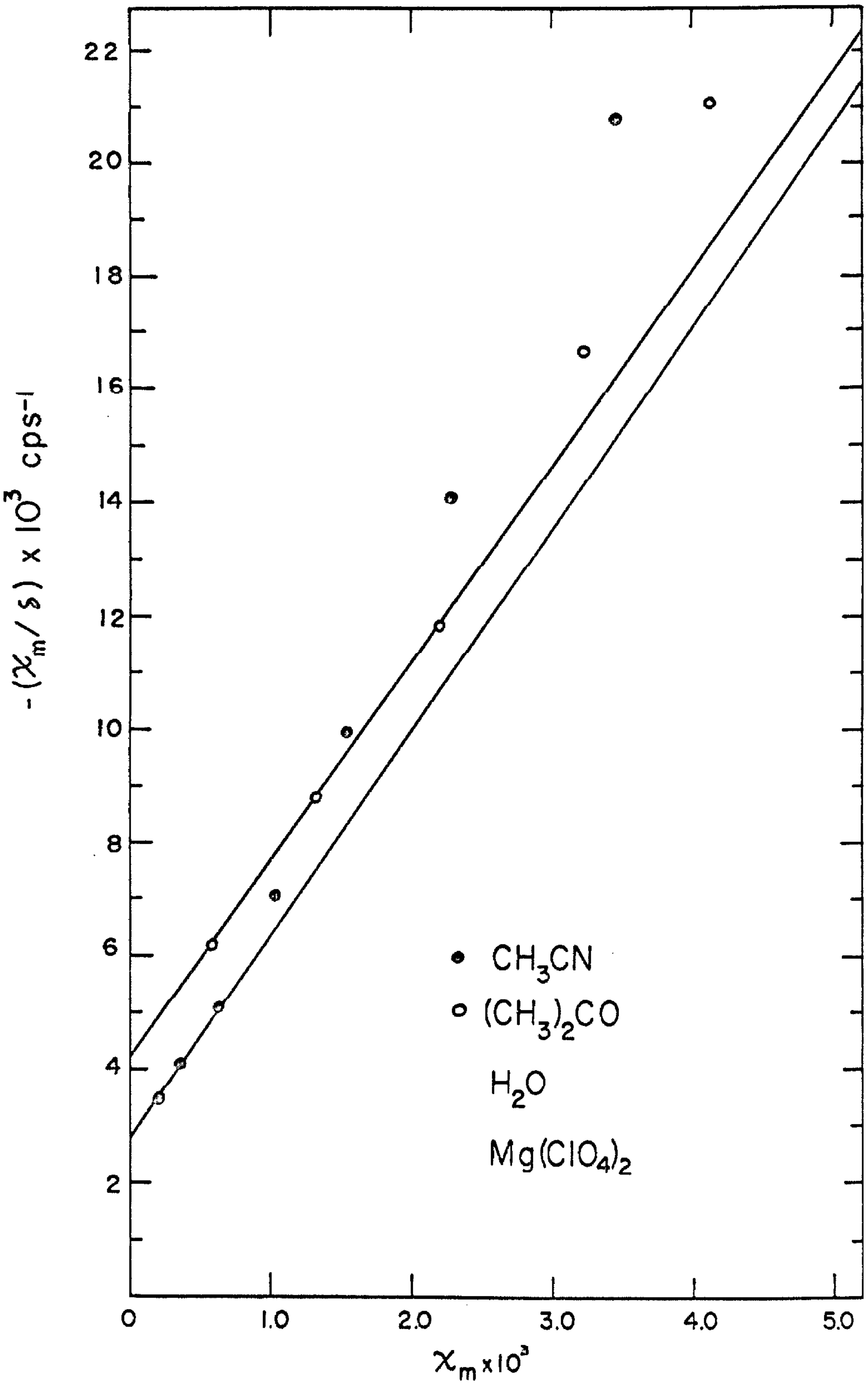

Figure 14. Extrapolation Plot for $Mg(ClO_4)_2/H_2O/CH_3CN$ and $Mg(ClO_4)_2/H_2O/(CH_3)_2CO$

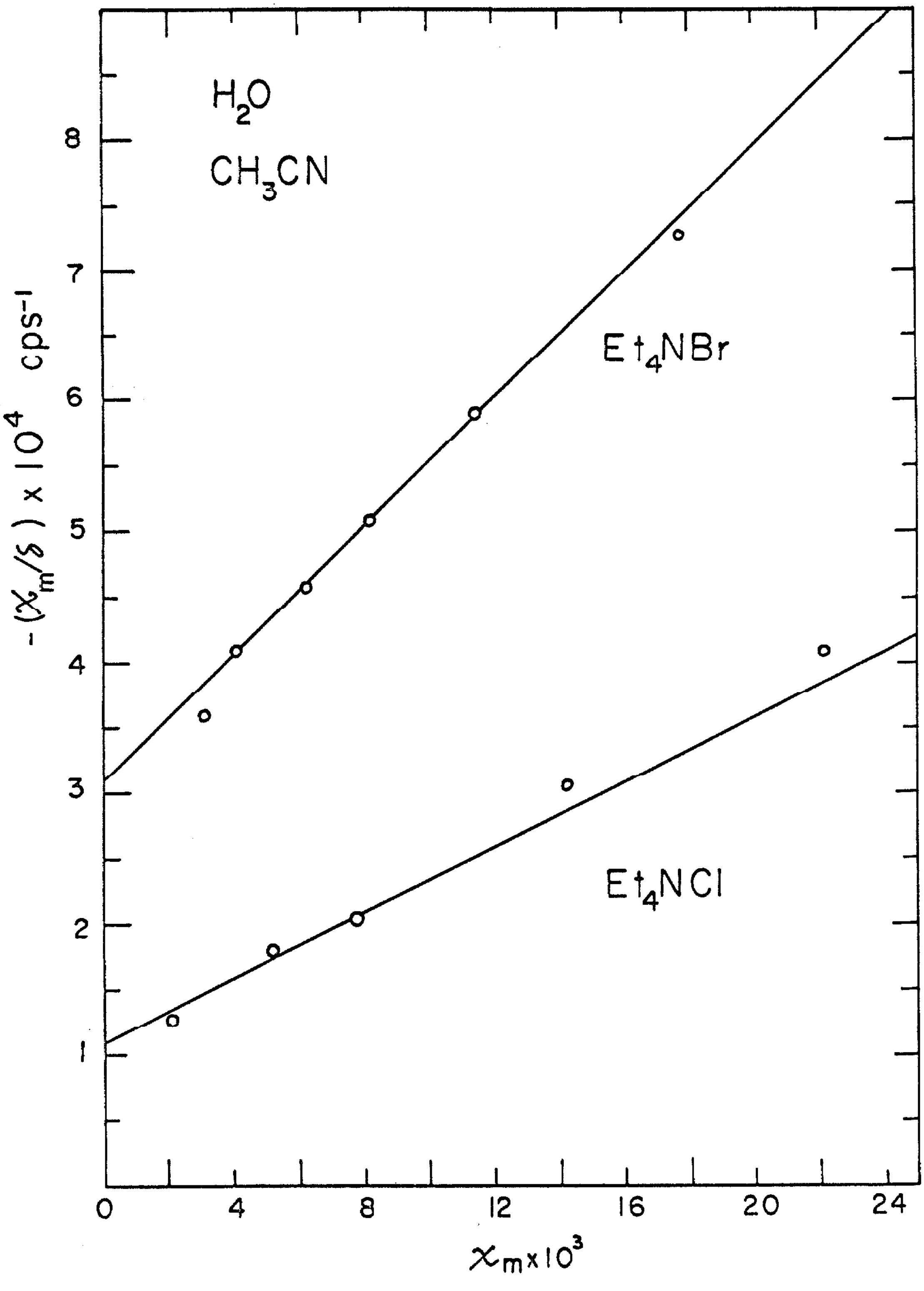

Figure 15. Extrapolation Plot for $Et_4NBr/H_2O/CH_3CN$ and $Et_4NCl/H_2O/CH_3CN$

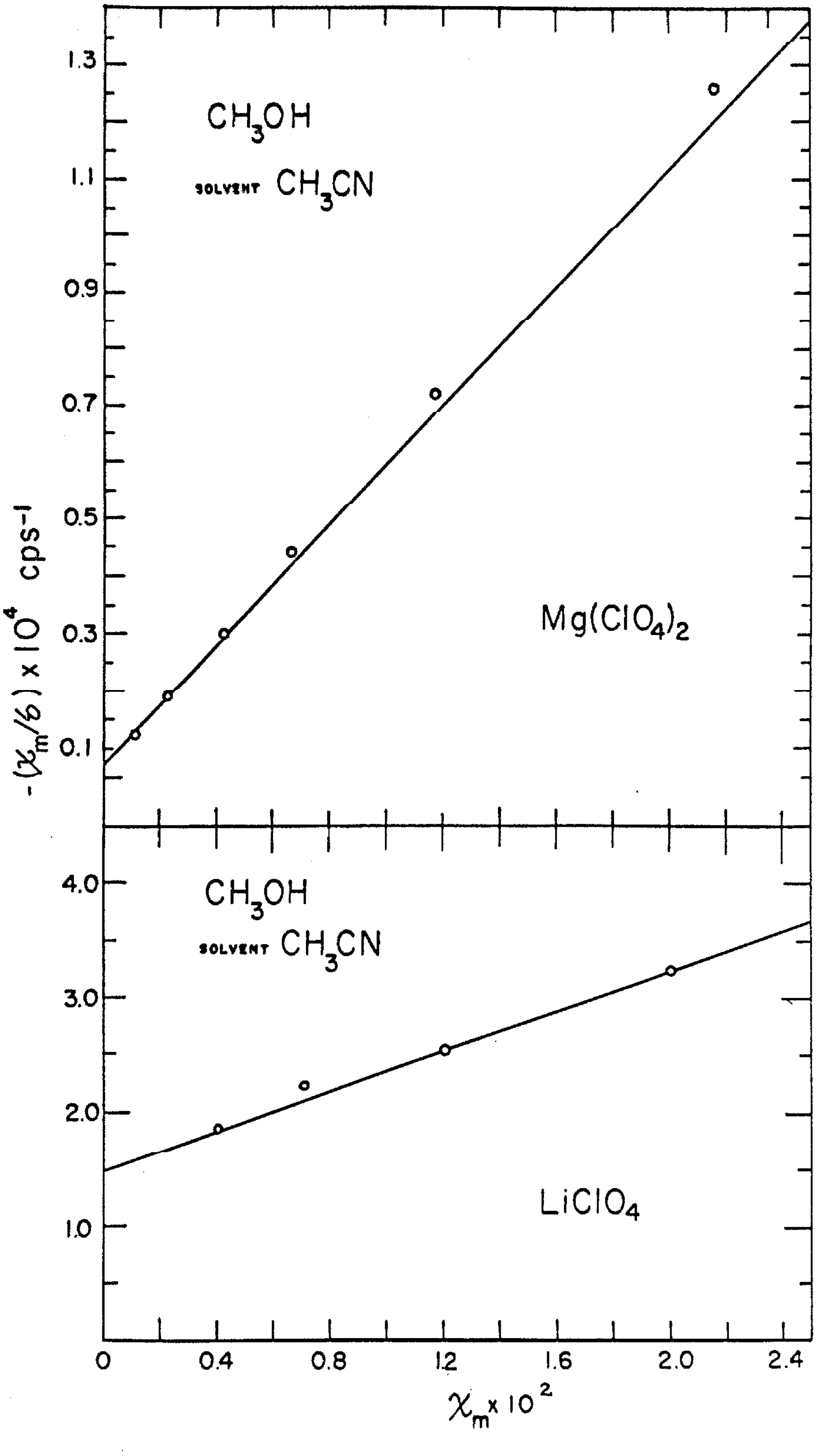

Figure 16. Extrapolation Plot for $LiClO_4/CH_3OH/CH_3CN$ and $Mg(ClO_4)_2/CH_3OH/CH_3CN$

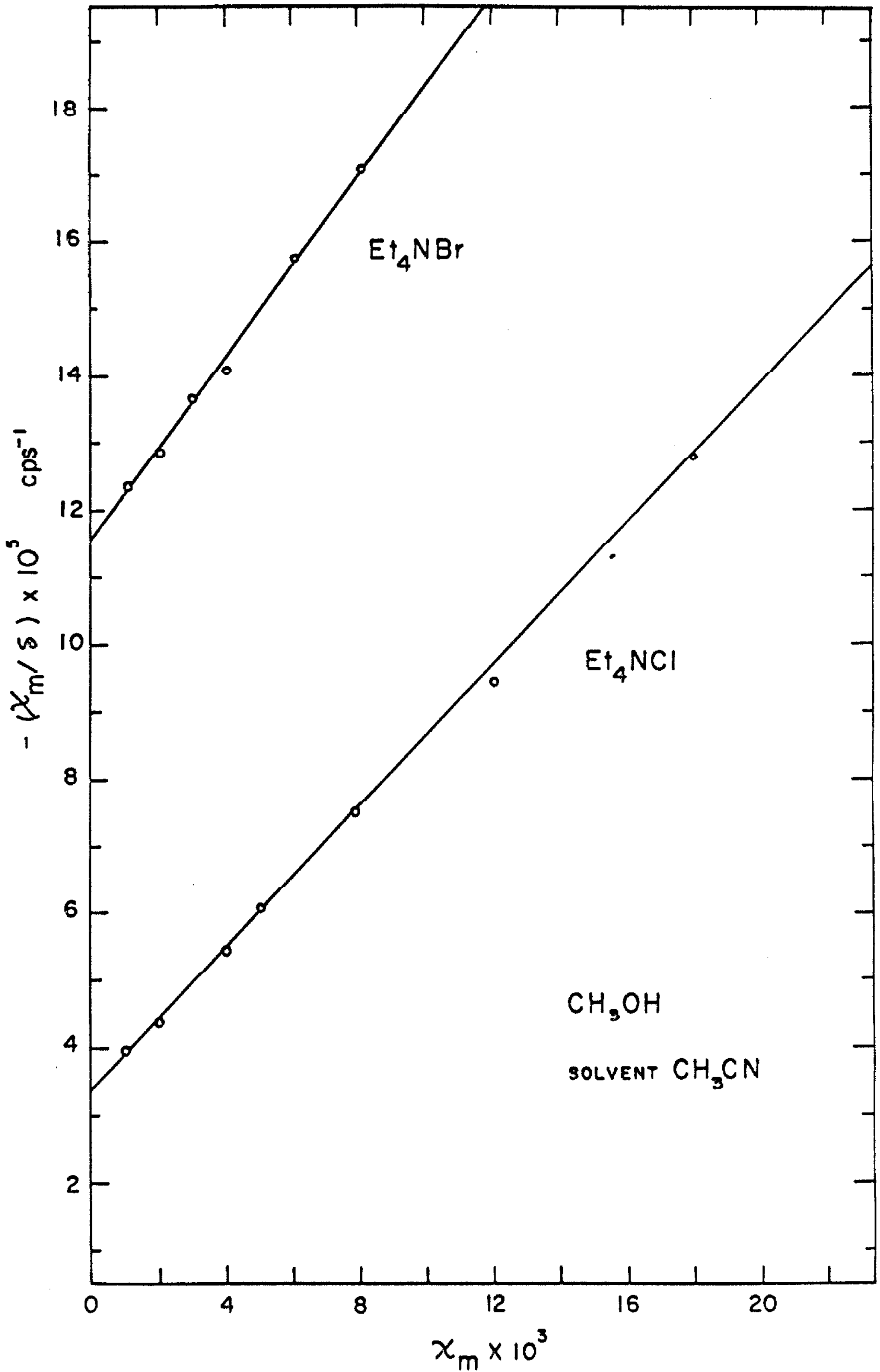

Figure 17. Extrapolation Plot for $Et_4NBr/CH_3OH/CH_3CN$ and $Et_4NCl/CH_3OH/CH_3CN$

TABLE 2

H_2O - Acetone

Ion	K x 10^{-2}	δ_c (cps)	δ_p (ppm)
Na^+	0.37 ± 0.05	-46 ± 5	-2.92 ± 0.1
Li^+	0.98 ± 0.05	-84 ± 5	-3.55 ± 0.1
Mg^{++}	8.33 ± 0.05	-287 ± 10	-6.94 ± 0.2

H_2O - Acetonitrile

Na^+	0.37 ± 0.05	-46 ± 5	-2.41 ± 0.1
Li^+	1.20 ± 0.05	-94 ± 5	-3.19 ± 0.1
Mg^{++}	13.05 ± 0.05	-278 ± 10	-6.25 ± 0.2
Br^-	0.77 ± 0.05	-43 ± 5	-2.33 ± 0.1
Cl^-	1.15 ± 0.05	-85 ± 5	-3.03 ± 0.2

CH_3OH - Acetonitrile

Na^+	0.40 ± 0.1	-35 ± 10	-2.74 ± 0.2
Li^+	0.60 ± 0.05	-108 ± 5	-3.96 ± 0.1
Mg^{++}	7.20 ± 1	-190 ± 60	-5.33 ± 1
Br^-	0.64 ± 0.05	-122 ± 5	-4.20 ± 0.1
Cl^-	1.55 ± 0.05	-197 ± 5	-5.44 ± 0.1

extrapolation of the electrolyte shifts to infinite dilution of methanol is rather difficult. Additional studies concerning electrolytic shifts at low methanol concentration will be made at a later date using CD_3OH.

In the case of the cation and anion complexation of water and methanol in acetone and acetonitrile, the results of the analysis indicate that $K_{Mg^{++}} > K_{Li^+} > K_{Na^+}$ for both solvents and that $K_{Cl^-} > K_{Br^-}$ in acetonitrile.

These results are reasonable since the relative orders of magnitude for the interaction between metal ion and water or methanol are expected to increase in the order $Mg^{++} > Li^+ > Na^+$. The results for the anion equilibrium constants are also reasonable since the relative orders of magnitude for the hydrogen-bonding interaction of water to solvent, Br^- and Cl^- increases in the order $Cl^- > Br^- > (CH_3)_2CO > CH_3CN$.

A less obvious situation arises when the complex formation constants are compared for the various ion complexes in the two solvents. The results indicate that $K_{CO} < K_{CN}$. At the present time, it is not clear that the solvation of ions in acetone is greater than in acetonitrile. If this were the case, and the only factor involved, we would expect that the ratio of K_{CO} to K_{CN} to be greater than unity which is the result obtained in this study. It is clear, however, that other factors must be considered as well as the problem concerning ion solvation.

We note, as mentioned previously, that the results of the high salt concentration data concerning the electrolyte shifts at infinite dilution of water suggest that either the state of aggregation of ions (such as ion pairs, ion quadrupoles, etc.) is lower in acetone than in acetonitrile or that the fraction of the ion water molecule complexes is greater in acetone due to a weaker ion solvation.

Since both effects are probably involved, further studies concerning the nature of ion solvation in these solvents are required before more definitive statements can be made regarding the variation in the equilibrium constant for the various ion complexes as the solvent is changed.

For the moment, we shall bypass this problem and consider the analysis of the polarization shifts for the various ion water and methanol complexes. In this work, we have defined the polarization shift for the ion complexes of water as $\delta_P = \delta_e + \delta_H$ in order to ascertain the effects due to both ion and solvent interactions.

E. INTERPRETATION OF POLARIZATION SHIFTS

The factors which contribute to the proton chemical shift which arise from the polarization of molecules, such as water by ions, were briefly discussed in the introduction. The principal contributions to this shift were suggested some time ago (6-9) and are: (1) a contribution to the proton screening due to the distortion of the electronic structure of the chemical bond which contains the proton of interest by both ion and solvent molecules and (2) a contribution (negative or positive) to the shielding constant due to the anisotropy in the magnetic susceptibility of neighboring groups.

The early success of the electric field approach in estimating orders of magnitudes of chemical shifts effected by various groups (23,24) has placed a considerable amount of significance on its value. As a result, its later application to many problems has tended to be conservative.

In the earlier studies by Hindman (9) and by Schneider and Strehlow (14), it was assumed that the shifts brought about by the polarization of water by ions could be interpreted in terms of a model which involves the calculation of electric fields effected by the ion. In both cases, however, there is no way of knowing whether or not such calculations are reasonable since these calculations can be compared only to the observed shifts which include both structure-breaking and polarization effects. The estimation of the structure-breaking contribution is extremely complex and is subject to considerable uncertainty.

In the following sections, the results of calculations based on the electric field approach as well as the results concerning the shifts which arise from solvent magnetic anisotropy considerations will be discussed.

Since the experimentally-determined polarization shifts reported in this work do not involve the large uncertainties concerning the structure-breaking effect as in the bulk water case, comparison between calculated and observed values can be made in an effort to elucidate the nature of the polarization effected by ions on molecules such as water.

1. Evaluation of the Shift Due to Neighbor Anisotropy

In 1957 Pople (29) and McConnell (30) derived expressions which enabled the estimation of a chemical shift contribution due to neighboring groups possessing magnetic anisotropy.

This contribution can be negative or positive depending on both the relative orientation of the anisotropic group, γ, and on $\Delta\chi$, the difference between the parallel and perpendicular components of the magnetic susceptibility of the group.

This contribution is given by:

$$\delta_{M.A.} = \frac{\Delta\chi\,(1 - 3\cos^2\gamma)}{3\,r_N^3\,N_0} \tag{5}$$

where $\vec{r}_N$ is the distance vector from the position of nucleus in question to the origin of the anisotropy and

N_0 is Avogadros number. γ is defined as that angle between the bond axis and the symmetry axis of the anisotropic group.

In so far as the present work is concerned, two difficulties arise: (1) The difference in the susceptibility for acetone ($C=O$) and acetonitrile ($C\equiv N$) are not known accurately, and (2) the equilibrium hydrogen bond distance and angle for acetone hydrogen-bonded to water are also not known.

Approximate values for the anisotropic contribution for the protons of water hydrogen-bonded to these solvent molecules can be obtained, however, by making some reasonable assumptions.

The differences in susceptibility for acetylene and ethylene were calculated by Pople (31). The results were -19.4×10^{-6} and $+8.6 \times 10^{-6}$ emu/mole, respectively. More recent crystal susceptibility measurements by de Vellpin (32) yield $(\chi_x - \chi_z) = +8.92 \times 10^{-6}$ emu/mole for the $C=C$ bond. (x is the bond axis and z is the axis perpendicular to the nodal plane).

The anisotropy of $C\equiv N$ and $C\equiv C$ has been examined by Goldstein and Reddy (33). They obtain -16.5×10^{-6} emu/mole for both $C\equiv N$ and $C\equiv C$.

We shall assume that $\Delta\chi_{CN} = -16.5 \times 10^{-6}$ emu/mole and $\Delta\chi_{CO} = +8.6 \times 10^{-6}$ emu/mole.

2. The Electric Field Contribution

For molecules in an electric field, the change in shielding due to the electric field can be expanded in a power series in E, i.e.,

$$\delta_E = \frac{1}{3}\sum_{\lambda}\left\{\sum_{\eta}\delta_{\lambda\lambda\eta}E_\eta + \frac{1}{2}\sum_{\eta}\sum_{\gamma}\delta_{\lambda\lambda\eta\gamma}E_\eta E_\gamma + \cdots\right\} \qquad (6)$$

where η, γ, and λ represent the various molecule fixed Cartesian co-ordinates x,y, and z. $\delta_{\lambda\lambda\eta}$ and $\delta_{\lambda\lambda\eta\gamma}$ represent the various components of the shielding tensor when the electric field is in the η or γ direction.

In order for the electric field approach to be useful it is clear that the series must converge with a reasonably small number of terms.

The application of the electric field approach to molecular systems has been discussed by Buckingham (23), Stephens (24), Musher (25) and by Chan and Iwamasa (26). For molecules in general, the calculation of the electric field dependent part of the chemical shift is no simple matter. A great simplification can be made, however, by considering the molecule as consisting of two parts, one which involves the nucleus of interest and another which does not. The case of a proton directly bonded to an atom X which in turn may or may not be bonded to other atoms has been treated by Buckingham (23).

In an axially symmetric X-H bond, the electric field dependent part of the chemical shift can be expressed by:

$$\delta_E = -k_E E_z - bE^2 \qquad (7)$$

where z is defined as the symmetry axis of the X-H bond. b and k_E are the familiar quadratic and linear electric field coefficients. E_z is the component of the total electric field, $\vec{E}$, parallel to the X-H bond axis at the proton.

This equation is essentially the starting point for the calculations which concern the effects of an electric field on an X-H bond. Despite the apparent simplicity of this expression, its use is complicated by the fact that both b and k_E are not universal constants. Values for these coefficients must be available therefore before calculations concerning the electric field contribution can be made.

Estimations concerning the magnitude of these coefficients have varied (23-27) and in some cases used with little physical justification. Since Buckingham's paper (23), values for the linear coefficient, k_E, from -3.4×10^{-12} to -2.0×10^{-12} have been used in the literature. Since the linear contribution, in general, contributes appreciably to the shift, this large variation can give rise to results which are meaningless unless careful attention is made concerning its actual value.

The variation in the quadratic coefficient has been expected to be small in comparison to the changes in the linear coefficient and is often approximated by the value obtained by Marshall and Pople for the case of the hydrogen atom (28). A more detailed discussion concerning the quadratic electric field coefficient will be presented later.

3. Interpretation of the Infinite Dilution Shifts for Water and Methyl Alcohol in Acetone and in Acetonitrile

Although the infinite dilution shift for water in acetonitrile was reported previously (16), no calculations were made concerning the interpretation of the electric field dependent part of the shift. The present value of the infinite dilution shift for water in acetonitrile, -1.64 ppm, differs from that previously given, due to a volume susceptibility correction error in (16). To our knowledge, neither the report of the infinite dilution shift for methanol in acetonitrile nor its interpretation has been made previously.

In the case of weak hydrogen-bonding, e.g. $HCCl_3$ in various amine solvents, the infinite dilution shifts were interpreted on the basis of a combined electric field and neighbor magnetic anisotropy contribution (27). The results agreed favorably in so far as the model and treatment were concerned.

In Table 1 infinite dilution shifts for water and methanol were given for several organic solvents. All values are reported relative to gaseous water or methanol. The raw data were taken from several articles and were recalculated according to $\delta_H = \delta_{obs.} - \frac{2\pi}{3} \chi_v$ (solvent). The shifts for methanol are reported relative to the OH resonance of gaseous methanol.

Despite the favorable results obtained for the hydrogen-bonding of chloroform to various amine solvents, it is not clear whether the approach based on electric field and magnetic anisotropy considerations is applicable for all protons involved in hydrogen bonds. We will consider the applicability of the approach to the solvents, acetone and acetonitrile.

It is imperative that the infinite dilution shifts for water and methanol in these solvents be considered since knowledge of the solvent field is required in later calculations.

To obtain approximate values for the electric fields produced by the solvent molecule, it is necessary to determine the neighbor magnetic anisotropic contribution to the chemical shift as well as to determine appropriate values for the linear electric field coefficient for water and methanol. In the following, we shall use -0.75×10^{-18} for the quadratic electric field coefficient.

a. Calculations Concerning Methyl Alcohol

Estimations concerning the neighbor magnetic anisotropic contribution to the infinite dilution shift for methyl alcohol in acetonitrile can be approximated by use of equation 5 .

For reasonable $C\equiv N$ hydrogen bonds to protons, $(r_{N...H})$ 2.58 Å(27), the anisotropic contribution due to the solvent molecule is approximately +0.67 ppm. (The origin of the anisotropy is taken at the center of the

$C \equiv N$ bond).

Estimation concerning the C-O bond anisotropy can be made by considering the C-C bond anisotropy. Grant and Paul (34) list several references for the C-C bond anisotropy; a reasonable value is $+3.0 \times 10^{-6}$ emu/mole. The corresponding contribution to the chemical shift is approximately +0.5 ppm.

Since the difference between the gas phase shift for water and methanol (OH) is of this order of magnitude, we shall assume that this difference originates, for the most part, from magnetic anisotropic considerations.

Earlier considerations concerning the proton resonances of methane and ethane were interpreted on this basis (17). In this case, ethane is too low field relative to methane by 0.70 ppm. An approximate calculation assuming a C-C bond anisotropy of $+3.0 \times 10^{-6}$ emu/mole yields -0.5 ppm for the anistropic shift, which agrees reasonably with the experimental observation. It is of interest to note that this shift is negative. In the case of methanol, the resonance shifts to high field, due to the angular dependent part of $\delta_{M.A.}$.

It is now possible to calculate the electric field dependent part of the infinite dilution shift, δ_H, and solve for E_s (the solvent field) as a function of the linear electric field coefficient, assuming a quadratic electric field coefficient of -0.75×10^{-18}.

The results of calculations for several reasonable values of $\delta_{M.A.\ (CH_3CN)}$ suggest that the variation in the solvent field is small for reasonably small changes in the anisotropic contribution.

To obtain the solvent field, we are faced with the problem of picking some appropriate value for the linear coefficient. For reasonable N···H hydrogen-bond distances of 2.5 Å, the value of the linear coefficient is about -3.0×10^{-12}.

Earlier work by Berkeley and Hanna (27) concerning linear coefficients for the C-H bond indicates a value of about this magnitude. It is expected that $k_{CH} \gtrsim k_{OH}$ but not vice-versa.

The corresponding value of the solvent field is approximately 0.66×10^6 statvolts/cm. This agrees quite well with the solvent fields calculated by Berkeley and Hanna (27) using a lone pairwave function of the form Ψ_{LP} $(2s + \lambda 2P)/(1+ \lambda^2)^{\frac{1}{2}}$ where λ is a hyberdization parameter. The calculated field for sp^3 hyberdization for a hydrogen-bond length of 2.4 Å was 0.65×10^6 esu and for sp^2 hyberdization about 0.70×10^6 esu.

b. Calculation Concerning Water in Acetone and in Acetonitrile and Methanol in Acetone

Since the electric field contribution to δ_H for water in acetonitrile is approximately the same as for methanol (after correction for the C-0 bond anisotropic contribution), the solvent field contribution is the same, *i.e.*, 0.66×10^6 esu for water in acetonitrile.

The electric field plus solvent magnetic anisotropic part of δ_H, *i.e.*, δ_D, for methanol and water in acetone and acetonitrile are compared in Table 3.

TABLE 3

δ_D ppm

solute/solvent	CH_3CN	$(CH_3)_2CO$
CH_3OH	-1.66	-2.57
H_2O	-1.64	-2.15

The solvent field for acetone is expected to be very close if not slightly larger than the field produced by acetonitrile.

The magnetic anisotropic contribution using $\Delta\chi_{C=O} = +8.6 \times 10^{-6}$ emu/mole is -0.45 ppm for a linear hydrogen-bond model (one in which the carbonyl bond axis is co-linear to the OH bond axis and $r_N = 2.2$ Å). Note that the sign is opposite to the anisotropic contribution for acetonitrile.

The electric field contribution in the case of water in acetone is (-2.15 + 0.45) or -1.70 ppm while for water in acetonitrile it is (-1.64 -0.68) or -2.32 ppm.

In the case of methanol, the electric field contribution in the case of acetone is (-2.57 + 0.45) or -2.12 ppm while for acetonitrile it is (-1.66 - 0.68) or -2.34 ppm.

In both cases, the results seem to be quite puzzling. Since the value of the linear coefficient for water should be approximately the same for the two hydrogen-bonded species, acetone and acetonitrile, the above results would indicate that the solvent field for acetone would be smaller than for acetonitrile. The same applies to the data concerning methanol.

It appears therefore that the solvent anisotropic contribution in the case of acetone is incorrect.

No matter what the anisotropic solvent contribution is, however, it is clear that the difference in δ'_D in the case of acetone is larger than for acetonitrile, with water at high field relative to methanol in both cases. This observation is significant for it indicates the importance of a possible cross-solvent field interaction in the case of water hydrogen-bonded to acetone (see Figure 18). In this case, although the resultant

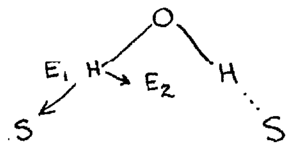

Figure 18. Cross-Solvent Field Interaction

field produced by the two solvent molecules at the proton is larger than that produced by one, the parallel component of that resultant along the OH bond axis is smaller. In the case of acetone the cross-field contribution amounts to some 0.42 ppm (assuming that the effective linear coefficients for methanol and water are the same). In the case of acetonitrile this difference is only 0.02 ppm indicating a negligible cross-field interaction.

The results of the problem concerning the anisotropic contribution due to acetone as solvent can be rationalized if we assume that the hydrogen-bonded species in the case of acetone are not linear (defined previously). Instead we shall assume the bent model given in Figure 19.

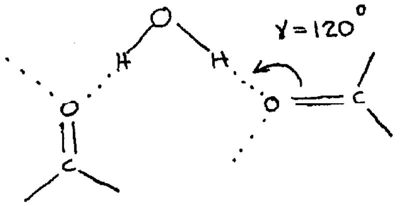

Figure 19. Hydrogen-bonding to H_2O by Acetone

We assume that the hydrogen-bonded species in the case of water or methanol hydrogen-bonded to acetonitrile are linear (Figure 20).

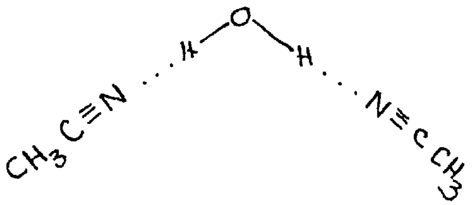

Figure 20. Hydrogen-bonding to H_2O by Acetonitrile

If we now use $\gamma = 120°$, the magnetic anisotropic contribution is +1.1 ppm for acetone, opposite in sign to that for $\gamma = 180°$. In this case, the electric field contribution at the proton of methanol hydrogen-bonded to acetone is $+105 \times 10^6$ esu, a field which is considerably high, especially when one considers typical fields produced by anions hydrogen-bonded to methanol or water. The fields for Br^- and Cl^- at typical hydrogen-bonding distances are 0.86×10^6 esu and 1.02×10^6 esu, respectively, for a $OH \cdot\cdot X^-$ distance of 3.35 Å for Br^- and 3.15 Å for Cl^-.

The anisotropic contribution is, however, very sensitive to the angle between the OH bond and the anisotropic group. In actuality, we should not really expect to have $\gamma = 120°$. In the solid state, packing considerations alter this angle, *e.g.* for acetic acid, this angle gets as large as 144° and for formic acid, 122° (35). In the liquid, due to solvent fields, this angle will be expected to be larger than 120°.

Since the $C=O...H-O$ hydrogen-bond distance is not known for acetone and water, it is not possible to calculate an actual compression angle from the NMR data. The solvent field for an angle of 120° is, however, probably too high. Calculations can be performed for different angles. For 124°, the anisotropic contribution is +0.29 ppm. This corresponds to a more reasonable value for the solvent field of about 0.8×10^6 esu. For 125°, the anisotropic contribution is +0.05 ppm and the solvent field about 0.75×10^6 esu.

Since we already know that the field due to acetonitrile is about 0.66×10^6 esu, a value of 0.8 to 0.75×10^6 esu, for the solvent field produced by acetone at the proton is reasonable.

The actual solvent field at the proton due to the solvent molecule in the case of acetone is certainly less clear than for acetonitrile, especially if the bent configuration is involved.

One way of getting around this problem is to assume that the effects of the electron and nuclear charge distribution from the rest of the solvent molecule is small compared to the field produced by the lone pair. This assumption was made by Berkeley and Hanna (27) who pointed out that due to the great uncertainties in the location and magnitude of the bond dipoles, it is not profitable to treat this effect quantitatively. An approximate estimate of the maximum contribution to the electric field at the $HCCl_3$ proton from the remaining electrical asymmetries in the various amine solvents was estimated to be less than 5% of the contribution from the lone pair. The applicability of this assumption obviously depends on the orientation and location of the solvent molecule relative to the proton whose shielding is being calculated.

At typical hydrogen-bonding distances, the dipole approximation is particularly bad, and for this reason more than any other considerations, the true field produced by the solvent cannot be calculated using such simple models.

If we consider the field at the proton due to the lone pair for a hydrogen-bond distance of 2.2 Å, the corresponding solvent field produced by a sp^2 hyberdized lone pair is about 0.80×10^6 esu (27). This value agrees reasonably well with the earlier considerations. We must remember that this value was obtained from the neglect of other contributions which may arise from the rest of the solvent molecule.

If we now assume that the solvent field for acetone is indeed 0.8×10^6 esu, it is possible to calculate an approximate value for the infinite dilution shift for water and compare it with experiment. We mentioned briefly before that the effect of a cross-field interaction was possibly responsible for the larger difference in δ_D for water and methanol in acetone compared with the difference for these molecules in acetonitrile. The secondary field at the proton due to the solvent field produced by acetone can be approximated to be about 1/4 the primary field.

The calculated value of the infinite dilution shift for water in acetone is $\delta_H = -3.0 \times 0.68 - 0.75 \times 0.49 + 0.29 = -2.04 - 0.37 + 0.29 = -2.12$ ppm. The resultant solvent field in the case of the water acetone complex is $(E^1{}_s) = 0.8 \times 10^6$, $(E^2{}_s) = 0.2 \times 10^6$, $E_t = 0.68 \times 10^6$, $E_t{}^2 = 0.49 \times 10^{12}$. The agreement with experiment, -2.15 ppm, is quite good and is to a certain extent fortuitous due to the uncertainties in hydrogen-bonding distances, etc. but does show the importance of the cross-field interaction in reducing the value for the calculated infinite dilution shift. If the cross-field is neglected, we obtain $\delta_H\text{calc.} = +0.29 - 3\text{x}.8 - 0.75\text{x}.64 = +0.29 - 2.4 - 0.48 = -2.57$ ppm.

Although these calculations are by no means quantitative, the difference in the infinite dilution shifts for water or methanol in acetone and acetonitrile is real and accurate to at least 1 or 2%. This difference cannot be accounted for unless some model is invoked, such as the bent hydrogen-bonded species for water or methanol complexed to acetone. The accuracy of the calculations obviously depends upon hydrogen-bonding distances and in the anisotropy of the susceptibility of the solvent and solute molecules. The present calculations are not meant to be quantitative but are useful in the sense of testing various models by making certain reasonable assumptions.

From these considerations, it appears that the hydrogen-bonding of water or methanol to acetonitrile can be interpreted on the basis of an electric field approach combined with magnetic anisotropy considerations. It is less clear if the electric field approach can be applied to the case of water or methanol hydrogen-bonded to acetone. In the present calculations we have treated this case as if it were applicable.

These results assume that $k_E(CH_3OH) = k_E(H_2O)$. In actuality, we expect that $k_E(H_2O) < k_E(CH_3OH)$ but such distinctions cannot be determined from the infinite dilution shifts alone.

4. Interpretation of Anion Polarization Shifts for Water and Methyl Alcohol

In the case of methanol polarized by anion, both k_E and b can be uniquely determined within the limits defined by equation 7 since polarization shifts were obtained for both bromide and chloride. The result obtained was $k_E = -1.63$ and $b = -3.15$. In the calculations, the $H...X^-$

distance for Br^- was taken to be 2.39 Å and for Cl^-, 2.19 Å (35). These values were obtained from O-H...X^- distances using 0.98 Å for the OH bond. The values are taken to be representative (minimum) hydrogen-bond distances in the liquid. The corresponding fields produced by the anion at the proton methane are 0.86×10^6 esu for Br^- and 1.02×10^6 esu for Cl^-.

Although the value of the linear coefficient is reasonable by itself, the value together with $b = -3.15$ is entirely unrealistic.

In order to understand why such is the case, it is necessary to understand what physical factors influence these coefficients.

For the case of S state atoms, the electric field problem can be solved exactly (28). Because of the symmetry of the atom, the linear variation of the shielding constant is zero. The results which includes both paramagnetic and diamagnetic contributions were found to be (28):

$$\sigma_{\parallel} = - \frac{439\ a^3}{mc^2\ 120}\ E^2 \qquad \text{parallel field case}$$

$$\sigma_{\perp} = - \frac{193\ \ a^3}{45\ mc^2}\ E^2 \qquad \text{perpendicular field case} \tag{8}$$

In the parallel field case, there is no paramagnetic contribution due to axial symmetry. In both cases, the distortion of the charge cloud by the electric field produces a deshielding of the proton.

This reduction is greatest when the applied magnetic field is perpendicular to the electric field since, in this case, there is a hindrance to the flow of electrons due to the lack of axial symmetry. The diamagnetic contribution corresponds to the partial removal of charge from the vicinity of the nucleus by the electric field corresponding to a reduction in the mean expectation of 1/r. The diamagnetic contribution is greatest when the magnetic field is parallel to the electric field because of the angular dependence of the charge cloud relative to the electric field.

For molecules, the effects of an electric field are comprehensible on a similar basis except that the shielding of the nucleus can now become affected by a term linear in E. The relative importance of the linear and quadratic variation of the shielding constant is obviously dependent on the orientation and magnitude of the applied electric field. When there is rapid tumbling of the molecule with the applied electric field, the linear term averages to zero. This is not, of course, the case when the electric field approach is used to study possible field effects due to electronegative or polar substituents.

In order to understand what factors influence the linear and quadratic coefficients for molecule, it is of interest to consider the Buckingham model (23). In this case, a hydrogen atom perturbed by a point charge λ, a distance r away, is placed in an electric field. It can be shown that the dependence of the chemical shift on the electric field is given by:

$$\delta_E = -2b(\lambda/r^2)\,E_{\parallel} - b\ E^2 \qquad (9)$$

where λ is the charge, r, the distance separating the charge from the atom, $E_{\parallel}$, the parallel component of the applied static electric field, and b the value obtained by Marshall and Pople (28). The quadratic coefficient is the same in this case for the simple reason that the model still involves a hydrogen atom. In this case, the linear coefficient is larger than the quadratic by at least a factor of 2 or 3. Any calculation which yields a smaller value is indicative of the inadequacy of the electric field approach based on this model. This was found to be the case of anion polarization of methanol.

In a more realistic situation, the b coefficient is expected to vary. For hydrogens involved in bonds the value will be slightly smaller but the variations in this term for different molecules should be small compared to the variations in the linear coefficient for various proton environments. If this is not the case, the electric field approach defined by equation 10 is inadequate.

In order to obtain approximate variations in the quadratic coefficient, it is of interest to re-examine the solution for the hydrogen atom in an electric field. Within the limitations of the Buckingham model, calculations for the b coefficient obtained by changing the orbital exponent of the 1s function for hydrogen should be representative of the variations in this coefficient for various proton environments in molecules. The result is just:

$$\text{a)}\quad \sigma_{\parallel} = -\frac{439}{120mc^2}\left(\frac{a}{z}\right)^3 E^2 \quad \text{parallel field case}$$

(10)

$$\text{b)}\quad \sigma_{\perp} = -\frac{193}{45mc^2}\left(\frac{a}{z}\right)^3 E^2 \quad \text{perpendicular field case}$$

where z is the orbital exponent, *i.e.*, exp (-zr/a).

For reasonable values of z between 0.75 and 2.0, the b coefficient varies from 2.0 to 0.1. These values only give us a range of possible extreme values for the quadratic coefficient. Due to the fact that protons in molecules are not hydrogen atoms perturbed by point charges, it is not possible to say what value in this range is realistic. To be sure, however, this value will change for various proton environments. Values outside this range would be expected to be extremely improbable. The value obtained from the anion data was -3.15×10^{-18}.

More recent calculations based on a quantum mechanical approach concerning the effects of an electric field on nuclear magnetic shielding in molecules (26), have indicated that the quadratic coefficient for the hydrogen molecule is approximately -0.56×10^{-18}.

If a value of -0.75×10^{-18} is used for the quadratic coefficient, no agreement can be found for the polarization shifts for either Br^- or Cl^- methanol complexes. Typical linear coefficients obtained in this manner are much too large, i.e., 6 to 8 x 10^{-12}. Such values for typical H...X^- distances would imply effective charges on the order of 10 to 14 x 10^{-10} esu (using -0.6 x 10^{-18} does not change the conclusions).

Although the arguments presented here are by no means definitive, the experimental results clearly indicate an inadequacy in the electric field approach based on the Buckingham model in so far as anion polarization shifts are concerned.

Furthermore, since the shielding of the molecule in the presence of an electric field can be expanded in a power series of $\vec{E}$, an approximation of the linear and quadratic coefficients is sufficient to show the applicability of the electric field approach in general, independent of any particular model.

In the specific case cited for the anion methanol complex, the linear and quadratic coefficients were of the same order of magnitude (in units of ppm). This is suggestive of the fact that orders of E greater than E^2 must be considered. The electric field approach for estimating anion polarization shifts for methanol by equation 10 is, consequently, inappropriate.

More refined calculations based on a quantum mechanical approach concerning the problem of polarization must be performed, therefore, before anion polarization shifts are understood on a quantitative basis.

Calculations concerning linear and quadratic coefficients for the anion-water complex are considerably more complicated than for the methanol case due to the fact that only one proton of water is hydrogen-bonded to the anion. The other proton remains hydrogen-bonded to the solvent (Figure 21). For this reason, it is not possible to solve for meaningful values of the coefficients even though three unknowns relating to this problem have been determined experimentally, i.e., the bromide-water complex shift, the chloride-water complex shift, and the infinite dilution shift for water in acetonitrile. The reason why one cannot do a calculation as was done for methanol is because of the fact that the anion produces an electric field at H_A which is comparable in magnitude to the solvent field at H_A.

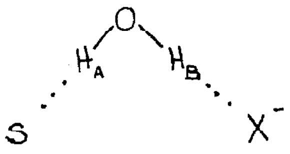

Figure 21. Anion-Water Complex

The chemical shift of the water-anion complex can be approximated by:

$$\delta(H_2O,\ X^-, S) = \frac{\delta(CH_3OH,\ X^-) + \delta_{H_A}}{2} \qquad (11)$$

where δ_{H_A} is the shift at proton A which includes the solvent field, neighbor magnetic anisotropic effects due to the solvent molecule, and the secondary (not negligible) electric field produced by the anion at proton A. δ (CH_3OH, X^-) is the shift affected on the OH proton in methanol by the anion X^-. The C — O bond anisotropic contribution is +0.5 ppm. The effect of the solvent field at H_B is neglected. The ratio of the field produced by the solvent molecule at H_B to the field produced by the ion at H_B is about 1/10.

Although equation 11 cannot be used to calculate electric field coefficients, it can be used to calculate approximate shifts for the water-anion complex to test the reasonableness of the model.

The variation in the electric field produced by the solvent molecule can be computed as a function of k_E for a constant value of +0.68 ppm for the magnetic anisotropic contribution for CH_3CN and for a fixed value of $b = -0.75 \times 10^{-18}$. For reasonable values between -1.6×10^{-12} and -3.5×10^{-12}, the electric field varies between 0.97 to 0.58×10^6 esu . If we use the value of 0.66×10^6 esu for the solvent field obtained earlier and use the corresponding value of +0.68 ppm for the magnetic anisotropic contribution, the chemical shift for the water-anion complex can be computed. The results are -2.37 ppm for the bromide complex and -2.97 ppm (Cl^-);2.33 (Br^-) and -3.03 ppm (Cl^-) obtained experimentally.

The results obtained are useful in the sense that they illustrate the effect of the secondary electric field produced by the anion on the proton of water hydrogen-bonded to the solvent. They also show that the calculated shifts based on the electric field calculation are consistent with the model in which only one proton of water is hydrogen-bonded to the anion.

If the electric field approach is used to compute polarization shifts, the above calculation indicates that a linear coefficient around -3.0×10^{-12} is required for proper characterization (using $b = 0.75 \times 10^{-18}$), in agreement with our earlier consideration of the infinite dilution shifts. Actually this value of k_E is probably slightly high due to the fact that the value of $\delta(CH_3OH, X^-)$ will overestimate the actual $OH...X^-$ contribution in the water-anion complex.

The value of $k_E = -3.0 \times 10^{-12}$ can now be used to compute chemical shifts for the methanol-anion complex. The calculations are -3.55 ppm for the bromide complex and -4.44 ppm for the methanol-chloride complex. The results are low in both cases when compared with the experimental values of -4.20 ppm for $Br^- \ CH_3OH$ and -5.44 ppm for the methanol-chloride complex which implies that the value of k_E and b used in the calculations for methanol-anion complexes is meaningless.

Although the portion of the water molecule which is hydrogen-bonded to the solvent molecule can be approximated by the electric field approach, the proton of the water molecule which is hydrogen-bonded to the anion can not. The results are consistent with the analysis of the methanol-anion polarization shifts given earlier.

It is important to note here that the electric fields produced by the anions are larger than those produced by the solvent. Calculated fields produced by Br^- and Cl^- at the proton in the O-H...X^- configuration are 0.86×10^6 and 1.02×10^6 statvolts/cm, respectively, for an O-H...X^- distance of 3.35 Å for Br^- and 3.15 Å for Cl^-. It seems apparent that when the electric field gets large, as in the case of anion polarization, the electric field approach is no longer adequate. It is expected, therefore, that this would also be the case for protons which are hydrogen-bonded to strong proton acceptors, such as dimethylsulfoxide and pyridine.

5. Interpretation of Cation Polarization Shifts

The interpretation of polarization shifts effected by cations is complicated by the fact that distortion in the electron distribution at the oxygen lone pair is expected. This distortion is brought about by the effects due to partial charge transfer and overlapping of the electron orbitals of the metal ion with the oxygen lone pair. As a consequence, the electron density at the proton of water or methanol will change.

Some orders of magnitude estimates concerning the linear electric field coefficient can be made, however, by assuming that the simple Buckingham model still applies. In this case, a value for an effective k_E can be obtained from the experimentally-determined polarization shifts, δ_p , for the various cations in the two solvents for water and methanol by calculating the electric field at the proton assuming a model for the cation methanol or water complex. In these calculations both solvent field and electric fields effected by the ion are included.

In this work, we shall assume a symmetric water or methanol complex represented in Figure 22.

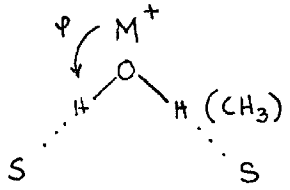

Figure 22. Model for the Cation Complex

There is an apparent disagreement, however, in the literature with regard to the orientation of water molecules in the field of an alkali ion (36). In Figure 22, M^+ represents the cation and the angle φ used in the the calculations was 128° for water and 125.5° for methanol. We assume a covalent radii for oxygen of 1.47 Å. This value was obtained from X ray crystallographic determinations of $O...M^+$ distances in hydrated crystals.

Values used for ionic radii, used in the calculations for the cations investigated, were Na^+ (0.97 Å), Li^+ (0.68 Å), and Mg^{++} (0.66Å) (37).

The results of the calculations concerning the cation dependent linear electric field coefficient determined by the method described above are summarized in Figure 23 for several values of the solvent field for water in acetonitrile.

It is clear that no matter what one uses for the solvent field, the linear coefficient for these ions

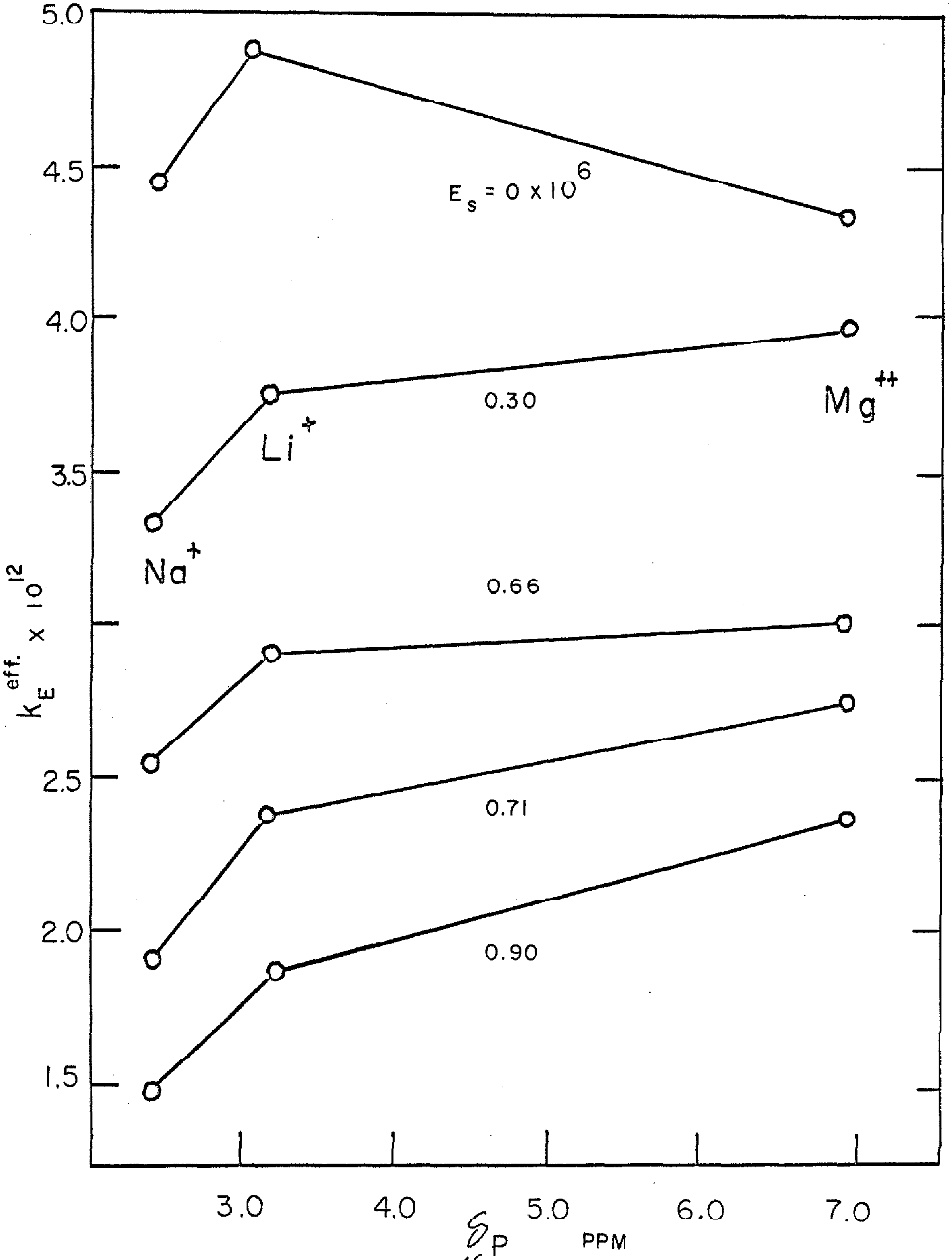

Figure 23. Variation in $k_E^{eff.}$ as a function of solvent field E_s.

is different. In principle, we would be inclined to believe that the linear coefficient would be in the order $Na^+ < Li^+ < Mg^{++}$ which is the result we obtain for solvent fields greater than 0.30 x 10^6 statvolts/cm. For a more realistic value of the solvent field, *i.e.*, 0.66 x 10^6 esu for acetonitrile (the field obtained by earlier considerations), the ordering of the effective k_E's is what one expects.

If we consider the simple Buckingham type of formalism to be representative of the specific polarization effects, the current results would suggest that repulsion effects (at the oxygen lone pair due to the cation) are just as important as specific charge transfer polarization effects. The present treatment, however, does not enable us to separate each of the two counteracting effects.

Earlier calculations concerning the nuclear magnetic shielding constants of alkali ions in crystals and dilute aqueous solutions of these ions by Ikenberry and Das indicate that both charge transfer and repulsive effects are important (38).

The relative importance of the two effects obviously depends upon both the charge on the ion and the number of electrons associated with the cation.

The specific effects of repulsion and charge transfer can be seen upon comparison of the effective linear electric field coefficients for the various ions. The value of k_E for Mg^{++}, for example, is not twice as large as for Li^+. Since the ionic radii of these ions are nearly the same, the fact that the ratio is the effective k_E's, i.e., $k_E^{eff.}$ (Mg^{++}) / $k_E^{eff.}$ (Li^+) is not 2.0 is indicative of the greater degree of repulsion in the case of Mg^{++}.

The results obtained for water and CH_3OH in CH_3CN ($E_s = 0.66 \times 10^6$ esu, M.A. = 0.68 ppm) are summarized in Table 4 for Na^+, Li^+, and Mg^{++}.

TABLE 4

Ion	H_2O/Acetonitrile	CH_3OH/Acetonitrile
	$k_E^{eff.} \times 10^{-12}$	$k_E^{eff.} \times 10^{-12}$
Na^+	-2.6 ± 0.2	-1.8 ± 0.4
Li^+	-2.9 ± 0.2	-2.4 ± 0.2
Mg^{++}	-3.0 ± 0.3	-1.8 ± 1

All of the present considerations are less clear in the case of water polarized by these ions in acetone.

The major problem concerns the nature of the solvated ion-water complex. In Section D-2b we discussed the possibility of a bent hydrogen-bonded water-acetone complex.

In the case of a solvated ion-water complex we are confronted with a similar problem. We shall assume for the moment that the acetone-solvated ion-water complex is also one in which the acetone-water hydrogen bond is not linear as is illustrated in Figure 24.

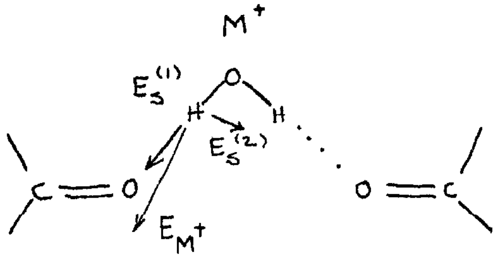

Figure 24. Cation-Water-Acetone Complex

The resultant field, E_R, is in this case the vector sum of $E(M^+)$, $E_s^{(1)}$, and $E_s^{(2)}$. We assume as before that the additional contributions to the solvent field which arise from the electrical asymmetries in the solvent molecule is small compared to the field produced by the lone pair.

The results obtained for water in acetone using $\delta_{M.A.} = +0.29$ ppm are summarized in Table 5 along with the calculated values for the resultant field at the proton.

TABLE 5

H_2O/Acetone

Ion	$E_R^{\parallel}$	E_R^2	$k_E^{eff.} \times 10^{12}$
Na^+	1.07	1.35	-2.06 ± 0.2
Li^+	1.17	1.67	-2.51 ± 0.2
Mg^{++}	1.65	3.50	-2.81 ± 0.3

$E^{\parallel}$ is in units of 10^6 esu and E^2 in units of 10^{12} esu^2.

In the case of cation polarization of water or methanol the linear coefficient can be obtained from the experimentally-determined polarization shifts. A variation in this coefficient for different cations is indicative of the inadequacy of the electric field approach based on equation 7 using a constant value for the linear electric field coefficient. If the case of cation water or methanol polarization were describable in terms of an electrostatic field approach which did not involve specific polarization effects at the oxygen, the linear electric field coefficient would be the same for all cations. Variations in this coefficient for the different ions are therefore indicative of specific polarization effects (both repulsive and charge transfer) at the oxygen lone pair. Subsequent distortions will also occur in the bonding electrons of water and methanol. The relative variations in the linear electric field coefficient are consistent with the relative degree of polarization which one would expect on the basis of ion size and charge.

It is clear that additional studies concerning O^{17} chemical shifts are desirable in order to ascertain a more quantitative description of the oxygen lone pair polarization by various cations.

Luz and Yagil (39) recently studied O^{17} chemical shifts of water in aqueous 1:1 electrolyte solutions. In this work, it was shown that most cations give rise to an upfield shift of about the same order of magnitude, whereas shifts due to anions differed considerably from one to another. No divalent ions were considered.

Since the data involve bulk water as solvent, the observed shifts are still extremely complicated. Quantitative partitioning of the observed chemical shifts in terms of the two counteracting (structure-breaking and polarization contribution) effects still remains a formidable problem.

The results of the preceding calculations can be rationalized by considering the polarization distortion of the oxygen lone pair.

In a previous section, the Buckingham treatment which introduced an effective charge, λ , was briefly discussed. For hydrogen-bonded systems and others which do not involve specific polarization at the oxygen, the value of λ originally chosen is not expected to vary upon complex formation since the oxygen is not directly involved. In the case of the polarization of water by cation, however, the complexation occurs at the oxygen lone pair. Consequently, the value of λ chosen for the reference state (monomer hydrogen-bonded to solvent) can no longer be used in order to estimate shifts affected by the cation. The results of the preceding calculations clearly bear this out.

An expression for the electric field contribution, analogous to the Buckingham treatment for water polarized by cations, can be determined by considering a different equation charge λ' given by:

$$\lambda' = \lambda_o + \epsilon_1 E_0 + \epsilon_2 S \qquad (12)$$

where E_o is the electric field at the oxygen effected by the cation and S the overlap integral, $\langle \Psi_{L.P.} | \Psi_{M^+} \rangle$ between the oxygen lone pair and metal ion orbitals. In this case, it is easily shown that:

$$\delta_E = -2b\left(\frac{\lambda_0}{R^2} + \frac{\epsilon_1 E_0}{R^2} + \frac{\epsilon_2 S}{R^2}\right)\mathcal{E}_{11} - b\,\mathcal{E}^2$$

$$-\frac{2b\lambda_0\epsilon_1 E_0}{R^4} - b\left(\frac{\epsilon_1 E_0}{R^2}\right)^2 - \frac{2b\lambda_0\epsilon_2 S}{R^4} - b\left(\frac{\epsilon_2 S}{R^2}\right)^2 \qquad (13)$$

$$\sim 2\epsilon_1\epsilon_2 S E_0 b / R^4$$

where $\mathcal{E}$ is the total field at the proton produced by the cation and solvent and $\mathcal{E}_{11}$ the component of this field parallel to the OH bond axis.

It is of interest to note that in addition to the Buckingham k_E given by $2b\lambda/R^2$, seven additional terms arise. These are essentially small for large cations with a small charge, but their contribution can become appreciable in the case of small ions or ions with a large charge.

These calculations combined with the previous results concerning the linear electric field coefficient clearly indicate that calculations concerning polarization shifts affected by cations must include the effects of the polarization of the oxygen lone pair in some manner if any meaningful results are to be obtained.

The preceding analysis concerning the estimation of the linear electric field coefficient by using the experimentally-determined polarization shifts is not unique. These calculations served as a basis of checking the reasonableness of the cation-water complex model which included the effects of both solvent and cation fields at the proton.

It is possible to make similar calculations as before with the exception of using the hydrogen-bonded monomer as a starting basis for the calculations. In this case the value of δ_c (complex shift relative to the hydrogen-bonded monomer) can be used to estimate the linear electric field coefficient. Since the solvent field in the cation-water complex is nearly the same as in the hydrogen-bonded monomer, the problems concerning the solvent field are essentially bypassed. These results are summarized in Table 6 for water and methanol in the various solvents. Again, the results verify the earlier considerations concerning the effect of the cation on the linear electric field coefficient.

TABLE 6

H_2O/Acetone

Ion	δ_C (ppm)	$E_M{}^+$	$\overset{''}{E}_M{}^+$	$k_E^{eff.}$
Na^+	-0.83 ± 0.1	0.493	0.340	-1.89 ± 0.1
Li^+	-2.02 ± 0.1	0.595	0.48	-3.65 ± 0.1
Mg^{++}	-4.78 ± 0.2	1.205	0.98	-3.76 ± 0.2
		H_2O/Acetonitrile		
Na^+	-0.83 ± 0.1	0.493	0.340	-1.89 ± 0.1
Li^+	-1.73 ± 0.1	0.595	0.48	-3.01 ± 0.1
Mg^{++}	-4.62 ± 0.2	1.205	0.98	-3.60 ± 0.2
		CH_3OH/Acetonitrile		
Na^+	-0.58 ± 0.5	0.500	0.412	-0.94 ± 0.5
Li^+	-1.89 ± 0.1	0.605	0.516	-3.12 ± 0.1
Mg^{++}	-3.17 ±~1	1.227	1.055	-1.93 ±~1

The fields are expressed in units of 10^6 and k_E in units of 10^{-12}.

F. SUMMARY

There are several important factors which bear emphasis. In this work, we have shown that the magnitude of the linear electric field coefficient varies depending on ion size and charge for the case of cation polarization of water or methanol molecules. This clearly indicates that specific effects of polarization at the oxygen lone pair must be considered if any quantitative calculations concerning polarization shifts due to cations are to be made. Treatments based on static electric field models which do not take this into account are meaningless.

In the case of anion polarization of water or methanol, the results obtained in this work indicate that once again the electric field approach is inadequate.

It is apparent that before polarization shifts are understood on a quantitative basis, the problem must be approached from a proper quantum mechanical formulation of the polarization phenomena and not from the electric field approach as has been done in the past.

In the case of very weak polarization, such as chloroform hydrogen-bonded to various nitrogen bases (27), it was shown that the electric field plus the magnetic anisotropy approach was satisfactory. This also appears to be the case for water and methanol in acetonitrile. In many cases, however, no clear distinction can be made concerning the electric field effect. To be sure, in some manner the observed shift may be dependent on electric field terms but the question of how good the linear and quadratic field dependence description is will always arise. Even if this point could be settled, the problem of what linear, quadratic, etc., coefficients are to be used still remains a formidable one. It is clear that considerable caution must be made when one is concerned with the general problem of polarization in reference to magnetic shielding calculations.

The results of the present work clearly indicate that the observed chemical shifts for water in aqueous electrolytic solutions cannot be treated in terms of the simple electric field approach based on the Buckingham type of formalism. In future calculations, one must treat these shifts on more quantitative grounds than the electric field approach can offer.

Although the results of the present calculations based on the electric field approach are by no means definitive, the models employed and the results of the calculations are instructive in several respects.

At least three inferences prove to be of special interest from the chemists' viewpoint: (1) the preferential attack of only one proton of water to the anion, (2) the non-linear water-acetone hydrogen bond, and (3) the importance of both charge transfer and repulsion effects in the polarization of water or methanol by various cations.

In this work, we mentioned that the polarization shifts obtained could be interpreted in terms of an ion-water or ion-methanol complex. Calculations concerning the effects of an electric field were subsequently made on the basis of this model only to gain insight into the problem of the polarization of these molecules by ions.

There are three aspects of the present problem which need to be considered in more detail for the case of the cation complexation of water.

(1) Overlap Consideration. In the ion-water molecule complex, the occupied orbitals of the ion and the water molecule lone pair orbitals overlap to some extent. As a result, strong repulsive forces exist between them. This force is short range in nature and arises mainly from the Pauli principle. The electrostatic attraction of the ion to the water molecule is counterbalanced by the repulsive force at the observed ion-water molecule distance.

(2) Polarization Distortion. In reality, the electron distribution of both the ion and water molecule is distorted as a result of the complex formation. The polarization itself may come about from electrostatic interactions, exchange interactions, and overlap interactions. The wave functions of the ion and molecule are consequently modified relative to their respective free gas state functions. A manner of taking this into account is to mix some of the excited state functions of the ion-water molecule complex into the ground state configuration (42).

(3) Charge Transfer Covalency. To a certain extent, a small transfer of charge from the oxygen lone pair to the unoccupied orbitals of the metal ion is also possible. The extent of this contribution is, however, thought to be

small in comparison to the overlap consideration and the polarization distortion (38).

It is hoped that a study will be initiated in the near future to consider these aspects in more detail.

In recent years there has been an increasing effort towards the characterization of ion molecule complexes in aprotic solvents (40). Ionic interactions in solutions of aprotic solvents have already been studied in a variety of ways (1), but the results have received varied interpretation.

Definitions of various types of complexes, such as contact ion pairs and solvent separated or shared ion pairs, are now well understood. More and more experimental evidence is becoming available which suggest that distinctions between the two can be made.

In the course of this work, we have also made an infrared spectroscopic study of the solutions whose magnetic resonance data we have reported in this section.

Although earlier studies concerning various salt solutions of water in acetone and in acetonitrile (41) and methanol in acetonitrile (13) have been reported, the interpretation of their results was not completely in agreement with the present NMR studies. For this reason, the infrared spectra of these solutions were reinvestigated in greater detail. The results of this study are presented in Part II.

G. APPENDIX

Table of Electrolyte Shifts

$Mg(ClO_4)_2/H_2O$/Acetone

(Shifts are relative to internal TMS)

0.010 M $Mg(ClO_4)_2$

W (molal)	δ cps
0.011	-253
0.021	-250
0.040	-244
0.051	-238
0.099	-221
0.115	-215
0.150	-205
0.235	-196
0.33	-189
0.52	-185
0.65	-184
0.855	-184
1.24	-185.5
1.50	-186.5
1.73	-187.5

0.023 M $Mg(ClO_4)_2$

W (molal)	δ cps
0.015	-312.5
0.025	-310
0.040	-306
0.051	-300
0.081	-283
0.135	-260
0.311	-222.5
0.54	-206
0.681	-202
0.855	-198
1.11	-195.5
1.445	-195.2
1.798	-196

0.038 M $Mg(ClO_4)_2$

W (molal)	δ cps
0.021	-345.5
0.055	-339
0.095	-323
0.145	-302
0.245	-266
0.382	-242
0.540	-227
0.754	-216
0.952	-211
1.23	-207.5
1.625	-205.5

0.056 M $Mg(ClO_4)_2$

W (molal)	δ cps
0.015	-357.5
0.041	-355.5
0.065	-351
0.151	-327
0.255	-302
0.390	-275
0.585	-250
0.745	-238
1.014	-226.5
1.27	-220
1.70	-215

(DATA FOR $Mg(ClO_4)_2/H_2O$/Acetone - Cont'd)

0.072 M $Mg(ClO_4)_2$

W (molal)	δ cps
0.025	-360
0.052	-358.5
0.070	-356
0.175	-334
0.265	-312
0.402	-287.5
0.702	-253
1.05	-233
1.40	-224
1.79	-220

0.122 M $Mg(ClO_4)_2$

W (molal)	δ cps
0.02	-371
0.05	-368
0.09	-364
0.155	-359
0.270	-347
0.392	-332
0.650	-302
0.905	-281
1.192	-264
1.455	-253
1.750	-244

0.209 M $Mg(ClO_4)_2$

W (molal)	δ cps
0.060	-369
0.095	-368
0.165	-365
0.306	-356.5
0.465	-345
0.750	-321
1.23	-288
1.75	-268

0.464 M $Mg(ClO_4)_2$

W (molal)	δ cps
0.065	-370.6
0.142	-370
0.265	-367.5
0.415	-365
0.685	-360
1.325	-342.5
1.755	-328.5

$Et_4NBr/H_2O/CH_3CN$

(Shifts are relative to internal TMS)

0.0645 M Et_4NBr

M H_2O	δ cps
0.0250	-137.0
0.1352	-135.5
0.3093	-135.0
0.5650	-136.5
0.9439	-138.5
1.6425	-142.0

0.1553 M Et_4NBr

M H_2O	δ cps
0.0250	-139.0
0.0837	-139.0
0.2106	-139.0
0.4876	-140.0
0.8722	-143.0
1.2605	-144.0

0.2811 M Et_4NBr

M H_2O	δ cps
0.0303	-144.5
0.1119	-144.5
0.2895	-145.0
0.5557	-146.5
0.9542	-147.5
1.4147	-149.0

0.4408 M Et_4NBr

M H_2O	δ cps
0.0195	-150.5
0.1011	-150.5
0.2569	-150.5
0.4647	-151.0
0.6688	-152.0
0.9228	-153.0

$NaClO_4/H_2O$/Acetone

(Shifts are relative to CH_3 of solvent)

2.11 M H_2O

M $NaClO_4$	δ
0	- 63.5
0.225	- 71.3
0.347	- 73.8
0.372	- 73.8
0.569	- 76.5
1.26	- 82.8
1.82	- 84.8

1.19 M H_2O

M $NaClO_4$	δ
0	- 54.5
0.656	- 74.0
1.61	- 82.5
2.42	- 84.3
3.46	- 84.8

(DATA FOR $NaClO_4/H_2O$/Acetone - Cont'd)

0.926 M H_2O

M $NaClO_4$	δ
0	-52.5
0.372	-67.8
0.893	-77.3
1.04	-79
1.26	-80.8
1.32	-80.8

0.658 M H_2O

M $NaClO_4$	δ
0	-49.5
0.193	-58.3
0.459	-68.8
0.857	-76.3
1.615	-81.8
2.365	-83.8

$NaClO_4/H_2O/CH_3CN$

(Shifts are relative to CH_3 of solvent)

1.34 M H_2O

M $NaClO_4$	δ
0	-23
0.197	-29.5
0.476	-36.5
0.510	-36.8
0.946	-43.0
1.772	-48.3
3.741	-54.0

0.686 M H_2O

M $NaClO_4$	δ
0	-16.8
0.53	-17.7
0.71	-21.0
0.75	-21.0
0.94	-25.2
1.03	-24.5
2.10	-35.7

2.13 M H_2O

M $NaClO_4$	δ
0	-31.5
0.62	-42.0
0.65	-42.8
1.10	-47.5
1.55	-47.5
2.48	-53.0

$LiClO_4/H_2O/(CH_3)_2CO$

(Shifts relative to internal TMS)

0.19 M $LiClO_4$

M H_2O	δ
0.042	-224.5
0.064	-224
0.099	-223.5
0.158	-222
0.198	-220.2
0.255	-219
0.341	-217
0.425	-215
0.515	-214
0.603	-213
0.805	-209
0.886	-208
1.200	-206
1.398	-205
1.720	-204

0.31 M $LiClO_4$

M H_2O	δ
0.025	-239
0.055	-238.5
0.115	-237.5
0.198	-235
0.275	-233.5
0.425	-230
0.550	-227.5
0.659	-225
0.791	-224
0.915	-223
1.298	-216
1.492	-215.5
1.680	-215.5

0.09 M $LiClO_4$

M H_2O	δ
0.061	-204
0.150	-202
0.241	-200
0.553	-195
0.872	-193
1.081	-192.5
1.648	-194.5

0.74 M $LiClO_4$

M H_2O	δ
0.042	-260
0.141	-259.5
0.374	-256.5
0.570	-255
0.930	-249
1.280	-245
1.595	-242

(DATA FOR $LiClO_4/H_2O/(CH_3)_2CO$ - Cont'd)

0.54 M $LiClO_4$

M H_2O	δ
0.030	-254
0.155	-250
0.285	-248
0.490	-243
0.710	-241
1.061	-235
1.415	-230

1.24 M $LiClO_4$

M H_2O	δ
0.120	-266
0.209	-265
0.315	-263.5
0.450	-263.5
0.595	-262.5
0.780	-262
1.15	-257.5
1.420	-256
1.596	-254.5

$Mg(ClO_4)_2/CH_3OH/CH_3CN$

(Shifts relative to internal TMS)

0.013 M $Mg(ClO_4)_2$

M H_2O	δ
0.211	-151
0.340	-146
0.549	-146
0.911	-148

0.025 M $Mg(ClO_4)_2$

M H_2O	δ
0.098	-185
0.200	-168
0.341	-157
0.640	-154
1.018	-155

0.055 M $Mg(ClO_4)_2$

M H_2O	δ
0.091	-222
0.298	-190
0.575	-177
0.825	-171

0.103 M $Mg(ClO_4)_2$

M H_2O	δ
0.121	-246
0.248	-232.5
0.390	-219
0.556	-202
0.796	-188

(DATA FOR $Mg(ClO_4)_2/CH_3OH/CH_3CN$ - Cont'd)

0.160 M $Mg(ClO_4)_2$

M H_2O	δ
0.101	-270
0.175	-267
0.348	-257
0.582	-242
0.761	-231
1.046	-218

0.291 M $Mg(ClO_4)_2$

M H_2O	δ
0.105	-289
0.305	-284
0.371	-282
0.786	-267

0.537 M $Mg(ClO_4)_2$

M H_2O	δ
0.135	-300
0.445	-298
0.710	-295
0.965	-291

Data for $LiClO_4$, Et_4NBr, and Et_4NCl for methanol in acetonitrile were originally obtained by Dr. Hans Lutje and can be found in his notebook. The data were rechecked for certain values of salt and methanol concentrations and were found to be reproducable to within ± 2 cps.

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PART II

INFRARED STUDIES ON THE POLARIZATION OF WATER AND METHANOL

BY

$NaClO_4$, $LiClO_4$, $Mg(ClO_4)_2$, Et_4NClO_4, Bu_4NI,
Et_4NBr, and Et_4NCl IN AN APROTIC SOLVENT

A. INTRODUCTION

One of the most important and complex problems in the study of electrolytic solutions is that concerning the details of the specific ion-ion and ion-solvent interactions. A great amount of work has already been done in an effort to study the nature of these solutions, but the majority of these studies do not yield quantitative information concerning specific interaction details. The results have received a wide latitude of interpretation, and as a consequence there exists in the literature considerable disagreement even over very fundamental points.

The matter of the existence of an appreciable difference in the interaction of solvent water molecules with cations and anions is not entirely settled. The state of ion aggregation in non-aqueous solvents is, in many cases, unclear. Even in cases where considerable ion pairing is known to exist the exact nature of the ion pair itself has been ambiguous (1,2).

The extent of association of solute molecules, such as water with ions in an aprotic solvent, is also not known. The particular cases cited are but a few of the many unanswered problems concerning ion solvation.

The study of electrolytic solutions by electrical conductance measurements and by optical spectroscopy has been reviewed by Davies (3). More recently, studies concerning the nature of aqueous electrolytic solutions have been made using the methods of magnetic resonance spectroscopy. Much of the earlier work in this area is discussed by

Craig (4) and reviewed by Kavanau (5).

The infrared spectra of aqueous electrolytic solutions have been previously investigates (6 -10) and discussed by Perelygin (11).

It is apparent that the absorption features of the bulk water data are such that little quantitative information concerning ion interactions or nature of ion complexes can be obtained. A single broad band centered at about 3400 cm^{-1} is observed for bulk water.

This band is presumed to arise from the 0-H stretching vibrations associated with the various hydrogen-bonded species of liquid water. The addition of salt causes a broadening and slight shifting to lower frequencies in the bulk water band. Quantitative determination of frequency shifts in this case is not possible since the bands which characterize the various hydrogen-bonded water molecules and ion-water complexes are strongly superimposed.

To a certain extent, better results have been obtained from the study of the absorption band at 4.7 mμ (2130 cm^{-1}) which is thought to arise from the combination $\nu_2 + \nu_R$ where ν_2 is the bending frequency and ν_R, the intermolecular vibrational frequency of water. This band undergoes a regular displacement (6,8,10) the extent of which becomes greater as the salt concentration is increased.

In contrast to the study concerning the single broad absorption feature of the fundamental in the bulk water data, Waldron (12) studied the influence of various anions on the bands corresponding to the OH and OD stretching vibrations in HOD for various ratios of H_2O/D_2O.

Since the OH and OD bands of HOD are to a certain extent overlapped by the bands due to H_2O and D_2O, respectively, frequency shifts for the various anion complexes cannot be accurately obtained. Furthermore, large salt concentrations (several moles per liter) are necessary to produce appreciable changes in the spectrum. Under these conditions, it is extremely difficult to obtain any detailed information concerning the nature of the ion complexes in these solutions.

In dilute solutions of water in acetone or acetonitrile, a more favorable situation occurs. Two partially overlapping bands in the region of the OH fundamental are observed. The two bands can be assigned to the symmetric and antisymmetric vibrations of hydrogen-bonded water complexes which have C_{2v} symmetry.

The addition of salt to these dilute water solutions alters the infrared spectra in the region of the OH fundamental in a dramatic manner. In addition to the symmetric and antisymmetric bands due to the water monomer hydrogen-bonded to the solvent, additional bands appear which can, in certain cases, be clearly distinguished apart from the monomeric bands.

Shcherba and Sukhotin (13) were the first to investigate the behavior of the OH and OD stretching bands for light and heavy water in solution with various salts in acetonitrile. The authors report the appearance of the new bands in the spectra of the salt solutions shifted in the direction of lower frequency and ascribe them to water molecules which have entered into the solvation sphere of the cations. The shift is explained in terms of the polarization of the water molecules by the electric field produced by the cation. No influence of the anion on the water spectrum was observed. The assignment of the complex bands due to the ion-water complex and hydrogen-bonded monomer is still difficult, however, but to a certain extent of overlapping between monomer and complex bands.

These solutions are, however, a better defined system compared to the case where bulk water is used as solvent in so far as polarization studies are concerned.

More recently, Perelygin (11) has investigated the effects of various ions on the absorption band (O-H stretch) for methanol in dilute salt solutions of methanol in acetonitrile. The absorption feature, in this case, is easier to analyze compared to water since only one band appears for the hydrogen-bonded monomer. The location and assignment of the various complex band positions due to the complex and uncomplexed monomer is, however, still complicated by the overlapping of these bands. This is especially true of the methanol complex of $NaClO_4$.

Although it appears that the essential experiments have already been done in order to elucidate the nature of the various ion complexes of water or methanol in acetonitrile, there still remains a considerable amount of uncertainty concerning the interpretation, assignment, and location of the various complex bands. Furthermore, some of the conclusions made by these authors (11,13) are not in agreement with the results of the NMR studies concerning these solutions reported in Part I.

Since knowledge of the various ion complexes of water (or methanol) is critical in the interpretation of the NMR data, we have decided to reinvestigate the infrared spectra of these solutions in greater detail. In this study, a more accurate determination of the location of the various complex bands has been made. In this part of the thesis, an investigation of the influence of $NaClO_4$, $LiClO_4$, $Mg(ClO_4)_2$, Et_4NClO_4, Bu_4NI, Et_4NBr, and Et_4NCl on the infrared spectrum of the OH stretching vibration of water and methanol in acetonitrile is presented. An analysis of the frequency shifts as well as band assignments are discussed for the various ion complexes of water and methanol.

B. EXPERIMENTAL

All of the infrared measurements reported in this work were made using a Beckman IR-7 prism grating spectrometer.

A set of (0.0972 and 0.0963 mm) CaF_2 cells obtained from the Perkin-Elmer Corporation was used throughout the entire study.

Frequency calibrations in the 2800 to 4000 cm^{-1} region were made by certain intervals of the spectral measurements by comparison of the spectrum of water vapor using the present apparatus with the spectrum reported by Plyler, Danti, Blaine, and Tidwell (14). Deviations from the recorded wave number and those given by PDBT (14) were approximately ± 1 cm^{-1}. The region from 2400 to 2700 cm^{-1} was checked by comparison of the absorption band for HBr. Deviations in this region were approximately ± 1 cm^{-1}. Single beam operation was used in both cases.

The information pertaining to the salts and solvents used in this study was previously described in the experimental section of Part I.

The spectra of dilute solutions of water and methanol in acetonitrile were obtained using double beam operation. Neat acetonitrile was used in the reference cell. "Background" absorption was checked by running acetonitrile versus acetonitrile.

The spectra of the salt solutions of water (or methanol) in acetonitrile were also obtained by double beam operation. For each of the salts studied in this work, a series of spectra were recorded in order to bring out certain spectral features of interest.

Each salt solution was prepared by adding anhydrous acetonitrile to the dry salt. "Background" absorption for each of the salt solutions was checked and recorded by running the anhydrous salt solution versus the same solution. Methanol or water was then added to the anhydrous salt solution. A first series of spectra were recorded for each salt solution containing small amounts of water or methanol using the corresponding "dry" salt solution as reference. A second series of spectra were recorded for the same salt solutions containing water or methanol using neat acetonitrile in the reference cell. The recorded spectra in the region from 3400 to 3800 cm^{-1} and from 2400 to 2850 cm^{-1} were identical to the corresponding salt solution spectra obtained in the first series.

These spectra are characterized by absorptions due to the various ion complexes of water or methanol as well as for the non-ion complexed water or methanol molecules. The location of the various complex band positions is rather difficult in these cases due to problems in overlapping between the ion complexed and non-ion complexed monomer bands.

In order to bypass this problem of band overlapping between monomer and complex, small amounts of water or methanol were added to the neat acetonitrile reference cell. Since double beam operation was again used, the monomer bands of the reference and the sample begin to cancel each other out. At some appropriate concentration of water or methanol in the reference cell, the monomer bands are completely eliminated from the recorded spectrum. The resulting spectrum then represents a spectrum of the complex bands. The location of band positions for the various ion complexes in the latter series of spectra is easily made in contrast to the earlier composite spectra of Shcherba and Sukhotin (13) and Perelygin (11).

All of the infrared spectra reported in this work were obtained using a spectral width between 0.5 to 1mm and at a chart rate of 50 cm^{-1}/inch. The measurements were made at a temperature of approximately 35° C.

C. RESULTS

1. The O-H Stretching Vibration Spectrum of Dilute Solutions of CH_3OH, CH_3OD, H_2O, and D_2O in Acetonitrile

The spectra associated with the OH stretching vibration of various alcohols and water in aprotic solvents have already been investigated (11, 13, 15, 16, 17, 18-21). The objectives of these studies, naturally, are to elucidate the nature of hydrogen-bonding in these systems. The results of these studies have, to a certain extent, established the foundation for the interpretation of the spectral features of the OH stretch for water in acetonitrile as well as for the ion complexes of water in acetonitrile.

A brief summary of the spectral features of water and methanol in acetonitrile is given below.

In dilute solutions of methanol in acetonitrile, the $0 \rightarrow 1$ (fundamental) transition which corresponds to the OH stretch is characterized by a single band at 3542 cm^{-1}. For water, two diffuse and partially overlapping bands at 3635 cm^{-1} and 3545 cm^{-1} corresponding to the antisymmetric and symmetric vibrations, respectively, are observed. The frequencies given above represent the band maxima for the OH stretch for water and methanol at concentration less than 0.4 molal. Below this concentration, the maximum is fairly constant ($\pm$ 5 cm^{-1}). At higher concentrations, however, the band maxima shifts to lower frequency presumably due to the formation of higher order polymeric species, such as water-water dimers, etc. Figure 1 represents the

O-H stretching fundamental at various methanol concentrations in acetonitrile. Figure 2 represents the O-H stretching fundamental for water at various concentrations in acetonitrile.

The results of the low concentration data concerning the band positions for methanol and water in acetonitrile are summarized in Table 1.

TABLE 1

Observed Frequencies for the OH (OD) Vibrational Transition (0→1 Stretch) for CH_3OH, CH_3OH, H_2O, and D_2O in Acetonitrile

Water	ω_1^{OH} (sym.) cm^{-1}	ω_3^{OH} (antisym.) cm^{-1}
H_2O	3545	3635
D_2O	2595	2700
Methanol	ω_{OH} cm^{-1}	
CH_3OH	3542	
CH_3OD	2615	

The nature of various species of water (or methanol) upon dissolution in an aprotic solvent, such as acetonitrile, has been the subject of previous infrared spectral investigations(15,17,21,22). These studies have more or less established the fact that the frequencies reported above can be attributed to a monomeric hydrogen-bonded species.

Figure 1. Infrared Spectrum of the OH Stretching Vibration for Methanol in Acetonitrile

	Moles Methanol/kgm CH_3CN
A	0
B	0.170
C	0.305
D	0.397
E	0.623
F	0.940

Figure 2. Infrared Spectrum of the OH Stretching Vibration for Water in Acetonitrile

	Moles Water/kgm CH_3CN
A	0
B	0.168
C	0.264
D	0.407
E	0.492
F	0.643
G	0.903
H	1.303

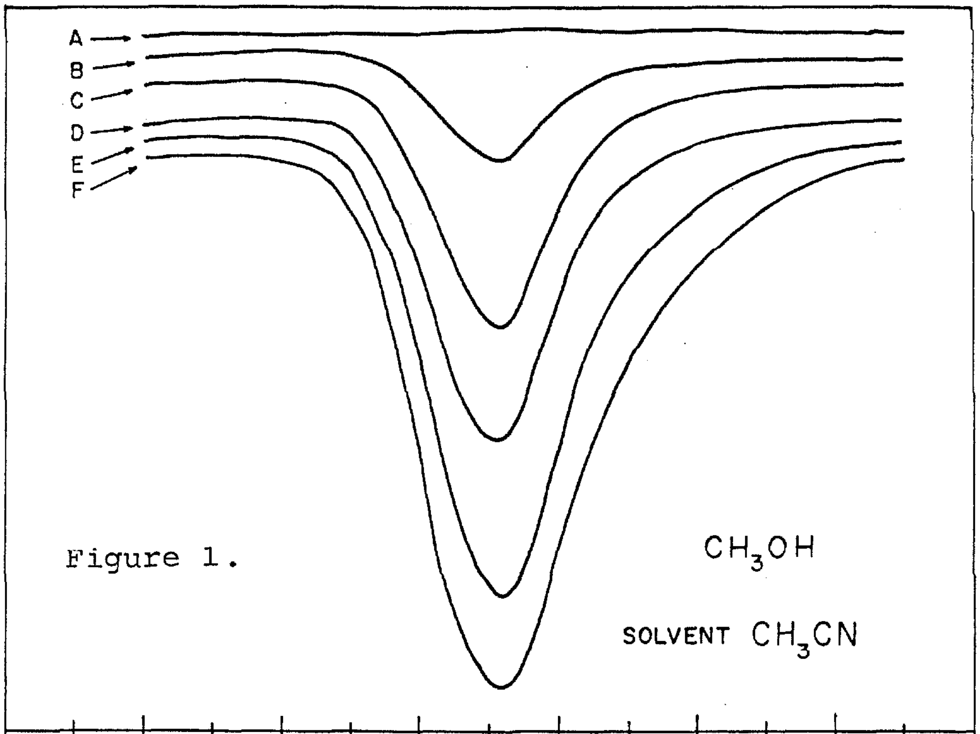


Figure 1.

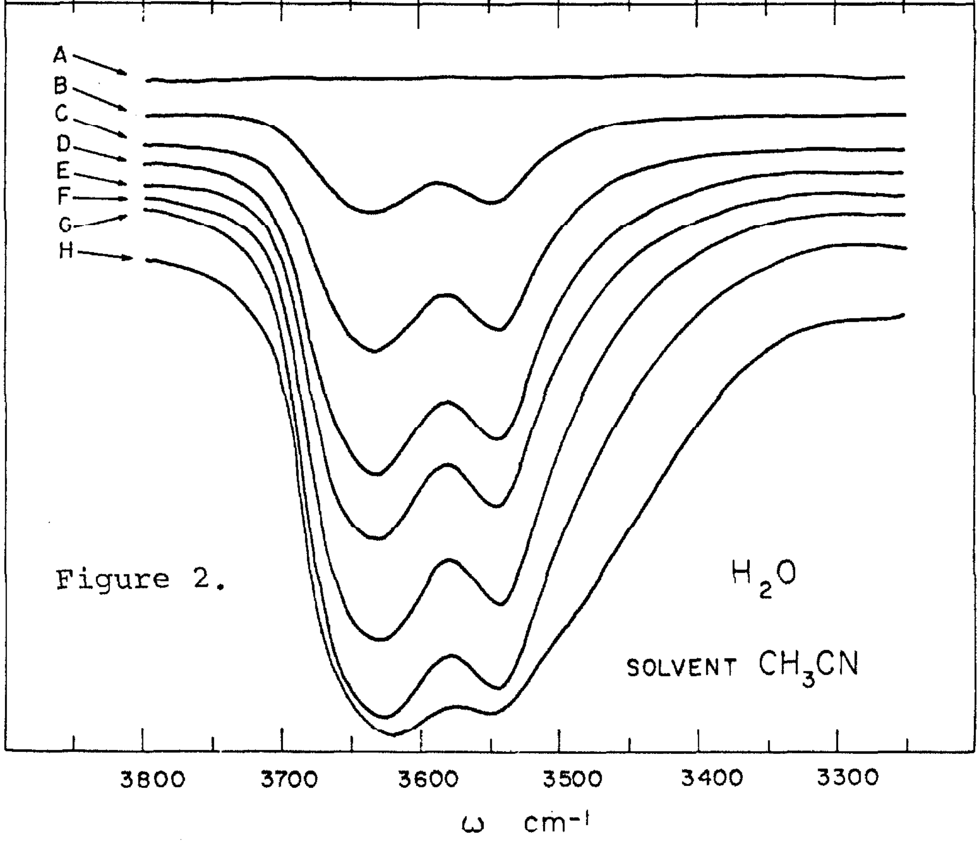


Figure 2.

In Figure 3, a summary is given for the variation in the absorbency (log I /I) for water and methanol as a function of the water (or methanol) concentration in acetonitrile.

It is apparent that at concentration greater than 0.5 molal the plot is not linear. This deviation can be ascribed to the formation of higher order methanol or water polymers (dimers, trimers, etc.) in acetonitrile.

Despite all of the earlier infrared studies which have been made in order to determine the various species (such as water or methanol monomers, dimers, trimers, etc.) in aprotic solvents, the nature of the various solvent-solute species is still not completely understood.

Recently, Barrow _et_. _al_. (20) made an infrared spectroscopic study concerning the association of water with various bases in CCl_4. Evidence was reported for one water to one base and one water to two base association complexes. At low base concentrations, it is suggested that the one to one complex predominates while at high base concentrations the one water to two base association complex predominates.

The association of phenol in water saturated carbon tetrachloride solutions was investigated by Badger and Greenough (21). Evidence was given for the possible configuration of a 2 phenol to one water molecule complex. It is also noted that phenol forms 2/1 intermolecular compounds with several organic solvents, for example, acetone (23) and acetamide (24), and that vapor pressure measurements suggest the presence of 2/1 complexes in the binary liquid systems with methanol, ethanol and acetone (25) as the second component.

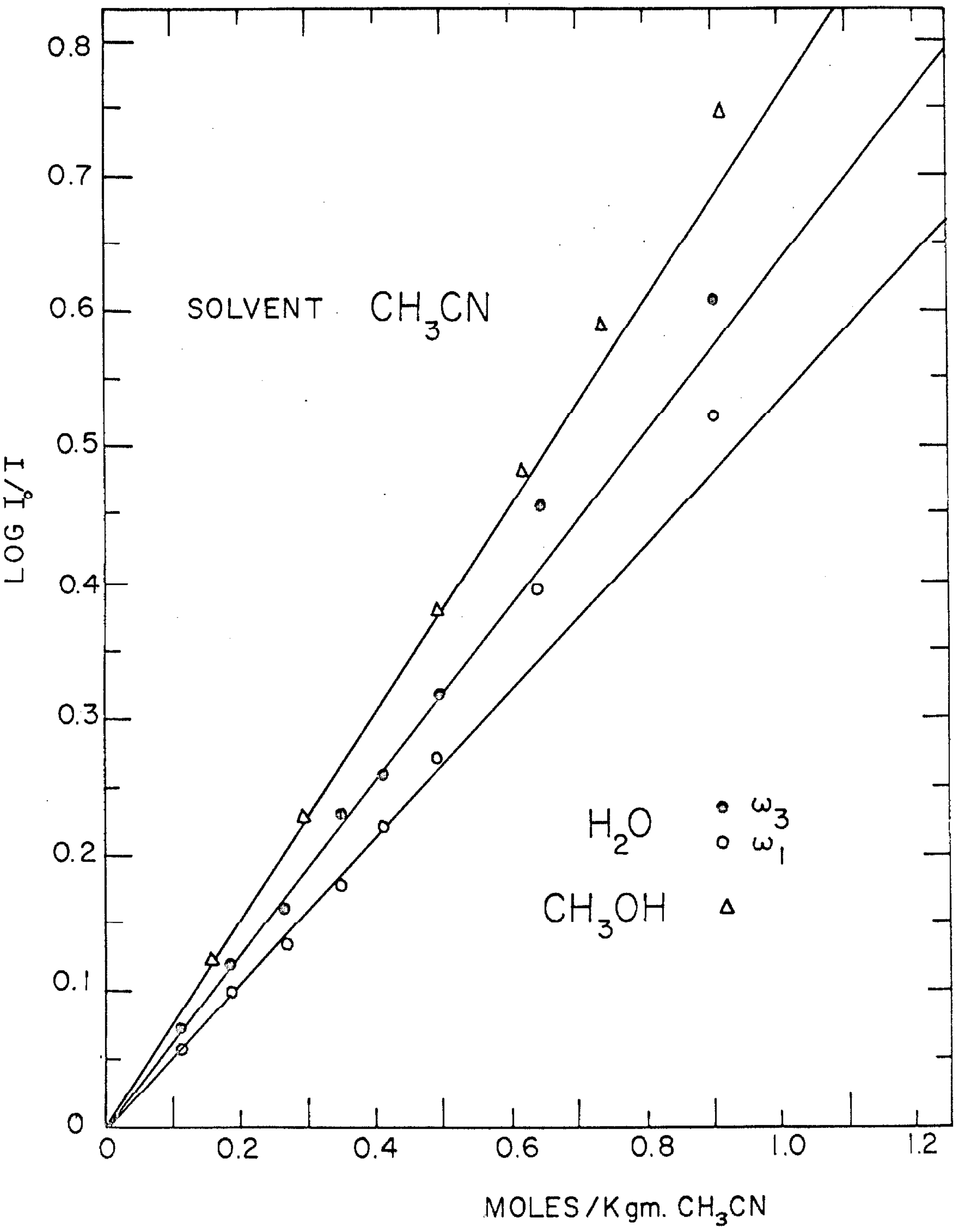
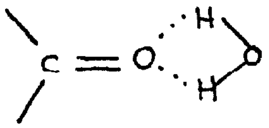


Figure 3. Plot of Absorbance vs. Methanol or Water Concentration

The results of the nuclear magnetic resonance data concerning water at low concentrations in acetone and acetonitrile discussed in Part I are consistent with the one water to two base association complex. This interpretation is in agreement with the results obtained by Barrow (20).

The elucidation of more detailed information, such as the structural features for the various one to one or one to two association complexes for water in various solvents, is a problem which is also of considerable interest.

The earlier infrared measurements of water in acetone, for example, by Errera, Gaspart, and Sock (17) were interpreted in terms of species of the type:

 .

This structure is questionable, however, in view of the nuclear magnetic resonance data. It appears that further work will have to be done in this area before the structural features of these hydrogen-bonded complexes can be established.

2. The Infrared Spectra of the Ion Complexes of Methanol in Acetonitrile

In general, the spectrum of the O-H stretching vibration of methanol in the presence of various diamagnetic salts is quite complicated. In the case of Et_4NClO_4, however, no shift or appearance of a new band in the region of the O-H stretching fundamental was observed. Because of this observation, the perchlorate or tetraalkylammonium ion was used as a counter ion for studying the effects due to Na^+, Li^+, Mg^{++}, I^-, Br^-, and Cl^-.

The spectra of the methanol complexes of $NaClO_4$, $LiClO_4$, $Mg(ClO_4)_2$, Et_4NBr, Bu_4NI, and Et_4NCl in acetonitrile are characterized by the appearance of a single band on the low frequency side of the band ascribed to the monomeric (methanol hydrogen-bonded to the solvent) species.

The influence of Cl^-, Br^-, and I^- on the OH stretching frequency of methanol (OH) in acetonitrile is illustrated in Figures 4, 5, and 6. In each of these figures, A represents the "background" absorption when no methanol is present; B, the hydrogen-bonded monomer spectrum in the absence of salt; C, the composite salt methanol spectrum; and D, the complex band spectrum obtained by the method discussed under the experimental section of Part II. The anion shifts for methanol (OD) are summarized in Figures 7, 8, and 9.

The apparent magnitude of the anion shifts are in the expected order, i.e., $Cl^- > Br^- > I^-$.

The spectra reported here are representative of the spectra obtained at low salt and low methanol concentrations. At higher methanol or salt concentrations, the spectral features obviously change due to the presence of higher order salt aggregates and methanol complexes. Since we are primarily interested with the various species at low salt and low methanol concentrations, only these will be considered here.

Figure 4. $Bu_4NI-CH_3OH-CH_3CN$

0.501 M	Bu_4NI
0.325 M	CH_3OH

Figure 5. $Et_4NBr-CH_3OH-CH_3CN$

0.295 M	Et_4NBr
0.302 M	CH_3OH

Figure 6. $Et_4NCl-CH_3OH-CH_3CN$

0.306 M	Et_4NCl
0.395 M	CH_3OH

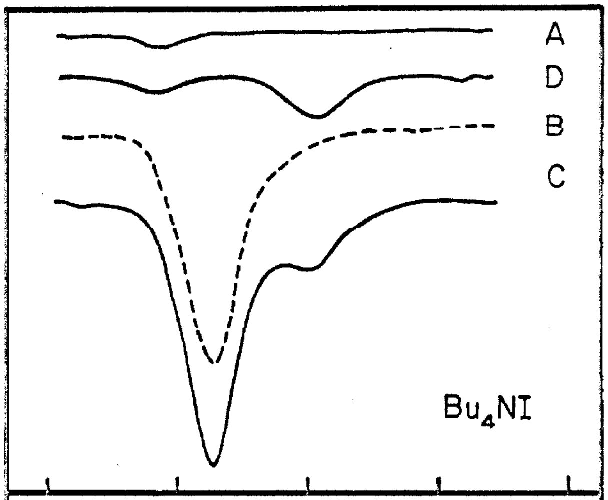


Figure 4.

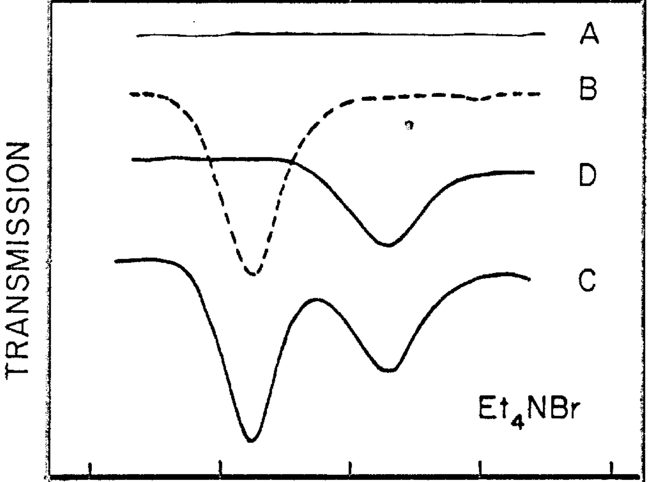


Figure 5.

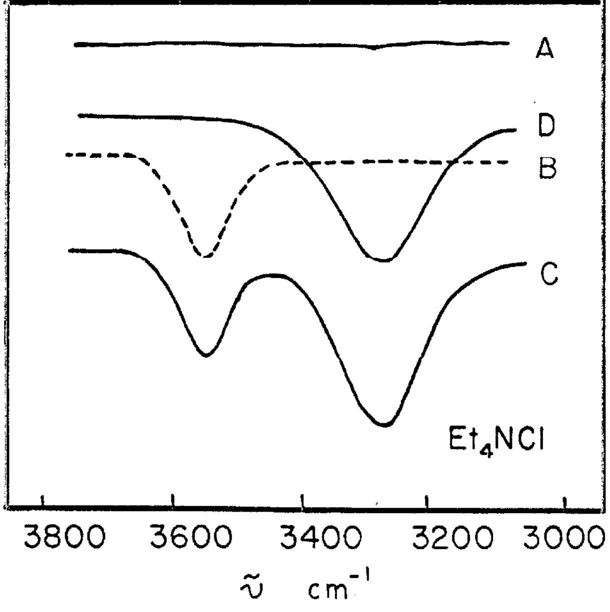


Figure 6.

Figure 7. $Bu_4NI-CH_3OD-CH_3CN$

Figure 8. $Et_4NBr-CH_3OD-CH_3CN$

Figure 9. $Et_4NCl-CH_3OD-CH_3CN$

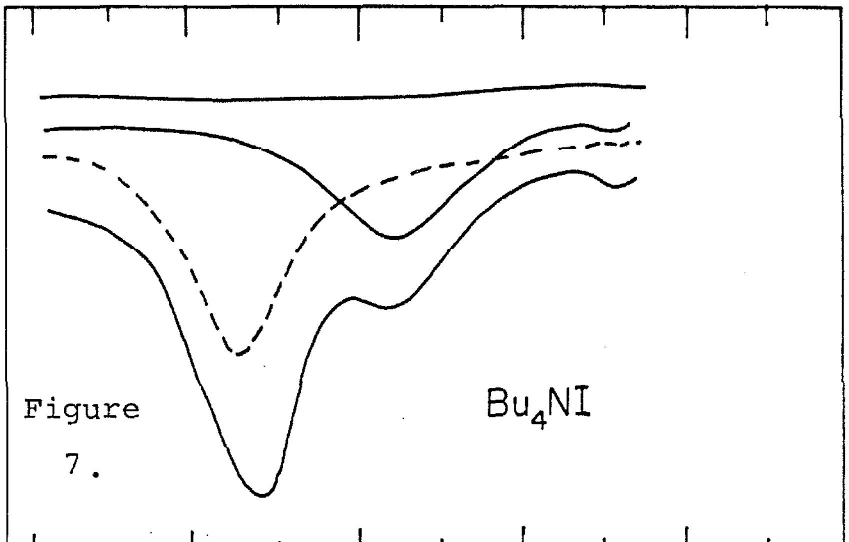
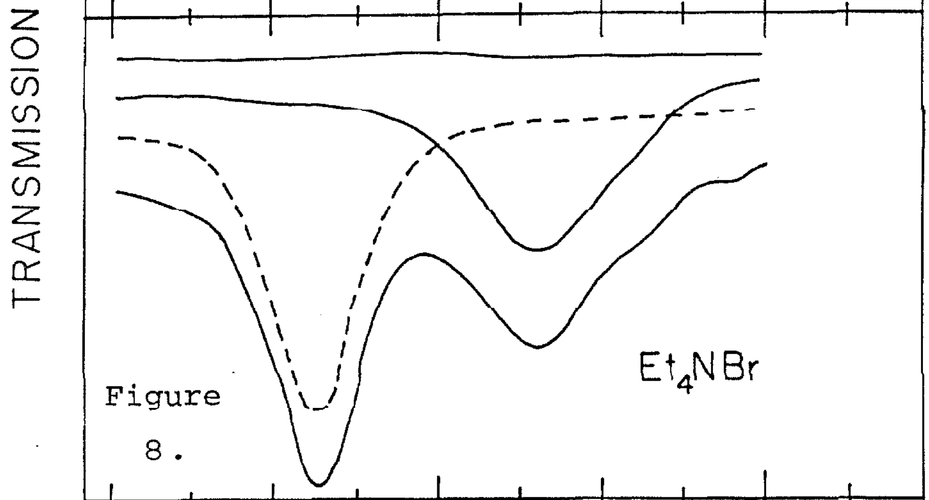


Figure 7.



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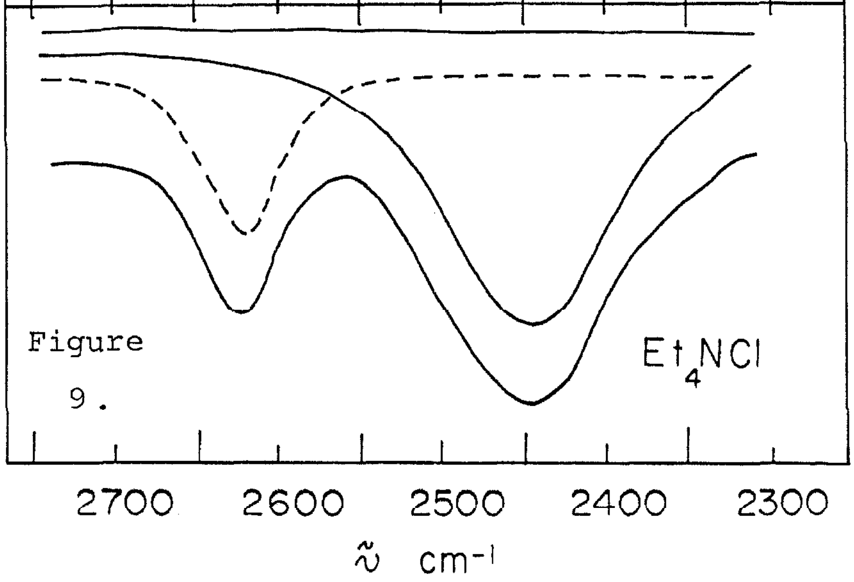


Figure 9.

The influence of Na^+, Li^+, and Mg^{++} on the OH stretching vibration for methanol (OH) in acetonitrile is illustrated in Figures 10, 11, and 12 and for methanol (OD) in acetonitrile in Figures 13, 14, and 15.

3. The Infrared Spectrum of the Ion Complexes of H_2O and D_2O in Acetonitrile

The infrared spectrum of the OH stretching vibration of water and heavy water in acetonitrile consists of two partially resolved bands corresponding to the symmetric and antisymmetric vibrations. The spectra of the ion complexes of water are similar. In this case, the spectrum is characterized by the appearance of two bands on the low frequency side of the bands attributable to the monomeric species.

The influence of Cl^-, Br^-, and I^- on the OH (OD) stretching frequency is illustrated in Figures 16, 17, and 18 for H_2O in acetonitrile, and in Figures 19, 20, and 21 for D_2O in acetonitrile.

The influence of Na^+, Li^+, and Mg^{++} on the OH stretching vibration for water in acetonitrile is illustrated in Figures 22, 23, and 24 and for D_2O in acetonitrile in Figures 25, 26, and 27.

A summary of observed band maxima is given in Table 2.

Figure 10. $NaClO_4-CH_3OH-CH_3CN$

0.521 M	$NaClO_4$
0.265 M	CH_3OH

Figure 11. $LiClO_4-CH_3OH-CH_3CN$

0.287 M	$LiClO_4$
0.231 M	CH_3OH

Figure 12. $Mg(ClO_4)_2-CH_3OH-CH_3CN$

0.069 M	$Mg(ClO_4)_2$
0.275 M	CH_3OH

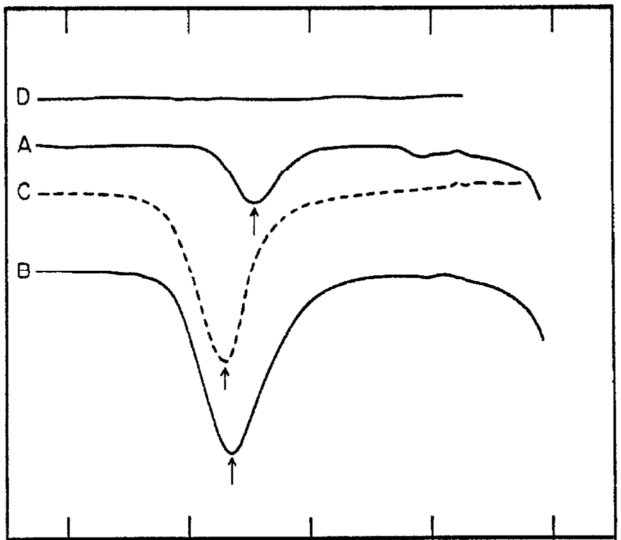


Figure 10.

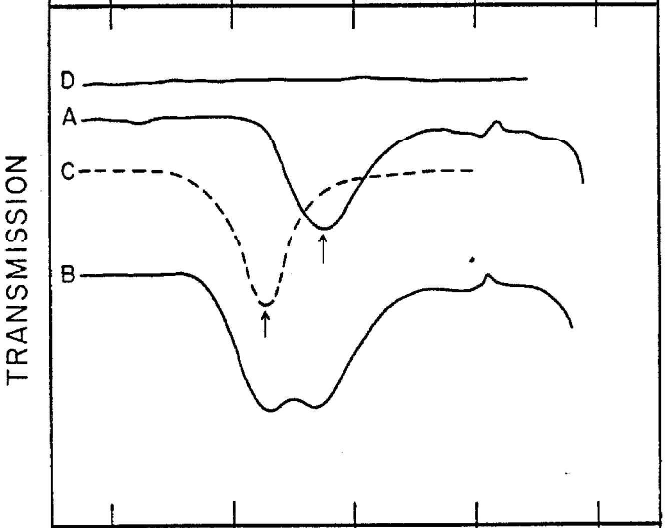


Figure 11.

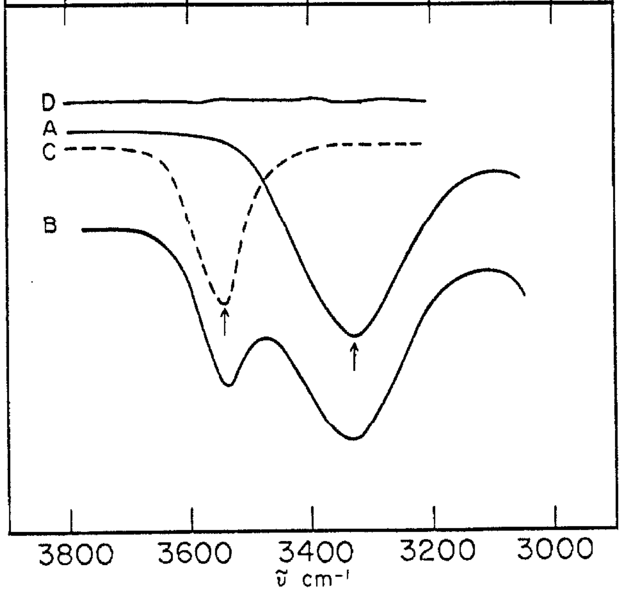


Figure 12.

Figure 13. $NaClO-CH_3OD-CH_3CN$

Figure 14. $LiClO_4-CH_3OD-CH_3CN$

Figure 15. $Mg(ClO_4)_2-CH_3OD-CH_3CN$

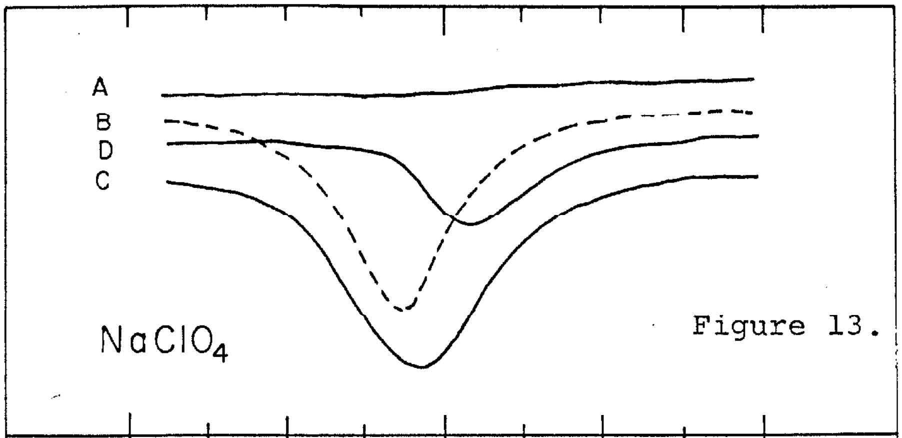
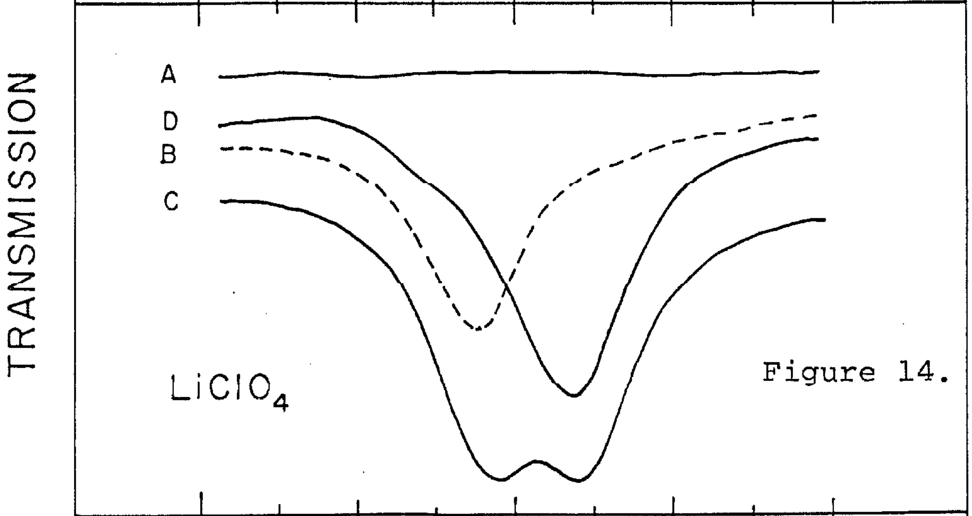


Figure 13.



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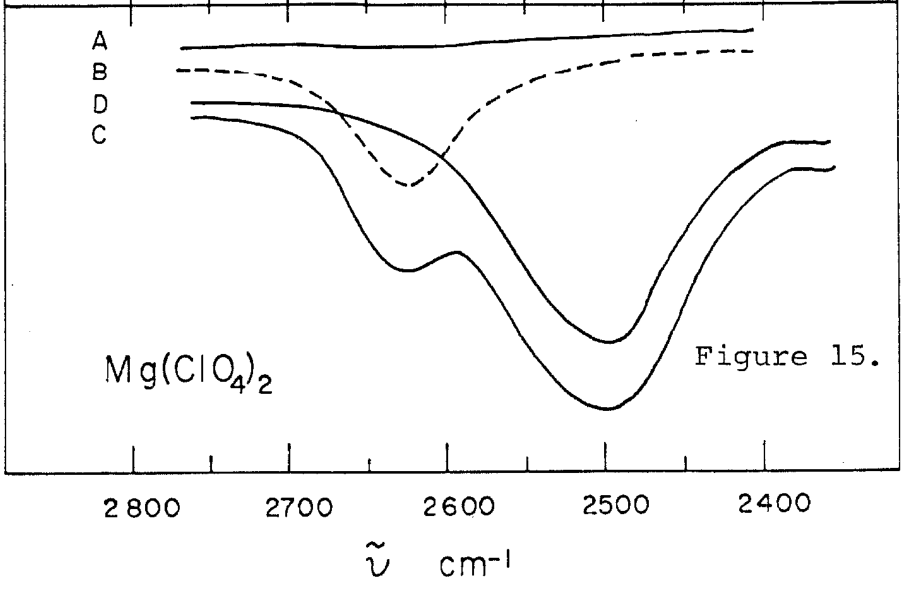


Figure 15.

Figure 16. $Bu_4NI-H_2O-CH_3CN$

0.312 M Bu_4NI

0.715 M H_2O

Figure 17. $Et_4NBr-H_2O-CH_3CN$

0.302 M Et_4NBr

1.021 M H_2O

Figure 18. $Et_4NCl-H_2O-CH_3CN$

0.505 M Et_4NCl

1.105 M H_2O

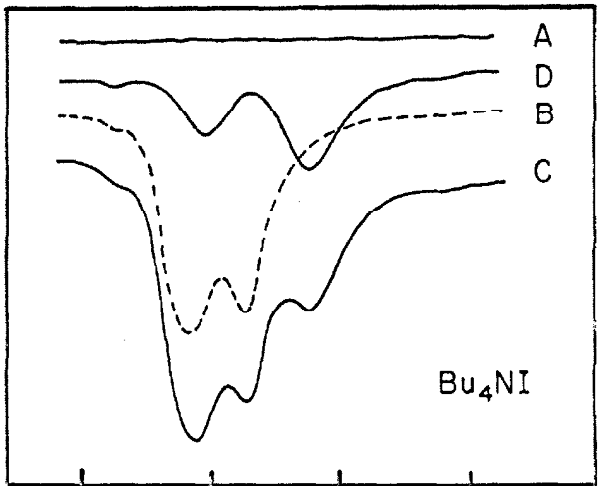
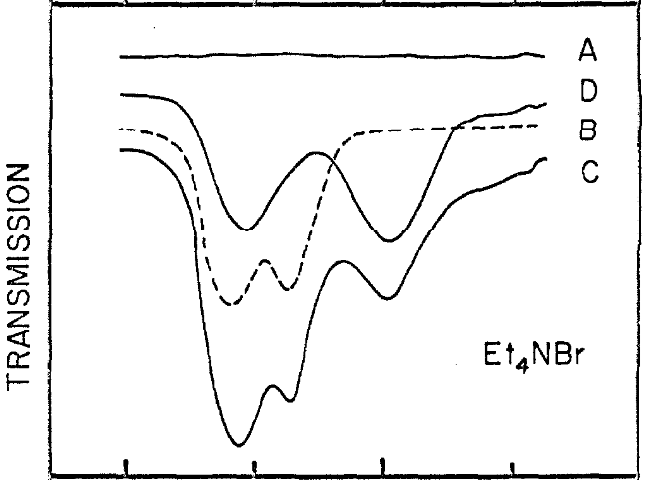


Figure 16.



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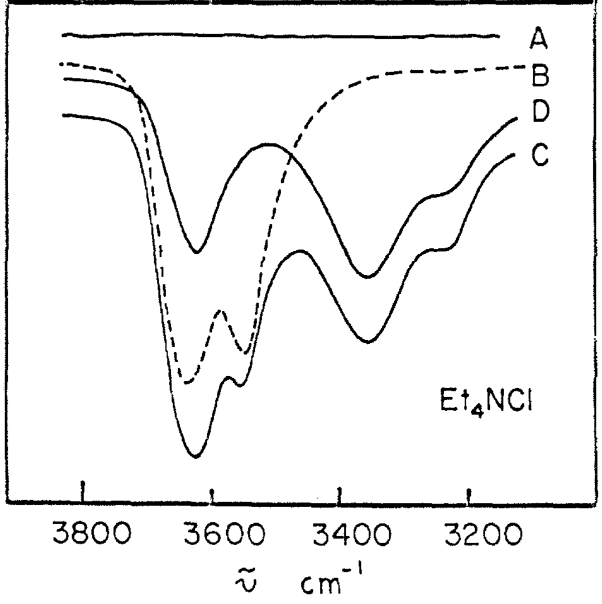


Figure 18.

Figure 19. $Bu_4NI-D_2O-CH_3CN$

0.375 M	Bu_4NI
0.604 M	D_2O

Figure 20. $Et_4NBr-D_2O-CH_3CN$

0.206 M	Et_4NBr
1.175 M	D_2O

Figure 21. $Et_4NCl-D_2O-CH_3CN$

0.437 M	Et_4NCl
0.944 M	D_2O

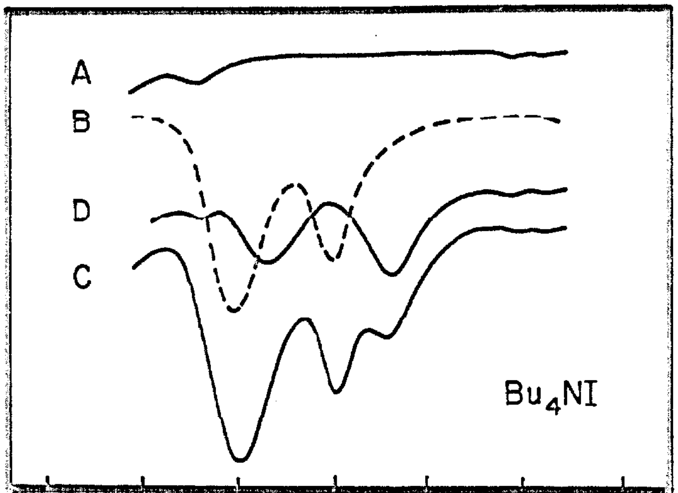


Figure 19.

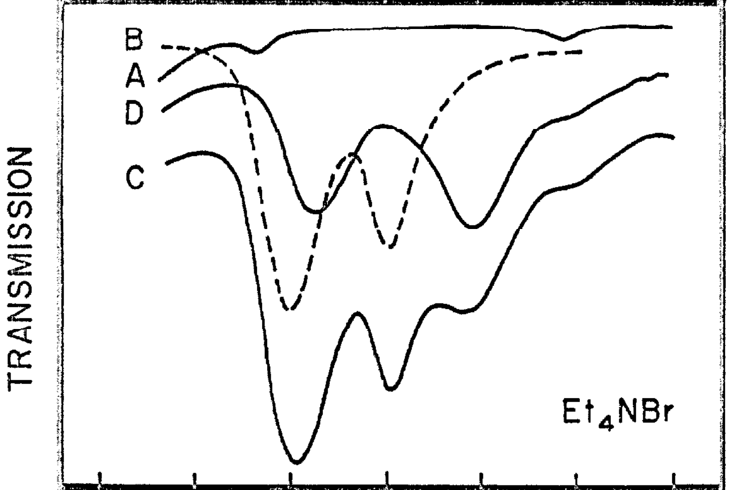


Figure 20.

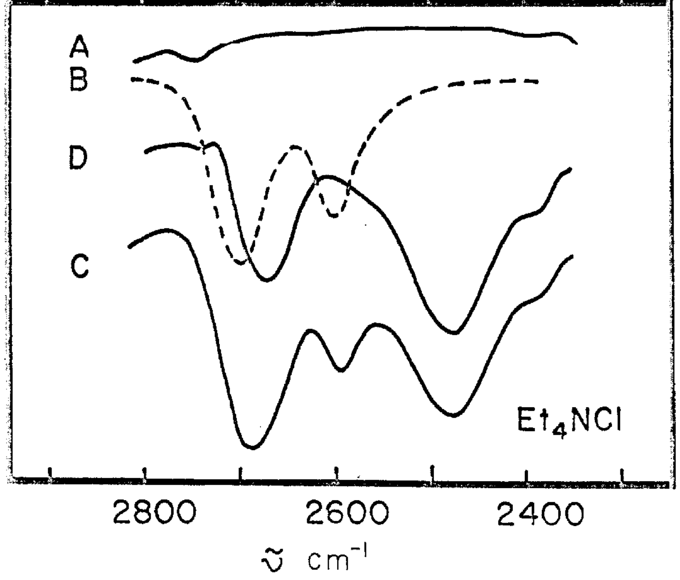


Figure 21.

Figure 22. $NaClO_4$-H_2O-CH_3CN

0.442 M	$NaClO_4$
0.769 M	H_2O

Figure 23. $LiClO_4$-H_2O-CH_3CN

0.497 M	$LiClO_4$
0.998 M	H_2O

Figure 24. $Mg(ClO_4)_2$-H_2O-CH_3CN

0.205 M	$Mg(ClO_4)_2$
0.321 M	H_2O

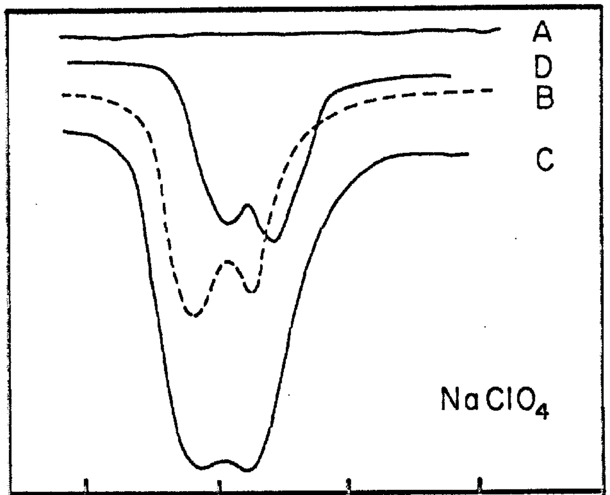


Figure 22.

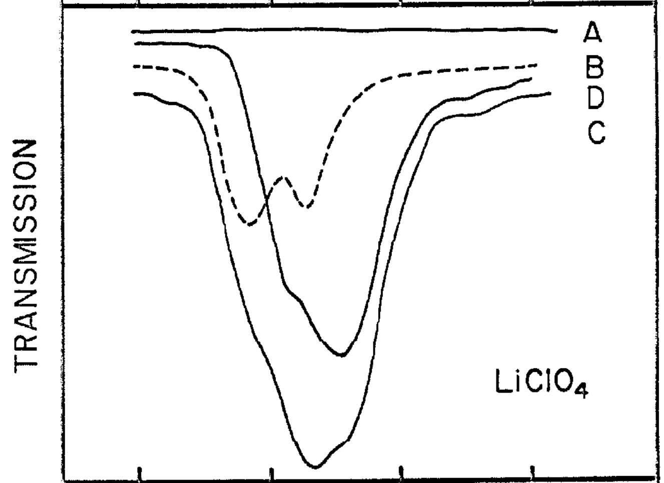


Figure 23.

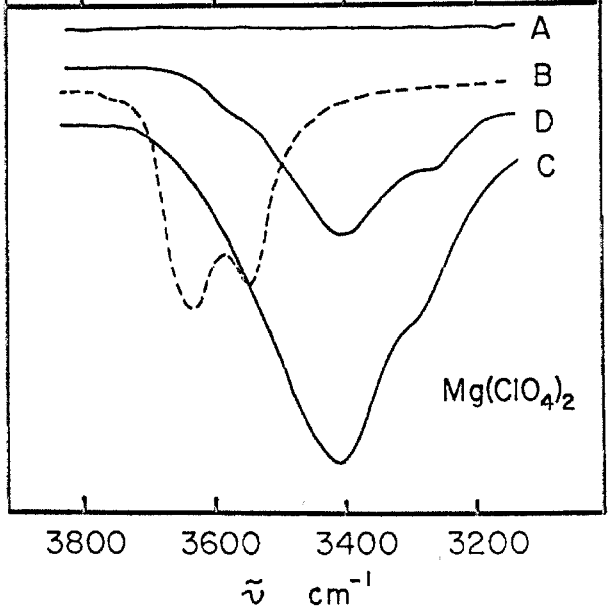


Figure 24.

Figure 25. $NaClO_4$-D_2O-CH_3CN

0.432 M $NaClO_4$
0.566 M D_2O

Figure 26. $LiClO_4$-D_2O-CH_3CN

0.217 M $LiClO_4$
0.766 M D_2O

Figure 27. $Mg(ClO_4)_2$-D_2O-CH_3CN

0.042 M $Mg(ClO_4)_2$
0.580 M D_2O

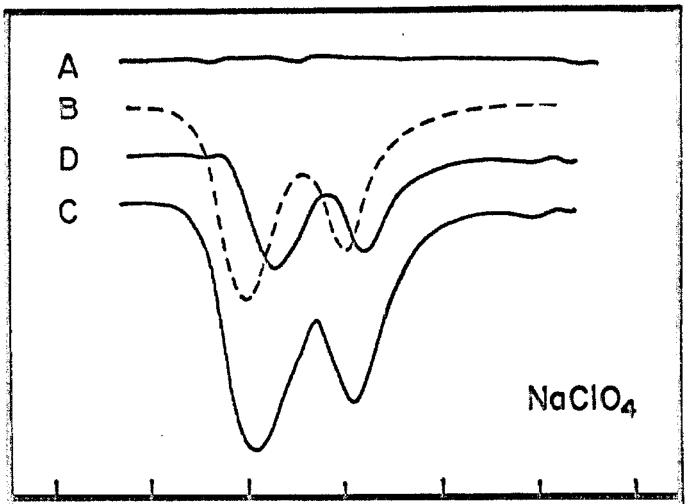


Figure 25.

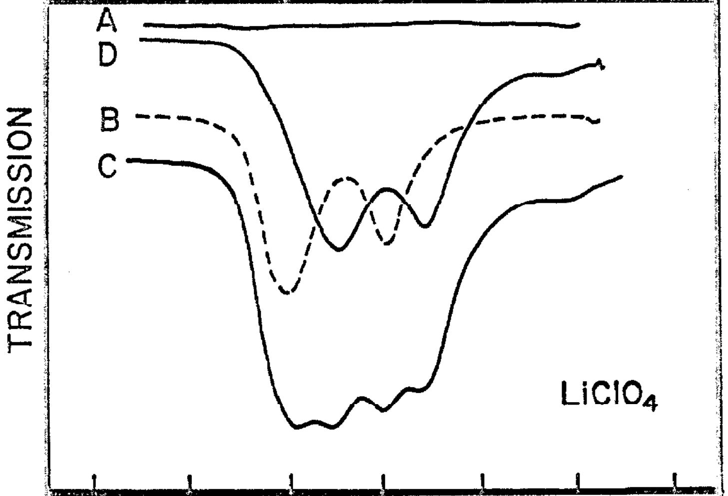


Figure 26.

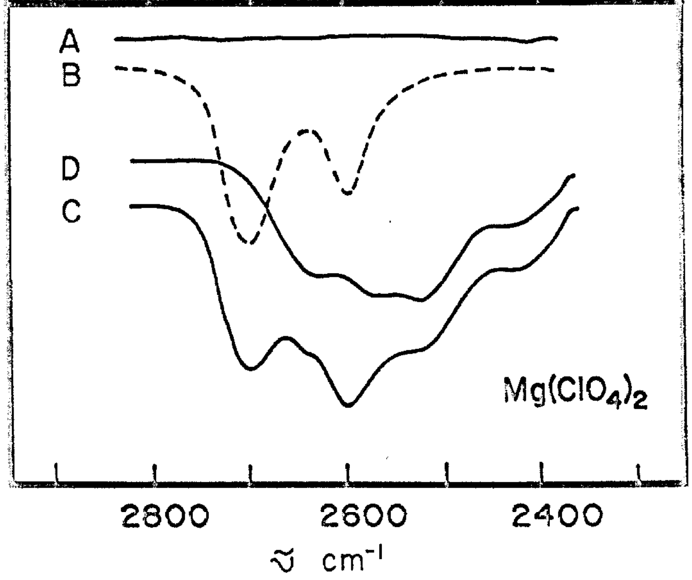


Figure 27.

TABLE 2

Observed Band Maxima (cm^{-1}) for the OH (OD) Vibrational Transition (0→1 stretch) for CH_3OD, CH_3OH, H_2O and D_2O for Several Diamagnetic Salts. (s = shoulder)

	CH_3OH	CH_3OD	H_2O	D_2O
Gas	3687	2720	3756 3656	2788 2671
CH_3CN	3542	2620	3635 3545	2700 2595
$NaClO_4$	3490	2592	3583 3510	2670 2575 2420 (s)
$LiClO_4$	3450	2565	3570 (s) 3490 3300 (s)	2645 2555 2420 (s)
$Mg(ClO_4)_2$	3330	2495	3525 (s) 3400 3300 (s)	2630 2492 2420 (s)
Bu_4NI	3380	2522	3605 3430	2670 2535
Et_4NBr	3335	2490	3615 3390	3675 2508 2400 (s)
Et_4NCl	3275	2440	3620 3356 3225 (s)	2670 2475 2400 (s)

D. ASSIGNMENT OF BAND POSITIONS

1. Assignment of Band Positions for Methanol

a. Assignment of the Anion-Methanol Complex Bands

In the case of the various anion complexes of methanol, the assignment of the complex band is definitive since only one band is involved. The band positions are I^- (3380 cm^{-1}), Br^- (3335 cm^{-1}), and Cl^- (3275 cm^{-1}).

In Figure 28, the probable structural configurations of the anion-methanol complex are summarized along with the band positions for the complex.

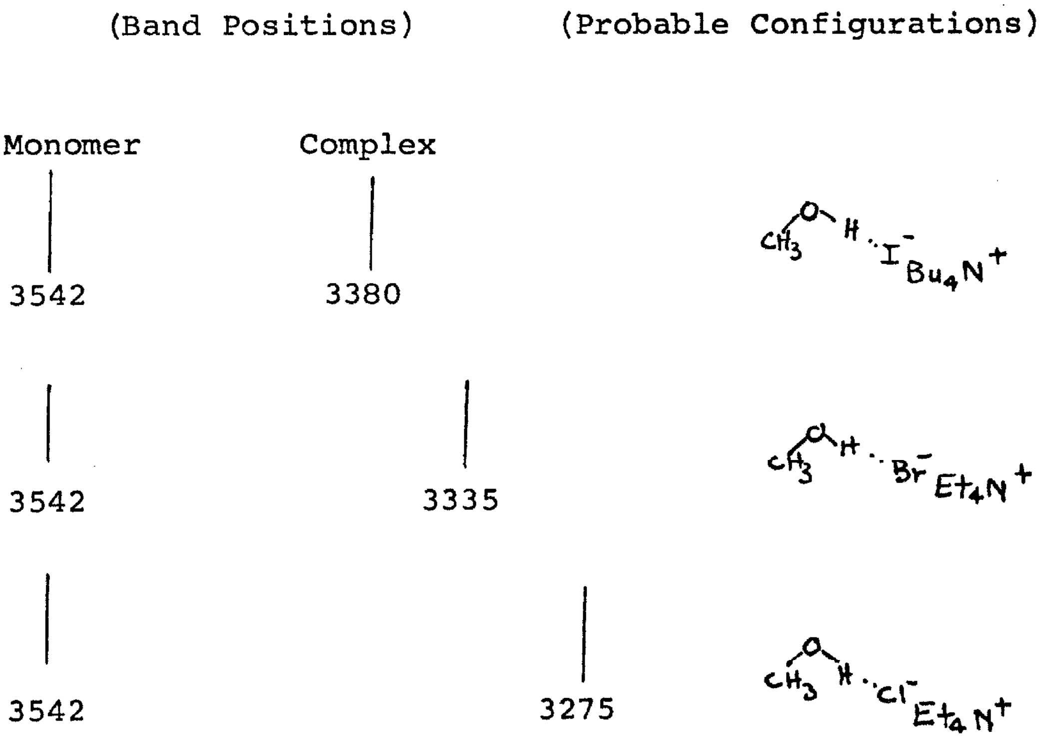


Figure 28. Anion Band Positions for CH_3OH

b. Assignment of the Cation-Methanol Complex Bands

In the case of the various cation complexes of methanol in acetonitrile, the assignment is also clear. The band positions are Na^+ (3490 cm^{-1}), Li^+ (3450 cm^{-1}), and Mg^{++} (3330 cm^{-1}).

In Figure 29, the probable structural configurations of the cation-methanol complexes are summarized along with the band positions for these complexes.

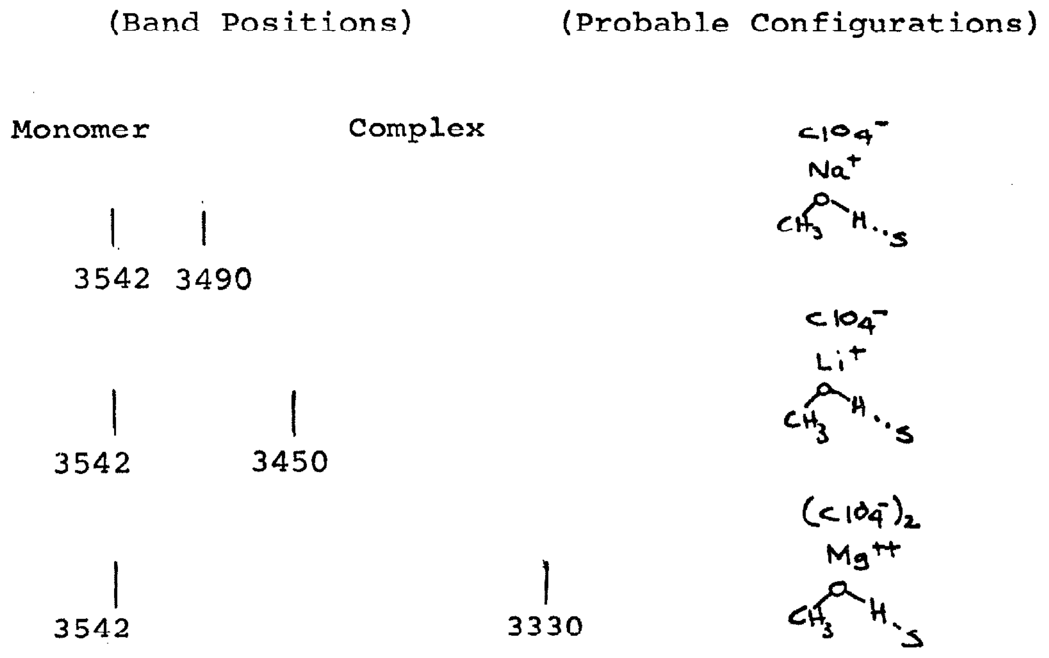


Figure 29. Cation Band Positions for Methanol

At the present time, there is no way of knowing whether an ion pair species is involved in the methanol complex. There is some evidence, however, which indicates that a contact ion pair might be involved for salts dissolved in acetonitrile. This evidence will be presented in Part III.

2. Assignment of the Various Ion Complex Bands for H_2O and D_2O in Acetonitrile

Since the spectral features of the complex bands for water and heavy water are essentially the same except for frequency differences, we shall treat these two cases simultaneously.

a. Assignment of the Anion-Water Complex Bands

In the case of water, two bands are observed in the region of the OH fundamental. For reasons which will be discussed later, we shall assign the low frequency band to the $OH \cdots X^-$ stretching vibration and the high frequency complex band to the $OH \cdots S$ (solvent) stretching vibration.

The observed frequency shifts for H_2O and D_2O are summarized in Table 3 for Br^-, Cl^-, and I^-. Figure 30 illustrates the configuration for the anion complex of water and heavy water.

It is especially important to note that in the composite spectrum it appears that only one complex band is present. The high frequency band for the anion complex of water is only slightly shifted so that it is buried underneath the antisymmetric vibration of the monomeric band. This explains the reason for the apparent appearance of only one shifted band for the anion complexes of water, an observation which appeared to be quite puzzling to Shcherba and Sukhotin (13).

For Et_4NCl, a third band appears at about 3220 cm^{-1}

TABLE 3

Observed Frequencies of the OH (OD) Stretching Vibration for Water and Heavy Water in Acetonitrile

	H_2O		D_2O	
	$\omega_{OH\cdots X^-}$	$\omega_{OH\cdots S}$	$\omega_{OD\cdots X^-}$	$\omega_{OD\cdots S}$
I^-	3430	3605	2535	2670
Br^-	3390	3615	2508	2675
Cl^-	3356	3620	2475	2670
Monomer	3545	3635	2595	2700

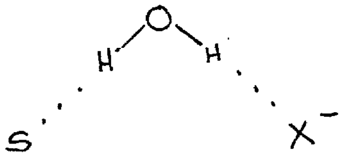
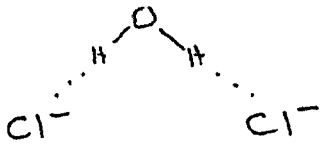


Figure 30. Anion-Water Complex

for H_2O and about 2400 for D_2O. No band near this frequency was observed for methanol. This band could arise from either $2\nu_2$ or the low frequency stretching vibration for the dichloride complex of OH_2, i.e.,



b. Assignment of the Cation-Water Complex Bands

The assignment of the complex bands due to the various cation complexes of water in acetonitrile is straightforward. The observed frequency shifts for H_2O and D_2O are summarized in Table 4 for Na^+, Li^+, and Mg^{++}. The structural configuration for the cation complex is illustrated in Figure 31.

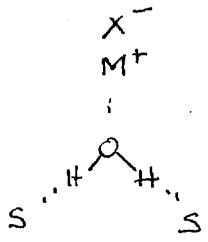


Figure 31. Cation-Water Complex

TABLE 4

Observed Frequencies of the OH (OD) Stretching Vibration for H_2O and D_2O in Acetonitrile

	H_2O		D_2O	
Ion	ω_1 (cm^{-1})	ω_3 (cm^{-1})	ω_1 (cm^{-1})	ω_3 (cm^{-1})
Na^+	3510	3583	2575	2670
Li^+	3490	3570	2555	2645
Mg^{++}	3400	3525	2492	2630
Monomer	3545	3625	2595	2700

In the course of this work, an attempt was also made to determine whether or not the bending frequency was changed upon complex formation. The spectra for some of the anion and cation complexes of water in acetonitrile are summarized in Figures 32 through 36. These spectra show that a change does occur, but these shifts are small in comparison to the shifts observed in the stretching vibration upon ion complexation.

The band maxima for water hydrogen-bonded to acetonitrile occurs at 1635 cm^{-1}. For the iodide and chloride complex of water the band maxima are 1625 cm^{-1} and 1640 cm^{-1}, respectively. For the sodium, lithium, and magnesium ion complexes of water the band maxima are 1643, 1655, and 1667 cm^{-1}, respectively. The uncertainties in the location of the band maxima are about $\pm$ 5 to 10 cm^{-1}.

These shifts can be understood in terms of a small change in the bending force constant. In the case of the anion complexes the bending force constant decreases, whereas in the case of cation complexation the bending force constant increases. We also note that changes in the stretching force constant and in the interaction constant which represents the coupling between the two stretching vibrations of water also affect the bending frequency. This change over a large range of coupling interaction constants and force constants amounts, however, to about 5 cm^{-1} at the maximum.

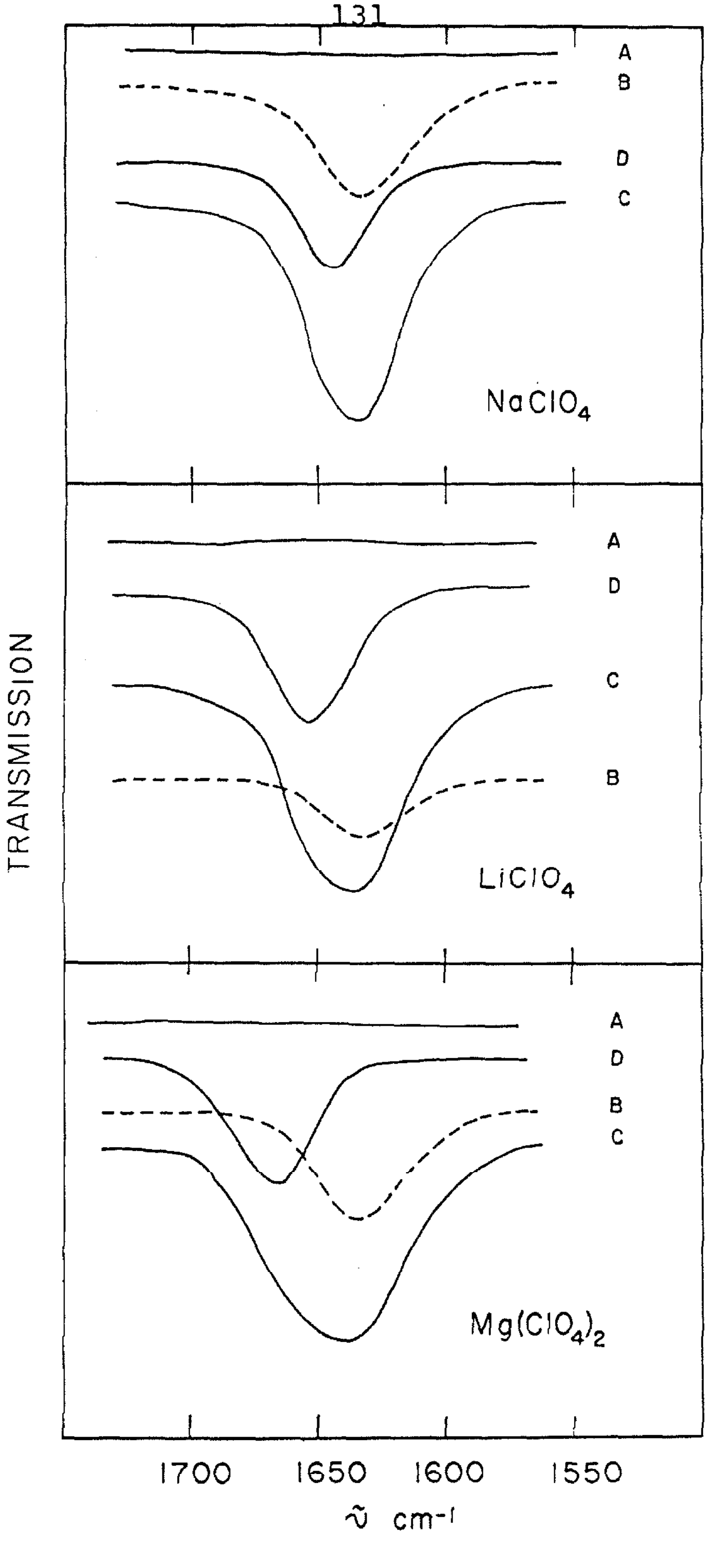


Figure 32.

Figure 33.

Figure 34.

Spectra for H_2O, solvent=CH_3CN

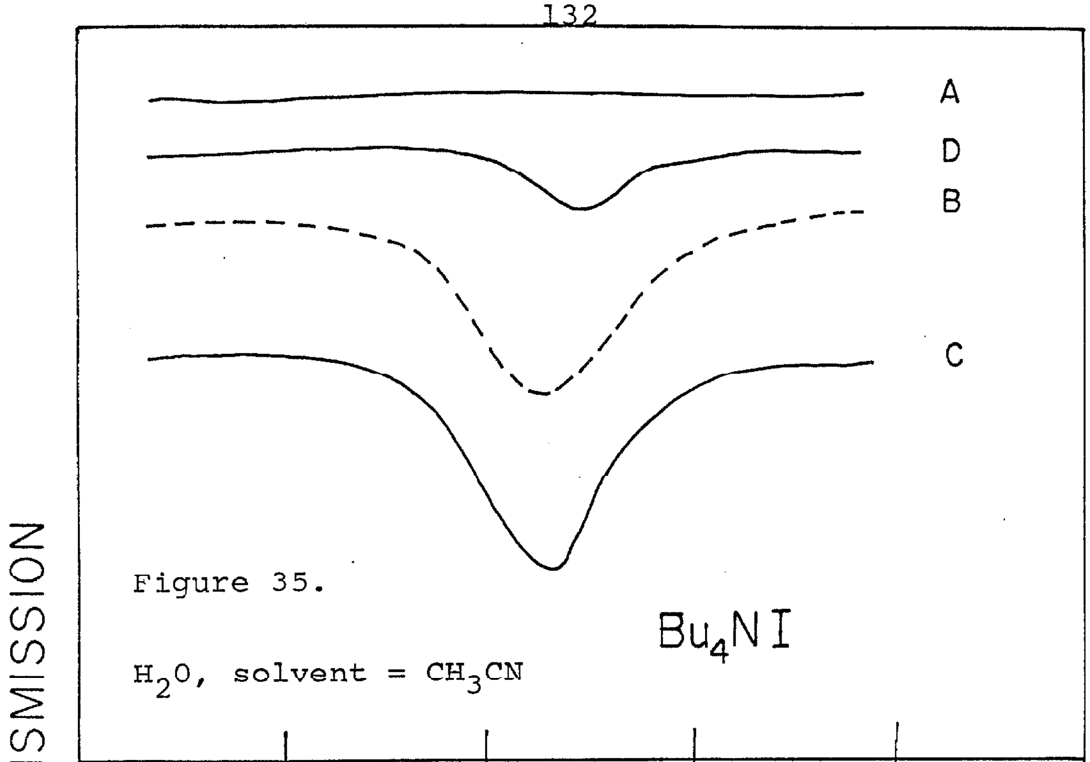


Figure 35.

H_2O, solvent = CH_3CN

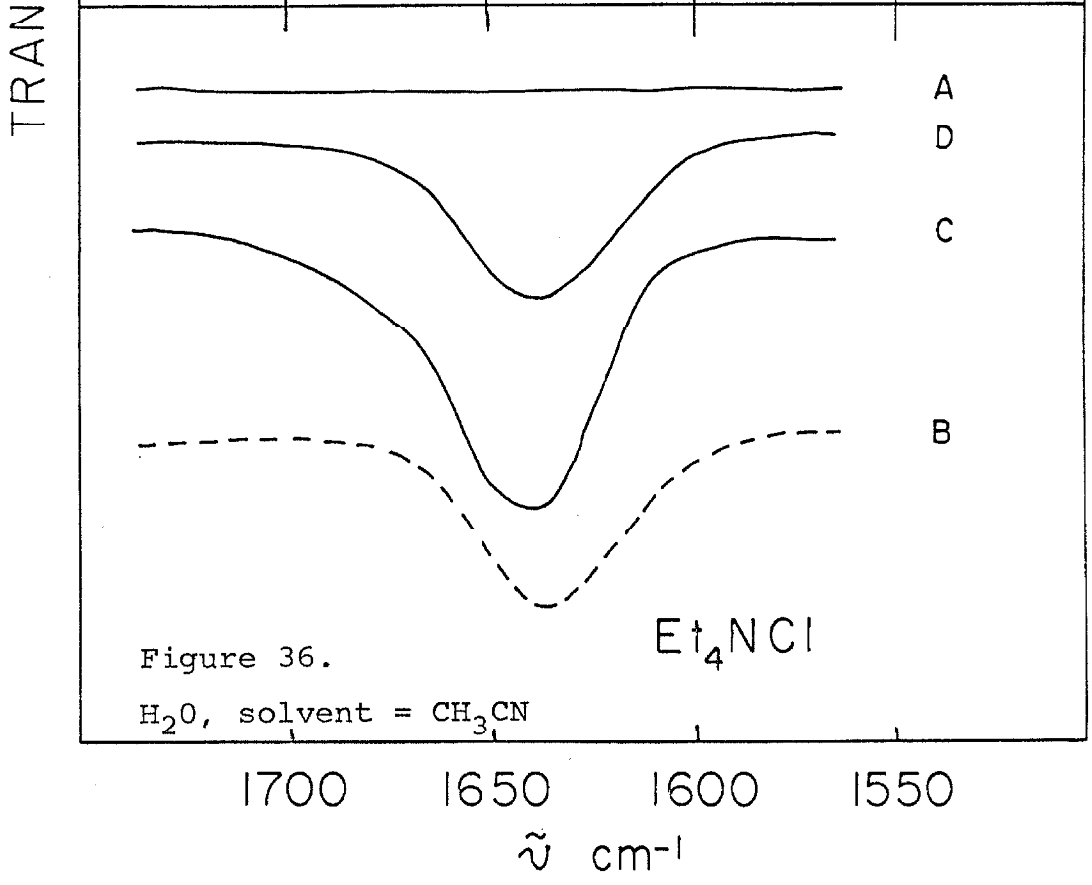


Figure 36.

H_2O, solvent = CH_3CN

E. ANALYSIS

In the previous section, assignment of band positions were made for the various ion complexes of methanol and water in acetonitrile. This information is clearly indispensable towards our understanding of the nature of the various types of complex species in salt solutions of an aprotic solvent.

Various aspects of this problem which were concerned with the assignment of complex bands, intensities and the interpretation thereof, were originally considered by Perelygin (11) and by Shcherba and Sukhotin (13). However, in view of the considerable amount of overlapping between the monomer and complex bands, the assignment and interpretations are severely handicapped.

For this reason, the extraction of detailed information concerning the effects of polarization (changes in force constant, etc.) on the hydrogen-stretching vibration could not be made. Such detailed information on the spectral changes which occur upon complex formation is clearly desirable if the factors which bring about these changes are to be understood on more quantitative grounds. In this section we report the results of a detailed analysis of the frequency shifts in the hydrogen-stretching vibration for water and methanol complexed to various ions.

Since the problem concerning the complexation of ions to molecules (such as water or methanol) is intimately related to the problem concerning hydrogen-bonding, it is instructive to consider some of the theoretical aspects which have already been developed in this area.

The study of the factors which involve hydrogen-bonding and its significance in various chemical and biological systems have been the subject of considerable investigation and review (26). A brief summary of the results which are pertinent to the present problem concerning the various ion complexes of water and methanol will be presented.

It is now well established that the infrared bands in the spectral region from 3200 cm^{-1} to 3800 cm^{-1} for water and methanol and from 2200 cm^{-1} to 2800 cm^{-1} for D_2O and CH_3OD arise from the OH and OD stretching vibrations, respectively. In the case of methanol in acetonitrile, the OH stretching vibration is characterized by a single band at 3545 cm^{-1} whose width at half height is about 100 cm^{-1} for a 0.3 molal solution. For water in acetonitrile, the OH stretching vibration is characterized by two diffuse partially overlapping bands at 3545 cm^{-1} and 3635 cm^{-1}. The band widths are about the same as for methanol. Changing the solvent has an affect on both the frequency and band width.

Several theories have been proposed in order to interpret the observed frequency shifts, band intensities, and widths for the hydrogen stretching vibration in hydrogen-bonded systems.

It is now recognized that an appropriate expression for the actual potential energy surface which describes vibrational problem in hydrogen-bonded systems is required if quantitative information on spectral changes is desired. Earlier treatments of this problem, however, have been based on various models which only roughly approximate the actual potential energy surface. In the majority of cases, the merits or limitations of the treatment are not discussed. As a result a certain amount of ambiguity still remains over the interpretation of the spectral changes effected by hydrogen-bond formation. The interpretation of spectral changes in the hydrogen-stretching vibration in systems which involve ion complexation is even less clear.

For this reason, most of the recent experimental and theoretical studies on hydrogen-bonding have been concerned with the determination of a more accurate expression for the potential energy surface.

The most detailed study of the hydrogen-stretching vibration in various hydrogen-bonded systems was recently completed by Chan and Fung (18). In this study a general highly anharmonic potential is used to describe the stretching vibration.

As shown by Chan and Fung, to a first approximation, the infrared spectra of the OH stretching vibration in hydrogen-bonded systems can be characterized by a one-dimensional potential function involving the coordinates of the hydrogen. Since the one-dimensional potential function only represents a cross section of the multidimensional potential energy surface, there are certain limitations associated with it. For example, it cannot explain the unusual band widths and intensities observed for the hydrogen-stretching vibration in hydrogen-bonded systems. A more accurate model obviously should include other interaction terms in the potential function such as those involving the couplings between the hydrogen-stretching motion with the remaining vibrational degrees of freedom. Chan and Fung felt that the coupling between the A-H stretch and the A-B stretch in the A-H···B hydrogen bond complex is more important than the other degrees of freedom and have also treated this case.

1. Nature of Anharmonicities in the Hydrogen-Stretching Vibration in Hydrogen-Bonded Systems

Despite the limitations which are inherent in the one-dimensional model, several features of the infrared spectra of a hydrogen-bonded system can be understood.

For example, the unusual spacing of the vibrational energy levels in the hydrogen-bonded complexes if one aspect of the general problem which can be understood in terms of the one-dimensional model.

When methanol is placed in a solvent such as acetonitrile, the vibrational energy levels are quite irregular. Experimentally, one band is observed in the fundamental region; however in the first overtone region two bands are observed with a separation of only 525 cm^{-1}. The next two bands are separated by 2425 cm^{-1}. The relatively close spacing of the bands in the region of the first overtone is referred to as doubling (15).

This doubling phenomena can be understood in terms of a double minimum potential function. Splittings or so-called doubling phenomena in the fundamental or overtone regions will be observed in the case of the double minimum potential depending upon the relative acidity of the proton involved in the hydrogen bond and the basicity of the proton acceptor.

The basic features of the infrared spectra of the various ion complexes of methanol are the same as those for methanol hydrogen-bonded to various solvents (such as acetone, acetonitrile, dimethylsulfoxide, etc.). Since no doubling in the fundamental region is observed this suggests that the depth of the second minima (OH···X$^-$) relative to the first minima (OH···X) is not as large as is observed in the case of carboxylic acids where doubling is observed (18). The same is true for the various cation complexes of methanol.

The double minimum potential function is clearly anharmonic. The nature of the anharmonicity is, however, of a rather unusual nature since a second minima is involved. The anharmonicity is, in this sense, quite different from the usual anharmonicities encountered in the Morse-type function.

In the case of gaseous methanol, for example, the potential for the OH stretching vibration can be characterized by an anharmonic Morse-type function. The energy levels for this type of function can be approximated by:

$$\omega_e(n+\tfrac{1}{2}) - \omega_e x_e(n+\tfrac{1}{2})^2 \tag{1}$$

where ω_e represents the stretching frequency in the absence of anharmonicity and n represents the vibrational quantum number.

It is possible to determine the first order anharmonicity term, $\omega_e X_e$, for the OH stretching vibration by fitting the observed vibrational levels to equation 3. The results obtained by fitting the 0→3 and 0→4 transitions for gaseous methanol are $\omega_e(\mathrm{OH}) = 3850\ \mathrm{cm}^{-1}$ and $\omega_e X_e(\mathrm{OH}) = 85.0\ \mathrm{cm}^{-1}$. A comparison between the observed and calculated values for the stretching vibration in methanol is summarized in Table 5.

TABLE 5

Calculated and Observed Transition Frequencies for Methanol (Gas) for $\omega_e X_e = 85.0\ \mathrm{cm}^{-1}$ and $\omega_e(\mathrm{OH}) = 3850\ \mathrm{cm}^{-1}$

Transition	$\omega_{calc.}\ (cm^{-1})$	$\omega_{OBS.}\ (cm^{-1})$	Reference
0→1	3680	3682	(27)
0→2	7190		
0→3	10530	10530	(28)
0→4	13700	13700	(29)
0→5	16700		

A value for ω_e for the deuteron-stretching vibration in CH_3OD can be obtained from:

$$\omega_e(OH) = \left[\left(\frac{m_O + m_H}{m_O + m_D}\right)\left(\frac{m_D}{m_H}\right)\right]^{\frac{1}{2}} \omega_e(OD) \qquad (2)$$

The calculated value for $\omega_e(\mathrm{OD})$ is $2802.5\ \mathrm{cm}^{-1}$. A value for $\omega_e X_e(\mathrm{OD})$ can be obtained from

$$\omega_e X_e(OD) = \left[\omega^{0\to 1}_{OBS.}(OD) - \omega_e(OD)\right]/2 \qquad (3)$$

using the reported value of $2720\ \mathrm{cm}^{-1}$ for the 0→1 fundamental for CH_3OD gas (30). The result is $\omega_e X_e(\mathrm{OD}) =$

41.25 cm^{-1}. The anharmonic contribution for the deuteron-stretching vibration is approximately one half of the anharmonic contribution for the hydrogen-stretching vibration. The actual ratio of $\omega_e x_e$(OH)/ $\omega_e x_e$(OD) is 2.06.

For comparison, the anharmonic contributions for various hydrogen-bonded complexes of methanol and HOD are summarized in Table 6. The numerical values for ω_e can be computed directly from the results obtained by Chan and Fung (18). The value for the anharmonic contribution is given by: $\Delta = \omega_e - \omega_{obs.}^{0\to 1}$. Values for ω_e(OD) were obtained using a value of 0.7279079 for the reduced mass ratio $(\mu OH/\mu OD)^{\frac{1}{2}}$. For the reduced mass we have used $\frac{1}{m_o}+\frac{1}{m_H}=\frac{1}{\mu_{OH}}$.

The results of the preceding calculations are of interest for at least two reasons: (1) The calculation shows that the anharmonicity contribution in the case of the hydrogen-bonded complexes is of the same order of magnitude as that obtained for the gas despite the fact that two completely different types of potentials are involved. Within the limitations of the one-dimensional model, the anharmonic contribution increases by about a factor of two upon complex formation; (2) The ratio of the anharmonic contribution for the OH and OD stretching vibrations is lower than what can be expected on the basis of a reduced mass dependence between ΔOH and ΔOD. In the case where higher order than quartic terms in the potential function are neglected and second-order perturbation theory is adequate in the calculation of the anharmonic contributions, the ratio of ΔOH/ ΔOD should be approximately $(\mu OD/\mu OH) \approx$ 2.

TABLE 6

	CH_3OH			CH_3OD			
	$\omega_{0\to1}^{(OH)}$	$\omega_e(OH)$	Δ_{OH}	$\omega_{0\to1}^{(OD)}$	$\omega_e(OD)$	Δ_{OD}	Δ_{OH}/Δ_{OD}
DMSO	3400	3730.2	330.2	2513	2715.2	202.2	1.63
THF	3505	3882.4	377.4	2586	2826.0	240.0	1.57
PD	3520	3890.8	370.8	2600	2832.1	232.1	1.60
CO	3525	3906.4	381.4	2615	2843.5	228.5	1.67
CN	3542	3924.9	382.9	2620	2857.0	237.0	1.62

	HOD			HOD			
	$\omega_{0\to1}^{(OH)}$	$\omega_e(OH)$	Δ_{OH}	$\omega_{0\to1}^{(OD)}$	$\omega_e(OD)$	Δ_{OD}	Δ_{OH}/Δ_{OD}
DMSO	3470	3822.5	352.5	----	2782.4	-----	----
THF	3550	3951.2	401.2	2590	2876.1	286.1	1.40
PD	3565	3976.9	411.9	2615	2894.8	279.8	1.47
CO	3580	4010.5	430.5	2630	2919.3	289.3	1.49
CN	3585	4022.3	437.3	2636	2927.9	291.9	1.50

In the case where second-order perturbation theo- is inadequate, this ratio can be calculated in a more rigorous way by the Chan-Fung treatment (18). The one-dimensional potential function for the hydrogen-stretching vibration in this treatment is expressed by:

$$V_{OH} = A_{OH} \left(X^4 + B_{OH} X^2 + C_{OH} X \right) \tag{4}$$

where the represent a displacement in dimensionless, and A, B, and C are the various parameters which describe the characteristics of the double minimum potential. The corresponding potential for the deuteron-stretching vibration is given by:

$$V_{OD} = \frac{A_{OH}}{\left(\frac{\mu_{OD}}{\mu_{OH}}\right)^{2/3}} \left(X^4 + \left(\frac{\mu_{OD}}{\mu_{OH}}\right)^{\frac{1}{3}} B_{OH} X^2 + \left(\frac{\mu_{OD}}{\mu_{OH}}\right)^{\frac{1}{2}} C_{OH} X \right) \tag{5}$$

In this case, the ratio of Δ_{OH}/Δ_{OD} can be computed for arbitrary values of the anharmonic constants in the potential function. The various vibrational energy levels can be computed for different values of B_{OH} and C_{OH} by diagonalizing the enrgy matrix using quartic oscillation functions for the basis set. The result of some calculations for methanol in acetonitrile when $(\mu_{OH}/\mu_{OD})^{-1} = 1.88733$ gave a ratio of 2.01468.

The earlier results concerning this ratio for methanol and HOD hydrogen-bonded to various solvent molecules are smaller than the calculated ratio of 2.0 by 40 and 60%, respectively. To a certain extent, the location of the band maxima can be responsible for these results.

This is particularly true for HOD since there is a problem of band overlapping between the bands of H_2O and D_2O in the region of the OH and OD absorptions for HOD. Even in this difficult case where errors can be as large as 20 or 30 cm^{-1} for the OD band, it is not possible to account for a 60% drop in this ratio. Similar arguments can be made for the methanol data. In this case, however, the location of the band maxima is easier to determine and is accurate to at least $\pm$ 5 cm^{-1}.

At this point it is important to note that the calculated values for ω_e were obtained from a method which involves the determination of the three parameters A, B, and C in equation 4 such that the band maxima of the three lowest frequency transitions observed in the infrared and near infrared is reproduced. The fitting of the various computed energy levels using the band maxima is a common procedure, but this does not necessarily imply that it is correct. In the case of a gas where discreet bands are observed for the various vibrational and rotational energy states, the frequency for the $0 \rightarrow 1$ vibrational transition, for example, can be accurately determined. In the case of the liquid, however, where broad bands are observed, the location of the $0 \rightarrow 1$ transition is not defined. The band maxima, in these cases, are usually taken to approximate the actual vibrational transition. In cases where several different types of species give rise to absorptions in the same spectral region of interest, it is clear that the band maxima do not represent any individual species but rather an "average" vibrational transition.

The uncertainties involved in the use of the band maxima for representing the vibrational transition for the hydrogen-bonded complex in solution will also affect the calculated values for ω_e and hence, the ratio of ΔOH/Δ OD.

Other factors can be expected to influence this ratio: (1) In the calculations, we have only tested the case where cubic and quartic contributions were considered. It is possible that higher order contributions in the zero-order potential function must be considered; (2) As mentioned previously, the one-dimensional model does not include couplings of the hydrogen-stretching vibration to other vibrational degrees of freedom. Since the vibrational energy levels are affected by these couplings, the omission of these additonal interaction terms in the potential function can yield erroneous results for quantities which are sensitive to small changes in the parameters which describe the actual potential energy surface.

All of these considerations are expected to be of some importance, but it is still difficult to account for the large drop in the calculated ratio of ΔOH/Δ OD for the various solvent hydrogen-bonded complexes of methanol and HOD. We conclude, therefore, that the origin of this discrepancy comes from another consideration. One other factor remains to be considered. In the Chan-Fung treatment, the potential function is given by a Taylor-series expansion. The function was chosen such that the over-all shape of the potential energy is reproduced with the least number of parameters. Since the nature of the doubling phenomena was under consideration, this expansion was naturally taken close to the maxima in the double minimum potential. Furthermore, the convergence of the variational calculations is much more rapid for this choice of origin. As a result, however, the potential function may not fit accurately the true potential in the region of the two minima. In this case, one cannot expect accurate values for the curvature or the force constant in the region of the equilibrium OH distance. Even in the case of a small deviation, a 1 to 5% error is possible for calculated values of ω_e.

In view of this consideration, it is not unreasonable that such large discrepancies were observed for the calculated values of λ OH/λ OD for the various hydrogen-bonded complexes of methanol and HOD.

Despite the similarities between systems (such as methanol or water hydrogen-bonded to acetonitrile and methanol or water complexed to various ions), the latter proves to be a more difficult case for analysis. An analysis concerning the calculation of anharmonicity and force constants generally involves knowledge of overtone frequencies. For this reason, an attempt was made to obtain the band positions in the overtone region for the various ion complexes of water and methanol in acetonitrile.

In the case of water, heavy water, and CH_3OD, no well-defined overtone bands were observed due to either solvent interference or a significant amount of band overlapping between the overtone bands of the monomer with those of the complex.

In the case of methanol (OH), a more favorable situation occurs. In the case of the chloride-methanol complex, a new band can be clearly distinguished from the monomer overtone bands. The new band appears at about 6250 cm^{-1} and can be assigned to the 0→3 transition for the $(OH\cdots Cl^{-})$ stretch. The 0→2 transition is much weaker and appears in the region of solvent interference. The 0→4 and 0→5 bands are more difficult to observe. The assignment of band positions are questionable in these cases. The results for bromide and iodide are even less obvious even for the 0→3 transition since this band is now overlapped by the 0→2 band for the methanol monomer.

Because of insufficient experimental information, it is not possible to determine a potential energy curve as was previously done for the case of methanol of HOD hydrogen-bonded to various solvents. The problem of an adequate treatment of the ion complex system is thus complicated due to the lack of experimental information.

2. Analysis of the Ion Complexes of Methanol

In order to obtain a better understanding of the effects of polarization on the hydrogen-stretching vibration in the various ion complexes of methanol, it is clear that an approach other than what was previously described must be made. In the following, we shall consider how the harmonic part of the observed frequency shift varies as the anharmonicity is changed.

As mentioned previously, the over-all anharmonic contribution to the OH and OD hydrogen or deuteron-stretching vibration for the 0 → 1 fundamental can be expressed by:

$$\Delta_{OH} = \omega_e\,(OH) - \omega_{0\rightarrow 1}\,(OH)$$

and

$$\Delta_{OD} = \omega_e\,(OD) - \omega_{0\rightarrow 1}\,(OD) \tag{6}$$

Since

$$\omega_e\,(OD) = \omega_e\,(OH)\quad(\mu OH/\mu OD)^{\frac{1}{2}} \tag{7}$$

we may express ω_e (OH) in the following manner:

$$\omega_e(OH) = \frac{\omega_{0\rightarrow 1}^{OH} - \left(\frac{\Delta_{OH}}{\Delta_{OD}}\right)\omega_{0\rightarrow 1}^{OD}}{1 - \left(\frac{\Delta_{OH}}{\Delta_{OD}}\right)\left(\frac{\mu_{OH}}{\mu_{OD}}\right)^{\frac{1}{2}}} \tag{8}$$

This expression is particularly useful for it shows how harmonic part varies as the anharmonicity is changed.

It is clear that ω_e(OH) can be extracted from the 0 → 1 fundamental for the OH and OD stretching vibrations is the ratio of ΔOH/ΔOD is known. From the previous discussion, a reasonable estimate for this ratio is 2.

As a test for the sensitivity of ω_e and hence the force constant, we have calculated ω_e from equation 8 using various values for ΔOH/ΔOD.

In Figures 37 and 38, a summary is given for the variation of ω_e as a function of ΔOH/ΔOD for the various ion complexes of methanol. Figure 37 represents the cation data and Figure 38 represents the anion data.

The results of the calculations summarized in these figures clearly shows that ω_e is extremely sensitive to small changes in ΔOH/ΔOD; especially as this ratio ap-

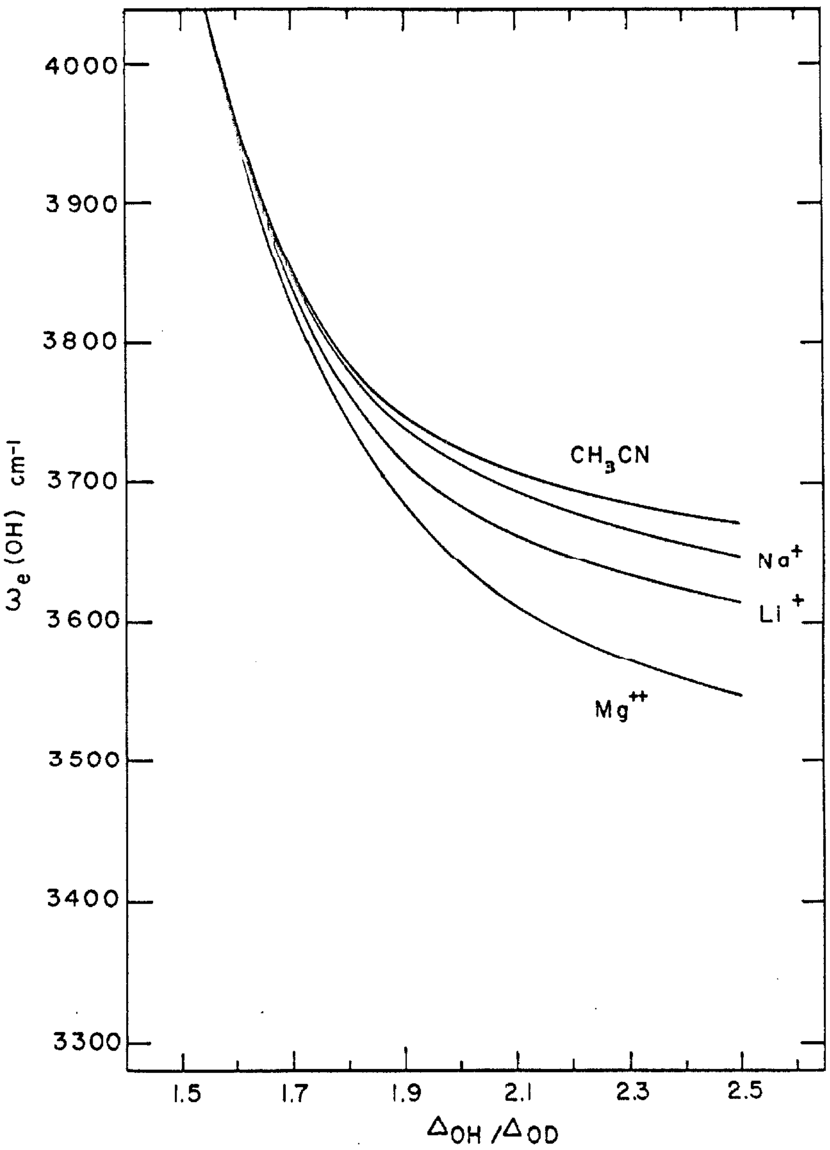


Figure 37. Plot of $\omega_e(OH) = \dfrac{\omega^{OH}_{0\to1} - \left(\frac{\Delta_{OH}}{\Delta_{OD}}\right)\omega^{OD}_{0\to1}}{1 - \left(\frac{\Delta_{OH}}{\Delta_{OD}}\right)\left(\frac{\mu_{OH}}{\mu_{OD}}\right)^{\frac{1}{2}}}$ as a Function of $\dfrac{\Delta\,OH}{\Delta\,OD}$ for Various Cation Complexes of Methanol in Acetonitrile

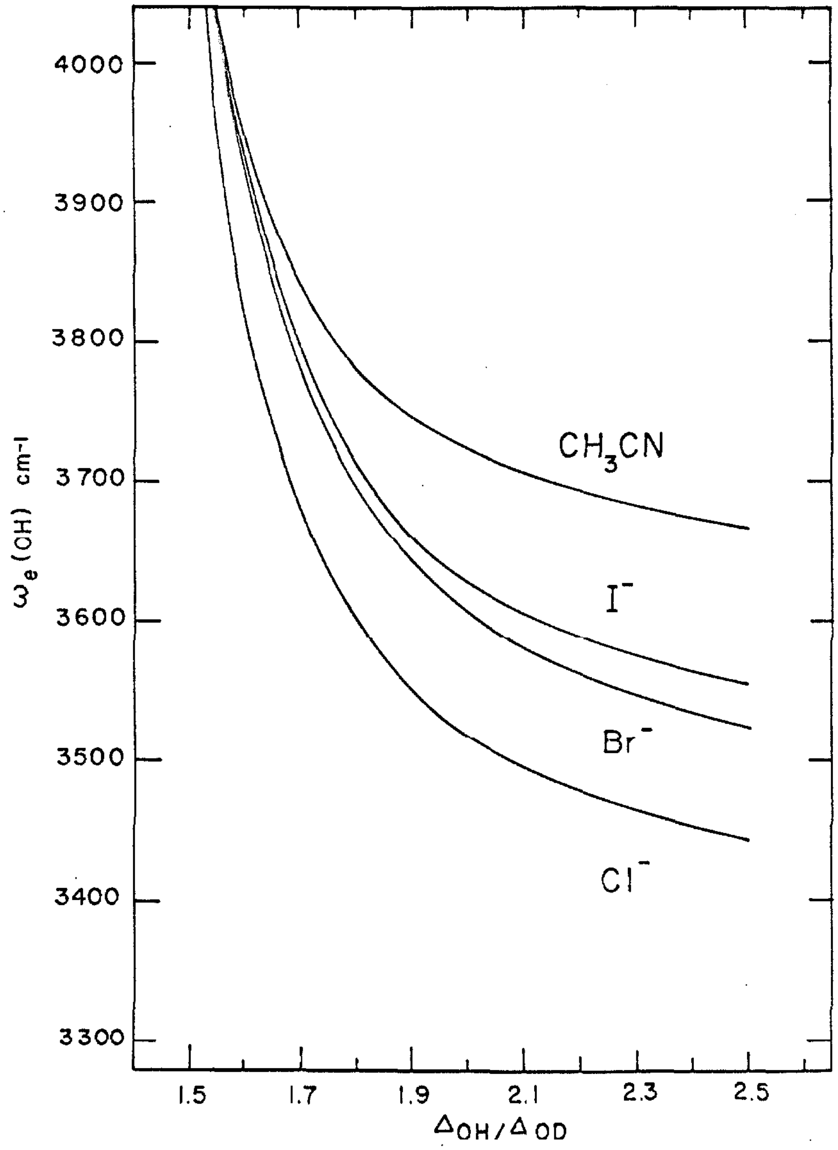


Figure 38. Plot of $\omega_e(OH) = \dfrac{\omega^{OH}_{0\rightarrow1} - \left(\frac{\Delta_{OH}}{\Delta_{OD}}\right)\omega^{OD}_{0\rightarrow1}}{1 - \left(\frac{\Delta_{OH}}{\Delta_{OD}}\right)\left(\frac{M_{OH}}{M_{OD}}\right)^{\frac{1}{2}}}$ as a Function of $\dfrac{\Delta\,OH}{\Delta\,OD}$ for Various Anion Complexes of Methanol in Acetonitrile

proaches $(\mu_{OD}/\mu_{OH})^{\frac{1}{2}}$. Furthermore, it can be seen that for ratios much smaller than 1.8, the harmonic frequency for the various cation complexes approach each other. This implies that the force constants for the various ion complexes are nearly the same, a conclusion which contradicts the earlier results obtained from the proton magnetic resonance studies. The polarization shifts for the OH proton of water and methanol clearly indicated the non-negligible distortion in the electronic environment of the proton upon complex formation. As a result of this polarization, a change in the harmonic frequency is to be anticipated.

As mentioned above, a value of 2 for this ratio is reasonable and in this region it is clear that ω_e extracted in this manner is not too sensitive to the choice of this ratio.

In Table 7, a summary of force constants is given for the various ion complexes of methanol in acetonitrile for Δ OH/Δ OD ratios of 1.9 and 2.0. Although these calculated force constants are by no means absolute, they do give us an insight into the polarization distortion which has occurred in the various ion complexes. Similar calculations were made for methanol and HOD in the various organic solvents previously discussed. The results are summarized in Table 8.

TABLE 7

CH_3OH in CH_3CN

	ω_e(OH)cm^{-1}		k(md/Å)	
(ΔOH/ΔOD)	1.9	2.0	1.9	2.0
CH_3CN	3754.3	3729.5	7.87	7.77
Na^+	3745.9	3716.4	7.84	7.72
Li^+	3716.4	3685.7	7.72	7.59
Mg^{++}	3682.5	3641.8	7.58	7.41
I^-	3659.8	3628.6	7.48	7.36
Br^-	3644.6	3608.9	7.42	7.28
Cl^-	3553.2	3521.7	7.05	6.93

TABLE 8

HOD and CH_3OH in Various Organic Solvents

CH_3OH	$\omega_e(OH)$ cm^{-1}		k (md/Å)	
$(\Delta_{OH}/\Delta_{OD})$	1.9	2.0	1.9	2.0
DMSO	3589.0	3567.2	7.20	7.11
THF	3677.0	3657.1	7.55	7.47
PD	3707.3	3685.7	7.68	7.59
CO	3745.6	3720.5	7.83	7.70
CN	3754.3	3729.6	7.87	7.77
HOD				
THF	3579.4	3576.0	7.16	7.14
PD	3664.2	3652.8	7.50	7.45
CO	3699.5	3685.7	7.65	7.59
CN	3716.2	3701.0	7.72	7.65

Although it is apparent that the force constant decreases as the ratio Δ_{OH}/Δ_{OD} is increased, it is not obvious how the anharmonicity Δ varies upon the strength of the hydrogen-bonding or ion-complexation interaction. In order to answer this question, it is necessary to know how the separate higher order anharmonic terms affect the overall anharmonic contribution.

An estimate of the separate cubic and quartic contribution to the overall anharmonic contribution can be made by using the results obtained from the Chan-Fung one-dimensional model previously discussed. Although the form of the potential used by these authors reflects the anharmonic character of the double minimum potential, it is more instructive to re-express their potential in more conventional form, *i.e.*,

$$V' = ax^4 + bx^3 + cx^2 \qquad (9)$$

where a, b, and c are the quartic, cubic, and quadratic constants, respectively. x represents the Cartesian coordinate displacement which describes the vibration along the $OH\cdots B$ axis.

These coefficients are related to the coefficients given by Fung and Chan by a translation. The coefficients are given by:

quartic constant $a = A/k^4$
cubic constant $b = 4d\ A/k^3$
quadratic constant $c = A(6d^2 + B)/k^2$

where k is defined by $(\hbar^2/8\mu A)^{\frac{1}{2}}$ and d is the translation in dimensionless space from the origin of the Chan-Fung potential to the center of the first minima.

In Table 9, values for the quartic, cubic, and quadratic constants are summarized for HOD and methanol in various organic solvents.

TABLE 9

Parameters of the Double Minimum Potential $V=ax^4+bx^3+cx^2$

<u>HOD</u>	$a(cm^{-1}/\AA^4)$	$b(cm^{-1}/\AA^3)$	$c(cm^{-1}/\AA^2)$	d
Dimethylsulfoxide	35.850	-54.174	22.186	2.5097
Tetrahydrofuran	43.175	-61.303	23.352	2.4317
<u>p</u>-Dioxane	44.780	-62.808	23.657	2.4167
Acetone	47.754	-65.178	24.058	2.3772
Acetonitrile	49.036	-66.154	24.200	2.3601
<u>CH_3OH</u>				
Dimethylsulfoxide	31.802	-49.834	20.813	2.5506
Tetrahydrofuran	39.394	-57.603	22.546	2.4663
<u>p</u>-Dioxane	38.899	-57.412	22.646	2.4844
Acetone	40.333	-58.549	22.824	2.4582
Acetonitrile	41.160	-59.424	23.043	2.4530

The results of the present calculations clearly indicate the non-negligible variation in all three constants for HOD and methanol in various base solvents.

Approximate values for the cubic and quartic contributions to the 0 → 1 fundamental can be obtained using standard second-order perturbation theory.

The energy level of the n^th vibrational state is given by:

$$W_n = h\nu(n+\tfrac{1}{2}) + \frac{3a}{4\alpha^2}(2n^2+2n+1) - \frac{b^2}{h\nu 8\alpha^3}(30n^2+30n+11) \qquad (10)$$

where n is the vibrational quantum number; a, the quartic constant; b, the cubic constant; and α is given by $(2\mu c/\hbar^2)^{\frac{1}{2}}$.

The 0 → 1 fundamental is:

$$\omega_{0\rightarrow 1} = \omega_e + 4A'a - 60b^2B' \qquad (11)$$

where $A' = \frac{3}{4}\alpha^2 hc$

and $B' = \frac{1}{8}(\hbar c)^{3/2}\omega_e\alpha^3$

b and a are expressed in units of cm^{-1}/cm^3 and cm^{-1}/cm^4, respectively. ω_e is in units of cm^{-1}.

In Table 10 values for the quadratic contribution (ω_e), the cubic contribution (K), and the quartic contribution (Q) are summarized for the 0 → 1 fundamental (OH) stretching vibration in HOD and methanol in various organic solvents.

The numerical values for ω_e can be computed directly from the results obtained from B. M. Fung (18) since $\omega_e = 2\Lambda\sqrt{6d^2+B}\,/\pi c\hbar$, where Λ is in ergs and ω_e is in cm^{-1}. The computation of the cubic and quartic contributions depend, however, on what one uses for the reduced mass for HOD and CH_3OH since both contributions depend on α .

The cubic and quartic constants summarized in Table 9 were obtained by using $1/\mu_{OH} = 1/m_H + 1/m_O$.

TABLE 10

Calculated Values for the Harmonic, Cubic, and Quartic Contributions for Methanol and HOD

$\underline{CH_3OH}$	ω_e (cm^{-1})	K (cm^{-1})	Q (cm^{-1})	$\omega_{0\to1}^{calc.}$	$\omega_{obs.}^{0\to1}$
DMSO	3730.2	-337.2	74.3	3467.3	3400
THF	3882.4	-384.0	84.9	3583.3	3505
PD	3890.8	-380.2	83.5	3594.1	3520
CO	3906.4	-387.2	85.9	3605.1	3525
CN	3924.9	-391.2	86.8	3620.5	3540

<u>HOD</u>	ω_e (cm^{-1})	K (cm^{-1})	Q (cm^{-1})	$\omega_{0\to1}^{calc.}$	$\omega_{obs.}^{0\to1}$
DMSO	3822.5	-335.2	76.8	3564.1	3470
THF	3951.2	-387.4	69.5	3653.3	3550
PD	3976.9	-396.3	89.9	3670.5	3565
CO	4010.4	-412.7	93.7	3691.5	3580
CN	4022.3	-420.2	96.2	3698.3	3585

The difference between the calculated values for the 0 → 1 transition and the observed 0 → 1 band maxima is about 3%. In this case, where higher order than quartic contributions are not considered, the separate anharmonic contributions are approximately: 10% and 2% of the harmonic contribution given by ω_e for the cubic and quartic contributions, respectively. It is important to note that the cubic contribution is negative, whereas the quartic contributions is positive. As a result, the over-all anharmonicity is a reflection of how the cubic contribution varies relative to the quartic contribution. Since a decrease in all contributions apparently occurs as the basicity of the solvent molecule is increased, it is rather difficult to determine how the actual over-all anharmonicity will be affected upon hydrogen-bonding or ion complexation.

We note that this decreasing trend in the calculated values for the cubic and quartic contributions may not reflect the actual trend. Since a translation of the origin to the first minima does not involve a new expansion about this origin, the parameters which were used to calculate the cubic and quartic contributions still reflect the fact that the expansion was taken near the maxima of the double minimum potential. For this reason, the calculated separate cubic and quartic contributions do not necessarily have to reflect the actual anharmonicity for these hydrogen-bonded systems.

The results of these calculations,however, do give us an insight into the approximate orders of magnitude of the separate higher order contributions. These results indicate that the omission of the higher order than quartic terms in the potential function is not a bad approximation.

A more realistic value for the actual anharmonic contribution for the various solvent hydrogen-bonded or ion complexes of methanol can be obtained from the results of the earlier calculations presented in Tables 7 and 8. A summary of over-all anharmonic contributions to the hydrogen-stretching vibration for the various complexes of methanol when $\Delta_{OH}/\Delta_{OD} = 2.0$ is given in Table 11.

The results summarized in Table 11 show an apparent increase in the anharmonicity as the perturbation effected by the ions is increased, whereas the anharmonicities reported for the various solvent hydrogen-bonded complexes show an irregular trend. It is possible in the latter case that an error is involved, due to the location of the band maxima for the methanol (OD) solvent complex. Since the values for the over-all anharmonicity are quite sensitive to the location of the $0 \rightarrow 1$ fundamental for both OH and OD stretching vibrations small errors in the location of the band maxima for the complex can give rise to such results. For this reason, too much emphasis should not be placed on the actual values reported. Despite the uncertainties involved, the trend observed for the anharmonic contribution for the various cation complexes is probably correct. Thus, as the force constant decreases, the anharmonicity increases.

TABLE 11

Anharmonicity Contribution for Various Methanol Complexes

$\Delta_{OH}/\Delta_{OD} = 2.0$

Complexing Group	Δ_{OH} cm^{-1}	Δ_{OD} cm^{-1}
CH_3CN (CN)	189.5	94.8
Na^+	226.4	113.2
Li^+	235.7	117.9
Mg^{++}	311.8	155.9
I^-	238.6	119.3
Br^-	273.9	137.0
Cl^-	246.7	123.4
Acetone (CO)	195.5	97.8
para Dioxane (pD)	165.7	82.9
Tetrahydrofuran (THF)	152.1	76.1
Dimethylsulfoxide (DMSO)	167.2	83.6

3. Analysis of the Frequency Shifts for the Ion Complexes of Water

In Section 2a, a description of the spectral features was given for the hydrogen-stretching vibration for some ion complexes of H_2O and D_2O in acetonitrile. It is desirable, at this point, to re-summarize briefly the experimental observations for the ion complexes of water which are to be explained in this section.

In the case of the ion complexes of methanol in acetonitrile, the $0 \rightarrow 1$ fundamental for the hydrogen-stretching vibration is characterized by a single band typical of the expected spectral features of a weakly hydrogen-bonded HYZ molecule.

In the case of the ion complexes of water in acetonitrile, however, two bands are observed in the region of the hydrogen-stretching fundamental. These bands are shifted to low frequencies by different amounts relative to the two bands observed for water in acetonitrile in the absense of salt. Two distinct cases are apparent: (1) The spectra of dilute water solutions in the presence of the perchlorate salts of Na^+, Li^+, or Mg^{++} are characterized by "approximately" equal low frequency shifts relative to the corresponding high frequency and low frequency band for water in acetonitrile. (2) The spectra of dilute water solutions in the presence of the tetraalkylammonium salts of I^-, Br^-, or Cl^- are characterized by an unequal low frequency shift relative to the two bands for water in acetonitrile. The high frequency band for the complex appears to be only slightly shifted from the high frequency band for water in acetonitrile, whereas the low frequency band of the complex shifts to low frequencies by an amount typical of the anion shifts observed for methanol.

The origin of these bands have been, in the past, a subject of some conjecture (31). It is now generally more agreed, however, that (at least for dilute solutions of water in weakly hydrogen-bonding solvents) the two bands correspond to the two hydrogen-stretching vibrations of a symmetrically hydrogen-bonded water complex. Previous authors (22) have assigned the high frequency band to the antisymmetric stretch and the low frequency counterpart to the symmetric stretch. We note, however, that a resonance interaction between the two stretching motions can occur in this case due to coupling between the two stretching vibrations. Since the separation between the two bands is dependent upon this interaction, the assignment of the two bands in terms of the symmetric and antisymmetric vibrations can be interchanged depending upon the sign and magnitude of the coupling interaction constant. The above assignment is correct for the case when the interaction constant is zero or negative. For increasing positive values, the separation between the two bands continues to decrease. The band which corresponds to the antisymmetric stretch shifts to lower frequencies whereas the band which corresponds to the symmetric stretch shifts to higher frequency. The two bands eventually cross each other for some positive interaction constant.

The extension of the preceding discussion to include ion complexes of water which are symmetrically hydrogen-bonded and complexed is straightforward. Two bands shifted relative to the monomer bands which correspond to the anti-symmetric and symmetric stretching vibrations of the ion water complex can be anticipated. Some examples of such complexes are illustrated in Figure 39.

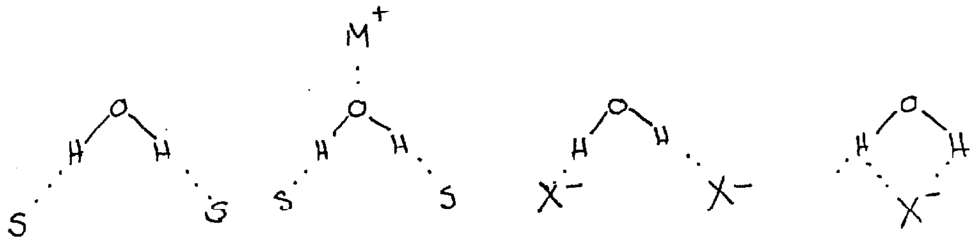


Figure 39. Some Symmetric Ion-Water Complexes

In Figure 39, S represents a solvent molecule; M^+, a cation; and X^-, an anion.

In general, not only will the stretching force constant be altered upon complexation, but the interaction constant between the two OH stretching vibrations can also be affected. A more rigorous analysis of this problem must clearly consider all of the couplings of the hydrogen-stretching vibration to the remaining vibrational degrees of freedom. As a first approximation, however, we shall consider changes in the stretching force constant and in the coupling interaction constant between the two OH stretching vibrations.

Before proceeding it is desirable at this point to consider what spectral features can be expected for an asymmetric water complex . Some examples of such complexes are illustrated in Figure 40.

For anion complexation of water, the earlier proton magnetic resonance studies indicated that only one proton of water was involved in a hydrogen bond to the anion. The other can still remain hydrogen-bonded to the solvent. In such a complex, the two hydrogen-stretching vibrations are no longer equivalent. Two bands are observed, one which characterizes the hydrogen-stretching vibration for the proton hydrogen-bonded to the anion, and the other which characterizes the hydrogen-stretching vibration for the proton hydrogen-bonded to the solvent. It is a misnomer, in this case, to characterize the anion complex bands in terms of the symmetric and antisymmetric stretching vibrations. Since the low frequency component of the anion water complex bands is shifted by an amount observed earlier for the methanol anion complexes, we have assigned this band to the $OH...X^-$ stretching vibration and the high frequency component to the $OH\cdots S$ stretching vibrations.

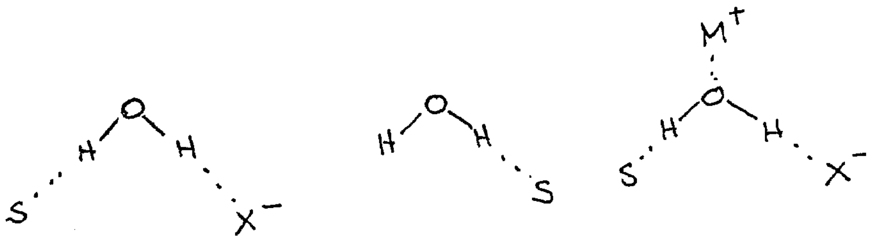


Figure 40. Some Asymmetric Ion Water Complexes

In order to express the preceding discussion for the ion complexes of water in more quantitative terms, it is desirable to discuss how the two OH stretching vibrations for the various ion complexes are affected by the quadratic terms in the potential function. Certain spectral features will become apparent in the light of this discussion.

It is clearly not possible, at the present time, to determine an expression for the actual potential energy surface which characterizes the hydrogen-stretching vibrations for these ion-water complexes. The problems involved in the determinations of parameters involved in such an expression was discussed previously for the ion complexes of methanol. These problems obviously still exist for the ion complexes of water.

Despite these difficulties, however, it is possible to obtain some insight into the overall problem even though an expression for the actual potential surface can not be obtained. The problem of the determination of an overall anharmonic contribution to the hydrogen-stretching vibration for the various ion complexes of water will be considered following this discussion.

a. General Theory

In the calculation of vibrational frequencies of polyatomic molecules, it is necessary to set up the kinetic and potential energy expressions in terms of the same set of coordinates. The particular set of coordinates is arbitrary, but an appropriate choice in the coordinates can usually lead to a reduction in the complexity of the equations which describes the motion of the various atoms in the molecule. A very useful set of coordinates has been introduced by Wilson (32). The potential and kinetic energies are expressed, in the treatment, in terms of what are referred to as internal coordinates (i.e., bond stretching, angle bending, etc.).

According to the method of Wilson, a set of internal coordinates, S_K , can be constructed from the set of Cartesian displacement coordinates by:

$$S_K = \sum_{i}^{3N} B_{Ki} \, q_i \qquad (12)$$

where the B_{Ki}'s have been determined by Wilson for angle bending, bond stretching, etc. The expression for the potential energy in the internal coordinate representation is:

$$2V = \sum_{i,j}^{3N-6} F_{ij} \, S_i \, S_j \qquad (13)$$

where the F_{ij} are the force constants associated with the various vibrations.

The vibrational kinetic energy is generally expressed in terms of the Cartesian displacement coordinates, i.e.,

$$2T = \sum_{i=1}^{3N} m_i \dot{q}_i^{2} \tag{14}$$

where N is the number of atoms, and m_i is the mass of the i^th^ atom. The kinetic energy can be expressed in terms of the internal coordinates by making the following transformation:

$$\dot{q}_i = \sum_{i=1}^{3N} (B^{-1})_{ik} \dot{S}_k \tag{15}$$

In terms of the internal coordinates,

$$\begin{aligned} 2T &= \sum_i m_i \sum_k (B^{-1})_{ik} \dot{S}_k \sum_j (B^{-1})_{ij} \dot{S}_j \\ &= \sum_i m_i \sum_{k,j} (B^{-1})_{ik} (B^{-1})_{ij} \dot{S}_k \dot{S}_j \qquad (16) \\ &= \sum_{k,j}^{3N-6} G^{-1}_{kj} \dot{S}_k \dot{S}_j \end{aligned}$$

where

$$G^{-1}_{kj} \equiv \sum_{i}^{3N} m_i \, (B^{-1})_{ik} \, (B^{-1})_{ij} \tag{17}$$

defines the well-known inverse $\underset{\sim}{G}$ matrix elements.

General expressions for the matrix elements of G for various n atom systems are given by Wilson (32). The corresponding inverse G matrix elements, G^{-1}_{ij} , can be obtained by computing the inverse of $\underset{\sim}{G}$.

Equations 13 and 16 now constitutes the necessary relationships which describe the vibrational motion of the atoms in the molecule.

Lagrange's equation in the internal coordinate representation is given by:

$$\frac{d}{dt}\left(\frac{\partial T}{\partial \dot{S}_i}\right) + \frac{\partial V}{\partial S_i} = 0 \qquad (i = 1, 2, \cdots 3N-6) \tag{18}$$

Since $$2\,\frac{\partial T}{\partial \dot{S}_i} = \sum_{j} (G^{-1}_{ij})\, \ddot{S}_j \tag{19}$$

and $$2\,\frac{\partial V}{\partial S_i} = \sum_{j} F_{ij}\, S_j \tag{20}$$

the 3N-6 equations which describe the vibrational motion are:

$$\sum_{j}^{3N-6} G^{-1}_{ij}\, \ddot{S}_j + \sum_{j}^{3N-6} F_{ij}\, S_j = 0 \tag{21}$$

The solutions are of the type $S_j = C_j \cos 2 \pi \nu t$. Substitution of these trial functions and their second derivatives leads to

$$\sum_j (F_{ij} - G^{-1}_{ij}) C_j = 0 \tag{22}$$

Non-trivial solutions will exist for the C_j's only if the determinant of the coefficients is zero, i.e.,

$$| \underset{\sim}{F} - \underset{\sim}{G}^{-1} \lambda | = 0 \tag{23}$$

where F is the matrix constructed from the potential function and the elements of $\underset{\sim}{G}^{-1}$ are obtained from the kinetic energy expression. λ defines the roots of the secular determinant and is related to the frequency ν by $4 \pi \nu^2$. It is sometimes more convenient to rewrite this secular determinant by multiplying though by $|\underset{\sim}{G}|$ to give:

$$|\underset{\sim}{G}| \, | \underset{\sim}{F} - \underset{\sim}{G}^{-1} \lambda | = | \underset{\sim}{G} (\underset{\sim}{F} - \underset{\sim}{G}^{-1} \lambda) | \; . \tag{24}$$

Therefore: $$| \underset{\sim}{G} \underset{\sim}{F} - \lambda | = 0 \tag{25}$$

Thus, if the matrix elements of $\underset{\sim}{F}$ and $\underset{\sim}{G}$ are known, it is possible to solve for the 3N-6 values of λ by solving equation 23 or 25 . These expressions constitute the "Wilson FG Method" of obtaining the various vibrational frequencies. Other methods of obtaining vibrational frequencies are known which do not involve the solving of the secular determinant. The actual computation of vibrational frequencies reported in this work was not calculated by the Wilson FG Method and will be discussed in section 3d. The expression of the vibrational problem in terms of the secular determinant given by equation 25 is, however, particularly useful in illustrating certain features which will be of interest to us.

b. The F and G Matrices for Water

For the non-linear XY molecule, the internal coordinates are expressed in terms of the two distances and the angle between the three atoms α .

Since we will be interested in two cases: (1) the case where the two XY stretching vibrations are equivalent and (2) the case where the two XY shielding vibrations are not equivalent, it is convenient to write down the expression for the potential function for the more general case where the force constants for the two XY vibrations are not equal. In this case:

$$2V = F_{ss}\Delta r_1^2 + 2F_{ss'}\Delta r_1 \Delta r_2 + F_{s's'}\Delta r_2^2 + F_{\alpha\alpha}\Delta\alpha^2 + 2F_{s\alpha}\Delta r_1 \Delta\alpha + 2F_{s'\alpha}\Delta r_2 \Delta\alpha \qquad (26)$$

where Δr_1 refers to the change in the XY distance for one bond and Δr_2 the change in the other. s and s' refer to stretch and α refers to the bend.

The $\underset{\sim}{F}$ matrix in the internal coordinate representation for this potential is:

$$\underset{\sim}{F} = \begin{pmatrix} F_{ss} & F_{ss'} & F_{s\alpha} \\ F_{s's} & F_{s's'} & F_{s'\alpha} \\ F_{s\alpha} & F_{s'\alpha} & F_{\alpha\alpha} \end{pmatrix} \tag{27}$$

General expressions for the matrix elements of $\underset{\sim}{G}$ for various n atom systems are given in (32). For the non-linear XY_2 molecule, the elements of $\underset{\sim}{G}$ in the internal coordinate representation are:

$$\begin{aligned} G_{11} = G_{22} &= \mu_X + \mu_Y \\ G_{12} = G_{21} &= \mu_X \cos\alpha \\ G_{13} = G_{31} &= -\frac{\mu_X \sin\alpha}{r_{XY}} = G_{23} = G_{32} \end{aligned} \tag{28}$$

and $$G_{33} = \left\{ \mu_Y + 2\mu_X (1 - \cos\alpha) \right\} / r_{XY}^2$$

In the case where the two XY stretching vibrations are equivalent, it is useful to define a set of symmetry coordinates given by:

$$S_1 = \frac{1}{\sqrt{2}}(\Delta r_1 + \Delta r_2) \qquad \text{Symmetric Stretch}$$

$$S_2 = \Delta\alpha \qquad \text{Bend} \qquad (29)$$

$$S_3 = \frac{1}{\sqrt{2}}(\Delta r_1 - \Delta r_2) \qquad \text{Antisymmetric Stretch}$$

since this choice of coordinates allows the secular determinant to be factored into two determinants of lower order. In terms of the symmetry coordinates, the potential function is given by:

$$\begin{aligned} 2V = {} & F_{ss}(S_1^2 + 2S_1S_3 + S_3^2)/2 + F_{ss'}(S_1^2 - S_3^2) \\ & + F_{\alpha\alpha}S_2^2 + F_{s's'}(S_1^2 - 2S_1S_3 + S_3^2)/2 \\ & + \sqrt{2}\,F_{s\alpha}(S_1S_2 + S_3S_2) + \sqrt{2}\,F_{s'\alpha}(S_1S_2 - S_3S_2) \end{aligned} \qquad (30)$$

The $\underset{\sim}{F}$ matrix in the symmetry coordinate representation is

$$\underset{\sim}{F} = \begin{pmatrix} \left(\frac{F_{ss}}{2} + F_{ss'} + \frac{F_{s's'}}{2}\right) & \frac{\sqrt{2}}{2}(F_{s\alpha} + F_{s'\alpha}) & \frac{1}{2}(F_{ss} - F_{s's'}) \\ \frac{\sqrt{2}}{2}(F_{s\alpha} + F_{s'\alpha}) & F_{\alpha\alpha} & \frac{\sqrt{2}}{2}(F_{s\alpha} - F_{\alpha'\alpha}) \\ \frac{1}{2}(F_{ss} - F_{s's'}) & \frac{\sqrt{2}}{2}(F_{s\alpha} - F_{s'\alpha}) & \left(\frac{F_{ss}}{2} - F_{ss'} + \frac{F_{s's'}}{2}\right) \end{pmatrix} \qquad (31)$$

For water $F_{ss} = F_{s's'}$ and $F_{s\alpha} = F_{s'\alpha}$ so that

$$\underset{\sim}{F} = \begin{pmatrix} F_{ss} + F_{ss'} & \sqrt{2}\; F_{s\alpha} & 0 \\ \sqrt{2}\; F_{s\alpha} & F_{\alpha\alpha} & 0 \\ 0 & 0 & F_{ss} - F_{ss'} \end{pmatrix} \qquad (32)$$

The corresponding G matrix is given approximately by:

$$\underset{\sim}{G} = \begin{pmatrix} G_{11} + G_{12} & \sqrt{2}\; G_{13} & 0 \\ \sqrt{2}\; G_{13} & G_{33} & 0 \\ 0 & 0 & G_{11} - G_{12} \end{pmatrix} \qquad (33)$$

We shall now discuss the results observed for the various ion water complexes in terms of the above results.

c. Effect of Symmetry on the Spectral Features for the Various Ion Complex of Water

(i) C_{2v} Symmetry (Cation Shifts)

In the case of the complexation of water to various hydrogen-bonding agents or to cations where the molecule may still retain C_{2v} symmetry, the form of the $\underset{\sim}{F}$ matrix is conveniently expressed by equation 32. For a symmetrically hydrogen-bonded water complex the secular determinant in the symmetry coordinate representation can be approximated by:

$$\begin{vmatrix} (G_{11}+G_{12})(F_{ss}+F_{ss'})-\lambda & \sqrt{2}\,G_{13}\,F_{\alpha\alpha} & 0 \\ \sqrt{2}\,G_{13}\,F_{ss} & F_{\alpha\alpha}G_{33}-\lambda & 0 \\ 0 & 0 & (F_{ss}-F_{ss'})(G_{11}-G_{12})-\lambda \end{vmatrix} \simeq 0 \tag{34}$$

since G_{13} is small compared to $(G_{11}+G_{12})\cdot G_{33}$, the symmetric stretching and bending frequencies are given approximately by:

$$4\pi^2\omega_1^2 \simeq (F_{ss}+F_{ss'})(G_{11}+G_{12}) \quad \text{Symmetric Stretch}$$

$$4\pi^2\omega_2^2 \simeq F_{\alpha\alpha}G_{33} \quad \text{Bend} \tag{35}$$

The antisymmetric stretch is

$$4\pi^2\omega_3^2 \simeq (F_{ss}-F_{ss'})(G_{11}-G_{12}) \tag{36}$$

Since G_{12} and $F_{ss'}$ are negative quantities for H_2O (or D_2O), the antisymmetric stretch is expected to be at higher frequencies relative to the symmetric stretch. The separation between the two frequencies, however, varies depending upon the magnitude of $F_{ss'}$. As $F_{ss'}$ becomes larger, i.e., more negative, the separation ($\omega_3 - \omega_1$) increases.

As the nature of the complexing group is varied, a change in the values of F_{ss}, $F_{ss'}$, $F_{\alpha s}$ and $F_{\alpha\alpha}$ can be expected. The changes which occur upon ion complexation can be understood as follows: Let $F_{ss} = F_{ss}^{o} + \Delta F_{ss}$ represent the force constant for the OH vibration in the symmetric ion water complex where F_{ss}^{o} represents the force constant for the symmetric hydrogen-bonded monomer and where ΔF_{ss} denotes the change in the force constant upon ion complexation. In this case, the symmetric and antisymmetric stretching frequencies are given by:

$$4\pi^2 \nu_1^2 \approx (F_{ss}^{o} + F_{ss'} + \Delta F_{ss})(G_{11} + G_{12})$$

and

$$4\pi^2 \omega_3^2 \approx (F_{ss}^{o} - F_{ss'} + \Delta F_{ss})(G_{11} - G_{12}) \qquad (37)$$

Since the change in $F_{ss'}$ is expected to be small the overall frequency shift for the two stretching vibrations is given by:

$$4\pi^2(\omega_1^2 - \omega_1^{o\,2}) = \Delta F_{ss}\,(G_{11} + G_{12})$$

and

$$4\pi^2(\omega_3^2 - \omega_3^{o\,2}) = \Delta F_{ss}\,(G_{11} - G_{12}) \qquad (38)$$

Thus, in the case where ΔF_{ss} is negative both stretching vibrations are shifted to lower frequencies relative to the hydrogen-bonded monomer by approximately equal amounts.

Experimentally, this appears to be the case observed for the various cation complexes of water in acetonitrile.

The preceding discussion applies to D_2O as well as for H_2O. There are, however, some differences in the spectral features which are worth noting: (1) The separation between ω_3 and ω_1 for D_2O is slightly larger than for H_2O. The reason for this expected observation is that

$$\frac{(\omega_3-\omega_1)(H_2O)}{(\omega_3-\omega_1)(D_2O)} \approx \left(\frac{G_{11}(D_2O)}{G_{11}(H_2O)}\right)^{\frac{1}{2}} \tag{39}$$

In the case of D_2O, G_{11} is smaller than G_{11} for H_2O so that $(\omega_3-\omega_1)$ H_2O is less than $(\omega_3-\omega_1)$ D_2O; (2) The observed band widths for both vibrations in the case of D_2O are approximately 50% of those for H_2O presumably because of smaller vibrational coupling between the donor and acceptor stretching vibrations (18). For these reasons, there is less band overlapping between the two stretching vibrations. The quality of the experimental data for D_2O, as a consequence, is better than for H_2O.

(ii) C_s Symmetry (Anion Shifts)

For an asymmetric water molecule complex, the complex no longer has C_{2v} Symmetry. If we let the force constant for the $\underline{O}H\cdots X^-$ stretch be F_{ss} and the force constant for the $\underline{O}H\cdots S$ stretch be $F_{s's'}$ the $\underset{\sim}{F}$ matrix in the symmetry coordinate representation is

$$\underset{\sim}{F} = \begin{pmatrix} F_{s's'}+F_{ss'}+\frac{\Delta F}{2} & \sqrt{2}\,F_{s\alpha} & \frac{\Delta F}{2} \\ \sqrt{2}\,F_{s\alpha} & F_{\alpha\alpha} & 0 \\ 0 & 0 & F_{s's'}-F_{ss'}+\frac{\Delta F}{2} \end{pmatrix} \tag{40}$$

where we have let $F_{ss} = F_{s's'} + \Delta F$.

Since the matrix elements involving $F_{s\alpha}$ and G_{13} are small compared to the other terms, the $\underset{\sim}{F}\underset{\sim}{G}$ matrix is approximately:

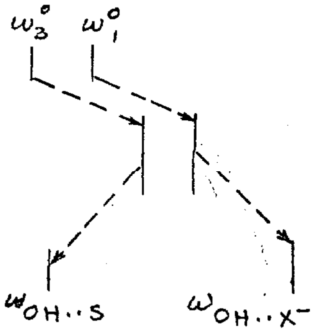
$$\underset{\sim}{F}\underset{\sim}{G} \simeq \begin{pmatrix} \left(F_{s's'} + F_{ss'} + \frac{\Delta F}{2}\right)(G_{11} + G_{12}) & 0 & \frac{\Delta F}{2}(G_{11} - G_{12}) \\ 0 & F_{\alpha\alpha} G_{33} & 0 \\ \frac{\Delta F}{2}(G_{11} + G_{12}) & 0 & \left(F_{s's'} - F_{ss'} + \frac{\Delta F}{2}\right)(G_{11} - G_{12}) \end{pmatrix} \tag{41}$$

The secular determinant breaks into two blocks so that we can consider the effect on the two stretching vibrations from:

$$(\underset{\sim}{F}\underset{\sim}{G})' = \begin{pmatrix} \left(F_{s's'} + F_{ss'} + \frac{\Delta F}{2}\right)(G_{11} + G_{12}) & \frac{\Delta F}{2}(G_{11} - G_{12}) \\ \frac{\Delta F}{2}(G_{11} + G_{12}) & \left(F_{s's'} - F_{ss'} + \frac{\Delta F}{2}\right)(G_{11} - G_{12}) \end{pmatrix} \tag{42}$$

To first order, the roots of the $(\underset{\sim}{F}\underset{\sim}{G})'$ matrix are given by the elements on the principal diagonal; however, in general for our problem the off-diagonal elements are comparable to the difference between the two diagonal elements so that the two states become essentially scrambled.

In Figure 41, we have illustrated the importance of taking into consideration the off-diagonal elements in the FG' matrix.



(off-diagonal elements = ODE)

ODE small compared to the difference between the diagonal elements.

ODE not small compared to the difference between the diagonal elements.

Figure 41. Influence of $\Delta F(G_{11} \pm G_{12})$ on the Two Stretching Vibrations for an Asymmetric Water Complex

For a decrease in force constant (i.e., $\Delta F < 0$), the simple theory predicts that the two bands are shifted to lower frequencies approximately equally to first order. If the off-diagonal elements are included, one root moves to lower frequencies while the other shifts towards . The magnitude of this "repulsion" depends upon the ratio of the off-diagonal elements to the difference between the diagonal elements and hence should increase as ΔF increases. In the limit where ΔF is very large, the higher frequency band should equal approximately ω_3^o .

Clearly, this is one way of looking at the problem for our present case. We could and perhaps should have discussed our observations in terms of the FG matrix in the internal coordinate representation instead of the symmetry coordinate representation. As expected, as $(\Delta F(G_{11} \pm G_{12}))^{\frac{1}{2}}$ becomes much larger than the frequency difference between ω_3^o and ω_1^o , the interaction between the two stretching motions can be ignored and hence the frequencies obtained by the diagonal elements of the FG matrix corresponds simply to the pure stretching motion of the OH··S and

OH··X⁻ vibrations.

It is clear that in the case where the complex has C_s symmetry only one band will appear to move if ΔF is large. The experimental observations concerning the anion-water shifts are in agreement with the preceding discussion. The results of the observed frequency shifts relative to the hydrogen-bonded monomer of water for the various anion complexes of H_2O and D_2O are compared in Table 12.

TABLE 12

Shifts in cm^{-1} for H_2O and D_2O Relative to the Monomer Hydrogen-bonded in Solvent

	H_2O		D_2O	
	OH··S	OH··X⁻	OD··S	OD··X⁻
I⁻	30	100	33	60
Br⁻	20	155	25	87
Cl⁻	15	189	30	120
CH_3CN	0	0	0	0

d. Calculation of Frequency Shifts and Force Constants for the Ion Complexes of Water

The frequencies for the two stretches for the various ion complexes of water were made using the normal coordinate analysis program discussed below. This program was written by S. I. Chan.

In terms of the column matrices, $\underset{\sim}{S}$ and $\dot{\underset{\sim}{S}}$ (made up of the internal coordinates and their time derivatives), the kinetic and potential energies are:

$$2T = \dot{\underset{\sim}{S}}^{+}\ \underset{\sim}{G}^{-1}\ \dot{\underset{\sim}{S}} \tag{43}$$

and

$$2V = \underset{\sim}{S}^{+}\ \underset{\sim}{F}\ \underset{\sim}{S} \tag{44}$$

where $\underset{\sim}{S}^{+}$ is the conjugate transpose matrix of $\underset{\sim}{S}$; $\underset{\sim}{G}^{-1}$, the inverse to matrix; and $\underset{\sim}{F}$, the force constant matrix in the internal coordinate representation.

The normal coordinate (column matrix $\underset{\sim}{Q}$) are related to the internal coordinates by a linear transformation

$$\underset{\sim}{S} = \underset{\sim}{L}\ \underset{\sim}{Q} \text{ and } \underset{\sim}{S}^{+} = \underset{\sim}{Q}^{+}\ \underset{\sim}{L}^{+} \tag{45}$$

In the normal coordinate representation

$$2T = \dot{\underset{\sim}{Q}}^{+}\ \underset{\sim}{E}\ \dot{\underset{\sim}{Q}} \tag{46}$$

and

$$2V = \underset{\sim}{Q}^{+}\ \underset{\sim}{\lambda}\ \underset{\sim}{Q} \tag{47}$$

where $\lambda_{ij} = \lambda_i \delta_{ij}$; $\lambda_i = 4\pi^2 \omega_i{}^2$ and $E_{ij} = \delta_{ij}$.

Upon substitution into equations 46 and 47 we obtain:

$$2T = \dot{\underset{\sim}{Q}}^{+}\ \dot{\underset{\sim}{L}}^{+}\ \underset{\sim}{G}^{-1}\ \dot{\underset{\sim}{L}}\ \dot{\underset{\sim}{Q}} \tag{48}$$

and

$$2V = \underset{\sim}{Q}^{+}\ \underset{\sim}{L}^{+}\ \underset{\sim}{F}\ \underset{\sim}{L}\ \underset{\sim}{Q} \tag{49}$$

We therefore seek a transformation matrix $\underset{\sim}{L}$, such that:

$$\underset{\sim}{L}^{+}\ \underset{\sim}{G}^{-1}\ \underset{\sim}{L} = \underset{\sim}{E} \tag{50}$$

and

$$\underset{\sim}{L}^{+}\ \underset{\sim}{F}\ \underset{\sim}{L} = \underset{\sim}{\lambda} \text{ (diagonal)} \tag{51}$$

To do this, we define a unitary transformation $\mathbf{T}$ ($\mathbf{T}^{+} = \mathbf{T}^{-1}$) which diagonalizes the inverse G matrix, *i.e.*,

$$\mathbf{T}^{-1}\,\mathbf{G}^{-1}\,\mathbf{T} = \mathbf{C} \text{ (diagonal)} \qquad (52)$$

The $\mathbf{C}$ matrix can then be reduced to the unit matrix by the transformation:

$$\mathbf{D}\,\mathbf{T}^{-1}\,\mathbf{G}^{-1}\,\mathbf{T}\,\mathbf{D} = \mathbf{E} \qquad (53)$$

where

$$\mathbf{D} = \begin{pmatrix} \frac{1}{c_{11}^{1/2}} & & 0 \\ & \frac{1}{c_{22}^{\frac{1}{2}}} \ddots & \\ 0 & & \frac{1}{c_{nn}^{\frac{1}{2}}} \end{pmatrix} \qquad (54)$$

equation 50 is now satisfied, but this Afine transformation in general does not reduce the transformed $\mathbf{F}$ matrix to diagonal form. We seek, therefore, another unitary transformation $\mathbf{M}$ such that $\mathbf{F}$ becomes diagonal, *i.e.*,

$$\mathbf{M}^{-1}\,\mathbf{D}\mathbf{T}^{-1}\,\mathbf{F}\,\mathbf{T}\,\mathbf{D}\,\mathbf{M} = \boldsymbol{\lambda} \text{ (diagonal)} \qquad (55)$$

The $\mathbf{G}^{-1}$ matrix is unchanged under this transformation since

$$\mathbf{M}^{-1}\,\mathbf{D}\,\mathbf{T}^{-1}\,\mathbf{G}^{-1}\,\mathbf{T}\,\mathbf{D}\,\mathbf{M} = \mathbf{M}^{-1}\,\mathbf{E}\,\mathbf{M} = \mathbf{E} \qquad (56)$$

The transformation which satisfies equations 50 and 51 is then given by:

$$\mathbf{L} = \mathbf{T}\,\mathbf{D}\,\mathbf{M} \qquad (57)$$

and

$$\mathbf{L}^{+} = \mathbf{M}^{-1}\,\mathbf{D}\,\mathbf{T}^{-1} \qquad (58)$$

The normal coordinate can be obtained from:

$$\underset{\sim}{Q} = \underset{\sim}{L}^{-1} \underset{\sim}{S} \tag{59}$$

where

$$\underset{\sim}{L}^{-1} = \underset{\sim}{L}^{+} \underset{\sim}{G}^{-1} \tag{60}$$

A preliminary calculation on water was made using the known force constants for water (gas) obtained from the work of Benedict, Gailar, and Plyler (33).

The G matrix elements used in the calculations were computed using:

$$m_H = 1.6733400 \times 10^{-23} \text{ gm.}$$

$$m_D = 3.3441199 \times 10^{-23} \text{ gm.}$$

$$m_O = 2.6557299 \times 10^{-22} \text{ gm.}$$

and

$$\alpha = 104.5^{\circ}$$

The numerical values for the matrix elements of F and G for H_2O and D_2O are summarized in Table 13.

In order to obtain information on frequency shifts for water effected by ion complexation, it is desirable to know how the stretching and bending vibrations are affected by changes in the various force constants. Some insight into the problem of frequency shifts in the hydrogen-stretching vibration can be obtained by examining the variation in frequency effected by changes on the stretching force constant, F_{ss}, and the interaction constant, $F_{ss'}$.

In the cation complexes of water, the two hydrogen-stretching vibrations are equivalent so that $F_{ss} = F_{s's'}$.

TABLE 13

Matrix Elements of F and G for H_2O and D_2O

A. F Matrix for H_2O and D_2O (F in mdynes/Å)

$F_{ss} = F_{ss'} = 8.82541$

$F_{s's} = F_{ss'} = -0.10042$

$F_{s\alpha} = F_{\alpha s} = 0.252345/r$

$F_{s'\alpha} = F_{\alpha s'} = F_{s\alpha}$

$F_{\alpha\alpha} = 0.76814/r^2$

B. G Matrix for H_2O and D_2O (G in $gm^{-1} \times 10^{23}$)

	H_2O	D_2O
$G_{11} = G_{22}$	6.3526160	3.3668676
$G_{12} = G_{21}$	-0.94384594	-0.94384594
$G_{13} = G_{31}$	-3.6452124/r	-3.6452124/r
$G_{32} = G_{32}$	-3.6452124/r	-3.6452124/r
G_{33}	$0.1289400/r^2$	$0.0692250/r^2$

A series of calculations were made to study how the frequency associated with the symmetric and antisymmetric vibrations of water are affected by changes in F_{ss} and $F_{ss'}$. In the calculations, we have kept $F_{ss'}$ constant and varied F_{ss} over a range of 7.5 to 10.0 mdynes/Å. Two sets of calculations were made; one for $F_{ss'} = -0.1004$ and another for $F_{ss'} = 0.09$ md/Å. The results are summarized in Figure 42. It is apparent that such small changes in the interaction constant have a negligible affect on the stretching vibrations. The large shifts in frequency are clearly associated with changes in the stretching force constant F_{ss}. For $F_{s\alpha}$ and $F_{\alpha\alpha}$ we have used the values reported by BGP (33).

In an asymmetric anion complex of water, the two OH stretching vibrations are no longer equivalent so that $F_{ss} \neq F_{s's'}$. As before, we shall let $F_{ss} = F_{OH\cdots X^-}$ represent the force constant associated with the $OH\cdot\cdot X^-$ vibration and $F_{s's'} = F_{OH\cdot\cdot S}$ represent the force constant associated with the OH··S stretching vibration. The variation in the stretching frequencies as a function of the $F_{OH\cdot\cdot X^-}$ stretching force constant for $F_{ss'} = -0.1, -0.06$ and 0 mdynes/Å is illustrated in Figure 43 for the case where $F_{OH\cdots S}$ is 9.1 md/Å. As in the case of the cation complexes, the most significant changes in frequency are clearly effected by changes in the $F_{OH\cdot\cdot X^-}$ stretching force constant. The changes in $F_{ss'}$ result in a much smaller variation in frequency but are significant in the sense that the separation between the two stretches are affected by this constant. The calculated separation between the

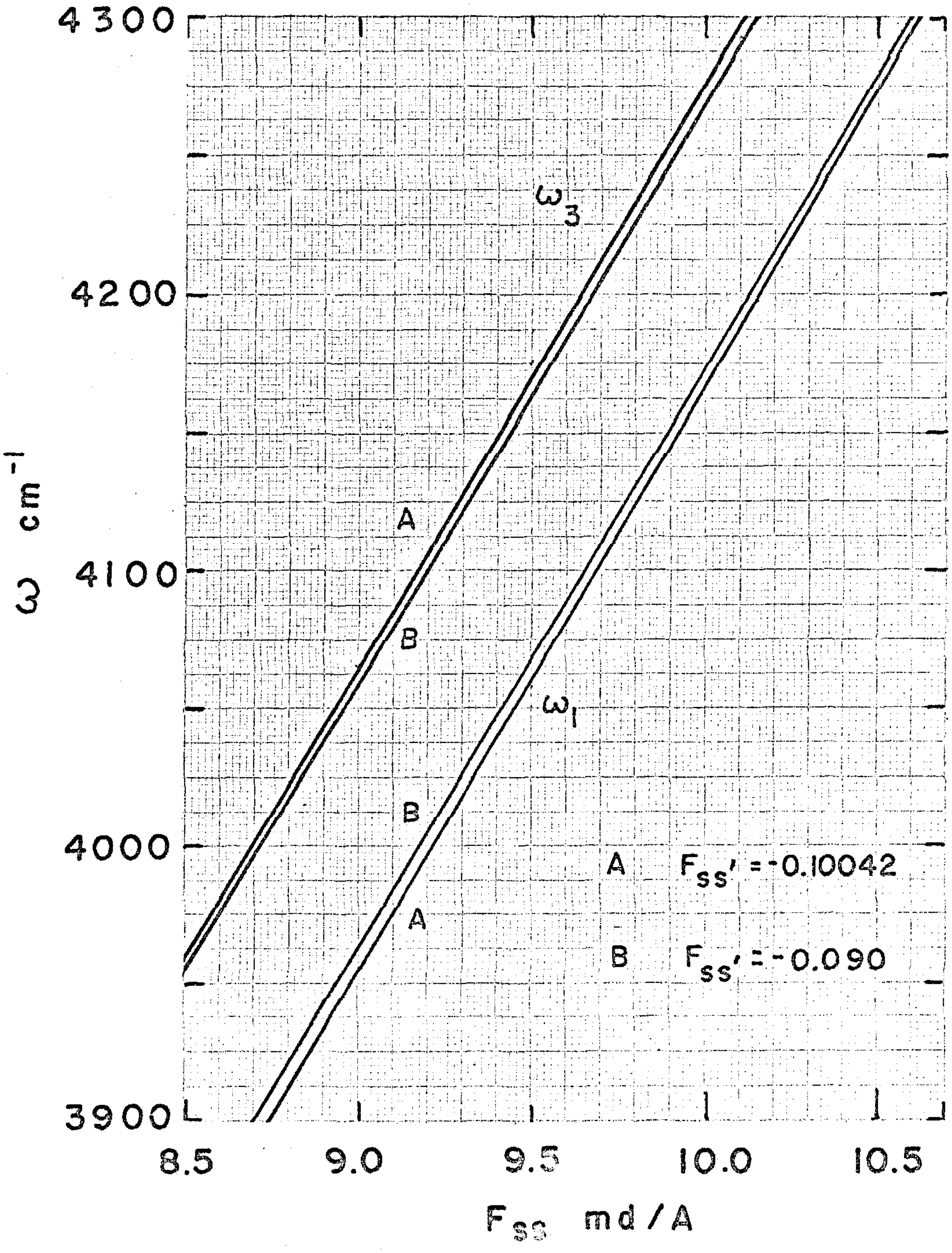


Figure 42. Variation of ω_3 and ω_1 as a function of the $\underset{\sim}{OH}\cdot\cdot S$ force constant for $F_{ss'}$ = -0.10042 and -0.090.

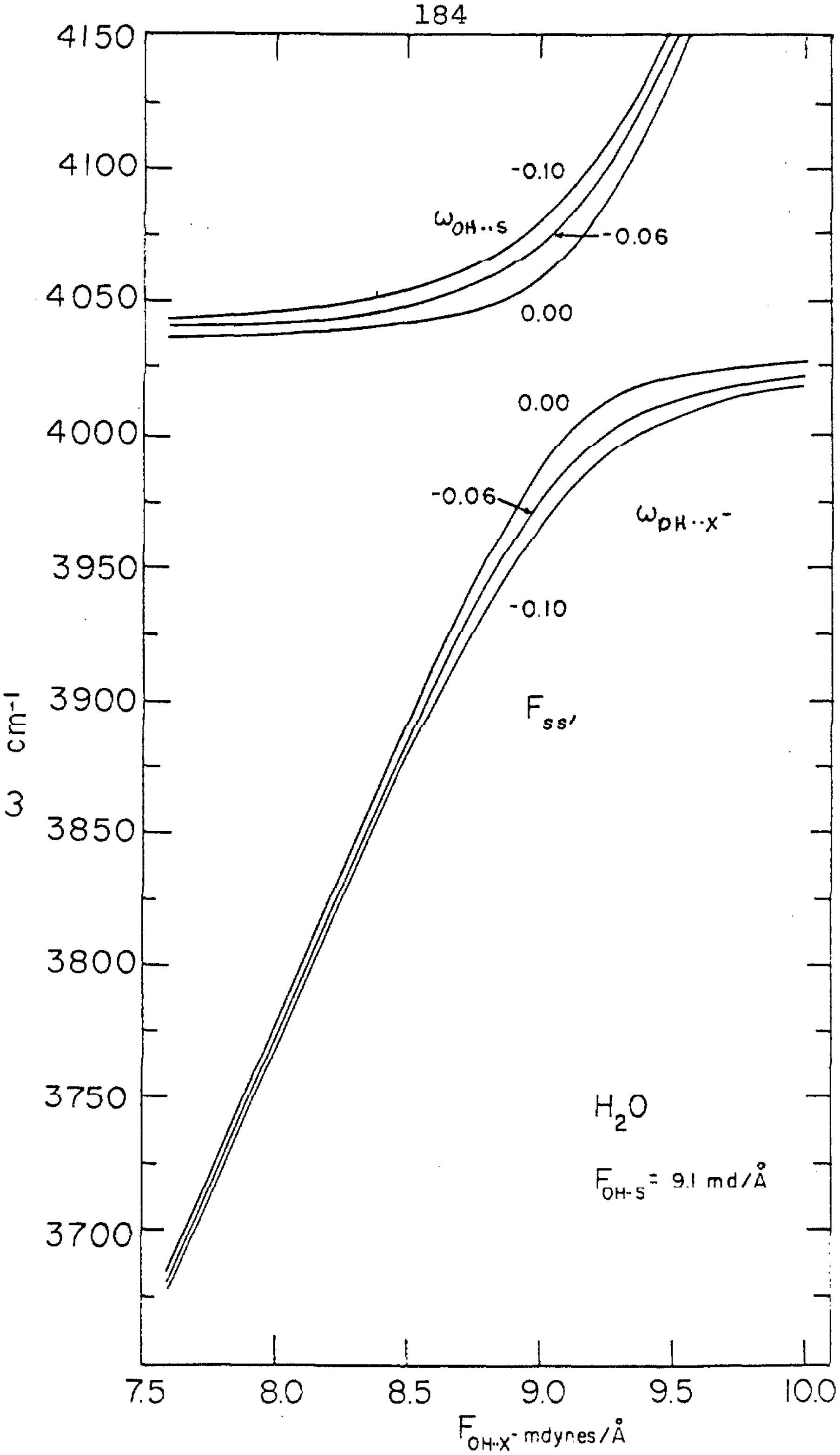


Figure 43. Variation of $\omega_{OH\cdot\cdot S}$ and $\omega_{OH\cdot\cdot X^-}$ as a Function of the $\underline{OH}\cdot\cdot X^-$ force constant for $F_{ss'}$ = 0, -0.06, and -0.10 md/Å and $F_{\underline{OH}\cdot\cdot S}$=9.1 md/Å .

two stretching vibrations for water when $F_{ss'} = -0.10$ is about 115 cm^{-1}. A value of $F_{ss'}$ of -0.06 reduces this separation to about 90 cm^{-1}. The observed separation for the various ion complexes of water is not constant but is about 90 cm^{-1} which suggests that a value of about -0.60 md/Å for the interaction constant would be appropriate in the calculation of frequency shifts.

The results of these calculations now serve as a basis for the analysis of the various ion-water complex spectra.

(i) Force Constants for the Cation Complexes of Water

Despite the preceding information concerning the variation in frequency in terms of changes in the force constant, it is still impossible to obtain force constants for the various ion complexes of water since knowledge of the anharmonic contributions are not known.

If we assume, however, that the arguments presented previously for the case of methanol can be applied to water, values for the anharmonicity contributions and force constants can be obtained. The results concerning the ratio of Δ_{OH}/Δ_{OD} for gaseous water summarized in Table 14 suggests that a ratio between 1.8 to 2.0 is reasonable.

Values for the "overall" anharmonicity contribution for the various cation complexes of water can be obtained from:

$$\Delta_{OH}^{sym.} = \omega_e^{sym.}(OH) - \omega_{0\to 1}^{sym.}(OH) \tag{61}$$

TABLE 14

Data for H_2O and D_2O (gas)

Reference 33

	$\omega_{0\rightarrow1}$	ω_e	Δ (cm^{-1})
H_2O (ω_1)	3656	3832.17	175.52
H_2O (ω_3)	3756	3942.53	186.74
D_2O (ω_1)	2671	2783.80	112.34
D_2O (ω_3)	2788	2888.78	100.73

$\Delta_1(OH)/\Delta_1(OD) = 1.904$

$\Delta_3(OH)/\Delta_3(OD) = 1.905$

$$\Delta^{sym.}_{OD} = \omega_e^{sym.}(OD) - \omega^{sym.}_{0\to1}(OD) \tag{62}$$

or from the corresponding expressions for the antisymmetric stretch. In this case, we can write:

$$\omega_e(OH) - \left(\frac{\Delta OH}{\Delta OD}\right)\omega_e\ (OD) = \omega^{OH}_{0\to1} - \left(\frac{\Delta OH}{\Delta OD}\right)\omega^{OD}_{0\to1} \tag{63}$$

A plot of the left hand side of equation 63 can be made as a function of the force constant F_{ss} using the calculated frequencies $\omega_e(OH)$ and $\omega_e(OD)$ obtained from the normal coordinate analysis program. Two sets of calculations were made using a value for $(\Delta OH/\Delta OD)$ of 1.9 and 2.0.

We have also used two different values for F_{ss}, of -0.10 and -0.060 md/A to illustrate the effect due to changes in the interaction constant. The results are represented by the solid line in Figure 44 for the symmetric stretch. The force constants for the various cation complexes of water can be determined by plotting the right hand side of equation 63 on the solid line. As in the case of methanol, the force constant is not too sensitive to ratios of $\Delta OH/\Delta OD$ near 2.

Similar plots concerning the antisymmetric stretch were made. The results, however, do not agree with those presented for the symmetric stretch. Since the success of the present analysis depends upon the accuracy in the location of the stretching fundamental, small errors can give rise to erroneous results. The location of the band maxima corresponding to the symmetric stretch is

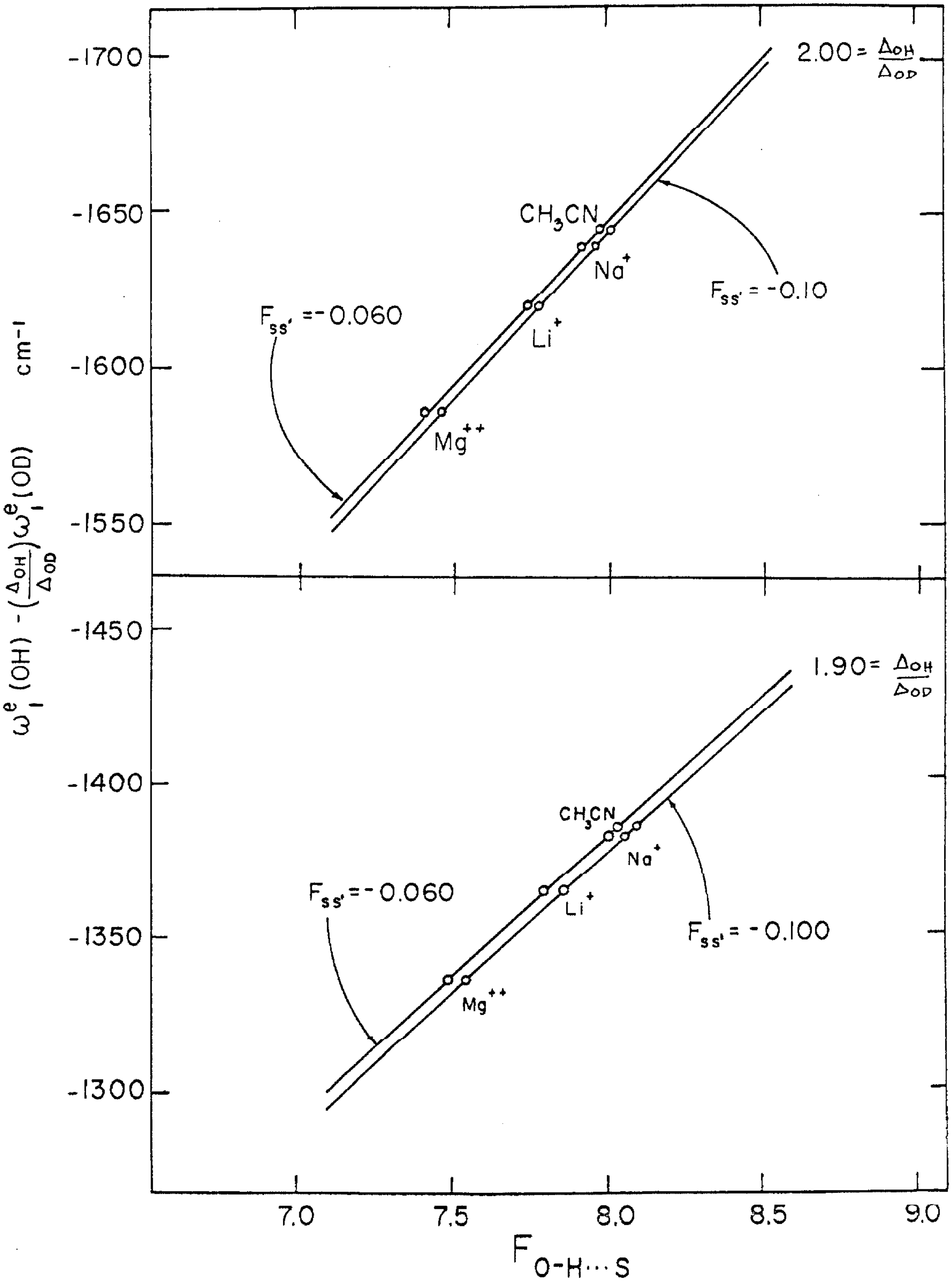


Figure 44. Variation of ω_1^e (OH) - $(\Delta_{OH}/\Delta_{OD})\,\omega_1^e$ (OD) as a function of the OH··S force constant for $F_{ss} = -0.06$ and-0.100 and $(\Delta_{OH}/\Delta_{OD})$ = 1.90 and 2.00.

certainly more accurate than for the antisymmetric stretch. For this reason, we feel that the results obtained from the symmetric stretch is more representative of the actual force constants involved in these complexes.

The variation in the symmetric and antisymmetric stretch for water as a function of F_{ss} is illustrated in Figure 45 for the case when $F_{ss'} = -0.06$ md/A. The solid lines are used to illustrate the relative positions of ω_{e_1} and ω_{e_3} for the various cation complexes. The corresponding illustration for D_2O is summarized in Figure 46.

(ii) Force Constants for the Anion-Water Complex

In the case of the anion-water complexes, the "overall" anharmonic contribution is given by:

$$\Delta_{OH} = \omega_e(OH\cdot\cdot X^-) - \omega_{0\rightarrow 1}(OD\cdot\cdot X^-) \tag{64}$$

$$\Delta_{OD} = \omega_e(OD\cdot\cdot X^-) - \omega_{0\rightarrow 1}(OD\cdot\cdot X^-) \tag{65}$$

so that

$$\omega_e(OH\cdot\cdot X^-) - \left(\frac{\Delta_{OH}}{\Delta_{OD}}\right)\omega_e(OD\cdot\cdot X^-) = \omega_{0\rightarrow 1}(OH\cdot\cdot X^-) - \left(\frac{\Delta_{OH}}{\Delta_{OD}}\right)\omega_{0\rightarrow 1}(OD\cdot\cdot X^-) \tag{66}$$

As in the case of the cation complexes, a plot of the left hand side of equation 66 can be made as a function of the $F_{OH\cdot\cdot X^-}$ force constant using the calculated frequencies for $\omega_e(OH\cdot\cdot X^-)$ and $\omega_e(OD\cdot\cdot X^-)$ obtained from the normal coordinate analysis program.

In the calculations it is necessary to assume some

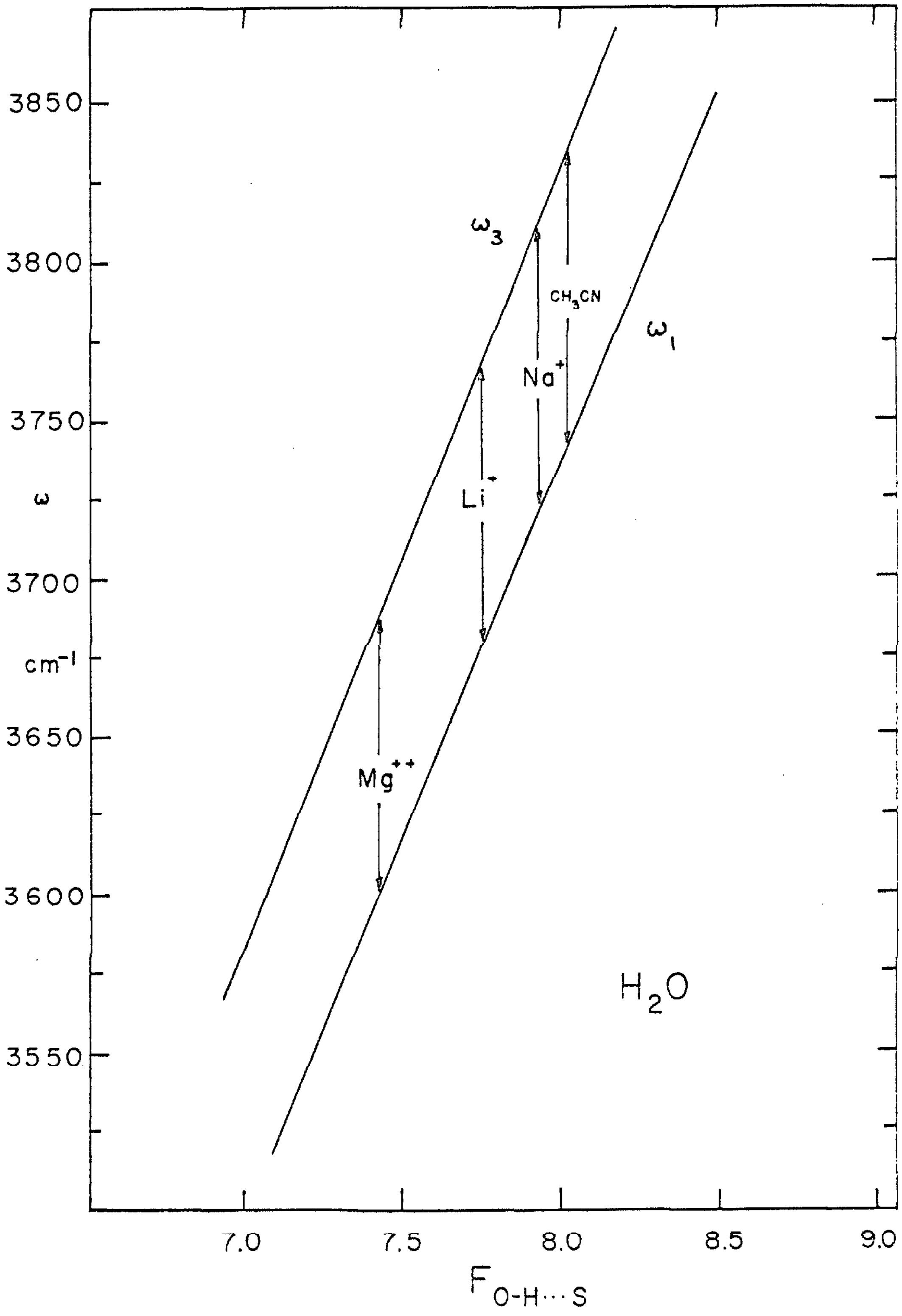


Figure 45. Variation of ω_3 and ω_1 as a function of the OH··S force constant for the cation complexes of H_2O.

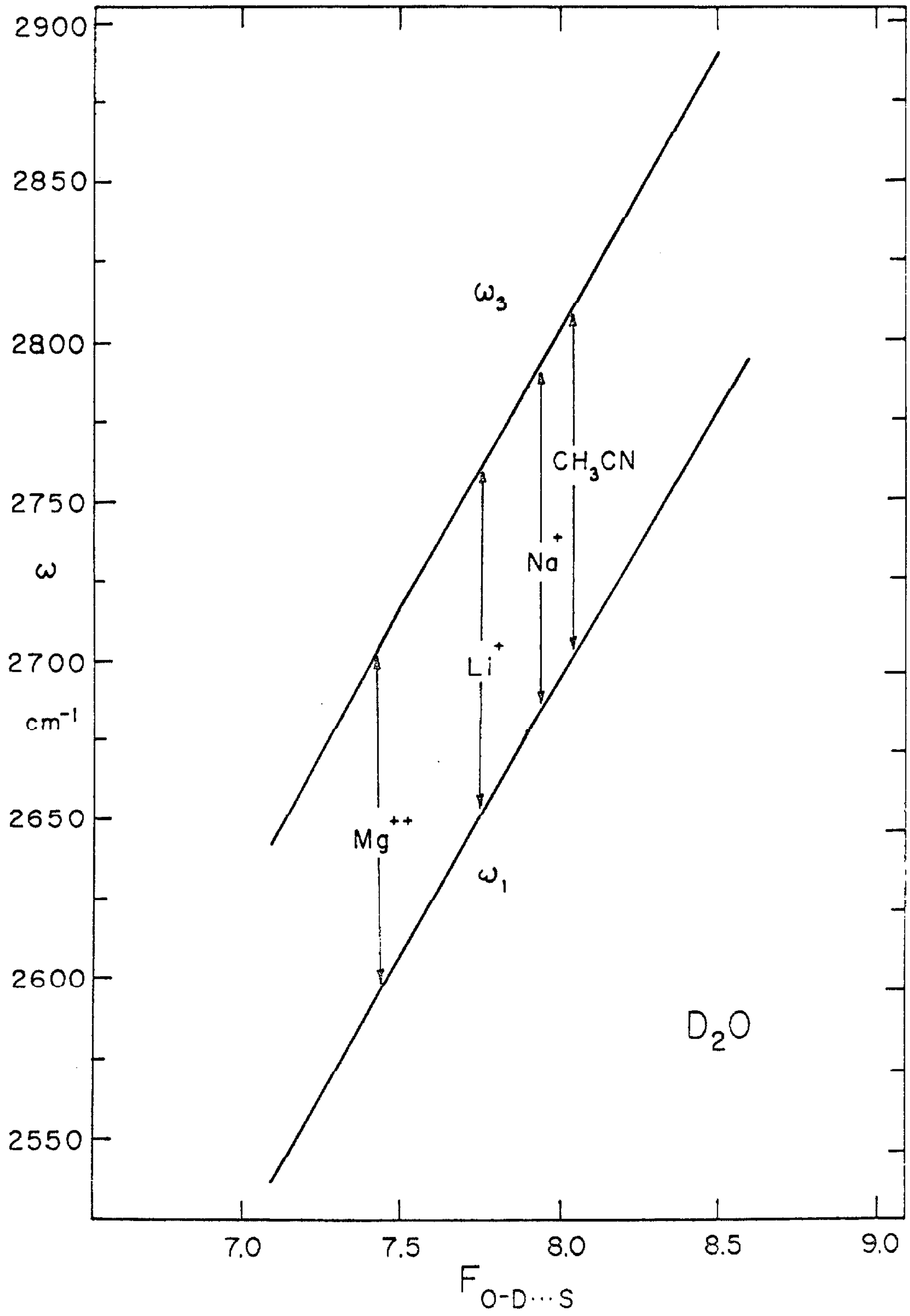


Figure 46. Variation of ω_3 and ω_1 as a function of the OD··S force constant for the cation complexes of D_2O

value for the OH··S stretching force constant. We shall assume that a representative value for the OH··S force constant in the anion complex is given by the OH··S stretching vibration force constant in the water complex of acetonitrile, i.e., 8.05 md/Å. A value of $F_{SS'} = 0.06$ md/Å was used for the interaction constant. The results are represented by the solid curve in Figure 47. As before, two sets of calculations were made using $(\Delta_{OH}/\Delta_{OD}) = 1.9$ and 2.0. The results of plotting the right hand side of equation 66 for the various anion complexes of water on the curve are represented by the open circles in Figure 47.

In Figure 48 a summary is given for the variation in ω_e (OH··S) and ω_e (OH··X$^-$) when $F_{OH\cdot\cdot S} = 8.05$ and $F_{SS'} = -0.06$ md/Å. An appropriate range in $F_{OH\cdot\cdot X^-}$ from 7.0 to 8.5 was chosen to illustrate the frequency shifts effected by anion complexation to H_2O. The solid vertical lines locate the frequencies and OH··X$^-$ force constant associated with the various anion-water complexes. In Figure 49 a similar summary is given for the anion complexes of D_2O.

A summary of force constants for the various ion complexes of water is given in Table 15 for the case where $F_{SS'} = -0.06$ and $(\Delta_{OH}/\Delta_{OD}) = 2.0$.

Approximate values for the anharmonic contribution can be obtained from $\omega_e - \omega_{0\rightarrow 1}$ using the appropriate values of ω_e associated with the force constants for the various ion complexes reported in Table 15. In Table 16, a summary is given for the anharmonic contributions for the various ion complexes of H_2O and D_2O for a ratio of Δ_{OH}/Δ_{OD} of 2.0.

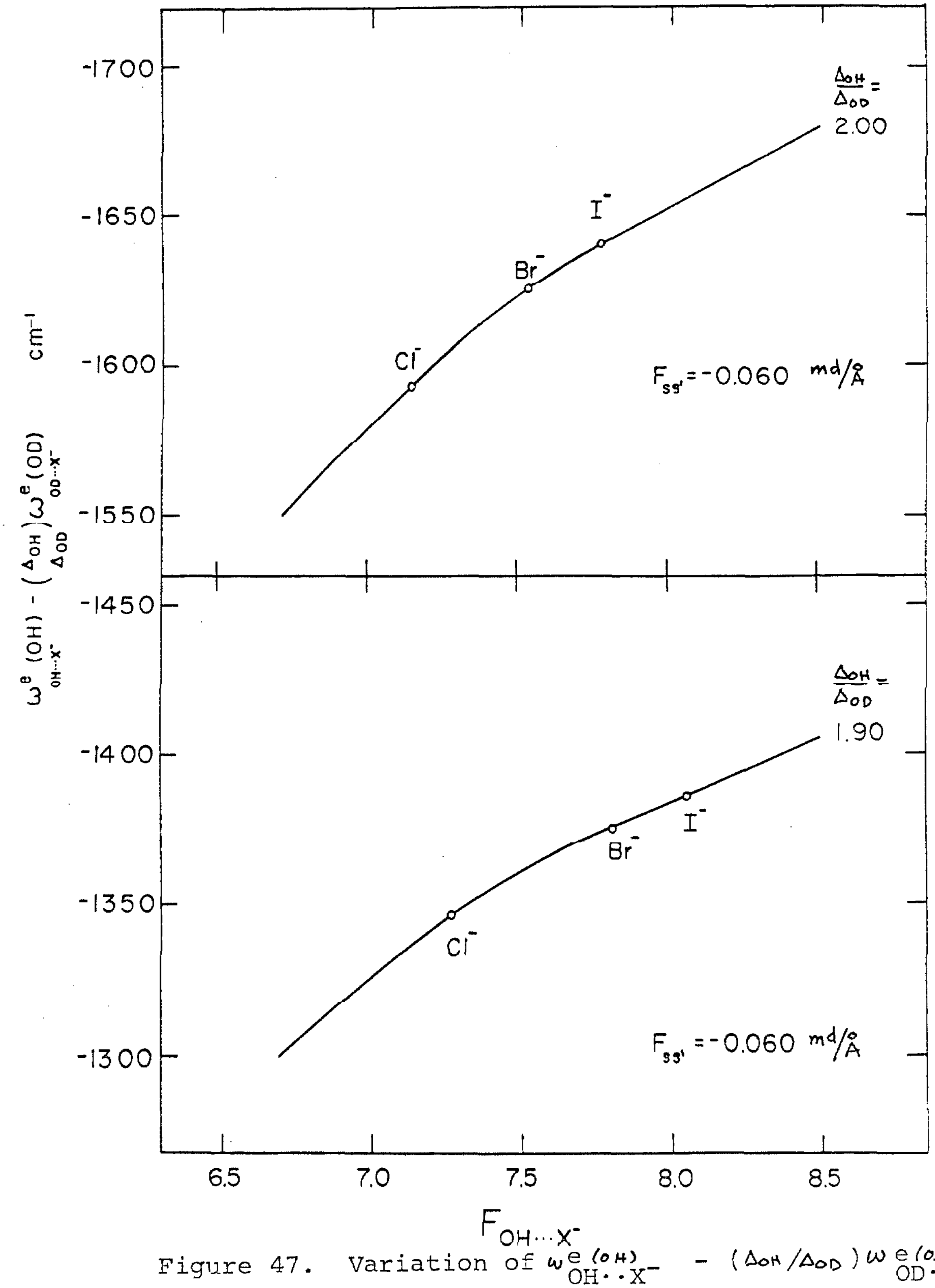


Figure 47. Variation of $\omega^{e\,(OH)}_{OH\cdot\cdot X^-} - (\Delta_{OH}/\Delta_{OD})\,\omega^{e\,(OD)}_{OD\cdot\cdot X^-}$ as a function of the OH··X⁻ force constant for $F_{ss'} = -0.060$ and $(\Delta_{OH}/\Delta_{OD}) = 1.90$ and 2.00.

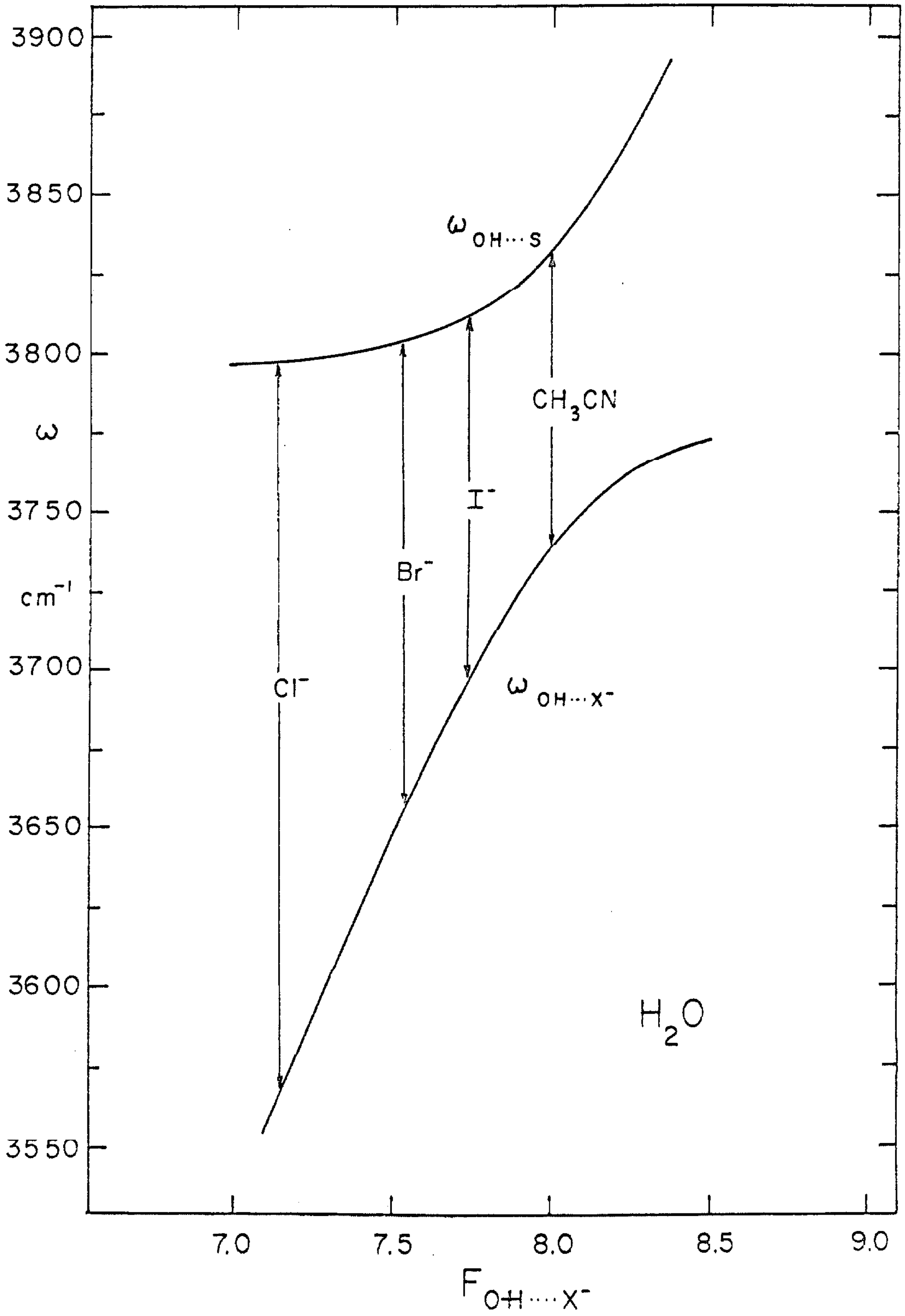


Figure 48. Variation of $\omega_{OH..S}$ and $\omega_{OH..X^-}$ as a function of the $\underline{OH}\cdot\cdot X^-$ force constant for the anion complexes of H_2O.

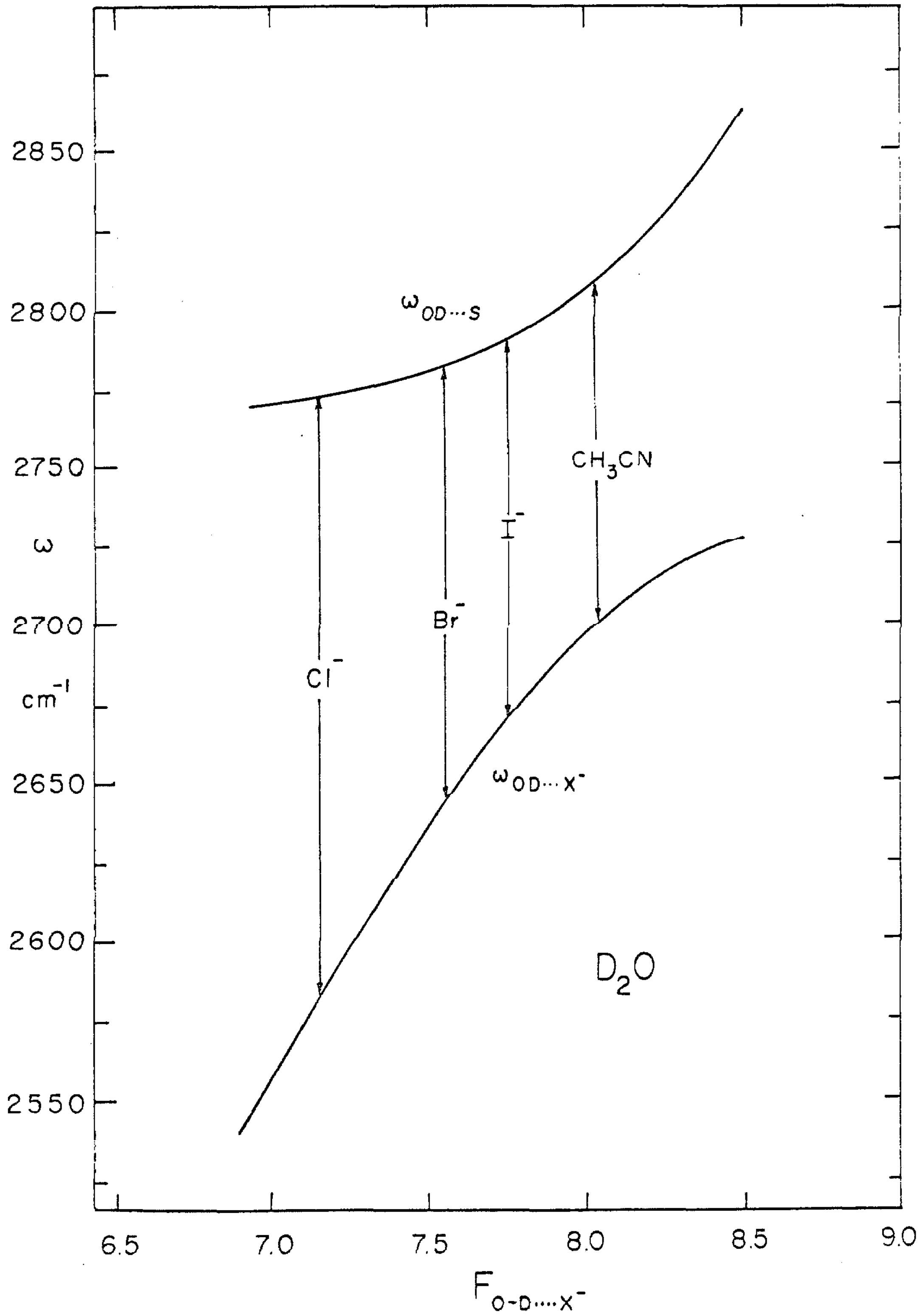


Figure 49. Variation of $\omega_{OD \cdot \cdot S}$ and $\omega_{OD \cdot \cdot X^-}$ as a function of the OD··X⁻ force constant for the anion complexes of D_2O.

TABLE 15

Table of Force Constants in mdynes/A

Complexing Group	$F_{OH\cdot\cdot S}$	$F_{OH\cdot\cdot X^-}$
CH_3CN	8.05	
Na^+	7.94	
Li^+	7.75	
Mg^{++}	7.40	
I^-	8.05	7.75
Br^-	8.05	7.55
Cl^-	8.05	7.15

TABLE 16

Anharmonic Contributions for H_2O in cm^{-1}

	ω_3	ω_1	$\Delta_3(OH)$	$\Delta_1(OH)$
CH_3CN	3830	3740	195	200
Na^+	3810	3720	210	227
Li^+	3770	3650	160	200
Mg^{++}	3680	3600	200	155

	$\omega_{OH\cdot\cdot S}$	$\omega_{OH\cdot\cdot X^-}$	$\Delta_{OH\cdot\cdot S}$	$\Delta_{OH\cdot\cdot X^-}$
I^-	3810	3695	265	205
Br^-	3805	3655	265	190
Cl^-	3795	3570	214	175

F. SUMMARY

In this part of the thesis, we have attempted to account for the frequency shifts in the OH stretching vibration for the various ion complexes of methanol and water for the case where the polarization is dominated by either the cation or anion. Spectra were also reported for D_2O and CH_3OD. These studies were made to supplement the studies of H_2O and CH_3OH. The bands attributed to the various solvated ion complexes of methanol and water have been assigned and interpreted in terms of the symmetry and structure of the solvated complex.

The analysis of the infrared frequency shifts in the OH and OD stretching vibration for the various anion complexes of water and D_2O suggests that only one proton of water is involved in a hydrogen bond to the anion. This result is consistent with the earlier results obtained from the proton magnetic resonance studies.

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PART III

Infrared and Proton Magnetic Resonance Studies on the Polarization of Water and Methanol by NaI, LiI, and LiBr in an Aprotic Solvent

A. INTRODUCTION

In Parts I and II, the results of a proton magnetic resonance study and infrared spectroscopic study on dilute solutions of water and methanol in an aprotic solvent in the presence of $NaClO_4$, $LiClO_4$, $Mg(ClO_4)_2$ Et_4NClO_4, Bu_4NI, Et_4NBr, and Et_4NCl were reported. Since the effects of Et_4NClO_4 on the proton chemical shift and on the OH stretching vibration of water and methanol are negligible, the corresponding perchlorate or tetraalkylammonium salts of Na^+, Li^+, Mg^{++}, I^-, Br^-, and Cl^- were used to investigate the case where the polarization is dominated by one ion. The chemical shifts and OH stretching frquency shifts were then interpreted on the basis of shifts representative of the polarization effected by either anion or cation.

In general, the polarization of water or methanol in an aprotic solvent by various diamagnetic salts can be affected by both cation and anion. Since the earlier studies have already indicated that both anion and cation complexation is possible, it is expected that salts, such as NaI, NaBr, LiBr, LiI, LiCl, $Mg(Br_2)$ etc., will reflect the effects of polarization by both anion and cation.

As mentioned previously, a considerable amount of work has already been done in an effort to understand in a quantitative manner the ion-induced proton chemical shifts in bulk water. It is clear that the bulk water data (IR and NMR) are such that quantitative information on the details of specific interactions between ions and between ions and solvent molecules is difficult to obtain. Even in the case where large counter ions (such as perchlorate or tetraalkylammonium ions) are used to study the effects of polarization by the very small ions, the effect of structure breaking by both ions makes the interpretation of the IR and NMR data formidable. Even if we assume that the structure-breaking effect has been adequately interpreted, the problem which concerns the specific effects of polarization still remains.

In a proton magnetic resonance study of bulk water salt solutions, the observed water resonance is an average over the various water-water aggregates and the ion complexes of water. The separation of the observed polarization in terms of the polarization effected by individual molecular complexes is desirable but difficult. The analysis of the bulk water is further complicated by the fact that extremely large salt concentrations (10-25 molar) were required to observe appreciable chemical shifts (0.5 to 1 ppm). As a consequence, the shifts reflect the complicated state of ion-ion interactions at high concentrations as well as the ion-solvent interactions. The extraction of quantitative information on the nature of the polarizing ion or ions is difficult to obtain under these conditions. Similar problems are encountered in the interpretation of the infrared studies on aqueous salt solutions.

In contrast to the bulk water studies, it is possible to extract more specific information on the nature of the polarizing ions for water and methanol complexes in aprotic salt solutions. The interpretation of the chemical shifts (NMR) and frequency shifts (IR) is still a difficult task and is by no means trivial. The advantage of the present proton magnetic resonance studies over the PMR studies of bulk water was discussed previously. In the case of the infrared studies, the spectral features are such that more quantitative information on specific interactions, which can be extracted from the data, is available. For this reason, a more detailed analysis of the problem of ion complexation is possible.

In this part we shall report the results of some infrared and nuclear magnetic resonance studies for the case where the polarization of water is affected by diamagnetic salts where both anion and cation complexation occurs. We have restricted our present study to water and methanol in acetone and acetonitrile in the presence of NaI, LiI, and LiBr. An attempt was made to also study the chemical shifts effected by LiCl, NaBr, and NaCl. These salts unfortunately have an extremely low solubility in acetone or acetonitrile so that it was not possible to obtain data for these salts. Other salts, such as CdI_2 and MgI_2, are however soluble. It is hoped that, in the future, similar PMR and IR studies will be made using these salts.

B. EXPERIMENTAL

The experimental aspects of the infrared and proton magnetic resonance studies were previously discussed in the experimental section of Parts I and II.

NaI was obtained from Allied Chemical Corporation; LiBr, from Matheson, Coleman, and Bell; and LiI from Lithium Corporation of America. Each of the anhydrous salts were recrystallized from a mixture of acetonitrile and carbon tetrachloride and redried at 110-120° C.

C. INFRARED STUDIES

One of the most interesting questions to which this study can address itself concerns the nature of the ion complexes of water. In general, electrolytic solutions are characterized by a complex set of equilibria between numerous association complexes. If these solutions are to be characterized in a quantitative manner, it is necessary to determine what the various complexes are. Although one can, in principle, write down various complexes and the equilibria between them, it is still necessary and desirable to perform experiments which will hopefully enable us to determine and substantiate the important specie(s).

The investigation of the OH stretching vibration of water in these dilute aprotic salt-water solutions offers a method of identifying various complex species. In this case, the water molecule is used to explore its immediate environment and thus offers a method of learning something about the polarized water molecule as well as about the nature of the polarizing ions.

The results reported in this part were obtained by the method previously described in Part II. In this work, we have studied the effects of NaI, LiI, and LiBr on the OH stretching vibration of methanol and water in acetonitrile and on the OD stretching vibration of D_2O in acetonitrile.

1. RESULTS

a. The OH Stretching Vibration Spectrum of the Ion Complexes of Methanol in Acetonitrile

The infrared spectrum in the region of the OH stretching vibration for dilute solutions of methanol in acetonitrile in the presence of NaI, LiI, and LiBr is characterized by the appearance of two or more bands on the low frequency side of the band which is attributable to the hydrogen-bonded monomer.

In Figures 1, 2, and 3 representative spectra are summarized for methanol in the presence of NaI, LiI, and LiBr, respectively, for a salt-to-water concentration of about 1 to 2. The resulting spectra are expected to be concentration dependent since the fraction of the various ion-methanol complexes is concentration dependent. Figure 4 illustrates how the methanol spectrum changes as the LiI concentration is increased keeping the methanol concentration constant.

b. The OH and OD Stretching Vibration Spectrum of the Ion Complexes of H_2O and D_2O in Acetonitrile

The infrared spectrum in the region of the OH stretching vibration for dilute solutions of water in acetonitrile in the presence of NaI, LiI, and LiBr is characterized by the appearance of several bands on the low frequency side of the bands attributable to the water monomer (hydrogen-bonded to the solvent).

Figure 1. NaI-CH_3OH-CH_3CN

0.468	M	NaI
0.402	M	CH_3OH

Figure 2. LiI-CH_3OH-CH_3CN

0.258	M	LiI
0.524	M	CH_3OH

Figure 3. LiBr-CH_3OH-CH_3CN

0.246	M	LiBr
0.578	M	CH_3OH

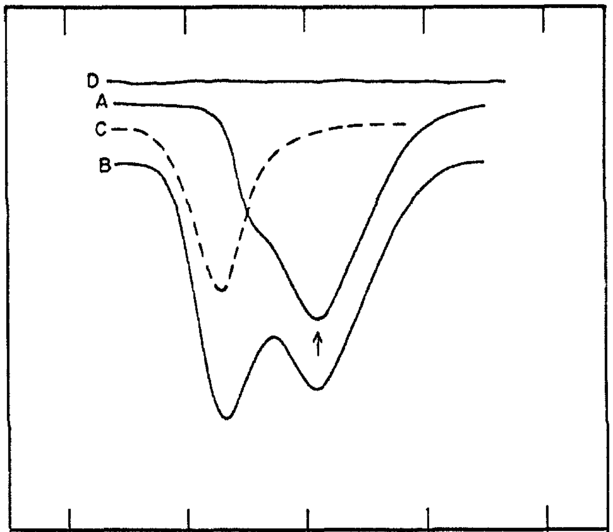


Figure 1.

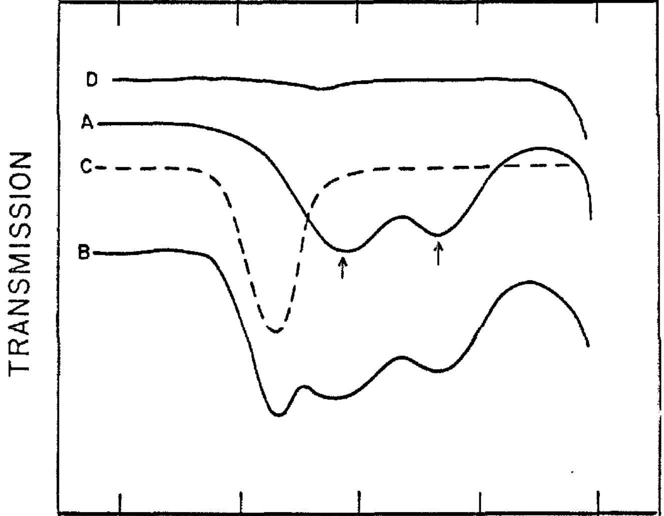


Figure 2.

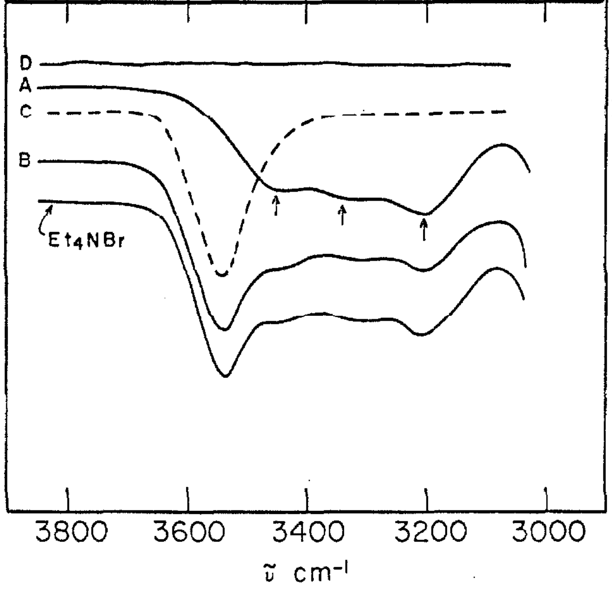


Figure 3.

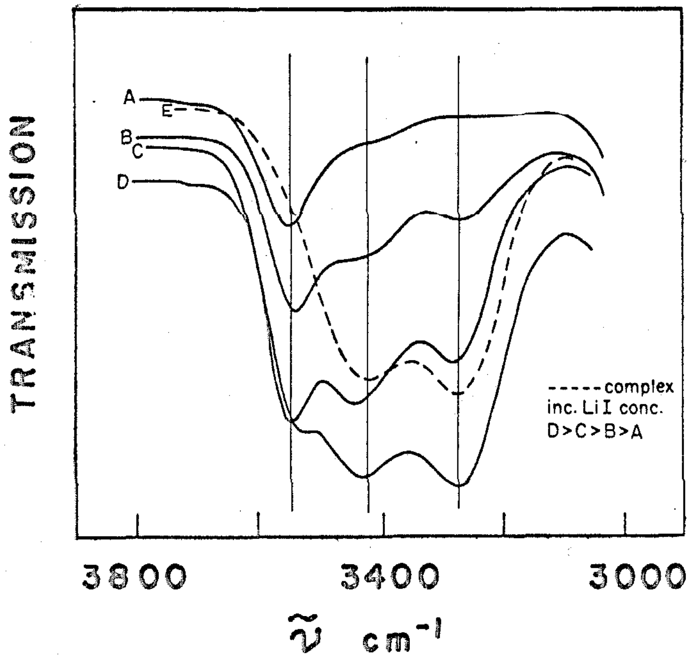


Figure 4. Effect of increasing LiI concentration on the OH stretching vibration of methanol in acetonitrile. Solid curves represent composite spectra which includes both monomer and complex bands. The dashed curve represents only the LiI complex bands.

In Figures 5, 6, and 7 representative spectra are summarized for H_2O in acetonitrile in the presence of NaI, LiI, and LiBr, respectively, for a salt-to-water concentration ratio of about 1 to 2.

In Figures 8, 9, and 10 similar spectra are summarized for D_2O in acetonitrile in the presence of NaI, LiI, and LiBr, respectively.

A summary of band maxima is given in Table 1.

2. Assignment of Band Positions

a. Assignment of the Ion Complex Bands for Methanol

The assignment of the complex band positions of the methanol complexes of NaI, LiI, and LiBr is complicated by the fact that more than one complex must be considered. This is immediately apparent when one looks at the infrared spectrum in the region of the OH stretching vibration. The spectrum is characterized by the appearance of two or more bands on the low frequency side of the band which is attributable to the monomeric hydrogen-bonded methanol solvent complex. The spectrum consists of a statistically weighted sum of absorption bands for the various methanol molecules with different neighboring configurations whose frequencies, absorption coefficients, and band widths are modified by the intermolecular interactions. In the case where the frequency separation between two or more bands are smaller than their band widths, a single band will be observed whose width will depend on the individual band widths, intensities, and frequencies.

Figure 5. NaI-H_2O-CH_3CN

0.395 M NaI

0.687 M H_2O

Figure 6. LiI-H_2O-CH_3CN

0.259 M LiI

0.512 M H_2O

Figure 7. LiBr-H_2O-CH_3CN

0.352 M LiBr

0.601 M H_2O

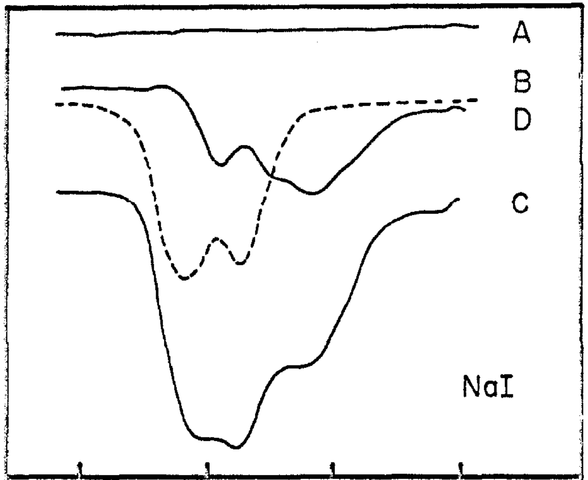


Figure 5.

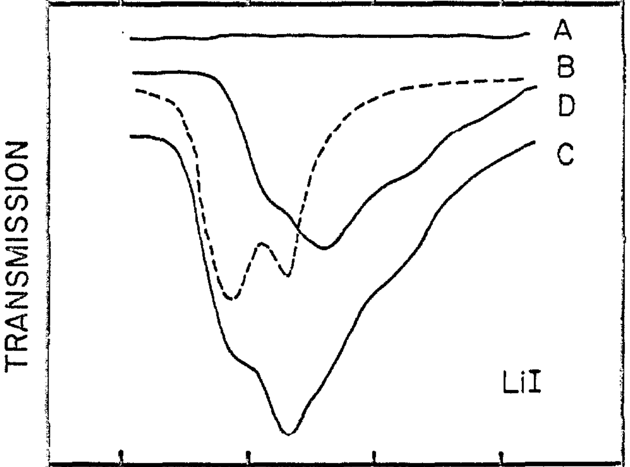


Figure 6.

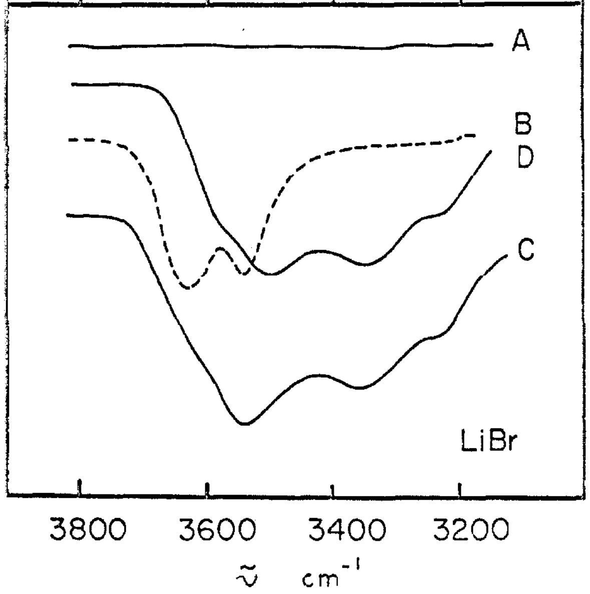


Figure 7.

Figure 8. $NaI-D_2O-CH_3CN$

0.382 M NaI

0.645 M D_2O

Figure 9. $LiI-D_2O-CH_3CN$

0.153 M LiI

0.414 M D_2O

Figure 10. $LiBr-D_2O-CH_3CN$

0.290 M LiBr

0.584 M D_2O

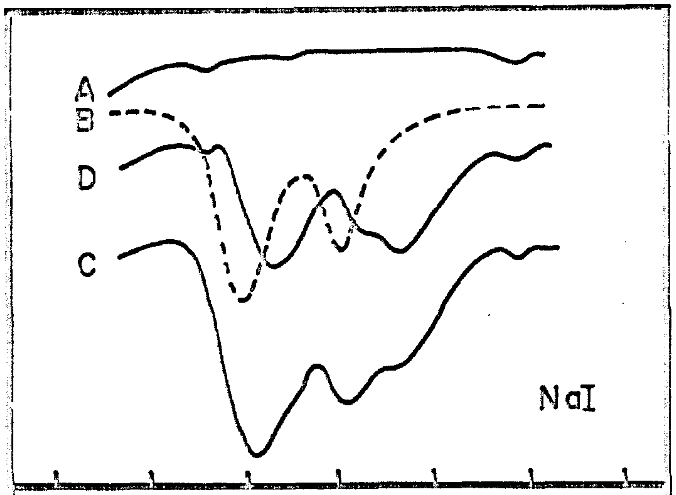


Figure 8.

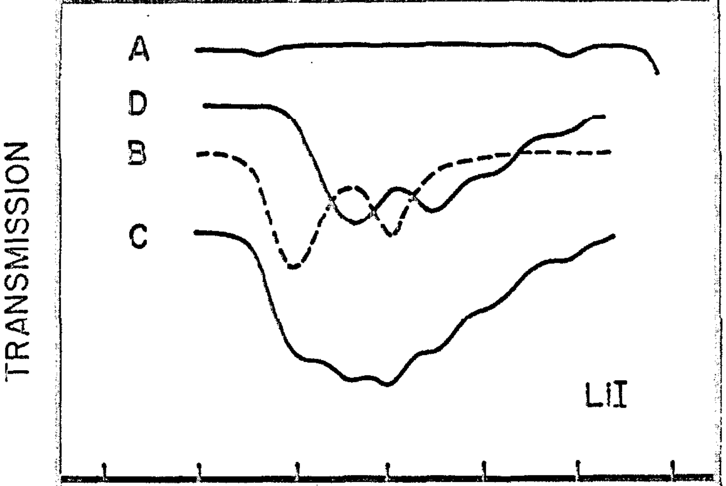


Figure 9.

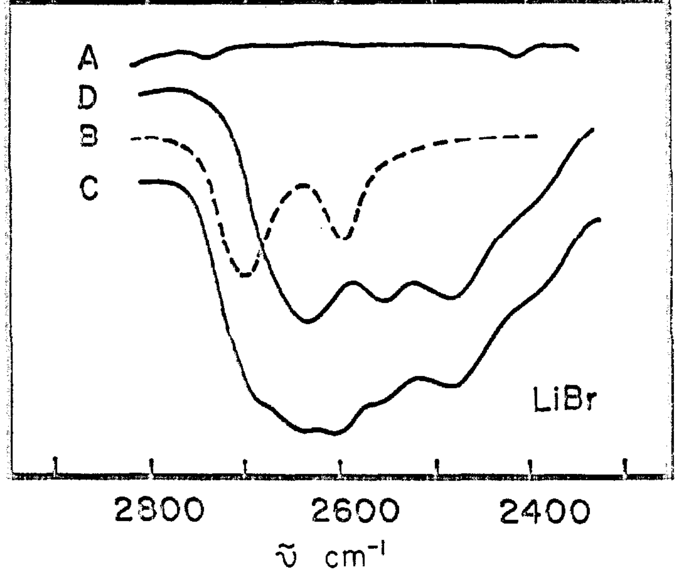


Figure 10.

TABLE 1

Observed Band Maxima (cm^{-1}) for the OH(OD) Vibrational Transition (0 → 1 Stretch) for CH_3OH, H_2O, D_2O in Acetonitrile for LiI, LiBr, and NaI (s = shoulder)

Salt/Solute	CH_3OH	H_2O	D_2O
NaI	3490 (s)	3580	2665
	3381	3500	2567
		3440	2533
LiI	3425	3570 (s)	2625
	3265	3490	2550
		3372 (s)	2485 (s)
LiBr	3450	3570 (s)	2635
	3310	3500	2553
	3200	3350	2482
		3250	2400 (s)

It is convenient, at this point, to consider some of the possible configurations for the ion-methanol complex. The earlier studies by Savedoff (1) and Olson and Konecny (2) on the electrical conductance of electrolytes in acetone have shown that association between the ions of the dissolved salt occurs. At reasonably low salt concentrations the ion pair association is expected to be important. The following ion pair dissociation constants were reported (1):

Salt	$K_D \times 10^4$ (25° C)
LiCl	0.033
LiBr	2.19
LiI	69.1
Bu_4NCl	16.6

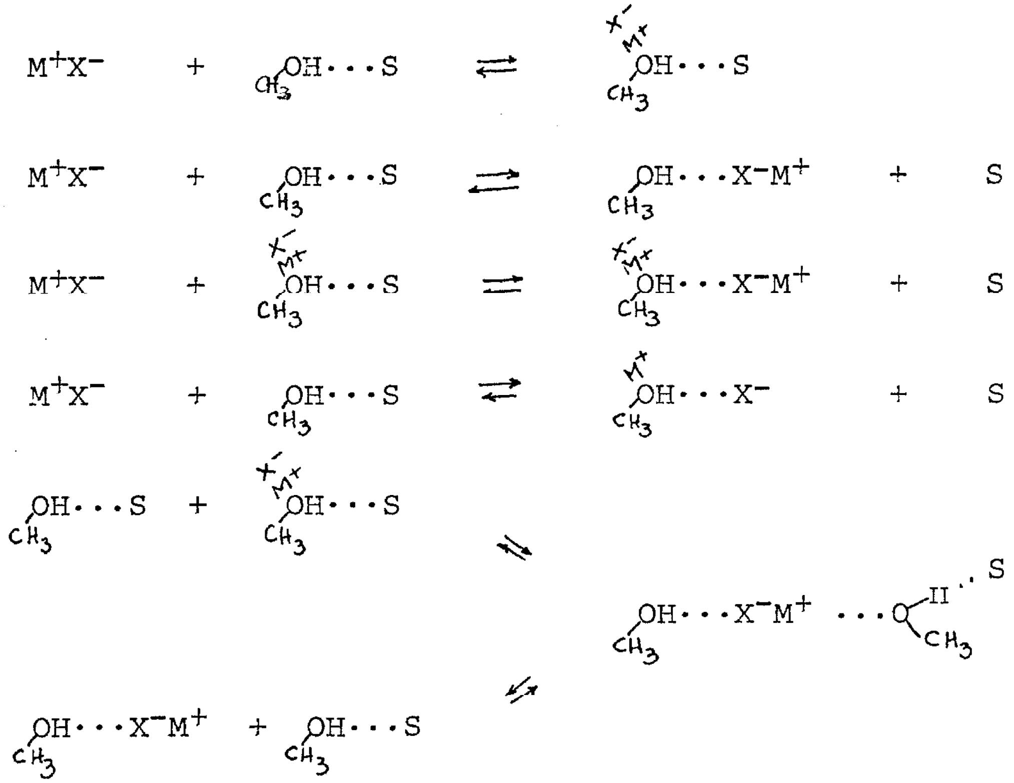
It is suggested that in the LiCl ion pair, the ions are in contact, while in LiI, the ion pair is formed from fully solvated ions. LiBr is thought to represent an intermediate case where only one solvent molecule may separate the ion pair (1). These suggestions are, however, questionable since there is no way of establishing definitively the nature of the ion pair from conductance measurements.

When water is introduced into these dry salt solutions, the dissociation of the ion pair increases. The effect of added water on the LiBr ion pair dissociation constant in acetone was studied by Olson and Konecny (2). The results are summarized below:

M H_2O	$K_D \times 10^4$ (25° C)
0	2.19
0.251	2.56
1.65	8.52
3.15	17.6
7.92	95.0

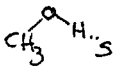
Although these studies give us some information on the association of these salts in an aprotic solvent, it is clear that other studies are required before these results can be adequately interpreted.

In the following, we shall consider some of the possible equilibria involved in the case of the ion complexation of methanol in acetonitrile:

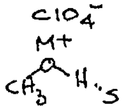


where M^+X^- represents a solvated ion pair and S represents a solvent molecule. It is convenient to let:

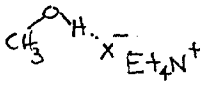
A =



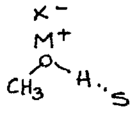
B =



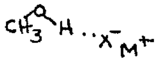
C =



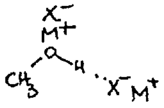
D =



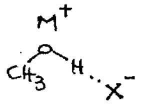
E =



F =

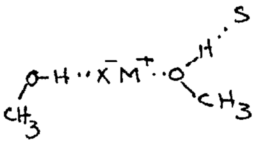


G =



and

H =



(i) Assignment of the Band Positions for the Methanol Complexes of NaI

In order to discuss the possible band positions for the methanol complexes of NaI, the band maximum of the methanol complexes of $NaClO_4$ and Bu_4NI are used as a reference.

In the case of complex D, a band centered at about 3490 cm^{-1} can be expected. To a first approximation, the band position for complex G can be estimated by taking the sum of the cation and anion shifts previously observed for $NaClO_4$ and Bu_4NI which would be about 3330 cm^{-1}. The actual frequency is expected to be slightly lower. In the case of complex E, a band should appear near the one observed for Bu_4NI (3380 cm^{-1}). The actual band positions for complexes D and E, however, can vary depending on the influence of the counter ion. As mentioned previously, the influence of the perchlorate or tetraalkylammonium ions on the OH stretching vibration is negligible so that in the case of the complexation of iodide to methanol, for example, the presence of the Bu_4N^+ cation (even if a contact ion pair were involved) is not expected to contribute to the over-all polarization effected by the anion. In the case of smaller cations or cations with large charges, however, the over-all polarization effected by the anion can be influenced by the cation especially if a contact ion pair is involved. Two factors can be expected to influence the anion polarization of methanol: (1) The cation is expected to polarize the anion and (2) In a contact ion pair configuration the anion does not completely screen out the cation so that the effects on cation polarization of the anion-methanol hydrogen bond must be considered. The same arguments also apply to the over-all polarization effected by the cation. As a result of these counter ion polarization effects the band positions for the anion or cation methanol complex bands of NaI do not necessarily have to correspond with the band maxima observed for the anion or cation methanol complex band of $NaClO_4$ and Bu_4NI. The effect counter ion polarization, however, can be expected to be small for NaI so that the cation and anion methanol complex bands of NaI should be near those observed for $NaClO_4$ and Bu_4NI.

In the case of complex F, a band should appear near complex G. A slight shift to higher frequencies is also expected. In Figure 11, a summary is given for the probable band positions and assignments for the various ion complexes of NaI with methanol. The non-appearance of a band or shoulder at about 3330 cm^{-1} or lower suggests that the equilibrium constant for the formation of complex G is

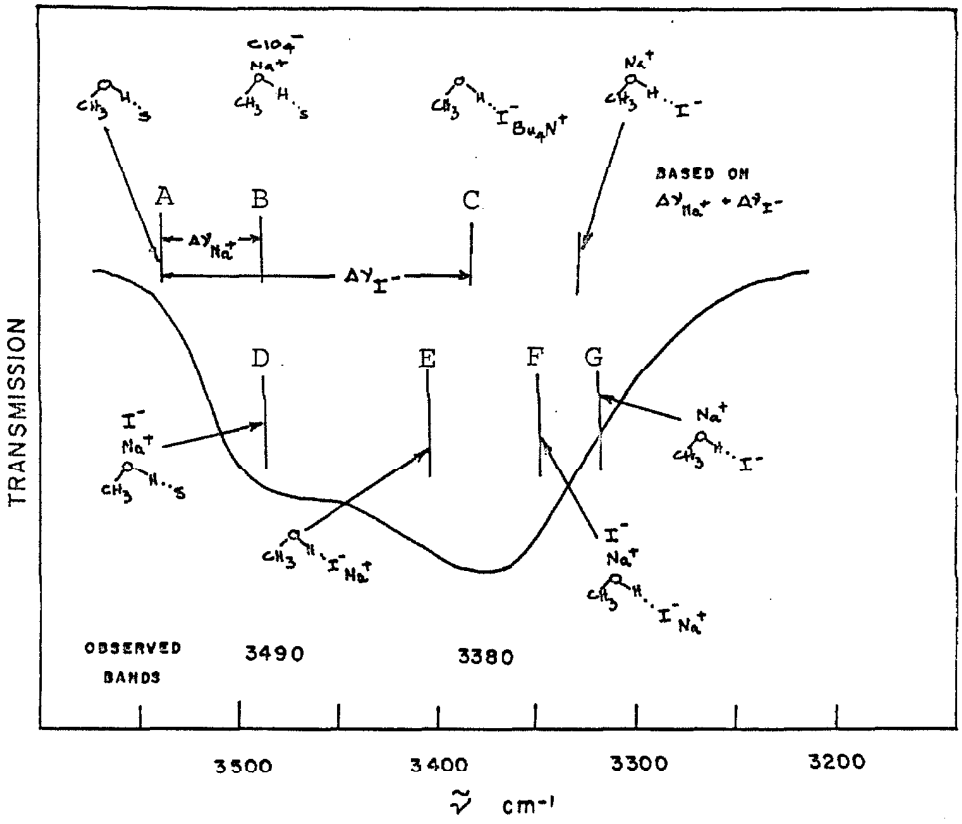


Figure 11. Band Assignments for the NaI Complexes of Methanol

quite small relative to the formation constants for the other methanol complexes of NaI. The large breadth of the 3381 cm^{-1} band is indicative of the presence of at least two bands separated by a frequency less than their individual band widths.

(ii) Assignment of the LiI Complex Bands for Methanol

In Figure 12, a similar analysis of the various possible band positions for the methanol complexes of LiI is presented. Since the effects of counter ion polarization of lithium by iodide is expected to be small, a band centered at about 3450 cm^{-1} can be expected for complex D. An approximate band position for complex G is 3542 - (162 + 92) = 3290 cm^{-1}. Band maxima for species E and F will depend upon the effects of counter ion polarization of iodide by lithium.

The observed complex band spectrum of the methanol complexes of LiI consists of two relatively distinct bands at 3425 cm^{-1} and 3265 cm^{-1}. It is important to note that the high frequency band (3425 cm^{-1}) for the LiI methanol complex appears at a lower frequency relative to the cation band for the $LiClO_4$ methanol complex (3450 cm^{-1}). The difference in frequency is 25 cm^{-1}. This shift may indicate that some kind of counter ion polarization is involved. It is possible that a counter ion polarization of lithium by the perchlorate or iodide ion occurs, and that this effect is greater for perchlorate than for iodide. If this is the case, the 3425 cm^{-1} band can be

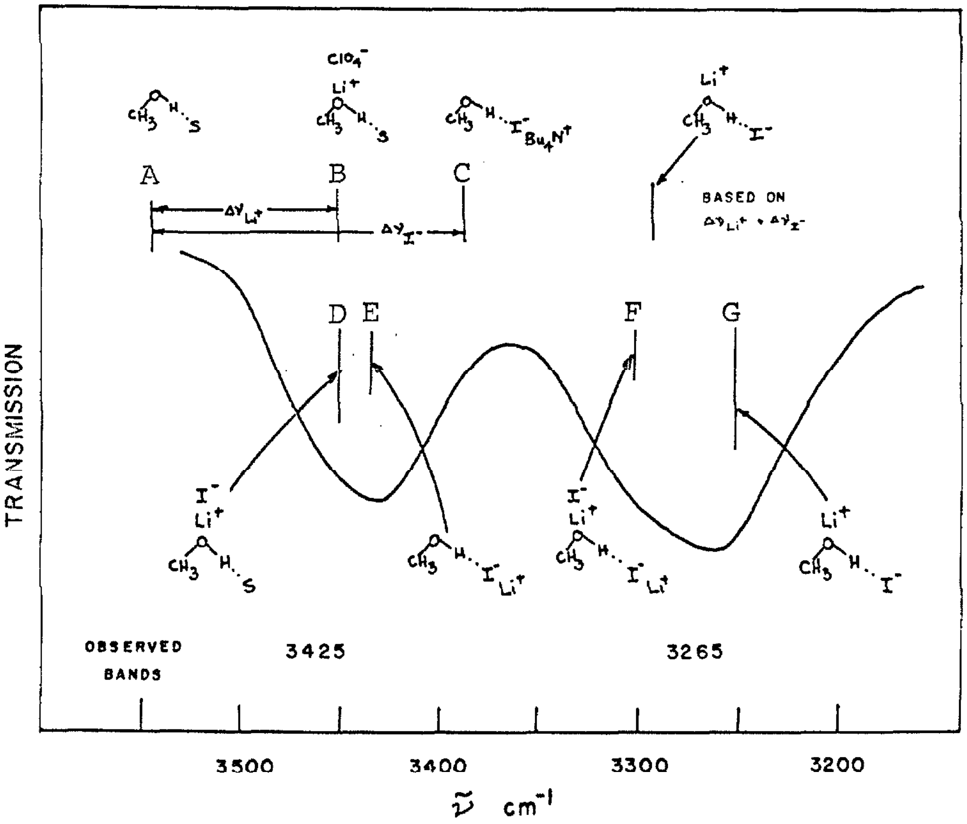
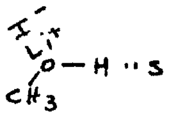
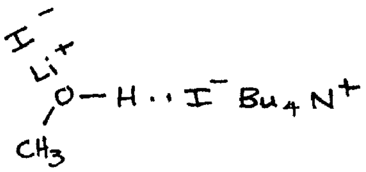


Figure 12. Band Assignments for the LiI Complexes of Methanol

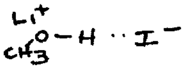
assigned to complex D. We would prefer to believe, however, that the low frequency shift of 25 cm^{-1} arises from the presence of two bands due to complexes D and E. The effect of counter ion polarization of iodide by lithium is expected to shift the anion complex band to higher frequencies. Since the frequency separation between the two bands would be less than their band widths, the presence of complex E would result in an apparent low frequency shift.

The low frequency complex band for the LiI methanol complex (3265 cm^{-1}) clearly indicates some kind of double ion perturbation since this band is lower in frequency by 115 cm^{-1} relative to the iodide methanol complex band. If we assume that the effects of counter ion polarization of iodide by lithium occurs, a band at frequencies greater than 3290 cm^{-1} can be expected for complex F. This frequency, however, is only a first approximation estimate for the frequency which can be assigned to the sandwich ion pair methanol complex represented by complex G. If complex G does exist, the actual frequency can be expected to be slightly lower than 3290 cm^{-1}.

As a result of these considerations, it is clear that a definitive assignment of the band at 3265 cm^{-1} can not be made. This band could arise from either complex F or G or both. For this reason, an additional study was made on a solution of methanol in the presence of excess iodide (Bu_4NI) to which small amounts of $LiClO_4$ were added. In this case, the predominant complex is the anion complex of methanol, <u>i</u>.<u>e</u>., $CH_3OH \cdots I^- Bu_4N^+$. The addition of $LiClO_4$, however, forms LiI which can now form the  $\overset{I^{-}\cdots Li^{+}}{\underset{CH_3}{O}}-H\cdots S$ complex. Since the concentration of I^- is larger than that of Li^+, the complex expected to also form is:



$$\overset{I^{-}\cdots Li^{+}}{\underset{CH_3}{O}}-H\cdots I^{-}\,Bu_4N^{+} \qquad = \text{I.}$$

This complex should have an OH stretching vibration similar to the  $\overset{Li^{+}}{\underset{CH_3}{O}}-H\cdots I^{-}$ complex. Thus, the determination of the band position of complex I will enable us to determine whether or not the 3265 cm^{-1} LiI methanol complex band is due to complex G or to complex F.

The results of this study are summarized in Figure 13. These spectra clearly show that no new band occurs at frequencies much lower than the 3265 cm^{-1} LiI methanol complex band, and that the band maximum for complex I is about 3250 cm^{-1}. It is important to also note the band which appears at about 3300 cm^{-1} in the Bu_4NI-$LiClO_4$-CH_3OH-CH_3CN spectrum. At high $LiClO_4$ concentrations this band disappears due to the strong overlapping between the iodide and I complex bands. This band can be assigned to the double ion pair methanol complex F. The fact that the low frequency band of the LiI methanol complex is at 3265 cm^{-1} is indicative of the presence of complex F. These results now enable us to assign the 3260 cm^{-1} band to complex F and G.

We also note that the complex band spectra do not enable us to distinguish differences between

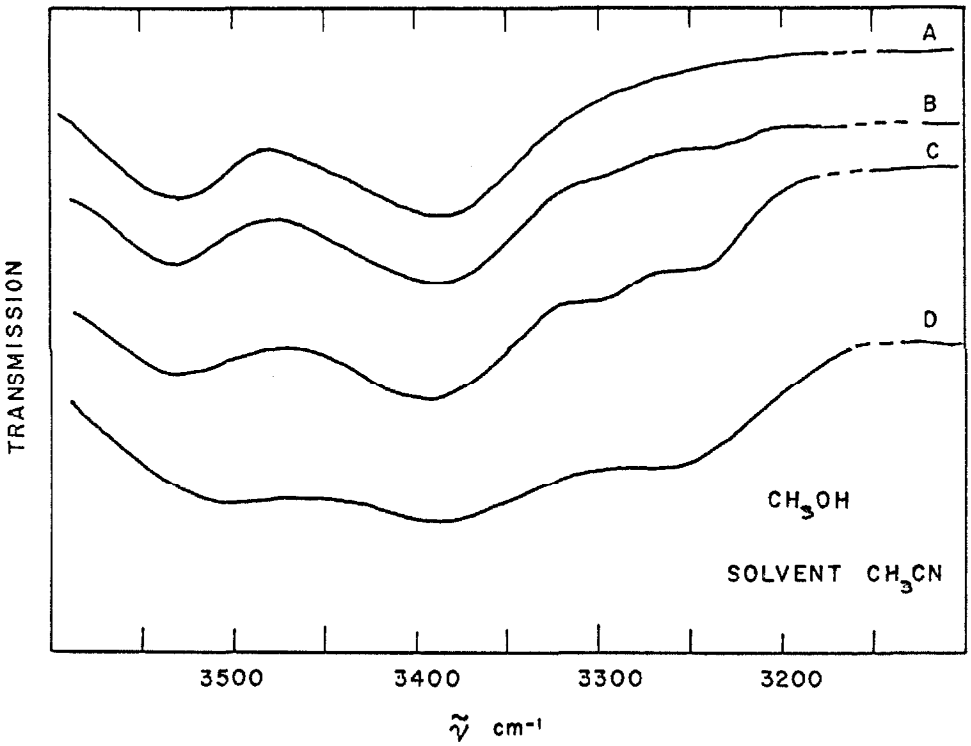
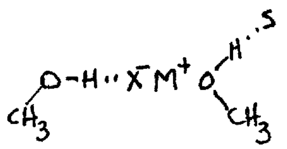
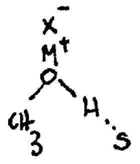
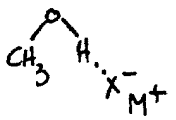


Figure 13. Infrared Spectrum of the OH stretching vibration of methanol in acetonitrile as a function of Bu_4NI and $LiClO_4$ concentrations. Spectrum A represents the complex bands of methanol for a solution of Bu_4NI and methanol in acetonitrile. Spectra B, C, and D represent the complex bands of methanol for the same Bu_4NI-methanol solution except that $LiClO_4$ has been added to the solution. The concentration of $LiClO_4$ increases in the order B, C, D.

 and  

(iii) Assignment of the LiBr Complex Bands

In Figure 14, a similar analysis of the various possible band positions for the LiBr methanol complexes is presented. The 3450 cm^{-1} band can be attributed to complex D and E, the 3310 cm^{-1} band to complex F, and the 3200 cm^{-1} band to complex G. The effect of added $LiClO_4$ to a solution of Et_4NBr on the infrared spectrum of methanol in acetonitrile is summarized in Figure 15. The addition of $LiClO_4$ gives rise to a band at about 3200 cm^{-1} and no bands at lower frequencies. This observation allows us to assign the 3200 cm^{-1} band in the LiBr methanol spectrum to complex G. The band at 3310 cm^{-1}, as a consequence, can be assigned to complex F.

b. Assignment of the Complex Bands of Water and Heavy Water for NaI, LiI, and LiBr

The interpretation of the various complex bands for water and heavy water which involves the effects of both anion and cation can be rationalized in terms of similar arguments given for methanol. In this case, however, two bands will be involved for each ion-water complex.

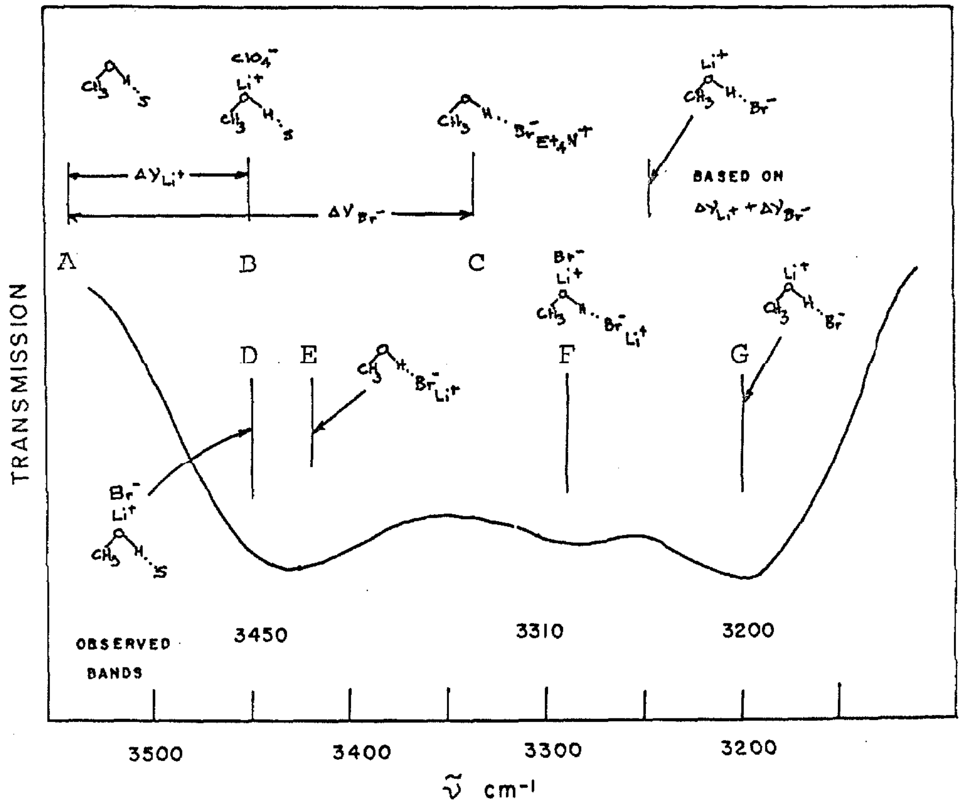


Figure 14. Band Assignments for the LiBr Complexes of Methanol

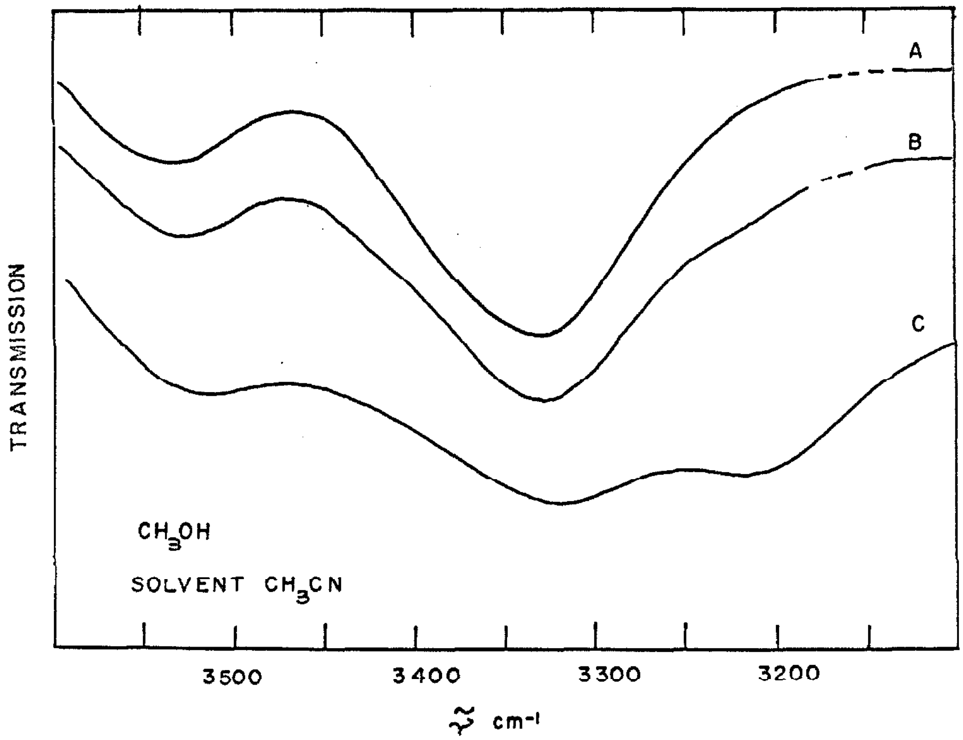


Figure 15. Infrared Spectrum of the OH Stretching Vibration of Methanol in Acetonitrile as a Function of Et_4NBr and $LiClO_4$ Concentrations

Spectrum A represents the complex bands of methanol for a solution of Et_4NBr and methanol in acetonitrile. Spectra B and C represent the complex bands of methanol for the same Et_4NBr-methanol solution except that $LiClO_4$ has been added to the solution. The concentration of $LiClO_4$ increases in the order B, C.

The two frequencies for the various complexes will depend upon the nature of the polarizing ion as well as on the symmetry of the complex. In the following, we shall consider the same complexes that were considered for methanol.

In the case of a symmetric ion-water complex, two bands corresponding to the symmetric and antisymmetric stretching vibrations of the water complex are expected. In view of the earlier results and discussions concerning frequency shifts for water reported in Part II, approximately equal low frequency shifts in both the symmetric and antisymmetric stretching vibrations would occur. The magnitude of this shift will depend on the nature of the polarizing ions.

In the case of an asymmetric ion-water complex, however, one band will appear to shift more so than the other. The magnitude of the shifts will also depend on the nature of the polarizing ions.

(i) Assignment of the NaI Complex Bands for Water and Heavy Water

In the case of NaI and H_2O in acetonitrile, two intense bands at 3580 cm^{-1} and 3438 cm^{-1} and two shoulders at 3495 cm^{-1} and 3370 cm^{-1} appear in the region of the OH stretch. In order to discuss the assignment of the various complex bands, it is convenient to refer to the previous band assignments for the perchlorate and tetraalkylammonium salts.

In Figure 16, a summary of the analysis of the possible band positions for the various NaI complexes of water is presented. In the case of complex D a pair of bands corresponding to the symmetric and antisymmetric stretch is expected at frequencies close to the observed frequencies for the cation-water complex of $NaClO_4$ represented by complex B. In the case of complex E, a pair of bands can be expected at frequencies close to the observed frequencies for the anion-water complex of Bu_4NI denoted by complex C. A slight shift in frequency can be expected due to a counter ion polarization effect of iodide by the sodium ion. The low frequency band which corresponds to the OH anion stretch is expected to shift to high frequency while the high frequency band corresponding to the OH·· solvent stretch shifts to lower frequencies. The shift in the high frequency OH··solvent band is expected to be quite small in view of the small shifts observed in this band for the different asymmetric anion water complex bands (*i.e.*, I^-, 3605 cm^{-1}; Br^-, 3615 cm^{-1}; and Cl^-, 3620 cm^{-1}). An approximate position for the OH··solvent band for complex G is rather difficult to determine, but its frequency will be less than the antisymmetric stretching frequency of complex D. In the case where the difference in force constant between the two OH stretching vibrations is large, the OH··solvent stretching band for complex G will be very close to the antisymmetric stretching frequency of complex D. The OH··solvent stretching band for complex F is expected to be close to the OH··solvent stretching band for complex G. A slight shift to low frequencies

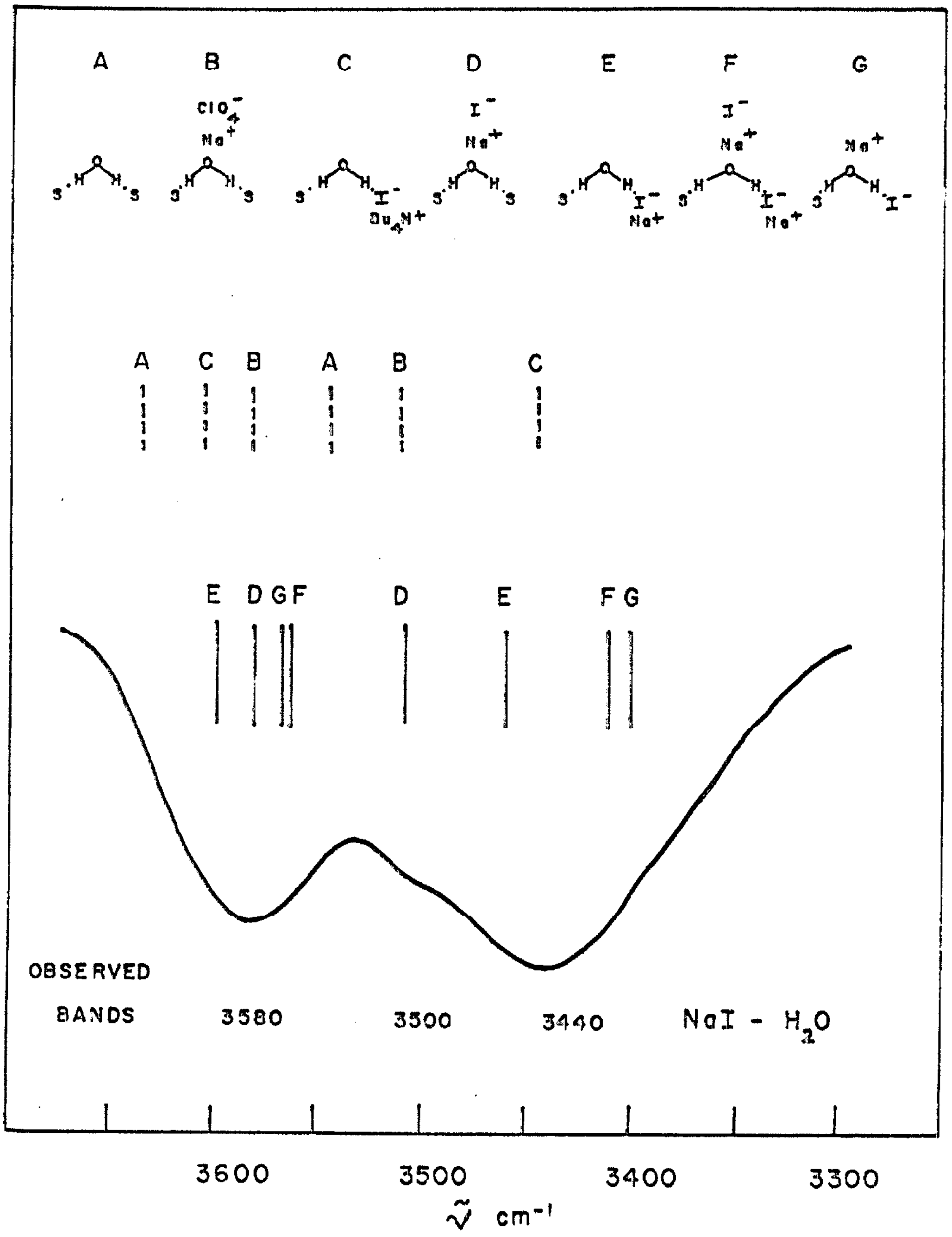


Figure 16. Band Assignments for the NaI complexes of H_2O. The dashed vertical lines represent the observed band maxima for the $NaClO_4$-H_2O and Bu_4NI-H_2O complex. The solid vertical lines represent the approximate band maxima for the various NaI complexes of H_2O. The solid curve represents the observed spectrum of NaI and H_2O in acetonitrile.

can be expected due to the effects of counter ion polarization of the iodide by the sodium ion. The OH anion stretching band for complexes F and G will appear at frequencies less than the observed frequency for the anion-water stretching vibration for the asymmetric anion-water complex of Bu_4NI.

In the following, we shall assume that the various ion complexes of water are the same as those for methanol. In this case, we can assign an approximate band position for F and G by looking for a band or shoulder at frequencies less than that assigned to the low frequency OH anion stretching vibration for the tetraalkylammonium-halide complex of water in the observed spectrum. For NaI, this assignment is rather difficult since no new band or shoulder appears at frequencies lower than the OH anion stretching vibration for the $Bu_4NI - H_2O$ complex. The large breadth of the 3440 cm^{-1} band, however, suggests that complex F and possibly complex G is present. For these reasons, we have assigned an approximate band position of 3400 cm^{-1} for complex G. In the case of complex F, the anion OH stretching vibration is expected to be close to the anion OH stretching frequency for complex G. A slight shift to higher frequencies can be expected due to counter ion polarization of iodide by the sodium ion.

Thus the assignment of the complex bands for H_2O appears to be straightforward.

In Figure 17, a summary of the analysis is given for the NaI complexes of D_2O. Since the analysis is the same as for H_2O, we shall not bother to restate the preceding

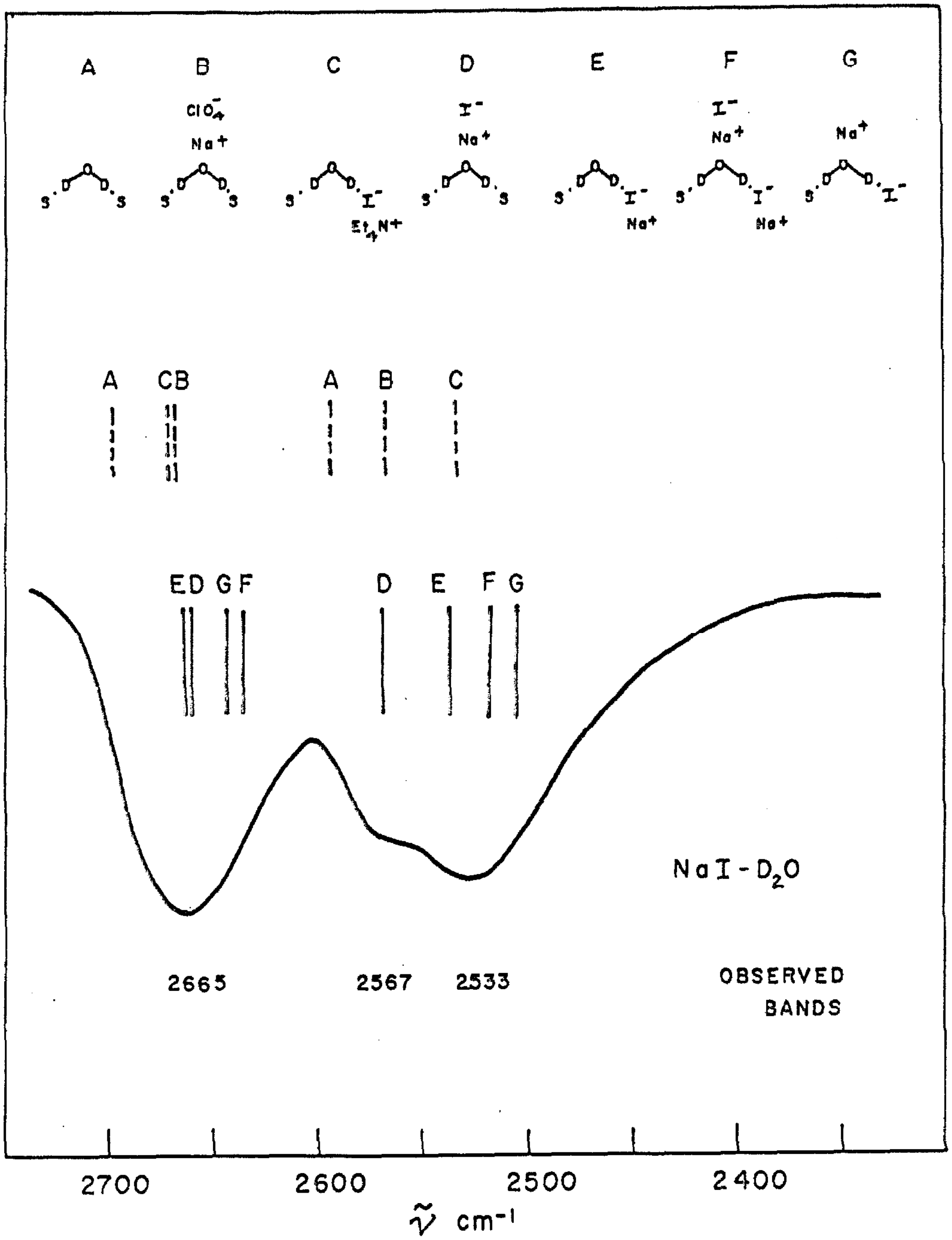


Figure 17. Band assignments for NaI complexes of D_2O. The dashed vertical lines represent the observed band maxima for the $NaClO_4$-D_2O and Bu_4NI-D_2O complex. The solid vertical lines represent the approximate band maxima for the various NaI complexes of D_2O. The solid curve represents the observed spectrum of NaI and D_2O in acetonitrile.

arguments. For D_2O in acetonitrile, the 2665 cm^{-1} band can be assigned to at least three unresolved bands due to the antisymmetric stretch of complex D and the OH solvent stretch of complexes E, F, and possibly G. The shoulder at 2570 cm^{-1} corresponds to the symmetric stretch of complex D, and the band at 2535 cm^{-1} consists of the two unresolved bands corresponding to the OH anion stretching vibration of complexes E and F. Since the OH anion stretching vibration of complexes F and G are expected to be relatively close to one another, it is not possible to determine the existence of complexes G and F from the experimental data. The large breadth of the 2533 cm^{-1}, however, does provide some evidence for the existence of either F or G or both.

(ii) Assignment of the LiI Complex Bands for Water and Heavy Water

In Figure 18, a similar analysis of the various possible band positions for the water complexes of LiI is presented. The prediction of the complex band spectra is complicated by the fact that the band positions for the various LiI complexes of water are all relatively close to one another. In this case, one very broad asymmetric band in the region from 3650 cm^{-1} to 3350 cm^{-1} could be observed with a band maximum at about 3500 cm^{-1}. Depending on the relative amounts of each complex, their intensities, and band widths the spectrum will change. Even

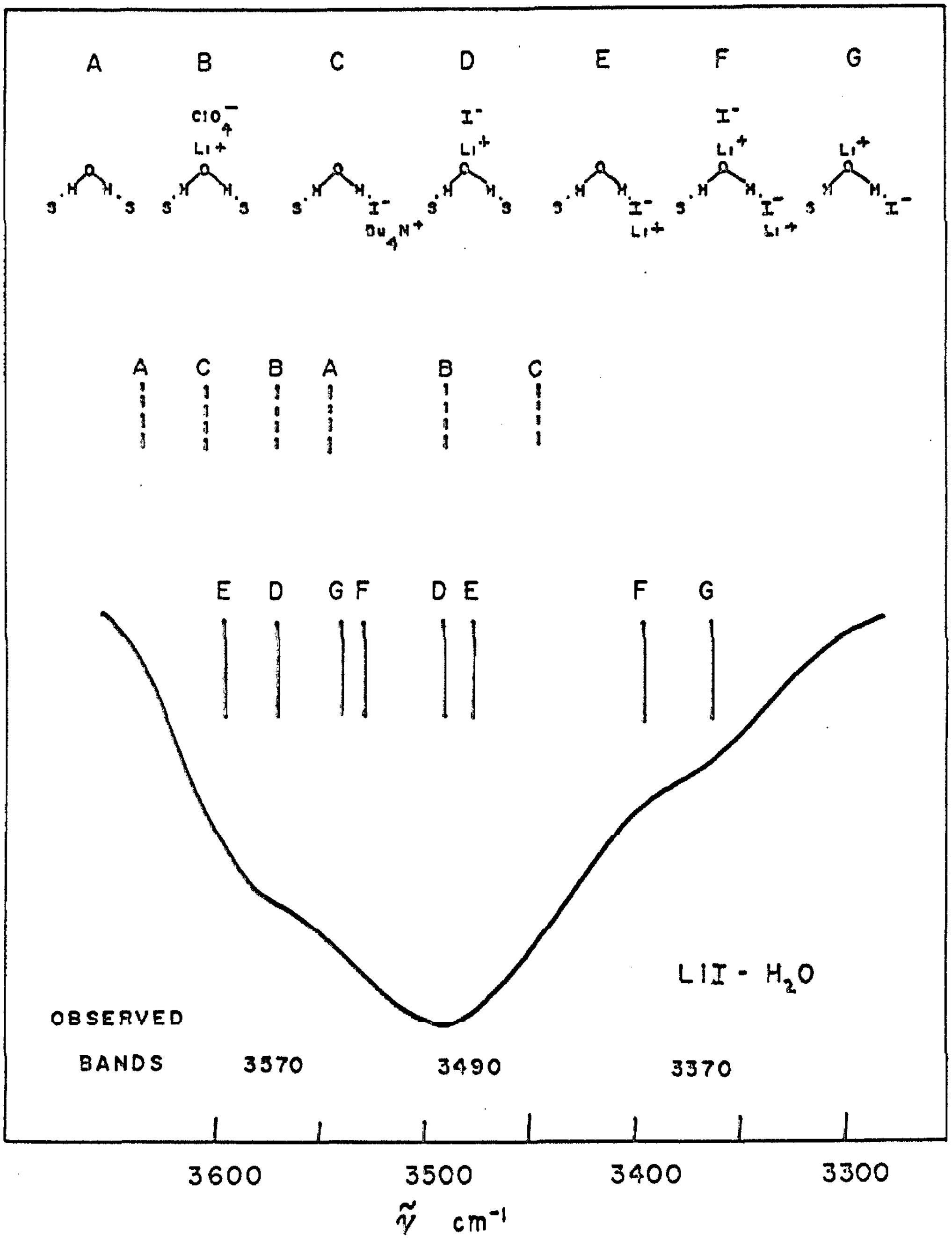


Figure 18. Band assignments for the LiI complexes of H_2O. The dashed vertical lines represent the observed band maxima for the $LiClO_4$-H_2O and Bu_4NI-H_2O complex. The solid vertical lines represent the approximate band maxima for the various LiI complexes of H_2O. The solid curve represents the observed spectrum of LiI and H_2O in acetonitrile.

under the "best conditions", however, only shoulders are expected in view of the relatively even frequency distribution in the band positions for the various LiI complexes of water.

The observed spectrum of the LiI water complexes consists of a broad asymmetric band centered at about 3483 cm^{-1} with two shoulders at about 3570 cm^{-1} and 3370 cm^{-1}. In view of the earlier methanol studies where evidence was given for the probable existence of both complexes F and G, we have assigned the shoulder at 3370 cm^{-1} to the OH anion stretching vibration of complexes F and G. The shoulder at 3570 cm^{-1} can be assigned to the antisymmetric stretching vibration of complex D and the OH···solvent stretching vibration of complex E. The band maximum at 3483 cm^{-1} is due essentially to the symmetric stretch of complex D and the OH anion stretch of complex E. The presence of complexes F and G can be expected to give rise to a band centered at about 3535 cm^{-1} which would correspond to the OH solvent stretching vibration in F and G. For relatively low salt concentration, however, the concentration of these complexes is expected to be small in comparison to complex D. In this case, these bands would not be observed as a result of the strong overlapping between the bands of complexes E and D.

In Figure 19, a similar analysis of the various possible band positions for the LiI complexes of D_20 is presented. In this case, the expected band positions for the various LiI complexes of D_20 are such that three band maxima may be observed. The observed spectrum consists

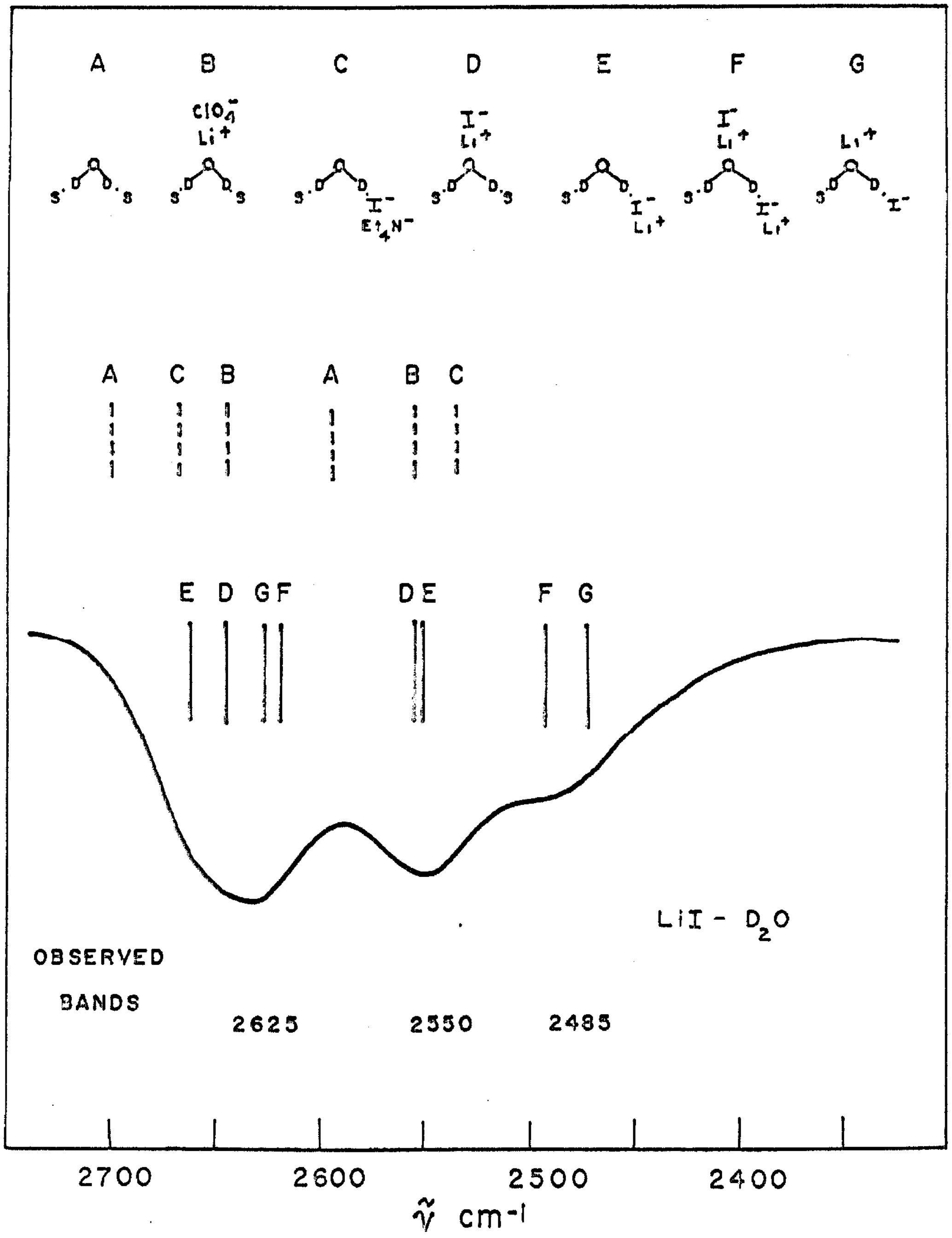


Figure 19. Band assignments for the LiI complexes of D_2O. The dashed vertical lines represent the observed band maxima for the $LiClO_4$-D_2O and Bu_4NI-D_2O complex. The solid vertical lines represent the approximate band maxima for the various LiI complexes of D_2O. The solid curve represents the observed spectrum of LiI and D_2O in acetonitrile.

of two distinct bands (band maximum: 2625 cm^{-1} and 2550 cm^{-1}) and a shoulder at about 2485 cm^{-1}. The observed band at 2625 cm^{-1} can be assigned to the four unresolved bands due to the antisymmetric stretch of complex D and the OH solvent stretching vibration of complexes E, F, and G. The band at 2550 cm^{-1} is a result of two strongly superimposed bands due to the symmetric stretching vibration of complex D and the OH anion stretching vibration of complex E. The shoulder at 2485 cm^{-1} can be assigned to the OH anion stretching vibration of complexes F and G.

(iii) Assignment of the LiBr Complex Bands for Water and Heavy Water

In Figure 20, a summary of the analysis of the various possible band positions for the water complexes of LiBr is presented.

The observed spectrum consists of two shoulders at 3570 cm^{-1} and 3240 cm^{-1} and two maxima, one at 3500 cm^{-1} and the other at 3350 cm^{-1}. The shoulder at 3570 cm^{-1} can be assigned to the antisymmetric stretching vibration of complex D and the OH solvent stretching vibration of complexes E, F, and G. The band maxima at 3500 cm^{-1} can be assigned to the symmetric stretch of complex D and the OH anion stretching vibration of complex E. In view of the earlier methanol studies where evidence was given for the probable existence of both complexes F and G for LiBr, we have assigned the shoulder at 3240 to the OH anion stretching vibration of complex G and the band maxima at

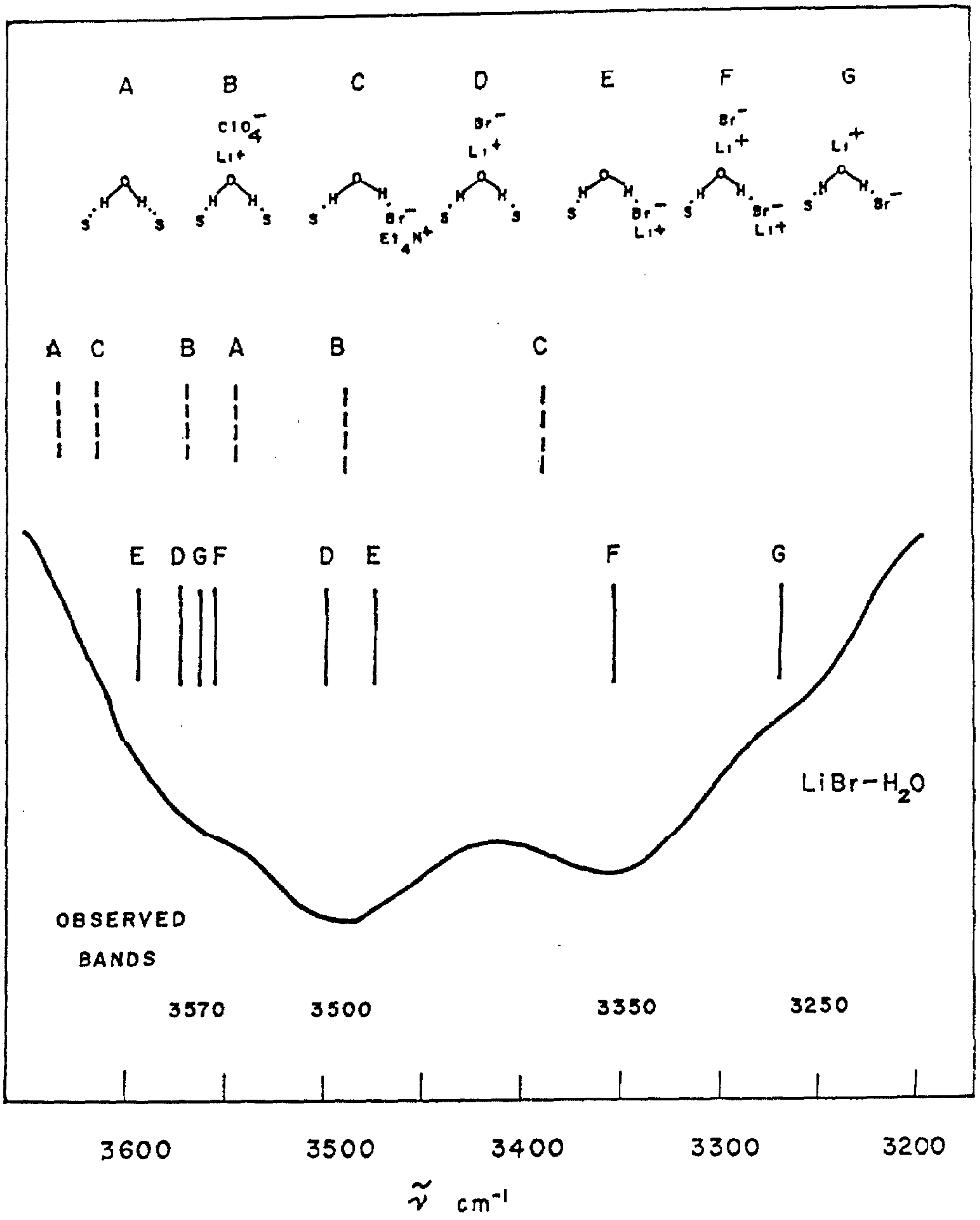
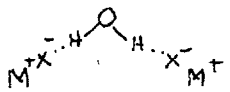


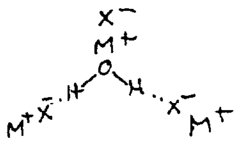
Figure 20. Band assignments for the LiBr complexes of H_2O. The dashed vertical lines represent the observed band maxima for the $LiClO_4$-H_2O and Et_4NBr-H_2O complex. The solid vertical lines represent the approximate band maxima for the various LiBr complexes of H_2O. The solid curve represents the observed spectrum of LiBr and H_2O in acetonitrile.

3350 cm^{-1} to the OH anion stretching vibration of complex F.

In Figure 21, a similar analysis of the various possible band positions for the LiBr complexes of D_2O is presented. The observed spectrum consists of three band maxima of 2635 cm^{-1}, 2553 cm^{-1}, and 2482 cm^{-1} with a shoulder at about 2400 cm^{-1}. In this case, the band maximum at 2635 cm^{-1} can be assigned to the antisymmetric stretching vibration of complex D and the OH solvent stretching vibration of complexes E, F, and G. The band maximum at 2553 cm^{-1} consists of two strongly superimposed bands due to the symmetric stretching vibration of complex D and the OH anion stretching vibration of complex E. The band at 2482 can be assigned to the OH anion stretching vibration of complex F and the shoulder at 2400 cm^{-1} to the OH anion stretching vibration complex G.

As mentioned previously in Part II, other possible ion-water complexes at high salt concentrations must be considered. These complexes will be of the type where both solvent molecules in the hydrogen-bonded water complex are replaced by an anion, *i.e.*,





At the salt concentrations investigated, however, the concentration of these additional water complexes can be expected to be small so that their contributions to the over-all spectral features will be small.

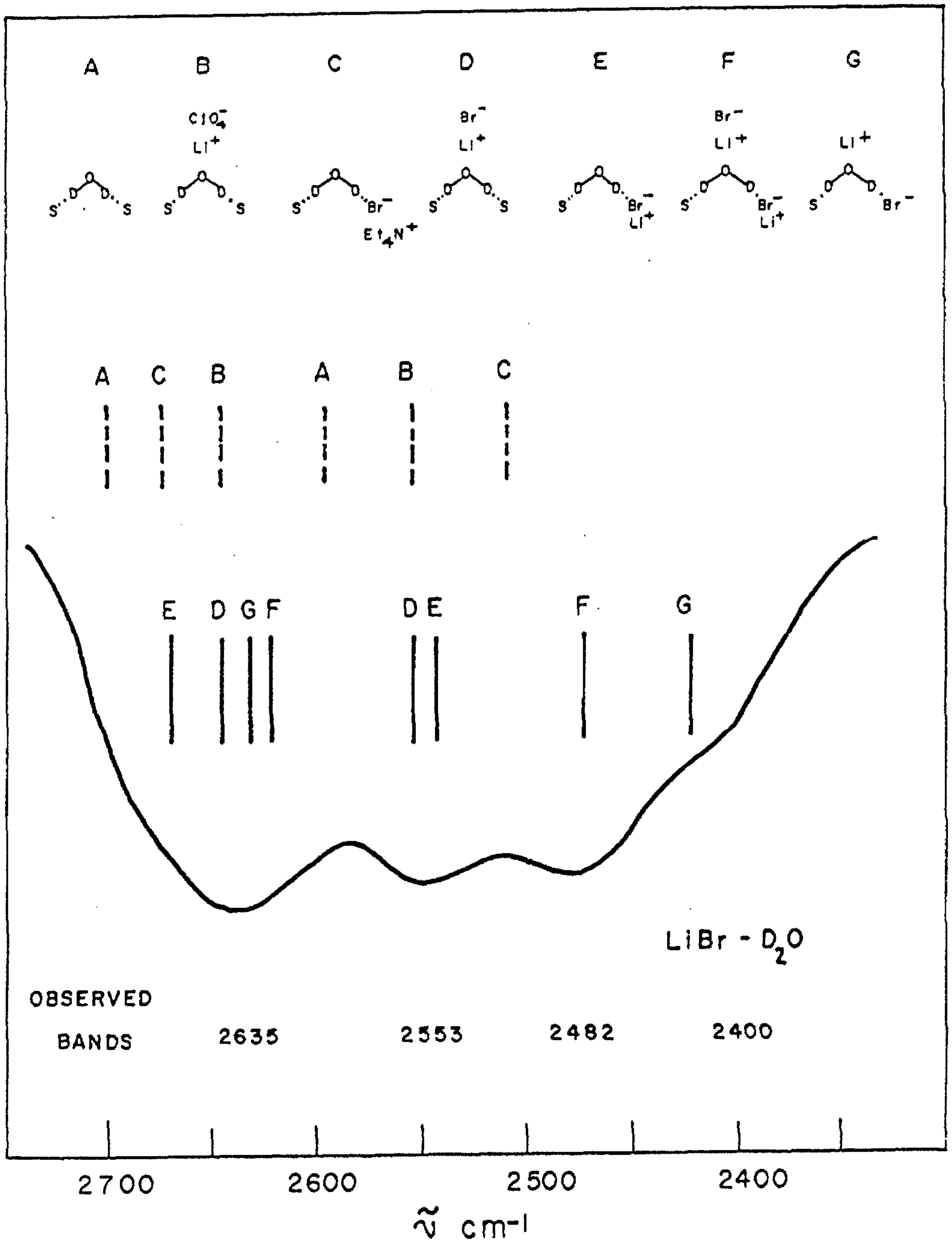


Figure 21. Band assignments for the LiBr complexes of D_2O. The dashed vertical lines represent the observed band maxima for the $LiClO_4$-D_2O and Et_4NBr-D_2O complex. The solid vertical lines represent the approximate band maxima for the various LiBr complexes of D_2O. The solid curve represents the observed spectrum of LiBr and D_2O in acetonitrile.

D. PROTON MAGNETIC RESONANCE STUDIES

In section C, the results obtained from the infrared spectroscopic study on the OH stretching vibration were reported and discussed for the various ion complexes of water and methanol in acetonitrile. The study has contributed much towards the understanding of the various ion water complexes in an aprotic solvent and on the nature of the polarizing ions. The determination of quantitative information concerning the details of the polarization effected by the various ions is, however, rather difficult to obtain due to the large extent of band overlapping. Even in the case where only one band is involved, it is still difficult to determine an accurate value for the transition frequency for the OH fundamental stretch due to the large band widths which are characteristic of the hydrogen-stretching vibration in hydrogen-bonded systems.

In this section, we wish to report the results of a proton magnetic resonance study on the polarization of water and methanol effected by NaI, LiI, and LiBr in an aprotic solvent. The chemical shifts of the OH proton(s) were studied as a function of both salt and water concentrations. In constrast to the earlier infrared studies where frequency shifts cannot be accurately determined, the chemical shifts obtained from the proton resonance studies can be measured to an accuracy of at least a few parts per million.

1. Results

a. Electrolyte Shifts

The electrolyte shifts for water polarized by LiI and LiBr in acetone and acetonitrile are summarized in Figures 22, 23, 24, and 25. The data for LiBr in methanol in acetonitrile are summarized in Figure 26. The electrolyte shift data for NaI are summarized in Appendix 1 for water in acetone and acetonitrile.

b. Polarization Shifts

The electrolyte shifts extrapolated to infinite dilution of water (polarization shifts) reported as a function of the salt concentration are summarized in Figure 27 for water and methanol in acetonitrile and for water in acetone in Figure 28.

2. Analysis of the Polarization Shifts

a. Water and Methanol in Acetonitrile

The polarization shifts for water and methanol in acetonitrile by NaI, LiI, and LiBr can be interpreted in terms of the sum of the polarization effected by the various ion water or methanol complexes. In the following, we shall consider these complexes:

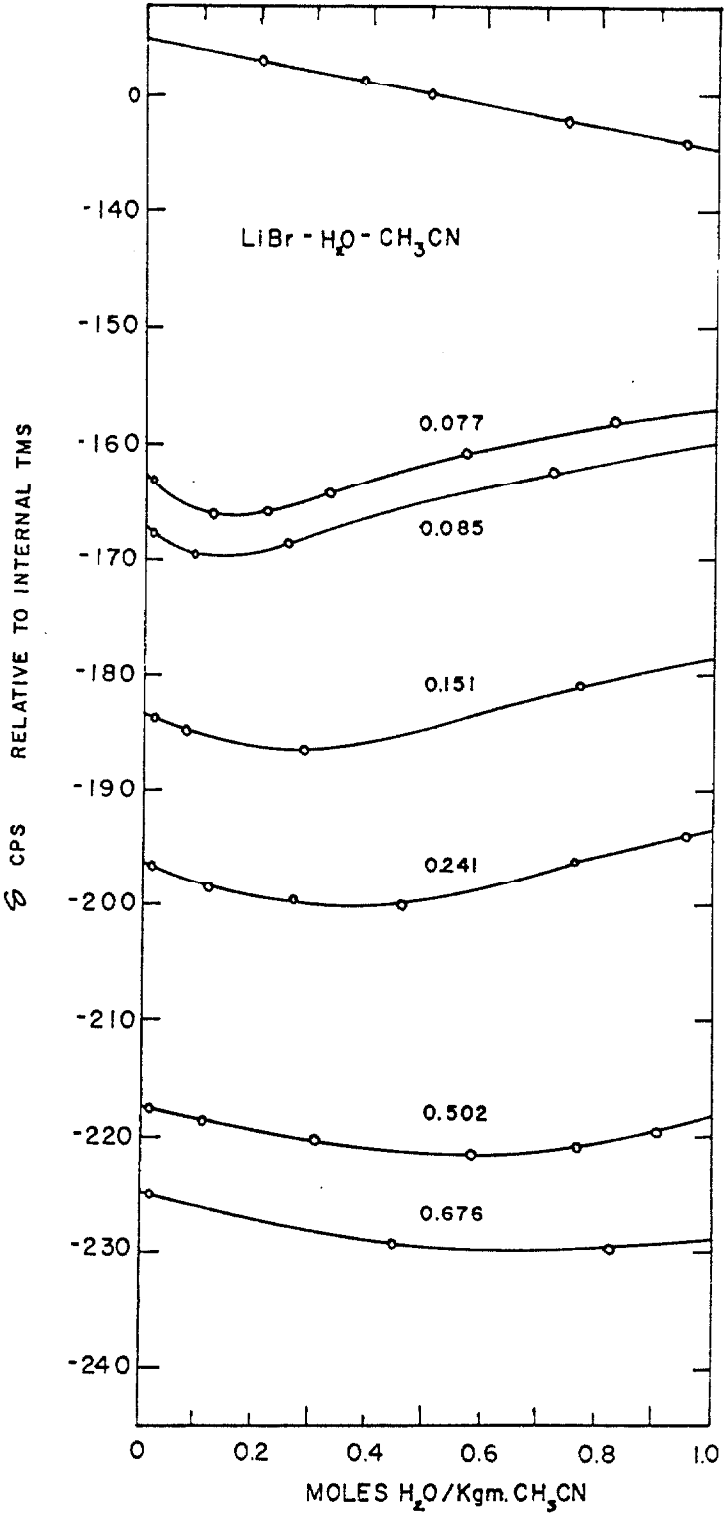


Figure 22. Electrolyte Shift Curves for LiBr and H_2O in Acetonitrile

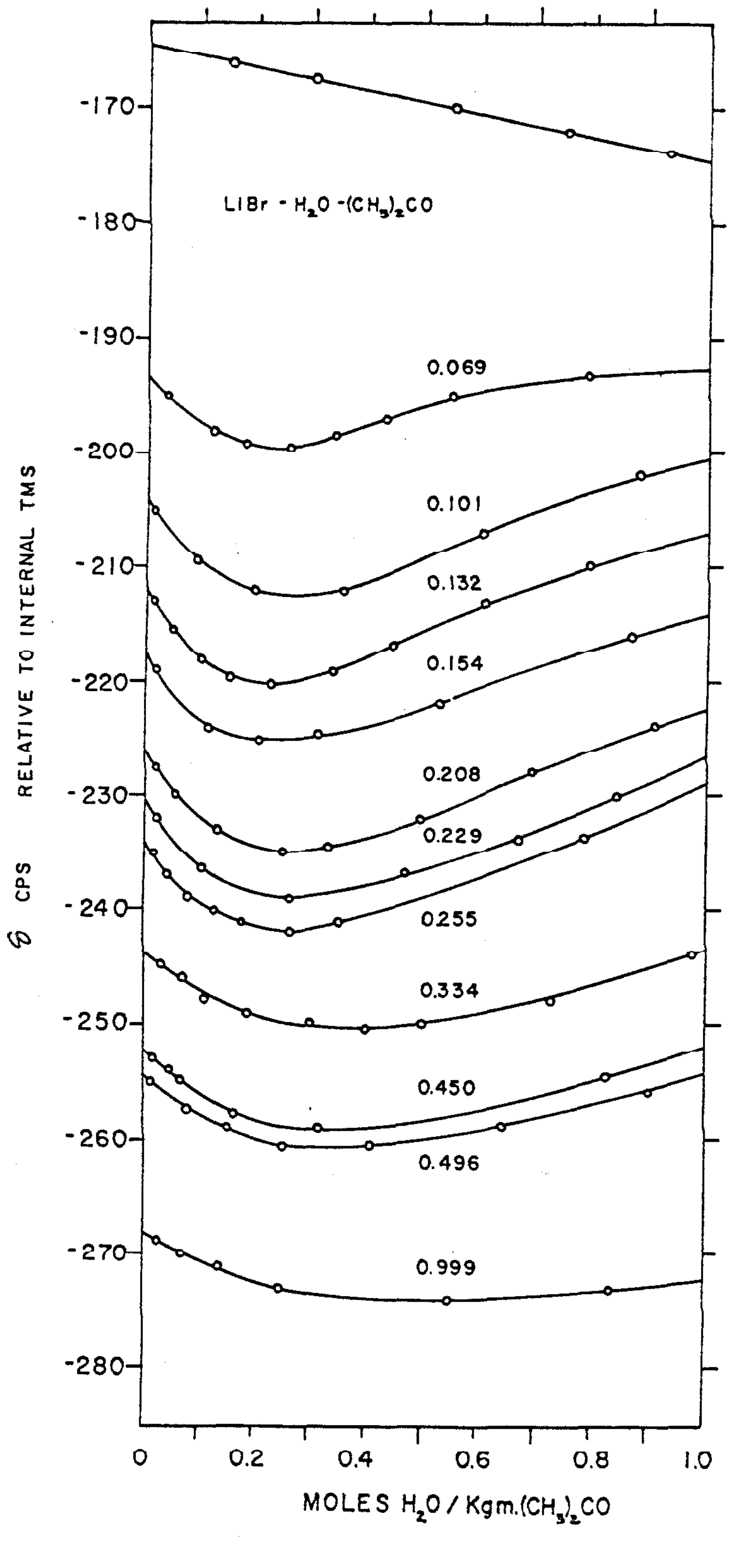


Figure 23. Electrolyte Shift Curves for LiBr and H_2O in Acetone

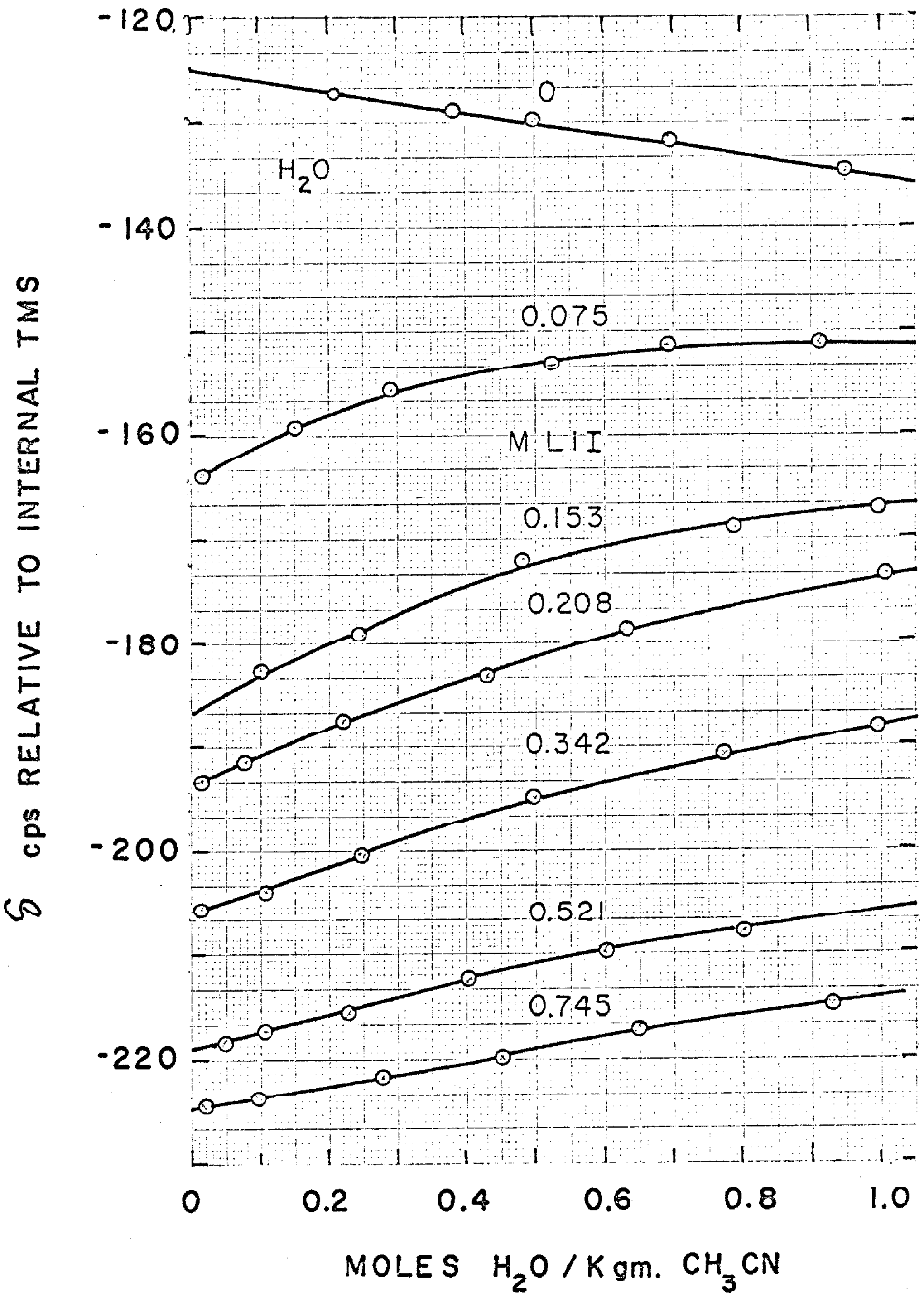


Figure 24. Electrolyte shift curves for LiI and H_2O in acetonitrile.

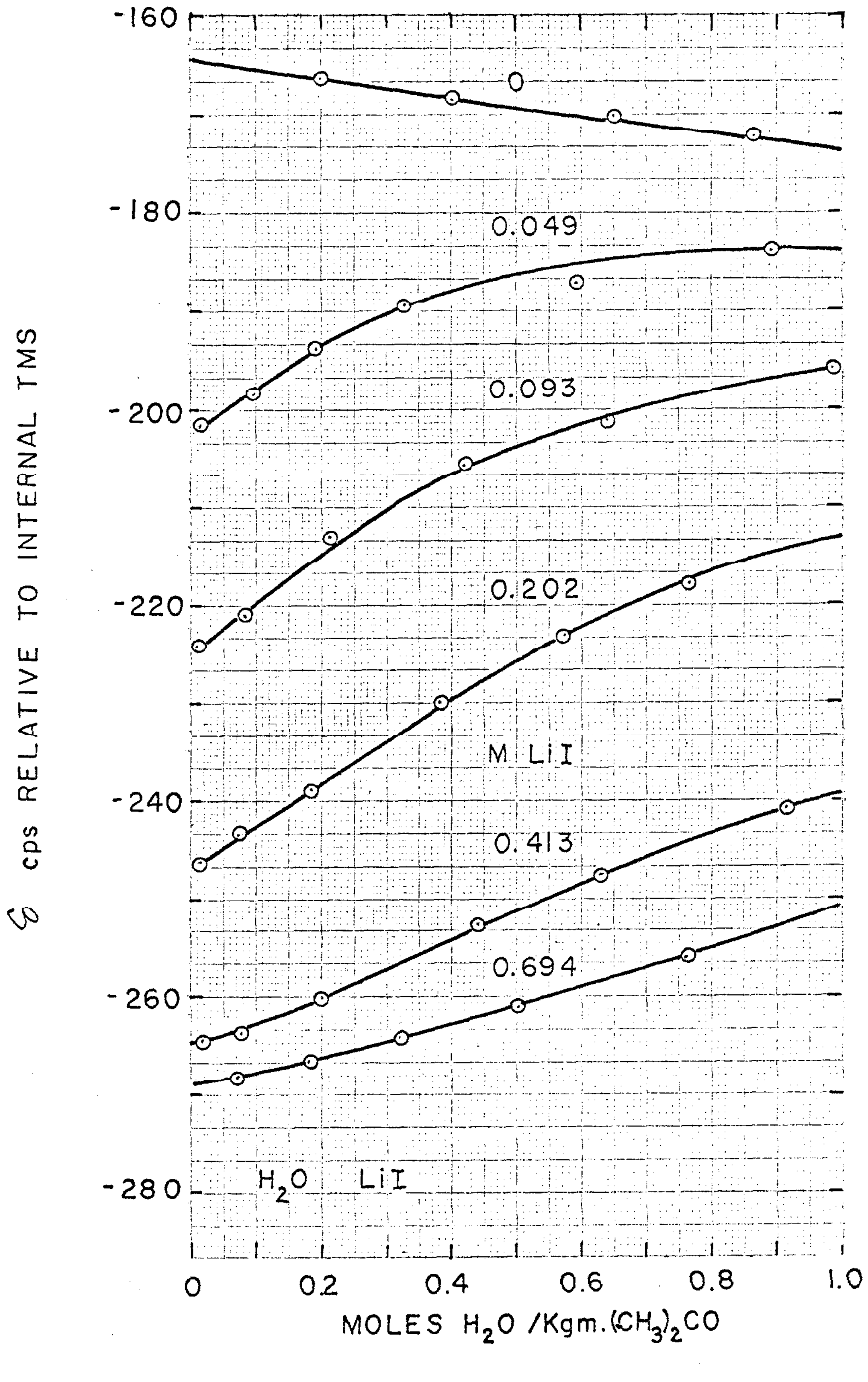


Figure 25. Electrolyte shift curves for LiI and H_2O in acetone.

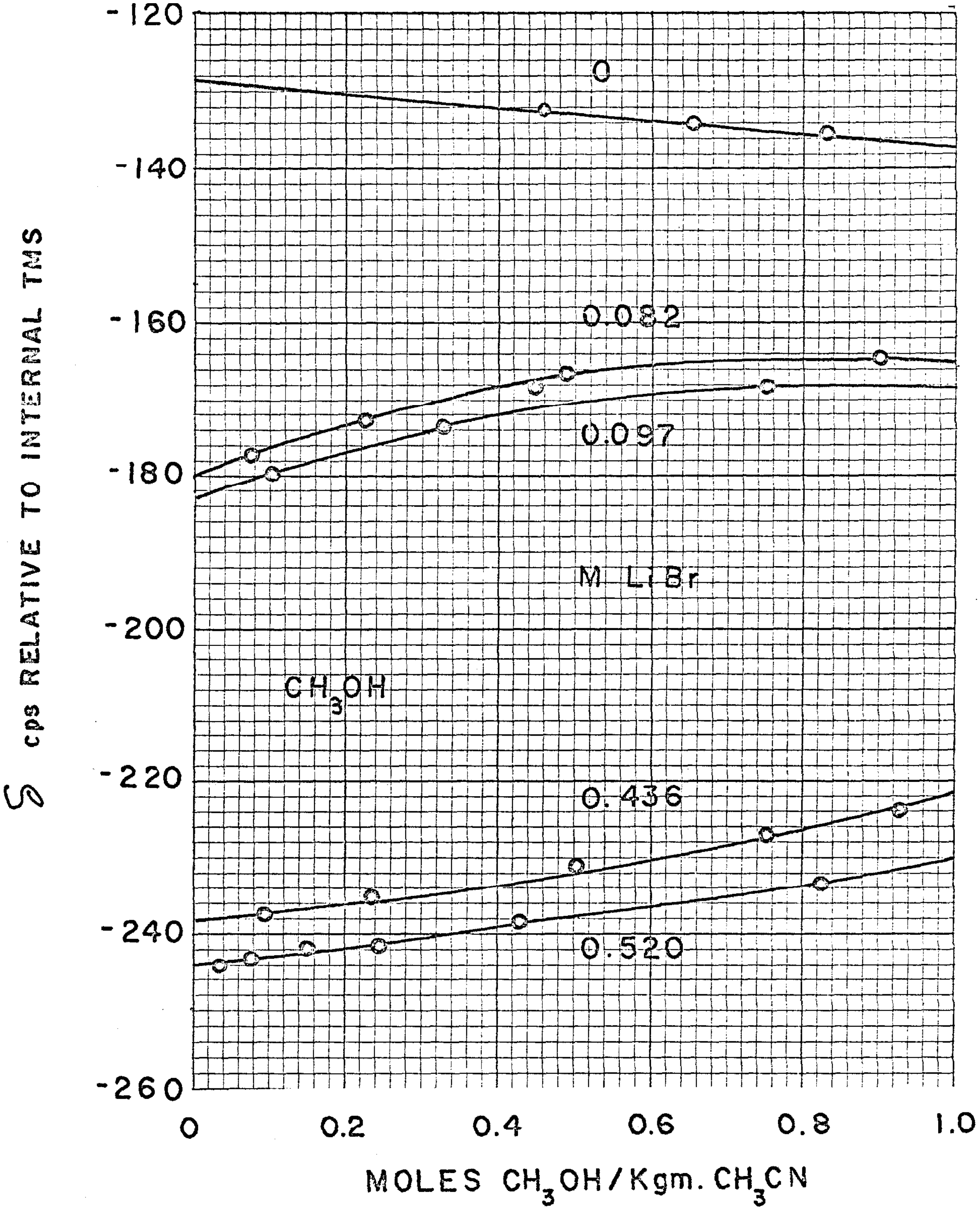


Figure 26. Electrolyte shift curves for LiBr and CH_3OH in acetonitrile.

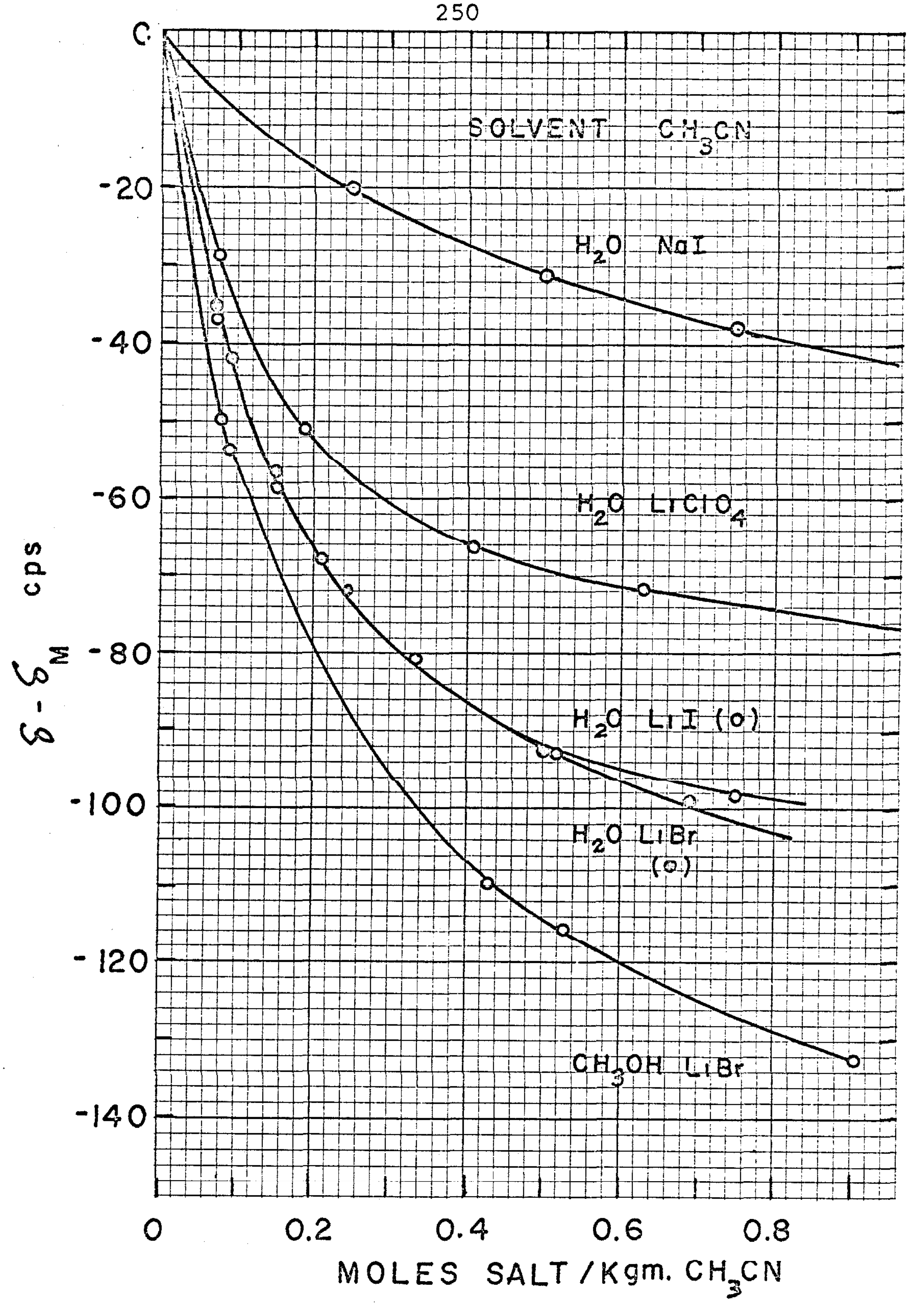


Figure 27. Polarization curves for water in acetonitrile for NaI, LiI, and LiBr and for methanol in acetonitrile for LiBr.

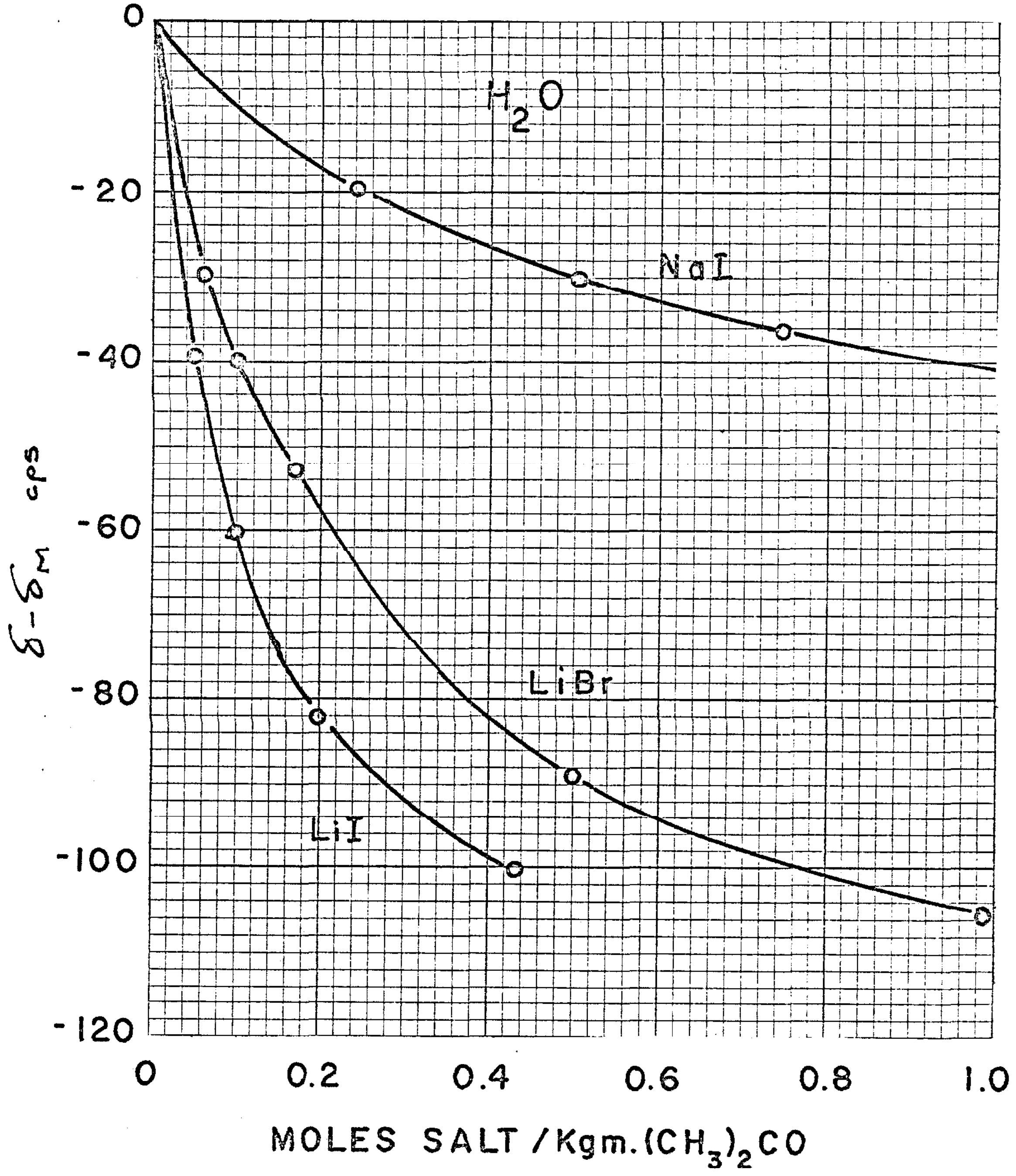
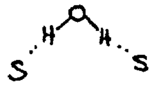
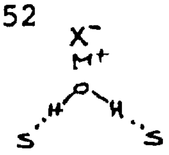
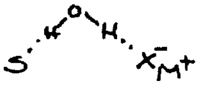
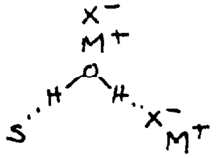


Figure 28. Polarization curves for water in acetone for NaI, LiI, and LiBr.

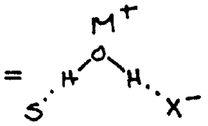
A =


B =


C =


D =


and

E =


The formation of these complexes is given by the following equilibria:

$$A + M^+X^- \overset{K_B}{\rightleftarrows} B \tag{1}$$

$$A + M^+X^- \overset{K_C}{\rightleftarrows} C \tag{2}$$

$$A + M^+X^- \overset{K_E}{\rightleftarrows} E \tag{3}$$

$$B + M^+X^- \overset{K_D}{\rightleftarrows} D \tag{4}$$

$$C + M^+X^- \overset{K_D'}{\rightleftarrows} D \tag{5}$$

In the limit of rapid exchange (exchange of water molecules from one environment to another), the chemical shielding constant is:

$$\sigma = \sigma_A f_A + \sigma_B f_B + \sigma_C f_C + \sigma_D f_D + \sigma_E f_E \tag{6}$$

where σ_A, σ_B, σ_C, σ_D, and σ_E are the shielding constants for the water protons in the various water complexes and f_A, f_B, f_C, f_D, and f_E are the equilibrium fraction of complexes in solution. If we take the hydrogen bonded to the solvent monomer A as reference, the chemical shift can be written as:

$$\delta \text{ (relative to A)} = \delta_B f_B + \delta_C f_C + \delta_E f_E + \delta_D f_D \tag{7}$$

so that

$$W\delta = \delta_B [B] + \delta_C [C] + \delta_E [E] \delta_D [D] \tag{8}$$

where W is the total water concentration and [B], [C], [D], and [E] are the equilibrium concentrations of complexes B, C, D, and E. The equilibrium concentration of each complex is given by:

$$[B] = K_B [M^+X^-] [H_2O] \tag{9}$$

$$[C] = K_C [M^+X^-] [H_2O] \tag{10}$$

$$[E] = K_E [M^+X^-] [H_2O] \tag{11}$$

$$[D] = (K_D K_B + K'_D K_C) [H_2O] [M^+X^-]^2 \tag{12}$$

The equilibrium water and solvated ion pair concentrations can be expressed in terms of the total salt and water concentrations and are given by:

$$m = [M^+X^-] + [H_2O][M^+X^-](K_B + K_C + K_E) + 2[H_2O][M^+X^-]^2 (K_D K_B + K'_D K_C) \tag{13}$$

and

$$W = [H_2O] (1 + [M^+X^-](K_B + K_C + K_E) + (K_D K_B + K'_D K_C) [M^+X^-]^2 \tag{14}$$

In the limit of infinite dilution of water $[M^+X^-] \approx m$.

In this case, the chemical shift is given by:

$$\delta = \frac{(\delta_B K_B + \delta_C K_C + \delta_E K_E) \; {}_m + \delta_D (K_B K_D + K_C K_D') \chi_m^2}{1 + {}_m (K_B + K_C + K_E) + (K_D K_B + K_D' K_C) \chi_m^2} \tag{15}$$

where χ_m is the salt mole fraction, and the K's are mole fraction equilibrium constants.

For cases where K_C, K_E, K_D, and K_D' or where δ_C, δ_E, and δ_D' are small, the preceding expression for δ reduces to:

$$\delta = \frac{\delta_B K_B \chi_m}{1 + K_B \chi_m} \tag{16}$$

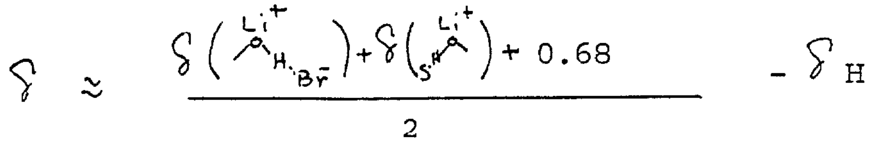
which is the expression used to analyze the earlier polarization shifts reported in Part I.

This interpretation is reasonable in view of the small K's and δ's for the perchlorate or tetraalkylammonium water complexes.

For NaI, LiI, and LiBr, however, these K's and δ's are not expected to be so small that these additional contributions to the chemical shift can be neglected. The interpretation of the observed chemical shifts at infinite dilution, therefore, must include the contributions which arise from the different ion water complexes.

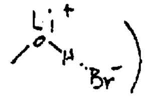
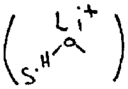
The quantitative partitioning of the observed shifts in terms of the separate ion water complex contributions is clearly desirable but rather difficult to obtain since there is no way at the present time to determine the actual K's and δ's for all of the water complexes in question. An approximate estimate of the separate ion water complex contributions can be obtained, however, by estimating values for K and δ for each complex.

In Table 1, a summary is given for the approximate K's and δ's for the various ion complexes of NaI, LiI, and LiBr for water and methanol in acetonitrile. Values for K and for the perchlorate salts of Na^+ and Li^+ reported in Part I can be used to estimate values for δ_B and K_B. For K_C (Br^-), an upper limit can be obtained from the previous results obtained from the Et_4NBr-water complex. Since the effects of counter ion polarization are not small in the case of the anion LiBr water complex, the actual K will be somewhat smaller. The same will be true for the chemical shift. A value for K_C (I^-) is rather difficult to obtain since the shifts effected by Bu_4NI on water are extremely small. This suggests that both K and δ are small for the iodide water complex. In the case of the anion complexation of NaI and LiBr, the effect of counter ion polarization is expected to make K and δ even smaller. A value of $K_C = 20$ was used to estimate the contribution from complex C with a δ_C of -20 cps for LiI and $K_C = 25$ and $\delta_C = -25$ cps for NaI. The formation constant for complex E is also difficult to estimate. Some preliminary calculations based on the resulting values of $\delta_{obs.}$ obtained for different values of K_E suggest that K_E (LiI) is greater than K_E (LiBr) which is reasonable in view of the greater electrostatic interaction between Li^+ and Br^- relative to Li^+ and I^-. In the calculations we have used a value of $K_E(LiI) = 60$ and $K_E(LiBr) = 30$. Approximate values for the chemical shift for complex E can be obtained by calculating the electric field at the proton produced by the cation and solvent as well as the anion. The chemical shift for complex E relative to the water monomer (hydrogen-bonded to the solvent) is given approximately by:



$$\delta \approx \frac{\delta\left(\overset{\mathrm{Li^+}}{\diagup\mathrm{O}\diagdown_{\mathrm{H}\cdots\mathrm{Br^-}}}\right)+\delta\left(\overset{\mathrm{Li^+}}{_{\mathrm{S}\cdots\mathrm{H}}\diagup\mathrm{O}\diagdown}\right)+0.68}{2} - \delta_H$$

where 0.68 represents the solvent magnetic anisotropic contribution, and δ_H is the polarization shift of the water monomer relative to water (gas). Values for

δ () and δ () can be calculated from

$$\delta = -k_E E_{//} - 0.75 E^2$$

where E represents the total field at the proton due to the cation and anion for one case and the cation and the solvent for the other. $E_{//}$ is the parallel component of the total field. In the calculations we have used a value of -2.9×10^{-12} for the linear electric field coefficient. The resulting values are $\delta_E(LiBr) = -170$ cps and $\delta_E(LiI) = -140$ cps. To a first approximation, $K_D \gtrsim K_C$ and $K_D' \gtrsim K_B$ so that $(K_BK_D + K_CK_D') \gtrsim 2\,K_BK_C$. For

δ_D and a value slightly lower than δ_E was used to estimate the chemical shift in order to account for the effect of counter ion polarization.

Similar arguments and calculations were made to obtain estimates for K and δ for ion complexes of methanol.

In Table 2, a summary is given for the approximate K's and δ's for the various ion complexes of NaI, LiI, and LiBr for water and methanol in acetonitrile.

TABLE 2

H_2O	K_B K'_D	K_C K_D	K_E	δ_B	δ_C	δ_E	δ_D
NaI	37	25	5	- 46	- 25	- 80	- 70
LiI	120	20	60	- 94	- 20	-140	-130
LiBr	120	40	30	- 94	- 30	-160	-140
CH_3OH							
NaI	40	20	5	- 35	- 85	-120	-115
LiI	60	15	60	-108	- 80	-180	-170
LiBr	60	35	30	-108	-110	-200	-180

In Figure 30 a comparison is made between the calculated polarization shifts based on the approximate constants summarized in Table 1 for the polarization of water in acetonitrile effected by LiI and LiBr and for methanol in acetonitrile effected by LiBr.

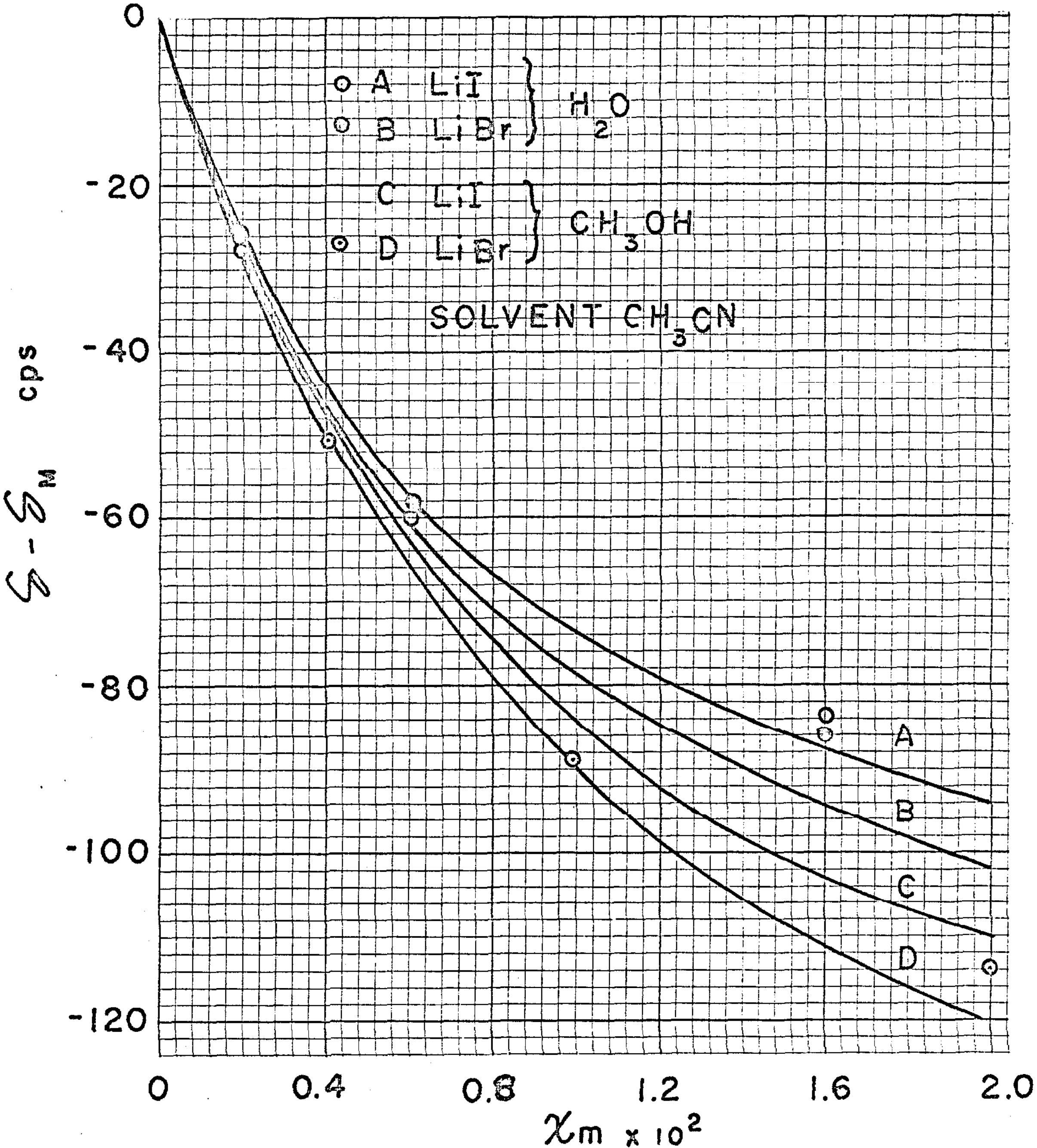


Figure 30. Comparison between calculated and experimentally determined polarization shifts for CH_3OH and H_2O for LiI and LiBr in acetonitrile. A, B, C, D represent the calculated curves, and the circles represent the experimental data.

In Figure 31, a comparison is made between the calculated and observed electrolyte shifts at infinite dilution of water and methanol for NaI in acetonitrile.

The interpretation of the infinite dilution shifts for water polarized by NaI, LiI, and LiBr in acetone will not be made at this time. Additional studies (such as an investigation of the infrared spectrum of the OH stretching vibration of water in acetone in the presence of these salts) are desirable before the chemical shifts can be adequately interpreted.

3. Discussion of Electrolyte Shifts

As previously mentioned, the analysis of the infinite dilution shifts forms one aspect of the general problem on the study of ion-ion and ion-solvent or solute interactions. The electrolyte shifts reported in this work represent a comprehensive study of the variation in the chemical shift of water as a function of both water and salt concentrations. These shifts represent an average over all the various complexes of water (water-ion complexes, water monomers, water-water dimers, higher order ion-water solvated complexes, etc.) As a consequence, the analysis of the shifts over the entire range studied is considerably more complicated than the analysis of the electrolyte shifts at infinite dilution of water. The extension of the discussion presented for the analysis of the infinite dilution shifts to include additional complexes (such as water-water dimers, higher order ion-water associa-

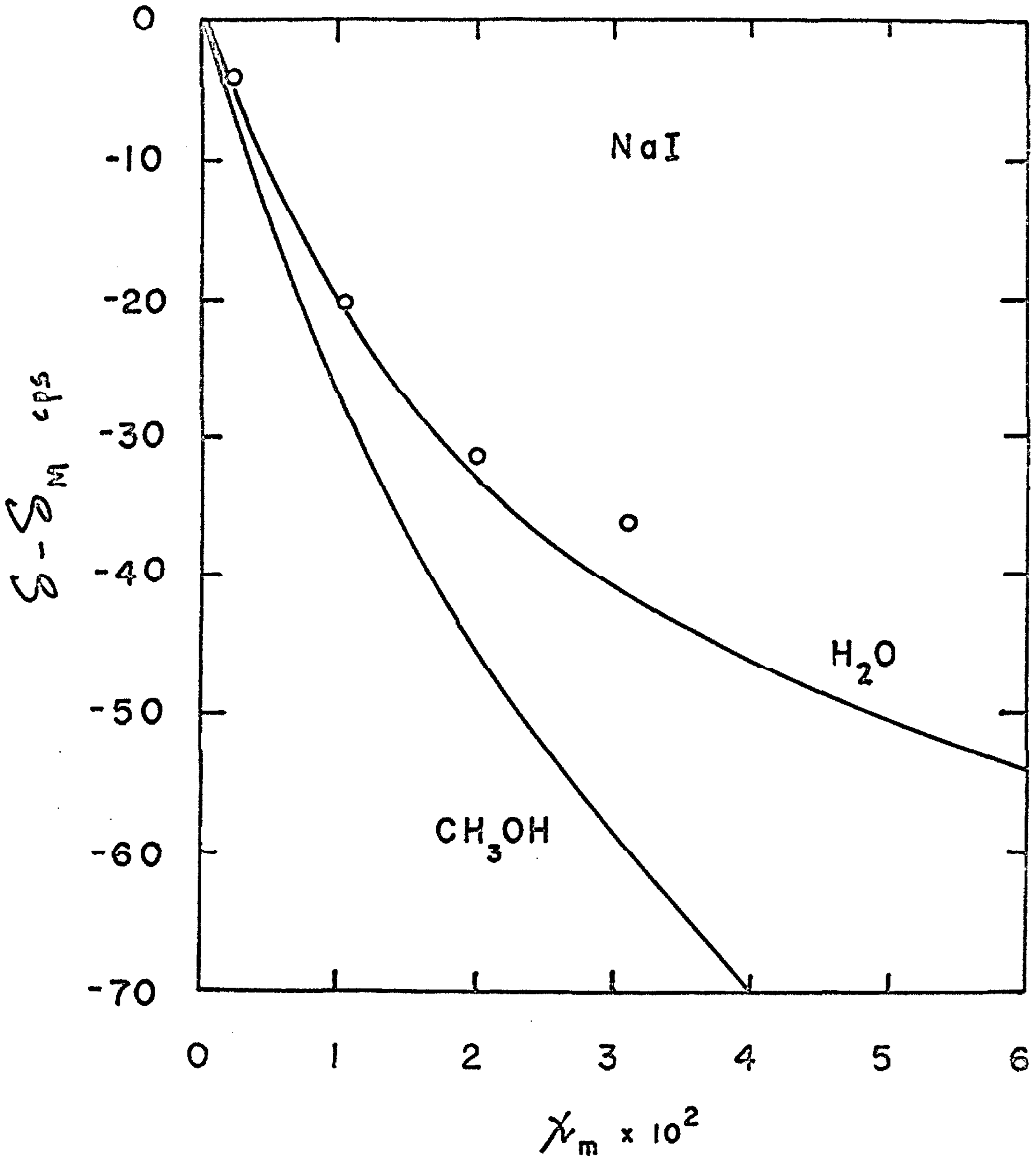


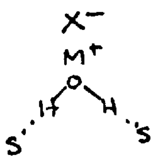
Figure 31. Comparison between calculated and experimentally determined polarization shifts for H_2O and NaI in acetonitrile. The solid curve represents the calculated polarization shifts. The circles represent experimental data. A calculated curve for CH_3OH and NaI in acetonitrile is also presented.

tion complexes, etc.) is straightforward in principle, but the amount of necessary bookkeeping does not warrant such an analysis at the present time.

There is one feature in the electrolyte shift curve which is worth noting. For all of the salts investigated in this work, the electrolyte shift curves are such that the shift at infinite dilution of water is the largest shift observed for any given salt concentration with the exception of LiBr in acetone and in acetonitrile. For this salt a dip in the electrolyte shift curve occurs at low water concentrations (Figures 22 and 23). No dip was observed for LiBr solutions of methanol in acetonitrile. The reason for this observation is not yet completely understood but probably results from the association of more than one molecule of water to an ion pair. Whether or not a dip will be observed will depend upon the magnitude of the various complex formation constants and the chemical shifts of the various ion-water complexes. Despite the complexity of this problem it is hoped that work will be initiated in the near future to analyze the electrolyte shifts for at least low water concentrations.

4. Summary

In this part, we have reported and discussed the results obtained from an infrared and proton magnetic resonance study on the polarization of water and methanol by various diamagnetic salts where both cation and anion complexation occurs. In the analysis of the infinite dilution shifts we have considered contributions to the chemical shift from the following species:



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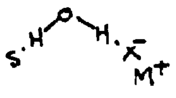
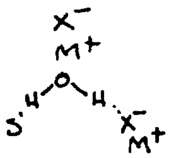


E



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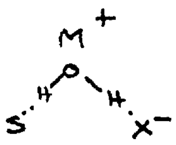
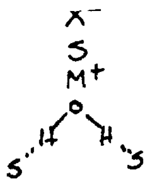


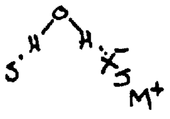
G

since the infrared data have indicated the probable existence of complexes of the types of structures given above.

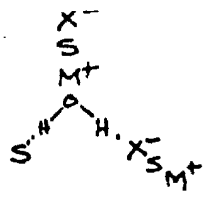
The earlier electrical conductance studies by Savedoff (1), however, have indicated the possible existence of an ion pair of the type M$^+$SX$^-$, where M$^+$SX$^-$ represents an ion pair separated by one solvent molecule. In this case, there will be other ion-water complexes such as:



H



I



J

Since the observed electrolyte shifts depend on the chemical shifts of each ion-water complex in solution and its concentration, it is necessary to know the structure of the various ion complexes of water as accurately as possible. To illustrate the importance of these additional complexes, we shall consider the equilibrium between the solvated water monomer, M$^+$SX$^-$, and complex H.

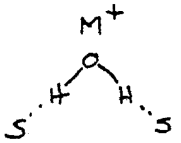
The concentration of this complex is $[H] = K_H [H_2O][M^+SX^-]$. The concentration of M^+SX^- can be expressed in terms of M^+X^- since

$$M^+X^- + S \underset{}{\overset{K'_s}{\rightleftharpoons}} M^+SX^-$$

so that

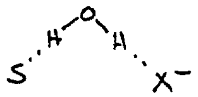
$$[H] = K_H\ K_s\ [H_2O][M^+SX^-].$$

One can generalize to single ion-water complexes of the type



K

and



L

and rule out the importance of these complexes in the concentration range of interest since the ion pair dissociation constants are on the order of 10^{-4}. A reasonable estimate of $K_s = K'_s [S]$ is 10^{-2} so that the total concentration of single cation-water complexes is

$$[D] + [H] + [K] = \left\{(K_D + 10^{-2}K_H)[M^+X^-] + 10^{-2}K_K[M^+X^-]^{\frac{1}{2}}\right\}[H_2O].$$

Since K_D K_H K_K, the contribution to the chemical shift from complexes H and K can be ignored. Similar arguments can be presented for complexes I, J, and L.

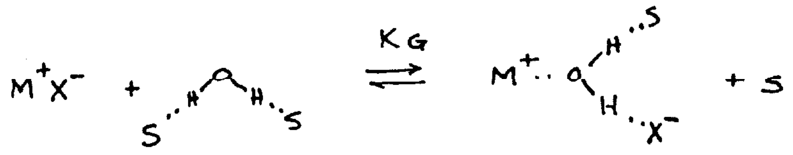
The observed chemical shift as a result of complexes D, E, F, G, H, I, and J relative to the hydrogen-bonded water monomer is:

$$W\delta = \left\{ (\delta_D K_D + \delta_E K_E + \delta_G K_G) + (\delta_H K_H + \delta_I K_I)\ K_s \right\} [M^+X^-][H_2O]$$
$$+ 2\left\{ (K_D K_E \delta_F) + (K_H K_I \delta_J)\ K_s^2 \right\} [M^+X^-][H_2O]$$

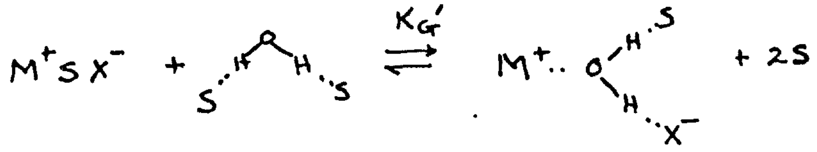
On the basis of the preceding discussion, we would expect that complexes H, I, J, K, L, and M are all relatively unimportant in the estimation of the chemical shift over the concentration range of interest. If these conclusions were not the case, one might observe species of the type given by H, I, and J in the infrared spectrum since the effect of counter ion polarization in these complexes is small. While the results in the case of NaI and LiBr do not enable us to make any conclusions, the results for LiI suggest that complexes of the type given by complex I and L are relatively unimportant.

It is important to note that the infrared studies can distinguish differences between complexes of the type given by F and G, but they cannot distinguish differences between complexes of the type given by J and G.

The formation of complex G probably proceeds via the contact ion pair, i.e.,



as well as by solvent displacement, i.e.,



In this case, the total concentration of G is given by:

$$[G] = [H_2O][M^+X^-]\ (K_G + K_sK_G').$$

This expression shows the importance of the insertion of the water molecule in the contact ion pair and is in agreement with the earlier results obtained by Olson and Konecny (2) on the variation of the ion pair dissociation constant for LiBr in acetone in the presence of small amounts of water.

E. APPENDIX

Table of Electrolyte Shifts

$NaI/H_2O/(CH_3)_2CO$

(Shifts relative to CH_3 of solvent)

3.556 M H_2O

M NaI	δ
0	-68.0
0.071	-68.8
0.101	-70.2
0.748	-80.6
1.185	-83.5
1.868	-85.8
2.197	-87.0
2.583	-87.7

0.914 M H_2O

M NaI	δ
0	-46.8
0.109	-54.2
0.501	-69.5
1.014	-78.4
1.150	-80.3
1.916	-83.5

2.513 M H_2O

M NaI	δ
0	-58.0
0.441	-73.0
0.900	-79.5
1.300	-82.8
2.071	-85.8

NaI/H_2O/CH_3CN

(Shifts are relative to CH_3 of solvent)

0.992 M H_2O

M NaI	δ
0.2651	-29.5
0.5554	-39.8
0.7114	-43.7
1.431	

1.467 M H_2O

M NaI	δ
0.214	-28.5
0.558	-39.8
0.923	-46.2
0.973	-47.5
1.054	-48.0

2.237 M H_2O

M NaI	δ
0.250	-34.0
0.463	-39.5
0.846	-47.0
1.21	-48.5

F. REFERENCES

1. L.G. Savedoff, J. Am. Chem. Soc., 88, 664 (1966).
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Proposition I

It is proposed that the U.V., visible, and IR absorption spectra of some transition metal ions be investigated in various aprotic solvents in order to obtain information concerning the strength of the ligand field in transition metal solvent complexes.

The absorption spectra (U.V., visible, and IR) of transition metal ions in aqueous solution have already received considerable attention (1,2).

There are several aspects of the general problem concerning the nature of complex formation in solutions which warrants attention. Until recently, it seemed sufficient to establish the number of metal ions and the ligands (other than solvent molecules) in a complex in solution. It is being increasingly realized, however, that the solvent molecules in the coordination spheres of complex species in solution are of no less importance than that of the other ligands in determining their physical and chemical properties (3). The symmetry of complexes formed in solution depends on the properties of the transition metal and ligands as well as that of the solvent.

Recently, more emphasis is being placed on various transition metal complexes in nonaqueous solvents (4). For this reason, it is important that information concerning the complex formation of various transition metal ions in these nonaqueous solvents be known.

It is proposed that the U.V., visible, and IR absorption spectra of a series of transition metal ions be investigated in various aprotic solvents in order to obtain information concerning the strength of the ligand field in these transition metal-solvent complexes.

It is to be noted that a number of transition metal ions in aprotic solvents have already been investigated (4), but in most cases no quantitative information concerning ligand field strengths was obtained.

A preliminary study of the complexation of acetone, acetonitrile, dimethylsulfoxide, and benzonitrile to Ni (II) has been made.

Previous investigators have studied the nickel (II) complex of H_2O (5), NH_3 (6), and dimethylsulfoxide (6-9). In the nickel (II) complex of H_2O and NH_3, the crystal field splitting parameter $\Delta = 10$ Dq was estimated to be 8,500 and 11,500 cm^{-1}, respectively (5). No value was reported for DMSO.

The coordination chemistry of nickel (II) is of reasonable complexity in which species of square planar, tetrahedral, and octahedral symmetries are found (4).

Ni (II) has a d^8 configuration. In water Ni (II) is thought to form the octahedral high spin $Ni(H_2O)_6^{++}$ complex (5).

With the d^8 configuration in the ground state, a considerable Jahn-Teller distortion is expected (5). This distortion is so great that Ni (II) can form characteristic four coordinated low spin complexes (5).

The spectra of the four coordinated low spin Ni (II) complexes are however, quite different from the Ni (II) high spin octahedral complexes. For this reason, it is relatively simple to decide on what type of complex one has by comparing the absorption spectra of the unknown complex with one whose configuration is already known (10).

In this preliminary study, the absorption spectra of the Ni (II) complexes of acetone, acetonitrile, dimethylsulfoxide, and benzonitrile are all like the high spin Ni $(H_2O)_6^{++}$ complex spectra. For this reason, the preliminary data obtained thus far have been interpreted in terms of the high spin d^8 octahedral configuration.

The theoretical aspects of the d^8 octahedral configuration have already been discussed by Orgel (11), Tanabe and Sugano (12), Jorgensen (5,10) and others.

The free ion states of Ni (II) in terms of the usual spectroscopic notation are ^1S, ^1D, ^1G, ^3P, and ^3F. In the presence of a crystal field, all of the singlet and triplet terms become split with the exception of the ^1S and ^3P terms. The labeling of the levels according to how their wavefunctions transform under the symmetry operations of the O_h group is given in Table 1.

TABLE 1

$^1S \longrightarrow {}^1A_{1g}$

$^1G \longrightarrow {}^1T_{1g}$, $^1T_{2g}$, ^1E_g, and $^1A_{1g}$

$^3P \longrightarrow {}^3T_{1g}$

$^1D \longrightarrow {}^1T_{2g}$, ^1E_g

$^3F \longrightarrow {}^3T_{1g}$, $^3T_{2g}$, and $^3A_{2g}$

A schematic energy diagram for some of the levels of a d^8 ion in a ligand field of O_h symmetry is given by Orgel (11) as a function of the crystal field splitting parameter Dq and is illustrated in Figure 3. The vertical lines (this study) represent the variation in the crystal field splitting for the various solvent complexes of Ni (II).

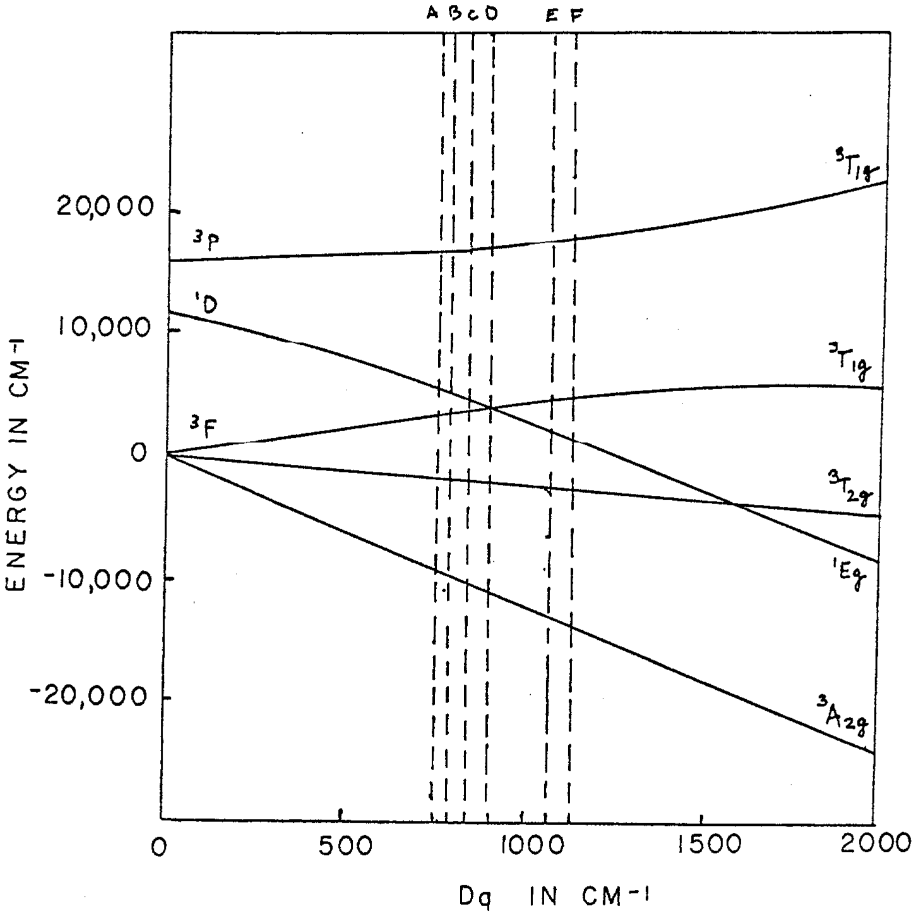

Figure 3. Energy Diagram for Ni (II) Octahedral Symmetry $Ni(S_6)^{++}$ Complex. Reference (11)

In Table 2, the various band positions for anhydrous Ni $(ClO_4)_2$ in acetone, acetonitrile, dimethylsulfoxide, benzonitrile, water, and ammonia are summarized. (All spectra were recorded on a Cary model 14 spectrometer using 1 cm cells).

TABLE 2

Band Positions in mμ

	$^3T_{1g}$(P)	^1E_g(D)	$^3T_{1g}$(F)	$^3T_{2g}$(F)
Acetone	405	665	780	
DMSO	420	775	690	
Water	400	655	720	
C_6H_5CN		620	720	1025
CH_3CN	372	715	610	
NH_3	368	780	600	

The crystal field splitting Δ = 10 Dq (cm^{-1}) can be obtained approximately from Figure 3. These values are summarized in Table 3.

TABLE 3

	Solvent	Δ (cm^{-1})
A	Acetone	7,600
B	DMSO	8,000
C	Water	8,500
D	C_6H_5CN	9,100
E	CH_3CN	10,750
F	NH_3	11,500

The values for water and ammonia were previously reported (5).

The extent of the crystal field splitting depends on several factors which includes the nature of the transition metal ion as well as the ligand.

From an electrostatic point of view, it is clear that ligands with a large negative charge and those that can approach the metal ion closely should provide the greatest crystal field splitting. Since the crystal field splitting arises from a strong interaction of the ligands with orbitals that point directly between them and a weak interaction with those that point in between, molecules (such as ammonia or acetonitrile) should produce greater crystal field splittings than water or acetone. This appears to be the case for the solvents studied.

It is proposed that other solvents (such as various alkyl cyanides, pyridine, dimethylformaide, dioxane, tHf, methanol) be studied. A series of substituted benzonitriles, substituted pyridines, and NH_2OH, CH_3NOH, etc. would also be interesting.

Similar studies concerning other transition metal ions in these solvents would also be of interest.

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PROPOSITION II

Studies Concerning the Effects of Various Guanidinium Salts on the Toxicity of Clostridium Botulinum Toxin (A)

This proposition is concerned with the effects of various guanidinium salts on the toxicity of Clostridium Botulinum toxin, type A.

The behavior of urea as a denaturing agent for Cl. Botulinum toxin is well known. In some cases, guanidine (G) has been used as the denaturant. The concentration at which guanidine detoxifies the protein, however, is much lower than the concentration required by urea (1). In the presence of 6 M urea, the toxin rapidly loses its toxicity. Within 15 minutes, the specific activity (LD_{50}/mg T) is reduced to less than 5% of the original activity. For guanidine similar results are observed at 4 M (1).

Because of the fact that urea and guanidine have different "critical" concentrations, it was of interest to see if any noticeable effects on the detoxification of Cl. Botulinum toxin (type A) could be observed for various guanidinium salts.

A preliminary study of this subject was done approximately 6 years ago (2). No conclusions were drawn at that time, but the results although qualitative were striking. The following salts were investigated: guanidinium hydrochloride, sulfate, adipate, oxalate, benzoate, thiocyanide, and D,L and meso tartarate. Guanidine benzoate was found to have the most noticeable effect, detoxifying at less than 0.8 M, while the addition of guanidine sulfate was found not to have any effect on the toxicity of the solution even up to saturation molalities. The rest of the compounds varied considerably as far as the critical concentration is concerned. Conventional biological methods were used to determine the relative toxicity by injecting small amounts of the prepared solution into laboratory animals and determining the specific activity.

In retrospect, this preliminary study was perhaps not the study to do. It is well known that certain compounds (such as oxalic acid) can themselves be lethal to animals. Thus, by measuring the toxicity in the above manner, we have not necessarily determined the protein toxicity. It is a necessary requirement to determine the effects of each of the various solutions in the absence of the toxin as well as for the toxin-salt solutions.

Cl. Botulinum toxin (type A) is a globular protein with a molecular weight of about 1×10^6. It is known that in the case of urea addition at 6 M, where the specific activity is less than 5% of the original activity the primary structure of the protein is broken down. The average molecular weight of the urea-toxin solutions determined by ultracentrifuge studies was 22,500 indicating considerable denaturization (3).

Since this information clearly indicates an alternate approach to the study of toxicity, the following experiment is proposed. Solutions of the toxin are to be prepared in which the salt concentration for various guanidinium salts is varied. A "relative" toxicity for the protein can be obtained by analysis of the molecular weight composition of the various solutions. (We assume that denaturization of the primary structure of Cl. Botulinum will occur at some salt concentration for some of the guanidinium salts). If intermediate molecular weights are obtained which are above 22,500, these solutions will have to be checked by the bioassay approach.

Concurrent studies with various K^+ or Na^+ salts of the anions used with guanidine must also be made so that specific anion-protein interactions can be eliminated or considered. At present, it is likely that the guanidinium ion is the species responsible for denaturization and hence detoxification, but anion effects have not yet been ruled out.

Such studies when compared with previous bioassay results concerning toxin-salt solutions should reveal any inadequacies in the former approach if contradictory results are obtained. The bioassay study of toxin-salt solutions combined with studies concerning guanidine salt solutions in the absence of the toxin should, however, be meaningful. It is especially important to determine any correlation between defragmentation and toxicity. The present proposal should lend information concerning this point.

After the results have been obtained, one is faced with the problem of explaining the results. We assume for the moment that different critical concentrations will be found for the various guanidinium salts. Studies concerning guanidine-anion association come immediately to mind since association of these ions would be expected to hinder the effectiveness of the guanidinium ion as denaturant.

Freezing point measurements as well as electrical conductance measurements are standard approaches to the problem of ion association. Early studies should be concerned with these methods since no data are available concerning the association of various anions with the guanidinium ion in aqueous solutions.

It is also possible to study relaxation times and line broadening of the N^{14} nuclear magnetic resonance in the various guanidinium solutions. The change in the electrical asymmetry at the nitrogen nucleus in $C^{+}(NH_2)_3$ caused by strong ion-ion interactions should manifest itself in a line broadening of the nuclear resonance due to the interaction of the quadrupole moment with the gradient of the asymmetric field at the nitrogen nucleus. Consequently, a line broadening or a shortening of the relaxation time is equivalent to the inference of an interaction on the part of the guanidinium ion by anion.

Measurements of the line width may not prove to be as profitable as one might hope for since the nitrogen resonances are usually quite broad to start out with, and one might not see the desired effect. This method is especially plagued with problems concerning saturation, magnetic field inhomogenuities, etc.

More fruitful results can perhaps be obtained by use of recently developed spin echo techniques for the measurement of spin lattice and spin-spin relaxation times. Experiments can be performed in which ion-ion interactions can be monitored by studying relaxation time changes for various guanidinium salts in the solid state as well as for aqueous solutions.

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Proposition III

Calculation of the Ground State Paramagnetic Contribution to the Proton Magnetic Shielding Constant in H_2O

Calculations on the proton magnetic shielding constant for water have been presented by Das and Ghose using a localized LCAOMO function (1). They obtain for $(\sigma^{P}_{AVE})_{G}$ a value of -64.2 ppm. By using the Hellman-Feynman theorem, one can evaluate this term without a knowledge of the ground state wavefunction. The value calculated here is -71.7 ppm. Within the limits of accuracy of the Hellman-Feynman theorem, $(\sigma^{P}_{xx})_{G}$ calculated using the LCAOMO function is 40% low and $(\sigma^{P}_{zz})_{G}$ is 21% high.

The Hamiltonian for a molecule in a magnetic field is given by:

$$\mathcal{H} = \frac{1}{2m}\sum_{k}\left(\vec{p}_k - \frac{e}{c}\vec{A}_k\right)^2 - \vec{\mu}_I\cdot\vec{H}_0 + V(\vec{r}_k) \qquad (1)$$

where $\vec{p}_k$ is the momentum vector operator for the k^{th} electron; $\vec{A}_k$, the magnetic vector potential; $\vec{\mu}_I$, the magnetic dipole moment of the nucleus; $\vec{H}_0$, the external magnetic field; and $V(\vec{r}_k)$, the electrostatic potential.

The expression for the components of the shielding tensor can be obtained by considering the energy proportional to μH_0 using the Hamiltonian given above. If one uses a variational wavefunction given by $\psi = \psi_0 + \vec{H}_0\cdot\vec{\psi}_1$, the expression for $\sigma_{\nu\lambda}$ can easily be shown to be:

$$\sigma_{\nu\lambda} = \frac{e^2}{2mc^2}\langle\Psi_0|\sum_k \frac{r_k^2\delta_{\nu\lambda} - (r_k)_\nu (r_k)_\lambda}{r_k^3}|\Psi_0\rangle - \frac{e^2}{2mc^2}\langle\Psi_0|\sum_k \frac{\vec{R}\cdot\vec{r}_k\,\delta_{\nu\lambda} - R_\nu\,(r_k)_\lambda}{r_k^3}|\Psi_0\rangle - \frac{2e}{mc}\langle\Psi_0|\sum_k (l_k)_\nu/r_k^3\,|\Psi_{1\lambda}\rangle \qquad (2)$$

The above expressions are often written in the following fashion:

$$\sigma = \sigma^d + (\sigma^P)_G + \sigma^P)_{EX} \qquad (3)$$

where σ^d is the diamagnetic contribution,
$\sigma^P)_G$ is the ground state paramagnetic contribution
and $\sigma^P)_{EX}$ is the excited state paramagnetic contribution often referred to as the high frequency term.

In so far as the calculations for $(\sigma^P)_G$ for H_2O are concerned, Das and Ghose have preformed a calculation for this term using a localized LCAOMO function. Their value for $(\sigma^P_{AVE})_G = \frac{1}{3}\{(\sigma^P_{xx})_G + (\sigma^P_{yy})_G + (\sigma^P_{zz})_G\}$ is -64.2 ppm.

A simple and rapid manner of calculating $(\sigma^P_{AVE})_G$ can be accomplished by using the Hellman-Feynman theorem which states that the total electric field at a nucleus neglecting minor vibrational effects is zero (2). The electric field due to the electrons is counterbalanced by the nuclear charges in the molecule, hence:

$$\langle\Psi_0|\sum_k \frac{\vec{r}_k}{r_k^3}|\Psi_0\rangle = \sum_N{}' \frac{Z_N\vec{r}_N}{r_N^3} \qquad (4)$$

The expression for $(\sigma^P_{\nu\lambda})_G$ then reduces to:

$$(\sigma^P_{\nu\lambda})_G = -\frac{e^2}{2mc^2}\left\{\vec{R}\cdot\sum_N{}' \frac{Z_N\vec{r}_N}{r_N^3}\,\delta_{\nu\lambda} - R_\nu \sum_N{}' \frac{Z_N(r_N)_\lambda}{r_N^3}\right\} \qquad (5)$$

One can also write this expression in terms of the permanent dipole moment of the molecule through the relation $\vec{\mu}_o = \eta e(R-R_n)$. Substitution of this expression for R yields the diagonal components of the shielding tensor.

$$(\sigma_{\lambda\lambda}^{P})_G = \frac{-e^2}{2mc^2} \sum_N{}' \frac{\xi_N}{r_N^3} \left\{ \left(\frac{\vec{\mu}_o}{\eta e} + \vec{R}_N\right) \cdot \vec{r}_N - \left(\frac{\vec{\mu}_o}{\eta e} + \vec{R}_N\right)_\lambda (\vec{r}_N)_\lambda \right\} \qquad (6)$$

Application to the Water Molecule

Figure 1 shows the schematic diagram for H_2O showing the choice of coordinates used in the present calculations. The HOH bond angle is taken to be 105°, and the OH bond distance as 0.96 Å. The nuclear centroid from the oxygen is 1/5 $r_0 \cos\frac{\theta}{2} = 0.1168$. The various components of distances used in the calculations are given below (r in Å):

$r_0 = 0.96$
$r_H = 0.76$
$(r_0)_y = 0$
$(r_0)_z = 0.58$

$(r_H)_x = 1.52$
$(r_H)_y = 0$
$(r_H)_z = 0$
$(R_N)_x = 0.47$
$(R_N)_y = 0$
$(R_N)_z = 0.80$

$r_{0_3}^3 = 0.88$
$r_H = 3.53$
$(\mu_o)_x = 0$
$(\mu_o)_y = 0$
$(\mu_o)_z = {}_o = 1.84$ D

The value for μ_o / ne is 3.86×10^{-10} and $e^2/2mc^2 = 1.41 \times 10^{-13}$

Using expression (5) the diagonal components of the shielding tensor are given by:

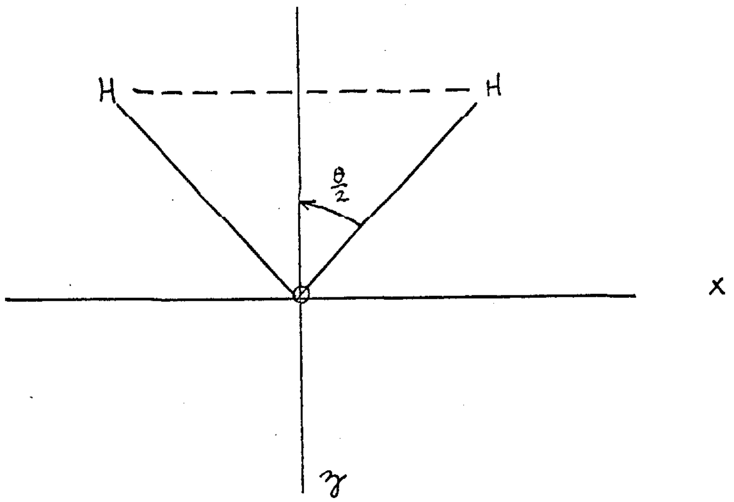

Figure 1. Schematic Diagram for H_2O

Making use of the fact that certain terms are zero in the above expressions, the final expressions are given below:

$$(\sigma^{p}_{xx})_G = -\frac{e^2}{2mc^2}\left\{R_z\left(\frac{\zeta_O(r_O)_z}{r_O^{3}} + \frac{\zeta_H(r_H)_z}{r_H^{3}}\right)\right\}$$

$$(\sigma^{p}_{yy})_G = \frac{-e^2}{2mc^2}\left\{R_x\left(\frac{\zeta_O(r_O)x}{r_O^{3}} + \frac{\zeta_H(r_H)x}{r_H^{3}}\right) + R_z\left(\frac{\zeta_O(r_O)_z}{r_O^{3}} + \frac{\zeta_H(r_H)_z}{r_H^{3}}\right)\right\}$$

$$(\sigma^{p}_{zz})_G = \frac{-e^2}{2mc^2}\left\{R_x\left(\frac{\zeta_O(r_O)x}{r_O^{3}} + \frac{\zeta_H(r_H)x}{r_H^{3}}\right)\right\}$$

It is obvious from the above expression that $(\sigma^{p}_{yy})_G = (\sigma^{p}_{zz})_G + (\sigma^{p}_{xx})_G$

RESULTS

	$\sigma_{\lambda\lambda}$ ppm	Das and Ghose $\sigma_{\lambda\lambda}$ Localized LCAOMO (ppm)
$(\sigma^{p}_{xx})_G$	- 59.5	-35.6
$(\sigma^{p}_{yy})_G$	-107.6	-93.6
$(\sigma^{p}_{zz})_G$	- 48.1	-60.7
$(\sigma^{p}_{AVE.})_G$	- 71.7	-64.2

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PROPOSITION IV

Study of the Electrical Conductance of Various Aprotic Salt Solutions in the Presence of Low Concentrations of Dissolved Solute Molecules

The equivalent conductances at infinite dilution of salt and the ion pair dissociation constants K_D are to be determined for a series of inorganic salts (such as LiBr, LiI, LiCl, NaI, etc.) in an aprotic solvent such as acetonitrile as a function of water or methanol concentrations.

A considerable amount of work has already been done in an effort to understand the nature of aqueous electrolytic solutions by electrical conductance measurements (1,2). In the case of non-aqueous solvents, however, the literature is quite sparse. It is the purpose of this proposition to study the electrical conductance of aprotic salt solutions in the presence of small amounts of dissolved water or methanol concentration. In many cases, it is important to know how the presence of small amounts of dissolved molecules (such as water or methanol) affects the dissociation of ions in an aprotic solvent. Such information can be of importance in the interpretation of kinetic experiments (3). In addition it is of importance to know the details of the factors which influence the dissociation of these ions under "dry" conditions where no water is present for different aprotic solvents. The investigation of second order rates for SN 2 reactions of lithium and tetra-n-butylammonium halides in acetone, for example, was studied by Winstein et. al. (4). In this study, it was observed that the nucleophilicities of the tetra-n-butylammonium halides showed the order Cl>Br>I, the exact opposite of the commonly accepted order which can be based on the reactions of lithium halides as nucleophiles(5). These results can be rationalized in terms of the different degree of association of these ions in an aprotic solvent such as acetone.

Although some electrical conductance studies have already been made in an effort to obtain dissociation constants for various salts in an aprotic solvent, it is clear that a considerable amount of careful work still needs to be made along these lines before the nature of ions in various aprotic solvents can be clearly understood. The study of the electrical conductance of these solutions will by no means answer all of the questions which con-concern the nature of the ions in an aprotic solvent. The results, however, can be of considerable value in guiding our interpretation of these solutions.

In the course of the work presented in this thesis, a literature search was made to find studies on the electrical conductance of salt solutions of acetonitrile. The study of the dissociation of several tetralkylammonium halides in acetonitrile was studied by Popov _et_. _al_. (6,7), but salts (such as NaI, LiI, LiBr, etc.) have not been reported to this author's knowledge. A statement presented by Shcherba and Sukhotin (8) on the electrical conductance of LiI and LiBr in acetonitrile indicates that these salts are highly ionized, but no reference to the actual experimental data could be found.

It is the purpose of this proposition, therefore, to study the electrical conductance of aprotic salt solutions in the presence of small amounts of dissolved water or methanol. Particular attention will be made on the equivalent conductances and dissociation constant as a function of the water or methanol concentration for NaI, LiI, LiBr, and MgI_2 in acetonitrile. Comparisons will be made with $NaClO_4$, $LiClO_4$, and $Mg(ClO_4)_2$. Similar studies can be extended to include other solvents (such as acetone, dimethylformamide, etc.)

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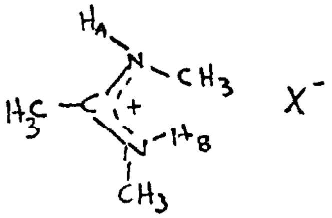
Proposition V

A Study Concerning the Non-Equivalent N-H Hydrogen-Bonding in Acetamidinium Compounds by Infrared Spectroscopy

The nuclear magnetic resonance of unsubstituted and symmetrically substituted aliphatic amidinium salts in dimethyl sulfoxide was observed by Hammond and Newman (1). In particular, for acetamidinium chloride in DMSO, two nitrogen proton signals are observed separated by 55 cps, the low field resonance being slightly broader. The corresponding widths at half height was 11 and 13 cps. The spectra for the N-CH_3 resonanceare more complicated. They (1) analyze the spectra as consisting of two overlapping doublets (J = 5 cps) centered at -171.5 and -176.5 cps relative to external tetramethyl silane. The N-H resonances are at -554 and -609 cps. The C-CH_3 resonance is unsplit and occurs at -137.5 cps.

Arguments are presented for the possible interpretation of the observed spectra. These authors (1) conclude that the most favorable conformation for this molecule is the one in which one nitrogen proton is in the inside configuration and the other in an outside configuration. See Figure 1.



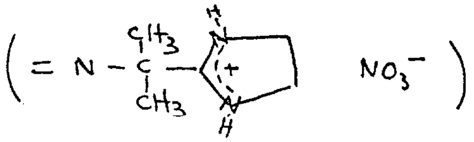
H_A = outside

H_B = inside

Figure 1. Possible configuration of acetamidinium$^+X^-$

A tentative spectral assignment is given to the N-H protons.

Due to the similarity of the NMR resonance of N-H in



(-608 cps) compared with the N-H resonance at -609 cps, the outside proton is assigned to the low field N-H resonance. The low field N-CH_3 resonance is also assigned to the outside N-CH_3. For the moment, there is no reason to doubt these assignments. The observation of a difference in 55 cps for the N-H protons is however of some interest. No attempts were made either qualitatively or quantitatively to obtain orders or magnitudes for these protons in magnetically non-equivalent positions. If one is concerned with this problem, it is essential that one have an idea of the nature of the interactions which occur at the site of interest.

There are a number of points which need to be clarified before the origin of the magnetic non-equivalence of the N-H protons can be understood. A difference in the neighbor magnetic anisotropic contribution from the C-N and C-C bonds is expected to contribute to the over-all shift between H_A and H_B as well as the effect of the solvent and anion electric field at the two protons. For the moment, it is of interest to determine if both N-H protons are equivalently hydrogen bonded or not hydrogen bonded to the solvent.

Since the spectral features of the N-H stretching vibration of a free N-H and a hydrogen bonded N-H vibration are quite different, *i.e.*, stretching frequency, band widths, intensities, etc., it is proposed that an infrared study of acetamidinium chloride in DMSO be made in the region of the NH stretching vibration. N-H protons involved in hydrogen bonds are known to give broad absorption bands in the region from 1700 to 3400 cm^{-1}. Typical band widths at half intensity are on the order of 100-200 cm^{-1} (2). N-H protons without hydrogen bonds yield relatively sharp absorption bands (25-70 cm^{-1}) in the region from 3500 to 3700 cm^{-1} (2).

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