

Neutron Inelastic Scattering Studies of Water and Ionic Solutions

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FOREWORD

This is one of a continuing series of reports designed to present accounts of progress in saline water conversion and the economics of its application. Such data are expected to contribute to the long-range development of economical processes applicable to low-cost demineralization of sea and other saline water.

Except for minor editing, the data herein are as contained in a report submitted by the contractor. The data and conclusions given in the report are essentially those of the contractor and are not necessarily endorsed by the Department of the Interior.

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NEUTRON INELASTIC SCATTERING STUDIES OF WATER
AND IONIC SOLUTIONS

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I. INTRODUCTION

Measurements at a molecular level of changes induced in the bonding, in the structured units, and in the associated diffusive motions of H₂O molecules by the addition of ionic solutes to water can provide information for testing theories and developing more unique and quantitative models for the structure and kinetics of ionic solutions than are now available. Such information could provide a deeper insight into the basic forces governing the structure and motions in saline solutions, and would be basic to the development and improvement of efficient large-scale desalination procedures. This, for example, is stressed in recent theories by Samoilov⁽¹⁾⁽²⁾ for the mechanism of salting out from aqueous solutions.

As reviewed previously,⁽³⁾ a surprising number of models can account for a number of the observed thermodynamic properties of bulk water, while differing significantly at a molecular level. In particular, the structure size and long-range ordering of the associated units, and the fraction and lifetime of unbonded "monomers" have differed significantly between models. In more recent years a number of theories have been devised which attempt in a quantitative manner at a molecular level to account for the space-time correlation of the motions of H₂O molecules in water, including: the vibrations of bonded molecules, the diffusive kinetics of individual molecules and of clusters, and the damping of and coupling to vibrational modes by diffusive motions. Data at a molecular level are of particular use in further developing and refining such models.

The influence of ions on the structure of water, the existence and the nature of hydrated species in electrolytic solutions, and the changes in diffusive kinetics of H_2O molecules caused by ions in solution have been the subject of both experimental and theoretical investigations. The results of a number of such investigations are briefly summarized in Table I.

The role of the water structure and the ability of ions either to break the structure or to incorporate into it has been of particular interest. Efforts have been made to classify salts or ions as "structure-makers or -breakers," depending on whether their solutions result in a more or less unique and tightly bonded coordination of H_2O molecules than in water or whether the molecules are more or less mobile than in water. However, the assignment of ions to such classes has not been in accord for all measurements.

There appears little doubt that the concept of hydration is a valid one and that hydrated species involving specific cation-water coordinations exist. In certain cases ⁽⁵⁾⁽⁶⁾ (KOH and KSCN) there are indications that ions may incorporate into the water structure even at higher concentrations. At lower concentrations and temperatures there is evidence that remnant "water-like" regions may coexist with hydrated ions. More generally, however, the ions break down the existing structure of pure water by a combination of charge, polarization, and steric effects. The coordination, strength of bonding, thermolability, and cooperative effects of anions and cations in the formation of new complexes depend strongly on the size and charge of the ions and the nature of the ion- H_2O interaction.

Evidence has been cited⁽⁷⁾⁽⁸⁾⁽⁹⁾ that at higher concentrations of ions having strong fields (i.e., Li^+ , Ca^{+2} , Al^{+3}) the molecular coordinations strongly resemble those of the corresponding solid hydrates. In addition, a degree of covalent bonding between a metal ion and the oxygen of a H_2O molecule may occur in both solution complexes and solid hydrates.⁽¹⁰⁾⁽¹⁴⁾ The complexes formed by certain large highly charged ions (i.e., Eu^{+3} , Er^{+3} , and La^{+3})⁽¹⁵⁾⁽¹⁶⁾⁽¹⁷⁾ may in turn be able to cause a further reordering of H_2O molecules beyond the primary hydration.

Neutron inelastic scattering (N.I.S.) has been applied previously to studies of water,⁽¹⁸⁾ non-aqueous liquids,⁽¹⁹⁾ and intermolecular frequencies and binding of H_2O molecules in minerals and solid salt hydrates. Detailed descriptions of this technique and reviews of both the experimental results and their theoretical evaluation for water and other liquids are in the literature.⁽²⁰⁾⁽²¹⁾ The observed vibrational spectra are not limited by symmetry or optical selection rules and all vibrations and diffusive motions occurring within the interaction time of 10^{-11} - 10^{-12} seconds will be observed. Due to the large scattering cross section for hydrogen relative to oxygen and the ions, the observed spectra will correspond to vibrations and to diffusive motions of water molecules.

In the present experiments N.I.S. has been used to study the intermolecular vibrations of water molecules below 900 cm^{-1} as a function of temperature and of concentration for a selected series of dissolved anions and cations and for some corresponding solid hydrates. The intermolecular frequencies observed at lower temperature have been compared, where possible, to those observed for H_2O molecules in the corresponding solid hydrates of the salts.

Simultaneously the broadening of the incident line by diffusive motions of H₂O molecules (the quasi-elastic component) has been measured and the results compared with the functional behavior predicted by different theories of diffusion. Effects of different ions and of temperature on the diffusion kinetics and related parameters has been determined.

II. SUMMARY OF RESULTS TO DATE OF THE PRESENT INVESTIGATION

The intermolecular frequencies between 900 cm⁻¹ and 8 cm⁻¹ of H₂O molecules in water and aqueous solutions of LaCl₃, CaCl₂, MgCl₂, CsI, CsCl, KSCN, KI, KBr, KCl, KF, NaCl, LiNO₃ and LiCl have been measured by slow neutron inelastic scattering. In addition, the diffusive kinetics of H₂O molecules in aqueous solutions of LaCl₃, MgCl₂, CsCl, KSCN, KCl, KF, NaCl, LiCl have been investigated and compared to water. The dependence of observed spectral changes on temperature, on concentration and on ionic size and charge were studied. Simultaneous changes were observed for both the intermolecular frequencies and the diffusive motions of H₂O in ionic solutions relative to pure water and were specific to the ions present, their concentrations, and the temperature. They result from the modification of water structure and the formation of hydrated complexes by ions.

For solutions of salts having a small and/or highly charged ion (i.e., LaCl₃, MgCl₂, LiCl and KF) new maxima appear at frequencies similar to those of the rocking, wagging, and twisting librational modes and to the ion-water stretching frequencies of H₂O molecules in the corresponding solid salt hydrates. They intensify with increasing concentration. While increasing temperature with these frequencies broaden

they persist to 75°C. At lower temperatures (1°C and 25°C) where the diffusive motions are in accord with a delayed diffusion model, these salts cause a corresponding decrease in the self-diffusion coefficients, D , and increase in the residence times, τ_0 , relative to pure water. D increases and τ_0 decreases with increasing temperature, but remain respectively smaller and larger than for pure water. However, at higher temperatures the diffusive kinetics depart from the simple jump diffusion behavior.

The data indicate that such small and/or highly charged ions break existing water structure and form complexes having local ordering and bonding similar to that of H_2O molecules in the corresponding solid salt hydrates. The strong ion-water coordinations and electrostriction of the solvent gives rise to a higher activation energy for H_2O molecules than in pure water and these ions thus act as positive hydrators.

Solutions of salts with larger singly charged ions (i.e., CsCl, KCl) also show new frequencies, but in contrast, at lower temperatures these are broader and less pronounced than for the smaller or highly charged ions. These solutions increase D and decrease τ_0 relative to pure water, acting as "negative hydrations." At higher temperatures maxima characteristic of ion-water coordinations appear more prominent and suggest that at such temperatures, relative to lower temperatures, the ion-water bonding may be more important than the H_2O - H_2O bonding in pure water.

Values of the intermolecular frequencies, the diffusion coefficients, and residence times obtained are in reasonable numerical agreement with those obtained from other techniques. For cases where the delayed diffusion model is not valid, a tentative explanation for the observed diffusion kinetics has been presented.

III. NEUTRON SCATTERING

A. Neutron Spectrometer

The neutron inelastic scattering spectrometer, shown in Figure 1, has been in operation at the Union Carbide Sterling Forest Research Center in Tuxedo for approximately four years.

A beam of thermal neutrons from the reactor passes through liquid-nitrogen-cooled, polycrystalline beryllium before striking the sample. The Be serves as a low-pass filter, transmitting only those neutrons with energies ≤ 5.2 meV (millielectron volts). Below this sharply-defined cutoff, the intensity of neutrons decreases rapidly; so that the energy distribution in the incident beam is asymmetric, with an average energy of 4 meV and a full width, at half maximum of about 1 meV. Such a beam of neutrons is termed "cold," since its average energy is small compared to the average thermal excitation energy at room temperature ($kT = 25$ meV). The beam impinges on the sample to be studied, and the neutrons scattered from the sample are interrupted by a rotating collimator. The velocities, and hence the energy distribution of the scattered neutrons, are determined by measuring the flight time over a 5-meter flight path between the chopper and the neutron detectors. Counts from the detectors are recorded, with their flight times, in a PDP-5 on-line computer acting, in this instance, as a multi-channel analyzer. By comparing the energy distribution of the scattered neutrons with that of the initial beam, one obtains a spectrum of energy gains from which the distribution of molecular vibration frequencies can be determined.

The sample thickness is chosen so that a neutron scatters once and only once in the sample. In such a scattering event, the neutron interacts with the nucleus of an atom bound in the molecule but does not have sufficient energy to break molecular bonds. Since the mass of the molecule is generally large compared to the neutron mass, the recoil energy of the molecule as a unit may be neglected. However, the neutron may gain or lose quantized units of energy corresponding to a transfer of molecular energy from or to the neutron. In our type of measurement, only those neutrons that have gained energy are observed.

B. Sample Preparation and Treatment of Data

The samples were contained in an aluminum holder shielded with cadmium. A thin layer of an inert polymer film was electrodeposited on the cell which afforded corrosive protection and did not contribute to the background significantly.

For the spectra taken at -25°C the samples were cooled by flowing liquid nitrogen boil-off gas through a channel in the sample holder; the temperature was controlled to $\pm 2^{\circ}\text{C}$. Care was taken to prevent the condensation of water vapor on the scattering surfaces of the sample. For the spectra taken at $+1^{\circ}\text{C}$, the sample was cooled by rapidly circulating water from an ice-water bath. The cooling system was shielded to avoid the scattering of neutrons by the coolant. Collimation of the sample was such that neutrons were only scattered from the liquids having maximum thickness of 0.5 mm.

Measurements have been made to determine the degree of spectral distortion arising from both multiple scattering (as described in detail in

Appendix I) and from background subtraction. Spectra distortion due to multiple scattering has been found to be negligible.

For thin samples, the background subtraction is important, the background was measured at each angle and for different cells. While, in general, the background was nearly flat and constant, small variances with both angle and cell were observed. However, it was shown that spectra independent of the cell were systematically obtained after background subtraction. The measured neutron spectra were corrected for measured background, for counter efficiency, for chopper transmission, and for the transmission of aluminum in the beam. Measurements were made to ensure the reproducibility and the reality of their features. Typical standard deviations are shown as calculated from the number of counts and of background counts per channel. Spectra were also repeated using independent counter banks, electronics, memory sections of the time-of-flight analyzer, and using identical freshly prepared samples. In addition, runs with different solutions were interspersed over the total duration of the experiment.

The solid curves in neutron spectra were "faired" through the data points. It was required for the maxima or shoulders shown that they reproduce under the conditions described above and that in addition, while their relative intensities varied, they also occurred in spectra for different angles and temperatures. In particular, where a singularity is marginal with regard to statistical error on a given spectrum it was assigned only if it appeared at more than one scattering angle, temperature, and concentration.

The kinetics and parameters that characterize diffusive motions (discussed below) may be obtained from the variation in intensity and the width of the broadened quasi-elastic maximum with scattering angle. Before the width can be estimated from the broadened maximum, the low-frequency inelastic contribution must be estimated and subtracted from the observed spectrum to obtain the true quasi-elastic contribution. Brockhouse⁽²²⁾ and others⁽²³⁾ have noted that the inelastic spectrum of water near the quasi-elastic peak resembles that from a gas of mass 18. The gas scattering spectrum, weighted with the incident neutron distribution, has been scaled to fit the spectra in the region of the quasi-elastic maximum and used to estimate and thus to subtract the inelastic contribution.

As vanadium scatters neutrons almost entirely in an incoherent, elastic manner, its spectrum yields the energy distribution of the incident beam. The incident distribution of energies was so determined at each scattering angle, and a typical example is given in Figure 2. The primary Be Bragg (Be 100 plane) cutoff occurs at channel 165 (i.e., 0.0052 eV). The fall off in intensity above channel 170 represents the distribution of neutrons having energies less than 0.005 eV. Additional secondary cutoffs due to Be and Al and BeO impurity in the beryllium, determined by emission spectroscopy, appear between channels 135 to 160. Other secondary cutoffs due to Al and BeO occur also above channel 168. These maxima have been included in the broadened incident distribution for the quasi-elastic analysis.

It was found that the instrumental broadening and the shape of the distribution could be reproduced by folding a Gaussian resolution function of a 32 μ -sec. width into the reactor spectrum which, for low energies, has a distribution of flight times, t , proportional to $\frac{1}{t^{5.8}}$ as shown in Figure 1. This spectrum was further broadened by "folding in" Lorentzian functions of varying half-widths at half-maximum, Γ (Figure 1), for comparison with observed quasi-elastic maximum. The values of Γ were chosen to yield the optimum agreement in shape between observed maxima and the broadened incident distribution.

C. Related Computer Programs

Computer programs for the IBM 360 Model 50 have been developed during the current contract period and are used for the following purposes:

- (a) To subtract the appropriate cell background as well as contributions of gas-like diffusion of water molecules,
- (b) To select the Lorentz width, Γ , and shape fit the theoretical curve to the experimental points of the quasi-elastic maximum,
- (c) To generate theoretical curves of Γ vs. K^2 based on either the pure jump model or the more general jump model and to calculate corresponding values of the self-diffusion constants, residence times, activation energies, and Debye temperatures.

These computer programs will be applied to the data of the proposed experiments and extended to other models as warranted.

IV. RESULTS AND DISCUSSION

A. Water

Previous N.I.S. ⁽¹⁸⁾⁽²¹⁾ investigations of water at 25°C have reported the presence of a broad torsional component at about 460 cm⁻¹ and weak lower frequency maxima associated with vibrations involving stretching and bending of hydrogen bonds. In accord with these assignments and previous results on D₂O, spectra for H₂O-D₂O mixtures (not shown) taken in this investigation showed additional partially resolved maxima at 425 cm⁻¹ and 360 cm⁻¹. The ratios of these frequencies to those for water are those expected for HDO and D₂O torsional modes, respectively; the intensity ratios correspond to the relative numbers of H₂O, HDO and D₂O in the mixture. The weak lower frequency maxima were invariant under deuteration. In the spectra of Figure 3, this broad torsional maximum at 1°C appears composed in part of three broad, partially resolved maxima at about 860±70cm⁻¹, 590±45 cm⁻¹ and 454±30 cm⁻¹ which are outside statistical error and are sample dependent.

Indeed, Larsson and Dahlborg ⁽¹⁸⁾ reported asymmetry in the torsional maximum in the neutron spectrum which they point out may indicate the presence of another component at about 1.5 to 2 times the peak frequency of the broad torsional maximum. They further argue that this asymmetry is real and does not arise from multi-phonon effects, from multiple scattering or from background. In like manner, Draegert and Williams ⁽²⁴⁾ report an asymmetry in the infrared hindered rotational band which they note makes it probable that this band consists of two or more unresolved components. Considering the uncertainties, the

frequencies of the three maxima in the neutron spectra of Figure 3 appear close to the three broad torsional components recently reported in the Raman⁽²⁵⁾ and hyper-Raman⁽²⁶⁾ spectra of water at about $740 \pm 25 \text{ cm}^{-1}$, $550 \pm 25 \text{ cm}^{-1}$ and $425 \pm 25 \text{ cm}^{-1}$ with full widths at half-maximum ranging between $200\text{-}250 \text{ cm}^{-1}$. These have been observed to shift as torsions under deuteration and have, from symmetry considerations, been assigned to four coordinated tetrahedral species with C_{2v} symmetry. Both the Raman spectra and the neutron spectra of Figure 3 show these components to decrease in intensity with increasing temperature. Walrafen⁽²⁷⁾ has associated this behavior with the distortion and breaking up of the C_{2v} species. Since the neutron spectra are not subject to symmetry selection rules and all species would contribute, the presence of these components suggests that the relative number of such tetrahedrally four-coordinated species may be appreciable at 1°C . With increasing temperature the three maxima first broaden and then disappear.

At $+95^\circ\text{C}$ (not shown), the median of the torsional maximum was shifted down by about 40 cm^{-1} from its position at 1°C and only weak vestiges of certain of the lower frequency maxima persist. These results indicate that appreciable association still exists at 95°C . The shifting and broadening of the torsional maximum with increasing temperature correlates with the small increases in the average O-O distance and thermal amplitudes observed by x-ray diffraction, an increase in the number of non-tetrahedrally oriented, lower than four-coordinated water molecules, and an increase in anharmonicity and multi-phonon contributions due to an increase in the average thermal amplitude fluctuations. As discussed below, a corresponding increase in the "diffusive freedom" of H_2O molecules

due to breaking of bonds and a related "loosening of the water structure" give rise to an increased diffusive broadening of the incident line resulting in the quasi-elastic maximum.

Upon freezing, the broad torsional envelope present in water shifted up abruptly by 100 cm^{-1} and narrows as the nearest neighbor O-O distance changes from 2.96 \AA in water to 2.76 \AA in ice at 0°C . In contrast, the torsional maximum in SO_2 hydrate, which has the same frequency and shape as that of hexagonal ice due to identical O-O distances and local ordering, shows no such abrupt shift at 0°C . Thus, the sudden shift at the melting point for the torsional maximum in ice reflects a change in the local coordination at the phase transition. The identity⁽²⁸⁾ of the torsional maximum and the variance of lower frequencies between ice and the hydrate indicate^{that} the former frequencies reflect similar local order while the latter reflect the different long-range ordering between these solids.

In addition to the shift of the torsional frequencies, all the inelastic maxima broadened and decreased in intensity relative to ice in the spectrum of water at 0°C ; this was particularly pronounced for maxima below the frequency of the torsional components which, however, appeared so strongly damped that any one-to-one correspondence for hexagonal ice in that region must be considered tenuous.⁽²⁸⁾ In accord with recent x-ray diffraction measurements⁽²⁹⁾⁽³⁰⁾⁽³¹⁾ showing the loss of correlation in O-O distances at about 10 \AA and the presence of large thermal amplitudes,⁽²⁹⁾ the damping and broadening may be associated with the presence of strong anharmonicity and associated multi-phonon effects,

variations in the bonded species, and imperfections in the structural ordering of water. Indeed, the Debye temperature observed for water ($\theta_D = 123^\circ\text{C}$) is low compared to the temperature at 1°C implying a highly excited or "hot lattice" and large amplitudes.

The above results can be tentatively explained in terms of a distortion and breaking down of tetrahedrally four-coordinated species and the formation of a variety of species with lower coordinations in the manner proposed previously by a number of authors to explain both the spectroscopic and thermodynamic properties of water. (20)(27)(32-36) At low temperatures, four-coordinated tetrahedrally bonded species would exist in a poorly ordered, highly excited and defected structure. Bound molecules would vibrate with large amplitudes breaking bonds and re-orienting with thermal fluctuations. With increasing temperature, the equilibrium would shift toward a lower average degree of coordination. The relaxation of molecules would occur at a faster rate. Thus, it would be possible that ions having the proper steric size and not too high a charge, might, especially at lower concentrations, fit into such a poorly-ordered and defected water structure. Others, with small size and/or high charge, could readily break down the structure and form new "hydration structures." The degree to which an ion would modify the water structure could depend on the variance of this structure with temperature.

B. The Inelastic Spectra of Ionic Solutions

The spectra for neutrons scattered from H_2O molecules in ionic solutions have been investigated as a function of ionic size and charge, of concentration, and of temperature. In all cases the spectra showed changes relative to water which depended on solute (Figures 4 - 14), concentration (Figures 6, 7, 8, 9), and temperature (Figures 13,14). For certain solutes at lower concentrations the observed departures from the water spectrum were smaller. To visually emphasize such smaller variations, "difference curves" as obtained from a channel-by-channel subtraction of the water spectrum from that of a salt solution are also shown.

The low frequency (900 cm^{-1} to 8 cm^{-1}) vibrational spectra show the following general features and trends:

At low concentrations many of the frequencies characteristic of pure water persist with new frequencies characteristic of ion-water interactions. With increasing concentration/^{the}former frequencies give way to the latter in a manner specifically determined by the ions. Evidence for the co-existence of water-cation coordinations and of water structure have been previously reported. Beck⁽⁹⁾ and Danilow and Neumark⁽³⁷⁾ have argued that at lower temperatures the radial distribution functions of a number of salt solutions retain maxima of pure water. Recent infrared measurements⁽²⁴⁾ on alkali-halide solutions show that while spectral changes due to ion water interactions occur, the spectra in part resemble that of water. Evidence for the co-existence of hydrated ions with pure water structure has also come from the P.M.R. studies of Fabricand et al⁽³⁸⁾

on 1-1 electrolytes. They argue that the H_2O molecules not near ions have nearly the same proton relaxation rate as for pure water. In addition Luz and Yagil⁽³⁹⁾ interpret the O^{17} shifts for 1-1 electrolytic solution to indicate that direct ion-adjacent- H_2O interactions and not overall changes of the solvent structure are involved.

With increasing concentrations the inelastic spectra of aqueous solutions containing small and/or highly charged ions show the most pronounced departures from that for pure water. In the spectra of 4.6m solutions of LiCl , KF and MgCl_2 , and in 3.5m solutions of LaCl_3 (Figures 4 and 5) new maxima appear in the 800 cm^{-1} to 200 cm^{-1} regions at similar frequencies to those observed⁽¹⁰⁾ and assigned⁽¹²⁾ to "rocking, twisting, and wagging" librational modes and the H_2O -ion stretching frequencies of H_2O molecules in the corresponding solid hydrates (Table II). An exact correspondence of frequencies is not implied as both the resolution in this frequency region and the weakness of certain of the lines in both the solid hydrates and the liquid precludes a one-to-one correspondence. However, the similarity between the spectra of the solid hydrate and the solutions with increasing concentration is emphasized in the spectra and difference curves of Figures 6 to 9. In like manner, such a similarity is also shown in a comparison of the spectrum of solid $\text{LiNO}_3 \cdot 3\text{H}_2\text{O}$ (Figure 9) with that of this salt melted in its waters of crystallization. In addition, for other salts similar changes are observed which correlate with ion size and charge as illustrated by the spectra and difference curve in the progressions of Figures 11 and 12. As shown, changes in the inelastic portion of the spectra are accompanied by significantly large changes in the quasi-elastic region. The departures from the spectrum of water increase in the progressions:

- (1) $KI < KBr < KCl < KF$; with decreasing anion size (Figure 10)
- (2) $NaCl < CaCl_2 < LaCl_3$; with increasing cation charge for nearly the same radius (Figure 11)
- (3) $CsCl < KCl < NaCl < LiCl$; with decreasing cation size for a given charge (Figure 12)

The increase in the quasi-elastic maxima with decreasing size and increasing charge reflect decreases in the diffusion coefficients and increases in the residence times and the Debye temperatures (as will be discussed in Section IV(C)).

The observed new frequencies in solutions are similar within resolution to those reported for H_2O -cation frequencies in Raman and I.R. spectra (as shown in Table II) which have been associated with short (2.0 - 2.2 Å) coordination distances and strong, partially covalent- H_2O cation interactions. ⁽¹²⁾⁽¹⁰⁾⁽⁴⁰⁾ The larger anions of low charge primarily perturb this H_2O -cation interaction by forming weak hydrogen bonds. At concentrations of 4.6m and above (having 12 H_2O molecules or less per salt molecule) these strongly coordinated waters in the primary hydration layer should contribute significantly to the spectrum as observed.

The above results are in accord with those of previous x-ray diffraction, Raman, ionic mobility, and electronic transition measurements. Beck, ⁽⁹⁾ and Danilow and Neumark ⁽³⁷⁾ have argued for the co-existence of "hydrate-like" and "water-like" regions at low concentrations. At higher concentrations evidence has been cited for a local hydrate-like ordering for a number of salts ⁽⁷⁾⁽¹⁴⁾⁽¹⁷⁾⁽³⁷⁾⁽⁴¹⁾ including $LaCl_3$, $LiCl$, $MgCl_2$ and KF .

As noted by McCall and Douglass⁽⁴²⁾ and others,⁽⁴³⁾ such "hydrate-like" structures are quasi-stable and H₂O molecules have finite lifetimes for exchange.⁽⁴⁴⁾⁽³⁸⁾⁽⁴⁵⁾⁽⁴⁶⁾

In addition to a strong cation-H₂O interaction in the primary hydration layers, a pronounced increased rigidity in the bonding of secondary or higher hydration layers may also be caused by ions having large charge-to-radius ratios; this effect is more significant at lower concentrations. Thus, small or highly-charged ions rapidly break down the structure of pure water and form strong ion-water local coordinations similar to those found in solid hydrates. In addition, a strong electrostriction of H₂O molecules in higher hydration layers may result which gives rise to a higher activation energy even at lower concentrations, as the overall bonding strength of the H₂O molecules would be stronger than the H₂O-H₂O bonds in pure water. Indeed, it will be seen below that corresponding changes observed in the diffusive freedom of H₂O molecules strongly support these observations. Frank and Evans⁽¹⁷⁾ have argued for the existence of a "super-lattice" structure in solutions of both LaCl₃ and EuCl₃, and that the influence of a highly-charged cation on the fluidity of the solution provides "a certain mechanical strength or rigidity in the iceberg it forms around itself." They also pointed out that the "iceberg building tendency" occurs in LiCl and KF solutions, although the new spectral maxima for the latter solutions are not either as intense or well-defined as those in the spectra of the LaCl₃ solution.

As shown in Figure 13 for the case of a 3.5m LaCl₃ solution, the new non-water frequencies persist but increasingly broaden with both increasing scattering angle and temperature. The former broadening is

probably due to an increase in multi-phonon contributions as discussed below and in more detail in Appendix II. The persistence of these frequencies with temperature is in keeping with their assignments to vibrations of H₂O molecules in primary hydration complexes with stronger bonding than for pure water. Similar results were obtained for the MgCl₂, KF, and LiCl solutions.

In contrast to small or highly-charged ions, solutions of large ions with low charge (i.e., Cs⁺, K⁺, Br⁻ and I⁻) have spectra in which existing water frequencies are primarily broadened and smeared out at lower temperatures. As will be discussed, the diffusive freedom of H₂O molecules is also increased relative to pure water. Thus, the water structure appears to be "weakened" or broken down and replaced by a weak coordination due to such ions. However, at high temperatures where a greater thermal disruption of the structure has also occurred the primary influence of the ions may be to form complexes. Thus, from nuclear relaxation and self-diffusion data, Hertz et al.⁽⁴⁷⁾ have noted that the structure-breaking tendency of many of these salts is very much stronger at low temperatures than at higher temperatures. Such local complexes would be quasi-stable and H₂O molecules could exchange between them on a time average. The neutron spectra at high temperatures also show partially resolved torsional components characteristic of water-ion interactions whose frequencies depend on both cation and anion. Thus, in solutions not having one small or highly-charged ion, both cation and anion can strongly affect water coordinations. Walrafen⁽⁴⁸⁾ has reported the observation of librational frequencies similar to those for the solid hydrates for a number of 1-1

salt solutions.⁽⁴⁹⁾ The intensities and frequencies of these components did not appreciably change with temperature and showed a strong anion and weak cation dependence. They were thus assigned to ion-water interactions in the first hydration sheath. The orientation of H_2O molecules in the H_2O -ion complex has been reported by Lawrence and Kruh.⁽⁵⁰⁾ It has been shown from x-ray diffraction on solutions of 1-1 electrolytes that the cations are positioned on the dipole axes of the H_2O molecules and the anions on the O-H axes. Ordering about a given ion occurs which in general is larger for anions than for cations.

As noted by Hindman,⁽⁵¹⁾ Grayson,⁽⁵²⁾ and others,⁽⁵³⁾ with increasing cation size and decreasing charge, the cation-water interaction decreases and the cation-water coordination approaches the strength of H_2O - H_2O coordination in pure water. However, increasing radius of monovalent anions also weakens the anion- H_2O interaction relative to the bonding in pure water. Thus, the average activation energy for the bulk solvent may be smaller for salts like CsCl and KCl relative to pure water, while the primary cation-hydration with stronger bonding and more unique coordinations than pure water may also exist and give rise to the observed frequencies characteristic of ion-water coordinations.

In this regard the concentration behavior of KSCN should be noted. At 4.6m the spectrum of the KSCN solution showed only small deviations from the spectra of pure water in the inelastic region and an increased broadening of its quasi-elastic peak. In contrast, at 18.5m, weak new inelastic frequencies appeared and the elastic maximum was sharper than for pure water. Thus, in the above sense, KSCN acts to initially loosen or break the structure of water and then at high concentrations its solution has a structure in which the H_2O molecules are more rigidly bonded

than for pure water. It has been suggested⁽⁶⁾ that, in contrast to Br^- and I^- , the nearly linear SCN^- ion may be incorporated into channels and hence does not break down the water structure as rapidly due to its weak ionic bonding and consequently weak negative hydration. In accord, a tentative explanation for the observed features would be that at lower concentration, the K^+ and SCN^- fit into the water structure but slightly distort it so as to lower the activation energy and increase the diffusional freedom. At the high concentration, the water structure would be broken down and only the primary hydration waters, more tightly bonded than in pure water, would be observed.

As for water, the presence of diffusing molecules and large vibrational amplitudes indicate considerable anharmonicity (hence, of higher phonon terms) in the spectra of their solutions. This is particularly true for the more dilute solutions where contributions to the spectra may arise from H_2O molecules beyond the first hydration layer of the ions. Thus, at best, the "quasi-hydrate" coordinations discussed must have finite lifetimes in the sense discussed by McCall and Douglass,⁽⁴²⁾ but these may vary strongly with the ion as discussed by Jackson, Lemons, and Taube.⁽⁴⁵⁾ The condition for the use of the one-phonon approximation for the inelastic scattering of a neutron from harmonic oscillator of frequency ω are given by

$$\frac{\hbar^2 K^2}{2M(\hbar\omega)} \frac{(kT)}{\hbar\omega} \ll 1$$

As $|K|^2 = k_0^2 + k_f^2 - 2k_0 k_f \cos \phi$, then $|K|^2$ and $\frac{|K|^2}{2M} \cdot \frac{1}{\hbar\omega}$ decreases with decreasing ϕ . Where $|K|^2$ is the square of the momentum transfer, k_0 and

k_i are the initial and final momentum vectors for a neutron respectively, M is the mass of the scattering unit, T is the temperature, and θ is the scattering angle. Therefore spectral maxima corresponding to "one-phonon" peaks would be most pronounced at small angles and lower temperatures (see Appendix II). Indeed, such behavior is observed for the "quasi-hydrate" frequencies (Figs. 4 & 13) which become significantly sharper and better defined at smaller angles and at lower temperatures. In like manner, it is seen in Figs. 4 to 10 & 12 that small and/or highly charged ions sharpen the hydrate peaks while larger ions of lower charge broaden ion-water frequencies. In addition, changes in the broad background due to ions are evident at the smaller values of $h\nu$. Thus, the difference curves for LiCl and NaCl are negative, indicating a reduction in the multi-phonon background relative to pure water. In contrast, the difference curves are slightly positive for CsCl and KCl between channels 100 and 140, indicating an increase in multi-phonon effects. Thus, small or highly-charged ions which form hydrate-like coordinations also decrease in higher phonon terms corresponding to a decrease in anharmonicity, or an increased binding strength for H_2O molecules. The reverse is true for large ions which "loosen" the water structure and decrease the average binding potential of the water molecule.

The above inelastic neutron scattering results for ionic solution can be viewed in terms of "structure-making" or "structure-breaking" concepts and in terms of "positive" or "negative" hydration as given by Samoilov.⁽⁵⁴⁾⁽⁵⁵⁾ For the salts with small or with multiple-charged cations (i.e., Al^{+3} , La^{+3} , Mg^{+2}) the strong coordination ion-water interactions cause a reduction in anharmonicity in average vibrational amplitude, and

in the diffusional freedom due to electrostrictive effects. Such ions could be termed as positive hydrators and would increase the average activation energy relative to pure water. In contrast, large ions of low charge (Cs^+K^+ , I^- , Br^- , SCN^-) at lower concentrations primarily broaden the frequencies of pure water, increase the anharmonicity average vibrational amplitudes and increase the diffusive freedom acting as negative hydrators. Such ions would loosen and break down the water structure and would not restrict large numbers of H_2O molecules or form as strong a H_2O -ion primary coordination as small or highly-charged ions. In addition, for salts that do not contain a single very small and/or highly-charged ion both the anion and the cation appear to play important roles in determining the ion-water coordinations at higher concentrations.

The quantitative analysis of the quasi-elastic maxima will now be considered. Indeed, it will be seen that these results support the above observations and conclusions based upon the inelastic portions of the spectra.

C. Diffusive Motions of H_2O Molecules in Water and Ionic Solutions (The Quasi-Elastic Component)

Both the widths and areas of the diffusively broadened incident lines for the ionic solutions show pronounced variations from those of water (Figures 15 & 16). These changes correlate with those observed in the inelastic spectra. The following general trends are observed relative to water:

- (1) For cations of essentially the same radius, but differing ionic charge, the quasi-elastic area increases regularly with increasing charge, i.e., $\text{NaCl} < \text{CaCl}_2 < \text{LaCl}_3$ (Figure 11).
- (2) For cations of a given charge, the area increases regularly with decreasing ionic radius, i.e., $\text{CsCl} < \text{KCl} < \text{NaCl} < \text{LiCl}$ (Figure 12); $\text{SrCl}_2 < \text{CaCl}_2 < \text{MgCl}_2$; and $\text{LaCl}_3 < \text{AlCl}_3$.
- (3) For salts with common cation the area increases regularly with decreasing anionic radius, i.e., $\text{KI} < \text{KBr} < \text{KCl} < \text{KF}$ (Figure 10).
- (4) For monovalent anions the above variations are considerably larger than those for monovalent cations. (Figure 10 vs. Figure 12).
- (5) With increasing concentration, there is a regular increase in the size of the quasi-elastic maxima (as for KSCN , LiCl and for KF and MgCl_2 in Figures 6, 7 & 8).
- (6) For small and/or highly-charged ions (i.e., La^{+3} , Al^{+3} , Mg^{+2} , Li^+ , F^-) the width of the quasi-elastic maximum narrows relative to water with increasing concentration.
- (7) For large singly-charged ions (i.e., Cs^+ , K^+ , Br^- , I^- , SCN^-) the quasi-elastic maxima are broadened relative to water. At higher concentrations of KSCN it can become narrower than for water.

In general, an increase in the area of the quasi-elastic maximum, as discussed quantitatively below, reflects an increase in the average Debye temperature (or a decrease in the average vibrational amplitudes) of bound water molecules due to ion-water interactions. In like manner, a narrowing of the quasi-elastic peak reflects a decrease in the diffusional freedom of H_2O molecules. Thus, the relative changes in the area and the widths of the quasi-elastic maxima correlate regularly with ionic charge, size and polarizability.

For water and certain salt solutions the quantitative dependence of the half-width at half-maximum on the momentum transfer squared (K^2)

(Figures 15 and 16) have been

determined. As described in Section III, a full multi-phonon or "gas model" cross section with a mass of 18 was used to estimate and to subtract the inelastic background under the quasi-elastic peak. After background subtraction the shapes of the curves were found to correspond to Lorentzian broadenings of the incident energy distributions to within statistics (Figure 2). The values of Γ were chosen to yield the optimum match in shape between the observed quasi-elastic maxima and the Lorentzian broadened incident energy distribution. The principal features of the Γ vs. K^2 curves are:

- (1) For water at $25^\circ C$, the widths of the incident line as a function of scattering angle are in numerical agreement with the results of Larsson and Dahlborg⁽¹⁸⁾ and with recent high resolution studies of Bojarik et al.⁽⁵⁶⁾ No non-instrumental maxima, of the type previously reported,⁽⁵⁷⁾

were observed in the immediate vicinity of the incident line. All weak maxima which were observed in the region of the "quasi-elastic" peak appeared to be instrumental and persisted in the spectra of water and of ionic solutions. Their origins in all cases could be related to primary or secondary Bragg cutoffs of impurities (determined to be present by emission spectroscopy) present in the Be filter or of materials in the flight path (see Figures 2 and 4).

(2) For Ionic Solutions

(a) At 1°C and 25°C the solutions of LaCl_3 , MgCl_2 , KF , and LiCl , which show "quasi-hydrate" inelastic frequencies, have Γ vs. K^2 curves (Figure 15) which lie below that of water and which are flatter at larger values of K^2

In contrast, for solutions of CsCl , KCl , and KSCN the Γ vs. K^2 curves lie above water, are less flat, and are increasing at larger K^2 values. At small K^2 values all the curves approach the origin as $\Gamma = \pi DK^2$, as expected for simple diffusion.

(b) With increasing temperature (50° and 75°C), the Γ vs. K^2 curves (Figure 16) become less flat at high K^2 values and approach a more linear behavior for the "structure breakers" (i.e., CsCl , KSCN and KCl).

The full solid curves in Figures 15 and 16 represent a fit to the Γ vs. K^2 curves by the simple "jump-diffusion" limit of the general Singwi-Sjölander model as given by

$$\Gamma = \frac{\hbar}{\tau_0} \left[1 - \frac{e^{-2W}}{1 + K^2 D \tau_0} \right] \quad (63)$$

τ_0 is the residence time, D is self-diffusion coefficient, and e^{-2W} is the Debye-Waller factor.

The Debye-Waller factor was first obtained from the angular variation of the quasi-elastic area (as described below). Values of D and τ_0 were then chosen to yield the optimum fit to Γ vs. K^2 and to minimize residuals. τ_0 is primarily determined by Γ at large K^2 values where $\Gamma \rightarrow \hbar/\tau_0$. As e^{-2W} is close to unity, D is mainly determined by the slope at the origin. Figure 15 shows that agreement is obtained for the data at 1°C, 25°C and certain of the data at 50°C, with the jump diffusion model which accounts for the functional shape of Γ vs. K^2 over the observed range of K^2 values and give values of D and τ_0 in numerical agreement with those obtained by other techniques (Tables III & IV). In contrast, at higher temperatures the validity of this simple model is subject to question as considered below. Solutions of salts like LaCl_3 , MgCl_2 , KF and LiCl which with increasing concentration showed the rapid growth of frequencies in the inelastic spectra similar to those of the solid hydrates, cause a pronounced decrease in D and increase in τ_0 . This undoubtedly arises from an increase in the activation energy and reflects, in part, the strong cation-water coordination in the primary hydration layer and, in part, stronger hydrogen bonding and polarization forces in higher hydration layers. Frank and

Evans⁽¹⁷⁾ have commented that the size of a frozen patch decreases in the progression $\text{Al}^{+3} > \text{Mg}^{+2} > \text{Ca}^{+2} > \text{Sr}^{+2} > \text{F}^- \geq \text{Li} > \text{Na} > \text{Cl}^-$. Glueckauf⁽⁵⁸⁾ has calculated from the electrostrictive influence of ions in solution that the time average number of water molecules in the "iceberg" about the cations for La^{+3} , Nd^{+3} , Yb^{+3} , Er^{+3} , Be^{+2} , Fe^{+3} , Cr^{+3} and Al^{+3} is nearly twice as large as for Li^+ , Ba^{+2} , Sr^{+2} , Ca^{+2} and Mg^{+2} . Also, Jackson, Lemons and Taube⁽⁴⁵⁾ have shown from P.M.R. studies that exchange of water between the solvent and the hydration shell is much slower for Al^{+3} , Ga^{+3} and Be^{+2} than for Mg^{+2} , Sn^{+2} , Ba^{+2} , Hg^{+2} and Bi^{+3} . From an x-ray study of LiCl solution, Brady⁽⁷⁾ has concluded that Li^+ is a highly hydrating ion with Li^+ affecting the solvent more than Cl^- . Li^+ gives rise to most orientation of solvent water.

In contrast, solutions of salts like CsCl and KSCN which primarily broadened the inelastic frequencies of pure water and showed no pronounced new frequencies at these concentrations cause an increase in D and a decrease in τ_0 . Hence, such salts break or loosen the water structure and cause a decrease in the activation energy.

From values of τ_0 and D , an estimate of the "jump-lengths" ℓ can be obtained from the relation $D = 1/6 \frac{\ell^2}{\tau_0}$ (as given in theories of random walk and of Brownian motion). In the "jump-diffusion" model there is no implicit distinction between jumps of an entire H_2O molecule and re-orientation jumps involving the breaking of a hydrogen bond and a re-orientation of one or more protons of a H_2O molecule. The former would involve a distance about that of an O-O distance in water (3 Å) or would be characteristic of equilibrium water positions for a given solution; the average distance due to a rotational jump could be shorter. The

jump distances at 1° and 25° for most salts and water are less than 3 Å, typically about 1.5 Å. In addition, while large variations in both D and τ_0 occur with different salts, the values of λ^2 show little variation and could be plausible if the "jumps" corresponded to rotations or at least combinations of rotations and translations of H_2O molecules.

From the relationships⁽⁵⁴⁾ $\tau = \tau_0 e^{+U/kT}$ and $D = D_0 e^{-U/kT}$, estimates of the activation energies of H_2O molecules were made. These vary from 2.6 kcal per mole for water, to 3.0 for KF, to 3.4 kcal mole for $MgCl_2$. While these values will be considered as approximate in view of the present accuracy of the data, their magnitudes are reasonable.⁽⁴³⁾⁽⁴⁸⁾⁽⁵⁴⁾⁽⁵⁹⁻⁶¹⁾

Estimates of the energy to break a hydrogen bond vary from about 2.8 kcal per mole⁽⁴⁸⁾ to 3.7 kcal per mole⁽⁶²⁾ for water. Valiev and Enel'yanov⁽⁴³⁾ reported from spin-echo measurements that Mg^{+2} ions increase the activation energy relative to water by about 2.6 kcal per mole. The activation energies for H_2O molecules in KCl and KSCN solutions appear slightly lower than that for pure water in keeping with their role as weak "structure-breakers."

The jump diffusion limit requires that the area of the quasi-elastic maximum to be proportional to a Debye-Waller factor,⁽⁶³⁾ e^{-2W} , where $2W = 1/6K^2R^2$ or $2W \approx K^2 \left(\frac{\pi}{2Mk\Theta_D} \cdot \frac{6T}{\Theta_D} \right)$. Hence, as K^2 varies as $\sin^2 \phi/2$, the area should show a specific angular variation which was indeed observed. From the angular variation of the quasi-elastic area, values of R^2 , the mean-square displacement of vibration, or of Θ_D , effective Debye temperatures were obtained. The values of R are typically 0.5 Å and are reasonably large compared to the average O-O distance of about 2.9 Å in water. For the structure-makers, the values of Θ_D are systematically higher than for pure water. Thus, for solutions at 1°C, Θ_D varies from 150°K±15°K for pure water to about 200°K±15°K for $MgCl_2$

and LaCl_3 . In contrast, Θ_D for the structure-breakers occurs within error of the value for pure water. The low values of $k\Theta_D$ as compared to kT and of the average vibrational amplitudes compared to the O-O distances, are characteristic of an excited or "hot lattice" in which H_2O molecules vibrate with large amplitudes and bond dissociation and re-orientation of molecules can occur due to thermal fluctuations. These features are consistent with the anharmonicities and multi-phonon effects, as discussed above. The presence of the ions with strong field (i.e., Mg^{+2} , La^{+3} , F^-) causes a decrease in the anharmonicity and an increase in the Debye temperature. The magnitude of the value of Θ_D obtained for water is in reasonable agreement with those previously reported.⁽²⁰⁾ In addition, it is of interest that both the direction and the magnitude of the increase in the Θ_D observed, correlate with the glass transition temperatures and their dependence on salt concentration observed by Angell, Saxe and Bressel.⁽⁶⁴⁾ Egelstaff⁽⁶⁵⁾ and others⁽⁶⁸⁾ have pointed out that the simple jump diffusion model may not be applicable for large K^2 values and at higher temperatures in water where recoil and a free particle behavior must also be considered. The experimental problem for the larger K^2 values is therefore whether the observed tendency of Γ to flatten and to approach a constant value indeed reflects a delay time and, hence, an approach to $\Gamma = \hbar/\tau_0$ (in accord with the jump model) or whether appreciable contributions from a "free particle" behavior are also occurring. Contributions from a "free particle motion" should cause a departure from a Lorentzian shape, but background and statistical errors could preclude small but significant variations from being detected.

However, departures should also occur from the specific temperature behavior for the Γ vs. K^2 curves of the simple jump model which can be observed (see Appendix II). For this purpose, it is convenient to express the observed dependence of Γ vs. K^2 in terms of the dimensionless parameters $\Gamma/kT = y$ and $\frac{\hbar DK^2}{kT} = x$, for a series of temperatures. The simple jump-diffusion model then becomes

$$y = \frac{\hbar}{\tau_0 kT} \left[1 - \frac{e^{-2W}}{1 + \frac{kT\tau_0}{\hbar} x} \right]$$

Then, for small x (i.e., small K^2) $y = x$, independent of temperature and corresponds to the simple diffusion limit. The "jump model" passes to this long time limit. However, for short enough time intervals (large K^2 values) the motion must be more similar to that of a free particle. (65)(66)(19) The simple jump model does not pass to this limit correctly. Various models (63)(65)(66) have been proposed that pass to both limits. They estimate that a "free particles" behavior would contribute to the quasi-elastic broadening when the parameter $\frac{K^2 D^2 M}{kT}$ (the ratio of the characteristic correlation time for a free particle to that of diffusion motion) is not small compared to unit as for large values of K^2 ; of the mass M or of D . In principle, the mass M need not be the mass of an individual water molecule but could correspond to the total mass of the water molecules within a range in which they move in a correlated manner. (67) Thus, if discrete "clusters" were to exist, this mass could be the "cluster mass." However, it does not necessarily imply the existence of clusters.

For large values of $\hbar DK^2/kT$, the value of Γ/kT increases with increasing temperature for a jump diffusion model, but, in general, decreases if significant contribution from free particle limit is present.

From the observed dependences of y vs. x at 1°C , 25°C , 50°C , and 75°C , the following general trends were observed:

- (1) For the smaller values of x , all the curves approach the straight line, $y = x$, characteristic of simple diffusion. Thus, all temperature values of D (listed in Table III) were extracted assuming Γ vs. $\frac{1}{DK^2}$ at the small K values.
- (2) In all solutions of salts at larger values of x , y departs from and falls below the $y = x$ line. However, at these larger values the values of y for most salts increase in going from 1° to 25° in accord with the temperature behavior of the jump diffusion model.
- (3) Above 25° for most salts, "an inversion temperature" is reached such that a further temperature increase then causes y to decrease as expected for significant contribution from free particle behavior.

At and above this inversion temperature validity of the simple jump model is questionable. The "inversion" temperature is characteristic to a given salt, occurring at higher temperatures for structure-makers like LaCl_3 and MgCl_2 . In contrast, water has an inversion point near 25°C , and KSCN shows no temperature behavior characteristic of jump diffusion above 1°C .

- (4) For "structure-breakers" like KCl and CsCl , a free particle contribution is observed below 25°C . However, at temperatures above 50°C , an increase in y with temperature is again observed.

No attempt will be made here to account for all of the above observations as models capable of quantitatively explaining uniquely all the observed features and the specific ion dependence in the temperature regions where the simple jump model fails are lacking. However, if it is assumed that in addition to jumps of individual molecules, groups of H_2O molecules can move in a correlated manner, a qualitative plausible justification for some of the above trends can be obtained. As emphasized above, it is not assumed that such groups are well defined "clusters" or "icebergs." They are defined only in a "dynamic" sense that the motions of molecules are not independent but comprise the motions of a number of molecules described by a correlation function within an average range.

An increase in either the correlation mass or the associated D for such a group can increase the parameter $\frac{K^2 D^2 M}{kT}$ and, hence, cause a departure from a simple jump model. Thus, in water above $25^\circ C$, and in $4.6m$ KSCN above $1^\circ C$, motions of correlated groups may be occurring and contributing to the quasi-elastic spectrum, KSCN may weaken the water structure and increase the freedom of such groups even at $1^\circ C$. In contrast, small or highly charged ions like La^{+3} , Mg^{+2} and F^- restrict the motions of such groups until a higher temperature is reached. Indeed, such ions can form strong ion water coordinations and increase the activation energy of molecules even at low salt concentrations. In contrast, CsCl and KCl at $4.6m$ (12 H_2O per ion pair) may rapidly break up the water structure including any correlated groups so as to decrease the mass in the above parameter faster than any increase in D with increasing temperature so that it approaches the simple diffusion as τ_1 (time during which

continuous diffusion takes place) increases compared to τ_0 . While this explanation must be considered as tentative, it appears that for any model that considers correlated motions the effects of both ions and temperature on the degree of correlation must also be considered.

V. SUMMARY AND CONCLUSIONS

Numerous models have been proposed for the specific structure and ordering of the associated "clusters" in water. While the neutron scattering results do not provide a unique and definitive determination of such structures, they do, together with recent Raman and x-ray measurements, provide additional information on certain characteristics of these units. Even at 1°C water structure must be considered as a highly excited or "hot-lattice" for which the thermal temperature is much above the effective Debye temperature. The bonding of H₂O at 1°C molecules has decreased relative to ice causing an abrupt downward shift in the torsional frequencies. This reflects the increase in the nearest neighbor O-O distance observed by x-rays. The potential of molecular bonding is anharmonic; the vibrational amplitudes are large; bonds are breaking by thermal energy; and jump re-orientation of H₂O molecules are occurring. At 1°C the librational frequencies observed by N.I.S. indicate that an appreciable number of four-bonded species exist; such species have been observed by Raman. With increasing temperature, the broadening and downward shift of the torsional frequencies indicate a displacement of the equilibrium of species toward lower coordinations in accord with the models of Nemathy and Scheraga⁽³³⁾ and Vand and Senior⁽³⁶⁾. The relaxation rates for breaking

bonds and jump orientations are also increasing with temperature. However, librational frequencies and vestiges of translational frequencies appear even at $+95^{\circ}\text{C}$ indicating a considerable degree of association still persists. At lower temperatures the diffusion kinetics, the relaxation times and the diffusion coefficients can be quantitatively explained on the basis of structural re-arrangements involving the breaking of bonds and subsequent activated jump relocations of individual molecules.

The neutron scattering results for the ionic solutions support the concept of hydration as both useful and valid and are in agreement with the recent conclusions of Walrafen.⁽⁴⁸⁾ Hydrated complexes exist for which the bonding and coordination is determined by the ions. At low concentrations, frequencies of pure water and of hydrated ions can co-exist. The former rapidly give way to the latter which intensify with increasing concentration. The degree of the disruption of water structure with increasing concentration uniquely depends upon the specific ion-water interactions. Small and/or highly-charged ions which form strong ion-water bonds break down the water structure rapidly and form complexes having local orderings similar to corresponding solid hydrates. This similarity of local ordering in both the solid and concentrated liquid states reflects the presence of strong, unique ion-water interactions which may be partially covalent as suggested by Plane and others.⁽¹⁴⁾⁽¹²⁾⁽⁴⁰⁾

Large ions of lower charge also break or weaken the water structure but in contrast to the small and highly-charged ions, form more weakly coordinated complexes. For such ions the strength of primary H_2O -ion coordinations in any complexes may be either weaker or stronger than between molecules in pure water, and are determined by both anion and

cation effects. (48)(51)(53)

The present measurements show that the type of complex strongly determines the diffusive mobility of the water molecules. Certainly at lower temperatures the concept of "positive and negative hydration" of Samoilov⁽⁵⁴⁾ can be used to characterize changes in the diffusion of H₂O solvent molecules due to ionic solutes. The motions of H₂O molecules in most ionic solutions can be described in terms of activated or delayed jumps for which the magnitudes of the self-diffusion coefficients and of the residence times are both primarily determined by changes in an activation energy. The small or highly-charged ions, which form "quasi-hydrate-like" cation-water coordinations raise the activation energy. In contrast, large ions of low charge lower it. In like manner, the former increase the Debye temperature and lower anharmonicity while the latter decrease the Debye temperature and increase anharmonicity. These results suggest that the degree to which ions break water structure and "reinforce" or "loosen" the binding of solvent molecules at low concentrations

is directly related to the ion-water forces which give rise to the formation of the above complexes. Future investigations on the concentration dependence of the diffusive motions should provide more definitive information on this subject.

VI. FUTURE WORK

The neutron spectra for selected "structure-making" and "structure-breaking" salts will be studied as a function of concentration.

The proposed measurements will be carried out at 1°C for the following reasons:

- (a) At low temperatures the jump-diffusion model for water molecules in ionic solutions appears valid.
- (b) The spectral differences are enhanced at lower observation temperatures.

These data will provide information on the concentration dependence of different salts for modifying the water structure, for forming hydration complexes, and for modifying the diffusive kinetics and related parameters. At low concentration, information will be obtained on changes in the coordination, binding, and diffusive motions of solvent water due to specific ions. The rate at which complexes are formed and the diffusive motions modified, with concentration, would be obtained. Self-diffusive coefficients, relaxation times and activation energies as function of concentration, could be derived. At higher concentrations, information on the structures, binding, relaxation times, and activation energies of primary hydration waters would be obtained.

Data will also be taken for salts having different anions but similar cations to those already studied. It has been reported that in solutions cations with strong fields perturb the strength of the hydrogen bond with the anion. ⁽¹⁰⁾⁽⁴⁰⁾ For cations with weaker fields, the results

of the neutron measurements to date indicate that the anion plays an important role in the coordinations and the kinetics of water molecules. To supplement data already taken for many chlorides, measurements of three monovalent salts (e.g., CsBr, KI, KBr) will be made in order to determine relative "structure-breaking" effects of the anions and the formation of non-water-like structured units. Measurements are also proposed for two other salts for the purpose of investigating anionic changes ($\text{La}(\text{NO}_3)_3$ and LiNO_3). It is expected that NO_3^- ion modification of the La^{+3} super lattice noted by Frank⁽¹⁷⁾ can be observed. In addition, the high solubility of these nitrates in water allows the preparation of solutions with low water-to-ion ratios, so that the structure and dynamics characteristic of water in the primary hydration layer of a strong "structure-making" cation can be observed.

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TABLE I

PARTIAL SUMMARY OF RESULTS ON THE STRUCTURE OF HYDRATED SPECIES
AND IONIC AQUEOUS SOLUTIONS

| TECHNIQUE - SOLUTES | INFORMATION OBTAINED |
|---|---|
| <u>X-RAY</u> Ag(NO ₃), Pb(NO ₃) ₂ Ba(NO ₃) ₂ , Th(NO ₃) ₃ UO ₂ (NO ₃) ₂ , LiI RbBr, LiBr | (a) Th ⁺³ and UO ₂ ⁺² have a regular or "super" arrangement in the liquid. The ions are surrounded only by H ₂ O molecules. Ag, Pb, and Ba nitrates show a large fraction of disassociated (gas-like) molecules. I ⁻ , Br ⁻ , Rb ⁺ show no arrangement but only a broad interference between heavy ion and surrounding molecule. |
| KCl, NaCl, LiCl | (b) At low temperatures these solutions showed the second maximum in the radial distribution curve of pure water which is interpreted to show inhomogenous structure at low temperatures, with "water-rich" regions. |
| LiCl, LiBr, RbCl | (c) 4.0 and 2.58 molal LiBr and RbBr retained the principal diffraction maximum of water. In more concentrated solution (i.e., 13m LiCl) the structure of the solutions resembles that of the corresponding hydrated salt. |
| KOH, KCl | (d) For KOH, the K ⁺ substitutes for an H ₂ O in the quasi-tetrahedral water structure while the OH ⁻ occupy interstitial positions. For KCl, the Cl ⁻ breaks down H ₂ O structure by distorting the tetrahedral coordination and squeezing out H ₂ O molecules. |
| LiCl | (e) The water structure is broken by Li ⁺ ions. Hydrated Li ⁺ then pack around Cl ⁻ ions giving a hydration number of 8-9. The hydrated Li ⁺ ions have four water molecules in a tetrahedral configuration about the ion. |
| ErCl ₃ and ErI ₃ | (f) H ₂ O molecules are firmly held in an octahedral arrangement around the Er ⁺³ ions. There is evidence for an "ice-like" ordering of H ₂ O molecules resulting from the higher degree of orientation about the cation. |

TABLE I (Continued)

| TECHNIQUE | SOLUTES | INFORMATION OBTAINED |
|--------------|--|--|
| <u>X-RAY</u> | (continued) | (g) For lithium and sodium halide solutions 7-9 water molecules occupy the first hydration layer of the halide ions. Their number increases slightly with ion size. Second and third hydration layers are correlated with the anions. The region of influence of Li^+ and Na^+ is in general smaller than that of the anions and corresponds to first and second hydration layers. The halide ions lie along the OH axes, while cations lie on the dipolar axes of the primary waters. Considerable ion-ion contact was detected in the cesium salt solutions but not in the others. |
| | 2.5, 5.0 and 10 m. LiCl, LiBr, NaI and CsCl 2.5 and 5.0 m. LiI, NaCl, CsBr 2.5 m. CsI | |
| <u>RAMAN</u> | concentrated ($>4N$) solutions of Li, Ca, Al, Cr and Th nitrates were compared to their corresponding solid salt hydrates | (h) From a correspondence of frequencies in the region $700\text{ cm}^{-1} - 1600\text{ cm}^{-1}$ between the solutions and the solid hydrates, it was concluded that the relative placement of the ions in the concentrated solutions is characteristic of the solid hydrate. |
| | Solutions of the nitrates, sulfates and perchlorates of Cu, Zn, Hg, In, Mg, Tl and Ga | (i) Lines in the $360 - 400\text{ cm}^{-1}$ region assigned to metal - O stretching frequency of cation-water complexes. Increased binding of the hydration sheath is correlated to increased ionic charge. There is considerable electron sharing in the metal-oxygen bond. |
| | LiCl, NaCl, KCl, NH_4Cl , LiBr, KBr, NH_4Br , KNO_3 , $\text{Ca}(\text{NO}_3)_2$, Li_2SO_4 | (j) A similar conclusion was reached from IR studies for metal-oxygen bonding in solid hydrates. |
| | | (k) Strongly hydrated units exist in electrolyte solutions. Librational frequencies of H_2O molecules in the primary hydration layer of the ions are observed between 900 cm^{-1} and 400 cm^{-1} . Reasonable agreement is obtained for $\text{O}-\text{HOH}\cdots\text{Cl}$ and $\text{O}-\text{HOH}\cdots\text{Br}$ librations in solutions and those reported for solid hydrates. |
| | Concentrated solutions of $\text{In}_2(\text{SO}_4)_3$, $\text{In}(\text{ClO}_4)_3$, $\text{In}(\text{NO}_3)_3$ | (l) Changes in the region below 500 cm^{-1} indicated formation of large, highly-ordered clusters of H_2O molecules centered on In^{+3} ions and extending several water molecules in depth. Solutions become more ordered with decreasing temperature. NO_3^- and SO_4^{2-} tended to displace H_2O molecules from the hydration sphere of the cations at $+25^\circ\text{C}$. |

TABLE I (Continued)

| TECHNIQUE - SOLUTES | INFORMATION OBTAINED |
|--|--|
| <u>ELECTRONIC SPECTRA</u> | |
| CoCl ₂ , CoBr ₂ , CoI ₂ and NiCl ₂ , NiSO ₄ , Ni(NO ₃) ₂ | (m) The observed frequencies below 500 cm ⁻¹ , characteristic of a cation complex, appear within 30 cm ⁻¹ of the corresponding solid hydrate in each case. |
| ErCl ₃ , Er(NO ₃) ₃ | (n,o) In the solutions thermally activated lattice vibrations were seen which closely paralleled those of the solid hydrate. The structures in the spectra of the solution were more diffuse than in the solid spectra. They become more diffuse with decreasing concentration. The cation appears surrounded by a quasi-solid-like patch which can support lattice vibrations. Frank and Evans have argued that a similar "super-lattice" may be associated with La ⁺³ ions in solution. |
| <u>ISOTOPIC MOBILITY</u> | |
| Concentrated LiNO ₃ | (p) The solution contains aggregates with molecular orientations similar to the crystal lattice of the solid hydrate. |
| <u>SOLUBILITY</u> | |
| KSCN | (q) The nearly linear SCN ⁻ to an extent occupy channels in the water structure. |
| <u>N.M.R.</u> | |
| Indium halides | (r) Evidence exists for In(H ₂ O) ₆ ⁺³ complexes in solution. |
| General review of data for many salts | (s) In general, the hydrated ion destroys the structure of water and forms complexes of type (Me(H ₂ O) ₆). However, ions may enhance strength of hydrogen bonds of H ₂ O molecules beyond the first hydration layer due to polarization. Vibrations of the complex are in general not harmonic. |
| 1-1 Electrolytes | (t) The ion-water complex is treated as a molecular species and effective hydration numbers are calculated. A decrease in the effective hydration number occurs with increasing ionic radius. Among halide ions, it is suggested that only the F ⁻ forms a hydrate structure. The larger halide ions "break down" the water structure. A "Structure making" effect is suggested for Li ⁺ . |

TABLE I (Continued)

| TECHNIQUE - SOLUTES | INFORMATION OBTAINED |
|---|---|
| <u>N.M.R. O^{17} ABSORPTION</u> | |
| Aqueous solutions of H^+ , Li^+ , Be^{+2} , Mg^{+2} , Ba^{+2} , Sn^{+2} , Hg^{+2} , Ga^{+3} , Bi^{+3} | (u) Exchange times for H_2O molecules between the hydration shell of an ion and the solvent were obtained. For Al^{+3} , Be^{+2} , and Ga^{+3} , the time exceeds 10^{-4} sec. while for all others it is less than 10^{-4} sec. |
| <u>QUADRUPOLE RELAXATION</u> | |
| KCl, CsCl, NaCl, LiCl, $MgCl_2$, $AlCl_3$ | (v) K^+ and Cs^+ increase the rotational freedom of H_2O molecules in the hydration sphere of the ion. In contrast, Na^+ , Li^+ , Mg^{+2} and Al^{+3} reduce it. |
| <u>PROTON RELAXATION</u> | |
| Alkali halide solutions | (w) The configuration of H_2O molecules is more stable about Li^+ , Na^+ or F^- ions than for pure water. While for all other ions, it is less stable. The degree of stability decreases with increasing ionic radius. |
| <u>THEORY</u> | |
| Alkali-metal cations and halid anions | (x) Estimates of interaction energies of ions with their nearest H_2O molecules have been obtained using ICAO-MO theory. The change in the energy of electrons on hydration decreases in the sequence $Li^+ > Na^+ > K^+ > Rb^+ > Cs^+$. The energy changes are smaller for anions than for cations. The translational mobility of H_2O molecules close to the ion should increase in going from Li^+ to Cs^+ . The Raman studies summarized above also indicate metal-oxygen electron sharing in aqueous solutions. Infrared studies yield similar results for the solid salt hydrates. |

TABLE I (Continued)

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TABLE II

LOW FREQUENCY MOTION OF H₂O MOLECULES IN IONIC SOLUTION
(All Frequencies in cm⁻¹)

| <u>LaCl₃</u> | <u>MgCl₂</u> | <u>LiCl</u> | <u>KF</u> | <u>NaCl</u> | <u>KCl</u> | <u>KSCN</u> | <u>CsCl</u> | <u>H₂O</u> | |
|-------------------------|--|--------------------|---------------------------|-------------|------------|-------------|-------------|-----------------------------|-------------------|
| | | | 1000 | 1060 | 1000 | | 1170 | | |
| 884±40 | 884 | 884 | | | | 884 | 884 | 860 | |
| | 706 | 706 | 706 | | | | | | |
| 670±40 | (714) ^a (607) ^b (615) ^c | (660) ^d | | 670 | | | | (722) ^g | Rock |
| | 575 | | 522 | | | | | | |
| 522±40* | (487) ^b (536) ^c | 498 | | 547 | 522 | | 547 | 590 (550) ^g | Wag |
| | | | 475 | | | 480 | | | |
| 461±15 (425)* | 454 (464) ^c | (430) ^d | | 434 | 454 | | 434 | 454 (450) ^g | Twist |
| | | 398 | 416 | | | 398 | | | |
| 398±15 | 382 (380) ^b (384) ^a | | | 366 | 381 | | 381 | | M-O Stretch |
| 351±15 | 337 | 351 | 337 | | | | | | |
| 267±15 | | | 250 | | 245 | | 250 | | |
| 222±15 | 222 (200) ^c | 225 | 222 (252) ^h | | | 220 | | 222 | |
| 168 | 180 | 168 | 143 | | 158 | 168 | 165 | 175±5 (175) ^e | H-bond Stretch |
| | | | | | | | | 60±3 (60) ^g | |

* Frequencies observed by N.I.S. in the solid hydrate.

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TABLE III

SELF-DIFFUSION COEFFICIENTS AND AVERAGE
RESIDENCE TIMES FOR WATER MOLECULES IN IONIC SOLUTIONS

| | | "Structure-Breakers" | | | | | "New Structure-Makers" | | | |
|---|------|----------------------|------|------|------------------|------|------------------------|------|-------------------|-------------------|
| | | CsCl | KSCN | KCl | H ₂ O | NaCl | LiCl | KF | MgCl ₂ | LaCl ₃ |
| Dx10 ⁵ cm ² /sec | 1°C | 0.9 | 1.0 | 0.8 | 0.8 | 0.9 | 0.6 | 0.6 | 0.4 | 0.5 |
| | 25°C | 2.8* | 3.5* | 3.2* | 2.7* | 1.9 | 1.3 | 0.9 | 0.8 | 0.5 |
| | 50°C | 3.1* | 6.4* | 4.0* | 4.2* | 2.2 | 2.2 | 1.8 | 1.2 | 1.0 |
| | 75°C | 3.9* | 8.3* | 4.3* | 4.5* | 4.6* | 4.1* | 2.8* | 1.9 | 1.4 |
| τ ₀ x10 ¹² sec. | 1°C | 1.4 | 1.7 | 2.0 | 2.4 | 3.4 | 3.2 | 3.7 | 5.7 | 7.9 |
| | 25°C | | | | | 2.0 | 2.1 | 1.8 | 2.8 | 2.5 |
| | 50°C | | | | | 1.2 | 1.1 | 1.6 | 1.7 | 2.2 |
| | 75°C | | | | | | | | 1.5 | 1.4 |

1. All solutions are 4.6 molal except 3.5 molal for LaCl₃ solution and 3.4 molal for KCl solution at 1°C.
2. Values with * were obtained from the slope near origin of Γ vs. K² curves. These values were used whenever simple jump diffusion model is not valid. Accordingly, no corresponding values of τ₀ are given.

TABLE IV

SUMMARY OF REPORTED VALUES FOR SELF-DIFFUSION
COEFFICIENTS AND AVERAGE RESIDENCE TIMES FOR
WATER MOLECULES IN IONIC SOLUTION

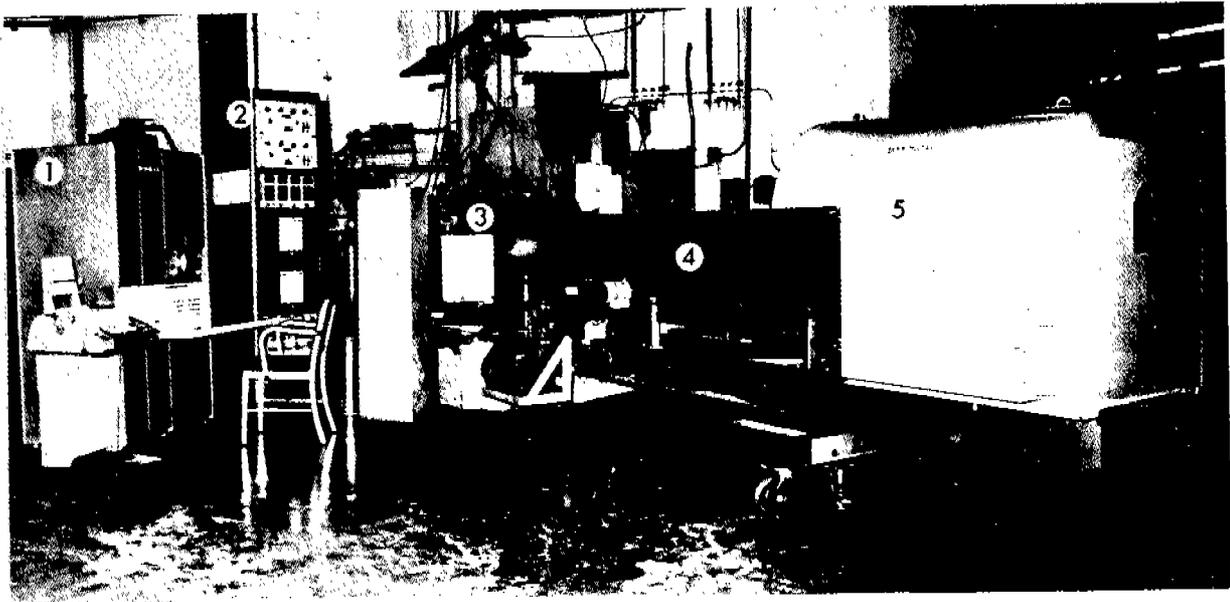
| Dx10 ⁵ cm ² /sec | Temp (°C) | CsCl | KSCN | KCl | H ₂ O | NaCl | LiCl | KF | MgCl ₂ | LaCl | Ref |
|--|----------------|-----------------------------------|------|----------------------------------|------------------|--|------------------------------------|----------------------------------|-------------------|------|-------|
| | 0 | 1.45 (4m) | | | | 1.1 | 0.78 (4m) | 0.76 (4m) | 0.73 (4m) | | |
| 1 | | | | | 0.97 | | | | | | (b) |
| 10 | | | | 1.74 (3f) | 1.68 | 1.19 (4f) | | | | | (c) |
| 23 | | | | 2.38 (3.45M) | 2.47 | 1.8 (3.5M) | 1.13 (5.6M) | 1.23 (5.55M) | 0.8 (3.0M) | | (d) |
| 25 | 2.70 (3.6m) | | | | 2.54 | | 1.75 (3.8m) | | | | (e) |
| 25 | | | | | 2.57 | 1.85 (4f) | | | | | (c) |
| 25 | | | | | 2.13 | | | | | | (b) |
| 25 | 2.92 (4m) | | | 2.63 (4m) | 2.5 | 1.60 (5m) | | | | | (a) |
| 25(?) | 2.7 (4.6M) | | | 2.4 (4.6M) | | 1.6 (4.6M) | 1.4 (4.6M) | | 0.45 (4.6M) | | (f) |
| 50 | | | | | 3.94 | | | | | | (b) |
| 75 | | | | | 6.27 | | | | | | (b) |
| 80 | 6.70 (4m) | | | 6.49 (4m) | 8.0 | 4.82 (5m) | 4.65 (4m) | 5.08 (4m) | | | (a) |
| τx10 ¹² sec | 0 | | | | 3.6 | | | | | | (g) |
| | 0 | | | | 2.5 | | | | | | (h) |
| | 25 | Cs ⁺ 3.1 (<2.0m) | | K ⁺ 3.3 (<2.9m) | | Na ⁺ Cl ⁻ 6.6 3.3 (<3.3 m) | Li ⁺ 29.0 (<3.9m) | F ⁻ 6.0 (<3.5m) | | | (i) † |
| | 25 | | | | 1-2 | | | | | | (j) |

† Result as reported by Fabricand et al are based on τ/τ^0 and τ^0 was taken as 3.5×10^{-12} from Bloembergen et al. See Fabricand's original paper.

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Figure 1

The Union Carbide neutron-time-of-flight spectrometer.



1 ON-LINE COMPUTER 2 CONTROL UNIT 3 SAMPLE STATION
 4 FLIGHT PATH 5 BF₃ COUNTER CHAMBER

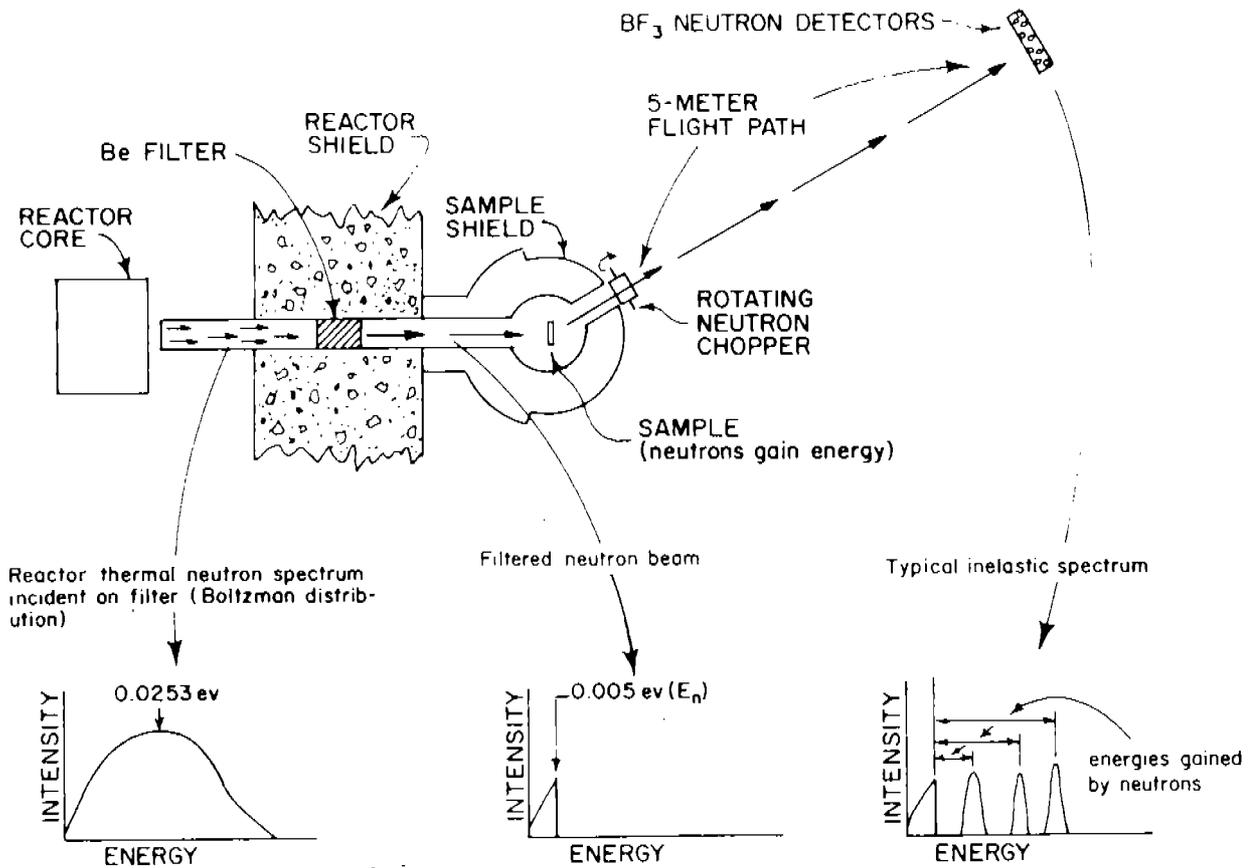


Figure 2

The time-of-flight spectrum of the elastic peak of vanadium is shown for a 65° scattering angle. The primary and secondary Bragg cutoffs of Be, Al, BeO and Be₂C are indicated. The impurities were determined present by emission spectroscopy. The solid line represents an optimum fit through the data points with a $32 \mu\text{-sec.}$ reactor spectrum varying as $1/t^n$ $n = 5.9$ broadened by a Gaussian of width $\Delta t = 32 \mu\text{-sec.}$ for the instrumental broadening. Similar vanadium spectra were measured at other scattering angles at which quasi-elastic measurements were made. This initial spectral distribution was further broadened by "folding in" a Lorentz function with varying half-width at half-maximum for comparison with the data. Examples of such broadened curves are also shown with half-widths indicated. Typical fits to observed quasi-elastic maxima are also shown. The independence of the spectral shapes for water to cell thickness are illustrated by a comparison of the spectra observed using cells having maximum thicknesses of 0.25 mm and 0.5 mm (see Appendix I for details).

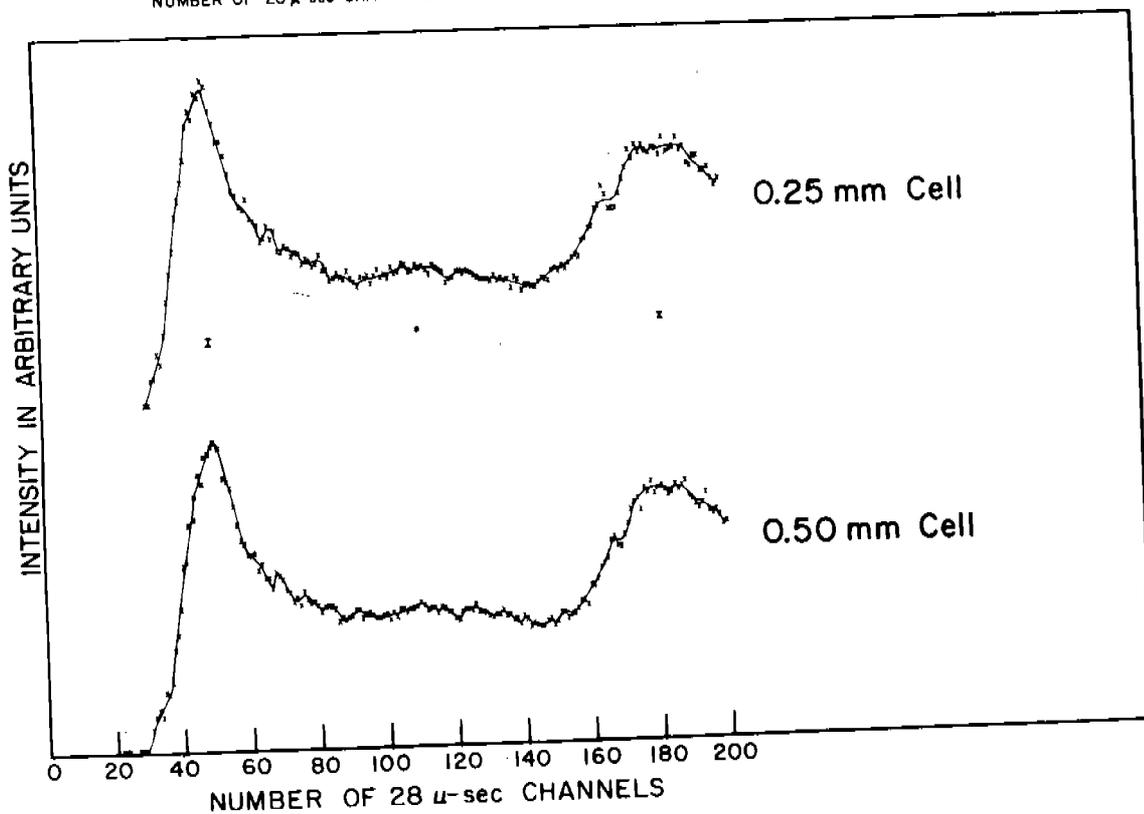
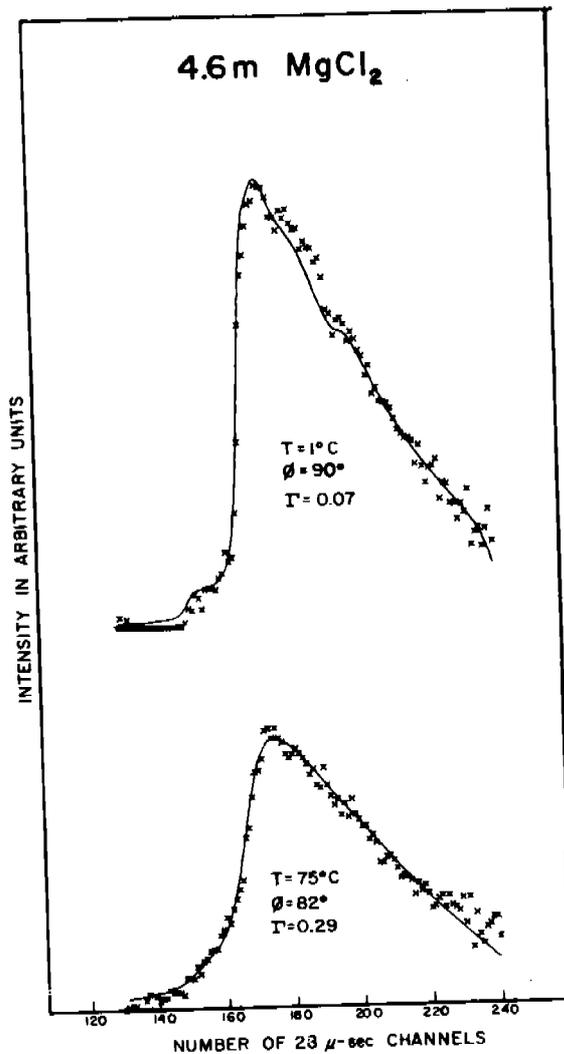
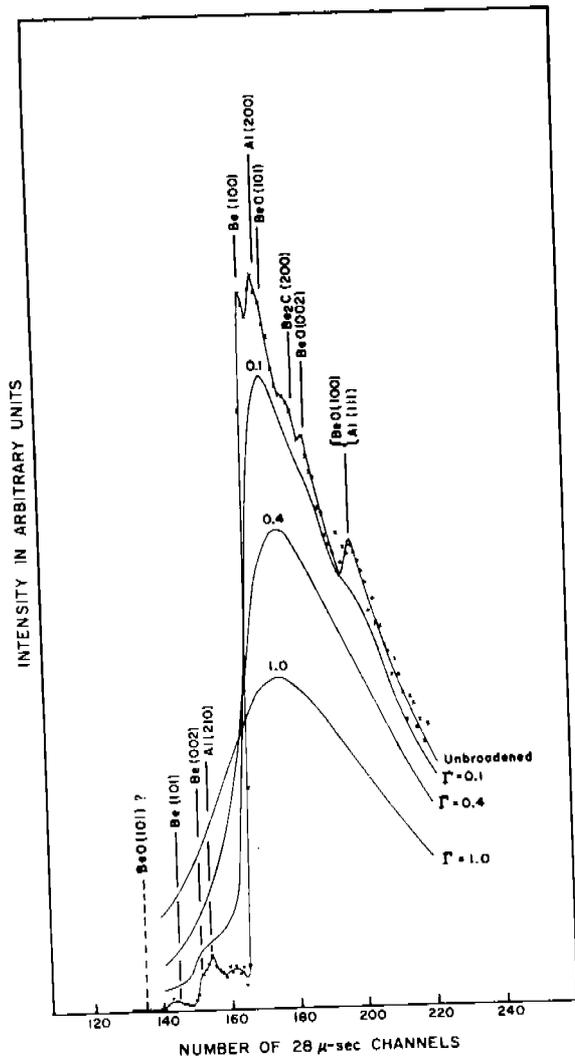


Figure 3

The time-of-flight spectra and the corresponding one-phonon frequency distributions for water at 1°C and 90° scattering angle are compared to those at a 45° scattering angle at 25°, 50° and 75°C. Partially resolved broad maxima appear in the torsional region above 400 cm⁻¹ which become less well defined with increasing temperature. Similar maxima appear, within resolution, in spectra taken at other angles.

The frequency distributions were calculated, assuming both the validity of cubic one-phonon cross section and a Debye-Waller factor of unity. If these approximations were strictly valid, the frequency distributions at a given temperature coincide for data taken at different angles which is not observed. Similar conclusions have been reached and discussed in detail by Larsson and Dahlborg. (18)

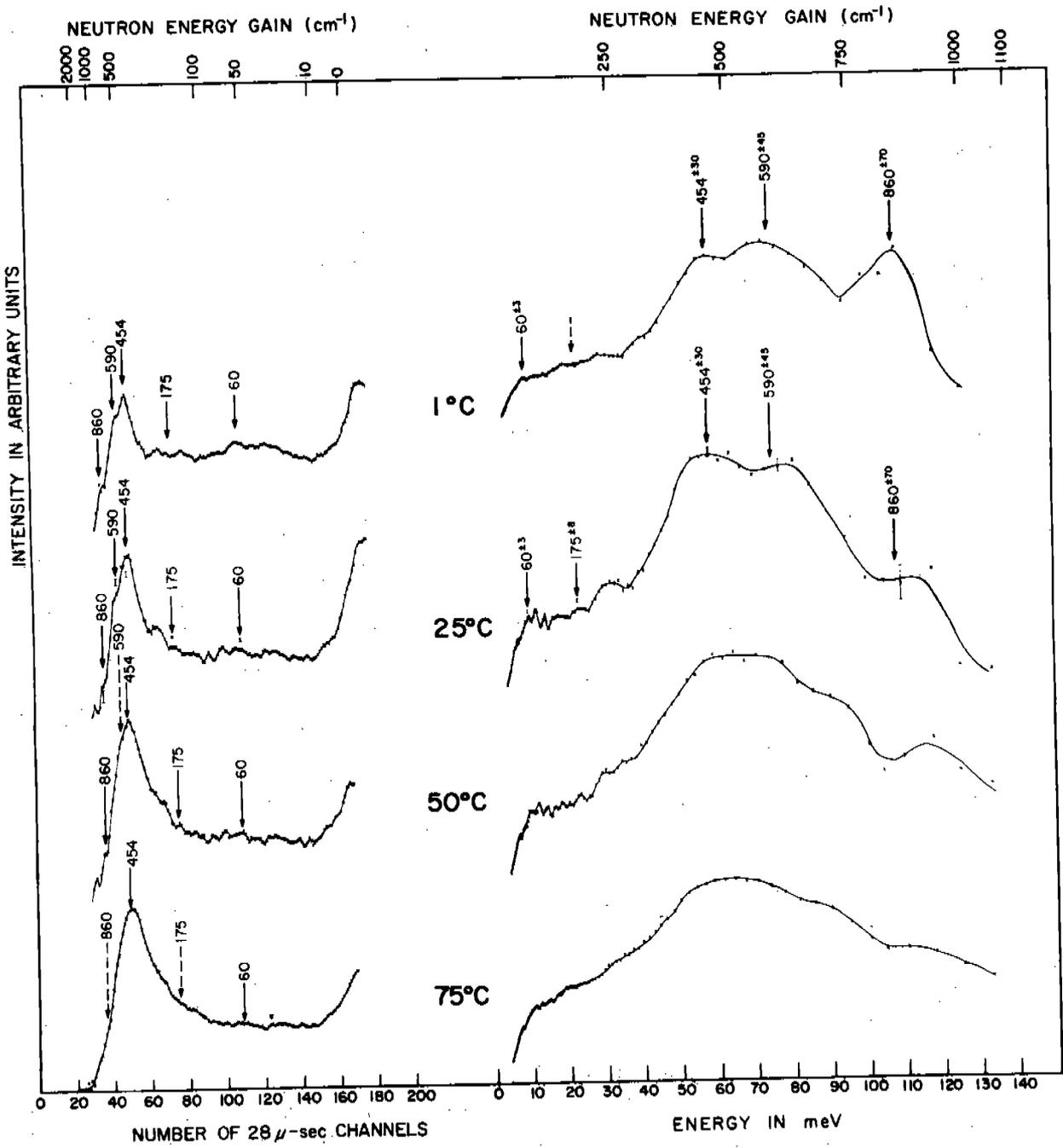


Figure 4

The time-of-flight spectra at 1°C for 4.6m MgCl₂, KF, LiCl and a 3.5m LaCl₃ are compared with their corresponding solid salt hydrates at -25°C. and all spectra were measured at 45° scattering angle except that for KF solution which was measured at 65°. The sharpness of the frequencies in the liquid and their correspondence to those in the solid hydrates appear most pronounced at these concentrations for LaCl₃ and LiCl. At higher concentrations, as shown in Figures 6 and 7, the similarity of the frequencies for MgCl₂ and KF solutions to those in the respective solid becomes more pronounced. The corresponding frequency distributions calculated in the one-phonon approximation from the spectra of this figure are shown in Figure 5. The frequencies of the spectral maxima and shoulders are given in cm⁻¹. The dashed arrows indicate a weak shoulder as determined by shape changes in the time-of-flight distribution at higher frequencies where their intensities are suppressed by the population factor and by the reduction of the figure. However, they appear as partially resolved components in the corresponding frequency distributions. In a number of cases (i.e., MgCl₂·6H₂O and LaCl₃·6H₂O) individual maxima in the liquid and appear unresolved in the solid, as indicated. However, these maxima appear in spectra taken at different angles and temperatures. Instrumental maxima arising from secondary Bragg cutoffs of Be, BeO, Be₂C, and Al in the primary beam are indicated. Typical errors calculated from observed and background counts are shown.

Figure 4 (continued)

The incoherent neutron spectra of a number of solid hydrates have been reported previously^{(78) (79)} as observed at a scattering angle of 90° and at 25°C . However, it was found that the sharpness and resolution of the maxima observed here for these hydrates appear markedly increased in spectra taken at 45° scattering angle and at -25°C .

INTENSITY IN ARBITRARY UNITS

NEUTRON ENERGY GAIN (cm^{-1})

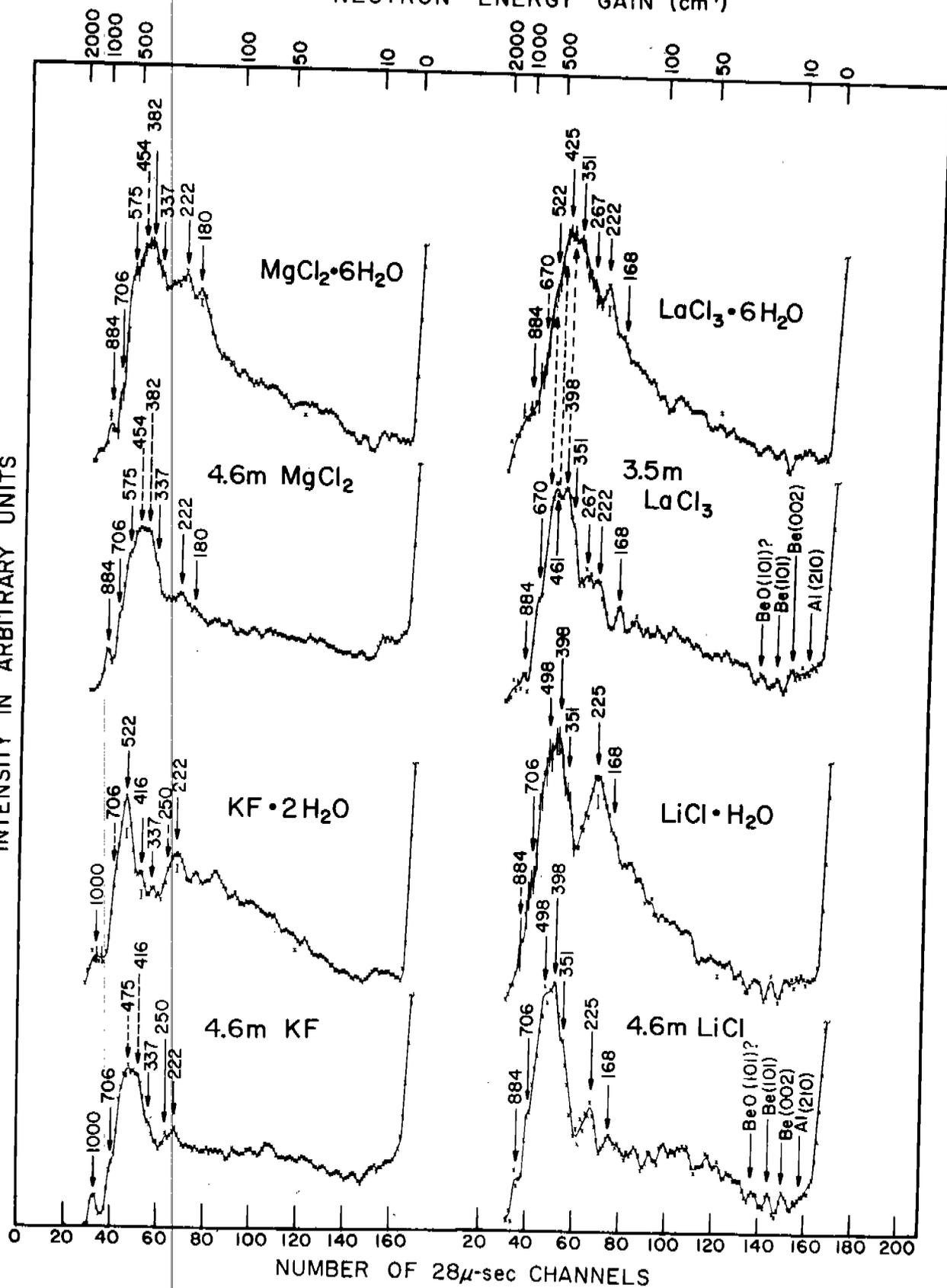


Figure 5

The frequency distribution corresponding to the time-of-flight spectra of Figure 4 for the solid hydrates and solutions of LaCl_3 , MgCl_2 , KF and LiCl , are shown. They were calculated assuming a one-phonon cross section for the inelastic spectra. The energies of the maxima in the frequency distributions are given in cm^{-1} . The energies at which these maxima occur in the time-of-flight spectra of Figure 4 are also given in parenthesis for comparison. It can be seen that any shifts of the peak frequencies due to the temperature dependence of the one-phonon cross section in general are one channel or less.

$\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ (1) was measured at -25°C and at 45° scattering angle, and $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ (3) was taken at 25°C and 65° scattering angle.

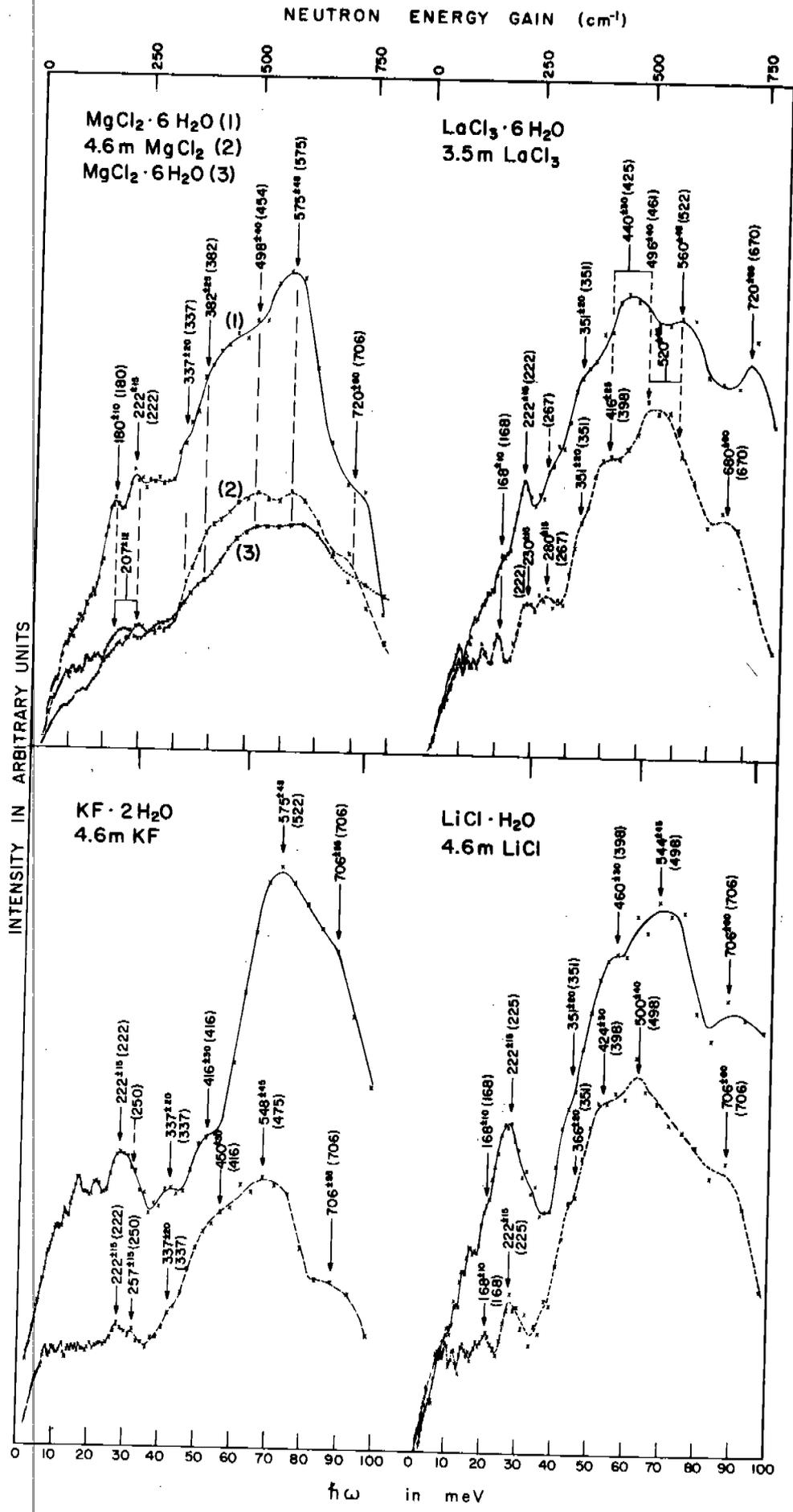


Figure 6

The time-of-flight spectra and the corresponding difference curves for neutrons scattered at 65° angle from 1.0 m, 3.5 m, 5.5 m MgCl_2 and from $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ at 25°C . The two frequencies at 454 cm^{-1} and 382 cm^{-1} which appeared unresolved in the -25°C spectrum of $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ (Figure 3) appear partially resolved in the above spectrum. The difference curves were obtained by a channel-by-channel subtraction of the water spectrum from that of the salt solution or the solid hydrate. The only purpose of these curves is to emphasize trends and to aid in the recognition of spectral regions where differences occur. They are not to be interpreted as spectra of species present in the salt solutions but not in pure water, and only the more major features and maxima should be considered as statistically significant. As a result of normalization procedures the net area in the inelastic region (channels 30 to 145) is set equal to zero, hence, an intensity enhancement in one region is compensated for by an apparent decrease in another.

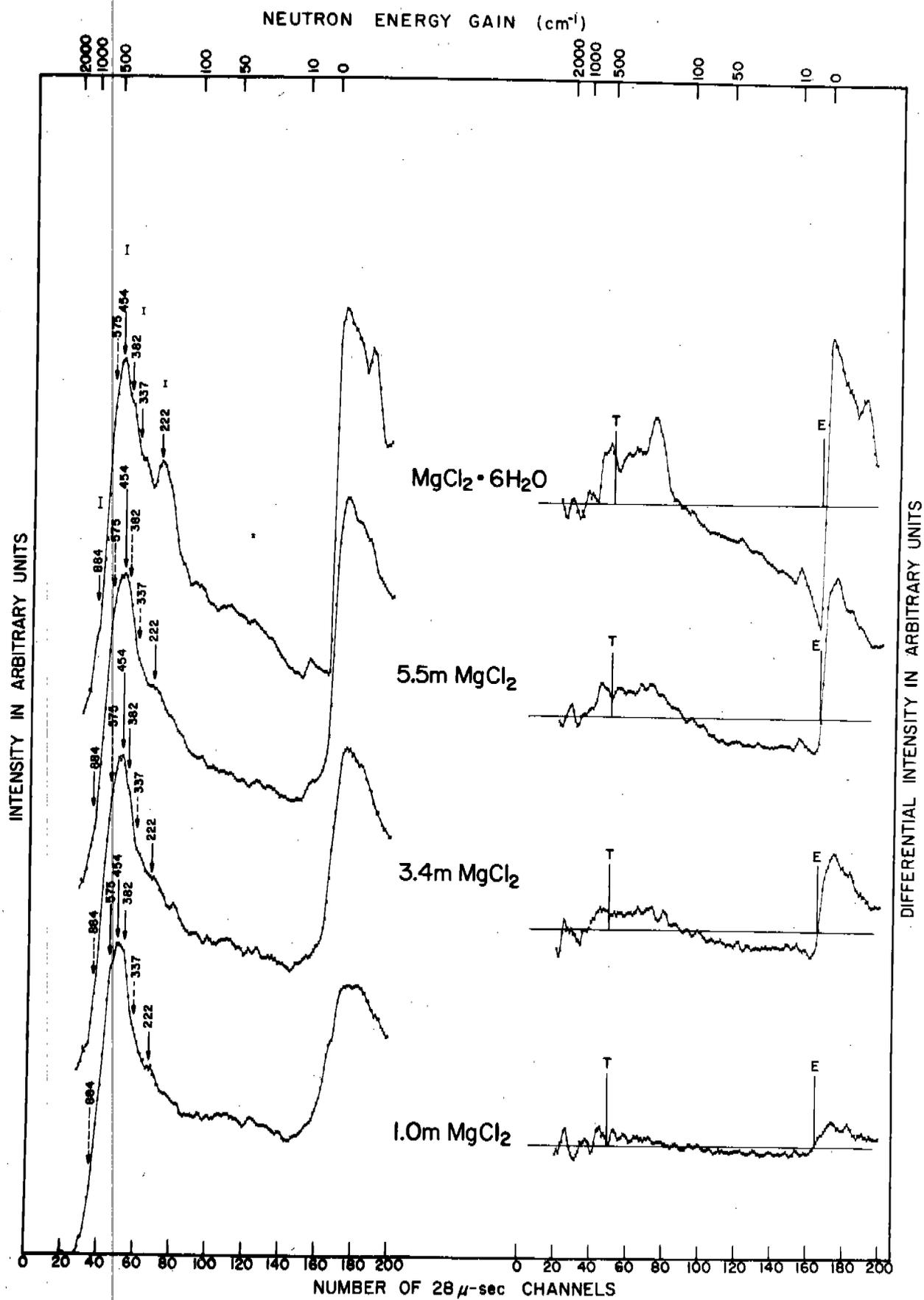


Figure 7

The time-of-flight distributions and the corresponding difference curves for neutrons scattered at a 65° angle from 4.6m and 17.0m KF and from $\text{KF}\cdot 2\text{H}_2\text{O}$ at 25°C . In addition, the time-of-flight spectra and corresponding difference curves are also shown for comparison. With increasing concentration the spectra of the KF solutions appear to approach that of solid $\text{KF}\cdot\text{H}_2\text{O}$. In contrast, the spectra of KSCN show a much less pronounced departure from the water spectra with increased concentration. With the concentration ranges shown the torsional maximum is observed to shift to higher frequencies and the quasi-elastic maximum to sharpen and intensify relative to water with increasing KF concentration. In contrast, 4.6m KSCN shows a broad and less intense quasi-elastic maximum than water and a slight broadening to lower energies of the torsional maximum. However, in 18.5m solution of KSCN the quasi-elastic maximum appears sharper and more intense than for water.

Figure 8

The concentration dependence of the neutron time-of-flight spectra and corresponding frequency distribution for LiCl are shown for data taken at a 45° scattering angle. Data are shown for solutions at 25°C and for the solid hydrate at $+25^\circ$ and -25°C . Maxima appear better resolved at the lower temperatures for the solid hydrates. The spectra of the solution with increasing concentration become similar to that observed at -25°C for the solid hydrate.

NEUTRON ENERGY GAIN (cm^{-1})

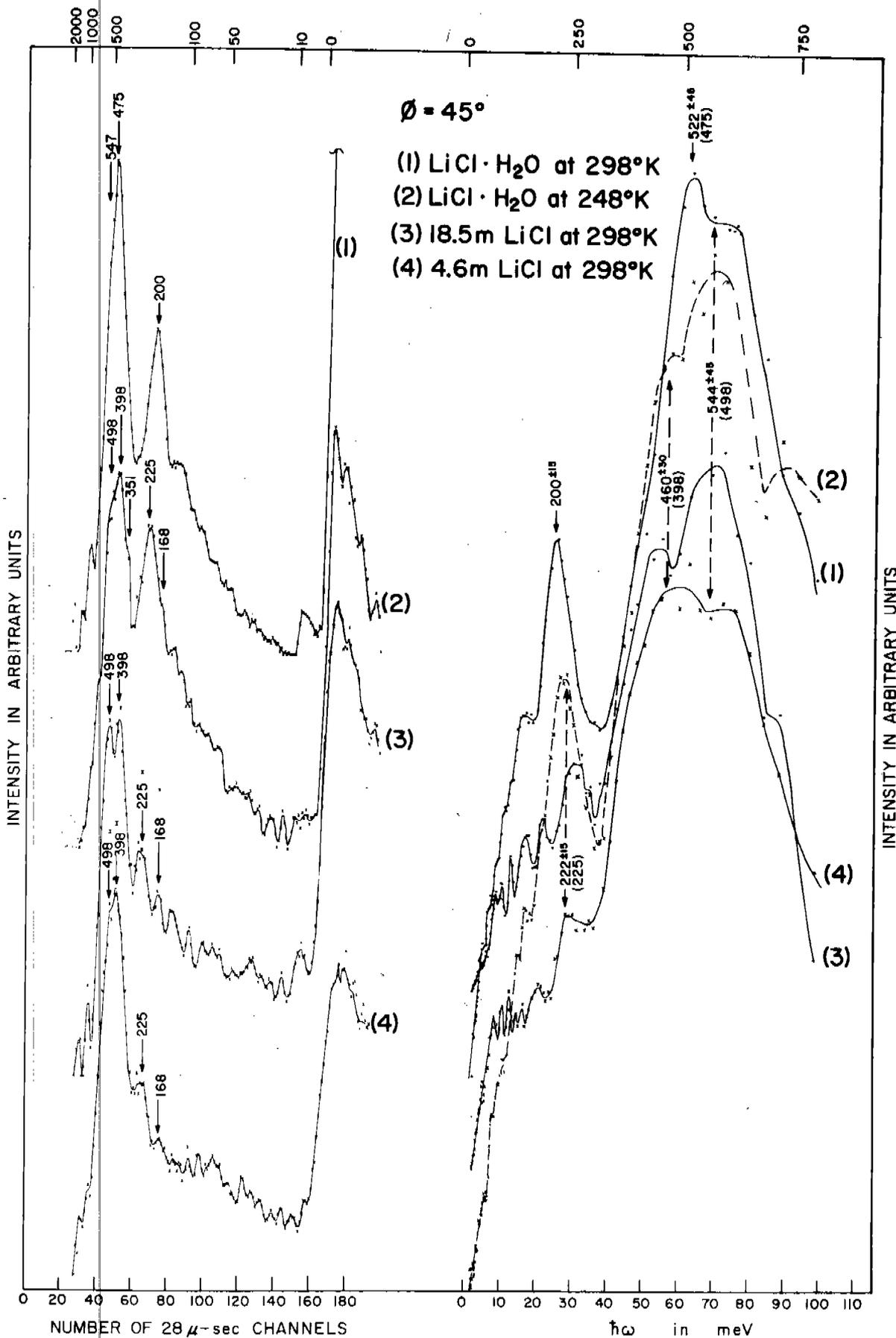


Figure 9

The time-of-flight spectra, the frequency distributions, and the differential curves for neutrons scattered at 65° from solid $\text{LiNO}_3 \cdot 3\text{H}_2\text{O}$ and 18.5m of LiNO_3 obtained by melting the solid hydrate in its waters of crystallization are compared. The frequency distributions corresponding to the neutron spectra of Figure 5 at 65° for KF as a function of concentration are also shown.

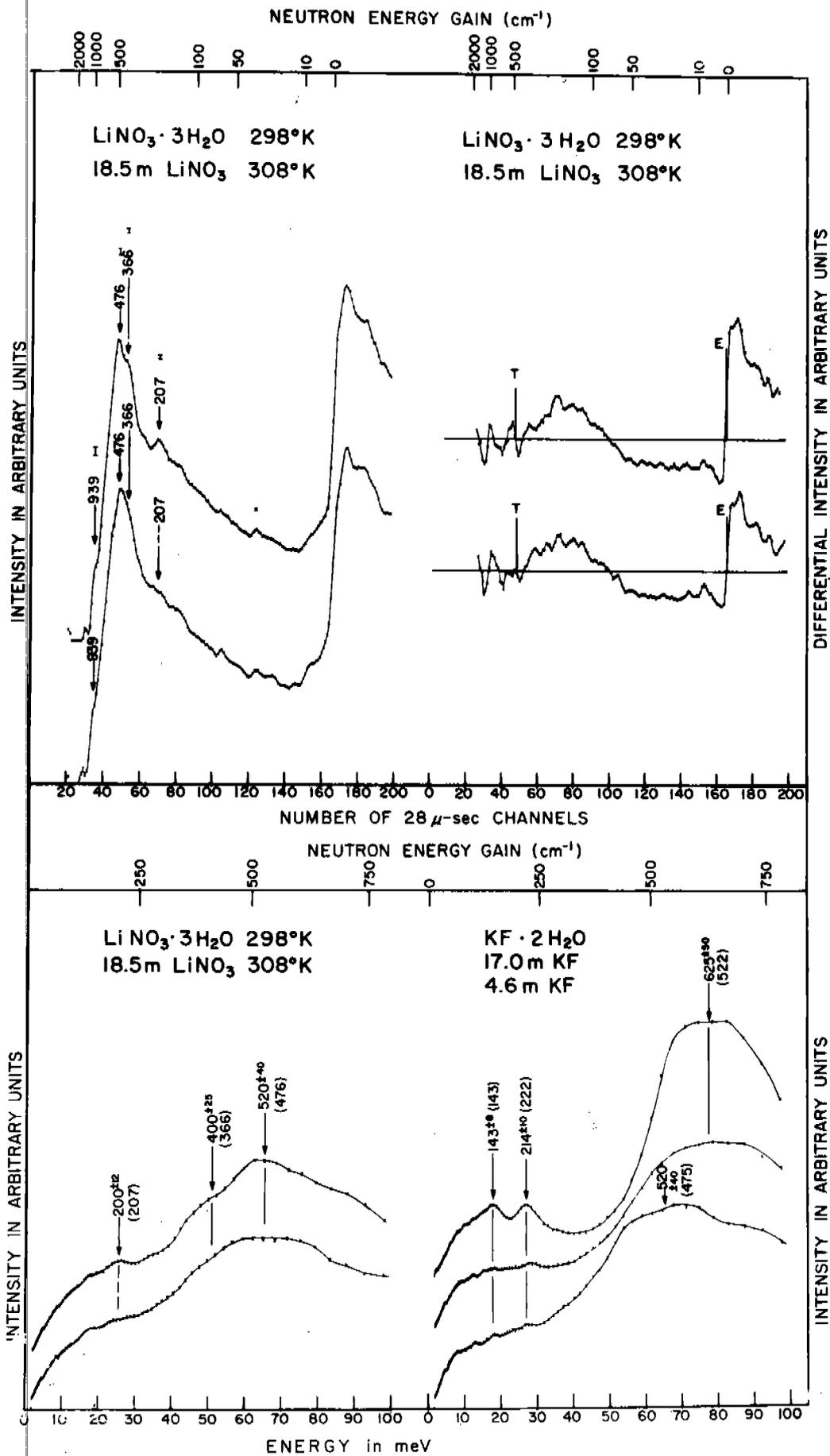


Figure 10

The time-of-flight and difference spectra for 4.6m of four potassium halides at 25°C and a scattering angle of 65°. The effect of varying anion size is shown.

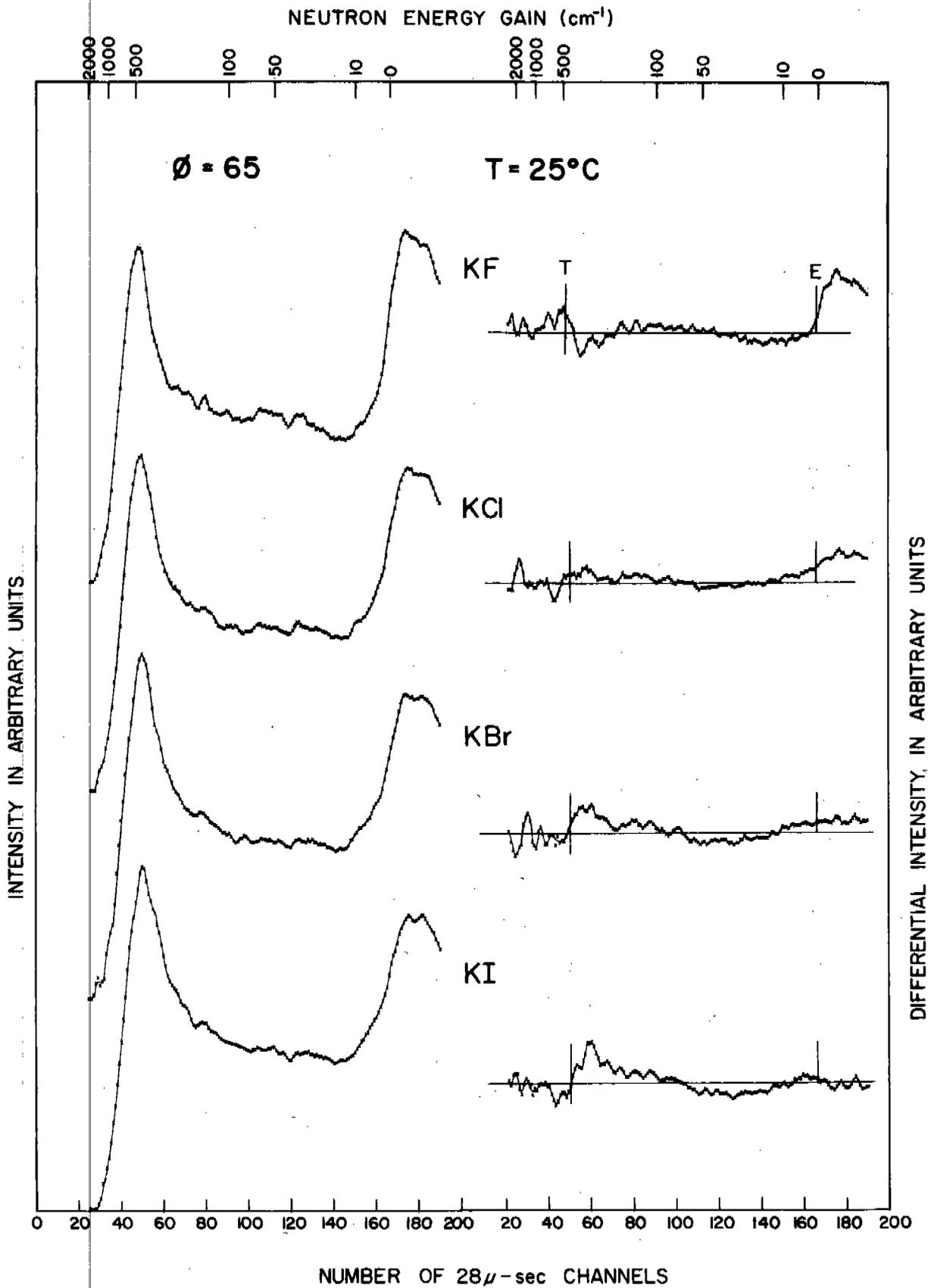


Figure 11

The time-of-flight and the difference curves for 3.5m sodium, calcium and lanthanum chlorides. As these cations have each essentially the same radius, the spectra show departure from that of pure water as a function of ionic charge.

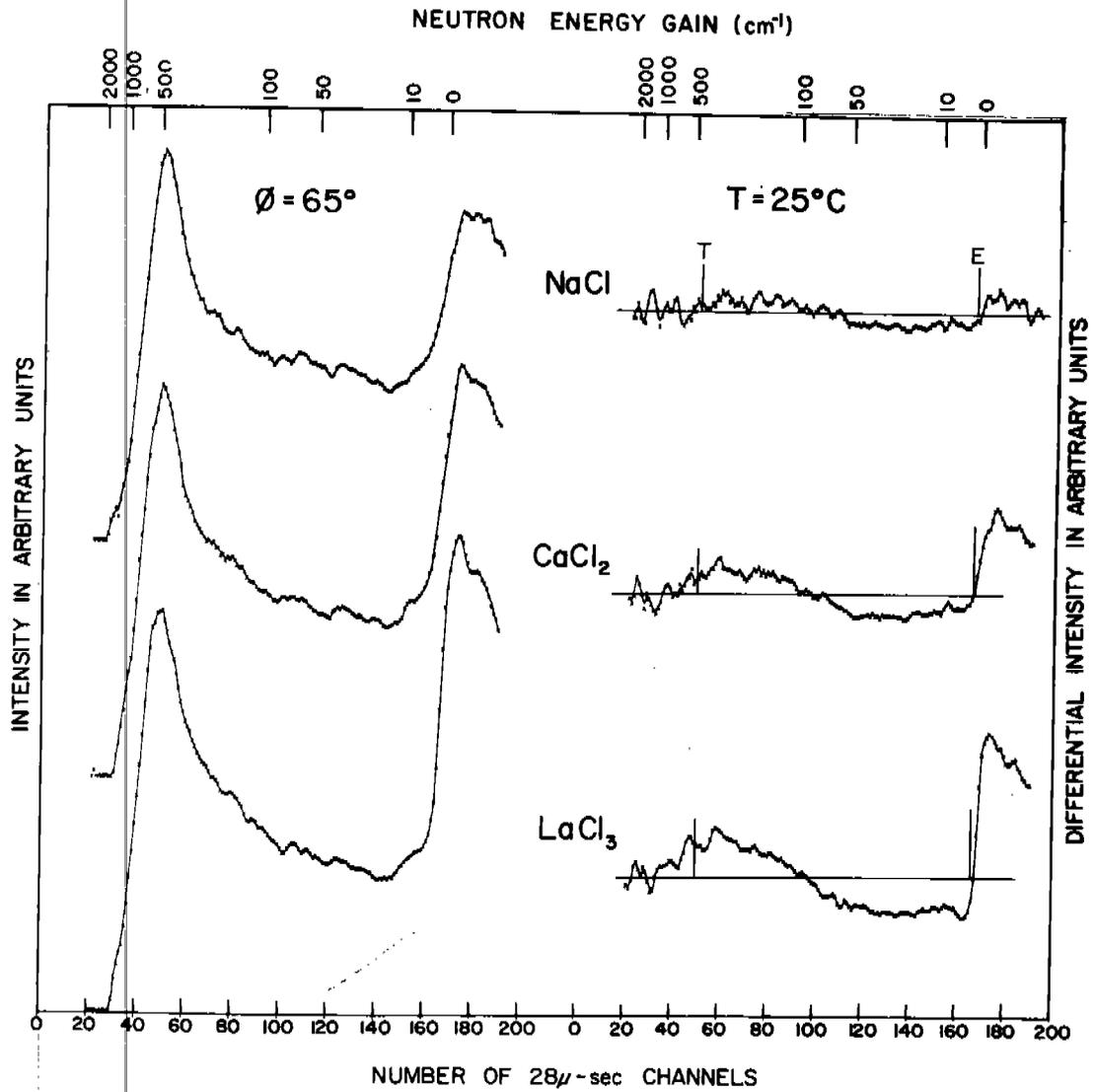


Figure 12

The time-of-flight and difference curves for 4.6m solutions of lithium, potassium, sodium and cesium chlorides. The effects of varying the ionic radius are shown. Departures from the water spectrum increase regularly with decreasing ionic radius (i.e., $\text{CsCl} < \text{KCl} < \text{NaCl} < \text{LiCl}$).

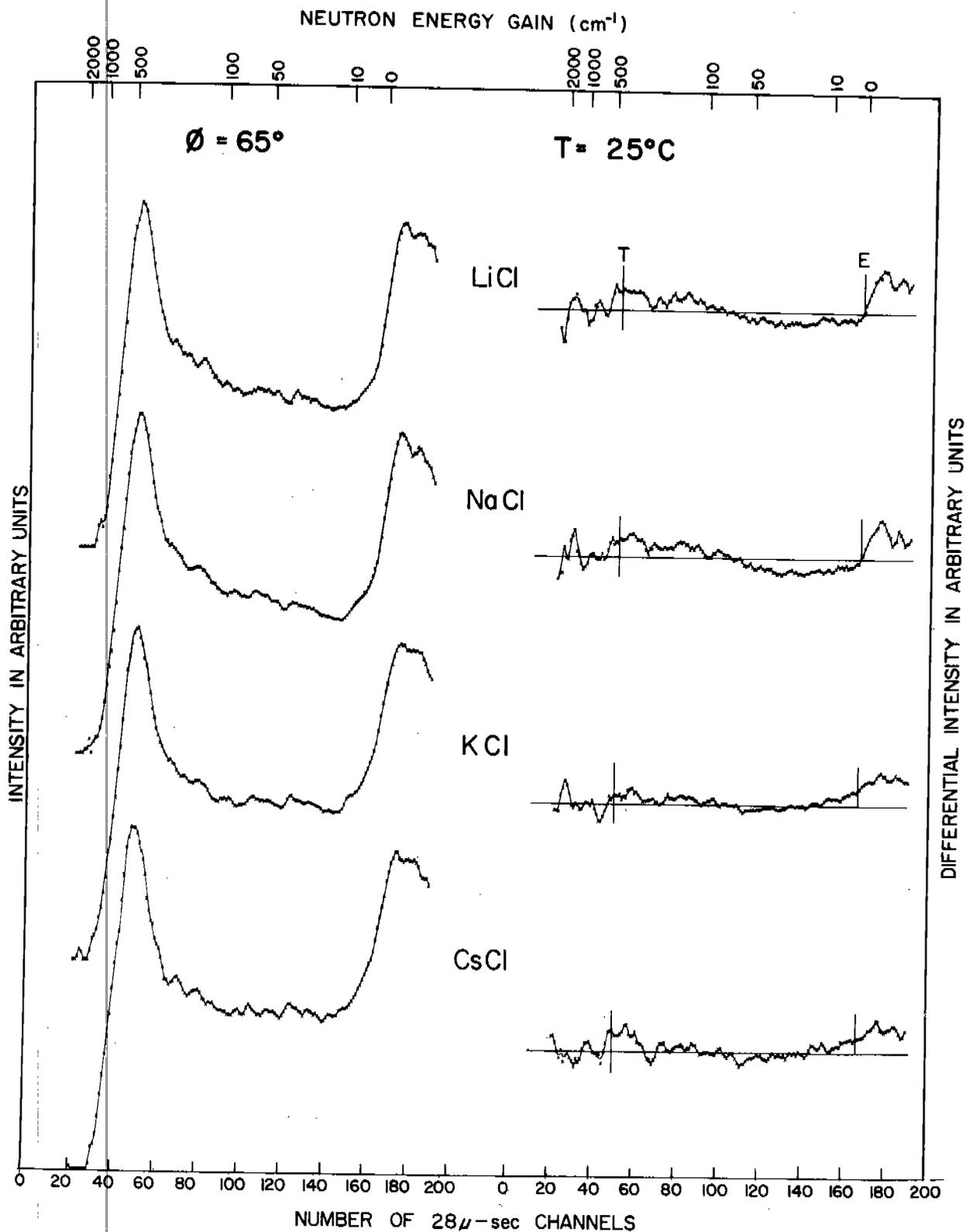


Figure 13

The time-of-flight distributions of neutrons scattered at 45° from 3.5M LaCl_3 solutions at 1° , 25° , 50° and 75°C are shown on the left. Many of the inelastic maxima present at 1°C persist to higher temperatures although broadened and less well resolved. The angular dependence (see Appendix II) of the LaCl_3 solution spectra is shown on the right with curves recorded at 1°C and scattering λ 's of 45 , 55 , 75 and 90° .

The areas under the curves on the left are normalized to a constant value over channels 30-145 to emphasize spectral features in the inelastic region. The righthand curves demonstrate that although they are broadened, the frequencies in the inelastic region persist with increased scattering angle and also allow a comparison of the quasi-elastic maxima with varying scattering angles. These curves have been normalized to the same constant area but over channels 30-240. This procedure results in a suppression of spectral features in the inelastic region; note however the consistency of features in the topmost left and righthand curves which are for the same data under the two different normalization procedures.

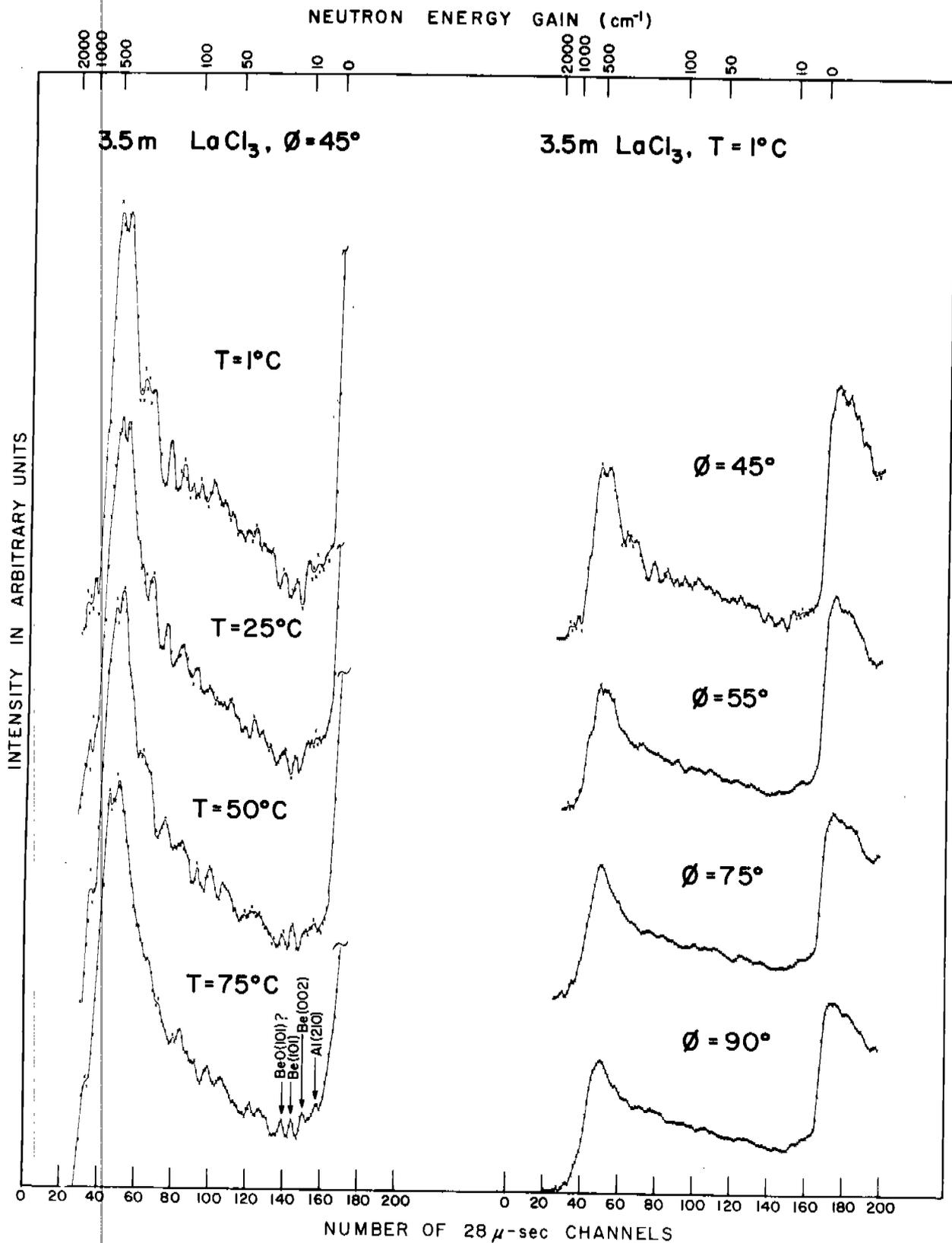


Figure 14

The time-of-flight distributions of neutrons scattered at an angle of 45° from 4.6m CsCl, CsI, KCl and KSCN are compared at temperatures of 25°C and 75°C . These salts (see text) are normally considered to be structure-breakers. It should be noted that, unlike water (see Figure 3), partially resolved torsional maxima appear at 75°C the frequencies of which depend on both cation and anion, and are associated with primary hydration water in H_2O -ion complexes as described in the text.

NEUTRON ENERGY GAIN (cm⁻¹)

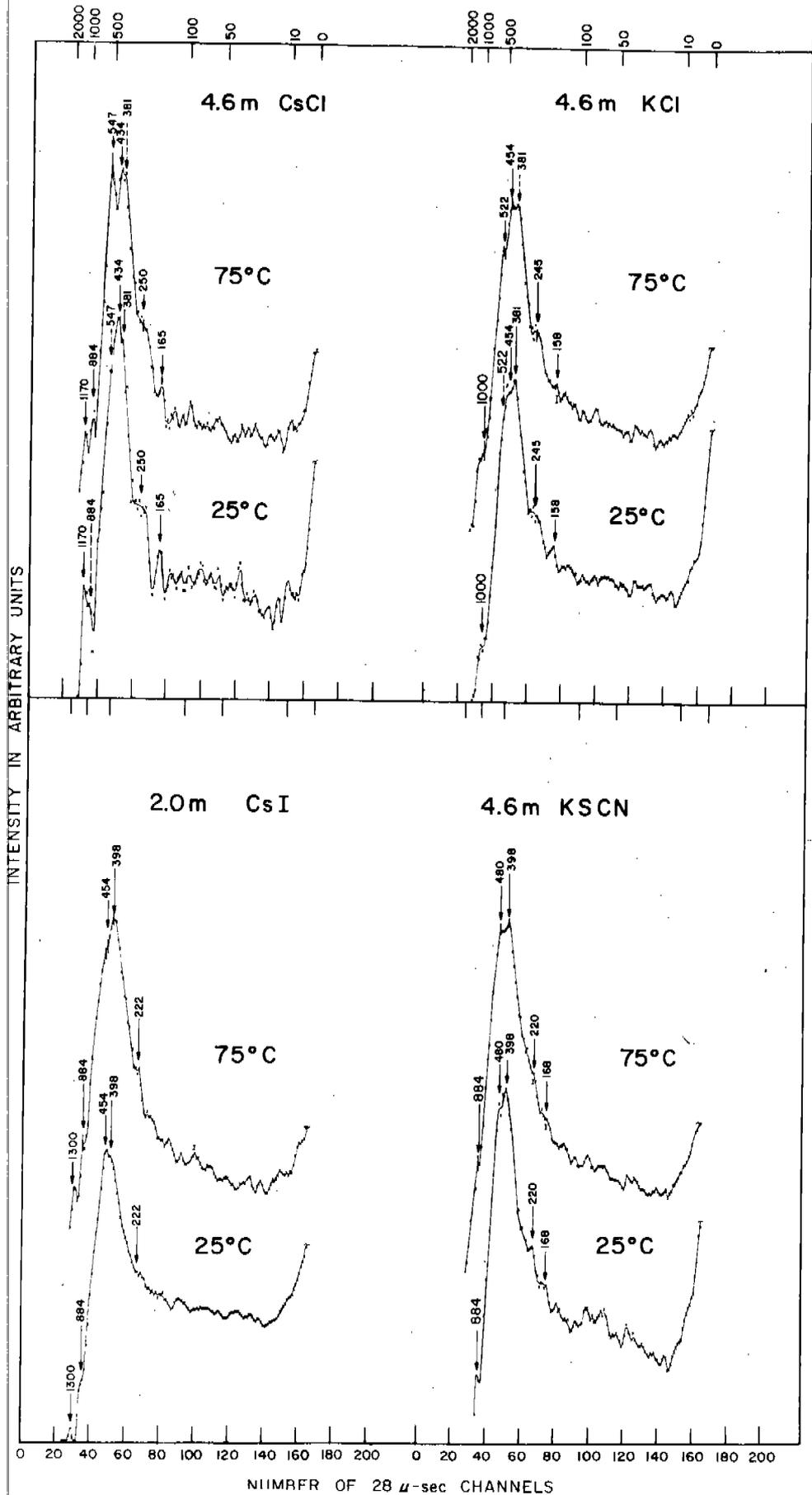


Figure 15

The observed values of Γ , the Lorentz-half-width at half maximum, as function of K^2 , the momentum transfer squared, are shown for water and salts containing small or highly charged ions. Note that at each temperature the curves of Γ vs. K^2 for all these lie below that for water solutions. These results are for 4.6 mola1 solutions excepting for the 3.5m LaCl_3 .

The values of Γ vs. K^2 obtained by Larsson (19) for water are also shown for comparison and appear in agreement with those of the present measurement. (The 1°C , 50°C , and 75°C data were taken from Larsson's experimental curve (18).) The full solid lines through the data points represent fits to the data minimizing residuals with the simple jump diffusion (63) relationships

$$\Gamma = \frac{\hbar}{\tau_0} \left(1 - \frac{e^{-2W}}{1 + \tau_0 D K^2} \right)$$

The values of D_0 and τ_0 of Table III were so obtained. A partially solid and dotted line indicates a departure from the temperature behavior of the simple jump model as described in the text. For such data, only a value of D has been extracted from the relation $\Gamma = \hbar K^2 D$ and the observed shape near the origin. The errors shown represent the limits to which a value of Γ could be varied

Figure 15

without incurring variations outside of statistical accuracy between an observed quasi-elastic maximum and the Lorentzian broadened incident energy distribution (Figure 2). Small but real departures from a true Lorentzian shape especially in the wings cannot be precluded. Such departures could occur where the temperature dependence of the simple jump diffusion model is no longer valid (see discussion in Appendix II).

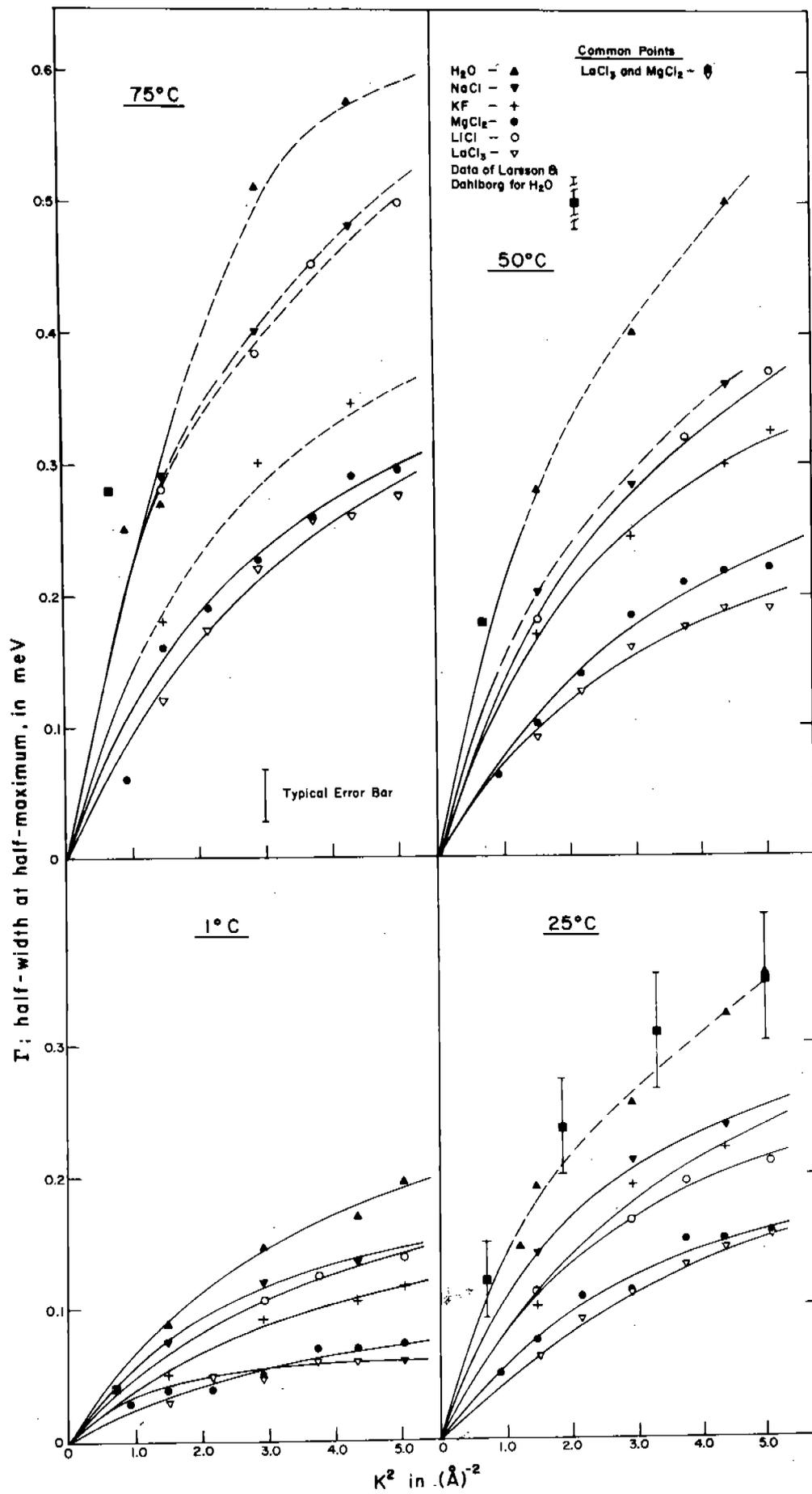
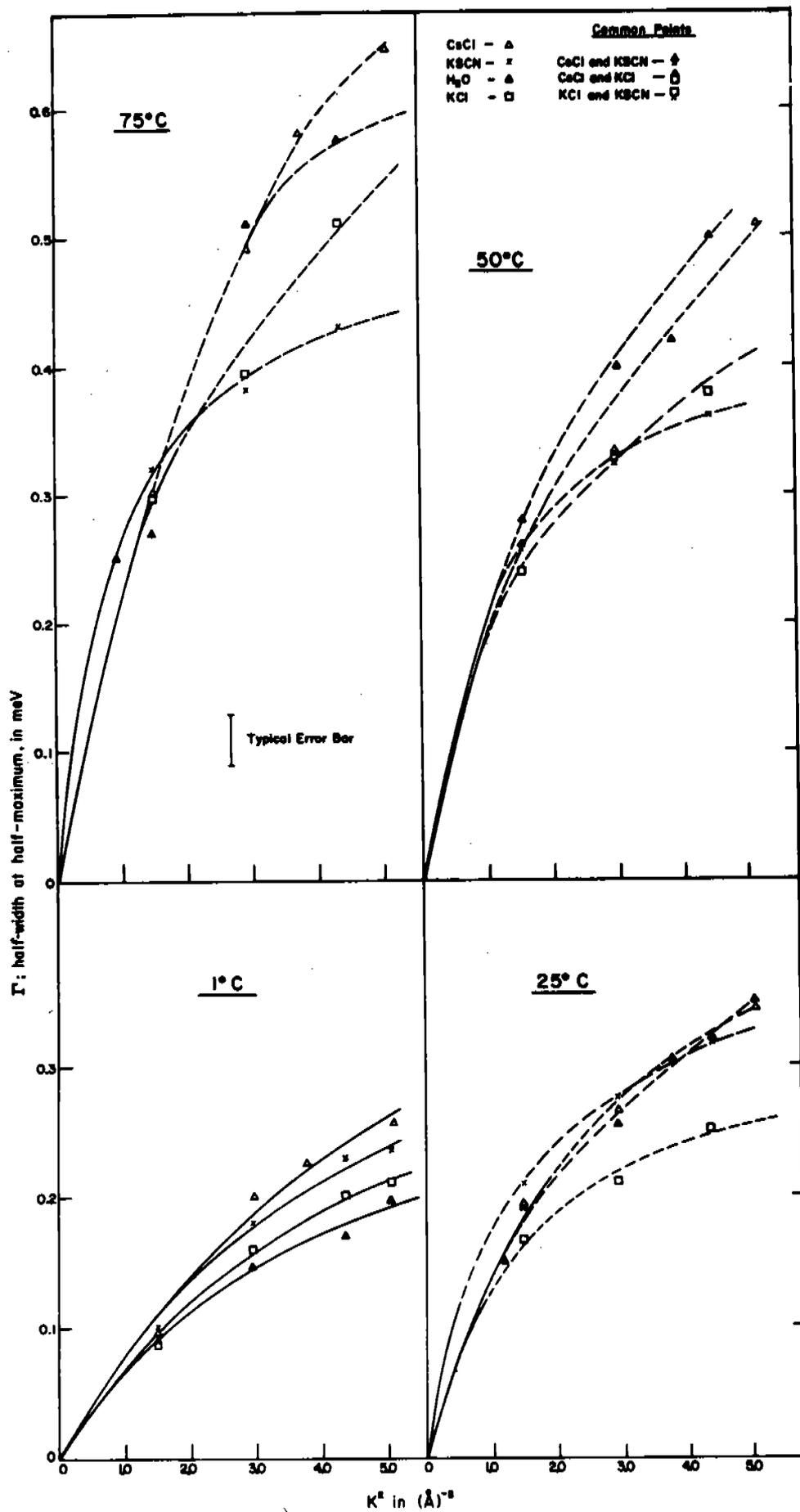


Figure 16

The observed values of Γ vs. K^2 are shown for water and aqueous solutions of salts having large, singly-charged ions at 1°C , 25°C , 50°C and 75°C . The concentration of all the solutions was 4.6m except for the KCl at 1°C which was 3.2m in concentration. At 1°C the Γ vs. K^2 curves for these salts all lie systematically above that for water in contrast to the corresponding curves for the salts in Figure 15. With increasing temperature the Γ vs. K^2 cross that for water and at 75°C with the possible exception of CsCl, lie below that for water.



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APPENDIX ITHE EFFECTS OF MULTIPLE SCATTERING AND CELL DESIGN

Larsson⁽⁶⁸⁾ reported that upon running the spectra (at 30° scattering angle) for a 0.5 and 0.2 mm cell, that the intensity ratio is not far from 2.5:1 over the entire energy scale as it should be for thin samples. A 0.2 mm sample was then considered as a "real thin" sample. In addition, a number of quasi-elastic studies have been made⁽⁶⁹⁻⁷³⁾ using effective cell thicknesses in terms of the number of hydrogens per square centimeter which were equivalent to our 0.5 mm cell for water.

In the present investigation the choice of cell thickness and design was based upon a number of considerations and measurements in addition to literature recommendations. In particular, the following features should be noted:

- (1) It was found that a thin cover plate of Al over a thin layer of water or a series of capillary grooves tended to bow and increase the sample thickness especially at the higher temperatures. Therefore, a cell design similar to that reported by Cribier and Jacrot⁽⁷⁰⁾ was adapted except that the water was contained in grooves precision pressed into the Al cover plate which was backed by a flat sheet of Cd. When the Al plate was then fastened in place the grooves served to strengthen the plate against measurable bowing as well as to contain the solutions. The spacings and collimations of the cell were such that for the range of scattering angles used

no significant fraction of the neutrons incident upon one water-filled groove could, upon scattering, pass through a second before going down the flight path. Thus, the maximum thickness was 0.5 mm, while the average thickness was about 0.42 mm.

- (2) A number of cell thicknesses between 0.17 mm and thickness above 0.5 mm have been measured. The comparison of the spectra of 0.25 with a 0.5 mm maximum thickness cell shows that these spectra are identical in shape within statistics.

Care should be taken when reducing the cell thickness to the 0.2 mm range that any differences seen with varying sample thicknesses do not occur from signal-to-noise ratios being uncertain and background corrections which are made to all spectra; i.e., a background correction for a thin cell is much more important and must be determined much more accurately than one for a thicker cell. This became evident when the spectrum of the 0.17 mm cell was measured. To ensure this not only the cell thickness but also the cell geometry have been varied such that the signal-to-noise ratio also varied to a significant degree. It was required that not only should this spectrum reproduce for two different sample thicknesses but for cells of these thicknesses having significantly different backgrounds that any variations or similarities in the spectrum were not fortuitously due to the way the background was handled.

APPENDIX IITHE OBSERVED BROADENING OF THE INCIDENT LINE AND ITS RELATIONSHIP TO THEORY

As noted in the text, diffusive motions in water or in the ionic solutions result in a series of small energy transfers that effectively broaden the incident neutron energy distribution and give rise to the so-called "quasi-elastic" peak. In principle, highly accurate data would be desirable to allow the following features of the "quasi-elastic maxima" to be investigated in detail and quantitatively correlated with theoretical models.

- (a) The functional form of shape of broadened distribution
- (b) The half-width at half-maximum as a function of the scattering angle
- (c) The angular dependence of the area of this maximum
- (d) The temperature behavior of both the area and the width.

In practice, precise data on the shape is difficult to obtain, and uncertainties in shape, particularly near the "wings" of the broadened curve, may result from the manner in which the contribution of the inelastic portion of the spectrum is estimated and subtracted. In the present investigation (as discussed in detail in our Annual Report for 1967) the observed temperature and the angular dependences of this background were well approximated by a spectrum of neutron scattered from a "gas of mass 18." A similar behavior was also noted by Brockhouse⁽²²⁾ and others.⁽²³⁾ This background results from small inelastic multiple transitions between the closely spaced levels of the continuum limit of the anharmonic potential in which H₂O molecules are bound. Upon subtracting such a background, all the resultant quasi-elastic maxima were observed,

within statistics, to be Lorentzian. However, small but significant deviations in shape may exist, but be obscured for cases where the broadening and the inelastic background are both large; for example, at high temperatures, and, in certain cases, at high K^2 values. Nevertheless (as will be discussed below), such undetectable departures in shape may also correspond to changes in the functional variation of the Γ vs. $/K^2/$ curves with temperature which can be detected. In addition, as reviewed by Larsson,⁽²¹⁾ until recently there have been discrepancies outside of experimental error on the measured values of the width as a function of the angle for pure water at -25°C . Further, in view of the errors, a number of models appear able to account for their observed angular variations of the widths. It is therefore desirable to study a number of aqueous systems so that the numerical values of characteristic parameters such as self-diffusion, coefficients and residence times which result from the application of a specific theory may be compared with values from other techniques.

For a model, the motions of a H_2O molecule are in general specified by a space-time correlation function, $G(\vec{r}, t)$. $G(\vec{r}, t)$ states the probability that a particle at $\vec{r} = 0$ will be at a position \vec{r} at a later time, t . It has been determined that the cross section and hence the intensity for neutrons scattered into a solid angle Ω after gaining or losing an energy $\hbar\omega = E_f - E_0$ and a momentum of $\hbar\vec{k}$ from a molecular vibration is given⁽⁷⁴⁾ by

$$\frac{d^2\sigma}{d\Omega dE_f} = \sqrt{\frac{E_f}{E_0}} \frac{Na^2}{2\pi} \int_{-\infty}^{+\infty} dt \int_{-\infty}^{+\infty} d\vec{r} e^{i(\vec{k}\cdot\vec{r}-\omega t)} G(\vec{r}, t).$$

The double fourier integral term is called, $S(\vec{K}, \omega)$, "the scattering law" and depends only on the molecular dynamics of the system. The problem then is to obtain for a model $G(\vec{r}, t)$. For an associated or hydrogen bonded liquid such water of any model should attempt to include:

- (a) The intermolecular vibrations
- (b) The diffusive motions
- (c) Correlations between diffusive and vibratory motions, damping of low frequency modes into diffusive motions, and anharmonicity and multi-phonon effects
- (d) The possibility of combined motions of individual water molecules as well as motions involving correlated motions of groups of molecules.

While $G(\vec{r}, t)$ represents the general solution to the equations of motions, it must, for any model, approach specific functional limits at both very short and very long times. As the neutron interaction time is $\frac{1}{Kv_0}$ (where v_0 is the velocity of the incident neutrons) then for the curves of Γ vs. K^2 , large K^2 values correspond to short times and small K^2 values will correspond to long times. For very short times (large K^2 values) a particle in a liquid will approach the behavior of a free classical gas with $G(\vec{r}, t) = \left(\frac{1}{\pi^{3/2}} \frac{1}{v_0^3} \frac{1}{t^{3/2}} \right) \times \exp(-r^2/(v_0 t)^2)$, where $v_0 = (2kT/M)^{1/2}$ and M is the mass of the diffusing unit. This leads to a quasi-elastic width given by $2\Gamma = 2.356 \left(\frac{kT}{M} \right) \hbar K$. In contrast, for long time, classical diffusion is approached with

$$G(\vec{r}, t) \longrightarrow (4\pi Dt)^{-3/2} \exp(-r^2/2(Dt))$$

where D is the self-diffusion coefficient. This gives a Lorentzian broadening of the incident line with a $\Gamma = \hbar DK^2$. Thus, any correct model should in general provide information on the mass of the diffusing unit for very large K^2 values and allow a value of D to be obtained from the slope of Γ vs. K^2 at the origin. Then the important differences between models and the different assumptions on the binding of H_2O molecules to structured units and the relationship of this binding to the diffusive kinetics will occur at times (or K^2 values) intermediate to the above limits. In order to correctly describe this "intermediate region" it would be necessary, for example, to solve the Langevin equation for the system

$$\frac{d^2\vec{r}}{dt^2} + \eta \frac{d\vec{r}}{dt} = \vec{F}(t) \quad \text{and to}$$

specify η , the viscous damping coefficient, and $M\vec{F}(t)$, the stochastic driving force. Unfortunately, an exact knowledge of these latter quantities implies a more quantitative and specific knowledge of water than is presently available. In practice therefore, certain specific types of diffusive motions are assumed, and their corresponding Γ vs. K^2 dependences calculated and tested against the measurements. In the present experiment for water and ionic solutions as a first approximation, we have compared the observed dependence of Γ with K^2 as a function of temperature with the delayed diffusion model. (63)(75) It is assumed that the molecule reorients or jumps between sites with a separation l with an average time between jumps given by

$$\tau_0 = 1/6 \frac{l^2}{D}.$$

It is further assumed that τ_0 is at least an order of magnitude larger than the vibrational period so that a molecule performs many oscillations between

jumps. Between bonding sites the molecule moves as a free particle with a transit time $\tau_1 = \ell \left(\frac{M}{2kT} \right)^{1/2}$. If this time much shorter than the period between the jumps these motions can be neglected as the gas-like motions are delayed by the fact that the molecules are first bound for a relaxation time τ_0 . This "model" does not specify if the "jump" associated with τ_0 is due to a reorientation of a molecule in the structure or if a water molecule breaks from the structure and "jumps." Such information would be contained in the specific temperature dependence of τ_0 and D . For arbitrary values of τ_1 and τ_0 , the broadening of the incident line is, in general, not Lorentzian. When $\tau_0 \ll \tau_1$, the "quasi-elastic" peak is Lorentzian with $\Gamma = \hbar DK^2$, corresponding to the long time limit discussed above. In the limit $\tau_0 > \tau_1$, the diffusion takes place by a series of activated jumps, the quasi-elastic maximum is again Lorentzian but now with

$$\Gamma = \frac{\hbar}{\tau_0} \left(1 - \frac{e^{-2w}}{1 + K^2 \tau_0 D} \right)$$

which again for small K^2 (i.e., long times) approaches $\hbar K^2 D$ or classical diffusion. However, for large K^2 , Γ approaches \hbar/τ_0 . Thus, as this Γ , for large K^2 values (i.e., short times) does not approach the necessary limit of the classical gas, it must only be considered as at best an approximation for times intermediate between the diffusion and gas model limits. Indeed, these authors show that for large K^2 the quasi-elastic peak is not Lorentzian broadened and the cross section is a series expansion in $\frac{K^2 D^2 M}{kT}$ for which the above expression for Γ is the first term. Hence, for very short times, the motions must correspond to diffusion of a gas with a correlation time, $\tau_g = \frac{DM}{kT}$ as given by kinetic theory. From

fluctuation theory, a diffusing particle goes an average distance

$(\Delta X^2)^{1/2} = (2Dt)^{1/2}$ in a time t . If a neutron is to be scattered with a momentum transfer \vec{K} by "interacting" over a distance (ΔX) with the diffusive motion, the interaction time t_{obs} must be $\geq \frac{1}{2DK^2}$. For simple Langevin diffusion, $\frac{kT}{M} = \frac{D}{\tau_g}$ where τ_g is the characteristic time for diffusion to begin. (66)

Then, when $\frac{\tau_g}{\tau_{\text{obs}}} \approx \frac{D^2 K^2 kT}{M}$ is less than one, diffusive motions will be seen. When this ratio is greater than one, individual gas-like or free particle-like motions of particles will be observed. Thus for small K^2 values of diffusive motions are observed while for large K^2 values of free particle-like motions are observed. Now if the Langevin diffusion is delayed by a residence time, τ_0 , then the jumps will appear as diffusive motions with $D = 1/6 \frac{\tau_0^2}{\tau_0}$ for $\frac{\tau_{\text{obs}}}{\tau_0} > \frac{1}{1/3 \ell^2 K^2}$ or at small K^2 values. For large K^2 values again of individual particle motions would be observed while for intermediate times, i.e., $\frac{\tau_0}{1/3 \ell^2 K^2} > t_{\text{obs}} > \frac{kT}{MD}$ all lines would be broadened according to the uncertainty principle, i.e., $\Gamma = \hbar/\tau_0$. In the above expressions the mass M need not be that of an individual water molecule rather it could correspond to the total mass of the water molecules within a range in which they effectively move in a correlated manner. Thus, beyond this range the vibrational modes would damp into diffusive motions. However, if discrete "clusters" were to exist, then this mass would be the "cluster mass." However, it does not imply the existence of cluster.

In the data for water and ionic solutions at small K^2 values, the values of Γ appear to approach the origin linearly in accord with $\Gamma = \hbar DK^2$, the necessary behavior for the long time classical diffusion limit of any correct correlation function. The problem is then at the

larger values of K^2 at which data are taken whether within the error Γ is uniquely approaching the limit $\Gamma = \hbar/\tau_0$ of the delayed diffusion model or if significant contributions of "free-particle" motions are in addition contributing. Particularly at higher temperatures where the curves of Γ vs. K^2 become less "flat" and τ_g is increasing, contributions from a gas behavior may be significant. Unfortunately, for experimental reasons measurements cannot always be extended to sufficiently large K^2 values so that an approach to a constant value of Γ is convincing. Indeed, if the curve does not bend sufficiently within the observed range of K^2 values, a number of different models⁽⁶³⁾⁽⁷⁶⁾⁽⁷⁷⁾ appear able to equally well account for the functional dependence of Γ vs. K^2 . For example, this has been particularly true for data for pure water at 25°C. In principle, contributions from free particle motions or deviations from the simple jump limit might be detected by corresponding departures from a Lorentzian shape. However, as discussed above, background subtraction and the accuracy of the data may preclude such departures from a Lorentzian broadening being detected. A more sensitive empirical determination results from the predicted temperature behavior as follows: We define the dimensionless parameters $\Gamma/kT = y$ and $\frac{\hbar DK^2}{kT} = x$. Then, for the jump diffusion limit

$$y = \frac{\hbar}{\tau_0 kT} \left(1 - \frac{e^{-2x}}{1 + \frac{kT\tau_0}{\hbar} x} \right)$$

For small K (i.e., small x) $y = x$ and is temperature independent. For large x , $y \rightarrow \hbar/\tau_0/kT$ and as τ_0 would decrease (exponentially) with increasing T , y would therefore increase. In contrast, the gas model would predict

$y = (2 \ln 2x)^{1/2} \left(\frac{\hbar}{\tau_g} \frac{1}{kT} \right)^{1/2}$ so that, in contrast to the jump model, y decreases with increasing T .

Egelstaff⁽⁶⁵⁾ has proposed a general model for the intermediate time range in liquids. In addition to the jump diffusion of individual molecules, strongly correlated globules of molecules are assumed to cooperatively diffuse together. The ratio of "globule mass" to the molecular mass as noted by Sjölander⁽⁶⁷⁾ and by Larsson⁽²¹⁾ is related to the relative number of degrees of freedom that may go into diffusive modes, i.e., the larger the cluster the lower the number of such degrees of freedom. Thus, in their extensive studies of liquid pentane and glycerol which are like water, the relative number of degrees of freedom is small at low temperature and increases rapidly with temperature corresponding to a rapid breakup of the structured units with temperature. For the motion of the "globules"

$$y = (2 \ln 2x)^{1/2} \left(\frac{\hbar}{\tau_g^2 + (\hbar/4kT)^2} \cdot \frac{1}{kT} \right)^{1/2}$$

This model also passes to the gas limit for high temperature and to classical diffusion for long times or small K^2 values. $1/\tau_g = \xi$ is the "friction constant" and $\tau_g = \frac{4\pi}{3} (M/v_a)(R_g)^3 \frac{D}{kT}$ where M and v_a respectively are the masses and volumes of molecules and R_g is the correlation range. As for the gas model, with increasing temperature, D/kT and hence τ_g would increase, and y would decrease. However, it should be noted that no specific temperature-dependence is assigned to R_g which could decrease with increasing temperature and tend to reduce τ_g . For this reason, it is best to compare observed changes in y at a series of temperatures the separations

of which are not very large compared to difference between the melting and boiling points of water.

In general, the passage to a gas behavior is attributed to an increase in τ_g given above by

$$\tau_g = \frac{4\pi}{3} (M/v_a)(R_g)^3 D/kT$$

due to D/kT increasing with temperature. If we consider that at the inversion point $\tau_0 = \tau_g$, then we define a value of $K_c^2 = (kT/M_c D^2)$ where $M_c = \frac{4\pi}{3}(M/v_a)R_g^3$. For $K^2 \gg K_c^2$ gas behavior is observed and K_c^2 would decrease with increasing T due to increasing D . Thus, with increasing temperature K_c^2 would decrease into measurable range of K^2 and gas behavior is observed. For a solution of a "structure making" salt where a solid hydrate-like ordering of H_2O molecules may exist, diffusion of correlated groups of H_2O molecules may be restricted so that K_c^2 would be large and the jump-diffusion of individual H_2O molecules would primarily contribute to the half-width Γ within our range of high K^2 values. In contrast, the addition of a "structure breaker" like KSCN would increase the ability of such correlated aggregates to diffuse and hence lower K_c^2 .

The maxima in the inelastic region will also in part be broadened by diffusive motions of the molecules. Thus, as discussed in the text, the following general trends are observed in the spectra:

- (a) The addition of a salt that sharpens and intensifies the quasi-elastic maximum also tends to sharpen the associated inelastic maxima relative to pure water

- (b) Both quasi-elastic and inelastic maxima are sharper at small angles and quickly broaden and decrease in intensity with increasing angle
- (c) Maxima (within resolution) do not shift appreciably as expected for coherent effects. Indeed solid salt hydrates as for pure water have been treated as incoherent scatterers. (78)(79)

In general, the width of the inelastic maxima will be determined in part by the resolution and width of the incident line and the relaxation processes and rates. In addition, for an associated liquid such as water, both dispersions in size and type of the bonded clusters and in the associated intermolecular frequencies may also contribute to broadening lines. Thus, Springer⁽²⁰⁾ has argued that the large width of the torsional maximum for pure water could not be explained in terms of a Doepler term or gas-model width for a mass of 18. He tentatively ascribed this width to a multiplicity of species of the type suggested by Cross et al.⁽³²⁾ Although, as suggested in this work, the presence of more than one torsional component can in part explain this. However, for certain of the solutions in the present paper the intermolecular frequencies appear better defined than for pure water (for example, see the LaCl_3 spectra of Figure 13) and the Doepler broadening associated with a "high energy or gas-model limit"⁽⁸⁰⁾ appears too large to account for their widths (being 30 meV near channel 49 and 8-10 meV at channel 100)--in agreement with Larsson⁽²¹⁾ who has recently concluded the gas-model limit is inadequate to explain the observed water spectrum.

The features a-c above are more in accord with the more general features proposed for a number of recent models⁽⁷⁵⁾⁽⁶⁷⁾. The self correlation function is taken as $G_s(r,t) \approx \int G_s^D(R,t) G_s^V(\overline{R-r},t) d\overline{R}$ where G^D describes the diffusive and G^V the vibrational motion. Upon performing the double fourier transform an expression results for the scattering law $S_s(K,a) \approx \int S_s^D(K\omega') S_s^V(K,(\omega-\omega')) d\omega'$. For the vibrational part $S_s^V(K,(\omega-\omega'))$ can be expanded in a multiphonon series, each term of which is effectively further broadened by folding in the dispersion of the diffusive energy transfers expressed by $S_s^D(K,\omega')$. The zero phonon term would give rise to the quasi-elastic maximum discussed and the remaining terms to the inelastic spectrum. Further, as Sjölander⁽⁸⁰⁾ and others⁽⁸¹⁾ have argued, the zero and one-phonon terms would give rise to maxima superimposed upon a relative smooth and continuously differentiable background arising from higher phonon terms. Thus, for diffusive motions leading to a Lorentzian function the zero phonon term would give $S^D(K,\omega) \frac{e^{-2W}\Gamma(K)}{\Gamma^2(K) + \omega^2}$ the one-phonon term would be:

$$S^1(\overline{K},\omega) \sim K^2 e^{-2W} \int \frac{g(\nu)d\nu}{\nu(e+h\nu/kT-1)} \frac{\Gamma(K)}{(\omega-\nu)^2 + \Gamma^2(K)}$$

where $h\omega$ is the energy transfer and ν is the frequency of the mode. The width of a maximum would reflect both the frequency distribution (ν) and the diffusive broadening through $\Gamma(K)$. At small scattering angles all maxima should sharpen as:

- (1) The contribution of higher phonon terms should decrease with decreasing angle.⁽⁸²⁾ Thus, zero and one-phonon singularities would become more pronounced relative to the background.

- (2) $\Gamma(K)$ for small angles, hence, for small (K) would approach hDK^2 and hence decrease, thus reducing the diffusive broadening of all lines
- (3) e^{-2W} the Debye-Waller factor would increase toward unity with decreasing angle and intensify the area of the elastic and inelastic components.

Thus, as observed, both quasi-elastic and inelastic lines should be sharpest at small angles and rapidly de-intensify and broaden with increasing angle as a result of both increases in the number of higher phonon terms and in the diffusive broadening. Further, individual inelastic maxima may broaden at different relative rates as the Debye factor differs for individual modes. Indeed, Springer⁽²⁰⁾ and others⁽¹⁸⁾ have noted that even for pure water more than one "effective Debye temperature is necessary to account for the spectrum."

The addition of small and/or highly charged ions to water can sharpen inelastic maxima relative to pure water by one or more of the following:

- (1) Increasing $2W$ and relatively reducing high phonon contribution
- (2) Decreasing the relaxation rate and the self-diffusion coefficient hence decreasing any diffusive broadening.
- (3) Forming more unique associated species than in pure water.

This is particularly true at higher concentration of salts where the majority of the H_2O molecules would be in the primary hydration layer. Thus the frequency distribution (ν_{obs}) observed would not be an average over as wide a distribution of species as for pure water.

- (4) Coupling between diffusive motions and slow or low frequency vibrations in the liquid phase could dampen the low frequency tail of the $g(\omega)$ for a mode and thus, compared to a solid lattice, narrow the frequency dispersion.