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Far-Infrared Studies on the Intermolecular Dynamics of Systems Containing Water. The Influence of Ionic Interactions in NaCl, LiCl, and HCl SolutionsEvangelos Zoidis,^{†,‡} Jack Yarwood,^{*,†} and Marcel Besnard[‡]

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We report, for the first time, extended very far IR (VFIR) intensity data ($2.5\text{--}30\text{ cm}^{-1}$) for solutions of NaCl, LiCl, and HCl in water over the accessible concentration ($0\text{--}10\text{ M}$) and temperature ranges (-100° to 80°C). This allows dynamic processes in the $0.2\text{--}2.0\text{ ps}$ regime to be probed, a suitable choice in view of much experimental data which shows that dynamic processes in this regime are important in liquid water. We have interpreted the data by consideration of (a) conductivity processes, shown only to be important at lowest frequencies, (b) changes in the rotational and translational dynamics of the water molecules, (c) $\text{M}^+\text{H}_2\text{O}$ rattling modes, and (d) modifications of the water network “structure” and collective dynamics for different ions. The changes in intensity with concentration and temperature have been shown to be consistent with the expected changes of the ion-containing water network for different ion types.

1. Introduction

We have recently been involved in a project¹ designed to characterize the effects, on vibrational spectra, of ultrarapid chemical exchange processes which have been predicted² and shown³ to be relevant to systems containing hydrogen-bonded networks, including aqueous systems. We have already established⁴ that isotropic Raman band broadening due to such effects can be detected, but the separation of the exchange and vibrational relaxation ($1/T_2$) contributions is expected⁵ to be extremely difficult. In the far-IR region the spectral intensity is dependent on fluctuations of the total dipole density, and there are no complications associated with vibrational relaxation. Furthermore, the $2\text{--}30\text{ cm}^{-1}$ region is associated with dynamic processes occurring on a $0.2\text{--}2.5\text{ ps}$ time scale—exactly in the time regime expected^{6–8} for the forming and breaking of hydrogen bonds in aqueous/network systems. This region ought therefore to afford direct evidence of such processes if they can be effectively distinguished from the other contributions^{9–11} to the overall spectrum (dipolar rotational and translational motions and ionic conductivity). To attempt to distinguish these various processes, we have made a detailed comparison of the very far-IR, VFIR ($2\text{--}30\text{ cm}^{-1}$), spectra of water, NaCl solutions,¹² LiCl solutions,¹¹ and concentrated acid (HCl) solutions. It is anticipated that proton exchange in the water hydrogen-bonded network will be enhanced by the presence of H_3O^+ ions since it is known^{13,14} that the mobility of such ions is extremely high. Ionic conductivity and “hydration” will, of course, also contribute to the spectra, but largely at lower frequencies.¹¹ Hence the need to use NaCl and LiCl solutions where ionic processes occur without the ultrahigh mobilities of the H_3O^+ ion. The

aim was therefore to detect effects due to such ultrarapid protonic mobility directly (in a unique way) in the frequency regime of interest. Although hydrogen-bonded networks have been probed using picosecond and femtosecond lasers,^{8,15–17} we are not aware of measurements in the very far-infrared region (below 50 cm^{-1}).

2. Experimental Section

The measurements were performed using a polarizing (Martin-Puplett) Fourier transform spectrometer (Beckmann-RIIC FS720) recently refurbished by Graseby-Specac. The instrument was equipped with a InSb hot electron detector (QMC Industrial Instruments, Ltd), which operated at liquid helium temperature. The infrared source was stabilized with a Specac power supply. The transmitted-signal was preamplified (ULN-10A, QMC Industrial Instruments, Ltd.) and further amplified by a lock-in amplifier (SR510, Stanford Research Systems). To improve the signal-to-noise ratio at low frequencies, the radiation was modulated at 81.5 Hz using a variable speed chopper unit. This had been found to be the optimum frequency of our detector system according to the observed characteristic noise curve, measured using a Hewlett-Packard signal analyzer. The spectral resolution was approximately 2 cm^{-1} . This instrumental configuration allowed us to record a very far-IR absorption spectra in the frequency range from 2.6 to 30 cm^{-1} with high reproducibility over a long time period. In most cases, the average of two spectra was calculated. The spectrometer itself was evacuated, whereas nitrogen gas was blown into the sample compartment and liquid cell, to avoid condensation of water vapor on the polyethylene cell windows.

A well-known problem^{18,19} in the conventional infrared absorption technique is the effect of the internal reflection losses

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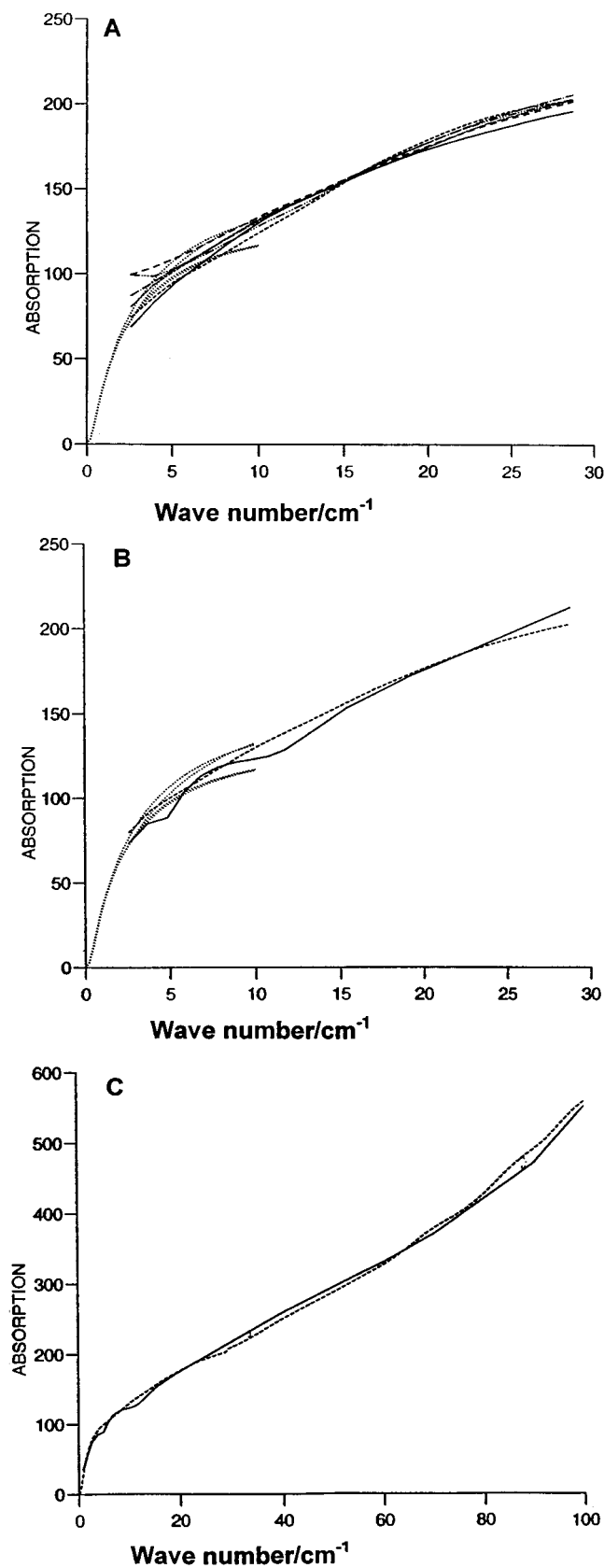


Figure 1. (A) Absorption spectrum of water between 2.5 and 30 cm^{-1} at 20 $^{\circ}\text{C}$ showing reproducibility at different thicknesses with a liquid helium-cooled detector. (B) Quality of agreement between our observed data at 20 $^{\circ}\text{C}$ (solid line), those of Birch⁹ (dotted line) and calculated spectra between 2.5 and 10 cm^{-1} based on Debye model (eq 1) with different relaxation times between 8 and 9.5 ps (see Table 1). (C) Similar data for water at 20 $^{\circ}\text{C}$ obtained up to 100 cm^{-1} using a Golay detector. Our data (solid line) compared with those of Birch et al.⁹

in the cell. Depending on the magnitude of this effect, the absolute intensity and the slope of the absorption spectrum is subject to large errors. One way to alleviate this problem is the use of a cell with two different path lengths.

However, for such a strongly absorbing liquid, where the intensity varies by more than 100 neper cm^{-1} over the frequency range 2–30 cm^{-1} , it is difficult to construct a cell of optimum thickness. Nevertheless, in Figure 1A we show the excellent reproducibility obtained in measuring the very far IR spectra of water using the two thickness method for difference combinations of a pair of path lengths between 30 and 250 μm . In this range, we succeeded in constructing cells thick enough to avoid severe internal reflection losses but thin enough to give sufficient optical transmission through water (and the electrolyte solutions). All the path lengths were measured independently using a micrometer and, where appropriate, using mid-IR interference fringes.

Aqueous solutions of LiCl and NaCl, with concentrations varying respectively from 0.2 to 8M, or 0.2 to 5M, were prepared by dissolving the pure solutions (LiCl, Aldrich 99%.; NaCl, Analar 99/9%) in distilled water. Concentrated HCl (BDH, certified 36%) was diluted in distilled water in order to obtain concentrations varying from 0.20 to 10M. No further purification of commercial chemicals was attempted.

3. Data Handling and Analysis

For polar molecules, accurate experimental data are required over the whole frequency range between the microwave and far-infrared regions (ref 18, chapter 5) in order to assess the effects of long ranged potentials. In other words, a quantitative analysis enabling the calculation of the total dipole moment auto correlation function (DACF) requires data between 0.1 and 200 cm^{-1} .^{18–20} However, the spectral density above 30 cm^{-1} has been shown¹⁹ to have a negligible (<2%) effect on the DACF. On the contrary, data in the microwave region dramatically affects the long time decay of the DACF (and will, of course, have some effect over the whole time domain). To calculate the DACF it is thus necessary either to make direct microwave measurements or to assume that the data between 0 and 5 cm^{-1} follow a single Debye relaxation process,²⁰ viz,

$$\epsilon''(\omega) = [\epsilon_0 - \epsilon_\infty] \omega \tau_D / (1 + \omega^2 \tau_D^2) \quad (1)$$

In effect, this involves fitting the data in the 2.5–5.0 cm^{-1} region to simulated microwave data assuming a Debye process with variable parameters ($\epsilon_0 - \epsilon_\infty$) and τ_D (as described previously²⁰). Such a process has been checked for liquid water where a variety of literature microwave data^{10,21,23,24} are available and has been found to produce very good agreement with our lowest (VFIR) measurements (see Figure 1B). It would have been tempting to use that approach here but for two reasons we have not done so.

(1) It is known²² that the low-frequency data are dominated by the ionic conductivity contribution (second term in eq 2) to the total dielectric loss, i.e.,

$$\epsilon''(\omega) = \frac{\Delta \epsilon \omega \tau_D}{1 + \omega^2 \tau_D^2} + \frac{\sigma_{dc}}{\epsilon_v \omega} \quad (2)$$

where $\Delta \epsilon = \epsilon_0 - \epsilon_\infty$ and ϵ_v is the permittivity of vacuum. Extrapolation to zero frequency²⁰ is therefore likely to introduce large errors from the conductivity term. (2) The inclusion of data between 2.5 and 30 cm^{-1} does not, in practice, help to

TABLE 1: Comparison of the Dielectric Data for Water at Different Temperature near Ambient

H ₂ O	ϵ_0	ϵ_∞	τ_1 [ps]	τ_2 [ps]	ϵ_2^a
Mason and Hasted ²¹ (20 °C)	80.31	4.32	9.33		
Kaatz ²³ (30 °C)	76.58	4.73	7.28		
Kaatz ²⁴ (25 °C)	78.36	5.26	8.27		
Barthel ¹⁰ (20 °C)	78.36	4.48	8.32	1.02	6.18

^a The second permittivity increment.

distinguish short-ranged effect between the different solutions studied here.

We have therefore focused attention on the spectral density differences in our interpretation.

4. Comparison with Literature

4.1. Liquid Water. Before proceeding to the analysis of our data on electrolyte solutions, we examine the data for liquid water which provide a basis for the quality assessment of our measurements. In Figure 1A the spectrum of liquid water at 20 °C is shown in the range 2.6–30 cm⁻¹ together with the most recent literature data in the VFIR⁹ and in the microwave regions.^{9,10,21} There is a very good agreement, within our experimental error (which is no greater than $\pm 5\%$). Similar results are obtained in the FIR-spectrum (Figure 1C) between 30 cm⁻¹ – 100 cm⁻¹, at 50 μ m path length, and using a Golay detector. Our data show no obvious band at 50 cm⁻¹, as found and discussed in previous studies.^{9,25,26} The dielectric properties of water have also been studied extensively in the past.^{23,24} It was found that the relaxation behavior up to at least 1.7 cm⁻¹ is governed by a single exponential. On the high-frequency side, a second process has been discovered,⁹ but there is still some uncertainty about whether this process is real. Kaatz and Ulendorf²⁴ suggested that one Debye process suffices to fit the data only up to about 40 GHz and Barthel et al.¹⁰ also come to the conclusion that, according to the far-IR results of Hasted et al.,²⁷ only the assumption of an *additional* exponential fast process (see Table 1) yields a satisfactory fit up to about 14 cm⁻¹.

To emphasize the quality of our lowest frequency VFIR data, the result of independent microwave experiments of pure water are shown in Figure 1B, as generated (up to 10 cm⁻¹) using a Debye-relaxation process and dielectric parameters from the literature (see Table 1). It is observed that the results from the different experiments are very similar up to ~ 2 cm⁻¹, whereas above ~ 5 cm⁻¹ none of those data can adequately describe our VFIR data.

4.2. Expected Influence of Added Ions. The spectral density in the region 2.5–30 cm⁻¹, of principal interest in this work, is expected to be influenced in these solutions by a number of different “known”, but often not clearly understood, phenomena. These include (a) the translational and reorientational motions of the water.^{9,10,28} Indeed, the data below 5 cm⁻¹ form the high-frequency (relatively short time) part of the overall diffusion process. (b) A contribution from the ionic conductivity (via translational motion) of the (hydrated) ions. This effect is likely to dominate²² the dielectric loss at low frequency (see eq 2). For LiCl solutions, it has been found²² that the conductivity contribution to $\alpha(\nu)$ is certainly significant at 10 cm⁻¹. It is, however, unclear how this contribution is influenced by cation (or anion) size or hydration number, but it clearly must increase as σ_{dc} increases (Table 2). (c) The spectral density must be influenced by the large intense bands at ~ 200 cm⁻¹ and ~ 600 cm⁻¹ respectively associated with the translational (ν_t) and rotational motions (ν_{rot}) of the water network. Since it is well-

TABLE 2: Conductivities, Heats of Hydration, Residence Times, and Debye Relaxation Time Ratios for Ions in Aqueous Solution

	$\sigma_{dc}/\Omega^{-1} \text{ cm}^{-1}$	$\Delta H_{hyd}/\text{kJ mol}^{-1}$	τ_h^D/τ_w^D ⁴²	residence time ⁴³ /ps
Na ⁺	0.021	444	1.6	22
Li ⁺	0.020	559		50
H ₃ O ⁺	0.111	1129		
Cl ⁻		340		16

TABLE 3: Dielectric Permittivities and Relaxation Times for Water NaCl Solutions and HCl Solutions as a Function of Temperature

T/°C	ϵ_0	ϵ_∞	τ_D/ps
	H ₂ O		
0	88.3	5.28	18.0
10	84.3	5.19	12.8
20	80.3	4.32	9.3
30	76.7	4.28	7.3
50	73.2	4.22	5.9
50	69.9	4.22	4.8
60	66.6	4.28	4.0
75	62.1	4.39	3.1
	NaCl (5M)		
5	84	4.6	10.0
25	73	4.4	6.9
45	71	4.1	5.0
65	70	3.7	3.5
85	69	3.4	1.9
	HCl (5M)		
-110	99	16.0	88
-70	96	5.8	32
-40	94	5.0	19
-10	92	4.6	11
20	84	4.1	8.2
50	82	3.9	6

known^{11,32} that the network is perturbed on the addition of ions, we must expect a change in $\alpha(\nu)$ at a much lower wavenumber (as found by Birch et al.¹² in 1981). (d) Finally, we note that Dodo et al.²⁹ have recently shown how the far IR spectra (of electrolyte solutions) can include (at >200 cm⁻¹) a contribution from “ion rattling” motions in a solvent cage^{30,31} (see below).

The FIR-spectra of a variety of electrolytes have been reported previously.^{12,27,29} However, most of these are relatively old and lack continuity in the 2–50 cm⁻¹ region. Spectra of hydrochloric acid have not been reported, as far as we know, in the far-IR region. Our main purpose here is to classify the differences in the spectral behavior of the acid and those of the Na⁺ and Li⁺ electrolyte solutions compared with water. The question arises as to whether there is a significant difference between the HCl spectrum and that of the salts which might be attributed to the high proton mobility of solutions containing the hydroxonium ions.

It is worth noting that, for such high ion concentrations, 0.2 to 5 M, or higher, the solutions are likely to be highly nonideal in a thermodynamic sense. This may introduce unknown factors into the total dipole density, especially at lowest frequencies.

5. Results and Discussion

5.1. NaCl and LiCl Solutions. (a) *Spectral Range 5–30 cm⁻¹.* Now let us consider the detailed changes found in this region with concentration and temperature for the Na⁺, Li⁺ ions in water. The comparison of $\alpha(\nu)$ as a function of concentration is shown in Figures 2 and 3 for the two electrolyte solutions studied. There are significant differences in behavior for the different cations. For NaCl the $\alpha(\nu)$ intensity remains relatively invariant with concentration in this range. However, for LiCl

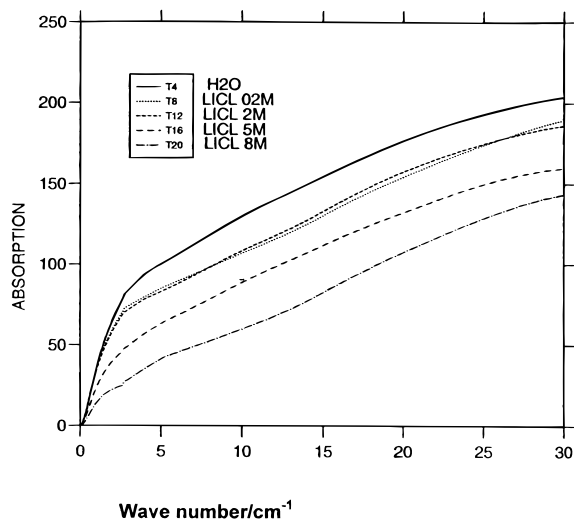


Figure 2. Very-far-IR spectra of LiCl solutions in water at 20 °C and at different concentrations.

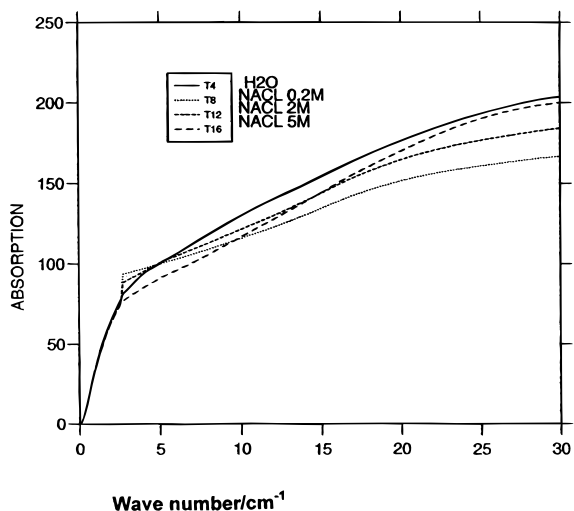


Figure 3. Same as Figure 2 but for NaCl solutions.

(Figure 2) the $\alpha(\nu)$ intensity decreases substantially with concentration (even at lowest concentration) showing a similar trend to, but with differences in, absolute $\alpha(\nu)$ values from what was found previously.¹¹

It is clear that our data follow the same trend as found previously, i.e., that the intensity falls consistently with increasing concentrations. However, our absolute $\alpha(\nu)$ values are somewhat below those reported by Dodo et al.¹¹ Gratifyingly, however, our data agree nicely with the predicted levels of absorption using *their* model. Two contributions to $\alpha(\nu)$ were initially considered by them to be relevant. First, the contribution of ionic conductivity (eq 2) and second, the reorientation of the water molecule total dipole moment. For LiCl, in agreement with Dodo et al.,¹¹ we find that the reduction in intensity on going from pure water to LiCl solutions is much greater than would be expected from the reduction of water “concentration” in making up the solutions. Indeed, detailed calculations of the mole fractions of water in the solutions show that the amount of water is not significantly different on going from LiCl to NaCl. However, the spectral behavior in the 10–30 cm^{-1} region is very different. In the LiCl (Figure 2) there is a large decrease in the $\alpha(\nu)$ values compared with those for pure water, especially at the highest concentrations. For NaCl, however (Figure 3), there is very little difference between the spectra of the solutions and the pure H₂O, especially when the adjustment for water

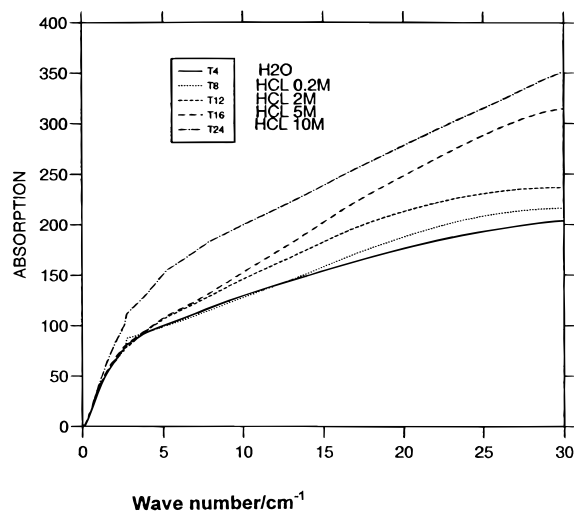


Figure 4. Same as Figure 2A but for HCl solutions.

“concentration” has been taken into account. Since the ionic conductances of the two electrolytes are the same (Table 2), this profound behavioral difference cannot be due to the conductivity contributions. There are now two other possible reasons for changes of spectral behavior between LiCl and NaCl. Since the heat of hydration is very much higher for Li⁺ than that for Na⁺ (Table 2), it follows that the motional hindrance of the dynamics of the water molecule is expected to be higher for Li⁺ than for Na⁺. This has recently been confirmed⁴³ by a MD simulation which measures the residence times of water in the first solvation shell of Li⁺ (50 ps) and Na⁺ (22 ps). This would lead to a differential change in the absorption coefficient in the 10–30 cm^{-1} region.

(b) 40–100 cm^{-1} Spectral Region. Dodo et al.²⁹ have recently reexamined the far IR spectra of a series of ions in aqueous solution in order to elucidate the influence, in the 10–80 cm^{-1} region, of the role of M⁺/solvent “rattling” (oscillating) modes,³⁰ which have also been studied by molecular dynamics simulation.³¹ It is shown, through the expected dependence of such spectra on ionic mass, that above 40 cm^{-1} the absorption coefficients were expected (as found) to be in the order

$$\text{NaCl} > \text{LiCl} > \text{H}_2\text{O}$$

These data are consistent with a Na⁺/H₂O “rattling” band (412 ± 12 cm^{-1}) at a lower frequency than that of Li⁺/H₂O as found by Williams et al.³⁷ Our data (see Figure 5) are consistent with this scenario, but such considerations do not give the full picture, and it may be seen from Figures 5 and 6 that there are different orders of absorption intensity depending on the frequency considered and the ionic concentration.

Certain ions are well-known to cause a modification of the water network³² (so-called structure “making”). Such modification is expected to have a significant effect on the band profiles of the $\nu_t(\text{H}_2\text{O})$ and $\nu_r(\text{H}_2\text{O})$ intermolecular bands at 200 and 600 cm^{-1} , respectively.³³ These spectral density changes will, of course, affect $\alpha(\nu)$ at lower frequencies and will be responsible for part of the changes which are observed, changes which therefore arise from a balance of at least two phenomena. Certainly, the difference in the hydration numbers residence times and thermodynamics of M⁺–H₂O of interactions (Table 2) will lead to subtle differences for both phenomena.

5.2. Aqueous Acid Solutions. Examination of Figure 4, and comparison with the data from Figures 2 and 3 (see also Figures 5 and 6), shows that the $\alpha(\nu)$ data for HCl in aqueous solution

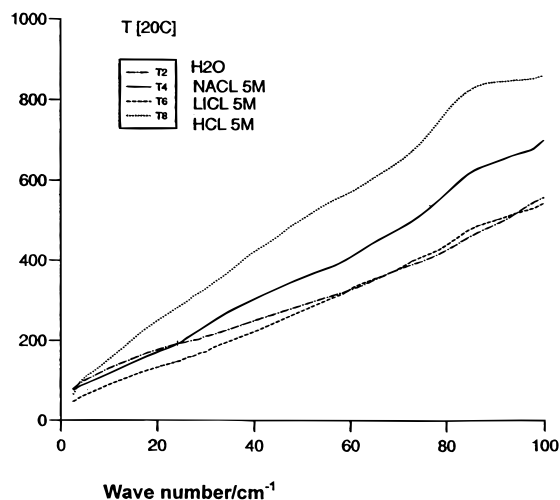


Figure 5. Very-far-IR spectra of LiCl, NaCl, and HCl all at the same concentrations (5 M) and temperature.

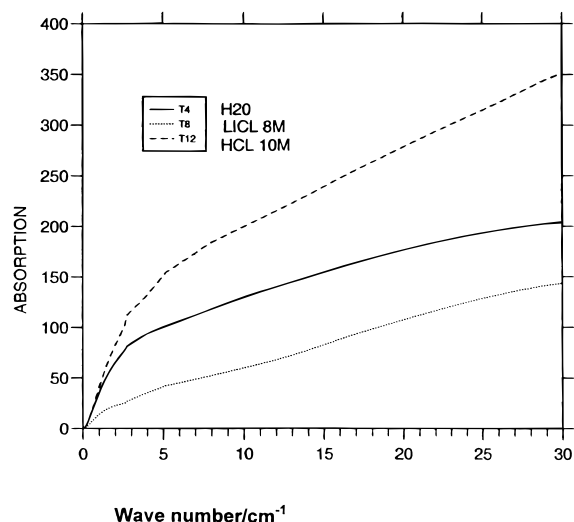


Figure 6. Same as Figure 5A except at higher concentrations for LiCl and HCl.

at a given concentration (again adjusting for the water concentration in the different mixtures) is always greater than that of either the pure water or the cationic (Li^+ or Na^+) solutions. There could be several reasons why this is the case.

(a) The first is that the contribution for the σ_{ac} increase is larger or that there is an implicit time dependence of the conductivity process^{29–31} in the region $\nu > 5 \text{ cm}^{-1}$. We emphasize that, as far as we are aware, accurate absorption coefficient information is reported here for the first time.

(b) The second is that the water structure and dynamics are modified to such an extent, by the formation of a H_3O^+ containing network, that the spectral envelope between 100 and 700 cm^{-1} is severely disturbed. Indeed, Zundel (over a period of 25 years) has shown consistent infrared evidence^{32,35} for the formation of a continuum of states in proton containing media. His spectra,³² and those of others,^{35,36} show consistently a drastic reduction of intensity in the vibrational region of the spectrum ($\sim 600 \text{ cm}^{-1}$) which could lead to the observed very far-IR intensity enhancement. A severe broadening of the far IR spectrum of water was observed by Williams as long ago as 1968.³⁷ On the other hand, the diffusion process of water has been shown to be severely restricted on becoming involved in cation ionic hydration^{41,42} with τ_h^D/τ_w^D (Debye) relaxation times being considerably higher than 1 (Table 2). This might reduce

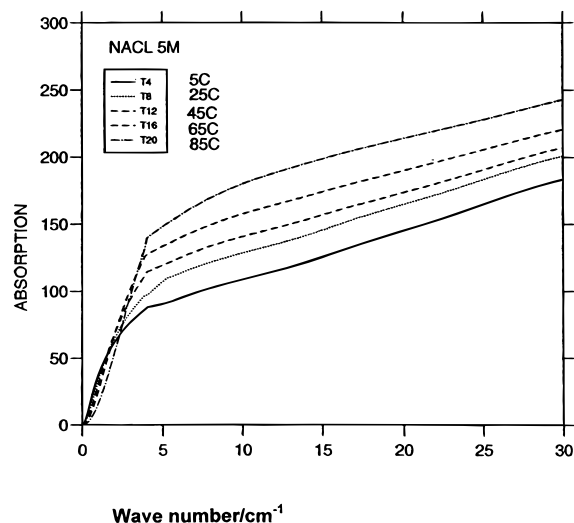


Figure 7. Very-far-infrared spectra of 5 M NaCl solutions between 5 and 80°C .

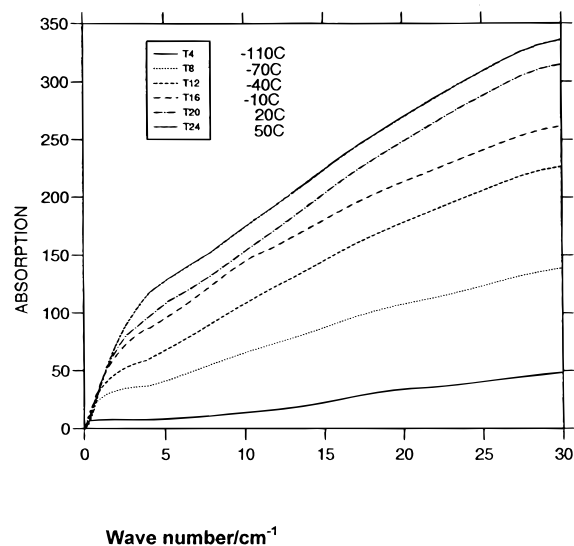


Figure 8. Very-far-infrared spectra of 5 M HCl solutions between -110 and 50°C .

the far-IR wing of water for Na^+ and Li^+ solutions compared with that of water, especially if water molecule motion is restricted on a picosecond time scale by the hydration process.

Thus, even if H_3O^+ is a structure maker³⁹ in aqueous solution, leading to a stronger water network, it seems likely that the band broadening caused by a large increase in rapidly fluctuating proton polarizability is responsible for the observed effects in the $30\text{--}100 \text{ cm}^{-1}$. It should be noted, however, that there is a decrease in the Rayleigh wing of water³⁸ when acid is added. It would appear that this may be caused by complex motional effects due to changes in the structure of the water network. It is noted in this context that a recent Kerr effect study (OKE) on aqueous solutions³⁹ shows that, at a given temperature, the weighting of slow (τ_1) process (relative to that of fast, processes (τ_2)) increases linearly with concentration. This reflected in the measured polarizability function using Rayleigh scattering. The dipole function (via VFIR) obviously behaves differently.

5.3. Effects of Changing the Temperature. For both cation and H_3O^+ containing solutions (Figures 7 and 8) there is an increase in the VFIR intensity with increasing temperature. In the case of H_3O^+ solutions the perturbation is particularly severe, especially at low temperatures. This could again be due to the effects of restricted rotational and translational and/or due to

shifts upward in the far-IR bands between 200 and 600 cm^{-1} . At a given concentration, OKE studies show the weighting of the collective τ_1 (slow) process increases with decreasing temperature and that of τ_2 (fast) processes increases with increasing temperature. As maybe expected, the importance of the fast processes are more important at high temperature and collective effects are more important at low temperatures. This is, however, the opposite of the OKE behavior found for water itself.³⁹ Thus, the effect found for HCl over and above those of water (changes in water intensity with temperature in the VFIR are very modest⁴⁰) are due to the large increase in proton polarizability due to the large network structural change on dissolving HCl in water.

6. Summary and Conclusions

The extension of the frequency window over which ionic solutions have been studied (to $\sim 30 \text{ cm}^{-1}$) has allowed us to explore the effects of ion type and concentration on the short time dynamic behavior. For NaCl in water the changes of spectral density were small, even at 5 M concentrations, and allowed us to study effects due to more perturbative ions. For LiCl in H_2O , with a high energy of hydration and a larger exothermic enthalpy of dissolution, there was a large decrease in intensity compared with water. This is due to the shift and/or shape change in the rotational and translational bands of water in the 200–700 cm^{-1} region due to network breaking and restricted H_2O molecule motion (up to ~ 10 ps residence times in the solvation shell.⁴¹ But there could also be a contribution due to the higher frequency of the $\text{Li}^+\text{H}_2\text{O}$ “rattling” mode caused by the lower mass. For HCl in water the effects were reversed. The water network structure was enhanced, collective dynamics become more important³⁹ and there was a huge increase in the VFIR intensity (cf water). This is caused by a large increase in proton polarizability, giving a large fluctuating transition dipole and extreme broadening of the whole far IR spectrum. This interpretation was confirmed by a temperature study which showed large increases in intensity with temperature, again reflecting the sensitivity of the total dipole function to changes in the fast (proton induced) dynamics in aqueous acid solutions.

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