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The High Frequency Raman Band of Water in Electrolyte Solutions

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The high frequency Raman band of water is studied in electrolyte solutions. The relative scattering yield as a function of Raman frequency is shown to be a very sensitive parameter. Distinct regions of the band are seen to be influenced specifically by the anions resp. the cations. Depolarization ratio measurements confirm these findings.

Introduction

Several theories have been proposed to explain the width of the high frequency Raman band of water, extending from 2.900 to 3.750 cm^{-1}. It was suggested that this band consists of three overlapping component bands, two fundamentals: $\nu_1(a_1)$ and $\nu_3(b_1)$, and one overtone: $2\nu_2(a_1)$.[1,2] Although there exists general agreement as to the presence of several component bands, the assignment to the various fundamentals and/or overtones is a matter of serious discussion.[3,4] On the other hand Buys and Chopin[5] assume that ion-water complexes and structures with a different degree of hydrogen bonding contribute to various extent to the complex Raman band. Thermodynamic calculations of Stevenson[6] however seem to rule out the assumption of a variable monomer concentration in liquid water and electrolyte solutions.

A criterion that has been used in interpreting Raman spectral data of aqueous electrolyte solutions was the intensity and the scattering yield S/S_o.[3,7,8,10] In those studies, however, the total intensity of the band, defined as the total planimetered surface, was considered, rather than the intensity or the scattering yield as a function of the Raman frequency. Moreover the experiments were confined to solutions of the alcali halides. The conclusions of all these investigations are however, unanimous in stating that the anion-effect is in the order $F^- < Cl^- < Br^- < I^-$ and that there is no reason to assume any cation effect.

It is the purpose of this report to show that more specific information can be obtained by studying the relative scattering yield and the degree of depolarization of electrolyte solutions as a function of the Raman frequency. Moreover the scope of this work is enlarged by the examination of mixed electrolyte solutions and of solutions with several divalent cations.

Experimental Section

The techniques for the preparation of the solutions, calibration of the spectra and calculation of the optical correction, have been described in a previous report.[3] The relative scattering yield for a solution *versus* the yield for pure water S_o is defined as

$$\frac{S}{S_o} = \frac{I_a(s)}{I_a(H_2O)} \times \frac{R_o(s)}{R_o(H_2O)} \times \frac{x(H_2O)}{x_s} \qquad (1)$$

wherein $\frac{I_a(s)}{I_a(H_2O)}$ is the ratio of the observed intensity of Raman radiation for the electrolyte solution *versus* the intensity for pure water, and $\frac{R_o(s)}{R_o(H_2O)}$ is the optical correction factor. Plots of S/S_o *versus* the Raman frequency ν (in cm^{-1}) have been made. The lowest value of S/S_o is indicated in the tables by $(S/S_o)_{min}$ and the corresponding Raman frequency by $(\nu_{min})_P$. Thus all the data related to specific values carry the index P to distinguish them from values relating to the whole band. If the minimum for S/S_o extends over a rather broad region the indication pl (plateau) is listed for $(\nu_{min})_P$. The Raman frequency at which this plateau ends towards the high frequency region is tabulated under the heading: end pl. The same system of symbols is used for the values of maximum relative scattering yield. Depolarization ratio's ρ were measured by the method of Rank and Kagarise. In Figures 1 and 2 are shown typical plots of S, ρ, and S/S_o *versus* ν for concentrated NaI and $MgCl_2$ solutions.

Spectra. (a) *Single Electrolyte Solutions.* The concentrations and the corresponding spectral parameters for the solutions of electrolytes investigated are tabulated in Table I.

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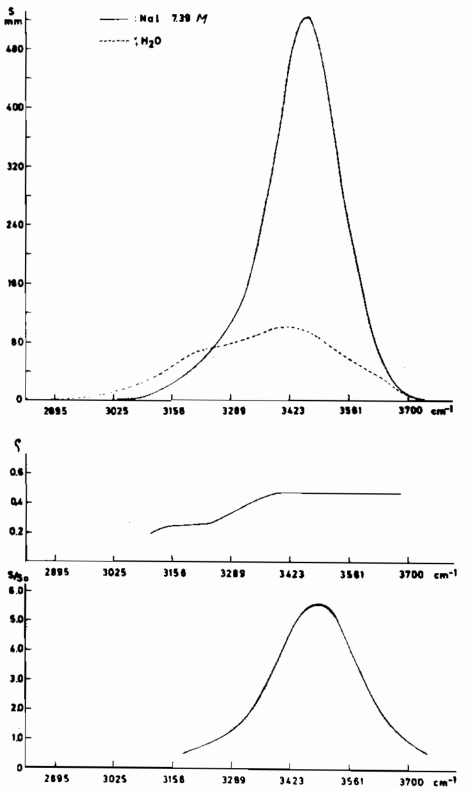

Figure 1. Curves of the scattering yield S, the depolarization ratio ρ and the relative scattering yield S/S_o as a function of Raman frequency for H_2O (dotted curve) and conc. NaI solution.

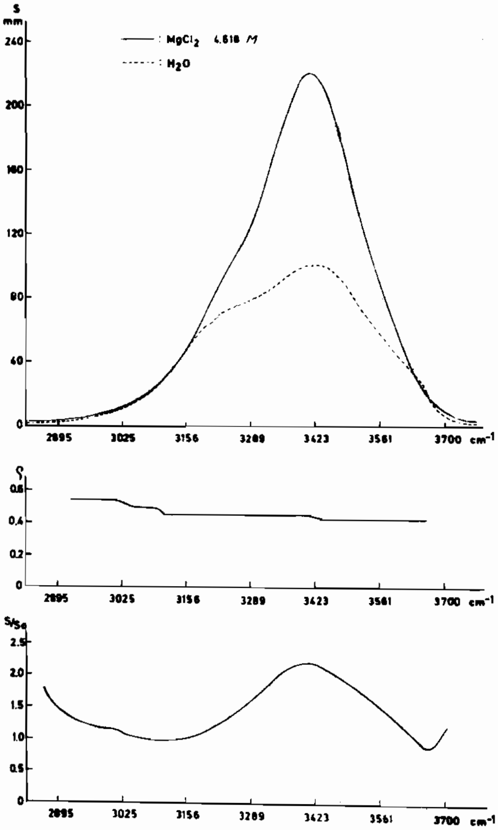

Figure 2. Curves of the scattering yield S, the depolarization ratio ρ and the relative scattering yield S/S_o as a function of Raman frequency for H_2O (dotted curve) and conc. $MgCl_2$ solution.

Table I.

	conc.	$(S/S_o)_{max}$	$(\nu_{max})_P$ cm^{-1}	$(S/S_o)_{min}$	$(\nu_{min})_P$ cm^{-1}	end pl cm^{-1}	x_s
LiCl	1.10	1.17	3440	0.95	3163	—	0.020
	2.20	1.39	3494	0.95	3163	—	0.041
	3.50	1.55	3441	0.97	3160	—	0.063
	4.40	1.81	3454	0.97	3163	—	0.080
	6.00	1.99	3454	0.92	3140	—	0.109
	8.80	2.47	3454	0.91	3140	—	0.162
NaCl	0.59	1.09	3495	1.00	pl	3305	0.010
	1.19	1.21	3502	0.92	pl	3140	0.021
	2.39	1.43	3495	0.78	pl	3140	0.043
	3.50	1.55	3478	0.65	pl	3216	0.064
	4.10	1.69	3509	0.56	pl	3140	0.076
	4.79	1.76	3468	0.53	pl	3140	0.085
KCl	1.00	1.15	3488	0.93	pl	3192	0.016
	1.06	1.21	3510	0.95	pl	3187	0.016
	2.00	1.30	3491	0.81	pl	3203	0.037
	2.82	1.51	3523	0.71	pl	3141	0.054
	3.00	1.47	3475	0.71	pl	3141	0.056
	3.42	1.57	3481	0.71	3048	—	0.064
	3.50	1.52	3482	0.62	pl	3220	0.067
	3.68	1.69	3496	0.64	pl	3141	0.071
LiBr	0.58	1.20	3536	0.97	pl	3233	0.010
	1.00	1.20	3522	0.94	pl	3267	0.018
	1.16	1.40	3536	0.95	pl	3233	0.021
	2.00	1.45	3495	0.90	pl	3174	0.037
	2.32	1.56	3495	0.75	pl	3140	0.045
	3.50	1.85	3495	0.80	pl	3174	0.065
	4.64	2.22	3522	0.71	pl	3186	0.087
NaBr	0.47	1.15	3551	0.99	pl	3306	0.008
	0.94	1.27	3508	0.90	pl	3186	0.017
	1.89	1.55	3522	0.71	pl	3140	0.034
	3.50	1.91	3485	0.82	pl	3223	0.065
	3.78	2.05	3495	0.73	pl	3140	0.070
	4.80	2.48	3495	0.67	—	3140	0.090
KBr	0.63	1.27	3536	0.88	pl	3193	0.011
	1.26	1.38	3495	0.83	pl	3193	0.023
	2.52	1.82	3522	0.72	pl	3183	0.046
	3.36	2.00	3495	0.73	pl	3186	0.065
	4.20	2.10	3481	0.63	pl	3186	0.082
NaI	0.48	1.45	3550	1.10	pl	3306	0.008
	0.97	1.58	3522	1.10	pl	3306	0.009
	3.90	3.09	3522	0.67	—	3140	0.077
	7.39	5.61	3491	0.35	—	3140	0.172
	7.60	6.03	3495	0.44	pl	3140	0.178
KI	0.72	1.48	3550	0.98	pl	3140	0.013
	1.44	1.82	3522	0.92	pl	3140	0.027
	2.89	2.67	3522	0.70	pl	3140	0.056
	5.72	4.22	3491	0.40	pl	3140	0.124
	5.78	4.50	3508	0.43	—	3140	0.125
$BaCl_2$	0.667	1.27	3488	0.90	pl	3166	0.012
	1.000	1.30	3485	0.86	pl	3217	0.018
	1.200	1.37	3487	0.81	pl	3165	0.021
	1.477	1.45	3477	0.71	pl	3155	0.027
$CdCl_2$	1.085	1.22	3525	1.02	3208	—	0.020
	1.661	1.43	3532	1.06	3175	—	0.031
	2.014	1.42	3539	1.08	3202	—	0.038
	2.076	1.44	3519	1.02	3182	—	0.040
	2.609	1.48	3525	1.02	3169	—	0.050
$CdBr_2$	1.002	1.33	3532	1.00	3162	—	0.019
	1.756	1.60	3532	1.01	3195	—	0.033
	2.361	1.83	3539	1.07	3259	—	0.046
	2.522	1.90	3539	1.08	3182	—	0.049
$MgCl_2$	1.181	1.33	3464	0.88	3083	—	0.021
	2.362	1.65	3450	0.85	3077	—	0.043
	3.001	1.76	3450	0.86	3122	—	0.055
	4.618	2.25	3402	1.00	3110	—	0.088
$ZnCl_2$	2.072	1.38	3560	0.98	3188	—	0.038
	2.989	1.70	3542	0.98	3195	—	0.057

For all the solutions containing the ions Na^+ and K^+ curves of S/S_o *versus* ν similar to that of Figure 1 are obtained. Below about 3150 cm^{-1} the S/S_o value is very low and rather constant. Taking account of an error of about 2% on each intensity measurement, the data of Table III (section b1), show that the values of $(S/S_o)_{max}$ and of $(\nu_{max})_P$ are constant for constant halide ion concentration.

Table II.

electrolyte	l_{x^-}	electrolyte	$l_{M^{n+}}$
KCl	0.17	NaCl	–0.09
NaCl	0.17	NaBr	–0.09
LiCl	0.17	NaI	–0.09
$BaCl_2$	0.17	KCl	–0.09
$MgCl_2$	0.13	KBr	–0.09
$ZnCl_2$	0.12	KI	–0.09
$CdCl_2$	0.11	$BaCl_2$	–0.17
NaBr	0.28		
KBr	0.28		
LiBr	0.28		
$CdBr_2$	0.18		
NaI	0.59		
KI	0.59		

Table III.

x	$(S/S_o)_{max}$	$(\nu_{max})_P$ cm^{-1}	$(S/S_o)_{min}$	$(\nu_{min})_P$ cm^{-1}	end pl cm^{-1}	n_{Hg}^{546}
LiCl(1), KCl(2) $M=1$						
0	1.15	3470	1.02	pl	3221	1.343
1/5	1.13	3477	0.97	pl	3221	1.343
2/5	1.12	3463	1.01	pl	3268	1.343
1/2	1.12	3477	1.02	pl	3268	1.343
3/5	1.13	3456	1.02	pl	3175	1.343
4/5	1.12	3505	1.00	pl	3221	1.343
NaCl(1). KCl(2) $M=1$						
1/5	1.10	3471	0.96	pl	3268	1.344
2/5	1.11	3485	1.00	pl	3221	1.344
1/2	1.12	3471	0.98	pl	3222	1.344
3/5	1.13	3484	1.00	pl	3268	1.344
4/5	1.14	3484	1.00	pl	3222	1.344
LiCl(1), KCl(2) $M=3.5$						
0	1.52	3482	0.62	pl	3220	1.367
1/5	1.52	3468	0.65	pl	3130	1.367
2/5	1.51	3482	0.77	pl	3174	1.366
1/2	1.51	3455	0.81	pl	3174	1.366
3/5	1.57	3455	0.90	pl	3174	1.365
4/5	1.55	3468	1.00	pl	3220	1.364
1	1.55	3441	0.97	3160	—	1.363
LiCl(1), NaCl(2) $M=3.5$						
0	1.55	3478	0.65	pl	3216	1.366
1/5	1.50	3475	0.76	pl	3219	1.365
2/5	1.50	3482	0.84	pl	3219	1.364
1/2	1.50	3482	0.75	pl	3219	1.364
3/5	1.50	3455	0.90	pl	3219	1.363
4/5	1.50	3455	0.91	pl	3219	1.363
1	1.55	3441	0.97	3160	—	1.363
NaCl(1), KCl(2) $M=3.5$						
0	1.52	3482	0.62	pl	3220	1.367
1/5	1.55	3450	0.67	pl	3216	1.367
2/5	1.57	3478	0.71	pl	3216	1.367
1/2	1.55	3478	0.65	pl	3216	1.367
3/5	1.59	3478	0.71	pl	3216	1.366
4/5	1.63	3478	0.71	pl	3216	1.366
1	1.55	3478	0.65	pl	3216	1.366
NaBr(1), KBr(2) $M=3.5$						
1/5	1.92	3481	0.90	pl	3219	1.380
2/5	1.96	3481	0.91	pl	3219	1.380
1/2	1.95	3481	0.88	pl	3219	1.380
3/5	1.94	3481	0.88	pl	3219	1.380
4/5	1.90	3485	0.79	pl	3223	1.380
1	1.91	3485	0.82	pl	3223	1.380

For dispositive ions and for LiCl, however, the S/S_o value starting from 2900 cm^{-1} has a reasonably high value, eventually even higher than unity (Figure 2). Figures 1 and 2 are illustrative of the two different kinds of curves encountered in this work. In Figures 3a and 3b, $(S/S_o)_{max}$ is plotted as a function of molar concentration of electrolyte. Figure 4 shows the decrease of $(S/S_o)_{min}$, with increasing molar concentration for solutions containing the cations Na^+, K^+, Ba^{2+}. The slopes l_{x^-} and $l_{M^{n+}}$ of these curves, defined by the equations:

$$(S/S_o)_{max} = 1 + l_{x^-} N_{x^-} \qquad (2)$$

$$(S/S_o)_{min} = 1 + l_{M^{n+}} N_{M^{n+}} \qquad (3)$$

are tabulated in Table II. N is the normality of the respective ions in solution. It is evident from these data that the $(S/S_o)_{max}$ values are determined by the nature of the halide ion, the $(S/S_o)_{min}$ values by the nature of the cation.

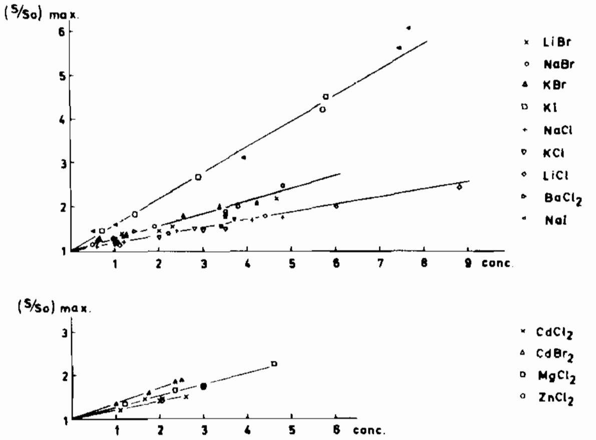

Figure 3. Plots of $(S/S_o)_{max}$ as a function of molar concentration.

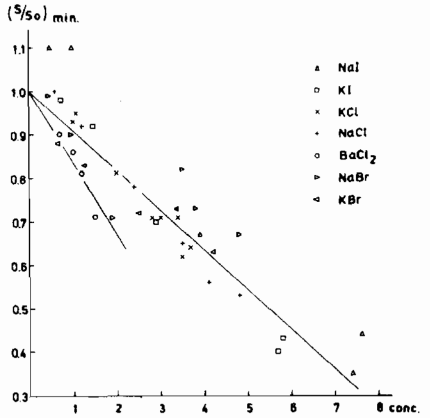

Figure 4. Plots of $(S/S_o)_{min}$ as a function of molar conncentration.

(b) *Binary Electrolyte Solutions.* In order to isolate the extent of any cation effect clearly, binary electrolyte solutions were investigated in the same way as the single electrolyte solutions. From the data in the preceding section it can be seen that the halide ions are most effective in influencing the $(S/S_o)_{max}$ values, and that deviations from the constant value of $l_{Cl^-}=0{,}17$ for instance, are only observed for so called complexing ions Mg^{2+}, Zn^{2+}, Cd^{2+}. For the other ions Na^+, K^+, Li^+, and Ba^{2+} the obvious conclusion would then be that there is no cation effect whatsoever. It is this conclusion, however erroneous, that has been drawn by most other authors.[3,7,8,10] Indeed, the observations concerning $(S/S_o)_{min}$, indicating that the slope value $l_{M^{n+}}$ for this parameter is only determined by the nature of the cation, were overlooked in previous investigations, because attention was focussed only on the total planimetered scattering yield of the band. In the binary solutions with constant halide ion concentration, however, slight deviations can be observed which can be ascribed to cation effects. Three groups of solutions have been investigated.

(1) *Binary Alcali Halide Solutions with Constant Halide Ion Concentration.* The spectral parameters for these solutiions are listed in Table III. The volume fraction x of electrolyte number 1 *versus* electrolyte number 2, defined by

$$x = \frac{v_1}{v_1 + v_2} \tag{4}$$

was used as concentration parameter.

Spectra for each binary system were recorded at different total molar concentrations *M*, from 1 to 3.5 molar.

(2) *Binary Solutions of $BaCl_2$ and KCl.* In this series of solutions the total ionic strength I was kept constant. The data for these solutions are collected in Table IV. From the data for the extreme values of chloride ion concentration 1.33 and 2.00 resp. 2.00 and 3.00 it is seen that $(S/S_o)_{max}$ is again mainly a function of this concentration. The $(S/S_o)_{min}$ values on the other hand seem to be dependent on the ratio of the concentration of Ba^{2+} to K^+. The spectral area covered by the minimum and the maximum are more or less constant.

The data of sections (b1) and (b2) therefore show that there is no mutual influence of ion effects to be observed: $(S/S_o)_{max}$ is a function of the concentration and the nature of the halideion only and $(S/S_o)_{min}$ values are only determined by the concentration and the nature of the cations. This statement is clearly illustrated by the fact that both $(S/S_o)_{max}$ and $(S/S_o)_{min}$ values for the systems $BaCl_2/KCl$ and the $(S/S_o)_{max}$ values for the system $MgCl_2/KCl$ (to be treated in the next section) can be calculated with reasonable accuracy using the l-values of Table II and assuming additivity of ion effects.

(3) *Binary Systems of $MgCl_2$ and KCl.* In this system a theoretical possibility existed of detecting complex-ion formation. Therefore the Job-method was used to investigate this possibility. In all the solutions the sum of concentrations of Mg^{2+} and Cl^- was kept constant and equal to 5 *M*. The parameter f, describing the ratio between the chloride ion concentration and this sum was varied over a range from 0.7 to 0.9.[9] The data for these series are collected in Table V. $(S/S_o)_{max}$ is seen to increase linearly with f, but there is no conclusive evidence for complex formation.

Table IV.

(Ba^{2+})	(K^+)	(Cl^-)	$(S/S_o)_{max}$	$(S/S_o)_{max}$ calcd.	$(\nu_{max})_P$ cm^{-1}	$(S/S_o)_{min}$	$(S/S_o)_{min}$ calcd.	$(\nu_{min})_P$ cm^{-1}	end pl cm^{-1}	n_{Hg}^{546}
					$BaCl_2/KCl$ I=2					
0.667	—	1.334	1.27	1.23	3488	0.90	0.89	pl	3166	1.3543
0.632	0.105	1.369	1.25	1.23	3512	0.91	0.89	pl	3192	1.3537
0.580	0.258	1.418	1.23	1.24	3518	0.87	0.89	pl	3161	1.3530
0.500	0.500	1.500	1.25	1.26	3490	0.86	0.88	pl	—	1.3542
0.462	0.616	1.540	1.24	1.26	3488	0.82	0.87	pl	3166	1.3551
—	2.000	2.000	1.31	1.34	3500	0.83	0.82	pl	3214	1.3520
					$BaCl_2/KCl$ I=3					
1.000	—	2.000	1.30	1.34	3485	0.86	0.83	pl	3217	1.3582
0.967	0.097	2.031	1.35	1.35	3492	0.92	0.83	pl	3196	1.3637
0.922	0.231	2.075	1.33	1.35	3489	0.88	0.82	pl	3164	1.3636
0.750	0.750	2.250	1.36	1.38	3515	0.84	0.80	pl	3192	1.3631
—	3.000	3.000	1.47	1.51	3475	0.71	0.73	pl	3141	1.3600

Table V. $MgCl_2/KCl$

Molar conc.		Conc.				Contrib. to I			
KCl	$MgCL_2$	Cl^-	f	$(S/S_o)_{max}$	$(\nu_{max})_P$ cm^{-1}	KCl	$MgCl_2$	$(S/S_o)_{max}$ calcd.	$(S/S_o)_{min}$
0.50	1.50	3.50	0.700	1.45	3454	0.09	0.39	1.48	0.84
1.25	1.25	3.75	0.750	1.48	3454	0.21	0.33	1.54	0.88
2.00	1.00	4.00	0.800	1.55	3464	0.34	0.26	1.60	0.77
2.75	0.75	4.25	0.850	1.63	3449	0.47	0.20	1.66	0.79

(c) *Depolarization Ratio Measurements.* The degree of depolarization ρ is plotted as a function of the Raman frequency ν (in cm^{-1}) in Figure 5 for pure water and for several types of electrolyte solutions. The plot for pure water confirms the findings of Schultz and Hornig[7] and of Weston.[8] In Figure 6 a similar plot is made for $MgCl_2$ solutions.

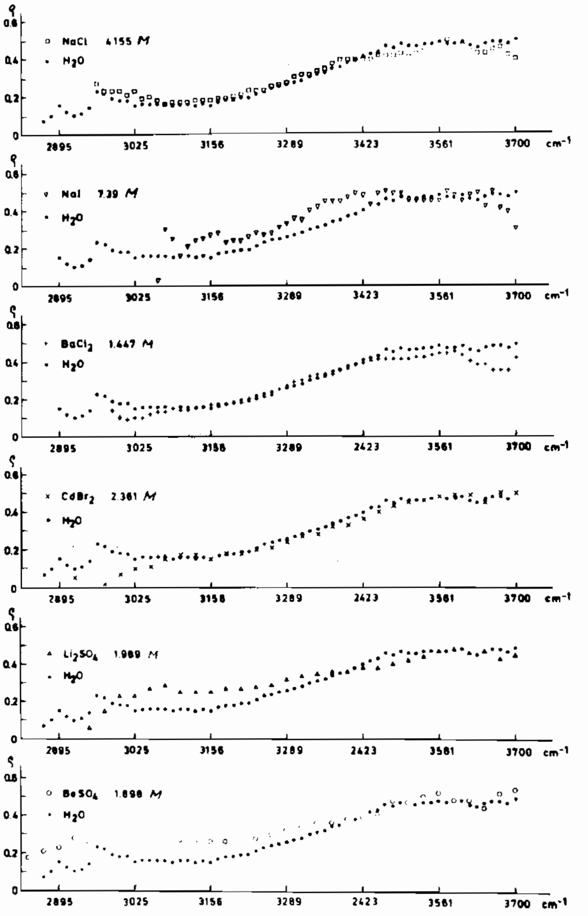

Figure 5. Plots of the depolarization ratio ρ as a function of Raman frequency for the OH-band in electrolyte solutions and in pure water.

Results and Discussion

The experimental data clearly bear out two important points. First, the anion-effect is confined specifically to the high frequency region of the OH Raman band and results in linear increase of the relative scattering yield $(S/S_o)_{max}$ in this portion of the OH-Raman band, with increasing halide ion concentration. This increase can be described by the described by the coefficient l_{x^-} in equation (2) and it is seen that $l_{Cl^-} < l_{Br^-} < l_{I^-}$. Similarly a specification effect results in a decrease of $(S/S_o)_{min}$, which is observed only in the low frequency region of the band. Secondly, in the case of alkalihalide solutions and of binary solutions of $BaCl_2/KCl$, no interference between the cation- and the anion-effect can be observed; $(S/S_o)_{max}$ and $(S/S_o)_{min}$ are seen to be only dependent on the nature and the concentration of the anion respectively the cation. Only in presence of the cations Mg^{2+}, Zn^{2+}, and Cd^{2+} the l_{Cl^-} values are seen to be decreased with respect to those observed in the alcalihalide solutions. Therefore, a discussion of the intensity relations in the low frequency region, as determined by the nature of the cations should be devided into two sections. Indeed whereas for Na^+, K^+, and Ba^{2+} constant values of $l_{M^{n+}}$ in equation (3) are observed, for Mg^{2+}, Zn^{2+}, and Cd^{2+} the situation is obviously more complex.

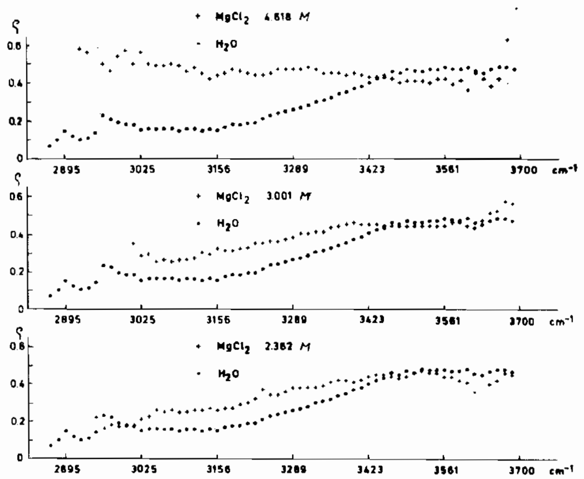

Figure 6. Plots of the depolarization ratio ρ as a function of Raman frequency for the OH-band in $MgCl_2$ solution.

The depolarization ratio data confirm more or less the division of the OH-Raman band into two regions. For all the electrolyte solutions studied the ρ value in the high frequency region defined above is about 0.4 to 0.5. This is very close to the value for pure water. In the low frequency region however again two groups of cations are seen to produce a different effect. Solutions containing Na^+, Ba^{2+}, and Cd^{2+} (Figure 3) show the ρ value of pure water in the low frequency region whereas Li^+, Be^{2+}, and Mg^{2+} (Figure 3, 4) yield higher values than the value of pure water. This comparison could be interpreted in terms of coupling of energy levels or of disturbance of the symmetry of the molecule as a result of strong intermolecular coupling. Although such effects ought to be strongest in the concentrated solutions studied, the experimental material is too scarce to allow a definite conclusion. Further experiments on the surrounding of the oxyanions in water solution, that will be reported in the next paper, allow more refined discussion of the structural background of the experimental material reported here.

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