Anomalous Contact-Ion Pairing in the Glassy States of "Dilute" Aqueous Lithium and Sodium Perchlorate Solution

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Aqueous D_2O solutions of lithium (0.5, 1, and 3 M) and sodium (1 and 3 M) perchlorate have been studied by FT-IR spectroscopy in their glassy states at 80 K, and their IR spectra compared with those of 1.0 M D_2O solutions recorded from 300 to 235 K. Evidence for strongly increasing contact-ion pairing in going from ambient temperature to the glassy state is based on the development of a second band in the ν_1 band region centered at high frequency of the band from "free" perchlorate and complete loss of degeneracy in the ν_3 and ν_4 band region. On the basis of curve resolution of the ν_1 band region, increasing contact-ion pairing is much more pronounced for sodium than for lithium perchlorate. The spectral features of contact-ion paired perchlorate are consistent with at most C_{2v} symmetry with bidentate binding. Anomalous increase in contact-ion pairing on hyperquenching into the glassy state is attributed to water's density maximum and the anomalies of supercooled water and "dilute" aqueous solutions. Spectral features of ion-pairing are weakly observable already at 300 K in the ν_1 and ν_3 band region and become more pronounced on cooling to 235 K. Significance of the results is discussed with respect to (i) differences in local geometry of contact-ion pairs in aprotic donor solvents, (ii) vapor-deposited alkali metal perchlorates isolated in a water matrix, (iii) thermodynamic continuity of states between vapor-deposited amorphous water, hyperquenched glassy water and normal supercooled water, and (iv) cryofixation of polyelectrolyte-type biomolecules such as nucleic acid sodium salts.

Introduction

In aqueous solution the perchlorate ion ClO_4^- is one of the least associating anions and it requires solvents of much lower dielectric permittivity than that of water to induce formation of contact-ion pairs and aggregates (see refs 1 and 2 for recent reviews, and refs 3−5 for reviews of older literature). Whereas Raman and IR spectroscopy generally can detect only contact-ion pairs, conductance measurements in addition reflect the presence of solvent-separated/solvent-shared ion pairs and therefore are more sensitive for detecting ion association effects. According to D'Aprano's conductance studies of perchlorate solutions at 25 °C,[6] perchlorate association is negligible for lithium and marginal for sodium cations in a concentration range up to 0.06 M. Because of that, aqueous perchlorate solutions in particular with lithium and sodium as cations are routinely used in equilibrium studies on complex formation for obtaining a "constant ionic medium"[3] or in Raman spectroscopic studies as an internal standard.[4] In the older literature on aqueous alkali metal perchlorate solution studies by Raman spectroscopy it was concluded that association is absent,[4,7−10] but in more recent studies small but significant association effects were reported for concentrated solutions.[11−13] This is probably due to improved instrumentation, and it involved careful analysis of the intense symmetric stretching band of the free perchlorate anion for a weak second component band from the contact-ion pair.[11−13]

Evidence for contact-ion pairing has been reported, however, for vapor deposited lithium and sodium perchlorate in a water matrix[14−16] and for the aqueous solutions hyperquenched into the glassy states.[17] These were IR spectroscopic studies where contact-ion pair formation was deduced from splitting of the

degenerate antisymmetric stretching vibration. Interpretation of loss of degeneracy by contact-ion pairing is difficult and in most cases not unambiguous. This increase in contact-ion pairing on quenching into the glassy state is unexpected because for aqueous electrolyte solutions studied on heating from ambient temperature, contact-ion pairing is known to *increase* with increasing temperature, mainly because of the parallel occurring decrease of water's dielectric permittivity.[4,5,18]

Here we report an FT-IR spectroscopic study of contact-ion pairing in the glassy states of "dilute" (i.e., 0.5−3 M) lithium and sodium perchlorate solutions in D_2O. This is an extension of the previous IR spectroscopic study,[17] but because of the highly improved quality of the spectra and improved curve resolution of overlapping bands by comparison of derivative curves,[19] we can quantify here contact-ion pairing in the nondegenerate symmetric perchlorate stretching band region. On the basis of contact-ion pairing observable in the nondegenerate normal mode, we then interpret the spectral changes in the degenerate normal modes. The spectral pattern of the contact-ion pair obtained from glassy solution allows to detect evidence for ion-pairing even for 1 M solution at ambient temperature and in supercooled solution.

This study is a continuation of our previous reports on anomalous increase in contact-ion pairing in "dilute" aqueous electrolyte solution in their supercooled and glassy states.[17,20,21] We have attributed this anomalous increase to water's density maximum and the anomalies of supercooled water and dilute aqueous solutions which are caused by structural changes toward a more open, fully hydrogen-bonded tetrahedral network in a comparatively small temperature region (see refs 22−25 for

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reviews). These structural changes continue on "hyperquenching" liquid water on cooling at $\approx 10^6 - 10^7$ K s^{-1} into the glassy state.[26-29] Our conjecture is consistent with our recent report of comparable anomalous increase of density and of contact-ion pairing on increasing supercooling.[21] By "dilute" we understand in this and our earlier studies electrolyte solutions at concentrations still showing the anomalies of supercooled water, although to a lesser extent.

The spectral changes characteristic for contact-ion pairing in the glassy states of hyperquenched lithium and sodium perchlorate solutions are then compared with those reported by Devlin and co-workers for vapor deposited lithium and sodium perchlorate in a water matrix,[14-16] and their assignment of the spectral changes in terms of contact-ion pairing is supported by our more detailed analysis. At first sight it is rather surprising that similar anomalous increase in contact-ion pairing occurs on both hyperquenching an electrolyte solution and matrix-isolation of the vapors. Therefore, these findings are next discussed in the context of the much debated thermodynamic continuity, or discontinuity, of states between vapor-deposited amorphous solid water (ASW), hyperquenched glassy water (HGW), and normal supercooled water. Recent experimental studies are consistent with thermodynamic continuity of states.[30,31] Thus, the surprising observation of comparable anomalous contact-ion pairing in the glassy states of vapor-deposited and hyperquenched electrolyte solution is consistent with continuity of states.

Our observation of pronounced contact-ion pairing even in "dilute" glassy aqueous solution of lithium and sodium perchlorate must have implications for so-called "cryofixation" of biomolecules into the glassy state.[32] Therefore, pronounced formation of contact-ion pairs (or salt bridges) is to be expected in particular on "cryofixation" of biomolecules which are polyelectrolytes, e.g., of sodium salts of nucleic acids. This aspect will also be discussed.

Experimental Section

LiClO$_4$·3H$_2$O (Merck, compound no. 10538) and NaClO$_4$·H$_2$O (Fluka, compound no. 71852) of p.a. quality were dried over P$_2$O$_5$, and solutions were made with D$_2$O (99.7%). Films of the glassy, or vitrified, solutions were made by "hyperquenching" of aerosol droplets on a CsI window held at 78 K. For further experimental details on this technique see refs 20 and 21. Changes in the concentration of the solute during the various stages of the procedure are estimated as $\pm 5\%$.[33]

The IR spectra were recorded in transmission on Biorad's FTS 45 at 2 cm^{-1} resolution (except for 3 M sodium perchlorate D$_2$O solution in Figure 7, (see below, which was recorded at 4 cm^{-1} resolution), by coadding between 500 and 1000 scans, and 2000 scans for the background (DTGS detector, UDR1; zero-filling factor 2; low-pass filter at 1.12 kHz; triangular apodization). Peak maxima are given in the Figures to 0.1 cm^{-1} and were found to be reproducible to a few tenths of a wavenumber. Water vapor was subtracted from each spectrum. Data processing was performed with Grams/32 (Galactic). The sloping background was subtracted with a multipoint spline-function routine. The effects of base line correction were controlled by comparing second derivative curves of the original bands with those of the bands after subtraction of the sloping background. Because of the low intensity of the composite ν_1 band, curve resolution had to be controlled by comparison of second derivative curves of the experimental composite bands with those of the sum of the curve-fitted component bands instead of using fourth derivative curves.[19] This comparison of

TABLE 1: Curve-Fitting Analysis of the ν_1 Band Region (from 850 to 980 cm^{-1}) of 0.5, 1, and 3 M Lithium Perchlorate Solution in D$_2$O, and of 1 and 3 M Sodium Perchlorate D$_2$O Solution, Recorded at 80 K in Their Glassy States[a]

cation/ concentration	ν_{max} (cm^{-1})	height	fwhh (cm^{-1})	% Gauss	% relative area and assignment
Li$^+$/0.5 M	917.7	0.0408	23.1	77	82, F
	928.6	0.0233	9.5	100	18, B
Li$^+$/1 M	920.3	0.0237	22.8	90	75, F
	929.2	0.0187	9.7	86	25, B
Li$^+$/3 M	922.1	0.0479	21.4	82	62, F
	929.7	0.0607	10.8	100	38, B
Na$^+$/1 M	917.4	0.0120	19.1	32	34, F
	931.9	0.0316	16.4	74	66, B
Na$^+$/3 M	917.9	0.00665	16.5	29	17, F
	933.4	0.0376	17.2	84	83, B

[a] ν_{max} (in cm^{-1}) are the peak frequencies; fwhh is the full width at half-height of the curve-fitted component bands; F indicates "free" perchlorate; B, bound (contact-ion paired) perchlorate; % Gauss are the values when using a sum of Gaussian and Lorentzian peak shapes.

second (or fourth) derivatives allows reliable curve resolution of highly overlapping bands and development of this criterion for "goodnes-of-fit" was essential for reliable curve resolution of perchlorate's ν_1 band region.[19] All second derivative curves are shown inverted. The scaling factors in the figures refer to the ordinate scale.

Simulation of the second derivative curves in the ν_1 band region of 1 M lithium perchlorate solution shown in Figure 8b, see below, was done with a selfwritten computer program which is based on the Grams/32 software.[34] This program allowed to generate synthetic peaks with defined peak parameters, calculate the second derivative curves, and to compare interactively the experimental second derivative with the simulated one.

Results and Assignment

An aquated unperturbed perchlorate anion of T_d symmetry generates vibrational bands at ≈ 932 (ν_1, A$_1$, R), ≈ 460 (ν_2, E, R), 1115 (ν_3, F$_2$, (IR, R) and ≈ 630 cm^{-1} (ν_4, F$_2$, IR, R) where IR and R denote infrared and Raman activity. In the IR spectrum of 1 m NaClO$_4$ in aqueous solution, a weak band at 933 cm^{-1} has been observed and attributed to the ν_1 (A$_1$) vibration of ClO$_4^-$ with its T_d symmetry perturbed.[13] Lowering of the local symmetry around ClO$_4^-$ causes band splittings of degenerate vibrations, i.e. of all vibrations except ν_1, and in favorable cases the new local symmetry can be determined from these band splittings.[1-5,12,13] Chabanel et al.[1] have reviewed recently contact-ion pairing and aggregation of lithium and sodium perchlorates in aprotic donor solvents and their Table 1 gives the correlation between vibrational modes of ClO$_4^-$ in environments of decreasing symmetry. Contact-ion pairing generates a new set of bands, somewhat displaced from those of the hydrated ion. Although the number of perchlorate bands is essentially doubled by the presence of free and contact-ion paired (or bound) perchlorate, their separation and quantitative evaluation is often impossible owing to insufficient separation. Contact-ion pairing is seen most clearly by doubling of the nondegenerate ν_1 band, whereas interpretation of band splittings of the degenerate bands is often ambiguous. We will speak in the following of "free" perchlorate but understand that it can contain varying amounts of solvent-shared and/or solvent separated ion pairs which generally are spectroscopically undistinguishable.[1,2]

D$_2$O was used throughout as solvent because its librational band is shifted sufficiently to low frequency to allow, by careful
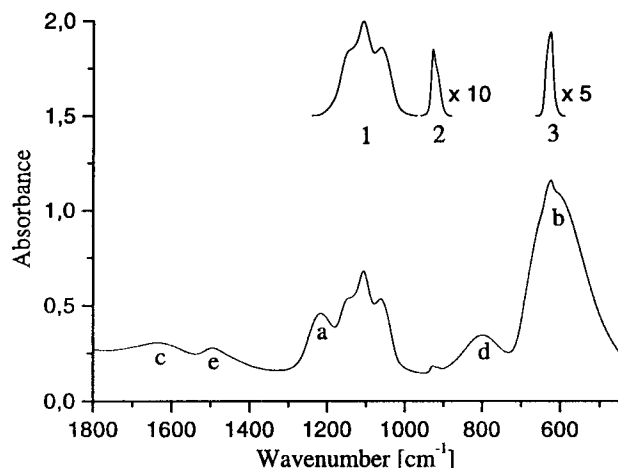
Figure 1. IR spectrum of 1 M lithium perchlorate D_2O solution recorded at 78 K in its glassy state (bottom) and perchlorate's ν_3, ν_1, and ν_4 band region after subtraction of the solvent (top, shifted upward, and numbered 1–3). Solvent bands are marked as a–e.

subtraction of the solvent spectrum, quantitative evaluation of the ν_1 band region for contact-ion pairing. Figure 1 shows for demonstration purposes the experimental IR spectrum (lower curve) of a hyperquenched and glassy 1 M $LiClO_4$ solution in D_2O from 1800 to 450 cm^{-1} and the ν_1, ν_3 and ν_4 band regions of the perchlorate ion after subtraction of the solvent (upper curves, labeled 2, 1 and 3), with ordinate scaling factors as given in the figure. The ν_2 band region at $\approx$460 cm^{-1} was not accessible in D_2O solution.

In the following figures we show as so-called "experimental" bands spectra of the perchlorate ion but after subtraction of the solvent spectrum. The number of component bands in composite band profiles was determined by deconvolution and by second and fourth derivative curves. The curve-fitted component bands are also shown in several of the figures.

ν_1 Band Region in Glassy Solution. We start with this region because, as pointed out above, it is most informative for observing contact-ion pairing. The ν_1 band shape is asymmetric in all the spectra of glassy lithium and sodium perchlorate solutions in D_2O shown here, and the composite band profile can be resolved into two component bands. Figure 2 shows for glassy $LiClO_4$ solution in D_2O the influence of concentration on the relative intensities of the two component bands. Curves a–c show spectra of glassy 0.5, 1, and 3 M $LiClO_4$ D_2O solution recorded at 80 K (solid), the curve-fitted component bands and their sum (broken). Curves a'–c' give the comparison of the second derivative of the composite band profile (solid) with that of the sum of the curve-fitted component bands (broken) where optimal correspondence is used as our criterion for the "goodness-of-fit". The relative intensity of the component band centered at low frequency (918–922 cm^{-1}) decreases with increasing concentration from 82% (a) to 75 and 63% (b and c), whereas that of the component band at high frequency increases. We therefore assign the component band at $\approx$929 cm^{-1} to contact-ion paired $Li^+ClO_4^-$, and that at low frequency to "free" ClO_4^-. IR activity of the band assigned to "free" perchlorate indicates perturbation of the anion by formation of solvent-shared/solvent-separated ion pairs because this band is IR inactive for T_d symmetry.[1] The band parameters and those of all other curve-fits of the ν_1 band region are listed in Table 1. The full width at half-height (fwhh) of the curve-fitted component bands of "free" perchlorate is between 21 and 23 cm^{-1}, whereas those of the contact-ion paired perchlorate is only 10–11 cm^{-1} (Table 1). This broadening of the component
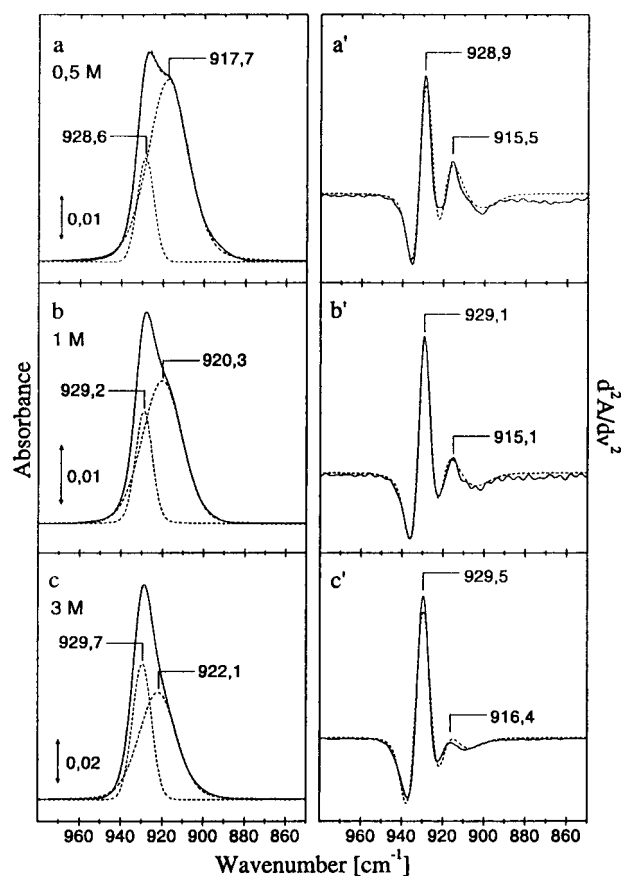

Figure 2. Effect of concentration on perchlorate's ν_1 band region: (a–c) IR spectra of 0.5, 1, and 3 M lithium perchlorate D_2O solution recorded in their glassy states at 80 K and their curve-fitted component bands (broken lines indicate the sum of the curve-fitted component bands); (a'–c') the comparison of the second derivatives of the spectra (solid) with that of the sum of the curve-fitted component bands (broken, "best" fit with respect to this comparison).

bands assigned to "free" perchlorate is attributed to the presence of significant amounts of solvent-shared/solvent-separated ion pairs. For the lithium salt the peak maximum of the "free" perchlorate band shifts in going from 1 to 3 M solution by 1.8 cm^{-1} to higher frequency, whereas for the sodium salt the shift is only 0.5 cm^{-1} (Table 1). This may reflect different amounts of solvent-separated/solvent-shared ion pairs in the two glassy alkali metal salt solutions.

In Figure 3 we compare contact-ion pairing in glassy 1 M lithium perchlorate D_2O solution with that in 1 M sodium perchlorate solution. Curves a and b show the original composite bands and the curve-fitted component bands, a' and b', the comparison of second derivative curves. The relative intensity of the component band at high-frequency assigned to contact-ion paired perchlorate increases in going from the lithium to the sodium cation from 25 to 66%.

We note that the composite band structure in the ν_1 band region cannot be caused by $^{35}Cl/^{37}Cl$ isomer splittings because band separation and relative intensities depend on both the cation and the concentration (see Table 1).

ν_3 Band Region in Glassy Solution. In Figure 4 we demonstrate the effect of the concentration for the experimental IR spectra (without solvent subtraction) of 0.5, 1, and 3 M lithium perchlorate solution (curves a–c). Their second derivatives are shown as curves a'–c'. The broad band at high-frequency centered at $\approx$1215 cm^{-1} is the D_2O deformation band. The antisymmetric stretching vibration centered at ambient

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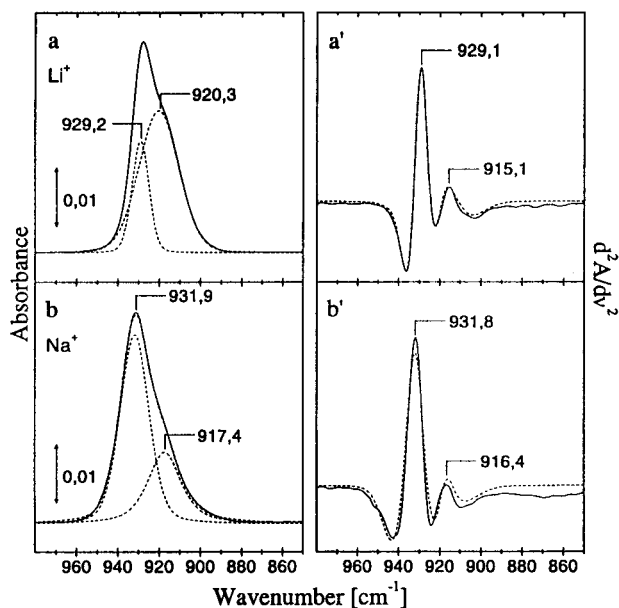*J. Phys. Chem. B, Vol. 103, No. 37, 1999* **8019**

Figure 3. Effect of alkali cation on perchlorate's ν_1 band region: IR spectra of 1 M lithium (a) and sodium (b) perchlorate D_2O solution recorded in their glassy states at 80 K (broken = sum of the curve-fitted component bands); (a′, b′) the comparison of the second derivatives of the spectra (solid) with that of the sum of the curve-fitted component bands (broken, "best" fit).
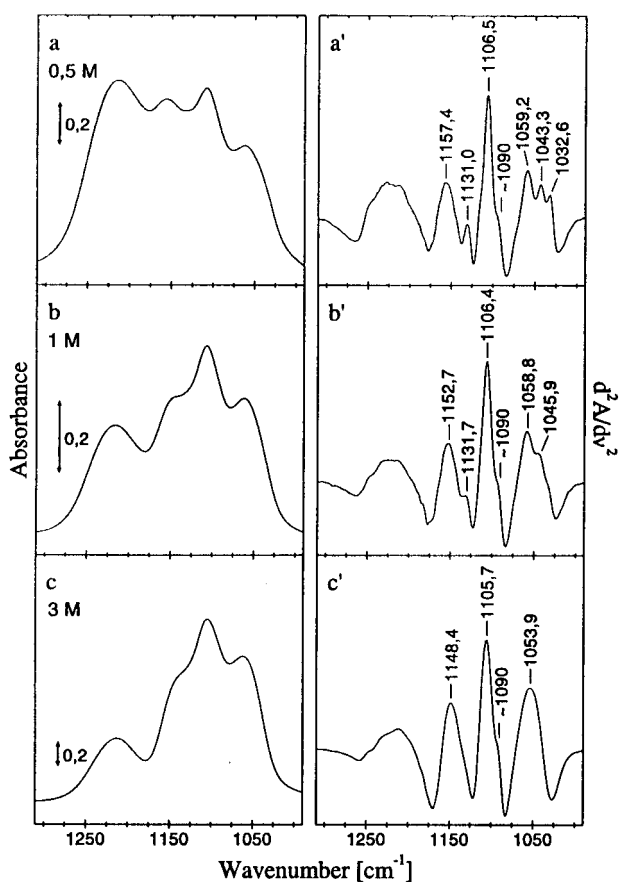

Figure 4. Effect of concentration on perchlorate's ν_3 band region: (a–c) IR spectra of 0.5, 1, and 3 M lithium perchlorate D_2O solution recorded in their glassy states at 80 K; (a′ to c′) their second derivatives. The broad band at ≈1215 cm^{-1} is from the solvent.

temperature at ≈1115 cm^{-1} in unperturbed perchlorate contains three component bands in the experimental spectra a to c. Curve

resolution of the component bands was attempted but gave no reliable results because of the multitude of highly overlapping band components. By comparison with the curve-fitted component bands of the ν_1 band region shown in Figure 2, it is obvious that the composite band of the ν_3 band region must also contain the spectrum of "free" perchlorate. A more quantitative estimation was not attempted because the molar infrared intensities of the component bands are not known and can vary considerably in going from "free" oxyanion to contact-ion paired anion.[4]

The second derivatives a′ and b′ show several further small splittings and shoulders, in addition to the three main component bands. These splittings are absent in 3 M solution (c′), probably because of the larger bandwidth. Except for the band centered at ≈1131 cm^{-1}, we attribute these additional small splittings and shoulders to the ^{35}Cl and ^{37}Cl isotopomers of "free" and contact-ion paired perchlorate. Decius and Murhammer[35] have first shown this isotopic effect for IR spectra of ClO$_4^-$ in KI matrixes. In this matrix, the ν_3 doublet was completely resolved with separation of 13 cm^{-1}, and the ν_4 doublet was partially resolved with separation of 3 cm^{-1}. Such isotopic effects are usually ignored in solution because bandwidths are larger than in matrixes, and the contribution of ^{37}ClO$_4^-$ is only seen by band asymmetry on the low-wavenumber side. The attribution of the ν_3 asymmetry to the isotopic structure has been confirmed by Chabanel et al.[1] for an IR spectrum of a dilute NaClO$_4$–MeCN (acetonitrile) solution (see their Figure 1, with separation of 15 cm^{-1}). In glassy aqueous solution recorded at 78 K, band narrowing had been observed before in comparison to spectra recorded at ambient temperature, and therefore, these isotopomer splittings become observable. Several of the small splittings in curves a′–c′ show the expected separations of 13–15 cm^{-1}. Only the band centered at 1131 cm^{-1} is separated by at least 26 cm^{-1} from the major component band at higher frequency which seems too large for assignment to an isotopomer, and it is attributed either to another perchlorate species or to one of the side lobes of the major component bands. We note that a second derivative curve of the IR spectrum of glassy D_2O does not show sharp peaks in the spectral regions depicted in Figure 4 and in the other Figures.

The effect of the cation is shown in Figure 5 for 1 M lithium and sodium perchlorate solution in D_2O. Curves a and b are the spectra of the lithium and sodium salt, a′ and b′ their second derivatives. The separation of the main components centered at high and low frequency decreases in going from the lithium to the sodium salt, and the isotopomer fine structure is barely observable in the second derivative of the sodium salt spectrum.

ν_4 Band Region in Glassy Solution. Figure 6 compares the spectrum of (a) 1 M lithium perchlorate solution in D_2O (a) with that of the (b) 1 M sodium salt (b). The second derivatives are shown as a′ and b′. The weak peak at 659 cm^{-1} in a and a′ is attributed to the deformation mode of CO$_2$ enclosed (enclathrated) in the D_2O water matrix.[36] The spectral features of the composite bands and of their second derivatives are very similar, and only small changes of at most 1 cm^{-1} occur in going from the lithium to the sodium salt (a′–b′). The three distinct peaks observable in the derivative curves at ≈639, 632, and 624 cm^{-1} indicate loss of degeneracy of the F$_2$ mode of "free" perchlorate. As discussed above for the ν_3 band region, loss of degeneracy and assignment of the distinct peaks is possible in several ways and will not be attempted here. However, it is unlikely that these splittings of 7–8 cm^{-1} are caused by an isotope effect because that gives rise to splitting of 3 cm^{-1} only.[2,35]
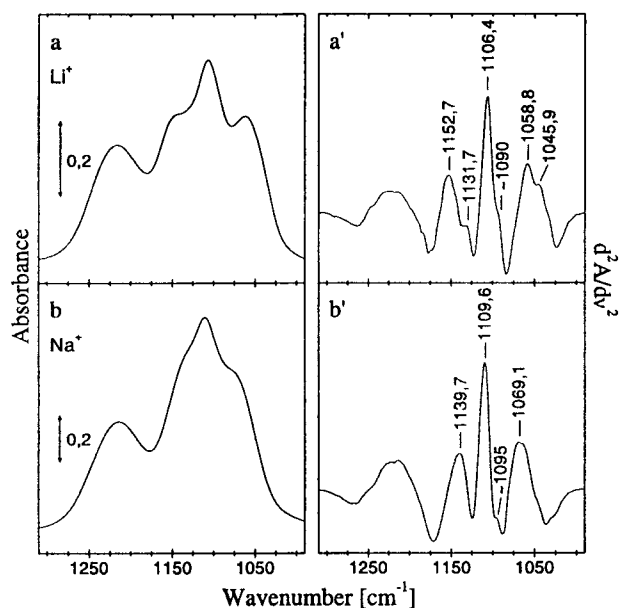
Figure 5. Effect of alkali cation on perchlorate's ν_3 band region: IR spectra of 1 M lithium (a) and sodium (b) perchlorate D_2O solution recorded in their glassy states at 80 K; (a', b') their second derivatives.

Figure 6. Effect of alkali cation on perchlorate's ν_4 band region: IR spectra of 1 M lithium (a) and sodium (b) perchlorate D_2O solution recorded in their glassy states at 80 K; (a', b') their second derivatives.
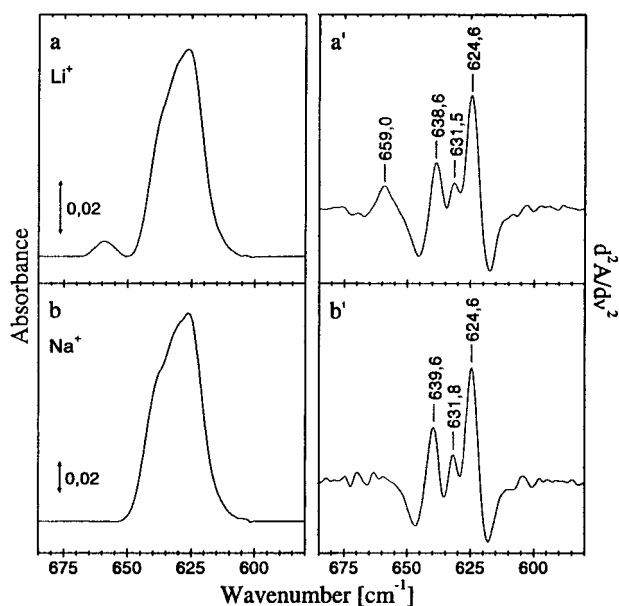
Concentration effects are also only minor and the spectrum of a 3 M glassy lithium perchlorate D_2O solution (not shown) is nearly identical to that of the 1 M solution. Similar observation has been reported by Chabanel et al.[1] for $LiClO_4$ in MeCN solution.

Figure 7 shows for glassy sodium perchlorate D_2O solutions the influence of concentration on the relative intensities of the two component bands in the ν_1 band region, and on the shape of second derivative curves in the ν_3 and ν_4 band region. Spectral features of glassy 1 M solution are depicted on the left side, those of 3 M solution on the right side. The ν_1 band region shows the experimental composite bands and the curve-fitted component bands (a and b). The relative intensity of the component band at high-frequency assigned to contact-ion pairs increases in going from the 1 M to the 3 M solution from 66 to 83% (see Table 1). For the ν_3 (a', b') and ν_4 (a'', b'') band region
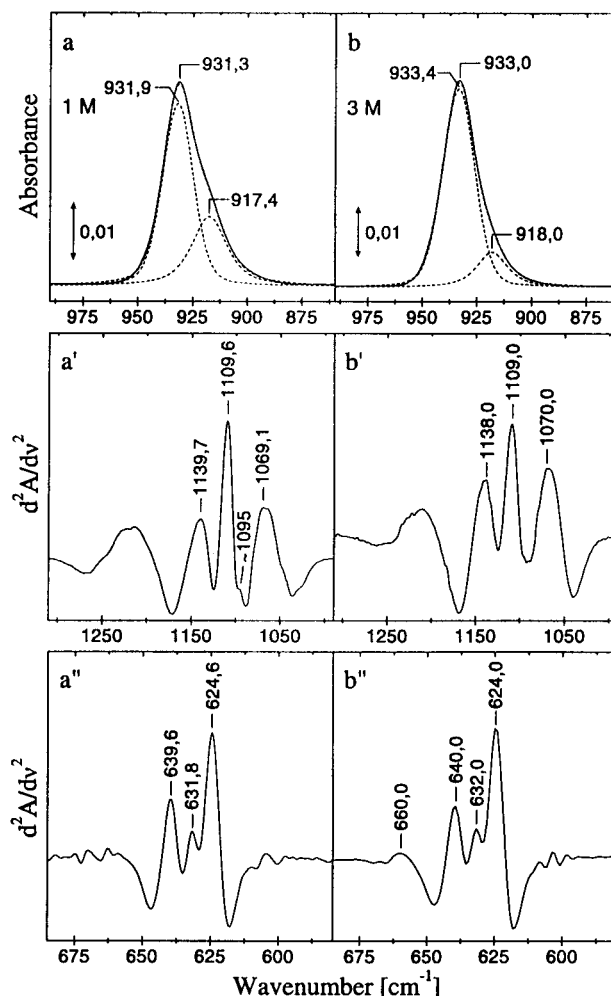

Figure 7. Effect of concentration on perchlorate's ν_1, ν_3, and ν_4 band region for 1 M (a) and 3 M (b) sodium perchlorate D_2O solution recorded in their glassy states at 80 K: (a, b) the ν_1 band region and the curve-fitted component bands; (a', b') second derivatives of the ν_3, and (a'', b'') of the ν_4 band region.

the second derivatives of the glassy solutions are shown for comparison.

Evidence for Ion Pairing at Ambient Temperature and in Supercooled Solution. Figure 8 displays evidence for increasing ion pairing on cooling a nonemulsified 1 M lithium (b) and sodium (c) perchlorate solution from 300 to 270 K in form of second derivative curves of the ν_1 band region. Emulsifier bands interfere in this spectral region, and therefore supercooled solutions could not be investigated. Asymmetry of the negative lobe at high frequency increases with decreasing temperature for both the lithium and sodium salt. This could be an indication for buildup of a weak second band at low frequency of the main band, with similar fwhh (see, e.g., Figure 10c in ref 37).

Alternatively, the same asymmetry can be generated by buildup of a second weak band at *high* frequency when it has a smaller fwhh than that of the main band. This is demonstrated in Figure 8a where the band shapes of the second derivative curves of Figure 8b have been simulated. The fwhh of the component band at high frequency used in the simulation is half of that of the main band. Similar ratio of fwhhs was obtained from curve-fitting analysis of the ν_1 band region in glassy solution at 80 K (see Table 1). The parameters of the simulation are listed in Table 2. This second component band cannot be separated from the main band even in fourth derivative
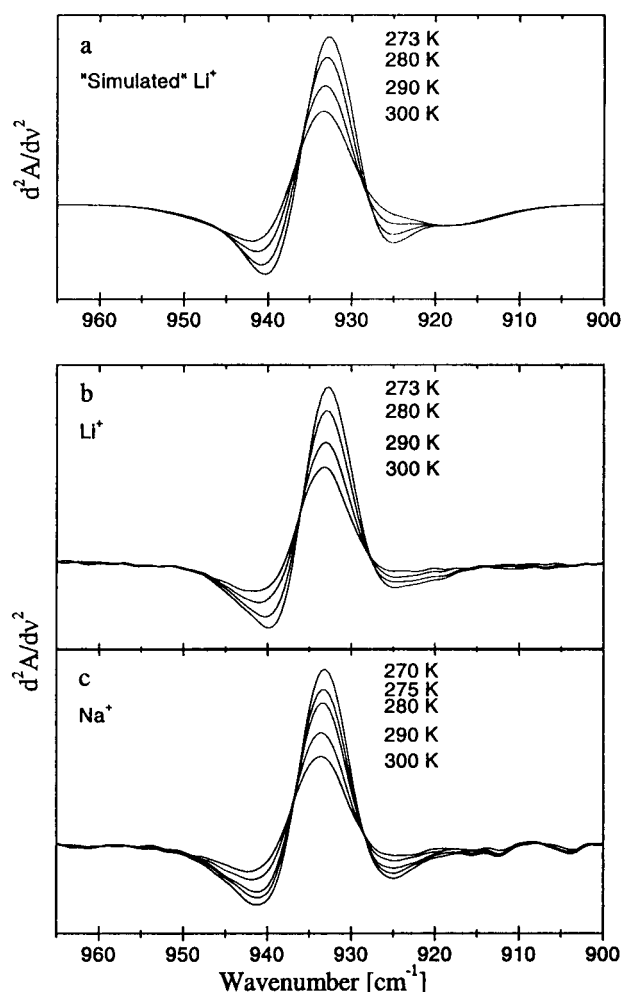
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Figure 8. (a) Simulated derivative curves with the parameters listed in Table 2. Evidence for increasing ion pairing on cooling from 300 to 273 K in form of second derivative curves of the ν_1 band region of (b) 1 M lithium and (c) sodium perchlorate D_2O solution. Note increasing asymmetry of the negative lobes as the solutions where cooled from 300 to 290, 280, and 273 K.

TABLE 2: Simulation of Increasing Asymmetry in Second Derivative Curves of 1 M Lithium Perchlorate Solution on Cooling from 300 to 273 K (see Figure 8)[a]

temperature (K)	ν_{max} (cm^{-1})	height	fwhh (cm^{-1})	% relative area
300	931.6	0.01	18	87
	933.8	0.003	9	13
290	931.4	0.01	18	82
	933.5	0.0045	9	18
280	931.0	0.01	18	76
	933.2	0.0062	9	24
273	930.7	0.01	18	73
	932.9	0.0074	9	27

[a] See Table 1 for footnotes. 100% Gauss bands were used in the simulation.

curves because of strong overlap and its low relative intensity (see, e.g., Figure 7, curves c, in ref 19, for the influence of relative band intensity on separability of highly overlapping bands).[38,39] The peak maxima of both simulated component bands shift on cooling to lower temperature (see Table 2). For 1 M glassy lithium perchlorate solution recorded at 80 K, peak maxima of the two curve-fitted component bands are centered at 929.7 and 920.3 cm^{-1}. Therefore, separation of the two component bands increased from 2.2 cm^{-1} at 300 K to 8.9 cm^{-1} at 80 K (Tables 1 and 2). This shift of peak maxima and their
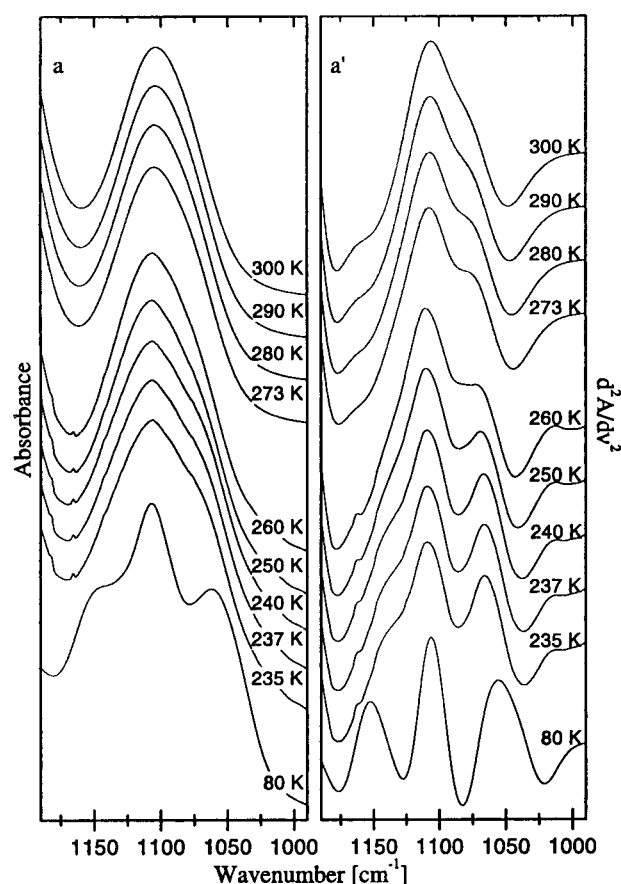

Figure 9. Evidence for increasing ion pairing on cooling from 300 to 235 K in the ν_3 band region of (a) 1 M lithium perchlorate D_2O solution and (a′) its second derivative. The spectra were recorded (from top to bottom) at 300, 290, 280, 273 K (without emulsifier), 260, 250, 240, 237, 235 K (emulsified). Bottom: for comparison the spectrum of 1 M glassy lithium perchlorate solution recorded at 80 K and its second derivative. Note development of a shoulder at ≈1075 cm^{-1} with decreasing temperature.

separation is much more than expected on the basis of a simple linear extrapolation of the values simulated for spectra recorded from 300 to 273 K, to the glassy spectrum recorded at 80 K.[40]

We cannot differentiate whether buildup of a weak second component band occurs at low or at high frequency of the principal band. In the latter case, the simulation depicted in Figure 8a shows that the relative area of the second component band increases from 13% at 300 K to 27% at 273 K (Table 2). The value for 273 K is about the same as that obtained for contact-ion pairs in glassy 1 M lithium perchlorate solution (Table 1). Since perturbation of perchlorate strongly increases on further cooling into the supercooled and glassy state, we expect that the second component band is more likely caused by solvent-shared ion pairs than by contact-ion pairs. Identifying the Raman spectroscopic features of ion pairing in dilute aqueous alkali metal perchlorate solution is not trivial, and we refer to ref 12 for a lucid discussion of the problems.

Figure 9 shows for 1 M lithium perchlorate solution the spectral changes in the ν_3 band region on cooling from 300 to 235 K: (a) are the recorded spectra, (a′) their second derivative curves. The spectrum of the glassy solution recorded at 80 K and its second derivative are shown below for comparison. Band asymmetry of the main band centered at ≈1108 cm^{-1} develops on cooling from 300 K mainly at low frequency, and a shoulder or separate band can be observed at ≈1075 cm^{-1}. These changes go in the direction observed in the spectrum of the glassy

solution where band splitting of the ν_3 band region is much more pronounced at low frequency than at high frequency. Therefore, increasing band asymmetry on cooling to 235 K is attributed to increasing perturbation by contact-ion pairing. This is consistent with our previous studies of increasing contact-ion pairing in supercooled solution where nitrate and thiocyanate were used as anions.[20,21] A small change of the peak maximum in emulsified solution by 3 cm^{-1} is an artifact caused by emulsification. Similar small changes in peak maxima on emulsification had been observed before.[20,41]

Discussion

One of the intentions of our continuing studies of anomalous contact-ion pairing in "dilute" aqueous electrolyte solutions in their glassy states is to ascertain the spectral patterns characteristic for contact-ion pairing and then to compare these with those at ambient temperature and in supercooled solution. The advantage of spectroscopic studies at low temperatures is that in general fwhhs of bands are expected to be smaller than those at ambient temperature. Therefore, separation of highly overlapping bands can be easier. In addition, the temperature dependence of peak maxima can be different for the various species and curve resolution into distinct bands easier.

We have pointed out before[20] that for the "dilute" aqueous solutions hyperquenched into the glassy state, liquid−liquid phase separation into a water-rich and a solute-rich phase is unlikely because their enthalpy of mixing is negative at ambient temperature. This holds also for the aqueous lithium perchlorate solution studied here.[42] Phase separation during hyperquenching is possible only when the enthalpy of mixing becomes positive on cooling which seems unlikely.

Local Geometry of Contact-Ion Pairs. The spectral changes on contact-ion pairing in glassy aqueous D$_2$O solution are on the whole very similar for both the lithium and sodium salt: in the ν_1 band region the band assigned to contact-ion pairs is at high frequency of the "free" perchlorate band, and both the ν_3 and ν_4 band region are split into three component bands. Differences occur with respect to relative areas of the bands due to the contact-ion pairs in the ν_1 band region (see Figure 3 and Table 1, 25% for 1 M lithium salt and 66% for 1 M sodium salt) and with respect to the amount of splitting in the ν_3 band region (see Figure 5a′ and b′, $\Delta\nu_3$, i.e., high-wavenumber minus low-wavenumber component band, is $\approx$94 cm^{-1} for the lithium salt and $\approx$71 cm^{-1} for the sodium salt). The latter can be accounted for by differences in the polarizing power of the two cations,[2,43] whereas the former had also been observed for contact ion pairing in 4 M aqueous solution[11] and in aprotic donor solvents.[1] Therefore, both cations generate on contact-ion pairing similar local symmetry at the perchlorate. Since both the ν_3 and ν_4 band region are split into three main component bands, this local symmetry is likely to be C_{2v} or less.[1] This reduction of symmetry on contact-ion pairing is generally attributed to bidentate binding of the cation, but we are aware of Beattie and Parkinsons' warning that even complete loss of degeneracy of perchlorate's ν_3 band does not prove bidentate binding.[44] Alternatively, superposition of the spectral features of "free" perchlorate with those of contact-ion paired perchlorate of C_{3v} symmetry can also give three component bands. This seems unlikely because for 3 M glassy sodium perchlorate solution, where the ν_1 band region is dominated by the component band of the contact-ion pair, splitting of the ν_3 and ν_4 band region into three component bands is still obvious (see Figure 7).

Although the ν_1 band region of 0.5, 1 and 3 M glassy lithium perchlorate solution in D$_2$O is dominated by the component band

assigned to "free" perchlorate (see Table 1, 82, 75, and 62% relative band area), its corresponding ν_3 band region shows distinct splitting into three component bands and is very similar despite the 6-fold change in concentration (see Figure 4, curves a−c). This requires that with increasing concentration, decreasing band intensity of the "free" perchlorate band at $\approx$1107 cm^{-1} is roughly compensated by increasing intensity of the center component from the contact-ion pair, and that the molar intensity of the latter is higher than that of the former. Apparently the decrease in "free" perchlorate with increasing concentration and the simultaneous increase in contact-ion pairs cannot be determined from the band shape of the ν_3 band region alone, and it requires evaluation of the ν_1 band region for estimation of "free" and contact-ion paired perchlorate. Since their relative molar infrared intensities are not known, this is not possible at present. Increased infrared intensity of the symmetric streching vibration of oxyanions has been observed on complexation and attributed to increasing mutual admixture of the A$_1$ component of the antisymmetric and the symmetric stretching mode as the polarization of the anion increases (see ref 45a for review). Thus for the symmetric stretching modes the ratio of contact-ion paired to "free" perchlorate molar intensity is likely to be >1.

Spectral features characteristic for ion pairing are observable already at ambient temperature and in supercooled solution (see Figures 8 and 9). However, even at 235 K, which is the lowest temperature accessible in supercooled (metastable) emulsified solution without formation of ice or crystalline hydrate, perturbation of perchlorate is still less than in the glassy state (see Figure 9). Therefore, contact-ion pairing must have continued on hyperquenching into the glassy state, in the same manner observed in our previous studies with nitrate and thiocyanate anions.[20,21] Our estimation of the temperature range where water and a solute become immobilized on hyperquenching into the glassy state is 230−200 K.[21] Thus, further pronounced contact-ion pairing must have occurred on hyperquenching between 235 and $\approx$200 K.

Comparison with Contact-Ion Pairing in Aprotic Donor Solvents. For alkali metal perchlorates dissolved in aprotic donor solvents, the local symmetries around perchlorate are different in LiClO$_4$ and NaClO$_4$ contact-ion pairs. Chabanel et al.[1,2] point out that ClO$_4$$^-$ must be monodentate in LiClO$_4$ and bidentate in NaClO$_4$, and that the ClO$_4$ groups prefer C_{3v} symmetry in LiClO$_4$ and at most C_{2v} symmetry in NaClO$_4$. The component band of LiClO$_4$ is shifted in the ν_1 band region to high frequency of the band from "free" perchlorate, whereas for the NaClO$_4$ contact-ion pair the opposite shift to low frequency occurs.

Evidently, the local symmetry of LiClO$_4$ and NaClO$_4$ contact-ion pairs must be different in glassy aqueous solution from that in aprotic donor solvents. Our assignment of spectral changes on contact-ion pairing in glassy solution to bidentate binding of at most C_{2v} symmetry is in line with that reported for NaClO$_4$ in aprotic donor solvents but the reversal of peak position of the contact-ion pair band in the ν_1 band region from low frequency to high frequency of the "free" perchlorate band indicates further subtle differences. For the lithium salt, the differences between contact-ion pairing in aqueous glassy solution and in aprotic donor solvents are much more pronounced.

Normal coordinate model calculations by Hester and co-workers[45] performed for metal complexes of several oxyanions including perchlorate may shed some light on the reversal of peak position of the contact-ion pair band in the ν_1 band region from high frequency in glassy D$_2$O water matrix and in aqueous solution[5,11−13] to low frequency in aprotic donor solvents.[1,2]

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These calculations show that "the symmetric stretching mode is seen to be slightly raised by increasing the M$-$O bond strength and lowered by the polarization effect. The net result of both effects operating together would be to produce but little change" in this mode from its value in the free anion.[45a] This holds for all the anions and local geometries considered in the study.[45a] Therefore, the reversal of peak positions of contact-ion paired alkali metal perchlorate can be attributed to small changes in polarization and M$-$O bond strength between water and aprotic donor solvents.

Comparison with Contact-Ion Pairing in Vapor-Deposited Matrixes. Three independent IR studies of the perchlorate contact-ion pairs in rare gas matrixes have come to the same conclusion: the most stable geometry has C_{2v} symmetry with bidentate binding.[14,44,46] Devlin and co-workers[14-16] have further studied contact-ion pairing in vapor-deposited amorphous water as matrix material and their results with lithium and sodium cations are compared here with our studies in hyperquenched glassy aqueous solution. Formation of contact-ion pairs in vapor-deposited matrixes was deduced from splitting of the triply degenerate ν_3 band into three components which indicates complete loss of degeneracy. However, as pointed out above, this argument can be misleading. Consideration of the spectral effects in the nondegenerate ν_1 band region gives direct support for contact-ion pairing as shown in this study. This type of work requires FT-IR spectroscopy with its remarkably enhanced signal-to-noise ratio. Since dispersive IR-spectroscopy had been used for the studies of perchlorate contact-ion pairing in vapor-deposited H$_2$O matrixes, interference by the water bands precluded quantitative evaluation of the ν_1 band region and only the intense ν_3 band region had been analyzed.[14-16] This comparison can be only approximate because electrolyte/water vapor ratios are not known for the vapor-deposited matrixes; only the percentages of water/argon vapors is given.[14-16] The effect of using D$_2$O as solvent instead of H$_2$O, as in our previous study and in the vapor-deposited matrixes, seems to be minor because splitting of perchlorate's ν_3 band region in glassy H$_2$O and D$_2$O solution was about the same.

This comparison first shows that the ν_3 band region spectrum of lithium perchlorate in vapor-deposited H$_2$O matrix, which had been assigned to the contact-ion pair (see Figure 4b in ref 14) can contain significant amounts of the "free" perchlorate band, despite its splitting into three component bands. Therefore, for lithium perchlorate in vapor-deposited H$_2$O matrix the proposed contact-ion pairing is consistent with our extended analysis of the ν_1 band region but the relative amounts of contact-ion paired and "free" perchlorate are uncertain.

Second, the $\Delta\nu_3$ splitting of perchlorate's antisymmetric F$_2$ stretching mode has been considered as sensitive indicator for perturbation of the anion by the polarizing power of the cation, smaller values of $\Delta\nu_3$ corresponding to less perturbation.[1,2,14-16,47] $\Delta\nu_3$ splittings of 85 and 67 cm^{-1} were obtained for Li$^+$ClO$_4^-$ and Na$^+$ClO$_4^-$ contact-ion pairs in vapor-deposited water matrixes (see Table 3 in ref 14). We have previously reported remarkably similar $\Delta\nu_3$ splittings of 86 and 60 cm^{-1} for 1 M lithium and sodium perchlorate H$_2$O solutions recorded in their glassy states at 20 K.[17] These values were only approximate because separation of the band components was not sufficient, in particular for the sodium salt, to allow reliable determination of peak maxima.

The second derivatives of the ν_3 band region reported here and the more extended range of concentrations allows a more detailed comparison. Second-derivative curves of highly overlapping composite bands are used routinely for determining the number and peak position of the component bands, and the shift in peak maximum is minor.[19,48] From Figure 4 we see that the $\Delta\nu_3$ splittings are 95, 83, and 79 cm^{-1} for 0.5, 1, and 3 M glassy lithium perchlorate D$_2$O solution, whereas the $\Delta\nu_3$ splittings calculated from their second derivatives decrease only from 98 cm^{-1} for 0.5 M solution to 94 cm^{-1} for 1 and 3 M solution (most intense peaks are used for $\Delta\nu_3$). $\Delta\nu_3$ splittings of 71 and 68 cm^{-1} are obtained from second derivatives of 1 and 3 M glassy sodium perchlorate D$_2$O solution (see Figure 7). $\Delta\nu_3$ splittings calculated from second derivatives appear more reliable because overlap of band components in the spectra of the sodium salt is too strong to allow reliable estimation of peak frequencies without curve resolution. Comparison of $\Delta\nu_3$ splittings from hyperquenched solutions with those from vapor-deposited matrixes shows that for both sets of spectra more pronounced splitting is observed for the lithium than for the sodium salt.

Devlin and co-workers[15] display in their Figure 1 for a C_{2v} (bidentate) configuration the dependence of alkali metal perchlorate ν_3 and ν_1 stretching mode frequencies on ΔF_{Cl-O} (i.e., the difference between Cl$-$O stretching force constants of noncoordinated and metal-coordinated Cl$-$O bonds). These calculations were performed in a similar manner developed by Hester and co-workers.[45] The calculated and estimated $\Delta\nu_3$ splittings decrease in magnitude in a regular fashion for Li$^+$ClO$_4^-$ from 226 cm^{-1} in pure argon matrix, to 181, 148, 105, and 85 cm^{-1} for Li$^+$ClO$_4^-$ with 1, 2, 3, and 4 water molecules, respectively. The value of 85 cm^{-1} is the same as that obtained with a pure vapor-deposited water matrix and therefore indicates full hydration of the contact-ion pair. This value has to be compared with our $\Delta\nu_3$ splitting of 95$-$79 cm^{-1} obtained from the original spectrum (Figure 4), or of 98$-$94 cm^{-1} from their second derivatives. $\Delta\nu_3$ splittings from second derivatives of the sodium perchlorate solutions vary from 71 to 68 cm^{-1}. Splittings from second derivatives are more reliable than those read from original highly overlapping spectra, and therefore, the former should be used in plots of wavenumber versus ΔF_{Cl-O}.

A contradictory aspect of these force constant calculations is that in the ν_1 band region the peak position of the Li$^+$ClO$_4^-$ contact-ion pair *decreases* with increasing ΔF_{Cl-O} (see Figure 1 in ref 15) whereas we have found the opposite, i.e., the band assigned to the contact-ion pair is centered at high frequency of that from "free" perchlorate (see Figure 2 and Table 1). Since the position of this band depends in an opposite manner on both polarization and M$-$O bond strength,[45] as pointed out above, this difference might be caused by exaggerated inclusion of polarization effects.

In the above comparison we had to neglect possible effects of microporosity of the vapor-deposited amorphous water matrix on the spectral features of the co-deposited electrolytes because these are not known. They can be investigated by heating the vapor deposits up to $\approx$120 K for removal of micropores by sintering.[49-51]

Relevance for Continuity of States between ASW and HGW. The results of this study on aqueous alkali metal perchlorate solution are further support for our conjecture that increase of contact ion pairing in the supercooled and glassy state is a "supercooled water anomaly". Since the anomalies of supercooled water and dilute aqueous solutions are caused by water's density maximum, the similarity of the spectral features on hyperquenching an aqueous electrolyte solution and on deposition of vapors into the glassy state seems to be a contradiction. However, recent studies have shown that ASW

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and HGW have the same structural state[28,52,53] and can be thermodynamically connected with normal and supercooled water.[30,31] On heating both ASW and HGW up to 150 K, the same calorimetrically distinct state of viscous water (water A) is obtained.[31] Thus, the surprising observation of comparable anomalous contact-ion pairing in the glassy states of vapor-deposited and hyperquenched electrolyte solution is consistent with thermodynamic continuity of states between ASW and HGW, and between HGW and normal supercooled water.

One of the reviewers pointed out that alternatively one can view our observation of increasing contact-ion pairing on cooling in terms of competition with the solvation of the individual ions and that of the ion pair, whose coordination number was shown to increase in aprotic solvents on cooling,[16,54] and the tendency of supercooled water to approach a tetrahedral four-coordinated local structure. This alternative view could eventually lead to a more detailed understanding than the thermodynamic one given above. However, at present, the properties of supercooled water are not known well enough for further analysis of its effects on contact-ion pair formation. In this context we mention a Monte Carlo simulation on contact-ion pairing in two different models for water by Goldman and Backx.[55] One model (ST2 water) was relatively water-like; the other model, in effect a polar solvent, had the same dipole moment as ST2 water, but it did not have the ST2-model's point-charge distribution. Goldman and Backx found that the two water models differed with respect to contact-ion pairing, the ST2 water-like solvent exerting a stronger and qualitatively different dissociation force on the contact-ion pair relative to the behavior of the polar solvent. Similar structural differences between normal and deeply supercooled water could account for the unexpected temperature dependence of contact-ion pairing.

Relevance for Cryofixation of Biomolecules. The goal of cryofixation is to immobilize, or "freeze-in", the native state of dynamic structures and the momentary distribution of all components in a system.[32] This is impossible for small molecules and ions even by "hyperquenching", and earlier studies[17,20,21] have demonstrated increasing contact-ion pairing with decreasing temperature. In this study extensive formation of contact-ion pairs between the sodium cation, one of the biologically important cations, and the perchlorate anion, one of the least associating anions, clearly suggests that anomalous increase in contact-ion pairing has to be considered in particular in cryofixation of biomolecules which are polyelectrolytes such as sodium salts of nucleic acids. It is conceivable that anomalous increase in contact-ion pairing triggers conformational changes of a biomolecule. For the practice of cryofixation of biological specimens for, e.g., electron microscopic studies it is important whether or not subsequent changes of the biomolecule's structure, caused by increasing contact-ion pairing, are fast enough to cause detectable structural changes.[32] This depends on the relative rates of quenching and of conformational change and on the spatial resolution of the technique.

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