Raman Studies of Lithium Coordination in Molten and Aqueous Environments

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ABSTRACT

Raman spectra have been obtain for alkali metal chloride melts and for very concentrated solutions of alkali metal chlorides and perchlorates. The frequency maximum and the intensity of Raman scattered light from molten alkali metal chlorides decreased from lithium to cesium. In very concentrated solutions of lithium chloride a weak polarized band at about 380 cm$^{-1}$ was assigned to an inner-sphere LiCl(H$_2$O)$_n$ where n is probably three. In more dilute aqueous lithium chloride and perchlorate a polarized band at 255 cm$^{-1}$ has been assigned to the Li-O symmetric stretching motion of Li(H$_2$O)$_4^+$. The need for excellent depolarization data and normalization factors to account for temperature and frequency dependence of Raman intensity will be emphasized.

INTRODUCTION

The structure and dynamics of the coordination sphere of lithium ion in molten salts and in aqueous solution has been the subject of considerable research(1-7). Light scattering(1), inelastic neutron scattering(2,3) and theoretical calculations(4) for molten alkali metal halide salts indicated a tendency for local ordering of halide ions in the lithium coordination sphere. Diffusion of lithium ion is accompanied by the halide ion atmosphere(6). Similar studies of concentrated aqueous solution of lithium salts by X-Ray(5), neutron diffraction(3) and Raman(7) methods indicated a moderately well defined hydration sphere for lithium. A coordination number of about four has been inferred for lithium ion in both the molten and aqueous phases although penetration of lithium ion into the coordination sphere of a neighbour lithium suggests a short lifetime of a coordinated ligand.

Raman spectroscopy has been employed to study structural arrangements and species concentration in electrolytes in the solid, molten and aqueous
phases(6,7). Spectroscopic data such as: the number of bands, the frequency of band maxima, infrared and Raman activities and intensities, polarization characteristics and spectral profiles, provide information about the dynamic microscopic local structure. In particular, Raman intensity measurements probe the very nature of the chemical bond by virtue of the fact that the band intensity is proportional to the square of the polarizability derivative with respect to the change in the normal coordinate, \(Q\) associated with the normal mode\([\alpha/\delta Q]\)(6,7). Since bond polarizability, \(\alpha\) is a function of electron density it is possible to relate the Raman intensity to the electron density. In the hard-sphere model ionic liquids do not generate Raman intensity. The question arises as to whether or not the mutual polarization(8) of the alkali metal ion and the coordinated halide or water ligand is sufficient to give rise to detectable Raman intensity.

It must be emphasized that the actual quantity measured in the Raman experiment, the scattering cross section, \(\partial \sigma / \partial \Omega\) has both temperature and frequency dependent factors that are especially important in the low wavenumber region of the spectrum at the high sample temperature normally employed for molten salts. The use of a normalized or reduced intensity, \(R(\omega)\) to create a spectrum that is directly proportional to the intrinsic Raman scattering activity is essential for measurements in the low wavenumber region(6,7,9). Within the double harmonic approximation the use of the \(R(\omega)\) spectrum removes a temperature and frequency dependent band asymmetry and permits comparison of spectra obtained at different temperatures(9). Furthermore it is essential to carefully measure light scattered in both the parallel, \(R_\parallel\) and perpendicular, \(R_\perp\) orientations in order to detect weak isotropic intensity \(R_{\text{ISO}}\) due the symmetric motions.

Raman spectroscopy is a fast process. Collision encounters that last for only a few picoseconds will be sticky enough for an ion-pair to vibrate several times and give rise to Raman intensity. However this property also presents the problem of how to account for the Raman intensity in terms of a species with a defined geometry or symmetry. Environmental broadening and possible exchange broadening may result in a broad symmetric Raman band that by itself cannot provide information on species geometry or even coordination number. Raman intensity in the isotropic spectrum can be attributed to a symmetric stretching mode of some entity but the concept of a species with a defined geometry has little meaning. Interpretations based on lattice models can be misleading because they tend to under-emphasize the dynamic properties and infer too much order.

**EXPERIMENTAL**

Raman spectra were measured with a Coderg PHO Raman spectrophotometer. The 514.5nm (500 mW, green) and 488.0nm (500mW, blue) line of a Control laser model 52 system were used to excite the sample. Plasma lines were removed with a narrow band-pass interference filter. Peak positions were
calibrated against laser plasma lines. The slit widths were set at 2.0 cm$^{-1}$. Raman spectra were obtained for samples in quartz containers with 6 to 10 mm paths. The container walls were masked to reduce reflection and Raman scattering from the glass. Spectra of solutions were were recorded for samples at 25 °C and there was no evidence to indicated local laser heating. Spectra of the melts were obtained in a in furnace with temperature regulated to ± 5 K. Raman spectra obtained for $I_{||}$ and $I_{\perp}$ polarizations for orientations $x(zz)y$ and $x(zx)y$. Polarization of the incident beam was controlled by a half-wave plate and the 90° scattered light was analyzed with Polaroid films which accepted parallel or perpendicular polarized light. A quarter wave-plate before the entrance slit served to compensate for grating polarization preference.

The Raman scattered light was detected with a PMT cooled to 250 K. Analogue spectra were output on a strip-chart recorder. Digital data files were created by integration of the photon counts with a home-built box-car averager interfaced to the Memorial University VAX 8800 computer. In the present case either two data points were collected per wavenumber. At least five identical sets of data were collected for each spectrum. Spectra were signal averaged and smoothed once with a three point Savitsky- Golay smoothing function. A baseline program was applied which corrected the measured intensity for the fourth power frequency factor and then set the lowest data point to zero and the highest data point to 999 on a relative intensity scale. This form of the data is defined as our $I(\omega)$ spectrum which should be independent of excitation frequency. The same baseline program was applied with the option to correct for the fourth power scattering factor, the temperature factor, $B = [1-\exp (-hc \omega /kT)]$ and the frequency factor, $\omega$, to give the reduced or $R(\omega)$ spectrum which is directly proportional to a point by point relative scattering activity, $S_Q(\omega)$ in terms of mass weighted normal coordinates, $Q$, in the double harmonic approximation. $R_Q(\omega)$ is the form of the Raman spectrum that most closely approaches the vibrational density of states (6-9). The relationship between the $I(\omega)$ and $R_Q(\omega)$ forms of the spectra is given by Eq. 1.

$$S_Q(\omega) \propto R_Q(\omega) = I(\omega) \cdot \omega \cdot B$$

It is our preference to plot the spectrum in the $R_Q(\omega)$ form because the Bose-Einstein factor removes the state dependent temperature factor of the excited state transitions and leaves the effect that is due to concentration changes.

Sample were prepared from recrystallized and carefully dried reagent salts. Aqueous samples of LiCl, LiBr and LiClO$_4$ were prepared by weight with to give solutions with known mole ratios of water to salt, $R$, which were confirmed with density measurements.

RESULTS and DISCUSSION

In a very concentrated solution of lithium chloride($R = 3$) a weak, polarized Raman band at about 380 cm$^{-1}$ has been assigned previously(7) to the Li-O motion of the hydrated lithium ion, Li$^{+}(H_2O)_4$. However the present studies
have shown that this band is more likely due to the Li-Cl motion of the inner-sphere ion-pair LiCl(H$_2$O)$_n$ where $n$ is probably three. The Raman spectra from an aqueous solution of LiCl with $R = 2.8$ (Fig. 1) clearly show the band at 380 cm$^{-1}$ for the $R_{iso}$ spectrum. Raman bands due to the hydrogen-bonded motions of water have also been identified at about 50, 200, and from 300 to 900 cm$^{-1}$ (7). Additional studies with LiCl in D$_2$O indicated that the band was insensitive to deuterium substitution while the Raman spectra from an aqueous LiBr solution with $R = 2.7$ showed that a similar band was shifted to 340 cm$^{-1}$. It appears that for very concentrated solutions of LiCl and LiBr the anion penetrates the coordination sphere of Li$^+$ to give an inner-sphere ion-pair with characteristic Raman bands for the Cl$^-$ and Br$^-$ at 380 and 340 cm$^{-1}$. These Raman bands provide a potential probe for more quantitative studies of ion-pair formation. Furthermore, in more dilute aqueous LiCl, LiBr and LiClO$_4$ a polarized band at 255 cm$^{-1}$ has now been detected and assigned to the Li-O symmetric stretching mode of Li(H$_2$O)$_4^+$. Raman spectra (Fig. 2) for aqueous LiCl with $R = 6.9$ and for LiClO$_4$ with $R = 10.5$ both show the polarized band at about 255 cm$^{-1}$ with halfwidth of about 60 cm$^{-1}$. The band is accentuated in aqueous LiClO$_4$ because the ClO$_4^-$ disrupts the hydrogen-bond structure of water and causes a decrease in the relative intensity of the band due to the O-H$^*-\equiv$O stretching mode at about 200 cm$^{-1}$. Bands due to the M-O stretching modes of aqueous divalent and trivalent cations have been reported (7) but the present work represents the first definitive result for a univalent cation.

Light scattering studies from molten alkali metal halides and their mixtures indicate significant Raman intensity in the 20 to 500 cm$^{-1}$ region. The scattered light is highly polarized and appears to arise from short-range, short-lived ion-pairs or aggregates which do not have well defined geometries on the ps time scale of the measurement. For the alkali metal halides the peak maxima and halfwidths in the $R(\omega)$ format are both anion and cation dependent. The wavenumber values for the peak maxima and halfwidths (parentheses) for the chlorides are: LiCl at 990 K, 310(350); NaCl at 1140 K, 215(260); KCl at 1110 K, 167(180); RbCl at 1090 K, 136(150); CsCl at 960 K, 118(130). The fact that the wavenumber values are reduced by about 0.7 for the molten alkali metal bromides suggests a mode of vibration which involves relative vibrational motion of both the anion and the cation and precludes the symmetric stretching mode of a species of symmetry as high as tetrahedral or octahedral.

Raman spectra of molten mixtures of LiCl with CsCl and KCl gave Raman spectra which gave rise bands which had characteristic intensity in regions which corresponded to that for each of the separate components. For instance in the mixtures of CsCl with LiCl there were two maxima in the spectra at about 420 and 120 cm$^{-1}$ corresponded to the separate maxima in pure LiCl and pure CsCl. Raman spectra for the isotropic intensity for pure LiCl and for the LiCl + 5 CsCl mixture (Fig. 3) illustrate these features. In molten LiCl the Raman intensity is highly polarized and very broad with peak maximum about 310 cm$^{-1}$ and halfwidth of 350 cm$^{-1}$. The large halfwidth reflects the wide range of
environments associated with the Li-Cl vibrational motions of the ion aggregates. For the CsCl mixture with LiCl the peak maximum of the LiCl band shifted to about 420 cm\(^{-1}\) and the halfwidth decreased to about 140 cm\(^{-1}\). Polarized intensity due to CsCl was observed at about 120 cm\(^{-1}\). Addition of CsCl has the effect of reducing the range of environments for the Li-Cl vibrations because the more massive Cs\(^+\) counter ions present a more static environment.

The present Raman studies have demonstrated that intensity due to the Li-Cl vibrational motions may be identified in very concentrated aqueous solutions and the molten salts. Raman studies of aqueous lithium halide solutions under hydrothermal conditions should prove interesting.

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Fig. 1.
Raman spectra in the $R(\omega)$ format for saturated LiCl ($R = 2.8$) at 25 °C.

Fig. 2.
Raman spectra of $R_{iso}$ for aqueous LiCl ($R = 6.9$) (A) and aqueous LiClO$_4$ ($R = 10.5$) (B). The best fit curve resolved components are indicated.
Fig. 3.
Raman spectrum for the $R_{iso}$ component of molten LiCl at 990 K (A) and the molten mixture of LiCl in 5 CsCl at 875 K (B).