Temperature dependence of the Raman scattering spectrum of molten CsCl

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Abstract. Light scattering measurements have been carried out in molten CsCl over the temperature range 945–1245 K. Assuming the molten salt system to be a quasi-harmonic oscillator, we have found that the integrated intensity of the spectra increases with temperature at rates that exceed those anticipated for first-order scattering. The spectral variation of the intensity shows that the excess scattering, due mainly to second-order summation or difference bands, occurs in the low-frequency region (up to 80 cm^{-1}) and the high-frequency tail (above 150 cm^{-1}). The average depolarization ratio $\bar{\rho}_d$ of the spectra remains constant with temperature, but the depolarization ratio spectrum shows that (a) $\rho_d(\bar{\nu})$ increases with T up to ≈ 60 cm^{-1} and (b) decreases with T above 60 cm^{-1}. This is explained as due to a transition of the ions that contribute most strongly to the scattering from an anistropic environment, determined by binary collisions, to a more isotropic environment determined by the average local structure.

1. Introduction

In a series of publications (Mitchell and Raptis 1983, Raptis *et al* 1983, Bunten *et al* 1984, 1986, Raptis and Mitchell 1987) we have reported and discussed light scattering from molten alkali and alkaline earth halides. The main features and conclusions from those studies can be summarized as follows

(i) There are three contributions to all spectra—narrow and broad central lines and a non-central component.

(ii) The narrow central line is relatively depolarized and of almost exponential frequency dependence. It dominates for $\bar{\nu} < 50$ cm^{-1}. The scattering in this region is determined by diffusive-type processes and is reminiscent of the depolarized light scattering by condensed inert gases (see, e.g., McTague *et al* 1969, Gornall 1970).

(iii) Around 100–200 cm^{-1} the narrow central component merges into a non-central feature that is observed as a peak in MgCl$_2$, MgBr$_2$ and CaI$_2$, a shoulder in Li halides, alkali iodides and other alkaline earth halides, and a slight departure from a smooth spectrum in other alkali halides. In all cases the onset of this intermediate component can be detected by a change in the slope in semi-logarithmic plots of the spectra. It is also evident in the depolarization ratio spectra which show much lower values in this region compared to the low-frequency region. It has been proposed in

a semi-empirical model (Bunten *et al* 1984) that this component corresponds to first-order Raman scattering (optic modes) from regions of short-range order in the melt. Whether these modes are resolved in the spectra depends largely on the lifetimes of these regions.

(iv) In the high-frequency region the broad central component dominates and all spectra exhibit exponential decays with well defined relaxation times. Scattering in this region has been attributed to the second-order Raman effect in which short-range interactions between ions (binary collisions) are most important. Mahan's model (Mahan 1973), which assumes binary collisions in a polarizable hard-sphere fluid, gives good agreement for the relaxation times in alkaline earth chlorides but less so for the bromides. In molten alkali halides there is qualitative agreement.

(v) The integrated intensity of the spectra has been found to increase in the direction of increasing ionic polarizability.

(vi) In the case of alkali halide melts and for a given halide ion the average depolarization ratio increases with increasing cation size. An empirical relation has been obtained giving the depolarization ratio as a function of cation and anion radii (Fairbanks *et al* 1986). It is noteworthy that Cs melts, particularly CsCl, show much higher depolarization ratios than the rest of the melts.

In spite of all the above evidence complete interpretation of the light scattering spectra has not been possible, mainly because all features are highly broadened and therefore it is difficult to separate the overlapping spectral components described above. The theoretical calculations of Madden and Board (1987), Madden and O'Sullivan (1990, 1991), Madden *et al* (1991) and O'Sullivan and Madden (1991) give some insight. In particular they confirm the suggestion that the scattering in the intermediate-range region is due to collective excitations, which they assign to fluctuations in the longitudinal charge current (longitudinal optic modes). However, the spectra are found to be due to a combination of processes in which there is a large degree of mutual cancellation, and the calculations are too complex to have been extended to the ions of higher atomic number, such as Cs^+, which show the highest depolarization ratios. Two questions which require further investigation are:

(a) What kind of microscopic anisotropy causes depolarized light scattering in a macroscopically isotropic medium? Mitchell and Raptis (1983) and Raptis *et al* (1983) have suggested that the anisotropy may be either spatial or dynamical depending on whether the average local order happens to be anisotropic or the anisotropy is induced by transient interactions.

(b) What type of scattering (first- or second-order) occurs in the various spectral regions?

In order to obtain further information about these aspects, and consequently a better understanding of the scattering processes in an ionic liquid, we have studied in detail the temperature dependence of the light scattering spectra of molten CsCl over the range 945–1245 K. Both quantitative (intensities) and qualitative (lineshapes, depolarization ratios) analyses of these spectra have been carried out, with the former being restricted to a maximum temperature of 1190 K because of a slight attack of the silica cell above 1200 K. There are several reasons for choosing molten CsCl as the ionic liquid for this study. Firstly CsCl is a stable compound with a relatively low melting point (918 K) and so offers a good range of temperatures for study. Secondly in its high-purity grade molten CsCl shows no trace of attack on the silica cell up to

≈ 1200 K and over long periods of time. Finally it shows the highest depolarization ratio of all the molten salts studied.

2. Experimental procedures

The experimental set-up used for the present work was the same as in previous studies (see, e.g., Mitchell and Raptis 1983). Briefly, high purity (BDH, Analar grade) CsCl powder was dried *in situ* inside a spectroscopic quality silica cell at moderate temperatures ($\approx 200\,^\circ$C) under vacuum. The salt was then melted in an argon atmosphere. The silica cell was appropriately positioned inside a vacuum-operated furnace (Raptis 1983) of very-low-temperature gradients. Prior to the measurement of spectra at each temperature the molten salt was allowed to 'relax' for some time until convective fluctuations had stopped; this was necessary in order to minimize background scattering. Small renormalizations of the recorded intensities were made (with reference to the intensity of the lowest-temperature spectrum) to account for the slight variation with temperature of the solid angle of collection which is a function of the refractive index of the melt (Raptis 1986). At temperatures below 1100 K the thermal background from the sample was negligible and was ignored, but above this temperature separate scans were made with the laser beam off and the resulting spectrum was subsequently subtracted from the overall spectrum of the melt.

The 4880Å Ar$^+$ laser line was used throughout the experiments at a constant power of 100 mW at the sample. The position of the laser beam inside the sample was kept fixed to ensure that the conditions of data collection were the same from one temperature to the next. Slow scan speeds were used for the low-frequency region to ensure accurate measurements of the rapidly decreasing spectrum. The spectral slit width was 2 cm^{-1}.

3. Results and discussion

Figure 1 shows the polarized (I_{xx}—parallel polarization of incident and scattered light) and depolarized (I_{yx}—perpendicular polarization) spectra of molten CsCl for the lowest temperature (945 K) and the highest (1190 K) for which reliable intensity measurements were possible. There is an increase in intensity for both I_{xx} and I_{yx} as T increases. This trend is continuous throughout the temperature range. The departure from almost exponential decay of the high- and low-frequency regions, and the change of slope in between, indicate the presence of the three spectral regions mentioned in the introduction.

Since it is not possible to assess from figure 1 the rate at which the intensity increases with temperature we have calculated both the differential and integrated fractional change of intensity with reference to the lowest-temperature ($T_0 = 945$ K) spectrum. The differential fractional change

$$\kappa(T,\bar{\nu})_{\text{obs}} = \frac{I(T,\bar{\nu})_{\text{obs}} - I(T_0,\bar{\nu})_{\text{obs}}}{I(T_0,\bar{\nu})_{\text{obs}}} \tag{1}$$

at two temperatures (1070 and 1190 K) and for total (depolarized plus polarized) scattering is shown in figure 2. The solid lines correspond to predicted values, assuming
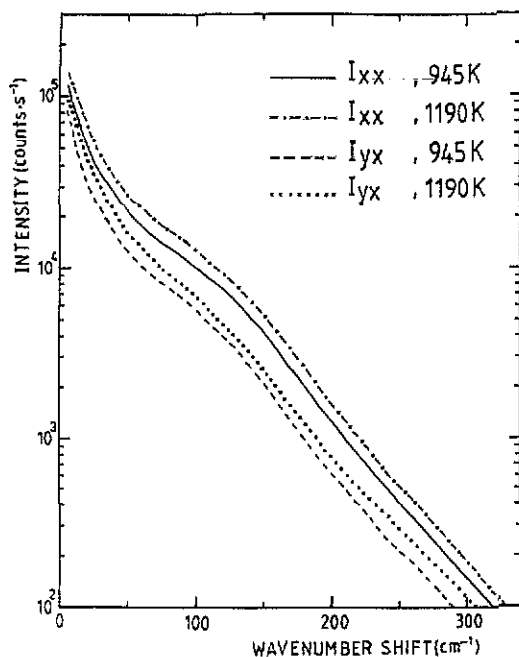
Figure 1. Polarized and depolarized Raman spectra of molten CsCl. Solid line, I_{xx}, 945 K; dashed line, I_{yx}, 945 K; chain line, I_{xx}, 1190K; dotted line, I_{yx}, 1190 K.

first-order scattering, calculated from the equation

$$I(T,\bar{\nu})_{\text{pr}} = I(T_0,\bar{\nu})_{\text{obs}} \frac{n(T,\bar{\nu})+1}{n(T_0,\bar{\nu})+1} \tag{2}$$

which is valid for single-particle scattering on the Stokes side of the spectrum. The quantity

$$n(T,\bar{\nu}) = \frac{1}{\exp(hc\bar{\nu}/kT)-1} \tag{3}$$

is the Bose–Einstein thermal factor.

The observed and predicted values of the integrated fractional intensity changes are obtained from the expression

$$\kappa(T) = \left(\int I(T,\bar{\nu})\,\mathrm{d}\bar{\nu} - \int I(T_0,\bar{\nu})\,\mathrm{d}\bar{\nu} \right) \Big/ \int I(T_0,\bar{\nu})\,\mathrm{d}\bar{\nu} \tag{4}$$

and are given in table 1 for polarized, depolarized and total scattering. The average values of depolarization ratio

$$\bar{\rho}_{\text{d}}(T) = \int I_{yx}(T,\bar{\nu})\,\mathrm{d}\bar{\nu} \Big/ \int I_{xx}(T,\bar{\nu})\,\mathrm{d}\bar{\nu} \tag{5}$$

are also given.

It is apparent from table 1 that the rates at which the integrated intensities of polarized and depolarized scattering increase with temperature are almost identical;
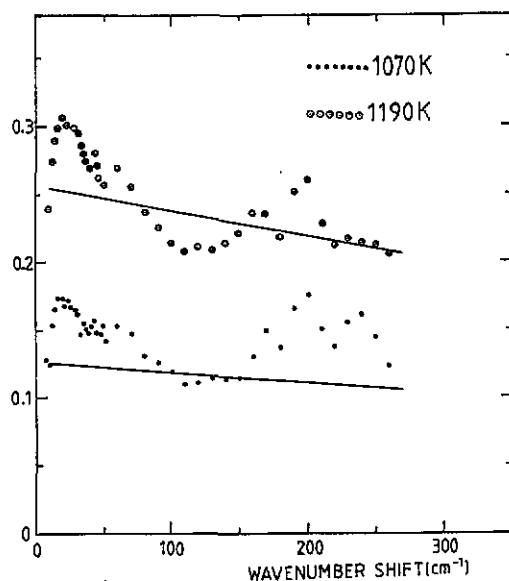
Figure 2. Spectra of fractional intensity change $\kappa(T, \bar{\nu})$ for total scattering $(I_{xx} + I_{yx})$ of molten CsCl at 1070 K (●) and 1190 K (○); reference temperature $T_0 = 945$ K. Solid lines show the intensity changes expected for first-order scattering.

Table 1. Integrated fractional increase of intensity κ for polarized (I_{xx}), depolarized (I_{yx}) and total $(I_{xx} + I_{yx})$ scattering from molten CsCl at various temperatures with reference to the corresponding spectra at $T_0 = 945$K (see text for details). The fifth column shows predicted values κ_{pr} assuming an $n(T, \bar{\nu}) + 1$ temperature dependence of the intensity (first-order scattering). The sixth and seventh columns show the extrapolated value of $\rho_d(\bar{\nu} \to 0)$ and the average depolarization ratio $\bar{\rho}_d = \rho_d(t = 0)$.

T (K)	κ_{xx}	κ_{yx}	κ_{xx+yx}	κ_{pr}	$\rho_d(\bar{\nu} = 0)$	$\rho_d(t = 0)$
945 (T_0)	—	—	—	—	0.678	0.616
1010	0.078	0.075	0.077	0.061	0.693	0.623
1070	0.139	0.140	0.139	0.118	0.710	0.624
1130	0.187	0.185	0.186	0.175	0.710	0.625
1190	0.249	0.250	0.249	0.235	0.725	0.634

consequently the total scattering increases at the same rate and $\bar{\rho}_d$ remains almost constant. However, the observed rate of increase is significantly greater than that anticipated for first-order scattering. This implies that higher-order scattering (predominantly second-order) also occurs in the melt.

The spectral variation of the intensity change (figure 2) also provides some insight into the dominant type of scattering in the various spectral regions. Firstly the pattern of this variation is remarkably similar for all four temperatures above T_0. In the low-frequency region (up to ≈ 80 cm^{-1}) the intensity increase is well above the level expected for first-order scattering. In the intermediate region (80–160 cm^{-1}) the intensity falls to the level (or just below) expected for first-order scattering. This is strong evidence that scattering in this region is first order and supports the suggestions put forward previously that collective excitations occur which correspond to residual optic modes. Further support for this suggestion comes from the fact that the peak position of the reduced-intensity spectrum in CsCl (Mitchell and Raptis 1983), 118 cm^{-1}, lies at the mid-point of the intermediate spectral region if the latter is defined

from the spectral dependence of the intensity increase in figure 2. This is very close to the frequency corresponding to the Debye temperature of the solid, 120 cm^{-1}. Finally in the high-frequency region the intensity levels appear to be above those anticipated for first-order scattering, providing evidence that the spectral tails are dominated by second-order (summation) processes.

Although the overall depolarization ratio $\overline{\rho}_d$ remains constant with temperature the spectral variation

$$\rho_d(\overline{\nu}) = I_{yx}(\overline{\nu})/I_{xx}(\overline{\nu}) \tag{6}$$

shows significant change with temperature. Figure 3 shows $\rho_d(\overline{\nu})$ for molten CsCl at T_0 and 1190 K. In the low-frequency region $\rho_d(\overline{\nu})$ increases gradually with T while in the intermediate- and high-frequency regions it decreases. At the highest temperature (1190 K) $\rho_d(\overline{\nu} \to 0)$ approaches the theoretical maximum value of 0.75—that is, complete depolarization.
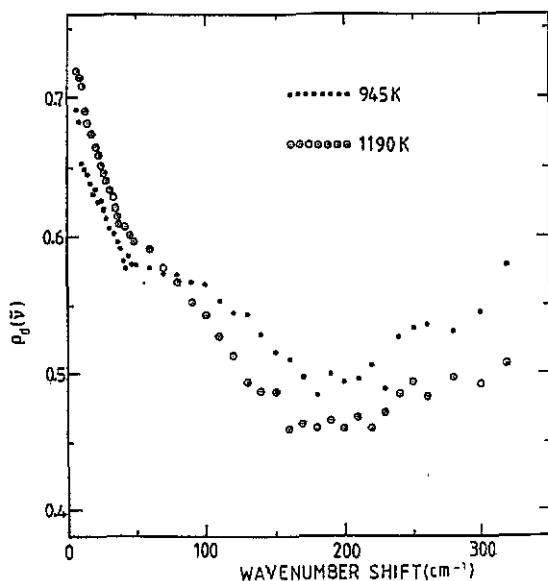

Figure 3. Depolarization ratio spectrum, $\rho_d(\overline{\nu})$, of molten CsCl at 945 K ($\bullet$) and 1190 K ($\circ$).

Because of the overlap of the three contributions to the spectra it is difficult to understand this behaviour in the frequency domain. In figure 4 we show the time dependence of the depolarization ratio

$$\rho_d(t) = I_{yx}(t)/I_{xx}(t) \tag{7}$$

where

$$I(t) = \int_0^\infty \frac{2\pi c I(\overline{\nu})}{k_s^4} \exp(-h\overline{\nu}c/2k_B T)\cos(2\pi\overline{\nu}ct)\,d\overline{\nu}. \tag{8}$$

Note that $\rho_d(t)$ is not the transform of $\rho_d(\overline{\nu})$. It can be seen that $\rho_d(t=0) = \overline{\rho}_d$ is almost invariant with temperature (see table 1). $\rho_d(t)$ increases as t increases,
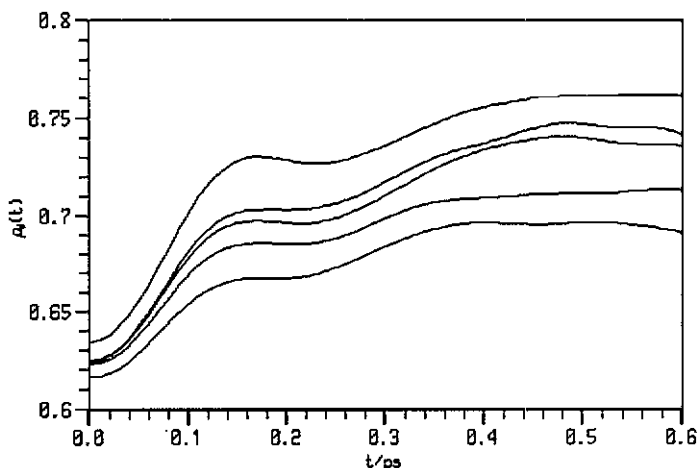
Figure 4. Depolarization ratio spectrum, $\rho_d(t)$, of molten CsCl at, in ascending order, $T = 945, 1010, 1070, 1130$ and 1190 K.

then reaches a limiting value about which it undergoes damped oscillations. (Note that there will be some errors in $\rho_d(t)$, particularly at high t, since $I(\bar{\nu})$ must be extrapolated to $\bar{\nu} = 0$.)

Fairbanks *et al* (1986) have explained the values of $\rho_d(t = 0)$ for the series of molten alkali halides by a simple model. The scattering is dominated by those pairs of ions which are closest together, and thus have the largest distortions of their polarisabilities, either due to direct electron cloud overlap or Coulomb field or field gradient. (Note that Raman scattering is strictly due to four-particle correlations, but these can be factorized approximately into two-particle correlations where higher-order correlations are weak.) The degree of depolarization is determined by the ratio of net quadrupolar terms (total depolarization, i.e. $\rho_d = 0.75$) to dipolar terms (no depolarization), which in turn is determined by the ratio of the polarisabilities of the interacting ions. For ions of similar polarisabilities (such as Cs^+ and Cl^-) the dipoles on the two ions tend to cancel, so ρ_d is high, while for dissimilar ions the net dipole is large and so ρ_d is low.

This model can now be extended to explain the t-dependence, and hence the $\bar{\nu}$-dependence, of ρ_d. As t increases we must now consider the resulting correlation of the original pair(s) of ions. These were close together at $t = 0$ and move further apart as t increases. The environment of both ions becomes more like the *average* environment of such ions in the melt; for CsCl the average local coordination is a disordered octahedron (see McGreevy and Pusztai 1990). This average environment must be more isotropic than that of the ions when in close contact, whatever salt is considered, so $\rho_d(t)$ must rise. (Complete isotropy corresponds to no net dipole, but only to quadrupole or higher-order terms, i.e. complete depolarization.) The ions then oscillate within their coordination 'cage' before eventually diffusing, on average after several picoseconds, into a different 'cage'. This oscillation, being of an ion within a cage of oppositely charged ions, could be considered as an overdamped (i.e. local) optic mode. The value of $\rho_d(t)$ about which the oscillation occurs will be determined by the degree of anisotropy in the average local structure. For NaCl the octahedral coordination is retained but with a larger proportion of vacancies than in CsCl (McGreevy and Pusztai 1990). The greater anisotropy should therefore lead to

lower values of $\rho_d(t)$ than for CsCl, in accord with the experimental data.

Increasing temperature will have little effect on $\rho_d(t = 0)$, since at the closest approach of two ions the interionic potential is rising very steeply. However, it will cause an increase in the degree of disorder in the average local coordination shell (around the minimum of the potential) which corresponds to a more isotropic environment and hence greater depolarization. This explains the data shown in figures 3 and 4. Given that $\rho_d(t = 0)$ changes little with temperature, while $\rho_d(t \gg 0)$ increases, one would expect $\rho_d(\bar{\nu} \to 0)$ to increase (being mostly due to long-t processes) while $\rho_d(\bar{\nu} \gg 0)$ will decrease to keep $\bar{\rho}_d$ constant. This is precisely what is observed. It is also consistent with the suggestion of Mitchell and Raptis (1983) and Raptis *et al* (1983) in that the degree of anisotropy at $t \to 0$ is determined by dynamical processes, while that at long t is spatial (structural) in origin.

4. Conclusions

We have shown that the temperature variation of the intensity of the light scattering spectrum of molten CsCl can be explained if the scattering is due to second-order processes at high and low $\bar{\nu}$, and first-order processes at intermediate $\bar{\nu}$. The variation of the depolarization ratio with frequency and temperature has been explained in terms of fluctuations of ions within their local coordination environment.

Acknowledgments

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