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Light scattering by alkali halides melts: a comparison of shell-model and rigid-ion computer simulation results

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Abstract. Molecular dynamics computer simulations with shell-model potentials have been used to calculate the light scattering (Raman) spectra of molten LiCl. A significant improvement in the level of agreement with experiment is found over previous simulations with rigid-ion potentials. The improvement is attributed to the better description of the relaxation of the charge-density fluctuations in the shell-model simulations

1. Introduction

Recently, molecular dynamics simulations have been used to calculate the (Raman) light scattering spectrum for NaCl, LiF and LiCl (Madden *et al* 1991, Madden and O'Sullivan 1990). The light scattering spectrum is related to the spectrum of the fluctuations in the total polarizability of the sample. For an isotropic fluid, there are two independent spectra which are given by the fluctuations in the isotropic and anisotropic parts of the polarizability tensor. The calculation of the light scattering spectrum from simulation data thus requires a computationally tractable model for the fluctuations in the polarizability of the system induced by the interionic interactions. Such a model has been developed for ionic systems based upon the results of *ab initio* electronic structure calculations (Fowler and Madden 1984). This model has been described extensively elsewhere (Madden and Board 1986). The interaction-induced polarizability is decomposed into contributions from four separate mechanisms; the dipole-induced dipole mechanism, (which is the dominant influence in atomic fluids (Birnbaum 1984)), a short-range term which describes the effects of near-neighbour interactions in the compression and overlap of ionic charge clouds, and terms which depend on the electric field and field gradient experienced by a given ion.

Good agreement was found between the experimental integrated intensity (Mitchell and Raptis 1983) and the simulation data in NaCl. The lineshapes were also found to agree remarkably well with experiment in NaCl and LiCl, especially at low frequencies ($< 100 \text{ cm}^{-1}$). At higher frequencies 'shoulders' appear in the experimental spectra which seem to appear at different frequencies in the calculations. The results for LiCl from the rigid-ion calculations are compared with the experimental data of Giergiel *et al* (1984) in figures 1 and 2. The discrepancy described above is particularly prominent in the anisotropic spectrum.

In a recent paper, the anisotropic light scattering lineshape has been analysed theoretically and its shape has been related to that of the mass and charge dynamical

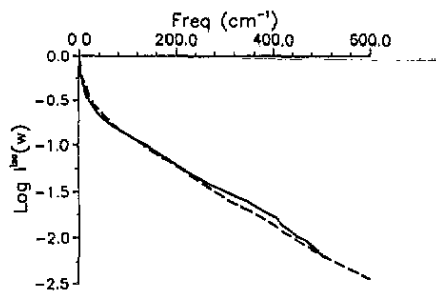


Figure 1. Comparison of the simulated isotropic spectrum of LiCl from a rigid-ion model simulation (broken line) (Madden *et al* 1991) with the experimental data of Giergiel *et al* (1984) (solid line).

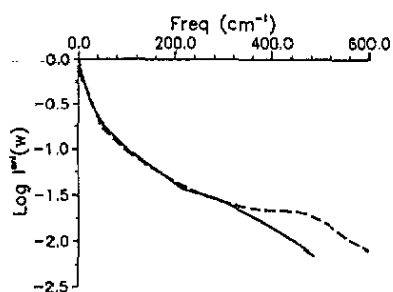


Figure 2. Comparison of the simulated anisotropic spectrum of LiCl from a rigid-ion model simulation (broken line) (Madden *et al* 1991) with the experimental data of Giergiel *et al* (1984) (solid line).

structure factors (Madden and O'Sullivan 1991). It was argued that the high frequency shoulder appearing in the anisotropic spectrum reflects a propagating longitudinal charge-density wave, or 'plasmon'-like oscillation, of well defined frequency.

The purpose of this paper is to report a shell-model (Sangster and Dixon 1976) simulation study of LiCl and the subsequent light scattering spectrum calculation. The motivation for this is to investigate whether the high frequency discrepancy in the rigid-ion calculation is due to (i) the failure of the rigid-ion potential to reproduce the characteristic frequency of the plasmon-like oscillation of the system or (ii) a weakness in the model used to calculate the ionic polarizability. The rigid-ion potential does not contain ion polarization effects and consequently the strength of the average coulomb interaction between ions is overestimated. The shell-model includes ion polarization effects and it is known to give a better description of the relaxation of the charge density in the melt (Hansen and McDonald 1986, Rovere and Tosi 1986). We will compare the behaviour of the ion current correlation functions in rigid-ion and shell-model simulations of LiCl in order to demonstrate the source of the improvement in the light scattering lineshape.

2. The computer simulation

The shell-model has been described fully by Sangster and Dixon (1976). They report the results of molecular dynamics simulations of several systems using shell-model potentials. The shell-model includes the effects of polarization on the ion dynamics by describing one or more of the ionic species as a point mass ion connected to a massless shell of charge Y through a harmonic spring of force constant K . These parameters are derived from the low- and high-frequency dielectric constants of the crystal (ϵ_0 , ϵ_∞) and following this method we derived shell-model parameters for LiCl from the dielectric constants of (Lowndes and Martin 1969) and these are given in table 1. The charge on the core is then determined such that the sum of shell and core charges is equal to the ionic charge, in this case $\pm |e|$.

We have developed a vectorized code that only allows for the anion species to be polarizable, and treats the cations as rigid ions. At a given timestep of the simulation, the ion cores are moved together with their shells as in a rigid-ion simulation. Next

Table 1. Shell model parameters for LiCl obtained from the high- and low-frequency dielectric constants for the system following Sangster and Dixon (1976) (Y_2 is in units of $|e|$, K is in units of e^2/V).

Y_2	K	R_0
-2.901	87.13819	7.195

the ion cores remain stationary in time whilst the shells are iteratively relaxed against their springs (using a steepest descent algorithm) until an equilibrium configuration is achieved. The force calculation differs from that of a rigid-ion simulation in the following manner; short-range forces are taken to act only between the shells for anion-anion interactions and shells with cores for anion-cation interactions, coulomb forces are taken to act between all shell-shell and shell-core interactions with the exception of an ion with its own core. This coupling is accounted for through the harmonic spring. The short-range forces are derived from a Fumi-Tosi (1964) type potential as tabulated by Sangster and Dixon (1976) and the coulomb forces are calculated using the Ewald summation technique as in a rigid-ion simulation.

We have performed a computer simulation of LiCl at 933 K using this shell-model algorithm. The system size was 216 ions contained in a cubic simulation cell of side $L = 17.25 \text{ \AA}$ to be consistent with the experimental density (Janz 1967). A timestep of $0.679 \times 10^{-15} \text{ s}$ was used, which is considerably smaller than that used in the rigid-ion simulation ($0.7 \times 10^{-14} \text{ s}$). The choice of timestep is dictated by the requirement that the steepest descent algorithm must converge rapidly. Under the conditions described it typically required three or less iterations to satisfy the convergence criterion. This was chosen to be such that the shell forces were taken to be in equilibrium if the RMS shell force was less than one thousandth of a typical interionic force ($\sim e^2/\sigma^2$ where e is the electronic charge and σ is a Fumi-Tosi diameter).

With this criterion good energy conservation was achieved (a drift of less than one part in 10^5 in 1000 steps). An equilibration period of 12 000 steps was first made. Data were then collected over 32 000 steps. The code ran on a single-processor of a Cray XMP-48 machine and required 0.8 s cpu-time per time step. The calculation of the induced polarizability correlation functions proceeded in exactly the same way as in the rigid-ion case (Madden *et al* 1991).

The structure in the simulation was verified by calculation of the partial radial distribution functions which were compared with those obtained from the rigid-ion simulation (O'Sullivan 1990). We found the same qualitative differences between these rigid-ion and shell-model simulation calculations as has been found in previous comparative studies of this type for the lighter alkali halides, in particular that of NaI (Sangster and Dixon 1976), i.e. we found there to be very little difference in both $g_{+-}(r)$ and $g_{--}(r)$ between the two models, but in the shell-model $g_{++}(r)$ is shifted towards lower r values indicating that cations can make closer approaches to each other than in the rigid-ion simulation. In the region of the first peak, $g_{++}(r)$ and $g_{--}(r)$ are distinctly different in both shell-and rigid-ion model calculations, but in the shell model this difference persists right out until these functions become flat.

The diffusion coefficients were calculated from the ion mean square displacement functions and were found to be $D_+ = 8.1 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ and $D_- = 4.8 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ compared with the corresponding rigid-ion values (O'Sullivan 1990) $D_+ = 10.2 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ and $D_- = 6.6 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$.

3. Relaxation of mass and charge densities

The dynamical excitations within the melt are best investigated through the spectra of the mass and charge density currents. The longitudinal mass and charge current $C_{mm}^l(k, \omega)$ and $C_{qq}^l(k, \omega)$ are given by

$$C_{aa}^l(k, \omega) = \text{Re} \int_0^\infty dt e^{-i\omega t} C_{aa}^l(k, t) \quad (1)$$

with

$$C_{aa}^l(k, t) = \left\langle \left(\sum_{j=1}^N -i a_j k \cdot v_j(t) e^{-ik \cdot r_j(t)} \right) \left(\sum_{n=1}^N i a_n k \cdot v_n(0) e^{ik \cdot r_n(0)} \right) \right\rangle \quad (2)$$

and a_j is either the mass or charge of ion j .

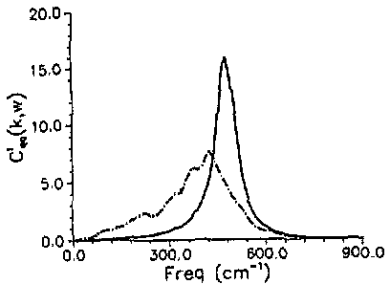


Figure 3. Comparison of the spectrum of the longitudinal mass current $C_{mm}^l(k, \omega)$ (defined by equation (3)) at $k = 0.364 \text{ \AA}^{-1}$ calculated from a rigid-ion model simulation of LiCl (solid line) (Madden *et al* 1991) with that from our shell-model simulation (dash-dotted line).

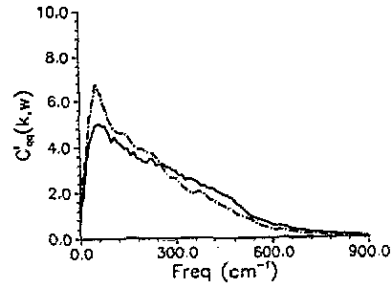


Figure 4. Comparison of the spectrum of the longitudinal mass current $C_{mm}^l(k, \omega)$ (defined by equation (3)) at a value of k close to the principle peak in the structure factor ($k = 2.06 \text{ \AA}^{-1}$) calculated from a rigid-ion model simulation of LiCl (solid line) (Madden *et al* 1991) with that from our shell-model simulation (dash-dotted line).

In figure 3 we compare the spectra of the longitudinal charge currents calculated at $k = 0.364 \text{ \AA}^{-1}$ from the rigid-ion (Hansen and McDonald 1986, Rovere and Tosi 1986) and shell-model simulation data. The existence of a propagating charge-density wave is quite clear from both simulations. In the rigid-ion result the frequency of this propagating mode is seen to be about 520.0 cm^{-1} . The shell-model frequency is quite significantly downshifted as expected, and the peak is seen to appear at about 380.0 cm^{-1} .

In the rigid-ion simulations we showed that the frequencies associated with the longitudinal and transverse charge densities (ω_{LO} and ω_{TO} , respectively) were connected by a Lyddane-Sachs-Teller relationship (Madden and O'Sullivan 1991)

$$\omega_{LO}^2 - \omega_{TO}^2 = \omega_p^2 = \sum_{\nu} \frac{4\pi\rho_{\nu} z_{\nu}^2 e^2}{m_{\nu}} \quad (3)$$

where ω_p is the plasma frequency. In the polarizable fluid, which the shell-model represents, we expect the expression for the plasma frequency to be modified to

account for the dielectric permittivity associated with ion polarization. If we model the situation as a system in which the ionic charges are embedded in a medium with relative permittivity ϵ_∞ (due to the electronic polarization) then the plasma frequency becomes

$$\omega_{p,\text{shell}}^2 \sim \frac{1}{\epsilon_\infty} \omega_{p,\text{rigid ion}}^2 \quad (4)$$

From this relationship we expect ω_{LO} in the shell-model results to be lower than the rigid-ion value by a factor of roughly $\epsilon_\infty^{-1/2}$. For LiCl ϵ_∞ is 2.25 (Janz 1967) and so the expected shell value for ω_{LO} is 350.0 cm^{-1} , in good agreement with what we have observed.

Besides shifting the charge-density wave frequency in this way, inclusion of electronic polarization seems to have considerably broadened the spectral peak relative to the rigid-ion spectrum at the same value of k . This suggests a stronger damping of the plasmon in the shell-model simulations.

At higher k this propagating mode disappears as the phase factors in equation (2) cause the interionic contributions to disappear and the spectra become incoherent. In figure 4 we show the function $C_{qq}^1(k, \omega)$ at a value of k close to the principal peak of the structure factor for both rigid-ion and shell-model simulations. The distinctive charge density wave feature has disappeared at this value of k . The functions are similar to the spectrum of the velocity autocorrelation function. The spectral density is shifted to lower frequencies in the shell model case; this reflects a reduction in the oscillatory frequencies of the lithium ion.

4. Light scattering spectrum

The results obtained for the integrated intensities of the light scattering spectra were the same, within the statistical uncertainty, as obtained in the rigid-ion case. This result is consistent with the observation that the structure of the melt, as seen in the partial radial distribution functions, is very similar in the two cases. Furthermore, it implies that there is good agreement between the shell-model and experimental depolarization ratios for LiCl, as previously noted for the rigid-ion case (Madden *et al* 1991).

The isotropic and anisotropic light scattering lineshapes calculated from the shell-model simulations are compared with the experimental data of Giergiel *et al* (1984) in figures 5 and 6. The most notable feature of these results is the marked improvement between the calculated and experimental anisotropic lineshapes, relative to the rigid-ion results shown in figure 2. The shifting and broadening of the plasmon by the inclusion of electronic polarization is responsible for this change.

5. Conclusion

The excellent agreement between the simulated and experimental spectra for LiCl confirms the validity of the model which has been used for the fluctuating polarizability in the melt. We would expect the ionic polarization effects on the ion dynamics to be less pronounced in NaCl than in LiCl as the polarizability density (i.e. ϵ_∞) is

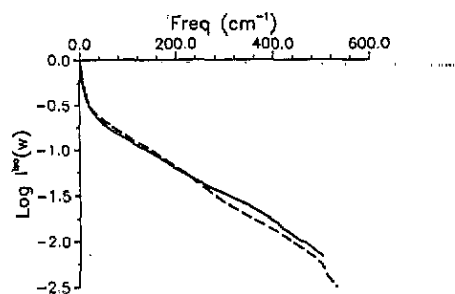


Figure 5. Comparison of the simulated isotropic spectrum of LiCl from our shell-model simulation (broken line) with the experimental data of Giergiel *et al* (1984) (solid line).

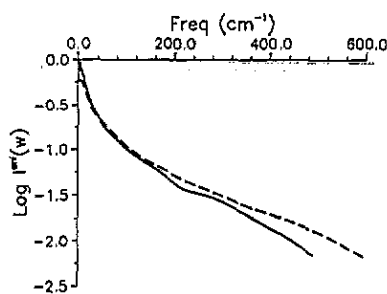


Figure 6. Comparison of the simulated anisotropic spectrum of LiCl from our shell-model simulation (broken line) with the experimental data of Giergiel *et al* (1984) (solid line).

substantially lower. We therefore would not expect shell-model dynamics for NaCl to significantly alter the lineshape calculated with the rigid-ion model. We have already noted the good agreement with experiment obtained in the rigid-ion calculations for NaCl.

Finally, we note that the improvement in the calculated lineshape for LiCl, when polarization effects are introduced in the ion dynamics, confirms the assignment of the prominent bump seen in the wings these spectra to the plasmon or charge-density wave (Madden and O'Sullivan 1991).

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