

Low-energy excitations in a low-viscous glass-forming liquid

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MS received 15 July 2011; revised 6 February 2013

Abstract. Polarized and depolarized low frequency Raman spectra of a liquid mixture, viz. 0.15LiCl–0.85H₂O, has been analysed in detail in order to elucidate the temperature and polarization characteristics of quasi-elastic line and Boson peak. The employed fitting procedure shows more convincingly that the Boson peak contribution to the overall low frequency Raman pattern is present even in this low-viscous liquid. The degree of disorder in this liquid is not so high and certain micro-ordering effects may take place due to hydrogen bonding. The results are discussed in the framework of the current phenomenological status of the field.

Keywords. Low-frequency Raman; Boson; liquids; Raman spectroscopy; low-viscous liquid.

1. Introduction

Low-energy excitations in amorphous solids and especially their presence and dependence on external stimuli have been the subject of extensive experimental and theoretical examinations over the last years (Shuker and Gammon 1970; Jackle 1981; Yannopoulos 2000; Taraskin *et al* 2001; Johari 2002; Grigera *et al* 2003; Johari 2003a, b; Lubchenko and Wolynes 2003; Gurevich *et al* 2003; Chumakov *et al* 2004). However, several aspects of low-energy excitations phenomenology are still under debate. In brief, the low frequency Raman spectrum of all amorphous solids and super-cooled liquids are dominated by an asymmetric intense peak, known as the Boson peak (BP), which is absent in the spectra of their crystalline counterparts. Many works have been dedicated so far to the elucidation of the origin of BP. One of the most popular, at least in the past decade, suggested a relation of this peak and the existence of an intermediate range of structural order in the glass. However, the existence of BP in the liquid state (above T_m) has challenged this approach (Yannopoulos *et al* 2003; Kalampounias *et al* 2006). The difficulty in formulating a successful theory about the dependence of the spectral features of BP with respect to a change of an external stimulus (such as temperature, pressure, confinement, etc) has led to the quest for phenomenological correlations which usually claim universal behaviour for glasses. However, it has been shown that such correlations are not based on a well established basis (Yannopoulos and Papatheodorou 2000).

Being disordered systems, viscous liquids might be expected to show a Boson peak in their low frequency Raman spectra. As reviewed in the literature (Angell 1995; Corset

1996; Kalampounias 2012), these features have been registered and analysed in numerous substances like glycerol and its analogues. However, no information exists regarding Boson peaks in ordinary, low-viscous liquids with certain ordering effects, like hydrogen bonding.

There are several obstacles for studies of Boson peak in ordinary liquids. At room temperature, Boson peak is usually hidden under the envelope of the so-called quasi-elastic scattering. The latter appears as a single line centred at $\omega_0 = 0$ presumably arising due to the coupling of light to localized structural defects (Theodorakopoulos and Jäckle 1976). Therefore, studies of low-frequency Raman features usually need a great deal of computational work based on various models in order to decompose Boson peak and quasi-elastic contribution. More and more refined fitting methods enable us to separate composite low-frequency Raman spectra to individual components which are being published and new theoretical approaches are elaborated (Yannopoulos *et al* 2002; Kalampounias *et al* 2006; Kalampounias 2008, 2011).

In this paper, we report the first observation of a Boson peak in the low frequency Raman spectra of a low-viscous liquid, viz. 0.15LiCl–0.85H₂O. The viscosity of this liquid at 298 K is many orders of magnitude less than that of glycerol. Low frequency Raman scattering has been utilized to elucidate the temperature dependence of quasi-elastic line and Boson peak and discuss their polarization characteristics.

2. Experimental

Filtering liquid 0.15LiCl–0.85H₂O through a 0.22 m Fluoropore (Millipore company) filter at 40 °C into the cells ensured that the sample was dust free. All the cells were sealed after filling. The Raman cells were made of fused silica tubing having 6 mm OD, 4 mm ID and 3–5 cm in length.

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All the cells were transparent, clear, free of optical defects and dust free.

Right-angle, Stokes-side Raman spectra were recorded with a 0.85 m double monochromator (Spex 1403). The excitation source was an Ar⁺ laser (Spectra Physics) operating at 488.0 nm line with an output power of about 100 mW to avoid heating the liquid. The instrumental resolution was fixed at 1.5 cm⁻¹ for the whole set of measurements. Temperature-dependent Raman measurements in the range from liquid-N₂ to room temperature were performed using a homemade cryostat and the temperature was controlled with an accuracy of ~0.5 K. Both scattering geometries, VV and HV were employed. The signal after detection by a water-cooled photomultiplier and amplification by standard electronic equipment was transferred to a computer. Each spectrum is the result of several accumulations (more than ten) in order to substantially enhance the signal-to-noise ratio. A calibration procedure with a neon lamp and CCl₄ sample was frequently done, during spectra accumulation, to account for possible shifts of the monochromator's gratings and to fix polarization, respectively.

3. Results and discussion

The room temperature polarized and depolarized Raman spectra of liquid 0.15LiCl–0.85H₂O are shown in full range (50–3800 cm⁻¹) in figure 1. Dashed lines represent the bending and stretching vibrations attributed to water. Raman spectra of LiCl–H₂O have been studied by Tao *et al* (1991) in great detail. The low-frequency vibrational spectrum of pure water, which has been reported by several investigators (see e.g. DeSantis *et al* 1987), is very similar to that of aqueous LiCl solutions, including the bands near 70, 110, 180 and ~314 cm⁻¹. Despite extensive study of the Raman spectrum of water, the origin of these bands

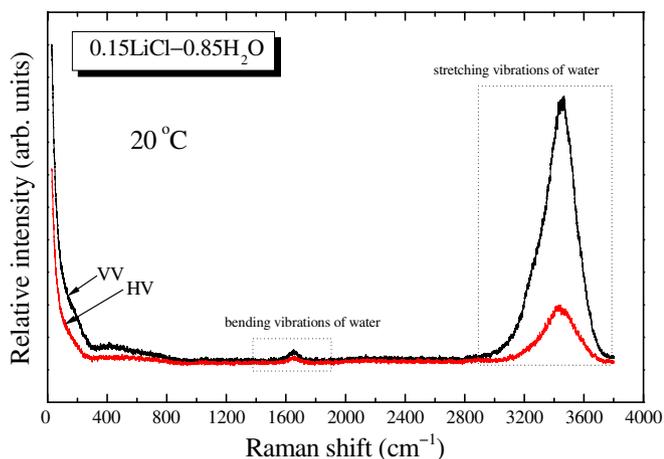


Figure 1. Polarized (VV) and depolarized (HV) Stokes-side Raman spectra of 0.15LiCl–0.85H₂O liquid at room temperature. Spectral conditions: $\lambda_0 = 488$ nm, resolution = 1.5 cm⁻¹, time constant = 1.0 and increment rate = 2.5 cm⁻¹/s.

is still controversial. The bands around ~70 and 110 cm⁻¹ have been assigned to the flexing mode of an O–O–O unit by Walrafen (1964). Other researchers have assigned these bands to disorder the induced localized transverse (Rousset *et al* 1990) or longitudinal (Aliotta *et al* 1986) acoustic phonons. The band at ~180 cm⁻¹ is assigned to the O–O stretching mode (Walrafen 1964). For 30 mol% LiCl solutions, all water molecules belong to LiCl hydration shells, so there is little change for the formation of O–O–O bridges (Tao *et al* 1991). If Walrafen's assignments were correct, we would expect a dramatic decrease in the intensity of ~70 and 110 cm⁻¹ bands in the concentrated solutions, which is not observed (Tao *et al* 1991).

The depolarization ratio $\rho(\omega) = I_{HV}(\omega)/I_{VV}(\omega)$ was calculated in the low-frequency region of interest (<350 cm⁻¹) and is presented in figure 2 for pure water and for 0.15LiCl–0.85H₂O mixture, respectively. The ratio is almost ~0.7 for water and slightly lower in the case of LiCl aqueous solution. Furthermore, the depolarization ratio was found to be independent of temperature.

Working in the harmonic approximation, Shuker and Gammon (1970) showed that the first order Stokes scattered intensity in amorphous solids can be cast in the form (Shuker and Gammon 1970):

$$I_{\text{exp}i} \propto C(\omega)g(\omega)[n(\omega) + 1]/\omega, \quad (1)$$

where ω is the frequency, $C(\omega)$ the photon–phonon (Raman) coupling coefficient that reflects activity of the vibrational excitations in scattering light, $g(\omega)$ the vibrational density of states and $n(\omega)$ the Bose factor, $n(\omega) = [\exp(\hbar\omega/kT) - 1]^{-1}$, \hbar the Planck constant, k the Boltzmann constant and T the temperature. Making the

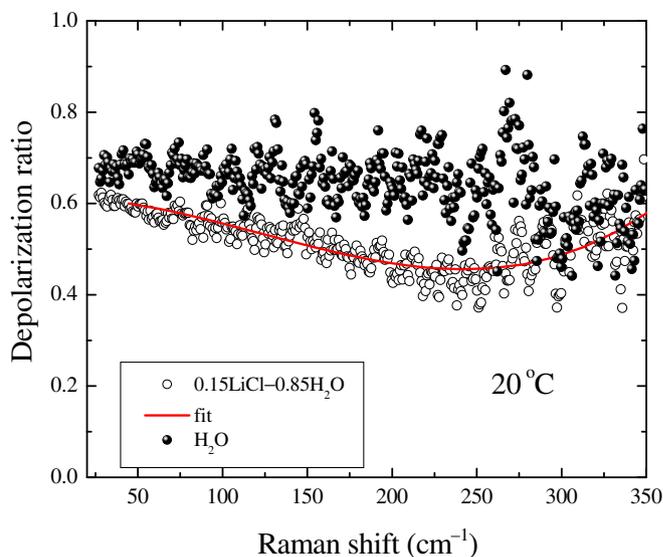


Figure 2. Experimental depolarization ratio for pure water (solid circles) and for 0.15LiCl–0.85H₂O liquid (open circles) at room temperature. Solid line represents total fitting (see text for details).

assumption that the vibrational densities of states follow Debye law, $g(\omega) \propto \omega^2$, one can rewrite (1) as

$$I_{\text{exp}t} \propto C(\omega)\omega[n(\omega) + 1]. \quad (2)$$

Debye approximation can be accepted for disordered solids and super-cooled liquids that remain in a microscopically liquid state below their equilibrium melting temperature, T_m . It should be said in all fairness that such an approximation is far from being justified when applied to liquids above T_m , as in our case.

Using the assumptions introduced in (2), the quasi-elastic line profile can be represented (Theodorakopoulos and Jäckle 1976) as:

$$I_{\text{exp}t}^{\text{QE}} \propto \omega[n(\omega) + 1] \frac{A\tau}{1 + \omega^2\tau^2}, \quad (3)$$

where A is a constant, τ a characteristic time and the quasi-elastic line width (half-width at half height) is $\Omega_{\text{QE}} = (2\pi c\tau)^{-1}$, where c is the speed of light.

Based on the approximations introduced in (2), one can derive an expression for the Boson peak profile as:

$$I_{\text{R}}^{\text{BP}} \propto \omega[n(\omega) + 1] \left\{ \omega^2 \left[g_{\text{TA}}(\omega)E_{\text{TA}} + \frac{2}{3}g_{\text{LA}}(\omega)E_{\text{LA}} \right] \right\}, \quad (4)$$

where E_i is the light-to-vibration coupling parameter for transversal (TA) and longitudinal (LA) acoustic phonons and $g_i(\omega)$ the space Fourier transform of the correlation function of the disorder in an amorphous solid.

Using the correlation function of the disorder of a Gaussian form, one arrives at Boson peak of an asymmetric quasi-Gaussian profile. However, it is inadequate to fit a large number of experimental data for various substances. Use of an exponential form of the disorder correlation function changes the profile of Boson peak from Gaussian-like to Lorentzian-like, which seems to fit better with the measured spectra.

Writing the space correlation function of the disorder as:

$$G_{\text{dis}}(r) = \exp \left\{ - \left[(r^2 + R_1^2)^{1/2} - R_1 \right] / R_2 \right\}, \quad (5)$$

where r is the distance, R_2 the structure correlation radius and R_1 a measure of the steepness of the correlation function of the disorder, one gets:

$$g_{\text{TA}}(\omega) = 4\pi c \frac{\Omega_{2,\text{TA}}}{\Omega_{1,\text{TA}}} \exp \left(\frac{\Omega_{2,\text{TA}}}{\Omega_{1,\text{TA}}} \right) \frac{K_1[z_{\text{TA}}(\omega)]}{z_{\text{TA}}^2(\omega)}, \quad (6a)$$

$$g_{\text{LA}}(\omega) = \left(\frac{c_{\text{TA}}}{c_{\text{LA}}} \right)^5 4\pi c \frac{\Omega_{2,\text{LA}}}{\Omega_{1,\text{LA}}} \exp \left(\frac{\Omega_{2,\text{LA}}}{\Omega_{1,\text{LA}}} \right) \frac{K_1[z_{\text{LA}}(\omega)]}{z_{\text{LA}}^2(\omega)}, \quad (6b)$$

where $K_1(x)$ is the modified Bessel function of the second kind, $\Omega_{1,i}$ and $\Omega_{2,i}$ are the parameters of Boson peak (the former is close to the Boson peak frequency and the latter is

a measure of the type of Boson peak profile), c_i the speed of sound in a medium and $z_i(\omega) = (\omega^2 + \Omega_{2,i}^2)^{1/2} / \Omega_{1,i}$.

The bands arising from inter-molecular vibrational modes, also present in the spectra, have been fitted. The method employed enables one to model real lines of an intermediate between Gaussian and Lorentzian form by an analytical function, which is analogue to Voigt function, that has an analytical counterpart in the time domain. It is based on the model time-correlation function written in the form:

$$G_{\text{V}}(t) = \exp \left\{ - \left[(t^2 + \tau_1^2)^{1/2} - \tau_1 \right] / \tau_2 \right\}, \quad (7)$$

where τ_1 is close to the vibrational frequency modulation time τ_v and τ_2 to the dephasing time τ_d . These characteristic times are widely used in studies of liquid dynamics. For a review on this subject, see Turrell (1997a, b), Kirillov (1998), and Kalampounias *et al* (2003a, b).

Fourier transform of (7) can be performed analytically giving the vibrational line profile as:

$$I(\omega) = 2nc \exp(\tau_1/\tau_2) \left(\tau_1^2/\tau_2 \right) K_1(x)/x, \quad (8)$$

where $K_1(x)$ is the modified Bessel function of the second kind, ω_0 the peak wavenumber, $n = 2$ if $\nu_0 = 0$ and $n = 1$ if $\nu_0 \neq 0$ and $x = \tau_1[4\pi^2c^2(\omega - \omega_0)^2 + 1/\tau_2^2]^{1/2}$.

In many cases, also as in our case, the presence of low-lying vibrational modes obstructs the analysis of the low frequency spectrum. A representative example of the fit is shown in figure 3 for the polarized (VV) low frequency

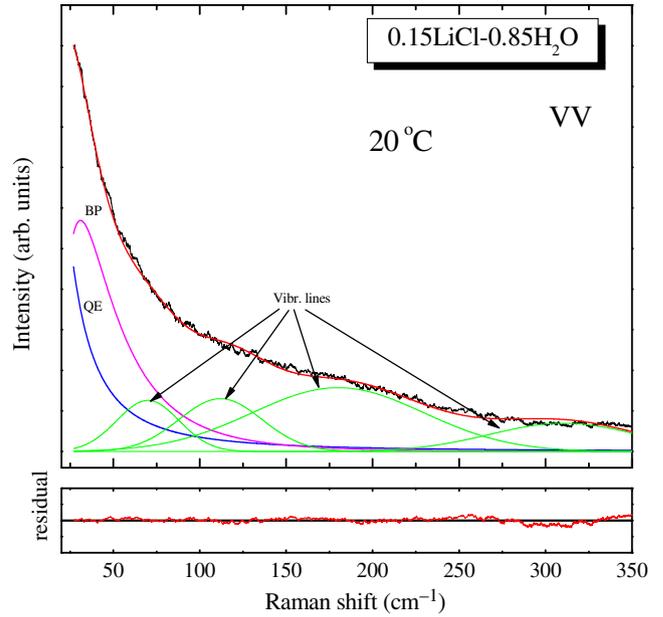


Figure 3. Representative fitting example for experimental polarized (VV) low-frequency Raman spectrum of 0.15LiCl-0.85H₂O liquid at room temperature. Lower panel represents fitting residual indicating goodness of fit. See text for details concerning fitting procedure.

Table 1. Fitting parameters at room temperature.

Parameter	VV spectrum	HV spectrum
Ω_{QE} (cm^{-1}) (Quasi-elastic half-width at half-maximum)	7.0	6.98
Ω_{QE}^{\max} (cm^{-1}) (Boson peak maximum frequency)	30.0	29.6
ν_1 (cm^{-1}) (peak frequency)	70.0	69.8
τ_v (ps) (vibrational relaxation time)	3.09	3.10
τ_ω (ps) (vibrational frequency modulation time)	0.0279	0.0282
ν_2 (cm^{-1}) (peak frequency)	110.0	109.7
τ_v (ps) (vibrational relaxation time)	3.43	3.42
τ_ω (ps) (vibrational frequency modulation time)	0.0294	0.0287
ν_3 (cm^{-1}) (peak frequency)	180.0	179.8
τ_v (ps) (vibrational relaxation time)	3.75	3.77
τ_ω (ps) (vibrational frequency modulation time)	0.0310	0.0293
ν_4 (cm^{-1}) (peak frequency)	314.0	313.7
τ_v (ps) (vibrational relaxation time)	3.78	3.81
τ_ω (ps) (vibrational frequency modulation time)	0.0317	0.0297

Raman spectrum at room temperature. The success of the approach followed becomes evident from the almost perfect fittings obtained in the way described above and from the fact that all vibrational features have zero intensity at $\omega = 0$ as well. Parameters of the overlapping contributions to the low-frequency Raman pattern of 0.15LiCl–0.85H₂O liquid are collected in table 1. It should be noticed that a surprisingly excellent agreement of calculated values for VV and HV spectra has been found. The quasi-elastic line width (HWHH) Ω_{QE} , Boson peak frequency and parameters of the low frequency vibrational band ν_1 , τ_v and τ_ω (the peak frequency, vibrational relaxation time and vibrational frequency modulation time, respectively), are the same with deviations less than 1%.

A comment is worth mentioning here concerning the temperature dependence of one of the most interesting parameters of the fitting, viz. the position of the Boson peak maximum. The former is depicted in figure 4 for the VV scattering geometry. The frequency of the Boson peak experiences maximum substantial softening as the system is driven from the glass to the melt through the super-cooled regime. The nature of Boson peaks is far from being understood even in the case of disordered solids. Therefore, in viscous liquids and even in water, low-frequency features are usually interpreted in terms of the damped-oscillator and Gaussian-cage models (Zwick and Landa 1994). There is a strong evidence, however, that in glasses, Boson peak features may arise due to micro-ordering effects (Yannopoulos *et al* 1997). In liquid 0.15LiCl–0.85H₂O, strong hydrogen bonding exists and this circumstance may favour the development of short-range ordering effects.

The interpretation given in this study is based on ideas common for amorphous solids. It should be emphasized that other approaches to the same experimental data are possible. For example, the de-polarized Raman spectra may be considered as caused by the rotation of the probe molecules (Rodríguez and McHale 1988). Such an approach, which

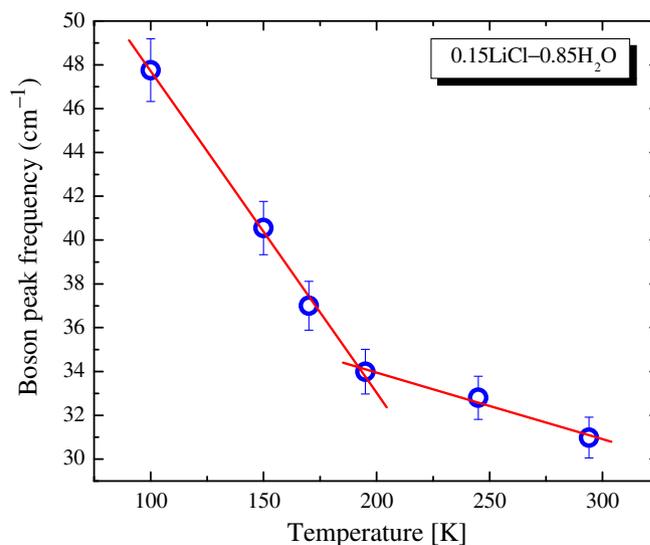


Figure 4. Temperature dependence of Boson peak frequency in 0.15LiCl–0.85H₂O glass-forming binary system for VV scattering geometry after scaling with Bose factor. Solid lines are drawn as guides to eye to indicate abrupt change at about 200 K near glass transition temperature.

is entirely based on the ideas of the dynamics of liquids has been successfully applied to dimethyl formamide (Rodríguez and McHale 1988). The low frequency Raman features resembling Boson peak may arise due to translation motions of the probe molecule as described for low frequency Raman features of liquid water (Corongiu and Clementi 1993). Relatively confined environments influence the low frequency inelastic neutron scattering spectrum of water (Belissent-Funel *et al* 1993). The wide variety of mutually excluding assignments shows that much more theoretical work is needed in order to clarify nature of the low frequency Raman pattern of ordinary liquids.

4. Conclusions

Temperature and polarization dependent low frequency Raman scattering study for 0.15LiCl–0.85H₂O glass-forming mixture has been performed. A joint detailed analysis for both polarized (VV) and depolarized (HV) spectra has clearly revealed the frequency dependence of the depolarization ratio for the low-frequency components. The main conclusion to be made is as follows. The fitting procedure employed shows convincingly that Boson peak contribution to the overall low frequency Raman pattern is present even in ordinary low viscous liquids. This means that the degree of disorder in these liquids is not so high, and certain micro-ordering effects may take place due to hydrogen bonding. Further studies are required in order to support this statement.

Acknowledgement

The author wishes to thank Prof G N Papatheodorou and Dr G A Voyiatzis for providing experimental facilities.

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