

# Low frequency excitations in amorphous polycarbonate studied by Raman spectroscopy

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Low frequency excitations in amorphous polycarbonate-bisphenol A have been studied by laser Raman spectroscopy in the frequency region  $5 \text{ cm}^{-1} < \Delta\bar{\nu} < 200 \text{ cm}^{-1}$ . Depolarized spectra were recorded at temperatures between ambient and 85 K, the reduced intensity spectra show no temperature dependence. Two bands are resolved in the reduced intensity spectrum: a strong band around  $96 \text{ cm}^{-1}$  and a weak band around  $45 \text{ cm}^{-1}$ ; these are attributed to the effects of longitudinal and transverse phonon waves originating in backbone motion. The low frequency Raman intensities provide information on the density of state  $g(\omega)$  from which the specific heat,  $C_v$ , of polycarbonate has been calculated. This is found to vary with temperature in a manner similar to the calorimetrically measured  $C_v$  in the low temperature range  $\sim 1 \text{ K} < T < 4 \text{ K}$ .

(Keywords: amorphous; polycarbonate; phonons; low frequency; Raman; specific heat)

## INTRODUCTION

Amorphous materials studied by laser Raman spectroscopy in the low frequency region  $\Delta\bar{\nu} < 200 \text{ cm}^{-1}$  show a characteristic broad band. This phenomenon has been observed in a number of structurally disordered materials including inorganic glasses<sup>1,2</sup>, polymer glasses<sup>3-5</sup> and organic liquids<sup>6,7</sup>. Another characteristic feature of the amorphous phase is the non-Debye behaviour of the specific heat at very low temperatures,  $T \lesssim 4 \text{ K}$ <sup>8,9</sup>. There has been a great deal of theoretical interest in the anomalous specific heat of glasses. The double well potential model<sup>10</sup> has successfully described the specific heat of amorphous materials at temperatures  $T < 1 \text{ K}$ .

The low frequency Raman spectrum can provide information on the density of states  $g(\omega)$  in the low frequency region<sup>11</sup>. In the quasi-harmonic approximation the specific heat is given by:

$$c_v = k \int_{\omega_{\min}}^{\omega_{\max}} g(\omega) \left( \frac{\hbar\omega}{kT} \right)^2 \frac{e^{\hbar\omega/kT}}{[e^{\hbar\omega/kT} - 1]^2} d\omega \quad (1)$$

According to the theory of Shuker and Gammon<sup>11</sup>

$$I_R = \sum_b c_b g_b(\omega) \quad (2)$$

where  $I_R$  is the reduced light scattering intensity given by:

$$I_R = I_{\text{obs}} \omega [1 - e^{-\hbar\omega/kT}] \quad (3)$$

Since the coupling coefficient  $c_b$  in the low frequency part of the spectrum varies as the square of the frequency<sup>4</sup>

equation (2) becomes:

$$I_R/\omega^2 \propto \sum_b g_b(\omega) \quad (4)$$

Assuming that the bands  $b$  have the same proportional dependence then the function  $I_R/\omega^2 \propto g(\omega)$  in the low frequency region and thus may be used for the calculation of specific heat values<sup>12</sup>.

## EXPERIMENTAL

Low frequency depolarized Raman spectra ( $I_{\text{VH}}$ ) in the frequency region  $5 < \Delta\bar{\nu} < 200 \text{ cm}^{-1}$  were obtained from a Cary 82 triple monochromator spectrometer. The sample was illuminated by an argon-ion laser beam (model 164 Spectra-Physics) operating on the green 514.5 nm line and with an output power between 400 and 600 mW. A continuous flow cryostat (Oxford Instruments CF 104) was used for the low temperature Raman scattering measurements. The temperature accuracy was within  $\pm 2 \text{ K}$  over the period recording the spectrum. The uncertainty due to the temperature gradient between the position of the temperature sensor and the scattering volume was estimated to be  $\pm 5 \text{ K}$ .

Polycarbonate-bisphenol A manufactured by the General Electric Co. under the commercial name Lexan was supplied in the form of a clear transparent sheet. Gel permeation chromatography (g.p.c.) determined an approximate molecular weight of  $3 \times 10^4$ . X-ray diffraction showed no evidence of order in the sample. The sample that was used in the Raman scattering experiment was cut into a cube shape of  $1 \text{ cm}^3$  dimensions and polished to a good optical finish.

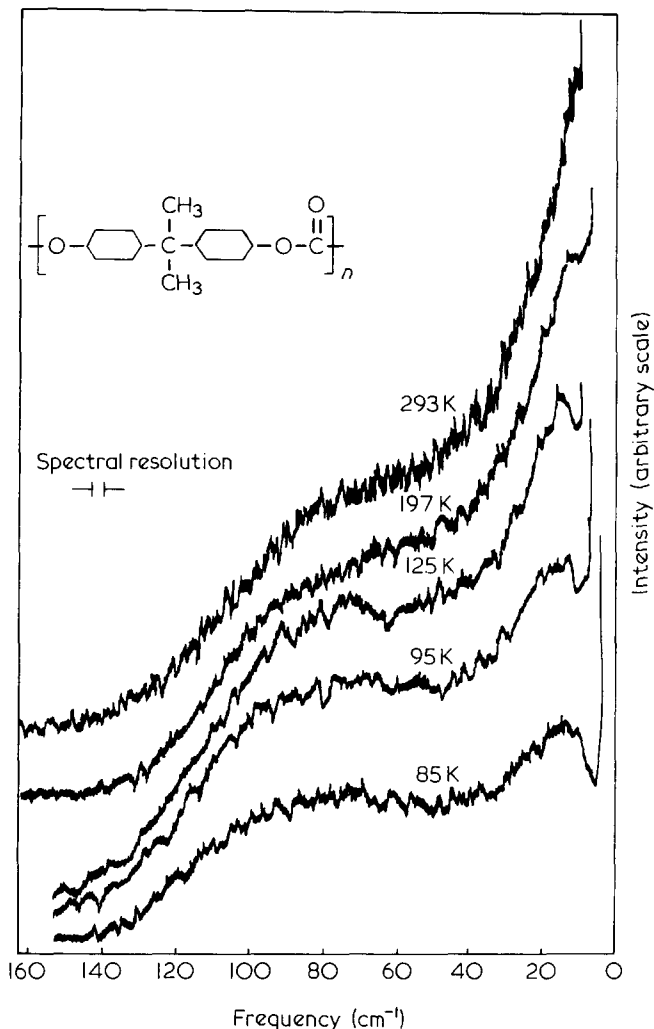


Figure 1 Low frequency Raman spectra from amorphous polycarbonate at temperatures of 293 K, 197 K, 125 K, 95 K, 85 K

RESULTS

Low frequency depolarized Raman scattering spectra from amorphous solid polycarbonate were recorded at temperatures of 293 K, 197 K, 125 K, 95 K and 85 K and are shown in Figure 1. The broad Rayleigh line at high temperatures screens the low frequency features of the spectrum below 30 cm<sup>-1</sup>. As the temperature is reduced the spectra become better resolved and a second peak appears at about 17 cm<sup>-1</sup>. The Stokes reduced intensity spectra was calculated for the four temperatures and the  $I_R$  spectra show a maximum at about 96 cm<sup>-1</sup> (Figure 2). The band at 96 cm<sup>-1</sup> also appears in the far-infrared spectrum. Another weaker and narrower band makes its appearance at 169 cm<sup>-1</sup>, which is absent in the Raman spectrum, while the broad width of the FIR 96 cm<sup>-1</sup> band might possibly obscure a narrow band at lower frequency. The similarity in the shape of the  $I_R$  curves (within experimental error) demonstrates a first order scattering behaviour. The asymmetric shape of the reduced intensities reveals the existence of at least two major overlapping bands. Assuming a symmetric shape for the band around 96 cm<sup>-1</sup>, a second band is thus resolved at 45 cm<sup>-1</sup> as seen in Figure 3, a similar method has been used by Furakawa *et al.*<sup>13</sup>. At very low frequencies the strong Rayleigh line obscures the Raman scattering intensities. An approximation needs to be made for the

shape of the Rayleigh wing by estimating the extrapolation to the base line. The same procedure has been adopted also by other workers such as Fraser<sup>14</sup> and Snyder *et al.*<sup>15</sup>.

The values of  $I_R/\omega^2$  are plotted in Figure 4 and these also demonstrate a first order temperature dependence. In the continuous broad distribution of the density of states,  $I_R/\omega^2$  with frequency shift, two distinct regions are distinguished: the low frequency region below 50 cm<sup>-1</sup> and the higher and broader region extending up to about 150 cm<sup>-1</sup>.

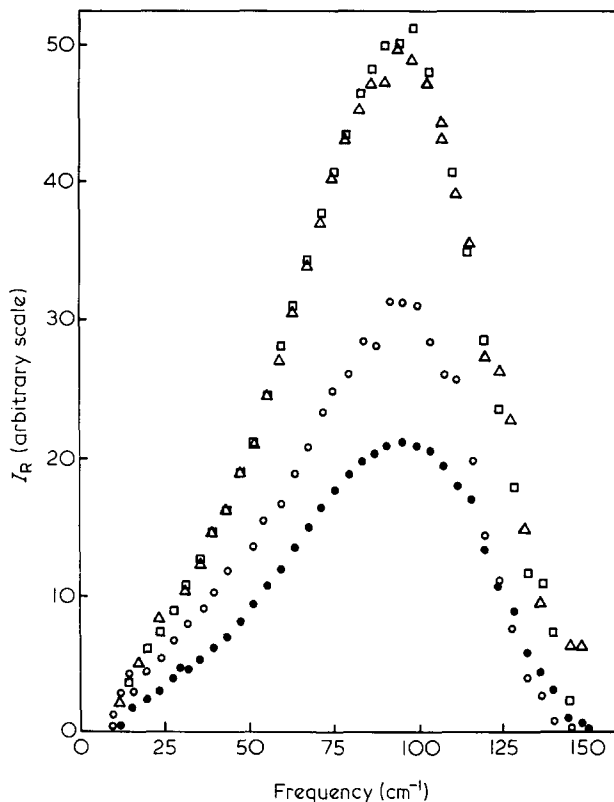


Figure 2 Reduced Raman scattering intensities  $I_R$  from amorphous polycarbonate at temperatures 197 K (O), 125 K (□), 95 K (Δ), 85 K (●)

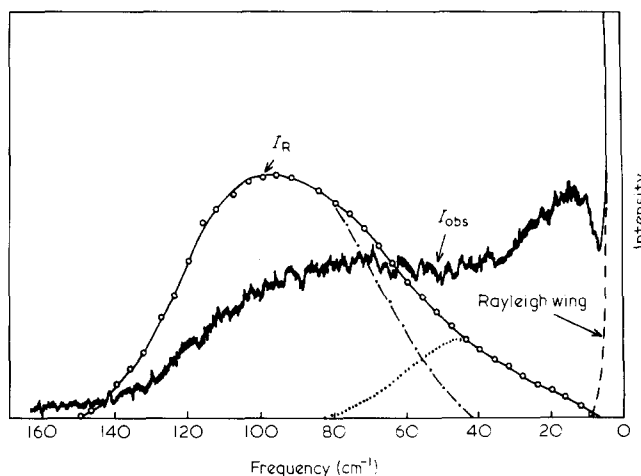
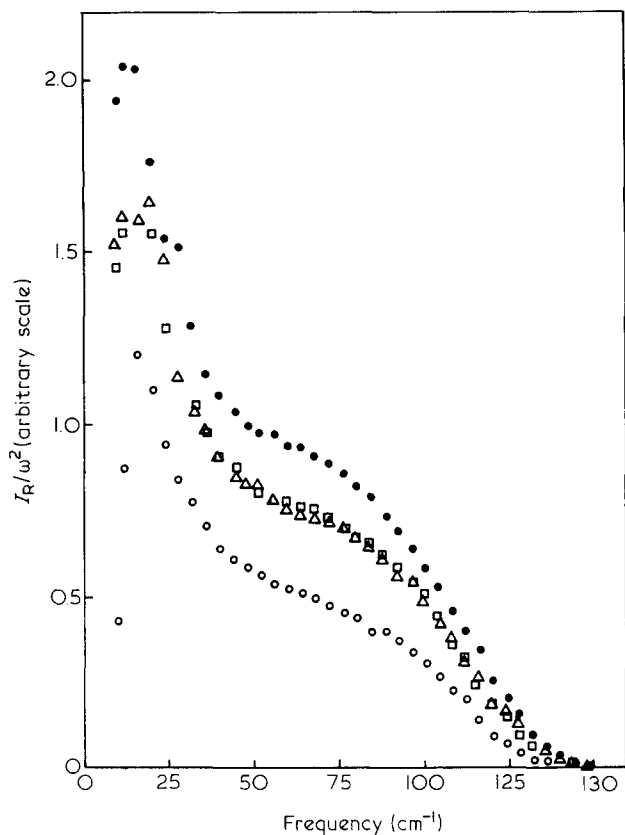


Figure 3 Low frequency Raman spectrum for polycarbonate at 85 K. The reduced intensity  $I_R$  is resolved into two peaks centered at about 96 cm<sup>-1</sup> (---) and 45 cm<sup>-1</sup> (.....)



**Figure 4** The function  $I_R/\omega^2$  for amorphous polycarbonate at temperatures of (O) 197 K, (□) 125 K, (△) 95 K and (●) 85 K

## DISCUSSION

There are some similarities between the Raman spectrum from polycarbonate, and that from poly(methyl-methacrylate)<sup>12</sup>. They both show two characteristic features at frequencies below  $200\text{ cm}^{-1}$ : in PMMA a broad band is centered around  $80\text{ cm}^{-1}$  and a narrow band at about  $17\text{ cm}^{-1}$ . The peak at  $17\text{ cm}^{-1}$  in the polycarbonate spectrum appears to have a stronger relative intensity than the one in the PMMA spectrum.

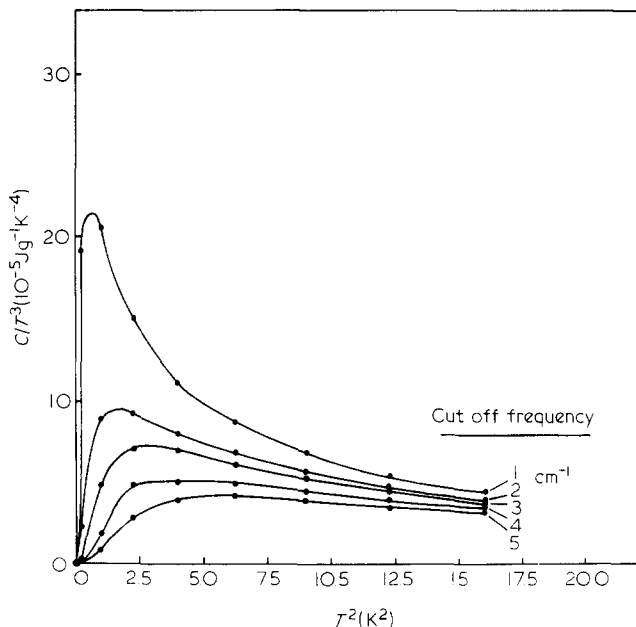
The specific heat  $C_v$  has been calculated through relation (1), for temperatures  $T < 4\text{ K}$ . Values for the density of states,  $g(\omega)$ , were calculated from the reduced intensities  $I_R$  through equation (4). The function  $I_R/\omega^2$  was thus calculated for cut-off frequencies from  $1\text{--}5\text{ cm}^{-1}$  at  $1\text{ cm}^{-1}$  intervals and normalized to unity. A similar technique has been used previously<sup>12</sup>. The normalized  $I_R/\omega^2$  was then identified with the density of states  $g_N(\omega)$  of one repeat unit in the polymer chain. If we assume that the vibrating unit associated with the Raman band is a repeat unit of the polymer<sup>16</sup> and also that all vibrating units contribute to the spectrum, then the density of states is:

$$g(\omega) = Ng_N(\omega) \quad (5)$$

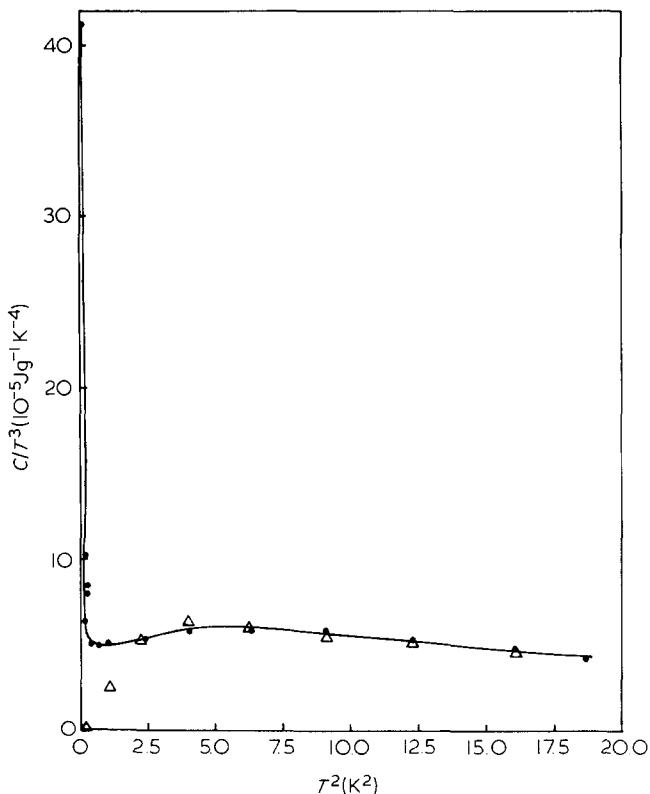
The parameter  $N$  represents the number of repeat units per gram and is used as a fitting parameter. The values of  $C/T^3$  calculated in this way (for cut-off frequency  $4\text{ cm}^{-1}$ ), **Figure 5**, vary with temperature in a similar manner as the calorimetrically observed specific heat<sup>17</sup> in the temperature range  $1.5\text{ K} < T < 4\text{ K}$  as seen in **Figure 6**. In **Figure 6** the specific heat of the polycarbonate obtained from Raman data is fitted to the calorimetric data. The

Raman data were normalized to the calorimetric values by varying the parameter  $N$  in equation (5). The Raman derived  $C/T^3$  values are not directly the 'excess' specific heat above the expected Debye value. The actual Raman values for  $C/T^3$  are slightly smaller than the calorimetric values by about 17%.

It is usually assumed that the Raman scattering intensities decrease near zero frequencies. If a vibrational mode exists in the frequency region  $\Delta\bar{\nu} < 8\text{ cm}^{-1}$  it could



**Figure 5** Specific heat of amorphous polycarbonate shown as  $C/T^3$  with temperature squared at cut-off frequencies from 1 to  $5\text{ cm}^{-1}$



**Figure 6** Specific heat of amorphous polycarbonate as  $C/T^3$  with  $T^2$  variation. △ Raman data; ○ data from Cieloszyk *et al.* (ref. 17); ● data from Stephens (ref. 19)

contribute to the specific heat to account for the above differences and bring the  $C/T^3$  Raman values coincident with the calorimetric values. Instrumental limitations though do not allow the investigation of Raman scattering in this very low frequency region.

It is interesting to compare the frequencies where the two peaks occur in the reduced spectrum with the Debye frequencies calculated<sup>18</sup> through the formula:

$$\bar{\nu}_D = \frac{v}{2\pi c} \left[ \frac{2\pi^2 N \rho n}{M_0 m} \right]^{1/3} \quad (6)$$

where  $v$  is the mean sound velocity,  $M_0$  the monomer unit weight,  $N$  Avogadro's constant and  $\rho$  the mass density of the polymer. The numbers  $n$  and  $m$  represent the number of degrees of freedom per vibrating unit and the number of molecules per vibrating unit, respectively. Data were obtained by Cieloszyk *et al.*<sup>17</sup>. By substituting  $v = v_t$ , where  $v_t$  is the transverse wave sound velocity, and  $n = 4$ ,  $m = 1$ , the Debye frequency is  $\bar{\nu}_D = 44 \text{ cm}^{-1}$ . Substituting  $v = v_l$ , the longitudinal sound velocity, the Debye frequency is calculated to be  $\bar{\nu}_D = 93.5 \text{ cm}^{-1}$ ; both values are near to the two Raman frequencies in the reduced intensity spectrum.

Similar calculations have been made for poly(methyl methacrylate)<sup>12</sup> and Debye frequencies near to the Raman frequencies in the low frequency spectrum were also obtained. Polystyrene is another example where the calculated Debye frequency of  $86 \text{ cm}^{-1}$  (for  $n = 6$ ,  $v = 1.67 \cdot 10^5 \text{ cm s}^{-1}$ <sup>19</sup>, and assuming that the vibrating unit is the aromatic side group) coincide with the observed frequency in the reduced Raman spectrum of Spells *et al.*<sup>4</sup>. On the other hand if the vibrating unit is taken as the whole repeat unit in the polystyrene chain, the calculation yields a Debye frequency of  $\sim 73 \text{ cm}^{-1}$ . This is the frequency where approximately the sharp peak in the low frequency Raman spectrum of crystalline isotactic PS should occur in the reduced intensity spectrum.

In all of these examples the value of  $n$  is either 6 or 4 whereas the vibrating unit is either the whole repeat unit or just the side group. The similarity in the low frequency Raman scattering behaviour of different glassy polymers and the corresponding Debye frequencies is interesting but does not provide sufficient information to classify the existence of the two low frequency Raman peaks in terms of certain structural dynamic mechanisms. It seems likely that phonon waves are responsible for the two Raman bands in the low frequency spectrum. Vibrations of

various degrees of freedom which could be separated into the two main types of backbone or side group motion, can contribute to these bands. In the case of polycarbonate there is furthermore evidence that the transverse sound wave is responsible for the small peak while the higher frequency band is due to the longitudinal sound waves. The picture of phonon-like waves in the low frequency Raman region acting as heat carriers at temperatures  $T < 4 \text{ K}$  in glassy polymers is supported by the agreement between specific heat calculation from Raman data and the calorimetric specific heat values and also the fact that the Debye frequencies fall in the region  $\Delta\bar{\nu} < 200 \text{ cm}^{-1}$ .

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