

Boson Peak in Low-Frequency Raman Spectra of Polymethylmethacrylate

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Abstract—The role of the local field, anharmonicity, and degree of disorder in the formation of the boson peak has been studied. The low-frequency Raman spectrum of a model polymethylmethacrylate crystal with disorder elements was calculated using the method of atom-atom potentials taking into account the effect of local fields on the spectrum. The calculations were carried out for a crystal containing rigid molecules of an isotactic polymethylmethacrylate oligomer and for a structure with flexible molecules.

Keywords: boson peak, Raman spectra, anharmonicity, modeling.

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INTRODUCTION

The low-frequency Raman spectra (RS) and infrared absorption spectra of disordered materials (amorphous, glassy, polymers) have a broad band referred to as the boson peak [1–8]. The boson peak reflects the fundamental properties of the medium and is associated with the excess density of vibrational states.

The temperature dependence of the shape of the boson peak is most often analyzed using the theory proposed in [9]. The model of harmonic oscillators identified with quasi-local vibrations of various large-scale structural groups in disordered media has been used to describe the mechanism of the occurrence of the boson peak, its universal form, position, and width. The anharmonicity (A) in the interaction of the oscillators and the assumption that they are affected by a random statistical force were additionally taken into account. These assumptions make it possible to explain the universal shape of the boson peak its position (ω^*) and width taking into account the anharmonicity parameter, the random force distribution width δf and the reduced mass M of the harmonic oscillator:

$$\omega^* = \sqrt{3A^{1/6}(\delta f)^{1/3}/\sqrt{M}}. \quad (1)$$

Experimental data have shown that theory [9] gives satisfactory agreement not for all disordered media. It was necessary to introduce additional parameters that take into account anharmonicity [10], the rigidity of structural of structures [11], and the temperature dependence of the phonon state density [12]. With a large number of parameters, the predictive attractiveness of theoretical conclusions weakens. It is of interest to clarify the contributions of different mechanisms to the shape of the boson peak and the conditions of their strongest manifestation.

Currently, the easiest way to do this is by studying molecular compounds, because, first, theory for them has been developed and programs for calculating optical and dynamic properties have been designed that give results in excellent agreement with experimental data; second, they are characterized by a low melting temperature, so that at room temperature, their anharmonicity cannot be ignored; third, molecules with branched end groups have a flexible structure. According to [13], the scattered light intensity is proportional

to the density of vibrational states $g(\nu)$ and the matrix element of the coupling $C(\nu)$ of vibrational modes with light:

$$J(\nu) = g(\nu)C(\nu)[n(\nu) + 1]/\nu, \quad (2)$$

which makes it possible to determine $C(\nu)$.

For ordered molecular crystals, $g(\nu)$ is calculated from data by solving the dynamic problem, and $C(\nu)$ is described by a second-rank tensor. Its elements are proportional to the derivatives of the dielectric susceptibility with respect to the normal coordinate.

For molecular crystals, the susceptibility depends on the polarizability of molecules, the local field, and the distance between molecules [14]. In this work, using the methods developed in [14] to solve the dynamic and electrooptical problem, we calculated the contributions of each of the parameters (normal vibration modes, dependences of the derivatives of the dielectric susceptibility with respect to the normal coordinate, anharmonicity) that affect the position and shape of the boson peak.

The study subject was polymethylmethacrylate (PMMA), for which the frequency dependence $C(\nu)$ was determined experimentally [12]. Results of X-ray diffraction studies are presented in [15]. Conformational characteristics are described in [16, 17].

CALCULATION OF THE VIBRATION INTENSITY

The most effective way to determine the low-frequency spectrum of disordered media is Dean's method [18]. The idea of the computational procedure based on this method is as follows: the center of gravity is determined from data [15] (bond lengths and angles of the PMMA monomer) and the coordinates of the atoms relative to it are calculated. Next, the other molecules surrounding the molecule are determined using the multiplication rules. Specifying the arrangement of atoms in the molecule and taking into account the field of intermolecular forces, we obtain the elements of the dynamic matrix.

The interaction potential is represented in the form [19, 20]

$$U = U_s + U_b + U_t + U_{vdW} + U_e, \quad (3)$$

where U_s , U_b , U_t , U_{vdW} , and U_e are the potential energies of the valence bonds, valence and torsion angles, the van-der-Waals interactions, and Coulomb forces, respectively:

$$U_s = 1/2 \sum_1^N K_s (r_k - r_e)^2 \quad (4)$$

(K_s is the rigidity of the valence bond, k is the bond number in the molecule, N is the number of valence bonds, r_k is the bond length, r_e is the equilibrium bond length);

$$U_b = 1/2 \sum_1^M K_b (\alpha_m - \alpha_e)^2 \quad (5)$$

(K_b is the elasticity of the bond angle, m is the bond angle number, M is the number of bond angles, α_m is the value of the bond angle, α_e is its equilibrium value);

$$U_t = 1/2 \sum_n K_t (1 + \cos(n^\theta \vartheta + \delta_n)) \quad (6)$$

(K_t is a constant);

$$U_e = \sum_{i \neq j} \frac{q_i}{r_{ij}} q_j \quad (7)$$

(q_i, q_j are the partial charges).

In the calculations, we used the values of the coefficients obtained in [16] for the potentials U_s, U_b, U_t , and U_e .

The Van-der-Waals intermolecular interactions was described using the atom-atom potential method [21]. The interatomic interaction potential U_{vdW} was used in the form

$$U_{vdW} = \sum_{i,j} \left(\frac{-A_{ij}}{r_{ij}^6} + B_{ij} \exp(-c_{ij}r_{ij}) \right). \quad (8)$$

The calculations of U_{vdW} were carried out using the following coefficients [22]: $A_{CC} = 370 \text{ kcal} \cdot \text{\AA}^6/\text{mol}$, $B_{CC} = 68700$, $C_{CC} = 3.6 \text{ \AA}^{-1}$, $A_{HH} = 31 \text{ kcal} \cdot \text{\AA}^6/\text{mol}$, $B_{HH} = 3890 \text{ kcal/mol}$, $C_{HH} = 3.76 \text{ \AA}^{-1}$, $A_{OO} = 420 \text{ kcal} \cdot \text{\AA}^6/\text{mol}$, $B_{OO} = 82000 \text{ kcal/mol}$, $C_{OO} = 3.9 \text{ \AA}^{-1}$.

The force constants in the equations of motion of the molecules were determined by direct differentiation of the potential energy written in the form of pairwise atom-atom interactions.

The number of atoms in the structure was about 15 000 because with a further increase in the number of atoms, the elements of the dynamic matrix did not change. In the calculation of the spectrum of vibrations, the resulting structure was considered as a single molecule, the interactions between atoms within the monomers were calculated using formulas (3)–(7), and the interactions between monomers were calculated as van-der-Waals interactions using (8).

In the calculation of the frequency spectrum in the rigid molecule approximation, changes in the monomer conformations were not allowed. In the case of flexible molecules, changes in the bond angles and lengths were taken into account.

The disordered PMMA crystal was a structure consisting of flexible molecules with orientational and translational disorder.

The eigenvalues of the matrices of disordered structures were determined using the Dean method. Based on the calculations (of the density of vibrational states), histograms were obtained which show the probability of the occurrence of spectral line frequencies in the selected frequency range.

The Raman spectrum is described by three parameters: frequency, intensity, and line width. The line intensity is proportional to the derivative of the susceptibility with respect to the normal coordinate.

Calculating the intensity for each vibration, we obtain the desired range. It should be borne in mind that the scattered radiation intensity depends on the tensor of the effective field, the structural Lorentz factor, which is expressed in terms of lattice sums and their derivatives with respect to the normal coordinate, and the magnitude of the effective polarizability and its derivative. A detailed description is given in [14].

In Fig. 1, curve 1 represents the calculated spectrum of an ordered PMMA crystal with rigid molecules; curve 2 shows the calculated density histogram of the vibrational states $g(\omega)$ of disordered PMMA with flexible molecules; curve 3 is the calculated intensity of the low-frequency Raman spectrum of this PMMA with consideration of the anharmonicity of the vibrations and the local field at a temperature of 300 K. As we can see, the theoretical (curve 3) and experimental (curve 4) [1] results are practically the same.

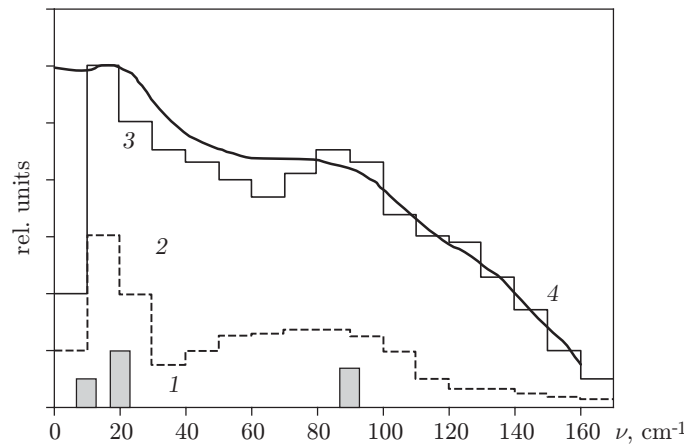


Fig. 1.

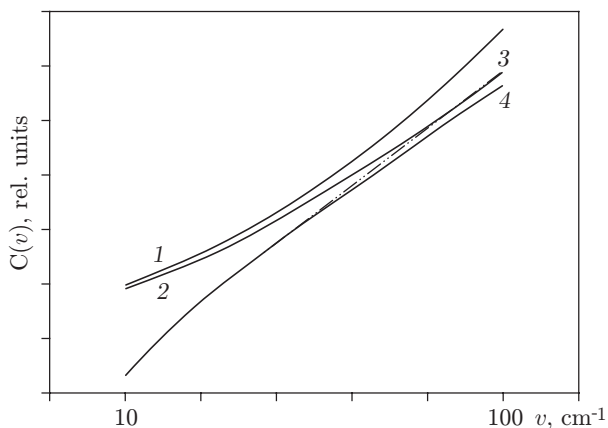


Fig. 2.

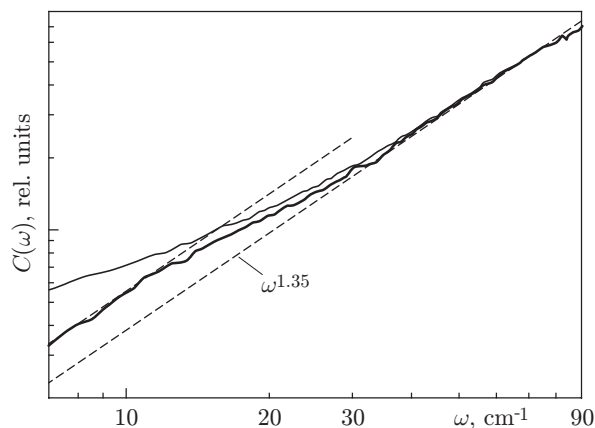


Fig. 3.

DISCUSSION OF THE RESULTS

In the calculation of crystalline polymethylmethacrylate with one rigid molecule in the cell, lines were obtained around frequencies of 7, 20, and 90 cm^{-1} of orientation vibrations (see Fig. 1, curve 1). Accounting for the anharmonicity of vibrations does not introduce significant changes to the calculated spectrum. The shift does not exceed 2 cm^{-1} .

In Fig. 1, curve 4 represents the experimental Raman spectrum of polymethylmethacrylate at a temperature of 300 K [1]. Comparison of curves 1 and 4 shows that for an ordered crystal with rigid molecules, the spectrum of PMMA is different from the experimental one. Therefore, we considered a flexible molecule of polymethylmethacrylate. Since the end groups of atoms of the flexible molecule are more mobile, the potential energy of intermolecular interactions has several minima, resulting in disorder in the structure of PMMA with flexible molecules.

The spectrum of polymethylmethacrylate taking into account the disorder in the arrangement of flexible molecules, anharmonicity, and local fields in the calculation of the intensities of lines is shown in Fig. 1, curve 3. As can be seen, it is consistent with the experimental spectrum of the boson peak of PMMA (curve 4). This shift of the maxima of the lines reaches 30 cm^{-1} , which indicates the importance of taking into account the flexibility of the molecules. In this case, the interaction potential has several minima.

Thus, the boson peak reflects the vibrational properties of the medium and is related to the excess density of vibrational states due to the absence of long-range order. The selection rules for the phonon wave vector k are not satisfied due to violation of the translational symmetry, and all phonon states can be involved in light scattering. Accounting for local fields for the disordered polymer also affects the occurrence of additional vibration density and changes in the intensity of the lines.

An important factor in the temperature dependence of the intensity $J(\nu)$ is $C(\nu)$. The dependence $C(\nu)$ for glass was investigated in [23]. The changes in the value of $C(\nu)$ with varying frequency and temperature were calculated. The behavior of $C(\nu)$ with temperature can show the role of anharmonicity in the calculation of the spectrum with flexible molecules.

Figure 2 shows curves of $C(\nu)$ versus frequency neglecting anharmonicity at a temperature of 300 K (curve 2) and taking into account anharmonicity (curve 1). The results of similar calculations at a temperature of 30 K show that at lower temperatures, anharmonicity plays a less significant role. The dependence of $C(\nu)$ on frequency at 30 K neglecting anharmonicity is shown by curve 4, and taking into account anharmonicity by curve 3 (the plots are on a logarithmic

scale). The results agree with the experimental data given in [12] (Fig. 3).

CONCLUSIONS

The calculation of the vibration spectrum of PMMA using the atom-atom potential method showed that the broad bands in the spectrum of PMMA may be due to vibrations of flexible chains of oligomers, with disorder and anharmonicity taken into account. Local fields play an important role in the increase in the density of vibrations. Consequently, for substances with flexible molecules, the main contribution to the boson peak is explained by the multi-minimum energy potential. Anharmonicity makes a significant contribution at high temperatures, due to the temperature dependence of $C(\nu)$.

