EFFECT OF LOADING ON THE VIBRATIONS OF THE MOLECULES OF CERTAIN POLYMERS WITH A PLANE ZIGZAG SKELETON

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The main-chain vibrational frequency shifts are calculated on the basis of a simplified model for a series of loaded polymers with a plane zigzag skeleton. The dispersion curves and distribution functions for the free and loaded molecules are compared.

It has been experimentally established that stretching polymer molecules leads to a shift of the vibration frequencies active in infrared spectroscopy [1, 2]. This shift is chiefly caused by a change in the stiffness of the molecule and to a lesser extent by a change in the kinematic interactions. The relation between the frequency shift of the skeletal vibrations and the tensile load has already been estimated for polyethylene and polyoxymethylene [3] and similar calculations have also been made for polypropylene [4]. A shift of the optically active frequencies under load has also been observed in connection with a series of polymers of the type \((-\text{CR}_1\text{CR}_2-)\)\(^n\). Accordingly, using a simplified model of the molecule, we have investigated the effect of loading on the normal vibrations of certain materials of this kind. The dependence of the frequency shifts on the tensile load, together with the corresponding dispersion curves, can be used in analyzing the vibrational spectra of the loaded molecules. The frequency distributions as a function of the tensile load, obtained on the basis of the dispersion curves, are useful for estimating the potential of the inelastic neutron scattering method in relation to the investigation of loaded polymers, as well as in studying their thermodynamic properties.

Choice of Model

When a tensile load is applied along the axis of a polymer molecule, its skeleton is most strongly deformed. This leads, in particular, to a frequency shift that affects the skeletal vibrations but not those of the side groups. The intermolecular forces do not have much effect on the frequency shift. Thus, in order to calculate the vibrational spectrum of the loaded molecule it is logical to choose a simplified model that describes only the vibrations of the main chain. We propose to employ a universal model consisting of an infinite two-dimensional zigzag chain with tetrahedral angles and two atoms in the unit cell [5]. The masses \(m_1\) and \(m_2\) are equal to the masses of the groups \(R_1\) and \(R_2\), respectively, which are regarded as simple dynamic units. The fact that the exact and not the reduced group masses are employed gives values of the frequencies and the frequency shifts that are somewhat too low when the interactions in the main chain and the side groups are quantities of the same order, but does not affect the relative value of the frequency shifts. The valence-force field is taken in its simplest form, i.e., only the diagonal terms of the force constant matrix are nonzero. Values of the force constants are taken from [5].

This model describes the skeletal vibrations most accurately if they are not intermixed with substituent vibrations. Nonetheless, in the first approximation it can be used to establish the principal features of the behavior of the normal vibrations of loaded polymer molecules, including those for which a detailed vibrational analysis has not been made.

Calculation Procedure

Free Molecule. In this case the vibrational spectrum is obtained by solving the secular equation for the one-dimensional crystal-molecule [5]

$$|D(\delta) - \lambda(\delta)I| = 0,$$  \hspace{1cm} (1)

where \(D(\delta)\) is the dynamic matrix; \(\delta\) is the phase difference between neighboring unit cells in the chain; \(I\) is the unit matrix; the order of the matrices is \(3n\), \(n\) is the number of atoms in the unit cell.

$$\lambda_i(\delta) = 4\pi^2 c^2 \nu^2(\delta).$$  \hspace{1cm} (2)

Here, \(\nu_i(\delta)\) is the wave number; \(c\) is the speed of light; the index \(i\) is used to number the frequency branches. Since \(\nu_i(\delta) = \nu_i(-\delta)\), the dispersion curves can be obtained by solving Eq. (1) in half the Brillouin zone \(0 \leq \delta \leq \pi\). The vibrations with \(\delta = 0\) are potentially active in infrared spectroscopy. For a one-dimensional crystal with two atoms in the unit cell not lying on the axis of the molecule we get two optical (\(\perp\) and \(\parallel\) vibrations) and four acoustic vibrational branches corresponding to rotation of the molecule about the axis and translation in the three Cartesian axes at \(\delta = 0\).

Equation (1) for the complex matrix is equivalent to the real equation [6]

$$\begin{vmatrix}
D'(\delta) - \lambda(\delta)I & -D''(\delta) \\
D''(\delta) & D'(\delta) - \lambda(\delta)I
\end{vmatrix} = 0,$$  \hspace{1cm} (3)

where \(D'(\delta) = \text{Re}D(\delta); \ D''(\delta) = \text{Im}D(\delta)\).

The dispersion curves serve as a basis for constructing the normal vibration frequency distribution functions

$$D(\nu) = M \sum_i \Delta \delta_i(\nu).$$  \hspace{1cm} (4)

Here, \(\Delta \delta_i(\nu)\) is the number of vibrations of the \(i\)-th branch corresponding to the frequency interval \(\nu - \nu' + \Delta \nu\); the normalizing factor \(M\) is so selected that the total number of vibrations \(3N = \int D(\nu) d\nu\); \(N\) is the number of atoms in the chain.

Loaded Molecule. Stretching the molecule leads to a change in its geometry and hence to a change in the interactions. The potential energy for uniformly deformed polymer molecules is known [7]. The vibrational spectrum of the loaded molecule is the spectrum of the small vibrations about the equilibrium position corresponding to the deformed configuration. This can be calculated in the same way as the spectrum of the unloaded molecule if the values of the force constants and geometric parameters of the deformed molecule are introduced into (1).

For small deformations the potential energy function can be expanded in a series. The variation of the internal coordinates (valence bonds, valence angles, internal rotation angles) is determined by the system of equilibrium equations

$$\frac{\partial V}{\partial \rho_j} = f_j,$$  \hspace{1cm} (5)

where \(V\) is the deformation potential energy; \(\rho_j\) is a small but finite change of the \(j\)-th internal coordinate; \(f_j\) is the load component corresponding to \(\rho_j\). System of equations (5) reduces to the form

$$\frac{\partial V(\rho)}{\partial \rho_j} = \sum_j F_{j'}(\rho) \rho_j = f_j,$$  \hspace{1cm} (6)