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Phonon mode coupling and Fano-type antiresonance in polyethylene

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With 6 figures

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I. Introduction

Polyethylene (PE) is a nonpolar partially crystalline polymer. The crystalline regions have lateral dimension of several hundred Ångströms and are embedded in an amorphous polymer matrix. Crystalline polyethylene belongs to the orthorhombic crystal system with point group D_{2h} . In the far infrared spectral region PE shows a strong absorption line at 73 cm^{-1} and a very weak band at 109 cm^{-1} , which is observable only at low temperature up to about 120 K [1, 2]. Both bands are superimposed on a continuous background absorption. They have been recognized to result from external lattice vibrations of the crystalline portions of the polymer [3, 4]. The corresponding optical phonons belong to the B_{1u} (73 cm^{-1}) and B_{2u} (109 cm^{-1}) representations of D_{2h} , where, as shown in figure 1, the two sublattices vibrate along the b -axis and in a -axis direction, respectively. The transition dipole moments of both modes are normal to the elongations of the PE-chains.

A recent detailed investigation of the temperature dependence of the far infrared absorption of PE by Frank et al. has revealed several remarkable features of the structure of the absorption which have not yet been satisfactorily explained [5]. Figure 2 shows the absorption coefficient of PE as a function of frequency for several temperatures between 4 K and 414 K, just below the melting temperature $T_m = 430\text{ K}$. The weak B_{2u} -band decreases with rising temperature and vanishes at 120 K. The absorption strength of the B_{1u} -band is constant up to 80 K. Above that temperature the absorption decreases gradually

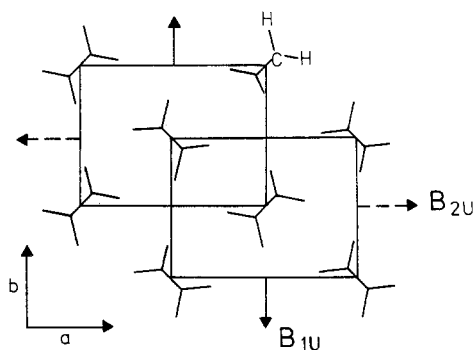


Fig. 1. Cross section of unit cell of PE. The arrows indicate the translational motion of the B_{1u} (73 cm^{-1}) phonon (full arrow) and the B_{2u} (109 cm^{-1}) phonon (broken arrow)

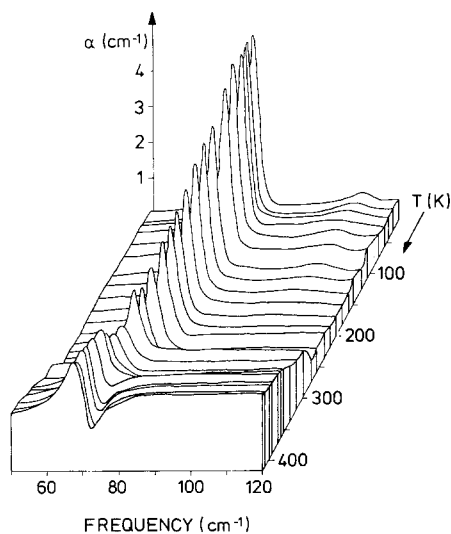


Fig. 2. Far infrared absorption of PE (6011 L) at various temperatures after [5]

in contrast to the behaviour of the absorption strength of a usual Reststrahlen-phonon. The absorption line is symmetric up to 310 K as it is expected for a narrow one phonon line. Above 310 K the line becomes more and more asymmetric and a pronounced antiresonance emerges at the high frequency wing of the line, which becomes deeper with rising temperature. In the following we will give a conceivable explanation for this anomalous behavior of the B_{1u} -line within the framework of a simple phenomenological theory.

II. Theory

The strong antiresonance suggests an explanation according to Fano's treatment of interference distortion of atomic transitions [6]. Basically the line shape of a transition between discrete energy levels may be distorted by interference of the states of the discrete spectrum with those of a continuous spectrum. Similar effects have also been found for various interacting excitations in solids [7, 8]. The measurements shown in figure 2 represent the first observation of a Fano-type antiresonance in a polymer.

For polyethylene we assume that the amplitude X_0 of the B_{1u} optical phonon is linearly coupled with the amplitudes X_μ of an infrared active continuum of vibrational modes. This continuum is at least partially responsible for the continuous background absorption. The most general dynamical equation of the coupled vibrational modes driven by an external electric field E has in quasi harmonic approximation the form

$$\begin{aligned}
 (\omega_0^2 - \omega^2 - i\omega\gamma_0)X_0 + \sum_{\mu} L_{0\mu}X_{\mu} &= Z_0E \\
 L_{\mu 0}X_{\mu} + (\omega_{\mu}^2 - \omega^2 - i\epsilon)X_{\mu} &= Z_{\mu}E \\
 \mu = 1 \dots N &
 \end{aligned}
 \tag{1}$$

where Z_0 and Z_{μ} are suitably normalized effective charges [9] containing local field corrections, and $L_{0\mu} = L_{\mu 0}$ are phenomenological coupling coefficients being generally complex. The resonance frequency and the damping constant of the uncoupled discrete phonon of amplitude X_0 are ω_0 and γ_0 , respectively, ω_{μ} is the frequency of a continuum vibration and ϵ is infinitesimal as we will not take into account explicitly a finite

damping of the continuum modes. Our model defined by equation 1 is an extension of *Barker* and *Hopefield's* theory of the infrared dispersion of coupled optical phonons [9]. A mechanical analogue of the coupled system of oscillators may be set up as shown figure 3. Elongation of a continuum vibration exerts a force on the discrete oscillator and the elongation of the discrete mode exerts forces on all continuum modes according to the coupling coefficients $L_{0\mu}$. The coupling establishes fixed phase relations among the modes. The antiresonance in the absorption spectrum occurs due to destructive interference of the dipole moments of the discrete phonon Z_0X_0 and those of the continuum modes $\sum_{\mu} Z_{\mu}X_{\mu}$.

The electric susceptibility of the system of coupled oscillators is given by

$$\chi = \sum_{i,j=0}^N Z_i G_{ij} Z_j + \chi_{\infty}
 \tag{2}$$

where χ_{∞} is the (real) susceptibility at optical frequencies and the response matrix $\underline{G} = G_{ij}$ of the coupled system is defined by

$$\underline{G}^{-1} = \begin{pmatrix} g_0^{-1} & L_{01} & \dots & L_{0N} \\ L_{10} & g_1^{-1} & 0 & \dots & 0 \\ \vdots & 0 & \ddots & & \\ L_{N0} & \vdots & & g_N^{-1} & \end{pmatrix}
 \tag{3}$$

Here $g_0 = (\omega_0^2 - \omega^2 - i\omega\gamma_0)^{-1}$ and $g_{\mu} = (\omega_{\mu}^2 - \omega^2 - i\epsilon)^{-1}$ are the classical response functions of the uncoupled discrete phonon and the continuum vibrations, respectively.

The matrix \underline{G} can easily be determined. We find:

$$G_{00} = G_0$$

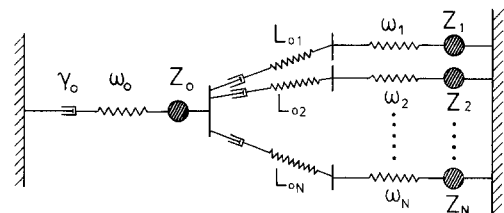


Fig. 3. Mechanical model illustrating the coupled oscillator system defined by equation 1

$$\begin{aligned}
 G_{0\mu} &= -L_{0\mu}g_{\mu}G_0 \\
 G_{\mu\gamma} &= g_{\mu}\delta_{\mu\gamma} + L_{0\mu}g_{\mu}L_{0\gamma}g_{\gamma}G_0 \\
 \mu, \gamma &= 1 \dots N.
 \end{aligned} \tag{4}$$

In these expressions

$$G_0 = (g_0^{-1} - \Delta)^{-1} = (\Omega_0^2 - \omega^2 - i\omega\Gamma_0)^{-1} \tag{5}$$

with

$$\Delta = \Delta' + i\Delta'' = \sum_{\mu=1}^N L_{0\mu}^2 g_{\mu}$$

$$\Omega_0^2 = \omega_0^2 - \Delta',$$

$$\omega\Gamma_0 = \omega\gamma_0 + \Delta'' \text{ and}$$

$\delta_{\mu\gamma}$ is the Kronecker symbol.

Inserting the response function equation 4 into equation 2 we can write the electric susceptibility as a sum:

$$\chi = \chi_c + \chi_a + \chi_{\infty} \tag{6}$$

where

$$\chi_c = \sum_{\mu=1}^N Z_{\mu}^2 g_{\mu} \tag{7}$$

is the contribution of the vibrational continuum and

$$\chi_a = F_0^2 G_0$$

with $F_0 = Z_0 - \Delta$ and

$$A = \Delta' + i\Delta'' = \sum_{\mu=1}^N Z_{\mu} L_{0\mu} g_{\mu} \tag{8}$$

is the susceptibility due to the discrete phonon. Equations 7 and 8 shows that χ_c is unaffected by the interaction whereas the response of the discrete phonon is renormalized. The resonance frequency and the damping constant of the interacting discrete phonon are $\Omega_0 = \omega_0 - \Delta'$ and $\Gamma_0 = \gamma_0 - \Delta''/\omega$, respectively, where the "self energy" Δ depends only on the coupling coefficients $L_{0\mu}$. Thus the frequency renormalization may occur even if the continuous spectrum is optically inactive as it is usually the case if a well defined excitation interacts with a continuum. The coupling also changes the effective charge of the discrete phonon which becomes $F_0 = Z_0 - \Delta$. In contrast to Δ the coefficient A depends on the coupling coefficients $L_{0\mu}$ and the charges of

the continuum phonons Z_{μ} . Thus the occurrence of A requires the coupling of the discrete phonon with continuous excitations and the infrared activity of the continuum modes. Because A is generally a complex quantity, F_0 and thus F_0^2 become complex. This is just the reason why the absorption line shape of the discrete phonon deviates from that of a simple damped oscillator and may show an antiresonance. The susceptibility χ as given by equations 6 to 8 is formally equal to the composite electron-phonon Green's function, which has been derived by *Balkanski et al.* [8] in discussing distorted Raman-scattering lines shapes in semi-conductors. It is obvious that the physical meanings of the parameters Δ and A are different.

The optical absorption coefficient is given by

$$\alpha(\omega) = \frac{4\pi\omega}{nc} \text{Im}\chi \tag{9}$$

where n is the refractive index and c the velocity of light. According to equation 6 $\alpha(\omega)$ may be decomposed into:

$$\alpha(\omega) = \alpha_c(\omega) + \alpha_a(\omega) \tag{10}$$

with α_c the absorption of the continuous background and α_a the absorption coefficient of the renormalized discrete phonon. In the limit $\varepsilon \rightarrow 0$ for α_c the well known result is obtained:

$$\alpha_c(\omega) = \frac{4\pi\omega}{nc} \text{Im} \sum_{\mu} Z_{\mu}^2 g_{\mu} \xrightarrow{\varepsilon \rightarrow 0} \frac{2\pi}{c} Z^2(\omega) D(\omega) \tag{11}$$

where $D(\omega)$ is the density of states of the vibrational continuum and the index μ of Z_{μ} has been replaced by the continuously varying frequency ω . This formula has been frequently used to describe impurity induced infrared absorption in defective crystals [10] and the absorption of amorphous materials [11]. The absorption coefficient reproduces the density of states multiplied by a generally frequency dependent oscillator strength which is in our terminology the square of the effective charge $Z(\omega)$ of the continuum.

The absorption of the discrete phonon $\alpha_a(\omega)$ is additively superimposed on $\alpha_c(\omega)$. Using equations 5 and 8 we get

$$\alpha_d(\omega) = \frac{4\pi\omega}{nc} \frac{Re F_0^2 \omega \Gamma_0 + Im F_0^2 (\Omega_0^2 - \omega^2)}{(\Omega_0^2 - \omega^2)^2 + (\omega \Gamma_0)^2} \quad [12]$$

with

$$Re F_0^2 = (Z_0 - A')^2 - A''^2$$

and

$$Im F_0^2 = 2A''(A' - Z_0).$$

Examining this equation, we see that when $Im F_0^2 = 0$ we have the usual symmetric oscillator absorption line if we assume A and A' to be independent of frequency. The second term in the nominator yields an asymmetric additive contribution to the absorption profile due to the factor $\Omega_0^2 - \omega^2$, which is only present if F_0^2 or equally A has an imaginary part. This term gives the contribution of the interference between the discrete phonon and the continuum modes. We rewrite equation 12 and obtain for the total absorption coefficient

$$\alpha(\omega) = \alpha_c(\omega) + \alpha_d^{(0)} \frac{1 + \mathcal{W}(\Omega_0^2 - \omega^2)/\omega \Gamma_0}{1 + (\Omega_0^2 - \omega^2)^2/(\omega \Gamma_0)^2} \quad [13]$$

with

$$\alpha_d^{(0)} = \frac{4\pi Re F_0^2}{nc \Gamma_0} = \frac{4\pi \{(Z_0 - A')^2 - A''^2\}}{nc \Gamma_0}$$

and

$$\mathcal{W} = \frac{Im F_0^2}{Re F_0^2} = \frac{2A''(A' - Z_0)}{(Z_0 - A')^2 - A''^2}.$$

In this equation \mathcal{W} may be regarded as an asymmetry parameter, which vanishes for symmetric line shapes ($A'' = 0$). The coefficient $\alpha_d^{(0)}$ is the absorption coefficient at the renormalized resonance frequency Ω_0 . It is connected with the integral absorption due to the discrete phonon by:

$$\int \alpha_d(\omega) d\omega = \frac{\pi}{2} \Gamma_0 \alpha_d^{(0)} \quad [14]$$

if $\Gamma_0 \ll \Omega_0$.

The parameter $\alpha_d^{(0)}$ may be modified by the phonon interaction, even if the absorption line is symmetric with $\mathcal{W} = 0$. If this situation

applies, $\alpha_d^{(0)}$ is the peak absorption of the line measured above α_c . Further we note that the depth of the antiresonance is limited by the thermodynamic requirement $\alpha = \alpha_c + \alpha_d > 0$. This implies the upper boundary of the asymmetry parameter $|\mathcal{W}| > 2\alpha_c/\alpha_d^{(0)}$.

In the case of a narrow resonance, $\Gamma_0 \ll \Omega_0$, the expressions $\Omega_0^2 - \omega^2$ and $\omega \Gamma_0$ in the above equations may be replaced by $\Omega_0^2 - \omega^2 \simeq 2\Omega_0(\Omega_0 - \omega)$ and $\omega \Gamma_0 \simeq \Omega_0 \Gamma_0$. Then it is easily shown that $\alpha(\omega)$ describes just a Fano line shape function of the form:

$$\alpha(\omega) = \alpha_c(\omega) - \sigma + \sigma \frac{(q + \varepsilon)^2}{(1 + \varepsilon^2)} \quad (15)$$

where $\varepsilon = (\omega - \Omega_0)/(\Gamma_0/2)$ is the reduced energy variable and $\sigma = \frac{4\pi}{nc} \frac{(A'')^2}{\Gamma_0}$ and

$q = (Z_0 - A')/A''$ are the Fano asymmetry parameters [6].

III. Temperature dependence of the model parameters

The model parameters $\alpha_d^{(0)}$, \mathcal{W} , Ω_0 and Γ_0 , introduced in the last section, are generally frequency dependent quantities which are determined by the dynamics of PE. As we don't know the dynamical properties and particularly the coupling mechanism in the partially crystallized polymer, we will assume these parameters to be constant in the vicinity of the resonance frequency of the discrete phonon. This is obviously a very crude approximation, because the asymmetric absorption line extends at higher temperatures over about 20 cm^{-1} (see fig. 2), a frequency range where the background absorption $\alpha_c(\omega)$ shows a non-negligible variation. Therefore we had to specify for each temperature a frequency dependent absorption coefficient $\alpha_c(\omega)$ in order to obtain a reasonable coincidence between the experimental and theoretical absorption curves. This introduces a considerable uncertainty into the model parameters as derived from the experimental data. Figure 4 shows a typical fitted absorption curve with the hypothetical continuous absorption $\alpha_c(\omega)$. The renormalized resonance frequency Ω_0 and the damping constant Γ_0 as functions of temperature determined by this fitting proce-

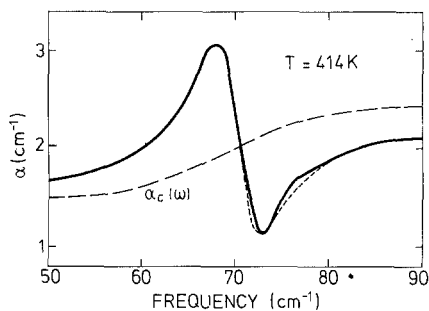


Fig. 4. Absorption coefficient $\alpha(\omega)$ at 414 K. Full line: experimental curve; broken line: fitted curve; $\alpha_c(\omega)$: hypothetical continuum absorption

ture are given in figure 5. For all temperatures we found $\Gamma_0 \ll \Omega_0$. The damping constant is much smaller than the extension in frequency of the asymmetric absorption line. For large asymmetry, $W \gg 1$, Γ_0 is equal to the frequency difference between the peak absorption and the antiresonance minimum. Though in the case $\Gamma_0 \ll \Omega_0$ the *Fano* formula equation 15 applies, we have evaluated $\alpha_d^{(0)}$ and W after equation 13 because using these parameters the integral absorption determined by $\alpha_d^{(0)}$ and the asymmetry of the lineshape specified by W are well separated. The renormalized resonance frequency Ω_0 and the damping constant Γ_0 as functions of temperature determined by this fitting procedure are given in figure 5 and the results for $\alpha_d^{(0)}$, W and $\alpha_c(\Omega_0)$ are shown in figure 6. The coupling between the phonon continuum and the discrete phonon sets in at approximately 80 K and increases in strength with rising temperature. This is indicated by the continuous decrease of $\alpha_d^{(0)}$ and the frequency Ω_0 . Up to about 310 K the line shape

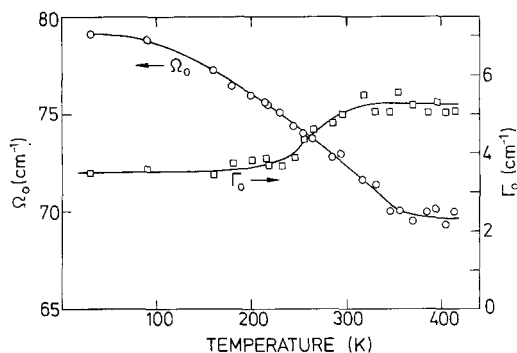


Fig. 5. Resonance frequency Ω_0 and damping constant Γ_0 as functions of temperature

is symmetric, thus $W = 0$ and A is real below this temperature. Also A' is very small up to 260 K, which can be seen from the only slightly increasing damping constant Γ_0 . Around 300 K the background absorption and the mode coupling change drastically. At 290 K the continuum absorption $\alpha_c(\Omega_0)$ rises within 10 K to twice its lower temperature value. In the same temperature region the line width Γ_0 increases strongly and the line shape becomes asymmetric, thus A is now complex yielding an asymmetry parameter $W > 0$. When the temperature is further raised, W increases strongly and the absorption strength $\alpha_d^{(0)}$ may be extrapolated to zero at about the melting temperature $T_m = 430$ K of crystalline PE.

IV. Discussion

The coupling mechanism of the discrete B_{1u} -phonon of crystalline PE to a continuum of infrared active modes introduces the question for the physical nature of this continuum. We discuss two conceivable mechanisms:

a) The PE crystallites with a mean edge-length of 300–500 Å contain crystal defects of several species. Here the most important and at the same time simplest one is the so called “kink”-defect formed by two neighbored gauche positions of three successive CH_2 -groups [12]. Because of the relaxation of the k -selection rule, such defects contribute to some extent to the continuous background absorption. This has been proved by investigating annealed material. Annealing lowers the number of defects in the crystallites and always reduces the background absorption. However, a strong influence of the kinks on the temperature behaviour of the line distortion is unlikely, since the concentration of kinks between room temperature and the melting point does not vary remarkably [13].

b) The continuum of vibrational modes of the amorphous parts of the material must also be taken into account. Again due to the lack of translational symmetry all modes of the amorphous portions are infrared active [11]. The coupling mechanism may be given by the transition of chains from the crystalline parts into the amorphous regions, leaving the crystallite surfaces in a distance of ca. 4 Å corresponding to the b -axis length of the

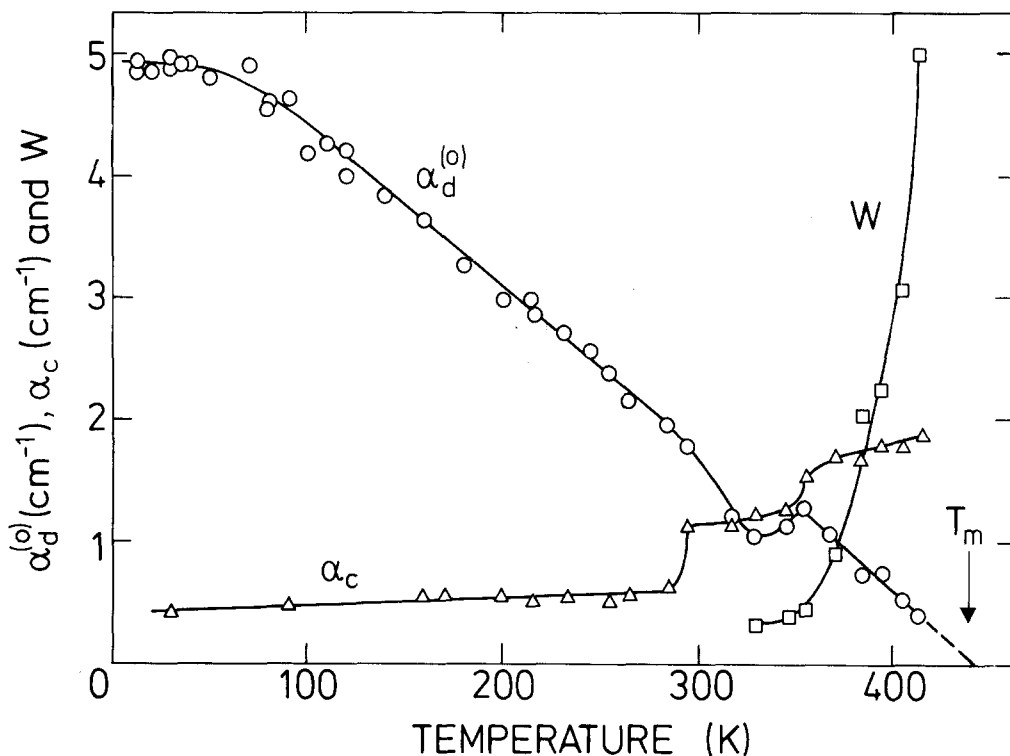


Fig. 6. Peak absorption $\alpha_d^{(0)}$, asymmetry parameter W and continuum absorption $\alpha_c(\Omega_0)$ as functions of temperature. T_m is the melting temperature of crystalline PE

crystal. The similarity of the mean chain distance in the amorphous parts to the b -axis value can explain the observed fact, that the band intensity of the 73 cm^{-1} band is so much stronger than that of the 109 cm^{-1} (see fig. 1 and 2), an experimental observation having no stringent explanation up to now. From symmetry relations the two bands corresponding to two transversal vibrations in b -axis-direction (73 cm^{-1} , B_{1u}) and a -axis-direction (109 cm^{-1} , B_{2u}) should not vary drastically in their absorption intensity. Till now we have argued that the absorption strength of 73 cm^{-1} band and thus Z_0 is large at low temperatures and is diminished with rising temperature by the mode coupling. If we assume, that the effective charge of the discrete phonon of 73 cm^{-1} Z_0 is equal or close to zero, than the effect would be still existent (see eq. 13), since A' would produce a "transfer" of absorption strength from the continuum to the discrete phonon. By the coupling via b -axis this would be only the case for the 73 cm^{-1} phonon, not for the 109 cm^{-1} mode.

In order to gain a complete understanding of the microscopic phonon processes in PE additional experiments are necessary. In particular materials with different crystallinity should be investigated. Furthermore other partially crystalline polymers are interesting, because it is very probable that phonon interactions of the type discussed here are not restricted to PE.

Summary

The decrease of the absorption strength of 73 cm^{-1} line in polyethylene and the strong antiresonance occurring above 310 K at the high frequency wing of the line are explained by assuming a Fano type coupling between the 73 cm^{-1} phonon and a continuum of infrared active vibrational modes. The parameters determining the line shape are deduced from experimental absorption curves and conceivable coupling mechanisms are discussed.

Zusammenfassung

Die Abnahme der Absorption der 73 cm^{-1} -Bande in Polyäthylen und die starke Antiresonanz, die oberhalb 310 K auf der hochfrequenten Seite der Bande einsetzt, werden erklärt durch Annahme einer

Fano-Kopplung zwischen dem 73 cm^{-1} -Phonon und einem Kontinuum von infrarot-aktiven Schwingungsmoden. Die Parameter, die die Linienform bestimmen, werden aus den experimentellen Absorptionskurven abgeleitet und Kopplungsmechanismen diskutiert.

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