Vibrational analysis of the tight (110) fold in polyethylene

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The defect density of states of the tight (110) fold in polyethylene has been calculated by the method of Green's functions in the frequency range 500–1400 cm^{-1}. Resonance modes of the (110) fold calculated at 1348, 1342 and 1288 cm^{-1} are assigned to infrared bands at 1346–1347 and 1342–1343 cm^{-1} and near 1295 cm^{-1}. These bands were observed in polyethylene single crystals by Painter *et al.* and Spells *et al.* and in fold crystals of the long n-alkane $C_{198}H_{398}$ by Ungar and Organ. It is shown that (110) folds (approximately *g'g'ggtg*) also contribute to the *gtg/gtg'* band at 1368 cm^{-1}. In contrast to the (200) fold, the (110) fold does not exhibit a localized gap mode near 700 cm^{-1}. The calculations allow the observed infrared bands to be assigned to defect modes of the (110) fold without introducing the qualitative concept of 'distorted *gg* conformations' used in the literature.

(Keywords: polyethylene, single crystals, chain folding, defect modes, Green's function method, (110) fold)

INTRODUCTION

The fold structure of polyethylene single crystals has been the subject of considerable interest and discussion. Infrared spectroscopy is particularly sensitive to conformational defects: in the infrared spectra of n-alkanes and polyethylene there are, for example, three distinct bands at 1308, 1353 and 1368 cm^{-1}, which are generally assigned to the conformational defects[1–4] *gg* (1353 cm^{-1}) and *gtg/gtg'*(1308, 1368 cm^{-1}).

Folds represent another kind of conformational defect and are more difficult to detect spectroscopically. One reason for this is that the concentration of folds is much smaller than the concentration of conformational defects mentioned above. The demonstration of some of these relatively weak fold bands has become feasible by modern infrared spectroscopic techniques (Fourier transform infrared spectroscopy, difference and Fourier self-deconvolution techniques).

Painter *et al.*[5] investigated samples of solution-grown polyethylene by means of Fourier transform infrared (*FT*i.r.) spectroscopy. They were able to assign a band at 1346 cm^{-1} and a band near 1295 cm^{-1} to regular fold conformations. Other interesting infrared spectra were obtained by Spells *et al.*[4] and by Ungar and Organ[6]. Spells *et al.*[4] investigated several polyethylene crystals grown from solution under different conditions. Ungar and Organ[6] considered samples of solution-grown crystals of the long n-alkane $C_{198}H_{398}$ and compared the spectra of well characterized once-folded chain crystals with the spectra of extended chain crystals.

To understand the experimental spectra we need model calculations that analyse the characteristic frequencies of defect vibrations. As far as we know, the characteristic frequencies of fold conformations in polyethylene have so far been calculated only for the tight (200) fold[7]. Ungar and Organ[6] also mentioned that vibrational calculations for other fold types are needed. In the present paper results of vibrational calculations concerning the tight (110) fold are presented and assigned to infrared bands observed by Painter *et al.*[5], Spells *et al.*[4] and Ungar *et al.*[6]. The assignments are based on quantitative agreements between calculated and observed frequencies. In principle it is possible to calculate not only the band frequencies but also the intensities by using the electro-optical parameters of Jona *et al.*[8]. But the calculation of such intensities would not be useful because a quantitative comparison between calculated intensities of defect modes in polyethylene and experimentally observed intensities is not possible for two reasons. First, the defect concentrations are not known. Second, the experimentally observed intensities of the infrared bands mentioned above are extremely weak. They are visible only in difference spectra or by means of self-deconvolution.

METHOD OF CALCULATION

The defect frequencies of the (110) fold were calculated by the Green's function method.

Polymer chains in single chain approximation are systems with one-dimensional periodicity. For such systems, Schmid[9] has developed a semi-analytical method to calculate exactly the phonon Green's function. This method is a generalization of the semi-analytical Green's function theory for polymer skeletons developed previously by Schmid and Hölzl[10]. The term 'semi-analytical' means that the Green's function is represented analytically as a function of relatively few complex polynomial roots and that these roots are calculated not analytically but numerically.

If the Green's function is known for a given frequency ω, one can calculate exactly the unperturbed density of states $g_0(\omega)$ as well as the change in the density of states due to (conformational or mass) defects $\Delta g(\omega) = g(\omega) -$

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$g_0(\omega)$. Consequently, the densities of states are obtained as smooth curves rather than histograms. Furthermore, direct calculation of the difference density of states $\Delta g(\omega)$ has the advantage over other normal mode calculations that the defect modes do not need to be separated from the unperturbed modes.

The Green's function method allows the calculation of the difference density of states for isolated defects. The influence of interfering neighbouring defects or chain ends is completely ruled out. Nevertheless, interactions between defects can be investigated by considering defect clusters[11].

The semi-analytic method of Schmid has been applied in the past mainly to the skeletal model of polyethylene[11]. However, the method is not limited to simplified models. Results of the method for polyethylene with all degrees of freedom have been presented by Hägele *et al.*[12], who used a special force field: the shell model of Hahn and Richter[13]. In the present paper the method of Schmid is applied for the first time to polyethylene with all degrees of freedom by using the well known valence force field of Snyder[1].

In addition investigating the (110) fold we also applied the Green's function method to the conformational defects *g*, *gg*, *gtg*, *gtg'*, and *ggtgg*. These results will be presented in a forthcoming paper[14].

Basic relations of Green's function method

The Green's function of the unperturbed problem is defined by[15–17]

$$(D_0 - \omega^2 1) r_0(\omega^2) = 1$$

D_0 is the mass weighted dynamical matrix of the unperturbed problem:

$$D_0 = M^{-1/2} B^{\mathrm{T}} F B M^{-1/2}$$

where:

F = matrix of force constants in internal coordinates (force field of Snyder[1]);

B = Wilson's B matrix[18];

M = matrix of masses (diagonal).

The density of states $g_0(\omega)$ of the unperturbed problem is

$$g_0(\omega) = \frac{2\omega}{\pi N_{\mathrm{f}}} \operatorname{Im} \operatorname{Tr} r_0(\omega^2)$$

$N_{\mathrm{f}} = 3sN$, where N = number of unit cells, Tr = trace, s = number of atoms in the unit cell, and $r_0(\omega^2) = \lim_{\varepsilon \to 0} + r_0(\omega^2 + \mathrm{i}\varepsilon)$.

The difference density of states $\Delta g(\omega)$, i.e. the difference between the perturbed density of states $g(\omega)$ and $g_0(\omega)$, obeys the relation:

$$\begin{aligned}\Delta g(\omega) &= g(\omega) - g_0(\omega)\\ &= \frac{2\omega}{\pi N_{\mathrm{f}}} \operatorname{Im} \operatorname{Tr} \left[r_0(\omega^2) J \frac{1}{1 - r_0(\omega^2) J} \right]\end{aligned}$$

This equation is only valid if the defect matrix $J = D_0 - D$ (D = dynamical matrix of the defect problem) is independent of the frequency. This is always true for pure conformational defects. The corresponding relation for a frequency dependent matrix $J(\omega^2)$ is slightly more complicated[19]. This is interesting if mass defects are taken into account.

Force field and geometry

The present results are based on the widely used valence force field of Snyder[1], including the tetrahedral geometry (i.e. valence angles of 109.5°) and the bond lengths $r_{\mathrm{C-C}} = 1.54$ Å* and $r_{\mathrm{C-H}} = 1.093$ Å. The calculations were done for two conformations (I and II) of the (110) fold. Conformation I is characterized by the dihedral angles −113.8°/−111.1°/87.4°/108.2°/−6.5°/113.2° (approximately *g'g'ggtg*), which were obtained by minimization of the static energy[20]. These values for the dihedral angles are similar to the results of other authors[21,22], including the extremely small *gauche* angle of 87.4°.

In contrast to the realistic dihedral angles of conformation I, conformation II is characterized by idealized dihedral angles of −113°/−113°/113°/113°/0°/113° (*g'g'ggtg*). Unlike conformation I, this idealized conformation is not compatible with a crystalline packing of neighbouring stems. Nevertheless, it was included in the calculations for two reasons. First, comparison of the results for conformations I and II shows that the experimentally observed bands of *Table 2* can be quantitatively understood without the qualitative concept of so called 'distorted *gg*-sequences' discussed in the literature[5–7,23]. Second, the comparison shows that the force field of Snyder[1] can be applied to the tight (110) fold, although Snyder used idealized dihedral angles to fit his force field.

RESULTS

The difference density of states $\Delta g(\omega)$ due to the (110) fold was calculated by the method of Green's function in the frequency range 500–1400 cm^{-1}. The computed frequencies of the resonance and localized modes due to the (110) field in conformations I and II are listed in *Table 1*. Conformation I shows resonance modes at 1374, 1372, 1348, 1342, 1288, 1101, 1082.5, 954, 844 and 820 cm^{-1} and localized modes at 1160, 1139, 1135 and 553 cm^{-1}. Conformation II shows resonance modes at 1374.5, 1366, 1350, 1346, 1286, 1106, 1081.5, 952, 838 and 822 cm^{-1} and localized modes at 1158.5, 1138.5,

Table 1 Calculated defect frequencies (cm^{-1}) of conformation I (dihedral angles determined by energy minimization) and conformation II (idealized dihedral angles) of the (110) fold in the frequency range 500–1400 cm^{-1}

(110)-fold	
Conformation I	Conformation II
1374	1374.5
1372	1366
1348	1350
1342	1346
1288	1286
1160 loc.[a]	1158.5 loc.
1139 loc.	1138.5 loc.
1135 loc.	1137 loc.
1101	1106
1082.5	1081.5
954	952
844 (very broad)	838
820	822
553 loc.	554 loc.

[a] Loc., localized gap modes

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* 1 Å = 10^{-1} nm

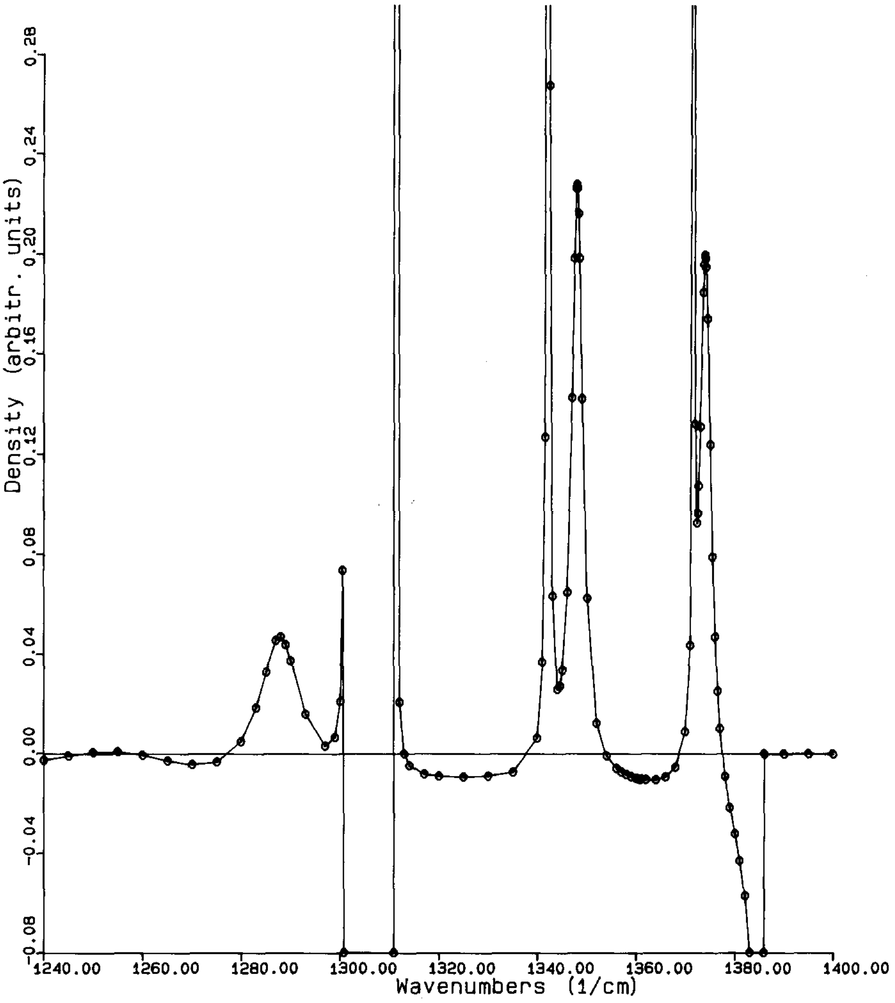

Figure 1 Difference density of states $\Delta g(\omega)$ of the tight (110) fold (conformation I) in the polyethylene chain

1137 and 554 cm^{-1}. In the total frequency range 500–1400 cm^{-1}, the maximal frequency shift between conformation I and conformation II is only 6 cm^{-1}. All defect frequencies were determined with an accuracy of at least ± 1 cm^{-1}.

Figure 1 shows the difference density of states due to conformation I in the frequency range 1240–1400 cm^{-1}, which at present is the range of the most important infrared investigations to elucidate the fold structure in polyethylene. One sees sharp resonance modes at 1342, 1348, 1372 and 1374 cm^{-1} and a broader resonance mode at 1288 cm^{-1}. The other peaks in $\Delta g(\omega)$ at 1301, 1311 and 1385 cm^{-1} are trivial because they coincide with peaks in the density of states of the unperturbed chain.

Table 2 shows our proposed assignment of our calculated defect frequencies of the (110) fold to infrared bands experimentally observed by Painter *et al*[5], Spells *et al.*[4] and Ungar and Organ[6]. These assignments are based on quantitative agreements between calculated and observed bands.

Comments on the force field

To fit his force field, Snyder[1] used the spectra of various n-alkanes in all-*trans* and *gauche* conformations and the spectrum of all-*trans* polyethylene. In the normal coordinate calculations of n-alkanes, Snyder used a *gauche* angle of 113°. Taking the example of *gauche*-n-butane, Snyder[1] showed that small changes of the dihedral angles result only in small frequency shifts. If the *gauche* angle is changed by 10° (from 110 to 120°), the maximal frequency shift is 7 cm^{-1} in the range 700–1400 cm^{-1} and only 3 cm^{-1} between 1200 and 1400 cm^{-1}.

Table 2 Assignment of calculated defect frequencies (cm^{-1}) of the (110) fold to experimentally observed infrared bands in References 4–6

Calculated (conformation I)	Observed		
	Painter *et al.*[5]	Spells *et al.*[4]	Ungar and Organ[6]
1374	1368	1369[a]	1369
1348	1346	1347	1346
1342	–	1343	1342
1288	1293–1296	1295	1298

[a] From the spectrum of *Figure 3* in Reference 4

The *gauche* angles of conformation I deviate by less than 5° from the *gauche* angle of 113° used by Snyder, except for the *gauche* angle of 87.4° where the difference is 25.6°. The *trans* angle of conformation I differs by only $-6.5°$ from the idealized *trans* angle of Snyder (0°). Therefore, the force field of Snyder can be applied to these small deviations. Furthermore, many normal coordinate calculations for polyethylene and (cyclo-) alkanes have been done with Snyder's force field using a *gauche* angle of 120° instead of 113°[1,3,7,23].

Because of the difference of 25.6° in the third *gauche* angle one cannot conclude that Snyder's force field can be fully applied to conformation I. Therefore, we have also calculated the defect frequencies of an approximate conformation of the (110) fold *g'g'ggtg* with *gauche* angles of 113° and an ideal *trans* angle of 0° (conformation II). This is a conformation to which the force field of Snyder can be applied. The defect frequencies of this approximate conformation II and the results for the realistic conformation I are similar (compare *Table 1*). In the frequency range 500–1400 cm^{-1} the maximal frequency shift is 6 cm^{-1}. The resonance modes at 1288, 1342, 1348 and 1374 cm^{-1} of conformation I, which we assign to experimental bands (see *Table 2*), are shifted to 1286, 1346, 1350 and 1374.5 cm^{-1} in conformation II. The shift is at most 4 cm^{-1}. We therefore assume that possible variations in the force field due to the extreme *gauche* angle of 87.4° would only cause frequency shifts of a similar order. Thus our assignments should not be influenced by these very small frequency shifts.

Our assignments are discussed in the next section.

DISCUSSION OF THE ASSIGNMENTS

Bands at 1342 and 1346 cm^{-1}

Painter *et al.*[5] investigated various samples of polyethylene in the frequency range 1250–1400 cm^{-1} by *FT*i.r. techniques. All difference spectra between single crystals of polyethylene grown from solution and the same sample after treatments which reduce the number of folds (annealing, quenching from the melt, extrusion) show a positive band at 1346 cm^{-1}. This band is, therefore, assigned to regular fold conformations in single crystals of polyethylene grown from solution. This assignment is confirmed by the fact that the band could not be seen in melt-quenched samples. However, Painter *et al.* were not able to assign this band at 1346 cm^{-1} to a specific fold type.

Single crystals of polyethylene grown from solution under different crystallization temperatures and different solvents were studied by Spells *et al.*[4] by means of Fourier transform infrared spectroscopy. Applying the method of Fourier self-deconvolution[24], Spells *et al.* were able to resolve two bands at 1347 and 1343 cm^{-1} located in the shoulder of the band at 1351 cm^{-1}, which is assigned to the *gg* conformation[1,25]. These bands were found in all single crystals of polyethylene under consideration which showed different proportions of {110} and {100} sectors, which indicates corresponding proportions of folds along {110} and {100} planes. Single crystals containing only {110} sectors as well as single crystals with large proportions (up to 55%) of {100} sectors showed bands at 1347 and 1343 cm^{-1}. Again, it was not possible to assign these bands to a specific fold type[4].

To investigate this question experimentally, Ungar and Organ[6] studied the very long n-alkane $C_{198}H_{398}$. By crystallizing this material from dilute solution under appropriate conditions, it is possible to produce single crystals consisting of extended chains (sample E) as well as single crystals consisting of chains with exactly one fold (sample F). The electron microscope shows that sample F consists of regular lozenge shaped single crystals, indicating the predominance of {110} fold planes[6]. Using *FT*i.r. methods Ungar and Organ determined the difference spectrum between these two samples, which contains the spectral information of the folds. After Fourier self-deconvolution, they found two bands at 1346 and 1341.7 cm^{-1}, just as Spells *et al.*[4] had done, but 1 cm^{-1} lower. Therefore, these bands may result from (110) folds. This assignment is confirmed by our calculations, which yielded two resonance modes at 1348 and 1342 cm^{-1} for the (110) fold.

Ungar and Organ[6] were able to assign the band at 1346 cm^{-1} to tight (110) folds, but they could not extract information about folds from the other band at 1342 cm^{-1} which they also observed because they couldn't exclude that this band may be due to end *gauche* defects. Although the fold crystal contains as many chain ends as the extended chain crystal, it may contain more end *gauche* defects because chain ends may have more conformational possibilities due to neighbouring folds[6]. An increased number of end *gauche* defects should give rise to bands at 1342 cm^{-1} according to the work of Maroncelli *et al.*[2].

Our result that (110) folds give rise to bands at 1342 cm^{-1} is confirmed by the fact that a band at 1343 cm^{-1} was observed also in single crystals with exclusively {110} sectors[4]. Thus the existence of a band at 1342 cm^{-1} in the infrared spectrum of polyethylene can no longer be considered to be specific for (200) folds.

Band at 1295 cm^{-1}

Painter *et al.*[5] observed that the low frequency tail of the broad band at 1303 cm^{-1} is very sensitive to conformational changes. Treatments which reduce the number of folds in the single crystals of polyethylene result in a narrowing of the low frequency tail of this band. Accordingly, in the difference spectrum of this frequency region, there is a relatively broad positive band, which is assigned to regular fold structures by Painter *et al.* for the same reasons as the band at 1346 cm^{-1}. The position of this band depends on the treatment. For example, the difference spectrum between solution-grown single crystal mats and the same sample after melting and quenching shows a positive difference band at 1293 cm^{-1}. The difference spectrum between the single crystal mat and the same sample after annealing (2 h) shows a positive band at 1296 cm^{-1}.

A broad band at 1295 cm^{-1} in the difference spectra between single crystals of polyethylene with varying proportions of {110} sectors was also observed by Spells *et al.*[4]. However, their *ad hoc* assignment to the *gtg* and *gtg'* wagging mode suffers from the fact that the latter is observed at 1308 cm^{-1} (Reference 1) and calculated between 1309 cm^{-1} (Reference 26) and 1313 cm^{-1} (References 2 and 14).

Related observations were also made by Ungar and Organ[6]. The difference spectrum F–E at 110 K shows a band at 1298 cm^{-1}. This band must be due to (110) folds because it does not appear in the extended chain crystal (E). Chain ends are no object in this frequency range.

Our calculations give a natural explanation of these bands. There are several conformational defects which show a relatively broad resonance mode in the frequency range considered: the (110) fold at 1288 cm^{-1} (see *Figure 1*), *gtg* and *gtg'* at 1293 cm^{-1} (Reference 14), and the (200) fold at 1283 cm^{-1} (Reference 14). On the other hand, the defects *g* and *gg* do not show any resonance mode in this frequency range.

Thus, our calculations show that the band observed near 1295 cm^{-1} may be caused either by (110) folds or by *gtg*/*gtg'* defects. Contributions of (200) folds are less probable because the frequency of the calculated resonance mode is comparatively low (1283 cm^{-1}). Our assignment is also supported by an observation of Spells *et al.*[4]; from the temperature dependence of the band at 1295 cm^{-1} one may conclude that this band should consist of at least two different components. One component may be the (110) fold and the other the defects *gtg* and *gtg'*.

Band at 1368 cm^{-1}

The infrared spectra of Painter *et al.*[5] and Spells *et al.*[4] all show a band at 1368 cm^{-1}, which is generally assigned to *gtg* and *gtg'* conformations[1,4]. The calculated defect frequencies of the conformations *gtg* and *gtg'* are 1367 cm^{-1} (Reference 2), 1375 cm^{-1} (Reference 26) and 1373 cm^{-1} (Reference 14), respectively. Contributions of (110) folds to the band at 1368 cm^{-1} are conjectured by Ungar and Organ[6] because the structure *gtg* is also contained in the (110) fold, which has approximately the conformation *g'g'ggtg*. This conjecture is confirmed by our calcuations.

The difference density of states of the (110) fold in conformation I (see *Figure 1*) shows two sharp resonance modes at 1372 and 1374 cm^{-1}. In conformation II these modes occur at 1366 and 1374.5 cm^{-1}, respectively. Thus the higher frequency resonance mode is practically independent of the details in the differences of conformation I and II. Furthermore, a single *gtg* defect shows a resonance mode at 1373 cm^{-1} (Reference 14). We therefore conclude that the resonance mode at 1374 cm^{-1} is due to the *gtg* conformation in the (110) fold.

Distorted gg conformations

To elucidate the fold structure of polyethylene, cycloalkanes have been studied too. According to X-ray structure investigations of Kay and Newman[27] and of Trzebiatowski *et al.*[28] cycloalkanes crystallize in the form of two parallel chain segments which are connected by two tight folds of conformation *ggtgg*. This conformation corresponds to (200) folds in polyethylene. In the infrared spectrum, cycloalkanes show a band at 1342 cm^{-1} (References 7 and 23), which is assigned by Grossmann *et al.*[29] to the fold conformation since the frequency of this band remains constant and the intensity decreases (lower fold concentration) when the molecular weight of the cycloalkanes is increased. Krimm and Jakes[23] made a complete normal coordinate analysis of the cycloalkane $(CH_2)_{34}$ on the basis of the conformation determined by Newman and Kay (fold *ggtgg*). This calculation yielded a fold frequency at 1355 cm^{-1}, which was assigned to the infrared band at 1342 cm^{-1} despite the relatively large difference between theory and experiment. On the other hand, the conformational defect *gg*, which is formally contained in *ggtgg* and which is assigned to the infrared band at 1353 cm^{-1} (Snyder[1]), has a calculated resonance mode at 1354 cm^{-1} (References 1 and 2) or 1355 cm^{-1} (Reference 14). The relatively large deviation between theoretical and experimental result is tentatively explained by Krimm and Jakes[23], who assume 'distortions', i.e. 'distorted' or 'strained' *gg* conformations in the real fold conformation coming from steric hindrances of the hydrogen atoms.

Since that time, bands in polyethylene occurring in this frequency region have been qualitatively ascribed to 'distorted' or 'strained' *gg* conformations[5,6]. The band observed at 1346 cm^{-1} in polyethylene is supposed by Ungar and Organ[6] to be due to 'strained' *gg* pairs in the (110) fold. Thus, the term 'distorted' or 'strained' *gg* conformations is used as a qualitative argument due to the lack of calculations. The question is left open whether the frequency shifts to be explained are induced only by geometrical distortions or also by force field modifications.

Our calculations, the first calculations on the (110) fold as far as we know, show that resonance modes at 1346 and 1350 cm^{-1} are produced already by the sequence *g'g'ggtg* with ideal dihedral angles (conformation II; i.e. neither geometrical distortions nor changes in the force field). These resonance modes are very close to the bands experimentally observed at 1342–1343 and 1346–1347 cm^{-1}. The influence of realistic dihedral angles (i.e. geometrical disotrtions, no force field distortions) has also been investigated. Conformation I shows resonance modes at 1342 and 1348 cm^{-1}, which are, by 4 and 2 cm^{-1}, slightly lower than the corresponding resonance modes of the idealized conformation II.

Thus we have two results. First, the calculated resonance modes of the (110) fold at 1342 and 1348 cm^{-1} (conformation I) can be assigned directly to the observed infrared bands at 1342–1343 and 1346–1347 cm^{-1}. The qualitative concept of 'distorted *gg* conformations' is not needed. It is, above all, the mere sequence of *gauche* and *trans* positions, *g'g'ggtg*, of the (110) fold which gives rise to resonance modes between 1340 and 1350 cm^{-1}. Second, the influence of geometrical distortions obtained by minimization of the static energy on the frequency of the resonance modes of the (110) fold between 1340 and 1350 cm^{-1} is relatively small. If the idealized dihedral angles (conformation II) are replaced by the more realistic ones of conformation I, the decrease of the frequency is in the range 2–4 cm^{-1}.

Other spectral regions

Other spectral regions of the n-alkane $C_{198}H_{398}$ were also studied by Ungar and Organ[6]. They report that the difference spectrum F–E between the single crystal with folds mainly along {110} plains and the extended chain single crystal displays only a broad and weak absorption in the range 690–715 cm^{-1}. This observation agrees with our calculations for the (110) fold, which do not show any localized mode in this frequency region in the band gap below the $k=0$ rocking mode at 720 cm^{-1} (calculated: 716 cm^{-1}).

On the other hand, calculations for the (200) fold show a localized mode at 714 cm^{-1} (References 7 and 14). Furthermore, after the investigations of cycloalkanes by Krimm and Jakes[23], (200) folds in polyethylene are expected to yield an infrared absorption band at 700 cm^{-1}. Thus, the observation of an infrared band at 700 cm^{-1} would be typical for (200) folds. However, until now it has not been possible to observe such a band in polyethylene. Therefore, from the hitherto known fold bands in the infrared spectrum of polyethylene, it is not possible to identify (200) folds since the infrared band at 1342 cm^{-1}, which has been considered up to now as typical for (200) folds, may also be due to (110) folds.

The calculated difference density of states of the (110) fold shows a sharp resonance mode at 820 cm^{-1}. This is interesting because other conformational defects like *g*, *gg*, *gtg* and *gtg'* do not have any sharp resonance modes in the frequency region below 880 cm^{-1} (Reference 14).

Only the (200) fold shows a resonance mode at 825 cm^{-1}, but it is substantially broader. The resonance mode at 820 cm^{-1} is interesting for yet another reason: it is the only mode which is noticeably influenced by geometric distortions of the dihedral angles. The defect mode is much more localized in conformation I (the resonance mode is much sharper) than in conformation II. None of the other modes show any spectacular differences between the two conformations.

To our knowledge, in this spectral region of polyethylen only one weak band at about 805 cm^{-1} was observed by Snyder[1]. It would be very interesting to look for fold specific absorptions in polyethylene in the range around 820 cm^{-1} using modern infrared methods (*FT*i.r., difference and self-deconvolution techniques).

SUMMARY

The characteristic defect frequencies of the tight (110) fold in polyethylene have been calculated using the Green's function method. The (110) fold shows, among others, calculated resonance modes at 1374, 1348, 1342 and 1288 cm^{-1}, which can be assigned to infrared bands observed in solution-grown polyethylene crystals and in solution-grown crystals of the n-alkane $C_{198}H_{398}$ at 1368, 1346, 1342 and near 1295 cm^{-1} (References 4–6).

The assigment of Painter *et al.*[5] is thus confirmed that bands at 1346 cm^{-1} and near 1295 cm^{-1} are due to regular fold conformations in solution-grown polyethylene crystals and, additionally, these bands can be assigned particularly to the tight (110) fold. This assignment was also made by Ungar and Organ[6], based on their experimental investigations of the n-alkane $C_{198}H_{398}$. Likewise, the conjecture of Ungar and Organ that the (110) fold (approximately *g'g'ggtg*) contributes to the *gtg/gtg'* band at 1369 cm^{-1} could be confirmed.

An infrared band at 1342 cm^{-1} in polyethylene was hitherto considered as typical for (200) folds[7]. However, the calculations presented in this paper show that (110) folds may also contribute to the infrared band at 1342 cm^{-1}. (200) fold calculations in polyethylene show a localized mode at 714 cm^{-1} (References 7 and 14). In contrast, our (110) fold calculations do not show any localized mode in this frequency range. Thus the observation of an infrared band at 700 cm^{-1} would be typical for (200) folds.

The infrared band at 1346 cm^{-1} is characteristic for (110) folds. Similarly, the observed infrared band near 1295 cm^{-1} (References 4–6) signifies the existence of (110) folds, but with less evidence, since *gtg/gtg'* defects may contribute to this band, too. The (110) fold (conformation I) also shows a sharp resonance mode at 820 cm^{-1}. Therefore, infrared investigations to elucidate the fold conformation in polyethylene should take into account the frequency range about 820 cm^{-1}.

It was shown that the qualitative concept of 'distorted *gg* conformations' is not needed for the (110) fold. The resonance modes between 1340 and 1350 cm^{-1} (conformation II: 1346 and 1350 cm^{-1}; conformation I: 1342 and 1348 cm^{-1}) are primarily determined by the sequence of *gauche* and *trans* positions *g'g'ggtg* of the mere (110) fold. These calculated resonance modes of the tight (110) fold provide a good explanation for the observed infrared bands at 1342 and 1346 cm^{-1} in polyethylene single crystals.

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REFERENCES

1 Snyder, R. G. *J. Chem. Phys.* 1967, **47**, 1316
2 Maroncelli, M., Qi, S. P., Strauss, H. L. and Snyder, R. G. *J. Am. Chem. Soc.* 1982, **104**, 6237
3 Jona, P., Gussoni, M. and Zerbi, G. *J. Mol. Struct.* 1985, **119**, 329
4 Spells, S. J., Organ, S. J., Keller, A. and Zerbi, G. *Polymer* 1987, **28**, 697
5 Painter, P. C., Havens, J., Hart, W. W. and Koenig, J. L. *J. Polym. Sci.* 1977, **15**, 1223
6 Ungar, G. and Organ, S. J. *Polymer Commun.* 1987, **28**, 232
7 Zerbi, G. and Gussoni, M. *Polymer* 1980, **21**, 1129
8 Jona, P., Gussoni, M. and Zerbi, G. *J. Appl. Phys.* 1985, **57** (3), 834
9 Schmid, C. *J. Phys. C: Solid State Phys.* 1973, **6**, L458
10 Schmid, C. and Hölzl, K. *J. Polym. Sci.* 1972, **10**, 1881
11 Hölzl, K., Schmid, C. and Hägele, P. C. *J. Phys. C: Solid State Phys.* 1978, **11**, 9
12 Hägele, P. C., Hahn, H., Michler, E. and Schmid, C. *Progr. Coll. Polym. Sci.* 1979, **66**, 213
13 Hahn, H. and Richter, D. *Coll. Polym. Sci.* 1977, **255**, 111
14 Wolf, S., Hägele, P. C. and Schmid, C. in preparation
15 Ludwig, W. 'Festkörperphysik', Akademische Verlagsgesellschaft, Wiesbaden, 1978
16 Maradudin, A. A., Montroll, E. W., Weiss, G. H. and Ipatova, I. P. 'Theory of Lattice Dynamics in the Harmonic Approximation', Academic Press, New York, 1971
17 Schmid, C. *Coll. Polym. Sci.* 1979, **257**, 561
18 Wilson, E. B., Decius, J. C. and Cross, P. C. 'Molecular Vibrations', McGraw-Hill, New York, 1955
19 Hägele, P. C., Wolf, S. and Schmid, C. *Phys. Stat. Sol. b* 1988, **149**, 521
20 Schmieg, C., Grossmann, H. P. and Hägele, P. C. *Polymer* 1989, in press
21 Petraccone, V., Allegra, G. and Corradini, P. *J. Polym. Sci. C* 1972, **38**, 419
22 Reneker, D. H., Mazur, J., Colson, J. P. and Snyder, R. G. *J. Appl. Phys.* 1980, **51** (10), 5080
23 Krimm, S. and Jakes, J. *Macromolecules* 1971, **4**, 605
24 Kauppinen, J. K., Moffatt, D. J., Mantsch, H. H. and Cameron, D. G. *Appl. Spectrosc.* 1981, **35**, 271
25 Zerbi, G., Piseri, L. and Cabassi, F. *Mol. Phys.* 1971, **22**, 241
26 Zerbi, G. *Adv. Chem.* 1983, **203**, 487
27 Kay, H. F. and Newman, B. A. *Acta. Cryst. B* 1968, **24**, 615
28 Trzebiatowski, T., Dräger, M. and Strobl, G. R. *Makromol. Chem.* 1982, **183**, 731
29 Grossmann, H. P., Arnold, R. and Bürkle, K. R. *Polym. Bull.* 1980, **3**, 135