Defect modes for (200), *GGTGG*, tight fold re-entry in polyethylene single crystals*

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Lattice dynamical calculations on *trans*-planar polyethylene chains containing conformational defects of the type *GGTGG* have been carried out. The purpose of the work is to predict the points in the vibrational infra-red and/or Raman spectrum at which a tight, (200) type, fold should show absorptions and/or scattering. Calculations are verified for the cyclic hydrocarbon $C_{34}H_{68}$ which contains two *GGTGG* defects. The usefulness and limitations of the vibrational spectrum as evidence for the existence of (200) tight folds are discussed. Two infra-red bands near 1342 cm^{-1} and a third near 700 cm^{-1} may indicate *GGTGG* defects in single crystals. Raman spectra seem insensitive to such defects.

INTRODUCTION

The detailed structure of folded-chain lamellae of polymeric materials has attracted the attention of many workers who used various physical and chemical techniques for its determination.

At present two main aspects of the structure of polymer folded-chain lamellae are being investigated, namely: (i) the type of re-entry of the polymer chain in the crystal; (ii) the type and nature of the fold surface.

The type of re-entry has been reviewed by Keller[1] and discussed in detail by Wunderlich[2]. Additional data have been derived from neutron scattering experiments on perdeuteropolyethlene. From these studies Sadler and Keller have reached the following conclusions: (a) in solution neutron scattering results on grown single crystals are consistent with the model of chain-folding into layers in an adjacently re-entrant manner; (b) in melt-crystallized samples, chains scatter as individual entities, thus supporting the random re-entry model[3]. These results do not completely agree with some previous infrared studies[4]‡.

While the attention of most of the workers in this field has focussed on the type of re-entry and the direction of propagation of the fold, relatively little attention has been given to the possibility of finding experimental evidence for the nature of the fold surface and the actual structure of the folding region of the polymer chain.

Wunderlich has summarized our knowledge of the nature of the fold surface, indicating that, even if buried folds are found about 25 A below the upper surface, the number of relatively sharp folds increases closer to the surface. However, the final folds occur rather close to the overall lamellar surface. The existence of a sizeable number of loose cilia and of what is probably a small number of long loose loops seems to be proven[2].

One of the physical techniques whose potentialities have not yet been fully explored is the vibrational infra-red and Raman spectrum. The main question to be answered is whether the vibrational spectrum is able to give reliable and useful indications of the structure of the fold. Assuming that accurate experiments on well-characterized samples have been performed, a complete analysis of the spectrum cannot be carried out on qualitative and correlative grounds, but must be supported by some quantitative evaluation of the molecular dynamics of polymer chains containing some sort of conformational defect, which may represent structures likely to occur in single crystal lamallae.

In this paper we focus our attention on a tight fold of the type *GGTGG* which propagates the polyethylene chain along the (200) crystallographic plane. Assuming that *GGTGG* folds exist, the question we wish to answer is where should the characteristic vibrations (if any) occur in the vibrational spectrum?

Results of calculations and comparisons with experimental data in model molecules are presented and discussed in this publication. The more difficult problem of folding along the (110) plane will be dealt with in another paper.

Method of calculation

The standard methods adopted in normal coordinate calculations cannot be used for the calculation of the normal frequencies and normal modes of such a large molecule. Following our usual approach[10,12] we applied the Negative Eigenvalue Theorem[13] and calculate the density of vibrational states $g(\omega)$ for this system[14]. By reducing the resolving power of our computer experiments we can narrow the steps in the histogram of $g(\omega)$

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[‡] For a discussion on the state of the art in this field see ref 5

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and reach exact eigenvalues for those normal modes of particular interest in the present study. The vibrational displacements (eigenvectors) were calculated using Wilkinson's inverse iteration method[15,16].

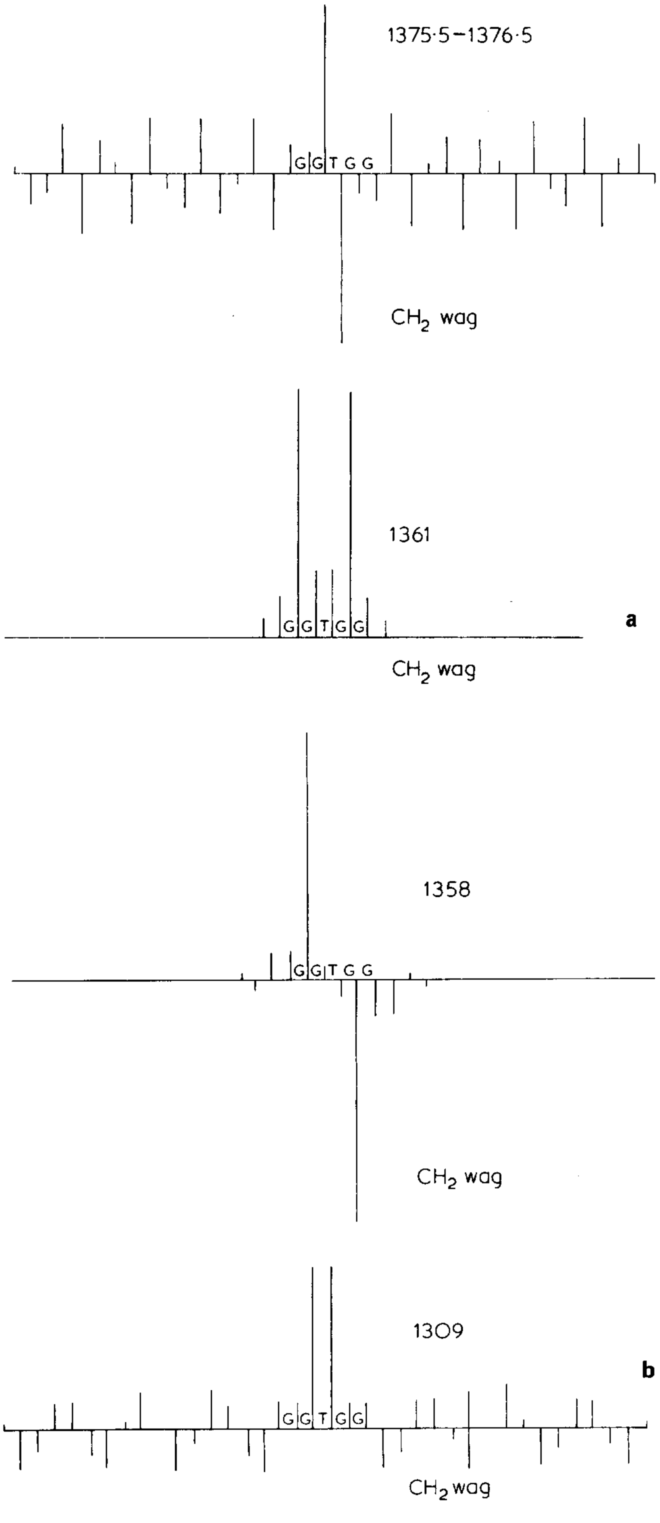
We have not calculated all of the 342 normal modes but we have sampled eigenvalues and eigenvectors in a few spectral regions where the experimental spectra of $C_{34}H_{68}$ and of PE single crystals showed seemingly interesting bands. In other words, we have used the infra-red and Raman spectra of $C_{34}H_{68}$ and of PE single crystals as a guide, keeping in mind that since the concentration of defects is relatively small in PE single crystal, only bands with a sizeable intensity would be likely to be observed in actual PE samples.

RESULTS AND DISCUSSION

Several calculations of $g(\omega)$ and of the corresponding vibrational amplitudes made over the whole spectral range have ensured that the vibrations of the all-*trans* section of the hydrocarbon chain show the characteristic vibrational features of an all-*trans* single chain of polyethylene[17,18]. The shape of the spectroscopically active modes ($k=0$) of the all-*trans* host lattice have been verified and their frequencies found to coincide with the expected singularities in the density of states as expected for polyethylene. The most important frequency cut-offs and frequency gaps have been verified.

Following the indications derived from the experimental infra-red and Raman spectra of the cyclic $C_{34}H_{68}$ molecule (which will be discussed later in this paper) calculations were made in various spectral regions and characteristic modes arising from the *GTGG* defect have been found as illustrated in *Figure* 1. With the exception of the mode located at 714 cm^{-1} all the other modes are resonance modes which occur within frequency regions spanned by the dispersion curves of the perfect all-*trans* lattice. A coupling of the defect modes with the vibrations of the host lattice is then expected as indeed is shown by calculations. The extent of localization and cooperativity of the defect modes depend on the type of motion, on the geometrical distortion of the chain and on the consequent varying extent of mechanical coupling.

We shall examine the characteristics of the frequencies and modes displayed in *Figure* 1. The first interesting modes are two quasi-degenerate resonances calculated to lie at 1376.5 and 1375.6 cm^{-1} which correspond to a large out-of-phase wagging motion of the two CH_2 groups connected by the cetral *trans* bond, and accompanied by a



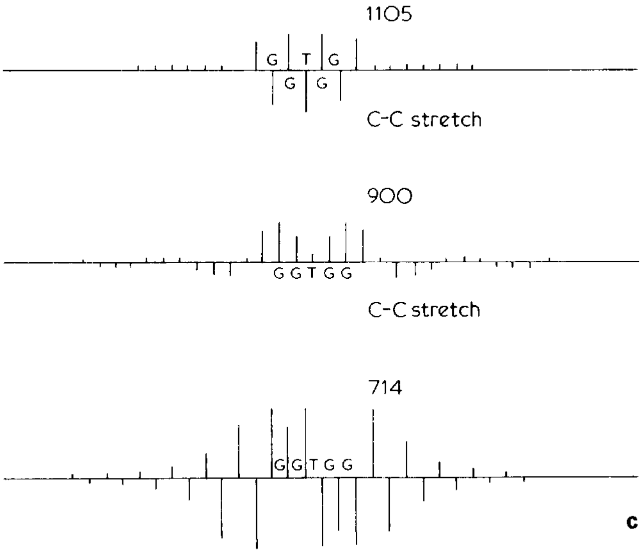


Figure 1 (a), (b) and (c) Calculated resonance modes of a *GGTGG* defect in all-*trans* host polyethylene lattice ($C_{38}H_{78}$). Vibrational amplitudes in terms of group coordinates (CH_2 wagging, C—C stretching, CH_2 rocking) are plotted on a straight line which represents the molecular model stretched out for sake of graphical display. The *GGTGG* defect lies in the middle of the chain as indicated. Frequencies are in cm^{-1}

highly cooperative wagging motions of the other CH_2 groups of the host *trans* lattice. The corresponding in-phase motion of the same two CH_2 groups is calculated at 1309 cm^{-1} and again shows some cooperativity with the *trans* host lattice.

Two highly localized resonance modes are calculated to lie at 1361 and 1358 cm^{-1} and correspond to the out-of-phase and in-phase motions of the two CH_2 groups located between the two C–C bonds in *gauche* conformation. These two modes are highly localized at the defect, while the other portion of the chain remains pratically still.

It is interesting to notice that the defect modes in the CH_2 wagging region near 1350 cm^{-1} show that in this spectral range the *GGTGG* defect behaves as if it were made up of *GG and GTG* defects moving independently. We find that this observation will be of importance in the discussion below.

In the lower frequency region of the spectrum defect modes are calculated to be at 1105,900 and 714 cm^{-1}. The mode calculated to lie at 714 cm^{-1} is of particular interest. From the dispersion curves of all-*trans* polyethylene below the limiting $k = 0$ CH_2 rocking mode at 720 cm^{-1}, we find a large frequency gap which extends as far as the cut off of the ω_5 branch at 550 cm^{-1}. This frequency gap is practically the only one available in the dispersion curves of PE below 1500 cm^{-1} [17]. The existence of a *GGTGG* defect then generates a defect mode just out of the frequency band spanned by the CH_2 rocking motions of the host *trans* lattice. From the shape of the vibration at 714 cm^{-1} we notice that a cluster of CH_2 groups, which comprises the defect, is performing mainly a rocking motion. From the shape of the vibration we do not yet consider this mode as a real gap mode since it shows a certain degree of cooperativity. A similar case of resonance at the edge of the frequency band was pointed out by Hölzl and Schmid in the study with the Green Function of the defect modes of a simplified polyethylene chain in the lower frequency region of the spectrum[19]. An analogous near-the-edge cooperative motion was found by Rubcic and Zerbi in the case of poly(vinyl chloride) containing head-to-head defects[20].

For the sake of completeness we have made similar calculations on models containing *G*, *GG* or *GTG'* defects, respectively, and found no near-the-edge defect modes. It seems that this mode is characteristic of the *GGTGG* defect.

The modes calculated at 1105 and 900 cm^{-1} are the results of a complicated mixture of several internal coordinates, but can mainly be described as localized C–C resonance modes. A discussion of these modes is given below.

INFRA-RED AND RAMAN SPECTRA OF CYCLIC $C_{34}H_{68}$

We cannot check the validity of our calculations by comparison with the spectra of a single crystal of PE since we do not yet know for sure whether the type of defect studied in this paper actually occurs and since many other kinds of defect are certainly known to exist in the disordered part of these crystals, thus complicating the issue. A clean model to be used as a test of the calculation is the cyclic hydrocarbon $C_{34}H_{68}$. The X-ray structure determined by Newman and Kay[8] shows that two segments of 15 CH_2 groups in a planar zigzag conformation are joined by two defects, each containing 2 additional CH_2 groups. The conformational sequence at the defect is substantially *GGTGG*.

We have recorded the infra-red and Raman spectrum of a sample of $C_{34}H_{68}$ kindly provided by Professor S. Krimm. Normal coordinate calculations on a simplified model of this molecule (point mass model) were reported by Tasumi *et al.*[21]; normal mode calculations on a complete model were reported by Jakes and Krimm[22]. Our calculations are in substantial agreement with the latter authors even if our vibrational assignment of the experimental spectrum differs slightly.

The infra-red spectra were recorded on Perkin-Elmer spectrometers models 125 and 180. Raman spectra were recorded with Jarrel Ash and Spex spectrometers.

CALCULATIONS

Model The tight fold re-entry with a propagation of the polymer chain along the (200) plane can be achieved when a *GGTGG* conformational defect is introduced in a *trans*-planar chain. This type of defect (i) is consistent with the diamond lattice model; (ii) is energetically plausible[6,7]; and (iii) involves as few carbon atoms as required by other kinds of study[1,2]. Two nearly *GGTGG* folds are found in the cyclic molecule $C_{34}H_{68}$ whose structure has been determined by Newman and Kay[8]. The results of our calculations will then be compared with the vibrational infra-red and Raman spectra of this molecule.

Here, we calculate the vibrational spectrum of a hydrocarbon chain consisting of two *trans*-planar chains made up by 17 CH_2 groups joined in the middle by a defect with *GGTGG* conformation. The whole hydrocarbon studied has formula $C_{38}H_{78}$. The considerable length of the *trans* arms (*trans* host lattice) ensures that the model approaches the physical situation which may eventually be found in a single crystal lamella. Chain end effects due to short *trans* segments are in this way removed. For a better understanding of some of the results obtained from the *GGTGG* defect, calculations were extended to other similar models containing *G*, *GG*, *GTG* and *GTG'*.

Force field The force field derived by Snyder[9] from analysis of the spectra of n-hydrocarbons in the liquid state was used. Tetrahedral geometry is adopted; C–C and C–H bond lengths are taken to be 1.54 and 1.1 A, respectively. Synder has shown that slight variations of the geometry from the assumed one do not affect the results of the vibrational analysis.

Figures 2 and 3 report the infra-red and Raman spectrum, respectively, of crystalline $C_{34}H_{68}$, which possesses C_{2h} symmetry; its 300 normal modes are divided in

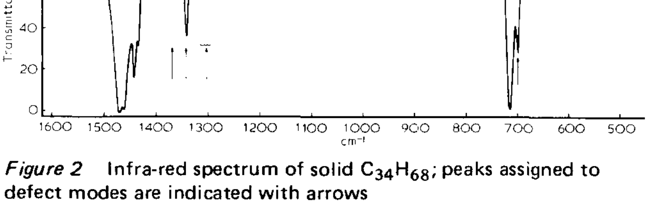


Figure 2 Infra-red spectrum of solid $C_{34}H_{68}$; peaks assigned to defect modes are indicated with arrows

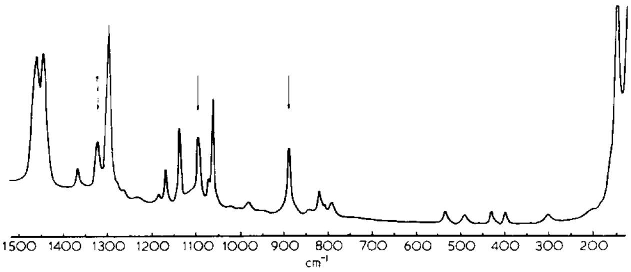


Figure 3 Raman spectrum of solid $C_{34}H_{68}$; peaks assigned to defect modes are indicated with arrows

Table 1 Most significant defect mode frequencies of a *GGTGG* defect placed in the middle of a *trans*-planar polymethylene chain. Comparison with the vibrational spectrum of crystalline $C_{34}H_{68}$

Calculated (cm^{-1})	Observed (cm^{-1})
1375	1368 i.r.
1361	1342 i.r.
1358	
1309	1304 i.r.
1105	1096 Raman
900	891 Raman
714	700 i.r.

the following symmetry species: 77 A_g, 73 A_g, 74 A_u and 76 B_u. *g* and *u* modes are Raman and infra-red active, respectively. The vibrational assignment of many of the normal modes of this molecule has been already discussed by Jakes and Krimm[5]. We focus our attention in this case only on those normal modes which may be characteristic of the defects; most of the defect modes are localized at the defects. Since they are so far away from each other, it is reasonable to assume that they are vibrationally uncoupled such that accidental degenracy between in-phase and out-of-phase *g* and *u* modes may occur. The calculated defect modes should then be found both in the infra-red and in the Raman spectrum at the same frequencies. The experimental results (*Figures* 2 and 3) do not show pairs of coincident infra-red and Raman bands. This is only due to the different spectral intensities in infra-red and Raman and to the intrinsic weakness of the Raman spectrum.

The *trans*-planar segment of this molecule shows the traditional spectral band progressions observed for solid paraffins in the infra-red and the typical spectral features in the Raman. A few peaks suitably labelled in *Figures* 2 and 3 cannot be easily assigned to the *trans*-planar segment and may originate from the defect.

In *Table* 1 we report the proposed association between calculated defect modes and observed bands in the infra-red or Raman spectra of the cyclic $C_{34}H_{68}$ molecule. Predictions from the calculations are satisfactorily verified in the experimental spectrum of the cyclic hydrocarbon molecule.

DISCUSSION

Once the calculations on defect modes have been verified for a molecule which certainly contains the same kind of defect, a critical analysis of the uniqueness of the calculated frequencies must be made. In other words, it may well happen that other kinds of conformational defects give rise to normal frequencies which nearly coincide with those calculated for the *GGTGG* defect. An answer to this question must be given both from experiments and/or calculations. In this section we will attempt critically to analyse this problem using the available information from theory and/or experiments. We limit our analysis to the case of the calculated defect modes of the *GGTGG* defect.

The defect modes calculated at 1105 and 900 cm^{-1} and observed in the Raman spectrum of solid $C_{34}H_{68}$ at 1095 and 891 cm^{-1}, respectively, can be shown not to be uniquely characteristic of a *GGTGG* defect. The 1095 cm^{-1} band has gained great popularity in the field of structure and spectroscopy of lipids. Every time some *gauche* distortion is introduced into *trans* hydrocarbon chains a Raman peak develops near this frequency. This band became known as the '*gauche* band' and has been used to probe the structure of lipids and membranes[23]. A weak peak is also observed in the infra-red spectra of liquid hydrocarbons and polyethylene. We have shown that practically all energetically acceptable conformational defects give rise to resonance modes, all occuring in a very narrow frequency range centered at about 1090 cm^{-1} [24]. With regard to the peak observed in the Raman spectrum near 890 cm^{-1} in $C_{34}H_{68}$ it is also observed as a broad feature in the Raman spectrum of solution-grown (*Figure 4*) as well as in melt-crystallized PE for which two different kinds of re-entry have been proposed from neutron scattering experiments[3].

An analogous situation is found in the Raman spectrum for the mode calculated at 1309 cm^{-1} and observed in the infra-red spectrum of $C_{34}H_{68}$ at 1304 cm^{-1}. Indeed, the Raman spectra of several kinds of polyethylene all show a weak broad scattering on the high frequency side of the strong peak, which is assigned to the CH_2 twisting motion near 1300 cm^{-1}. This broad scattering is certainly evidence of disorder[25], but is not characteristic of a *GGTGG*-type defect.

This discussion allows us to draw the first important conclusion, namely that those defect modes of the *GGTGG* defect which show some activity in the Raman spectrum of $C_{34}H_{66}$ cannot be considered unique if observed in the Raman spectra of PE single crystals. We then learn that the Raman spectrum may not be so useful in the search for

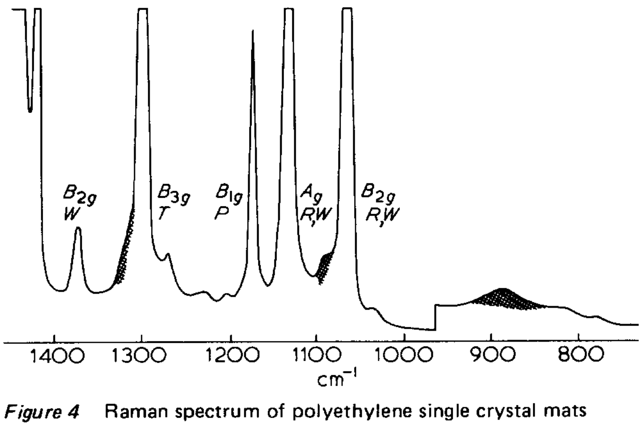


Figure 4 Raman spectrum of polyethylene single crystal mats grown from solution (kindly provided by Dr. Sadler and Professor Keller); Hatched regions correspond to those where defects modes calculated for (200)-type *GGTGG* re-entry may occur, see text

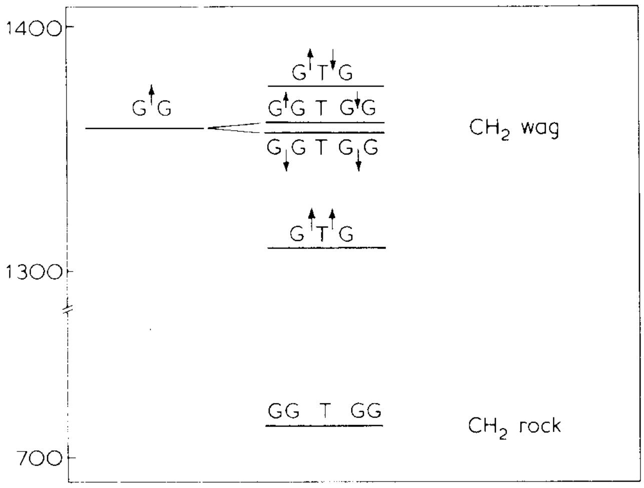


Figure 5 Calculated vibrational levels associated with *GG* and *GGTGG* defects. Arrows indicate approximately the location on the defect, and the direction of the displacement of the wagging motions

(200)-type tight fold defects or perhaps for any kind of fold*.

We must therefore focus our attention only on the infra-red spectrum, with the wagging modes near 1360 cm^{-1}, the wagging mode near 1309 cm^{-1} and the near-the-edge rocking mode at 700 cm^{-1}, all certainly observed in the infra-red spectrum of $C_{34}H_{68}$.

The medium strength absorption of $C_{34}H_{68}$ at 1342 cm^{-1} has been subject of some discussion in the literature with reference to the problem of the nature of the fold surface of PE single crystals[22,26]. A recent review by Coleman and Painter discusses the present state of the art[27]. Fourier transform infra-red difference spectroscopy of several samples of PE have clearly indicated that an absorption band at 1346 cm^{-1} is characteristic of the fold surface of solution-grown PE single crystals[28].

It is generally accepted from calculations and experiments that the conformational disorder which can occur in the amorphous regions of PE or in liquid n-alkanes gives rise to absorption bands at 1368, 1353 and 1305 cm^{-1} mainly due to the wagging motions of the CH_2 groups in the disordered material[9,29]. In particular, the band at 1351 cm^{-1} in $C_{34}H_{68}$ and at 1346 cm^{-1} in PE solution grown single crystals has been ascribed to distorted *GG* structures[22,27]. Coleman and Painter conclude that if the assignment is correct it follows that the fold in PE single crystals as revealed by the band at 1346 cm^{-1} is tight[27]. No distinction between (200)- and (110)-type defects is attempted.

If this is so we must conclude that the band observed in $C_{34}H_{68}$ is only due to the *GG* section of the tight fold and that the wagging motion of the CH_2 at the *GG* group is dynamically uncoupled with its neighbour, separated by a *trans* bond. The question which remains to be answered is how to distinguish between a *GGTGG* defect and a *GG* defect.

In *Figure* 5 the calculation of defect modes made on a model with only one *GG* defect are compared with the results from a *GGTGG* defect of *Figure* 1. The defect mode from a *GG* defect is calculated at 1359 cm^{-1} and is a highly localized resonance wagging mode of the CH_2 between two *gauche* bonds (*Figure* 6). The splitting of such a mode into the in- and out-of-phase motions in *GGTGG* is small thus showing that the mechanical coupling is itself small.

The modes calculated as lying near 1375 and 1309 cm^{-1} arise from the *GTG* section of the *GGTGG* defect; while this may be meaningful in deciding on the existence of a *GGTGG* structure in a simple cyclic molecule such as $C_{34}H_{68}$, it will be of no help in the case of PE single crystals, since many other *GTG* structures occur in the disordered part of PE single crystals.

Of crucial importance, then, is the possibility of the experimental observation of the out-of-band mode below the $k=0$ CH_2 rocking mode. In order to ensure that the mode near 700 cm^{-1} is characteristic of *GGTGG* defect we have undertaken calculations in this frequency range for a model containing *G*, *GG*, *GTG* and *GTG'* defects. None of these structures generate a defect below the $k=0$ CH_2 rocking mode.

CONCLUSIONS

We have reported calculations of vibrational frequencies and vibrational displacements of normal modes generated by the introduction of a *GGTGG* conformational defect in an otherwise all-*trans* host lattice of polyethylene. Using special numerical techniques, calculations were undertaken on large molecular models in order to simulate as closely as possible, the real situation in a PE single crystal.

The validity of the predictions of the calculations has been checked by the fact that the predicted modes are observed in the infra-red or Raman spectra of the cyclic hydrocarbon $C_{34}H_{68}$ in the solid state, where it is known that the molecule contains two *GGTGG* defects.

The calculations in this paper provide a set of frequencies and corresponding amplitudes which may be useful in

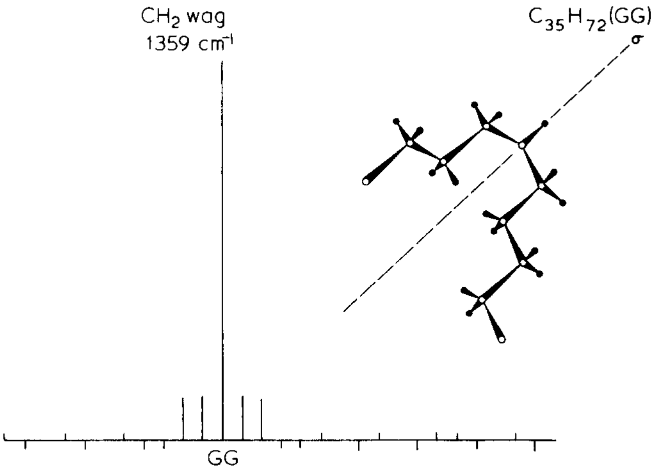


Figure 6 Calculated resonance mode of *GG* defect in all-*trans* host polyethylene lattice. The vibrational amplitudes in terms of the CH_2 wagging group coordinate are indicated on a straight line which represents the molecular model stretched out for the sake of graphical display. The *GG* defect lies in the middle of the molecule as indicated. On the right side is given a sketch of the shape of the chain with *GG* conformation

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* An additional failing of the Raman spectrum is that since organic molecules are generally poor scatterers, small concentrations of scattering species cannot be revealed. In PE single crystals the concentration of defects relative to the perfect part is certainly small.

§ A doublet is observed in the infra-red spectrum of $C_{34}H_{68}$ at 1342 and 1351 cm^{-1}. The assignment of the 1351 cm^{-1} component to a defect mode or to one of the components of the sequences of CH_2 wagging from the *trans*-planar sections of the molecule cannot be made on any logical grounds.

structural studies of simple cyclic molecules when evidence for the *GGTGG* structure is sought.

A critical analysis based on calculations and experimental spectroscopic observations on samples of $C_{34}H_{68}$, PE single crystals and solid and liquid n-alkanes shows that some of the modes cannot be taken as characteristic and unique of the *GGTGG* defect.

It is concluded that the Raman spectrum does not seem to be a good source of experimental information for the study of the detailed structure of the defect in PE; but the infra-red spectrum does contain some useful information.

In the CH_2 wagging region (1380–1300 cm^{-1}) the *GGTGG* defect contributes to the infra-red spectrum providing signals originating independently from the *GG* and *GTG* sections of the defect. While the signals from *GTG* blend into the absorption from the disordered part of PE single crystals, only the mode near 1342 cm^{-1}, due to the distorted *GG* defect, can be clearly isolated.

The question raised at the beginning of this paper and which was the reason of this work can then be answered as follow. Calculations on several model systems and experiments on $C_{34}H_{68}$ suggest that a simultaneous appearance in the infra-red spectrum of two bands near 1342 cm^{-1} and one near 700 cm^{-1} (certainly below the CH_2 in-phase rocking mode of the *trans*-planar chain) may be evidence for the existence of *GGTGG* defects in PE single crystals. Further studies on polyethylene are now required.

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