

# DEFECT INDUCED INFRA-RED ABSORPTION OF POLYMERS

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## ABSTRACT

Polymeric systems never possess an ideal structure but contain a considerable amount of chemical and structural imperfections. The vibrational properties of polymer systems considered as defect containing crystals are discussed. The features of the infra-red and Raman spectrum are qualitatively predicted. The major advancement of the vibrational spectroscopy of these systems is the present possibility of calculation of the density of vibrational states both for ideal and defect containing molecules. The use of the density of states for the interpretation of the vibrational spectra of these systems is discussed and its limitations are pointed out.

The vibrational spectrum of solid polyethylene is analysed and conclusions on the existence of various types of conformational defects are derived. A possible interpretation of the spectrum of polyethylene single crystals is suggested.

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The advancement of the studies of normal vibrations of macromolecules has closely followed the development and availability of large and fast computers. The theoretical concepts of the vibrations of periodic infinite structures developed a long time ago<sup>1-4</sup> can equally be applied to the study of normal vibrations of polymeric systems. Since we are generally dealing with polymeric materials which can be considered as organic crystals, intramolecular forces are at least one order of magnitude larger than the intermolecular ones. Most of the spectroscopic work on polymers has been carried out on the assumption of a chemically perfect infinite and isolated chain where intermolecular interactions have been neglected.

The first theoretical treatment of the vibrations of chain molecules was presented by Higgs<sup>5</sup> and has been reformulated in different ways by several authors<sup>6-10</sup>. The first application to real polymers was presented by Tasumi *et al.*<sup>11</sup> and by Lin *et al.*<sup>12</sup>. Most of the work has been limited to simple polymers and to  $k = 0$  modes for which experimental spectroscopic data were available. Moreover since for hydrocarbon-like polymers reliable (i.e. reasonably transferable) force fields were available structural information could then be derived. The purpose of such a calculation is twofold; (a) Spectroscopists wish to base their analysis of the vibrational spectrum on a theoretical basis which also provides a quantitative description of the normal modes<sup>13</sup>. Moreover if a satisfactory fitting between the calculated and the experimental spectrum is found using potential constants derived

from model compounds, further support for the transferability of the force field is acquired<sup>14,15</sup>. (b) The structural chemist wishes to calculate the spectrum of different possible models of an unknown polymer<sup>16</sup>. Comparison with experiment may be the clue to the determination of its structure. Combination of experimental and theoretical data both from x-ray work and from the vibrational spectrum has proved to be an important tool for structural determinations on polymers<sup>17</sup>.

A major change in the spectroscopy of polymers occurred when neutron diffraction studies were found able to provide either the density of states by means of time-of-flight experiments<sup>18-22</sup> or the actual phonon dispersion curves measured as functions of  $k$ <sup>23</sup>. Efforts have been made for the calculation of the phonon spectra of polymers in one or three dimensions throughout the first Brillouin zone<sup>24</sup>. One- or two-phonon density of states were calculated<sup>24</sup>. The interpretation of the peaks in the time-of-flight neutron spectra or in the derived density of states was made more certain by such calculations<sup>24</sup>. In the author's laboratory attempts have also been made to extend these calculations to polymer chains other than the well known traditional organic polymers. Hydrogen-bonded systems can be considered as chain molecules and their spectral features can be interpreted with the same principles and the same tools as those previously adopted for organic polymers. The work so far carried out seems to be useful for a more detailed interpretation of the vibrational spectra of these substances<sup>25-27</sup>.

It has been generally realized, however, by most of the workers in this field that several features observed in the infra-red, Raman and inelastic neutron scattering (i.n.s.) spectra of polymeric materials cannot be accounted for on the basis of the lattice dynamics of ideal systems. Several absorption peaks which could not be ascribed either to  $k = 0$  modes, or to multiphonon processes, were said to originate from the so-called 'amorphous' or 'imperfect' part of the polymer chain<sup>28</sup>. This assumption is well justified since a certain amount of amorphous substance is known to occur even in the most crystalline samples of polymeric materials<sup>29</sup>.

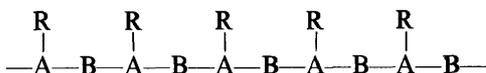
Our interest has thus been focused mainly on the analysis of the infra-red and/or Raman peaks which occur in addition to those of the perfect crystal. Our purpose was twofold: (a) to understand the lattice dynamics of a defect-containing chain and explain its vibrational spectrum; (b) obtain from the so-interpreted infra-red spectrum information on the nature and structure of the so-called amorphous regions of the polymer sample. This problem is far from being solved and a large amount of work is still needed.

The vibrational problem of defect containing crystals has been dealt with both theoretically and experimentally in several papers<sup>30-32</sup> and the main spectral modifications arising from a perturbation of the perfect lattice by the defects have been qualitatively predicted in general and quantitatively verified in a few cases<sup>33</sup>. The peculiar chemical nature and chemical structure of an organic polymer requires consideration of several additional types of defects which are not found in simpler inorganic crystals. Intrachain defects must first be considered before the interchain ones are taken into account. The orders of magnitude of intra- and inter-chain forces are different because in organic polymers chemical units are linked by covalent bonds while van der Waals type forces act between chains.

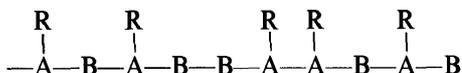
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Let us briefly discuss the types of defects expected in a polymer crystal and point out those which have been considered so far in a detailed treatment

of the vibrational spectrum. A monomer unit of the type  $\begin{array}{c} \text{R} \\ | \\ \text{A}-\text{B} \end{array}$  will be taken as a working model; the necessary limitations or extensions of the discussion which follow should be considered when a different type of monomer unit is considered. If the stereospecific polymerization is not perfect the regular repetition of chemical units of the type



(head-to-tail isotactic sequence) will be interrupted either by a switching of the order of presentation of the monomer unit:



or by an irregular stereoregular structure taken up by the substituent. Chemical defects and stereoregular defects are then introduced and their existence should, in principle, be shown by the vibrational spectrum. Even if the polymerization reaction has occurred in a perfect way, once the chain has been made it will taken up the most 'comfortable' position in space corresponding to a minimum in its conformational energy. The obtained geometry is characterized by a screw operation. Several factors may force the translationally regular growing segment to fold, bend or twist thus giving rise to a complicated framework which may change when mechanical or thermal treatments are applied to the sample. Conformational defects are then introduced. As the last step intermolecular factors force, when possible, molecular chains to pack into a three-dimensional lattice. The perfect packing may be altered by many causes which give rise to several types of lattice defects some of which are encountered also in simple crystals while others are peculiar to the polymer system<sup>29</sup>.

The present discussion is restricted to the case of intramolecular defects which are more likely to be observed in the vibrational spectra. The vibrational perturbations by intermolecular imperfections can be considered second-order effects (both in frequency and intensity) and are neglected in what follows.

Our studies are based mainly on the knowledge of the density of the states  $g(\nu)$  for a polymeric system either with perfect structure or in the various possible imperfect states which can be reasonably conceived on the basis of thermodynamical or structural arguments. Moreover the desired density of states should account for most of the structural details of the polymer molecule. Calculations must then be performed on real polymer chains taking into account all vibrating atoms without simplifications (e.g. point masses, etc.). Suitable methods for the exact calculation of  $g(\nu)$  and related quantities for a perfect polymer chain with translational symmetry have been presented previously<sup>34</sup> but cannot be applied in the present case. It is required to construct a dynamical matrix which contains the desired random distribu-

tion of defects. A method has been proposed<sup>35-37</sup> which allows us to construct a dynamical matrix starting from a set of Wilson's type internal displacement coordinates<sup>38</sup>. The linear transformation between the internal displacement coordinates  $R$  and the cartesian displacement coordinates  $X$  is generally written in matrix notation as

$$\mathbf{R} = \mathbf{B}\mathbf{X} \quad (1)$$

If  $\mathbf{F}_R$  is the force constant matrix in  $R$  space, the vibrational potential energy is written as

$$2V = \tilde{\mathbf{R}}\mathbf{F}_R\mathbf{R} \quad (2)$$

which can be transformed into

$$2V = \tilde{\mathbf{X}}\tilde{\mathbf{B}}\mathbf{F}_R\mathbf{B}\mathbf{X} = \tilde{\mathbf{X}}\mathbf{F}_X\mathbf{X} \quad (3)$$

The symmetrical dynamical matrix is written as

$$\mathbf{D} = \mathbf{M}^{-\frac{1}{2}}\mathbf{F}_X\mathbf{M}^{-\frac{1}{2}} \quad (4)$$

where  $\mathbf{M}$  is a diagonal matrix whose elements are the atomic masses. Since  $g(\nu)$  is desired, all matrices appearing in equations 1 to 4 must refer to a very large system which should consist of the largest possible number of atoms thus generating a very high population of vibrational degrees of freedom. The unavoidable practical computational difficulties (computer storage and computing time) on these very large matrices can be handled reasonably by: (i) the generation of large matrices from small starting submatrices which refer to one chemical repeat unit, (ii) the solution of the eigenvalue problem by the so-called negative eigenvalue theorem (n.e.t.)<sup>39</sup>. While generating the large matrix it is then possible to introduce the randomness properly chosen. Various types of defects can then be introduced to the problem whose dynamics we wish to study. Geometry defects, force constant defects and mass defects enter the dynamical problem through equations 1, 3 and 4 respectively. Equation 4 has the advantage of being symmetrical and the application of n.e.t. is immediate.

The effect on the vibrational spectrum of a simple crystal by the introduction of defects has been already discussed in several papers. It has been predicted and experimentally verified that out-of-band or gap modes give rise to characteristic absorption due to localized modes and moreover that all band modes may be activated thus mapping the density of vibrational states  $g(\nu)$  of the regular crystals. We look for the same phenomenon in the vibrational spectra of polymers, being aware of the differences between the crystals theoretically studied and those which are the subject of the present paper.

Attempts to build a dynamical matrix of a polymer with conformational defects were originally presented by Jannink<sup>40</sup>; later a discussion on a simplified model of a polymer molecule whose defects are represented only by force constant impurities was presented by Opaskar and Krimm<sup>41</sup>. Studies on mass and conformational defects of real polymers have been carried out in the author's laboratory<sup>35-37, 42</sup>.

For the general types of organic polymer crystals we must consider the large number of atoms per primitive unit cell which give rise to many

frequency branches in the dispersion relation which generally cover most of the vibrational spectrum (3500 to 0  $\text{cm}^{-1}$ ). From previous work<sup>10,43</sup> we know that some frequency branches are practically independent of  $k$  giving rise to strong singularities in the density of states plot. Some others are strongly coupled giving rise to crossing or mutual interactions clearly displayed by a detailed calculation. With the exception of mass defects where isotopic impurities only are introduced (e.g. H impurity in perdeuteropolyethylene)<sup>35</sup> for organic polymer crystals we expect that out-of-band modes will not occur and must consider gap or in-band modes. Neglecting isotopic impurities, for real polymers stereoregular or conformational defects introduce drastic changes in the geometry as well as in the force constant matrices which enter the dynamical matrix. Among the normal modes corresponding to the eigenvectors of the defect-containing dynamical matrix of equation 4 we should be able to find modes which are highly localized in a chain (i.e. only the atoms at the defect and a few neighbouring ones move, the rest of the chain remains still) or are coupled with the motion of the perfect lattice. Opaskar and Krimm<sup>41</sup> have tried to suggest criteria for predicting the amount of localization of the various vibrational modes in terms of the extent of coupling with the host lattice. Their treatment is, however, confined to a very simplified chain model. The problem seems to us more complicated since each of the defects considered involves several atoms thus generating several resonances whose coupling between themselves or with the host lattice depends on the nature of the defect introduced.

Exact judgement on the localization of the modes is only possible when the eigenvectors for these vibrating systems are known. In the author's laboratory some work is in progress for the calculation of polarization vectors. Since we still lack detailed knowledge of the displacement vectors, for the time being we judge the extent of localization of the mode at the defect by locating its characteristic frequencies and by judging their sensitiveness to change in the surrounding medium in the lattice considered (see later). The following cases can generally be expected:

(i) The spatial arrangement of the atoms and the corresponding force constants of the defect generate in-band resonances highly localized within the defect and not coupled with the rest of the chain. The frequencies of the modes occur, however, within the frequencies transmitted by the host lattice.

(ii) The spatial arrangement of the atoms and the corresponding force constants of the defects generate modes which are coupled with other phonons of the host lattice thus introducing a large perturbation into the displacements and to a lesser extent into the frequencies of the other phonons.

The final expected results can be summarized as follows:

(a) The translational symmetry is removed and the shape of the phonon waves is slightly perturbed. As a result activation of the whole density of states of the perfect lattice should occur.

(b) If the concentration of defects is small the localized defect modes will also give their contribution to the experimental spectrum. Superimposed on the  $g(\nu)$  of the host lattice it is expected that the density of states due to the defects should be detected.

(c) If the concentration of defects is not small the modes of the defects may interact and the phonons of the host crystal will be strongly perturbed. The whole density of states will then be perturbed. A calculation of the density of states from the dynamical matrix containing a large concentration of defects may predict the experimental spectrum of an amorphous substance since, because of a lack of any symmetry, each mode should become active.

Our work is mostly based on the comparison of the calculated density of states with the experimental vibrational spectrum (infra-red, Raman, i.n.s.). This method may be the subject of criticism and we wish to point out its limitations. We feel, however, that its cautious use may provide useful information.

It is known<sup>44</sup> that the absorption coefficient for defect-induced one phonon absorption is given by the expression :

$$I(\nu) = DM(\nu)^2 g(\nu) \quad (5)$$

where  $D$  is the concentration of defects,  $M(\nu)$  is the frequency-dependent transition moment which depends on the perturbation introduced by the defect, and  $g(\nu)$  is the density of states of the perfect host lattice. Several studies on simpler inorganic crystals have shown that the frequency-dependent transition moment may sometimes substantially modify the features of the predicted vibrational spectrum if compared with the one assumed to depend only on  $g(\nu)$ . Determination of the electronic distribution of atoms or molecules is, however, a very difficult task which is still the subject of several extensive theoretical studies. Quite often the calculated dipole unweighted density of states can be compared reasonably with the experimental infra-red, Raman or i.n.s. spectra<sup>45</sup>.

In the case of organic crystals the prediction of the transition moment is even more complex and remains an unsolved problem even for small molecules comprising a few atoms<sup>46, 47</sup>. It is then impossible to introduce reliable dipole transition moments into equation 5 for the calculation of the experimental infra-red or Raman spectrum. The cross section for inelastic neutron scattering experiments is simpler to calculate but it requires, however, knowledge of the polarization vectors<sup>24</sup>. We content ourselves with the use of the dipole unweighted  $g(\nu)$ . Several reasonable justifications support our decision:

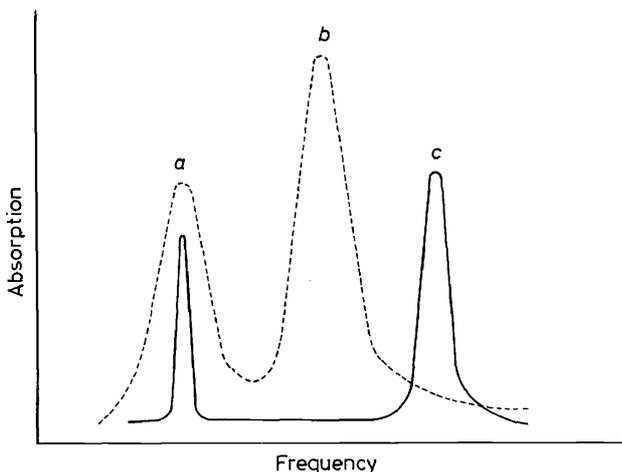
(i) Because, as already mentioned, intramolecular forces are considerably larger than the intermolecular ones, the derived density of states is strongly peaked. The activation of  $g(\nu)$  peaks may quite probably result in peaks in the vibrational spectrum. While frequency fitting can be taken into account, obviously no comparison with peak intensity should in general be made.

(ii) The use of dipole unweighted  $g(\nu)$  is based on just the same principles as were adopted in the interpretation of the vibrational spectrum by means of normal coordinate analysis. Normal coordinate calculations have been used in the last decade by many authors and have led to acceptable conclusions. The typical situation (which may be used as an example) of the interpretation of the vibrational spectrum of a small molecule in terms of normal coordinate analysis is graphically depicted in a work by Zerbi and Sandroni for the case of biphenyl<sup>48</sup>. In normal coordinate analysis no prediction of the band intensity is generally done and strong or weak bands are equally used

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in fitting frequencies. Some Russian authors have attempted to predict band intensity for polyatomic molecules<sup>49</sup> but it is felt that the starting data are somewhat empirical. It has to be added that the use of  $g(\nu)$  for polymeric systems allows us to display additional features arising from the large model adopted, unattainable from calculation on model compounds.

Let us consider the three possible situations depicted in *Figure 1* which can occur in a comparison between calculated  $g(\nu)$  and the experimental



*Figure 1.* Examples of extreme situations which may occur in a comparison between the experimental absorption spectrum of a polymer (dashed) and a calculated  $g(\nu)$  (full line).

spectrum. Case (a): coincidence of peaks (irrespective of their intensity) can be considered a positive factor in the comparison; Case (b): It is very unlikely that a very few modes (or even no modes) in  $g(\nu)$  gain such a high intensity to exhibit a strong absorption. Even if this case cannot be excluded it can be considered very unlikely. The infra-red peaks should have other origins (defects, etc.). Case (c): The existence of a  $g(\nu)$  peak with no corresponding i.r. band may well be explained in terms of the existence of a local symmetry within the molecule which compensates dipoles.

Next step in the interpretation of the observed vibrational spectrum of a defect-containing polymer is the identification of the possible extra peaks due to modes at the defect.

The theoretical prediction of the peak position is generally carried out by calculating  $g(\nu)$  on the following models:

(a) A long repetition of the basic unit  $-(A)_n-X-(A)_n-$ , where A represents a repeating unit of the host lattice and X a defect of any type;  $n$  has to be taken large enough to avoid or to minimize end effects.

(b) A long repetition of the basic unit  $-(A)_n-X-(A)_m-$  where  $n$  and  $m$  can take any values at random.

(c) Calculations (a) and (b) are repeated on models with different  $n$  and  $m$ ,

i.e. by changing the concentrations of the defects relative to the number of units of the host lattice. The calculated population of frequencies of the characteristic  $g(\nu)$  peak should follow the same trend.

It is then possible to identify in the calculated  $g(\nu)$  the singularities arising from the host lattice and those arising from the localized defect modes which we take as characteristic of that particular group of atoms occurring in the defect. The independence (i.e. localization) of the mode is assured by calculations (a), (b) and (c).

It is obvious that the identification of the peaks in terms of some group of atoms or of some structural features is strongly model-dependent, i.e. the choice of the model may affect the conclusions. As usual in normal coordinate calculations applied to structural analysis, computations become meaningful only when they are based on reasonable geometries (they must be likely on energetic considerations) and on reliable force fields. The use of  $g(\nu)$  is based on these same principles. We may quote as an example the work on polyethylene by Snyder<sup>50</sup> who bases his interpretation on normal coordinate calculations of various rotamers of linear paraffins and the work Zerbi *et al.*<sup>37</sup> on the same substance based on the calculation of  $g(\nu)$ .

An additional simplification has been accepted in the present work, namely we neglect interchain interactions and limit our calculations to polymer chains isolated from their neighbours. This approximation is certainly well justified on the basis of the results of earlier work on perfect polymers<sup>10, 24, 43</sup>. As already discussed, intermolecular forces are weaker than the intramolecular ones and their effect on the vibrational spectrum can be considered as a perturbation. Furthermore  $k = 0$  space group splitting has been observed for a very few polymers, namely for polyethylene<sup>28</sup> and for orthorhombic polyoxymethylene<sup>51</sup>. Comparison of the density of states along the 100 symmetry direction for a three-dimensional crystal of polyethylene (PE) and that for a single chain of PE<sup>24</sup> shows that the features from the three-dimensional lattice do not dramatically change the  $g(\nu)$ , with the exception of the very low energy region which is not generally considered in our studies. To our knowledge most of the spectra of polymers have been satisfactorily interpreted on the basis of line group modes (isolated chain). Opaskar and Krimm in their analysis of defect-containing PE<sup>41</sup> report the density of states for a three-dimensional crystal, but their conclusions could be equally well derived from a single chain model which they subsequently adopt for polyvinyl chloride.

## POLYETHYLENE

The case of PE has been treated in the author's laboratory using the approach just discussed. The mechanism of the opening of the double bond during polymerization was determined through comparison of the experimental spectra of several copolymers of ethylene and deuterioethylene with the density of states calculated for various isotopically impure polyethylenes. It was shown that the reaction occurs through the *cis* opening of the double bond<sup>35</sup>.

Of particular interest for a critical study of the applicability of this type of study to the interpretation of the structure of solid polymers is the recent

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work by Zerbi *et al.* on conformationally impure PE chain<sup>37</sup>. It is well known that the vibrational spectrum of crystalline PE shows absorptions which cannot be ascribed to  $k = 0$  fundamental transitions<sup>28</sup>. The knowledge of the  $k = 0$  one phonon spectrum is fairly certain as a result of extensive experimental as well as theoretical studies on a single chain or on a three-dimensional crystal<sup>24</sup>. Several absorption peaks, however, were left unassigned or were associated qualitatively with the so-called 'amorphous' bands. We have carried out new careful experimental studies on samples of highly crystalline PE and studied the temperature dependence of its infra-red spectrum. The main unexplained infra-red peaks are observed at 198 (w), 252 (w), 386 (w), 538 (m),  $\sim 1075$  (m), 1128 (w), 1300 (m), 1350 (m), 1367 (m), 1440 (m)  $\text{cm}^{-1}$  (Figures 2, 3). By raising the temperature the peak

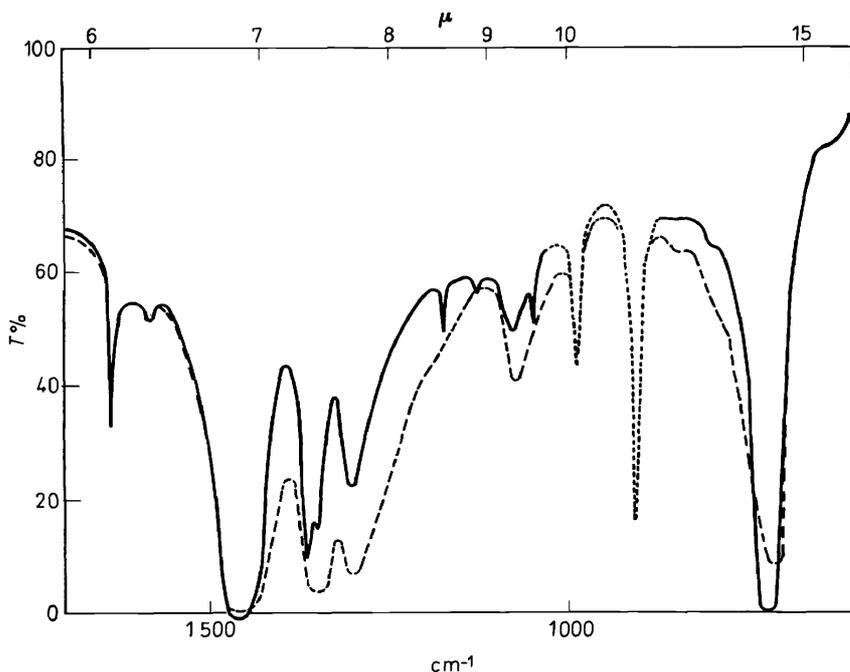


Figure 2. Section of the infra-red spectrum of polyethylene: full line denotes solid at room temperature; dashed line refers to the melt; dotted line denotes absorption due to vinyl end groups.

at  $538 \text{ cm}^{-1}$  broadens and shifts slightly, and a new band appears at  $300 \text{ cm}^{-1}$ . The factor group  $k = 0$  doublets of the rocking at  $720\text{--}730 \text{ cm}^{-1}$  and bending modes at  $1463\text{--}1471 \text{ cm}^{-1}$  respectively decreased their distance and disappear at the melting point. The peaks at  $1050$  and  $1075 \text{ cm}^{-1}$  coalesce into a broader absorption with maximum at  $1073 \text{ cm}^{-1}$ ; the peaks at  $1128$  and  $1173 \text{ cm}^{-1}$  disappear. More interesting is the doublet at  $1350$  and  $1367 \text{ cm}^{-1}$  (Figure 4). The component at  $1350 \text{ cm}^{-1}$ , weaker than that at  $1367 \text{ cm}^{-1}$  at  $25^\circ \text{C}$ , increases its relative intensity with temperature while the

sample is still solid. It reaches the same intensity at the melting point and becomes more intense in the melt. The Raman spectrum of crystalline PE reported by other authors<sup>52-54</sup> shows at least two lines (at  $\sim 1465$  and  $\sim 720$   $\text{cm}^{-1}$ ) which cannot be accounted for in terms of line or space factor group  $k = 0$  modes.

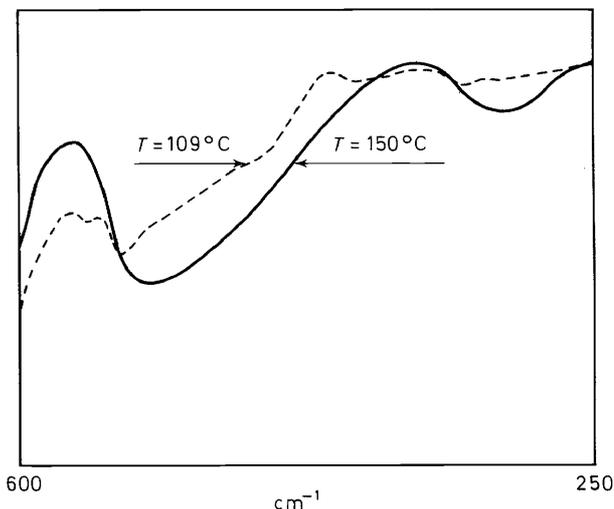


Figure 3. Far infra-red spectrum of polyethylene at two different temperatures.

Since it is well known that a solid sample of highly crystalline PE contains a non-negligible amount of amorphous material<sup>29</sup> we have constructed a dynamical matrix for conformationally impure PE and calculated the corresponding density of states  $g(\nu)$ . The choice of the model (i.e. the types of possible conformational defects) was guided by thermodynamical considerations on the types and relative concentrations of the various rotamers which should be considered. The use of an Ising model for the determination of the concentrations of conformational defects at various temperatures was also adopted<sup>55</sup>. The model adopted consists of 200  $\text{CH}_2$  units joined in *trans* conformation for the ideal case. Kinks and folds in the *trans* chain were introduced (in a *regular* or *random* way) by the insertion of the following types of X defects  $X = G, GG, GTG, GTTG, GGTGG$ . The segment of 200 units was extracted as a 'well balanced' section of a sequence of 5000 units. Density of state values were calculated and compared with the experiments. The following conclusions were derived.

The whole density of states  $g(\nu)$  of the perfect host crystal becomes activated (Figure 5). The i.r. peaks at 1440, 1300, 1128, 1075  $\text{cm}^{-1}$  coincide satisfactorily with singularities in the density of states calculated. The broad feature with peaks at  $\sim 538$   $\text{cm}^{-1}$  and at  $\sim 252$   $\text{cm}^{-1}$  is accounted for as the activation

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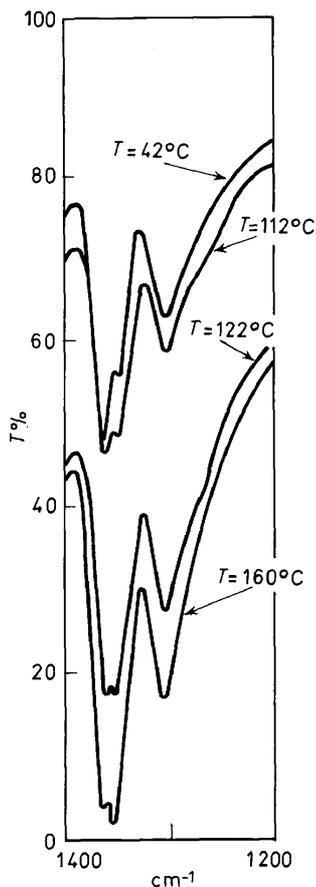


Figure 4. Temperature dependence of the infra-red spectrum of polyethylene from 1200 to 1400  $\text{cm}^{-1}$ .

of the whole  $\nu_5$  and  $\nu_9$  acoustical branches. The asymmetrical swing toward higher frequencies of the  $720 \text{ cm}^{-1}$  peak and that toward lower frequencies of the peak at  $1300 \text{ cm}^{-1}$  are in this way accounted for. The Raman peak at  $\sim 1465 \text{ cm}^{-1}$  corresponds to the singularity at  $\sim 1470 \text{ cm}^{-1}$  which is infra-red active for the perfect case. Localized defect modes are located at  $1367$  and  $1350 \text{ cm}^{-1}$ . The peak at  $1350 \text{ cm}^{-1}$  arises from a contribution of GG and GTG defects; the peak at  $1367 \text{ cm}^{-1}$  comes from GTTG defects.

The limitation of our study with regard to intensity is well depicted in the case of the rocking mode at  $720 \text{ cm}^{-1}$ . While a weak peak is observed in  $g(\nu)$ , a strong infra-red band is found in the experiment. We consider this case a typical example of the necessity for cautious use of  $g(\nu)$ . However, the large amount of positive comparison in other regions of the spectrum convinces us that the comparison is satisfactory and capable of providing reliable structural conclusions. The assignment of the doublet at  $1367$  and

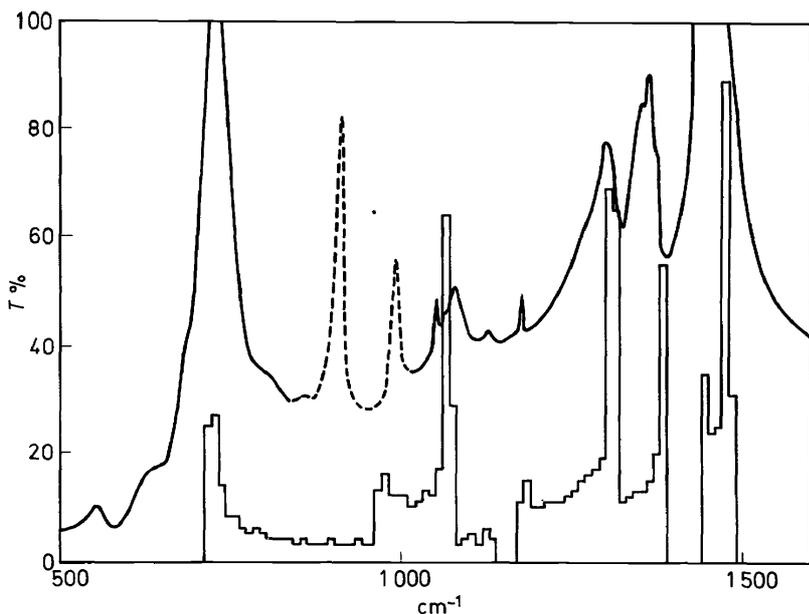


Figure 5. Comparison between the infra-red spectrum of crystalline polyethylene and the density of states  $g(\nu)$  for a perfect single chain crystal; dashed line denotes absorption due to vinyl end groups.

$1350\text{ cm}^{-1}$  to defect local modes is accepted on this ground. Indeed while we do not need a  $g(\nu)$  singularity in this frequency range to be matched with those of the perfect lattice, peaks are calculated at these frequencies when certain types of defects are introduced. The existence of these defects is thermodynamically and structurally reasonable; moreover the force field adopted is reliable. We consider this assignment fairly reasonable.

The same conclusions would have been reached if normal coordinate analysis on such a large model were carried out. According to our approach, however, normal coordinate calculations on smaller models would lead to different conclusions which have already been presented in the literature. With the hope of explaining the additional features of the vibrational spectrum of PE, Snyder<sup>50</sup> has recently carried out an extensive normal coordinate analysis of several rotamers of hydrocarbons. He has mainly focused his attention on the various rotamers of *n*-hexane and *n*-heptane. His calculations suggest a different assignment of the doublet at  $1367$  and  $1350\text{ cm}^{-1}$ . Moreover all the extra peaks in the spectrum of PE are assigned by this author to special conformations (i.e. to localized defect modes). The difference in assignment must be mainly ascribed to the model adopted by Snyder compared with ours. The main difference in the model which Snyder adopted is that he uses short chain model compounds which are much different from the very long chain we adopt in our calculations. Intra-molecular coupling may be different for some of the fundamentals thus providing a different vibrational assignment, even if the same force field has been used. Also Snyder has never taken into account the activation of the

whole phonon spectrum of the perfect lattice which is claimed instead by us. Whatever is the right interpretation, both factors may well be active and a quantitative distinction between them can only be made when intensity factors are taken into account. This problem requires further study.

Structural information can then be derived from our analysis. Indications are found from the vibrational spectrum that a solid sample of PE contains crystalline and amorphous parts. This information is not new but confirms what is already known from other sources. Indications are found for the existence of GG, GTG and GTTG sequences in the amorphous part. Heat treatment increases the concentration of GG and GTG units with respect to the GTTG ones when the sample is still solid thus proving an increase of coiling of the polymer chain while in the solid. In the melt the concentration of GG becomes larger. The structure of PE in the liquid phase can be roughly described as consisting of short *trans* segments in addition to other conformations. The concentration of GG and GTG sequences has increased. The question as to how long should a *trans* segment be to give rise to frequencies approaching the limiting  $k = 0$  fundamentals should be treated in connection with the problem of the existence of phonons and of quasi-lattice structures in liquids.

The results obtained on solid PE can be used to discuss the problem of the structure of the fold in PE single crystals for which three extreme models have been proposed in the literature, namely: (i) tight-fold re-entry, (ii) switchboard type, (iii) loosely-looped fold<sup>29</sup>. The spectrum of solution-grown single crystals shows<sup>56</sup> the doublet at 1350 and 1367  $\text{cm}^{-1}$  assigned by us to GG + GTG and GTTG sequences respectively. For the sake of completeness we have carried out a calculation of  $g(\nu)$  on PE of the type  $-(\text{T})_m-\text{GGTGG}-(\text{T})_n-$  ( $m = n$  and  $n \neq m$ ) which is characteristic of the tight-fold re-entry. We have found a  $g(\nu)$  peak at 1350  $\text{cm}^{-1}$ . The existence of the experimental peak at 1350  $\text{cm}^{-1}$  seems to support the possibility of GGTGG tight-fold re-entry; however, the existence of the second peak at 1367  $\text{cm}^{-1}$  indicates the existence of a considerable amount of other conformations inconsistent with the model of tight-fold re-entry. The model of irregular re-entry should then be favoured unless we consider the various intermediate models recently re-proposed for a reconciliation of many of the experimental data collected from various sources. The model of composite-fold surface proposed by Keller<sup>29</sup> would not contradict but instead support our experimental and theoretical data. Our conclusions also are not in contradiction with the recent proposal of the 'ciliated'<sup>57</sup> single crystals which are, however, included in Keller's composite-fold model.

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