polymer review

Twistons and phase transitions in polymethylene systems: a spectroscopic study

M. Del Zoppo and G. Zerbi*
Dipartimento Chimica Industriale, Politecnico, Piazza L. Da Vinci 32, Milano, Italy
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The transport and diffusion properties observed for solid n-alkanes and the premelting phenomena in polymethylene systems imply that molecular chains possess conformational flexibility coupled to longitudinal mobility. Most of the authors have proposed models based on the creation and mobility of conformational kinks whose existence is not proven by spectroscopy. The existence of 'twistons' has been postulated. In this work vibrational i.r. and/or Raman spectroscopy is used as a probe for twistonic excitations. The conditions for the spectroscopic observation of twistons are discussed. The temperature dependence of the spectra of n-alkanes from the orthorhombic to 'α' (or 'pseudohexagonal') and to melt phases is studied and the spectra are interpreted in the attempt to find evidence of twistons. As a test case of the theoretical predictions the spectra of n-alkanes in urea clathrates are discussed. Indications are found that twistons start being produced while still in the orthorhombic phase when the lattice starts expanding. The 'α' phase (or premelting state) may be considered as a 'soft' phase consisting of a collection of twistonic chains out of register because of the propagation of twistons which also generate the spectroscopically observed surface disordering and diffusion.

(Keywords: polymethylene; twistons; phase transitions)

INTRODUCTION

Materials consisting of chain molecules in which monomer units are linked only by σ bonds show peculiar physical properties generally accounted for in terms of the large torsional flexibility of the whole chain. There exists in nature a very large variety of such chain molecules whose peculiar properties make them useful for specific technological applications.

The understanding of the correlations between molecular (crystal) structure and properties is not easy and has attracted the attention of many authors who have tackled the problem with a variety of experimental techniques or with various kinds of theoretical models. Two lines of thought are generally followed in the literature, namely some authors describe the physical phenomena associated with such chain molecules in terms of simplified supermolecular models in which the microscopic molecular reality is overlooked; some others try to focus on specific intra- or intermolecular elementary phenomena at the molecular level.

The simplest class of molecules whose physical properties still need to be rationalized at the molecular level is the n-alkanes, the extreme case of which is polyethylene. An understanding of this simpler series of molecules may provide a better understanding of the structure–property relationships of more complex polymethylene systems (fatty acids, surfactants, phospholipids, energy storage systems, etc).

As discussed below, the amount of work carried out on polymethylene systems is enormous; many different experimental and/or theoretical techniques have been applied to elucidate the structure–property relationships. In this work, vibrational spectra are used as a probe in order to derive information on the dynamics and structure of such systems.

The peculiarities of the physical properties of these materials specifically related to their molecular flexibility are exhibited both in the solid and liquid (solution) states. Theories and experiments necessarily require that these two phases be treated separately.

In this work, materials are studied in the solid state. Our main target is the proposal of a molecular model which can account for the available experimental data including the new results obtained from vibrational spectroscopy and presented in this work. The outcome of this work results in the need to consider some new physics generally overlooked in polymer circles.

THE MOLECULAR AND CRYSTAL STRUCTURE OF n-ALKANES

Solid n-alkanes with the general formula $CH_3(CH_2)_{n-2}CH_3$ (hereafter referred to as C_n) are polymorphic[1] and there is unquestionable experimental evidence that molecules with an odd number of carbon atoms crystallize in an orthorhombic lattice with two molecules per unit cell while even chains crystallize either in triclinic or monoclinic lattices, depending on their length[2]. The existence of small impurities may change such a rule[3].

The first peculiarity of these systems is the existence of an intermediate phase just before melting. The structure of this new phase has been variously described as

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* To whom correspondence should be addressed

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'pseudohexagonal', 'α', 'rotator', etc. (hereafter referred to as 'α'). The temperature range of existence of such a phase depends on the chain length and is pressure dependent[4], disappearing in the pressure range of 2.5×10^5–3.0×10^5 kPa. The appearance of the 'α' phase is accompanied by the onset of some kind of conformational disorder whose nature and molecular topology need to be described. Other minor transitions are observed at $T<T_\alpha$ for longer n-alkanes[5], e.g. C_{33}.

Knowledge of the origin and of the properties of the 'α' phase is acquiring an increasing importance due to its relevance in applied and basic material science. For this reason it has already been the focus of interest of many studies. Topics of major interest to be understood are the local and/or collective molecular structure, flexibility and mobility which produce transport of matter (diffusion) and seem to be the origin of the melting process.

The existence of the 'α' phase has been unquestionably proven by d.s.c.[6,7]; its nature and structure have been studied by X-ray scattering[5,8–11], neutron scattering[12–16], i.r. and Raman spectroscopy[7,17–19], n.m.r.[20–23], and dielectric absorption[24]. The conclusions reached by these studies are not always in agreement (often because of the intrinsic limitations of each technique). The main reason for the disagreement lies in the fact that molecules in this phase are almost certainly highly mobile exhibiting motions with characteristic times compatible or incompatible with the physical probes used in the experiments.

STATE OF THE ART FOR THE 'α' PHASE

The picture which emerges from X-ray diffraction is that upon heating, the orthorhombic lattice lamellae with chains perpendicular to the lamellar plane expand anisotropically[2] since chains move apart; at T_α the crystal becomes pseudohexagonal with chains still parallel to each other and still orthogonal to the lamella plane (for $n<26$), the main difference being the existence of an 'orientational disorder' of the chains[2]. The orientational disorder is a common structural feature of many bilayered systems of biological importance[25,26]. N.m.r. experiments confirm the existence of some kind of orientational disorder[23] which is further described by the early inelastic neutron scattering experiments as a rotational jump diffusion consistent with a circular random walk model, with an estimated[12] dipole relaxation time of 3.5 ps.

I.r. and Raman spectra on C_{19} provide a more detailed molecular description of the 'α' phase[19]. Evidence is found that in this phase the orthorhombic lattice has unquestionably mostly disappeared while interlamellar forces have weakened*. By means of selective deuteration and intensity measurements it has been estimated that ~25% of the chain ends are tilted exhibiting a *gauche* conformation in positions C2–C3 and C3–C4, while the centre of the lamella does not contain any defect[19]. The concept and evidence of 'surface disordering' emerge from such a study, thus introducing the idea that chains may perform a longitudinal motion parallel to the chain axis. The preferential surface disordering is also shown in the spectroscopic studies by Maroncelli *et al.*[28]. The existence of a longitudinal motion is confirmed by quasi elastic neutron scattering. Ewen and Richter[29] found evidence in C_{33} of preferential longitudinal translational jumps of one CH_2 unit. These results are in agreement with those recently reported by Guillaume *et al.*[30] showing that translational diffusion (of two CH_2) is effective with a translational diffusion constant $D=6\times10^{-6}\,\mathrm{cm^2\,s^{-1}}$ for C_{19} at 300 K. However a rotational process also takes place. The nature of the rotational motion (instantaneous jumps, continuous rotational diffusion, large amplitude oscillations, etc.) is still controversial and is a matter of active discussion among various groups[12,14,16].

The fact that n-alkane molecules in or near the 'α' phase are capable of diffusing out of the lamella has been shown by recent d.s.c. experiments by Ungar and Keller[31] and by both d.s.c. and spectroscopic experiments by Zerbi *et al.*[32]. These studies show that starting from a mechanical mixture of n-alkanes of slightly different chain length, upon annealing in or near the 'α' phase one obtains some kind of co-crystal. The rate of diffusion increases noticeably by applying pressure to the starting mixture (i.e. by increasing the physical contact between particles)[31]. However, no indication is obtained in these kinds of experiments on whether the diffusion is longitudinal or translational.

THEORETICAL MODELS

Theoretical models accompanied by increasingly larger computational studies have been developed in order to account for the experimental observations which have been presented over the past few years. Calculations on 'static' models of crystalline n-alkanes based on semi-empirical non-bonded atom–atom potentials account for both the orthorhombic and monoclinic arrangements[33]. In these systems, however, one also has to take into account the existence of the additional 'α' phase. The basic concept generally accepted is that such chain molecules in the solid phase are necessarily performing some kind of collective and/or localized roto-translational motion with the possible generation and intramolecular diffusion of conformational defects.

Several authors have tried to describe these phenomena with theoretical and/or numerical models. The literature before 1968 is clearly reviewed and discussed by McClure[34]. McClure himself, in an attempt to calculate the change in the lattice energy accompanying the rotational phase transition, proposed a specific model for the rotation mechanism. McCullough[35] shows that a rigid rotation coupled with translation is a low-energy intermolecular process by which an intramolecular response mechanism can be accommodated and points out the relevance of longitudinal chain translation as a low-energy mechanism for chain motion.

The models mentioned above neglect the contribution of entropic terms due to molecular intra- and intermolecular vibrations which, instead, are taken into account by Kobayashi[36], who performed a lattice dynamical calculation of the thermodynamic functions in the 'α' phase, using a model of co-operative rotation accompanied by a small translational fluctuation along the chain axis.

More recently, computer simulations have been introduced as a powerful tool for the study of the dynamics and structures of molecular systems and have also been used for n-alkanes. Monte Carlo calculations[37] suggest that the translational motion of the molecules is very

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* Casal *et al.* found an indication that a fraction of the material in the 'α' phase may still contain two highly perturbed molecules per 'unit cell'[27]

active and independent of the rotational motion of the chains considered as rigid units.

A step forward in the understanding of the 'α' phase has been made by numerical calculations of molecular dynamics by Ryckaert *et al.*[38,39], who introduced an additional degree of freedom by allowing the onset of some kind of conformational flexibility through the formation of kinks which are capable of diffusing along the molecular chain. Ryckaert *et al.* found that translational diffusion plays an important role and cannot be disregarded when considering the formation of kinks and the roughening of the interlayer interface, where intramolecular defects mainly occur.

A different scenario of the pretransitional state emerges from the recent numerical simulation calculation by Sumpter *et al.*[40]. Their conclusions are that rotational isomeric defects are created and quenched very rapidly and substantially do not diffuse large distances along the chains. Moreover, there are little or no correlated motions of any defect. The origin of the transport of matter or lamellar thickening is ascribed to a temperature-dependent random generation of defects whose lifetimes are very short (a few picoseconds). We observe that unfortunately the conformational roughening of the lamella surface identified with certainty by vibrational spectroscopy does not enter into the fascinating and seemingly comprehensive scenario by Sumpter *et al.*.[40].

Surface roughening is indeed supported by the statistical mechanical calculations recently presented[41]. From the study of a polymethylene chain inserted in its own three-dimensional lattice simulated by a given external potential, it is shown that chain end distortions are initially favoured and, with increasing temperature, kink formation and longitudinal translation of the molecular chains sustain the disordering process.

VIBRATIONAL SPECTROSCOPY AS A PROBE FOR MOLECULAR MOBILITY

In this paper the possible use is discussed of data from vibrational i.r. and Raman spectroscopy as a probe for the study of the molecular flexibility and mobility of these systems. Vibrational studies of n-alkanes can be separated into three main classes, namely (1) band frequencies, (2) band intensities and (3) band shapes and widths. While (1) is well established, (2) and (3) are still being actively studied.

From i.r. and/or Raman spectra, the orthorhombic structure is confirmed[42] and the setting angle between chains is measured[43]. The all *trans* conformation of the chains is unquestionably proven[44] and its actual length is measured by LAM Raman spectroscopy[45]. The existence of a few well defined conformational defects (e.g. *GTG'*, *GG*, end-*TG*[46–47] and *GGTGG*[48]) and their location within the chain can be directly determined[49]. The above techniques applied to the case of C_{19} have provided the description of the 'α' phase as already discussed earlier[19].

I.r. intensities[50] interpreted on the basis of electro-optical parameters[51] have allowed the effective equilibrium charges on the C–H groups to be measured and charge fluxes in σ bonded systems (e.g. n-alkanes and polyethylene) to be studied. Moreover, the intensities of the i.r. active defect modes have been accounted for[52].

The third spectroscopic class observable in the i.r. and Raman spectra of n-alkanes which has received less attention is band shape [for complicated molecular systems information can also be obtained from band widths $\Delta\nu_{1/2}$ = half-width at half height (HWHH)]. From the theory of band shapes discussed elsewhere[53], it is known that Raman spectra contain information both on vibrational and reorientational relaxation phenomena. For this reason, our analysis is mainly focused on the Raman spectra of n-alkanes.

It is known that the Raman scattering tensor can be separated into anisotropic angular-dependent and isotropic amplitude-dependent contributions which can be measured from the depolarization ratios $\rho = I_{\perp}/I_{//}$ of the Raman lines[53]. While the amplitude-dependent term is related to the purely vibrational temperature-independent relaxations, the angular-dependent term also contains a contribution from the relaxations due to angular-dependent motions.

These results have been used to study the Raman spectra of liquid n-alkanes of increasing length, mostly focusing on the totally symmetric CH_2 stretching (d^+) (isotropic) and on the antisymmetric CH_2 stretching (d^-) (anisotropic) modes as probes of the overall rotations of the whole molecules. The case of a relatively short n-alkane, butane, is reported in *Figure 1*[54]. *Figure 1* shows clearly that the FWHH of d^- increases with increasing temperature while that of d^+ is temperature independent. The slope of HWHH/T is chain length dependent and reaches a plateau for $n > 6$ carbon atoms. This indicates that while shorter chains in the liquid phase can perform end-over-end tumbling motions in any direction, for longer chains there exists a preferential longitudinal direction about which the molecule can rotate.

The first conclusion is that if n-alkane chains perform large amplitude overall rotations their motion should be detected from the HWHH of the d^- mode. However, it is known that chains are highly flexible and can perform low frequency motions coupled with overall rotations.

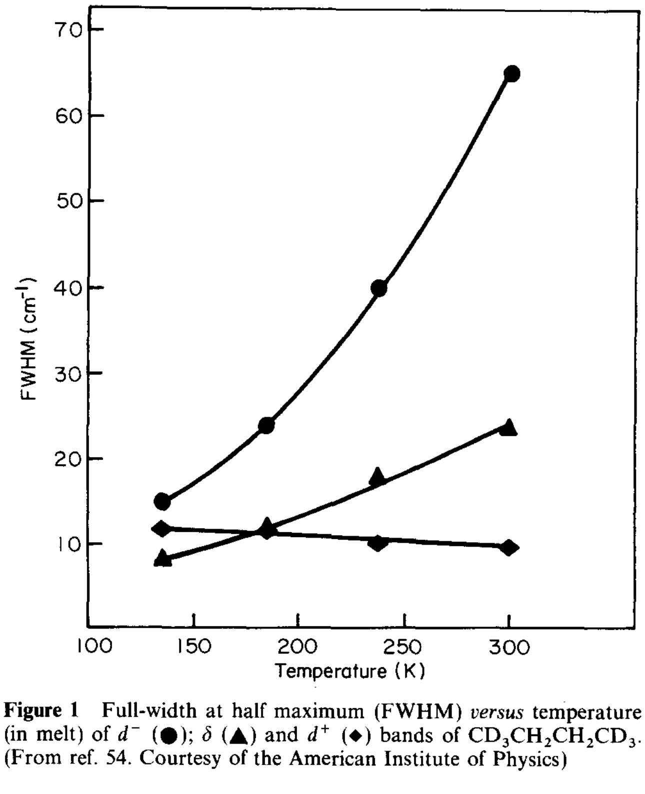


Figure 1 Full-width at half maximum (FWHM) *versus* temperature (in melt) of d^- (●); δ (▲) and d^+ (◆) bands of $CD_3CH_2CH_2CD_3$. (From ref. 54. Courtesy of the American Institute of Physics)

This is certainly verified experimentally from the study of the temperature-dependent low frequency i.r. and Raman spectra of solid n-alkanes[55]. Since the torsional potential is fairly flat the mean vibrational amplitudes associated with torsional motions must be relatively large. In such a case if an anharmonic coupling exists between the C–H stretching and the torsional motions the d^- frequency can be modulated by the torsional motions. In all the theoretical models presented in the literature the frequency of the torsional mode which couples with high frequency internal modes is a determining step. The energy initially stored in the C–H stretching is quickly relaxed into the torsional motions through some preferential channel, thus shortening the lifetime of the high frequency vibrational level and hence causing temperature-dependent broadening[56]. The direct spectroscopic evidence of some kind of coupling is given by the selective photoisomerization experiments with i.r. light by Räsänen and Bondybey[57]. Other models have been proposed, which all substantially converge to similar physics.

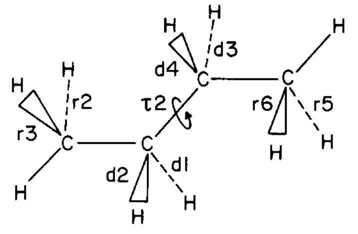
The spectroscopic concept which thus follows is that not only overall rotations (librations) but also torsional motions can contribute to the broadening of d^-. The question which still needed to be clarified was whether not only the band shapes, but also the frequencies of the CH_2 stretching modes could be affected by a coupling with the torsional modes. The problem can be treated either considering anharmonic terms[58] of the potential or in the harmonic approximation by classical normal coordinate calculations. By symmetry considerations it can be shown that coupling with torsions cannot affect d^+ while it may affect d^-. Numerical calculations made both on *trans* planar and distorted (frozen) structures show that when harmonic coupling terms of the type C–H stretching/C–C torsion are introduced d^- shifts (*Table 1*)[59]. It follows that if the originally *trans* planar chain becomes torsionally distorted, the frequency maximum of the d^- mode is expected to shift.

However, any normal coordinate calculation depends on the numerical values and sign of the force constants used. While these calculations prove that d^- shifts, the direction and the amount of such a change depend on the number used as input. It is a known fact in spectroscopic circles that the numerical values of harmonic force constants are to be considered with a very critical attitude and are often quite arbitrary.

Table 1 Comparison between CH_2 stretching frequencies calculated with a harmonic force field (neglecting Fermi resonance) for $CD_3(CH_2)_4CD_3$ with and without stretching–torsion interaction in all-*trans* planar geometry and in a distorted geometry (rotation of all torsional angles 60°). From ref. 59

$f_{r\tau}=0$		$f_{r\tau}=0.05$ (mdyn rad^{-1})	
Planar geometry			
2931	d^-	2950	d^-
2921		2930	
2909		2910	
2899		2899	
2895	d^+	2895	d^+
2891		2891	
2887		2887	
2884		2884	
Distorted geometry			
2933	d^-	2949	d^-
2923		2932	
2909		2912	
2895		2896	
2892	d^+	2892	d^+
2889		2889	
2887		2887	
2885		2885	

Table 2 Calculated *ab initio* (4-31G) interaction stretching–torsion force constants at first and second nearest neighbours



First neighbour interaction (mdyn rad^{-1})		Second neighbour interaction (mdyn rad^{-1})	
$f_{\tau2/d1}$	−0.0002	$f_{\tau2/r2}$	0.0019
$f_{\tau2/d2}$	0.0002	$f_{\tau2/r3}$	−0.0019
$f_{\tau2/d3}$	−0.0002	$f_{\tau2/r5}$	0.0019
$f_{\tau2/d4}$	0.0002	$f_{\tau2/r6}$	−0.0019

An attempt has been made to move away from the unavoidable bias of molecular modelling by recourse to quantum mechanical *ab initio* calculations. In this case, the electronic wavefunction determines the vibrational potential focusing not only on one particular interaction but providing a complete description of the redistribution of the electrons when torsional angles change. Calculations have been made by extracting the harmonic terms from the *ab initio* vibrational potential. From such harmonic terms we learn that: (1) there exists an interaction between the torsional modes about the C–C bond and the C–H stretching of the second neighbour CH_2 group (*Table 2*), i.e. the nature of the C–H bond changes when the torsional angle changes and vice versa, and (2) the d^- mode shifts upward when the molecule becomes conformationally distorted[60] (*Figure 2*), i.e. the C–H bond becomes stiffer and shortens when the torsion changes from $\tau=180°$. In conclusion, if the *trans* n-alkane chain becomes conformationally distorted we expect the frequency of d^- to shift upward. The extent of frequency shift depends on the extent of conformational distortion. It is then possible to distinguish spectroscopically between inter- and intramolecular angular-dependent relaxations (due to librotorsional motions) and purely torsional deformations.

It should be pointed out that different kinds of conformational distortions can take place in a polymethylene chain. The first and most popular kinds of distortions are the classical conformational kinks (e.g. *G*, *GG*, *GTG'*, end-*TG*, *GGTGG*, etc.) generally pinned at a given site of the molecule (point or localized defects). The vibrational spectroscopy of such point defects has been widely treated and is well established in the literature[61]. Normal modes characteristic of a few point defects have been calculated and experimentally observed in many systems. These modes are a very useful probe in the structural analysis of polymethylene chains. The characteristic normal modes of the defects used as structural probes are mostly the CH_2 wagging motions.

The fact that C–H stretching is extremely sensitive to minute changes of the chemical environment has

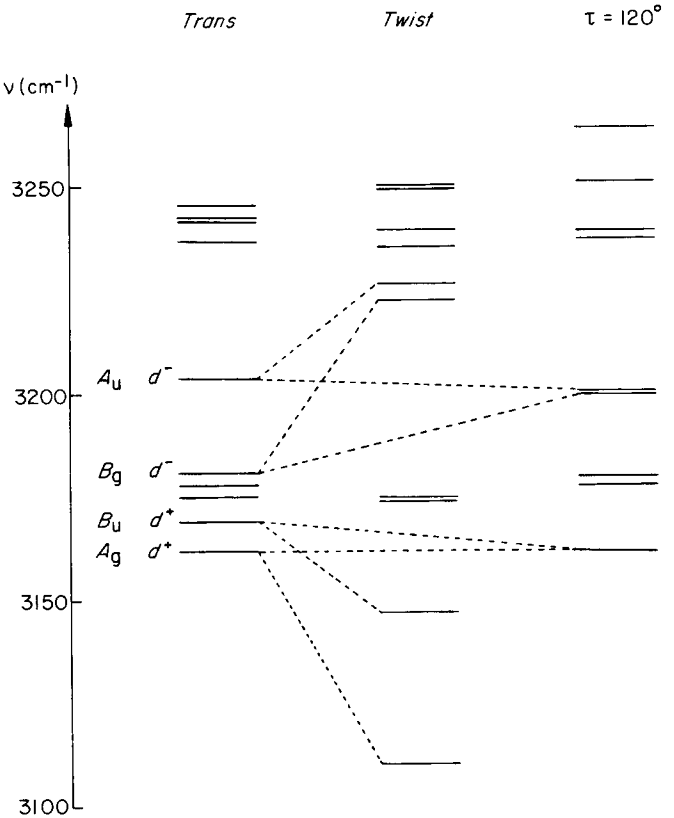


Figure 2 Diagram of calculated (*ab initio* 4-31G) frequencies in the C–H stretching region of butane constrained in different conformations. (From ref. 60)

been shown in the experimental studies by McKean *et al.*[62]. These studies generated a cascade of subsequent papers[63–65] based on quantum chemical calculations with the aim of justifying the C–H bond length/C–H stretching frequency linear relationship presented by McKean *et al.*

However, another kind of conformational distortion has to be considered and is currently being studied by various groups. This distortion is a long gentle conformational twist (collective distortion) either pinned or mobile possibly showing characteristic normal modes in the i.r.-Raman spectra. As mentioned above, our recent calculations on slightly distorted chains indicate that even in the case of a collective long twist the frequency of the d^- mode shifts upward (*Figure 2*).

A TEST CASE: THE VIBRATIONAL SPECTRA OF n-ALKANES IN UREA CHANNELS

It is well known that n-alkane molecules can form clathrates with urea; n-alkanes occupy the channels formed by the network of hydrogen bonds between urea molecules. Chains are thus isolated from one another and are suitable targets for the study of intra- and intermolecular dynamics as isolated entities. Long n-alkane chains are substantially all *trans* as shown by X-ray scattering experiments[66] and by LAM Raman spectroscopy[67]. Recent X-ray and neutron scattering experiments have proven that n-alkane chains in urea clathrate perform longitudinal translational motions on a picosecond time-scale[68,69]. Temperature-dependent Raman spectra are presented by Zerbi *et al.*[59], Snyder *et al.*[70] and Kobayashi *et al.*[71]. These experiments can be interpreted as discussed above and in reference 59, thus showing that chains are performing both librational (broad HWHH of d^-) and torsional motions (upward shift of d^-) which become frozen in the low temperature phase of the urea clathrates (*Figure 3*). Wood *et al.* have presented a model which accounts for both band broadening and frequency shift and derive a value of 0.52×10^{-2} Gy^2 (for C_{20} at 300 K) for the mean square angular displacement[58]. This model does not favour the site hopping theory proposed by several authors. On the other hand, the model of Wood *et al.* neglects the longitudinal translations which, instead, are shown to be important for the interpretation of data from X-ray spectroscopy and neutron scattering.

In conclusion, there is a sufficient body of experimental and theoretical evidence that in urea clathrate long n-alkane chains do not substantially generate point defects and are able to perform longitudinal translations and librotorsional motions. It has to be remarked that, contrary to the results of numerical calculations, n-alkane chains in urea channels are capable of performing longitudinal diffusive-type motions without the need of a sizeable concentration of point defects. Moreover, in these numerical studies a possible coupling of longitudinal translations with collective librotorsional motions has not yet been considered to be a relevant phenomenon.

An important observation needs to be made here regarding the experimental and theoretical concepts discussed above. The amplitude of the librotorsional motions becomes an important factor when considering the various phases in which these systems can exist. The experimentally observed features in urea clathrates which fit nicely with theory are enhanced by the fact that molecules find themselves in a molecular surrounding which allows much freedom to their flexibility. In considering polymethylene chains in the orthorhombic or 'α' phase the space available may be less and the intermolecular forces may be larger, thus hindering large amplitude, low frequency motions and making the experimental observations less noticeable. This is the case for crystalline n-alkanes, as discussed below.

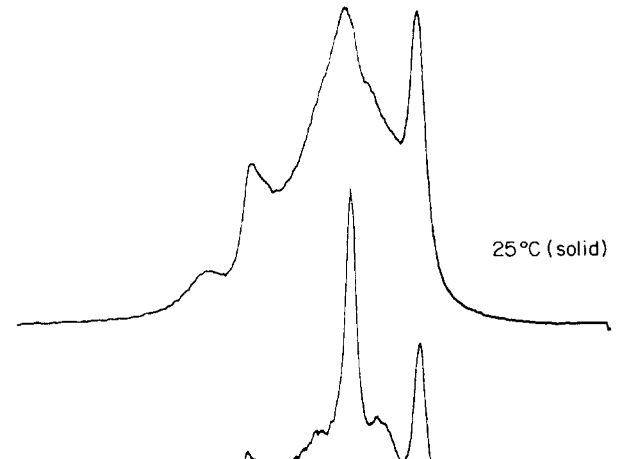


Figure 3 Temperature dependence of the Raman spectrum in the C–H stretching range of $C_{25}H_{52}$ in urea clathrate. (From ref. 59. Courtesy of the American Institute of Physics)

THE CASE OF CRYSTALLINE n-ALKANES

The vibrational spectroscopic information discussed above for n-alkanes in urea clathrates is not always reproduced in the case of crystalline n-alkanes, thus indicating that the physics of these systems in urea channels and in their own lattice may be different.

The experimental spectroscopic observations on solid crystalline n-alkanes and other polymethylene molecules (e.g. fatty acids, polyethylene, organic perowskytes, etc.), which need to be explained are the following:

1. Temperature-dependent Raman spectra from the solid orthorhombic phase, through the 'α' phase to the melt in the CH_2 stretching range, show that d^- modes do not broaden before melting. We have observed this for some n-alkanes[59], for fatty acids and for polyethylene[72] (*Figures 4* and *5*).
2. In the 'α' phase of n-alkanes the d^- mode in the Raman spectrum shows the onset of scattering on the higher frequency side. This is also observed in the i.r. spectra of fatty acids[60].
3. In the 'α' phase chain diffusion occurs as shown from d.s.c.[31] and i.r. spectroscopy experiments[32].
4. Surface melting takes place with the formation of specific kinks at the end of the polymethylene chain while inside the chain remains *trans* planar[73].
5. The integrated i.r. intensities of the various modes of polymethylene chains decrease with increasing temperature. The decrease starts already in the crystalline orthorhombic phase and proceeds in a smooth way; at T_α a large discontinuity is observed and then there is a further decrease until T_{melt} is reached. These very relevant data are presented and discussed by Snyder *et al.*[74].

On the basis of what has been discussed earlier, observation (1) indicates that large amplitude librotorsional motions do not take place both in the crystalline and in the 'α' phase. On the other hand, because of observation (3) another origin for the diffusional translational motion needs to be found.

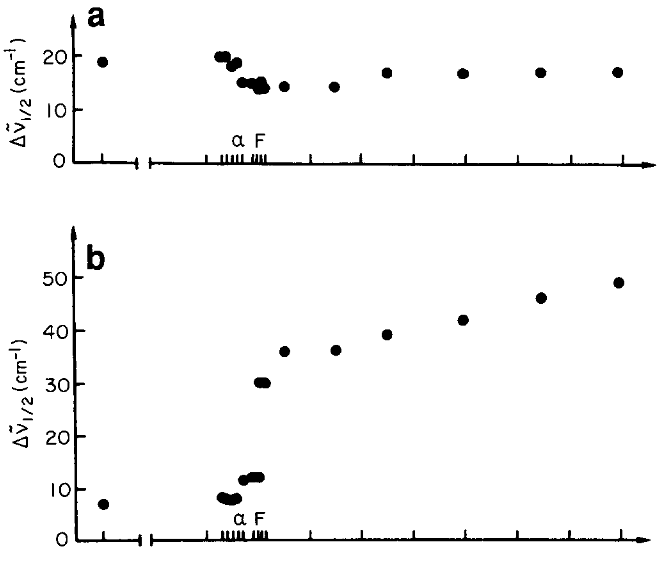


Figure 4 Temperature dependence of $\Delta\nu_{1/2}$ of (a) d^+ and (b) d^- modes in $C_{21}H_{44}$. The values of $\Delta\nu_{1/2}$ are derived from the lower frequency symmetric side of the band. (From ref. 59. Courtesy of the American Institute of Physics)

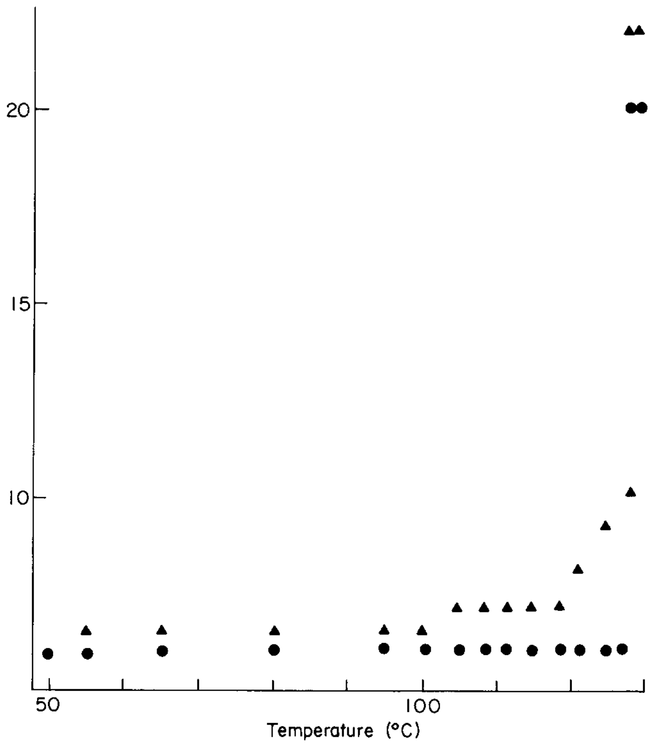


Figure 5 Temperature dependence of $\Delta\nu_{1/2}$ of the d^- mode in polyethylene (from ref. 72). The values of $\Delta\nu_{1/2}$ (●) are derived from the lower frequency symmetric side of the band; (▲) $\Delta\nu_{tot}$

THE SOLITON (TWISTON) MODEL

Among the models which stress the importance of roto-translational motions coupled with some kind of internal twisting of the chain, of particular relevance to us is the model proposed by Mansfield and Boyd[75]. This model is based on conformational energy calculations for a three-dimensional crystal using non-bonded atom–atom potentials. These calculations indicate the possibility for a chain to be twisted inside the crystal by means of a gentle collective distortion which propagates along the chain across the crystal and in so doing causes transport of matter. This is not a point defect (such as the Reneker defect), instead the twist consists of a fairly uniform succession of small bond torsions and it propagates without local barrier to its advance. The twisted domain (hereafter referred to as Utah twist or 'twiston') is rather localized ($\sim 12\,CH_2$ units in polyethylene). The activation energy estimated by Mansfield is $\sim 42\,kJ\,mol^{-1}$.

The twiston model postulates that the molecular process underlying chain transport may involve: the initial formation of a twisted section near the surface of the crystal; the smooth longitudinal propagation of the twist through the crystal; and the disappearance of the twist at the opposite crystal surface leaving the chain rotated by 180° and translated by half the repeat unit.

With some physically reasonable simplifications the twiston can be described as a 'conformational soliton' which is obtained as the solution of the following Hamiltonian:

$$H=\sum_i [V(\theta_i)+\tfrac{1}{2}ma^2\dot{\theta}_i^2+\tfrac{1}{2}C(\theta_i-\theta_{i+1})^2]$$

$$V(\theta)=A(1-\cos 2\theta)$$

where θ_i is a rotational degree of freedom associated with the CH_2 unit, $V(\theta)$ is a periodic potential which results from the crystal field, m is the mass of a CH_2 unit and a is the distance of each unit from the chain axis. The harmonic term, with coupling constant C, models the strong covalent bonds. If θ_i does not change much from one CH_2 unit to another (as is the case for the Utah twist) one can make the continuous approximation and consider the solution of the sine Gordon Hamiltonian. The soliton solution:

$$\theta(x-x_0-vt)=4\tan^{-1}\exp[\pm\gamma(x-x_0-vt)]$$

describes a twist of the chain very similar (except for the neglect of translational mismatch) to the Utah twist[76]. In the absence of friction the soliton propagates with the same shape and velocity. Using some molecular parameters Mansfield[77] estimated this velocity to be $\sim 10^5\,cm^{-1}\,s$.

The idea of the existence of solitons is also presented by Fukao[78], who calculates the formation energy for a *GTG'* and end-*TG* defects to be too large to account for the phase transition. From the two-state model of Fukao the defect formation energy is estimated to be $\sim$4.2 kJ mol^{-1}. This energy is consistent with the idea of the existence of a 'soliton-type' defect. Fukao develops his theory for a paraffin molecule in urea clathrate.

The existence of twistons justifies the longitudinal diffusion [observation (3)] and the 'surface melting' [observation (4)]. If twistons exist they should be revealed by spectroscopy.

VIBRATIONAL SPECTROSCOPY OF CONFORMATIONAL SOLITONS (TWISTONS) IN POLYMETHYLENE SYSTEMS

We present here a brief attempt to outline the theoretical and experimental aspects of soliton (twiston) spectroscopy. There are two ways of approaching the problem, namely to consider the twiston as a conformational defect involving a large portion of the chain. This implies considering the system as a two-phase model in which one phase is unperturbed and the other phase contains the twistons; and considering the system as a one-phase model which transforms from the orthorhombic to the 'α' phase. In this case, the system as a whole transforms with temperature with an expansion of the lattice even before T_α with a parallel onset of chain flexibility. The 'α' phase is described as a collection of chains whose mobility is very large, thus allowing the formation and propagation of twistons which generate the transport of matter.

In the case of a *two-phase model*, in order to observe spectroscopic markers due to twistons the following conditions must be satisfied:

1. The instantaneous concentration of such objects must be sizeable, which implies that their energy of formation must be small.
2. The lifetime of such objects must be sufficiently long to allow the system to perform a large number of vibrational cycles so as to provide an acceptable and observable band width. This implies that the velocity of the twiston be below a certain threshold.
3. The object must have some of its normal frequencies different from those of the host lattice; moreover, their intrinsic transition moments (hence the i.r. intensities) must be non-negligible.

We discuss below the implications of the above conditions. An observable concentration of twistons as conformational defects of $\sim$5% would imply a formation energy of $\sim$8.4 kJ mol^{-1} at 300 K, i.e. in the range of values estimated by Fukao.

Since the soliton is intrinsically mobile along the polymethylene chain its longitudinal motion can be described as hopping between adjacent CH_2 sites $\sim$2.5 Å apart. On each site the twiston sits for a certain time during which atoms perform a certain number of cycles of vibration. Since the vibrational mean lifetime is inversely proportional to the band width (BWHM) for BWHM $\sim 20\,cm^{-1}$, $\tau \sim 2$ ps and the corresponding velocity of the twiston is $\sim 10^4\,cm\,s^{-1}$.

Normal mode calculations (which included frequencies as well as i.r. absorption intensities) on all-*trans* n-nonadecane and on a soliton containing nonadecane have shown that a few normal frequencies characteristic of the soliton are calculated to be different from the all-*trans* chain[79]. The i.r. spectrum of n-nonadecane in the 'α' phase shows a few extra weak peaks in the frequency range predicted by calculations; however, claiming that such results can be taken as evidence of solitons is still too hazardous.

Attempts to identify the twistons in a possible two-phase model have been made by studying the C–H stretching range on the basis of the concepts discussed earlier. From the experimental viewpoint we have first studied the temperature-dependent i.r. spectrum of $C_{36}D_{74}$ which is known to contain isotopic impurities and isolated C–H or CH_2 groups (which we expected to provide a clean spectrum in the $3000\,cm^{-1}$ range). Unfortunately the spectrum is crowded by many bands (of difficult assignment) where temperature-dependent site splittings are the main feature. We then turned to the i.r. spectra (near $2200\,cm^{-1}$) of selectively deuterated fatty acids with the CD_2 groups in a preselected position. A temperature-dependent broad absorption is observed at frequencies higher than the d^- mode as calculation predicts.

If, instead, one considers the temperature dependence of a *one-phase model* at temperatures below, through and above T_α we have to look for evidence of an overall phenomenon common to all chains in the system. We know, on the other hand, that the phenomenon of flexibility must lead to chain diffusion and surface melting in the 'α' phase.

Contrary to what is observed for n-alkanes in urea clathrates, for n-alkanes in their own lattice Raman active d^- modes neither broaden nor shift upward thus indicating that if twistonic motions occur they cannot occur with low frequencies and large amplitudes. However, their existence seems to be required by other n-alkyl systems when placed in a suitable environment. Indeed, as part of our spectroscopic search for twistons the Raman spectra of a solid aqueous solution of *n*-decylammonium chloride (DACl) recently reported by Picquart *et al.*[80] and further studied by us[81] are very exciting. These systems present several phases whose identification has been attempted using various physical techniques. We focus on the so-called S_1 and S_2 phases for a 20% solid aqueous solution of DACl. The experimental conditions for the existence of these two phases are described in reference 80. What is relevant to us is that the d^- Raman active mode in phase S_1 is a narrow and symmetric band at $2878\,cm^{-1}$; the corresponding d^- mode of phase S_2 occurs as a narrow and symmetric band at 2890 cm^{-1}, i.e. 12 cm^{-1} higher.

The authors of these spectra elaborate qualitatively on the possible existence of interdigitated structures. From our viewpoint the identification of the supermolecular structure is inessential. Based on what has been discussed above we are strongly tempted to think that the d^- mode of phase S_2 originates from all-*trans* decyl chains which perform collective torsional motions of a 'twistonic' nature. Evidence that chains are all-*trans* with no *gauche* structures (or a negligible amount) comes from the lack of the well known scattering near 1080 cm^{-1} characteristic of G defects and from the observation of the LAM mode. The narrow width of the d^- Raman line shows that chains are not performing libronic motions but eventually only twistonic-torsional motions. A similar situation is observed in the so-called 'interdigitated' phase of DACl studied using spectroscopy and X-ray diffraction by Schenk *et al.*[82]. It is interesting noticing that the temperature factors in X-ray scattering for the skeletal atoms of DACl indicate a remarkable static and/or dynamic disorder[82], thus supporting the idea of torsional flexibility.

The fact that in this case one can observe an upper shift of the d^- modes implies (as in the case of urea clathrates) that the molecules have a large torsional flexibility (i.e. the torsional amplitudes are relatively large and their frequencies are lower if compared with the flexibility of n-alkanes in their own lattice; in other words the S_2 phase is 'softer' than the 'α' phase of n-alkanes). Further relevant spectroscopic information comes from the temperature dependence of the i.r. intensities presented and discussed by Snyder *et al.* [observation(5)].

From the experiments by Snyder, the intensity changes follow the thermal expansion of the lattice with their onset already in the crystalline orthorhombic phase and with a sudden drop at T_α. The temperature coefficients ($\delta = \partial \ln I / \partial T$) below and above T_α are different with $\delta_{\mathrm{orth}} < \delta_\alpha$. Snyder suggests as an explanation for such observations that the high frequency modes are coupled with the low frequency skeletal torsional modes of the n-alkanes molecules thus inducing intensity changes.

In our work we have considered the possible origin of such temperature-dependent intensity changes:

1. Assuming that the electronic properties do not change by a slight twist of the chain (constant electro-optical parameters), the intensity decrease may be simply due to the changes in the geometry of the chain.
2. If intramolecular electronic properties change with torsional angles (the electro-optical parameters change) intensity may change with increasing chain torsion.
3. Strong interchain interactions take place in the crystal and weaken when the lattice expands (electro-optical parameters are temperature dependent and change when the lattice expands).
4. Harmonic and/or anharmonic coupling of the high frequency oscillators with the low frequency torsional modes exists. In such a case it is expected that the coupling of C–H stretching is less than that of CH_2 bending, which in turn is less than that of CH_2 rocking.

We have tried to analyse the above four hypotheses and to obtain some theoretical estimate of possible changes. Case (1) was simply verified using the data obtained in reference 79. There we calculated the frequencies and intensities of n-nonadecane in the all-*trans* conformation and in the conformation of the Utah twist described by Mansfield *et al.*[75]. Both the dynamical parameters (force constants) and the intensity parameters (electro-optical parameters) were kept constant and only the geometry was changed. The calculated intensities summed over each frequency range (e.g. CH stretching, CH_2 bending and CH_2 rocking) or even the total intensity summed over all the modes are practically identical in the two structures considered.

We have verified hypothesis (2) with *ab initio* quantum mechanical calculations (4-31 *G* basis set) on a simple n-alkane in the coplanar and twisted structure[60]. Because of the size and the complexity of the calculation we were limited to consider only n-butane. The calculated electronic properties (hence the electro-optical parameters) change from one geometry to the other, but the partial intensity sums over each frequency range or the total sum over the whole spectrum remains practically constant.

For case (3), the electro-optical interactions between chains in a crystal lattice could not be calculated in a reasonably simple way. In the absence of highly polar chemical groups or of highly polarizable delocalized π electrons sizeable changes of the effective atomic point charges and charge fluxes along the network of σ bonds are unlikely when the crystal expands and the molecules twist. Moreover the approximation of the 'Hornig's gas oriented model' (no electrical interactions among molecules in a lattice) for crystalline n-alkanes seems to work very satisfactorily[43].

We are left with the hypothesis of a harmonic and/or anharmonic coupling between high frequency modes and torsional modes. At low temperatures in the orthorhombic lattice chains are fully *trans* planar and many torsional normal modes are forbidden by i.r. strictly because of symmetry requirements. When the molecular skeleton becomes distorted coupling of the high frequency modes and the torsions is turned on, the symmetry of the molecules is lowered, and all modes become in principle i.r. active and intensity is transferred from the strong high frequency modes to the torsional modes. As a result, we predict a temperature-dependent 'bleaching' of the high frequency modes with the transfer of intensity to the many torsional modes (and eventually to lattice modes) which change frequencies and amplitudes along with the expansion of the lattice. The bleaching is expected to be larger the lower the frequency of the internal modes (larger coupling) as is indeed observed experimentally. Further theoretical work is needed on this problem.

DISCUSSION AND CONCLUSIONS

We have indicated that the vibrational i.r. and/or Raman spectra can be used as a probe for the study of chain flexibility and mobility of polymethylene systems. The combined use of frequency, intensity and band width of Raman lines allows us to distinguish between large and small amplitude overall librations and/or torsional chain motions.

While n-alkanes in urea clathrates perform large amplitude librotorsional motions, the same molecules when embedded in their own lattice (either orthorhombic or 'α') do not have room (or hindering forces are too strong) for exhibiting such large amplitude motions.

However, the surface melting detected by i.r. spectroscopy and the diffusion processes detected by i.r. spectroscopy and by other independent physical techniques for the material while still in the 'solid' require the existence of twistonic motions i.e. of torsional motions coupled to longitudinal translations without involving librational motions.

The spectra observed do not give indications contrary to the existence of twistons. A strong indication in favour of twistons is the observed temperature-dependent i.r. intensity. This experiment leads to the choice of a one-phase system. If the intensity behaviour is taken as evidence of twistons, they start being turned on by the expansion of the lattice while still in the orthorhombic phase. The 'α' phase consists of a collection of twistonic chains out of register because of the propagation of twistons which also generate surface disordering and diffusion.

The understanding of the physics of mobility and premelting phenomena based on several experimental observations in n-alkanes is challenged by the very large numerical simulation calculations presently being performed. Since we look at these phenomena from the viewpoint of vibrational spectroscopy (frequencies, intensities and band shapes) support to the numerical results will come only when the reported vibrational data are accounted for by such numerical simulations.

The 'premelting' phenomena which generally lead to surface disordering in many solid polymethylene systems can then be originated by the generation of twistonic excitations which are turned on when the lattice relaxes by increasing the temperature. The pinning of twistons into conformational kinks may also be envisaged but is not proven.

Twistons may be generated whenever the environment (i.e. the lateral packing) of the polymethylene chains is 'loose' or 'soft'. More attention should then be paid in terms of twistons in the case of liquid crystals, gels and mesogenic-type systems.

Finally, the existence of a twistonic phase capable of generating transport of matter may be an important transient state in the process of crystallization of polymethylene chains. Moreover, the temperature-dependent lamellar thickening of crystalline polyethylene is likely to be originated by twistonic motions.

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