

Conformational solitons or twistons in polymethylene chains: lattice dynamics and infra-red spectra

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It has been shown that the lattice of *n*-alkanes can host some molecules which contain a large and gentle conformational twist with properties similar to a conformational soliton. We calculated its vibrational spectrum and discuss under which conditions it may be observed experimentally. The observed vibrational spectrum of nonadecane is discussed in the search for such solitons or twistons.

(Keywords: solitons; twistons; lattice dynamics)

INTRODUCTION

It is generally accepted that the conformational flexibility of polymethylene chains is the origin of several peculiar physical properties (e.g., phase transitions, relaxation phenomena and transport properties) shown by all the materials which contain such molecular systems as main constituents. Local conformational changes introduce specific and energetically discrete conformational defects in the polymethylene chain. These are variously labelled as twists, kinks and jogs and have been widely studied both theoretically and experimentally^{1,2}. The study of the geometry, mobility and energetics of a collective conformational flexibility has not yet received much attention in spite of its growing importance.

We focus our attention on collective conformational defects and try to define the conditions under which the existence of such defects, either pinned at or mobile along the chain, could be probed by the vibrational infra-red spectrum. In the search for possible structures the calculated infra-red spectra will be compared with experimental data on systems which are more likely to contain such structures.

THE CASE OF *n*-ALKANES

More than ten years ago the study of relaxation processes and the thickening of the lamellae in polyethylene (PE) required the introduction of the concept of transport of matter through materials in the crystalline phase. At first the motion of localized defects was assumed to cause these phenomena. Topologically localized conformational defects such as the Reneker twist³ or the Pechold kink⁴ were presented and studied. However, following Fröhlich's idea⁵ a collective motion of the chain seems to better justify several experimental observations. Such phenomena imply a collective molecular motion which requires the rotation and the twisting of the whole molecular chain about its axis and a translation along the same axis. Solid state n.m.r. measurements supported this view⁶. The problem has been dealt with in detail by Mansfield and Boyd⁷ who have shown with conformational energy calculations that the orthorhom-

bic crystal of *n*-hydrocarbons can host chains with twisted structures (180° twist). The twisted regions are localized on about 12 CH₂ groups and can propagate smoothly along the chain and across the crystal.

The problem of the transport of matter in solid *n*-alkanes has been encountered more recently in a spectroscopic study of the phase transitions in odd-numbered *n*-alkanes. These materials show solid-solid (S₁-S₂) and solid-liquid (S₂-L) phase transitions. The temperature range under which the S₂ phase (variously labelled as 'rotatory' or 'pseudo-hexagonal' or 'α' phase) exists narrows with chain length and is maximum for *n*-nonadecane C₁₉H₄₀ (hereafter referred to as C19)⁸. The study of the vibrational spectra of C19⁹ has indicated that in the S₂ phase approximately 25% of the chains have moved out of the crystal lamellae by a longitudinal motion and have tilted their heads with localized *gauche* (*g*) conformations in positions 2-3 or 3-4 of the molecule (end-*g* defects). Evidence is found that the remaining chains are in a *trans*-planar conformation. The motion of the chains must occur only through a longitudinal sliding of the whole molecule chain. The same phenomenon has been postulated in the study of the vibrational spectra of fatty acids¹⁰ and has been supported by statistical mechanical calculations¹¹. Transport of matter throughout a crystalline phase of *n*-alkanes has been unquestionably observed in calorimetric and infra-red studies of a mechanical mixture of two *n*-alkanes with different lengths which evolve into a co-crystal upon annealing in the S₂ phase^{12,13}. In these experiments because samples consisted of a mixture of finely powdered materials there was no possibility of distinguishing between longitudinal or translational motions. Based on the values of longitudinal and transverse diffusion coefficients obtained from neutron measurements on similar materials longitudinal motions were preferred.

The existence of libro-twisting motion of alkyl chains has been shown to account for the observed frequencies and band profiles of the CH₂ stretching motions easily observed as strong signals in the Raman spectra of materials containing polymethylene chains^{14,15}. Such collective overall libro-torsional motions are clearly

observed by n.m.r. or Raman spectra of *n*-alkanes as urea clathrates¹⁶.

CONFORMATIONAL SOLITON AND TWISTONS

The work by Mansfield and Boyd⁷ introduced the concept of a torsional wave (Utah twist¹⁷) which propagates along the chain through the crystal and moves site by site the chain within the crystal. The subject of solitary waves, or solitons, travelling through a material is still the subject of studies in various fields of physics¹⁸⁻²⁰. Mansfield noticed that the potential felt by a single CH₂ group can be described in terms of two variables: a rotational variable for a motion about the long axis and a translational variable for a motion parallel to the long axis²¹. Both linear and non-linear forces are taken into account and the resulting solution of the equation of motion describes a conformational soliton travelling along the chain with a velocity $v \sim 10^5 \text{ cm s}^{-1}$ (ref. 22) evaluated from molecular constants used in conformational energy calculations and molecular geometries²¹. The concept of conformational soliton has also been introduced for polymethylene chains by Skinner and Wolynes¹⁷. Taylor has presented a similar concept based on a realistic molecular model to account for poling in polyvinylidene fluoride (PVDF)²².

The conformational soliton proposed in references 7 and 17 is a theoretical generalization extracted from the concept of a mobile collective conformational defect as described in references 7 and 22. In these works each atom in the molecule has its coordinates and the geometry of the whole twisted chain can be described with precise values of the torsional angles ϕ_i . Although the travelling soliton wave can be described by a smooth and continuous function of the ϕ_i variable of the problem, the conformational defect obeys the constraints by valence bonds, valence angles⁷ and by the surrounding discrete lattice. The energy minimum is found for a discontinuous sequence of torsional angles⁷.

For sake of clarity we label as conformational *soliton* the ideal and analytically tractable solitary wave as derived in references 17 and 21 from an idealized model of the polymethylene chain. We label as *twiston* the numerically determined realistic collective mobile conformational defect as described in reference 7 for PE and in reference 22 for PVDF.

THE SEARCH FOR TWISTONS

The evidence for the existence of twistons is only indirect and direct experimental evidence is extremely difficult to obtain. The conditions under which solitons or twistons could be observed in the vibrational spectrum are discussed below.

We mainly focus on the twiston in polymethylene chains because it describes an object with a more realistic and tractable structure. The case of PVDF has been presented elsewhere²².

Let us first assume that such defect is immobile, i.e. it is pinned at a given site within the polymethylene chain. The formation energy for such a defect is calculated by Mansfield and Boyd⁷ to be 10 kcal mol^{-1} , which is rather high. However, it is well known that calculations reported in the literature on conformational defects are strongly model dependent. If we assume that the formation energy

of the twiston is relatively small, their concentration at kT is sizeable and, in principle, it could be observed by optical vibrational spectroscopy. Indeed the pinned twiston will have its own normal modes, thus generating localized or resonance states in the vibrational spectrum²⁴.

If this is the case, it is possible to calculate its vibrational infra-red spectrum in terms of both frequencies and intensities. Since the spectra of *n*-hydrocarbons have been extensively studied over several decades the calculation of frequencies is made possible by the availability of a very reliable quadratic valence force field²⁵. The calculation of absorption intensities is a very recent achievement in molecular spectroscopy²⁶⁻²⁸. Intensity parameters are available for an acceptable prediction of the absorption coefficients²⁸.

Let us first treat the lattice dynamics of polyethylene as a one-dimensional lattice in its full *trans*-planar structure. Application of standard numerical methods of lattice dynamics for perfect^{29,30} and disordered^{31,32} lattices allows the calculation of the one phonon density of state $g_p(\omega)$ of the perfect chain. We then introduce in the lattice an isolated twiston with the geometry given in reference 17 and calculate $g_{dis}(\omega)$. The vibrational density of states, g_{tw} , due to the twiston is given by:

$$g_{tw}(\omega) = g_{dis}(\omega) - g_p(\omega)$$

$g_{tw}(\omega)$ is plotted as a histogram in *Figure 1* in the energy range most meaningful for structurally sensitive normal modes. From *Figure 1* it is clear that in going from the perfect chain to the conformationally disordered one some normal modes of the all *trans* 1-*d* lattices are lost, while new ones specifically associated with the modes of the twiston appear in $g(\omega)$. In our analysis we focus our attention on those frequencies of the twiston which turn out to be more isolated from those of the perfect 1-*d* lattice.

The plot of $g_{tw}(\omega)$ in *Figure 1* indicates the possible locations of modes characteristic of the pinned twiston, but no indication is given on the corresponding dipole transition moments which determine intensities. Intensities indicate which modes are more likely to be observed experimentally in the i.r. spectrum.

We have then carried out the calculation of the complete infra-red spectrum of a finite molecule, namely *n*-nonadecane (hereafter referred to as to C19) with various structures and in terms of frequencies and absorption intensities. We had studied the vibrational infra-red and Raman spectra of C19 in the three phases, S₁ (orthorhombic), S₂ 'α' and melt previously and had shown that in the S₂ phase 25% of the chains have moved out of the crystal lamellae⁹. If such an overall longitudinal molecular motion is caused by the twistons the spectrum

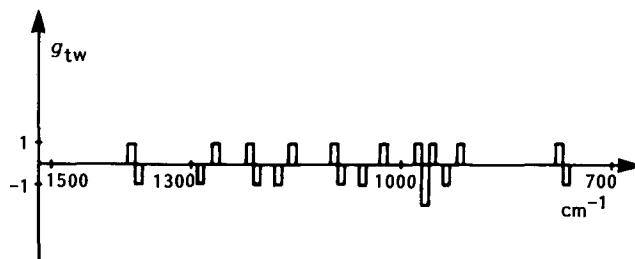


Figure 1 Difference of one phonon density of states for a chain of 50 CH₂ groups containing one Utah twist (see text)

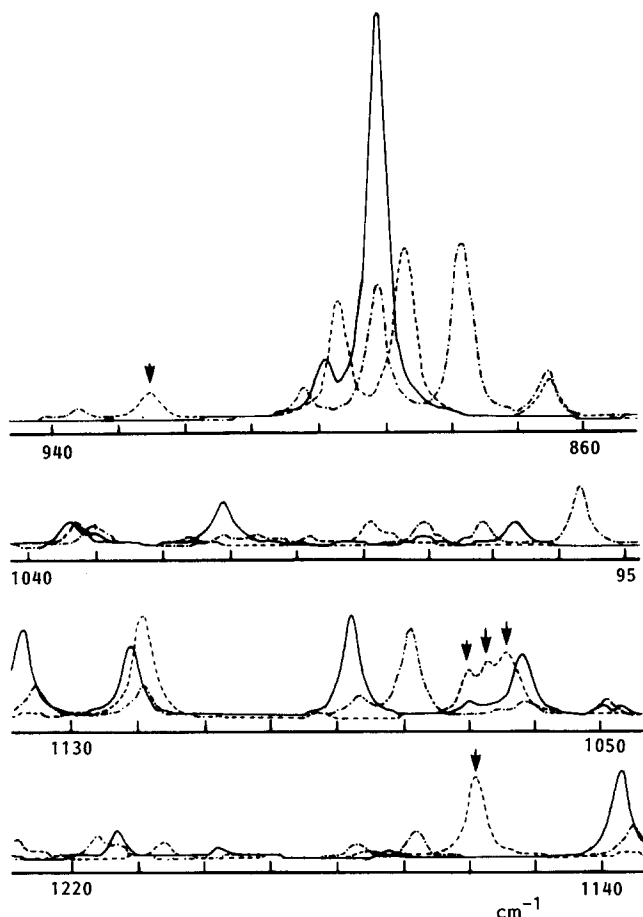


Figure 2 Calculated infra-red spectra of $C_{19}H_{40}$ in (—), *trans* conformation; (---), with one end -TG defect, and (-·-·) with a soliton-like distortion. BWHM 5 cm^{-1} . Arrows indicate the calculated bands for a soliton-like distorted molecule which seem more relevant in a comparison with the experimental spectrum

of phase S_2 is the more likely candidate for shown spectral features, if any, associated with such conformational collective defects.

In *Figure 2* we report the calculated infra-red spectra of *trans* planar C19 (phase S_1), C19 molecules with end-*gauche* conformational defects (identified in the S_2 phase) and C19 containing a pinned Mansfield and Boyd twiston. The calculated frequencies for the first two cases are in good agreement with the experimental and calculated frequencies in reference 9. Moreover they agree with the calculations reported in reference 33. We also calculated absorption intensities which agree with the experimental ones. The spectra calculated in *Figure 2* consider each phase separately, i.e. the spectra refer to samples with 100% of each phase. The experimental spectrum of C19 in the S_2 phase is satisfactorily reproduced by the weighted coaddition of the calculated spectra $\sim(0.75 S_1 + 0.25 S_2)$.

As seen in *Figure 2* the calculated spectrum of C19 with a twiston has an infra-red spectrum very different from the other structures of C19. The results for this finite molecule agree with the results of lattice dynamical calculations on much longer chains reported in *Figure 1*. For real samples, however, a mixture with unknown percentages of the three samples must be considered. Strong overlapping then occurs and obscures many of the signals of the twiston. One must then look for absorption bands free from overlapping, and allow for some small

uncertainty in the calculated quantities due to obvious uncertainties in the parameters used in the calculations.

As predicted in *Figure 1* we located interesting isolated signals possibly due to the twiston in the following spectral ranges: (i) at 1159 cm^{-1} near a much weaker signal of TG structures at 1168 cm^{-1} , (ii) in the $1070\text{--}1064\text{ cm}^{-1}$ range we observe a broad and structured band separated from a TG signal at 1079 cm^{-1} and a signal of all *trans* conformation at 1062 cm^{-1} and (iii) a weak but well isolated band at 925 cm^{-1} separated from the absorptions due to the TG conformation at 957 and 936 cm^{-1} . All these bands originate from coupled skeletal C-C stretchings within the twiston.

We then turn to the experimental infra-red spectra of C19. *Figure 3* gives a section of the experimental infra-red spectra of crystalline (*trans*-planar) C19 and α -phase C19. It is surprising to find features in the spectrum of α -phase C19 predicted by calculations to belong to twistons. These have not yet been shown to be due to end-*gauche* C19 even after very careful vibrational analysis (32,33). It has been noted previously (9,33) that other kinds of localized defects (e.g. GTG' and GG) show characteristic absorptions in the infra-red spectrum which are different from those we assign here to twistons.

THE VIBRATIONAL SPECTRUM OF A MOBILE TWISTON

No vibrational analysis can be proposed if the mobility of the twiston is not considered. So far we have discussed the spectrum of a pinned twiston. Let us now consider the discrete structure of a polymethylene chain and assume that the twiston spends a certain time Δt at a given site of the molecule before making a very fast hop to the nearest site which is at a distance of $\sim 2.5\text{ \AA}$. While sitting at one site the twiston is performing its normal modes of vibration. In a first and very crude approximation the lifetime, τ , of the vibrational mode of the twiston is the time spent by the twiston at each molecular site. In other words one can consider how many cycles of oscillations atoms can perform before hopping. τ is inversely proportional to the bandwidth at half maximum, BWHM. If it is too small bands become too large, are

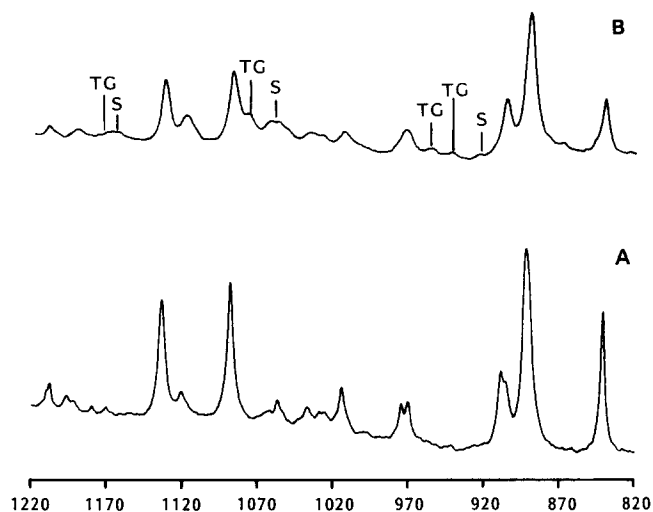


Figure 3 Experimental infra-red spectra of $C_{19}H_{40}$ in the crystalline phase at 19°C (A) and in the ' α ' phase at 31°C (B) in the region $1220\text{--}820\text{ cm}^{-1}$. The assignments to non-planar conformations (TG defect, S: soliton-like distortion) derive from the calculated spectra of *Figure 2*

smear out in the whole spectrum and cannot be observed. For a BWHM of 20 cm^{-1} , taken as a reasonable limit for the experimental observation of weak bands, $\tau \approx 2\text{ ps}$. The upper limiting speed of propagation of the twiston in order to be observed in the infra-red spectrum is then approximately 10^4 cm s^{-1} . In this very crude model other relaxation phenomena which affect band shape and band width^{14,15,31} are neglected.

CONCLUSIONS

The theoretical calculation of the vibrational infra-red spectrum of a polymethylene chain containing a pinned and immobile Mansfield and Boyd twiston (or Utah soliton) shows that several modes of this object are different from those of the *trans*-planar chain. Thus, signals characteristic of this object should, in principle, be found experimentally if its concentration is sizeable at kT, i.e., if its formation energy is low. However, no reliable information can be obtained unless absorption intensities are calculated to allow the identification of modes which are not too weak or too overlapped with the other phonons of the perfect *trans*-planar lattice. The mobility of the twiston along the chain involves the bandwidth of the potentially observable infra-red active modes.

A few coincidences between the calculated spectra and those observed for *n*-nonadecane in the $S_2\ \alpha$ phase make the problem extremely interesting and stimulate further work. The fact that modes of the twiston are possibly observed experimentally sets an approximate upper value to its velocity of propagation along the chain. The estimated velocity of $\sim 10^4\text{ cm s}^{-1}$ is interestingly very close to the value estimated by Mansfield²¹ of $\sim 10^5\text{ cm s}^{-1}$.

A necessary observation regarding C19 is that chains are short relative to the size of the Mansfield Boyd twiston. Hence even if the twistons exist their shape and motion may be similar, but not identical, to those of the Mansfield and Boyd twistons. Some kind of motion, however, even if slow, must exist because 25% of the chains have moved out of the crystal lamella⁹ and have been able to diffuse.

We wish to stress the potential importance of lattice dynamical calculations and of infra-red spectroscopy in the study of the collective motions which may occur in chain molecules. We do not claim that with certainty we have identified defects precisely like Mansfield Boyd twistons in the S_2 phase of C19, but we certainly find interesting coincidences between calculations and experiments. Both need further study.

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