Notes

On the Origin of the Infrared 690-cm^{-1} Band of Polyethylene: Molecular Twist Boundaries or Binary Combinations?

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Introduction

Recently Reneker, Mazur, and Fanconi (RMF) reported infrared evidence for the existence of molecular twist boundaries in semicrystalline polyethylene (PE), i.e., twisted segments in otherwise planar polymethylene chains.[1] Their evidence centers on a broad infrared band whose frequency they refer to as 680 cm^{-1}. This band, RMF note, appears weakly in the spectrum of solution-crystallized PE[2,3] and more strongly in samples of PE that have been quenched and then partially annealed.[4] On the basis of normal coordinate and intensity calculations, RMF argue that the infrared spectrum of twisted segments of the type described in ref 6 will have a band between 680 cm^{-1} and 715 cm^{-1}, depending on how tight the twist is. Therefore, they concluded that the bands observed in this region indicate the presence of twisted segments with about nine CH_2 groups in the 180° twist.

For the purposes of this note it is important to emphasize that *two* different bands are involved and that they are associated with different PE morphologies. One is associated with solution[2,3] and bulk[5]-crystallized PE. We will call this band the "690-cm^{-1} band" since it has this frequency at low temperatures (<100 K).

The other band, which is much more intense and appears at 680 cm^{-1}, was reported by Hendra et al.[4] for a partially annealed PE "glass". To our knowledge this band has not been reported elsewhere. We will refer to it as the "680-cm^{-1} band" to distinguish it from the 690-cm^{-1} band. It is the assignment of the 690-cm^{-1} band that is the subject of this report.

Our assignment of the 690-cm^{-1} band of PE is based on the observation that this band, or a complex of bands that is centered about 690 cm^{-1}, is also present in the infrared spectra of long, crystalline *n*-alkanes at low temperature. In this case the bands cannot be associated with twisted segments, since the chains in *n*-alkane crystals are known to be planar zigzag. We have found also that the relative intensity of the band, or the summed intensity of the bands, if there is more than one, is about the same as that of the 690-cm^{-1} band observed for polyethylene. Thus the polyethylene band near 690 cm^{-1} appears to be associated with *planar* chains and will appear even in the absence of twisted segments. We note that this interpretation does not apply to the 680-cm^{-1} band reported for the partially warmed glass by Hendra et al.[4]

Experimental Observations

Unless otherwise noted, all spectra were measured with the use of an evacuatable Nicolet Model 8000 FTIR spectrometer. For sample temperatures below 77 K, a CTI Model 21 closed-cycle helium refrigerator equipped with a temperature controller was used. The *n*-alkanes measured were of high purity, 99.6–99.9 mol %, and are described in ref 7.

n-Alkanes. The infrared spectrum of a film of the orthorhombic form I of n-$C_{36}H_{74}$[8] at 40 K is shown in Figure 1 in the 825–600-cm^{-1} region. Weak bands are observed near 685 and 677 cm^{-1}, which are similar in frequency and intensity to the 690-cm^{-1} band of PE. The infrared spectra of other crystalline *n*-alkanes at low temperature show similar bands. These may be seen in Figure 2, which summarizes the spectra of the *n*-alkanes C_{18}, C_{20}–C_{30}, and C_{36}.[13]

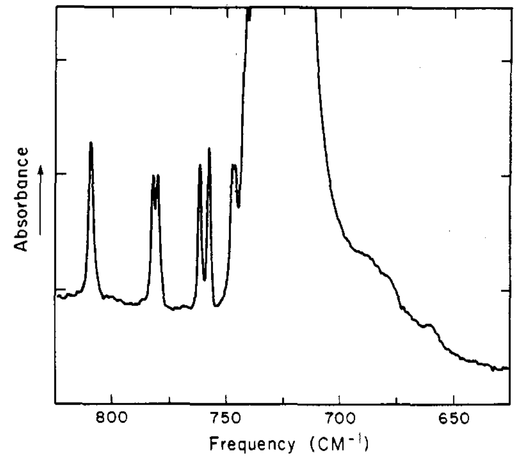

Figure 1. Infrared spectrum of the orthorhombic form I of n-$C_{36}H_{74}$ at 40 K.

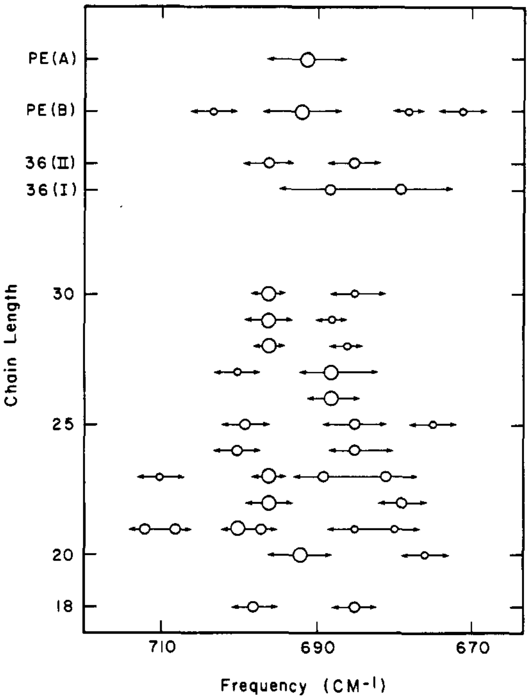

Figure 2. Summary of the low-temperature infrared spectra of the *n*-alkanes (n = 18, 20–30, 36; bands for two orthorhombic forms of n-$C_{36}H_{72}$ are included: 36(I) and 36(II) (see ref 8)) and polyethylenes (A = high molecular weight; B = low molecular weight, ~2000). The circles indicate the band positions and the size of the circles the intensity; half-widths (HWHH) are indicated by the arrow lengths.

In general, the low-temperature *n*-alkane spectra show more than one band in the 700–670-cm^{-1} region, and these bands are significantly broader (FWHH ≅ 6 cm^{-1}) than the rocking-mode bands (FWHH < 2 cm^{-1}). However, the intensity-weighted average frequency computed for the

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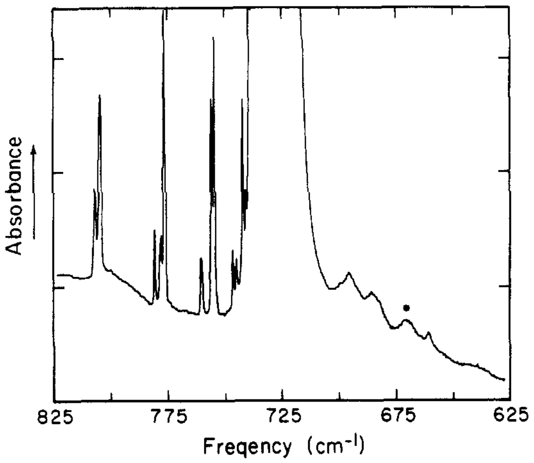

Figure 3. Infrared spectra of a mixture of the orthorhombic forms I and II of n-$C_{36}H_{74}$ at 77 K. (The approximate ratio of form I to form II is 1:2. The asterisk indicates an impurity band.)

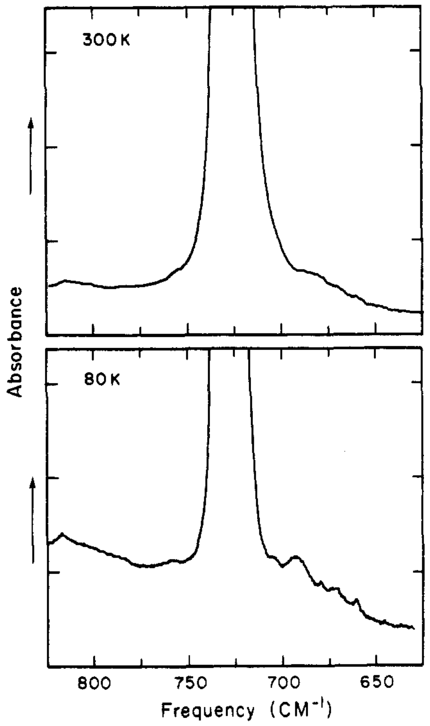

Figure 4. Infrared spectra of low molecular weight (MW ≅ 2000) polyethylene at 300 and 80 K.

spectra shown in Figure 2 is 690 cm^{-1}, which is also the frequency observed for the band of interest in PE.

The disposition of the bands in the complex near 690 cm^{-1} is somewhat dependent on crystal structure. This is evident from a comparison of Figures 1 and 3. These figures show the 690-cm^{-1} bands for two crystal modifications of n-$C_{36}H_{74}$.[8] Figure 1 is for the orthorhombic form I; Figure 3 is for a mixture of the orthorhombic forms I and II in the approximate ratio 1:2. There are differences between the two spectra in the 690-cm^{-1} region. The 687- and 678-cm^{-1} bands in the spectrum of the orthorhombic form I appear to be shifted to 695 and 685 cm^{-1} in form II. Another difference is in the band widths, which are significantly narrower in the spectrum of form II.

Polyethylene. Figure 4 shows the infrared spectra (780–600 cm^{-1}) of a melt-crystallized sample of a low molecular weight PE ($\bar{M}_n$ = 1790, $\bar{M}_w/\bar{M}_n$ = 1.1) at 300 and 80 K. At 300 K, there is a band near 680 cm^{-1} that is broad and nearly featureless, but, at 80 K, several components become apparent. A band at 691 cm^{-1} dominates the region. Figure 5 shows the low-temperature spectrum of a film of PE of a much higher molecular weight. Again there is a band at 691 cm^{-1}, but in this case it is not accompanied by satellite bands.

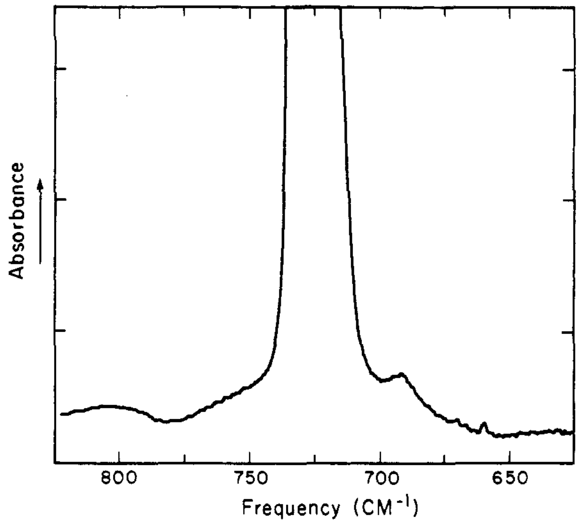

Figure 5. Infrared spectra of polyethylene (MW ≫ 2000) at 10 K.

The half-width (FWHH) of the 690-cm^{-1} band of PE (Figure 5) is around 9–12 cm^{-1} while the various individual bands observed near 690 cm^{-1} in the n-alkane spectra have smaller widths, around 6 cm^{-1}. The relative values of these widths are consistent with the idea that the 690-cm^{-1} band of PE is comprised of an overlapping complex of narrower bands. Many low-intensity band complexes of this sort have been found in other regions of the infrared spectrum of crystalline n-alkanes and polyethylene and have been assigned to specific binary combinations of the fundamentals.[9]

The intensities of the 690-cm^{-1} band in different spectra can be compared by using the intensity of the band at 660 cm^{-1} as an internal standard. The latter band appears in all the infrared spectra of the crystalline polyethylenes and n-alkanes that we measured. Earlier studies[5,10] indicate this band belongs to the CD rocking mode of a CHD methylene isolated in an otherwise undeuterated trans chain. Such groups are present as a result of naturally occurring deuterium. Thus, the 660-cm^{-1} band can serve as an intensity standard, and, using it as such, we find that, to within 30%, the intensities of the 690-cm^{-1} band observed in our high and low molecular weight samples are the same. Also, these intensities, to within a factor of 2, are equal to the sum of the intensities of the individual component bands in the spectra of crystalline n-$C_{21}H_{44}$ and n-$C_{36}H_{74}$.

Assignment of the 690-cm^{-1} Band

We propose an assignment for the 690-cm^{-1} band that appears to account for the following features: (i) its frequency; (ii) its unusual breadth; (iii) its multiplicity in the n-alkane spectra; (iv) its intensity; (v) its sensitivity to crystal structure. In brief, its assignment is to certain binary combinations comprised of in-plane skeletal bending modes and out-of-plane skeletal twisting modes. These combinations fall in the proper frequency region and have the proper symmetry to interact through Fermi resonance with the 720-cm^{-1} fundamental. Through this interaction, their intensities, which are unusually large for binary bands, are accounted for.

It is convenient to discuss the assignment in terms of the two dispersion curves, ν_5 and ν_9, which are associated with in-plane skeletal bending and out-of-plane skeletal

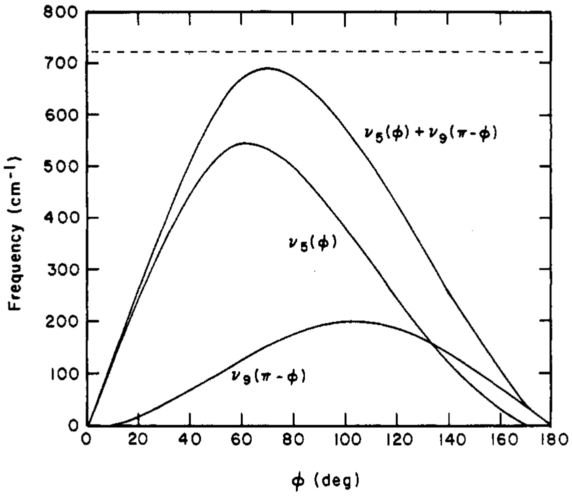

Figure 6. Zone-center frequencies of the binary combinations obtained by adding $\nu_5(\phi)$ and $\nu_9(\pi - \phi)$. The dashed line indicates the frequency near 725 cm^{-1} of the intense methylene rocking mode fundamental, from which the binary combinations borrow intensity. (See text and ref 9 for a fuller explanation.)

twisting modes, respectively. These curves are depicted in Figure 6 for the isolated chain. Interchain interaction in the crystal complicates the picture, but its effect is primarily in the frequency region near the zone center (ϕ = 0 and π). Thus, the isolated-chain approximation is quite good in the region in which we are interested, since it is well away from the zone center. The ν_5 and ν_9 curves in Figure 6 were computed with a standard valence force field[11] and then scaled somewhat so that their cut-off frequencies have the generally accepted values determined from neutron scattering. These values are 550 cm^{-1} for ν_5 and 200 cm^{-1} for ν_9.[12]

The two possible zone-center combinations are $\nu_5(\phi) + \nu_9(\phi)$ and $\nu_5(\phi) + \nu_9(\pi - \phi)$.[9] The latter combination, shown in Figure 6, has a critical point at 690 cm^{-1}, nearly exactly at the frequency of the band in question.

The symmetry of half the binary combinations $\nu_5(\phi) + \nu_9(\pi - \phi)$ is correct for interaction with the 720-cm^{-1} band. This can be easily shown for a chain having an odd number of carbons. The point group of this chain is C_{2v}. If symmetry species A_1 and B_1 contain the in-plane modes (ν_5) and A_2 and B_2 contain the out-of-plane modes (ν_9), then the binaries $A_1 + B_2$ and $B_1 + A_2$ have the B_2 symmetry of the 720-cm^{-1} fundamental so that interaction will occur. A similar argument can be made for even chains. We note that the interaction between the 720-cm^{-1} fundamental and the binary combinations is actually very weak, just sufficient to make the binary combinations observable.

For PE, effectively an infinitely long chain, the result is a single, broad band at 690 cm^{-1} that consists of a continuum of overlapping components. For the *n*-alkanes, the frequency separation between the binaries is large enough to permit individual bands to appear. The higher frequency components tend to be the more intense because they are closer to and hence can interact more strongly with the 720-cm^{-1} fundamental. The fact that these bands depend on chain length and crystal structure is now understandable, since both these factors are known to influence the frequencies of the component fundamentals.

Summary

In a recent publication, an infrared band in the spectrum of solid polyethylene was associated with the presence of molecular twist boundaries.[1] Actually, two different bands are involved. One of these appears at 690 cm^{-1} in the spectra of bulk- and solution-crystallized polyethylene; the other, which is much more intense, is reported to appear at 680 cm^{-1} in the spectrum of a partially annealed polyethylene glass obtained by rapid quenching of the melt.[4] In their paper on twist boundaries, the authors refer to both bands as the "680 cm^{-1} band".

We are concerned here with the assignment of the 690-cm^{-1} band. Bands similar in frequency and intensity are observed in the spectra of long crystalline *n*-alkanes, which are known to be comprised of planar chains. An analysis of these bands indicates that the 690-cm^{-1} band is to be assigned to a Fermi-resonance-enhanced series of binary combinations. The assignment accounts well for the main features of the 690-cm^{-1} band.

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Registry No. $C_{18}H_{38}$, 593-45-3; $C_{20}H_{42}$, 112-95-8; $C_{21}H_{44}$, 629-94-7; $C_{22}H_{46}$, 629-97-0; $C_{23}H_{48}$, 638-67-5; $C_{24}H_{50}$, 646-31-1; $C_{25}H_{52}$, 629-99-2; $C_{26}H_{54}$, 630-01-3; $C_{27}H_{56}$, 593-49-7; $C_{28}H_{58}$, 630-02-4; $C_{29}H_{60}$, 630-03-5; $C_{30}H_{62}$, 638-68-6; $C_{36}H_{74}$, 630-06-8; polyethylene, 9002-88-4.

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(13) These spectra were measured with the use of an IR-7 Beckman infrared spectrometer with a resolution of better than 2 cm^{-1}. The *n*-alkanes were measured in KBr pellets. Several of the *n*-alkanes were also measured as films with the Nicolet FTIR spectrometer. The spectra are the same in both cases except near 667 cm^{-1}, where the Beckman spectra show anomalies due to the intense CO_2 band at this frequency.

Reduction of the Unperturbed Dimensions of the Main Chain When Ethyl Groups Are Attached to a Poly(methylene) Backbone

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Branched and linear polymers with the same number of bonds, *N*, have different mean square radii of gyration, $\langle s^2 \rangle$.[1] The ratio of the two $\langle s^2 \rangle$ is commonly denoted by *g*. The value of *g* in the unperturbed state can be calculated by random flight statistics,[1] rotational isomeric state theory,[2,3] or the wormlike-chain model.[4] Rotational isomeric state theory most easily takes into account the influence of a branch on the probability for occupancy of individual rotational isomers accessible to bonds near a

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