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Studying the length of *trans* conformational sequences in polyethylene using Raman spectroscopy: a computational study[☆]

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Abstract

The long standing question of how long a *trans* sequence in a polyethylene needs to be in order to contribute to the all-*trans* Raman bands at 1060 and 1130 cm^{-1} is addressed. Various hexadecane, $C_{16}H_{34}$, conformers were studied using ab initio type calculations revealing vibrational frequencies and intensities. We found that only *trans* sequences longer than 10 *trans* bonds reveal Raman intensity primarily selectively at the same frequencies as the C–C stretching modes arising from crystalline polyethylene. Since it is statistically highly unlikely that such long *trans* sequences occur in the amorphous phase, intensity arising from all-*trans* sequences not belonging to crystalline structure may only be expected as a consequence of strong non-equilibrium conditions (e.g. shear), or the presence of tie-molecules. © 2001 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Vibrational spectroscopy is known as one of the major analytical tools to characterize polymer samples. Detailed information on quantities such as configuration, conformation, chemical composition and orientation can be obtained using infrared or Raman spectroscopy [1–3]. Although even a polymer like polyethylene (PE) has been extensively studied using vibrational spectroscopy, there are still items of significant interest, which require further study. This particularly applies to spectral intensities and their change upon temperature, morphology, etc.

From previous studies on the Raman spectra of alkanes as model systems for polyethylene, we have obtained gratifying results, which demonstrate the applicability of quantum mechanical modelling to describe features in the Raman spectra of alkanes and polyethylene (semi-) quantitatively correct. Firstly, the shift of the Raman C–C stretching bands upon applying strain has been described [4]. Secondly, using octane, dodecane and hexadecane as models to describe parts of the Raman spectrum of PE [5–7], the effect of conformation on the spectral intensities was studied. The experimentally observed temperature dependence of the integrated intensity in the 0–600 and the 700–1000 cm^{-1} range of the Raman spectrum of alkanes and PE could be rationalized (originating from differences in chain conformation). The practical insensitivity towards conformation of the intensity in the 1300 cm^{-1} was recovered. The two all-*trans* C–C stretching bands were found to react very differently with respect to conformational changes. These findings could be compared to experimental data, and therefore provide a further rationalization of the experimentally observed features. Finally, using calculated Raman intensities, a very acceptable value for the *trans–gauche* energy difference was obtained for pentane [8]. The feasibility of this type of calculations make that several of the early interpretations presented by Snyder and other authors [9–11] long time ago can now be confirmed on basis of ab initio calculated data, whereas previous studies involving interpretation have often relied on force fields which were parametrised using the vibrational frequencies. Here, the ab initio methodology provides independent and, in this respect, unbiased information. Moreover, the ab initio calculations provide frequencies and intensities.

A still unresolved issue concerns the sensitivity of Raman spectroscopy in probing short all-*trans* sequences in a polyethylene chain. The part of the Raman spectrum covering the C–C stretching range reveals three distinct features:

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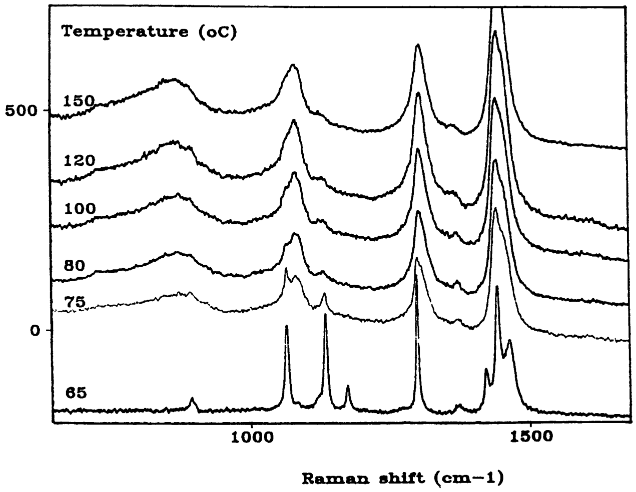

Fig. 1. Raman spectra recorded from $C_{36}H_{74}$ in the C–C stretching range. Note the persistence of spectral intensity at 1060 and 1130 cm^{-1} while the melting point of $C_{36}H_{74}$ is 76°.

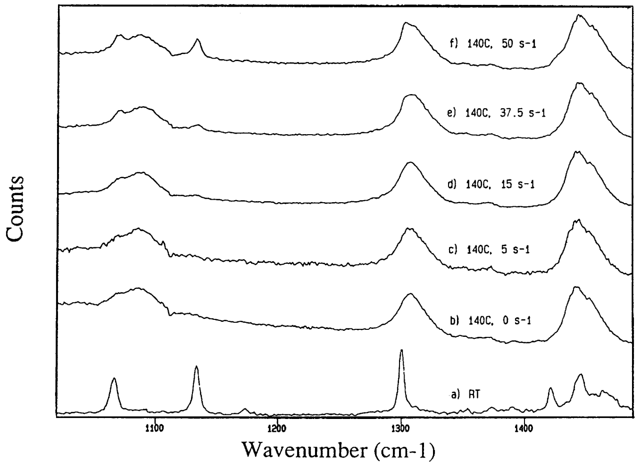

Fig. 2. Effect of shear rate on the Raman spectrum of a high density polyethylene sample at 140°C, in the melt (reproduced with permission from Chai et al. [15]).

two sharp bands centred at 1060 and 1130 cm^{-1}, representing the asymmetric and the symmetric C–C stretching of all-*trans* PE chains, respectively, and a broad band centred around 1080 cm^{-1}. Because crystalline PE consists of all-*trans* PE chains (neglecting chain folds), in a semi-crystalline PE the former two bands primarily probe the level of crystallinity. The broad 1080 cm^{-1} band is characteristic of the conformationally disordered chain and reflects the presence of either amorphous phase or the melt phase of PE or (long) alkanes. The bands at 1060 and 1130 cm^{-1} are attributed to the all-*trans* chain, not necessarily to crystalline polyethylene. This is not always sufficiently appreciated, as often bands like these are referred to as crystalline bands, whereas they usually are (the $k = 0$) modes of a single all-*trans* chain [12,13]. Upon melting, the 1D-translational periodicity is broken and for that reason the spectrum changes dramatically. On the other hand, for semi-crystalline polyethylene, it seems that by far most of the intensity in the 1060 and 1130 cm^{-1} region does arise from crystalline structure.

Having said this, there is an interest to detect, in the end quantify, all-*trans* sequences as these may be present in oriented amorphous material or in the melt, as such a small quantity may nevertheless have a more than proportional influence on properties, e.g. as tie-molecules. Indications for persistence of all-*trans* sequences, when identified with Raman intensity at 1060 and 1130 cm^{-1}, has been obtained from experiments in which a polyethylene was heated from room temperature up to the melt, see Fig. 1 [14], and from an experiment in which a melt was made subject to a flow, see Fig. 2 [15]. Also in oriented polymers, a fraction of the amorphous phase is considered oriented [16], suggesting (short) *trans* sequences for polyethylene. Regarding analysis of the Raman spectrum, however, we are not aware of any study that has addressed from which length of the all-*trans* segment onwards the same spectrum as that of the infinite, all-*trans*, polyethylene chain is retained. Some authors speak of “sufficient number of consecutive C–C bonds in all-*trans* disposition” and “not enough consecutive C–C bonds in all-*trans* disposition” [17], and therefore, no detailed conclusions can be drawn from such studies.

As there are no experimental means to selectively study the dependence of the Raman spectrum at the level of specific individual chain conformation, in the light of the present study, the intensity distribution in the C–C spectral range, the computational approach successfully applied in our previous studies [4–8] was adopted. The errors in the Hartree–Fock calculated frequencies are well-recognised, and lead to an overestimation of the frequencies by about 10%. Regarding intensities, we emphasize that we do not refer to absolute Raman scattering cross sections here, but to relative changes. This study is primarily concerned with results obtained on a series of hexadecane conformers. For practical reasons, a limited number of conformers were selected, and qualitative conclusions will be drawn, but though based on trends in quantitative data. The results presented in the present study refer to isotropic Raman scattering data.

2. Computational methods

The calculations were performed using the GAUSSIAN 98W suite of programs [18] running on an IBM Netfinity server. All geometries were fully optimised within C_1-symmetry using the 6-31G* basis set (individual gradients of the order of 10^{-5} hartree/bohr, the root-mean-force of the order of a few times 10^{-6} hartree/bohr).

The calculated modes can be identified with the experimentally observed modes by enumeration of the total number of observed Raman active modes and considering the symmetry of the modes and by making reference to, e.g.

Table 1

Ab initio (6-31G* basis) calculated Raman vibrational frequencies for hexadecane, $C_{16}H_{34}$, for various lengths of the all-*trans* segment. Frequencies in cm^{-1}, in brackets the Raman intensities in Å^4. Only those Raman data are presented for which the intensity is at least one (in the given units). The all-*trans* hexadecane is said to have all 15 C–C bonds in the *trans* sequence, likewise the conformation designated '13 C–C *trans*' has 13 C–C bonds in a *trans* sequence. The *trans* sequence has been allocated in the middle of the molecule, so that except for the all-*trans* structure all chain ends involve *gauche* bonds. In bold those frequencies lying close to the experimental '1060' (calculated 1140) and '1130' (calculated near 1245) cm^{-1} frequencies related to the asymmetric and symmetric C–C stretch vibrations, respectively. Occasionally, when two calculated frequencies are very close (typically within 2 wavenumbers, the average frequency is given and the total, co-added, intensity. Finally, the designation T stands for the observation that this vibration is located in the *trans* sequence (was only checked for vibrations in the experimental '1060' (calculated 1140) and '1130' (1245) cm^{-1} frequency region

	15 C–C in *trans* (=all-*trans*) 13 consecutive *trans* bonds	13 C–C in *trans* 11 consecutive *trans* bonds	10 C–C in *trans* 8 consecutive *trans* bonds	8 C–C in *trans* 6 consecutive *trans* bonds	8 C–C in *trans* 6 consecutive *trans* bonds	6 C–C in *trans* 4 consecutive *trans* bonds	4 C–C in *trans* 2 consecutive *trans* bonds
Total energy (hartree)	− 625.714723 0 *gauches*	− 625.711540 2 *gauches* gtttttttttttg	− 625.711396 2 *gauches* ttgttttttttgt	− 625.705410 6 *gauches* gtgttttttgggg	− 625.711395 2 *gauches* tttgttttttgtt	− 625.705023 6 *gauches* tgggttttgtggt	− 625.700544 9 *gauches* gtgggttgggtgg
Relative energy (kcal/mol)	0	+ 2.0	+ 2.1	+ 5.8	+ 2.1	+6.1	+ 8.9
1030–1230 cm^{-1} range	1056 (1.3)	1041 (5)	1035 (1)	1058 (1)	1050 (1)	1035 (4.5)	1031 (6)
	1078 (2) 1109 (3.3) **1138 (23)** **1140 (37)** **1144 (2)** 1181 (12)	1068 (5) 1093 (2) 1101 (1.5) 1123 (1.2) **1138 (22) T** **1141 (16) T** 1151 (3.3)	1050 (1.2) 1101 (3.9) 1116 (3.5) 1119 (2.6) 1129 (7.1) **1141 (26) T** 1162 (27)	1069 (3.2) 1081 (2.1) 1102 (1.2) 1108 (1) 1122 (3.2) **1135 (3.1)** **1140 (13.1) T** **1142 (8) T** 1150 (7.2) 1165 (15) 1171 (7) 1175 (4.6) 1187 (8.3)	1075 (1) 1096 (1.4) 1114 (3.6) 1129 (7.6) **1138 (13)** **1140 (9.9)** **1141 (17.8) T** 1162 (22.7) 1173 (8.7) 1185 (8) 1229 (1.2)	1092 (4) 1099 (5.3) 1108 (7) 1120 (2) 1127 (4) **1137 (11) T** 1150 (11) 1155 (5) 1179 (2) 1182 (12) 1190 (5.6) 1227 (2.2)	1089 (6.4) 1096 (2.6) 1117 (3.5) **1133 (4.6) mainly T** **1145 (3.0)** 1153 (8.2) 1168 (2.8) 1174 (2.4) 1188 (3.3) 1190 (9) 1194 (2.9)
Total intensity in range	81	89	97	78	94	76	55
1230–1305 cm^{-1} range	**1246 (48)**	**1244 (28)**	1230 (1.1)	**1249 (5.7)**	**1247 (5.9)**	**1250 (6.3)**	**1251 (2.6)**
			1247 (10) 1300 (5.2) 1303 (2.7)	1279 (1.2) 1285 (2.4)	1299 (6.7) 1301 (2.8)	1276 (1.6) 1282 (1.5)	1262 (3.6) 1285 (1.4)
Total intensity in range	48	28	19	9.3	15.4	9.4	7.6

the octane frequencies published by Snyder [11]. This procedure has been explained and applied in earlier work [5–7]. Because we will use alkanes as model systems for polyethylene, it is important to recognize that a set of vibrational bands will generally correspond to a single band in the ('infinite') polyethylene chain, e.g. the fact that three of the calculated frequencies of octane exhibiting Raman activity are identified with the single 1060 cm^{-1} band in PE is in accordance with the splitting observed when shortening the length of the alkane, viz. Ref. [11] Table V. To become practical, the calculated Raman spectra in this spectral range have been subdivided in the 1030–1230 and the 1230–1305 cm^{-1} calculated frequency ranges. For polyethylene, the former range would correspond to the 1060 cm^{-1} C–C stretching band, and the latter range refers to the 1130 cm^{-1} C–C stretching band.

3. Results and discussion

We have calculated the vibrational spectra for a series of hexadecane, $C_{16}H_{34}$, for various lengths of the *trans* sequence. When all-*trans*, $C_{16}H_{34}$ has 15 C–C bonds in the extended chain segment. In addition to this all-*trans* sequence, we have calculated the conformers with 13, 10, 8, 6 and 4 C–C bonds in an extended chain segment. This is equivalent to a sequence of 11, 8, 6, 4 and 2 *trans* bonds, respectively. For all these conformers, the *trans* sequence was located in the central part of the hexadecane chain; the chain ends had predominantly *gauche* bonds. The precise constitution in terms of *trans* and *gauche* bonds is given in the second row of Table 1.

In Table 1, the computed HF energies of the HF/6-31G* optimized structures have been collected. It is known, from higher level quantum calculations and by comparison of those data with experimental data [19–22], that these values qualitatively yield the correct relative order for the conformers, but absolute values are off by a factor of about 2. The correct base value for a single *gauche* bond is about 0.5 kcal/mol (e.g. ttgtt compared to ttttt). For the HF/6-31G* level, the energy penalty related to a single *gauche* bond in an alkane chain is close to 1 kcal/mol, whereas, two consecutive *gauche* bonds make this value practically double [22]. Thus, by comparing the relative energy of each calculated conformer to the number of *gauche* bonds in that conformer (both values are given in the top of Table 1), we see that the relative energies in Table 1 are in good agreement with the literature value of around 1 kcal/mol for a *gauche* at the 6-31G* level of computation.

We now focus on the Raman frequencies and intensities in order to access the length of a *trans* sequence required to reveal Raman intensity at the experimental 1060 and 1130 cm^{-1} Raman shifts. The experimental 1060 cm^{-1} band is identified with a computed frequency close to 1140 cm^{-1}, whereas the experimental 1130 cm^{-1} corresponds to a computed frequency in the range near 1245 cm^{-1} [4–6]. In order to avoid confusion between calculated and experimental frequencies, we will refer to the C–C stretching bands as '1060' and '1130', respectively, when we refer to computed intensity values, but for clarity phrase, the well-known experimental frequency values in quotes.

The first observation based on the data presented in Table 1 is that upon shortening of the *trans* sequence in the hexadecane, overall intensity is distributed over a larger number of frequencies. This seems in agreement with experimental observations of a very broad background coming up upon melting polyethylene, as shown in Fig. 5.13 of Ref. [23], as well as the spectra on $C_{36}H_{74}$ shown in Fig. 1. Furthermore, whereas in the calculated 1230–1305 cm^{-1} range (experimental 1130 cm^{-1} range), the total intensity drops very quickly upon shortening the *trans* sequence, i.e. introducing more *gauche* bonds in the chain, the total intensity in the calculated range 1030–1230 cm^{-1} remains much more constant. This is precisely what is observed upon heating (introducing *gauche* bonds) in polyethylene: the experimental 1130 cm^{-1} almost vanishes, whereas, the 1060 cm^{-1} band is replaced by a very broad band centred around 1080 cm^{-1}.

The data in Table 1 printed in bold represent the frequencies close to the corresponding bands in the all-*trans* hexadecane, and therefore indirectly to the polyethylene all *trans* '1060' and '1130' cm^{-1} frequencies. The vibrational modes with frequency close to a calculated value of 1245 cm^{-1} (experimental 1130 cm^{-1} band in PE) have, throughout the series of species comprising Table 1, the same character. The C-atoms are, alternating along the chain, moving towards and away from the chain in a direction perpendicular to the (all-*trans*) chain segment, but the mode is not localised in the *trans* part of the chain. The modes with their calculated frequency close to 1140 cm^{-1} ('1060' cm^{-1} band), however, are primarily located in the *trans* sequence. This is particularly so for the second variant of the hexadecane with six *trans* bonds, i.e. column 6, with the 1138 cm^{-1} mode being localised in the ttt sequence at the chain end, whereas the 1141 cm^{-1} band represents a mode located in the central 6 *trans* bond (tttttt) sequence. Irrespective of the number of *trans* bonds in sequence, however, we observe that some intensity is retained for both the '1060' and the '1130' cm^{-1} band. Thus, we conclude that it seems very short *trans* sequences do contribute to the intensity of the C–C stretching bands at 1060 and 1130 cm^{-1} in polyethylene.

In addition, we note that there is some correspondence with the calculated data presented in Refs. [5,6]. In that earlier work, we started from the all-*trans* form of the alkane and consecutively incorporated *gauche* bonds in the central part of the chain. In that sense, the reverse was done from what we did in the present study, namely having the central part *trans* and the *gauches* at the chain ends. When one, two or even three *gauche* bonds are present in the octane, Raman intensity was found to reside at the '1130' cm^{-1} frequency

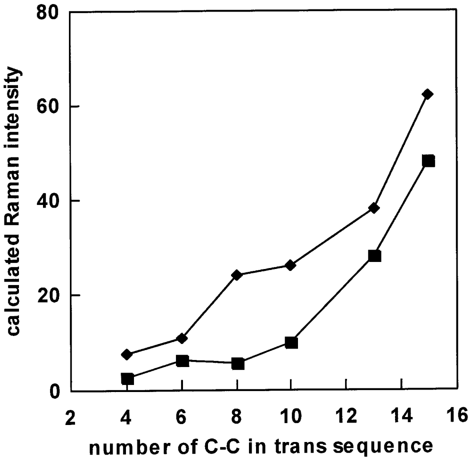

Fig. 3. Calculated dependence (HF/6-31G*) of the intensity of the Raman bands for frequencies near the all-*trans* 1140 (◆) and 1245 cm^{-1} (■) frequencies in hexadecanes (i.e. sums of intensities printed in bold in Table 1).

(see Fig. 2 in Refs. [5,6]). On the contrary, the part representing the asymmetric C–C stretching band (‘1060’ cm^{-1}), calculated range 1030–1230 cm^{-1}, changed drastically upon conformational changes with a redistribution over this spectral range.

We thus observe intensity is retained at the C–C stretching frequencies, but what is the extent to which short *trans* sequences contribute to the intensity of the stretching bands? Intensity contributing to the ‘1060’ and ‘1130’ bands is decreasing readily, as can be seen from the data shown in Fig. 3. Interestingly, since the number of longer *trans* sequences will decrease upon increasing temperature and finally going into the melt, the observation from the calculations that intensity drops more quicker for the high frequency band (‘1130’) than the low frequency band (‘1060’) is in full agreement with experimental behaviour upon heating polyethylene from room temperature up to 126°C (Fig. 5.14 in Ref. [23]), which provides us with another qualitative feature supporting the present level of calculations. As for both bands, the calculated intensity drops more than proportional with the shortening of the length of the *trans* sequence, viz. the non-linearity of the curves displayed in Fig. 3, it is at least questionable whether a short *trans* sequence will raise sufficient intensity to be detected in an actual polyethylene Raman spectrum (even after some advanced analysis of the bands). In addition, quantification will be practically impossible: (i) the ab initio results are a qualitative guide only, and (ii) there is a wide variety in conformers, each with a different intensity distribution.

We now come to the most crucial point in our discussion. The 1060 and 1130 cm^{-1} bands in polyethylene are attributed to all-*trans*, extended, chains. Researchers are trying to quantify the amount of non-crystalline extended chain material by analysing the relative intensity in these spectral regions [17]. What we therefore need is the length of the all-*trans* chain which does selectively contribute to the 1060 and 1130 cm^{-1} intensity, but which does not have further distribution of intensity because in that case it contributes to the broad amorphous feature centred around 1080 cm^{-1}. We have observed that very short *trans* sequences do contribute to the ‘1060’ and ‘1130’ bands. However, from the data in Table 1, we also observe that for most of the short sequences, significant part of the intensity is distributed over a broad spectral domain. Basically, only *trans* sequences which retain almost all intensity in the ‘1060’ and ‘1130’ cm^{-1} bands (calculated 1140 and 1245 cm^{-1}) can therefore be regarded as contributing as extended chain to the bands also representing crystalline polyethylene. From the data in Table 1, we see that this is the case for 11 consecutive *trans* bonds, but not anymore for the conformer having eight consecutive *trans* bonds. The transition thus takes place around 10 *trans* bonds in sequence. Any shorter *trans* sequence will in some way contribute to the broad amorphous feature centred around 1080 cm^{-1}.

For the amorphous phase, the probability of finding 10 bonds in a *trans* sequence is, however, very low. Based on Monte Carlo simulations, de Pablo et al. [24] noted that at 200°C, sequences of six *trans* conformations can still be distinguished in the distribution. From analysis of the Monte Carlo data reported by Sariban et al. [25], we found that *trans* sequences of 10 are highly improbable. Therefore, only strong non-equilibrium states can have such sequences in quantifiable amount. One possible such non-equilibrium state is shear, and this may explain the experimental results presented by Chai et al. [15]. Another possibility is tie-molecules linking crystalline domains. Presence of a significant fraction of such molecules seems the only way to explain the results from the analysis brought forward by Rodriguez-Cabello et al. [17]. However, any such method requires extremely careful curve-fitting, as in the past it was shown that uncritical procedures may lead to invalidation of previously suggested procedures (Ref. [14] represents the example with respect to the third, interlamellar, phase in semi-crystalline polyethylene).

4. Conclusions

On basis of ab initio Hartree–Fock calculations on conformers of hexadecane, we found that very short *trans* sequences, down to a length of two or even a single *trans* bond, adds intensity to the frequency corresponding to the ‘infinite’ all-*trans* chain. The intensity of such peaks drops very quickly, however, much quicker than the all-*trans* segment length shortens. However, when we look at all vibrational modes calculated within the spectral range also comprising the all-*trans* range ‘1060’ and ‘1130’ cm^{-1} bands, for *trans* sequences shorter than about 10, the intensity distribution is broadly spread, contributing to the signal representing the amorphous phase rather than adding to the ‘crystalline’ bands at experimental Raman shifts 1060 and 1130 cm^{-1}. Only *trans* sequences longer than about 10 are found to add more or less selectively to the same C–C stretching Raman bands as characteristic for crystalline polyethylene. That we can not make a more precise statement is because any deviation from an infinitely long all-*trans* chain introduces an intensity distribution, and therefore conclusions must be drawn on basis of dominant intensities in this spectral range.

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