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Relationship between the Distortion of Polyene Chains from Planarity and the Raman Activity of the In-Phase CH Out-of-Plane Wag

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Summary: The relationship between the distortion of polyene chains from planarity and the Raman activity of the in-phase CH out-of-plane wag is examined by performing density functional theory calculations. The vibrational wavenumbers, vibrational modes, Raman activities and infrared absorption intensities of several oligoene (or polyene) molecules are calculated for model structures having various kinds of distortion around the CC double and/or single bond(s). The results of calculations show that the molecular distortion induces the Raman activity of the in-phase CH out-of-plane wag which should be Raman-inactive for the planar structure. The Raman activity of the in-phase CH out-of-plane wag is particularly enhanced when the molecule is uniformly helical. The origin of a weak Raman band at about 1010 cm^{-1} of *trans*-polyacetylene is discussed on the basis of the calculated results.

Keywords: in-phase CH out-of-plane wag; molecular distortion; polyacetylenes; polyenes; Raman spectroscopy

Introduction

In the present paper, the relationship between the distortion of polyene (or oligoene) chains from planarity and the Raman activity of the in-phase CH out-of-plane wag is examined by performing density functional theory calculations. The vibrational pattern of the in-phase CH out-of-plane wag (hereafter abbreviated as the Wag) of $C_{14}H_{16}$ is depicted in Figure 1. The purpose of this study is to check the validity of a band assignment that a weak band observed at about 1010 cm^{-1} in the Raman spectrum of *trans*-polyacetylene (abbreviated as *trans*-PA) is due to the Wag activated in the Raman spectrum by molecular distortion.[1]

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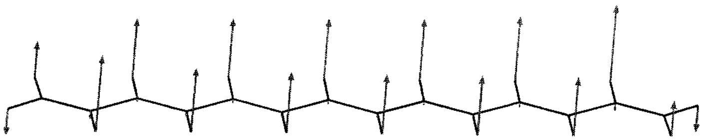

Figure 1. Calculated vibrational pattern of the in-phase CH out-of-plane wag of $C_{14}H_{16}$.

The subject treated in the present study is not confined to the matter of a mere band assignment but is directly related to an issue of more global interest, i.e., the planarity or nonplanarity of molecules with strong π-electron conjugation. Recently, two of the present authors (AS and MT), together with three other co-authors, carried out a similar study on *trans*-stilbene, one of the most basic organic molecules, and showed that this molecule is slightly distorted in solution.[2] This prompted us to conduct the present study on polyenes which have fundamental importance in not only materials science but also biological science.

In the infrared spectrum of *trans*-PA, an intense band is observed at about 1010 cm^{-1}, which is undoubtedly assignable to the Wag.[3] In the Raman spectrum, on the other hand, a weak band is observed at about the same wavenumber.[1] The selection rule for the planar structure of *trans*-PA dictates that the Wag should be infrared-active but Raman-inactive. However, this vibrational mode may be observed in the Raman spectra of polyene chains which have no center of symmetry due to distortion around the CC double and/or single bond(s). It is therefore important to evaluate the Raman activity of the Wag of distorted polyene chains by theoretical calculations to confirm or rule out the possibility of observing a Raman band from this mode.

The seven species of C_nH_{n+2} with even numbers of n (4, 6, 8, 10, 12, 14, and 16) are treated in the present study. Hereafter, C_nH_{n+2} is called the C_n species.

Calculations

First, the structural parameters of the oligoene (or polyene) molecules were optimized by density functional theory calculations using the B3LYP functional[4,5] in combination with the 6-311+G** basis set. Then, the normal frequencies, normal modes, and their Raman and infrared intensities were calculated for model structures having some distortions from planarity, which were obtained by changing the torsional angle(s) around the CC double and/or single bond(s) at 4° intervals from the planar *trans* form. The structural parameters of the model structures other than the pre-fixed torsional angles were kept at the same values as those of the geometry-optimized structures.

The torsional angle around the C=C bond is denoted as θ and that around the C–C bond as τ. The angle θ is defined around the C=C bond in the C–C=C–C linkage, and the angle τ around the C–C bond in the C=C–C=C linkage in a way consistent with the IUPAC recommendations.[6] Thus, in the case of the planar structure, both of θ and τ are equal to 180°. Changes in θ and τ from the planar structure are expressed as $\Delta\theta$ and $\Delta\tau$, which are positive for a clockwise torsion around the respective bond, and negative for an anticlockwise torsion.

The two versions of GAUSSIAN98 were used in the following way. The Rev.A.7 version[7] was used at a network parallel execution mode with Linda (embedded in GAUSSIAN98) on a cluster of four CPUs (Pentium III, 500 MHz) operating with RedHat Linux6.0. The Rev.A.11.3 version[8] was used on three separate computers having CPUs of Pentium 4 (2.4 or 2.8 GHz) operating with RedHat Linux 7.2 or 8.0.

The calculated wavenumbers are multiplied by a single scale factor of 0.9735, which was determined to obtain the best fit between the calculated wavenumbers and the observed wavenumbers of the C_4, C_6, C_8, and C_{10} species.[9,10,11,12]

Results and Discussion

1. Optimized geometries of the C_n species. The optimized geometries of all the C_n species treated in the present study were found to have the planar all-*trans* form with C_{2h} symmetry. The calculated lengths of the C=C and C–C bonds are given in Figure 2. In this figure, the effect of π-electron conjugation is clearly indicated. Briefly, the length of the C=C bond in the middle of each molecule is the longest among the C=C bonds, and the C–C bond in the middle is the shortest among the C–C bonds. Even the length of the terminal C=C bond is longer than that of the C=C bond of ethylene (1.3288 Å), and the length of the C–C bond next to the terminal C=C bond is significantly shorter than that of the C–C bond of ethane (1.5304 Å).

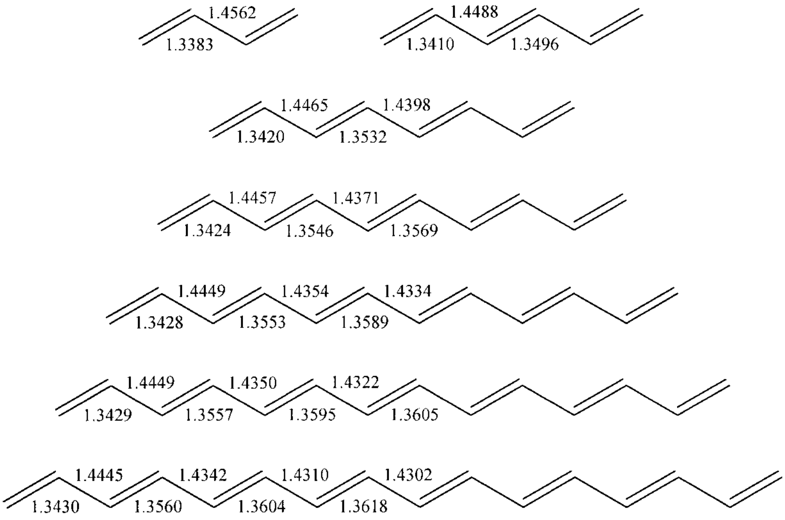

Figure 2. Calculated lengths of the C=C and C–C bonds of the C_4 to C_{16} species.

2. Effect of distortion around the central C=C double bond on the Raman activity of the Wag. First, the effect of distortion around the central C=C bond on the Raman intensities of the Wag is examined for the C_6, C_{10}, and C_{14} species, which have a C=C bond in the center of the molecule. The results of calculations are shown in Figure 3, where the calculated Raman activities of the Wag are plotted against $\Delta\theta$. In this figure, the calculated Raman activities of the Wag are null at $\Delta\theta=0°$ (planar *trans* structure) for all the three molecules, as expected. The following two points are noted.

(1) In similarity with the in-phase CH out-of-plane wag of the ethylenic CH=CH group of *trans*-stilbene,[2] the Wag of the C_n species acquires the Raman activity when the molecule is distorted from the planar all-*trans* form, and the Raman activity increases with increasing $\Delta\theta$.

(2) The number of conjugated C=C bonds (i.e., the length of π-electron conjugation) seems to have a great effect on the enhancement of the Raman activity with molecular distortion. At $\Delta\theta=20°$, the calculated Raman activity of the Wag of the C_{14} species is 917.2 $Å^4amu^{-1}$, whereas that of the C_6 species is only 48.0 $Å^4amu^{-1}$ and that of the C_{10} species 252.9 $Å^4amu^{-1}$. This means that the activity enhancement is not proportional to the chain length. The differences in the degree of activity enhancement cannot be explained by the local structural

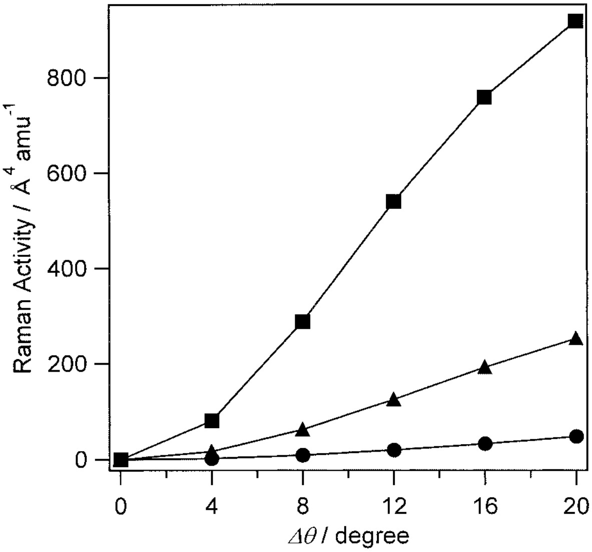

Figure 3. Raman activities of the in-phase CH out-of-plane wag calculated for model structures of the C_6, C_{10}, and C_{14} species with distortion around the central C=C bond. ●=C_6, ▲=C_{10}, ■=C_{14}.

differences either, since the calculated lengths of the central C=C bonds of the C_6, C_{10}, and C_{14} species are 1.3496, 1.3569, and 1.3605 Å, respectively; the difference in bond lengths between the C_{14} and C_{10} species is 0.0036 Å, whereas that between the C_{10} and C_6 species is 0.0073 Å. All these results seem to indicate that the activity enhancement depends nonlinearly on the electronic structure of the entire conjugated chain.

3. Effect of distortion around the central C–C single bond on the Raman activity of the Wag. Next, the effect of distortion around the central C–C bond on the Raman intensities of the Wag is examined for the C_4, C_8, C_{12}, and C_{16} species, which have a C–C bond in the center of the molecule. The results of calculations are shown in Figure 4, where the calculated Raman activity of the Wag is plotted against $\Delta\tau$. The results in Figure 4 show a general trend similar to those in Figure 3, indicating that the distortion around the central CC bond, whether it is a double bond or a single bond, causes the enhancement of the Raman activity of the Wag to a similar degree. In the case of the C_{16} species, an imaginary frequency is obtained for

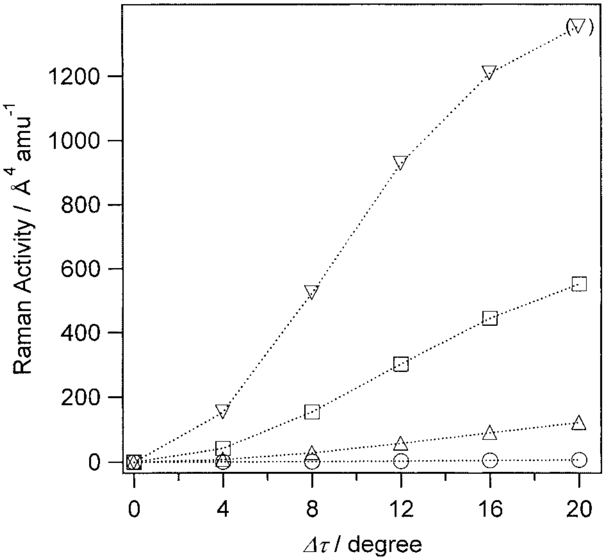

Figure 4. Raman activities of the in-phase CH out-of-plane wag calculated for model structures of the C_4, C_8, C_{12}, and C_{16} species with distortion around the central C–C bond. ○=C_4, △=C_8, □=C_{12}, ▽=C_{16}.

$\Delta\tau$=20°. This means that this model structure is definitely unstable. Accordingly, the calculated Raman activity is given in parentheses in Figure 4.

4. Effect of distortion around a C=C or a C–C bond at different positions in the C_{14} species on the Raman activity of the Wag. For the C_{14} species, the effect of distortion around a C=C bond or a C–C bond at different positions in the molecule on the enhancement of the Raman activity of the Wag is examined. Since there are six axes of internal rotation, i.e., three C=C and three C–C bonds, in this molecule, the internal rotations around the C=C bonds are denoted as $\Delta\theta_i$ (i=1, 3, and 5) and those around the C–C bonds as $\Delta\tau_j$, (j=2, 4, and 6), as depicted in Figure 5. The results of calculations are also shown in Figure 5 in the same way as in Figures 3 and 4.

It is clearly shown in Figure 5 that the enhancement of the Raman activity of the Wag is maximal for the distortion around the central C=C bond ($\Delta\theta_1$), and it decreases as the relevant bond is shifted from the center towards the terminal. The enhancement of the Raman activity is minimal for $\Delta\tau_6$, and it seems to level off at $\Delta\tau_6$=20°. These results confirm that π-electron conjugation is most important for the enhancement of the Raman activity of the Wag. The effect of π-electron conjugation is largest in the center of the molecule and it gradually diminishes on going from the center to the terminal, as indicated in the bond lengths given in Figure 2; the $C_7{=}C_8$ bond is the longest and the $C_1{=}C_2$ bond is the shortest among the C=C bonds, and the C_6–C_7 bond is the shortest and the C_2–C_3 bond is the longest among the C–C bonds.

5. The Raman activities of the Wag calculated for two model structures of the C_{14} species uniformly distorted over the entire molecule. The Raman activities of the Wag described

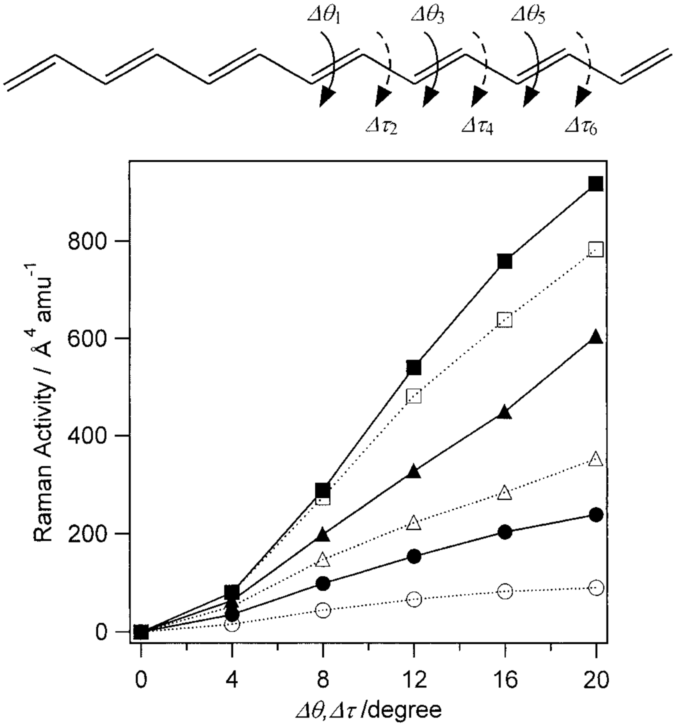

Figure 5. Raman activities of the in-phase CH out-of-plane wag calculated for model structures of the C_{14} species with distortion around a C=C bond or a C–C bond at different positions. ■=$\Delta\theta_1$, □=$\Delta\tau_2$, ▲=$\Delta\theta_3$, △=$\Delta\tau_4$, ●=$\Delta\theta_5$, ○=$\Delta\tau_6$.

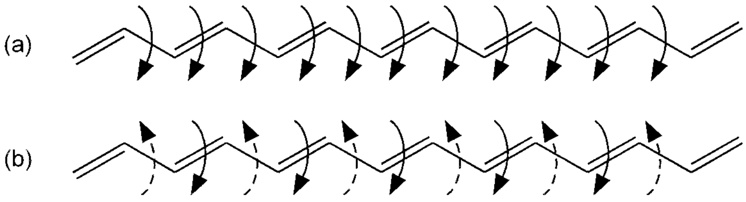

Figure 6. Two uniformly distorted model structures. (a)=helical model, (b)=alternately distorted model.

above for the model structures distorted around particular bonds are actually much smaller than the calculated Raman activities of the in-phase C=C stretch and the in-phase C–C stretch of the same molecule. For example, the calculated Raman activities of the in-phase C=C stretch and the in-phase C–C stretch of the C_{14} species with $\Delta\theta_1$=20° are, respectively, 170268.3 and 56214.5 $Å^4amu^{-1}$, whereas, as already mentioned, the calculated Raman activity of the Wag is only 917.2 $Å^4amu^{-1}$, a value smaller than those of the in-phase C=C stretch and the in-phase C–C stretch by two orders of magnitude. For smaller values of $\Delta\theta$ and $\Delta\tau$, differences between the Raman activities of the Wag and those of the in-phase C=C stretch and the in-phase C–C stretch are larger. Under such circumstances, it would be difficult to observe the Raman band arising from the Wag.

In order for the Raman activity of the Wag of a polyene chain including *trans*-PA to have a reasonably large value, the possibility of a slightly but uniformly distorted chain should be examined. The effect of distortion may be additive for such a chain, leading to a observable Raman activity. For this purpose, two kinds of model structures are considered; one is a helical structure with $\Delta\theta_i$ =2.4° and $\Delta\tau_j$ =4.4° and the other is an alternately distorted structure with $\Delta\theta_i$=2.4° and $\Delta\tau_j = -4.4°$. These model structures are schematically depicted in Figure 6. If $\Delta\theta_i$ or $\Delta\tau_j$ takes the above value, the total energy increases by about 0.1 kcal mol^{-1} per bond from the most stable planar structure.

The Raman spectra calculated for these two model structures and the planar structure of the C_{14} species are compared with the observed Raman spectrum of *trans*-PA in Figure 7. The observed Raman spectrum of *trans*-PA in this figure is the one arranged from a spectrum published in Ref. 13. This spectrum is best suited for comparison with the results of density functional theory calculations, because it was observed under an off-resonant condition with

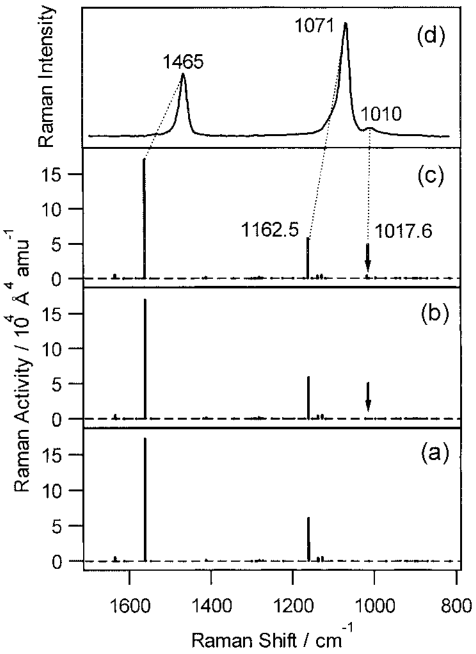

Figure 7. Raman spectra calculated for model structures of the C_{14} species, and the observed Raman spectrum of *trans*-polyacetylene. (a)=planar structure, (b)=alternately distorted structure, (c)=helical structure, (d)=observed Raman spectrum of *trans*-polyacetylene.

1064-nm excitation. The calculated wavenumber (scaled) and Raman activity of the Wag are 1017.6 $\mathrm{cm^{-1}}$ and 4178.6 $\mathrm{Å^4amu^{-1}}$ for the helical structure, and 1021.5 $\mathrm{cm^{-1}}$ and 521.7 $\mathrm{Å^4amu^{-1}}$ for the alternately distorted structure. It is noted that the Raman activity is much larger for the helical structure, although the absolute values of $\Delta\theta_i$ and $\Delta\tau_j$ are equal in the two model structures. Apparently, the cancellation of the polarizability derivatives with respect to the Wag occurs between $\Delta\theta_i$ and $\Delta\tau_j$ for the alternately distorted structure. The calculated wavenumbers of the in-phase C=C stretch (1561.9 $\mathrm{cm^{-1}}$) and the in-phase C–C stretch (1162.5 $\mathrm{cm^{-1}}$) for the helical structure are considerably higher than the corresponding Raman bands observed for *trans*-PA (the correspondence between the observed and calculated bands being indicated with dotted lines in Figure 7). This is attributable to the fact that *trans*-PA contains conjugated segments much longer than the C_{14} species. The relative magnitudes of the Raman activities calculated for the in-phase C=C stretch and the in-phase C–C stretch (170604.7 and 57674.5 Å^{4}amu^{-1}, respectively, for the helical structure) of the C_{14} species are opposite to the relative intensities of the Raman bands at 1465 and 1071 cm^{-1} of *trans*-PA. Since various factors are to be considered to explain this discrepancy, it is not appropriate to discuss this issue in detail in this paper. It should be noted, however, that the relative Raman activities of the line due to the Wag at 1017.6 cm^{-1} and that due to the in-phase C–C stretch at 1162.5 cm^{-1} of the helical structure are close to the relative intensities of the 1010 cm^{-1} band and the 1071 cm^{-1} band of *trans*-PA.

6. Raman spectra calculated for the C_n species in the helical structure. As described above, the helical structure seems to be important in that the Raman spectrum calculated for the C_{14} species in this structure has some similarity with the Raman spectrum observed for *trans*-PA. Then, the Raman spectra of all the C_4 to C_{16} species in the helical structure (i.e., having the same set of $\Delta\theta_i$ and $\Delta\tau_j$ as used for the helical structure of the C_{14} species) are calculated. The results are shown in Figure 8 in the 1220 – 950 cm^{-1} region, together with the observed Raman spectrum of *trans*-PA. The following points are noted in the spectra in Figure 8.

(1) The intense line due to the in-phase C–C stretch shifts to lower wavenumbers as the chain length becomes longer; the calculated wavenumbers (scaled) are 1193.7 cm^{-1} for the C_4 species and 1157.6 cm^{-1} for the C_{16} species, decreasing by 6.0 cm^{-1} on an average as the carbon number increases by 2. If this decreasing rate in wavenumber continues with increasing carbon number, the observed 1071 cm^{-1} band of *trans*-PA would correspond to a chain of about 44 carbons. However, since the decreasing rate is expected to fall with increasing carbon number, it is more probable that the observed 1071 cm^{-1} band corresponds to longer chains.

(2) The line due to the Wag (indicated with an arrow in each spectrum in Figure 8) also shifts to lower wavenumbers as the chain length becomes longer. However, its decreasing rate in wavenumber is much smaller than that of the in-phase C–C stretch; the decreasing rate for the Wag is about 1.1 cm^{-1} per two carbons on an average but smaller for longer chains. Accordingly, it may be considered that the wavenumber position of the Wag depends only slightly on the chain length.

(3) The calculated Raman activity of the Wag increases with increasing carbon number in its absolute value as shown in Figure 9. On the other hand, the calculated Raman activity of the in-phase C–C stretch (and the in-phase C=C stretch as well, although not shown in Figure 9) also increases rapidly with increasing carbon number. However, the degree of increase in the Raman activity of the Wag exceeds that of the in-phase C–C stretch. This is made clear by

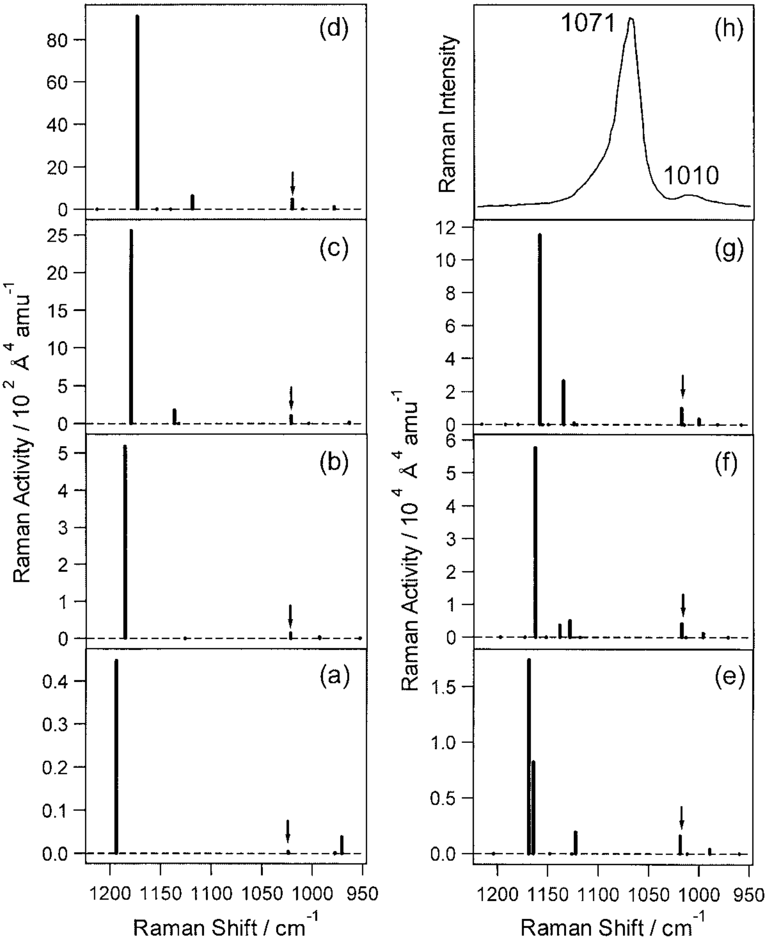

Figure 8. Raman spectra calculated for the C_4 to C_{16} species in the helical structure, and the observed Raman spectrum of polyacetylene. (a)=C_4, (b)=C_6, (c)=C_8, (d)=C_{10}, (e)=C_{12}, (f)=C_{14}, (g)=C_{16}, (h)=observed Raman spectrum of *trans*-polyacetylene.

taking the ratio between the Raman activity of the Wag and that of the in-phase C–C stretch. This ratio for each C_n species is also given in Figure 9. In the calculation of the ratio for the C_{12} species, the following measure was taken. The calculated Raman spectrum of the C_{12} species in Figure 8(e) has a medium-activity line at 1164.1 cm^{-1} in addition to an intense line at 1168.7 cm^{-1}. This is due to a mixing between the in-phase C–C stretch and a CH in-plane bend which happens to be very close in wavenumber to the former. Since the Raman activity of the 1164.1 cm^{-1} line seems to be borrowed from the in-phase C–C stretch, the sum of the Raman activities of the two lines should be attributed to the in-phase C–C stretch of the C_{12} species.

The Raman activity ratio given in Figure 9 increases almost linearly with the carbon number. A similar trend is found to exist for the ratio between the Raman activity of the Wag and that of the in-phase C=C stretch in the 1660–1540 cm^{-1} region (data not shown in Figure 9). This means that the Raman activity of the Wag of the helical structure increases *faster* with

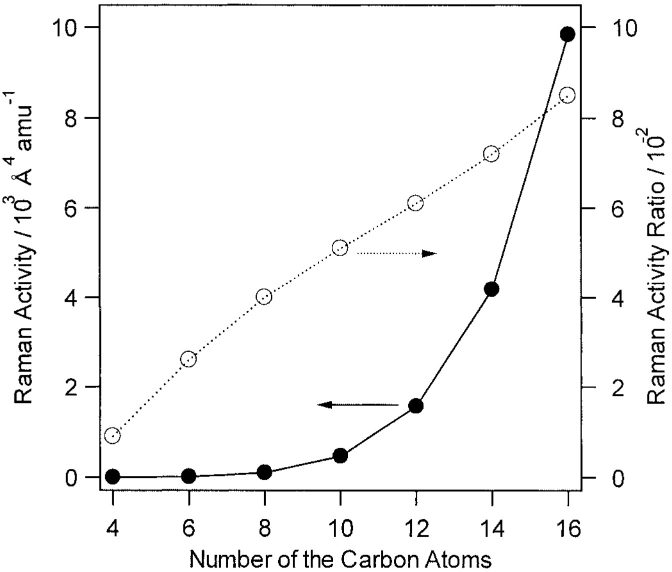

Figure 9. Raman activities of the in–phase CH out–of plane wag calculated for the C_4 to C_{16} species, and the Raman activity ratio between the in-phase CH out-of-plane wag and the in-phase C–C stretch for the C_4 to C_{16} species.

increasing carbon number than the Raman activities of the in-phase C=C stretch and the in-phase C–C stretch, which are considered to be the vibrational modes most closely associated with the electronic structure of the π-conjugated chain.

Thus, it should be emphasized that, for the helical structure, the Raman activity of the Wag increases extraordinarily with increasing chain length, although the wavenumber position of the Wag depends only slightly on the chain length. In other words, the Raman activity of the Wag and its wavenumber position seem to behave almost independently. This is an important result obtained in the present study. Although this result appears somewhat self-contradictory, a simple explanation appealing to chemical intuition is not available for it at present.

7. The origin of the Raman band at 1010 cm^{-1} of *trans*-PA. In a paper published in 1984,[1] Takeuchi et al. discussed this issue in some detail. A few possibilities which had been proposed until then were considered less probable in view of the experimental results obtained for copolymers of normal and deuterated acetylenes. The activation of the Wag in the Raman spectrum due to molecular distortion remained as the most probable possibility. The results of the present study are consistent with the conclusion of Takeuchi et al., if *trans*-PA consists of slightly helical chains. Deuterated *trans*-PA has a weak Raman band at 746 cm^{-1}, which is assignable to the in-phase CD out-plane wag.[1] In the calculated Raman spectra of the deuterated C_{14} species, the corresponding line is found at 744.0 cm^{-1} with the Raman activity of 1478.3 Å^{4}amu^{-1}, in support of the above assignment of the 746 cm^{-1} band of *trans*-PA.

From the calculated results shown in Figures 8 and 9, it seems that even a helical structure with $\Delta\theta_i$ and $\Delta\tau_j$ smaller than those used in the present calculations may account for the observed Raman spectrum of trans-PA, if such helical structure is long enough. It is not unlikely that *trans*-PA consists of such helical chains that are very close to the planar structure.

Conclusion

The in-phase CH out-of-plane wag of a polyene chain, which should be Raman-inactive for the planar all-*trans* structure, acquires a Raman activity when the chain is distorted around the

CC double and/or single bond. The Raman activity is particularly enhanced for a uniformly helical chain. The results of calculations performed in the present study support the assignment of the Raman band of *trans*-polyacetylene at about 1010 cm^{-1} to the in-phase CH out-of-plane wag, if *trans*-polyacetylene consists of slightly helical chains.

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