

NORMAL VIBRATIONAL ANALYSIS OF CIS-POLYACETYLENE

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ABSTRACT

The normal vibrational calculation was carried out on *cis*-polyacetylene(PA) and its model compound, *cis, trans*-2, 4-hexadiene. Based on the observed IR and Raman frequencies, force constants relevant to the *cis*-structure were refined. Finally a force field common for *cis*-PA, *trans*-PA and three model molecules was obtained. The observed spectra of *cis*-PA were theoretically assigned and the similarities and differences between the *cis*- and *trans*-conjugate systems were discussed on the basis of normal coordinate calculation.

INTRODUCTION

The molecular chain of polyacetylene(PA) is a long conjugate system with alternating single and double carbon-carbon bonds and it has some geometric isomers such as *cis*- and *trans*-PA, according to the configuration of the double bonds. In present work, the normal vibrational calculation was carried out on *cis*-PA and its model compound, *cis, trans*-2, 4-hexadiene(CTHD). The normal mode analyses of *trans*-PA^[1] and its model molecules, *trans, trans*-2, 4-hexadiene(TTHD)^[2], *trans, trans*-1, 4-diphenyl-butadiene(TTDP)^[3] were published in previous papers. The same procedure was taken for *cis*-PA and CTHD. Based on the observed IR and Raman frequencies, force constants relevant to the *cis*-structure were refined. Finally a force field common for *cis*-PA, *trans*-PA and three model molecules was obtained. The observed spectra of *cis*-PA were theoretically assigned and the similarities and differences between the *cis*- and *trans*-conjugate systems were discussed on the basis of normal coordinate calculation.

NORMAL MODE ANALYSIS

The principle and computer programs employed in the present calculation was the same as in the previous papers^[1,2]. Similar structural parameters were taken for *cis*-PA and CTHD: bond length, C = C 1.34Å, C-C 1.48Å, C-CH₃ 1.50Å; bond angle, around unsaturated carbon 120°, around methyl carbon, 109°29'.

1. *Cis, trans*-2, 4-hexadiene (CTHD)^[2]

CTHD is a planar conjugate molecule of 16 atoms. The two carbon-carbon double bonds are in *cis*- and *trans*-configurations respectively. The methyl groups at the molecular ends are so oriented in space that the molecule has the lowest potential energy and all the distances between hydrogen atoms are greater than the van der Waals distance. Thus the molecular model has C_s symmetry. Its 3N-6 = 42 normal vibrational modes belong to A' and A'' symmetry species, respectively.

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2. Symmetry of *cis*-polyacetylene(*cis*-PA)

The molecular chain is depicted in Fig.1. All atoms are in the same plane and all carbon-carbon double bonds exist in *cis*-configuration. This structure was shown to be even more stable than the benzene-ring-like long conjugate system in which there is no single and double bond alternation^[4].

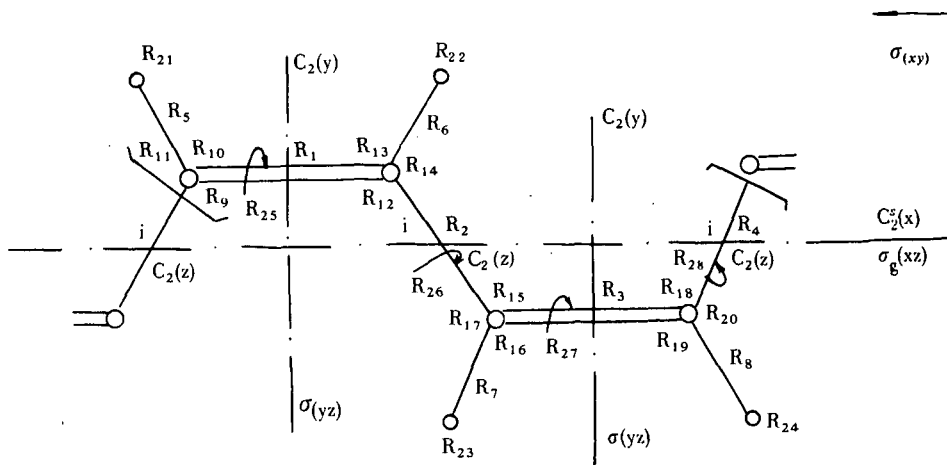


Fig. 1 Symmetry elements and internal coordinates for *cis*-PA

C_2 , i , σ = symmetry elements

$R_1 \cdots R_{28}$ = internal coordinates

It is shown in Fig. 1 that there are eight symmetry elements: 3 two-fold rotation axes C_2^x , C_2^y , C_2^z ; 3 symmetry planes $\sigma_{(xy)}$, $\sigma_{g(xz)}$, $\sigma_{(yz)}$; a symmetry center i and identity E . Therefore its line group is isomorphic to point group D_{2h} . Its repeat unit consists of four carbon and four hydrogen atoms, and thus it should have $3N-4 = 20$ normal modes. Their symmetry distribution is

$$\Gamma_{cis-PA} = 4A_g^R + 4B_{1g}^R + 2B_{2g}^R + B_{3g}^R + 2A_u^{IR} + B_{1u}^{IR} + 3B_{1u}^{IR} + 3B_{3u}^{IR}$$

24 possible normalized symmetry coordinates (Table 1) were obtained, by means of the character table for D_{2h} point group. These normalized symmetry coordinates had the similar definition with those of model molecules and 4 of them were redundancies.

3. The IR and Raman spectra of *cis*-PA and their assignment

All the observed frequencies used in this computation were from literature.

The IR spectra of *cis*-PA were published by Shirakawa^[5] in 1971. Recently, the results of photoacoustic infrared spectroscopy (PAS) of *cis*-PA^[6] and polarized infrared spectra of highly oriented *cis*-PA^[7] confirmed most of Shirakawa's assignment. A correction was made to symmetry species of two IR-active C—H stretching vibrations. The studies on Raman spectra of *cis*-PA were done by Kuzmany^[8] and Lefrant^[9,10] respectively, and the empirical assignment was given by the former.

The assignment employed in the present work is given in Table 2. Certain corrections were made by us for several peaks and were discussed, in three classes, as follows:

(1) It is known that there must be the bands of *trans*-configuration in a Raman spectrum of *cis*-PA, because of the *trans*-segments formed during polymerization, as well as the isomerization

Table 1 Definition of normalized symmetrical coordinates of *cis*-PA

Symmetry	Symbol	Definition	Explanation
A _g	$\nu_{(C=C)}$	$S_1 = \frac{1}{\sqrt{2}}(R_1 + R_3)$	C = C stretchings
	$\nu_{(C-C)}$	$S_2 = \frac{1}{\sqrt{2}}(R_2 + R_4)$	C — C stretchings
	$\nu_{(C-H)}$	$S_3 = \frac{1}{2}(R_5 + R_6 + R_7 + R_8)$	C—H stretchings
	$\delta_{(C-H)}$	$S_4 = \frac{1}{\sqrt{8}}(R_{10} - R_{11} + R_{13} - R_{14} + R_{16} - R_{17} + R_{19} - R_{20})$	$\begin{array}{c} \\ \text{C—H in-plane bendings} \end{array}$
	$\delta_{(C=CC)}$	$S_5 = \frac{1}{\sqrt{12}}(2R_9 - R_{10} - R_{11} + 2R_{12} + R_{17} - R_{19} + R_{20} + 2R_{18} - R_{19} - R_{20})$	C = CC deformations
B _{1g}	$\nu_{(C-C)}$	$S_6 = \frac{1}{\sqrt{2}}(R_2 - R_4)$	C — C stretchings
	$\nu_{(C-H)}$	$S_7 = \frac{1}{2}(R_5 - R_6 - R_7 + R_8)$	C—H stretchings
	$\delta_{(C-H)}$	$S_8 = \frac{1}{\sqrt{8}}(R_{10} - R_{11} - R_{13} + R_{14} - R_{16} + R_{17} + R_{19} - R_{20})$	$\begin{array}{c} \\ \text{C—H in-plane bendings} \end{array}$
	$\delta_{(C=CC)}$	$S_9 = \frac{1}{\sqrt{12}}(2R_9 - R_{10} - R_{11} - 2R_{12} + R_{13} + R_{14} - 2R_{15} + R_{16} + R_{17} + 2R_{18} - R_{19} - R_{20})$	C = CC deformations
B _{2g}	$\omega_{(C-H)}$	$S_{10} = \frac{1}{2}(R_{21} + R_{22} + R_{23} + R_{24})$	C—H out-of-plane bendings
	$\tau_{(C=C)}$	$S_{11} = \frac{1}{\sqrt{2}}(R_{25} - R_{27})$	C = C torsions
B _{3g}	$\omega_{(C-H)}$	$S_{12} = \frac{1}{2}(R_{21} - R_{22} - R_{23} + R_{24})$	C—H out-of-plane bendings
A _u	$\omega_{(C-H)}$	$S_{13} = \frac{1}{2}(R_{21} + R_{22} - R_{23} - R_{24})$	C—H out-of-plane bendings
	$\tau_{(C=C)}$	$S_{14} = \frac{1}{\sqrt{2}}(R_{25} + R_{27})$	C = C torsions

Table 1 (Continued)

Symmetry Symbol	Definition	Explanation
$\tau_{(C-C)}$	$S_{15} = \frac{1}{\sqrt{2}}(R_{26} + R_{28})$	C - C torsions
B_{1u}	$\omega_{(C-H)}$	$S_{16} = \frac{1}{2}(R_{21} - R_{22} + R_{23} - R_{24})$ C-H out-of-plane bendings
	$\tau_{(C-C)}$	$S_{17} = \frac{1}{\sqrt{2}}(R_{26} - R_{28})$ C - C torsions
B_{2u}	$\nu_{(C=C)}$	$S_{18} = \frac{1}{\sqrt{2}}(R_1 - R_3)$ C = C stretchings
	$\nu_{(C-H)}$	$S_{19} = \frac{1}{2}(R_5 + R_6 - R_7 - R_8)$ C-H stretchings
	$\delta_{(C-H)}$	$S_{20} = \frac{1}{\sqrt{8}}(R_{10} - R_{11} + R_{13} - R_{14} - R_{16} + R_{17} - R_{19} + R_{20})$ = C-H in-plane bendings
	$\delta_{(C=CC)}$	$S_{21} = \frac{1}{\sqrt{12}}(2R_9 - R_{10} - R_{11} + 2R_{12} - R_{13} - R_{14} - 2R_{15} + R_{16} + R_{17} - 2R_{18} + R_{19} + R_{20})$ C = CC deformations
B_{3u}	$\nu_{(C-H)}$	$S_{22} = \frac{1}{2}(R_5 - R_6 + R_7 - R_8)$ C-H stretchings
	$\delta_{(C-H)}$	$S_{23} = \frac{1}{\sqrt{8}}(R_{10} - R_{11} - R_{13} + R_{14} + R_{16} - R_{17} - R_{19} + R_{20})$ = C-H in-plane bendings
	$\delta_{(C=CC)}$	$S_{24} = \frac{1}{\sqrt{12}}(2R_9 - R_{10} - R_{11} - 2R_{12} + R_{13} + R_{14} + 2R_{15} - R_{16} - R_{17} - 2R_{18} + R_{19} + R_{20})$ C = CC deformations

by Laser resource while measuring. The peaks at 1292 cm^{-1} , 1130 cm^{-1} and 1008 cm^{-1} were the typical Raman frequencies of *trans*-PA for C—C stretching, C—H in-plane bending and C—H out-of-plane bending respectively^[1,8,9], and therefore were not used in present assignment.

(2) The assignment from literature^[8] and some mismatches between the bands of *cis*-PA and those of deuterated one were corrected here and, on the basis of their ratios of isotopic shift, new assignment was given as C—H in-plane bending, instead of C—C stretching, for the peak at 1252 cm^{-1} ; C—H out-of-plane bending, rather C—C stretching, for that at 915 cm^{-1} ; and two C—C stretchings for those at 1070 and 985 cm^{-1} , respectively.

(3) The peak at 820 cm^{-1} was not assigned by Kuzmany^[8] as it was too weak in his spectrum. A strong band was observed by Lefrant^[9,10] at 820 cm^{-1} and probably it was the frequency of C—H out-of-plane bending for *cis*-PA.

Table 2 Observed frequencies and preliminary assignment for *cis*-PA*

	Symmetry	$\nu(\text{CH})_x$	$\nu(\text{CD})_x$	$\nu(\text{CH})_x/\nu(\text{CD})_x$	Preliminary assignment
Raman	A _g	3090m	2315w	1.34	C—H stretching
		1544vs	1460vs	1.05	C=C stretching
		1252vs	987s	1.27	=C—H in-plane bending + C—C stretching
		985m	965w	1.02	C—C stretching
	B _{1g}	3030m	2260m	1.34	C—H stretching
		1170m	930w	1.26	=C—H in-plane bending + C—C stretching
		1070sh	987s	1.08	C—C stretching
		445w	406vw	1.09	C=CC deformation
	B _{2g}	820vw	670vw	1.22	C—H out-of-plane bending
		295vw	265vw	1.11	C=C torsion
	B _{3g}	915s	767w	1.20	C—H out-of-plane bending
IR	A _u				C—H out-of-plane bending
					C=C torsion
	B _{1u}	740vs	548vs	1.35	C—H out-of-plane bending
	B _{2u}	3057vw	2275vw	1.34	C—H stretching
					C=C stretching
	B _{3u}	1249w	947w	1.32	=C—H in-plane bending
		3044w	2255m	1.35	C—H stretching
		1329s	1050s	1.27	=C—H in-plane bending
		446vs	402vs	1.11	C=CC deformation + =C—H in-plane bending

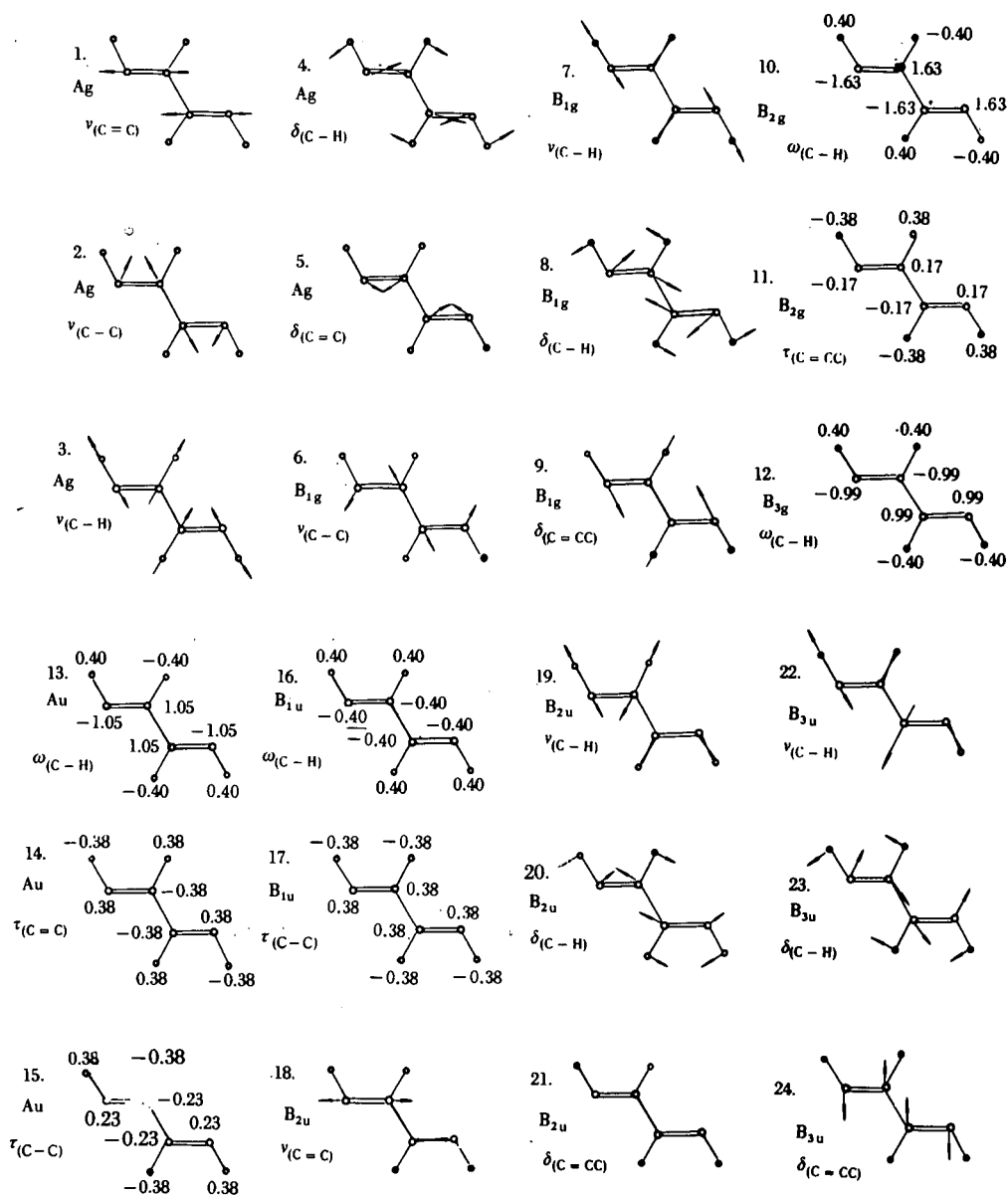
* Band Intensity: vs = very strong; s = strong; m = medium; w = weak;
vw = very weak; sh = shoulder.

COMPUTATION RESULTS AND DISCUSSION

The force field common for *trans*-PA and TTHD and TTDP^[1] was transferred to the present computation. All the observed spectral frequencies of *cis*-PA and model molecule CTHD were considered in the refinement. Only the force constants relevant to *cis*-structure were refined and those related to *trans*-structure were kept unchanged. The computation results were listed in Table 3.

(1) Only 20 normal vibrational modes with non-zero frequencies were obtained for *cis*-PA, though 24 possible normalized symmetry coordinates were employed, which is consistent with the analysis of its molecular symmetry. The relative vibrational amplitudes of various modes of *cis*-PA (Fig. 2) gave a clear explanation to the 4 zero-frequency modes. They are, respectively, two C=CC deformations (S_5 and $S_{2,1}$) and two C—C torsions (S_{15} and S_{17}).

(2) The potential energy distribution (PED) data obtained from the calculation showed that our assignment to IR and Raman spectra of *cis*-PA was reasonable. Most of vibrational modes for *cis*-PA had the contributions of several empirical modes, which is quite similar to *trans*-PA. Not only did this show us the strong interaction within its conjugate system, but also presented some rational interpretations to the isotopic shift ratios of several observed frequencies for *cis*-PA. For instance, the Raman bands at 1252 and 1170 cm^{-1} (Table 2), which had the isotopic shift ratios of 1.27 and 1.26 respectively, were assigned empirically as C—H in-plane bendings with considerable

Fig. 2 Vibrational Modes for *Cis*-PA

addition of C—C stretchings, because the isotopic shift ratio of a typical C—H bond vibration generally is about 1.35. And the corresponding calculated frequencies of 1259 and 1166 cm^{-1} (Table 3) gave out the PED data of $\delta_{(\text{C-H})}(56) + \nu_{(\text{C-C})}(22)$ and $\delta_{(\text{C-H})}(74) + \nu_{(\text{C-C})}(20)$ respectively, which were in good agreement with our preliminary assignment.

(3) Computed with the force constants obtained, the *cis*-PA's average absolute and relative deviations of calculated from observed frequencies were 15 cm^{-1} and 1.3%, respectively. This indicates that both the vibrations of macromolecules and their model molecules can be described by this set of force constants.

Table 3 Calculated and observed frequencies of *cis*-

Symmetric Species	Cals. (cm ⁻¹)	Obs. (cm ⁻¹) Raman IR	PED * (%)
Ag	3110	3090m	$\nu_{(C-H)}(96)$.
	1555	1544vs	$\nu_{(C=C)}(51)$, $\delta_{(C-H)}(25)$, $\nu_{(C-H)}(12)$
	1259	1252vs	$\delta_{(C-H)}(56)$, $\nu_{(C-C)}(22)$, $\nu_{(C=C)}(21)$
	967	985m	$\nu_{(C-C)}(62)$, $\delta_{(C-H)}(19)$.
B _{1g}	3042	3030m	$\nu_{(C-H)}(98)$.
	1166	1170m	$\delta_{(C-H)}(74)$, $\nu_{(C-C)}(20)$.
	1032	1070sh	$\nu_{(C-C)}(91)$.
	457	445w	$\delta_{(C=C)}(95)$.
B _{2g}	824	820vw	$\omega_{(C-H)}(100)$.
	296	295vw	$\tau_{(C-C)}(93)$.
B _{3g}	921	915s	$\omega_{(C-H)}(100)$.
Au	1047		$\omega_{(C-H)}(50)$, $\tau_{(C=C)}(27)$, $\tau_{(C-C)}(23)$
	260		$\tau_{(C=C)}(44)$, $\tau_{(C-C)}(55)$.
B _{1u}	735	740vs	$\omega_{(C-H)}(89)$, $\tau_{(C-C)}(11)$.
B _{2u}	3017	3057vw	$\nu_{(C-H)}(97)$
	1466		$\nu_{(C=C)}(68)$, $\nu_{(C-H)}(20)$, $\delta_{(C-H)}(11)$.
	1237	1249w	$\delta_{(C-H)}(83)$, $\nu_{(C=C)}(13)$.
B _{3u}	3056	3044w	$\nu_{(C-H)}(99)$.
	1345	1329s	$\delta_{(C-H)}(89)$, $\nu_{(C-H)}(11)$.
	440	446vs	$\delta_{(C=C)}(77)$, $\delta_{(C-H)}(17)$.

* Only the PED data more than 10% are included.

(4) The normal vibrational analysis of *trans*-PA^[1] showed that calculated C=C and C—C stretching frequencies extremely deviated from the observed values because of its long conjugate length. But this did not happen for *cis*-PA. It shows that the π -electron cloud in *cis*-PA has more localization and the conjugation in *cis*-PA is more alternate than in *trans*-PA. This is likely responsible for the large disparities in molecular structure, vibrational characteristics and conductivity between *cis*-PA and *trans*-PA.

(5) *Cis*-PA should have 9 IR-active vibrational modes as determined by its molecular symmetry, while only 6 bands were observed in the IR spectral experiments. The other 3 bands were predicted by the calculation to be C—H out-of-plane bending(Au), backbone's torsion(Au) and C=C stretching(B2u), and the calculated frequencies were 1047, 260 and 1466 cm⁻¹ respectively, and this would be verified by the future spectral experiments.

Up to now, a common refined force field suitable to all the five molecules, TTHD, TTDP, CTHD, *trans*- and *cis*-PA was obtained in several steps. It is noticed that we succeeded in employing a single set of force constants for both *trans*- and *cis*-PA, as well as for both small and macro-molecules. The normal vibrational analysis is expected to be applied to other polymer systems and their model compounds.

Keywords:

Polyacetylene; IR of Polyacetylene; Raman spectra of polyacetylene; Vibrational spectra of

polyacetylene; Vibrational analysis of polyacetylene.

REFERENCES

- [1] Wang, J.; Jing, X. and Feng, Z., *Chinese J. Polym. Sci.*, **1981**, 5(4), 316.
- [2] Wang, J.; Jing, X. and Feng, Z., *Spectrosc. & Spectral Anal.*, **1985**, 5(6), 46.
- [3] Wang, J.; Jing, X. and Feng, Z., The 4th Conference on Molecular Spectrosc. Preprints, Suzhou, China, **1986**, 135.
- [4] Jing, X.; Wang, F. and Cao, Y., *Exploration of Nature*, **1985**, 4(4), 17.
- [5] Shirakawa, H. and Ikeda, S., *Polym. J.*, **1971**, 2, 231.
- [6] Will, F. G. and McDonald, R. S., *J. Chem. Phys.*, **1983**, 78(10), 5847.
- [7] Piaggio, P.; Dellepiane, G.; Piseri, L.; Tubino, R. and Taliani, C., *Solid State Commun.*, **1984**, 50(10), 947.
- [8] Kuzmany, H., *Phys. Stat. Sol. (b)*, **1980**, 97, 521.
- [9] Lefrant, S.; Lichtmann, L. S.; Temkin, H.; Fitchen, D.B.; Miller, P.C.; Whitwell, G.E. and Burlitch, J.M., *Solid State Commun.*, **1979**, 29, 191.
- [10] Lefrant, S., *J. Physique, Colloq.*, **1983**, C3-247.