

NORMAL VIBRATIONAL ANALYSIS OF TRANS-POLYACETYLENE

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ABSTRACT

The results of normal vibrational analyses of *trans*, *trans*-2, 4-hexadiene and the backbone of *trans*, *trans*-1, 4-diphenyl-butadiene were used in the normal mode computation of *trans*-polyacetylene (PA). Only 8 non-zero calculated frequencies were obtained which obeys the rule of $3N-4$. The potential energy distribution (PED) data were in good agreement with the empirical assignment of Shirakawa et al. and Kuzmany, but most of the vibrational frequencies of *trans*-PA had contributions from several empirical modes, indicating the more complicity in *trans*-PA molecular vibration than in the model molecule case. The calculated C = C and C—C stretching frequencies of *trans*-PA were over 200cm^{-1} higher and lower than the observed ones, respectively, due to the longer effective conjugate length in the *trans*-PA. This was shown by the dependence of the PED-weighted average frequencies of C = C and C—C stretchings on the force constants $f(\text{C}=\text{C})^2$ and $f(\text{C}-\text{C})^2$.

INTRODUCTION

The molecular chain of *trans*-polyacetylene (*trans*-PA) is a planar conjugate system with alternating single and double carbon-carbon bonds (Fig. 1). Recently, the studies on its molecular structure were made by means of infrared (IR) and Raman, spectroscopy. But few were made on its normal vibrational analysis. The calculations which were made on *trans*-PA were only for its IR-active^[1] or Raman-active modes^[2,3], or its in-plane vibrational modes^[4,5].

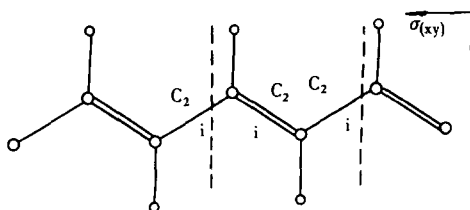


Fig. 1 Molecular structure and symmetry elements for *trans*-PA.
C₂, i, σ = symmetrical elements

β -Carotene was considered as its model molecule, but finally different force fields were employed in the calculation for β -carotene and *trans*-PA^[2].

In this paper, a normal vibrational analysis of *trans*-PA (Fig. 2) was made based on those of *trans*, *trans*-2, 4-hexadiene (TTHD) and the backbone of *trans*, *trans*-1, 4-diphenyl-butadiene (TTJD), in order to get a refined force field suitable to both *trans*-PA and its model molecules. A theoretical assignment to the vibrational spectra of *trans*-PA was expected.

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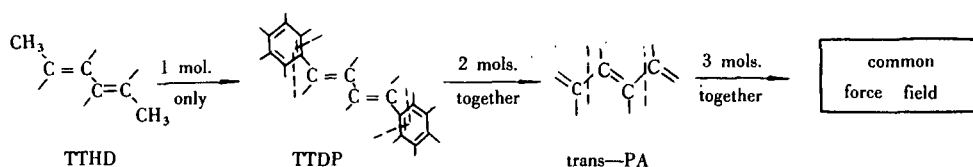


Fig. 2 Working way of the present paper

CALCULATING METHOD

The method of Wilson's *GF* matrix^[7] was used in the present work. The principle of this method can be described in the following determinant equation

$$|GF - E\lambda| = 0 \quad (1)$$

where *F* designates force constant matrix which is related to the potential energy of molecular vibration, *G* stands for the kinetic energy matrix associated with the atomic mass and molecular configuration and conformation, *E* is a unit matrix and λ is eigenvalue matrix of the equation,

$$\lambda_i = 4\pi^2 C^2 v_i^2 \quad (2)$$

Therefore the molecular vibrational frequencies v_i can be obtained from equation (1).

The computer program used in the present work was kindly provided by S. Krimm of the University of Michigan, U. S. A. and the computations of the polymer and its model molecules were conducted on an M-160H computer from Hitachi Co.. The structure parameters used in the computations were listed in Table 1.

Table 1 Structural parameters used in the calculation

	TTHD		TTJD		<i>trans</i> -PA	
Bond Length (Å)	C = C	1.34	C = C	1.34	C = C	1.34
	C—C	1.48	C—C	1.48	C—C	1.48
	C—CH ₃	1.50	C—C(Benz.)	1.39	C—H	1.08
	C—H	1.08	C—H	1.08		
Bond Angle (°)	C = C—C	120	C = C—C	120	C = C—C	120
	C = C—H	120	C = C—H	120	C = C—H	120
	C—C—H	120	C—C—H	120	C—C—H	120
	C—C—H(Methyl)	109°28'	C—C—C(Benz.)	120		
	H—C—H(Methyl)	109°28'				

NORMAL ANALYSES OF MODEL MOLECULES

1. *Trans*, *trans*-2, 4-hexadiene (TTHD)^[8]

TTHD (Fig. 2) is a molecule of 16 atoms, with all carbon atoms in the same plane and two conjugate double bonds in *trans* configuration. The methyl groups are so oriented in space that one of the C—H bonds is in the molecular plane and exactly in the *cis* position to the adjacent C = C

bond. Therefore, TTHD belongs to C_{2h} symmetry. TTHD should have $3N-6 = 42$ normal vibrational modes and their symmetry distribution is

$$\Gamma_{\text{TTHD}} = 14A_g^R + 7B_g^R + 8A_u^{IR} + 13B_u^{IR}$$

40 observed frequencies were obtained from its IR and Raman spectra. The average absolute deviation of its calculated from observed frequencies is 14 cm^{-1} .

2. *Trans, trans*-1, 4-diphenyl-butadiene(TTDP) and its backbone (TTJD)^[9]

TTDP is a conjugate molecule with 30 atoms and 2 carbon-carbon double bonds in its backbone. Most of its observed frequencies are those of benzene rings, which have little to do with the conjugate backbone. Therefore, its backbone part was taken as the simplified model (TTJD) for the normal vibrational analysis of *trans*-PA. The observed frequencies of TTJD were obtained by comparing the IR and Raman spectra of TTDP with those of compounds which have benzene rings in their molecules.

TTJD is also of C_{2h} symmetry and the symmetrical distribution of its 24 normal vibrational modes is

$$\Gamma_{\text{TTJD}} = 9A_g^R + 3B_g^R + 4A_u^{IR} + 8B_u^{IR}$$

The refined force constants obtained from the calculation of TTHD were taken as the initial value, then refined further for both TTHD and TTJD. The average absolute deviation of TTHD and TTJD of calculated from observed frequencies is 16 cm^{-1} , showing that it is a satisfactory initial force field for the normal vibrational analysis of *trans*-PA.

NORMAL VIBRATIONAL ANALYSIS OF TRANS-PA

1. Symmetry of its molecular chain

The planar and alternating conjugate structure of *trans*-PA was verified by the experimental results of the Raman spectra^[10], X-ray diffraction^[11] and the calculation results of molecular orbit theory^[12-14]. This structure was thought to be even more stable than that of benzene ring-like conjugate structure which has the same carbon-carbon bond lengths^[15].

Only two carbon and two hydrogen atoms are included in the repeat unit of its planar alternating structure (Fig. 1). The line group of *trans*-PA is isomorphic to C_{2h} point group. As two rotations whose axes are perpendicular to the molecular chain become impossible, there should be $3N-4 = 8$ normal vibrational frequencies for *trans*-PA. The symmetry distribution of its 8 normal modes is

$$\Gamma_{\text{trans-PA}} = 4A_g^R + B_g^R + A_u^{IR} + 2B_u^{IR}$$

The definition of its internal coordinates was consistent with that for model molecules, as shown in Fig. 3 and Table 2. The interaction between repeat units was considered in the computation of polymer chain.

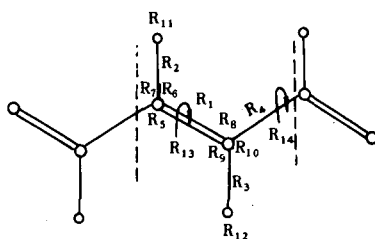


Fig. 3 Definition of internal coordinates for *Trans*-PA

Table 2 Explanation to internal coordinates of *Trans*-PA

Internal Coordinates	Explanation
R_1	C = C stretchings
R_2, R_3	C—H stretchings
R_4	C—C stretching
R_5, R_8	C = CC deformations
R_6, R_9	C = CH deformations
R_7, R_{10}	C—CH deformations
R_{11}, R_{12}	C—H out-of-plane bendinags
R_{13}	C = C torsion
R_{14}	C—C torsion

A set of 12 normalized symmetry coordinates of *trans*-PA were obtained from the internal coordinates by means of the character table for C_{2h} group as shown in Table 3. There were 4 redundances because there should be only 8 normal vibrational frequencies for *trans*-PA and this was confirmed by IR^[1,16] and Raman^[17] results.

Table 3 Definition of normalized symmetrical coordinates of *trans*-PA

Symmetry	Symbol	Definition	Explanation
Ag	$\nu(\text{C}=\text{C})$	$S_1 = R_1$	C = C stretching
	$\nu(\text{C}-\text{H})_s$	$S_2 = 1/\sqrt{2}(R_2 + R_3)$	C—H symmetrical stretchings
	$\nu(\text{C}-\text{C})$	$S_3 = R_4$	C—C stretching
	$\delta(\text{C}=\text{CC})_s$	$S_4 = 1/\sqrt{12}(2R_5 - R_6 - R_7 + 2R_8$	C = CC symmetrical deformations.
	$\delta(\text{C}-\text{H})_s$	$\frac{-R_9 - R_{10}}{2}(R_6 - R_7 + R_9 - R_{10})$	
Bg	$\omega(\text{C}-\text{H})_s$	$S_6 = 1/\sqrt{2}(R_{11} - R_{12})$	C—H symmetrical out-of-plane bendings
Au	$\omega(\text{C}-\text{H})_a$	$S_7 = 1/\sqrt{2}(R_{11} - R_{12})$	C—H asymmetrical out-of-plane bendings
	$\tau(\text{C}=\text{C})$	$S_8 = R_{13}$	C = C torsion
	$\tau(\text{C}-\text{C})$	$S_9 = R_{14}$	C—C torsion
Bu	$\nu(\text{C}-\text{H})_a$	$S_{10} = 1/\sqrt{2}(R_2 - R_3)$	C—H asymmetrical stretchings
	$\delta(\text{C}=\text{CC})_a$	$S_{11} = 1/\sqrt{12}(2R_5 - R_6 - R_7$	C = CC asymmetrical deformations
	$\delta(\text{C}-\text{H})_a$	$\frac{1}{2}(R_6 - R_7 - R_9 + R_{10})$	

2. The IR and Raman spectra of *trans*-PA and their assignment

All the observed IR and Raman frequencies of *trans*-PA used in this computation came from literature.

The infrared spectra of *trans*-PA were published by Shirakawa^[1] in 1971. The assignment was given on the basis of symmetry analysis and deuteration. After that, the experimental results of photoacoustic infrared spectroscopy (PAS)^[18] of *trans*-PA and polarized infrared spectra of highly oriented *trans*-PA^[16] confirmed Shirakawa's assignment.

The Raman spectra of *trans*-PA were obtained and assigned initially by Shirakawa^[10] in 1973. Kuzmany^[17] studied the Raman spectra of *trans*-PA and deuterated *trans*-PA. The peak at 1090–1120 cm⁻¹ was assigned as the C—H in-plane bending, as it had a considerable isotopic shift (Table 4). The peak at 1292 cm⁻¹ was considered as a vibrational frequencies of C—C stretching, due to its less isotopic shift. According to the results of these two authors, we gave the empirical assignment of *trans*-PA spectra as listed in Table 4.

Table 4 Observed frequencies and preliminary assignment for *trans*-PA

Symmetry Reference			$\nu_{(\text{CH})_x}$	$\nu_{(\text{CD})_x}$	$\nu_{(\text{CH})_x}/\nu_{(\text{CD})_x}$	Preliminary Assignment
Raman	Ag	[17]	2990w*	2230m	1.34	C—H stretching
		[17]	1470—1520	1370—1450	1.07	C=C stretching
	Bg	[17]	1292w	1207	1.07	C—C stretching
		[17]	1090—1120s	856—870s	1.28	=C—H in-plane bending
		[17]	1008s	745m	1.35	C—H out-of-plane bending
IR	Au	[1,16]	1015vs	752vs	1.35	C—H out-of-plane bending
	Bu	[1,16]	3013m	2231m	1.35	C—H stretching
		[1,16]	1292vw	916vw	1.41	=C—H in-plane bending

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

3. Computation results and discussion

The refined force constants from two model molecules (TTHD, TTJD) were taken as the initial value in the calculation of *trans*-PA. All the force constants (except $f(\text{C}=\text{C})^2$ and $f(\text{C}—\text{C})^2$, as explained latter) of the three molecules (TTHD, TTJD and *trans*-PA) were refined together and the refined force field obtained was given in Table 5. Those irrelative to the vibrations of *trans*-PA were not listed in the table.

The observed and calculated frequencies of *trans*-PA are shown in Table 6. The main results are as follows:

(1) Only 8 non-zero calculated frequencies were obtained, which obeys the rule of $3N-4$. Of the 12 normalized symmetry coordinates of *trans*-PA (Table 3), the frequencies of 4 vibrational modes are zero. These four modes are depicted in Fig. 4. Obviously, S_4 , S_{11} , S_8 , S_9 are stretching, Y-direction displacement, torsional movement around C=C bond and torsional movement around C—C bond of the whole macromolecular chain, respectively. They are beyond the general assumptions for normal mode analysis.

Table 5 Refined force constants of *trans*-PA*

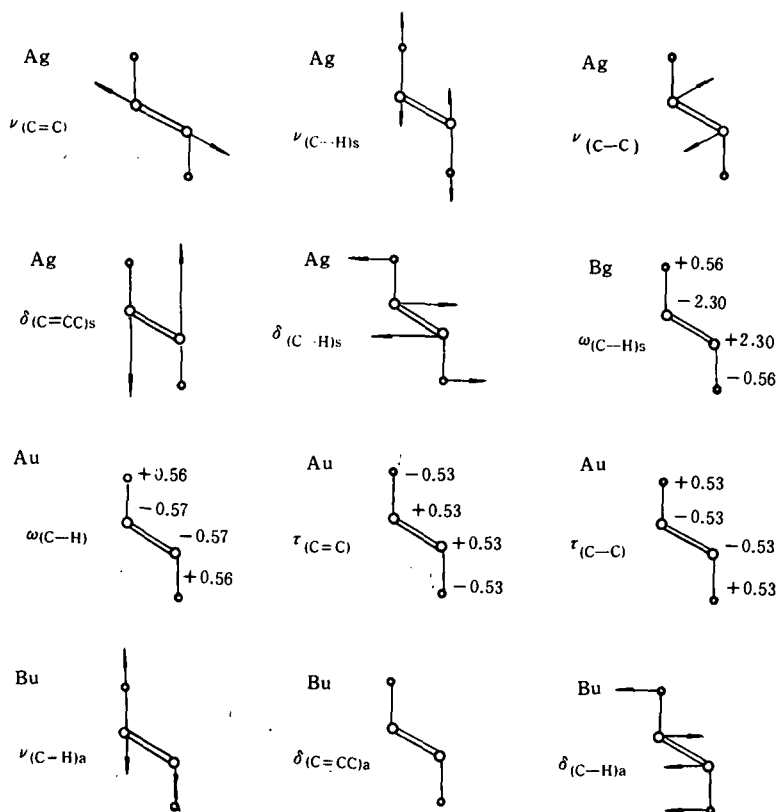
No.	Symbol	Value	No.	Symbol	Value
1.	$f(\text{C}=\text{C})^2$	7.7279	18.	$f(\text{C}=\text{C})(\text{C}=\text{CH})$	-0.0732
2.	$f(\text{C}-\text{H})^2$	4.9043	19.	$f(\text{C}-\text{C})(\text{C}-\text{H})$	-0.1037
3.	$f(\text{C}-\text{C})^2$	5.6177	20.	$f(\text{C}-\text{C})(\text{C}=\text{CC})$	0.6111
4.	$f(\text{C}=\text{CC})^2$	1.6112	21.	$f(\text{C}-\text{C})(\text{C}-\text{CH})$	0.5056
5.	$f(\text{C}=\text{CH})^2$	0.7036	22.	$f(\text{C}-\text{H})(\text{C}=\text{CH})$	0.0776
6.	$f(\text{C}-\text{CH})^2$	0.2661	23.	$f(\text{C}-\text{H})(\text{C}-\text{CH})$	0.7538
7.	$f(\text{CHOPL})^2$	0.3369	24.	$f(\text{C}=\text{CC})(\text{C}=\text{CH})$	-0.0691
8.	$f(\text{C}=\text{C TOR})^2$	0.3145	25.	$f(\text{C}=\text{CC})(\text{C}-\text{CH})$	-0.0714
9.	$f(\text{C}-\text{C TOR})^2$	0.1618	26.	$f(\text{C}=\text{CH})(\text{C}-\text{CH})$	-0.0340
10.	$f(\text{C}=\text{C})(\text{C}-\text{H})$	0.0	27.	$f(=\text{TOR})(-\text{TOR})$	0.2229
11.	$f(\text{C}=\text{C})(\text{C}-\text{C})$	1.1257	28.	$f(\text{CHOPL})(=\text{TOR})$	0.1480
12.	$f(\text{C}=\text{C})(\text{C}=\text{CC})$	0.1033	29.	$f(\text{CHOPL})(-\text{TOR})$	-0.1636
13.	$f(\text{HCCCH})_{\text{cv}}$	-0.0114	30.	$f(\text{HCCCH})_{\text{c}\omega}$	0.0049
14.	$f(\text{HC}=\text{CH})_{\text{tv}}$	-0.0157	31.	$f(\text{HC}=\text{CH})_{\text{t}\omega}$	-0.0400
15.	$f(\text{HC}-\text{CH})_{\text{tv}}$	-0.0183	32.	$f(\text{HC}-\text{CH})_{\text{t}\omega}$	-0.0415
16.	$f(\text{C}=\text{CC})(\text{C}-\text{CH})_{\text{c}\delta}$	-0.0867	33.	$f(\text{C}=\text{CC})(\text{C}=\text{CH})_{\text{c}\delta}$	0.5210
17.	$f(\text{C}=\text{CC})(\text{C}=\text{CC})_{\text{t}\delta}$	0.3987	34.	$f(\text{CC}-\text{C})(\text{C}-\text{CC})_{\text{t}\delta}$	-0.1407

- * 1. The force constants are in mdyn/Å for stretching, mdyn. Å/(rad)² for bending, mdyn/rad for stretching-bending.
2. The force constants $f(\text{C}=\text{C})^2$ and $f(\text{C}-\text{C})^2$, which came from the refinement of model molecules, were not refined in the computation of *trans*-PA.
3. Subscripts: t = interaction between those in different side of the molecular chain, c = interaction between those in the same side of molecular chain. v, δ and ω are the same as shown in Table 3.

Table 6 Calculated and observed frequencies of *trans*-PA*

Symmetry	Calc. (cm ⁻¹)	Obs.(cm ⁻¹) Raman	IR	Potential energy distribution (%)
Ag	2993	2990		$\nu_{(\text{C}-\text{H})_{\text{S}}}(86)$, $\delta_{(\text{C}=\text{CC})_{\text{S}}}(13)$.
Ag	1747	1470		$\nu_{(\text{C}=\text{C})}(34)$, $\delta_{(\text{C}-\text{H})_{\text{S}}}(47)$, $\delta_{(\text{C}=\text{CC})_{\text{S}}}(18)$.
Ag	1122	1120		$\delta_{(\text{C}-\text{H})_{\text{S}}}(68)$, $\delta_{(\text{C}=\text{CC})_{\text{S}}}(17)$.
Ag	1036	1292		$\nu_{(\text{C}-\text{C})}(59)$, $\delta_{(\text{C}-\text{H})_{\text{S}}}(21)$, $\delta_{(\text{C}=\text{CC})_{\text{S}}}(16)$.
Bg	1023	1008		$\omega_{(\text{C}-\text{H})_{\text{S}}}(100)$.
Au	966		1015	$\omega_{(\text{C}-\text{H})_{\text{a}}}(82)$, $\tau_{(\text{C}=\text{C})}(18)$.
Bu	3007		3013	$\nu_{(\text{C}-\text{H})_{\text{a}}}(99)$.
Bu	1290		1249	$\delta_{(\text{C}-\text{H})_{\text{a}}}(65)$, $\delta_{(\text{C}=\text{CC})}(30)$.

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

Fig. 4 Vibrational modes for *trans*-PA

(2) The potential energy distribution (PED) data obtained from the computation were in good agreement with the empirical assignment of Shirakawa et al. and Kuzmany. But most of the vibrational frequencies of *trans*-PA had contributions from several empirical modes, indicating the more complicity in *trans*-PA molecular vibrations than in the model molecule case.

(3) After the refinement of the force field for the model molecules and *trans*-PA, where the C=C and C-C stretching modes were not included, the average absolute and relative deviations of calculated from observed frequencies were 20 cm^{-1} and 1.8%, respectively. The agreement of the calculated with observed frequencies for *trans*-PA indicates this set of force constants are acceptable to both *trans*-PA and its model molecules.

(4) There were large differences between calculated and observed frequencies for C=C and C-C stretching vibrations, due to the much longer effective conjugate length of *trans*-PA than its model molecules. For the olefins of limited conjugate length, the conjugate-length dependence of the observed frequencies for C=C stretching vibration is given by^[19]

$$\nu_{\text{C}=\text{C}} = 1450 + \frac{915}{2N_{\text{C}=\text{C}}} \quad (3)$$

in which $N_{\text{C}=\text{C}}$ stands for the number of carbon-carbon double bonds in a conjugate system. It can be well seen that the observed frequency of C=C stretching vibration is heavily dependent on its effective conjugate length. Obviously, 1470 cm^{-1} is a typical band of long conjugate system of *trans*-PA.

In our computation, the bond lengths of $C \equiv C$ and $C - C$ were transferred from butadiene. This was insufficient to account for the effect of conjugation. We tried to get proper $f(C \equiv C)^2$ and $f(C - C)^2$ for both small and macro-molecules. But our attempt proved unsuccessful. So the force constants $f(C \equiv C)^2$ and $f(C - C)^2$ were transferred from TTHD and TTJD to *trans*-PA without further refinement. The worse agreement of the calculated with observed frequencies for these two modes was the evidence for the much higher conjugation degree in *trans*-PA than in model molecules.

To account for the influence of $f(C \equiv C)^2$ and $f(C - C)^2$ on the calculation results, we decreased $f(C \equiv C)^2$ and increased $f(C - C)^2$ in different proportion in the computation. There was much change in the potential energy distribution (PED), but not in corresponding frequency value. So the PED-weighted average value of calculated frequencies for $C \equiv C$ and $C - C$ stretching modes was adopted. It can be seen from Fig. 5 that the PED-weighted average value $\bar{\nu}_{(C \equiv C)}$ and $\bar{\nu}_{(C - C)}$ decreases and increases respectively towards the observed frequencies with rising $f(C \equiv C)^2$ and $f(C - C)^2$ correction. This tendency shows that the conjugation in *trans*-PA made its double bond weakened and single bond strengthened.

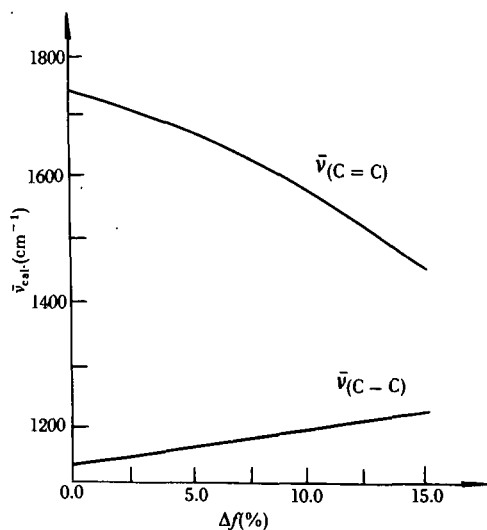


Fig. 5 Dependence of the PED-weighted average frequencies of $C \equiv C$ and $C - C$ stretchings on $f(C \equiv C)^2$ and $f(C - C)^2$

(5) The satisfactory results were obtained when the above force field relevant to the *trans*-structure was transferred to the normal vibrational analysis of *cis*-polyacetylene^[6]. Not only does this confirm the results mentioned above, but also shows the nice transférability of the force field.

Keywords:

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

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