LOCAL AND OVERALL VIBRATIONS OF POLYMER CHAINS

T. SHIMANOUCHI

Department of Chemistry, Faculty of Science,
University of Tokyo, Japan

ABSTRACT

Internal motions of polymer chains are classified into the local and the overall vibrations. The frequencies and modes of the latter are sensitive to the conformation of the chains. The discrimination between these two kinds of modes is explained, taking the 1,2-dichloroethane molecule as an example. The overall vibrations of n-$C_{36}H_{74}$ chain molecule, $(CH_2)_{34}$ ring molecule and polypeptide chain are discussed.

INTRODUCTION

Translational and rotational motions of biopolymer molecules have been studied in detail by means of electrophoresis, sedimentation, diffusion, viscosity, osmotic pressure and other measurements and the information on the molecular weight, molecular shape and hydration has been acquired. However, the internal motions of biopolymer molecules remain to be explored, although they may be closely related with the properties and biological functions[1, 2].

The internal motions of small molecules have been widely studied by infra-red and Raman spectroscopy. The spectra obtained provide almost full information of the vibrational states of small molecules. However, for the large molecules they give only limited information, the important parts of internal motions being left undetermined.

This fact is due to the number of degrees of freedom of the internal motion. For instance, the myoglobin molecule has 2600 atoms and the internal freedom is 7800. It is impossible to know full details of all these motions. In order to overcome this situation, the author suggested separating the motions into local vibrations and overall vibrations, emphasized the need for study of the latter, and calculated the frequencies of the longitudinal acoustical vibrations of the α-helix[2–4]. Peticolas and his co-workers also attempted to calculate the frequencies of these modes[1, 5].

The frequencies of the overall vibrations are highly sensitive to the length or overall shape of a large molecule and give helpful information as to the conformations of polymer chains. In the present paper the discrimination between local and overall vibrations is first described, 1,2-dichloroethane being taken as an example; then overall vibrations are discussed for paraffin and polypeptide molecules.

1,2-DICHLOROETHANE

The infra-red and Raman spectra of 1,2-dichloroethane have been studied in detail by Mizushima and his co-workers[6–8]. The spectra in the solid state show that the molecule takes the *trans* form. The assignments of the bands are given as shown in column 4 of *Table 1*[9]. These assignments are based on the PED elements in normal coordinate treatments. However, the mode is differently described when we calculate the atomic displacements in each vibration. The motion of the *i*th atom for the *a*th normal vibration is given by

$$\left.\begin{aligned} x_i^a &= x_i^0 + d(L_x)_{xi}^a \sin 2\pi c\nu_a t \\ y_i^a &= y_i^0 + d(L_x)_{yi}^a \sin 2\pi c\nu_a t \\ z_i^a &= z_i^0 + d(L_x)_{zi}^a \sin 2\pi c\nu_a t \end{aligned}\right\} \tag{1}$$

where x_i^0, y_i^0 and z_i^0 are the Cartesian coordinates of the *i*th atom in the equilibrium position, ν_a is the wavenumber of the *a*th vibration, $(L_x)_{xi}^a$, $(L_x)_{yi}^a$ and $(L_x)_{zi}^a$ are the elements of the L_x matrix defined by

$$\mathbf{X} = L_x\mathbf{Q} \tag{2}$$

($\mathbf{X}$ is the Cartesian displacement vector and $\mathbf{Q}$ the normal coordinate vector.) The coefficient d is given by

$$d = 6.84\,(T^{\frac{1}{2}}/\nu_a) \tag{3}$$

(T is the absolute temperature), when the L_x matrix elements are calculated using the atomic weight unit for the mass and the ångström unit for the length and when the sum of the kinetic and potential energies for each vibration is assumed to be kT. *Figures 1, 2* and *3* show the values of x_i^a, y_i^a and z_i^a, when we take −90°, −80°, . . ., 80° and 90° for $2\pi c\nu_a t$. For almost all the atomic displacements the lines drawn are overlapped and just give the area of displacements.

The result of the interpretation of these figures is given in column 5 of *Table 1*. The ν_6 (CCCl symmetrical deformation) vibration is assigned to the molecule elongation mode. This is a kind of Cl . . . Cl stretching mode, other atoms following the movement of the Cl atoms. The ν_{10} (CC torsion) and ν_{18} (CCCl antisymmetrical deformation) vibrations are assigned to the molecule deformation modes, since the two Cl atoms move in one direction and the central CH_2—CH_2 group moves in the opposite direction. The ν_{17} (CCl antisymmetrical stretching) vibration is similar. However, this mode does not cause the deformation of the whole molecule and is assigned to the local translation of the CH_2—CH_2 group.

Other modes are almost pure local vibrations. For ν_1, ν_2, ν_3, ν_7, ν_8, ν_{11}, ν_{12}, ν_{14}, ν_{15}, ν_{16} the Cl and C atoms are almost fixed and they are just the hydrogen vibrations. For ν_9 and ν_{13} (CH_2 rocking) vibrations the two carbon atoms move slightly and they are assigned to the twisting and rotation modes of the CH_2—CH_2 group, respectively. For the ν_4 (CC stretching) vibration the two Cl atoms are almost fixed and it is just the local CH_2—CH_2 stretching mode.

For the ν_5 (CCl symmetrical stretching) vibration the two Cl atoms are

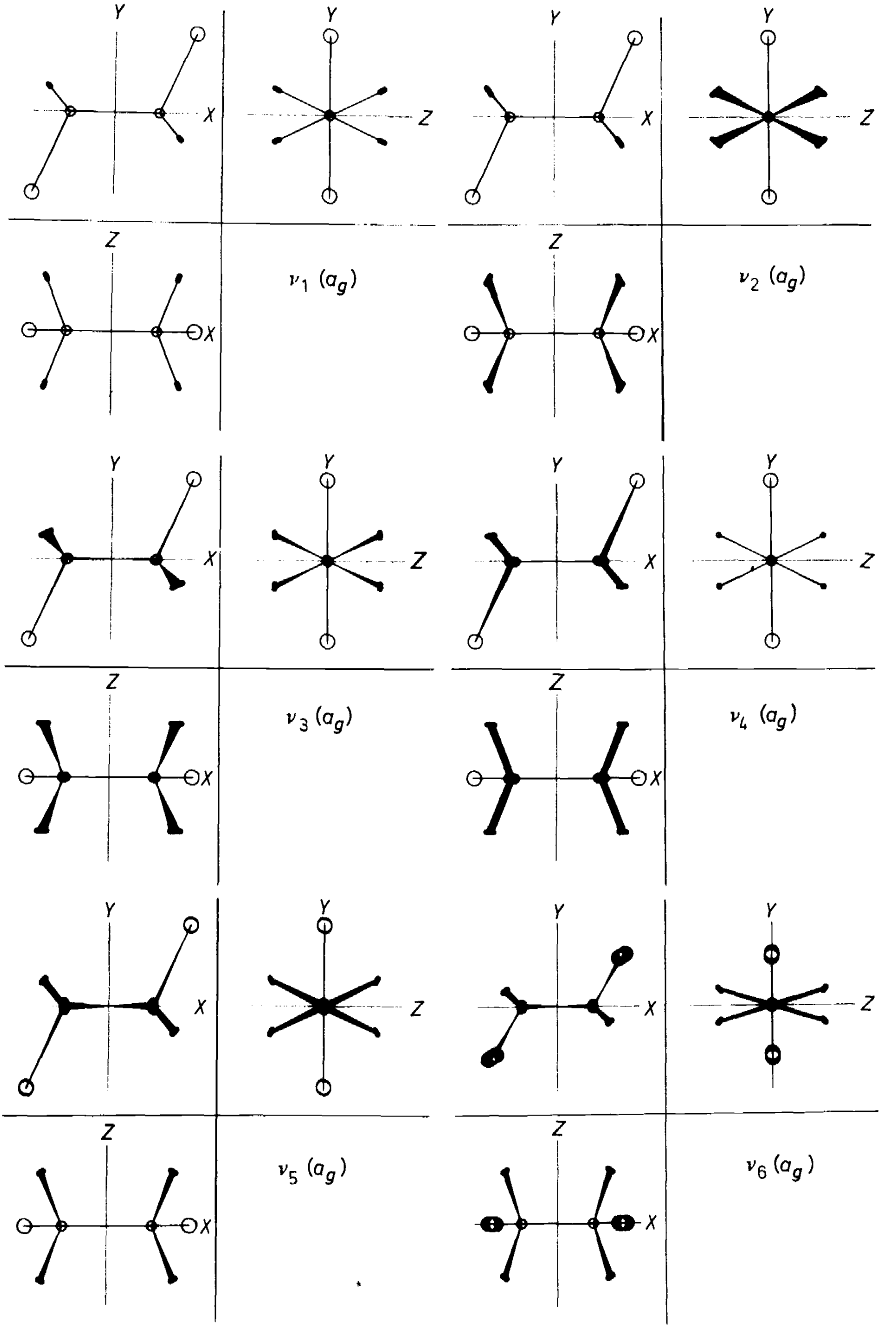
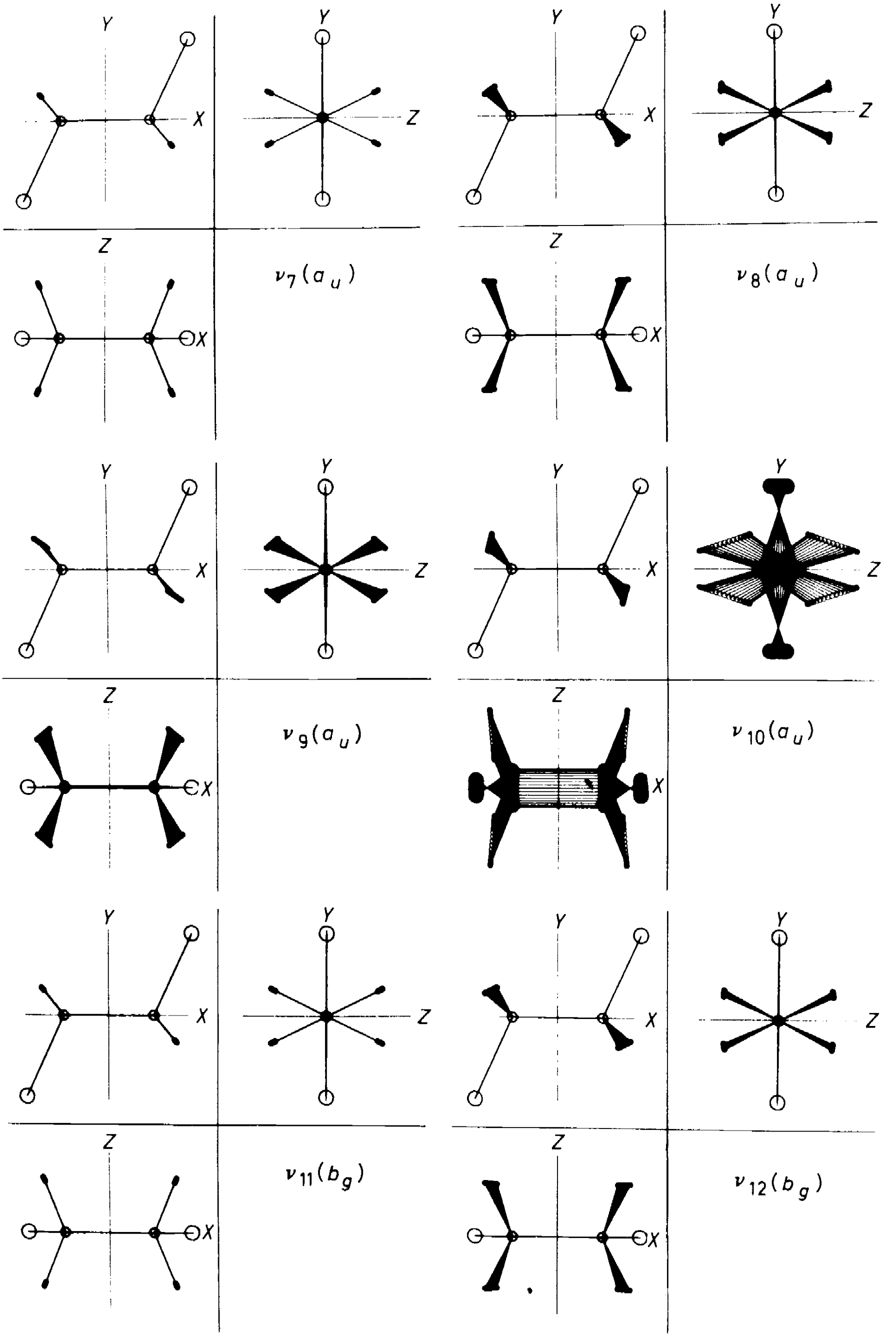


Figure 1. Atomic displacements in the normal vibrations of the 1,2-dichloroethane molecule. (The *trans* form. Classical dynamics and the harmonic approximation are used. The amplitudes are 2.5 times larger than those at 300 K.)



$\nu_7(a_u)$

$\nu_8(a_u)$

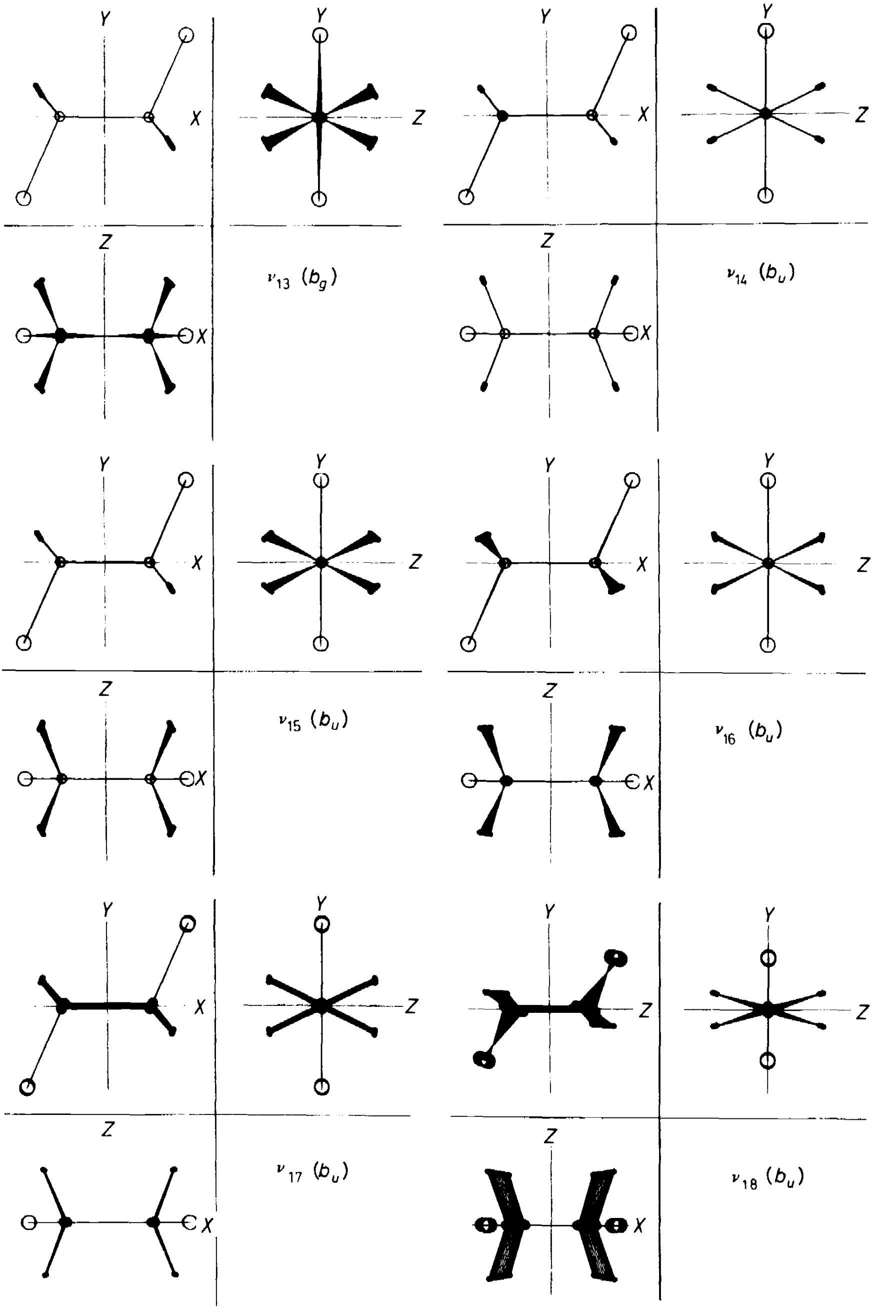
$\nu_9(a_u)$

$\nu_{10}(a_u)$

$\nu_{11}(b_g)$

$\nu_{12}(b_g)$

Figure 2. Atomic displacements in the normal vibrations of 1,2-dichloroethane (continued).



ν_{13} (b_g)

ν_{14} (b_u)

ν_{15} (b_u)

ν_{16} (b_u)

ν_{17} (b_u)

ν_{18} (b_u)

Figure 3. Atomic displacements in the normal vibrations of 1,2-dichloroethane (continued).

also almost fixed and it is assigned to the local rotation of the $CH_2—CH_2$ group.

As far as the atomic masses are concerned, the $Cl—CH_2—CH_2—Cl$ molecule is approximately the Cl . . . Cl diatomic molecule. The Cl . . . Cl stretching mode ν_6 is clearly the overall vibration. The two modes, ν_{10} and ν_{18} are also the overall vibrations, in which the $CH_2—CH_2$ group moves perpendicular to the Cl . . . Cl direction. All the other vibrations are local, the hydrogen atoms or the $CH_2—CH_2$ group moving locally and the two Cl atoms being almost fixed.

Table 1. Normal vibrations of the 1,2-dichloroethane molecule (transform)

		obs.	Assignments	
		cm^{-1}	(from PED)	(from L_x)
a_g	ν_1	2957	CH_2 stretch.	CH_2 stretch.
	ν_2	1445	CH_2 sciss.	CH_2 sciss.
	ν_3	1304	CH_2 wag.	CH_2 wag.
	ν_4	1052	CC stretch.	$(CH_2—CH_2)$ stretch.
	ν_5	754	CCl stretch.	$(CH_2—CH_2)$ rotation.
	ν_6	300	CCCl deform.	$(CH_2Cl—CH_2Cl)$ stretch. (molecule elongation)*
a_u	ν_7	3005	CH_2 stretch.	CH_2 stretch.
	ν_8	1123	CH_2 twist.	CH_2 twist.
	ν_9	773	CH_2 rock.	CH_2 rock.
	ν_{10}	123	CC torsion	$(CH_2—CH_2)$ translation (molecule deformation)*
b_g	ν_{11}	3005	CH_2 stretch.	CH_2 stretch.
	ν_{12}	1264	CH_2 twist.	CH_2 twist.
	ν_{13}	989	CH_2 rock.	CH_2 rock.
b_u	ν_{14}	2983	CH_2 stretch.	CH_2 stretch.
	ν_{15}	1461	CH_2 sciss.	CH_2 sciss.
	ν_{16}	1232	CH_2 wag.	CH_2 wag.
	ν_{17}	728	CCl stretch.	$(CH_2—CH_2)$ translation
	ν_{18}	222	CCCl deform.	$(CH_2—CH_2)$ translation (molecule deformation)*

* Overall vibrations.

n-$C_{36}H_{74}$ CHAIN MOLECULE

The normal hydrocarbon molecules take the extended zigzag form, in which all the C—C conformations are *trans*, in the crystal. The normal vibrations of these molecules have been studied in detail[10] and the result is summarized as the dispersion curve of a one-dimensional crystal (*Figure 4*). As this figure shows, the ν_5 and ν_9 vibrations are acoustical modes, to which the overall vibrations belong. All the other vibrations appearing in the region higher than 700 cm^{-1} are optical modes, which correspond to the local vibrations.

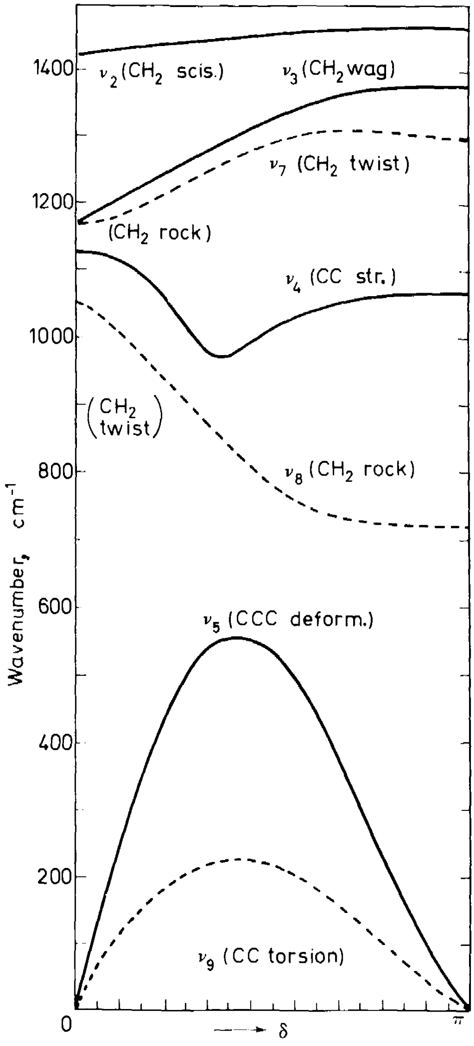


Figure 4. Frequency versus phase difference (δ) relationship for polymethylene chain (ν_4 and ν_5 are coupled strongly and ν_5 vibrations with small phase differences are assigned to the CC stretching mode. See text. The curves for ν_1 and ν_6 appearing in the 3000 cm^{-1} region are omitted.)

Figure 5 shows the Raman spectra of n-$C_{36}H_{74}$ and the correspondence between the spectra and the dispersion curve. A progression of bands appearing in the low frequency region is the longitudinal acoustical vibrations[11]. The lowest frequency band at 67.4 cm^{-1} is assigned to the accordion-like vibration.

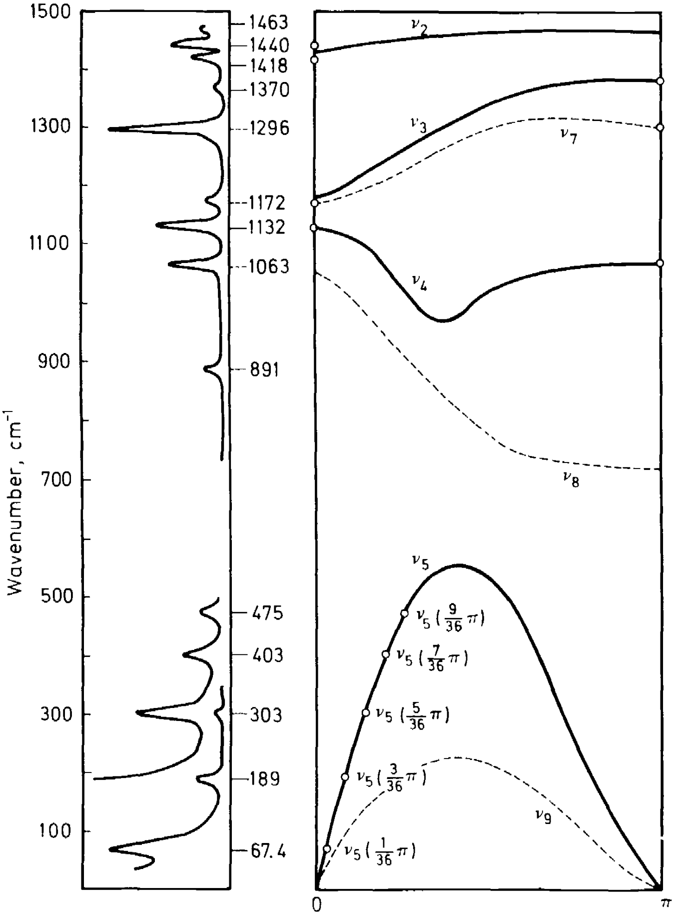


Figure 5. Raman spectra and band assignments of n-$C_{36}H_{74}$ in the crystalline state. (The 891 cm^{-1} Raman band is assigned to the methyl group rocking vibration.)

This vibration was first found and assigned by Mizushima and the author[12] in 1944 for the smaller normal paraffin molecules and the frequencies are expressed by

$$\nu = 2400/N_C \text{ cm}^{-1} \tag{4}$$

where N_C is the number of carbon atoms. The form of the equation is based on

$$\nu = (1/2l)(E/\rho)^{\frac{1}{2}} \tag{5}$$

where ν is the frequency of the accordion-like vibration of a rod, the length, the density and Young's modulus of which are l, ρ and E, respectively.

Equation 4 gives the frequency accurately, when the number of carbon atoms is large. In *Table 2* the frequencies calculated from equation 4 are compared with those observed by Schaufele and the author in 1967[11]. This equation is useful for the study of the length of a hydrocarbon chain[11] and also the thickness of the single polyethylene crystal[13].

Table 2. Accordion-like vibrational frequencies of polymethylene chains utilizing equation 4

No. of C atoms	Calc. (cm^{-1})	Obs.* (cm^{-1})	No. of C atoms	Calc. (cm^{-1})	Obs.* (cm^{-1})
18	131	133	32	75	76
20	120	114	36	67	67
24	100	98	44	55	57
28	86	85	94	26	26

* See ref. 11.

The accordion-like vibration is a typical overall vibration. Other parts of the dispersion curve for ν_5 and ν_9 in *Figure 4* are related with other kinds of overall vibrations. The modes of these vibrations are given in *Figure 6*, those of the lowest frequency ones are drawn in *Figure 7*, and their frequencies are given in *Figure 8* as a function of the number of carbon atoms.

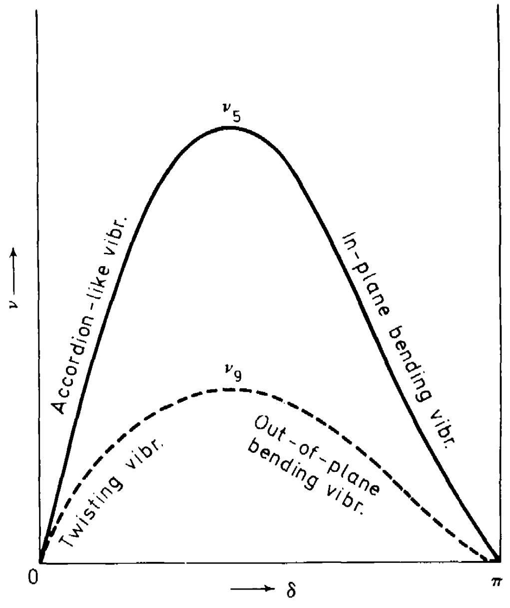


Figure 6. Frequency versus phase difference curves for acoustical vibrations of the polymethylene chain and their vibrational modes as overall vibrations.

In *Figures* 9 and *10* a couple of the overall vibrations of *n*-$C_{36}H_{74}$ are shown as examples. The modes given in *Figure 5* and the PED elements[14] show that the accordion-like vibration belongs to the CC stretching mode and not to the CCC bending mode.

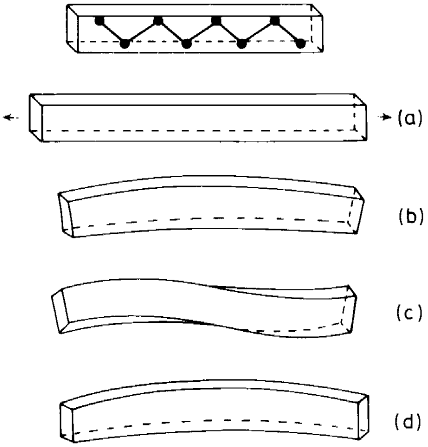


Figure 7. Lowest frequency modes for four kinds of overall vibrations of the polymethylene chain cited in *Figure 6*. (a) accordion-like vibrations, (b) in-plane bending vibrations, (c) twisting vibration and (d) out-of-plane bending vibration.

The phase differences of the one-dimensional crystal are the problem of interest and are discussed by Shimanouchi and Tasumi[14] and by Peticolas *et al.*[5]. When the extended or helix chain consists of *n* units, the phase difference found for neighbouring units is given by $m\pi/(n + 1)$, where *m* is the order of vibration and $m = 1$ for the accordion-like vibration. Accordingly, the phase difference for the CC stretching mode is given by $m\pi/n_C$, since the chain has $n_C - 1$ CC bonds. Similarly the phase differences for the CCC bending mode and for the CC torsional mode are given by $m\pi/(n_C - 1)$ and $m\pi/(n_C - 2)$, respectively. In accord with the above assignment the phase differences for the normal paraffin molecules are given by $m\pi/n_C$ better than by $m\pi/(n_C - 1)$[14].

$(CH_2)_{34}$ RING MOLECULE

The laser-Raman scattering by $(CH_2)_{34}$ was measured and the normal vibrations were calculated by Schaufele, Tasumi and Shimanouchi[15, 16]. This molecule takes approximately the form given in *Figure 11* and has overall vibrations more complex than those of the *n*-paraffin chains. *Figure 12* gives some of them which correspond to the observed low frequency Raman bands. The accordion-like vibrations of this rectangular molecule are expected to have frequencies close to that of n-$C_{15}H_{32}$. The frequency calculated for the latter is 160 cm^{-1} which is not far from the observed value, 145 cm^{-1}.

POLYPEPTIDE CHAIN

The overall vibrations of protein molecules may be very complex and are one of the aims of this series of researches. So far no observed Raman band has been assigned to this sort of vibration. The only way of estimating the modes and the frequencies is to transfer the force constants from small molecules with similar structures and to calculate the normal modes and the frequencies. Calculations have been made for the right-handed α-helix of poly-L-alanine and the relation between the length of the helix and the frequency of the accordion-like vibration was estimated[3, 5]. The helix rod has other overall vibrations similar to those shown in *Figure 7*. The frequencies of these vibrations are also functions of the length of the rod and are estimated from the low frequency dispersion curve[3, 5]. Some of the overall vibrations of protein molecules like myoglobin or lysozyme may be similar to those shown in *Figure 12*. However, there may be other vibrations the amplitudes of which are considerably larger.

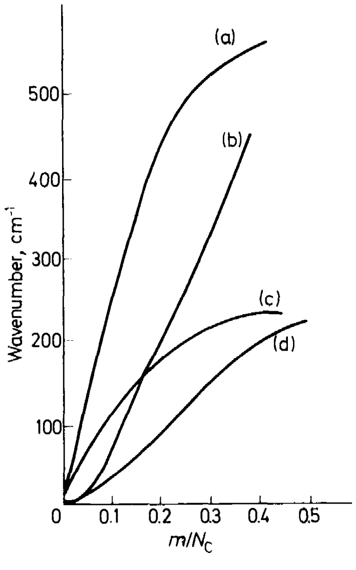


Figure 8. Frequencies of four kinds of overall vibrations of the polymethylene chain as functions of the order of vibration m and the number of carbon atoms n_C. As for (a), (b), (c) and (d), see *Figure 7*.

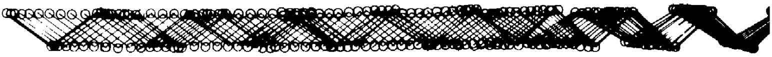


Figure 9

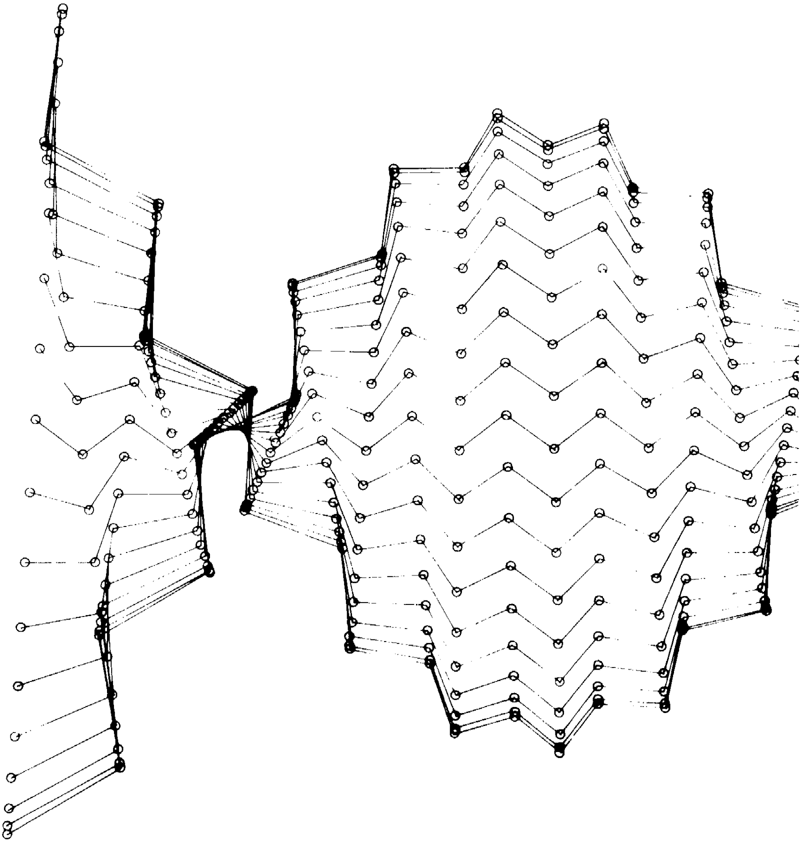
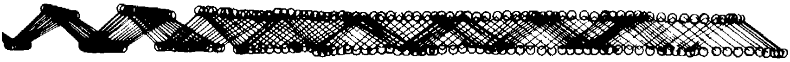


Figure 10

Figure 9. Atomic displacements of $C_{36}H_{74}$ for the accordion-like vibration at 300 K (Classical dynamics and the harmonic approximation are adopted and equation 1 is used. The methylene groups are treated as one dynamical unit.)



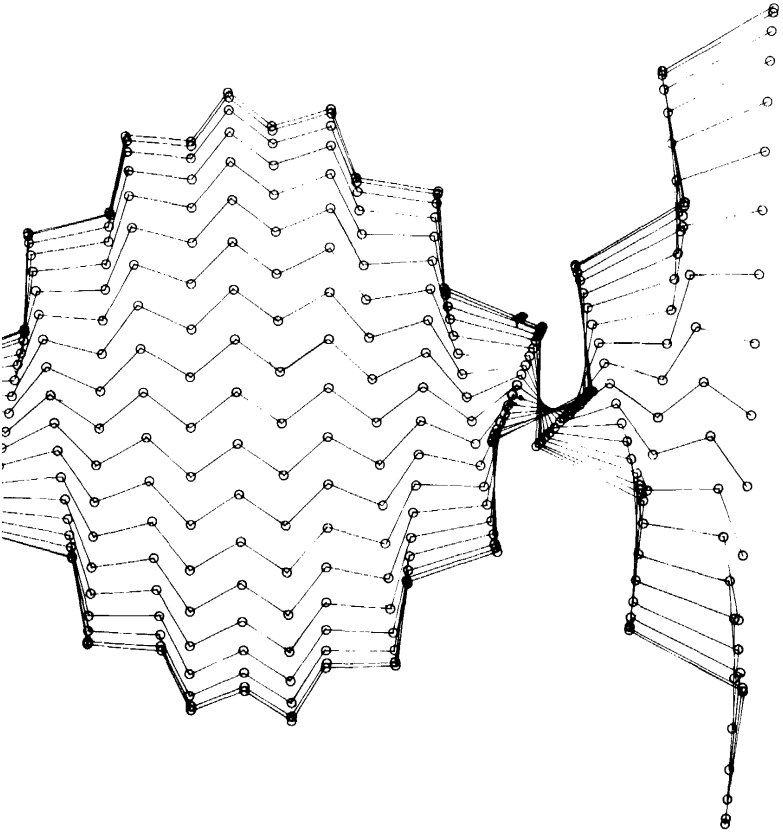


Figure 10. Atomic displacements of $C_{36}H_{74}$ for the lowest frequency 'gerade' mode belonging to the in-plane bending vibration at 300 K. (See *Figure 9*. The calculated frequency is 12 cm^{-1}.)

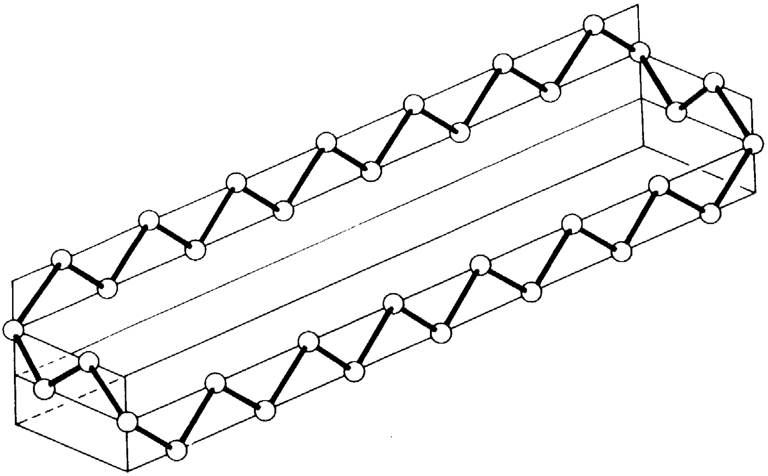


Figure 11. Approximate structure of the $(CH_2)_{34}$ ring molecule in the crystalline state.

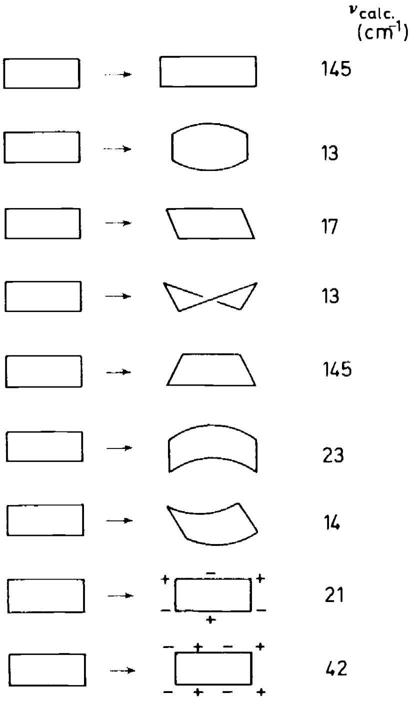


Figure 12. Overall vibrations of the $(CH_2)_{34}$ molecule.

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