Normal Coordinate Treatment and Assignment of Infrared Absorption Bands of Polyvinyl Chloride

By Takehiko SHIMANOUCHI and Mitsuo TASUMI

(Received September 16, 1960)

In the analysis of infrared absorption spectra it is often of considerable importance to calculate the frequencies of the normal vibrations. Recent developments in high-speed computers have made it possible to calculate the normal vibrations of complex molecules. We have calculated the frequencies of the polyvinyl chloride molecule using the force constants transferred from simple molecules. These results suggest a modification of the assignment proposed in former studies[1,2] and will be reported in the present paper.

Method of Calculation and Results

The normal coordinate treatment was carried out on assuming that the polyvinyl chloride molecule is syndyotactic and takes the extended zigzag form with the repeating unit made up of two monomer units. The unit cell for this structure is shown in Fig. 1. This model belongs to a group isomorphous with to the point group C_{2v}[1], and in Table I symmetry species, selection rules, and dichroic properties are given.

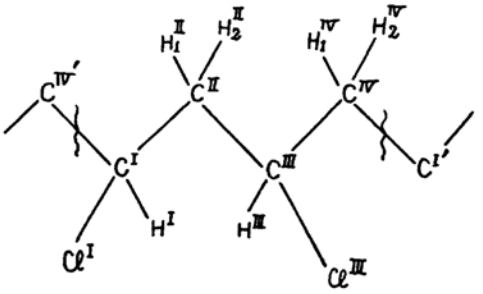


Fig. 1. Unit cell for syndyotactic structure of polyvinyl chloride.

TABLE I. SYMMETRY SPECIES, SELECTION RULES, AND DICHROISM FOR SYNDYOTACTIC POLYVINYL CHLORIDE*

C_{2v}	E	C_2	σ_v	σ_g	Number of frequencies	IR (Dichroism)	R
A_1	1	1	1	1	9	σ	active
A_2	1	1	−1	−1	7	inactive	active
B_1	1	−1	1	−1	9	σ	active
B_2	1	−1	−1	1	7	π	active

* As to the notation, see Ref. 1.

TABLE II. INTERNAL COORDINATES

Bond lengths ;		Bond angles ;			
R^{I}	$C^{I}-C^{II}$	Θ^{I}	$C^{IV\prime}-C^{I}-C^{II}$	φ_1^{II}	$C^{I}-C^{II}-H_1^{II}$
R^{II}	$C^{II}-C^{III}$	Θ^{II}	$C^{I}-C^{II}-C^{III}$	φ_2^{II}	$C^{I}-C^{II}-H_2^{II}$
R^{III}	$C^{III}-C^{IV}$	Θ^{III}	$C^{II}-C^{III}-C^{IV}$	φ_3^{II}	$C^{III}-C^{II}-H_1^{II}$
R^{IV}	$C^{IV}-C^{I\prime}$	Θ^{IV}	$C^{III}-C^{IV}-C^{I\prime}$	φ_4^{II}	$C^{III}-C^{II}-H_2^{II}$
r_1^{I}	$C^{I}-Cl^{I}$	θ^{I}	$Cl^{I}-C^{I}-H^{I}$	φ_1^{III}	$C^{II}-C^{III}-H^{III}$
r_2^{I}	$C^{I}-H^{I}$	θ^{II}	$H_1^{II}-C^{II}-H_2^{II}$	φ_2^{III}	$C^{II}-C^{III}-Cl^{III}$
r_1^{II}	$C^{II}-H_1^{II}$	θ^{III}	$H^{III}-C^{III}-Cl^{III}$	φ_3^{III}	$C^{IV}-C^{III}-H^{III}$
r_2^{II}	$C^{II}-H_2^{II}$	θ^{IV}	$H_1^{IV}-C^{IV}-H_2^{IV}$	φ_4^{III}	$C^{IV}-C^{III}-Cl^{III}$
r_1^{III}	$C^{III}-H^{III}$	φ_1^{I}	$C^{IV\prime}-C^{I}-Cl^{I}$	φ_1^{IV}	$C^{III}-C^{IV}-H_1^{IV}$
r_2^{III}	$C^{III}-Cl^{III}$	φ_2^{I}	$C^{IV\prime}-C^{I}-H^{I}$	φ_2^{IV}	$C^{III}-C^{IV}-H_2^{IV}$
r_1^{IV}	$C^{IV}-H_1^{IV}$	φ_3^{I}	$C^{II}-C^{I}-Cl^{I}$	φ_3^{IV}	$C^{I\prime}-C^{IV}-H_1^{IV}$
r_2^{IV}	$C^{IV}-H_2^{IV}$	φ_4^{I}	$C^{II}-C^{I}-H^{I}$	φ_4^{IV}	$C^{I\prime}-C^{IV}-H_2^{IV}$

---

[1] S. Krimm and C. Y. Liang, *J. Polymer Sci.*, **22**, 95 (1956).

[2] S. Narita, S. Ichinohe and S. Enomoto, ibid., **37**, 273, 281 (1959).

TABLE III. INTERNAL SYMMETRY COORDINATES

$$\mathrm{A}_1 \quad S_1 = \frac{1}{2}(\Delta R^{\mathrm{I}} + \Delta R^{\mathrm{II}} + \Delta R^{\mathrm{III}} + \Delta R^{\mathrm{IV}})$$

$$S_2 = \frac{1}{2}(\Delta r_1^{\mathrm{II}} + \Delta r_2^{\mathrm{II}} + \Delta r_1^{\mathrm{IV}} + \Delta r_2^{\mathrm{IV}})$$

$$S_3 = \frac{1}{\sqrt{2}}(\Delta r_2^{\mathrm{I}} + \Delta r_1^{\mathrm{III}})$$

$$S_4 = \frac{1}{\sqrt{2}}(\Delta r_1^{\mathrm{I}} + \Delta r_2^{\mathrm{III}})$$

$$S_5 = \frac{1}{\sqrt{2}}(\Delta \Theta^{\mathrm{I}} + \Delta \Theta^{\mathrm{III}})$$

$$S_6 = \frac{1}{\sqrt{2}}(\Delta \Theta^{\mathrm{II}} + \Delta \Theta^{\mathrm{IV}})$$

$$S_7 = \frac{1}{\sqrt{2}}(\Delta \theta^{\mathrm{I}} + \Delta \theta^{\mathrm{III}})$$

$$S_8 = \frac{1}{\sqrt{2}}(\Delta \theta^{\mathrm{II}} + \Delta \theta^{\mathrm{IV}})$$

$$S_9 = \frac{1}{\sqrt{8}}(\Delta\varphi_1^{\mathrm{II}} + \Delta\varphi_2^{\mathrm{II}} + \Delta\varphi_3^{\mathrm{II}} + \Delta\varphi_4^{\mathrm{II}} + \Delta\varphi_1^{\mathrm{IV}} + \Delta\varphi_2^{\mathrm{IV}} + \Delta\varphi_3^{\mathrm{IV}} + \Delta\varphi_4^{\mathrm{IV}})$$

$$S_{10} = \frac{1}{\sqrt{8}}(\Delta\varphi_1^{\mathrm{II}} - \Delta\varphi_2^{\mathrm{II}} - \Delta\varphi_3^{\mathrm{II}} + \Delta\varphi_4^{\mathrm{II}} - \Delta\varphi_1^{\mathrm{IV}} + \Delta\varphi_2^{\mathrm{IV}} + \Delta\varphi_3^{\mathrm{IV}} - \Delta\varphi_4^{\mathrm{IV}})$$

$$S_{11} = \frac{1}{2}(\Delta\varphi_2^{\mathrm{I}} + \Delta\varphi_4^{\mathrm{I}} + \Delta\varphi_1^{\mathrm{III}} + \Delta\varphi_3^{\mathrm{III}})$$

$$S_{12} = \frac{1}{2}(\Delta\varphi_1^{\mathrm{I}} + \Delta\varphi_3^{\mathrm{I}} + \Delta\varphi_2^{\mathrm{III}} + \Delta\varphi_4^{\mathrm{III}})$$

Four redundancies are included among these coordinates.

$$\mathrm{A}_2 \quad S_1 = \frac{1}{2}(\Delta R^{\mathrm{I}} + \Delta R^{\mathrm{II}} - \Delta R^{\mathrm{III}} - \Delta R^{\mathrm{IV}})$$

$$S_2 = \frac{1}{2}(\Delta r_1^{\mathrm{II}} + \Delta r_2^{\mathrm{II}} - \Delta r_1^{\mathrm{IV}} - \Delta r_2^{\mathrm{IV}})$$

$$S_3 = \frac{1}{\sqrt{2}}(\Delta \Theta^{\mathrm{II}} - \Delta \Theta^{\mathrm{IV}})$$

$$S_4 = \frac{1}{\sqrt{2}}(\Delta \theta^{\mathrm{II}} - \Delta \theta^{\mathrm{IV}})$$

$$S_5 = \frac{1}{\sqrt{8}}(\Delta\varphi_1^{\mathrm{II}} + \Delta\varphi_2^{\mathrm{II}} + \Delta\varphi_3^{\mathrm{II}} + \Delta\varphi_4^{\mathrm{II}} - \Delta\varphi_1^{\mathrm{IV}} - \Delta\varphi_2^{\mathrm{IV}} - \Delta\varphi_3^{\mathrm{IV}} - \Delta\varphi_4^{\mathrm{IV}})$$

$$S_6 = \frac{1}{\sqrt{8}}(\Delta\varphi_1^{\mathrm{II}} - \Delta\varphi_2^{\mathrm{II}} - \Delta\varphi_3^{\mathrm{II}} + \Delta\varphi_4^{\mathrm{II}} + \Delta\varphi_1^{\mathrm{IV}} - \Delta\varphi_2^{\mathrm{IV}} - \Delta\varphi_3^{\mathrm{IV}} + \Delta\varphi_4^{\mathrm{IV}})$$

$$S_7 = \frac{1}{2}(\Delta\varphi_2^{\mathrm{I}} - \Delta\varphi_4^{\mathrm{I}} - \Delta\varphi_1^{\mathrm{III}} + \Delta\varphi_3^{\mathrm{III}})$$

$$S_8 = \frac{1}{2}(\Delta\varphi_1^{\mathrm{I}} - \Delta\varphi_3^{\mathrm{I}} - \Delta\varphi_2^{\mathrm{III}} + \Delta\varphi_4^{\mathrm{III}})$$

One redundancy is included.

$$\mathrm{B}_1 \quad S_1 = \frac{1}{2}(\Delta R^{\mathrm{I}} - \Delta R^{\mathrm{II}} - \Delta R^{\mathrm{III}} + \Delta R^{\mathrm{IV}})$$

$$S_2 = \frac{1}{2}(\Delta r_1^{\mathrm{II}} - \Delta r_2^{\mathrm{II}} + \Delta r_1^{\mathrm{IV}} - \Delta r_2^{\mathrm{IV}})$$

$$S_3 = \frac{1}{\sqrt{2}}(\Delta r_2^{\mathrm{I}} - \Delta r_1^{\mathrm{III}})$$

$$S_4 = \frac{1}{\sqrt{2}}(\Delta r_1^{\mathrm{I}} - \Delta r_2^{\mathrm{III}})$$

$$S_5 = \frac{1}{\sqrt{2}}(\Delta \Theta^{\mathrm{I}} - \Delta \Theta^{\mathrm{III}})$$

$$S_6 = \frac{1}{\sqrt{2}}(\Delta \theta^{\mathrm{I}} - \Delta \theta^{\mathrm{III}})$$

$$S_7 = \frac{1}{\sqrt{8}}(\Delta\varphi_1^{\mathrm{II}} + \Delta\varphi_2^{\mathrm{II}} - \Delta\varphi_3^{\mathrm{II}} - \Delta\varphi_4^{\mathrm{II}} - \Delta\varphi_1^{\mathrm{IV}} - \Delta\varphi_2^{\mathrm{IV}} + \Delta\varphi_3^{\mathrm{IV}} + \Delta\varphi_4^{\mathrm{IV}})$$

$$S_8 = \frac{1}{\sqrt{8}}(\Delta\varphi_1^{\mathrm{II}} - \Delta\varphi_2^{\mathrm{II}} + \Delta\varphi_3^{\mathrm{II}} - \Delta\varphi_4^{\mathrm{II}} + \Delta\varphi_1^{\mathrm{IV}} - \Delta\varphi_2^{\mathrm{IV}} + \Delta\varphi_3^{\mathrm{IV}} - \Delta\varphi_4^{\mathrm{IV}})$$

$$S_9 = \frac{1}{2}(\Delta\varphi_2^{\mathrm{I}} + \Delta\varphi_4^{\mathrm{I}} - \Delta\varphi_1^{\mathrm{III}} - \Delta\varphi_3^{\mathrm{III}})$$

$$S_{10} = \frac{1}{2}(\Delta\varphi_1^{\mathrm{I}} + \Delta\varphi_3^{\mathrm{I}} - \Delta\varphi_2^{\mathrm{III}} - \Delta\varphi_4^{\mathrm{III}})$$

One redundancy is incuded.

$$\mathrm{B}_2 \quad S_1 = \frac{1}{2}(\Delta R^{\mathrm{I}} - \Delta R^{\mathrm{II}} + \Delta R^{\mathrm{III}} - \Delta R^{\mathrm{IV}})$$

$$S_2 = \frac{1}{2}(\Delta r_1^{\mathrm{II}} - \Delta r_2^{\mathrm{II}} - \Delta r_1^{\mathrm{IV}} + \Delta r_2^{\mathrm{IV}})$$

$$S_3 = \frac{1}{\sqrt{8}}(\Delta\varphi_1^{\mathrm{II}} + \Delta\varphi_2^{\mathrm{II}} - \Delta\varphi_3^{\mathrm{II}} - \Delta\varphi_4^{\mathrm{II}} + \Delta\varphi_1^{\mathrm{IV}} + \Delta\varphi_2^{\mathrm{IV}} - \Delta\varphi_3^{\mathrm{IV}} - \Delta\varphi_4^{\mathrm{IV}})$$

$$S_4 = \frac{1}{\sqrt{8}}(\Delta\varphi_1^{\mathrm{II}} - \Delta\varphi_2^{\mathrm{II}} + \Delta\varphi_3^{\mathrm{II}} - \Delta\varphi_4^{\mathrm{II}} - \Delta\varphi_1^{\mathrm{IV}} + \Delta\varphi_2^{\mathrm{IV}} - \Delta\varphi_3^{\mathrm{IV}} + \Delta\varphi_4^{\mathrm{IV}})$$

$$S_5 = \frac{1}{2}(\Delta\varphi_2^{\mathrm{I}} - \Delta\varphi_4^{\mathrm{I}} + \Delta\varphi_1^{\mathrm{III}} - \Delta\varphi_3^{\mathrm{III}})$$

$$S_6 = \frac{1}{2}(\Delta\varphi_1^{\mathrm{I}} - \Delta\varphi_3^{\mathrm{I}} + \Delta\varphi_2^{\mathrm{III}} - \Delta\varphi_4^{\mathrm{III}})$$

As only the vibrations in which corresponding atoms in all the unit cells move in phase are optically active for such high polymers, the calculation was done for these modes of vibration according to the method applied to polyethylene[3]. The internal coordinates and the internal symmetry coordinates used are given in Tables II and III. For the internal coordinates only the bond lengths and angles are taken and the angles of internal rotation about the C–C bond are excluded. Therefore, in this calculation the torsional vibrations of the zigzag chain are not considered, but this has comparatively little effect on the other calculated frequencies.

The potential field used is the Urey-Bradley type[4].

$$2V = K(\mathrm{C{-}C})\sum_{R}(\Delta R)^2 + K(\mathrm{C{-}H})_{\mathrm{CHH}}\sum_{r_a}(\Delta r_a)^2 + K(\mathrm{C{-}H})_{\mathrm{CHCl}}\sum_{r_b}(\Delta r_b)^2$$

---

[3] T. Shimanouchi and S. Mizushima, *J. Chem. Phys.*, **17**, 1102 (1949).

[4] T. Shimanouchi, ibid., **17**, 245, 734, 848 (1949).

$$\begin{aligned}
&+K(\mathrm{C{-}Cl})\sum_{r_c}(\varDelta r_c)^2\\
&+H(\mathrm{C{-}C{-}C})\times(1.54)^2\sum_{\varTheta}(\varDelta\varTheta)^2\\
&+H(\mathrm{H{-}C{-}H})\times(1.09)^2\sum_{\theta_a}(\varDelta\theta_a)^2\\
&+H(\mathrm{H{-}C{-}Cl})\times(1.09)\times(1.77)\sum_{\theta_b}(\varDelta\theta_b)^2\\
&+H(\mathrm{H{-}C{-}C})_{\mathrm{CHH}}\times(1.09)\times(1.54)\sum_{\varphi_a}(\varDelta\varphi_a)^2\\
&+H(\mathrm{H{-}C{-}C})_{\mathrm{CHCl}}\times(1.09)\times(1.54)\sum_{\varphi_b}(\varDelta\varphi_b)^2\\
&+H(\mathrm{Cl{-}C{-}C})\times(1.77)\times(1.54)\sum_{\varphi_c}(\varDelta\varphi_c)^2\\
&+F(\mathrm{C}\cdots\mathrm{C})\sum_{Q}(\varDelta Q)^2+F(\mathrm{H}\cdots\mathrm{H})\sum_{q_a}(\varDelta q_a)^2\\
&+F(\mathrm{H}\cdots\mathrm{Cl})\sum_{q_b}(\varDelta q_b)^2\\
&+F(\mathrm{H}\cdots\mathrm{C})_{\mathrm{CHH}}\sum_{q_c}(\varDelta q_c)^2\\
&+F(\mathrm{H}\cdots\mathrm{C})_{\mathrm{CHCl}}\sum_{q_d}(\varDelta q_d)^2\\
&+F(\mathrm{Cl}\cdots\mathrm{C})\sum_{q_e}(\varDelta q_e)^2+\text{linear terms}
\end{aligned}$$

where R, r_a, r_b, r_c, $\varTheta$, θ_a, θ_b, φ_a, φ_b, φ_c, Q, $q_a\cdots q_e$ represent the following bond lengths, bond angles, and interatomic distances indicated in parentheses.

$R(R^{\mathrm{I}}, R^{\mathrm{II}}, R^{\mathrm{III}}, R^{\mathrm{IV}})$

$r_a(r_1{}^{\mathrm{II}}, r_2{}^{\mathrm{II}}, r_1{}^{\mathrm{IV}}, r_2{}^{\mathrm{IV}})$

$r_b(r_2{}^{\mathrm{I}}, r_1{}^{\mathrm{III}})$

$r_c(r_1{}^{\mathrm{I}}, r_2{}^{\mathrm{III}})$

$\varTheta(\varTheta^{\mathrm{I}}, \varTheta^{\mathrm{II}}, \varTheta^{\mathrm{III}}, \varTheta^{\mathrm{IV}})$

$\theta_a(\theta^{\mathrm{II}}, \theta^{\mathrm{IV}})$

$\theta_b(\theta^{\mathrm{I}}, \theta^{\mathrm{III}})$

$\varphi_a(\varphi_1{}^{\mathrm{II}}, \varphi_2{}^{\mathrm{II}}, \varphi_3{}^{\mathrm{II}}, \varphi_4{}^{\mathrm{II}}, \varphi_1{}^{\mathrm{IV}}, \varphi_2{}^{\mathrm{IV}}, \varphi_3{}^{\mathrm{IV}}, \varphi_4{}^{\mathrm{IV}})$

$\varphi_b(\varphi_2{}^{\mathrm{I}}, \varphi_4{}^{\mathrm{I}}, \varphi_1{}^{\mathrm{III}}, \varphi_3{}^{\mathrm{III}})$

$\varphi_c(\varphi_1{}^{\mathrm{I}}, \varphi_3{}^{\mathrm{I}}, \varphi_2{}^{\mathrm{III}}, \varphi_4{}^{\mathrm{III}})$

$Q(\mathrm{C}^{\mathrm{IV}'}\cdots\mathrm{C}^{\mathrm{II}}, \mathrm{C}^{\mathrm{I}}\cdots\mathrm{C}^{\mathrm{III}}, \mathrm{C}^{\mathrm{II}}\cdots\mathrm{C}^{\mathrm{IV}}, \mathrm{C}^{\mathrm{III}}\cdots\mathrm{C}^{\mathrm{I}'})$

$q_a(\mathrm{H}_1{}^{\mathrm{II}}\cdots\mathrm{H}_2{}^{\mathrm{II}}, \mathrm{H}_1{}^{\mathrm{IV}}\cdots\mathrm{H}_2{}^{\mathrm{IV}})$

$q_b(\mathrm{H}^{\mathrm{I}}\cdots\mathrm{Cl}^{\mathrm{I}}, \mathrm{H}^{\mathrm{III}}\cdots\mathrm{Cl}^{\mathrm{III}})$

$q_c(\mathrm{C}^{\mathrm{I}}\cdots\mathrm{H}_1{}^{\mathrm{II}}, \mathrm{C}^{\mathrm{I}}\cdots\mathrm{H}_2{}^{\mathrm{II}}, \mathrm{C}^{\mathrm{III}}\cdots\mathrm{H}_1{}^{\mathrm{II}}, \mathrm{C}^{\mathrm{III}}\cdots\mathrm{H}_2{}^{\mathrm{II}}, \mathrm{C}^{\mathrm{III}}\cdots\mathrm{H}_1{}^{\mathrm{IV}}, \mathrm{C}^{\mathrm{III}}\cdots\mathrm{H}_2{}^{\mathrm{IV}}, \mathrm{C}^{\mathrm{I}'}\cdots\mathrm{H}_1{}^{\mathrm{IV}}, \mathrm{C}^{\mathrm{I}'}\cdots\mathrm{H}_2{}^{\mathrm{IV}})$

$q_d(\mathrm{C}^{\mathrm{IV}'}\cdots\mathrm{H}^{\mathrm{I}}, \mathrm{C}^{\mathrm{II}}\cdots\mathrm{H}^{\mathrm{I}}, \mathrm{C}^{\mathrm{II}}\cdots\mathrm{H}^{\mathrm{III}}, \mathrm{C}^{\mathrm{IV}}\cdots\mathrm{H}^{\mathrm{III}})$

$q_e(\mathrm{C}^{\mathrm{IV}'}\cdots\mathrm{Cl}^{\mathrm{I}}, \mathrm{C}^{\mathrm{II}}\cdots\mathrm{Cl}^{\mathrm{I}}, \mathrm{C}^{\mathrm{II}}\cdots\mathrm{Cl}^{\mathrm{III}}, \mathrm{C}^{\mathrm{IV}}\cdots\mathrm{Cl}^{\mathrm{III}})$

For the first calculation we used the force constants transferred from polyethylene[3], 1, 2-dichloroethane[5], and 1, 1, 2, 2-tetrachloroethane[6]. These force constants are indicated as Set 1 in Table IV. The molecular constants assumed are also given in Table IV. From these values the characteristic values, L-matrix, potential energy distribution, and Jacobian $\partial(\nu_1\cdots\nu_k)/\partial(K_1\cdots K_n)$ were calculated with the use of the PC-1 computer built in the Department of Physics, The University of Tokyo. In the next calculation, taking into account the results of the first calculation and the observed values, we introduced the new force constants, Sets 2 and 3 given in Table IV, and repeated the calculation in the same way. In the case of Set 2 the force constants are adjusted so that the calculated frequencies show the best agreement with the observed values of polyvinyl chloride. Set 3 was obtained by modifying the former sets in such a way as to make the calculated frequencies correspond reasonably to the observations for deuterated polyvinyl chloride also.

TABLE IV. FORCE CONSTANTS (in millidyn./Å)[a] AND INTRAMOLECULAR TENSION (κ) (in millidyn. Å)

		Set 1	Set 2	Set 3
1	$K(\mathrm{C{-}C})$	2.8[b]	3.10	3.00
2	$K(\mathrm{C{-}H})_{\mathrm{CHH}}$	4.2[b]	4.15	4.15
3	$K(\mathrm{C{-}H})_{\mathrm{CHCl}}$	3.90[d]	4.10	4.10
4	$K(\mathrm{C{-}Cl})$	1.81[c]	1.65	1.70
5	$\kappa(\mathrm{-CHH-})$	0.2[b]	0.21	0.20
6	$\kappa(\mathrm{-CHCl-})$	0.10[c]	0.10	0.10
7	$H(\mathrm{C{-}C{-}C})$	0.2[b]	0.20	0.20
8	$H(\mathrm{H{-}C{-}H})$	0.4[b]	0.36	0.38
9	$H(\mathrm{H{-}C{-}C})_{\mathrm{CHH}}$	0.15[b]	0.09	0.12
10	$H(\mathrm{H{-}C{-}Cl})$	0.05[c]	0.06	0.06
11	$H(\mathrm{H{-}C{-}C})_{\mathrm{CHCl}}$	0.15[c]	0.15	0.15
12	$H(\mathrm{Cl{-}C{-}C})$	0.10[c]	0.10	0.10
13	$F(\mathrm{C}\cdots\mathrm{C})$	0.3[b]	0.50	0.45
14	$F(\mathrm{H}\cdots\mathrm{H})$	0.1[b]	0.06	0.08
15	$F(\mathrm{H}\cdots\mathrm{C})_{\mathrm{CHH}}$	0.4[b]	0.43	0.41
16	$F(\mathrm{H}\cdots\mathrm{Cl})$	0.80[c]	0.80	0.80
17	$F(\mathrm{H}\cdots\mathrm{C})_{\mathrm{CHCl}}$	0.40[c]	0.45	0.45
18	$F(\mathrm{Cl}\cdots\mathrm{C})$	0.60[c]	0.50	0.55

Molecular constants

$r(\mathrm{C{-}C})=1.54\,\text{Å}$, $r(\mathrm{C{-}H})=1.09\,\text{Å}$, $r(\mathrm{C{-}Cl})=1.77\,\text{Å}$,
All the bond angles=109°28′

a F' is assumed to be $-0.1\,F$.
b Transferred from polyethylene[3].
c Transferred from 1,2-dichloroethane[5].
d Transferred from 1,1,2,2-tetrachloroethane[6].

The calculated frequencies are compared with the observed in Tables V and VI, in which the assignments of bands based on the calculated potential energy distribution are also given.

Discussion

Polyvinyl Chloride (PVC). — Of the three infrared active species, A_1, B_1 and B_2, only B_2

---

[5] S. Mizushima, I. Nakagawa, I. Ichishima and T. Miyazawa, ibid., 22, 1614 (1954).

[6] K. Naito, I. Nakagawa, K. Kuratani, I. Ichishima and S. Mizushima, ibid., 23, 1907 (1955).

TABLE V. CALCULATED AND OBSERVED FREQUENCIES OF POLYVINYL CHLORIDE (in cm^{-1}) and assignments

Calcd.			Obs.^{d}		Assignment
1^{a}	2^{b}	3^{c}			
2891 2880	2969 2969	2969 2968	2967	w σ	CH str. (B_1), (A_1)
2921 2919	2911 2910	2905 2905	2920	m σ	CH_2 antisym. str. (B_1), (B_2)
2905	2871	2873	2849	w σ	CH_2 sym. str. (A_1)
			2820	vvw σ	
1501	1425	1459	1427	s σ	CH_2 bend. (A_1)
1392	1340	1360	1381	vw π	CH_2 wag. (B_2)
1397	1343	1367	1352	vw σ	CH_2 wag. (B_1)
1225	1246	1245	1330	m σ	CH bend. (A_1)
1227	1245	1244	1250	s σ	CH bend. (B_1)
			1243	vvw σ	
1190	1210	1208	1228	w π	CH bend. (B_2)
			1197	w π	
1030	1063	1054	1125	vw π	CC str. (B_2)
1076 1028	1103 1089	1100 1071	1096	m σ	CC str. (A_1), (B_1)
1016	976	993	963	m σ	CH_2 rock. (B_1)
1026	930	977	926	vw σ	CH_2 twist. (A_1)
874	832	849	833	w π	CH_2 rock. (B_2)
			693	m σ	
663	639	651	635	s σ	CCl str. (A_1)
			615	s σ	
639	624	633	603	w σ*	CCl str. (B_1)
			487	vw	
444	458	452	430	w	CCC def. (B_1)
343	328	338	363	w	CCl bend. (A_1)
313 290	294 283	303 290	315	vw	CCl bend. (B_2) CCl bend. (B_1)
			182 160	w w	torion (A_1, B_2)
			102	vw	

a Calculated from the force constants, Set 1.
b Calculated from the force constants, Set 2.
c Calculated from the force constants, Set 3.
d See Refs. 1, 2, 7—11.
* As to the dichroism of the 603 cm^{-1} band we shall report later.

should have parallel dichroism when the molecular chains are oriented along the stretching direction. As shown in Table V the observed parallel bands correspond reasonably to the calculated B_2 frequencies. The perpendicular bands, also, show good correspondence with the calculated A_1 and B_1 frequencies. The main points of the present assignment are summarized as follows:

1) Both of the two CH stretching frequencies which belong to the A_1 and B_1 species are assigned to the band at 2967 cm^{-1}. The former assignment1) of the CH stretching mode (A_1) to the 2820 cm^{-1} band is improper because of the weak interaction between the two CH bonds. This is also the case for 1, 1, 2, 2-tetrachloroethane, in which the two CH bonds are situated nearer than in polyvinyl chloride. The CH stretching frequency of this compound appears only at 2990 cm^{-1} in infrared spectra and at 2989 cm^{-1} in Raman spectra6).

2) Krimm and Liang1) assigned the A_1 and B_1 CH bending modes to the bands at 1330 cm^{-1} and 1250 cm^{-1}, respectively, However, because of the weak interaction between the two CH bonds such great splitting can not be expected. This expectation is confirmed clearly by our calculation. The calculated Jacobian shows that both of these frequencies depend similarly on the force constants H(H–C–Cl), $H(\text{H–C–C})_{\text{CHCl}}$, F(H···Cl), $F(\text{H}\cdots\text{C})_{\text{CHCl}}$, and κ_{CHCl}, and it is impossible to separate them. The corresponding frequencies are found in 1, 1, 2, 2-tetrachloroethane at 1304 cm^{-1} (A_u)

TABLE VI. CALCULATED AND OBSERVED FREQUENCIES OF DEUTERATED POLYVINYL CHLORIDE (in cm^{-1}) AND ASSIGNMENTS

Calcd.		Obs.[c]	Assignment
1[a]	3[b]		
2120 2111	2177 2169	2228 m σ	CD str. (A_1, B_1)
2164 2163	2151 2152	2159 vw σ	CD_2 antisym. str. (B_1, B_2)
2095	2090	2122 vw σ	CD_2 sym. str. (A_1)
1218	1225	1273 w σ	CC str.+CD_2 bend. (A_1)
1254	1261	1251 m π	CC str.+CD_2 wag. (B_2)
1170	1189	1112 s σ	CC str.+CD_2 wag. (B_1)
		1091 sh ?	
1024	1028	1041 sh σ	CD bend.+CC str. (B_1)
998	986	1017 vs σ	CD_2 bend.+CD bend. (A_1)
		958 sh σ	
938	930	937 s π ?	CD_2 wag.+CD bend. (B_2)
909	905	904 sh π ?	CD_2 rock.+CD_2 wag. (B_1)
844	858	886 vw ?	CD bend.+CD_2 bend. (A_1)
		836 w π ?	
806	807	806 w π	CD bend.+CD_2 wag.+CD_2 rock. (B_2)
820 805	822 771	787 s σ	CD bend.+CD_2 rock.+CCl str. (B_1) CD_2 twist.+CCl str. (A_1)
685	672	680 vw π	CD_2 rock. (B_2)
		628 m σ	
591	574	594 m σ	CCl str.+CD_2 twist. (A_1)
		573 w σ	
586	575	568 m σ	CCl str.+CD_2 rock. (B_1)
374	391		CCC def. (B_1)
330	322		CCl bend. (A_1)
279	272		CCl bend. (B_2)
260	260		CCl bend. (B_1)

a Calculated from the force constants, Set 1.
b Calculated from the force constants, Set 3.
c See Ref. 2.

and 1308 cm^{-1} (B_g) for the trans from, and at 1280 cm^{-1} (A) and 1243 cm^{-1} (B) for the gauche form. Even in the gauche form the splitting does not exceed 40 cm^{-1}. So, at first it seemed reasonable to assign the 1250 cm^{-1} band to both A_1 and B_1 CH bending modes and the 1330 cm^{-1} band to the CH_2 wagging mode (B_1). On the other hand the change of the dichroism observed for PVC films of varying degrees of stretching (which will be reported later) shows that the 1330 and 1250 cm^{-1} bands should belong to A_1 and B_1 species, respectively. This fact can be understood if we assume that strong coupling takes place between one of the CH bending modes and the CH_2 wagging or twisting mode, and the large splitting of frequencies occurs, though it is inconsistent with the results of our calculation. This deviation may be due to the incompleteness of the force constants given in Table IV. Ambiguity is still remaining as to this point; our final assignments are shown in Table V.

3) The bands at 1228, 963 and 833 cm^{-1} are assigned to CH bending (B_2), CH_2 rocking (B_1), and CH_2 rocking (B_2) frequencies, respectively, according to the results of the calculation. The 1228 cm^{-1} band was assigned by Krimm et al.[7] to the overtone of the 615 cm^{-1} band. However, this band remains definitely in the spectrum of the highly syndyotactic polymer for which the 615 cm^{-1} band is observed as a shoulder of the 603 cm^{-1} band. Kawasaki et al.[8] suggested that the very weak band found at 1243 cm^{-1} may be assignable to the overtone of the 615 cm^{-1} band.

4) The bands at 2820, 1197, 693 and 615 cm^{-1} are not assigned. The 693 cm^{-1} band is associated with the atactic structure and the 615 cm^{-1} band with the syndyotactic structure, which is not in the ordered configuration,

---

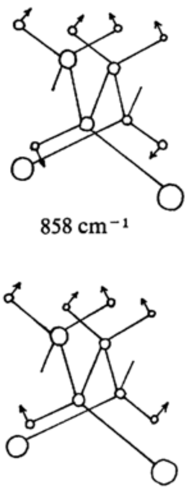
7) S. Krimm, A. R. Berens, V. L. Folt and J. J. Shipman, *Chem. & Ind.*, **1958**, 1512.

8) A. Kawasaki et al., *Abstr. of Symposium on the Infrared and Raman Spectroscopy (Tokyo)*, p. 41 (1959).

because they can not be observed for the sample prepared by radiation-induced polymerization of a urea-vinyl chloride complex[7,9-11]. The band at 1197 cm^{-1} seems to behave analogously, but in a less distinct manner.

5) The band at 926 cm^{-1} is only tentatively assigned to the CH_2 twisting frequency. It is known that for some vibrational modes, such as CH_3 rocking vibrations in ethane and CH_2 twisting vibrations in 1, 2-dichloroethane, the calculated frequencies deviate considerably from the observed[4,12-14]. Therefore, it may be undesirable to assign the 926 cm^{-1} band to the CH_2 twisting mode simply because it corresponds to the calculated value of 977 cm^{-1}. More detailed investigation of the intramolecular potential field seems to be necessary to settle this problem.

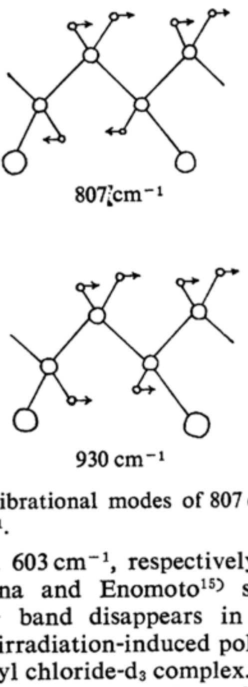
Deuterated Polyvinyl Chloride.—1) The infrared spectrum of deuterated PVC was reported by Enomoto et al.[2] Compared with the spectrum of normal PVC, it is quite complicated and hard to analyze, as many bands are found in the 800 cm^{-1} to 1300 cm^{-1} region. From the results of the present calculation and the observed dichroism tentative assignments are proposed for the main bands. The calculated potential energy distribution and L-matrix indicate that a strong coupling of two or more modes occurs for most bands of deuterated PVC. For example, for the calculated 858 cm^{-1} (A_1) vibration, in-phase coupling of the CD_2 and CD bending modes occurs while in the case of the calculated 986 cm^{-1} (A_1) vibration, out-of-phase coupling occurs. This is shown in Fig. 2. The in-phase mode is expected to be weak in intensity, and it probably corresponds to the very weak band at 886 cm^{-1}. The intensity of the out-of-phase mode is strong and it undoubtedly corresponds to the very strong band at 1017 cm^{-1}. A similar situation is found for the calculated 807 cm^{-1} (B_2) and 930 cm^{-1} (B_2) vibrations (see Fig. 3). The 930 cm^{-1} mode is expected to be strong and corresponds to the strong parallel band at 937 cm^{-1}, and the 807 cm^{-1} mode is weak and corresponds to the weak band at 806 cm^{-1}.



858 cm^{-1}

986 cm^{-1}

Fig. 2. Vibrational modes of 858 cm^{-1} and 986 cm^{-1}.



807 cm^{-1}

930 cm^{-1}

Eig. 3. Vibrational modes of 807 cm^{-1} and 930 cm^{-1}.

2) The bands at 594 cm^{-1} and 568 cm^{-1} are assigned to the CCl stretching frequencies (A_1 and B_1). These bands correspond to those at 635 cm^{-1} and 603 cm^{-1}, respectively, of normal PVC. Asahina and Enomoto[15] showed that the 628 cm^{-1} band disappears in the sample obtained by irradiation-induced polymerization of a urea-vinyl chloride-d_3 complex. Therefore, this band is the contribution of the atactic structure and corresponds to the 690 cm^{-1} band of normal PVC. The deuterated PVC prepared by Enomoto et al. was kindly made available to us. We measured the spectrum of this sample using a grating spectrometer (Perkin-Elmer Model 112G) and found a new band at about 573 cm^{-1}, which probably corresponds to the 615 cm^{-1} band of normal PVC. All four bands of deuterated PVC are perpendicular.

As stated above the observed infrared absorption bands, including their dichroism, can

---

[9] T. Shimanouchi, S. Tsuchiya and S. Mizushima, *J. Chem. Phys.*, **30** 1365 (1959).

[10] T. Shimanouchi, S. Tsuchiya and S. Mizushima, *The High Polymer* (*Kobunshi*), **8**, 202 (1959).

[11] S. Krimm, A. R. Berens, V. L. Folt, and J. J. Shipman, *Chem. & Ind.*, **1959**, 433.

[12] I. Nakagawa and S. Mizushima, *J. Chem. Phys.*, **21**, 2195 (1953).

[13] I. Nakagawa, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **74**, 848 (1953).

[14] I. Nakagawa, ibid., **77**, 1030 (1956).

[15] M. Asahina and S. Enomoto, ibid., **81**, 1374 (1960).

be satisfactorily accounted for on the basis of the calculation of normal vibrations. This gives a further confirmation of the syndyotactic configuration for the crystalline part of polyvinyl chloride. The remaining important problem is to study the potential field more thoroughly, and for this purpose the comparative investigation of other polymers and related compounds will be indispensable.

We wish to thank Professor H. Takahashi for making available the PC-1 computer. Thanks are also due to Dr. K. Nambu and Mr. S. Enomoto, who kindly gave us various samples of polyvinyl chloride.

Department of Chemistry
Faculty of Science
The University of Tokyo
Hongo, Tokyo