S. MIZUSHIMA - T. SHIMANOUCHI · I. HARADA

REEXAMINATION OF CONFORMATIONS
OF SOME MOLECULES

REEXAMINATION OF CONFORMATIONS
OF SOME MOLECULES

S. MIZUSHIMA *Pontifical Academician,*

T. SHIMANOUCHI and I. HARADA

SVMMARIVM — Novae spectrorum Raman et infrarubrorum 1,2 dichloroetani mensiones, variis adhibitis ad experimenta facienda condicionibus, congruunt cum computationibus de interiore rotatione, per viam quantomechanicam effectis; ita et priores nostrae conclusiones confirmantur et nova elementa praebentur.

Introduction

For the past forty years the structures of a large number of molecules have been studied in our laboratory in relation to internal rotation about single bonds as axes [1]. During this period when we found something new which could not be explained satisfactorily from the conclusions so far obtained, we have always reexamined the molecular structure of 1,2-dichloroethane $ClH_2C\text{-}CH_2l$ which was the first substance of our series of researches. The reexaminations including those of Raman and infrared spectra, dielectric constant, electron diffraction and entropy, have often given

us clues to the explanation of the experimental results found newly for the internal rotation in many other polyatomic molecules including those of polymers.

Our earlier conclusion arrived at in 1940's was that in the gaseous and liquid states and in solutions the molecules of 1,2-dichloroethane assume the trans and gauche forms (See Fig. 1), and in the solid state only the trans form, although the lattice mode due to rotation changes on crossing the transition point [2] (See Fig. 2). (Hereafter the trans form with symmetry C_{2h} is abriviated as T and the gauche form with symmetry C_2 as G. The solid above the transition point is denoted as solid I and that below this point as solid II). The equilibrium ratio between T and G in the gaseous state and in dilute solutions was also determined.

The incentive of the present remeasurement was given by the recent development of the experimental techniques together with our success in making a package of computor programs for the calculation of vibrational and torsional frequencies and vibrational modes [3] so that we can now make clear some points left undetermined in our previous work. Figs. 3-6 give the spectra we remeasured which support our previous results.
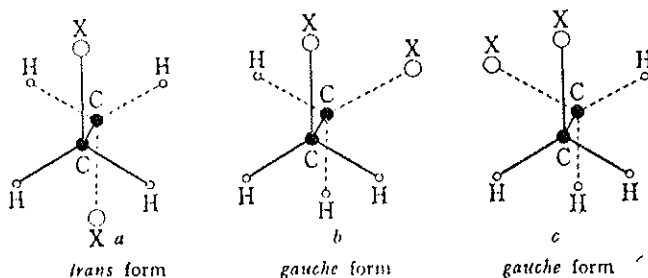

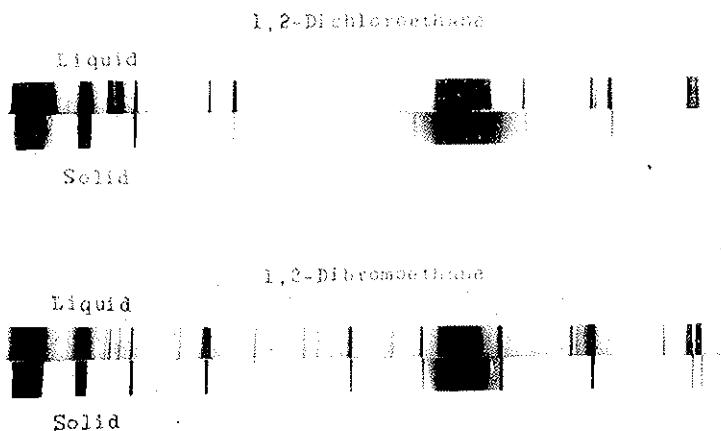FIG. 1 — Stable conformations of 1,2-dihalogenoethanes.

FIG. 2 — Raman spectra of 1,2-dichloroethane in the liquid and solid states (1937).

1,2-dichloroethane in solid II

In our previous papers [4] we considered the crystal field has a center of symmetry which allows three kinds of rotatory vibrations to appear in the Raman effect. At that time we found only two lines, because the photographic method did not allow us to detect satisfactorily low frequency Raman lines which are masked by the wings of the strong unmodified lines. With the use of the laser as an excitation source and the suitable photomultiplier system as a detector, the experimental difficulties in this frequency region have been overcome and satisfactory results of the measurement have been obtained as shown in Fig. 6.

Meanwhile, X-ray analysis of this substance (solid I and II) was made by LIPSCOMB and his collaboraters who showed
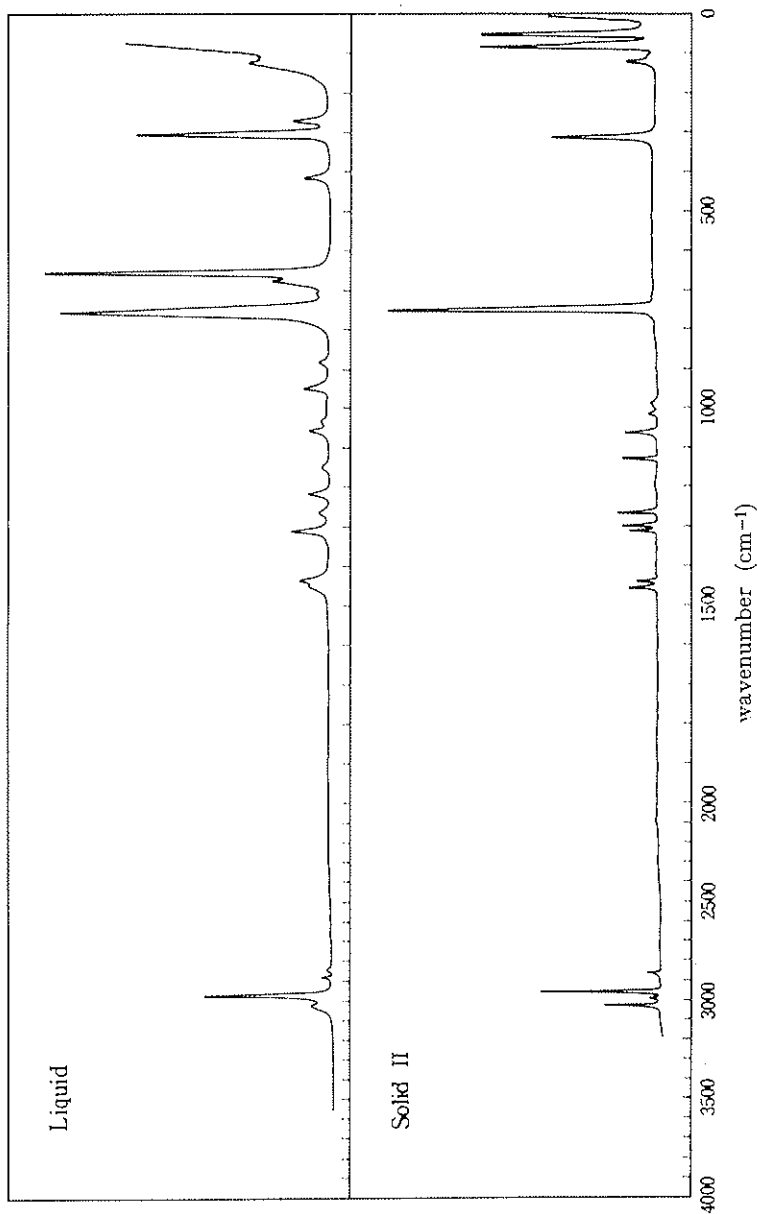
3

Fig. 3 — Raman spectra of 1,2-dichloroethane in the liquid and solid II (at liquid nitrogen temperature) states.
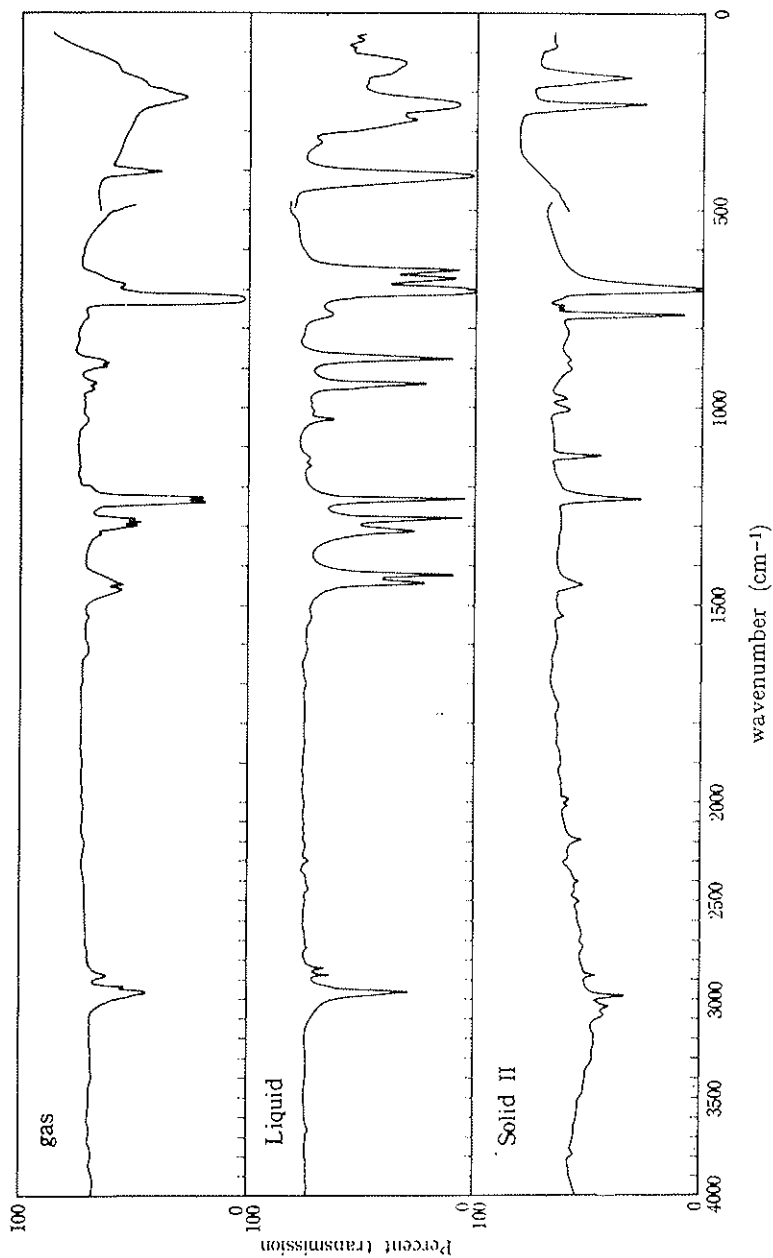
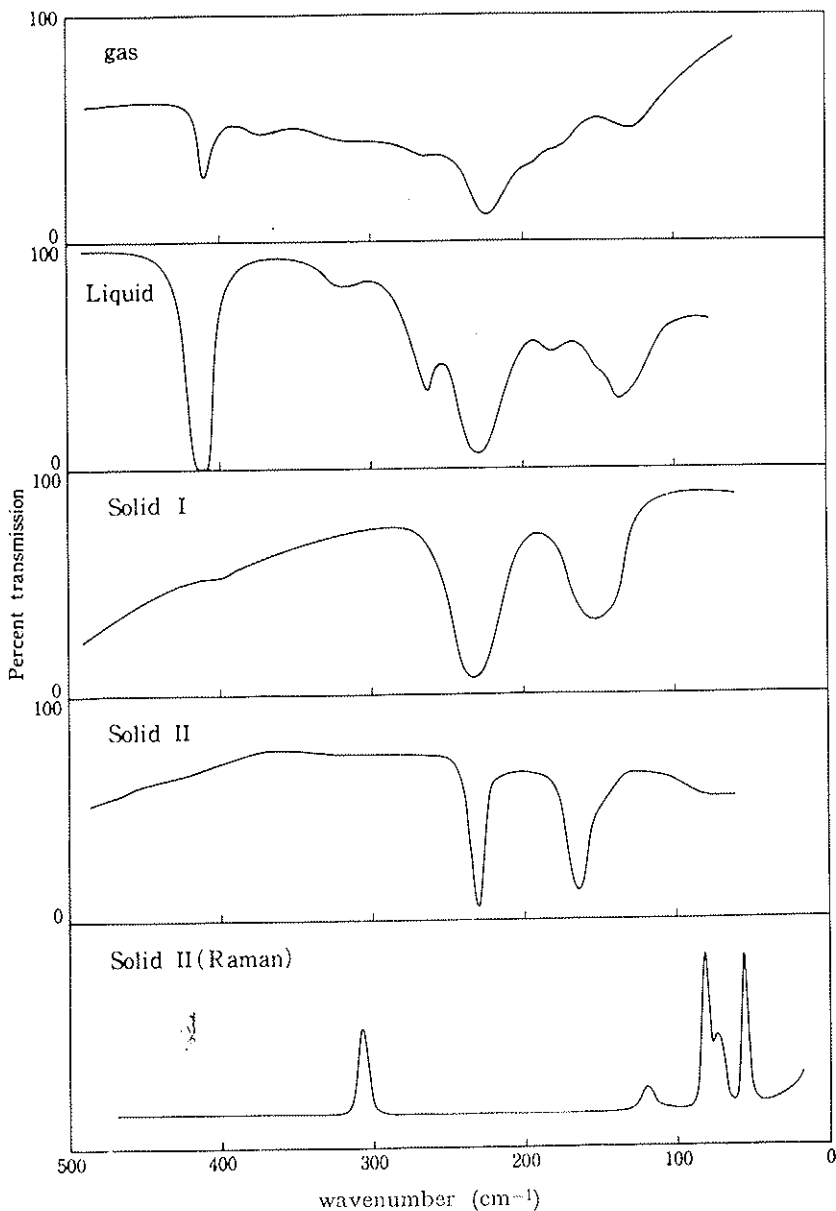FIG. 4 — Infrared spectra of 1,2-dichloroethane in the gaseous, liquid and solid II states.

FIG. 5 — Far-infrared spectra of 1,2-dichloroethane in the gaseous, liquid, solid I (at the temperature of dry-ice and ethanol mixture) and solid II (at liquid nitrogen temperature) states and Raman spectra in the solid II state in the same wavenumber region.
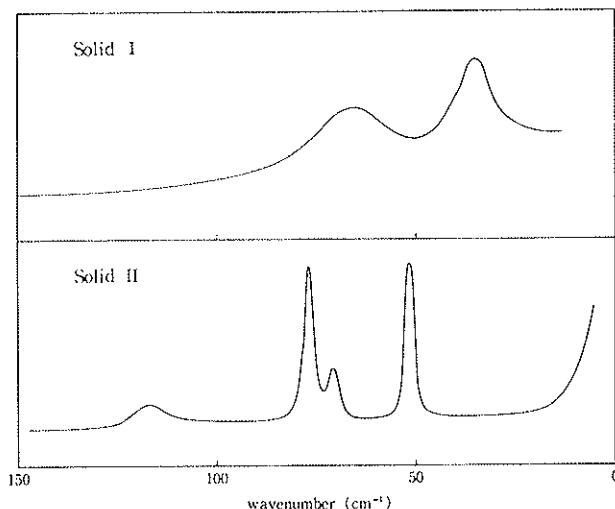
FIG. 6 — Low frequency Raman spectra of 1,2-dichloroethane in the solid I and II states.

that the unit cell contains two molecules and the crystal field does have a center of symmetry [5, 6]. Therefore, the three rotatory vibrations said above are Raman active. However, to be more exact, we have to take into account the interaction between molecules which results in symmetric and antisymmetric rotatory vibrations and we expect six Raman lines of the frequencies ν_{x1}, ν_{x2}, ν_{y1}, ν_{y2}, ν_{z1} and ν_{z2}. Here z denotes the direction of the molecular axis or the axis joining two chlorine atoms and x and y denote those of the axes, both perpendicular to z axis.

Of these frequencies the highest one corresponds to ν_{z1} or ν_{z2}, because the moment of inertia about the molecular axis is much less than those about the other two. Thus we can assign the Raman band observed at 118 cm^{-1} to ν_{z1} or ν_{z2}, but very probably to both of them, since we may consider the molecular interaction in this case is too small to observe

7

two separate bands. Similarly we may assign the band observed at 56 cm^{-1} to both ν_{y1} and ν_{y2}, if we take the axes in such a way that the interaction between molecules is greatest for ν_{x1} and ν_{x2}, these being assigned to the bands observed at 78 cm^{-1} and 73 cm^{-1}.

The assignment made above is most probable, but if the interaction between molecules is much stronger than we expected as above, we may have to assign the observed bands at 78 cm^{-1} and 56 cm^{-1} to ν_{x1} and ν_{x2}. In this case the band observed at 73 cm^{-1} is assigned to ν_{y1} and that at 56 to ν_{y2} which falls on ν_{x2}.

1,2-dichloethane in solid I

In our previous paper [4] we considered the free rotation about the molecular axis sets in above the transition point. This was found to be consistent with the result of X-ray analysis [5, 6] published soon after our previous paper. From this we can understand the result of the present experiment that the band at 118 cm^{-1} of solid II assigned to ν_{z1} and ν_{z2} disappears in the Raman spectrum of solid I (See Fig. 6).

Since the free rotation about the molecular axis sets in above the transition point, the moments of inertia about x and y axes are equal to each other. Therefore, the fact that two bands are observed at 60 cm^{-1} and 40 cm^{-1} is to be explained as due to the difference in the restoring forces between the two rotatory vibrations about x and y axis. Both of these bands are broad enough to consider that ν_{x1} falls on ν_{x2} and ν_{y1} on ν_{y2}. This seems to be the probable assignment.

If, however, the interaction between molecules is stronger, we may make an alternative assignment as we did for solid II. In this case we assign one of the two bands to ν_{x1} and ν_{y1} delete (falling on each other) and the other to ν_{x2} and ν_{y2}.

It is to be noted that the observed bands become broader as the temperature is raised and the broadness of the higher frequency band becomes remarkable near the melting point. Evidently all the bands explained above disappear in the liquid state.

In Table II all the Raman and infrared frequencies observed in the solid state are listed. It is seen that the mutual exclusion rule holds and we are sure that the molecule of 1,2-dichloroehtane is in the trans form with the center of symmetry. Furthermore, the agreement between the observed and calculated values is more satisfactory than that reported previously [1]. Thus we could confirm our previous conclusions.

It may not be out of place to make a remark on the difference in the torsional frequency (about C-C single bond as axis) between the liquid and solid states. (See the infrared spectra shown in Fig. 5). The frequency 125 cm^{-1} observed in the liquid state changes to 153 cm^{-1} in solid I and to 164 cm^{-1} in solid II. The higher frequencies observed in the solid state can be explained as due to the crystal field which stabillizes the trans form in this state. (See Table I and Fig. 5). Furthermore, we would like to note that tbe vibration band at 223 cm^{-1} previously observed by us and assigned to CCCl antisymmetric deformation mode [7] was also observed by PITZER et al [8]. As shown in Fig. 5 this band was more clearly observed at 230 cm^{-1} (liquid) and at 234 cm^{-1} (solid II) in the present experiment.

1,2-dichloroethane in the liquid and gaseous states

Our previous conclusion that the molecules of 1,2-dichloroethane in the liquid and gaseous states assume both the trans and gauche forms, has also been confirmed by the more precise measurement of the present experiment (See Table II).

TABLE I — *Vibrational spectra of 1,2-dichloroethane in the solid state.*

Raman	infrared	calcd.	assignments (trans)	
—	3040	3012 (a_u)	ν_7	CH$_2$ antisym. str.
3013 ⎫ * 2985 ⎭	—	2998 (b_g)	ν_{11}	"
—	2980	2965 (b_u)	ν_{14}	CH$_2$ sym. str.
2966	—	2949 (a_g)	,,	"
—	2880	—	($\nu_2 + \nu_{15}$)	
2869	—	—	($2\nu_2$)	
1457 ⎫ * 1438 ⎭	—	1445 (a_g)	ν_2	CH$_2$ scis.
—	1450	1453 (b_u)	ν_{15}	"
1311 ⎫ * 1300 ⎭	—	1305 (a_g)	ν_3	CH$_2$ wag.
1263	—	1265 (b_g)	ν_{12}	CH$_2$ twist.
—	1236	1233 (b_u)	ν_{16}	CH$_2$ wag.
—	1128	1132 (a_u)	ν_8	CH$_2$ twist.
1124	—	—	($\nu_5 + \nu_6$)	
1058	—	1052 (a_g)	ν_4	CC str.
1009 ⎫ * 995 ⎭	—	991 (b_g)	ν_{13}	CH$_2$ rock.
—	1006	—	($\nu_{17} + \nu_6$)	
—	976	—	($\nu_5 + \nu_{18}$)	
—	900	—	($\nu_5 + \nu_{10}$)	
—	768	768 (a_u)	ν_9	CH$_2$ rock.
747	—	759 (a_g)	ν_5	CCl. str.
—	700	713 (b_u)	ν_{17}	"
300	—	300 (a_g)	ν_6	CCCl deform.
—	234	230 (b_u)	ν_{18}	"
—	164	136 (a_u) **	ν_{10}	CC torsion
118	—	—	lattice vibration	
78	—	—	"	
73	—	—	"	
56	—	—	"	

* The spliting of the frequencies into doublet can be explained as due to crystal field.

** The values listed in the third column were calculated from the force constants of the molecules in the liquid state.

TABLE II — *Vibrational spectra of 1,2-dichloroethane in the liquid state.*

Raman	infrared	calcd.	gauche	assignments	trans
—	—	3009	v'_{11}	CH$_2$ antisym. str.	v_7
2996	—	3001	v'_1	"	v_{11}
—	2980	2960	v'_{12}	CH$_2$ sym. str.	v_{14}
2950	—	2954	v'_2	"	v_1
2873	2878	—	$(v'_{13}+v'_3)$		v_2+v_{15}
2843	2842	—	$(2v'_3)$		$2v_2$
1446	1449	1432	v'_{13}	CH$_2$ scis.	v_{15}
1431	1428	1431	v'_3	"	v_2
—	1318	1316	v'_4	CH$_2$ wag.	—
1306	—	—	—		v_3
—	1288	1289	v'_{14}	CH$_2$ wag.	
1263	—	—	—		v_{12}
—	1235	—	—		v_{16}
1209	—	1207	v'_5	CH$_2$ twist.	—
1142	1143	1146	v'_{15}	"	—
—	1125	—	—		v_8
1052	—	—	—		v_4
1033	1030	1030	v'_6	CC str.	—
—	—	—	—		v_{13}
942	942	939	v'_7	CH$_2$ rock.	—
880	880	889	v'_{16}	"	—
—	768	—	—		v_9
754	—	—	—		v_5
709	708	—	—		v_{17}
675	672	669	v'_{17}	C-Cl str.	—
655	652	655	v'_8	"	—
411	410	411	v'_{18}	CCCl deform.	—
299	—	—	—		v_6
262	265	263	v'_9	CCCl deform.	—
—	230	—	—		v_{18}
—	125	—	—		v_{10}
122	—	128	v'_{10}	CC torsion	—

11

All the Raman and infrared frequencies not observed in the solid state can be assigned to the gauche form which has the symmetry C_2 and which, therefore, can show the same frequencies in both the Raman and infrared spectra. The result of calculation which is more exact than the previous one confirms that the assignment of observed frequencies are correct. This is also shown from the observed envelopes of the infrared absorption bands in the gaseous state. (See Figs. 4 and 7 and Table III) [9]. The difference in the relative intensity in the infrared spectra between the liquid and gaseous states is due to the difference in the equilibrium ratio of the number of the trans and gauche molecules as explained in our previous papers.

Quantum mecanical treatment of internal rotation

The quantum mechanical treatment of the internal rotation of 1,2-dichloroethane is to be made as an asymmetric top problem. Since the reduced moment of inertia as well as the potential function depends on the internal rotation angle, both the kinetic energy and potential energy parts of the SCHRÖDINGER equation become the functions of internal rotation angle.

Assuming a reasonable type of potential as a function of internal rotation angle, we have solved the wave equation numerically. In Figs. 8 and 9 are shown the energy levels obtained in this way and in Fig. 10 the eingenfuctions corresponding to the energy levels in the gaseous state. As can be seen from this figure, the eingenfuctions belonging to the trans form only have appreciable values in the neighborhood of the trans state and those belonging to the gauche form in the neighborhood of the gauche state. Thus it is shown our proposition of rotational isomers is also supported from quantum mechanical point of view.
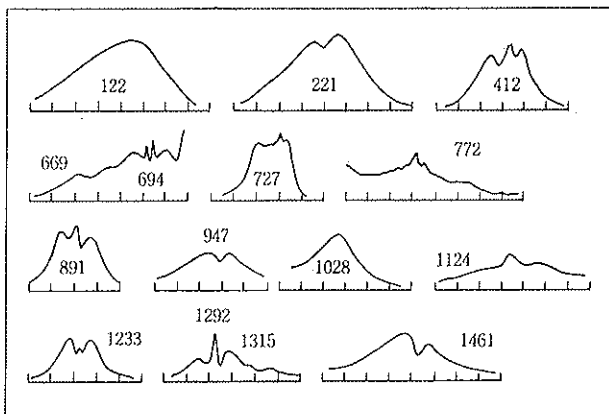
FIG. 7 — Infrared band envelopes of 1,2-dichloroethane (Ordinate denotes absorbance in different scale for each band and abscissa denotes frequency in units of 10 cm⁻¹).

TABLE III — *Assignment and types of infrared bands of 1,2-dichloroethane.*

| Frequency in cm^{-1}	Molecular form	Assignment		Band type	
				Predicted	Observed
122	trans	A_u	torsion	C	C?
221	trans	B_u	C-Cl def.	B + (A)	B
412	gauche	B	C-Cl def.	A + C	A + C
669	gauche	A	C-Cl str.	B	B
694	gauche	B	C-Cl str.	A + C	A + C
727	trans	B_u	C-Cl str.	A + (B)	A + B
772	trans	A_u	CH_2 rock.	C	C
891	gauche	B	CH_2 rock.	A + C	A + C
947	gauche	A	CH_2 rock.	B	B
1028	gauche	A	C-C str.	B	?
1124	trans	A_u	CH_2 twist.	C	C
1233	trans	B_u	CH_2 wag.	A + (B)	A + (B)
1292	gauche	B	CH_2 wag.	A + C	A + C
1315	gauche	A	CH_2 wag.	B	B
1461	trans	B_u	CH_2 bend.	B + (A)	B

13
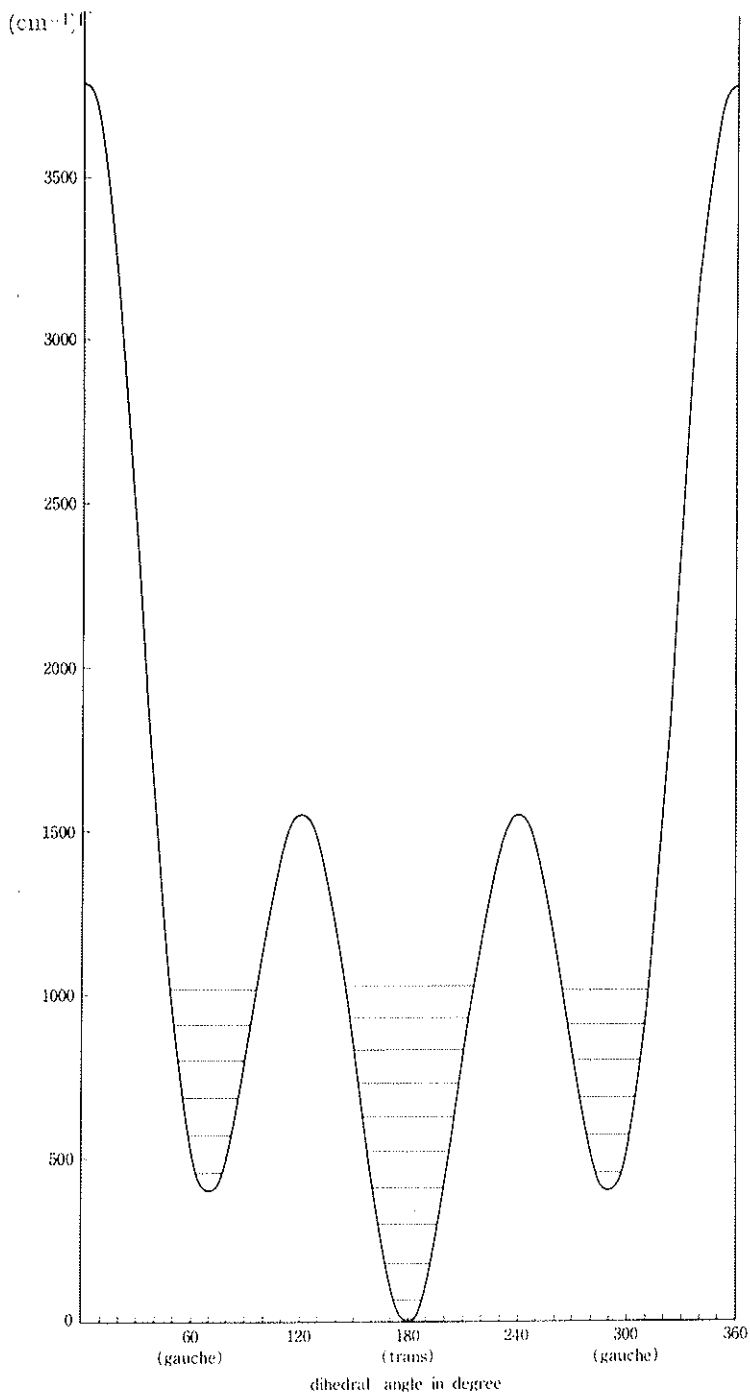
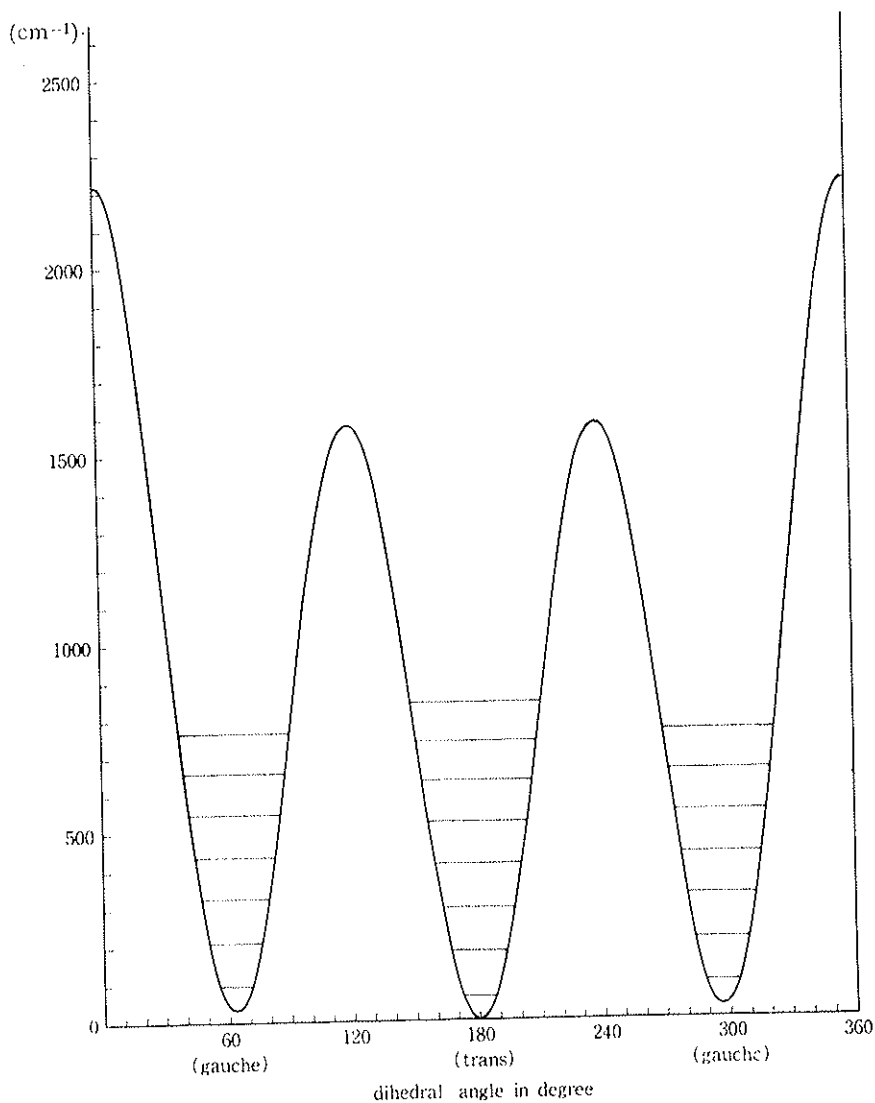Fig. 8 — Potential energy and energy levels for the internal rotation of 1,2-dichloroethane in the gaseous state.

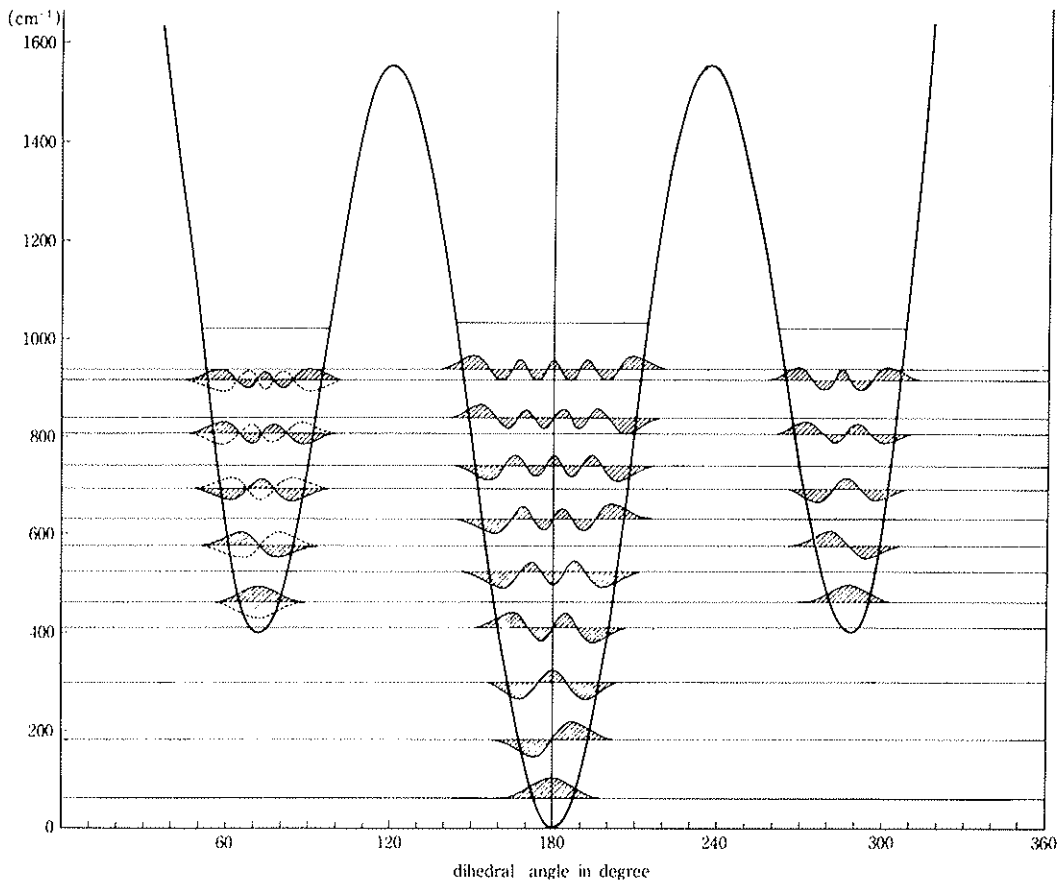FIG. 9 - Potential energy an denergy levels for the internal rotation of 1,2-dichloroethane in the liquid state.

FIG. 10 — Energy levels and eigenfuctions for the internal rotation of 1,2-dichloroethane in the gaseous state. Each energy level beloging to the gauche form consists of the symmetric and antisymmetric ones, the eigenfuction of the latter being given by the dotted lines.
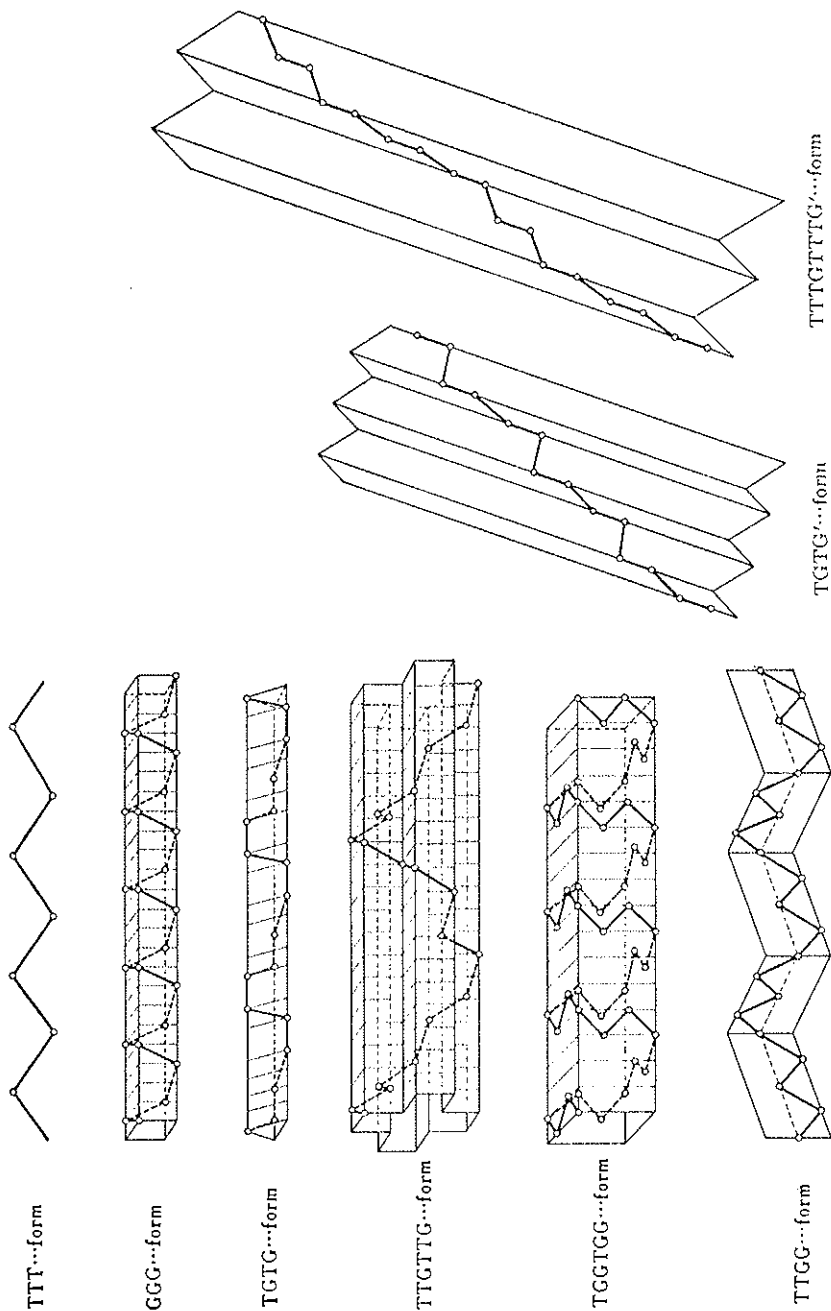
Fig. 11 — Various conformations of n-paraffin molecules.

Chain molecules of hydrocarbons

Molecules consisting of C-C single bond chains always exhibit T or G in their unit structure. The simplest conformation is found in n-paraffin molecules in the solid state and is denoted as TTT--- (See Fig. 11). An interesting spectroscopic result obtained first by us [10] was that each n-paraffin (up to C=16) shows a strong Raman line with frequencies inversely proportional to the number of carbon atoms. The calculation of normal vibrations assigned this mode to the accordion-like motion of an extended carbon chain [10]. Later it was also shown [11] that this relationship holds up to C=94 and can be used to measure the thickness of the single crystal of polyethylene [12].

In the liquid or amorphous states n-paraffins can show different conformations, some of which are shown in Fig. 11. If the hydrocarbon chain contains a C=C double bond or bonds, the conformation of the molecule does not always show what has been described above. The internal rotation about a single bond next to a double bond behaves differently and the stable positions may correspond to cis and skew positions instead of the trans and gauche positions [13].

REFERENCES

[1] Paper up to 1961 are summarized in S. MIZUSHIMA, « Pure and Applied Chemistry », 7, 1 (1963).

[2] MIZUSHIMA, S., MORINO, Y., WATANABE, I., SHIMANOUCHI, T. and YAMAGUCHI, S., « J. Chem. Phys. », 17, 591 (1949).

[3] SHIMANOUCHI, T., « Computer programs for normal coordinate treatment of polyatomic molecules (Department of Chemistry, University of Tokyo, 1968) ».

[4] ICHISHIMA, I. and MIZUSHIMA, S., « J. Chem. Phys. », 18, 1420 (1950). See also MIZUSHIMA, S. and MORINO Y., « Proc. Ind. Acad. Sci. », 8A, 315 (1938).

[5] MILBERG, M.E. and LIPSCOMB, W.N., « Acta Cryst. », 4, 369 (1951).

[6] REED, T.B. and LIPSCOOMB, W.N., « Acta Cryst. », 6, 45 (1953).

[7] MIZUSHIMA, S., MORINO, Y. and SHIMAOOUCHI, T., « Sci. Pap. Inst. Phys. Chem. Res (Tokyo) », 40, 87 (1942).

[8] BONN, C.R., FREEMAN, N.W., GWINN, W.D., HOLLENBERG, J.L. and PITZER, K.S., « J. Chem. Phys. », 21, 719 (1953).

[9] MIZUSHIMA, S., SHIMANOUCHI, T., ICHISHIMA, I. and KAMIYAMA, H., « Rev. Universelle des Min. », 15, 447 (1959).

[10] MIZUSHIMA, S. and SHIMANOUCHI, T., « J. Am. Chem. Soc. », 71, 1320 (1949).

[11] SCHAUFELE, R.F. and SHIMANOUCHI, T., « J. Chem. Phys. », 47, 3605 (1967).

[12] PETICOLAS, W.L., HIBLER, G.W., LIPPERT, J.L., PETERLIN, A. and OLF, H., « Applied Physics Letters », 18, 87 (1971).

[13] SHIMANOUCHI, T., ABE, Y. and ALAKI, Y., « Polymer Journal », 2, 199 (1971).