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INFRARED AND RAMAN SPECTRA OF 1,2
- DICHLOROETHANE AND ITS DEUTERIUM
COMPOUND IN THE GASEOUS, LIQUID AND
SOLID STATES

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ABSTRACT

The infrared and Raman spectra of 1,2-dichloroethane and its deuterium compound in the gaseous, liquid and solid states have been remeasured in the wide range of wave length by the experimental techniques developed recently. Normal coordinate treatments have been made for crystals as well as for free molecules by use of computer programs made by us, and all the vibrational frequencies observed for free molecules and crystals have been assigned satisfactorily. Our previous conclusions of the existence of the trans and gauche forms

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have been confirmed spectroscopically and, furthermore, supported theoretically by the quantum mechanical treatment of the internal rotation.

I. INTRODUCTION

Since the early days of 1930's the structure of a large number of molecules have been studied in our laboratory in relation to the internal rotation about single bonds as axes as summarized by MIZUSHIMA (1954 and 1963). During this period and even after that, when we found something new which could not be explained satisfactorily from the conclusion so far obtained, we have always reexamined the molecular structure of 1,2-dichloroethane $\text{ClH}_2\text{C}-\text{CH}_2\text{Cl}$ which was the first substance of the series of our researches. The reexaminations including those of infrared and Raman spectra, dielectric constants, electron diffraction and entropy, have often given us clues to the explanation of the experimental results found newly for the internal rotations of many other polyatomic molecules including those of polymers. The conclusion arrived at in early 1940's and published by MIZUSHIMA, MORINO and SHIMANOUCI (1942) was that in the gaseous and the liquid states the molecules of 1,2-dichloroethane assume the trans and gauche forms, but in the solid state only the trans form (see Fig. 1). It was also found by MIZUSHIMA and MORINO (1938) that the bands due to the rotational lattice modes change on crossing the transition point at -96°C .

While we have been extending our researches along this line, other authors e. g. OZORA, NAKAGAWA and ITO (1970) and KVESETH (1974), have made measurements on this substance by various experimental methods. The results are in good agreement with ours.

The incentive of the present remeasurement and calculation was given by the recent development of the experimental

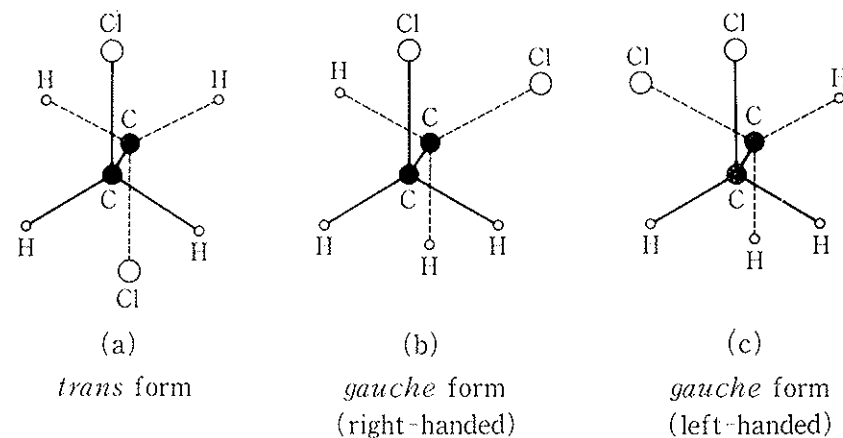


Fig. 1 — Stable conformations of 1,2-dichloroethane.

techniques together with our success in making a package of computer programs by SHIMANOUCI (1968) and those by TAKEUCHI, INAGAKI, HARADA and SHIMANOUCI (1973, 1975) for the more accurate calculation of the vibrational and torsional frequencies and vibrational modes so that we can make clear some points left undetermined in our previous work.

II. EXPERIMENTAL

The infrared spectra were measured with a Japan Spectroscopic 402G Grating Spectrometer except for those in the long wave length region where a Hitachi FIS-1 Vacuum Spectrometer was used. The Raman spectra were recorded using a JEOL JRS-400D Spectrometer with a CR-3 argon ion laser (5145\AA).

The sample of $\text{ClD}_2\text{C}-\text{CD}_2\text{Cl}$ used was that of Merck Sharp & Dohme of Canada.

TABLE 1 — *Atom-pair potentials* *

	A (Kcal mol ⁻¹)	B (Å ⁻¹)	C (Kcal Å ⁶ mol ⁻¹)	Reference**
H...H	2654	3.74	27.3	(1)
C...H	8766	3.67	125	(1)
C...C	83630	3.60	568	(1)
H...Cl	11290	3.627	281	—
C...Cl	87130	3.577	1283	—
Cl...Cl	229000	3.513	2900	(2)

* The form of the potential functions used in this calculation is Buckingham exp-6 type, $V(r) = A \exp(-Br) - Cr^{-6}$, where r is less than 6 Å. The H...Cl and C...Cl potential parameters were adjusted to give the fit with the observed lattice frequencies.

** (1) WILLIAMS (1967) and (2) DASHEVSKY (1970).

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 used in the experiment by MIZUSHIMA and MORINO (1938) did not allow us to detect satisfactorily low frequency Raman lines which tended to be masked by the wings of the strong unmodified lines. With the use of a laser as an exciting source and a 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. 3.

Soon after our above paper (1950) was published, the X-ray analysis of crystalline 1,2-dichloroethane was made by MILBERG and LIPSCOMB (1951) and REED and LIPSCOMB (1953) and LIPSCOMB and WANG (1961) who showed that the unit cell contains two molecules and the crystal field has a center of symmetry as we expected. Therefore, the three rotatory vibrations mentioned above are Raman active. How-

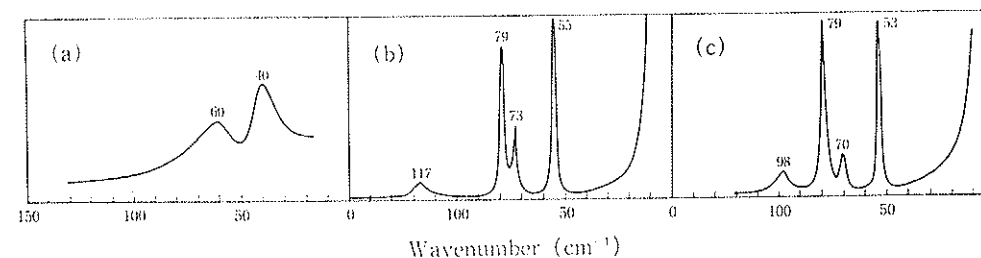


FIG. 3 — Raman spectra of polycrystalline 1,2-dichloroethane in the lattice mode region. (a) C₂H₄Cl₂ above the transition point, (b) C₂H₄Cl₂ at 77°K (below the transition point) and (c) C₂D₄Cl₂ at 77°K.

ever, to be more exact, we have to take into account the interaction between molecules which results in symmetric anti-symmetric rotatory vibrations and we expect six Raman bands: two for every three axes x , y and z , of which z is chosen as the molecular axis, or the axis joining two chlorine atoms and x and y as the axes, both perpendicular to the z axis (x lies in the ClCCl plane).

The bands observed at 117 cm⁻¹ for C₂H₄Cl₂ below the transition point which has the highest frequency can be assigned to the rotatory oscillation about the z axis, because the moment of inertia about the molecular axis is much less than those of the other two, and the change of frequency is greatest on deuteration (98 cm⁻¹ for C₂D₄Cl₂). It is very probable that this broad band corresponds to one of the two rotatory vibrations about the z axis and the other is too weak to detect. Of the remaining four modes, two arising from the rotatory vibrations with the strong intermolecular interactions are expected to appear at higher frequencies. Thus we can assign the bands at 79 cm⁻¹ and 73 cm⁻¹ of C₂H₄Cl₂ and those at 79 cm⁻¹ and 70 cm⁻¹ of C₂D₄Cl₂ to these modes of vibrations. The remaining two with weaker interactions for rotatory vibrations are then assigned to 55 cm⁻¹ for C₂H₄Cl₂ and 53 cm⁻¹ for C₂D₄Cl₂, respectively. The calcul-

TABLE 2 — Observed and calculated frequencies of the *trans* form (cm^{-1}) *

(a) Raman active modes

Mode	$\text{CICH}_2\text{CH}_2\text{Cl}$		$\text{ClCD}_2\text{CD}_2\text{Cl}$	
	obs. (Raman)	calc.	obs. (Raman)	calc.
ν_1 (a_g) CH ₂ sym. str.	2979	2955	—	2167
	2960		2179	
	2964		2180	
ν_2 (a_g) CH ₂ sciss.	—	1430	—	1162
	1431		1160	
	1458		1164	
	1437		1161	
ν_3 (a_g) CH ₂ wag.	1310	1319	—	1039
	1306		1036	
	1313		1035	
	1301		1025	
ν_4 (a_g) CC str.	1057	1049	—	913
	1052		909	
	1060		916	
	1057		906	
ν_5 (a_g) CCl str.	772	775	—	697
	754		708	
	748		694	
ν_6 (a_g) CCCI def.	305	295	—	290
	302		299	
	305		302	
	300		298	
ν_{11} (b_g) CH ₂ antisym. str.	3001	3002	—	2265
	3005		2264	
	3009		2272	
ν_{12} (b_g) CH ₂ twist.	1267	1260	—	981
	1263		975	
	1265		972	
	1263		967	
ν_{13} (b_g) CH ₂ rock.	996	1001	—	765
	989		768	
	992		767	

TABLE 2 (continued)

(b) Infrared active modes

Mode	$\text{CICH}_2\text{CH}_2\text{Cl}$		$\text{ClCD}_2\text{CD}_2\text{Cl}$	
	obs. (IR)	calc.	obs. (IR)	calc.
ν_7 (a_u) CH ₂ antisym. str.	3009	3009	—	2268
	3005		2271	
	3040		2280	
ν_8 (a_u) CH ₂ twist.	1124	1126	817	800
	1124		817	
	1135		820	
	1132		820	
ν_9 (a_u) CH ₂ rock.	772	774	—	578
	768		568	
	768		568	
ν_{10} (a_u) torsion	122	123	—	114
	125		128	
	164		151	
ν_{14} (b_u) CH ₂ sym. str.	2983	2976	2185	2186
	2957		2178	
	2980		2179	
ν_{15} (b_u) CH ₂ sciss.	1461	1460	1085	1079
	1450		1077	
	1460		1081	
	1447		1081	
ν_{16} (b_u) CH ₂ wag.	1233	1243	944	939
	1230		941	
	1236		941	
	1232		941	
ν_{17} (b_u) CCl str.	727	731	707	702
	709		689	
	700		683	
ν_{18} (b_u) CCCI def.	221	219	—	207
	230		217	
	234		218	

* For each vibration the first row gives the frequency in the gaseous state, the second that in the liquid state and the third that in the solid state. When the splittings due to the crystal field are observed, they are given in the third and fourth rows.

TABLE 3 — Observed and calculated frequencies of the gauche form (cm^{-1})*

(a) Raman active modes

Mode	CICH ₂ CH ₂ Cl		ClCD ₂ CD ₂ Cl	
	obs. (Raman)	obs. (IR)	calc.	obs. (IR)
ν_1 (a) CH ₂ antisym. str.	3005	3005	3005	2266
ν_2 (a) CH ₂ sym. str.	2966 2957	2968 2957	2968	2176
ν_3 (a) CH ₂ sciss.	1446	1448	1448	1154
ν_4 (a) CH ₂ wag.	1315	1315 1312	1307	1050
ν_5 (a) CH ₂ twist.	1214 1209	1212	1212	924
ν_6 (a) CC str.	1033	1028 1032	1029	827
ν_7 (a) CH ₂ rock.	950 942	947 944	943	759 737**
ν_8 (a) CCl str.	670 655	669 655	668	624 612
ν_9 (a) CCCI def.	263 262	272	274	240
ν_{10} (a) torsion	122	125	121	117

(b) Infrared active modes

CICH₂CH₂Cl

TABLE 3 (continued)

(b) Infrared active modes

Mode	CICH ₂ CH ₂ Cl		ClCD ₂ CD ₂ Cl	
	obs. (Raman)	obs. (IR)	calc.	obs. (Raman)
ν_{11} (b) CH ₂ antisym. str.	3005	3005	3006	2266
ν_{12} (b) CH ₂ sym. str.	2957	2957	2962	2176
ν_{13} (b) CH ₂ sciss.	1431	1436 1433	1442	1067 1059
ν_{14} (b) CH ₂ wag.	1289	1292 1286	1285	1020
ν_{15} (b) CH ₂ twist.	1142	1146 1143	1147	827
ν_{16} (b) CH ₂ rock.	880	891 880	885	712
ν_{17} (b) CCl str.	675	694 678	697	638
ν_{18} (b) CCCI def.	411	410 412	413	370

* For each vibration the first row gives the frequency in the gaseous state and the second row gives that in the liquid state.

** The two Raman and infrared bands are ascribed to the Fermi resonance between ν_7 and $\nu_8 + \nu_{10}$. In the gaseous state ν_{10} becomes lower in frequency and the Fermi resonance does not occur.

TABLE 4 — Observed and calculated lattice frequencies (cm^{-1})

Species	Mode *	CICH ₂ CH ₂ Cl		ClCD ₂ CD ₂ Cl	
		obs.	calc.	obs.	calc.
A _g	R _z	117	111.6	98	94.4
	R _y	79	79.2	79	75.4
	R _x	55	50.4	53	50.0
B _g	R _z	—	97.0	—	86.5
	R _y	73	73.0	70	71.4
	R _x	(55)	49.9	(53)	48.8
A _u	T _a	—	83.8	—	82.5
	T _c	—	47.4	—	46.7
B _u	T _b	—	51.3	—	50.5

* The dominant modes are given. R_x, R_y and R_z stand for the rotatory lattice vibrations about the axes x, y and z, respectively (see the text). T_a, T_b and T_c stand for the translation lattice vibrations along the crystal axes a, b and c, respectively.

ation shows the former correspond to the rotatory vibrations about the y axis and the latter to those about the x axis (as shown in Table 4).

Since the free rotation about the molecular axis sets in above the transition point, the bands at 117 cm^{-1} assigned to the rotatory vibration about the z axis of C₂H₄Cl₂ disappears completely, as is expected. Furthermore, the moments of inertia about the x and y axes become equal to each other and so the two different bands observed at 60 cm^{-1} and 40 cm^{-1} are to be explained from the difference in the restoring forces between the two rotatory vibrations. As shown in Fig. 3 these two bands are so broad that each of them can be assigned to every two bands (symmetric and antisymmetric rotatory vibrations) observed below the transition point. We would like to note that these bands become broader, as the tempera-

ture 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 Figs. 4 and 6 and Tables 2 and 4 all the infrared and Raman frequencies observed in the solid state are shown. It is seen that the mutual exclusion rule holds and we are sure that the molecule of 1,2-dichloroethane in this state assume the trans form with a center of symmetry. Furthermore, the agreement between the observed and calculated values is more satisfactory than those reported in our previous papers cited above. This is also the case for C₂D₄Cl₂.

It may not be out of place to make a remark on the difference of the torsional frequency (about the C-C single bond as axis) between the liquid and solid states. (See the infrared spectra shown in Fig. 6 and Table 2*b*). The frequency 125 cm^{-1} observed for C₂H₄Cl₂ in the liquid state changes to 153 cm^{-1} in the solid state above the transition point and to 164 cm^{-1} below this point. The same tendency of the increase in frequency is also observed for C₂D₄Cl₂. The higher frequencies observed in the solid state can be explained as due to the crystal field which stabilizes the trans form in this state. Furthermore, we would like to note that the vibration band at 223 cm^{-1} of C₂H₄Cl₂ previously observed by us and assigned to the CCl antisymmetric deformation mode by MIZUSHIMA, MORINO and SHIMANOUCI (1942) was also observed by BONN *et al.* (1953). As shown in Fig. 6*a* this band is more clearly observed at 230 cm^{-1} (liquid) and at 234 cm^{-1} (solid below the transition point) in the present experiment. The corresponding bands of C₂D₄Cl₂ were found to appear at 217 cm^{-1} (liquid) and at 218 cm^{-1} (solid), respectively. (See Fig. 6*a*).

B) Liquid and Gaseous States

Our previous conclusion that the molecule of 1,2-dichloroethane in the liquid and gaseous states assume both the trans

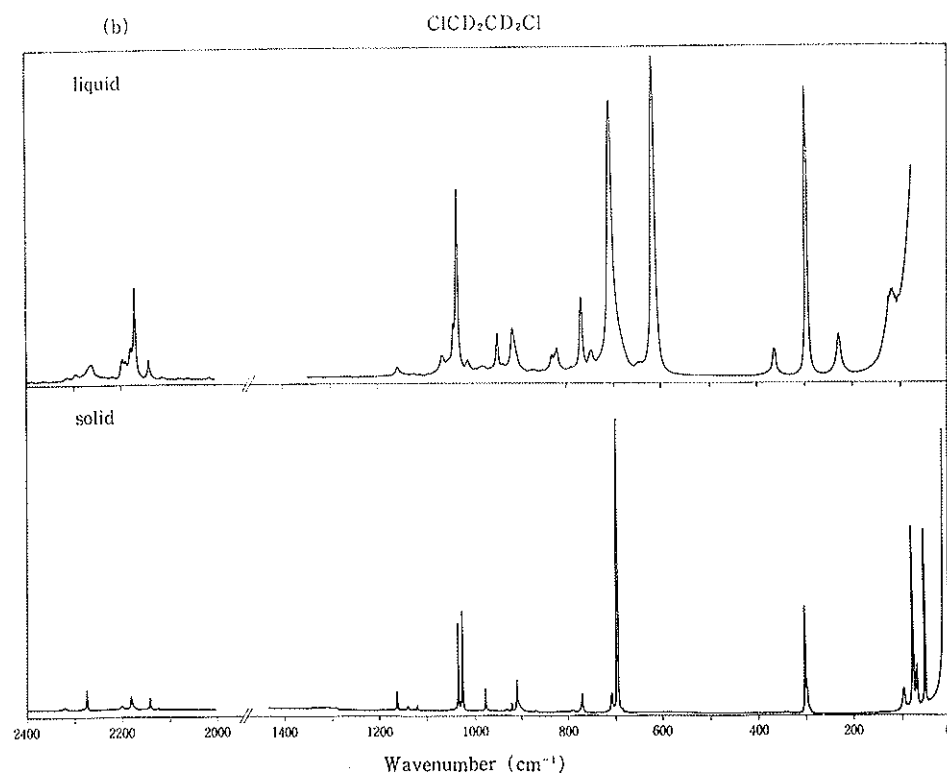
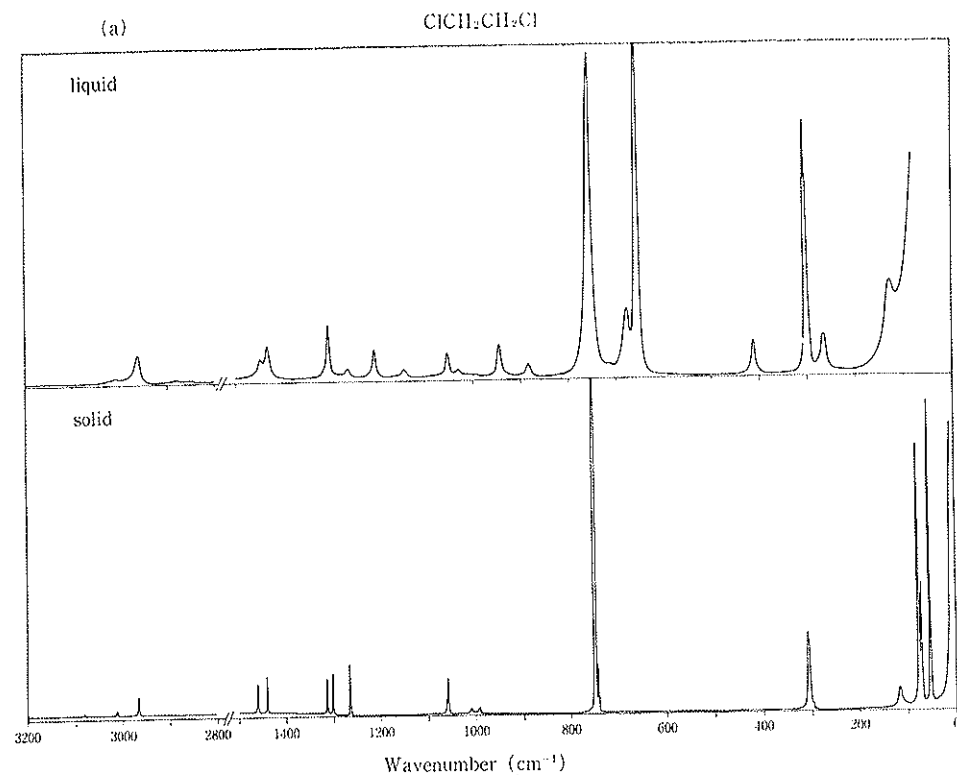


FIG. 4 — Raman spectra in the liquid and solid (at 77°K) states. (a) $\text{C1H}_2\text{-CH}_2\text{Cl}$ and (b) $\text{C1D}_2\text{C-CD}_2\text{Cl}$.

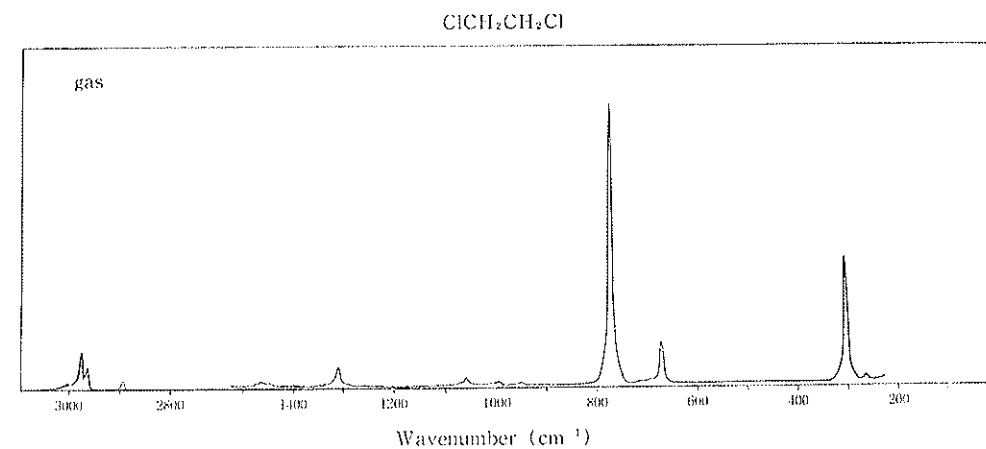


FIG. 5 — Raman spectrum of $\text{C1H}_2\text{C-CH}_2\text{Cl}$ in the gaseous state (60 torr at 24°C).

and the gauche forms has been confirmed by the more exact measurements of the present work. (See Figs. 4, 5 and 7 and Tables 2 and 3).

All the infrared and Raman frequencies (except for those arising from the trans form deformed in the liquid state as reported by MIZUSHIMA, MORINO and SHIMANOUCI (1942)) can be assigned to the gauche form which has the symmetry C_2 and which, therefore, can show the same frequencies in both the infrared and Raman spectra. The results of the present calculation which is more exact than those reported by us previously, confirm that the assignment of the observed frequencies is correct. The envelopes of the infrared absorption bands in the gaseous state observed by us (1959) are in good agreement with this assignment. The difference in the relative intensity of the bands between the liquid and gaseous states is due to the difference in the equilibrium ratio between the trans and the gauche molecules as explained in our previous papers. (See, e. g. MIZUSHIMA, 1954).

C) Quantum Mechanical 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 torsion angle, both the kinetic energy and potential energy parts of the Schrödinger equation become the functions of the torsion angle. The torsional Hamiltonian for the case where the potential barrier is an even function of torsion angle, θ , is expressed as:

$$H_t = \frac{1}{2} p_\theta^2 F(\theta) p_\theta + \frac{1}{2} \sum_k V_k (1 - \cos k\theta),$$

where $p_\theta = -(\partial/\partial \theta)$ and $F(\theta)$ is the effective inverse moment of inertia. The solution of the Schrödinger equation is obtained by solving the secular equation for the Hamiltonian matrix. Each matrix element is set up, using the free rotor wave function as the basis set. The computer program for the calculation of the torsional energy levels written by INAGAKI, HARADA and SHIMANOCHI (1973) was used for the present purpose. Since we know experimentally the torsional frequencies of the trans form, the energy difference between the trans and gauche forms, and the torsion angle of the gauche form, we can obtain the numerical values of V_k 's for $k = 1, 2$ and 3 as $1866.7, -1110.9$ and 1917.5 cm^{-1} , respectively. Furthermore, using proper structural parameters, we can calculate $F(\theta)$ numerically as:

$$\begin{aligned} F(\theta) = & 1.2458 - 0.2848 \cos\theta + 0.6346 \cos 2\theta \\ & - 0.2540 \cos 3\theta + 0.2164 \cos 4\theta - 0.1212 \cos 5\theta \\ & + 0.0842 \cos 6\theta - 0.0522 \cos 7\theta \text{ (cm}^{-1}\text{)}. \end{aligned}$$

Thus for the first eight transitions of the trans form the frequencies are calculated as $119.5, 116.8, 114.0, 111.0, 108.1, 104.8, 101.6$ and 98.2 cm^{-1} and the first four transitions of the gauche form as $117.6, 115.4, 113.0$ and 110.4

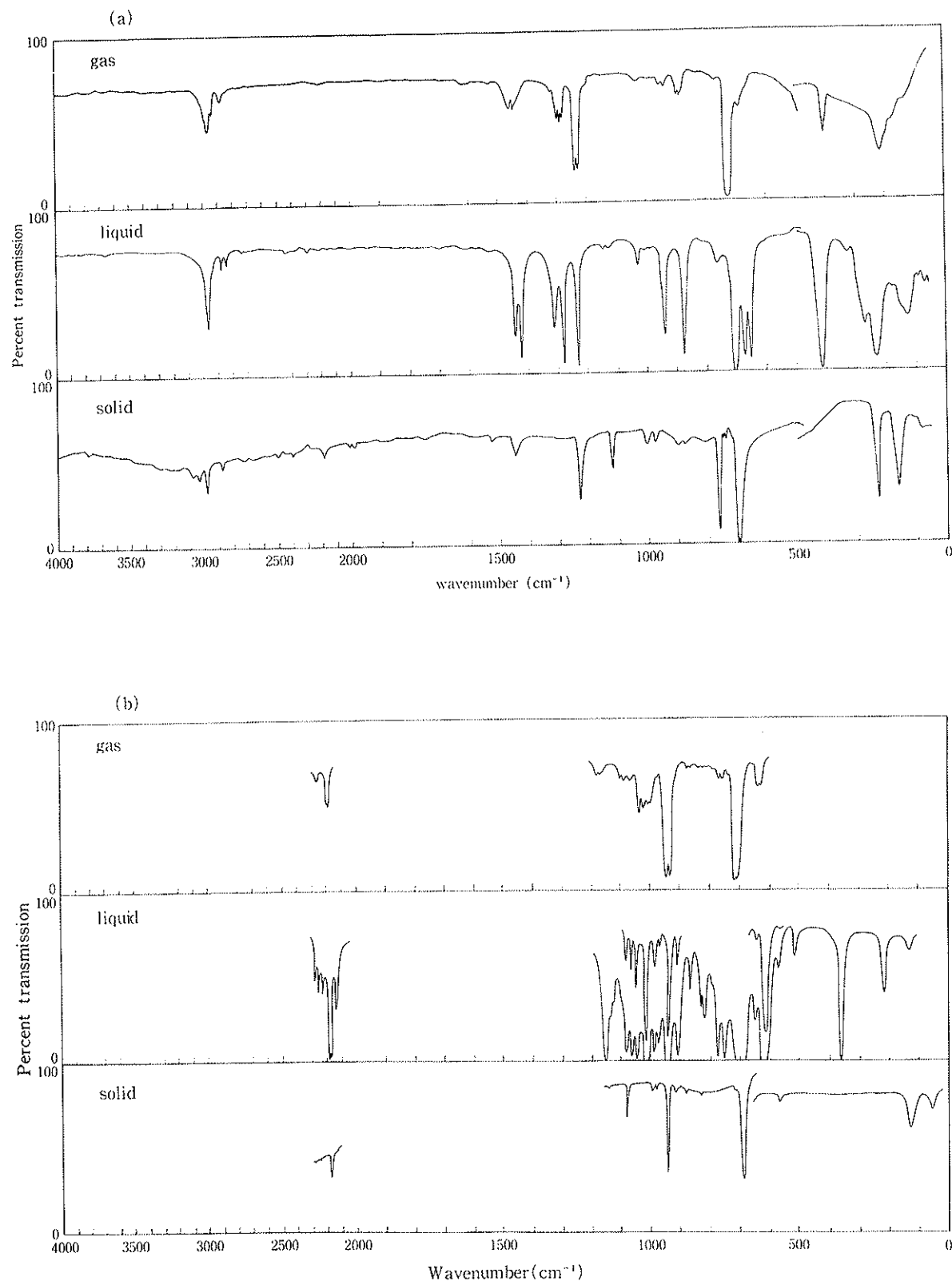


FIG. 6 — Infrared spectra of 1,2-dichloroethane in the gaseous, liquid and solid (at 77°K) states. (a) $\text{CIH}_2\text{C-CH}_2\text{Cl}$ and (b) $\text{CID}_2\text{C-CD}_2\text{Cl}$.

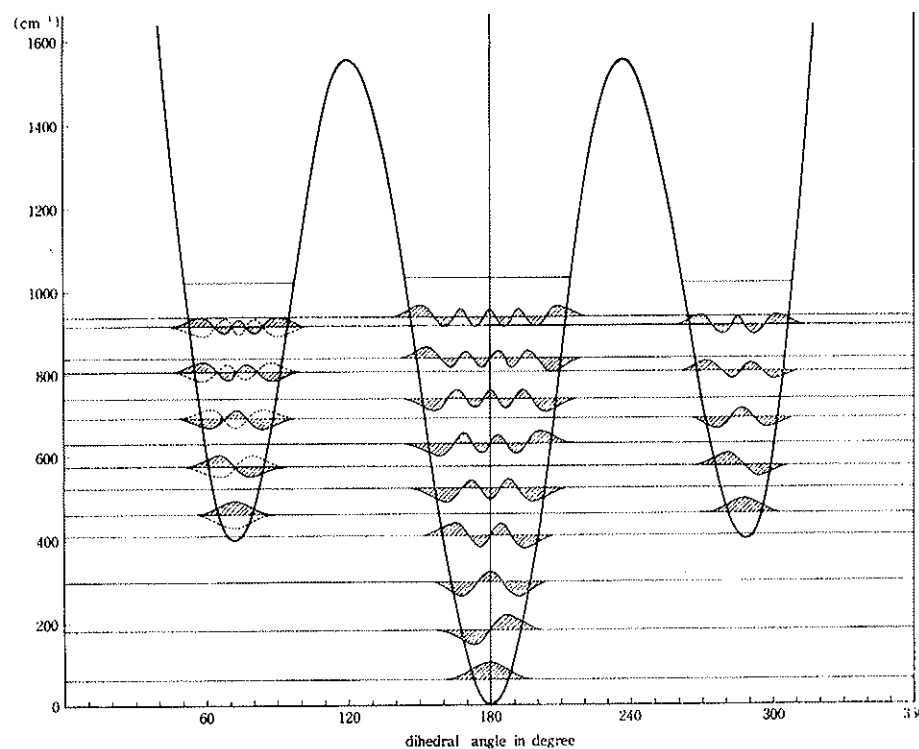


FIG. 7 — Energy levels and eigenfunctions for the internal rotation of 1,2-dichloroethane in the gaseous state. Each energy level belonging to the gauche form consists of the symmetric and antisymmetric ones, the eigenfunctions of the latter being denoted by the dotted lines.

cm^{-1} . The eigenfunctions belonging to the trans form have appreciable values only in the neighborhood of the trans state and those belonging to the gauche form only in the neighborhood of the gauche state. Thus it is shown that our proposition of rotational isomerism is also supported from the quantum mechanical point of view.

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