

# Vibration Spectra and Rotational Isomerism of Chain Molecules. VII.<sup>1)</sup> 1-Chloro-, 1-Bromo-, and 1-Iodopropanes, and 1-Chloro-, 1-Bromo-, and 1-Iodobutanes

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The Raman and infrared spectra of 1-chloro-, 1-bromo-, and 1-iodopropanes,  $\text{CH}_3\text{CH}_2\text{CH}_2\text{X}$  ( $\text{X}=\text{Cl}$ ,  $\text{Br}$ , and  $\text{I}$ ), and 1-chloro-, 1-bromo-, and 1-iodobutanes,  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{X}$  ( $\text{X}=\text{Cl}$ ,  $\text{Br}$ , and  $\text{I}$ ), were measured for the gaseous, liquid, glassy, and crystalline states. The normal vibration frequencies were calculated, a consistent set of force constants explaining the frequencies of basic halogenoalkanes being assumed. The rotational isomerism was studied on the basis of the spectral observations and the normal coordinate calculations. The enthalpy differences among the rotational isomers were examined.

The study of the vibration spectra and rotational isomerism of 1-halogenopropanes was started by Mizushima and coworkers<sup>2)</sup> and Radinger and Wittek<sup>3)</sup> about thirty years ago. Many studies have been made by means of Raman and infrared,<sup>4–17)</sup> microwave,<sup>18,19)</sup> and electron-diffraction<sup>20)</sup> measurements. As a result, it has been established that the *trans* (T) form exists in the crystalline state except 1-fluoropropane for which the *gauche* (G) form exists<sup>7a,b)</sup> and both the T and G forms exist in the liquid and gaseous states. The enthalpy difference between the T and G forms has also been determined by many investigators.<sup>4–6,10,11,17–20)</sup> However, as has been indicated previously,<sup>17)</sup> the reported values of the enthalpy difference are quite different from one another and there are some disagreements in the vibrational assignments among different authors. These problems remain to be settled.

The rotational isomerism of 1-halogenobutanes has been studied also by means of Raman and infrared,<sup>4–9,14,16,21–25)</sup> and electron-diffraction<sup>26)</sup> measurements. Ukaji and Bonham<sup>26a)</sup> concluded that 1-chlorobutane had an isomer distribution of 37% TG, 24% GG', 17% GG, 11% TT, and 11% GT in the gaseous state at room temperature. Snyder and Schachtschneider<sup>14)</sup> observed the infrared spectra of  $\text{CH}_3(\text{CH}_2)_n\text{Cl}$  ( $n=1-5$ ) in the crystalline (annealed solid) and glassy (unannealed solid) states and obtained the refined valence force field through the normal coordinate analysis. They indicated that the vibrational spectra of 1-chlorobutane in the crystalline state are explained by the existence of the TT form and those in the glassy state by the coexistence of the TT form and the TG form with the *gauche* CC–CCl axis. More recently, Crowder and coworkers<sup>7,8)</sup> interpreted the vibrational spectra of 1-fluoro- and 1-iodoalkanes, taking into account only two among various isomers, the all-*trans* form and the form which has a *gauche* conformation about the CC–CX axis and a *trans* conformation about the remaining axes. Thus, the whole aspect of the rotational isomers existing in the various states of 1-halogeno-

butanes is still unknown and the enthalpy differences among the isomers have not yet been determined.

In the previous papers,<sup>27–31)</sup> we compared the Raman and infrared spectra of unbranched ethers, paraffins, and sulfides in the crystalline, glassy, liquid, and gaseous states with the results of normal vibration calculations and determined the rotational isomers existing in each state. As a continuation of such studies, the same method has been applied to 1-halogenopropane and 1-halogenobutane molecules. The results show that the method is useful in the study of rotational isomerism. In the course of the research, several new findings including the identification of less stable rotational isomers and the enthalpy differences among the isomers in the liquid state have been obtained. The present paper describes the rotational isomerism and vibrational assignments of 1-halogenopropanes,  $\text{CH}_3\text{CH}_2\text{CH}_2\text{X}$ , and 1-halogenobutanes,  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{X}$  ( $\text{X}=\text{Cl}$ ,  $\text{Br}$ , and  $\text{I}$ ).

## Experimental

Samples used in the present study were purchased from Tokyo Kasei Kogyo Co., Ltd. and were distilled prior to the measurements. The Raman and infrared spectra were measured for the gaseous, liquid, glassy, and crystalline states by the method reported previously.<sup>27,28,30)</sup>

The glassy state for the Raman measurements was obtained by immersing the sample enclosed in an ampoule in liquid nitrogen for rapid cooling, and that for the infrared measurements by depositing the sample onto a cooled window of KBr or KRS-5.

For the determination of the enthalpy difference, the Raman spectra in the liquid state were recorded twice at each of nine different temperatures between  $-105$  and  $15^\circ\text{C}$  for 1-chloropropane, nine different temperatures between  $-100$  and  $15^\circ\text{C}$  for 1-bromopropane, eight different temperatures between  $-85$  and  $15^\circ\text{C}$  for 1-iodopropane, and eight different temperatures between  $-90$  and  $15^\circ\text{C}$  for 1-chloro-, 1-bromo-, and 1-iodobutanes. The Raman spectra in the gaseous state were also measured three times at each of four different temperatures between  $23$  and  $80^\circ\text{C}$  for 1-chloropropane.

## Normal Coordinate Treatment

The normal coordinate treatment of the unbranched halogenoalkanes (see Table 1) was carried out with a computer program NCTB<sup>32)</sup> and a HITAC 8700/8800

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TABLE 1. PROCEDURE OF THE LEAST-SQUARES CALCULATION

(i) Chloroalkanes					
Step	$C_3H_7Cl^{(a)}$	$C_4H_9Cl^{(b)}$	$C_5H_{11}Cl^{(c)}$	$ClC_3H_6Cl^{(d)}$	$ClC_4H_8Cl^{(e)}$
1	T (19)	TT (26)			
2	G (17)	TG (13)			
3			TTT (29)		
4			TTG (18)	GG (19) TG (12) TT (13)	GTG' (24)
5		GT (5) GG (11)	TGT (14) TGG (11) GTG (9) GTG' (8)		TTT (17) TTG (20) TGG (18) GTG (16) GGG (17)
(ii) Bromoalkanes					
Step	$C_3H_7Br^{(a)}$	$C_4H_9Br^{(b)}$	$C_5H_{11}Br^{(c)}$	$BrC_3H_6Br^{(d)}$	$BrC_4H_8Br^{(e)}$
1	T (19)	TT (24)			
2	G (16)	TG (14)			
3			TTT (31)		
4			TTG (29)	GG (19) TG (10) TT (7)	GTG' (24)
5		GT (4) GG (8)	TGT (10) GTT (7) TGG (10) GTG (10) GTG' (7)		TTT (19) TTG (20) TGT (17) TGG (20) GTG (16) GGG (19)
6	$CH_3CHDCH_2Br^{(e)}$ $CH_3CH_2CHDBr^{(e)}$	T (17) T (16)	G (6) G (5)	G' (6) G' (9)	
(iii) Iodoalkanes					
Step	$C_3H_7I^{(a)}$	$C_4H_9I^{(b)}$	$C_5H_{11}I^{(c)}$	$IC_3H_6I^{(d)}$	
1	T (19)	TT (24)			
2	G (13)	TG (15)			
3			TTT (28)		
4			TTG (16)	GG (19) TG (13) TT (19)	
5		GT (7) GG (13)	TGT (12) GTT (9) TGG (14) GTG (10) GTG' (11)		
(iv) Fluoroalkanes					
Step	$C_3H_7F^{(f)}$	$C_4H_9F^{(f)}$	$C_5H_{11}F^{(f)}$		
1	G (17)	TG (24)			
2			TTG (27)		
3	T (9)	TT (7)			
4			TTT (6)		
5		GT (3) GG (1)	TGT (3) GTT (3)		

TABLE 1. CONTINUED

The least-squares calculation begins with the simplest halogenoalkanes given in the first step and the first set of force constants is determined so as to give the best fit between the observed and calculated frequencies. This set of force constants gives the definite vibrational assignments of the halogenoalkanes given in the second step and the second set of force constants is subsequently determined from the observed frequencies in this step in addition to those in the first step. By repeating this procedure, the final set of force constants is obtained. The figures in parentheses give the numbers of observed frequencies used for the least-squares calculation. The observed frequencies of the CH and CD stretching vibrations are not included in the calculation and accordingly the force constants associated with these vibrations are not refined. The results of the following references are utilized in the least-squares calculation. a) This study and Ref. 13. b) This study. c) Ref. 34. d) Ref. 35. e) Ref. 15. f) Ref. 7.

computer system at the Computer Center of the University of Tokyo. The calculation made it possible to assign the observed Raman and infrared bands to individual rotational isomers and to determine a consistent set of force constants of halogenoalkanes. Structural parameters and symmetry coordinates used in the calculation and a final set of the force constants will be reported in a separate paper.<sup>33)</sup>

The force constants of halogenoalkanes were determined in the following way. The force constants associated with a methyl or methylene group which is not bound directly to a halogen atom were assumed to be the same as those for the paraffin molecules.<sup>32)</sup> The force constants associated with the halogen atom, including those of the methyl or methylene group adjacent to the halogen atom, were refined in the least-squares adjustment. The initial values for the chlorine part were transferred from the result by Snyder and Schachtschneider.<sup>14)</sup> The initial values for the bromine and iodine parts were estimated from the corresponding values of the chlorine part. Some of the halogenoalkane force constants including those which were unestimable from the observed frequencies were assumed to be the same values as those for the corresponding paraffin force constants.

Table 1 shows the procedure of the least-squares calculation. The calculation began with the simplest halogenoalkanes in the extended form, and then the molecules to be treated were extended to the longer halogenoalkanes and the non-extended forms. In the force constant refinement, we also used the observed frequencies of the deuterated derivatives of 1-bromopropane,<sup>15)</sup> 1-halogenopentanes,<sup>34)</sup> 1,3-dihalogenopropanes,<sup>35)</sup> and 1,4-dihalogenobutanes.<sup>34)</sup> A total of 23 force constants associated with the chlorine part were determined from 336 Raman and infrared frequencies of 21 forms of 5 molecular species, 21 force constants associated with the bromine part from 419 frequencies of 29 forms of 7 molecular species, and 23 force constants associated with the iodine part from 242 frequencies of 16 forms of 4 molecular species.

The normal vibration calculation of fluoroalkanes was also carried out in the same way as the other halogenoalkanes on the basis of the experimental data by Crowder and Mao.<sup>7)</sup> The procedure of the least-squares calculation of fluoroalkanes is also included in Table 1. A total of 22 force constants associated with the fluorine part were determined from 100 Raman and infrared frequencies of 10 forms of 3 molecular species.

## Results

Figures 1—16 show the Raman and infrared spectra in the gaseous, liquid, glassy, and crystalline states. The observed frequencies and the vibrational assignments based on the calculated potential-energy distributions are listed in Tables 2—7. The observed spectra were analyzed with reference to the results of the normal coordinate treatment. The values of enthalpy differences obtained from the intensity variation of the Raman bands with temperature are given in Figs. 17 and 18.

In the following subsections, the rotational isomerism of the individual halogenopropane and halogenobutane molecules is described.

**1-Halogenopropanes.** These molecules have two possible rotational isomers, T and G, as given in Table 1 of Part I of this series.<sup>27)</sup> The observed Raman and infrared spectra and the calculated frequencies are compared in Figs. 7 and 8. These figures show that the T form exists in the crystalline state of 1-chloro-, 1-bromo-, and 1-iodopropanes and the T and G forms coexist in the glassy, liquid, and gaseous states.

The individual rotational isomers of each molecule are discriminated from each other by the Raman key bands of the liquid state, their frequencies being given in parentheses: T form (364 and 723 cm<sup>-1</sup>) and G form (292, 424, 648, and 787 cm<sup>-1</sup>) of 1-chloropropane, T form (311 and 648 cm<sup>-1</sup>) and G form (274, 402, 563, and 777 cm<sup>-1</sup>) of 1-bromopropane, and T form (288 and 593 cm<sup>-1</sup>) and G form (390, 503, and 763 cm<sup>-1</sup>) of 1-iodopropane. These Raman bands were used for the determination of the enthalpy difference between the T and G forms of each molecule. Figure 17 shows the obtained results of the enthalpy differences in the liquid state. As is evidently seen in Fig. 17, the G form is slightly more stable than the T form for any of 1-chloro-, 1-bromo-, and 1-iodopropanes in the liquid state.

The enthalpy difference in the gaseous state of 1-chloropropane was also determined. The  $\Delta H_{G-T}$  value of  $15 \pm 30$  cal/mol and  $-210 \pm 100$  cal/mol were obtained from the pairs of the Raman bands at 663 and 745 cm<sup>-1</sup> and at 793 and 745 cm<sup>-1</sup>, respectively. Thus, the G form is as stable as or slightly more stable than the T form in gaseous 1-chloropropane.

**1-Halogenobutanes.** These molecules have five possible isomers, TT, TG, GT, GG, and GG',<sup>27)</sup> where the first and second conformation symbols in each isomer designation are those for the CC-CC and CC-CX axes,

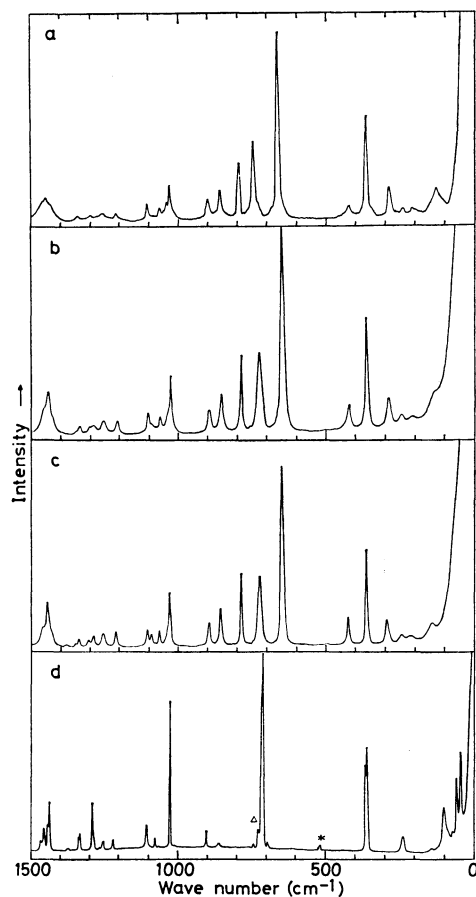


Fig. 1. Raman spectra of 1-chloropropane.

a: Gas (23 °C), b: liquid (23 °C), c: liquid (-100 °C), d: crystal (liquid nitrogen temperature). Following symbols are used in Figs. 1—16. \*: Emission line of Ar<sup>+</sup>, Δ: origin unknown, ×: impurity.

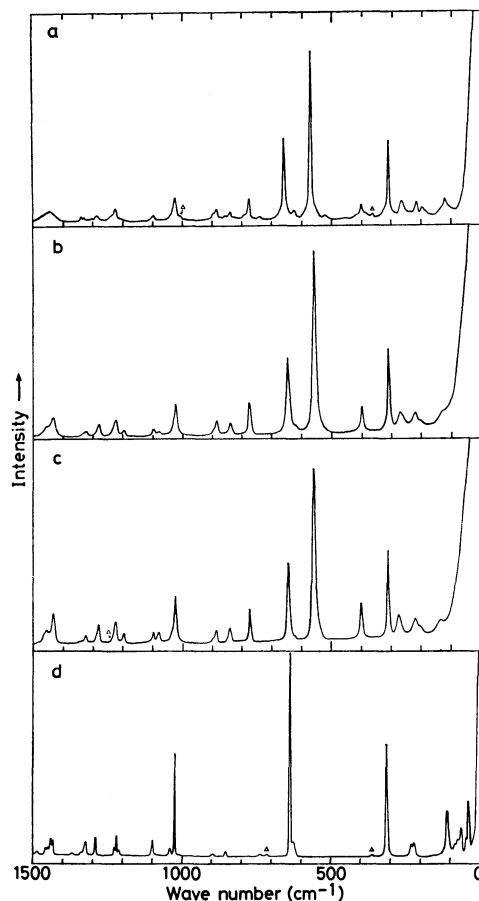


Fig. 3. Raman spectra of 1-bromopropane.

a: Gas (23 °C), b: liquid (23 °C), c: liquid (-90 °C), d: crystal (liquid nitrogen temperature). The symbol is explained in the caption of Fig. 1.

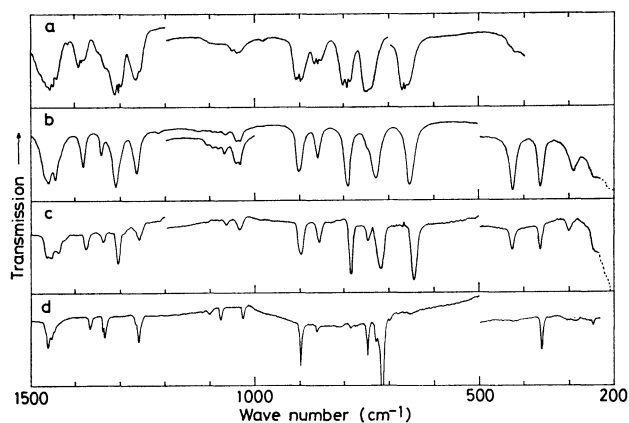


Fig. 2. Infrared spectra of 1-chloropropane.

a: Gas (room temperature), b: liquid (room temperature), c: glass, d: crystal.

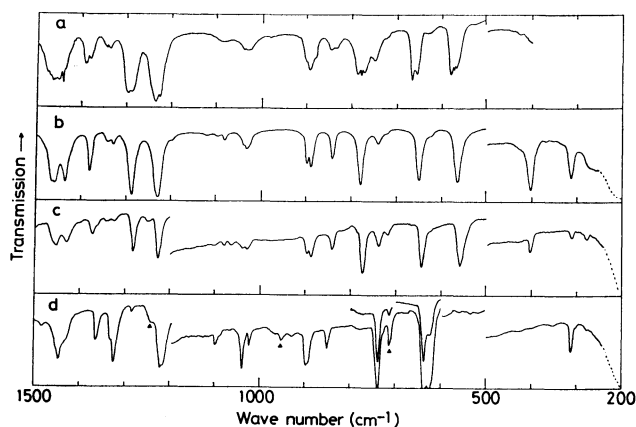


Fig. 4. Infrared spectra of 1-bromopropane.

a: Gas (room temperature), b: liquid (room temperature), c: glass, d: crystal.

The symbol is explained in the caption of Fig. 1.

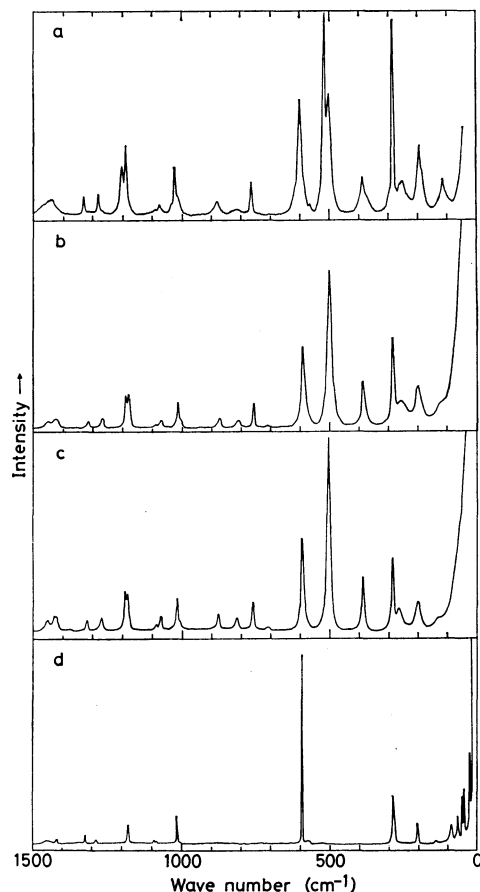


Fig. 5. Raman spectra of 1-iodopropane.  
a: Gas (23 °C), b: liquid (23 °C), c: liquid (-80 °C),  
d: crystal (liquid nitrogen temperature).

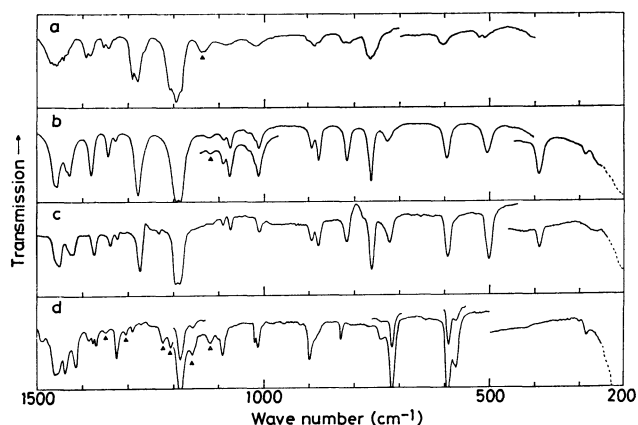


Fig. 6. Infrared spectra of 1-iodopropane.  
a: Gas (room temperature), b: liquid (room temperature), c: glass, d: crystal.  
The symbol is explained in the caption of Fig. 1.

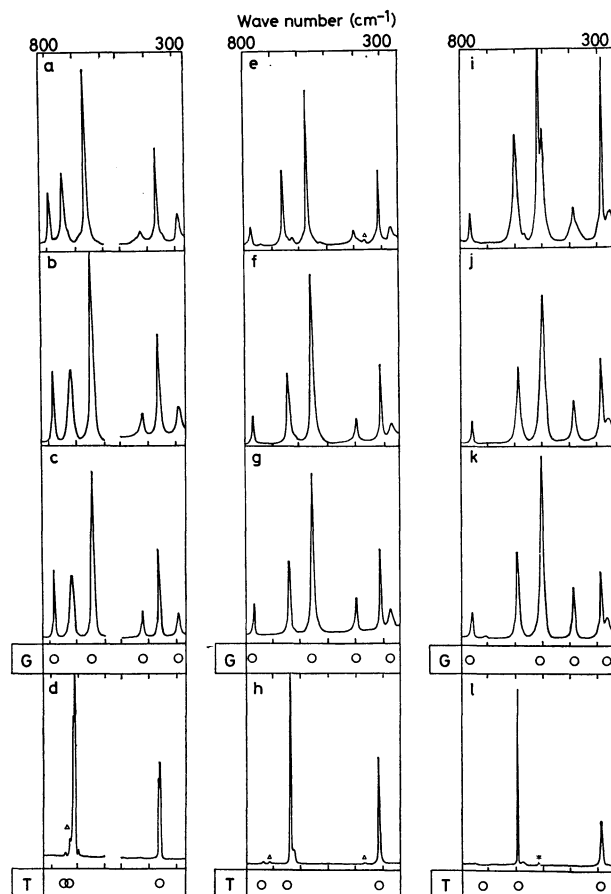


Fig. 7. Comparison between the Raman spectra and the calculated frequencies of 1-halogenopropanes.

1-Chloropropane,  
a: gas (23 °C), b: liquid (23 °C), c: liquid (-100 °C),  
d: crystal (liquid nitrogen temperature).  
1-Bromopropane,  
e: gas (23 °C), f: liquid (23 °C), g: liquid (-90 °C),  
h: crystal (liquid nitrogen temperature).  
1-Iodopropane,  
i: gas (23 °C), j: liquid (23 °C), k: liquid (-80 °C),  
l: crystal (liquid nitrogen temperature).  
The symbols are explained in the caption of Fig. 1.

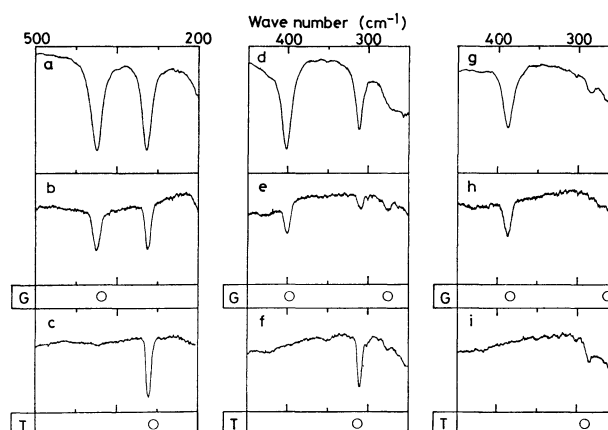


Fig. 8. Comparison between the infrared spectra and the calculated frequencies of 1-halogenopropanes.

1-Chloropropane,  
a: liquid (room temperature), b: glass, c: crystal.  
1-Bromopropane,  
d: liquid (room temperature), e: glass, f: crystal.  
1-Iodopropane,  
g: liquid (room temperature), h: glass, i: crystal.

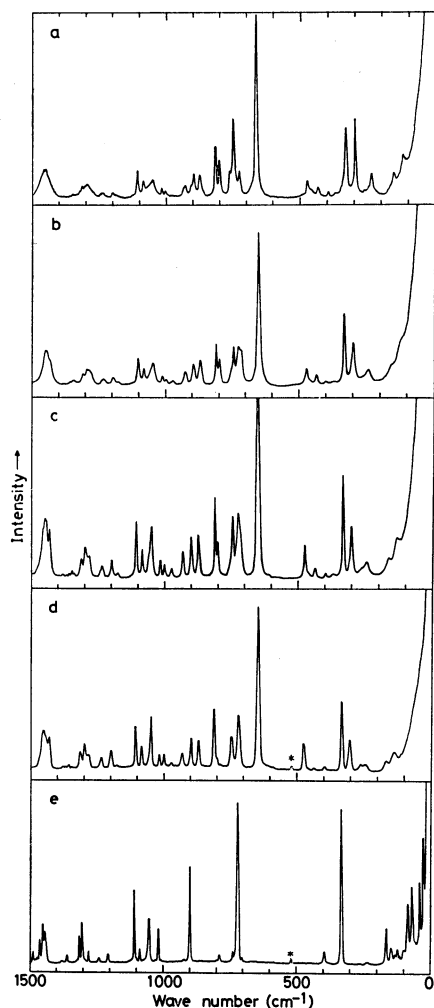


Fig. 9. Raman spectra of 1-chlorobutane.  
a: Gas (23 °C), b: liquid (23 °C), c: liquid (−90 °C),  
d: glass (liquid nitrogen temperature), e: crystal  
(liquid nitrogen temperature).  
The symbol is explained in the caption of Fig. 1.

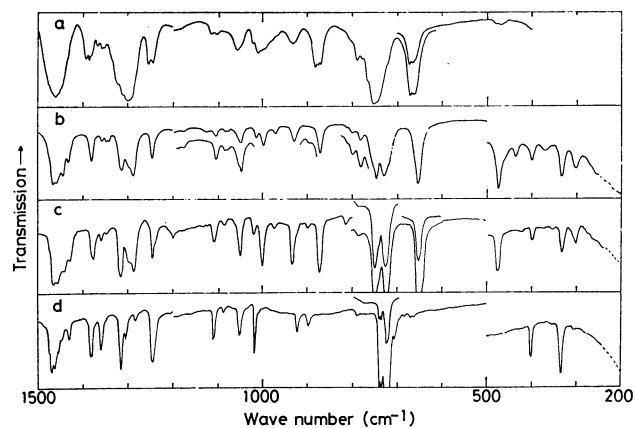


Fig. 10. Infrared spectra of 1-chlorobutane.  
a: Gas (room temperature), b: liquid (room temperature), c: glass, d: crystal.

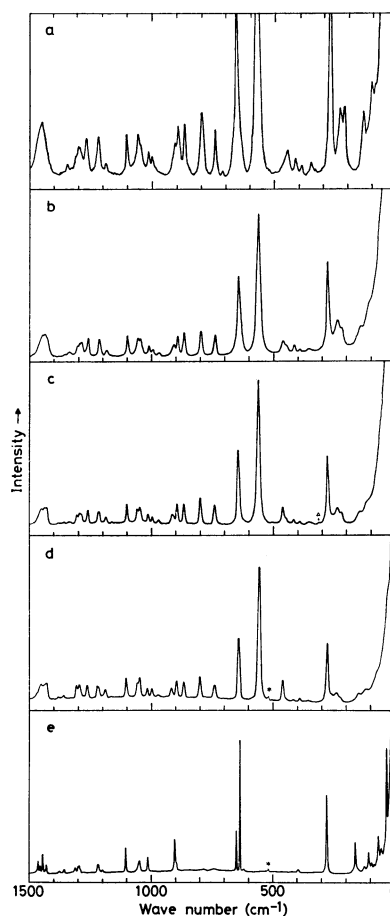


Fig. 11. Raman spectra of 1-bromobutane.  
a: Gas (23 °C), b: liquid (23 °C), c: liquid (−90 °C),  
d: glass (liquid nitrogen temperature), e: crystal  
(liquid nitrogen temperature).  
The symbols are explained in the caption of Fig. 1.

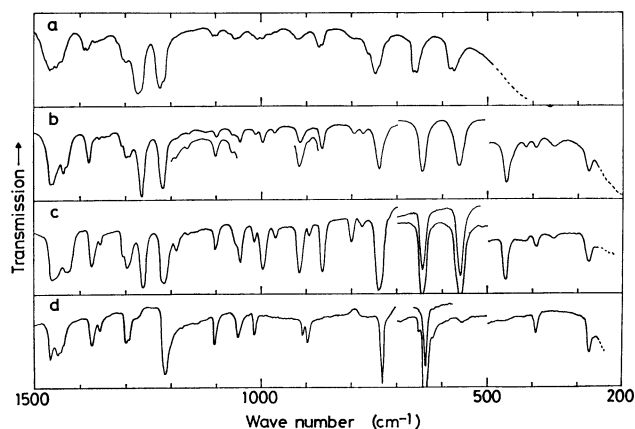


Fig. 12. Infrared spectra of 1-bromobutane.  
a: Gas (room temperature), b: liquid (room temperature), c: glass, d: crystal.

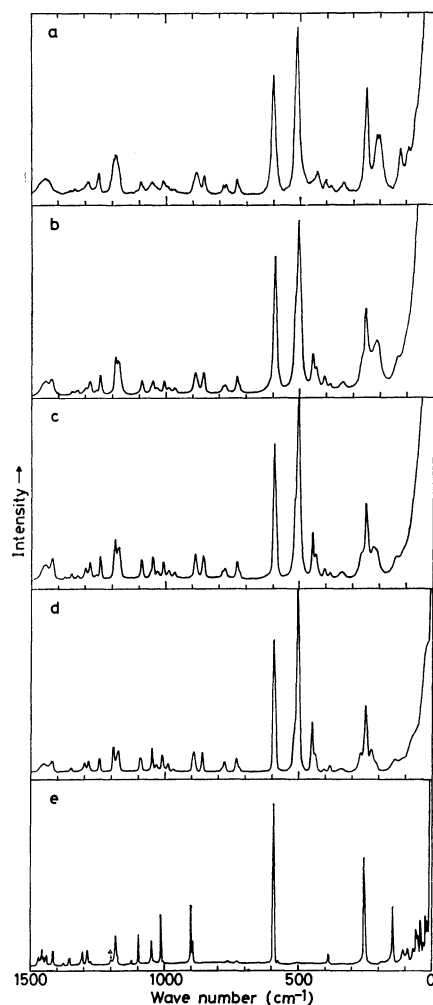


Fig. 13. Raman spectra of 1-iodobutane.  
a: Gas (23 °C), b: liquid (23 °C), c: liquid (-95 °C),  
d: glass (liquid nitrogen temperature), e: crystal  
(liquid nitrogen temperature).  
The symbol is explained in the caption of Fig. 1.

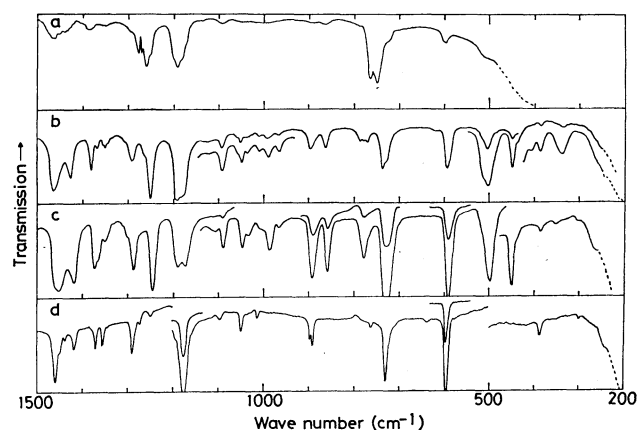


Fig. 14. Infrared spectra of 1-iodobutane.  
a: Gas (room temperature), b: liquid (room temperature),  
c: glass, d: crystal.

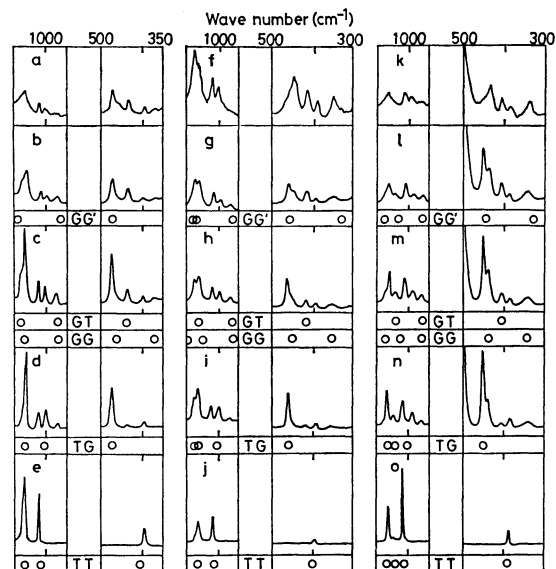


Fig. 15. Comparison between the Raman spectra and the calculated frequencies of 1-halogenobutanes.

1-Chlorobutane,  
a: gas (23 °C), b: liquid (23 °C), c: liquid (-90 °C),  
d, glass (liquid nitrogen temperature), e: crystal  
(liquid nitrogen temperature).  
1-Bromobutane,  
f: gas (23 °C), g: liquid (23 °C), h: liquid (-90 °C),  
i: glass (liquid nitrogen temperature), j: crystal  
(liquid nitrogen temperature).  
1-Iodobutane,  
k: gas (42 °C), l: liquid (23 °C), m: liquid (-95 °C),  
n: glass (liquid nitrogen temperature), o: crystal  
(liquid nitrogen temperature).

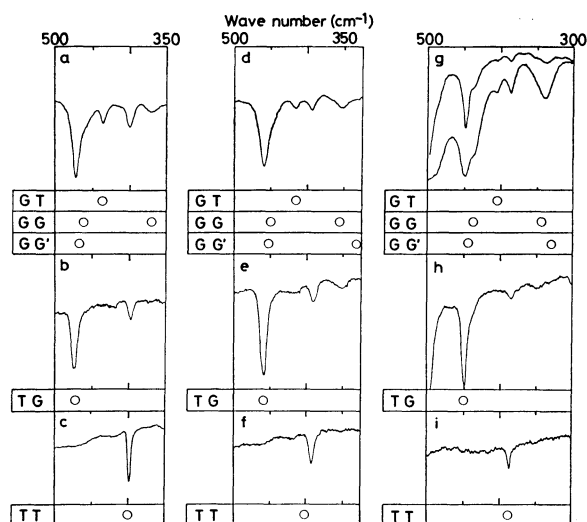


Fig. 16. Comparison between the infrared spectra and the calculated frequencies of 1-halogenobutanes.

1-Chlorobutane,  
a: liquid (room temperature), b: glass, c: crystal.  
1-Bromobutane,  
d: liquid (room temperature), e: glass, f: crystal.  
1-Iodobutane,  
g: liquid (room temperature), h: glass, i: crystal.

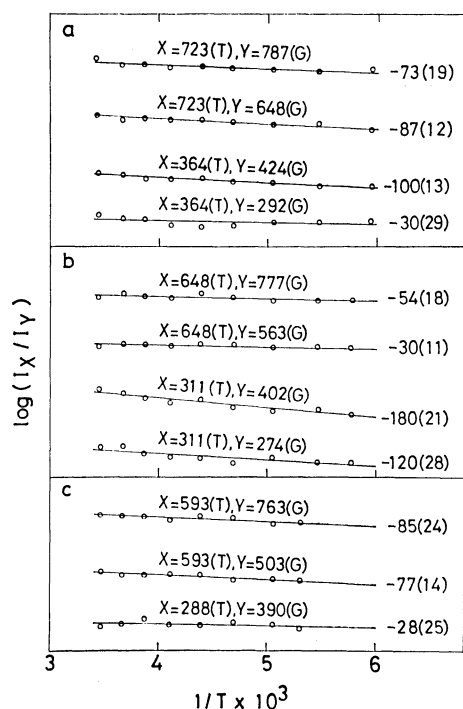


Fig. 17. Enthalpy differences between the T and G forms of 1-halogenopropanes.

a: 1-Chloropropane, b: 1-bromopropane, c: 1-iodopropane.

X and Y denote the band pairs ( $\text{cm}^{-1}$ ). The values of  $\Delta H_{G-T}$  (cal/mol) are given on the right side of the straight lines. The standard deviations obtained by the method of least-squares are also given in parentheses.

respectively. The observed Raman and infrared spectra and the calculated frequencies are compared in Figs. 15 and 16.

For 1-chlorobutane (see Figs. 15a—e and 16a—c), the spectra in the crystalline state show that only the TT form exists. The Raman band at  $397\text{ cm}^{-1}$  and the infrared band at  $400\text{ cm}^{-1}$  persisting in the crystalline state can be explained only by the existence of the TT form. In the glassy, liquid, and gaseous states, the observed spectra are explained by the coexistence of the TT, TG, GT, and GG forms. The Raman band at  $476\text{ cm}^{-1}$  and the infrared band at  $474\text{ cm}^{-1}$  in the glassy state, whose intensities relative to those of other bands increase in going from the liquid state to the glassy state, can be explained only by the existence of the TG form. The Raman band at  $437\text{ cm}^{-1}$  and the infrared band at  $436\text{ cm}^{-1}$  observed in the liquid state are assigned to the GT form, while the Raman bands at  $458$  (a shoulder of the  $474\text{ cm}^{-1}$  band) and  $370\text{ cm}^{-1}$  and the infrared bands at  $458$  (a shoulder of the  $473\text{ cm}^{-1}$  band) and  $370\text{ cm}^{-1}$  in the liquid state are assigned to the GG form.

For 1-bromobutane (see Figs. 15f—j and 16d—f), the comparison between the observed spectra and the calculated frequencies indicates that the TT form exist in the crystalline state. The Raman band at  $397\text{ cm}^{-1}$  and the infrared band at  $394\text{ cm}^{-1}$  are assigned only to the TT form. The glassy-, liquid-, and gaseous-

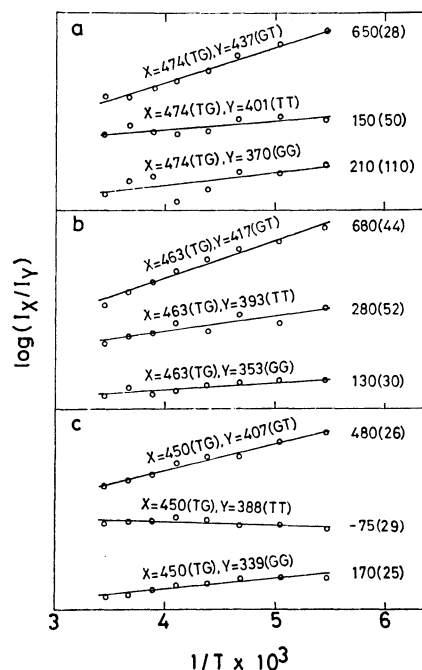


Fig. 18. Enthalpy differences among the TT, TG, GT, and GG forms of 1-halogenobutanes.

a: 1-Chlorobutane, b: 1-bromobutane, c: 1-iodobutane.

X and Y denote the band pairs ( $\text{cm}^{-1}$ ). The values of  $\Delta H_{Y-X}$  (cal/mol) are given on the right side of the straight lines. The standard deviations obtained by the method of least-squares are also given in parentheses.

state spectra show the coexistence of the TT, TG, GT, and GG forms in these states. The Raman band at  $462\text{ cm}^{-1}$  and the infrared band at  $459\text{ cm}^{-1}$  in the glassy state, whose intensities are enhanced as compared with those of the liquid state at room temperature, are assigned only to the TG form. The existence of the GT form is confirmed by the Raman and infrared bands at  $417\text{ cm}^{-1}$  in the liquid state, and the existence of the GG form is also clear from the observation of the Raman bands at  $448$  (a shoulder of the  $463\text{ cm}^{-1}$  band) and  $353\text{ cm}^{-1}$  and the infrared bands at  $445$  (a shoulder of the  $459\text{ cm}^{-1}$  band) and  $352\text{ cm}^{-1}$  in the liquid state. In the gaseous state, the Raman spectral pattern around  $450\text{ cm}^{-1}$  is different from that in the liquid state. The existence of the TG and GG forms is, however, confirmed definitely by the observation of the Raman bands at  $1000$  and  $350\text{ cm}^{-1}$ , respectively.

For 1-iodobutane (see Figs. 15k—o and 16g—i), the spectra of the crystalline state are explained by the existence of the TT form and those of the glassy, liquid, and gaseous states by the coexistence of the TT, TG, GT, and GG forms similarly to the cases of 1-chloro- and 1-bromobutanes. The Raman band at  $389\text{ cm}^{-1}$  and the infrared band at  $387\text{ cm}^{-1}$  in the crystalline state are assigned only to the TT form and the Raman band at  $452\text{ cm}^{-1}$  and the infrared band at  $449\text{ cm}^{-1}$  in the glassy state only to the TG form. The Raman band at  $407\text{ cm}^{-1}$  and the infrared band at  $406\text{ cm}^{-1}$  in the liquid state indicate the existence of the GT form and the Raman bands at  $438$  (a shoulder of the  $450$



TABLE 2. OBSERVED FREQUENCIES AND VIBRATIONAL ASSIGNMENTS OF 1-CHLOROPROPANE

Observed frequency (cm <sup>-1</sup> ) <sup>a)</sup>							Assignment <sup>b)</sup>
Gas		Liquid		Glass	Crystal		
R	IR	R	IR	IR	R	IR	
1452 W, b	1464 S, sh		1464 S, sh	1463 M	1465 VW	1463 M	CH <sub>2</sub> scis
	{ 1457 S 1450 S, sh }	1458 W, sh	1457 S	1453 M	1453 W	{ 1455 M 1448 W, sh }	CH <sub>3</sub> op-d-deform CH <sub>3</sub> ip-d-deform
	1441 M, sh	1443 M	1442 S	1438 M	{ 1441 W, sh 1434 M }	1443 W, sh	CH <sub>2</sub> scis (T)
		1431 VW,sh*	1436 M, sh	1425 VW, sh			CH <sub>2</sub> scis (G)
1343 VW	{ 1395 M 1388 M 1383 M, sh 1352 W, sh }	1382 VW	1381 M	1378 M	1372 VW	{ 1375 W, sh 1372 W }	CH <sub>3</sub> s-deform
		1347 VW, sh	1352 VW, sh				CH <sub>2</sub> wag (G)
	1335 M, sh	1337 W	1339 M	1339 M	{ 1336 VW 1332 VW }	{ 1343 W 1338 M }	CH <sub>2</sub> wag (T)
1304 VW	{ 1315 S 1307 S 1300 S }	1305 VW, sh	1306 S	1307 M			CH <sub>2</sub> wag (G)
1259 VW		1288 VW	1300 M, sh	1295 VW, sh	{ 1288 M 1284 VW, sh }		CH <sub>2</sub> twist (T)
	{ 1266 S 1258 M, sh }		1266 M, sh	1266 W, sh	{ 1262 VW, sh 1254 VW }	{ 1268 VW, sh 1262 M }	CH <sub>2</sub> wag (T)
		1256 W	1260 S	1261 M			CH <sub>2</sub> twist (G)
1212 VW		{ 1217 VW, sh 1209 W }	1211 VW	1215 VW	1220 VW		CH <sub>2</sub> twist (T) CH <sub>2</sub> twist (G)
1108 W	{ 1098 VW, b }	{ 1104 W 1090 VW, sh }	1103 VW 1090 VW	1105 VW	1104 W	1104 VW	CC stretch (T) CC stretch (G)
1079 VW			1078 VW	1080 VW	1078 VW	1079 W	CH <sub>3</sub> op-rook (T)
1067 W	{ 1068 VW, sh }	{ 1063 W 1038 W, sh 1027 M }	1063 W	1065 W			CC stretch (G)
1042 W, sh	{ 1051 W }		1038 W				CH <sub>3</sub> op-rock (G)
1032 M	{ 1038 W }		1030 W	1035 M			
899 W	{ 908 S 903 S, sh 898 S }	899 W, sh*	899 S	897 S	1028 VS	1029 W	CC stretch (T)
					{ 904 W 898 S }		CH <sub>3</sub> ip-rock (T)
		895 W	895 S, sh		861 VW	863 VW	CH <sub>3</sub> ip-rock (G) CH <sub>2</sub> rock (T)
857 M	{ 866 M 859 M 852 M, sh }	856 W	856 M	857 M			CH <sub>2</sub> rock (G)
793 S	{ 802 S 793 S 787 S }	787 S	789 VS	786 VS			CH <sub>2</sub> rock (G)
745 S	748 S, b	723 S	746 W, sh	748 M	745 VW 728 VW	748 S 730 VW, sh	CH <sub>2</sub> rock (T) Origin unknown
			727 S	720 S	{ 717 S, sh 712 VS 698 VW }	715 VS	CCl stretch (T)
							<sup>13</sup> CCl stretch (T)?
663 VS	{ 671 S 665 S 658 S }	648 VS	651 VS	645 VS			CCl stretch (G)
422 VW		424 W	425 VW	425 VW			CCC deform (G)
364 S		364 S	365 VW	362 VW	{ 367 S, sh 361 S }	361 VW	CCC deform (T)
288 M		292 M	291 VW	296 VW			CCCl deform (G)
242 VW		248 W	246 VW	245 VW	241 W	245 VW	CCCl deform (T)
207 VW		214 VW					CH <sub>3</sub> torsion (G)
130 W		140 VW			145 W		CC torsion (T, G)

Observed frequency (cm <sup>-1</sup> ) <sup>a)</sup>								Assignment <sup>b)</sup>
Gas		Liquid		Glass	Crystal			
R	IR	R	IR	IR	R	IR		
					1485 VW	1484 VW	Overtone or combination?	
	1464 S		1464 S			1463 W, sh	CH <sub>2</sub> scis	
1452 VW, sh	1451 S	1458 VW, sh	1458 S	1453 M	{1457 VW 1450 VW	1458 M, sh 1446 S	CH <sub>3</sub> op-d-deform CH <sub>3</sub> ip-d-deform	
1443 W	1443 M, sh	1436 W	1435 S	1428 M	{1438 W 1432 W	{1440 M, sh 1433 W, sh	CH <sub>2</sub> scis	
1387 VW	{1393 M 1383 M	1381 VW*	1382 S	{1375 M 1363 W, sh	1365 VW	1368 M	CH <sub>3</sub> s-deform (G) CH <sub>3</sub> s-deform (T)	
1338 VW	1348 VW	1336 VW, sh	1343 VW	1342 VW			CH <sub>2</sub> wag (G)	
1331 VW	1340 VW	1326 VW	1330 W	1327 VW	{1335 VW, sh 1321 W	{1336 M, sh 1327 S	CH <sub>2</sub> wag (T)	
1288 VW	1296 S 1288 S	1290 VW, sh 1283 VW	1287 VS	1283 S	{1289 W	1291 VW	CH <sub>2</sub> twist (T) CH <sub>2</sub> twist (G)	
				1253 VW		1245 VW, sh	Origin unknown	
1233 VW, sh	1235 VS	1233 VW, sh	1233 VS, sh	1226 VS	{		CH <sub>2</sub> wag (G)	
1226 W	1227 VS	1226 W	1228 VS		{1226 VW 1219 W	{1222 S 1218 S	CH <sub>2</sub> wag (T)	
		1213 VW*			1211 VW		CH <sub>2</sub> twist (T)	
1200 VW		1198 VW	1200 W				CH <sub>2</sub> twist (G)	
1099 VW		1100 VW	1099 VW	1102 VW	1099 W	1099 W	CC stretch (T)	
	1085 W, b	1081 VW	1082 VW	1080 VW			CC stretch (G)	
		1041 VW, sh*	1042 W, sh	1065 W	1039 W	1039 M	CH <sub>3</sub> ip-rock (G)	
1027 W	1033 W, b	{1031 W, sh 1025 M	{1032 M 1025 W, sh	1040 W	{		CH <sub>3</sub> op-rock (T) CH <sub>3</sub> op-rock (G)	
1008 VW, sh				1029 W	1025 S	1025 W	CC stretch (T)	
							Origin unknown	
						953 VW	Origin unknown	
896 VW, sh	{903 W, sh 895 M	896 VW, sh	897 M	896 M	895 VW	{898 M 894 M, sh	CH <sub>3</sub> ip-rock (T)	
887 VW	883 W, sh	886 W	888 M	888 M			CC stretch (G)	
856 VW	848 W	850 VW, sh			{852 VW	851 W	CH <sub>2</sub> rock (T)	
840 VW	836 W	840 W	841 M	842 M	{		CH <sub>2</sub> rock (G)	

TABLE 3. CONTINUED

Observed frequency (cm <sup>-1</sup> ) <sup>a)</sup>							Assignment <sup>b)</sup>
Gas		Liquid		Glass	Crystal		
R	IR	R	IR	IR	R	IR	
{792 VW, sh 778 W	{788 M 780 M 773 M	777 M	778 S	774 <sub>4</sub> VS			CH <sub>2</sub> rock (G)
742 VW	752 W		740 W	738 M 720 VW	736 VW 714 VW	738 VS 714 W	CH <sub>2</sub> rock (T) Origin unknown
660 S	{666 S 657 S	648 S	648 S	644 VS	638 VS	637 VS	CBr stretch (T)
627 W	630 W, b	620 VW, sh	620 VW, sh		625 VW, sh	623 VW, sh	2 × 313 cm <sup>-1</sup> or <sup>13</sup> CBr stretch (T)?
572 VS	{580 S 573 S 567 S	563 VS	563 VS	559 VS			CBr stretch (G)
523 VW							Origin unknown
401 W		402 M	401 VW	402 VW			CCC deform (G)
363 VW					363 VW		Origin unknown
311 S		311 S	312 VW	311 VW	313 S	311 VW	CCC deform (T)
268 W		274 W	273 VW	277 VW			CCBr deform (G)
					232 W		CH <sub>3</sub> torsion (T)
217 W		224 W			222 W		CCBr deform (T)
198 VW		205 VW, sh					CH <sub>3</sub> torsion (G)
122 W		133 W					CC torsion (T)
					115 W, sh 111 M 86 W, sh 77 W, sh 65 M 48 W, sh 39 M		Lattice vibrations

a), b) See a) and b), respectively, of Table 2.

TABLE 4. OBSERVED FREQUENCIES AND VIBRATIONAL ASSIGNMENTS OF 1-IODOPROPANE

Observed frequency (cm <sup>-1</sup> ) <sup>a)</sup>							Assignment <sup>b)</sup>
Gas		Liquid		Glass	Crystal		
R	IR	R	IR	IR	R	IR	
		1469 VW, sh*	1460 S			1488 W	591 + 898 cm <sup>-1</sup> ?
						1473 W, sh	CH <sub>2</sub> scis
	1458 M 1443 W, sh }	1455 W	1456 S	1452 M	{ 1460 VW 1454 VW 1448 VW 1443 VW }	1460 S	CH <sub>3</sub> op-d-deform
					{ 1451 S 1438 S }		CH <sub>3</sub> ip-d-deform
1435 W, b		1433 W	1435 M, sh }				CH <sub>2</sub> scis (G)
		1427 W	1428 S }	1423 M	{ 1418 VW	1415 S	CH <sub>2</sub> scis (T)
1383 VW	{ 1392 M 1383 M }	1378 VW	1380 S	1376 M	{ 1375 VW 1367 VW }	{ 1386 W 1376 W 1370 W }	CH <sub>3</sub> s-deform
						1349 VW	Origin unknown
	{ 1354 W 1343 W }	1338 VW, sh*	1344 M	1340 W			CH <sub>2</sub> wag (G)
1332 W		1323 W	1328 W	1325 VW	1324 W	1325 M	CH <sub>2</sub> wag (T)
						1304 VW	Origin unknown
1282 W	{ 1291 S 1279 S }	1285 VW, sh*			1286 VW	1289 VW	CH <sub>2</sub> twist (T)
		1273 W	1279 S	1275 S			CH <sub>2</sub> twist (G)
						1212 VW	Origin unknown
						1206 VW	Origin unknown

TABLE 4. CONTINUED

Observed frequency (cm <sup>-1</sup> ) <sup>a)</sup>							Assignment <sup>b)</sup>
Gas		Liquid		Glass	Crystal		
R	IR	R	IR	IR	R	IR	
1202 M	{1208 S 1195 VS	1194 M	1195 VS	1194 VS			CH <sub>2</sub> wag (G)
1189 M	1185 VS, sh	1184 M	1185 VS	1186 VS	1182 W	1185 VS	CH <sub>2</sub> wag (T), CH <sub>2</sub> twist (T)
						1158 W, sh	Origin unknown
	1133 W		1121 VW			1117 W	Origin unknown
1089 VW	{1083 W, b	{1088 VW	1089 VW	1090 VW	{1092 VW 1087 VW	1090 M	CC stretch (T)
1076 W		{1073 W	1075 W	1075 W			CC stretch (G)
1035 VW, sh		1032 VW, sh	1036 VW, sh				CH <sub>3</sub> op-rock (G)
1024 M	{1016 W, b	{1019 M	1020 W, sh		1016 W	1020 W	CC stretch (T)
1013 W, sh		{1011 W, sh	1012 M	1010 W	1011 VW	1013 W	CH <sub>3</sub> op-rock (T), CC stretch (G)
895 VW, sh	{888 M	{894 VW, sh	895 M	895 M	898 VW	{898 M 880 W, sh	CH <sub>3</sub> ip-rock (T)
880 W		{879 W	880 M	880 M			CH <sub>3</sub> ip-rock (G)
	823 W, sh	828 VW, sh			828 VW	829 W	CH <sub>2</sub> rock (T)
817 VW	812 W	816 VW	816 M	817 M			CH <sub>2</sub> rock (G)
765 W	765 M	763 M	764 S	762 S			CH <sub>2</sub> rock (G)
		711 VW	726 W	722 M	724 VW	716 VS	CH <sub>2</sub> rock (T)
602 S	603 W	593 S	594 M	593 S	594 VS	591 VS	CI stretch (T)
					578 VW	575 W	<sup>13</sup> CI stretch (T)
{518 VS 503 S	{523 W 512 W	503 VS	503 M	500 S			CI stretch (G)
388 W		390 M	388 VW	388 VW			CCC deform (G)
285 VS		288 S	285 VW	270 VW	{286 S	285 VW	CCC deform (T)
256 W		263 W	263 VW				CCI deform (G)
					240 VW		CH <sub>3</sub> torsion (T)
197 M		203 M			206 M		CCI deform (T)
189 W, sh							CH <sub>3</sub> torsion (G)
116 W		130 VW			144 VW		CC torsion (T)
					116 VW	}	Lattice vibrations
					91 M		
					69 M		
					53 S		
					46 S		
					28 S		

a), b) See a) and b), respectively, of Table 2.

cm<sup>-1</sup> band) and 339 cm<sup>-1</sup> and the infrared bands at 438 (a shoulder of the 449 cm<sup>-1</sup> band) and 339 cm<sup>-1</sup> indicate the existence of the GG form. In the gaseous state, a trend similar to the case of 1-bromobutane is observed in the Raman spectral pattern around 440 cm<sup>-1</sup>. The existence of the TG and GG forms is confirmed by the observation of the Raman bands at 995 and 337 cm<sup>-1</sup>, respectively.

It is not probable that the GG' form of 1-bromobutane exists, since no bands are observed in the gaseous, liquid, or glassy state around its characteristic frequency of 331 cm<sup>-1</sup>. The distance between the terminal methyl group and the bromine atom seems to be too short for the GG' form to be stable. Thus, it is also improbable that the GG' form of 1-chloro- or 1-iodobutane

exists, although its existence is uncertain from the normal coordinate analysis because of the coincidence of the frequencies of the GG' and other forms.

As has been described above, the key bands for the individual isomers of each molecule in the skeletal deformation region have become clear. These key bands were used for the determination of the enthalpy differences among the isomers in the liquid state. Figure 18 shows the obtained results of the enthalpy differences.

For 1-chlorobutane, the intensity ratios of the Raman bands at 370 (GG form) and 474 cm<sup>-1</sup> (TG form), those at 401 (TT form) and 474 cm<sup>-1</sup>, and those at 437 (GT form) and 474 cm<sup>-1</sup> gave the enthalpy differences,  $\Delta H_{GG-TG} = 210 \pm 110$  cal/mol,  $\Delta H_{TT-TG} = 150 \pm 50$  cal/

TABLE 5. OBSERVED FREQUENCIES AND VIBRATIONAL ASSIGNMENTS OF 1-CHLOROBUTANE

Observed frequency (cm <sup>-1</sup> ) <sup>a)</sup>									
Gas		Liquid		Glass		Crystal		Assignment <sup>b)</sup>	
R	IR	R	IR	R	IR	R	IR		
1454 M, b	1460 VS, b	1480 VW, sh	1476 M, sh	1483 VW, sh	1474 M, sh	1488 W	1486 VW	CH <sub>2</sub> scis	
		1468 M, sh*	1467 VS	1468 W, sh	1465 S	{1477 VW 1471 VW}	{1475 M, sh 1469 S}	CH <sub>2</sub> op-d-deform, CH <sub>2</sub> scis	
		1458 M*	1460 VS	1454 M	1456 S	{1462 W 1451 M}	{1462 S 1454 M, sh}	CH <sub>2</sub> scis, CH <sub>3</sub> op-d-deform	
		1447 M	1446 S	1443 M	1442 M, sh	1444 M	1447 W, sh	CH <sub>3</sub> ip-d-deform	
		1434 W, sh	1433 M	1432 M	1428 M, sh	1438 W, sh	1432 W	CH <sub>2</sub> scis	
1348 VW	{1393 M 1387 M 1368 W 1359 W 1352 W 1340 W, sh 1322 M, sh}	1383 VW	1383 M	1380 VW	1377 M	1378 VW	1383 M	CH <sub>3</sub> s-deform	
		1369 VW		1370 VW					CH <sub>2</sub> wag (TG)
		1358 VW	1360 VW	1360 VW	1359 W	1360 VW	1362 M		CH <sub>2</sub> wag (TT, GG)
		1346 VW	{1349 VW 1344 W}	1346 VW	1348 VW				CH <sub>2</sub> wag (GT)
			1319 M, sh						CH <sub>2</sub> wag (GG, GT)
1313 W, sh	1312 S, sh	1311 W	1316 M	1315 W	1315 S	{1324 VW 1314 W}	{1316 S 1307 W}	CH <sub>2</sub> wag (TG)	
1297 W	1300 VS	1300 W	1302 M, sh	1299 W	1298 M, sh	1303 M		CH <sub>2</sub> wag (TT, GG)	
		1285 W, sh	1291 S	1284 VW	1285 S			CH <sub>2</sub> twist (TT, TG)	
1250 VW	{1253 M 1244 M}	1242 VW, sh	1248 M	1242 VW, sh	1245 M	1280 VW	1284 VW	CH <sub>2</sub> wag (TG), CH <sub>2</sub> twist (GT)	
		1234 VW	1234 VW, sh	1236 W	1237 W, sh	1240 VW	1246 S	CH <sub>2</sub> twist (TT)	
		1230 VW, sh						CH <sub>2</sub> wag (TT), CH <sub>2</sub> twist (GT)	
1238 VW								CH <sub>2</sub> twist (TG)	
1228 VW								CH <sub>2</sub> twist (GG)	
1198 W	1195 VW					1205 W	1208 VW	CH <sub>2</sub> twist (TT)	
		1198 VW	1200 VW 1190 VW	1199 W	1200 W			CH <sub>2</sub> twist (TG)	
		1178 VW, sh	1178 VW	1178 VW				CH <sub>2</sub> twist (GT)	
1107 W	{1113 W 1102 W}	1107 W	1106 W	1108 M	1106 W	{1109 S 1100 VW}	1109 M	CH <sub>2</sub> twist (GG)	
1085 W		1084 W	1085 VW	1086 W	1083 VW	1087 W	1088 VW	CC stretch (TT, TG, GT)	
1064 W, sh	1057 W		1080 VW					CH <sub>2</sub> rock (TT), CH <sub>3</sub> ip-rock (TG), CC stretch (GT)	
		1058 W, sh	1058 VW, sh					CH <sub>3</sub> op-rock (GG)	
1050 W	1050 W, sh	1050 W	1051 W	1049 M	1048 M	1052 M	1052 M	CC stretch (GG, GT)	
1017 VW	1023 W, sh	1015 VW	1017 W	1018 W	1017 W	1017 M	1018 M	CC stretch (TT)	
1000 VW	1010 W	998 VW	1000 W	1000 W	999 M			CC stretch (TG)	
976 VW	972 W, sh	972 VW	973 VW	973 VW	972 VW			CH <sub>3</sub> ip-rock (GG), CH <sub>3</sub> op-rock (GT)	
929 VW	934 W	932 VW, sh	932 W	932 W	931 M			CH <sub>2</sub> rock (TG)	
		927 W			922 VW, sh	920 VW	924 W	CH <sub>3</sub> op-rock (TT), CH <sub>2</sub> rock (GG, GT)	
897 W		896 W	898 VW	899 W	897 VW	900 S	898 W	CH <sub>2</sub> ip-rock (TT, GT)	
876 W	{882 M 877 M 872 M}	872 W	875 M	872 W	870 S			CH <sub>3</sub> op-rock (TG), CH <sub>2</sub> rock (GG)	
813 M		811 M	812 VW	813 M	812 VW			CH <sub>2</sub> rock (TG)	
800 M		800 W	801 VW	803 VW, sh	804 VW, sh			CC stretch (GG), CH <sub>2</sub> rock (GT)	
761 W	790 M		783 W	786 VW	783 VW	788 VW	787 VW	CH <sub>2</sub> rock (TT)	
	767 M, sh	755 VW, sh	757 M, sh					CH <sub>2</sub> rock (GG, TT)	
	753 VS	746 M	747 S	746 W	747 VS			CH <sub>2</sub> rock (TG)	
					738 M, sh	{743 VW 738 VW}	{740 S 736 S}	CH <sub>2</sub> rock (TT)	

TABLE 5. CONTINUED

Observed frequency (cm <sup>-1</sup> ) <sup>a)</sup>								Assignment <sup>b)</sup>
Gas		Liquid		Glass		Crystal		
R	IR	R	IR	R	IR	R	IR	
748 S	743 VS	727 M	730 S	721 M	723 VS	{725 S 718 VS	722 VS	CCl stretch (TT)
726 W	722 M, sh	718 M, sh	718 M, sh					CCl stretch (GT)
665 VS	{671 S 663 S	653 VS	653 VS	647 VS	650 VS			CCl stretch (TG, GG)
473 W		474 W	473 VW	476 W	474 VW			CCC deform (TG)
459 VW, sh		458 VW, sh	458 VW, sh					CCC deform (GG)
434 VW		437 VW	436 VW	438 VW				CCC deform (GT)
397 VW		401 VW	399 VW	398 VW	398 VW	397 W	400 VW	CCC deform (TT)
370 VW		370 VW	370 VW	370 VW				CCC deform (GG)
332 S		334 S	333 VW	334 S	332 VW	333 VS	334 VW	CCC deform (TT)
298 S		302 M	300 VW	305 W	302 VW			CCCl deform (TG), CCC deform (GT)
262 VW		265 VW, sh		266 VW				CCC deform (TG), CCCl deform (GT)
238 VW		243 VW		247 VW				CCCl deform (GG)
154 VW		161 VW		170 VW		237 VW		CH <sub>3</sub> torsion (TT)
120 VW		125 VW		139 W		166 M		CCCl deform (TT)
						148 W		
						133 VW		
						124 W		
						100 VW		
						85 M		
						69 S		
						41 S		
						28 S		
								Torsions (TT) and lattice vibrations

a), b) See a) and b), respectively, of Table 2.

TABLE 6. OBSERVED FREQUENCIES AND VIBRATIONAL ASSIGNMENTS OF 1-BROMOBUTANE

Observed frequency (cm <sup>-1</sup> ) <sup>a)</sup>								Assignment <sup>b)</sup>
Gas		Liquid		Glass		Crystal		
R	IR	R	IR	R	IR	R	IR	
		1488 VW*	1473 W, sh	1488 VW, sh		1478 VW		CH <sub>2</sub> scis
	1465 M	1465 W, sh*	1466 S	1468 W, sh	1462 S	1462 W	1466 M	CH <sub>3</sub> op-d-deform, CH <sub>2</sub> scis
1453 M, sh		1456 W, sh*	1458 S, sh			1454 VW	1448 M	CH <sub>2</sub> scis
1448 M	1452 M, sh	1448 M	1452 M, sh	1448 M		1443 W	1442 M	CH <sub>3</sub> ip-d-deform
	1442 M, sh	1438 M	1437 S					CH <sub>2</sub> scis
		1429 W, sh	1430 M, sh	1427 M	1430 S	{1433 VW 1428 W	1435 W, sh	CH <sub>2</sub> scis
	{1390 W 1386 W 1368 VW	1381 VW	1382 M	1378 VW	1378 M	1376 VW	1375 M	CH <sub>3</sub> s-deform
			1370 VW, sh		1368 M, sh			CH <sub>2</sub> wag (TG)
1363 VW		1357 VW	1360 VW	1356 VW	1358 W	1356 VW	1358 W	CH <sub>2</sub> wag (TT)
			1355 VW					CH <sub>2</sub> wag (GG)
			1347 VW					CH <sub>2</sub> wag (GT)
1343 VW		1337 VW	1340 VW					CH <sub>2</sub> wag (GG, GT)
1308 W, sh	1307 M, sh	1305 W	1308 W, sh	1305 W	1308 M, sh	1312 W		CH <sub>2</sub> twist (TT,TG)
1295 W	1300 M	1295 W	1299 M	1294 W	1298 M	{1300 W 1296 W	{1299 M 1293 M	CH <sub>2</sub> wag (TT, TG)
	1297 M	1288 W	1293 M		1292 M, sh			CH <sub>2</sub> twist (GG,GT)
1267 M	1272 VS	1262 M	1267 VS	{1273 VW 1261 W		{1275 VW 1270 VW	1277 VW	CH <sub>2</sub> twist (TT)
					1263 VS			CH <sub>2</sub> twist (TG, GG, GT)

TABLE 6. CONTINUED

Observed frequency (cm <sup>-1</sup> ) <sup>a)</sup>								Assignment <sup>b)</sup>
Gas		Liquid		Glass		Crystal		
R	IR	R	IR	R	IR	R	IR	
1217 M	{1224 VS 1217 S, sh	1220 W, sh* 1215 M	1219 VS	1218 W	{1222 VS 1217 VS	{1217 W 1209 VW, sh	1213 S	CH <sub>2</sub> wag (TG, GG, GT) CH <sub>2</sub> wag (TT)
1189 VW		1186 VW	1189 VW	1198 VW	1203 W, sh	1199 VW		CH <sub>2</sub> rock (TT)
1155 VW		1160 VW	1164 VW	1187 W	1189 W			CH <sub>2</sub> twist (TG, GT)
1103 M	{1107 W 1100 W	1100 M	1100 W	1162 VW	1164 VW			CH <sub>2</sub> twist (GG)
				1101 M	1103 W	1104 M	1104 M	CC stretch (TT, GT)
					1100 W, sh			CC stretch (TG)
	1074 VW, sh		{	1080 VW				CC stretch (GT)
			1064 VW					CH <sub>3</sub> op-rock (GG)
1060 M	1057 W	1057 M	1053 VW, sh	1056 W, sh	1056 W, sh	1056 W, sh	{	{CC stretch (TT), CH <sub>3</sub> ip-rock (TG)
1048 W, sh	1048 W, sh	1048 M	1048 W	1046 M	1047 M	1047 W	1051 M	{CH <sub>2</sub> twist (TT), CC stretch (TG, GT)
1013 W	{1022 VW, sh 1008 W	1013 W	1014 VW	1014 W	1016 W	1013 W	1016 W	CC stretch (TT)
1000 VW	997 W	997 VW	996 W	996 W	997 S			CC stretch (TG)
973 VW, sh		972 VW	970 VW	969 VW	970 W			CH <sub>3</sub> ip-rock (GG), CH <sub>3</sub> op-rock (GT)
915 VW, sh	918 W	915 VW, sh	915 W	913 W	916 S			CH <sub>2</sub> rock (TG, GG)
907 W, sh		907 W					908 W	CH <sub>3</sub> op-rock (TT), CH <sub>2</sub> rock (GT)
896 M		893 M	895 VW	893 W	895 W	{902 M 897 W, sh	898 W	CH <sub>3</sub> ip-rock (TT)
869 M	{873 W 868 W	868 M	867 M	864 W	865 S			CH <sub>3</sub> op-rock (TG), CH <sub>2</sub> rock (GG), CH <sub>3</sub> ip-rock (GT)
800 S	800 W	799 M	797 W	801 M	801 W			CH <sub>2</sub> rock (TG), CC stretch (GG)
	783 W	777 VW*	777 W	775 VW	778 W	776 VW		CH <sub>2</sub> rock (TT, GT)
743 M	{764 W, sh 748 S	740 M	742 S	740 W	740 VS			CH <sub>2</sub> rock (TG, GG, GT)
	738 M, sh		732 M, sh		733 VS	741 VW	733 VS	CH <sub>2</sub> rock (TT)
658 VS	{664 M 657 M	643 S	646 S	640 S	642 VS	{649 M 636 VS	{650 VW, sh 637 VS	CBr stretch (TT, GT)
					621 VW	620 VW	620 W, sh	<sup>13</sup> CBr stretch (TT)?
576 VS	{582 M 574 M	562 VS	564 S	558 VS	558 VS			CBr stretch (TG, GG)
456 VW, sh		463 W	459 VW	462 M	459 VW			CCC deform (TG)
448 W		448 VW, sh	445 VW, sh	448 VW, sh	444 VW, sh			CCC deform (GG)
415 VW		417 VW	417 VW	419 VW	417 VW			CCC deform (GT)
390 VW		393 VW	393 VW	392 VW	392 VW	397 VW	394 VW	CCC deform (TT)
350 VW		353 VW	352 VW	355 VW	352 VW			CCC deform (GG)
276 VS		279 S	277 VW	278 S	275 VW	280 S	274 VW	CCC deform (TT, GT), CCBBr deform (TG)
				267 W, sh				CCC deform (TG)
232 S		238 M		242 W				CCBr deform (GT)
215 S		224 M, sh		227 VW, sh				CH <sub>3</sub> torsion
138 M		143 W		153 VW		162 M		CCBr deform (TT)
105 W		115 VW		122 VW		125 VW		CC torsion
						108 W		
						93 VW		
						84 VW		
						67 M		
						57 W		
						42 VW, sh		
						36 S		
								Torsion (TT) and lattice vibrations

a), b) See a) and b), respectively, of Table 2.

TABLE 7. OBSERVED FREQUENCIES AND VIBRATIONAL ASSIGNMENTS OF 1-IODOBUTANE

Observed frequency (cm <sup>-1</sup> ) <sup>a)</sup>								Assignment <sup>b)</sup>
Gas		Liquid		Glass		Crystal		
R	IR	R	IR	R	IR	R	IR	
1448 W, b	1465 VW, sh	1466 VW*	1474 W, sh 1463 S	1481 VW 1465 VW, sh	1458 VS, sh	1470 VW 1457 W	1459 S	CH <sub>2</sub> scis CH <sub>3</sub> op-d-deform, CH <sub>2</sub> scis
	1460 W	1453 W, sh*	1457 S, sh	1452 W	1451 VS	1452 VW	1450 M, sh	CH <sub>2</sub> scis
	1452 W, sh	1446 W	1445 M, sh			1441 VW	1438 VW	CH <sub>3</sub> ip-d-deform
	1437 W, sh	1429 W	1431 M, sh	1430 W, sh				CH <sub>2</sub> scis
		1423 W, sh*	1425 M, sh	1424 W				CH <sub>2</sub> scis
1355 VW			1419 M		1419 S	1417 W	1419 W	CH <sub>2</sub> scis
	1384 W	1379 VW	1380 M	1377 VW	1373 S	{1377 VW 1372 VW}	1371 W	CH <sub>3</sub> s-deform
		1368 VW	1367 W	1366 VW	1365 M, sh			CH <sub>2</sub> wag (TG)
1339 VW	1352 VW	1353 VW	1354 W, sh 1350 W	1353 VW	1353 W	1354 VW	1356 W	CH <sub>2</sub> wag (TT, GG)
1289 VW		{1343 VW 1333 VW	1343 W, sh 1336 VW, sh	1343 VW 1332 VW	1333 VW, sh			CH <sub>2</sub> wag (GT)
		1303 VW	1306 VW, sh	1302 W	1304 W, sh	1308 W		CH <sub>2</sub> wag (GG)
	1298 VW, sh		1295 W, sh					CH <sub>2</sub> wag (GT)
1250 W		1288 W	1290 W	1287 W	1288 S	{1290 W 1276 VW}	{1289 M 1274 VW}	CH <sub>2</sub> twist (TT, TG)
	{1278 M 1271 M, sh			1272 VW	1272 W, sh			CH <sub>2</sub> wag (TT)
	1261 M	1263 VW	1264 W, sh	1263 VW				CH <sub>2</sub> twist (GG)
1193 M, sh	1252 M, sh	1248 W	1250 VS	1247 W	1246 VS		1250 VW	CH <sub>2</sub> twist (GT)
						1201 VW		CH <sub>3</sub> twist (TT, TG, GG, GT)
	{1203 M, sh 1193 M	1191 M	1192 VS	1192 W	1190 M			Origin unknown
1185 M	1183 M, sh	1183 M	1183 VS, sh	1182 W, sh		{1187 W, sh 1183 W		CH <sub>2</sub> wag (TG, GG)
1095 W		1175 M, sh	1175 VS, sh	1176 W	1173 M	1178 VW	1175 VS	CH <sub>2</sub> wag (TT, GT)
		1153 VW, sh*		1157 VW	1153 W, sh			CH <sub>2</sub> rock (TT), CH <sub>2</sub> twist (GT)
			1122 VW					CH <sub>3</sub> ip-rock (TG)
	1094 VW	1093 W	1093 W	1093 W	1089 VW	1098 W	1095 VW	CC stretch (GG)
1050 W		1089 VW, sh		1091 W, sh				CC stretch (TT, TG)
		1059 VW, sh	1058 VW, sh					CC stretch (GT)
		1049 W	1050 VW	1050 W	1047 VW	1050 W	1049 W	CH <sub>3</sub> op-rock (GG)
1010 W			1037 VW	1039 VW, sh				CC stretch (TT, TG)
		1032 VW, sh	1032 VW, sh	1036 VW	1035 VW, sh	{1034 VW 1024 VW}	1029 VW	CH <sub>2</sub> twist (TT, TG)
		1008 W	1011 VW	1013 W	1008 VW, sh	{1014 M 1006 VW}	1013 VW	CH <sub>3</sub> ip-rock (GT)
995 VW		990 VW	991 VW	990 VW	987 W			CH <sub>2</sub> twist (TT, TG)
970 VW		968 VW	968 VW	970 VW	966 VW, sh			CC stretch (TT)
889 W	898 VW	896 W, sh	896 W	895 W, sh	893 W	{901 M 895 W	{898 W 892 M	CC stretch (TG)
		889 W	891 VW, sh	892 W				CH <sub>3</sub> ip-rock (GG), CH <sub>3</sub> op-rock (GT)
		886 W, sh						CH <sub>2</sub> rock (TG, GT)
860 W	{870 VW 863 VW	861 W	863 W	861 W	859 W			CH <sub>3</sub> ip-rock (TT), CH <sub>3</sub> op-rock (TT)
786 W	790 VW, sh	786 VW	787 W	792 VW, sh	788 VW, sh			CH <sub>2</sub> rock (GG)
778 W		779 VW	779 W	781 VW	778 W			CH <sub>3</sub> op-rock (TG), CH <sub>2</sub> rock (GG)
	{765 VS 759 VS, sh 750 VS		772 W	763 VW	765 VW, sh	764 VW	762 VW	CC stretch (GG)
								CH <sub>2</sub> rock (TG, GT)



TABLE 7. CONTINUED

Observed frequency (cm <sup>-1</sup> ) <sup>a)</sup>								Assignment <sup>b)</sup>	
Gas		Liquid		Glass		Crystal			
R	IR	R	IR	R	IR	R	IR		
736 W		736 W	735 M	735 W	728 M	{	731 VW	730 S	CH <sub>2</sub> rock (TG, GG)
728 VW, sh	724 W, sh	728 W, sh	726 M, sh	723 VW, sh					CH <sub>2</sub> rock (TT, GT)
601 S	600 W	593 S	592 M	593 S	590 M	{	595 S	596 VS	CI stretch(TT, GT)
							592 VS		
							589 S		
							577 VW		<sup>13</sup> CI stretch (TT)?
		515 S, sh	518 VW, sh	517 M, sh	520 VW, sh				CI stretch (GG)
511 VS		506 VS	504 W	503 VS	500 W				CI stretch (TG)
453 VW, sh		450 M	449 VW	452 M	449 VW				CCC deform (TG)
436 VW		438 W, sh	438 VW, sh	442 W, sh	435 VW				CCC deform (GG)
408 VW		407 W	406 VW	407 VW					CCC deform (GT)
385 VW		388 VW	387 VW	386 VW	384 VW	389 VW	387 VW		CCC deform (TT)
337 W		339 VW	339 VW	341 VW	348 VW				CCC deform (GG)
		267 M, sh	268 VW	270 W	267 VW				CCC deform (TG, GT)
251 S		251 S	247 VW	250 M		256 S	245 VW		CCC deform (TT), CH <sub>3</sub> torsion (TG)
		231 M, sh		230 W					CH <sub>3</sub> torsion (TT)
		223 M, sh*							CH <sub>3</sub> torsion (GG)
213 M		212 M		213 VW, sh					CCI deform (TG, GT)
203 M									CCI deform (GG)
		190 W, sh*		188 VW					CH <sub>3</sub> torsion (GT)
127 M		132 W		141 W		149 M			CCI deform (TT), CC torsion (TT)
96 W		110 VW		114 VW		112 W			Torsions and lattice vibrations
						95 W			
70 VW				75 VW		74 W			
						60 W			
						55 W			
						45 M			
						34 VW			
						25 M			
						20 W			

a), b) See a) and b), respectively, of Table 2.

TABLE 8. ROTATIONAL ISOMERS OF 1-HALOGENOPROPANES AND 1-HALOGENOBUTANES

	Gas				Liquid				Glass				Crystal
CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> F <sup>a)</sup>	T	G			—				T	G			G
CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> Cl	T	G			T	G			T	G			T
CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> Br	T	G			T	G			T	G			T
CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> I	T	G			T	G			T	G			T
CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> F <sup>b)</sup>	—				TT	TG	GT	GG	—				TG
CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> Cl	TT	TG	GT	GG	TT	TG	GT	GG	TT	TG	GT	TT	TT
CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> Br	TT	TG	GT	GG	TT	TG	GT	GG	TT	TG	GT	GG	TT
CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> I	TT	TG	GT	GG	TT	TG	GT	GG	TT	TG	GT	GG	TT

a) Refs. 7 and 19. b) Ref. 7.

mol, and  $\Delta H_{\text{GT-TG}} = 650 \pm 28$  cal/mol, respectively. The relatively large error is estimated for the  $\Delta H_{\text{GG-TG}}$  value because of the very weak intensity of the band at 370 cm<sup>-1</sup>. Thus, the stability of the rotational isomers in the liquid state is in the order of TG, TT, GG, and GT, with the TG form being the most stable.

For 1-bromobutane, the intensity ratios of the Raman bands at 353 (GG form) and 463 cm<sup>-1</sup> (TG form), those at 393 (TT form) and 463 cm<sup>-1</sup>, and those at 417 (GT form) and 463 cm<sup>-1</sup> gave the enthalpy differences,  $\Delta H_{\text{GG-TG}} = 130 \pm 30$  cal/mol,  $\Delta H_{\text{TT-TG}} = 280 \pm 52$  cal/mol, and  $\Delta H_{\text{GT-TG}} = 680 \pm 44$  cal/mol, respective-

ly. In the liquid state, the stability of the rotational isomers is in the order of TG, GG, TT, and GT.

For 1-iodobutane, the enthalpy differences,  $\Delta H_{GG-TG} = 170 \pm 25$  cal/mol,  $\Delta H_{TT-TG} = -75 \pm 29$  cal/mol, and  $\Delta H_{GT-TG} = 480 \pm 26$  cal/mol were obtained from the pairs of the Raman bands at 339 (GG form) and 450  $\text{cm}^{-1}$  (TG form), those at 388 (TT form) and 450  $\text{cm}^{-1}$ , and those at 407 (GT form) and 450  $\text{cm}^{-1}$ , respectively. Thus, the stability of the rotational isomers in the liquid state is in the order of TT, TG, GG, and GT.

**Comparison with Previous Results.** Table 8 shows the rotational isomers of 1-halogenopropanes and 1-halogenobutanes existing in the various states, including those of 1-fluoropropane and 1-fluorobutane reported by Crowder and Mao.<sup>7)</sup> In the crystalline state, 1-fluoropropane takes the G form and 1-fluorobutane takes the TG form, in contrast with other 1-halogenopropanes and 1-halogenobutanes.

Many investigations<sup>2-6,8-18,20)</sup> indicated for 1-chloro-, 1-bromo-, and 1-iodopropanes that the T form exists in the crystalline state and the T and G forms coexist in the glassy, liquid, and gaseous states. These conclusions have been further confirmed by the present normal vibration calculation of these compounds in conjunction with longer halogenoalkanes.

The quite different values of the enthalpy differences were reported by many authors<sup>4-6,10,11,18-20)</sup> for 1-halogenopropanes. Tanabe and Saeki<sup>17)</sup> discussed this problem and obtained their values of the enthalpy differences by the absolute-intensity method and the temperature-variation method applied to the infrared spectra of the liquid state. The values by the latter method were  $\Delta H_{G-T} = -140$  cal/mol for 1-chloropropane,  $\Delta H_{G-T} = 220$  cal/mol for 1-bromopropane, and  $\Delta H_{G-T} = 580$  cal/mol for 1-iodopropane. However, the present results show that the G form is more stable than the T form by about 100 cal/mol for these three compounds in common in the liquid state. Tanabe and Saeki mentioned that the good air-tightness of the high temperature cell allowed the experiment at temperatures higher than the boiling point of 1-chloro- or 1-bromopropane. This implies that the enthalpy differences obtained are those at pressures higher than 1 atm. The disagreement between their and our values is ascribed, at least in part, to the above fact. As for gaseous 1-fluoropropane, the  $\Delta H_{G-T}$  value of  $-50 \pm 30$  cal/mol was obtained by the microwave measurement.<sup>19)</sup>

There has been disagreement concerning the assignment of the  $\text{CH}_2$  twisting bands of 1-halogenopropanes. Snyder and Schachtschneider<sup>14)</sup> assigned the 1292  $\text{cm}^{-1}$  band of 1-chloropropane to the *trans*  $\text{CH}_2$  twisting mode on the basis of the normal vibration calculation of many kinds of chloroalkanes and Hayashi *et al.*<sup>15)</sup> assigned the 1288  $\text{cm}^{-1}$  band of 1-bromopropane to the *trans*  $\text{CH}_2$  twisting mode. These assignments agree with those by Brown and Sheppard<sup>9)</sup> and Komaki *et al.*<sup>11)</sup> On the other hand, Tanabe and Saeki<sup>17)</sup> had doubts of these assignments from the viewpoint that the twisting frequencies of the  $\text{CH}_2$  group (adjacent to  $\text{CH}_3$ ) in 1-halogenopropanes should be lower than that of propane, 1278  $\text{cm}^{-1}$ , and that the twisting frequency of the  $\text{CH}_2$  group (adjacent to  $\text{CH}_3$ ) should be lower

than the wagging frequency of the  $\text{CH}_2$  group (adjacent to halogen) in the *trans* form. Thus, they assigned the 1256, 1200, and 1180  $\text{cm}^{-1}$  bands of 1-chloro-, 1-bromo-, and 1-iodopropanes, respectively, to the *trans*  $\text{CH}_2$  twisting mode. In the present study, however, the Raman band of 1-chloropropane at 1288  $\text{cm}^{-1}$ , the Raman and infrared bands of 1-bromopropane at 1289 and 1291  $\text{cm}^{-1}$ , respectively, and the Raman and infrared bands of 1-iodopropane at 1286 and 1289  $\text{cm}^{-1}$ , respectively, all of which are definitely observed in the crystalline state (see Figs. 1—6), are assigned consistently to the *trans*  $\text{CH}_2$  twisting mode on the basis of our normal vibration calculation including the data of longer halogenoalkanes. Tanabe and Saeki did not assign these bands to any vibration of the T form of 1-halogenopropanes. Also, their grounds for interpreting the spectra are not appropriate, since it is generally acceptable that the twisting frequency of the  $\text{CH}_2$  group (adjacent to  $\text{CH}_3$ ) can be higher than the twisting frequency of a single isolated  $\text{CH}_2$  group in propane owing to the vibrational coupling between the two  $\text{CH}_2$  twisting modes in 1-halogenopropanes, and that it can be higher than the wagging frequency of the  $\text{CH}_2$  group (adjacent to halogen) owing to the mass effect by the halogen atom. The situation is almost the same for the *gauche* twisting frequencies.

Many studies<sup>4-9,14,16,21-26)</sup> have been made on the rotational isomerism of 1-halogenobutanes. Ukaji and Bonham<sup>26a)</sup> proposed for 1-chlorobutane an isomer distribution of 37% TG, 24% GG', 17% GG, 11% TT, and 11% GT in the gaseous state and Momany *et al.*<sup>26b)</sup> proposed for 1-bromobutane 36% TT, 24% TG, 24% GT, and 16% GG in the gaseous state by the electron-diffraction method. Snyder and Schachtschneider<sup>14)</sup> concluded for 1-chlorobutane that the TT form exists in the crystalline state and the TT and TG forms coexist in the glassy state on the basis of the comparison of the crystalline- and glassy-state spectra and of the normal coordinate analysis. Crowder and Ali<sup>8a)</sup> interpreted the spectra of 1-iodobutane, taking into account only two among various isomers, the TT and TG forms. In the present study, it has been also found that the GT and GG forms of each of 1-halogenobutanes exist in the gaseous, liquid, and glassy states in addition to the TT and TG forms. However, the existence of the GG' form was not identified in any state of these compounds. The skeletal deformation vibrations of 1-chlorobutane<sup>22)</sup> and 1-bromobutane<sup>22,23)</sup> were discussed in relation to the identification of existing rotational isomers. The results of these studies, however, do not agree with ours.

Studies concerning the relative stability of the isomers of 1-halogenobutanes have not yet been fully made. So far, only the apparent enthalpy difference between the mixture of the TT and GT forms and that of the TG and GG forms has been determined from the C-Br stretching bands of 1-bromobutane by the infrared and Raman methods,<sup>5,6)</sup> and the relative stabilities of the *trans* and *gauche* conformations about the CC-CX and CC-CCX axes have been estimated by the electron-diffraction method.<sup>26)</sup> In the present study, it has been possible to determine the enthalpy differences among the

individual isomers of 1-chloro-, 1-bromo-, and 1-iodobutanes, as the key bands in the skeletal deformation region have been clarified.

### Discussion

Several consistent trends have been observed for 1-halogenopropanes and 1-halogenobutanes. (1) The forms existing in the various states are same for all the compounds except 1-fluoroalkanes (Table 8). (2) The enthalpy difference  $\Delta H_{G-T}$  in the liquid state is about  $-100$  cal/mol for 1-halogenopropanes studied in this work in common. For 1-halogenobutanes in the liquid state, the GT form is the least stable and the TG form is the most stable with an exception that the TT form of 1-iodobutane is slightly more stable than the TG form (Figs. 17 and 18). (3) The force constants of the halogen part<sup>33</sup> show a systematic trend in their values.

The diagonal force constants of the CCX skeletal deformation for different halogen atoms are about the same and the frequency shifts are mainly due to the difference in the masses of halogen atoms. Together with the similarity of the relative stabilities of the rotational isomers, this is one of the principal reasons for the similarity of the spectral patterns. Thus, the skeletal deformation region of 1-halogenobutanes has good key bands for discriminating the individual isomers. In particular, the bands in the  $300-500$   $\text{cm}^{-1}$  region of 1-halogenobutanes are explicit examples, since these bands are associated predominantly with the CCC skeletal deformation (see Tables 5-7) and the frequency shift due to the mass difference is smaller than that for 1-halogenopropanes. In the study of the longer halogenoalkanes,<sup>34</sup> the key bands in the skeletal deformation region are efficiently used together with those in the skeletal stretching and  $\text{CH}_2$  rocking regions.

It is noticed for the halogenoalkane molecules studied in this work except 1-iodobutane that the most stable isomer in the liquid or glassy state does not exist in the crystalline state. This is reasonably understood by considering that the T or TT form is less stable than the G or TG form by only  $100-300$  cal/mol in the liquid state and the intermolecular forces favoring the T or TT form in crystal may well overwhelm the intramolecular forces favoring the G or TG form.

Care must be taken in the interpretation of the Raman spectra in the gaseous state on the analogy of that in the liquid state. An apparent band or shoulder observed only in the gaseous-state Raman spectra can be that due to some rotational isomer which is not identified in the liquid-state spectra, part of the rotational contour of the vibrational band, or a hot band. The relative peak intensities of the bands belonging to the same isomer can also be different from those in the liquid state. Such examples are found in the Raman spectra of 1-iodopropane. The C-I stretching band of the G form is observed as doublet at  $518$  and  $503$   $\text{cm}^{-1}$ . This doublet may be the contour of the B-type vibration since the corresponding infrared band is also observed as the B-type doublet. The relative peak intensities of the  $602$  and  $285$   $\text{cm}^{-1}$  bands, both assigned to the T form, in the gaseous-state spectrum are significantly

different from those in the liquid-state spectrum. In the cases of 1-bromo- and 1-iodobutanes, the relative intensities of the Raman bands in the gaseous state at  $448$  and  $456$   $\text{cm}^{-1}$  and at  $436$  and  $453$   $\text{cm}^{-1}$ , respectively, are different from those in the liquid state.

As has been shown in the present work, the skeletal deformation vibrations are useful for the determination of the enthalpy differences because of the relatively few overlapping bands due to different isomers. The measurement of the Raman spectra in this region is more effective for this purpose than that of the infrared spectra. Experiments of the temperature dependence of Raman intensities, especially at lower temperatures, can be performed without much difficulty, but the measurement of infrared intensities is difficult because of the interference by infrared emissions from the sample and the reference experimental apparatus.

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