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Infrared Spectra of Crystalline  $\text{CHCl}_3$  and  $\text{CDCl}_3$ 

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The infrared spectra for the fundamental absorption bands,  $\nu_1$ ,  $\nu_2$ ,  $\nu_4$  and  $\nu_5$ , of  $\text{CHCl}_3$  and  $\text{CDCl}_3$  have been measured in polycrystalline films. For the C-H or C-D bending band a triplet has been observed in the pure crystal. The spectra of a mixed crystal ( $\text{CHCl}_3$ : $\text{CDCl}_3$ ) have also been studied over the entire concentration range. The space group of crystalline chloroform has been determined to be  $D_{2h}^{14}$ . The intensity of the band changes, going from the gas to the solid, depending on the symmetry species to which the vibrational mode belongs; the  $A_1$  bands increase in intensity, while the E bands decrease. The C-H stretching band shows an especially remarkable increase.

Recently the infrared spectra of chloroform in the solid state have been reported on by several investigators.<sup>1-3)</sup> The crystal spectra observed so far, however, do not always agree with one another. For instance, a triplet was found for the C-H bending band by Lisitsa and Tsiashchenko,<sup>1)</sup> while a doublet was found by Maklakov, Nikitin and Purkina<sup>2)</sup> and by Denariez.<sup>3)</sup> We have here studied carefully the infrared spectra of crystalline chloroform and deuterio-chloroform, and obtained the definite spectra for the stable, well-annealed phase.

A qualitative analysis of crystalline spectra generally establishes only the site group of the molecule, but it can sometimes make possible the unique determination of the space group. In the present work, the spectra are also measured for the  $\text{CHCl}_3$ : $\text{CDCl}_3$  mixed crystals at various concentrations; this is done to clarify the mechanism of the band splittings. The splittings observed in the crystal field can make it possible to determine the space group, when used in connection with the results of X-ray diffraction and the Raman spectra.

On the other hand, considerable attention has been paid to the infrared intensities in condensed

phases.<sup>4-11)</sup> The absolute intensities have already been measured for a number of simple molecules in the solid state. These studies attempted to compare the intensities in the solid state with those in the gaseous state. Large intensity changes are observed in benzene and ethylene, especially for the C-H stretching bands, while the intensity changes in carbon disulfide and carbon tetrachloride are relatively small and are interpreted as "ideal field effects." However, the observed intensity changes are not yet fully understood. The intensity behavior observed in chloroform may be useful in making theoretical progress on this problem, as our preliminary data<sup>12)</sup> suggested.

4) J. L. Hollenberg and D. A. Dows, *J. Chem. Phys.*, **37**, 1300 (1962); *ibid.*, **39**, 495 (1963).

5) G. M. Wieder and D. A. Dows, *ibid.*, **37**, 2990 (1962).

6) D. A. Dows, *Spectrochim. Acta*, **22**, 1479 (1966).

7) H. Yamada and W. B. Person, *J. Chem. Phys.*, **40**, 309 (1964).

8) H. Yamada and W. B. Person, *ibid.*, **41**, 2478 (1964); *ibid.*, **43**, 2519 (1965).

9) H. B. Friedrich and W. B. Person, *ibid.*, **39**, 811 (1963); H. B. Friedrich, H. Yamada and W. B. Person, *ibid.*, **43**, 4180 (1965); J. M. P. J. Versteegen, H. Goldring, S. Kimel and B. Katz, *ibid.*, **44**, 3216 (1966).

10) C. F. Cook, W. B. Person and L. C. Hall, *Spectrochim. Acta*, **23A**, 1425 (1967).

11) T. L. Brown, *J. Chem. Phys.*, **43**, 2780 (1965).

12) A. Kimoto and H. Yamada, This Bulletin, **40**, 243 (1967).

1) M. P. Lisitsa and Iu. P. Tsiashchenko, *Opt. Spectry. (USSR)*, **6**, 396 (1959).

2) L. A. Maklakov, V. N. Nikitin and A. V. Purkina, *ibid.*, **15**, 178 (1963).

3) M. M. Denariez, *J. Chim. Phys.*, **62**, 323 (1965).

### Experimental

Extra pure chloroform (Wako Pure Chemical Industries Ltd.) was washed with water in order to remove any alcohol present as a preservative. It was then dried over calcium chloride and distilled (bp 61.0–61.5°C). Deuterated chloroform was obtained from the Showa Denko, Ltd.; the purity stated was 99.8%. In the infrared spectrum of  $\text{CDCl}_3$  some weak bands of  $\text{CHCl}_3$  were discerned, from which the amount of  $\text{CHCl}_3$  was estimated to be less than 0.7%. Commercial, extra-pure  $\text{CS}_2$  and  $\text{CCl}_4$  were used as solvents.

The technique for obtaining the spectrum has been described in the literature.<sup>4–7</sup> The sample in the gas phase was sprayed through a needle valve (VLV-II, Shinsei Sangyo Ltd.) onto a KRS-5 window, which was kept at the temperature of liquid nitrogen in a cold, glassy cell. Although the present study has been mostly concerned with sprayed samples, sample film was also made by cooling the liquid in a cold, metallic cell with KRS-5 windows. The temperature of the sample was determined to be 100°K in both of cases by use of a copper-constantan thermocouple.

The sample film was annealed as follows: after the sample film had been prepared at 100°K, it was gradually warmed 40 degrees and then again cooled down to 100°K. This process was repeated until the spectrum no longer showed any change. The spectrum varied with the deposition rate of the sample. The spectrum of the sample without annealing was slowly transformed to that of well-annealed film. That is, the slower the deposition, the better-annealed the film was obtained. The deposition rate, controlled by opening the needle valve, was 4–6 min per  $\mu$  of thickness. The film thickness was measured from the interference fringes observed at 2.5  $\mu$ . The spectra of well-annealed films prepared by the two different methods coincided completely with each other. In order to detect any preferred orientation of the film, spectra were also measured in polarized light. No appreciable changes in the spectra were found, however.

The spectra were obtained using a Jasco DS-402G spectrometer in the 400–4000  $\text{cm}^{-1}$  region. The spectral slitwidths were 0.7–1.0  $\text{cm}^{-1}$  for  $\nu_1$ , 0.8  $\text{cm}^{-1}$  for  $\nu_4$ , and 0.6–1.4  $\text{cm}^{-1}$  for  $\nu_2$  and  $\nu_5$ .

The index of refraction of the sample film was estimated to be  $n_{100^\circ\text{K}} = 1.61$  for both  $\text{CHCl}_3$  and  $\text{CDCl}_3$ ; estimation was made from the Lorenz-Lorentz equation using the following values:<sup>13)</sup>

$$n_D^{288^\circ\text{K}} = 1.448, d^{288^\circ\text{K}} = 1.498, d^{100^\circ\text{K}} = 1.93$$

for  $\text{CHCl}_3$  and

$$n_D^{293^\circ\text{K}} = 1.445, d^{293^\circ\text{K}} = 1.500 \text{ and } d^{100^\circ\text{K}} = 1.95$$

for  $\text{CDCl}_3$ .

The integrated absorption intensity was obtained from the curve of the absorbance *vs* the wave number, according to:

$$B = (\rho l)^{-1} \int \ln(T_0/T) d\nu \quad (1)$$

where the concentration,  $\rho$ , was calculated to be 16.2

mol/l from the densities for both  $\text{CHCl}_3$  and  $\text{CDCl}_3$ . Intensities in solutions were measured using a 0.1 mm cell with KRS-5 windows.

For the measurement of mixed crystals, the vapor of mixtures of  $\text{CHCl}_3$  with  $\text{CDCl}_3$  were deposited onto the cold substrate; the films deposited were also annealed. The  $(\text{CHCl}_3/\text{CDCl}_3)$  ratios were assumed to be equal to those in the liquid.

### Results and Discussion

Figures 1 and 2 show the four fundamentals observed for crystalline  $\text{CHCl}_3$  and  $\text{CDCl}_3$ . The dotted lines represent the curves of unannealed samples, and the solid lines, those of well-annealed samples. After annealing, the  $\nu_1$  and  $\nu_2$  bands belonging to  $A_1$

TABLE 1. OBSERVED FREQUENCIES FOR FUNDAMENTAL BANDS OF CHLOROFORM ( $\text{cm}^{-1}$ )

Band <sup>a)</sup>	Gas <sup>b)</sup>	Liquid	Solid <sup>c)</sup>
$\nu_1(A_1)$	3034	3015	{ (3024) 3007
$\nu_4(E)$	1221	1216	{ 1225 (1221) 1210 1206
$\nu_5(E)$	769	756	{ ~765 756 ~738
$\nu_2(A_1)$	681	669	{ (677) 673

a) G. Herzberg, "Molecular Spectra and Molecular Structure," Vol. II, D. Van Nostrand Company, Inc., Princeton, N. J. (1945), p. 316.

b) J. Morcillo, J. Herranz and J. Biarge, *Spectrochim. Acta*, **15**, 110 (1959).

c) In parentheses are the bands which disappeared by annealing.

TABLE 2. OBSERVED FREQUENCIES FOR FUNDAMENTAL BANDS OF DEUTERO-CHLOROFORM ( $\text{cm}^{-1}$ )

Band <sup>a)</sup>	Gas	Liquid	Solid <sup>d)</sup>
$\nu_1(A_1)$	2262 <sup>b)</sup>	2260	{ (2260) 2250
$\nu_4(E)$	915 <sup>b)</sup>	909	{ 911 902 898
$\nu_5(E)$	747 <sup>c)</sup>	732	{ ~740 727 ~722
$\nu_2(A_1)$	651 <sup>a)</sup>	646	{ (655) 651

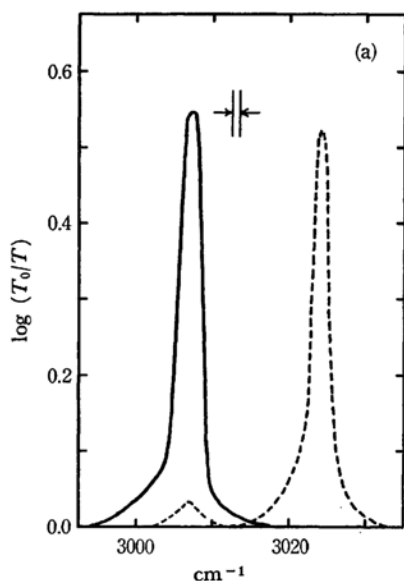
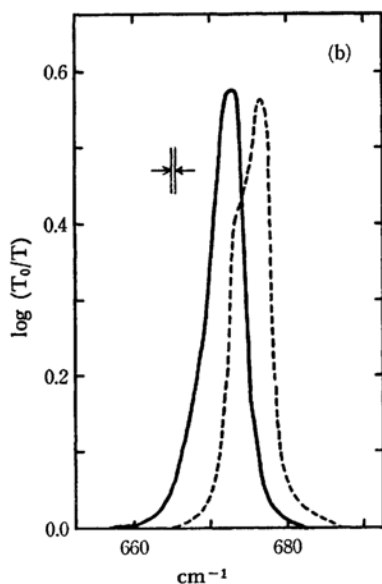
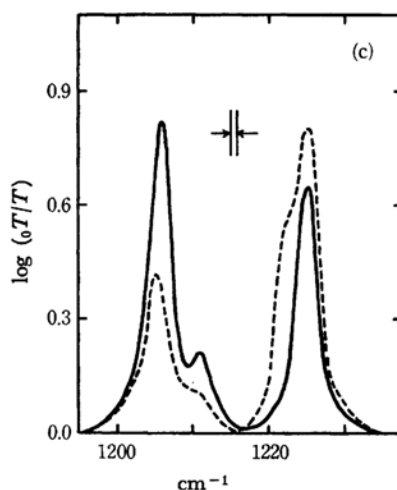
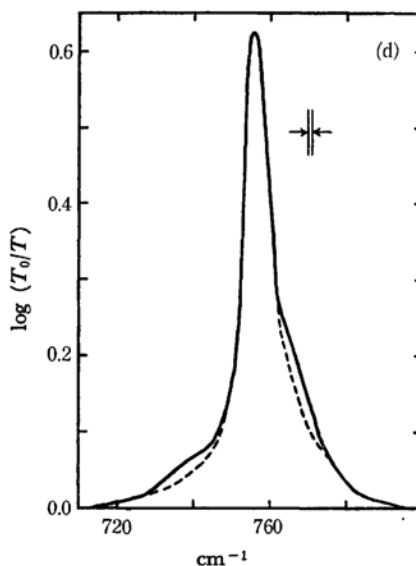
a) Ref. a in Table 1.

b) Ref. 3.

c) J. R. Madigan, F. F. Cleveland, W. M. Boyer and R. B. Bernstein, *J. Chem. Phys.*, **18**, 1081 (1950).

d) In parentheses are the bands which disappeared by annealing.

13) J. Timmermans, "Physico-Chemical Constants of Pure Organic Compounds," Elsevier Publishing Co., Inc., New York (1950); "Beilsteins Handbuch der Organischen Chemie," Drittes Ergänzungswerk, Band 1, System Nr. 1–15, Springer-Verlag, Heidelberg (1958).

Fig. 1. (a),  $\nu_1$ .Fig. 1. (b),  $\nu_2$ .Fig. 1. (c),  $\nu_4$ .Fig. 1. (d),  $\nu_5$ .Fig. 1. Fundamental bands of crystalline  $\text{CHCl}_3$ .

— annealed, --- unannealed sample

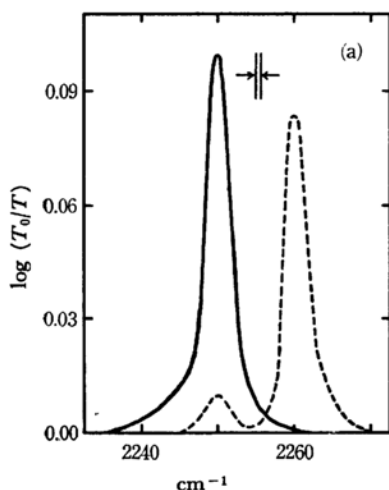
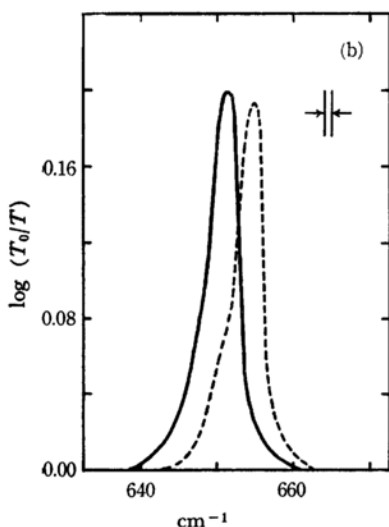
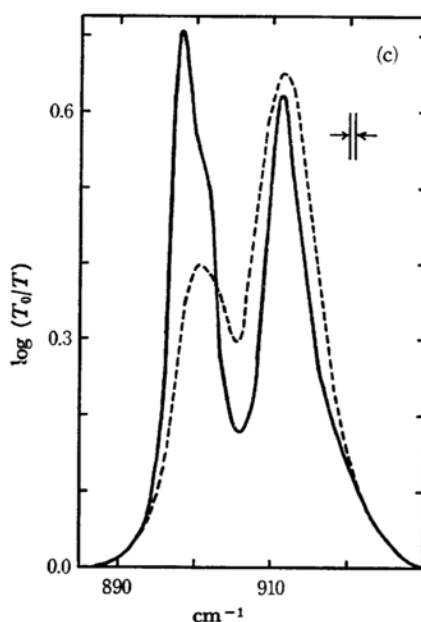
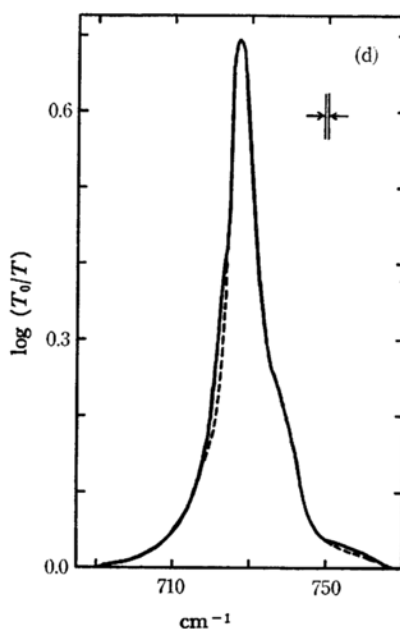
species shift to the low-frequency side, while the  $\nu_4$  and  $\nu_5$  bands belonging to E species split into three components. Three peaks are clearly resolved in the  $\nu_4$ , C-H bending band. The  $\nu_1$  and  $\nu_2$  bands are slightly asymmetric, suggesting that there are additional peaks on the low-frequency sides. The observed frequencies at the band peaks are listed in Tables 1 and 2.

In order to ascertain why the spectra obtained for the unannealed samples differed considerably from those for the well-annealed samples, a differential thermal analysis of  $\text{CHCl}_3$  has been undertaken. No thermal anomaly, however, was detected over the

300–390°K temperature range, with the exception of that at the melting point, 209°K. This means that solid  $\text{CHCl}_3$  does not show any phase transition. This is consistent with the results of the pure quadrupole resonance study by Gutowsky and McCall.<sup>14</sup> The spectra obtained for the unannealed samples, therefore, are those of the metastable or amorphous form, partly mixed with those of the stable form.

The C-H and C-D bending bands,  $\nu_4$ (E), in the mixed crystals ( $\text{CHCl}_3$ :  $\text{CDCl}_3$ ) are shown in Figs. 3

14) H. S. Gutowsky and D. W. McCall, *J. Chem. Phys.*, **32**, 548 (1960).

Fig. 2. (a),  $\nu_1$ .Fig. 2. (b),  $\nu_2$ .Fig. 2. (c),  $\nu_4$ .Fig. 2. (d),  $\nu_5$ .

and 4 at various concentrations. Figure 5 shows the frequencies of the absorption maxima in both the  $\nu_4$ - $\text{CHCl}_3$  and  $\nu_4$ - $\text{CDCl}_3$  regions for the mixtures of  $\text{CHCl}_3$  and  $\text{CDCl}_3$ . In the mixed crystal four peaks are observed for the  $\nu_4$  bands. As the concentration of  $\text{CHCl}_3$  decreases, the two inner peaks increase in intensity, while the two outer peaks decrease. When  $\text{CHCl}_3$  was considerably diluted with  $\text{CDCl}_3$  (97.4%), the two outer peaks disappeared and a complete doublet at 1213.8 and 1220.0  $\text{cm}^{-1}$  was observed. The spacing of the two inner peaks remains almost constant at 6–8  $\text{cm}^{-1}$ , independent of the concentration. Let us now designate the four peaks as  $\nu_4^1$ ,  $\nu_4^2$ ,  $\nu_4^3$ , and  $\nu_4^4$  respectively, from high to low frequencies. Then  $\nu_4^2$  and  $\nu_4^3$  can be assigned to the components split by the site group or by removing the degeneracy in the crystal field, and  $\nu_4^1$ ,  $\nu_4^3$  and  $\nu_4^4$  in the pure  $\text{CHCl}_3$  or  $\text{CDCl}_3$ , to the components split by the factor group. One of

Fig. 2. Fundamental bands of crystalline  $\text{CDCl}_3$ .

the factor group components overlaps with  $\nu_4^3$ , the site group component. The four peaks observed in the mixed crystal, therefore, may be interpreted as a superposition of the components split by the site group upon those split by the factor group at various rates. The C–D bending band behaves in the same way as the C–H bending band, but its splitting is relatively small.

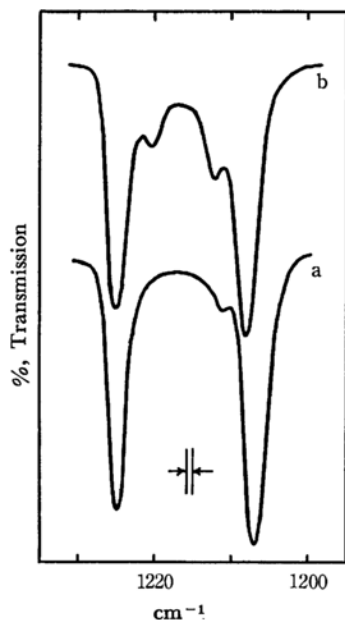
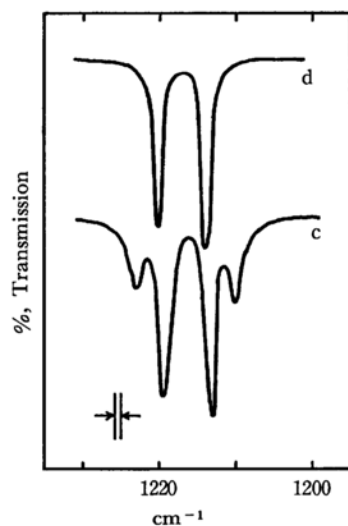
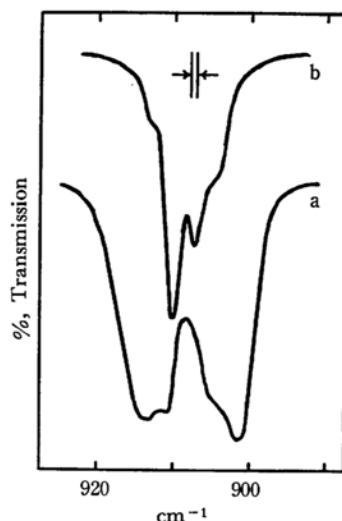
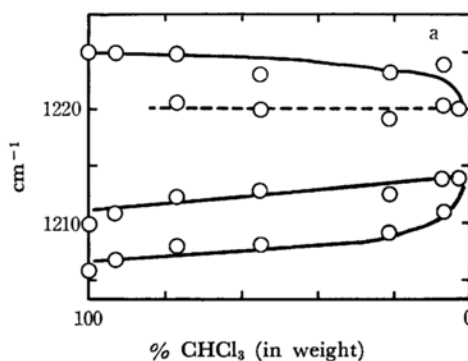
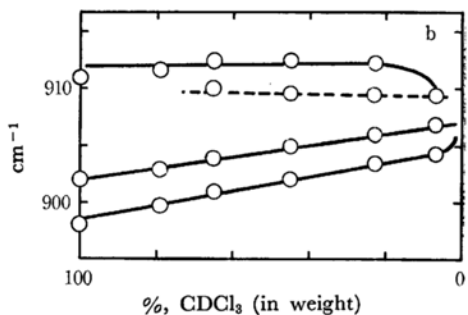
Fig. 3. a)  $\text{CDCl}_3$  7.2%, b) 23.2%.

Fig. 3. c) 79.3%, d) 97.4%.

Fig. 3. Spectra in  $\nu_4\text{-CHCl}_3$  region for mixture of  $\text{CHCl}_3$  and  $\text{CDCl}_3$ .

Although the spectra of the  $\text{CHCl}_3$ :  $\text{CDCl}_3$  mixed crystal have already been reported by Maklakov *et al.*<sup>2)</sup> and by Denariez,<sup>3)</sup> their sets of results coincide with neither each other nor the present spectra. Maklakov *et al.*, observing a singlet at a very dilute solid solution, concluded that a factor-group splitting is predominant in crystalline  $\text{CHCl}_3$ . On the contrary, Denariez observed a doublet at the concentration of 1%, indicating that a site-group splitting is rather predominant. These differences may be caused by the use of unannealed or incompletely

Fig. 4. Spectra in  $\nu_4\text{-CDCl}_3$  region for mixture of  $\text{CHCl}_3$  and  $\text{CDCl}_3$ .a)  $\text{CHCl}_3$  34.8% b) 94.5%.Fig. 5. a) Frequencies of absorption maxima in  $\nu_4\text{-CHCl}_3$  region for mixtures of  $\text{CHCl}_3$  and  $\text{CDCl}_3$ .Fig. 5. b) Frequencies of absorption maxima in  $\nu_4\text{-CDCl}_3$  region for mixtures of  $\text{CHCl}_3$  and  $\text{CDCl}_3$ .

annealed films. In many cases, the crystal splittings observed are not in harmony with those theoretically predicted, even for simple molecules, because the

natural abundance of isotopic molecules and sometimes the Fermi resonance<sup>15)</sup> complicate the crystal spectra or because the magnitudes of the band splittings are small. However, the C-H bending band of  $\text{CHCl}_3$  is not affected by these influences. Here it is a typical example for the site- and factor-group splittings.

The structure of crystalline chloroform may be inferred from the results of group theoretical analysis.<sup>16)</sup> In the mixed crystal of  $\text{CHCl}_3$  diluted by  $\text{CDCl}_3$ , the  $A_1$  bands remain single, while the E bands split into two components. On the other hand, in the pure crystal the  $A_1$  bands probably split into two components (if we count the asymmetric tail as a peak), while the E bands split clearly into three components. The unit-cell groups which explain these splitting are  $C_{2v}$ ,  $D_{2h}$ ,  $C_{3v}$ , etc. (20 altogether), all with the  $C_s$ -site symmetry. Referring to the Raman spectrum of crystalline  $\text{CHCl}_3$ ,<sup>17)</sup> we note that none of the peak frequencies of the infrared spectrum coincide with those of the Raman spectrum. This suggests that there exists a mutual exclusion between the infrared and Raman spectra, namely, the inversion symmetry in the unit-cell group.

An X-ray diffraction study of the chloroform single crystal has been made in our university,<sup>18)</sup> and the possible space group has been found to be either  $C_{2v}^9$  or  $D_{2h}^{16}$  with four molecules per unit-cell. While we were making this X-ray study, Fourme and Renaud<sup>19)</sup> reported the crystal structure independently, giving the same space group. From the vibrational spectra described above, we can easily discard the possibility of  $C_{2v}^9$  with the  $C_1$  site symmetry. Consequently, the space group of crystalline  $\text{CHCl}_3$  must be  $D_{2h}^{16}$  with the  $C_s$  site symmetry. The correlation diagram is shown in Fig. 6.

Molecule	Site	Unit cell
$C_{3v}$	$C_s$	$D_{2h}^{16}$
$\nu_i$ $A_1$ IR, R	A'	$A_g$ — R
$A_2$ — —		$B_{1g}$ — R
$\nu_j$ E IR, R	A''	$B_{2g}$ — R
		$B_{3g}$ — R
		$A_u$ — —
		$B_{1u}$ IR, b —
$i=1,2,3; j=4,5,6$		$B_{2u}$ IR, a —
		$B_{3u}$ IR, c —

Fig. 6. Correlation diagram for crystalline  $\text{CHCl}_3$ .

15) For example, R. Kopelman, *J. Chem. Phys.*, **44**, 3547 (1966).

16) R. S. Halford, *ibid.*, **14**, 8 (1946); H. W. Winston and R. S. Halford, *ibid.*, **17**, 607 (1949); D. F. Hornig, *ibid.*, **16**, 1063 (1948).

17) M. Ito, *ibid.*, **40**, 3128 (1964). In this article only two components have been reported for the E species. In later works three components have been observed (private communication).

18) Y. Tomiie *et al.*; The cell dimension is determined to be  $a=7.14$ ,  $b=9.80$  and  $c=5.84$  Å,  $Z=4$ .

Returning to Figs. 3 and 4 for the C-H and C-D bending vibration,  $\nu_4$ ,  $\nu_4^4$  should be assigned to the  $B_{1u}$  component, since it is the strongest among the three peaks in the pure crystal.  $\nu_4^1$  and  $\nu_4^3$  are assigned to  $B_{3u}$  and  $B_{2u}$ , respectively or *vice versa*.  $\nu_4^4$  is almost equal in intensity to the sum of  $\nu_4^1$  and  $\nu_4^3$ . Thus,  $\nu_4^1$ ,  $\nu_4^3$  and  $\nu_4^4$  correspond to the c, a, and b (or to be a, c, and b)-axis components of the crystal respectively, and the C-H bond of  $\text{CHCl}_3$  lies on the ac plane. Taking the angle between the C-H bond and the a axis  $\theta$ , the infrared intensities of  $B_{2u}$  (a) and  $B_{3u}$  (c) components are related as:

$$I(B_{2u})/I(B_{3u}) = \tan^2 \theta,$$

if the oriented gas model can be assumed. The observed intensity ratio gives  $\theta=25^\circ$ . The parameters for the  $\text{CHCl}_3$  crystal reported by Fourme and Renaud lead to a value of  $14^\circ$  for this angle. Notwithstanding the ambiguity in separating each component of the  $\nu_4$  band and the assumption of the oriented gas model, these are in good agreement. Assuming the molecular orientation shown in Fig. 7,<sup>19)</sup> we may expect the  $B_{3u}$  (c) component of the  $A_1$  band, as well as the  $B_{2u}$  (a) component of the E band, to be very weak. This may be the reason why the splittings of  $A_1$  bands are not resolved clearly in the pure crystal.

The crystal structure of  $\text{CDCl}_3$  is considered isomorphous to that of  $\text{CHCl}_3$ , since the same trends in band splittings are observed.

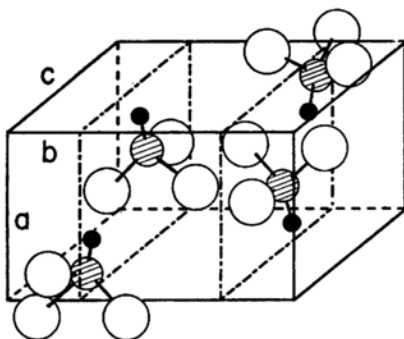


Fig. 7. Molecular orientation in the crystal. (After the structure given by Fourme and Renaud.)

As has been mentioned above, the band splittings may be well interpreted as the factor group for the pure crystals and as the site group for the dilutely-mixed crystals, in accordance with the crystal structure. It is of great interest for us what kind of forces give rise to such splittings of the bands; in other words, what kind of intermolecular potentials contribute to the splittings. As has been indicated by

19) R. Fourme and M. Renaud, *Compt. rend.*, **263B**, 69 (1966); The parameter for H atom  $z/c=0.7200$  should be corrected to be 0.0720 (private communication).

Hexter<sup>20)</sup> and Dows,<sup>21)</sup> when the dipole-dipole interaction potential is predominant, the isotopic relation governing any particular factor group holds:

$$\frac{\Delta\nu_H}{\Delta\nu_D} = \frac{\nu_D}{\nu_H} \frac{I_H}{I_D} \quad (2)$$

Here,  $\Delta\nu$  represents the magnitude of band splitting,  $\nu$ , the wavenumber, and  $I$ , the intensity of the band.  $\text{CHCl}_3$  and  $\text{CDCl}_3$  are denoted by the suffixes H and D respectively. Examining this formula for the  $\nu_4$  band, we must take  $|\nu(\text{B}_{2u}) - \nu(\text{B}_{3u})|$  as  $\Delta\nu_H$  or  $\Delta\nu_D$  for the factor-group splitting. The observed values are  $\Delta\nu_H = 15 \text{ cm}^{-1}$  and  $\Delta\nu_D = 9 \text{ cm}^{-1}$ . Then, the left side in Eq. (2) gives 1.7, while the right side gives a quite different value, 0.23, using the gas-phase intensities. Even though we substitute  $I_H$  and  $I_D$  for the solid intensities, the right side still gives the same value. This suggests that some potential other than the dipole-dipole potential plays an important role in the splitting of the  $\nu_4$  band. Presumably atom-atom potentials,  $\text{H}\cdots\text{Cl}$  interactions, contribute to the coupling of the  $\nu_4$  vibration, which is similar to the vibrations which arise primarily from hydrogen motions, of methylchloride<sup>21,22)</sup> and ethylene.<sup>23)</sup> On the other hand, the  $\nu_5(\text{E})$  of the C-Cl stretching vibration may split due to the dipole-dipole coupling, much as does the  $\nu_3$  of methyl chloride,<sup>20-22)</sup> because the intensity of this band is extremely large. Detailed calculations of the splittings will be published elsewhere.

The absolute intensities of the fundamental bands in the crystals are given in Tables 3 and 4, while the intensities between different phases are compared in Tables 5 and 6. The maximum error involved in the intensity measurements is 15% for the solids. Lambert's law plots of  $B\rho l$  vs.  $l$  are shown in Fig. 8. As for the solid intensities of  $\text{CHCl}_3$ , Lisitsa *et al.*<sup>1)</sup> early reported values for the polycrystalline films

TABLE 3. ABSOLUTE INTENSITIES OF CRYSTALLINE CHLOROFORM

Band	$\nu_{\max}$ ( $\text{cm}^{-1}$ )	$\Delta\nu_{1/2}$ ( $\text{cm}^{-1}$ )	B (darks)	
			This work	Lisitsa <i>et al.</i> <sup>a)</sup>
$\nu_1(\text{A}_1)$	3007	3.5	1200	170
$\nu_4(\text{E})$	$\begin{Bmatrix} 1225 \\ 1210 \\ 1206 \end{Bmatrix}$	$\begin{Bmatrix} 2.8 \\ - \\ 2.6 \end{Bmatrix}$	2700	320
$\nu_5(\text{E})$	$\begin{Bmatrix} 765 \\ 756 \\ 738 \end{Bmatrix}$	$\begin{Bmatrix} - \\ 10.0 \\ - \end{Bmatrix}$	19000	3200
$\nu_2(\text{A}_1)$	673	5.0	1600	—

a) Ref. 1.

20) R. M. Hexter, *J. Chem. Phys.*, **33**, 1833 (1960).

21) D. A. Dows, *ibid.*, **35**, 282 (1961).

22) D. A. Dows, *ibid.*, **33**, 1342 (1960).

23) D. A. Dows, *ibid.*, **36**, 2836 (1962).

TABLE 4. ABSOLUTE INTENSITIES OF CRYSTALLINE DEUTERO-CHLOROFORM

Band	$\nu_{\max}$ ( $\text{cm}^{-1}$ )	$\Delta\nu_{1/2}$ ( $\text{cm}^{-1}$ )	B (darks)
$\nu_1(\text{A}_1)$	2250	4.0	300
$\nu_4(\text{E})$	$\begin{Bmatrix} 911 \\ 902 \\ 898 \end{Bmatrix}$	$\begin{Bmatrix} 6.0 \\ - \\ 6.1 \end{Bmatrix}$	8900
$\nu_5(\text{E})$	$\begin{Bmatrix} 740 \\ 727 \\ 722 \end{Bmatrix}$	$\begin{Bmatrix} - \\ 10.4 \\ - \end{Bmatrix}$	20000
$\nu_2(\text{A}_1)$	651	5.2	1100

TABLE 5. ABSOLUTE INTENSITIES OF CHLOROFORM IN VARIOUS PHASES (darks)

Band	Gas <sup>a)</sup>	Liquid	Solid	Solution $\text{CS}_2$
$\nu_1(\text{A}_1)$	44	707 <sup>b)</sup>	1200	559 <sup>b)</sup>
$\nu_4(\text{E})$	4200	2900 <sup>c)</sup>	2700	3000
$\nu_5(\text{E})$	27000	30000 <sup>c)</sup> 28600 <sup>d)</sup>	19000	24000
$\nu_2(\text{A}_1)$	600	—	1600	490

a) Ref. b in Table 1. See also, Ref. 26 and D. C. McKean, Dissertation, Oxford (1953).

b) R. E. Kagarise, U. S. Naval Research Laboratory Report, 5906(1963); See also, M. T. Forel, J. P. Leiknamand M. L. Josien, *J. Chim. Phys.*, **57**, 1103 (1960).

c) G. M. Irons and H. W. Thompson, *Proc. Roy. Soc. (London)*, **A298**, 160 (1967).

d) A. C. Gilby, J. Burr, Jr., W. Krueger and B. Crawford, Jr., *J. Phys. Chem.*, **70**, 1525 (1966).

TABLE 6. ABSOLUTE INTENSITIES OF DEUTERO-CHLOROFORM IN SOLID AND SOLUTION (darks)

Band	Solid	Solution	
		$\text{CS}_2$	$\text{CCl}_4$
$\nu_1(\text{A}_1)$	300	—	160
$\nu_4(\text{E})$	8900	9500	9600
$\nu_5(\text{E})$	20000	15200	—
$\nu_2(\text{A}_1)$	1100	490	540

obtained by cooling the liquid. Their values, shown in Table 3, are quite small, being only about 15% of the present values. As has been previously discussed for crystalline benzene,<sup>24)</sup> measurement by cooling the liquid makes for considerable errors in determining the intensity, because the assumption that the product,  $\rho l$ , of the concentration and the path length remains constant as it was frozen from the liquid to the solid will be in error.

24) H. Yamada and W. B. Person, *ibid.*, **38**, 1253 (1963).

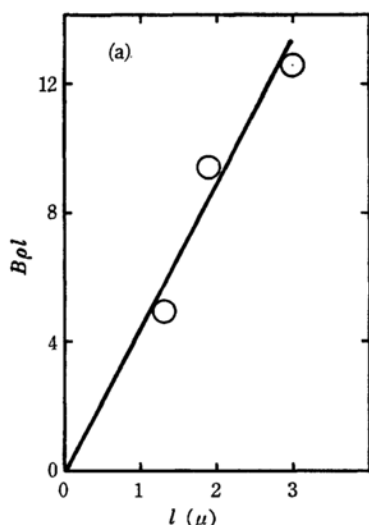


Fig. 8. (a) Lambert's law plots for  $\nu_4$  of crystalline  $\text{CHCl}_3$ .

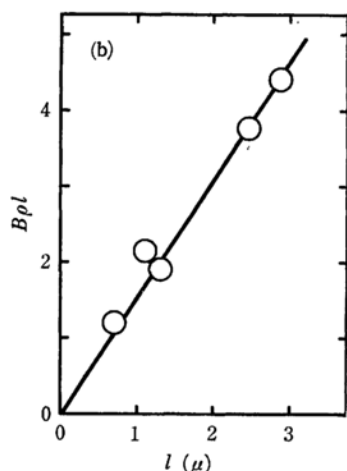


Fig. 8. (b) Lambert's law plots for  $\nu_2$  of crystalline  $\text{CDCl}_3$ .

For  $\text{CHCl}_3$ , the  $\nu_1$  and  $\nu_2$  bands increase in intensity going from the gas to the solid, while the  $\nu_4$  and  $\nu_5$  bands decrease. As may be seen from the Table 5, these trends can be roughly seen to be in order from the gas to the solution and to the solid. The increase in intensity for the  $\nu_1$  band of  $\text{CHCl}_3$ , going from the gas to the solid, is remarkable. However, most of this increase is observed when it goes from the gas to the solution. Some of the authors<sup>25</sup> who measured the intensity of the  $\nu_1$

band in dilute solutions (in  $\text{CCl}_4$  and  $\text{CS}_2$ ) attributed it to the effect of molecular association, similar to hydrogen bonding, though this point is not clear.

An interesting phenomenon has been reported that for this  $\nu_1$  vibration, the first overtone is much stronger in intensity than the fundamental band, suggesting an abnormal weakness of the fundamental  $\nu_1$  in the gas phase.<sup>26</sup>

In the crystal the interatomic distances between an H atom and its nearest Cl atoms are calculated from previously-reported data<sup>19</sup> to be as follows: molecule whose central carbon lies on the same  $C_2$  plane as the H atom), 3.12 Å for H...Cl (for a Cl atom of another molecule whose central carbon also lies in the same  $C_2$  plane), and larger than 3.7 Å for all others. Comparing these values with the van der Waals distance, 3.00 Å, for H...Cl, it seems that the hydrogen is surrounded by the three Cl atoms and that no special H...Cl linkage is formed. It is doubtful, therefore, that the observed intensity changes are due to any special association of the molecules.

At any rate, it is worth noting that the bands belonging to  $A_1$  species of the molecule increase in intensity, while the bands belonging to E species decrease, going from the gas to the solid. That is, the intensity varies depending on the symmetry species of the vibrational mode. Since the molecular axis of chloroform coincides with the short axis of the molecular ellipsoid, the field effects predict that the intensity will increase for the  $A_1$  modes and decrease for the E modes. Thus, the qualitative trends observed are the same as those expected from the field effects, though the magnitudes of the observed changes are considerably larger than those predicted. If we compare the intensities of  $\text{CDCl}_3$  between the solution and the solid, the  $A_1$  bands increase in intensity from the solution to the solid, while the E bands remain unchanged or decrease. Similar trends are observed in  $\text{CHCl}_3$ .

The intensity behavior observed in chloroform is quite different from those observed in benzene<sup>4</sup> and ethylene.<sup>5</sup> It also differs from those observed in  $\text{CCl}_4$ <sup>10</sup> and  $\text{CS}_2$ <sup>7</sup> where the "ideal field effects" is concerned. As for the C-H stretching bands, the intensity increases in  $\text{CHCl}_3$  as well as in acetylene,<sup>6</sup> while it decreases in benzene and ethylene. If we interpret this behavior in terms of the "delocalization moment,"  $M_D$ ,<sup>10</sup>  $M_D$  should have the same sign as that of the intrinsic moment or exceed the intrinsic moment greatly.

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25) C. M. Huggins and G. C. Pimentel, *ibid.*, **23**, 1244 (1955); S. Singh and C. N. R. Rao, *J. Phys. Chem.*, **71**, 1074 (1967); W. E. Thompson and G. C. Pimentel, *Z. Elektrochem.*, **64**, 748 (1960); See also, G. C. Pimentel and A. L. McClellan, "The Hydrogen Bond," H. W. Freeman and Company, San Francisco (1960), pp. 120, 197.

26) C. C. Robinson, S. A. Tare and H. W. Thompson, *Proc. Roy. Soc.*, **A269**, 492 (1962).



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