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Citation: *The Journal of Chemical Physics* **18**, 346 (1950); doi: 10.1063/1.1747629

View online: <http://dx.doi.org/10.1063/1.1747629>

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tion of unlike pairs was introduced. Assuming no interpenetration for the fluorocarbon pairs, and no interpenetration for the fluorocarbon-hydrocarbon pairs, an interpenetration factor, " $d$ " was calculated for  $n$ -pentane. The value for " $d$ " should be essentially the same for all normal hydrocarbons in similar fluorocarbon solutions, however, this awaits further experimental investigation.

#### ACKNOWLEDGMENT

The authors wish to thank Professor J. G. Aston for the loan of the Cryogenic Laboratory Standard Thermocouple #S-5 for use in calibrating the thermocouples used in this research. They wish to thank The Minnesota Mining and Manufacturing Company for sponsoring the program under which this work has been carried out.

## Substituted Methanes. I. Raman and Infra-Red Spectral Data, Assignments, and Force Constants for Some Tribromomethanes\*

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(Received August 17, 1949)

As a part of a systematic investigation of the vibrational spectra of substituted methanes and ethanes, Raman displacements, semiquantitative relative intensities, quantitative depolarization factors, and infra-red absorption frequencies in the region 700–5000  $\text{cm}^{-1}$  have been obtained for  $\text{CBr}_3\text{H}$ ,  $\text{CBr}_3\text{Cl}$ , and  $\text{CBr}_4$ . Details about the design of the infra-red spectrograph are given. The Raman and infra-red spectral data in the literature for  $\text{CBr}_3\text{H}$ ,  $\text{CBr}_3\text{D}$ ,  $\text{CBr}_3\text{F}$ ,  $\text{CBr}_3\text{Cl}$ , and  $\text{CBr}_4$  have been collected, tabulated, and critically examined in comparison with the present results and a decision was made as to the probable values of the Raman and infra-red data at the present time. Assignments of the observed Raman and infra-red bands, consistent with the selection rules, were made for all of the molecules. Finally, force constants were calculated for the five molecules, using a potential energy function containing all possible second degree terms.

#### INTRODUCTION

SUBSTITUTED methanes and ethanes in which the substituents are single atoms—not radicals—are being systematically investigated in this laboratory. It is hoped that Raman displacements, relative intensities, quantitative depolarization factors, infra-red absorption spectra in the region 400–5000  $\text{cm}^{-1}$ , force constants, and thermodynamic properties may eventually be obtained for all such molecules for which the present information is incomplete and for which samples can be obtained. The present paper presents results obtained in an investigation of a series of methanes of the type  $\text{CBr}_3\text{X}$ .

#### EXPERIMENTAL DETAILS

The Raman displacements were obtained partly with a Hilger E-518 spectrograph having a dispersion of 307  $\text{cm}^{-1}/\text{mm}$  (63A/mm) at 4500A, and partly with a two-prism spectrograph constructed in this laboratory which has a dispersion of 162  $\text{cm}^{-1}/\text{mm}$  (33A/mm) at 4500A. The spectrograms were obtained on Eastman 103-J plates with Hg 4358A as the exciting line, using

the experimental arrangement and technique previously described.<sup>1</sup>

The relative intensities were obtained with the aid of a Gaertner microdensitometer<sup>2</sup> by the formerly used method.<sup>1,3</sup> The relative intensities are only semiquantitative since no correction was made for variation in the sensitivity of the plates with wave length and since calibration marks were not placed upon each spectrogram but only upon a master calibration plate with the same type of emulsion.

The depolarization factors were obtained by a well-tested, quantitative method.<sup>4</sup> The two exposures corresponding to the vertical and horizontal components of the electric vector were obtained simultaneously, calibration marks were placed upon each spectrogram, and separate calibration curves were prepared for each Raman line; corrections were made for failure of the reciprocity law, for real or apparent polarization produced by the spectrograph or other optical parts in the path of the scattered beam, and for convergence errors.

The infra-red absorption spectra were obtained with a self-recording infra-red spectrometer constructed in this laboratory. The arrangement of the optical parts and the radiation path in this spectrometer are shown in Fig. 1. The source  $N$  is a Nernst glower. The mirrors

\* Presented at the Chicago meeting of the American Physical Society, November, 1948, papers C1 and C2; abstract in *Phys. Rev.* **75**, 333 (1949).

<sup>†</sup> The experimental portion of this paper gives results obtained in an investigation carried out at the Illinois Institute of Technology by Mr. Shirley E. Rosser in partial fulfillment of the requirements for the degree of Master of Science at the University of Virginia.

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<sup>1</sup> Forrest F. Cleveland, *J. Chem. Phys.* **11**, 1 (1943).

<sup>2</sup> S. Jacobsohn and W. H. Kliever, *J. Opt. Soc. Am.* **25**, 244 (1935).

<sup>3</sup> Forrest F. Cleveland, *J. Chem. Phys.* **11**, 227 (1943); *Year Book of the American Philosophical Society* (1942), pp. 104–105.

<sup>4</sup> Forrest F. Cleveland, *J. Chem. Phys.* **13**, 101 (1945).

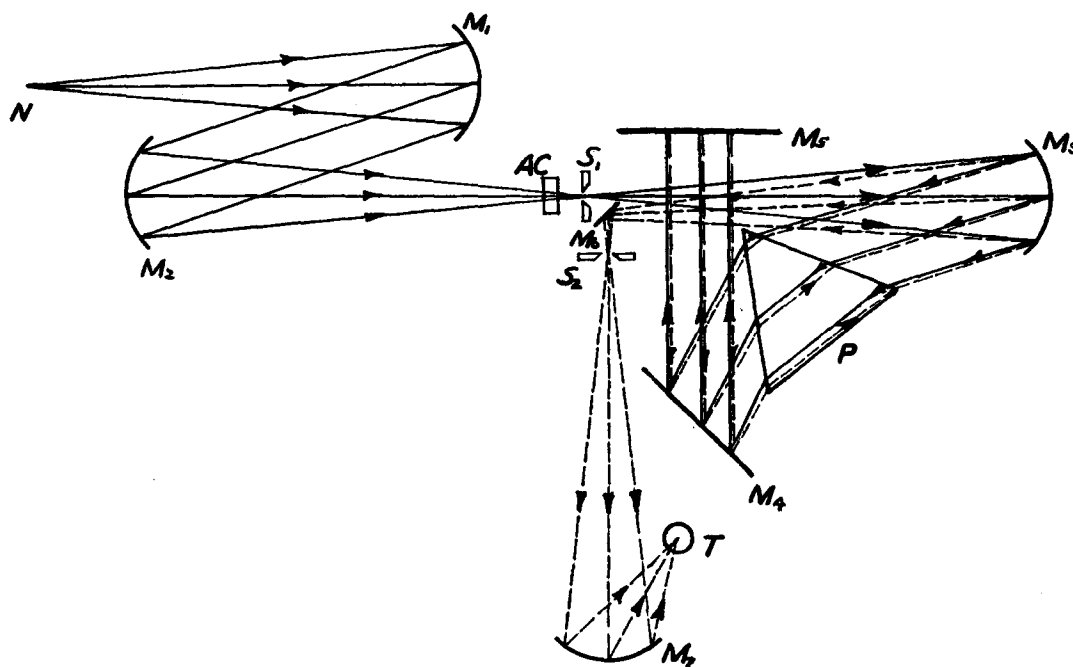


FIG. 1. Arrangement of the optical parts in the infra-red spectrometer.

$M_1$ ,  $M_2$ , and  $M_7$  are spherical and are all 5 cm in diameter; for  $M_1$  and  $M_2$ , the focal lengths were 30 cm, while for  $M_7$  it was 10 cm.  $AC$  is the absorption cell and the entrance and exit slits  $S_1$  and  $S_2$  are Gaertner L162b bilateral slits. The collimating mirror  $M_3$  is parabolic,  $10^\circ$  off-axis, and has a focal length of 30 cm and a diameter of 5 cm.  $M_4$ ,  $M_5$ , and  $M_6$  are plane mirrors and the prism  $P$  is of rocksalt with 6 cm base and 4 cm height; it can be replaced by a similar KBr prism. The thermocouple  $T$  is a compensated Weyrich thermocouple obtained from the Department of Physics of the University of Michigan through the courtesy of Professors H. M. Randall and E. F. Barker.

The slit-width varied from 0.30 mm near  $3000\text{ cm}^{-1}$  to 3.00 mm in the  $700\text{--}1000\text{ cm}^{-1}$  region. Since no amplification was used, the resolving power was not very good; it of course varies for different regions of the spectrum and depends upon the slit-width and the intensity of the bands, so that it is not possible to give a single value for all conditions; the most closely spaced bands that were resolved in the present investigation were  $26\text{ cm}^{-1}$  apart (at  $925\text{ cm}^{-1}$ ), but no attempt was made to find whether this was the limit for resolution.

#### RAMAN AND INFRA-RED SPECTRAL DATA

For use in the force constant calculations to be discussed in a subsequent section, and in thermodynamic calculations to be discussed in a later paper, it was desired to have the best possible values of the Raman and infra-red spectral data. Consequently, all of the compounds for which samples could be obtained ( $\text{CBr}_3\text{H}$ ,  $\text{CBr}_3\text{Cl}$ , and  $\text{CBr}_4$ ) were reinvestigated. In

addition, the previous data in the literature were collected, tabulated, and critically examined in comparison with the present results and finally a decision was made as to the probable values of the Raman and infra-red data.

#### Tribromomethane (Bromoform, $\text{CBr}_3\text{H}$ )

The sample of tribromomethane was kindly furnished by the Dow Chemical Company, Midland, Michigan; it was originally of the "technical" grade, but was carefully purified by use of a distilling column. The spectrograms were obtained with the sample in the liquid state at approximately  $30^\circ\text{C}$ . The exposure time on the plate giving the best lines for depolarization measurements was 7 hr. at a slit-width of 0.09 mm. On this plate all previously reported lines were obtained, except for the one at  $1439\text{ cm}^{-1}$  which has never been obtained with sufficient intensity to permit depolarization measurements, even qualitative ones. In fact, this line could not be obtained in the present investigation even on frequency spectrograms with very long exposures.

Raman spectral data have been obtained in ten previous investigations<sup>5-14</sup> and infra-red data have been

<sup>5</sup> A. S. Ganesan and S. Venkateswaran, *Ind. J. Phys.* **4**, 195 (1929).

<sup>6</sup> S. Bhagavantam and S. Venkateswaran, *Proc. Roy. Soc. London* **A127**, 360 (1930).

<sup>7</sup> S. Bhagavantam, *Ind. J. Phys.* **5**, 35 (1930).

<sup>8</sup> See reference 7, p. 59.

<sup>9</sup> S. Venkateswaran, *Phil. Mag.* **15**, 263 (1933).

<sup>10</sup> J. Cabannes and A. Rousset, *Ann. de physique* **19**, 229 (1933).

<sup>11</sup> J. T. Dahr, *Ind. J. Phys.* **9**, 189 (1934).

<sup>12</sup> O. Redlich and W. Stricks, *Sitz. Akad. Wiss. Wien IIb*, **145**, 192 (1936).

<sup>13</sup> A. A. Sidorova, *Acta Physicochimica* **7**, 193 (1937).

<sup>14</sup> V. Tatevsku, *J. Phys. Chem. U.S.S.R.* **20**, 129 (1946).

TABLE I. Raman and infra-red spectral data for liquid tribromomethane (CBr<sub>3</sub>H), including calculated frequencies and assignments.\*

PR	N	$\Delta\nu$	PV	AD	Raman					PR	PS	Infra-red					$\nu_c$	Theoretical	
					$I$	V	B	$\rho$	CR			$\nu$	$I$	N	PV	AD		$I$	Assignment
155	10	154.3	0.5	45	0.8	0.78	0.77	0.85	D			1	128	—	—	116	$\nu_8 - \nu_2$	E	
222	10	222.5	0.5	100	0.2	0.22	0.11	0.45	P			2	219.0	2.0	—	153.8	$\nu_6$	E	
												1	250	—	—	222.5	$\nu_3$	A <sub>1</sub>	
												1	308	—	—	(231)	$(\nu_2 - 2\nu_6)$	A <sub>1</sub> +E	
												1	379	—	—	308	$2\nu_6$	A <sub>1</sub> +E	
												2	390.0	2.0	—	376	$\nu_3 + \nu_6$	E	
												2	431.5	1.5	—	385	$\nu_2 - \nu_6$	E	
540	10	539.3	0.9	35	0.1	0.13	0.06	0.18	P			3	538.0	1.3	—	433	$\nu_5 - \nu_3$	E	
655	10	655.5	1.0	15	0.7	0.5	0.53	0.72	D	(674)	w	3(4)	661.0	1.3	—	540.4	$\nu_2$	A <sub>1</sub>	
										774	s	2	773.5	0.5	s	652.3	$\nu_5$	E	
												1	797	—	—	761	$\nu_2 + \nu_3$	A <sub>1</sub>	
										875	m	2(3)	872.5	2.5	m	809	$\nu_5 + \nu_6$	A <sub>1</sub> +A <sub>2</sub> +E	
												1	(969)	—	—	877	$\nu_3 + \nu_5$	E	
														—	—	990	$\nu_4 - \nu_6$	A <sub>1</sub> +A <sub>2</sub> +E	
1143	7	1144.3	1.7	15	0.7	0.5	6/7	0.54	D	1143	vs	3(5)	1143.1	0.6	vs	1147.2	$\nu_4$	E	
—	4	(1439.0)	3.0	vw						1309	m	2	1298.5	10.5	m	1298	$\nu_4 + \nu_6$	A <sub>1</sub> +A <sub>2</sub> +E	
												1	2283	—	—	1416	$\nu_2 + \nu_3 + \nu_5$	E	
3017	8	3020.9	1.6	60	0.3	0.22	0.24	0.64	P	3004	vs	5	3010.4	12.7	vs	2288	$2\nu_4$	A <sub>1</sub> +E	
												1	4142.0	—	50	3022.5	$\nu_1$	E	
												1	4326.0	—	52	4165	$\nu_1 + \nu_4$	E	
												1	4453.4	—	23	4319	$\nu_1 + \nu_4 + \nu_6$	A <sub>1</sub> +A <sub>2</sub> +E	
												2	4463.9	0.1	22	4437	$\nu_1 + \nu_2 + \nu_3 + \nu_5$	E	
												1	4492.8	—	32	4473	$\nu_1 + \nu_4 + 2\nu_6$	A <sub>1</sub> +A <sub>2</sub> +2E	
												1	4680.1	—	26	4485	$\nu_1 + 2\nu_5 + \nu_6$	A <sub>1</sub> +A <sub>2</sub> +2E	
												1	4820.2	14.4	44	4704	$\nu_1 + \nu_2 + \nu_4$	E	
												3	4820.2	14.4	44	4820	$\nu_1 + \nu_4 + \nu_5$	A <sub>1</sub> +A <sub>2</sub> +E	
												1	5240.4	—	77	5243	$\nu_1 + 2\nu_2 + \nu_4$	E	
												3	5314.9	40.8	66	5309	$\nu_1 + 2\nu_4$	A <sub>1</sub> +E	
												1	5775.0	—	45	5820	$2\nu_1 - \nu_3$	A <sub>1</sub>	
												4	5950.6	37.4	81	6042	$2\nu_1$	A <sub>1</sub>	
												1	6128.9	—	6	6196	$2\nu_1 + \nu_6$	E	
												1	6334.3	—	20	6264	$2\nu_1 + \nu_3$	A <sub>1</sub>	
												1	6442.0	—	17	6486	$2\nu_1 + 2\nu_3$	A <sub>1</sub>	
												2	6537.3	22.2	21	6581	$2\nu_1 + \nu_2$	A <sub>1</sub>	
												3	6810.0	66.0	11	6697	$2\nu_1 + \nu_5$	E	
												3	7067.0	50.6	74	7186	$2\nu_1 + \nu_4$	E	
												1	7752	—	—	7725	$2\nu_1 + \nu_2 + \nu_4$	E	
												2	8224.3	108.8	7	8330	$2\nu_1 + 2\nu_4$	A <sub>1</sub> +E	
												3	8688.3	10.2	51	8687	$3\nu_1 - \nu_3 - \nu_6$	E	
												1	9524	—	—	9507	$3\nu_1 + 2\nu_3$	A <sub>1</sub>	
												4	9781.5	46.5	16	9718	$3\nu_1 + \nu_5$	E	
												1	9901	—	—	9940	$3\nu_1 + \nu_3 + \nu_5$	E	
												1	10101	—	—	10141	$3\nu_1 + 2\nu_2$	A <sub>1</sub>	
												1	10417	—	—	10373	$3\nu_1 + 2\nu_5$	A <sub>1</sub> +E	
												2	11111	0.0	—	11084	$3\nu_1 + \nu_3 + \nu_4 + \nu_5$	A <sub>1</sub> +A <sub>2</sub> +E	
												3	11282.7	31.1	—	11351	$3\nu_1 + 2\nu_4$	A <sub>1</sub> +E	
												1	12453	—	—	12460	$4\nu_1 + \nu_3 + \nu_6$	E	

\*  $\Delta\nu$  is the Raman displacement in cm<sup>-1</sup>,  $I$  is the relative intensity,  $\rho$  is the depolarization factor of the Raman line,  $\nu$  is the infra-red absorption frequency in cm<sup>-1</sup>,  $\nu_c$  is the calculated frequency in cm<sup>-1</sup>; PR = present results, N = number of times the band has been observed in independent investigations, PV = the probable value of the Raman displacement or infra-red frequency, AD = the average deviation of the individual values from the mean, V = Venkateswaran (see reference 9), B = Bhagavantam (see reference 8), CR = Cabannes and Rousset (see reference 10), PS = the polarization state (depolarized D, polarized P); uncertain frequencies are enclosed in parentheses; under the infra-red intensities, w = weak, m = medium, s = strong, vs = very strong, and the numbers give percent absorption.

obtained in thirteen previous investigations.<sup>15-27</sup> The present results and the previous data are summarized and compared in Table I. The Raman displacements are given at the left and the fifth column gives the relative intensities of the Raman lines; the values listed are those obtained in the present investigation, the previously obtained values being only visual estimates. The depolarization factors obtained in four independent investigations are given in columns six to nine. It was thought best not to take a mean of these values, since

the reliability of the experimental methods used in determining depolarization factors varies so widely, but rather to list the individual values side by side for comparison, and finally—as has been done in column ten—to decide from the polarization data which lines are depolarized (*D*) and which are polarized (*P*). Only four investigators<sup>6-8, 13</sup> have observed the very weak Raman line at 1439 cm<sup>-1</sup>; this line failed to show on the spectrograms in the present study even after very prolonged exposures. It thus seems quite probable that this line may have been due to an impurity. Sidorova,<sup>13</sup> one of the four, also reported Raman lines for the liquid at 580, 695, and 1292 cm<sup>-1</sup> with intensities of 30, 30, and 10 (on a basis of 100 for the strongest Raman line); since these three lines were not observed in any of the other nine investigations, it seems certain that they must have been due to impurities. Sidorova<sup>13</sup> also reported the following  $\Delta\nu(I)$  values for the solid state: 42(5), 156(8), 220(10), 538(9), 654(7), 696(1), 1145(5), 1294(1), 1448(0), and 3020(6). These solid state data also include the four Raman displacements attributed above to impurities in the liquid sample.

<sup>15</sup> J. W. Ellis, Phys. Rev. **23**, 48 (1924).

<sup>16</sup> Easley, Fenner, and Spence, Astrophys. J. **67**, 185 (1928).

<sup>17</sup> J. Lecomte, Comptes Rendus **196**, 1011 (1933).

<sup>18</sup> B. Timm and R. Mecke, Zeits. f. Physik **98**, 363 (1935).

<sup>19</sup> E. Trabert and K. Schaum, Zeits. f. wiss. Phot. **35**, 153 (1936).

<sup>20</sup> A. Maione, Nuovo Cimento **14**, 361 (1937).

<sup>21</sup> G. Emschwiller and J. Lecomte, J. de phys. et rad. **8**, 130 (1937).

<sup>22</sup> Yeou Ta, Comptes Rendus **206**, 1371 (1938).

<sup>23</sup> A. Carrelli and P. Tulipano, Nuovo Cimento **15**, 1 (1938).

<sup>24</sup> P. Barchewitz and M. Parodi, J. de phys. et rad. **10**, 143 (1939).

<sup>25</sup> W. Gordy, J. Chem. Phys. **7**, 163 (1939).

<sup>26</sup> G. L. Jenkins and J. W. Straley, Phys. Rev. **68**, 99 (1945).

<sup>27</sup> E. K. Plyler, J. Chem. Phys. **16**, 1008 (1948).

TABLE II. Raman spectral data, calculated frequencies, and assignments for liquid deuterotribromomethane (CBr<sub>3</sub>D).\*

Observed $\Delta\nu$	$I_e$	Calculated $\nu_c$	Assignment	Type
153.4	8	153.4	$\nu_6$	E
221.6	10	221.4	$\nu_3$	A <sub>1</sub>
519.3	7	517.6	$\nu_2$	A <sub>1</sub>
628.5	5b	631.8	$\nu_5$	E
840	3b	844.6	$\nu_4$	E
856.5	3	850	$\nu_3 + \nu_5$	E
2247	4b	2247.6	$\nu_1$	A <sub>1</sub>

\*  $I_e$  = visually estimated relative intensity, b = broad; other symbols have the same meaning as in Table I.

TABLE III. Raman spectral data, calculated frequencies, and assignments for liquid fluorotribromomethane (CBr<sub>3</sub>F).

Observed $\Delta\nu$	$I_e$	$\rho$	Calculated $\nu_c$	Assignment	Type
150	14	$\frac{7}{8}$ *	150	$\nu_6$	E
218	20	0.1	218	$\nu_3$	A <sub>1</sub>
306	3.3	$\frac{7}{8}$ *	306	$\nu_5$	E
398	10	0.04	398	$\nu_2$	A <sub>1</sub>
743	m	$\frac{7}{8}$ *	743	$\nu_4$	E
1069	w	0.42	1069	$\nu_1$	A <sub>1</sub>

\* Given as 6/7 in a later paper, M. L. Delwaulle and F. Francois, J. de physique 7, 15 (1946).

The infra-red data are given in the central part of Table I. For the 661-cm<sup>-1</sup> frequency, the band has been observed four times, but one of the values seemed unreliable and hence was not included in the mean value; likewise, one of the values for the 872.5-cm<sup>-1</sup> band and two of the values for the 1143.1-cm<sup>-1</sup> band seemed to differ from the other values by an amount greater than the expected experimental error, and were excluded in taking the mean. In general, the infra-red spectra have not been studied as frequently as the Raman spectra and the average deviations for the infra-red are greater

than for the Raman, especially for the higher frequencies.

Jenkins and Straley<sup>26</sup> obtained infra-red frequencies for two of the bands for both the liquid and gaseous states; for the liquid they obtained 1142.4 and 3012.0 cm<sup>-1</sup> and for the gaseous state they obtained 1147.7 and 3049.2 cm<sup>-1</sup>.

### Deuterotribromomethane (CBr<sub>3</sub>D)

No infra-red data were found for deuterotribromomethane and Raman data have been reported only by Redlich and Stricks.<sup>12</sup> The values obtained by them are compared with the present calculated values in Table II. No depolarization factors were found for this molecule.

### Fluorotribromomethane (CBr<sub>3</sub>F)

Likewise, no infra-red data were found for fluorotribromomethane and Raman data have been reported only by Delwaulle and Francois.<sup>28</sup> Their values, the present calculated values, and the assignments are given in Table III.

### Chlorotribromomethane (CBr<sub>3</sub>Cl)

The sample of chlorotribromomethane also was furnished by the Dow Chemical Company. Since it was a solid at room temperature, the spectrograms were obtained with benzene and CCl<sub>4</sub> solutions; both solutions upon exposure to the light from the arcs developed a deep brown coloration, presumably due to the liberation of bromine; to keep them colorless during the exposure five percent by volume of *n*-amylene was added.

Previous spectral data have been reported in two<sup>29,30</sup> Raman and in one<sup>29</sup> infra-red investigations. The

TABLE IV. Raman and infra-red spectral data for chlorotribromomethane (CBr<sub>3</sub>Cl, liquid or solution), including calculated frequencies and assignments.\*

PR	N	Raman				Infra-red				Theoretical			
		$\Delta\nu$	$I$	$\rho$	DF	$\nu$	$I_e$	$\nu$	$\nu_c$	Assignment	Type	$\nu_c$	Assignment
		PV	AD	PR	DF	PR	PS	PR	PR	LVT			
141	3	140.3	0.9	70	$\frac{7}{8}$ **	0.83	D		140.3		$\nu_6$		E
210	3	211.3	1.8	100	0.5	0.64	P		211.5		$\nu_3$		A <sub>1</sub>
									211.3		$\nu_5$		E
269	3	268.3	1.6	3	—	—			281		2 $\nu_6$		A <sub>1</sub> +E
326	3	326.7	0.9	100	0.05	0.35	P		326.7		$\nu_2$		A <sub>1</sub>
677	3	677.0	2.0	35	0.7	0.93	D		667		$\nu_4$		E
748	2(3)	745.0	3.0	5	0.7	—			740		$\nu_1$		A <sub>1</sub>
								887	m		$\nu_3 + \nu_4$ or $\nu_4 + \nu_5$		E or A <sub>1</sub> +A <sub>2</sub> +E or E
								(968)	m		or $\nu_1 + \nu_6$		
								(1150)	m		$\nu_1 + \nu_3$ or $\nu_1 + \nu_5$		A <sub>1</sub> or E
								(1310)	m		$\nu_1 + 2\nu_3$ or $\nu_1 + 2\nu_5$		A <sub>1</sub> or A <sub>1</sub> +E
									1354		2 $\nu_4$		A <sub>1</sub> +E

\* DF = Delwaulle and Francois (see reference 30), LVT = Lecomte, Volklinger, and Tchakirian (see reference 29); other symbols have the same meaning as in Table I.

\*\* Given as 6/7 in a later paper, M. L. Delwaulle and F. Francois, J. de phys. et rad. 7, 15 (1946).

<sup>28</sup> M. L. Delwaulle and F. Francois, Comptes Rendus 214, 828 (1942).

<sup>29</sup> Lecomte, Volklinger, and Tchakirian, Comptes Rendus 204, 1927 (1937).

<sup>30</sup> M. L. Delwaulle and F. Francois, Comptes Rendus 214, 226 (1942).

TABLE V. Raman and infra-red data for tetrabromomethane (CBr<sub>4</sub>, solution), including calculated frequencies and assignments.\*

PR	N	Raman				$\rho$	PS	Infra-red				$I_e$	Theoretical		
		$\Delta\nu$	PV	AD	$I$			$\nu$	$I_e$	$\nu$	PV	AD	$\nu_e$	Assignment	Type
122	3(4)	122.5	0.3	100	$\frac{7}{8}^{**}$	0.71	D			1	(164)	—	122.5	$\nu_2$	E
										1	182	—	182.5	$\nu_4$	$F_2$
182	4	182.5	0.5	40	$\frac{7}{8}^{**}$	0.72	D			1	213	—	221	$\nu_3 - \nu_1 - \nu_4$	$A_1 + E + F_1 + F_2$
267	4	267.2	1.2	70	0.05	0.00	P			1	(266)	—	267.2	$\nu_1$	$A_1$
										1	303	—	306	$\nu_2 + \nu_4$	$F_1 + F_2$
										1	365	—	366	$2\nu_4$	$A_1 + E + F_2$
										1	454	—	450	$\nu_1 + \nu_4$	$F_2$
671	4	670.7	1.8	10	$\frac{7}{8}^{**}$	0.83	D			2	666	1.0	670.7	$\nu_3$	$F_2$
								(734)	s	1	(734)	—	794	$\nu_2 + \nu_3$	$F_1 + F_2$
								931	w	1	931	—	938	$\nu_1 + \nu_3$	$F_2$
								1118	w	1	1118	—	1121	$\nu_1 + \nu_3 + \nu_4$	$A_1 + E + F_1 + F_2$

\* The symbols have the same meaning as in Table I.

\*\* Given as 6/7 in a later paper, M. L. Delwaulle and F. Francois, J. de phys. et rad. 7, 15 (1946).

Raman and infra-red data, calculated frequencies, and assignments are given in Table IV. One of the previous Raman displacements was excluded in taking the mean for the 745.0-cm<sup>-1</sup> frequency since it seemed to be considerably too low. The relatively few infra-red data are given in columns nine to eleven; of the four infra-red frequencies obtained in the present work, three are enclosed in parentheses as uncertain.

#### Tetrabromomethane (Carbon Tetrabromide, CBr<sub>4</sub>)

This compound was included in the present investigation as still another molecule of the type CBr<sub>3</sub>X, despite the fact that it represents the very special case in which X=Br. The sample was furnished by the Dow Chemical Company, and like CBr<sub>3</sub>Cl, was a solid at room temperature; accordingly, it was investigated in an approximately saturated benzene solution. Initial attempts to obtain the Raman spectrum resulted in a marked formation of cloudiness in the solution when it was exposed to the mercury arcs, thus ruining the spectrogram. This difficulty was eliminated by renewing the solution in the Raman tube at half-hour intervals during the exposures. The infra-red spectrum was also obtained in benzene solution.

Previous Raman spectral data have been obtained in three<sup>30-32</sup> and infra-red data also in three<sup>17, 24, 29</sup> other investigations. Two of the previous Raman spectra were obtained with CCl<sub>4</sub> solution,<sup>30, 32</sup> one with benzene solution.<sup>31</sup> One of the previous infra-red spectra<sup>17</sup> was obtained in CS<sub>2</sub> solution. The results are given in Table V.

#### Iodotribromomethane (CBr<sub>3</sub>I)

Iodotribromomethane, CBr<sub>3</sub>I, is a logical sixth member of this series, but no Raman or infra-red data could be found in the literature for this molecule and it was not possible to locate a sample for investigation.

<sup>31</sup> A. Dadiou and K. W. F. Kohlrausch, Sitz. Akad. Wiss. Wien IIa, 139, 717 (1930).

<sup>32</sup> A. Langseth, Zeits. f. Physik 72, 350 (1931).

### ASSIGNMENTS

#### The CBr<sub>3</sub>X Molecules

The CBr<sub>3</sub>X molecule has a symmetry corresponding to the point group C<sub>3v</sub>. According to the well-known selection rules,<sup>33</sup> the molecule should therefore have three non-degenerate, totally symmetrical vibrations of type A<sub>1</sub> and three doubly degenerate vibrations of type E. All of these are allowed in both the Raman and infra-red spectra and furthermore all binary combinations and all overtones are allowed in both spectra.

The assignments of the observed frequencies for CBr<sub>3</sub>H, consistent with these selection rules, are given at the right in Table I.<sup>34</sup> It was possible to assign all of the Raman and infra-red frequencies in the region of the fundamental frequencies (128-3025 cm<sup>-1</sup>) as fundamentals, first overtones, or binary combinations, with the exception of the infra-red frequency at 250 cm<sup>-1</sup> and the doubtful Raman displacement at 1439 cm<sup>-1</sup>. The assignment given for the 250-cm<sup>-1</sup> frequency is not too certain, for difference tones should coincide more exactly with the observed frequency than is here the case. For the overtone and combination frequencies above 3100 cm<sup>-1</sup>, the agreement of the calculated and observed values is generally not as exact as for the lower frequencies. This may be due partly to the influence of anharmonicity, but it is probably also due in large part to the greater inaccuracies in the experi-

<sup>33</sup> Cf. Meister, Cleveland, and Murray, Am. J. Phys. 11, 239 (1943).

<sup>34</sup> The numbering of the vibrational frequencies follows the procedure of G. Herzberg, *Infrared and Raman Spectra of Polyatomic Molecules* (D. Van Nostrand Company, Inc., New York, 1945), which is also in line with the agreement of molecular spectroscopists at the Symposium on Molecular Structure and Spectroscopy, held at Ohio State University (1948). The largest frequency of the most symmetrical type (A<sub>1</sub> in this case) is designated  $\nu_1$ , the next largest  $\nu_2$ , and so on up to  $\nu_n$ , where  $n$  is the number of frequencies of type A<sub>1</sub> (here  $n=3$ ); one then proceeds to the next most symmetrical type (here type E), designating the first frequency of this type  $\nu_{n+1}$ , the next  $\nu_{n+2}$ , etc.; this process is continued until all of the fundamentals have been numbered. Thus, the lowest frequency of the most unsymmetrical type (here  $\nu_6$ ) is designated  $\nu_m$ , where  $m$  is the number of distinct fundamental frequencies.

mental data since the values reported by different investigators are not in very good agreement in this region.

The assignments for the  $\text{CBr}_3\text{D}$  molecule are given in Table II. The  $840, 856.5\text{-cm}^{-1}$  doublet appears to be due to Fermi resonance between  $\nu_4$  and the combination frequency  $\nu_3 + \nu_5$ . All of the remaining observed frequencies are fundamentals.

The assignments for the  $\text{CBr}_3\text{F}$  molecule are given in Table III. For this molecule, all of the observed frequencies are fundamentals, no overtone or combination frequencies having been observed as yet.

The assignments for the  $\text{CBr}_3\text{Cl}$  molecule are given in Table IV. The point requiring the greatest comment in this assignment is that of the  $211\text{-cm}^{-1}$  frequency. Simanouti<sup>35</sup> has carried out normal-coordinate treatments for 16 substituted methanes, including  $\text{CBr}_3\text{Cl}$ ; 102 fundamental frequencies were calculated with 28 distinct force constants and the mean deviation of the calculated and observed values was 1.4 percent. According to his calculations, two fundamental frequencies fall together near  $211\text{ cm}^{-1}$  for  $\text{CBr}_3\text{Cl}$ , one an  $A_1$ , the other an  $E$ -type frequency. This is not inconsistent with the fact that in the present investigation the depolarization factor for the 211 line has an abnormally large value for a polarized line; this could be caused by the superposition of the polarized  $A_1$  and the depolarized  $E$  frequencies.

If the  $211\text{-cm}^{-1}$  line is indeed due to the coincidence of these two lines, the coincidence must be nearly exact (within about  $5\text{ cm}^{-1}$ ), for examination of the polarization spectrograms obtained by the authors shows no displacement or shading of the weak component relative to the strong component, as would be the case if a polarized and a depolarized line were nearly but not quite coincident. Furthermore, the width of the  $211\text{-cm}^{-1}$  line is not abnormally great, which would indicate that if the line is double the superposition must be nearly exact.

If one assigns two fundamentals to the observed  $211\text{-cm}^{-1}$  line, it is then necessary to assign the line observed at  $268.3\text{ cm}^{-1}$  as the first overtone of the  $140.3\text{-cm}^{-1}$  fundamental; this overtone would fall at  $280.6\text{ cm}^{-1}$ , or  $12.3\text{ cm}^{-1}$  from the observed value. While this may be the correct assignment, it seems doubtful that the combined effects of anharmonicity and experimental error in determining the Raman displacements would be greater than about  $5\text{ cm}^{-1}$ ; hence the  $12.3\text{-cm}^{-1}$  difference seems rather large.

An alternative explanation would be to assign the observed Raman displacement at  $268.3\text{ cm}^{-1}$  as the  $E$  fundamental and the  $211.3\text{-cm}^{-1}$  line as the  $A_1$  fundamental, ascribing its large depolarization factor to the fact that it is a deformation vibration; Wolkenstein and Eliashevich<sup>36</sup> have pointed out that the depolarization

factors of pure deformation vibrations are usually large, even for totally symmetrical ( $A_1$ ) vibrations. However, if this assignment is made, Simanouti's calculated value for the  $E$  fundamental would be in error by  $57\text{ cm}^{-1}$  or 21 percent and this does not seem possible in view of the good agreement he has obtained for the large number of other frequencies in the extended series of similar molecules.

Consequently, it seems that the most probable assignment is the one given in Table IV, where—in agreement with Simanouti—the 211 line is considered to correspond to the two fundamentals in nearly exact coincidence. A clear-cut decision on the assignment of this  $E$  frequency must, however, await the investigation of the 211 frequency, in either the Raman or infra-red spectra, with sufficient resolution to obtain the rotational contour of the band, from which one should be able to determine whether it is a normal parallel ( $A_1$ -type) band or whether it is a superposition of a parallel and a perpendicular ( $E$ -type) band. Unfortunately, the spectrographs available to the authors do not have sufficient dispersion to make this test possible in their laboratory.

If the  $268\text{-cm}^{-1}$  line were assigned as  $\nu_6$ , rather than as  $2\nu_6$  as suggested by Simanouti, the assignments given in Table IV would be changed otherwise only by the omission of the alternative combination bands which involve  $\nu_6$ .

### The $\text{CBr}_4$ Molecule

The  $\text{CBr}_4$  molecule has a greater symmetry than the  $\text{CBr}_3\text{X}$  molecules, namely, that corresponding to the point group  $T_d$ . According to the well-known selection rules,<sup>33</sup> the molecule should therefore have one totally symmetrical type  $A_1$  vibration, allowed in the Raman, forbidden in the infra-red; one doubly degenerate type  $E$  vibration, allowed in the Raman, forbidden in the infra-red; and two triply degenerate type  $F_2$  vibrations, allowed in both the Raman and infra-red spectra. All binary combinations of these frequencies are allowed in the Raman spectrum, but only the ones  $A_1 \times F_2$ ,  $E \times F_2$ , and  $F_2 \times F_2$  are allowed in the infra-red. Moreover, while all overtones of these frequencies (at least up to the fourth overtone) are allowed in the Raman spectrum, only the overtones of the triply degenerate  $F_2$  frequencies are allowed in the infra-red.

The assignments for  $\text{CBr}_4$ , consistent with these selection rules, are given in Table V. All of the observed Raman and infra-red frequencies have been accounted for as fundamentals, binary combinations, or first overtones, with the exception of the  $213\text{-}$  and  $1118\text{-cm}^{-1}$  infra-red bands, which had to be assigned as ternary combinations, and the  $164\text{-cm}^{-1}$  infra-red band for which no explanation could be found.

The values of the fundamental frequencies of the five molecules which the authors regard as the most probable values at the present time are collected for ease of comparison and for ready reference in Table VI.

<sup>35</sup> T. Simanouti, J. Chem. Phys. 17, 245 (1949).

<sup>36</sup> M. Wolkenstein and M. Eliashevich, Acta Physicochimica U.R.S.S. 20, 525 (1945).

## CALCULATION OF FORCE CONSTANTS

Although force constants have been given by other investigators for the molecules considered in this study, no single investigator considered all of the molecules of the  $\text{CBr}_3\text{X}$  set. In most cases, the sequence  $\text{CH}_4 \rightarrow \text{CBr}_4$  was investigated in order to find a general set of force constants for the sequence. In this way, several atoms were changed in going from one molecule to another, while in the present investigation an attempt was made to determine the variation in force constants when only one atom was changed. In other cases interaction constants were omitted from the calculations which on the basis of the present work are quite large. Furthermore, the other investigators did not always agree on the values for the fundamental frequencies to be used in determining the force constants. So, for these reasons, it was felt that a consistent treatment of the  $\text{CBr}_3\text{X}$  molecules using the best known values of the fundamental frequencies would furnish information about the behavior of the force constants.

The Wilson  $FG$  matrix method<sup>37</sup> was used in the calculations. The potential energy function used for  $\text{CBr}_3\text{H}$ ,  $\text{CBr}_3\text{D}$ ,  $\text{CBr}_3\text{F}$ , and  $\text{CBr}_3\text{Cl}$  was the following:

$$2V = k_D(\Delta D)^2 + k_a[(\Delta d_1)^2 + (\Delta d_2)^2 + (\Delta d_3)^2] \\ + 2k_{ad}[(\Delta D)(\Delta d_1 + \Delta d_2 + \Delta d_3)] \\ + 2k_{ad}[(\Delta d_1)(\Delta d_2 + \Delta d_3) + (\Delta d_2)(\Delta d_3)] \\ + d^2k_a[(\Delta \alpha_{12})^2 + (\Delta \alpha_{23})^2 + (\Delta \alpha_{13})^2] \\ + d^2k_\beta[(\Delta \beta_1)^2 + (\Delta \beta_2)^2 + (\Delta \beta_3)^2] \\ + 2dk_{D\alpha}[(\Delta D)(\Delta \alpha_{12} + \Delta \alpha_{23} + \Delta \alpha_{13})] \\ + 2dk_{D\beta}[(\Delta D)(\Delta \beta_1 + \Delta \beta_2 + \Delta \beta_3)] \\ + 2dk_{d\beta}[(\Delta d_1)(\Delta \beta_1) + (\Delta d_2)(\Delta \beta_2) + (\Delta d_3)(\Delta \beta_3)] \\ + 2d^2k_{\alpha\alpha}[(\Delta \alpha_{12})(\Delta \alpha_{23} + \Delta \alpha_{13}) + (\Delta \alpha_{23})(\Delta \alpha_{13})] \\ + 2dk_{d\beta}'[(\Delta d_1)(\Delta \beta_2 + \Delta \beta_3) + (\Delta d_2)(\Delta \beta_1 + \Delta \beta_3) \\ + (\Delta d_3)(\Delta \beta_1 + \Delta \beta_2)]$$

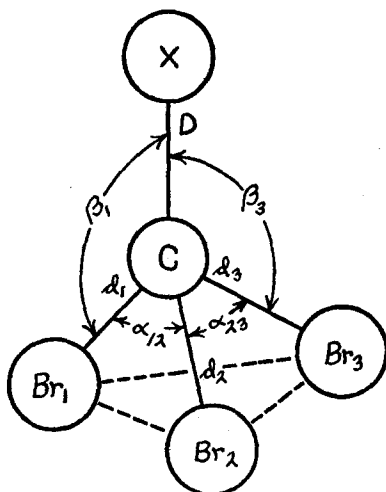


FIG. 2. Equilibrium bond distances and bond angles for a  $\text{CBr}_3\text{X}$  molecule.

TABLE VI. Probable values of the fundamental vibrational frequencies for the tribromomethanes (liquid or solutions).

Type	De- gen- eracy	$\text{CBr}_3\text{H}$	$\text{CBr}_3\text{D}$	$\text{CBr}_3\text{F}$	$\text{CBr}_3\text{Cl}$	$\text{CBr}_4$	De- gen- eracy	Type
$A_1$	1	3020.9	2247	1069	745.0			
$A_1$	1	539.3	519.3	398	326.7	267.2	1	$A_1$
$A_1$	1	222.5	221.6	218	211.3			
$E$	2	1144.3	848.2	743	677.0	670.7	3	$F_2$
$E$	2	655.5	628.5	306	211.3	182.5	3	$F_2$
$E$	2	154.3	153.4	150	140.3	122.5	2	$E$

$$+ 2dk_{d\alpha}[(\Delta d_1)(\Delta \alpha_{12} + \Delta \alpha_{13}) + (\Delta d_2)(\Delta \alpha_{12} + \Delta \alpha_{23}) \\ + (\Delta d_3)(\Delta \alpha_{13} + \Delta \alpha_{23})] \\ + 2d^2k_{\beta\beta}[(\Delta \beta_1)(\Delta \beta_2 + \Delta \beta_3) + (\Delta \beta_2)(\Delta \beta_3)] \\ + 2dk_{d\alpha}'[(\Delta d_1)(\Delta \alpha_{23}) + (\Delta d_2)(\Delta \alpha_{13}) + (\Delta d_3)(\Delta \alpha_{12})] \\ + 2d^2k_{\alpha\beta}[(\Delta \beta_1)(\Delta \alpha_{12} + \Delta \alpha_{13}) + (\Delta \beta_2)(\Delta \alpha_{12} + \Delta \alpha_{23}) \\ + (\Delta \beta_3)(\Delta \alpha_{13} + \Delta \alpha_{23})] \\ + 2d^2k_{\alpha\beta}'[(\Delta \beta_1)(\Delta \alpha_{23}) + (\Delta \beta_2)(\Delta \alpha_{13}) \\ + (\Delta \beta_3)(\Delta \alpha_{12})].$$

The equilibrium bond distances and bond angles are shown in Fig. 2.

Because  $\text{CBr}_4$  has greater symmetry than the other  $\text{CBr}_3\text{X}$  molecules, it was necessary to modify the potential energy function so that for this molecule one has

$$2V = k_d[(\Delta d_1)^2 + (\Delta d_2)^2 + (\Delta d_3)^2 + (\Delta d_4)^2] \\ + 2k_{dd}[(\Delta d_1)(\Delta d_2 + \Delta d_3 + \Delta d_4) \\ + (\Delta d_2)(\Delta d_3 + \Delta d_4) + (\Delta d_3)(\Delta d_4)] \\ + d^2k_\alpha[(\Delta \alpha_{12})^2 + (\Delta \alpha_{13})^2 + (\Delta \alpha_{14})^2 \\ + (\Delta \alpha_{23})^2 + (\Delta \alpha_{24})^2 + (\Delta \alpha_{34})^2] \\ + 2d^2k_{\alpha\alpha}[(\Delta \alpha_{12})(\Delta \alpha_{13} + \Delta \alpha_{14} + \Delta \alpha_{23} + \Delta \alpha_{24}) \\ + (\Delta \alpha_{13})(\Delta \alpha_{14} + \Delta \alpha_{23} + \Delta \alpha_{34}) \\ + (\Delta \alpha_{14})(\Delta \alpha_{24} + \Delta \alpha_{34}) \\ + (\Delta \alpha_{23})(\Delta \alpha_{24} + \Delta \alpha_{34}) + (\Delta \alpha_{24})(\Delta \alpha_{34})] \\ + 2d^2k_{\alpha\alpha}'[(\Delta \alpha_{12})(\Delta \alpha_{34}) \\ + (\Delta \alpha_{13})(\Delta \alpha_{24}) + (\Delta \alpha_{14})(\Delta \alpha_{23})] \\ + 2dk_{d\alpha}[(\Delta d_1)(\Delta \alpha_{12} + \Delta \alpha_{13} + \Delta \alpha_{14}) \\ + (\Delta d_2)(\Delta \alpha_{12} + \Delta \alpha_{23} + \Delta \alpha_{24}) \\ + (\Delta d_3)(\Delta \alpha_{13} + \Delta \alpha_{23} + \Delta \alpha_{34}) \\ + (\Delta d_4)(\Delta \alpha_{14} + \Delta \alpha_{24} + \Delta \alpha_{34})] \\ + 2dk_{d\alpha}'[(\Delta d_1)(\Delta \alpha_{23} + \Delta \alpha_{24} + \Delta \alpha_{34}) \\ + (\Delta d_2)(\Delta \alpha_{13} + \Delta \alpha_{14} + \Delta \alpha_{34}) \\ + (\Delta d_3)(\Delta \alpha_{12} + \Delta \alpha_{14} + \Delta \alpha_{24}) \\ + (\Delta d_4)(\Delta \alpha_{12} + \Delta \alpha_{13} + \Delta \alpha_{23})].$$

Since the symmetry coordinates and  $G$  matrices for a  $\text{CY}_3\text{X}$  and a  $\text{CY}_4$  molecule have already been given in a previous publication,<sup>38</sup> they will not be repeated here. Also, because the  $F$  matrices are somewhat the same as those obtained previously<sup>38</sup> they will not be given again, because once the form of the potential energy function and the symmetry coordinates are known, these matrices can be found very simply by the method given in reference 38.

Tetrahedral angles were assumed and the following constants were used: for the reciprocals of the masses of

<sup>37</sup> E. B. Wilson, Jr., J. Chem. Phys. 7, 1047 (1939); 9, 76 (1941).

<sup>38</sup> A. G. Meister and F. F. Cleveland, Am. J. Phys. 14, 13 (1946).



TABLE VII. Force constants for  $\text{CBr}_3\text{H}$  and  $\text{CBr}_3\text{D}$  ( $10^5$  dynes/cm).

Type	$\text{CBr}_3\text{H}$	$\text{CBr}_3\text{D}$
$k_D$	4.8847	4.8809
$k_d$	2.8987	2.8965
$k_{dd}$	0.27567	0.32250
$k_{dD}$	0.058900	0.058900
$*k_{D\gamma}$	0.24448	0.24448
$k_{da}$	0.17662	0.17662
$k_{da'}$	-0.10884	-0.10884
$k_{a\beta}$	0.13597	0.13597
$k_{a\beta'}$	-0.079581	-0.079581
$k_{\alpha\alpha}$	0.33399	0.33133
$k_{\alpha\alpha'}$	0.067920	0.065377
$k_{\alpha\beta}$	0.021329	0.021329
$k_{\alpha\beta'}$	0.00000	0.00000
$k_{\beta\beta}$	0.16044	0.16326
$k_{\beta\beta'}$	-0.0013706	-0.0013706

$$*k_{D\gamma} = k_{D\alpha} - k_{D\beta}.$$

the atoms,

$$\mu_C = 5.0153 \times 10^{22},$$

$$\mu_H = 5.9762 \times 10^{23},$$

$$\mu_D = 2.9905 \times 10^{23},$$

$$\mu_F = 3.1702 \times 10^{22},$$

$$\mu_{Cl} = 1.6988 \times 10^{22},$$

and

$$\mu_{Br} = 7.5372 \times 10^{21} \text{ g}^{-1};$$

and for the equilibrium values of the bond distances,<sup>39</sup>

$\text{C}-\text{Br} = 1.91\text{\AA}$  for  $\text{CBr}_3\text{H}$ ,  $\text{CBr}_3\text{D}$ ,  $\text{CBr}_3\text{F}$ , and  $\text{CBr}_3\text{Cl}$ ;

$\text{C}-\text{Br} = 1.92\text{\AA}$  for  $\text{CBr}_4$ ;

$\text{C}-\text{H} = \text{C}-\text{D} = 1.093\text{\AA}$ ;

$\text{C}-\text{F} = 1.44\text{\AA}$ ;

and

$\text{C}-\text{Cl} = 1.76\text{\AA}$ .

It will be noted that most of the force constants are expressed to five significant figures which is greater, in most cases, than the number of significant figures occurring in the frequencies used to determine force

constants. This greater number of significant figures was retained in order to insure agreement in all cases between the observed and calculated frequencies to the nearest  $\text{cm}^{-1}$ . Since the error in the observed frequencies may be greater than one  $\text{cm}^{-1}$ , the force constants cannot, of course, be considered as having been reliably established to five significant figures.

In order to obtain force constants for the  $\text{CBr}_3$  group, the  $\text{CBr}_3\text{H}$  and  $\text{CBr}_3\text{D}$  molecules were considered. Using the observed fundamental frequency values of Redlich and Stricks,<sup>12</sup> force constants for these two molecules were determined which gave calculated values for the frequencies that agreed to within  $0.1 \text{ cm}^{-1}$  of the observed values. These constants are given in Table VII. Since there are sixteen force constants and only twelve fundamental frequencies, it was necessary to make assumptions concerning the values of four of the force constants. The value of  $k_{dD}$  was taken from the work of Stepanov<sup>40</sup> while the value of  $k_{\beta\beta}$  was obtained from the work of Decius.<sup>41</sup> However, no value could be found in the literature for  $k_{a\beta'}$  so it arbitrarily was assumed to be zero, although the value given for  $k_{a\beta}$  actually is for the difference ( $k_{a\beta} - k_{a\beta'}$ ) which becomes  $k_{a\beta}$  when  $k_{a\beta'}$  is made zero. Finally, the linear combination  $k_{D\alpha} - k_{D\beta} = k_{D\gamma}$  was used since the two constants  $k_{D\alpha}$  and  $k_{D\beta}$  occur only once in the  $F$  matrices and as this linear combination.

Although two sets of force constants were determined for these two molecules, this calculation is not presented as proof that the force constants for  $\text{CBr}_3\text{H}$  and  $\text{CBr}_3\text{D}$  are considerably different. Rather it indicates how the force constants are affected when anharmonicity are neglected and force constants are modified in order to get good agreement between the calculated and observed values of the fundamental frequencies. Actually, in the investigation of the other tribromomethanes, the mean values of the force constants of the two sets were used and the calculated

TABLE VIII. Force constants for some tribromomethanes ( $10^5$  dynes/cm).

Type	$\text{CBr}_3\text{H}$ and $\text{CBr}_3\text{D}$			$\text{CBr}_3\text{F}$	$\text{CBr}_3\text{Cl}$			$\text{CBr}_4$			
	Present	Decius	Stepanov	Present	Set I	Set II	Simanouti	Present	Decius	Simanouti	Stepanov
$k_D$	4.8828	5.04	5.02	4.9531	2.9565	2.9565	2.7684	—	—	—	—
$k_d$	2.8976	2.840	2.886	2.8976	2.8976	2.8976	2.4073	2.8976	2.840	2.3379	2.945
$k_{dd}$	0.29910	0.186	0.147	0.29910	0.29910	0.29910	0.35465	0.15437	0.186	0.35465	0.147
$k_{dD}$	0.058900	0.000	0.0589	0.02654	0.20890	0.20890	0.41186	—	—	—	—
$*k_{D\gamma}$	0.24448	0.000	-0.168	-0.035300	-0.24818	-0.24818	-0.21094	—	—	—	—
$k_{da}$	0.17662	0.179	0.286	0.17662	0.17662	0.17662	0.19563	0.17662	0.179	0.19563	0.336
$k_{da'}$	-0.10884	-0.0995	0.000	-0.10884	-0.10884	-0.10884	0.00000	-0.12211	-0.0995	0.00000	0.000
$k_{a\beta}$	0.13597	0.160	0.286	0.13886	0.16567	0.29918	0.22952	—	—	—	—
$k_{a\beta'}$	-0.079581	-0.0796	0.000	-0.081027	0.094430	-0.16118	0.00000	—	—	—	—
$k_{\alpha\alpha}$	0.33266	0.291	0.257	0.33266	0.33266	0.33266	0.34155	0.29473	0.291	0.33933	0.261
$k_{\alpha\alpha'}$	0.066648	0.0367	0.0192	0.066648	0.066648	0.066648	0.053479	0.034934	0.0367	0.025999	0.0192
$k_{\alpha\beta}$	0.021329	0.000	0.0173	0.013707	0.021889	0.060851	0.053479	—	—	—	—
$k_{\alpha\beta'}$	0.00000	0.000	0.000	0.00000	0.00000	0.00000	0.00000	—	—	—	—
$k_{\beta\beta}$	0.16185	0.161	0.187	0.30015	0.25468	0.44497	0.33795	—	—	—	—
$k_{\beta\beta'}$	-0.0013706	-0.00137	0.0249	-0.049727	-0.019260	-0.036487	0.053479	—	—	—	—
$k_{\alpha\alpha'}$	—	—	—	—	—	—	—	0.010579	0.0106	0.00000	0.000
$k_{D\alpha}$	—	0.000	0.000	—	—	—	0.00000	—	—	—	—
$k_{D\beta}$	—	0.000	0.168	—	—	—	0.21094	—	—	—	—

$$*k_{D\gamma} = k_{D\alpha} - k_{D\beta}.$$

<sup>39</sup> L. R. Maxwell, J. Opt. Soc. Am. **30**, 374 (1940).

<sup>40</sup> B. I. Stepanov, Acta Physicochimica U.R.S.S. **20**, 174 (1945).

<sup>41</sup> J. C. Decius, J. Chem. Phys. **16**, 214 (1948).

fundamental frequencies given in Table I for  $\text{CBr}_3\text{H}$  and in Table II for  $\text{CBr}_3\text{D}$  were obtained using this mean set of force constants.

The above procedure served to establish the force constants of the  $\text{CBr}_3$  group which were used for  $\text{CBr}_3\text{F}$  and  $\text{CBr}_3\text{Cl}$ . The values of  $k_D$  for these molecules were obtained by splitting out<sup>37</sup> the C—F and C—Cl stretching frequencies for the type  $A_1$  vibrations. Other force constants were determined from the probable values of the observed fundamental frequencies given in Table VI. In Table VIII the force constants which were obtained for  $\text{CBr}_3\text{F}$  and  $\text{CBr}_3\text{Cl}$  are given as well as the mean set for  $\text{CBr}_3\text{H}$  and  $\text{CBr}_3\text{D}$  taken from Table VII.

It will be noted that two sets of force constants have been given for  $\text{CBr}_3\text{Cl}$ . This results from the fact that the value of one of the type  $E$  fundamental frequencies is uncertain as was mentioned previously in the section on assignments. The first set of force constants was obtained assuming that the value of the frequency was  $211.3\text{ cm}^{-1}$  while the second set resulted when the value  $268.3\text{ cm}^{-1}$  was used. Although the two sets of force constants appear to be reasonable, the much higher values of  $k_\beta$ ,  $k_{\alpha\beta}$ , and  $k_{\alpha\beta}'$  obtained in Set II might indicate that the force constants of Set I are to be preferred over those of Set II.

For  $\text{CBr}_4$  the values of  $k_d$  and  $k_{d\alpha}$  were taken from the mean set for  $\text{CBr}_3\text{H}$  and  $\text{CBr}_3\text{D}$  while the value of  $k_{d\alpha}'$  was taken from the work of Decius.<sup>41</sup> The remaining force constants were determined from the probable values of the observed fundamental frequencies given in Table VI and in Table VIII the force constants for  $\text{CBr}_4$  are indicated.

Force constants for the tribromomethanes determined by Decius,<sup>41</sup> Simanouti,<sup>35</sup> and Stepanov,<sup>40</sup> also are given in Table VIII for comparison. Simanouti used a Urey-Bradley type potential energy function but he gave relations between his force constants and those of the modified valence force type potential energy function used in this investigation. The values in the columns headed Simanouti were calculated using his equations and force constants. Decius assumed  $k_{dD}$ ,  $k_{D\alpha}$ ,  $k_{D\beta}$ ,  $k_{\alpha\beta}$ , and  $k_{\alpha\beta}'$  were zero while Stepanov neglected  $k_{d\beta}'$ ,  $k_{d\alpha}'$ , and  $k_{\alpha\alpha}'$ . Since some of these interaction

constants seem large when compared with the bending force constants, it seems that the present values of the force constants are to be preferred over those of these two investigators. The agreement between the present values of the force constants and those determined by the other investigators in most cases is good although it seems that all the other investigators used a value of  $k_D$  for  $\text{CBr}_3\text{H}$  and  $\text{CBr}_3\text{D}$  which was too high. The lower value obtained in this investigation is believed to be a better value since the other investigators found calculated values for the C—H and C—D frequencies which were greater than the observed values. This resulted from their attempt to determine a C—H stretching force constant which would remain the same in the sequence  $\text{CH}_4 \rightarrow \text{CX}_3\text{H}$ .

Finally, it should be indicated that Stepanov<sup>42</sup> calculated fundamental frequencies for the  $\text{CBr}_3\text{F}$  molecule using force constants which he obtained in an earlier work. However, the reference he gives to this work is in error and it was not possible to determine the values of the force constants he used since they were not given in the later paper.<sup>42</sup>

#### ACKNOWLEDGMENTS

The microdensitometer used in this investigation was obtained with a grant from the Penrose Fund of the American Philosophical Society; the Hilger E-518 spectrograph was obtained, in part, with a grant from the Permanent Science Fund of the American Academy of Arts and Sciences; and the optical parts for the two-prism spectrograph were obtained with a grant from The Society of the Sigma Xi.

The infra-red spectrometer was carefully constructed in the Illinois Institute of Technology shop by Mr. Max Schoenherr and was modified somewhat by Mr. Walter L. Hadlock, both of whom contributed many original ideas to its design. The samples used in the experimental part of the paper were furnished by the Dow Chemical Company, Midland, Michigan, through the courtesy of Mr. Walter W. Cooper. The drawing used for Fig. 1 was prepared by Mr. Dusan J. Ljubenko.

The authors are grateful for all of this assistance.

<sup>42</sup> B. I. Stepanov, *Comptes Rendus U.R.S.S.* **45**, 56 (1944).