

## The Normal Vibrations of Polyatomic Molecules as Treated by UreyBradley Field

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# The Normal Vibrations of Polyatomic Molecules as Treated by Urey-Bradley Field

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A method of setting up the vibrational secular equation for polyatomic molecules of "Urey-Bradley field" type is described. By this method the vibration frequencies of  $\text{CCl}_4$ ,  $\text{CBr}_4$ ,  $\text{CH}_4$ ,  $\text{CD}_4$ ,  $\text{CCl}_3\text{Br}$ ,  $\text{CCl}_2\text{Br}_2$ ,  $\text{CClBr}_3$ ,  $\text{CCl}_3\text{H}$ ,  $\text{CCl}_2\text{H}_2$ ,  $\text{CClH}_3$ ,  $\text{CCl}_3\text{D}$ ,  $\text{CCl}_2\text{D}_2$ ,  $\text{CClD}_3$ ,  $\text{CH}_3\text{D}$ ,  $\text{CH}_2\text{D}_2$ , and  $\text{CHD}_3$  molecules have been calculated. The 102 fundamental frequencies calculated using 28 distinct force constants are in satisfactory agreement with the observed, with a mean deviation of 1.4 percent.

WHEN the simple valence force field or the central force field is used as the potential function, the vibration frequencies of polyatomic molecules often cannot be calculated satisfactorily. In such cases it is most adequate to use the Urey-Bradley field, which contains both force constants related to changes in the distances between non-bonded atoms and force constants associated with changes in bond lengths and bond angles. In the present paper, the frequencies of the normal vibrations of numerous methane derivatives are calculated using this type of potential field.

## POTENTIAL ENERGY

Pentatomic methane derivative molecules  $\text{CXYZU}$  are dealt with (Fig. 1). The Urey-Bradley field type of potential function is expressed as

$$V = \sum_{i=1}^4 [K_i' r_i \Delta r_i + \frac{1}{2} K_i (\Delta r_i)^2] + \sum_{i < j} [H_{ij}' r_{ij}^2 \Delta \alpha_{ij} + \frac{1}{2} H_{ij} (r_{ij} \Delta \alpha_{ij})^2] + \sum_{i < j} [F_{ij}' q_{ij} \Delta q_{ij} + \frac{1}{2} F_{ij} (\Delta q_{ij})^2], \quad (1)$$

where  $r$ 's are the bond lengths,  $\alpha$ 's the bond angles,  $q$ 's the distances between atoms not bonded directly, and  $r_{ij}$  represents  $(r_i r_j)^{1/2}$ .  $K'$ ,  $K$ ,  $H'$ ,  $H$ ,  $F'$ , and  $F$  are the force constants, the last two of which are the repulsion constants between non-bonded atoms.

Through the relation

$$q_{ij}^2 = r_i^2 + r_j^2 - 2r_i r_j \cos \alpha_{ij}, \quad (2)$$

we can represent  $\Delta q_{ij}$  by  $\Delta r_i$ ,  $\Delta r_j$ , and  $\Delta \alpha_{ij}$ :

$$\Delta q_{ij} = s_{ij} \Delta r_i + s_{ji} \Delta r_j + (t_{ij} t_{ji})^{1/2} (r_{ij} \Delta \alpha_{ij}) + \{ t_{ij}^2 (\Delta r_i)^2 + t_{ji}^2 (\Delta r_j)^2 - s_{ij} s_{ji} (r_{ij} \Delta \alpha_{ij})^2 - 2t_{ij} t_{ji} (\Delta r_i) (\Delta r_j) + 2t_{ij} s_{ji} (\Delta r_i) (r_{ij} \Delta \alpha_{ij}) + 2t_{ji} s_{ij} (\Delta r_j) (r_{ij} \Delta \alpha_{ij}) \} / 2q_{ij}, \quad (3)$$

where

$$s_{ij} = (r_i - r_j \cos \alpha_{ij}) / q_{ij}, \\ s_{ji} = (r_j - r_i \cos \alpha_{ij}) / q_{ij}, \\ t_{ij} = r_j \sin \alpha_{ij} / q_{ij}, \\ t_{ji} = r_i \sin \alpha_{ij} / q_{ij}. \quad (4)$$

In these equations,  $r_i$ ,  $r_j$ ,  $\alpha_{ij}$ , and  $q_{ij}$  denote equilibrium values. From Eqs. (1) and (2) the potential energy is obtained as a function of valence-force coordinates:

$$V = \sum_i \left[ K_i' r_i + \sum_{j(\neq i)} F_{ij}' s_{ij} q_{ij} \right] (\Delta r_i) + \sum_{i < j} [H_{ij}' r_{ij} + F_{ij}' q_{ij} (t_{ij} t_{ji})^{1/2}] (r_{ij} \Delta \alpha_{ij}) + \frac{1}{2} \sum_i \left[ K_i + \sum_{j(\neq i)} (t_{ij}^2 F_{ij}' + s_{ij}^2 F_{ij}) \right] (\Delta r_i)^2 + \frac{1}{2} \sum_{i < j} [H_{ij} - s_{ij} s_{ji} F_{ij}' + t_{ij} t_{ji} F_{ij}] (r_{ij} \Delta \alpha_{ij})^2 + \sum_{i < j} [-t_{ij} t_{ji} F_{ij}' + s_{ij} s_{ji} F_{ij}] (\Delta r_i) (\Delta r_j) + \sum_{i \neq j} [t_{ij} s_{ji} F_{ij}' + t_{ji} s_{ij} F_{ij}] \times (r_j / r_i)^{1/2} (\Delta r_i) (r_{ij} \Delta \alpha_{ij}). \quad (5)$$

In this equation all  $\Delta r$ 's are independent variables, but all  $\Delta \alpha$ 's are not and the relation among the latter is not simple. When it is assumed, however, that all the bond angles are tetrahedral in the equilibrium position, the following relation among six  $\Delta \alpha$ 's can be obtained, neglecting

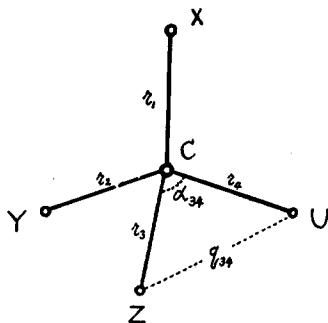


FIG. 1. Coordinates used.

higher terms of  $\Delta\alpha$ 's.

$$\sum_{i < j} (\Delta\alpha_{ij}) + (\sqrt{2}/8) \left\{ 3 \sum_{i < j} (\Delta\alpha_{ij})^2 + 4 \sum_{i \neq j \neq k} (\Delta\alpha_{ij})(\Delta\alpha_{ik}) \right\} = 0. \quad (6)$$

As the atoms are in equilibrium position, from Eqs. (5) and (6) are obtained:

$$r_i K_i' + \sum_{j (\neq i)} s_{ij} q_{ij} F_{ij}' = 0, \quad (7)$$

$$r_{ij}^2 H_{ij}' + r_{ij} q_{ij} (t_{ij} t_{ji})^{1/2} F_{ij}' + \kappa = 0, \quad (8)$$

where  $\kappa$  is a new molecular constant which may appropriately be called "intramolecular tension." Finally, the potential energy can be expressed as follows:

$$\begin{aligned} V = & \frac{1}{2} \sum_i \left[ K_i + \sum_{j (\neq i)} (t_{ij}^2 F_{ij}' + s_{ij}^2 F_{ij}') \right] (\Delta r_i)^2 \\ & + \frac{1}{2} \sum_{i < j} [H_{ij} - s_{ij} s_{ji} F_{ij}' + t_{ij} t_{ji} F_{ij} \\ & \quad + (3\kappa/\sqrt{8} r_{ij}^2)] (r_{ij} \Delta\alpha_{ij})^2 \\ & + \sum_{i < j} [-t_{ij} t_{ji} F_{ij}' + s_{ij} s_{ji} F_{ij}'] (\Delta r_i) (\Delta r_j) \\ & + \sum_{i \neq j} [t_{ij} s_{ji} F_{ij}' + t_{ji} s_{ij} F_{ij}'] \\ & \quad \times (r_j/r_i)^{1/2} (\Delta r_i) (r_{ij} \Delta\alpha_{ij}) \\ & + \sum_{i \neq j \neq k} (\kappa/\sqrt{2} r_{ij} r_{ik}) (r_{ij} \Delta\alpha_{ij}) (r_{ik} \Delta\alpha_{ik}). \end{aligned} \quad (9)$$

TABLE I. Observed frequencies<sup>a, b</sup> and force constants of CX<sub>4</sub> molecules.

	Frequencies (cm <sup>-1</sup> )				Force constants* (10 <sup>8</sup> dynes/cm)			
	A	E	T	T	K	H	F'	F
CCl <sub>4</sub>	458	218	314	776	1.76	0.080	-0.097	0.656
CBr <sub>4</sub>	269	122	183	667	1.43	0.045	-0.078	0.493
CH <sub>4</sub>	2914	1499	1306	3018				
CD <sub>4</sub>	2085	1036	997	2259	4.79	0.41	0	0.077

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

<sup>b</sup> See reference 10.

\* As the anharmonicity and liquid perturbation are neglected, the force constants mean the effective values. In the case of CH<sub>4</sub> and CD<sub>4</sub> the force constants are determined so that the calculated frequencies agree with the observed as well as possible.

## SECULAR EQUATION

To express the vibrational kinetic energy with the valence-force coordinates, the method developed by E. B. Wilson<sup>1</sup> is used and the normal vibrations can be calculated from the secular equation

$$|GF - E\lambda| = 0. \quad (10)$$

## TETRAHEDRAL MOLECULES, CX<sub>4</sub>

For the four frequencies, A, E, and two T's, of CX<sub>4</sub> molecules, the following F and G matrices are obtained:

$$\left. \begin{aligned} G_A &= \mu, \\ F_A &= K + 4F, \end{aligned} \right\} \quad (11)$$

$$\left. \begin{aligned} G_E &= 3\mu, \\ F_E &= H - \frac{1}{3}F' + \frac{1}{3}F, \end{aligned} \right\} \quad (12)$$

$$\left. \begin{aligned} G_T &= \begin{pmatrix} \mu + \frac{4}{3}\mu_0 & -\frac{8}{3}\mu_0 \\ -\frac{8}{3}\mu_0 & 2\mu + \frac{16}{3}\mu_0 \end{pmatrix}, \\ F_T &= \begin{pmatrix} K + \frac{4}{3}F' + \frac{4}{3}F & \frac{2}{3}(F' + F) \\ \frac{2}{3}(F' + F) & H - \frac{8}{3}F' + \frac{1}{3}F \end{pmatrix}, \end{aligned} \right\} \quad (13)$$

where  $\mu$  and  $\mu_0$  are the reciprocals of the masses of the X atom and C atom, respectively. This result is in good agreement with those of Rosenthal<sup>2</sup> and Urey and Bradley.<sup>3</sup>

From four observed frequencies four force constants, K, H, F', and F, are calculated. The other constants can be expressed with F'; that is, K' is expressed with Eq. (7) and  $\kappa$  with Eq.

TABLE II. Force constants (10<sup>8</sup> dynes/cm).

$H_{\text{CICBr}}$	0.0303
$F'_{\text{CICBr}}$	-0.0872
$F_{\text{CICBr}}$	0.575

TABLE III. The vibration frequencies of chlorobromomethanes (cm<sup>-1</sup>). ( $r_{\text{CCl}} = 1.77\text{\AA}$ ,  $r_{\text{CBr}} = 1.92\text{\AA}$ ,  $\alpha$  = the tetrahedral angle.)

	CCl <sub>3</sub> Br			CCl <sub>2</sub> Br <sub>2</sub>			CClBr <sub>3</sub>				
	Obs.	Calc.	$\Delta\%$ per cent	Obs.	Calc.	$\Delta\%$ per cent	Obs.	Calc.	$\Delta\%$ per cent		
A <sub>1</sub>	710	714	0.6	A <sub>1</sub>	720	727	1.0	A <sub>1</sub>	734	724	1.4
	418	422	1.0		370	383	3.5		326	333	2.1
	243	246	1.2		230	242	5.2		210	210	0.0
E	765	758	0.9		141	150	6.4	E	674	671	0.4
	289	294	1.7	B <sub>1</sub>	759	740	2.5		210	211	0.5
	187	184	1.6		252	259	2.8		139	137	1.4
				B <sub>2</sub>	672	674	0.3				
					230	226	1.7		266	Overtone	
				A <sub>2</sub>	164	164	—				
					318	Overtone					

<sup>1</sup> E. Bright Wilson, Jr., J. Chem. Phys. 7, 1047 (1939); 9, 76 (1941).

<sup>2</sup> Jenny E. Rosenthal, Phys. Rev. 45, 538 (1934).

<sup>3</sup> H. C. Urey and C. A. Bradley, Phys. Rev. 38, 1969 (1931).

(8), since  $H'$  is considered to be zero in this molecule. In this case Eq. (7) becomes

$$\kappa = -r_{ij}^2 F_{ij}' \sin \alpha_{ij}. \quad (14)$$

The results of calculation are given in Table I. The negative values of  $F'$  show that the forces between non-bonded atoms are repulsive, as pointed out by Urey and Bradley.<sup>3</sup> The magnitude of the values of  $F'$  and  $F$  are found to be reasonable when some of them are compared with the interatomic forces of argon, krypton, and the like.<sup>4,5</sup>

#### CCl<sub>3</sub>Br, CCl<sub>2</sub>Br<sub>2</sub>, AND CClBr<sub>3</sub>

In the case of CX<sub>3</sub>Y and CX<sub>2</sub>Y<sub>2</sub> molecules, the **F** and **G** matrices are factored because of the symmetry properties, the details of which have been already given.<sup>1,6-8</sup> Of the twelve necessary constants, the values of  $K_{\text{CCl}}$ ,  $H_{\text{ClCCl}}$ ,  $F'_{\text{ClCl}}$ ,  $F_{\text{ClCl}}$ ,  $K_{\text{CBr}}$ ,  $H_{\text{BrCBr}}$ ,  $F'_{\text{BrBr}}$ , and  $F_{\text{BrBr}}$  are assumed to be the same as those of CCl<sub>4</sub> and CBr<sub>4</sub>. For the values of  $F'_{\text{ClBr}}$ ,  $F_{\text{ClBr}}$ , and  $\kappa$ , the arithmetical means of those of CCl<sub>4</sub> and CBr<sub>4</sub> are used. The remaining constant  $H_{\text{ClCBr}}$  is calculated from the frequency 164 cm<sup>-1</sup> of CCl<sub>2</sub>Br<sub>2</sub> molecule. The force constants thus obtained are given in Table II. Table III gives the calculated frequencies using these constants. The observed frequencies are taken from the Raman spectra measured by Lecomte and collaborators,<sup>9</sup> but the assignments are somewhat different.

TABLE IV. The vibration frequencies of deuteromethanes (cm<sup>-1</sup>).

CH <sub>3</sub> D				CH <sub>2</sub> D <sub>2</sub>				CHD <sub>3</sub>			
Obs.	Calc.	$\Delta$ per cent		Obs.	Calc.	$\Delta$ per cent		Obs.	Calc.	$\Delta$ per cent	
A <sub>1</sub>	2982	2958	0.8	A <sub>1</sub>	2974	2983	0.3	A <sub>1</sub>	2992	3005	0.2
	2205	2204	0.0		2139	2160	1.0		2141	2115	1.2
	1306	1315	0.7		1450	1407	3.0		1046	1010	3.4
E	3030	3026	0.1		1036	1022	1.3	E	2269	2253	0.7
	1477	1435	2.8	B <sub>1</sub>	3020	3026	0.2		1299	1265	2.6
	1156	1164	0.7		1090	1101	1.0		982	1022	4.1
				B <sub>2</sub>	2255	2254	0.0				
					1235	1241	0.5				
				A <sub>2</sub>	1286	1285	0.1				

<sup>4</sup> Y. Morino, I. Watanabe, and S. Mizushima, Sci. Pap. I. P. C. R. (Tokyo) **39**, 348 (1942).

<sup>5</sup> Takehiko Simanouti, Bull. I. P. C. R. (Tokyo) **23**, 314 (1944).

<sup>6</sup> J. E. Rosenthal and H. H. Voge, J. Chem. Phys. **4**, 134 (1936).

<sup>7</sup> J. Wagner, Zeits. f. physik. Chemie **B45**, 69 (1940).

<sup>8</sup> Takehiko Simanouti, Bull. I. P. C. R. (Tokyo) **21**, 825 (1942).

<sup>9</sup> Lecomte, Volklinger, and Tchakirian, Comptes Rendus **204**, 1927 (1937).

TABLE V. Force constants (10<sup>5</sup> dynes/cm).

$K_{\text{CCl}} = 1.75$	$K_{\text{CH}} = 4.8(\text{CH}_4), 4.5(\text{CH}_3-), 4.2(\text{CH}_2-), 3.9(\text{CH}-)$	
$H_{\text{ClCCl}} = 0.1$	$H_{\text{HCH}} = 0.4$	$H_{\text{ClCH}} = 0.05$
$F'_{\text{ClCl}} = -0.1$	$F'_{\text{HH}} = 0.0$	$F'_{\text{CH}} = -0.05$
$F_{\text{ClCl}} = 0.65$	$F_{\text{HH}} = 0.1$	$F_{\text{CH}} = 0.8$

#### CH<sub>3</sub>D, CH<sub>2</sub>D<sub>2</sub>, AND CHD<sub>3</sub>

In calculating the frequencies of these molecules the force constants necessary are only four, which are given in Table I. The calculated values are compared (Table IV) with the observed which have been reviewed by Dennison<sup>10</sup> and Halverson.<sup>11</sup>

#### CCl<sub>3</sub>H, CCl<sub>2</sub>H<sub>2</sub>, CClH<sub>3</sub>, CCl<sub>3</sub>D, CCl<sub>2</sub>D<sub>2</sub>, AND CClD<sub>3</sub>

In these molecules the bond angles deviate from tetrahedral by several degrees.<sup>12</sup> In the present calculation the tetrahedral angles are assumed, and in consequence some deviations are unavoidable. In view of this approximation, only rounded values of force constants are assumed (Table V). The values of  $K_{\text{CH}}$ ,  $H_{\text{ClCH}}$ ,  $F'_{\text{CH}}$ , and  $F_{\text{CH}}$  are determined so that the

TABLE VI. The vibrational frequencies of chloro- and deuteriochloromethanes (cm<sup>-1</sup>).

CCl <sub>4</sub>				Obs.	Calc.	$\Delta \nu$ per cent			
	A	458	456	0.4					
	E	218	224	2.7					
	T	314	318	1.3					
		776	787	1.4					
				$\Delta \nu$ per cent					
	Obs.	Calc.	$\Delta \nu$ per cent		Obs.	Calc.	$\Delta \nu$ per cent		
CCl <sub>3</sub> H	A <sub>1</sub>	364	357	1.9	CCl <sub>3</sub> D	A <sub>1</sub>	367	357	2.7
		667	670	0.5			651	659	1.2
		3033	2988	1.5			2256	2170	3.8
	E	260	267	2.7		E	262	266	1.5
		760	745	2.0			738	728	1.4
		1205	1252	3.9			908	922	1.5
CCl <sub>2</sub> H <sub>2</sub>	A <sub>1</sub>	283	292	3.2	CCl <sub>2</sub> D <sub>2</sub>	A <sub>1</sub>	—	290	—
		704	718	2.0			—	694	—
		1429	1439	0.8			—	1053	—
		2984	2992	0.3			—	2162	—
	B <sub>1</sub>	899	847	5.8		B <sub>1</sub>	—	677	—
		3048	3015	1.1			—	2216	—
	B <sub>2</sub>	737	715	3.0		B <sub>2</sub>	—	705	—
		1266	1302	2.8			—	957	—
	A <sub>2</sub>	1155	1127	2.4		A <sub>2</sub>	—	802	—
CClH <sub>3</sub>	A <sub>1</sub>	732	724	1.1	CClD <sub>3</sub>	A <sub>1</sub>	701	706	0.7
		1355	1367	0.9			1029	1011	1.7
		(2920)	2981	2.1			2161	2134	1.3
	E	1020	966	5.2		E	775	731	5.7
		1460	1433	1.8			1081	1036	4.2
		3047	3028	0.6			2300	2239	2.6
CH <sub>4</sub>	A	2916	2960	1.5	CD <sub>4</sub>	A	2085	2093	0.4
	E	1499	1480	1.3		E	1036	1047	1.1
	T	1306	1324	1.4		T	997	996	0.1
		3018	3037	0.6			2259	2259	0.0

\* For the recently observed frequencies in Tables IV and VI the writer is indebted to the reviewer of the Journal of Chemical Physics, to whom he wishes to express his thanks.

<sup>10</sup> David M. Dennison, Rev. Mod. Phys. **12**, 208 (1940).

<sup>11</sup> Frederick Halverson, Rev. Mod. Phys. **19**, 100 (1947).

<sup>12</sup> Y. Morino and M. Kimura, private communication.

calculated values agree with the observed as well as possible. Four values of  $K_{CH}$ , 4.8, 4.5, 4.2, and  $3.9 \times 10^5$  dynes/cm, are those of  $CH_4$ ,  $CClH_3$ ,  $CCl_2H_2$ , and  $CCl_3H$ , respectively. Those values can be used successfully also in the calculation of the vibration frequencies of ethane ( $K_{CH}=4.5$ ) and polyethylene ( $K_{CH}=4.2$ ).<sup>13</sup> That the  $K_{CH}$  force constant is different in these molecules seems to be due to the difference of CH bond length.<sup>14</sup> For the values of  $\kappa$ , the weighted means of those obtained from Eq. (14) and the values of  $F'$  in Table V are taken. The calculated and the observed frequencies are compared in Table VI. The frequencies of  $CCl_4$ ,  $CH_4$ , and  $CD_4$  are recalculated using these force constants. The observed frequencies of the other molecules are taken from the Raman and the infra-red data (liquid state).<sup>15</sup>

### CONCLUSION

Taking into account that the assumptions are very simple and that the assumed force constants are only 28 (strictly speaking 20), the results obtained for 102 frequencies are satisfactory. As the anharmonicity, liquid state frequency shift, and bond angle deviation from

tetrahedral are neglected, the difference of several percent between the calculated and the observed values is unavoidable.

Thus we can conclude that the Urey-Bradley field is an adequate type of potential function to explain the vibration frequencies of polyatomic molecules and, therefore, the repulsive forces between non-bonded atoms are not negligible compared with the bond stretching or bending forces.

By means of almost the same method, Sanichiro Mizushima, Yonezo Morino, and the author have already calculated the skeletal vibrational frequencies of propane, *n*-butane, *n*-pentane, *n*-hexane, other normal long-chain paraffins,<sup>16</sup> and the rotational isomers of dichloroethane.<sup>17</sup> The vibrations of ethane, hexahaloethanes, acetate ion, glycine, and polyethylene (including its deuterio and fluoro derivatives) are also calculated. All these calculations have given good results, the details of which will be reported in the near future.

The author wishes to express his sincere thanks to Professor S. Mizushima for helpful suggestions and advice, and also to Professor Y. Morino for the constant interest he has shown throughout the research.

<sup>13</sup> Takehiko Simanouti, unpublished work.

<sup>14</sup> T. Simanouti and H. Baba, unpublished work.

<sup>15</sup> George Herzberg, *Infrared and Raman Spectra of Polyatomic Molecules* (D. Van Nostrand Company, Inc., New York, 1945).

<sup>16</sup> S. Mizushima and T. Simanouti, *Proc. Imp. Acad. Tokyo* **20**, 86 (1944).

<sup>17</sup> S. Mizushima, Y. Morino, and T. Simanouti, *Sci. Pap. I. P. C. R. (Tokyo)* **40**, 87 (1942).