Force Constants for Some Halomethanes

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Force Constants for Some Halomethanes*

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(Received November 25, 1947)

Valence-type force constants, including several interaction terms, have been deduced from some of the experimentally observed fundamental vibration frequencies of the molecular sequence CX_4, CX_3Y, CX_2Y_2, CXY_3, and CY_4 in which X may be chlorine or bromine, Y hydrogen or deuterium. By assuming that the force constants are invariant for the different molecules and by neglecting several interaction constants associated with two bending motions, the number of distinct constants was reduced to 28, from which, after slight adjustment, 100 vibration frequencies were calculated. The quality of the fit with the experimental frequencies is indicated by a reasonably low root mean square deviation between calculation and observation (1.1 percent for 82 frequencies) and by the success of the constants in predicting 22 of the frequencies which were not used in the initial numerical evaluation of the constants.

I. INTRODUCTION

IN the study of the vibrational spectra of polyatomic molecules it is at present not feasible to calculate the vibrational frequencies *a priori*, even in the harmonic oscillator approximation, since the quantum mechanical problem of deducing internuclear potential functions, solved in principle by Born and Oppenheimer[1] has not in practice been developed sufficiently to allow explicit representations of the potential energy associated with small displacements of the nuclei from their equilibrium configuration, except for very simple molecules. In order, therefore, to facilitate the interpretation of the structure of increasingly complex molecules from their vibrational spectra, it has proved worth while to calculate empirically the values of force constants for various types of quadratic potential functions. Two types of such functions have been principally used: central and valence force systems. In either system, the number of constants in the most general quadratic form, even after consideration of symmetry, generally exceeds the number of independent data, i.e., the observed frequencies. The situation may, of course, be improved if isotopically substituted molecules have been studied experimentally. On the other hand, most attempts to fit the observed spectra with the minimum number of parameters, as with a diagonal potential function (no interaction constants), are less and less successful as the size of the molecule increases.

It is the purpose of this paper to continue the attempt, initiated by Crawford and Brinkley[2] and others, to obtain a set of force constants, including some interaction terms, which can be used without change for a variety of molecules to predict the vibration frequencies with reasonable precision. The molecules involved constitute the sequence CX_4, CX_3Y, CX_2Y_2, CXY_3, and CY_4 in which X may be either Cl or Br and Y either H or D.

II. COORDINATE BASIS AND KINETIC ENERGY MATRIX ELEMENTS

A coordinate basis of the valence type has been chosen and the following nomenclature adopted:

$$R = \Delta(C-X),$$
$$r = \Delta(C-Y),$$
$$\alpha = \Delta(X-C-Y),$$
$$\beta = \Delta(X-C-X),$$
$$\eta = \Delta(Y-C-Y).$$

I.e., the Roman letters are used to denote bond stretches and Greek letters designate bond bendings.

The potential and inverse kinetic energy matrix elements relative to such a basis are identified by the following scheme of notation. The f or g

[1] M. Born and J. R. Oppenheimer, Ann. d. Physik **84**, 457 (1927).

[2] B. L. Crawford, Jr. and S. R. Brinkley, Jr., J. Chem. Phys. **9**, 64 (1941).

identifying a potential energy or inverse kinetic energy matrix element respectively is followed by literal subscripts designating which types of valence coordinates are involved. When this much is specified there remain several possibilities in most cases: these are distinguished by the use of numerical superscripts. As an example, consider the matrix element corresponding to a combination of $H-C$ stretching and $H-C-Cl$ bending. Since the H may or may not be common to the pair of coordinates, $f_{r\alpha}{}^1$ if used in case the H is common and $f_{r\alpha}{}^2$ is used when different H atoms are involved. All such combinations will be identified below by figures giving the numbering of coordinates and tables in which the individual f matrix elements are defined relative to the numbered coordinates.

The individual g matrix elements have not been tabulated here, since it is planned to present an extensive tabulation of these quantities, both algebraically and numerically, in a forthcoming paper. They have been computed by the vector method of Wilson.[3]

The molecular parameters which enter the calculations of the inverse kinetic energy matrix elements are the reciprocal masses of the individual atoms, the reciprocals of the interatomic distances, and trigonometric functions of the bond angles. The following numerical values have been adopted in these calculations:

Mass (atomic wt. units)		Distance (A)	
C	12.01	C$-$Cl	1.75
Cl	35.457	C$-$Br	1.88
Br	79.916	C$-$H	1.093
H	1.008	C$-$D	1.093
D	2.0147		

All bond angles have been assumed tetrahedral, i.e., 109°28′.

Refined studies of rotational spectra and electron diffraction may indicate small variations in bond lengths in different molecules, but the present assumption of constancy is consistent with that of the invariance of the force constants.

III. SYMMETRY FACTORING

A. General Procedure

Once the matrix elements have been set up in a valence coordinate basis, it is still necessary to transform them to a symmetry coordinate basis in order to realize the fullest factoring of the secular determinant possible by group theory. Previously, this has been accomplished by forming, more or less by inspection, linear combinations of the valence coordinates which exhibit the transformation properties characteristic of the irreducible representations of the point group of the molecule. In the following treatment, use is made of a more systematic method developed by Lippman[4] in an unpublished work. According to Lippman's method, there exist transformation formulas of the form

$$f_{ip, jq}{}^{(k)} = \sum_{m=1}^{v_{ij}} \gamma_{ij}{}^m a_{ip, jq}{}^{(k)m} f_{ij}{}^m \qquad (1)$$

Here $f_{ip, jq}{}^{(k)}$ is a potential energy matrix element in a symmetry coordinate basis, (fully factored) formed from valence coordinates of the ith and jth classes (corresponding to particular bond stretches and/or deformations as described above, such as $H-C$ stretching and $H-C-Cl$ bending). The summation index, m, refers to the various possible valence coordinate matrix elements of this particular pair of coordinate types, with v_{ij} the number of such different matrix elements, $f_{ij}{}^m$. The indices p and q in the general case may have a maximum range of 3, but for the sequence of molecules presently to be considered, the maximum number of symmetry coordinates which are formed from any given valence coordinate type appearing in a given irreducible representation (identified by the index k) is only one, and the indices p and q which are associated with this possible multiplicity, assume only the value of unity and will henceforth be omitted. Under these conditions, the "symmetry coefficients," $a_{ij}{}^{(k)m}$, and the "multiplicities," $\gamma_{ij}{}^m$, can be determined as follows. Let u_i denote the number of valence coordinates in the ith set and let $\beta_{ij}{}^m$ denote the number of times $f_{ij}{}^m$ occurs in the first row of F_{ij}, the submatrix of F which corresponds to all rows of coordinates of type i and all columns of coordinates of type j. Then

$$\gamma_{ij}{}^m = \beta_{ij}{}^m \left(\frac{u_i}{u_j}\right)^{\frac{1}{2}} \qquad (2)$$

[3] E. B. Wilson, Jr., J. Chem. Phys. 9, 76 (1941).

[4] Caro Lippman, private communication, Harvard University.

TABLE I. Characters and frequency distribution for CX_4.

T_d	E	$8C_3$	$6\sigma_d$	$6S_4$	$3S_4{}^2=3C_2 n_R$	n_β	n'	n	Selection rule
A_1	1	1	1	1	1	1	1	1	1	$R(p)$
A_2	1	1	−1	−1	1	0	0	0	0	I
E	2	−1	0	0	2	0	1	0	1	$R(d)$
F_1	3	0	−1	1	−1	0	0	0	0	I
F_2	3	0	1	−1	−1	1	1	0	2	$IR, R(d)$
χ^R	4	1	2	0	0					
χ^β	6	0	2	0	2					
χ'	1	1	1	1	1					
χ	9	0	3	−1	1					

and, when $i = j$

$$a_{ii}^{(k)m} = \frac{u_i}{h} \sum_{r \epsilon H_{im}} \chi_r^{(k)}, \qquad (3)$$

where h is the order of the group, $\chi_r^{(k)}$ is the character of the rth group element in the kth irreducible representation, and the summation is to be extended over the set of those group elements, H_{im},† which have the property of sending the first coordinate of the ith type into one whose order number is m, which is in turn defined as the order number of any column in the first row of F_{ii} occupied by f_{ii}^m. When $i \neq j$

$$a_{ij}^{(k)m} = \frac{\pm(\beta_{ij}^1)^{\frac{1}{2}} \sum_{t(m)} a_{jj}^{(k)t(m)}}{\beta_{ij}^m (\sum_{t(1)} a_{jj}^{(k)t(1)})^{\frac{1}{2}}}, \qquad (4)$$
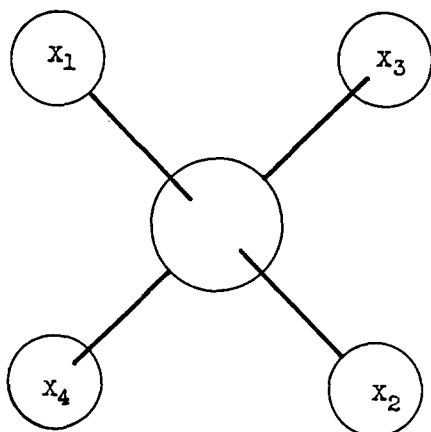

FIG. 1. Coordinates for CX_4. $R_i = \Delta CX_i$, $\beta_i = \Delta X_1 CX_2$, $\beta_2 = \Delta X_1 CX_3$, $\beta_3 = \Delta X_1 CX_4$, $\beta_4 = \Delta X_2 CX_3$, $\beta_5 = \Delta X_3 CX_4$, $\beta_6 = \Delta X_4 CX_2$.

† H_{im} is one of the cosets determined by H_{i1}, the subgroup which leaves the first coordinate of the ith set invariant.

where

$$a_{jj}^{(k)t(m)} = a_{jj}^{(k)m}, \qquad (5)$$

and the summations over $t(m)$ and $t(1)$, respectively, are extended over those columns in which f_{ij}^m and f_{ij}^1 appear in the first row of F_{ij}.

These expressions become especially simple when $\chi_1^{(k)} = 1$ (dimension of the irreducible representation equals unity). They are then

$$a_{ij}^{(k)m} = \chi_r^{(k)}, \qquad r \epsilon H_{im}, \qquad (6)$$

and, in particular, for the totally symmetric representation

$$a_{ij}^{(1)m} = 1. \qquad (7)$$

The transformation scheme for the inverse kinetic energy matrix elements is identical with that for the potential energy matrix just described.

B. The CX_4 and CY_4 Molecules

The initial assumption of tetrahedral angles compels consideration of T_d symmetry for these molecules. The coordinates are numbered as in Fig. 1. The symmetry factoring is illustrated by Table I.

The first six rows and columns in Table I define the irreducible representations and their characters. The columns headed n_R and n_β give, respectively, the number of times symmetry coordinates formed from each of these valence coordinates appear in the factored secular equation. In general, $n_i^{(k)}$ is found from the character relation,

$$n_i^{(k)} = \frac{1}{h} \sum_i \rho_i \chi_j^{(k)} \chi_j^i †† \qquad (8)$$

$$n_i^{(k)} = \frac{u_i}{h} \sum_{r \epsilon H_{i1}} \chi_r^{(k)}.$$

where ρ_j is the number of elements in the jth class, $\chi_j^{(k)}$ the character of the jth class in the kth irreducible representation, and χ_j^i the character of the jth class in the representation afforded by the ith set of valence coordinates; this latter quantity is merely the number of coordinates of the ith set taken into themselves by a given group element of the jth class.

In this scheme, in general, there may exist redundant coordinates: the column headed n'

†† Lippman (reference 4) has shown that this expression can be contracted to

TABLE II. Force constants for the CX_4 molecule.

	R				β					
	1	2	3	4	1	2	3	4	5	6
R	$f_R{}^1$	$f_R{}^2$	$f_R{}^2$	$f_R{}^2$	$f_{R\beta}{}^1$	$f_{R\beta}{}^1$	$f_{R\beta}{}^1$	$f_{R\beta}{}^2$	$f_{R\beta}{}^2$	$f_{R\beta}$
β					$f_\beta{}^1$	$f_\beta{}^2$	$f_\beta{}^2$	$f_\beta{}^2$	$f_\beta{}^3$	$f_\beta{}^2$

TABLE III. Multiplicities and symmetry coefficients for CX_4.

	R		$R\beta$		β		
$f_{ij}{}^m$	$f_R{}^1$	$f_R{}^2$	$f_{R\beta}{}^1$	$f_{R\beta}{}^2$	$f_\beta{}^1$	$f_\beta{}^2$	$f_\beta{}^3$
$\gamma_{ij}{}^m$	1	3	$(6)^{\frac{1}{2}}$	$(6)^{\frac{1}{2}}$	1	4	1
A_1	1	1	1	1	1	1	1
E	0	0	0	0	1	$-\frac{1}{2}$	1
F_2	1	$-\frac{1}{3}$	$(3)^{-\frac{1}{2}}$	$-(3)^{-\frac{1}{2}}$	1	0	-1

gives the number of redundancies in each factor, while the last column represents the net order of each factor. The entries of the last column are readily determined by equations similar to (8) with $\chi_j{}^i$ replaced by χ_j, where χ_j is to be determined, for example, by the method of Rosenthal and Murphy,[5] and is merely the character of the complete set of genuine vibrations (internal displacements involving no displacement of the center of mass and no rotation) of the molecule.

The selection rules are given in the last column, where R means Raman active, IR means infrared active, I means inactive in both spectra, p and d mean polarized and depolarized, respectively.

Table II defines the potential energy matrix elements relative to the valence coordinate basis.

Note that the terms of the type $f_{ii}{}^m$ are abbreviated as $f_i{}^m$. Finally, the symmetry analysis of the CX_4 molecule is completed by tabulating the multiplicities and symmetry coefficients (Table III).

Thus, by the use of Eq. (2), the symmetry factored $\mathfrak{F}\ddagger$ matrices become

$$A_1: \quad f_R{}^1 + 3f_R{}^2 \quad (6)^{\frac{1}{2}}(f_{R\beta}{}^1 + f_{R\beta}{}^2)$$
$$f_\beta{}^1 + 4f_\beta{}^2 + f_\beta{}^3$$
$$E: \quad f_\beta{}^1 - 2f_\beta{}^2 + f_\beta{}^3$$
$$F_2: \quad f_R{}^1 - f_R{}^2 \quad (2)^{\frac{1}{2}}(f_{R\beta}{}^1 - f_{R\beta}{}^2)$$
$$f_\beta{}^1 - f_\beta{}^3$$

in which the elements below the principal diagonal have been omitted on account of the symmetry of the matrices.

The corresponding $\mathcal{G}$ matrices are:

	CCl₄		CBr₄	
	R	β	R	β
A_1:	.02820	0	.01251	0
		0		0
E:		.02763		.01062
F_2:	.13922	$-.12688$	.12354	$-.11811$
		.16342		.13272

[5] J. Rosenthal and G. M. Murphy, Rev. Mod. Phys. **8**, 317 (1936).
‡ Roman symbols stand for matrices relative to the valence coordinates and script symbols for matrices relative to symmetry coordinates.

In this case, the redundancy in the A_1 factor is revealed directly by the vanishing column; this corresponds, of course, to the condition:

$$\sum_{l=1}^{6} \beta_l = 0. \qquad (9)$$

In the general case, the redundancy may appear in the $\mathcal{G}$ matrix only as a linear dependence between the columns.

In the analysis of the remaining molecules, the $\mathfrak{F}$ matrices will not be given explicitly, since they can be constructed immediately once a table corresponding to Table III has been given.

The treatment of the CY_4 molecule is formally identical with that just given for CX_4, requiring only the substitution of coordinates r for R and η for β. The $\mathcal{G}$ matrices are:

	CH₄		CD₄	
	r	η	r	η
A_1:	0.99206	0	0.49634	0
		0		0
E:		2.4912		1.2464
F:	1.1031	-0.20314	0.60736	-0.20314
		2.0325		1.2027
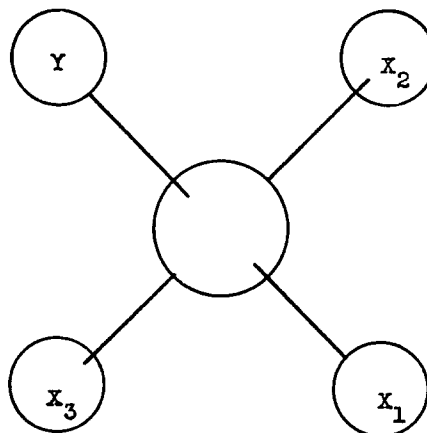
FIG. 2. Coordinates for CX_3Y: for CXY_3, permute X and Y, R and r, substitute η for β. $R_i = \Delta CX_i$, $r = \Delta CY$, $\alpha_i = \Delta X_i CY$, $\beta_1 = \Delta X_2 CX_3$, $\beta_2 = \Delta X_1 CX_2$, $\beta_3 = \Delta X_1 CX_2$.

TABLE IV. Characters and frequency distribution for CX_3Y.

C_{3v}	E	$2C_3$	$3\sigma v$	n_R	n_r	n_α	n_β	n'	n	Selection rule
A_1	1	1	1	1	1	1	1	1	3	$IR, R(p)$
A_2	1	1	-1	0	0	0	0	0	0	I
E	2	-1	0	1	0	1	1	0	3	$IR, R(d)$
χ^R	3	0	1							
χ^r	1	1	1							
χ^α	3	0	1							
χ^β	3	0	1							
χ'	1	1	1							
χ	9	0	3							

TABLE V. Force constants for the CX_3Y molecule.

| | R | | | r | α | | | β | | |
	1	2	3	1	1	2	3	1	2	3
R	f_R^1	f_R^2	f_R^2	f_{Rr}^1	$f_{R\alpha}^1$	$f_{R\alpha}^2$	$f_{R\alpha}^2$	$f_{R\beta}^2$	$f_{R\beta}^1$	$f_{R\beta}^1$
r				f_r^1	$f_{r\alpha}^1$	$f_{r\alpha}^1$	$f_{r\alpha}^1$	$f_{r\beta}^1$	$f_{r\beta}^1$	$f_{r\beta}^1$
α					f_α^1	f_α^2	f_α^2	$f_{\alpha\beta}^2$	$f_{\alpha\beta}^1$	$f_{\alpha\beta}^1$
β								f_β^1	f_β^2	f_β^2

C. The CX_3Y and CXY_3 Molecules

These molecules possess the point group symmetry C_{3v}. The coordinates are numbered in accordance with Fig. 2. Tables IV to VI give the details of the symmetry factoring.

The nine fundamental frequencies are accounted for by two third-order determinants, one of which is doubly degenerate. The redundancy anticipated in the totally symmetric factor is obviously associated with the α- and β-coordinates.

The table of multiplicities and symmetry coefficients is considerably condensed by noting the identical symmetry properties of the coordinates R, α, and β.

The symmetry treatment of the CXY_3 molecule is almost identical when the substitutions r for R and η for β are performed. In addition, however, the matrix element f_α^2 must be replaced by f_α^3, the former involving two $X-C-Y$ bendings with a common Y and the latter two such coordinates with a common X.

The $\mathcal{G}$ matrices for the different factors of the molecules of this class are now given in numerical form:

	A_1 R	A_1 r	A_1 α	E R	E α	E β
CCl₃H:	0.05596	-0.04807	0.04486	0.13922	-0.13016	0.08972
		1.07532	-0.07770		1.40744	-0.10058
			0.08170			0.09553
CCl₃D:	0.05596	-0.04807	0.04486	0.13922	-0.13016	0.08972
		0.57960	-0.07770		0.78502	-0.10058
			0.08170			0.09553
CBr₃H:	0.04027	-0.04807	0.04176	0.12354	-0.12861	0.08352
		1.07532	-0.07233		1.39815	-0.09498
			0.06636			0.07167
CBr₃D:	0.04027	-0.04807	0.04176	0.12354	-0.12861	0.08352
		0.57960	-0.07233		0.77574	-0.09498
			0.06636			0.07167

	A_1 r	A_1 R	A_1 α	E r	E α	E η
CClH₃:	1.01981	-0.04807	0.07182	1.10308	-0.10320	0.14364
		0.11147	-0.12346		0.94016	0.28168
			1.01627			2.26190
CClD₃:	0.52409	-0.04807	0.07182	0.60736	-0.10320	0.14364
		0.11147	-0.12346		0.52521	0.07421
			0.60133			1.22452
CBrH₃:	1.01981	-0.04807	0.07182	1.10308	-0.09855	0.14364
		0.09578	-0.12346		0.92319	0.29770
			1.01627			2.26190
CBrD₃:	0.52409	-0.04807	0.07182	0.60736	-0.09855	0.14364
		0.09578	-0.12346		0.50825	0.08023
			0.60133			1.22452

In tabulating these matrices, columns in the A_1 factor corresponding to a symmetry coordinate of type β in the case of CX_3Y and η in the case of CXY_3 have been omitted since they are exactly the negatives of the columns headed by α. This is evidence of the redundancies

$$\sum_{l=1}^{3} (\alpha_l + \beta_l) = 0 \qquad (10)$$

and

$$\sum_{l=1}^{3} (\alpha_l + \eta_l) = 0 \qquad (11)$$

in CX_3Y and CXY_3, respectively. In such cases it has been shown[3] that a column (and row) of $\mathcal{G}$ involved in the linear dependence may be ignored, provided an appropriate transformation is made upon $\mathcal{F}$, resulting in a reduction of its order by unity.

D. The CX_2Y_2 Molecule

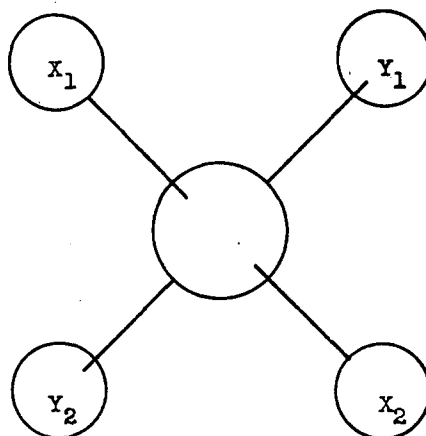Coordinates are numbered in accordance with Fig. 3. Tables VII to IX give the symmetry fac-

FIG. 3. Coordinates for CX_2Y_2. $R_i = \Delta CX_i$, $r_i = \Delta CY_i$, $\alpha_1 = \Delta X_1 C Y_1$, $\alpha_2 = \Delta X_1 C Y_2$, $\alpha_3 = \Delta X_2 C Y_2$, $\alpha_4 = \Delta X_2 C Y_1$, $\beta = \Delta X_1 C X_2$, $\eta = \Delta Y_1 C Y_2$.

toring, based on the assumption of C_{2v} symmetry.

The A_1 factors for these molecules contain redundancies involving symmetry coordinates of types α, β, and η. In this case, the α-column has been omitted in the tabulation:

CCl$_2$H$_2$:

A_1:	R	r	β	η	B_2:	r	α
	0.08371	−0.05551	−0.06344	0.10157		1.10308	−0.06798
		1.04757	0.06344	−0.10157			0.62088
			0.09092	−0.11608	B_1:	R	α
				1.84669		0.13922	−0.18407
A_2:	α						1.55544
	1.25944						

CCl$_2$D$_2$:

A_1:	R	r	β	η	B_2:	r	α
	0.08371	−0.05551	−0.06344	0.10157		0.60736	−0.06798
		0.55185	0.06344	−0.10157			0.41340
			0.09092	−0.11608	B_1:	R	α
				1.01679		0.13922	−0.18407
A_2:	α						0.93302
	0.63702						

CBr$_2$H$_2$:

A_1:	R	r	β	η	B_2:	r	α
	0.06803	−0.05551	−0.05906	0.10157		1.10308	−0.14595
		1.04757	0.05906	−0.10157			0.59546
			0.06990	−0.10805	B_1:	R	α
				1.84669		0.12354	−0.18188
A_2:	α						1.54538
	1.25092						

CBr$_2$D$_2$:

A_1:	R	r	β	η	B_2:	r	α
	0.06803	−0.05551	−0.05906	0.10157		0.60736	−0.14595
		0.55185	0.05906	−0.10157			0.38799
			0.06990	−0.10805	B_1:	R	α
				1.01679		0.12354	−0.18188
A_2:	α						0.92297
	0.62851						

TABLE VI. Multiplicities and symmetry coefficients for the CX_3Y molecule.

	(R, α, β)		$(R, \alpha, \beta)r$	r
	f_R^1	f_R^2	f_{Rr}^1	f_r^1
	$f_{R\alpha}^1$	$f_{R\alpha}^2$		
	$f_{R\beta}^2$	$f_{R\beta}^1$	$f_{r\alpha}^1$	
	f_α^1	f_α^2		
	$f_{\alpha\beta}^2$	$f_{\alpha\beta}^1$	$f_{r\beta}^1$	
	f_β^1	f_β^2		
$\gamma_{ij}{}^m$	1	2	$(3)^{\frac{1}{2}}$	1
A_1	1	1	1	1
E	1	$-\frac{1}{2}$	0	0

IV. CALCULATION OF FORCE CONSTANTS

At this point it becomes essential to simplify the calculations by making some reasonable assumptions which will eliminate many of the 53 force constants which have been defined in Part III. The remarkable constancy of hydrogen-carbon stretching frequencies suggests putting all interaction constants involving this coordinate (r) equal to zero. Moreover, the large separation of such frequencies ($\sim$3000 cm^{-1}) from the remaining ones ($<$1500 cm^{-1}) justifies an approximation of practical importance; such frequencies may be factored using the method described by Wilson.[3] A further approximation is made by similarly assuming that all interaction constants involving the hydrogen-carbon-hydrogen coordinate (η) vanish. Finally, it has been quite arbitrarily assumed that all interactions between the angular coordinates α and β (hydrogen-carbon-halogen and halogen-carbon-halogen) can be put equal to zero, although a few

TABLE VII. Characters and frequency distribution for CX_2Y_2.

C_{2v}	E	C_2	σ_v	$\sigma_{v'}$	n_R	n_r	n_α	n_β	n_η	n'	n	Selection rule
A_1	1	1	1	1	1	1	1	1	1	1	4	$IR, R(p)$
B_2	1	-1	-1	1	0	1	1	0	0	0	2	$IR, R(d)$
A_2	1	1	-1	-1	0	0	1	0	0	0	1	$R(d)$
B_1	1	-1	1	-1	1	0	1	0	0	0	2	$IR, R(d)$
χ^R	2	0	2	0								
χ^r	2	0	0	2								
χ^α	4	0	0	0								
χ^β	1	1	1	1								
χ^η	1	1	1	1								
χ'	1	1	1	1								
χ	9	1	3	3								

small interaction terms of the types $\alpha\alpha$ and $\beta\beta$ have been retained.

After making these assumptions, only 28 non-vanishing constants are left to be dealt with; 100 distinct fundamental vibration frequencies are to be calculated, of which 82 have actually been observed. The actual process used in determining the force constants consisted first in selecting numerical values for combinations of the constants appearing in secular determinants of order unity which fit the corresponding observed frequencies.‡‡ Utilization of the approximate factoring of the $(C-Y)$ stretching frequency gives, in all, 32 separate relations from which the force constants given in Table X have been determined.

Following these calculations, the second order determinants of the CXY_3 molecule were next investigated, and the resulting constants, which differ only very slightly, owing to a slight change

TABLE VIII. Force constants for the CX_2Y_2 molecule.

	R		r		α				β	η
	1	2	1	2	1	2	3	4		
R	f_R^1	f_R^2	f_{Rr}^1	f_{Rr}^1	$f_{R\alpha}^1$	$f_{R\alpha}^1$	$f_{R\alpha}^2$	$f_{R\alpha}^2$	$f_{R\beta}^1$	$f_{R\eta}^1$
r			f_r^1	f_r^2	$f_{r\alpha}^1$	$f_{r\alpha}^2$	$f_{r\alpha}^2$	$f_{r\alpha}^1$	$f_{r\beta}^1$	$f_{r\eta}^1$
α					f_α^1	f_α^3	f_α^4	f_α^2	$f_{\alpha\beta}^1$	$f_{\alpha\eta}^1$
β									f_β^1	$f_{\beta\eta}^1$
η										f_η^1

in the inverse kinetic energy matrix elements, from a similar treatment previously given by Noether[6] are given in Table XI.

The values of $f_\alpha^1 - f_\alpha^3$ and f_η^1 are in reasonable agreement with the values given in parentheses which may be obtained from Table X.

There are now sufficient data to compute the individual values of the following force constants: f_R^1, f_R^2, $f_{R\alpha}^1$, f_r^1, f_α^1, f_α^2, f_α^3, f_α^4, and f_η^1. By inserting numerical values of f_R^1, f_R^2 in the F_2 factor for CX_4, the A_1 factor of CX_3Y, and the B_1 factor of CX_2Y_2, six additional linear combinations of constants may be computed for each value of $X = $ Cl and $X = $ Br. After such a calculation, all the force constants assumed to be non-vanishing can be individually determined. As a matter of fact, there exist at this point several

‡‡ The experimental frequencies used for these calculations are given later in Table XIII.
[6] H. D. Noether, J. Chem. Phys. **10**, 664 (1942).

TABLE IX. Multiplicities and symmetry coefficients for CX_2Y_2.

	R f_{R^1} f_{R^2}	Rr f_{Rr^1}	$R\alpha$ $f_{R\alpha^1}$ $f_{R\alpha^2}$	$R(\beta, \eta)$ $f_{R\beta^1}$ $f_{R\eta^1}$	r f_{r^1} f_{r^2}	$r\alpha$ $f_{r\alpha^1}$ $f_{r\alpha^2}$
$\gamma_{ij}{}^m$	1 1	2	(2)$^{\frac{1}{2}}$ (2)$^{\frac{1}{2}}$	(2)$^{\frac{1}{2}}$	1 1	(2)$^{\frac{1}{2}}$ (2)$^{\frac{1}{2}}$
A_1	1 1	1	1 1	1	1 1	1 1
B_2	0 0	0	0 0	0	1 −1	1 −1
A_2	0 0	0	0 0	0	0 0	0 0
B_1	1 −1	0	1 −1	0	0 0	0 0

	$r(\beta, \eta)$ $f_{r\beta^1}$ $f_{r\eta^1}$	α f_{α^1} f_{α^3} f_{α^4} f_{α^2}	$\alpha(\beta, \eta)$ $f_{\alpha\beta^1}$ $f_{\alpha\eta^1}$	β, η f_{β^1} $f_{\beta\eta^1}$ f_{η^1}
$\gamma_{ij}{}^m$	(2)$^{\frac{1}{2}}$	1 1 1 1	2	1
A_1	1	1 1 1 1	1	1
B_2	0	1 −1 −1 1	0	0
A_2	0	1 −1 1 −1	0	0
B_1	0	1 1 −1 −1	0	0

checks involving the constants which do not give quite consistent results, but by taking slightly adjusted values, the final numerical results are obtained in Table XII.

The following constants have been put equal to zero: f_{Rr^1}, $f_{R\eta^1}$; f_r^2, $f_{r\alpha^1}$, $f_{r\alpha^2}$, $f_{r\beta^1}$, $f_{r\eta^1}$, and $f_{r\eta^2}$; $f_{\alpha\beta^1}$, $f_{\alpha\beta^2}$, $f_{\alpha\eta^1}$, $f_{\alpha\eta^2}$; $f_{\beta\eta^2}$; f_η^2, and f_η^3.

The relative smallness of the interaction constants involving two bending coordinates suggests that most such constants could have been omitted without impairing the quality of the fit and helps to justify the arbitrary omission of many constants of similar type. On the other hand, the interaction constants between carbon-halogen stretching and the lower frequency bending coordinates ($R\alpha$ and $R\beta$) are relatively large and undoubtedly have real physical significance.

TABLE X. Force constants calculated from one-dimensional factors of the methane derivatives.

	$X = Cl$	$X = Br$
f_r^{1a}	5.04±0.02^b	
f_η^1	0.523±0.01^c	
$f_{R^1}+3f_{R^2}$	4.379	3.397
$f_{\beta^1}-2f_{\beta^3}+f_{\beta^2}$	1.013	0.8324
$f_{\alpha^1}-f_{\alpha^3}-f_{\alpha^4}+f_{\alpha^2}$	0.7719	0.6707
$f_{\alpha^1}-f_{\alpha^3}+f_{\alpha^4}-f_{\alpha^2}$	0.6239	0.5594

[a] Here and throughout this paper the units of the force constants are 10^5 dyne cm^{-1}, for two stretching coordinates, 10^{-3} dyne for one stretching and one bending coordinate, and 10^{-11} dyne cm for two bending coordinates.
[b] Average and standard deviation for 20 separate calculations; C—H and C—D results, which show a real difference due to anharmonicity, have been averaged together.
[c] Average and standard deviation for 4 separate calculations.

TABLE XI. Force constants for the CXY_3 molecule.

	$X = Cl$		$X = Br$	
f_{R^1}	3.383		2.840	
$f_{R\alpha^1}$	0.3401		0.3045	
$f_{\alpha^1}+f_\eta^1+2f_{\alpha^3}$	1.156		1.0711	
$f_{\alpha^1}-f_{\alpha^3}$	0.721	(0.698)	0.6393	(0.615)
f_η^1	0.538	(0.523)	0.5351	(0.523)

Table XII shows comparable force constants computed by Stepanov[6a] who reported values not only for the bromine and chlorine derivatives, but also for the fluorine derivatives of this same series. It is noteworthy that these values are, on the whole, in good agreement, the present author having been unaware of the work of Stepanov at the time he undertook these calculations. In particular, the calculations are based upon the same assignments for the CX_2Y_2 molecule, about which there has been some controversy. The principal differences in the numerical values are to be attributed to varying assumptions about negligible constants, Stepanov having chosen to ignore the class of interaction constants involving:

(i) Bond stretching with a bending having neither bond in common with the stretching.
(ii) Bond bendings having no bonds in common. This accounts for Stepanov's zeros for $f_{R\alpha^2}$, $f_{R\beta^2}$, f_{α^4}, and f_{β^3}.

On the other hand, Stepanov found finite, although, for the most part, relatively small values

TABLE XII. Force constants for chloro- and bromomethanes.

	$X = Cl$		$X = Br$	
f_{R^1}	3.383	3.533^a	2.840	2.856^a
f_{R^2}	0.332	0.265	0.186	0.147
$f_{R\alpha^1}$	0.340	0.588	0.305	0.492
$f_{R\alpha^2}$	−0.164	0	−0.152	0
$f_{R\beta^1}$	0.338	0.661	0.342	0.568
$f_{R\beta^2}$	−0.249	0	−0.190	0
f_r^1	5.04	5.023	5.04	5.023
f_{α^1}	0.687	0.777	0.589	0.673
f_{α^2}	0.009	0.115	−0.005	0.084
f_{α^3}	−0.034	0.056	−0.026	0.042
f_{α^4}	−0.065	0	−0.060	0
f_{β^1}	1.136	1.133	1.061	0.937
f_{β^2}	0.092	0.098	0.134	0.067
f_{β^3}	−0.037	0	0.039	0
f_η^1	0.530	0.525	0.530	0.525

[a] These values have been obtained by averaging the results in reference 6a.

[6a] B. Stepanov, Acta Physicochimica 20, 174 (1945).

TABLE XIII. Comparison of calculated and observed frequencies: chloro- and bromomethanes; methane and deuteromethane.

Molecule	Irr. Rep. Type of Coord.		$X = Cl$ $\tilde{\nu}_{calc.}$ (cm⁻¹)	$\tilde{\nu}_{exp.}$ (cm⁻¹)	Δ (%)	$X = Br$ $\tilde{\nu}_{calc.}$ (cm⁻¹)	$\tilde{\nu}_{exp.}$ (cm⁻¹)	Δ (%)
CX_4	A_1	R	458	458	0.0	269	269	0.0
	E	β	218	218	0.0	123	123	0.0
	F_2	R	785	785	0.0	672	672	0.0
		β	314	314	0.0	183	183	0.0

Molecule	Irr. Rep. Type of Coord.		$Y=H$ $\tilde{\nu}_{calc.}$ (cm⁻¹)	$\tilde{\nu}_{exp.}$ (cm⁻¹)	Δ (%)	$Y=D$ $\tilde{\nu}_{calc.}$ (cm⁻¹)	$\tilde{\nu}_{exp.}$ (cm⁻¹)	Δ (%)	$Y=H$ $\tilde{\nu}_{calc.}$ (cm⁻¹)	$\tilde{\nu}_{exp.}$ (cm⁻¹)	Δ (%)	$Y=D$ $\tilde{\nu}_{calc.}$ (cm⁻¹)	$\tilde{\nu}_{exp.}$ (cm⁻¹)	Δ (%)
				$X=Cl$						$X=Br$				
CX_3Y	A_1	r	3040	3030	+0.3	2240	2257	−0.7	3037	3023	+0.5	2237	2247	−0.4
		R	677	672	+0.7	656	655	+0.2	541	539	+0.4	522	519	+0.6
		$\beta(\alpha)$	354	363	−2.5	352	364	−3.3	223	222	+0.5	223	222	+0.5
	E	α	1221	1217	+0.3	887	908	−2.3	1137	1142	−0.4	820	848	−3.3
		R	744	760	−2.1	736	738	−0.3	645	656	−0.7	637	629	+1.3
		β	258	261	−1.1	257	262	−1.9	154	154	0.0	154	153	+0.6
CX_2Y_2	A_1	r	2993	2984	+0.3	2174			2993	2988	+0.2	2174		
		$\eta(\alpha)$	1437	1423	+1.0	1064			1413	1388	+1.8	1043		
		R	710	702	+1.1	674			578	576	+0.3	545		
		$\beta(\alpha)$	288	283	+1.8	286			180	174	+3.4	179		
	B_2	r	3073	3048	+0.8	2283			3078	3061	+0.6	2281		
		α	902	899	+0.3	731			809	810	−0.1	665		
	A_2	α	1177	1155	+1.9	836			1091	1090	+0.1	773		
	B_1	α	1267	1266	+0.1	936			1183	1183	0.0	870		
		R	737	737	0.0	723			638	637	+0.2	621		
CXY_3	A_1	r	2958	2928	+1.0	2127	2136	−0.4	2958	2932	+0.9	2126	2134	−0.4
		$\eta(\alpha)$	1350	1355	−0.4	1024	1029	−0.5	1301	1305	−0.3	984	987	−0.3
		R	733	732	+0.1	693	695	−0.3	613	610	+0.5	573	577	−0.7
	E	r	3078	3047	+1.0	2294	2287	+0.3	3080	3061	+0.6	2293	2294	0.0
		η	1455	1460	−0.3	1044	1058	−1.3	1446	1450	−0.3	1041	1053	−1.1
		α	1020	1020	0.0	771	775	−0.5	938	957	−2.0	703	717	−2.0

Molecule	Irr. Rep. Type of Coord.		$Y=H$ $\tilde{\nu}_{calc.}$ (cm⁻¹)	$\tilde{\nu}_{exp.}$ (cm⁻¹)	Δ (%)	$Y=D$ $\tilde{\nu}_{calc.}$ (cm⁻¹)	$\tilde{\nu}_{exp.}$ (cm⁻¹)	Δ (%)
CY_4	A_1	r	2914	2914	0.0	2062	2085	−1.1
	E	η	1498	1499	−0.1	1059	1054	+0.4
	F_2	r	3080	3020	+2.0	2297	2258	+1.7
		η	1337	1306	+2.4	1003	996	+0.7

for some of the constants which have been ignored by the present author, namely: $f_{Rr}{}^1 = 0.088$, 0.059; $f_r{}^2 = 0.029$, 0.029; $f_{r\alpha}{}^1 = 0.364$, 0.310; $f_{r\eta}{}^1 = 0.225$, 0.225; $f_{\alpha\beta}{}^1 = 0.063$, 0.056; $f_{\alpha\eta}{}^1 = 0.042$, 0.042; $f_\eta{}^2 = -0.024$, -0.024; the numerical values being cited for chlorides and bromides in that order.

There seems to be little physical ground for a choice between these sets of parameters at present, because the wider range of Stepanov's calculations, including the other halides (and refer-ences to a notable series of calculations for various hydrocarbons) are in part compensated by the application of the present calculations to the deuterium analogues which were not considered in Stepanov's paper.

Finally, Table XIII gives a direct comparison between calculated and experimental frequencies.

The authors from whose work the experimental frequencies have been taken are as follows: CCl₄, CBr₄, CH₄, and CD₄, Langseth[7] and data cited

[7] A. Langseth, Zeits. f. Physik 72, 350 (1931).

by Herzberg;[8] CCl₃H, Nielsen and Ward;[9] CCl₃D, Wood and Rank;[10] CBr₃H and CBr₃D, Redlich and Stricks,[11] Barchewitz and Parodi;[12] CClH₃, Bennett and Meyer;[13] CClD₃, Noether;[6] CBrH₃, Barker and Plyler;[14] CBrD₃, Noether;[6] CCl₂H₂, Corin and Sutherland,[15] Wagner;[16] CBr₂H₂, Wagner,[16] Delwaulle.[17]

All the frequencies were recalculated using the slightly adjusted values of the constants given in Table XII, the approximate factoring of the $C-Y$ stretching modes not being used except in

the case of the A_1 factor of CX_2Y_2. Naturally, the fit is somewhat better in the simpler factors, such as those of CX_4, from which the constants were more or less directly determined. Good confirmation of the assumed potential functions is found, however, in the comparison of the calculations with observed values for the E factor of CX_3Y and the A_1 factor of CX_2Y_2 which were not used in obtaining the force constants; these frequencies are underlined in the table. For the 82 frequencies for which experimental data were available, the root mean square difference between calculation and observation is 1.1 percent.

It must be remembered, however, that the assignment of the fundamentals for the methylene halides is not certain. Spectroscopic data for the deutero-methylene halides would provide an interesting test of the potential functions which have been developed here.

ACKNOWLEDGMENT

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The Fluorescence of Solid Acetone*

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IT has been known for some time that acetone vapor, illuminated by wave-length 3130A, shows a weak blue fluorescence spectrum.[1,2] It occurred to us that the fluorescence should be intensified in the solid state at 83°K, both because of increased density and reduced number of collisions. This intensification has been found. We find this fluorescence also in a rigid solvent (isopentane, ether, and ethyl alcohol) at 83°K.[3]

The fluorescence spectrum consists of a broad band, beginning at about 4000A and extending to about 5000A, with a broad maximum at approximately 4556A. The spectrum shows no resolved structure at dispersions of 150A per mm and at 16A per mm. Methyl ethyl and diethyl ketones were examined under the same conditions, and show similar short- and long-wave limits, with intensity maxima at 4675 and 4707, respectively. The latter ketones were photographed only at the lower dispersion. No indication of the well-known fluorescence of biacetyl was obtained in any of these cases.

The absorption level of acetone[4] in the vapor

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