would be about 3.0 debye. This primary component evidently is mostly canceled by the large, oppositely-directed atomic hybridization moment of the apex oxygen. If we subtract the observed moment from the primary moment, an approximate value for the atomic

moment, 2.5 debye, is obtained. This value is not unreasonable, considering the one unbalanced electron in the sp^2 orbital directed along the symmetry axis. However, hybridization in the end oxygens, which is neglected, may be important.

The Vibration Frequencies of the Halogenated Methanes and the Substitution Product Rule*

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The extension of the Teller-Redlich product rule to the substitution of different atoms or groups, which was previously applied to the methyl benzenes, is here applied to the halogenated methanes. The rule is found to hold accurately enough to be useful in assigning fundamental frequencies or in computing unobserved fundamentals.

SEVERAL years ago Pitzer and Scott extended the Teller-Redlich product rule to the substitution of methyl groups for hydrogen atoms in certain hydrocarbons.[1] Similar extensions of the isotopic product rule have been made by others.[2] The present paper presents the results of applying the substitution product rule to the halogen derivatives of methane.

The recent force constant-frequency calculations of Stepanov,[3] Decius,[4] Pace,[5] and others[6-8] yield more detailed information on these simple compounds. The application of these force constants to more complex molecules would give, in principle, the desired guidance to spectral assignments. However, normal coordinate calculations become very laborious for larger molecules of low symmetry. Consequently, while the product rule yields less information, its ease of application makes it particularly valuable. This will be illustrated with some methane derivatives of low symmetry in the present paper.

In the earlier paper the product ratio τ was defined as

$$\tau = \prod_i \left(\frac{\nu_i'}{\nu_i}\right) \left[\prod_j \left(\frac{I_j}{I_j'}\right) \prod_k \left(\frac{M_k}{M_k'}\right)\right]^{\frac{1}{2}}, \qquad (1)$$

where the prime mark indicates the substituted mole-

cule and where the indices i, j, and k cover all the vibrations, rotations, and translations, respectively, of a given symmetry type. The other symbols ν, I, and M refer to vibration frequencies, moments of inertia, and molecular masses, respectively.

An examination of normal coordinate theory shows that in every case τ will be given by a product of mass and bond distance ratios and a ratio of force constants. In isotopic substitution one assumes no change in bond distances or force constants, hence the factors depending on these quantities are unity. Then it is customary to combine the mass ratio with the terms in square brackets in Eq. (1) so as to yield a theoretical value for the ratio of frequencies.

However, the substitution of new atoms changes bond distances and force constants as well as masses. Thus, a reliable theoretical value of τ is not available. It seems best to combine all of the observable quantities in the form of Eq. (1), so that the τ-values for similar substitutions will be comparable. Furthermore, the theory does not indicate exactly the same τ-value for all examples of a given substitution. The cross terms in the potential expression enter in different ways. Also the distances and principal force constants for a given bond may vary slightly from one molecule to another. Consequently, we do not expect exact constancy of these substitution product ratios but rather will wish to see whether the variation is small enough to make them useful. The vibration frequency assignments for CH_4, CH_3F, CH_3Cl, CH_3Br, CH_2F_2, CH_2Cl_2, CH_2Br_2, CHF_3, $CHCl_3$, $CHBr_3$, CF_4, CCl_4, CBr_4, CF_3Cl, CF_2Cl_2, $CFCl_3$, CF_3Br, CF_2Br_2, $CFBr_3$, CCl_3Br, CCl_2Br_2, and $CClBr_3$ seem sufficiently reliable to be used in the determination of the τ-values and their constancy.

The experimental frequency values adopted in the

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[1] K. S. Pitzer and D. W. Scott, J. Am. Chem. Soc. **65**, 803 (1943).

[2] See, for example, Mizushima, Morino, and Shimanouchi, Sci. Papers Inst. Phys. Chem. Research (Tokyo) **40**, 87 (1942).

[3] B. Stepanov, Acta Physicochim. U.R.S.S. **20**, 174 (1945).

[4] J. C. Decius, J. Chem. Phys. **16**, 214 (1948).

[5] E. L. Pace, J. Chem. Phys. **18**, 881 (1950).

[6] Meister, Rosser, and Cleveland, J. Chem. Phys. **18**, 346 (1950).

[7] Zietlow, Cleveland, and Meister, J. Chem. Phys. **18**, 1076 (1950).

[8] E. K. Plyler and W. S Benedict, J. Research Natl. Bur. Standards **47**, 202 (1951).

TABLE I. Product ratios for the substitution of Y for X.

Compounds	Sym. type	F for H	Cl for F	Br for Cl
(Examples with one stretching motion)				
CX_4, CY_4	A_1	0.31	0.51	0.59
CH_3X, CH_3Y	A_1	0.27	0.52	0.59
CF_3X, CF_3Y	A_1	0.27	0.53	0.59
CCl_3X, CCl_3Y	A_1	0.25	0.53	0.58
CBr_3X, CBr_3Y	A_1	0.25	0.55	0.58
average for one stretching		0.27	0.53	0.58
(Examples with one bending motion)				
CX_4, CY_4	E	0.29	0.50	0.56
CH_3X, CH_3Y	E	0.25	0.53	0.54
CF_3X, CF_3Y	E	0.29	0.48	0.56
CCl_3X, CCl_3Y	E	0.27	0.53	0.59
CBr_3X, CBr_3Y	E	0.26	0.52	0.59
CH_2X_2, CH_2Y_2	A_2	0.22	0.51	0.59
CF_2X_2, CF_2Y_2	A_2	0.25	0.50	0.59
CCl_2X_2, CCl_2Y_2	A_2	0.25	0.56	0.58
CBr_2X_2, CBr_2Y_2	A_2	0.25	0.56	0.58
CH_2X_2, CH_2Y_2	B_1	0.28	0.48	0.59
CF_2X_2, CF_2Y_2	B_1	0.31	0.50	0.52
CCl_2X_2, CCl_2Y_2	B_1	0.31	0.49	0.59
CBr_2X_2, CBr_2Y_2	B_1	0.30	0.49	0.59
average for one bending		0.27	0.51	0.58
(Examples with one stretching and one bending motion)				
CX_4, CY_4	T_2	0.086	0.23	0.34
CHX_3, CHY_3	A_1	0.102	0.23	0.34
CFX_3, CFY_3	A_1	0.098	0.22	0.33
$CClX_3$, $CClY_3$	A_1	0.099	0.23	0.34
$CBrX_3$, $CBrY_3$	A_1	0.099	0.22	0.34
CH_2X_2, CH_2Y_2	A_1	0.085	0.25	0.34
CF_2X_2, CF_2Y_2	A_1	0.093	0.24	0.33
CCl_2X_2, CCl_2Y_2	A_1	0.087	0.25	0.33
CBr_2X_2, CBr_2Y_2	A_1	0.083	0.26	0.34
CH_2X_2, CH_2Y_2	B_2	0.054	0.27	0.36
CF_2X_2, CF_2Y_2	B_2	0.058	0.27	0.34
CCl_2X_2, CCl_2Y_2	B_2	0.060	0.26	0.35
CBr_2X_2, CBr_2Y_2	B_2	0.054	0.29	0.36
av for 1 stretching and 1 bending		0.082	0.25	0.34
(av stretching)×(av bending)		0.073	0.27	0.34
(Examples with one stretching and two bending motions)				
CHX_3, CHY_3	E	0.016	0.13	0.20
CFX_3, CFY_3	E	0.019	0.12	0.20
$CClX_3$, $CClY_3$	E	0.017	0.13	0.20
$CBrX_3$, $CBrY_3$	E	0.018	0.14	0.20
av for 1 stretching and 2 bendings		0.017	0.13	0.20
(av stretching)×(av bending)^2		0.020	0.14	0.20

TABLE II. Spectral assignments and product ratios for CX_2YZ molecules. (Revised assignments marked r.)

Molecule	CH_2FCl[9]	CH_2FBr[10]	CH_2ClBr[8]	CF_2HCl[8]
A'	2993	2993	2987	3023
	1470	1461	1402	1311
	1351	1313(r)	1225	1178
	1068	1050	728	809
	760	630	606	595
	385	314	226	422
A''	3048	3053	3060	1347
	1236	1227	1130	1116
	1004	940(r)	852	365
Mole wt	68.5	113.0	129.4	86.5
$I_x \times 10^{39}$	16.1	23.3	40.5	17.2
$I_xI_y \times 10^{78}$	29.3	45.3	112.0	200.0
Reference	CH_2F_2	CH_2F_2	CH_2Cl_2	CF_3H
Ratio (obs) A' expected	0.26 / 0.27	0.078 / 0.092	0.35 / 0.34	0.27 / 0.27
Ratio (obs) A'' expected	0.49 / 0.51	0.28 / 0.30	0.59 / 0.58	0.50 / 0.51

Molecule	CF_2HBr[12]	CF_2BrCl[12]	CCl_2HF[8]	CCl_2HBr[8]
A'	3003	1102	3023	3040
	1280	872	1304	1168
	1135	648	1079	719
	718	(400)	742	604
	576	(380)	458	330
	(380)calc	(200)	276	220
A''	1344	1150	1242	1211
	1108	440	804	760
	323	300	368	215
Mole wt	130.9	165.4	102.9	163.9
$I_x \times 10^{39}$	28.2	56.0	12.2	44.4
$I_xI_y \times 10^{78}$	291.5	1085	890	1690
Reference	CF_3H	CF_3Cl	CH_2Cl_2	$CHCl_3$
Ratio (obs) A' expected	0.097 / 0.092	0.081 / 0.092	0.066 / 0.073	0.34 / 0.34
Ratio (obs) A'' expected	0.28 / 0.30	0.31 / 0.30	0.27 / 0.27	0.60 / 0.58

Molecule	CCl_2FBr[10]	CBr_2HF[10]	CBr_2HCl[8]	CBr_2FCl[10]
A'	1069	3015	3034	1063
	779(r)	1295(r)	1189	802
	501	1063	746	462
	334	620	570	340(r)
	303(r)	358(r)	278	267(r)
	215	171	168	160
A''	825(r)	1170(r)	1144	741
	390	704	657	306(r)
	203(r)	295(r)	201	195(r)
Mole wt	181.9	191.9	208.3	226.3
$I_x \times 10^{39}$	54.8	14.9	32.2	42.7
$I_xI_y \times 10^{78}$	2380	5370	6550	7540
Reference	CCl_2HBr	CBr_2H_2	CBr_2H_2	CBr_2HCl
Ratio (obs) A' expected	0.077 / 0.073	0.064 / 0.073	0.018 / 0.020	0.063 / 0.073
Ratio (obs) A'' expected	0.27 / 0.27	0.26 / 0.27	0.14 / 0.14	0.27 / 0.27

force constant treatments mentioned above are used in the present calculations, the latest vapor phase data being employed where available.

We accept the recent assignment for CF_3Br.[9] The general assignment for CCl_2Br_2 given by Plyler and Benedict is correct, but we have substituted the more precise Raman frequencies listed in the *Landolt-Börnstein Tabellen*.[10] This involves the interchange of the 174 and 230 cm^{-1} frequencies in the Landolt-Börnstein assignment. The new assignment for CF_2Cl_2[8] must replace that of Thompson and Temple,[11] whose assignments for CF_3Cl and $CFCl_3$ are accepted, however.

The moments of inertia were obtained from various sources in the literature or calculated from the appropriate bond distances and angles. Values are quoted in g-cm^2 units. Since these values contribute little uncertainty, they will not be discussed in detail.

Table I contains the calculated product ratios for the compounds listed above. For a single motion the average deviation from the mean is about 8 percent for

[9] W. F. Edgell and C. E. May, J. Chem. Phys. **20**, 1822 (1952).
[10] *Landolt-Bornstein Tabellen* (Verlag Julius Springer, Berlin, 1951), Sixth Edition, Vol. I, parts 2 and 3.

[11] H. W. Thompson and R. B. Temple, J. Chem. Soc. **90**, 1422 (1948).

the substitution of F for H but only about 3 percent for the substitution of one halogen for another. Where more than one motion is involved one would expect the variation to be greater. This is found particularly in the case of one bending and one stretching motion with substitution of F for H. Here we find examples equivalent to the combination of the extreme ratios for the single component motions. It may be noted, however, that for a given symmetry type a higher degree of constancy obtains for each type of motion. Also it appears that the ratios for the substitution of Cl for H would be more nearly constant than those for F for H. This is readily verified by observing that the higher values of τ for F for H substitution are followed by relatively low values for Cl for F substitution. It may be seen from Table I that the average product ratios for two or more motions closely approximate the product of the averages for the single component motions. We believe the agreement found in Table I is good enough to allow the method to be used in interpreting other spectra.

The assignments for the CX_2YZ molecules are given in Table II. The frequencies are in cm^{-1} and the moments of inertia in $g\text{-}cm^2$ units. All possible molecules of this type (with H, F, Cl, or Br) are included. A number of the assignments given in the *Landolt-Börnstein Tabellen*[10] are inconsistent with the polarization of the Raman bands. The present assignments have removed all these inconsistencies. No changes were required in the assignments of Plyler and Benedict[8] or of Plyler and Acquista.[12] For the four molecules not investigated by Plyler, revision of the previous assignments was necessary. In one case a single pair of frequencies was interchanged as indicated by (r), and in the other three cases two pairs of frequencies were interchanged in order to obtain satisfactory agreement with the τ-values and the polarization data. For CF_2HBr one frequency was not observed, but the value calculated by Stepanov appears to be quite satisfactory. The three lowest frequencies of A' symmetry in CF_2BrCl were estimated from combination and overtone bands.[12]

The completely unsymmetrical compound CHFClBr has been studied recently,[13] the observed frequencies and other relevant data being given in Table III. The agreement between observed and expected product ratios is very satisfactory.

TABLE III. Spectral frequencies and product ratio for CHFClBr[13].

Frequencies	3023, 1299, 1202, 1060, 772, 655, 426, 313, 220 cm^{-1}
Mole wt	147.4
$I_1I_2I_3 \times 10^{11}$	26800
Reference	$CHFCl_2$
Ratio (obs)	0 194
expected	0.20

[12] E. K. Plyler and N. Acquista, J. Research Natl. Bur. Standards 48, 92 (1952).
[13] E. K. Plyler and M. A. Lamb, J. Research Natl. Bur. Standards 46, 382 (1951).

TABLE IV. Spectral assignments and product ratios for iodomethanes. (Revised assignments marked r.)

Molecule	CH₃I[10]		CF₃I[9]		CH₂I₂[10]	
		2950		1073		2970
	A_1	1240	A_1	740	A_1	1348
		525		265(r)		485
						120
		3050		1185	A_2	1103(r)
	E	1420	E	540		
		890		286(r)	B_1	3050
						714(r)
					B_2	1028(r)
						567
Mole wt		142.0		195.9		267.9
$I \times 10^{39}$		$I_A = 0.55$		$I_A = 14.8$		$I_z = 131.2$
		$I_B = 10.0$		$I_B = 55.1$		$I_y = 3.20$
						$I_x = 135.5$
Reference		CH₃Br		CF₃Br		CH₂Br₂
Ratio (obs)	(A_1)	0.67	(A_1)	0.63	(A_1)	0.47
expected				0.67		0.47
Ratio (obs)	(E)	0.70	(E)	0.67	(B_2)	0.47
expected				0.70		0.47
Ratio (obs)					(A_2)	0.72
expected						0.70
Ratio (obs)					(B_1)	0.69
expected						0.70

Molecule	CH₂BrI[10]		CH₂ClI[10]	
		2978		2978
		1374		1392
	A'	1065(r)	A'	1126(r)
		616		718
		517		527
		144		194
		3053		3048
	A''	1150	A''	1183
		754(r)		801(r)
Mole wt		220 9		176.4
$I \times 10^{39}$		$I_z = 92.5$		$I_z = 51.9$
		$I_zI_y = 336$		$I_zI_y = 170$
Reference		CH₂Br₂		CH₂Cl₂
Ratio (obs)	(A')	0.45	(A')	0.15
expected		0 47		0.16
Ratio (obs)	(A'')	0.68	(A'')	0.40
expected		0.70		0.41

We find throughout Tables II and III that the τ values agree within a few percent with the relevant average τ-values from Table I.

The data for iodine compounds are generally less extensive or certain than those considered heretofore. The values available are included in Table IV. As before, the symbol (r) indicates a rearrangement of fundamental frequencies from an earlier assignment.

The reversal of the assignment of the two lowest frequencies of CF_3I is suggested by the product ratios. In the absence of polarization data and in view of the proximity of the two frequencies, this new assignment cannot be considered certain.

As we stated above, it is not possible to calculate reliable theoretical values for these ratios unless the detailed potential systems are known for each molecule. However, we may indicate the form that the ratios

TABLE V. Comparison of observed and calculated product ratios.

Substitution	F for H	Cl for F	Br for Cl	I for Br
Stretching				
Calc for no change in potential constant	0.23	0.73	0.67	0 79
Calc with average potential constant	0.26	0.54	0.61	0.69
Average obs	0.27	0.53	0.58	0.67
Bending				
Calc for no change in potential constant	0.19	0.57	0.61	0.72
Calc with average potential constant	0.33	0.50	0.58	...
Average obs	0.27	0.51	0.58	0.70

take when a simple valence potential system is assumed with no off-diagonal terms. Also we assume that the substitution concerns a terminal atom, i.e., one connected to the rest of the molecule by just one bond. We obtain from the usual theory

$$\tau \text{ (theory, stretching)} = \left(\frac{m}{m'}\right)^{\frac{1}{2}}\left(\frac{k'_{\text{str}}}{k_{\text{str.}}}\right)^{\frac{1}{2}}, \quad (2)$$

$$\tau \text{ (theory, bending)} = \frac{d}{d'}\left(\frac{m}{m'}\right)^{\frac{1}{2}}\left(\frac{k'_{\text{bend.}}}{k_{\text{bend.}}}\right)^{\frac{1}{2}}. \quad (3)$$

Here the primed quantities refer in each case to the substituted molecule, and d, k, and m refer to the bond distance, potential constant, and atomic mass, respectively. It is of interest to compare the observed average product ratios with those calculated from the above equations. The stretching force constants given by Pace[5] are used together with a value of 2.20×10^{-5} dyne/cm for the carbon-iodine stretching constant. The appropriate $X-C-Y$ bending constants, averaged over all types of substitution shown in Table I, are taken from the above-mentioned force-constant treatments.[4-8]

Table V gives these calculated product ratios together with the observed average values. The theoretical product ratios with the potential constants k' and k equal in each case are also listed for comparison.

The agreement between observed and calculated product ratios is very satisfactory. In connection with the averaged product ratios for the bending motions in the substitution of fluorine for hydrogen it must be remembered that there is a considerable variation with symmetry type in the relevant product ratios of Table I.

The observed τ-values are practically identical for both bending and stretching motion. This leads to an interesting relationship between force constants and bond distances

$$d\left(\frac{k_{\text{str}}}{k_{\text{bend}}}\right)^{\frac{1}{2}} \cong d'\left(\frac{k'_{\text{str}}}{k'_{\text{bend.}}}\right)^{\frac{1}{2}}. \quad (4)$$

This relationship would appear to hold within about 4 percent, so far as the observed product ratios are concerned. Since the use of the principal force constants of Decius and Pace gives more variation when substituted into Eq. (4), it is apparent that the off-diagonal potential terms must play a role in the close agreement found above.

CONCLUSIONS

We believe the tables presented above illustrate the value of the substitution product rule for halogen derivatives of hydrocarbons. This principle makes it possible to check an assignment or to calculate a single missing frequency with much less labor than that required for a force constant—normal coordinate treatment.

We intend to use these assignments as a basis for calculating the thermodynamic properties of the halogenated methanes. We are also continuing to apply the substitution product rule to halogen derivatives of higher hydrocarbons.