calculated moments, of *o*-chlorotoluene indicates that the "ortho" effect, which is usually ascribed to mutual induction, is absent or at least too small to be detected by dipole moment measurements in this compound.

The dipole moment of 3,3,3-trifluoropropene, 2.45, is intermediate in value between the vapor moment of benzotrifluoride, 2.86, and the moment, 2.36, of trifluoromethylacetylene,[14] determined from microwave spectra. It is interesting to note that the moment of the acetylenic compound containing the trifluoromethyl group is close to the vapor dipole moment, 2.34, of 1,1,1-trifluoroethane.

[14] J. N. Shoolery, R. G. Shulman, W. F. Sheehan, Jr., V. Schomaker and D. M. Yost, *J. Chem. Phys.*, **19**, 1364 (1951).

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[CONTRIBUTION FROM ARTHUR D. LITTLE, INC.]

An Assignment of Frequencies for the Methyl Halomethanes and Silanes $(CH_3)XY_3$, $(CH_3)_2XY_2$ and $(CH_3)_3XY$

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Complete assignments of frequencies based on spectroscopic data found in the literature are given for thirteen methyl halomethanes and silanes of the types $(CH_3)XY_3$, $(CH_3)_2XY_2$ and $(CH_3)_3XY$. It is pointed out that in these compounds there is relatively little interaction between methyl and skeletal frequencies.

In spite of the numerous difficulties involved, it has occasionally proved possible to make assignments of frequencies for large molecules, especially when relatively high symmetry is present. This has been done, for example, by Young, Koehler and McKinney[1] for the group IV tetramethyl compounds. A modification of their assignment, based on new experimental data, has been used by Lippincott and Tobin[2] to calculate the thermodynamic functions of lead, tin and germanium tetramethyls.

In this paper, assignments of fundamental frequencies are given for those methyl chloro-, bromo- and iodomethanes and silanes for which spectroscopic data have been published, considering the molecules to have C_{2v} or C_{3v} symmetry. Following Young, Koehler and McKinney, internal vibrations of the methyl groups are assumed to lie above 1200 cm.$^{-1}$. For the methanes, the CH_3 rocking frequencies lie roughly in the region 1000–1200 cm.$^{-1}$, skeletal frequencies below 1000 cm.$^{-1}$. For the silanes, the CH_3 rocking frequencies lie roughly in the region 800–900 cm.$^{-1}$, skeletal frequencies below about 800 cm.$^{-1}$.

Within any one of these regions, it is assumed that: (1) Frequencies corresponding to similar normal modes, such as symmetric C–H stretching, fall in the same region of the spectrum, regardless of symmetry species. (2) For a given type of vibration within a given symmetry species, symmetric modes lie below asymmetric modes. (3) Angle bending frequencies lie below bond stretching frequencies. (4) Characteristic bond frequencies do not change much in going along the series $X(CH_3)_4 \rightarrow XY_4$.

The Classification of the Normal Modes for the types of molecules considered in this paper is given in Table I. The notation follows that of Herzberg.[3]

TABLE I

NORMAL MODE CLASSIFICATIONS

$(CH_3)XY_3$

	A_1	A_2	E
CH_3 asym. stretching			ν_7
CH_3 sym. stretching	ν_1		
CH_3 asym. bending			ν_8
CH_3 sym. bending	ν_2		
CH_3 rocking			ν_9
C–X stretching	ν_3		
X–Y stretching	ν_4		ν_{10}
XY_3 rocking			ν_{11}
XY_3 bending	ν_5		ν_{12}
CH_3 torsion		ν_6	
Activity	R. pol., I.	Inactive	R., I.

$(CH_3)_2XY_2$

	A_1	A_2	B_1	B_2
CH_3 asym. stretching	ν_1	ν_{10}	ν_{15}	ν_{22}
CH_3 sym. stretching	ν_2		ν_{16}	
CH_3 asym. bending	ν_3	ν_{11}	ν_{17}	ν_{23}
CH_3 sym. bending	ν_4		ν_{18}	
CH_3 rocking	ν_5	ν_{12}	ν_{19}	ν_{24}
C–X stretching	ν_6		ν_{20}	
X–Y stretching	ν_7			ν_{25}
XC_2 bending	ν_8			
XY_2 bending	ν_9			
Skeletal twisting		ν_{13}		
Skeletal rocking			ν_{21}	ν_{26}
CH_3 torsion		ν_{14}		ν_{27}
Activity	R. pol., I.	R.	R., I.	R., I.

$(CH_3)_3XY$

	A_1	A_2	E
CH_3 asym. stretching	ν_1	ν_9	ν_{13}, ν_{14}
CH_3 sym. stretching	ν_2		ν_{15}
CH_3 asym. bending	ν_3	ν_{10}	ν_{16}, ν_{17}
CH_3 sym. bending	ν_4		ν_{18}
CH_3 rocking	ν_5	ν_{11}	ν_{19}, ν_{20}
C–X stretching	ν_6		ν_{21}
X–Y stretching	ν_7		
XC_3 bending	ν_8		ν_{22}
Skeletal rocking			ν_{23}
CH_3 torsion		ν_{12}	ν_{24}
Activity	R. pol., I.	Inactive	R., I.

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[1] C. Young, J. Koehler and D. McKinney, THIS JOURNAL, **69**, 1410 (1947).

[2] E. R. Lippincott and M. C. Tobin, "The Thermodynamic Functions of Lead Tetramethyl," "The Thermodynamic Functions of Tin Tetramethyl and Germanium Tetramethyl," ONR Reports No. 1 and 2, University of Connecticut, 1951.

[3] G. Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules," D. Van Nostrand Co., Inc., New York, N. Y., 1945.

TABLE II

FUNDAMENTAL FREQUENCIES OF $(CH_3)XY_3$ MOLECULES

	(CH_3)-CCl_3[a,b]	(CH_3)-$SiCl_3$[c,d]	(CH_3)-$SiBr_3$[e]
ν_1	2938	2912	2904
ν_2	1378	1265	1320
ν_3	1075	761	746
ν_4	522	450	314
ν_5	342	229	153
ν_6	..	..	..
ν_7	3002	2983	2977
ν_8	1432	1405	1396
ν_9	1179	807	(800)
ν_{10}	714	576	453
ν_{11}	308	229	186
ν_{12}	240	164	98

TABLE III

FUNDAMENTAL FREQUENCIES OF $(CH_3)_2XY_2$ MOLECULES

	$(CH_3)_2$-CCl_2[b,f]	(CH_3)-CBr_2[b,g,h,i]	$(CH_3)_2$-CI_2[h]	$(CH_3)_2$-$SiCl_2$[c]	$(CH_3)_2$-$SiBr_2$[e]
ν_1	2993	2994	(2990)	2980	2975
ν_2	2934	2922	(2900)	2910	2902
ν_3	1387	1376	(1370)	1401	1395
ν_4	1187	1179	(1170)	1265	1325
ν_5	1155	1142	(1110)	(850)	(850)
ν_β	653	626	551	691	682
ν_7	557	481	448	465	355
ν_8	360	310	270	231	208
ν_9	254	166	112	169	118
ν_{10}	2993	2994	(2990)	2980	2975
ν_{11}	1443	1434	(1430)	1410	1395
ν_{12}	1110	1098	(1100)	(850)	(850)
ν_{13}	284	246	112	177	166
ν_{14}	..	..	..	..	..
ν_{15}	2993	2994	(2990)	2980	2975
ν_{16}	2934	2968	(2900)	2910	2902
ν_{17}	1443	1434	(1430)	1401	1395
ν_{18}	1387	1376	(1370)	1265	1325
ν_{19}	1110	1098	(1090)	(850)	(850)
ν_{20}	913	900	868	804	797
ν_{21}	360	292	270	241	208
ν_{22}	2993	2968	(2900)	2980	2975
ν_{23}	1443	1434	(1430)	1401	1395
ν_{24}	1110	1098	(1050)	(850)	(850)
ν_{25}	653	585	551	533	426
ν_{26}	388	341	270	304	208
ν_{27}	..	..	..	..	..

TABLE IV

FUNDAMENTAL FREQUENCIES OF $(CH_3)_3XY$ MOLECULES

	$(CH_3)_3$-CCl[b,j]	$(CH_3)_3$-CBr[b,j]	$(CH_3)_3$-CI[j,k]	$(CH_3)_3$-$SiCl$[c,l]	$(CH_3)_3$-$SiBr$[e]
ν_1	2978	2982	2976	2970	2973
ν_2	2924	2918	2918	2902	2904
ν_3	1361	1358	1366	1315	1325
ν_4	1234	1235	1223	1260	1258
ν_5	1147	1142	1134	846	850
ν_6	812	805	801	637	635
ν_7	570	515	487	467	374
ν_8	372	303	259	242	213
ν_9	2978	2982	2863	2970	2973
ν_{10}	1445	1454	1448	1415	1398
ν_{11}	1026	1026	1021	846	850
ν_{12}	..	..	..	..	..
ν_{13}	2978	2982	2976	2970	2973
ν_{14}	2978	2982	2976	2970	2973
ν_{15}	2978	2960	2955	2902	2904
ν_{16}	1445	1454	1448	1446	1398
ν_{17}	1445	1454	1448	1446	1398
ν_{18}	1234	1235	1223	1250	1258
ν_{19}	1026	1029	1021	846	850
ν_{20}	1026	1029	1021	846	850
ν_{21}	925	932	927	760	758
ν_{22}	406	398	386	330	242
ν_{23}	304	268	227	187	178
ν_{24}	..	..	..	..	..

[a] T. Y. Wu, "Vibrational Spectra and Structure of Polyatomic Molecules," Edwards Bros., Ann Arbor, Mich., page 356. [b] J. Wagner, *Z. physik. Chem.*, **B45**, 341 (1940). [c] T. Shimanouchi, I. Tsuchiya and Y. Mikawa, *J. Chem. Phys.*, **18**, 1306 (1950). [d] L. Burnelle and J. Duchesne, *ibid.*, **20**, 1324 (1952). [e] H. Mutara and S. Hayashi, *ibid.*, **19**, 1217 (1951). [f] K. W. F. Kohlrausch and F. B. Köppl, *S. B. Akad. Wiss. Wien*, **143**, 537 (1935). [g] L. Kahovec and J. Wagner, *Z. physik. Chem.*, **B47**, 48 (1940). [h] L. Kahovec and K. W. F. Kohlrausch, *ibid.*, **B48**, 7 (1940). [i] F. Mortimer, R. Blodgett and F. Daniels, THIS JOURNAL, **69**, 822 (1947). [j] A. Dadieu, K. W. F. Kohlrausch and A. Pongratz, *S. B. Akad. Wiss. Wien*, **141**, 267 (1932). [k] L. Kahovec and J. Wagner, *Z. physik. Chem.*, **B42**, 123 (1939). [l] J. Duchesne, *J. Phys. Chem.*, **16**, 1006 (1948).

Spectra and Assignments.—The assignments to the normal modes are given in Tables II, III and IV. The assignments are based on spectra published in the references given in these tables. Essentially complete assignments have been published for $(CH_3)CCl_3$[4–7] and $(CH_3)SiCl_3$,[8] although there is considerable disagreement about the details of the former. Assignments for the skeletal modes of the methyl bromo- and chlorosilanes, based on a normal coördinate analysis using a Urey–Bradley potential function have been given by Shimanouchi[9] and Mutara.[10]

These assignments agree with those proposed in this paper, with the exception of minor differences noted below. The detailed assignment of frequencies is discussed in the succeeding sections.

Assignments

I. $(CH_3)XY_3$.—The assignment of frequencies for $(CH_3)CCl_3$ has been discussed by several workers, as mentioned above, and will only be sketched here. The A_1 and E skeletal frequencies are readily assigned as shown in Table II. The A_1 frequency ν_3 appears as a doublet at 1068 and 1082 cm.$^{-1}$; this is ascribed to Fermi resonance with the first overtone of 522 cm.$^{-1}$. The assignment of skeletal frequencies for the silicon compounds is exactly analogous to this assignment.[9,10] Of the extra-skeletal frequencies of $(CH_3)CCl_3$, 3002 and 2938 cm.$^{-1}$ are readily assigned on the basis of their position in the spectrum and the polarization of 2938 cm.$^{-1}$. 1432 and 1378 cm.$^{-1}$ are likewise easily assigned, 1378 cm.$^{-1}$ being polarized. 1432 cm.$^{-1}$ appears as a doublet at 1420 and 1444 cm.$^{-1}$. This is ascribed to Fermi resonance with the first overtone of 714 cm.$^{-1}$. Finally, 1179 cm.$^{-1}$ is assigned to the CH_3 rocking mode, on the basis of its depolarization, and its position in the spectrum.[1,3]

The assignment of the extra-skeletal frequencies for $(CH_3)SiCl_3$ and $(CH_3)SiBr_3$ was made in an analogous manner, except that 807 cm.$^{-1}$ was assigned to the CH_3 rocking frequency ν_9. The corresponding frequency is not observed in the spectrum of $(CH_3)SiBr_3$, but is estimated to lie at about 800 cm.$^{-1}$.

No attempt was made to assign the inactive A_2 CH_3 torsional frequency, since none of the observed spectra, except those of $(CH_3)CCl_3$ contained any large number of overtones which might give a clue as to its value. Smith, *et al.*,[5] estimate this frequency to lie at 205 cm.$^{-1}$ in $(CH_3)CCl_3$.

II. $(CH_3)_2XY_2$.—For most of the $(CH_3)_2XY_2$ compounds, the number of observed frequencies which could be reasonably assigned as skeletal fundamentals was less than the expected nine. This was generally ascribed to piling up of frequencies. Such piling up is to be expected, in view of the large masses of the constituent atoms, and the fact that the X–C and X–Y frequencies tend to fall in the same region of the spectrum.

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[4] T. Y. Wu, "Vibrational Spectra and Structure of Polyatomic Molecules," Edwards Bros., Ann Arbor, Mich., 1946, p. 356.

[5] D. C. Smith, G. M. Brown, J. R. Nielsen, R. M. Smith and C. Y. Liang, *J. Chem. Phys.*, **20**, 473 (1952).

[6] P. Venkateswarlu, *ibid.*, **20**, 1810 (1952).

[7] M. Zaki el-Sabban, A. G. Meister and F. F. Cleveland, *ibid.*, **20**, 1810 (1952).

[8] L. Burnelle and J. Duchesne, *ibid.*, **20**, 1324 (1952).

[9] T. Shimanouchi, I. Tsuchiya and Y. Mikawa, *ibid.*, **18**, 1306 (1950).

[10] H. Mutara and S. Hayashi, *ibid.*, **19**, 1217 (1951).

In the substituted methanes, the ν(C–C) frequencies $\nu_6(B_1)$ and $\nu_{20}(A_1)$ are assigned by analogy with $C(CH_3)_4$[1] and $(CH_3)_2CH_2$.[8] Likewise, the ν(C–Y) frequencies $\nu_{25}(B_2)$ and $\nu_7(A_1)$ are assigned by analogy to the simple dihalomethanes. ν_6 in $(CH_3)_2CBr_2$ appears as a doublet at 606 and 645 cm.$^{-1}$. This is ascribed to Fermi resonance with the first overtone of 310 cm.$^{-1}$. The position of ν_7 in $(CH_3)_2CI_2$ must be regarded as uncertain, since 488 cm.$^{-1}$ seems too high. Of the skeletal bending frequencies, ν_8 and ν_9 are assigned on the basis of the polarization data. This leaves the rocking frequencies ν_{21} and ν_{26}, and the twisting frequency ν_{13} to be assigned. The assignment of these is a bit uncertain, but by analogy to the chlorobromomethanes, etc., they may be assigned as shown in Table III. The assignment of the skeletal frequencies of $(CH_3)_2SiCl_2$ and $(CH_3)_2SiBr_2$ is analogous to these, and has been supported by a normal coördinate analysis.[9,10] Polarization data were available for $(CH_3)_2CCl_2$ and $(CH_3)_2CBr_2$, and were used as an aid in the assignments.

The assignment of the extra-skeletal frequencies is of necessity less certain than that of the skeletal frequencies, since on the basis of the Raman spectrum alone, it is difficult to determine whether a band found in, say, the CH_3 bending region is a fundamental frequency or an overtone. The course followed was to assign all observed lines as fundamentals whenever such assignment was reasonable. Thus, the 1187 cm.$^{-1}$ band in $(CH_3)_2CCl_2$ was assigned as a fundamental, since it lies in the CH_3 bending–CH_3 rocking region, but the 2733 cm.$^{-1}$ band in the same compound was considered to be an overtone, since it seems too low to be a C–H stretching fundamental. The Raman spectrum of $(CH_3)_2CI_2$ is incomplete, so that no extra-skeletal frequencies were observed. These were estimated from the spectra of $(CH_3)_2CCl_2$ and $(CH_3)_2CBr_2$. The estimated values may be corrected when infrared spectra become available for $(CH_3)_2CI_2$. Of the A_1 frequencies, ν_1, ν_2, ν_3 and ν_4 are assigned on the basis of the polarization data, and by analogy to $C(CH_3)_4$. The 2968 cm.$^{-1}$ band of $(CH_3)_2CBr_2$ is reported as weakly polarized; it is not assigned as an A_1 frequency because no band at this position is reported as polarized in any of the other compounds. The only other A_1 extra-skeletal frequency is ν_5, which is assigned to polarized lines at 1155, and 1142 cm.$^{-1}$. The remainder of the assignments requires no special comment, except for the B_2 $\delta(CH_3)$ frequency ν_{18}. This was rather arbitrarily assumed to be piled up with the A_1 $\delta(CH_3)$ frequency ν_3. As before, no assignments were made for the CH_3 torsional frequencies ν_{12} and ν_{27}.

The assignments for $(CH_3)_2SiCl_2$ and $(CH_3)_2SiBr_2$ were made in an analogous manner. The CH_3 rocking frequencies were not observed in the Raman spectra, but are estimated to lie at about 850 cm.$^{-1}$, by analogy with $Si(CH_3)_4$[1] and $(CH_3)_3SiBr$.[10]

III. $(CH_3)_3XY$.—Polarization measurements were available for $(CH_3)_3CCl$ and $(CH_3)_3CBr$ only.

For the substituted methanes, ν_6, ν_7 and ν_8 are easily assigned on the basis of the polarization measurements, and by analogy to $C(CH_3)_4$ and the simple monohalomethanes. ν_{21} is assigned by analogy to $C(CH_3)_4$. Of the two remaining skeletal frequencies, ν_{22} is assigned above ν_{23}, since this seemed to be the trend in such compounds as bromotrichloromethane, where one of the peripheral atoms is heavier than the other three. The line at 406 cm.$^{-1}$ in $(CH_3)_3CCl$ is assigned to ν_{22}, even though it is reported as weakly polarized, by analogy with the other two compounds, and the 415 cm.$^{-1}$ line in $C(CH_3)_4$.[1] The assignment in Table IV leaves unexplained the weak line at 514 cm.$^{-1}$ and the doubtful line at 574 cm.$^{-1}$ in the $(CH_3)_3CI$ spectrum. 514 cm.$^{-1}$ may be assigned as the first overtone of 259 cm.$^{-1}$. 574 cm.$^{-1}$, if it is real, is probably a difference tone.

The assignment of skeletal frequencies for $(CH_3)_3SiCl$ and $(CH_3)_3SiBr$ requires no special comment, except that for $(CH_3)_3SiCl$ differs from that of Shimanouchi[9] in that ν_{22} is assigned to the weak Raman line at 330 cm.$^{-1}$, rather than at 242 cm.$^{-1}$. The weak line at 700 cm.$^{-1}$ is assigned to the combination 242 + 467 cm.$^{-1}$.

The assignment of the extra-skeletal frequencies follows the same lines as in the case of the $(CH_3)_2XY_2$ compounds. There is the difference that in the $(CH_3)_3XY$ molecules, the A_2 frequencies are forbidden in both the Raman and infrared spectrum. They were assigned by assuming them to lie at the same positions as the corresponding E frequencies. Since none of the A_2 frequencies will lie below 1000 cm.$^{-1}$, the error, for such purposes as the calculation of thermodynamic functions, will be small.

In the halomethanes, the lower A_1 ν(C–H) frequency ν_2 is readily assigned on the basis of the polarization measurements. The other A_1 ν(C–H) frequency, ν_1, was assigned arbitrarily. No line at the position 2960 cm.$^{-1}$ is reported for $(CH_3)_3CCl$, and the polarization measurements were apparently not accurate enough to say whether or not the lines at this position in the other two compounds are polarized. There is again some difficulty in assigning the A_1 $\delta(CH_3)$ and CH_3 rocking frequencies. 1147, 1142 and 1134 cm.$^{-1}$ are probably the A_1 CH_3 rocking frequency ν_3. The lines at 1234, 1235 and 1223 cm.$^{-1}$ are in the right position for the A_1 $\delta(CH_3)$ frequency ν_4, but were reported as depolarized. A possible explanation is that the A_1 bands are only weakly polarized, and are piled up with the analogous E frequency ν_{18}. The assignment was made on this basis.

Of the E frequencies, ν_{19} is assumed to be piled up with ν_{20}, ν_{16} with ν_{17}, and ν_{13} with ν_{14}. The line assigned as a CH_3 rocking frequency at 1026 cm.$^{-1}$ is reported as depolarized in $(CH_3)_3CCl$, but 1029 cm.$^{-1}$ is reported as weakly polarized in $(CH_3)_3CBr$. The assignment was made, however, on the basis of the position of these bands.

The assignment of the extra-skeletal frequencies of $(CH_3)_3SiCl$ and $(CH_3)_3SiBr$ was made in like manner. The CH_3 rocking frequencies were assigned to weak Raman lines at 846 cm.$^{-1}$ in $(CH_3)_3SiCl$ and at 850 cm.$^{-1}$ in $(CH_3)_3SiBr$.

Discussion

The assignments given above are admittedly arbitrary in many respects, and could undoubtedly be improved by a careful re-examination of the Raman spectra, including polarization measurements of a high degree of accuracy. Infrared measurements at high dispersion would also be of great value, since something might be learned from band contours.

It is doubtful that a standard normal coördinate analysis would be feasible for the $(CH_3)_2XY_2$ and $(CH_3)_3XY$ compounds. Even if the work of reducing the high order matrices were carried out, the accuracy to be expected is not high, in view of uncertainties in the values of the force constants.

An interesting feature of the spectra is the small interaction between methyl group frequencies and skeletal frequencies. The methyl group frequencies change little in going from methanes to silanes, or from chlorides to bromides or iodides. The CH_3 rocking frequencies, which are really mixed skeletal–extra-skeletal frequencies, drop from about 1100 to about 800 cm.$^{-1}$ in going from methanes to silanes, but are insensitive to changes in type or number of halogen atoms within either group. These observations point to the methods of Edgell and Riethof[11] as a possible way of attacking the normal coördinate analysis of these compounds, especially if machine computers are available.

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(11) W. Edgell and T. Riethof, *J. Phys. Chem.*, **56**, 326 (1952).