542. *Infrared Spectra and Polar Effects. Part III.* Internal Spectral Relationships.*

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In the homologous series of the methyl halides, all the six fundamental frequencies can be shown to be interrelated so that a stepwise change in any one of them produces proportionate changes in the others. The frequencies can also be correlated directly with the stretching frequencies of the corresponding halogen acids. By using these relations the fundamentals of other CH_3X molecules have been predicted with reasonable precision from a simple knowledge of the H–X stretching frequencies. The theoretical implications of these findings are discussed.

IN earlier papers of this series,[1,2] the origins of shifts in characteristic group frequencies which are not sensitive to mass or coupling effects were discussed. Groups which show characteristic frequencies of this kind are usually of the type $>X \overset{\cdots}{-} Y$ where Y is attached only to X by a single or multiple bond, and it has been suggested that frequency shifts originate in changes in the electron density at X, which can be quantitatively related to the strengths of the inductive and mesomeric effects of the substituents at this point. This offers a satisfactory explanation of the many correlations which have been observed between group frequency shifts and physical properties such as pK_a values,[3] kinetic rates,[1,4,5] chelate stabilities,[6] atomic refractivity exaltations,[2] etc., which are primarily dependent on these same effects. However, the hypothesis has other important implications. Thus, in the system (RR′R″)X any systematic changes in R will affect all the mass-insensitive frequencies of R′X and of R″X by amounts proportional to the changes in the *I* and *M* effects introduced. The changes in these frequencies will therefore be interrelated. In principle any such relations which exist would be best studied by a comparison of the relative changes in force constants which occur on passing down a series such as CH_3F—CH_3I. However, owing to the uncertainties which arise from the choice of suitable force fields, values covering a very wide range have been suggested by various authors for the force constants of any one bond in this series. Provided, therefore, that mass effects are small in relation to electrical effects the direct comparison of the actual frequencies observed seems likely to be the more promising approach. We have therefore studied the six fundamental methyl group frequencies of CH_3X compounds to see how far they are interrelated.

The spectra of the methyl halides have been studied by a number of workers and we have made use of the best high-resolution data available.[7-10] Each of these molecules gives rise to six fundamentals consisting of two CH stretching modes (ν_1 and ν_4), two CH deformation modes (ν_2 and ν_5), a CH_3 rocking mode (ν_6), and the C–Halogen stretching mode (ν_3). The values for these are given in Table 1 together with the values for ν_1, corrected for Fermi resonance and for ν_3 after an appropriate correction for mass effects. The latter was carried out by treating CH_3–X as point masses with weights of M_{CH_3} and M_X, the corresponding reduced mass being given by $\mu_{CH_3X} = M_{CH_3}M_X/(M_{CH_3} + M_X)$. Precisely similar methyl-group fundamentals arise in other CH_3X compounds. Of the six fundamentals, ν_1, ν_4, and ν_5 are acknowledged to be mass-insensitive,[7] and a correction can be applied as above for the ν_3 mode. However, we have found that on passing down

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* Part II, *J.*, 1955, 4221.

[1] Bellamy, *J.*, 1955, 2818.

[2] *Idem, ibid.*, p. 4221.

[3] Goulden, *Spectrochim. Acta*, 1954, **6**, 129.

[4] Flett, *Trans. Faraday Soc.*, 1948, **44**, 767.

[5] Fuson, Josien, and Shelton, *J. Amer. Chem. Soc.*, 1954, **76**, 2297.

[6] Bellamy and Beecher, *J.*, 1954, 4491.

[7] Herzberg, " Infrared and Raman Spectra of Polyatomic Molecules," Van Nostrand, New York, 1945.

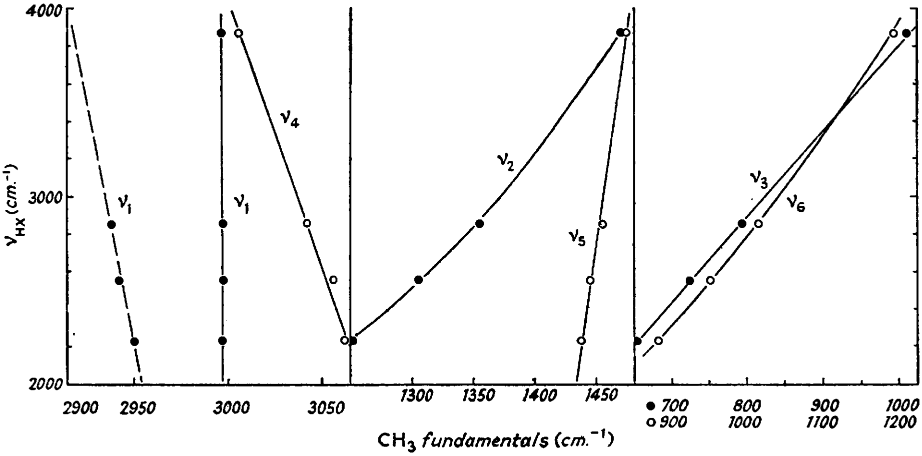
[8] Bernstein, Cleveland, and Voelz, *J. Chem. Phys.*, 1954, **22**, 193.

[9] Pickworth and Thompson, *Proc. Roy. Soc.*, 1954, *A*, **222**, 443.

[10] *Idem, Trans. Faraday Soc.*, 1954, **50**, 218.

the methyl halide series the changes in each of the six fundamentals are a direct function of the halogen electronegativity. As electronegativity is not a mass function this suggests very strongly that, in the ν_2 and the ν_6 mode also, electrical rather than mass effects are the predominating factor in inducing frequency shifts. Sheppard[11] has also reported a similar electronegativity relation for the ν_2 mode of a variety of methyl compounds.

This relation between the shifts shown by each fundamental and the electronegativities of the substituents is not very precise as electronegativity itself cannot be measured with precision. However, as a precisely similar relation can be shown to exist between the H–X stretching frequencies of the halogen acids and the halogen electronegativities, it should be possible to eliminate uncertainties arising in this way and to plot directly H–X stretching frequencies against the frequencies of each of the corresponding CH_3X fundamentals. The results are shown in the Figure and it will be seen that, apart from a slight curvature of the line joining the ν_2 frequencies—which may be associated with the effects of lone-pair repulsions—an excellent linear relation is realised in practice. The observed values have been used for the ν_1 frequencies, but the corresponding plot for these vibrations, corrected, where possible, for Fermi resonance, is indicated by the broken line of the Figure.



The values for the halogen acid stretching frequencies were again taken from the best available data[12–15] and are given in Table 1, together with the values after correction for mass effects. Vapour-phase data have been used in all cases in both Tables 1 and 2.

TABLE 1.

	HX (cm.⁻¹)		CH_3X frequencies (cm.⁻¹)							
			ν_1			ν_3				
X	Obsd.	Mass-corrected	Obs.	Corr.	ν_2	Obs.	Corr. $\frac{1}{3}\mu^{\frac{1}{2}}\nu$	ν_4	ν_5	ν_6
F	3961·4	3875	2964·5	—	1475·3	1048·2	1012·4	3005·7	1471·1	1195·5
Cl	2885·0	2856	2967·8	2938	1354·9	732·1	793·0	3041·8	1454·6	1015·6
Br	2558·6	2553	2972	2942	1305·1	611	724·6	3055·9	1445·3	952·0
I	2230·1	2230	2969·8	2950	1251·5	532·8	651·1	3062·2	1437·8	882·5

The Figure has a number of important implications which will be discussed separately.

Frequencies of Other CH_3X *Molecules*.—The prediction of the fundamentals of other CH_3X molecules directly from the corresponding mass-corrected H–X stretching

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[11] Sheppard, *Trans. Faraday Soc.*, 1955, **51**, 1465.

[12] Herzberg, "Molecular Spectra and Molecular Structure. Diatomic Molecules," Van Nostrand, New York, 1950.

[13] Mills, Thompson, and Williams, *Proc. Roy. Soc.*, 1953, *A*, **218**, 29.

[14] Thompson, Williams, and Callomon, *Spectrochim. Acta*, 1952, **5**, 313.

[15] Boyd and Thompson, *ibid.*, p. 308.

frequencies is one obvious application of this correlation. Thus, if from a point corresponding to the hydrogen stretching frequency of hydrogen cyanide a line is drawn across the Figure it intersects each of the six lines at a point corresponding fairly well to each of the six methyl fundamentals of methyl cyanide. Even with as complex a molecule as trichlorosilane a line drawn across at the H–Si stretching frequency gives a series of values in close agreement with the appropriate fundamentals of methyltrichlorosilane. The observed and the predicted values for a number of different CH_3X molecules studied in this way are compared in Table 2. In computing the ν_1 frequencies the broken line of the Figure has been used for compounds which show Fermi resonance, and the ν_3 frequencies have been approximately corrected for mass. It will be seen that the agreement obtained is reasonably good although the predicted values for the C–X stretching mode sometimes show less satisfactory agreement. This last may be in part due to the approximations made in mass correction, but it is probably associated also with the fact that there are differences in the properties of bonds formed by the overlapping of two sp^3 atomic orbitals from those given by the overlap of sp^3 with p as is the case with the methyl halides.[16] In one instance (acetaldehyde) the predicted values for the ν_3 and the ν_6 mode result in a reversal of the original assignments of these bands. This appears to be strong evidence for a correction of these assignments and affords an interesting example of one possible application of these relations.

These findings do not follow immediately from the electronegativity considerations advanced above. The mean of the two H–X stretching frequencies of H_2X compounds is a linear function of the electronegativity of X, but, although the slope is the same, the line is displaced from that given by a similar plot of the halogen acids.[2] The corresponding lines for H_3X and H_4X compounds are similarly further displaced. These displacements can be shown to be partly connected with the introduction of a new factor, the angle between the H–X bonds. As this angle factor enters into any corresponding plots for the methyl derivatives, it is self-cancelling in the comparisons made above, but the

TABLE 2.

	HX (cm.$^{-1}$)	CH$_3$X Frequencies (cm.$^{-1}$)												
	mass-	Sym. CH st.		Asym. CH st.		Sym. CH def.		Asym. CH def.		CH$_3$ rock		CH$_3$–X st.		
X	corrected	obs.	calc.	obs.	calc.	obs.	calc.	obs.	calc.	obs.	calc.	obs.	calc.	Ref.
CN ...	3263	2955	2930	3009	3027	1387	1408	1455	1460	1041	1091	920	895	7, *a*
CF$_3$...	3021	2975	2935	3034	3034	1409	1378	1442	1455	970	1046	830	706	*b*
SiCl$_3$	2275	2923	2949	2990	3060	1271	1259	1416	1441	807	892	764	540	*c*, *d*
CCl$_3$...	3033	2951	2934	3014	3035	1386	1384	1457	1456	1088	1049	867	681	*c*, *e*
C≡CH	3278	2941	2929	3008	3026	1382 *	1411	1452	1460	1053	1095	931	834	7, *f*
OH ...	3613	2844	2924	2977	3014	1455	1450	1477	1466	1171	1153	1034	1039	7
CHO	2790	2710	2939	2964 2915	3043	1370	1344	1425	1451	760	1001	917	740	7, *g*
SH ...	2590	2870	2943	3000	3050	1335	1313	1475 1430	1447	1060 957	959	704	683	*h*, *i*
CO$_2$H	2919	2935	2937	3027 2983	3039	1381	1364	1403 1431	1453	1184 1082	1027	996	719	7, *j*
NH$_2$	3292	2820	2930	2968	3025	1426	1412	1460	1460	1127	1096	1045	954	7, *k*
N$_3$ ...	3309	2931	2929	3000	3026	1351	1414	1482 1434	1461	1194 1118	1100	914	802	*l*
NCO	3503	2951	2925	2994	3018	1377	1440	1453	1465	1181 1107	1138	870	845	*l*, *m*

* Raman data.

a, Venkateswarlu, *J. Chem. Phys.*, 1951, **19**, 293; Williams, unpublished work. *b*, Cowan, Herzberg, and Sinha, *J. Chem. Phys.*, 1950, **18**, 1538. *c*, Gibson and McKinney, *J. Amer. Chem. Soc.*, 1951, **73**, 1431. *d*, Smith, *J. Chem. Phys.*, 1953, **21**, 1997. *e*, Venkateswarlu, *ibid.*, 1951, **19**, 298. *f*, Boyd and Thompson, *Trans. Faraday Soc.*, 1952, **48**, 493. *g*, Morris, *J. Chem. Phys.*, 1943, **11**, 230. *h*, Allen, Cross, and King, *ibid.*, 1950, **18**, 1412. *i*, Thompson and Skerrett, *Trans. Faraday Soc.*, 1940, **36**, 812. *j*, Weltner, *J. Amer. Chem. Soc.*, 1955, **77**, 3941. *k*, Cleaves and Plyler, *J. Chem. Phys.*, 1939, **7**, 563. *l*, Eyster, *ibid.*, 1940, **8**, 135, 369. *m*, Herzberg and Reid, *Discuss. Faraday Soc.*, 1950, **9**, 92.

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[16] Maccoll, *Trans. Faraday Soc.*, 1950, **46**, 369.

implicit assumption that there is no angle change in passing from the hydride to the corresponding methyl compound may well account for some of the minor discrepancies in Table 2.

Internal Relation.—The hypothesis that all the six fundamental methyl group frequencies of any molecule CH_3X must be directly and quantitatively related is clearly borne out by the results given in Table 2. If, for example, only the ν_1 C–H stretching of such a molecule is known, the remaining five fundamentals, together with the H–X stretching frequency, can be obtained from the Figure by reading across from a line drawn horizontally through the point at which this frequency occurs on the plot joining the ν_1 fundamentals.

The Slopes of the Lines in the Figure.—Perhaps the most significant feature of the Figure is the relative directions of the slopes of the lines joining the individual fundamental vibrations. Thus in descending the series CH_3F—CH_3I the C–H stretching frequencies rise and the C–H deformation frequencies fall. This is consistent with the C–H bonds' becoming progressively harder to stretch and easier to bend. When the mean H–X stretching frequency of methane is plotted as an ordinate in the Figure, the mean value of each pair of fundamental frequencies of ethane can be derived directly. It is interesting, however, that the latter points lie in each case between the points corresponding to CH_3F and to CH_3Cl. When the data are plotted in this way, therefore, the order in which the elements occur on any single line is not the order of their electronegativities but appears to be rather the order of the strengths of the C–X bonds as measured by their dissociation energies. The dissociation energy of the C–C bond of ethane, for example, is less than that of the C–F bond of CH_3F and greater than that of the C–Cl bond of CH_3Cl. Insofar as dissociation energies parallel the relative states of hybridisation it follows that in the C–X link a progressive increase in the *p* character occurs down the series, which is reflected in the progressive fall in the C–X frequencies. The C–F bond of methyl fluoride must therefore have more *s* character than the sp^3 C–C bond of ethane, whilst the corresponding bond in the other methyl halides must have more *p* character.

These conclusions are fully supported by a consideration of the directions of slope of the remaining lines. A progressive increase in *p* character in the C–X bonds must be accompanied by a progressive increase in the *s* character of the C–H bonds. These will therefore become progressively shorter, and their frequencies will rise down the same series. It will be seen from the Figure that the C–H stretching modes do alter in this way and that the slopes of the lines from the ν_1 and the ν_4 vibrations are in the opposite direction to those of the deformation and the C–X stretching modes. The non-parallelism of the lines joining the C–H stretching modes is of course due to the effect of Fermi resonance on the ν_1 vibration and after correction for this the lines are approximately parallel.

The directions of slope of the lines joining the CH deformation modes are also consistent with this interpretation. For the force constants and bond lengths of C–H links in sp^3, sp^2, and *sp* hybrids Walsh[17] noticed that an increase in *s* character results in a decrease in the bending force constants. He attributes this to a reduction in the directional character which he associates primarily with *p* hybridisation. Our own findings could be explained on this basis or perhaps equally well in terms of the repulsive effects of the charge cloud situated between the C–X atoms. In the C–F bond this cloud is highly concentrated and, as the link is short, fairly close to the carbon atom, whereas in the C–I bond it is more diffuse (lower ionisation potential) and further away so that it will offer less physical resistance to the deformation of the hydrogen atoms. The non-parallelism of the lines joining the separate CH deformation modes may also be explained on this basis, as a greater resistance would be offered in the case of the symmetrical deformation in which all the hydrogen atoms are brought up together than in the asymmetric deformation in which they are not.

It will therefore be seen that the directions of slopes of the lines in the Figure give a self-consistent picture of a regular increase in *p* character in the C–X link, with corresponding increases in the *s* character of the C–H links down the series CH_3F—CH_3I. This is also consistent with that suggested by Coulson[18] on the basis of the tetrahedral angles of

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[17] Walsh, *Discuss. Faraday Soc.*, 1947, **2**, 18.

[18] Coulson, " Victor Henri Memorial Vol. Contribution a l'Etude de la Structure Moleculaire," Desoer, Liège, 1948, p. 15.

the methyl halides. It is therefore interesting to consider how far the observed frequencies (corrected as necessary for resonance or mass effects) afford a true quantitative picture of the hybridisation changes in a limited series, such as this, in which the range of change is relatively small. This approach might permit the use of frequencies in following the course of hybridisation changes for some of those applications for which force constants have previously been employed.[19] It would be advantageous to substitute such a parameter, which can be measured with high precision, for one which is dependent on an arbitrary choice of force fields. That such a use is possible is strongly suggested by our earlier findings [1, 2] in which frequency shifts have been quantitatively related to *I* and *M* effects in a number of cases, as these effects will themselves be directly related to the changes in hybridisation which they produce at the central atom. The magnitude of the frequency shifts observed is not inconsistent with this suggestion, as can be shown from the observed changes in the tetrahedral angles in the methyl halide series. These correspond to changes in the sp^3 hybridisation ratios of about 5% over the whole series, and this is the order of change of the C–H stretching frequencies which, being least influenced by other factors, would be expected to provide the best measure of the hybridisation changes.

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[19] Duchesne, *Nature*, 1947, **159**, 62, 793; *J. Chem. Phys.*, 1951, **19**, 246; Heath, Linnett, and Wheatley, *Trans. Faraday Soc.*, 1950, **46**, 137; Walsh, *ibid.*, 1946, **42**, 60, 158.