THE EFFECTIVE ELECTRONEGATIVITY OF MOLECULES: CORRELATION WITH C—H AND M—CH₃ FREQUENCIES

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The ffective electronegativity criterion has been further elaborated and shown to be valid in the case of the C—H and M—CH₃ stretching frequencies (M=elements of the third to seventh group). The deviations of the C—H stretching in methyl and methylene fluorides has been explained to be due to the reinforcement of the inductive component of fluorine by the hybridization dipole moment of the methyl. The CH₃—MCl₃ compounds of the fourth group elements have larger shifts compared with the methyls of the same elements which has been suggested to be a result of the change in the effective electronegativity.

In the previous paper[1] it was shown that since the vibrational energy is a component of the total energy of a molecule which in turn depends on its electronic environment, it is possible to correlate the vibrational frequency in terms of the effective electronegativity particularly because the vibration involves all the bonds in a molecule for which the effective electronegativity is a fair representative.

Before entering into the discussion of the various implications it would be worth mentioning that the vibration of a molecule involves the normal modes, and that localization of a vibration in a particular bond is a valid approximation only when its frequency is not too close to that of the other possible vibrational modes. Strong coupling between the localized oscillators may result from the effect of substituents and it is conceivable that the rules of arithmetic mean would break down in such cases. In certain complexes with a heavy metal atom, as in Ligand field theory, it is sufficient to regard the mass of the molecule as localized and their treatment becomes simple. In the previous study[1] phosphorus in the phosphoryl compounds $RP(O)XY$ was taken as one such central atom. Here, the relationship has been demonstrated to hold for the C—H symmetric and asymmetric vibration in the methyl and methylene halides, and the CH₃—M stretching frequencies of the third to seventh group elements.

In the case of alkyl compounds the C—H stretching, bending, twisting, wagging and rocking modes have been shown to change with the product of the electronegativity of the substituents.[2] Similar results are obtained by the consideration of the effective electronegativity of the molecules which offers an advantage that the whole molecular environment is taken into account. The variation of the symmetric stretching vibrations for the methyl halides with the effective electronegativity is shown in Fig. 1. The corresponding asymmetric vibration appears not to be in much

agreement. This, to a certain extent could be due to the non-symmetric nature of this vibration where mass effect must be prominent. A closer examination of the various points in Fig. 1, however, does bear out the relationship with respect to the halides on the one hand and the various anionic groups on the other. In the case of the methylene halides also the symmetric C—H stretching follows a straight line (Fig. 2) as compared with the asymmetric vibration. It is of interest to note here that the effective electronegativity of the central carbon atom has been used in another correlation.[3] The similarity in results indicates the reliability of the present method.
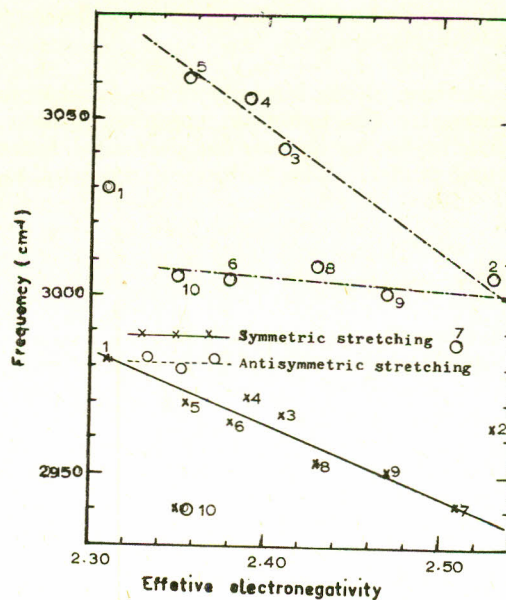

Fig. 1.—Dependence of the C—H stretching frequency of the methyl halides on the effective electronegativity.

1. CH₃D, 2. CH₃F, 3. CH₃Cl, 4. CH₃Br, 5. CH₃I, 6. CH₃CHO, 7. CH₃OH, 8. CH₃CN, 9. CH₃NC, 10. CH₃COO⁻.
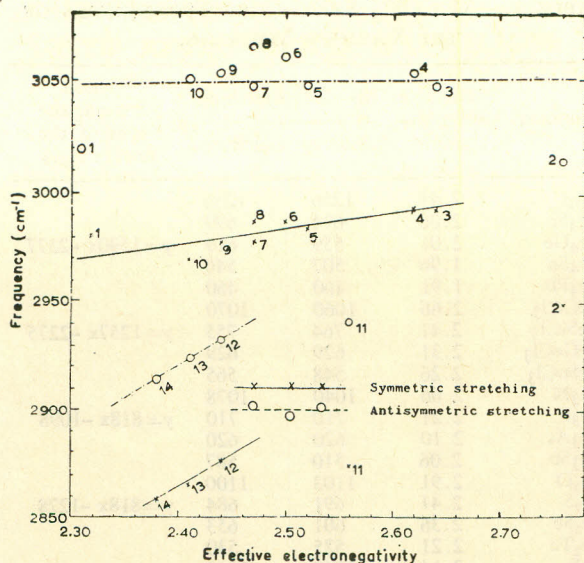
Fig. 2.—Dependence of the C—H stretching frequency of the methylene halides on the effective electronegativity.

1. CH_2D_2, 2. CH_2F_2, 3. CH_2FCl, 4. CH_2FBr, 5. CH_2Cl_2, 6. CH_2ClBr, 7. CH_2ClI, 8. CH_2Br_2, 9. CH_2BrI, 10. CH_2I_2, 11. CH_3CH_2F, 12. CH_3CH_2Cl, 13. CH_3CH_2Br, 14. CH_3-CH_2I.

The methyl substituted methylene halides seem to form a different class from the methylene dihalides as shown in Fig. 2. Change in hybridization due to the electron releasing methyl groups is suggested to be the reason for this deviation.[3] Here also the electron density changes can be rationalized by making use of the effective electronegativity. The electron-withdrawing substituents form a different class. This is seen in the case of the phosphoryl fluorides discussed earlier and the methyl (Fig. 1) and methylene fluorides (Fig. 2). Effective electronegativity clearly marks this deviation of the fluorides.

Nonlinear effects of fluorine might be expected in methyl fluoride when the hybridization dipole moment due to methyl is acting to reinforce the inductive component due to the electronegative fluorine. In such cases the overall moment will be unusually large. In the unsubstituted methane the electropositive hydrogen atoms are opposing the hybridization term. This distinction, it may be pointedout, is very relevant to the validity of an effective electronegativity criterion.

The nonlinear effects may be further elaborated by considering a molecule AB, the molecular orbital for which would be given by
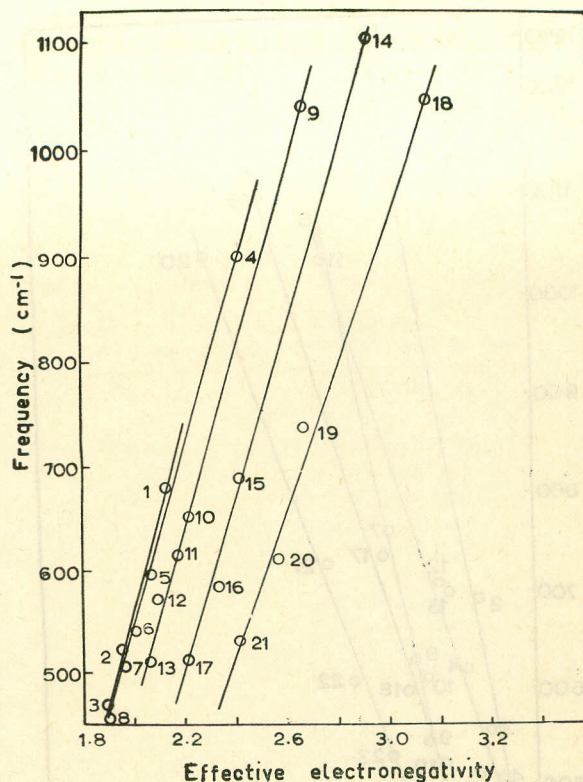
$$\Psi_{AB} = \Psi_A + \lambda \Psi_B \qquad (1)$$

Fig. 3.—Dependence of the M—CH_3 symmetric stretching frequency on the effective electronegativity of methyls of group III, IV, V, VI and VII elements.

1. Me_3B, 2. Me_3Ga, 3. Me_3In, 4. Me_4C, 5. Me_4Si, 6. Me_4Ge 7. Me_4Sn, 8. Me_4Pb, 9. Me_3N, 10. Me_3P, 11. Me_2PH, 12. Me_3As, 13. Me_3Sb, 14. Me_2O, 15. Me_2S, 16. Me_2Se, 17. Me_2Te, 18. MeF, 19. $MeCl$, 20. $MeBr$, 21. MeI.

where λ is dependent on the difference in electronegativity. The charge cloud would be displaced towards the more electronegative orbital. In the case of the fluorides the displacement would be towards fluorine. The high electronegativity of fluorine would be compensated by the contribution from the hybrid function due to the methyl. That the hybrid functions contribute collectively towards the overall moment supports the present electronegativity criterion.

It has been shown earlier that higher or lower shifts from the given range of characteristic frequency are observed depending on the electronegativity of the substituents. Because of a change in hybridization the shifts may be positive or negative depending on how the charge cloud has been displaced. That the whole effect is on the central atom is demonstrated by a definite periodicity in the variation of the electronegativity of the central atom. This was shown earlier[1] for the X-sensitive frequency of the phenyl group, mode q with the electronegativity of the phenyls
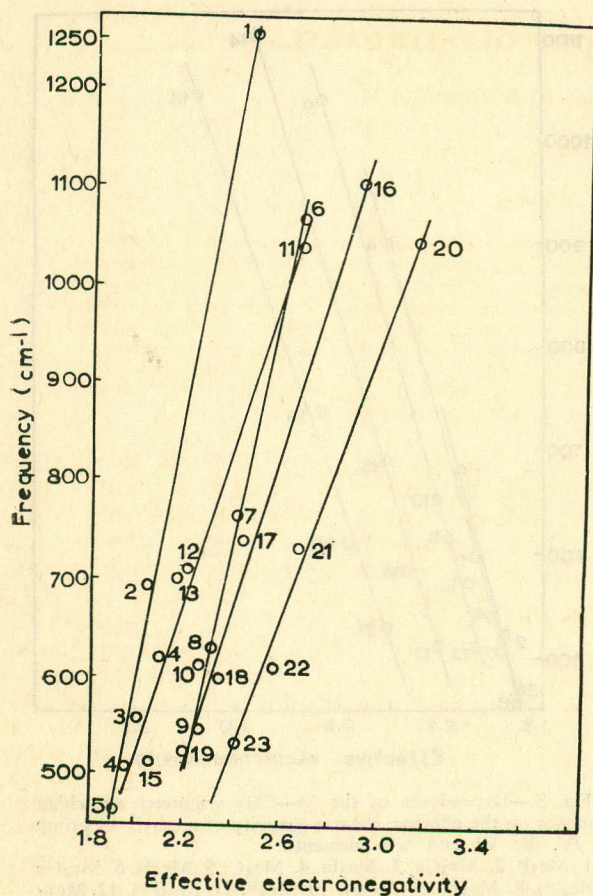
Fig. 4.—Dependence of the M—CH₃ antisymmetric stretch-ing frequency on the effective electronegativity of the methyls of group IV, V, VI and VII elements.

1. Me₄C, 2. Me₄Si, 3. MeGe, 4. Me₄Sn, 5. Me₄Pb, 6. Me-CCl₃, 7. MeSiCl₃, MeGeCl₃, 9. MeSnCl₃, 10. Me₂GeCl₂, 11. Me₃N, 12. Me₃P, 13. Me₂PH, 14. Me₃As, 15. Me₃Sb, 16. Me₂O, 17. Me₂S, 18. Me₂Se, 19. Me₂Te, 20. MeF, 21. MeCl, 22. MeBr, 23. MeI.

of the elements of the various groups. A similar relation has been found in the case of the methyls. Deviations occur from the expected values when the substituents are changed from a methyl to a trichloromethyl. The central atom electronega-tivity[4] would no longer be able to explain this. This is duly taken into account by the effective electronegativity of molecules. The periodicity in the case of the third to the seventh group methyls is shown in Figs. 3 and 4 where the sym-metric and antisymmetric stretching frequencies are plotted against the effective electronegativity. In Fig. 4, it may be noted that the CH₃—MCl₃ compounds of the fourth group elements have a different slope. This may be explained on the present basis to be due to a change in hybridization

TABLE 1.—M—CH₃ STRETCHING FREQUENCIES OF THE VARIOUS METHYLS.

Compound	Effective electrone-gativity	M—CH₃ stretching		Equation governing the slopes of the lines in Fig.4
		Observed	Calculated	
Me₄C	2.41	1256	1256	
Me₄Si	2.06	694	699	
Me₄Ge	2.01	559	619	y=1590x −2577
Me₄Sn	1.96	507	540	
Me₄Pb	1.91	460	460	
MeCCl₃	2.66	1060	1070	
MeSiCl₃	2.41	764	755	y=1257x −2275
MeGeCl₃	2.31	629	629	
MeSnCl₃	2.26	548	565	
Me₃N	2.66	1040	1078	
Me₃P	2.21	710	710	y=818x −1098
Me₃As	2.10	620	620	
Me₃Sb	2.06	510	587	
Me₂O	2.91	1103	1100	
Me₂S	2.41	691	684	y=818x −1278
Me₂Se	2.36	601	653	
Me₂Te	2.21	525	530	
MeF	3.14	1048	1048	
MeCl	2.66	732	708	y=707x −1172
MeBr	2.56	611	641	
MeI	2.41	532	530	

caused by the different and highly electronegative molecular environment which again maintains the periodicity. This is apparent from the slope of the line which is almost the same as for the fourth group methyls.

The change in hybridization is brought about by a modification of electron density around the central atom. Because of a large difference in the electronegativity of the two moieties, viz. CH₃ and MCl₃, the value of the parameter λ in equation (1) would be large and the charge cloud would be displaced towards MCl₃ resulting in an increase in the stretching frequency of the M—Me bond. Since the electronegativity of the central atom decreases as we go down the periodic table, the periodicity is expected to be maintained in the same molecular environment. It is possible to predict the frequencies from the effective electronegativities of analogous compounds and is shown in Table 1.

References

1. M.A.A. Beg, Pakistan J. Sci. Ind. Res., 11, 345 (1968.)
2. R.G. Jones and W.J. Orville-Thomas, Spec-trochim. Acta, 20, 291 (1964).
3. R.G. Jones, J.A. Ladd and W.J. Orville-Thomas, Spectrochim. Acta, 20, 1967 (1964).
4. R.D. Kross and V.A. Fassel, J. Am. Chem. Soc., 77, 5858 (1955).