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Berkeley, California

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THE SYMMETRICAL DEFORMATION FREQUENCIES OF
METHYL, SILYL AND GERMYL GROUPS

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March 1963

The Symmetrical Deformation Frequencies of Methyl, Silyl and Germyl Groups

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The symmetrical deformation frequencies of the MH_3 groups in compounds of the type $\text{H}_3\text{M-X}$ (where $\text{M} = \text{Si}$ or Ge , and where X may be bound to other atoms) increase with increasing electronegativity of the atom X . These correlations and the similar correlation for methyl groups may be explained in terms of the repulsions between the M-H bonding electrons and the M-X bonding electrons.

Introduction

It has been pointed out^{1,2} that the symmetrical deformation frequency

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- (1) N. Sheppard, Trans. Faraday Soc. 51, 1465 (1955).
 - (2) L. J. Bellamy and R. L. Williams, J. Chem. Soc., 2753 (1956).
-

of a $\text{CH}_3\text{—X}$ group may be correlated with the electronegativity of the atom X (which may be bound to other atoms). A plot of the symmetrical deformation frequency against the electronegativity of X yields a series of parallel straight lines, each line corresponding to X atoms from a particular horizontal row of the periodic table.¹ In order to test the generality of this type of correlation and to aid in the identification of substituted silanes and germanes, we have examined the existing infrared spectral data on silyl and germyl compounds.

Correlations with Electronegativity

The symmetrical deformation frequencies for silyl compounds and germyl compounds are presented in Tables I and II, respectively. Most of the frequency assignments are taken from the literature; those few cases in which we have made the assignments are marked in the tables. In making assignments, we have been aided by the fact that the absorption band attributable to a symmetrical deformation is generally very strong. The frequencies in Tables I and II have been plotted in Figure 1 against the

Pauling electronegativities³ of the atoms to which the silicon and germanium

- (3) L. Pauling, "The Nature of the Chemical Bond," 3rd ed., Cornell University Press, Ithaca, New York, 1960.
-

atoms are bound. It will be noted that the points roughly form two straight lines, one corresponding to the silyl compounds and the other corresponding to the germyl compounds. The slope of the silyl compound line is 48 cm^{-1} per electronegativity unit, and the slope of the germyl compound line is 30 cm^{-1} per electronegativity unit. These slopes may be compared with that for methyl compounds, approximately 65 cm^{-1} per electronegativity unit.^{1,4}

- (4) A single line drawn through all the methyl compound points, without regard for the periodic table grouping, would have a slope around 110 cm^{-1} per electronegativity unit.
-

It is interesting that if one plots the symmetrical deformation frequencies for either methyl, silyl or germyl groups against the single-bond covalent radius of X, one obtains a series of straight lines, each line corresponding to X atoms from a particular horizontal row of the periodic table. Because the covalent radius of an atom is closely related to its electronegativity, and because there seemed no advantage in breaking up each of the lines of Figure 1 into a family of lines, we have not presented these plots.

Table I. Symmetrical Deformation Frequencies of Silyl Groups.

Compound	Frequency (cm ⁻¹)	Reference
SiH ₃ F	990	a
SiH ₃ OCH ₃	975	b
SiH ₃ OSiH ₃	957	c
SiH ₃ Cl	949	a
(SiH ₃) ₃ N	944	d
SiH ₃ Br	929	a
SiH ₃ SSiH ₃	956	e
SiH ₃ CH ₃	940	f
SiH ₃ CN	920	g
SiH ₃ I	903	e
SiH ₃ SeSiH ₃	932	h
SiH ₃ PH ₂	904	i
SiH ₃ AsH ₂	890	j
SiH ₃ SiH ₃	876	k
SiH ₃ SiH ₂ SiH ₃	880	l
SiH ₃ GeH ₃	895	m

a Ref. (6).

b B. Sternbach and A. G. MacDiarmid, J. Am. Chem. Soc., 83, 3384 (1961).

c R. C. Lord, D. W. Robinson, and W. C. Schumb, J. Am. Chem. Soc., 78, 1327 (1956).

d D. W. Robinson, J. Am. Chem. Soc., 80, 5924 (1958).

e E. A. V. Ebsworth, R. Taylor, and L. A. Woodward, Trans. Faraday Soc., 55, 211 (1959).

Table I. References continued:

f S. Kaye and S. Tannenbaum, J. Org. Chem., 18, 1750 (1953);

I. F. Kovalev, Optika i Spektroskopiya, 8, 315 (1960).

g H. R. Linton and E. R. Nixon, Spectrochim. Acta, 10, 299 (1958).

h Ref. (7).

i H. R. Linton and E. R. Nixon, Spectrochim. Acta, 15, 146 (1959).

j J. E. Drake and W. L. Jolly, Chem. and Industry, 1470 (1962).

k G. W. Bethke and M. K. Wilson, J. Chem. Phys., 26, 1107 (1957).

We have taken the average of the in-phase and out-of-phase deformation frequencies, ν_2 and ν_6 .

l E. J. Spanier and A. G. MacDiarmid, Inorg. Chem., 1, 432 (1962).

Assignment by the author.

m E. J. Spanier and A. G. MacDiarmid, Inorg. Chem., 2, 215 (1963).

Assignment by the author.

Table II. Symmetrical Deformation Frequencies of Germyl Groups.

Compounds	Frequency (cm ⁻¹)	Reference
GeH ₃ F	859	a
GeH ₃ Cl	848	b
GeH ₃ Br	832	a
GeH ₃ CH ₃	842	c
GeH ₃ CN	832	d
GeH ₃ PH ₂	816	e
GeH ₃ AsH ₂	806	e
GeH ₃ SiH ₃	788	f
GeH ₃ GeH ₃	795	g

a J. E. Griffiths, T. N. Srivastava, and M. Onyszchuk, Canad. J. Chem., 40, 579 (1962).

b R. C. Lord and C. M. Steese, J. Chem. Phys., 22, 542 (1954).

c J. E. Griffiths, private communication.

d T. H. Goldfarb, J. Chem. Phys., 37, 642 (1962).

e J. E. Drake and W. L. Jolly, Chem. and Industry, 1470 (1962).

f E. J. Spanier and A. G. MacDiarmid, Inorg. Chem., 2, 215 (1963).

g V. A. Crawford, K. H. Rhee, and M. K. Wilson, J. Chem. Phys., 37, 2377 (1962). We have taken the average of the in-phase and out-of-phase deformation frequencies, ν_2 and ν_6 .

Discussion

Bellamy and Williams² explain the frequency shift on going from CH_3I to CH_3F in terms of a change in the hybridization of the carbon bonding orbitals; they assert that, in ascending this series, the C-H bonds gain p character (and hence increase in directional character) and the C-X bonds gain s character. Actually one finds very little evidence for any appreciable change in hybridization in the equilibrium configurations of either these compounds or the silyl halides, when one uses changes in bond angles as a measure of rehybridization. On going from CH_3I to CH_3Cl , the H-C-H bond angle decreases from 111.4° to 110.5° , a difference which is barely outside of the probable experimental error.⁵ For SiH_3Br , SiH_3Cl ,

(5) S. L. Miller et al., J. Chem. Phys. 20, 1112 (1952).

and SiH_3F , the X-Si-H bond angles are the same within experimental error: 108.5° , 108.9° , and 108.7° , respectively.⁶ Further evidence that only

(6) C. Newman, J. K. O'Loane, S. R. Polo, and M. K. Wilson, J. Chem. Phys. 25, 855 (1956).

minor changes in hybridization occur in these compounds is to be found in the relative constancy of the M-H symmetrical stretching frequency, ν_1 . In the CH_3I - CH_3F series, ν_1 decreases by only 5 cm^{-1} , and even after correcting for Fermi resonance, the decrease is only 12 cm^{-1} from CH_3I to CH_3Cl .² In the SiH_3I - SiH_3F series,^{6,7} which has no Fermi resonance, ν_1 increases by 14 cm^{-1} .

(7) H. R. Linton and E. R. Nixon, Spectrochim. Acta. 12, 41 (1958).

Any rehybridization which occurs in these series of compounds would most likely be just the opposite of that claimed by Bellamy and Williams. A large body of data⁸ indicates that, as the electronegativity of X increases,

(8) H. A. Bent, Chem. Revs. 61, 275 (1961).

the carbon orbital in the C-X bond gains p character, not s character.

We believe that the electrostatic repulsion between electrons in adjacent bonds, only briefly discussed as a possible explanation by Bellamy and Williams,² satisfactorily accounts for the frequency-electronegativity trends. As the electronegativity of the atom X in the H₃M-X group increases, the electron density in the M-X bond increases. This occurs because, as X becomes more electronegative, its bonding orbital becomes much more compact. A semi-quantitative idea of the change in bonding electron density as X becomes more electronegative can be gotten from Figure 2. It can be seen that as X becomes more electronegative, the repulsion between these bonding electrons and the M-H bonding electrons increases, even through the polarity of the M-X bond changes in the direction to make X relatively more negative. The more repulsion there is between the M-X and M-H bonding electrons, the more resistance is offered to the widening of the H-M-H bond angles. Consequently the potential well for the symmetrical deformation becomes steeper on one side, and the energy levels become more widely spaced.

In compounds of the first-row elements C, N, and O, the bonding electrons in adjacent bonds repel one another strongly, whereas in compounds of the second- and third-row elements (Si, P, S, etc.), these repulsions are much weaker.⁹ Thus one can explain the fact that the symmetrical deformation

(9) This explains why the bond angles in compounds such as NH₃ and H₂O are

Reference 9 continued:

large compared to those in compounds such as PH_3 and H_2S . It may also explain the slight trend in bond angles on going from CH_3I to CH_3Cl , and the absence of a trend on going from SiH_3Br to SiH_3F .

frequencies for methyl groups are quite high (1150-1475 cm^{-1}), whereas the corresponding frequencies for silyl and germlyl groups are relatively low (870-990 cm^{-1} and 780-860 cm^{-1} , respectively). As the M atom in the group $\text{H}_3\text{M-X}$ becomes larger, and the interaction between the M-X and M-H electrons becomes weaker, it is also to be expected that changes in the nature of the X atom will have a smaller effect on the bending frequencies of the molecule. Thus we find an explanation for the decrease in the slope of the frequency-electronegativity plot on going from methyl compounds to germlyl compounds.

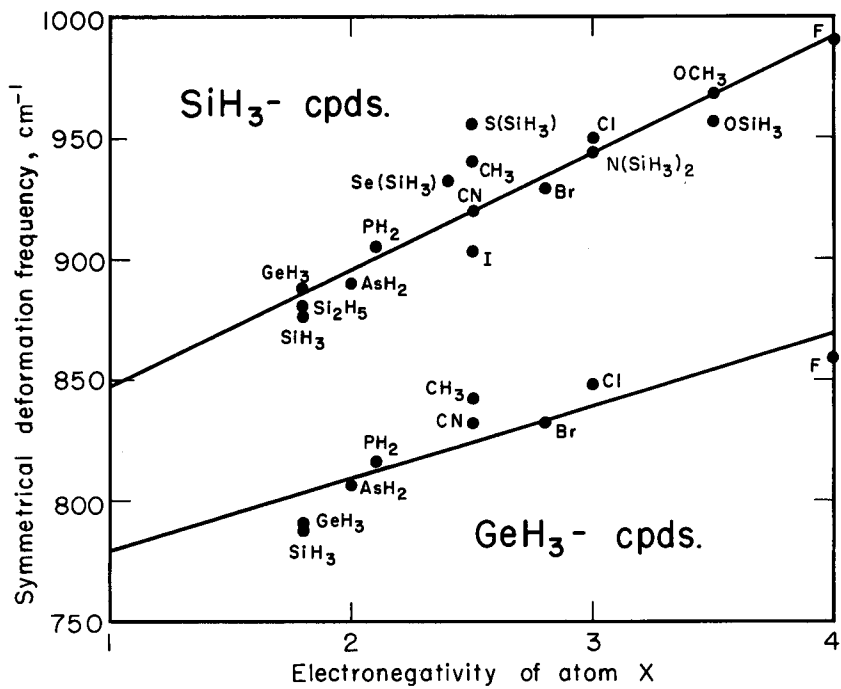
Acknowledgements

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Figure Captions

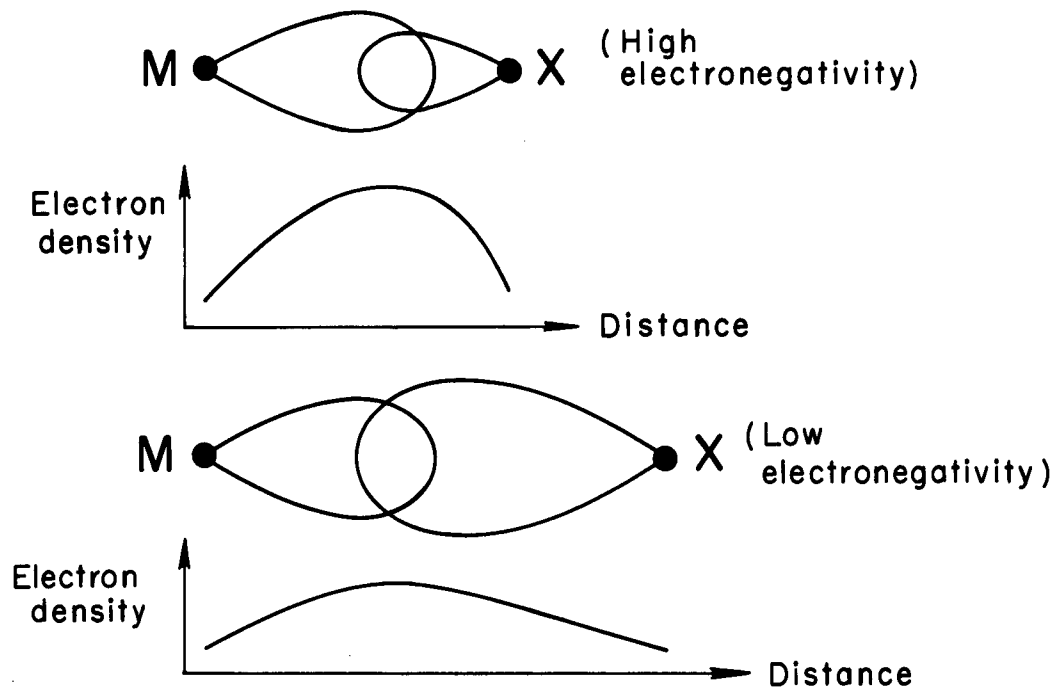
Figure 1. Symmetrical deformation frequencies for silyl compounds and germyl compounds versus electronegativities of the attached atoms.

Figure 2. Orbital overlap and resulting electron density in M-X bonds, for X of high electronegativity and for X of low electronegativity.



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Fig. 1



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Fig. 2

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