

frequency peptide carbonyl bands at 1640–1650  $\text{cm}^{-1}$  further increase in intensity as pD is increased to very high values. At the highest measured pD, however, only a single peptide carbonyl band is observed regardless of the number of peptide groups present. The observed complexity, therefore, is due to the fact that each peptide group is a different distance from the positive ammonium group and is influenced by its inductive effect to different degrees, thus giving rise to absorption bands of different frequency. It is therefore seen that the greater the number of peptide linkages, the larger is the number of low pD peptide carbonyl bands, resulting in an increasingly complex spectrum in this region.

The pK values for the over-all dissociation reactions were determined from plots of the type shown in Fig. 5 for triglycine. Similar plots were obtained for the other peptides. It is noted that the values obtained from two different absorption bands agree quite well for each dissociation step. The dissociation constants obtained from both spectral data and potentiometric measurement are listed in Table II.

### Discussion

It is interesting to observe that since the nature of the terminal amino group in the peptide species indicated in Plate I is reflected by the frequency of the peptide carbonyl, it is possible to identify each of the individual peptide species present in solution. At low and neutral pH the positive charge of the terminal amino group may be detected by the frequency of the adjacent peptide carbonyl group. This type of evidence, coupled with the solution conditions, would be useful in determining if a metal ion is coordinated to the terminal amino group. Similarly, the displacement of a proton from the peptide nitrogen atom by a metal ion would be expected to produce a large shift of the peptide carbonyl absorption to lower frequency. Effects of this type should be useful in the determination of the specific sites on the peptide molecule to which the metal ion becomes coordinated.

The variation of the relative intensities of ionized and un-ionized carboxyl absorptions with pH provide an interesting comparison of the zwitterion formation tendencies of the polyglycines. When one goes from

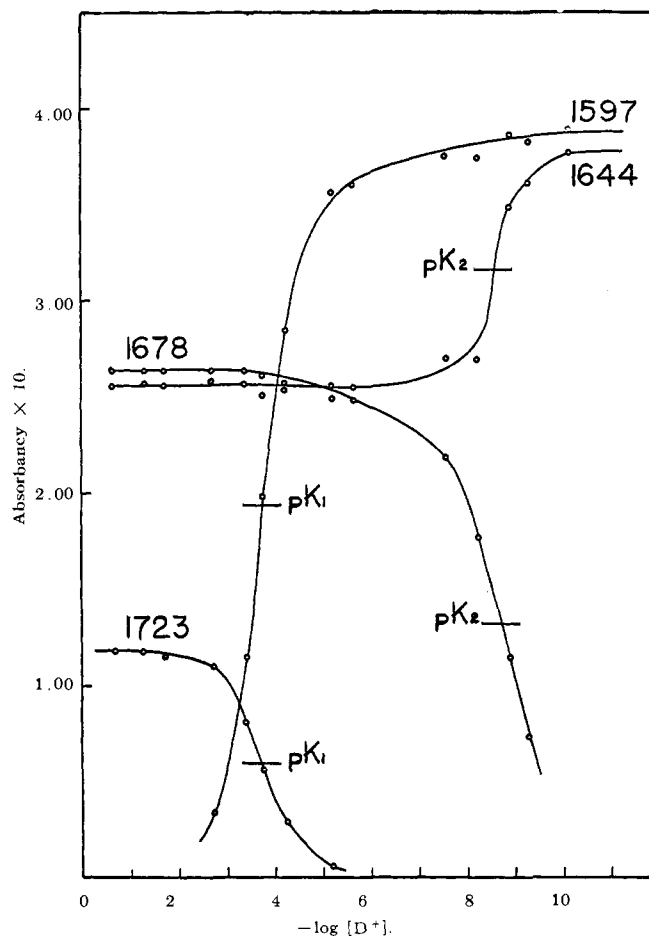


Fig. 5.—Variation of absorbance of glycyglycylglycine in  $\text{D}_2\text{O}$  as a function of  $-\log [D^+]$ ; frequency of absorption maxima indicated on curves.

glycine to tetraglycine, the carboxyl group is seen to persist to an increasing extent as the pH is increased in the acid range, whereas the carboxylate bands become less intense in the pH range just before they acquire maximum intensity. An analysis of this effect will be discussed in a future publication.

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## The Symmetrical Deformation Frequencies of Methyl, Silyl, and Germyl Groups

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

### Introduction

It has been pointed out<sup>1,2</sup> that the symmetrical deformation frequency of a  $\text{CH}_3-\text{X}$  group may be correlated with the electronegativity of the atom  $\text{X}$  (which may be bound to other atoms). A plot of the symmetrical deformation frequency against the electronegativity of  $\text{X}$  yields a series of parallel straight lines, each line corresponding to  $\text{X}$  atoms from a particular horizontal row of the periodic table.<sup>1</sup> 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

(1) N. Sheppard, *Trans. Faraday Soc.*, **51**, 1465 (1955).

(2) L. J. Bellamy and R. L. Williams, *J. Chem. Soc.*, 2753 (1956).

TABLE I

SYMMETRICAL DEFORMATION FREQUENCIES OF SILYL GROUPS

Compound	Frequency, cm. <sup>-1</sup>	Reference	Compound	Frequency, cm. <sup>-1</sup>	Reference
SiH <sub>3</sub> F	990	<sup>a</sup>	SiH <sub>3</sub> SCF <sub>3</sub>	940	<sup>i</sup>
SiH <sub>3</sub> OCH <sub>3</sub>	975	<sup>b</sup>	SiH <sub>3</sub> CH <sub>3</sub>	940	<sup>j</sup>
SiH <sub>3</sub> OSiH <sub>3</sub>	957	<sup>c</sup>	SiH <sub>3</sub> CN	920	<sup>k</sup>
SiH <sub>3</sub> Cl	949	<sup>a</sup>	SiH <sub>3</sub> I	903	<sup>l</sup>
(SiH <sub>3</sub> ) <sub>3</sub> N	944	<sup>d</sup>	SiH <sub>3</sub> SeSiH <sub>3</sub>	932	<sup>m</sup>
SiH <sub>3</sub> NCS	949	<sup>e</sup>	SiH <sub>3</sub> PH <sub>2</sub>	904	<sup>m</sup>
SiH <sub>3</sub> NCO	960	<sup>f</sup>	SiH <sub>3</sub> AsH <sub>2</sub>	890	<sup>n</sup>
SiH <sub>3</sub> Br	929	<sup>a</sup>	SiH <sub>3</sub> SiH <sub>3</sub>	876	<sup>o</sup>
SiH <sub>3</sub> SSiH <sub>3</sub>	956	<sup>g</sup>	SiH <sub>3</sub> SiH <sub>2</sub> SiH <sub>3</sub>	880	<sup>p</sup>
SiH <sub>3</sub> SCH <sub>3</sub>	959	<sup>h</sup>	SiH <sub>3</sub> GeH <sub>3</sub>	895	<sup>q</sup>

<sup>a</sup> Ref. 6. <sup>b</sup> B. Sternbach and A. G. MacDiarmid, *J. Am. Chem. Soc.*, **83**, 3384 (1961). <sup>c</sup> R. C. Lord, D. W. Robinson, and W. C. Schumb, *ibid.*, **78**, 1327 (1956). <sup>d</sup> D. W. Robinson, *ibid.*, **80**, 5924 (1958). <sup>e</sup> E. A. V. Ebsworth, R. Mould, R. Taylor, G. R. Wilkinson, and L. A. Woodward, *Trans. Faraday Soc.*, **58**, 1069 (1962). <sup>f</sup> E. A. V. Ebsworth and M. J. Mays, *J. Chem. Soc.*, 4844 (1962). <sup>g</sup> E. A. V. Ebsworth, R. Taylor, and L. A. Woodward, *Trans. Faraday Soc.*, **55**, 211 (1959). These authors have tentatively assigned the less intense of the two SiH<sub>3</sub> deformation bands to the A<sub>1</sub> modes. The reverse assignment would give a better electronegativity correlation. <sup>h</sup> B. Sternbach and A. G. MacDiarmid, *J. Inorg. Nucl. Chem.*, **23**, 225 (1961); an assignment analogous to that in reference *g* was made. <sup>i</sup> A. J. Downs and E. A. V. Ebsworth, *J. Chem. Soc.*, 3516 (1960); an assignment analogous to that in reference *g* was made. <sup>j</sup> S. Kaye and S. Tannenbaum, *J. Org. Chem.*, **18**, 1750 (1953); I. F. Kovalev, *Optika i Spektroskopiya*, **8**, 315 (1960). <sup>k</sup> H. R. Linton and E. R. Nixon, *Spectrochim. Acta*, **10**, 299 (1958). <sup>l</sup> Ref. 7. <sup>m</sup> H. R. Linton and E. R. Nixon, *Spectrochim. Acta*, **15**, 146 (1959). <sup>n</sup> J. E. Drake and W. L. Jolly, *Chem. Ind.* (London), 1470 (1962). <sup>o</sup> 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,  $\nu_2$  and  $\nu_6$ . <sup>p</sup> E. J. Spanier and A. G. MacDiarmid, *Inorg. Chem.*, **1**, 432 (1962); assignment by the author. <sup>q</sup> E. J. Spanier and A. G. MacDiarmid, *ibid.*, **2**, 215 (1963); assignment by the author.

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 Fig. 1 against the Pauling electronegativities<sup>3</sup> of the atoms to which the silicon and germanium 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 germlyl compounds. The slope of the silyl compound line is 48 cm.<sup>-1</sup> per electronegativity unit, and the slope of the germlyl compound line is 30 cm.<sup>-1</sup> per electronegativity unit. These slopes may be compared with that for methyl compounds, approximately 65 cm.<sup>-1</sup> per electronegativity unit.<sup>1,4</sup>

It is interesting that if one plots the symmetrical deformation frequencies for either methyl, silyl, or germlyl 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 Fig. 1 into a family of lines, we have not presented these plots.

### Discussion

Bellamy and Williams<sup>2</sup> explain the frequency shift on going from CH<sub>3</sub>I to CH<sub>3</sub>F 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

(3) L. Pauling, "The Nature of the Chemical Bond," 3rd Ed.; Cornell University Press, Ithaca, N. Y., 1960.

(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.<sup>-1</sup> per electronegativity unit.

TABLE II

SYMMETRICAL DEFORMATION FREQUENCIES OF GERMYL GROUPS

Compound	Frequency, cm. <sup>-1</sup>	Reference	Compound	Frequency, cm. <sup>-1</sup>	Reference
GeH <sub>3</sub> F	859	<sup>a</sup>	GeH <sub>3</sub> PH <sub>2</sub>	816	<sup>e</sup>
GeH <sub>3</sub> Cl	848	<sup>b</sup>	GeH <sub>3</sub> AsH <sub>2</sub>	806	<sup>e</sup>
GeH <sub>3</sub> Br	832	<sup>a</sup>	GeH <sub>3</sub> SiH <sub>3</sub>	788	<sup>f</sup>
GeH <sub>3</sub> CH <sub>3</sub>	842	<sup>c</sup>	GeH <sub>3</sub> GeH <sub>3</sub>	795	<sup>g</sup>
GeH <sub>3</sub> CN	832	<sup>d</sup>			

<sup>a</sup> J. E. Griffiths, T. N. Srivastava, and M. Onyszchuk, *Can. J. Chem.*, **40**, 579 (1962). <sup>b</sup> R. C. Lord and C. M. Steese, *J. Chem. Phys.*, **22**, 542 (1954). <sup>c</sup> J. E. Griffiths, *ibid.*, **38**, 2879 (1963). <sup>d</sup> T. H. Goldfarb, *ibid.*, **37**, 642 (1962). <sup>e</sup> J. E. Drake and W. L. Jolly, *Chem. Ind.* (London), 1470 (1962). <sup>f</sup> E. J. Spanier and A. G. MacDiarmid, *Inorg. Chem.*, **2**, 215 (1963). <sup>g</sup> 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,  $\nu_2$  and  $\nu_6$ .

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<sub>3</sub>I to CH<sub>3</sub>Cl, the H-C-H bond angle decreases from 111.4° to 110.5°, a difference which is barely outside of the probable experimental error.<sup>5</sup> For SiH<sub>3</sub>Br, SiH<sub>3</sub>Cl, and SiH<sub>3</sub>F, the X-Si-H bond angles are the same within experimental error: 108.5°, 108.9°, and 108.7°, respectively.<sup>6</sup> Further evidence that only minor changes in hybridization occur in these compounds is to be found in the relative constancy of the M-H symmetrical stretching frequency,  $\nu_1$ . In the CH<sub>3</sub>I-CH<sub>3</sub>F series,  $\nu_1$  decreases by only 5 cm.<sup>-1</sup>, and even after correcting for Fermi resonance, the decrease is only 12 cm.<sup>-1</sup> from CH<sub>3</sub>I to CH<sub>3</sub>Cl.<sup>2</sup> In the SiH<sub>3</sub>I-SiH<sub>3</sub>F series,<sup>6,7</sup> which has no Fermi resonance,  $\nu_1$  increases by 14 cm.<sup>-1</sup>.

Any rehybridization which occurs in these series of compounds would most likely be in just the opposite direction of that claimed by Bellamy and Williams. A large body of data<sup>8</sup> indicates that, as the electronegativity of X increases, the carbon orbital in the C-X bond gains p-character, not s-character.

We believe that the frequency-electronegativity trends may be accounted for in terms of two types of electrostatic repulsion: (1) repulsion between the M-H bonding electrons and the M-X bonding electrons and (2) repulsion between the M-H bonding electrons and nonbonding valence electrons on the X atom. (The first type of repulsion was only briefly discussed as a possible explanation by Bellamy and Williams.<sup>2</sup>) As these repulsions increase, 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. The fact that both types of repulsion become more important when the X atom becomes more electronegative is made reasonable by Gordy's observation<sup>9</sup> that electronegativities are proportional to the function  $(n+1)/r$ , where  $n$  is the number of valence electrons<sup>10</sup> and  $r$  is the covalent radius.

As the electronegativity of the atom X in the H<sub>3</sub>-M-X group increases, the electron density in the M-X bond increases. This occurs because, as X becomes

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

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

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

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

(9) W. Gordy, *Phys. Rev.*, **69**, 604 (1946).

(10) The function may be rewritten as  $(n'+5)/r$ , where  $n'$  is the number of nonbonding valence electron pairs on the atom.

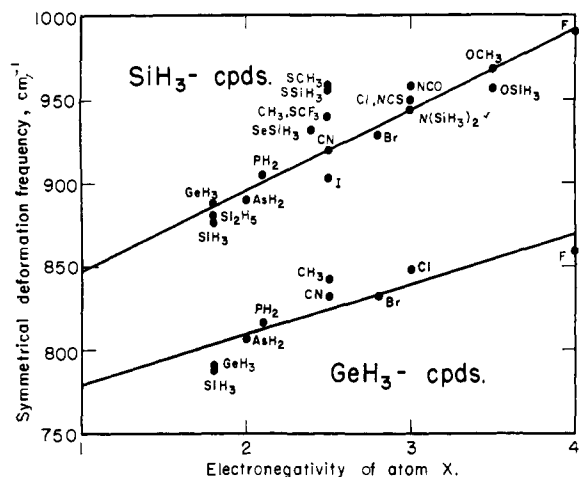


Fig. 1.—Symmetrical deformation frequencies for silyl compounds and germyl compounds *vs.* electronegativities of the attached atoms.

more electronegative, its bonding orbital becomes much more compact. A semiquantitative idea of the change in bonding electron density as X becomes more electronegative can be gotten from Fig. 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 though the polarity of the M-X bond changes in the direction to make X relatively more negative.<sup>11</sup>

If repulsion between the M-H and M-X bonding electrons were the only significant type of repulsion, then the  $MH_3$  symmetrical deformation frequencies for  $H_3M-SiH_3$  and  $H_3M-Br$  would be similar because the covalent radii of Si and Br are similar. In fact, the frequencies for  $H_3M-Br$  are considerably higher,

(11) Gillespie<sup>12</sup> has recently stated that "the repulsions exerted by bonding electron-pairs decrease with increasing electronegativity of the ligand," an assertion directly opposed to our ideas. We wish to point out here that the data which Gillespie quotes in support of his statement may be used as evidence for the exactly opposite statement. Thus the decrease in the bond angles in molecules of the type  $NX_3$ ,  $PX_3$ , and  $AsX_3$  with increasing electronegativity of X is probably in part due to the increased repulsion between the nonbonding electrons and the bonding electrons. (Lone-pair-bond-pair repulsions are more important than bond-pair-bond-pair repulsions.) Some of the increase in bond angle on going from  $NF_3$  to  $NH_3$  is probably due to rehybridization of the type discussed by Bent.<sup>8</sup> The small increase in bond angle on going from  $OF_2$  to  $H_2O$  is of opposite direction to that expected from the change in lone-pair-bond-pair repulsions, but is consistent with the expected rehybridization. The small increase is probably the resultant of these opposing forces.

(12) R. J. Gillespie, *J. Chem. Educ.*, **40**, 295 (1963).

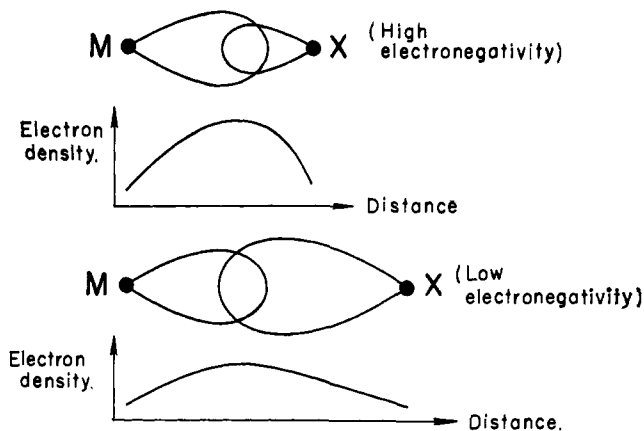


Fig. 2.—Orbital overlap and resulting electron density in M-X bonds for X of high electronegativity and for X of low electronegativity.

presumably because of the repulsive effect of the nonbonding electrons on the Br atom. The presence of the nonbonding electrons is also reflected in the fact that bromine has a much higher electronegativity than silicon.

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.<sup>13</sup> Thus one can explain the fact that the symmetrical deformation frequencies for methyl groups are quite high (1150–1475  $cm^{-1}$ ), whereas the corresponding frequencies for silyl and germyl groups are relatively low (870–990 and 780–860  $cm^{-1}$ , respectively). As the M atom in the group  $H_3M-X$  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 germyl compounds.

**Acknowledgments.**—The author has been greatly aided in this work by discussions with Professor G. C. Pimentel. This research was supported in part by the U. S. Atomic Energy Commission.

(13) This explains why the bond angles in compounds such as  $NH_3$  and  $H_2O$  are 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  $SiH_3F$ .