The spectra of these group IV (M = C, Si, Ge, and Sn) compounds show that induction from M increases in a sequence that qualitatively agrees with the Pauli-Gordy-Mulliken scale; the induction constant \( \sigma' \) for \((\text{CH}_3)_3\text{M}\) is \(- 0.3, - 0.72, - 0.76, \) and \(- 0.9\) in the four cases. M also acts as an electron acceptor, the effect increasing from Si via Ge to Sn; this and the induction determine the electron-density distribution in adjacent bonds. These concepts explain the anomalous behavior of the optical parameters and chemical shifts in the methyl derivatives of M. The analogy with the magnetic parameters indicates that the Olered-Rakhov electronegativity scale \( (\chi_\text{C}=2.6; \chi_\text{Si}=1.9; \chi_\text{Ge}=2.0; \chi_\text{Sn}=1.93) \) does not reflect the induction effects of M in pure form but provides a good measure of the sum of the electronic effects. The present results do not confirm the view that silicon transmits induction less readily than carbon.

Organic compounds of group IV elements are of some considerable interest \((M = C; Si, Ge, or Sn)\); the bond type varies in a regular fashion along the sequence. It becomes more metallic or ionic; moreover, the atom acquires specific features in its valency states. Carbon is always tetravalent in organic compounds, whereas Si and Ge exhibit valencies up to six when their higher orbitals are used, and tin up to eight \([1]\). Many major aspects of the atomic interactions remain unclarified, in spite of the very extensive work on these compounds; in particular, there is no generally accepted scale of electronegativities for the M, so the relative effects of induction and bond polarity cannot be evaluated. This is also reflected in discussions on the role of the \(d\)-orbitals of Si, Ge, and Sn, and also on the donor-acceptor bonds formed with the \(\pi\) and \(p\) electrons of \(-\text{CH}=\text{CH}_2, \text{C}_6\text{H}_5\) groups, and with oxygen, nitrogen, and so on \([1, 2]\).

I show here that valuable information can be derived from the intensities and frequencies of characteristic bands for the hydrides and alkyls of group IV; this clears up many obscure points in the literature. The results are compared with ones from NMR.

**Methods**

The IR data given below were recorded with IKS-12 and IKS-14 spectrophotometers in solution in \(\text{CCl}_4\) in cells of constant thickness. The integral intensities were deduced \((10-15\%)\) by planimetry along band contours for the optical density as a function of wave number; overlapping bands were separated graphically in a few cases, on the assumption that the bands were symmetrical. The compounds were made at the Institute of Organic Chemistry, Academy of Sciences of the USSR, by Mironov et al. \([3]\).

**Discussion**

The IR spectra give reliable information on the interactions only if the frequency and intensity describe the properties of kinematically isolated groups or bonds. The \(\nu(M-H)\) valence vibrations in the hydrides are strictly characteristics \([4, 5]\), so it is best to start with these.

My data \([5, 7]\) on the \(\nu_\text{MH}\) have been compared with those in the literature \([8]\) to show that \(\nu_\text{MH}\) for \(R^{(\text{f}+\text{r})}_n \text{MH}_n\) \((R\) being various radicals, with \(n\) from 1 to 3) is linearly related to Taft's \(\sigma'\) for the \(R^{(0)}\). Joint calculations \([5]\) on \(f\), the force constant for the \(M-H\) bond, have been made for over 60 hydrides with this structure; \(f_\text{MH}\) obeys the linear relation

\[
\tilde{f}_\text{MH} = A + B \sum_{i=1}^{3} \sigma_i' \tag{I}
\]

\((A = 4.55, 2.82, 2.61, \text{and } 2.1 \text{ for } C, \text{Si, Ge, and Sn respectively, while } B = 0.037 \pm 0.002 \text{ for all}).\) This means that \(f_\text{MH}\) has a direct relation to \(\nu_\text{MH}\), so any frequency shift is a direct indication of the effects of \(R^{(0)}\). The physical significance of (I) is that the \(f\) (frequencies) are governed by two terms, one of which, \(A\), is dependent only on \(M\); this governs the features of the \(M-H\) bond in the hypothetical diatomic molecule. The second, \(B\), is nearly constant \((\text{very slightly dependent on } M)\) and represents the perturbation of the electron shell of \(M\) by the adjacent radicals. This alters the effective nuclear charge and hence \(f\) for \(M-H\). The effect is additive; the \(R^{(0)}\) produce independent effects.

There is little difference between the \(f\) or \(\nu\) given by (I) and found by experiment, especially for \(\nu(\text{Si-H})\) and \(\nu(\text{Ge-H})\), for which there is abundant evidence \([7, 8]\). Phenyl radicals are the only ones to produce marked deviations, probably because of specific interactions between the \(\pi\)-electrons and the heteroatom \([1, 5]\).

* Lead is not considered here, because I have no data of my own on its compounds.
Figure 1 shows the changes in the parameters of M and of the M – H bond: U is ionization potential, \( \nu_{\text{MH}} \) is valence-vibration frequency in a given type of molecule, \( f \) is force constant of the M – H bond [the A of (I)], and \( r \) is the MH interatomic distance. Nearly all are relative to C (e.g., \( f_{\text{SiH}} / f_{\text{CH}} \)). Mulliken’s definition [9] gives the electronegativity of an atom in a valency state, \( \chi_M \), as determined by half the sum of U and the electron affinity E, which is only 10-15% of U for these M. The similar trends in U and A (Fig. 1) thus show that A reflects the variation in \( \chi_M \) in the carbon-tin series. Existing electronegativity scales show no marked difference between C and Si; on average \( \chi_c = 2.55 \) and \( \chi_{\text{Si}} = 1.84 \) [10, 35], and so we have that \( \chi_{\text{Ge}} = 1.75 \) and \( \chi_{\text{Sn}} = 1.58 \). This is almost exactly the largely neglected scale proposed by Mulliken in 1949 [10]. The induction constants \( \sigma_{\text{C}(\text{CH}_3)} = -0.30 \) and \( \sigma_{\text{Sn}(\text{CH}_3)} = 0.72 \) [36], similarly give \( \sigma_{\text{Ge}(\text{CH}_3)} = -0.76 \) and \( \sigma_{\text{Sn}(\text{CH}_3)} = -0.9 \).

This result agreed well with the integral IR intensities (i.e., B), which are more sensitive to effects from R than \( \nu_{\text{MH}} \) is. Relation (I) is only very rough for the B; all we can say is that there is a general tendency for the intensity to fall when alkyl radicals attached to M (e.g., 0 to –0.15) are replaced by more electronegative atoms such as hydrogen (\( \sigma_{\text{H}} = 0.49 \)) or chlorine (\( \sigma_{\text{Cl}} = 2.9 \)). Some of these results are given in Table 1; each line gives the total intensity B (liter/cm²-mole) and \( B_0 \), the intensity per MH bond. The B decrease from left to right; they also increase substantially from top to bottom, on account of rise in the dipole moment of the M – H bond. The intensity for \( \nu_{\text{SnH}} \) in \( (\text{CH}_3)_2\text{SnH} \) is about 9500 units in this scale [11], which is about that found in the analogous germane.

The polarities of the M – H bonds probably follow the \( \sigma_{\text{M}(\text{CH}_3)} \); Table 1 and (I) show that the frequency falls as B increases, which is due to reduced M – H bond energy on account of the greater contribution from ionic states and also to loss of polarity in this bond when M is attached to electronegative radicals. The changes in the optical parameters (Fig. 1) are caused by this effect (induction).

### Table 1

<table>
<thead>
<tr>
<th>M</th>
<th>( R_3\text{MH} )</th>
<th>( R_5\text{MH} )</th>
<th>( R_5\text{Cl-MH} )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( B )</td>
<td>( B_0 )</td>
<td>( B )</td>
</tr>
<tr>
<td>C</td>
<td>2500</td>
<td>2500</td>
<td>4200</td>
</tr>
<tr>
<td>Si</td>
<td>8850</td>
<td>8850</td>
<td>13250</td>
</tr>
<tr>
<td>Ge</td>
<td>10000</td>
<td>10000</td>
<td>16000</td>
</tr>
</tbody>
</table>

\( B \) = total intensity, \( B_0 \) = intensity per MH bond, R is alkyl, and \( \oplus \) represents solutions in CC\( \text{Cl}_3 \)H [6].

Frequency change due to induction is not peculiar to the hydrides and is [14] to be found in most characteristic frequencies in the structurally similar compounds of the M.

The valence vibrations of the \( \text{CH}_3 \) group are highly characteristic in molecules of general formula \( X-\text{CH}_3 \); they are unaffected by the mass of X, but they and those for \( \text{CH}_2 \) are very sensitive (in both frequency and intensity) to the electronic nature of X [15]. The molecular extinction coefficient \( \varepsilon \) for the doubly degenerate valence vibration \( \nu_{\text{CH}} \) is on average 100 units per \( \text{CH}_3 \) group in the normal and branched-chain hydrocarbons [16] but is only 10-15 for esters or halides [8, 17]. OR and CI are electronegative substituents, so the fall in intensity is expected (Table 1); the effect arises from the electrons, because the IR and Raman intensities are proportional to the numbers of \( \text{CH}_3 \) groups for \( n \)-paraffins not containing polar groups [16, 18]. This would lead us to expect that the intensity of \( \nu_{\text{CH}} \) for \( M(\text{CH}_3)_4 \) would increase as M becomes less electronegative, but this is not found, for it actually falls sharply, while the frequency rises. Thus Si, Ge, and Sn act as electron acceptors in relation to C – H bonds in methyl groups.

Table 2 gives IR characteristics for the valence vibrations of \( \text{CH}_3 \) in \( M(\text{CH}_3)_4 \); the first column gives results for \( (\text{CH}_3)_2\text{C}-\text{CH} = \text{CH}_2 \), because \( (\text{CH}_3)_2\text{C} \) was not available. This is not important, because the \( \text{CH}_3 \) groups are linked to a tetrahedral carbon atom, while \(-\text{CH}=\text{CH}_2 \) and \( \text{CH}_2 \) are nearly equal in induction [13]. Table 2 reveals the unexpected behavior of the frequencies and intensities; \( \nu_{\text{CH}} \) shows a fall in intensity by about a factor two in each case when carbon