Infrared Gas-phase Intensities and Gas–Crystal Frequency Shifts in Group IVB Hydrides

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IN the light of recent discussion[1] of electronegativity values for the elements C, Si, Ge, and Pb, it is of especial interest to examine the infrared intensities of the vibration bands of Group IVB hydrides and the bond polar properties μ and $d\mu/dr$ which can be determined from them.

The intensities, Γ, of ν_3 and ν_4 of SnH_4 have now been measured in this laboratory, thereby extending previous work on CH_4,[2] SiH_4,[3] and GeH_4.[4,5] Of the two sets of values of μ and $d\mu/dr$ derived from the intensities (Table 1), set (2) is preferred on the grounds of the chemical resemblances between SiH_4, GeH_4, and SnH_4: an experimental choice was not possible as no SiD_4 was available.

TABLE 1

		SnH_4	(1)	(2)	GeH_4	SiH_4	CH_4
ν_3 1905·89†	Γ_3 23·9 ± 5%	$d\mu/dr$*	± 1·62	±1·70	±1·38	±1·23	±0·61
ν_4 ~679	Γ_4 50·4 ± 10%	μ*	± 1·81	±1·63	±1·21	±1·58	±0·33
		μ/r_e		0·96	0·79	1·06	0·30
	Electronegativity (Ref. 1)			3	2·0	1·90	2·60

Units: Γ in cm.²/mmole, μ in D, $d\mu/dr$ in D/Å, ν in cm.$^{-1}$
* Normal co-ordinates from I. W. Levin and H. Ziffer, *J. Chem. Phys.*, 1965, **43**, 4023.
† G. R. Wilkinson, private communication.

Inspection of Table 1 shows that it is possible to choose a set of values of $d\mu/dr$ which increase smoothly from CH_4 to SnH_4. This choice then entails a change in the sign of μ passing from CH_4 to SiH_4. The following interpretation may then be offered. The change in $d\mu/dr$ reflects primarily the change in polarizability of the central atom, which will increase along the series C, Si, Ge, Sn. The direction of $d\mu/dr$ is taken to be $\overset{+}{X}\text{–}\overset{-}{H}$. The values of μ on the other hand are likely to reflect (a) the equilibrium bond moment, and hence the electronegativity difference between the atoms; and (b) the extent to which bonding electrons "follow" the bonding vibration. It seems plausible that the value and direction here chosen for μ_{CH} ($\overset{-}{C}\text{–}\overset{+}{H}$) results at least in part from factor (b). However the values of μ/r_e for SiH_4, GeH_4, and SnH_4 run nicely parallel to the electronegativities proposed for these elements,[1] for the direction here assumed ($\overset{+}{X}\text{–}\overset{-}{H}$).

A feature of the spectrum of SiH_4 is the considerable depression of both vibration frequencies on change of phase from gas to crystal.[6] The gas–crystal frequency shifts of GeH_4 and SnH_4 (Table 2) repeat this phenomenon, the shift $\Delta\nu_4$ for SnH_4 of 43 cm.$^{-1}$ (= 679 − 636 cm.$^{-1}$) being particularly high.

If the shift arises from dipole–dipole forces then the Haas–Ketelaar equation[6] should apply:—

$$\Delta\nu_1 = (n^2 + 2)\Gamma_1.N_S/18\pi^2$$

TABLE 2

	SiH_4	GeH_4	SnH_4	Units
Γ_3 (Gas)	13·9	14·3	23·9	cm.²/mmole
$\Delta\nu_3$ (Gas–crystal)* ..	13	19·7	25	cm.$^{-1}$
Γ_4 (Gas)	43·7	29·9	50·4	cm.²/mmole
$\Delta\nu_3$ (Gas–crystal)* ..	34	26·7	43	cm.$^{-1}$

* This shift measures the distance of the "centre of gravity" of the observed crystal band from the band centre in the gas.

In the absence of refractive index data it can only be said that, qualitatively, the frequency shifts run parallel to the gas intensities. In particular, there is a different sequence of values for Γ_3 or $\Delta\nu_3$ (Si < Ge < Sn) than is found for Γ_4 or $\Delta\nu_4$ (Ge < Si < Sn). It seems probable then that dipole–dipole forces are at least an important factor in determining the shifts.

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[5] I. W. Levin, *J. Chem. Phys.*, 1965, **42**, 1244.
[6] D. F. Ball and D. C. McKean, *Spectrochim. Acta*, 1962, **18**, 1029.