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NOTE

ULTRAVIOLET ABSORPTION SPECTRA OF PERETHYLPOLYGERMANES AND -POLYSTANNANES

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As shown by Gilman[1] and Kumada[2] silanes of general structure $R(SiR_2)_nR$ show ultraviolet absorption. The first absorption maximum is shifted to longer wave length with increasing number of metal atoms in the chain. Shorygin *et al.*[2] observed the same phenomenon in polygermanes. They also give the spectra of $(CH_3)_6Sn_2$ and $(CH_3)_{14}Sn_6$. The phenomenon of bathochromic shift with increasing chain length is not typical for metal chains. It also occurs in normal hydrocarbons for which Raymonda and Simpson[4] give an explanation in terms of their independent systems model. Pitt, Jones and Ramsey[5,6] use molecular orbital theory to account for the shift in metal chains.

According to the latter theory a plot of transition energy versus $2\cos[\pi/(n+1)]$ gives a straight line the slope of which is equal to $\beta_g+\beta_e$[6]. These β's are exchange integrals between orbitals of neighbouring metal atoms. The subscript g refers to the ground state and the subscript e to the first excited state.

TABLE 1

ULTRAVIOLET ABSORPTION SPECTRA OF POLYMETAL COMPOUNDS[a]

n	$CH_3[Si(CH_3)_2]_nCH_3$		$C_2H_5[Ge(C_2H_5)_2]_nC_2H_5$		$C_2H_5[Sn(C_2H_5)_2]_nC_2H_5$	
	λ_{max} (nm)	$h\nu$ (eV)	λ_{max} (nm)	$h\nu$ (eV)	λ_{max} (nm)	$h\nu$ (eV)
2	192	6.45	202 sh	6.14	232 sh[b]	5.34
3	215	5.77	217.5 sh	5.70	250 sh	4.96
4	235	5.28	233.5	5.31	290 sh	4.28
5	250	4.96	248	5.00	310	4.00
6	260	4.77	258	4.81	325[b]	3.82
8	272.5	4.55				

[a] Spectra were recorded in cyclohexane solution using a Cary Model 15 spectrometer. [b] *Cf.* 210 nm for $n=2$ and 246 nm for $n=6$ in the permethyl compounds[3].

Several perethylpolygermanes and -polystannanes have been prepared in this Institute[7,8] and their ultraviolet absorption spectra measured (Table 1). The wave lengths of maximum absorption of the perethylpolygermanes are slightly higher than the data given by Shorygin *et al.*[3] for permethylpolygermanes, but the tin data are

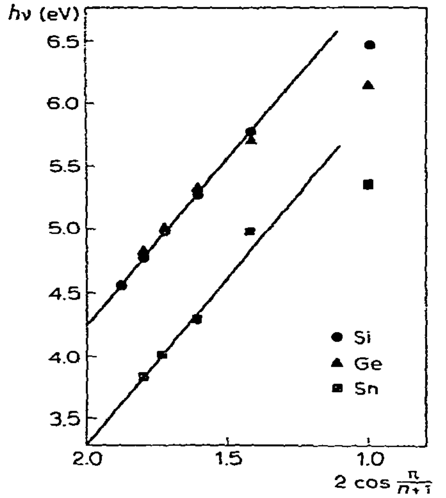

Fig. 1. Plot of $h\nu$ *vs.* $2\cos[\pi/(n+1)]$.

appreciably different.

Plots of transition energies corresponding with the data in Table 1, are given in Fig. 1. For comparison, transition energies of permethylsilanes[1] have been included. The silicon, germanium and tin lines are parallel. Thus, $\beta_g+\beta_e$ has equal value for Si–Si, Ge–Ge and Sn–Sn bonds. It amounts to -2.7 eV, compared to -1.7 eV for normal hydrocarbons[6].

In the series Si_2, Ge_2, Sn_2 metal–metal bond energies are approximately 3.0, 2.8 and 2.2 eV[9]. Assuming that β_g will parallel this change and, therefore, will increase to a less negative value, β_e has to decrease to a more negative value. This result indicates an increasing overlap of atomic orbitals which are the basis of the excited state molecular orbitals, in the series $Si \leqslant Ge < Sn$.

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