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ULTRAVIOLET PHOTOELECTRON SPECTROSCOPIC STUDY OF M–S σ BONDING ENERGY AND OF SPIROCONJUGATION EFFECTS IN GROUP IVA THIOSPIRANES

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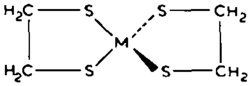
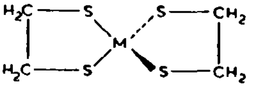
Summary

He(I) and He(II) ultraviolet photoelectron spectra of tetrathiometallaspiranes  (M = C, Si, Ge, Sn) yield data for quantitative characterization of several structural effects. Spiroconjugation of the lone pair orbitals of the sulfur atoms is indicated by the splitting patterns of the n_s ionization bands in the low IE region (8–9 eV); quantitative evaluation confirms that there is a marked decrease of the spiroconjugation effects with increasing size of M. Energy values are assigned by UP spectral analysis to M–S σ bond orbitals which show a small variation with M between ca. 10 and 11 eV, consistent with the small electronegativity variation, and to C–S bond orbitals in the spirane rings, fairly constant around 13.5 eV. Ionizations of the quasi-valence 4*d* orbitals in the Sn derivative are identified at 34.38 and 35.42 eV, and suggest, by comparison with other known Sn compounds, a considerably high overall electronegativity of the ligands in the present compound.

Introduction

As a part of a program of systematic investigation of the electronic structure of metal-organic compounds by UV-photoelectron spectroscopy (UPS) [1], we undertook a comparative study of the UP spectra, and of the corresponding structural implications, of a series of Group IVA tetrathiospiranes  (M = C, Si, Ge, Sn). The C compound has been investigated

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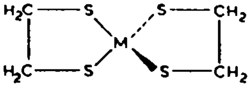
previously [2], and was reexamined giving results in good agreement with the previous findings in order to include the He(II) spectra and to provide data for comparisons. The Pb compound is unknown and is probably less stable; for the Sn compound, a preliminarly UPS study was reported [3], but the spectra were less resolved and in part at variance with ours, and furthermore were obtained only for He(I) irradiation.

Our interest in the above class of compounds was dictated by their relatively simple molecular structure, which should enable description of the electronic structure involving the S atoms and the M–S σ bonds, and by the presence of spiroconjugation [2,4–7], the extent of which can be conveniently measured by UPS [2], and can be studied in the present series as a function of the nature of the central atom M.

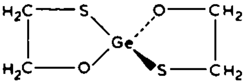
As a result, we can not only confirm the analysis of the spiroconjugation effect put forward by Kobayashi et al. [2] for the C compound, but also extend its interpretation to spiranes with larger central atoms, and more generally present an assignment of the UP spectra of the whole series, including quantitative evaluation of the M–S σ bond energies, in the usual framework of Koopmans' approximation [8].

Experimental

The investigated spiranes



(M = C, Si, Ge, Sn) were prepared by published methods [9–12] and their purities confirmed by their physical constants. For comparison purposes, the mixed dioxadithiospirane



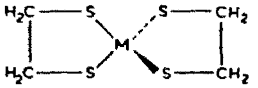
was also prepared [11] and its UPS recorded; instability, lack of reliable literature references on the synthesis, and possible complications by bridged polymeric structures prevented a full investigation of the whole series of corresponding dioxadithiospiranes.

Experimental structure determinations for the investigated molecules have not been reported; we assumed, as in previous work [2], an effective D_{2d} molecular point symmetry for the spiranes structure throughout the series of MS_4 spiranes, with approximate T_d environment around the M atom. Actually, non-planarity of the MS_2C_2 rings probably causes a further symmetry lowering from T_d, as discussed in ref. [2] but, to a first approximation the assumption of D_{2d} symmetry appears to be in reasonable agreement with UPS data, although minor effects due to lower symmetry are sometimes evident, e.g. in the splitting of the e(D_{2d}) pair of n_s orbitals in the C-spirane (see below).

UP spectra were measured in gas phase at temperatures in the range 110–130°C, except for M = Sn (160–170°C). The spectrometer was a Perkin-Elmer PS-18 instrument equipped with dual (He(I)/He(II)) source (Helectros Dev. Co.), and spectra were calibrated by known signals of reference gases (CH_3I, Ar and self-ionising He). All the compounds were completely stable under the employed conditions of UPS measurements. Our He(I) data are in excellent agreement with previous reports for M = C [2], but show marked qualitative and quantitative differences from previous findings for M = Sn [3].

Spectral assignments were assisted by comparison with quantum-mechanical computations of the MNDO type [13] (for M = C, Si) and the extended Hückel model EHT type [14] for the whole series, using the usual parametrization and assuming a D_{2d} geometry with standard values of interatomic distances and angles (C–S 1.81, Si–S 2.15, Ge–S 2.25, Sn–S 2.43 Å, S–Si–S 100, S–Ge–S 103°).

Results and discussion

The UP spectra of the investigated series of metallaspiranes 

(M = C, Si, Ge, Sn) allow a fairly detailed quantitative description of most significant features of their electronic structure. The relevant IE data, together with the gross assignments, are listed in Table 1, which also gives a comparison of experimental IEs with computed orbital energy (Koopmans) values for the MS_4, and the MO_2S_2 spiranes, respectively. The experimental spectra for He(I) and He(II) excitation are reproduced in Figs. 1 and 2.

Generally speaking, the UP spectra are fairly well resolved, at least in the low IE region ($\leq$ 15 eV); the assignments were performed by empirical procedures based both on comparison with assigned spectra of related simple molecules and on the effect of varying the excitation source (the decrease of relative intensity of S ionizations under He(II) being an indication of the participation of S atomic orbitals in the ionised levels), assisted by comparison with computed orbital energies (EHT and MNDO); the latter quantities were, as usual, somewhat higher in absolute values than the experimental IEs, but their sequence usually matched very closely the sequence of levels inferred from empirical assignment criteria, apart from a few minor inversions (typically artifacts of the adopted computational methods), which are discussed below.

For classification and assignment purposes, the experimental UP spectra of all investigated substances can be divided into at least five distinct regions:

Region A. Narrow bands, occurring with (partial) resolution into 4 components between ca. 8 and 9 eV IE, and of strongly decreasing relative intensity in He(II), are assigned to ionization of combination of the four sulfur lone pairs n_S (or of $n_S + n_O$ in the GeO_2S_2 derivative).

Region B. Broader, but still resolved bands between approximately 10.3 and 11.1 eV are due to ionization of the higher lying couple of M–S σ bonding orbitals.

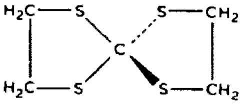
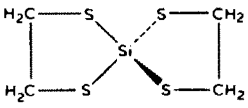
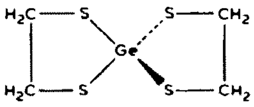
Region C. A series of less resolved bands extending from ca. 11.5 to 12.6 eV contains the ionization signals from the remaining σ (M–S) orbitals, probably overlapping and mixed with the highest σ orbitals of the aliphatic part of the spirane rings (σ(C–C)).

Region D. Around 13.5 eV, a broad but well defined band is assigned as the ionizations of the ring σ(C–S) bands; at higher energies ionization of σ(C–C) and σ(C–H) orbitals sets in, giving rise to a somewhat shapeless band contour, generally with a broad maximum around 15.2 eV.

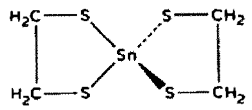
(Continued on p. 348)

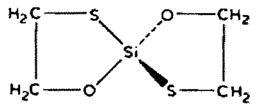
TABLE I

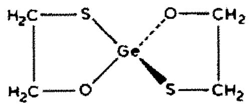
EXPERIMENTAL AND CALCULATED IONIZATION ENERGIES (eV) FOR SOME THIOSPIRANES OF GROUP IVA [a]

Region										
	Assignment [b]	Exp.	MNDO	EHT	Assignment [b]	Exp.	MNDO	EHT	Exp.	EHT
A	$n_S(a_2)$	8.23	10.17	12.00	$n_S(a_2)$	8.64	10.68	12.51	(8.62)	12.54
										12.70 [b]
	$n_S(e)$	8.75	10.37	12.29	$n_S(b_2)$	9.00	10.80	12.76	(8.87)	12.74
		9.00	10.37	12.29	$n_S(e)$	9.37	10.64	12.81	9.10	12.78
	$n_S(b_2)$	9.32	10.94	13.08		9.37	10.64	12.81	9.10	12.78
B	σ(M–S)	10.72	12.34		σ(M–S)	10.88	12.25		10.67	
	σ(M–S)	11.07	12.35		σ(M–S)	10.88	12.25		10.67	
C	σ(M–S)	11.89	13.46		σ(M–S)	11.70	12.53		11.77	
	σ(C–C)		13.66		σ(C–C)		13.71			
			13.79						12.18	
	σ(H–C–C–H)	11.58	13.88			12.61				
									12.46	
	σ(M–S)		14.77		σ(M–S)		13.91			
D	σ(C–S)	13.65			σ(C–S)	13.47			13.50	
	σ(C–S)	13.65			σ(C–S)	13.47			13.50	
E					$2D_{5/2}$					
					$2D_{3/2}$					

[a] Shoulders in parentheses. [b] Assuming D_{2d} symmetry. [c] σ ring.







	Assignment[h]	Exp.	EHT	Region	Assign-ment	MNDO	EHT	Exp.	EHT
A	$n_\pi(a_2)$	(8.80)	12.52[h]	A			12.11		12.33
			12.59						
	$n_\pi(b_2)$	(8.80)	12.67				12.40		12.53
	$n_\pi(e)$	9.06	12.93		n_S	10.54	12.75	9.18	12.83
		9.06	12.93		n_S	10.66	12.86	9.45	12.94
B	σ(M–S)	10.37		A′	n_O	11.03	13.66	10.16	13.80
	σ(M–S)	10.37			n_O	11.79	13.69	10.38	13.88
C	σ(M–S)	11.57		B				10.94	
				+				11.33	
				C				11.70	
	σ(C–C) σ(M–S)	12.16						(11.99)	
								12.48	
D	σ(C–S)	13.44						13.65	
	σ(C–S)	13.44						14.62	
E		34.38							
		35.42							

Region E. A spectral feature of particular interest is the occurrence of ionization signals from the quasi-valence orbitals of $4d$ type for the Sn compounds; although rarely and sometimes only indirectly observed, they are nevertheless of considerable interest for an evaluation of the total charge distribution in the investigated molecules. In the present case, the $^2D_{(5/2,3/2)}$ $(4d)$ doublet of Sn in the corresponding spirane was found at 34.38–35.42 eV; the corresponding Ge $3d$ ionization is expected at somewhat higher IEs, towards the limits of the He(II) range, and was not, in fact, observed in our experiments.

We now comment briefly on the spectral features in each of the above mentioned characteristic regions, providing a more detailed support for the proposed assignments, and discussing the implications and the correlations with the electronic and molecular structures of the series of metallaspiranes with special reference to the electronic structure of the sulfur atoms and of their bonds.

Region A. The n_s ionization bands of neutral (thioether-type) sulfur atoms are usually the lowest in the UP spectra of the corresponding molecules, and for organic compounds appear at energies slightly larger than 8 eV (cf. 10.47 eV in H_2S [15]; 9.42 eV in CH_3SH [16]; 8.67 eV in $(CH_3)_2S$ [17]; down to ~ 8.4 eV in cyclic compounds of $S(CH_2)_n$ type [2]). In the present compounds there are four n_S electron pairs, expected to give rise to three ionization peaks (1/1/2, $a_2/b_1/e$) in the ideal D_{2d} symmetry, or up to four peaks for lower-symmetric distortions in the molecular geometry. These multiplets appear between ca. 8.2 and 9.4 eV for all spiranes investigated here, with center of gravity around 8.8–9.0 eV, and overall splitting decreasing in the order C > Si > Ge > Sn. This assignment of such band systems to MOs almost purely based on atomic S $3p$ orbitals is supported by the strong decrease of relative intensity on passing from He(I) to He(II) excitation (see Fig. 1). The splittings between the n_S levels have been discussed by Kobayashi et al. [2], at least for the C compound, and originate mainly in the through-space conjugation within each MS_2C_2 ring and in the "spiroconjugation" effect resulting from interaction between the antisymmetric n_S couples of both MS_2C_2 rings. Thus for all the investigated compounds the separate n_S singlets, when distinguishable, correspond to the symmetric and antisymmetric ring-ring contribution of antisymmetric n_S ring couples, separated in a single LCBO treatment [2] by 4 β (β being the inter-ring S–S resonance integral for spiroconjugation), whereas the double component band corresponds to the degenerate or nearly degenerate symmetric n_S couples of the two rings, which cannot, by symmetry, undergo spiroconjugation inter-ring effects. The energy difference between the latter double component, and the center of gravity of the split singlets should be, in the simplest LCBO model, equal to 2 β' (through-space intra-ring S–S resonance integral).

The experimentally observed trends show that the overall splitting, i.e. the influence of the spiroconjugation effect, decreases in the order C > Si > Ge > Sn, as expected from the increasing size of M and thus the increasing S–S inter-ring distance; actually, for the Sn compound the separate components could not be detected, but showed up as shoulders on the composite band profile. The centers of gravity are not significantly affected by the nature of M; the value for Si is slightly higher (9.09 against an average of 8.88 eV), but it is doubtful whether this effect has a simple meaning, in the light of the subsequent considerations; in any case, the insensitivity of the average n_S ionization energy to the nature of M supports the view that the ionized orbitals are purely S in character, with very small, if any, admixture

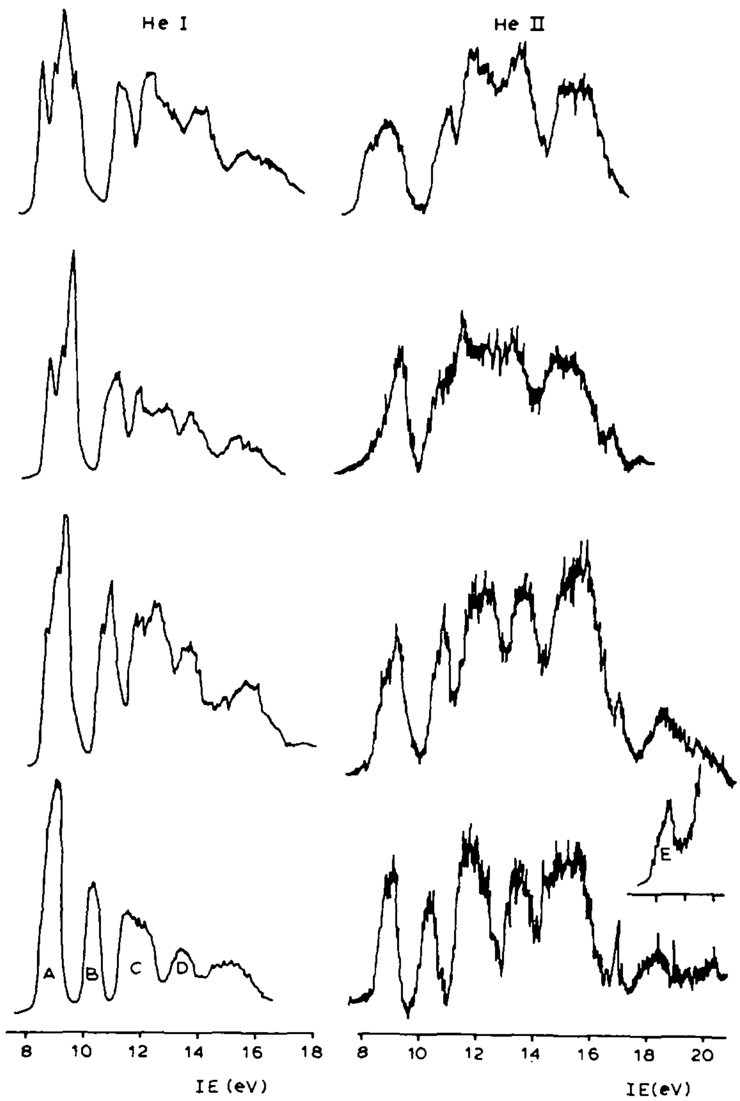
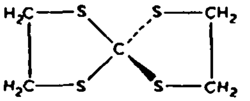
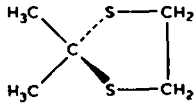


Fig. 1. Gas-phase UP spectra of $M(S_2C_2H_4)_2$ (from top to bottom M = C, Si, Ge, Sn).

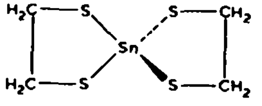
of M. A small inductive effect due to the environment of M can be seen from the comparison of the n_S centers of gravity of 8.82 in



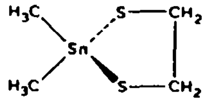
against 8.73 eV in



[18] or 8.93 in



against 8.71 eV in



[18].

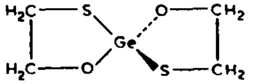
TABLE 2

RESONANCE INTEGRALS FOR S-S SPIROCONJUGATION (β') AND THROUGH-SPACE CONJUGATION (β) DETERMINED FROM THE EXPERIMENTAL IONIZATION ENERGIES

M	IE (eV) of n_S singlets (center of gravity)	IE (eV) of n_S doublet	IE (eV) of n_S (total) (center of gravity) $\simeq A_s$	β' (eV)	β (eV)
C	8.78	8.87	8.82	0.05	0.27
Si	8.82	9.37	9.09	0.27	0.09
Ge	8.73	9.10	8.92	0.18	0.04
Sn	8.80	9.06	8.93	0.13	0.00

One can also, following the simple LCBO scheme, try to extract values for β'(SS) and β(SS) from the experimental IE data and the results of such an analysis is presented in Table 2. However, such a simple model is probably inadequate because of neglect of ring-σ (as already pointed out in ref. [2]) and M-d interactions; but, in fact, the values reported in Table 2 correctly reproduce the decreasing trend of β' and β with increasing size of M, except for β' for M = C, the low value for which could perhaps be the result of lower symmetric distortions.

The existence of spiroconjugation effects is supported by theoretical calculations by both the MNDO and EHT methods, which confirm that all four n_S levels are the highest occupied MOs, well separated (with one exception) from the lower lying ones, and the decreasing trend of spiroconjugation splitting on going from C to Sn is also qualitatively reproduced. The quantitative agreement is less satisfactory: the computed overall spiroconjugation splitting is smaller than the experimental, particularly with MNDO, and even the relative ordering is sometimes inverted, e.g. the unsplit doublet, which is experimentally the lowest in orbital energy for Si, Ge and Sn (as expected also on the ground of the naive LCBO model), is predicted to be in the highest position for Si by MNDO, and EHT predicts overlap of a σ(C-C) orbital within the n_S composite band of Sn, which does not fit the experimental data. On the whole, however, quantum-mechanical predictions, although of low accuracy, confirm the occurrence of spiroconjugation and help in rationalising its origin and the observed trends through the investigated C to Sn series.

The mixed thiospirane  exhibits somewhat different spectral patterns in region A (see Fig. 2), in keeping with its lower symmetry, and with the expected energy separation between n_S and n_O levels. Actually, the experimental pattern is made up of two doublets (9.18-9.45 and 10.16-10.38 eV), with the former assigned essentially to the n_S, and the latter to the n_O couples, although calculations suggest a significant intermixing, which is however certainly not large, since the decrease in the intensity of the former doublet is much more pronounced in the He(II) spectrum, thus showing a large contribution of S $3p$.

Region B. The M-S σ orbitals are considered to be the next to be ionized, in order

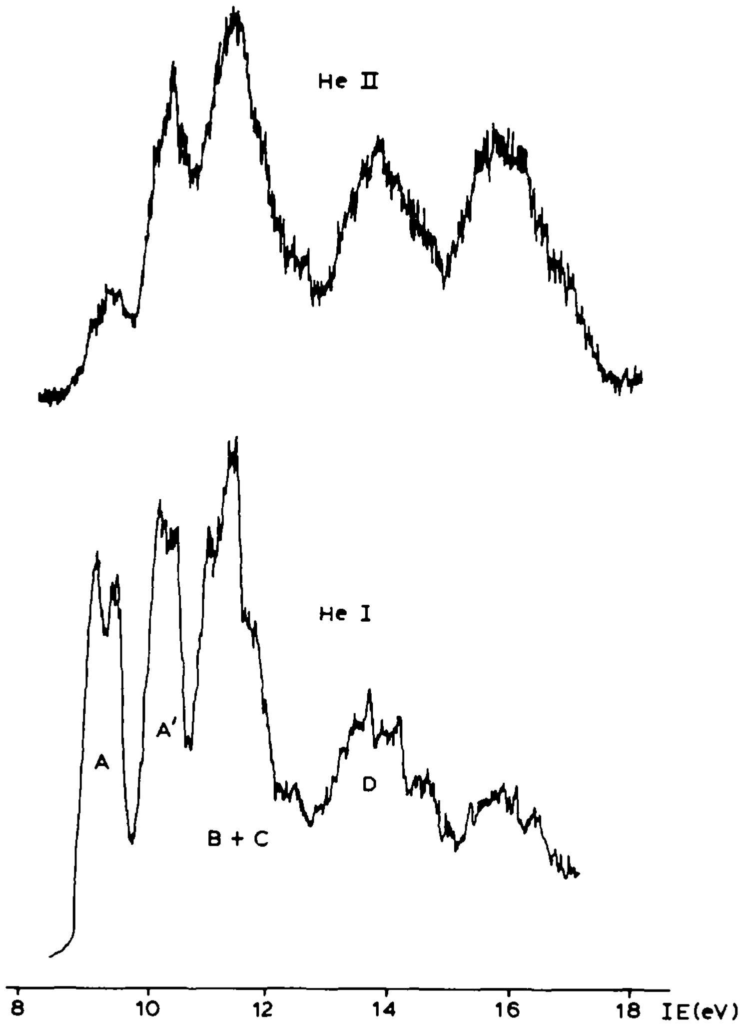
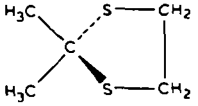
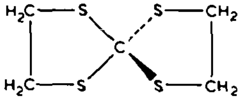


Fig. 2. Gas-phase UP spectra of $Ge(OSC_2H_4)_2$.

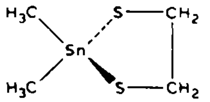
of increasing IE, both on the ground of empirical comparisons, and of theoretical predictions. The four M–S σ levels appear experimentally to be split into two doublets, the higher (in orbital energy) of which is fairly well separated from the neighbouring levels, and represents, in the UP spectrum, the section denoted by region B. Such separation is confirmed by theoretical predictions (actually in D_{2d} symmetry the higher doublet should be completely degenerate), and the situation lends itself to significant comparisons within the series, as well as with other related molecules. There is a slight decrease of ionization energy on going from the Si (10.88 eV) to the Sn compound (10.37 eV), which is consistent with increasing metallic character of M; again, the C compound does not fit in with this trend, and the practical identity of IE of σ(M–S) for M = C and M = Si is again reproduced by computation (MNDO). Another possible reason for the anomalous C behaviour could be lack of stabilising interactions with higher-lying *d* orbitals. Obviously, the overall effect of varying M throughout the series is larger for σ(M–S) than for n_S levels, since M orbitals are now directly involved in the former levels, and the same applies to changes in the environment of M; we can, e.g., compare the larger effect of methyl substituents on M (σ(M–S) at 10.53 in



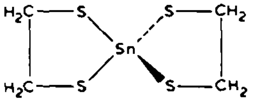
[18] against 10.90 eV (av.) in



and 9.80 in

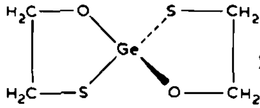


[18] against 10.37 eV in



It is difficult to set up a really significant comparison with IE values for σ(M–S) levels in other classes of metalorganic compounds; thus e.g. σ(M–S) levels are assigned much lower IEs in dithiochelates of organotin moieties (8.74 in $(CH_3)_3SnS_2CN(CH_3)_2$ or 8.53 eV in $(CH_3)_2Sn[S_2CN(CH_3)_2]_2$ [1]), and the differences would be even larger if we consider the second σ(M–S) couple of levels of tetrathiospiranes, but the low IE value reported for alkytin-dithiocarbamates or dithiophosphinates [1] is probably strongly influenced by the thiolic nature of the involved sulfur atoms, which belong to anionic ligands.

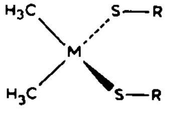
Less clear-cut is the situation for the mixed oxa-thiospirane



for which a composite band profile shows maxima or shoulders at 10.94, 11.32, 11.70, 11.99 and 12.18 eV, thus indicating less clear energy separation between the couples of σ(Ge–O) and σ(Ge–S) levels, a situation which can be described as merging of the B and C regions for this compound.

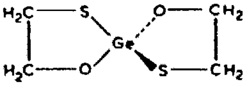
Region C. This region, extending approximately between 11.5 and 12.6 eV, is less well resolved, and contains the lower doublet of σ(M–S) levels, (now split), plus probably one level of the σ(C–C) type, and possibly some admixture of σ(C–H). Such admixtures are suggested particularly by MNDO predictions for the C and Si compounds, and are not unlikely on the ground of empirical correlations with related organic molecules, although occurrence of σ(C–C) or σ(C–H) ionizations below 14–15 eV is rather rare in linear organic chains. The resolution in the spectra of the present series of spiranes is rather limited, and does not allow identification and assignment of single components, nor significant structural comparisons.

Region D. A peculiar feature of the UP spectra of all investigated tetrathiospiranes is the occurrence of a broad band, distinctly separated from the neighbouring bands, with remarkably constant IE (13.55 ± 0.10 eV at the maximum). Both the quantum-mechanical calculations and comparison with other sulfur-containing organic molecules suggest that this band is due to ionization of the highest σ(C–S) bonds, probably to the two highest ones; for example, σ(CSH) appear at 13.9 eV in CH_3SH [16], while lower values (ca. 12–12.5 eV) were reported for



systems [18], probably due to the effect of methyl substituents at M.

The near-constancy at ca. 13.5 eV of our band D is consistent with the σ(C–S) assignment (no strong direct influences of M). Band D does not appear separately for

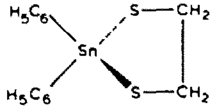


a more complicated profile being produced by extensive band overlapping.

Further ionization bands, beginning usually with a broad peak around 15 eV, are considered to be due to σ(CH) and the remaining σ(CC) bonds, and are not particularly informative about the electronic structure of the M atom and of its immediate environment.

The effects discussed above and the comparison between the different compounds along the series are presented diagramatically in Fig. 3 as a correlation diagram of the experimental IEs for the four tetrathiospiranes.

d Bands are expected from the Sn derivative, and are in fact, observed in He(II) at apparent b.e. values of 26.82 and 27.86 eV, due to excitation by the He(II) satellite at 48.10 eV. This corresponds to actual b.e. values of 34.38 and 35.42 eV for $^2D_{(5/2,3/2)}$(Sn 4d), which, if compared with e.g. 34.08–35.07 eV in



[1], 34.91–36.05 eV in $SnCl_4$ [19], and 32.59–33.61 eV in $(CH_3)_2SnCl_2$ [20], suggest that the environment exerts a considerable electron-withdrawing effect on Sn, the effective ligand electronegativity being not much lower than in the $SnCl_4$ molecule. This result is in agreement with the high value of $3d_{(5/2)}$ b.e. found for the same compound by Willimen et al. in a XPS study [21].

Conclusions

The UPS investigation of this series of tetrathiospiranes of Group IVA elements has revealed a number of features which help considerably in assigning and

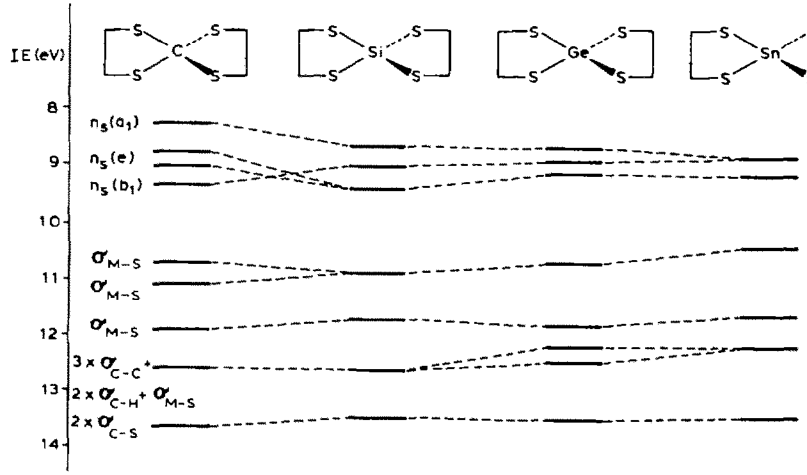


Fig. 3. Correlation diagram of the experimental I.E.'s for some tetrathiospiranes of Group IVA.

interpreting the electronic structure of the investigated molecules, and confirms the applicability and usefulness of the UPS technique for study of spirane-type organometallics. The UPS data yield good evidence for spiroconjugation effects and for their quantitative evaluation, and the dependence of these on the nature of M. The data also confirm the critical dependence of such spiroconjugation on inter-ring distances, and thus on the size of the central M atom. Trends in orbital energies of both M–S and C–S σ bonds are revealed by quantitative comparisons between corresponding spectral features (bands B, C and D); the overall effect is rather small, as expected on the ground of the small electronegativity difference between Si, Ge and Sn, while C has a special position, falling slightly outside the pattern for the heavier Group IVA elements. The series of molecules studied in the present work is also of interest in that the interpretation of the electronic structure can be reached by viewing the involved molecules either as a particular class of substituted organic molecules, or as tetrahedral coordination compounds, and this represents therefore a point of convergence for models typical of inorganic and of organic chemistry. It should also be noted that UPS investigations can be extended to quasi-valence orbitals (in the present case, $4d$ of Sn), which are significant since their b.e. values represent probes for the intramolecular potentials and atomic charge distributions, and make a significant contribution to the overall description of the molecular electronic structure.

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