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Vacuum ultraviolet and photoelectron spectra of dimethyl- and trimethyl-stannane

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Abstract

The vacuum ultraviolet spectra of dimethyl- and trimethyl-stannane between 220 and 110 nm are reported.

Comparison of the spectroscopic data (photoelectron and vacuum UV) for compounds of general formula $SnH_n(CH_3)_{4-n}$ have been used to reveal the effects of methylation on the stability of radical ions and the first Rydberg states. A comparison with results for the corresponding alkane, silane and germane series reveals a progressive increase in the energy of the valence electrons as the atomic number of the central atom increases.

Introduction

The structures of stannanes are similar to those of hydrocarbons, a carbon atom having been replaced by a tin atom. However, the presence of the tin atom considerably changes the properties of these compounds. In recent years, much work has been carried out in these compounds because of their theoretical interest (arising from the presence of the carbon–metal bond) and the practical applications of organotin species. Electron and photoelectron spectroscopy combined with quantum mechanical calculations are the best techniques for providing a more thorough understanding of the electronic structures of such compounds.

The aim of this work was to provide a consistent interpretation of the electron structure and spectroscopic properties of the stannane species $SnH_n(CH_3)_{4-n}$.To complement published data on this group of compounds, we have recorded for the first time the vacuum ultraviolet (VUV) spectra of $SnH_2(CH_3)_2$ and $SnH(CH3)_3$. The photoelectron and electron spectra of these compounds are discussed in the light of the results of SCF ab initio calculations.

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Experimental

Dimethyl- and trimethyl-stannane were prepared by reduction [1] with $LiAlH_4$ of dimethyltin dichloride and trimethyltin chloride in di-n-butyl ether. The dimethyltin dichloride and trimethyltin chloride were purchased (Merck), and used without further purification. The di-n-butyl ether was dried by refluxing over sodium metal under nitrogen and subsequent distillation. The reaction was also carried out under nitrogen. Most of the solvent was removed from the reaction mixture by trap-to-trap distillation before the product was fractionably disfilled on a suitable column under vacuum. The purity and identity of the product were checked by gas-phase IR spectroscopy [2,3].

The UPS spectra were recorded on a Perkin–Elmer PS18 photoelectron spectrometer and calibrated against Ar and Xe lines. The He(1) resonance line served as the ionization source.

The VUV spectra were recorded with a laboratory-made vacuum UV spectrometer of moderate resolution [4], and the radiation source was a windowless spark (BRV source) [5]. The main drawback with this type of source, the non-reproductibility of flashes, was overcome in two ways. A beam splitter which separates the sample and the reference is used, and as the spectrometer is entirely run by computer, we can use recording algorithms combining filtration and accumulation in real time. A 10 cm path-length cell equipped with lithium fluoride windows was used. Two photomultipliers (reference and sample) associated with two sodium salicylate coated windows were used as detector.

Theoretical methods

Ab initio SCF-MO calculations were undertaken using a relativistic pseudopotential to describe the tin core electrons as proposed by Durand et al. [6]. This type of ab initio pseudopotential takes account of major relativistic corrections (mass and Darwin corrections) and gave us good results in the study of the photoelectron spectrum of closely related molecules [7,8]. The basis set on the tin atom was a double ζ quality basis set (6) augmented by a set of d polarization orbitals ($\zeta = 0.20$) [9]. Dunning's ($9s5p$) Gaussian basis set contracted to ($4s2p$) for the carbon atom was used [10], while for the hydrogen atom the basis set was the ($2s$) contraction derived by Dunning from the ($4s$) primitive functions [10]. Calculations were performed with the PSHONDO program [11] at experimental geometries [12,13], assuming idealized C_2 and C_{3v} structures for dimethylstannane and trimethylstannane, respectively. The C–H bond length and the H–C–Sn bond angle were assumed to be 1.083 Å and 110.36°, respectively in all the methyl groups [14].

The theoretical IEs were calculated by use of Koopman's theorem. In the length of our experience we rescaled these IEs by nine tenths as proposed by Bertoncello et al. [15]. This scaling factor seems to be appropriate to give a fit to the experimental values when Koopman's theorem is used to calculate the IEs of tin derivatives.

The absorption frequencies of vacuum UV electronic spectra were estimated by use of the well known formula [16].

$$\nu = \mathrm{IE} - \frac{R}{(n-\delta)^2}$$

where n is the quantum number, R the Rydberg constant, and δ the quantum deffect.

For both dimethylstannane and trimethylstannane was used the set of term values that we deduced from the SnH_4, SnH_3CH_3, and $Sn(CH_3)_4$ electronic spectra [7,8,16]: 3.0 and 1.9 eV for the *ns* and *np* series, respectively.

Results and discussion

Photoelectron spectra

The photoelectron spectra of dimethyl- and trimethyl-stannane (Fig. 1, Table 1) each contain two clearly distinct regions. The first broad band, located between 9 and 11 eV in each spectrum, includes three poorly defined peaks with considerable overlap. The peak values in this broad band in the dimethylstannane spectrum are 10.00, 10.45 and 10.90 eV, in good agreement with previously reported values [18] of 10.0, 10.5 and 11.0 eV. The values for trimethylstannane are 9.65, 9.90 and 10.65 eV, also in good agreement with published values [19].

Dimethyl stannane. The electron structure of the valence shell of dimethylstannane indicated by the pseudopotential ab initio calculations is: 1*a*1, 2*b*2, 2*a*1, 3*a*1, 1*a*2, 2*b*2, 2*b*1, 4*a*1, 3*b*2.

The IE's calculated after correction are in good agreement with the experimental values, the deviation being less than 0.4 eV.

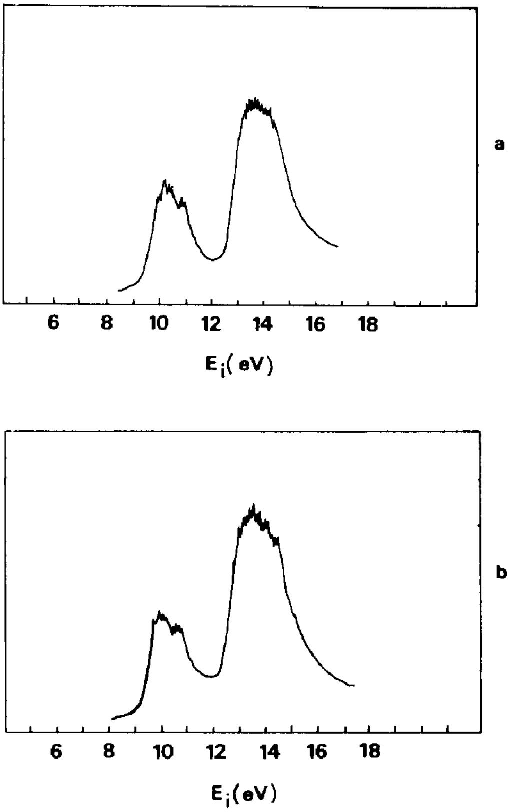

Fig. 1. Photoelectron spectra of (a): dimethyl- and (b): trimethylstannane.

Table 1

Calculated and experimental photoelectron spectra of dimethyl- and trimethyl-stannane

	MO	IE (eV)		Dominant character
		Calcd. [a]	exp [b]	
$SnH_2(CH_3)_2$	$3b_2$	9.57	10.00	σ(Sn–C)
	$4a_1$	10.02	10.45	σ(Sn–C)+ σ(Sn–H)
	$2b_1$	10.97	10.90	σ(Sn–H)
$SnH(CH_3)_3$	$4e$	9.56	9.65	σ(Sn–C)
	$4a_1$	10.33	10.60	σ(Sn–C)+ σ(Sn–H)
	$1a_2$	13.15	13.55	σ(C–H)

[a] Koopman SCF values rescaled by nine tenths. [b] This work. Other values reported in literature are (eV): $SnH_2(CH_3)_2$ [18]: 10.0, 10.5 and 11.0; $SnH(CH_3)_3$ [19]: 9.9 and 10.6.

The interpretation of the first ionization potentials of dimethylstannane involves interactions of the σ(C–Sn) and σ(Sn–H) bonds. The spectra of the methylstannanes are dominated by the Sn–C bond energy, which are lower than those for the Sn–H bond (in contrast to observations on the analogous family derived from methane [20,21]. Thus, the HOMO of dimethylstannane is formed almost exclusively by the antisymmetric combination of the two σ(Sn–C) orbitals. The b_2 orbital resulting from this combination is destabilized by about 0.65 eV compared with that for σ(Sn–C) of methylstannane [7] (Fig. 2). The a_1 orbital resulting from this mixture is, however, lowered sufficiently to be able to interact with the σ(Sn–H)

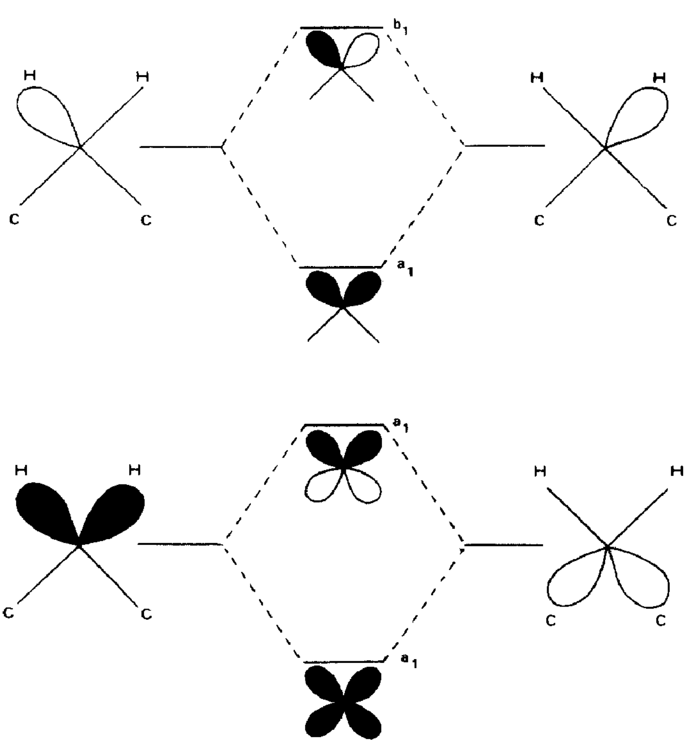

Fig. 2. Molecular orbitals of dimethylstannane.

orbitals. This leads to an antisymmetric combination (b_1) and to a more stable symmetric combination (a_1). As a result of symmetry, only the a_1 combination can interact with the a_1 orbital of σ(Sn–C). This is confirmed by the substantial contribution of Sn–H bonds to the $4a_1$ orbital, which causes a relative destabilization of this shell and brings it to 10.45 eV (whereas we would have expected an energy higher than that for the σ(Sn–C) level in methylstannane, situated a 10.65 eV).

The third IP of the first broad band (at 10.9 eV) is the b_1 orbital, and may be assigned to the asymmetric combination of the Sn–H bonds, the symmetrical combination giving to the deeper lower energy whose IP appears in the second broad band.

Trimethylstannane. The valence orbitals of trimethylstannane have the following symmetries: $1a1$, $1e$, $2a1$, $3a1$, $2e$, $3e$, $1a2$, $4a1$, $4e$.

The ionization energy of the HOMO results from the departure of one electron from a double degenerate orbital primarily involving the Sn–C bonds. This ionization is accompanied by a Jahn–Teller effect [22] which causes a splitting of the band (9.65 and 9.90 eV). The 0.25 eV Jahn–Teller splitting is much lower than that observed in the case of SnH_4 [23] and SnH_3CH_3 [24], namely 0.4 to 0.5 eV. It should nevertheless be noted that in both of these latter molecules this splitting involved principally the Sn–H bonds. It is possible that when bulky substituents such as methyl groups are present the splitting arising from a substantial geometric rearrangement is less important because of steric hindrance. This can be verified by examining the photoelectron spectrum of $Sn(CH_3)_4$. Although splitting in this case cannot be measured, it is obvious that the first broad band is much narrower than that for SnH_4.

The third band of the $SnH(CH_3)_3$ spectrum at 10.60 eV can be assigned to the ionization of the $4a_1$ orbital, which involves principally the symmetrical combination of the Sn–C bonds. The MO corresponding to the other bonds are shifted to the broad band centered at 13.5 eV.

Vacuum UV spectra

The gas phase electron spectra of dimethyl- and trimethyl-stannane (Fig. 3) show that neither compound absorbs below 200 nm. The shapes of these spectra are relatively similar and are characterized by broad bands, relatively unstructured and weakly resolved, and so difficult to interpret. In order to facilitate the VUV attribution, the first band in the spectrum was deconvoluted by a set of Gaussians to fit the experimental results. Although this fit is relatively arbitrary when the bands are complex and overlap considerably, it does furnish the order of magnitude of the oscillator strength of a band. The results are summarized in Table 2.

$SnH_2(CH_3)_2$. The lowest absorption of dimethylstannane is a shoulder at 178.3 nm. Calculations by use of 1 indicate a value of 171 nm. The estimated oscillator strength for this transition is 0.148, and it can be assigned to the excitation of a $3b_2$ electron towards the $6s$ Rydberg orbital. The term value (3.05 eV) is in good agreement with results for other organotin compounds [2,3,12]. The oscillator strength of 0.148 is reasonable for an essentially Rydberg transition.

A broad band centered at around 155 nm dominates the lower region of the spectrum. The fit of this part suggests several transitions within the broad band, the lowest being at 169 nm. This band could in principle be assigned to the $3b_2 \rightarrow 6s$

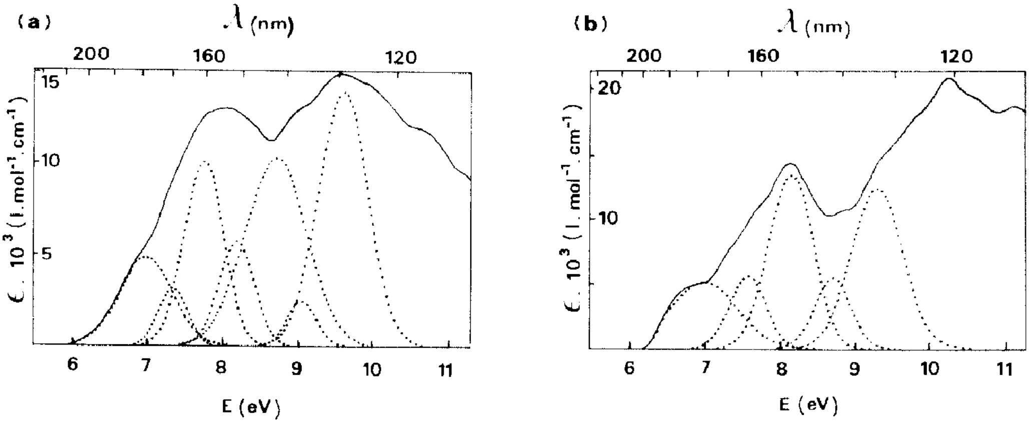

Fig. 3. Vacuum UV spectra of (a): dimethyl- and (b): trimethyl-stannane.

Rydberg transition, but on the basis of calculations on methyl- and tetramethylstannane [7,8], this band can be assigned preferentially to an excitation of the second occupied $4a_1$ level towards the diffuse $6s$ orbital (term value 3.13 eV). Similarly, the third transition situated a 161 nm can be interpreted as the $2b_1 \rightarrow 6s$ transition. The weak intensity of these bands agrees with their presumed Rydberg nature. This assignment is confirmed by the fact that the first three IP's in the photoelectron spectrum are 0.45 eV apart. The distance separating the first three Rydberg states is found to be about 0.40 eV, in keeping with the similarity generally observed between the Rydberg states and the parent ionic states.

As shown in Table 2, the higher absorptions can be assigned to Rydberg *p* transitions, which are mixed with valence type transitions. The assignment of these poorly resolved bands is uncertain and will not be discussed.

$SnH_2(CH_3)_3$. The lowest transition of trimethylstannane is a broad flat shoulder around 177 nm. The oscillator strength of this band is 0.206, indicating a notable intensity. On the basis of the photoelectron spectrum, this band is assigned to the $4e \rightarrow 6s$ transition (term value 2.92 eV). The corresponding Rydberg states are

Table 2

Vacuum UV spectra of dimethyl- and trimethyl-stannane. Tentative assignment

	(nm)	Oscillator strength	Transition
$SnH_2(CH_3)_2$	178.3 (171.1) [a]	0.128	$3b_2 \rightarrow 6s$
	169.0 (166.4)	0.052	$4a_1 \rightarrow 6s$
	160.7 (156.9)	0.225	$2b_1 \rightarrow 6s$
	152.0 (153.1)	0.114	$3b_2 \rightarrow 6p$
	142.8 (145.0)	0.362	$4a_1 \rightarrow 6p$
	137.2 (137.8)	0.042	$2b_1 \rightarrow 6p$
$SnH(CH_3)_3$	177.6 (182.9)	0.206	$4e \rightarrow 6s$
	163.8 (163.1)	0.121	$4a_1 \rightarrow 6s$
	152.3 (157.4)	0.354	$4e \rightarrow 6p$
	142.3 (142.5)	0.115	$4a_1 \rightarrow 6p$

[a] Values in parentheses are deduced using equation 1.

doubly degenerate and we can predict a Jahn–Teller coupling. The estimated intensity of this band, broad and relatively unstructured, agrees with this assignment. The next band in the fitted spectrum is at 164 nm, with an oscillator strength of 0.121. In the light of the assignment proposed for dimethylstannane, this transition is assigned to the excitation of level $4a_1$ towards the $6s$ orbital, rather than $4e \rightarrow 6p$. The term value of this excitation is 2.76 eV.

The second region of the spectrum is composed of bands between 160 and 135 nm. The most intense absorption at 152.5 nm has an oscillator strength of 0.354. This band can be assigned to an excitation toward the lowest Rydberg p states. The intensity of the band seem to be rather strong for a Rydberg transition (stronger that the transition towards $4s$ levels), although the term value of 1.63 eV is in good agreement with expectations for this type of transition. It is thus probable that the excited Rydberg p state involves a non-negligible mixture with antibonding valence levels (σ(Sn–C). These levels will be particularly low in these molecules because of the low Sn–C bonding energy. This phenomenon enables the peak at 142 nm to be assigned to the $4a_1 \rightarrow 6p$ transition (term value of 1.88 eV) observed, with an oscillator strength of 0.115.

The following regions of the spectrum contain the other transitions towards Rydberg levels, characterized by intense transitions.

Conclusion

As a summary of the photoelectron spectra, Fig. 4 presents a diagram of the changes in experimental IP values and their assignment for the $SnH_n(CH_3)_{4-n}$ compounds. Figure 5 shows the correlation with the electron spectra.

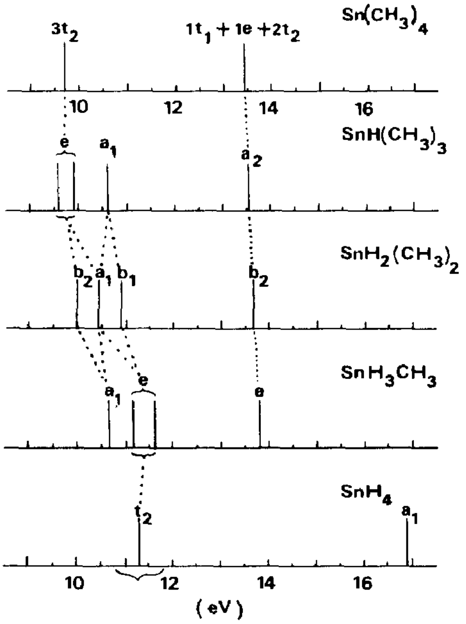

Fig. 4. Schematic evolution of stannane derivatives PES.

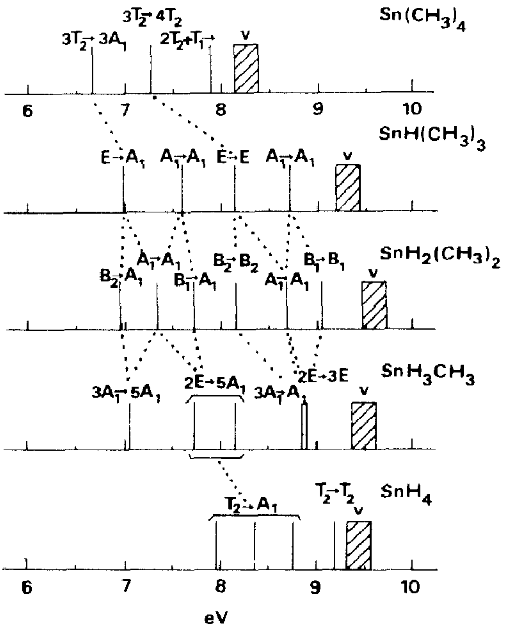

Fig. 5. Correlation of electronic spectra of stannane derivatives.

Figure 4 shows that the progressive substitution of hydrogen atoms by methyl groups causes IP shifts towards lower energies. This is due to the gradual destabilization of the Sn–C bond brought about by methylation. The high ionization energy of stannane is evidently due to the fact that this ionization arises from an Sn–H rather than from an Sn–C orbital. Shifts of this type have been reported for the analogous series of derivatives of other group 14 elements. The observed shifts nonetheless depend significantly on the nature of the central atom. When we go from XH_4 to $X(CH_3)_4$, the first IP decreases by 3.39, 2.25, 2.23, 1.57 eV for X-C, Ge, Si, Sn, respectively.

The lowest VUV absorption of $SnH_n(CH_3)_{4-n}$ compounds corresponds to a Rydberg transition towards 6*s* orbitals arising from the excitation of the σ(Sn–C) bond, except of course for SnH_4 where the bond in question is σ(Sn–H). As can be seen from the photoelectron spectrum, progressive substitution of hydrogen atoms by methyl groups is accompanied by a red shift of the first band, which is 46 nm lower in tetramethylstannane than in stannane. Similar shifts have been observed in the electron spectra of homologues the $MH_n(CH_3)_{3-n}$ derivatives of Group 14 other elements, although they are weaker in those cases: methane and neopentane are separated by 30 nm, and silane and tetramethylsilane by 34 nm. On going from carbon to tin, it can be seen that the red shift is due to increase in the degree of methylation, in contrast to observations for the photoelectron spectrum. This would suggest that permethylation of the SnH_4 molecule stabilizes the first excited Rydberg state more than the first ionic state. In contrast, the ground state CH_4^+ is stabilized more by permethylation that the parent Rydberg state [25,26].

The shift resulting from the presence of a heavy atom can be analyzed. Comparison of the photoelectron spectra of $XH(CH_3)_{4-n}$ compounds with the same degree of methylation, reveals that an increase in the atomic number of the central atom is accompanied by a decrease in the ionization energy. The same phenomenon is observed in the photoelectron spectra: a progressive red shift of the absorption spectrum is observed on going from the alkanes to the stannanes. This can be easily accounted for in terms of the fact that the first transition involves levels which involve the bonding orbitals between the central atom and the substituents. The passage from alkanes to stannanes is thus dominated by the considerable instability of tin atom valence electrons.

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