THE VACUUM ULTRAVIOLET SPECTRUM OF STANNANE

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The vacuum UV spectrum of SnH_4 has been recorded up to 110 nm (12 26 eV) This spectrum has been interpreted by ab initio calculations (SCF + CI), using a *relativistic* pseudopotential to describe the core electrons of the tin atom. The spectrum consists of a broad band composed of three maxima (at 8 73, 9 53 and 11 33 eV). The transitions below 9 50 eV have been attributed to transitions to diffuse Rydberg states (6s and 6p). The other bands are due essentially to valence transitions

1. Introduction

There is an obvious interest in stannanes both as hydrocarbon analogues and because of their unique organometallic chemistry Organostannane compounds have recently been implicated in certain environmental problems [1] In particular, the biological methylation of inorganic tin in sea water and the subsequent reaction of the first formed organostannic compounds are not well understood Certain photochemical reactions have been proposed as a mode of reaction of these stannanes These hypotheses are difficult to justify, however, while the UV spectra of these compounds are unknown

In fact, there is little experimental or theoretical data on tin derivatives, particularly on their electronic structure or excited states *Only* the photoelectron spectra of stannane [2] and some of its derivatives have been recorded [3], *only* the electronic spectrum of $SnCl_4$ (recorded in 1972 by Iverson and Russel [4]) and those of certain stannane polymers (recorded up to 170 nm) are known [5]

Theoretical aspects have been covered in a number of papers, the fundamental states of stannanes [6], radical ions [7,8] and most recently the chemical reactivity of organostannic compounds [9]

An experimental and theoretical study of the

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electronic spectrum of SnH_4 is described in this paper. The vacuum UV spectrum of this compound has been recorded to a wavelength of 110 nm. The ab initio calculation of this spectrum has been carried out using a relativistic pseudopotential to describe the tin core electrons.

2. Experiment

21 VUV spectrometer

The spectrum of SnH_4 was recorded using a laboratory-made vacuum UV spectrometer of moderate resolution [10] The radiation source is a windowless spark (BRV source [11]) which has the advantage of producing high-energy flashes containing wavelengths down to ≈ 50 nm The main drawback with this type of source, the non-reproducibility of flashes, has been overcome in two ways A beam splitter which separates the sample and the reference is used and as the machine is entirely run by computer, we are able to use recording algorithms combining filtration and accumulation in real time

The monochromator is equipped with a holographic grating on a toric support

The 10 cm path-length cell is equipped with lithium fluoride windows Radiation flux is measured by a combination of two photomultipliers (reference and sample) associated with two sodium salicylate coated windows

The tin hydride was obtained by reduction of SnCl₄ by L1AlH₄ The reaction was carried out under vacuum in ether using the method described by Finholt et al [12] After several vacuum distillations, the purity of the SnH₄ was checked by IR analysis [13]

The vacuum UV spectrum was recorded at ambient temperature and an average pressure of 10 mTorr

22 The spectrum

The spectrum obtained (fig 1) shows no nota-

ble absorption until ≈ 7.75 eV (160 nm) The first band, centered at 8 86 eV (140 nm) is relatively intense ($\epsilon = 17.2 \times 10^3$)

This band is comparable to the 125 nm band in the spectrum of methane [14] which has an intensity of the same order of magnitude (f = 0.36) However, it is far more intense than the first band in the spectrum of silane, at 7 95 eV (158 nm), recorded by Alexander et al [15] which has been attributed to a forbidden transition

The last part of the spectrum shows an intense band with a peak at 964 eV (129 nm) This band is asymmetric towards longer wavelengths. The final broad band shows a maximum at $\approx 10.04 \text{ eV}$ (124 nm)



ev

10

9

Fig 1 VUV spectrum of SnH₄ (----—) experimental spectrum, () deconvolution of the spectrum

3. Theoretical calculations

31 Methods

All calculations were undertaken using a relativistic pseudopotential to describe the tin core electrons [16] This type of pseudopotential gave us good results in the study of the SnH_4^+ ion [8] and in the interpretation of the photoelectron spectrum of SnH_4 Ab initio calculations on valence electrons were carried out, using a 4s,4p basis set contracted to double ζ (2s,2p) [16] This basis was completed by adding d orbitals on the tin atom ($\zeta = 0.2$) and two p-orbitals on each hydrogen atom ($\zeta = 0.7, 0.2$)

In order to take into account the diffuse states obtained in the vacuum UV spectrum, we have included a series of Rydberg s and p orbitals on the central atom The exponent of these atomic orbitals was optimized using the energy of the first Rydberg state of SnH_4 , which was calculated, to



Fig 2 Variation of second-order Møller–Plesset energy of ground state and first excited state of SnH_4 with the ζ of the Rydberg orbital

the second order, by Møller–Plesset perturbation The results, presented in fig 2, show that the value of the transition between the ground and first excited state is relatively sensitive to the gaussian coefficients used The optimum value $\zeta = 0.021$ thus obtained has been used in the remaining calculations

The ground state energy and that of the first four excited states have been evaluated by configuration interaction, combining variation and perturbation

Initially, a multiconfigurational reference subspace (S_0) was constructed on the SCF wavefunction of the ground state This subspace comprising 150 mono-, di- and tri-excited determinants of the ground state, was constructed using the CIPSI algorithm [17] This allows incorporation of all quasi-degenerate determinants in S_0 with the excited states studied

In a second stage, the correlation energy of S_0 was evaluated to the second order by the Møller-Plesset perturbation method In the course of this calculation, the 5000 most important determinants in the wavefunction were selected (subspace M) In order to evaluate the correlation energy as accurately as possible, we have used a method of successive diagonalisations of more and more important parts of the subspace M An extrapolation, similar to that proposed by Buenker et al [18], allows the most accurate evaluation possible (combining variational and perturbational results) of the second-order correlation energy To estimate the total correlation energy and the influence of tetra-excited determinants of S_0 , we have evaluated the influence of the unlinked clusters, as proposed by Davidson [19]

32 Results

The principal results on the first four excited states of SnH_4 are shown in table 1 It can be noted that the transition energies are not noticeably dependent on the degree of approximation used to evaluate the correlation energy We can simply note that taking the correlation energy of the unlinked clusters into account brings the first two transitions considerably closer together

Transition moments were calculated from mul-

Calculated	transitions	of SnH ₄

State	Nature ^{a)}	$\frac{\Delta E^{(b)}}{(eV)}$	ΔE^{c} (eV)	$\Delta E^{(d)}$ (eV)	Ω^{e}	$f^{(1)}$
$\overline{S_1}$	$T_2 \rightarrow A_1^R$	8 45	8 56	8 38	0 897	0 495
S ₂	$T_2 \rightarrow T_2^{R}$	9 85	9 39	917	0 406	0 111
S ₃	$T_2 \rightarrow A_1^V$	10 56	10 55	10 27	1 458	1 604
S4	$T_2^{\vee} \rightarrow T_2^{\vee}$	11 82	12 01	11 8	1 239	1 335

 ^{a)} Most important determinant in the multiconfigurational development

- ^{b)} Transition calculated by Møller-Plesset perturbation (491000 determinants)
- c) Transition calculated by partial diagonalisation of the previous space and extrapolation
- ^{d)} Same as c) with the contribution due to the unlinked cluster taken into account
- e) Transition moments
- f) Oscillator strength

ticonfigurational density matrices obtained from S_0 perturbed in the first order by the Møller-Plesset method Mulliken population analysis was undertaken on density matrices

The results obtained on the four first excited states and on the ground state are presented in table 2 Populations have been regrouped in order to distinguish valence orbitals from d orbitals and diffuse Rydberg orbitals

4. Discussion

Stannane of T_d symmetry has eight valence electrons occupying an a_1 orbital and a triply degenerate t_2 orbital Only transitions from the ground state to the excited T_2 states will be active in the absorption spectrum This means that all

Table 2 Mulliken population analysis of the five first singlet states of SnH_4

State	Population on Sn				Total
	total	R _s	R _p	d	population on H
ground	3 145	0 022	0 029	0 076	1 214
S ₁	3 656	0 807	0 118	0 062	1 086
S ₂	3 783	0 120	1 000	0 065	1 054
S ₃	3 196	0 199	0 000	0 079	1 213
S ₄	3 301	0 108	0 028	0 094	1 174

triply degenerate excited states are susceptible to a Jahn-Teller distortion Only orbital transitions of the following type are possible $a_1 \rightarrow t_2$, $t_2 \rightarrow t_2$, $t_2 \rightarrow a_1$ or $t_2 \rightarrow e$, this latter transition involves excitation to d orbitals The experimentally measured spectrum is a series of at least three bands with maxima at 8 86, 9 64 and 10 04 eV

In order to facilitate the analysis of the spectrum and its comparison with theoretical results, we have carried out a deconvolution which apart from a certain arbitrary character, given the poor separation of the bands, allows us to evaluate, approximately, the oscillator strength The results thus obtained are presented in table 3

4.1 First region of the spectrum

The first broad absorption observed is, in fact, a mixture of several bands superimposed on each other, an intense band centered at 8 74 eV with an oscillator strength of 0 221 and probably two weaker bands at lower energy This absorption causes the strong asymmetry of the first band towards higher wavelengths

Theoretical calculations show that, in this region, the only transition, calculated at 8 38 eV with an oscillator strength of 0 495, is of type $t_2 \rightarrow a_1$ We have also been able to show that no forbidden transitions would occur at longer wavelength It is worth noting that a very weak band is observed towards longer wavelength in the optical spectrum of methane (at 8 80 eV) [14] and of SiH₄ (at 7 95 eV) [15] No satisfactory interpretation has been put forward to explain the presence of these bands (singlet-triplet transition, forbidden valence transition, [20]) In the electronic impact spectrum of CH₄ this band is no longer visible [21]

In the case of SnH_4 we can give a simple explanation for the strong low-energy deformation of this first band In fact, it corresponds to a transition to a T_2 state with a strong Rydberg s component This is indicated by examination of the Mulliken populations of the state concerned (table 2) A charge of 0 807 electron can be taken from the 6s orbital, this is accompanied by a strong reduction in the hydride character of SnH_4 , the charge on each hydrogen atom drops to 0 128 electron

	$\frac{\bar{\nu}_{max}}{(10^3 \mathrm{cm}^{-1})}$	€ max	Deconvolution		
		$(10^3 \ell \text{mol}^{-1} \text{cm}^{-1})$	$\overline{\nu}_{\max}^{a)}$ (10 ³ cm ⁻¹)	oscillator strength	
first band	71 50 (8 86)	17 2	64 05 (7 94)	0 168	
			67 30 (8 34)	0 112	
			70 49 (8 74)	0 221	
second band	77 80 (9 64)	20 9	76 10 (9 43)	0 687	
			78 09 (9 68)	0 074	
third band	82 10 (10 04)	178	81 84 (10 14)	0 081	
			85 25 (10 56)	0 443	
	89 00 (11 03)	13 4	89 95 (11 15)	0 132	

Table 3 Experimental VUV spectrum of SnH₄

^{a)} The values in parentheses are given in units of eV

This assignment is consistent with that proposed by Robin [20] for interpretation of the first intense bands of the methane (at 9 69 eV) and silane (at 8 99 eV) spectra The strong intensity (for a Rydberg transition) of this band can also be noted in the spectrum of methane with an oscillator strength from 0 26 to 0 36 [14]

The practically pure Rydberg character of the first excited state of SnH_4 must cause a certain similarity to the ion radical SnH_4^+ Examination of the first observed band in the photoelectron spectrum shows a strong splitting caused by the Jahn-Teller effect (and spin-orbit coupling) into three portions separated by 0.4 eV This splitting, which is less visible in the vacuum UV spectrum, explains the deformation of the spectrum towards longer wavelength A deformation of the spectrum (fig 1) can, in fact, be seen There are three distinct regions separated by $\approx 0.40 \text{ eV}$

The assignment of this band to a Rydberg s transition is confirmed by evaluation of the corresponding term value which is $\approx 3.07 \text{ eV}$ This is a reasonable value for the tin atom, the $t_2 \rightarrow R_s$ transition of methane has a value of 3.92 eV and of SiH₄ 3 41 eV

42 The second band

The second band was calculated at 9 17 eV with an oscillator strength four times weaker than the previous transition It corresponds to a $t_2 \rightarrow t_2$ transition Examination of the population analysis of the excited state shows its character to be essentially Rydberg p The weak intensity of this band compared to the $t_2 \rightarrow a_1$ transition (\mathbf{R}_s) is understandable as in a model atom it corresponds to a forbidden transition ($\Delta l = 0$) In the experimental spectrum this band is hidden by the considerably more intense bands which precede and follow it

43 Last part of the spectrum

The following spectral bands involve valence transitions The third band, calculated at 10 27 eV with an oscillator strength of 1 60 is the most intense band in the experimental spectrum, situated at 9 43 eV (f = 0.687) This band is primarily due to a valence transition $t_2 \rightarrow a_1$, however mixed with this is a significant contribution from transitions to diffuse states (0 199 electron in R_s) The polarization of the Sn-H bond is similar to that found in the ground state

The fourth transition, calculated at 118 eV, can be attributed to the fourth spectral band It corresponds to an essentially valence transition $t_2 \rightarrow t_2$ It is worth noting, as for the Rydberg transitions, the low intensity of the $t_2 \rightarrow t_2$ transitions compared to the corresponding $t_2 \rightarrow a_1$

It is noteworthy that all the transitions calculated here correspond to an experimental spectrum limited to 11 26 eV (110 nm) There is no significant d-orbital interaction The total charge on these orbitals remains essentially the same as in the ground state

It is necessary to comment on the proximity of calculated and experimental values While the calculated states correspond to transitions to diffuse orbitals (Rydberg states or radical ions [8]), the calculated results obtained are in excellent agreement with experimental values, both for the position and intensity of the bands However, as soon as the virtual valence orbitals are involved in excitation, the quality of the theoretical results is reduced (with an error of ≈ 1 eV) This can be partly explained by the fact that we have used a pseudopotential to describe the tin core electrons The interaction of diffuse orbitals with the core of the atom is weak (these orbitals are not very penetrating), however, when an electron is in a much more *penetrating* virtual valence orbital, then the core-valence interaction becomes more significant and causes the observed shift in the corresponding transitions

5. Conclusion

The vacuum UV spectrum of SnH_4 shows a number of bands between 150 and 110 nm These have been assigned with the aid of an ab initio calculation The first transitions, observed below 9 5 eV, correspond to transitions to Rydberg levels These bands are followed (above 9 5 eV) by essentially valence transitions ($t_2 \rightarrow a_2$ and $t_2 \rightarrow t_2$)

The first band of the spectrum, which involves an excited 6s Rydberg state, shows a strong deformation towards long wavelength This is comparable to a similar effect observed in the photoelectron spectrum of SnH_4 The net red shift of the whole spectrum as compared to the spectra of SiH_4 and CH_4 is also noteworthy

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