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PHOTOELECTRON SPECTRUM OF TETRAVINYLSTANNANE, $Sn(CH{=}CH_2)_4$

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Summary

The HeI and HeII photoelectron spectra of tetravinylstannane are reported and assigned on the basis of comparison with the spectra of other Group IVB tetravinyl derivatives and by correlation of the electronic structures of ethene and stannane.

Introduction

The electronic structures of various MX_4 derivatives (M = C, Si, Ge, Sn, Pb) have been studied by photoelectron (PE) spectroscopy. The X substituents were halogen atoms [1,2], methyl [3,4] and allyl groups [5—7] and their combinations. Of the tetravinyl compounds only the cases with M = C and Si were studied [8,9] and the partial assignment of PE spectra was made on the basis of the assumed D_{2d} symmetry. Recently, the molecular geometries in the gas phase have been determined by electron diffraction for tetravinylsilane [10] and tetravinylstannane [11], showing them to be of S_4 symmetry. We report here the PE spectrum of tetravinylstannane.

Experimental

The PE spectra of the commercially available sample (Riedel de Haën AG) were recorded on a Vacuum Generators UV G3 instrument [12] under low resolution ($\simeq$30 meV). The spectra were calibrated by an addition of small amounts of xenon to the sample flow.

Results and discussion

The HeI and HeII PE spectra of $Sn(CH{=}CH_2)_4$ are shown in Figs. 1 and 2, respectively. The assignment of the spectra is made by comparison with the

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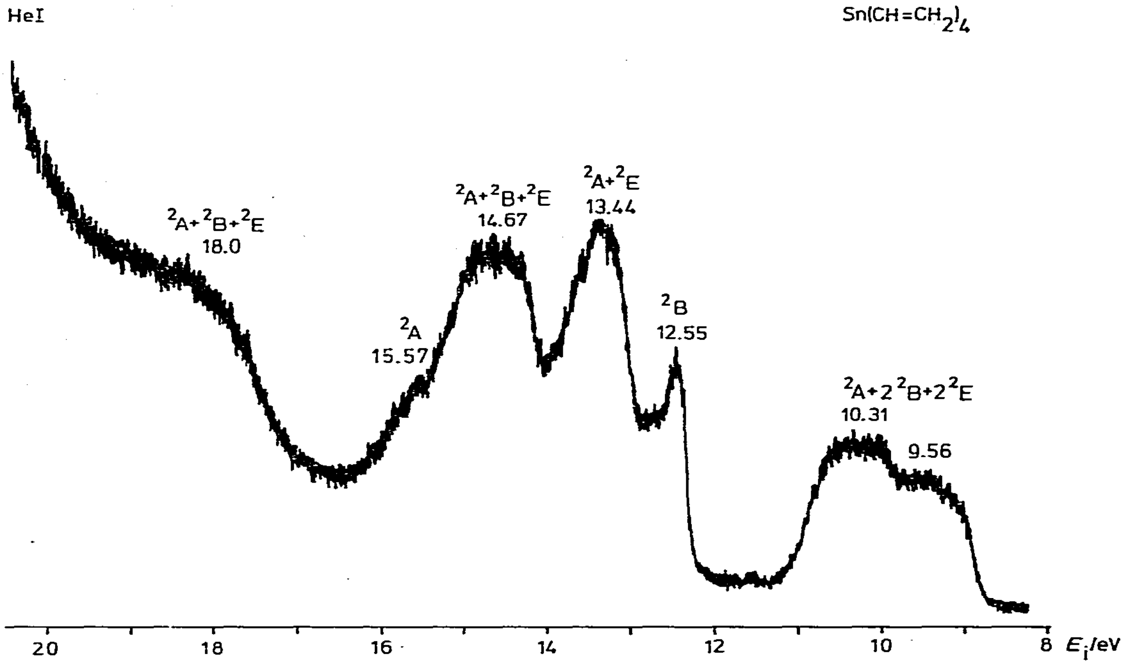

Fig. 1. HeI PE spectrum of Sn(CH=CH$_2$)$_4$.

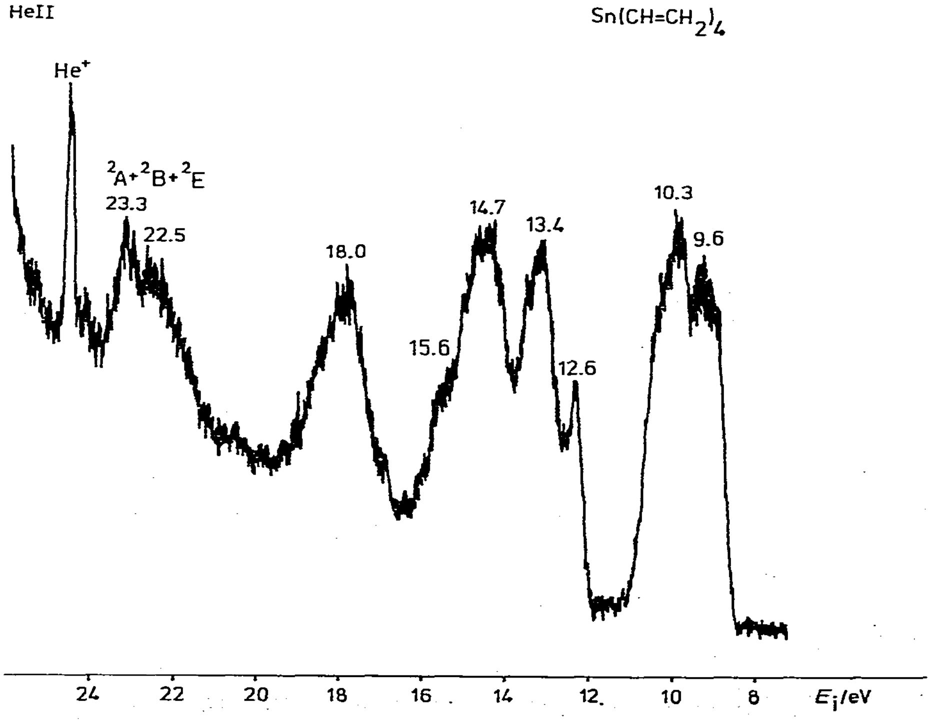

Fig. 2. HeII PE spectrum of Sn(CH=CH$_2$)$_4$.

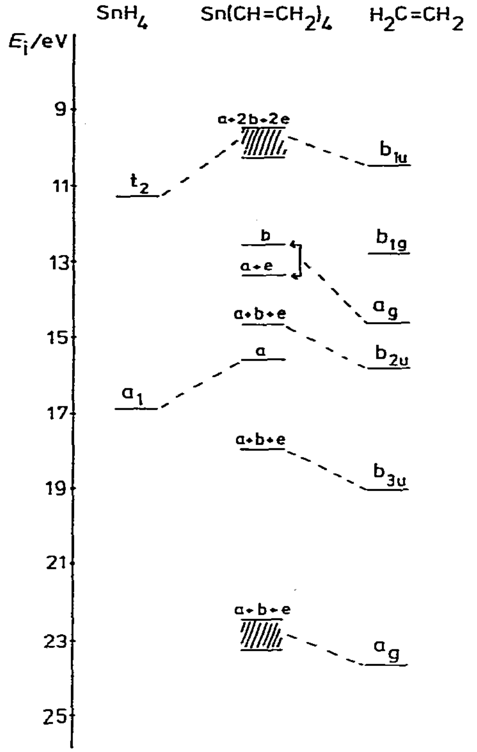

Fig. 3. Energy level diagram of SnH_4, $Sn(CH{=}CH_2)_4$ and $H_2C{=}CH_2$. The dashed areas correspond to unresolved systems in the PE spectra.

molecular fragments: stannane and four ethene molecules, which can be thought of as building blocks for the title compound. The energy levels and their assignments shown in Fig. 3 were taken from the PE spectra of stannane [13] and ethene [14]. The analysis of Fig. 3 shows that the unresolved systems at 9.56 and 10.31 eV comprise five ionizations, two of them corresponding to predominantly Sn—C bonding orbitals and the other three to π orbitals of vinyl groups. This conclusion is supported by the PE spectra of tetravinylmethane [8] and tetravinylsilane [9], where ionizations from three π and two Si—C bonding orbitals in the 9.5—10.5 eV region were the only parts of the spectra assigned. Three π orbitals belong to $a + b + e$ symmetry species in the S_4 point group, while those of Sn—C (or Si—C) bonding orbitals belong to $b + e$ species. The exact ordering of the states in the unresolved systems (9.5—10.5 eV region) cannot be established by these arguments, but the HeII spectrum indicates mixing of the Sn—C and π-type levels. Thus, the intensities of the systems at 9.56 and 10.31 eV are raised by approximately the same amount on going from HeI to HeII excitation, which indicates that the Sn—C and π-type orbitals are involved in both unresolved systems. If this were not the case, a different behaviour of the ionization cross-sections for the two groups of systems could be expected. Furthermore, as in $C(CH{=}CH_2)_4$ and $Si(CH{=}CH_2)_4$, the ^2E systems could be split by vibronic interactions, and hyperconjugative interactions between vinyl substituents (via d_π orbitals on the Sn atom) could also be expected. The rest of the spectrum is similar to that of tetravinylsilane [9] and by analogy our assignment can be extended to the latter. Every orbital in the ethene molecule can be correlated with the group of three orbitals in tetravinylstannane belonging to $a + b + e$ species lying close in energy. This orbital pattern is produced by weak mutual interactions of vinyl groups. With this assumption the systems at (12.55, 13.44), 14.67, 18.0, (22.5 and 23.3) eV can be assigned to the ionization of four groups of orbitals ($a + b + e$ species in each group) located mainly on the vinyl ligands. Two possible assignments of the systems at 12.55 and 13.44 eV are: ^2A and $^2B + {}^2E$; ^2B and $^2A + {}^2E$, but the qualitative reasoning used in this work does not allow a choice to be made. The 15.57 eV system can be assigned to ionization of a Sn—C bonding orbital of a symmetry (Fig. 3). Thus, all the bands with ionization energies up to 24 eV in the PE spectrum of Sn(CH=CH$_2$)$_4$ have been assigned and indicate a rather weak interaction between the vinyl groups and between them and the central atom.

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