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Short Communication

Photoelectron Spectra of Cyclopolysilanes

Rudolf Janoschek[1], **Edwin Hengge**[2], **Harald Stüger**[2], and **Laszlo Nyulaszi**[3]

[1] Institut für Theoretische Chemie, Karl-Franzens-Universität, A-8010 Graz, Austria
[2] Institut für Anorganische Chemie, Technische Universität, A-8010 Graz, Austria
[3] Institut für Anorganische Chemie, Technische Universität, H-1521 Budapest, Hungary

Summary. He (I) PE spectra of cyclopentasilane and cyclohexasilane show excellent agreement with STO-3 G+ ab initio calculations. The HOMO in both compounds is of σ(SiSi) 3 p character. First IP's appear at 9.4 and 9.6 eV respectively.

Keywords. Ab initio calculations; Cyclopolysilanes; PE-spectra.

Photoelektronenspektren von Cyclopolysilanen (Kurze Mitt.)

Zusammenfassung. Die He (I) PE-Spektren der Cyclosilane Si_5H_{10} und Si_6H_{12} zeigen ausgezeichnete Übereinstimmung mit STO-3 G+ ab initio Rechnungen. Beide Ringe besitzen HOMO's mit σ (SiSi) 3 p Charakter. Die ersten Ionisierungspotentiale liegen bei 9.4 bzw. 9.6 eV.

A number of polysilane molecules have been studied experimentally and theoretically to understand the electronic structure, specifically the Si-Si linkages, which are very important in the chemistry of these compounds. The Si-Si bonding is believed to be an important factor in the formation of radical anions containing delocalized electrons, the UV absorption spectra, and the formation of coloured charge transfer complexes with electron acceptors such as tetracyanoethylene [1]. Silicon hydrides recently attracted particular attention because they proved to be suitable for theoretical studies at higher levels [2–4]. However, more experimental data are needed to complement the theoretical results, consequently it was decided to record the hitherto unknown He (I) photoelectron spectra of cyclopentasilane and cyclohexasilane. This should allow the direct comparison between the observed and calculated vertical ionization energies [5]. The observed He (I) photoelectron spectra of Si_5H_{10} and Si_6H_{12} are presented in Fig. 1, which contains also the calculated SCF, Koopmans theorem, ionization potentials. Numerical values are summarized in Table 1. Experimental and theoretical data seem to be in excellent agreement. At low energies both spectra show several bands arising from ionizations from orbitals predominately σ-(SiSi) in character. In both compounds the respective HOMO's have σ-(SiSi) 3 p character (Fig. 2). The HOMO in Si_6H_{12} is more stable

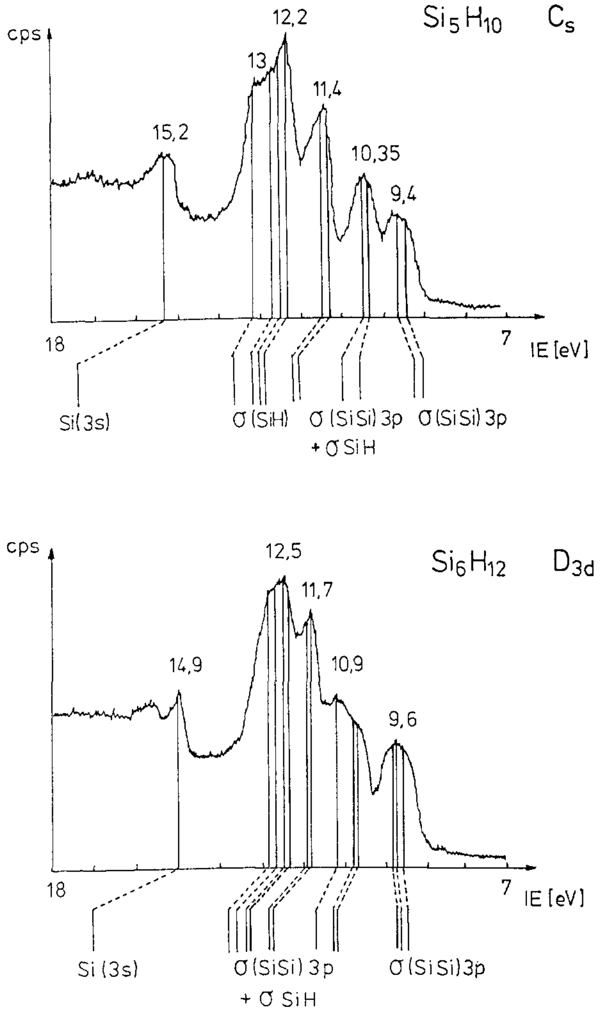

Fig. 1. He(I) PE spectra of Si_5H_{10} and Si_6H_{12} and assignment by Koopmans ionization energies obtained by STO−3G+ ab initio calculations

than in the five membered ring as seen by its somewhat higher ionization potential. In general, however, homoatomic chains have ionization potentials that decrease with increasing chain length. The unusual stability of the HOMO in Si_6H_{12} compared to Si_5H_{10} might be explained by decreased ring strain in the six membered ring. This unproven generalization, however, is strongly questioned by the reversed order of the first ionization potentials in the carbon analogues cyclopentane and cyclohexane [6]. With increasing ionization potentials SiH contributions also increase gradually. Ionizations from SiH orbitals occur at higher ionization potentials, typically 12–14 eV, which is in good agreement with those observed for the chain structures [1]. However, in the cyclic compounds the orbital energy separation between σ-(SiSi) and (SiH) orbitals seems to be smaller than for the chain structure. Ionization potentials near 15 eV may be attributed to Si (3 s) electrons.

Experimental

Cyclopentasilane and cyclohexasilane were synthesized and purified by well known procedures [7, 8]. Silanes show extreme sensitivity with respect to oxygen and they need special handling for recording

Table 1. Experimental and calculated IP's (eV) and symmetries of molecular orbitals of Si_5H_{10} and Si_6H_{12}

Si_5H_{10}			Si_6H_{12}		
Exp.	Calc.		Exp.	Calc.	
9.4	9.10	A'	9.6	9.41	A_{1u}
	9.37	A''		9.52	E_g
10.35	10.53	A'	10.9	11.10	E_u
	10.86	A''		11.62	A_{1g}
11.4	11.95	A'	11.7	12.69	E_u
	12.07	A''			
12–13	12.91	A'	12–13	13.32	E_g
	13.03	A''		13.50	A_{1g}
	13.22	A'		13.67	A_{2u}
	13.67	A'			
15.2	17.38	A'	14.9	17.04	A_{2u}

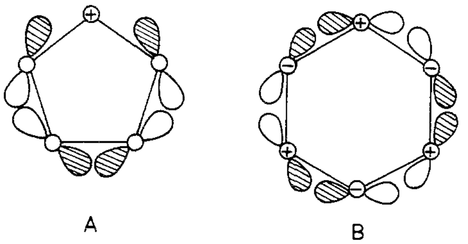

Fig. 2. Shape of HOMO's in Si_5H_{10} (**A**) and Si_6H_{12} (**B**). Hydrogen atoms have been omitted for clarity. The + and − signs indicate the non-planarity of the silicon cycles (+ = above, − = below the paper plane)

the photoelectron spectra. For each measurement a small amount of the compound was condensed under nitrogen into a vacuum tight flask. After connection to the spectrometer the liquid silanes were cooled with liquid nitrogen and the flasks evacuated. The samples were then gently warmed until the vapour pressure was sufficient to record the spectra. The spectrometer (described elsewhere [9]) had a resolution of 45 meV (FWHM) at the $Ar^2P_{1/2}$ line. The spectra were calibrated with methyl iodide.

Ab initio calculations were performed on a VAX 3200 computer using the Gaussian 82 suite of programs employing a STO-3 G basis set extended with a silicon (s, p) set with an exponent of 0.0331. This basis set has been shown to produce calculated ionization potentials in excellent agreement with the experiment. C_s (Si_5H_{10}) and D_{3d} (Si_6H_{12}) symmetries have been assumed throughout, according to experimental investigations [10, 11]. Full details of the computational procedure employed may be found elsewhere [5].

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