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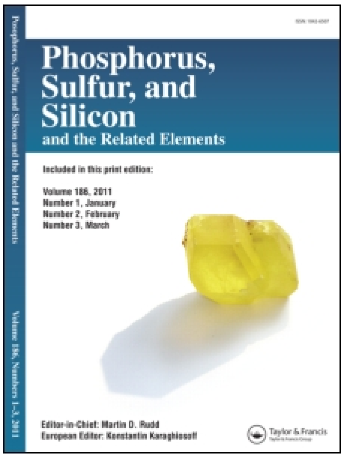

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PHOTOELECTRON SPECTRA AND QUANTUMCHEMICAL CALCULATIONS OF PERCHLOROCYCLOPOLYSILANES

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PHOTOELECTRON SPECTRA AND QUANTUMCHEMICAL CALCULATIONS OF PERCHLOROCYCLOPOLYSILANES

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Dedicated to Professor Edwin Hengge on occasion of his 60th birthday

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He(I)-PE-spectra of perchlorocyclopolysilanes $(SiCl_2)_4$, $(SiCl_2)_5$ and $(SiCl_2)_6$ are recorded and interpreted by semiempirical PM3 calculations. HOMOs may be described by antibonding π^* interactions of σ(SiSi)3p and (Cl)3p lone pair orbitals. First ionization potentials appear near 9 eV and increase in the order $Si_4 < Si_6 < Si_5$. HOMO-LUMO studies suggest, that intramolecular charge transfer might be responsible for the unusual low energy of UV absorption bands.

Key words: Photoelectron spectra; PM3 calculations; perchlorocyclopolysilanes; UV-absorption energies; ionization potentials.

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INTRODUCTION

In the last decades UV photoelectron spectroscopy turned out to be an excellent method to gain further insight into bonding properties of compounds containing silicon-silicon bonds. He(I)-PE-spectra of various cyclic and linear perhydro- and permethyloligosilanes have been recorded and interpreted theoretically at various levels of accuracy.[1-3] Isolated bands between 8–10 eV usually appear and are readily assigned to ionizations from the Si—Si bond system. Ionization potentials and PE-band splitting patterns strongly depend on structure and size of the Si—Si framework and on the nature of substituents attached to it.

Only little is known about the influence of halogen groups and other substituents containing "lone pairs" on the Si—Si skeleton in oligosilanes. Recently we recorded the UV absorption spectra of perhalocyclosilanes and derived a qualitative model for their assignment.[4] Now we want to report about the He(I)-PE-spectra of perchlorocyclooligosilanes and their interpretation by semiempirical PM3 calculations. Particular attention will be paid to the interaction of Si—Si bonding and Cl "lone pair" orbitals. HOMO-LUMO studies will be used to further elucidate the nature of the unusual low energy UV absorption bands.

CALCULATIONS

Semiempirical calculations were performed applying the PM3 method.[7] As experimental geometries of perchlorocyclopolysilanes are not yet available, complete geometry optimizations of $(SiCl_2)_4$, $(SiCl_2)_5$ and $(SiCl_2)_6$ had to be carried out yielding bond lengths and angles represented in Table I. The four-membered ring exhibits a square planar skeleton (D_{4h} symmetry), the five-membered ring is irregularly puckered (C_1), and the six-membered ring adopts chair conformation (D_{3d}). The calculated Si—Si bond lengths of 2.46 Å exceed the usual standard values by 4 percent. In contrast, Si—Cl bond distancies and Cl—Si—Cl angles apparently reflect standard values. All the calculated geometries have been confirmed as true energy minima by the calculated sets of harmonic vibrational frequencies.

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Photoelectron spectra of perchlorocyclopolysilanes are depicted in Figure 1 together with the calculated vertical ionization potentials. Table II shows the calculated SCF, Koopmans theorem, ionization potentials. In accordance with the computational results four ionization regions immediately can be distinguished in the photoelectron spectra of $(SiCl_2)_4$, $(SiCl_2)_5$ and $(SiCl_2)_6$:

1) Low intensity ionization bands appearing in the PE-spectra at high energies may be attributed to electron expulsion from orbitals with predominant (Si)3s character. PM3 calculations predict ionizations of Si(3s) electrons between 14.8 and 16.7 eV (The spectrum of $(SiCl_2)_4$ additionally exhibits bands at 15.6 and near 17 eV arising from traces of N_2 in the sample, what, however, does not affect the quality of the residual spectrum).

2) Ionizations from orbitals describing the Si—Cl bonds are calculated quite close to each other between 12.7 and 14.6 eV. In the photoelectron spectra the corresponding bands strongly overlap to form a broad poorly resolved hump in that region also visible in the PE-spectra of other compounds containing Si—Cl bonds like $SiCl_4$ or H_3SiCl.[8]

3) Ionization energies of Cl(3p) lone pairs are computed between 11.3 and 12.0

TABLE I
PM3 calculated geometries (Å, deg.) of perchlorocyclopolysilanes

Molecule	Symmetry	r Si-Si	r Si-Cl	∢Cl-Si-Cl	∢Si-Si-Si
$(SiCl_2)_4$	D_{4h}	2.454	2.051	106.1	90.0
$(SiCl_2)_5$[a]	C_1	2.460	2.060	106.2	108.0±0.5
$(SiCl_2)_6$	D_{3d}	2.463	2.059	105.4	109.7

[a] The five membered ring is slightly puckered (±0.1 Å)

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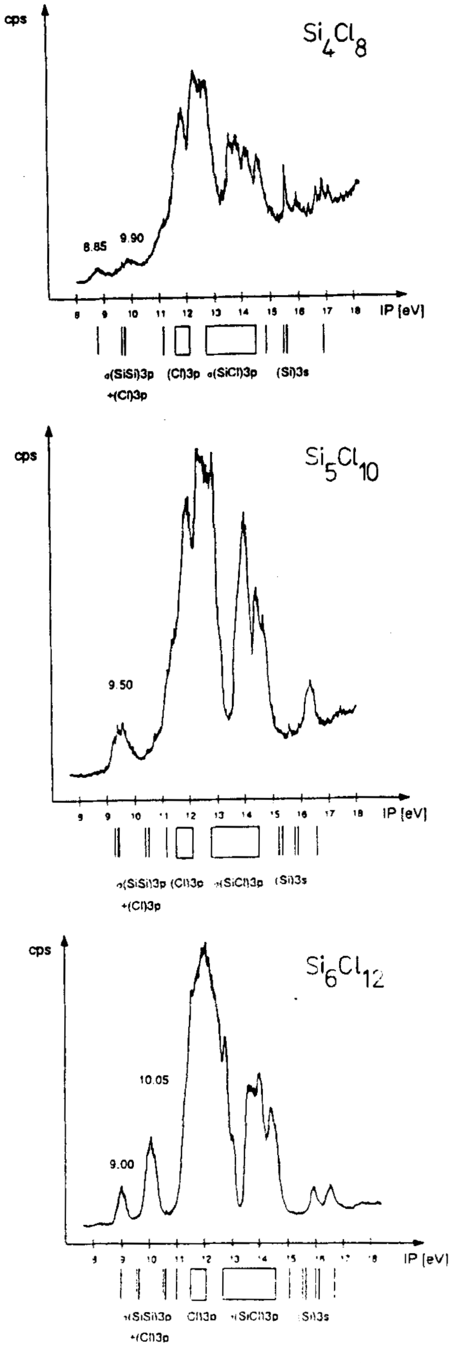

FIGURE 1 He(I) PE-spectra of perchlorocyclopolysilanes and PM3 calculated ionization energies.

TABLE II
PM3 calculated, Koopmans theorem, ionization potentials (eV) of perchlorocyclopolysilanes (*e* = doubly degenerate MOs).

$(SiCl_2)_4$	$(SiCl_2)_5$	$(SiCl_2)_6$	
8.85	9.19	8.98	
9.75-e	9.21	9.61-e	π^*[σ(SiSi)3p -(Cl)3p]
11.03	10.30	10.58-e	
	10.31	10.98	
	11.10		
11.34	11.40	11.43-e	
11.35-e	11.40	11.44-e	
11.35	11.41	11.44	
11.49	11.41	11.46	
11.52-e	11.41	11.62	
11.57	11.51	11.62	
11.81	11.55	11.63-e	
11.94	11.56	11.63-e	(Cl)3p
11.95-e	11.65	11.96	
	11.65	11.98-e	
	11.88	12.00	
	11.88	12.00-e	
	11.88		
	11.99		
	11.99		
12.69	12.82	12.82	
12.97-e	12.83	12.95-e	
13.28-e	13.09	13.21-e	
13.80	13.10	13.43-e	
14.34	13.61	13.92	σ(SiCl)3p
14.35	13.61	13.95	
	13.70	14.19-e	
	13.70	14.61	
	14.41		
	14.46		
14.80	15.20	15.05	
15.47-e	15.20	15.49-e	
16.91	15.84	16.02-e	(Si)3s
	15.84	16.67	
	16.67		

eV. Due to the large number of the corresponding orbitals very close in energy the PE-spectra again only show broad structureless bands.

4) Particularly important for the description of the bonding situation in the compounds investigated are ionization bands with energies below 11 eV. Similar bands appear in the PE-spectra of other compounds containing Si—Si bonds and usually are assigned to ionizations from orbitals with large σ(SiSi) contributions.[9,10] For the series of perchlorocyclopolysilanes PM3 calculations predict several low energy ionizations with intensity ratios of 1:2:1 for $(SiCl_2)_4$ (D_{4h}; B_{2g}, E_u, B_{2u}),

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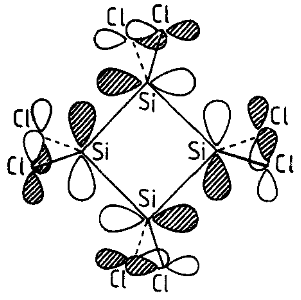

FIGURE 2 Antibonding π^* interaction of the σ(SiSi)3p orbital and (Cl)3p lone pairs in octachlorocyclotetrasilane.

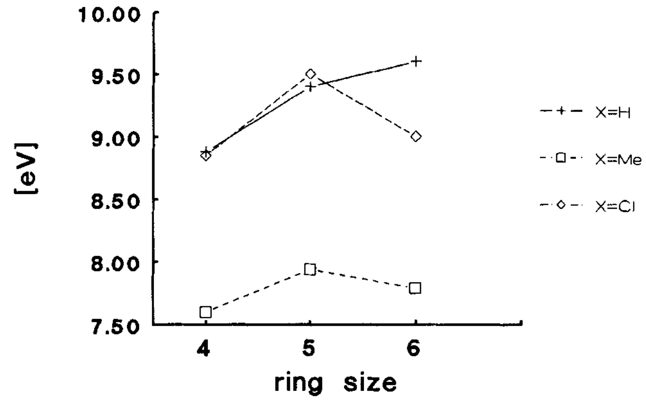

FIGURE 3 First ionization energies of cyclopolysilanes $(SiX_2)_n$, (X = H, Cl, Me) versus ring size.

TABLE III

Expansion coefficients in the HOMO for a Si—Cl unit in different perchlorocyclopolysilanes.

		$(SiCl_2)_4$	$(SiCl_2)_5$	$(SiCl_2)_6$
Si	3s	0.00	0.14	0.00
	$3p_x$	0.00	0.14	0.00
	$3p_y$	-0.37	0.02	0.00
	$3p_z$	0.00	0.00	-0.30
Cl	3s	0.00	0.00	0.00
	$3p_x$	0.00	-0.13	0.00
	$3p_y$	0.24	-0.01	0.00
	$3p_z$	0.00	0.04	0.21

2:2:1 for $(SiCl_2)_5$ (C_1; all A) and 1:2:2:1 for $(SiCl_2)_6$ (D_{3d}; A_{1u}, E_g, E_u, A_{1g}). PE-spectra are consistent with the calculations although several bands are overlapping or superimposed by bands with much higher intensity arising from ioni-

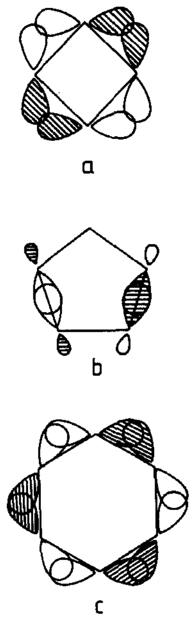

FIGURE 4 Silicon contributions to the HOMOs of perchlorocyclopolysilanes. a), c) σ-(SiSi)3p orbital for an even number of centers. b) σ-(SiSi)3s-3p orbital for an odd number of centers.

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ations of Cl(3p) electrons (compare Figure 1). In order to achieve improved assignment of calculated ionization potentials, cationic states of $(SiCl_2)_4$ additionally have been investigated. $(SiCl_2)_4^+$ exhibits reduced symmetry ($D_{4h} \rightarrow D_{2d}$) due to Jahn-Teller distortion. The Jahn-Teller splitting of the formerly degenerate E_u-state turned out to be 0.6 eV and very likely can be assigned to the weak shoulders at 9.9 and near 11 eV in the PE-spectra. The orbitals responsible for the lowest ionization bands may be described by antibonding π^* interactions of σ(SiSi)3p orbitals and (Cl)3p lone pairs. To allow better understanding their principal shape is sketched in Figure 2. Similar interactions have recently been identified as the reason for the lowering of ionization energies of permethylpolysilanes compared to the unsubstituted silicon hydrides [compare Reference 2], where the HOMOs are pure σ(SiSi)3p orbitals.

DISCUSSION

Ionization Energies

Perchlorocyclopolysilanes exhibit first ionization energies near 9 eV quite similar to the corresponding parent silicon hydrides. The destabilizing π^*-interaction of σ(SiSi)3p and (Cl)3p orbitals, therefore, is nearly equalized by the inductive stabilization of the SiSi-bonds by the electronegative Cl-substituents. In Figure 3 first ionization potentials of cyclopolysilanes $(SiX_2)_n$ (X = H, Me, Cl) are plotted versus ring size. Cyclic silicon hydrides show increasing first ionization energies with increasing ring size, what perhaps might be due to the decreasing ring strain,

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whereas in the series of perchloro- and permethylcyclopolysilanes the five-membered rings exhibit the highest values. The high symmetries of four- and six-membered rings, D_{4h} and D_{3d}, respectively, prevent any stabilizing (Si)3s contribution to mix into the corresponding HOMOs. Expansion coefficients of the HOMOs of $(SiCl_2)_4$ and $(SiCl_2)_6$, presented in Table III, exhibit non-zero numerical values for 3p orbitals only. A bonding orbital of the type σ(SiSi)3p can be constructed because of the even number of silicon atoms in the rings (Figures 4a and c). The lack of symmetry restrictions in the five-membered ring allows (Si)3s orbitals also to contribute to the HOMO (Table III shows non-zero expansion coefficients for 3s and 3p orbitals), what stabilizes the resulting bonding orbital (Figure 4b) compared to the HOMOs in the four- and six-membered rings. This might be a reasonable explanation for the unexpected order of the first ionization energies in permethyl- and perchlorocyclopolysilanes, although it does not explain their different sequence in the corresponding hydrosilanes.

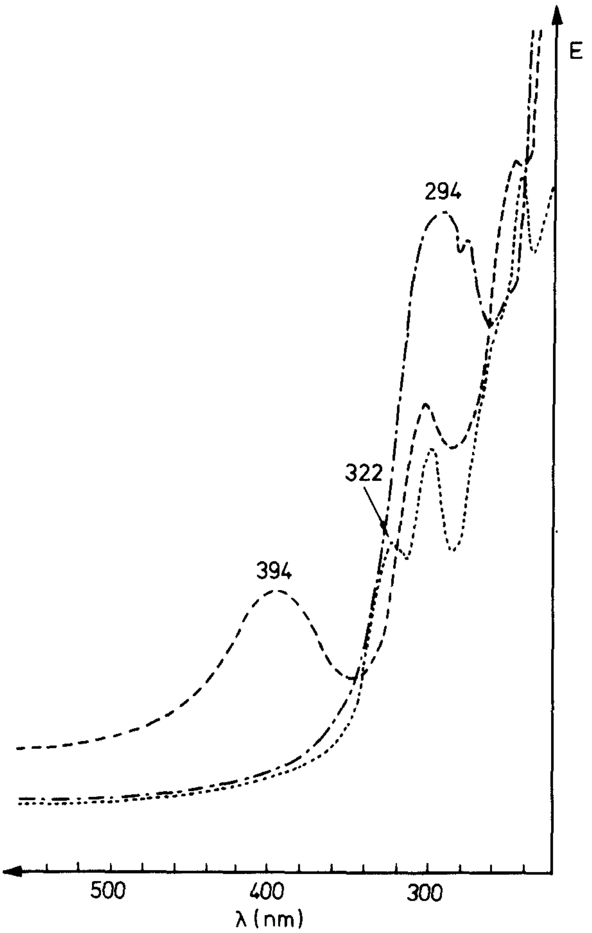

FIGURE 5 UV/Vis absorption spectra of perchlorocyclopolysilanes $(SiCl_2)_n$. ------ : $(SiCl_2)_4$; ······ : $(SiCl_2)_5$; -·-·-· : $(SiCl_2)_6$.

Low Energy UV Absorption Bands

$(SiCl_2)_4$, $(SiCl_2)_5$ and $(SiCl_2)_6$ exhibit UV absorption bands at remarkably low energies of 3.11, 4.17 and 3.81 eV (Figure 5),[4] respectively, compared to 5.68 eV for $(SiH_2)_5$ and 6.36 eV for $(SiH_2)_6$ [Reference 3]. Although reliable calculations of electronic transition energies are not yet possible for perchloropolysilanes, a closer look at HOMOs and LUMOs might lead to better understanding of this phenomenon. Calculated HOMO and LUMO energies of perchloro- and perhydrocyclopolysilanes are represented in Table IV. Figure 6 illustrates, that HOMO energies remain nearly unchanged upon chlorination, whereas the LUMOs are stabilized by about 2 eV. Their unusual low energy is caused by the increased positive charge (electron deficiency) of the silicon core in the ground state of the chloro-derivatives due to the influence of the electronegative substituents, which is clearly documented by the atomic populations of silicon with numerical values of 3.81 in perhydro-, but only 3.54 in perchloropolysilanes. The LUMOs in either series of cyclopolysilanes are composed of antibonding σ^*(SiSi)4s Rydberg-type

TABLE IV

PM3 calculated HOMO and LUMO energies (eV) and their difference (ΔE) of perhydro- and perchloropolysilanes.

	HOMO	LUMO	ΔE
$(SiH_2)_4$	-9.12	-1.76	7.36
$(SiH_2)_5$	-9.62	-1.82	7.80
$(SiH_2)_6$	-9.90	-1.86	8.04
$(SiCl_2)_4$	-8.85	-3.66	5.19
$(SiCl_2)_5$	-9.19	-3.79	5.40
$(SiCl_2)_6$	-8.98	-4.08	4.90

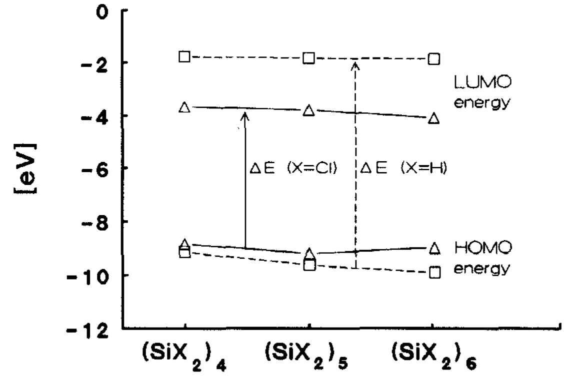

FIGURE 6 Differencies of PM3 calculated HOMO and LUMO energies of cyclopolysilanes $(SiX_2)_n$. (□------: X = H; Δ——: X = Cl; n = 4,5,6).

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contributions. Thus, due to the different character of the HOMOs, electronic excitations are not of the same nature in unsubstituted and in perchlorocyclopolysilanes as already has been argued in Reference 4. In the first case the electronic transitions are of the kind [σ(SiSi)3p → σ^*(SiSi)4s]. In the second case charge transfer from chlorine to silicon occurs with excitation of an electron from the π^*[σ(SiSi)3p-(Cl)3p] type HOMO to a σ^*(SiSi)4s orbital. However, at this point of the discussion it has to be mentioned, that the character of the LUMO can considerably deviate from that of the lowest excited, singly occupied orbital, which we actually want to discuss [Reference 2].

EXPERIMENTAL

$(SiCl_2)_4$, $(SiCl_2)_5$ and $(SiCl_2)_6$ were synthesized and purified using standard procedures already described in literature.[5,6] With regard to the extreme sensitivity of the compounds investigated against humidity and air all manipulations had to be carried out under inert gas atmosphere. Photoelectron spectra were recorded with a Leybold-Heraeus UPG 200 spectrometer. For each measurement a small amount of the corresponding compound was introduced directly into the spectrometer under dry nitrogen via a solids probe inlet. All photoelectron spectra were calibrated with argon (15, 76 eV).

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