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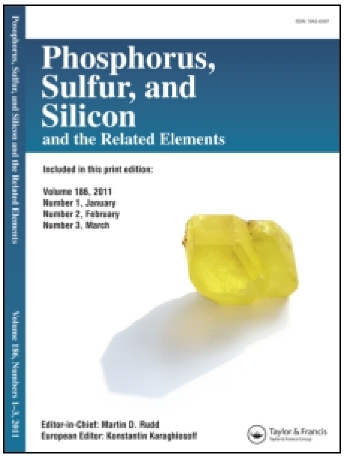

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PE AND UV SPECTRA OF LINEAR AND CYCLIC POLYSILANES AND ASSIGNMENT BY AB INITIO CALCULATIONS

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PE AND UV SPECTRA OF LINEAR AND CYCLIC POLYSILANES AND ASSIGNMENT BY *AB INITIO* CALCULATIONS†

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Ab initio calculations have been performed on linear and cyclic polysilanes including permethyl-substituted compounds. Koopmans' approximation was used for assigning experimentally obtained PE and UV spectra. The PE spectrum of octamethylcyclotetrasilane and the UV spectra of cyclopenta- and cyclohexasilane are presented for the first time.

Key words: Ab initio calculations; linear and cyclic polysilanes, PE and UV spectra.

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INTRODUCTION

Since the early 1960's the question, why certain polysilane high polymers or siloxene derivatives exhibit colour, is still controversial. First UV/vis-spectroscopic investigations were strongly impeded by the insolubility of the compounds in question and therefore just led to empirical statements.[1] Recently, the discovery that polysilanes may serve as photo-resists in microlithography intensified the search for a theoretical explanation of the unusual electronic properties of Si–Si bonds. PE and UV/vis-spectroscopic investigations of numerous linear and cyclic polysilanes resulted in first theoretical models.[2,3] For cyclosilane derivatives bearing substituents with free electron pairs (halogen and methoxy groups) we succeeded in deriving a model from the measured absorption spectra assigning the unusual long wavelength absorption bands to intramolecular charge transfer transitions.[4]

Theoretical treatment of extended polysilane systems at higher levels of accuracy, however, are rare. Higher silicon hydrides prove to be particularly suitable for theoretical studies because calculations nowadays can be performed with high accuracy even for larger molecules. In this work we report for the first time the UV spectra of cyclopentasilane and cyclohexasilane. Together with the PE and UV spectra of linear polysilanes and selected methylsilanes they are

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† We are saddened by the death of Prof. Dr. O. E. Polansky to whom this paper is dedicated.

interpreted by *ab initio* calculations. Emphasized are the differences between linear and cyclic silicon hydrides and the influence of methyl group introduction on the polysilane systems.

EXPERIMENTAL

Cyclopentasilane and cyclohexasilane were synthesized and purified using standard procedures already described in literature.[5,6] Due to the extreme sensitivity of the compounds investigated against oxygen, all manipulations need to be carried out under inert gas atmosphere. UV spectra were recorded between 190 and 300 nm on a Perkin Elmer Lambda 5 spectrophotometer in sealed quartz cells of 1 cm path length using spectral grade isopentane dried over $LiAlH_4$ and distilled prior to use. Absorption maxima were measured by scanning the spectrum at least twice and were always reproducible to <0.5 nm. The extinction coefficients are considered accurate to at least ±10%.

COMPUTATIONAL METHODS

Ab initio SCF calculations were performed on a VAX 3200 computer using the GAUSSIAN 82 program.[7] The STO-3G basis set employed, expectedly yields Koopmans' theorem ionization energies systematically lower than the experimental ionization potentials. In contrast, calculated ionization energies by the use of the split valence 3-21G basis set are too high. An intermediate basis set is produced by extending the STO-3G basis with a silicon (s, p) set with an exponent of 0.0331.[8] It is shown in Table I that this augmented STO-3G basis set is useful for the calculation of ionization energies and that the same extension of the 3-21G basis set does not lead to an improvement.

A similar basis test was performed for the calculation of electronic transition energies (compare Table II). The STO-3G as well as the 3-21G basis sets are both unsuitable for useful calculations of excitation energies. Augmented silicon basis sets are obligatory. Excited states were calculated employing the STO-3G basis set augmented by a diffuse (s, p) set on each Si atom with an exponent of 0.015.[9] The use of limited basis sets shows a strong sensitivity of calculated ionization and excitation

TABLE I

Effect of different basis sets on lowest Koopmans ionization potentials (eV) of silicon compounds

	STO-3G	STO-3G+ sp(0.0331)	3-21G	3-21G+ sp(0.0331)	Exp.
SiH_4	11.42	12.49	13.16	13.20	12–13
Si_2H_6	8.68	10.15	11.00	11.05	10.53
Si_3H_8	7.95	9.60	10.44	10.49	9.87
c-Si_4H_8	6.78	8.88	9.81	9.83	—
Si_2Me_6	7.72	8.33	9.31	9.38	8.69

TABLE II

Effect of different basis sets on lowest electronic transition energies (eV) of silicon compounds

	STO-3G	STO-3G+ sp(0.015)	3-21G	3-21G+ sp(0.015)	Exp.
SiH_4	18.40	8.81	11.71	10.02	8.9
Si_2H_6	13.96	6.92	9.52	8.29	>6.4
Si_3H_8	12.27	6.54	8.70	7.99	>6.4
c-Si_4H_8	11.61	5.83	6.76	6.71	—
Si_2Me_6	13.53	6.08	9.02	7.45	6.17

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energies with respect to the augmented functions. Ionization energies only need appropriate descriptions of the doubly occupied valence orbitals. In contrast, excitation energies need two sets of well described orbitals. These are the valence orbitals from which excitations occur, as well as the singly excited orbitals. With one additional (s, p) set per Si atom a compromise must be achieved by which the ionization energies have partially lost their accuracy. The calculation of excited states was performed by the method of "improved virtual orbitals" (IVO).[10] The main advantage of the IVO method, which is identical to a limited expansion of configurations (CI), is the generation of two sets of singly excited orbitals for singlet and triplet states. The orbital from which excitation takes place is singly occupied. Excitation energies simply are differences between orbital energies and show Koopmans theorem accuracy.

PE SPECTRA OF POLYSILANES AND ASSIGNMENT

Photoelectron (PE) spectra of silanes and the assignment of ionization potentials by quantum chemical calculations are already described in literature.[11-14] Electron delocalization and valence band structure in linear polysilanes, Si_nH_{2n+2}, in particular the valence band broadening with increasing length of the chain, have been discussed repeatedly. PE spectra of linear polysilanes of up to $n = 6$ silicon atoms are composed of three parts which can be interpreted as follows:

(1) ionizations from σ(Si–Si) bonds in the range 9.5–11 eV;

(2) ionizations from σ(Si–H) bonds in the range 12–13.5 eV;

(3) ionizations from orbitals with dominating Si(3s) contributions in the range 15–17 eV.

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Theoretical studies within the framework of HMO theory start with the assumption that the interaction between σ(Si–Si) and σ(Si–H) bond orbitals is small and, therefore, can be neglected.[11] The study of Si–Si bonds without considering the adjacent Si–H bonds, however, leads to significant deviations of up to 1 eV between "calculated", i.e. optimal fitting of experimental data by the Hückel formulas, and measured values. A further disadvantage of the HMO formalism is associated with the assignment because the participation of specific Si atomic orbitals such as 3s and 3p cannot be identified.

The assignment of PE spectra by means of the semi-empirical CNDO method allows the distinction between 3s and 3p atomic orbital contributions, but even the lowest ionization potentials deviate from the measured values by 3 eV.[12]

Recently reported *ab initio* calculations using the 3-21G(d) basis set and applying Koopmans' theorem show the hitherto best agreement between calculated and experimental ionization potentials.[14] As expected d-orbitals were found to be meaningless for the description of valence MO's.

In the following section *ab initio* calculations for ionization potentials of a series of silanes applying Koopmans' theorem are described. Answers to the following questions were expected:

(1) Is there a significant interaction between Si–Si and Si–H bond orbitals?

(2) What is the difference of the PE spectra for linear and cyclic polysilanes?

(3) What kind of influence has permethylation on the PE spectra?

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The following systems have been investigated:

Si_nH_{2n+2} $n = 1, \ldots, 5$
$c\text{-}(SiH_2)_n$ $n = 4, 5, 6$
Si_nMe_{2n+2} $n = 2, 3$
$c\text{-}(SiMe_2)_4$

Linear polysilanes Si_nH_{2n+2}. Standard geometry data were used for silicon hydrides: Si–Si = 2.34 Å, Si–H = 1.48 Å, <SiSiH = 110°, <SiSiSi = 110°; all-trans conformation was assumed for the species with $n = 4$ and 5. The calculated Koopmans' theorem ionization potentials are summarized in Table III. As depicted in Figure 1, our results are in excellent agreement with experimentally obtained PE spectra.[12] In the range of σ(Si–Si) and σ(Si–H) ionizations the maximum deviation of calculated from experimental values[11a,12] is 0.7 eV. The energetically lowest $n - 1$ ionizations of Si_nH_{2n+2} are assigned to orbitals with dominating σ(Si–Si)3p contributions. These orbitals, however, also contain σ(Si–H) contributions which are larger than those of σ(C–H) in linear hydrocarbons. The C(2p):H(1s) ratio of the expansion coefficients in the HOMO's of linear hydrocarbons is 5:1, whereas the corresponding Si(3p):H(1s) ratio of linear silicon hydrides is 3:1. For polysilanes with $n \geq 4$, the density of peaks in the σ(Si–H) range of the PE spectra is too high to allow resolution. Degenerate point groups appear for the systems $SiH_4(T_d)$ and $Si_2H_6(D_{3d})$ so that Jahn–Teller splittings of the orbitals T_2 and E_g, E_u, respectively, should be accounted for. The highest n ionization energies of Si_nH_{2n+2} are assigned to low lying orbitals with dominating Si(3s) contributions. In this case the requirements of Koopmans' theorem become doubtful. Concomitantly Si(3s) ionization cannot be resolved in the PE spectra of higher polysilanes.

TABLE III

Calculated Koopmans ionization potentials (eV) and symmetries of molecular orbitals of linear polysilanes

SiH_4	T_d	12.49	19.78			
		F_2	A_1			
Si_2H_6	D_{3d}	10.15	12.16	13.12	18.39	20.69
		A_{1g}	E_g	E_u	A_{2u}	A_{1g}
Si_3H_8	C_{2v}	9.60	10.82	12.14	12.68	12.69
		B_2	A_1	B_1	B_2	A_2
		13.01	13.50	17.80	19.61	21.17
		A_1	B_1	A_1	B_2	A_1
Si_4H_{10}	C_{2h}	9.12	10.76	11.05	12.21	12.48
		A_g	A_g	B_u	B_g	A_u
		12.82	12.95	13.08	13.76	17.62
		B_u	A_g	B_g	A_u	B_u
		...	21.45			
			A_g			
Si_5H_{12}	C_{2v}	8.85	10.61	11.02	11.15	12.19
		B_2	A_1	A_1	B_2	B_1
		12.32	12.74	12.79	12.92	13.31
		A_2	B_1	A_1	B_2	A_2
		13.86	17.52	...	21.60	
		B_1	A_1		A_1	

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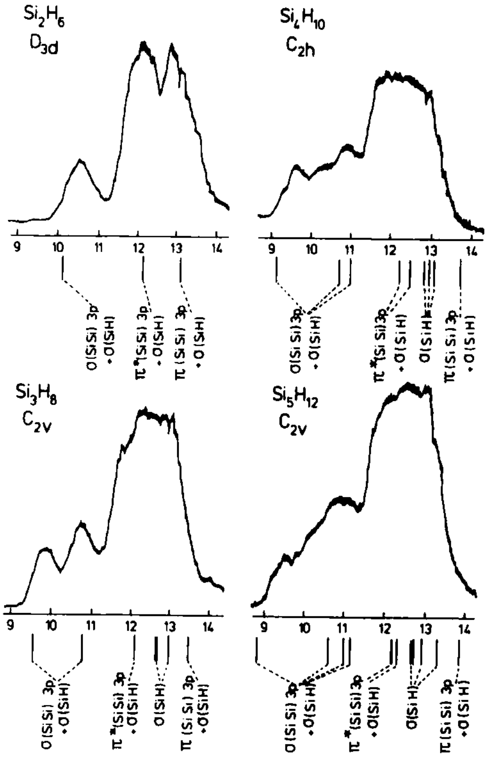

FIGURE 1 Assignment of PE spectra of linear silanes Si_nH_{2n+2} ($n = 2, 3, 4, 5$).

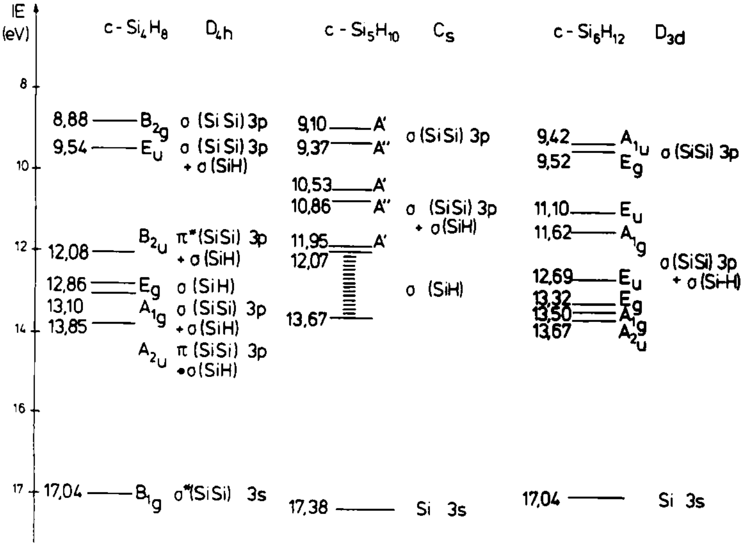

FIGURE 2 Calculated Koopmans ionization potentials of cyclic polysilanes $(SiH_2)_n$ ($n = 4, 5, 6$) and assignment.

Cyclic polysilanes $(SiH_2)_n$. The hypothetic cyclotetrasilane was calculated in D_{4h} symmetry. This restriction is justified by the low destabilization with respect to the folded D_{2d} structure of only 0.5 kcal/mol.[15] The conformation of cyclopentasilane is of the type "half-boat" (C_s symmetry), and that of cyclohexasilane is "chair" (D_{3d} symmetry).[16] Alternative conformations such as "boat" (C_{2v}) do not yield significant changes in the ionization energies. A Si–Si distance of 2.36 Å was used for the four-membered ring, and 2.34 Å for five- and six-membered rings.

Calculated valence ionization energies and their interpretation are similar to those of linear polysilanes (Figure 2). However, the trend of the ionizations from the HOMO's with respect to the increasing ring size is reversed. These HOMO's now are pure σ(Si–Si)3p orbitals with no or negligibly small σ(Si–H) contributions. The reversed order of lowest ionization energies very well might be due to the decreasing ring strain. The energetic separation of Si–Si and Si–H ionizations is less pronounced in cyclosilanes than in linear silanes. For the four-membered ring the fourth σ(Si–Si) MO is embedded between σ(Si–H) MO's. In the six-membered ring Si–Si contributions in the valence MO's continuously decrease with decreasing orbital energies, and Si–H contributions increase.

Permethylated silanes. The molecules Si_2Me_6 and Si_3Me_8 were calculated using the following geometry data: Si–Si = 2.34 Å, Si–C = 1.87 Å, C–H = 1.09 Å, <SiSiC = 110°, <SiCH = 110°, <SiSiSi = 118°.

Calculated Koopmans ionization energies of selected permethylated silanes are presented in Figure 3 together with the σ(Si–Si)3p energy levels of the corresponding hydrosilanes demonstrating the significant destabilization of the σ(Si–Si) orbitals in the methyl compounds.[10,13] Although these orbitals are energetically well separated from those dominated by σ(Si–C) contributions, there is, in contrast to earlier assumptions,[13] a destabilizing interaction between

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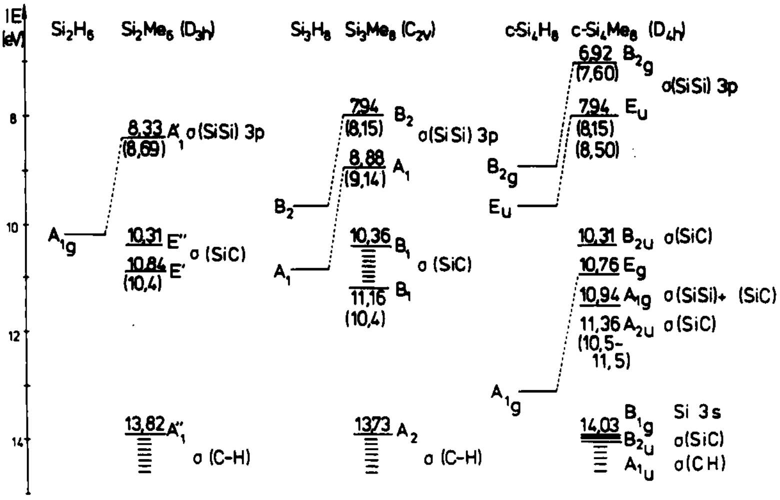

FIGURE 3 Effect of methylation on σ(Si–Si) orbitals of Si_2H_6, Si_3H_8, and c-Si_4H_8 and calculated Koopmans ionization potentials of the corresponding permethyl-silanes. IP's obtained from PE spectra[13,17] are displayed in brackets.

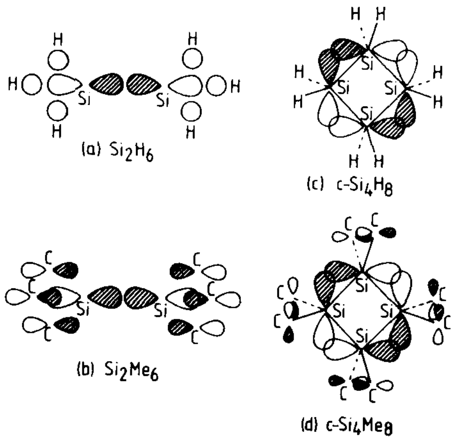

FIGURE 4 HOMO's of (a) disilane (A_{1g}) and (b) hexamethyldisilane (A_1'), (c) cyclotetrasilane (B_{2g}) and (d) octamethylcyclotetrasilane (B_{2g}).

σ(Si–Si) and σ*(Si–C) (Figure 4(b)) instead of the stabilizing σ(Si–Si)–σ(Si–H) interaction in silicon hydrides (Figure 4(a)). The onset of orbitals with dominating σ(Si–C) contributions is separated from the lowest σ(C–H) orbitals by 3 eV, but in the lower lying MO's both contributions are mixed. Even the lowest valence MO's with Si(3s) contributions are strongly destabilized with respect to silicon hydrides.

The destabilization of σ(Si–Si) orbitals in octamethylcyclotetrasilane is 2 eV with respect to the unsubstituted species Si_4H_8, although there is no stabilizing σ(Si–Si)3p–σ(Si–H) interaction in Si_4H_8 for symmetry reasons (Figure 4(c)). The

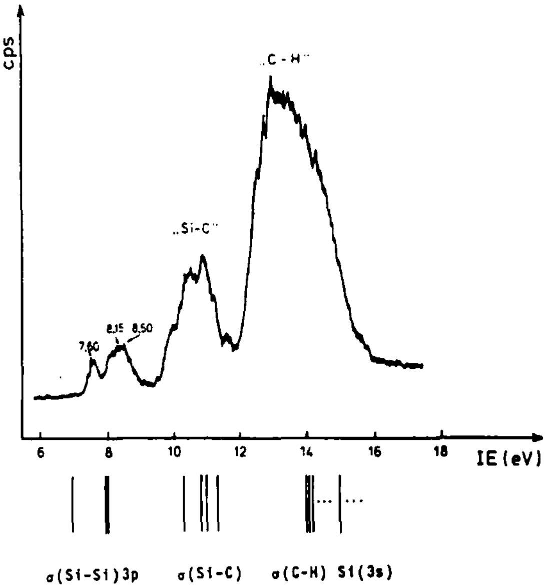

FIGURE 5 PE spectrum and Koopmans ionization potentials of octamethylcyclotetrasilane.

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destabilizing σ(Si–Si)3p–π^*(Si–C) interaction probably causing the low ionization potentials of Si_4Me_8 is depicted in Figure 4(d). The fourth σ(Si–Si) MO is embedded between σ(Si–C) MO's. This is in agreement with the PE spectrum if a Jahn–Teller splitting of the degenerate E_u orbitals is taken into account (Figure 5).[17]

UV SPECTRA OF POLYSILANES AND ASSIGNMENT

UV spectra of linear polysilanes, Si_nH_{2n+2}, show increasing bathochromic shifts of the first absorption bands with increasing chain length. The lowest electronic transition energies for linear polysilanes with $n = 2, \ldots, 5$ silicon atoms are >6.4, >6.4, 5.96, 5.68 eV, respectively. Continuous absorption occurs at higher energies.[11,18]

Theoretical interpretations of UV spectra of polysilanes have been tried within the framework of HMO theory. The lowest excited states should be described by so-called HOMO→LUMO excitations which are of the type σ(Si–Si)→ σ^*(Si–Si) where the LUMO's are antibonding valence MO's.

In contrast, *ab initio* calculations have shown that vacant orbitals are not appropriate tools for the description of excited states. On the one hand these orbitals do not reflect the nature of excited states wave functions; on the other hand their energies show an arbitrary sequence. In general unoccupied orbitals energetically lie above the ionization limit.[10] Saturated compounds such as polysilanes do not have bound excited states which can be described by means of antibonding valence orbitals. Even the lowest excited orbitals are Rydberg-like and can only be described by silicon AO's of the type 4s and/or 4p (Figure 6). These notations should not be taken literally due to the lack of strict orthogonality between the basis functions for the description of valence orbitals, 3s and 3p, and Rydberg orbitals, 4s and 4p. Split valence basis sets such as 3-21G make the diffuse character of excited orbitals less visible (by occupation numbers or excitation energies) than minimal basis sets (STO-3G). Extended basis sets no longer allow an unambiguous distinction between "valence" basis functions and "diffuse" functions. Furthermore, the importance of additional diffuse basis functions decrease with increasing size of the molecules (Table II).

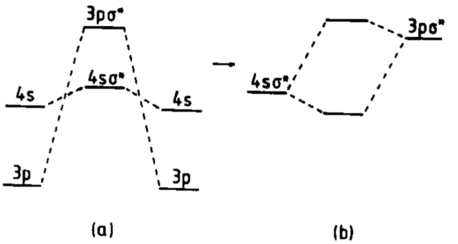

FIGURE 6 Orbital correlation diagrams for the stabilizing effect of Rydberg 4s AO's on the antibonding 3pσ^* interaction. The combination (b) of the initially constructed antibonding 3pσ^* and 4sσ^* MO's (a) leads to a stabilized lowest antibonding MO.

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Ab initio calculations of electronic transition energies and excited states wave functions have been performed for a series of polysilanes in order to answer the following questions:

(1) What is the reason for the bathochromic shifts of UV absorption bands of linear polysilanes with increasing length of the chains?

(2) What is the assignment of the bands in the UV spectra?

(3) What causes the differences in the UV spectra of linear and cyclic polysilanes?

(4) What kind of influence has permethylation on the UV spectra?

Linear polysilanes Si_nH_{2n+2}. The use of vacant valence orbitals is unsuitable for the description of excited states not only within the framework of HMO theory[11] but also for *ab initio* calculations[10,14] as shown in Figure 7. The calculated excitation energies turn out to be too high and the bathochromic shift with increasing chain length by far is overestimated due to the strong stabilization of the LUMO's (3pσ*). The use of atomic functions of the types 4s and 4p causes drastic stabilization of the empty orbitals which now exhibit constant energies slightly above the ionization limit. Thus, lowest unoccupied orbitals (LUMO) are artefacts of unsufficient theories because their energies tend towards the ionization limit with increasing expansion of the basis set. Improved virtual orbitals (IVO), however, which are singly excited MO's, are found below the ionization limit and, therefore, represent bound states. With increasing chain length they are slightly destabilized, but this trend appears to be weaker compared to the corresponding HOMO's.

In Table IV the four lowest excited states are characterized by excitation energies and orbital transitions for Si_nH_{2n+2} ($n = 2, \ldots, 5$). In all cases the excitations occur from the corresponding HOMO's of the type σ(Si–Si)3p. The

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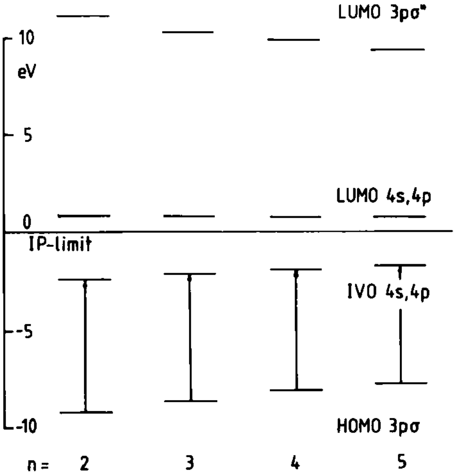

FIGURE 7 HOMO, first excited MO (IVO), Rydberg-like LUMO, and valence LUMO in linear polysilanes Si_nH_{2n+2} ($n = 2, 3, 4, 5$).

TABLE IV

Calculated Koopmans transition energies and their assignment to UV spectra of linear polysilanes

Molecule		ΔE (eV) calc.	Assignment (Orbitals)	ΔE (eV) exp.[a]	ε
SiH_4	T_d	8.81	$F_2 \rightarrow A_1$ (4s)	8.9	
		9.81	F_2 (4p)	9.6	
Si_2H_6	D_{3d}	6.92	$A_{1g} \rightarrow A_{1g}$ (4sσ) fb.	>6.4	
		7.23	A_{2u} (4sσ^*)		
		7.41	E_u (4pπ)		
		7.92	A_{1g} (4pσ) fb.		
Si_3H_8	C_{2v}	6.54	$B_2 \rightarrow A_1$ (4sσ^*)	>6.4	
		6.81	A_1 (4s, 4pσ^*)		
		6.85	B_2 (4s, 4pσ)		
		6.94	B_1 (4pπ) fb.		
n-Si_4H_{10}	C_{2h}	6.28	$A_g \rightarrow A_g$ (4s, 4pσ^*) fb.		
		6.42	B_u (4sσ^*)	5.96	8010
		6.51	B_u (4s, 4pσ^*)		
		6.58	A_u (4pπ)		
n-Si_5H_{12}	C_{2v}	6.14	$B_2 \rightarrow A_1$ (4sσ^*)	5.68	6220
		6.20	A_1 (4sσ^*)		
		6.38	B_2 (4pσ)		
		6.41	B_1 (4pπ) fb.		

[a] Reference 11.

frequently discussed bathochromic shift observed in the UV spectra of linear polysilanes usually is considered as a unique spectral property due to the silicon–silicon bond acting as a chromophore, probably by employing vacant d-orbitals of the silicon atom.[11,18] However, *ab initio* calculations do not show any participation of d-orbitals in low-lying excited states. Additionally the present calculations seem to belie any unique electronic properties of the silicon–silicon bond. According to Figure 8, excitation energies of linear polysilanes and the homologous alkanes exhibit nearly the same shift to lower energies with increasing length. Only the absolute values of the transition energies differ by 3 eV, what also is reflected by the ionization potentials. For $n \geq 3$ the lowest excited orbitals are of the type σ^*(Si–Si)4s. Excited π(Si–Si)4p MO's are found in third or fourth place 0.3–0.4 eV above the lowest excited MO's. Even in short

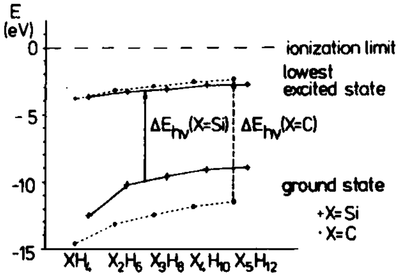

FIGURE 8 Lowest Koopmans ionization potentials and electronic transition energies ΔE of linear alkanes and silanes X_nH_{2n+2} ($n = 1, 2, 3, 4, 5$).

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chains the excited states are energetically separated by only 0.1 eV, what explains the observed UV continuum.

Cyclic polysilanes $(SiH_2)_n$. Compared to linear polysilanes cyclosilanes exhibit some interesting features (Table V). As well as the first ionization potentials the lowest excitation energies also increase with increasing ring size. The five- and six-membered rings show low-lying excited states with excitations from the HOMO-1. The lowest excited MO of the hypothetic four-membered ring is 4s, 4p-σ in character, the 4p-π MO appears in third place. The five-membered ring has a lowest excited MO with 4s, 4p-σ^* character. The same situation is found for the six-membered ring in boat conformation. However, in chair conformation the lowest excited MO is composed of axial 4p AO's in order to form a π^*-like MO. Numerous symmetry-forbidden transitions (fb.) facilitate the assignment of the UV absorption bands. In the five-membered ring with C_s symmetry all transitions are symmetry-allowed. The two measured absorption maxima at 5.68 and 6.23 eV can be assigned to the calculated $A' \rightarrow A'$ transitions at 5.89 and 6.34 eV, respectively. The six-membered ring shows two conformers with comparable energies. For the chair conformation (D_{3d} symmetry) the four lowest transitions are symmetry-forbidden so that the measured peak at 6.36 eV must be assigned to the $B_1 \rightarrow A_1$ transition from the HOMO-1 in boat conformation (C_{2v} symmetry) calculated at 6.65 eV.

TABLE V

Calculated Koopmans transition energies and their assignment to UV spectra of cyclic polysilanes

Molecule		ΔE (eV) calc.	Assignment (Orbitals)	ΔE (eV) exp.[a]	ε
c-Si_4H_8	D_{4h}	5.83	$B_{2g} \rightarrow A_{1g}$ (4s, 4pσ) fb.		
		5.85	E_u (4s, 4p) non-bond.		
		6.06	A_{2u} (4pπ) fb.		
		6.36	B_{1g} (4s, 4pσ^*) fb.		
c-Si_5H_{10}	C_s	5.89	$A' \rightarrow A'$ (4s, 4pσ^*)	5.68	3000
		6.19	A'' (4s, 4pσ^*)		
		6.25	$A'' \rightarrow A'$ (4s, 4pσ^*)		
		6.34	$A' \rightarrow A'$ (4s, 4pσ^*)	6.23	14000
		6.58	A'' (4s, 4pσ^*)		
c-Si_6H_{12}	D_{3d}	6.50	$A_{1u} \rightarrow A_{1g}$ ($4p_{ax}\pi^*$) fb.		
		6.73	E_u (4s, 4pσ) fb.		
		6.73	A_{2u} (4sσ^*) fb.		
		6.77	$E_g \rightarrow A_{1g}$ ($4p_{ax}\pi^*$) fb.		
		6.98	E_u (4s, 4pσ)		
c-Si_6H_{12}	C_{2v}	6.55	$A_2 \rightarrow A_1$ (4s, 4pσ^*) fb.		
		6.65	$B_1 \rightarrow A_1$ (4s, 4pσ^*)	6.36	6000
		6.74	$A_2 \rightarrow A_1$ (4s, 4pσ^*) fb.		
		6.79	B_2 (4s, 4pσ)		
		6.79	B_1 (4s, 4pσ^*)		
		6.82	$B_1 \rightarrow A_1$ (4s, 4pσ^*)		
		6.85	B_2 (4s, 4pσ) fb.		
		6.87	B_1 (4s, 4pσ^*)		

[a] This work.

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Permethylated polysilanes. Introducing methyl groups into polysilanes significantly reduces their excitation energies.[10,18] The effect of permethylation on the excited states of Si_2H_6, Si_3H_8, and c-Si_4H_8 is shown in Figure 9, together with the assignment of experimentally obtained UV maxima. Doubly occupied orbitals in the ground state, in particular, exhibit much stronger destabilization than singly excited orbitals. The destabilization of the former was already discussed by involving antibonding σ^*(Si–C) contributions in the chapter about the PE spectra. Excited 4p-π orbitals are less destabilized by methylation than excited 4s, 4p-σ or σ^* orbitals (compare Fig. 9). Therefore, 4p-π orbitals in Si_2Me_6, Si_3Me_8, and Si_4Me_8 now are found in second place 0.2–0.3 eV above the lowest excited MO's which show 4s-σ character. For Si_4Me_8 two peaks with very low intensity were measured at 4.04 and 4.89 eV. Those are assigned to D_{4h}-symmetry-forbidden transitions which have lost their strict forbiddeness by the rotation of methyl groups. The $B_{2g} \rightarrow E_u$ transition is assigned to the peak with high intensity at 5.38 eV.

Recently published transition energies of permethylated polysilanes using a semi-empirical method of linear combination of sp^3 hybridized atomic orbitals do not reflect general features of UV spectra such as the manifold of states and assignment.[19] *Ab initio* calculations where additional diffuse functions are included do not indicate any silicon 3s contribution, neither in the HOMO's nor in excited orbitals. However, the semi-empirical method mentioned above could allow to fit some experimental data correctly, independent of the quality of the underlying theory, if the parameters are chosen appropriately.

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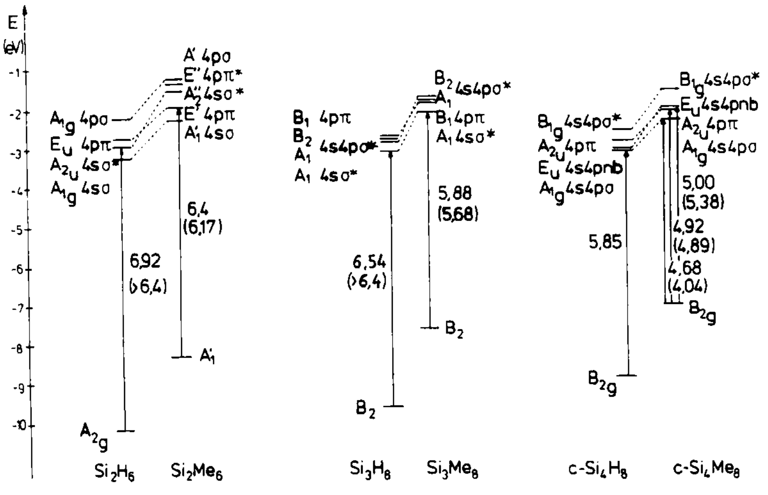

FIGURE 9 Effect of methylation on excited states of Si_2H_6, Si_3H_8, and c-Si_4H_8, and assignment of experimentally obtained UV maxima[4,18] (experimental values in brackets).

REFERENCES

1. E. Hengge, *Chem. Ber.* **95,** 648 (1962).
2. C. G. Pitt, L. L. Jones and B. G. Ramsay, *J. Am. Chem. Soc.* **89,** 5471 (1967).
3. C. G. Pitt, *J. Am. Chem. Soc.* **91,** 6613 (1969).
4. H. Stüger and E. Hengge, *Monatsh. Chem.* **119,** 873 (1988).
5. E. Hengge and G. Bauer, *Monatsh. Chem.* **106,** 503 (1975).
6. E. Hengge and D. Kovar, *Z. Anorg. Allg. Chem.* **459,** 123 (1979).
7. J. S. Binkley, M. J. Frisch, D. J. DeFrees, R. Krishnan, R. A. Whiteside, H. B. Schlegel, E. M. Fluder and J. A. Pople, GAUSSIAN 82, Carnegie-Mellon University, Pittsburgh, PA (1982).
8. W. J. Hehre, L. Radom, P. V. R. Schleyer and J. A. Pople, *Ab initio Molecular Orbital Theory* (Wiley, New York, 1986).
9. T. H. Dunning and P. J. Hay in *Modern Theoretical Chemistry* Ed.: H. F. Schaefer (Plenum, New York, 1977), Vol. 3, Chap. 1.
10. E. A. Halevi, G. Winkelhofer, M. Meisl and R. Janoschek, *J. Organomet. Chem.* **294,** 151 (1985).
11. (a) F. Fehér, Forschungsbericht des Landes Nordrhein-Westfalen, Nr. 2632, Westdeutscher Verlag (1977); (b) Y. Harada, J. N. Murrell and H. H. Sheena, *Chem. Phys. Lett.* **1,** 595 (1968); R. Roberge, C. Sandorfy, J. I. Matthews and O. P. Strausz, *J. Chem. Phys.* **69,** 5105 (1978).
12. H. Bock, W. Ensslin, F. Fehér and R. Freund, *J. Am. Chem. Soc.* **98,** 668 (1976).
13. H. Bock and W. Ensslin, *Angew. Chem.* **83,** 435 (1971); *Angew. Chem. Int. Ed. Engl.* **10,** 404 (1971).
14. J. T. Nelson and W. J. Pietro, *J. Phys. Chem.* **92,** 1365 (1988). After this manuscript was finished correlation corrected low-lying ionization energies of linear polysilanes were reported using electron propagator theory. Calculated ionization potentials are in agreement with measured values by 0.1–0.2 eV. J. V. Ortiz and J. W. Mintmire, *J. Am. Chem. Soc.* **110,** 4522 (1988).
15. A. F. Sax, *Chem. Phys. Lett.* **127,** 163 (1986).
16. Z. Smith, A. Almenningen, E. Hengge and D. Kovar, *J. Am. Chem. Soc.* **104,** 4362 (1982).
17. H. Bock, B. Solouki, H. Stüger and E. Hengge (unpublished results).
18. H. Gilman, W. H. Atwell and G. L. Schwebke, *J. Organomet. Chem.* **2,** 369 (1964).
19. A. Herman, *Chem. Phys.* **122,** 53 (1988).

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