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The Electronic Spectra of the Alkyl, Fluorine and Chlorine Substituted Derivatives of Silane*

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The main characteristics of the ultraviolet absorption spectra of simple alkyl, fluorine and chlorine derivatives of silane are described. The interpretation of these spectra is discussed in relation to the respective photoelectron spectra, the Rydberg-valence-shell distinction and involvement of $3d$ atomic orbitals.

Key words: Silane, alkyl, fluorine, and chlorine substituted derivatives of ~

1. Introduction

A great deal of work has been done on the electronic spectra of silane derivatives. The results are, however, scattered in the literature and it is felt that a comprehensive article could be useful at this stage. The present paper is meant to be intermediate between a review and an original contribution. It is based partly on spectra published previously by various authors including ourselves. As to the alkyl and fluorine substituted silanes these have been treated in detail in one of our recent publications [1] and only a short description of their main characteristics will be given. To this a treatment of the spectra of chlorine substituted silanes will be added.

2. Experimental

The spectra determined by us were measured on a model 225 1 m McPherson vacuum UV spectrometer and a model PS-16 Perkin-Elmer photoelectron instrument with a HeI source. All spectra mentioned in this paper were obtained in the vapor phase. More details are given in [1].

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* Dedicated to Professor Dr. Hermann Hartmann on the occasion of his 65th birthday.

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The methods used for the purification of alkyl and fluorosilanes were also given in [1]. The chlorine derivatives were treated as follows:

The materials were purified by high vacuum distillation at reduced pressure then by gc on either of three columns: 22 ft silicone oil DC 200 on Chromosorb WAW (A), 8 ft di-iso-decyl phthalate (B), 8 ft dimethyl sulfonane (C), or 6 ft Porapak Q (D), all at room temperature and using a helium flow rate of 25 ml/min.

$HSiCl_3$ (Silicon Chem.) was degassed at $-196°$ and $-130°$, distilled at $-78°$ and purified on column A; retention time, 9.6 min.

Me_2SiHCl (Pierce Chem. Co.) and Me_3SiCl (Columbia Org. Chem. Co. Inc.) were degassed at $-160°$ and $-196°$, respectively and purified on column B; retention times, 5.8 and 7.2 min respectively.

In all cases the final purity was estimated to be 99.9%.

2.1. *Alkyl and Fluorine Derivatives of Silane*

The ultraviolet absorption spectra of silane and its derivatives generally consist of diffuse bands. They give no detailed information about the structure of the molecules in their excited states. These spectra can be interpreted in a general manner, however, by making use of the respective photoelectron spectra, Rydberg term values, analogies with the spectra of related carbon compounds and quantum chemical calculations.

The lowest excited states of paraffins are known to be of the Rydberg or, more exactly, of intermediate Rydberg–valence shell type. The originating orbital has t_2 symmetry in molecules having tetrahedral symmetry like methane or neopentane. This makes the transition of lowest energy allowed: $(3s \leftarrow t_2)$; $(^1T_2 \leftarrow {}^1A_1)$. Actually the first (3*s*) band is intense in the spectra of these molecules. It is followed by a pronounced minimum and a broad band containing the allowed member of the 3*p* manifold and members of the 3*d* manifold. Paraffins having approximate tetrahedral symmetry possess this type of spectrum [2]. Ethane has a spectrum of different appearance. Under D_{3d} symmetry triple degeneracy is no longer possible, instead we find two very close-lying originating orbitals, $1e_g$ and $3a_{1g}$, the former mainly populated in the C—H bonds, the latter in the C—C bond. (See, for example, [3] and [4].) The transition to 3*s* being symmetry-forbidden from both these orbitals the spectrum begins with a very weak band at its low-frequency end and is followed without an apparent minimum by intense bands belonging to the allowed 3*p* manifold. All normal paraffins have spectra close to the ethane type. It was proposed [1] to call these two types of spectra "round field" and "long field", a distinction which is helpful in understanding the UV spectra of saturated hydrocarbons.

The same applies to silane and the alkylsilanes. There is a complete analogy with the paraffins concerning the originating orbitals as well as the orbitals associated with the excited electron in the lower excited states. The first band in silane is $(4s \leftarrow t_2)$, 4*s* being a relatively small intermediate type Rydberg orbital. This has been shown convincingly by the *ab initio* SCF MO calculations of Schwarz [5, 6] and the Xα calculations of Roberge and Salahub [7], and it is the clue to the understanding of silane spectra. There is no evidence for an additional valence-shell type transition in this spectral region. The bands that follow at higher frequencies can be assigned to the $4p$ and $3d$ manifolds with significant valence-shell contributions. The spectrum of methyl silane is an example for a long field spectrum, that of tetramethyl silane for a round field spectrum. In general, longer alkyl chains and a low degree of substitution on the Si atom tend to favor long field spectra.

In fluoromethanes and alkyl-fluoromethanes and silanes the originating orbital is mainly populated in C—H and C—C bonds (except for CF_4 and SiF_4). The lowest electronic transitions still go to Rydberg levels. Fluorine substitution causes hypsochromic shifts in both the lowest photoelectron and UV bands. The shift is slight for mono- and difluoro derivatives but it is sizeable for trifluoromethanes and silanes. Fluorine substitution in long field silanes affects to a different degree the two close-lying originating orbitals. A consequence of this fluoroeffect is the sharpening of the lowest PE band due to a shift to higher energies of one of its contributors. At the same time the gap between the $4s$ and $4p$ bands in the UV spectra deepens because of the moving to higher frequencies of the transitions originating with the shifted ground state orbital. For this reason the UV spectra of the fluorocompounds tend to be closer to the round field type than those of the related methyl substituted compounds.

In summary, the UV absorption bands of alkyl and fluorine substituted silanes are due to transitions from a bonding σ-orbital to intermediate type Rydberg orbitals. There is no evidence for the involvement of $3d$ orbitals. (For an extensive list of references, see paper [1].)

2.2. Chlorine Substituted Silanes and Alkylsilanes

The spectra of chlorosilanes are very different from those of silane derivatives containing alkyl or fluorine substituents only. The highest occupied orbitals in the ground state are formed from chlorine lone pair atomic orbitals ($\overline{Cl}$) and all the observed UV transitions originate with these. The situation is very similar to that related to the alkyl halides which are discussed in detail by Turner [8]. Connected with this is the shift to higher energies of the photoelectron bands related to the bonding orbitals.

The simplest molecule of this kind is chlorosilane, SiH_3Cl. Its PE spectrum has been measured by several authors (9–11) who assigned the first PE band (11.61 eV, vertical) to ionization from the doubly degenerate chlorine lone pair orbital. The second band (13.4 eV) is assigned to the mainly Si–Cl bonding orbital (a_1) and the third one (13.7 eV) to the degenerate (e) SiH bonding orbital. The energies of these three bands are comparable with those of the analogous bands of CH_3Cl, 11.28, 14.4 and 15.5 eV, respectively. It is to be noted that SiH_3Cl has a *higher* IP than CH_3Cl, 11.61 compared with 11.28 eV, while the IP of GeH_3Cl (11.30 eV) is lower than that of SiH_3Cl.

Howell and Van Wazer (12) carried out an *ab initio* study of the role of *d* orbitals in chlorosilane. These authors included into the basis set first, 3*d* AOs on Si only, then on Cl only, and finally on both Si and Cl. The stabilization of the total energy amounted to about 2.5, 0.6 and 2.9 eV, respectively. This is a striking demonstration of the importance of the 3*d* AOs of the silicon atom. At the same time it is clear that in order to have a sizeable effect like this, the silane derivative must contain a substituent (Cl) having AOs with energies sufficiently close to those of the Si 3*d* AOs. This is not the case for alkyl and fluorosilanes. The frontier orbital in chlorosilanes is stabilized much less (by about 0.25 eV) and is of mixed $\overline{\mathrm{Cl}}(\pi)$ and antibonding (Si–Cl)π^* character. The overlap in the Si—Cl bond would be negative without the 3*d* orbitals but becomes positive when they are included. At the same time, the silicon atom becomes negative with respect to both the chlorine and the hydrogens. The effects of the inclusion of the 3*d* orbitals on the other MOs are also discussed by Howell and Van Wazer and are instructive. For our purposes it is sufficient to note that, provided Koopmans' theorem holds, these calculations correctly rationalize the increase of the IP from CH_3Cl to SiH_3Cl. It is interesting too that Bell and Walsh [13], on the basis of their UV absorption measurements, predicted this increase several years before the PE spectra became known. They observed that, for each silyl compound studied, the spectrum was shifted to higher frequencies relative to that of the corresponding methyl compound and they attributed this to the partial loss of lone-pair character and the gain in bonding character of the originating orbital on passing from the carbon to the silicon compounds, due to the intervention of the silicon 3*d* AOs.

The UV band of lowest frequency in alkyl chlorides is known to be $\sigma^* \leftarrow n(p\pi)$ where the σ^* orbital is antibonding in the C—Cl bond [14, 15]. On the basis of the above argument this band in SiH_3Cl is expected to move to higher frequencies. Actually, it has not been observed and it is likely to be hidden under the envelope of the more intense Rydberg bands. (Photochemists should not forget about it.) The $4s \leftarrow n(p\pi)$ and $4p \leftarrow n(p\pi)$ bands have been identified at 67,000 and 74,900 cm^{-1} respectively by Bell and Walsh [13]. The corresponding term values are 26,000 and 18,700 cm^{-1}, somewhat lower than those for the related carbon compounds.

We were hoping that the UV spectra of other monochlorosilanes could reveal the presence of the $\sigma^* \leftarrow n$ band and have therefore measured those of $(CH_3)_3Si—Cl$

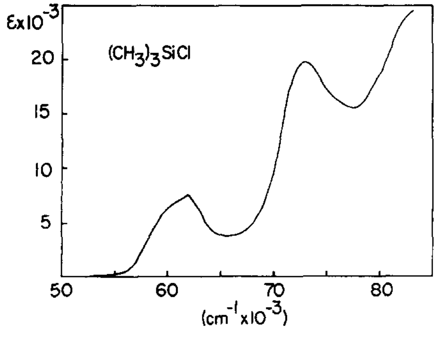

Fig. 1. The far-ultraviolet absorption spectrum of $(CH_3)_3SiCl$

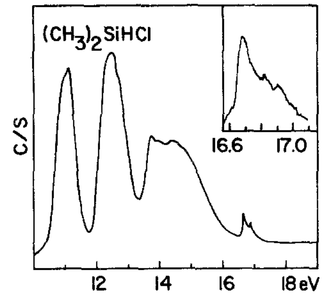

Fig. 2. The HeI photoelectron spectrum of $(CH_3)_2SiHCl$

and $(CH_3)_2SiHCl$. The PE spectrum of the former has already been reported by Block *et al.* [16]. The Jahn-Teller split $\overline{\text{Cl}}$ band of this compound gives two peaks, at 10.60 and 10.8 eV. The next three bands at 11.9, 12.0 and 12.3 eV must correspond to the *e*(Si—C) and a_1(Si—Cl) orbitals. A composite band follows, centered at 13.8 eV (CH_3) and a weak band at 16.2 eV (Si3*s*). The first band in the UV spectrum (Fig. 1) seems to contain three peaks near 60,000 (or somewhat lower), 61,900 and 62,300 cm^{-1}. They are badly overlapped. Two of the peaks might correspond to the Jahn-Teller split $4s \leftarrow n$ band with term values of the order of 25,000–27,000 cm^{-1}. The third peak might be the $\sigma^* \leftarrow n$ band but it is impossible to ascertain this. It can be alternatively interpreted as being due to residual vibrational fine structure. This would imply an Si—Cl frequency of about 400 cm^{-1} which has a ground state value of 487 cm^{-1} [17]. The 4*p* region is weak. The very strong peak at 73,000 cm^{-1} is likely to receive contributions from 3*d* and higher Rydberg and valence shell transitions.

$(CH_3)_2SiHCl$ has a better resolved PE spectrum (Fig. 2). The first band has again two peaks near 10.9 and 11.1 eV resulting probably from the lifting of the degeneracy of the $\overline{\text{Cl}}$ band. The *e*(Si—C) and a_1(Si—Cl) bands are at 12.2, 12.5 and 12.8 eV. They are followed by weaker bands at 13.8, 13.9 and 14.4 eV, a broad shoulder and a weak band at 16.8 eV. Attempts to make detailed assignments do not seem to be rewarding. In the UV spectrum (Fig. 3) the 4*s* bands can be assigned to the broad feature in the 63,000–65,000 cm^{-1} region with term values of about 25,000 cm^{-1}. The 4*p* band is better defined in this case, it is at 67,700 cm^{-1} giving a term value of 19,900 cm^{-1}.

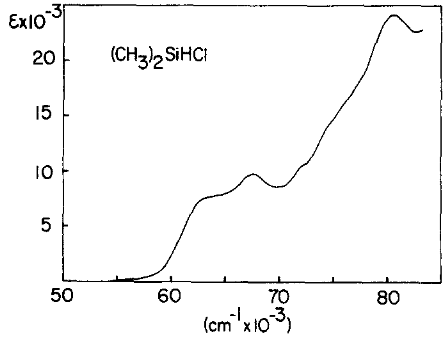

Fig. 3. The far-ultraviolet absorption spectrum of $(CH_3)_2SiHCl$

The PE spectra of SiH_2Cl_2, CH_3SiHCl_2 and $(CH_3)_2SiCl_2$ have been published by Frost *et al.* [10, 11], Cradock and Whiteford [9] and by Green *et al.* [18]. These authors observed the expected split in the Cl lone pair band. The UV absorption spectra of these compounds have been measured by Causley and Russell [19] who interpreted them in Rydberg terms. The spectra gave no sure indication of $\sigma^* \leftarrow n$ bands but for SiH_2Cl_2 they found a long tail at the low-frequency side of the first peak which is at the expected location.

The PE spectrum of $SiHCl_3$ was reported by Frost *et al.* [10, 11]. We found some fine structure on some of the bands (Figs. 4, 5). The first band is at 12.0 eV and it was assigned by Frost to ionization from the a_2(Cl) orbital on the ground that it is relatively sharp and that a_2 correlates to the frontier orbital of $SiCl_4$ which has t_1 symmetry. This assignment is rendered questionable, however, since the UV band of lowest frequency (70,700 cm^{-1}) is an intense one whereas a $4s \leftarrow a_2$ transition would be forbidden (Fig. 6). Thus an a_1 assignment for the first PE band appears to be more probable. The broad second band which has a pronounced shoulder (12.5 and 12.6 eV) can then contain a_2 and one of the e levels and the broad band at 13.1 eV the other e level. In this way all the lone pair orbitals ($a_1 + a_2 + e + e$) are accounted for.

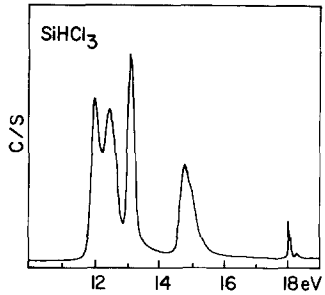

Fig. 4. The HeI photoelectron spectrum of $SiHCl_3$ (full spectrum)

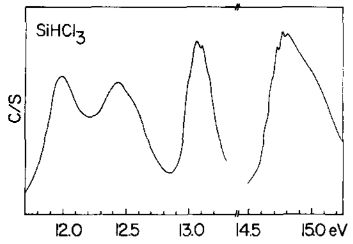

Fig. 5. The HeI photoelectron spectrum of $SiHCl_3$ (detail)

The 13.1 eV band exhibits a vibrational interval of about 400 cm^{-1}. This can be assigned to the Si—Cl stretching frequency (a_1) whose ground state value is 497 cm^{-1} [17]. This indicates some Si—Cl bonding character in the $e(\overline{\mathrm{Cl}})$ orbital.

The next band has two peaks (at 14.8 and 15.0 eV) which we assign to the e(Si—Cl) and a_1(Si—H) orbitals.

The fine structure of the 18.1 eV band (Si3*s*) exhibits a high vibrational frequency [10, 11], 2020 cm^{-1}. This can be assigned to the Si—H stretching vibration whose ground state frequency is 2274 cm^{-1} [17].

In the UV spectrum there are two well pronounced shoulders at 70,700 cm^{-1} and at 74,700 cm^{-1}. The first one has the right term value 26,000 cm^{-1} to be assigned to the $4s \leftarrow a_1$ transition. The second one is likely to receive contributions from the $4p \leftarrow a_1$ and $4s \leftarrow e$ (13.1 eV) transitions corresponding to term values 17,600 and 26,500 cm^{-1}, respectively. The strong peak at 79,300 cm^{-1} could be 3*d* but its intensity suggests that its main constituent is a valence shell transition.

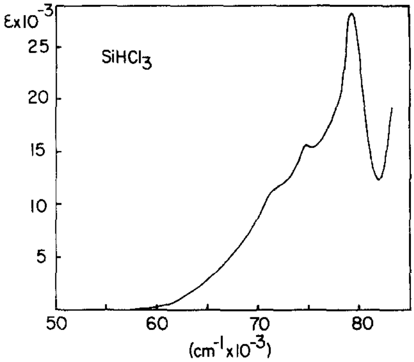

Fig. 6. The far-ultraviolet spectrum of $SiHCl_3$

It is more important to note (Fig. 6) that at the low frequency end of the spectrum there is a long tail more pronounced than in SiH_2Cl_2 which, if resolved, could be centered near 66,000 or 67,000 cm^{-1}. This corresponds to a term value of about 30,000 cm^{-1} which is too high for this type of molecule and since the 4*s* Rydberg bands could be unarbitrarily assigned to bands at higher frequencies we can assign the tail to the $\sigma^* \leftarrow n$ transition. It is about 10,000 cm^{-1} *higher* than in chloroform. This lends credibility to the suggestion that in the mono- and dichlorosilanes the $\sigma^* \leftarrow n$ band has shifted to higher frequencies relative to the corresponding carbon compounds and "disappears" underneath the stronger bands that are located there.

The UV spectrum of $SiCl_4$ has been discussed by Causley and Russell [20]. The PE spectrum was measured earlier by Green *et al.* [18]. According to these authors, the bands correspond, in order of increasing ionization energies, to the MOs $1t_1 < 3t_2 < 1e < 2t_2 < 2a_1$ for both CCl_4 and $SiCl_4$, where the first three are essentially chlorine lone pair levels and the last two are the bonding orbitals. The $1t_1$ IP is at 11.60 and 12.01 eV, the $3t_2$ at 12.40 and 12.85 eV for CCl_4 and $SiCl_4$, respectively. The most striking observation of Causley and Russell is the huge hypsochromic shift which the UV band of lowest frequency undergoes in passing from CCl_4 to $SiCl_4$, from 57,000 to 72,000 cm^{-1}. This observation, together with the general blue shift in chlorosilanes with respect to chloroalkanes observed by Bell and Walsh [13] and the *ab initio* study of SiH_3Cl by Howell and Van Wazer [12] seem to be good indications for $d\pi$-$p\pi$ mixing in chlorosilanes.

The bands in the PE spectra of chlorosilanes and methylchlorosilanes found in the literature or measured by us are compiled in Table 1.

Table 1. The photoelectron bands of some chlorosilanes corresponding to ionization from $np(\overline{\mathrm{Cl}})$, σ and Si3*s* orbitals

Molecule	$SiHCl_3$	$ClCH_2SiCl_3$	CH_3SiHCl_2	$(CH_3)_2SiCl_2$	$(CH_3)_2SiHCl$	$(CH_3)_3SiCl$
$np(\overline{\mathrm{Cl}})$	12.0	11.1	11.3	11.0	10.8	10.6
	12.5	11.5	11.8	11.5	11.1	10.8
	12.6	11.9	12.1	11.9		
	13.1	12.3	12.2			
		12.7				
		13.0				
σ	14.8	14.4	13.4	12.8	12.2	11.9
	15.0	14.5	13.8	13.3	12.5	12.0
		15.3	14.7	14.2	12.8	12.3
		15.5	14.9	14.5	13.8	13.3
		16.0	15.3	14.8	14.1	13.6
					14.5	13.9
					14.9	14.5
Si3*s*	18.13	17.70	17.40	16.81	16.68	16.20

An interesting case is that of $ClCH_2SiCl_3$. In the PE spectrum (Fig. 7) we find six bands in the $\overline{\mathrm{Cl}}$ region at 11.1, 11.5, 11.9, 12.3, 12.7 and 13.0 eV. Supposing that the —$SiCl_3$ part is ruled by near C_{3v} symmetry we expect four bands related to MOs formed from the six lone pairs of the three chlorine atoms. In $SiHCl_3$ the first band is at 12.0 eV, in $ClCH_2CCl_3$ at 11.45 eV. Thus it is reasonable to assign the four bands of highest energy to the —$SiCl_3$ part while the bands at 11.1 and 11.5 can be assigned to the $\overline{\mathrm{Cl}}$ linked to the carbon with the degeneracy of the lone pairs lifted. The resemblance of the 13.0 eV band to that of $SiHCl_3$ is particularly striking.

The UV spectrum of $ClCH_2SiCl_3$ consists of extremely broad bands and we had to renounce any attempt to make assignments.

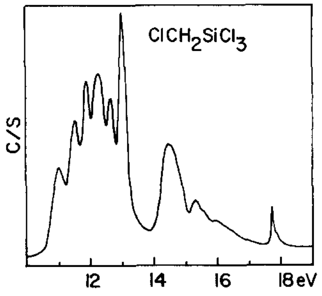

Fig. 7. The HeI photoelectron spectrum of $ClCH_2SiCl_3$

3. Conclusions

The orbitals related to the photoelectron band of lowest energy with which all known electronic transitions originate are bonding σ orbitals in the case of alkyl and fluorosilanes but essentially chlorine lone pair orbitals for chlorosilanes. The characteristic differences between the former and the latter are connected with this. There is a great deal of analogy between the spectra of alkyl and fluorosilanes and those of the respective carbon compounds. In both cases the spectra fall into one of two categories. They either resemble the spectrum of methane ("round field") or the spectrum of ethane ("long field"). An interesting "fluoroeffect" affects to a different degree the two close-lying originating orbitals in fluorosilanes. Si *3d* atomic orbitals do not seem to play any significant role in the case of alkyl and fluorosilanes.

In chlorosilanes the valence-shell type $\sigma^* \leftarrow \overline{\mathrm{Cl}}$ transition, well known for chloroalkanes, is not readily found. There is evidence for $d\pi$–$p\pi$ interaction for these molecules in both the ground and certain excited states. The hypsochromic shift of that band seems to be one of the consequences of this.

In general, most of the bands in these spectra can be interpreted as being due to transitions to Rydberg or intermediate Rydberg-valence-shell type excited states.

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