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PHOTOELECTRON AND PENNING ELECTRON SPECTROSCOPIC INVESTIGATION OF PHENYLHALOSILANES

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Summary

Penning ionization electron spectroscopy and CNDO/S calculations have been applied succesfully to the analyses of the UV photoelectron spectra of some phenyl-fluoro- and -chloro-silanes. The relative intensities of the π-type and the lone pair bands are enhanced in the Penning spectra compared with those of the UV photoelectron spectra.

Introduction

The first UV photoelectron spectra (UPS) studies of halogenosilanes were carried out more than a decade ago [1–5]. The investigations demonstrated the difference between the carbon and silicon derivatives. In examining the lone pair orbitals of the halides of Group IV it was found that the halosilanes have the highest *IP* values in the series. The shift to higher energy and the broadening of the halogen lone pair bands compared to those of the carbon analogues, which show the typical non-bonding shape, indicate that there is considerable $(d–p)\pi$ bonding between the lone pairs and the silicon atom. Frost et al. [6,7] were the first to show that the effect of σ-type orbitals of the correct symmetry is similar to that of the *d*-orbitals and that selection between the two effects is rather difficult.

In this work we continue the UPS and Penning spectroscopic investigation of the organosilicon compounds. In the previous papers [9,10] we presented studies of trimethylsilyl-substituted aromatic compounds. In this paper we deal with the following phenylhalosilanes: $PhSiF_3$ (I), $PhSiMeF_2$ (II), $PhSiCl_3$ (III), $PhSiMeCl_2$ (IV), and $PhSiMe_2Cl$ (V).

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Experimental

The electron spectra were obtained at an ejection angle of 90° with respect to the metastable or the photon beams by means of a hemispherical analyzer. The sample vapor was introduced into the collision chamber through a sample nozzle at ca. 25°C. Metastable neon atoms, Ne★ ($^3P_2$, 16.62 eV) were produced by impact of 60 eV electrons; at this energy the contributions of Ne★ ($^3P_0$, 16.72 eV) atoms and photons are negligible [8]. For the measurement of the UPS, pure helium and neon gases were discharged to produce the He(I) (21.21 eV) and Ne(I) (16.85 and 16.67 eV) radiations. The low energy component of the Ne(I) resonance lines made little contribution to the spectra.

During the Penning experiments it was found that a few second after introducing a fluoro derivative into the reaction chamber, the metastable atoms were deactivated and so the experiment was spoiled. About 20 min after the sample flow was closed, the source of metastable atoms was regenerated. In the case of some other fluoro derivatives we found a similar effect, but we could measure the chloro compounds without difficulties.

Results and discussion

Figures 1 and 2 show the He(I) UPS spectra of the investigated compounds in comparison with the spectrum of $PhSiMe_3$ (VI) [9]. Figure 3 shows the Ne(I)

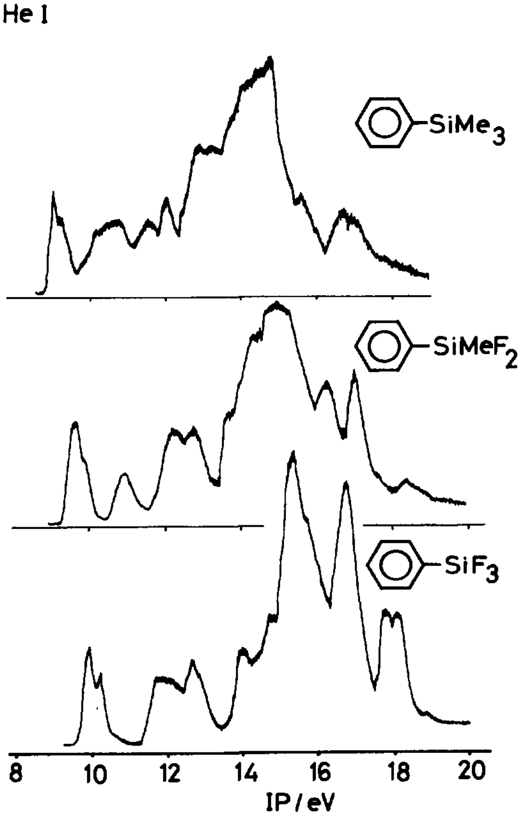

Fig. 1. He(I) photoelectron spectra of phenylfluorosilanes.

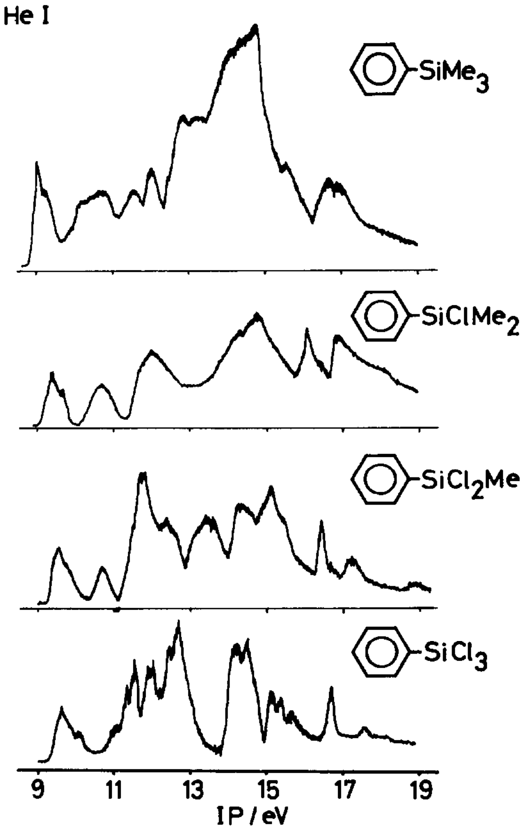

Fig. 2. He(I) photoelectron spectra of phenylchlorosilanes.

photoelectron spectra and Ne* Penning ionization electron spectra of the chloro derivatives. Some of the observed and calculated vertical ionization potentials for these compounds are listed in Tables 1 and 2. The calculated *IP* values were

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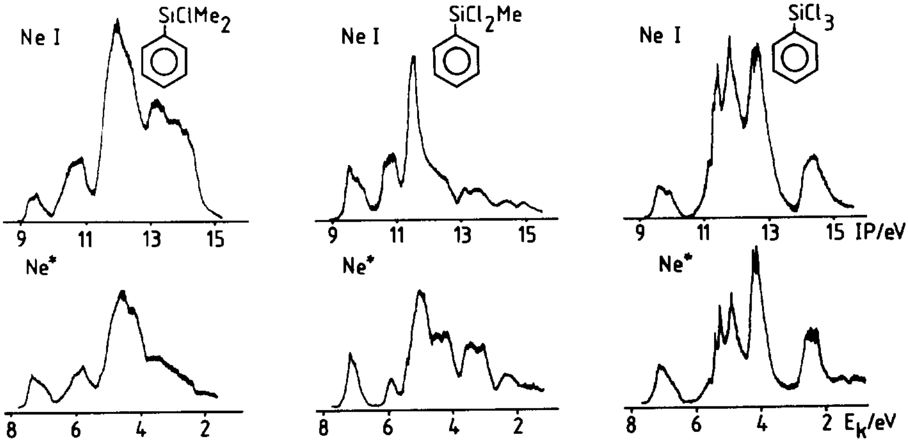


Fig. 3. Ne(I) UPS and Ne* PIES of phenylchlorosilanes.

TABLE 1

CALCULATED[a] AND OBSERVED IONIZATION POTENTIALS[b] OF PHENYLFLUOROSILANES

$PhSiF_3$ (I)			$PhSiMeF_2$ (II)			$PhSiMe_3$ (VI)			Assignment	Benzene	
A	B	C	A	B	C	A	B	C		A[c]	C
10.23	9.28	9.18	9.55	9.08	8.97	9.05	8.91	8.80	a', e_{1g}, π_3	9.25	9.03
9.85	9.17	9.13	9.75	9.07	9.03	9.30	9.01	8.97	a'', e_{1g}, π_2	9.25	9.03
11.70	10.80	10.68	10.9	10.38	10.29	10.10	10.19	10.16	$Si-C_{Ar}$		
				12.03	11.84	10.70	10.96	10.89	$Si-C_{Me}$		
			12.2				11.14	11.11	$Si-C_{Me}$		
12.2	12.14	12.10		12.03	11.99	11.60	11.99	11.95	a'', e_{2g}	11.53	11.98
12.65	12.52	12.44	12.7	12.60	12.51	12.05	12.36	12.33	a_{2u}, π_1	12.38	12.35
14.00	13.65	13.37	13.7	13.61	13.31	12.8	12.92	12.84	a', e_{2g}	11.53	11.98
14.7	14.77	14.75	14.0–14.4	14.62	14.41	13.3	14.14	14.14	a'', e_{1u}	13.98	14.62
				14.41	13.88						
15.3–15.8	14.54	13.87							$n(F)$		
	14.56	13.90									
	14.60	14.25									
				14.78	15.49	13.9–14.7	14.33	14.40	CH_3		
16.7	15.11	15.21	14.7–15.2	14.97	14.71		15.00	15.03	a', e_{1u}	13.98	14.62
	15.50	14.38		15.26	14.74				$n(F)$		
	15.71	14.53		15.67	15.07						
	15.86	15.26									

[a] Corrected values, see text. [b] In eV: A, experimental; B, CNDO/S calculation with *d* orbitals; C, CNDO/S calculation without *d* orbitals. [c] Ref. 12.

TABLE 2

CALCULATED[a] AND OBSERVED IONIZATION POTENTIALS[b] OF PHENYLCHLOROSILANES

$PhSiCl_3$ (III)			$PhSiMeCl_2$ (IV)			$PhSiMe_2Cl$ (V)			$PhSiMe_3$ (VI)			Assignment	Benzene	
A	B	C	A	B	C	A	B	C	A	B	C		A[c]	C
9.55	9.15	9.10	9.52	9.08	8.97	9.3	9.03	8.93	9.05	8.91	8.80	a', e_{1g}, π_3	9.25	9.03
9.85	9.20	9.14	9.75	9.11	9.08	9.7	9.06	9.03	9.30	9.01	8.97	a'', e_{1g}, π_2	9.25	9.03
11.10	10.40	10.24	10.7	10.25	10.13	10.4	10.19	10.08	10.10	10.19	10.16	Si–C_{Ar}		
									10.7	10.96	10.89	Si–C_{Me}		
										11.14	11.11	Si–C_{Me}		
	11.30	11.10		11.19	10.95	(10.9)	10.74	10.55						
11.35	11.34	11.12		11.24	11.05		11.66	11.50						
11.48	11.37	11.29	11.6	11.74	11.44							n(Cl)		
11.86	11.97	11.59		11.88	11.70	11.9								
	12.01	11.69												
	12.11	12.06		12.07	12.05		11.95	11.86	11.60	11.99	11.95	a'', e_{2g}	11.53	11.98
	12.29	12.02	12.2									n(Cl)		
12.68	12.67	12.40	12.6	12.42	12.25		11.98	11.88	12.05	12.36	12.33	a_{2u}, π_1	12.38	12.35
	13.33	13.11		12.61	12.43	12.4	12.16	12.15				n(Cl)		
	13.64	13.52	13.1	13.25	13.19		12.77	12.62						
14.1	14.01	13.95	13.6	13.67	13.58	13.2	13.18	13.10	12.8	12.92	12.84	a', e_{2g}	11.53	11.98
	14.81	14.77	14.3	14.73	14.69	13.8	14.22	14.21	13.3	14.14	14.14	a'', e_{1u}	13.98	14.62
14.4	15.06	14.97		15.03	14.97	14.2	15.01	15.02	13.9	15.00	15.03	a', e_{1u}	13.98	14.62

[a] Corrected values, see text. [b] In eV: A, experimental; B, CNDO/S calculation with *d* orbitals; C, CNDO/S calculation without *d* orbitals. [c] Ref. 12.

obtained using a CNDO/S method and were corrected by the formula [11]:

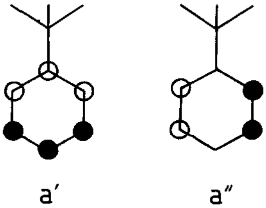
$$IP_i = -0.74\,\epsilon_i + 1.7\ \text{eV} \qquad (1)$$

The first two bands of the spectra can be unambiguously derived from the $e_{1g}(\pi)$ orbitals of the benzene. Both the spectra and the calculations show the inductive effect of the halogen atoms. The Si–C_{Ar} bond lies in the nodal plane of the a''-type orbitals. (The nodal plane of the molecules in the C_s point group is supposed to be perpendicular to the plane of the benzene ring.) Therefore the effect of the substituent is weaker for these orbitals than for the a' orbitals (see Fig. 4). This shows that the orbitals of a' symmetry are stabilized strongly for I relative to VI, and while the HOMO level in VI is of a'' symmetry, it is of a' in I. The order of the first two orbitals in II cannot be determined. In the spectrum, the two *IP* values are very close and the calculations change the order of the two orbitals, depending on the basis set (with or without *d*-orbitals) used. Considering the chlorosilanes, a similar effect can be seen but the $-I$ effect is weaker than in the fluoro derivatives and an exchange of orbitals doesn't occur.

The assignment of the innermost π_1 orbitals is more uncertain than in VI [9]. As mentioned above, the Penning experiment with fluorosilanes was unsuccesful, therefore the position of the π_1 orbitals can only be found on the basis of the calculations and a comparison with I. Accordingly, the position of the π_1 bands in I and II are nearly the same, at 12.65 and 12.70 eV, respectively. The stabilization is about 0.6 eV compared to VI. In the case of the chloro derivatives the lone pair orbitals of the chlorine appear in the uncertain area, causing difficulties in the assignment. Nevertheless, on the basis of a careful comparison of the relative intensities of the Penning and photoelectron bands we can conclude that the positions of the π_1 bands are 12.68 eV in III, 12.35 eV in IV and 12.4 eV in V. However, according to the calculations and spectra this area probably contains several peaks corresponding to other ionizations.

The orbitals producing the well-observable broad band between 10.1 and 11.2 eV in every spectrum is mainly distributed on the Si–C_{Ar} and Si–C_{Me} bonds. The lowest orbital corresponds to the Si–C_{Ar} bonds.

The bands originating from the e_{2g} (σ) orbitals of benzene (a' and a'' in the C_s point group) can be identified in fluorosilanes. It is more complicated to find the bands of the a''-type because there are some other *IP* close to them, e.g. the Si–C_{Ar} band in I or an Si–C_{Me} band in II. The a''-orbitals are nearly unaffected by the substitution (from benzene to I the shift is only 0.6 eV). The a' orbitals are very sensitive and the stabilization from benzene to I is 2.5 eV.



a′ a″

Fig. 4. Orbital symmetry in the C_s point group.

TABLE 3

NUMBER AND SYMMETRY OF ORBITALS IN GROUPS SiX, SiX_2 AND SiX_3

Group	SiX bond	Lone pairs
≡SiX	a_1	a_1+e
$=SiX_2$	a_1+b_1	$2a_1+2b_1+a_2+b_2$
$-SiX_3$	a_1+e	$2a_1+a_2+3e$

The analyses of the inner σ-orbitals are difficult because in that region the lone pair bands of fluorine, as well as the bands associated with an ionization from the methyl groups, appear. Probably the peak at 14.7 eV in I corresponds to ionization of one of the e_{1u} orbitals (a''). The calculations suggest the position of the a' component is at about 15.2 eV. The spectrum of II contains a broad region between 14 and 16 eV which may be ascribed to ionizations from CH_3 and the lone pairs of the fluorines. According to our calculations this band includes the e_{1u} orbitals (at about 14.6 eV (a'') and 14.9 eV (a')).

The assignment of the σ-orbitals originating from the e_{2g} benzene orbitals in the chloro compounds are uncertain. The reason is, as mentioned above, that in this region the intensive lone pair bands appear. On the other hand the calculations show a strong mixing of orbitals and the derivation from benzene orbitals is sometimes rather an illusory one.

The UP spectrum of $PhSiCl_3$ can be analyzed especially easily even in the higher energy region. In this case there is no disturbing methyl group and the Si–Cl bands or the halogen lone pair bands appear in the lower energy part of the spectrum. Therefore a comparison with the benzene places the positions of the e_{1u} (a'' and a'), b_{2u}, b_{1u} and a_{1g}-type peaks in the following order: 14.1 (14.8), 14.4 (15.0), 15.1 (15.7), 15.6 (16.1), 16.6 (20.8) eV. The calculated results (without *d*-orbitals) are in bracket.

The correct assignment of the other part of the spectra is difficult, due to the lone pairs of the halogens. The number and symmetry of the expected peaks for the ≡SiX, $=SiX_2$ and $-SiX_3$ groups can be seen in Table 3. Naturally, in a phenyl-substituted group the original symmetry decreases and the number of expected peaks increases. Therefore several closely lying bands appear in the spectra of the fluoro derivatives (from 15 to 18 eV) and of the chloro compounds (from 11 to 13 eV).

The assignments in the literature of the lone pair orbitals are based on CNDO/2 calculations or even on intuition. According to our calculations, some of them contain significant contributions from the compounds' other orbitals. Moreover, the values for the lone pairs are generally near to each other and sometimes the calculated difference between them is 0.1 eV or less. Therefore a proper calculated orbital ordering cannot be expected. Since in the C_s point group the group theoretical orbital character is meaningless, we didn't characterise these orbitals.

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