OVERLAPPING CORE TO VALENCE - CORE TO RYDBERG TRANSITIONS
AND RESONANCES IN THE XUV SPECTRA OF SiF$_4$

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Core to Valence/Rydberg Excitations in SiF$_4$

Overlapping core to valence – core to Rydberg transitions
and resonances in the XUV spectra of SiF$_4$ [+]

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Abstract

By comparison of the Si 2p absorption spectra of molecular and
solid SiF$_4$ the local character of the resonances above threshold and the valence or Rydberg character of the lines at threshold have been established. After checking the reliability of
the Z + 1 model on the core-spectra of SF$_6$, an assignment of
the SiF$_4$ lines, based on SCF calculations for the Z + 1 analogue PF$_4^+$, is presented which is consistent with the experimental data.

1. Introduction

Different assignments, summarized in table 1, have
been proposed for the lines detected at the 2p-threshold
of molecular SiF_4 (Zimkina and Vinogradov 1971). Hayes
and Brown (1972) assign all lines to a single Rydberg
series, whereas Robin (1975) ascribes the low energy
doublet to core to valence transitions and all the ad-
joining lines to Rydberg transitions of different symme-
tries. Resonances localized within the molecule have
been invoked for the explanation of the maxima at 117
eV and 133 eV (Zimkina and Vinogradov 1971, Dehmer 1972).

To clarify the situation, theoretical and additional ex-
perimental investigations have been performed. First,
the Si2p spectrum of solid SiF_4 has been measured. The
absorption of molecules in the condensed phase forms an
'operational yardstick' to judge the valence – Rydberg
character (Robin 1974) and the local character of reso-
nances. Second, theoretical term values for the core ex-
cited states have been obtained within the framework of
the equivalent ionic core virtual orbital model (Schwarz
1976, 1977) by SCF calculations on PF_4^+. The main con-
clusion is that core to valence and core to Rydberg ex-
citations of different symmetry are strongly overlapping
and that both assignments given in the literature have
to be revised.

2. Experimental Results

The 7.5 GeV electron synchrotron DESY served as a light
source. The experimental setup has been described else-
where (Comes et al. 1973). Solid SiF_4 films were pre-
pared by condensation onto thin carbon films cooled to
~50 K. The absorption spectra of gaseous and solid
SiF_4 are shown in figs. 1 and 2. The absolute cross-
sections refer to the gas phase data. By varying the
gas pressure from 0.4 to 2 mbar the influence of satu-
ration on the gas phase absorption has been eliminated.
Only relative values have been determined for solid SiF_4.

Our data for molecular SiF_4 agree with those of Zimkina
and Vinogradov (1971) and of Hayes and Brown (1972). A
doublet followed by a series of lines shows up at the
Si 2p-threshold. Strong maxima at 117 eV and 133 eV
dominate the spectrum above 115 eV. Si 2s excitations
give rise to the maximum at 160 eV.

No dramatic change occurs upon solidification. The broad
resonance bands above 115 eV and the low energy doublet
persist. The three lowest members of the group of lines
around 110 eV are broadened but still can be identified.
In contrast, the higher members are completely smeared
out. All lines are shifted towards higher energies by
approximately 0.2 eV (see Tab. 1). Two shoulders emerge
at 113 eV and 142 eV.

3. SCF calculations

Within the equivalent ionic core virtual orbital model
EICVOM (Schwarz 1976, 1977) the term value of a core
excited state - i. e. the energy difference between
the excited state and the corresponding ionization
limit - is approximated by the negative value of the
virtual orbital energy of the final orbital in the
equivalent ionic core species. The latter one is ob-
tained by increasing the nuclear charge of the core
excited atom by one, that is PF_4^+ in the case of Si
2p-excited SiF_4.

Before applying the model to SiF_4, we considered it
useful to check its accuracy on a very similar system,
SF_6, the core excitation spectra of which are well
understood. In this case the $Z + 1$ analogue is ClF_6^+.
MO-SCF calculations have been performed with the
MUNICH program system. The cartesian gaussian basis
sets of Roos and Siegbahn (1970) are contracted to
the split valence shell type ([7s3p/3s2p] for F,
[10s6p/4s3p] for Cl) and augmented by diffuse func-
tions on the central atom (4s, 4p, 3d with exponents
0.1, 0.03, 0.01, (0.003)). The calculated virtual
orbital energies are given in Tab. 2.

Highly resolved S2p spectra, which slightly differ
in the absolute energies, have been reported by

Nakamura et al. (1971), Gluskin et al. (1977) and
Hitchcock and Brion (1978). The most probable term
values are compared with the theoretical estimates
in Tab. 2. The deviation of a few tenths of an eV is
due to reorganization and polarization (external cor-
relation) effects which are counterbalanced by the
exchange correction (see e. g. Radler et al. 1976)
and nonexternal correlation contributions (see Schwarz
and Buenker 1976). The nearly exact cancellation of
errors in the case of the lowest two empty orbitals
of antibonding type from the valence shell with high
S3s and S3p population seems fortuitous.

Using a similar basis set as above but in addition
augmented by a polarization d-function with exponent
0.7 at the center, corresponding calculations have
been performed on PF_4^+. The virtual orbital energies
are given in Tab. 3.

The symmetry order of the virtual orbitals below the
ionization threshold is the same in both molecules.
However due to the smaller number of electronegative
fluorine atoms and the smaller electronegativity of
Si/P^+ as compared to S/Cl^+, all virtual orbitals in
SiF_4/PF_4^+ are less strongly bound than those in SF_6/ClF_6^+.

4. Discussion

Obviously the $Si2p_{3/2} \rightarrow \sigma^* (a_1)$ and $2p_{1/2} \rightarrow \sigma^* (a_1)$ transitions are the origin of the doublet at 106.13 and 106.68 eV. The persistance of the lines upon solidification (fig. 2) forms a strong evidence for the core to valence character of the transitions involved. The ratio of the oscillator strengths of the two lines (1:1.1) for molecular and solid SiF_4 considerably deviates from the statistical ratio of 2:1. It implies that the $2p \rightarrow \sigma^* (a_1)$ exchange integral K is comparable to the 2p spin orbit coupling constant λ. From our data a value of K = 0.12 eV is obtained (Onodera and Toyozawa 1967) which harmonizes with predominant valence character of the final orbital. The considerable width of the lines indicates strong coupling to molecular vibrations due to the antibonding character of the final orbital.

The latter statement also holds for the lines at 108.9 eV and 109.4 eV which we assign to $2p_{3/2} \rightarrow \sigma^* (t_2)$ and $2p_{1/2} \rightarrow \sigma^* (t_2)$ transitions. The core to valence character of these transitions manifests itself in the insensitivity to solidification. Since the t_2 orbital has strong Si 3p population it seems reasonable that the $Si2p \rightarrow \sigma^* (t_2)$ transitions are less intense than the transitions from Si2p to the $\sigma^* (a_1)$ orbital, which is of dominant Si3s character. Due to the tetra-

hedral symmetry of SiF_4, the intensity ratio $\sigma^* (a)/ \sigma^* (t)$ is significantly smaller than in octahedral SF_6 (Hitchcock and Brion 1978), where $2p \rightarrow \sigma^* t$ is orbitally forbidden. The valence character of the t_2 orbital also explains why transitions to it give rise to a strong absorption band in the F1s spectrum of SiF_4 (Zimkina and Vinogradov 1971). Because of the triple degeneracy of the t_2 orbital we expect the Jahn-Teller interaction to give rise to shoulders on both sides of the main peaks (Toyozawa and Inoue 1966). Due to the overlap of different absorption bands we only see the low energy vibronic shoulder at 108.4 eV.

Rydberg transitions are responsible for the lines in the gaseous phase at higher energies. Rydberg orbitals extend beyond the cage formed by the F-ligands and therefore are quenched in solid SiF_4. The assignment of the lines, which again can be grouped in spin-orbit pairs, is given in table 1. The ionic character of the SiF_4 bond explains the vibronic broadening of the Rydberg lines (Schwarz 1977, **Radler et al. 1976). The broadening prevents the probably weak $2p \rightarrow 4p$ transitions to be detected, whereas they are resolved in the considerably less ionic SF_6 although orbitally forbidden (Nakamura et al. 1971, Gluskin et al. 1977, Hitchcock and Brion 1978). Sharp Rydberg lines have also been detected in the Si 2p spectrum of the covalently bound SiH_4 (Butscher et al. 1979).**

XPS measurements (Perry and Jolly 1972) place the $2p_{3/2}$ ionization limit at 111.6 eV. The experimental term values are in agreement with the calculated virtual orbital energies of PF_4^+ (Tab. 3) except for the low energy doublet. Due to reorganization, correlation- and exchange-effects deviations of about 1 eV between experimental and calculated term values, based on this model, are quite general for core to valence excitations (e. g. Radler et al. 1976, Schwarz and Buenker 1976). The experimental term values of the lowest a_1 and t_2 final orbitals are 5.5 and 2.7 eV. The corresponding term values from valence electron excitations are about 4.6 and 2.5 eV (Robin 1974). These values fit into the rule that term values from valence excitations are usually smaller than those from core excitations (Butscher et al. 1979).

It is also interesting to compare the term values with those of the related molecule SiH_4 (Butscher et al. 1979). For the totally symmetric orbitals they are larger in SiF_4. This is probably due to penetration of the a_1 orbitals into the molecular interior, which is more positively charged in the ionic molecule SiF_4. Contrarily the final orbitals of t and e symmetry are destabilized in SiF_4 as compared to SiH_4, showing that the repulsion by the negatively charged fluorine ligands dominates, since the penetration into the positive molecular core

is suppressed because of the nonzero angular momentum of these orbitals.

The strong maxima above the Si 2p ionization threshold are due to transitions to final states mainly localized within the molecule (Zimkina and Vinogradov 1971, Dehmer 1972, Koch and Sonntag 1979). The backscattering of the excited electron by the F-ligands gives rise to resonances above the ionization limit. According to multiple scattering Xα calculations performed by Paulytchev et al. (1979) the maximum at 117 eV is mainly due to $2p \to e$ transitions whereas $2p \to t_2$ transitions are responsible for the maximum at 133 eV. The absence of these resonances in the Si2p-spectrum of SiH_4 demonstrates the essential role of the F-ligands. Similar resonances in the S2p-spectra of SF_6 have been analyzed in great detail (see e. g. Koch and Sonntag 1979). Our results for solid SiF_4 confirm the local character of the resonances. The shoulder at 142 eV in solid SiF_4 is probably due to the backscattering of the excited electron by the next nearest shell of neighbouring atoms. A corresponding maximum shows up at 143 eV in the spectrum of solid SiH_4 (Butscher et al. 1979).

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Table 1: Experimental energy positions for the maxima in the Si 2p spectrum of molecular and solid SiF_4. Our assignment is given together with the assignments proposed by Hayes and Brown (1972) and by Robin (1975)

| Energy positions (eV) | | Assignment | | |
molec. SiF_4	solid SiF_4	Hayes-Brown	Robin	this work
106.13 ± 0.2	106.35 ± 0.2	$2p_{3/2} \to 4s$	$2p_{3/2} \to \sigma^*$	$2p_{3/2} \to \sigma^*$ (3s)
106.68 ± 0.2	106.9 ± 0.2	$2p_{1/2} \to 4s$	$2p_{1/2} \to \sigma^*$	$2p_{1/2} \to \sigma^*$ (3s)
108.4 ± 0.2	108.7 ± 0.3	$2p_{3/2} \to 5s$	$2p_{3/2} \to 4s$	vibr.
108.9 ± 0.2	109.2 ± 0.2	$2p_{1/2} \to 5s$	$2p_{1/2} \to 4s$	$2p_{3/2} \to \sigma^*$ (3p)
109.4 ± 0.2	106.6 ± 0.3	$2p_{3/2} \to 6s$	$2p_{3/2} \to 4p$	$2p_{1/2} \to \sigma^*$ (3p), $2p_{3/2} \to 4s$
110.0 ± 0.2		$2p_{1/2} \to 6s$, $2p_{3/2} \to 7s$	$2p_{1/2} \to 4p$, $2p_{3/2} \to 3d$	$2p_{1/2} \to 4s$, $2p_{3/2} \to 3d$
110.7 ± 0.2		$2p_{1/2} \to 7s$ $2p_{3/2} \to 8s$	$2p_{1/2} \to 3d$	$2p_{1/2} \to 3d$, $2p_{3/2} \to 5s$, 4d
111.4 ± 0.3		$2p_{1/2} \to 8s$		$2p_{1/2} \to 5s$, 4d
	112.9 ± 0.5			
117.2 ± 0.5	117.4 ± 0.5			$2p \to e$ [a]
133 ± 0.5	130 ± 0.5			$2p \to t_2$ [a]
	142 ± 0.5			
160 ± 0.5	160 ± 0.5			2s excitation

[a] According to $X\alpha$-calculations of Paulytschev et al. (1979)

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Table 2 Virtual orbital energies ε for ClF_6^+ and experimental S2p-term values T for SF_6 (see text) in eV

type of orbital	ε (calc)	T (exp) (± 0.2 eV)	$|\varepsilon|$-T
σ^* ($3s\,a_{1g}$)	-8.60	8.3	+0.3
σ^* ($3p\,t_{1u}$)	-4.71	4.5	+0.2
4s	-2.51	3.0	-0.5
4p	-1.98	2.2	-0.2
3d (t_{2g})	-1.44	} 1.7	-0.3
3d (e_g)	-1.38		
5s	-1.20	} 1.4	-0.3
5p	-1.00		

Table 3 Virtual orbital energies ε for PF_4^+ and experimental Si2p-term values T for SiF_4 in eV

type of orbital	ε (calc)	T (exp)*	$|\varepsilon|$-T
σ^* ($3sa_1$)	-4.40	5.5 $\pm$ 0.2	-1.1
σ^* ($3pt_2$)	-2.56	2.7 $\pm$ 0.2	-0.1
4s	-2.08	2.2 $\pm$ 0.2	-0.1
4p	-1.61	-	
3d(t_2)	-1.28	} 1.5 $\pm$ 0.2	-0.2
3d(e)	-1.25		
5s	-1.05	}	
5p	-0.93	} 0.8 $\pm$ 0.3	
4d			

*) using 111.6 and 112.2 eV as Si2p-IPs (Perry and Jolly 1972)

Figure captions

Fig. 1   Si 2p, 2s absorption spectra of molecular and solid SiF_4. The absolute cross sections refer to the spectrum of molecular SiF_4 only. The uncertainty is $\pm$ 25 %.

Fig. 2   Asorption spectra of molecular and solid SiF_4 at the Si 2p threshold. The assignment and the ionization potentials are indicated.
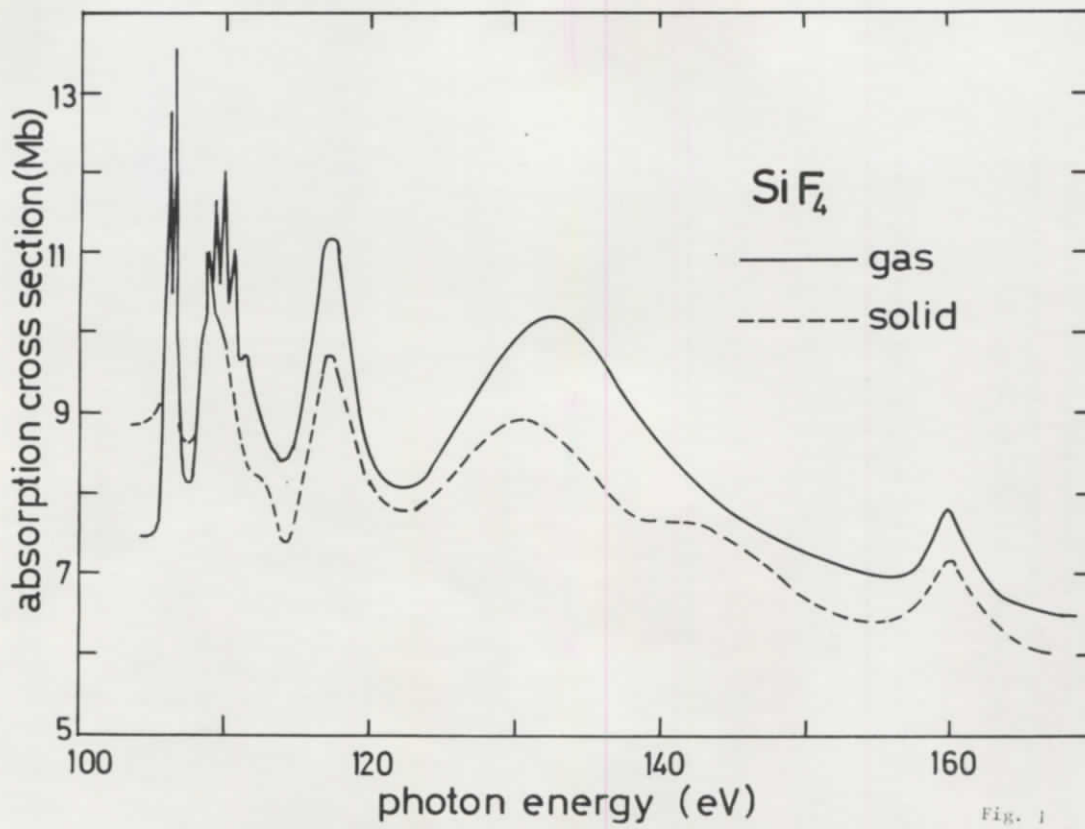
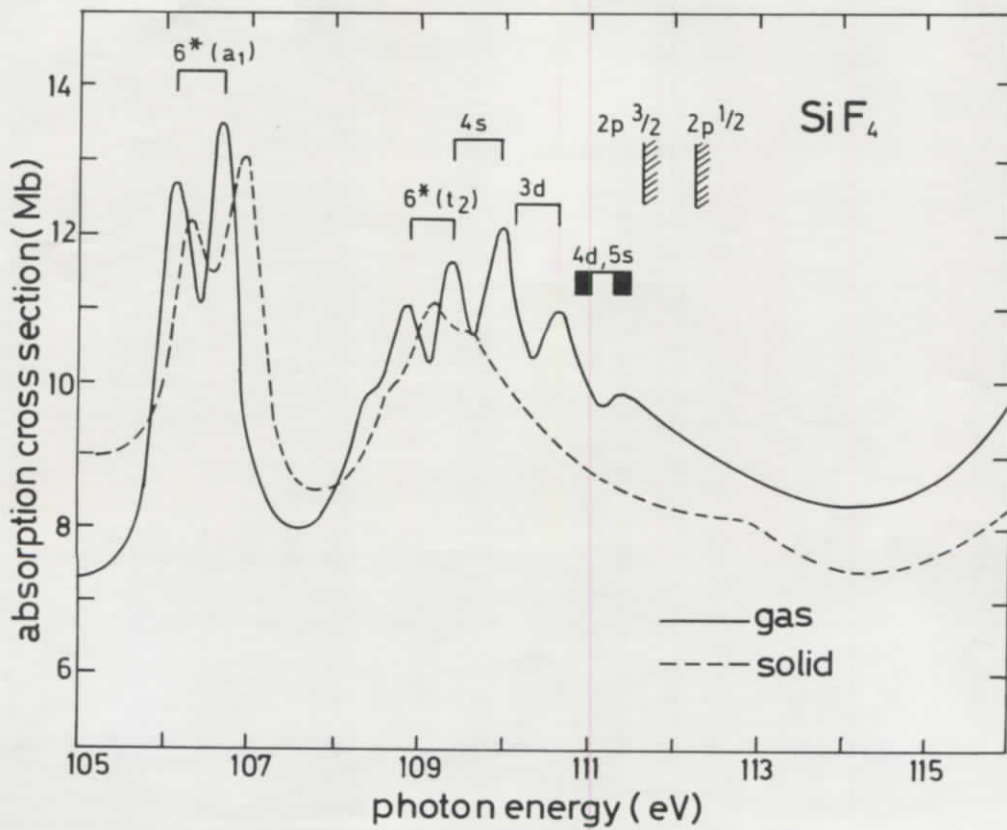Fig. 1

Fig. 2