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The Photoelectron Spectrum of SiF_2

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Silicon difluoride, SiF_2, is one of a number of interesting high-temperature species whose chemistry and structures are of considerable interest.[2] Photoelectron spectroscopy provides information on the electronic structures of chemical species,[3] and in some respects this technique is well adapted for studying high-temperature species. We report here the observation of the photoelectron spectrum of SiF_2 obtained with He(I) radiation.

Experimental Section

Silicon difluoride was continuously prepared by flowing SiF_4 (Matheson) over pure silicon (Kochlight) at *ca.* 1150° as described by Timms, *et al.*[4] The efflux of the reactor was admitted directly to the collision chamber of the spectrometer *via* a 1 cm length of 1 mm id tubing. The pressure in the reactor was *ca.* 0.1 Torr while in the analyzer it was less than 5×10^{-5} Torr. The 127° sector photoelectron spectrometer with electron retardation has been described previously.[5] Two modifications improved the resolution and reduced the scattered electron intensity. The length of the analyzer entrance slit was reduced to 1 cm and a grounded 1×4 mm slit was placed between the source slit and the analyzer entrance slit. Both resolution and sensitivity deteriorated in the presence of SiF_2, although both could be restored by cleaning the source. Several attempts were made to obtain a spectrum at a resolution better than 60 meV full width at half maximum; however, none was successful. Calibration was carried out using argon and SiF_4 as internal standards. The vertical ionization potentials of SiF_4, listed in Table I, were measured separately with both He(I) and He(II) radiation.

Results and Discussion

The photoelectron spectra observed as a function of silicon temperature are illustrated in Figure 1. At the higher temperatures three new bands appear. These bands increase with increasing temperature and depend on the SiF_4 mass flow. In addition, the ratio of the intensities of the two new bands at lowest ionization potential is independent of temperature and mole fraction of SiF_4. As it has been shown previously[2] that SiF_4 and SiF_2 constitute 99.5% of the reactor efflux, we assign these new bands to SiF_2 and the vertical ionization potentials are listed in Table I. The first vertical ionization potential agrees well with the electron impact value of 11.0 ± 0.5 eV.[6]

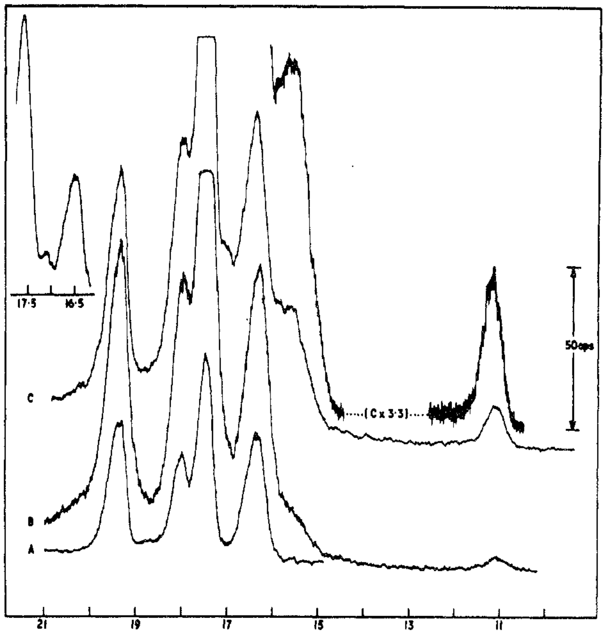

Figure 1. Photoelectron spectra of SiF_4 + Si as a function of silicon temperature: (A) T 25°, (B) T ~1100°, (C) T ~1200°. The inset is a slow scan under the conditions of spectrum C.

Table I. Experimental Vertical Ionization Potentials and Relative Intensities for SiF_2 and SiF_4

	This work				Vert	Rel	Vert
	Vert IP	Rel int			IP[e]	int[e]	IP[f]
SiF_2	11.08	1.0					
	15.57	~3					
	17.08	~3					
		b	*c*	*d*			
SiF_4	16.45	1.00	1.00	1.00	16.46	1.00	16.46
	17.54	1.17	1.44	0.74	17.55	0.93	17.54
	18.09	0.61	0.75	0.32	18.09	(0.35)	18.12
	19.48[a]	0.95	1.70	0.70	19.51	(0.42)	19.52
	21.49[d]			0.31			

[a] Vibrational structure was observed on this band at 19.31, 19.36, 19.40, 19.45, 19.48, 19.54, and 19.57 eV. The spectrum was similar to that shown in Figure 1 of W. E. Bull, B. P. Pullen, F. A. Grimm, W. E. Moddeman, G. K. Schweitzer, and T. A. Carlson, *Inorg. Chem.*, 9, 2474 (1970). [b] Relative intensities for the spectrometer with electron retardation. [c] Corrected relative intensities for spectrum obtained on the instrument described in D. W. Turner, *Proc. Roy. Soc., Ser. A*, 307, 15 (1968). [d] Data obtained with He(II) radiation on the instrument described by Turner in the reference in footnote *c*. [e] See the reference in footnote *a*. [f] P. J. Bassett and D. R. Lloyd, *Chem. Phys. Lett.*, 3, 22 (1969).

It appears that SiF_2 deposited under collision-free conditions behaves differently from SiF_2 that has been pumped through a tube long with respect to its diameter.[2] Thus, in order to look for less stable species, the sampling time was reduced by eliminating tubing bends after the reactor and by reducing the volume between the reactor and sampling constriction. The average sampling time in the former reactor is *ca.* 2 sec, while in the modified reactor it was 0.2 sec. However, although the signal intensity was lower, no differences were observed in the spectrum. As SiF_2 experiences a large number of wall collisions before ionization, hot bands were not considered a problem in the interpretation of the spectrum.

Silicon difluoride is a bent triatomic molecule ($\theta = 101°$) having one more electron than NO_2 ($\theta = 134°$) and two more than CO_2 ($\theta = 180°$). SiF_2 is isoelectronic with SO_2[3,7] and a representation of its electronic structure is

$$\ldots(4a_1)^2(3b_2)^2(1b_1)^2(5a_1)^2(4b_2)^2(1a_2)^2(6a_1)^2\ldots{}^1A_1$$

The band at 11.1 eV is assigned to ionization from the $6a_1$ orbital. This orbital involves atomic orbitals from both the

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central and ligand atoms and is weakly antibonding.[8] As might be anticipated from the discussion of AB_2 molecules by Walsh,[9] this band shifts to lower ionization potential as the ionization potential of the central atom decreases in the series O_3, SO_2, and SiF_2.[10]

The second and third bands of SiF_2 are partly hidden by the bands of SiF_4. However, both the bandwidths and relative intensities of the second and third bands with apparent vertical ionization potentials of 15.6 and 17.1 eV indicate that they result from ionization from at least two molecular orbitals each. This is reasonable as the splittings of the $1a_2$, $4b_2$ and $1b_1$, $5a_1$ pairs is small for O_3, SO_2, and NO_2.[10] These orbital pairs correlate with the π_g and π_u orbitals in linear AB_2 molecules and, as they are expected to be somewhat localized on B,[9] will appear at higher ionization energies than similar orbitals in SO_2.[3,7] The spectrum of SiH_2F_2 has two fairly narrow bands at 12.85 and 15.20 eV assigned to ionization from molecular orbitals associated with the SiH bonding and two broad and more intense bands between 15.5-16.5 and 17-19 eV assigned to the $1a_2$, $4b_2$ and $1b_1$, $5a_1$, $3b_2$ orbital groups, respectively.[11] These broad bands are very similar to the second and third bands observed for SiF_2. SiH_3F exhibits a band at 16.1 eV which has been assigned to fluorine "lone pair" ionization[12] and NSF also has two bands between 15.5 and 16.5.[13] Thus, one is tempted to assign the second band in SiF_2 to the $1a_2$, $4b_2$ pair and the third band to the $1b_1$, $5a_1$ pair.

It is of interest to compare this orbital assignment based on Koopmans' theorem with the information available from ultraviolet emission and absorption spectra of SiF_2. There is substantial evidence[14,15] that the ultraviolet absorption with a vibrationless transition at 44,109 cm^{-1} corresponds to the transition

$$\ldots(4b_2)^2(1a_2)^2(6a_1)(2b_1),\ {}^1B_1 \leftarrow \ldots(4b_2)^2(1a_2)^2(6a_1)^2,\ {}^1A_1$$

Recently,[16] absorption in the vacuum ultraviolet with a vibrationless transition at 62,214 cm^{-1} has been assigned to the transition

$$\cdots(4b_a)^2(1a_2)(6a_1)^2(2b_1),\ {}^1B_2 \leftarrow \cdots(4b_2)^2(1a_2)^2_2(6a_1)^2,\ {}^1A_1$$

This suggests that the spacing between the $6a_1$ and $1a_2$ orbitals should be 18,105 cm^{-1} (2.24 eV) and, thus, there should be a band in the photoelectron spectrum at $11.08 + 2.24 = 13.32$ eV. Clearly no such band is present. The photoelectron and ultraviolet absorption data are compatible if the vacuum ultraviolet absorption at 62,214 cm^{-1} is reassigned to ${}^3B_2 \leftarrow {}^1A_1$ as a near ultraviolet system with a vibrationless transition at 26,310 cm^{-1} has been observed and assigned to ${}^3B_1 \leftarrow {}^1A_1$.[17] This revised assignment leads to a splitting of the $6a_1$ and $1a_2$ orbitals of 35,904 cm^{-1} (4.45 eV) which compares well with the difference in ionization energies of the first two bands in the photoelectron spectrum (4.49 eV). The ${}^1B_2 \leftarrow {}^1A_1$ transition would then be predicted to lie at *ca.* 80,000 cm^{-1}.[18]

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Registry No. SiF_2, 13966-66-0.

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(18) Note Added in Proof. The electronic spectrum of SiF_2 has been discussed in a recent theoretical paper: B. Wirsam, *Chem. Phys. Lett.*, 22, 360 (1973).

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Synthesis of *closo*-1,7-$B_{10}C_2H_{12}$ from *nido*-2-B_5CH_9

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Until now, direct routes to two-carbon carboranes have involved treating boron hydrides with acetylenes, alkenes, and atomic carbon species.[1] Many other two-carbon carboranes have been discovered by subjecting known two-carbon carboranes to chemical oxidation, hydroboration, pyrolysis, photolysis, or electrical discharge.[1,2] We now report a unique synthesis of a closed two-carbon carborane accomplished by joining two units of a one-carbon carborane.

Experimental Section

Techniques for the preparation and purification of 2-B_5CH_9 have been described elsewhere.[3,4]

In a typical pyrolysis, 0.0968 g of 2-B_5CH_9 (1.29 mmol) was sealed in a 100-cm^3 Pyrex bomb and heated to 250° for 84 hr. A total of 2.32 mmol of hydrogen was generated. The volatile borane products (0.040 g, 41.5 wt % conversion to two-carbon carboranes) were separated on a 25 ft × $^1/_4$ in. glass vpc column at 210° (10% Apiezon L on firebrick). The products (see Table I) were identified by their characteristic R_f values, mass spectra, and ^{11}B nmr spectra. The 1,7-$B_{10}C_2H_{12}$ derivative was also identified by comparison of its melting point and ir spectrum with those of an authentic sample. Neither the 1,2- nor 1,12-$B_{10}C_2H_{12}$ isomer was detected.

In a separate experiment, 0.0707 g of 3-$CH_3B_5CH_8$[3,4] (0.794 mmol) was pyrolyzed for 2 days at 250°. The only product was 0.0093 g of a clear liquid. Boron-11 nmr, proton nmr, and mass spectra showed this liquid to be a B-methylated 1,6-$B_8C_2H_8(CH_3)_2$ species (0.063 mmol, 16% conversion). No B-methylated $B_{10}C_2H_{10}(CH_3)_2$ species were detected.

Results and Discussion

The gas-phase pyrolysis of 2-B_5CH_9 at 250° proceeds in two identifiable directions. In one pathway, two molecules of *nido*-2-carbahexaborane(9) apparently fuse, face to face, to

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