TABLE VI

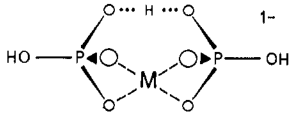
CALCULATED COMPOSITIONS OF A SOLUTION CONTAINING 0.008 MOL L.$^{-1}$ OF ORTHOPHOSPHATE, 0.008 MOL L.$^{-1}$ OF CALCIUM(II), AND 0.15 MOL L.$^{-1}$ OF POTASSIUM NITRATE AT 37°[a]

pH	[Ca^{2+}]	[H_3PO_4]	[$H_2PO_4^-$]	[HPO_4^{2-}]	[Orthophosphate] as			[$CaH_2PO_4^+$]	[$CaHPO_4^0$]	[Orthophosphate] as	
					$H_5(PO_4)_2^-$	$H_4(PO_4)_2^{2-}$	$H_3(PO_4)_2^{3-}$			$CaH_3(PO_4)_2^-$	$Ca_2H_2(PO_4)_2^0$
3.0	779	54	652	*	27	46	*	21	*	*	*
3.5	778	18	697	*	10	52	*	22	*	*	*
4.0	777	6	712	1	3	54	*	23	*	*	*
4.5	776	2	714	4	1	54	*	23	1	1	*
5.0	774	1	705	14	*	53	*	22	2	2	*
5.5	767	*	672	42	*	48	1	21	6	5	3
6.0	737	*	578	115	*	36	3	18	16	11	24
6.5	664	*	390	246	*	16	5	11	31	15	87
7.0	585	*	192	381	*	4	3	5	42	10	163

[a] $10^5 \times$ concentrations in mol l.$^{-1}$; concentrations less than 5×10^{-6} mol l.$^{-1}$ are shown by an asterisk.

oxygens. Alternative forms for II and III are IIa and IIIa. Such structures are idealistic since consideration of the solvent molecules is omitted and they probably represent only the most stable of a number of configurations contributing to the properties of the solution. However the linkage shown in III, involving two metal ions and one hydrogen bond, is similar to that between adjacent tetrahedra in solid calcium monohydrogen orthophosphate;[24] the linkage in IIa binds adjacent tetrahedra in barium monohydrogen orthophosphate,[25] and the linkage shown in IIIa is present in calcium dihydrogen orthophosphate monohydrate.[26]

IIa



IIIa

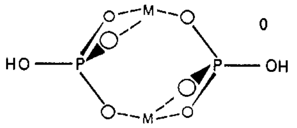


Table VI lists the calculated composition of a solution containing 0.008 mol l.$^{-1}$ of calcium(II), 0.008 mol l.$^{-1}$ of orthophosphate, and 0.15 mol l.$^{-1}$ of potassium nitrate as the pH varies from 3.0 to 7.0. The values in Tables III–V for $F = 0.80$ have been used in the calculations. For none of the pH values shown were [PO_4^{3-}] or [$CaOH^+$] greater than 5 x 10^{-6} mol l.$^{-1}$.

Acknowledgment.—I am grateful to H. Kinns of the Australian National University for assistance with the computing and to P. S. Hallman, W. A. E. McBryde, R. Montgomery, and D. D. Perrin for helpful discussions.

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(24) G. MacLennan and C. A. Beevers, *Acta Crystallogr.*, **8**, 579 (1955).

(25) R. C. L. Mooney, Report TID-5212, U. S. Atomic Energy Commission, Washington, D. C., Sept 1955, p 165.

(26) G. MacLennan and C. A. Beevers, *Acta Crystallogr.*, **9**, 187 (1956).

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Binding Energy of the "2p" Electrons[1] of Silicon in Various Compounds

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The binding energy of the "2p" electrons[1] of silicon in 16 compounds was measured by means of photoelectron spectroscopy. It was found that the binding energy for this orbital ranged from *ca.* 107 eV for Na_2SiF_6, in which the silicon atom is surrounded by strongly electron-withdrawing atoms, to *ca.* 99 eV for the element. These values are discussed from the viewpoint of the influence of the atoms directly bonded to the silicon. In addition, the binding energies for the "2p" orbitals of silicon, phosphorus, and sulfur have been correlated through structures having identical surrounding atoms. Interpretation of these experimental results has been aided by atomic SCF calculations on several configurations of silicon, phosphorus, and sulfur.

Photoelectron spectroscopy of electrons in inner-shell orbitals offers considerable promise as a physical tool for chemical investigations. Indeed, the forerunners[3] in this field have seen fit to apply the acronym ESCA to it, where ESCA stands for electron spectroscopy for chemical analysis.

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[1] The designation of the atomic orbital for which a binding energy is measured is put in quotation marks, *e.g.*, "2p," since the inner orbitals of molecules are somewhat delocalized and hence are not identical with the corresponding atomic inner orbitals.

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[3] K. Siegbahn, C. Nordling, A. Fahlman, R. Nordberg, K. Hamrin, J. Hedman, G. Johansson, T. Bergmark, S. E. Karlsson, I. Lindgren, and B. Lindberg, *Nova Acta Regiae Soc. Sci. Upsal.*, [4] **20** (1967).

Part of the rites of introducing a physical technique to broad usage in chemistry is the investigation of a series of compounds of a given element. In this paper, we are looking at the binding energy of an inner orbital of silicon in such a series, since the ESCA technique has not previously been applied to this element for which there is much chemistry and a wide diversity of compounds.

Experimental Section

Photoelectron Spectroscopy.—The photoelectron spectrometer employed in this work is a scaled-up version (35-cm radius) of a unit previously described.[4] This instrument, which is kept in an iron-free room, has been fitted[5] with a small-sized computer to process the operation of the instrument.

Both magnesium and aluminum were employed as anodes in the X-ray source, with most of the data being obtained by means of the magnesium radiation. All of the silicon-containing samples but one were solids. The "1s" binding energy of carbon was used as the energy reference line. For every compound studied, at least one measurement was made with a sample that was a mixture of the compound and graphite. We determined the carbon "1s" binding energy for graphite to be 283.0 eV by measuring the energy of the line relative to the carbon "1s" binding energy in different carbon-containing compounds reported by Nordberg, *et al.*[6] If graphite were not mixed with the sample, the carbon "1s" line from hydrocarbon contamination of the vacuum system (which has been shown to exhibit a carbon "1s" binding energy of 286.0 eV) served as the reference.

We believe that the use of graphite as a reference line is much to be preferred to the usual referencing to hydrocarbon contaminants (principally from the O-ring seals in our case), since the carbon "1s" line may vary from one kind of contaminant to another. Furthermore, the hydrocarbon line results from a thin surface layer which may be more easily affected by the gross sample than the essentially nonreactive particles of graphite. An example of this kind of problem with the contaminant was found in the study of sodium hexafluorosilicate, where the accustomed spacing between the carbon "1s" peaks of the hydrocarbon contamination and the graphite was not observed. Thus, with the hydrocarbon contaminant as the reference standard, a value of 103.6 eV was obtained for the single silicon "2p" line of sodium hexafluorosilicate, whereas the use of graphite as the reference standard gave a value of 10.72 eV for this very same line. On the basis of the physical form of the graphite particles, we argue that the value of 107.2 eV is the correct one and this value, which is several electron volts larger than any of the other binding energies reported herein, lies in the range to be expected for a silicon atom surrounded by six fluorine atoms in accord with the reported data on sulfur[2] and phosphorus.[7] It should be noted that, in addition to serving as a calibration standard, the graphite also ought to reduce surface-charge buildup on poorly conducting samples.

The spectrometer was also calibrated by means of photoelectron lines from copper, produced by magnesium, aluminum, and chromium Kα radiation, and the above values for the carbon "1s" binding energy of graphite and of hydrocarbon contaminants were thus confirmed. A small nonlinearity due to a residual external field was discovered and corrections for this nonlinearity were applied to the measured energies. In no case did the correction exceed 0.2 eV. The work function of the spectrometer was not measured but is taken to be 3.7 eV, as determined for other aluminum spectrometers of this type.[8]

The solid sources were prepared either by sprinkling the sample–graphite mixture onto an adhesive tape or by pressing it into a brass mesh. Since the siloxane, $[(CH_3)_2SiO]_n$, used in this study is a viscous liquid of very low volatility, the source in this case was prepared by dipping the mesh into the liquid.

Theoretical Calculations.—Some *ab initio* LCAO–MO–SCF calculations[9] were done on silicon, phosphorus, and sulfur atoms in their lowest energy states (chosen according to Hund's rule) for selected configurations of the valence orbitals. A minimum-basis set of Slater-type orbitals was used, with all orbital exponents being throughly optimized. The configurations studied and their respective terms are $s^2p^2(^3P)$, $sp^3(^5S)$, $sp^2(^4P)$, $s^2pd(^3F)$ $sp^2d(^5F)$, $spd(^4F)$, and the neon core (^1S) with all valence electrons stripped off. The ionic charge for a given configuration will, of course, vary from silicon to phosphorus to sulfur. Thus, the sp^3 configuration corresponds to Si^0, P^+, and S^{2+}, while spd corresponds to Si^+, P^{2+}, and S^{3+}.

Samples.—The compounds studied in this work were all taken from our collection of silicon compounds and represent materials of good purity. They were prepared according to standard procedures and were recrystallized when made in solution. Those samples which were hygroscopic or otherwise air sensitive were handled in a drybag and transferred rapidly into the spectrometer which was then immediately pumped out.

Results and Discussion

Experimental Data.—The various silicon compounds on which meaningful reproducible data were obtained are listed in Table I in order of decreasing binding energy. The binding energies of the various compounds are listed in column 3 of this table while columns 4 and 5 give, respectively, the number of replicates on which each binding energy was based as well as its standard deviation. The standard deviations are indications of the reproducibility of the measurements

TABLE I
EXPERIMENTAL "2p" BINDING ENERGIES OF SILICON IN VARIOUS COMPOUNDS

Compound	Nearest atoms to Si	Binding energy, eV	No. of replicates	Std dev, eV
Na_2SiF_6	6 F	107.4[a]	3	0.1
$(HSiO_{3/2})_\infty$	1 H, 3 O	104.2	2	0.6
SiI_4	4 I	103.8	2	0.6
$(SiO)_\infty$	x Si, $(4 - x)$ O	103.5	2	0.9
$(SiS_2)_\infty$	4 S	103.1	4	0.7
$(SiO_2)_\infty$, quartz	4 O	103.0	6	0.2
$[(CH_3)_2SiO]_n$	2 O, 2 C	102.8	5	0.3
$(C_6H_5)_3SiOH$	1 O, 3 C	102.4	6	0.7
$(C_6H_5)_4Si$	4 C	102.4	4	0.3
SiB_4	4 B	102.4; 99.2[b]	3	0.1; 0.1
Zn_2SiO_4	4 O	102.2	2	0.3
$(SiC)_\infty$	4 C	102.2; 99.2[b]	2	0.9; 0.9
$(Na_2SiO_3)_n$	4 O	102.0	4	0.3
$(C_6H_5)_2Si(OH)_2$	2 O, 2 C	101.9	2	0.2
$(SiN_4)_\infty$	4 N (?)	101.8	3	0.6
$(C_6H_5)_3SiSi(C_6H_5)_3$	3 C, 1 Si	101.3	4	0.1
Si_∞	4 Si	~99	1	. . .

[a] Referenced to graphite; value of 103.6 eV obtained by referencing to pump oil (see text). [b] Two peaks observed; the lower binding energy is ascribed to elemental silicon or a related reduced form.

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[4] R. Nordberg, J. Hedman, P. F. Hedén, C. Nordling, and K. Siegbahn, *Ark. Fys.*, **37**, 489 (1968).

[5] A. Fahlman, R. G. Albridge, R. Nordberg, and W. M. LaCasse, *Rev. Sci. Instrum.*, in press.

[6] R. Nordberg, J. Hedman, P. F. Hedén, U. Gelius, C. Nordling, and K. Siegbahn, submitted for publication.

[7] M. Pelavin, D. N. Hendrickson, J. M. Hollander, and W. L. Jolly, *J. Phys. Chem.*, **74**, 1116 (1970).

[8] A. Fahlman, S. Hagström, K. Hamrin, R. Nordberg, C. Nordling, and K. Siegbahn, *Ark. Fys.*, **31**, 479 (1966).

[9] B. Roos, C. Salez, A. Viellard, and E. Clementi, "A General Program for Calculation of Atomic SCF Orbitals by the Expansion Method," IBM Research Laboratory, San Jose, Calif. 95114.

and are therefore to be used in considering observed differences in the bond energies. However, if one is concerned with absolute values of the binding energies, consideration must be given also to the other error contributions, such as uncertainties in the spectrometer work function and in the energies of the calibration line and X-ray radiation.

It should be noted in Table I that two silicon "2p" lines were observed for silicon carbide, SiC. We have ascribed the line with the lower binding energy (99.2 eV) to contamination with elemental silicon and hence have placed silicon carbide at 102.2 eV in the tabulation. Measurements were also made on calcium silicide, $CaSi_2$, lithium silicide, Li_4Si, and silicon phosphide, SiP. The binding energies of these compounds lie somewhere in the neighborhood of those of elemental silicon and silicon carbide. Not surprisingly, the sample of silicon phosphide exhibited two silicon "2p" binding energies, with one of them being ascribable to an oxidation product. Even though great care was taken to avoid surface oxidation in handling lithium silicide, it was difficult to prepare a source which would give an electron spectrum containing a silicon "2p" line. Somewhat related behavior was observed with silica gel, which showed an oxygen "1s" peak but no peaks attributable to silicon. Heating the sample for several hours at 1000° caused the silica "2p" peak to show up, presumably through elimination of a surface layer of water sufficiently thick as to be virtually impenetrable to the electrons emitted from the silicon atoms.

Influence of Neighboring Atoms.—It is still somewhat of an open question as to whether molecules in the solid state will show nearly the same inner-orbital binding energies which they exhibit as gases.[10] Elucidation of this question requires more comparative studies of solid and gaseous samples than are yet available. In a few specific cases, attempts have been made to calculate the magnitude of "molecular and lattice potentials"[3,6,11,12] in solids; however, widely applicable methods of estimating the solid-state effect are not available. A further difficulty in interpreting data obtained on solids occurs because the photoelectron method does not probe deeply into a condensed phase and thus there may be surface effects. In the remainder of this discussion we shall assume that the solid-state and surface effects are small or nearly compensatory, so that they will be ignored for the molecular solids studied here.

In all of its compounds (except perhaps the silicides of highly electropositive metals, *e.g.*, Li_4Si) silicon is covalently bonded to its nearest neighbor atoms. Further, silicon does not bear unshared pairs of electrons, so that a silicon atom in any molecule to be found in a solid or liquid is well protected from surrounding molecules by its neighboring atoms and the substituent groups of which they form a part. On this basis, we choose to interpret the observed binding energies in terms of the effects of the nearest-neighbor atoms to silicon in the respective molecule.

In the second column of Table I, the number and kinds of atoms which hold the position of nearest neighbor to the silicon are listed. Inspection of this column shows that there is some tendency for the silicon atoms in the compounds toward the top of the table to be surrounded by groups which withdraw electrons more than do the neighboring groups of the silicon in the compounds toward the bottom. However, as illustrated by Figure 1, in which the Si "2p" electronic binding energy is plotted against an estimation of the effective electrical charge on the silicon atom in the various compounds studied, most of the binding energies lie in the narrow range of 101–104 eV. The effective charges employed in Figure 1 were obtained from averaged electronegativity values,[13] using either the Pauling[14] or Hannay–Smyth[15] equation relating electronegativity difference to the ionic character of a single bond and making small adjustments for specific electron-withdrawing effects.[16] No attempt was made to estimate the effective electrical charge on the silicon atom by either semiempirical or *ab initio* quantum mechanical procedures since the "charge on an atom"[17]

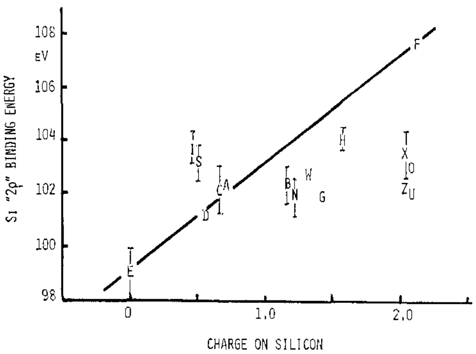

Figure 1.—The silicon "2p" binding energy in various compounds *vs.* the charge on the silicon atom empirically estimated from single-bond polarities. The line in this plot is drawn through those compounds which contain a silicon atom that is not expected to accept electrons from its neighboring atoms. The letters stand for the following compounds: A, $(C_6H_5)_4Si$; B, $(C_6H_5)_3SiOH$; C, SiC; D, $(C_6H_5)_3SiSi(C_6H_5)_3$; E, Si_∞; F, Na_2SiF_6; G, $(C_6H_5)_2Si(OH)_2$; H, $(HSiO_{3/2})_\infty$; I, SiI_4; N, $(Si_3N_4)_\infty$; O, $(SiO_2)_\infty$ (quartz); S, $(SiS_2)_\infty$; U, $(Na_2SiO_3)_n$; W, $[(CH_3)_2SiO]_n$; X, $(SiO)_\infty$; Z, Zn_2SiO_4.

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[10] K. Siegbahn, C. Nordling, G. Johansson, J. Hedman, P. F. Heden, K. Hamrin, U. Gelius, T. Bergmark, L. O. Werme, R. Manne, and Y. Baer, "ESCA Applied to Free Molecules," North-Holland Publishing Co., Amsterdam, 1969.

[11] C. S. Fadley, S. B. M. Haystrom, M. P. Klein, and D. A. Shirley, *J. Chem. Phys.*, **48**, 3779 (1968).

[12] W. L. Jolly and D. N. Hendrickson, UCRL Report 19050, July 1969; submitted for publication.

[13] M. L. Huggins, *J. Amer. Chem. Soc.*, **75**, 4123 (1953).

[14] L. Pauling, "Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960, pp 97–102.

[15] N. B. Hannay and C. P. Smyth, *J. Amer. Chem. Soc.*, **68**, 171 (1946).

[16] *E.g.*, R. W. Taft, "Steric Effects in Organic Chemistry," M. S. Newman, Ed., Wiley, New York, N. Y., 1956, Chapter 13, p 556.

[17] The charge on an atom is obtained from SCF calculations through an electron population analysis, according to R. S. Mulliken, *J. Chem. Phys.*, **23**, 1833, 1841, 2338, 2343 (1955).

in a molecule is a bookkeeping entry[18] which results from the LCAO (linear combination of atomic orbitals) approximation and which is very sensitive to calculational details such as the size of the basis set used in an SCF computation.[19]

It should be noted that the points in Figure 1 form a scatter pattern so that there is no simple correlation between atomic charge estimated from single-bond polarities and the binding energy of the silicon "2p" electron for the various compounds.

An Atom-Based Interpretation.—The results of the *ab initio* atomic SCF calculations carried out on silicon, phosphorus, and sulfur are presented in Table II. The various configurations calculated for each of these atoms are listed in order of decreasing stability as measured by the total atomic energy given in the fourth column of this table. As expected, the configurations lie in the same ordering with respect to energy for silicon, phosphorus, and sulfur, and this order corresponds to an increase in the positive charge of the atom as well as to promotion to higher orbitals for a given atomic charge. Not surprisingly, the energy of the 2p inner orbital becomes an increasingly larger negative number when going down the listing of configurations of decreasing overall atomic stability. It is interesting to note that the exponent of this 2p orbital does not vary systematically with its energy or with the total energy of the atom. In all three cases the largest 2p exponent (and hence the smallest orbital radius) corresponds to the spd configuration, and the smallest exponent (largest radius) to the neon-core configuration.

TABLE II

MINIMUM-BASIS-SET SLATER–ORBITAL SCF CALCULATIONS ON SILICON, PHOSPHORUS, AND SULFUR ATOMS OR THEIR IONS

Atom	3rd-shell confign	State[a]	Energies, eV		Slater 2p orbital exponent
			Total	2p orbital	
Si^0	s^2p^2	^3P	−7,838.85	−108.97	4.9724
Si^0	sp^3	^5S	−7,836.79	−109.84	4.9736
Si^0	s^2pd	^3F	−7,834.08	−115.46	5.0050
Si^0	sp^2d	^5F	−7,830.44	−115.53	4.9887
Si^+	sp^2	^4P	−7,829.02	−120.03	4.9911
Si^+	spd	^4F	−7,820.43	−123.77	5.0172
Si^{4+}	(Neon)	^1S	−7,738.61	−162.15	4.9457
P^+	s^2p^2	^3P	−9,239.85	−151.79	5.4953
P^+	sp^3	^5S	−9,236.43	−152.56	5.4947
P^+	s^2pd	^3F	−9,229.78	−156.07	5.5170
P^+	sp^2d	^5F	−9,225.26	−156.32	5.5059
P^{2+}	sp^2	^4P	−9,216.81	−165.91	5.5122
P^{2+}	spd	^4F	−9,204.30	−168.97	5.5359
P^{5+}	(Neon)	^1S	−9,076.19	−216.08	5.4549
S^{2+}	s^2p^2	^3P	−10,762.51	−202.01	6.0135
S^{2+}	sp^3	^5S	−10,757.76	−202.56	6.0121
S^{2+}	s^2pd	^3F	−10,748.06	−205.28	6.0325
S^{2+}	sp^2d	^5F	−10,742.36	−205.53	6.0220
S^{3+}	sp^2	^4P	−10,722.93	−218.87	6.0302
S^{3+}	spd	^4F	−10,706.60	−221.35	6.0517
S^{6+}	(Neon)	^1S	−10,522.59	−276.87	5.9626

[a] According to Hund's rules, these are all ground states.

Following the well-established procedure of discussing molecules in terms of theory appertaining to isolated atoms, we see from Table II that increasing the charge on an atom by removing either an s, p, or d electron from the valence shell causes an increase in the binding energy of the 2p inner-shell electron. This is in accord with the generally accepted idea[3] that an increase in the electron-withdrawing power of the neighboring atoms in a molecule leads to an increase in inner-shell-orbital binding energy.

According to the usual valence-bond theory, p_π–d_π bonding acts as a feedback mechanism to reduce the charge separation between a second-row atom and a strongly electron-withdrawing substituent.[20] Such addition of electronic charge to a d orbital of a second-row atom in a molecule ought to cause a decrease in the "2p" orbital energy of that atom; and this is seen to be true for isolated atoms from comparison of the sp^2 and sp^2d configurations for either silicon, phosphorus, or sulfur in Table II.

We are now in a position to give a theoretical interpretation for the scattering of the points in Figure 1. Let us draw a line through those chemical structures in which p_π–d_π bonding is not expected to any extent. These structures are the hexafluorosilicate anion, SiF_6^{2-}, tetraphenylsilane, $(C_6H_5)_4Si$, hexaphenyldisilane, $(C_6H_5)_3SiSi(C_6H_5)_3$, and elemental silicon, Si_∞. It should be noted that all of the points in Figure 1, except those of silicon tetraiodide and silicon disulfide, lie below this line. We shall then take the perpendicular distance between a point lying below the line and the line as a measure of the number of electrons involved in p_π–d_π bonding for that particular compound. From the difference in 2p binding energies between the sp^2 and sp^2d configurations in Table II, one might guess that for each electron volt which a point lies below the line in Figure 1 there is approximately 0.2 e^- involved in p_π–d_π bonding.

Now consider the stepwise substitution of carbon by oxygen atoms on a silicon atom, according to the interpretation given in the paragraph above. In going from $(C_6H_5)_4Si$ to $(C_6H_5)_3SiOH$ to $(C_6H_5)_2Si(OH)_2$ to SiO_2, we see in Figure 1 that the substitution of the

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(18) It is known that the Hartree–Fock limit may be reached by using unusual combinations of atomic orbitals (AO's). For example, all of the AO's may be assigned to a single atom in a so-called one-center calculation and, even at the Hartree–Fock limit where calculated properties such as the dipole moment should be correct, a population analysis of a one-center calculation will assign all of the electrons to the particular atom chosen as the center. In order to get a *balanced* basis set, which by its definition will give meaningful charges on the atoms, one would presumably employ a very large number of AO's, with these being reasonably distributed between the constituent atoms. Examples of one-center calculations for silane in restricted basis sets are the following: R. B. Hake and K. E. Banyard, *J. Chem. Phys.*, **44**, 3523 (1966); E. L. Albasing and J. R. A. Cooper, *Proc. Phys. Soc. (London)*, **85**, 1133 (1965); R. Moccia, *J. Chem. Phys.*, **40**, 2164 (1964).

(19) Present-day *ab initio* SCF computations are generally carried out with 25–75 Gaussian-type orbitals per molecule. As yet unpublished SCF studies made in our laboratory show that the calculated charge on the atom is particularly sensitive to the exact choice of basis set for this size range of basis sets as applied to compounds of second-row elements. Therefore, it is unwise today to turn to *ab initio* calculations for values of charges on atoms in molecules. Obviously, the charges calculated from semiempirical procedures (such as the extended-Hückel, CNDO, or INDO methods) are also highly suspect; particularly when one considers that a Slater minimum-basis set usually gives a very poor dipole moment.

(20) Theoretical evidence for $p\pi$–$d\pi$ bonding and for such electronic feedback results from a recent *ab initio* LCAO–MO–SCF calculation: L. C. D. Groenweghe, H. Marsmann, L. J. Schaad, and J. R. Van Wazer, *J. Amer. Chem. Soc.*, in press.

first carbon by oxygen leads to the introduction of some π-bond feedback (*ca.* 0.3 e^-) which is increased by the substitution of the second carbon almost to the value corresponding to complete substitution (*ca.* 0.9 e^-). Moreover, according to this interpretive scheme, there is somewhat less electronic feedback from the oxygen to the silicon in the long-chain dimethylsiloxane than in diphenylsilanediol, in which the silicon also exhibits two oxygen and two carbon atoms as nearest neighbors. Similarly, the silicate salts, Zn_2SiO_4 and Na_2SiO_3, seem to utilize about 0.2 e^- more in Si–O p_π–d_π bonding than is found for quartz. The qualitative sensibleness of these conclusions leads one to believe that the atoms-in-molecule interpretation given here for the data is not unreasonable.

Comparison of Different Atoms in Similar Compounds.—Recent work[7] on the binding energies of "2p" electrons associated with phosphorus in various compounds as well as published data[3] on sulfur compounds may be compared with the measurements reported here for the "2p" electrons of silicon. We believe that such a comparison between different atoms with respect to variations in their binding energies may be carried out in a fruitful manner by contrasting compounds in which there are the same kind and number of atoms similarly surrounding each of the atoms being compared.

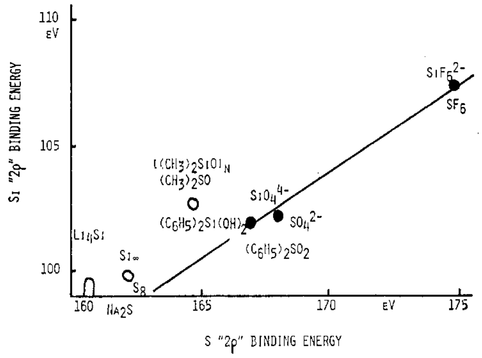

Figure 2.—The "2p" binding energies of silicon *vs.* those of sulfur for compounds having the same number, kind, and arrangement of nearest-neighbor atoms (solid points). The open points correspond to structures which are closely related but do not fulfill all of the specifications for the solid points. The line has the same slope as the line drawn through the points in a similar plot of silicon and sulfur 2p binding energies for the various atomic configurations given in Table II.

In comparing silicon with sulfur, the respective hexafluoro structures, the respective anions of the ortho oxy acids, and the pair of compounds in which the nearest neighbor atoms consist of two phenyl groups and two oxygen atoms make up a series of such related silicon and sulfur compounds. We also expect some concordance between "2p" binding energies of this series, and the binding energies for the elements as well as for the alkali metal binary compounds. Perhaps even the contrast between the silicon binding energy of polydimethylsiloxane and the sulfur binding energy of dialkyl sulfoxide will also be in line with the series.

The "2p" binding energies of such pairs of related compounds are plotted in Figure 2, in which the line has been given a theoretical slope. This slope was obtained from a similar plot (which also gave a straight line, with little scatter of the points) of the values representing the various atomic configurations of Table II for the silicon and sulfur atoms. In the case of both the experimental "2p" binding energies and the atomic SCF calculations of 2p binding energies, we find that the change in binding energy with electron-withdrawing power of the substituents is about 1.5 times greater for the sulfur than for the silicon.

In Figure 3, the "2p" binding energy of silicon is compared in the same way with that of phosphorus, and it is seen that in this case the results from the atomic SCF calculations do not agree as well with the experimental points as in Figure 2. From the experimental measurements, we conclude that the effect of an increase or decrease in the electron-withdrawing power of the nearest-neighbor atoms has about the same effect on the silicon as on the phosphorus "2p" binding energy. However, the atomic SCF calculations indicate that the change in "2p" binding energy with change in electron-withdrawing power of the substituents is somewhat greater for the phosphorus than for the silicon.

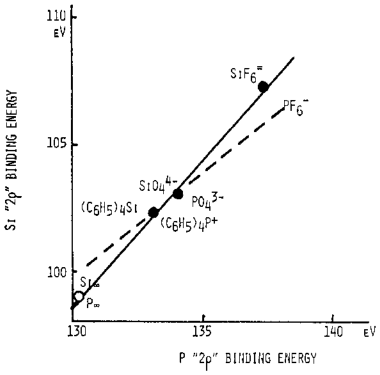

Figure 3.—The "2p" binding energies of silicon *vs.* those of phosphorus for compounds having the same number, kind, and arrangement of nearest-neighbor atoms (solid points). The open point in this figure corresponds to a structure which is closely related but does not fufill all of the specifications for the solid points. The solid line has been drawn through the experimental points and the dotted line gives the slope corresponding to the 2p binding energies of various atomic configurations.

Finally in Figure 4, a comparison is made between the "2p" binding energies of phosphorus and sulfur for similar related compounds. Again, as would be expected from the previous relationships of Figures 2 and 3, there is not good agreement between the slope of the line obtained from the SCF calculations and that representing the experimental data. However, in either case, it is seen that an increase or decrease in electron-withdrawing power of the substituents leads to a greater change in "2p" binding energy of the sulfur than of the phosphorus.

In summary, according to the atomic SCF calcula-

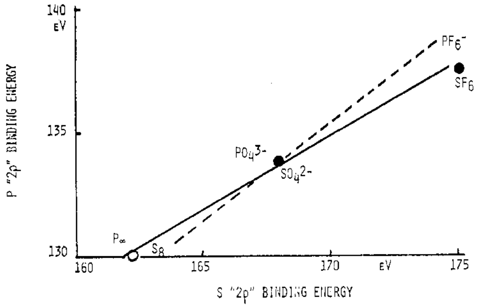

Figure 4.—The "2p" binding energies of phosphorus *vs.* those of sulfur for compounds having the same number, kind, and arrangement of nearest-neighbor atoms (solid points). The open point in this figure corresponds to a structure which is closely related but does not fulfill all of the specifications for the solid points. The solid line goes through the experimental points and the dotted line gives the slope corresponding to the 2p binding energies of various atomic configurations.

tions presented in Table II, the effect of removing a valence-shell electron on the binding energy of the 2p inner-shell electron increases gradually when going from phosphorus to silicon to sulfur. On the other hand, the experimental data indicate that the change in "2p" binding energy by removing a certain amount of valence charge through sharing of electrons with neighboring atoms is about the same for silicon and phosphorus but is considerably greater for sulfur. Both the theoretical and experimental results show an increasing effect with increasing atomic number.

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High-Resolution Photoelectron Spectroscopy of Carbon and Silicon Tetrafluorides[1]

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High-resolution photoelectron spectra of CF_4 and SiF_4 obtained with 584-Å radiation are reported. The spectra are interpreted by relating the photoelectron bands to the energies of the molecular orbitals of the two molecules. Vibrational fine structure observed on the photoelectron bands is assigned to vibrational states of the resulting ions. Evidence of the participation of d orbitals in the bonding of SiF_4 is discussed.

In this paper we report the high-resolution photoelectron spectra of carbon tetrafluoride and silicon tetrafluoride using 584-Å radiation of a helium discharge lamp. Low-resolution spectra of these compounds have been reported[4,5] using the retarding grid type of instrument. These spectra failed to indicate the vibrational fine structure of some of the photoelectron bands which are of considerable help in interpreting the spectra. In this paper we have reexamined the molecular orbital energy level sequences utilizing the additional information available from the high-resolution spectra and suggest new assignments for the molecular orbital sequences in CF_4 and SiF_4. Assignments for the vibrational modes which are excited upon ionization are also discussed.

Discussion

Carbon Tetrafluoride.—The photoelectron spectrum of carbon tetrafluoride consists of three bands (see Figure 1); the first band starts at 15.67 eV, rises smoothly to a maximum intensity at 16.25 eV, and extends into the second smooth band which has a maximum at 17.46 eV. The third band exhibits vibrational fine structure which consists of two series of peaks each with a separation of 0.10–0.11 eV. The first series which has the more intense peaks displays ionization energies of 18.27, 18.37, 18.48, 18.58, 18.69, and 18.80 eV with the maximum intensity of the band coinciding with the 18.58-eV vibrational peak. The second less intense series has maximum intensities at 18.33, 18.44, 18.54, 18.65, 18.76, and 18.87 eV.

Except for our observation of the fine structure on the third band, these data agree very well with the photoelectron spectrum reported by Bassett and Lloyd.[5] Frost, *et al.*,[4] have also reported the photoelectron spectrum of CF_4 and cite vertical ionization energies of 15.9, 17.2, and 18.5 eV. The onset of ionization at 15.67 eV agrees quite well with the recent reports of 15.56,[6]

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