The germanium–sulfur and –selenium compounds may be of the "iso" type too, but since their spectra show no strong absorptions attributable to bonds between the pseudohalo groups and the germanium above ~300 cm.$^{-1}$ a definite conclusion cannot be drawn.

The vibrations of the pseudohalo groups which can be referred to as pseudosymmetric do not give strong enough absorptions to have been detected in the spectra of any of the six compounds and, accordingly, structure arguments based on the positions of these absorptions cannot be applied.

If, as seems probable, the silicon compounds are of the iso type, the sizes of the Si–N–C bond angles are of interest in view of the fact they may point to the presence or absence of d_π–p_π bonding between the sp^3d^2 hybridized silicon and the nitrogen.[11]

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K-Edge X-Ray Absorption of Arsenic Compounds

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Since we have recently been investigating certain areas of arsenic chemistry[1] as well as the use of K-edge X-ray absorption in characterizing compounds of transition metals,[2] it seemed desirable to look at the K-edge absorption spectra of a number of arsenic compounds. Outside of $AsCl_3$ and a number of interstitial metal arsenides,[3] we have been able to find no literature on K-edge absorption spectra of arsenic compounds. The samples were run on a General Electric XRD-5 single-crystal monochromator employing a scintillation counter moved at a continuous rate of 0.04° (2θ)/100 sec. Under these conditions, the diffractometer clearly and cleanly resolves the low-energy spike in the permanganate spectrum.

All of the compounds investigated in this study (listed in Table I) exhibited similar spectra, as typified by Figure 1. Within an experimental error of several electron volts, the position of point A in Figure 1 was found to be the same for all of the compounds investigated. Although the distance from A to B varied somewhat from compound to compound, this variation was not as great as the change in the distance between B and C. According to the treatment[2] which seems to be generally applicable to the transition metals, the maximum, labeled B in Figure 1, should correspond to a transition from the 1s to a vacant p level, and that labeled C to a kind of ionization or "escape" energy for the 1s electron. Furthermore, the distance, ΔE, from the maximum at C to the minimum at D should be a measure of the radius of the first coordination sphere around the arsenic through the Bragg relation, $r_1 = (151/\Delta E)^{1/2}$.

TABLE I

MEASURED PARAMETERS IN X-RAY ABSORPTION MEASUREMENTS OF ARSENIC COMPOUNDS

Compound	Replicate runs	Escape potential, e.v.[a]	Estd. av bond length, Å.
As_2O_5[c]	5	93	1.85
		95	1.83
		93	1.85
		96	1.87
		94	1.85
As_2S_5	3	83	2.45
$(NH_2C_6H_5)AsO(OH)_2$	2	100	1.95
$(C_6H_5)_3AsO$	3	98	1.81
$(C_6H_5)_3AsCH_3{}^+Cl^-$	2	82	1.89
Na_3AsO_4	2	99	1.71
$Na_2(CH_3)AsO_4$	2	101	1.63
$H_4As_2O_7$	2	95	1.88
AsI_3	2	40	2.38
$AsCl_3$	3	73	2.20
AsF_3	2	90	1.90
$(C_6H_5)_3As$	2	77	1.93
$As(OCH_3)_3$	4	86	1.78
$As(OC_2H_5)_3$	1	87	1.70
As_2O_3	2	90	1.80
$As_2(NCH_3)_3$	2	87	1.69
$As[N(CH_3)_2]_3$	1	92	1.90
AsS (amorphous)	2	84	2.02
AsS (crystalline)	2	91	1.87

[a] Difference from A to C (see Figure 1). [b] $r_1 = (151/\Delta E)^{1/2}$ (see Figure 1). [c] The reproducibility of the data is typified by these five independent runs on arsenic pentoxide.

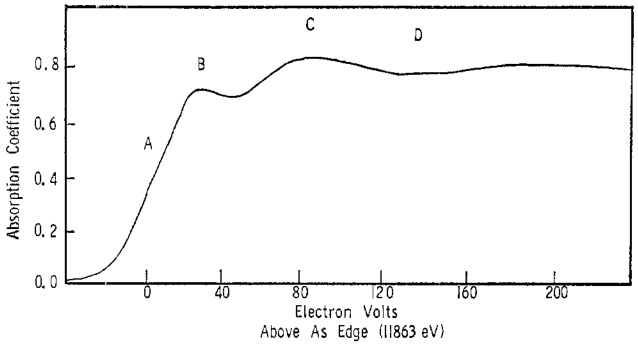

Figure 1.—K-edge X-ray absorption spectrum of As_2O_5. The labeled features are discussed in the text. A is the half-maximum of the adsorption edge.

In a purely electrostatic model, as successfully applied to third-row transition metal complexes,[2] the energy of C varies almost exactly as the conventional ionization potential of the equivalently charged gaseous ions. Such correspondence is not observed in the arsenic compounds where, for example, the difference

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(1) *E.g.*, J. R. Van Wazer, K. Moedritzer, and D. Matula, *J. Am. Chem. Soc.*, **86**, 807 (1964); M. D. Rausch, J. R. Van Wazer, and K. Moedritzer, *ibid.*, **86**, 814 (1964); and K. Moedritzer and J. R. Van Wazer, *Inorg. Chem.*, **3**, 139 (1964).

(2) R. M. Levy, *J. Chem. Phys.*, **43**, 1846 (1965); R. M. Levy and J. R. Van Wazer, *Advan. Anal. Chem. Instrumentation*, in press.

(3) D. Coster and G. H. Klamer, *Physica*, **1**, 889 (1934); W. Eberbeck, *Z. Physik*, **149**, 412 (1957).

in ionization potential between As^{+2} and As^{+5} is 100 e.v. while the energies of peak C for As_2O_5 and As_2O_3 differ by only 5 e.v. There is also only a small correlation between the average electronegativity of the substituents and the energy of peak C, as can be seen from Table I. However, as expected, a high electron density on the arsenic atom consistently favors the escape of a 1s electron from the arsenic, represented by the escape-potential peak C.

Although the electrostatic model only poorly predicts the characteristics of the transitions in the lower energy regions, it fares much better when employed to estimate bond distances[2] from the C–D distance in Figure 1. This is shown by the following bond distances (Å.), where the values determined from diffraction studies[4] are given in parentheses behind those estimated from the K-edge absorption data: AsF_3, 1.9 (1.72); $AsCl_3$, 2.2 (2.25); AsI_3, 2.4 (2.54); Na_3AsO_4, 1.7 (1.75); and As_4O_6, 1.9 (1.79). We may conclude that, while details of σ and π bonding strongly influence the bound electronic levels on the arsenic atoms, a 1s electron with energy sufficient to surmount the attractive Hartree potential behaves approximately as a free electron in an ionic lattice.

The composite data on the arsenic compounds studied are presented in Table I.

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[4] L. E. Sutton, Ed., Tables of Interatomic Distances and Configuration in Molecules and Ions, The Chemical Society, London, 1958.

Correspondence

On the Supposed Reaction between Sulfur Hexafluoride and Hydrogen Iodide

Sir:

Padma and Murthy[1] have recently reported that sulfur hexafluoride is completely reduced by hydrogen iodide in the gas phase after 6 hr. at room temperature (30 ± 2°) and propose an analytical method based on the equation

$$SF_6 + 8HI = H_2S + 4I_2 + 6HF$$

Previously published work has shown that SF_6 undergoes chemical disruption only under powerful conditions such as exposure to alkali metal systems[2,3] and to attack by strong Lewis acids.[4] In the course of an investigation into the reactions of SF_5-containing compounds, we were unable to achieve reduction of the SF_5 group in the fluorocarbon derivatives $SF_5(C_2F_5)_nCl$[5] using either HI or H_2S at temperatures up to 200°. Furthermore, we could not detect any reaction between pure SF_6 and H_2S, contrary to an early report.[6] These observations prompted us to investigate the claim that reduction of SF_6 is readily brought about by hydrogen iodide.

In our experiments dry, oxygen-free gaseous mixtures of HI and SF_6 (8:1 molar ratio) under atmospheric pressure were allowed to stand in the dark at 25–35° for 72 hr. On analysis no trace of hydrogen sulfide, hydrogen fluoride, or free iodine could be detected, SF_6 being recovered unchanged. When the experiments were repeated with the gas mixtures exposed to ultraviolet radiation no products derivable from SF_6 were found, although iodine formed by the photodecomposition of HI was present.

The reducibility of the SF_5 group in compounds of the formula SF_5X depends largely on the nature of the attached group X. Perfluoroalkyl–SF_5 compounds and SF_6 are not reduced by sodium iodide in acetone, whereas SF_5Cl, S_2F_{10}, and $S_2F_{10}O$ react readily.[7] The trend is further illustrated by the reaction with anhydrous $AlCl_3$ in which chlorine and chlorides of sulfur are formed.[4] In this reaction SF_6 requires a temperature of 180–200° for its decomposition whereas $SF_5(C_2F_4)_nCl$ and S_2F_{10} react exothermally at room temperature.

The results reported by Padma and Murthy,[1] who did not state how they characterized their SF_6 sample, are consistent with the presence of a large proportion of S_2F_{10} (b.p. 29°) or even $S_2F_{10}O$ (b.p. 31°) in their material.

Sulfur hexafluoride was obtained as a by-product from the reaction of SF_4 with chlorine monofluoride.[8] The gas was freed from traces of SF_5Cl, SF_4, and Cl_2 by scrubbing with aqueous sodium hydroxide and aqueous potassium iodide consecutively, before being dried by passage through concentrated sulfuric acid and over phosphorus pentoxide. Gas–liquid chromatography on Florube A grease[8] indicated a single component. The infrared spectrum of the gas was identical in detail with the published spectrum[9] of pure SF_6 and no absorption attributable to S_2F_{10} (*e.g.*, the 826 cm.$^{-1}$ band[10]) was present.

Hydrogen iodide was prepared by the reaction of iodine with boiling tetralin.[11] The gaseous product was entrained in a stream of dry, oxygen-free nitrogen and collected in a liquid air cooled trap. Repeated transfer of the material between cooled traps *via* U tubes packed with powdered KI served to remove traces of tetralin and unreacted iodine.

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[2] H. C. Cowen, F. Riding, and E. Warhurst, *J. Chem. Soc.*, 4168 (1953).
[3] G. C. Demitras and A. G. MacDiarmid, *Inorg. Chem.*, **3**, 1198 (1964).
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[5] J. R. Case, N. H. Ray, and H. L. Roberts, *J. Chem. Soc.*, 2070 (1961).
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[11] J. Houben, J. Boedler, and W. Fischer, *Chem. Ber.*, **69B**, 1766 (1936).