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Preliminary communication

GENERATION OF DIMETHYLGERMATHIONE AND DIMETHYLSILATHIONE AND THEIR DETECTION IN THE GAS PHASE BY PHOTOELECTRON SPECTROSCOPY

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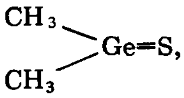
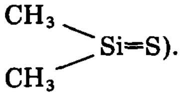
Summary

We report in this paper the first spectroscopic detection (photoelectron spectroscopy) of germathiones and silathiones, which previously had been characterized only by chemical trapping [1].

Dimethylgermathione and dimethylsilathione were generated from the corresponding trimers $(Me_2MS)_3$ (M = Ge or Si). Upon pyrolysis (250—300°C, 5×10^{-2} mbar), the photoelectron spectrum of each trimer is completely changed (Fig. 1 and 2). The number of bands observed suggests the presence of two species. Since pyrolysis of trimers can lead to monomeric and dimeric species, and dimerization reaction of monomer cannot be excluded, we also determined the ionization potentials characteristics of the n-butylgermathione dimer $(n\text{-}Bu_2GeS)_2$ (Fig. 3).

We also noticed that for a temperature about 20° of the decomposition temperature of the trimer, a decrease in intensity of band 1 corresponds to a slight increase in the intensities of bands 3 and 5.

In the light of these observations, the very intense band 1 (Fig. 1 and 2) can only arise from the ionization of the non-bonding pair of sulfur of the monomeric form (8.6 eV for  $(CH_3)_2Ge{=}S$, 9.15 eV for  $(CH_3)_2Si{=}S$). This ionization obscures the first two ionizations of the dimer (present in low proportions). Band 2 (9.55 eV for $Me_2Ge{=}S$ and 10.10 eV for $Me_2Si{=}S$), characteristic of the π

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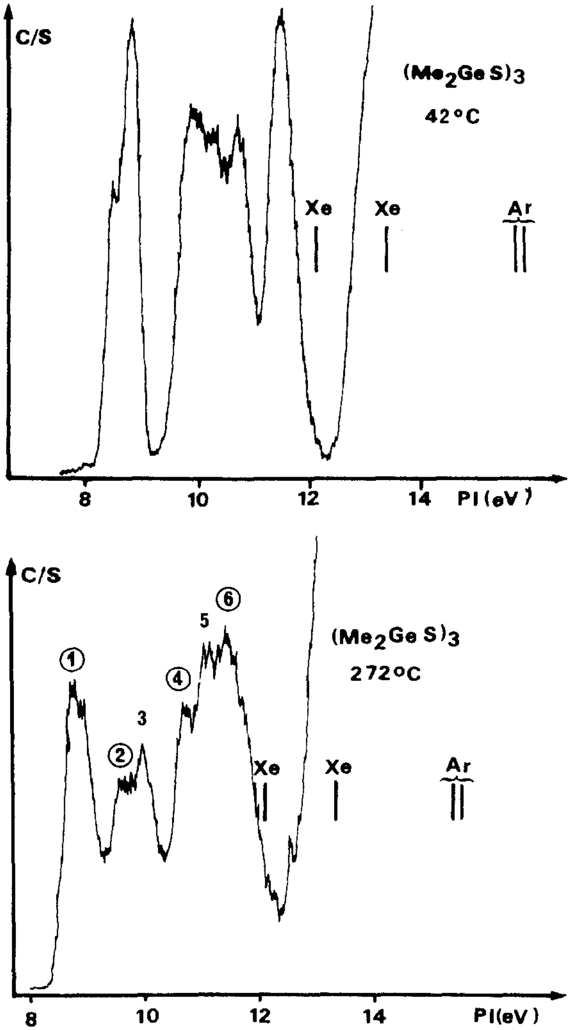

Fig. 1. Photoelectron spectra of $(Me_2GeS)_3$ at 42 and 272° C.

ionization of the Ge=S and the Si=S bonds, decreases in intensity as the irradiation changes from He(I) to He(II) [2], at the same time as band 1. From this observation and from the value of 9.45 eV observed for the second ionization potential of the dimer of di-n-butylgermathione, we attribute the two bands 3 and 5 to the dimer. Bands 4 and 6 are associated with ionizations of the Ge—S and Ge—C bonds (10.75, 11.47) or the Si—S and Si—C bonds (11.05, 12.10) of the monomer.

These assignments are in agreement with theoretical ionization potentials calculated for these two species (Table 1). For dimethylgermathione we used the PS HONDO program and introduced polarization and correlations interpair corrections [3]; in the case of the silathione, the MNDO method [4], which gives correct ionization potentials of organic molecules, was used [5].

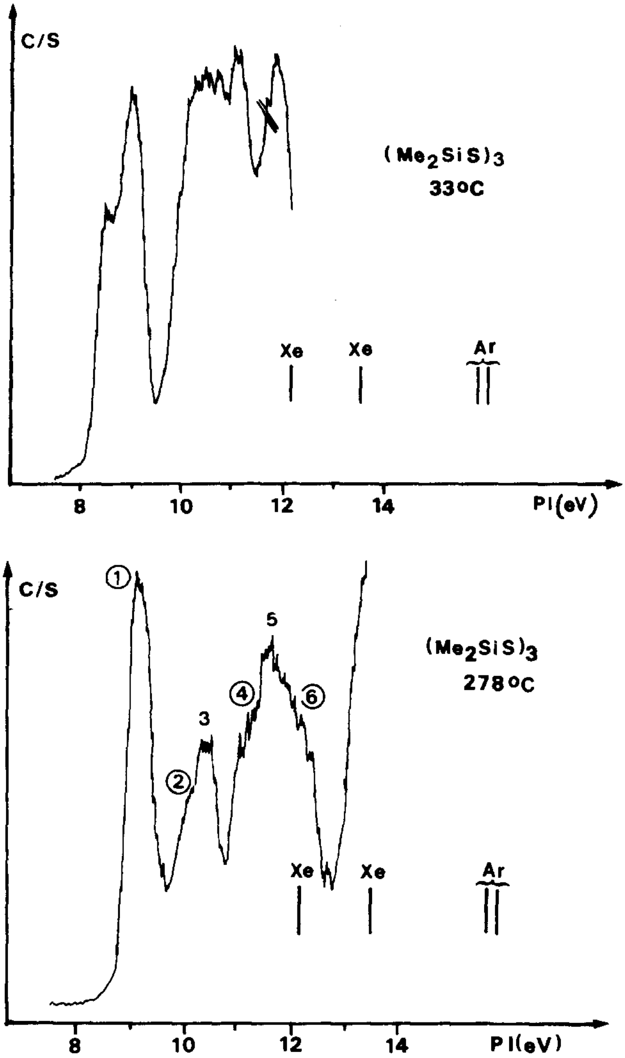

Fig. 2. Photoelectron spectra of (Me$_2$SiS)$_3$ at 33 and 278° C.

TABLE 1

EXPERIMENTAL AND CALCULATED VERTICAL IONIZATION POTENTIALS

Germathione						Silathione		
Vertical ionization potentials	Calculated ionization potentials[a]					Vertical ionization potentials	Assignment	Koopmans[b]
	Assignment	Koopmans	Pol.	Corr.	Estimated			
8.6	n(S)	8.88	−0.73	0.32	8.48	9.15	n(S)	9.46
9.55	π(Ge=S)	9.32	−0.55	0.40	9.17	10.10	π(Si=S)	10.12
10.75	σ(Ge—S)	11.33	−0.59	0.28	11.08	11.05	σ(Si—S)	11.71
11.47	σ(Ge—C)	12.72	−0.20	0.19	12.3	12.10	σ(Si—C)	12.62

[a] PS HONDO Program: pseudo potentials and double ζ gaussian bases with polarization functions ϕ(Ge) = 0.25; ϕ(S) = 0.54. Structural parameters Ge—S 2.02 Å [6], Ge—C 1.99 Å. [b] Optimized structural parameters by MNDO method: Si—S 1.894 Å; Si—C 1.836 Å; C—Si—S 122.7°.

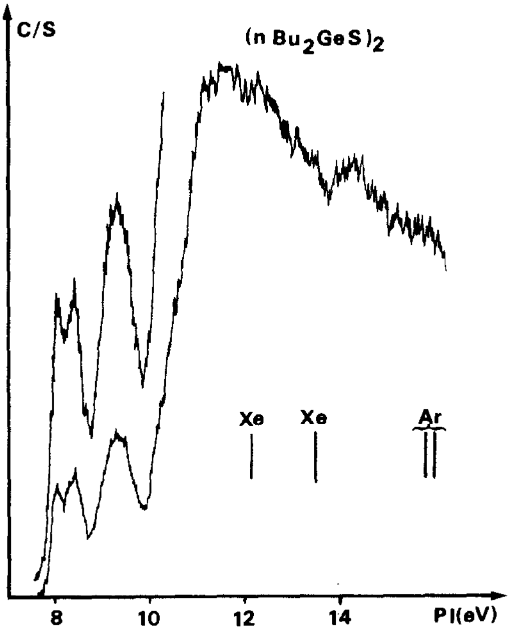

Fig. 3. Photoelectron spectra of (n-Bu$_2$GeS)$_2$.

Experimental

Spectra were recorded with a Perkin—Elmer PS 18 photoelectron spectrometer with an He(I)/He(II) Helectros source. In the probe used the evaporation chamber is separated by about 30 cm from the ionization chamber by a metal tube in which the evaporated sample could be heated independently without affecting unvaporized material. The spectra were calibrated with the $^2P_{1/2}$ and $^2P_{3/2}$ lines of Ar or Xe.

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