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Publication Date
1979
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Prepared for the U. S. Department of Energy
under Contract W-7405-ENG-48

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The He I Photoelectron Spectroscopy 
of Heavy Group IV-VI Diatomics

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January 1979

ABSTRACT

The He I photoelectron spectra of the Group IV-VI diatomics GeO, GeS, GeSe, GeTe, SnS, SnSe, and SnTe are presented. The outermost valence structure of these molecules is similar to that observed in the lighter series CO, CS, etc. of this valence iso-electronic group; in each case a relatively sharp peak is assigned to ionization from the nominally non-bonding 3σ orbital and a broader band to ionization from the 1π orbital. At higher binding energies the spectra exhibit several peaks where only a single peak is expected, from the (2σ)⁻¹ hole state. This structure is assigned as correlation peaks resulting from configuration interaction among hole states of \( ^2\Sigma^+ (\Omega = 1/2) \) symmetry. Semi-empirical CNDO-MO calculations have been performed for these molecules, and the results are used to interpret the observed trends. In addition, a simple molecular orbital model is employed to estimate the importance of spin-orbit coupling in the valence electronic structure of the heavy IV-VI ions.

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I. INTRODUCTION

Considerable effort in ultraviolet photoelectron spectroscopy (UPS) has been focussed on elucidating periodic trends in the electronic structure of molecules that are isoelectronic in the valence shells. Recently, the use of high temperature ovens in UPS research has allowed heavier molecules to be studied in the vapor phase. For the (Group VI) dichalcogenides $\text{O}_2$, $\text{S}_2$, $\text{Se}_2$, $\text{Te}_2$, and the two III-VII series $\text{TlX} \ (X = \text{F, Cl, Br, I})$ and $\text{InX} \ (X = \text{Cl, Br, I})$, the molecular orbital intensity patterns and relative energy ordering remain similar in the heavier molecules. As the atomic numbers of the constituent atoms increase, however, spin-orbit effects become dominant, leading to large splittings between the $\Omega$ sub-states and in some cases to non-statistical intensity ratios. In addition, the transition from Hund's case (a) coupling in the light molecules to case (c) coupling for the heavier molecules results in a relaxation of symmetry conditions for configuration mixing of multiplets within the initial and final states. Hence, many-electron correlation effects become increasingly important, making a one-electron molecular orbital description inappropriate for relativistic molecules.

The photoelectron spectrum of $\text{Bi}_2^+$ was recorded recently in this laboratory. In addition to the expected large spin-orbit splittings, it showed a reversal in the binding energy ordering of the outermost molecular orbitals relative to that observed for the lighter homologues of this group, $\text{N}_2$ and $\text{PN}$. 
Further studies on the Group V series are hampered by the instability of the diatomic molecules in the vapor phase. In contrast, the vapors of most of the isoelectronic Group IV-Group VI compounds consist primarily of the IV-VI diatomic molecules at temperatures below 1000°K. Hence, the IV-VI molecules are suitable for further study of the variation of valence molecular orbital structure with molecular weight.

The He I spectra of the IV-VI molecules GeX (X = S, Se), SnX (X = S, Te), and PbTe have recently been reported by Wu and Fehlner⁶ and that of SiO by Colbourn, et al.⁷ In the work of Wu and Fehlner,⁶ the low binding energy regions of these spectra, containing the outermost $2\Sigma^+$ and $2\Pi$ ionization bands, were presented. Except for the GeS⁺ spectrum, however, they did not report the weaker structure expected to lie at higher binding energies. Such structure results from electron correlation between the inner $(\sigma)^{-1}$ primary hole states and closely lying excited ionic states as observed in the photoelectron spectra of CO⁺ and CS⁺. In this work, we present additional He I spectra for the GeX and SnX molecules in which the correlation states are evident, as well as the previously unpublished spectra of GeO, GeTe, and SnSe. Our peak assignments are based on semi-empirical LCAO-MO-SCF calculations, band shape and intensity arguments and comparison with photoelectron data for the lighter members of this series. A simple molecular orbital model is employed to estimate the spin-orbit splittings and the importance of $2\Sigma^+$ ($\Omega = 1/2$) and $2\Pi$ ($\Omega = 1/2$) mixing in
the final ionic state. Finally, the observed trends in relation to the general valence electronic structure of the Group IV-VI molecules.

II. EXPERIMENTAL

The spectra were recorded in a modified Perkin-Elmer PS-18 photoelectron spectrometer operating at a nominal energy resolution of 80-90 meV (FWHM) as measured on the Xe 5p_{1/2}-5p_{3/2} doublet. The oven and experimental procedure have been described in detail elsewhere. Because of continuous deposition of the sample on critical surfaces, the energy resolution and peak position could vary considerably during a single run (which took from one to ten hours). Energy calibration was done by introducing Xe and N\textsubscript{2} together with the sample in separate runs.

The samples were obtained commercially. All samples were of at least 99.9\% purity and were used without further purification. The GeO sample was loaded into the spectrometer under a dry nitrogen atmosphere, while all other samples were loaded in air. Only in the vaporization of the SnS sample were appreciable impurities encountered. Near 400°C, an intense spectrum of SnCl\textsuperscript{2+} was observed as identified from the He I UPS data of Evans and Orchard. The intensity of these bands decreased at higher temperatures and eventually disappeared after several hours. To confirm the data obtained with the SnS sample, additional experiments were performed using SnS\textsubscript{2}. 
At elevated temperatures SnS$_2$ is unstable with respect to disproportionation, i.e., SnS$_2$(s) \textcolor{red}{\rightarrow} SnS(g) + S$_2$(g). The spectra at lower temperatures (~400°C) were characteristic of S$_2$ while at higher temperatures a spectrum identical to that observed in the SnS vaporization was dominant.

The oven temperatures at which the spectra were recorded were: GeO (570°C), GeS (380°C), GeSe (405°C), GeTe (550°C), SnS (610°C), SnSe (590°C), and SnTe (650°C). The thermocouple that monitored the temperature was in contact with a slightly cooler part of the oven; hence, the actual sample temperatures may have been up to 30°C higher. At these temperatures the vapor pressures of the MX(g) molecules were between 10$^{-14}$ and 10$^{-16}$ as extrapolated from the vapor pressure data for these systems, and mass spectroscopic studies have shown in each case that the MX(g) diatomic molecule is the principal component in the vapor phase.

In high temperature UPS experiments the analysis of the vibrational fine structure is complicated by the fact that the ground state molecule is in a thermal distribution of vibrational levels. This is particularly important for heavy molecules, for which the vibrational frequencies of the neutral ground states are small. The thermal vibrational distributions for the molecules studied in this work are given in Table I. For the heavier members of this series, particularly the MSe and MTe diatomics, the vibrational excitation is extensive, with significant populations up to v" = 4. The effect of this
distribution is to wash out the fine structure of the closely lying $^2\Sigma^+$ and $^2\Pi$ levels. In addition, the band shapes yield less information concerning geometry changes upon photoionization because the Franck-Condon envelope is thermally averaged over many initial and final vibrational transitions.

III. THEORETICAL

The ground electronic state of a IV-VI diatomic can be represented by the single determinental wavefunction

$$\Psi(1^1\Sigma^+) = \mathcal{A}(10) \left\{ 1\sigma^2 \ 2\sigma^2 \ 3\sigma^2 \ 1\pi^4 \right\}$$  \hspace{1cm} (1)$$

where we have explicitly considered only the outermost filled valence molecular orbitals, and $\mathcal{A}(N)$ represents the $N$-electron antisymmetrizer. Neglecting relativistic interactions at this point, photoionization from the $\pi$ shell and any of the $\sigma$ shells will result in $^2\Pi$ and $^2\Sigma^+$ ionic states, respectively.

To estimate the binding energies of these orbitals, we have performed semi-empirical CNDO\textsuperscript{17} valence molecular orbital calculations for the molecules discussed in this paper. The calculations were carried out using an extensively modified CNDO code parameterized for atoms through Xe ($Z = 54$).\textsuperscript{18} Calculations employing both nsnp and nsnp(n+1)d basis were performed. The overall molecular orbital character and energy level ordering for these basis sets were similar. Because the unoccupied d orbitals make a negligible contribution to the spin-orbit matrix elements discussed below, only the nsnp
basis results are reported here. Equilibrium bond lengths were taken from reference (19).

The orbital eigenvalues are compared with the experimental binding energies in Tables II and III. The eigenvalues have been empirically reduced by 15% to account for final ionic state relaxation. This factor was estimated by averaging the percentage errors of the CNDO eigenvalues from the experimental binding energies for the lighter members of this series (CO, CS, and SiO). Table IV summarizes the Mulliken population analyses for the valence molecular orbitals.

For the heavier members of both the GeX and the SnX series, spin-orbit interactions become appreciable and remove the degeneracy of the $\Omega = 1/2$ and $\Omega = 3/2$ sublevels of the $^2\Pi$ ionic state. In addition, the ionic states of the heavier molecules are more appropriately described in a $(\omega,\omega)$ (Hund's case (c)) rather than a $(\Lambda,\Sigma)$ (Hund's case (a)) coupling scheme. In the former coupling scheme, the closely spaced $^2\Sigma^+_{1/2}(3\sigma)^{-1}$ and $^2\Pi_{1/2}(1\pi)^{-1}$ ionic states can interact strongly and the resulting $\Omega = 1/2$ states can be expressed as linear combinations of the $(\Lambda,\Sigma)$ states; i.e.,

$$\psi(\Omega = 1/2) = a\psi(2^2\Sigma^+_{1/2}) + b\psi(2^1\Pi_{1/2}) \quad . \quad (2)$$

This interaction has been shown to be very important in rationalizing the observed spin-orbit splittings in the UPS spectra of $I_2$ and the cesium halides.
To estimate the importance of these final ionic state interactions, we used an approximate spin-orbit model based on the CNDO wavefunctions. This method parallels similar semi-empirical calculations by others.\textsuperscript{23-25} The molecular spin-orbit operator was approximated as

$$\mathcal{H}_{SO} = \sum_{N} \sum_{i} \zeta_{N}^{\text{eff}} \mathbf{I}_{N} \cdot \mathbf{s}_{i}$$

(3)

where the sums over \(N\) and \(i\) refer to atomic centers and electrons, respectively, and where \(\zeta_{N}^{\text{eff}}\) is the effective atomic spin-orbit coupling constant as defined by Grimm.\textsuperscript{25} In a \(|\Lambda \Sigma \Omega \rangle\) basis, the \((3\sigma)^{-1}\) and \((1\pi)^{-1}\) final ionic states can be represented by the single determinants

\begin{align*}
2_{\Sigma^{+}}^{1/2}: \quad & |0 1/2 1/2 1/2\rangle = \mathcal{A}(9) \{ \ldots 3\sigma \alpha(5) 1\pi^{+} \alpha(6) \\
& \times 1\pi^{+} \beta(7) 1\pi^{-} \alpha(8) 1\pi^{-} \beta(9) \} \\
2_{\Pi^{1/2}}^{1/2}: \quad & |1 1/2 -1/2 1/2\rangle = \mathcal{A}(9) \{ \ldots 3\sigma \alpha(5) 3\sigma \beta(6) \\
& \times 1\pi^{+} \alpha(7) 1\pi^{-} \beta(8) 1\pi^{-} \beta(9) \} \\
2_{\Pi^{3/2}}^{1/2}: \quad & |1 1/2 1/2 3/2\rangle = \mathcal{A}(9) \{ \ldots 3\sigma \alpha(5) 3\sigma \beta(6) \\
& \times 1\pi^{+} \alpha(7) 1\pi^{+} \beta(8) 1\pi^{-} \alpha(9) \}
\end{align*}

where the degenerate \(-(\Lambda+\Sigma)\) combinations have not been given. Since \(\mathcal{H}_{SO}\) of Eq. (3) is only a one-electron operator, and

noting the identity \(\mathbf{I} \cdot \mathbf{s} = l_{z} s_{z} + \frac{1}{2} (l^{+} s_{-} + l^{-} s_{+})\), the non-zero matrix elements are readily evaluated as
\begin{align*}
\langle 2\Pi_{3/2}|\mathcal{H}_{\text{SO}}|2\Pi_{3/2}\rangle &= \langle 1\pi_\alpha|\mathcal{H}_{\text{SO}}|1\pi_\alpha\rangle = -A/2 \\
\langle 2\Pi_{1/2}|\mathcal{H}_{\text{SO}}|2\Pi_{1/2}\rangle &= \langle 1\pi_\beta|\mathcal{H}_{\text{SO}}|1\pi_\beta\rangle = A/2 \\
\langle 2\Sigma^+_1/2|\mathcal{H}_{\text{SO}}|2\Pi_{1/2}\rangle &= \langle 3\sigma_\beta|\mathcal{H}_{\text{SO}}|1\pi_\alpha\rangle = \epsilon
\end{align*}

where $A$ is proportional to the spin-orbit splitting within a given electronic term. The $3\sigma$ and $1\pi$ wavefunctions were taken from the calculated molecular orbitals of the ground state as a Koopmans' approximation to the hole-state wavefunctions. We can then obtain the matrix elements of $\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_{\text{SO}}$ to give the total interaction matrix

\begin{table}
\begin{tabular}{c|ccc}
& $2\Pi_{3/2}$ & $2\Pi_{1/2}$ & $2\Sigma^+_1/2$
\hline
$2\Pi_{3/2}$ & $E(2\Pi) - 1/2A$ & 0 & 0 \\
$2\Pi_{1/2}$ & 0 & $E(2\Pi) + 1/2A$ & $\epsilon$ \\
$2\Pi_{1/2}$ & 0 & $\epsilon$ & $E(2\Sigma^+)$
\end{tabular}
\end{table}

where $\mathcal{H}_0$ is the electrostatic Hamiltonian. For the purpose of the calculation, $E(2\Pi)$ was set equal to zero and $E(2\Sigma^+)$ was varied until the $2\Pi_{3/2} - 2\Sigma^+_1/2$ separation resulting from the diagonalization matched experiment. The values of $\zeta^\text{eff}_n$ and the appropriate matrix elements, as well as the calculated spin-orbit splittings, are summarized in Table V.
IV. RESULTS

The He I spectra of the seven molecules studied are shown in Figs. 1-5, with the assignments of the prominent bands labeled. The peaks marked S are photoelectron bands from the GeX$^+$ diatomic produced by the He I $\beta$ satellite line at 23.07 eV. The assignments and experimental binding energies for the GeX and SnX molecules are summarized in Tables II and III, respectively.

A. The GeX Series

Below 12 eV, the spectra of the GeX$^+$ ions exhibit two close, intense ionization features (Figs. 1 and 2). In this binding energy range, two ionic states corresponding to the $(3\sigma)^{-1}$ and $(1\pi)^{-1}$ hole states are predicted. The UPS spectra of the lighter members of this series, CO, $^{27}$CS, $^{28}$ and SiO, $^{7}$ characterize the $3\sigma$ and $1\pi$ MO's as non-bonding and bonding, respectively; the $(3\sigma)^{-1}$ ionization bands consist primarily of a strong $v'' = 0$ to $v' = 0$ transition while the $(1\pi)^{-1}$ band exhibits a broad Franck-Condon envelope with vibrational frequencies lower than in the ground state molecule. On this basis we assign the sharper, narrower band in each of these spectra to the $^2\Sigma^+(3\sigma)^{-1}$ state and the broader band to the $^2\Pi(1\pi)^{-1}$ ionic state. We note that this level ordering is further supported by the CNDO-MO calculations (see Table II).

Figure 3 shows the overlapping bands of the $^2\Sigma^+$ and $^2\Pi$ states of GeO$^+$ and GeS$^+$ on an expanded energy scale. In
these two molecules the thermal excitation of the neutral ground state is not extensive and photoemission should be predominantly from the v" = 0 level. For the 2Π state of GeO⁺, a vibrational progression of 740 ± 70 cm⁻¹ is observed, with an approximate spin-orbit splitting of 360 ± 50 cm⁻¹. This vibrational spacing is roughly 25% less than that of the neutral ground state, in qualitative agreement with its bonding character. In GeS⁺, the vibrational spacing and the spin-orbit splitting of the 2Π₁/₂, 3/₂ levels is evidently very close, since only one fine structure frequency of 590 ± 100 cm⁻¹ could be extracted with our limited resolution. This spacing is in reasonable agreement with ~500 cm⁻¹ obtained by Wu and Fehlner, who characterize this orbital as only weakly bonding. The vibrational spacings of the 2ℓ⁺(3σ)⁻¹ levels could not be discerned.

Due to the small vibrational frequencies expected for the ionic states (v' < 400 cm⁻¹) and the extensive thermal excitation of the neutral ground states (see Table I), the vibrational structure of the GeSe⁺ and GeTe⁺ ions could not be resolved. In addition, the 2Π₁/₂ and 2Π₃/₂ spin-orbit partners are also not well resolved, even though for GeTe⁺ this splitting is predicted to be several tenths of an eV (see Table V). The overlap of the vibrationally excited Franck-Condon envelopes is at least partially responsible for the lack of observed structure.

At higher binding energies, a single ionization band corresponding to the B²Σ⁺(2σ)⁻¹ state is predicted (the (1σ)⁻¹ hole state will not be observed because its binding energy lies
above the He I resonance line energy of 21.2 eV). In GeO+ a weak band is observed at a vertical I.P. of 15.16 eV with vibrational spacing of $780 \pm 125 \text{ cm}^{-1}$. The structure and low intensity of this band is similar to the $(2\sigma)^{-1}$ ionization observed in CO+, CS+, SiO+, N2+, and P2+. A decrease in the vibrational spacing relative to the neutral ground state ($986 \text{ cm}^{-1}$) is in agreement with the slight bonding character of the $2\sigma$ orbital as predicted by the molecular orbital calculations. The small intensity of the $(2\sigma)^{-1}$ level results presumably from the low photoionization cross section of the Ge 4s atomic orbital which largely comprises the $2\sigma$ molecular orbital (see Table IV).

The spectra of the GeS, GeSe, and GeTe, however, show several weak ionization bands in this energy range. This structure is attributed to primary photoelectric excitation of the GeX+ ions rather than to inelastic processes, because the relative intensities of these bands were invariant with temperature. These peaks are tentatively assigned to correlation or configuration interaction (CI) satellites arising from many-electron effects involving the $(2\sigma)^{-1}$ primary hole state. Similar CI states have been observed in the soft x-ray and He I and He II spectra of CO+, N2+, and CS+. From theoretical studies on these lighter homologues, however, we expect one of the CI levels to be predominantly $(2\sigma)^{-1}$ primary hole state in character. If we assign the band at 15.16 eV in GeO+ to the B2Σ+(2σ)−1 hole state, then the
binding energy of the 2σ orbital in the heavier molecules should lie below ~15 eV, because the atomic ionization potentials decrease as one proceeds down the GeX series. Applying this reasoning and using the calculated binding energies of the 2σ orbitals given in Table II, we have tentatively assigned the \( B^2 \Sigma^+(2\sigma)^{-1} \) states for the GeX\(^+\) ions. The fact that the intensity of the \((2\sigma)^{-1}\) hole state is shared nearly equally among several bands in the spectra of GeSe\(^+\) and GeTe\(^+\), however, indicates that configuration mixing is much greater than that found for the CX\(^+\) homologues. Therefore, the designation of one of these levels to the \( B^2 \Sigma^+(2\sigma)^{-1} \) ionic state can be considered only tentative.

Configuration interaction calculations for CO\(^+\), CS\(^+\), and \( N_2^{+32} \) indicate that the excited ionic configuration most strongly coupled to the single-hole \( 2\Sigma^+ \) ionic state is

\[
\psi(2\Sigma^+) = \mathcal{A}(9) \left\{ 1\sigma^2 \ 2\sigma^2 \ \ 3\sigma^1 \ 1\pi^3 \ 2\pi^1 \right\}.
\]

Satellite lines based on this configuration derive their intensities from both the \((2\sigma)^{-1}\) and \((3\sigma)^{-1}\) primary hole state although those satellites associated with the \((2\sigma)^{-1}\) hole state are found to be more intense. A more complete assignment of the correlation states is severely hampered by the lack of additional theoretical or experimental information on the highly excited ionic states of the GeX\(^+\) ions. The situation is further complicated by the fact that these molecular ions are best described in Hund's case (c) coupling, in which \( \Omega = 1/2 \)}
excited states \( ^2\Sigma_{1/2}^-, \, \, ^2\Pi_{1/2}, \, ^4\Delta_{1/2}, \text{etc.} \) may also interact with the \((2\sigma)^{-1}\) and \((3\sigma)^{-1}\) hole states.

In addition to the features ascribed to the GeX\(^{+}\) diatomics, our spectra of both GeO\(^{+}\) and GeTe\(^{+}\) contain ionization bands from other species. For the temperature range in which the GeO\(^{+}\) spectrum was taken, the vapor has been reported to consist of the \((\text{GeO})_{n=1,2,3}\) species in the approximate ratio 3:1:1.\(^{10}\) The intensities of the bands at 8.5 - 11 eV and 13 - 14 eV in the GeO\(^{+}\) spectrum varied with temperature independently of the intense features at 11.4 eV: these bands are thus clearly not associated with GeO\(^{+}\). Although they are weaker than the above ratio would imply, they lie at slightly lower binding energies than the main peaks in GeO\(^{+}\), as would be expected in polymeric species.

To obtain a theoretical estimate of the level structure of these polymeric molecules, CNDO-MO calculations were performed for \((\text{GeO})_2\) and \((\text{GeO})_3\) using the approximate geometries derived from infrared analysis.\(^{33}\) The resulting eigenvalue spectra of these molecules are concentrated in the regions 8.7 - 11 eV and 13.5 - 16.0 eV. This is in qualitative agreement with both the UPS spectrum and the appearance potential IP's of 8.7 ± 1 eV and 8.6 ± 1 eV for \((\text{GeO})_2\) and \((\text{GeO})_3\), respectively.\(^{10}\) It seems probable that these weak features in the GeO\(^{+}\) spectrum are due to the \((\text{GeO})_{n=2,3}\) species.

In addition to direct vaporization, GeTe also undergoes the disproportionation reaction, GeTe(s) + Ge(s) + \( \frac{1}{2} \) Te\(_2\)(g).\(^{16}\)
The presence of Te\textsuperscript{2+} in our spectrum of GeTe\textsuperscript{+} was readily identified by comparison with the UPS data of Streets and Berkowitz.\textsuperscript{3}

B. The SnX Series

The He I UPS spectrum of SnS\textsuperscript{+} is shown in Fig. 4 and the spectra of SnSe\textsuperscript{+} and SnTe\textsuperscript{+} in Fig. 5. We note that the same general features and trends observed in the GeX\textsuperscript{+} series are evident in these spectra; a sharp narrow band assigned to the \(2\Sigma^{+}(3\sigma)^{-1}\) ionic state and the broader spin-orbit split \(2\Pi(1\pi)^{-1}\) ionization band. In the spectrum of SnTe\textsuperscript{+}, the \(2\Pi_{1/2}\) and \(2\Pi_{3/2}\) states are clearly discernable and the intensity ratio \(2\Pi_{1/2}: 2\Pi_{3/2}\) is greater than the predicted statistical ratio of 1:1. As in the heavier GeX\textsuperscript{+} ions, we again note the extensive structure at higher binding energies, which is tentatively assigned to configuration interaction satellites of the \(2\Sigma^{+}\) primary hole states. More satellite bands appear, and they cover a wider range of binding energies than in the GeX\textsuperscript{+} ions, which is consistent with the larger number of low lying excited valence states found in the absorption spectra of the neutral SnX molecules.\textsuperscript{34}

The position of the \(B^{2\Sigma^{+}(2\sigma)^{-1}}\) hole state is indicated for each spectrum, based on the results of the CNDO-MO calculations. Of course no \(B^{2\Sigma^{+}(2\sigma)^{-1}}\) state can be said to exist, though several \(2\Sigma^{+}\) states are apparent: configuration interaction has distributed the \(B^{2\Sigma^{+}(2\sigma)^{-1}}\) state over all of these peaks.

Finally, we note that the spectrum and assignment of the SnS\textsuperscript{+} ion reported here differs markedly from that given by
Wu and Fehlner. In their work, ionization bands centered at 9.55 eV and 10.2 eV were observed, and the relative intensities of these bands were found to be temperature dependent. The 9.55 eV peak was assigned to the decomposition product, $S_2^+$, while the band at 10.2 eV was assigned to the SnS$^+$ ion. In our studies involving the vaporization of SnS(s), however, no bands attributable to $S_2^{+35}$ were observed, in agreement with the vapor pressure data of Colin and Drowart, who did not observe $S_2(g)$ in detectable quantities. To check our spectrum of SnS$^+$ obtained by the direct vaporization of SnS(s), additional experiments employing SnS$_2$(s) were performed. At temperatures below 450°C, the spectrum of $S_2^+$ was dominant and the strong $^2\Pi_g$ ionization band of $S_2^+$ at 9.41 eV masked the spectrum of SnS$^+$. The spectra at temperatures near 600°C, however, were identical to that found in the SnS(s) vaporization. Furthermore, the band shapes of the $A^2\Sigma^+$ and $X^2\Pi$ levels in our SnS$^+$ spectrum are very similar to those observed for the other GeX$^+$ and SnX$^+$ ions and are consistent with band shapes expected for nominally non-bonding and bonding molecular orbitals, respectively. Hence, we believe the spectrum given in Fig. 4 represents the SnS$^+$ ion, while the ionization bands observed by Wu and Fehlner must arise at least in part from impurities or high temperature reaction products.
IV. DISCUSSION

The sharply peaked bands of the $^2\Sigma^+(3\sigma)^{-1}$ levels of the GeX$^+$ and SnX$^+$ ion characterize the 3\(\sigma\) molecular orbital as essentially non-bonding. Furthermore, in a higher-resolution spectrum of GeS$^+$, Wu and Fehlner reported a small increase in the vibrational spacing ($\Delta v \sim 25$ cm$^{-1}$) in the $^2\Sigma^+(3\sigma)^{-1}$ band relative to the neutral ground state. This indicates that for GeS$^+$, at least, the 3\(\sigma\) orbital is actually weakly anti-bonding. In contrast, the calculated overlap populations tabulated in Table III suggest that the 3\(\sigma\) orbital is weakly bonding for all GeX and SnX molecules. A similar situation is found in the heavy Group III-VII diatomics (InX, TlX; \(X = Cl, Br, I\)) for which the molecular bond is considered somewhat ionic in nature, i.e., \(M^+ - X^-\). For these molecules, which are isoelectronic with the IV-VI series, extended Huckel calculations predict the 3\(\sigma\) orbital to be predominately (\(\sim 75\%\)) localized on the In or Tl atom and to be nominally nonbonding. Because of this localization, however, ionization from the 3\(\sigma\) orbital leads to an increase in the ionic character of the III-VII bond, i.e., \(M^{++} - X^-\), resulting in a shortening of the bond length and an increase in the vibrational frequency of the (3\(\sigma\))$^{-1}$ hole state. Hence, the shape of the $^2\Sigma^+(3\sigma)^{-1}$ photoelectron peak is characteristic of an anti-bonding orbital. Although the atomic orbital composition of the 3\(\sigma\) orbital in the IV-VI diatomics is similar to that of the III-VII series, the localization on the Group IV atom is smaller, giving less
ionic character (see Table IV). Thus, the small increase in the polarity of the IV-VI bond upon ionization from the 3σ orbital is somewhat canceled by the loss of covalent bond overlap. Therefore, in the more ionic IV-VI molecules GeO and GeS (as determined by the extend of charge transferred from the Group IV to the Group VI atom), the resulting $2\Sigma^+(3\sigma)^{-1}$ photoelectron bands will have the structure of a slightly anti-bonding level, while in the more covalent molecules, MSe and MTe, these bands will have the structure of a non-bonding orbital.

A similar argument explains the large decrease in vibrational spacing ($\sim25\%$) in the $2\Pi(1\pi)^{-1}$ ionic state of GeO$^+$, even though the overlap population of the $1\pi$ orbital is small compared to that in most of the other GeX and SnX molecules. Because the $1\pi$ orbital is primarily localized on the Group VI atom (>70%), ionization from this orbital decreases the ionic character of the bond, and therefore increases the bond length. Hence, the $2\Pi$ band exhibits a broader Franck-Condon envelope and smaller vibrational frequency than would otherwise be expected.

For both the GeX and SnX series, an energy stabilization of the 3σ orbital relative to the $1\pi$ orbital develops with increasing molecular weight. A similar trend was observed in the (isoelectronic) Group V-V series, in which the $2\Pi-2\Sigma(3\sigma)^{-1}$ energy ordering reverses between N$_2^+$ and P$_2^+$ and their separation increases in going to Bi$_2^+$. Süzer, et al.,$^5$ found a linear relationship between the internuclear distance and the energy
separation between the $(3\sigma)^{-1}$ and $(1\pi)^{-1}$ ionic states of these V-V molecules. This correlation was based on the interpretation of Price\textsuperscript{35} in which the $3\sigma$ orbital supplies little bonding energy at short internuclear distances because the nuclei have been pulled through some of the $3\sigma$ electron cloud. Hence, for the light diatomics, e.g., N\textsubscript{2}, the $3\sigma$ orbital is destabilized relative to the $1\pi$ and lies at lower binding energy. As the valence atomic orbitals become larger in the heavier atoms, the internuclear distance increases, thereby increasing (decreasing) the bonding effectiveness of the $3\sigma$ orbital ($1\pi$ orbital).

A similar explanation should apply to the IV-VI diatomics, to explain the large differences between the $2_\Pi - 2_\Sigma^+(3\sigma)^{-1}$ energy separation in the light CX\textsuperscript{+} ions and that in the heavy GeX\textsuperscript{+} and SnX\textsuperscript{+} ions. Wu and Fehlner suggest that the rapid decrease in the $2_\Pi - 2_\Sigma^+(3\sigma)^{-1}$ separation from the light to heavy IV-VI molecules results from a sharp decrease in the $\pi$-type interaction between the atoms. This conclusion is qualitatively supported by the fact that the $1\pi$ CNDO-MO overlap population for CO, .2343, is significantly larger than the overlap populations for the $1\pi$ orbitals in the GeX and SnX molecules (see Table IV). The particularly small $1\pi$ overlap population of GeO as compared to the other GeX and SnX molecules results from the small atomic $p\pi$ overlap due to the large difference in size between the Ge(4p) and O(2p) atomic orbitals. In addition, the overlap population of the
3σ orbital in CO is -0.0130, indicating that it is anti-bonding in character, while the overlap populations for the 3σ orbitals in the GeX and SnX molecules are all positive. These trends in overlap populations are consistent with the explanation given by Price to describe changes in the bonding character of 3σ and 1π orbitals between the second row and heavier isoelectronic molecules. Within the GeX and SnX series, however, the relative stabilities of the 3σ and 1π orbitals change only slowly with increasing bond length; the \( \frac{2\Pi - 2\Sigma^+}{\Sigma} \) energy difference decreases by 0.71 eV from GeO⁺ to GeTe⁺ with a corresponding increase in bond length of 0.72 Å, while between CO⁺ and GeO⁺ the energy separation decreases by 2.38 eV for a 0.50 Å bond length increase. The trends within these heavy series are more readily interpreted on the basis of their calculated charge distributions (see Table IV). As noted previously the 1π orbital is localized principally on the chalcogenide while the 3σ orbital is more equally distributed between both atoms. Hence, as one proceeds down the GeX or SnX series, the ionization potentials of the \( (3\sigma)^{-1} \) and \( (1\pi)^{-1} \) hole states decrease, following the decrease in ionization potential of the chalcogenide ns and np atomic orbitals. The 1π energy will decrease faster, however, because it has the proportionally higher Group VI atomic character. Finally, the \( \frac{2\Pi - 2\Sigma^+}{\Sigma} \) energy separation does not vary linearly with internuclear distance for the IV-VI molecules unlike the isoelectronic V-V diatomics. The simple relationship between
atomic orbital overlap and bond length observed for the homonuclear V-V series is less appropriate in the heteronuclear IV-VI molecules because the two atoms have differences in both orbital size and atomic potentials.

If the spin-orbit interaction between the \( \Omega = 1/2 \) substates is neglected, the constant \( A \) defined by Eqs. (4a) and (4b) would give the energy separation between the \( 2\Pi_{1/2} \) and \( 2\Pi_{3/2} \) ionic states. From Table V it is seen that for GeO\(^+\), GeS\(^+\), and SnSe\(^+\) the \( A \) values compare favorably with the experimental splittings, while for GeSe\(^+\), GeTe\(^+\), and SnTe\(^+\) they are significantly larger than experiment. The \( 1\Pi \) orbital is predominantly chalcogenide in character; hence the calculated \( A \) values reflect the spin-orbit splitting of the np shell of the Group VI atom. With the inclusion of \( \Omega = 1/2 \) interaction, the agreement with experimental for the GeSe\(^+\), GeTe\(^+\), and SnTe\(^+\) ions is significantly improved while for the others the interaction matrix elements, \( \xi \), are small and have little effect.

These results are very different from the findings of Berkowitz, et al., 22 for a similar \( 2\Pi_{1/2} - 2\Sigma_{1/2}^+ \) spin-orbit interaction in the ionic states of the cesium halides. For the CsX\(^+\) ions, the off-diagonal matrix elements were approximated as \( A/\sqrt{2} \) based on the assumption that the matrix elements \( \langle 2\Sigma|\xi(r)|2\Pi \rangle \) are well approximated by \( \langle 2\Pi|\xi(r)|2\Pi \rangle = Z/r^3 \). When applied to the GeX\(^+\) and SnS\(^+\) ions this approximation clearly results in off-diagonal energies which are overall much larger than those calculated by Eq. (4c). The relatively small
interaction matrix elements obtained by Eq. (4c) result primarily from the symmetry properties of the $1\pi$ and $3\sigma$ orbitals. The $1\pi$ and $3\sigma$ orbitals are composed of an antisymmetric (ungerade) combination of $p\sigma$ atomic orbitals and a symmetric (gerade) combination of $p\pi$ atomic orbitals, respectively. Hence, the matrix elements given by Eq. (4c) and expanded in an LCAO basis have large contributing terms of opposite sign. The resulting $\Omega = 1/2$ interaction energy therefore depends on the relative magnitudes of these terms which are ultimately determined by the detailed wavefunctions for the $3\sigma$ and $1\pi$ orbitals. This result is a simple consequence of the more general selection rule, that $g$ and $u$ symmetry states cannot be connected by the totally symmetric spin-orbit operator. As a result the heavy homonuclear V-V diatomics, such as $\text{Bi}_2^+$ do not exhibit a shift in the $2\Pi_{u,1/2}$ and $2\Pi_{u,3/2}$ spin-orbit splitting, because the $2\Sigma^+ - 2\Pi_{u,1/2}$ interaction is strictly forbidden.

Finally, we noted that in the case in which the $2\Pi_{1/2}$ and $2\Pi_{3/2}$ states were well separated, $\text{SnTe}^+$ (Fig. 4), the $2\Pi_{1/2}: 2\Pi_{3/2}$ intensity ratio was found to be greater than the statistical ratio of 1:1. This was also observed in the UPS spectrum of $\text{Bi}_2^+$, where the $2\Pi_{1/2} : 2\Pi_{3/2}$ intensity ratio was reported to be 1.5:1. Such a difference in cross section between the $\pi_{1/2}$ ($\omega = \lambda - 1/2$) and $\pi_{3/2}$ ($\omega = \lambda + 1/2$) components of the bound $\pi$ molecular orbital is analogous to that observed for the $j = \ell \pm 1/2$ spin-orbit components of relativistic atoms. In $\text{Hg}^+$, for instance, the $2D_{5/2} : 2D_{3/2}$ branching ratio varies between
2.5 and the statistical value of 1.5 for photon energies between 18 eV and 30 eV. Qualitatively, this behavior has been attributed to the differences between the \( j = l - 1/2 \) and \( j = l + 1/2 \) bound state radial wavefunctions (the \( j = l - 1/2 \) radial function lies closer to the nucleus than the \( j = l + 1/2 \) component) and the differences in the kinetic energies of the continuum electrons at a given photon energy. These considerations lead to the generalization that \( \sigma_{l+1/2}/\sigma_{l-1/2} \) branching ratio is greater than the statistical value if the partial cross sections are rising, while the ratio is less than statistical if the cross sections are falling. Extending these arguments to the IV-VI molecules in which \( \sigma_{\pi 3/2}/\sigma_{\pi 1/2} \) is less than unity, the partial cross sections of the \( \pi_{1/2} \) and \( \pi_{3/2} \) molecular orbitals are evidently decreasing at the He I photon energy (21.2 eV). Furthermore, the kinetic energies of the photoelectrons are much greater than the spin-orbit splitting of the \( 2\pi_{1/2} \) and \( 2\pi_{3/2} \) states at this photon energy. Hence, the cross section differences are primarily caused by the difference in the \( \pi_{1/2} \) and \( \pi_{3/2} \) bound state wavefunctions and not to relative kinetic energy effects. Additional studies at various photon energies particularly near the \( 2\Pi_{1/2, 3/2} \) thresholds would provide the necessary data to extend these qualitative theories for the heavy atoms to relativistic molecules.
ACKNOWLEDGMENT

This work was supported by the Division of Chemical Sciences, Office of Basic Energy Sciences, U. S. Department of Energy under contract No. W-7405-Eng-48.
Table I

THERMAL VIBRATIONAL DISTRIBUTIONS OF
THE GeX and SnX NEUTRAL GROUND STATES

<table>
<thead>
<tr>
<th>Molecule</th>
<th>$v''$ (cm$^{-1}$)$^a$</th>
<th>$T$ (°C)</th>
<th>Vibrational Population (% of $N_0$)</th>
</tr>
</thead>
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<tr>
<td></td>
<td></td>
<td></td>
<td>$N_1$</td>
</tr>
<tr>
<td>GeO</td>
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<td>19</td>
</tr>
<tr>
<td>GeS</td>
<td>575.8</td>
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</tr>
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<td>GeSe</td>
<td>406.8</td>
<td>405</td>
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<tr>
<td>GeTe</td>
<td>323.4</td>
<td>550</td>
<td>57</td>
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<tr>
<td>SnS</td>
<td>487.7</td>
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</tr>
<tr>
<td>SnSe</td>
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<td>590</td>
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</tr>
<tr>
<td>SnTe</td>
<td>259.5</td>
<td>650</td>
<td>67</td>
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$^a$) Reference 20.
Table 11. Experimental and theoretical I.P.'s for the GeX (X = Os,Se,Te) molecules.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Ionic State</th>
<th>Experimental I.P.'s (eV)(^a)</th>
<th>This Work(^b)</th>
<th>Wu + Fehlner(^c)</th>
<th>Theory (eV)(^d)</th>
</tr>
</thead>
<tbody>
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<td>GeX</td>
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<td>---</td>
<td>---</td>
<td>11.61</td>
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<td></td>
<td>(X^2\Pi_{1/2,3/2})</td>
<td>11.40(5)</td>
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<td>---</td>
<td>11.81</td>
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<td>(v' \sim 740(70) \text{ cm}^{-1})</td>
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<tr>
<td></td>
<td>(s. o. \sim 360(40) \text{ cm}^{-1})</td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>(\tilde{B}^2\Pi_{1/2})</td>
<td>15.16(2)</td>
<td>---</td>
<td>---</td>
<td>15.21</td>
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<td>(\tilde{C}^2\Pi_{1/2})</td>
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<td>30.97</td>
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<td>GeS</td>
<td>(X^2\Pi_{1/2,3/2})</td>
<td>10.36(5)</td>
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<td>10.17</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(s. o. \sim 590(100) \text{ cm}^{-1})</td>
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<td></td>
<td></td>
<td></td>
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<td>(\tilde{A}^2\Pi_{1/2})</td>
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<tr>
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<td>CI State</td>
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<td>(\tilde{C}^2\Pi_{1/2})</td>
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<td>22.22</td>
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<td>(X^2\Pi_{1/2})</td>
<td>9.96(5)</td>
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<tr>
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<td>(\tilde{C}^2\Pi_{1/2})</td>
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<td>(X^2\Pi_{1/2})</td>
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<td>9.55</td>
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<td>(\tilde{B}^2\Pi_{1/2})</td>
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<td>(\tilde{C}^2\Pi_{1/2})</td>
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<td>20.63</td>
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\(^a\)Vertical ionization potentials. Uncertainties are specified in parenthesis.

\(^b\)Ref. (6).

\(^c\)Empirical ionization potentials, empirically reduced by 0.85 to reflect final ionic state relaxation.
Table 111. Experimental and theoretical I.P.'s for the SnX (X = S, Se, Te) molecules.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Ionic State</th>
<th>This Work (eV)</th>
<th>Wu + Fehlner</th>
<th>Theory (eV)</th>
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<tbody>
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<td>SnS</td>
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<td>$A^2E_{1/2}$</td>
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<td>CI State</td>
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<td>CI State</td>
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<td>$C^2E_{1/2}$</td>
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<td>$C^2E_{1/2}$</td>
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<td>SnTe</td>
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<td>$A^2E_{1/2}$</td>
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<td>9.39</td>
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<td>$B^2E_{1/2}$ (?)</td>
<td>11.91(1)</td>
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<td>CI State</td>
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<td>$C^2E_{1/2}$</td>
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<td>18.89</td>
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*Vertical ionization potentials. Uncertainties are specified in parenthesis.
*Ref. (6).
*Koopmans theorem ionization potentials. Empirically reduced by 0.85 to reflect final ionic state relaxation.
Table IV,

Population Analysis of the Valence MO's

<table>
<thead>
<tr>
<th>Molecule</th>
<th>IV 1a</th>
<th>VI 1a</th>
<th>IV 2a</th>
<th>VI 2a</th>
<th>IV 3a</th>
<th>VI 3a</th>
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<td>GeO</td>
<td>0.1035</td>
<td>0.1070</td>
<td>0.7887</td>
<td>0.0009</td>
<td>0.0666</td>
<td>0.0006</td>
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<td>GeS</td>
<td>0.2058</td>
<td>0.0754</td>
<td>0.7911</td>
<td>0.0177</td>
<td>0.0600</td>
<td>0.0118</td>
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<td>GeSe</td>
<td>0.2648</td>
<td>0.1014</td>
<td>0.5875</td>
<td>0.0315</td>
<td>0.4583</td>
<td>0.0175</td>
</tr>
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<td>GeTe</td>
<td>0.5446</td>
<td>0.0915</td>
<td>0.4938</td>
<td>0.0702</td>
<td>0.4498</td>
<td>0.0430</td>
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<td>SnS</td>
<td>0.3307</td>
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<td>0.7765</td>
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<td>0.6487</td>
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<table>
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<th>IV 1a</th>
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<th>IV 2a</th>
<th>VI 2a</th>
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<td>0.6412</td>
<td>0.0234</td>
<td>0.0653</td>
<td>0.1855</td>
</tr>
<tr>
<td>CeTe</td>
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<td>6.1090</td>
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<td>0.0310</td>
<td>0.1260</td>
<td>0.1468</td>
</tr>
<tr>
<td>SnSe</td>
<td>3.8120</td>
<td>6.1830</td>
<td>0.5588</td>
<td>0.0150</td>
<td>0.0839</td>
<td>0.1504</td>
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<tr>
<td>SnTe</td>
<td>3.7980</td>
<td>6.2051</td>
<td>0.5472</td>
<td>0.0236</td>
<td>0.1153</td>
<td>0.1298</td>
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</tbody>
</table>
Table V
SUMMARY OF SPIN-ORBIT CALCULATIONS (meV)

<table>
<thead>
<tr>
<th>Molecule</th>
<th>$\zeta_{IV}^{a}$</th>
<th>$\zeta_{VI}^{b}$</th>
<th>A</th>
<th>E</th>
<th>$^2\Pi_{1/2}-^2\Pi_{3/2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>GeO</td>
<td>134</td>
<td>20</td>
<td>49</td>
<td>19</td>
<td>51</td>
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<tr>
<td>GeS</td>
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<td>54</td>
<td>72</td>
<td>5</td>
<td>71</td>
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<tr>
<td>GeSe</td>
<td>127</td>
<td>232</td>
<td>204</td>
<td>-60</td>
<td>161</td>
</tr>
<tr>
<td>GeTe</td>
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<td>521</td>
<td>423</td>
<td>-183</td>
<td>288</td>
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<tr>
<td>SnS</td>
<td>319</td>
<td>53</td>
<td>107</td>
<td>-44</td>
<td>98</td>
</tr>
<tr>
<td>SnSe</td>
<td>312</td>
<td>232</td>
<td>251</td>
<td>15</td>
<td>250</td>
</tr>
<tr>
<td>SnTe</td>
<td>312</td>
<td>521</td>
<td>475</td>
<td>135</td>
<td>390</td>
</tr>
</tbody>
</table>

a) For the Group IV atoms, $\zeta_{IV,p}^{a}$ and $\zeta_{IV,p}^{+}$ obtained from Landé Interval rule for the lowest multiplets of the ns$^2$ and ns$^2$np configurations, respectively.

b) The oxygen and sulfur atomic s.o. parameters taken from reference (25). For Se and Te the intermediate coupling values for $\zeta_{VI,p}$ were used. See S.-T. Lee, S. Suzer, and D. A. Shirley, Chem. Phys. Lett. 41, 25 (1976).

c) Values in parenthesis are tentative due to the severe overlapping of the $^2\Pi_{1/2}$ and $^2\Pi_{3/2}$ ionization bands.
REFERENCES


   (b) We obtained the GeS, GeSe, SnS, and SnSe samples from Research Organic/Inorganic Chemical Corp., Sun Valley, CA 91352; GeO and SnS₂ from Atomergic Chemetals Corp., Plainview, NY 11803; SnTe from Alfa Products, Beverly, MA 01923; and GeTe from ICN Pharmaceuticals, Inc., Plainview, NY 11803.


FIGURE CAPTIONS

Figure 1. The He I photoelectron spectra of GeO$^+$ and GeSe$^+$. The bars above the $B^2\Sigma_1^+$ ionization band indicate the position of the vibrational levels.

Figure 2. The He I photoelectron spectra of GeSe$^+$ and GeTe$^+$. The bars above the $B^2\Sigma_1^+$ ionization band indicate the position of the vibrational levels.

Figure 3. Higher resolution spectra of GeO$^+$ and GeS$^+$ showing the $2\Sigma^+(3\sigma)^{-1}$ and $2\Pi(1\pi)^{-1}$ ionization bands on expanded energy scales. The bars indicate the approximate positions of the vibrational levels of the $2\Pi(1\pi)^{-1}$ ionic state.

Figure 4. The He I photoelectron spectrum of SnS$^+$. The position of the $B^2\Sigma_1^+$ state in SnTe$^+$ is uncertain and is shown in parentheses.
Fig. 1
Fig. 2
Fig. 3 XBL 789-10910
Fig. 4

CI STATES

SnS

A^2 \Sigma^+_\frac{1}{2}

B^2 \Sigma^+_\frac{1}{2}

\times 2 \Pi_{\frac{3}{2}, \frac{3}{2}}

\times 5

Counts (arbitrary units)

Binding energy (eV)
Sn Se$^+$

Sn Te$^+$

Counts (arbitrary units)

Binding energy (eV)

Fig. 5
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