HIGH-TEMPERATURE PHOTOELECTRON SPECTROSCOPY: A STUDY OF ATOMIC AND MOLECULAR ANTIMONY

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The gas-phase vacuum ultraviolet photoelectron spectra of Sb₄, Sb₂ and Sb have been recorded; the Sb₂ and Sb being produced by superheating a flowing Sb₄ beam. The molecular spectra are interpreted using Hartree-Fock-Slater calculations whereas the spectrum of atomic antimony is compared with that recorded previously for atomic arsenic and bismuth. In the Sb₂⁺ (X $^{2}\Pi_{u}$) state, the spin-orbit splitting is measured as 0.34 ± 0.04 eV. The measured first-band onset of Sb₂ of 8.36 ± 0.10 eV is used to derive the dissociation energy, D_{0}^{0} , in Sb₂⁺ (X $^{2}\Pi_{u,3/2}$) as 3.37 ± 0.14 eV.

1. Introduction

High-temperature gas-phase photoelectron spectroscopy (PES) has proved, in recent years, to be an extremely valuable technique for investigating the electronic structure of atoms and molecules which have negligible vapour pressure at room temperature [1-3]. For example, of the homonuclear molecules formed from the group V elements, N_2 is the only molecule whose photoelectron spectrum can be recorded at room temperature. The photoelectron spectra of P_2 [4], P_4 [5,6], As_2 , As_4 [7,8] and Bi_2 [9] have all been recorded by heating the corresponding solid elements. Of the group V atoms phosphorus, arsenic and bismuth have been generated for PES investigation by high-temperature methods whereas nitrogen atoms have been more conveniently prepared in the gas phase by microwave discharge of molecular nitrogen diluted with an inert gas [10]. In the case of antimony, however, only the photoelectron spectrum of Sb_4 has been recorded previously [11].

In this present work, the photoelectron spectra of Sb_2 and Sb are presented for the first time and an improved spectrum of Sb_4 has been obtained, allowing comparison to be made with the corresponding spectra of the other group V atoms and homonuclear molecules. Although the valence ionization energies of atomic antimony are well established from optical spectroscopy [12,13], only the first ionization energy of Sb₂ has been measured previously. However, the values quoted in the literature differ considerably. 9.3 ± 0.2 eV was obtained from extrapolation of Rydberg series measurements [14] whereas 8.4 ± 0.3 eV [15] and 8.64 ± 0.06 eV [16] were derived from electron impact mass spectrometric experiments.

2. Experimental

The photoelectron spectrum of Sb₄ was recorded by evaporating antimony powder from a carbon furnace heated to temperatures in the range 970-1070 K. This is consistent with existing vapour pressure data as the main vapour species in equilibrium with solid antimony is known to be Sb₄ at temperatures between 500 and 1400 K [17]. Vapour-phase mixtures of Sb and Sb₂ were obtained by passing Sb₄ through a heated graphite cylinder placed between the antimony supply and the photon beam. The Sb: Sb₂ ratio in the ionization region of the spectrometer could be increased by increasing the length of this graphite superheater or by increasing the temperature difference between the furnace and superheater. Temperature readings taken with an optical pyrometer and a chromel-alumel thermocouple showed that the

0301-0104/86/\$03.50 © Elsevier Science Publishers B.V. (North-Holland Physics Publishing Division) temperature of the graphite superheater was typically ≈ 600 K higher than the furnace temperature when spectra attributable to Sb₂ and Sb were obtained. Directly heated copper antimonide (Cu₃Sb) samples also gave spectra assignable to Sb₂/Sb mixtures but these were in general weaker than the spectra obtained from solid antimony. As a result, all the spectra reported in this work were obtained from solid antimony samples.

The photoelectron spectrometer and radiofrequency induction heating method used have been described previously [1,18]. Spectral calibration was achieved using the HeI (21.22 eV) photoelectron spectra of methyl iodide and argon, and the NeI (16.85 eV) photoelectron spectrum of methyl iodide.

3. Computational details

As in our recent work on As_2 and As_4 [8], Hartree-Fock-Slater calculations [19,20] have been performed on Sb₂ and Sb₄ in order to interpret their experimental photoelectron spectra. In these calculations, the outermost 5s and 5p antimony orbitals were treated as valence orbitals and double-zeta valence basis sets were used with the atomic cores kept frozen. Vertical ionization energies were estimated by Slater's transition state method [21] which takes account of relaxation effects on ionization to a large extent. Relativistic effects were included by a perturbational approach [22], which has been successfully applied previously in the interpretation of the photoelectron spectra of a number of molecules containing heavy atoms [23,24].

For the Sb₂ calculations, the ground-state equilibrium bond length of 2.48 Å, as determined by a vapour-phase laser-induced fluorescence study [25], was used whereas for Sb₄ a tetrahedral ground-state geometry was assumed [26] with an Sb–Sb internuclear distance of 2.88 Å, as estimated from the known ground-state equilibrium bond lengths in As₂, Sb₂ and As₄ [25,27].

4. Results and discussion

At the outset of this work the aim was to record the photoelectron spectrum of Sb_4 and compare it with that recorded earlier [11]. The Sb₄ beam could then be superheated to decompose the tetrameric antimony molecules into smaller units. However, on taking a sample of antimony powder in a carbon furnace and gradually increasing the temperature to 570 ± 50 K, the HeI photoelectron spectrum of Sb₄O₆ was recorded. This spectrum was in good agreement with the known HeI photoelectron spectrum of Sb_4O_6 [28]. Furthermore this result was independently confirmed by heating Sb_2O_3 (s) under identical conditions to that used for solid antimony and an identical spectrum to that seen from solid antimony was observed. Hence, although all samples of solid antimony that were used were of purity 99% or better, as stated by the manufacturer's specifications, presumably some surface oxide was present in all samples and this was observed to vaporize at fairly low temperatures.

On further heating of solid antimony samples to 1020 ± 50 K, the spectrum shown in fig. 1 is obtained. This could be immediately identified as Sb₄ by comparison with the previous work of Elbel et al. [11]. As shown in table 1, the band maxima measured in this work compare favourably with those quoted by Elbel et al. [11]. However, the



Fig. 1. The HeI photoelectron spectrum of Sb₄ obtained from solid antimony heated to 1020 ± 50 K. Ordinate: counts s⁻¹. Abscissa: ionization energy (eV).

Orbital ionized	Experimental VIP this work	Experimental VIP ref. [11]	Non-relativistic HFS VIP	Relativistic HFS VIP	Relativistic state
1e	7.81 ± 0.02	7.84	6.78	6.43	u _{3/2}
	8.22 ± 0.02	8.20			-, -
2t ,	8.70 ± 0.01	8.69	7.43	7.18	e _{5/2}
-	9.06 ± 0.01	9.06		7.36	u _{3/2}
2a ₁	9.74 ± 0.02	9.82	8.24	8.13	e _{1/2}
1t ₂	-	-	12.82	13.44	e _{5/2}
	-	-		13.45	u _{3/2}
1a ₁	-	-	17.84	17.93	e _{1/2}

 Table 1

 Comparison of the calculated and observed vertical ionization energies (eV) of Sb₄

additional structure seen by these workers between 10.5 and 16.0 eV ionization energy, which was tentatively assigned to shake-up bands and bands attributable to the Sb₄ $(1t_2)^{-1}$ ionization, was not seen in this work. The assignment of the Sb₄ spectrum presented in ref. [11] was based on the known assignment of the P₄ photoelectron spectrum [5,6] as well as molecular orbital energies and molecular wavefunctions computed for the neutral molecules N₄, P₄, Sb₄ and As₄ using the semi-empirical SCC X α method. However, ionization energies were not calculated directly and the effects of relativity were not included in these calculations. Consequently a full analysis of the experimental spectrum in terms of the ionic states obtained from Sb₄ in the molecular double group was not possible. This can be readily achieved using the relativistic HFS calculations performed in this present work.

If the valence orbitals of Sb_4 are considered as linear combinations of antimony 5s and 5p atomic orbitals which reflect the tetrahedral symmetry of the molecule, then the electronic ground-state configuration of Sb_4 can be written, using a valence orbital numbering system, as

 $(1a_1)^2(1t_2)^6(2a_1)^2(2t_2)^6(1e)^4.$

Consideration of the orbital energies computed by Elbel et al. [11] for the group V tetrahedral molecules shows that HeI (21.22 eV) radiation should be energetic enough to ionize from the 1e, $2t_2$, $2a_1$ and $1t_2$ molecular orbitals. Also, on the basis of the HFS calculations performed for Sb₄ in this work (table 2), it is expected that the $2t_2$ and

 $2a_1$ molecular orbitals are largely Sb(5p) in character with small contributions from Sb(5s) orbitals whereas the 1t₂ and 1a₁ molecular orbitals are expected to be mainly Sb(5s) in character with small admixtures of Sb(5p) atomic orbitals. The 1e molecular orbital is entirely Sb(5p) in character. Of the monopositive ionic states obtained by oneelectron ionization from the valence molecular orbitals, only the states obtained from the $(2t_2)^{-1}$ and $(1t_2)^{-1}$ ionizations will show spin-orbit splittings (see table 1). As the $2t_2$ level is mainly Sb(5p) in character the maximum value of this splitting for the $(2t_2)^{-1}$ ionization is expected to be, approximately $\frac{3}{2} \zeta_{Sb(5p)}$ [29]. Taking $\zeta_{Sb(5p)}$ as 0.41 eV [12,13], $\frac{3}{2} \zeta_{Sb(5p)}$ is calculated as 0.61 eV. In contrast, the splitting of the states derived from the $(1t_2)^{-1}$ ionization is expected to be a lot smaller as the 1t₂ neutral molecular orbital is mainly Sb(5s) in character with only a small Sb(5p) contribution. With this information and using the results of the HFS calculations listed in table 1, the photoelectron spectrum shown in fig. 1 can be assigned. The fifth band in fig. 1 centred at 9.74 eV ionization energy is attributed to the $e_{1/2}$ state

Table	= 2							
HFS	Mulliken	population	analysis	for	the	valence	orbitals	of
Sb.								

Orbital	% Sb(5s) character	% Sb(5p) character
1e	_	100
$2t_2$	7	93
2a1	22	78
1t ₂	93	7
1a ₁	80	19

arising from the $(2a_1)^{-1}$ ionization. The bands at 8.70 and 9.06 eV are assigned to spin-orbit components, $e_{5/2}$ and $u_{3/2}$, obtained from the $(2t_2)^{-1}$ ionization. As anticipated, the experimental separation of these bands, 0.36 ± 0.02 eV, is lower than the maximum value of 0.61 eV. Also the band at 9.06 eV ionization energy is approximately twice the intensity of the band at 8.70 eV, as expected on the basis of the number of components of the $e_{5/2}$ and $u_{3/2}$ states. The remaining two bands in the spectrum at 7.81 and 8.22 eV are approximately equally intense (fig. 1) and must arise from a Jahn-Teller splitting of the $u_{3/2}$ state obtained from the $(1e)^{-1}$ ionization. This assignment is consistent with previous assignments of the P_4 and As₄ spectra [5-8] and the observed separation of the peak maxima, 0.41 ± 0.04 eV, compares favourably with the corresponding separations of 0.36 eV [5,6] and 0.34 ± 0.02 eV [7,8] measured for the P_4 and As_4 cases respectively. Although bands associated with the $(1t_2)^{-1}$ and $(1a_1)^{-1}$ ionizations are expected above 11.0 eV, a careful search of the 11.0-20.0 eV ionization energy region revealed no features that could be associated with Sb_4 . This is probably due to the fact that the $1t_2$ and 1a, molecular orbitals are mainly Sb(5s) in character and the Sb(5s) photoionization cross section has been calculated to be approximately an order of magnitude lower than the Sb(5p) cross section at the HeI photon energy [30].

When Sb₄ vapour was passed through a graphite superheater decomposition of Sb₄ into Sb₂ and Sb occurred. Photoionization of the pyrolysis products with HeI radiation yielded spectra of the type shown in fig. 2, which was recorded with a furnace temperature of 1100 \pm 50K and a superheater temperature of 1700 ± 50 K. Initially this spectrum was thought to be due to ionization of atomic antimony (X ${}^{4}S_{3/2}$) to the ${}^{3}P_{0}$, ${}^{3}P_{1}$ and ${}^{3}P_{2}$ ionic states arising from removal of one of the 5p electrons in atomic antimony. However, the asymmetry of the bands showed that there were other contributions present other than those of atomic antimony. As a result, the photoelectron spectrum of this ionization energy region was recorded using NeI radiation (16.85 eV) in order to obtain improved experimental resolution. Two limiting types of NeI spectra were recorded. The first, shown in



Fig. 2. The HeI photoelectron spectrum obtained from a superheated Sb₄ beam. A furnace temperature of 1100 ± 50 K was used with a superheater temperature of 1700 ± 50 K. Ordinate: counts s⁻¹. Abscissa: ionization energy (eV).

fig. 3 and obtained under conditions very similar to those used to obtain fig. 2, was recorded at a furnace temperature of 1000 ± 50 K and a superheater temperature of 1550 ± 50 K. The second type, shown in fig. 4, was recorded at a furnace temperature of 1250 ± 50 K and a superheater temperature of 1850 ± 50 K. Initially, fig. 4 was the simplest spectrum to analyze as the peak maxima of the sharp bands seen in this spectrum were in good agreement with the expected band positions for the Sb⁺(5s²5p², ${}^{3}P_{0,1,2}) \leftarrow$ Sb(5s²5p³, ${}^{4}S_{3/2}$ ionizations from optical spectroscopy [12,13] (see table 5 below). The relative atomic band intensities obtained from fig. 4, when corrected for analyser transmission, were also in reasonably good agreement with the 1:3:5 ratio expected on the basis of the degeneracy of the ionic state. Hence, although fig. 4 contains some residual Sb₂ contributions, it allows the band positions and intensities of atomic antimony in the 8.0-10.0 eV ioniza-



Fig. 3. The NeI (16.85 eV) photoelectron spectrum obtained from a superheated Sb₄ beam. A furnace temperature of 1000 \pm 50 K was used with a superheater temperature of 1550 \pm 50 K. Contributions from the weaker NeI (16.67 eV) line are represented with a broken horizontal line (----). Ordinate: counts s⁻¹. Abscissa: ionization energy (eV).



Fig. 4. The NeI (16.85 eV) photoelectron spectrum obtained from a superheated Sb₄ beam. A furnace temperature of 1250 \pm 50 K was used with a superheater temperature of 1850 \pm 50 K. Contributions form the weaker NeI (16.67 eV) line are represented with a broken horizontal line (----). Ordinate: counts s⁻¹. Abscissa: ionization energy (eV).

tion energy region to be determined. In comparison, figs. 2 and 3 whilst clearly showing these atomic components, also contain a much larger molecular contribution. Notably, a resolved sharp feature was observed in fig. 3 at 9.26 ± 0.01 eV which was assigned on the basis of the calculations shown in table 3 and the known photoelectron spectrum of Bi₂ [9] to the Sb₂⁺($^{2}\Sigma_{g}^{+}$) \leftarrow Sb₂(X¹ Σ_{g}) process associated with the $(2\sigma_{g})^{-1}$ ionization of diatomic antimony. Fig.2 also shows evidence of a broad maximum on the high ionization energy side of the Sb⁺(³P₀) \leftarrow Sb(⁴S_{3/2})component. When the known photoelectron spectrum of atomic antimony, suitably adjusted for a small change in experimental resolution between the NeI and HeI photon sources, is subtracted from fig. 2, three bands remain at 8.72 ± 0.02 eV, 9.06 ± 0.02 eV and 9.26 ± 0.01 eV. As shown in table 3, the first two band maxima are assigned to spin-orbit components arising from the $(1\pi_u)^{-1}$ ionization of Sb₂ and the third band arises from the $(2\sigma_{a})^{-1}$ Sb₂ process. Fig. 2 resembles qualitatively that recorded for bismuth vapour [9] in that both spectra exhibit the same atomic and molecular contributions overlapped in a very similar way. No further bands were observed associated with diatomic antimony in the 10.0-20.0 eV ionization energy range despite the fact that contributions from the $(1\sigma_{\mu})^{-1}$ and $(1\sigma_{o})^{-1}$ processes were expected in this region. This probably arose, as with the $(1t_2)^{-1}$ ionization in Sb₄, because these ionizations are essentially Sb(5s) in character (see table 4) and hence are expected to be of low intensity relative to the bands in the 8.0-10.0 eV region because of the low 5s: 5p photoionization cross-section ratio in atomic antimony at the HeI wavelength [30].

The onset of the first band of Sb_2 has been measured in this work as 8.36 ± 0.10 eV. This compares with previous determinations of the first adiabatic ionization energy of Sb_2 of 8.4 ± 0.3 eV [15] and 8.64 ± 0.06 eV [16] by electron impact mass spectrometry as well as 9.3 ± 0.2 eV [14] derived from Rydberg series measurements. Normally for a small diatomic molecule the study of Rydberg series in the vacuum ultraviolet absorption spectrum would be expected to yield a more accurate value for the first ionization energy than either an electron impact mass spectrometric study

Orbital ionized ^{a)}	Ionic state	Experimental VIP this work	Non-relativistic HFS VIP	Relativistic HFS VIP	
1π _u	² Π _{µ,3/2}	8.72±0.02	8.47	8.07	
	${}^{2}\Pi_{\mu,1/2}$	9.06 ± 0.02		8.53	
$2\sigma_{e}$	${}^{2}\Sigma_{R,1/2}$	9.26 ± 0.01	8.73	8.76	
1σ _u	${}^{2}\Sigma_{u,1/2}$		12.97	13.96	
1 og	${}^{2}\Sigma_{g,1/2}$		18.00	18.57	

Table 3 Comparison of the calculated and observed vertical ionization potentials (eV) of Sb₂

^{a)} Orbital numbering refers to valence molecular orbitals only.

or a PES investigation. However, in the case of Sb₂ only four Rydberg states were identified [14] and they were thought to be components of three separate series. Hence the ionization energy derived from the vacuum UV absorption spectrum [14] must be viewed with caution. Nevertheless, the value obtained in ref. [14], 9.3 ± 0.2 eV, is closer to the PES adiabatic ionization energy for the Sb₂ $(2\sigma_{a})^{-1}$ ionization, 9.26 ± 0.01 eV, than the band onset of the first Sb, band. As a result, it is possible that the Rydberg states seen in ref. [14] are all members of series which converge to the $A^2 \Sigma_{\alpha 1/2}$ state of Sb_2^+ obtained via the $(2\sigma_{\alpha})^{-1}$ ionization of the neutral molecule. Measurement of the onset in the first band of Sb₂ also allows an estimate to be made of the dissociation energy, D_0^0 , in the ground state of the ion, $Sb_2^+(X^2\Pi_{u,3/2})$. Assuming $Sb_2(X^1\Sigma_g^+)$ dissociates to $Sb({}^4S_{3/2})$ and $Sb({}^{4}S_{3/2})$ and $Sb_{2}^{+}(X {}^{2}\Pi_{u,3/2})$ dissociates to $Sb^{+}({}^{3}P_{0})$ and $Sb({}^{4}S_{3/2})$, then the band onset measured in this work, 8.36 ± 0.10 eV, can be combined with the first ionization energy of atomic antimony, 8.64 eV [12,13], and the known dissociation energy, D_0^0 , in Sb₂(X¹ Σ_g^+), 3.09 ± 0.04 eV [15,32], to yield D_0^0 , in the ground state of the ion as 3.37 + 0.14 eV.

Table 4 HFS Mulliken population analysis for the valence orbitals of Sb₂

Orbital	% Sb(5s) character	% Sb(5p) character
1π,		100
2 σ,	15	85
1σ.	96	4
1σ,	86	14

As stated earlier, the peak maxima measured for the three sharp bands in fig. 4 show good agreement with the ionization energies of atomic antimony $(5s^25p^3, {}^4S_{3/2})$ to the ionic states $(5s^25p^2, {}^{3}P_{0.1,2})$ as derived from optical spectroscopy [12,13]. The experimental relative intensities of these peaks, corrected for analyser transmission, are in reasonably good agreement with the intensity ratios of 1:3:5 expected on the basis of ionic state degeneracy (table 5). Two other bands associated with antimony $(5p)^{-1}$ ionizations corresponding to the transitions $Sb^{+}(^{1}D_{2}) \leftarrow Sb(^{4}S_{3/2})$ and $Sb^+({}^1S_0) \leftarrow Sb({}^4S_{3/2})$ are expected at 10.22 and 11.60 eV respectively [12,13]. However, despite a careful search no evidence for these bands was found. A similar result has been obtained in photoelectron investigations of the lighter group V atoms. However, for atomic bismuth a weak feature associated with the ${}^{1}D_{2} \leftarrow {}^{4}S_{3/2}$ ionization has been observed [9]. In the limit of L-S coupling the spin selection rule $\Delta S = 1/2$, for the change in spin between the atom and the ion, is expected to hold and hence only triplet and quintet ionic states are accessible from an initial quartet state. Equally in the limit of j-j coupling, the lowest J = 3/2state of the group V atom arising from the initial ns^2np^3 configuration correlates with the configuration (3/2, 1/2, 1/2) whereas for the p² ionic configuration the J = 0 and J = 2 states, that convert to the ${}^{1}S_{0}$ and ${}^{1}D_{2}$ states in the L-S limit, both correlate with the (3/2, 3/2) configuration [33]. Hence as the (3/2, 3/2) configuration cannot be obtained from (3/2, 1/2, 1/2) the intensity of photoelectron bands to these J = 0 and J = 2 ionic states will also be zero in the j-j limit. However, as pointed out previously [9], the situation may be

Table 5 Experimental ionization energies and relative photoelectron band intensities of atomic antimony $(X {}^{4}S_{3/2})$

Ionic state	Observed IP (band maximum; this work) (eV)	Expected IP from optical data [12,13] (eV)	Experimental relative intensity ^{a)}
$^{3}P_{0}$	8.62±0.01	8.64	1.6±0.3
³ P ₁	9.00 ± 0.01	9.02	3.0 ± 0.3
³ P,	9.32 ± 0.01	9.34	5.0
$^{1}D_{2}$	-	10.22	-
${}^{1}S_{0}$	-	11.60	-

^{a)} Corrected for analyser transmission function.

further complicated in the heavier atoms and ions by configurations containing contributions from low-lying, formally unoccupied d levels. Nevertheless the appearance of the ${}^{1}D_{2}$ state of Bi⁺ in the photoelectron spectrum of atomic bismuth indicates that a coupling scheme intermediate between the L-S and j-j limits in both the atom and ion is appropriate for this element. As part of this present investigation, we have reproduced the HeI photoelectron spectra quoted in ref. [9] for vapour-phase mixtures of Bi and Bi₂. Superheating a Bi/Bi, effusive beam gave a clean spectrum of bismuth atoms and the relative intensities of the atomic peaks obtained from the HeI spectrum were in good agreement with those quoted in ref. [9]. It is interesting that the intensity ratio of the ${}^{3}P_{0}$, ${}^{3}P_{1}$ and ${}^{3}P_{2}$ peaks remains, within experimental error, virtually constant at 1:3:5 for the group V elements arsenic, antimony and bismuth [8,9] whereas the $^{1}D_{2}$ peak is only seen for bismuth. Clearly, accurate calculations of photoelectron band intensities would be extremely useful to help explain the origin of these intensity changes and it is hoped that this work will help to initiate theoretical studies in this area. A study of the photoelectron band intensities of the group V elements as a function of photon energy would also be extremely valuable.

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