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High-temperature Photoelectron Spectroscopy

A Study of Atomic and Molecular Arsenic

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The He(I) photoelectron spectra of As_4 and As_2 have been recorded from heated solid arsenic and copper arsenide. The spectra were interpreted with the aid of Hartree-Fock-Slater calculations. Pyrolysis of As_2 vapour has enabled the photoelectron spectrum of atomic arsenic to be recorded. The spectra obtained demonstrate the ability of photoelectron spectroscopy to monitor the vapour-phase composition above solid arsenic or a metal arsenide as a function of temperature.

Currently much molecular-beam epitaxy research is centred on the preparation of the III-V semiconductors such as gallium arsenide because of their desirable electrical and optical properties.[1,2] One method of preparation of such semiconductors involves the co-deposition of the constituents from the vapour phase onto a solid substrate. In the preparation of gallium arsenide crystals by vapour deposition a convenient arsenic source is tetrameric arsenic, As_4, which is readily obtainable from the evaporation of polycrystalline arsenic at relatively low temperatures. In contrast, As_2 is only obtained in the vapour phase at higher temperatures. Recently, however, it has been demonstrated that As_2 has a higher sticking coefficient than As_4 on solid substrates, and use of As_2 as the arsenic source results in higher quality GaAs crystals than those prepared *via* As_4. Clearly, therefore, control of the vapour-phase composition above solid arsenic is a desirable feature of gallium arsenide crystal-growth experiments. Possible ways of monitoring the vapour above solid arsenic as a function of temperature include mass spectrometry and photoelectron spectroscopy (p.e.s.).

In this paper, although the u.v.-photoelectron spectra of As_2 and As_4 have been recorded previously,[3] improved spectra of these molecules are presented. Also, the photoelectron spectrum of atomic arsenic is presented for the first time. On the basis of these spectra, the ability of p.e.s. to monitor the vapour-phase composition above solid arsenic as a function of temperature is demonstrated.

Experimental

The major vapour species in equilibrium with solid arsenic in the temperature range 400-850 K is known to be As_4.[4] As a result, the photoelectron spectrum of As_4 could be recorded fairly easily by evaporating solid arsenic in the temperature range 450-550 K from an inductively heated graphite furnace.

To obtain As_2 as the major vapour-phase species two methods were used: (a) an effusive beam of As_4 was superheated in a graphite pyrolyser to 1100-1300 K. This produced a high vapour phase As_2:As_4 ratio. (b) Copper arsenide (Cu_3As, 99% Cerac Inc.) heated to 1200-1400 K in a carbon furnace was found to be a clean source of As_2. The As_2 spectra obtained from both routes were in good agreement although the superheated As_4 spectra always contained residual contributions from As_4. Atomic

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arsenic was produced by further superheating arsenic vapour to temperatures in the region 1650–1850 K.

The photoelectron spectrometer and inductive heating method used in this study have both been described previously.[5,6] Spectral calibration was achieved using the He(Iα) (21.22 eV) photoelectron spectra of methyl iodide, ethyl iodide, argon and water and the He(Iβ) (23.09 eV) photoelectron spectrum of water. Calibrant gases were added to the vapours under investigation before spectra were recorded.

Computational Details

In order to interpret the photoelectron spectra of As_2 and As_4, vertical ionization energies have been calculated using the Hartree–Fock–Slater (HFS) method of Baerends *et al.*[7] The details of the method have been outlined elsewhere,[8,9] but the main feature of the HFS procedure involves using Slater's local-exchange approximation[10] to simplify the exchange terms that appear in the Hartree–Fock method. The exchange scaling factor, α, is held constant in this work at 0.7. An LCAO expansion is used, while matrix elements are calculated by an efficient numerical integration scheme. The STO basis set used was of double-zeta quality and only the 4*s* and 4*p* orbitals were treated as valence orbitals. Inner orbitals were treated as part of the frozen core. Vertical ionization energies were estimated using an extension of Slater's transition-state method,[11] which allows for relaxation effects on ionization. Relativistic effects were allowed for by a perturbational method developed by Snijders *et al.*[12,13] which has been successfully applied previously in the interpretation of the photoelectron spectra of a number of molecules containing heavy atoms.[14–16]

For As_2 and As_4 all calculations were performed at the ground-state equilibrium geometry of the neutral molecule. For As_2, the equilibrium bond-length used was 2.10 Å, obtained from rotational analysis of an electronic-emission spectrum of As_2,[17] and for As_4 the As—As equilibrium distance in a tetrahedral geometry was taken as 2.44 Å, as determined from vapour-phase electron-diffraction studies.[18]

Results and Discussion

The He(I) photoelectron spectrum of As_4 obtained on heating solid arsenic to temperatures in the range 450–500 K is shown in fig. 1. The spectrum shows five band maxima and is very similar to that obtained previously for As_4 by Elbel *et al.*[3] Apart from the five bands shown in fig. 1, no other bands were seen in the As_4 spectrum in this work.

By analogy with N_4 and P_4,[19–21] the valence electronic configuration of As_4 can be written as $(1a_1)^2(1t_2)^6(2a_1)^2(2t_2)^6(1e)^4$.

The valence-orbital energies of the neutral group V tetrahedral molecules, N_4, P_4, As_4 and Sb_4, have previously been computed by Elbel *et al.*[21] using the semi-empirical SCC-Xα method and consideration of these energies shows that the $1e$, $2t_2$, $2a_1$ and $1t_2$ orbitals of As_4 should be accessible with He(I) radiation. In tetrahedral symmetry the arsenic 4*p* orbitals transform as $e+a_1+t_1+2t_2$, whereas the 4*s* orbitals transform as a_1+t_2. Thus, of the occupied orbitals in neutral As_4, the $1a_1$ and $1t_2$ levels are expected to be mainly As(4*s*) in character, whereas the $2a_1$ and $2t_2$ levels are expected to be composed mainly of As(4*p*) orbitals. The $1e$ molecular orbital is solely comprised of As(4*p*) contributions. This is borne out by our HFS calculations on neutral As_4 (see table 1). Of the states obtained by one-electron ionization from the As_4 valence orbitals, only the ionic states obtained from the $(2t_2)^{-1}$ and $(1t_2)^{-1}$ ionizations will exhibit spin-orbit splitting. As the $2t_2$ level is mainly As(4*p*) in character the maximum value of this splitting for the $(2t_2)^{-1}$ ionization is expected to be $3/2\ \mathscr{G}_{As(4p)}$.[22] Taking $\mathscr{G}_{As(4p)}$ from known term values in atomic arsenic,[23,24] $3/2\ \mathscr{G}_{As(4p)}$ is calculated as 0.27 eV.

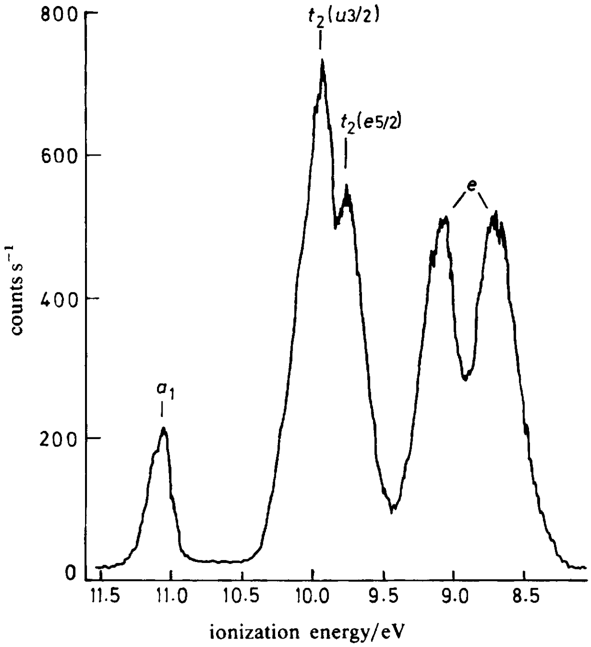

Fig. 1. The He(I) photoelectron spectrum of As_4, obtained by heating solid arsenic in the temperature range 450–550 K.

Table 1. HFS Mulliken population analysis for the valence orbitals of As_4

orbital	As(4*s*) character (%)	As(4*p*) character (%)
$1e$	—	100
$2t_2$	8	92
$2a_1$	25	75
$1t_2$	92	8
$1a_1$	78	22

In contrast, the splitting of the states derived from the $(1t_2)^{-1}$ ionization is expected to be much smaller because the As(4*p*) contribution to this orbital is much lower.

The previous assignment[3] of the He(I) photoelectron spectrum of As_4 was achieved by comparison with the known experimental assignment of P_4.[19,20] In fig. 1 the first two bands, centred at 8.76 and 9.10 eV, respectively, were assigned to components of a $(1e)^{-1}$ ionization and the two bands at 9.78 and 9.96 eV were assigned to components of a $(2t_2)^{-1}$ ionization. The band centred at 11.09 eV was assigned to the $(2a_1)^{-1}$ ionization. This assignment is consistent with the relativistic HFS transition-state calculations performed in this work (see table 2). As expected, the observed splitting of the $(2t_2)^{-1}$ band into $e_{5/2}$ and $u_{3/2}$ components of 0.18 ± 0.03 eV is lower than the limiting value of 0.27 eV and the $u_{3/2}$ component, at 9.96 eV, is more intense than the $e_{5/2}$ component, at 9.78 eV, as anticipated from statistical weight considerations. The splitting of the first two bands, associated with the $(1e)^{-1}$ ionization, must arise from a Jahn–Teller effect. The observed splitting, 0.34 ± 0.02 eV, is similar in magnitude to that found in the spectrum of P_4(0.36 eV)[19,20] and Sb_4 (0.41 eV).[21,25] As mentioned previously, no further bands of As_4 were observed, despite the fact that bands associated with the $(1t_2)^{-1}$

Table 2. Comparison of the calculated and observed vertical ionization potentials (eV) of As_4

orbital ionized	experimental v.i.p. this work	experimental v.i.p.[a] ref. (3)	non-relativistic HFS v.i.p.	relativistic HFS v.i.p.	relativistic state
$1e$	8.76±0.01 9.10±0.01	8.92 9.28	7.91	7.73	$u_{3/2}$
$2t_2$	9.78±0.02 9.96±0.01	9.86 10.06	8.71	8.57 8.66	$e_{5/2}$ $u_{3/2}$
$2a_1$	11.09±0.01	11.16	9.72	9.67	$e_{1/2}$
$1t_2$	— —	— —	15.53	15.78 15.78	$e_{5/2}$ $u_{3/2}$
$1a_1$	—	—	22.29	22.28	$e_{1/2}$

[a] The values quoted in ref. (3) differ from those obtained in this work because of the approximate calibration method used in the earlier work.

ionization were expected in the 15.5–17.0 eV region. However, at the He(I) photon energy the As(4*s*) photoionization cross-section is expected to be at least two orders of magnitude lower than the As(4*p*) cross-section[26] and, as the $1t_2$ molecular orbital is largely As(4*s*) in character (table 1), it is therefore not surprising that contributions from the $(1t_2)^{-1}$ ionization are not observed experimentally.

As mentioned previously, pyrolysis of As_4 vapour gave rise to As_2 spectra that still contained residual amounts of As_4. However, heating copper arsenide proved to be a much cleaner source of As_2 and the As_2 spectrum obtained under these conditions is shown in fig. 2. This shows three band maxima at 9.82±0.01, 9.96±0.01 and 10.22±0.01 eV. The valence electronic configuration of As_2 can be written as $(1\sigma_g)^2$ $(1\sigma_u)^2$ $(2\sigma_g)^2$ $(1\pi_u)^4$ and, on the basis of the HFS transition-state calculations performed in this work (tables 3 and 4), the observed bands can be attributed to ionization of $As_2(X\,^1\Sigma_g^+)$ to the As_2^+ states $^2\Pi_{u,3/2}$, $^2\Pi_{u,1/2}$ and $^2\Sigma^+_{g,1/2}$ derived by one-electron ionization from the $1\pi_u$ and $2\sigma_g$ valence molecular-orbitals of the neutral molecule. Comparison of the As_2 spectrum with that presented in ref. (3) shows that the spin-orbit splitting in the $(1\pi_u)^{-1}$ band has been resolved in this work, whereas in the earlier work it was unresolved. The measured value, 0.14±0.02 eV, compares favourably with that obtained from the relativistic HFS calculations of 0.18 eV. An independent check of this spin-orbit separation can be obtained in the following way:[14] in the $As_2^+(^2\Pi_u)$ state the $\pi_{1/2}$ and $\pi_{3/2}$ molecular orbitals can be written simply as:

$$\pi_{1/2}=\frac{1}{\sqrt{2(1+S)}}\,(\pi^{A}_{1/2}+\pi^{B}_{1/2})$$

$$\pi_{3/2}=\frac{1}{\sqrt{2(1+S)}}\,(\pi^{A}_{3/2}+\pi^{B}_{3/2})$$

where S is the overlap integral $\langle\pi^{A}_{1/2,3/2}|\pi^{B}_{1/2,3/2}\rangle$. Neglecting off-diagonal spin-orbit matrix elements of the form $\langle\pi^{A}_{1/2}|\mathrm{Hso}|\pi^{B}_{1/2}\rangle$, the spin-orbit splitting in the $^2\Pi$ state can be written as

$$\Delta=\frac{1}{2(1+S)}\,(\mathscr{G}_A+\mathscr{G}_B)$$

where $\mathscr{G}_A$ and $\mathscr{G}_B$ are the atomic spin-orbit constants on centres A and B, respectively. Setting $\mathscr{G}_A=\mathscr{G}_B=\mathscr{G}_{As}$, then $\Delta=\mathscr{G}_{As}/(1+S)$. Also, taking $\mathscr{G}_{As}=0.18$ eV[23,24] and $S=0.3$,

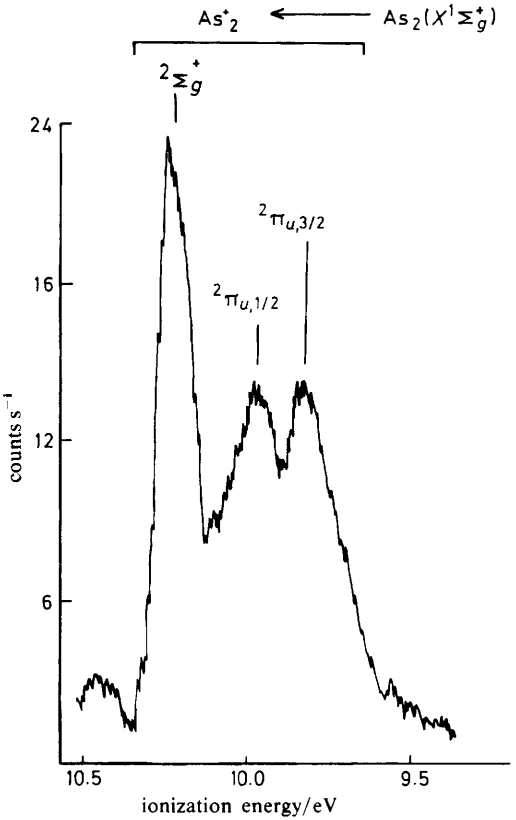

Fig. 2. The He(I) photoelectron spectrum of As_2, obtained by heating copper arsenide to temperatures in the region 1200–1400 K.

Table 3. Comparison of the calculated and observed vertical ionization potentials (eV) of As_2

orbital[a] ionized	ionic state	experimental v.i.p. this work	experimental v.i.p.[b] ref. (3)	non-relativistic HFS v.i.p.	relativistic HFS v.i.p.
$1\pi_u$	$^2\Pi_{u,3/2}$	9.82	10.12	9.59	9.40
	$^2\Pi_{u,1/2}$	9.96			9.58
$2\sigma_g$	$^2\Sigma_{g,1/2}$	10.22	10.39	9.83	9.79
$1\sigma_u$	$^2\Sigma_{u,1/2}$	—	15.32	15.12	15.55
$1\sigma_g$	$^2\Sigma_{g,1/2}$	—	—	21.38	21.60

[a] Orbital numbering refers to valence molecular orbitals only. [b] Differences arise from the band maxima measured in this work and those quoted in ref. (3) because of the approximate calibration method used in the earlier work.

Δ is evaluated as 0.14 eV, in agreement with the experimentally observed value. This calculation is obviously approximate, but confirms that the experimental value for the $As_2^+(^2\Pi_u)$ spin-orbit splitting is reasonable.

Table 4. HFS Mulliken population analysis for the valence orbitals of As_2

orbital	As(4*s*) character (%)	As(4*p*) character (%)
$1\pi_u$	—	100
$2\sigma_g$	15	85
$1\sigma_u$	96	4
$1\sigma_g$	87	13

Inspection of the ionization potential region above 10.5 eV showed no further features that could be assigned to As_2. In particular, no evidence was obtained for the weak band observed previously at 15.32 eV[3] or the As_2 'shake-up' structure seen in the earlier work.[3] On the basis of the calculations performed in this work (see table 3), the $(1\sigma_u)^{-1}$ ionization is expected to give a band at *ca.* 15.5 eV. However, the $1\sigma_u$ orbital in the neutral molecule is mainly As(4*s*) in character (table 4) and, because of the unfavourable As(4*s*:4*p*) cross-section ratio noted earlier, it is expected that the $(1\sigma_u)^{-1}$ band would be extremely weak relative to the $(1\pi_u)^{-1}$ and $(2\sigma_g)^{-1}$ bands at lower ionization energy. Nevertheless, the observation of the $(1\sigma_u)^{-1}$ band in ref. (3) may be due to the greater sensitivity of the Leybold spectrometer used in ref. (3) to low-energy electrons over the spectrometer used in this work.

Experimentally, the onset of the first band of As_2 has been measured as 9.52 ± 0.05 eV. This compares with previous values for the first adiabatic ionization energy of As_2 of 10.1 ± 0.2 eV from Rydberg series measurements[29] and 11.0 ± 0.5 eV from electron-impact mass spectrometry.[30,31] Although, because of experimental difficulties, the adiabatic first ionization energy of a molecule measured by electron-impact mass spectrometry is often too high, the use of Rydberg series usually leads to an ionization energy which is at least an order of magnitude more accurate than the corresponding value measured from photoelectron spectroscopy. However, in ref. (29) only six Rydberg states of As_2 have been observed and it was thought that they were components of three separate Rydberg series. As a result, the ionization energy quoted in this reference must only be regarded as an approximate value and higher members of each series would be required before the ionization energy can be more firmly established by this method. However, for the photoelectron band corresponding to the $(2\sigma_g)^{-1}$ ionization, the adiabatic and vertical ionization energies coincide at 10.22 ± 0.01 eV, a value which is in good agreement with the ionization energy obtained from electronic spectroscopy.[29] Hence, it is possible that the Rydberg states observed in ref. (29) are components of series converging to the second ionization energy of As_2, *i.e.* the $(2\sigma_g)^{-1}$ ionization. Further measurements on Rydberg states close to the convergence limit would obviously be necessary to investigate this suggestion.

The band onset for the process $As_2^+(X\ ^2\Pi_{u,3/2}) \leftarrow As_2(X\ ^1\Sigma_g^+)$ can also be used to derive a value for the dissociation energy, $D_0^{\ominus}$, of $As_2^+(X\ ^2\Pi_{u,3/2})$. Assuming, as seems likely, that $As_2(X\ ^1\Sigma_g)$ dissociates to $As(^4S_{3/2})$ and $As(^4S_{3/2})$, and $As_2^+(X\ ^2\Pi_{u,3/2})$ dissociates to $As^+(^3P_0)$ and $As(^4S_{3/2})$, then the first band onset of As_2 can be combined with the known dissociation-energy, $D_0^{\ominus}$, of $As_2(X\ ^1\Sigma_g)$ of 3.96 ± 0.03 eV[32] and the first ionization energy of atomic arsenic, 9.79 eV,[23,24] to yield $D_0^{\ominus}$ in $As_2^+(X\ ^2\Pi_{u,3/2})$ of 4.23 ± 0.08 eV.

On superheating As_2 vapour to temperatures in the range 1650–1850 K, spectra were recorded in the 9.0–10.5 eV ionization-energy region which exhibited contributions from both As_2 and atomic arsenic (see fig. 3). Subtraction from fig. 3 of the known As_2 spectrum gave three bands with maxima in good agreement with those expected for the ionizations $As^+(^3P_0, ^3P_1, ^3P_2) \leftarrow As(^4S_{3/2})$ and with relative intensities approximately equal to the statistically expected ratio of 1:3:5 (see table 5). Ionization from the 4*p* shell of neutral arsenic $[As(4s^24p^3), ^4S_{3/2}]$ is expected to give five ionic states $^3P_2$, $^3P_1$,

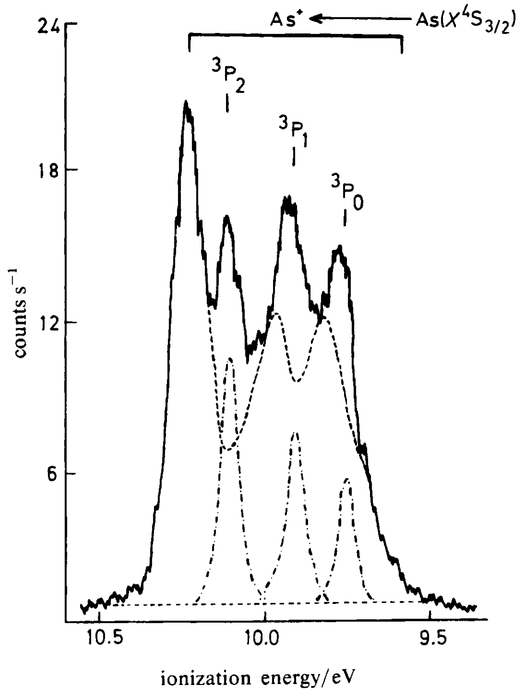

Fig. 3. The He(I) photoelectron spectrum obtained by superheating an As_2 beam to temperatures in the region 1650–1850 K. (- - -) As_2; (- · - · -) As.

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

ionic state	observed i.p.[a]	expected i.p.[b]	experimental relative intensity[c]
$^3P_0$	9.78 ± 0.01	9.79	1.9 ± 0.5
$^3P_1$	9.91 ± 0.01	9.92	3.1 ± 0.3
$^3P_2$	10.09 ± 0.01	10.10	5.0
$^1D_2$	—	11.04	—
$^1S_0$	—	12.59	—

[a] Band maximum; this work. [b] From optical data [ref. (23) and (24)]. [c] Corrected for analyser transmission.

$^3P_0$, $^1D_2$ and $^1S_0$. However, in L–S coupling the photoelectron spin selection rule shows that the ionizations $^1D_2 \leftarrow {}^4S_{3/2}$ and $^1S_0 \leftarrow {}^4S_{3/2}$ are formally forbidden, and indeed bands associated with these processes were not observed experimentally. This is also the case in the He(I) photoelectron spectrum of nitrogen,[27] phosphorus[6] and antimony[25] atoms, where only the $^3P_{0,1,2} \leftarrow {}^4S_{3/2}$ ionization was observed despite the fact that the $^1D_2 \leftarrow {}^4S_{3/2}$ and $^1S_0 \leftarrow {}^4S_{3/2}$ ionizations are known to be in the He(I) range. In contrast, the photoelectron spectrum of bismuth[28] shows a weak band due to the process $Bi^+(^1D_2) \leftarrow Bi(^4S_{3/2})$ as well as bands due to the ionizations $Bi^+(^3P_0, {}^3P_1, {}^3P_2) \leftarrow Bi(^4S_{3/2})$. The appearance of the $^1D_2$ band indicates that the L–S coupling scheme is inappropriate for this element and, in fact, the observed spectrum has been interpreted qualitatively in terms of a coupling scheme intermediate between the L–S and j–j limits.[28]

Apart from the assignment of the experimental spectra, this study has demonstrated how p.e.s. can be used to monitor the composition of the vapour above solid arsenic or a metal arsenide as a function of temperature and as indicated earlier, this could be useful in the *in situ* monitoring of vapour composition in the preparation of arsenic-containing semiconductors by chemical vapour-deposition methods. A similar photoelectron investigation to the one reported here is also in progress on antimony vapour. As has been established from other studies,[4] it has been found that the relative proportions of Sb_4, Sb_2 and Sb above solid antimony can be controlled simply by varying the temperature and this allows the electronic structure of these species to be probed with p.e.s.

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