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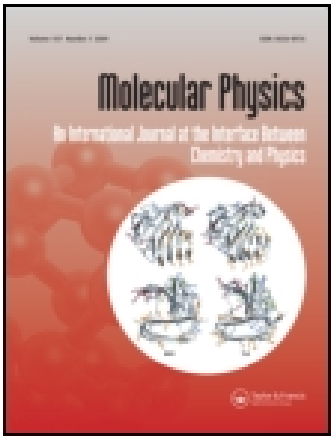

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Structure and ionization potentials of clusters containing heavy elements

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Structure and ionization potentials of clusters containing heavy elements I. Homonuclear group V clusters up to hexamers

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Homonuclear clusters X_m of heavy group V atoms (X = As, Sb) up to $m = 6$ have been studied with valence *ab initio* self consistent field/configuration integration calculations using energy-adjusted pseudopotentials. Several structures have been investigated and results are given for bond lengths (R_e), atomization energies (D_e) and vertical ionization potentials of the ground states. Comparison with experimental and other theoretical values is made where possible.

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1. Introduction

For several years, metal clusters of main group elements have been of special interest from both the experimental and the theoretical point of view (see e.g. [1–6, 74] and references cited therein); in particular alkaline and alkaline-earth clusters have been studied intensively over the last few years [1, 2]. Much less is known, on the other hand, about group III through group VI clusters, especially for the heavier elements of these groups [3–12, 70–73]. All-electron *ab initio* calculations are very rare here due to the large computational effort involved. Pseudopotentials are the only way to keep this effort within reasonable limits and thus have been used in several theoretical studies [7, 8, 12]. The main idea of the pseudopotential method which is reviewed in [14–18] is that only the valence electrons are treated explicitly while the core is represented by a pseudopotential. Additionally, relativistic effects, which become more and more important for the fourth- and fifth-row elements considered in the present work, can be included in the pseudopotentials in a simple way [13]. Using pseudopotentials does not mean a significant loss in accuracy as shown in recent papers [19–21] and, one more merit of the method, all elements of the same group can be treated on an equal footing. Pseudopotential parameters have been published previously by our group for nearly all the main group elements [19, 22–24].

In the last few years, ionization potentials of mixed clusters of alkaline atoms and antimony and tellurium, respectively, (M_nX_m; M = Li, Na, K, Cs; X = Sb, Te; n, $m \leqslant 6$) have been measured by mass spectroscopy [25–28] but, up to now, little is known about the structure and the type of bonding in these clusters. Pseudopotential calculations could provide considerable insight here. Moreover, as mentioned above, corresponding compounds with other homologous atoms (X = As, Se) which, to our knowledge, have not yet been investigated experimentally can be treated in a similar way. In a forthcoming article [29], we shall report on pseudopotential calculations for these mixed M_nX_m clusters (M = Li, Na, K, Rb, Cs; X = As, Sb),

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whereas we set the stage for this study in this and a subsequent paper [30], by presenting results for homonuclear group V (As, Sb) and group VI (Se, Te) clusters X_m with $m \leqslant 6$. (Results for alkali clusters M_n (M = Li, Na, K; $n \leqslant 4$) where M is treated as a one-electron atom were published several years ago [68]. Increasing computer efficiency has now enabled the treatment of the electron-rich clusters of group V and group VI [30] elements.) Several structures of X_m have been studied; bond lengths (R_e), atomization energies (D_e) and vertical ionization potentials (IP) have been calculated. Comparison with experimental and other theoretical values is made in the few cases where it is possible. We also compare our results to those for light-element group V and group VI clusters (P_m, S_m).

2. Method

Let us begin with a short review of our method which has been described in detail in several papers [19, 22–24, 31]. We use a valence model Hamiltonian (in atomic units)

$$H_{\text{mod}} = -\frac{1}{2}\sum_i \Delta_i + V_{\text{sp}} + \sum_{i<j}\frac{1}{r_{ij}} + \sum_{\lambda<\mu}\frac{Q_\lambda Q_\mu}{r_{\lambda\mu}}. \tag{1}$$

i, j denote valence electrons; λ, μ are core indices and Q_λ, Q_μ are core charges. V_{sp} is a semilocal pseudopotential:

$$V_{\text{sp}} = -\sum_{\lambda,i}\frac{Q_\lambda}{r_{\lambda i}} + \sum_{\lambda,i}\sum_{l,j} B_{lj}^\lambda \exp\left(-\beta_{lj}^\lambda r_{\lambda i}^2\right) P_l^\lambda + V_{\text{pol}}. \tag{2}$$

P_l^λ is the projection operator on angular momentum l with respect to core λ. V_{pol} is a core-polarization potential of the type

$$V_{\text{pol}} = -\sum_\lambda \frac{1}{2}\alpha_\lambda \mathbf{f}_\lambda^2, \tag{3}$$

with

$$\mathbf{f}_\lambda = \sum_i \mathbf{r}_{\lambda i} r_{\lambda i}^{-3}\left[1 - \exp\left(-\delta_\lambda r_{\lambda i}^2\right)\right] - \sum_{\mu(\neq\lambda)} Q_\mu \mathbf{r}_{\lambda\mu} r_{\lambda\mu}^{-3}. \tag{4}$$

Here α_λ is the dipole polarizability of core λ and $\mathbf{f}_\lambda$ is the field generated at the site of core λ by the valence electrons and other cores. The cut-off factor (with parameter δ_λ) in (4) and the parameters B_{lj}^λ, β_{lj}^λ in (2) are adjusted to single-valence-electron atomic data, to experimental and Dirac–Fock (DF) values of the first ionization potential, and to experimental excitation energies of the valence electron. As the core-polarization potential is explicitly included in our semilocal pseudopotential V_{sp}, frozen-core DF pseudopotentials (V_{DF})

$$V_{\text{DF}} = V_{\text{sp}} - V_{\text{pol}} \tag{5}$$

are easily available without changing the pseudopotential parameters (see (2)) [31]. Furthermore, due to our adjustment, relativistic effects are implicitly included in V_{DF}. The fitting procedure is described in detail in [31]. All pseudopotential parameters used in this work have already been published [19].

In the present work, molecular geometries, atomization energies and ionization potentials are determined. We firstly performed valence self consistent field (SCF)

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calculations with our model Hamiltonian (see (1)) using the programs MOLPRO [32–35] and TURBOMOLE [36], both containing energy gradients for geometry optimization. Additionally, in the case of the dimers the influence of both valence and core–valence correlation on the spectroscopic properties was studied. For this purpose, geometries were optimized with and without our core-polarization potential V_{pol} (see (3)). As the core-polarization potential has not yet been implemented in MOLPRO or TURBOMOLE, we used the program MELD [37] modified by our group. Including V_{pol}, valence correlation energies were calculated by means of configuration interaction with single and double excitations (*SD-CI*), and the contribution of quadruple excitations was estimated by means of Davidson's correction [38] (*SD-CI* + *Q*). For larger clusters ($m > 2$), valence correlation effects were taken into account by means of the coupled-electron pair approximation (CEPA-1) using MOLPRO, at the SCF geometries (except for geometries of X_5 and X_6 with very low stability which are unbound at the SCF level). Our Gaussian basis sets (GTO) for As and Sb have the size (6s6p1d)/[4s4p1d]. In view of subsequent investigations on M_nX_m clusters (M = Li, Na, K, Rb, Cs; X = As, Sb, Se, Te) [29, 67], where negatively charged X_m^- ions may be expected, we augmented a 4s4p basis set [39] by two diffuse s and p functions, respectively. The s and p exponents which are tabulated in table 1 were energy-optimized in SCF calculations for the atomic ground states using the program PSATOM [40], whereas the d exponents were optimized in atomic CEPA-1 calculations.

With the exception of the dimers X_2 (X = As, Sb), the geometry of the X_m clusters ($m \leqslant 6$) was optimized at the SCF level only. For this geometry, calculations including valance correlation were performed for the neutral X_m cluster and the singly charged ions X_m^+ in order to determine the atomization energies (D_e) and the (vertical) ionization potentials (*IP*). (It has been shown in recent papers [41–43] that there is no qualitative change in geometry between SCF and the valence-correlated level.) In the case of the dimers X_2, additionally, vibrational frequencies ω_e were determined by calculating (total) valence energies at four or five points around the minimum of the potential curve (with $\Delta R_e = 0{\cdot}1\ a_0$) and fitting these values to third-degree polynomials at each level of approximation. In the following section, our results for R_e, D_e and *IP* are tabulated and discussed.

Table 1. Exponents and contraction coefficients of the (6s6p1d)/[4s4p1d] basis sets for As and Sb.

X	s-Exp.	Coeff.	p-Exp.	Coeff.	d-Exp.	Coeff.
As	3·22023	0·19231	1·70184	−0·10724	0·34800	1·0
	1·93051	−0·49866	0·53185	0·24023		
	0·30240	0·64280	0·22134	0·52114		
	0·12783	1·0	0·09257	1·0		
	0·05364	1·0	0·03825	1·0		
	0·01596	1·0	0·01596	1·0		
Sb	1·71462	1·99629	2·00127	0·25620	0·24201	1·0
	1·53857	−2·39893	1·66073	−0·38772		
	0·27181	0·47592	0·29376	0·36534		
	0·14004	1·0	0·13648	1·0		
	0·07289	1·0	0·06662	1·0		
	0·05008	1·0	0·03191	1·0		

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Table 2. Bond lengths (R_e), dissociation energies (D_e) vibrational frequencies ω_e and ionization potentials (IP) of X_2 molecules.

X			R_e/a_0†	D_e/eV*	ω_e/cm^{-1}	IP/eV
As	V_{DF}	SCF	3·86	0·38	491	8·67
		SD-CI + *Q*	3·99	2·68	433	9·38
		CEPA-1	4·01	2·78	424	9·41
	V_{sp}	SCF	3·83	0·48	479	8·72
		SD-CI	3·92	2·32	476	9·31
		SD-CI + *Q*	3·96	2·84	420	9·44
	exp.[a]		3·97	3·93	430	12 9·89 ± 0·10[b]
Sb	V_{DF}	SCF	4·56	−0·32	315	7·67
		SD-CI + *Q*	4·72	1·79	282	8·34
		CEPA-1	4·76	1·91	243	8·39
	V_{sp}	SCF	4·53	−0·24	341	7·81
		SD-CI	4·59	1·50	401	8·42
		SD-CI + *Q*	4·70	1·99	280	8·55
	exp.[a]		4·70	3·13	270	8·5 ± 0·3

[a] [44, 45].
[b] [71].
† $1\,a_0 \approx 5{\cdot}291\,77 \times 10^{-11}$ m.
* $1\,eV \approx 2{\cdot}602\,18 \times 10^{-19}$ J.

3. Results and discussion

Let us start with discussion of the dimers X_2 which have been intensively studied both experimentally and theoretically. Our results for bond lengths (R_e), atomization energies (D_e), vibrational frequencies (ω_e) and vertical ionization potentials (IP) of the $^1\Sigma_g^+$ ground state of As_2 and Sb_2 are summarized at various levels of approximation in table 2.

At the SCF level, the bond lengths R_e are shortened by core-polarization in all cases (see the results with V_{DF} and V_{sp}) but the reduction is only $\sim 0{\cdot}03\,a_0$. Taking valence correlation into account, R_e significantly increases (by $\Delta R_e \leqslant 0{\cdot}2\,a_0$ with both CEPA-1 and *SD-CI* + *Q*). Contributions of quadruple excitations are rather small for As_2 ($\sim 0{\cdot}04\,a_0$) but larger for Sb_2 ($\Delta R_e = 0{\cdot}1\,a_0$). At this level of approximation, R_e with V_{DF} is by $\leqslant 0{\cdot}05\,a_0$ longer than with V_{sp}, similarly as at the SCF level. Compared with experiment [44, 45], the agreement of our best calculated bond lengths (V_{sp}, *SD-CI* + *Q*) is very good, with a deviation $\leqslant 0{\cdot}01\,a_0$.

Atomization energies are usually considerably enlarged by valence correlation effects; but the influence of core–valence correlation is rather small again ($D_e \approx 0{\cdot}2$ eV at the *SD-CI* + *Q* level) both for As_2 and for Sb_2. Our calculated atomization energies are by about 1 eV too small compared with experiment. This deviation can still be reduced by augmenting the one-particle basis set. For example, with another d and one f function (both unoptimized), we obtained the following changes in atomization energies: 0·29 eV (As_2) and 0·21 eV (Sb_2). (Note that R_e is only negligibly affected by basis-set extension ($\Delta R_e \sim 0{\cdot}01\,a_0$).) Size-consistency

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effects are substantial as can be seen by comparing our *SD-CI* and *SD-CI* + *Q* results (about 0·5 eV). Deviations of ω_e (at the highest level of approximation: V_{sp}, *SD-CI* + *Q*) from the experimental values are in all cases smaller than 10 cm^{-1}.

We now turn to ionization potentials *IP*. For group V dimers, the $^1\Sigma_g^+ \rightarrow {}^2\Pi_u$ ionization has been studied. As already mentioned for R_e and D_e, core-polarization is relatively unimportant ($\Delta IP \leqslant 0{\cdot}15$ eV) both at SCF and *CI* level, but the effect increases within a group of the Periodic Table as expected. The deviations from experimental values are rather small for Sb_2 (< 0·1 eV) but, for As_2 our calculated value strongly disagrees with the experimental one ($\Delta IP \sim 2{\cdot}6$ eV). In the latter case, the experimental value of the ionization potential from [44] and [45] seems to be unreliable. In several recent papers, values of about 9·8 eV [8, 48, 71] are reported which are in much better agreement with our pseudopotential result ($\Delta IP \approx 0{\cdot}4$ eV). (Compared with atomization energies, the differences between calculated and experimental ionization potentials are significantly smaller because the correlation errors partly cancel here.) Our calculated ionization potentials are in all cases smaller than the experimental ones; extension of the basis sets to (6s6p2d1f)/[4s4p2d1f] increases the ionization potentials by 0·15 eV (As_2) and 0·10 eV (Sb_2), respectively.

Finally, we come to comparison with other theoretical work. Calculations with the local density method for As_2 led to good results for bond length and vibrational frequency, but the atomization energy as well as the ionization potential were overestimated, as usual with this method [49]. A bond length of 3·98 a_0 and an ionization potential of 9·8 eV for As_2 is obtained with all-electron coupled-cluster calculations [50]. Pseudopotential calculations for As_2 have been performed by Meier *et al.* [12]; their results obtained at the highest level of approximation (4s4p1d basis set, Davidson-corrected multireference *CI* with single and double excitations (*MRD-CI*)) are 4·10 a_0 for R_e, 2·59 eV for D_e, 430 cm^{-1} for ω_e and 9·33 eV for *IP*. Using similar methods [51], results have been reported by Wang *et al.* [8] for As_2 ($R_e = 4{\cdot}01\ a_0$, $\omega_e = 426\ cm^{-1}$, $D_e = 3{\cdot}24$ eV) and Sb_2 ($R_e = 4{\cdot}88\ a_0$, $D_e = 2{\cdot}17$ eV). Excellent agreement is obtained for R_e by Musolino *et al.* [52] using model potentials combined with the local density method, but D_e is overestimated by 0·4 eV.

We now turn to the discussion of our results for As_m and Sb_m clusters ($3 \leqslant m \leqslant 6$). We have studied several structures which are shown in figure 1. Our results for R_e, D_e and *IP* are summarized in tables 3 (for As_m) and 4 (for Sb_m). (In addition, results for $m = 2$ are listed in these tables. To enable a comparison at the same level of approximation, we took for R_e the SCF and for D_e and *IP* the CEPA-1 values of table 2, respectively.)

For $m = 3$, three different structures have been investigated (D_{3h}, C_{2v} and $D_{\infty h}$) and it is found that the stability increases from $D_{\infty h}$ ($2\sigma_g^2\ 2\sigma_u^2\ 1\pi_u^4\ 1\pi_g^3$) over D_{3h} ($2a_1'^2\ 2e'^4\ 1a_2''^2\ 1e''^1$) to C_{2v} ($4a_1^2\ 2b_1^2\ 1b_2^2\ 1b_2^1$ or $1a_2^1$) both for As_3 and Sb_3. In the case of As_3, $D_{\infty h}$ is about 1·5 eV higher in energy than D_{3h} and about 1·6 eV higher than C_{2v}, at the CEPA-1 level. Due to the partially occupied doubly degenerate highest occupied orbital (HOMO), C_{2v} is preferred over D_{3h}; Jahn–Teller distortion leads to two geometries: an 'acute' isosceles triangle (apex angle $\gamma < 60°$) and an 'obtuse' one ($\gamma > 60°$). Both structures have virtually the same ground state energies when valence correlation effects are taken into account ($^2A_2$ and $^2B_2$). At the CEPA-1 level, e.g., ΔD_e is 0·02 eV only, for both As_3 and Sb_3. In both cases, the smaller of the triangle sides is larger than the X_2 bond lengths ($\geqslant 0{\cdot}3\ a_0$), while the larger side is by $\leqslant 0{\cdot}3\ a_0$ shorter than the nearest-neighbour distance in the bulk metal (As: 4·71 a_0; Sb: 5·48 a_0). Experimental values are available for both molecules.

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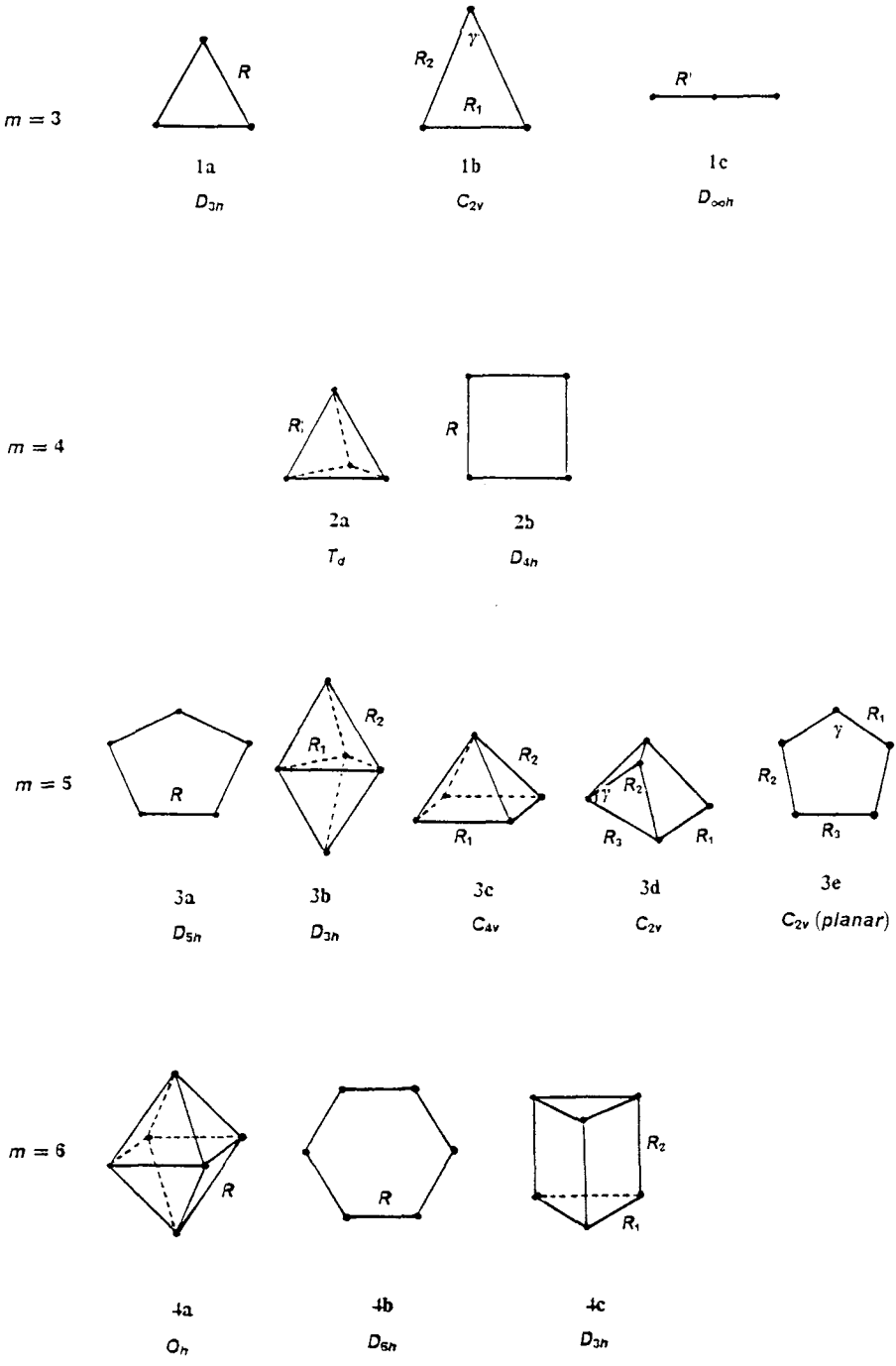

Figure 1. Structures of X_m clusters (X = As, Sb).

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Table 3. Bond lengths (R_e) (in a_0), atomization energies (D_e) and ionization potentials (IP) of As_m clusters ($m \leqslant 6$). Experimental values in parentheses.

m			Geometry	D_e^{SCF}/eV	$D_e^{CEPA\text{-}1}$/eV		$IP_\nu^{CEPA\text{-}1}$/eV
2			$R = 3{\cdot}86$ [a] ($3{\cdot}97$) [c]	– –	$2{\cdot}78$ [b] ($3{\cdot}93$) [c]	$^1\Sigma_g^+ \rightarrow {}^2\Pi_u$	$9{\cdot}41$ [b] (12 [c] $9{\cdot}78$ [f] $9{\cdot}83$ [g] $9{\cdot}89 \pm 0{\cdot}10$ [h])
3	1*a*	D_{3h}	$R = 4{\cdot}37$	$0{\cdot}12$	$3{\cdot}78$	$^2E'' \rightarrow {}^1A_1'$	$6{\cdot}77$
	1*b*	C_{2v}	$R_1 = 4{\cdot}18$ $R_2 = 4{\cdot}48$ $\gamma = 56°$	$0{\cdot}63$	$3{\cdot}92$	$^2B_2 \rightarrow {}^1A_1$	$7{\cdot}04$ ($< 7{\cdot}3$ [g] $7{\cdot}46 \pm 0{\cdot}10$ [h])
			$R_1 = 4{\cdot}60$ $R_2 = 4{\cdot}28$ $\gamma = 65°$	$0{\cdot}41$	$3{\cdot}90$	$^2A_2 \rightarrow {}^1A_1$	$7{\cdot}01$
	1*c*	$D_{\infty h}$	$R = 4{\cdot}02$	$-1{\cdot}35$	$2{\cdot}32$	$^2\Pi_g \rightarrow {}^3\Sigma_g^-$	$7{\cdot}20$
4	2*a*	T_d	$R = 4{\cdot}67$ ($4{\cdot}60$) [d]	$2{\cdot}32$	$7{\cdot}17$	$^1A_1 \rightarrow {}^2E$	$8{\cdot}54$ ($8{\cdot}75$ [e] $\leqslant 8{\cdot}49$ [g] $8{\cdot}63 \pm 0{\cdot}10$ [h])
	2*b*	D_{4h}	$R = 4{\cdot}60$	$0{\cdot}40$	$5{\cdot}08$	$^3A_{1g} \rightarrow {}^2E_g$	$7{\cdot}93$
5	3*a*	D_{5h}	$R = 4{\cdot}35$	$1{\cdot}19$	$7{\cdot}27$	$^2E_1'' \rightarrow {}^3A_1'$	$8{\cdot}18$
	3*b*	D_{3h}	$R_1 = 5{\cdot}91$ $R_2 = 4{\cdot}55$	$-0{\cdot}02$	–	$^2E' \rightarrow {}^3A_1'$	–
	3*c*	C_{4v}	$R_1 = 4{\cdot}60$ $R_2 = 4{\cdot}70$	$1{\cdot}08$	$7{\cdot}09$	$^2B_1 \rightarrow {}^1A_1$	$5{\cdot}66$
	3*d*	C_{2v}	$R_1 = 4{\cdot}62$ $R_2 = 4{\cdot}66$ $R_3 = 4{\cdot}53$ $\gamma = 70°$	$0{\cdot}81$	$6{\cdot}61$	$^2B_2 \rightarrow {}^3A_2$	$6{\cdot}15$

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Table 3. Continued

m			Geometry	D_e^{SCF}/eV	$D_e^{CEPA\text{-}1}$/eV		$IP_\nu^{CEPA\text{-}1}$/eV
	$3e$	C_{2v} (planar)	$R_1 = 4{\cdot}51$ $R_2 = 4{\cdot}17$ $R_3 = 4{\cdot}55$ $\gamma = 107°$	1·66	7·39	$^2B_2 \rightarrow {}^1A_1$	8·50 $(7{\cdot}95 \pm 0{\cdot}10^{(h)})$
6	$4a$	O_h	$R = 4{\cdot}95$	−2·08	–	$^3T_{2u} \rightarrow {}^4A_{1g}$	–
	$4b$	D_{6h}	$R = 4{\cdot}33$	1·48	8·86	$^1A_{1g} \rightarrow {}^2E_{1u}$	8·67
	$4c$	D_{3h}	$R_1 = 4{\cdot}60$ $R_2 = 4{\cdot}68$	2·97	9·85	$^1A_1' \rightarrow {}^2E''$	7·91

(a) SCF value (see table 2).
(b) CEPA-1 value at SCF geometry (see table 2).
(c) [44, 45].
(d) [46].
(e) [10].
(f) [8].
(g) [48].
(h) [71].

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Table 4. Bond lengths (R_e) (in a_0), atomization energies (D_e) and ionization potentials (IP) of Sb_m clusters ($m \leqslant 6$). Experimental values in parentheses.

m			Geometry	D_e^{SCF}/eV	$D_e^{CEPA\text{-}1}$/eV		$IP_\nu^{CEPA\text{-}1}$/eV
2			$R = 4{\cdot}56$ [a] ($4{\cdot}70$) [c]	– –	$1{\cdot}91$ [b] ($3{\cdot}13$) [c]	$^1\Sigma_g^+ \rightarrow {}^2\Pi_u$	$8{\cdot}39$ [b] ($8{\cdot}5 \pm 0{\cdot}3$) [d]
3	1*a*	D_{3h}	$R = 5{\cdot}11$	$-0{\cdot}38$	$2{\cdot}94$	$^2E'' \rightarrow {}^1A_1'$	$6{\cdot}39$
	1*b*	C_{2v}	$R_1 = 4{\cdot}91$ $R_2 = 5{\cdot}23$ $\gamma = 56°$	$0{\cdot}08$	$3{\cdot}04$	$^2B_2 \rightarrow {}^1A_1$	$6{\cdot}58$ ($7{\cdot}5 \pm 0{\cdot}1$ [e] $9{\cdot}2 \pm 0{\cdot}3$ [d])
			$R_1 = 5{\cdot}33$ $R_2 = 5{\cdot}02$ $\gamma = 64°$	$-0{\cdot}14$	$3{\cdot}02$	$^2A_2 \rightarrow {}^1A_1$	$6{\cdot}54$
	1*c*	$D_{\infty h}$	$R = 4{\cdot}72$	$-1{\cdot}98$	$1{\cdot}38$	$^2\Pi_g \rightarrow {}^3\Sigma_g^-$	$6{\cdot}45$
4	2*a*	T_d	$R = 5{\cdot}28$	$1{\cdot}70$	$5{\cdot}83$	$^1A_1 \rightarrow {}^2E$	$7{\cdot}79$ ($7{\cdot}85$) [e] ($7{\cdot}7 \pm 0{\cdot}3$) [d]
	2*b*	D_{4h}	$R = 5{\cdot}16$	$0{\cdot}05$	$4{\cdot}01$	$^3A_{1g} \rightarrow {}^2E_g$	$7{\cdot}29$
5	3*a*	D_{5h}	$R = 5{\cdot}07$	$0{\cdot}21$	$5{\cdot}71$	$^2E_1'' \rightarrow {}^3A_1'$	$7{\cdot}41$
	3*b*	D_{3h}	$R_1 = 5{\cdot}63$ $R_2 = 5{\cdot}44$	$-0{\cdot}89$	–	$^2E' \rightarrow {}^3A_1'$	–
	3*c*	C_{4v}	$R_1 = 5{\cdot}23$ $R_2 = 5{\cdot}52$	$0{\cdot}56$	$5{\cdot}87$	$^2B_1 \rightarrow {}^1A_1$	$5{\cdot}29$
	3*d*	C_{2v}	$R_1 = 5{\cdot}37$ $R_2 = 5{\cdot}40$ $R_3 = 5{\cdot}29$ $\gamma = 70°$	$0{\cdot}28$	$5{\cdot}48$	$^2B_2 \rightarrow {}^3A_2$	$5{\cdot}69$

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Table 4. Continued

m			Geometry	D_e^{SCF}/eV	$D_e^{CEPA\text{-}1}$/eV		$IP_\nu^{CEPA\text{-}1}$/eV
	$3e$	C_{2v} (planar)	$R_1 = 5{\cdot}25$ $R_2 = 4{\cdot}89$ $R_3 = 5{\cdot}28$ $\gamma = 107°$	0·71	5·80	$^2B_2 \rightarrow {}^1A_1$	7·68
6	$4a$	O_h	$R = 5{\cdot}60$	−1·64	–	$^3T_{2u} \rightarrow {}^4A_{1g}$	–
	$4b$	D_{6h}	$R = 5{\cdot}05$	0·20	6·87	$^1A_{1g} \rightarrow {}^2E_{1u}$	7·75
	$4c$	D_{3h}	$R_1 = 5{\cdot}35$ $R_2 = 5{\cdot}43$	2·30	8·40	$^1A_1' \rightarrow {}^2E''$	7·20

(a) SCF value (see table 2).
(b) CEPA-1 value at SCF geometry (see table 2).
(c) [44, 45].
(d) [25].
(e) [47].

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For As_3, Yoo *et al.* [48] as well as Zimmerman *et al.* [71] measured the adiabatic ionization potential and reported values less than 7·3 eV [48] and 7·46 eV [71] which are both in good agreement with our calculated value for the vertical ionization potential of 7·04 eV. For the ionization potential of Sb_3, several references have been found [25, 47, 48]. In the first reference [25], the deviation from our pseudopotential value is rather large ($\sim$ 2·7 eV). In view of the results for the X_4 clusters (X = As, Sb) where the deviations between theoretical and experimental ionization potentials are smaller by an order of magnitude (about 0·1 eV), it is possible that the value measured for Sb_3 in [25] (by Knudson effusion mass spectroscopy) refers to a state different from that considered in our calculations. The second reference [47] is nearer to our calculated value; the deviation is still about 1 eV, but it should be mentioned that measurements by electron impact ionization as done in [47] often yield too high ionization potentials [48]. In a recent paper, Yoo *et al.* [48] estimated the adiabatic ionization potential of Sb_3, by scaling those of P_3 and As_3, to approximately 6·34 eV which means a deviation of only about 0·2 eV from our calculated value. To the best of our knowledge, only two other theoretical studies exist for As_3 and Sb_3 [53, 54]. In the first paper, an empirical many-body potential energy function was used to determine the structures of As_m, Sb_m and Bi_m microclusters up to seven atoms [53]. For a cluster size of $m = 3$, a linear $D_{\infty h}$ geometry was found to be the most stable one for As_3 and Sb_3, in disagreement with our results. (Only for Bi_3 was a triangular ground state obtained [53].) More reliable are the results of Balasubramanian *et al.* [54] who performed extensive CASSCF/MRCI calculations using relativistic pseudopotentials for all group V trimers. Their calculated bond angles agree very well with ours in all cases, whereas their bond lengths are larger by about 0·2 a_0 than our SCF optimized ones, due to valence correlation effects which increase bond distances as shown above in the case of dimers X_2 (see table 2).

For $m = 4$, a planar (D_{4h}) and a tetrahedral structure (T_d) have been considered (see figure 1). Geometry optimization for the planar X_4 molecules (X = As, Sb) has been started at a rhombic structure (D_{2h}) (electronic configuration $3a_g^2\ 2b_{3u}^2\ 2b_{2u}^2\ 1b_{1g}^2\ 1b_{1u}^2\ 1b_{2g}^1\ 1b_{3g}^1$) which converges to the square one (D_{4h}) (electronic configuration $2a_{1g}^2\ 2e_u^4\ 1b_{2g}^2\ 1b_{1g}^2\ 1a_{2u}^2\ 1e_g^2$). (Singlet states are less favoured in this case.) The bond lengths in D_{4h} symmetry are 4·60 a_0 for As_4 and 5·16 a_0 for Sb_4, i.e. shorter by about 0·1 a_0 than the corresponding values of the T_d structure ($2a_1^2\ 2t_2^6\ 1e^4$). For As_4 in T_d symmetry an experimental value of 4·60 a_0 is given [46] which agrees well with our calculated one. T_d is very probably the ground state for As_4 and Sb_4; we find this geometry to be more stable than D_{4h} by about 2 eV at the CEPA-1 level, in qualitative agreement with both experimental (see e.g. [55–61, 71]) and theoretical investigations (see e.g. [10, 12, 52, 61–65, 72]) for As_4 (and P_4) clusters. Ionization potentials are in good agreement with experimental data both for As_4 [10, 48, 71] and Sb_4 [25, 47]. The deviations are in both cases smaller than 0·3 eV. We now turn to comparison with other calculations on As_4 and Sb_4. Meier *et al.* [12] determined an As–As bond distance of 4·73 a_0 which is only 0·06 a_0 longer than ours. In that paper [12], the stability with respect to dissociation into two As_2 units is given. The value of 1·79 eV corresponds well with ours (1·61 eV) but is smaller than the experimental one (2·35 eV [58]). A value of 8·74 eV is reported for the ionization potential from the 1e orbital of As_4 [12] in agreement with experiment (8·75 eV) and our value (8·54 eV). Andzelm *et al.* [65] overestimate the experimental *IP* of As_4 by about 0·4 eV using model potentials (MPs) and local exchange–correlation spin density functionals (LSDs). For Sb_4, $R_e \approx 0{\cdot}1\,a_0$ larger than ours in the MP-LSD

calculations of Musolino *et al.* [52], but their atomization energy with respect to two Sb_2 units (3·39 eV [52] against 2·00 eV (this work), respectively) seems to be overestimated again. Empirical studies of Katircioglu and Erkoc [53] yield planar D_{4h} ground states for the X_4 clusters strongly disagreeing with experimental and theoretical results [55–65].

For $m = 5$, we have taken four different structures into account (D_{5h}, D_{3h}, C_{4v} and C_{2v}) which are shown in figure 1. (The latter, C_{2v}, is built up from a roof structure of X_4 (X = As, Sb) with a twofold coordinated fifth atom; Jones and Hohl [66] found this geometry to be the most stable one in the case of P_5.) For Sb_5, we find the C_{4v} geometry ($4a_1^2\ 1b_1^2\ 1b_2^2\ 3e^4\ 2b_1^1$) to be the most stable one at the CEPA-1 level whereas for As_5, D_{5h} ($2a_1'^2\ 2e_1'^4\ 2e_2'^4\ 1a_2''^2\ 1e_1''^3$) is lower in energy than C_{4v}; the $C_{4v} \rightarrow D_{5h}$ energy difference of 0·2 eV is just reversed for As_5. (Both for As_5 and Sb_5, D_{3h} ($3a_1'^2\ 2a_2''^2\ 2e'^4\ 1e''^4\ 3e'^3$) is the most unstable structure investigated here.) The three-dimensional C_{2v} geometry (electronic configuration $6a_1^2\ 1a_2^2\ 3b_1^2\ 2b_2^2\ 3b_2^1$) is less stable than the planar D_{5h} for As_5 and the C_{4v} one for Sb_5, but as in the case of X_3, the highest occupied molecular orbital in the planar symmetric form (D_{5h}) of X_5 (X = As, Sb) is spatially degenerate and our calculations confirm a Jahn–Teller distortion to a planar C_{2v} structure of lower symmetry (electronic configuration $6a_1^2\ 1a_2^2\ 3b_1^2\ 2b_2^2\ 3b_2^1$); the distortion of bond lengths is not very large ($\Delta R \approx 0{\cdot}2\,a_0$), however, and the bond angles change by less than 2° in both cases, and the energy difference between the D_{5h} and the distorted C_{2v} geometry is rather small (0·1 eV) both for As_5 and Sb_5. Compared to the most stable structures (C_{2v} (*planar*) for As_5 and C_{4v} for Sb_5), the three-dimensional C_{2v} geometry is less stable by 0·78 eV (As_5) and 0·39 eV (Sb_5), respectively. Unfortunately, neither experimental nor reliable theoretical work exists for Sb_5, and for As_5, only an experimental ionization potential of 8·63 eV is known [71] in good agreement with our calculated value of 8·54 eV. An empirical many-body potential [53] predicts a planar D_{5h} structure as ground state for the X_5 clusters (X = As, Sb).

Finally we turn to the discussion of our results for X_6 clusters (X = As, Sb). An O_h ($2a_{1g}^2\ 2t_{1u}^6\ 1e_g^4\ 1t_{2g}^6\ 1t_{2u}^4$) and a D_{6h} geometry ($2a_{1g}^2\ 1e_{1g}^4\ 2e_{2g}^4\ 1a_{2u}^2\ 1b_{1u}^2\ 1b_{2u}^2\ 2e_{1u}^4$) have been investigated (see figure 1). Additionally, a prismane analogue with D_{3h} geometry (electronic configuration $3a_1'^2\ 3e'^4\ 2a_2''^2\ 2e''^4$) is considered (see figure 1) which has been studied in the case of the homologous P_6 and As_6 clusters [66] and predicted to be the most stable structure for As_6 [66]. For both As_6 and Sb_6, we find D_{6h} to be lower in energy than O_h (for As_6, $\Delta E \approx 3{\cdot}6$ eV; for Sb_6, $\Delta E \approx 1{\cdot}8$ eV, at the SCF level), but D_{3h} is the most stable structure as predicted in preliminary calculations by Jones and Hohl [66]. Our calculated energy difference from the planar D_{6h} structure is 1·0 eV for As_6 and 1·5 eV for Sb_6, respectively, at the CEPA-1 level, i.e. the stability of D_{3h} is increased with increasing atomic number. Neither experimental nor theoretical investigations have been done on Sb_6 compounds, to our knowledge, except for the above-mentioned preliminary calculations on As_6 [66].

We now want to summarize our results. We have investigated several structures for X_m clusters with X = As, Sb and $m \leqslant 6$. For $m \geqslant 4$, we found three-dimensional structures to be the ground states (with the exception of As_5 where a distorted planar pentagon is found to have the lowest in energy) in agreement with reliable experimental and theoretical studies where available. The bond lengths obtained for the most stable structures in our calculations are $\approx 4{\cdot}6\,a_0$ for As_m and $\approx 5{\cdot}3\,a_0$ for Sb_m for the cases $3 \leqslant m \leqslant 6$. This is in good agreement with the experimentally known

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nearest-neighbour bond distances for the solid phase (4·71 a_0 (As) and 5·48 a_0 (Sb)) [69]. As expected, the atomization energy increases with increasing cluster size m and decreases within a group of the periodic table in all cases.

4. Conclusions

We have performed pseudopotential calculations on X_m clusters (X = As, Sb) up to $m = 6$. Thereby, we have investigated several structures for each cluster size m. Results are given for bond lengths, atomization energies and vertical ionization potentials. The results have been compared both with experimental and other theoretical values where available.

For the dimers X_2, the agreement with reliable data is high: the deviation of our calculated bond lengths from the experimental values, e.g., are $\leqslant 0{\cdot}01\, a_0$ (including correlation; $0{\cdot}1\, a_0$ at the SCF level), ionization potentials are accurate to about 0·4 eV.

For larger clusters, the geometry has been optimized at the SCF level only. The inaccuracy of bond lengths and bond angles due to that treatment is expected to be small as demonstrated for related compounds in several earlier papers [41–43]. The equilibrium structures are found to be three-dimensional geometries for $m \geqslant 4$, i.e., a tetrahedron for $m = 4$, a square pyramid for $m = 5$ and a trigonal prisma for $m = 6$. (As_5 with its distorted pentagonal planar structure is an exception.)

In the near future, similar calculations will be performed, in our laboratory, for the homologous Se_m and Te_m clusters [30] and for mixed clusters M_nX_m (M = Li, Na, K, Rb, Cs; X = As, Sb, Se, Te; $n, m \leqslant 6$) [29].

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