

An ab initio investigation of the molecules X_2 , CuX , Cu_2X and CuX_2 ($X = Si, Ge, \text{ and } Sn$)

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Abstract

The molecules X_2 , CuX , Cu_2X and CuX_2 ($X = Si, Ge \text{ or } Sn$) have been investigated by valence ab initio calculations using energy-adjusted pseudopotentials. The results for bond lengths R_e , harmonic frequencies ω_e and dissociation energies D_e are given for the ground state of these molecules. In the case of the Cu_2X molecules, two low-lying electronic states have been examined, 1A_1 and 3B_1 , and the singlet 1A_1 state was found to be the ground state. The experimental dissociation energies of the CuX , Cu_2X and CuX_2 molecules have been revised according to the molecular parameters derived in this work. A copper 19-valence-electron Dirac–Fock pseudopotential has been generated in order to check the one-valence-electron approximation in the case of the CuX molecules.

Keywords: Copper; Dissociation energies; Germanium; Mixed clusters; Silicon; Tin

1. Introduction

The interest in mixed clusters of group 11 and 14 elements stems from their relevance in such areas as heterogeneous catalysis, homogeneous nucleation and crystal growth [1–3]. Mass spectrometric investigations proved to be an efficient tool to gain insight into the chemistry of such mixed clusters, especially if their thermodynamic data are considered [4,5]. The majority of the experimental data for these mixed clusters is reported for the heavier elements of both groups [6–12]. As neither experimental nor theoretical data on their structure were available in the literature, the evaluation of their thermodynamic data utilizing the third law

method [5,13] had to be based on estimated molecular parameters, e.g. topology, dimensions, and vibrational frequencies. It is therefore important to obtain more detailed knowledge of the molecular parameters of such mixed clusters.

In a previous paper we reported on pseudopotential investigations of the molecules Cu_2Si_2 , Cu_2Sn_2 , Cu_4Si_4 and Cu_4Sn_4 [14]. For these clusters the relative stabilities of several possible structures were compared and their bonding situation was discussed. In this paper we present the results of pseudopotential calculations of the molecules X_2 , CuX , Cu_2X and CuX_2 , where X is Si, Ge and Sn . The molecular parameters derived for the CuX , Cu_2X and CuX_2 molecules are used to revise the interpretation of their heat of dissociation measurements according to the third law method. For

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copper, a 19-valence-electron pseudopotential fitted to numerical all-electron Dirac–Fock energies is presented and used for reference calculations in order to check the reliability of the one-valence-electron approximation for the copper atom in these heterometallic molecules.

2. Method

The use of the pseudopotential method not only has the advantage of reducing the computational effort, but also allows relativistic effects to be introduced in a rather simple way. The valence model hamiltonian (in atomic units) used in this work is

$$H_{\text{mod}} = -\frac{1}{2} \sum_i \Delta_i + V_{\text{SP}} + \sum_{i < j} \frac{1}{r_{ij}} + \sum_{\lambda < \mu} \frac{Q_\lambda Q_\mu}{r_{\lambda\mu}} \quad (1)$$

where V_{SP} is a semilocal pseudopotential of the form

$$V_{\text{SP}} = -\sum_{\lambda,i} \frac{Q_\lambda}{r_{\lambda i}} + \sum_{\lambda,i} \sum_{l,k} C_{lk}^\lambda \exp(-c_{lk}^\lambda r_{\lambda i}^2) P_l^\lambda + V_{\text{pol}} \quad (2)$$

$$P_l^\lambda = \sum_{m_l} |lm_l\rangle \langle lm_l|$$

Here, i and j are valence electron indices, whereas λ and μ are core indices and Q_λ and Q_μ are the corresponding core charges; P_l^λ is the projection operator onto the Hilbert subspace of angular momentum l with respect to core λ , and V_{pol} is a polarization potential of the type

$$V_{\text{pol}} = -\sum_\lambda \frac{1}{2} \alpha_\lambda f_\lambda^2 \quad (3)$$

$$f_\lambda = \sum_i r_{\lambda i} r_{\lambda i}^{-3} [1 - \exp(-\delta_\lambda r_{\lambda i}^2)] - \sum_{\mu(\neq \lambda)} Q_\mu r_{\lambda\mu} r_{\lambda\mu}^{-3} \quad (4)$$

Here α_λ is the dipole polarizability of core λ and f_λ is the field produced at the site of core λ by the valence electrons and other cores. For the one- and four-valence-electron pseudopotentials of copper [15] and silicon, germanium and tin [16], respectively, a single-electron-fit (SEFIT) procedure for

adjusting the pseudopotential parameters was employed (for details see ref. [15]), where the cut-off factor (with parameter δ_λ) in Eq. (4) and the parameters C_{lk}^λ and c_{lk}^λ in Eq. (2) are adjusted to single-valence-electron atomic data; i.e. to experimental and Dirac–Fock (DF) values of the first ionization potential, and to experimental excitation energies of the valence electron. The parameters of the 19- (copper, see Table 1) and 22-valence-electron pseudopotentials (germanium and tin, see ref. [17]) derived in this work have been generated using a multi-electron-fit (MEFIT) procedure outlined in Refs. [18] and [19], utilizing the programs JUSTPOT [20] and a modified version of MCHF77 [21]. However, in contrast to these literature procedures, we are using atomic ionization and excitation energies taken from numerical all-electron relativistic DF calculations [23] to introduce relativistic effects in the pseudopotentials. In order to do so one has to perform an averaging over LSJ states and this, of course, is possible only in certain cases. As the 22-valence-electron pseudopotentials for germanium and tin are primarily intended to be used in the calculation of the core–core interaction energies of the $\text{Cu}^+ \cdots \text{X}^{4+}$ pairs, it is reasonable to take into account even fairly high charged reference states. The six reference states actually used are ^3P for X, ^2P for X^+ , ^1S for X^{2+} , ^2S and ^2P for

Table 1
Parameters of the relativistic (DF) MEFIT pseudopotential for copper (in atomic units) and the contraction coefficients and exponents of the (8s7p6d)/[6s4p3d] GTO basis set

Q	l	C_{l_1}	C_{l_2}	c_{l_1}	c_{l_2}		
19	0	335.7557	70.74581	30.22	13.19		
	1	233.8472	53.55422	33.13	13.22		
	2	-31.33685	-3.130213	38.42	13.26		
		s	p	d			
		-0.185873	30.24566	0.003275	89.07806	0.051052	40.17160
		0.332262	14.16370	-0.126517	16.50540	0.216428	12.55179
		0.823154	10.11813	0.280692	5.49862	0.441168	4.57755
				0.811201	2.42599	0.511360	1.70176
	1.0	2.44411					
	1.0	0.99589	1.0	0.87156	1.0		0.61449
	1.0	0.14053	1.0	0.11952	1.0		0.19780
	1.0	0.06098	1.0	0.03077			
	1.0	0.01420					

X^{3+} , and 1S for X^{4+} . In the case of copper, seven low-lying feasible reference states of the neutral atom (Cu: 2S , 2D , 4F and 2P), the cation (Cu^+ : 1S and 3D) and the anion (Cu^- : 1S) were accessible. Only in two cases (4F , for Cu, and 3D , for Cu^+) is more than a simple averaging of LSJ states necessary. Although in the case of Cu^+ two LS states exist for $J = 2$ (3D and 1D), the LSJ states 3D_1 and 3D_3 can be used to calculate the energy of the 3D reference state according to

$$E(^3D) = \frac{1}{5}[2E(^3D_1) + 3E(^3D_3)] \quad (5)$$

since their nondiagonal elements of the spin-orbit Hamiltonian are zero. For the second case in question, 4F for Cu, only one LS state exists for $J = 9/2$ and therefore this reference energy can easily be calculated with the following equation

$$E(^4F) = E(^4F_{9/2}) - \frac{1}{2}\zeta_{(n+1)p} + \zeta_{nd} \quad (6)$$

The spin-orbit coupling constants $\zeta_{(n+1)p}$ and ζ_{nd} are taken from the energy splitting of the 2D and 2P states found for the neutral copper atom and scaled according to the $\langle r^{-3} \rangle$ expectation values of the 4F state. These estimated coupling constants agree quite well with that calculated utilizing Eq. (7)

$$\zeta(r_i) = \frac{\alpha^2}{2} Z' \langle r^{-3} \rangle_i \quad (7)$$

$$Z' = Z - \sigma$$

In Eq. (7) the fine structure constant α is equal to $e^2/\hbar c$ and the shielding constants σ for the different orbitals were taken from ref. [24].

From investigations of molecules containing group 11 elements [14,15] it became apparent that, in the case of a one-valence-electron pseudopotential, a simple treatment of the core-core interactions within a point charge model is not sufficient. Deviations from the point charge interactions have been derived from frozen-core SCF pseudopotential interaction curves of the $Cu^+ \dots X^{4+}$ pairs and fitted to an exponential function of the form $\Delta = D \exp(-\eta R)$ [25]. We applied the 19-valence-electron pseudopotential for copper (see Table 1) and the 22-valence-electron pseudopotentials for germanium and tin (for pseudo-

potential parameters see [17] and for the (5s5p6d) Gaussian type orbital (GTO) basis sets see [26]) derived in this work and took all electrons into account for silicon ((13s9p)/[6s5p] GTO basis set from [27]).

Valence self-consistent-field (SCF) calculations have been performed with the programs MELD [28] and MOLPRO [29] utilizing small basis sets that had been energy optimized for the ground state of the neutral atoms [30]. In the case of the copper one- and the silicon, germanium and tin four-valence-electron pseudopotentials, the small basis sets have been augmented by a diffuse function optimized at the corresponding anion to ensure a reliable description for possible anionic species (see also ref. [14]). By adding polarization functions, optimized to yield a maximum in the SCF binding energy of the dimers X_2 , we obtained a (4s4p1d)/[2s3p1d] GTO basis set for silicon, germanium and tin and a (5s2p)/[4s2p] GTO basis set for copper, further denoted as basis sets A (see Table 2). For calculations including correlation effects we also used extended GTO basis sets B. The (4s4p1d)/[2s3p1d] GTO basis sets of the group 14 elements have been augmented by two diffuse s, one diffuse p, and an f polarization function and the d functions were split into two sets yielding (6s5p2d1f)/[4s4p2d1f] GTO basis sets, and for copper we used an uncontracted (5s5p2d) GTO basis set from ref. [31] (basis sets B, see Table 2). The GTO valence basis sets A for silicon, germanium, tin and copper in combination with the four- and one-valence-electron pseudopotentials have been used in the calculations throughout the paper unless stated otherwise. For the 19-valence-electron pseudopotential of copper, an (8s5p6d) GTO basis set has been energy optimized for the 2S state. Two diffuse p functions optimized for the 2P state have been added. In the resulting (8s7p6d) GTO basis the smallest s exponent has been substituted by an s function optimized for the 1S state of the anion to give the final (8s7p6d)/[6s4p3d] GTO basis set (see Table 1; for notation see [32]). For calculations at the correlated level we added two f polarization functions taken from ref. [33] (4.962, 1.221) yielding an (8s7p6d2f)/[6s4p3d2f] GTO basis set.

Valence correlation effects have been investigated by the use of density functional methods

Table 2

Contraction coefficients and exponents of the (4s4p1d)/[2s3p1d] GTO valence basis set for silicon, germanium, and tin (four-valence-electron pseudopotential) and the (5s2p)/[4s2p] GTO basis set for copper (one-valence-electron pseudopotential), basis sets type A. The exponents of the extended (6s5p2d1f)/[4s4p2d1f] GTO basis sets of the group 14 elements are given in parentheses (basis sets type B). For copper also the exponents of the uncontracted (5s5p2d) GTO basis set from ref. [31] are given (basis set type B)

	s		p		d ^a	
Si	0.098990	3.74422	-0.065628	1.78884	1.0	0.26328
	-0.575218	1.47731	1.025761	0.30621	(1.0	0.3612)
	1.225102	0.24620			(1.0	0.0903)
			1.0	0.09072		
	1.0	0.09077	1.0	0.02556		
	(1.0	0.04)	(1.0	0.01)	(f:	0.382)
	(1.0	0.01)				
Ge	0.415665	2.65867	-0.147632	1.69403	1.0	0.19689
	-0.924999	1.74609	1.052100	0.28588	(1.0	0.2700)
	1.223723	0.24378			(1.0	0.0675)
			1.0	0.08517		
	1.0	0.09065	1.0	0.02405		
	(1.0	0.03)	(1.0	0.01)	(f:	0.359)
	(1.0	0.01)				
Sn	0.782576	1.80207	-0.297190	0.94306	1.0	0.13470
	-1.554097	1.21272	1.135154	0.22827	(1.0	0.1848)
	1.357978	0.21106			(1.0	0.0462)
			1.0	0.07132		
	1.0	0.08072	1.0	0.02319		
	(1.0	0.03)	(1.0	0.01)	(f:	0.267)
	(1.0	0.01)				
Cu (5s2p)	0.115510	2.22336	1.0	0.11952 ^b		
	-1.088861	0.70545	1.0	0.03077 ^b		
	1.0	0.14176				
	1.0	0.04626				
	1.0	0.01159				
Cu (5s5p2d)		1.98533		1.26180		0.5
		0.72369		1.08805		0.05
		0.16174		0.17134		
		0.06936		0.05646		
		0.03027		0.02068		

^a The d polarization functions for Si, Ge, and Sn were optimized by minimizing the SCF energy of the homonuclear dimers at the bonding distance obtained for the d exponents (Si: 0.424; Ge: 0.382; Sn: 0.253) taken from ref. [32]. In the case of the extended (6s5p2d1f)/[4s4p2d1f] GTO basis sets B the single d set is substituted by the two d functions given in parentheses.

^b The two smallest p exponents of the (8s7p6d) GTO basis set for the 19-valence-electron pseudopotential (see Table 1) are added as polarization functions.

[34,35]. We employed two different density functionals, one with the self-interaction correction of Stoll, Pavlidou and Preuss (SPP) [36] and the other with a gradient correction suggested by Perdew (GCP) [37] (for parameterization see [35] and references therein). Except for the cases where the copper 19-valence-electron pseudopotential is

used, calculations taking into account core-valence correlation effects (V_{pol} ; see Eq. (3)) have been performed. The density functional results have been checked by configuration interaction (CI) calculations with single and double excitations from the SCF reference configuration (CI-SD) including V_{pol} . The contributions of higher excitations have

been approximated by applying the Langhoff–Davidson size-consistency correction (+SCC) [38]. With the extended GTO basis sets, valence correlation effects have also been taken into account by means of the coupled-electron pair approximation (CEPA-1) in order to have a more reliable estimate for the bonding energies of the molecules investigated.

We also analyzed the chemical bonding by means of population analysis according to Davidson's method [39] further developed by Roby [40] and Ahlrichs and co-workers [41,42], which yields multicenter contributions to the chemical bond. This analysis is performed by a projection of the molecular electron density on a minimal atomic orbital basis taken from atomic calculations. This leads to a multicenter expansion of the molecular charge by means of shared electron numbers.

The calculation of the vibrational frequencies has been carried out for the optimized structures by fitting harmonic potentials for symmetry-adapted internal coordinates [43,44]. For optimization the internal coordinates belonging to the totally symmetric irreducible representation were used in the harmonic potential.

The reported experimental dissociation energies of the CuX, Cu₂X and CuX₂ molecules examined herein are based on estimated geometries and harmonic frequencies (see refs. [8–10]) and were determined utilizing the third-law method [13], which is based on the knowledge of the absolute entropy of the reactants. It allows calculation of the heat of reaction according to Eq. (8)

$$\Delta H_{\text{ref}}^{\circ} = -RT \ln K_p - T \Delta \left[\frac{G_T^{\circ} - H_{\text{ref}}^{\circ}}{T} \right] \quad (8)$$

In Eq. (8) $(G_T^{\circ} - H_{\text{ref}}^{\circ})/T$ is the free-energy function and Δ signifies the difference between the sum of the products and the sum of the reactants. The knowledge of the molecular parameters obtained in this work allows us to revise these experimental dissociation energies, since the free-energy functions are the only quantities not determined by the experiment. The revision of the dissociation energies is based on the particular reactions and measured equilibrium constants taken from the respective references [8–10]. The free energy functions of the atoms and molecules involved in these

reactions are either taken from the corresponding references or calculated using standard statistical thermodynamic expressions [13].

3. Results and discussion

Before we turn to the discussion of the molecular results, we comment briefly on the quality of the applied pseudopotentials and basis sets. The one-valence-electron pseudopotential for copper and the four-valence-electron pseudopotentials for silicon, germanium and tin have already been tested for atomic (Cu [15]; Si, Ge and Sn [16,45]) and molecular results (Cu [15,46]; Ge [47]; Sn [45,48]). The size and contraction pattern of the GTO basis sets given in Table 2 were chosen in such a way as to ensure a reliable description of atomic quantities (ionization and excitation energies and electron affinities). Numerical Hartree–Fock pseudopotential calculations have been taken as reference for these atomic test results. As expected, the largest errors using the contracted basis sets are found for the ionization energies (0.14 eV) and electron affinities (0.07 eV) of the group 14 elements, whereas the average error for copper and the excitation energies of the neutral group 14 atoms are negligible. To test the GTO basis sets and pseudopotential parameters utilized for the treatment of the group 14 elements in this paper, the ground state properties of the homonuclear dimers Si₂, Ge₂ and Sn₂ have been calculated (see paragraph on X₂ molecules).

Although the one-valence-electron approximation for copper has already been tested for the homonuclear diatomic molecule, the hydride [15,49] as well as the oxide [46], we performed test calculations on the diatomic CuX molecules (X is Si, Ge, and Sn). As the experimental data on these molecules are rather limited we adjusted a 19-valence-electron pseudopotential for copper on numerical DF energies (see Method section) to have a benchmark for the one-valence-electron pseudopotential. The errors for the SCF results using the DF pseudopotential derived in this work compared with the numerical all-electron DF results are of the order of 0.04 eV for the ionization and excitation energies and also for the

electron affinity. The 19-valence-electron quasirelativistic MEFIT,R pseudopotential for copper taken from ref. [18] (relativistic part fitted to one-valence-electron numerical DF energies) appears to be of similar quality with an average error of 0.07 eV for the relevant atomic energies.

3.1. X_2 molecules

We confine our calculations on Si_2 , Ge_2 and Sn_2 molecules to the $^3\Sigma_g^-$ ground state [50,51]. The results for bond lengths R_e , vibrational frequencies ω_e and dissociation energies D_e at different levels of approximation are listed in Table 3. The homonuclear dimers X_2 have been optimized at three different levels of approximation, the SCF, CI-SD + V_{pol} and CI-SD + SCC + V_{pol} level, using basis sets A. At the CI-SD + SCC + V_{pol} and CEPA-1 levels we also performed calculations with the extended (6s5p2d1f)/[4s4p2d1f] GTO basis sets B for the

bond lengths derived at the CI-SD + SCC + V_{pol} level of approximation using the smaller basis sets A. In addition, the valence correlation effects have been approximated at the SCF bond lengths employing density functional methods (SPP and GCP).

For Si_2 and Sn_2 , the bond lengths obtained at the SCF level are 4 pm shorter than the experimental values. If correlation effects (valence and core-valence, CI-SD + V_{pol}) are taken into account the calculated bond length for all three dimers increases by ≈ 3 pm. The inclusion of size-consistency corrections (+SCC) yields an even further increase of the bond lengths of ≈ 2 pm. At the highest level of approximation (CI-SD + SCC + V_{pol}) the calculated bond lengths for Si_2 and Sn_2 are within 1 pm of the experimental values. As no experimental data on the bond length of Ge_2 have been reported in the literature so far (the value occasionally referred to as such was originally

Table 3

Dissociation energies (in eV), bond lengths (in pm), and harmonic frequencies (in cm^{-1}) for the X_2 molecules ($X = Si, Ge, Sn$) in the ($^3\Sigma_g^-$) state^a

	R_e				ω_e			
	SCF	SCF + V_{pol}		Exp.	SCF	SCF + V_{pol}		Exp.
		CI-SD	+SCC			CI-SD	+SCC	
Si_2	221	224	226	225 ^b	575	532	490	511 ^b
Ge_2	236	239	241	–	317	290	276	274 ^c
Sn_2	271	273	276	275 ^d	218	198	192	190 ^d

	D_e							
	SCF	SCF + V_{pol}						Exp.
		SPP	GCP	CI-SD	+SCC	+SCC ^e	CEPA-1 ^e	
Si_2	1.83	2.62	2.93	2.34	2.59	3.00	3.07	3.21 ± 0.22^f
Ge_2	1.27	2.09	2.39	2.00	2.25	2.57	2.59	2.70 ± 0.07^g
Sn_2	1.07	1.92	2.17	1.79	1.98	2.31	2.31	1.93 ± 0.09^h

^a For abbreviations see text.

^b Ref. [59].

^c Ref. [60].

^d Ref. [61].

^e Results using the extended GTO basis sets B for the bond lengths obtained at the SCF + V_{pol} + CI-SD + SCC level employing the GTO basis sets A.

^f Ref. [62].

^g Ref. [58].

^h Ref. [63].

reported as an experimental estimate of ≈ 244 pm [52]), we give a brief comparison with other theoretical results. Calculations employing other pseudopotentials at the MRD-CI level (243–246 pm, see refs. [53–55]) and the MCSCF(CASSCF) level (244 pm [56]) generally yield a greater bond length for Ge_2 than the 241 pm (CI-SD+SCC+ V_{pol}) value derived in this work. It is interesting to note that our calculated bond length is similar to that obtained from an all electron CI calculation (242 pm) reported by Shim, Gingerich and co-workers [57,58]. In accordance with the excellent agreement between the experimental and our calculated Si_2 and Sn_2 bond lengths and the trends observed for the calculated values, we tend to assign a value of 240 pm for the equilibrium bond distance of the Ge_2 dimer in the $^3\Sigma_g^-$ ground state.

At the SCF level the vibrational frequencies of the X_2 dimers are overestimated (by 15%). If correlation effects are included, the calculated harmonic frequencies decrease considerably, and at the highest level of approximation (CI-SD+SCC+ V_{pol}) a good agreement with experimental values is found (see Table 3). The largest deviation from the reported experimental values is observed in the case of Si_2 , but our result is within the range given by other CI calculations as available in the literature [57,58,64–69].

From the dissociation energies listed in Table 3 it is obvious that correlation effects play an important role in the case of group 14 dimers. The GCP functional generally gives larger dissociation energies than the SPP density functional, but on the other hand these energies agree quite well with the results of the CEPA-1 calculations utilizing the extended (6s5p2d1f)/[4s4p2d1f] basis sets B and the experimental values (see Table 3). In the case of the Sn_2 molecule the dissociation energy is overestimated compared with the experimental value, whereas in the other two cases the calculated dissociation energies are somewhat too small, but for all three molecules the calculated dissociation energies are still within a reasonable error margin. Our results indicate that the smaller (4s4p1d)/[2s3p1d] basis sets A are not sufficient to give good approximations for the dissociation energies if basis set sensitive methods like CI-SD are employed, at least for the lighter congeners, in

agreement with the findings by other authors for the Si_2 and Ge_2 molecules (cf. [53–55,65, 68]). The results of the calculations for the Si_2 , Ge_2 and Sn_2 molecules further support the quality of the employed pseudopotential parameters and GTO basis sets. The (4s4p1d)/[2s3p1d] GTO valence basis sets are very well suited to deriving the structural parameters of these molecules and, with the GCP density functional, to give rather good approximations for the dissociation energies.

3.2. *CuX* molecules

The results for bond lengths R_e , vibrational frequencies ω_e and dissociation energies D_e for the $^2\Pi$ and $^4\Sigma^-$ states of the CuX molecules obtained with the copper one- and 19-valence-electron pseudopotentials at different levels of approximation are summarized in Tables 4 and 5. For the copper 19-valence-electron pseudopotential the bond lengths were optimized at the SCF, CI-SD and CI-SD+SCC levels. Moreover, SPP and GCP density functionals have been used to approximate valence correlation effects at the SCF bond lengths. Taking the copper one-valence-electron pseudopotential, the bond lengths were optimized at the SCF+ Δ , CI-SD+ Δ + V_{pol} and CI-SD+SCC+ Δ + V_{pol} levels. For the bond lengths obtained at the CI-SD+SCC+ Δ + V_{pol} level using the basis sets A, we also performed calculations at the correlated level (CI-SD+SCC+ Δ + V_{pol} and CEPA-1+ Δ + V_{pol}) employing the extended basis sets B. In addition, the valence correlation effects have been calculated using the SPP and GCP density functionals at the bond lengths obtained at the SCF+ Δ level.

The bond lengths calculated for the $^2\Pi$ and $^4\Sigma^-$ states using the copper one- and 19-valence-electron pseudopotentials, respectively, are essentially comparable at all levels of approximation. The largest deviations are found for the $^4\Sigma^-$ state if electron correlation effects (CI-SD and CI-SD+SCC) are taken into account. For the vibrational frequencies, somewhat larger deviations are observed than in the case of the bond lengths if the results obtained with the two pseudopotentials are compared. Generally, the smallest deviations between the results of the one- and the 19-valence-electron

Table 4

Dissociation energies (in eV), bond lengths (in pm) and harmonic frequencies (in cm^{-1}) for the CuX molecules (X = Si, Ge, Sn) in the doublet ($^2\Pi$) and quartet ($^4\Sigma^-$) state using the one-valence-electron pseudopotential for copper^a

	R_e			ω_e		
	SCF + Δ	SCF + Δ + V_{pol}		SCF + Δ	SCF + Δ + V_{pol}	
		CI-SD	+SCC		CI-SD	+SCC
CuSi $^2\Pi$	241	231	232	305	314	310
CuSi $^4\Sigma^-$	233	225	225	312	315	317
CuGe $^2\Pi$	247	237	238	219	228	225
CuGe $^4\Sigma^-$	240	232	232	209	228	228
CuSn $^2\Pi$	264	254	256	185	189	187
CuSn $^4\Sigma^-$	259	250	251	168	188	188

	D_e						
	SCF + Δ	SCF + Δ + V_{pol}				CEPA-1 ^b	Exp. ^c
		SPP	GCP	CI-SD+SCC	CI-SD+SCC ^b		
CuSi $^2\Pi$	0.49	1.69	1.67	1.52	1.74	1.72	2.26 ^d (2.12)
CuSi $^4\Sigma^-$	1.00	1.20	1.47	1.26	1.43	1.45	
CuGe $^2\Pi$	0.42	1.68	1.66	1.47	1.69	1.66	1.93 ^e (1.92)
CuGe $^4\Sigma^-$	0.79	0.96	1.21	1.07	1.25	1.26	
CuSn $^2\Pi$	0.47	1.64	1.62	1.45	1.66	1.63	1.73 ^f (1.80)
CuSn $^4\Sigma^-$	0.68	0.85	1.08	0.93	1.11	1.11	

^a For abbreviations see text.

^b Results using the extended GTO basis sets B for the group 14 elements and copper for the bond lengths obtained at the SCF + Δ + V_{pol} + CI-SD+SCC level employing the GTO basis sets A.

^c Revised experimental dissociation energies are given in parentheses.

^d Ref. [8].

^e Ref. [9].

^f Ref. [10].

pseudopotential are found for the $^2\Pi$ state at the correlated levels. It is important to note that for the one-valence-electron pseudopotential the frequencies obtained at the SCF + Δ level are only slightly increased upon inclusion of electron correlation effects. Thus, the frequencies calculated using the one-valence-electron pseudopotential at the SCF + Δ level are certainly reasonably good estimates. As a consequence of this result it seems to be sufficient to calculate geometry and vibrational frequencies using the copper one-valence-electron pseudopotential at the SCF + Δ level.

At the SCF + Δ level both copper pseudopotentials yield roughly the same dissociation energies and the high spin $^4\Sigma^-$ state is energetically favored. The situation is different if electron correlation

effects are included, and the CI-SD+SCC and the CEPA-1 results clearly establish the $^2\Pi$ state to be the ground state of the CuX molecules. Contributions from quadruple excitations (+SCC), which generally increase for systems with larger numbers of valence electrons, play an important role in the case of the 19-valence-electron pseudopotential and amount to more than two thirds of the calculated total valence correlation energy (CI-SD+SCC). In the case of the one-valence-electron pseudopotential approximation the situation is quite different, and the size-consistency correction makes only minor contributions to the valence correlation energy (< 0.1 eV). It is evident from our results that the one-valence-electron approximation underestimates the dissociation energies even

Table 5

Dissociation energies (in eV), bond lengths (in pm) and harmonic frequencies (in cm^{-1}) for the CuX molecules (X = Si, Ge, Sn) in the doublet ($^2\Pi$) and quartet ($^4\Sigma^-$) state using the 19-valence-electron pseudopotential for copper^a

		R_e			ω_e		
		SCF	CI-SD	+SCC	SCF	CI-SD	+SCC
CuSi	$^2\Pi$	239	231	230	278	313	309
	$^4\Sigma^-$	235	230	229	264	288	285
CuGe	$^2\Pi$	247	240	239	202	221	219
	$^4\Sigma^-$	246	241	240	178	198	198
CuSn	$^2\Pi$	262	256	255	175	189	188
	$^4\Sigma^-$	260	256	255	151	165	167

		D_e					
		SCF	SPP	GCP	CI-SD+SCC ^b	CEPA-1 ^b	Exp. ^c
CuSi	$^2\Pi$	0.49	1.10	1.35	1.51	1.99	2.26 ^d (2.12)
	$^4\Sigma^-$	0.89	0.91	1.41	1.17	–	
CuGe	$^2\Pi$	0.40	1.01	1.23	1.47	1.86	1.93 ^e (1.92)
	$^4\Sigma^-$	0.68	0.74	1.17	1.02	–	
CuSn	$^2\Pi$	0.48	1.08	1.28	1.50	1.85	1.73 ^f (1.80)
	$^4\Sigma^-$	0.64	0.69	1.09	0.98	–	

^a For abbreviations see text.

^b Results using the (8s7p6d)/[6s4p3d] GTO basis set extended by two f polarization functions (see text) and the extended GTO basis sets B for the group 14 elements.

^c Revised experimental dissociation energies are given in parentheses.

^d Ref. [8].

^e Ref. [9].

^f Ref. [10].

at the CEPA-1 level using the extended basis sets B. Interestingly, the density functional results (SPP and GCP) are in good agreement with the CI-SD+SCC and CEPA-1 results using the extended basis sets B. If we explicitly include the d shell correlation effects for the copper center by employing the 19-valence-electron pseudopotential and the extended (8s7p6d2f)/[6s4p3d2f] GTO basis set for copper as well as the extended basis sets B for the group 14 elements, we can calculate dissociation energies that are in good agreement with the revised experimental values.

Based on the discussed results, it can be concluded that the CuX molecules (X is Si, Ge and Sn) can be treated using the one-valence-electron pseudopotential for copper, although the dissociation energies are somewhat underestimated. Moreover, it was found that the geometries and vibrational frequencies can be established with sufficient accuracy at the SCF+ Δ level.

Nonetheless, the molecular parameters used to revise the experimental dissociation energies of the CuX molecules have been taken from the calculations employing the copper one-valence-electron pseudopotential at the correlated level of approximation (SCF+ Δ + V_{pol} +CI-SD+SCC). As evidenced by the above results, the dissociation energies of this set of molecules can be approximated using density functional methods.

3.3. Cu_2X molecules

The calculated geometry, harmonic frequencies and dissociation energies of the Cu_2X molecules in the $^1\text{A}_1$ and $^3\text{B}_1$ states are given in Table 6. According to the aforementioned results on the CuX molecules, the geometry and harmonic frequencies of the three atomic Cu_2X molecules have been optimized at the SCF+ Δ level utilizing the copper one-valence-electron pseudopotential. The

Table 6

SCF + Δ bond lengths (in pm), angles (in degrees), harmonic frequencies (in cm^{-1}) and dissociation energies^a (in eV) for the Cu_2X molecules (X = Si, Ge, Sn) in the singlet ($^1\text{A}_1$) and triplet ($^3\text{B}_1$) state using the one-valence-electron pseudopotential copper

		$R_{\text{X-Cu}}$	$\angle(\text{CuXCu})$	Harmonic frequencies			
				A_1		B_2	
Cu_2Si	$^1\text{A}_1$	239	84	313	63	294	
	$^3\text{B}_1$	233	140	203	53	412	
Cu_2Ge	$^1\text{A}_1$	245	79	241	43	213	
	$^3\text{B}_1$	238	141	193	45	288	
Cu_2Sn	$^1\text{A}_1$	262	79	193	37	185	
	$^3\text{B}_1$	256	134	168	43	235	

		D_e							
		SCF + Δ + V_{pol}							
		SCF + Δ	SPP	GCP	CI-SD	+SCC	+SCC ^b	CEPA-1 ^c	Exp. ^d
Cu_2Si	$^1\text{A}_1$	1.39	3.75	3.80	3.21	3.52	3.80	4.20	–
	$^3\text{B}_1$	1.90	3.51	3.77	3.04	3.31	3.54	–	–
Cu_2Ge	$^1\text{A}_1$	1.25	3.61	3.65	3.11	3.28	3.68	4.01	–
	$^3\text{B}_1$	1.57	3.13	3.37	2.75	2.86	3.25	–	–
Cu_2Sn	$^1\text{A}_1$	1.26	3.55	3.58	3.00	3.15	3.53	3.89	4.68 ^e (4.91)
	$^3\text{B}_1$	1.48	2.98	3.19	2.58	2.68	3.03	–	–

^a Dissociation energies are given at different levels of theory; for abbreviations see text.

^b Results using the extended GTO basis sets B for the group 14 elements and copper for the structures obtained at the SCF + Δ level employing the GTO basis sets A.

^c Results using the 19-valence-electron pseudopotential and the extended (8s7p6d2f)/(6s4p3d2f) GTO basis set for copper and the extended GTO basis sets B for the group 14 elements for the structures obtained at the SCF + Δ level employing the GTO basis sets A.

^d Revised experimental dissociation energies are given in parentheses.

^e Ref. [10].

dissociation energies have been calculated at the SCF + Δ geometry using different levels of approximation. Generally, at all correlated levels core-valence correlation effects are included (V_{pol}). For the treatment of valence correlation effects, CI-SD, CI-SD + SCC and also density functional methods (SPP and GCP) have been applied.

The geometry parameters of the $^1\text{A}_1$ state of the Cu_2X molecules are comparable with those already observed in the case of the Cu_2X_2 and Cu_4X_4 molecules [14]. The rather small angles are not related to any copper–copper bonding, as evidenced by the vanishing corresponding two-center-shared electron numbers $\sigma_{\text{Cu-Cu}}$ for these molecules. For the $^3\text{B}_1$ state, as expected for such carbene analogues [70,71], the bond lengths are shortened and the bond angles enlarged compared with those observed for the $^1\text{A}_1$ state. The low harmonic

frequencies calculated for both electronic states of the Cu_2X molecules are indicative of a high molecular flexibility. In particular, the potential energy surface is shallow along the Cu–Cu coordinate. This is in line with the intuitive picture of chemical bonds between copper and the group 14 elements X and only weak copper–copper interactions. Consequently, the only significant shared electron number obtained is the $\sigma_{\text{Cu-X}}$ two-center-shared electron number with a value of 1.0. Moreover, population analysis results give no indication of multicenter contributions for the Cu_2X molecules. Correlation effects related with excitations from the d shell of copper are investigated for the Cu_2Sn molecule by CI-SD calculations using the copper 19-valence-electron pseudopotential and the extended basis sets for both copper and the group 14 elements. For the $^1\text{A}_1$ state the Cu–Sn

bond length is somewhat shortened to 251 pm, compared with 262 pm obtained using the pseudopotential with the larger core size. More significant is the change for the Cu–X–Cu bond angle, which is lowered to 68°, corresponding to a Cu–Cu distance of 282 pm. This on the other hand is not yet a Cu–Cu distance short enough for direct copper–copper interactions to matter, if compared with the equilibrium distance of 222 pm in Cu₂ [59]. The situation is different in the case of the Cu₂Se molecule, where Cu–Cu distances between 250 and 260 pm calculated at various correlated levels (MP2, CPF, CCSD, CCSD(T)) have been reported and therefore in this case direct copper–copper interaction has been considered and further demonstrated by population analysis results [33]. On the other hand, probably the shortest known non-bonding Cu–Cu distance is reported at 235 pm [72].

At the SCF + Δ level the ³B₁ state is energetically favored by \approx 0.2–0.5 eV for the three Cu₂X molecules. If correlation effects are included the energetic sequence is altered, as can be seen from the results summarized in Table 6, and the singlet state becomes the ground state. Both core–valence and valence correlation effects equally favor the singlet state by \approx 0.4 eV each. What about spin–orbit coupling, can it favor a triplet ground state? We can estimate its effect on the singlet–triplet separation by taking the corresponding atomic values. Since spin–orbit coupling is partially quenched by the molecular field [73], it can serve as a sort of upper limit. For silicon and germanium the spin–orbit coupling effect is negligible, and for tin a stabilization of \approx 0.3 eV is estimated on the basis of atomic results. Taking this into account, we still feel confident in assigning the Cu₂X molecules a ¹A₁ ground state.

The Cu₂Sn molecule is the only one in this series with a known experimental dissociation energy, which on the other hand had to be based on estimated molecular parameters. The estimates for the bond lengths agree reasonably well with our calculated values, whereas neither of the assumed molecular topologies could be confirmed [10]. With the molecular parameters calculated here for the Cu₂Sn molecule, we have been able to revise this experimental dissociation energy, and found a slightly increased value of 4.91 eV. As expected

from the results for the CuX molecules, the calculations utilizing the one-valence-electron pseudopotential with valence correlation effects approximated by density functional methods (SPP and GCP with basis sets A) give comparable results to CI-SD + SCC calculations employing the extended basis sets B. Although these calculations yield the largest dissociation energies obtained with the one-valence-electron approximation, they underestimate the experimental value determined for the Cu₂Sn molecule by more than 1 eV. If we explicitly include correlation effects due to excitations from the d shell of the two copper centers in the calculations by means of the 19-valence-electron pseudopotential (extended basis sets for copper and tin) we calculate a dissociation energy of 3.89 eV for the Cu₂Sn molecule, which is still 1 eV less than the revised experimental value. As in the case of the CuX molecules the latter treatment gave good agreement between the calculated and the experimental dissociation energies, we believe that the reported experimental value is probably too high. This on the other hand is already evident from the so-called additivity rule usually applied to estimate such atomization energies (cf. [9,10]). If no multicenter contributions are present, as is the case here, the estimated dissociation energy of the Cu₂Sn molecule should not exceed 4 eV. Therefore we anticipate the CEPA-1 results obtained with the 19-valence-electron pseudopotential for copper (see Table 6) will be good approximations for the dissociation energies of the Cu₂X molecules. It is important to note also that the results at all levels indicate that the dissociation energies of the Cu₂X molecules are within a range of \approx 0.3 eV, i.e. the dissociation energy of these molecules seems to be predominantly determined by copper and shows only minor dependence upon changes in the X atom. This is in agreement with the results obtained for the CuX molecules, where both our CEPA-1 results and the revised experimental dissociation energies show a similar behavior (differences are < 0.3 eV).

3.4. CuX₂ molecules

The geometry and the harmonic frequencies for the ²B₁ state of the CuX₂ molecules have been calculated at the SCF + Δ level. For the established minimum structure of each molecule the

Table 7

SCF + Δ bond lengths (in pm) and harmonic frequencies (in cm^{-1}) plus dissociation energies^a (in eV) for the CuX_2 molecules (X = Si, Ge, Sn) in the 2B_1 state using the one-valence-electron pseudopotential for copper

	$R_{\text{X-X}}$	$R_{\text{X-Cu}}$	Harmonic frequencies		
			A_1		B_2
CuSi ₂	218	252	591	250	172
CuGe ₂	223	259	319	176	104
CuSn ₂	270	279	227	147	90

	D_e							
	SCF + Δ + V_{pol}							
	SCF + Δ	SPP	GCP	CI-SD	+SCC	+SCC ^b	CEPA-1 ^c	Exp. ^d
CuSi ₂	3.21	5.17	5.61	4.53	4.83	5.43	5.61	–
CuGe ₂	2.42	4.43	4.84	3.98	4.27	4.67	4.81	5.24 ^e (5.09)
CuSn ₂	2.10	4.13	4.49	3.67	3.91	4.26	4.62	4.05 ^f (4.33)

^a Dissociation energies are given at different levels of theory; for abbreviations see text.

^b Results using the extended GTO basis sets B for the group 14 elements and copper for the structures obtained at the SCF + Δ level employing the GTO basis sets A.

^c Results using the 19-valence-electron pseudopotential and the extended (8s7p6d2f)/(6s4p3d2f) GTO basis set for copper and the extended GTO basis sets B for the group 14 elements for the structures obtained at the SCF + Δ level employing the GTO basis sets A.

^d Revised experimental dissociation energies are given in parentheses.

^e Ref. [9].

^f Ref. [10].

dissociation energy has been approximated at different levels. Core–valence (V_{pol}) and valence correlation effects (CI-SD, CI-SD + SCC, SPP and GCP) have been included. At the CI-SD + SCC + V_{pol} level we also performed calculations employing the extended GTO basis sets B for the group 14 elements and copper. Furthermore, the dissociation energies have been also calculated at the CEPA-1 level including d shell correlation effects at the copper center (19-valence-electron pseudopotential). In Table 7 the results of these calculations and the known experimental dissociation energies are summarized.

The calculated bond lengths for the CuX_2 molecules (Cu–X and X–X) are similar to those determined for the corresponding, bent doubly bridged, butterfly structure of the Cu_2Si_2 (Cu–Si 249 and Si–Si 216 pm) and Cu_2Sn_2 molecules (Cu–Sn 276 and Sn–Sn 268 pm) [14]. It is interesting to note that the X–X bond lengths in both types of molecules (CuX_2 and Cu_2X_2) are very similar to the calculated ground state equilibrium distances for

the related homonuclear dimers (Si–Si 221 and Sn–Sn 271 pm). The harmonic frequencies calculated for the CuX_2 molecules indicate a rather flat potential energy surface in the minimum region. As in the case of the Cu_2X_2 molecules, the vibration according to the highest harmonic frequency can be characterized as the symmetrical X–X stretching mode and, therefore, exhibits the greatest variation on changing the X atoms. Moreover, the value for this harmonic mode of the CuX_2 and Cu_2X_2 molecules resembles quite well the harmonic frequency calculated for the related homonuclear dimer X_2 (Si 575, Ge 317, and Sn 218 cm^{-1}) at the SCF level using the GTO basis sets A from Table 2.

The population analysis for the CuX_2 molecules reveals that multicenter bonding is a prominent feature. This is consistent with the results obtained for the Cu_2X_2 and Cu_4X_4 molecules [14]. As an example, for the three-center-shared electron number σ_{CuSn_2} a value of 0.4 is found for CuSn_2 and the same value is obtained for the butterfly

structure of the Cu_2Sn_2 molecule [14]. The same holds for the two-center CuSn contribution in these molecules with a value of 0.75; taking into account that the three-center contribution is already included, it is clear that both contributions, two- and three-center, are of equal importance.

The experimental dissociation energies of the CuGe_2 and CuSn_2 molecules have been revised on the basis of their molecular parameters derived herein. We found the experimental value for CuGe_2 decreased to 5.09 eV and that for CuSn_2 increased to 4.33 eV (see Table 7).

From the calculated dissociation energies for the CuX_2 molecules, it is evident that correlation effects are very important. The contributions from core–valence correlation effects range from 0.4 to 0.6 eV (increasing from silicon to tin). The valence correlation energies derived with the GCP density functional is about the same as that obtained from the size consistency corrected CI-SD calculation utilizing the extended basis sets B. Moreover, size-consistency effects are important for all three molecules, as can be seen by comparison of the CI-SD and CI-SD+SCC results (≈ 0.3 eV). The effects observed are actually similar to those found for the X_2 dimers. For the CuGe_2 and CuSn_2 molecules the calculated dissociation energies are in reasonably good agreement with the revised experimental values.

Since the properties of the CuX_2 molecules seem to be dominated by the constituent X_2 fragments, it is interesting to see whether this is also reflected in the values of the dissociation energies of these molecules. The dissociation energies themselves show a rather large variation of ≈ 1 eV (CEPA-1 results, see Table 7). If the energies for binding of one copper atom to the X_2 fragments, as $D_e(\text{CuX}_2) - D_e(\text{X}_2)$, are calculated, we find a mean value of 2.35 eV and a deviation of < 0.2 eV (2.54 for CuSi_2 , 2.22 for CuGe_2 , and 2.31 for CuSn_2). This gives an indication that the copper binding energy to the X_2 fragments seems to be independent of the X atoms. This fact is in agreement with the observations of Kingcade and Gingerich for a series of mixed metal clusters of group 11 and 14 elements. They found that the group 11 element energy of binding to group 14 element fragments appears to be determined by the group

11 element rather than by silicon, germanium or tin [12].

4. Summary

We have performed pseudopotential calculations on small mixed compounds of copper and the group 14 elements X, viz. Si, Ge and Sn and also the homonuclear dimers of the latter. The results of atomic test calculations and of calculations for the diatomic CuX and X_2 molecules indicate that the employed pseudopotentials and GTO basis sets provide a reliable description for these atomic systems. Moreover, molecular calculations show that it is possible to treat copper as an one-valence-electron atom in these mixed compounds, although in some cases, the CuX and Cu_2X molecules, it is necessary explicitly to include the d shell correlation effects for the copper atom in order to get good agreement with the revised experimental dissociation energies.

It has been shown that the geometry of the molecules considered here can reliably be determined at the SCF level if core–core interactions are included. The results of the molecular calculations have been compared with experimental and other theoretical values as available in the literature. The molecular parameters obtained for the CuX , Cu_2X , and CuX_2 molecules have been used to revise their experimental dissociation energies.

For the Cu_2X molecules we found a $^1\text{A}_1$ ground state. The calculations employing the copper one-valence-electron pseudopotential yield Cu–Cu distances longer than 312 pm and population analysis results give no indication of direct copper–copper interactions. To address further the question of possible copper–copper interactions, we performed for the Cu_2Sn molecule calculations at the correlated level explicitly including the copper 3d shell using our copper 19-valence-electron pseudopotential. For the reoptimized geometry at CI-SD, level the Cu–Sn bond length is somewhat shortened to 251 pm, whereas the Cu–X–Cu bonding angle decreases to 68° . Although the Cu–Cu distance is shortened to 282 pm this is still too long for direct copper–copper interactions, as compared to the equilibrium distance of 222 pm in Cu_2 [59].

The geometric parameters obtained for the CuX_2 molecules are in good agreement with those earlier reported for the corresponding Cu_2X_2 and Cu_4X_4 molecules [14]. In all these cases X–X interactions play an important role and determine the structure of the molecules. In this context it is important to note that multicenter bonding is a prominent feature of molecules containing X_2 and X_4 backbones. This can be seen already from the three-center shared electron numbers observed for the CuX_2 molecules, the smallest molecules containing an X_2 backbone.

We were able satisfactorily to calculate the dissociation energies of the molecules studied here. The only significant deviation from the experimental results is observed for the Cu_2Sn molecule. We attribute this fact to a probably overestimated experimental dissociation energy in this case. If one considers the fact that the CuX_2 molecules, in contrast to the Cu_2X molecules, exhibit extensive multicenter bonding contributions, a considerably higher dissociation energy can be expected in the former case (cf. the so-called additivity rule, see refs. [9,10]). This exactly corresponds to the results of our calculations. It would certainly be interesting to see how the other yet unknown experimental values fit into this scheme and compare with our predicted dissociation energies.

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- 3.07669, 2.04613, 1.07177; $p = 16.2083, 14.9547, 5.17794, 2.47567, 1.06449$; $d = 99.9899, 32.6097, 12.6394, 5.19991, 2.07686, 0.76938$. Sn: $s = 33.8040, 12.5941, 8.12990, 1.72766, 0.80702$; $p = 19.3005, 7.95070, 4.14882, 1.78745, 0.75189$; $d = 7.68136, 5.31032, 2.35730, 1.12759, 0.54251, 0.27000$.
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