

## Calculated energy levels of thallium and eka-thallium (element 113)

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Multiconfiguration Dirac-Fock and relativistic coupled cluster results are reported for electron affinities, ionization potentials, and excitation energies of Tl and element 113 and their cations. Large basis sets are used, with  $l$  up to 6, the Dirac-Fock or Dirac-Fock-Breit orbitals found, and the external 35 electrons of each atom are correlated by the coupled-cluster method with single and double excitations. Very good agreement with experiment is obtained for the Tl transition energies. As in the case of elements 111 [Eliav *et al.*, Phys. Rev. Lett. **73**, 3203 (1994)] and 112 [Eliav, Kaldor, and Ishikawa, Phys. Rev. A **52**, 2765 (1995)], strong relativistic stabilization of the  $7s$  orbital is observed for E113, leading to dramatic reduction (relative to Tl) in the energies of excitation from  $d^{10}$  to  $d^9$  levels. Thus the  $d^{10}s \rightarrow d^9s^2$  energy of E113 $^{2+}$  is 0.1 eV, compared to 8 eV for Tl $^{2+}$ . It is predicted that divalent or trivalent compounds of E113 with an open  $6d^9$  shell could possibly exist. The calculated electron affinities of Tl and E113 are  $0.40 \pm 0.05$  and 0.6–0.7 eV, respectively. [S1050-2947(96)01106-7]

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### I. INTRODUCTION

Superheavy elements, up to eka-gold, element 111 ( $A = 272$ ), have now been experimentally created [1]. One reason for studying them, apart from the nuclear physics involved, is the hope that the strong relativistic effects for the heavier elements would lend them exotic chemical properties, unknown for their lighter analogs. Indeed, it has already been shown that the eka-gold (E111) atom has a  $d^9s^2$  ground state [2,3] instead of the  $d^{10}s^1$  configurations of the lighter coinage metals. Similarly, the divalent eka-mercury (E112) cation has a  $d^8s^2$  ground state instead of the  $d^{10}$  of  $M^{2+}$ ,  $M = \text{Zn-Hg}$  [4].

Neutral Tl and its ions (up to Tl $^{3+}$ ) have ground states with a full  $5d^{10}$  shell; the excitation energies from the  $5d$  orbital are rather high. We now consider the intriguing possibility that the relativistic stabilization of the  $7s$  and destabilization of the  $6d$  shell are strong enough to lower open- $6d$ -shell states (which have higher  $7s$  or  $7p$  occupancy) of some E113 (eka-thallium) ions until they become low-lying (or even ground) states. The group 13 element E113 would then behave, at least in the gas phase, like a transition element. Although Dirac-Slater [5] and multiconfiguration Dirac-Fock (MCDF) [6] calculations on the  $d^{10}$  states of E113 have been published long ago and its chemistry has been discussed [2,7], this possibility appears to be new.

Numerous calculations have been performed for the energy levels of thallium or its ions [8–17]. The available experimental data include, in addition to standard references [18–20], new data for Tl IV [21]. Experimentally known energy levels and ionization potentials of thallium are calculated here to check the accuracy and provide calibration for the data on E113. The electron affinity of Tl is not known

accurately [20] and the value reported below is expected to provide a standard result.

Accurate theoretical prediction of transition energies in heavy atoms requires high-order inclusion of both relativistic and correlation terms in the Hamiltonian. An *ab initio* relativistic-coupled-cluster (RCC) method incorporating both effects has been applied recently to a series of heavy atoms, including gold [22], mercury [4], several lanthanides and actinides [23], and elements 104 [24], 111 [3], and 112 [4]. Calculated transition energies were in very good agreement with known experimental values, usually within a few hundred wave numbers. Even higher accuracy was obtained for fine-structure splittings.

### II. METHOD

The relativistic coupled cluster method has been described in our previous publications [22,25], and only a brief review is given here. We start from the projected Dirac-Coulomb (or Dirac-Coulomb-Breit) Hamiltonian [26,27],

$$H_+ = H_0 + V, \quad (1)$$

where (in atomic units)

$$H_0 = \sum_i \Lambda_i^+ h_D(i) \Lambda_i^+, \quad (2)$$

$$h_D(i) = c \boldsymbol{\alpha}_i \cdot \mathbf{p}_i + c^2(\beta_i - 1) + V_{\text{nuc}}(i) + U(i), \quad (3)$$

$$V = \sum_{i < j} \Lambda_i^+ \Lambda_j^+ (V_{\text{eff}})_{ij} \Lambda_j^+ \Lambda_i^+ - \sum_i \Lambda_i^+ U(i) \Lambda_i^+. \quad (4)$$

Here  $h_D$  is the one-electron Dirac Hamiltonian. An arbitrary potential  $U$  is included in the unperturbed Hamiltonian  $H_0$  and subtracted from the perturbation  $V$ . This potential is chosen to approximate the effect of the electron-electron interaction; in particular, it may be the Dirac-Fock self-consistent field potential. The nuclear potential  $V_{\text{nuc}}$  includes the effect of finite nuclear size.  $\Lambda_i^+$  are projection operators onto the positive-energy states of the Dirac Hamiltonian  $h_D$ . Because of their presence, the Hamiltonian  $H_+$  has normalizable, bound-state solutions. This approximation is known as the no-(virtual-)pair approximation, since virtual electron-positron pairs are not allowed in intermediate states. The form of the effective potential  $V_{\text{eff}}$  depends on the gauge used. In Coulomb gauge it becomes (in atomic units, correct to the second order in the fine-structure constant  $\alpha$ ) [28]

$$V_{\text{eff}} = \frac{1}{r_{12}} + B_{12} + O(\alpha^3), \quad (5)$$

where the frequency-independent Breit interaction is

$$B_{12} = -\frac{1}{2r_{12}} [\boldsymbol{\alpha}_1 \cdot \boldsymbol{\alpha}_2 + (\boldsymbol{\alpha}_1 \cdot \mathbf{r}_{12})(\boldsymbol{\alpha}_2 \cdot \mathbf{r}_{12})/r_{12}^2]. \quad (6)$$

In  $q$ -number theory the Dirac-Coulomb-Breit Hamiltonian  $H_+$  is rewritten in terms of normal-ordered products of the spinor operators,  $\{r^+s\}$  and  $\{r^+s^+ut\}$  [26,29]

$$\begin{aligned} H &= H_+ - \langle 0|H_+|0\rangle \\ &= \sum_{rs} f_{rs} \{r^+s\} + \frac{1}{4} \sum_{rstu} \langle rs||tu\rangle \{r^+s^+ut\}, \end{aligned} \quad (7)$$

where  $f_{rs}$  and  $\langle rs||tu\rangle$  are, respectively, elements of one-electron Dirac-Fock and antisymmetrized two-electron Coulomb-Breit interaction matrices over Dirac four-component spinors. The effect of the projection operators  $\Lambda^+$  is now taken over by the normal ordering, denoted by the curly braces in the equation above, which requires annihilation operators to be moved to the right of creation operators as if all anticommutation relations vanish. The Fermi level is set at the top of the highest occupied positive-energy state, and the negative-energy states are ignored.

The no-pair approximation leads to a natural and straightforward extension of the nonrelativistic open-shell coupled-cluster (CC) theory. The multireference valence-universal Fock space coupled-cluster approach is employed here, which defines and calculates an effective Hamiltonian in a low-dimensional model (or  $P$ ) space, with eigenvalues approximating some desirable eigenvalues of the physical Hamiltonian. According to Lindgren's formulation of the open shell CC method [30], the effective Hamiltonian has the form

$$H_{\text{eff}} = PH\Omega P, \quad (8)$$

where  $\Omega$  is the normal-ordered wave operator,

$$\Omega = \{\exp(S)\}. \quad (9)$$

The excitation operator  $S$  is defined in the Fock-space coupled-cluster approach with respect to a closed-shell ref-

erence determinant. In addition to the traditional decomposition into terms with different total ( $l$ ) number of excited electrons,  $S$  is partitioned according to the number of valence holes ( $m$ ) and valence particles ( $n$ ) to be excited with respect to the reference determinant,

$$S = \sum_{m \geq 0} \sum_{n \geq 0} \left( \sum_{l \geq m+n} S_l^{(m,n)} \right). \quad (10)$$

The upper indices in the excitation amplitudes reflect the partitioning of the Fock space into sectors, which correspond to the different numbers of electrons in the physical system. This partitioning allows for partial decoupling of the open-shell CC equations, since the equations in each sector do not involve excitation amplitudes from higher sectors. The eigenvalues of the effective Hamiltonian (8) in a sector directly give the correlated energies in that sector with respect to the correlated (0,0) reference state. These transition energies may be ionization potentials, electron affinities, or excitation energies, according to the presence of valence holes and/or valence particles.

In the present application, we use the (0,0), (0,1), (0,2), (1,0), (2,0), and (1,1) sectors. The lower index  $l$  in (10) is truncated at  $l=2$ . The resulting coupled cluster with single and double excitations (CCSD) scheme involves the fully self-consistent, iterative calculation of all one- and two-body virtual excitation amplitudes, and sums all diagrams with these excitations to infinite order. Negative-energy states are excluded from the  $Q$  space, and the diagrammatic summations in the CC equations are carried out only within the subspace of the positive-energy branch of the Dirac-Fock spectrum.

### III. CALCULATIONS

Preliminary Dirac-Fock (DF) calculations were performed with the GRASP program [31]. A homogeneously charged nuclear model was assumed. The  $A$  values are 204 and 277 for Tl and E113, respectively. Both single and multireference calculations were of the optimized level (OL) type. The Breit operator was included by perturbation theory. When possible, the results were compared with those calculated by Desclaux's program [32]. The energies were rounded to the nearest  $100 \text{ cm}^{-1}$ . In comparison with experiment or with accurate calculations, DF and MCDF results turn out to be of comparable quality.

The Fock-space relativistic-coupled-cluster method was applied to several ionization states of the thallium and element 113 atoms. Three sequences of the open-shell CC calculations were carried out for Tl, starting from the closed-shell systems  $\text{TI}^{3+} 5d^{10}$ ,  $\text{TI}^+ 5d^{10}6s^2$ , or  $\text{TI}^- 5d^{10}6s^26p_{1/2}^2$  (the latter is a closed-shell configuration due to the large relativistic splitting of the  $p$  shell), and then adding or removing electrons according to the schemes

$$\begin{aligned} \text{TI}^{3+}(0,0) &\rightarrow \text{TI}^{4+}(1,0) \rightarrow \text{TI}^{5+}(2,0) \\ &\rightarrow \text{TI}^{2+}(0,1) \rightarrow \text{TI}^+(0,2) \\ &\rightarrow \text{TI}^{3+*}(1,1), \end{aligned} \quad (11)$$

TABLE I. Basis sets for Tl and element 113. Members of the well- or even-tempered  $s$ -basis series used in the various  $l$  sectors are given.

	Basis	Ref.	$s$	$p$	$d$	$f$	$g$	$h$	$i$
Tl	$35s27p21d15f9g6h4i$	[36]	1–35	9–35	13–33	17–31	21–29	24–29	25–28
113	$35s26p20d14f9g6h4i$	[37]	1–35	9–34	13–32	17–30	21–29	24–29	25–28

with valence particles (orbitals where electrons are added)  $6s$  and  $6p$  and valence holes (orbitals from which electrons are removed)  $5d$ ,

$$\begin{aligned} \text{Tl}^+(0,0) &\rightarrow \text{Tl}^{2+}(1,0) \rightarrow \text{Tl}^{3+}(2,0) \\ &\rightarrow \text{Tl}(0,1) \rightarrow \text{Tl}^-(0,2) \\ &\rightarrow \text{Tl}^{+*}(1,1), \end{aligned} \quad (12)$$

with valence particles  $6p$  and  $7s$  and valence holes  $6s$ , and

$$\text{Tl}^-(0,0) \rightarrow \text{Tl}(1,0) \rightarrow \text{Tl}^+(2,0), \quad (13)$$

with valence holes  $6p$ . Similar schemes are used for element 113, except for some changes in the selection of valence holes and particles in scheme (12) caused by the different relative orbital energies in the heavier atom. Electrons were added in the  $7p$  and  $8s$  orbitals in the (0,1) and (0,2) sectors and removed from  $6d$  and  $7s$  in the (1,0) and (2,0) sectors; a smaller  $P$  space was used in the (1,1) sector, comprising all one-electron excitations from  $6d_{5/2}$  or  $7s$  to  $7p_{1/2}$ .

The Dirac-Fock [29] and RCC [22,25] programs are both written for spherical symmetry, utilizing the angular decomposition of the wave function and CC equations in a central field. The energy integrals and CC amplitudes which appear in the Goldstone-type diagrams defining the CC equations are decomposed in terms of vector-coupling coefficients, expressed by angular-momentum diagrams, and reduced Coulomb-Breit or  $S$  matrix elements, respectively. The reduced equations for single and double excitation amplitudes

are derived using the Jucys-Levinson-Vanagas theorem [30] and solved iteratively. This technique makes possible the use of larger basis sets.

To avoid ‘‘variational collapse’’ [33], the Gaussian spinors in the basis are made to satisfy kinetic balance [34]. They also satisfy relativistic boundary conditions associated with a finite nucleus, described here as a sphere of uniform proton charge [29]. The atomic masses used are 204.37 for Tl and 297 for element 113. This higher  $A$  value is close to the other expected island of stability for elements around  $Z = 113$  [35]. For excitation processes increasing the number of  $7s$  electrons by one, the change of  $A$  from 277 to 297 will increase the excitation energy by about  $10^2 \text{ cm}^{-1}$ . The speed of light  $c$  is 137.035 99 a.u.

The uncontracted well-tempered basis set of Huzinaga and Klobukowski [36] was used for Tl, and the universal basis set of Malli, DaSilva, and Ishikawa [37] was selected for element 113. The basis sets, which go up to  $i$  orbitals ( $l=6$ ), are summarized in Table I. Atomic orbitals with the same  $l$  but different  $k$  number (e.g.,  $p_{1/2}$  and  $p_{3/2}$ ) are expanded in the same basis functions. Correlated shells include the external 35 electrons of each atom, i.e., the  $5s5p5d4f6s6p$  electrons of Tl and the  $6s6p6d5f7s7p$  electrons of 113. Virtual orbitals with high orbital energies have been found to contribute very little to correlation effects on excitation energies; orbitals higher than 100 a.u. are therefore eliminated from the calculation, effecting considerable savings in computational effort.

The DF and MCDF calculations were carried out in Helsinki, and the RCC computations were done at Tel Aviv University.

TABLE II. Ionization potential (IP), excitation energies (EE), and electron affinity (EA) of Tl ( $\text{cm}^{-1}$ ). Ground state is  $6s^26p^2P_{1/2}$ . DF — Dirac Fock. B — Breit correction. CP — core polarization. PT — perturbation theory. PP — pseudopotential. MCDF — multiconfiguration Dirac Fock plus Breit correction. RCC1 — relativistic coupled cluster, scheme (12). RCC2 — relativistic coupled cluster, scheme (13).

Method	Ref.	IP	EE				EA
			$6s^26p(^2P_{3/2})$	$5d^96s^26p(^2D_{5/2})$	$6s6p(^4P_{1/2})$	$6s^27s(^2S_{1/2})$	
DF+CP	[8]		7712				
DF+PT	[13]	51 157	8114				
DF+PT	[14]	49 140					
PP	[11]		7409				
PP	[12]		7397				
MCDF <sup>a</sup>		42 400		96 900	34 000		
DF		45 100	7600	98 500	47 700	<0	
RCC1		49 279	7710			26 456	
RCC2		48 575				2677	
Expt.	[18]	49 264	7793		45 220	26 478	

<sup>a</sup>The number of configurations used is one for the Tl ground state, four for the  $\text{Tl}^+$  ground state, five for  $\text{Tl } ^2D_{5/2}$ , and four for  $\text{Tl } ^4P_{1/2}$ .

TABLE III. Ionization potential (IP) and excitation energies (EE) of Tl cations ( $\text{cm}^{-1}$ ). RCC1 — relativistic coupled cluster, scheme (12). RCC3 — scheme (11).

	State		Expt.	RCC1	RCC3	DF	Other	
			Tl <sup>+</sup> , ground-state $5d^{10}6s^2\ ^1S_0$					
IP			164 765	165 062	165 568	148 400		
EE	$6s6p$	$^3P_0$	49 451	50 663	49 468	38 300		
		$^3P_1$	52 393	53 772	52 464		46 703 [15] 51 780 [10] 52 110 [17]	
		$^3P_2$	61 725	63 283	61 931			
		$^1P_1$	75 660	77 673	76 392		74 670 [15] 77 436 [10] 75 358 [17]	
	$5d^96s^26p$	$^3F_2$	110 387			104 600		
			Tl <sup>2+</sup> , ground-state $5d^{10}6s^1\ ^2S_{1/2}$					
IP			240 600	240 520	241 073	227 100	237 700 [9]	
EE	$5d^{10}6p_{1/2}$	$^2P_{1/2}$	64 157		64 668			
	$5d^{10}6p_{3/2}$	$^2P_{3/2}$	78 970		79 568			
	$5d^96s^2$	$^2D_{5/2}$		65 942		71 000		
		$^2D_{3/2}$		84 316				
			Tl <sup>3+</sup> , ground-state $5d^{10}\ ^1S_0$					
IP			409 100		408 582	397 500		
EE	$5d^96s$	$^3D_3$	75 052	75 357	73 407	76 100		
		$^3D_2$	78 647	78 915	77 105			
		$^3D_1$	93 676	94 343	92 307			
		$^1D_2$	96 727	97 287	95 494			
	$5d^96p$	$J=2$	147 635		147 092			
		$J=3$	149 841		149 417			
		$J=2$	166 425		166 295			
		$J=1$	167 499		167 365			
		$J=4$	167 672		167 441			
		$J=2$	170 334		170 142			
		$J=3$	172 272		172 313			
		$J=1$	175 290		174 855			
		$J=0$	181 083		183 141			
		$J=3$	187 667		187 798			
		$J=0$	188 233		188 455			
		$J=0$	190 144		190 417			
		$5d^86s^2$	$J=4$		164 877			
			$J=2$			173 975		
	$J=3$				182 432			
	$J=0$				188 597			
	$J=2$				190 192			
	$J=1$				194 508			
	$J=4$				198 483			
		$J=2$		208 031				
		$J=0$		237 061				
			Tl <sup>4+</sup> , ground-state $5d^9\ ^2D_{5/2}$					
IP					528 479	517 200		
EE	$5d^9$	$^2D_{3/2}$			19 140	18 200		
	$5d^86s$	$^4F_{9/2}$				96 400		
	$5d^76s^2$	$^4F_{9/2}$				220 200		
			Tl <sup>5+</sup> , ground-state $5d^8\ ^3F_4$					
EE	$5d^8$	$^3F_2$			8695			
		$^3F_3$			18 268			
		$^3P_0$			24 255			
		$^3P_2$			26 126			
		$^3P_1$			30 519			
		$^1G_4$			34 707			
		$^1D_2$			44 338			
		$^1S_0$			74 284			

TABLE IV. Ionization potentials and excitation energies of element 113 and its ions ( $\text{cm}^{-1}$ ). RCC1 — relativistic coupled cluster, scheme (12). RCCB1 — same, including the Breit term (6). RCC2 — scheme (13). RCCB3 — scheme (11), Breit term included. MCDF — multiconfiguration Dirac-Fock ( $N_l$  and  $N_u$  are the number of configurations for the lower and upper states, respectively).

State		RCC1	RCCB1	RCC2	DF	MCDF	$N_l, N_u$	
IP (EA of 113)		113 <sup>-</sup> , ground-state $7s^2 7p_{1/2}^2 \ ^3P_0$						
		5143	5035	5919	800			
IP		113, ground-state $6d^{10} 7s^2 7p_{1/2} \ ^2P_{1/2}$						
		59 417	59 115	58 810	57 200	53 900	1,4	
EE	$7s^2 7p_{3/2}$	$^2P_{3/2}$	22 831	22 528	25 100			
	$7s^2 8s$	$^2S_{1/2}$	35 401	35 124				
	$7s 7p_{1/2}^2$	$^2S_{1/2}$			61 500	54 500	1,4	
	$6d^9 7s^2 7p^2$	$^2D_{5/2}$			47 400	46 600	1,5	
IP		113 <sup>+</sup> , ground-state $6d^{10} 7s^2 \ ^1S_0$						
				RCCB3				
EE	$6d^9 7s^2 7p_{1/2}$	$J=2$	193 513	193 053	192 646	177 300	180 600	4,1
		$J=3$	59 870	60 927		51 600	54 200	4,4
	$6d^{10} 7s 7p_{1/2}$	$J=0$	62 943	63 972				
		$J=1$	62 598	63 051	61 245	50 000	52 400	4,10
	$6d^{10} 7s 7p_{3/2}$	$J=2$	68 080	68 489	66 868			
		$J=1$			92 208			
					107 182			
IP		113 <sup>2+</sup> , ground-state $6d^{10} 7s \ ^2S_{1/2}$						
EE	$6d_{3/2}^4 6d_{5/2}^5 7s^2$	$^2D_{5/2}$	270 167	269 706	271 096	258 500	255 000	1,3
	$6d_{3/2}^3 6d_{5/2}^6 7s^2$	$^2D_{3/2}$	236	933		5000		
	$6d^{10} 7p_{1/2}$	$^2P_{1/2}$	31 066	31 411				
	$6d^{10} 7p_{3/2}$	$^2P_{3/2}$			74 779			
					111 044			
IP		113 <sup>3+</sup> , ground-state $6d^{10} \ ^1S_0$						
EE	$6d^9 7s$	$^3D_3$	5384	6025	366 312	355 300	353 500	3,10
		$^3D_2$	8748	9477	8738	4400	7900	3,2
	$6d^8 7s^2$	$J=4$	18 185	19 561				
		$J=2$	25 187	26 321				
	$6d^9 7s$	$J=1$	37 845	38 113	35 093			
	$6d^8 7s^2$	$J=0$	42 705	43 970				
	$6d^9 7s$	$J=2$	43 612	44 077	38 721			
		$J=3$	48 708	49 723				
		$J=2$	57 002	57 938				
		$J=1$	58 780	59 797				
		$J=4$	61 959	62 963				
	$6d^9 7p_{1/2}$	$J=2$			85 322			
	$6d^9 7p_{3/2}$	$J=3$			88 789			
IP		113 <sup>4+</sup> , ground-state $6d^9 \ ^2D_{5/2}$						
EE	$6d^8 7s$	$^4F_{9/2}$			471 338	458 400	460 100	10,15
	$6d^9$	$^2D_{3/2}$			31 836	11 500	14 700	10,5
	$6d^7 7s^2$	$^4F_{9/2}$				30 100	22 200	10,10
						46 200	49 800	10,3
EE		113 <sup>5+</sup> , ground-state $6d^8 \ ^3F_4$						
	$6d_{3/2}^4 6d_{5/2}^4$	$^3F_2$			4980			
		$^3P_0$			21 552			
		$^3F_3$			31 711			
	$6d_{3/2}^3 6d_{5/2}^5$	$^3F_2$			37 108			
		$^3P_1$			39 461			
		$^1G_4$			44 579			
	$6d_{5/2}^2 6d_{5/2}^6$	$^1D_2$			68 692			
		$^1S_0$			92 441			

TABLE V. Properties of group 13 elements (eV). Experimental data from Ref. [19]; calculated data, present work. In order to give the best possible results for E113, the results quoted are those that correspond to the values calculated for Tl that agree best with experiment, i.e., IP1 to IP3 are from the RCC1 calculations, scheme (12), IP4 is from the RCC3 calculations, scheme (11), and the EA's are from the RCC2 calculations, scheme (13). The Breit-corrected results were used in the case of E113.

Property	B(expt)	Al(expt)	Ga(expt)	In(expt)	Tl(expt)	Tl(calc)	113(calc)
EA	0.277(10)	0.441(10)	0.30(15)	0.3(2)	0.2(2)	0.40(5)	0.68(5)
IP1	8.298	5.986	5.999	5.786	6.108	6.110	7.306
IP2	25.155	18.829	20.514	18.870	20.428	20.47	23.96
IP3	37.931	28.448	30.71	28.03	29.83	29.83	33.47
IP4	259.375	119.992	64.2 <sup>a</sup>	54.4 <sup>a</sup>	50.7 <sup>a</sup>	50.66	45.42

<sup>a</sup>Reference [18].

## IV. RESULTS AND DISCUSSION

### A. Tl

The ionization potential, electron affinity, and several excitation energies of neutral Tl are reported and compared with experiment and previous calculations in Table II. The DF values are off by 2000–4000  $\text{cm}^{-1}$ ; the RCC results (the Breit term is expected to be small and is therefore left out) show better agreement, with values obtained by using  $\text{Tl}^+$  as reference [scheme (12)] falling within 100  $\text{cm}^{-1}$  of experiment. The ionization potential calculated by scheme (13) is off by 700  $\text{cm}^{-1}$ ; this is not surprising, since  $\text{Tl}^+$  orbitals are expected to be more suitable for describing ionization (and excitation) than those of  $\text{Tl}^-$ . It is interesting to note that the lowest  $d^9$  state is very high, about 12 eV above the ground state. The electron affinity of Tl is not known experimentally; Hotop and Lineberger [20] provide a rough, semi-empirical estimate of 0.2(2) eV. A previous calculation [38] using pseudopotentials and nonrelativistic configuration interaction in the valence shell obtained 0.27 eV; the neglect of spin-orbit interaction in the Tl atom may introduce significant error. Our calculations with  $\text{Tl}^-$  orbitals predict an electron affinity of 0.42 eV. These results are expected to be more reliable than the value of 0.33 eV obtained with  $\text{Tl}^+$  orbitals. The difference between these values indicates the precision of the CCSD calculations; we therefore put our electron affinity (EA) at  $0.40 \pm 0.05$  eV. The smallest EA of an alkali metal Cs is 0.4716 eV. Compounds with the ceside ion  $\text{Cs}^-$  have been made. One could thus speculate [39] that molecular  $\text{Tl}^-$  compounds could also be made.

Ionization potentials and excitation energies of Tl cations are reported in Table III. The DF results differ from experiment by 1000–17 000  $\text{cm}^{-1}$ . RCC results agree with available experimental data to a few hundred wave numbers, even for the very high levels of  $\text{Tl}^{3+}$ . There is a large separation between  $d^9$  and  $d^{10}$  levels for all ions, with the former higher by 70 000–100 000  $\text{cm}^{-1}$ .

### B. Element 113

The first, Dirac-Slater calculation of the ionization potential of element 113 gave 39 200  $\text{cm}^{-1}$  [5]. MCDF (point nucleus, average level) calculations by Pyper and Grant [6] predicted 57 300  $\text{cm}^{-1}$ , which is closer to the RCC value. Ionization potentials and excitation energies of the atom and its cations are collected in Table IV. The salient feature of the results is the relativistic stabilization of the  $7s$  and  $7p$

orbitals relative to the  $6d$ , in line with the previous observations [3,4]. This stabilization is not sufficient to change the ground-state electron configuration, with the possible exception of the dication, and all E113 species have ground states with a maximum  $6d$  occupancy. The excitation energies from  $6d^n(7s+7p)^m$  to  $6d^{n-1}(7s+7p)^{m+1}$  are, however, much lower than for Tl: 5.8 eV for neutral E113 vs 12.2 eV for Tl, 7.4 vs 13.7 eV for the monocations (the  $d^9s^2p$  is the first excited state of  $\text{E113}^+$ , whereas  $\text{Tl}^+$  has several lower-lying  $d^{10}sp$  states), 0.7 vs. 9.3 eV for the triply charged ion, and 1.8 eV for  $\text{E113}^{4+}$  compared to 12 eV for  $\text{Tl}^{4+}$ . It should be noted that the numbers quoted for the neutral and quadruply charged species are DF values and may have larger errors than RCC results, but the trend is clear. Of special interest is the doubly charged ion. While the  $d^{10}s \rightarrow d^9s^2$  excitation energy of  $\text{Tl}^{2+}$  is 66 000  $\text{cm}^{-1}$ , the corresponding value for  $\text{E113}^{2+}$  is a mere 900  $\text{cm}^{-1}$ , and it is conceivable that more accurate calculations may reverse the order and produce a  $d^9s^2$  ground state.

The stabilization of the  $7s$  orbital and the relatively low  $d^{10} \rightarrow d^9$  excitation energies in  $\text{E113}^{2+}$  and  $\text{E113}^{3+}$  mean that  $d^9$  states may play an important role in compounds of the element. Thus the  $\text{E113}^{2+}$  ( $6d^97s^2$ ) ion could form compounds which are chemically analogous to both  $\text{Cu}^{2+}$  ( $3d^9$ ) and  $\text{Tl}^+$  ( $6s^2$ ) compounds. For  $\text{Tl}^{2+}$  this configuration is energetically more remote. One  $\text{Tl}^{2+}$  compound with an unpaired electron has been reported and structurally characterized [40] but no theoretical analysis of the electronic structure of its  $\text{Pt}^{2+}-\text{Tl}^{2+}-\text{Pt}^{2+}$  core has been performed. The electron paramagnetic resonance spectrum suggests that the unpaired electron is in a  $6s6p$  hybrid orbital. This shows that the main-group element thallium can have open-shell compounds.

Finally, the calculated electron affinity of E113 is about 0.68 eV, which is significantly higher than for Tl, due to the relativistic stabilization of the  $7p_{1/2}^2$  shell. The appearance of the element as an anion is even more likely than for Tl.

The ionization potentials and electron affinities of all group 13 elements are shown in Table V. Only B and Al have reliable experimental electron affinities. In order to map the periodic trends, modern measurements for Ga, In, and Tl would be most welcome. The periodic trend for IP2 and IP3 shows a “secondary periodicity.” This term was introduced by Biron [41] in 1915 to characterize the empirically observed similarity of chemical properties for every *second* row in a given column of the periodic system. It was later shown

[42] that the anomalously strong binding of the  $4s$  and  $4p$  valence electrons in row 4 elements is caused by the  $d$ -shell (or "scandide") contraction due to filling of the  $3d$  shell. The anomalously strong binding of the  $6s$  and  $6p$  electrons in row 6 is due to both relativistic effects and the lanthanide contraction (filling of the  $4f$  shell) [42,43]. The result is that both Ga and Tl show higher values of the first three consecutive ionization potentials than indium, situated between them.

## V. SUMMARY AND CONCLUSION

Ionization potentials, excitation energies, and electron affinities of Tl and element 113 are calculated. Very good agreement with the known EE's and IP's of Tl and its ions is obtained. The EA of Tl is estimated at  $0.40 \pm 0.05$  eV, which is probably more accurate than the semiempirical estimate of  $0.2(2)$  eV [20]. This relatively high value raises the possibility of Tl<sup>-</sup> compounds. The E113 levels are characterized by

considerable relativistic stabilization of the  $7s$  and  $7p$  orbitals relative to  $6d$ , leading to dramatic decreases of  $d^n(s+p)^m \rightarrow d^{n-1}(s+p)^{m+1}$  excitation energies relative to Tl. These excitation energies are particularly low for E113<sup>+2</sup> and E113<sup>+3</sup>, 0.1 and 0.7 eV, respectively. It is therefore possible that the E113<sup>2+</sup> ( $6d^9 7s^2$ ) ion will form compounds resembling at the same time both Cu<sup>2+</sup>( $3d^9$ ) and Tl<sup>+</sup>( $6s^2$ ) compounds. The calculated EA of E113 is 0.6–0.7 eV.

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