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# The dissociation energy of the new diatomic molecules SiPb and GePb

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The diatomic molecules SiPb and GePb were for the first time identified by producing high temperature vapors of the constituent pure elements in a "double-oven-like" molecular-effusion assembly. The partial pressures of the atomic, heteronuclear, and homonuclear gaseous species observed in the vapor, namely, Si, Ge, Pb, SiPb, GePb, Pb<sub>2</sub>, Ge<sub>n</sub>, and Si<sub>n</sub> ( $n=2-3$ ), were mass-spectrometrically measured in the overall temperature ranges 1753–1961 K (Ge–Pb) and 1992–2314 K (Si–Pb). The dissociation energies of the new species were determined by second- and third-law analyses of both the direct dissociation reactions and isomolecular exchange reactions involving homonuclear molecules. The selected values of the dissociation energies at 0 K ( $D_0^\circ$ ) are  $165.1 \pm 7.3$  and  $141.6 \pm 6.9$  kJ/mol, respectively, for SiPb and GePb, and the corresponding enthalpies of formation ( $\Delta_f H_0^\circ$ ) are  $476.4 \pm 7.3$  and  $419.3 \pm 6.9$  kJ/mol. The ionization efficiency curves of the two species were measured, giving the following values for the first ionization energies:  $7.0 \pm 0.2$  eV (SiPb) and  $7.1 \pm 0.2$  eV (GePb). A computational study of the species SiPb and GePb was also carried out at the CCSD(T) level of theory using the relativistic electron core potential approach. Molecular parameters, adiabatic ionization energies, adiabatic electron affinities, and dissociation energies of the title species were calculated, as well as the enthalpy changes of the exchange reactions involving the other Pb-containing diatomics of group 14. Finally, a comparison between the experimental and theoretical results is presented, and from a semiempirical correlation the unknown dissociation energies of the SiSn and PbC molecules are predicted as  $234 \pm 7$  and  $185 \pm 11$  kJ/mol, respectively. © 2007 American Institute of Physics. [DOI: 10.1063/1.2752803]

## I. INTRODUCTION

Within the general interest in metallic clusters that, besides their fundamental importance, stems mainly from the foreseen application in new catalysts, nanostructured alloys, and electronic devices,<sup>1–3</sup> the purpose of this work is to contribute to the knowledge of the chemical bond in intermetallic molecular species. Indeed, although the simple diatomic molecules are the fundamental building blocks of larger structures, basic information, such as the bond energy, is far from being complete across the entire periodic table.

Molecules containing group 14 elements have generated a special interest because of their possible application in areas such as new sensors and cluster materials.<sup>4–8</sup> Several studies were carried out investigating the adsorption properties and dynamics of lead on silicon and germanium substrates.<sup>9–13</sup> However, as Gigli *et al.*<sup>14</sup> previously pointed out, only half of the ten intragroup 14 heteronuclear diatomic molecules were energetically characterized, and, in particu-

lar, none of those contained lead. In our continuing effort to investigate and determine the thermodynamic properties of group 14 molecules, we present the results of high temperature Knudsen effusion mass spectrometry (KEMS) experiments, which enabled us to identify the new diatomics SiPb and GePb. Attention has been focused on these two molecules for the special interest aroused by the lead-containing molecules, where relativistic effects may have an important role in determining the energetics of the molecular aggregates.<sup>15–17</sup> No report on these species was previously published, apart from the mainly semiempirical calculations carried out by Mazzone<sup>18</sup> to examine the size-dependent effects in Si, Ge, Pb, Si–Pb, and Ge–Pb clusters.

In this KEMS study, the first experimental determination of the bond energy of SiPb and GePb is reported, together with their ionization energies. Quantum mechanical computations at the coupled cluster single and double excitations including the effect of connected triple excitations [CCSD(T) level] are also presented. This computational part has been performed first of all to get reliable information on the molecular parameters needed in analyzing the primary experi-

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mental data, and secondly to inquire into the performance of the CCSD(T) method in calculating the energetic properties of the heavy molecules under study.

## II. EXPERIMENT

The KEMS technique has been employed in this investigation. Its features are well summarized in Ref. 19 and in references cited therein. Details on our apparatus have been given previously.<sup>20</sup> Briefly, a single focusing 90° magnetic sector mass spectrometer was used. A secondary electron multiplier provided the detection of ions, which were produced from the vapors effusing from the Knudsen cell by electron impact with an electron emission current generally regulated at 1.0 mA. The ion source features allowed the determination of the ionization efficiency curves (IEC) by continuously varying the energy of the electrons up to 100 V.

Analogous to what was noted in Ref. 14, the large difference in volatility between pure Pb and either Ge or Si poses the problem of which sample to use in the Knudsen cell acting as the molecular source. Indeed, to promote the equilibrium formation of the diatomic heteronuclear molecules, a rather large partial pressure of both the constituent metal atoms must be realized in the Knudsen cell. On the other hand, molecular-effusion conditions must be met in the course of the experiment in order to preserve the relation between the measured ion current and the partial pressure realized inside the Knudsen cell (see Sec. IV B). Therefore, instead of a simple alloy of the two elements, a better and more convenient way to produce equilibrated partial pressures of the two atoms in the molecular source is to use an experimental approach quite similar to the double oven technique.<sup>21</sup> We used a crucible design similar to that employed by Hilpert and Ruthardt<sup>22</sup> and Gigli *et al.*<sup>14</sup> The upper crucible, which acts as the molecular source and is loaded with the lower fugacity metal (Ge or Si), was heated with a tungsten coil resistor while the lower crucible, loaded with lead and connected with a homemade tantalum tube (50 mm in length, 1.0 mm in internal diameter, and 0.05 mm in thickness), was kept in a much lower temperature zone of the assembly. Typically, with the upper compartment (loaded with Ge or Si) at 1800 K, the lower one (containing Pb) was at 1150 K. As a consequence, the flux of Pb vapors generated in the lower crucible was largely superheated in the upper compartment. Both crucibles were machined from high purity and high density graphite blocks. Temperatures of the Knudsen cell were measured with a W–Re/W–Re 5%/26% thermocouple, whereas those of the lower crucible with a Pt/Pt–Rh 10% thermocouple.

## III. COMPUTATIONAL METHODS

Due to the lack of experimental investigations on the spectroscopic parameters of the SiPb and GePb molecules, electronic structure calculations were carried out in order to determine the molecular constants necessary to calculate the thermodynamic functions needed for the data analysis. Besides SiPb, GePb, and the pertinent atomic species, calculations were performed for the positive and negative ions

SiPb<sup>±</sup> and GePb<sup>±</sup>. As detailed in Sec. V, in order to put into perspective the dissociation energies measured and calculated here, calculations were also performed for the other group 14 atoms, the homonuclear dimers (except C<sub>2</sub>), and selected intragroup 14 diatomics, such as SiSn, PbC, and PbSn. All the computations were carried out using the GAUSSIAN 03 program package.<sup>23</sup> The CCSD(T) level of theory was chosen together with increasingly larger basis sets up to the augmented correlation consistent polarized valence triple zeta (aug-cc-pVTZ) for C,<sup>24,25</sup> Si,<sup>26</sup> and Ge,<sup>27</sup> and up to aug-cc-pVTZ with small core relativistic pseudopotential (aug-cc-pVTZ-pp) for Sn and Pb.<sup>28</sup> As far as the SiPb, GePb, Si, Ge, and Pb species are concerned, quadruple zeta basis sets were also used to extrapolate the calculated dissociation energies of SiPb and GePb to the complete basis set limit (CBS). The molecular constants (harmonic vibrational frequencies and bond distances) and energetics, including adiabatic ionization energies (AIEs), adiabatic electron affinities (AEAs), term energies, and dissociation energies ( $D_0^0$ ) were computed for SiPb and GePb.

## IV. RESULTS

### A. Identification of ions

In the course of the experiments dedicated to the germanium-lead system, in addition to the atomic ions Ge<sup>+</sup> and Pb<sup>+</sup>, a number of germanium single ionized polymeric ions have been observed in the mass spectrum, up to Ge<sub>5</sub><sup>+</sup>. All these ions, as usual, were identified by the measurement of mass-to-charge ratios, isotopic abundances, shutter profiles, and IEC. The shutter profiles were obtained by interposing a movable slit (shutter) into the molecular beam in order to distinguish between ions produced from species in the beam and from residual gases with the same mass-to-charge ratio in the ionization region of the mass spectrometer. In addition, in the temperature range 1753–1961 K, the GePb<sup>+</sup> ion has been also identified. The isotopic abundance of this ion, distributed in the 274–284 amu range, overlaps with that of the Ge<sub>4</sub><sup>+</sup> ion, whose isotopic distribution spans between 280 and 304 amu. A careful analysis of the relative ion intensity of all the masses between 274 and 279, together with the superimposed masses, made it possible to unambiguously assign the observed ions to the GePb<sup>+</sup> molecular ion. Furthermore, in order to avoid this superposition of signals, the GePb<sup>+</sup> ion at  $m/q=278$  amu was monitored during the experiments.

The appearance energies (AEs) of the atomic and homonuclear species were determined by calibrating the energy scale with the well established ionization energy of gaseous gold, using the linear extrapolation method. The values so obtained compare favorably with previous determinations (selected literature data are reported in parentheses), confirming that the observed ions were formed by primary ionization processes (eV): Ge<sup>+</sup>, 7.9±0.3 [7.88 (Ref. 29)], Pb<sup>+</sup>, 7.4±0.3 [7.415 (Ref. 29)], Ge<sub>2</sub><sup>+</sup>, 7.8±0.3 [7.58–7.76 (Refs. 30–32)], Ge<sub>3</sub><sup>+</sup>, 8.3±0.3 [7.97–8.09 (Refs. 32 and 33)], and Ge<sub>4</sub><sup>+</sup>, 8.2±0.4 [7.87–7.97 (Refs. 32 and 33)]. A more thorough analysis has been performed on the ionization efficiency curves of the GePb<sup>+</sup> ion, whose AE was evaluated by means of four different methods proposed in the literature,<sup>34</sup>

TABLE I. Appearance energies (eV) of the SiPb<sup>+</sup> and GePb<sup>+</sup> ions obtained from the ionization efficiency curves by different methods of analysis.

	Vanishing current	Linear extrapolation	Semilog plot	Extrapolated voltage	Average value (proposed)
SiPb	7.05	6.90	7.16	6.92	7.0±0.2
GePb	7.45	6.94	7.02	7.04	7.1±0.2

namely, the vanishing current, linear extrapolation, semilog plot, and extrapolated voltage difference (Table I). The proposed value of AE(GePb), which is a first determination, is 7.1±0.2 eV and is based on data collected in the temperature range 1900–1960 K.

Ions similar to those found for the Ge–Pb systems were observed in our silicon-lead experiments. Indeed, atomic lead and silicon ions, together with a number of silicon polymer ions Si<sub>2</sub><sup>+</sup>, Si<sub>3</sub><sup>+</sup>, Si<sub>4</sub><sup>+</sup>, and Si<sub>5</sub><sup>+</sup>, have been identified in the mass spectrum. In this system, even if only in a handful of cases, the diatomic Pb<sub>2</sub><sup>+</sup> ion could also be detected in the spectrum, at the limit of instrumental sensitivity. In addition, the new molecular ion SiPb<sup>+</sup> has been observed. All ions have been identified as previously described for the Ge–Pb system. Once again, the AEs of the atomic and homonuclear species were in agreement with literature values (eV): Si<sup>+</sup>, 8.0±0.3 [8.149 (Ref. 29)], Pb<sup>+</sup>, 7.0±0.4 [7.415 (Ref. 29)], Si<sub>2</sub><sup>+</sup>, 7.5±0.3 [7.4±0.4 (Ref. 35) and 7.913 (Ref. 36)], Si<sub>3</sub><sup>+</sup>, 7.8±0.5 [8.0 (Ref. 35)], and Si<sub>4</sub><sup>+</sup>, 7.9±0.5 [7.6 (Ref. 35)]. The AE of the new molecule SiPb reported in Table I is the result of a more complete analysis and is an average of a number of determinations, giving the final value AE(SiPb) = 7.0±0.2 eV. In this case the ionization efficiency curves analyzed have been measured at 2280–2310 K.

In both the germanium-lead and silicon-lead systems, the aforementioned ion intensities have been recorded as a function of the temperature of the molecular source (upper crucible) to process the equilibrium data by the second- and third-law thermodynamic analyses. In order to minimize the possible superimposition with the signal of background ions and the possible effects of undetected fragmentations, the ion intensities of interest in the subsequent thermodynamic analysis were recorded at 10 and 11 eV electron energy for the Si–Pb and Ge–Pb systems respectively, and are reported in Tables II and III.

## B. Thermodynamic results

The measured ion intensities  $I_i^+$  were converted into partial pressures of the corresponding neutral species in the Knudsen cell through the usual relation:<sup>19</sup>  $P_i = k f_i I_i^+ T$ , where  $k$  is the instrument sensitivity constant and the factor  $f_i = (\sigma_i \gamma_i a_i)^{-1}$ , specific to each ion  $i$ , includes the electron impact ionization cross section  $\sigma$ , the multiplier gain  $\gamma$ , and the isotopic abundance  $a$ .

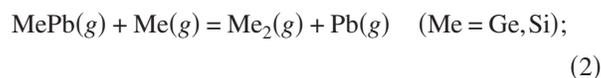
The instrument sensitivity constants have been evaluated with separate experiments exploiting the well known Au<sub>2</sub>(g) = 2Au(g) and Si<sub>2</sub>(g) = 2Si(g) equilibria for the Ge–Pb and Si–Pb systems, respectively. The individual constants for each experiment are reported in the footnotes to Tables II and III.

From the ion intensities of Tables II and III and the derived partial pressures, a number of gas phase equilibria could be studied in order to derive the dissociation energies of the new molecules GePb and SiPb.

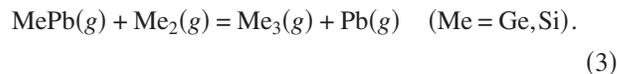
- (a) the direct dissociation reaction



- (b) the isomolecular exchange reactions with the corresponding dimers Ge<sub>2</sub> and Si<sub>2</sub>,



- (c) the isomolecular exchange reaction with the corresponding couple, dimer-trimer, of germanium and silicon clusters,



In addition, in the case of the Si–Pb system, by exploiting the observation of the Pb<sub>2</sub> molecule it has been possible to analyze two data points of the isomolecular exchange reaction of the SiPb molecule with this dimer,



It is useful to recall that while the values of the equilibrium constants for reaction (1) depend on the instrument sensitivity constants, all the other equilibria are independent of this parameter.

As a rule, equilibrium data were processed by the so-called second- and third-law analyses.<sup>19,37</sup> Briefly, the second-law procedure allows the determination of the enthalpy change at the average temperature of the experiment,  $\Delta_r H_{(T)}^\circ$ , by a least squares analysis of a van't Hoff plot,  $\ln K_p$  vs  $1/T$ , where  $K_p$  is the equilibrium constant. This value can be reduced to 0 K reference temperature through the use of the heat content functions,  $H_T^\circ - H_0^\circ$  (HCF<sub>0</sub>), of reactants and products. On the contrary, the third-law procedure, through the relation  $\Delta_r H_0^\circ = -RT \ln K_p - T \Delta_r [(G_T^\circ - H_0^\circ)/T]$ , where  $-(G_T^\circ - H_0^\circ)/T$  is the Gibbs energy function (GEF<sub>0</sub>), allows the determination of a  $\Delta_r H_0^\circ$  value at each experimental temperature point.

The necessary HCF<sub>0</sub> and GEF<sub>0</sub> of the various atomic and molecular species involved in equilibria (1)–(4) are discussed in Secs. IV D and IV E of this paper. In Sec. IV E we present also the analysis made for the selection of the ancillary enthalpies of atomization of the germanium, silicon, and

TABLE II. Ion intensities (A) measured in the experiments on the Ge-Pb system. [Values measured at 11 eV electron energy. The ratio to the corresponding values at the maximum ionization efficiency are 0.39, 0.35, 0.66, 0.56, and 0.40 for  $\text{Ge}^+$ ,  $\text{Pb}^+$ ,  $\text{GePb}^+$ ,  $\text{Ge}_2^+$ , and  $\text{Ge}_3^+$ , respectively. The corresponding specific factors ( $f$ ) are in the same order, 8.03, 10.39, 12.32, 6.73, and 10.03.]

Expt. <sup>a</sup>	$T$ (K)	$^{74}\text{Ge}^+$	$^{208}\text{Pb}^+$	$^{278}\text{GePb}^+$	$^{146}\text{Ge}_2^+$	$^{218}\text{Ge}_3^+$
1	1828	$8.10 \times 10^{-9}$	$1.17 \times 10^{-8}$	$1.20 \times 10^{-12}$	$3.65 \times 10^{-10}$	
	1891	$1.41 \times 10^{-8}$	$1.86 \times 10^{-8}$	$2.40 \times 10^{-12}$	$6.70 \times 10^{-10}$	
	1923	$1.80 \times 10^{-8}$	$2.00 \times 10^{-8}$	$2.55 \times 10^{-12}$	$9.00 \times 10^{-10}$	
	1924	$1.92 \times 10^{-8}$	$1.74 \times 10^{-8}$	$2.60 \times 10^{-12}$	$9.30 \times 10^{-10}$	
	1956	$2.45 \times 10^{-8}$	$2.07 \times 10^{-8}$	$3.10 \times 10^{-12}$	$1.26 \times 10^{-9}$	
	1883	$1.26 \times 10^{-8}$	$1.26 \times 10^{-8}$	$1.40 \times 10^{-12}$	$5.90 \times 10^{-10}$	
	1834	$7.80 \times 10^{-9}$	$8.10 \times 10^{-9}$	$6.50 \times 10^{-13}$	$3.50 \times 10^{-10}$	
	1802	$5.70 \times 10^{-9}$	$6.00 \times 10^{-9}$	$4.00 \times 10^{-13}$	$2.40 \times 10^{-10}$	
2	1907	$1.32 \times 10^{-8}$	$8.10 \times 10^{-9}$	$1.15 \times 10^{-12}$	$6.70 \times 10^{-10}$	
	1950	$1.80 \times 10^{-8}$	$9.90 \times 10^{-9}$	$1.50 \times 10^{-12}$	$1.00 \times 10^{-9}$	
3	1845	$7.80 \times 10^{-9}$	$1.14 \times 10^{-8}$	$1.00 \times 10^{-12}$	$3.40 \times 10^{-10}$	$1.80 \times 10^{-10}$
	1890	$1.14 \times 10^{-8}$	$1.67 \times 10^{-8}$	$1.90 \times 10^{-12}$	$5.40 \times 10^{-10}$	$2.60 \times 10^{-10}$
	1912	$1.47 \times 10^{-8}$	$2.04 \times 10^{-8}$	$3.00 \times 10^{-12}$	$7.50 \times 10^{-10}$	$3.50 \times 10^{-10}$
	1933	$1.71 \times 10^{-8}$	$2.55 \times 10^{-8}$	$3.90 \times 10^{-12}$	$9.00 \times 10^{-10}$	$4.40 \times 10^{-10}$
	1945	$1.89 \times 10^{-8}$	$2.90 \times 10^{-8}$	$4.50 \times 10^{-12}$	$9.00 \times 10^{-10}$	
	1956	$1.97 \times 10^{-8}$	$3.10 \times 10^{-8}$	$5.00 \times 10^{-12}$	$1.05 \times 10^{-9}$	$5.40 \times 10^{-10}$
	1945	$1.86 \times 10^{-8}$	$2.90 \times 10^{-8}$	$4.40 \times 10^{-12}$	$1.02 \times 10^{-9}$	
	1961	$1.94 \times 10^{-8}$	$3.10 \times 10^{-8}$	$5.30 \times 10^{-12}$	$1.02 \times 10^{-9}$	$5.10 \times 10^{-10}$
	1944	$1.89 \times 10^{-8}$	$3.00 \times 10^{-8}$	$4.50 \times 10^{-12}$	$9.75 \times 10^{-10}$	$4.65 \times 10^{-10}$
	1902	$1.23 \times 10^{-8}$	$2.10 \times 10^{-8}$	$2.70 \times 10^{-12}$	$6.10 \times 10^{-10}$	
	1880	$1.02 \times 10^{-8}$	$1.74 \times 10^{-8}$	$1.90 \times 10^{-12}$	$5.00 \times 10^{-10}$	$2.55 \times 10^{-10}$
	1824	$5.60 \times 10^{-9}$	$1.11 \times 10^{-8}$	$1.00 \times 10^{-12}$	$2.60 \times 10^{-10}$	
	1765	$3.10 \times 10^{-9}$	$6.90 \times 10^{-9}$	$4.50 \times 10^{-13}$	$1.29 \times 10^{-10}$	
4	1753	$2.90 \times 10^{-9}$	$6.20 \times 10^{-9}$	$3.50 \times 10^{-13}$	$1.11 \times 10^{-10}$	$6.20 \times 10^{-11}$
	1813	$5.50 \times 10^{-9}$	$1.13 \times 10^{-8}$	$9.00 \times 10^{-13}$	$2.65 \times 10^{-10}$	$9.15 \times 10^{-11}$
	1815	$5.90 \times 10^{-9}$	$1.13 \times 10^{-8}$	$1.05 \times 10^{-12}$	$2.45 \times 10^{-10}$	
	1851	$8.85 \times 10^{-9}$	$1.67 \times 10^{-8}$	$1.80 \times 10^{-12}$	$4.25 \times 10^{-10}$	$2.10 \times 10^{-10}$
	1882	$1.19 \times 10^{-8}$	$2.10 \times 10^{-8}$	$2.10 \times 10^{-12}$	$5.85 \times 10^{-10}$	$3.00 \times 10^{-10}$

<sup>a</sup>The instrument constant ( $\text{bar A}^{-1} \text{K}^{-1}$ ) is equal to 0.930, 1.307, 1.217, and 1.014 in experiments 1–4, respectively.

lead homonuclear molecules involved in the equilibria.

Coming back to the conversion of measured currents into partial pressures, we note that while the  $\sigma_i$  and  $\gamma_i$  values do not affect the second-law enthalpy changes of the studied reactions, the influence of these parameters on the third-law results deserves a brief comment. For the cross sections, experimental values are available for a number of atomic species,<sup>19</sup> whereas these data are still largely lacking even for simple molecules. Therefore, molecular cross sections must be estimated by approximate methods.<sup>19,38</sup> Cross sections for Pb, Ge, and Si atoms were experimentally determined by Freund *et al.*<sup>39</sup> as, respectively, 8.32, 7.46, and 6.69 Å<sup>2</sup>. A lower value for Pb (7.61 Å<sup>2</sup>) was obtained more recently<sup>40</sup> (all the above values are given at the respective maximum ionizing energy).

In order to test the sensitivity of our results to errors in the estimated molecular cross sections, we used two procedures: one based on the additivity of atomic cross sections reduced by a constant factor and one based on an empirical model devised by Hastie.<sup>38</sup> Using the additivity approach, which is the oldest approach and is still the method of choice in KEMS studies, a number of values for the reducing con-

stant have been proposed in the literature, generally ranging from 0.75 to 0.90 for diatomic species. The most recent assessment<sup>19</sup> gives for  $\sigma_{M_2}$  and  $\sigma_{M_4}$  the recommended values of, respectively,  $1.80\sigma_M$  and  $2.25\sigma_M$ , corresponding to additivity-reducing factors of 0.90 and 0.5625. Interpolation between these values would lead to the relation  $\sigma_{M_3} = 2.025\sigma_M$  for trimers, corresponding to a reducing factor of 0.675. In Hastie's model, the cross section of the species AB is calculated from the cross sections of elements isoelectronic with the ions  $A^+$  and  $B^-$ , their ionization energies, and the ionization energy of the species AB as well. Developed for ionic or polar molecules, the model has also been applied to covalent and homonuclear  $A_2$  species.<sup>14,38</sup> In the latter case, the element isoelectronic with the dipositive  $A^{2+}$  ion is involved in the calculation. In view of the low polarity of the SiPb and GePb molecules, as revealed by our calculations (the computed Mulliken charges on Pb atoms in the  $^3\Sigma^-$  ground electronic state are +0.07 and +0.16, respectively), we tentatively handled these molecules either as  $\text{Pb}^+\text{Me}^-$  species or "homonuclear-like." As Hastie's model was optimized for the atomic cross section set calculated by Mann<sup>41</sup>

TABLE III. Ion intensities (A) measured in the experiments on the Si–Pb system. [Values measured at 10 eV electron energy. The ratio to the corresponding values at the maximum ionization efficiency are 0.25, 0.49, 0.61, 0.56, 0.55, and 0.60 for Si<sup>+</sup>, Pb<sup>+</sup>, SiPb<sup>+</sup>, Si<sub>2</sub><sup>+</sup>, Si<sub>3</sub><sup>+</sup>, and Pb<sub>2</sub><sup>+</sup>, respectively. The corresponding specific factors (*f*) are, in the same order, 3.46, 7.49, 4.76, 1.32, 1.25, and 7.90.]

Expt. <sup>a</sup>	<i>T</i> (K)	<sup>28</sup> Si <sup>+</sup>	<sup>208</sup> Pb <sup>+</sup>	<sup>236</sup> SiPb <sup>+</sup>	<sup>56</sup> Si <sub>2</sub> <sup>+</sup>	<sup>84</sup> Si <sub>3</sub> <sup>+</sup>	<sup>420</sup> Pb <sub>2</sub> <sup>+</sup>
1	1992	5.49 × 10 <sup>-9</sup>	5.69 × 10 <sup>-9</sup>	3.57 × 10 <sup>-13</sup>			
	2114	1.29 × 10 <sup>-8</sup>	1.2 × 10 <sup>-8</sup>	8.33 × 10 <sup>-13</sup>	9.66 × 10 <sup>-10</sup>	6.45 × 10 <sup>-10</sup>	
	2224	5.88 × 10 <sup>-9</sup>	3.75 × 10 <sup>-8</sup>	8.33 × 10 <sup>-13</sup>			
2	2031	8.25 × 10 <sup>-9</sup>	6.25 × 10 <sup>-9</sup>	4.00 × 10 <sup>-13</sup>	4.20 × 10 <sup>-10</sup>	2.40 × 10 <sup>-10</sup>	
	2028	8.10 × 10 <sup>-9</sup>	6.20 × 10 <sup>-9</sup>	3.00 × 10 <sup>-13</sup>	4.50 × 10 <sup>-10</sup>	1.85 × 10 <sup>-10</sup>	
3	2030	7.80 × 10 <sup>-9</sup>	7.10 × 10 <sup>-9</sup>	4.00 × 10 <sup>-13</sup>	4.60 × 10 <sup>-10</sup>		
	2123	2.20 × 10 <sup>-8</sup>	1.50 × 10 <sup>-8</sup>	1.55 × 10 <sup>-12</sup>			
	2138	2.60 × 10 <sup>-8</sup>	1.44 × 10 <sup>-8</sup>	1.75 × 10 <sup>-12</sup>		1.44 × 10 <sup>-9</sup>	
	2139	2.31 × 10 <sup>-8</sup>	1.40 × 10 <sup>-8</sup>	1.80 × 10 <sup>-12</sup>	1.59 × 10 <sup>-9</sup>		
	2200	3.65 × 10 <sup>-8</sup>	2.00 × 10 <sup>-8</sup>	3.00 × 10 <sup>-12</sup>	2.60 × 10 <sup>-9</sup>		
	2207	3.25 × 10 <sup>-8</sup>	2.30 × 10 <sup>-8</sup>	2.80 × 10 <sup>-12</sup>	2.46 × 10 <sup>-9</sup>		
	2155	1.98 × 10 <sup>-8</sup>	1.59 × 10 <sup>-8</sup>	1.40 × 10 <sup>-12</sup>	1.16 × 10 <sup>-9</sup>		
	2162	1.90 × 10 <sup>-9</sup>	1.88 × 10 <sup>-8</sup>	3.00 × 10 <sup>-13</sup>	3.10 × 10 <sup>-11</sup>		
	2210	2.80 × 10 <sup>-9</sup>	2.75 × 10 <sup>-8</sup>	4.50 × 10 <sup>-13</sup>	2.80 × 10 <sup>-11</sup>		
4	2093	8.85 × 10 <sup>-10</sup>	1.34 × 10 <sup>-8</sup>	1.50 × 10 <sup>-13</sup>	8.40 × 10 <sup>-12</sup>		
	2171	2.00 × 10 <sup>-9</sup>	2.37 × 10 <sup>-8</sup>	4.50 × 10 <sup>-13</sup>	1.70 × 10 <sup>-11</sup>		
	2222	3.30 × 10 <sup>-9</sup>	3.45 × 10 <sup>-8</sup>	7.00 × 10 <sup>-13</sup>	3.10 × 10 <sup>-11</sup>		
	2305	5.90 × 10 <sup>-9</sup>	5.90 × 10 <sup>-8</sup>	1.55 × 10 <sup>-12</sup>	6.00 × 10 <sup>-11</sup>		5.50 × 10 <sup>-13</sup>
	2311	5.75 × 10 <sup>-9</sup>	5.90 × 10 <sup>-8</sup>	1.55 × 10 <sup>-12</sup>	5.70 × 10 <sup>-11</sup>		
	2314	5.15 × 10 <sup>-9</sup>	5.15 × 10 <sup>-8</sup>	1.20 × 10 <sup>-12</sup>	4.90 × 10 <sup>-11</sup>		5.00 × 10 <sup>-13</sup>
	2305	6.20 × 10 <sup>-9</sup>	4.10 × 10 <sup>-8</sup>	9.00 × 10 <sup>-13</sup>	5.65 × 10 <sup>-11</sup>		
	2312	5.75 × 10 <sup>-9</sup>	4.25 × 10 <sup>-8</sup>	1.20 × 10 <sup>-12</sup>	5.10 × 10 <sup>-11</sup>		
	2260	3.05 × 10 <sup>-9</sup>	2.80 × 10 <sup>-8</sup>	5.00 × 10 <sup>-13</sup>	2.40 × 10 <sup>-11</sup>		

<sup>a</sup>The instrument constant (bar A<sup>-1</sup> K<sup>-1</sup>) is equal to 0.794, 0.421, 0.795, and 1.034 in the experiments 1–4, respectively.

(the most commonly adopted values in high temperature mass spectrometry studies<sup>19</sup>), we applied the model using this set of values.

In view of the availability of experimental values for the Si, Ge, and Pb cross sections, and also considering that the SiPb and GePb species have a low charge separation, making them ill suited to Hastie's model, we decided to select the following values as the most reliable cross sections for molecular species, in Å<sup>2</sup>: 10.77, 11.35, 12.04, 16.86, 13.43, 18.80, and 14.98 for SiPb, GePb, Si<sub>2</sub>, Si<sub>3</sub>, Ge<sub>2</sub>, Ge<sub>3</sub>, and Pb<sub>2</sub>, respectively. These values were obtained by summing the experimental atomic cross sections (6.69, Si; 7.46, Ge; and 7.61, Pb) and by correcting the sum with a 0.90 multiplicative factor for the diatomic homonuclear species and with a 0.75 factor for the heteronuclear ones, as generally recommended. The procedure was iterated twice in the cases of triatomic species. In summary, the assumptions used are as follows:  $\sigma_{M_2} = 1.80\sigma_M$ ,  $\sigma_{M_3} = 2.52\sigma_M$ , and  $\sigma_{MM'} = 0.75(\sigma_M + \sigma_{M'})$ . The above listed  $\sigma$  values are to be compared with the corresponding values from the Hastie model, here reported in the same order from SiPb to Pb<sub>2</sub>: 8.32, 8.43, 6.89, 15.42, 7.06, 16.31, and 12.79. Finally, Hastie's  $\sigma$  for SiPb and GePb calculated according to his A<sup>2+</sup> B<sup>2+</sup> picture are 9.57 and 9.66, respectively.

For the gain factor  $\gamma_i$ , it is usually recommended that it be set proportional to the reciprocal square root of the molecular weight of the species *i*. This choice was also used in

the present study. A –0.4 power dependence instead of –0.5 has also been alternatively proposed.<sup>19</sup> The effect of this alternative has been tested on the third-law enthalpy changes.

For all the studied reactions the results of the second- and third-law analyses are reported in Tables IV and V together with the values of the derived dissociation energies for the GePb and SiPb molecules, calculated using the pertinent thermochemical cycles. A detailed discussion of these results is reported in Sec. V A.

The influence of both the cross sections and multiplier gain values on the equilibrium constants has been taken into account in assigning the uncertainties to the third-law enthalpies of reaction reported in Tables IV and V. The entire spread of values obtained with the various possible options has been taken as representative of an estimated standard deviation. As already mentioned, in this work, the instrumental constants have been derived from the study of known equilibria. Using the same criteria to estimate the  $\sigma$  and  $\gamma$  values both for these calibration equilibria and for the new equilibria under study, a partial compensation of errors occurs in the derivation of equilibrium constants.

### C. Quantum mechanical results

The optimized molecular parameters of both the neutral, GePb and SiPb, and ionic molecules, GePb<sup>+</sup>, GePb<sup>-</sup>, SiPb<sup>+</sup>, and SiPb<sup>-</sup>, computed with augmented triple zeta basis sets,

TABLE IV. Enthalpy changes for reactions (1)–(3) in the Ge–Pb system and derived dissociation energies of the GePb molecule (values in kJ/mol).

	GePb(g)=Pb(g)+Ge(g)	GePb(g)+Ge(g)=Ge <sub>2</sub> (g)+Pb(g)	GePb(g)+Ge <sub>2</sub> (g)=Ge <sub>3</sub> (g)+Pb(g)
Data points	28	27	13
Average temperature (K)	1881	1883	1888
Second-law $\Delta H_T^\circ$	163.1±7.7	−104.2±7.6	−167.1±12.2
Second-law $\Delta H_0^\circ$	154.0±7.7	−91.8±7.6	−163.4±12.2
Third-law $\Delta H_0^\circ$	142.2±6.8	−117.0±7.5	−192.6±15.3
Third-law trend (J/K mol) <sup>a</sup>	−6.1	−13.4	−15.6
Third-law uncertainties:			
standard deviation	1.3	1.5	1.7
error on $\sigma$ , $\gamma$	1.5	2.1	9.7
error on GEF <sub>0</sub>	3.9	3.9	3.9
total error	6.7	7.5	15.3
Error on auxiliary $D_0^\circ$ 's	...	7	20.2
Third-law $D_0^\circ$ (GePb)	142.2±6.8	144.0±10.3	135.4±25.3
Selected $D_0^\circ$ (GePb)		141.6±6.9	

<sup>a</sup>Here, the third-law trend is the temperature coefficient of an assumed linear dependence of the calculated third-law  $\Delta H_0^\circ$  vs  $T$ .

are listed in Table VI. Expectation values of  $S^2$  indicate negligible spin contamination for the ground states of the neutral, anion, and cation of the SiPb and GePb molecules, whereas  $\langle S^2 \rangle$  for the  $^3\Pi$  state of the neutrals is considerably greater than 2. The same trend is observed from the T1 diagnostic that shows a multireference character for values greater than 0.02.

The present single-reference CCSD(T) computations provide term symbols within the  $\Lambda$ - $S$  coupling scheme. In particular, according to this scheme, the outer electronic configuration for the neutral ground electronic states of GePb and SiPb is  $\sigma^2\pi^2(\pi_{p_x}^1\pi_{p_y}^1)$ , corresponding to  $X^3\Sigma^-$ , and for the two calculated excited states is  $\sigma^1\pi^3(\pi_{p_x}^2\pi_{p_y}^1)$ , corresponding to  $A^3\Pi$ , and  $\sigma^2\pi^2(\pi_{p_x}^2)$ , corresponding to  $a^1\Delta$ .

To validate our choice for the use of the bond distances and vibrational frequencies in the calculations for the GePb and SiPb thermal functions, CCSD(T) computations were performed at the same level of theory on homo- and heteronuclear group 14 diatomics that are spectroscopically characterized. The results are discussed in Sec. IV D. Briefly, there is an excellent agreement between the optimized and

experimental  $r_e$  with a maximum deviation of only 2% for the heaviest Pb<sub>2</sub> molecule. Also, the calculated vibrational frequencies differ by only a few percent for the lightest Ge<sub>2</sub> molecule and by approximately 26% for Pb<sub>2</sub>. The same level of theory applied to Si<sub>2</sub> reproduced a perfect agreement in both the equilibrium bond length and vibrational frequency.

Looking at the bond distance changes (see Table VI) upon removal of an electron from the highest occupied molecular orbital (HOMO) of the anion to obtain the neutral ground state ( $X^3\Sigma^-$ ) as well as upon removal of an electron from the ground state of the neutral to give the ground state of the cation, it is possible to attribute a bonding character to the  $\pi$  orbital of both GePb and SiPb. In fact, removal of an electron from the  $\pi$  orbital of the anion causes a lengthening of the bond distance of +0.07 Å for both GePb and SiPb in their  $X^3\Sigma^-$  state. This could be attributed to destabilization caused by reduction of the “bond order.” The same reasoning can explain the bond lengthening when an electron is removed from the HOMO of the neutral to obtain the cation ground electronic state, in which a further lengthening of the bond distance of more than 0.2 Å occurs. This is also con-

TABLE V. Enthalpy changes for reactions (1)–(4) in the Si–Pb system and derived dissociation energies of the SiPb molecule (values in kJ/mol).

	SiPb(g)=Pb(g)+Si(g)	SiPb(g)+Si(g)=Si <sub>2</sub> (g)+Pb(g)	SiPb(g)+Si <sub>2</sub> (g)=Si <sub>3</sub> (g)+Pb(g)	SiPb(g)+Pb(g)=Si(g)+Pb <sub>2</sub> (g)
Data points	23	20	4	2
Average temperature (K)	2172	2181	...	...
Second-law $\Delta H_T^\circ$	168.6±19.9	−143.2±19.4	...	...
Second-law $\Delta H_0^\circ$	163.0±19.9	−137.7±19.4	...	...
Third-law $\Delta H_0^\circ$	166.6±10.4	−154.3±10.2	−230.9±19.1	80.8±11.1
Third-law trend (J/K mol) <sup>a</sup>	−2.3	−7.5	...	...
standard deviation	4.2	3.7	6.0	2.0
error on $\sigma$ , $\gamma$	3.3	3.5	10.2	6.3
error on GEF <sub>0</sub>	2.9	2.9	2.9	2.9
total error	10.4	10.2	19.1	11.1
Error on auxiliary $D_0^\circ$ 's	...	7	17.5	1
Third-law $D_0^\circ$ (SiPb)	166.6±10.4	165.7±12.3	154.1±25.9	163.8±11.2
Selected $D_0^\circ$ (SiPb)		165.1±7.3		

<sup>a</sup>Here, the trend is the temperature coefficient of an assumed dependence of the calculated third-law  $\Delta H_0^\circ$  vs  $T$ .

TABLE VI. Optimized molecular parameters, bond distances ( $r_e$ ) in Å, harmonic vibrational frequencies ( $\omega_e$ ) in  $\text{cm}^{-1}$ , term energies ( $T_e$ ) in  $\text{cm}^{-1}$ , AIEs in eV, AEAs in eV, and dissociation energies ( $D_0^\circ$ ) in  $\text{kJ mol}^{-1}$ , calculated at the CCSD(T) level of theory with the aug-cc-pVTZ basis sets for C, Si, and Ge and the aug-cc-pVTZ-pp basis set for Sn and Pb.

Molecule	State	$r_e$	$\omega_e$	$T_e$	AIE	AEA	$D_0^\circ$	$\langle S^2 \rangle$	T1
SiPb	$X^3\Sigma$	2.582	321	...	7.48	1.87	239.6	2.015	0.0145
	$A^3\Pi$	2.465	348	1035.8				2.616	0.0529
	$a^1\Delta$	2.624	297	3911.2				...	0.0141
SiPb <sup>+</sup>	$X^2\Pi$	2.795	258	...				0.763	0.0215
SiPb <sup>-</sup>	$X^2\Pi$	2.511	338	...				0.762	0.0198
GePb	$X^3\Sigma$	2.630	211	...	7.38	1.85	237.4	2.012	0.0125
	$A^3\Pi$	2.513	230	1084.7				2.621	0.0445
	$a^1\Delta$	2.673	195	3854.6				...	0.0128
GePb <sup>+</sup>	$X^2\Pi$	2.845	171	...				0.760	0.0182
GePb <sup>-</sup>	$X^2\Pi$	2.560	222	...				0.760	0.0165
PbC	$X^3\Sigma$	2.191	565	...			248.1	2.014	0.0220
SiSn	$X^3\Sigma$	2.514	353	...			255.0	2.016	0.0131
SnPb	$X^3\Sigma$	2.804	167	...			222.5	2.013	0.0113

firming by the drawing, in Fig. 1, of the MO in question. Less clear is the character of the  $\sigma$  (HOMO-1) molecular orbital. In Fig. 1 a bonding character is apparent. On the contrary, the shortening of the bond distance by 0.05 Å for both the anions GePb<sup>-</sup> and SiPb<sup>-</sup> upon removal of an electron to give the corresponding neutral excited  $A^3\Pi$  states would indicate an antibonding character. However, it should be kept in mind that the rather high value of the T1 diagnostics suggests that care should be taken in using quantitatively the results for these excited states, for which a multireference representation may be important.

#### D. GePb and SiPb thermal functions

As stated in Sec. III, the quantum mechanical calculations for the GePb and SiPb molecules have been performed principally to determine reliable molecular parameters (Table VI) to be used in the evaluations of their thermal functions. Therefore, it is of interest to ascertain how well the computational method that has been used here reproduces the experimental parameters, when available, of similar molecules.

For all the group 14 homonuclear diatomics quite a number of measurements have been made on both the ground state and on low-lying excited states.<sup>42-46</sup> In addition, a few high level quantum mechanical computations are also

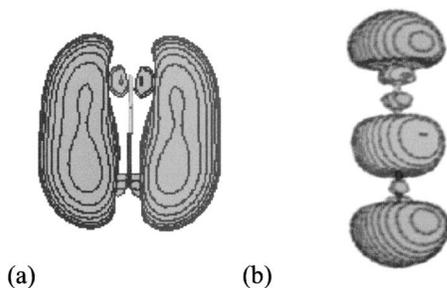


FIG. 1. Outer molecular orbitals of the ground electronic state of GePb: (a)  $\pi$ , HOMO; (b)  $\sigma$ , HOMO-1.

available<sup>47-49</sup> (see also references cited in Sec. IV E below). Among the group 14 heteronuclear diatomics, only some carbides involving the lighter elements and the GeSi,<sup>50</sup> SiSn,<sup>50</sup> and SnPb (Ref. 44) molecules have been partially studied by spectroscopic techniques. For three species, GeSi, SiSn, and GeSn, molecular parameters and  $\Lambda$ - $S$  term energies computed with an earlier local spin density-model potential method have been reported.<sup>51</sup> The GeSi species was also studied more recently by high level calculations.<sup>52-54</sup>

At the highest level of the calculations performed here, CCSD(T) with a triple zeta augmented basis set, the equilibrium distance and harmonic vibrational frequency of the Pb<sub>2</sub> ground state are predicted to be 2.865 Å and 139  $\text{cm}^{-1}$ , respectively, as compared to the experimental values of 2.9271 Å (Refs. 42 and 43) and  $(110 \pm 15) \text{cm}^{-1}$ .<sup>44</sup> The corresponding parameters for Sn<sub>2</sub> are calculated to be 2.740 Å and 196  $\text{cm}^{-1}$ , as compared to the experimental values of 2.746 Å and  $(186 \pm 15) \text{cm}^{-1}$ .<sup>44,55</sup> Similarly, for Ge<sub>2</sub> these computed values are 2.374 Å and 294  $\text{cm}^{-1}$ ; the experimental bond length is 2.368 Å and the vibrational frequency is 287.9  $\text{cm}^{-1}$  (Ref. 44) or  $(286 \pm 5) \text{cm}^{-1}$ .<sup>56</sup> Finally, the ground state molecular constants of the SnPb molecule are calculated to be  $r_e = 2.804 \text{Å}$  and  $\omega_e = 167 \text{cm}^{-1}$ , while the experimental vibrational frequency has been measured to be  $(148 \pm 15) \text{cm}^{-1}$ .<sup>44</sup> The SnPb ground state bond length has not been experimentally determined. Taking into account all these comparisons, it can be concluded that for the heteronuclear diatomics here of interest, GePb and SiPb, the CCSD(T) method, together with extended basis sets and pseudopotentials, is expected to predict reasonable internuclear equilibrium distances (within 2% of the experimental values), as well as vibrational frequencies. Indeed, calculated frequencies are larger than the experimental ones, but, with the exception of Pb<sub>2</sub>, within the experimental uncertainties. For these reasons, these values are likely to allow for a reliable computation of rotational and vibrational contributions to the thermal functions.

Quite a different picture occurs if we consider the calculated term energies. This may be expected because the spin-orbit interaction plays an ever increasing role on going down group 14. As a consequence, a pure  $\Lambda$ - $S$  scheme is no longer valid, and the only good quantum numbers are  $J$  and  $\Omega$ . As an example, let us consider the  $\text{Ge}_2$ ,  $\text{SnPb}$ , and  $\text{Pb}_2$  molecules, for which experimental data on the electronic energy levels are available. In the  $\Lambda$ - $S$  approximation used in the quantum mechanical method reported here, all the ground states are predicted to be  $^3\Sigma$ , while the first excited states,  $^3\Pi$ , are found at 415.5, 971.1, and 1168.2  $\text{cm}^{-1}$  above the ground state for  $\text{Ge}_2$ ,  $\text{SnPb}$ , and  $\text{Pb}_2$ , respectively. Using these values will severely overestimate the electronic contribution to the Gibbs energy functions  $\text{GEF}_0$ . Indeed, with these energy levels and their associated degeneracies, the values of these contributions, at 2000 K, are calculated to be 16.70, 14.87, and 14.31  $\text{J K}^{-1} \text{mol}^{-1}$ , while, using the experimentally known levels (see Table VIII and Ref. 44), the corresponding values are 15.74, 6.43, and 0.66  $\text{J K}^{-1} \text{mol}^{-1}$  for  $\text{Ge}_2$ ,  $\text{SnPb}$ , and  $\text{Pb}_2$ , respectively. It is evident from these values that on moving towards molecules with heavier atoms, the spin-orbit splitting of the degenerate sublevels of the  $^3\Sigma$  and  $^3\Pi$  terms spreads the levels on an ever increasing energy range and then lowers by a quite large amount the value of the electronic partition function. Consequently, at least for the heavier molecules, without a full account of the spin-orbit splitting interaction, the contribution of the electronic energy terms to the thermal functions can be seriously in error.

To tackle this problem and to reliably estimate these quantities, we resorted to an empirical approach based on correlating the electronic partition function ( $Q_{\text{el}}$ ) with the total number of electrons ( $n_{\text{el}}$ ) in the molecule. Thus,  $n_{\text{el}}$  will be used as a crude parameter in order to represent the complexity in the electronic structure. In this connection, it is appropriate to recall here that the Gibbs energy function  $\text{GEF}_0$  is a linear function of  $\ln Q_{\text{el}}$ , whereas the enthalpy content  $\text{HCF}_0$  depends on the first derivative of  $\ln Q_{\text{el}}$  with respect to temperature and, hence, on the ratio  $(dQ_{\text{el}}/dT)/Q_{\text{el}}$ .

Using the aforementioned experimental and computational data for the ground state and low-lying energy levels, it has been possible to evaluate the electronic partition function for all the homonuclear and some of the heteronuclear intragroup 14 diatomic molecules. This quantity calculated at  $T=2000$  K is reported in Fig. 2 as a function of  $n_{\text{el}}$ . Experimental values of the  $\omega$ - $\omega$  levels were used when available (namely, for all the homonuclear species and the  $\text{SnPb}$  molecule). For the  $\text{GeSi}$  and  $\text{SiSn}$  molecules the first excited  $^3\Pi$  state experimental energy<sup>73</sup> has been used together with the second calculated excited state.<sup>51</sup>  $Q_{\text{el}}$  values for the  $\text{GeSn}$  molecule were calculated from the theoretical electronic levels given in Ref. 51, while for the  $\text{GePb}$  and  $\text{SiPb}$  molecules the energy terms computed here (Table VI) were used. Finally, in the same figure the  $Q_{\text{el}}$  values for a number of group 13–group 15 isoelectronic diatomics with the intragroup 14 species are also included, as obtained by using the  $\omega$ - $\omega$  levels reported in a series of theoretical papers based on the multireference single double configuration interaction (MRS-

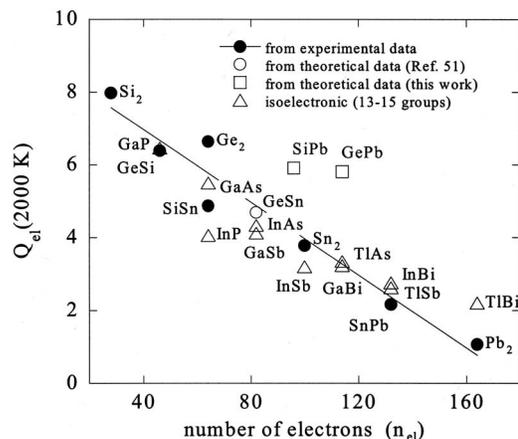


FIG. 2. Electronic partition function  $Q_{\text{el}}$  at  $T=2000$  K for the intragroup 14 and the isoelectronic intergroups 13–15 diatomics as a function of the total number of electrons in the molecule.  $Q_{\text{el}}$  are calculated from experimental (full circles) and computational (open symbols) values of term energies.

DCI) approach by Das and co-workers.<sup>57–65</sup> In Fig. 2, in accordance with the considerations made previously, the decrease in the partition function for the heavier molecules as a consequence of the increase of the spin-orbit splitting is quite apparent. In particular, if we consider only the experimentally derived values (full circles in Fig. 2), a reasonably good linear behavior is found (see the line in the figure). The overestimation due to neglecting the spin-orbit splitting is clearly illustrated in Fig. 2 by the large deviations of the new molecules of interest here, which lie outside the general trend. This deviation is more accentuated for  $\text{GePb}$  than for  $\text{SiPb}$ , as expected.

Therefore, in view of the correlation observed, the electronic partition functions of these newly observed molecules were derived from the corresponding linear fit shown in Fig. 2. While, in principle, such a plot can be constructed for any temperature, in order to obtain  $Q_{\text{el}}$  in the whole experimental temperature range we preferred to use this interpolation only at the average experimental temperature and to calculate the  $Q_{\text{el}}$  values thereafter by using the obtained values of  $dQ_{\text{el}}/dT$ , for all the temperatures of the range of interest, as described below in the next paragraphs. This procedure assures a better self-consistency between the estimated  $\text{GEF}_0$  and  $\text{HCF}_0$ . Note also that although we decided to fit only the experimentally derived values in order to interpolate  $Q_{\text{el}}$ , the calculated  $\text{GEF}_0$  does not change appreciably if all the points in Fig. 2 (with the obvious exception of the  $\text{GePb}$  and  $\text{SiPb}$  values) are included in the fitting procedure.

In view of the fairly satisfactory  $Q_{\text{el}}$  vs  $n_{\text{el}}$  correlation observed for the group of molecules of interest, a similar correlation was exploited for the first temperature derivative  $dQ_{\text{el}}/dT$ . Besides being necessary for calculating  $Q_{\text{el}}$  in the whole experimental temperature range from the interpolated value at the mean temperature of the experiments, the  $dQ_{\text{el}}/dT$  function is directly related to the  $\text{HCF}_0$  (see above) necessary to report to 0 K the high temperature reaction enthalpies derived by the second-law analysis. The plot of  $dQ_{\text{el}}/dT$  vs  $n_{\text{el}}$  is shown in Fig. 3 for  $T=2000$  K.

It is apparent that the observed trend is markedly different from that seen for  $Q_{\text{el}}$ . If only the experimental data are

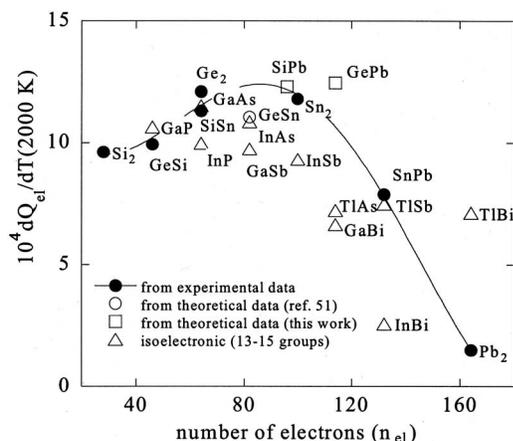


FIG. 3. Temperature derivative of  $Q_{el}$  at  $T=2000$  K for the intragroup 14 diatomics and the isoelectronic intergroups 13–15 diatomics as a function of the total number of electrons, calculated from the available experimental and computational data (same symbols as in Fig. 2).

used (full circles in Fig. 3), the  $dQ_{el}/dT$  term exhibits a well defined behavior with an intermediate maximum peak value, which can be fitted by a polynomial function (line drawn in Fig. 3). A very similar trend would be obtained from a plot of  $HCF_0$  for the group 14 monoatomic species either versus the atomic number or, as here, the number of electrons. This general trend is also confirmed by including the theoretical values of the aforementioned group 13–group 15 isoelectronic diatomics even if the overall picture is now more scattered. In such a situation, a polynomial interpolation such as that in Fig. 3 was used, at each temperature, to derive the  $dQ_{el}/dT$  values for the GePb and SiPb molecules.

The so obtained  $Q_{el}$  and  $dQ_{el}/dT$  values, together with the molecular parameters of the electronic ground state, calculated with the CCSD(T) method and reported in Table VI, allowed us to derive the  $GEF_0$  and  $HCF_0$  values reported in Table VII. As implied in the above discussion, the thermal functions were calculated by factorizing the internal partition function into electronic, vibrational, and rotational terms and by using the rigid-rotator harmonic-vibrator approximation for the nuclear motion. The inaccuracy due to ignoring the anharmonicity contribution is negligibly small compared to the other potential sources of error in primary data and molecular parameters.

TABLE VII. Gibbs energy functions ( $GEF_0$ ),  $-(G_T^\circ - H_0^\circ)/T$  in J/K mol, and heat content functions ( $HCF_0$ ),  $(H_T^\circ - H_0^\circ)$  in kJ/mol, for the gaseous molecules GePb and SiPb (standard pressure  $p^\circ = 1$  bar).

$T$ (K)	GePb		SiPb	
	$GEF_0$	$HCF_0$	$GEF_0$	$HCF_0$
1600	300.61	67.53	290.62	66.07
1700	303.17	71.72	293.12	70.16
1800	305.58	75.88	295.48	74.23
1900	307.86	80.01	297.70	78.27
2000	310.02	84.13	299.82	82.29
2100	312.07	88.23	301.82	86.30
2200	314.03	92.33	303.73	90.29
2300	315.89	96.41	305.56	94.27
2400	317.67	100.47	307.30	98.23

From the numerical estimates of the electronic partition functions made here, it is also possible to attempt an evaluation of the energy levels of the SiPb and GePb molecules. To this end a  $^3\Sigma$  ground state and a  $^3\Pi$  first excited state have been assumed, the same as those found in the other homonuclear and heteronuclear intragroup 14 molecules, where the corresponding  $\omega-\omega$  states are known. Even if such “back-calculation” of the energy levels from the  $Q_{el}$  is numerically somewhat ill defined, the spin-orbit splitting of the  $^3\Sigma$  state can nevertheless be proposed to be 440 and 620  $\text{cm}^{-1}$  for the SiPb and GePb molecules, respectively, while the calculated  $\omega-\omega$  levels of the  $^3\Pi$  state span the ranges 960–3050  $\text{cm}^{-1}$  (SiPb) and 1690–5350  $\text{cm}^{-1}$  (GePb). The energy difference between the  $0^+$  and 1 components of the  $^3\Sigma$  ground state, if compared with those of  $\text{Ge}_2$  (114  $\text{cm}^{-1}$ ),  $\text{Sn}_2$  (760  $\text{cm}^{-1}$ ),  $\text{SnPb}$  (1363  $\text{cm}^{-1}$ ), and  $\text{Pb}_2$  (5300  $\text{cm}^{-1}$ ), seems reasonable.

### E. Auxiliary thermal functions and atomization energies

As mentioned above, in order to obtain the enthalpy changes at 0 K for the reactions (1)–(4) from the partial pressure data, the knowledge of the  $HCF_0$ , (second-law analysis) and  $GEF_0$  (third-law analysis) of all the species involved is required. For all the atomic species, we adopted the values reported in Ref. 66. For the isomolecular processes (2)–(4), the thermodynamic functions of the homonuclear dimers and trimers must also be evaluated. Furthermore, to derive the dissociation energy of the newly identified diatomics from the enthalpy changes in reactions (2)–(4), the dissociation/atomization energies of the homonuclear species must be known. In the following paragraphs, we discuss the choices we made to select the above auxiliary properties. A summary is reported in Table VIII.

$\text{Si}_2$ . While the ground state properties of the silicon dimer  $\text{Si}_2$  have been known for a long time, the energetics and molecular parameters of the excited states have been investigated by both computational and experimental studies during the last two decades. The properties of the low-lying excited states relevant to the calculation of thermodynamic functions were obtained by negative ion photodetachment techniques.<sup>45,67</sup> The thermodynamic functions so derived are slightly, yet not insignificantly, different from those used by Schmude, Jr. *et al.* in their mass spectrometry study of  $\text{Si}_2$  (Ref. 35) (for example, the  $GEF_0$  at  $T=2200$  K are 274.30 and 274.85 J/K mol, respectively, from our calculation and from the work of Schmude, Jr. *et al.*). As the spectroscopic parameters used are the same in both cases, the difference is most probably due to the inclusion of the interaction between electronic and nuclear terms in our calculation. For the dissociation energy of  $\text{Si}_2$ , we used the most recent mass spectrometric value by Schmude, Jr. *et al.* ( $319 \pm 7$  kJ/mol).<sup>35</sup> In view of the above mentioned reevaluation of the  $GEF_0$ , this value has been readjusted to  $320 \pm 7$  kJ/mol.

$\text{Si}_3$ . Despite the considerable amount of experimental and theoretical investigations, the nature of the ground state of silicon trimer cannot be considered conclusively ascertained. Although recent density functional theory (DFT) cal-

TABLE VIII. Summary of the molecular data used to calculate the thermal functions ( $\text{GEF}_0$ , free energy function, in J/K mol, and  $\text{HCF}_0$ , heat content function, in kJ/mol) of the auxiliary homonuclear molecules: electronic state and energy in  $\text{cm}^{-1}$ , bond distances ( $r_e$ ) in Å, harmonic vibrational frequencies ( $\omega_e$ ) in  $\text{cm}^{-1}$ , and atomization energies in kJ/mol. The thermal functions are calculated at standard pressure  $p^\circ = 1$  bar.

Molecule	State	$T_e$	$r_e, \alpha^{a,b}$	$\omega_e(\omega_e x_e)^b$	Atomization energy	$\text{GEF}_0$	$\text{HCF}_0$	Ref.
						at $T=2000$ K	at $T=2000$ K	
$\text{Si}_2$	$^3\Sigma_g^-$	0	2.246	509	$320 \pm 7$	270.67	76.12	45,67
	$^3\Pi_u$	331	2.115	536				
	$^1\Delta_g$	3509	2.290	486				
	$^1\Pi_u$	4388	2.160	540				
	$^1\Sigma_g^+$	4726	2.230	365				
$\text{Si}_3$	$^1A_1$	0	2.177,78.10°	148,551,525	$705 \pm 16$	342.93	111.59	69,72–74
	$^3A_2'$	138						
	$^1B_2$	5243						
	$^3A_1$	7259						
	$^3B_1$	9033						
$\text{Ge}_2$	$^3\Sigma_g^0$	0	2.368	287.9(0.81)	$260.7 \pm 6.8$	294.81	80.01	75,76
	$^3\Sigma_g^1$	114	2.423	270				
	$^3\Pi_u^2$	337	2.320	308				
	$^3\Pi_u^1$	711	2.320	278				
	$^3\Pi_u^0^+$	1193	2.320	278				
	$^3\Pi_u^0^-$	1305	2.320	278				
	$^1\Delta_g$	3308	2.466	276				
	$^1\Sigma_1$	4941	2.443	204				
	$^1\Pi_u$	4943	2.323	303				
	$\text{Ge}_3$	$^1A_1$	0	2.132,83.2°				
$^3A_2'$		323						
$^1B_2$		2017						
$^1\Sigma_g^+$		4033						
$^3A_1$		6856						
$^3B_1$		8389						
$^3A_2$		7420						
$\text{Pb}_2$	$0_g^+$	0		110.2(0.34)	$83 \pm 1$	313.03	81.30	49,81
	$1_g$	5305		120.6(0.25)				
	$2_u$	5826		116				
	$1_u$	7818		126.5(0.40)				
	$2_g$	8150		111				
	$0_g^-$	9185		63				

<sup>a</sup>For  $\text{Ge}_3$  and  $\text{Si}_3$  (ground state: isosceles triangle,  $C_{2v}$ ); the first number is the shortest bond length and the second one is the apical angle.

<sup>b</sup>For  $\text{Ge}_3$  and  $\text{Si}_3$  no interaction between the electronic and nuclear motions was considered in calculating the thermal functions.

calculations seem to prefer a triplet ground state,<sup>68</sup> most theoretical studies indicate a  $^1A_1$  ( $C_{2v}$  symmetry, isosceles triangle) ground state, having a slightly lower energy than the  $^3A_2'$  ( $D_{3h}$ , equilateral triangle) state. For example, the energy difference between the two structures is calculated at 138, 1290, and 484  $\text{cm}^{-1}$ , respectively, at the QCISD(T),<sup>69</sup> MRSDCI,<sup>47</sup> and Davidson-corrected multireference configuration interaction<sup>70</sup> (MRCI) levels of theory. The energy order is reversed if a single-reference CI approach is used.<sup>70</sup> However, the existence of a  $^1A_1$  ground state is consistent with experimental observations.<sup>71–73</sup> Higher-lying  $^1B_2$ ,  $^3A_1$ , and  $^3B_1$  states were also predicted by theory and observed by photoelectron spectroscopy of the  $\text{Si}_3^-$  anion.<sup>72</sup> The geometrical parameters of the  $C_{2v}$  ground state were recently obtained by high-resolution rotational spectroscopy<sup>74</sup> ( $r_{\text{Si-Si}}=2.177$  Å, apical angle of 78.10°), and two out of three vibrational fre-

quencies are also known from IR-matrix experiments<sup>73</sup> (551 and 525  $\text{cm}^{-1}$ ). These experimental results are in excellent agreement with the aforementioned high level theoretical calculations. In order to calculate the thermal functions of  $\text{Si}_3$ , we used the experimental data when available, integrated with the QCISD(T) theoretical results<sup>69</sup> for the missing parameters. The values so obtained are close to those reported by Schmude, Jr. *et al.*<sup>35</sup> (e.g.,  $\text{GEF}_0$  differ by 0.25 J/K mol at 2000 K). Based on mass spectrometric experimental data and a reevaluation of previous work, those authors recommended for the atomization energy of  $\text{Si}_3$  the value of  $705 \pm 16$  kJ/mol. The correction to be applied to this value to take into account the slightly improved  $\text{GEF}_0$  obtained in the present work is approximately +0.4 kJ/mol, which is negligible compared to the error bar associated with the recommended value.

Ge<sub>2</sub>. Several spectroscopic studies have been carried out on the germanium dimer,<sup>46,56,75</sup> giving a rather rich set of molecular parameters for the ground and low-lying excited states of this molecule. These results, complemented with the most recent high level computational work,<sup>76</sup> were used to calculate the thermodynamic functions. The values so obtained are very close to those employed in the mass spectrometric study of Ref. 76. The dissociation energy of Ge<sub>2</sub> was also taken from that work, where a value of 260.7±6.8 kJ/mol was suggested.

Ge<sub>3</sub>. Similar to the Si<sub>3</sub> species, two nearly degenerate states (<sup>1</sup>A<sub>1</sub> with an isosceles triangle C<sub>2v</sub> structure and <sup>3</sup>A<sub>2</sub>' with a D<sub>3h</sub> equilateral triangle geometry) compete for the ground state of the germanium trimer. Most theoretical calculations,<sup>48,77,78</sup> as well as recent B3LYP DFT (Ref. 79) results tend to prefer the <sup>1</sup>A<sub>1</sub> singlet as the lowest energy state. For example, the <sup>3</sup>A<sub>2</sub>' state is calculated to be 323 cm<sup>-1</sup> higher than <sup>1</sup>A<sub>1</sub> at the CCSD(T) level of theory by Archibong and St-Amant.<sup>78</sup> These authors also succeeded in reproducing the order of excited states observed by photoelectron spectroscopy.<sup>46</sup> In view of this, to calculate the thermal functions we adopted the experimental information complemented with the CCSD(T) results. The most recent mass spectrometric atomization energy provided by Gingerich *et al.*<sup>80</sup> is 589.8±19 kJ/mol. On the basis of our calculated GEF<sub>0</sub> values, we should adjust this value by about -0.8 kJ/mol, a very small correction compared to the error bar given by the authors.

Pb<sub>2</sub>. The thermodynamic functions for the lead dimer were calculated by using the available experimental data<sup>81</sup> complemented with results from a RECP-based MRCI calculation.<sup>49</sup> The dissociation energy  $D_0^\circ(\text{Pb}_2) = 83 \pm 1$  kJ/mol, based on mass spectrometric work,<sup>82</sup> was taken from the IVTANTHERMO database.<sup>66</sup>

## V. DISCUSSION

### A. Thermochemical results

Before analyzing the results obtained from the thermodynamic treatment of the primary data, some comments are appropriate on the second- and third-law methods of analysis. These two independent methods, which have been applied in the present case to almost all the reactions studied [with the obvious exceptions of reaction (3) for Me=Si and reaction (4), for which very few data points could be taken; see Table III], do show advantages and shortcomings.<sup>19</sup> When thermal functions are sufficiently well established, third-law results are usually preferred because they are less sensitive to random errors and allow an easier identification of trends due to systematic errors, especially if temperature dependent. Second-law values, on the contrary, are more prone to errors dependent on the temperature. On the other hand, the second-law method relies much less on the thermal functions of the species involved and is certainly the most direct way to derive the enthalpy of the reaction from the original experimental data. In principle, therefore, agreement between the results obtained with these two methods is most reassuring on the overall quality of the primary data. As a consequence, in our laboratory, somewhat at variance with

the present prevailing attitude in the literature, both treatments have been used in the past and their results retained in the final selection of the enthalpy values to be proposed.

In the present work, from Tables IV and V, it is apparent that agreement between the second- and third-law analyses has been fully obtained only for the reactions involving the SiPb molecule. Even in these cases, however, somewhat larger than usual statistical errors associated with the enthalpies of reaction are apparent. Therefore, the necessary conclusion is that the quality of the primary collected data has not been optimal, probably as a consequence of the difficult experimental conditions to be met. However, we note that in the course of the experiments a rather large range of conditions were sampled in terms of partial pressure ratios of atomic species, which varied by factors equal to about 4 and 30 for the Pb-Ge and Pb-Si systems, respectively. This feature gives an indication of the attainment of proper equilibrium conditions during the experiments. Furthermore, we believe that, as detailed in Sec. IV D, the thermal functions of the newly observed species were estimated with reasonable accuracy. This, together with the well established thermal functions of the other gaseous species involved in the equilibria studied, makes the third-law values quite reliable. Moreover, in most of the cases the trends of the third-law values reported in Tables IV and V are acceptably small. Recalling that this drift in temperature of the third-law values provides a rather convincing figure of merit for the absence of temperature dependent errors, the reliability of the third-law values is also confirmed by these tests.

In conclusion, therefore, only the third-law values have been considered in deriving, from the enthalpy values of the various reactions studied, the dissociation energy of the GePb and SiPb molecules reported in Tables IV and V. The associated errors, derived with the proper propagation rules, take into account the aforementioned discussion on cross sections and multiplier gain parameters, the statistical uncertainty on the third-law enthalpies of reaction, and the uncertainties on the electronic GEF<sub>0</sub> estimates and on the ancillary atomization energies discussed in Sec. IV E. It can be seen how all the values obtained agree within their uncertainties, giving much confidence in the overall results. In particular, excellent agreement is evident between the dissociation energies derived by the study of the simple dissociation reactions and of the exchange reactions with homonuclear diatomics Si<sub>2</sub> and Pb<sub>2</sub> in the case of SiPb and with Ge<sub>2</sub> in the case of GePb. The final proposed values are  $D_0^\circ = 165.1 \pm 7.3$  kJ/mol and  $D_0^\circ = 141.6 \pm 6.9$  kJ/mol for the SiPb and GePb molecules, respectively. These values were calculated by averaging the third-law results from the various reactions, weighted with the pertinent number of experimental data. Using the pure element vaporization data from Ref. 66, the corresponding enthalpies of formation ( $\Delta_f H_0^\circ$ ) were calculated to be 476.4±7.3 kJ/mol (SiPb) and 419.3±6.9 kJ/mol (GePb). Finally, using the electronic states of SiPb and GePb derived in Sec. IV D, it is possible to evaluate the HCF<sub>0</sub> for the two species at 298 K and to then derive values for their respective enthalpies of formation at 298 K ( $\Delta_f H_{298}^\circ$ ) as 477.2±7.3 kJ/mol (SiPb) and 418.6±6.9 kJ/mol (GePb).

TABLE IX. Calculated [CCSD(T)] (with triple zeta augmented basis set) and experimental dissociation energies and enthalpy changes for isomolecular reactions of intragroup 14 molecules of contiguous rows in the periodic table (values in kJ/mol).

Reaction	Experimental $\Delta H_0^\circ$	Calculated $\Delta H_0^\circ$	Expt./Calc.	Expt. + $\Delta_{SO}^a$	Calc./ (Expt. + $\Delta_{SO}$ )
Homonuclear dissociations					
$\text{Si}_2(\text{g})=2 \text{Si}(\text{g})$	320.0	295.2	1.08	323.6	0.91
$\text{Ge}_2(\text{g})=2 \text{Ge}(\text{g})$	260.7	278.5	0.94	283.0	0.98
$\text{Sn}_2(\text{g})=2 \text{Sn}(\text{g})$	183.4	233.5	0.79	236.4	0.99
$\text{Pb}_2(\text{g})=2 \text{Pb}(\text{g})$	83.0	212.5	0.39	244.7	0.87
Heteronuclear dissociations					
$\text{SiPb}(\text{g})=\text{Si}(\text{g})+\text{Pb}(\text{g})$	165.1	239.6 257.9 <sup>b</sup>	0.69	265.3	0.90 0.97
$\text{GePb}(\text{g})=\text{Ge}(\text{g})+\text{Pb}(\text{g})$	141.6	237.4 252.2 <sup>b</sup>	0.60	250.2	095 1.01
$\text{SnPb}(\text{g})=\text{Sn}(\text{g})+\text{Pb}(\text{g})$	122.6	222.5	0.55	243.2	0.91
$\text{SiSn}(\text{g})=\text{Si}(\text{g})+\text{Sn}(\text{g})$		255.0			
$\text{PbC}(\text{g})=\text{Pb}(\text{g})+\text{C}(\text{g})$		248.1			
Isomolecular reactions					
$\text{PbC}(\text{g})+\text{Si}(\text{g})=\text{SiPb}(\text{g})+\text{C}(\text{g})$		8.5			
$\text{SiPb}(\text{g})+\text{Ge}(\text{g})=\text{GePb}(\text{g})+\text{Si}(\text{g})$	23.5	2.2		15.1	
$\text{GePb}(\text{g})+\text{Sn}(\text{g})=\text{SnPb}(\text{g})+\text{Ge}(\text{g})$	19.0	14.8		7.0	
$\text{SnPb}(\text{g})+\text{Pb}(\text{g})=\text{Pb}_2(\text{g})+\text{Sn}(\text{g})$	39.6	10.0		-1.4	

<sup>a</sup>Expt. +  $\Delta_{SO}$ : experimental values corrected for the difference between the spin-orbit couplings of products and reactants (see text for details).

<sup>b</sup>Complete basis set (CBS) limit evaluated from double to quadruple zeta quality results.

The dissociation energies presented here, being a first determination, do not lend themselves to a comparison with previous evaluations.

## B. Calculated and experimental dissociation energies

When we compare our experimental determinations with the outcome of the computational work, we first observe that the CCSD(T) computed dissociation energies largely overestimate the experimental results, with a calculated  $D_0^\circ(\text{SiPb}, \text{g})$  of 239.6 kJ mol<sup>-1</sup> vs 165.1 kJ mol<sup>-1</sup> and a calculated  $D_0^\circ(\text{GePb}, \text{g})$  of 237.4 kJ mol<sup>-1</sup> vs 141.6 kJ mol<sup>-1</sup> (Table IX). This overprediction increases as the mass of the molecule increases. These “as-calculated” dissociation energies will be used in Sec. V C to estimate the  $D_0^\circ$  of the intragroup 14 molecules not yet determined experimentally. However, in order to more accurately assess the quality of the CCSD(T) dissociation energies, a comparison with the experimental results should be made after adjusting either the calculated or the experimental values with the spin-orbit couplings for both the atoms and the molecules.<sup>28</sup> Indeed, it should be considered that in the computations performed here the relativistic effects are taken into account only through the use of the core pseudopotential. As anticipated, in order to put into perspective the performance of the CCSD(T) calculations, we calculated the  $D_0^\circ$  of the group 14 homonuclear diatomics and of the SnPb molecule at the same level of theory. The CCSD(T) values are reported in Table IX for the Si<sub>2</sub>, Ge<sub>2</sub>, Sn<sub>2</sub>, Pb<sub>2</sub>, and SnPb molecules.

For the atomic spin-orbit correction, the energy difference between the lowest  $J$  level of the <sup>3</sup> $P$  state and the  $J$ -averaged <sup>3</sup> $P$  state has been employed in literature<sup>28</sup> and is

easily calculated from the experimental atomic data of Ref. 29. The resulting values in kJ/mol are the following 0.35 (C), 1.79 (Si), 11.59 (Ge), 29.53 (Sn), and 101.96 (Pb). However, this procedure neglects the mixing<sup>83</sup> between the <sup>3</sup> $P_0$  and <sup>1</sup> $S_0$  states as well as the <sup>3</sup> $P_2$  and <sup>1</sup> $D_2$  states, which can be significant in the case of the Pb atom, where a correction based on first principles computation might be more appropriate.<sup>84</sup> For the molecules, while a partial quenching of the coupling due to the molecular field is expected to lead to smaller values, the evaluation nevertheless remains difficult. However, in some of the cases, the almost pure  $\Omega$  components of the <sup>3</sup> $\Sigma$  ground state are experimentally known. Therefore, the following values in kJ/mol of the differences between the 0 ground state and the average of the  $\omega$ - $\omega$  states of the <sup>3</sup> $\Sigma$  ground state can be calculated (values in kJ/mol): 0 (Si<sub>2</sub>),<sup>45</sup> 0.91 (Ge<sub>2</sub>),<sup>46</sup> 6.06 (Sn<sub>2</sub>).<sup>44</sup> For the Pb<sub>2</sub> molecule a significant mixing of the  $\Lambda$ - $S$  states occurs,<sup>83</sup> and for the SnPb molecule a considerable mixing can also be expected, complicating the evaluation of the correction. Once again, by neglecting these effects and taking into account the two lowest  $\omega$ - $\omega$  states (0 and 1), the following values, in kJ/mol, can be derived: 42.27 (Pb<sub>2</sub>) and 10.87 (SnPb). For GePb and SiPb, the pertinent corrections, 4.94 (GePb) and 3.51 (SiPb), have been tentatively evaluated by taking into account the 0<sup>+</sup>-1 splittings estimated here (see Sec. IV D). In order to compare experimental and calculated dissociation energies, these spin-orbit corrections  $\Delta_{SO}$  can be applied either to the calculated or to the experimental values. Both conventions have been used in the literature. Here, we added  $\Delta_{SO}$  to the experimental  $D_0^\circ$ , adopting the convention proposed in the original paper where the basis sets used in this work have been presented

(Ref. 28). The corrected values, hereafter named Expt. +  $\Delta_{SO}$ , are reported in the fifth column of Table IX. In the same table (sixth column) we also report the ratio between the calculated reaction energy and these “experimental” values inclusive of the estimated spin-orbit couplings. It is apparent that the deviations between the calculated and experimental values are now quite reasonable, with a comforting average value of  $0.93 \pm 0.05$  for this ratio, the more so considering that the extrapolations of these values to the CBS limit, which lies outside the scope of the current study, can be of the order of 15–20 kJ/mol (*vide infra* for the SiPb and GePb molecules) and the corrections due to the spin-orbit couplings do not take into account the aforementioned mixing of states, which in many cases may be significant.

To further improve the theoretical dissociation energies, an extrapolation was made to the CBS for the SiPb and GePb molecules by using the dissociation energies computed up to the quadruple zeta quality basis set with both the mixed exponential/Gaussian CBS formula proposed in Ref. 85 and that exploiting the  $n^{-3}$  dependence,<sup>86</sup> where  $n$  is the cardinal number of the cc-pVXZ basis sets. Total energies were used in both cases. The resulting values were, respectively, 256.9 and 259.0 (SiPb) and 251.2 and 253.3 (GePb). The average values of 257.9 and 252.2 kJ/mol, also reported in Table IX, are in agreement within the uncertainties with the experimental values tentatively corrected for the spin-orbit splittings: 265.3 and 250.2 kJ/mol for SiPb and GePb, respectively.

### C. Predicted dissociation energies of the yet unobserved intragroup 14 diatomics

As previously stated, the spin-orbit free dissociation energies calculated for the SiPb and GePb species largely overestimate the experimental values. Also overestimated are the  $D_0^\circ$  of the group 14 homonuclear diatomics (with the exception of Si<sub>2</sub>) and that of the SnPb molecule, as shown in Table IX. The ratio between the experimental and calculated dissociation energies varies from 1.08 for Si<sub>2</sub> to 0.39 for Pb<sub>2</sub>.

In order to make use of the data presented here for predicting the dissociation energies of the other intragroup molecules yet unobserved, we focused our attention on the aforementioned ratios between experimental (as such) and calculated (with augmented triple zeta basis sets) reaction energies, reported in the fourth column of Table IX. These uncorrected data were preferred in view of the uncertainties in the estimated corrections for the spin-orbit couplings. It is once again quite clear that a dependence of this ratio is observed on increasing the electronic complexity of these diatomics. This electronic complexity varies along the group 14 as a consequence of an interplay between a number of important contributions. The most prominent can be identified in the electron correlation, the scalar relativistic contributions (probably well accounted for by the used pseudopotentials), and the spin-orbit coupling. This last is known to play an important role. Indeed, as an example, while the Sn<sub>2</sub> molecule could be treated reasonably well in the  $\Lambda$ - $S$  coupling scheme in Ref. 87, the Pb<sub>2</sub> dissociation energy was found to be reduced by a factor of 2 by spin-orbit coupling. Balasubramanian and Pitzer<sup>83</sup> state that this interaction

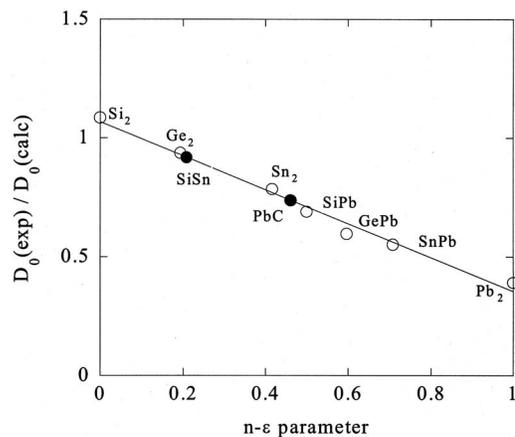


FIG. 4. Ratios of the calculated and experimental dissociation energies of intragroup 14 homonuclear and Pb-containing heteronuclear molecules (open circles). The full circles refer to the same ratio predicted for the yet unknown diatomics SiSn and PbC. Ratios are plotted as a function of the empirical parameter  $n-\epsilon$  (see text), which takes into account the total number of electrons of each molecule and the sum of the  $^3P_0$ - $^3P_1$  energy splittings of the constituent atoms.

mixes the  $^1\Sigma_g^+$  and  $^3\Sigma_g^-$  components, which results in a destabilization of the bond through mixing of the  $\sigma_g$  bonding with the  $\pi_g$  antibonding orbitals.<sup>88</sup>

In view of these considerations, we searched for a simple semiempirical way to describe this complexity and the related partial neglect of the electron correlation and spin-orbit coupling. To this end two contributions have been taken into account: the mere total number of electrons in each molecule  $n_{el}$  and the sum of the  $^3P_0$ - $^3P_1$  energy splittings of the constituent atoms,  $\sum \epsilon_{\text{split,atoms}}$ .<sup>29</sup> These two contributions have been incorporated in an overall parameter that we indicate as  $n-\epsilon$ , defined by the following relation:

$$n-\epsilon = w_{n_{el}} \frac{n_{el} - n_{el_{\min}}}{n_{el_{\max}} - n_{el_{\min}}} + w_{\epsilon_{\text{split}}} \frac{\sum \epsilon_{\text{split,atoms}} - \sum \epsilon_{\text{split,atoms}_{\min}}}{\sum \epsilon_{\text{split,atoms}_{\max}} - \sum \epsilon_{\text{split,atoms}_{\min}}}, \quad (5)$$

where  $w_{n_{el}}$  and  $w_{\epsilon_{\text{split}}} = 1 - w_{n_{el}}$  are the corresponding weights, and the subscripts min and max indicate the smallest and the largest values assumed by the two parameters in the series of molecules considered.

This parameter can be thought to represent the “complexity” of each species better than the crude indicator given by the total number of electrons because it includes a direct measure of the importance of spin-orbit effects, as given by the above mentioned atomic splitting. By studying the trend of the  $D_0^{\circ}(\text{expt})/D_0^{\circ}(\text{calc})$  ratio with the  $n-\epsilon$  parameter, a quite good linear relation ( $R=0.993$ ) could be found, with the optimized value  $w_{n_{el}}=0.646$ , as shown in Fig. 4. From the linear fit  $D_0^{\circ}(\text{expt})/D_0^{\circ}(\text{calc}) = -0.17337(n-\epsilon) + 1.0668$ , the corresponding ratio  $D_0^{\circ}(\text{expt})/D_0^{\circ}(\text{calc})$  for the yet unknown intragroup 14 molecule SiSn can be derived. This value, in turn, using the calculated CCSD(T) dissociation energy reported in Table IX, allows the prediction of a “pseudoexperimental”  $D_0^{\circ}(\text{SiSn}, g)$  value of 234 kJ mol<sup>-1</sup>. It can be estimated that this predicted dissociation energy should be

reliable within 7 kJ/mol, the standard error of the deviations between the experimental and calculated values of the known molecules in Fig. 4. An almost identical value,  $D_0^\circ(\text{SiSn})=235 \text{ kJ mol}^{-1}$ , is obtained with a much similar procedure using the differences between the calculated and the experimental  $D_0^\circ$  instead of their ratios.

Of some interest is also the possibility to attempt, with the same procedures, an estimate of the dissociation energy of the only still unknown Pb-containing intragroup 14 diatomic molecule: PbC. In this respect, it is worthwhile to note that in the correlation shown in Fig. 4 no carbon-containing molecules are included. Therefore, the reliability of this estimate is expected to be lower. The values obtained by the above reported procedures are  $D_0^\circ(\text{PbC})=183$  and  $D_0^\circ(\text{PbC})=192 \text{ kJ mol}^{-1}$  ( $D_0^\circ$  ratio and difference, respectively). Moreover, another opportunity is offered by the completion here realized of the determination of the dissociation energy of the series of diatomic molecules MePb (Me=Si, Ge, Sn, Pb). By exploiting, in much similar ways as those described previously, only the pertinent data of this series, it is possible to derive for the  $D_0^\circ(\text{PbC})$  a value of 177 kJ/mol. In conclusion, the dissociation energy of the molecule PbC can be estimated to be  $D_0^\circ(\text{Pb})=185 \text{ kJ/mol}$ , with an uncertainty of 11 kJ/mol, which is 1.5 times the standard error of the deviations between the experimental and calculated values of the known molecules in Fig. 4. This rather low value for the lead-carbon bond provides a simple rationale for the findings of Ref. 89. In this work the  $\text{PbC}_n$  clusters were invariably found to be in the preferred configuration with the lead atom in a terminal position. Indeed, with a carbon-carbon bond energy of 600 kJ/mol as deduced from the  $\text{C}_2$  molecule, the trade-off between two Pb–C and one Pb–C plus one C–C bonds is energetically much favored.

The main phenomena, which bring about the reported deviations from the experimental values of the dissociation energies calculated at the CCSD(T) level, have already been discussed. The lead-containing molecules in the intragroup 14 are still a challenge for any computational method. It is therefore of interest to analyze our results from the point of view of the energy of hypothetical reactions, where a partial compensation of the errors could occur, in the spirit of isodesmic reactions. With this in mind, the exchange reactions of MePb molecules involving Me atoms in contiguous rows of the periodic table have been taken into account. These reactions, together with the pertinent experimental and CCSD(T) energies, are reported in the last lines of Table IX. Compared to the simple dissociation to atom reactions, a better agreement between the calculated and pure experimental values is apparent, with a mean deviation of 18.4 kJ/mol. Thus, we can use the hypothetical exchange reaction between the PbC and SiPb molecules as an alternative method to estimate the PbC dissociation energy. Using the experimental  $D_0^\circ(\text{SiPb})$ , one obtains  $D_0^\circ(\text{PbC})=165.1+8.5=173.6 \text{ kJ/mol}$ . Moreover, giving confidence, on the contrary, to the spin-orbit coupling corrections estimated above as well as to the experimental data, we note that the difference between the experimental values adjusted for the spin-orbit coupling ( $\text{Expt.}+\Delta_{\text{SO}}$ ) and the calculated ones (i.e., 12.9, –7.8, and –11.4) monotonically decreases as the period

increases. A simple extrapolation to the exchange reaction involving the molecules PbC and SiPb permits us to estimate this difference as 22.2 kJ/mol. This allows us to correct the calculated value to  $8.5+22.2=30.7 \text{ kJ/mol}$ . Thus, the estimated dissociation energy ( $\text{Expt.}+\Delta_{\text{SO}}$ ) for the PbC molecule becomes  $265.3+30.7=296.0 \text{ kJ/mol}$ . Finally, using the aforementioned atomic spin-orbit coupling values and assuming that this effect is negligible in the PbC molecule, its dissociation energy is calculated to be 193.7 kJ/mol. These exchange reactions therefore give an average estimate for  $D_0^\circ(\text{PbC})$  of 184 kJ/mol, in very good agreement with the previously reported estimate, which was based on the interpolation of Fig. 4.

## D. Ionization energies and electron affinities

The calculated adiabatic ionization energies of 7.38 eV for GePb and 7.48 eV for SiPb overestimate the experimental values (Table I) by 3.9% and 6.9%, respectively, with the CCSD(T) AIE of GePb lying within the experimental uncertainties. In comparing these calculated and experimental values, it should be kept in mind that at the rather high temperatures of the experiments ( $\sim 1950$  and  $\sim 2300 \text{ K}$  for the GePb and SiPb molecules, respectively), the excited electronic levels of the neutral molecules can be significantly populated. However, if the energies of the electronic levels, as previously proposed in Sec. IV D, are used, the spreads in energy of the populated levels are found to be within 0.3 eV with a weighted average energy of 0.1 eV for both the molecules. Therefore, if the simple hypothesis of a unique ion state is assumed, the experimental values reported here underestimate the 0 K value by a small amount. As a consequence, the AIE value of the GePb molecules is brought into agreement, within the experimental uncertainty, with the computed value. The computed adiabatic EAs of 1.87 and 1.85 eV for SiPb and GePb, respectively, cannot be compared because no experimental determinations have been obtained.

## VI. CONCLUSION

By using the Knudsen effusion mass spectrometry method, the previously unknown molecular species GePb and SiPb were produced and identified in the high temperature vapors formed under the vaporization of pure elements in a double-oven-like molecular source. Several homogeneous equilibria were investigated as a function of temperature, involving the newly identified species and the homonuclear dimers and trimers.

The following chemophysical properties were determined: (i) dissociation energies at 0 K,  $165.1\pm 7.3 \text{ kJ/mol}$  (SiPb), and  $141.6\pm 6.9 \text{ kJ/mol}$  (GePb); (ii) first ionization energy,  $7.0\pm 0.2 \text{ eV}$  (SiPb), and  $7.1\pm 0.2 \text{ eV}$  (GePb).

A computational study of the GePb and SiPb species was also performed at the CCSD(T) level of theory using an electron core potential description for the Pb atoms. By comparing the experimental and theoretical results, some conclusions can be drawn.

The bond distances and vibrational frequencies obtained by the computational method used are of satisfactory to very good accuracy and can be used to evaluate the vibrational

tional part of thermal functions. On the contrary, since electronic levels calculated within the  $\Lambda$ - $S$  coupling scheme lead to a severe overestimation of the electronic partition function due to the neglect of the spin-orbit removal of degeneracy, which is important for these Pb-containing species, an evaluation of the electronic partition function is more satisfactorily accomplished using an empirical correlation.

The computed dissociation energies, once corrected for the estimated spin-orbit coupling effects and extrapolated to the complete basis set limit, are in good agreement with experimental data. Using a semiempirical correlation, the uncorrected computed dissociation energies were used to predict values of 234 and 185 kJ/mol, respectively, for the yet unknown dissociation energies of the SiSn and PbC molecules. Finally, we found that the experimental enthalpy changes of isomolecular reactions are better reproduced than dissociations to atoms at the CCSD(T) level.

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