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Mass spectrometric and computational study of SnPb in the gas phase

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The SnPb molecule has been identified in a Knudsen effusion mass spectrometry experiment. The direct dissociation reaction and two isomolecular exchange reactions involving the Sn₂ and Pb₂ molecules have been studied, in the 1426–1705 K range of temperatures, using both second and third law procedures. The $D_0^\circ(\text{SnPb},g)$ has been derived, for the first time, as (122.6 ± 4.0) kJ mol⁻¹. Density functional and *ab initio* calculations up to the coupled clusters level of theory were also performed. In addition, the anion dissociation energy $D_0^\circ(\text{SnPb}^-,g)$ of (179.2 ± 4.2) kJ mol⁻¹ was determined using the $D_0^\circ(\text{SnPb},g)$ mass spectrometric value derived in this investigation and literature data. © 2005 American Institute of Physics. [DOI: 10.1063/1.1825997]

I. INTRODUCTION

One piece of the information needed for a full understanding of a chemical bond is the energy stabilization that results. If one considers chemical bonds involving permutations of all the elements across the entire periodic system, much of the pertinent energetic information has been collected over the years (see, for example, Ref. 1) by the high temperature KEMS (Knudsen effusion mass spectrometric) technique which couples a Knudsen molecular source with a mass spectrometric analysis of the effusing beam.^{2–4}

Diatomic molecules, moreover, represent the first step in the understanding of the chemical bonding between atoms. Therefore, the importance of experimental determinations and theoretical evaluations on new diatomic molecules does not need to be underscored. In addition, the group-IVA elements are actively investigated for their various applications in many areas such as catalysis, sensor films, and new cluster materials.

Among the ten IVA intergroup heteronuclear diatomic molecules only half of them, SiC, GeC, SnC, GeSi, and SnGe, have experimentally characterized energetics at various levels of reliability (e.g., the GeC dissociation energy could be seriously in error as shown by Sari *et al.*⁵). The dissociation energy has not been measured for any of the IVA-Pb diatomics. On the contrary, the molecular parameters of the SnPb molecule, which are important ancillary data needed in the thermodynamic treatment of the primary KEMS results, have been determined in an extensive photoelectron study of the Sn₂⁻, Pb₂⁻, and SnPb⁻ anion by Ho *et al.*⁶

In this KEMS investigation, the SnPb gaseous molecule has been identified in the molecular beam effusing from an especially designed Knudsen cell. Its dissociation energy has

been measured both directly and by comparison with that of the homonuclear molecules Sn₂ and Pb₂. Experiments on the new gaseous molecule SnPb have also been complemented with a computational study of its properties up to the coupled clusters CCSD(T) level of theory.

II. EXPERIMENT

The basic features of the classical Knudsen effusion mass spectrometric apparatus employed have been previously described.⁷ A single focusing 30.5 cm radius of curvature, 60° magnetic sector mass spectrometer was used. The detector was a secondary electron multiplier. Ionization of the vapors effusing from the cell was accomplished with 70 V electrons while the electron emission current was regulated at 1.0 mA. Ionization efficiency curves (IEC) measurements were made by continuously varying the energy of the electrons up to 70 V.

The large difference in fugacity between pure Pb and Sn, together with the requirement of keeping the total pressure in the Knudsen cell within the molecular effusion conditions, would suggest using a sample with a reduced activity of Pb. While this, in principle, is easy to achieve by simply alloying Pb and Sn, a more convenient method of control is to regulate the relative partial pressures of the two elements. Therefore, we preferred an experimental approach which is, basically, the double oven technique.² More specifically, the design of the crucible used is similar to that employed by Hilpert *et al.*⁸ The principal Knudsen cell was suspended with tungsten rods within the hot zone where heating was accomplished with three tungsten strips. To this upper compartment containing Sn, was attached an auxiliary one, which, kept in a lower temperature zone (~50 mm in distance) and loaded with Pb, generated a flux of Pb vapor that was largely superheated in the upper compartment. Crucibles were machined from high purity high density graphite blocks, and temperatures were measured with Pt/Pt-Rh 10% thermo-

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TABLE I. Ion intensities measured in the experiments.

Experiment ^a	T/K	Ion intensities					
		¹²⁰ Sn ⁺ /A	²⁰⁸ Pb ⁺ /A	²³⁸ Sn ₂ ⁺ /A	⁴¹⁶ Pb ₂ ⁺ /A	³²⁶ SnPb ⁺ /A	
a)	1585	2.00e-09	5.10e-09			3.00e-13	
	1496	4.20e-10	9.30e-09			2.00e-13	
	1494	3.90e-10	2.50e-08			3.50e-13	
	1592	2.20e-09	6.90e-09			3.00e-13	
b)	1426	1.95e-10	3.10e-08		8.00e-13	2.00e-13	
	1429	2.20e-10	3.10e-08		8.50e-13	3.00e-13	
	1482	5.20e-10	4.30e-08		1.70e-12	7.00e-13	
c)	1480	2.80e-10	1.71e-08			1.50e-13	
	1507	6.70e-10	2.30e-08			5.50e-13	
	1528	8.85e-10	1.65e-08			4.00e-13	
	1557	1.38e-09	9.30e-09			3.00e-13	
d)	1421	3.00e-10	9.75e-09			2.00e-13	
	1476	6.30e-10	1.56e-08			2.00e-13	
	1549	1.62e-09	2.80e-08		5.00e-13	8.00e-13	
	1603	2.90e-09	4.40e-08			2.00e-12	
	1605	3.00e-09	4.50e-08	6.00e-12		2.00e-12	
	1582	2.34e-09	3.50e-08	4.30e-12		1.20e-12	
	1544	1.35e-09	2.22e-08	2.60e-12		7.00e-13	
	1636	4.30e-09	5.20e-08	9.00e-12		2.70e-12	
	1642	4.50e-09	5.00e-08	9.60e-12	1.20e-12	2.90e-12	
	1694	6.80e-09	6.90e-08	1.80e-11	1.90e-12	4.40e-12	
	1705	6.80e-09	7.00e-08	1.89e-11	2.10e-12	5.10e-12	
	e)	1455	3.70e-10	7.80e-09			1.00e-13
		1494	6.60e-10	1.35e-08			3.00e-13
1516		8.70e-10	1.68e-08	8.00e-13		3.00e-13	
1539		1.08e-09	1.77e-08	1.20e-12		4.00e-13	
1565		1.44e-09	2.04e-08	2.10e-12		5.50e-13	

^aInstrument sensitivity constants for the various experiments: $k/\text{bar A}^{-1} \text{K}^{-1} = 3.05, 1.74, 1.74, 1.87, 2.09$ for exp. (a)–(e).

couples. Temperature readings were checked by repeatedly observing the triple point of Ag. This molecular source made it possible to verify the equilibrium conditions for the molecule formation in a rather large range of pressure ratios $P_{\text{Pb}}/P_{\text{Sn}}$.

III. COMPUTATIONAL METHODS

Density-functional theory (DFT) and *ab initio* methods were employed for studying the structure, adiabatic ionization energy (IE), adiabatic electron affinity (EA), and dissociation energy (D_0°) of the electronic ground-state $X^3\Sigma$ of SnPb. The calculations were performed using the Becke three-parameter exchange functional with the Lee, Yang, and Parr correlational functional (B3LYP), the second- and fourth-order Møller–Plesset (MP2 and MP4) perturbation theory, and the coupled cluster singles and doubles excitations approach including the effect of connected triples excitations [CCSD(T)]. The basis sets used were the Stuttgart–Dresden–Bonn relativistic effective core potential (SDB) with large core correlation-consistent polarized valence triple- ζ (cc-pVTZ) pseudopotential basis set for Sn⁹ and the Stuttgart basis set with a relativistic large core (RLC) and effective core potential (ECP) for Pb.¹⁰ The adiabatic IE and EA were calculated using the relationships $(E_{\text{cation}} + \text{ZPE}_{\text{cation}}) - (E_{\text{neutral}} + \text{ZPE}_{\text{neutral}})$ and $(E_{\text{neutral}} + \text{ZPE}_{\text{neutral}}) - (E_{\text{anion}} + \text{ZPE}_{\text{anion}})$, respectively, where E is the total elec-

tronic energy of the optimized geometry and ZPE the zero-point energy. The computations were performed with the GAUSSIAN 98 program package.¹¹

IV. RESULTS

A. Identification of ions

Throughout these experiments, the single ionized species Sn⁺, Pb⁺, Sn₂⁺, Pb₂⁺, and SnPb⁺ were observed and identified by measurement of mass-to-charge ratios, isotopic abundances, shutter profiles, and IEC (ionization efficiency curves). To our knowledge, the heteronuclear species SnPb⁺ was identified here for the first time. For the elemental monomers and dimers, the appearance energy (AE) values were in agreement with literature data. For the newly identified molecule SnPb, the IEC did not show any significant fragmentation process. An analysis of the best ionization efficiency curve, measured at 1700 K, allowed for a determination of the ionization energy of the neutral molecule. The value here proposed of (6.7 ± 0.3) eV is an average of those derived by various methods:¹² Vanishing current (6.9), linear extrapolation (6.7), semilog plot (6.5), and extrapolated voltage difference (6.5). Ag and Pb were used as references in these determinations.

The measured ion currents are shown in Table I. From these ion currents, partial pressures of the atomic and molecular species were obtained with the relation $P_i = kf_i I_i^+ T$,

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 σ , the multiplier gain γ , and the isotopic abundance a . Also in Table I are the adopted values of the instrument sensitivity constants for each experiment. These values were determined before and after each experiment by quantitative silver calibration vaporizations and by assuming unit activity for Sn in the initial part of the experiments; in addition, further controls of the $\text{Sn}_2(g) = 2\text{Sn}(g)$ and $\text{Pb}_2(g) = 2\text{Pb}(g)$ equilibria were made over a range of temperatures different from those used for the molecule SnPb. Relevant data for the $\text{Sn}_2(g) = 2\text{Sn}(g)$ and $\text{Pb}_2(g) = 2\text{Pb}(g)$ equilibria were taken from the Ivtanthermo database.¹³ The multiplier gains were assumed to be proportional to the inverse square root of the pertinent ionic masses. The ionization cross sections of the atoms were taken from the experimental determination of Freund,¹⁴ $\sigma_{\text{Sn}} = 8.42$ and $\sigma_{\text{Pb}} = 7.27 \text{ \AA}^2$. In order to estimate the molecular ionization cross sections, various methods have been employed. With the selected choice (i.e., 0.75 times the sum of the cross sections of the constituent atoms $\sigma_{\text{Sn}_2} = 12.63$, $\sigma_{\text{Pb}_2} = 10.91$, and $\sigma_{\text{SnPb}} = 11.77 \text{ \AA}^2$) the specific factors f were: 3.837, 3.946, 6.791, 6.808, 6.830 for ^{120}Sn , ^{208}Pb , $^{238}\text{Sn}_2$, $^{416}\text{Pb}_2$, and $^{326}\text{SnPb}$, respectively.

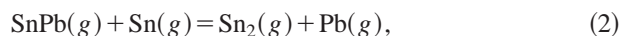
B. Reaction enthalpies and dissociation energy

The bond energy of the newly identified SnPb molecule was obtained from the thermodynamic study of the following gas-phase reactions:

the direct dissociation reaction



and two isomolecular exchange reactions



These last two reactions involve the dimers Sn_2 and Pb_2 for which the dissociation energy values of 183.4 ± 0.3^{15} and $83 \pm 1 \text{ kJ mol}^{-1}$ ^{16,17} are well known.

From the measured ion intensities and the derived partial pressures, equilibrium constants have been calculated for the equilibria (1)–(3). The equilibrium constants as a function of the temperature were then analyzed using the so-called second and third law methods.^{2–4} It is worthwhile to recall that 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-square analysis of a van't Hoff plot, $\ln K_p$ vs $1/T$. This value can be reduced to 0 K reference temperature through the use of the heat content functions, $H_T^\circ - H_0^\circ(\text{HCF}_0)$, of reactants and products. On the contrary, the third law procedure, through the relation $\Delta_r H_0^\circ = -RT \ln K_p - T\Delta[(G_T^\circ - H_0^\circ)/T]$, where $[(G_T^\circ - H_0^\circ)/T]$ are the Gibbs energy functions (GEF₀), allows the determination of a $\Delta_r H_0^\circ$ value at each experimental temperature point. 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. The pertinent data for

these procedures are reported in Table II for all reactions studied along side the derived dissociation energies of the SnPb molecule.

C. Thermal functions

The thermodynamic functions for the monoatomic elements as well as for the dimers were taken from the Ivtanthermo database.¹³ As mentioned before, many of the molecular parameters of the SnPb neutral molecule have been reported by Ho *et al.*⁶ In particular, we used the vibrational frequencies determined by Ho *et al.*⁶ for the ground and the first three low-lying electronic states of SnPb, together with their term energies. As for the bond lengths, Ho *et al.*⁶ could only determine the changes of the bond distance for different neutral electronic states upon photodetachment of the SnPb^- anion. Therefore, the bond length of 2.863 Å calculated at the CCSD(T) level of theory has been used together with the aforementioned experimental differences in bond lengths in order to evaluate the thermodynamic functions, HCF_0 and GEF_0 , of SnPb. Whenever possible the vibration–rotation interaction constant α_e has been estimated with the Pekeris relation for the anharmonic oscillator.¹⁸ These functions, calculated by taking into account the interdependence of electronic and internal motions ($Q = Q_{\text{tr}}(T, p) \cdot \sum_i q_{\text{rot}}(T, r_{e,i}) \cdot q_{\text{vib}}(T, \omega_{e,i}) g_i \cdot e^{\Delta \epsilon_i / RT}$), are reported in Table III together with the term energies and molecular parameters used.

D. Computational results

The optimized molecular parameters, zero-point vibrational energy (ZPE), adiabatic IE, adiabatic EA, and D_0° for the electronic ground state $X^3\Sigma^-(1\sigma^2 2\sigma^2 3\sigma^2 1\pi^2)$ of SnPb are listed in Table IV. At the highest level of theory, CCSD(T), the computed vibrational frequency of 156 cm^{-1} is in good agreement with the experimental value⁶ of $(148 \pm 15) \text{ cm}^{-1}$. There is no experimental bond distance available for SnPb, so the optimized value of 2.863 Å was used in the evaluation of its thermal functions as described previously.

In order to support the choice of the CCSD(T) level of theory for the computed molecular parameters, we performed calculations with the same level of theory and basis sets for Sn_2 , Pb_2 , and the SnPb^- anion whose molecular parameters are well known. There is an excellent agreement for the homonuclear molecules between our optimized bond distances and the experimental values. Specifically, we calculated a r_e of 2.798 Å for Sn_2 , only 2% larger than the spectroscopic value, and a r_e of 2.956 Å for Pb_2 , ~1% larger than the experimental one. For SnPb^- the bond distance is not spectroscopically determined, but the difference $r_e(\text{SnPb}^-, g) - r_e(\text{SnPb}, g)$ of 0.085 Å is known from the negative ion photodetachment investigation of Ho *et al.*⁶ The CCSD(T) computed $r_e(\text{SnPb}^-, g)$ is equal to 2.781 Å, and $r_e(\text{SnPb}^-, g) - r_e(\text{SnPb}, g) = 0.082 \text{ \AA}$, in perfect agreement with Ho *et al.*⁶ The computed harmonic vibrational frequency of 186 cm^{-1} for Sn_2 is the same than the value determined by Ho *et al.*,⁶ whereas the calculated frequency of 127 cm^{-1} for Pb_2 is ~15% larger than the experimental

TABLE II. Equilibrium data and reaction enthalpies (in kJ mol^{-1}) for reactions (1)–(3). Errors reported are the standard deviations.

Exp.	T/K	$\ln K_p(1)$	$\Delta H_0^\circ(1)$	$\ln K_p(2)$	$\Delta H_0^\circ(2)$	$\ln K_p(3)$	$\Delta H_0^\circ(3)$	
a)	1496	-1.27	121.6					
	1585	-1.01	126.0					
	1494	-1.62	125.9					
	1592	-0.61	121.3					
b)	1426	-1.79	121.7			-3.66	37.6	
	1429	-2.08	125.4			-3.88	40.4	
	1482	-1.70	125.7			-3.50	37.3	
c)	1480	-1.70	125.6					
	1507	-1.81	129.4					
	1528	-1.54	127.8					
	1557	-1.36	128.1					
d)	1421	-2.45	129.1					
	1476	-1.20	119.1					
	1549	-1.01	122.9			-3.30	36.5	
	1603	-0.86	125.6					
	1605	-0.80	125.0	3.77	-62.7			
	1582	-0.80	123.1	3.95	-63.9			
	1544	-1.29	126.2	4.08	-63.7			
	1636	-0.58	124.5	3.66	-62.7			
	1642	-0.64	125.9	3.57	-61.7	-3.27	38.6	
	1694	-0.29	125.3	3.69	-65.8	-3.13	38.1	
	1705	-0.42	128.0	3.61	-65.1	-3.19	39.3	
	e)	1455	-1.64	122.5				
		1494	-1.58	125.3				
		1516	-1.07	120.9	3.91	-60.2		
1539		-1.08	122.9	3.86	-60.7			
1565		-0.95	123.5	3.96	-63.2			
		Avg. Third law	124.8±2.6		-63.0±1.8		38.3±1.3	
		Trend ^a 10 ³	+5.1		-19.1		+0.7	
		Second Law $\Delta H_{(T)}^\circ$	127.8±10.7		-46.0±11.3		42.6±7.7	
		$\langle T \rangle$	1537		1600		1553	
		Second Law ΔH_0°	118.1±10.7		-59.3±11.3		46.8±7.7	
	Derived D_0°	124.8±2.6		120.4±1.8		121.3±1.6		

^aHere the trend is the temperature coefficient of an assumed linear dependence of the calculated third-law ΔH_0° vs T.

value. The calculated $\omega_e(\text{SnPb}^-,g)$ of 164 cm^{-1} overestimates the spectroscopic finding by only 3 cm^{-1} .

Moreover, from the computational results it is worthwhile to note that according to the Mulliken population the absolute value of atomic charges is extremely small, changing from 0.05 at the B3LYP level to 0.13 at the MP4 and CCSD(T) level. This together with the valence electronic structure $1\sigma^2 2\sigma^2 3\sigma^2 1\pi^2$ would suggest the presence of a double bond with a very little ionic contribution for the SnPb electronic ground state.

V. DISCUSSION

It should be noted that in the present study all the necessary thermodynamic functions of the atoms and molecules involved in the equilibria studied are known with a rather high degree of accuracy. Therefore, the third law analysis is preferred to the second law procedure. Nevertheless, a comparison between third and second law analyses is very useful in assessing the quality of the primary data.

The equilibrium data summarized in Table II show that for all the three equilibria studied, the 0 K reaction enthalpies derived from the third law agree with the second law values

within the uncertainty limits. Since the second law analysis is independent of the instrument sensitivity constant, this agreement is especially important in the case of reaction (1) whose equilibrium constant depends directly on this parameter and for which a larger set of data could be collected. Third law analysis of the pressure independent exchange reactions (2) and (3), in view of the compensation between reactants and products, is less sensitive to systematic errors in the auxiliary parameters, σ_i and γ_i , needed in converting ion intensities in partial pressures. However, the second law procedure for reactions (2) and (3) is still the more direct way of deriving $\Delta_r H_0^\circ$ from equilibrium constant measurements. Overall, in spite of the limited number of experimental points in the case of the isomolecular reactions (2) and (3), the agreement found for all the reactions studied gives confidence in the measurements. In addition, the drift in temperature of the third law values reported in the Table II provides a figure of merit for the absence of temperature trends in the equilibria studied. For the reason previously stated, the selected D_0° values reported in Table II are those derived from the third law enthalpies of reactions.

The quality of the primary data is also apparent from

TABLE III. Gibbs energy functions $-(G_T^\circ - H_0^\circ)/T$ and enthalpy contents $(H_T^\circ - H_0^\circ)$ for the gaseous molecule SnPb (standard pressure $p^\circ = 1$ bar).

T/K	$-(G_T^\circ - H_0^\circ)/T/\text{J K}^{-1} \text{mol}^{-1}$	$(H_T^\circ - H_0^\circ)/\text{kJ mol}^{-1}$
1000	286.274	41.583
1100	290.256	46.214
1200	293.925	50.803
1300	297.322	55.345
1400	300.482	59.843
1500	303.434	64.300
1600	306.201	68.720
1700	308.805	73.107
1800	311.261	77.465
1900	313.587	81.799
2000	315.793	86.110
2100	317.891	90.402
2200	319.891	94.677
2300	321.801	98.936
2400	323.629	103.182
2500	325.381	107.416

Electronic and molecular constants used (in cm^{-1})

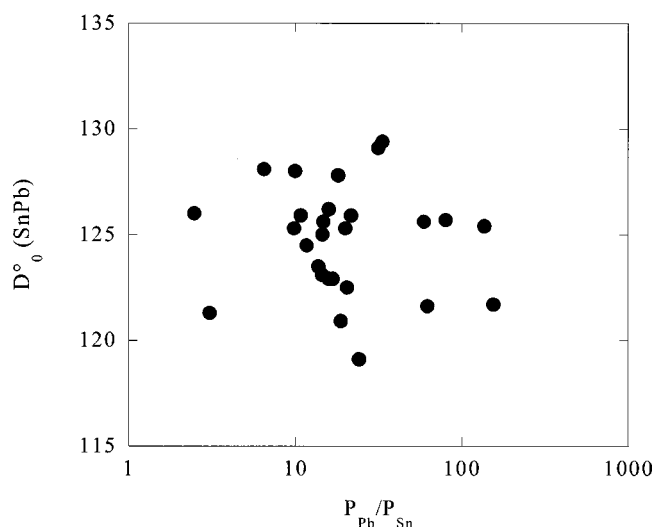
State	T_0	ω_e	$\omega_e x_e$	B_e	α_e
$^3\Sigma^-(0^+)$	0	148	0.4	0.027 250 94	8.524e-5
$^3\Sigma^-(1)$	1363	148	0.3	0.028 028 66	7.235e-5
$^3\Pi(2)$	2347	145		0.028 944 08	
$^3\Pi(1)$	5944	158		0.028 944 08	

Fig. 1 in which the third law D_0° values from reaction (1) are reported as a function of the partial pressure ratios of Pb and Sn. The equilibrium conditions shown have been sampled for a pressure ratio that spans almost two orders of magnitude without any dependence of the derived dissociation energy being observed.

An assessment of the reliability of the auxiliary parameters, electron impact cross sections and multiplier gains, used in converting ion intensities into pressures is useful both for estimating the overall uncertainty and selecting the final value of the dissociation energy. The uncertainty in the electron impact cross sections continues to be one of the main sources of error in the KEMS technique. For the atoms in the present study, the recent experimental determination by Freund *et al.*¹⁴ has been preferred with respect to the most common adoption of the complete set of values calculated by Mann.¹⁹ Different methods have been used in the past in estimating the diatomic molecule cross sections from the atomic values. The procedure used here for the assessment of the final data is the most common and assumes the additivity of atomic values reduced by the factor 0.75.⁴ However, other

TABLE IV. The optimized molecular parameters, r_e (in Å) and ω_e (in cm^{-1}), ZPE (in kJ mol^{-1}), adiabatic IE (in eV), adiabatic EA (in eV), and D_0° (in kJ mol^{-1}) computed at various levels of theory for the SnPb electronic ground state.

Method	r_e	ω_e	ZPE	IE	EA	D_0°
B3LYP	2.857	158	0.94	6.99	1.45	211.7
MP2	2.851	159	0.95	6.90	1.37	175.5
MP4	2.866	155	0.92	6.91	1.40	190.8
CCSD(T)	2.863	156	0.93	6.88	1.38	187.9

FIG. 1. Dissociation energies (in kJ mol^{-1}) of the molecule SnPb from reaction (1) as a function of the ratio of the partial pressures of lead and tin.

reducing factors, both lower and higher, have been proposed.⁴ Recently, a simple and accurate method has been proposed by Hastie.²⁰ This method, developed for ionic molecules, has been also adapted to species with significant covalency (up to 50%) and homonuclear dimers. For the sake of comparison, we used this method for all of the diatomics involved in the reactions (1)–(3). For the SnPb molecule the quantum-mechanical calculations indicated a very small charge separation. In this case, tentatively, the method has been used treating the molecule as homonuclear and, therefore, in the framework of the model, taking into account the elements isoelectronic with the Sn_2^+ and Pb_2^+ ions. The calculated cross sections, which are at the maximum of the ionization efficiency curve, have been reduced to the here used 70 eV energy of the ionizing electrons with the procedure suggested by Hastie.²⁰ Cross sections were also calculated by the additivity method with a reducing factor of 0.9. The resulting cross sections were as follows: (a) Hastie's method: Sn_2 (7.59), Pb_2 (7.02), SnPb (8.49); (b) reduced (0.9) additivity: Sn_2 (15.16), Pb_2 (13.09), SnPb (14.12). With the aforementioned alternative estimates of σ_i , which affect only the third law values, the following dissociation energies, in kJ mol^{-1} have been calculated: (a) Hastie's cross sections: Reaction (1) $D_0^\circ = 128.9$, reaction (2) $D_0^\circ = 118.0$ and reaction (3) $D_0^\circ = 119.8$; (b) reduced (0.9) additivity: reaction (1) $D_0^\circ = 122.4$ whereas for reactions (2) and (3) no variation with respect to the results of Table II is expected.

As for the multiplier gain, the inverse square root dependence on the mass is the largely prevailing choice found in the literature. However, the alternative choice of a mass^{-0.4} dependence,⁴ which once again has no influence on the second law values, significantly affects the direct dissociation reaction (1). Specifically, the third law D_0° value increases to $130.3 \text{ kJ mol}^{-1}$. Variations in the D_0° values derived by reactions (2) and (3), as before, are much smaller, $+0.3$ and -0.4 kJ mol^{-1} , respectively, as a consequence of the intrinsic compensation in the exchange reaction equilibrium constants.

As it is apparent from the results of Table II and the

preceding discussion, the $D_0^\circ(\text{SnPb},g)$ values which are derived by the analysis of the exchange reactions (2) and (3) are valuable for two important reasons. Firstly, they are in very close agreement. Secondly, these results are much less sensitive to different choices of the ancillary parameters needed in analyzing the primary data. On the other hand, the number of experimental points which could be collected is much smaller and at the limit of statistical significance. As a consequence, an average dissociation energy of (122.6 ± 4.0) kJ mol^{-1} for the SnPb molecule has been obtained by both weighting the values derived from equilibria (2) and (3) twice that from equilibria (1) and on the number of experimental points. The quoted error takes into account the preceding discussion.

Based on these results, the calculated CCSD(T) $D_0^\circ(\text{SnPb},g)$ largely overestimates the experimental value by 53%. This is not surprising because, at the same level of theory, the computed D_0° for the homonuclear diatomics, $D_0^\circ(\text{Sn}_2,g) = 205.3 \text{ kJ mol}^{-1}$ and $D_0^\circ(\text{Pb}_2,g) = 159.7 \text{ kJ mol}^{-1}$ also overestimate the experimental values by 12% and 92%, respectively. Clearly the evaluation of the dissociation energies of these molecules requires a higher level of treatment which would take full account of the relativistic effects. Qualitatively, it can be observed that the experimental value, $122.6 \text{ kJ mol}^{-1}$, here determined for the $D_0^\circ(\text{SnPb},g)$, is close to the average of the $D_0^\circ(\text{Sn}_2,g)$ ¹⁵ and $D_0^\circ(\text{Pb}_2,g)$ ^{16,17} dissociation energies of 183.4 and 83 kJ mol^{-1} . The computed dissociation energies parallel this behavior with the average of $182.5 \text{ kJ mol}^{-1}$ almost identical to the calculated $D_0^\circ(\text{SnPb},g)$. At the same level of theory, the computed adiabatic electron affinity underestimates the anion photoelectron spectroscopic value⁶ of 1.699 eV by $\sim 19\%$. On the contrary, the calculated adiabatic IE of 6.88 eV is in very good agreement with the experimentally determined value, $(6.7 \pm 0.3 \text{ eV})$, in this investigation. In order to compare these values one should take into account that, at the temperature of the experimental determination (1700 K), the first two low lying electronic levels of the neutral molecule, at 0.17 and 0.29 eV (see Table III) are significantly populated (33% and 14%, respectively). Therefore, while the resulting spread in energy of the neutral electronic levels is within the experimental error, with the simplifying hypothesis of the formation of an unique ion state, the agreement is even slightly improved. Moreover, it is possible to derive the dissociation energy of the SnPb^- anion using the $[D_0^\circ(\text{SnPb}^-,g) - D_0^\circ(\text{SnPb},g)]$ value of $(0.587 \pm 0.012) \text{ eV}$ precisely measured by Ho *et al.*⁶ and the $D_0^\circ(\text{SnPb},g)$ obtained in this investigation. The $D_0^\circ(\text{SnPb}^-,g)$ is then determined as $(179.2 \pm 4.2) \text{ kJ mol}^{-1}$ or $(1.857 \pm 0.044) \text{ eV}$.

VI. CONCLUSION

In this study the dissociation energy of the SnPb molecule has been determined for the first time via Knudsen

effusion mass spectrometry. In order to evaluate the mass spectrometric data of the three equilibria studied through both second and third law procedures, we performed DFT and *ab initio* calculations up to the CCSD(T) level of theory to obtain reliable values for the bond distance of the electronic ground state of SnPb. The $D_0^\circ(\text{SnPb},g)$ is derived as $(122.6 \pm 4.0) \text{ kJ mol}^{-1}$. From the analysis of the ionization efficiency curve, the $\text{IE}(\text{SnPb},g)$ is determined to be $(6.7 \pm 0.3) \text{ eV}$. This value compares well with the computed adiabatic IE of 6.88 eV. Moreover, from the $D_0^\circ(\text{SnPb},g)$ together with the $[D_0^\circ(\text{SnPb}^-,g) - D_0^\circ(\text{SnPb},g)]$ value we obtained a $D_0^\circ(\text{SnPb}^-,g)$ of $(179.2 \pm 4.2) \text{ kJ mol}^{-1}$ or $(1.857 \pm 0.044) \text{ eV}$.

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