

2000

Thermodynamic Stability of Sn₄, Sn₅, Sn₆, and Sn₇ Clusters by Knudsen Cell Mass Spectrometry

Giovanni Meloni

University of San Francisco, gmeloni@usfca.edu

R.W. Schmude

J.E. Kingcade

Karl A. Gingerich

Follow this and additional works at: http://repository.usfca.edu/chem_fac

 Part of the [Chemistry Commons](#)

Recommended Citation

Meloni, G., Schmude, R. W., Kingcade, J. E., & Gingerich, K. A. (2000). Thermodynamic stability of Sn₄, Sn₅, Sn₆, and Sn₇ clusters by Knudsen cell mass spectrometry. *Journal Of Chemical Physics*, 113(5)

This Article is brought to you for free and open access by the Chemistry at USF Scholarship: a digital repository @ Gleeson Library | Geschke Center. It has been accepted for inclusion in Chemistry Faculty Publications by an authorized administrator of USF Scholarship: a digital repository @ Gleeson Library | Geschke Center. For more information, please contact repository@usfca.edu.

Thermodynamic stability of Sn_4 , Sn_5 , Sn_6 , and Sn_7 clusters by Knudsen cell mass spectrometry

G. Meloni, R. W. Schmude, Jr.,^{a)} J. E. Kingcade, Jr.,^{b)} and K. A. Gingerich^{c)}

Department of Chemistry, Texas A&M University, P.O. Box 30012, College Station, Texas 77842-3012

(Received 3 April 2000; accepted 5 May 2000)

The Knudsen cell mass spectrometric method has been employed to measure the partial pressures of Sn_n ($n=1-7$) under equilibrium conditions above liquid tin or a tin-gold alloy, contained in a graphite Knudsen cell. From the all-gas analyzed equilibria the following atomization enthalpies $\Delta_a H_0^\circ(\text{Sn}_n)$, and enthalpies of formation, $\Delta_f H_{298.15}^\circ(\text{Sn}_n)$, in kJ mol^{-1} , have been obtained: Sn_4 , 750.2 ± 14 and 450.6 ± 14 ; Sn_5 , 990.2 ± 22 and 512.3 ± 22 ; Sn_6 , 1349.7 ± 28 and 452.8 ± 28 ; Sn_7 , 1644.2 ± 37 and 460.0 ± 37 . The atomization energies are compared with available theoretical values. © 2000 American Institute of Physics. [S0021-9606(00)02029-8]

I. INTRODUCTION

In recent years, there has been a large amount of research focused on the thermodynamic, electronic, and physical properties, and on the structure and reactivity of small inorganic clusters. The recent development of laser vaporization coupled with molecular beam technology has resulted in numerous studies of gas phase metal and semiconductor clusters.¹ This interest arises from their unique physical properties,² from the vital role that they play in the nucleation processes,^{3,4} from their potential use as functional units in quantum computers,⁵ and from their potential use as catalysts.^{6,7}

The present investigation of the tin clusters Sn_4 – Sn_7 has been part of our systematic investigation of thermodynamic properties of small group 14 clusters from Knudsen effusion measurements with a mass spectrometer.^{8–12} These investigations contribute to the knowledge of their thermodynamic properties and, together with the relevant spectroscopic and theoretical studies, to the knowledge of the bonding in such clusters.

The first mass spectrometric observation of tin clusters, Sn_2^+ – Sn_5^+ , has been reported by Honig, who evaporated tin from an open fused silica crucible.¹³ Drowart and Goldfinger¹⁴ have estimated the atomization energies of Sn_3 and Sn_4 from Honig's data. Gingerich *et al.*¹¹ evaporated tin from a graphite Knudsen cell and derived the third-law atomization energies of Sn_2 – Sn_7 , assuming linear geometries for the tin clusters.

The first theoretical study of Sn_2 – Sn_7 , using a molecular orbital method, was reported by Anderson.¹⁵ His calculations predicted linear, diamond, trigonal pyramid, hexagonal, and double capped pentagon geometries as the most stable structures for Sn_3 , Sn_4 , Sn_5 , Sn_6 , and Sn_7 , respectively. The

computed bond energies were smaller than the corresponding experimental values.¹¹

In recent years there has been an increasing number of experimental^{16–32} and theoretical^{26,33–36} investigations of small tin clusters.

In several mass spectrometric investigations of nonequilibrium vapor information on the relative stabilities of small tin clusters under various conditions of clusters formation was obtained. Vaporization by resistance heating¹⁶ or laser vaporization¹⁹ and subsequent cluster formation by cooling with He gas and ionization of the neutral clusters by 70 V electrons¹⁶ or photoionization¹⁹ were used in one set of investigations. Noda and co-workers^{20,21} analyzed the tin cluster ions from a liquid metal ion source. With this method clusters containing up to seven atoms were observed and enhanced stability was indicated for Sn_4^+ and Sn_6^+ ,²⁰ whereas the gas evaporation methods also produced intermediate size clusters with more than ten atoms and indicated preferred stability for $n=4, 6$, and 10. All investigators found that the Sn clusters behave similarly to those of silicon and germanium, having semiconductorlike covalent bonding. In comparing tin and lead clusters LaiHing *et al.*¹⁹ found a similar behavior, especially local maxima for $n=10$ for Si through Pb, whereas Saito and Noda²¹ found the mass spectra for Pb clusters to be different, reflecting metallic bonding. Ren and Ervin²⁵ studied the chemical reactivity of tin and lead cluster anions with oxygen by using a flow-tube reactor; they found there was a large variation in reactivity depending on cluster sizes. Ganteför *et al.*^{22,23} and Moravec *et al.*²⁷ observed the anion photoelectron spectra of tin clusters gaining important information about the ground and low-lying electronic states of the neutral species, and measured their electron affinities (EA). Shvartsburg and Jarrold²⁸ characterized the structures of tin clusters cations using a tandem quadrupole drift tube apparatus to measure the relative ion mobilities. Bachelors *et al.*^{30,31} used a micromechanical calorimeter in combination with a high-vacuum molecular beam apparatus to investigate thermal properties of isolated tin clusters, such as the formation enthalpy per atom. Yoshida and Fuke²⁹ examined the photoionization threshold of tin clusters with up

^{a)}Present address: Division of Natural Science and Nursing, Gordon College, 419 College Dr., Barnesville, Georgia 30204.

^{b)}Present address: Division of Natural Science, Blinn College, Brenham, Texas 77833.

^{c)}Electronic mail: gingerich@mail.chem.tamu.edu

to 41 atoms by laser photoionization with mass spectrometric detection and measured their ionization potentials. Negishi *et al.*³² studied the electronic properties of tin cluster anions and chlorine doped tin cluster anions and measured the threshold energies and the HOMO–LUMO gaps and electron affinities of Sn_n ($n=4-41$). They found that the Sn_n clusters with less than 30 atoms are semiconductor clusters, similar to the Si_n and Ge_n clusters.

In continuation of our studies of the thermodynamic stabilities of small tin clusters,^{11,17} we report here our results for the atomization energies and enthalpies of the formation of Sn_4 – Sn_7 . Our experimental values for the atomization energies are also compared with recent theoretical results from the literature. They have also been used, together with the experimental values for the electron affinities by Moravec *et al.*,²⁷ to derive the atomization energies of the corresponding cluster anions.

II. EXPERIMENT

The Knudsen effusion mass spectrometric method was employed to measure the partial pressures of Sn_4 , Sn_5 , Sn_6 , and Sn_7 clusters under equilibrium conditions. The experiments were performed with a Nuclide Corporation 12-90 HT single focusing magnetic deflection-type mass spectrometer. Details of the instrument and experimental procedure have been described elsewhere.³⁷

The tin molecules, Sn_4 – Sn_7 , were observed and measured in three different investigations. In series 1, a binary Sn–Au alloy in the molar ratio of 4.2:1.0 was contained within a graphite Knudsen cell. A graphite lined tantalum cell containing a 0.99 mole fraction of tin with minor traces of Cu, Ag, and Au was employed in series 2. The sample used in series 3 was tin inside a graphite cell. The electron energy used in each of the three series was 17, 18, and 20 V, respectively. More details about the experimental parameters used in these investigations can be found in Ref. 17. All gaseous species were identified from their mass-to-charge ratio, isotopic abundance, and ionization efficiency. At each measurement a movable slit was interposed into the molecular beam 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. The ionization energy of Sn_4 was measured as 8.7 ± 1.0 eV, using the literature ionization energies of Sn, 7.34 eV,³⁸ and of Au, 9.22 eV,³⁸ to calibrate the electron energy scale. The ion currents of Sn_5^+ , Sn_6^+ , and Sn_7^+ were too small for obtaining the respective ionization energies. The measured ion intensities of Sn^+ , Sn_4^+ , Sn_5^+ , Sn_6^+ , and Sn_7^+ , pertinent to the present investigation are listed in Table I.

The reference pressure calibration constant for atomic tin, k_{Sn} , was determined from the known $\text{Sn}_2(g) = 2 \text{Sn}(g)$ dissociation reaction, by combining the ion intensities of Sn^+ and Sn_2^+ , and the literature values of the dissociation enthalpy of $\text{Sn}_2(g)$ ($D_0^\circ = 183.4 \text{ kJ mol}^{-1}$).³⁹ The necessary Gibbs energy functions of $\text{Sn}(g)$ were taken from Gurvich *et al.*⁴⁰ and those for $\text{Sn}_2(g)$ were calculated using the molecular parameter determined by Pak *et al.*,³⁹ and the electronic excited states measured by Ho *et al.*⁴¹ In these calcu-

lations, the ionization cross section σ for Sn_2 was assumed to be 1.5 times that of $\text{Sn}(g)$;¹⁴ the multiplier gains were measured several times in series 1, resulting in $\gamma_{\text{Sn}_2}/\gamma_{\text{Sn}} = 0.88$. The pressure constants k_i for the clusters were then calculated from $k_i = k_{\text{Sn}}(\sigma_{\text{Sn}}\gamma_{\text{Sn}}n_{\text{Sn}})/(\sigma_i\gamma_i n_i)$, where σ , γ , and n are the cross section, multiplier gain, and isotopic abundance, respectively. The cross section for Sn was taken from Freund *et al.*⁴² and the molecular cross sections were assumed as 0.75 times the sum of the atomic value. The $\gamma_i/\gamma_{\text{Sn}}$ ratio used was equal to that measured for Sn_2 and Sn, implying cancellation of the mass and molecular effect.⁴³ The resulting values of k_i , in $\text{bar A}^{-1} \text{K}^{-1}$, are the following for series 1, 2, and 3: Sn, 0.074, 0.605, and 0.064; Sn_4 , 0.084, 0.687, and 0.072; Sn_5 , 0.078, 0.640, and 0.068; Sn_6 , 0.075, 0.614, and 0.065; Sn_7 , 0.577 and 0.061, for series 2 and 3, respectively.

III. RESULTS AND DISCUSSION

A. Thermal functions

The Gibbs energy functions, $(G_T^\circ - H_0^\circ)/T$ (GEF_0), and the heat content functions, $(H_T^\circ - H_0^\circ)$ (HCF_0), needed in the evaluation of the reaction enthalpies were taken from the literature for Sn.⁴⁰ Those for Sn_4 , Sn_5 , Sn_6 , and Sn_7 were calculated according to the statistical thermodynamic procedures, using the harmonic oscillator–rigid rotator approximation.⁴⁴ The geometries and bond lengths are shown in Fig. 1. The structures of Sn_4 , Sn_5 , Sn_6 , and Sn_7 clusters and the relative molecular parameters were obtained from Jackson,⁴⁵ which are revised values of those in Jackson *et al.*²⁶ The optimized molecular parameters of these molecules were obtained by local spin density calculations (LSD), carried out using the Hedin–Lundqvist (HL) exchange–correlation functional with the von Barth and Hedin (vBH) modification.

The Sn_4 ground state, 1A_g , has a planar rhombus geometry (D_{2h}) with Sn–Sn bond distances of 2.860 Å, the short diagonal of 3.078 Å, and the smaller bond angle equal to 65.1° . The vibrational frequencies, in cm^{-1} , are 66, 91, 112, 140, 153, and 170. Since all of the predicted electronic excited states, calculated by Dai and Balasubramanian,³³ lie more than 1.0 eV above the ground state, their contribution to the thermal functions below 1900 K is negligible.

The Sn_5 ground state, $^1A'_1$, is a distorted trigonal bipyramid with symmetry reduction to C_{2v} . The bond lengths, in Å, are 3.014 ($\times 4$) and 3.008 ($\times 2$) for the axial–equatorial distances, and 3.380 for the equatorial–equatorial distance with a bond angle of 107.5° . The vibrational frequencies, in cm^{-1} are 43, 51, 59, 88, 97, 103, 123, 139, and 151. The following 11 electronic excited states and respective energies, in cm^{-1} , based on theoretical work by Dai and Balasubramanian³⁴ were taken into account: 3B_2 (3791), 3B_1 (3791), 3A_2 (4678), 1A_2 (5001), $^3E''$ (5001), 1B_2 (5968), 1B_1 (5968), $^1E''$ (6049), $^3A'_2$ (6291), 1A_1 (6372), and 3A_1 (7340).

The Sn_6 ground state, $^1A_{1g}$, has a distorted octahedral geometry with a symmetry reduction to D_{4h} . The bond lengths, in Å are 3.033 ($\times 8$) for the axial–equatorial distances and 3.481 ($\times 4$) for the equatorial–equatorial dis-

TABLE I. Measured ion currents, in A, and third-law values, in kJ mol^{-1} , of the atomization enthalpies, $\Delta_a H_0^\circ$, of the Sn_4 , Sn_5 , Sn_6 , and Sn_7 clusters.

| T (K) | Ion intensities | | | | | $\Delta_a H_0^\circ$ Sn ₄ | $\Delta_a H_0^\circ$ Sn ₅ | $\Delta_a H_0^\circ$ Sn ₆ | $\Delta_a H_0^\circ$ Sn ₇ |
|----------|-----------------|------------------------------|------------------------------|------------------------------|------------------------------|---|---|---|---|
| | Sn ⁺ | Sn ₄ ⁺ | Sn ₅ ⁺ | Sn ₆ ⁺ | Sn ₇ ⁺ | | | | |
| Series 1 | | | | | | | | | |
| 1421 | 2.42E-8 | 3.11E-13 | | | | 750.2 | | | |
| 1448 | 4.12E-8 | 5.70E-13 | | | | 746.3 | | | |
| 1484 | 6.93E-8 | 8.79E-13 | | | | 744.9 | | | |
| 1526 | 1.45E-7 | 2.26E-12 | | | | 740.8 | | | |
| 1563 | 2.15E-7 | 3.40E-12 | | | | 743.9 | | | |
| 1579 | 2.53E-7 | 3.98E-12 | | | | 745.2 | | | |
| 1598 | 2.96E-7 | 4.98E-12 | | | | 748.9 | | | |
| 1611 | 3.82E-7 | 7.95E-12 | | | | 747.7 | | | |
| 1630 | 4.72E-7 | 1.06E-11 | 2.09E-13 | 1.43E-13 | | 749.1 | 982.6 | 1340.2 | |
| 1644 | 5.03E-7 | 9.24E-12 | 2.08E-13 | 1.29E-13 | | 750.3 | 986.5 | 1345.0 | |
| 1662 | 6.44E-7 | 1.13E-11 | 3.20E-13 | 1.43E-13 | | 747.8 | 986.1 | 1340.7 | |
| 1709 | 1.10E-6 | 1.52E-11 | 4.52E-13 | 2.15E-13 | | 743.1 | 980.6 | 1338.8 | |
| 1734 | 1.23E-6 | 1.50E-11 | 3.53E-13 | 9.80E-14 | | 747.6 | 983.2 | 1337.4 | |
| 1769 | 1.42E-6 | 9.45E-12 | 1.27E-13 | | | 747.7 | 977.3 | | |
| | | | | | Average | 746.7±2.8 ^a | 982.7±3.5 | 1340.4±2.9 | |
| Series 2 | | | | | | | | | |
| 1471 | 8.25E-9 | 3.81E-13 | | | | 755.0 | | | |
| 1526 | 1.91E-8 | 1.53E-12 | | | | 758.8 | | | |
| 1523 | 1.72E-8 | 7.95E-13 | | | | 754.3 | | | |
| 1604 | 4.86E-8 | 2.35E-12 | 1.20E-13 | | | 754.1 | 999.2 | | |
| 1648 | 9.78E-8 | 5.05E-12 | 2.55E-13 | 1.94E-13 | | 747.3 | 988.7 | 1344.6 | |
| 1715 | 1.78E-7 | 9.78E-12 | 3.75E-13 | 3.84E-13 | | 753.5 | 991.4 | 1357.8 | |
| 1800 | 3.73E-7 | 2.17E-11 | 1.47E-12 | 6.45E-13 | 7.00E-14 | 759.2 | 1005.2 | 1366.5 | 1650.9 |
| 1855 | 7.19E-7 | 4.53E-11 | 2.42E-12 | 1.09E-12 | 1.26E-13 | 753.7 | 992.7 | 1355.6 | 1639.3 |
| 1597 | 5.17E-8 | 2.10E-12 | 8.50E-14 | | | 746.0 | 986.1 | | |
| | | | | | Average | 753.5±4.5 | 993.9±7.1 | 1356.1±9.0 | 1645.1±8.2 |
| Series 3 | | | | | | | | | |
| 1552 | 1.95E-7 | 5.20E-12 | | | | 754.7 | | | |
| 1621 | 5.13E-7 | 1.88E-11 | 9.27E-13 | 5.22E-13 | 6.00E-14 | 754.0 | 999.5 | 1353.2 | 1640.8 |
| 1651 | 7.18E-7 | 2.85E-11 | 8.91E-13 | 7.15E-13 | 1.00E-13 | 755.5 | 994.2 | 1354.9 | 1641.8 |
| 1680 | 9.31E-7 | | | | 1.20E-13 | | | | 1647.7 |
| | | | | | Average | 754.7±0.7 | 996.9±3.7 | 1354.1±1.2 | 1643.4±3.7 |

^aThe error terms are standard deviations.

tances. The vibrational frequencies, in cm^{-1} , are 46 ($\times 2$), 54, 70, 89, 121, 128, 136 ($\times 2$), 160 ($\times 2$), and 177.

The Sn_7 ground state, $^1A'_1$, is a pentagonal bipyramid (D_{5h}) with the bond lengths equal to 3.17 Å ($\times 15$). The vibrational frequencies, in cm^{-1} , are 53, 55, 63, 69, 70, 82 ($\times 2$), 94, 104, 108, 109, 122, 133 ($\times 2$), 149.

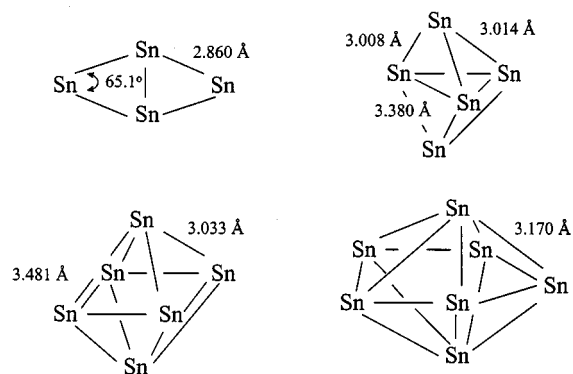


FIG. 1. Structures used in the evaluation of the Gibbs energy functions and the heat content functions listed in Table II.

Table II lists the thermal functions calculated for Sn_4 , Sn_5 , Sn_6 , and Sn_7 .

B. Atomization energies and enthalpies of formation

The enthalpy of the atomization reaction,

$$\text{Sn}_n(g) = n \text{Sn}(g), \quad n = 4-7, \quad (1)$$

TABLE II. The Gibbs energy functions, $(G_T^\circ - H_0^\circ)/T$ (GEF_0), in $\text{J K}^{-1} \text{mol}^{-1}$, and the heat content functions, $H_T^\circ - H_0^\circ$ (HCF_0), in kJ mol^{-1} , for the Sn_4 , Sn_5 , Sn_6 , and Sn_7 clusters.

| Species | | Temperature (K) | | | | | |
|-----------------|-------------------|-----------------|-------|-------|-------|-------|-------|
| | | 298.15 | 1400 | 1600 | 1800 | 2000 | 2200 |
| Sn ₄ | −GEF ₀ | 319.9 | 437.7 | 448.4 | 457.9 | 466.4 | 474.1 |
| | HCF ₀ | 20.87 | 112.1 | 128.7 | 145.4 | 162.0 | 178.6 |
| Sn ₅ | −GEF ₀ | 369.9 | 525.9 | 540.8 | 554.3 | 566.6 | 577.9 |
| | HCF ₀ | 27.56 | 155.0 | 181.6 | 208.3 | 234.7 | 260.6 |
| Sn ₆ | −GEF ₀ | 384.2 | 570.4 | 587.4 | 602.6 | 616.1 | 628.5 |
| | HCF ₀ | 32.56 | 178.5 | 205.1 | 231.7 | 258.3 | 284.9 |
| Sn ₇ | −GEF ₀ | 420.4 | 643.3 | 663.7 | 681.7 | 697.9 | 712.6 |
| | HCF ₀ | 39.28 | 212.8 | 244.4 | 275.9 | 307.5 | 339.1 |

TABLE III. Thermodynamic properties for the tin clusters Sn_4 – Sn_7 . All values are in kJ mol^{-1} .

| Cluster | $\Delta_a H_0^\circ$ | $\Delta_a H_{298.15}^\circ$ | $\Delta_f H_0^\circ$ | $\Delta_f H_{298.15}^\circ$ |
|---------------|----------------------|-----------------------------|----------------------|-----------------------------|
| Sn_4 | 750.2±14 | 754±14 | 455±14 | 451±14 |
| Sn_5 | 990.2±22 | 994±22 | 516±22 | 512±22 |
| Sn_6 | 1349.7±28 | 1354±28 | 458±28 | 453±28 |
| Sn_7 | 1644.2±37 | 1648±37 | 465±37 | 460±37 |

was evaluated according to the second-law method, based on a least-squares analysis of $\ln K_p$ vs $1/T$ plots, and according to the third-law method, using the relation $\Delta_f H_0^\circ = -RT \ln K_p - T\Delta[(G_T^\circ - H_0^\circ)/T]$.

For Sn_4 the second-law atomization enthalpy values obtained from the separate analysis of series 1 and series 2 are in good agreement with the third-law values. From series 1 the second and third law $\Delta_a H_0^\circ$, in kJ mol^{-1} , are 743.0 ± 11.8 and 746.7 ± 2.8 , respectively; from series 2 they are 754.9 ± 20.2 and 753.5 ± 4.5 , respectively. The atomization enthalpy, in kJ mol^{-1} , for Sn_4 is selected as 745.5 ± 4.1 and 754.0 ± 7.1 for series 1 and series 2, respectively, giving the third-law value twice the weight of the second-law value. From series 3 only a third-law evaluation is possible, due to few data points and the too small temperature range; the corresponding $\Delta_a H_0^\circ$ value, in kJ mol^{-1} , is 754.7 ± 0.7 .

For Sn_5 – Sn_7 the third-law $\Delta_a H_0^\circ$ values, in kJ mol^{-1} , of series 1, series 2, and series 3 are Sn_5 , 982.7 ± 3.5 , 993.9 ± 7.1 , and 996.9 ± 3.7 ; Sn_6 , 1341.2 ± 2.7 , 1356.1 ± 9.0 , and 1354.1 ± 1.2 ; Sn_7 , 1645.1 ± 8.1 and 1643.4 ± 3.7 for series 2 and series 3, respectively. The atomization enthalpy values of Sn_4 and Sn_5 clusters are slightly lower than the values reported by Gingerich *et al.*,¹¹ whereas the $\Delta_a H_0^\circ$ of Sn_6 and Sn_7 are higher. This is mainly due to their different thermal functions used; they were based on an assumed linear structure.

The recommended values for the atomization enthalpies of Sn_4 , Sn_5 , Sn_6 , and Sn_7 were obtained as the weighted average of the respective selected $\Delta_a H_0^\circ$ value, resulting from each series. The weight for each series was taken as the square root of number of data points. The resulting $\Delta_a H_0^\circ$ values, in kJ mol^{-1} or in eV, are Sn_4 , 750.2 ± 14 or 7.78 ± 0.15 ; Sn_5 , 990.2 ± 22 or 10.26 ± 0.23 ; Sn_6 , 1349.7 ± 28 or 13.99 ± 0.29 ; Sn_7 , 1644.2 ± 37 or 17.04 ± 0.38 . Here the uncertainties are the overall errors obtained as discussed in Schmude *et al.*⁴⁶ The corresponding values of $\Delta_a H_{298.15}^\circ$, $\Delta_f H_0^\circ$, and $\Delta_f H_{298.15}^\circ$ for Sn_4 , Sn_5 , Sn_6 , and Sn_7 have been derived from the $\Delta_a H_0^\circ$, using $\Delta_f H_0^\circ(\text{Sn}, g) = (301.3 \pm 1.5) \text{ kJ mol}^{-1}$, and $\Delta_f H_{298.15}^\circ(\text{Sn}, g) = (301.2 \pm 1.5) \text{ kJ mol}^{-1}$, from Gurvich *et al.*,⁴⁰ respectively, and the $H_{298.15}^\circ - H_0^\circ$ values from Table II. The enthalpies of formation were calculated employing the relation $\Delta_f H_T^\circ(\text{Sn}_n) = n\Delta_f H_T^\circ(\text{Sn}) - \Delta_a H_T^\circ(\text{Sn}_n)$, where T is 0 or 298.15 K. The thermodynamic properties for Sn_4 – Sn_7 clusters have been summarized in Table III.

From the $\Delta_a H_0^\circ$ values, the fragmentation energies or incremental dissociation energies, $\Delta_a H_0^\circ(\text{Sn}_n) - \Delta_a H_0^\circ(\text{Sn}_{n-1})$, can be derived. They are, in kJ mol^{-1} or eV, 346 or 3.59, 240 or 2.49, 360 or 3.73, and 295 or 3.06,

TABLE IV. A comparison of experimental atomization energies, in eV, with recent theoretical values for Sn_4 – Sn_7 .

| Cluster | Experiment | Theoretical | | |
|---------------|--------------------|-------------------|-------------------|--------------------|
| | This investigation | MRSDCI | BLYP ^a | CP-MD ^b |
| Sn_4 | 7.78±0.15 | 7.37 ^c | 8.28 | 10.94 |
| Sn_5 | 10.26±0.23 | 9.37 ^d | 10.89 | 14.83 |
| Sn_6 | 13.99±0.29 | | 13.92 | 19.00 |
| Sn_7 | 17.04±0.38 | | 16.84 | 23.16 |

^aReference 26.

^bReference 36.

^cReference 33.

^dReference 34.

for Sn_4 , Sn_5 , Sn_6 , and Sn_7 . Here the $\Delta_a H_0^\circ(\text{Sn}_3)$ of $(403.8 \pm 14.8) \text{ kJ mol}^{-1}$, or 4.19 eV,¹⁷ has been used to obtain the value for Sn_4 . The values confirm the qualitative conclusions of earlier nonequilibrium mass spectrometric observations of a preferred stability for Sn_4 and Sn_6 .^{16,20} The stability trend for the tin clusters is similar to that for the corresponding germanium clusters¹⁰ and silicon clusters.⁴⁷

It is also interesting to calculate the binding energies, or atomization enthalpies, of tin clusters anions for the reaction $\text{Sn}_n^-(g) = (n-1)\text{Sn}(g) + \text{Sn}^-(g)$, using the experimental values of their electron affinities (EA). The results, in eV, are 5.32, 8.71, 11.80, 15.16, and 17.89 for Sn_3^- , Sn_4^- , Sn_5^- , Sn_6^- , and Sn_7^- , respectively. The relation used is $\Delta_a H_0^\circ(\text{Sn}_n^-) = \Delta_a H_0^\circ(\text{Sn}_n) - \text{EA}(\text{Sn}) + \text{EA}(\text{Sn}_n^-)$. The experimental electron affinities were taken from Moravec *et al.*²⁷ for Sn_3 – Sn_7 , and from Thøgersen *et al.*⁴⁸ for the atomic tin. The corresponding fragmentation enthalpies, $\Delta_a H_0^\circ(\text{Sn}_n^-) - \Delta_a H_0^\circ(\text{Sn}_{n-1}^-)$, in eV, are 3.39, 3.09, 3.36, and 2.72 for Sn_4^- , Sn_5^- , Sn_6^- , and Sn_7^- , respectively.

C. Comparison of experimental and theoretical atomization energies

In recent years theoretical studies in predicting binding or atomization energies of small group 14 clusters, especially those of carbon and silicon, with chemical accuracy,⁴⁷ using the Gaussian 2 (G2) theory have become possible. The G2 theory has recently⁴⁹ also been applied with similar success to germanium clusters with up to five atoms,¹⁰ but has not yet been extended to tin clusters.

In Table IV we compare the experimental atomization energies of Sn_4 – Sn_7 obtained in the present investigation with the corresponding recent theoretical values.

Dai and Balasubramanian performed multireference singles and doubles configuration interaction calculations (MRSDCI) on Sn_4^{33} and Sn_5^{34} giving several electronic excited states with different geometries. The calculated atomization enthalpies are about 5% for Sn_4 and 9% for Sn_5 less than our respective recommended values.

The only theoretical calculations performed so far on Sn_6 and Sn_7 are those by Jackson *et al.*²⁶ and Wang *et al.*³⁵ Wang *et al.* performed *ab initio* total-energy pseudopotential calculations on neutral and negatively charged Sn_n ($n = 3$ – 10) clusters, giving the lowest-energy structures without details of the molecular parameters. Jackson *et al.*²⁶ cal-

culated the energy minimized structures for Sn₂–Sn₇ neutral and anionic clusters, also giving the molecular parameters, bond distances, and vibrational frequencies. The atomization enthalpies obtained by single-point calculations using the Becke–Lee–Yang–Parr gradient-corrected correlation functional (BLYP) at the Becke–Janak–Moruzzi–Williams correlation functional (BJMW) optimized geometry with zero-point corrections, are slightly higher than our values for Sn₄ and Sn₅, whereas they are in good agreement for Sn₆ and Sn₇. Lu *et al.*³⁶ carried out the Car–Parrinello *ab initio* molecular dynamics (CP-MD) simulated annealing of tin clusters up to 13 atoms to gain some insight into the dynamics of clusters formation. They also give values for the cohesive energies of these clusters (see Table IV), which are subject to a constant shift.

ACKNOWLEDGMENTS

The authors would like to thank the Robert A. Welch Foundation and the National Science Foundation for financial support of this work.

- ¹M. D. Morse, *Chem. Rev.* **86**, 1049 (1986).
- ²Y. Oshima and K. Takayanagi, *Z. Phys. D: At., Mol. Clusters* **27**, 287 (1993).
- ³J. Bernholc and J. C. Phillips, *Phys. Rev. B* **33**, 7395 (1986).
- ⁴*Physics and Chemistry of Finite Systems: From Clusters to Crystals*, edited by P. Jena, S. N. Khanna, and B. K. Rao (Kluwer Academic, Boston, 1992), Vols. 1 and 2.
- ⁵N. Hamada, in *Microclusters*, edited by S. Sugano, Y. Nishina, and S. Ohnishi (Springer-Verlag, Berlin, 1987), p. 180.
- ⁶D. N. Belton and S. J. Schmieg, *Surf. Sci.* **202**, 238 (1988).
- ⁷J. Haggin, *Chem. Eng. News* **65**, 9 (1987).
- ⁸K. A. Gingerich, H. C. Finkbeiner, and R. W. Schmude, Jr., *J. Am. Chem. Soc.* **116**, 3884 (1994).
- ⁹K. A. Gingerich, Q. Ran, and R. W. Schmude, Jr., *Chem. Phys. Lett.* **256**, 274 (1996).
- ¹⁰K. A. Gingerich, R. W. Schmude, Jr., M. Sai Baba, and G. Meloni, *J. Chem. Phys.* **112**, 7443 (2000).
- ¹¹K. A. Gingerich, A. Desideri, and D. L. Cocke, *J. Chem. Phys.* **62**, 731 (1975).
- ¹²K. A. Gingerich, D. L. Cocke, and F. Miller, *J. Chem. Phys.* **64**, 4027 (1976).
- ¹³R. E. Honig, *J. Chem. Phys.* **21**, 573 (1953).
- ¹⁴J. Drowart and P. Goldfinger, *Angew. Chem. Int. Ed. Engl.* **6**, 581 (1967).
- ¹⁵A. B. Anderson, *J. Chem. Phys.* **63**, 4430 (1975).
- ¹⁶T. P. Martin and H. Schaber, *J. Chem. Phys.* **83**, 855 (1985).
- ¹⁷K. A. Gingerich, E. A. Ramakrishnan, and J. E. Kingcade, Jr., *High Temp. Sci.* **21**, 1 (1986).
- ¹⁸J. C. Phillips, *J. Chem. Phys.* **87**, 1712 (1987).
- ¹⁹K. LaiHing, R. G. Wheeler, W. L. Wilson, and M. A. Duncan, *J. Chem. Phys.* **87**, 3401 (1987).
- ²⁰M. Watanabe, Y. Saito, S. Nishigaki, and T. Noda, *Jpn. J. Appl. Phys.* **27**, 344 (1988).
- ²¹Y. Saito and T. Noda, *Z. Phys. D: At., Mol. Clusters* **12**, 225 (1989).
- ²²G. Ganteför, M. Gausa, K. H. Meiwes-Broer, and H. O. Lutz, *Faraday Discuss. Chem. Soc.* **86**, 197 (1988).
- ²³G. Ganteför, M. Gausa, K. H. Meiwes-Broer, and H. O. Lutz, *Z. Phys. D: At., Mol. Clusters* **12**, 405 (1989).
- ²⁴D. S. Cornett, M. Peschke, K. LaiHing, P. Y. Cheng, K. F. Willey, and M. A. Duncan, *Rev. Sci. Instrum.* **63**, 2177 (1992).
- ²⁵X. Ren and K. M. Ervin, *Chem. Phys. Lett.* **198**, 229 (1992).
- ²⁶P. Jackson, I. G. Dance, K. J. Fisher, G. D. Willett, and G. E. Gadd, *Int. J. Mass Spectrom. Ion Processes* **157/158**, 329 (1996).
- ²⁷V. D. Moravec, S. A. Klopčic, and C. C. Jarrold, *J. Chem. Phys.* **110**, 5079 (1999).
- ²⁸A. A. Shvartsburg and M. F. Jarrold, *Phys. Rev. A* **60**, 1235 (1999).
- ²⁹S. Yoshida and K. Fuke, *J. Chem. Phys.* **111**, 3880 (1999).
- ³⁰T. Bachels and R. Schäfer, *Chem. Phys. Lett.* **300**, 177 (1999).
- ³¹T. Bachels, F. Tiefenbacher, and R. Schäfer, *J. Chem. Phys.* **110**, 10 008 (1999).
- ³²Y. Negishi, K. Kawamata, A. Nakajima, and K. Kaya, *J. Electron Spectrosc. Relat. Phenom.* **106**, 117 (2000).
- ³³D. Dai and K. Balasubramanian, *J. Chem. Phys.* **96**, 8345 (1992).
- ³⁴D. Dai and K. Balasubramanian, *J. Phys. Chem.* **100**, 19 321 (1996).
- ³⁵B. Wang, L. M. Molina, M. J. López, A. Rubio, J. A. Alonso, and M. J. Stott, *Ann. Phys. (Leipzig)* **7**, 107 (1998).
- ³⁶Z.-Y. Lu, C.-Z. Wang, and K.-M. Ho, *Phys. Rev. B* **61**, 2329 (2000).
- ³⁷K. A. Gingerich, in *Current Topics in Material Science*, edited by E. Kaldis (North-Holland, Amsterdam, 1980), Vol. 6, p. 345.
- ³⁸C. E. Moore, NRS-D-NBS 35, Natl. Bur. Stand. US, 1971.
- ³⁹K. Pak, M. F. Cai, T. P. Dzugas, and V. E. Bondybey, *Faraday Discuss. Chem. Soc.* **86**, 153 (1988).
- ⁴⁰*Thermodynamic Properties of Individual Substances*, edited by L. V. Gurvich, I. V. Veys, and C. B. Alcock (Hemisphere, New York, 1991), Vol. 2.
- ⁴¹J. Ho, M. L. Polak, and W. C. Lineberger, *J. Chem. Phys.* **96**, 144 (1992).
- ⁴²R. S. Freund, R. C. Wetzel, R. J. Shul, and T. R. Hayes, *Phys. Rev. A* **41**, 3575 (1990).
- ⁴³M. G. Inghram and R. J. Hayden, *Mass Spectrometry* (National Academy of Sciences, Washington, DC, 1954).
- ⁴⁴D. R. Stull and H. Prophet, in *Characterization of High Temperature Vapors*, edited by J. L. Margrave (Wiley Interscience, New York, 1971), p. 359.
- ⁴⁵P. Jackson (private communication).
- ⁴⁶R. W. Schmude, Jr., Q. Ran, and K. A. Gingerich, *J. Chem. Phys.* **99**, 7998 (1993).
- ⁴⁷K. Raghavachari and L. A. Curtis, in *Quantum Mechanical Electronic Structure Calculations with Chemical Accuracy*, edited by S. R. Langhoff (Kluwer Academic, The Netherlands, 1995), p. 173.
- ⁴⁸J. Thøgersen, L. D. Steele, M. Scheer, C. A. Brodie, and H. K. Haugen, *J. Phys. B* **29**, 1323 (1996).
- ⁴⁹P. W. Deutsch, L. A. Curtiss, and J. B. Blaudeau, *Chem. Phys. Lett.* **270**, 413 (1997).

Journal of Chemical Physics is copyrighted by AIP Publishing LLC (AIP). Reuse of AIP content is subject to the terms at: <http://scitation.aip.org/termsconditions>. For more information, see <http://publishing.aip.org/authors/rights-and-permissions>.