The Dimerization of $SnCl_2(g)$: Mass Spectrometric and Theoretical Studies

K. Hilpert,*,[†] S. Roszak,*,[‡,||] J. Saloni,[‡,||] M. Miller,[§] P. Lipkowski,[‡] and J. Leszczynski[||]

Institute for Materials and Processes in Energy Systems, Research Center Jülich, 52425 Jülich, Germany, Institute of Physical and Theoretical Chemistry, Wroclaw University of Technology, Wybrzeże Wyspiańskiego 27, 50-370 Wroclaw, Poland, Institute of Inorganic Chemistry and Metallurgy of Rare Elements, Wroclaw University of Technology, Wybrzeże Wyspiańskiego 27, 50-370 Wroclaw, Poland, and Computational Centre for Molecular Structure and Interactions, Jackson State University, Jackson, Mississippi 39217

Received: August 31, 2004; In Final Form: December 9, 2004

The vaporization of $SnCl_2(s)$ was investigated in the temperature range between 382 and 504 K by the use of Knudsen effusion mass spectrometry. The Sn^+, $SnCl^+$, $SnCl_2^+$, $Sn_2Cl_3^+$, and $Sn_2Cl_4^+$ ions were detected in the mass spectrum of the equilibrium vapor. The $SnCl_2(g)$ and $Sn_2Cl_4(g)$ gaseous species were identified, and their partial pressures were determined. The structure and vibrational properties of both species and corresponding fragmentation products were studied applying density functional theory and second-order Møller−Plesset perturbation theoretical approaches. Molecular parameters yielded thermodynamic functions by the use of statistical thermodynamics. The sublimation enthalpies of $SnCl_2(g)$ and $Sn_2Cl_4(g)$ at 298 K resulting from the second- and third-law methods are evaluated as 130.9 ± 6.2 kJ mol^{-1} and 155.8 ± 7.3 kJ mol^{-1}, respectively. The enthalpy changes of the dissociation reactions $Sn_2Cl_4(g) = 2\ SnCl_2(g)$ were obtained as $\Delta_d H°(298) = 106.8 \pm 6.2$ kJ mol^{-1}. The corresponding theoretical value amounts to 103.4 kJ mol^{-1}. The change of monomer properties due to the dimerization reaction is also discussed.

I. Introduction

The thermodynamic properties of tin(II) halides are of interest because of their applications in electric discharge lamps.[1] Knowledge concerning $SnBr_2$ [2] and SnI_2 [3] vapors has increased by our recent studies reported in the cited references. The thermodynamics of the $SnCl_2$ vapor was studied for the first time by Karpenko and Novikov.[4] The authors identified dimeric species by use of mass spectrometery and investigated the dimerization equilibrium by measuring the total pressure of saturated and unsaturated $SnCl_2$ vapors. No dimeric species, however, were observed in the subsequent mass spectrometry experiment.[5] The dimerization of $SnCl_2$ vapors was confirmed in more recent studies performed by Knudsen effusion mass spectrometry and transpiration methods.[6,7] Vapor pressure measurements above the liquid tin chloride suggest that the mole fraction of the dimer is decreasing at temperatures above 576 K. Thermodynamic data for $Sn_2Cl_4(g)$ obtained in the latter studies should be considered as preliminary due to the small content of this species in the vapor. The tin chloride vapor has been additionally studied by means of gas-phase Raman spectroscopy,[8,9] matrix isolation infrared[10] and Raman spectroscopy,[11] electron spectroscopy,[12] gas-phase electron diffraction,[13] and by synchrotron radiation photoemission.[14] Fields et al. have undertaken an attempt to deduce the structure and bonding of Sn_2Cl_4 dimers based on laser Raman spectroscopic studies and force constant calculations.[15] The authors suggest a single-chlorine bridged C_s symmetry structure and provide corresponding thermodynamic functions.

The experimental studies of monomers were supplemented by several theoretical investigations.[16−18] Very recently quantum chemical studies were also published for dimeric species of the general formula Sn_2X_4 (X = Cl, Br, I).[19−21] The results of Levy et al.[19] on the thermodynamic properties of $SnCl_2$ vapors are especially relevant to the presented study. The experimental data from the previous studies[6,7] were marged by the latter authors with thermochemical functions of gaseous $SnCl_2(g)$ and $Sn_2Cl_4(g)$ species derived from the molecular parameters computed by quantum chemical methods. Their results will be compared with those obtained by us in the Results and Discussion section.

The thermodynamic stability of dimeric and larger aggregates in the metal halide vapors is rather common.[22,23] In this work, for the first time the vapor composition over solid $SnCl_2$ was studied by the use of Knudsen effusion mass spectrometry. The properties of the monomer and dimer of $SnCl_2$ as well as corresponding molecular fragment cations were additionally investigated by the density functional theory (DFT) and second-order Møller−Plesset perturbation approaches. The structures and vibrational properties were calculated and compared with the available experimental and theoretical data. These results yielded thermodynamic functions of gaseous species needed for the third law treatment of partial pressure obtained by mass spectrometry. The dissociation enthalpy of the Sn_2Cl_4 complex was also calculated directly from the theoretically determined data. Additionally, the theoretical values of ionization and appearance potentials are reported and compared with the experimental values available in the literature. The nature of bonding involved in the dimerization of $SnCl_2$ in the gas phase was studied, applying the electron population analysis and the interaction energy decomposition scheme. The studies are

---

* Corresponding authors. (Hilpert) tel.: +49 2461 613280; fax: +49 2461 613699. (Roszak) tel.: +48 71 3202675; fax: +48 71 3203364.

[†] Research Center Jülich.

[‡] Institute of Physical and Theoretical Chemistry, Wroclaw University of Technology.

[§] Institute of Inorganic Chemistry and Metallurgy of Rare Elements, Wroclaw University of Technology.

[||] Jackson State University.

10.1021/jp0460691 CCC: $30.25

TABLE 1: Number of the Measurement Temperatures, *n*, Temperature Range of Run, Δ*T*, and Pressure Calibration Constant, *k*, in Runs 1−6 Performed for the Vaporization of $SnCl_2$(s)

run	n	ΔT/K	k/(Pa K^{-1} s)
1	12	384−504	$(1.32 \pm 0.07) \cdot 10^{-9}$
2	8	382−498	$(8.29 \pm 0.48) \cdot 10^{-10}$
3	14	383−500	$(1.14 \pm 0.06) \cdot 10^{-9}$
4	6	398−496	$(1.15 \pm 0.08) \cdot 10^{-9}$
5	12	388−498	$(1.06 \pm 0.05) \cdot 10^{-9}$
6	12	388−499	$(1.37 \pm 0.09) \cdot 10^{-9}$

TABLE 2: Ion Intensities Corrected for the Isotopic Distribution in Counts per Second Determined upon Vaporizing $SnCl_2$(s) in the Course of Run 5 and the Assignment of Ions to Their Neutral Precursors

	$SnCl_2$(g)			Sn_2Cl_4(g)	
T/K	Sn^+	$SnCl^+$	$SnCl_2^+$	$Sn_2Cl_3^+$	$Sn_2Cl_4^+$
498	$9.72 \cdot 10^5$	$6.60 \cdot 10^6$	$3.44 \cdot 10^6$	$3.90 \cdot 10^5$	$3.84 \cdot 10^4$
488	$5.51 \cdot 10^5$	$3.69 \cdot 10^6$	$1.92 \cdot 10^6$	$1.97 \cdot 100^5$	$1.99 \cdot 10^4$
478	$3.21 \cdot 10^5$	$1.88 \cdot 10^6$	$9.74 \cdot 10^5$	$8.81 \cdot 10^4$	$9.40 \cdot 10^3$
468	$1.62 \cdot 10^5$	$8.80 \cdot 10^5$	$4.58 \cdot 10^5$	$3.76 \cdot 10^4$	$4.06 \cdot 10^3$
458	$8.75 \cdot 10^4$	$4.34 \cdot 10^5$	$2.27 \cdot 10^5$	$1.73 \cdot 10^4$	$1.88 \cdot 10^3$
448	$4.62 \cdot 10^4$	$2.14 \cdot 10^5$	$1.13 \cdot 10^5$	$6.98 \cdot 10^3$	$8.27 \cdot 10^2$
438	$1.91 \cdot 10^4$	$8.74 \cdot 10^4$	$4.58 \cdot 10^4$	$2.43 \cdot 10^3$	$3.05 \cdot 10^2$
428	$8.26 \cdot 10^3$	$3.53 \cdot 10^4$	$1.89 \cdot 10^4$	$9.31 \cdot 10^2$	$1.35 \cdot 10^2$
418	$3.35 \cdot 10^3$	$1.57 \cdot 10^4$	$8.14 \cdot 10^3$	$3.47 \cdot 10^2$	$4.51 \cdot 10^1$
408	$1.52 \cdot 10^3$	$6.19 \cdot 10^3$	$3.15 \cdot 10^3$	$1.22 \cdot 10^2$	
398	$5.18 \cdot 10^2$	$2.24 \cdot 10^3$	$1.13 \cdot 10^3$	$3.58 \cdot 10^1$	
388	$2.11 \cdot 10^2$	$7.42 \cdot 10^2$	$4.01 \cdot 10^2$		

supplemented by the discussion of changes of properties in monomers undergoing the dimerization process.

II. Experimental Section

The vaporization measurements were carried out with a substantially modified single-focusing CH5 mass spectrometer[24] (Finnigan MAT, Bremen, Germany), which was equipped with a Knudsen cell machined from molybdenum. The knife-edged effusion orifice had a 0.5 mm diameter. Temperatures were measured with a chromel/alumel thermocouple calibrated at the melting point of silver. The vapor species were ionized with an emission current of 82 mA and an electron energy of 15−17 eV.

The $SnCl_2$ sample (nominal purity 99.999 mass percent) used for the measurements was supplied by Cerac Inc., Milwaukee, WI. Six independent runs were carried out. Table 1 gives details for the runs. The ion intensities obtained in the course of run 5 are given in Table 2 as an example. In addition, three mass-loss-isothermal measurements were performed in order to calibrate the Knudsen cell−mass spectrometer system.

III. Theoretical Approach and Computational Details

The geometries of the studied species were optimized applying the second-order Møller−Plesset perturbation theory (MP2)[25] and density functional theory (DFT) methods.[26] No symmetry constraints were imposed during the optimization process, and geometry searches were carried out for a number of possible isomers to ensure the location of the global minimum. At the DFT level of theory the location of true minima was confirmed by frequency calculations. The density functional theory (DFT) approach has utilized the Becke's three-parameter functional[27] with the Vosko et al. local correlation part[28] and the Lee et al.[29] nonlocal part (abbreviated as B3LYP). The calculations were performed using the relativistic effective core potentials (RECPs) developed by the Stuttgart group[30] and the SDB-aug-cc-pVTZ basis set[31] for tin and the all electron aug-cc-pVTZ basis for chlorine.[32] The f orbitals from the original basis sets were not included. The six-component representation was applied for the d orbitals. The above choice leads to 266 atomic orbitals for the largest studied system, the Sn_2Cl_4 molecule. Because of the ionic nature of the chemical bonds in the studied complexes, the applicability of selected basis sets was confirmed by the computation of the ionization potential of Sn and the electron affinity of Cl atoms. The calculated ionization potential of tin (7.14 eV) agrees well with the experimental value (7.342 eV).[33] The theoretical value of the electron affinity for Cl (3.46 eV) also agrees satisfactorily with the experimental value of 3.61 eV.[33] Vibrational frequencies and thermodynamic properties of the studied complexes were calculated applying the ideal gas, rigid rotor, and harmonic oscillator approximations.[34]

The total interaction energy calculated at the MP2 level

$$\Delta E_{\mathrm{MP2}} = E_{\mathrm{AB}} - E_{\mathrm{A}} - E_{\mathrm{B}} \qquad (1)$$

has been decomposed

$$\Delta E_{\mathrm{MP2}} = \Delta E_{\mathrm{HF}} + \epsilon_{\mathrm{MP}}^{(2)} \qquad (2)$$

into Hartree−Fock (ΔE_{HF}) and correlation components ($\epsilon_{\mathrm{MP}}^{(2)}$). The HF interaction energy decomposition was performed within the variational-perturbational scheme, corrected for the basis set superposition error (BSSE).[35] In the above scheme ΔE_{HF} is partitioned into electrostatic ($\epsilon_{\mathrm{el}}^{(10)}$) and Heitler−London exchange ($\epsilon_{\mathrm{ex}}^{\mathrm{HL}}$) first-order components and the higher order delocalization ($\Delta E_{\mathrm{del}}^{\mathrm{HF}}$) term. The delocalization energy accounts for the charge transfer, induction, and other higher order Hartree−Fock terms.[36,37] The correlation contribution $\epsilon_{\mathrm{MP}}^{(2)}$ was also corrected for BSSE. The electronic density distribution was studied applying Mulliken and natural bond orbital (NBO) population analyses schemes.[38]

The calculations were carried out using the Gaussian 98 suite of programs.[39] The interaction energy decomposition was performed applying the modified version[40] of the Gamess code.[41]

IV. Results and Discussion

Ions Observed in the Mass Spectrum and Their Assignment to Neutral Precursors. The ions recorded in the mass spectrum of vapor species being in the equilibrium over $SnCl_2$(s), together with the assignment to their neutral precursors, are shown in Table 2. The assignment of ions was carried out on the basis of the following rules: (a) ions originating from the same neutral precursor usually show similar temperature dependencies; (b) it is often observed[42] that, upon ionizing M_mX_n metal halide vapor species by electron impact, one halogen atom is split off, thereby forming abundant $M_mX_{n-1}^+$ ions. This assignment was, in addition, verified by the appearance potential measurements of different ions carried out in reference 43.

Intensities of the Cl^+ and $SnCl_3^+$ ions were observed in the mass spectra at the beginning of each run performed by the use of a fresh material. Depending on the run, the relative intensities of these ions varied from 0.04 to 0.14 for the $I(Cl^+)/I(SnCl^+)$ ratio and from 1.0×10^{-3} to 4.7×10^{-3} for the $I(SnCl_3^+)/I(SnCl^+)$ ratio. The origin of Cl^+ is unclear, whereas $SnCl_3^+$ is most probably a fragment of $SnCl_4$(g) resulting from the $SnCl_4$(s) impurity in the sample. It is well established that the tetravalent tin halides are much more volatile than the divalent tin halides.[44,45] Another possibility is a minor disproportionation of $SnCl_2$ to $SnCl_4$ and Sn in the reagent.[6] Both ions, Cl^+ and $SnCl_3^+$, decreased rapidly at the start measuring temperature (which was typically ca. 500 K) and disappeared after about 1

TABLE 3: Isothermal Vaporization Experiments for the Calibration of the System by the Use of Eq 6 (Clausing factor $C = 0.85$, orifice effusion area $A = 1.96 \cdot 10^{-7}$ m^2)

calibration	T/K	Δm/mg	Δt/min
1	499	14	65
2	498	93	456
3	483	37	543

h. A similar observation was reported in refs 5 and 46 upon studying the $SnCl_2$ vapors.

Partial Pressures. The ion intensities belonging to the mass spectrum of the equilibrium vapor of $SnCl_2$(s) at temperature T are related to the partial pressure $p(i)$ of species i by the following relation:[47]

$$p(i) = [k\,T\,\Sigma I(i)]/\sigma(i) \qquad (3)$$

where k and $\Sigma I(i)$ are the pressure calibration factor and the sum of the intensities of the ions originating from the same neutral precursor i. The term $\sigma(i)$ signifies the relative ionization cross section of species i.

Ion intensities of the Sn^+ and $Sn_2Cl_4^+$ ions were not recorded at the low experimental temperatures. For this reason, the fragmentation coefficients $I(Sn^+)/I(SnCl^+) = 0.212 \pm 0.013$ and $I(Sn_2Cl_4^+)/I(Sn_2Cl_3^+) = 0.113 \pm 0.010$ have been computed from all mass spectra where all of the ions could be detected. The calculated fragmentation coefficients have been finally used for the calculation of the sum of ion intensities originating from $SnCl_2$(g) and Sn_2Cl_4(g) as follows:

$$\Sigma\, I(SnCl_2) = 1.212\, I(SnCl^+) + I(SnCl_2^{\ +}) \qquad (4)$$

$$\Sigma\, I(Sn_2Cl_4) = 1.113\, I(Sn_2Cl_3^{\ +}) \qquad (5)$$

The pressure calibration factor was obtained in three independent measurements, by using the mass-loss Knudsen effusion technique combined with the mass spectrometry. Details concerning these measurements are given in Table 3. The following equation was used for the estimation of the calibration factor k in eq 3:

$$\frac{k}{\sigma(SnCl_2)} = \sqrt{\frac{2\Pi R}{MT}}\frac{\Delta m}{\Delta t\, CA} \Big/ \left(\sum I(SnCl_2) + \sqrt{2} \sum I(Sn_2Cl_4) \frac{\sigma(SnCl_2)}{\sigma(Sn_2Cl_4)} \right) \qquad (6)$$

where R = gas constant, M = molecular mass of $SnCl_2$, Δm = mass loss of the sample upon evaporation for time Δt from the Knudsen cell of the effusion area A. C represents a Clausing factor estimated from the effusion orifice geometry as 0.85. The relative ionization cross section $\sigma(SnCl_2)/\sigma(Sn_2Cl_4)$ was assumed to be 0.67. Mass spectrum used for the calibration of each run was interpolated to the respective temperature of the isothermal vaporization experiment in Table 3. The mean values of the three pressure calibration factors obtained in this manner for each run were adopted for the calculation of partial pressures. These values are reported in Table 1 and show the stability in the sensitivity of our instrument with time.

Partial pressures were evaluated by eq 3 for each measurement temperature. Figure 1 presents the partial pressures over $SnCl_2$(s) at different temperatures determined in run 5. Equations for the $SnCl_2$(g) and Sn_2Cl_4(g) partial pressures as functions of temperature are a result of the least squares computation for each individual run and are shown in Table 4. Selected equations were obtained by the computation of mean values of coefficients A and B determined for individual runs. The probable overall errors for partial pressures at 500 K, given in Table 4, are valid for the temperature range of the measurements listed in Table 1.

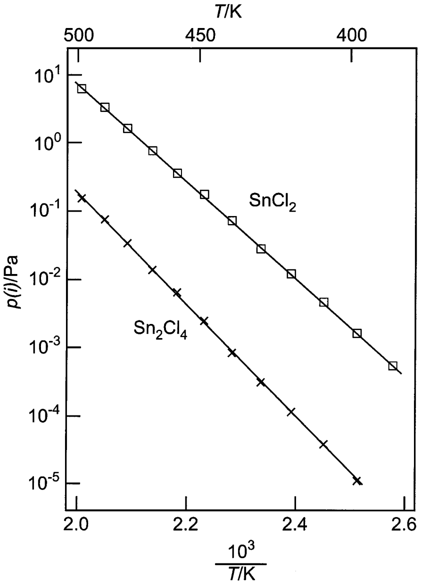

Figure 1. Partial pressures of the gaseous species over $SnCl_2$(s) at different temperatures obtained in run 5.

TABLE 4: Partial Pressures of $SnCl_2$(g) and Sn_2Cl_4(g) over $SnCl_2$(s) Obtained in All Runs (partial pressures at 500 K are given for comparison)

		$\ln p(i)$/Pa = $-A/T + B$		
i	run	A[a]	B[a]	$p(i)$/Pa[b] at 500 K
$SnCl_2$(g)	1	7049	14.960	7.3
	2	6947	14.753	7.2
	3	7020	14.901	7.3
	4	6804	14.465	7.2
	5	7128	15.122	7.3
	6	6856	14.568	7.2
mean:		6967 ± 122[a]	14.795 ± 0.248[a]	7.2[b]
Sn_2Cl_4(g)	1	8346	15.975	0.19
	2	8467	16.257	0.21
	3	8156	15.585	0.19
	4	7936	15.147	0.19
	5	8205	15.683	0.19
	6	8285	15.888	0.21
mean:		8233 ± 182[a]	15.756 ± 0.380[a]	0.20[c]

[a] Statistical error. [b] Probable overall error of ±43% valid for the entire temperature range. [c] Probable overall error of ±58% valid for the entire temperature range.

Equilibrium constants for the dissociation process of the dimeric Sn_2Cl_4 species:

$$Sn_2Cl_4(g) = 2SnCl_2(g) \qquad (7)$$

$$K_p{}^\circ(\text{eq 7}) = \frac{p(SnCl_2)^2}{p(Sn_2Cl_4)p^\circ} \qquad (8)$$

were calculated at each experimental temperature by the use of partial pressures where p° is a standard pressure of 101,325 Pa. The following selected equation describing the temperature dependence of $K_p{}^\circ$(eq 7) was obtained from all six runs:

$$\log K_p{}^\circ(\text{eq 7}) = -(5777 \pm 196)/T + (8.982 \pm 0.413) \qquad (9)$$

Molecular Structure of $SnCl_2$(g), Sn_2Cl_4(g), and Corresponding Molecular and Fragment Cations. Experimental

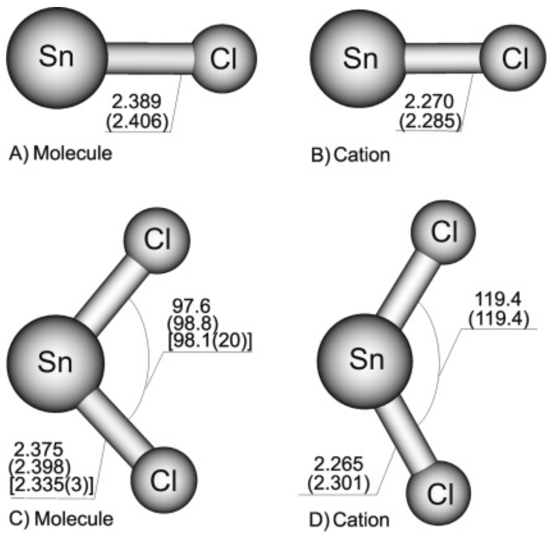

Figure 2. MP2, B3LYP (in parentheses), and experimental (in square brackets) structures of A) SnCl, B) $SnCl^+$, C) $SnCl_2$, and D) $SnCl_2{}^+$ species. Distances in angstrom, angles in degrees.

geometrical parameters available for monomer are well reproduced by the presented calculations (Figure 2). The validity of theoretically determined structures for other species is shown indirectly by the prediction of thermodynamic properties depending upon the structural parameters. The present calculation agree well with available theoretical structures for monomer[16−19] as well as with the structure of dimer.[19] The energetically preferred molecular structure for Sn_2Cl_4 is characterized by two chlorine atoms involved in a bridged bond and two terminal Sn−Cl bonds in the trans configuration (Figure 3). The molecular skeleton possesses C_s symmetry with a puckered four-membered ring. The terminal Cl atoms are not equivalent, indicating that the structure is controlled by many body intramolecular interactions. The energy barrier of the transition state separating the trans conformers (Figure 3) amounts to 5.0 kJ mol^{-1} (MP2 level). The value is reduced to 2.5 kJ mol^{-1} when the enthalpy correction is included (correction to enthalpy was calculated at the DFT level). The very low value of the barrier indicates the nonrigidity of the Sn_2Cl_4 skeleton. The second stable isomer possesses cis geometry and is only 5.4 kJ mol^{-1} higher in energy than the trans structure. The low energetical stable structure containing an Sn−Sn bond was not determined. The lack of such an isomer is consistent with the experimental IR spectra excluding the possibility of the metal−metal bond.[15] The somehow unusual molecular structure determined for Sn_2Cl_4 was also previously found for analogous bromine[20,21] and iodine[20] derivatives.

The fragmentation of molecules due to the ionization process leads to significant structural changes. The removal of an electron from the Sn atom enhances the bonding and leads to the 0.1 Å shorter bond distances in the $SnCl^+$ and $SnCl_2{}^+$ cations in comparison to parent neutrals (Figure 2). The $Sn_2Cl_3{}^+$ cation is characterized by three bridged chlorine atoms. The ionization of Sn_2Cl_4 leads to the complex with three nonequivalent bridged chlorine atoms (Figure 4). The predicted ionization potentials and appearance potentials for detected ionic species (Table 5) agree well with the experimental data available for fragments of $SnCl_2$. These findings indicate the proper theoretical description of neutral as well as cationic species and give us confidence in *AP* for the dimeric species.

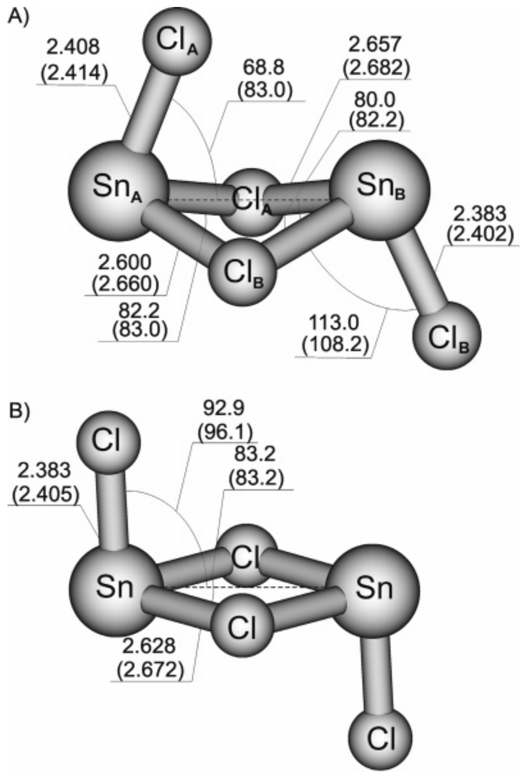

Figure 3. Geometry of trans isomer (C_s symmetry) of Sn_2Cl_4 (A) and the corresponding transition state (C_{2h} symmetry) (B) calculated at the MP2 and B3LYP (in parentheses) levels of theory. The puckering angle SnClClSn amounts to 138.8 at MP2 and 156.3 at B3LYP level. Distances in angstrom, angles in degrees.

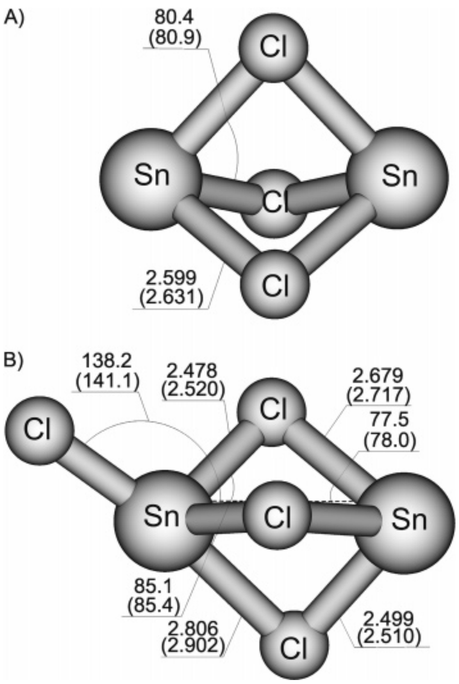

Figure 4. Cationic species − products of Sn_2Cl_4 fragmentation. (A) $Sn_2Cl_3{}^+$ (D_{3H} symmetry) and (B) $Sn_2Cl_4{}^+$ (C_s symmetry) calculated at the MP2 and B3LYP (in parentheses) levels of theory. Distances in angstrom, angles in degrees.

Thermodynamic Properties of $SnCl_2$(g) and Sn_2Cl_4(g). The second law enthalpies of sublimation reactions of $SnCl_2$(g) and Sn_2Cl_4(g) as well as of the dissociation of Sn_2Cl_4(g) species at 298 K were computed from the respective regression coefficients *A* given in Table 4 and in eq 9. Recalculation of the enthalpies from mean temperature of experiment to 298 K was performed by use of $H(T) - H(298\ \mathrm{K})$ functions for $SnCl_2$(g) and Sn_2-

TABLE 5: Theoretical and Experimental Ionization Potentials (IP) and Appearance Potentials (AP) (in eV) of Molecules and Ions Detected in the Mass Spectra of $SnCl_2$(g) and Sn_2Cl_4(g)

data source	IP $SnCl_2^+/SnCl_2$	AP $SnCl^+/SnCl_2$	AP $Sn^+/SnCl_2$	IP Sn^+/Sn	IP $Sn_2Cl_4^+/Sn_2Cl_4$	IP $Sn_2Cl_3^+/Sn_2Cl_4$
B3LYP	9.82	10.97	15.05	7.21	8.91	9.95
MP2	9.73	10.96	15.08	7.14	8.84	9.96
expt.	10.1 ± 0.4[a]	11.3 ± 0.4[a]	15.8 ± 1.0[a]	7.342[b]		

[a] Reference 43. [b] Reference 33.

TABLE 6: Thermochemical Functions for $SnCl_2$(g) and Sn_2Cl_4(g) Calculated from Theoretical Structures and Vibrations at the MP2 Level of Theory

	$SnCl_2$(g) $S°(298\text{ K}) = 304.10$ J mol^{-1} K^{-1} $H°(298\text{ K}) - H°(0\text{ K}) = 13.53$ kJ mol^{-1}		Sn_2Cl_4(g) $S°(298\text{ K}) = 456.88$ J mol^{-1} K^{-1} $H°(298\text{ K}) - H°(0\text{ K}) = 29.44$ kJ mol^{-1}	
T/K	$C_p°$/J mol^{-1} K^{-1}	$-[G°(T)\text{-}H°(298)]/T$ J mol^{-1} K^{-1}	$C_p°$/ J mol^{-1} K^{-1}	$-[G°(T) - H°(298)]/T$ J mol^{-1} K^{-1}
298.15	54.45	304.10	125.99	456.88
300	54.49	304.11	126.07	456.88
400	55.99	306.26	128.97	461.87
500	56.75	310.38	130.38	471.37
600	57.18	315.03	131.17	482.07
700	57.44	319.72	131.65	492.86
800	57.62	324.26	131.97	503.30
900	57.73	328.60	132.19	513.26
1000	57.82	332.71	132.35	522.70
1100	57.89	336.60	132.46	531.63
1200	57.94	340.29	132.55	540.08
1300	57.97	343.77	132.62	548.08
1400	58.00	347.08	132.68	555.66
1500	58.03	350.23	132.72	562.87

TABLE 7: Second and Third Law Enthalpies of Sublimation and Dissociation Reactions in the $SnCl_2$ System

reaction	run	$\Delta H°$(II law, 450 K)[a]	$\Delta H°$(III law, 298 K)[a]
$SnCl_2(s) = SnCl_2(g)$	1	135.0 ± 2.0	124.8 ± 1.3
	2	133.0 ± 1.7	124.7 ± 1.2
	3	134.4 ± 1.0	124.8 ± 1.2
	4	130.3 ± 2.0	124.3 ± 0.8
	5	136.5 ± 0.6	125.0 ± 1.3
	6	131.2 ± 1.0	124.5 ± 0.9
	mean:	133.4 ± 2.3	124.7 ± 3.7[b]
		$\Delta H°$(II law, 298 K) = 137.1 ± 5.8 kJ mol^{-1} [b]	
	selected:	$\Delta H°$(298 K) = 130.9 ± 6.2 kJ mol^{-1} [b]	
$2SnCl_2(s) = Sn_2Cl_4(g)$	1	159.8 ± 3.2	148.7 ± 1.4
	2	162.1 ± 2.0	148.5 ± 1.4
	3	156.2 ± 1.1	148.5 ± 1.4
	4	152.0 ± 1.5	148.1 ± 0.8
	5	157.1 ± 0.7	148.7 ± 1.0
	6	158.6 ± 1.8	148.5 ± 1.2
	mean:	157.6 ± 3.5	148.5 ± 6.3[b]
		$\Delta H°$(II law, 298 K) = 163.0 ± 7.2 kJ mol^{-1} [b]	
	selected:	$\Delta H°$(298 K) = 155.8 ± 7.3 kJ mol^{-1} [b]	
$Sn_2Cl_4(g) = 2\,SnCl_2(g)$	1	114.6 ± 2.8	100.6 ± 1.3
	2	109.0 ± 1.9	100.4 ± 0.9
	3	111.1 ± 1.2	100.7 ± 0.9
	4	108.6 ± 2.9	100.5 ± 0.9
	5	114.9 ± 0.9	101.0 ± 1.2
	6	105.2 ± 1.0	100.4 ± 0.6
	mean:	110.6 ± 3.8	100.6 ± 6.3[b])
		$\Delta H°$(II law, 298 K) = 113.0 ± 5.8 kJ mol^{-1} [b]	
	selected:	$\Delta H°$(298 K) = 106.8 ± 6.2 kJ mol^{-1} [b]	

[a] Statistical error. [b] Probable overall error.

Cl_4(g) calculated in this work (Table 6) and for $SnCl_2$(s).[45] The results of the second law evaluation are given in Table 7.

The enthalpy changes of the reactions collected in Table 7 were additionally evaluated according to the third-law method by the following equation:

$$\Delta_r H°(298\text{ K}) = -T\,[R \ln K_p° + \Delta_r GEF°(T)] \qquad (10)$$

where $\Delta_r GEF°(T) = \Delta_r[G°(T) - H°(298)]/T$ is the change of the Gibbs energy function for the reaction considered, obtained from the data of $SnCl_2$(s)[45] and from the data calculated in this work for the $SnCl_2$(g) and Sn_2Cl_4(g) gaseous species (Table 6). More recent thermochemical data for $SnCl_2$(s) reported in ref 48 are in excellent agreement with the respective data in the compiled work[45] used throughout the present study. Table 8 shows in detail the results of the third-law evaluation for run 5. The mean values of the third-law enthalpies obtained for each

TABLE 8: Third Law Evaluation of the Enthalpy Changes for Different Reactions Obtained in Run 5

	$SnCl_2(s) = SnCl_2(g)$			$2\ SnCl_2(s) = Sn_2Cl_4(g)$			$Sn_2Cl_4(g) = 2\ SnCl_2(g)$		
T/K	$K_p°$	$-\Delta_r GEF°$ J mol^{-1}K^{-1}	$\Delta H°$(298 K) kJ mol^{-1}	$K_p°$	$-\Delta_r GEF$ J mol^{-1} K^{-1}	$\Delta H°$(298 K) kJ mol^{-1}	$K_p°$	$-\Delta_r GEF°$ J mol^{-1}K^{-1}	$\Delta H°$(298 K) kJ mol^{-1}
498	$6.04\cdot10^{-5}$	167.116	123.4	$1.53\cdot10^{-6}$	184.815	147.5	$2.39\cdot10^{-3}$	149.417	99.4
488	$3.31\cdot10^{-5}$	167.216	123.5	$7.56\cdot10^{-7}$	184.873	147.4	$1.45\cdot10^{-3}$	149.559	99.5
478	$1.65\cdot10^{-5}$	167.336	123.8	$3.31\cdot10^{-7}$	184.975	147.7	$8.22\cdot10^{-4}$	149.698	99.8
468	$7.56\cdot10^{-6}$	167.477	124.3	$1.38\cdot10^{-7}$	185.122	148.1	$4.13\cdot10^{-4}$	149.833	100.4
458	$3.66\cdot10^{-6}$	167.639	124.4	$6.23\cdot10^{-8}$	185.314	148.1	$2.15\cdot10^{-4}$	149.964	100.8
448	$1.76\cdot10^{-6}$	167.822	124.5	$2.46\cdot10^{-8}$	185.553	148.4	$1.27\cdot10^{-4}$	150.092	100.7
438	$7.05\cdot10^{-7}$	168.027	125.2	$8.39\cdot10^{-9}$	185.839	149.1	$5.92\cdot10^{-5}$	150.216	101.2
428	$2.80\cdot10^{-7}$	168.254	125.7	$3.13\cdot10^{-9}$	186.173	149.4	$2.50\cdot10^{-5}$	150.336	102.1
418	$1.21\cdot10^{-7}$	168.504	125.8	$1.14\cdot10^{-9}$	186.556	149.5	$1.27\cdot10^{-5}$	150.452	102.1
408	$4.61\cdot10^{-8}$	168.777	126.2	$3.91\cdot10^{-10}$	186.989	149.8	$5.44\cdot10^{-6}$	150.565	102.6
398	$1.62\cdot10^{-8}$	169.074	126.6	$1.12\cdot10^{-10}$	187.474	150.4	$2.35\cdot10^{-6}$	150.674	102.9
388	$5.35\cdot10^{-9}$	169.395	127.2						
mean: [a]			125.0 ± 1.3			148.7 ± 1.0			101.0 ± 1.2

[a] Errors are standard deviations.

measurement temperature of a run are additionally incorporated in Table 7. Selected enthalpies result in an arithmetical mean of the second- and third-law values.

The dissociation enthalpy of 103.4 kJ mol^{-1} calculated at the MP2 level for the predicted gas-phase structures agrees well (within the error limits) with the experimental value, which is 106.8 ± 6.2 kJ mol^{-1}. The significant part of the dissociation energy is due to the energy correlation contribution. The dissociation enthalpy calculated by the B3LYP approach does not properly account for the correlation energy[49] and leads to the underestimated value of 70 kJ mol^{-1}.

Good agreement between the results of the six independent runs indicates the reproducibility and accuracy of the vaporization data of the present study. However, a difference of 12−15 kJ mol^{-1} exists between the enthalpies of sublimation and dimerization obtained by the second and third law. The second law values are systematically higher in comparison to the third law values. The selected value for the dissociation enthalpy of Sn_2Cl_4(g) (106.8 ± 6.2 kJ mol^{-1}) is very close to the values of 106.8 ± 3.6 kJ mol^{-1} and 101.0 ± 4.4 kJ mol^{-1} obtained for the dissociation of Sn_2Br_4(g)[2] and Sn_2I_4(g)[3], respectively. O'Brien and Mucklejohn[7] obtained a large difference between second law enthalpies of dissociation reaction of Sn_2Cl_4(g) below the melting temperature (82 ± 12 kJ mol^{-1}) and after melting (145 ± 8 kJ mol^{-1}). Recently, Levy et al.[19] merged the experimental data in ref 7 with their new estimated thermochemical functions of gaseous $SnCl_2$(g) and Sn_2Cl_4(g) species. The third law value of 104 ± 3 kJ mol^{-1} reported in ref 19 agrees excellently with the value obtained in the present study.

The sublimation enthalpy (131 ± 6 kJ mol^{-1}) of $SnCl_2$(g) at 298 K, obtained in the present study agrees with the value of 128 ± 3 kJ mol^{-1} in ref 6 and with the respective data in the thermochemical compilations.[44,45] A much lower sublimation enthalpy of $SnCl_2$(g) was obtained in ref 5 (114 ± 13 kJ mol^{-1}) and in ref 4 (105 kJ mol^{-1}). The sublimation enthalpy of Sn_2Cl_4(g) obtained in the present study, 155.8 ± 7.3 kJ mol^{-1}, is also higher than the values of 105 ± 19 kJ mol^{-1} (ref 7) and 130 kJ mol^{-1} (ref 4) obtained by other authors. To our knowledge there are no other reports available.

Thermochemical functions for $SnCl_2$(g) and Sn_2Cl_4(g) calculated in the present study for the third law evaluation are in excellent agreement with the other data available in the literature. For instance values of $[G°(500) - H°(298)]/T$ of −310.38 J mol^{-1} K^{-1} (present study), −312.21 J mol^{-1} K^{-1},[19] and −312.15 J mol^{-1} K^{-1} [45] are given for $SnCl_2$(g) in the cited sources. The $[G°(500) - H°(298)]/T$ value obtained for Sn_2Cl_4(g) in the present study (−471.37 J mol^{-1} K^{-1}) agrees with the value published in ref 19 (−474.72 J mol^{-1} K^{-1}). Therefore the applied thermodynamical functions are rather excluded as a possible reason for the discrepancy between the second and third law enthalpies evaluated in the study. The other reasons for this disagreement could be the temperature-dependent fragmentation of $SnCl_2$(g) and/or Sn_2Cl_4(g) due to electron bombardment. To check this, we analyzed the regression coefficients of the $\ln(IT) = A/T + B$ functions obtained for all ions individually in each run. The $SnCl_2^+$ and $SnCl^+$ ions show almost identical temperature dependence, whereas the regression coefficient A for the Sn^+ ions is systematically lower, resulting in the "apparent second law enthalpy" of approximately 8 kJ mol^{-1} less compared to those for the $SnCl^+$ and $SnCl_2^+$ ions. However, due to the relative low contribution of the Sn^+ ions in the mass spectrum of $SnCl_2$(g) (ca. 12%) this difference does not influence significantly the second law enthalpy of this species. In the case of ions originating from Sn_2Cl_4(g), the "apparent second law enthalpy" of the $Sn_2Cl_3^+$ ions is about 9 kJ mol^{-1} higher in comparison to molecular $Sn_2Cl_4^+$ ions. The $Sn_2Cl_3^+$ fragment ions contribute approximately 90% to the total mass spectrum of Sn_2Cl_4(g), thereby determining practically the regression coefficient of the temperature dependence of the partial pressure of this species. A possible temperature-dependent fragmentation of Sn_2Cl_4(g) to $Sn_2Cl_3^+$ would result in the overestimated second law sublimation enthalpy and the underestimated second law dissociation enthalpy of these species. This would lead to better agreement between the second and third law sublimation enthalpies of Sn_2Cl_4(g) and, to a larger extent, between the second and third law dissociation enthalpies of these species.

The Sn_2Cl_4 contribution to the total vapor pressure over $SnCl_2$(s,l) observed in the present study is similar to contributions obtained in references[4,7] Karpenko[4] determined that approximately 5% of the species exist at 493 K, which agrees with 4.7% at 570 K in ref 7 and with 2.8% at 500 K obtained in the present study (Table 4). Due to the much higher sublimation enthalpy of the dimeric species in comparison to monomers, this contribution increases with increasing temperature. The data in ref 7 for vapors over liquid $SnCl_2$ suggest a decrease of the dimer content in vapors from 4.7% at 570 K down to 0.2% at 690 K. Levy et al.[19] suggested that the above observation is erroneous, thus leading to a lower enthalpy of vaporization of the dimer in comparison to the monomer. In our opinion such a situation can take place after melting a substance of low

TABLE 9: MP2 Calculated Frequencies (cm^{-1}, with PED, %), Intensities (*A*, km mol^{-1}), and Raman Scattering Activities (R, A^4/AMU) (from B3LYP level) in the Infrared Spectrum of SnCl$_2$ and Sn$_2$Cl$_4$[a]

	SnCl$_2$			Sn$_2$Cl$_4$		
N	assignment and PED (%)	ν	*A* (R)	assignment and PED (%)	ν	*A* (R)
1	βSnCl(97)	147.6 [120^c,122^d]	2.4 (3.2)	τring(78)	42.6	2.9 (0.2)
2	νSnCl$_1$(+50), νSnCl$_2$(−51)	337.1 [330^{c}337^d]	105.6 (9.7)	βSn$_A$Cl$_{At}$(+79), βSn$_B$Cl$_{Bt}$(+14),	68.2	1.8 (0.1)
3	νSnCl$_1$(+49), νSnCl$_2$(+49)	359.1 [351^{c}354^d]	55.1 (19.9)	γSn$_A$Cl$_{At}$(+48) βring(23), γSn$_B$Cl$_{Bt}$ (−21),	73.7	0.2 (3.4)
4				βSn$_B$Cl$_{Bt}$(+81), βSn$_A$Cl$_{At}$(−18)	106.5	2.6 (2.8)
5				βring(55), γSn$_B$Cl$_{Bt}$(+33), γSn$_A$Cl$_{At}$(−5)	124.7	0.5 (1.9)
6				γSn$_B$Cl$_{Bt}$(+38), γSn$_A$Cl$_{At}$(+33), τring(19), βring(9)	132.4	2.6 (0.5)
7				νSn$_A$Cl$_{Bb}$(+29), νSn$_A$Cl$_{Ab}$(−29), νSn$_B$Cl$_{Bb}$(−19), νSn$_B$Cl$_{Ab}$(19),	143.4	0.5 (0.4)
8				νSn$_A$Cl$_{Ab}$(31), νSn$_A$Cl$_{Bb}$(+31), νSn$_B$Cl$_{Ab}$(−12), νSn$_B$Cl$_{Bb}$(−12), γSn$_B$Cl$_{Bt}$(+5)	220.7	155.8 (0.6)
9				νSn$_B$Cl$_{Bb}$(+34), νSn$_B$Cl$_{Ab}$(−34), νSn$_A$Cl$_{Ab}$(−15), νSn$_A$Cl$_{Bb}$(+15), νSn$_B$Cl$_{Bb}$(+32)	239.2	48.6 (0.7)
10				νSn$_B$Cl$_{Ab}$(+32), βring(9), νSn$_A$Cl$_{Ab}$(+9), νSn$_A$Cl$_{Bb}$(+9)	254.9	17.8 (11.9)
11				νSn$_B$Cl$_{Bt}$(+85), νSn$_A$Cl$_{At}$(+12)	329.7	38.4 (20.7)
12				νSn$_A$Cl$_{At}$(+88), νSn$_B$Cl$_{Bt}$(−10)	344.0	95.7 (7.0)

[a] The indices A and B correspond to the dimer skeleton from Figure 3; t and b stand for terminal and bridged atoms. Chlorine atoms Cl$_{Ab}$ and Cl$_{Bb}$ are equivalent symmetrically. [b] Abbreviations: ν, stretching; β, in-plane bending; γ, out-of-plane bending; τ, torsional vibration. The phases of internal coordinates are indicated by signs: the plus sign corresponds to the clockwise in-plane bending or the in-phase stretching (or the out-of-plane bending) vibrations; the minus sign has the opposite meaning. [c] Experimental value.[9] [d] Other theoretical.[1]

sublimation enthalpy and a large melting enthalpy, ΔH_{melt}. At melting point, the vaporization enthalpy of the monomer decreases by ΔH_{melt}, whereas the enthalpy of the dimer decreases by 2 times ΔH_{melt}. This can lead to a “maximum” dimer content at the melting point. Sublimation enthalpies at 500 K given in Table 7 and ΔH_{melt}(SnCl$_2$) = 14.5 kJ mol^{-1} [45] yield the vaporization enthalpies of SnCl$_2$(g) and Sn$_2$Cl$_4$(g) beyond the melting point as 112 kJ mol^{-1} and 121 kJ mol^{-1}, respectively. Even considering the possible uncertainties in the present study, the vaporization enthalpy of Sn$_2$Cl$_4$(g) remains larger in comparison to SnCl$_2$(g) which is a contradiction to a decrease in dimer content in vapors observed in ref 7.

The Nature of the Dimerization Process. The length of the terminal Sn−Cl bonds in the dimer is close to the distances found in the monomers. The bridged bonds are about 0.2 Å longer. Such a bond increase is expected in analogy to a phenomenon observed in the complexation processes of other compounds.[22] The Cl$_{terminal}$−Sn−Cl$_{bridged}$ angle in the dimer (about 90 degrees) can be considered as a perturbation to the angle characterizing the monomer. New bridged bonds Sn$_A$−Cl$_B$ and Sn$_B$−Cl$_A$ (Figure 3) are formed due to the concerted donation of electron pairs from chlorine to tin atoms. The process is complemented by the simultaneous relaxation of two other already existing bonds. The dimer molecule may be considered as a complex of two (A and B) interacting fragments according to the definition provided in Figure 3. The total interaction energy of the (SnCl$_2$)$_2$ complex amounts to 168.6 kJ mol^{-1}. The attractive interactions are dominated by the delocalization term ($\Delta E_{del}{}^{HF} = -350.2$ kJ mol^{-1}) corresponding mostly to the charge transfer energy. The above finding confirms the formation of the bond due to the electron pair donation. The addition of attractive electrostatic contribution ($\epsilon_{el}{}^{(10)} = -170.9$ kJ mol^{-1}) and repulsive exchange ($\Delta E_{ex}{}^{HL} = 408.2$ kJ mol^{-1}) terms leads to overall interactions at the Hartree−Fock level of −112.9 kJ mol^{-1} (ΔE_{HF}). The correlation correction increases the interactions by −45.7 kJ mol^{-1} (ϵ_{MP2}). The large difference between the interaction and dissociation energies (103.4 kJ mol^{-1} at the MP2 level) indicates the significant contribution of the stabilization due to the geometry relaxation.

The analysis of the electronic density distribution from the Mulliken as well as from the NBO scheme (Figure 5) leads to the similar qualitative conclusions. The atomic charges on the terminal Cl atoms are almost the same as the charges in the monomers. The bridged chlorines, despite being involved in two bonds, possess an atomic charge lower by only 0.02 electron from that of the terminal chlorines.

The calculated vibrational frequencies for SnCl$_2$ reasonably reproduce the experimental values (Table 9). We assume that the predicted dimer properties are of similar quality and that allows for a reasonable interpretation of the spectra. The calculated frequencies of the dimer closely agree with the theoretical values of Levy et al.[19] The aforementioned authors discussed the difficulties with the interpretation of Raman spectra based on speculations around the experimental record-

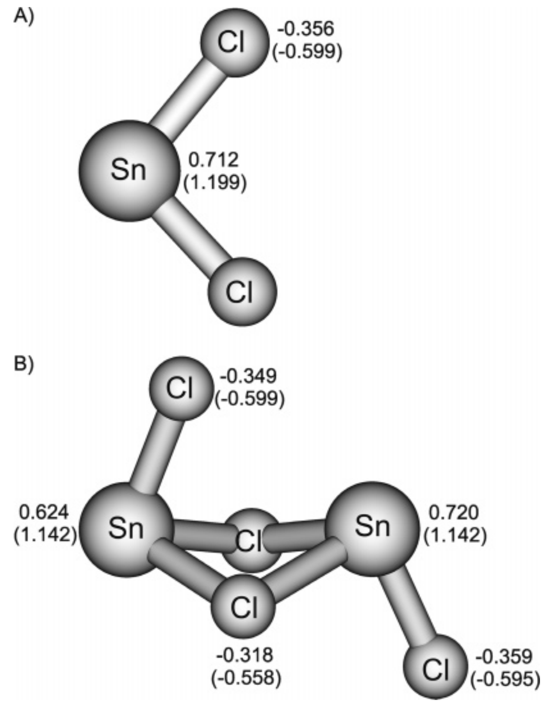

Figure 5. Mulliken and NBO (in parentheses) atomic charges for $SnCl_2$ and Sn_2Cl_4 molecules calculated at the MP2 level of theory. Charges in electrons.

ing.[15] The calculated potential energy distributions (PED) again indicate the local character of the dimerization reaction. The stretching vibrations of the terminal bonds are almost the same as the analogous vibrations in the monomer. The bridged bonds possess significantly different characteristics in comparison to the monomer. As was shown in the previous section the thermodynamic functions based on determined structures and frequencies lead to excellent agreement between experimental and calculated theoretical enthalpies.

Estimations of Probable Uncertainties of Data. The probable overall errors of the reaction enthalpies and of the partial pressures given in Tables 4 and 7 were estimated from the statistical errors and uncertainties of data used in the calculations. The following uncertainties were assumed for the computation of the overall errors: ±5 K for the absolute error of the temperature measurement, ±2 K at the lowest and ±2 K at the highest measurement temperature for the differential error, as well as ±30% for the $\sigma(Sn_2Cl_4)/\sigma(SnCl_2)$ quotient of the ionization cross sections used in the computation of $p(Sn_2Cl_4)$. Moreover, uncertainties of ±5 J mol^{-1} K^{-1} ($SnCl_2$(s) and $SnCl_2$(g)) and ±8 J mol^{-1} K^{-1} were assumed for the $[G°(T) - H°(298)]/T$ function for the species given in parentheses.

V. Conclusions

The vaporization of $SnCl_2$(s) was investigated over a temperature range between 382 and 504 K by the use of Knudsen effusion mass spectrometry. Dimeric species were observed besides monomers in the vapor, the latter being the main species in the equilibrium vapor. Electron impact mass spectra of $SnCl_2$(g) and Sn_2Cl_4(g) were determined at an electron energy of 15−17 eV. Enthalpies of sublimation of monomer and dimer species as well as the dissociation of dimers to monomers were determined by the use of the second and third law procedure. The difference of 12−15 kJ mol^{-1} between the second and the third law enthalpies was obtained for each reaction investigated. The recommended standard values of sublimation energy are 130.9 ± 6.2 kJ mol^{-1} and 155.8 ± 7.3 kJ mol^{-1} for $SnCl_2$(g) and Sn_2Cl_4(g), respectively. The experimentally determined enthalpy of the $Sn_2Cl_4 = 2SnCl_2$ reaction (applying thermodynamic functions of the species obtained by the use of statistical thermodynamic relations) ($\Delta_d H°(298) = 106.8 \pm 6.2$ kJ mol^{-1}) is in excellent agreement with the theoretically calculated value of 103.4 kJ mol^{-1}.

The interaction energy decomposition indicates the covalent nature (dominated by the charge transfer contribution) of the formed bridged Sn−Cl bonds. The terminal Sn−Cl bonds in the dimer possess properties very similar to those observed in monomers indicating the local character of the dimerization process.

Acknowledgment. This research has been supported by the Research Centre, Jülich, Germany, and by the Wroclaw University of Technology, Poland. It was also facilitated in part by NSF EPSCOR Grant No. 99-01-0072-08, CREST Grant No. HRD-01-25484, a Wroclaw University of Technology Grant, and the AHPCRC under agreement number DAAD19-01-2-0014, contract number DAAH04-95-C-0008, the contents of which do not necessarily reflect the position or policy of the government, and no official endorsement should be inferred. The Mississippi Center for Supercomputing Research and Wroclaw Center of Computing and Networking are acknowledged for a generous allotment of computer time.

References and Notes

(1) Hilpert, K.; Niemann, U. *Thermochim. Acta* **1997**, *299*, 49.
(2) Hilpert, K.; Miller, M.; Ramondo, F. *J. Phys. Chem.* **1991**, *95*, 7261.
(3) Hilpert, K.; Bencivenni, L.; Saha, B. *Ber. Bunsen-Ges. Phys. Chem.* **1985**, *89*, 1292.
(4) Karpenko, N. V.; Novikov, G. I. *Vestn. Leningrad. University Fiz. Khim.* **1967**, *4*, 72.
(5) Ciach, S.; Knowles, D. J.; Nicholson, A. J. C.; Swinler D. L. *Inorg. Chem.* **1973**, *12*, 1443.
(6) Mucklejohn, S. A.; O'Brien, N. W. *J. Chem. Thermodyn.* **1987**, *19*, 1079.
(7) O'Brien, N. W.; Mucklejohn, S. A. *J. Chem. Thermodyn.* **1987**, *19*, 1065.
(8) Perry, R. O. *Chem. Commun.* **1996**, 886.
(9) Beattie, I. R.; Perry, R. O. *J. Chem. Soc. A* **1970**, 2429.
(10) Andrews, L.; Frederick, D. L. *J. Am. Chem. Soc.* **1970**, *92*, 775.
(11) Ozin, G. A.; Voet, A. *J. Chem. Phys.* **1972**, *56*, 4768.
(12) Naegli, D.; Palmer H. B. *J. Mol. Spectrosc.* **1966**, *21*, 325.
(13) Nasarenko, A. Ya.; Spiridonov, V. P.; Butayev, B. S.; Zasorin, E. Z. *J. Mol. Struct.* **1985**, *119*, 263.
(14) Stranges, S.; Adam, M. Y.; Cauletti, C.; de Simone, M.; Furlani, C.; Piancastelli, M. N.; Decleva, P.; Lisini, A. *J. Chem. Phys.* **1992**, *97*, 4764.
(15) Fields, M.; Devonshire, R.; Edwards, H. G. M.; Fawcett, V. *Spectrochim. Acta, Part A* **1995**, *51*, 2249.
(16) Benavides-Garcia, M.; Balasubramanian, K. *J. Chem. Phys.* **1994**, *100*, 2821.
(17) Sicilia, E.; Toscano, M.; Mineva, T.; Russo, N. *Int. J. Quantum Chem.* **1997**, *61*, 571.
(18) Ricart, J. M.; Rubio, J.; Illas, F. *Chem. Phys. Lett.* **1986**, *123*, 528.
(19) Levy, J. B.; Jancso, G.; Hargittai, M. *J. Phys. Chem. A* **2003**, *107*, 10450.
(20) Saloni, J.; Roszak, S.; Miller, M.; Hilpert, K.; Leszczynski, J. *J. Phys. Chem. A* **2004**, *108*, 2418.
(21) Kolonits, M.; Reffy, B.; Jancso, G.; Hargittai, M. *J. Phys. Chem. A* **2004**, *108*, 6778.
(22) Hargittai, M. *Chem. Rev.* **2000**, *100*, 2233.
(23) Hargittai, M. *Coord. Chem. Rev.* **1988**, *91*, 35.
(24) Hilpert K. *Report Jül-1744, KFA Research Centre Jülich*; Jülich, Federal Republic of Germany.
(25) Møller C.; Plesset, M. S. *Phys. Rev.* **1934**, *46*, 618.
(26) Parr R. G.; Yang, W. *Density-Functional Theory of Atoms and Molecules*; Oxford University Press: New York, 1994.
(27) Becke, D. *J. Chem. Phys.* **1993**, *98*, 5648.
(28) Vosko, S. H.; Wilk, L.; Nusiar, M. *Can. J. Phys.* **1980**, *58*, 1200.
(29) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.
(30) Bergner, A.; Dolg, M.; Kuechle, W.; Stoll, H.; Preuss, H. *Mol. Phys.* **1993**, *80*, 1431.

(31) Martin, J. M. L.; Sundermann, A. *J. Chem. Phys*. **2001**, *114*, 3408.

(32) Woon, D. E.; Dunning, T. H., Jr. *J. Chem. Phys*. **1993**, *98*, 1358.

(33) *CRC Handbook of Chemistry and Physics*, 83rd ed.; Lide, D. R., Ed.; CRC Press: Boca Raton, 2002.

(34) Davidson, N. *Statistical Mechanics*; McGraw-Hill: New York, 1962.

(35) Sokalski, W. A.; Roszak, S.; Pecul, K. *Chem. Phys. Lett*. **1988**, *153*, 153.

(36) Jeziorski, B.; van Hemert, M. C. *Mol. Phys*. **1976**, *31*, 713.

(37) Chalasinski, G.; Szczesniak, M. M. *Mol. Phys*. **1988**, *63*, 205.

(38) Reed, E.; Curtiss, L. A.; Weinhold, F. *Chem. Rev*. **1988**, *88*, 899.

(39) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, revision A.4; Gaussian, Inc.: Pittsburgh, PA, 1998.

(40) Gora, R. W.; Bartkowiak, W.; Roszak, S.; Leszczynski, J. *J. Chem. Phys*. **2002**, *117*, 1031.

(41) Schmidt, M. S.; Baldridge, K. K.; Boatz J. A.; et al. *J. Comput. Chem*. **1993**, *14*, 1347.

(42) Bauer, S. H.; Porter R. F. In: *Molten Salt Chemistry*; Blander, M., Ed.; Interscience: New York, 1964; p. 671.

(43) Buchunan, A. S.; Knowles, D. J.; Swingler, D. L. *J. Phys. Chem*. **1969**, *73*, 4394.

(44) Yungman, V. S.; Medvedev, V. A.; Veits, I. V. G.; Bergman, A. *IVTANTHERMO − A Thermodynamic Database and Software System for the Personal Computer*; CRC Press and Begell House: Boca Raton, 1993.

(45) Barin, I. *Thermochemical Data of Pure Substances, Part I*; VCH: Weinheim, Germany, 1989; p. 610.

(46) Binnewies, M.; Schafer, H. *Z. Anorg. Allg. Chem*. **1974**, *407*, 327.

(47) Hilpert, K. *J. Electrochem. Soc*. **1989**, *136*, 2009.

(48) Gardner, P. J.; Preston, S. R. *Thermochim. Acta* **1991**, *185*, 219.

(49) Roszak, S.; Gee, R. H.; Balasubramanian, K.; Fried L. E. *Chem. Phys. Lett*. **2003**, *374*, 286.