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Response to “Comment on ‘Atomization energies and enthalpies of formation of the SnBi<sub>n</sub> (n=1–3) gaseous molecules by Knudsen cell mass spectrometry’ ” [J. Chem. Phys. 118, 4766 (2003)]

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**Response to “Comment on ‘Atomization energies and enthalpies of formation of the SnBi<sub>n</sub> ( n =1–3) gaseous molecules by Knudsen cell mass spectrometry” [J. Chem. Phys. 118, 4766 (2003)]**

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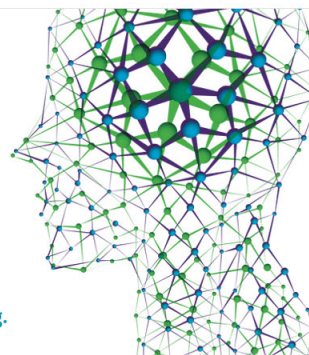
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## Response to “Comment on ‘Atomization energies and enthalpies of formation of the $\text{SnBi}_n$ ( $n=1-3$ ) gaseous molecules by Knudsen cell mass spectrometry’” [J. Chem. Phys. 118, 4766 (2003)]

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We are grateful to the authors of the Comment in Ref. 1 who have performed higher level calculations for the  $\text{SnBi}_2$  and  $\text{SnBi}_3$  molecules, studied by our group using the classical and invaluable technique of Knudsen cell mass spectrometry.<sup>2</sup> We would be delighted to see their new results in a publication, with all the details of the molecular parameters and energetics of the ground state and possible low-lying electronic states for the  $\text{SnBi}_2$  and  $\text{SnBi}_3$  molecules.

In order to evaluate the mass spectrometric equilibrium data, we need to calculate the thermal functions of the molecules investigated. So far no experimental spectroscopic investigations have been performed on the  $\text{SnBi}_2$  and  $\text{SnBi}_3$  molecules, and for this reason we have to rely on computational results. For the evaluation of the Gibbs energy functions,  $(G_T^o - H_0^o)/T$  ( $\text{GEF}_0$ ), of  $\text{SnBi}_2$ ,<sup>2</sup> we used the  $D_{\infty h}$  structure and the relative molecular parameters calculated at the B3LYP level of theory by the same authors. Figgen *et al.*<sup>1</sup> did not give the vibrational frequencies for the new computed equilibrium ground state geometry of  $\text{SnBi}_2$ . Therefore, we performed calculations on the  $^1A_1$   $\text{SnBi}_2$  ground state using the coupled-cluster method with single and double excitations including the effect of connected triple excitations (CCSD(T)). The basis sets employed were the Stuttgart relativistic large-core effective-core potentials (ECP) basis sets for Sn (Ref. 3) and Bi.<sup>4</sup> Employing the so computed vibrational frequencies,  $b_2 = 115 \text{ cm}^{-1}$ ,  $a_1 = 132 \text{ cm}^{-1}$ ,  $a_1 = 170 \text{ cm}^{-1}$ , and the structure from Ref. 1, we reevaluated the thermal functions of  $\text{SnBi}_2$ . The new  $\text{GEF}_0$  are lower than the previous reported values,<sup>2</sup> in particular they differ by  $11.7 \text{ J mol}^{-1} \text{ K}^{-1}$  at 900 K. This result is directly related to the value of the enthalpy of reaction (2), specifically the lower the  $\text{GEF}_0$  are for the reactant, the higher the enthalpy of reaction (2) will be according to the relation  $\Delta_r H_0^o = -RT \ln K_p - T\Delta[(G_T^o - H_0^o)/T]$ . This is translated in a larger atomization energy ( $\Delta_a H_0^o$ ) for  $\text{SnBi}_2$ . The revised  $\Delta_a H_0^o(\text{SnBi}_{2,g})$  value is  $(426.3 \pm 15.0) \text{ kJ mol}^{-1}$ . The  $\Delta_a H_0^o(\text{SnBi}_{2,g})$  value of Figgen *et al.*<sup>1</sup> computed at the CCSD(T) level of theory including spin-orbit (SO) contributions and using the Stuttgart relativistic small-core (RSC) ECP basis sets is approximately 5% larger than our revised

value. Also the  $\Delta_a H_0^o(\text{SnBi}_{3,g})$  computed using the CCSD(T) method with RSC-ECP basis sets is higher than the experimental value of  $(603.4 \pm 18.0) \text{ kJ mol}^{-1}$  of approximately 16%. This is not surprising for heavy metal molecules for at least two reasons. First, the SO coupling effects are not negligible. Figgen *et al.*<sup>1</sup> showed that the inclusion of SO contributions reduces the atomization energies by  $5 \text{ kJ mol}^{-1}$  for the  $\text{SnBi}$  molecule and by  $55 \text{ kJ mol}^{-1}$  for the  $\text{SnBi}_2$  molecule. Unfortunately, no CCSD(T)-SO calculations are reported for  $\text{SnBi}_3$ . The second reason is that a very high level of calculations (including high level of valence correlation) with large basis sets is needed to reproduce with accuracy the experimental results. Metz *et al.*<sup>5</sup> showed that using RSC-ECP basis sets and the CCSD(T) level of theory, the same quantum mechanical treatment used by Figgen *et al.*,<sup>1</sup> the computed  $\Delta_a H_0^o$  of the  $\text{PbO}$  molecule is approximately 33% higher than the experimental value. Only the use of very high level of calculation, namely two components multireference configuration interaction with single excitations, nine reference configurations and CCSD(T) spin-free-state shifts reproduced the experimental atomization energy in a nearly perfect way.<sup>5</sup>

A decision whether the theoretical values for the atomization enthalpies are accurate or whether our experimental values are closer to the actual  $\Delta_a H_0^o$  should come from very high level calculations.

The *ab initio* calculations performed for the computation of the vibrational frequencies of  $\text{SnBi}_2$ , used in the evaluation of the new thermal functions, have been performed employing the GAUSSIAN 98 suite of programs.<sup>6</sup>

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