2003

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

Giovanni Meloni
University of San Francisco, gmeloni@usfca.edu

Karl A. Gingerich

Giovanni Meloni and Karl A. Gingerich

Articles you may be interested in

Response to "Comment on 'Atomization energies and enthalpies of formation of the SnBi$_n$ (n=1–3) gaseous molecules by Knudsen cell mass spectrometry'" [J. Chem. Phys. 118, 4766 (2003)]

Giovanni Meloni[a)]
Department of Chemistry, University of California, Berkeley, California 94720

Karl A. Gingerich
Department of Chemistry, Texas A&M University, College Station, Texas 77842-3012

We are grateful to the authors of the Comment in Ref. 1 who have performed higher level calculations for the SnBi$_2$ and SnBi$_3$ molecules, studied by our group using the classical and invaluable technique of Knudsen cell mass spectrometry.[2] 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 SnBi$_2$ and 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 SnBi$_2$ and SnBi$_3$ molecules, and for this reason we have to rely on computational results. For the evaluation of the Gibbs energy functions, $(G_T^o - H_0^o)/T$ (GEF$_0$), of SnBi$_2$,[2] 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.*[1] did not give the vibrational frequencies for the new computed equilibrium ground state geometry of SnBi$_2$. Therefore, we performed calculations on the $^1A_1$ 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.[4] 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 SnBi$_2$. The new GEF$_0$ are lower than the previous reported values,[2] in particular they differ by 11.7 J mol^{-1} K^{-1} at 900 K. This result is directly related to the value of the enthalpy of reaction (2), specifically the lower the 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 SnBi$_2$. The revised $\Delta_a H_0^o(\text{SnBi}_{2,g})$ value is (426.3 ± 15.0) kJ mol^{-1}. The $\Delta_a H_0^o(\text{SnBi}_{2,g})$ value of Figgen *et al.*[1] 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 ± 18.0) 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.*[1] showed that the inclusion of SO contributions reduces the atomization energies by 5 kJ mol^{-1} for the SnBi molecule and by 55 kJ mol^{-1} for the SnBi$_2$ molecule. Unfortunately, no CCSD(T)-SO calculations are reported for 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.*[5] showed that using RSC-ECP basis sets and the CCSD(T) level of theory, the same quantum mechanical treatment used by Figgen *et al.*,[1] the computed $\Delta_a H_0^o$ of the 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.[5]

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 SnBi$_2$, used in the evaluation of the new thermal functions, have been performed employing the GAUSSIAN 98 suite of programs.[6]

[a)]Electronic mail: giovanni@radon.cchem.berkeley.edu

[1] D. Figgen, W. Müller, M. Schweizer, H. Stoll, and K. A. Peterson, J. Chem. Phys. **118**, 4766 (2003).

[2] G. Meloni and K. A. Gingerich, J. Chem. Phys. **116**, 6957 (2002).

[3] A. Bergner, M. Dolg, W. Kuechle, H. Stoll, and H. Preuss, Mol. Phys. **80**, 1431 (1993).

[4] W. Kuechle, M. Dolg, H. Stoll, and H. Preuss, Mol. Phys. **74**, 1245 (1991).

[5] B. Metz, H. Stoll, and M. Dolg, J. Chem. Phys. **113**, 2563 (2000).

[6] M. J. Frisch, G. W. Trucks, H. B. Schlegel *et al.*, GAUSSIAN 98, Revision A.9, Gaussian, Inc., Pittsburgh, PA 1998.