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On Comparison of Experimental Thermochemical Data with G3 Theory

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The results of assessments of methods for computing molecular thermochemical data can depend significantly on how comparison with experimental data is done. This is illustrated for two cases involving G3 theory: the energy of SiF_4 and the G2/97 test set.

In the past decade significant progress has been made in developing quantum chemical methods for accurately predicting molecular thermochemical data. An important part of the development of such quantum chemical methods is their critical assessment on test sets of accurate experimental data. We recently published a paper on the development of G3 theory[1] and its evaluation on the G2/97 test set.[2,3] Since then two papers have appeared that give different interpretations of the accuracy of G3 theory. Martin and Taylor[4] (MT) suggested that G3 theory has a "large error" for SiF_4, one of the molecules in the G2/97 test set, based on their theoretical calculations. This is in contradiction to our conclusions in ref 1. In another paper Montgomery et al.[5] reanalyzed the accuracy of G3 theory on the G2/97 test set and found that it had a smaller mean absolute deviation from experiment (0.94 kcal/mol) compared to our published value in ref 1 (1.01 kcal/mol). These two differences in the interpretation of the accuracy of G3 theory need further explanation. In this note we discuss in more detail the G3 error in the energy of SiF_4 and our criteria for assessments on the G2/97 test set.

Martin and Taylor[4] compared the G3 value of the atomization energy, ΣD_e, of SiF_4 (571.7 kcal/mol) with their "benchmark" value of 573.9 kcal/mol. They give the G3 error to be 2.2 kcal/mol compared to the benchmark value, and 4.1 if scalar relativistic corrections are included. They conclude that G3 exhibits a "large error" for SiF_4. The first point to be made about the analysis of MT is that they use their theoretical ΣD_e(SiF_4) to assess the G3 value. If G3 is strictly compared with experimental data, the conclusions are different. The directly measured experimental quantity for SiF_4 is its enthalpy of formation: $\Delta H_f^o(298\ \text{K}) = -385.98 \pm 0.2$ kcal/mol[6] or -386.18 ± 0.18 kcal/mol.[7] The G3 enthalpy of formation at 298 K (−384.9 kcal/mol) differs by only 1.1 kcal/mol from the first experimental value,[6] which is included in the G2/97 test set. The experimental atomization energy at 0 K, $\Sigma D_o(SiF_4)$, can be derived from the measured values for ΔH_f^o(298 K) of SiF_4 [−385.98], ΔH_f^o(0 K) of Si(g) [106.6 kcal/mol[6]], ΔH_f^o(0 K) of *F*(*g*) [18.47 kcal/mol[6]] and the temperature corrections of these species [0.76 kcal/mol for Si(cr),[6] 1.05 kcal/mol[6] for F_2(g),and 3.67 kcal/mol[4] for SiF_4]. The resulting experimental ΣD_o of 565.2 kcal/mol differs by only 1.1 kcal/mol from the G3 value of 564.1 kcal/mol. Finally, inclusion of the experimental zero-point energy (8.03 kcal/mol[4,8]) gives a $\Sigma D_e(SiF_4)$ of 573.2 kcal/mol, which differs by 1.4 kcal/mol from the G3 value of 571.7 kcal/mol.[9] Thus, G3 is quite accurate for SiF_4, based on the best available experiment data.

The second point to be noted about the MT results for G3 theory on SiF_4 is that it is incorrect to add a scalar relativistic correction to the G3 energies without re-optimizing the G3 higher level correction (HLC) parameter values. The overall mean absolute deviation for the G2/97 test set remains about the same when the HLC is re-optimized with relativistic corrections included.[10,11] When this is done, the error in the SiF_4 enthalpy of formation increases from 1.1 kcal/mol to 2.3 kcal/mol (or 2.0 kcal/mol if the MT relativistic correction is used). This error is much less than what is obtained by MT without re-optimization.

Martin and Taylor[4] have recommended a new value for the Si(g) atomic enthalpy of formation [107.2 ± 0.38 kcal/mol] that is based on their theoretical ΣD_e value and the experimental value for the ΔH_f^o of SiF_4. If we use this value, it would increase the error in ΣD_o and ΣD_e given by G3 theory by about 0.6 kcal/mol. We did not use the new value for the ΔH_f^o of Si(g) in the analysis above for the following reason. The new ΔH_f^o of Si(g) recommended by MT is obtained in part from the experimental ΔH_f^o of SiF_4, the quantity that we are calculating. Thus, including it in our derivation would introduce circular reasoning that should be avoided (see below for more discussion of this point).

We now address the second subject of this note. Montgomery et al.[5] reported that the mean absolute deviation of G3 theory is 0.94 kcal/mol for the G2/97 test set. In contrast we originally reported this mean absolute deviation as 1.01 kcal/mol for the G2/97 test set.[1,12] There are two reasons for the difference between the two analyses of the accuracy of G3 theory. First, Montgomery et al. eliminate four entries in the statistical analysis of the G2/97 test set: the enthalpies of formation of CF_2O, C_2F_4, and CH_2CHCl, and the ionization potential of B_2F_4. They do this because there is theoretical evidence that the experimental values are in error. In our analysis we have chosen not to throw out experimental data unless there is new experimental evidence that warrants it. In only one case is there such evidence, CF_2O.[2] In the other cases there is no new experimental evidence to

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support dropping the energies and, thus, we have not dropped them in our analysis. Second, Montgomery et al. have used "theoretical" atomic enthalpies of formation for Si[4] and Be[13] and experimental atomic enthalpies for all other elements in the calculation of molecular enthalpies of formation. We use experimental values for all elements, despite some uncertainty in the Si and Be values.[14] The reason that we do not use these "theoretical" atomic enthalpies is that they are derived in part from an experimental molecular enthalpy that is part of the test set, which may bias the assessment process. If the two changes noted above are not included in this analysis of the G2/97 test set, the mean absolute deviation is 1.01 kcal/mol for G3 theory the same as we reported in ref 1.[15] Thus, elimination of these items produces significant change.

The problem with using a "theoretical" value for an atomic enthalpy in assessments of thermochemical data is illustrated by the case of Si(g). The $\Delta H_{\mathrm{f}}^{\mathrm{o}}$(0 K) of Si(g) from the JANAF tables[6] is 106.6 ± 1.9 kcal/mol. The uncertainty was revised to 1.0 kcal/mol by Desai.[16] In 1992 Grev and Schafer suggested, on the basis of theoretical calculations combined with the experimental enthalpy of formation of SiH_4, a new value of 108.1 kcal/mol for the $\Delta H_{\mathrm{f}}^{\mathrm{o}}$(0 K) of Si(g). It was used by Montgomery et al.[17] in an earlier assessment study. As discussed above, MT in 1999 recommended a value of 107.15 ± 0.38 kcal/mol[4] based on "benchmark" calculations in combination with the experimental enthalpy of formation of SiF_4. This is the value used by Montgomery et al. in the assessment of G3 theory discussed here. In 1999 Dixon and Feller[18] also reported "benchmark" calculations on SiF_4 and indicated that there was not enough evidence to challenge the experimental value of $\Delta H_{\mathrm{f}}^{\mathrm{o}}$(0 K) of Si. Thus, the published "benchmark" calculations on this subject are conflicting and further work is welcome.

Montgomery et al.[5] assess their CBS-QB3 method on the G2/97 test set. The CBS-QB3 method is a modification of the CBS-Q method that is based on density functional geometries and zero-point energies. They have published two versions of this method, an earlier one based on localization using an extended basis set[17] and the latest based on localization using a minimal basis set.[5] Montgomery et al.[5] give the mean absolute deviation from experiment of the latest CBS-QB3 method as 1.10 kcal/mol for the G2/97 test set using their analysis scheme. Using our criteria it increases to 1.16 kcal/mol. The original version[17,19] of CBS-QB3has a mean absolute deviation of 1.21 kcal/mol[20] for the G2/97 test set using our criteria. Thus, there is some overall improvement due to the change in the localization procedure (1.21 to 1.16 kcal/mol). Note that the two versions of CBS-QB3 give different molecular energies in some cases. For example, SO_2 differs by 0.6 kcal/mol, CCl_4 by 2.4 kcal/mol, and C_6H_6 by 0.6 kcal/mol.[17,20]

In summary, we have shown that the results of assessments of methods for computing molecular thermochemical data can depend significantly on how comparison with experimental data is done. In all of our assessments[1−3] including our most recent on that presented the G3/99 test set,[21] we have avoided including any theoretical input in the experimental test set. If theoretical input is included in the experimental data, the resulting analysis may differ as shown by several examples in this note.

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References and Notes

(1) Curtiss, L. A.; Raghavachari, K.; Redfern, P. C.; Rassolov, V.; Pople, J. A. *J. Chem. Phys.* **1998**, *109,* 7764.

(2) Curtiss, L. A.; Raghavachari, K.; Redfern, P. C.; Pople, J. A. *J. Chem. Phys.* **1997**, *106,* 1063.

(3) Curtiss, L. A.; Redfern, P. C.; Raghavachari, K.; Pople, J. A. *J. Chem. Phys.* **1998**, 109, 42.

(4) Martin, J. M. L.; Taylor, P. R. *J. Phys. Chem. A* **1999**, *103,* 4427.

(5) Montgomery, J. A., Jr.; Frisch, M. J.; Ochterski, J. W.; Petersson, G. A.. *J. Chem. Phys.* **2000**, *112,* 6532.

(6) *NIST-JANAF Thermochemical Tables*, 4th ed.; Chase, M. W., Jr., Ed.; *J. Phys. Chem. Ref. Data* 1998, Monograph 9.

(7) Johnson, G. K. *J. Chem. Thermodyn.* **1986**, *18,* 801.

(8) McDowell, R. S.; Reisfeld, M. J.; Patterson, C. W.; Krohn, B. J.; Vasquez, M. C.; Laguna, G. A. *J. Chem. Phys.* **1982**, *77,* 4337.

(9) It should be also be noted that G3 theory it is not expected to be as accurate for D_e values as it is for $\Delta H_{\mathrm{f}}^{\mathrm{o}}$ or ΣD_o values because its HLC parameters have been derived to give the best agreement with experiment for enthalpies of formation. The HLC takes into account not only deficiencies in the total energies, but also deficiencies in other quantities such as zero-point energies.

(10) Kedziora, G. S.; Pople, J. A.; Rassolov, V.; Ratner, M. A.; Redfern, P. C.; Curtiss, L. A. *J. Chem. Phys.* **1999**, *110*, 7123.

(11) Kedziora, G. S.; Pople, J. A.; Rassolov, V.; Ratner, M. A.; Redfern, P. C.; Curtiss, L. A., submitted.

(12) Curtiss, L. A.; Raghavachari, K.; Redfern, P. C.; Pople, J. A. *J. Chem. Phys***. 2000**, *112,* 7374.

(13) Ochterski, J. W.; Petersson, G. A.; Wiberg, K. B. *J. Am. Chem. Soc.* **1995**, *117,* 11299.

(14) See ref 2 for details on the procedure used to calculate enthalpies of formation of molecules.

(15) Montgomery et al.[5] have also revised some of the experimental values with slightly different values. This has little overall effect on the results.

(16) Desai, P. D. *J. Phys. Chem. Ref. Data* **1986***, 15,* 967.

(17) Montgomery, J. A., Jr.; Frisch, M. J.; Ochterski, J. W.; Petersson, G. A. *J. Chem. Phys.* **1999**, *110,* 1.

(18) Feller, D.; Dixon, D. A. *J. Phys. Chem.* **1999**, *A103*, 6413.

(19) *Gaussian 98* (Revisions A.3); M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. G. Johnson, W. Chen, M. W. Wong, J. L. Andres, M. Head-Gordon, E. S. Replogle, and J. A. Pople, Gaussian, Inc., Pittsburgh, PA, 1998.

(20) Curtiss, L. A.; Redfern, P. C.; Frurip, D. J. *Reviews of Computational Chemistry*; Lipkowitz, K. B., Boyd, D. B., Eds.; Wiley-VCH: New York, 2000; Vol. 15, pp 147−202.