Comment on the Ionization Energy of B2F4

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Comment on the Ionization Energy of B2F4

Abstract
The Gn test sets(1) of accurate (uncertainty ≤ 1 kcal mol–1 ≈ 4 kJ mol–1) experimental data are widely employed in the development and assessment of quantum chemistry procedures. However, while all the data in the Gn sets nominally carry a sub-kcal mol–1 uncertainty, several of the experimental values show uncharacteristically large discrepancies when compared with values determined by high-level theoretical calculations. One of these questionable values is the adiabatic ionization energy (IE) of B2F4, for which the theoretical values calculated, for example, with the high-level G2 (1133.9, kJ mol–1),(1b) G3 (1135.4 kJ mol–1),(2) and G4 (1127.2 kJ mol–1)(3) procedures differ significantly from the experimental value of 1164.6 ± 1.0 kJ mol–1.(4)

Keywords
b2f4, comment, energy, ionization, GeoQUEST

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Comment on the Ionization Energy of B₂F₄

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The G2 test sets of accurate (uncertainty ≤ 1 kcal mol⁻¹ ≈ 4 kJ mol⁻¹) experimental data are widely employed in the development and assessment of quantum chemistry procedures. However, while all the data in the G2 sets nominally carry a sub-kcal mol⁻¹ uncertainty, several of the experimental values show uncharacteristically large discrepancies when compared with values determined by high-level theoretical calculations. One of these questionable values is the adiabatic ionization energy (IE) of B₂F₄, for which the theoretical values calculated, for example, with the high-level G2 (1133.9 kJ mol⁻¹)¹b G3 (1135.4 kJ mol⁻¹)² and G4 (1127.2 kJ mol⁻¹)³ procedures differ significantly from the experimental value of 1164.6 ± 1.0 kJ mol⁻¹.

Taken together with the general agreement between these and other high-level theoretical results, the discrepancies between theory and experiment for the ionization energy of B₂F₄ have called into question the accuracy of the experimental values. In the course of our own developments of quantum chemistry procedures, we have also been persistently concerned by the large discrepancies between theory and experiment for this quantity. However, as the reason behind the discrepancy was not clear, and in the absence of an alternative experiment for this quantity, the change in structure from B₂F₄ to B₂F₄⁺ diﬀers signiﬁcantly, leading to large normal mode displacements, so that it would be difficult experimentally to observe the ionization onset that corresponds to the adiabatic process. Indeed, both Montgomery et al.⁵ and Li and Fan⁶ suggest this possibility. However, in both cases, they focus on the change in geometry accompanying the vertical ionization, strengthens the case for either removing the experimental adiabatic ionization energy of B₂F₄ from the G2 test sets or (in the absence of an experimental redetermination) replacing it by a high-level theoretical value. For the time being, we recommend a value of 1132 kJ mol⁻¹ based on our W2w calculations. It would seem that retention of the current experimental value, which is now widely acknowledged to be quite poor, could lead to unnecessary distortions in the parametrization and assessment of the performance of new theoretical procedures.

Author Information

Notes

The authors declare no competing financial interest.

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References

(9) All calculations were performed using Gaussian 09: Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; et al. Gaussian 09, revision A.02; Gaussian, Inc.: Wallingford, CT, 2009.