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Comment on the Ionization Energy of B2F4

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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

Disciplines

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Comment on the Ionization Energy of B₂F₄Bun Chan,^{*,†,§} Adam J. Trevitt,[‡] Stephen J. Blanksby,^{‡,§} and Leo Radom^{*,†,§}[†]School of Chemistry, University of Sydney, Sydney, NSW 2006, Australia[‡]School of Chemistry, University of Wollongong, Wollongong, NSW 2522, Australia[§]ARC Centre of Excellence for Free Radical Chemistry and Biotechnology, Australia

The *Gn* test sets¹ of accurate (uncertainty ≤ 1 kcal mol⁻¹ \approx 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 \pm 1.0 kJ mol⁻¹.⁴

Taken together with the general agreement between these and other^{5,6} 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 value.^{3,5,6} In the course of our own developments of quantum chemistry procedures,⁷ 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 appropriately accurate experimental value, the value of 1164.6 kJ mol⁻¹ remains the one used in the *Gn* test sets.⁸

A likely cause for the discrepancy between the experimental and theoretical ionization energies is that the structures of B₂F₄ and B₂F₄⁺ differ 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 structure from *D*_{2h} (neutral B₂F₄) to *D*_{2d} (B₂F₄⁺ cation), but this rotation in fact is found to correspond to a relatively small energy change.⁶ Thus, the reason for the discrepancy between theory and experiment remains.

With these considerations in mind, we have calculated⁹ the vertical and adiabatic ionization energies of B₂F₄ using the high-level W2w composite procedure.¹⁰ Apart from confirming the change in symmetry from *D*_{2h} to *D*_{2d}, we observe large differences in the B–B and B–F bond lengths for B₂F₄ and B₂F₄⁺. For example (at the CCSD(T)/aug-cc-pVTZ level), the B–B bond length changes from 1.730 Å in B₂F₄ to 2.084 Å in B₂F₄⁺. Similarly, the B–F bond length changes from 1.321 Å in B₂F₄ to 1.271 Å in B₂F₄⁺. These results are consistent with those obtained by Li and Fan but were not commented on in their work. It is, however, precisely these structural differences that lead to a large difference between our calculated vertical (1277.8 kJ mol⁻¹) and adiabatic (1132.5 kJ mol⁻¹) ionization energies for B₂F₄. The large *structural change* accompanying the

ionization of B₂F₄ means that the experimental determination of the onset of the ionization process corresponding to an adiabatic transition may not be entirely trivial as the corresponding Franck–Condon factors are likely to be small. The large *energy change* associated with the vertical and adiabatically ionized structures means that there would be significant energy consequences connected with the difficulty in observing the ionization onset. The fact that the experimentally reported ionization energy (1164.6 kJ mol⁻¹) lies between our calculated adiabatic (1132.5 kJ mol⁻¹) and vertical (1277.8 kJ mol⁻¹) IEs is in accord with these arguments.

We believe that our analysis, which shows that there is a large energetic consequence of the change in geometry accompanying ionization, strengthens the case for either removing the experimental adiabatic ionization energy of B₂F₄ from the *Gn* 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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