Experiment 9: Comparison with Experimental Results

Bond dissociation, atomization energies and the NIST WebBook

> Tip
>
> **At a glance.** Two bond dissociations and five atomization energies, with five methods, def2-TZVP, a (99,590) grid and stability analysis: **78 jobs**. **You will learn** why radicals and atoms are hard, and why a computed electronic energy can't be compared directly with an experimental enthalpy.

Background

This experiment analyzes two bond dissociation reactions from the Minnesota 2015B database [1], one from the SR-MGN-BE107 subset [2], [3], [4] and one from the SR-TM-BE17 subset [2], [5], [6], [7], [8]. You will also look at total atomization energies from the W4-11 subset [9] of GMTKN55 [10].

Bond dissociations.

- **9a**: *tert*-butyl alcohol ⟶ *tert*-butyl radical + OH radical (C–O bond). ΔE_{ref} = **115.02 kcal/mol**.
- **9b**: FeCl ⟶ Fe + Cl [8]. The reference electronic dissociation energy is ΔE_{ref} = **78.5 kcal/mol**.

Use **stability analysis** in both cases, an integration grid of at least **(99,590)** (`XC_GRID 000099000590`) and the **def2-TZVP** basis set [11] (def2-QZVP would not fit within the free server's 10-minute limit for *tert*-butanol). Use the functionals MN15-L [12], MN15 [1], B3LYP [13], [14], [15], [16], [17] and PBE [18], plus the HF method [19], [20], [21], [22]. Collect the computed reaction energies and their errors in a table before you answer the questions.

Atomization energies. An atomization reaction breaks a molecule into its constituent atoms (see reaction 5c in Experiment 5). Study H_2, methane, ammonia, water and ozone with the same methods; for H_2, atomization and bond dissociation are the same reaction.

Molecule	Reference energy (kcal/mol)
H_2	109.5
CH_4	420.4
NH_3	298.0
H_2O	233.0
O_3	147.4

Total atomization energies are not very important chemically, but they are interesting computationally: they are a challenge for functional development and a good test of a functional's robustness and reliability.

Run the calculations

All inputs include `INTERNAL_STABILITY TRUE` and the (99,590) grid (`XC_GRID 000099000590`).

Enter your results

Record the **total energy**, **SCF cycles** and **wall time** of every job, then enter your seven reaction energies. Atomization reactions have big coefficients ($CH_4 \longrightarrow C + 4\,H$): mind the signs. The B3LYP/6-31G* row only needs the three species of the *tert*-butanol reaction.

Practice comment

Bond dissociation energies are everywhere in benchmark databases [1], [10], [12], [23], [24] because xc functionals must describe them correctly. Even simple reactions can be tricky. Breaking the C–O bond is easy in principle, but it produces two radicals, which are hard for theoretical methods (remember that KS-DFT, like HF, is in principle a single-determinant theory) [25]. For FeCl, the heavier element complicates things further. There is also no simple way to compare a computed result with an experimental one, as Truhlar and co-workers explain [6], [8]: going from the experimental value to a purely electronic one requires several corrections (zero-point energy, thermal contributions, spin–orbit coupling, …). That is why comparing computed and experimental values directly is discouraged unless you get help from a theoretician.

The atomization energies are one more example of why you should rely on modern functionals. A functional must describe not only the molecule but also the atoms, which are a completely different chemical species. HF lacks electron correlation, so it describes atoms very poorly and gives large errors. All density functional approximations include electron correlation in some approximate way [26], [27], [28], [29], [30], so they do better for atoms. Even so, we again advise non-experts to seek help from a theoretician in such cases.

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