SUB TWENTY WAVENUMBER COMPUTATIONAL PREDICTION OF MOLECULAR BOND ENERGIES AND THE INTRIGUING BDE OF F_2

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The determination of molecular bond dissociation energies (BDE) is a fundamental pursuit of chemistry. This is an area where computational approaches have proved useful, especially when addressing molecules or environments that are difficult to study in the lab. High-accuracy composite methods can typically compute bond-energies to within one kJ mol^{-1} via a series of additive energy increments, with corrections for relativistic effects, the vibrational zero-point energy, and the Born-Oppenheimer approximation.

Recently, the present authors explored an extension to the HEAT composite method, currently named KS-HEAT, which routinely reproduces the Active Thermochemical Tables (ATcT) total-atomization energies of small molecules to within 20 cm^{-1}. F_2, however, differs from the ATcT value by nearly 30 cm^{-1}. While fluorine-containing species are historically challenging to model, disagreement of this magnitude is surprising given the considerable level of theory and size of basis sets employed here.

To confound the issue, while the BDE predicted by KS-HEAT agrees closely with the combined ZEKE and IPP study of Yang *et al.* and the computational work of Csontos *et al.*, a recent CIPP study by Matthíasson *et al.* and the FPD value calculated by Feller *et al.* agree with the current ATcT assignment. As the BDE of F_2 influences the ATcT enthalpies of formation of all fluorine containing molecules, this is an important quantity to get "right". The details of these calculations are presented, and the BDE of F_2 is discussed.