Supplementary Material to

Analysis of transition state stabilization by non-covalent interactions in additions of organoboron reagents to fluoroketones using functional-group symmetry-adapted perturbation theory

Brandon W. Bakr[1] and C. David Sherrill[1, 2, a)]

[1)]*Center for Computational Molecular Science and Technology,*
School of Chemistry and Biochemistry, Georgia Institute of Technology, Atlanta,
GA 30332-0400

[2)]*School of Computational Science and Engineering, Georgia Institute of Technology,*
Atlanta, GA 30332-0280

(Dated: 30 May 2018)

---

a) Electronic mail: sherrill@gatech.edu

Figures	**Content**
I. General Material	
S1	π–π investigation for MP2 overbinding
S2	SAPT0/jDZ vs sSAPT0/jDZ vs MP2/aTZ-CP vs MP2/aTZ-CP + δ[CCSD(T)] for systems of reaction A
S3	SAPT0/jDZ vs sSAPT0/jDZ vs MP2/aTZ-CP for systems of study
S4	Relative deformation energies for systems of study as computed by MP2/aTZ

Because MP2 can overbind π-π interactions[1], we have verified the computed interaction energies for TS's with potential for π-π interactions are within 1 kcal mol^{-1} of the CP-corrected ωB97X-V/aug-cc-pVTZ level of theory, as seen in Figure S1, which has been shown to produce accurate interaction energies for a variety of complexes.[2]

For reaction A, sSAPT and MP2 agree that TS IVa is stabilized by 4 – 6 kcal mol^{-1} compared to the others, and that the other TS's have similar interaction energies (although MP2 and sSAPT disagree about whether IIIa is slightly stabilized or slightly destabilized compared to IIa and Va). For reaction B, sSAPT and MP2 agree that IIb is the most stable, followed by Vb and IVb at about 2 kcal mol^{-1} less stable, followed by IIIb which is much less stable. For reaction C, MP2 and sSAPT agree that IIc is the most stable, followed closely by Vc, with IVc being significantly less stable, and with IIIc being even less stable.

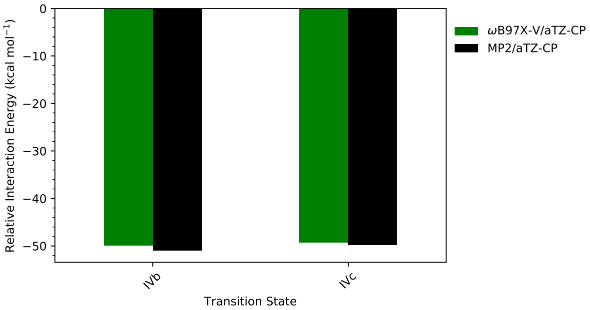

FIG. S1. The chosen reference method, counterpoise-corrected MP2/aTZ was tested against counterpoise-corrected ωB97X-V/aTZ on two systems where π-π interactions were suspected, due to aligned π faces. MP2/aTZ estimates are within 1 kcal mol^{-1} of ωB97X-V/aTZ indicating no large overbinding.

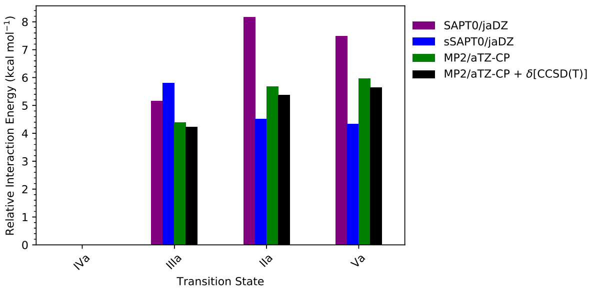

FIG. S2. Interaction energies are plotted relative to the most negative interaction energy estimated within each model chemistry (SAPT0/jaDZ, exchange-scaled sSAPT0/jaDZ, counterpoise-corrected MP2/aTZ, counterpoise-corrected MP2/aTZ + counterpoise-corrected δ[CCSD(T)/DZ]).

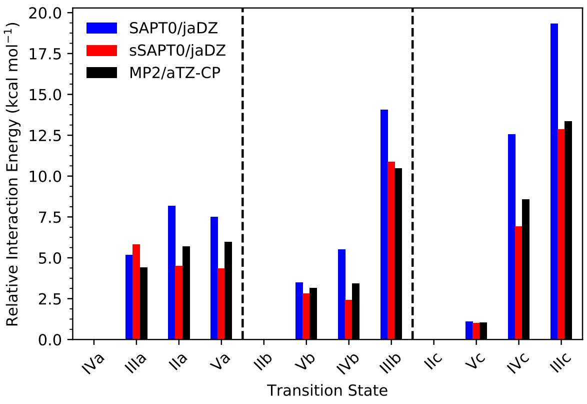

FIG. S3. Interaction energies are plotted relative to the most negative interaction energy estimated within each model chemistry (SAPT0/jaDZ, exchange-scaled sSAPT0/jaDZ and MP2/aTZ).

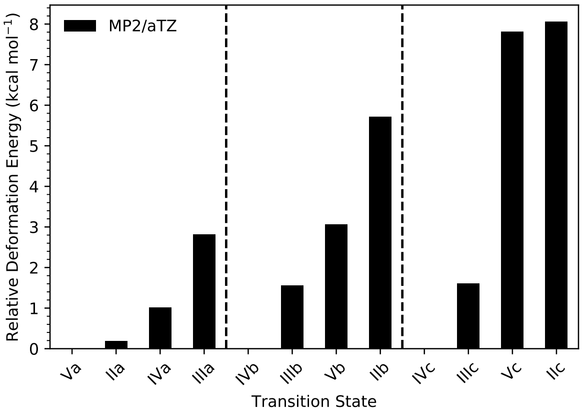

FIG. S4. The relative deformation energy of each transition state, as computed with MP2/aTZ, is plotted with respect to the minimum deformation energy in each reaction family (A, B, and C).

REFERENCES

[1] J. Antony and S. Grimme, *J. Phys. Chem. A*, 2007, **111**, 4862–4868.

[2] L. A. Burns, J. C. Faver, Z. Zheng, M. S. Marshall, D. G. A. Smith, K. Vanommeslaeghe, A. D. MacKerell, K. M. Merz and C. D. Sherrill, *J. Chem. Phys.*, 2017, **147**, 161727.