On the Performance of Different Methods and Basis Sets in Quantum Chemistry

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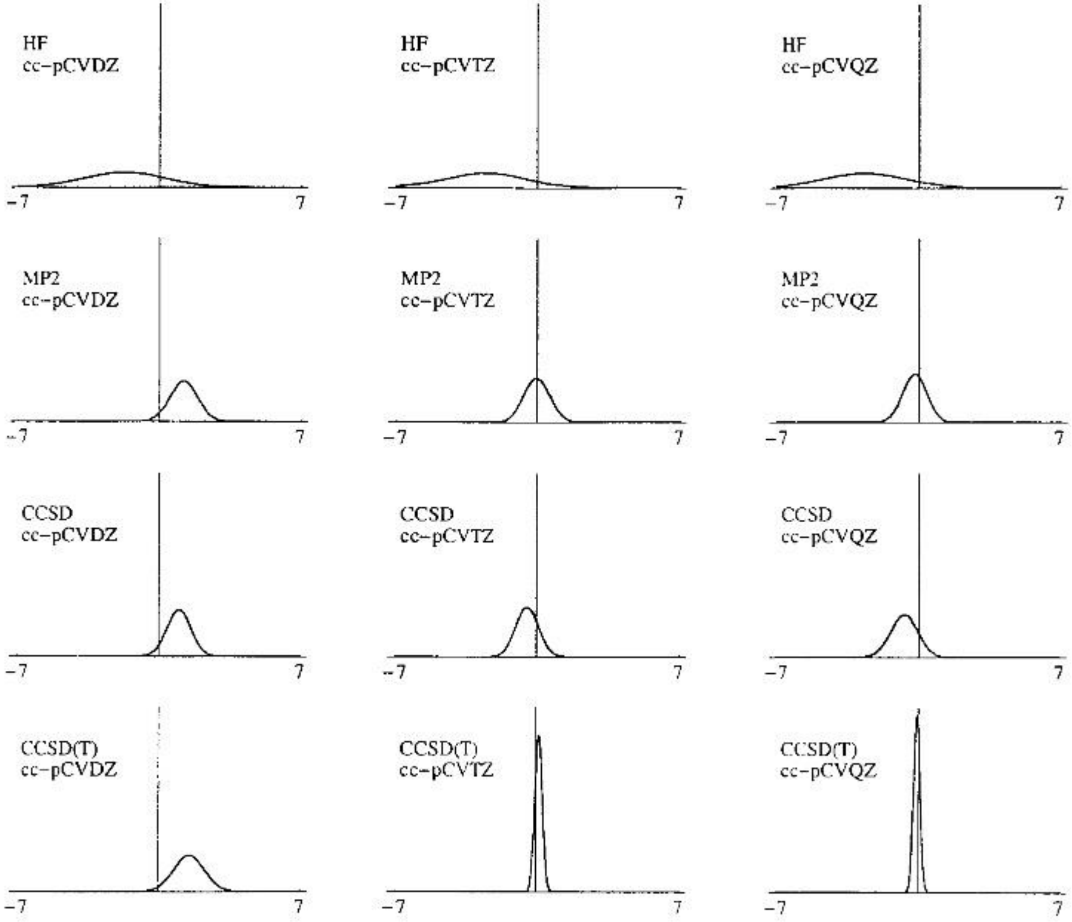
Performance for Bond Lengths



Normal distributions of errors in the calculated bond distances (pm) for 19 small molecules

Bak, Gauss, Jorgensen, Olsen, Helgaker, and Stanton, *J. Chem. Phys*. **114**, 6548 (2001)

Performance for Bond Lengths

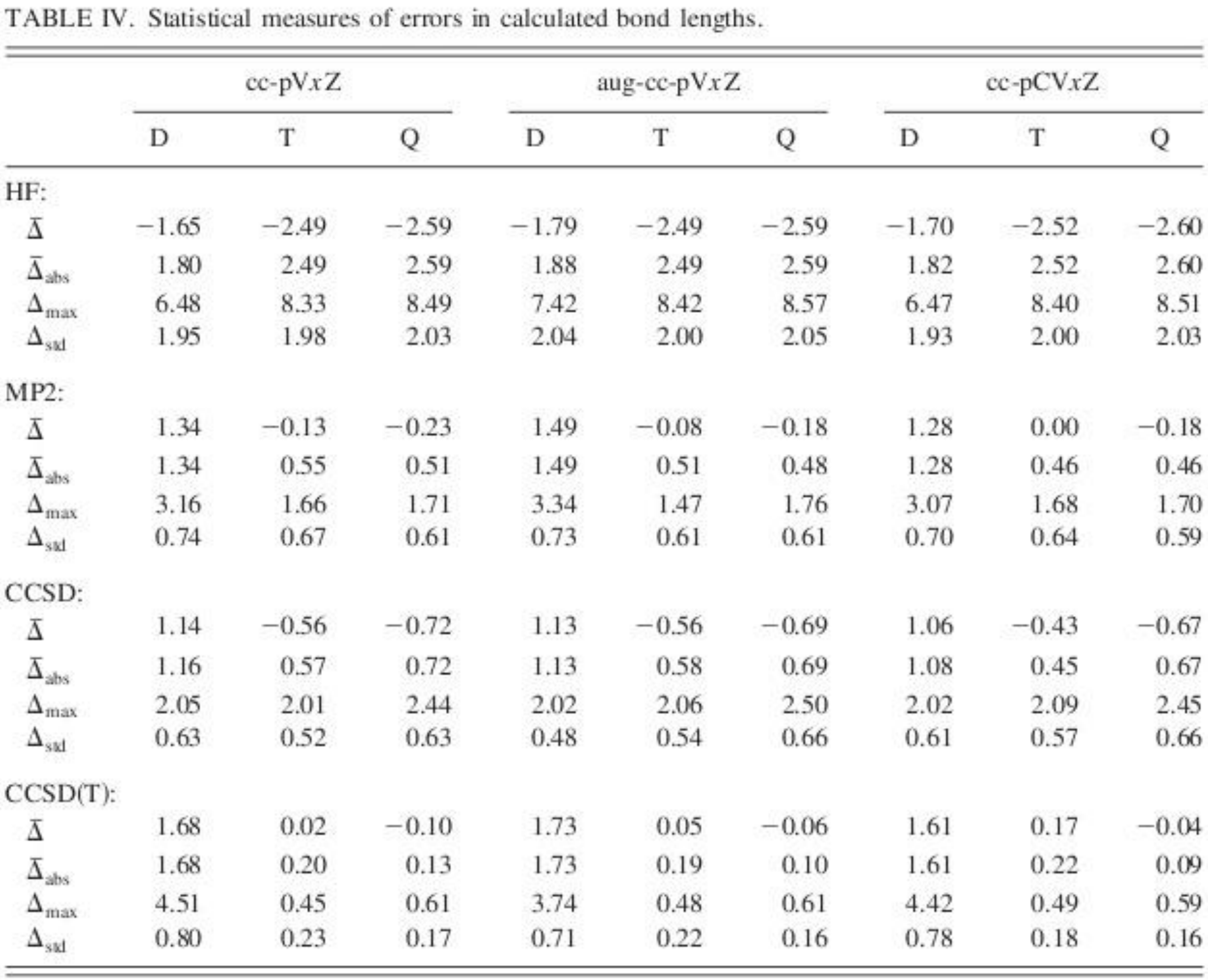
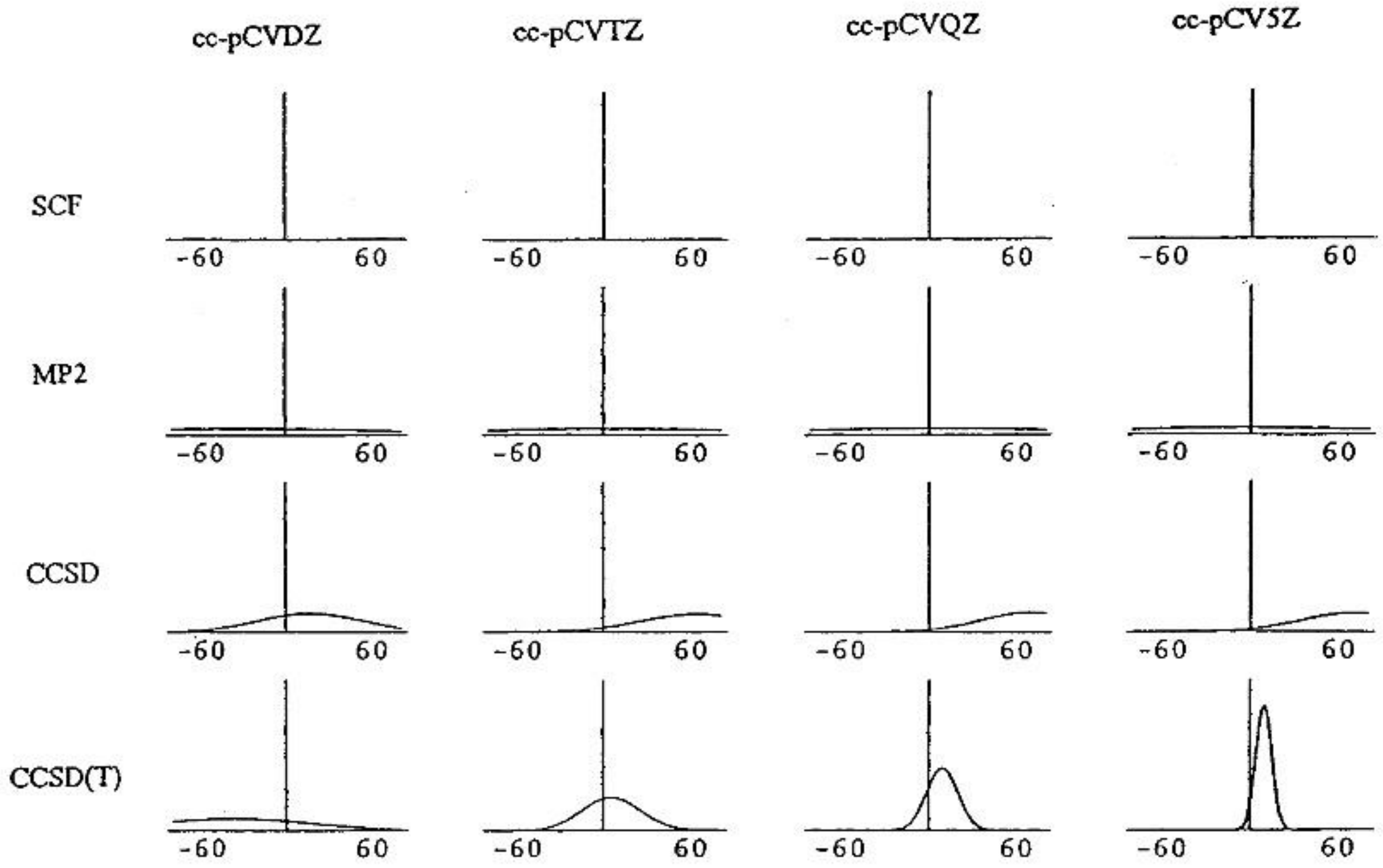


TABLE IV. Statistical measures of errors in calculated bond lengths.

	cc-pV*x*Z			aug-cc-pV*x*Z			cc-pCV*x*Z		
	D	T	Q	D	T	Q	D	T	Q
HF:									
$\bar{\Delta}$	−1.65	−2.49	−2.59	−1.79	−2.49	−2.59	−1.70	−2.52	−2.60
$\bar{\Delta}_{\mathrm{abs}}$	1.80	2.49	2.59	1.88	2.49	2.59	1.82	2.52	2.60
Δ_{max}	6.48	8.33	8.49	7.42	8.42	8.57	6.47	8.40	8.51
Δ_{std}	1.95	1.98	2.03	2.04	2.00	2.05	1.93	2.00	2.03
MP2:									
$\bar{\Delta}$	1.34	−0.13	−0.23	1.49	−0.08	−0.18	1.28	0.00	−0.18
$\bar{\Delta}_{\mathrm{abs}}$	1.34	0.55	0.51	1.49	0.51	0.48	1.28	0.46	0.46
Δ_{max}	3.16	1.66	1.71	3.34	1.47	1.76	3.07	1.68	1.70
Δ_{std}	0.74	0.67	0.61	0.73	0.61	0.61	0.70	0.64	0.59
CCSD:									
$\bar{\Delta}$	1.14	−0.56	−0.72	1.13	−0.56	−0.69	1.06	−0.43	−0.67
$\bar{\Delta}_{\mathrm{abs}}$	1.16	0.57	0.72	1.13	0.58	0.69	1.08	0.45	0.67
Δ_{max}	2.05	2.01	2.44	2.02	2.06	2.50	2.02	2.09	2.45
Δ_{std}	0.63	0.52	0.63	0.48	0.54	0.66	0.61	0.57	0.66
CCSD(T):									
$\bar{\Delta}$	1.68	0.02	−0.10	1.73	0.05	−0.06	1.61	0.17	−0.04
$\bar{\Delta}_{\mathrm{abs}}$	1.68	0.20	0.13	1.73	0.19	0.10	1.61	0.22	0.09
Δ_{max}	4.51	0.45	0.61	3.74	0.48	0.61	4.42	0.49	0.59
Δ_{std}	0.80	0.23	0.17	0.71	0.22	0.16	0.78	0.18	0.16

Bak, Gauss, Jorgensen, Olsen, Helgaker, and Stanton, *J. Chem. Phys*. **114**, 6548 (2001)

Performance for Vibrational Frequencies



Normal distributions of errors in the calculated harmonic frequencies (cm^{-1})
For BH, HF, CO, N_2, and F_2

Pawlowski, Halkier, Jorgensen, Bak, Helgaker, and Klopper, *J. Chem. Phys*. **118**, 2539 (2003)

Scale Factors

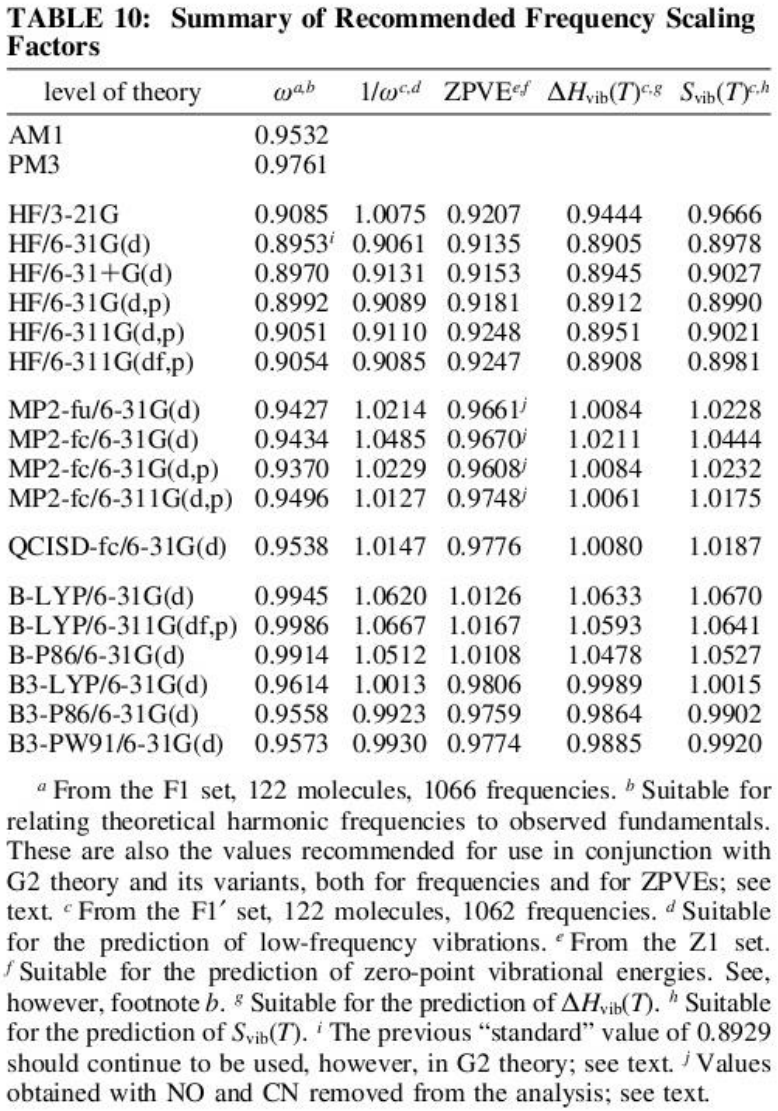


TABLE 10: Summary of Recommended Frequency Scaling Factors

level of theory	$\omega^{a,b}$	$1/\omega^{c,d}$	ZPVE^{e,f}	$\Delta H_{\text{vib}}(T)^{c,g}$	$S_{\text{vib}}(T)^{c,h}$
AM1	0.9532				
PM3	0.9761				
HF/3-21G	0.9085	1.0075	0.9207	0.9444	0.9666
HF/6-31G(d)	0.8953^{i}	0.9061	0.9135	0.8905	0.8978
HF/6-31+G(d)	0.8970	0.9131	0.9153	0.8945	0.9027
HF/6-31G(d,p)	0.8992	0.9089	0.9181	0.8912	0.8990
HF/6-311G(d,p)	0.9051	0.9110	0.9248	0.8951	0.9021
HF/6-311G(df,p)	0.9054	0.9085	0.9247	0.8908	0.8981
MP2-fu/6-31G(d)	0.9427	1.0214	0.9661^{j}	1.0084	1.0228
MP2-fc/6-31G(d)	0.9434	1.0485	0.9670^{j}	1.0211	1.0444
MP2-fc/6-31G(d,p)	0.9370	1.0229	0.9608^{j}	1.0084	1.0232
MP2-fc/6-311G(d,p)	0.9496	1.0127	0.9748^{j}	1.0061	1.0175
QCISD-fc/6-31G(d)	0.9538	1.0147	0.9776	1.0080	1.0187
B-LYP/6-31G(d)	0.9945	1.0620	1.0126	1.0633	1.0670
B-LYP/6-311G(df,p)	0.9986	1.0667	1.0167	1.0593	1.0641
B-P86/6-31G(d)	0.9914	1.0512	1.0108	1.0478	1.0527
B3-LYP/6-31G(d)	0.9614	1.0013	0.9806	0.9989	1.0015
B3-P86/6-31G(d)	0.9558	0.9923	0.9759	0.9864	0.9902
B3-PW91/6-31G(d)	0.9573	0.9930	0.9774	0.9885	0.9920

[a] From the F1 set, 122 molecules, 1066 frequencies. [b] Suitable for relating theoretical harmonic frequencies to observed fundamentals. These are also the values recommended for use in conjunction with G2 theory and its variants, both for frequencies and for ZPVEs; see text. [c] From the F1′ set, 122 molecules, 1062 frequencies. [d] Suitable for the prediction of low-frequency vibrations. [e] From the Z1 set. [f] Suitable for the prediction of zero-point vibrational energies. See, however, footnote *b*. [g] Suitable for the prediction of $\Delta H_{\text{vib}}(T)$. [h] Suitable for the prediction of $S_{\text{vib}}(T)$. [i] The previous "standard" value of 0.8929 should continue to be used, however, in G2 theory; see text. [j] Values obtained with NO and CN removed from the analysis; see text.

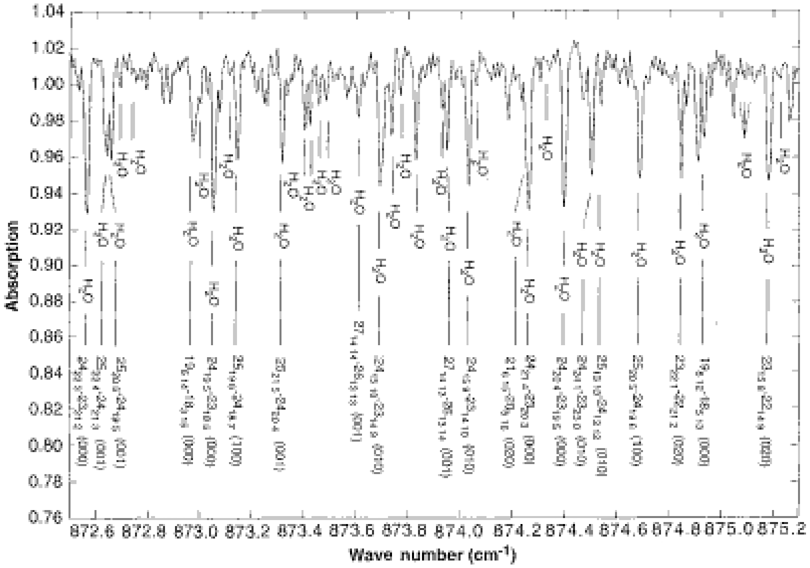
- Scale factors can *approximately* connect from theoretical ω to experimental ν (because anharmonicity usually 2-3%)
- Scale factors for frequencies not necessarily same as for ZPVE contributions to ΔH
- Errors in ZPVE can become among the largest ones for some computations

A. P. Scott and L. Radom, *J. Phys. Chem.* **100**, 16502 (1996)

Achieving Spectroscopic Accuracy

- Ab initio methods required to assign highly excited rovibrational levels in H_2O and prove the presence of water on the sun [Polyansky, Zobov, Viti, Tennyson, Bernath, Wallace, Science 277, 346 (1997)]

- The Born-Oppenheimer approximation must be accounted for to achieve 1 cm^{-1} agreement with rovibrational levels [Polyansky, Császár, Shirin, Zobov, Barletta, *Science 299,* 539 (2003)]



Polyansky et al, Science 277, 246 (1997)

Systematic Studies of Diatomics

- Dunning, Woon, Peterson, Kendall (1993, 1994)
  Basis set and correlation effects

- Martin (1994, 1998, 2001)
  Basis set and correlation effects

- Handy and Lee (1996)
  Effect of Diagonal Born-Oppenheimer Correction (DBOC) on bond lengths and vibrational frequencies of H_2, HF, N_2, F_2

- Helgaker, Gauss, Jørgensen, Olsen, Pawlowski, Halkier, Bak, Klopper (1997, 2003)
  Basis set and correlation effects

- Feller and Sordo (2000)
  Comparison of CCSD(T) and CCSDT

- Sinnokrot and Sherrill (2001)
  DFT provides fairly accurate anharmonicities

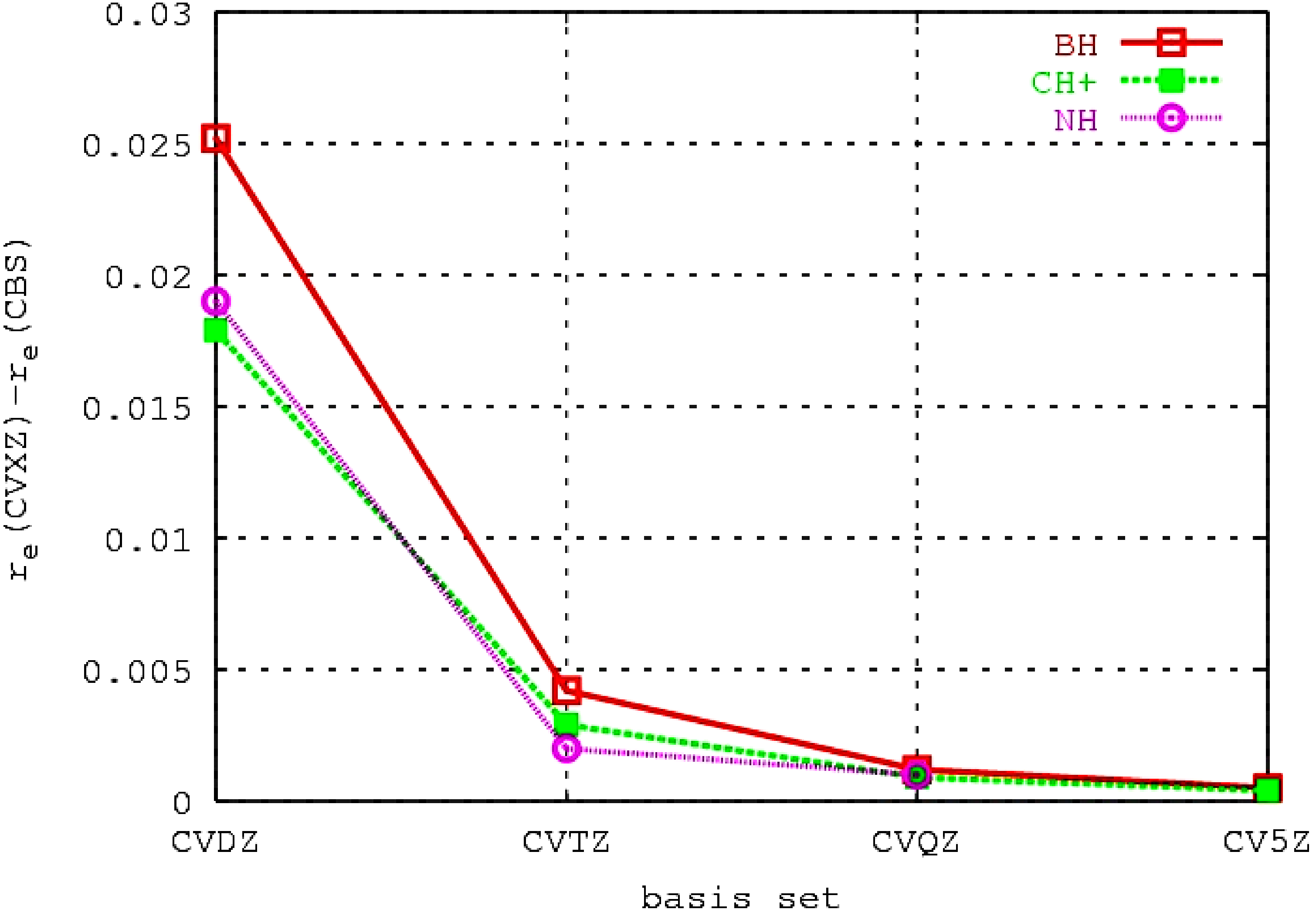
Comparison of Small Effects

- Basis set extrapolation beyond cc-pCV5Z
  - According to Halkier, Helgaker, Jørgensen, Klopper, Koch, Olsen, and Wilson *Chem. Phys. Lett. 286*, 243 (1998)
- Electron correlation beyond CCSD(T) using Full CI in a smaller basis
- Diagonal Born-Oppenheimer Correction (DBOC)
  - First-order correction to BO approximation
  - Computed at CI levels according to Valeev and Sherrill, *J. Chem. Phys*. **118**, 3921 (2003)

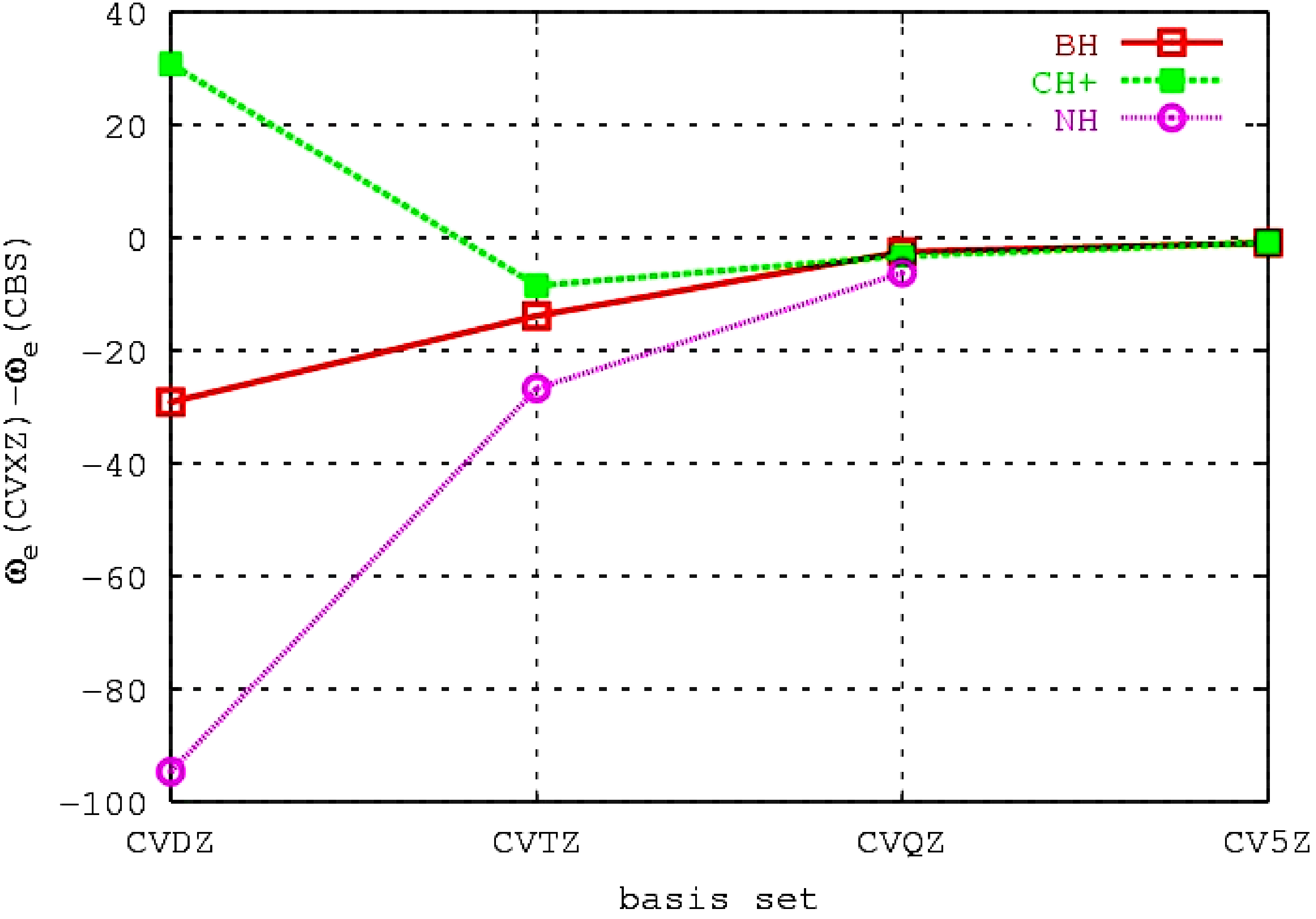
$$E_{DBOC} = \langle \Psi_e(r;R) | \hat{T_n} | \Psi_e(r;R) \rangle$$

- Scalar relativistic corrections
  - One-electron mass-velocity and Darwin terms using CCSD(T) densities

Convergence of r_e with Basis Set [CCSD(T) method]



Convergence of ω_e with Basis Set [CCSD(T) method]

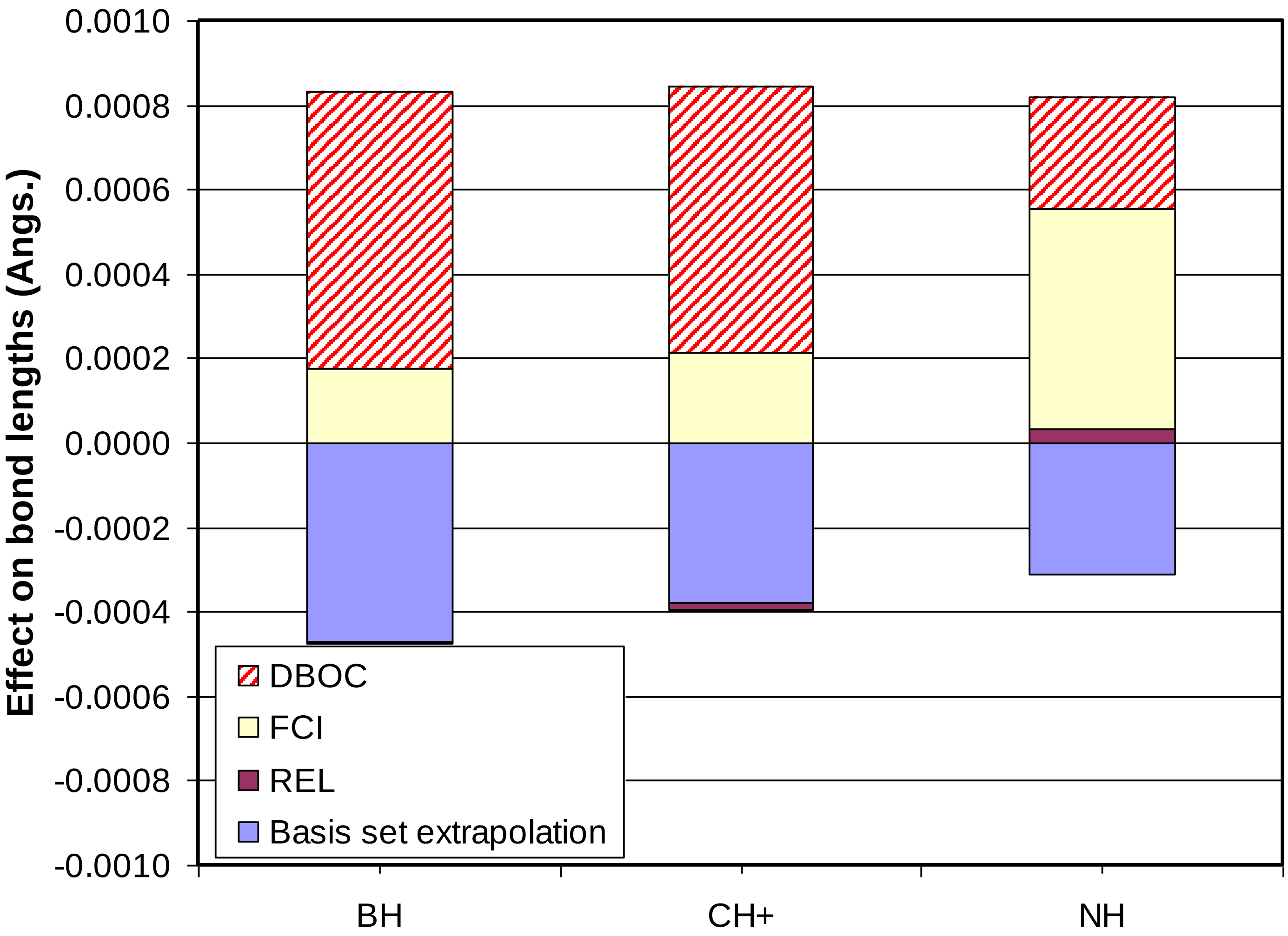


Full CI – CCSD(T)

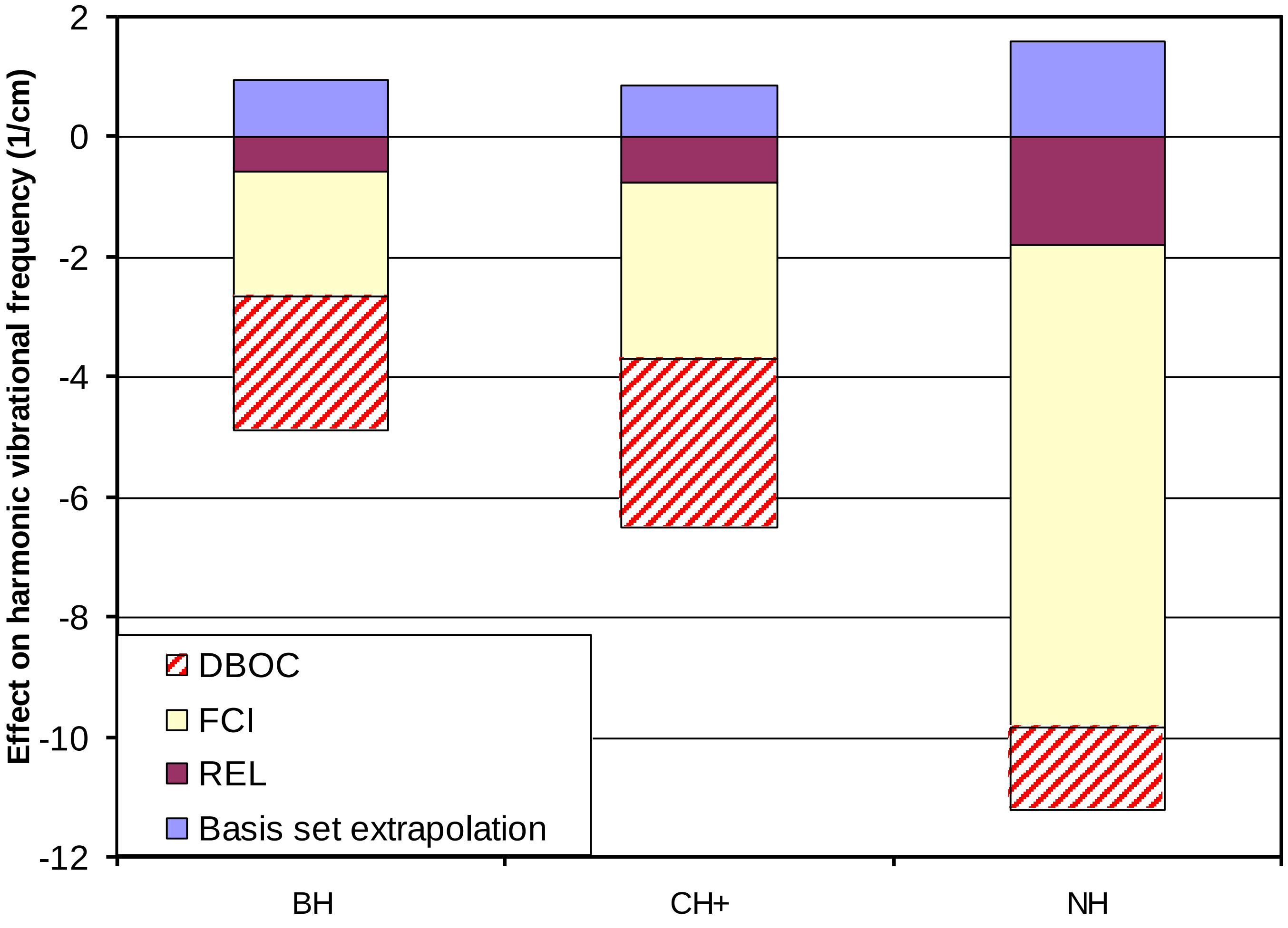
Basis	R_e	ω_e	$\omega_e x_e$	B_e	D_e	A_e
VDZ (BH)	0.00019	-1.93	0.2	-0.0035	0.00000	0.0012
VTZ	0.00020	-2.13	0.1	-0.0038	0.00000	0.0011
VQZ	0.00019	-2.13	0.2	-0.0030	0.00000	0.0011
V5Z	0.00019	-2.06	0.2	-0.0036	0.00000	0.0011
VDZ (CH+)	0.00018	-2.46	0.2	-0.0047	0.00000	0.0012
VTZ	0.00023	-3.00	0.2	-0.0059	0.00000	0.0013
VQZ	0.00022	-2.89	0.4	-0.0055	0.00000	0.0013
V5Z	0.00018	-2.77	0.5	-0.0052	0.00000	0.0016
VDZ (NH)	0.00058	-8.73	0.9	-0.0177	0.00000	0.0043
VTZ	0.00049	-7.59	0.9	-0.0156	0.00000	0.0038

B. Temelso, E. F. Valeev, and C. D. Sherrill, *J. Phys. Chem. A* **108**, 3068 (2004)

Effect of Small Corrections on r_e



Effect of Small Corrections on ω_e



Achieving Spectroscopic Accuracy

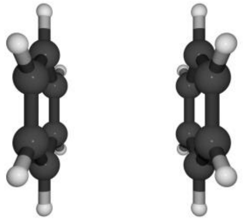
	BH		CH^+		NH	
	R_e (Å)	ω_e(cm^{-1})	R_e (Å)	ω_e(cm^{-1})	R_e (Å)	ω_e(cm^{-1})
Best Adiabatic†	1.22982	2366.34	1.12815	2858.06	1.03609	3283.03
Experiment	1.23217	2366.73	1.13090	2858	1.03675	3282.58
Error	-0.00235(a)	-0.39	-0.00275(b)	0	-0.00066	0.45

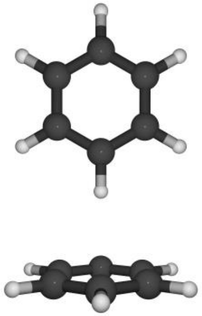
† $E=E_{\text{CBS CCSD(T)}} + E_{\Delta\text{FCI}} + E_{\text{Relativistic}} + E_{\text{DBOC}}$

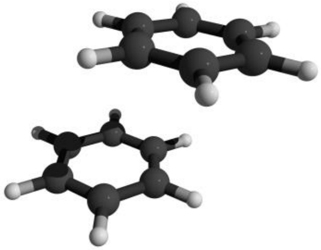
(a) **Comparable to estimated nonadiabatic contribution of 0.0025 Å**
[J. L. Martin, *Chem. Phys. Lett.* **283**, 283 (1998)]

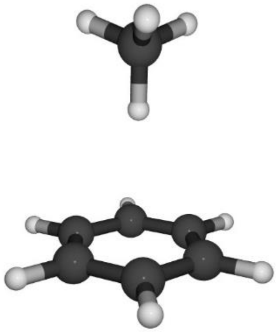
(b) **Isoelectronic to BH, so large (~0.0025 Å) nonadiabatic contribution expected**

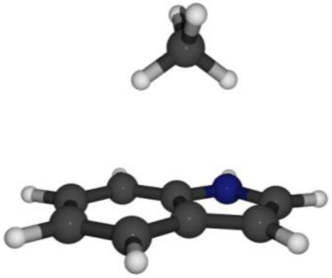
B. Temelso, E. F. Valeev, and C. D. Sherrill, *J. Phys. Chem. A* **108**, 3068 (2004)

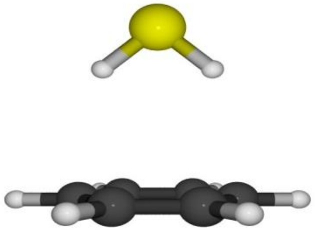


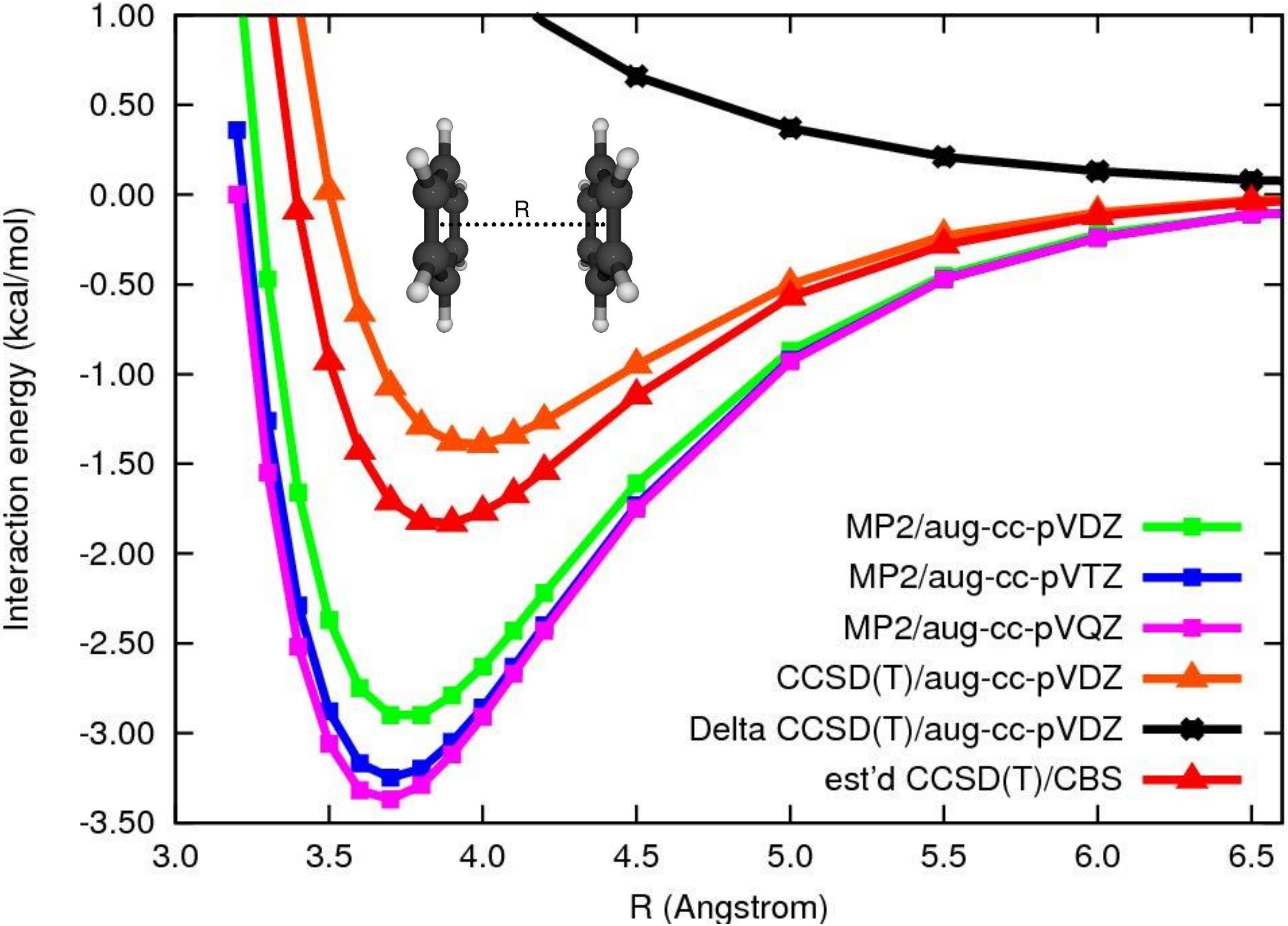




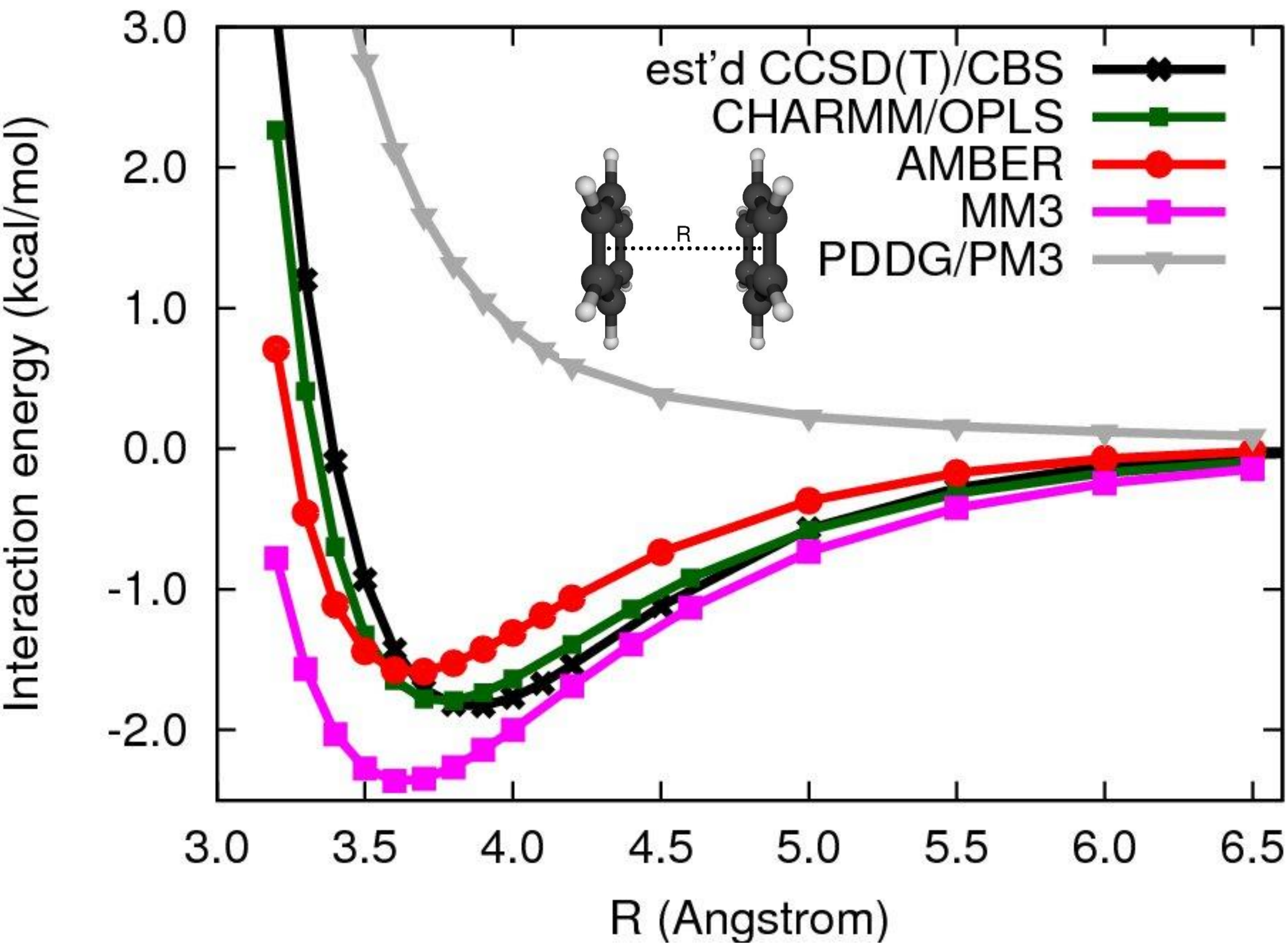




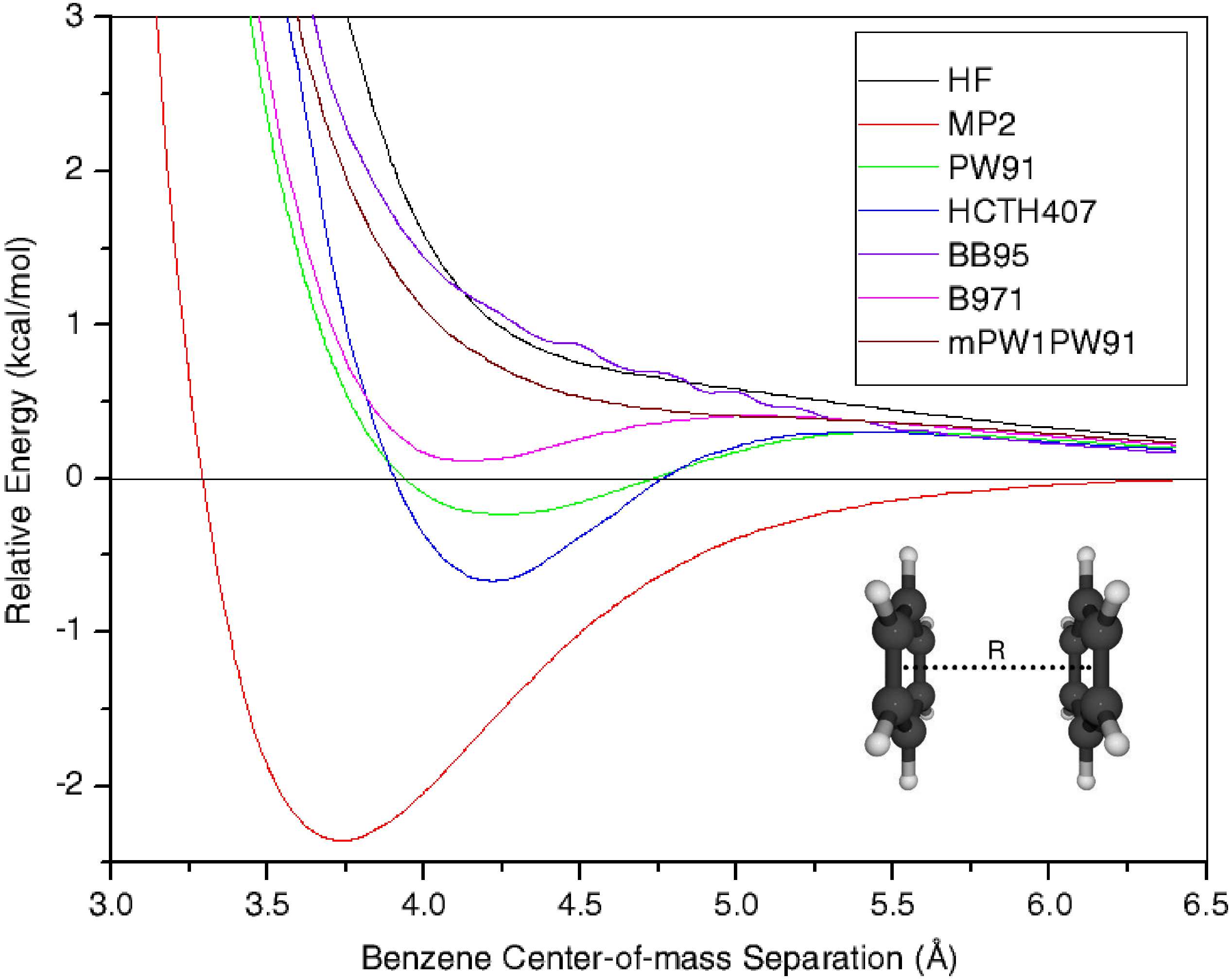




M. O. Sinnokrot and C. D. Sherrill, *J. Phys. Chem. A* **108,** 10200 (2004); C. D. Sherrill, to be published


3.0
2.0
1.0
0.0
-1.0
-2.0
Interaction energy (kcal/mol)
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
R (Angstrom)
est'd CCSD(T)/CBS
CHARMM/OPLS
AMBER
MM3
PDDG/PM3
R

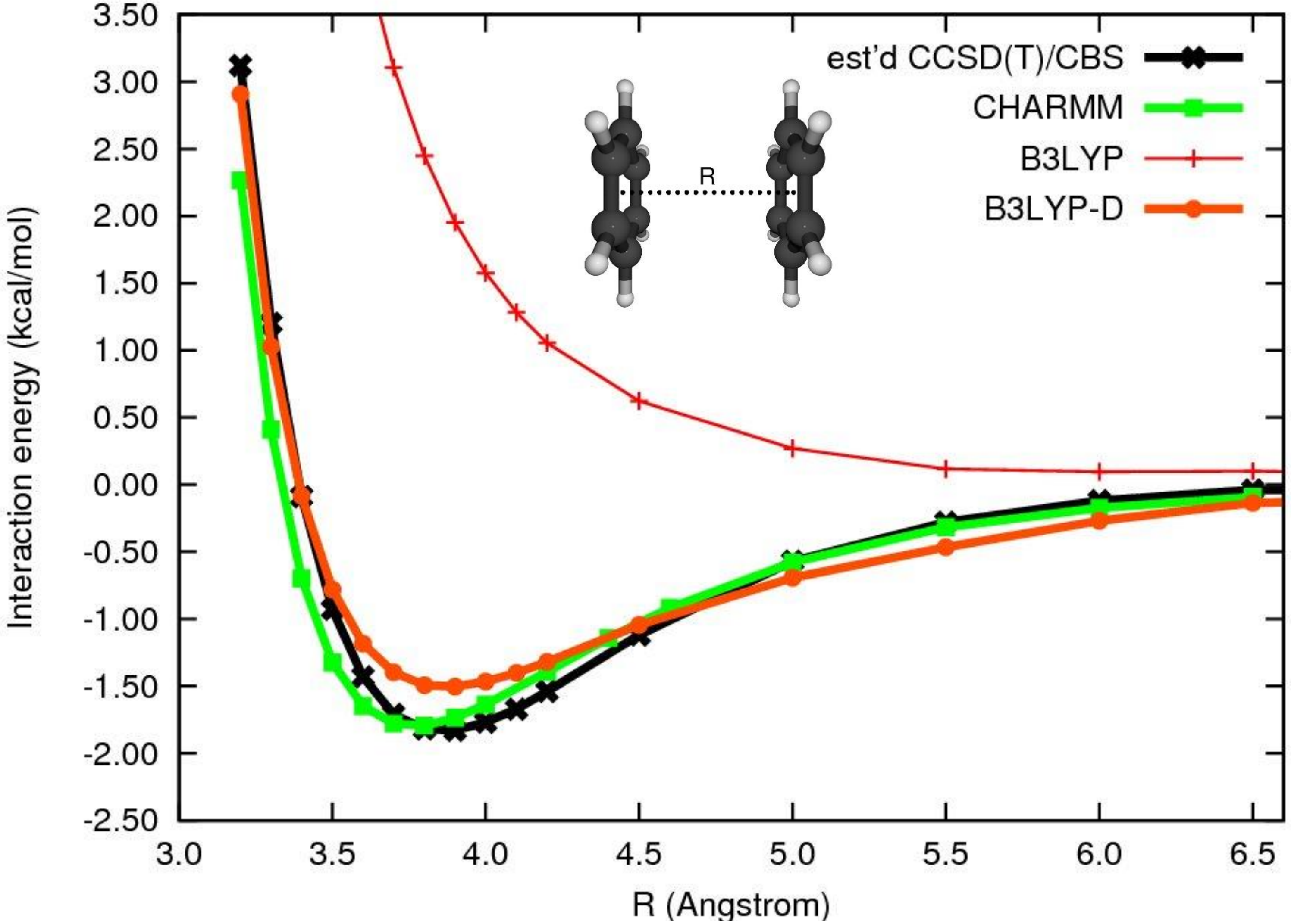
What about DFT?



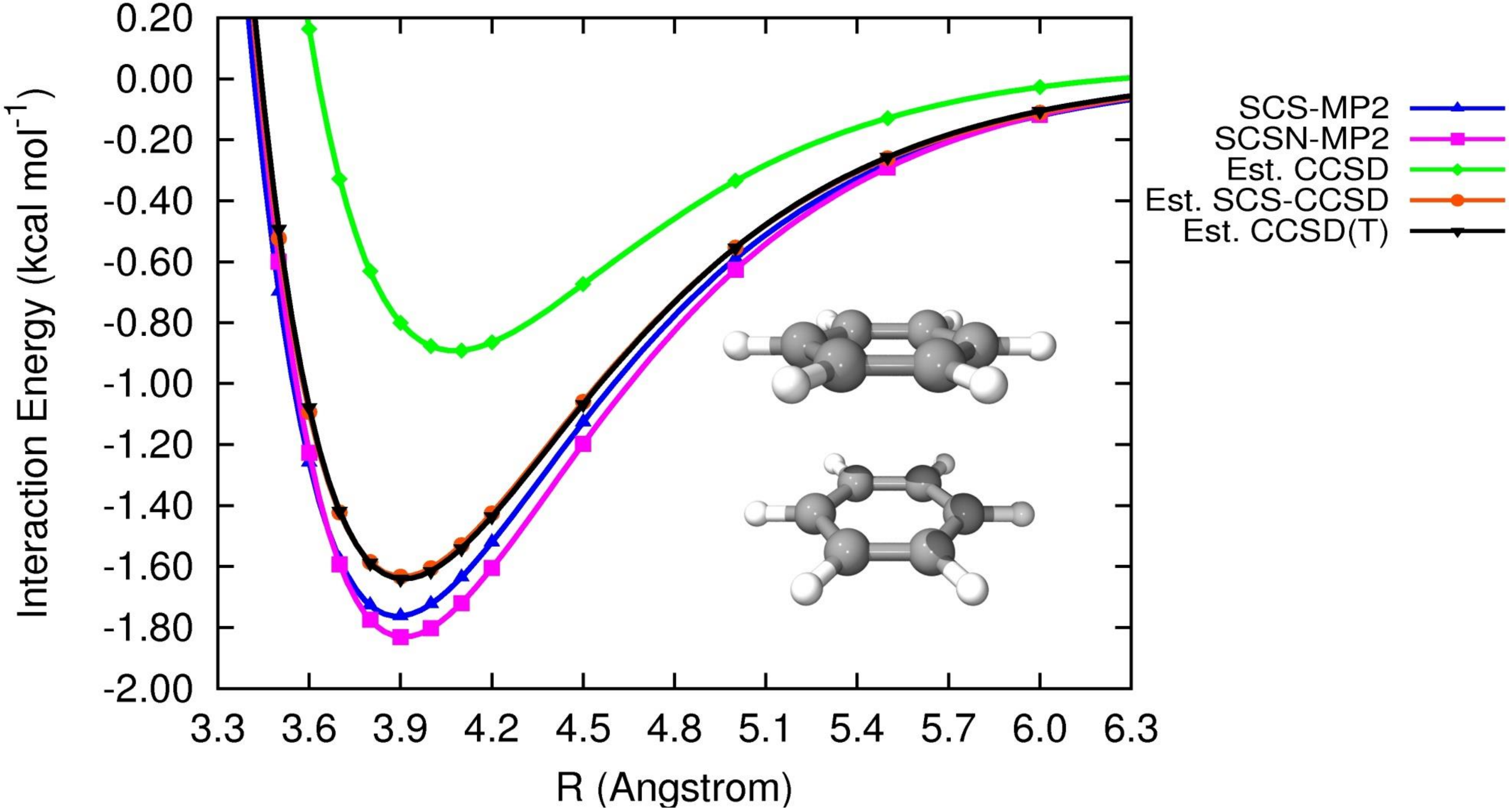
E. R. Johnson, R. A. Wolkow, and G. A. DiLabio, *Chem. Phys. Lett*. **394**, 334 (2004)

What about DFT-D?

S. Grimme, *J. Comput. Chem*. **25**, 1463 (2004); *J. Comput. Chem*. **27**, 1787 (2006)



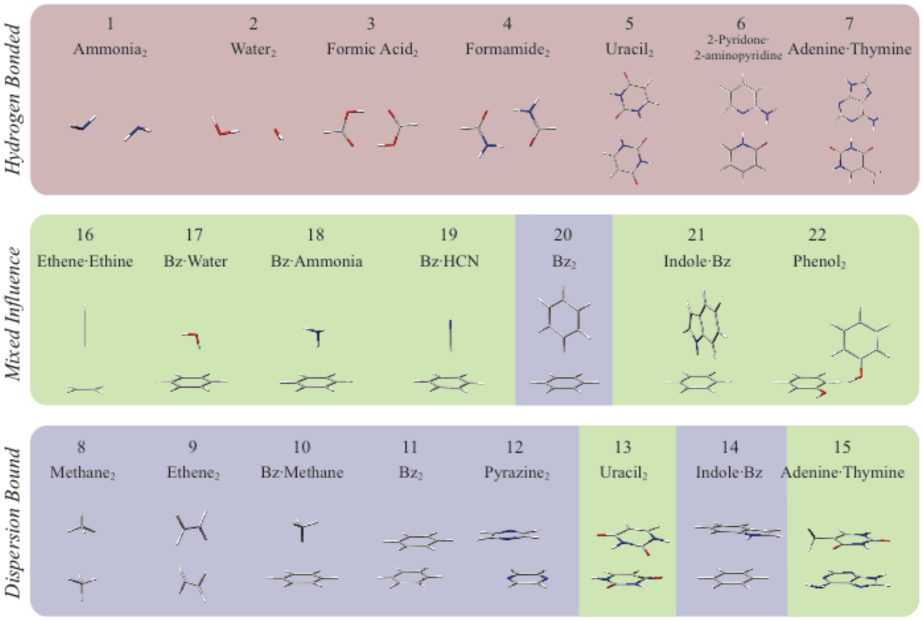
Benzene Dimer (est'd CBS limit)



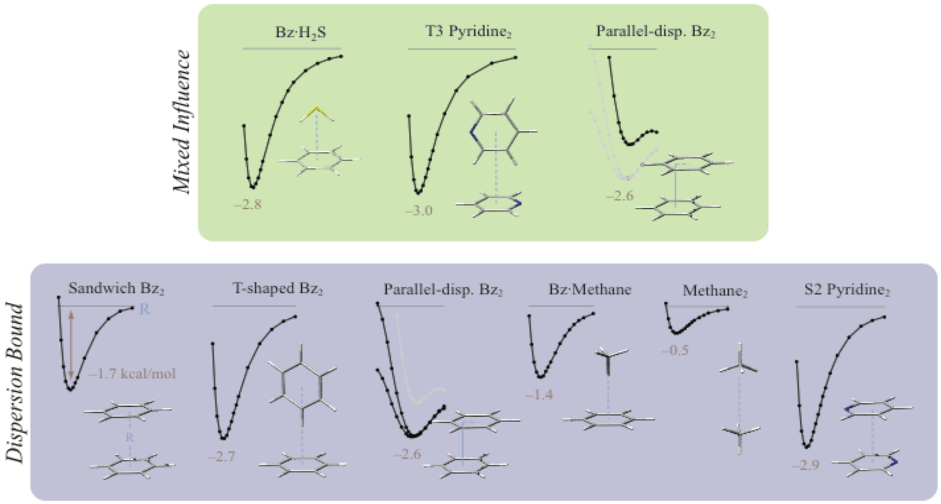
SCS-MP2 and SCSN-MP2: T. Takatani and C. D. Sherrill, Phys. Chem. Chem. Phys. **9**, 6106 (2007)
SCS-CCSD: T. Takatani, E. G. Hohenstein, and C. D. Sherrill, J. Chem. Phys. **128**, 124111 (2008)

Databases for Noncovalent Interactions

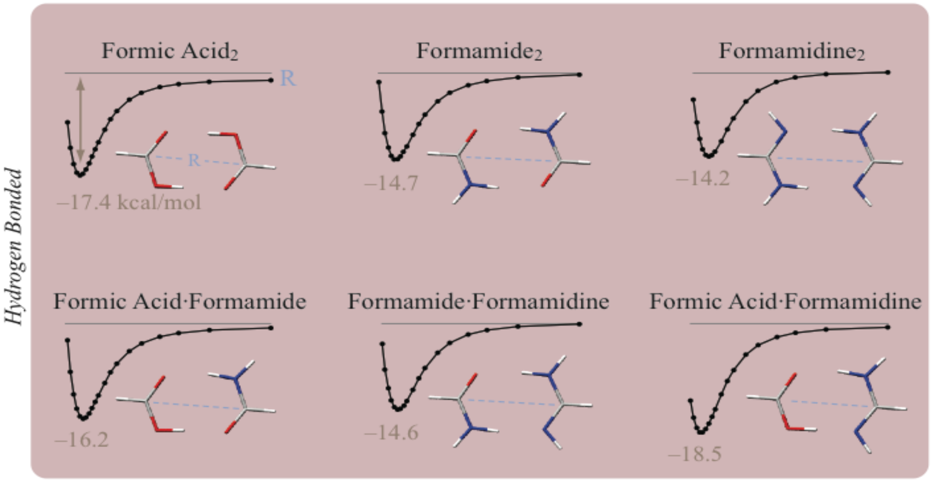
S22



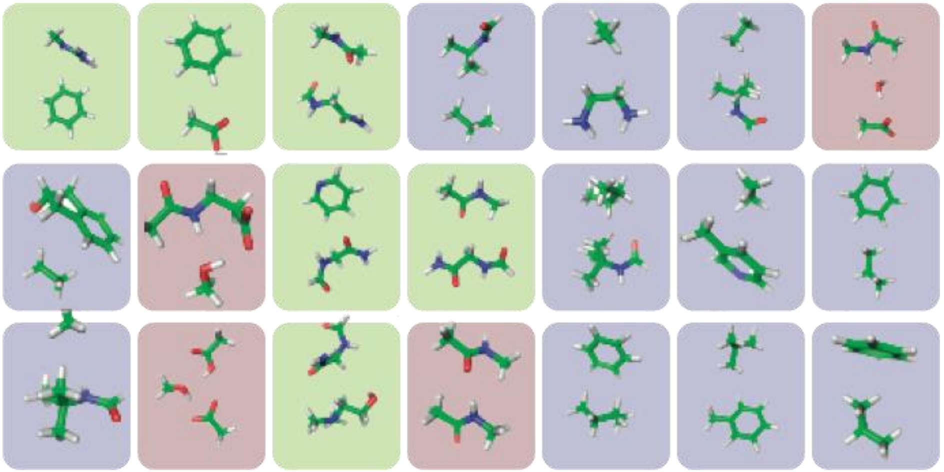
NBC10



HBC6

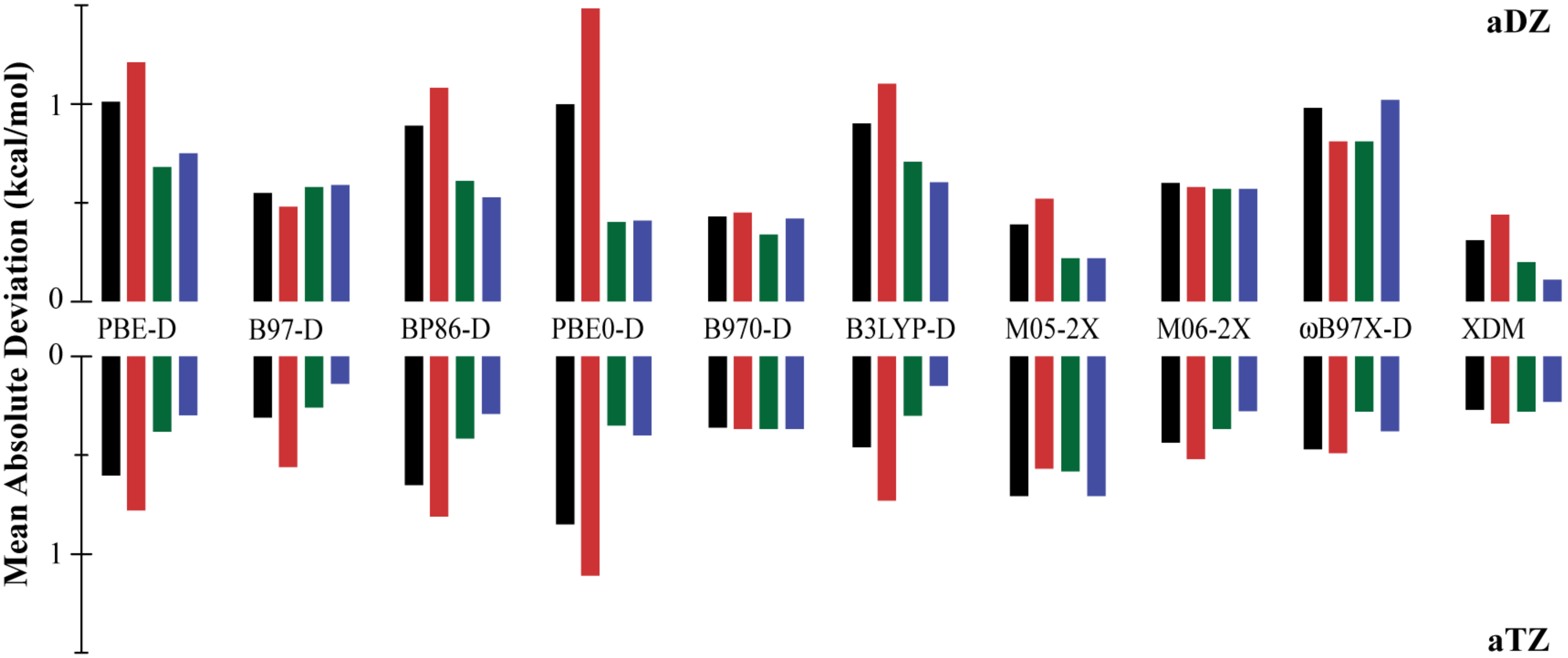


HSG



Testing Dispersion-Including DFT

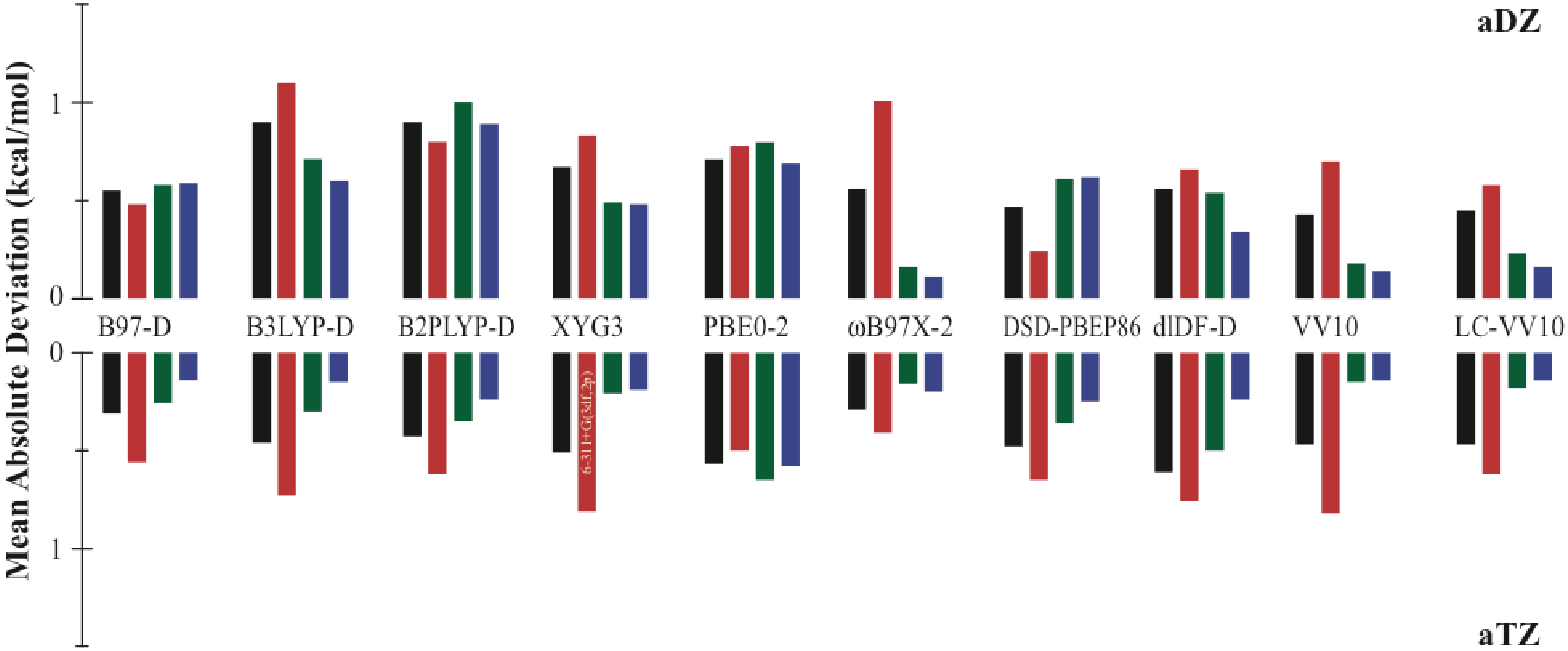
Averaged over 345 energies in the S22, NBC10 HBC6 and HSG test sets



L. A. Burns, A. Vazquez-Mayagoitia, B. G. Sumpter, and C. D. Sherrill, *J. Chem. Phys.* **134**, 084107 (2011)

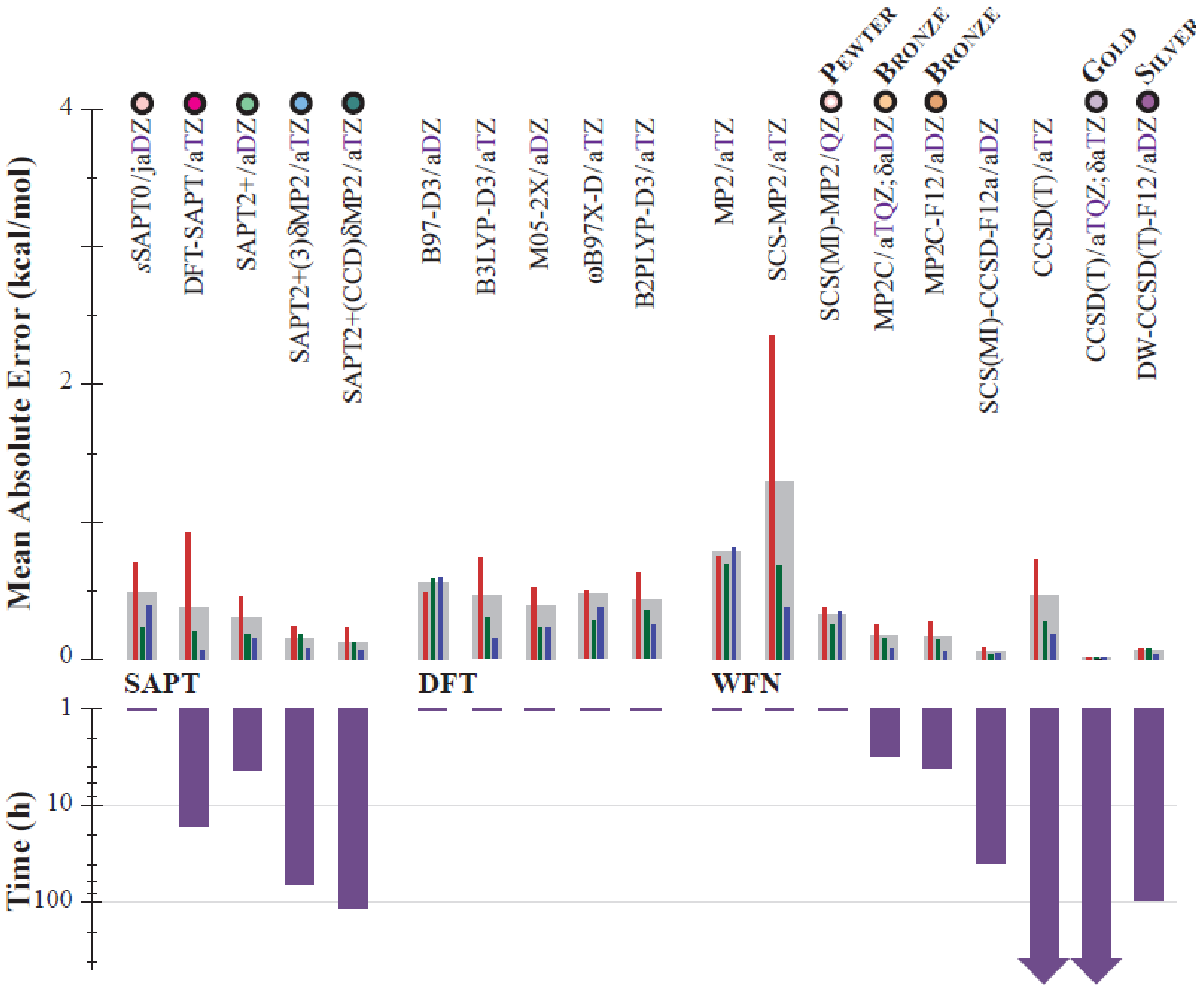
Testing Dispersion-Including DFT

Averaged over 345 energies in the S22, NBC10 HBC6 and HSG test sets



L. A. Burns, C. A. Cook, and C. D. Sherrill, manuscript in preparation

Grand Comparison: SAPT, DFT, WFT

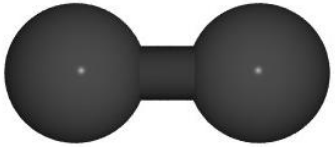


L. A. Burns, A. Vazquez-Mayagoitia, B. G. Sumpter, and C. D. Sherrill, *J. Chem. Phys.* **134**, 084107 (2011)

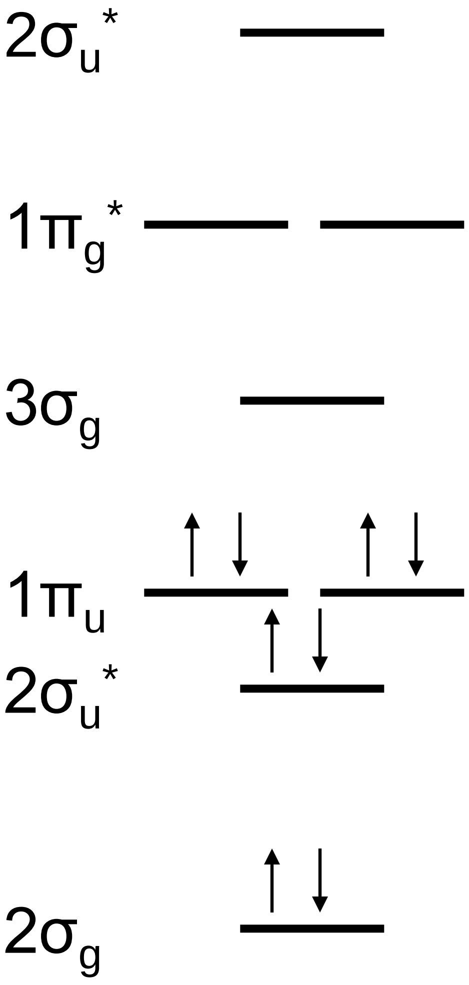
T. M. Parker, L. A. Burns, R. M. Parrish, A. G. Ryno, and C. D. Sherrill, *J. Chem. Phys.* **140**, 094106 (2014)

L. A. Burns, M. S. Marshall, and C. D. Sherrill, in preparation

C_2: Theoretical Challe

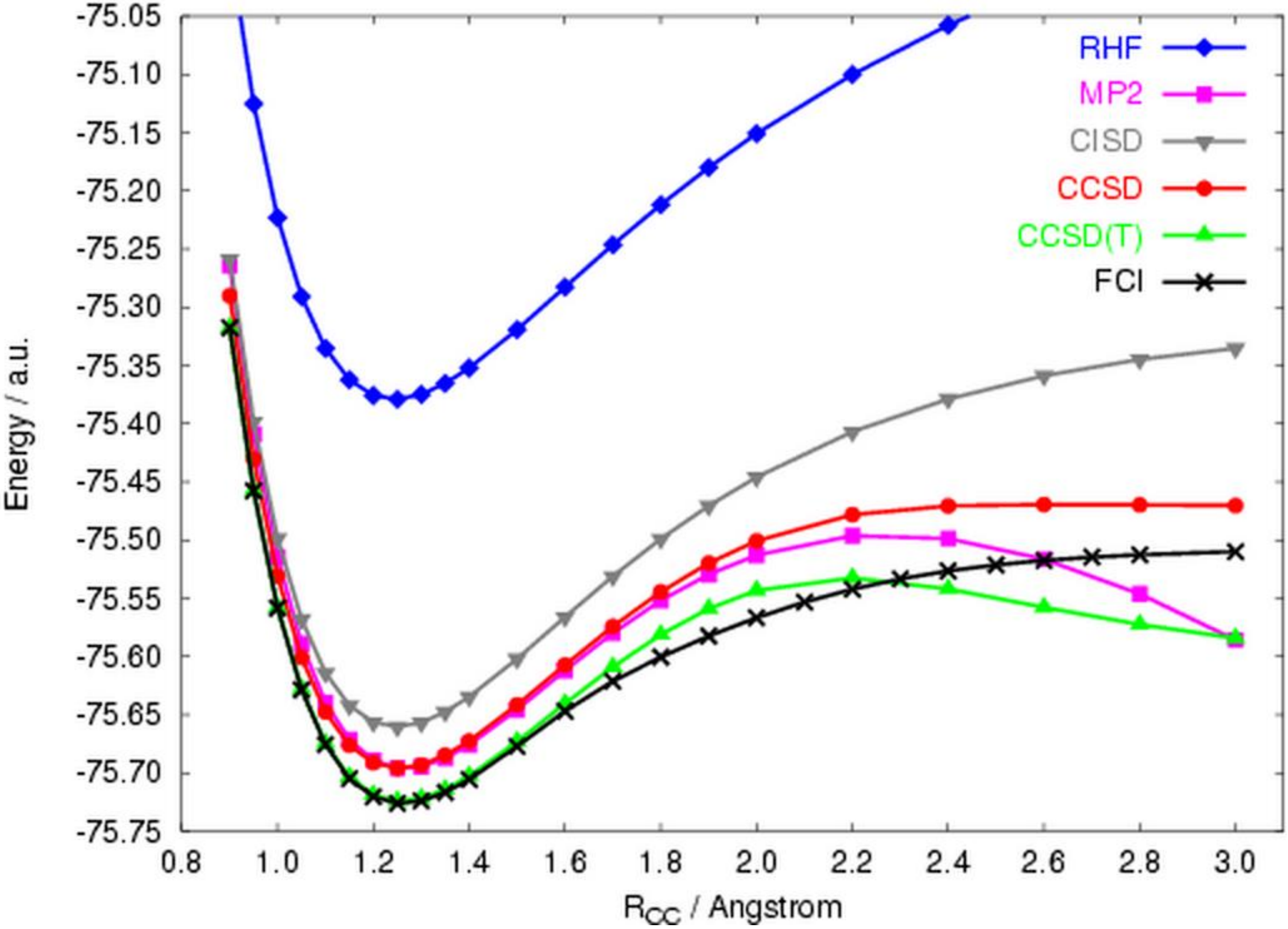


- Intermediate in combustion reactions; interstellar medium
- Very unusual bonding
- Many low-lying excited states; $^3\Pi_u$ state only 716 cm^{-1} up



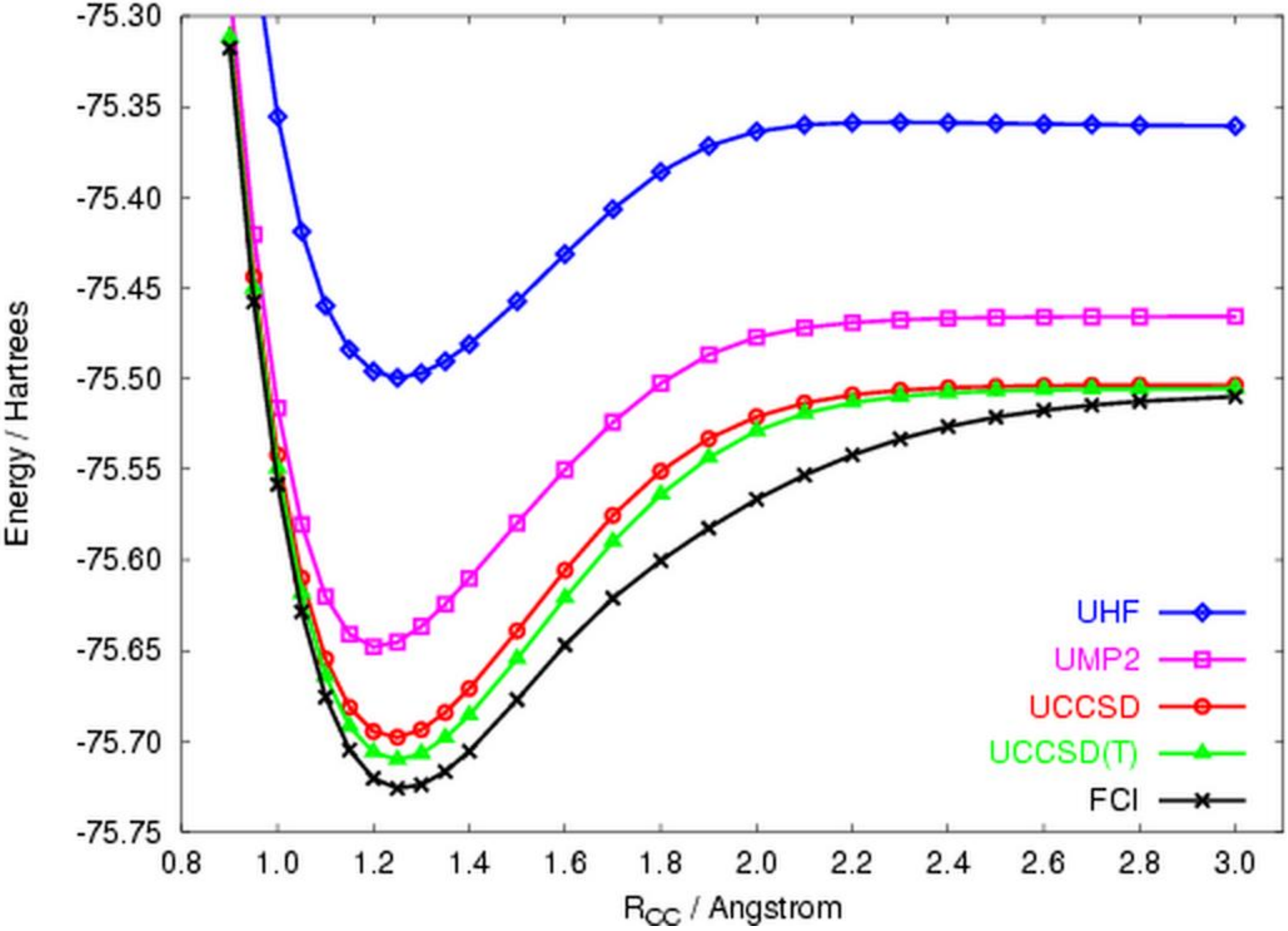
M. L. Abrams and C. D. Sherrill, *J. Chem. Phys*. **121**, 9211 (2004).
C. D. Sherrill and P. Piecuch, *J. Chem. Phys.* **122**, 124104 (2005).

RHF-based Correlated Methods

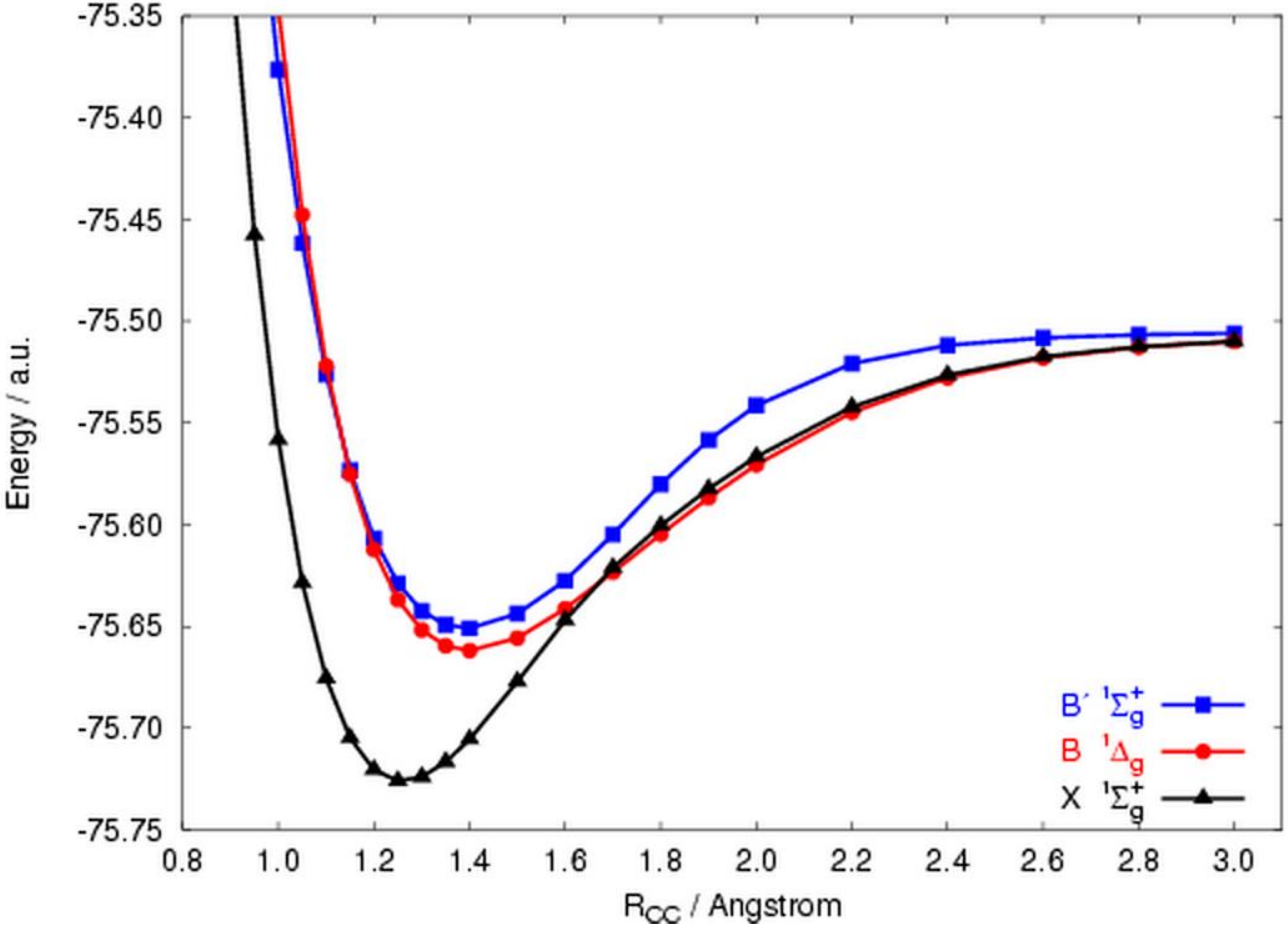


M. L. Abrams and C. D. Sherrill, *J. Chem. Phys*. **121**, 9211 (2004).

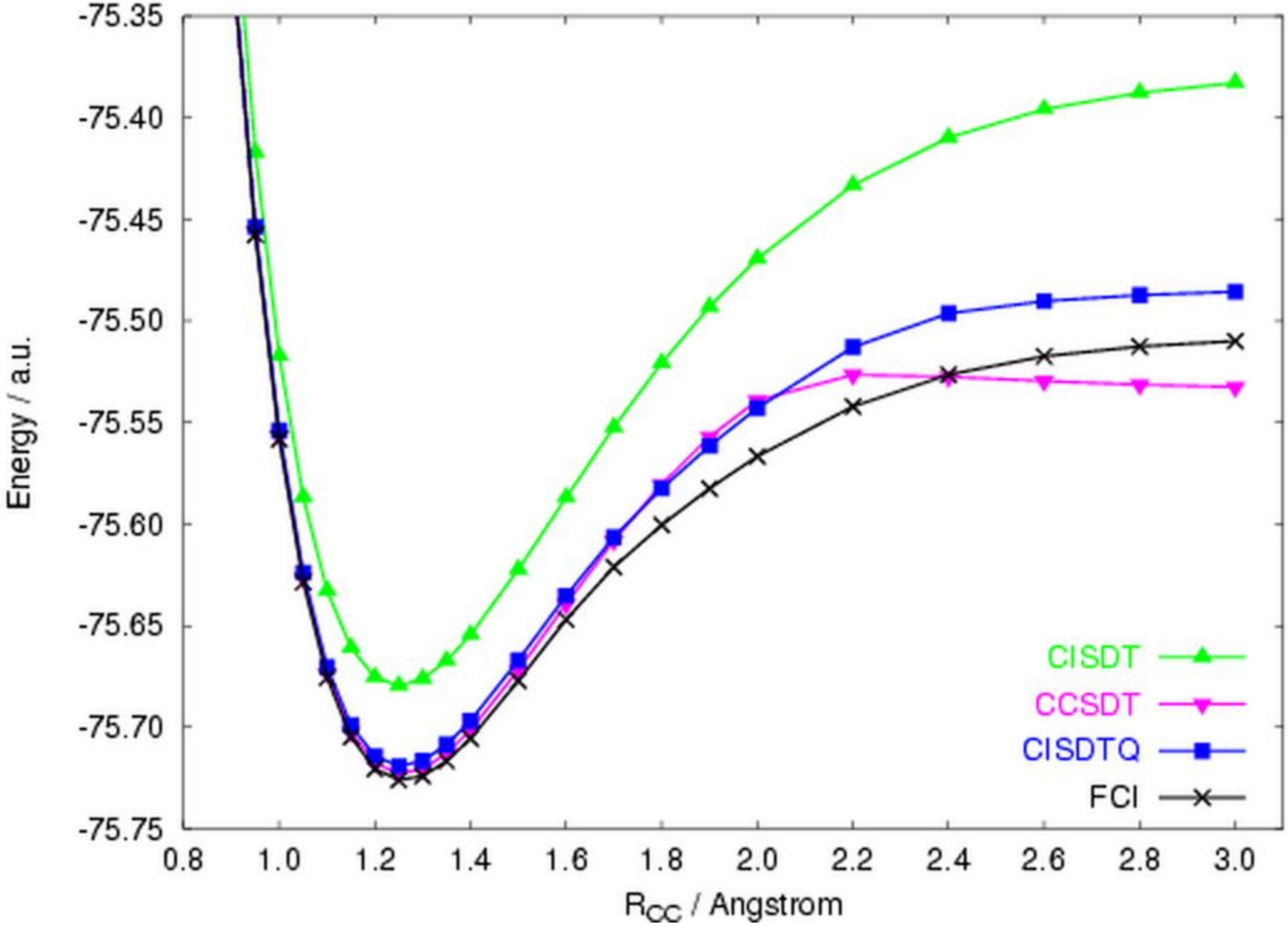
UHF-based Correlated Methods



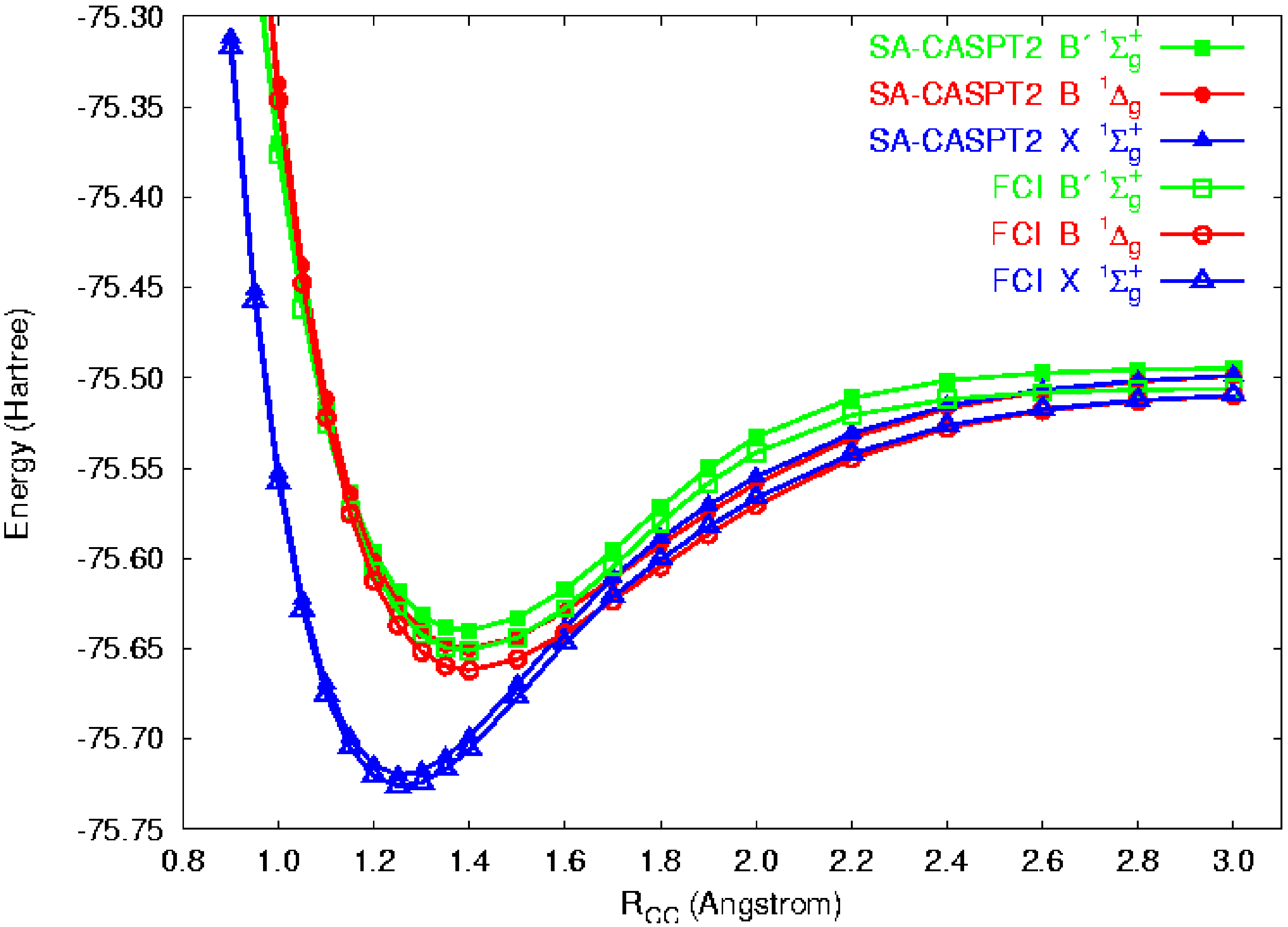
Real and Avoided Crossings



Higher-Order Correlation



Multireference Methods



C. D. Sherrill and P. Piecuch, *J. Chem. Phys*. **122**, 124104 (2005).