NIST
Computational Chemistry Comparison and Benchmark Database

A website which compares
computed and experimental
ideal-gas thermochemical properties
http://srdata.nist.gov/cccbdb

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http://www.nist.gov/compchem

How good is that ab initio calculation?

For predicting enthalpies.

For predicting geometries.

For predicting vibrational frequencies.

For this molecule.

For these molecules.

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CCCBDB Contents

- 680 molecules
- Enthalpies of formation, Entropies, Geometries, Vibrational frequencies
- **Experimental values**
- **Computed values**
- Comparisons
- Auxiliary information

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Properties

- Energetics
  - Enthalpies of formation
  - Atomization enthalpies
  - Reaction enthalpies
  - Barriers to Internal Rotation
- Entropies
  - Heat Capacities
  - Integrated Heat Capacities

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More Properties

- Geometries
  - Bond lengths and angles
  - Rotational Constants
  - Moments of Inertia
- Vibrational Frequencies
  - Intensities
  - Zero point energies

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Even More Properties

- Electrostatics
  - Dipole Moments
  - Quadrupole Moments
  - Polarizabilities
  - Charges
    - Mulliken
    - ESP
    - ChelpG

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Molecules in CCCBDB

- Small, gas-phase
- Mostly < 7 heavy atoms - hexane
- Mostly no atoms with atomic number >17 (chlorine). A dozen Br-containing molecules.
- 90 diatomics, 574 polyatomics
- 469 organic molecules,
  - 125 hydrocarbons
  - 145 CHO species
  - 16 amides

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Experimental Data in CCCBDB

- Enthalpy of formation ($\Delta_f H$) at 0K and 298.15K
- Entropy (S) at 298.15K
  - Vibrational frequencies
  - Geometries
  - Rotational Constants
  - Excited and/or degenerate electronic states
- Heat Capacities
- Dipole Moments
- Ionization Energies

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II.A.1. Listing of experimental data for H_2CO (Formaldehyde)

Enthalpy of formation (Hfg), Entropy, Integrated heat capacity (0 K to 298.15 K) (HH), Heat Capacity (Cp)

Property	Value	Uncertainty	units	Reference	Comment
Hfg(298.15K)	-108.70	0.50	kJ mol^{-1}	Gurvich	
Hfg(0K)	-104.86	0.50	kJ mol^{-1}	Gurvich	
Entropy (298.15K)	218.76		J K^{-1} mol^{-1}	Gurvich	
Integrated Heat Capacity (0 to 298.15K)	10.02		kJ mol^{-1}	Gurvich	
Heat Capacity (298.15K)	35.39		J K^{-1} mol^{-1}	Gurvich	

Information can also be found for this species in the NIST Chemistry Webbook

Vibrational levels (cm^{-1})

Mode Number	Symmetry	Frequency (cm^{-1})	Frequency Reference	Intensity (km mol^{-1})	Int. unc.	Intensity Reference	Comment
1	A_1	2782	1982Nak/Kon:3860	75.5	7.1	1982Nak/Kon:3860	
2	A_1	1746	1982Nak/Kon:3860	74.0	5.3	1982Nak/Kon:3860	
3	A_1	1500	1982Nak/Kon:3860	11.2	1.0	1982Nak/Kon:3860	
4	B_1	1167	1982Nak/Kon:3860	6.5	0.6	1982Nak/Kon:3860	
5	B_2	2843	1982Nak/Kon:3860	87.6	8.0	1982Nak/Kon:3860	
6	B_2	1249	1982Nak/Kon:3860	9.9	1.0	1982Nak/Kon:3860	

vibrational zero-point energy: 5,643.5 cm^{-1}
Calculated vibrational frequencies for H_2CO (Formaldehyde).

Rotational Constants (cm^{-1})

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Computational Data in CCCBDB

- Energies – Electronic,Vibrational
  - Torsional barriers (internal rotation)
  - HOMO-LUMO energies
- Geometries – Cartesians
- Charge Information – dipole moments, electric charges
- Derived Values
  - Vibrational zero-point energies
  - Atomization Enthalpies
  - Entropies
  - Products of moments of inertia

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III.A.1.c. Products of Moments of Inertia for H_2CO (Formaldehyde)

Products of moments of inertia. Units are 10^{-117} gm^3cm^6

Methods with predefined basis sets

semi-empirical	AM1	1.674
	PM3	1.500
	MNDOd	

Methods with standard basis sets

		3-21G	3-21G*	6-31G	6-31G*	6-31G**	6-31+G**	6-311G*	6-31G(2df,p)	cc-pVDZ	cc-pVTZ	aug-cc-pVDZ
hartree fock	HF	1.475	1.475	1.499	1.420	1.427	1.436	1.406	1.405	1.446	1.402	1.455
density functional	BLYP	1.724	1.724	1.760	1.666	1.664	1.685	1.633	1.632	1.691	1.617	
	B3LYP	1.631	1.631	1.664	1.576	1.576	1.592	1.548	1.547	1.602	1.535	1.605
	B3PW91	1.632	1.632	1.655	1.569	1.569	1.582	1.543	1.545	1.591	1.534	
	MPW1PW91	1.612	1.613		1.550	1.552	1.563	1.525		1.572	1.517	
	PBEPBE	1.722	1.613	1.749	1.657	1.656	1.673	1.629	1.625	1.679		1.686
Moller Plesset perturbation	MP2FC	1.721	1.721	1.785	1.621	1.602	1.623	1.588	1.569	1.641	1.566	1.674
	MP2FU	1.718			1.616	1.595	1.615	1.583		1.634		
	MP4				1.653			1.625				
Configuration interaction	CID				1.544			1.512				
	CISD				1.554	1.533						
Quadratic configuration interaction	QCISD	1.714			1.614		1.603	1.580				
	QCISD(T)				1.638			1.608				
Coupled Cluster	CCD				1.590			1.556				
	CCSD				1.605			1.572				
	CCSD(T)				1.635	1.607		1.605				

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Computations in CCCBDB

Methods

- AM1, PM3
- HF, ROHF
- MP2(full), MP2(frozen core), MP4
- BLYP, B3LYP, B3PW91, MPW1PW91, PBE
- CID, CISD
- QCISD, QCISD(T)
- CCD, CCSD, CCSD(T)
- G1, G2, G2MP2, CBS-Q

Basis Sets

- 3-21G, 3-21G*
- 6-31G, 6-31G*
- 6-311G*
- 6-31G**
- 6-31+G**
- cc-pVDZ
- cc-pVTZ
- ECPs

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3 dimensions of comparisons

1. Property
   - For example: Entropy
2. Molecule(s)
   - For example: C_2H_3
3. Quantum chemical model
   - For example: ROHF/6-31G*

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IV.B.1 Entropy Comparison at 298.15K for C_2H_3 (vinyl)

Experimental Value

Entropy ($J\,K^{-1}\,mol^{-1}$)	Uncertainty
232.84	

Entropy Differences (Calculated - Experiment)

Entropy ($J\,K^{-1}\,mol^{-1}$)
Click on an entry for details.

Methods with predefined basis sets

semi-empirical	AM1	6.39
	PM3	3.30
molecular mechanics	DREIDING	-3.35

Methods with standard basis sets

		STO-3G	3-21G	3-21G*	6-31G	6-31G*	6-31G**	6-31+G**	6-311G*	6-311G**	6-31G(2df,p)	cc-pVDZ	cc-pVTZ	a
hartree fock	HF	2.83	0.91	0.94	1.15	1.21	1.20	1.16	1.16	1.13	1.13	1.40	0.96	
	ROHF					0.65								
density functional	BLYP	1.70	1.17	1.18	1.31	1.57	1.57	1.64	1.49	1.47	1.51	1.81	1.37	
	B3LYP	1.42	0.87	0.90	1.03	1.28	1.30	1.35	1.22	1.22	1.24	1.54	1.16	
	B3LYPultrafine					0.87								
	B3PW91	1.42	0.91	0.93	1.03	1.30	1.31	1.36	1.25	1.26	1.28	1.57	1.23	
	MPW1PW91	1.35	0.85	0.94	1.03	1.25	1.25	1.31	1.22	1.21	1.23	1.51	1.14	

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Comparisons

- Theory to Experiment
- Theory to Theory
- Examples of theory performing poorly

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Accuracy depends on type of molecule

- More expensive calculations are required for:
  - Triple bonds
  - Heavier elements
- Need to classify molecules for comparisons

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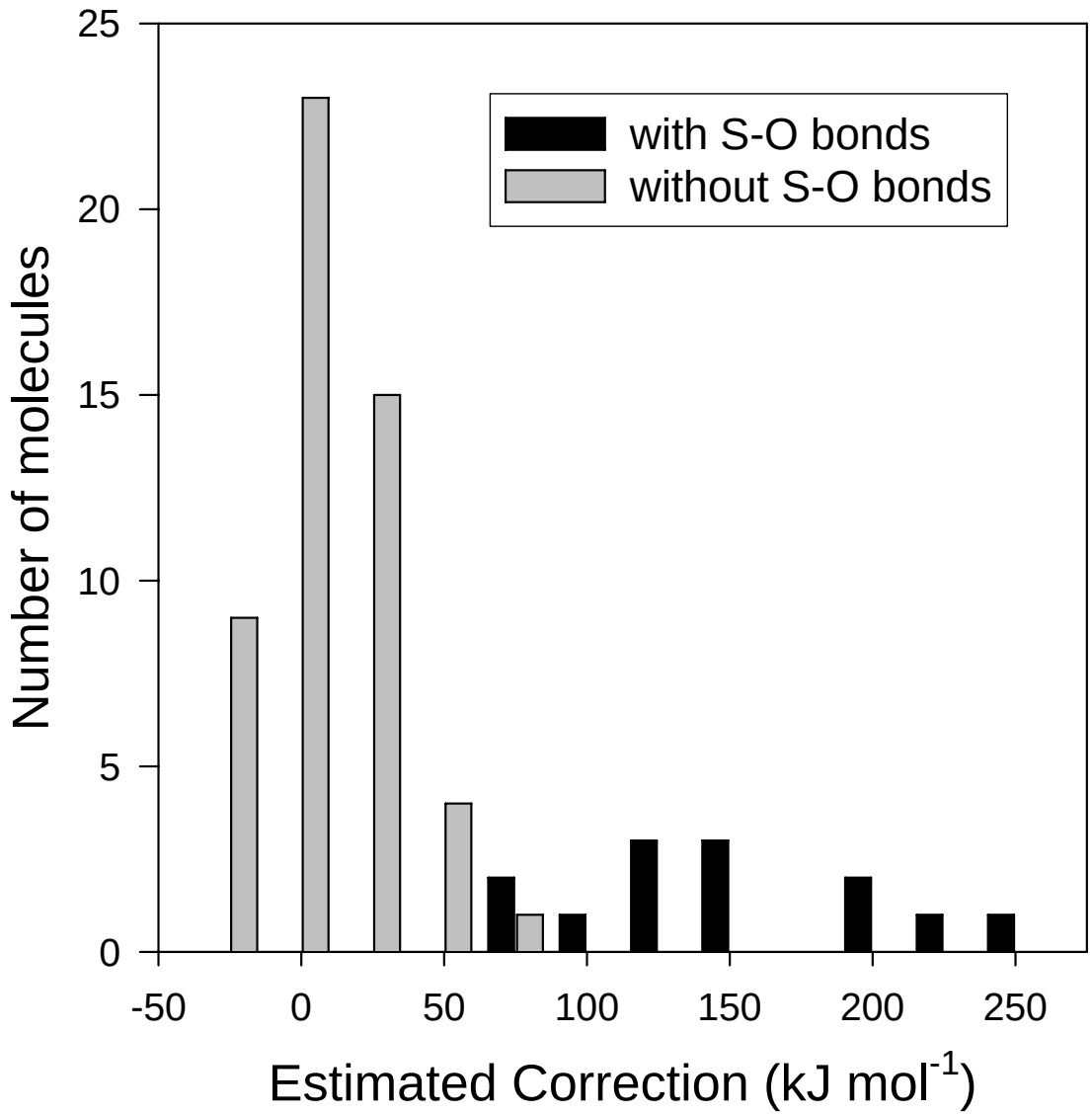
Atomization Enthalpies of molecules containing sulfur



http://sr

Need to classify molecules

- Bonds (C=N)
- Chemical groups (NH2, rings, aromatic, ethanes)
- Elements (must have P)
- Number of atoms
- Radicals
- Point Group
- C2H?Cl*
- No substructure searching

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Barriers to internal rotation

- Calculations for 88 molecules
- Experimental data for 36 molecules

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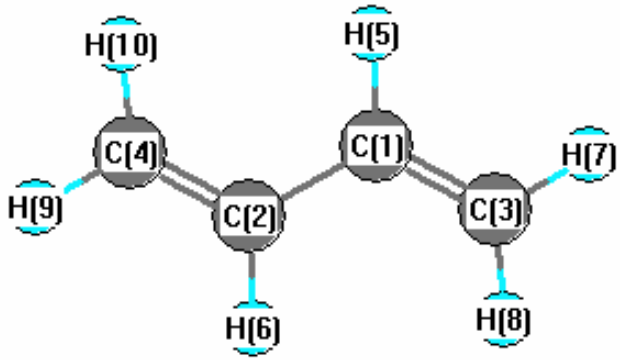
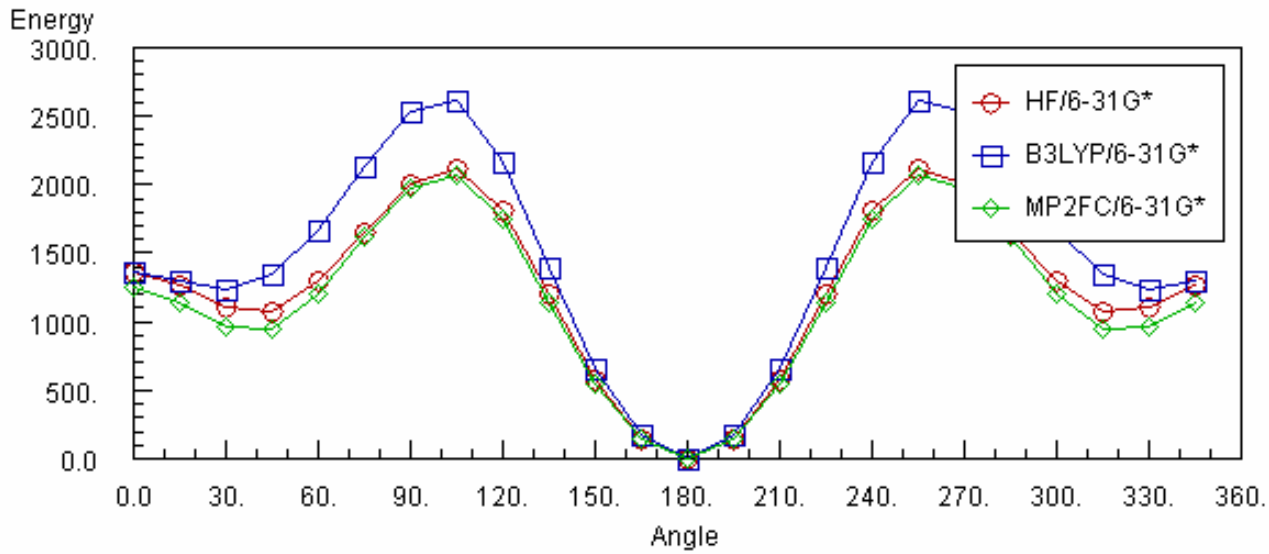


The following graph shows the energy (in cm^{-1}) as a function of the torsion angle (in degrees).

View Table | Help

NIST Data Viewer



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Cost versus Accuracy

What is the least expensive calculation that gives me the accuracy I need?

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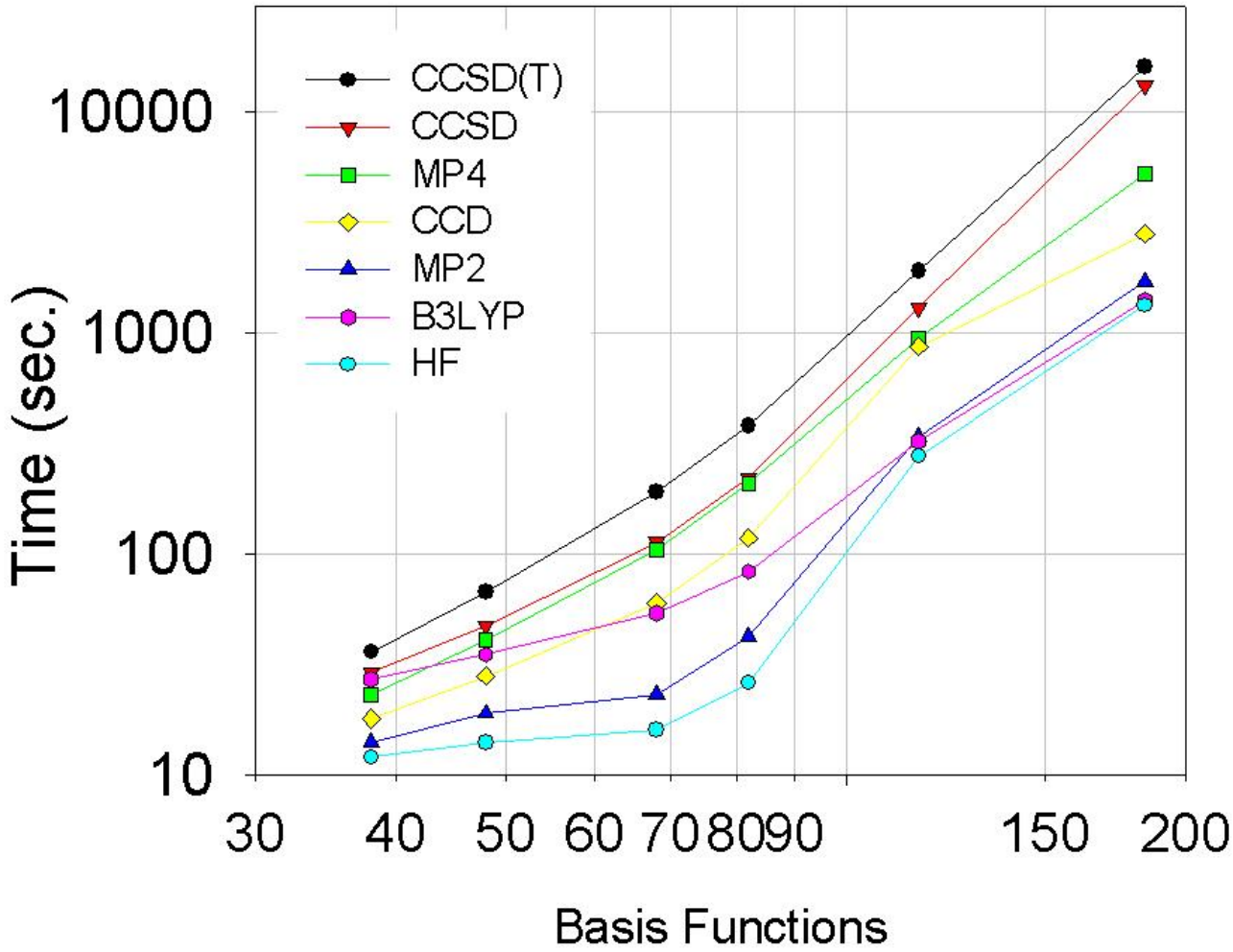
Cost



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What next?

- More Calculations
- Third row (Ga through Br)
- Transition metals
- Reaction Enthalpies
- Hydrogen bonded systems
- Uncertainties

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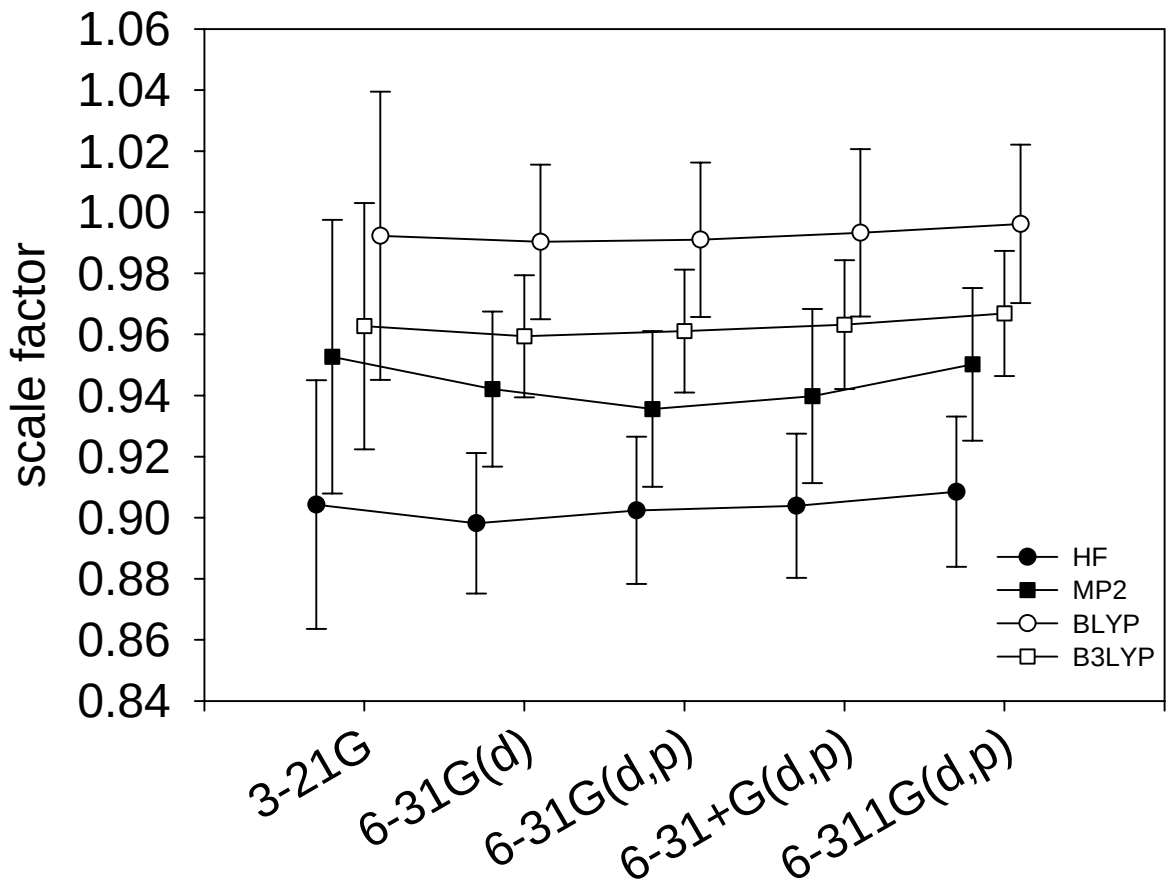
Vibrational Scaling Factors



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What would you like?

- Other molecules?
- Other properties?
- Other comparisons?
- Better ways of presenting the data?
- cccbdb@nist.gov

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CCCBDB

- 6 letters
- Charlie, Charlie, Charlie, Bravo, Delta, Bravo
- Ends in Bravo
- Google it

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Summary

- 680 molecules
- Enthalpies, Entropies, Heat Capacities, Geometries, Vibrations, Dipoles
- 100 000 calculations
- Comparisons
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