

CP2K - STFC Workshop

Four ways to vibrational frequencies

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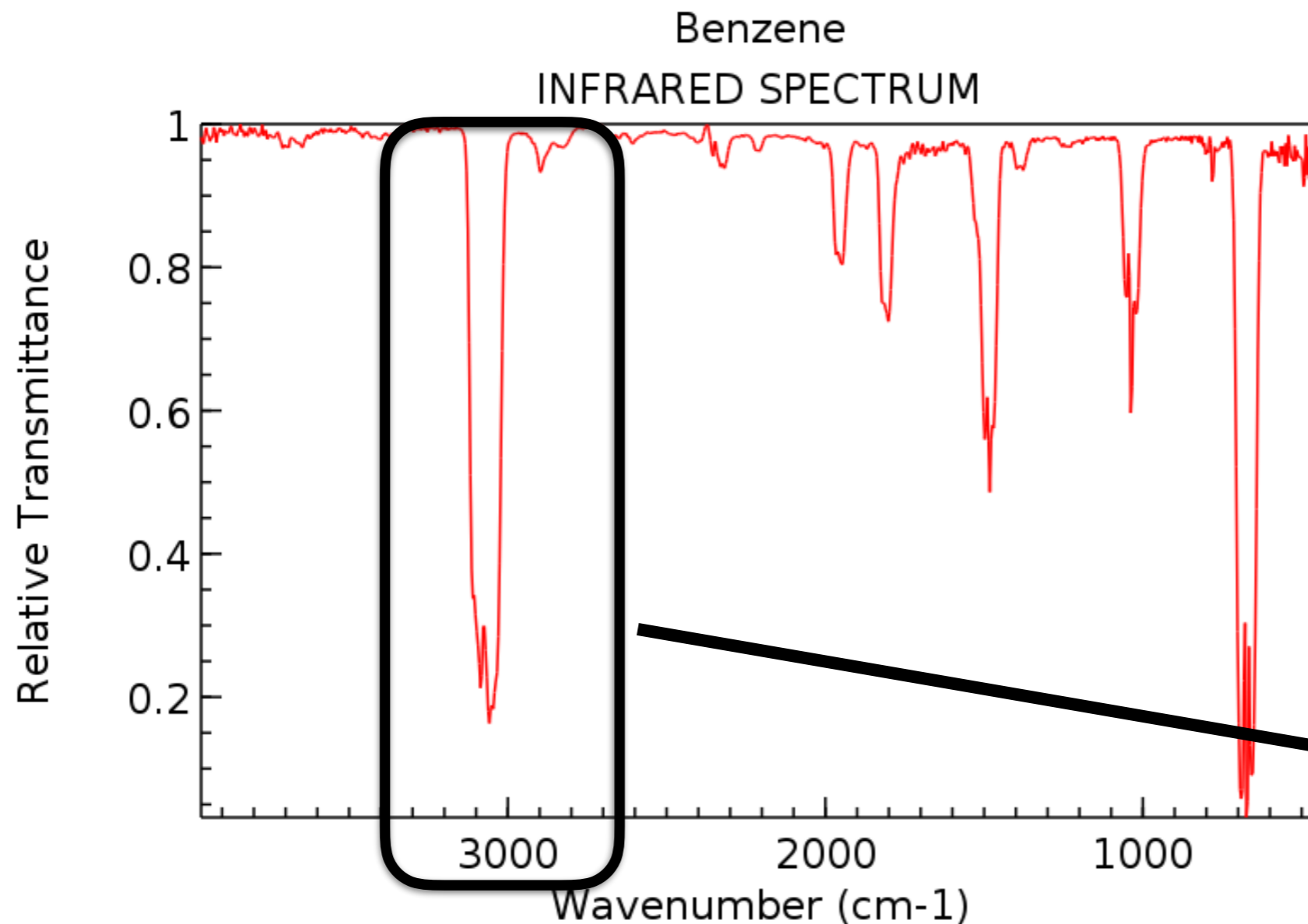
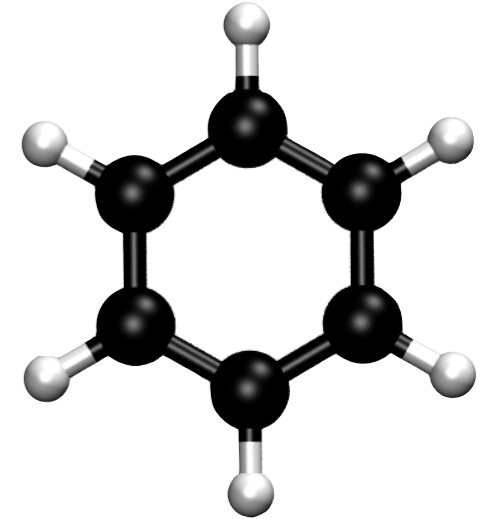
 @dbenoit1

E.A. Milne Centre

for Astrophysics

VIPER
Transforming Research

Let's calculate the C–H vibrational frequencies for benzene



NIST Chemistry WebBook (<https://webbook.nist.gov/chemistry>)

Mode [cm ⁻¹]	Exp.
2 [A _{1g}]	3074
20 [E _{1u}]	3064
7 [E _{2g}]	3057
13 [B _{1u}]	(3057)



STAND BY ME ESPRESSO
8oz 12oz

**The Classic one:
Full Hessian**

**The Thrifty one:
Partial Hessian**

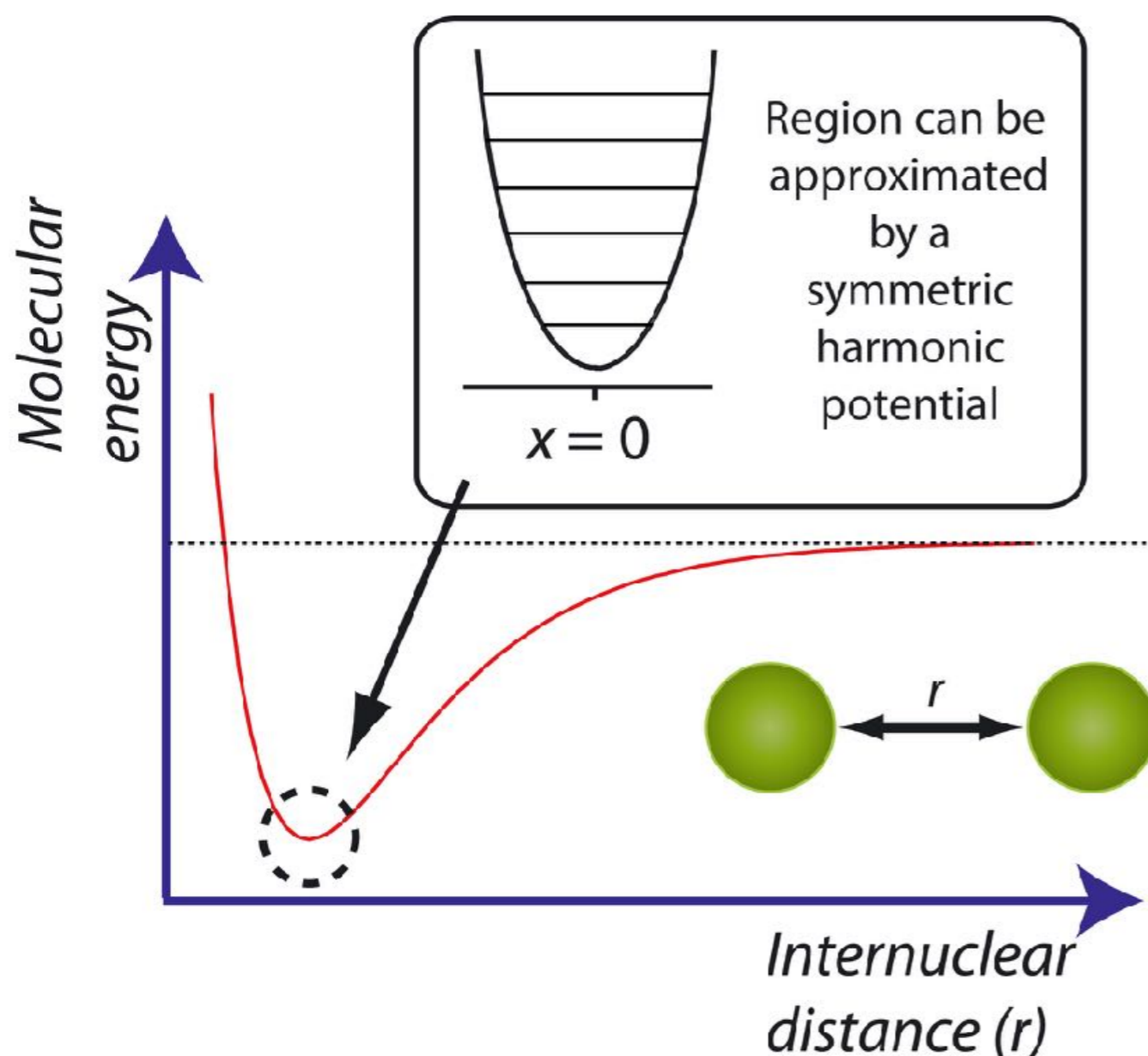
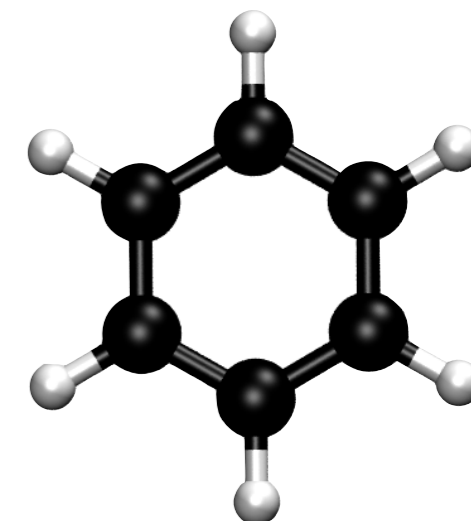
**The Sneaky one:
Mode selection**

**The Lazy one:
Molecular dynamics**



Choice 1: Full-Hessian based vibrational frequencies

- Any energy function for which we can calculate double derivatives can be used to predict IR spectrum



$$V(Q_i) = \frac{1}{2} \sum_i k_i \cdot (Q_i)^2$$

\uparrow
 $\frac{\partial^2 E}{\partial Q_i^2}$

Full Hessian CP2K input

- Calculates all the energy derivatives numerically
- Difference of gradients
- Embarrassingly parallel problem (independent $\Delta x, \Delta y, \Delta z$ displacements)

		31			32			33		
VIB		31			32			33		
VIB Frequency (cm ⁻¹)		3776.566304			3777.221187			3790.954407		
VIB Intensities		0.012069			0.012076			0.000004		
VIB Red.Masses (a.u.)		1.094382			1.094460			1.099934		
VIB Frc consts (a.u.)		0.569941			0.570377			0.581612		
ATOM	EL	X	Y	Z	X	Y	Z	X	Y	Z
1	H	0.00	0.01	0.02	-0.10	-0.17	-0.55	-0.07	-0.12	-0.39
2	C	-0.00	-0.00	-0.00	0.01	0.01	0.05	0.01	0.01	0.04
3	C	0.03	0.01	-0.03	-0.02	-0.00	0.01	-0.03	-0.01	0.03
4	H	-0.35	-0.08	0.36	0.18	0.04	-0.18	0.28	0.06	-0.28
5	C	0.04	0.02	0.01	0.02	0.01	0.00	-0.03	-0.02	-0.01
6	H	-0.43	-0.21	-0.12	-0.25	-0.13	-0.07	0.35	0.17	0.09
7	C	-0.00	-0.00	-0.00	0.01	0.01	0.05	-0.01	-0.01	-0.04
8	H	0.00	0.01	0.02	-0.10	-0.17	-0.55	0.07	0.12	0.39
9	C	0.03	0.01	-0.03	-0.02	-0.00	0.01	0.03	0.01	-0.03
10	H	-0.35	-0.08	0.36	0.18	0.04	-0.18	-0.28	-0.06	0.28
11	C	0.04	0.02	0.01	0.02	0.01	0.00	0.03	0.02	0.01
12	H	-0.43	-0.21	-0.12	-0.25	-0.13	-0.07	-0.35	-0.17	-0.09

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&MOMENTS
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&END
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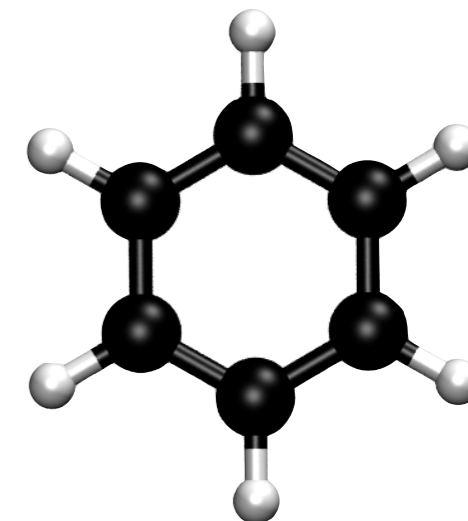
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INTENSITIES
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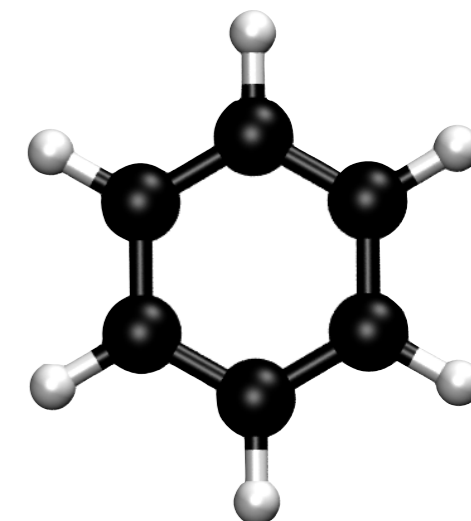
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Full-Hessian results

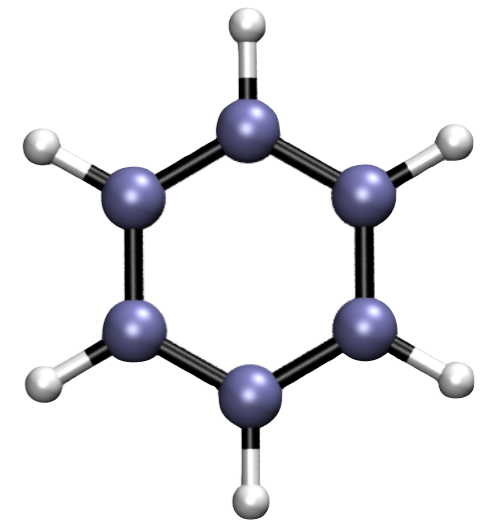
PBE/SVP-MOLOPT



Mode [cm ⁻¹]	Full Hessian	Exp.	Harmonic reference
2 [A1g]	3791	3074	3191
20 [E1u]	3777	3064	3181
7 [E2g]	3769	3057	3164
13 [B1u]	3762	3057	3174
RMSD (exp)	581	—	—
RMSD (Harmonic)	488	—	—

Choice 2: Partial Hessian

- Instead of calculating **all** frequencies and derivatives, we focus only on atoms that we are interested in
- **Freeze** the carbon atoms (blue) and only let the hydrogen atoms move (motion constraint)



$$H = \begin{pmatrix} H_{CC} & H_{CH} \\ H_{HC} & H_{HH} \end{pmatrix} \rightarrow H_{\text{partial}} = \begin{pmatrix} 0 & 0 \\ 0 & H_{HH} \end{pmatrix}$$

Partial Hessian CP2K input

MODULE QUICKSTEP: ATOMIC COORDINATES IN angstrom

Atom	Kind	Element	X	Y	Z	Z(eff)	Mass	
1	1	H	1	-0.164183	0.937027	0.338824	1.00	1.0079
2	2	C	6	-0.350910	0.636285	-0.654650	4.00	12.0107
3	2	C	6	-1.583921	0.020603	-0.989467	4.00	12.0107
4	1	H	1	-2.314290	-0.135736	-0.244831	1.00	1.0079
5	2	C	6	-1.835940	-0.382837	-2.325437	4.00	12.0107
6	1	H	1	-2.753111	-0.840221	-2.574231	1.00	1.0079
7	2	C	6	-0.852991	-0.173554	-3.326467	4.00	12.0107
8	1	H	1	-1.039682	-0.474385	-4.319921	1.00	1.0079
9	2	C	6	0.380014	0.442138	-2.991636	4.00	12.0107
10	1	H	1	1.110397	0.598458	-3.736261	1.00	1.0079
11	2	C	6	0.632048	0.845557	-1.655671	4.00	12.0107
12	1	H	1	1.549264	1.302822	-1.406834	1.00	1.0079

VIBI		16			17			18		
VIBIFrequency (cm ⁻¹)		3622.171552			3622.775629			3627.837689		
VIBIIntensities		0.000121			0.000132			0.000012		
VIBIRed.Masses (a.u.)		1.007940			1.007940			1.007940		
VIBIFrc consts (a.u.)		0.444205			0.444501			0.446991		
ATOM	EL	X	Y	Z	X	Y	Z	X	Y	Z
1	H	0.00	-0.00	-0.01	0.09	0.15	0.50	0.08	0.13	0.43
4	H	0.33	0.07	-0.34	0.24	0.05	-0.24	-0.27	-0.06	0.27
6	H	-0.45	-0.22	-0.12	0.26	0.13	0.07	-0.33	-0.16	-0.09
8	H	0.00	0.01	0.03	-0.10	-0.16	-0.51	-0.08	-0.13	-0.43
10	H	-0.33	-0.07	0.35	-0.24	-0.05	0.24	0.27	0.06	-0.27
12	H	0.45	0.22	0.12	-0.27	-0.13	-0.07	0.33	0.16	0.09

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&DFT
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...
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&PRINT
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&MOMENTS
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&END
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&END
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&END
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&GLOBAL
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RUN_TYPE VIBRATIONAL_ANALYSIS
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&END GLOBAL
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&VIBRATIONAL_ANALYSIS
```

```
FULLY_PERIODIC
```

```
INTENSITIES
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NPROC_REP 2
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&MOTION
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&CONSTRAINT
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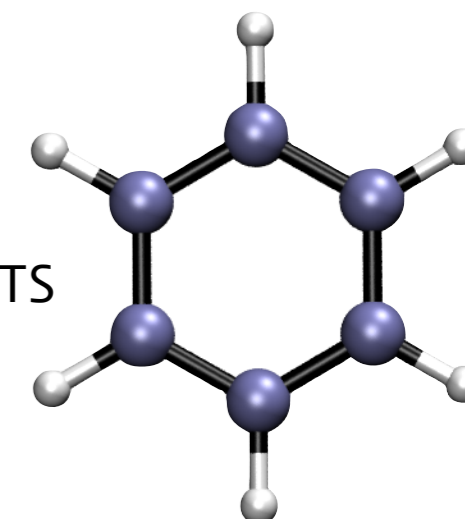
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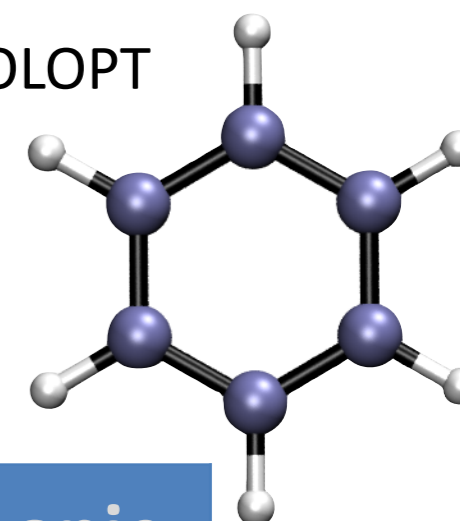
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Partial Hessian results

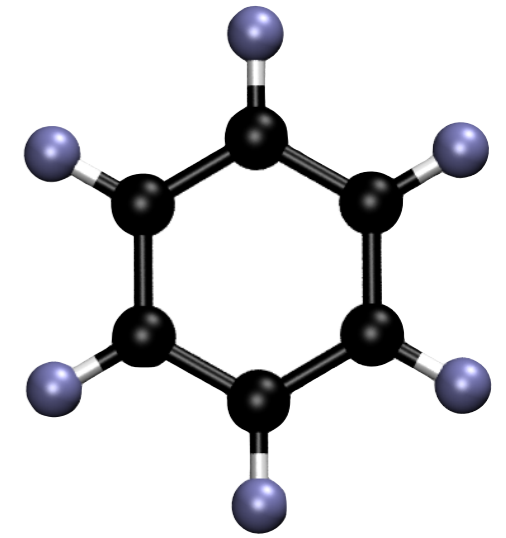
PBE/SVP-MOLOPT



Mode [cm ⁻¹]	Full Hessian	Partial Hessian	Exp.	Harmonic reference
2 [A _{1g}]	3791	3628	3074	3191
20 [E _{1u}]	3777	3623	3064	3181
7 [E _{2g}]	3769	3622	3057	3164
13 [B _{1u}]	3762	3619	3057	3174
RMSD (exp)	581	457	—	—
RMSD (Harmonic)	488	364	—	—

Choice 3: Mode selection

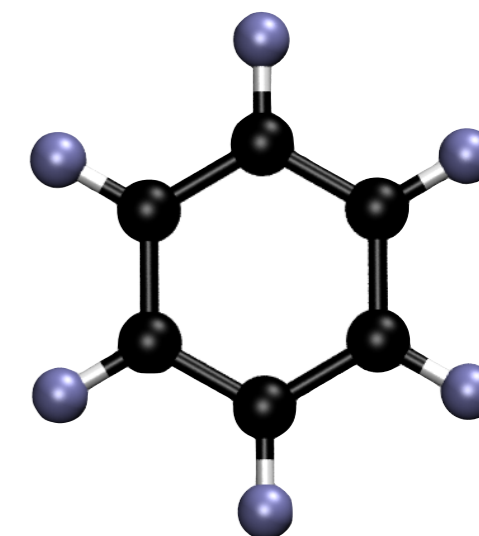
- Instead of freezing part of the system, we can try to pick out the modes that involve the atoms we are interested in
- This mode selective (mode tracking) approach is described in: Reiher and Neugebauer, J. Chem. Phys., 2003 **118** 1634
- It involves iterating the solutions of: $\mathbf{H}q_i = \epsilon_i q_i$ with a reasonable guess for the vibrational modes



Mode selection CP2K input

MODULE QUICKSTEP: ATOMIC COORDINATES IN angstrom

Atom	Kind	Element	X	Y	Z	Z(eff)	Mass	
1	1	H	1	-0.164183	0.937027	0.338824	1.00	1.0079
2	2	C	6	-0.350910	0.636285	-0.654650	4.00	12.0107
3	2	C	6	-1.583921	0.020603	-0.989467	4.00	12.0107
4	1	H	1	-2.314290	-0.135736	-0.244831	1.00	1.0079
5	2	C	6	-1.835940	-0.382837	-2.325437	4.00	12.0107
6	1	H	1	-2.753111	-0.840221	-2.574231	1.00	1.0079
7	2	C	6	-0.852991	-0.173554	-3.326467	4.00	12.0107
8	1	H	1	-1.039682	-0.474385	-4.319921	1.00	1.0079
9	2	C	6	0.380014	0.442138	-2.991636	4.00	12.0107
10	1	H	1	1.110397	0.598458	-3.736261	1.00	1.0079
11	2	C	6	0.632048	0.845557	-1.655671	4.00	12.0107
12	1	H	1	1.549264	1.302822	-1.406834	1.00	1.0079



&GLOBAL

...
RUN_TYPE VIBRATIONAL_ANALYSIS
&END GLOBAL

MSI TRACKED FREQUENCY (4) IS: 1101.733955 cm-1
MSI TRACKED FREQUENCY (12) IS: 950.994757 cm-1
MSI TRACKED FREQUENCY (13) IS: 3773.476473 cm-1
MSI TRACKED FREQUENCY (14) IS: 1172.140769 cm-1

&VIBRATIONAL_ANALYSIS

FULLY_PERIODIC
INTENSITIES
NPROC_REP 2

&MODE_SELECTIVE

ATOMS 1 4 6 8 10 12

&INVOLVED_ATOMS

INVOLVED_ATOMS 1 4 6 8 10 12

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INITIAL_GUESS ATOMIC

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EPS_MAX_VAL 1.0E-5

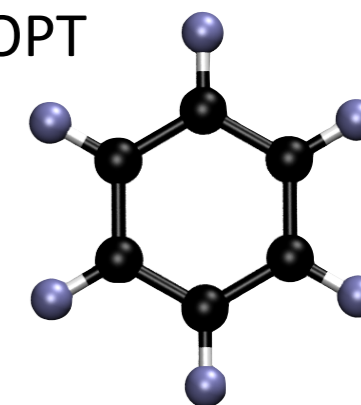
&END

&END

FREQUENCY AND CONVERGENCE LIST					
	FREQUENCY	INTENSITY	MAXVAL CRITERIA	NORM CRITERIA	CONVERGENCE
VIB	195.711	0.000299	0.107E-05	0.333E-05	YES
...					
VIB	1505.164	0.000610	0.243E-05	0.600E-05	YES
VIB	1566.289	0.003771	0.639E-05	0.153E-04	YES
VIB	1612.322	0.004823	0.252E-05	0.775E-05	YES
VIB	1651.464	0.003426	0.453E-05	0.831E-05	YES
VIB	3761.167	0.000901	0.178E-05	0.612E-05	YES
VIB	3766.778	0.002028	0.522E-05	0.937E-05	YES
VIB	3767.854	0.000991	0.254E-05	0.572E-05	YES
VIB	3773.476	0.011729	0.363E-05	0.122E-04	YES
VIB	3776.018	0.012046	0.224E-05	0.426E-05	YES
VIB	3789.009	0.001904	0.222E-05	0.770E-05	YES

Mode selection results

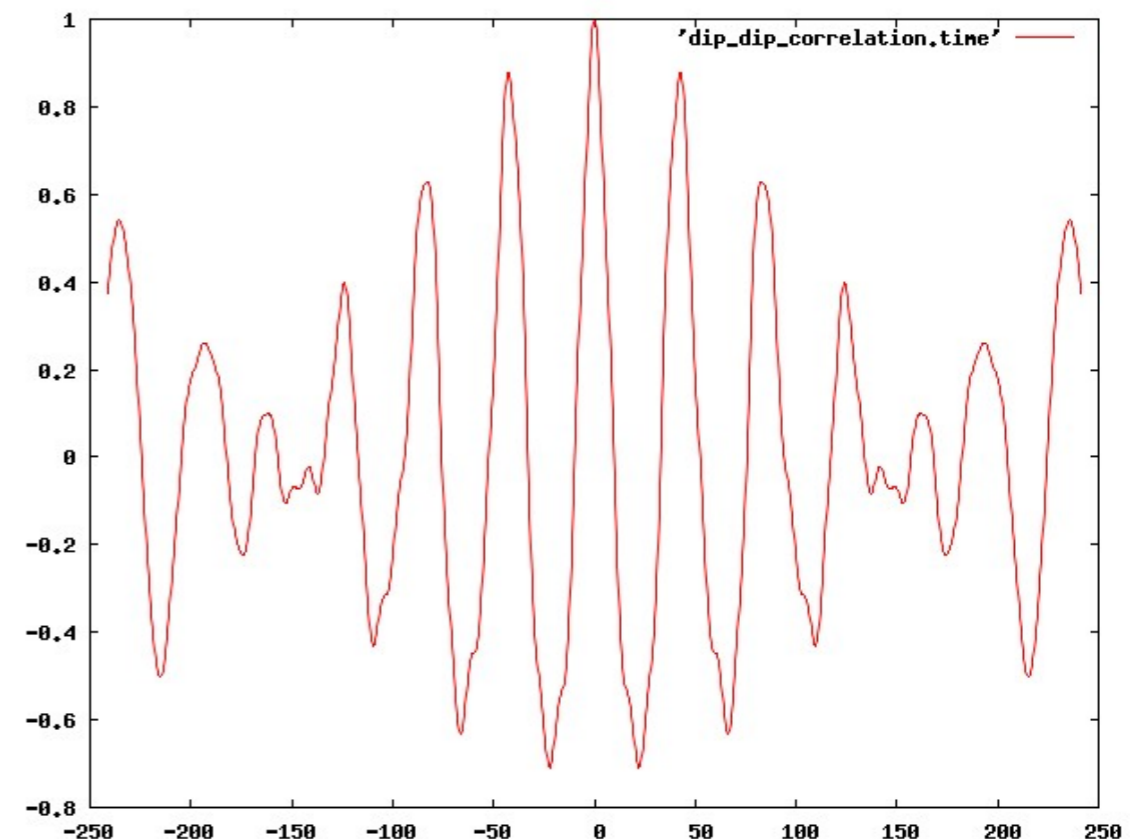
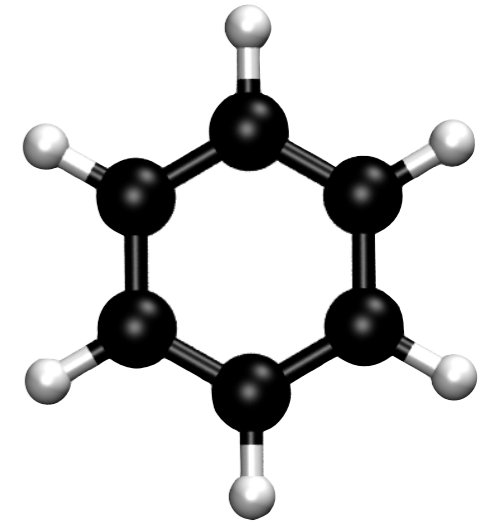
PBE/SVP-MOLOPT



Mode [cm ⁻¹]	Full Hessian	Partial Hessian	Mode selected	Exp.	Harmonic reference
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13 [B _{1u}]	3762	3619	3761	3057	3174
RMSD (exp)	581	457	580	—	—
RMSD (Harmonic)	488	364	486	—	—

Molecular dynamics CP2K input

- Atoms vibrate during MD simulations, so collecting the dipole autocorrelation function and extracting oscillator frequencies gives us a power spectrum
- You will need a reasonably long MD with smallish timestep and means of calculating FFTs and correlation functions
- See also: Thomas *et al*, PCCP, 2013, **15** 6608 (doi: 10.1039/c3cp44302g)



Choice 4: Molecular dynamics

- MD can be NVE or NVT (more often)
- Dipole moment needs to be saved to construct autocorrelation function
- Analysis tools are required to extract power spectrum (see for example https://www.cp2k.org/exercises:2015_ethz_mmm:infra_red)

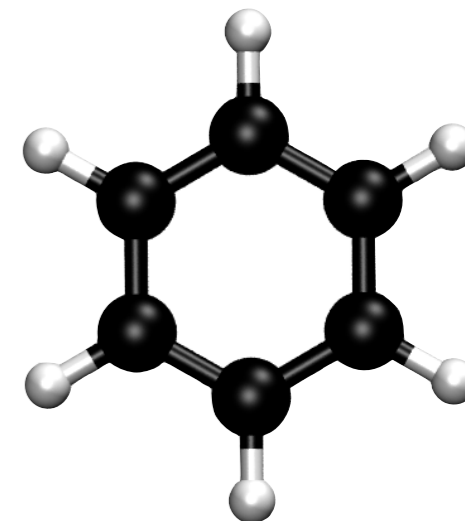
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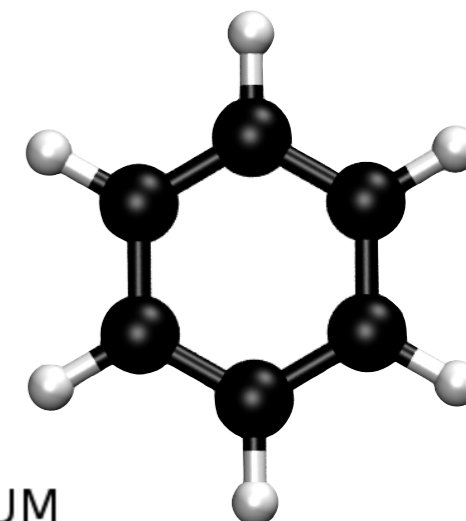
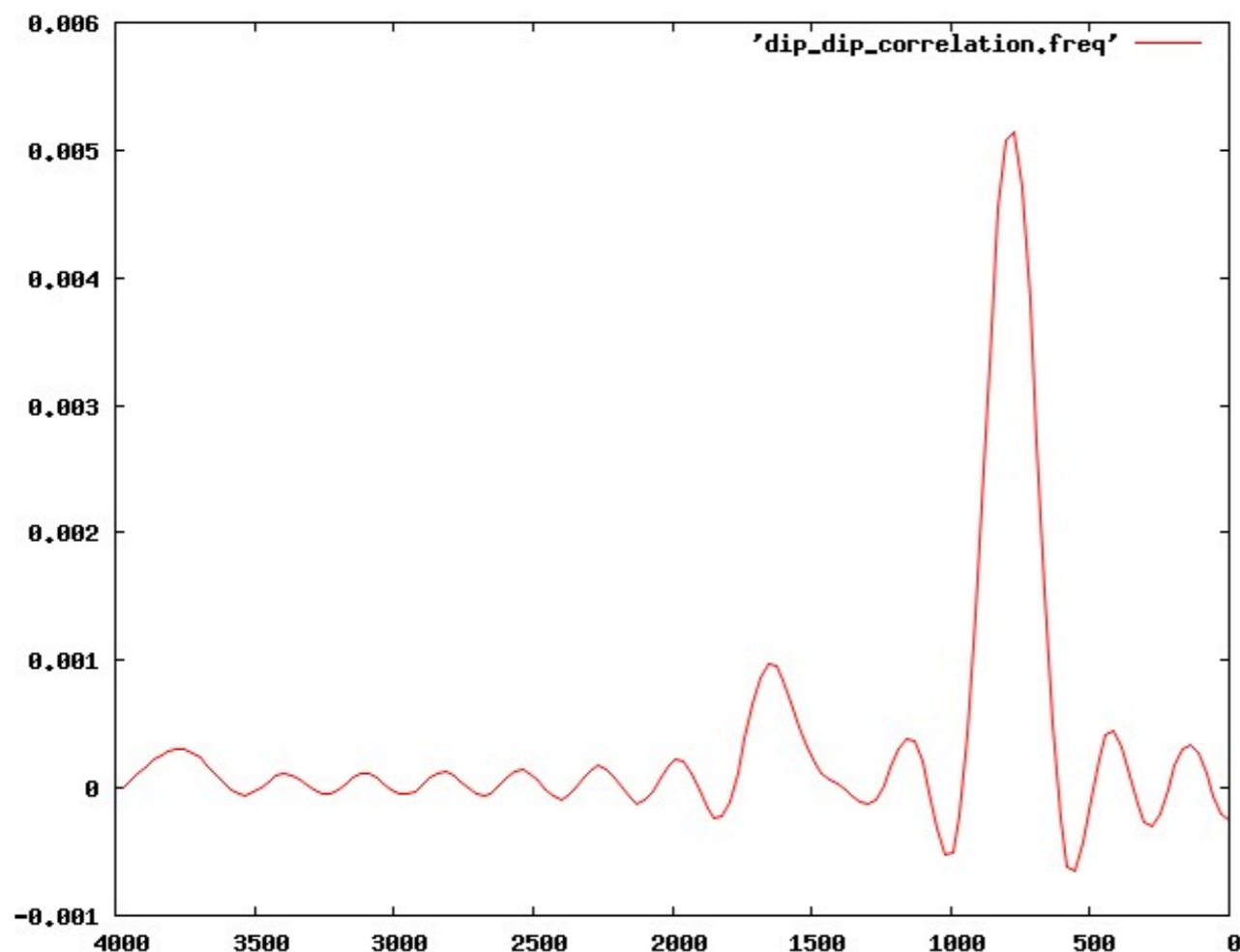
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  TEMPERATURE 1200
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&END MOTION

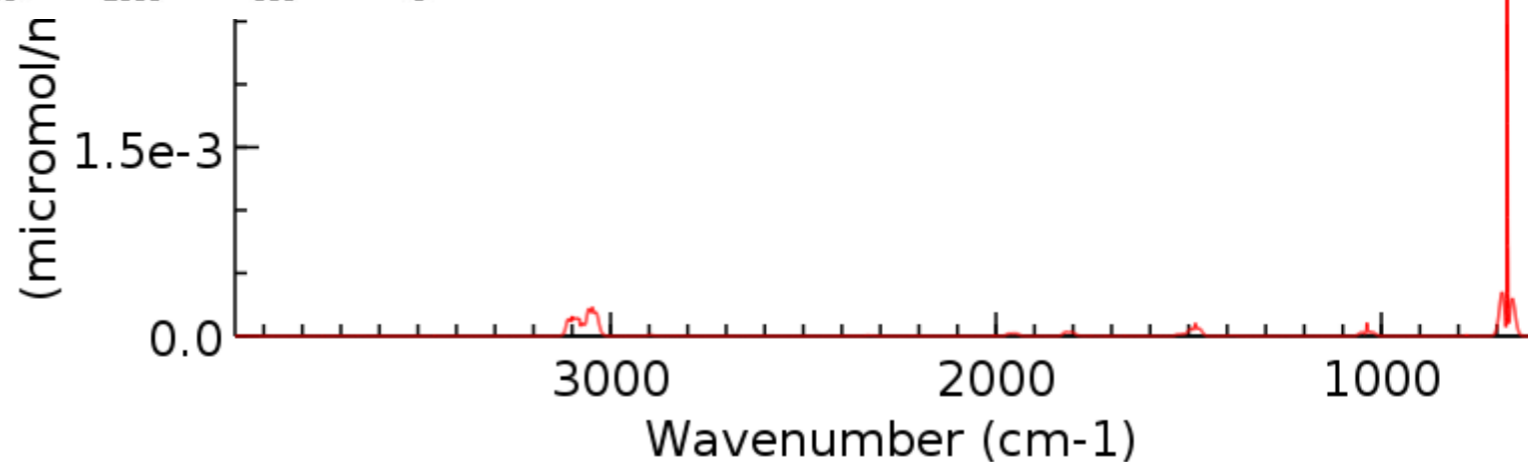
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Molecular dynamics results



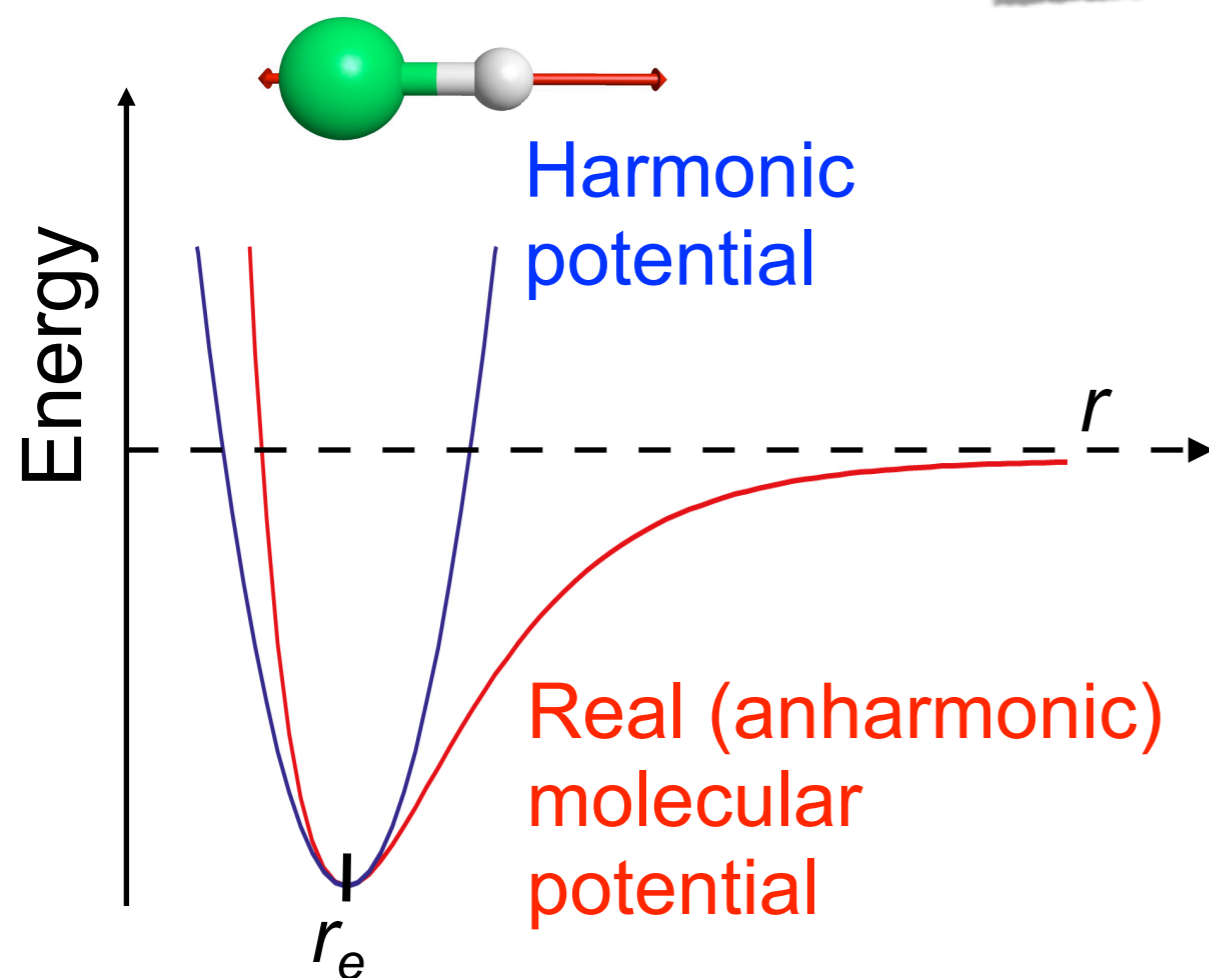
Benzene
INFRARED SPECTRUM



NIST Chemistry WebBook (<https://webbook.nist.gov/chemistry>)

What is anharmonicity?

- A symmetric harmonic potential is only an approximation to the real potential



JULY 1, 1929

PHYSICAL REVIEW

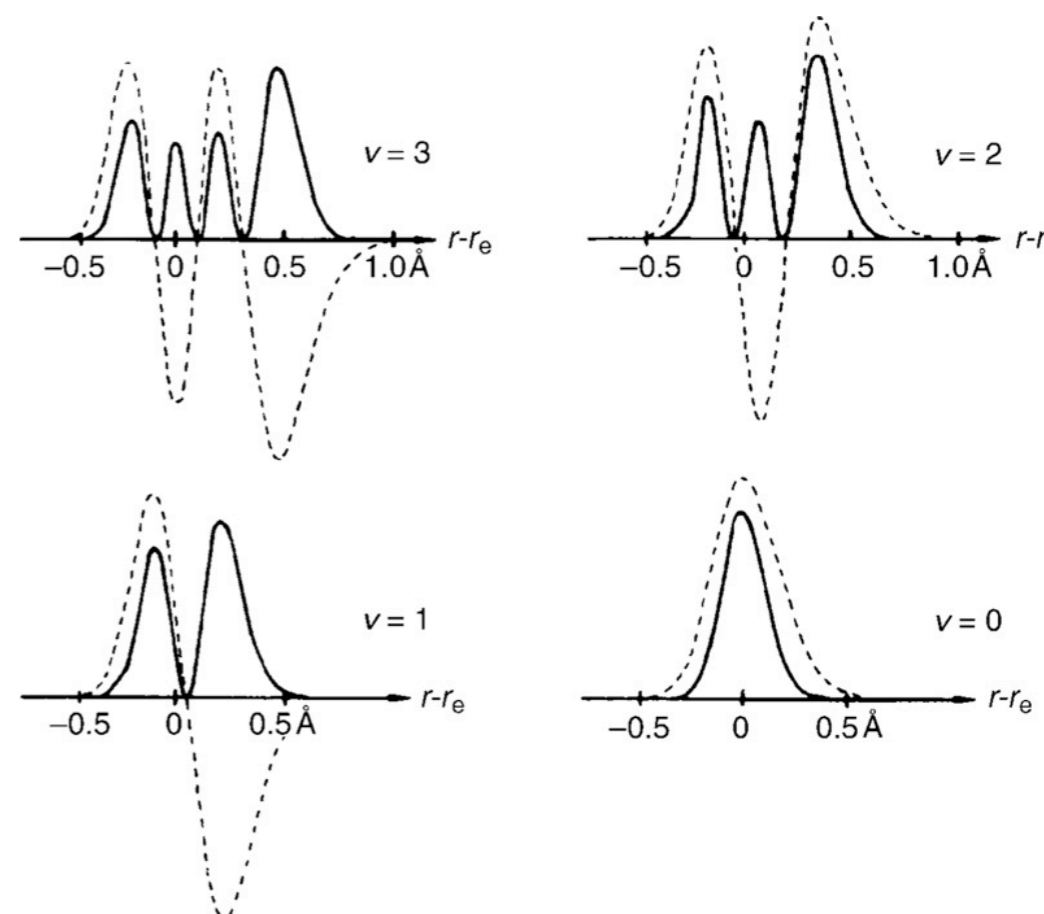
VOLUME 34

DIATOMIC MOLECULES ACCORDING TO THE WAVE MECHANICS. II. VIBRATIONAL LEVELS

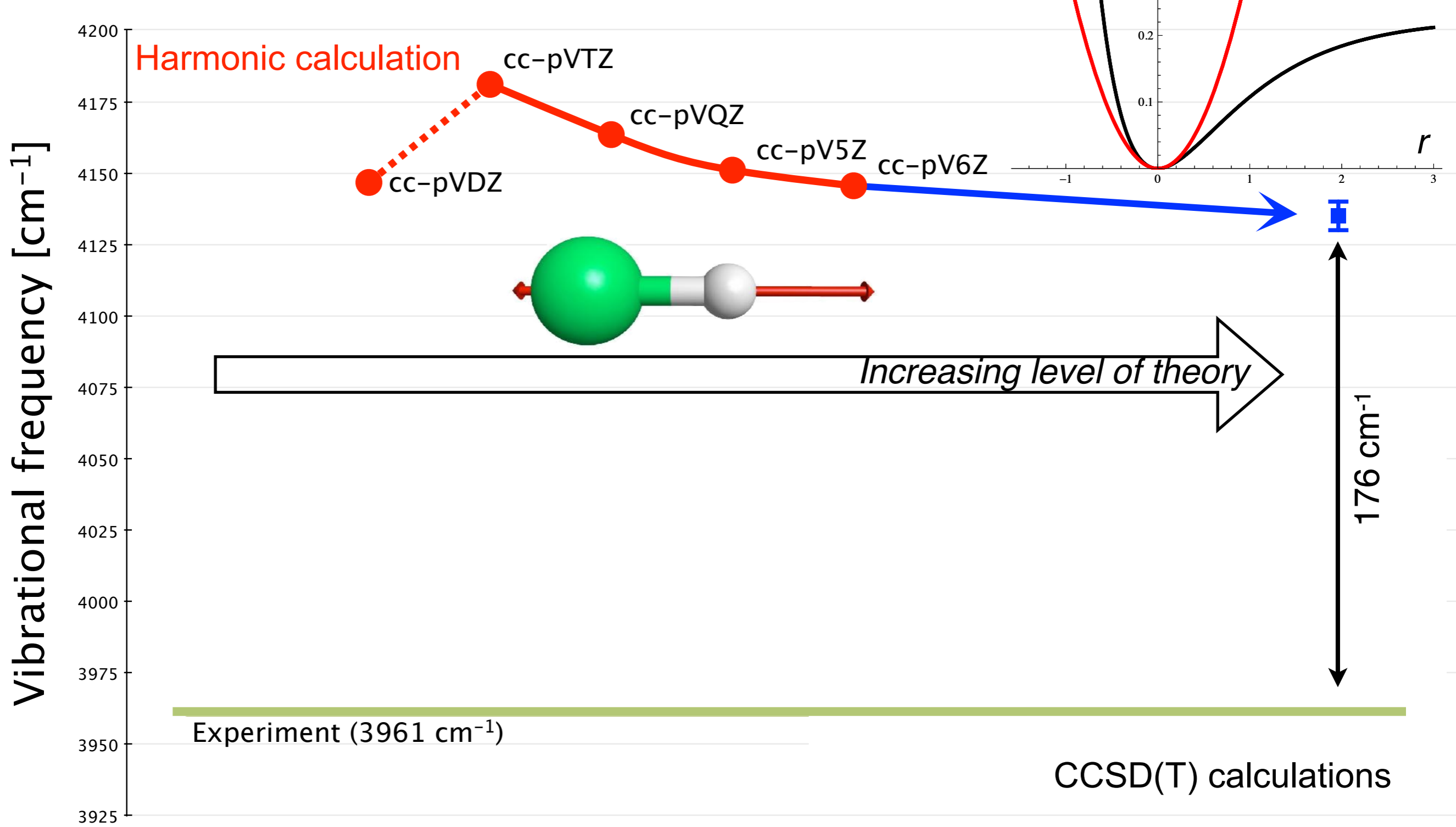
BY PHILIP M. MORSE

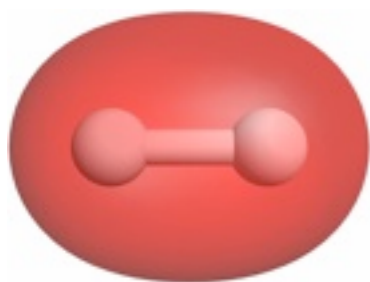
Palmer Physical Laboratory, Princeton University

(Received April 8, 1929)



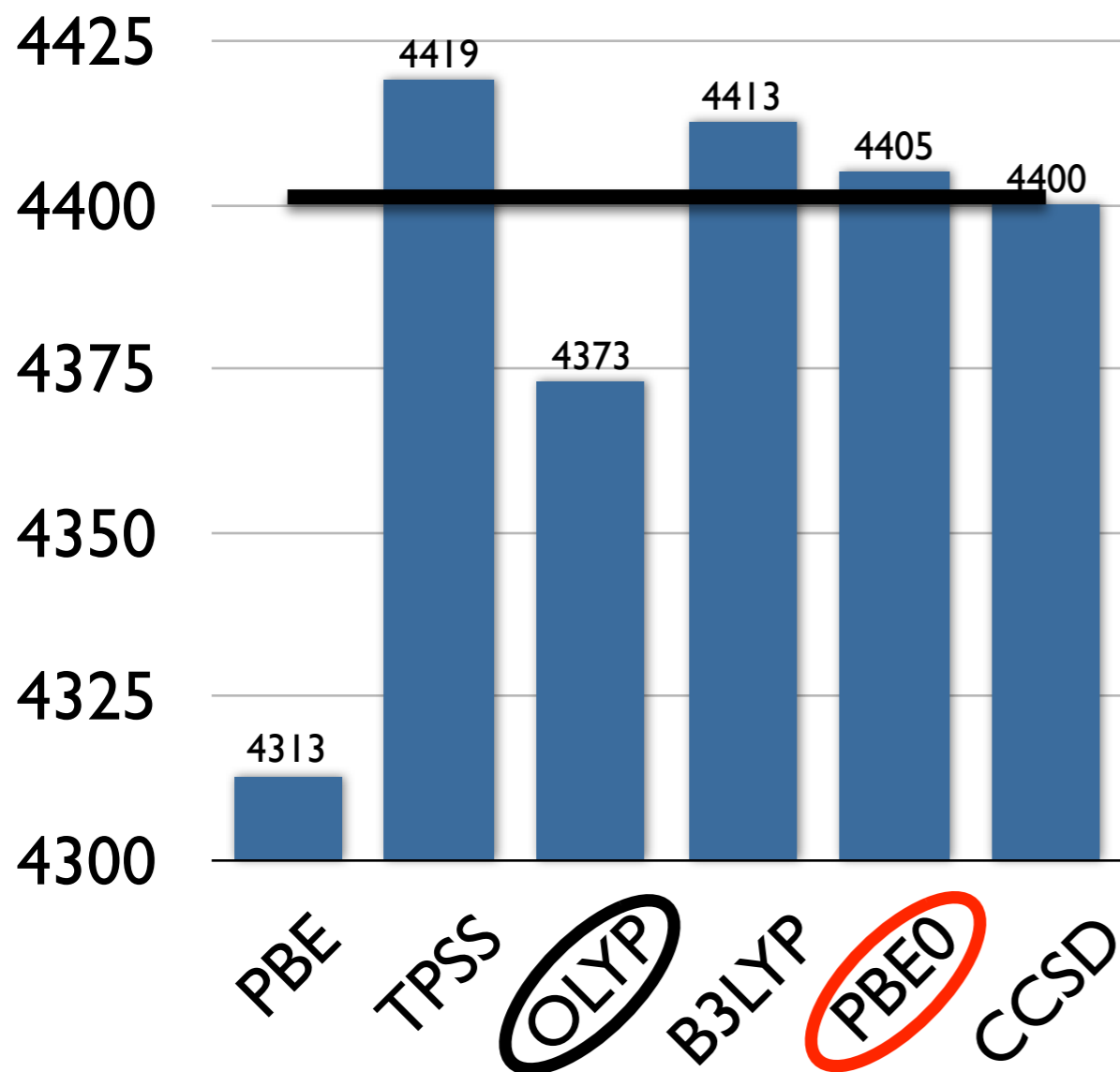
Let's use the harmonic approximation...



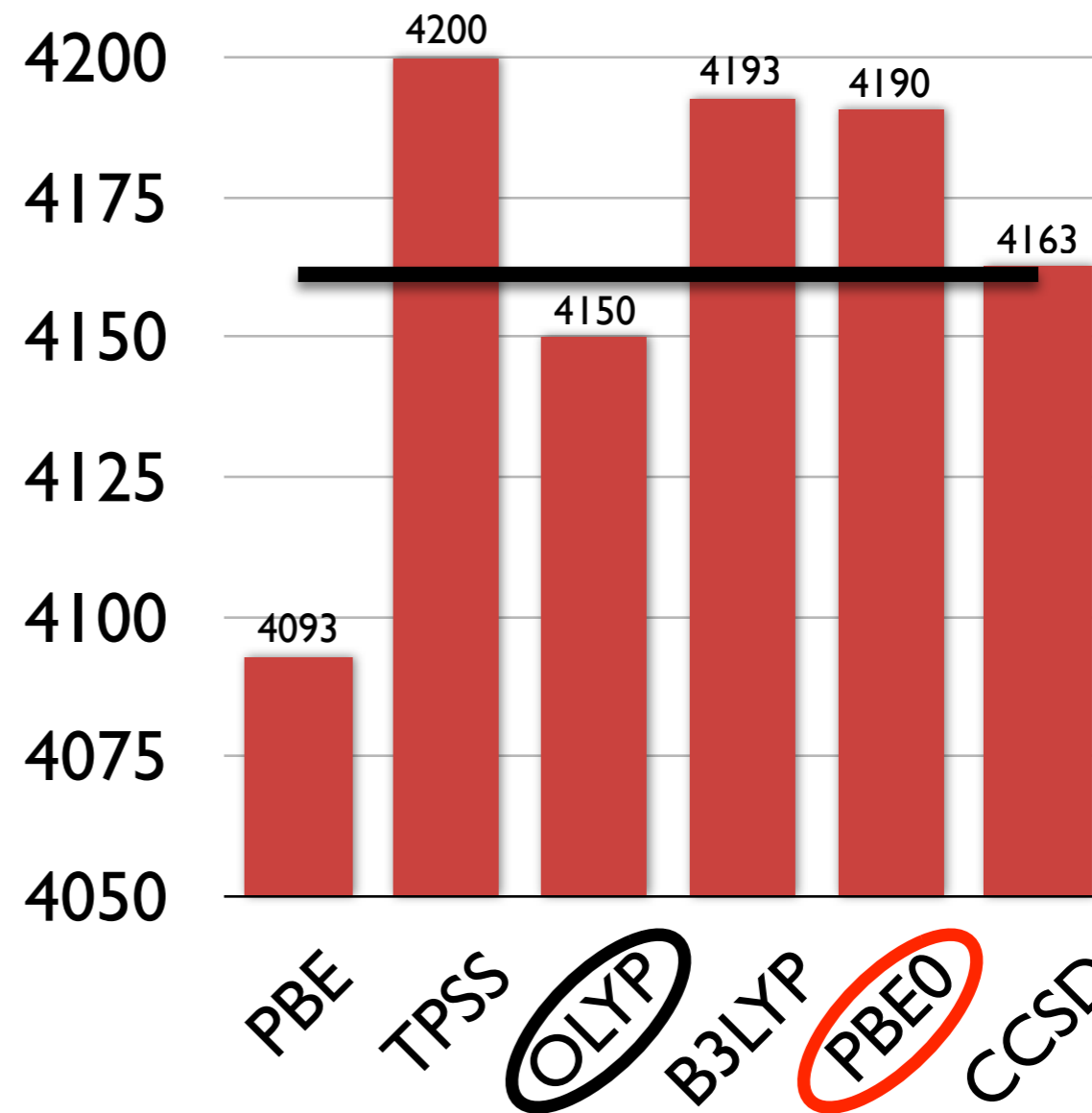


How accurate can we be?

“Harmonic” Frequency



Anharmonic Frequency



Basis set: QZVPP (ORCA)