

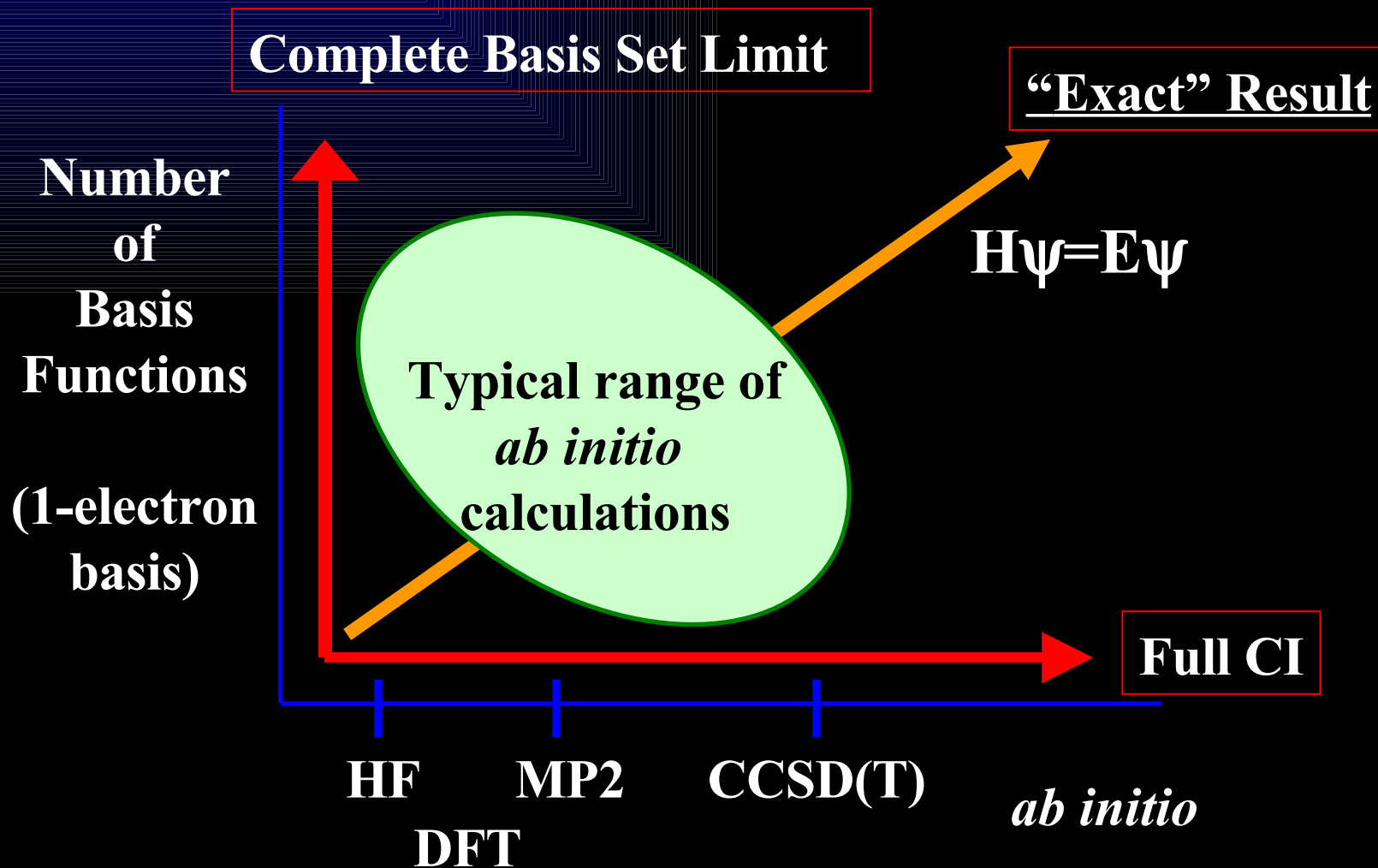
# Overcoming the Overestimation of Vibrational Frequencies: The Development of Frequency Scaling Factors for B3P86 in Combination with the Correlation Consistent Basis Sets

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# What Causes Errors in Calculated Frequencies

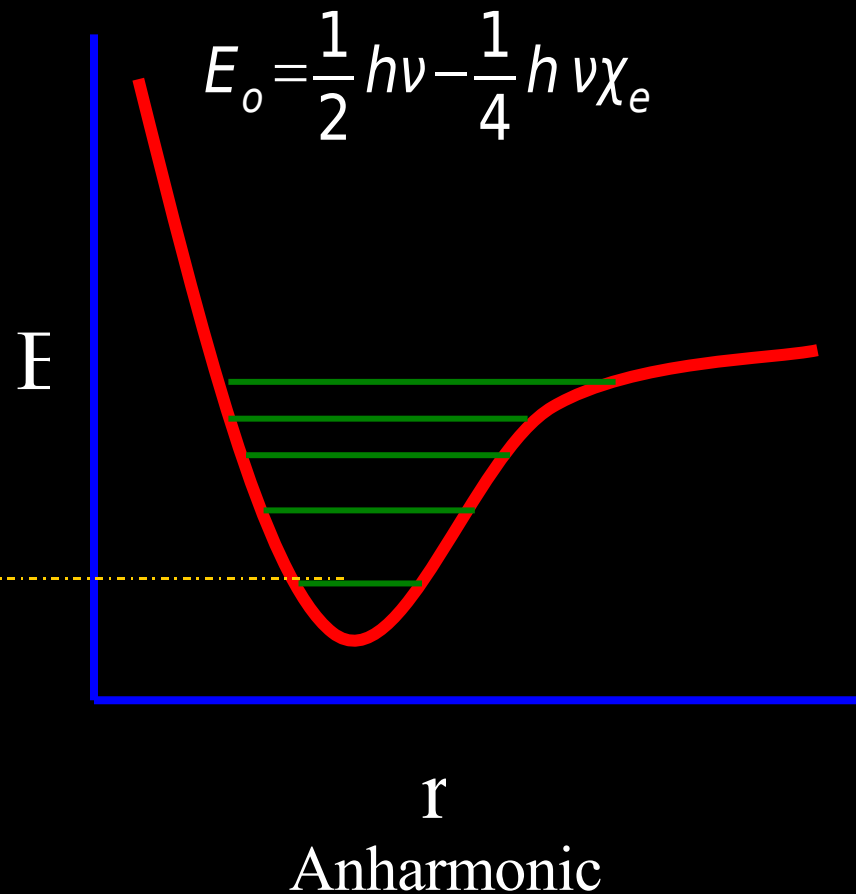
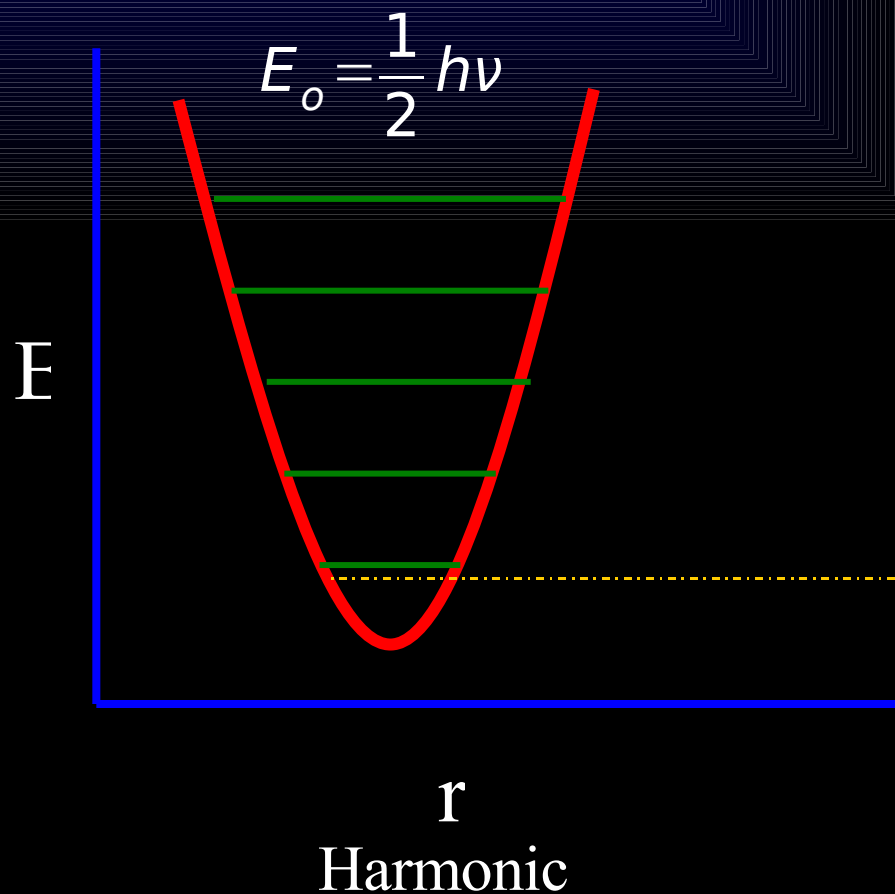
Approach to the “exact” solution to the Schrödinger Equation



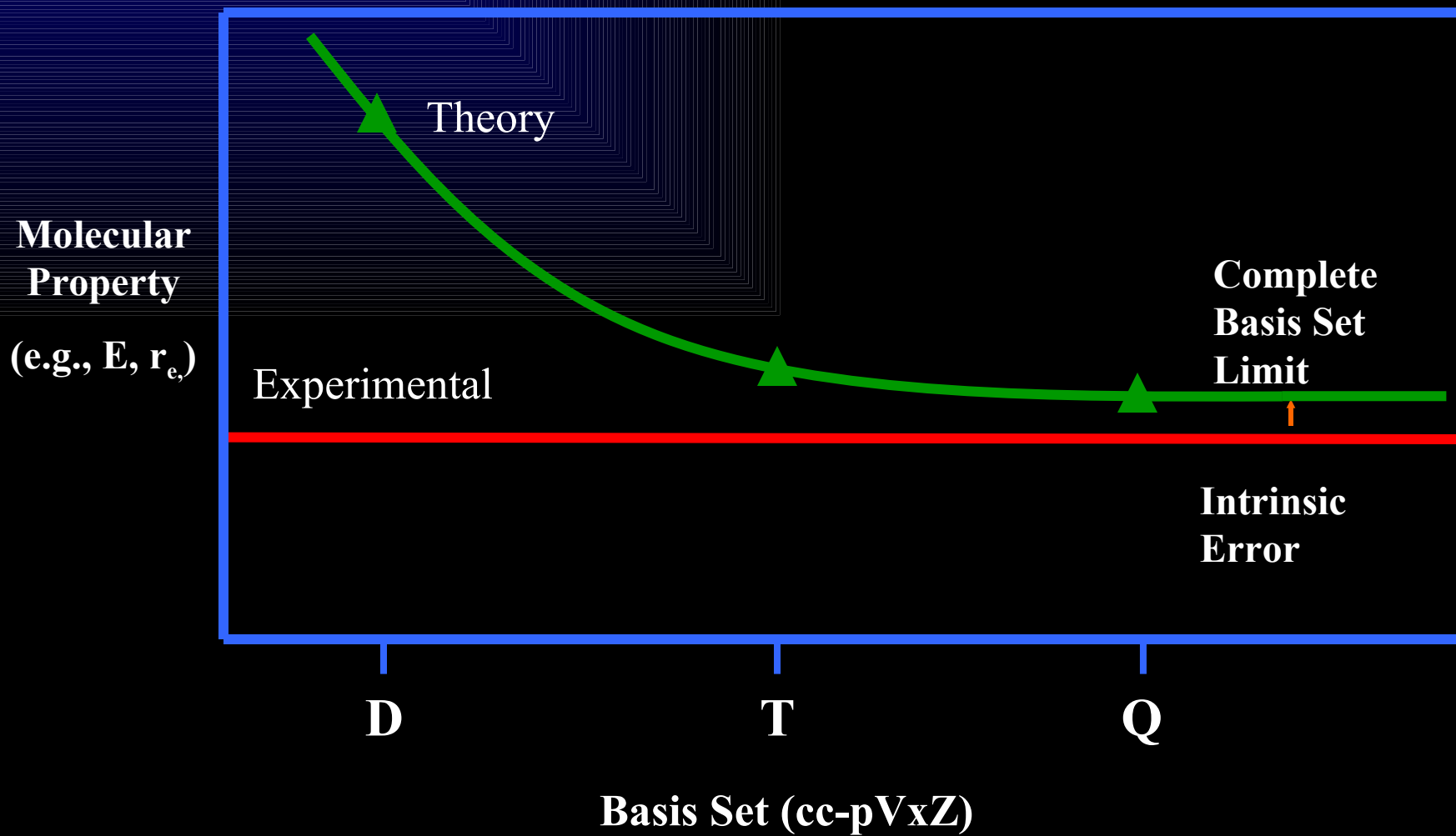
# Vibrational Frequency Scale Factors

Calculated harmonic frequencies are usually overestimated.

Common computational methods neglect **ANHARMONICITY**



# Correlation-Consistent Basis Sets



# Solution

- ❑ Errors between calculated and experimental frequencies are generally uniform.
- ❑ Scale factors are determined to reduce the error between calculated harmonic frequencies and experimental fundamental frequencies.
- ❑ With the use of scale factors, a molecule's calculated vibrational spectrum can be correlated with experiment accurately.
- ❑ Scale factors have been determined for a wide range of methods and basis sets combination (each unique).
- ❑ Until now no global set of scale factors have been determined for the correlation-consistent basis sets.

# Calculating Scaling Factors

- ❑ Calculations of high-end ( $>1000\text{ cm}^{-1}$ ) frequencies on 42 different organic molecules
- ❑ Comparison of calculated frequencies compared to those obtained experimentally through the use of residual values
- ❑ Minimizing the sum of all the residual values yields an optimal scaling factor

# Calculating Scaling Factors

$$\Delta_{\text{tot}} = \sum_i^{\text{all}} (\lambda \omega_i^{\text{theor}} - \nu_i^{\text{expt}})^2$$

$$\lambda = \frac{\sum_i^{\text{all}} \omega_i^{\text{theor}} \nu_i^{\text{expt}}}{\sum_i^{\text{all}} (\omega_i^{\text{theor}})^2}$$

$\lambda$  = Global scaling factor

$\Delta_{\text{tot}}$  = Sum of all residual values

$\omega_i^{\text{theor}} = i^{\text{th}}$  Calculated frequency

$\nu_i^{\text{expt}} = i^{\text{th}}$  Experimental frequency

Minimizing  $\Delta_{\text{tot}}$  provides the global scaling factor,  $\lambda$ .

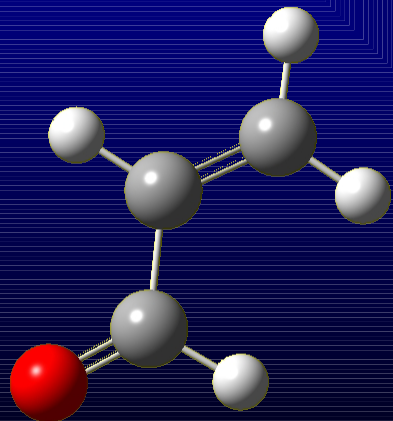
# High-End Frequency Scale Factors

Method	Basis Set	$\lambda_{\text{high}}$	$\text{rms}_{\text{ov}}$
B3P86	cc-pVDZ	0.9625	43
	cc-pVTZ	0.9627	37
	cc-pVQZ	0.9632	37
	aug-cc-pVDZ	0.9629	45
	aug-cc-pVTZ	0.9632	37
	aug-cc-pVQZ	-	-

# Root Mean Square Comparison

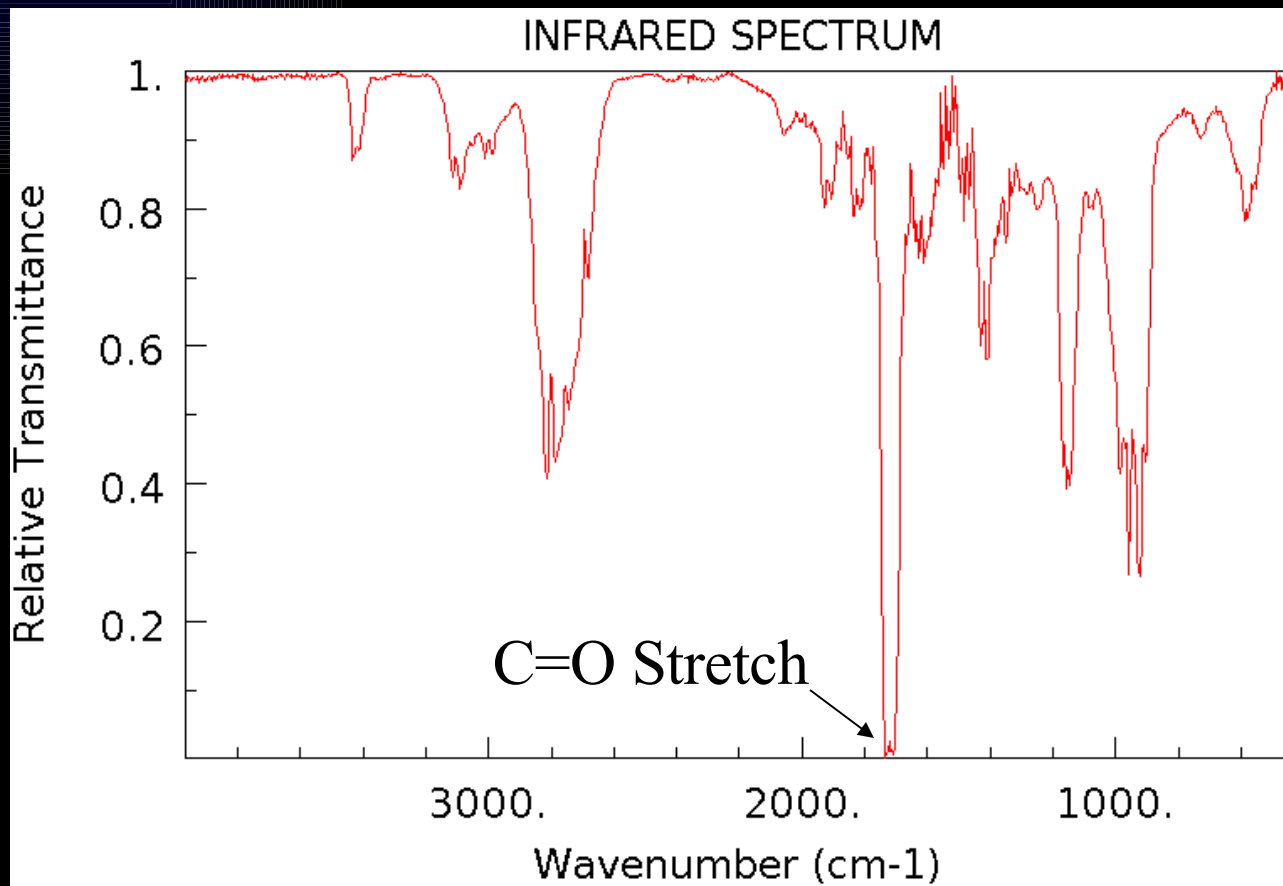
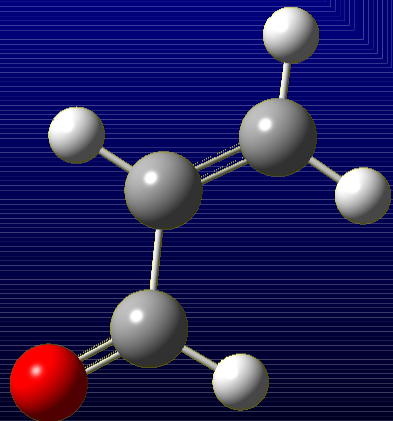
Method	Basis Set	rms <sub>before</sub>	rms <sub>after</sub>
B3P86	cc-pVDZ	95	43
	cc-pVTZ	91	37
	cc-pVQZ	90	37
	aug-cc-pVDZ	95	45
	aug-cc-pVTZ	91	37
	aug-cc-pVQZ	-	-

## 2-Propenal Values



Experimental	Calculated	Scaled	%Error (Before)	%Error (After)
1625	1698.3	1634.6	4.5	0.59
1724	1817.1	1748.6	5.4	1.4
2800	2881.4	2773.3	2.9	0.95
3000	3151.9	3033.7	5.1	1.1
3028	3198.9	3079.0	5.6	1.7
3103	3258.0	3135.8	5.0	1.1

# 2-Propenal Values



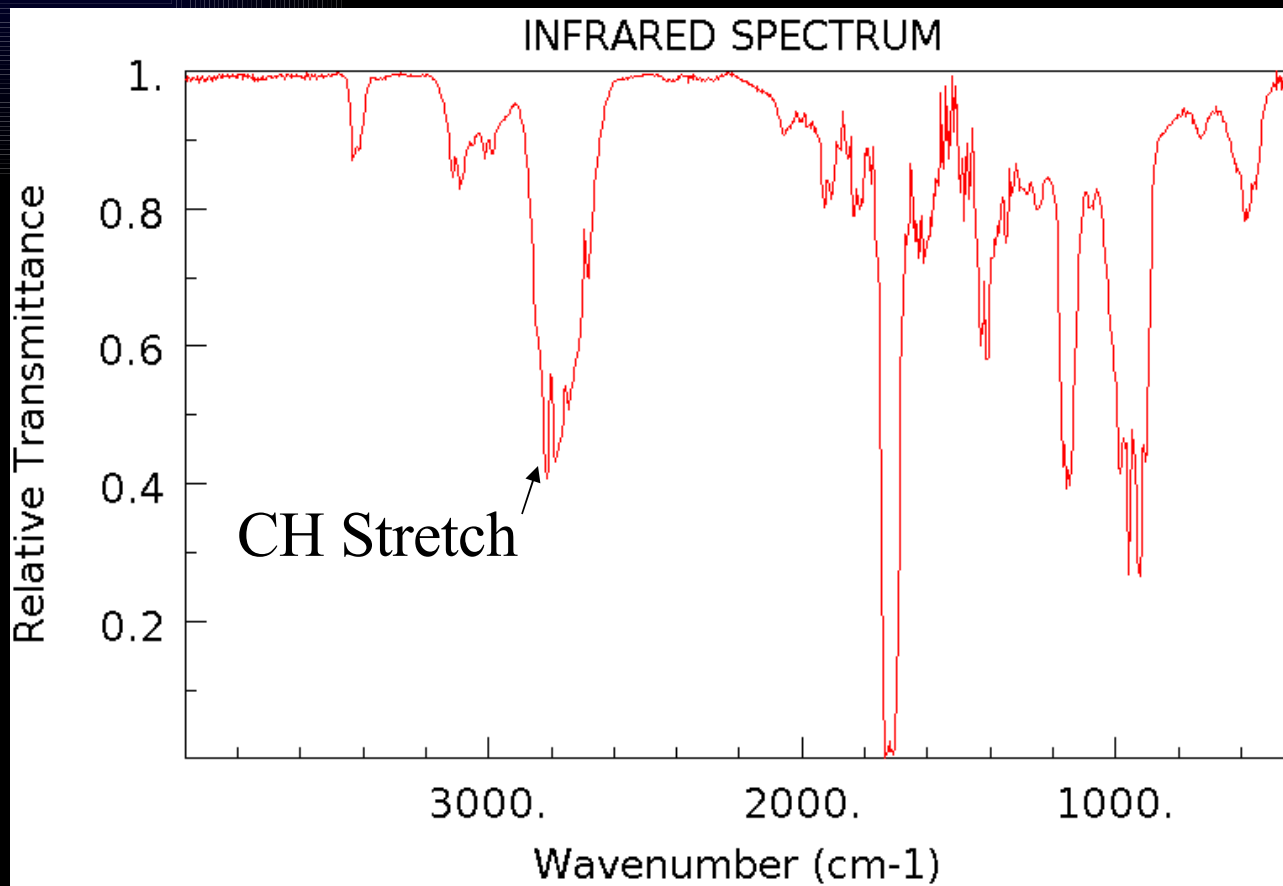
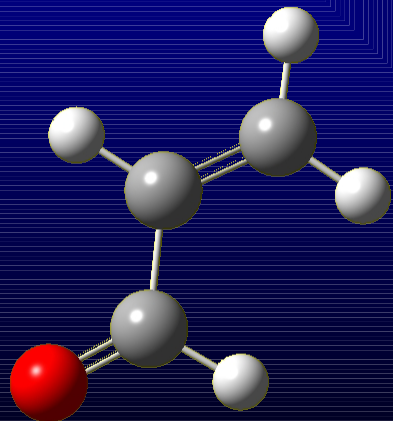
Experimental: 1724

Scaled: 1748.6

Experimental (before): 1734.4

Calculated (after): 1717.4

# 2-Propenal Values



Experimental: 2800

Scaled: 2773.3

Experimental (before): 2800

Calculated (after): 2880.95

# Conclusion

- ❑ Determined scale factors for high-end frequencies calculated by the B3P86 density functional theory method with the correlation consistent basis sets.
- ❑ Larger basis sets show improving accuracy with decreasing root mean square values and scale factors that approach 1.
- ❑ Scale factors improve the calculated values as shown by the over one half decrease in root mean square values after scaling.
- ❑ Other molecules not included in determining the scale factors also exhibit overall improved values.

# Future Work

- ❑ Finish scale factors for the aug-cc-pVQZ basis set
- ❑ Scale factors for...
  - Low frequencies ( $<1000 \text{ cm}^{-1}$ )
  - Thermodynamic values (entropy and enthalpy)
  - Zero-point energies

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