

# Vibrational Stark Effect: Theory and Analysis

# Vibrational Stark Effect

- Surface effect on bound ligands (interfacial)  
CO on metal surfaces
- Electrostatic environment in a protein (matrix)  
Fe-Bound CO, NO , Artificial amino acid CN
- Applied electric field (capacitor)  
Nitrile and carbonyl groups in molecules

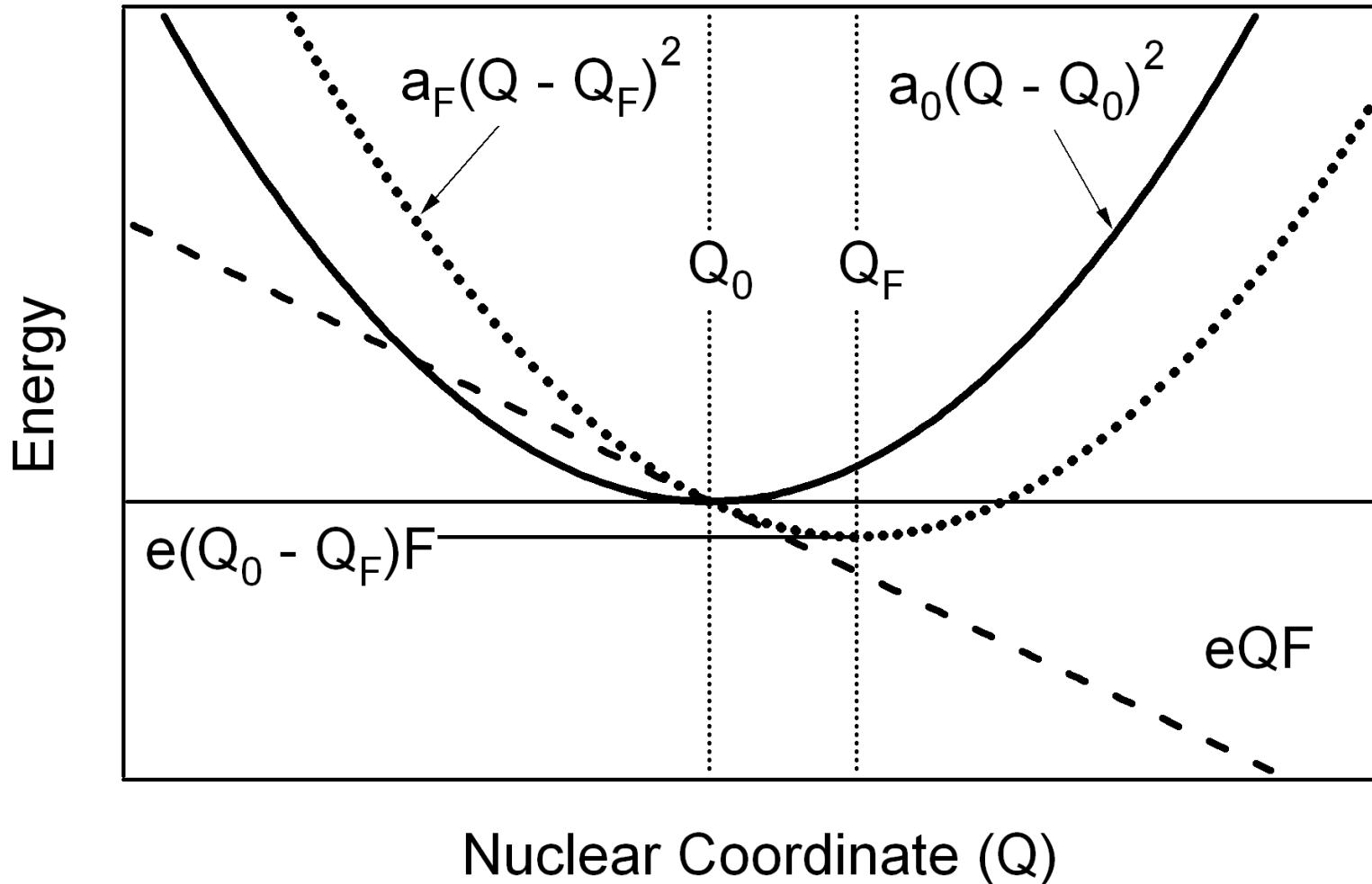
# Systematic study of CO and CN vibrations

Perform DFT calculations of frequencies and potential energy surfaces based on the eigenvector projection of the relevant CO or CN stretching mode.

Perform frequency calculations on geometry optimized structures at each electric field value and calculate the frequency.

Calculate the anharmonic potential energy surface and anharmonic correction at each projected geometry.

# Potential energy surface model



# Compare potential surfaces

$$U(Q) - \mu(Q)F = a_0(Q - Q_0)^2 + b_0(Q - Q_0)^3 - eQF$$

$$U_F(Q) = a_F(Q - Q_F)^2 + b_F(Q - Q_F)^3 - e(Q_F - Q_0)F$$

Eliminate higher order terms using the device

$$x_F = x_0(1 + \varepsilon)$$

The field-dependent coefficient and geometry changes are

$$a_F = \frac{a_0 + \frac{eF}{2} \left( \frac{1}{x_0} + 3 \frac{b_0}{a_0} \right)}{1 - \frac{eF}{2a_0x_0}} \quad b_F = b_0 \quad x_F = x_0 - \frac{eF}{2a_0}$$

# A quadratic surface becomes non-harmonic in an applied field

$$U(Q) - \mu(Q)F = a_0(Q - Q_0)^2 - eQF$$

$$U_F(Q) = a_F(Q - Q_F)^2 - e(Q_F - Q_0)F$$

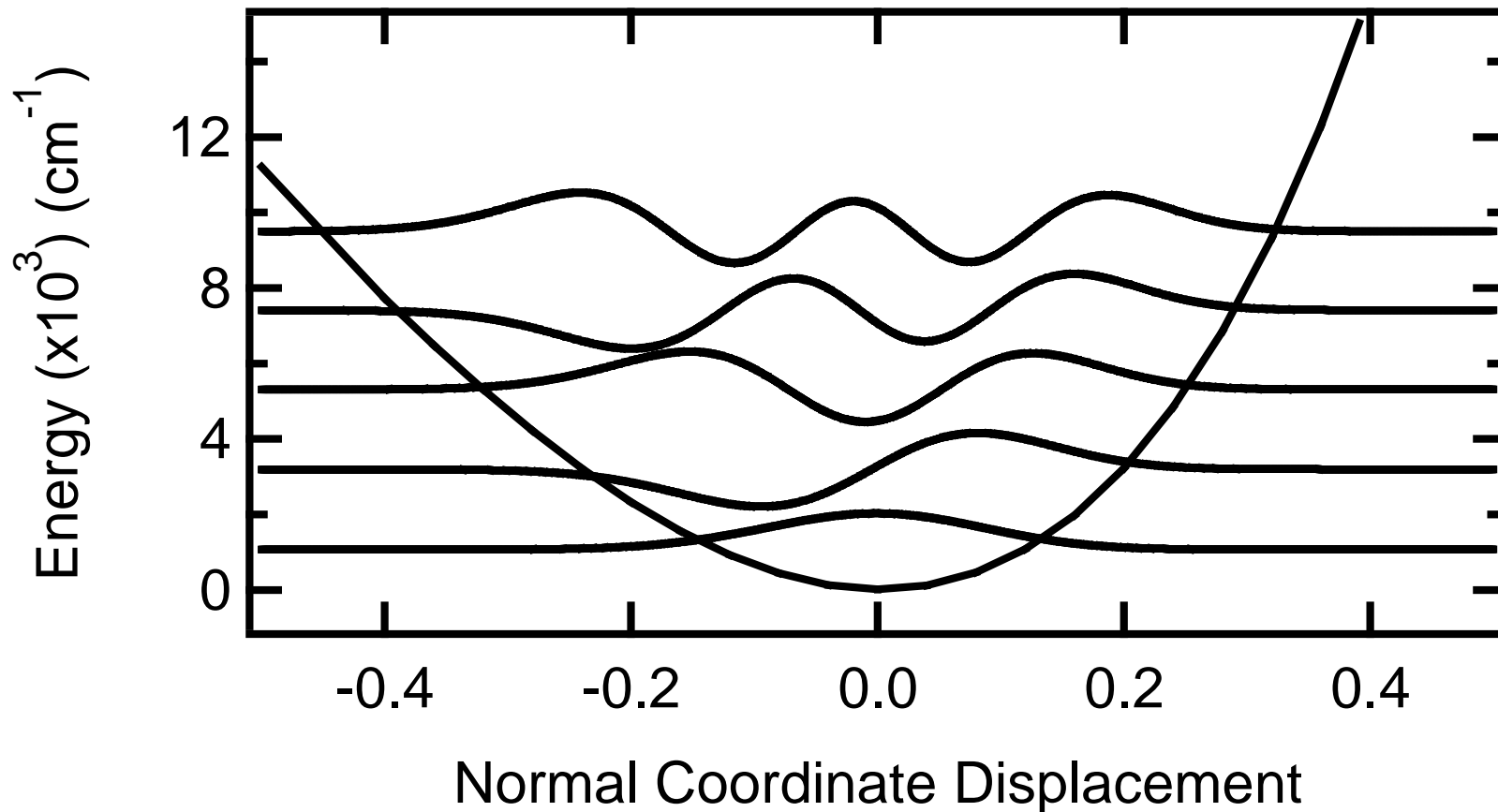
Eliminate higher order terms using the device

$$x_F = x_0(1 + \varepsilon)$$

The field-dependent coefficient and geometry changes are

$$a_F = a_0 \frac{1+x}{1-x} \quad x_F = x_0(1-x) \quad x = \frac{eF}{2a_0x_0}$$

# Anharmonic wavefunctions



Use Cooley-Numerov Algorithm to obtain eigenvalues and eigenfunctions for a polynomial model of PES

# Calculation of the Stark tuning rate

$$\Delta\mu = \frac{E_+ - E_-}{F_+ - F_-} = \frac{\Delta E}{\Delta F}$$

$$\Delta\mu_{tot} = \Delta\mu_{geom} + \Delta\mu_{anharm}$$

# Calculation of the transition polarizability

$$M(F) = M + AF$$

$$M = \left( \frac{\partial\mu}{\partial Q} \right) \langle \chi_0 | Q | \chi_1 \rangle \quad \langle \chi_0 | Q | \chi_1 \rangle = \sqrt{\frac{1}{2\alpha}} \quad \alpha = \frac{\mu\omega}{\hbar}$$

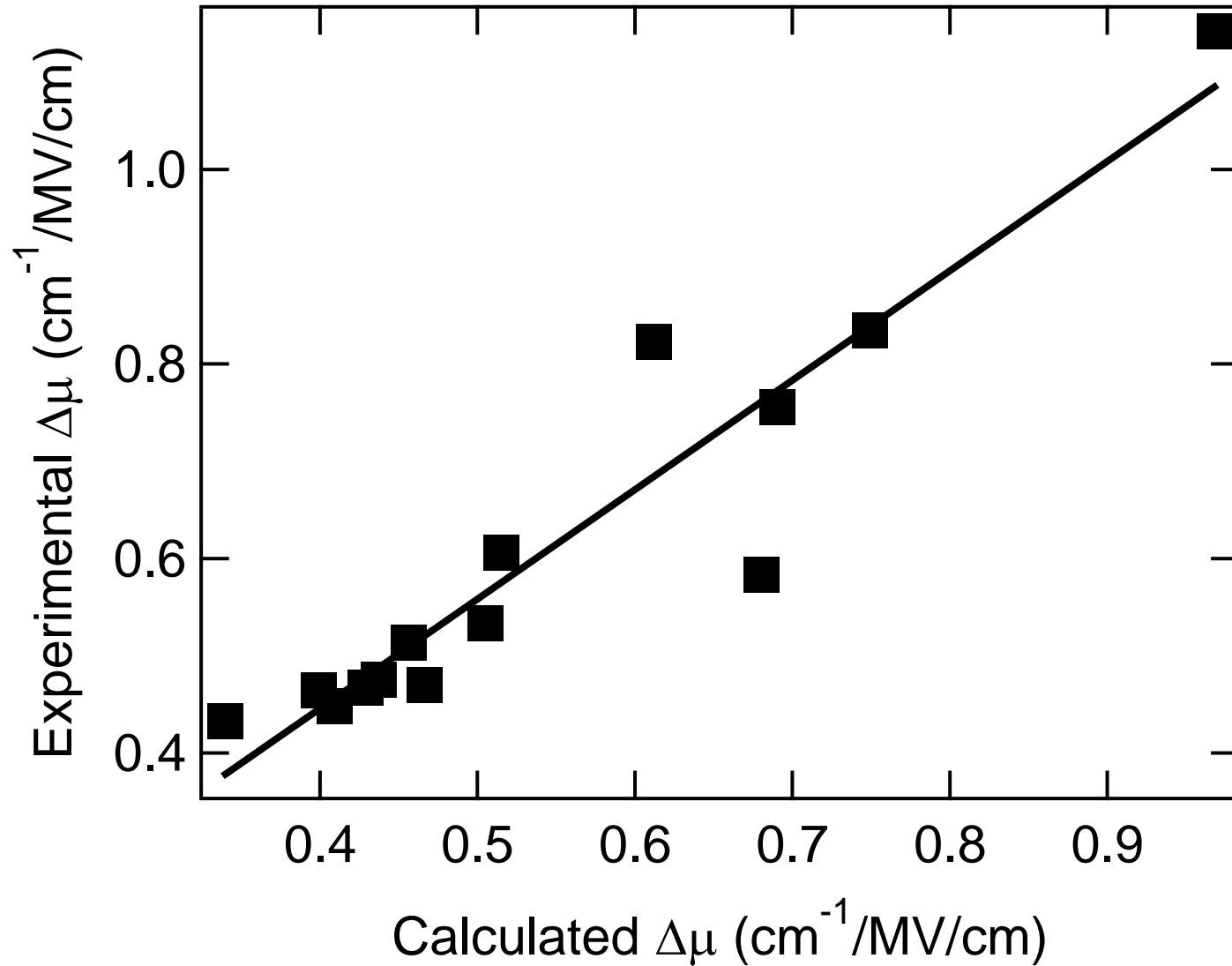
$$|A| = \frac{1}{2} \left( \left| \frac{|M_{1F+} \langle \chi_{0F+} | Q | \chi_{1F+} \rangle - |M_1 \langle \chi_0 | Q | \chi_1 \rangle|}{F_+} \right| + \left| \frac{|M_{1F-} \langle \chi_{0F-} | Q | \chi_{1F-} \rangle - |M_1 \langle \chi_0 | Q | \chi_1 \rangle|}{F_-} \right| \right)$$



# Correlation of $\Delta\mu$

| Molecule              | Stark Tuning Rate<br>Calculated <sup>A</sup><br>( $\text{cm}^{-1}/(\text{MV}/\text{cm})$ ) | Stark Tuning Rate<br>Calculated <sup>B</sup><br>( $\text{cm}^{-1}/(\text{MV}/\text{cm})$ ) | Stark Tuning<br>Rate<br>A + B | Stark Tuning Rate<br>Experimental<br>( $\text{cm}^{-1}/(\text{MV}/\text{cm})$ ) <sup>C</sup> |
|-----------------------|--|--|-------------------------------|--|
| acetone               | 0.253  | 0.437  | 0.690                         | 0.756  |
| CO                    | 0.010  | 0.457  | 0.467                         | 0.429 <sup>D</sup>   |
| CN <sup>-</sup>       | 0.019  | 0.204  | 0.223                         | -----  |
| HCN                   | 0.049  | 0.049  | 0.098                         | ----- <sup>E</sup>   |
| ACN                   | 0.068  | 0.272  | 0.340                         | 0.433  |
| BCN                   | 0.097  | 0.418  | 0.515                         | 0.606  |
| MVK                   | 0.214  | 0.398  | 0.612                         | 0.823  |
| NMP                   | 0.262  | 0.706  | 0.968                         | 1.142  |
| 4-chlorobenzonitrile  | 0.126  | 0.554  | 0.680                         | 0.584  |
| 3-chlorobenzonitrile  | 0.097  | 0.408  | 0.505                         | 0.534  |
| 2-chlorobenzonitrile  | 0.097  | 0.359  | 0.456                         | 0.514  |
| 4-methoxybenzonitrile | 0.146  | 0.603  | 0.749                         | 0.835  |
| propionitrile         | 0.078  | 0.321  | 0.399                         | 0.465  |
| butyronitrile         | 0.097  | 0.340  | 0.437                         | 0.475  |
| valeronitrile         | 0.088  | 0.321  | 0.409                         | 0.448  |
| hexanenitrile         | 0.097  | 0.369  | 0.466                         | 0.470  |

# Correlation of $\Delta\mu$

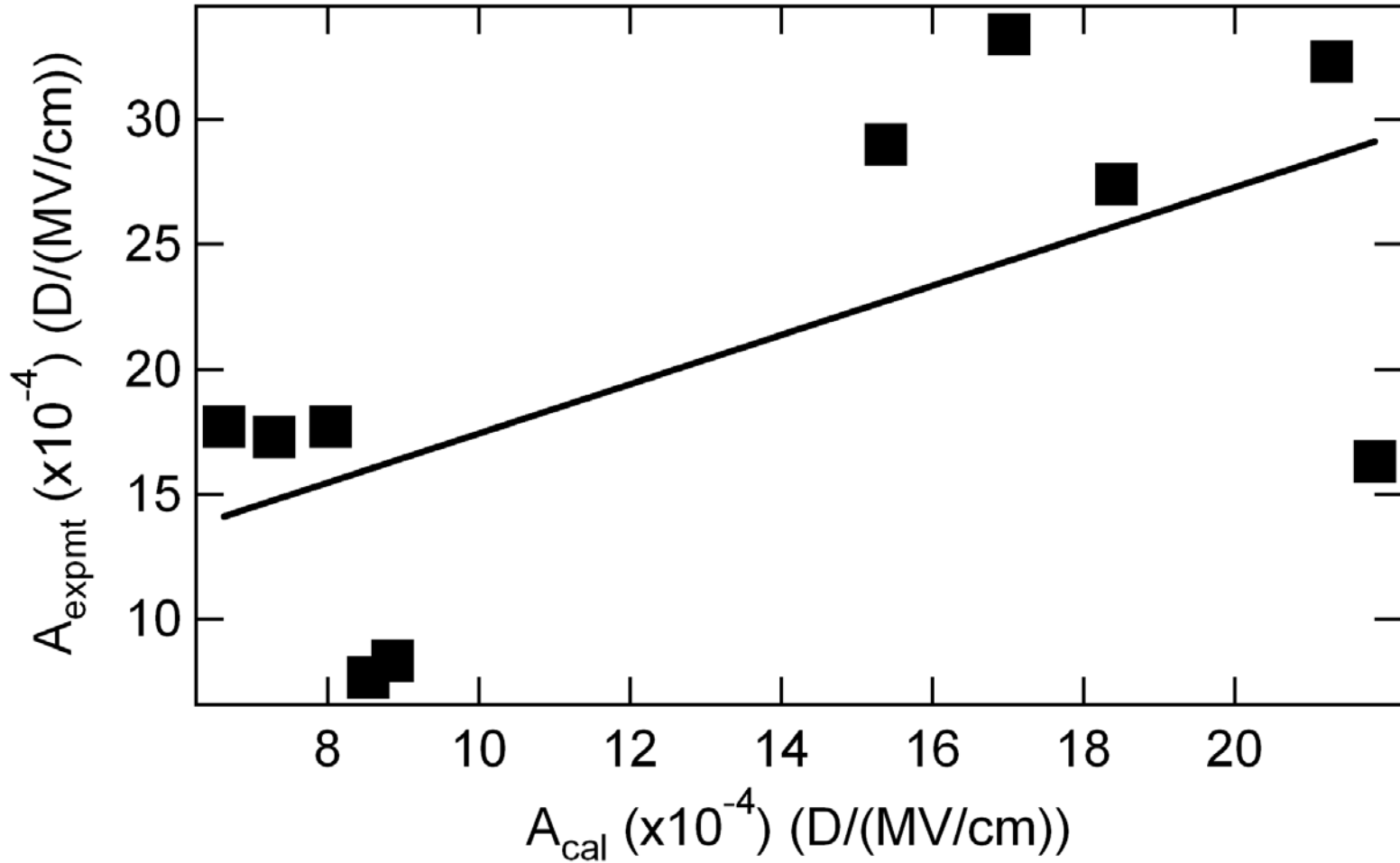


# Correlation of A

$$|A| = \frac{1}{2} \left( \left| \frac{|M_{1F+} \langle \chi_{0F+} | Q | \chi_{1F+} \rangle - |M_1 \langle \chi_0 | Q | \chi_1 \rangle|}{F_+} \right| + \left| \frac{|M_{1F-} \langle \chi_{0F-} | Q | \chi_{1F-} \rangle - |M_1 \langle \chi_0 | Q | \chi_1 \rangle|}{F_-} \right| \right)$$

| Molecule              | A  (x10 <sup>-4</sup> )<br>(D/(MV/cm)) <sup>I</sup> | A  (x10 <sup>-4</sup> )<br>(D/(MV/cm)) <sup>II</sup> | A  (x10 <sup>-4</sup> )<br>(literature values)<br>(D/(MV/cm)) <sup>III</sup> |
|-----------------------|---|--|--|
| acetone               | 2.81  | 2.05   | -----  |
| CO                    | 16.05   | 16.60  | -----  |
| CN <sup>-</sup>       | 37.45   | 37.46  | -----  |
| HCN                   | 5.81  | 5.90   | ----- <sup>IV</sup>  |
| ACN                   | 6.61  | 6.63   | 17.7   |
| BCN                   | 17.01   | 17.01  | 33.4   |
| MVK                   | 4.20  | 1.33   | -----  |
| NMP                   | 2.50  | 2.30   | -----  |
| 4-chlorobenzonitrile  | 20.91   | 21.28  | 32.3   |
| 3-chlorobenzonitrile  | 18.26   | 18.43  | 27.4   |
| 2-chlorobenzonitrile  | 15.40   | 15.38  | 29.0   |
| 4-methoxybenzonitrile | 21.31   | 21.85  | 16.3   |
| propionitrile         | 7.28  | 7.29   | 17.3   |
| butyronitrile         | 8.04  | 8.04   | 17.7   |
| valeronitrile         | 8.54  | 8.54   | 7.67   |
| hexanenitrile         | 8.86  | 8.86   | 8.34   |

# Correlation of A



# DFT case study CO in myoglobin

Calculate frequencies of CO vibrations in various geometries  
Compare to experiment and determine calibration  
of frequency, bond length and Mulliken charge.

A states - CO bound states. There are often multiple CO stretching frequencies. These have been attributed to specific interactions with residues such as histidine.

B states - Photolyzed CO states. CO is trapped inside the protein and yet its frequency is shifted due to interactions with particular groups.



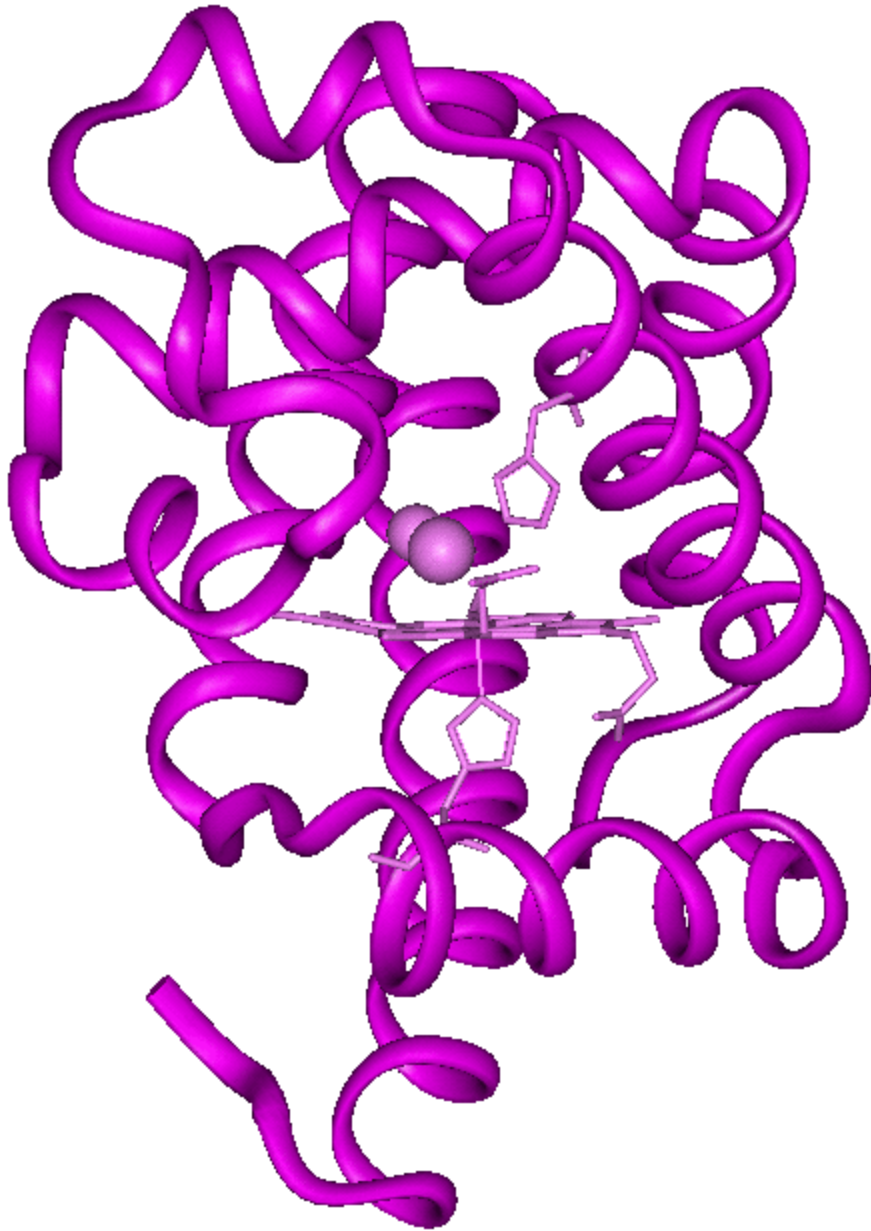
# MbCO

The peptide backbone is shown as a ribbon that follows the  $\alpha$ -helical structure of myoglobin.

The structure shown is at equilibrium.

Conformational substates are called **A states**.

Teng, Srajer, Moffat  
Nature Struct. Biol. (1994), 1, 701



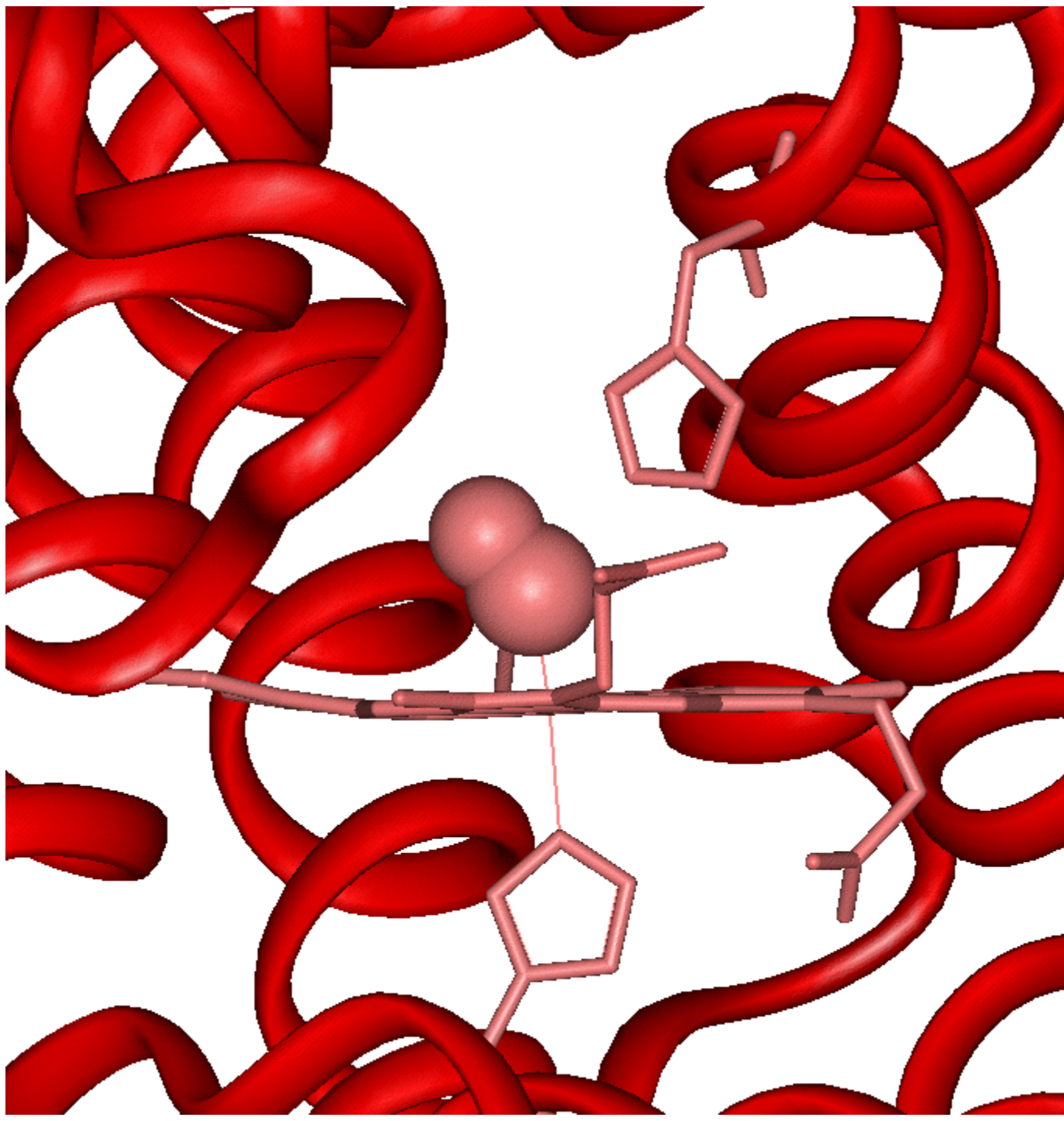
## Mb:CO

The photoproduct.

Iron moves out of the heme plane when CO is photolyzed.

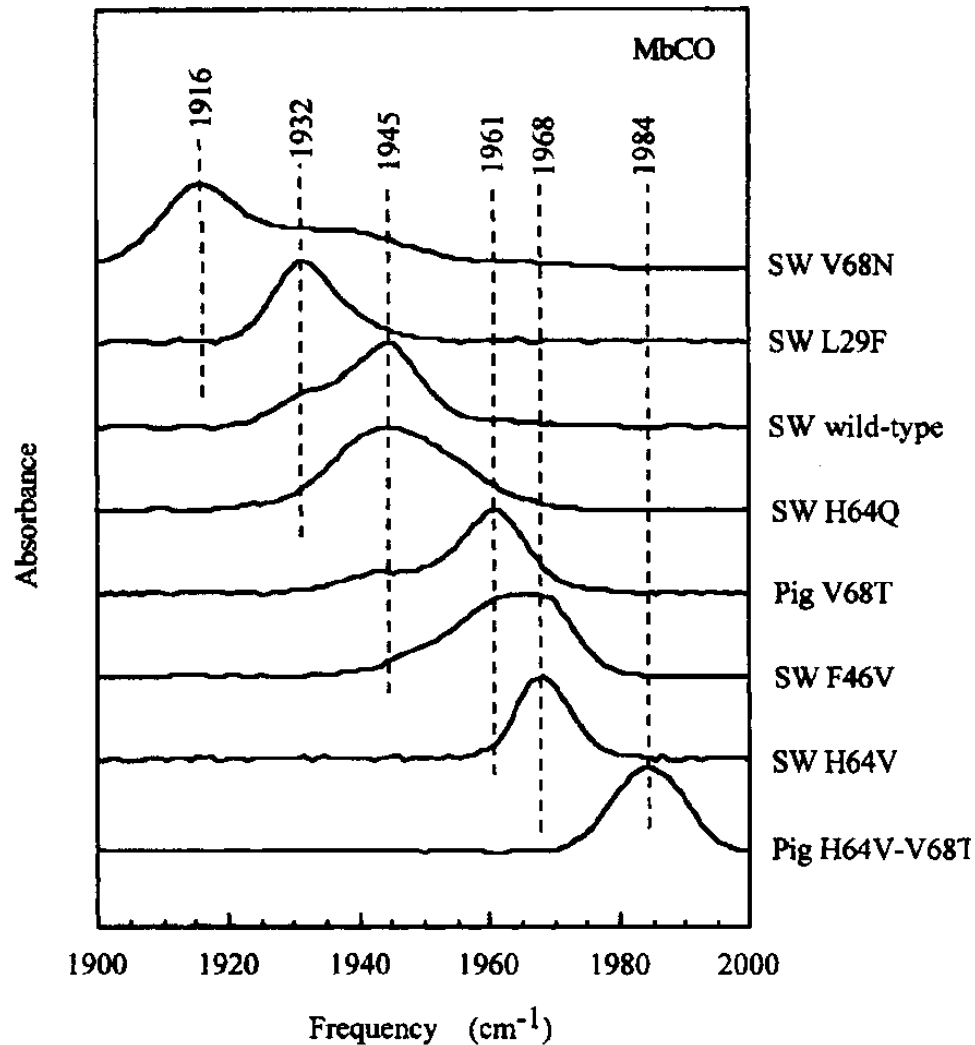
CO moves to a docking site and is parallel to the heme plane.

Conformational substates are called **B states**.

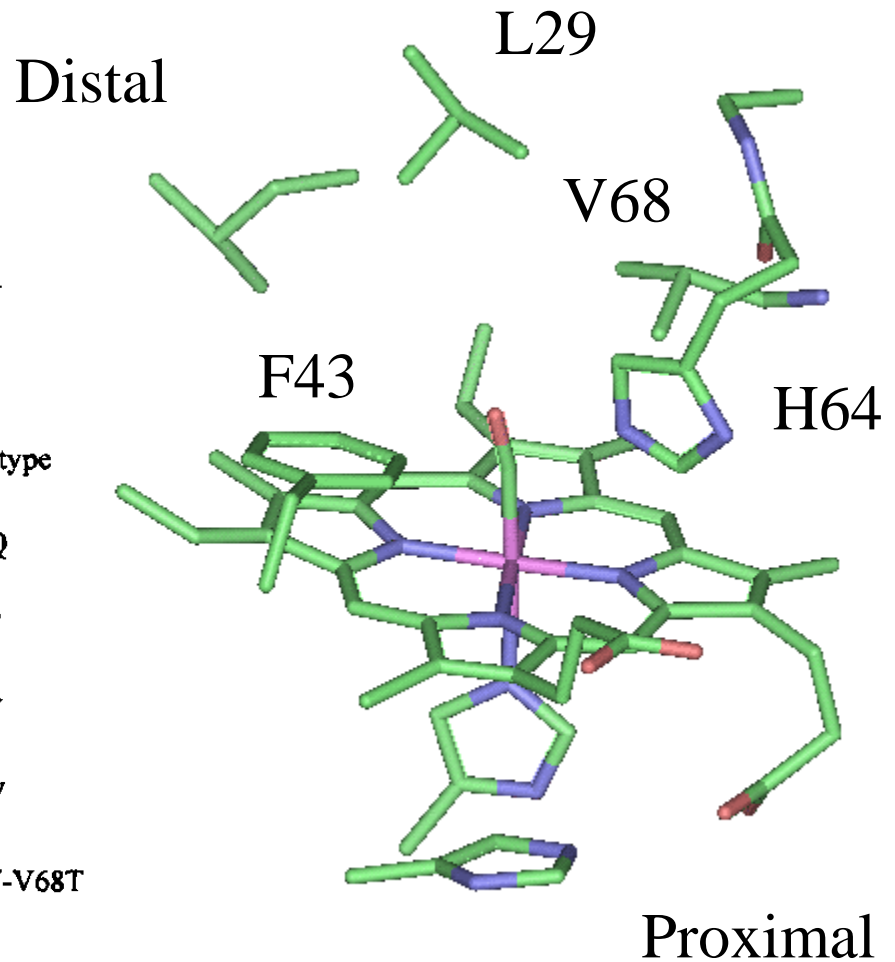
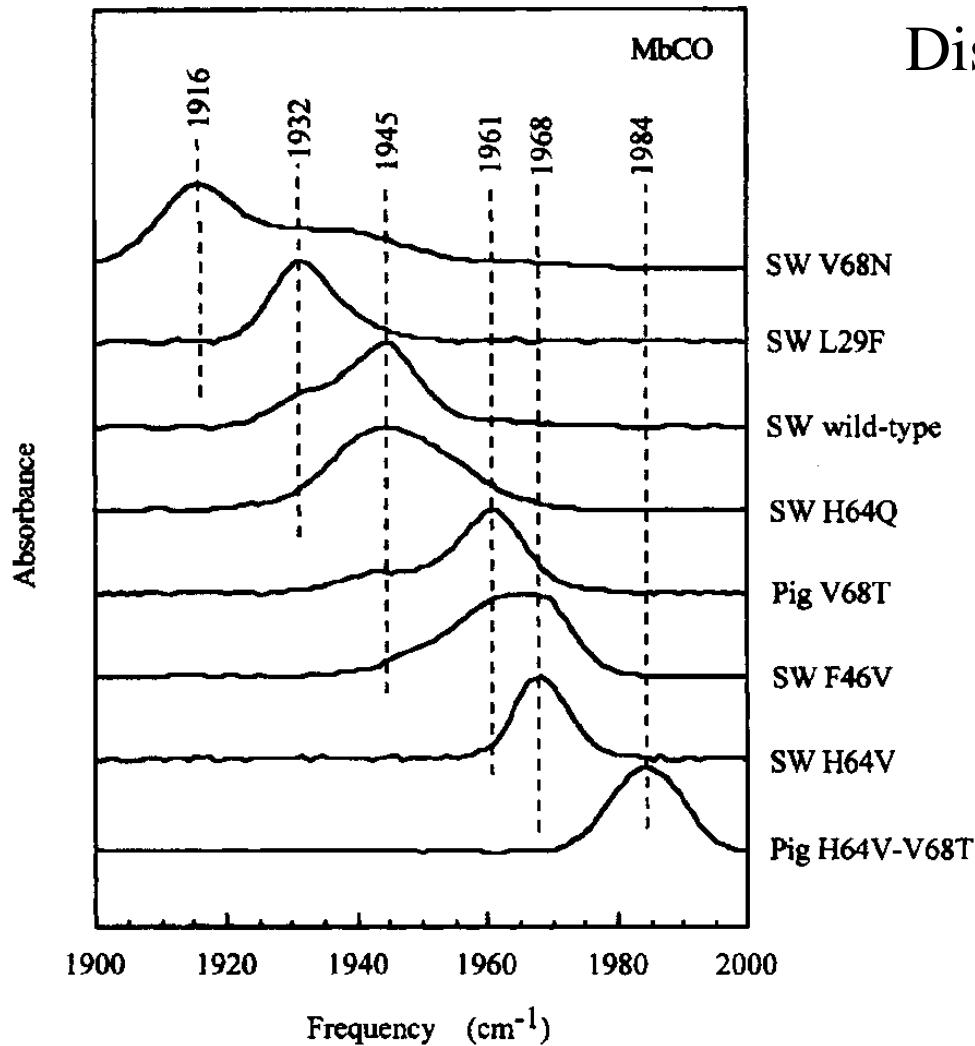




# The origin of the A states is the hydrogen bonding conformations to CO

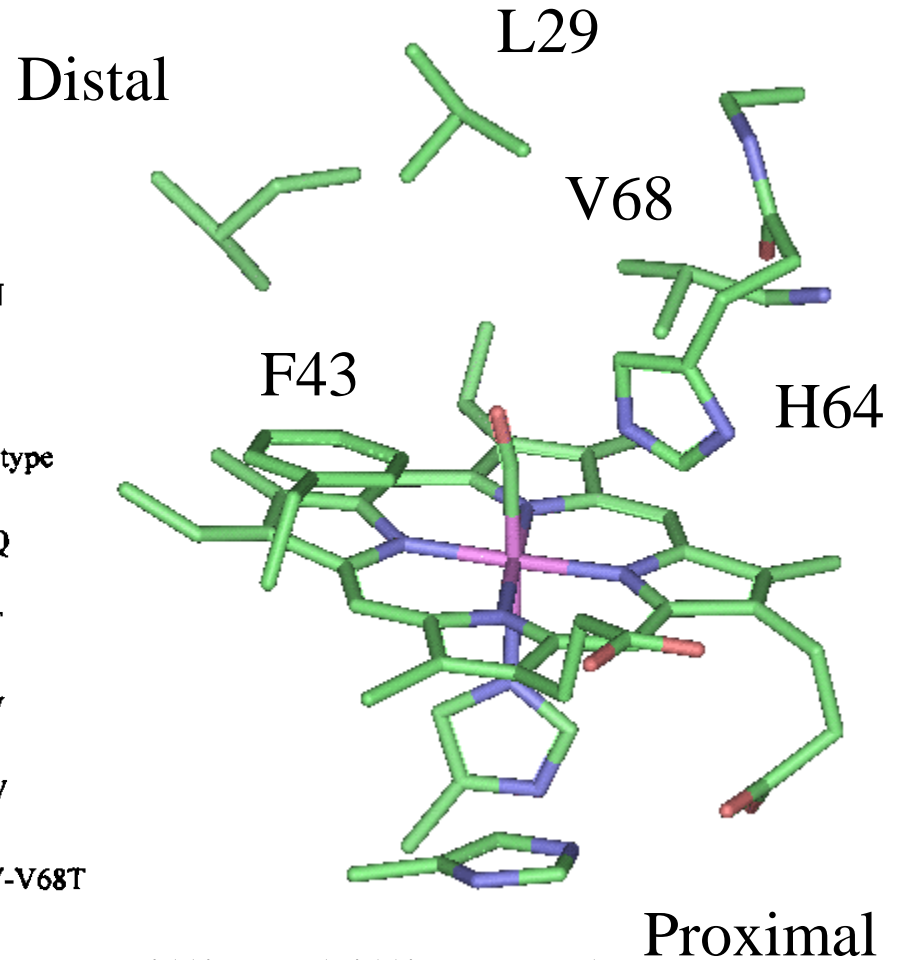
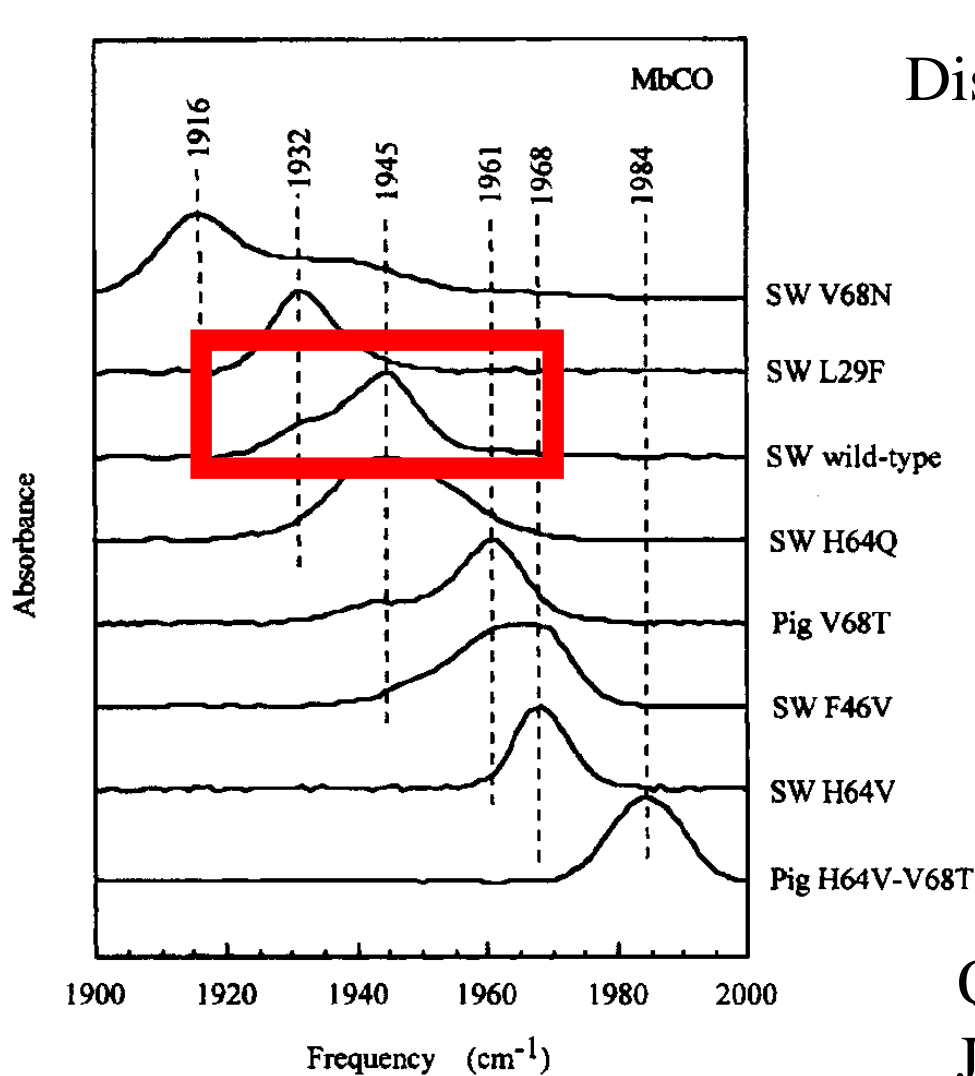


# A view of the distal pocket



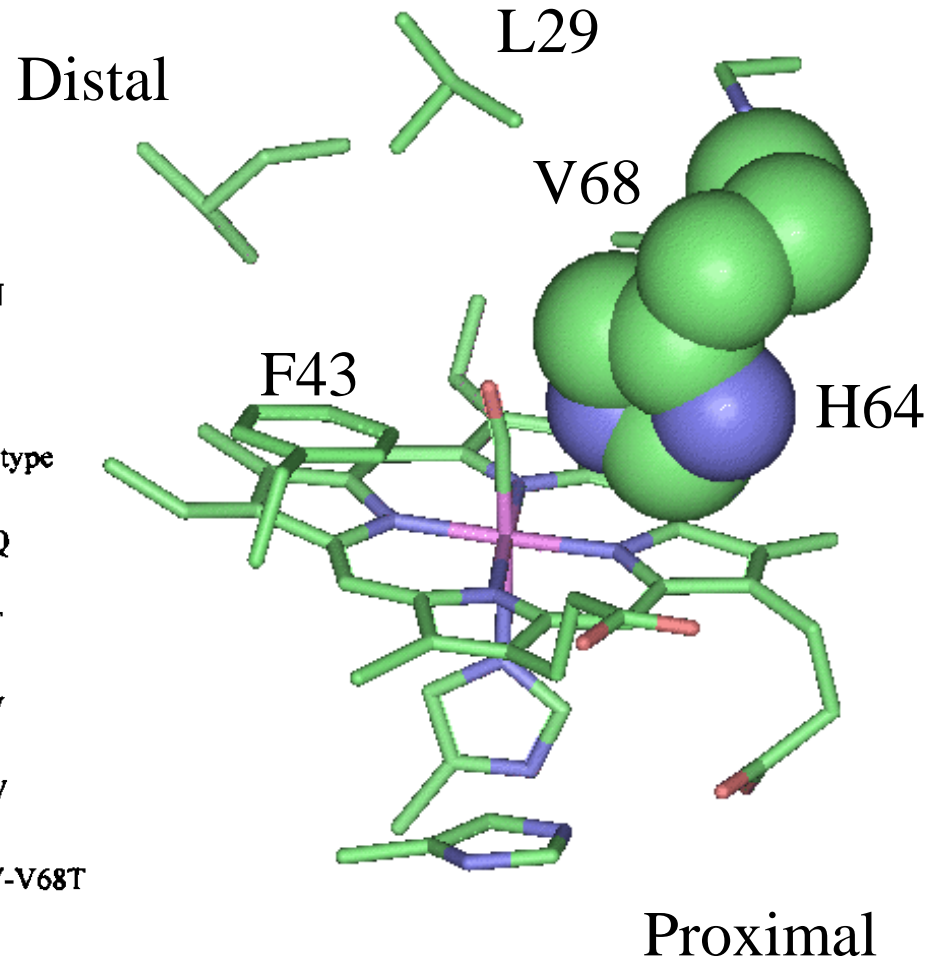
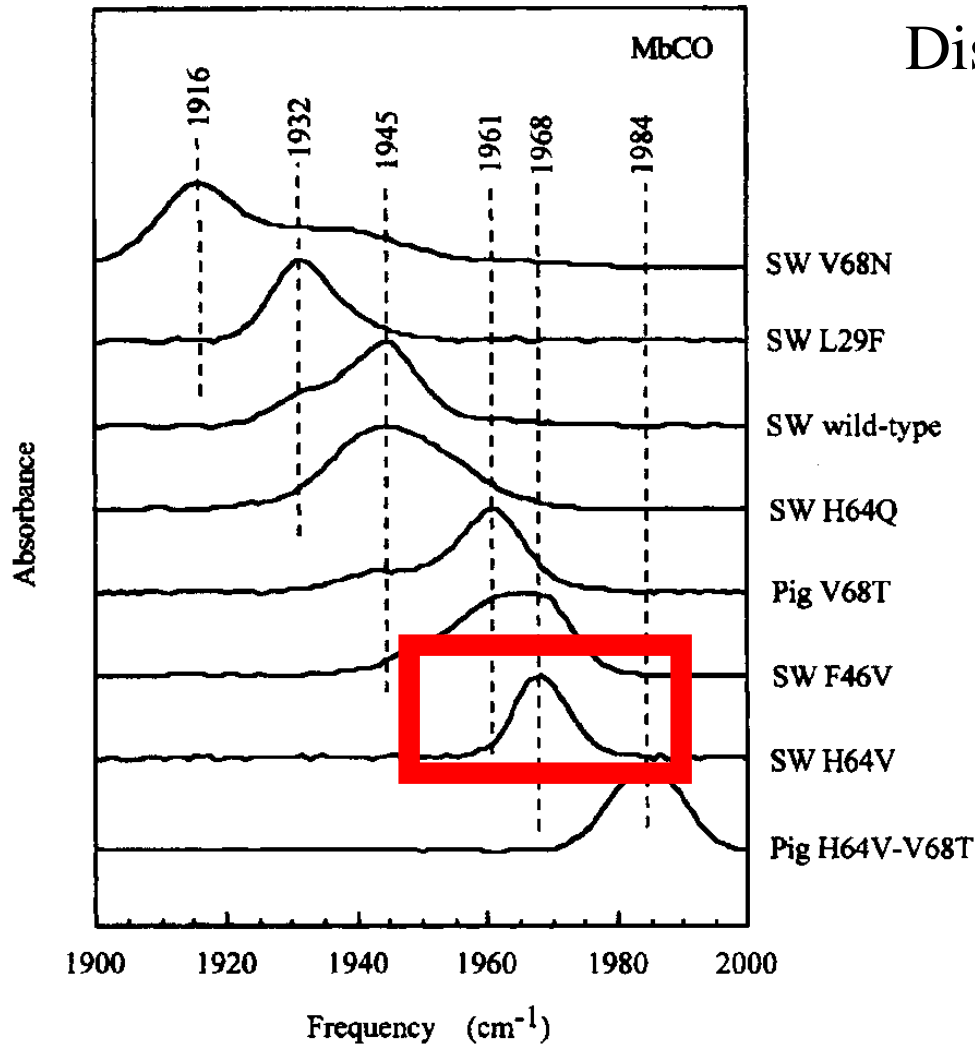
Protein Data Bank 2MGK

# Wild-type has multiple CO bands

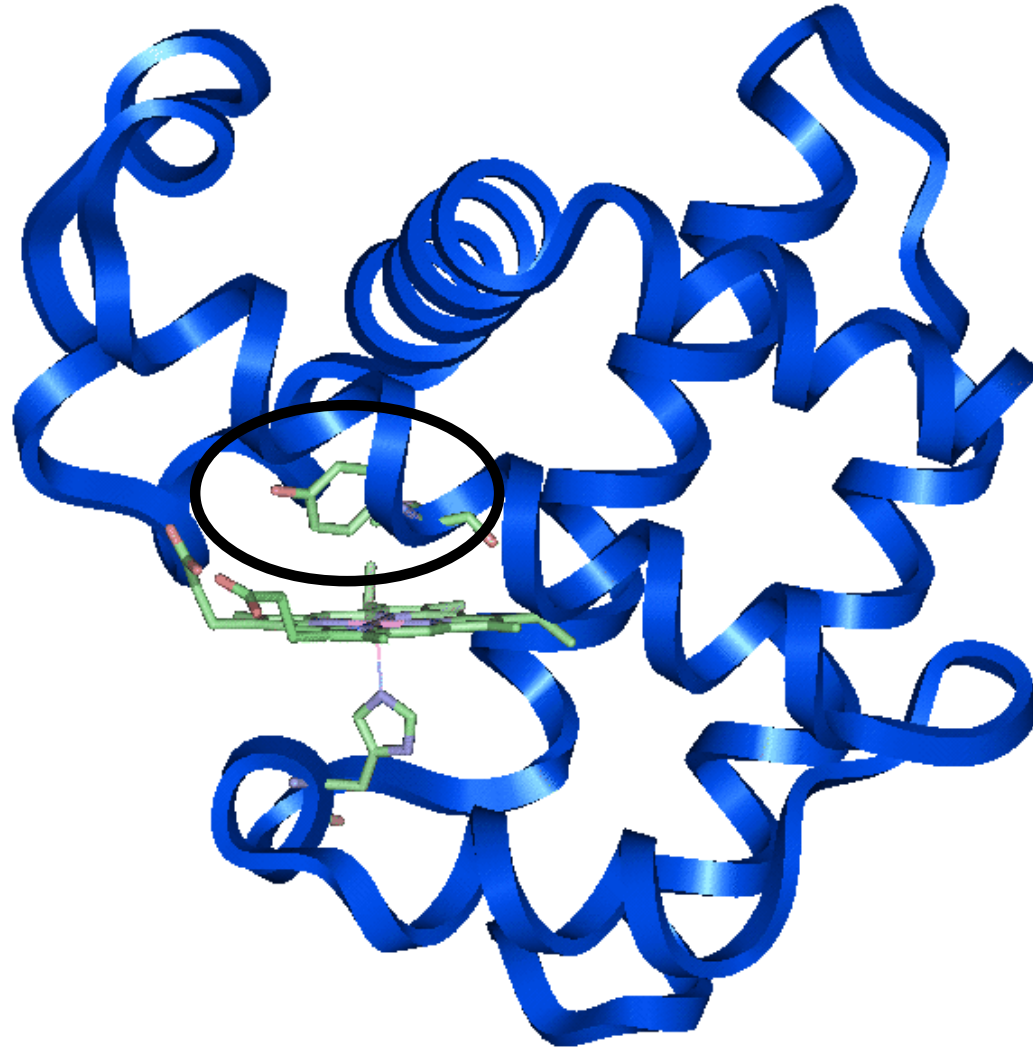


Quillin, Phillips et al.  
JMB 1993, 234, 140-155

# Distal histidine is key

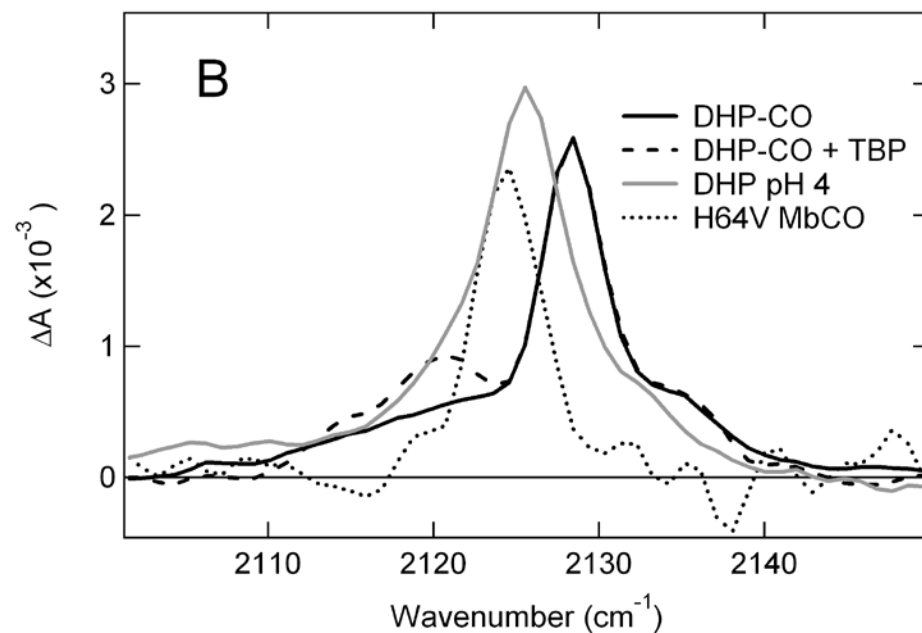
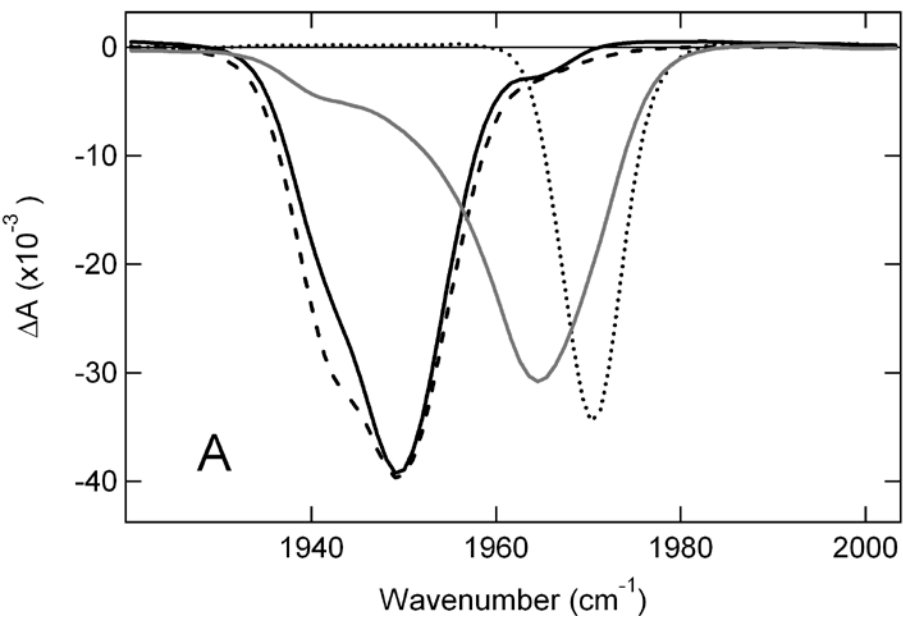


The substrate of DHP binding site is in the heme pocket

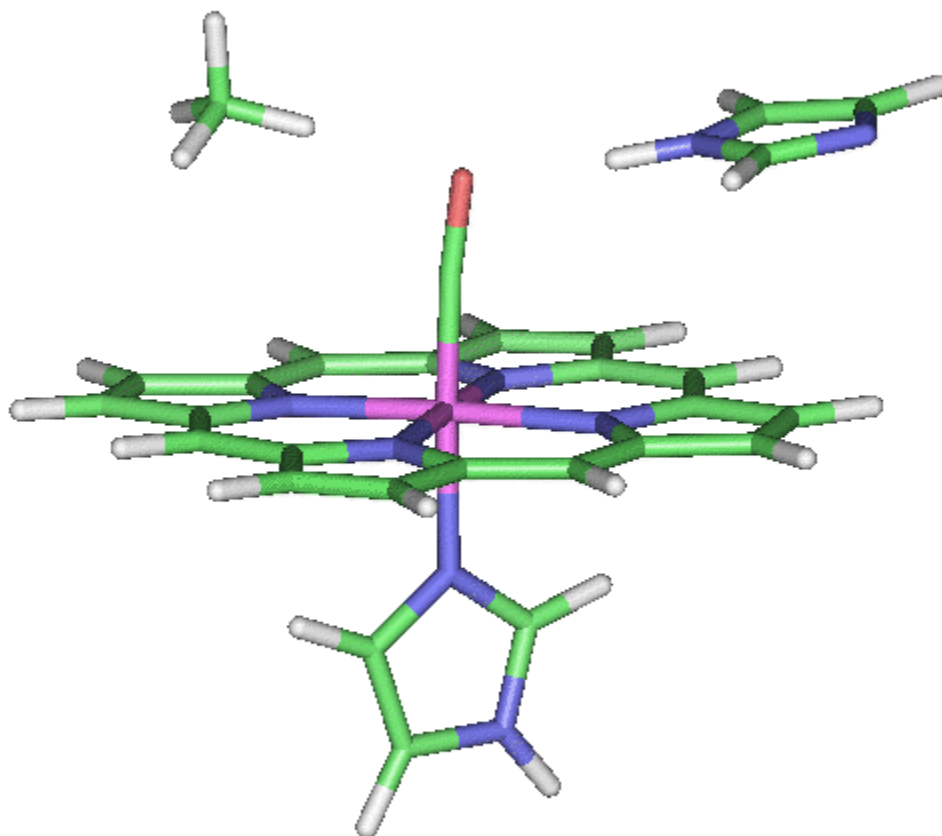


Lebioda et al., J.Biol.Chem. (2000) 275, 18712

# A-state and B-state CO vibrations in DHP

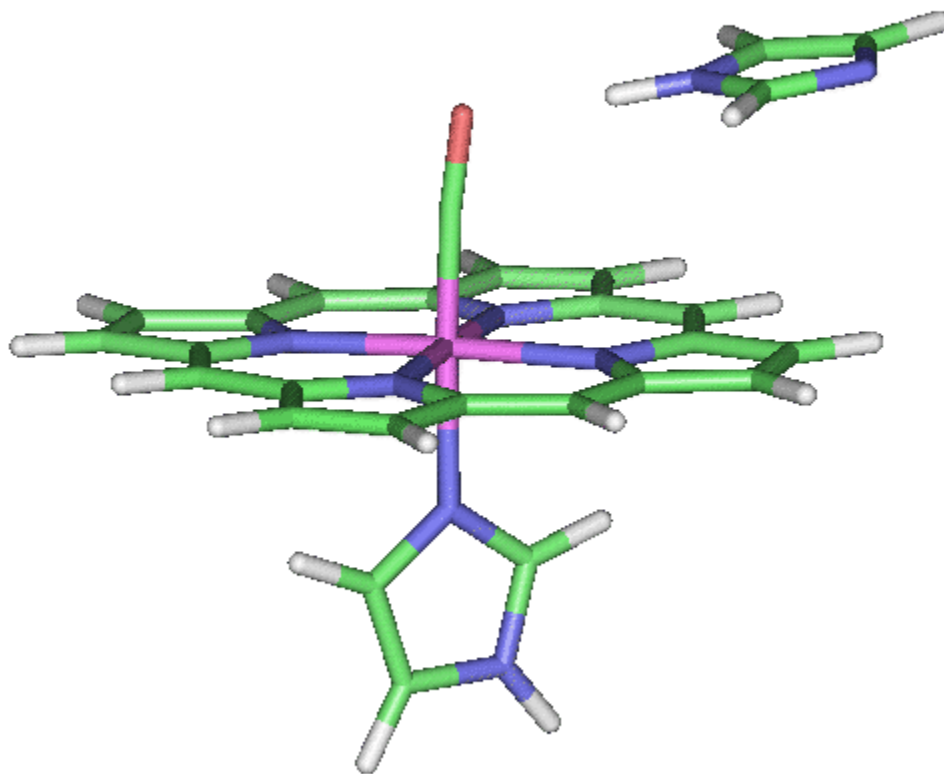


# DFT calculation of $\nu_{\text{CO}}$ frequencies



Multiple hydrogen bonding interactions

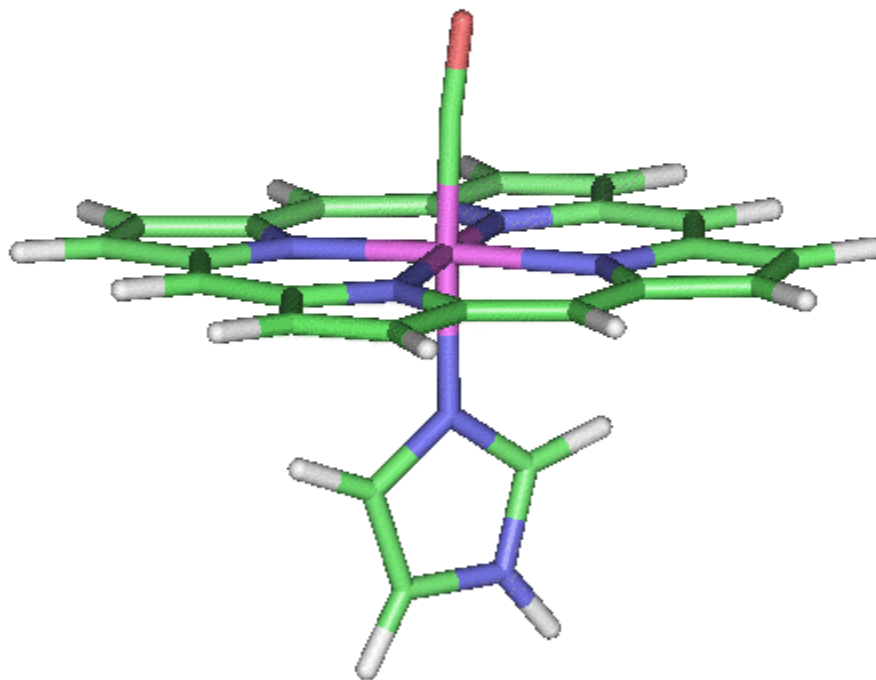
# DFT calculation of $\nu_{\text{CO}}$ frequencies



Single hydrogen bonding interaction



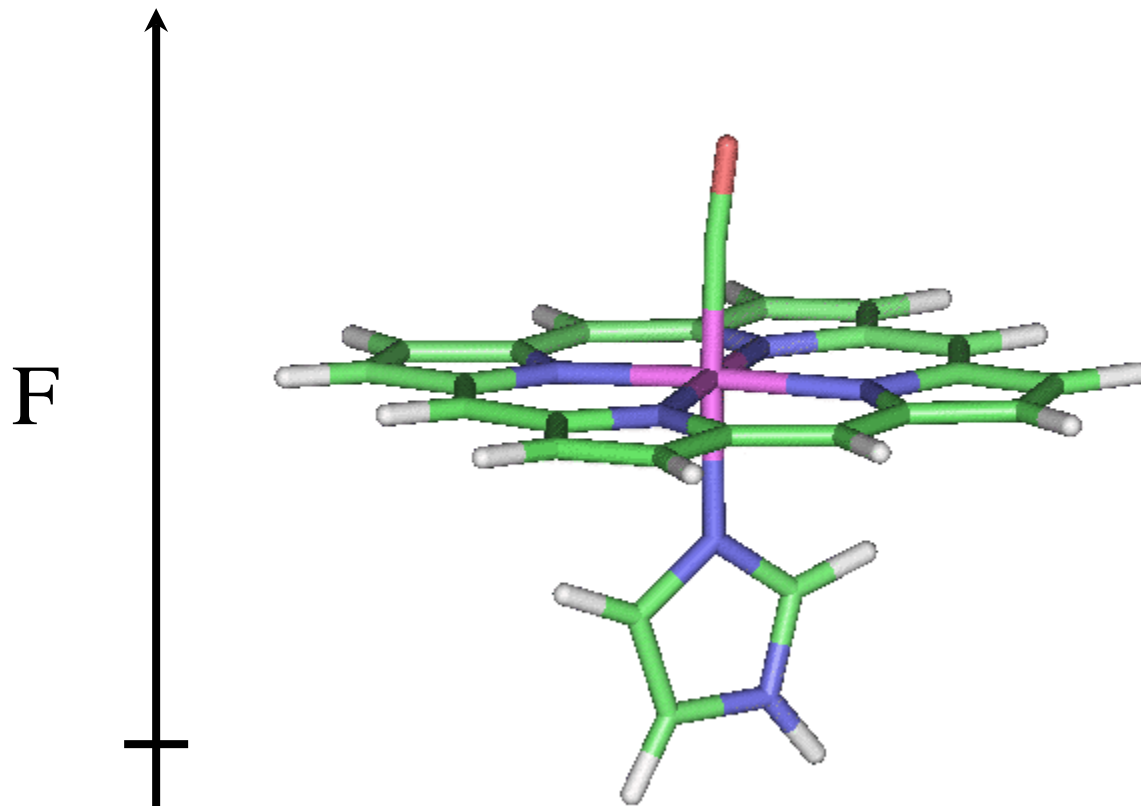
# DFT calculation of $\nu_{\text{CO}}$ frequencies



No hydrogen bonding interaction

# DFT calculation in an applied electric field

+ + + + + + + + + + +



# Electric field effect by DFT

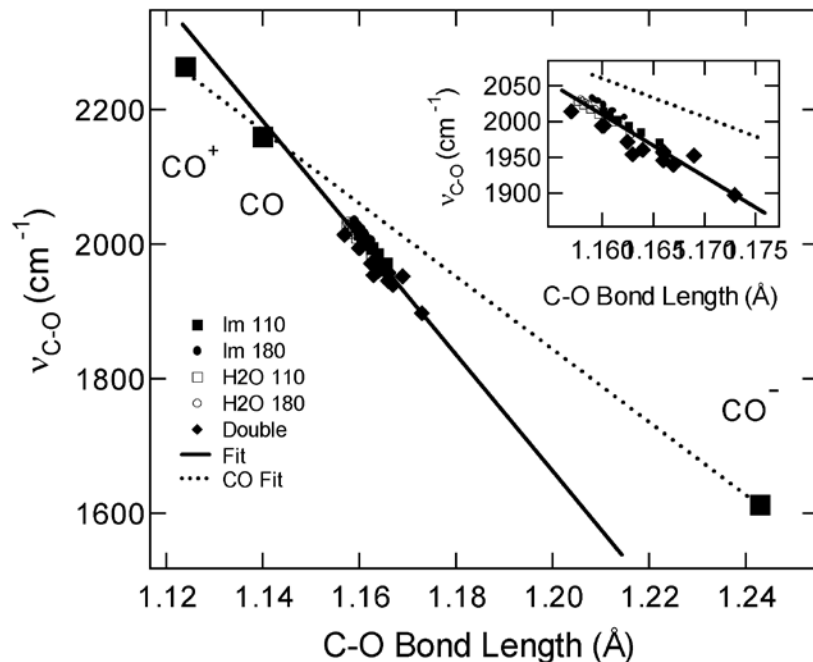
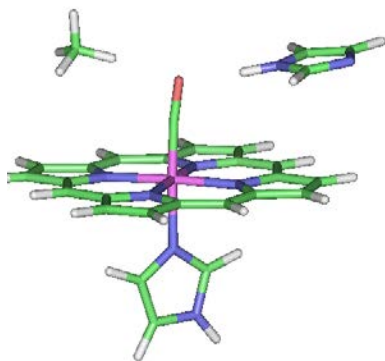
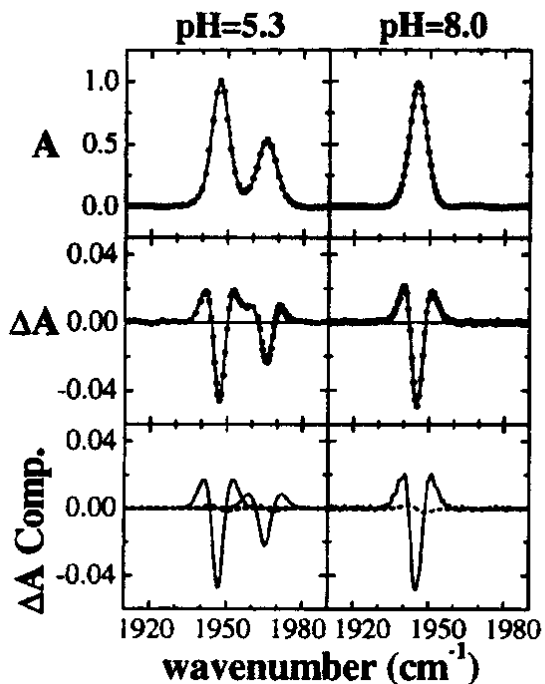
| MV/cm | Fe-C   | C-O    | $q_C$ | $q_O$  | $q_C+q_O$ | $q_C-q_O$ | $\nu_{CO}$ Eqn. 1 | $\nu_{CO}$ Eqn. 2 | $\nu_{CO}$ Eqn. 2 |
|-------|--------|--------|-------|--------|-----------|-----------|-------------------|-------------------|-------------------|
| -1    | 1.7864 | 1.1569 | 0.190 | -0.237 | -0.047    | 0.427     | 2021.4            | 2021.8            | 2015.7            |
| -0.5  | 1.7865 | 1.1572 | 0.190 | -0.238 | -0.048    | 0.428     | 2018.7            | 2020.3            | 2015.0            |
| 0     | 1.7861 | 1.1572 | 0.190 | -0.239 | -0.049    | 0.429     | 2018.7            | 2018.9            | 2014.5            |
| 0.5   | 1.7861 | 1.1573 | 0.190 | -0.239 | -0.049    | 0.429     | 2017.9            | 2018.8            | 2014.5            |
| 1     | 1.7858 | 1.1575 | 0.190 | -0.240 | -0.050    | 0.430     | 2016.2            | 2017.3            | 2013.8            |

Correlation is based on distance or Mulliken charge.

$$\nu_{CO} = 2168 - 8677 (R_{CO} - R_{CO}^0) \quad (1)$$

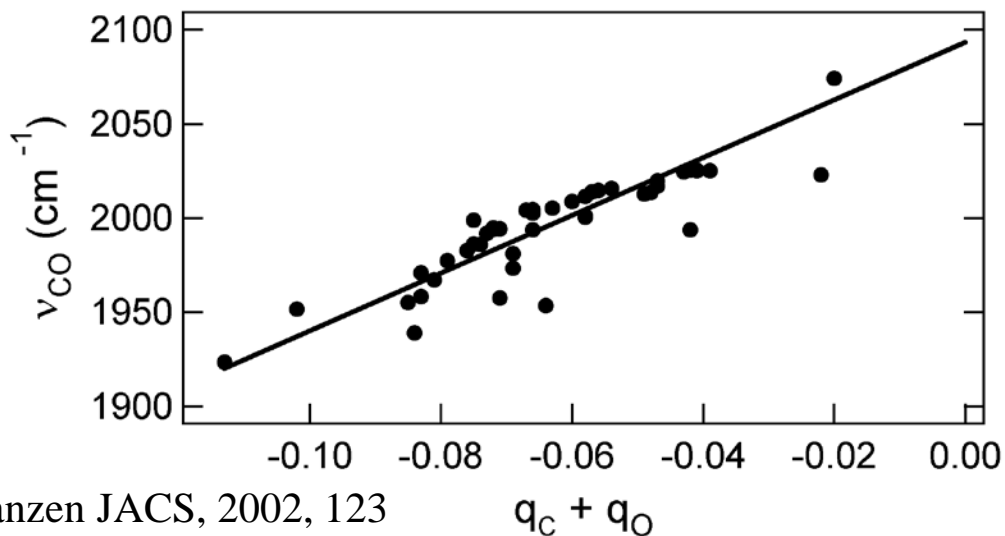
$$\nu_{CO} = \{2094 + 1535(q_C + q_O)\} \text{ cm}^{-1} \quad (2)$$

# DFT calculation of $\nu_{\text{CO}}$ frequencies



Stark tuning rate is  
 $2.4 \text{ cm}^{-1}/(\text{MV}/\text{cm})$ .  
 This is value predicted  
 from correlations shown  
 on right.

Park and Boxer  
 JPC 1999, 103, 9013

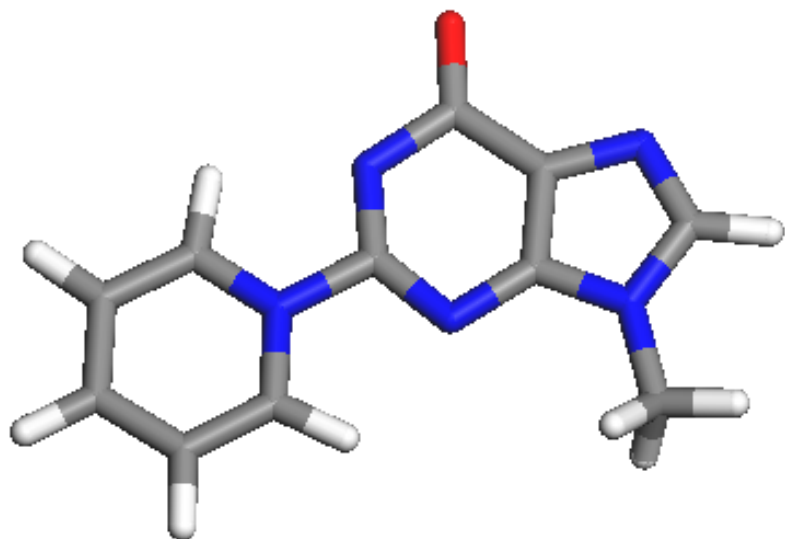


Franzen JACS, 2002, 123

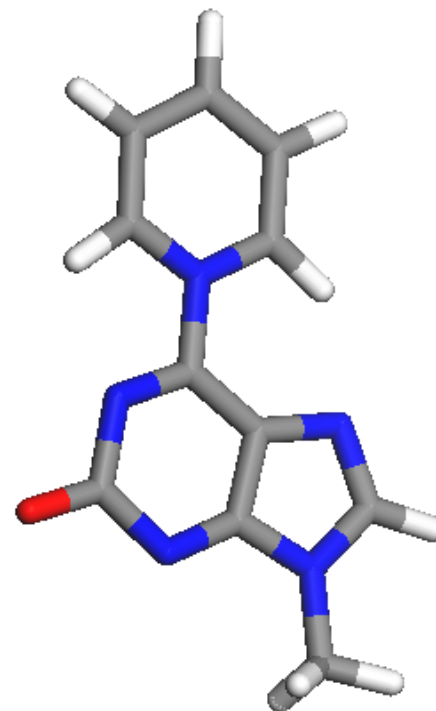
# Solvatochromism and Electrochromism by DFT

**NC State University**

# Xanthine Pyridinium Betaines



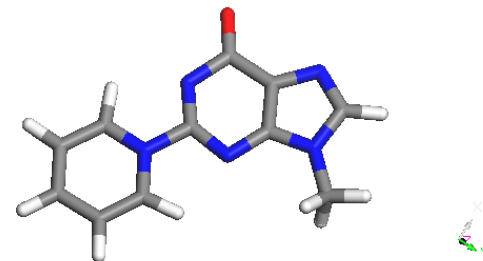
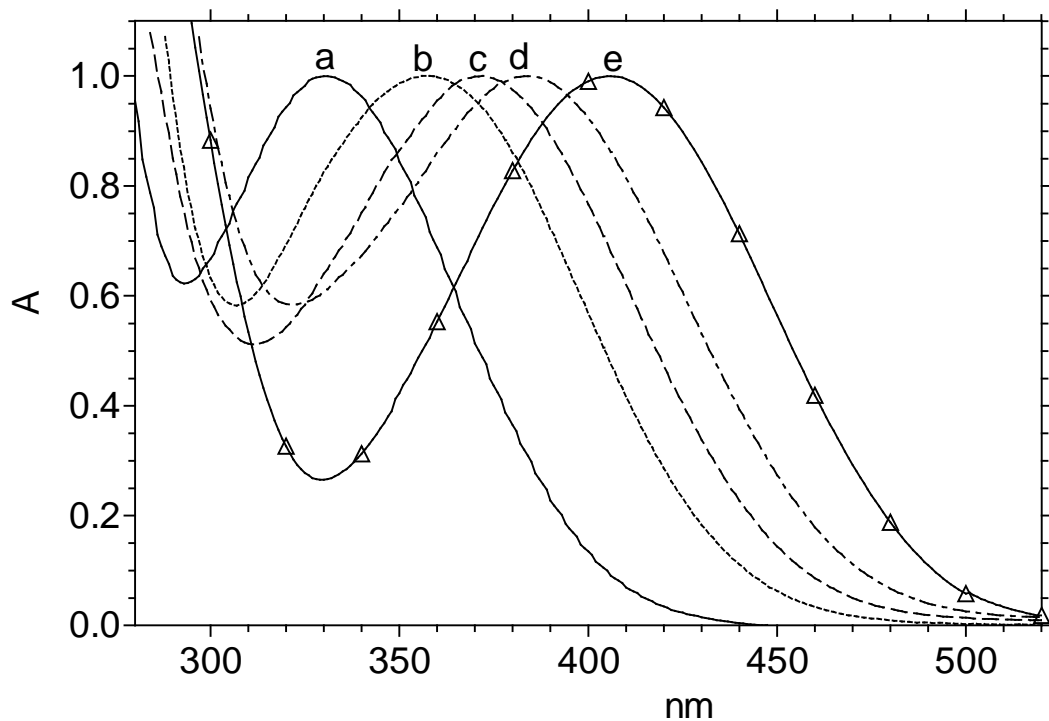
XPBM



XPBRM

A new class of solvatochromic molecules

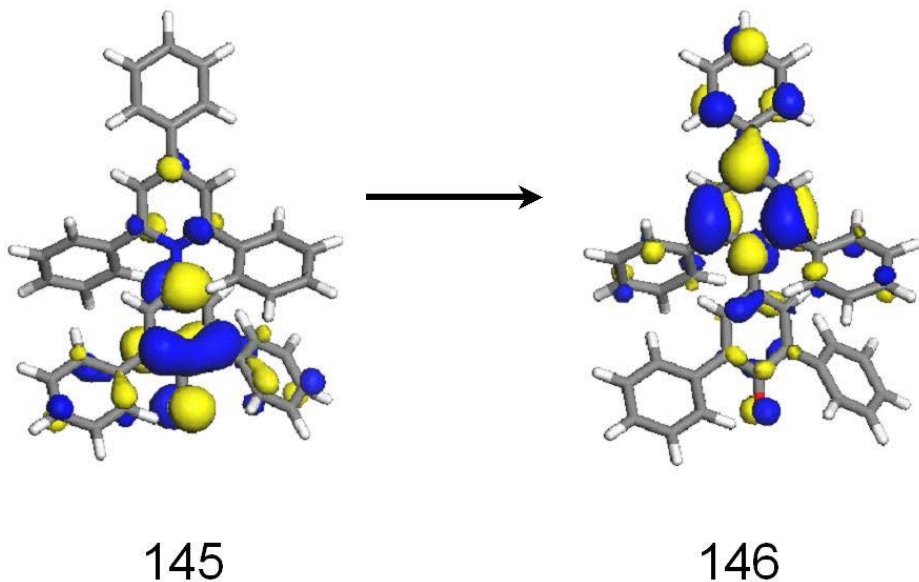
# Solvatochromism: solvent effect on absorption spectrum



- a Water
- b Ethanol
- c Butanol
- d Dimethylsulfoxide
- e Chloroform

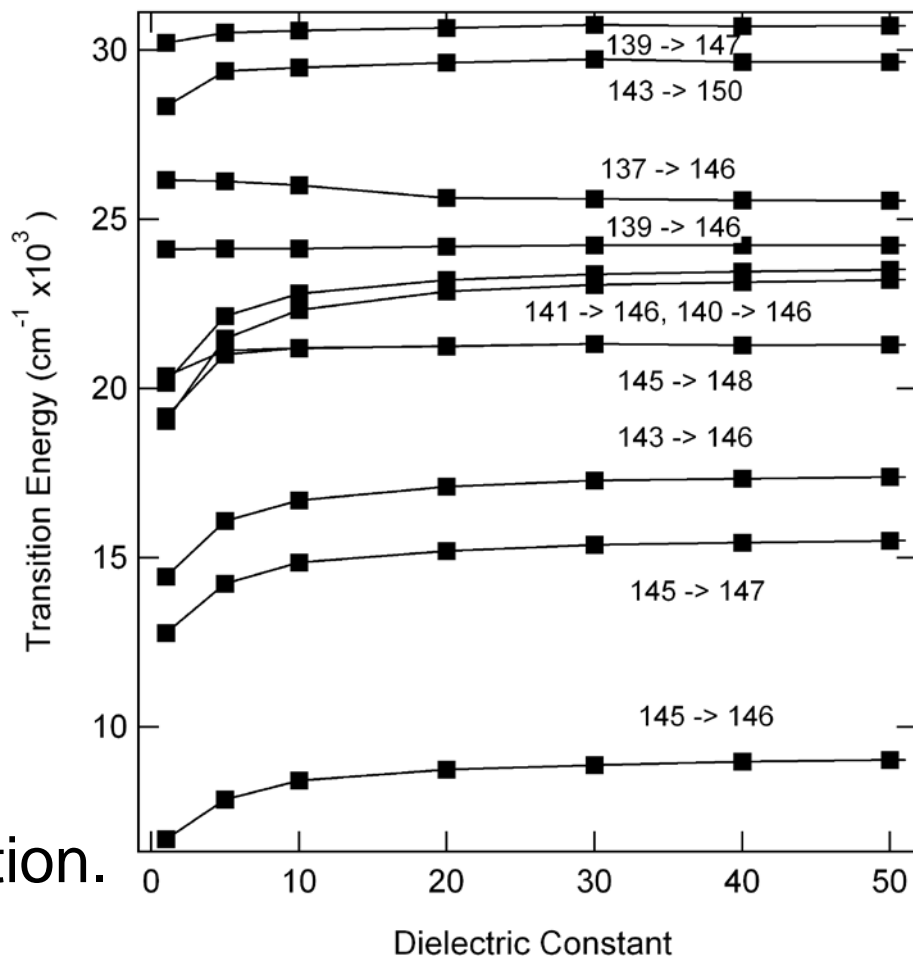
XPBs, a new class of solvatochromic molecules.

# Origin of Solvatochromism



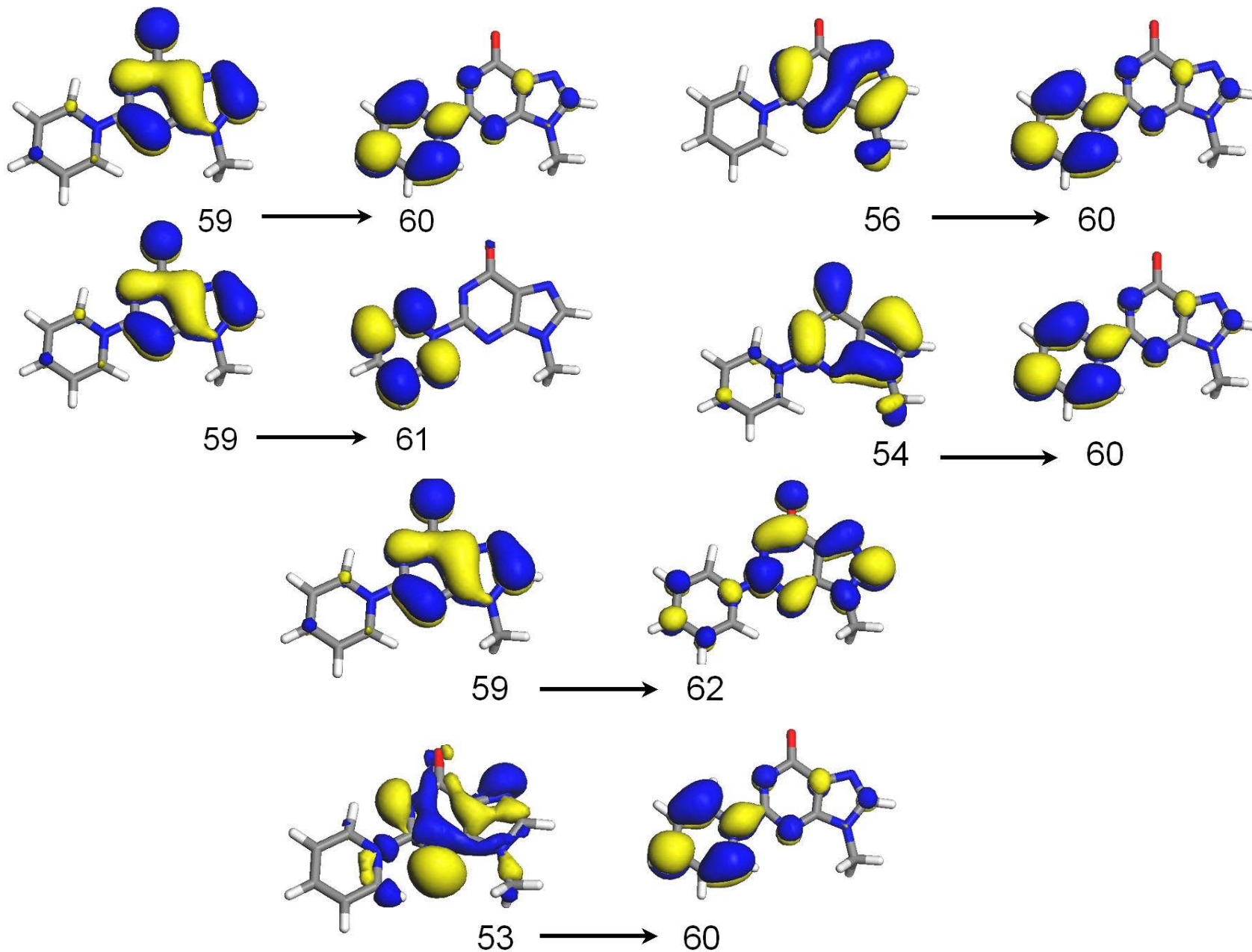
TD-DFT calculation shows that this is the intense transition. Energy is  $11,871 \text{ cm}^{-1}$ .

Classic solvatochromic molecule: Reichardt's dye  
Basis for the  $E_T(30)$  solvent polarity scale

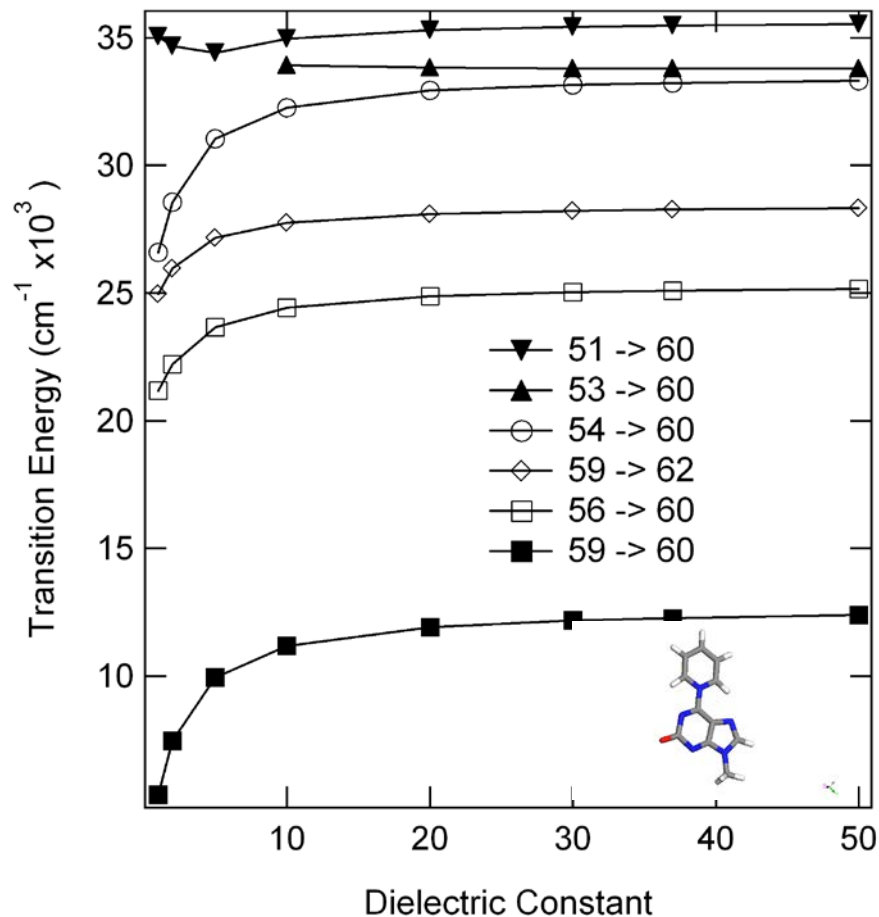
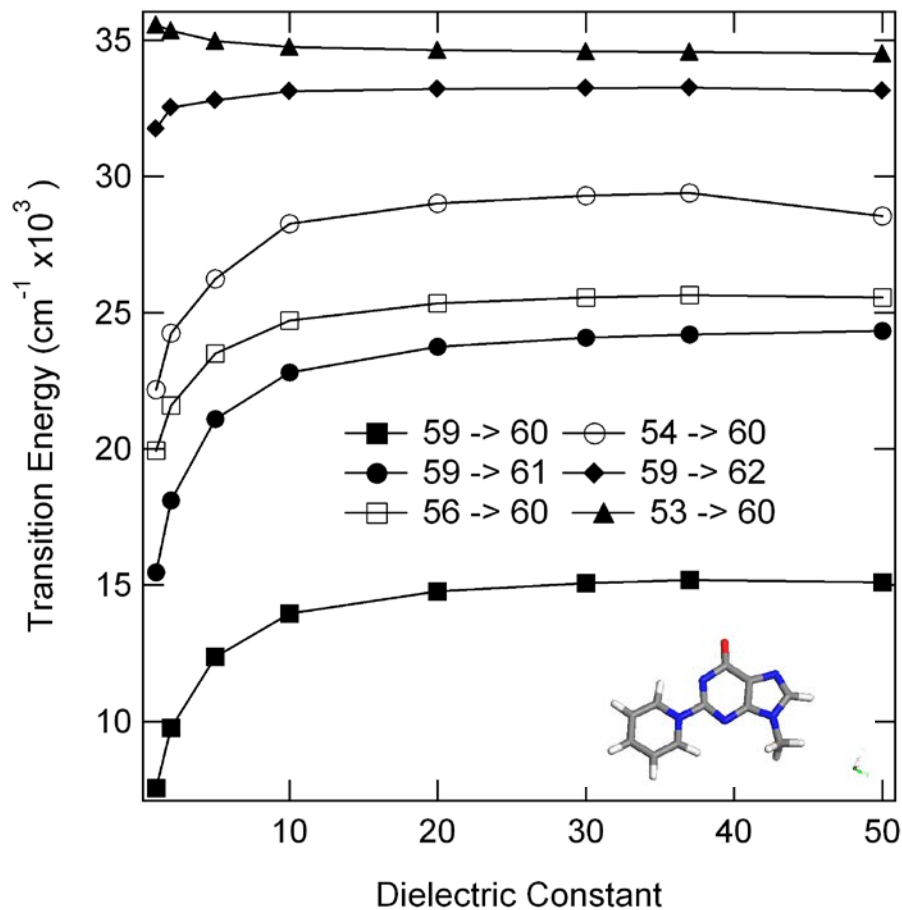




# Calculated transitions for XPBM

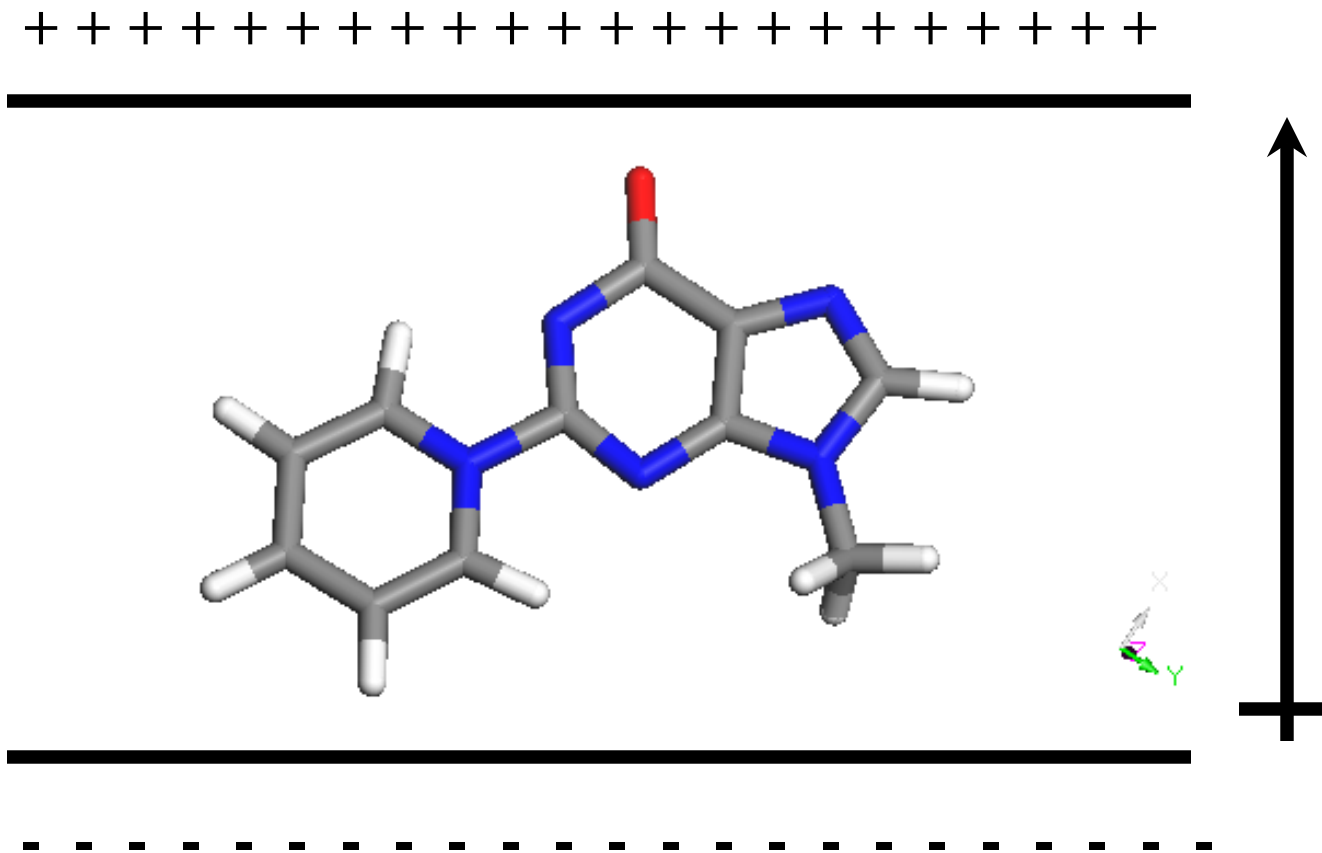


# DFT calculation of solvatochromism

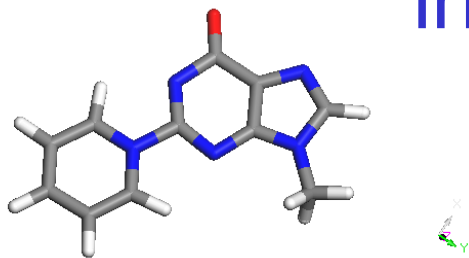


Use COSMO continuum dielectric model to obtain absorption spectra as a function of  $\epsilon$ . This is a model for solvatochromism.

# Electrochromism: the shift of the absorption spectrum in an applied electric field

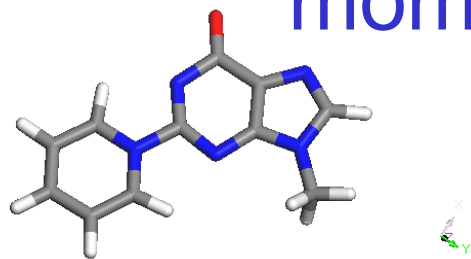


# Calculated electrochromism using DFT: Obtain the shift in wavenumber in an applied field



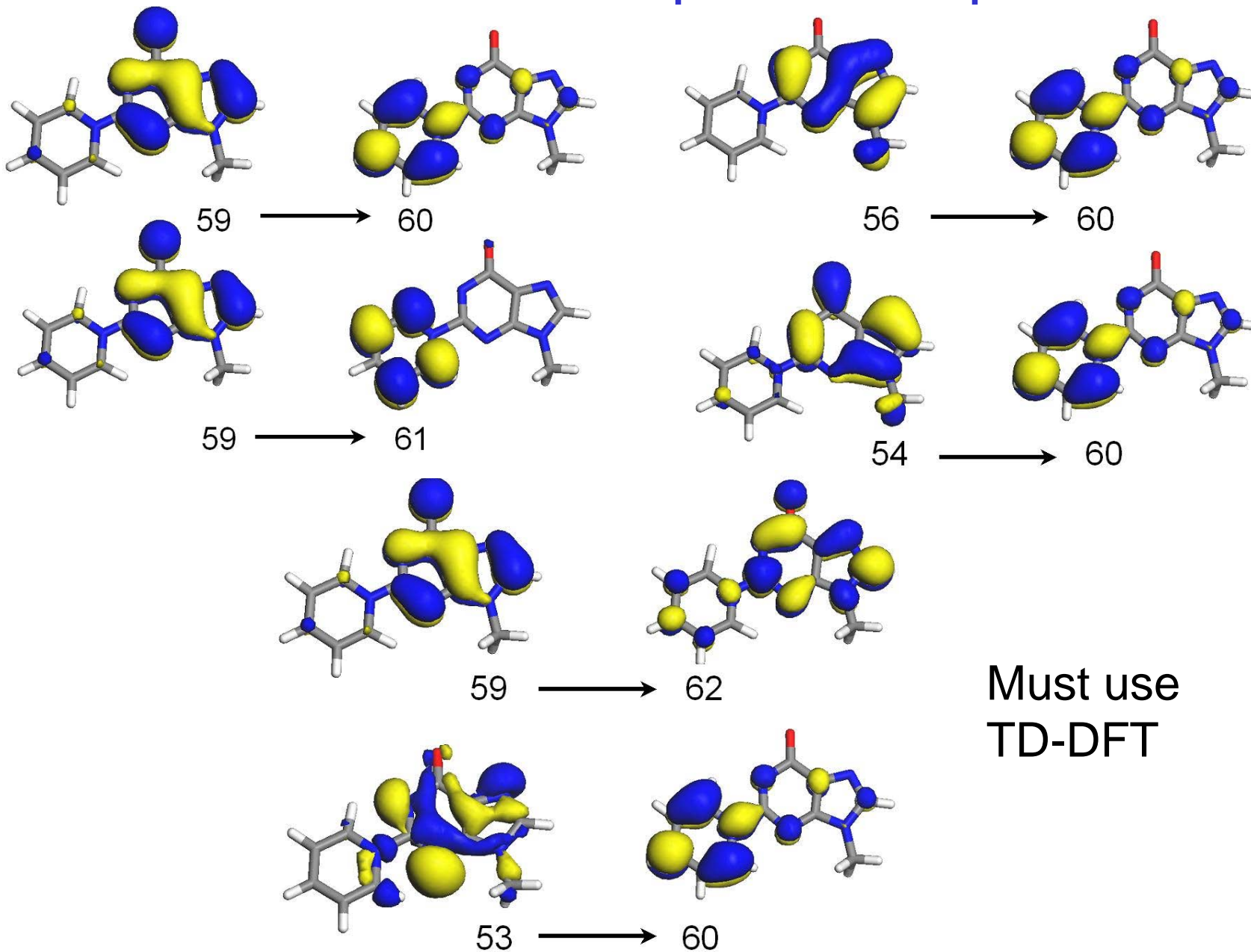
| Transition | $\epsilon = 1$ | $\epsilon = 5$ | $\epsilon = 10$ | $\epsilon = 15$ | $\epsilon = 20$ | $\epsilon = 30$ |
|------------|----------------|----------------|-----------------|-----------------|-----------------|-----------------|
| 59 → 60    | 605.5          | 1215.1         | 1333.7          | 1373.4          | 1393.2          | 1413.0          |
| 59 → 61    | 726.1          | 1411.0         | 1542.3          | 1588.0          | 1610.9          | 1633.7          |
| 56 → 60    | 703.1          | 1342.3         | 1469.5          | 1509.5          | 1529.5          | 1549.4          |
| 54 → 60    | 759.2          | 1322.2         | 1390.1          | 1416.8          | 1429.2          | 1440.5          |
| 59 → 62    | 153.2          | 119.3          | 69.1            | 60.8            | 56.1            | 51.7            |
| 53 → 60    | 211.9          | 595.6          | 219.3           | 194.8           | 197.3           | 200.8           |
| 59 → 63    | 46.9           | 126.5          | 179.4           | 445.1           | 209.2           | 276.1           |

# Calculated electrochromism using DFT: Convert the shift into a difference dipole moment using $U = -\Delta\mu \cdot F$



| Transition | $\epsilon = 1$ | $\epsilon = 5$ | $\epsilon = 10$ | $\epsilon = 15$ | $\epsilon = 20$ | $\epsilon = 30$ |
|------------|----------------|----------------|-----------------|-----------------|-----------------|-----------------|
| 59 → 60    | 3.5            | 7.0            | 7.6             | 7.9             | 8.0             | 8.1             |
| 59 → 61    | 4.2            | 8.1            | 8.8             | 9.1             | 9.2             | 9.4             |
| 56 → 60    | 4.0            | 7.7            | 8.4             | 8.7             | 8.8             | 8.9             |
| 54 → 60    | 4.4            | 7.6            | 8.0             | 8.1             | 8.2             | 8.3             |
| 59 → 62    | 0.89           | 0.68           | 0.40            | 0.35            | 0.32            | 0.30            |
| 53 → 60    | 1.2            | 3.4            | 1.3             | 1.1             | 1.1             | 1.2             |
| 59 → 63    | 0.27           | 0.73           | 1.0             | 2.5             | 1.2             | 1.6             |

# Which transitions correspond to experiment?

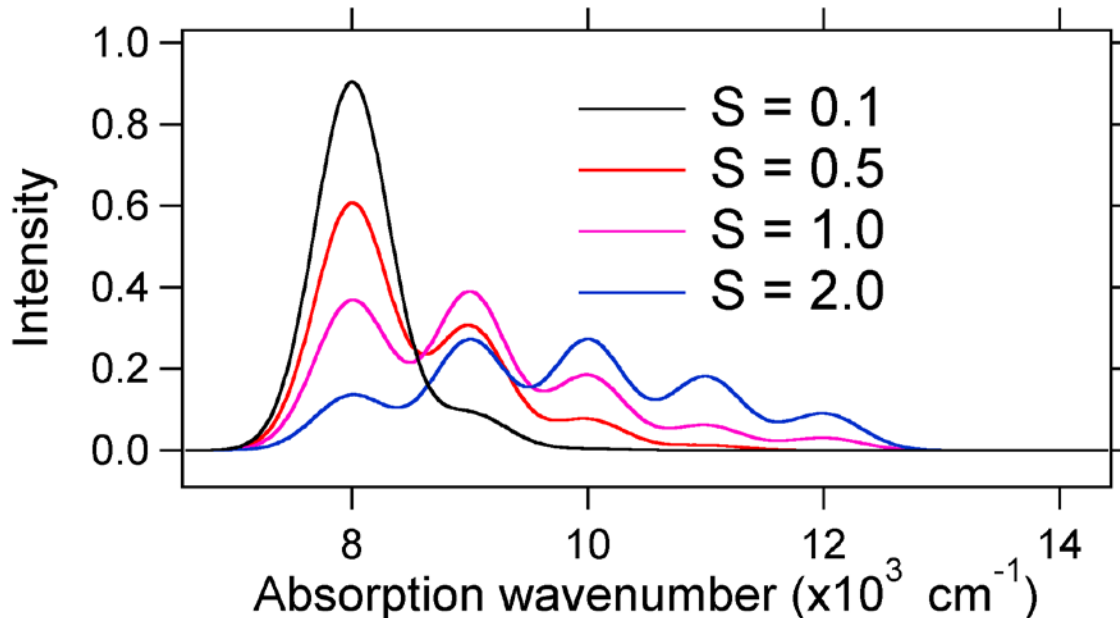
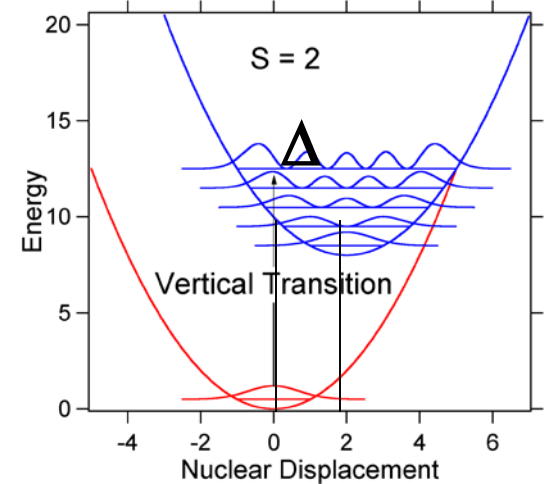
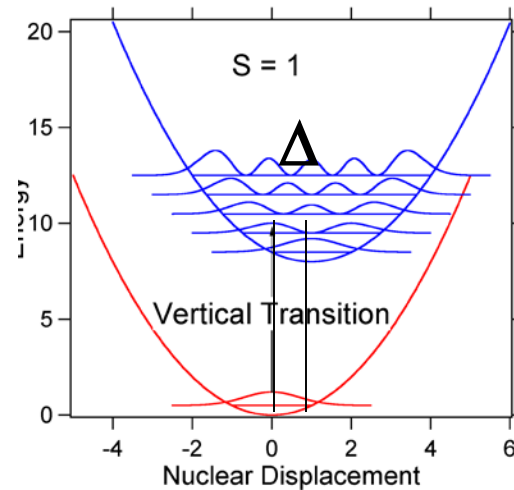
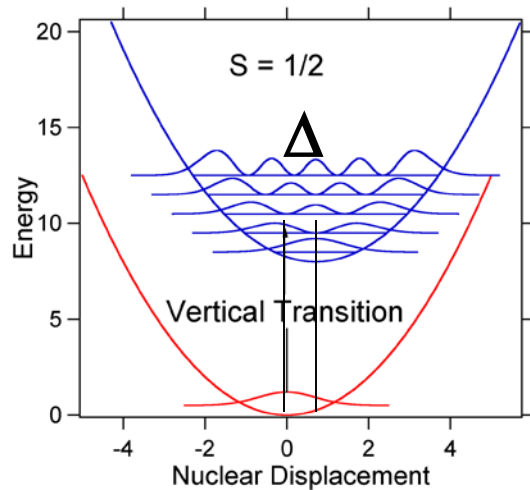


Must use  
TD-DFT

# Calculating Resonant Raman Cross Sections

- Perform an optical absorption calculation
- Identify relevant states (e.g. four orbital model)
- Perform a vibrational frequency calculation
- Project along eigenvectors for each normal mode
- Plot potential energy surfaces and determine displacements
- Use dimensionless deltas in time correlator to calculate  $\sigma_R$

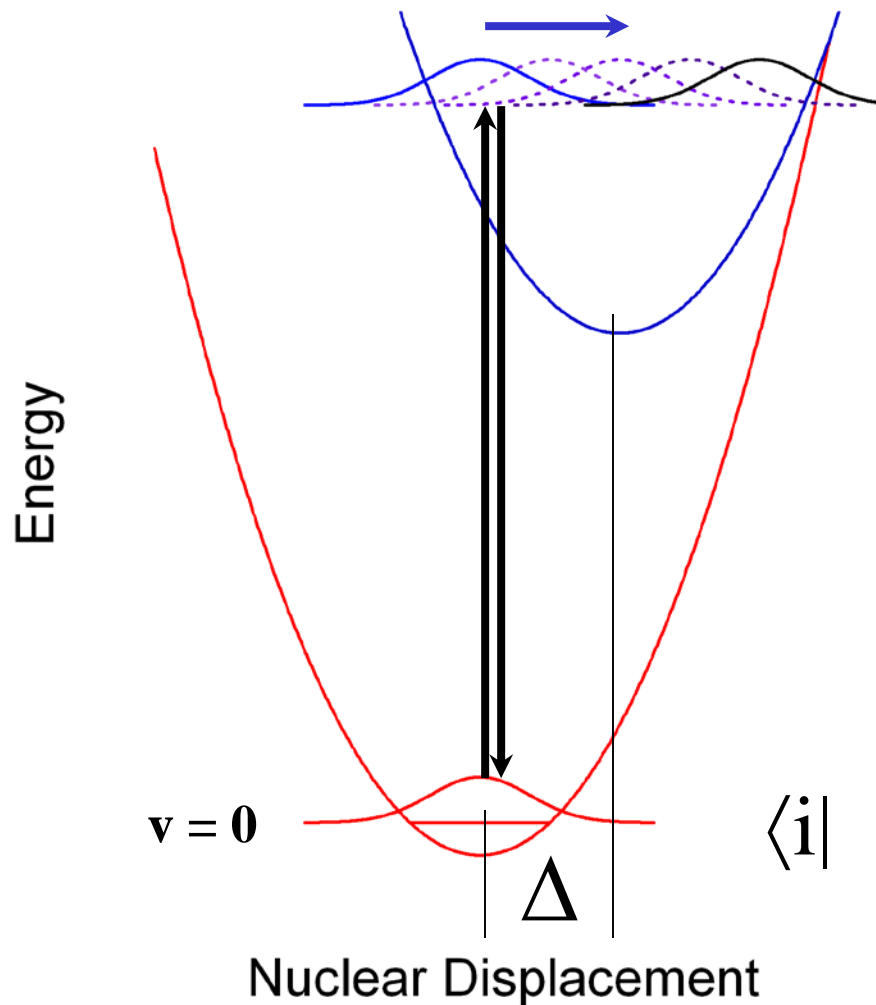
# The Franck-Condon factor determines the envelop of the absorption lineshape



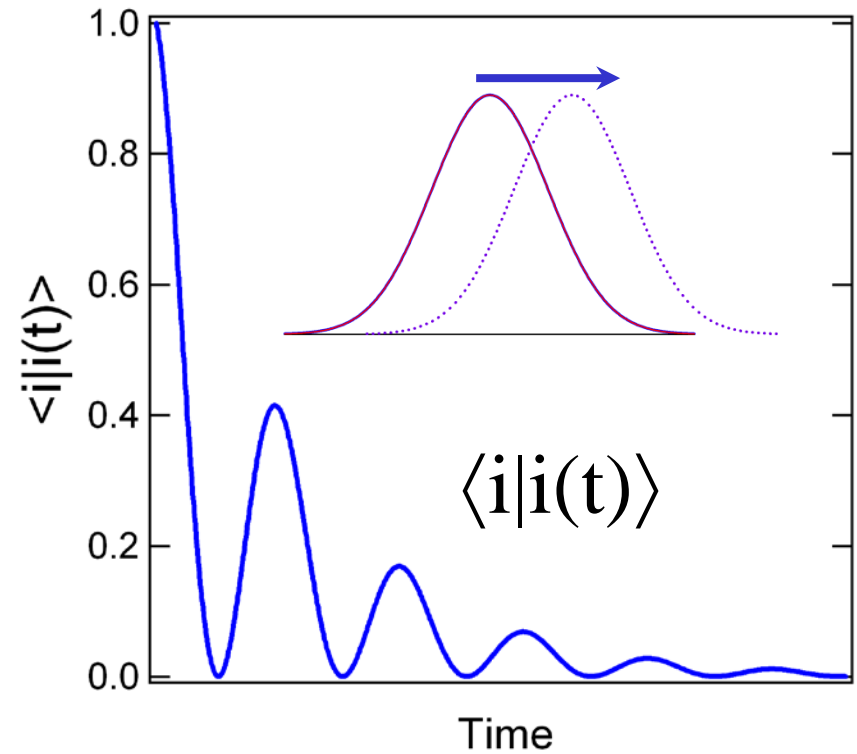
$S = \Delta^2/2$   
 $S$  is electron-phonon coupling  
 $\Delta$  is nuclear displacement



# Wavepacket dynamics: Absorption

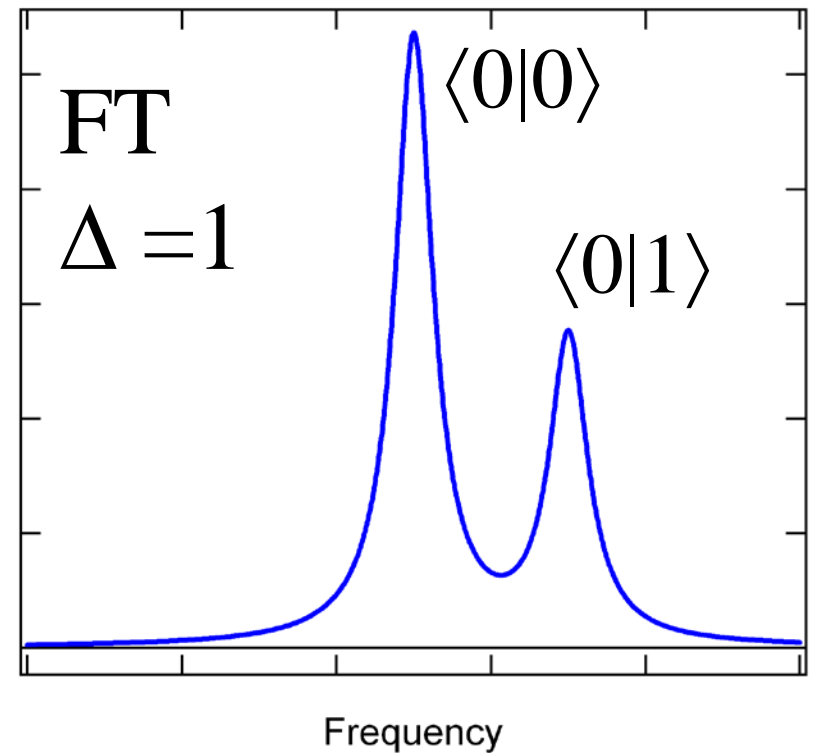
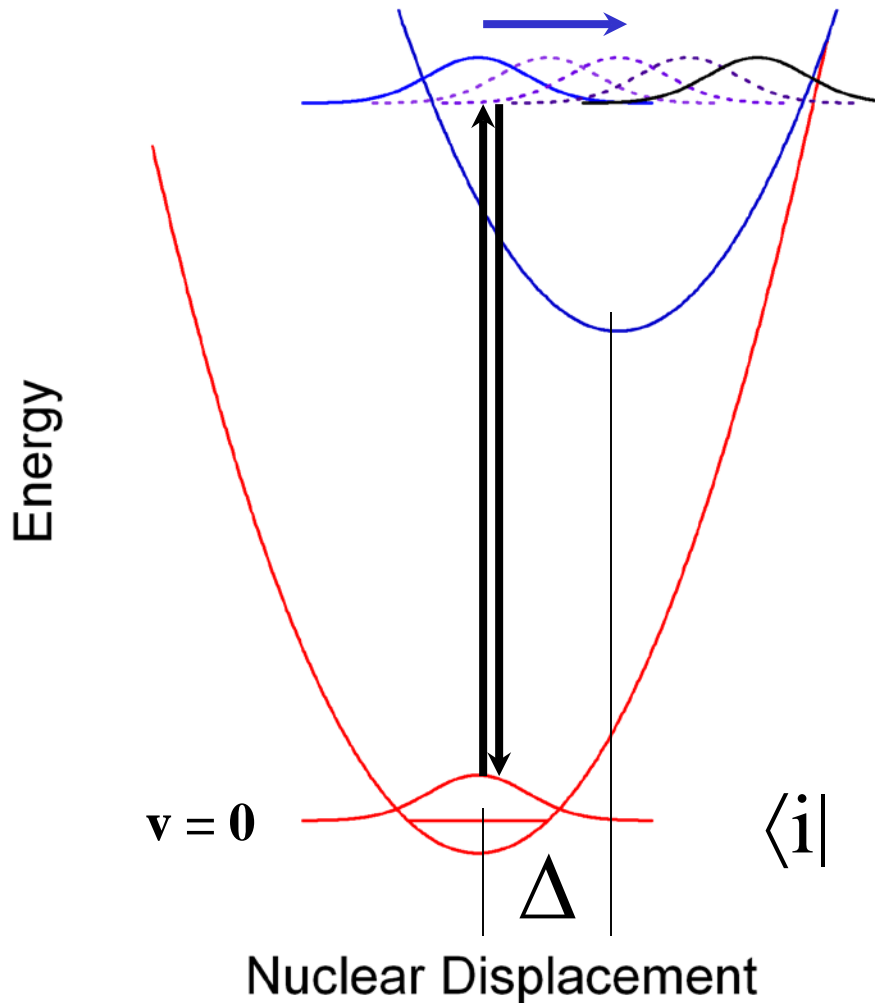


$$|\mathbf{i}(t)\rangle = e^{iHt}|\mathbf{i}\rangle$$

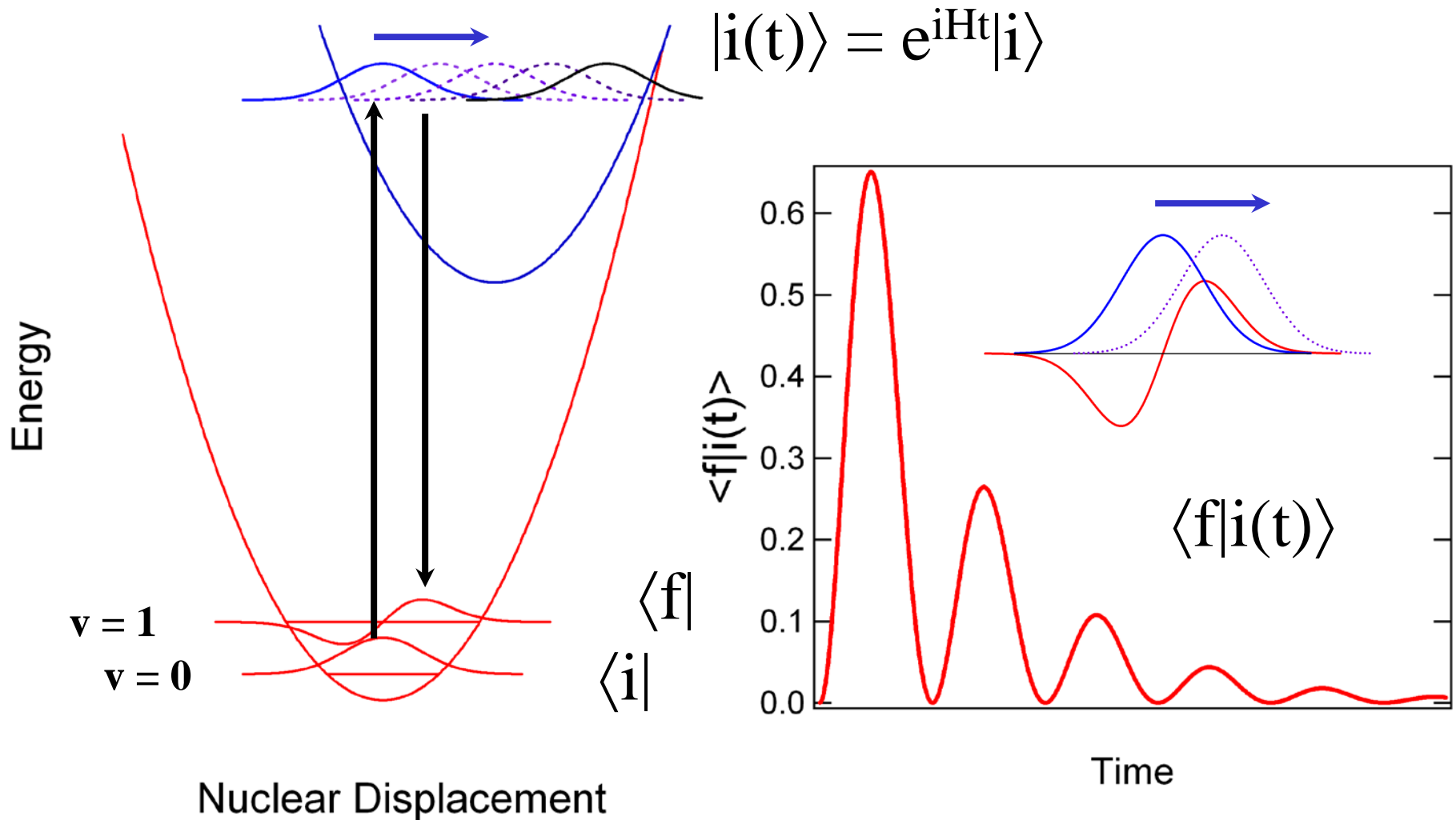


# Fourier transform of exponentially damped sinusoid is a Lorentzian

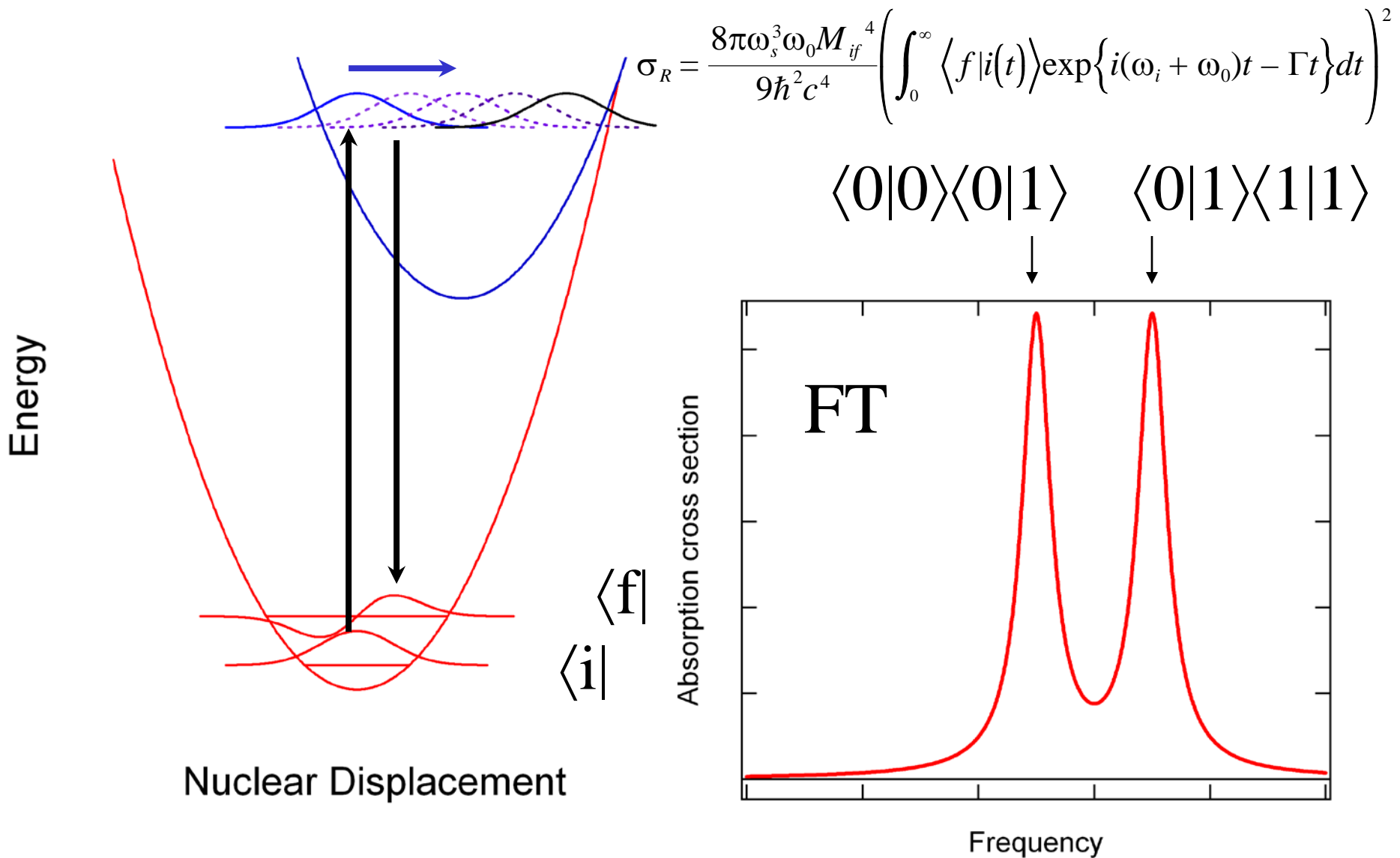
$$\sigma_A = \frac{2\pi\omega_0 M_{if}^2}{3\hbar c} \int_{-\infty}^{\infty} \langle i|i(t) \rangle \exp\{i(\omega_i + \omega_0)t - \Gamma t\} dt$$



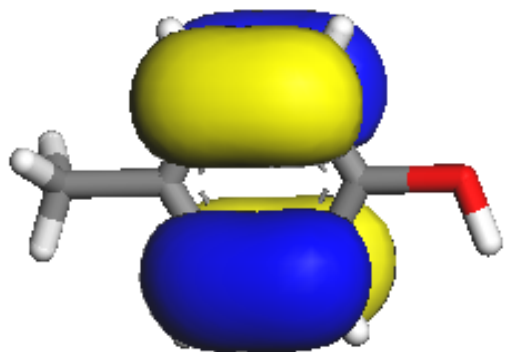
# Wavepacket dynamics: Raman



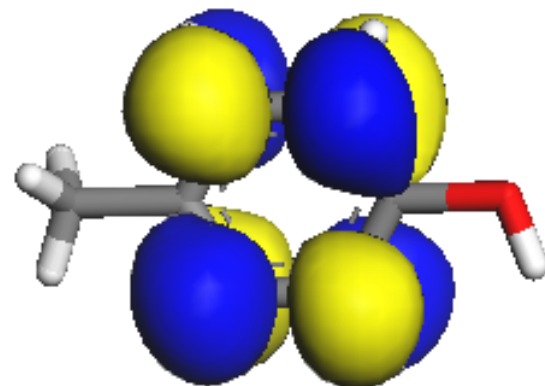
# FT of $\langle f|i(t)\rangle$ yields the REP



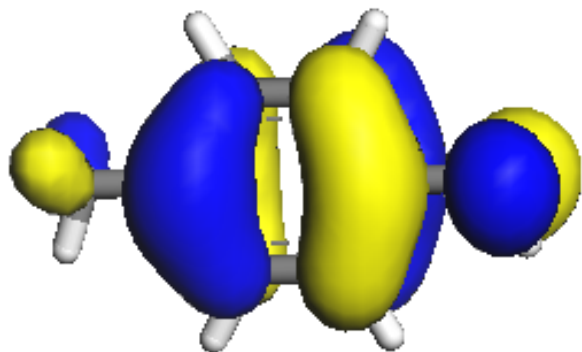
# Para-cresol transitions



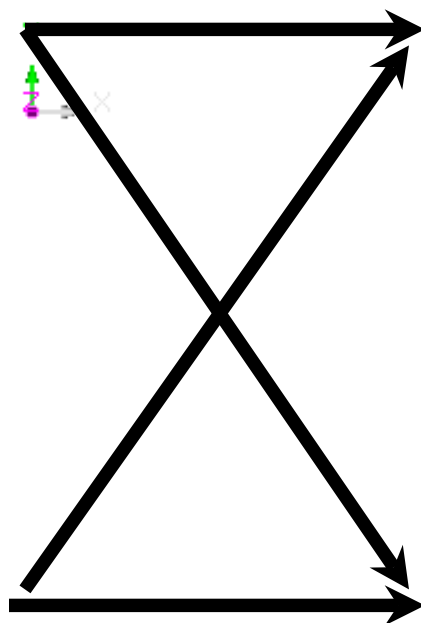
28



30

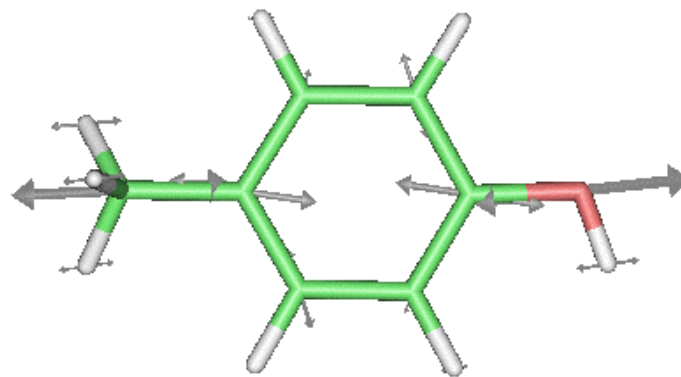
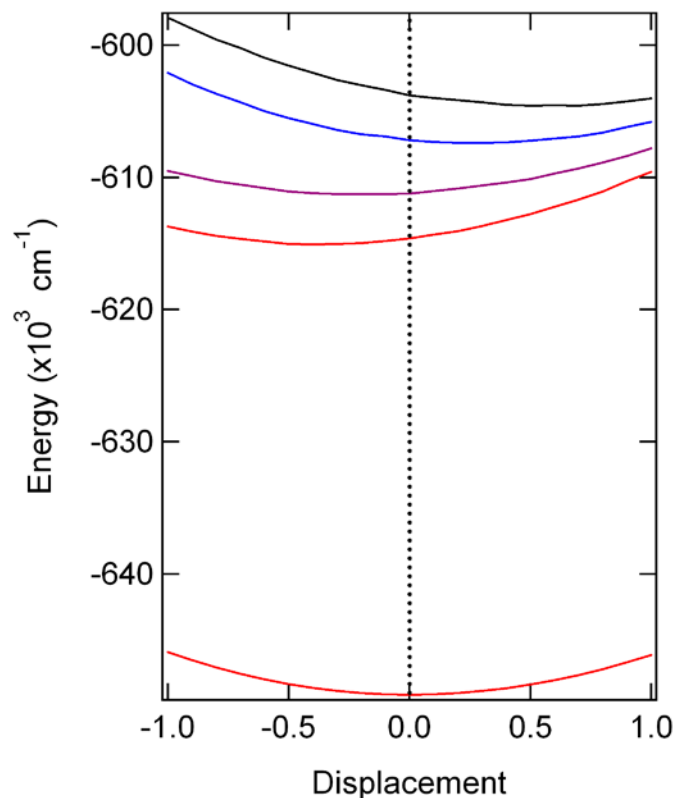


29



31

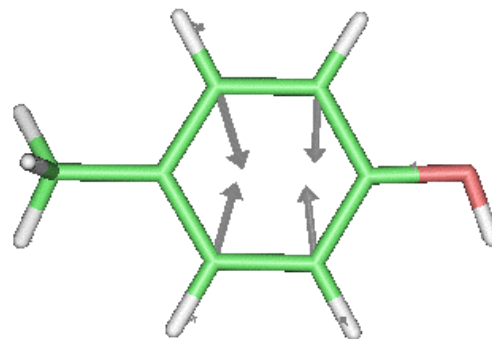
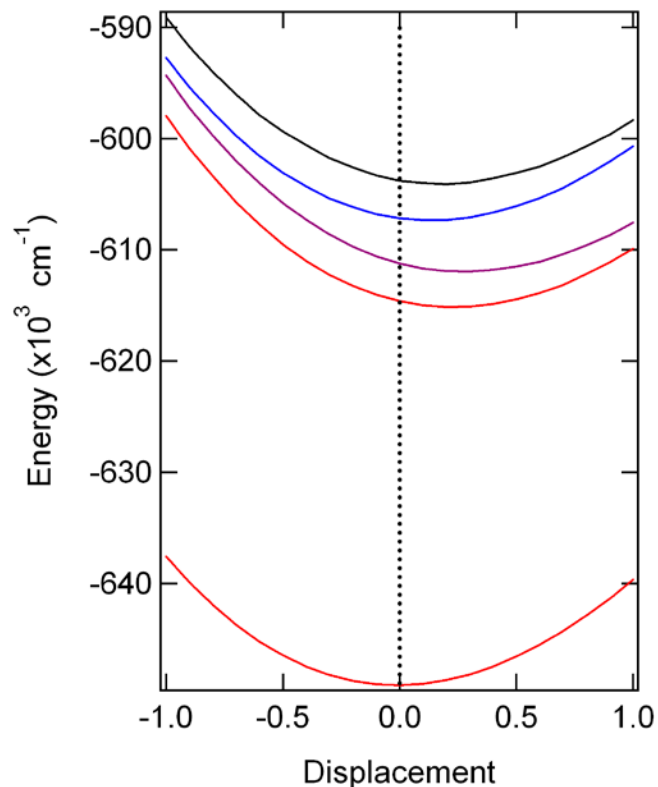
# Vibrational Modes of para-cresol A Model for Tyrosine



Mode 8:  $459 \text{ cm}^{-1}$

# Vibrational Modes of para-cresol

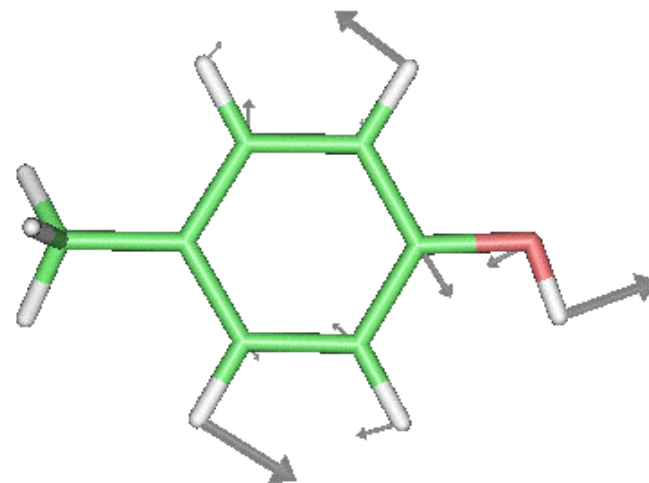
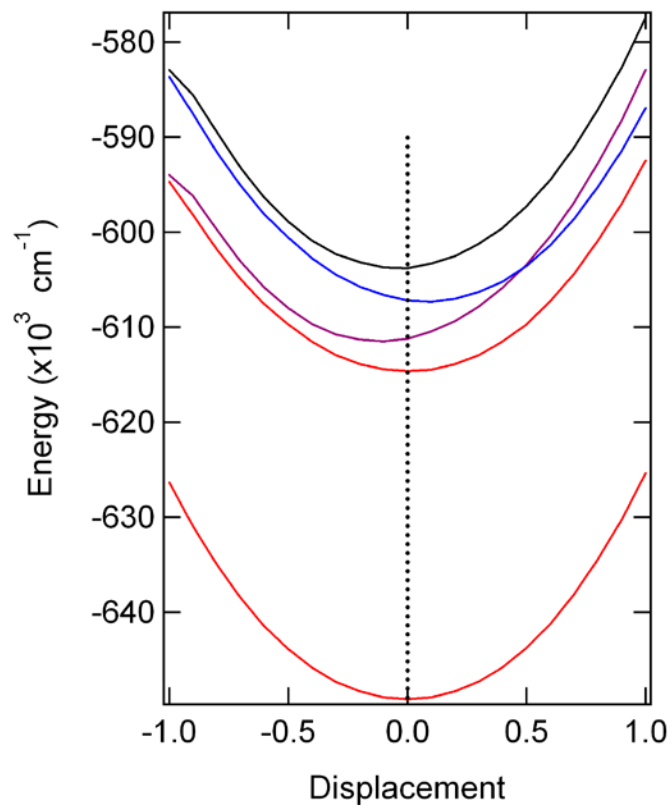
## A Model for Tyrosine



Mode 15:  $841 \text{ cm}^{-1}$

# Vibrational Modes of para-cresol

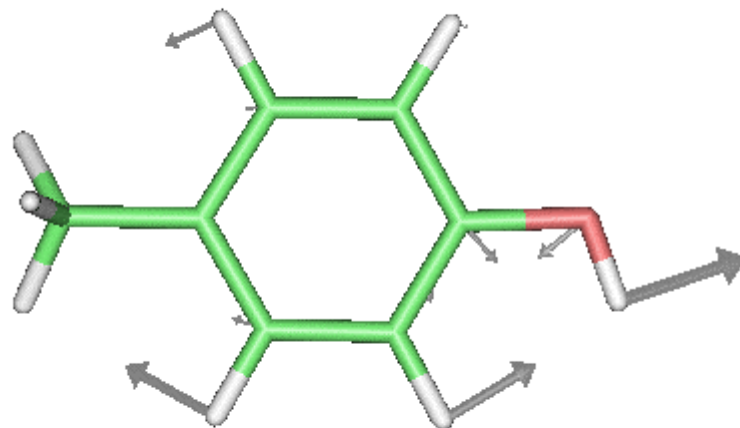
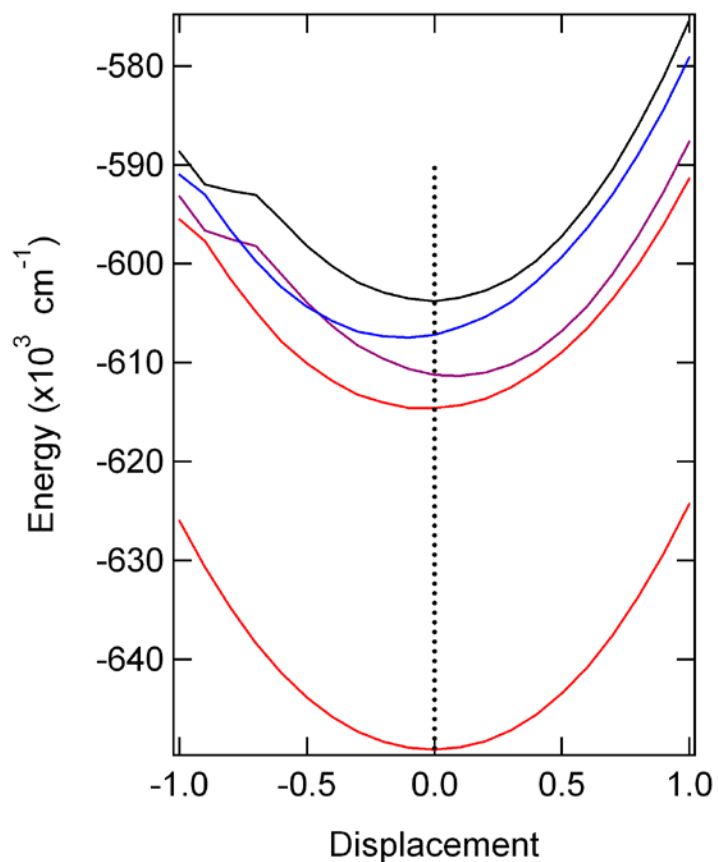
## A Model for Tyrosine



Mode 22:  $1148 \text{ cm}^{-1}$



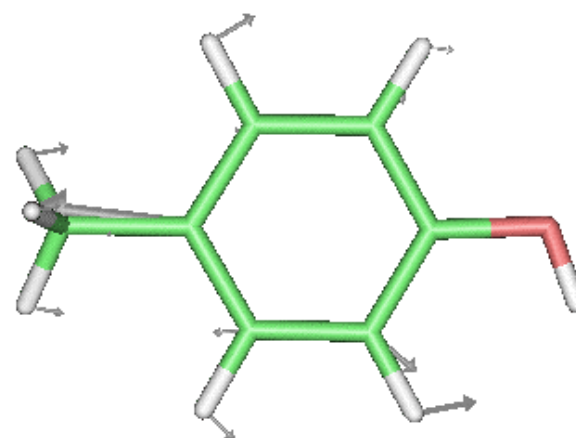
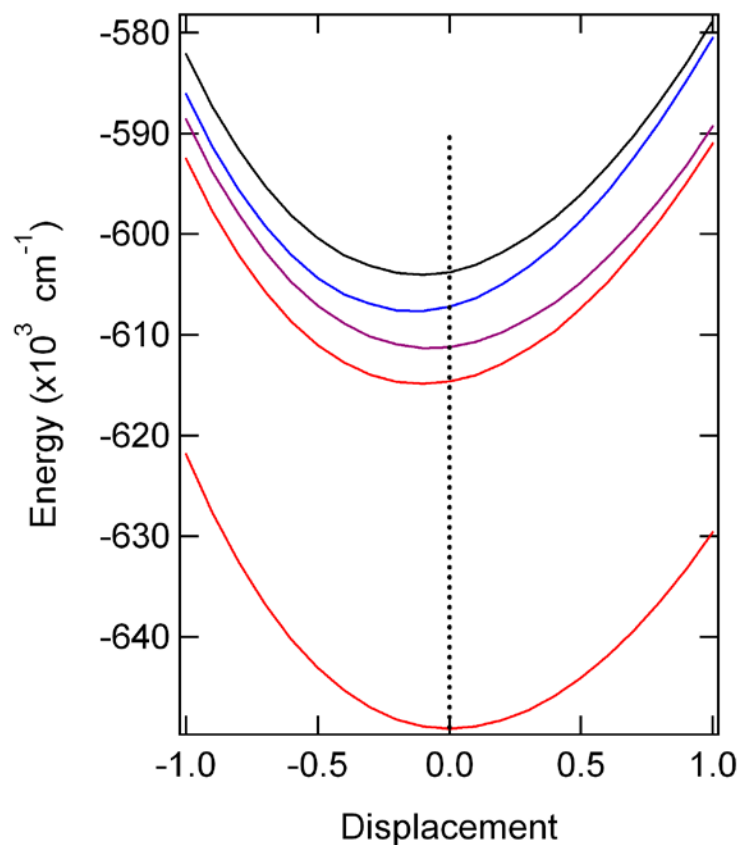
# Vibrational Modes of para-cresol A Model for Tyrosine



Mode 23:  $1185 \text{ cm}^{-1}$

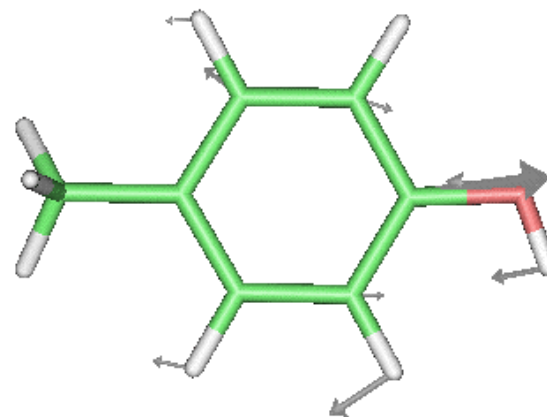
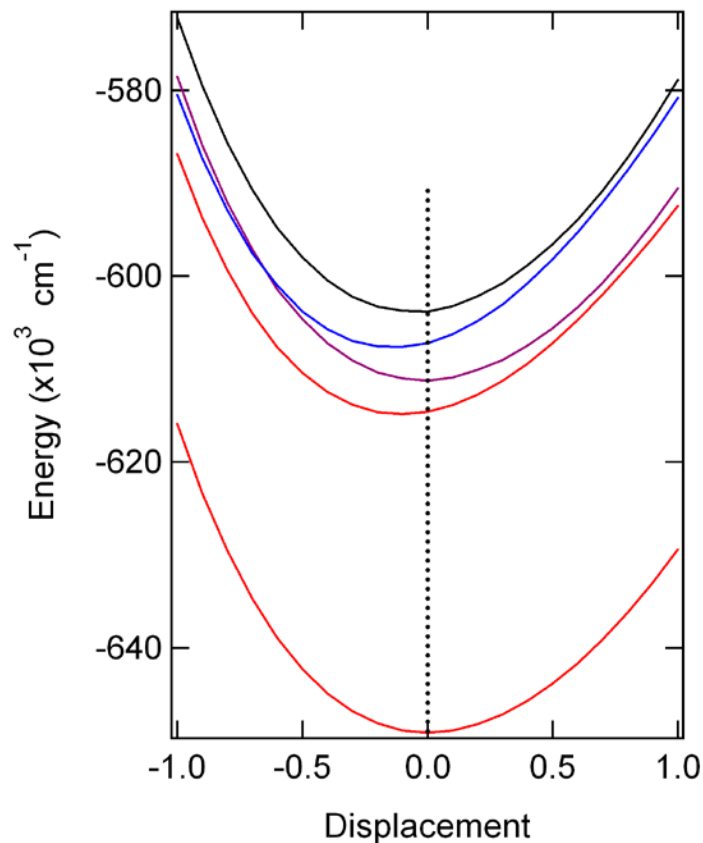
# Vibrational Modes of para-cresol

## A Model for Tyrosine



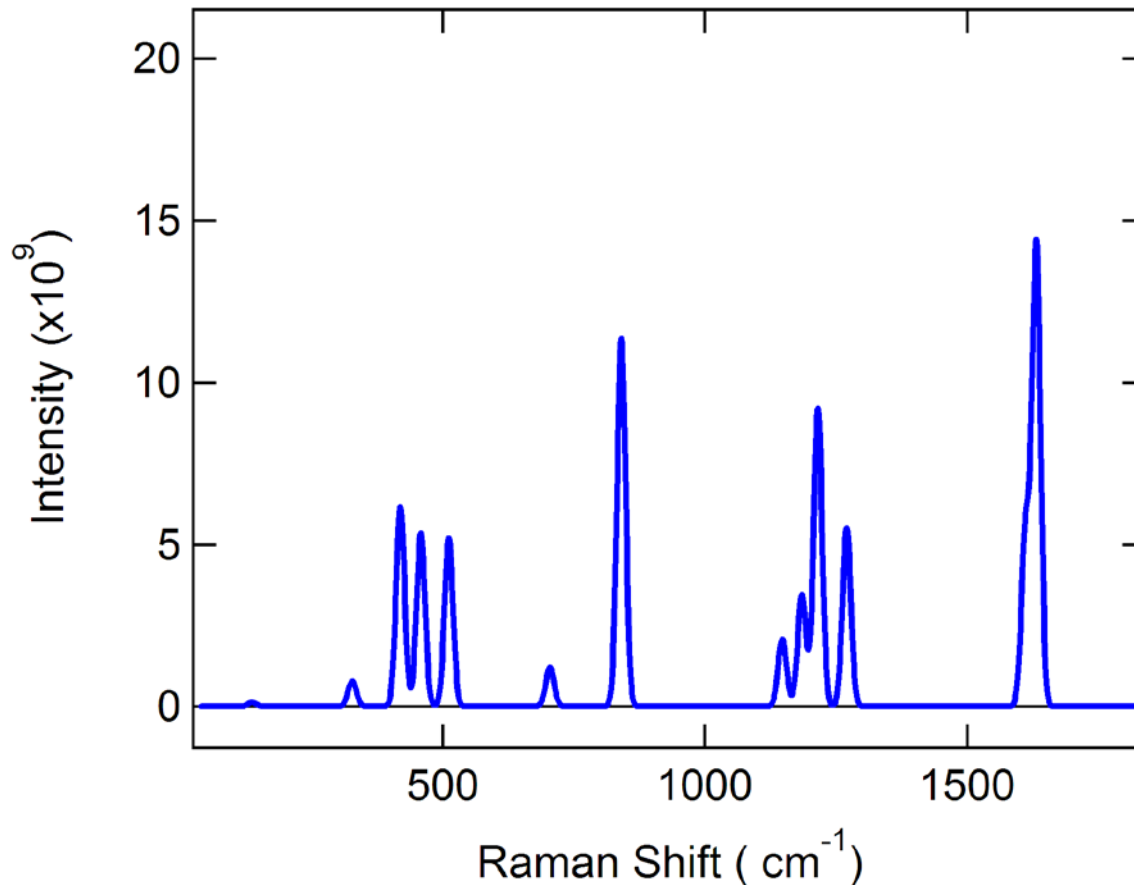
Mode 24:  $1216 \text{ cm}^{-1}$

# Vibrational Modes of para-cresol A Model for Tyrosine



Mode 25:  $1271 \text{ cm}^{-1}$

# Resonant Raman Spectrum for Tyrosine (GGA)



# Resonant Raman Spectrum for Tyrosine Compared

