

Vibrational Stark Effect: Theory and Analysis

NC State University

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

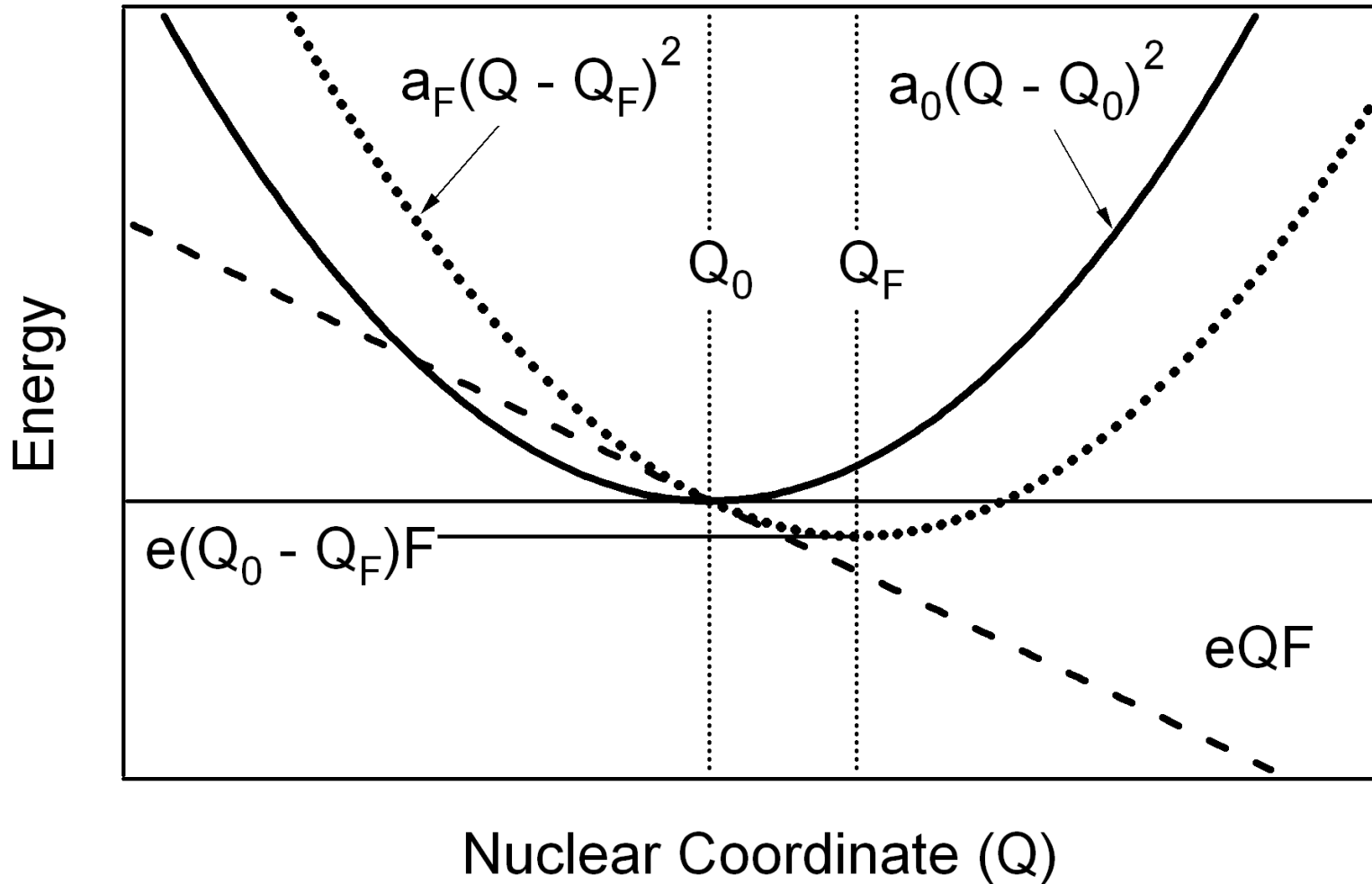
Systematic study of CO and CN vibrations

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

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

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

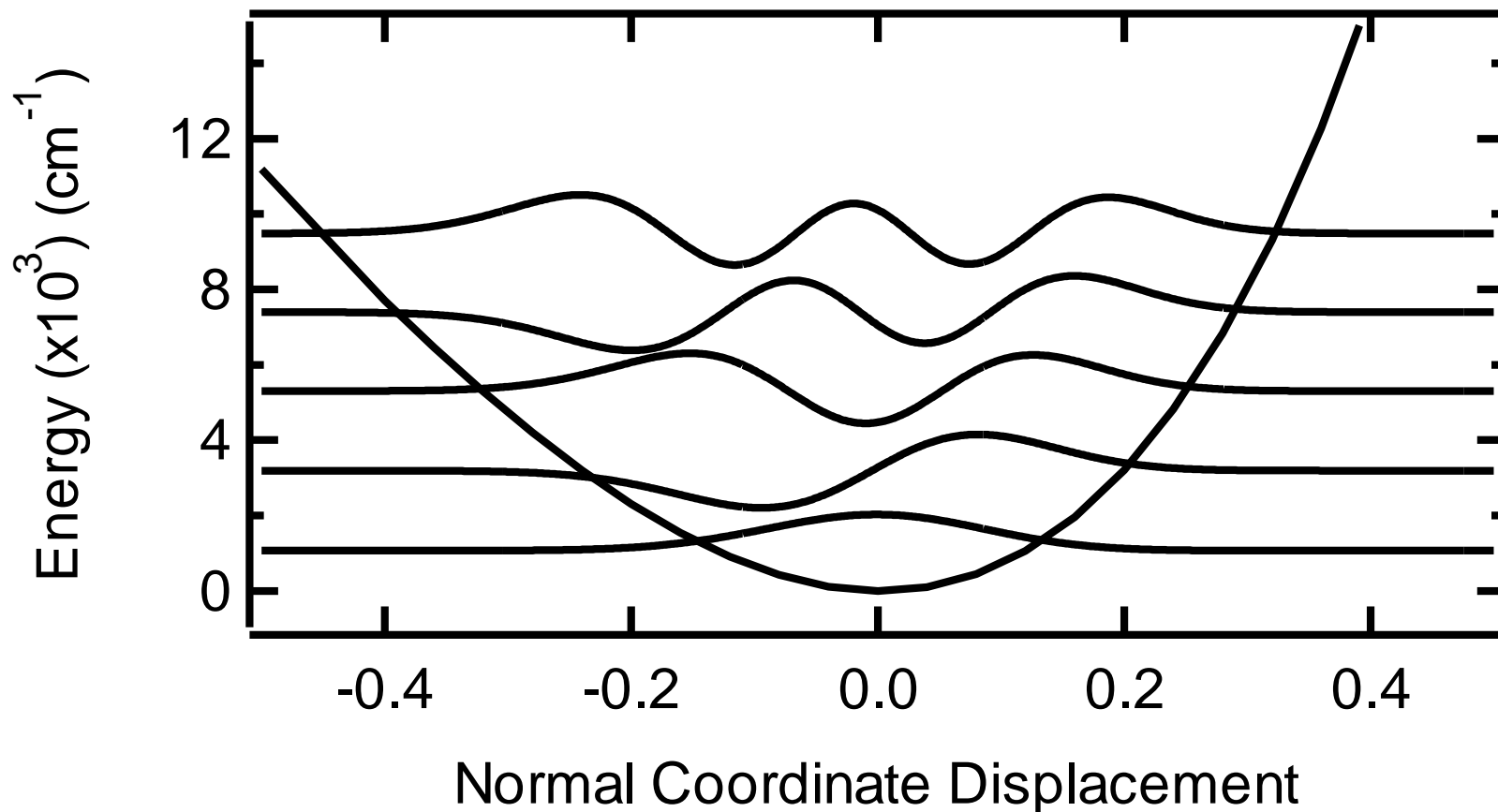
Eliminate higher order terms using the device

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

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

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

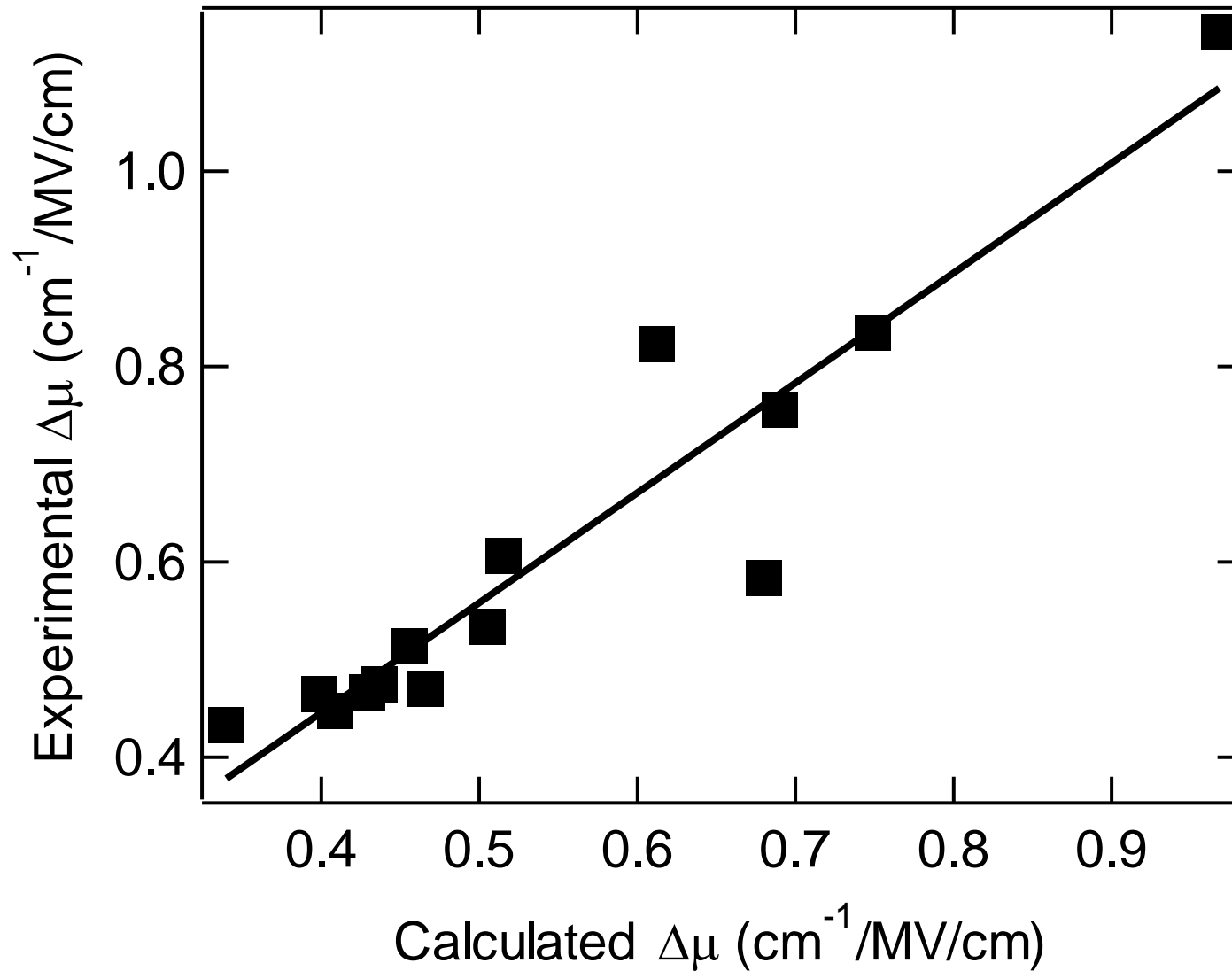
$$M = \left(\frac{\partial\mu}{\partial Q} \right) \langle \chi_0 | Q | \chi_1 \rangle \quad \langle \chi_0 | Q | \chi_1 \rangle = \sqrt{\frac{1}{2\alpha}} \quad \alpha = \frac{\mu\omega}{\hbar}$$

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

Correlation of $\Delta\mu$

Molecule	Stark Tuning Rate Calculated ^A (cm ⁻¹ /(MV/cm))	Stark Tuning Rate Calculated ^B (cm ⁻¹ /(MV/cm))	Stark Tuning Rate A + B	Stark Tuning Rate Experimental (cm ⁻¹ /(MV/cm)) ^C
acetone	0.253	0.437	0.690	0.756
CO	0.010	0.457	0.467	0.429 ^D
CN ⁻	0.019	0.204	0.223	-----
HCN	0.049	0.049	0.098	----- ^E
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 $\Delta\mu$

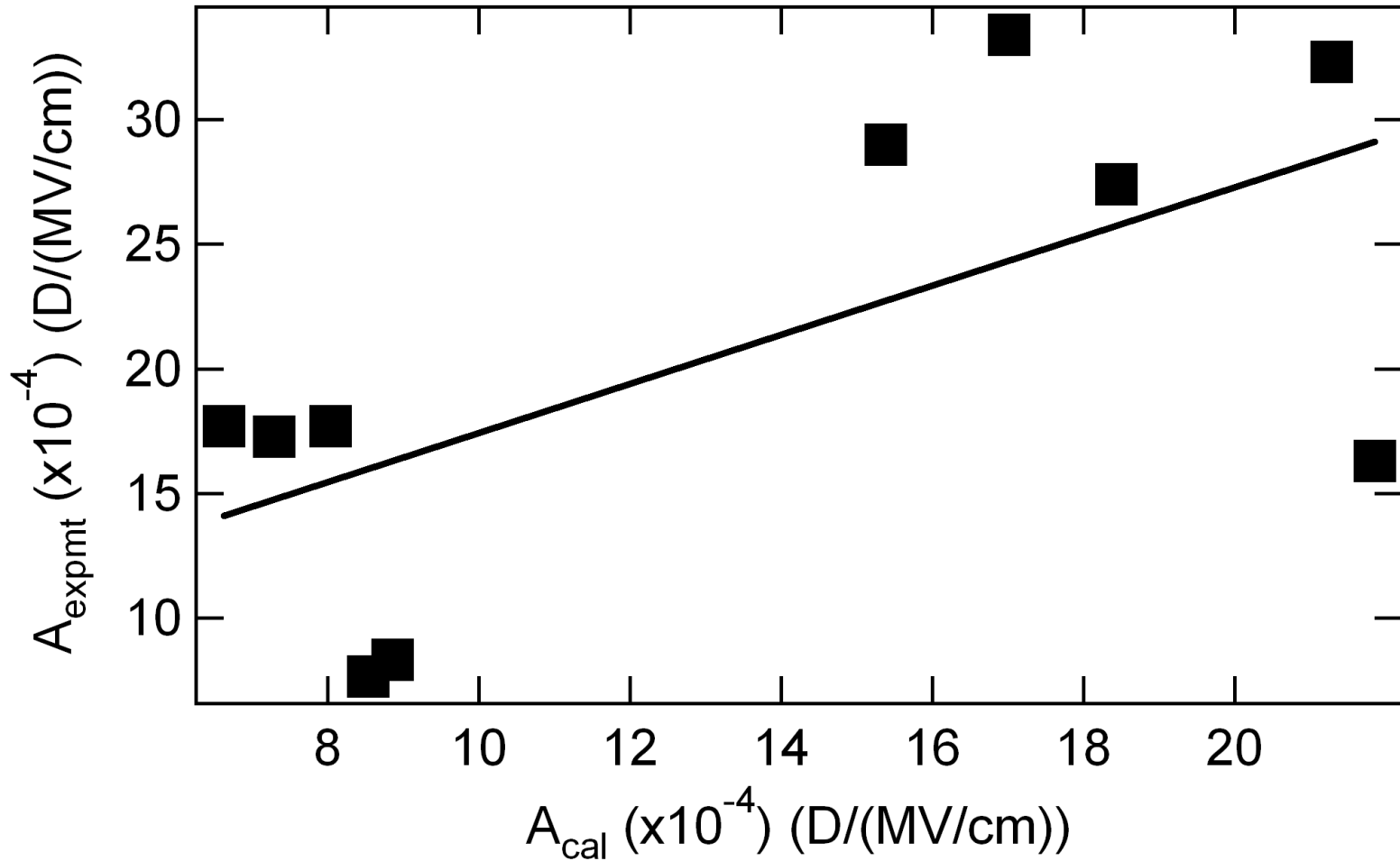


Correlation of A

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

Molecule	A (x10 ⁻⁴) (D/(MV/cm)) ^I	A (x10 ⁻⁴) (D/(MV/cm)) ^{II}	A (x10 ⁻⁴) (literature values) (D/(MV/cm)) ^{III}
acetone	2.81	2.05	-----
CO	16.05	16.60	-----
CN ⁻	37.45	37.46	-----
HCN	5.81	5.90	----- ^{IV}
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.



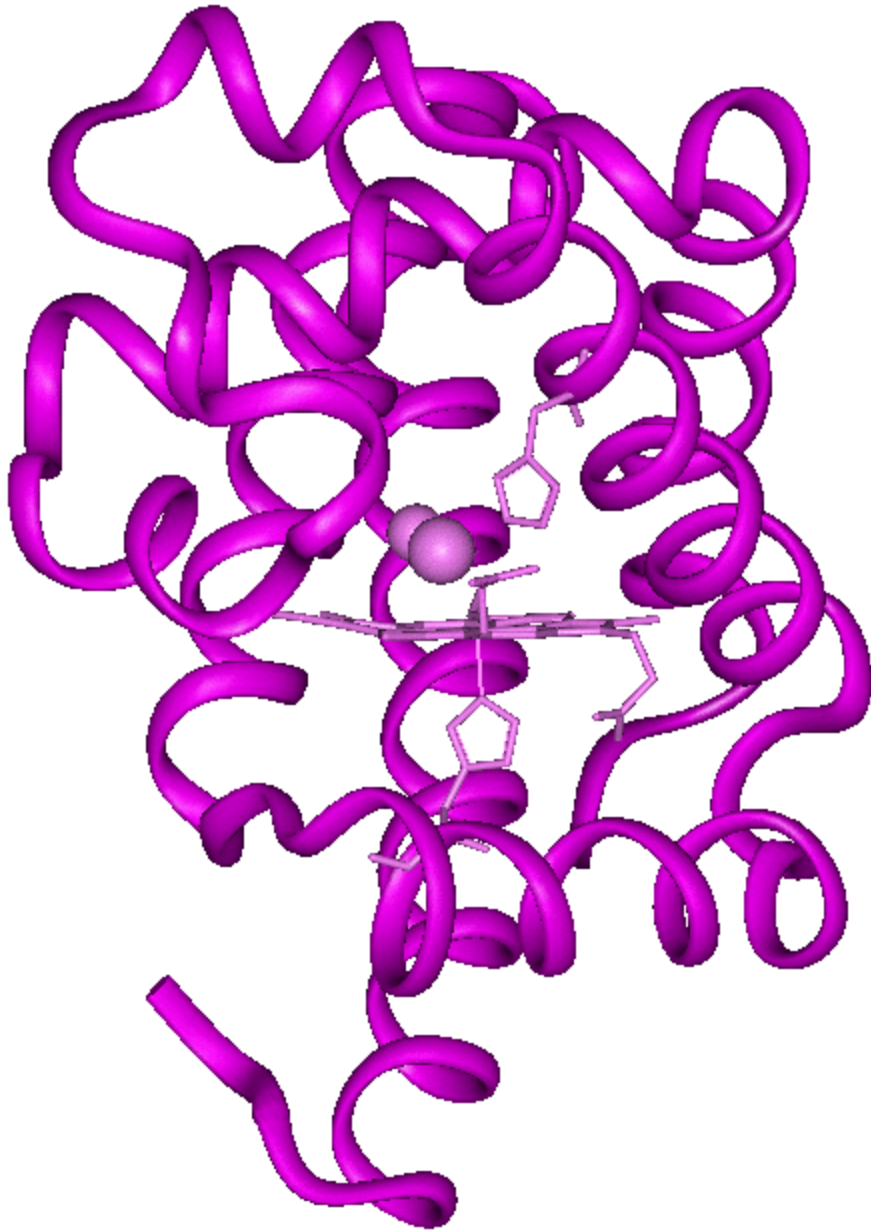
MbCO

The peptide backbone is shown as a ribbon that follows the α -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



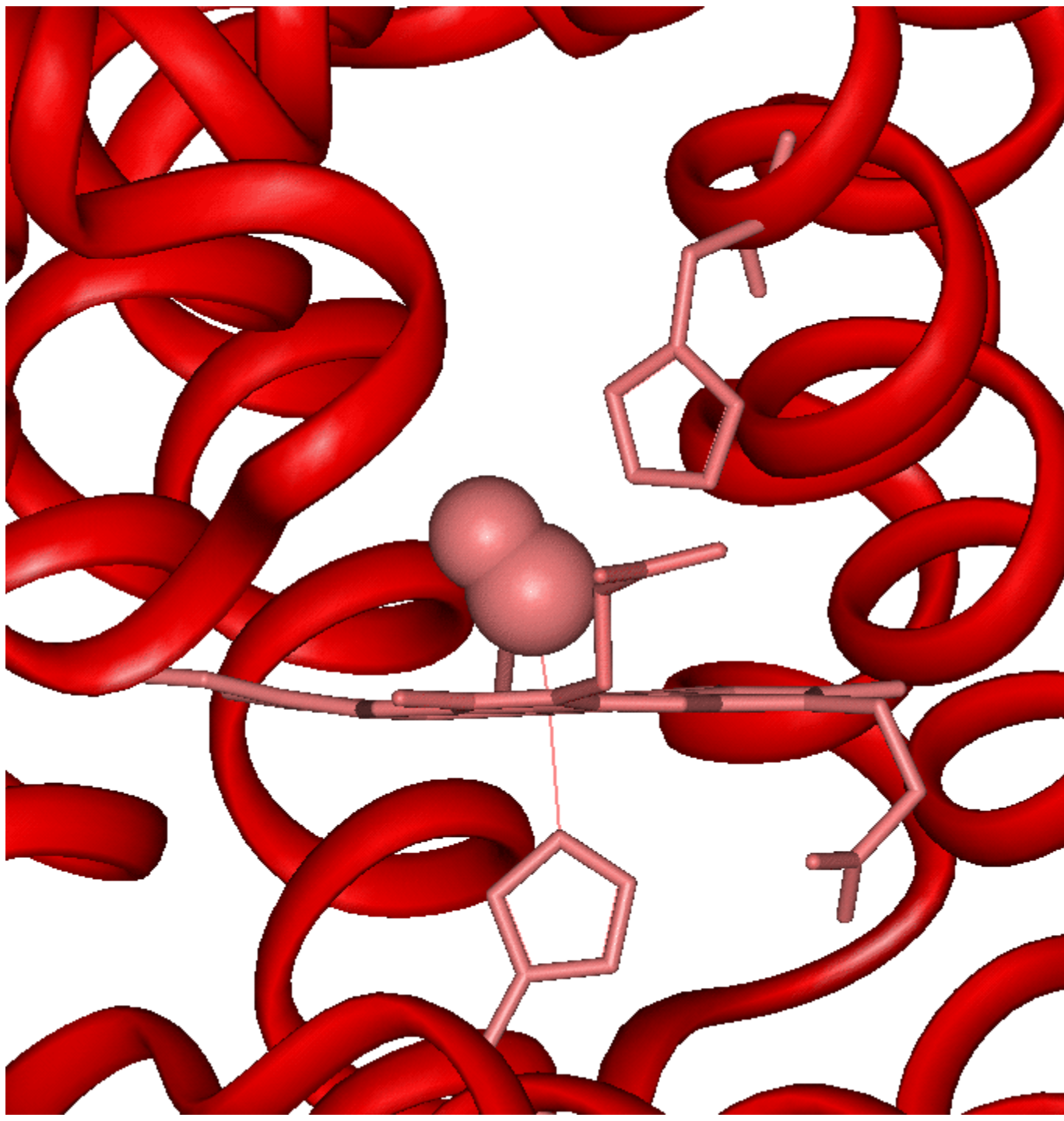
Mb:CO

The photoproduct.

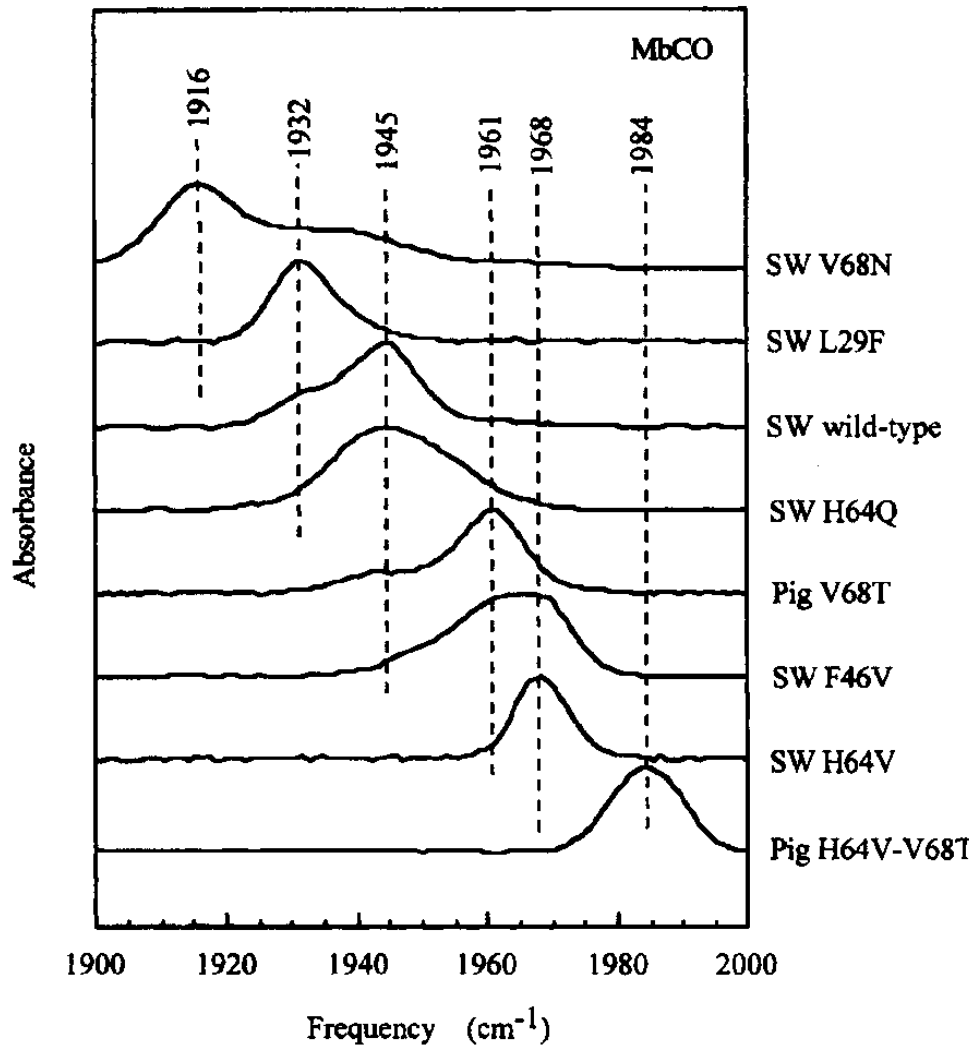
Iron moves out of the heme plane when CO is photolyzed.

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

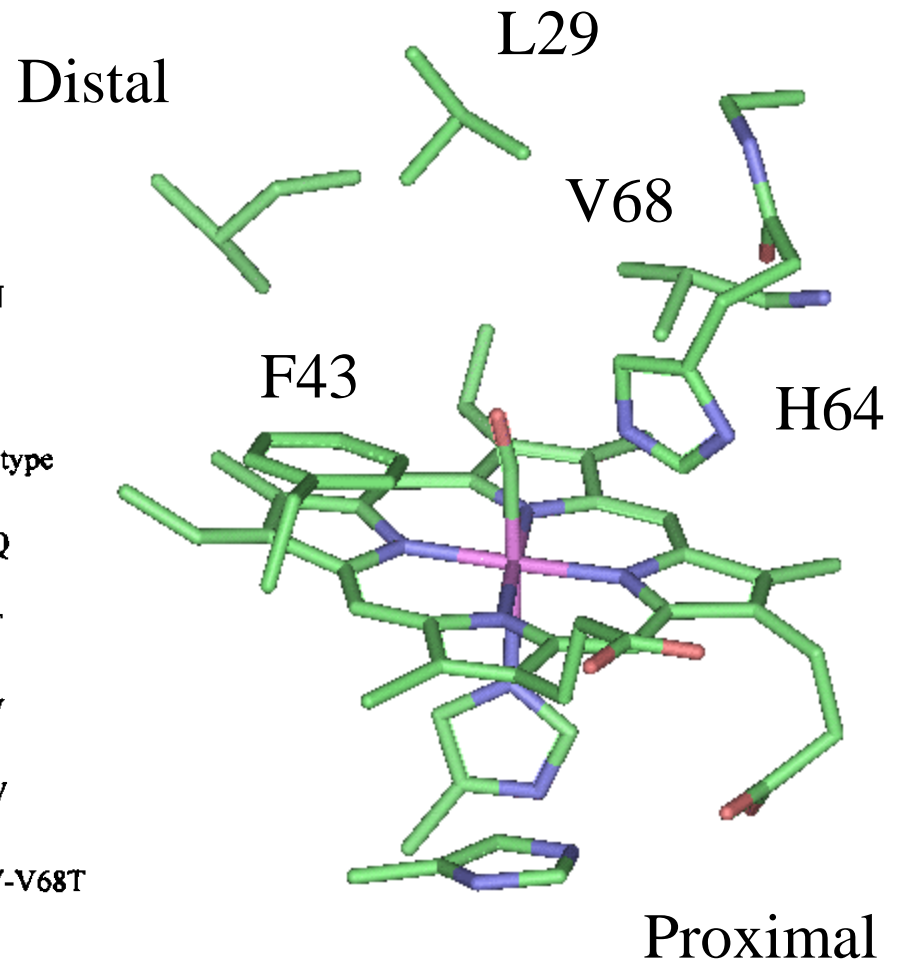
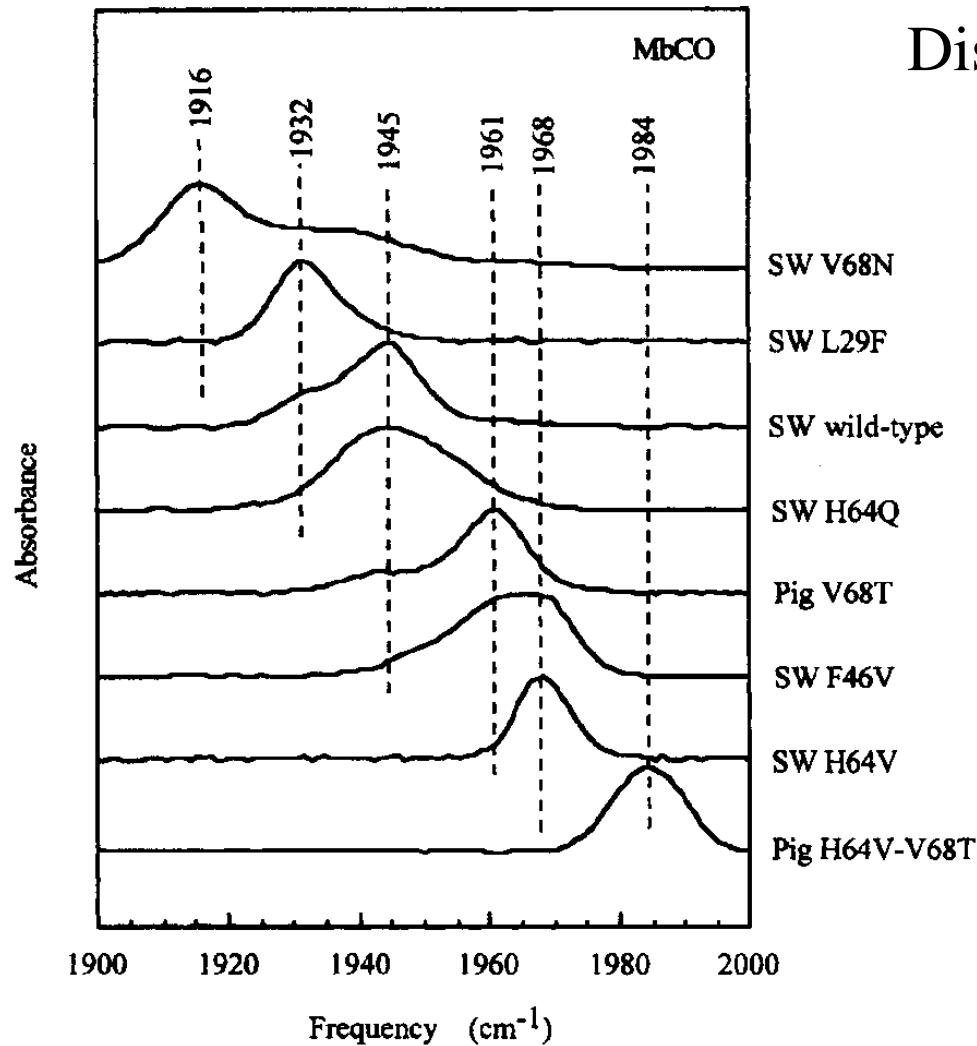
Conformational substates are called **B states**.



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

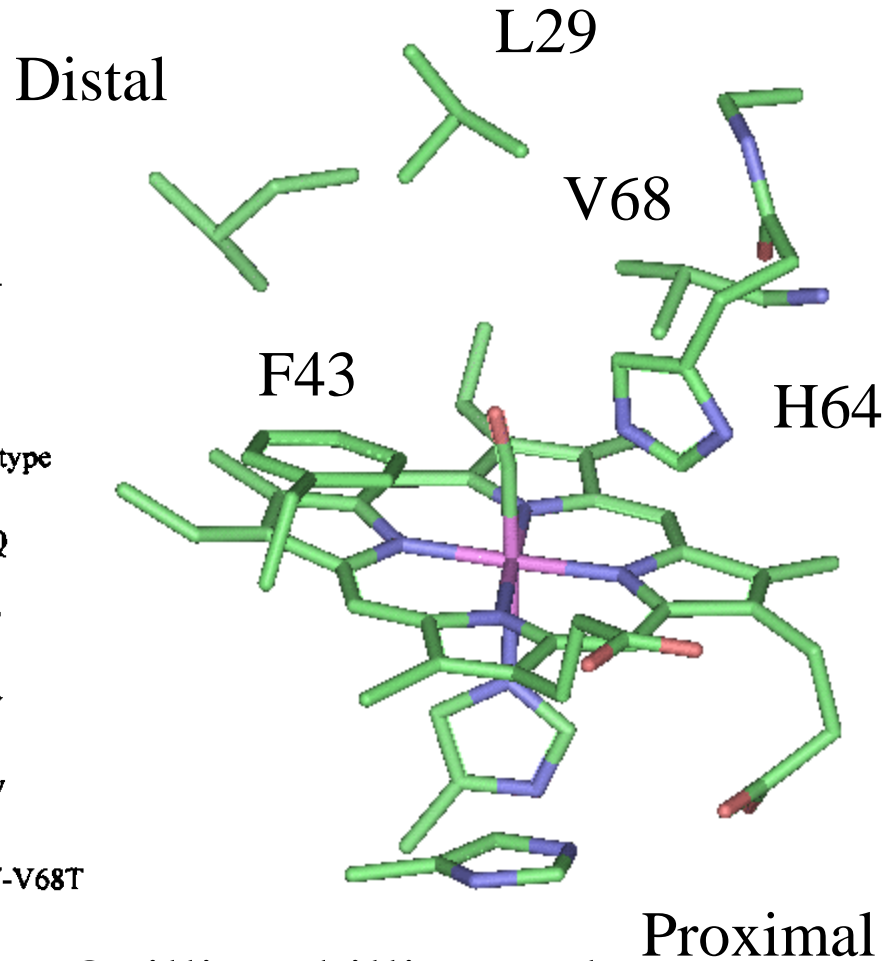
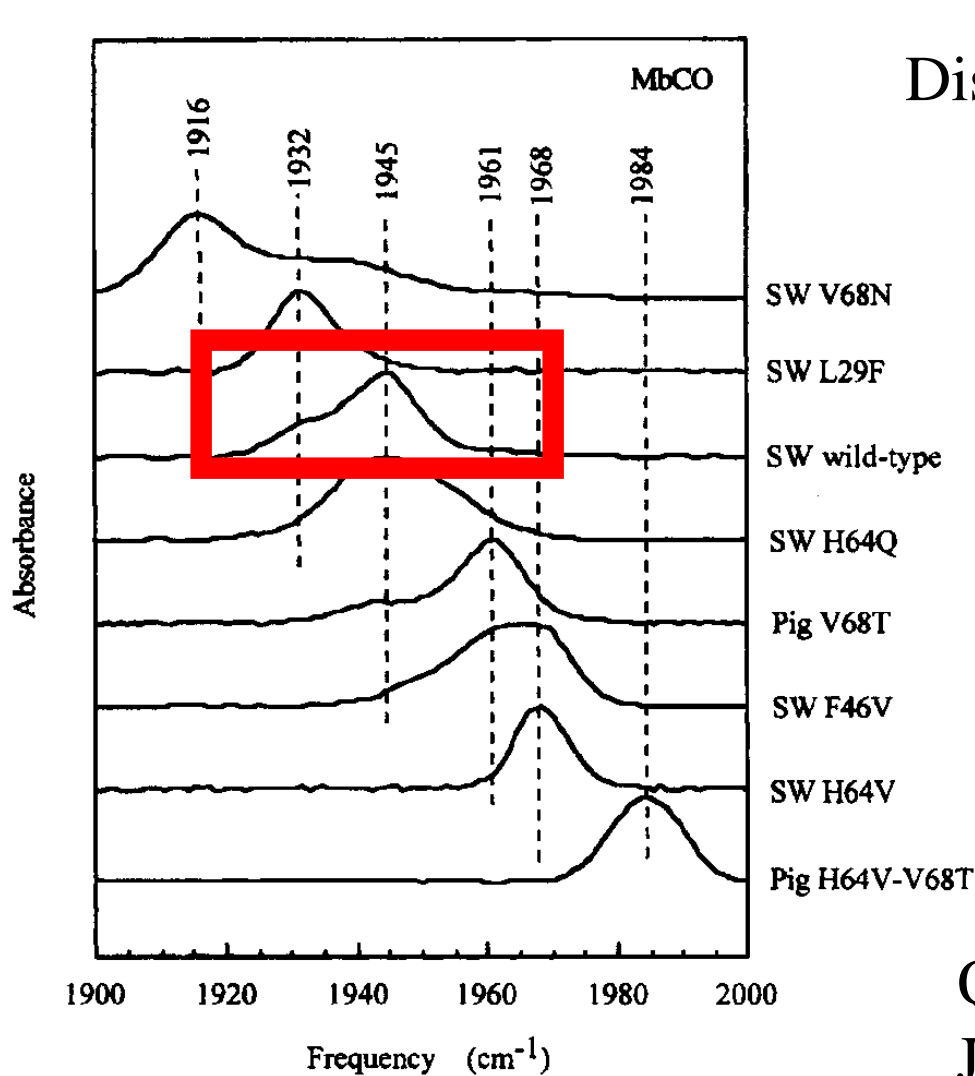


A view of the distal pocket



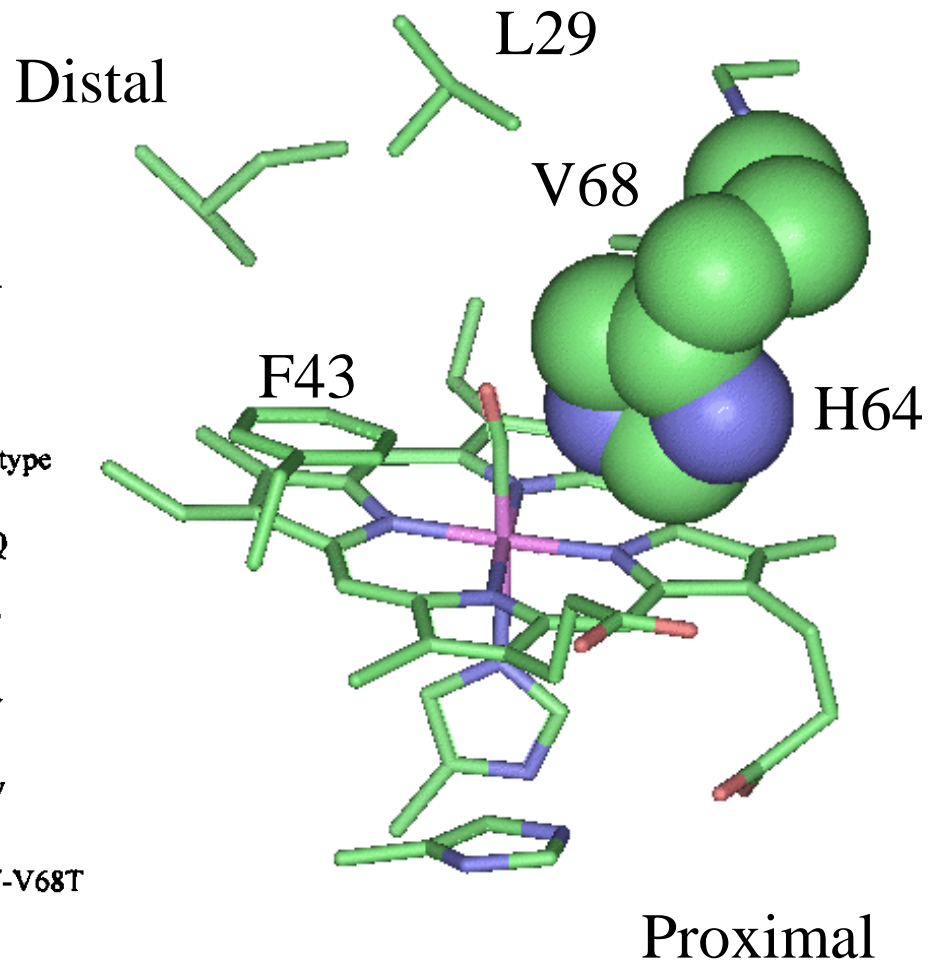
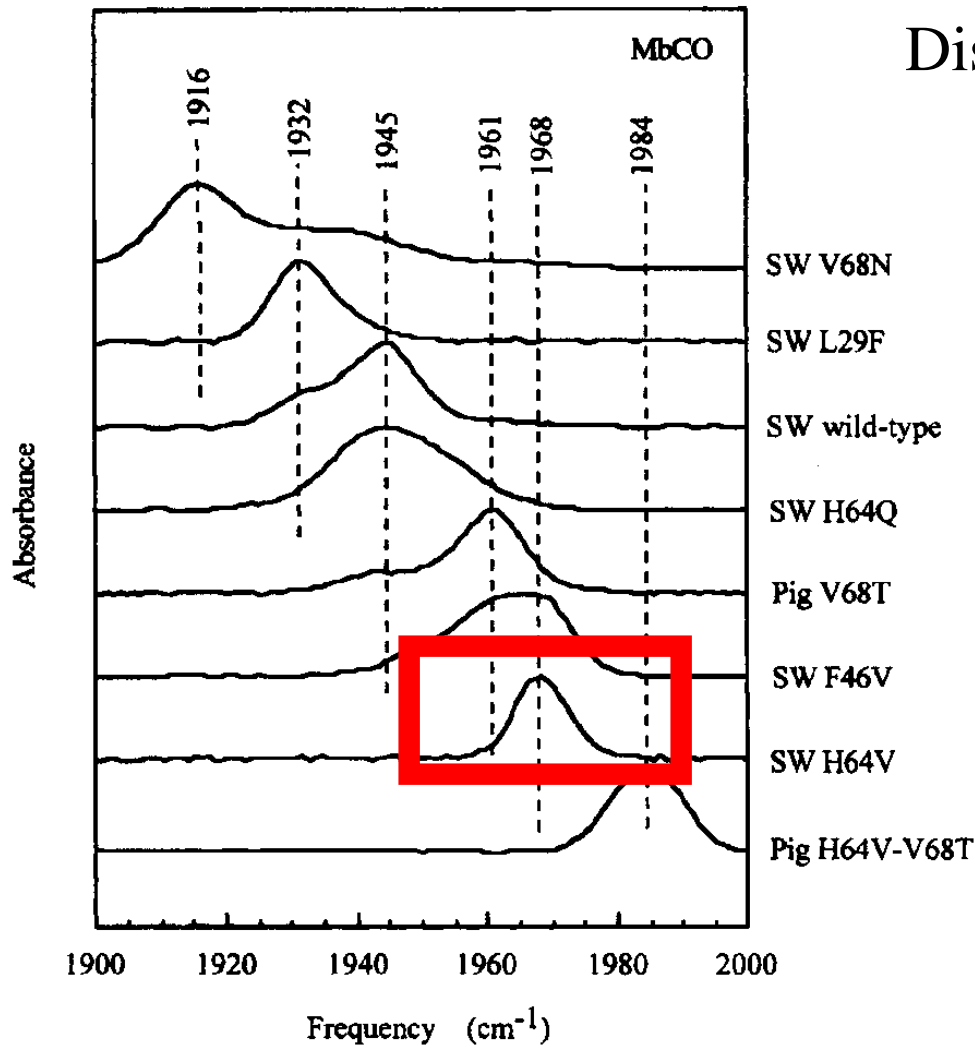
Protein Data Bank 2MGK

Wild-type has multiple CO bands

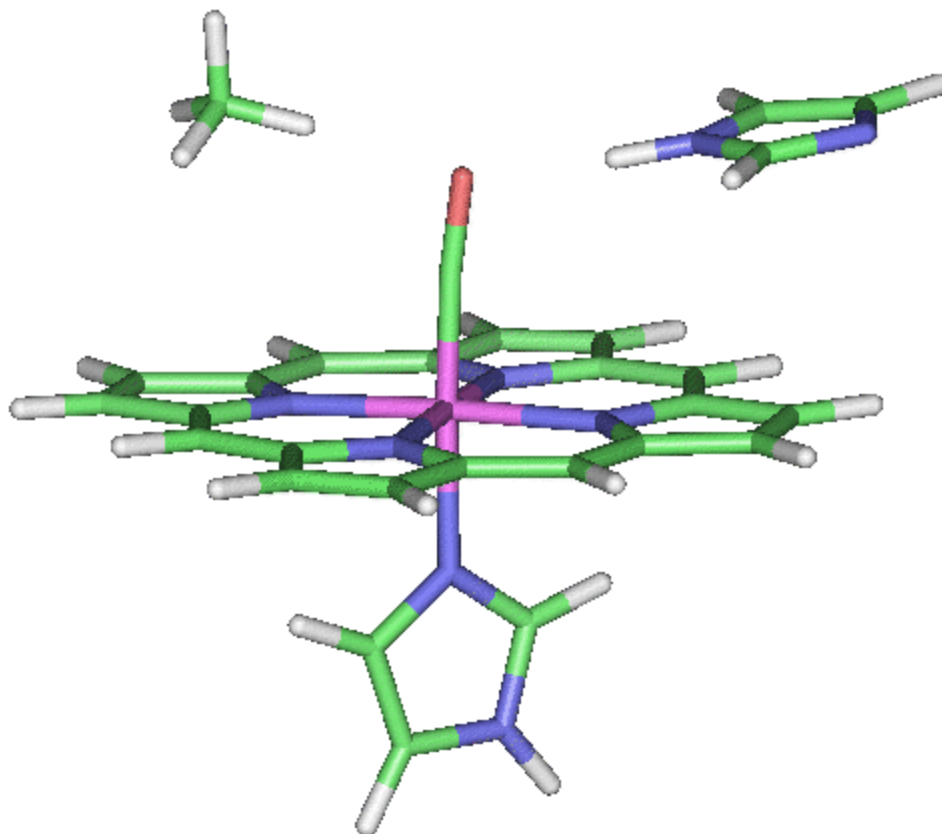


Quillin, Phillips et al.
JMB 1993, 234, 140-155

Distal histidine is key

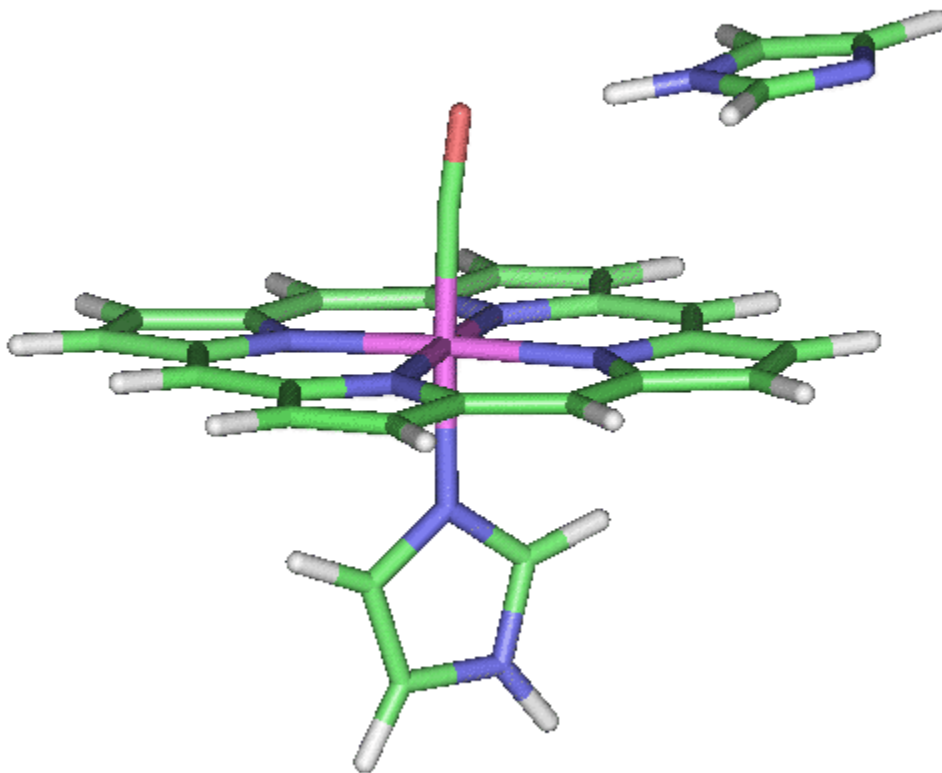


DFT calculation of ν_{CO} frequencies



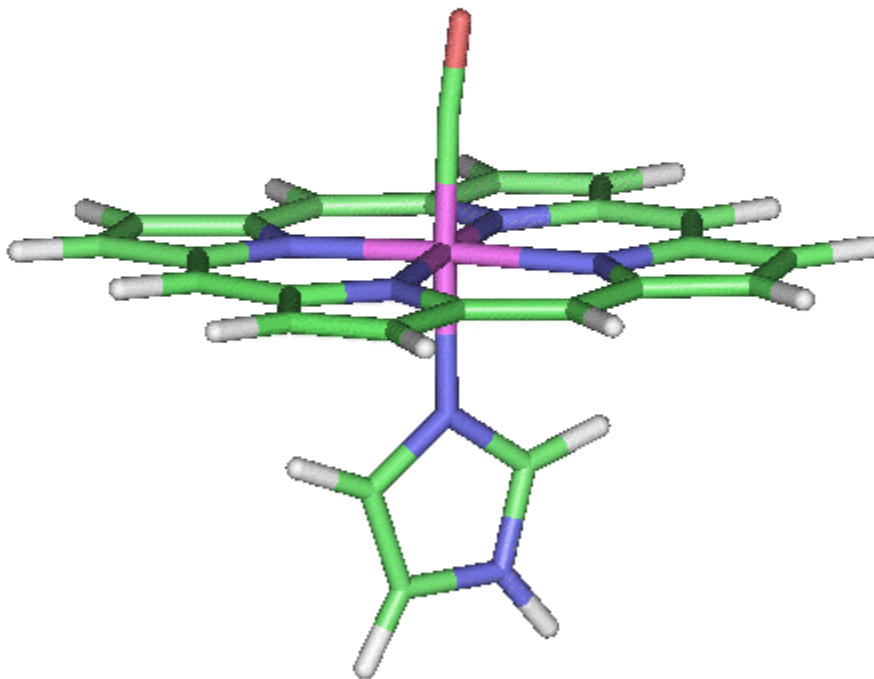
Multiple hydrogen bonding interactions

DFT calculation of ν_{CO} frequencies



Single hydrogen bonding interaction

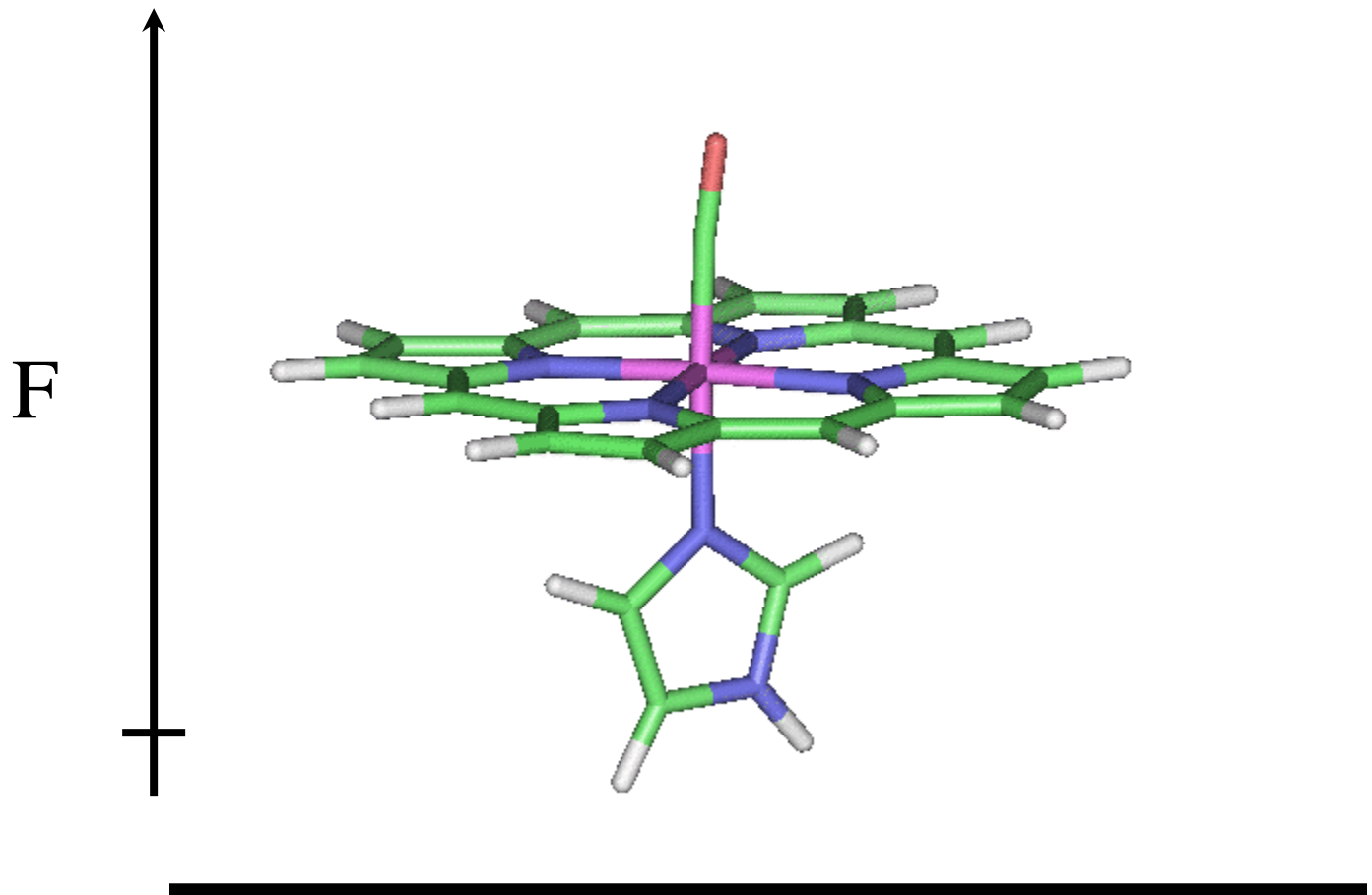
DFT calculation of ν_{CO} frequencies



No hydrogen bonding interaction

DFT calculation in an applied electric field

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Electric field effect by DFT

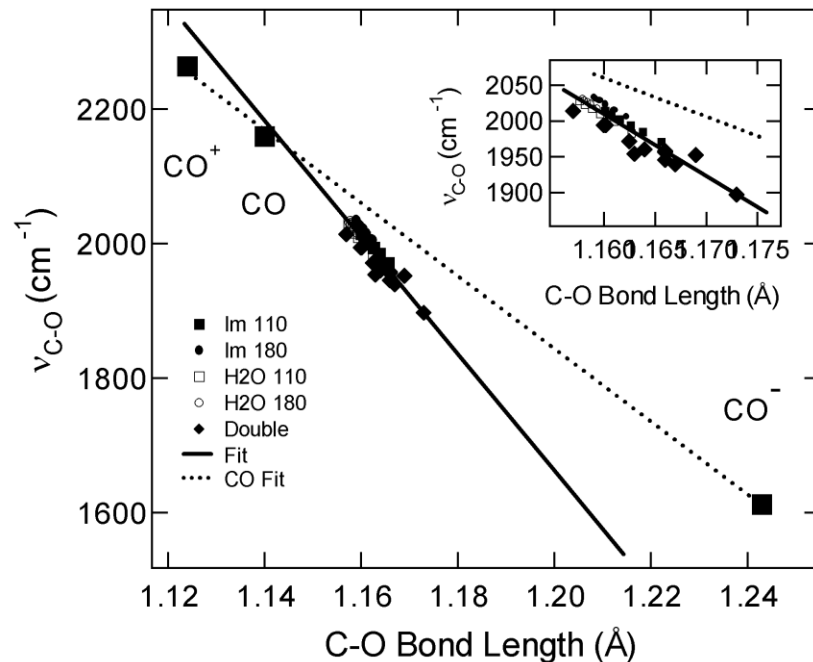
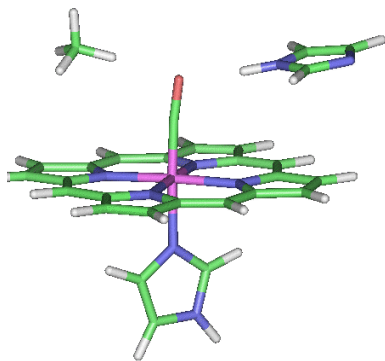
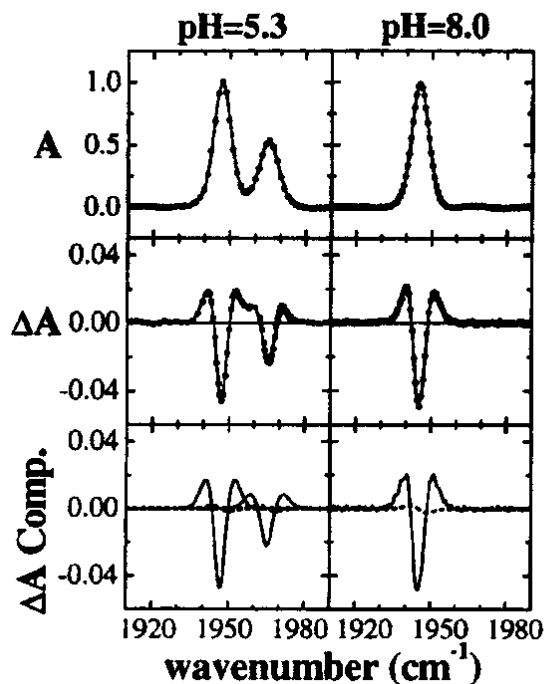
| MV/cm | Fe-C | C-O | q _C | q _O | q _C +q _O | q _C -q _O | v _{CO} Eqn. 1 | v _{CO} Eqn. 2 | v _{CO} Eqn. 2 |
|-------|--------|--------|----------------|----------------|--------------------------------|--------------------------------|------------------------|------------------------|------------------------|
| -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.

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

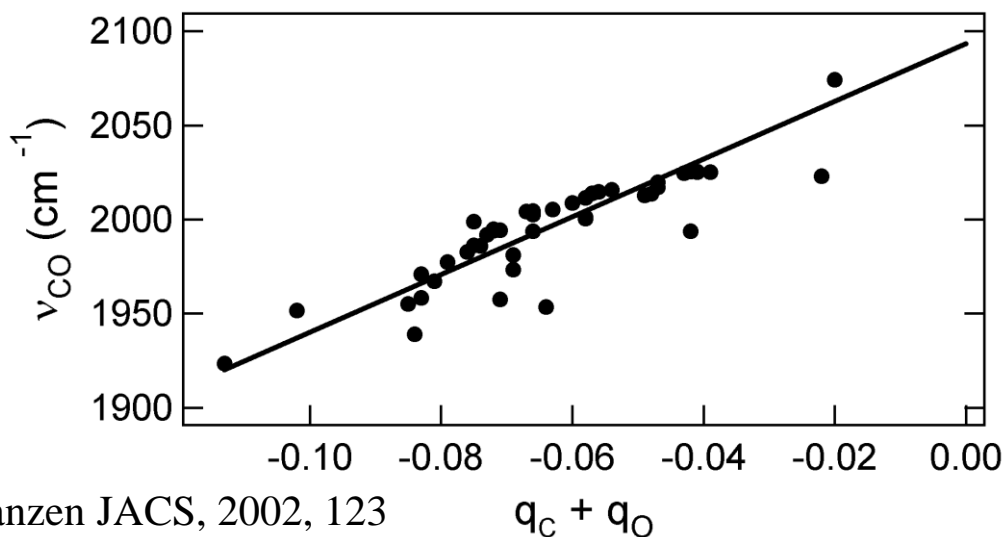
$$v_{\text{CO}} = \{2094 + 1535(q_{\text{C}} + q_{\text{O}})\} \text{ cm}^{-1} \quad (2)$$

DFT calculation of ν_{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