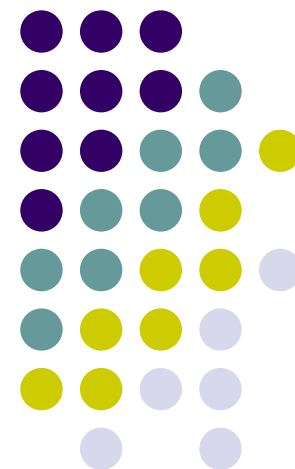


# Raman Spectroscopy

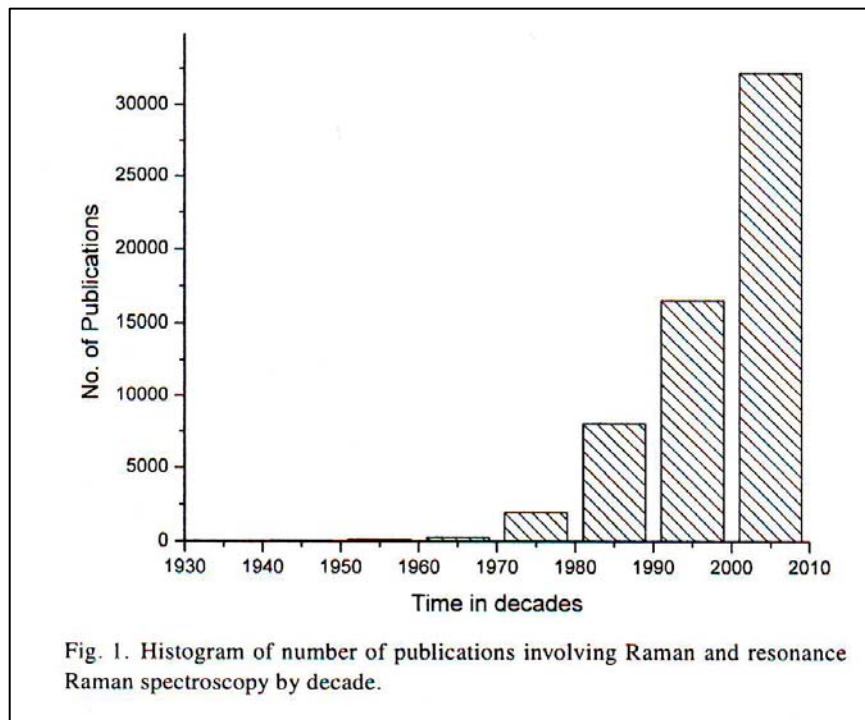
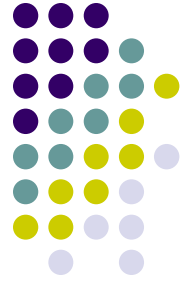
## Theory and Applications

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Dr. Florian Paulat  
(Lehnert Laboratory)



# Historical background



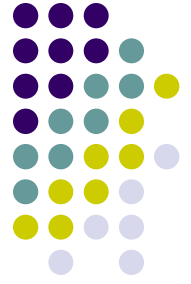
- 1920s: Prediction of inelastic scattering of light by molecules (Kramers, Heisenberg and Dirac)
- 1928: First report of inelastic scattering in water and alcohol vapors by Raman & Krishnan  
Technical limitation: light source
- 1960s: Development of Laser as intense monochromatic light sources



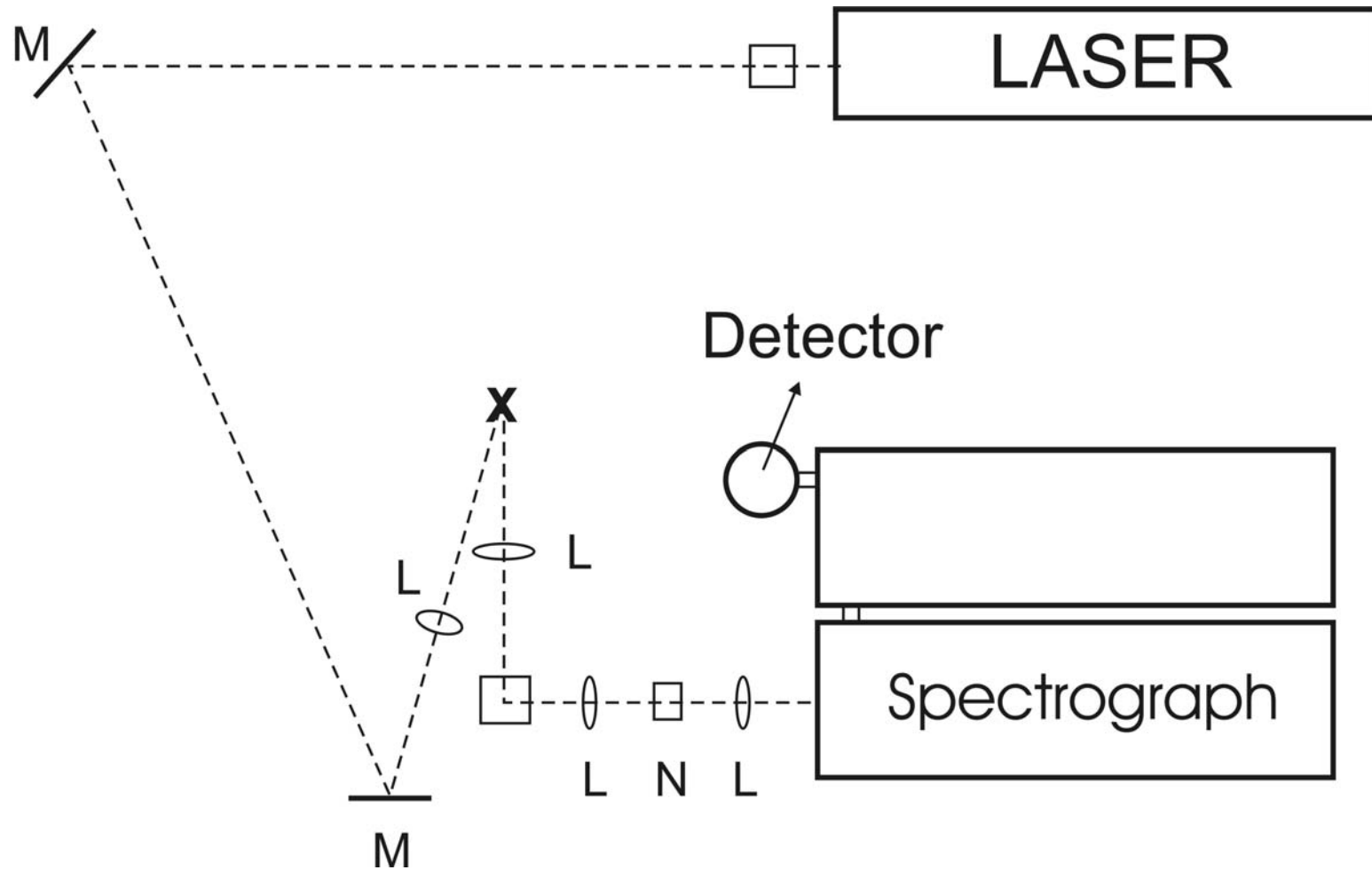
# Outline

## Assembly of a Raman spectrometer

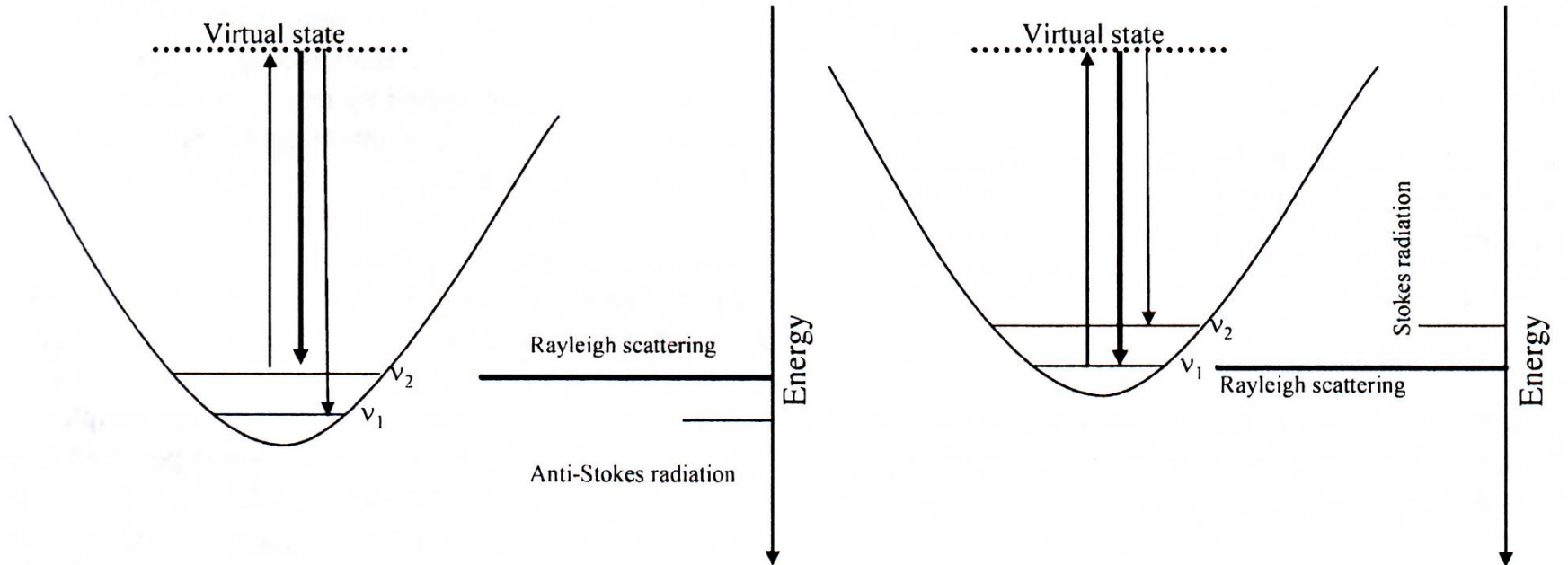
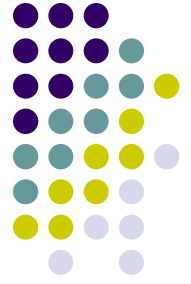
- 1) Theoretical background of:
  - Nonresonance Raman spectroscopy
  - Resonance Raman (rR) spectroscopy → A-,B- and C-Term enhancement mechanism
- 2) Resonance Raman spectroscopy of metalloporphyrins
  - Electronic structure of metalloporphyrins
  - Assignment of vibrational modes using DFT and rR spectroscopy
  - Identification of electronic transitions using rR spectroscopy



# Raman spectrometer

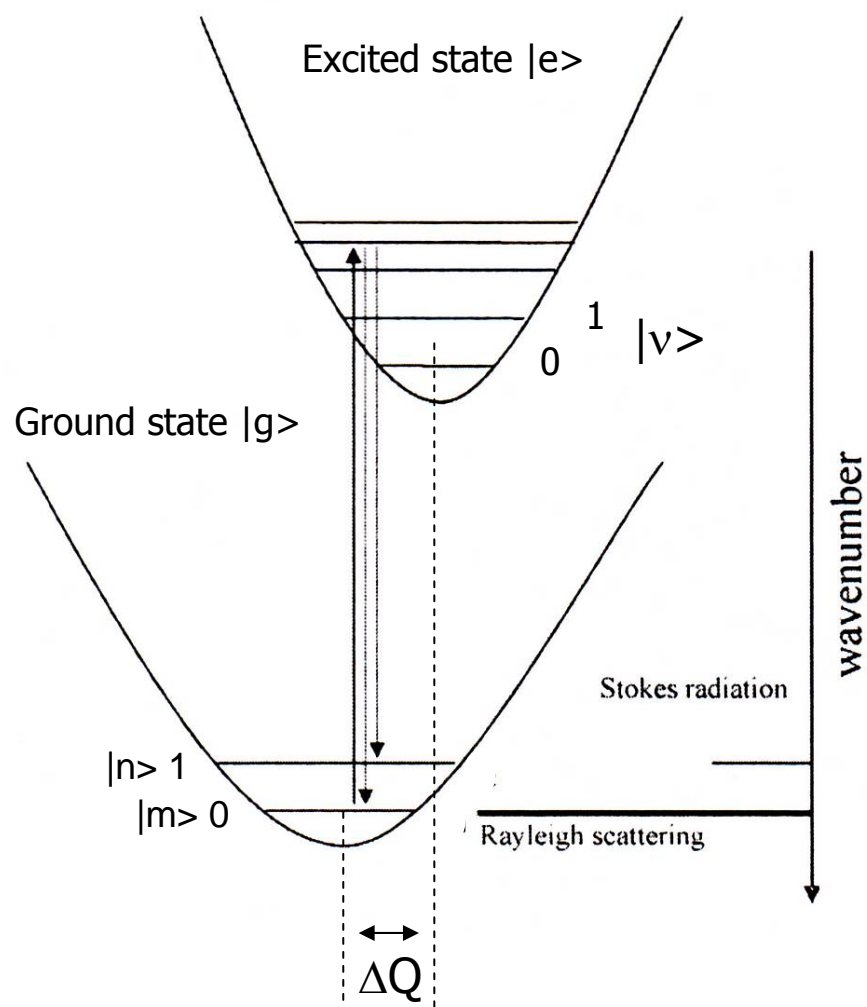


# 1) Nonresonance Raman



- $\sim 0.1\%$  is elastically (Rayleigh) and  $\sim 0.0001\text{-}0.00001\%$  inelastically scattered (Raman: Stokes; Anti-Stokes)  $\rightarrow$  LASER!
- IR: one photon  $\rightarrow$  direct absorption of light in IR region
- Raman: two photons  $\rightarrow$  UV, Vis and NIR excitation
- Stokes more intense than anti-Stokes (Boltzmann distribution)

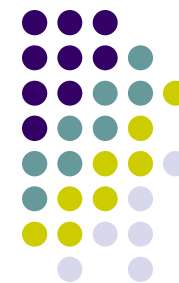
# Resonance Raman (rR) theory



- Harmonic potentials
- Intensity of a Raman line is proportional to  $\alpha^2$
- Polarizability:  $\alpha = A + B + C$ 
  - What is the meaning of the different mechanisms?
  - Following: Vibronic treatment of **Albrecht**: Starting from the quantum theoretical dispersion equation, using the Herzberg-Teller formalism he derived equations for A-, B- and C-Term enhancement.

(a) Tang, Albrecht in *Raman Spectroscopy*, Vol. 2, Plenum Press, New York, 1970.  
 (b) Albrecht, *J. Chem. Phys.* 1961, 34, 1476.

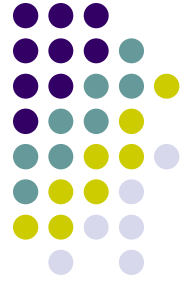
# rR – Enhancement Mechanism (A-Term)



$$A = \sum_{\nu} \frac{\langle e | \mu | g \rangle^2 \cdot \langle m | \nu \rangle \cdot \langle \nu | n \rangle}{E_{e,\nu} - E_{g,m} - E_0 + i\Gamma}$$

- In resonance:  $E_{e,\nu} - E_{g,m} \approx E_0$
- A proport. to electronic transition moment squared → **intense electronic transition** (dipole allowed)
- Vibrational overlap integrals (Franck-Condon factor):
  - a) = 0 for identical potential curves and
  - b)  $\neq 0$  only if displacement of potential curves ( $\Delta Q > 0$ ) → only **totally symmetric modes** ( $A_{1g}$ )

# rR – Enhancement Mechanism (B-Term)

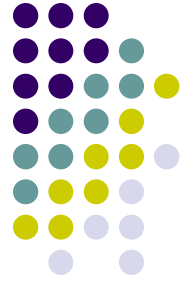


$$B = \sum_v \left[ D_v \cdot \sum_s \sum_j \frac{\langle e | h_j | s \rangle}{\Delta E_{e,s}} \cdot \left( \langle e | \mu | g \rangle \cdot \langle s | \mu | g \rangle \cdot \langle n | \nu \rangle \cdot \langle \nu | Q_j | m \rangle + \langle e | \mu | g \rangle \cdot \langle s | \mu | g \rangle \cdot \langle m | \nu \rangle \cdot \langle \nu | Q_j | n \rangle \right) \right]$$

- **Vibronic coupling** of another excited state  $|s\rangle$  with the resonant excited state  $|e\rangle$
- **Energetic separation of  $|e\rangle$  and  $|s\rangle$  must be small**
- Both transition dipole moments from  $|g\rangle$  to  $|e\rangle$  and  $|s\rangle$  must be nonvanishing  
→ **excited states must belong to allowed electronic transitions**
- $\langle \nu | Q_j | m, n \rangle$  connect  $|g\rangle$  and  $|e\rangle$  vibrational levels that differ by one quantum; when they are multiplied by Franck-Condon factors having same quantum numbers, the nominator does not! vanish even if there is no excited-state displacement  $\Delta Q$   
→ (totally) and **nontotally symmetric modes are enhanced via B-Term**
- Which modes are enhanced? → group theory (direct product)

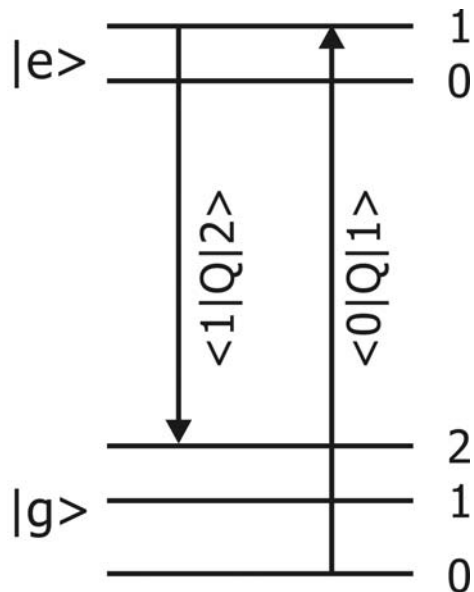


# rR – Enhancement Mechanism (C-Term)



$$C \propto \langle m|Q|v \rangle \cdot \langle v|Q|n \rangle$$

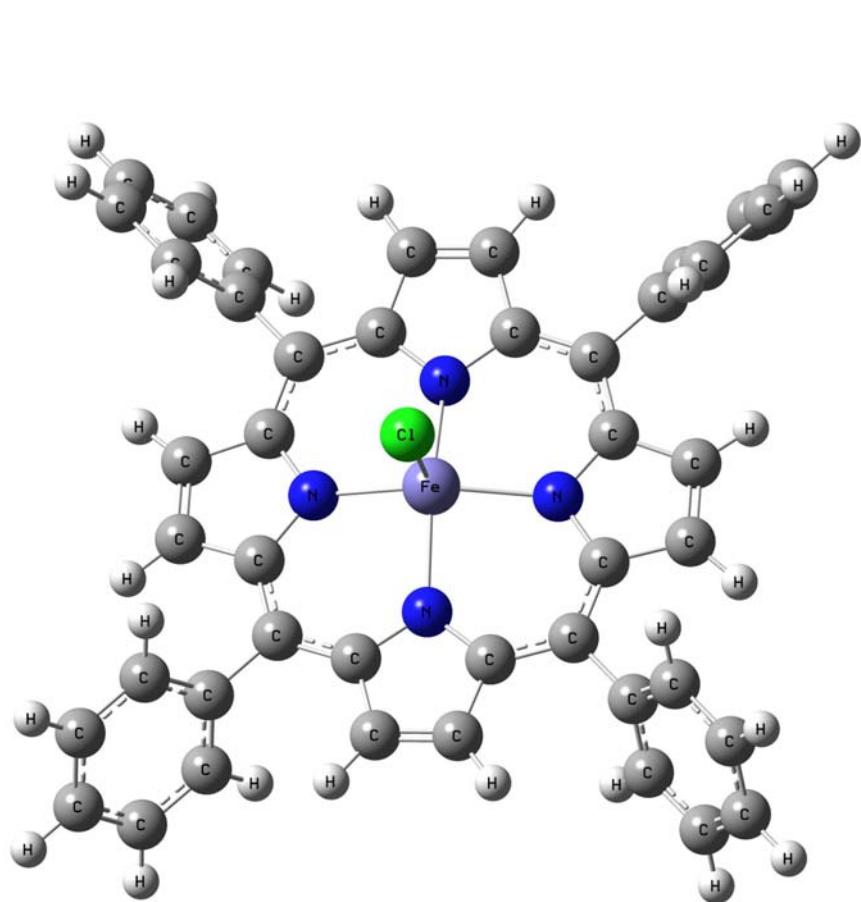
- Numerator contains two Q-dependent integrals, which connect vibrational levels of  $|g\rangle$  and  $|e\rangle$  differing by one quantum



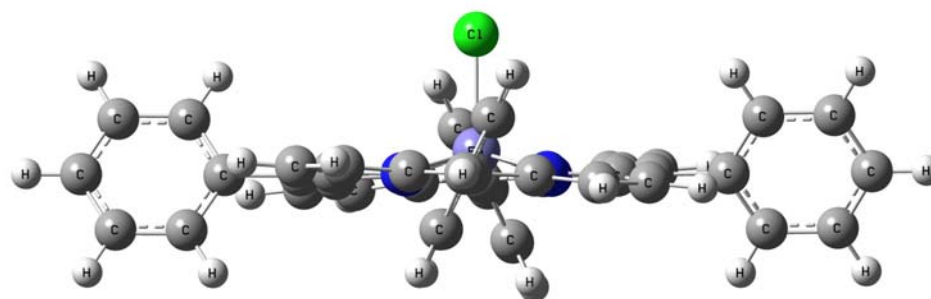
What kind of modes are enhanced by C-Term?

→ **Overtones (0→2)!!!**

## 2) Resonance Raman Spectroscopy of [Fe(TPP)Cl]



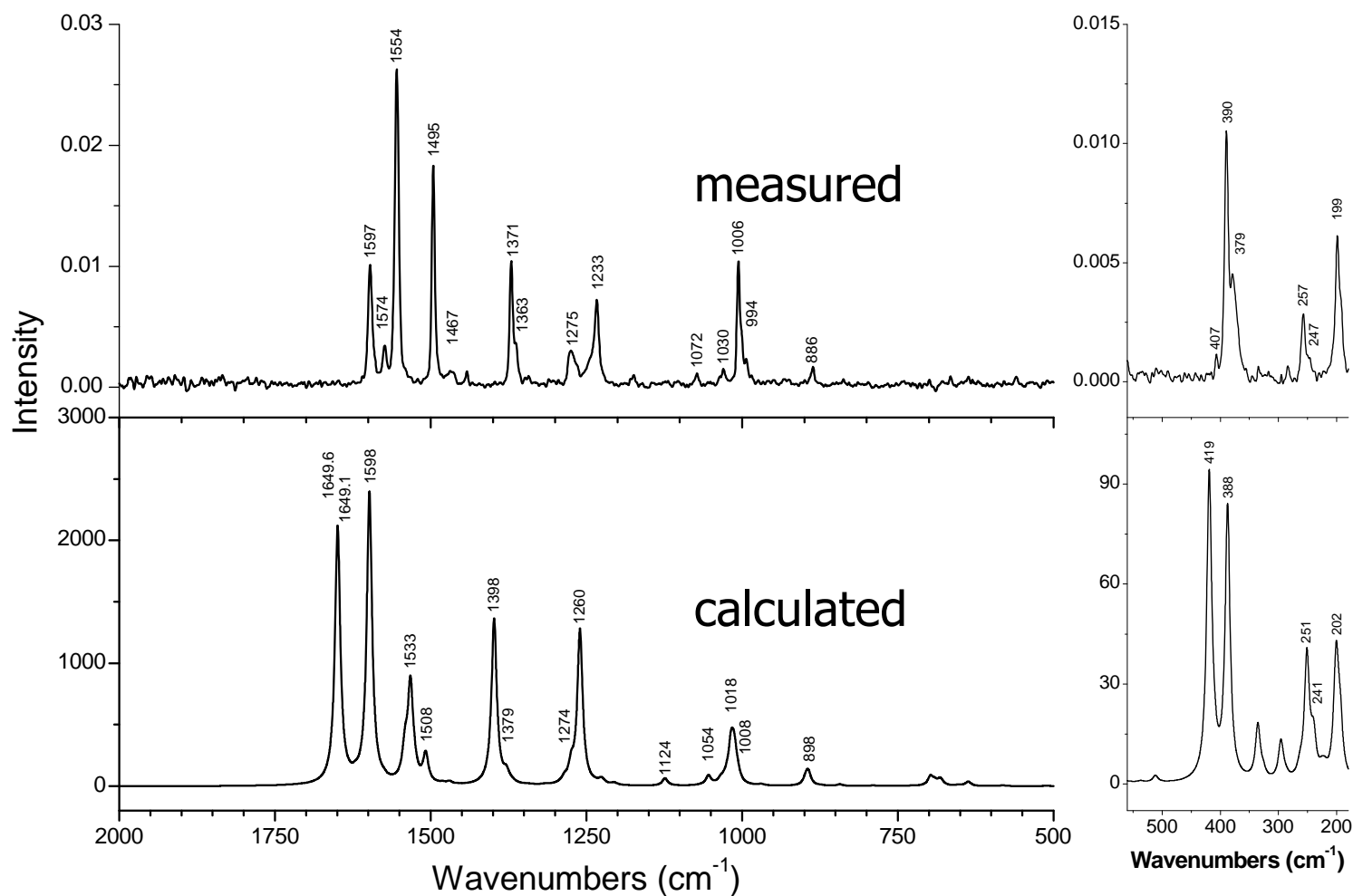
Optimized structure (B3LYP/LanL2DZ)



Vibrational Assignment:

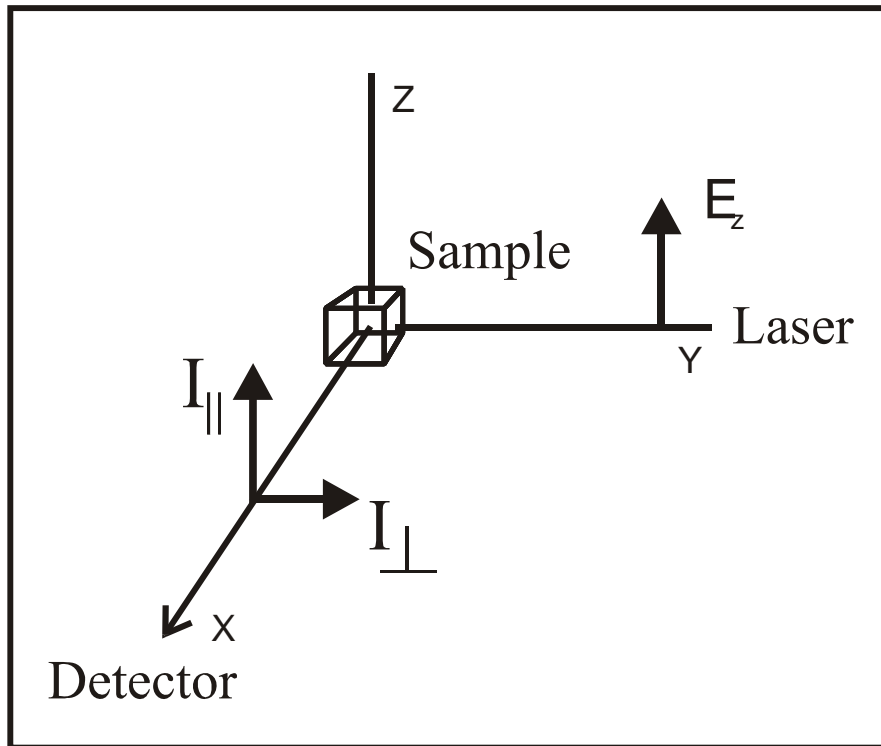
- 78 Atoms  $\rightarrow 3N-6 = 228$  vibrations!!!
- What tools to solve problem?
  - DFT calculations
  - Polarized rR spectroscopy ( $D_{4h}$  apply to the [M(TPP)] vibrations of [M(TPP)(Cl)])

# Nonresonance Raman Spectrum of [Fe(TPP)Cl] ( $\lambda_{exc.} = 1064 \text{ nm}$ )





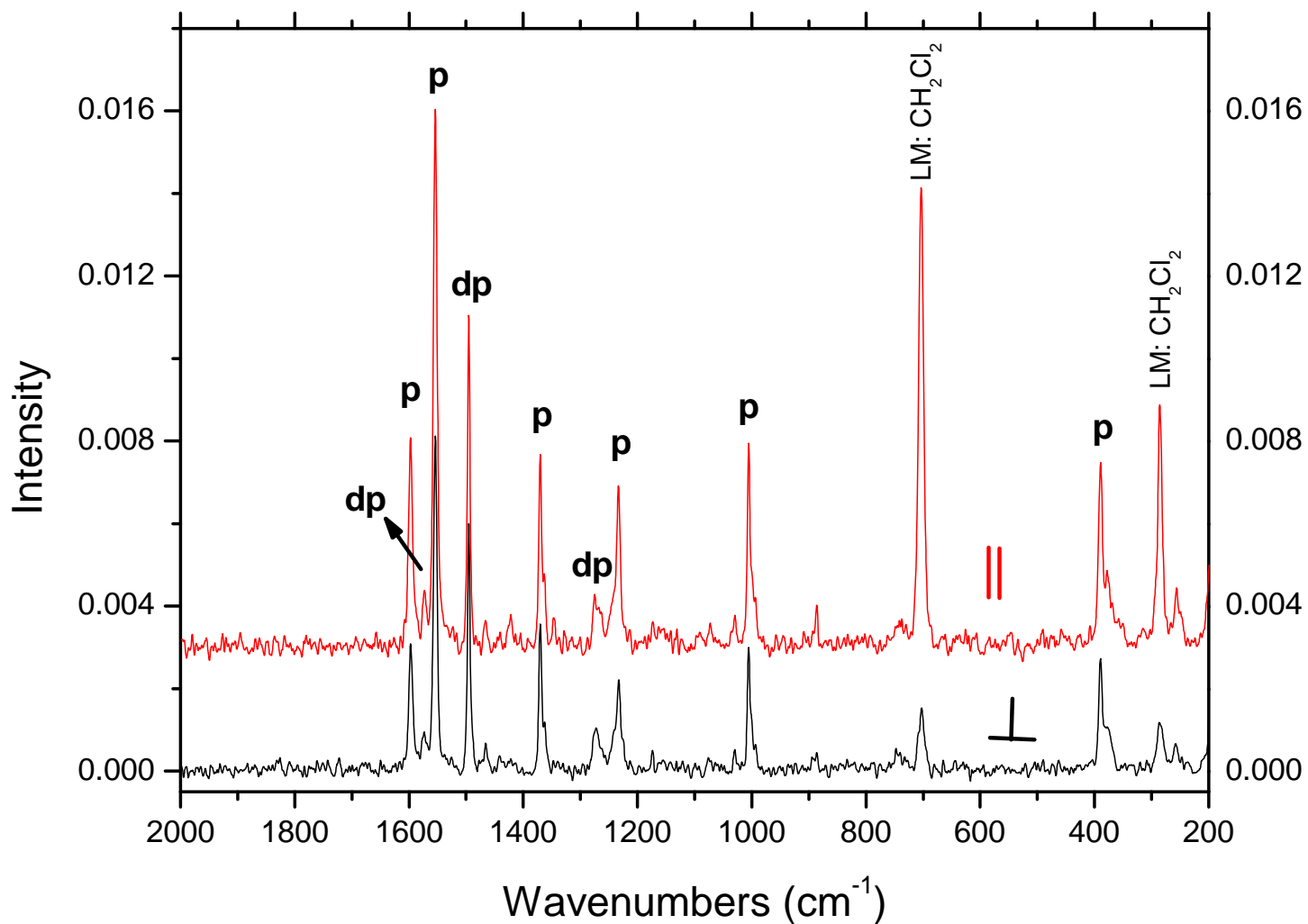
# Depolarization ratio $\rho$



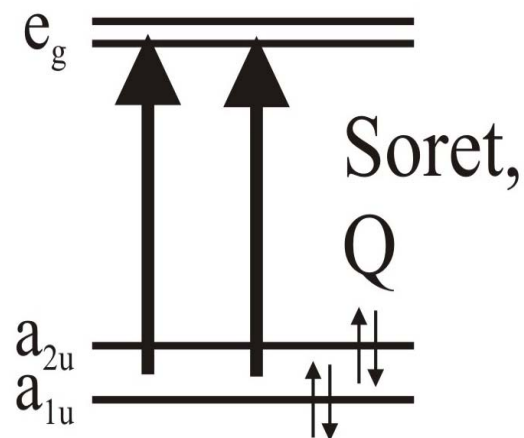
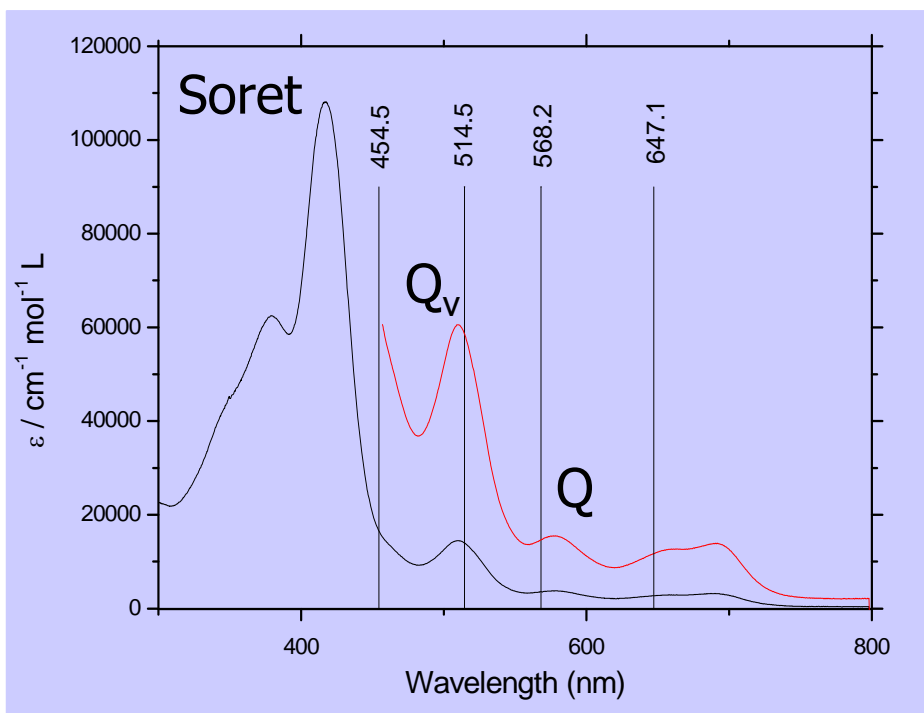
$$\rho = \frac{I_{\text{perpendicular}}}{I_{\text{parallel}}}$$

- $0 < \rho < \frac{3}{4}$  polarized (**p**;  $A_{1g}$  vibrations)
- $\rho = \frac{3}{4}$  depolarized (**dp**;  $B_{1g}$  and  $B_{2g}$  vibrations)
- $\rho > \frac{3}{4}$  anomalous Polarization (**ap**;  $A_{2g}$  vibrations; in nonresonance Raman forbidden!)

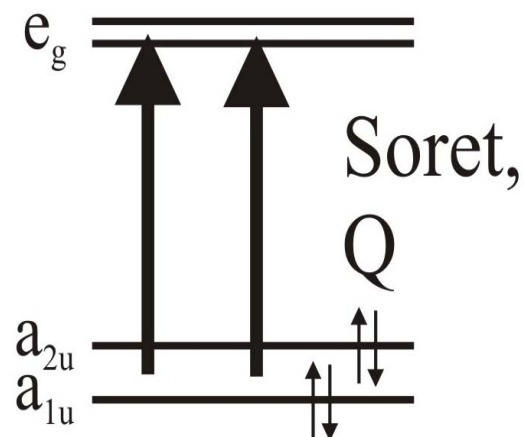
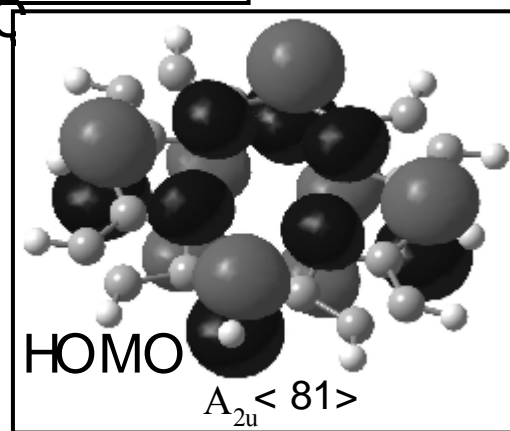
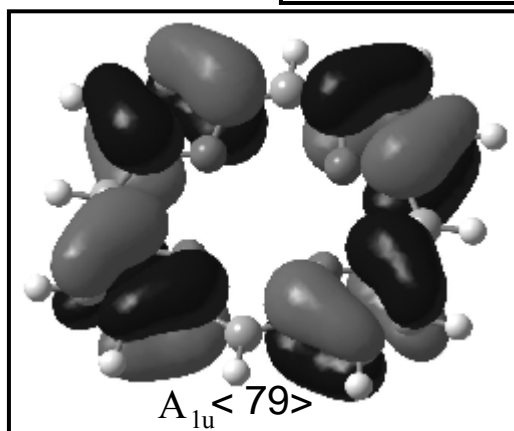
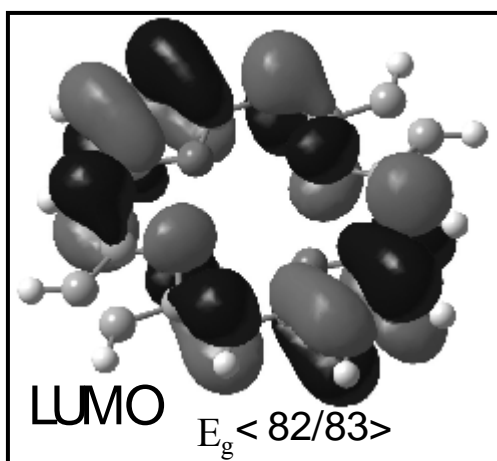
# Polarized nonresonance Raman Spectrum of [Fe(TPP)Cl] ( $\lambda_{\text{exc.}} = 1064 \text{ nm}$ )



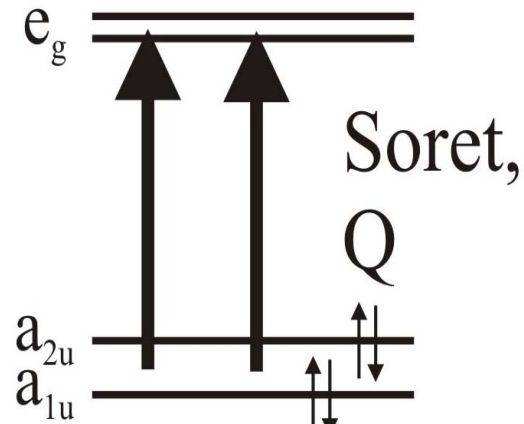
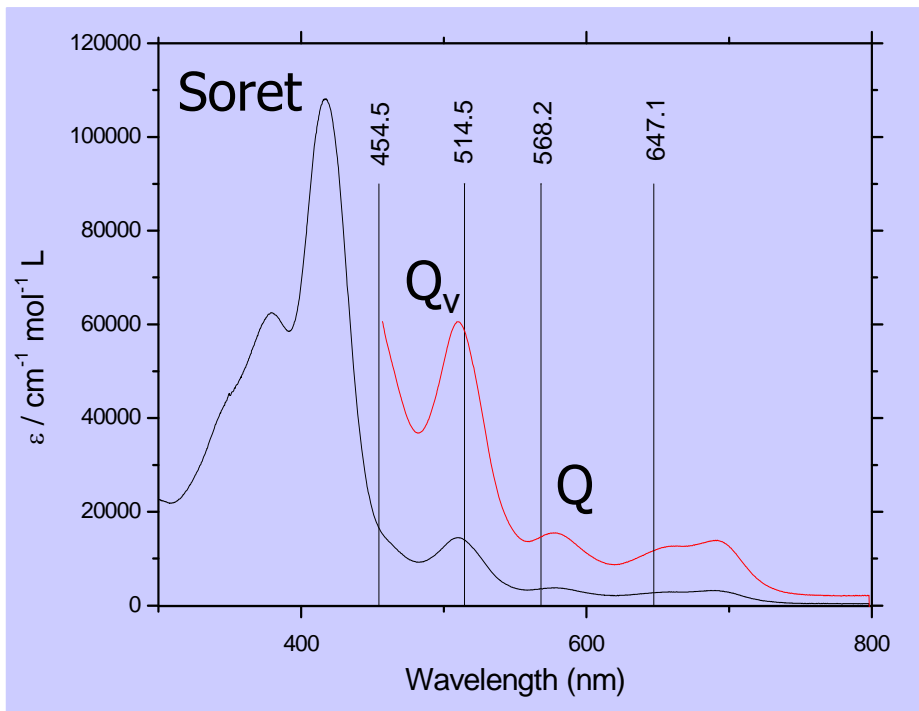
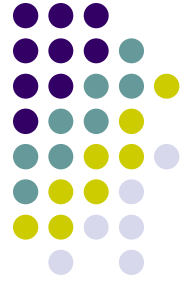
# Electronic structure of [Fe(TPP)Cl]: Gouterman model



# Electronic structure of [Fe(TPP)Cl]: Gouterman model



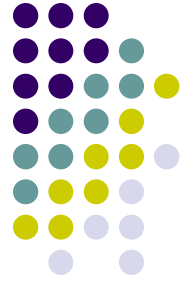
# Electronic structure of [Fe(TPP)Cl]: Gouterman model



- Both excited states have  $E_u$  symmetry ( $a_{1u} \times e_g = a_{2u} \times e_g = E_u$ )
- Strong CI leads to large splitting  
→ Soret and Q-band
- $Q_v$ : Vibronic mixing between Soret and Q excited states: Which vibrations are active? →  $E_u \times E_u = (A_{1g}) + B_{1g} + B_{2g} + A_{2g}$
- Distance between Q and  $Q_v$ ?



# Polarized rR spectroscopy of Metalloporphyrins



- A-Term: totally symmetric modes  $\rightarrow A_{1g}$  vibrations

A-Term proport. to  $\langle e|\mu|g\rangle^2 \rightarrow$  A-Term is dominant for intense electronic transitions

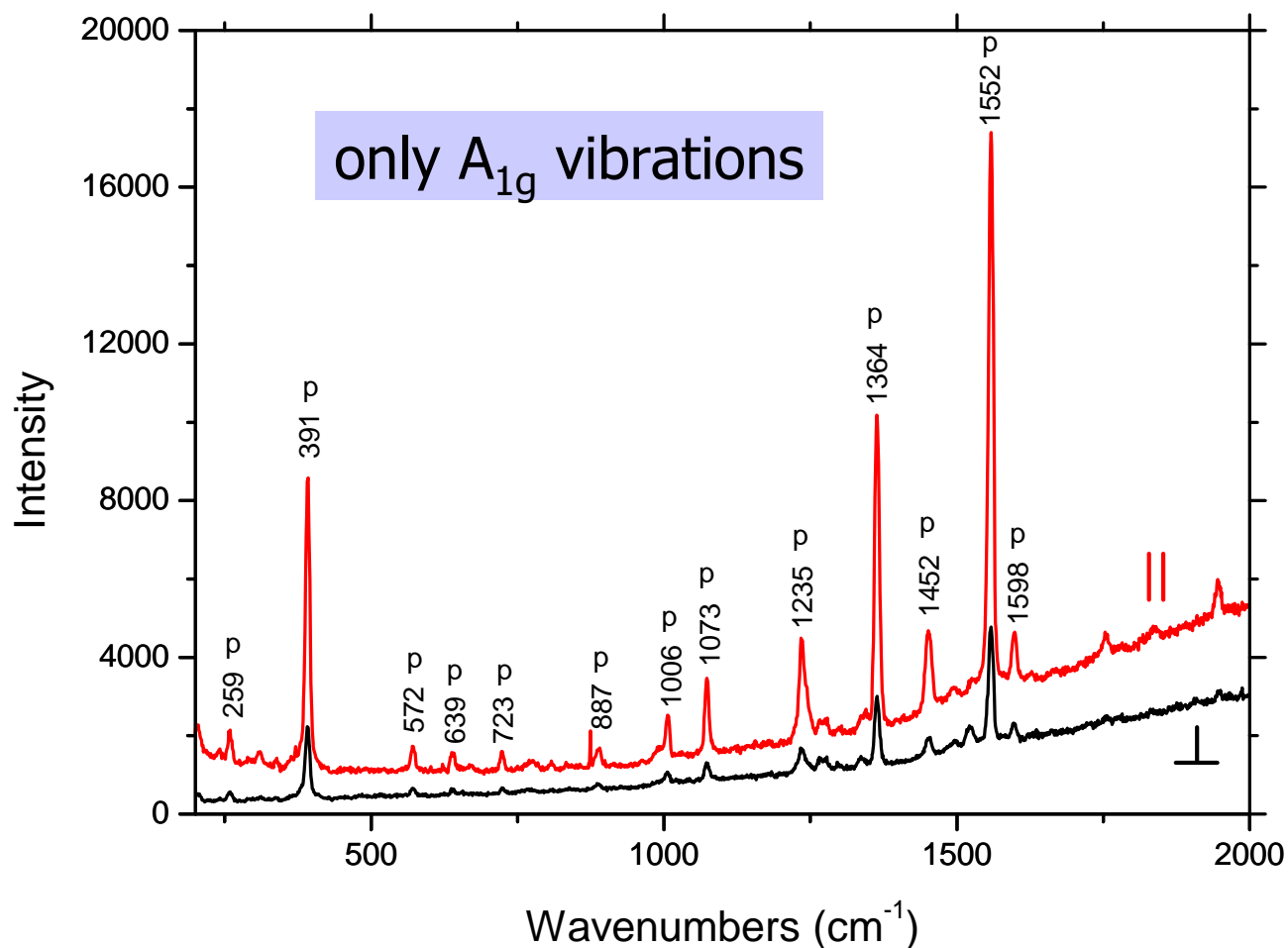
Metalloporphyrin:  $\rightarrow$  In Soret resonance enhancement of  $A_{1g}$

- B-Term: vibronic coupling  $\rightarrow$  nontotally symmetric modes which are active in mixing  $|e\rangle$  with  $|s\rangle \rightarrow B_{1g}, B_{2g}$  and  $A_{2g}$

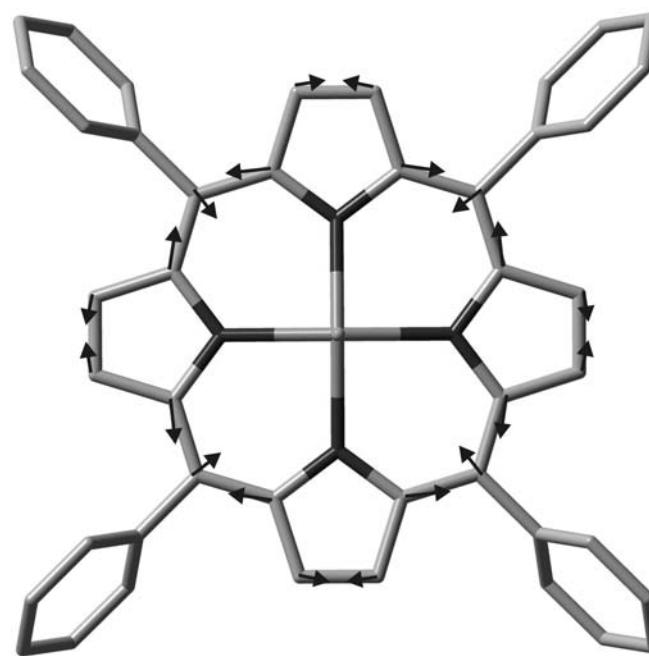
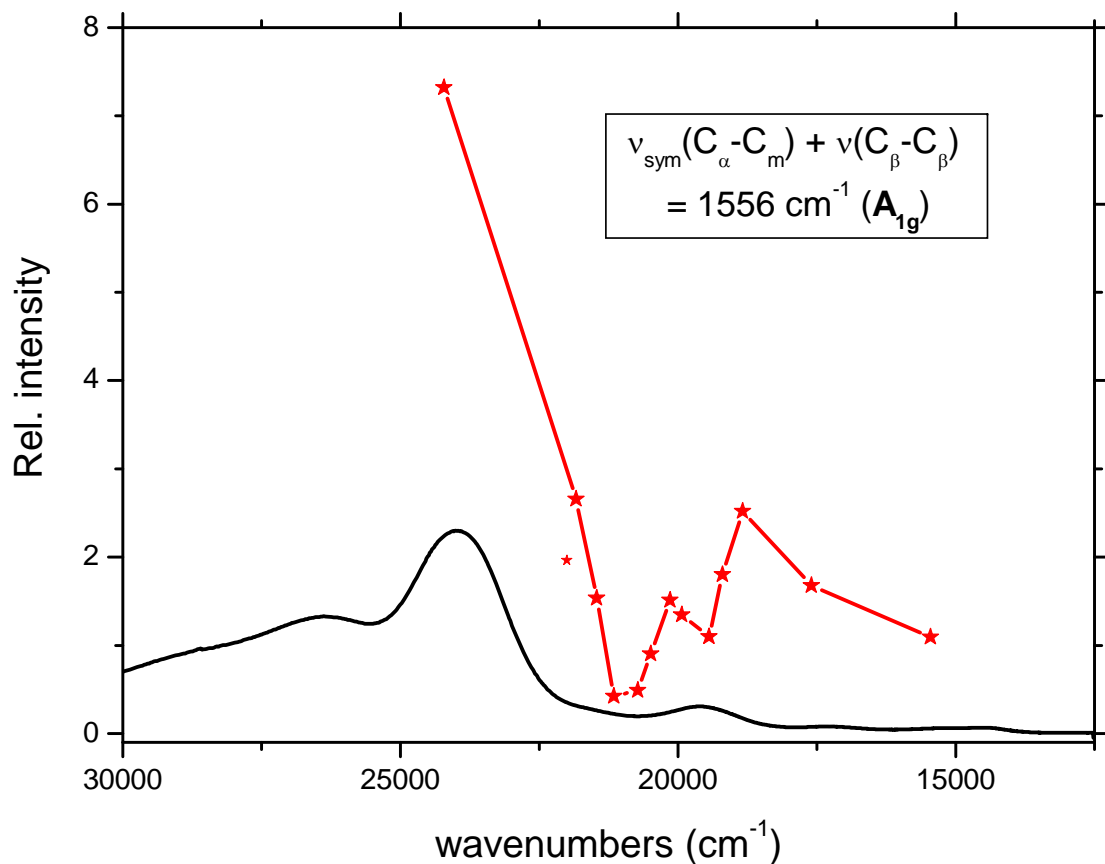
Metalloporphyrin:  $\rightarrow$  In Q resonance (vibronic mixing with Soret excited state) enhancement of  $B_{1g}, B_{2g}$  and  $A_{2g}$  modes

But: Q band is relative intense  $\rightarrow$  additional A-Term enhancement of  $A_{1g}$

# Polarized rR spectrum (Soret) of [Fe(TPP)Cl] at $\lambda_{\text{exc.}} = 454.5 \text{ nm}$

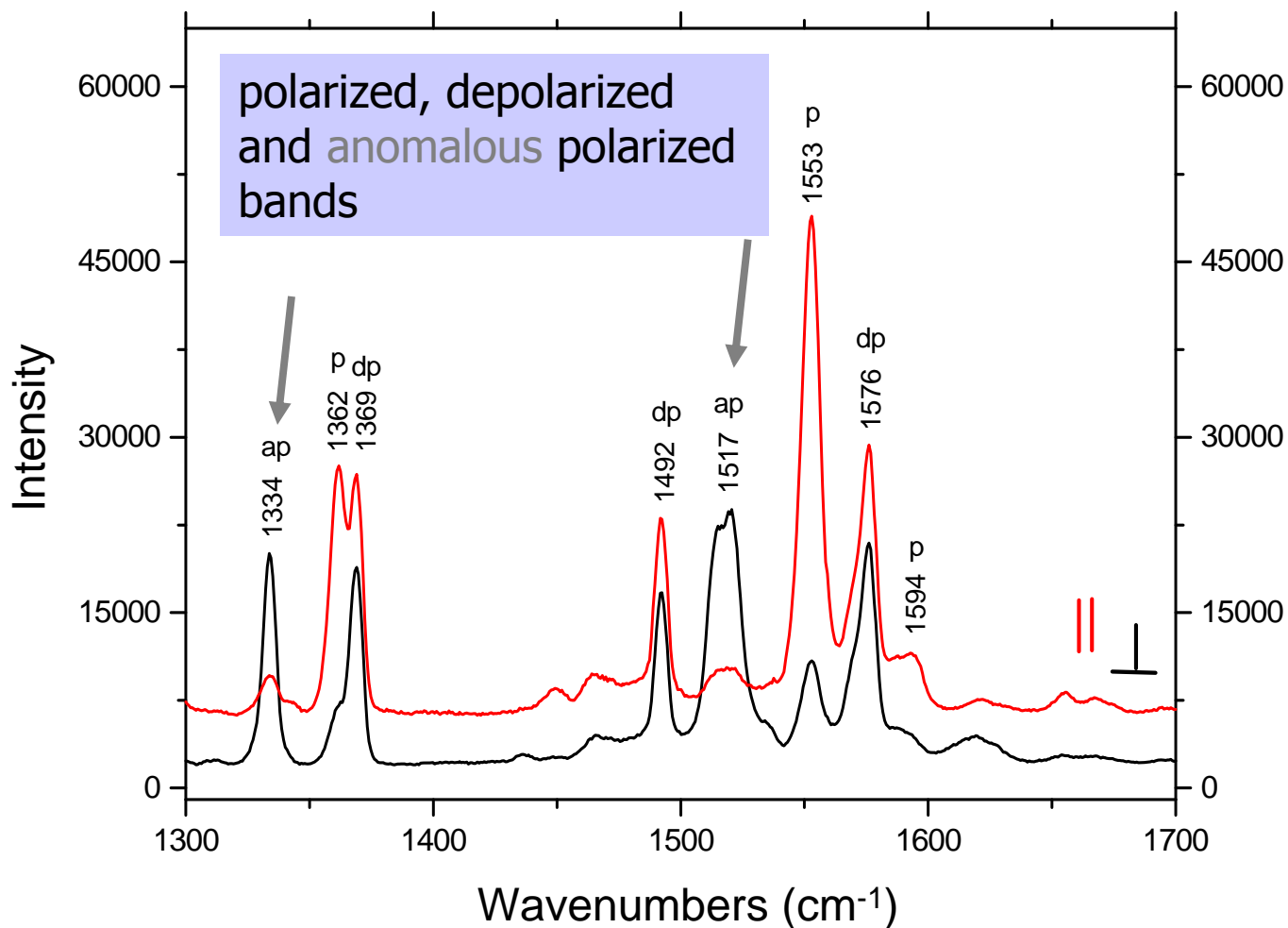


# rR: excitation profile [Fe(TPP)Cl]

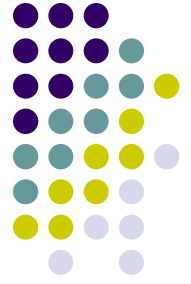


Symmetry?

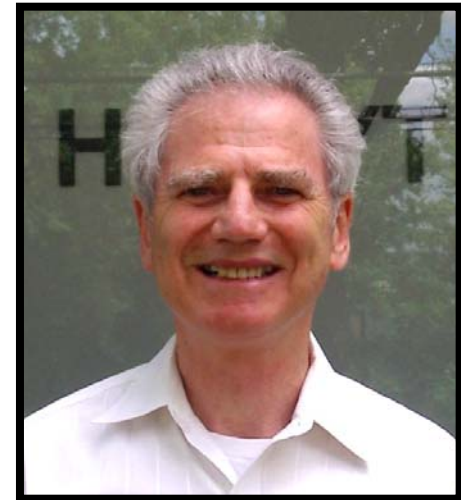
# Polarized rR spectrum ( $Q_V$ ) of [Fe(TPP)Cl] at $\lambda_{exc.} = 514.5$ nm



# Anomalous Polarization

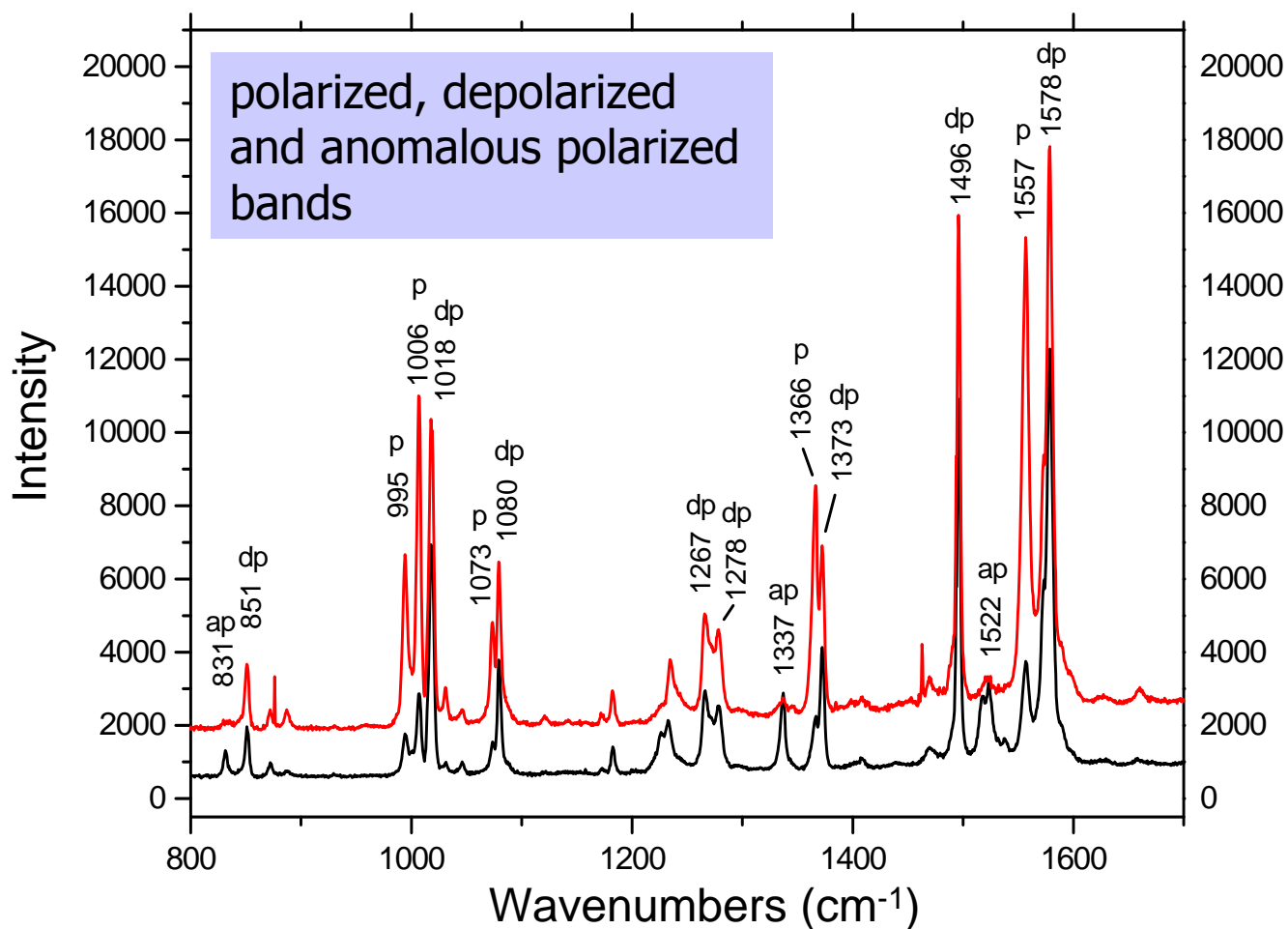


- **1934 Placzek:** Theoretical Prediction of anomalous polarization
- **1972 Spiro and Strekas:**  
almost 40 years later: first experimental determination of this effect: found in the resonance Raman spectra (depolarized measurements) of hemoglobin and cytochrome C

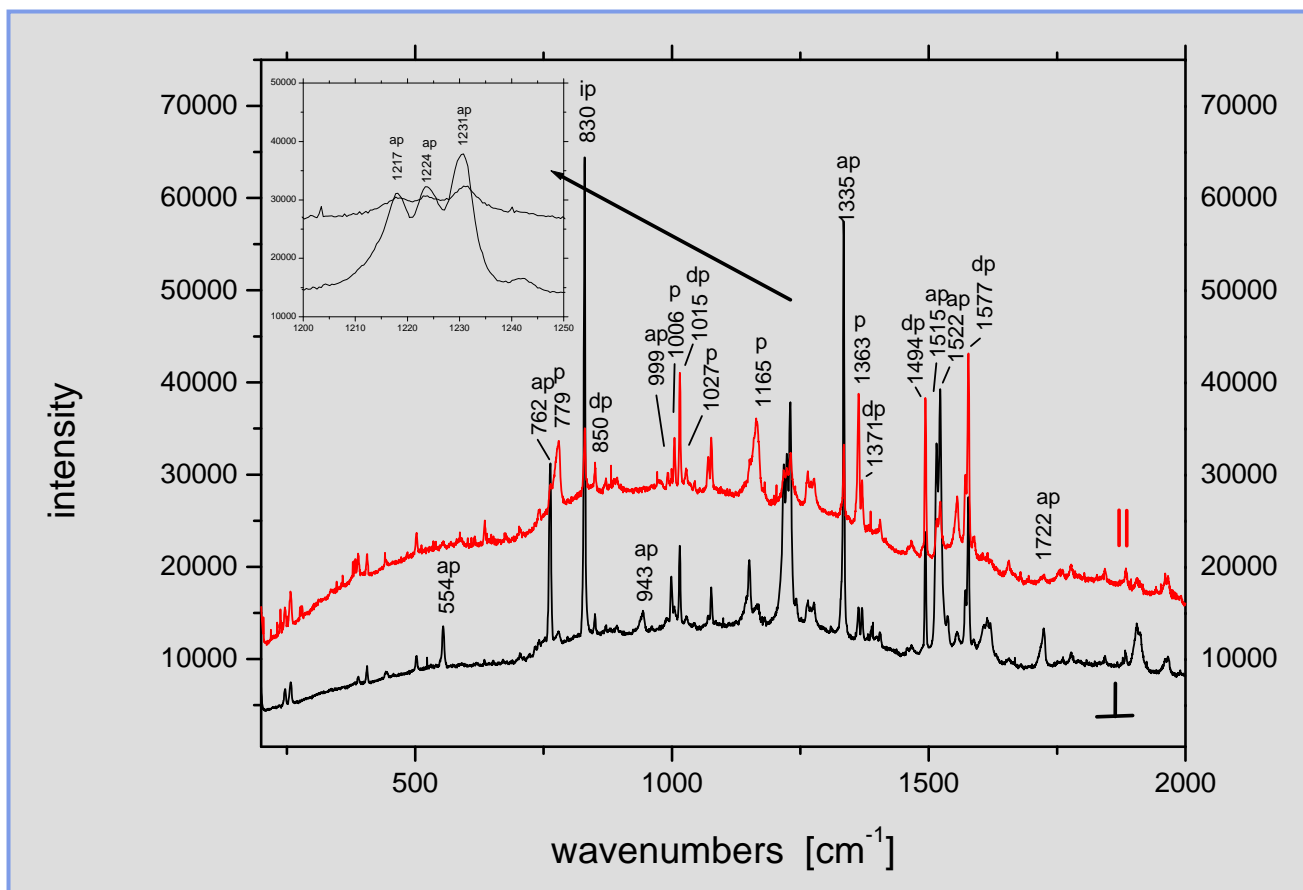


T. G. Spiro, T. C. Strekas, *Proc. Nat. Acad. Sci.* **1972**, Vol. 69 (No. 9), 2622-2626.

# Polarized rR spectrum (Q) of [Fe(TPP)Cl] at $\lambda_{\text{exc.}} = 568.2 \text{ nm}$



# [Fe(TPP)Cl]: rR spectrum with excitation in ? ( $\lambda_{exc.} = 647.1 \text{ nm}$ )



- low energy: anomalous polarized bands: out-of-plane vibrations of the phenylrings
- different enhancement compared to excitation in Q
- What is the nature of this electronic transition?
- TD-DFT calculations and MCD Spectra have to be analyzed in detail!

Gouterman: porphyrin( $a_{1u}/a_{2u}$ )  $\rightarrow$   $d\pi$  transition (again  $E_u$  symmetry  $\rightarrow$  strong CI with Soret and or Q (if near in energy)? TDDFT: very very complicated!!!)

# Summary (rR of Metalloporphyrins)



- **Complete assignment** of the nonresonance and resonance Raman spectra of [Fe(TPP)Cl] using DFT and polarized Raman
- **Assignment of additional vibrations** which are not present in the nonresonance case
- Resonance enhancement is related to the nature of the excited electronic transition → **Polarized resonance Raman assists in assigning electronic absorption bands**
- Identification of anomalous polarized bands ( $A_{2g}$ ) which are a **probe for vibronic mixing**
- Resonance enhancement very different for Soret,  $Q/Q_v$  and  $\sim 680\text{nm}$  bands
- What is the nature of the  $\sim 680\text{nm}$  feature? Gouterman: porphyrin( $a_{1u}/a_{2u}$ ) →  $d\pi$  transition

Paulat, F.; Praneeth, V. K. K.; Lehnert, N. *Inorg. Chem.* **2006**, *45*, 2835-2856.



# Available wavelengths for rR in the Lehnert group

