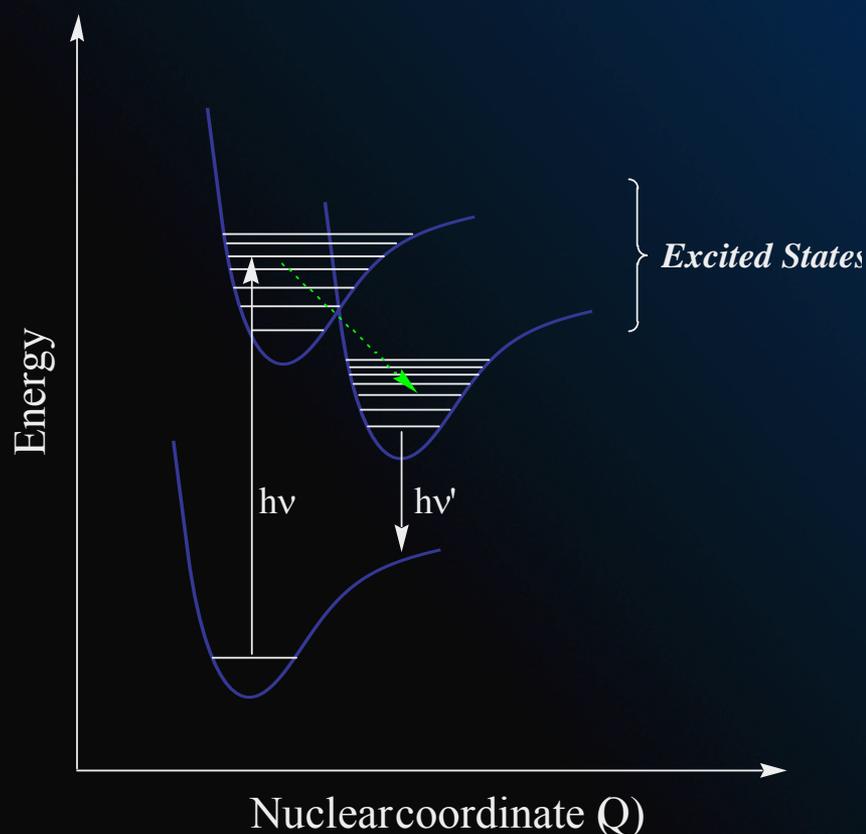


*Ultrafast Spin and Structural
Isomerization Dynamics in
Transition Metal Complexes*

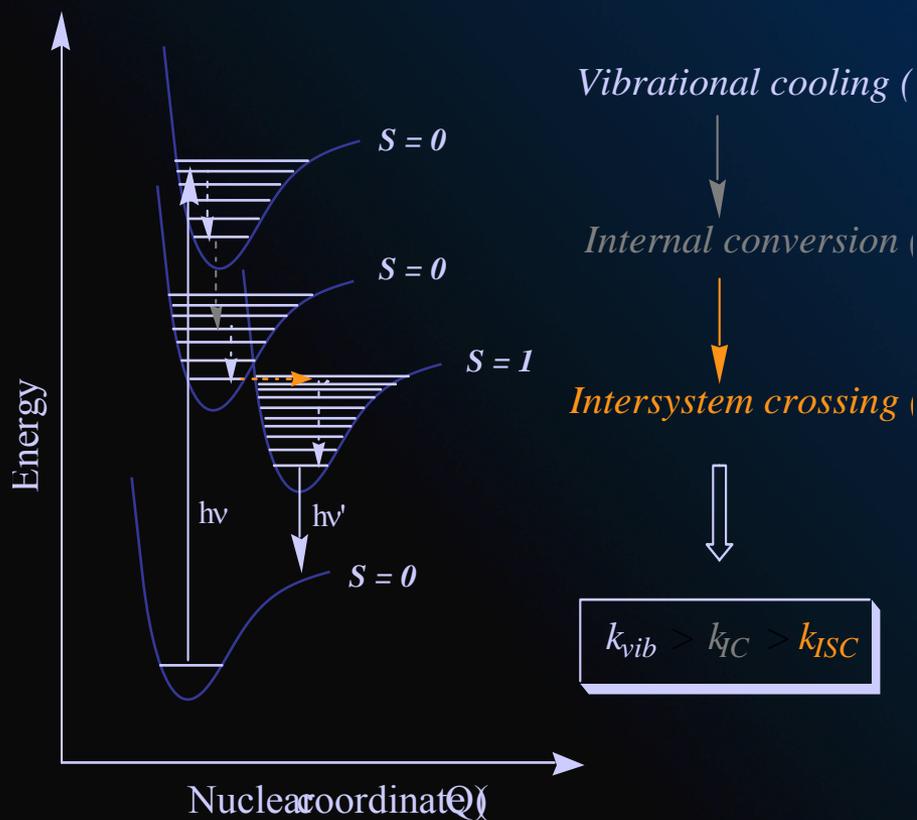
James K. McCusker
Department of Chemistry
Michigan State University

Excited-State Evolution



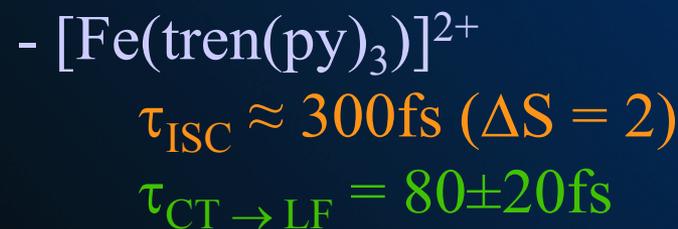
- What is the time scale of excited-state formation?
- Mechanistic details?
- To what extent do electronic, geometric, and other factors play a role?
- Can these processes be controlled?

Reassessing the “rules”



- classic picture of excited-state evolution suggests well-defined sequence of events

- *not realized in transition metal systems:*



Outline

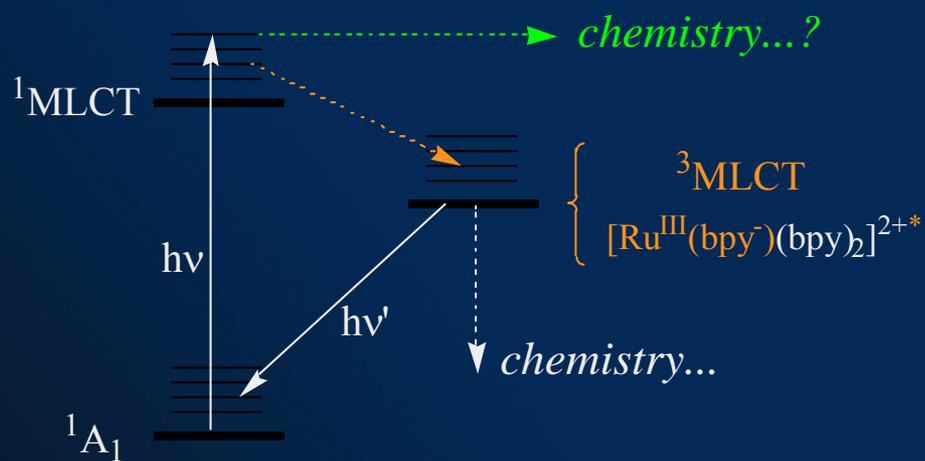
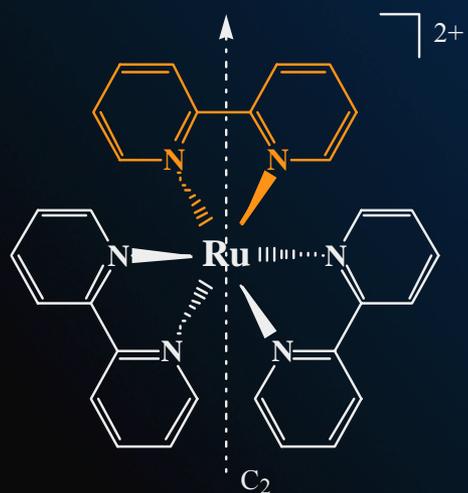
I. Introductory comments

→ II. Dynamics in charge-transfer states
- *LAM in CT state evolution*
- *solvent effects*

→ III. Charge-transfer to ligand-field dynamics
- *ultrafast dynamics in low-spin Fe^{II}*

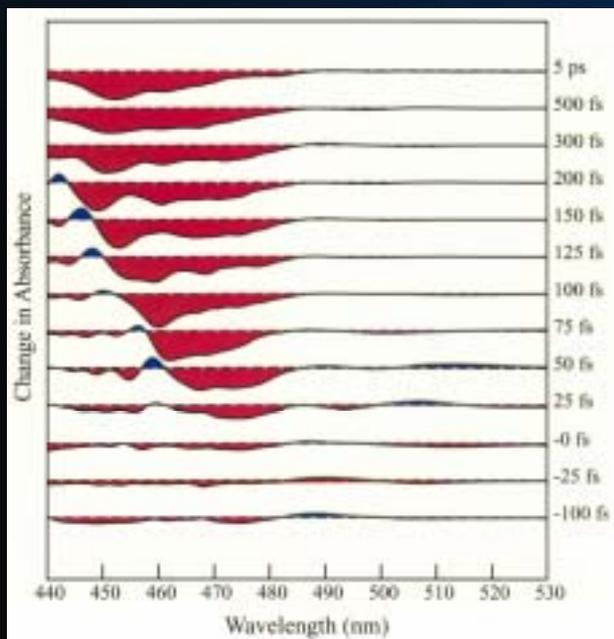
→ IV. Concluding comments

The Prototype: $[Ru(bpy)_3]^{2+}$



- perhaps the most widely studied of transition metal chromophores
- basis for most transition metal-based solar energy conversion schemes of the past two decades
- electronic structure is reasonably approximated as a three-level system

Basic photophysics of $[Ru(bpy)_3]^{2+}$



- charge localization
- non-diffusive solvation dynamics



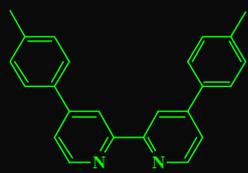
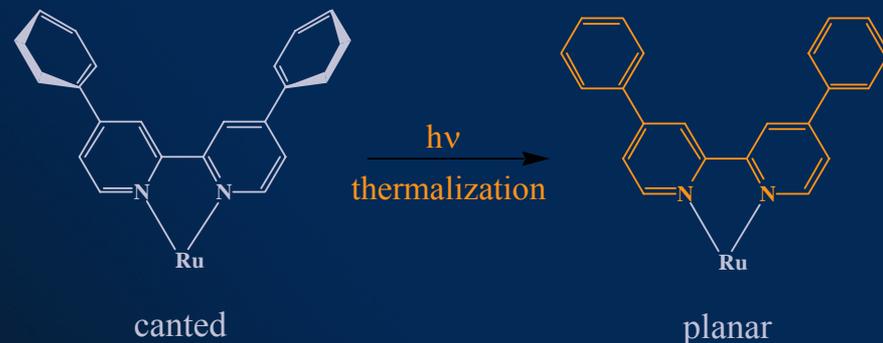
QuickTime™ and a
TIFF (LZW) decompressor
are needed to see this picture.



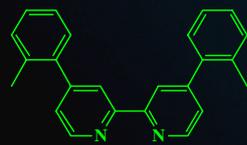
- time scale of 3MLCT formation
- methodology

LAM in CT-State Formation

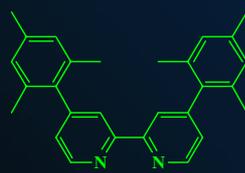
- anomalously strong emission from $[\text{Ru}(\text{dpb})_3]^{2+}$ ($\Phi_r \approx 0.2$)
- relatively narrow spectrum suggests nested potentials
- model involving aryl ring rotation coupled to $^3\text{MLCT}$ state formation was proposed



dptb



dotb



dmesb

k_{nr}	$5.2 \times 10^5 \text{ s}^{-1}$	$6.2 \times 10^5 \text{ s}^{-1}$	$9.6 \times 10^5 \text{ s}^{-1}$
$\Delta\nu$	16 cm^{-1}	42 cm^{-1}	67 cm^{-1}



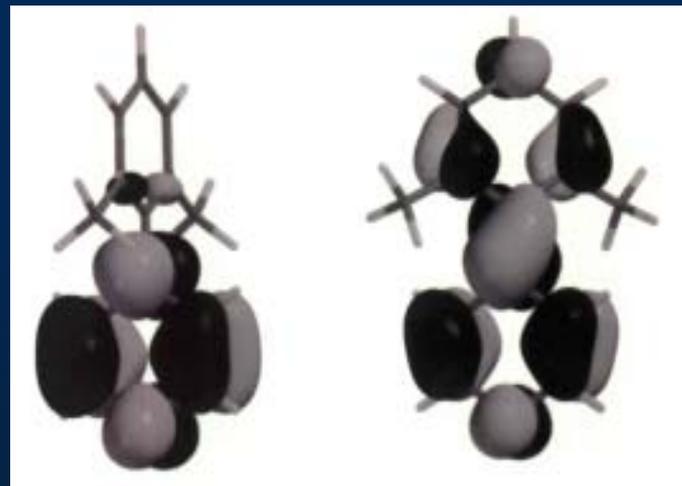
Intraligand electron delocalization

Calculated Structural Changes: $\Delta\theta$

4-phenylpyridine $\sim 45^\circ$

4-(o-tolyly)pyridine $\sim 35^\circ$

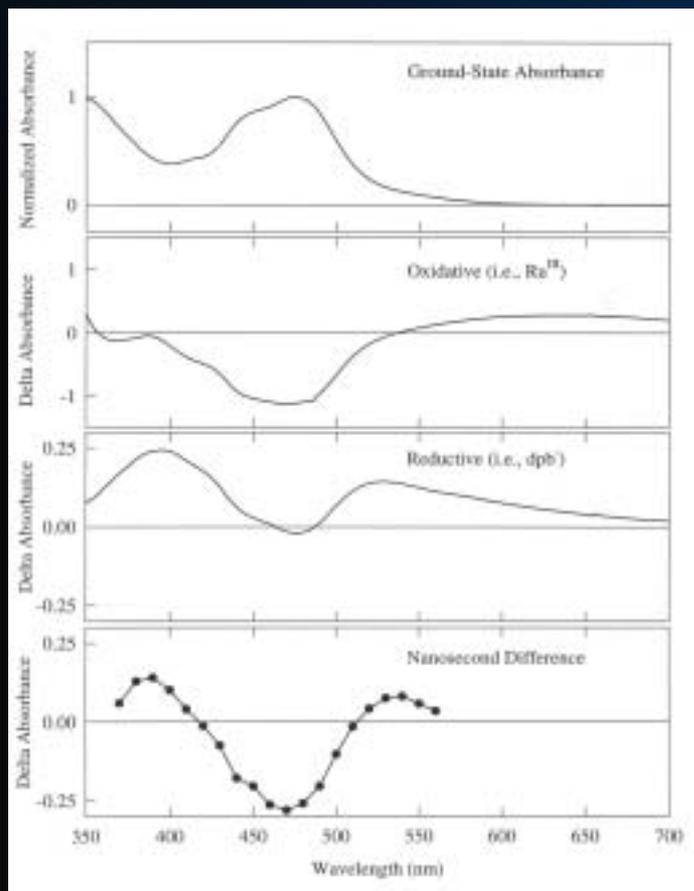
4-(2,6-(CH₃)₂Ph)pyridine $\sim 45^\circ$



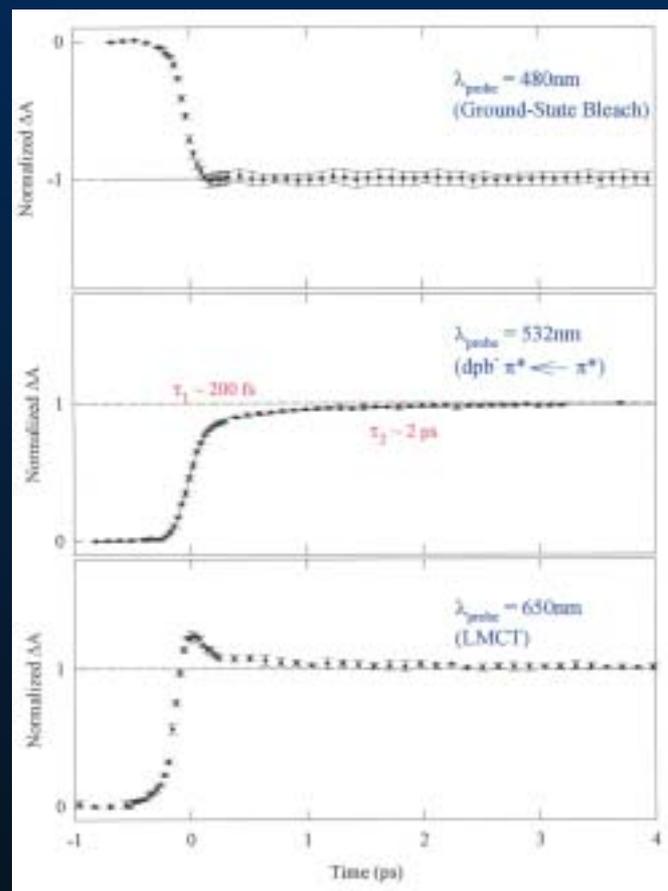
- increased conjugation between ring systems provides driving force for ring rotation
- larger transition dipole anticipated for structurally relaxed “anion”
- provides means for studying charge transfer processes occurring concomitant with large amplitude motion (LAM) of the chromophore

Spectroscopy of $[Ru(dpb)_3]^{2+}$

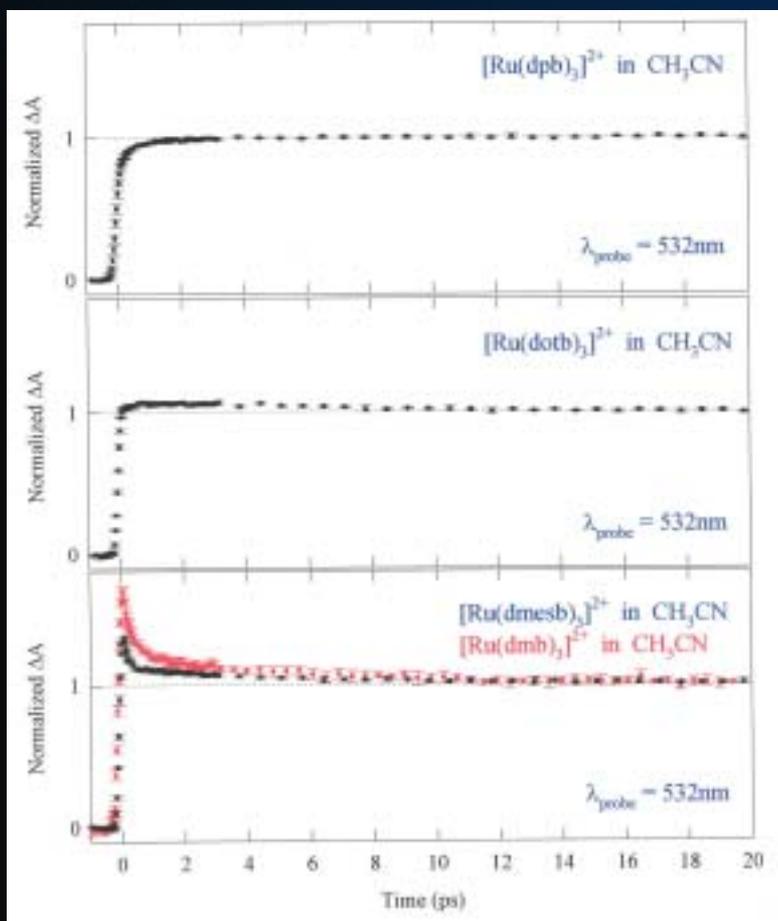
Spectroelectrochemistry



Time-resolved absorption

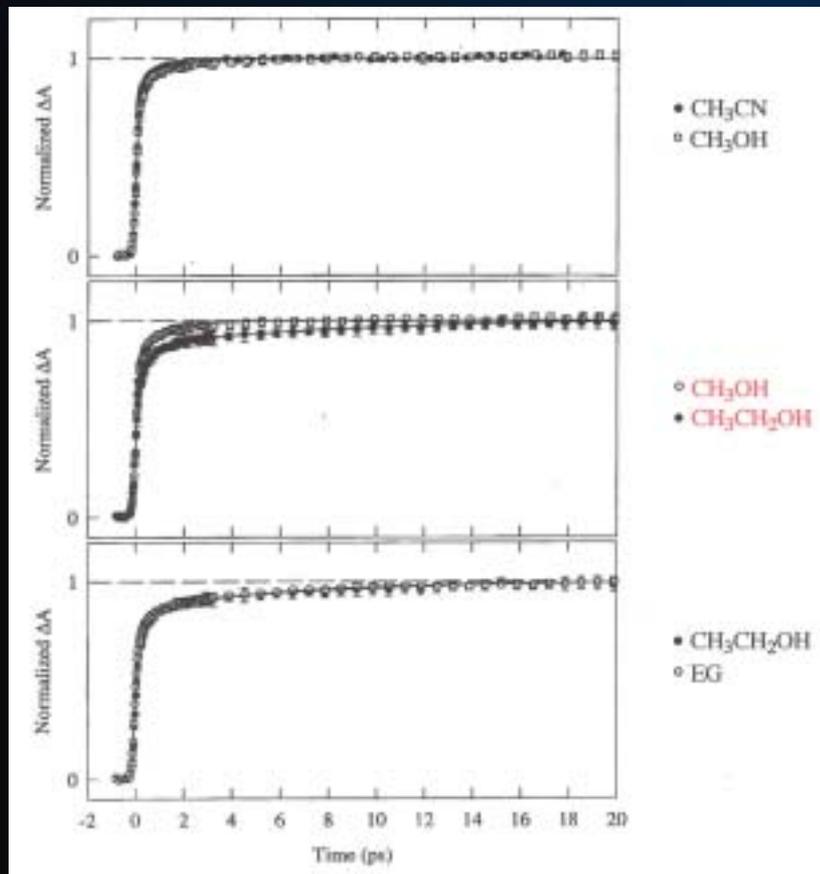


Dynamics of ring rotation



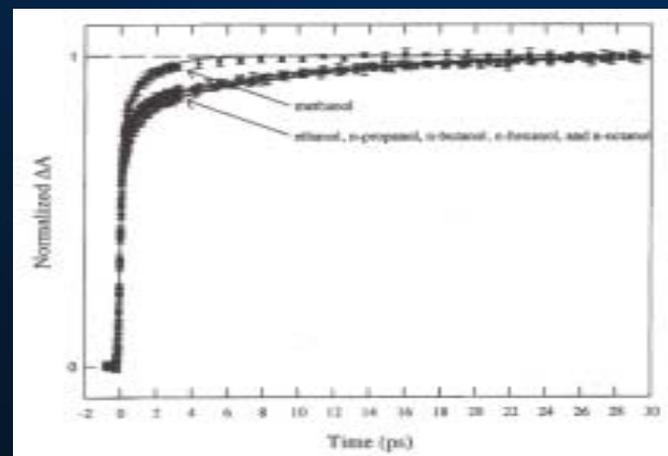
- rise time for dpb⁻ signal consistent with expected increase in transition dipole concomitant with ring rotation
- introduction of steric hindrance to ring rotation reflected in observed kinetics
- *wavelength dependence of dynamics likely due to the presence of overlapping signals of opposite sign (dpb⁻ and LMCT features)*

Solvent effects on rotation dynamics



• **mechanical** versus dielectric friction for ring rotation:

Solvent	η (cP)	ϵ	τ_L (ps)
CH ₃ OH	0.544	33.0	3.3
CH ₃ CH ₂ OH	1.074	25.3	9.8
CH ₃ (CH ₂) ₂ OH	1.945	20.8	39
CH ₃ (CH ₂) ₃ OH	2.544	17.84	72
CH ₃ (CH ₂) ₄ OH	3.619	15.13	120
CH ₃ (CH ₂) ₅ OH	4.578	13.03	167
CH ₃ (CH ₂) ₇ OH	7.288	10.30	319

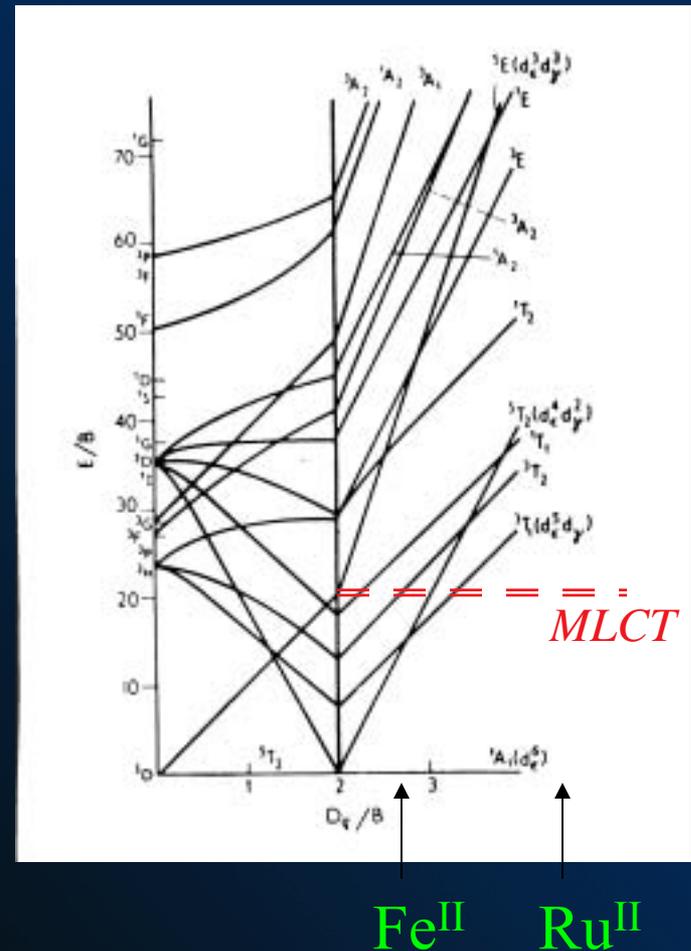


saturation effect inconsistent with bulk view of the solvent

Excited-State Dynamics of Fe^{II}

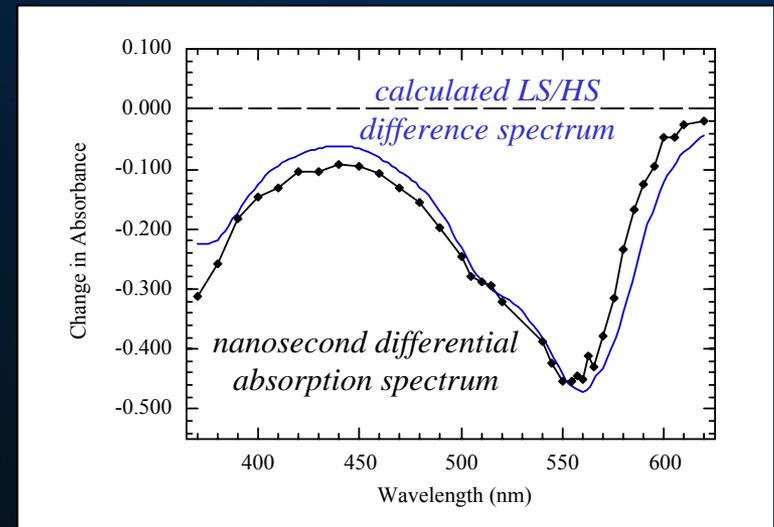
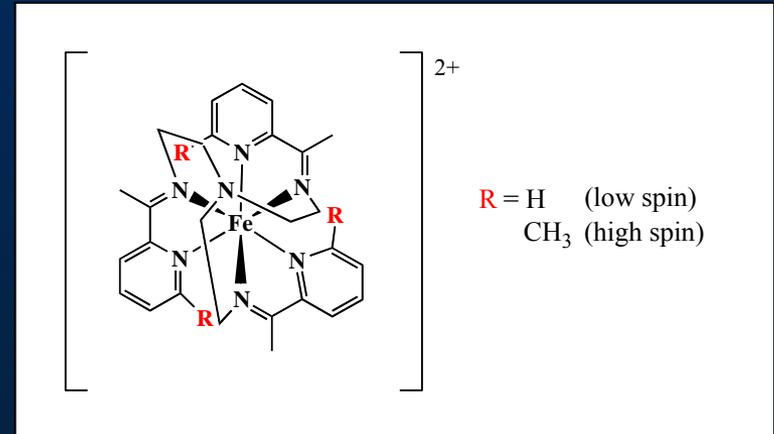
- significant change in electronic structure relative to Ru^{II}
- synthetic design allows for facile manipulation of relative energies of low-lying electronic states
- many connections to both basic and applied science
 - *biological*: low-spin/high-spin interconversion central to a number of metabolic processes involving Fe porphyrins
 - *materials*: potential applications in optical memory devices
 - *solar energy technology*: use as sensitizers for charge injection in mid-to-wide band gap semi-conductors

Tanabe-Sugano diagram for d⁶ transition metal ion



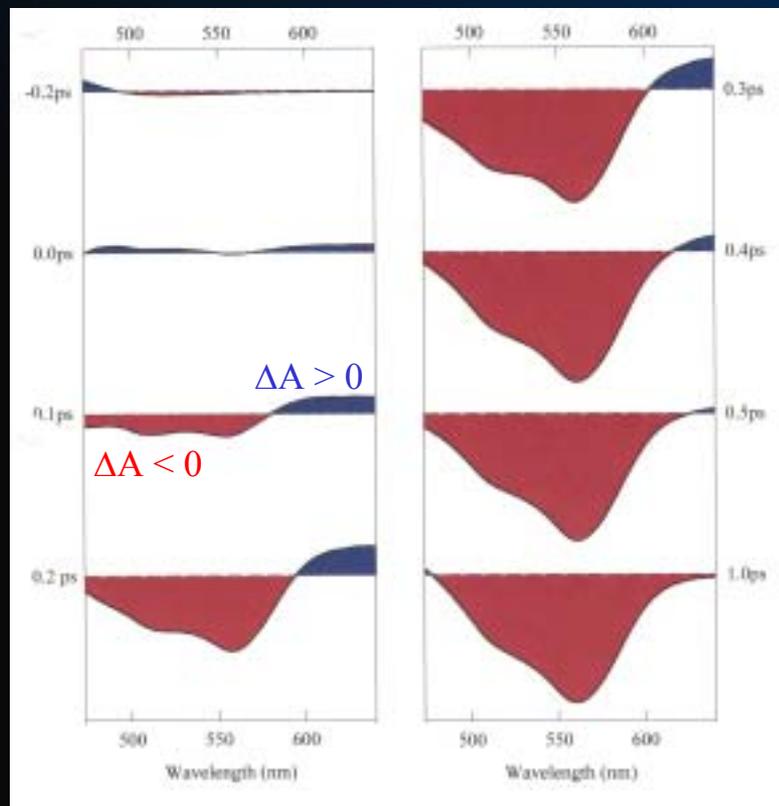
Photophysics of $[Fe(tren(py)_3)]^{2+}$

- need to explore basic photophysics of Fe^{II} chromophores in order to assess rates of intramolecular excited-state dynamics
- use of $[Fe(tren(py)_3)]^{2+}$ as a prototype:
 - near spin-crossover point, allowing for unambiguous characterization of lowest excited state as 5T_2
 - *large structural change accompanying 1A_1 to 5T_2 conversion*

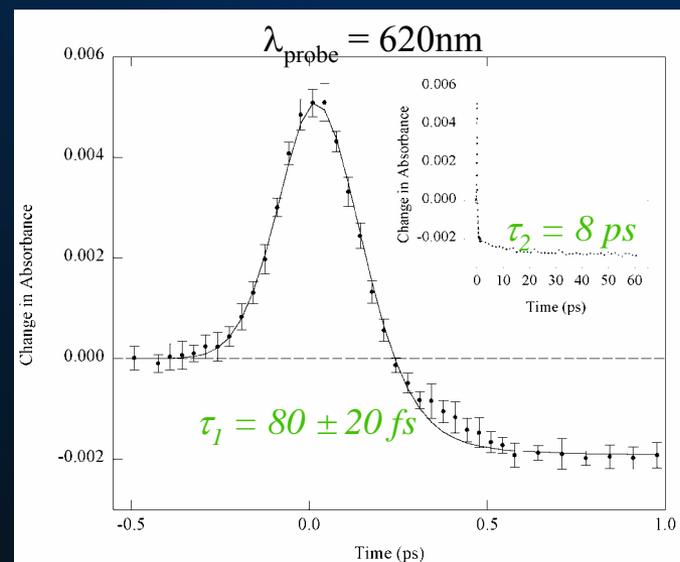


Ultrafast CT to LF conversion

- full spectrum data (left) shows formation of 5T_2 state in < 500 fs
- single-wavelength data (below) establishes CT-state deactivation to LF state(s) in < 100 fs



Transient absorption data for $[Fe(tren(py)_3)]^{2+}$ in CH_3CN solution following ~ 120 fs excitation at 400 nm.



Acknowledgments

Ru^{II} Polypyridyls

Niels Damrauer

Aimee Curtright

Fe^{II} Systems

Amanda Smeigh

Jeremy Monat

