

Ultrafast X-ray spectroscopy as a probe of nonequilibrium dynamics in ruthenium complexes

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Outline

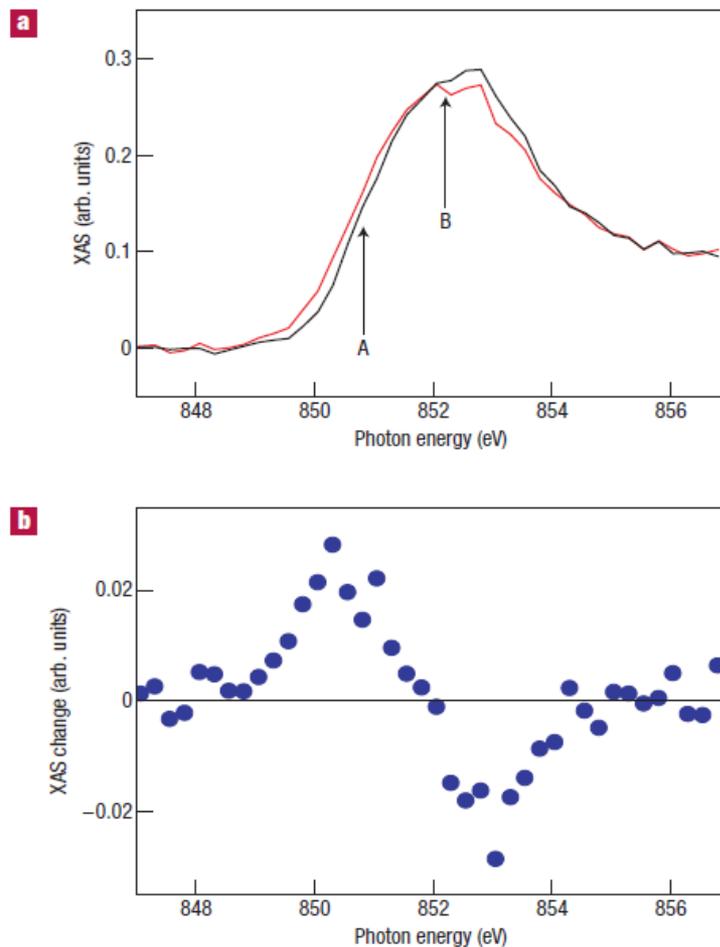
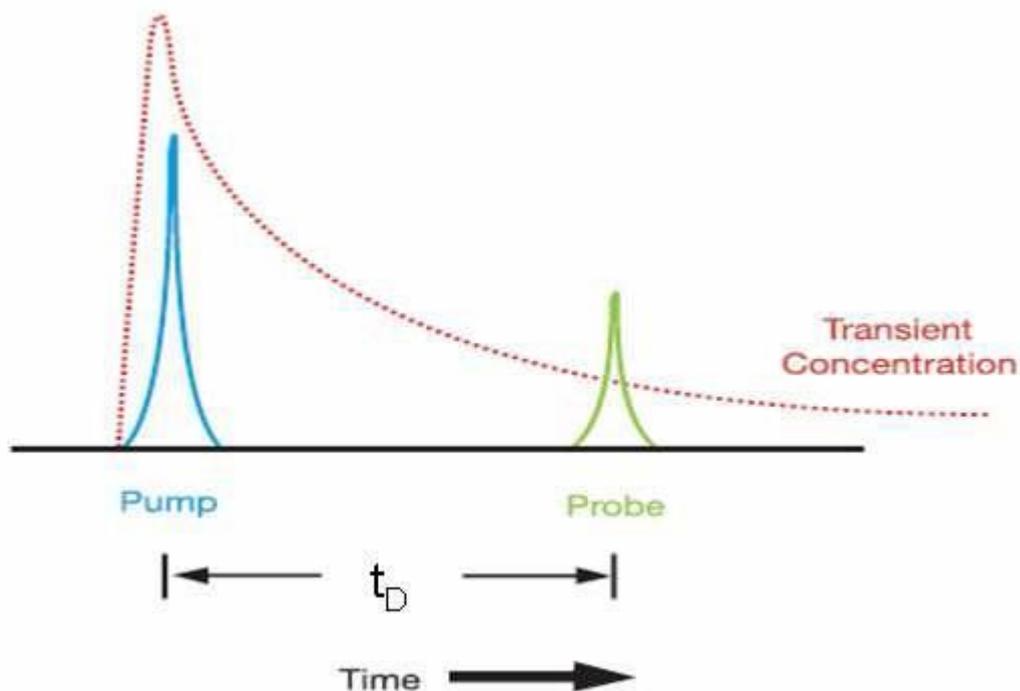
- Time dependent/pump-probe spectroscopy
- Nonequilibrium phenomena and decay
- Spin crossover systems: Fe and Ru complexes
- Dynamic spectroscopy on ruthenate complexes



Why nonequilibrium physics

- Solar cells, energy conversion
- Bond breaking, water and hydrogen conversion, photosynthesis
- Photoinduced magnetism, demagnetization

Pump-probe spectroscopy

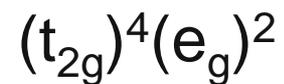
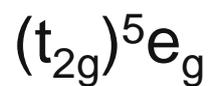
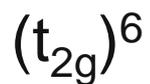
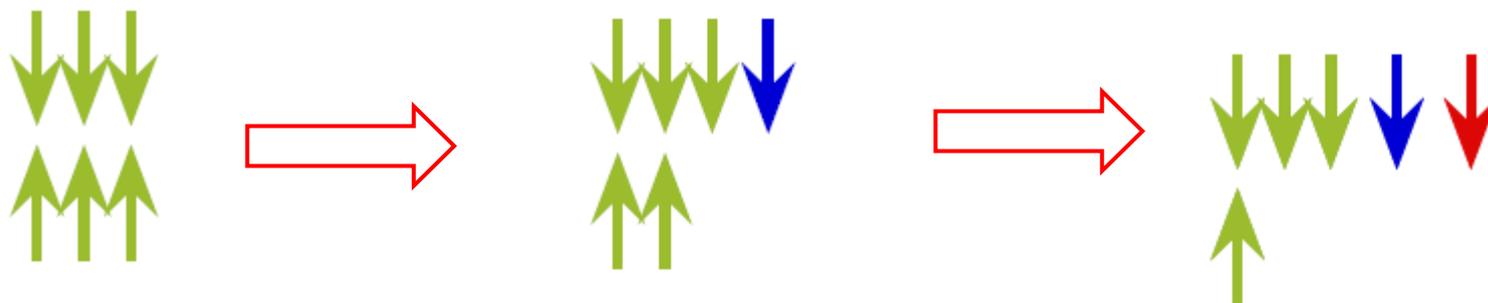


Stamm et al.

Figure 2 Femtosecond X-ray absorption spectra. **a**, XAS spectra obtained with linearly polarized femtosecond X-ray pulses at normal incidence. The absorption at the L_3 edge is shown for a 15-nm-thick Ni film 200 fs after (red line) and without (black line) laser excitation. The arrows A and B indicate energy positions where measurements in Fig. 3 were taken. **b**, Difference between the spectra in **a**.

An easier system

Fe spin cross over complexes



S=0

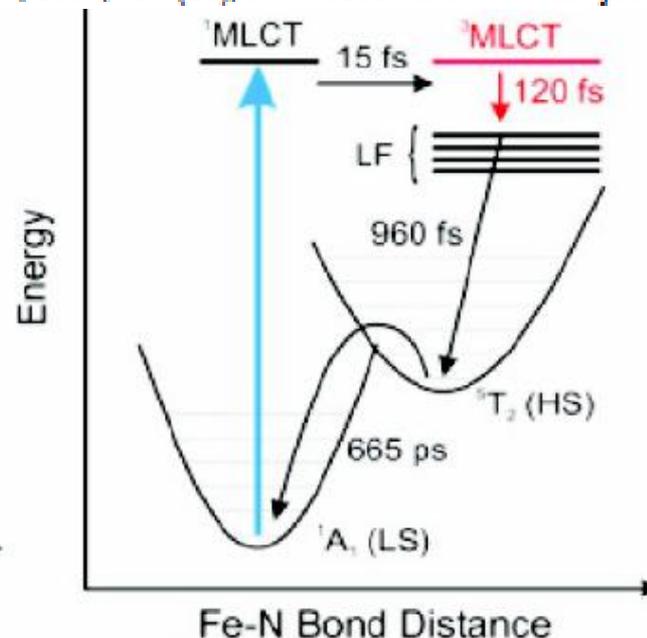
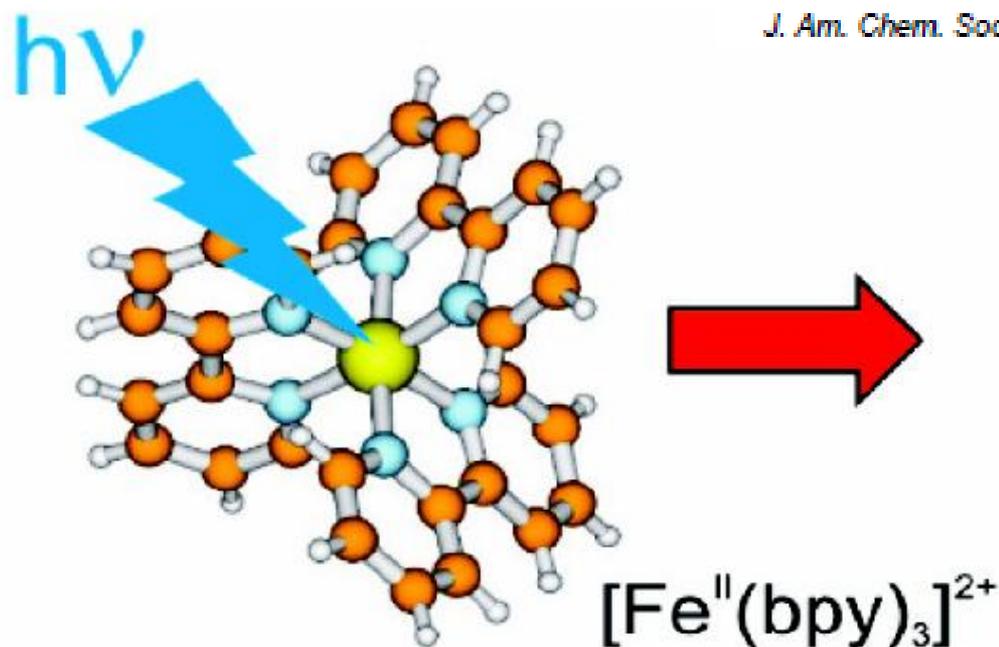
S=1

S=2

Fe spin crossover complexes

Wojciech Gawelda, Andrea Cannizzo, Van-Thai Pham,
Frank van Mourik, Christian Bressler, and Majed Chergui

J. Am. Chem. Soc., 2007, 129 (26), 8199-8206 • DOI: 10.1021/ja070454x

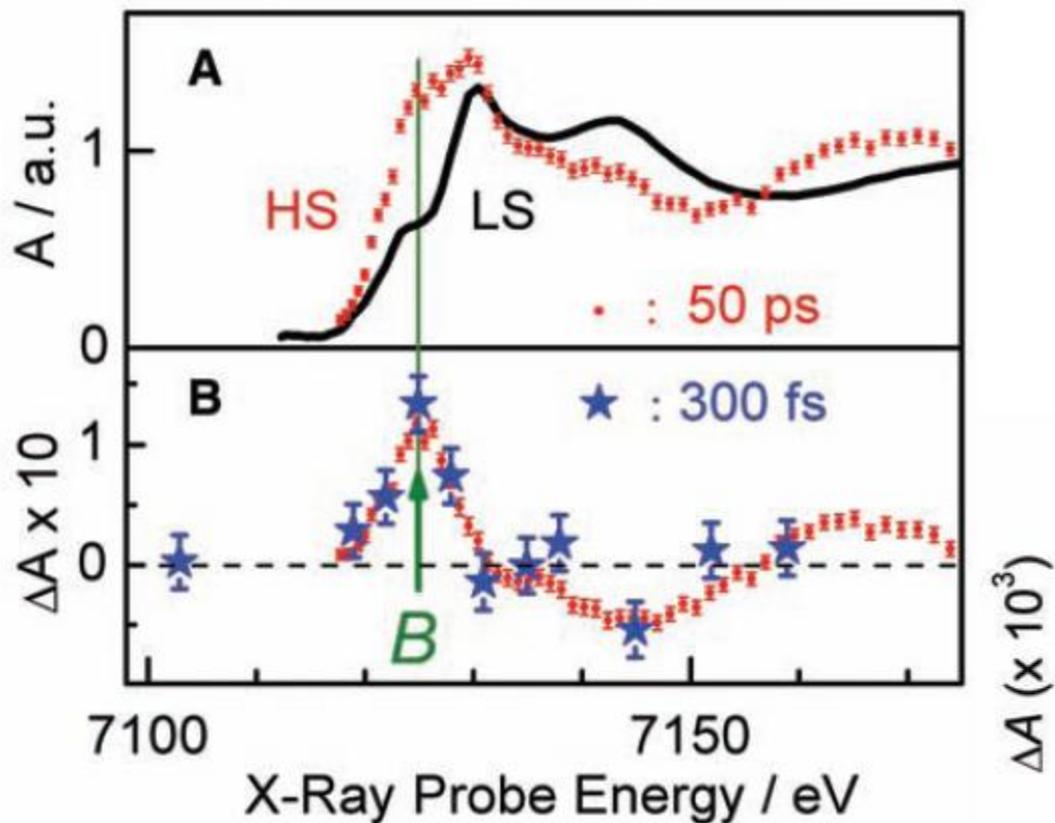


This process is on the time scale (≤ 20 fs)
of the highest frequency modes of the molecule,

The highest frequency mode in these systems is the
skeleton mode of the bpy ligand at 1607 cm^{-1} ,

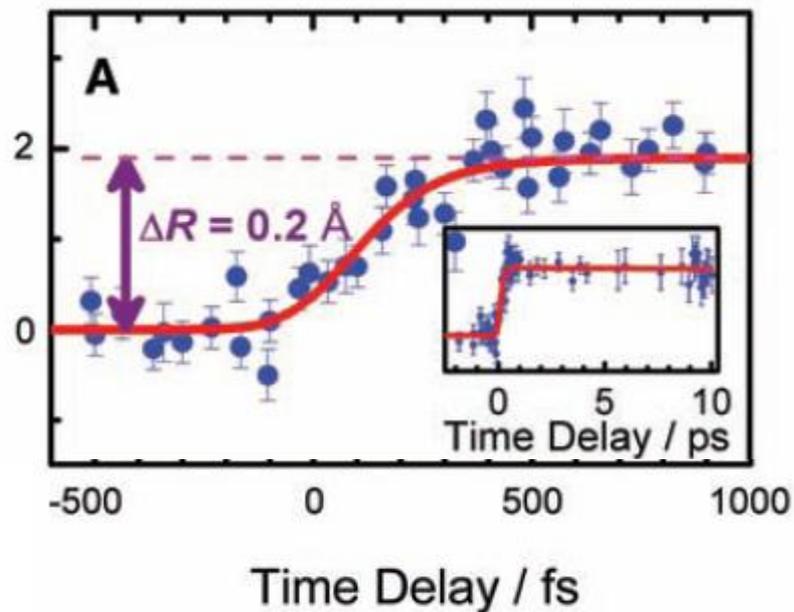
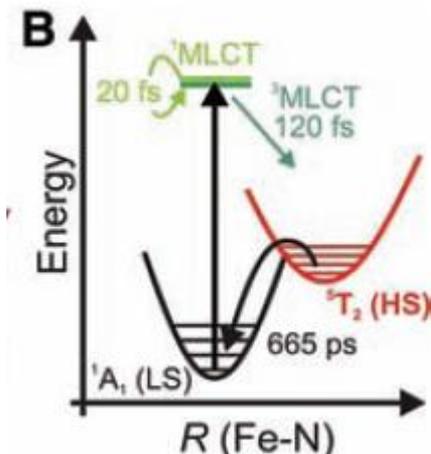
$$1607\text{ cm}^{-1} = 199\text{ meV} = 20.8\text{ fs}$$

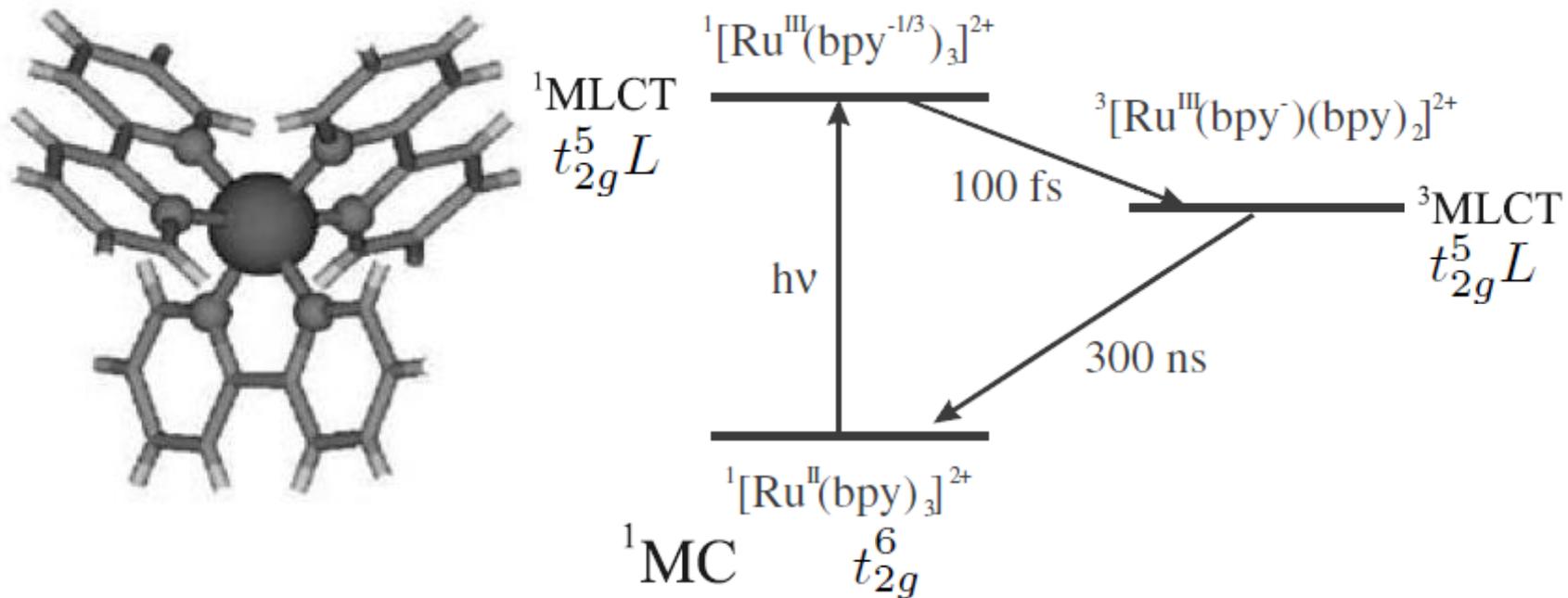
Lattice transitions



the derived relaxation time scale corresponds to the period of the Fe-N stretch mode, which lies in the 130- to 160-fs range for all Fe(II)-based complexes,

$$238 \text{ cm}^{-1} = 29.5 \text{ meV} = 140 \text{ fs}$$



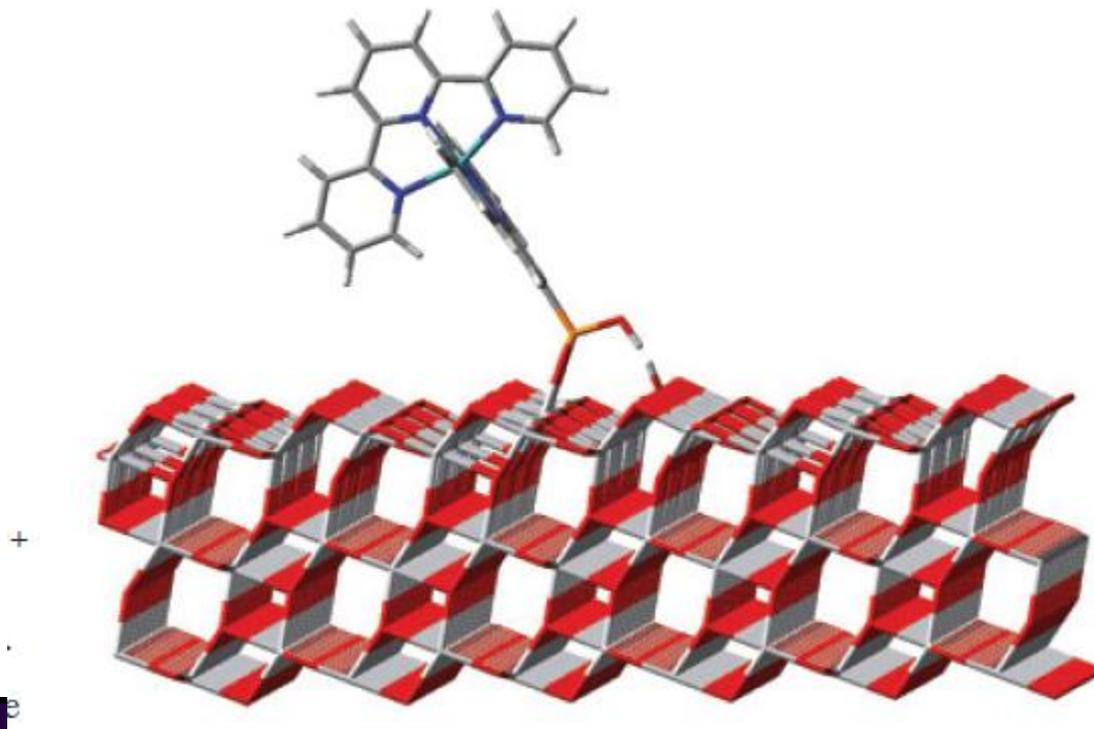


Photoexcitation with visible light: transition from metal to ligand

Since ligands not connected: localization on one of the bpy

We can connect the Ru-complex to, for example, TiO_2

Photoexcitation leads to a interfacial electron transfer
Into the conduction band of TiO_2

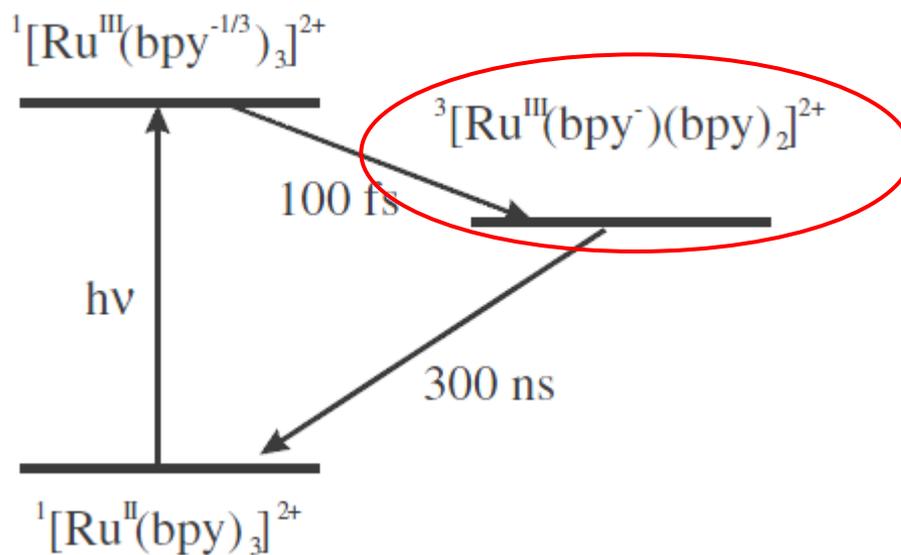


Can we calculate spectroscopy and make discriminating tests for different theoretical scenarios?

1. We do not understand the mechanism to go from singlet to triplet MLCT states in Ruthenium complexes
2. We do not understand much about dynamical spectroscopy

What has been done so far?

Transient-state spectroscopy

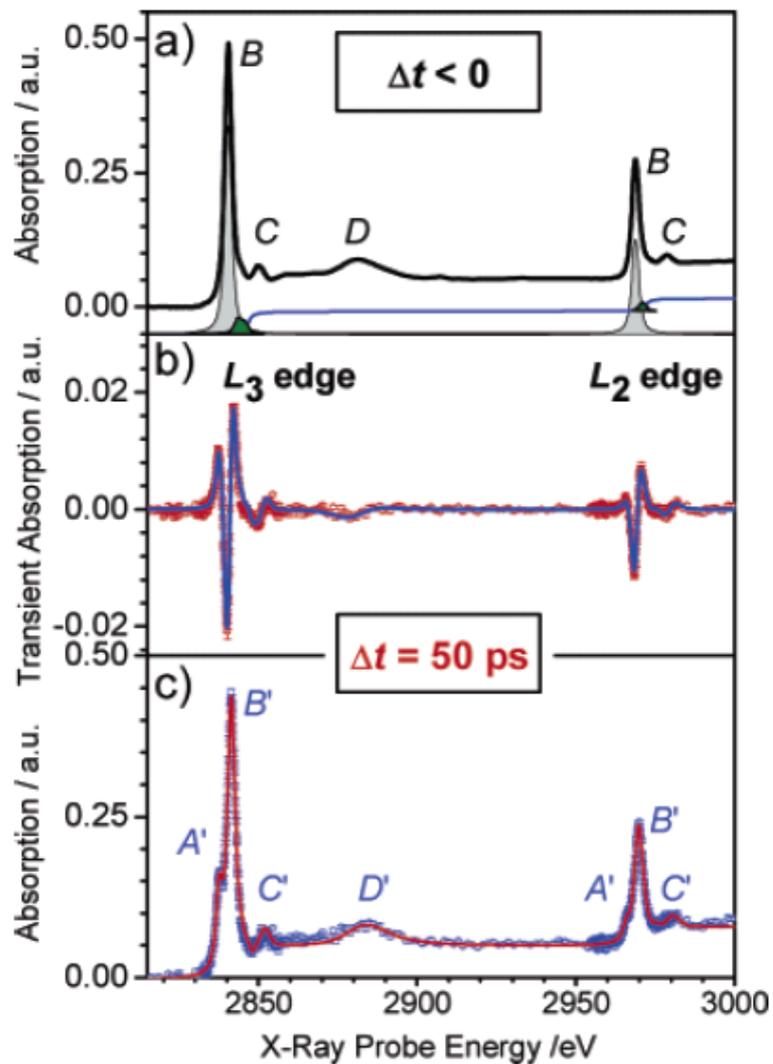


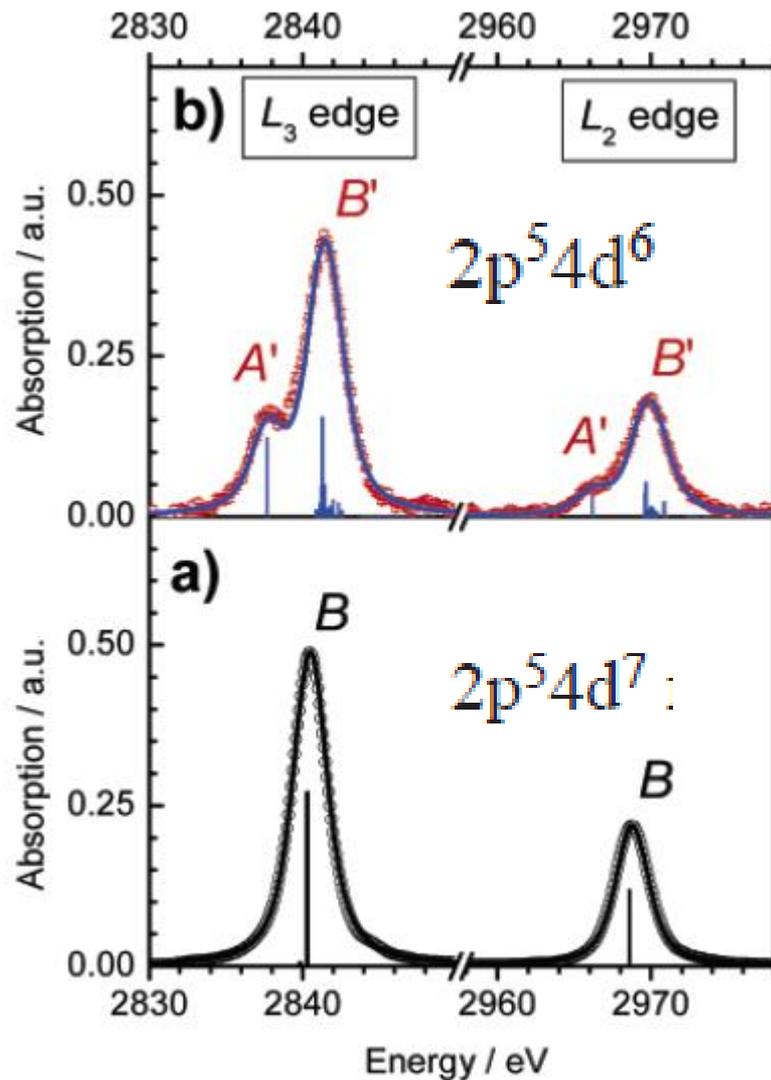
Measure XAS in a metastable excited states

Electronic and Molecular Structure of Photoexcited $[\text{Ru}^{\text{II}}(\text{bpy})_3]^{2+}$ Probed by Picosecond X-ray Absorption Spectroscopy

Wojciech Gawelda,^{†,‡} Melanie Johnson,^{†,‡} Frank M. F. de Groot,[§] Rafael Abela,[‡]
Christian Bressler,[†] and Majed Chergui^{*,†}

J. AM. CHEM. SOC. 2006, 128, 5001–5009





After excitation (50 ps)

Before excitation

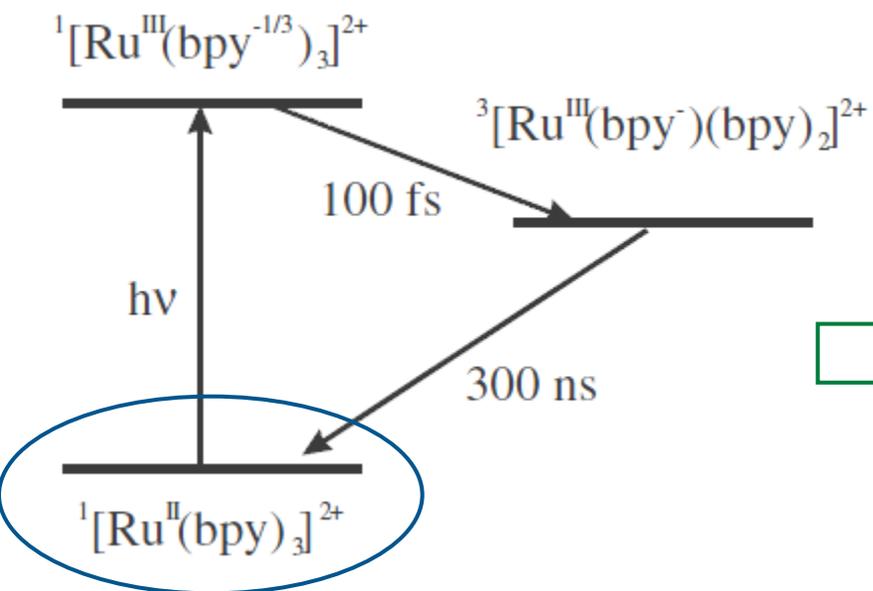
Typical atomic calculation

$$H_{\text{total}} = H_{\text{atom}} + H_{\text{crystal}} = H_{\text{atom}} + H_{O_h} + H_{D_3} + H_{\zeta LS}$$

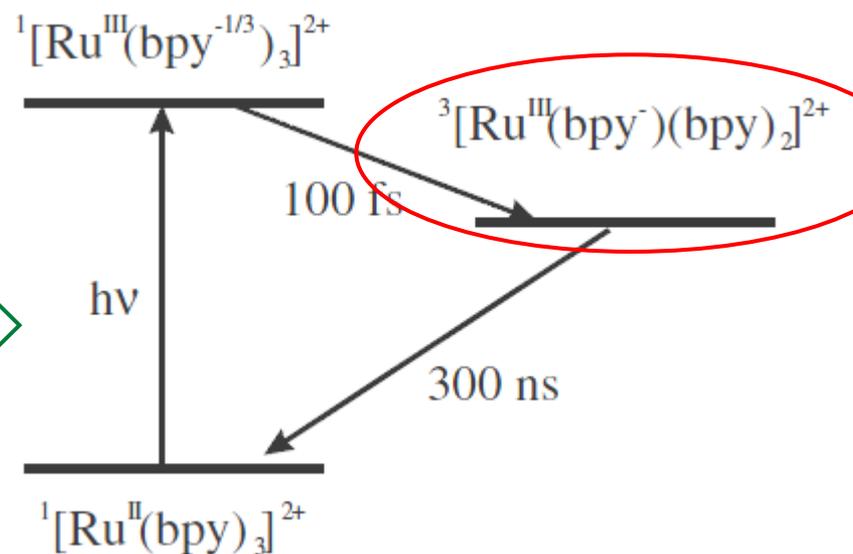
Note, the spectrum after excitation is not really an excited state
But starts from a $3d^5$ ground state

2000-2010

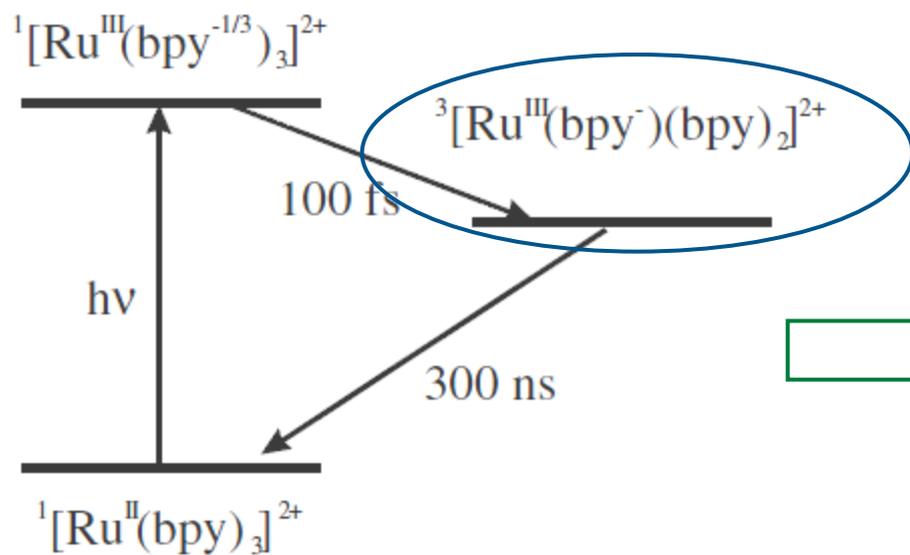
Conventional static/ground-state spectroscopy



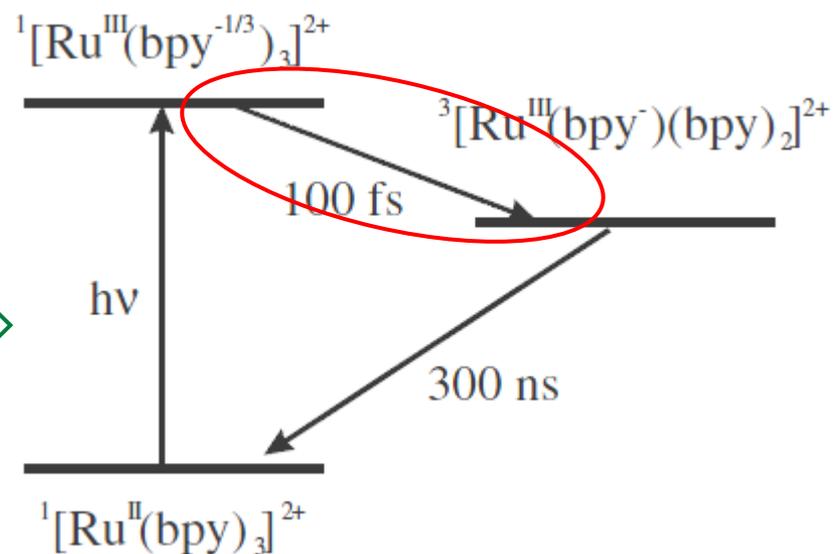
Transient/metastable-state spectroscopy



Transient/metastable-state state spectroscopy



Dynamic/nonequilibrium spectroscopy



Questions:

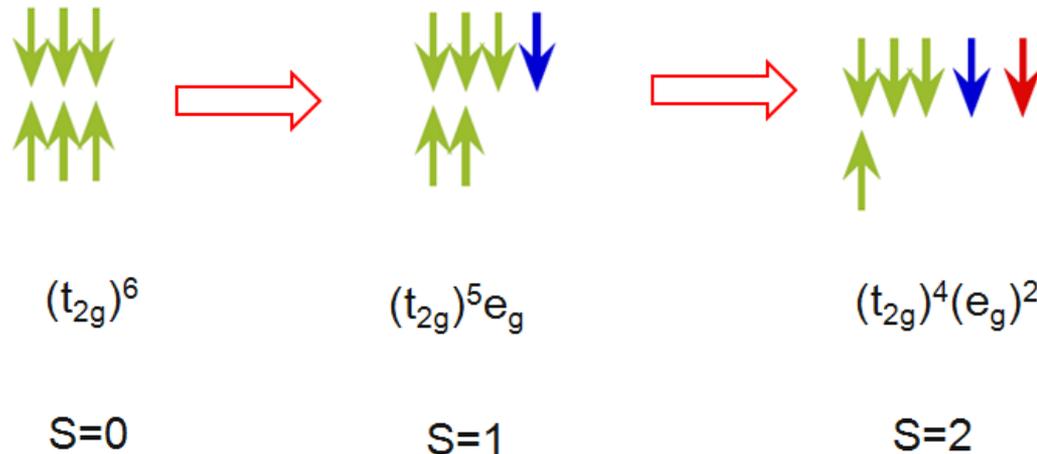
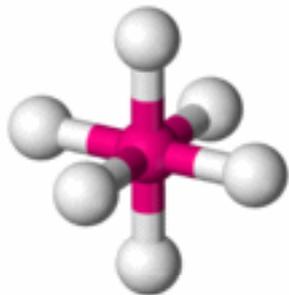
1. We do not understand the mechanism to go from singlet to triplet MLCT states in Ruthenium complex
 - Why does a photo excitation cause such a rapid decay?
 - Why does the decay occur into states that are significantly different in spin, but sometimes also orbital and metal-ligand distances?

2. We do not understand much about dynamical spectroscopy

Let us go back to Fe complexes which are better understood

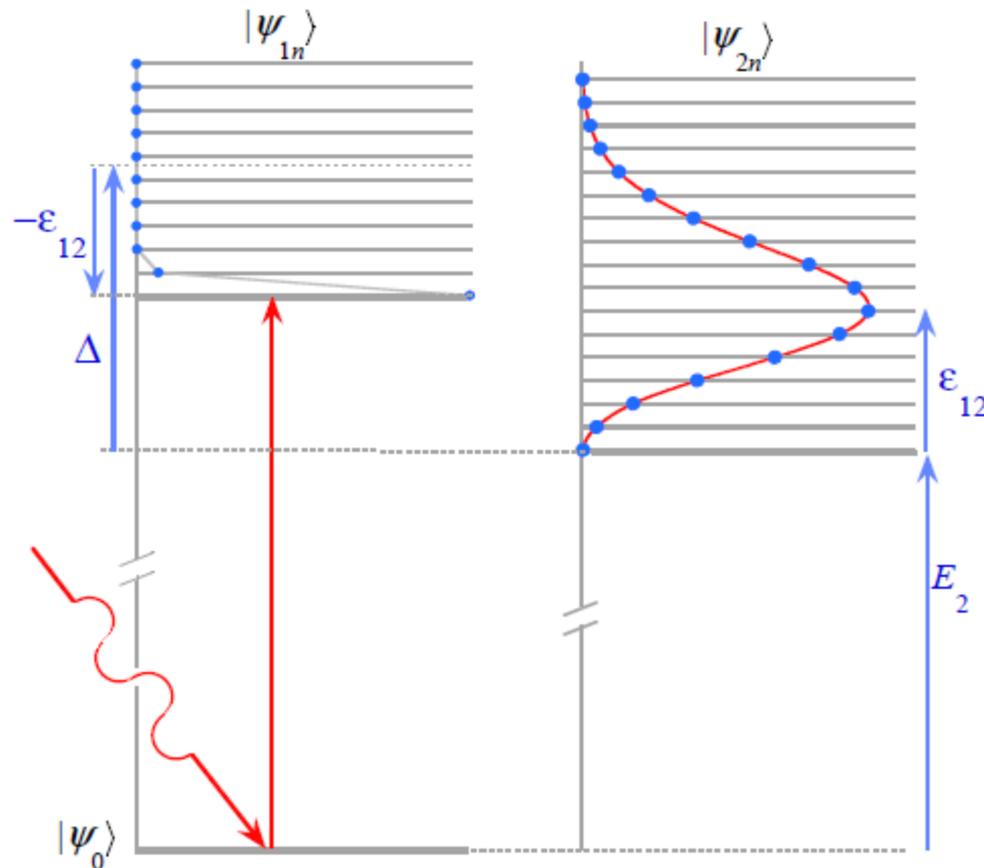
Why change in spin

- In a local octahedral surrounding, addition of local phonons does not cause a coupling of the $(t_{2g})^6$ and $(t_{2g})^4(e_g)^2$ to other configurations
- We need terms in the Hamiltonian that do not diagonalize in the same fashion as crystal fields and the local phonons. This can be the spin-orbit coupling, but also off-diagonal Coulomb terms or band effects
- The spin-orbit coupling can convert t_{2g} electrons into e_g electrons. To go from $(t_{2g})^6$ to $(t_{2g})^4(e_g)^2$ we need two steps.



Coupling between phonon continua

Suppose little change in initial photoexcitation, but major lattice change in coupling between states 1 and 2



Hamiltonian

$$H_0 = \sum_{i=1,2} E_i c_i^\dagger c_i + \hbar\omega a^\dagger a + \sum_{i=1,2} \sqrt{\varepsilon_i \hbar\omega n_i} (a^\dagger + a)$$

Energies of states energies of local coupling between electrons
vibronic stretching mode and stretching mode

coupling

$$H_1 = V(c_1^\dagger c_2 + c_2^\dagger c_1) \quad \text{Spin-orbit coupling at transition metal}$$

$$\hbar\omega = 30 \text{ meV}$$

Typical Fe-N stretching mode

$$V = 50 \text{ meV}$$

Typical spin-orbit coupling parameter

$$\varepsilon_{12} = \varepsilon_2 - \varepsilon_1 = 0.2 \text{ eV} \quad \text{Displacement of a few tenths of Angstrom}$$

PRL 104, 067401 (2010)

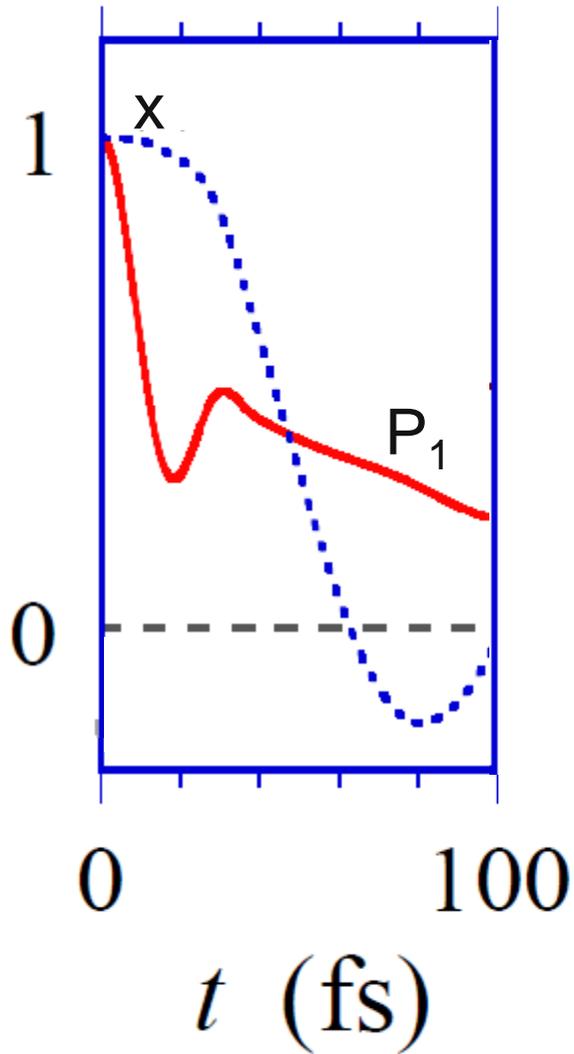
PHYSICAL REVIEW LETTERS

WCCA CIRLING
12 FEBRUARY 2010

Model of Ultrafast Intersystem Crossing in Photoexcited Transition-Metal Organic Compounds

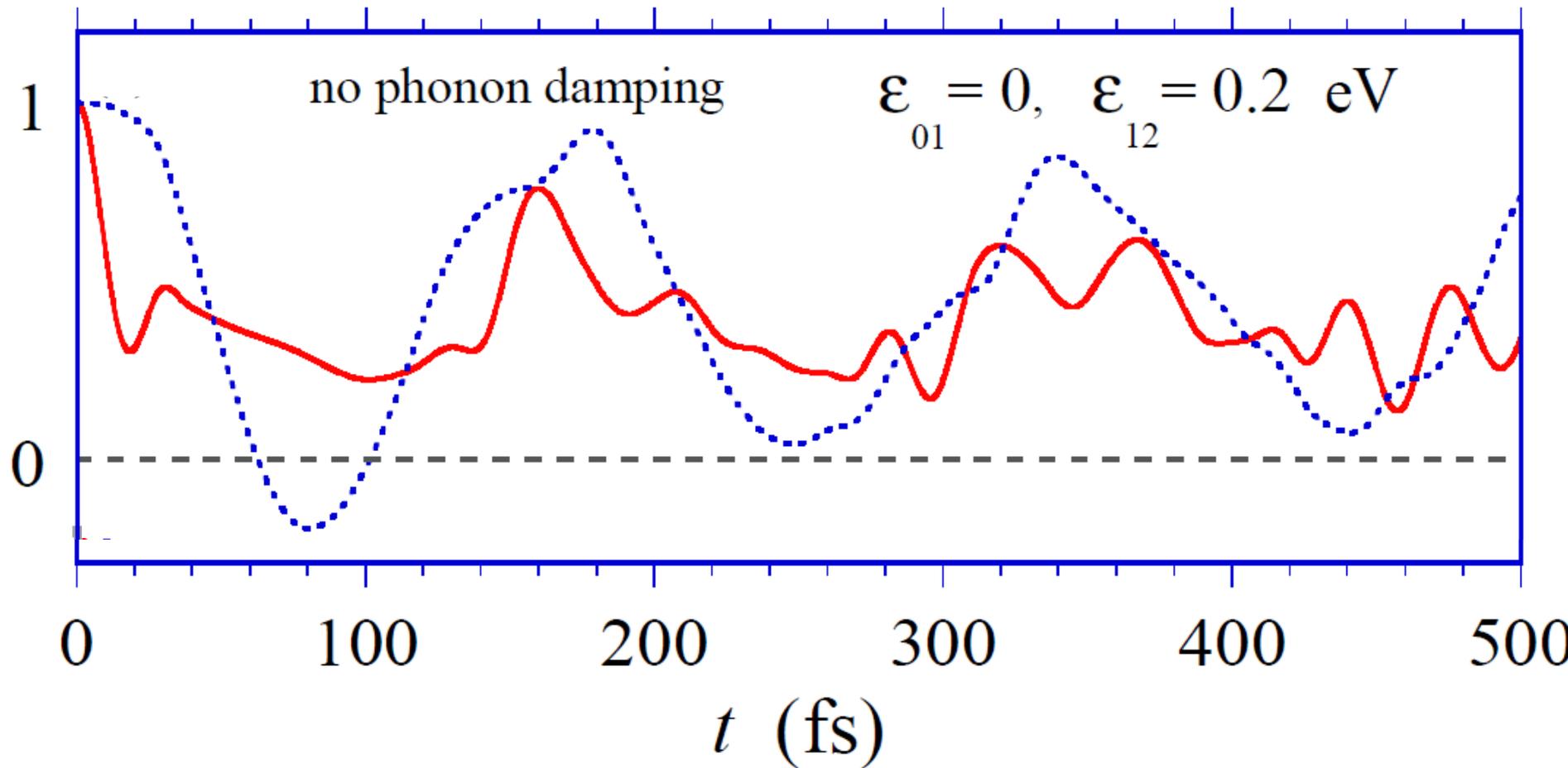
Michel van Veenendaal, Jun Chang, and A.J. Fedro

Two states and a local phonon

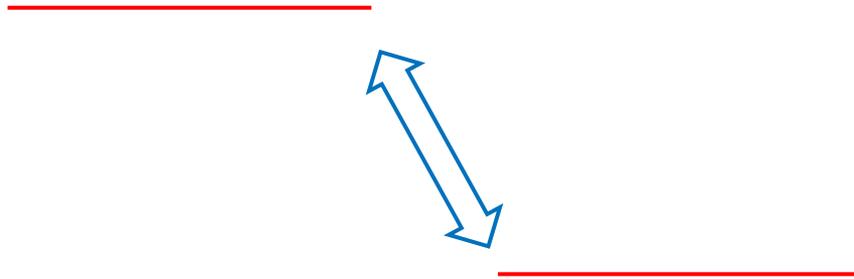


$$\varepsilon_{01} = 0, \quad \varepsilon_{12} = 0.2 \text{ eV}$$

Two states and a local phonon: recurrence effects



No decay, but oscillation

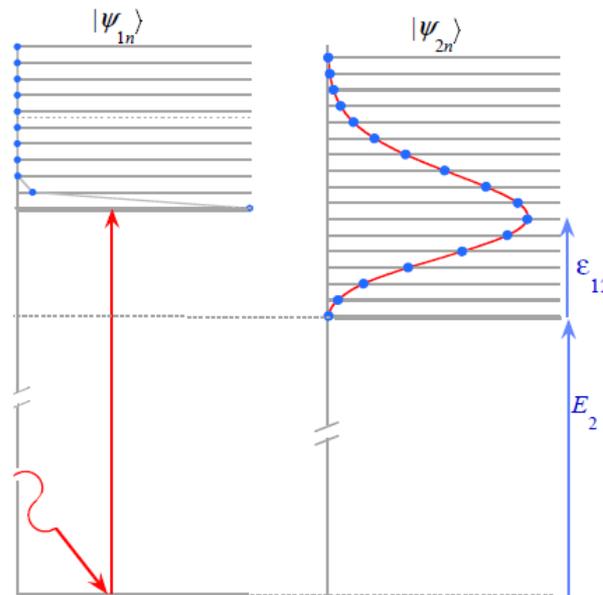
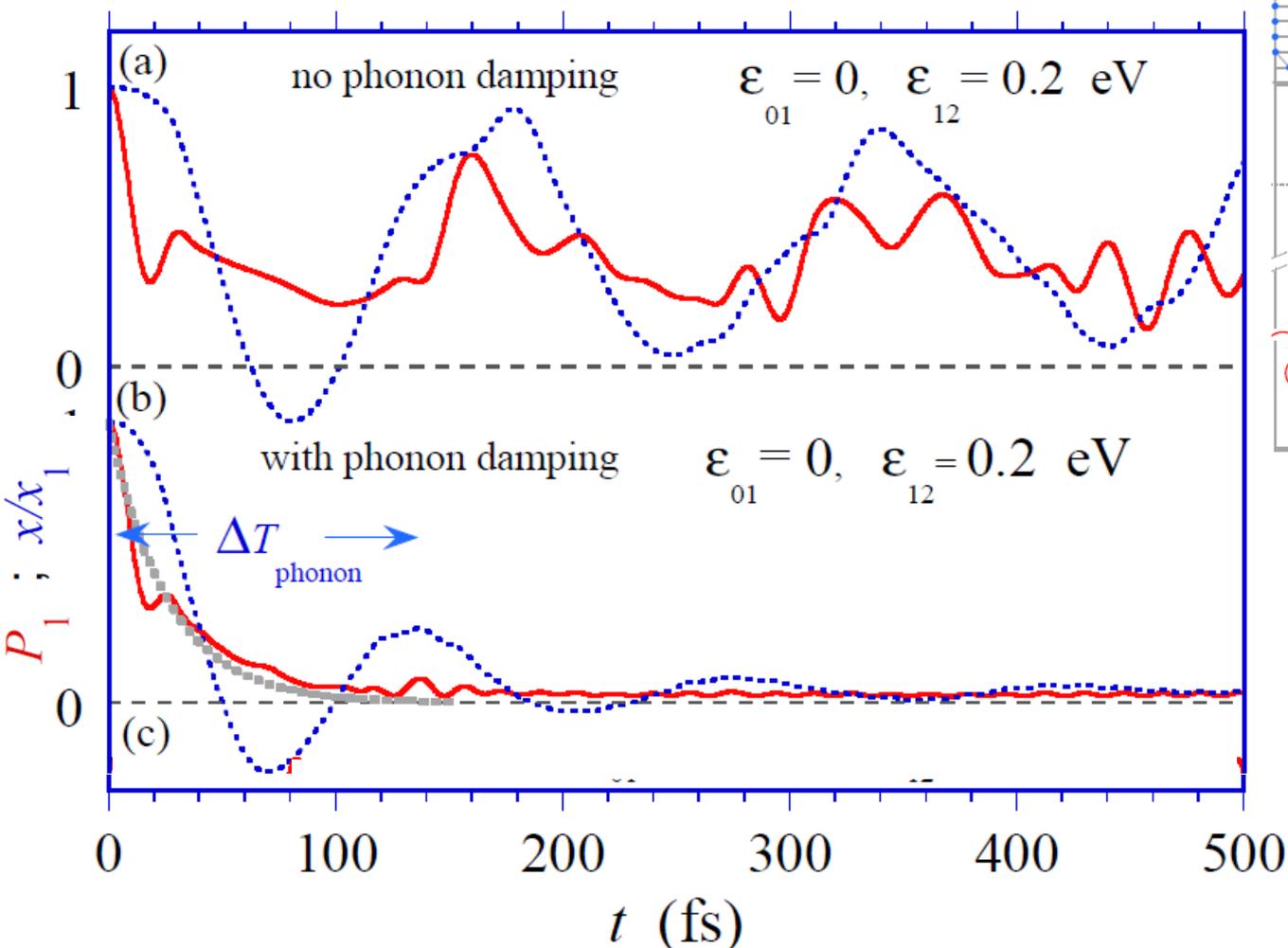


Why don't we observe decay?

- There are only a finite number of excited vibrational states
- The dephasing is incomplete so we observe a recurrence
- The system does not lose energy and keeps oscillating

We want to damp the oscillation of the local vibronic mode

Transition between two states



PRL 104, 067401 (2010)

PHYSICAL REVIEW LETTERS

week ending
12 FEBRUARY 2010

Model of Ultrafast Intersystem Crossing in Photoexcited Transition-Metal Organic Compounds

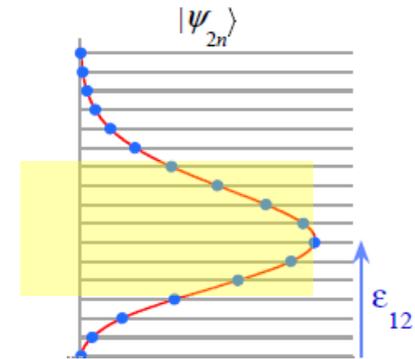
Introduced irreversibility



- “Continuum” of phonon states
- Loss of energy due to damping oscillations
- Irreversibility

Types of intersystem crossing

Fast dephasing: $V_{n0} = e^{-g} g^n / n!$



This can be viewed as an effective density of states

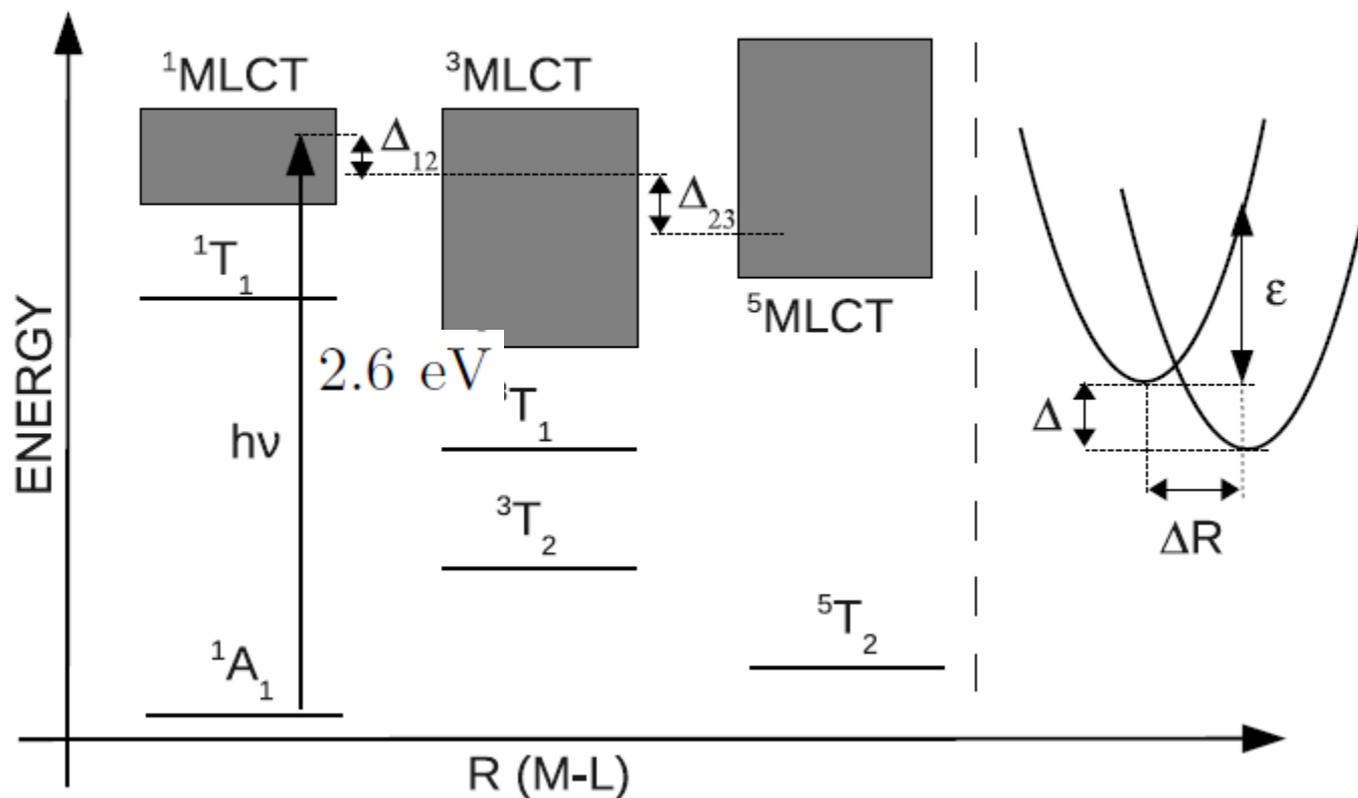
$$\rho(\epsilon) = e^{-\epsilon} g^\epsilon / [\hbar\omega\Gamma(\epsilon + 1)], \text{ with } \epsilon = E/\hbar\omega$$

$\Gamma(\epsilon + 1)$ is the gamma function

$$\Gamma_d = \pi V^2 \rho(\Delta - \epsilon) / \hbar$$

Optical spectroscopy:

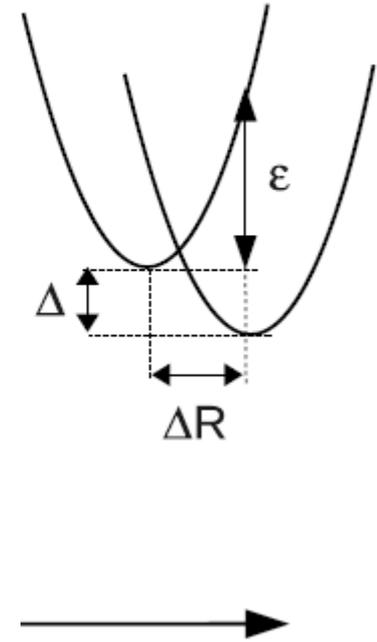
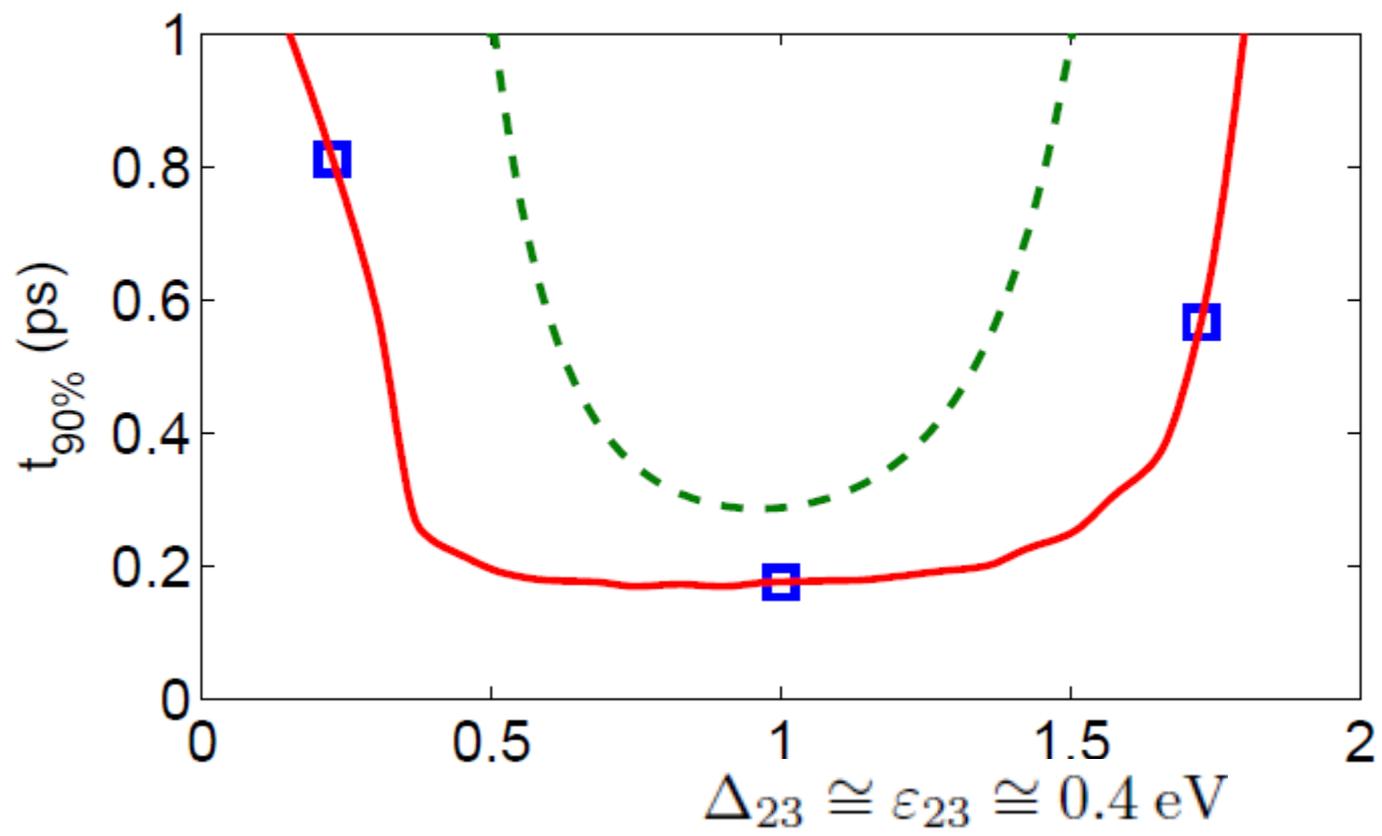
$$\epsilon_{12} = 0.2 \text{ eV} \quad \epsilon_{23} = 0.4 \text{ eV}$$



PHYSICAL REVIEW B 82, 075124 (2010)

Ultrafast cascading theory of intersystem crossings in transition-metal complexes

Jun Chang, A. J. Fedro, and Michel van Veenendaal

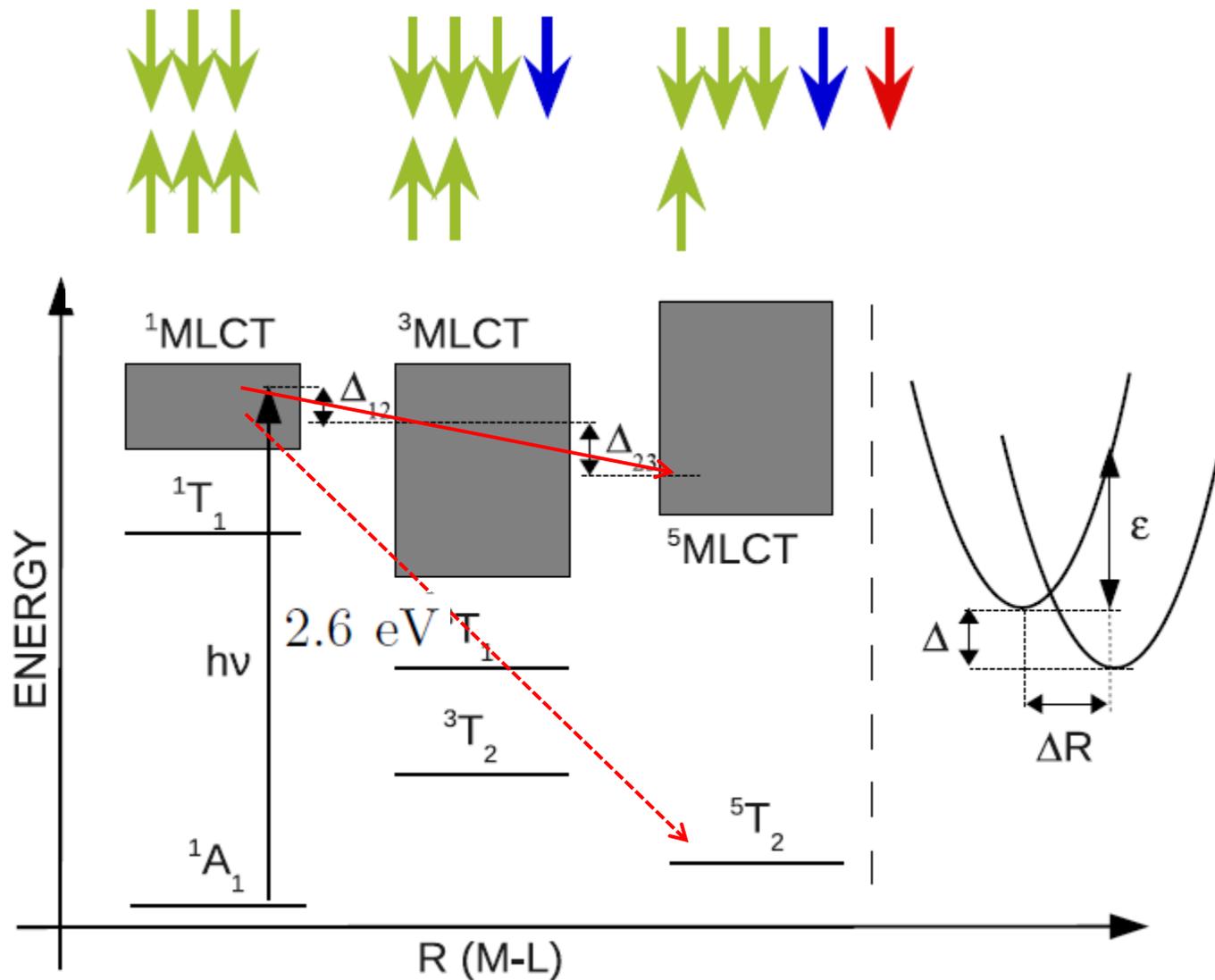


total energy bridged

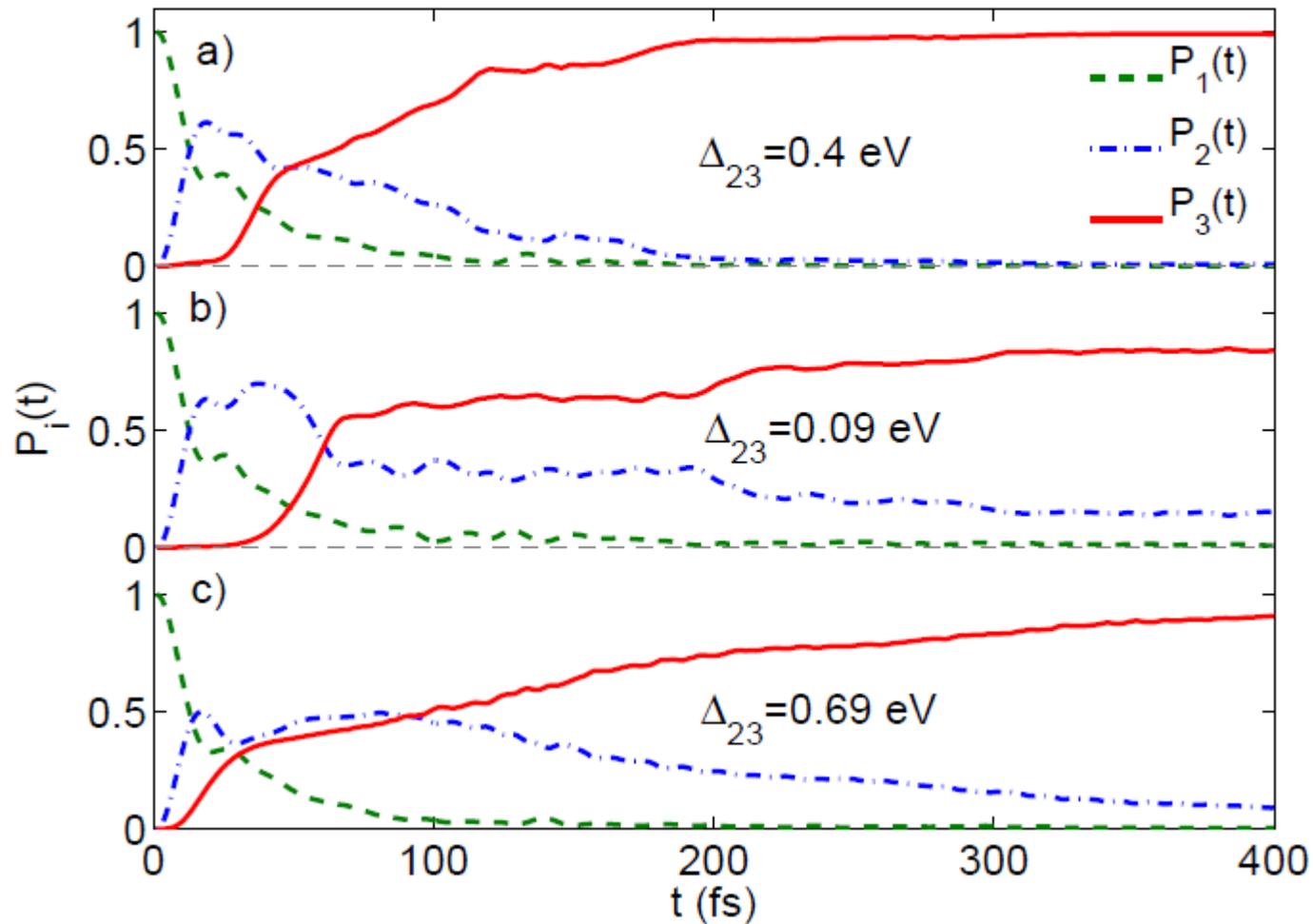
$$\Delta_{12} + \Delta_{23} \cong 0.32-0.88 \text{ eV}$$

Much less

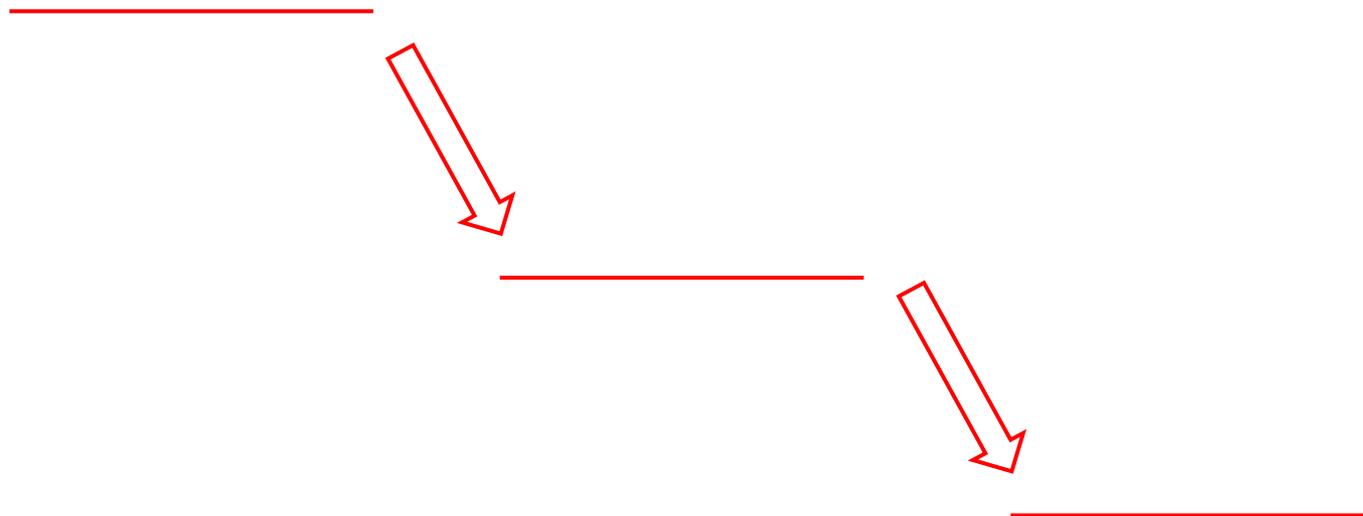
$$2.6 \text{ eV}$$



We cannot bridge the energy to 5T_2 on in less than a picosecond



Cascading phenomena

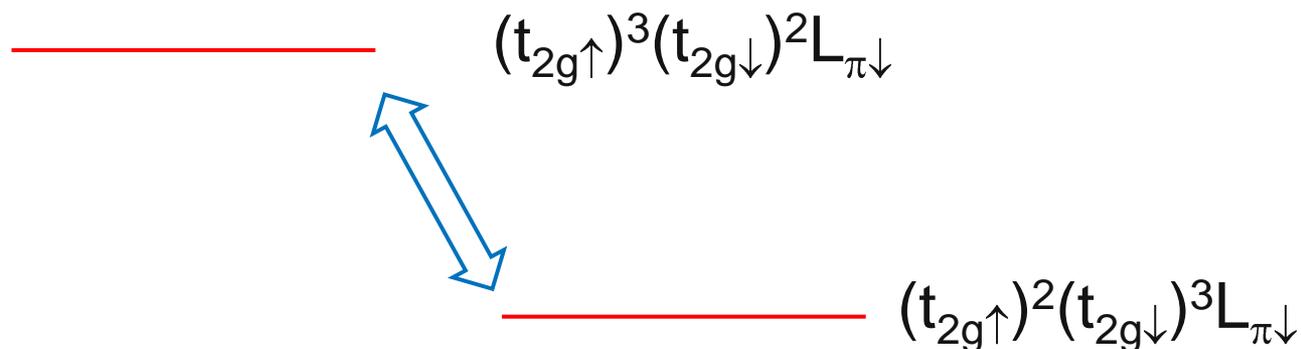


- Ultrafast spin transitions occur in the metal-to-ligand charge-transfer (MLCT) states
- Intersystem crossing from MLCT to metal-centered quintet state on larger timescale

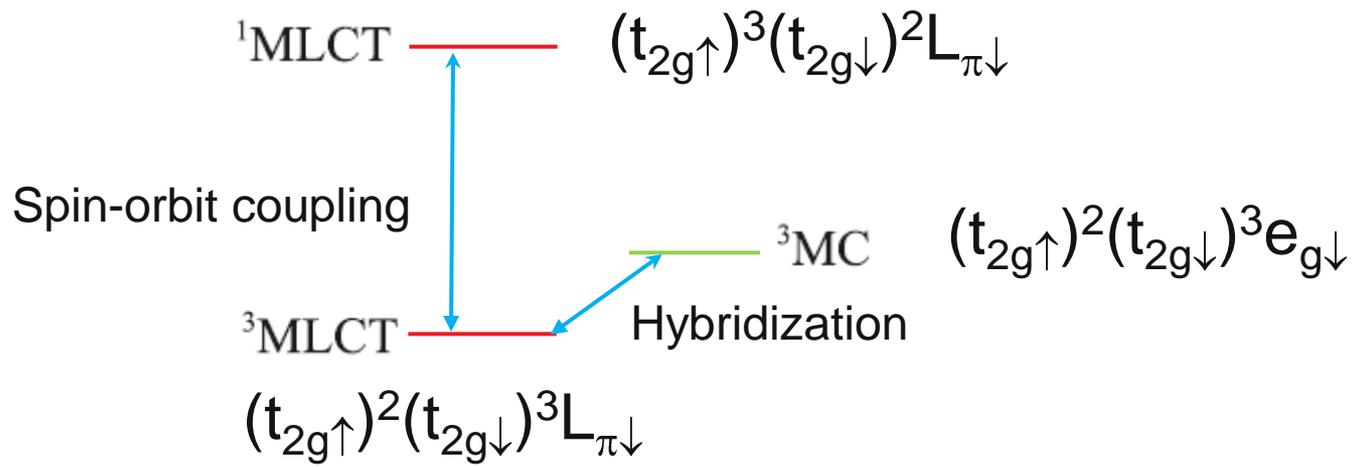
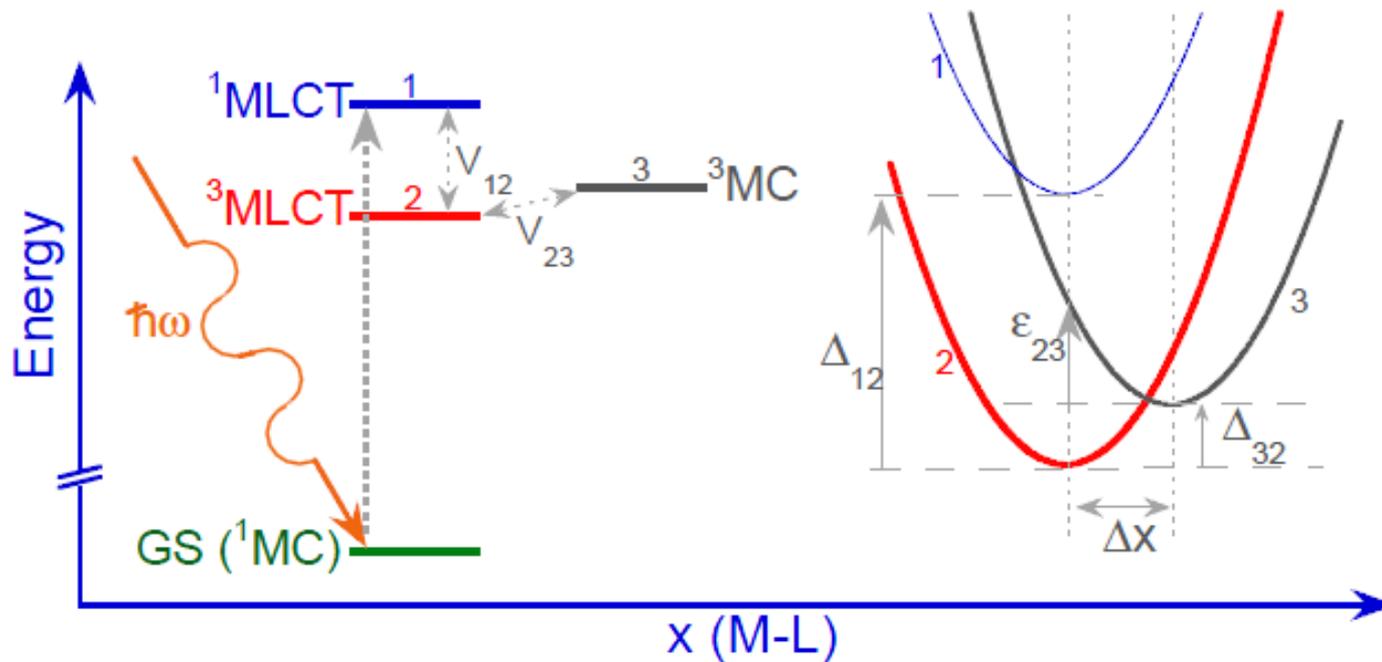
What's the problem with the ruthenium complexes?

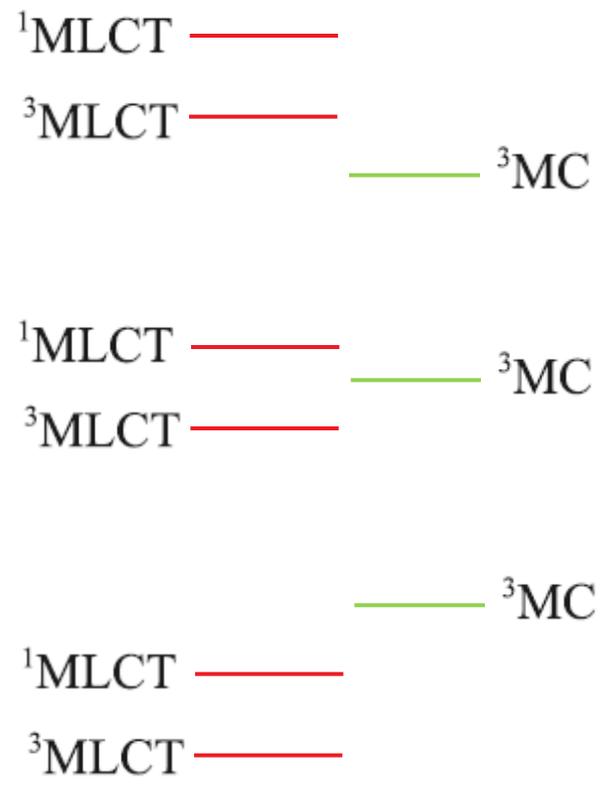
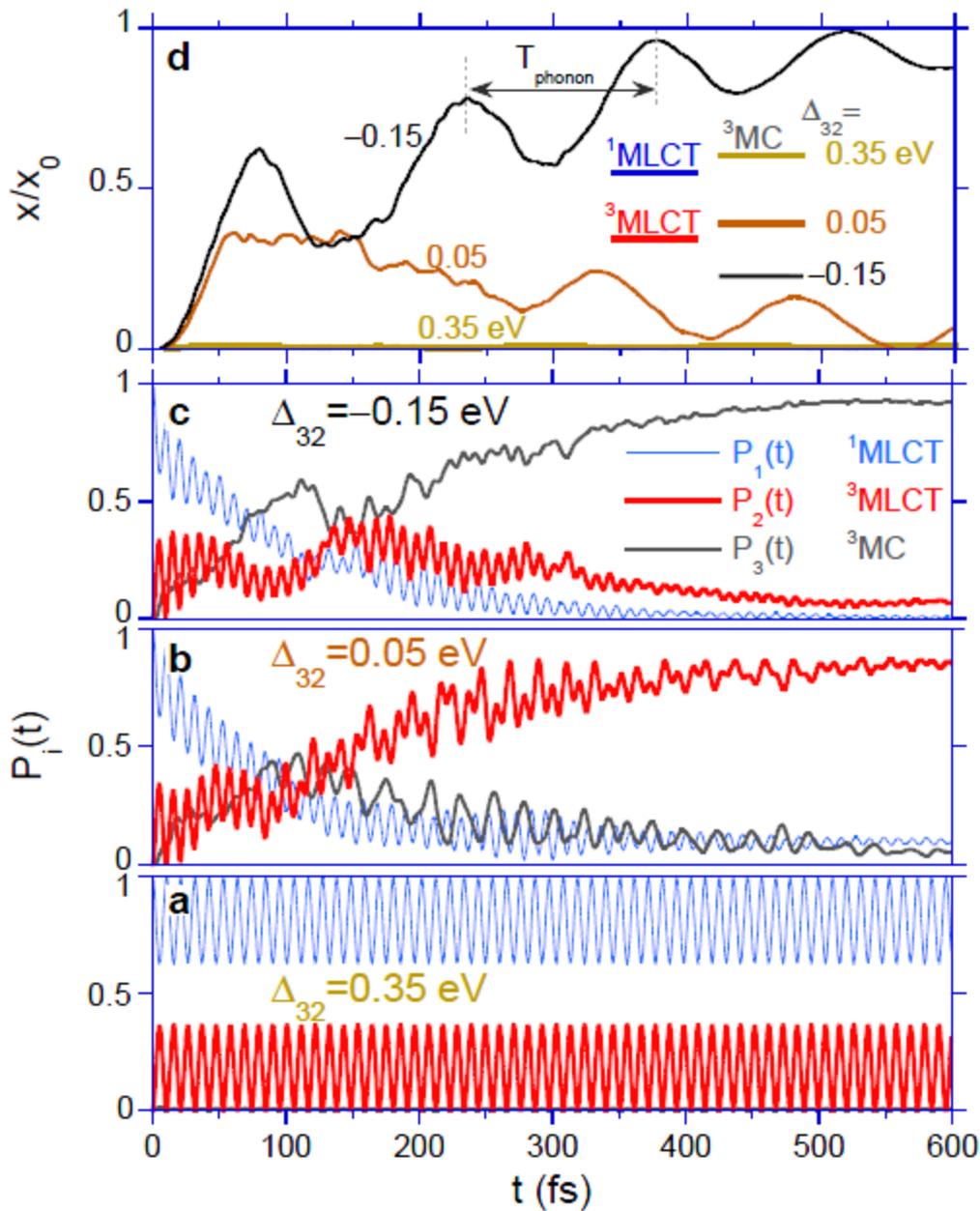
No decay, but oscillation

- Crystal field is much larger, so increase in crystal field due to converting t_{2g} to e_g not compensated by Hund's Coulomb exchange

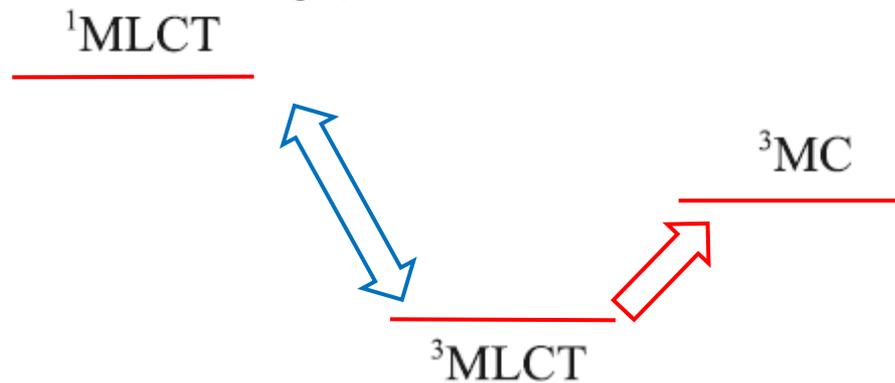


- No “Continuum” of phonon states since singlet and triplet have the same metal-ligand distance
- Would form an effective j

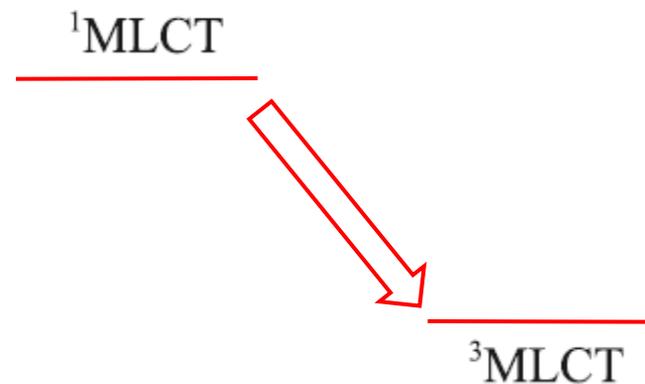
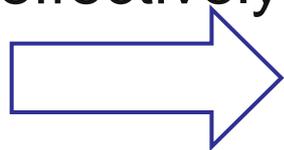




Cascading phenomena



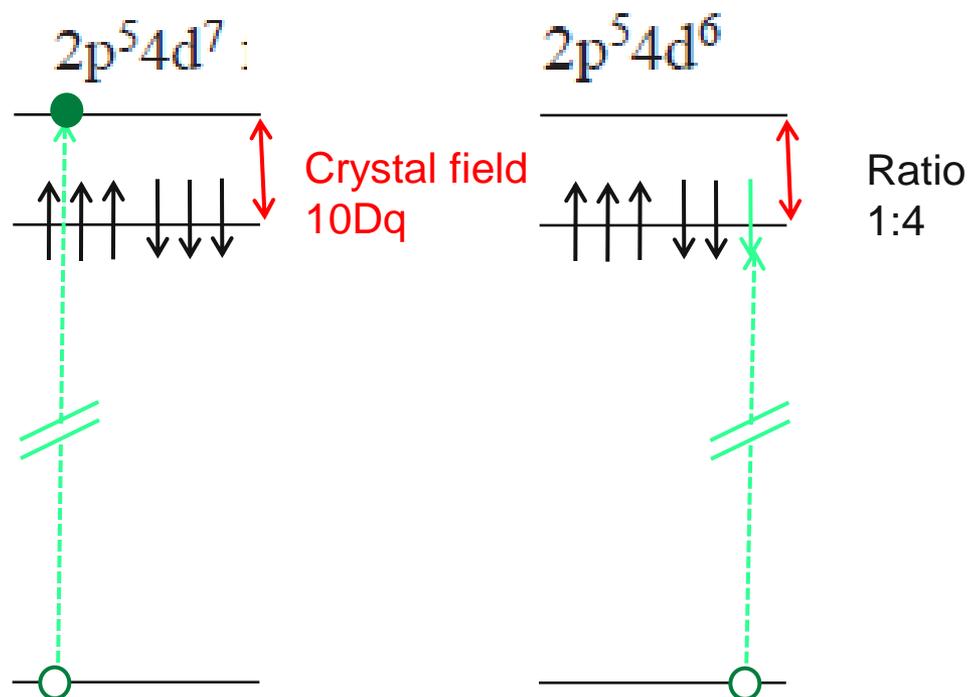
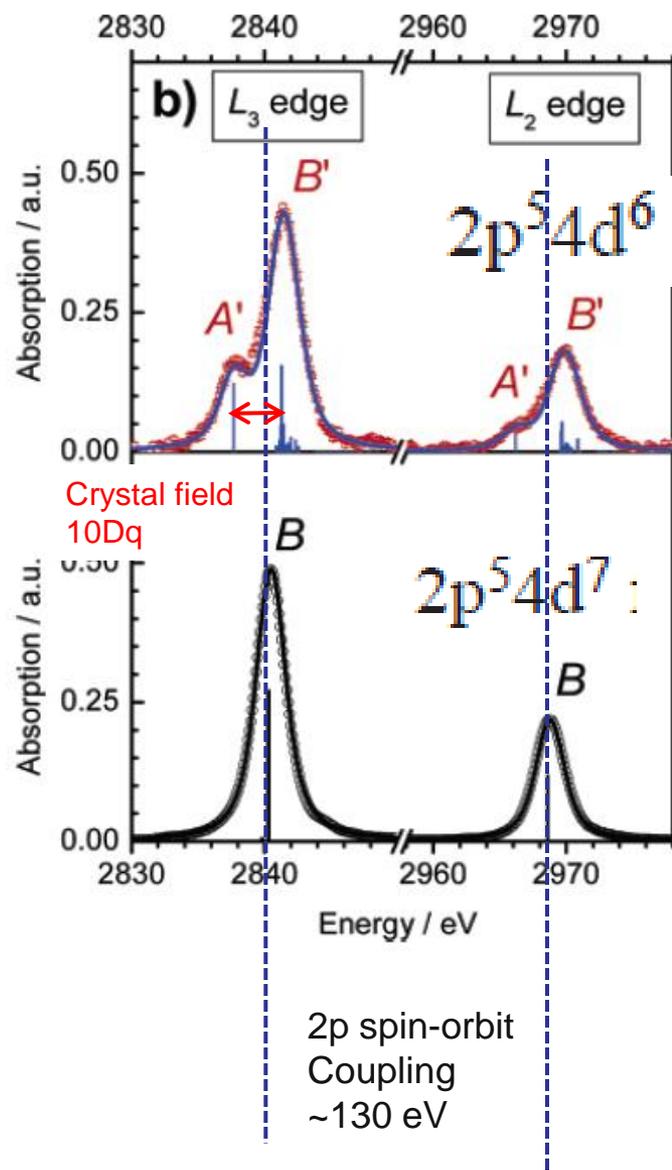
effectively



Questions:

1. We do not understand the mechanism to go from singlet to triplet MLCT states in Ruthenium complex
2. We do not understand much about dynamical spectroscopy
 - What do we need to add to calculate nonequilibrium spectroscopy
 - Can we actually expect changes in the line shape

Can we see this in dynamic XAS spectroscopy?



Typical atomic calculation

$$H_{\text{total}} = H_{\text{atom}} + H_{\text{crystal}} = H_{\text{atom}} + H_{O_h} + H_{D_3} + H_{\zeta LS}$$

Electronic and Molecular Structure of Photoexcited $[\text{Ru}^{\text{II}}(\text{bpy})_3]^{2+}$ Probed by Picosecond X-ray Absorption Spectroscopy

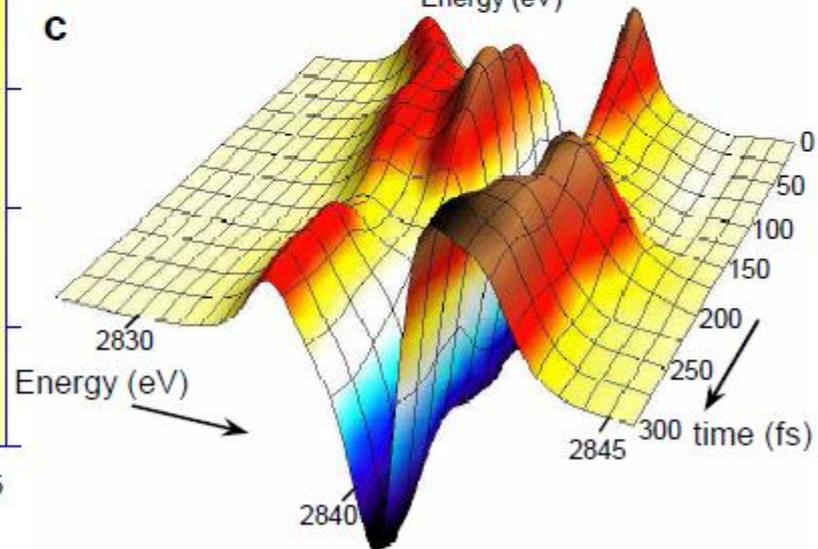
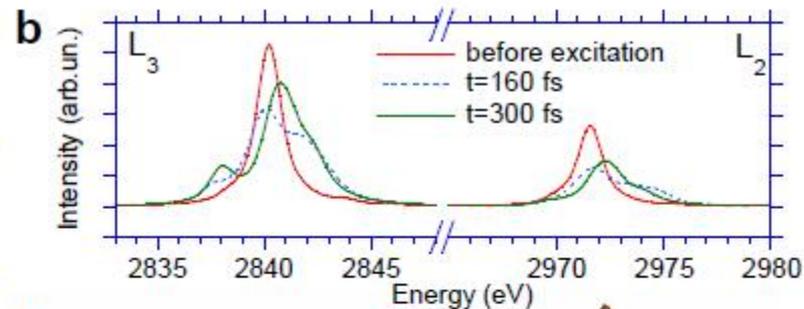
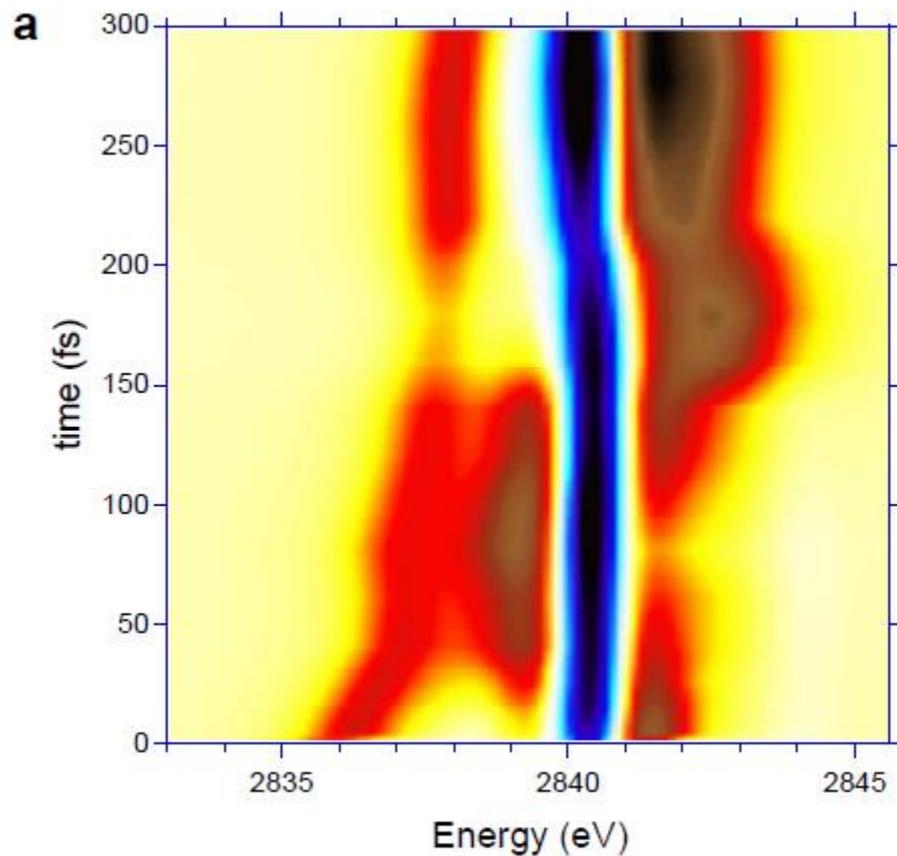
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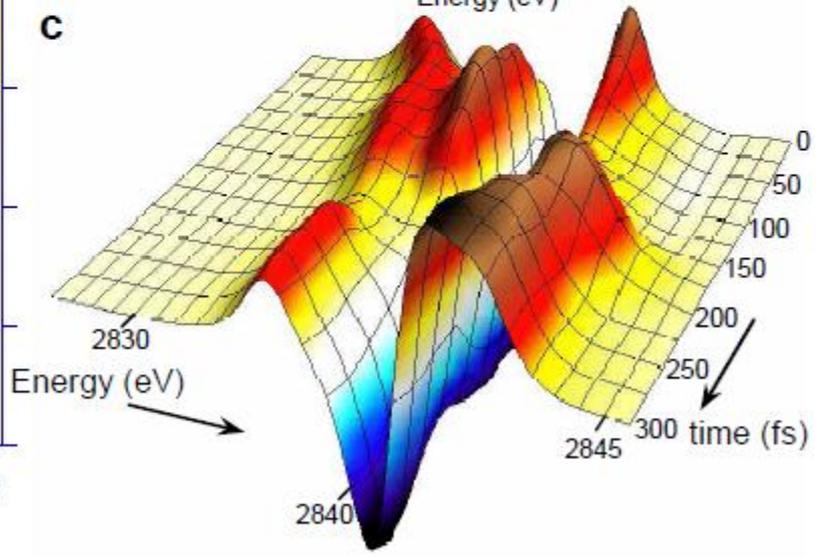
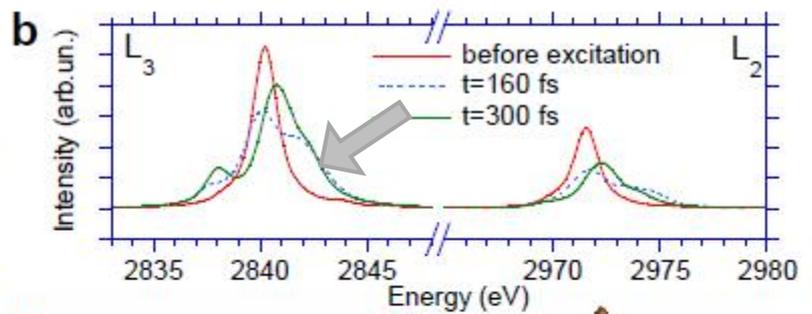
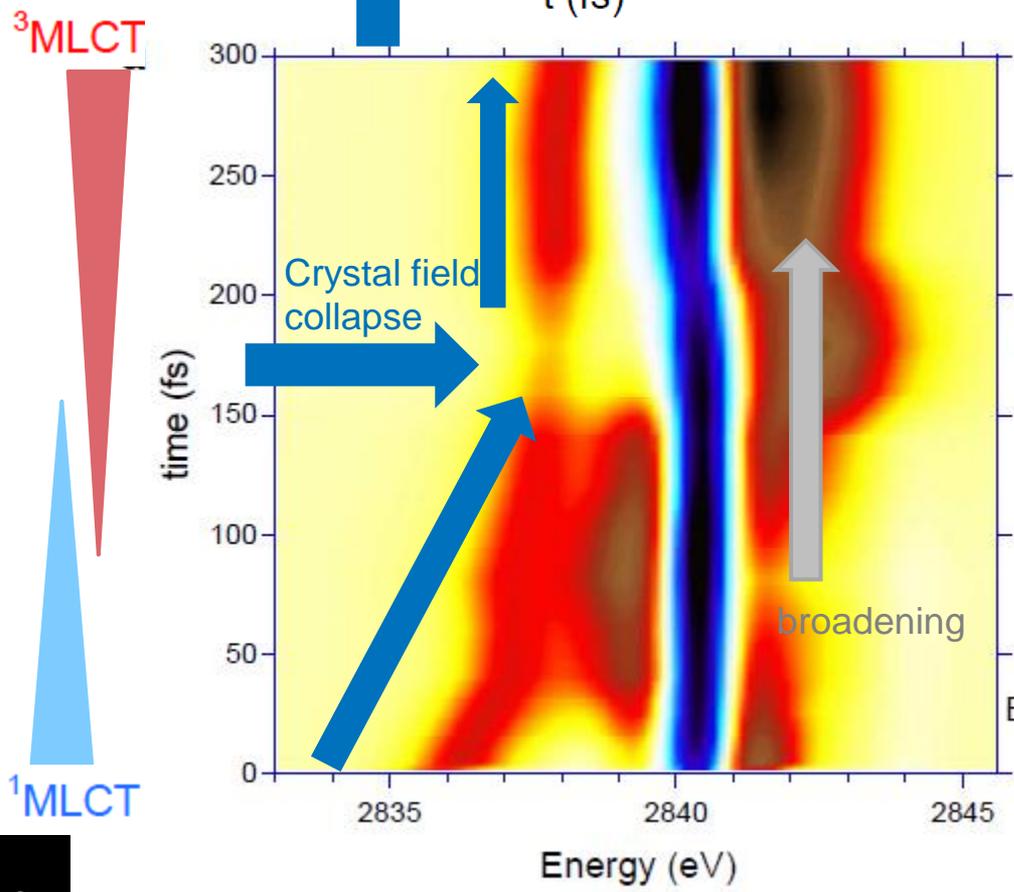
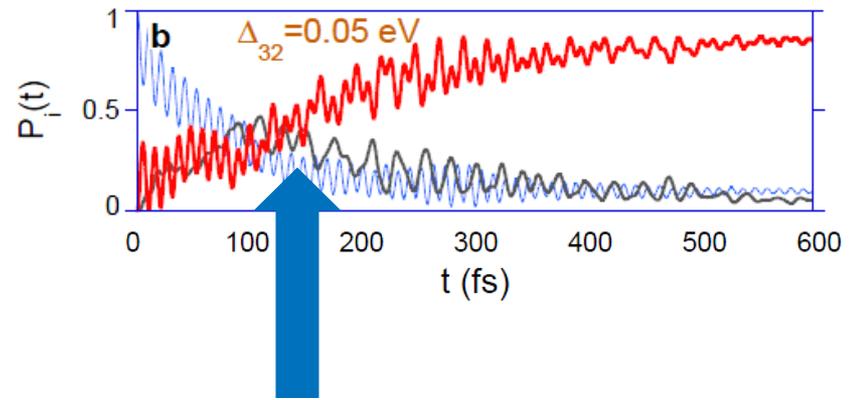
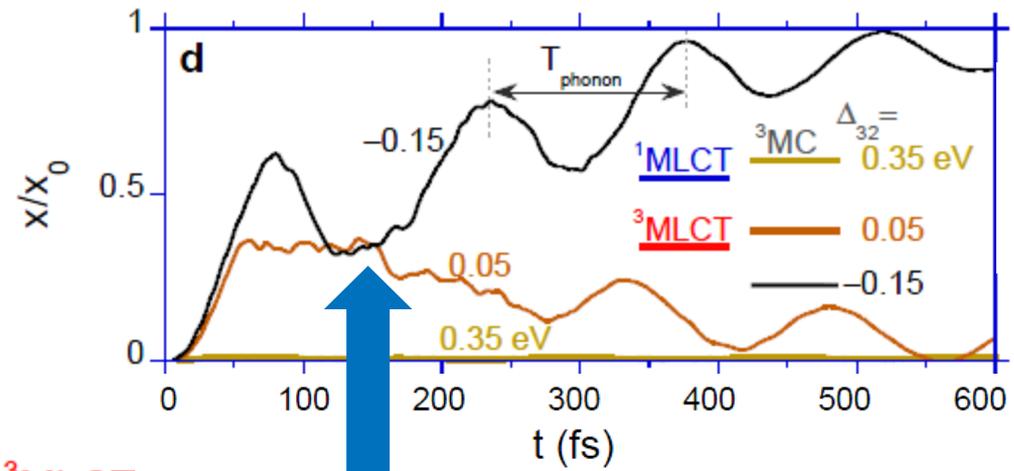
What needs to be changed and added?

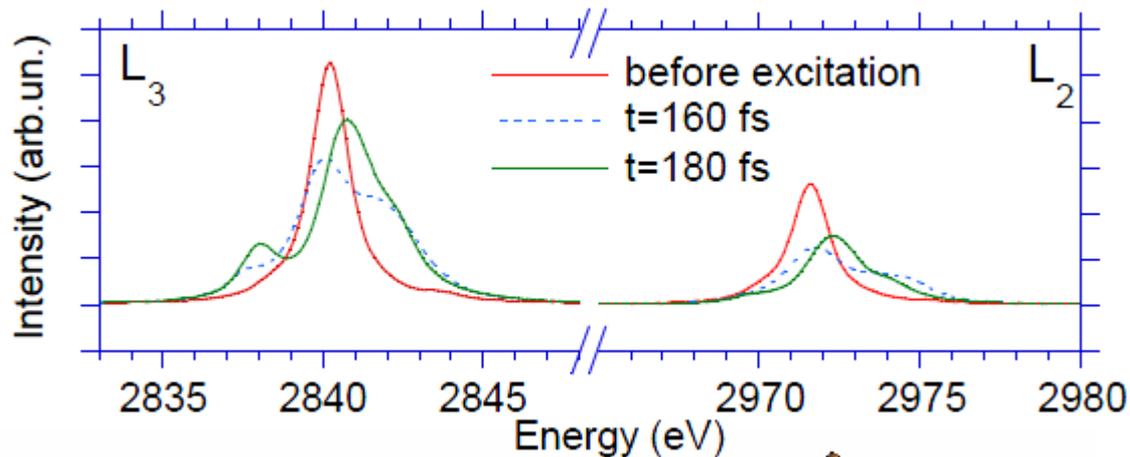
- The nonequilibrium effects change the ground state and final states
- We need to include the decay as described earlier
- The ligand states need to be included explicitly
- Changes in metal-ligand distance affect the crystal field and hybridization

$$10Dq' = (r/r')^5 10Dq$$
$$V' = (r/r')^{3.5} V$$

- Spin-orbit coupling not only changes spin but also the orbitals
- The metal-centered states need to be included







$$BR = I_{L_3} / I_{L_2}$$

$$BR=2 \xrightarrow{300 \text{ fs}} 3$$

$$BR = (2 + r) / (1 - r)$$

$$r = \langle \mathbf{L} \cdot \mathbf{S} \rangle / \langle n_h \rangle$$

Sum rules:

Thole and van der Laan

Spin flips lead to a change in L leading to a change in $\mathbf{L} \cdot \mathbf{S}$

Conclusions

- Without terms such as spin-orbit coupling, off-diagonal Coulomb terms, local phonon modes cannot couple different configurations with each other.
- Without a strong change in lattice constant, there is no phonon continuum and therefore no fast dephasing
- Decay of the phonons modes is essential for irreversibility.
- Showed the nature of the singlet to triplet MLCT crossing in Ru complexes
- The changes have a strong effect on the spectral line shape that are indicative of the underlying mechanism

Acknowledgments.— This work was supported by the U.S. Department of Energy (DOE), DE-FG02-03ER46097, and NIU's Institute for Nanoscience, Engineering, and Technology under a grant from the U.S. Department of Education. Work at Argonne National Laboratory was supported by the U.S. DOE, Office of Science, Office of Basic Energy Sciences, under contract DE-AC02-06CH11357.