# Towards Solvent Interactions in Modelling Infrared Spectra of Rhenium(I) Complex

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## Introduction

Different rates of the intersystem crossing (ISC) observed in various polar solvents[1,2]

The ISC is triggered by a light irradiation

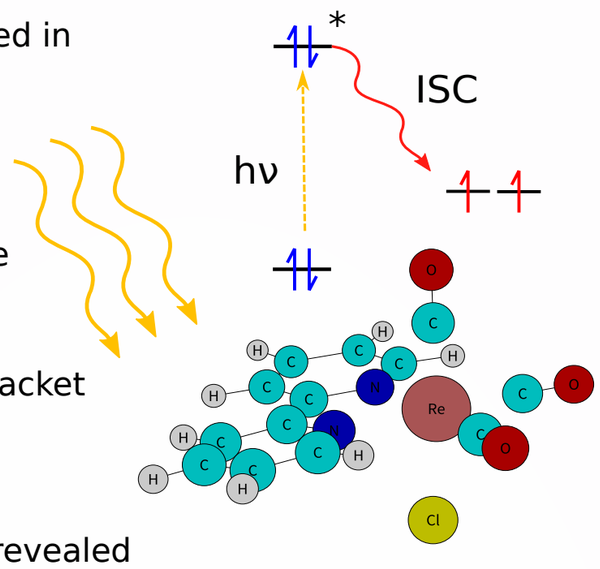
**Aim:** mimic the experiment at sub-ps and ps timescale

- State-of-the-art non-adiabatic dynamics
- An analysis based on virial theorem for computing the infrared spectra at sub-ps time scale

Uncovered relaxation processes:

- Ultrafast relaxation of the molecular spin-orbit wavepacket
- Non-adiabatic relaxation
- Vibrational relaxation of carbonyl modes
- Redistribution of solvent molecules

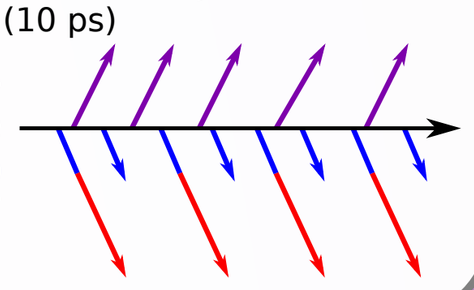
Correlation between solvent and vibrational relaxation revealed




## Methodology

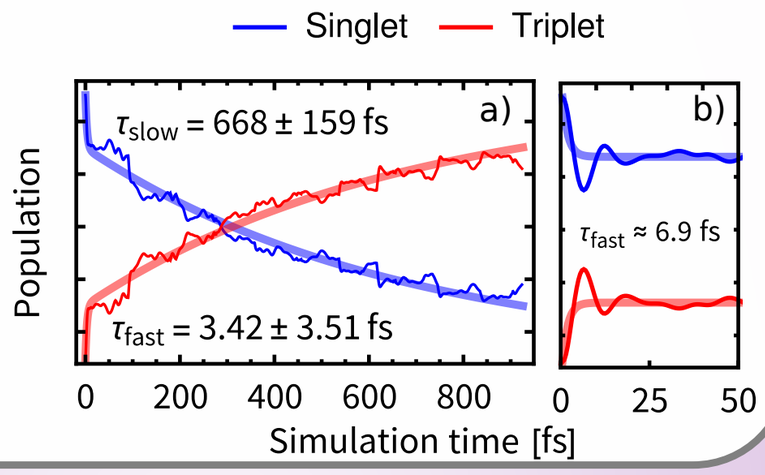
Combination of two computational approaches employed:

0) Initial conditions from ground state dynamics
1) Born-Oppenheimer dynamics in the lowest triplet state (5 ps)
2a) Non-adiabatic dynamics at sub-ps time scale
2b) Extended Born-Oppenheimer dynamics in the lowest triplet state (10 ps)



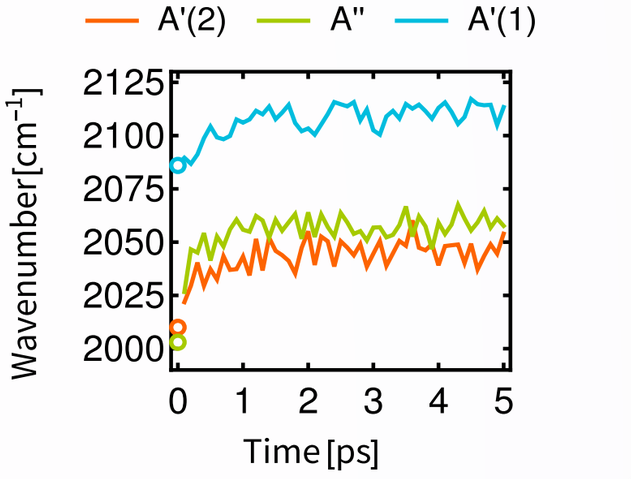

## Intersystem crossing

- Relaxation of the **molecular spin-orbit wavepacket**[3] (time constant $\tau_{fast}$)
  - Converting about 20 % of the electronic population
  - Confirmed by frozen-nuclei dynamics - b)
- Vibrational relaxation in a strong **non-adiabatic** regime (time constatnt $\tau_{slow}$) - a)
  - Conversion about 80 % of the singlet population to triplet states



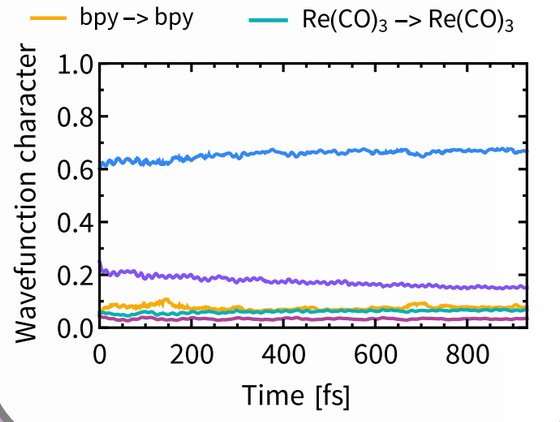

## Vibrational relaxation

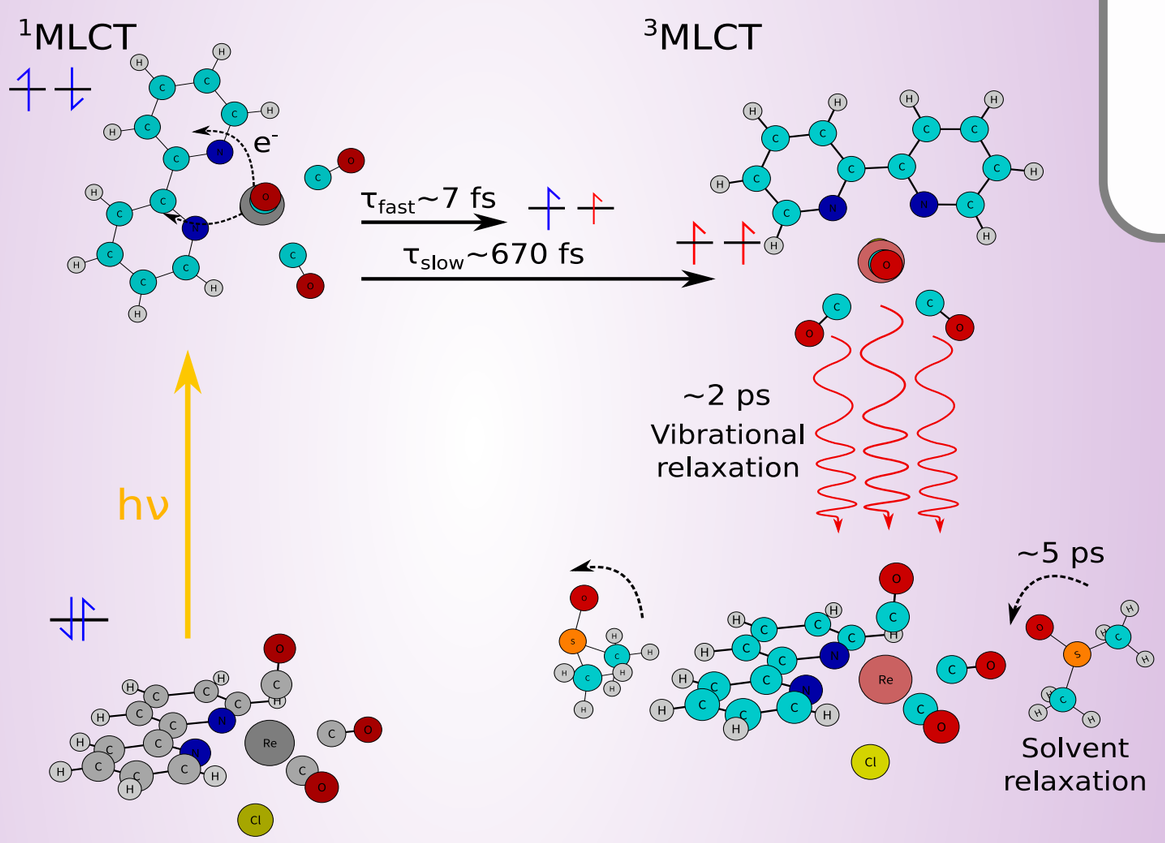
- New equilibrium approached in **2 ps**
- Total shift upwards (~**40 cm$^{-1}$**) in accord with the experiment




## WF character

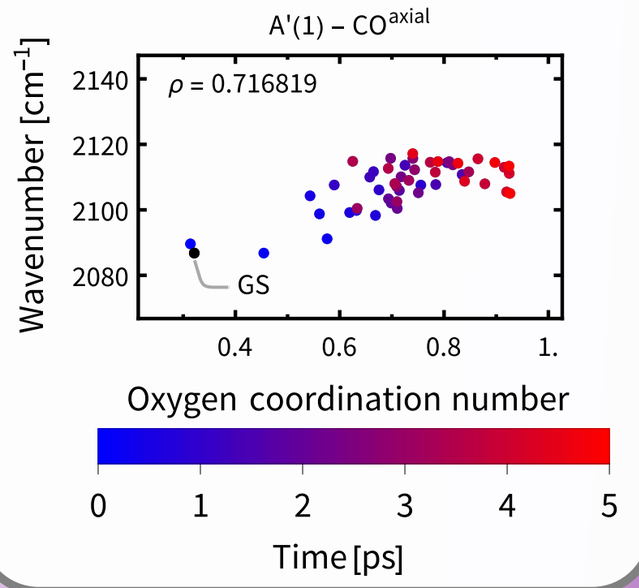
- Mixed MLCT and LLCT character (Re ⟶ bpy) & (Cl,$(CO)_3$ ⟶ bpy)
- Character of the wavefunction preserved during the whole non-adiabatic dynamics




## Vibration-solvation correlation

- Carbonyl modes frequencies
- DMSO oxygen coordination number to carbonyl ligands




## Acknowledgement

SZ and AV thank the Czech Science Foundation (grant 21-05180S) for support. This work was supported by the Ministry of Education, Youth and Sports of the Czech Republic through the e-INFRA CZ (ID:90140). SZ thanks IT4I for multiyear project OPEN-20-8.

[1] *A. Cannizzo, A. M. Blanco-Rodríguez, A. E. Nahhas, J. Šebera, S. Záliš, A. Vlček and M. Chergui, J. Am. Chem. Soc.* ***130****, 8967-8974 (2008)*
[2] *A. E. Nahhas, A. Cannizzo, A. M. Blanco-Rodríguez, S. Záliš, A. Vlček and M. Chergui, J. Phys. Chem. A* ***114****, 6361-6369 (2010)*
[3] *S. Mai and L. González, Chem. Sci.* ***10****, 10405-10411 (2019)*