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# Unraveling the electronic structure and photodissociation dynamics of metal carbonyls

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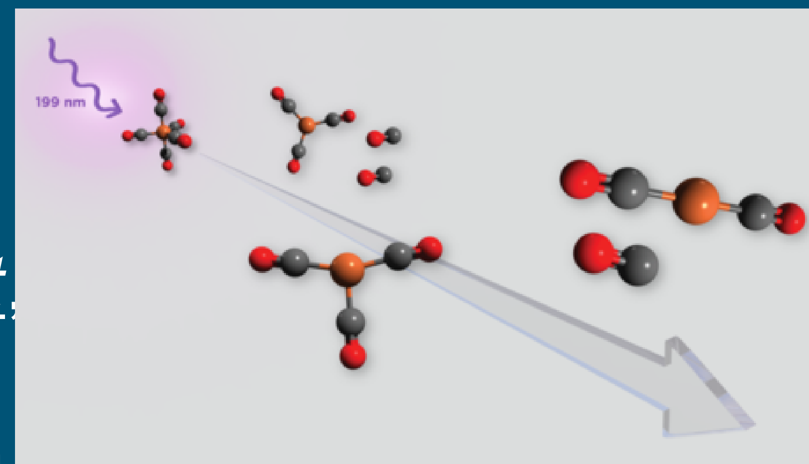
# Metal carbonyls in catalysis

Metal carbonyl compounds photodissociate in the UV to create reactive intermediates that aid catalysis




$Fe(CO)_5$ is known as the *prototypical model catalyst*, which photodissociates at 267 nm to form $Fe(CO)_4$

$Ni(CO)_4$ is highly toxic and is rarely used in modern industrial applications

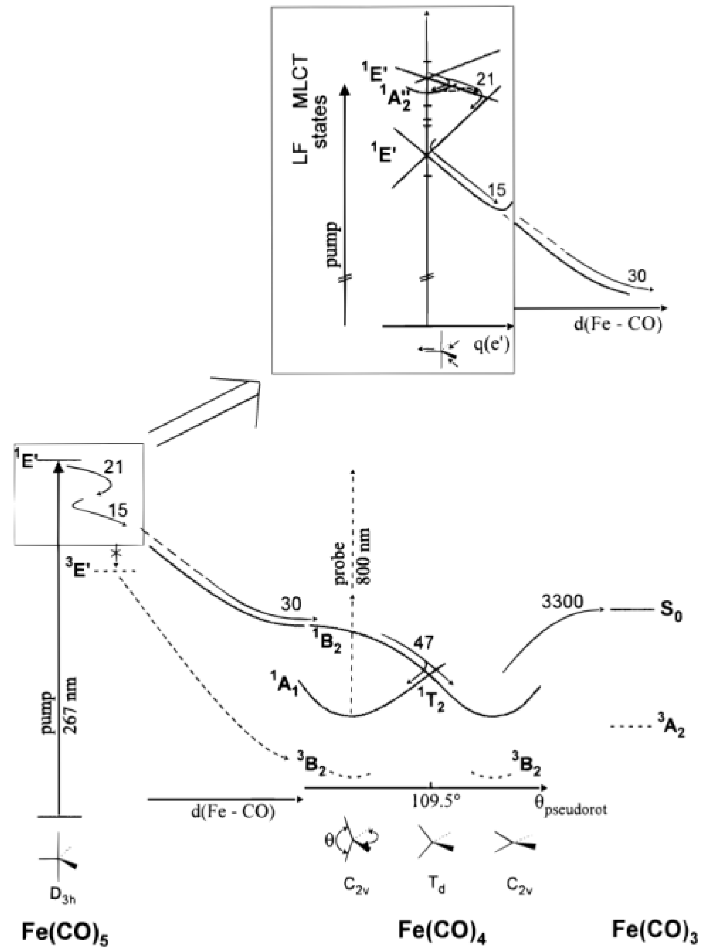
## In popular culture [ edit ]

"Requiem for the Living" (1978), an episode of *Quincy, M.E.*, features a poisoned, dying crime lord who asks Dr. Quincy to autopsy his still-living body. Quincy identifies the poison—nickel carbonyl.

# So why study specific $M(CO)_n$ photodissociation pathways?

## $M(CO)_n$ photodissociation pathways follow a standard set of rules:

- Pump at ~267 nm (4.6 eV) to excite a metal-to-ligand charge transfer (MLCT) state
- $M(CO)_n$ relaxes to a dissociative ligand field (LF) state ($S_1$)
- $M(CO)_n$ moves through a $S_0/S_1$ conical intersection (40-70 fs after excitation)
- $M(CO)_n$ -> $M(CO)_{n-1}$ + CO (~100 fs after excitation)



# $Fe(CO)_5$: prototypical metal carbonyl?

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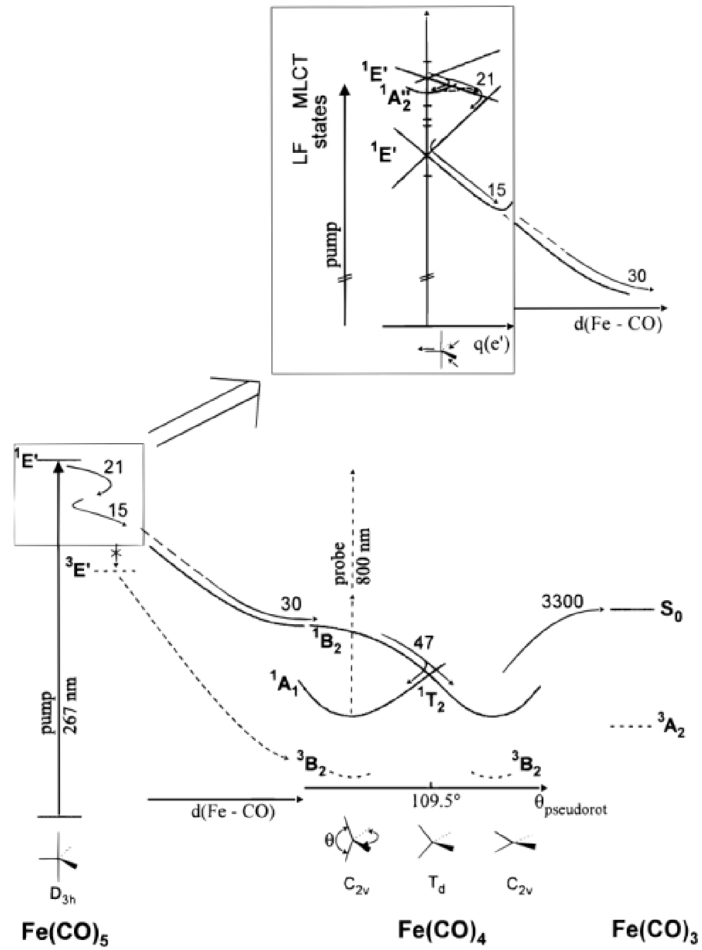
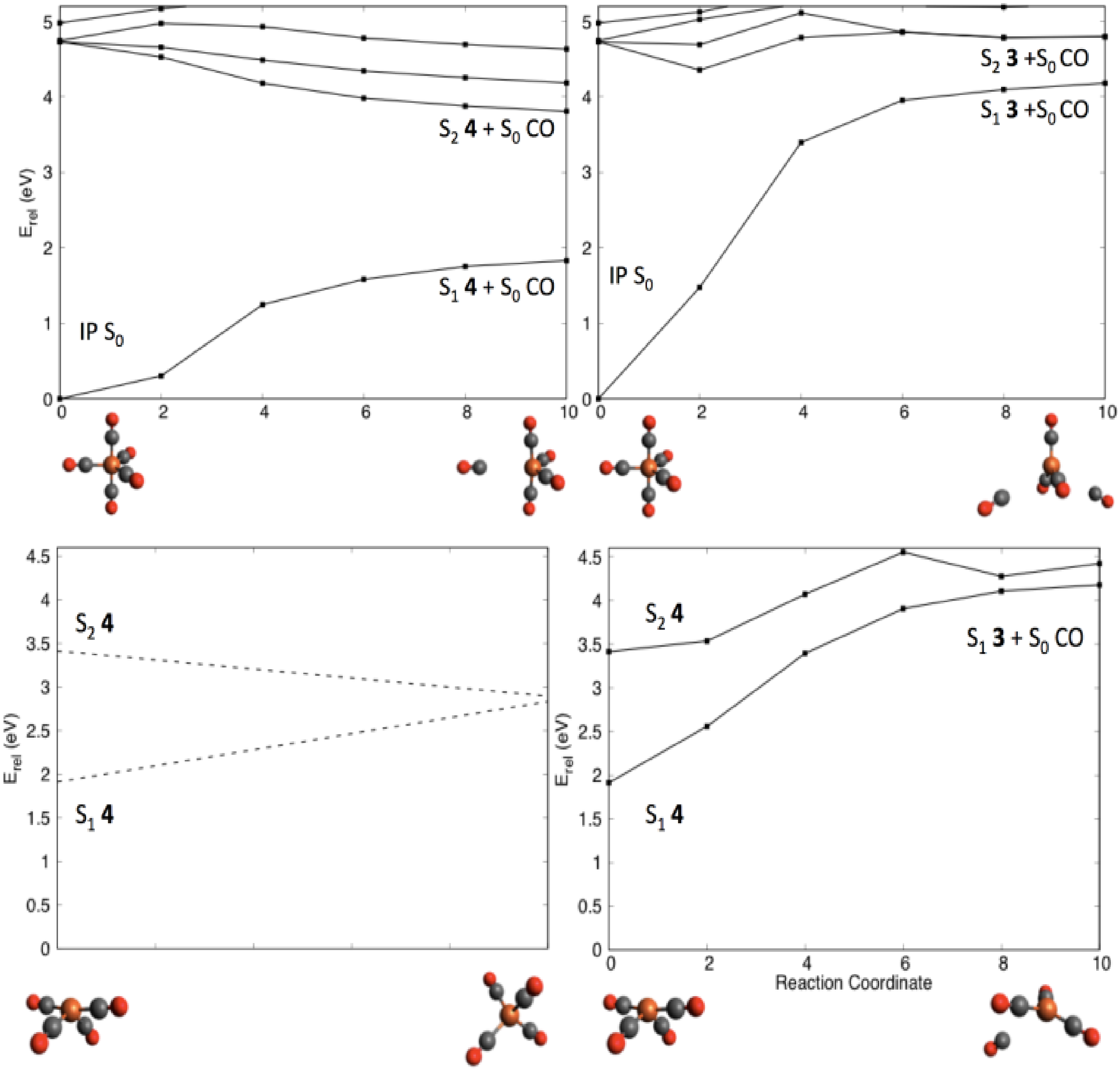



**However, the story is a bit more complicated than the rules imply…**

# $Fe(CO)_5$: prototypical metal carbonyl already breaking the rules




1. $Fe(CO)_4$ is a ground state triplet
2. $Fe(CO)_5$ dissociates to the $S_2$ state of $Fe(CO)_4$ before reaching the $S_1/S_2$ conical intersection
3. Additional pathways (concerted loss of CO) are possible!

# How does the electronic structure of $Ni(CO)_4$ differ from other $M(CO)_n$?

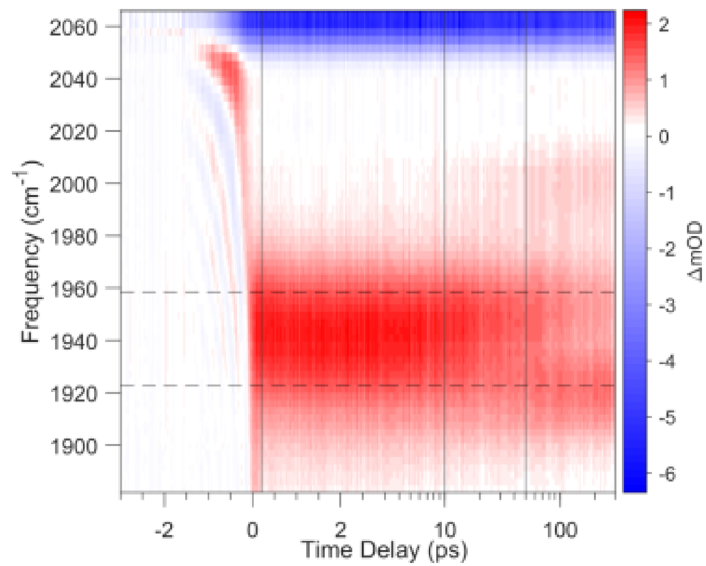
1. $Ni(CO)_4$ has a full d shell
2. No ligand field (LF) states, d→4s states proposed to act as dissociative states
3. Symmetry prevents $S_0/S_1$ conical intersection
4. $Ni(CO)_3$ luminescence is seen on a ns timescale post-dissociation!

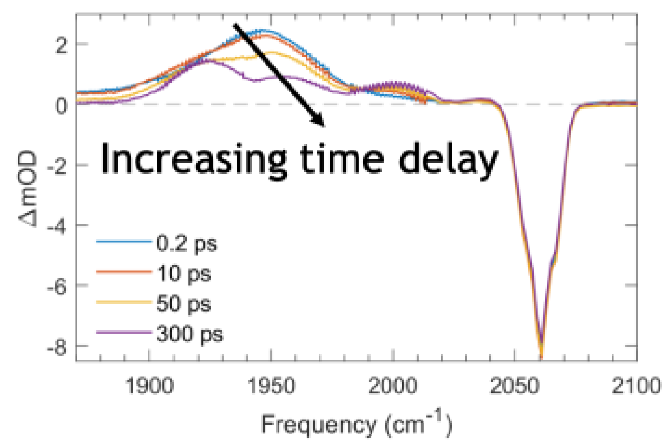
**If $Fe(CO)_5$ already challenges the standard model, how much does $Ni(CO)_4$ deviate?**

# Experimental and theoretical integration

Gas phase transient absorption spectroscopy:

- 267 pump, IR probe
- Observe IR spectrum changes in time
- Captures vibrational signatures of photodissociation products

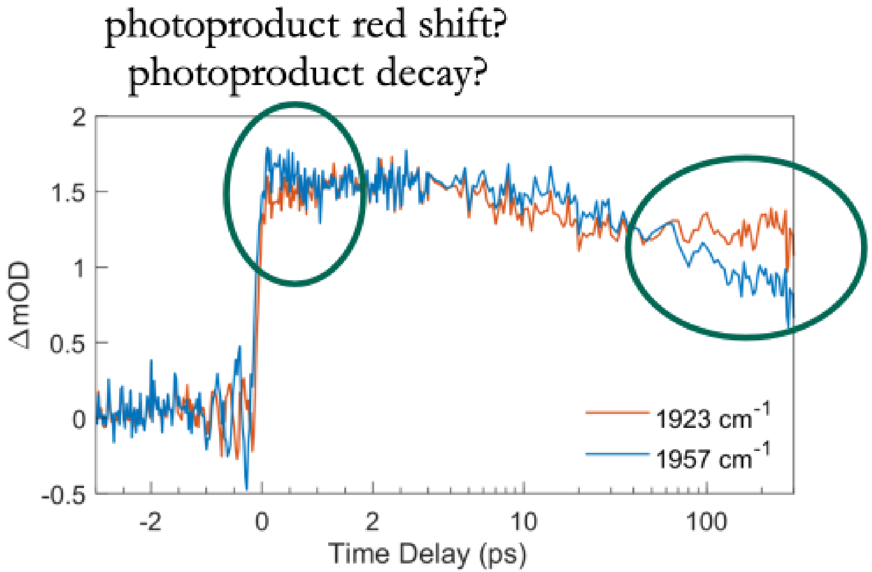


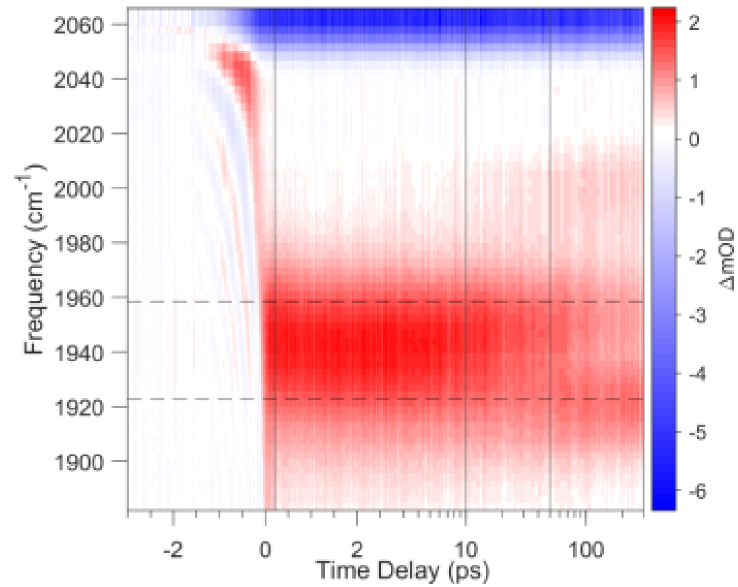




Krupa Ramasesha


Neil Cole-Filipiak

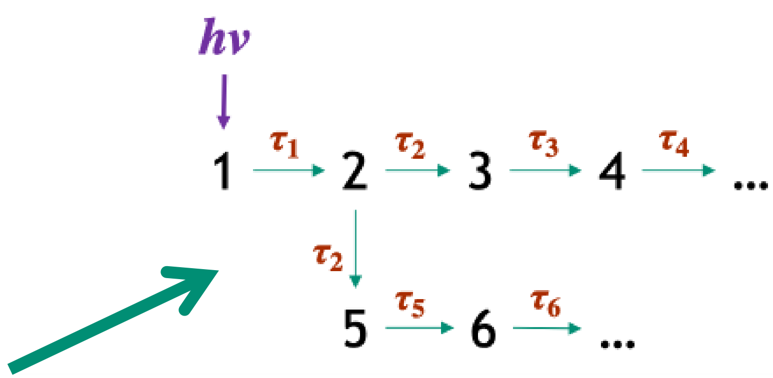
# Experimental and theoretical integration

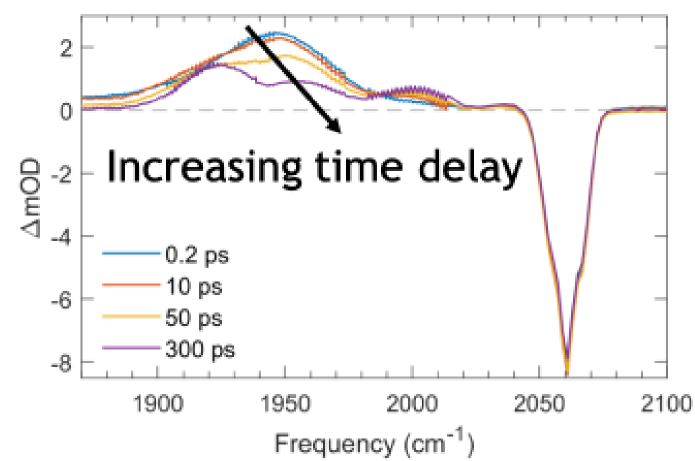



1957 cm$^{-1}$: <1 ps, 60 ps, $10^3$ ps

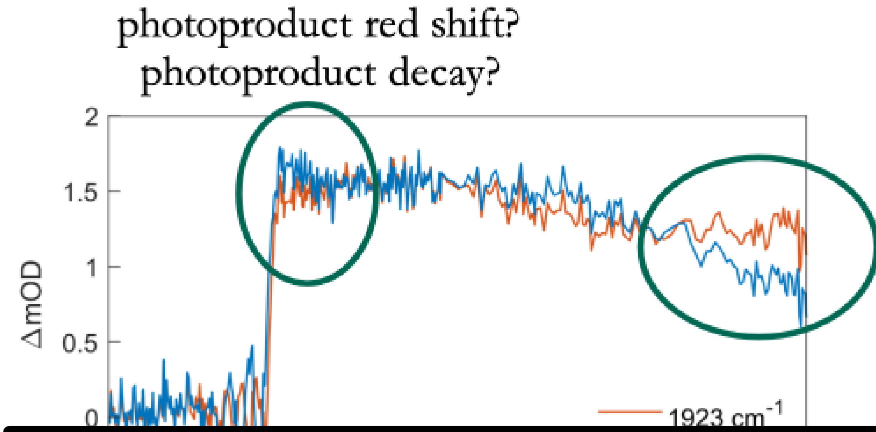
1923 cm$^{-1}$: <1 ps, 10 ps, $10^4$ ps

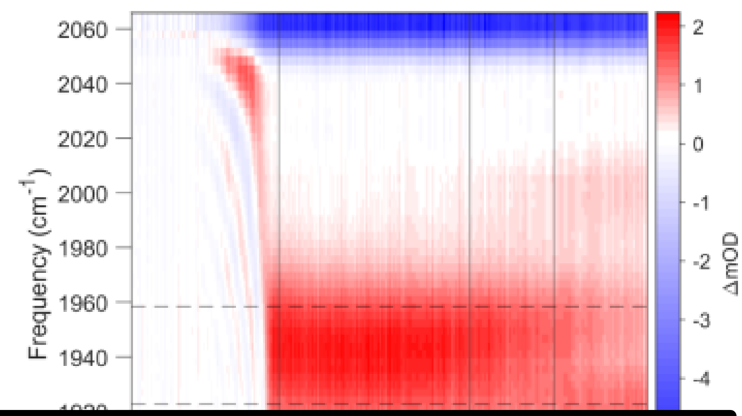



Experimental fitting provides a set of mysterious time constants corresponding to changes in the spectra

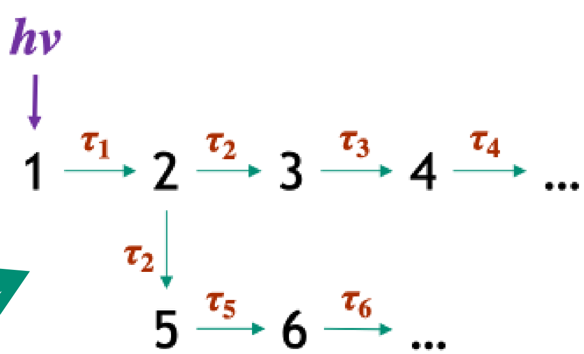
# Experimental and theoretical integration

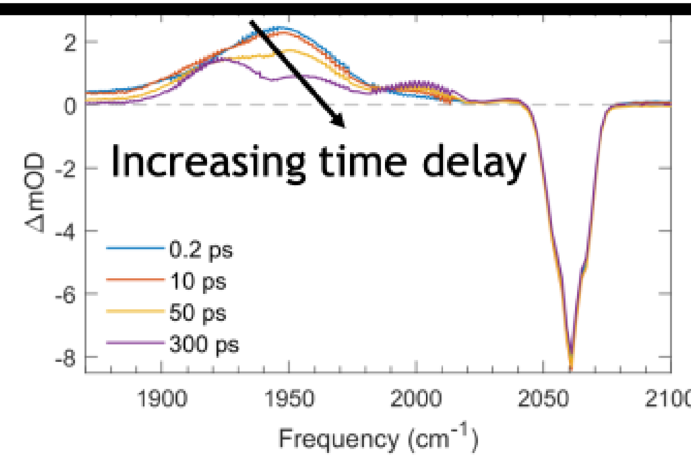



**Something is happening at the following times: 600 fs, 14 ps, and 55 ps**

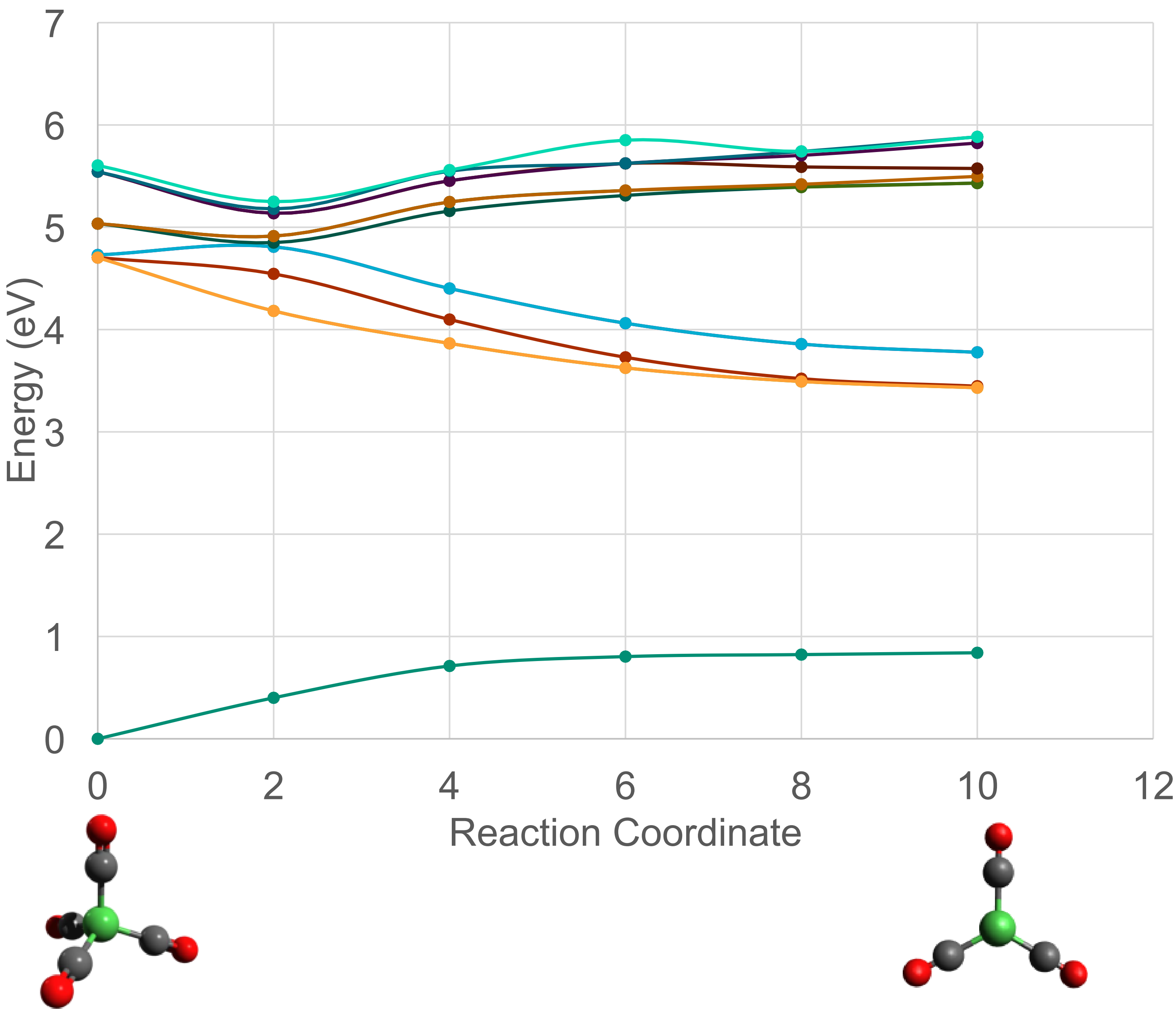
1923 cm$^{-1}$: <1 ps, 10 ps, $10^4$ ps




Experimental fitting provides a set of mysterious time constants corresponding to changes in the spectra

# $Ni(CO)_4$ dissociation pathways



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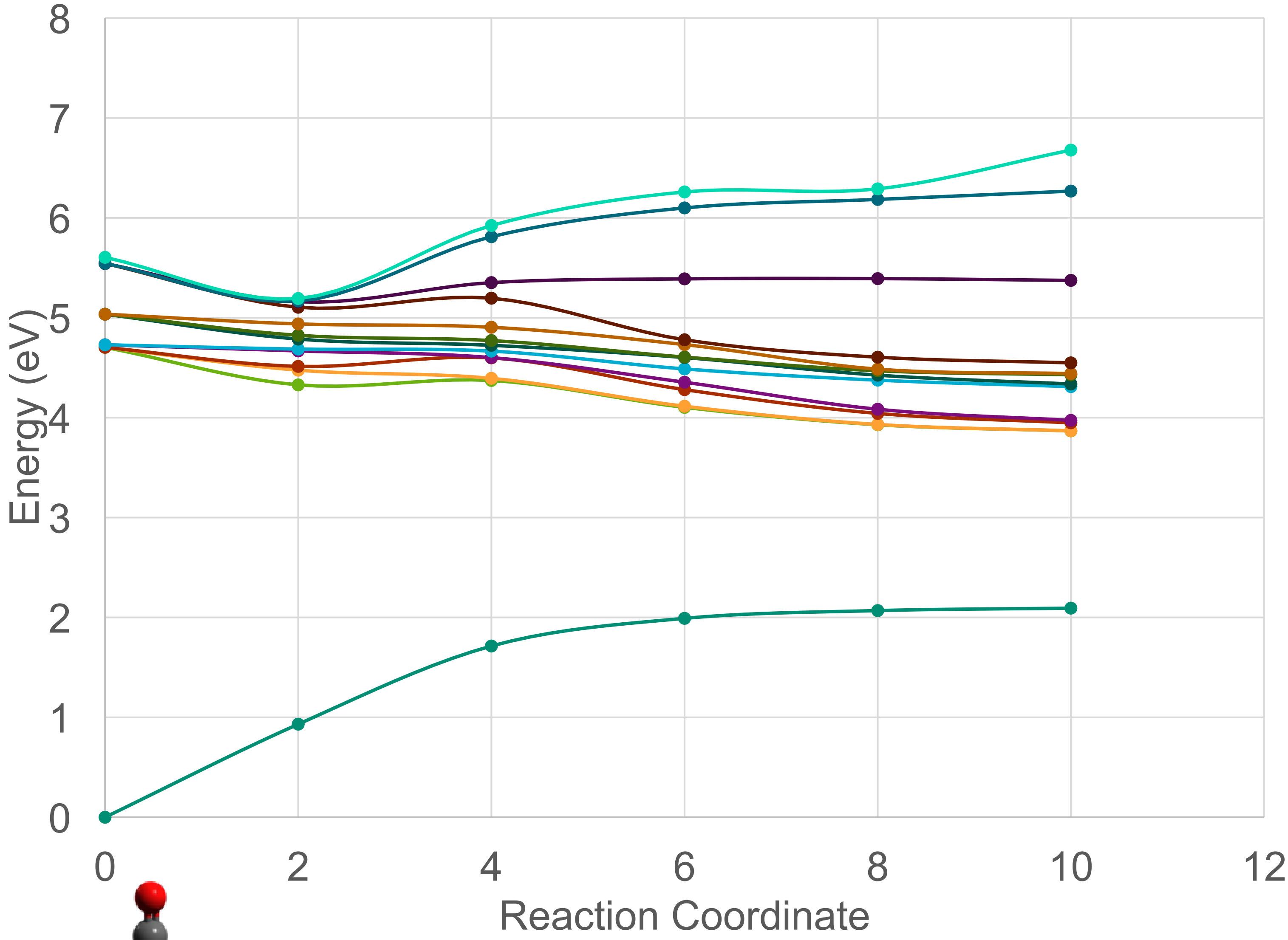
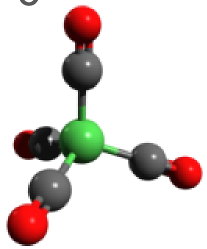
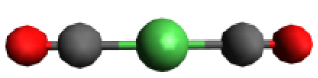
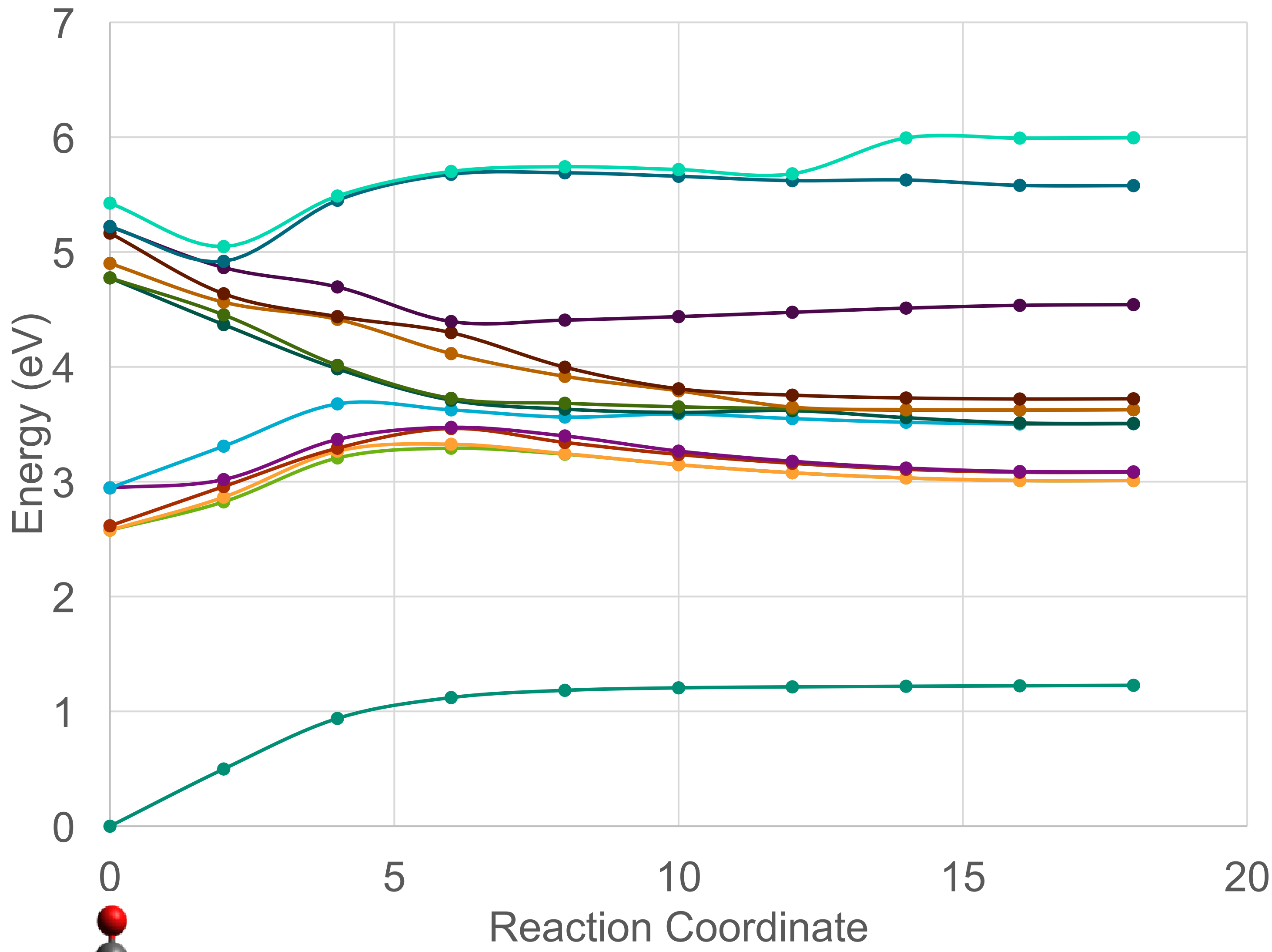
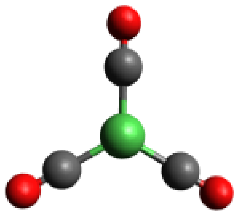


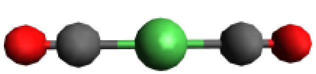





# $Ni(CO)_3$ dissociation pathway

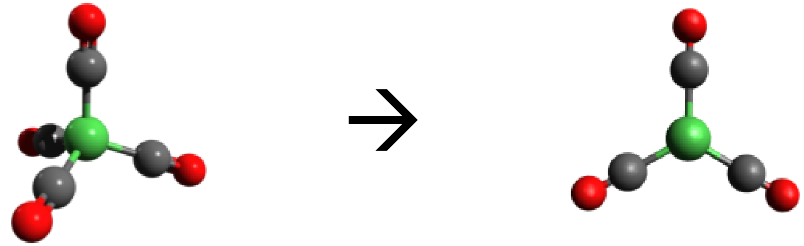


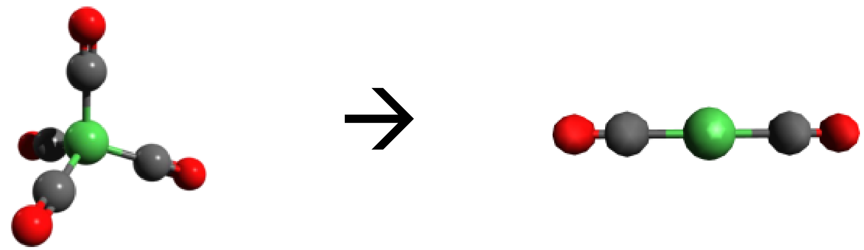


# Assigning time constants

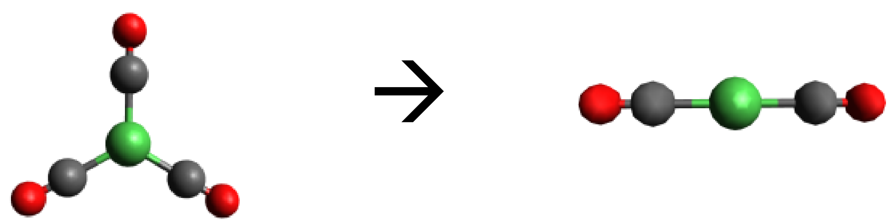
600 fs:



14 ps?



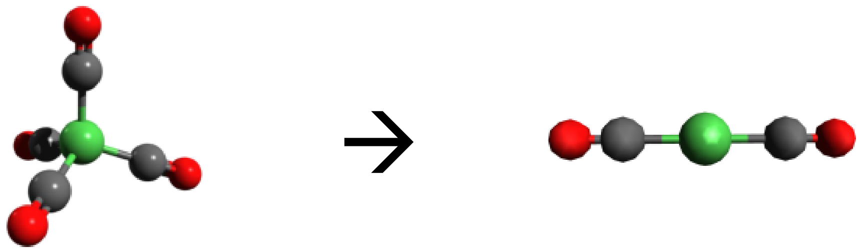
55 ps?

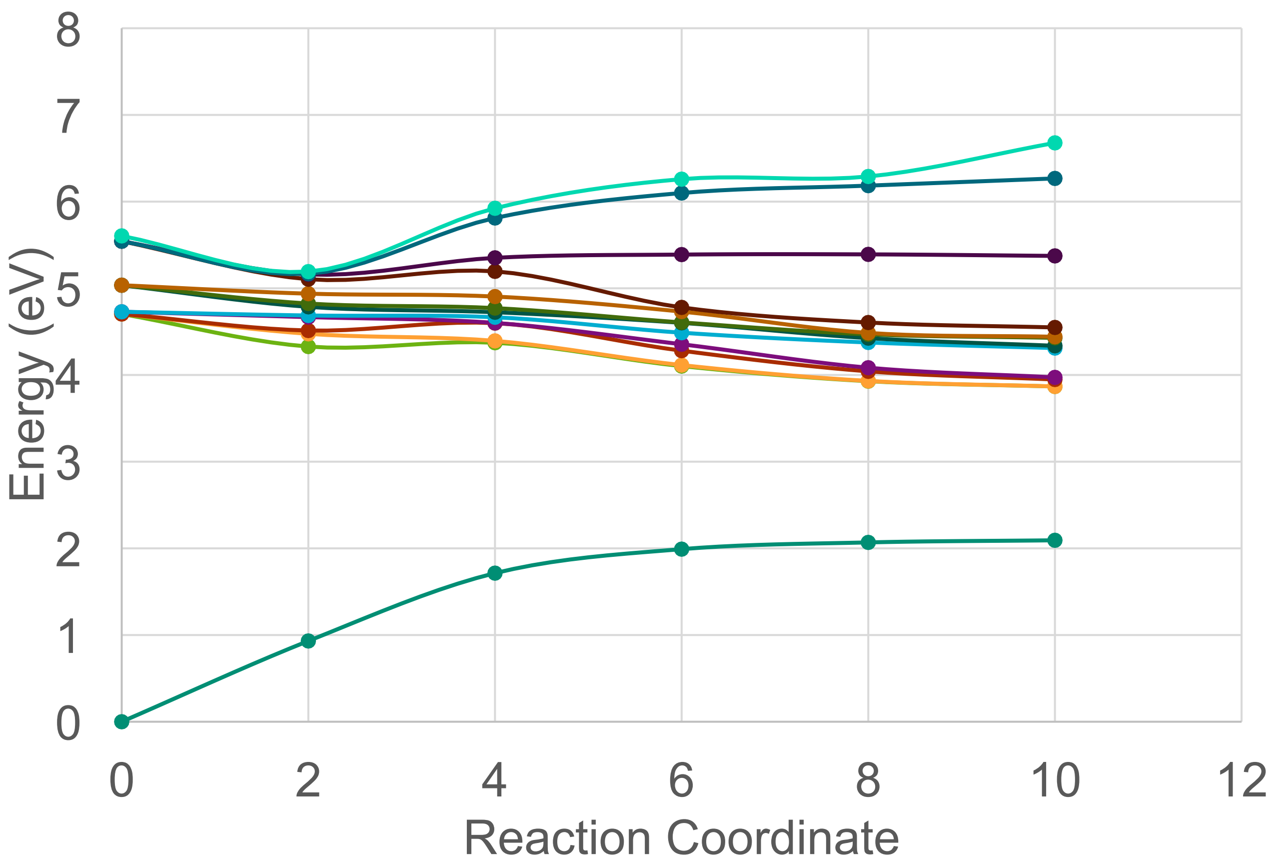


14 ps is a long timescale for such a small barrie

# Assigning time constants

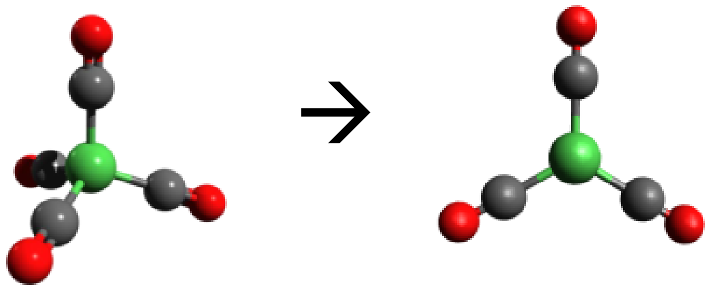
14 ps?

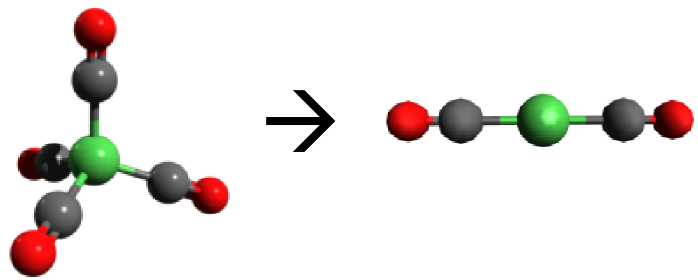




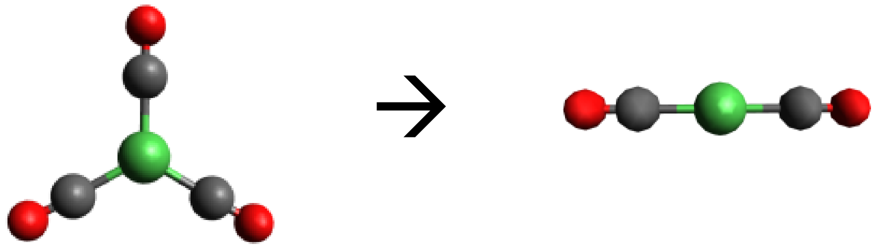

14 ps is a long timescale for such a small barrier

# Does 600 fs encompass both?



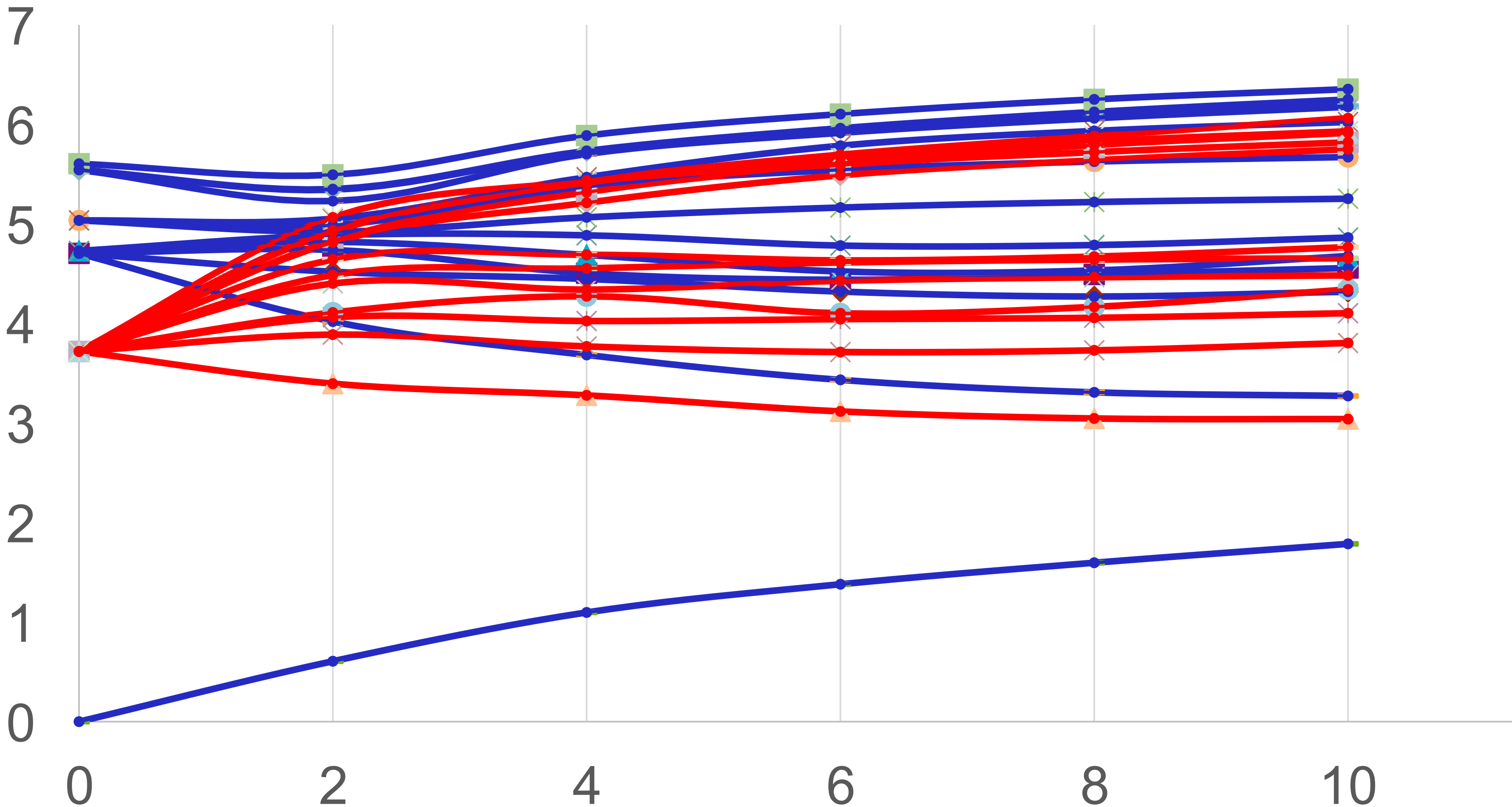


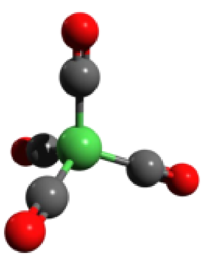
## Does 14 ps represent 3 → 2?

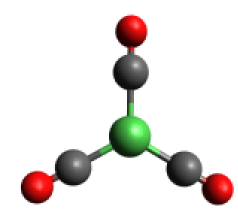


*<u>What else could be going on?</u>*

# Are there any triplet states in the vicinity?



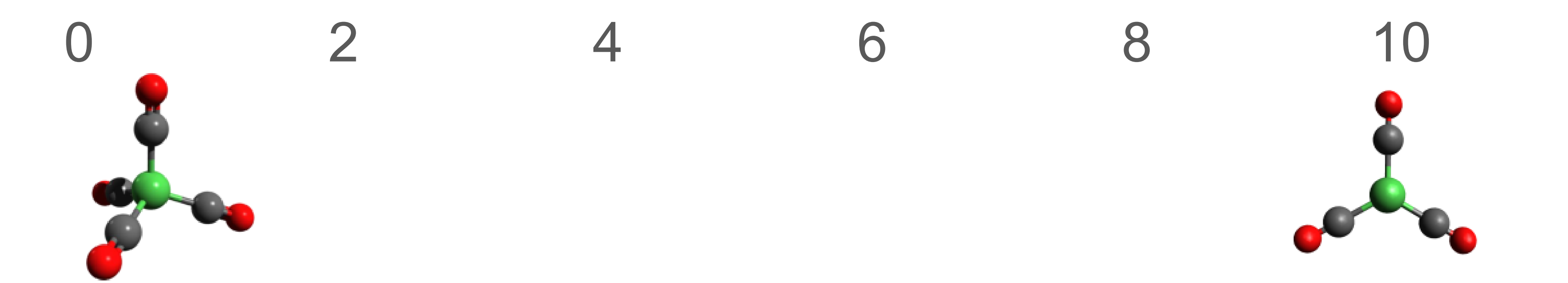


# Are there any triplet states in the vicinity?


We may be seeing intersystem crossing at 14ps or 55ps (in either $Ni(CO)_3$ or $Ni(CO)_2$):

Currently calculating

- Anharmonic frequencies of singlet and triplet species
- Spin-orbit coupling at key geometries



What can *ab initio* molecular dynamics tell us about these mechanisms?

# On-the-fly *ab initio* molecular dynamics

Pros:

- Powerful tool for determining reaction mechanisms, timescales, and spectra
- Gives electronic structure at each point along dynamical trajectory

Cons:

- Many trajectories needed for statistics
- Computationally expensive (relies on electronic structure, many trajectories needed to get statistics)

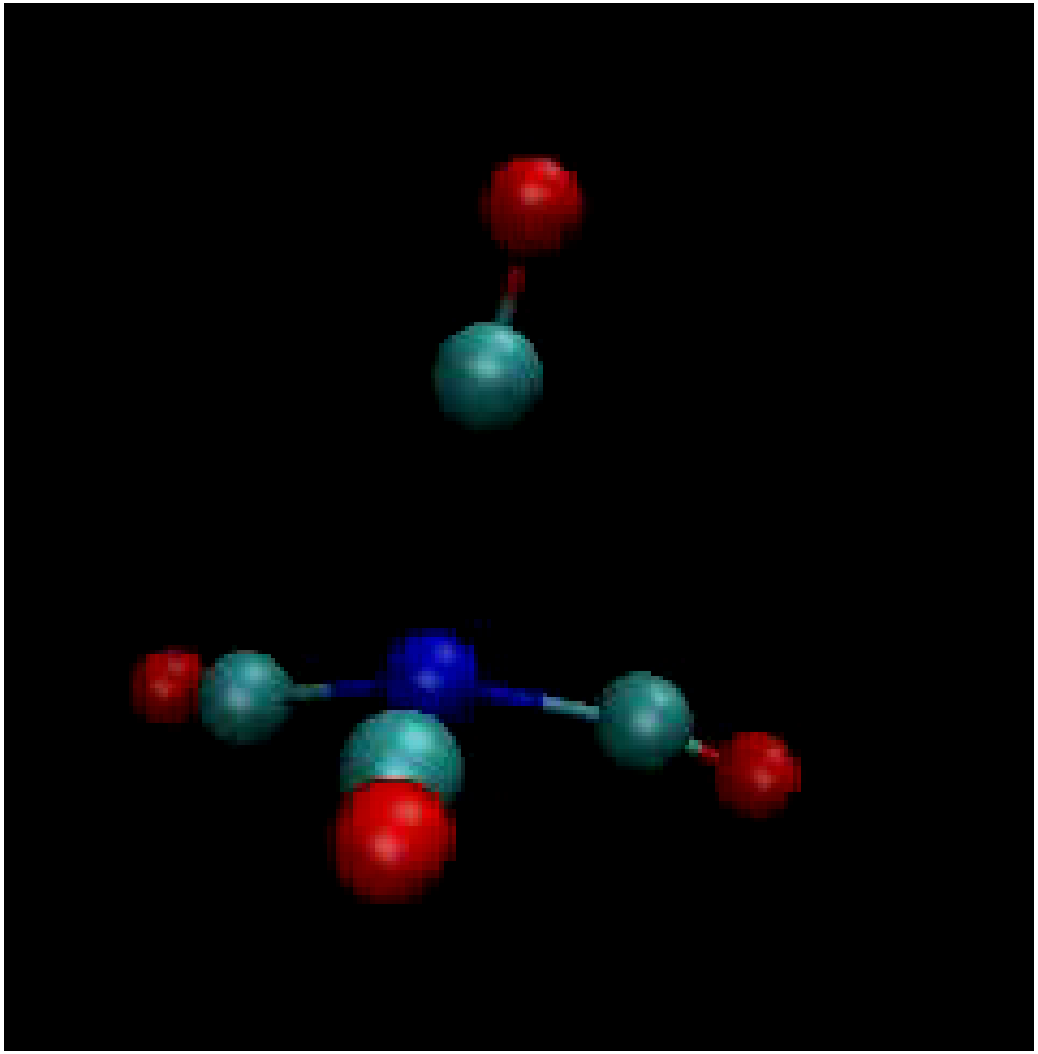
$$m_j \frac{d^2 x_j}{dt^2} = -\frac{\partial V}{\partial x_j}$$

← Potentials obtained on-the-fly from *ab initio* electronic structure calculations

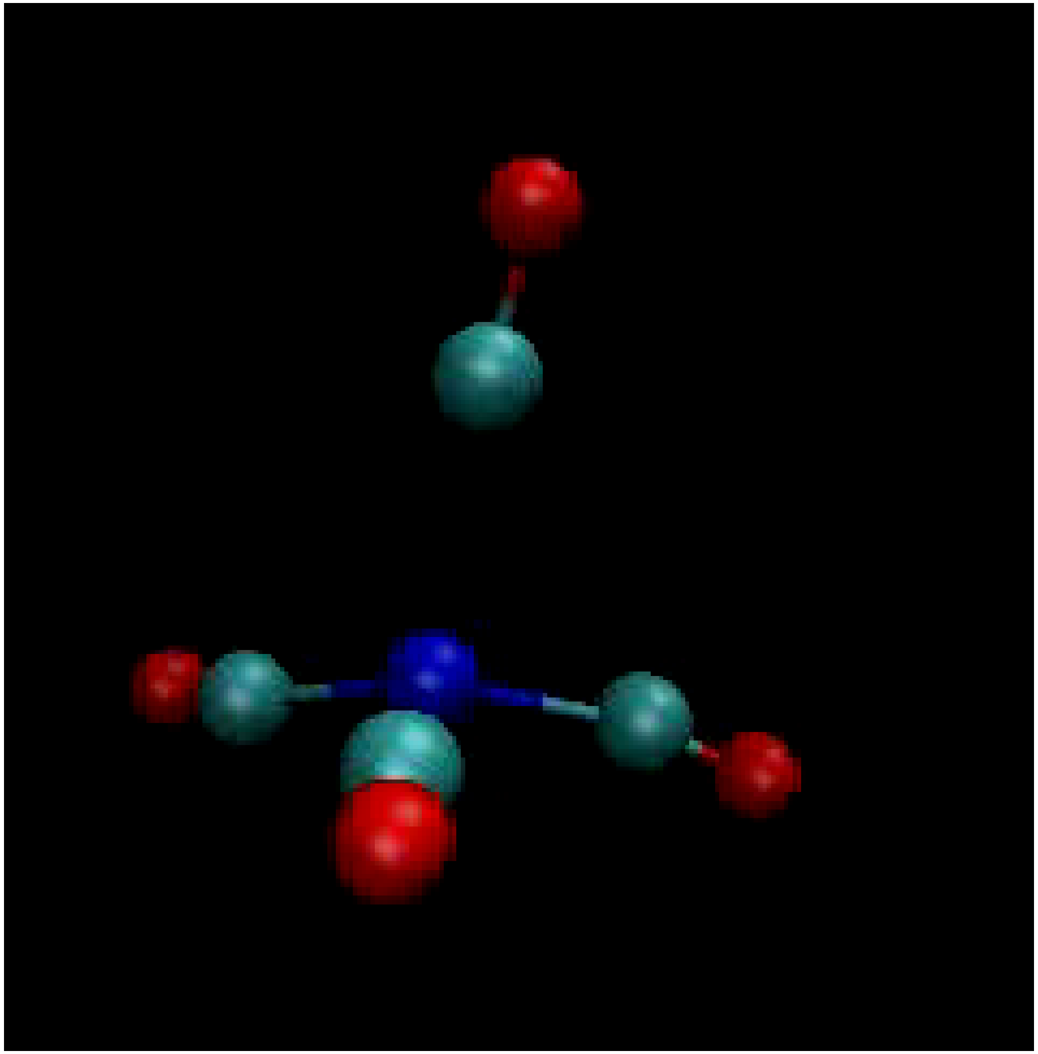
# Excited state AIMD on metal carbonyls is non-trivial

- High density of states is challenging for AIMD
- Treatment of non-adiabatic effects: Tully-type surface hopping
- Electronic structure method must have balance between accuracy and computational efficiency
- TDDFT PBE0/cc-pVDZ (C,O), Wachters+f (Ni) performed well in benchmark PES cuts

# Photodissociation dynamics over 1 ps



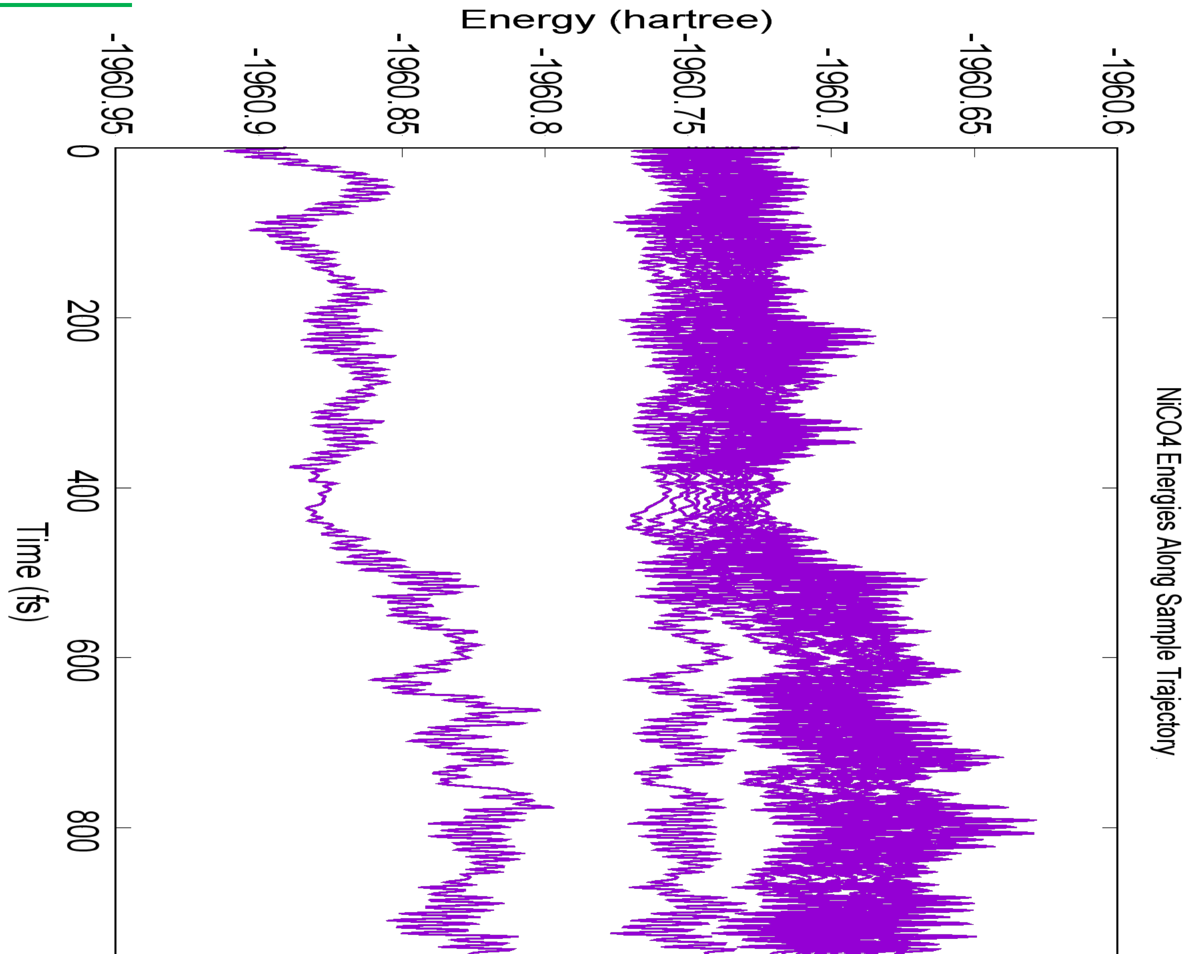
# Early results: photodissociation dynamics over 1 ps



- Dissociation seen at ~350ps
- Here: CO weakly interacting with $Ni(CO)_3$ up to 1 ps
- Further analysis of electronic state character (d→4s?), timescales, and branching yields underway

# Early results: dynamics over 1 ps

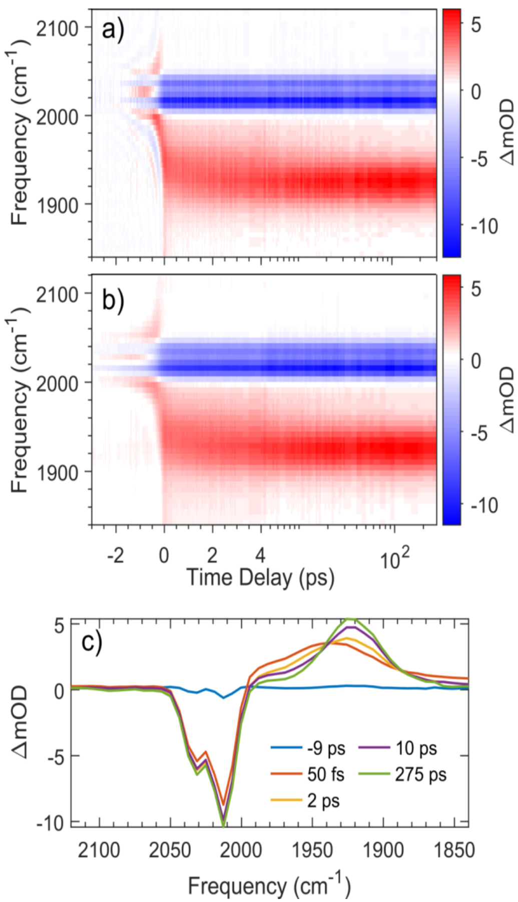
- High density of electronic states (15 states in 1eV)
- At ~550 fs, $Ni(CO)_3$ is formed on S1 surface, which separates away from $S_2$-$S_{15}$ → matches our 600fs time constant

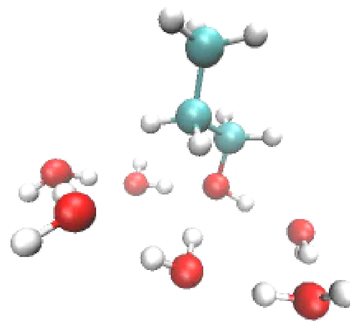


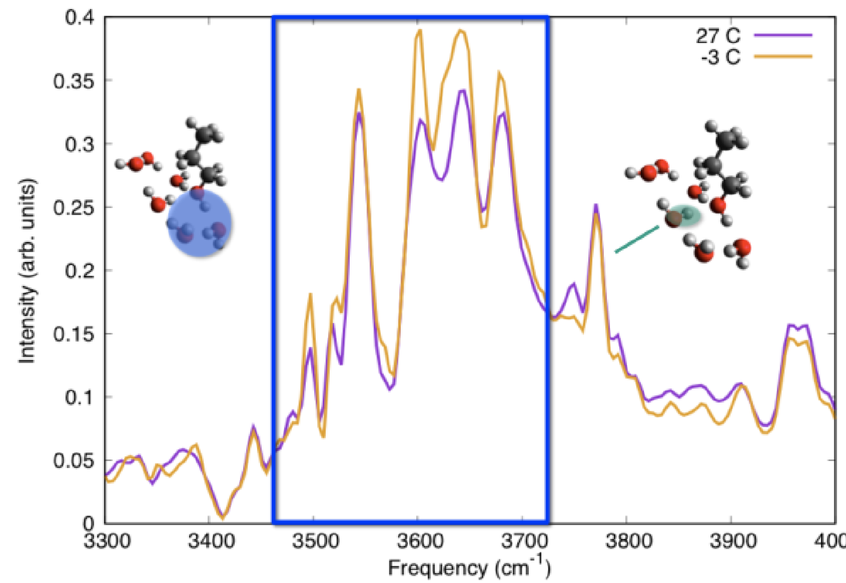

$S_1$

$S_0$

# Future goal of dynamics: predicting experimental observables





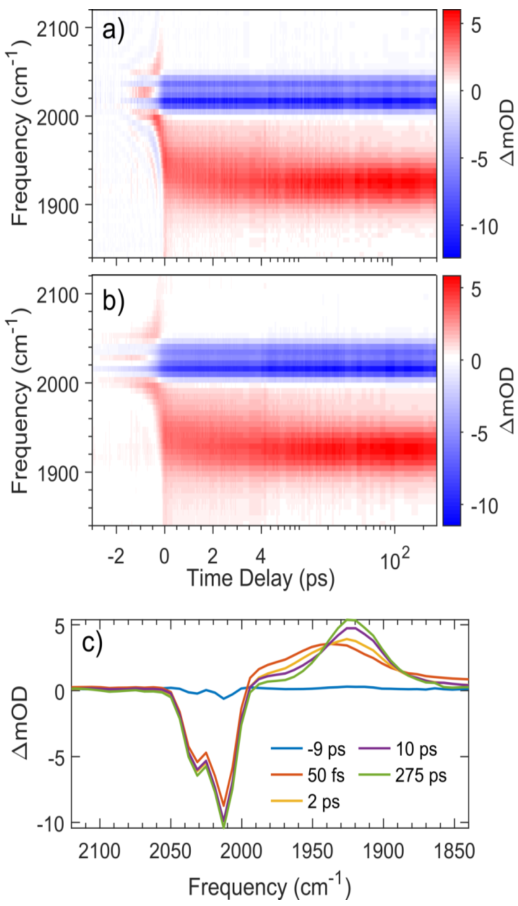

$$I(\omega) \propto \omega \int_{-\infty}^{\infty} dt\, e^{-i\omega t} \langle \vec{\mu}(0) \cdot \vec{\mu}(t) \rangle$$

- We can predict equilibrium spectra via AIMD
- Aim: create a windowing scheme to extract transient absorption spectra from excited state AIMD

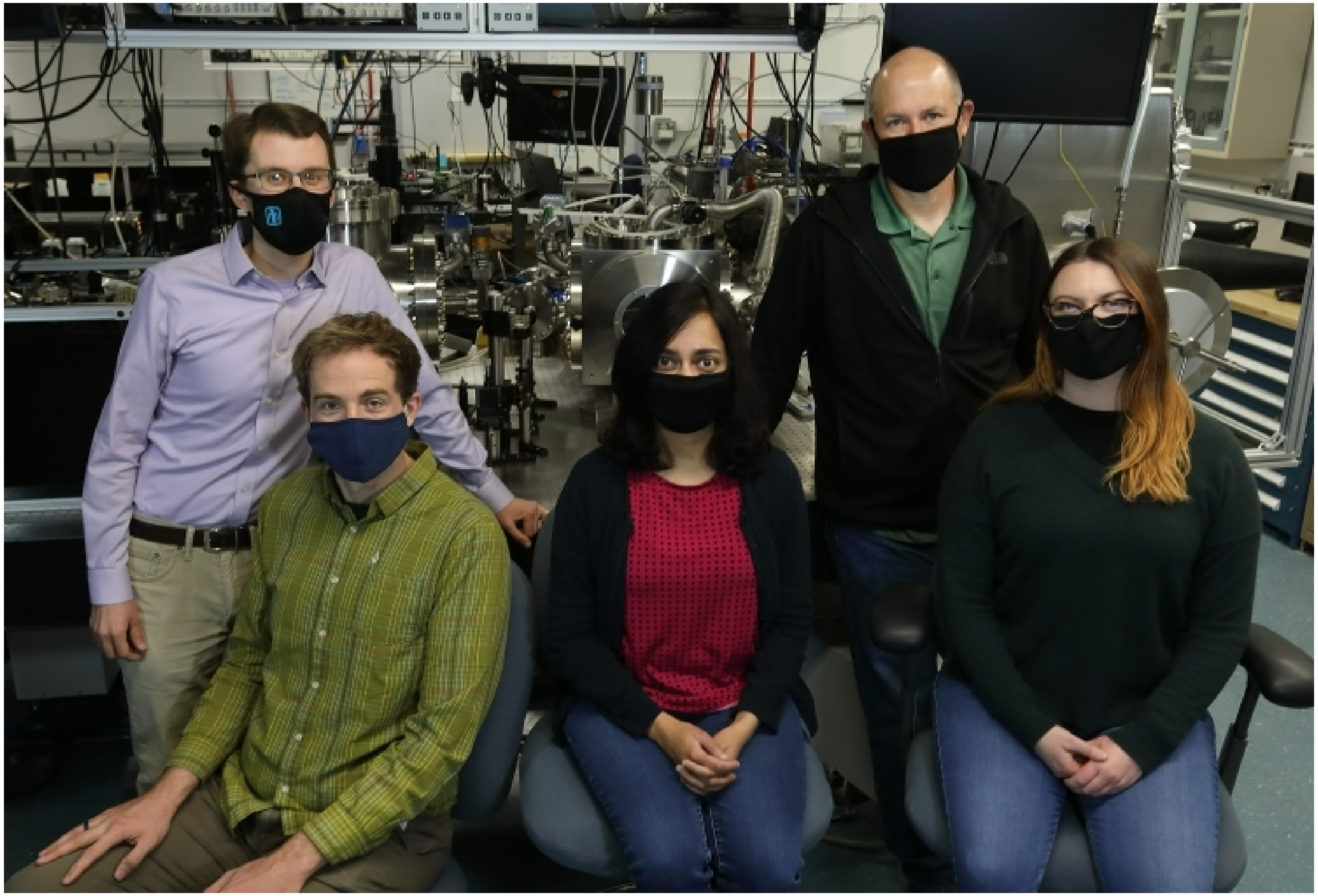
M.G. Vazquez de Vasquez, K.A. Carter-Fenk, L.M. McCaslin, E.E. Beasley, J.B. Simpson, H.C. Allen, “Inherent Interfacial Electric Fields and Fatty Alcohol and Acid Hydration as a Function of Temperature” (in review)

# Conclusions

- Experimental and theoretical confirmation of 600 fs dissociation timescale for $Ni(CO)_4 \rightarrow Ni(CO)_3 + CO$
- Potential energy surfaces indicate ***both concerted and sequential*** CO loss mechanisms
- Currently investigating role of triplet states
- Non-adiabatic dynamics: timescales, mechanisms, electronic character



# Acknowledgments



Top: Neil Cole-Filipiak, Paul Schrader
Bottom: Jan Troß, Krupa Ramasesha, Laura McCaslin

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