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Ultrafast Infrared Transient Absorption Spectroscopy of $Ni(CO)_4$ Photodissociation

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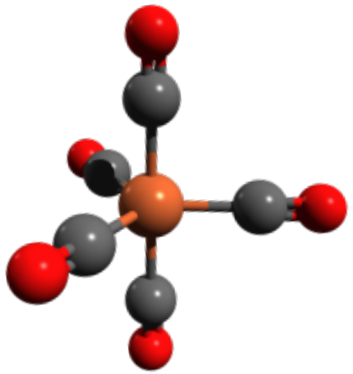
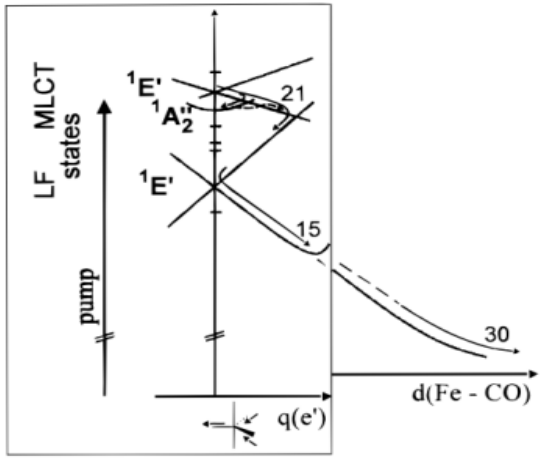
Metal Carbonyls

Family of transition metal carbonyls
- $Fe(CO)_5$, $Ni(CO)_4$, $W(CO)_6$, *etc.*

Models for ligand binding and catalysts

Typical electronic structure:
- bright MLCT ($\pi^*_{CO} \leftarrow$ d) states
- JT-distorted d$\leftarrow$d states





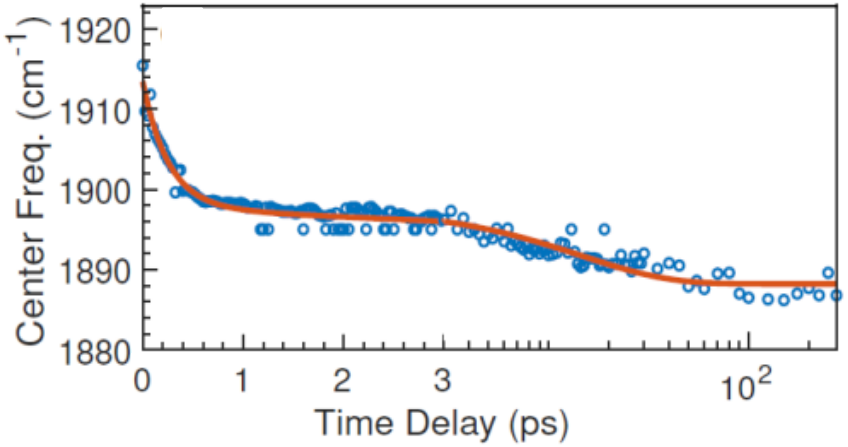
Ultrafast dissociation along repulsive electronic states

First CO lost in condensed phase followed by fast quenching

Different story in the gas phase...

Iron pentacarbonyl (IP) shows wavelength-dependent loss of multiple CO
- dissociations occur within excited singlet manifold
- TR-IY work at 267 nm showed sequential loss of two CO with τ <100 fs and ~3 ps

Recent work by our group at 267 nm and 200 nm
- use mid-IR as non-destructive probe
- IV



Leadbeater, Coord. Chem. Rev. **188**, 35 (1999)
Trushin *et al.*, JPCA **104**, 1997 (2000)

Cole-Filipiak *et al.*, JCP **154**, 134308 (2021)

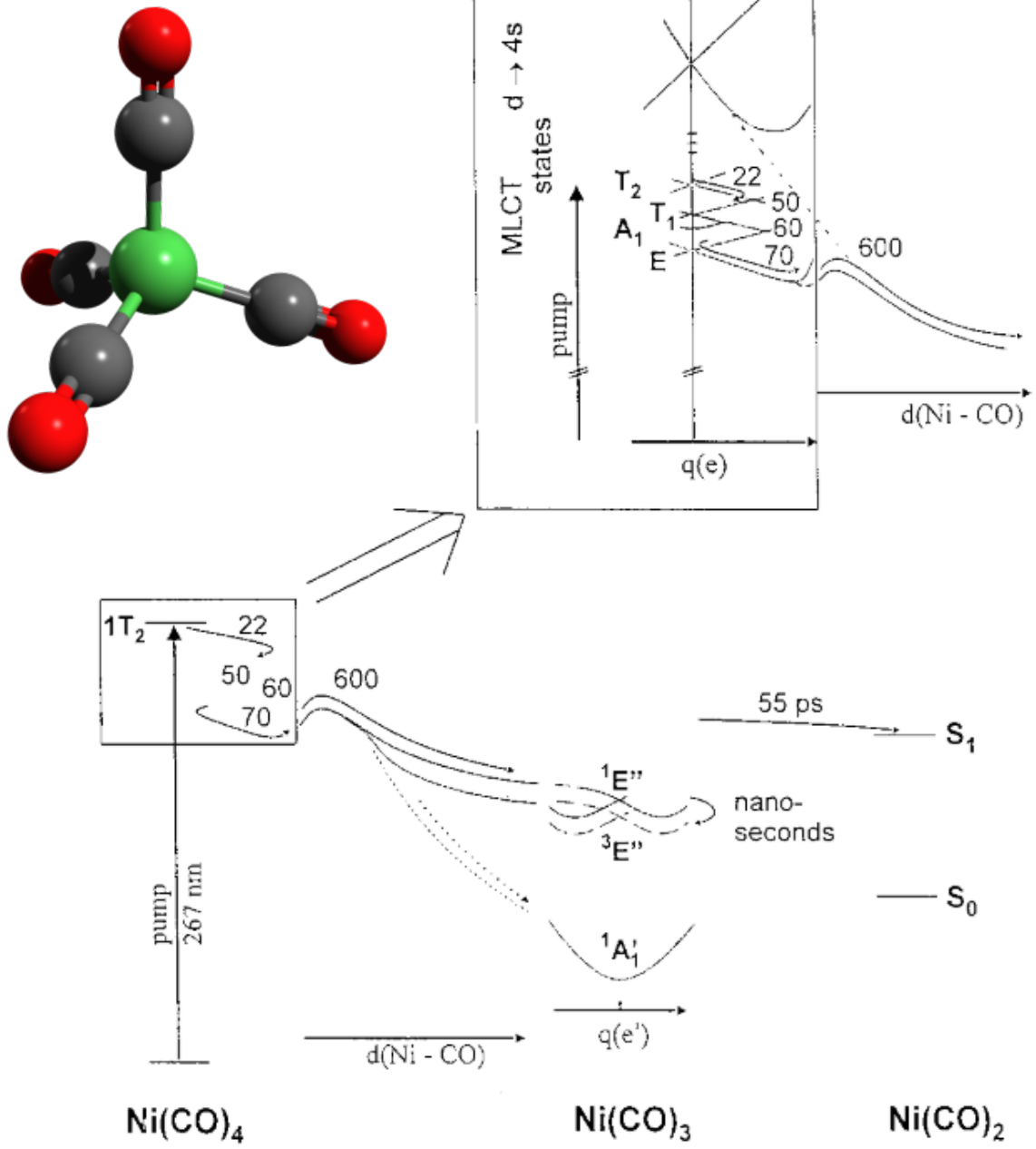
Nickel Tetracarbonyl

Different electronic structure full d shell
- MLCT crosses to repulsive 4s←d state
- Photoproducts show long lived luminescence

One previous ultrafast study using TR-IY at 267 nm
- Ultrafast IC from bright to repulsive states
- Excited state barrier to $Ni(CO)_3$ (S_1 and S_0)
- Pump-dependent time constant to $Ni(CO)_2$ (S_1)

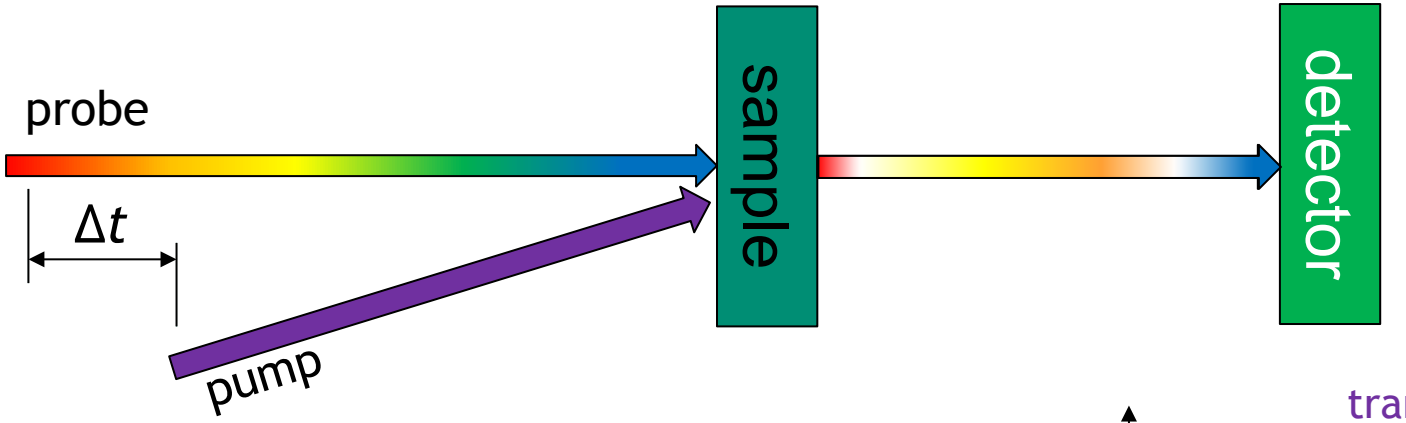
Sparse ~200 nm work using ns lasers
- Only two CO lost per 193 nm photon

Questions:
- Multiple electronic states of $Ni(CO)_3$?
- What are dynamics following 200 nm excitation?
- Why only two CO groups despite higher photon energies?



Reiner *et al.*, Chem. Phys. Lett. **195**, 169 (1992)
Schlenker *et al.*, JCP **93**, 7110 (1990)
Fuss *et al.*, JPCA **105**, 333 (2001)

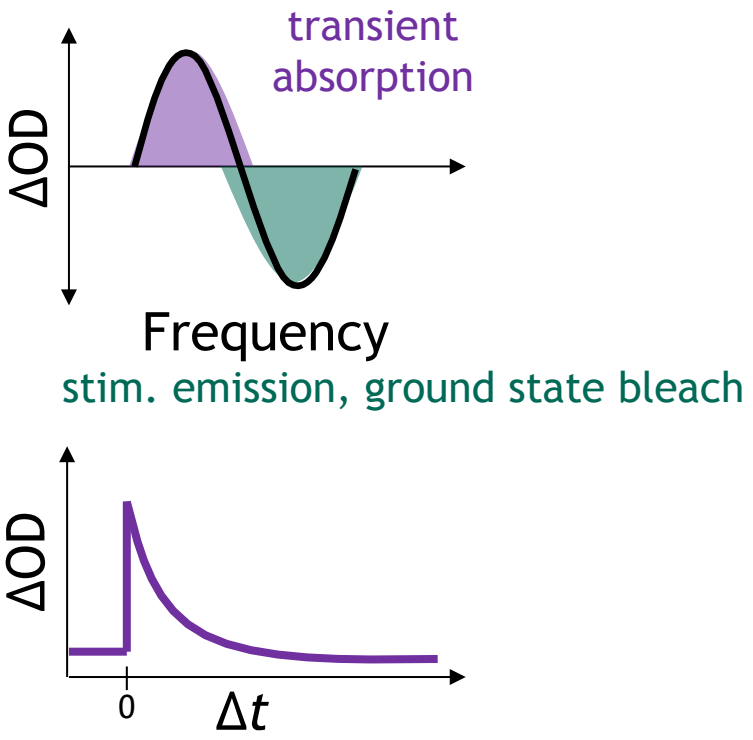
Ultrafast Transient Absorption Spectroscopy



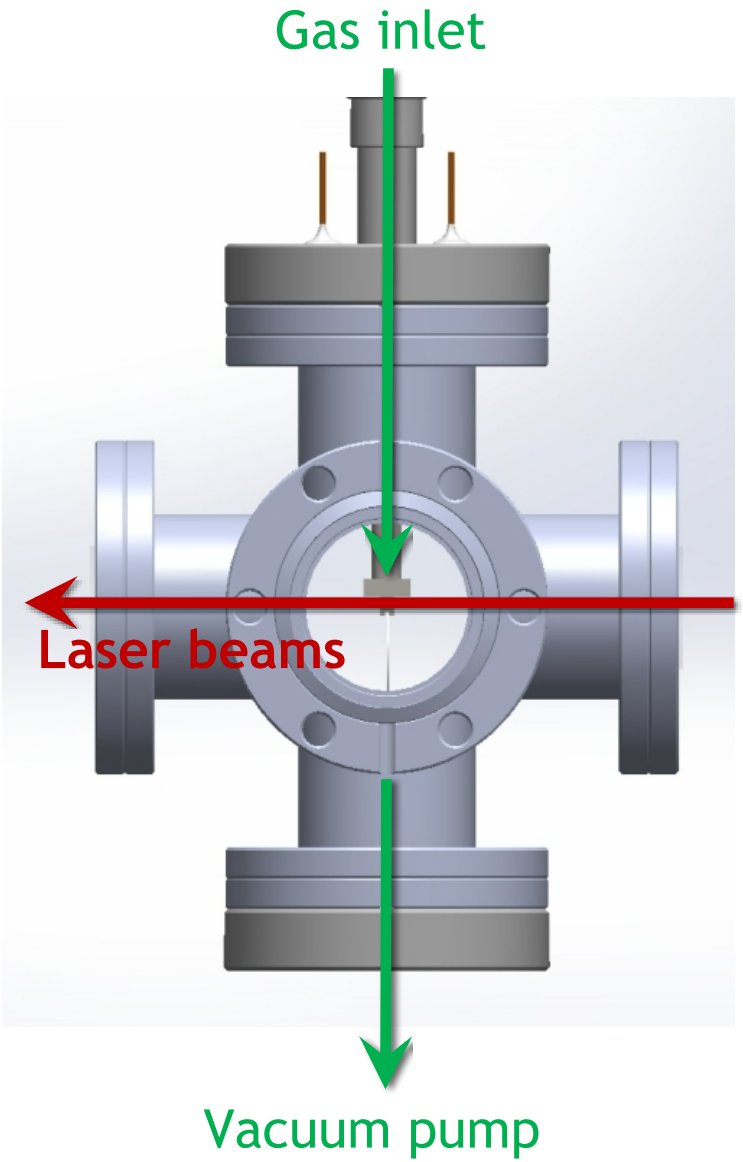
Pump
- THG from Ti:sapph, centered at 261 nm (4.7 eV)
- FHG, centered at 197 nm (6.3 eV)

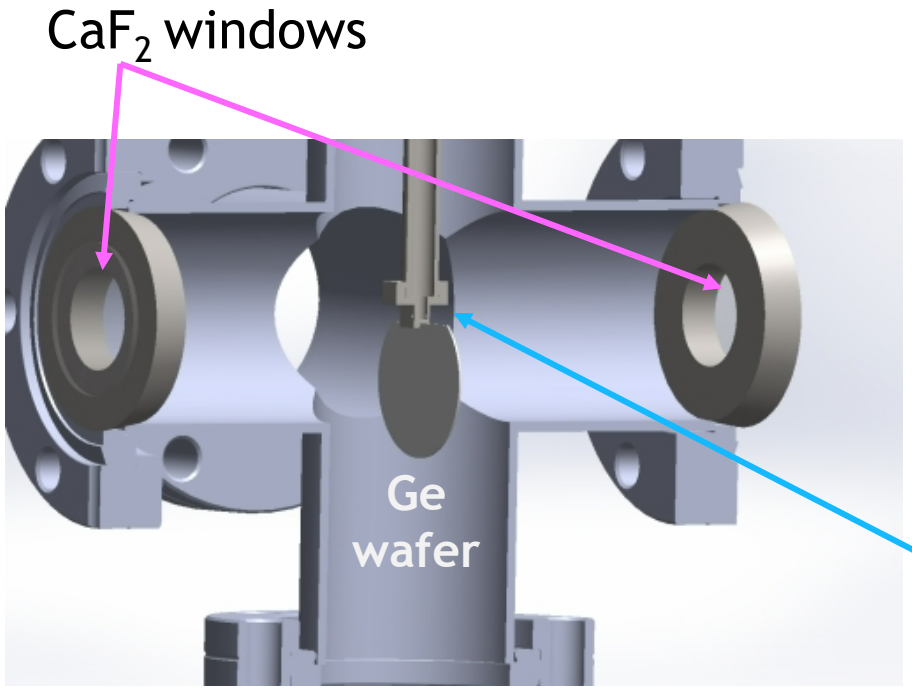
Probe
- DFG output of TOPAS centered at ~2000 cm^{-1}
- spectrum covers NT and $Ni(CO)_x$ photoproducts

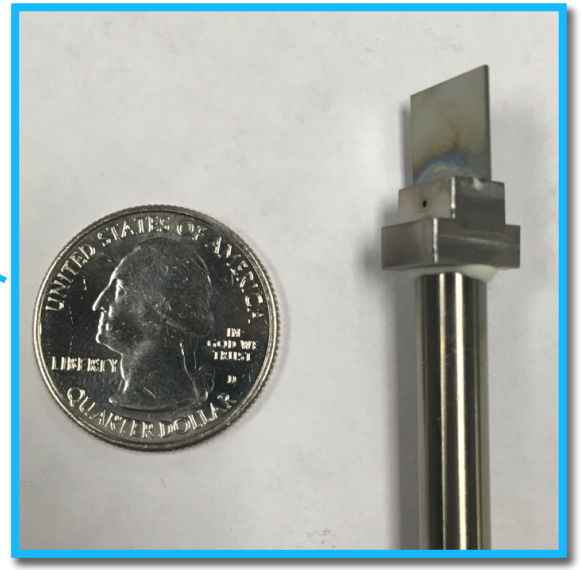
UV/mid-IR cross-correlation = 160–180 fs



Experimental Setup: Sample Cell

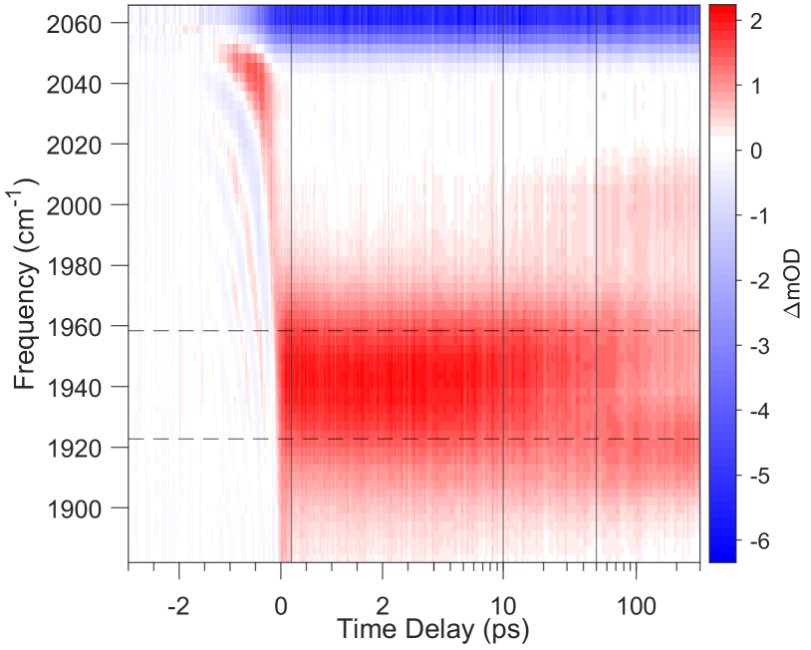


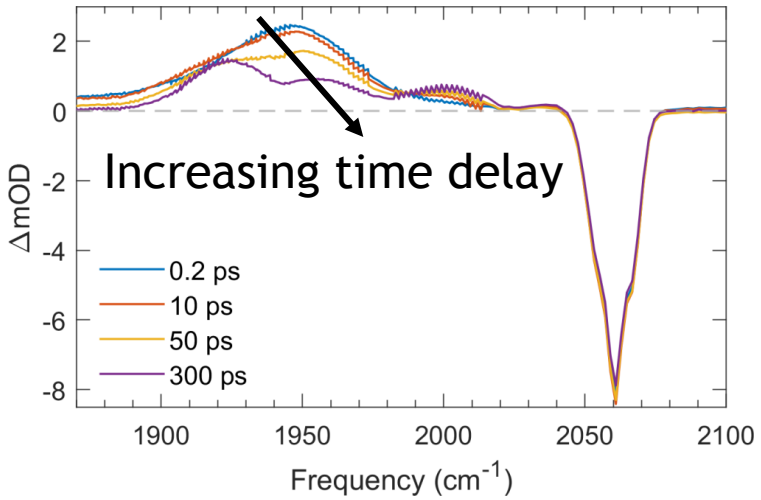




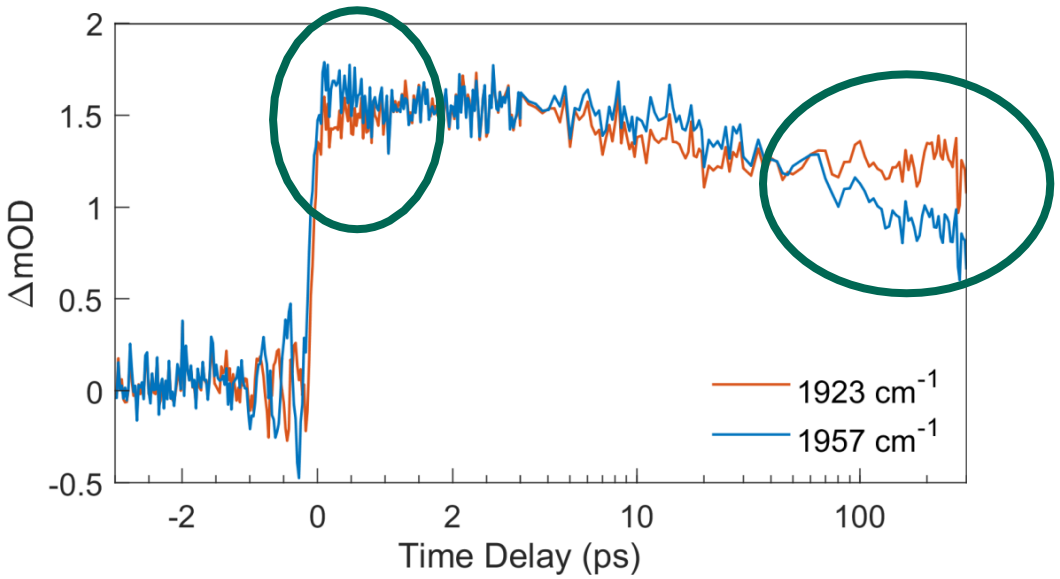
- windowless design at laser focus
- changeable cell with variable path lengths
- *in situ* UV/IR cross-correlation in Ge wafer

Photodissociation at 261 nm





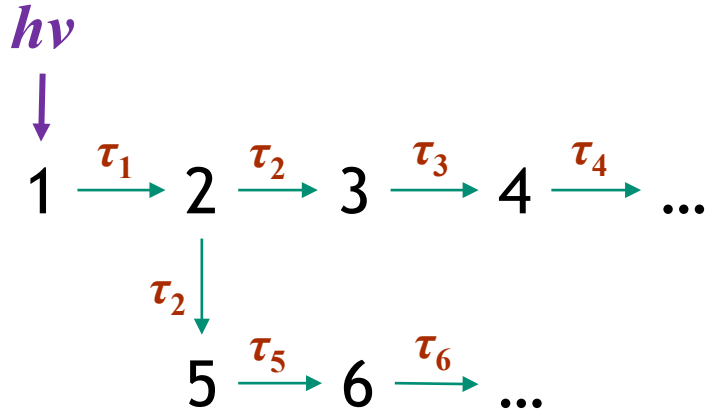
photoproduct red shift?
photoproduct decay?



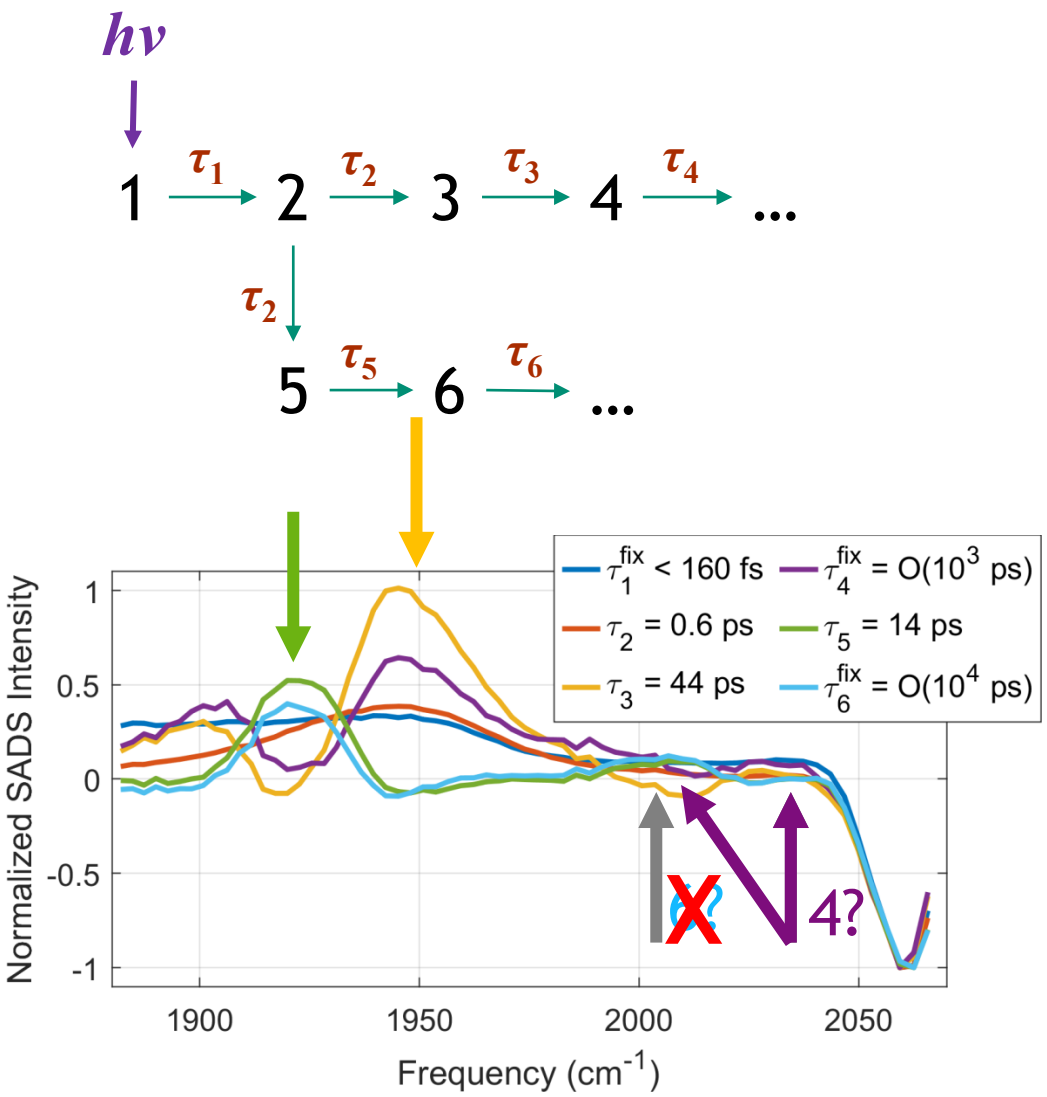
different final states

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

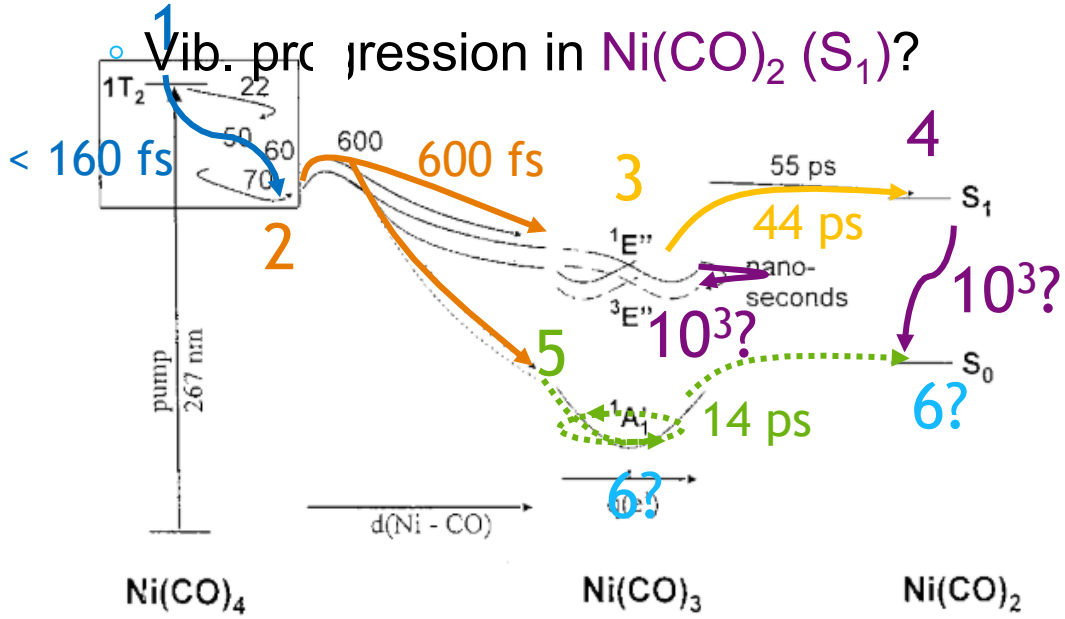
1923 cm^{-1}: <1 ps, 10 ps, 10^4 ps



Photodissociation at 261 nm



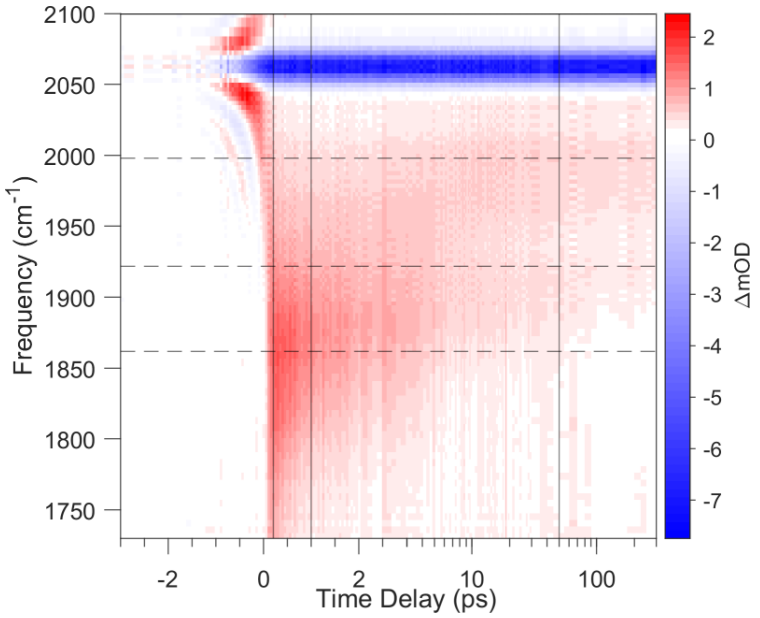
- $Ni(CO)_3$ (S_1) and $Ni(CO)_2$ (S_1) vib. freq.
  - Why is $Ni(CO)_2$ (S_1) higher freq.?
- $Ni(CO)_3$ (S_0) CO stretch Ar matrix = 2017 cm^{-1}
  - Suggests 6 quanta of excitation
- $Ni(CO)_3$ (S_0) at 2000 cm^{-1} doesn't make sense…
  - Vib. progression in $Ni(CO)_2$ (S_1)?



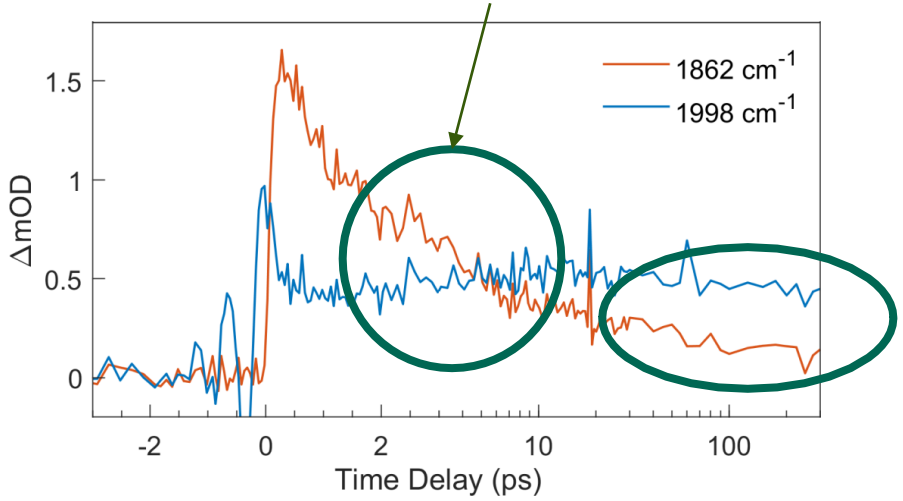
DeKock, Inorg. Chem. **10**, 1205 (1971)

Fuss *et al.*, JPCA **105**, 333 (2001)

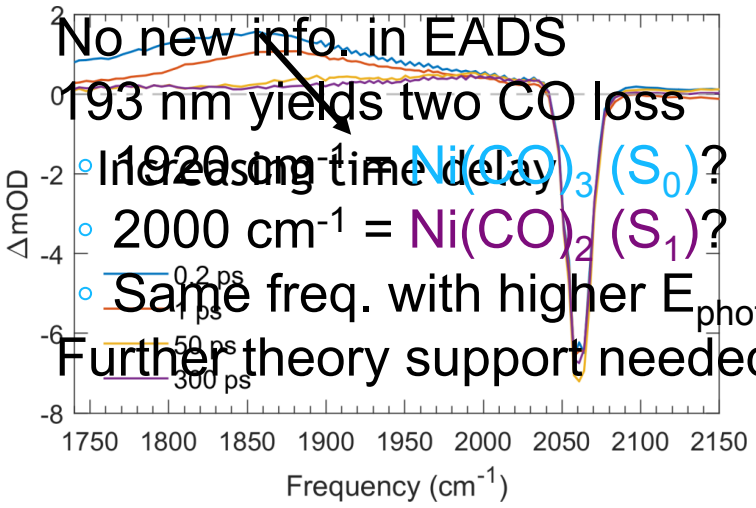
Photodissociation at 197 nm



matched growth/decay



same decay behavior



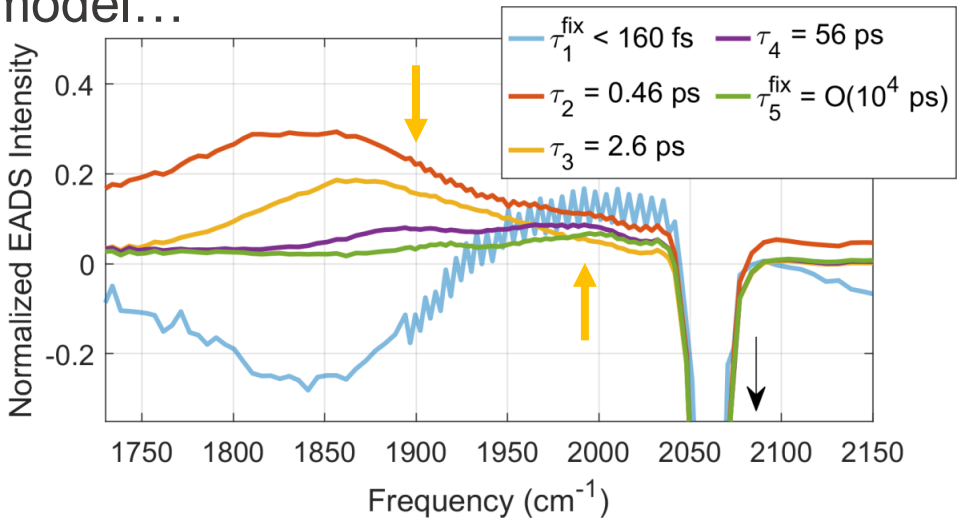
No new info. in EADS

193 nm yields two CO loss

- Increasing time delay 1920 cm^{-1} = $Ni(CO)_3$ (S_0)?
- 2000 cm^{-1} = $Ni(CO)_2$ (S_1)?
- Same freq. with higher E_{photon}?

Further theory support needed…

Similar analysis with sequential kinetic model…



Schlenker *et al.*, JCP **93**, 7110 (1990)

Conclusions and Future Work

Reproduce dynamics and time constants from previous 267 nm study
- Ultrafast dissociation of NT, followed by longer dissociation of $Ni(CO)_3$

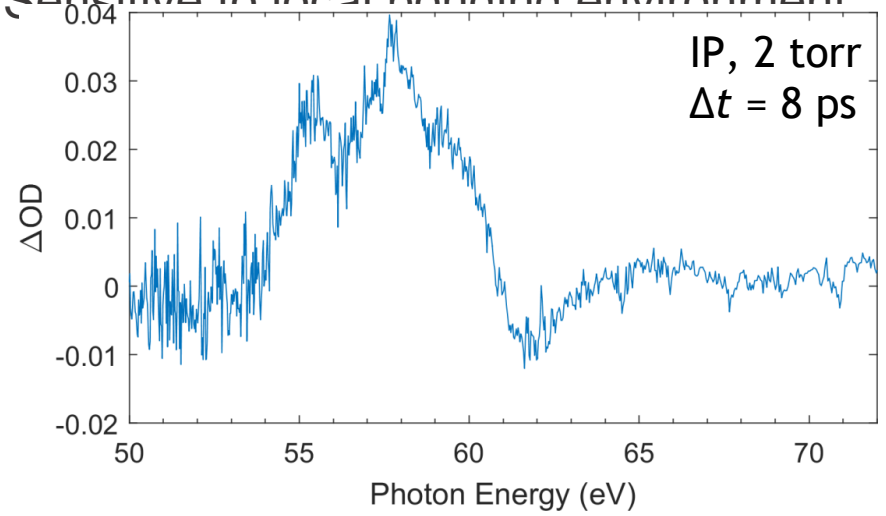
Evidence for additional decay pathway
- assigned as $Ni(CO)_3$ (S_0)

Vib. freq. of $Ni(CO)_2$ (S_1)?

First ultrafast study at 197 nm
- Fast initial IC
- Prompt dissociation within few ps
- Evidence for $Ni(CO)_3$ and $Ni(CO)_2$?
- Where is excess energy going?

Theory support
- excited state energies
- vibrational frequencies (of multiple electronic states)
- *ab initio* molecular dynamics?

XUV trans. abs. with newly commissioned set-up
- Follow metal 3p-to-valence transition energy
- Sensitive to local bonding environment



Acknowledgements

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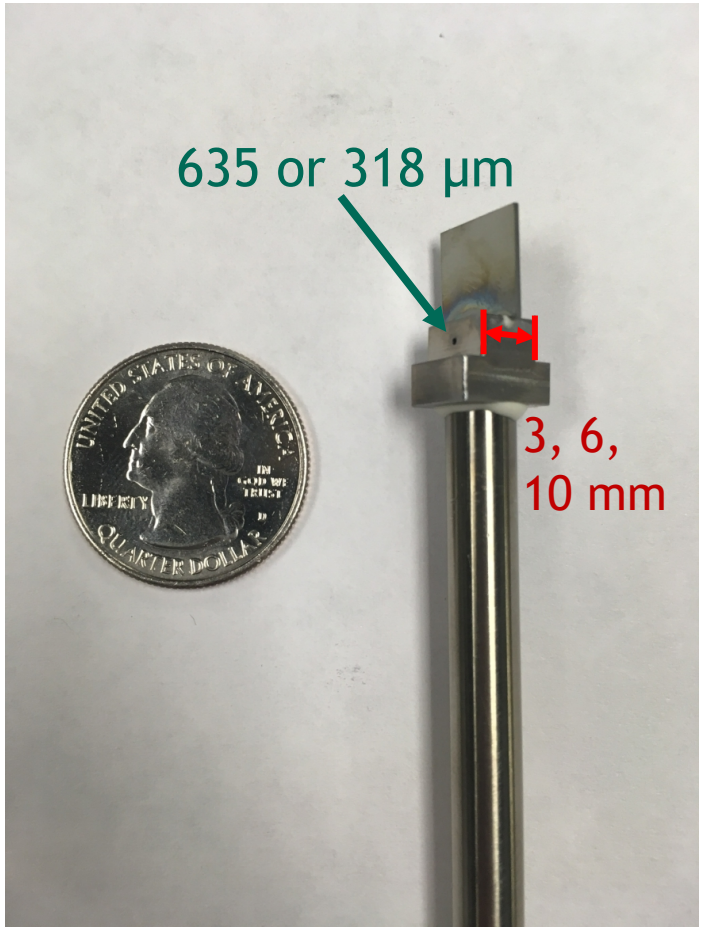
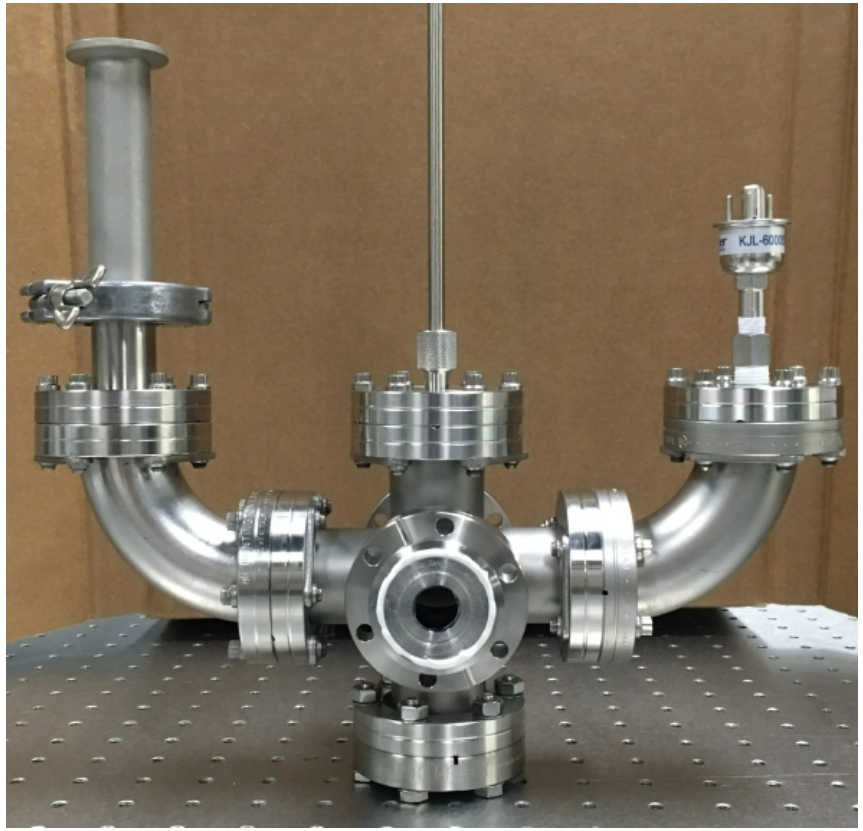
Krupa Ramasesha

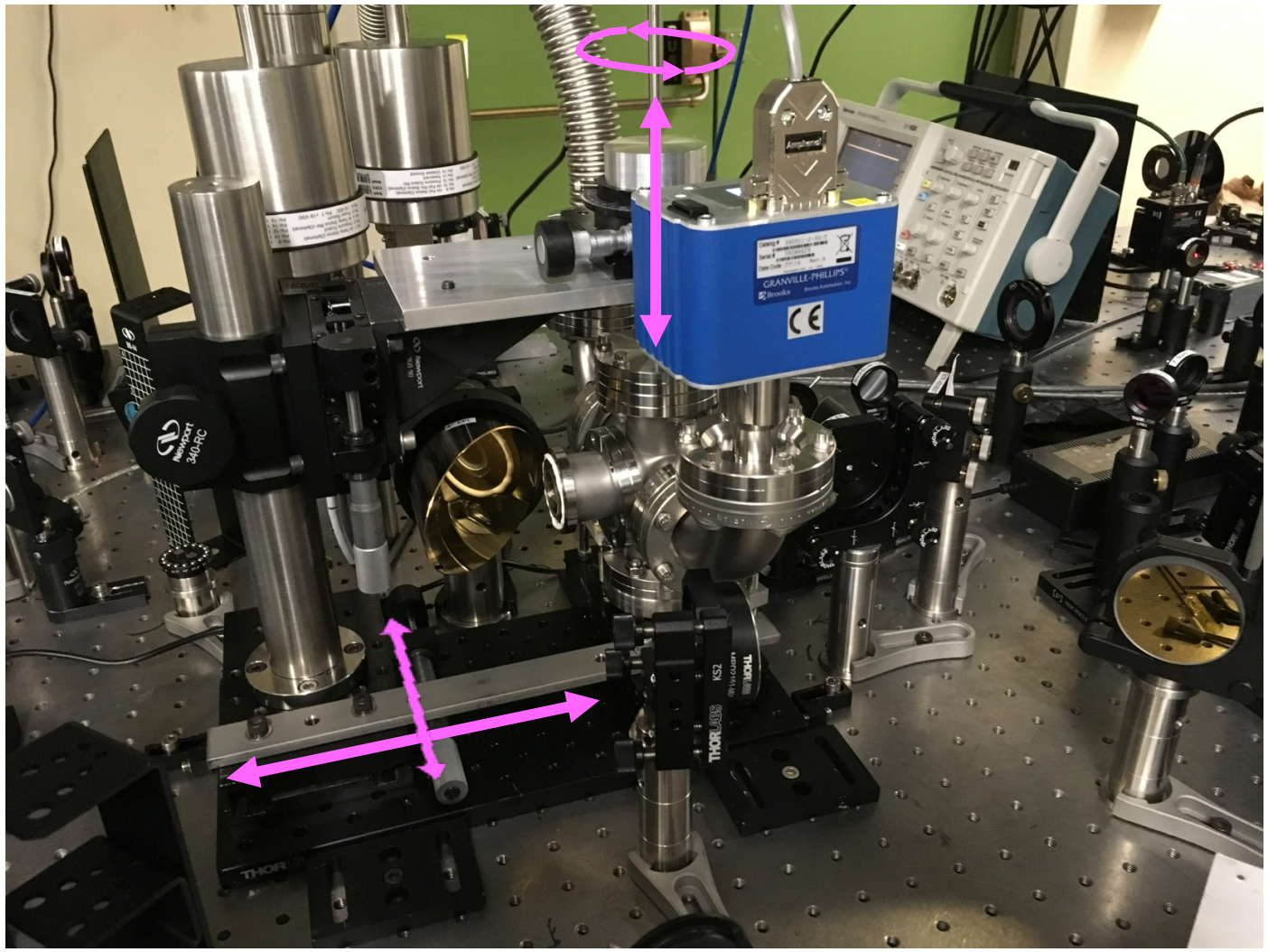
Questions?

Experimental Setup: Sample Cell



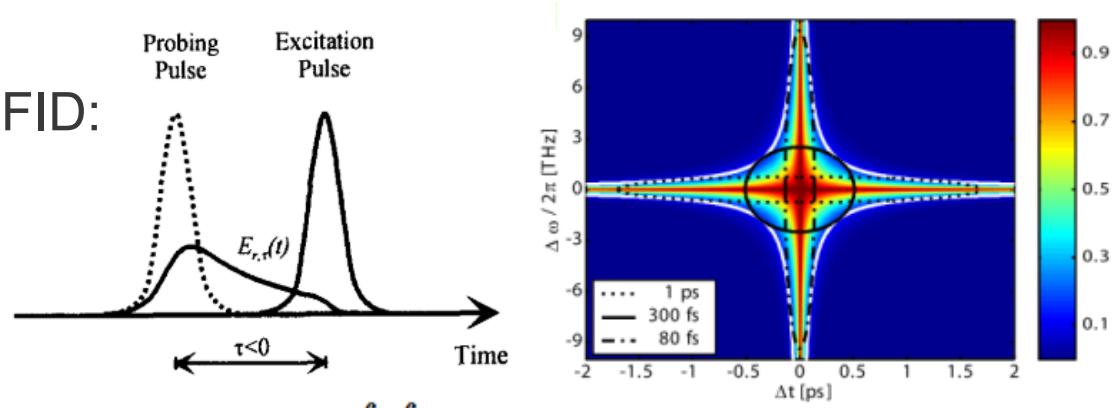


Experimental Setup: Sample Cell



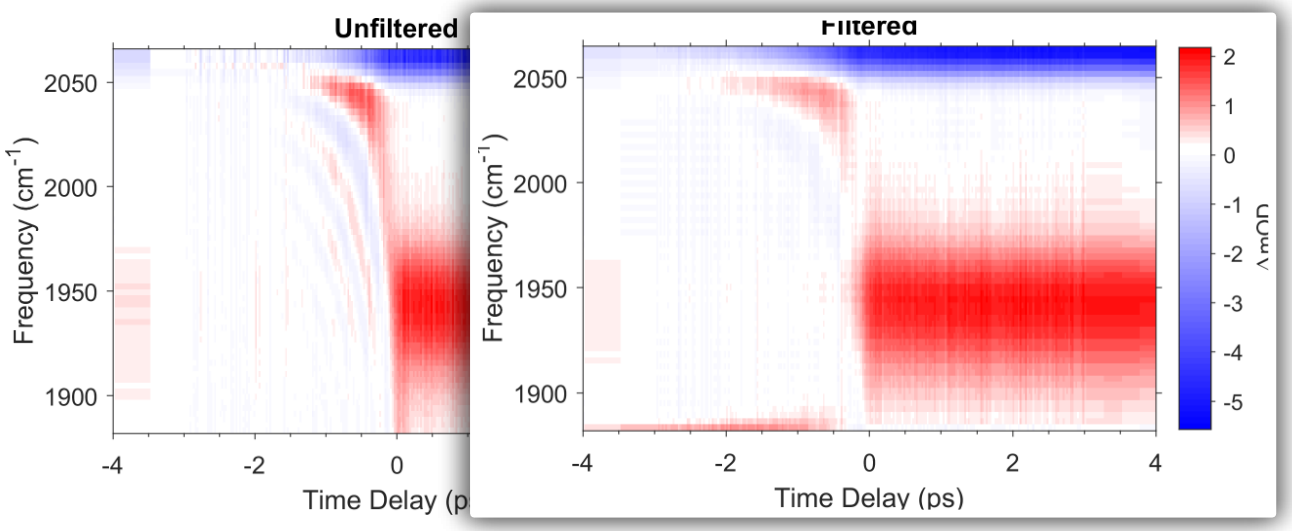
Perturbed Free-Induction Decay and Instrument Response Function

PFID:

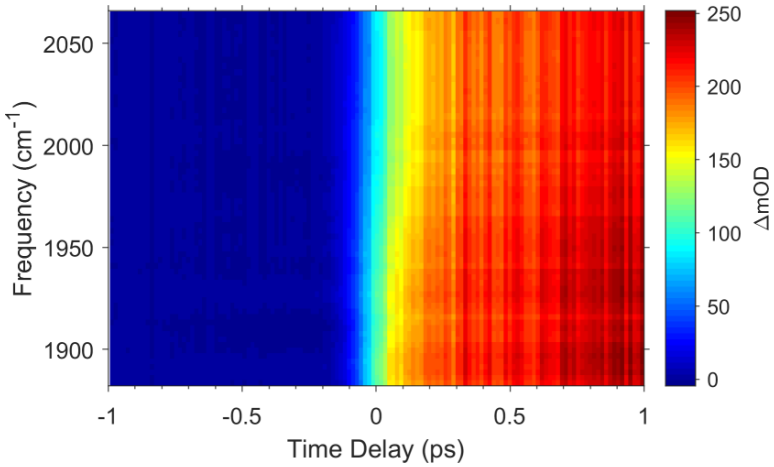


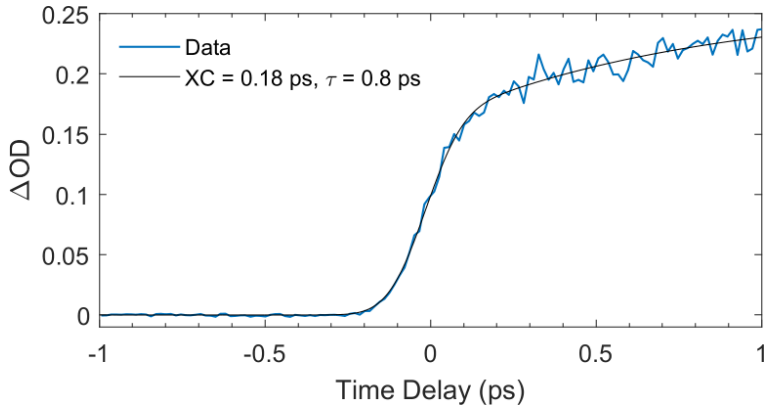
FFT: $\widehat{\Delta T_i}(\nu,\tau) = \int\int \Delta T_i(t,\omega)\exp\left[i(2\pi t\nu - 2\pi\omega\tau)\right]\mathrm{d}t\,\mathrm{d}\omega$

Filter: $\hat{f}(\nu,\tau) = \exp\left[-|\pi\nu t| + i(\pi\nu t)\right]$



IRF:





Hamm, Chem. Phys. **200**, 415 (1995)
Polack, Opt. Exp. **14**, 5823 (2006)

Energetics, Frequencies, and Excited States

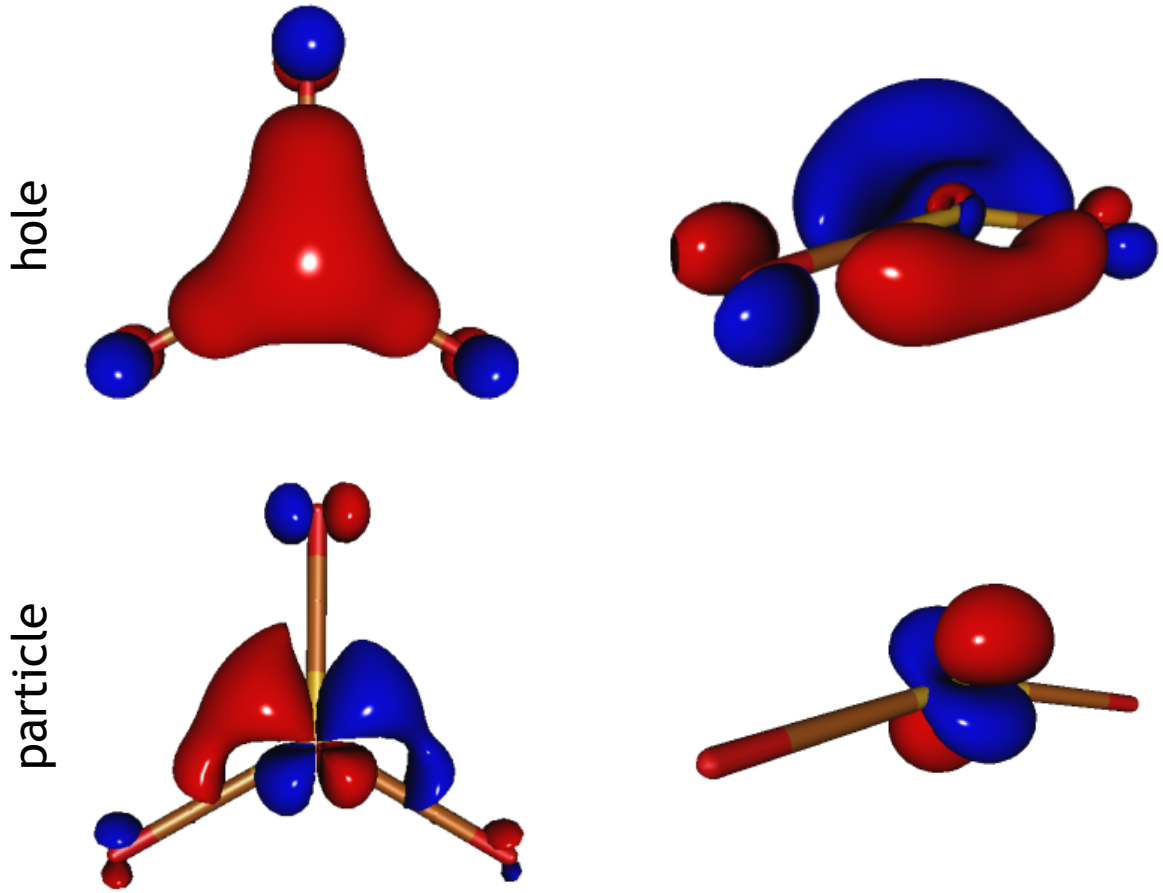
Bond dissociation energies (ground state)

- NT → $Ni(CO)_3$ + CO = 1.1 eV
- $Ni(CO)_3$ → $Ni(CO)_2$ + CO = 0.8 eV
- $Ni(CO)_2$ → NiCO + CO = 2.3 eV
- NiCO → Ni + CO = 1.3 eV

CO vibrational frequencies (ground state)

- NT = 2052 cm^{-1} (Ar matrix), 2061 cm^{-1} (jet)
- $Ni(CO)_3$ = 2017 cm^{-1} (Ar matrix)
- $Ni(CO)_2$ = 1967 cm^{-1} (Ar matrix)
- NiCO = 1996 cm^{-1} (Ar matrix), 2011 cm^{-1} (jet)

$S_1 \leftarrow S_0$ natural transition orbitals



Schlenker *et al.*, JCP **93**, 7110 (1990)

DeKock, Inorg. Chem. **10**, 1205 (1971)
Martinez and Morse, JCP **124**, 124316 (2006)
Asselin *et al.*, Mol. Phys. **106**, 1135 (2008)

CO Internal Energy and Product Branching

TABLE III. CO temperatures and weighing factors from the microcanonical statistical calculation.

Photolysis wavelength	Channel	Vibrational level	Temp. #1(K)	Temp. #2(K)
193 nm	excited	$v=0$	1600(0.50)	620(0.50)
	excited	$v=1$	1440(0.56)	260(0.44)
	excited	$v=2$	1260(1.0)	···
248 nm	excited(.75)	$v=0$	600(.600)	···
	ground(.25)	$v=0$	2600(.200)	1780(.200)
	excited(.05)	$v=1$	355(0.02)	···
	ground(.95)	$v=1$	2420(0.49)	1320(0.49)
	ground	$v=2$	2250(.50)	850(0.50)
308 nm	ground	$v=0$	1957(0.28)	1007(0.28)
	excited	$v=0$	280(0.43)	···

TABLE IV. $Ni(CO)_n$ fragment distributions from $Ni(CO)_4$ photolysis.

Photolysis wavelength	Excited state $Ni(CO)_3$	Excited state $Ni(CO)_2$	Ground state $Ni(CO)_3$	Ground state $Ni(CO)_2$
193 nm	···	100%	···	···
248 nm	70%	5%	···	25%
308 nm	60%	···	···	40%
450 nm	···	···	···	100%

Schlenker *et al*. JCP **93**, 7110 (1990)

Multiphoton dynamics

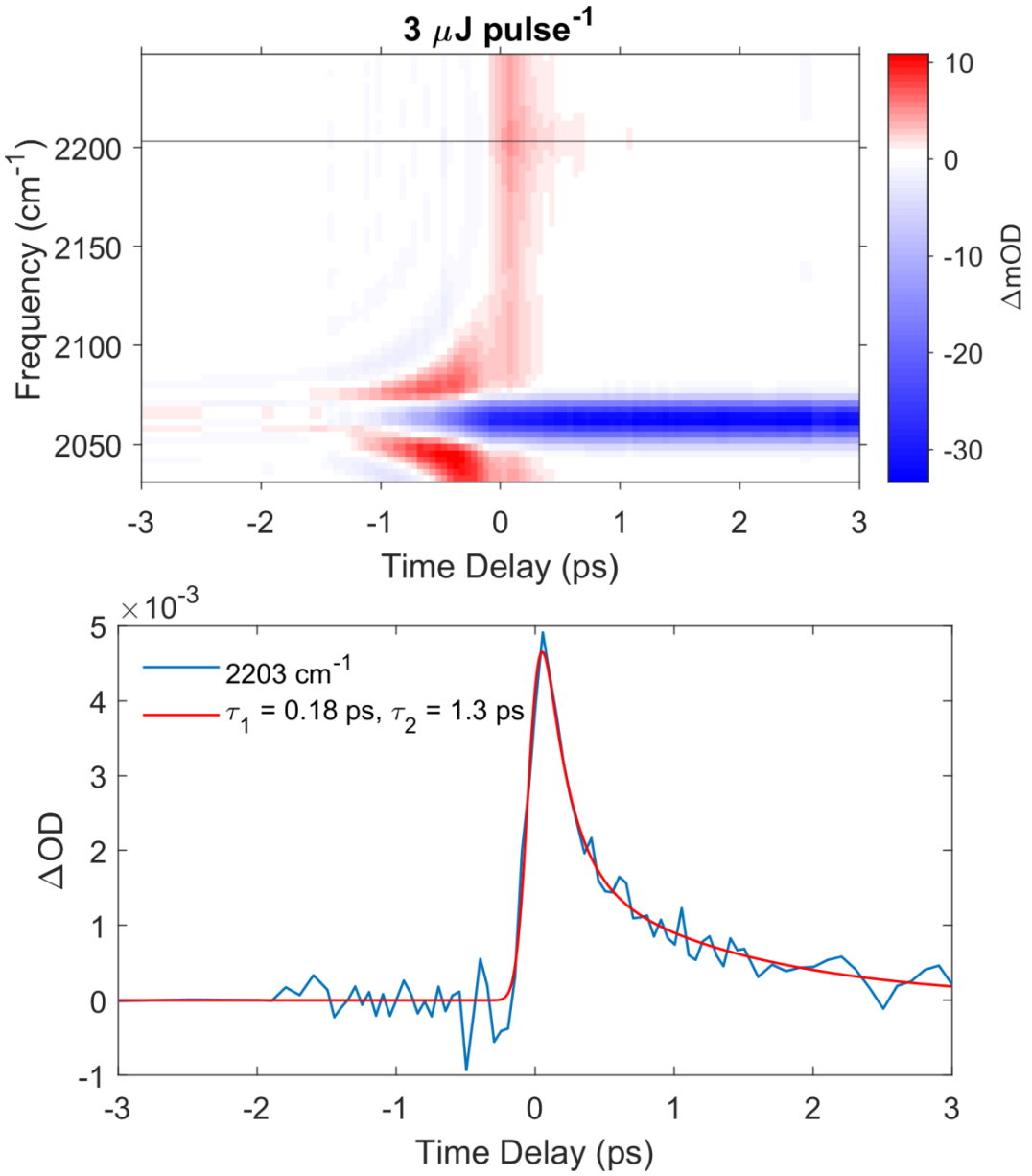
At 261 nm, additional peak at ~2200 cm^{-1}

Two-photon power dependence
- Likely corresponds to the dissociation time of $Ni(CO)_4^+$
- NT IE = 8.3 eV
- $NiC_3O_3^+$ AE ≈ 9 eV

Time constants inconsistent with one photon signal
- All features 1.0 ± 0.1 photons

Unlikely this contributes to previous (low power) or present results

No sign of two-photon behavior at 197 nm
- All features 1.1 ± 0.3 photons

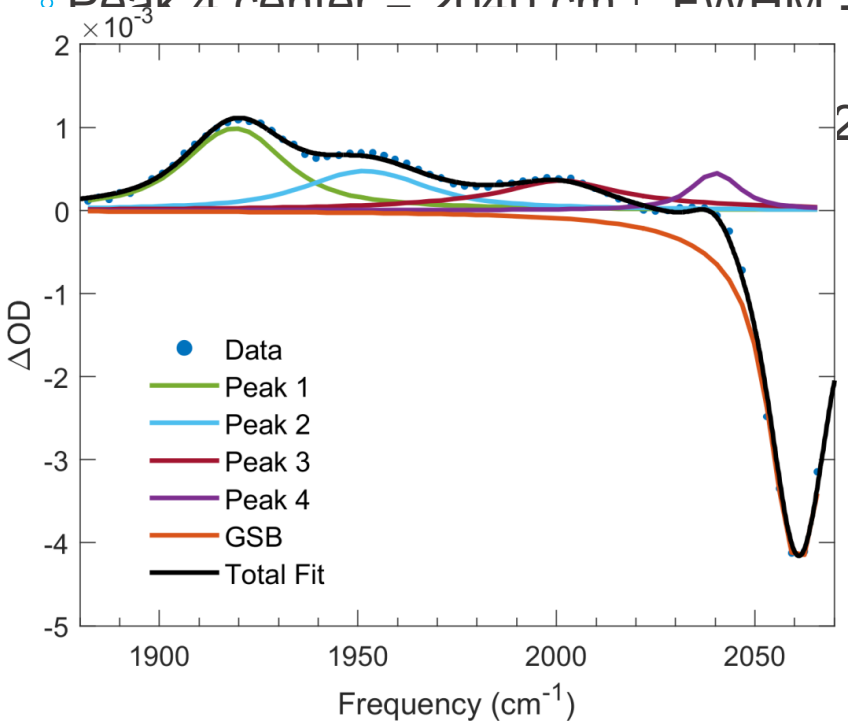


NIST Chemistry WebBook
Fuss *et al.*, JPCA **105**, 333 (2001)

Peak Lineshapes (pseudo-Voigt fits)

261 nm:

- Peak 1 center = 1919 cm^{-1}, FWHM = 49 cm^{-1}
- Peak 2 center = 1952 cm^{-1}, FWHM = 60 cm^{-1}
- Peak 3 center = 2001 cm^{-1}, FWHM = 62 cm^{-1}
- Peak 4 center = 2040 cm^{-1}, FWHM = 23.5 cm^{-1}



197 nm:

- Peak 1 center = 1900 cm^{-1}, FWHM = 282 cm^{-1}
- Peak 2 center = 2004 cm^{-1}, FWHM = 207 cm^{-1}
- GSB center = 2061 cm^{-1}, FWHM = 28 cm^{-1}