Monitoring Conical Intersections with Ultrafast X-Ray Spectroscopy – A Theoretical Perspective

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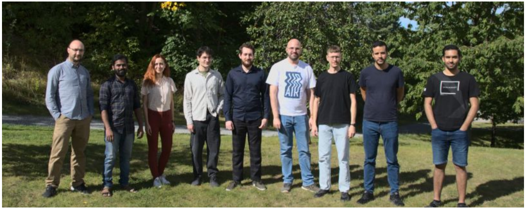
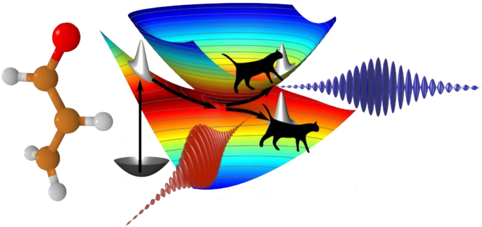
- **D. Jadoun, L. Restaino** R. Cuoto, B. Arslanoglu, T. Schnappinger, L. Borges, E. Davidsson, M. Gudem
- S. Mukamel, K. Bennett, Z. Zhang, K. Dorfmann

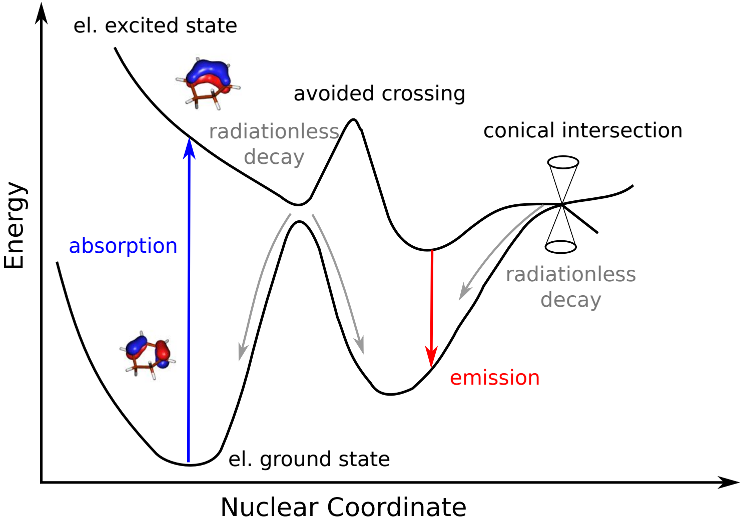


Overview



Overview – Non-adiabatic Dynamics in Molecules

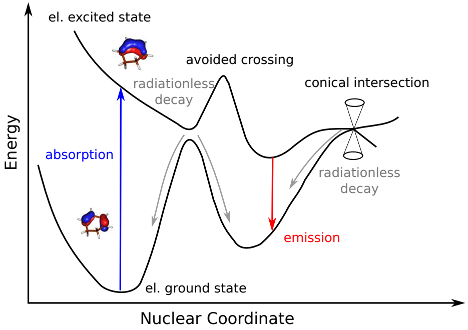
What Happens When a Molecule Absorbs a Photon?



Conical Intersection in Molecules

Abundant and Yet Elusive

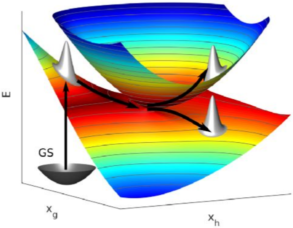
- Conical Intersections common in poly-atomic molecules
- Break down of the Born-Oppenheimer approximation
- Important in bio-molecules (vision, DNA damage/repair)
- Suncreens

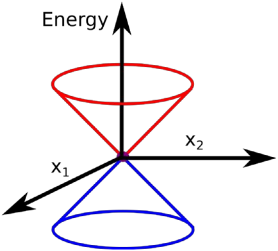


Conical Intersections

Nonadiabatic Dynamics with Degenerate Points

- Appear in poly-atomic Molecules
- Point of degeneracy (cone-shape, geometric phase)
- 2D branching space, $(N-2)$D seam space
- Break down of Born-Oppenheimer Approximation
- Nuclear and electronic DOF strongly mixed





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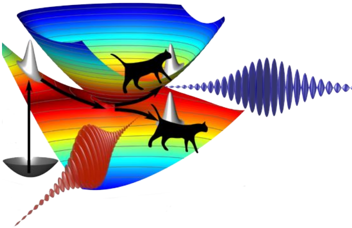
- Methods are based on pop. dynamics
- Change of vibrational frequencies
- Transient absorption
- Infrared/Optical pulses
- Challenge: rapidly decreasing energy gap
  $\rightarrow$ huge bandwidth needed
- Solution: X-ray/attosecond pulses
  (FEL, HHG sources)
- Detection via electronic coherences



herding Schrödinger's cats

M. Kowalewski et al., "Simulating Coherent Multidimensional Spectroscopy of Non-adiabatic Molecular Processes: From the Infrared to the X-Ray Regime", Chem. Rev., **117**, 12165 (2017).

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Overview - Techniques

Detecting conical intersections with XUV/X-Rays

- Transient absorption: easy to measure?
- Spontaneous emission: more information, harder to measure?
- Raman spectroscopy: CoIn fingerprints, not realized yet.
- Photoelectron spectroscopy: different selection rules.
- Time resolved diffraction: spatial information!
- Multidimensional HHG spectroscopy.

S. Jiang, M. Kowalewski, K. E. Dorfman, Opt. Express, 24, 4746 (2021).
M. Kowalewski, K. Bennett, and S. Mukamel, Struct. Dynam., **4**, 054101 (2017).
K. Bennett, M. Kowalewski, et al., Proc. Natl. Acad. Soc. USA, **115**, 6538 (2018).

T. Schnappinger, et al. Chem. Comm., **58**, 12763 (2022).

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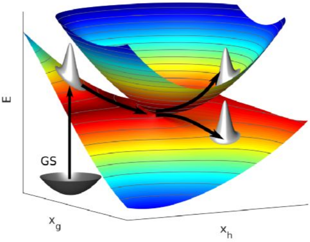
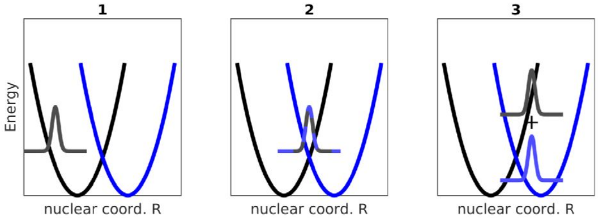
Detecting Electronic Coherences

The finger print of conical intersections

- Pump creates a wave packet
- Wave packet splits at CoIn
- Electronic super position
- $\rho_{ge} = \int \mathrm{d}R \Psi_g^*(R)\Psi_e(R)$





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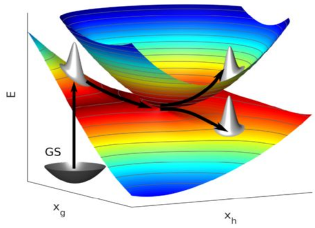
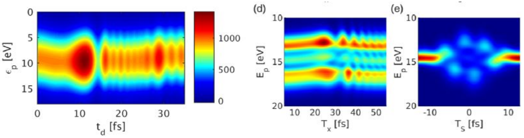
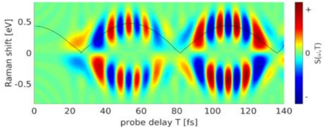
Overview: Detecting Electronic Coherences



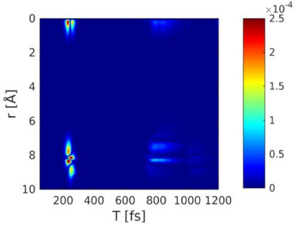
Time resolved photoelectron spectroscopy



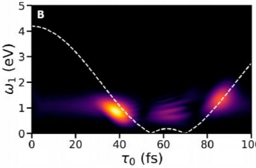
X-Ray Raman



Time resolved diffraction



2D-Dimensional techniques



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Different Spectroscopic Techniques

Probing different properties

- Time resolved photoelectron spectroscopy
  → Resolve coherent oscillations
  → Not tied to optical selection rules.
- X-ray Raman
  → Probe polarizability
  → Resolve energy gap directly
- Time resolved diffraction
  → Measure transition densities
  → Access location of coherence creation
- 2D-techiques
  → Extra information
  → Bypass time-bandwidth limit

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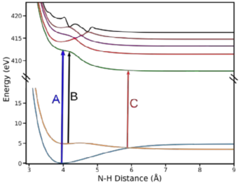
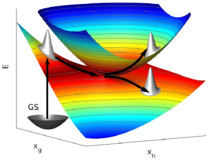
Theoretical Methods

Typical workflow

1. Quantum chemistry → Get potential energy surfaces



2. Wave packet dynamics → Time evolution of nuclei + el. states



3. Time Dependent Perturbation theory → Spectra
   Correlation functions: $\langle \hat{\mu}_{\mathbf{p}}(t')\hat{\mu}^{\dagger}_{\mathbf{p}}(t)\rangle$

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Wave Packet Dynamics

Coupled nuclear + electronic time evolution

- Reduced nuclear coordiantes
  $\rightarrow$ important molecular coordinates
  (e.g. bond-lengths).
- Represent nuclear WF in realspace.
- Solve TDSE:

$$i\frac{\partial}{\partial t}\begin{pmatrix}\chi_1^N\\ \chi_2^N\end{pmatrix} = \left[\begin{pmatrix}\hat{T}_N + \tau_{11} & \tau_{12}\\ -\tau_{12} & \hat{T}_N + \tau_{22}\end{pmatrix} + \begin{pmatrix}E_1 & 0\\ 0 & E_2\end{pmatrix}\right]\cdot\begin{pmatrix}\chi_1^N\\ \chi_2^N\end{pmatrix}$$

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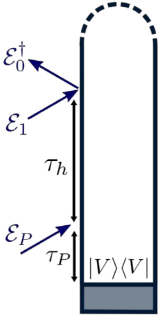
Time Dependent Perturbation Theory

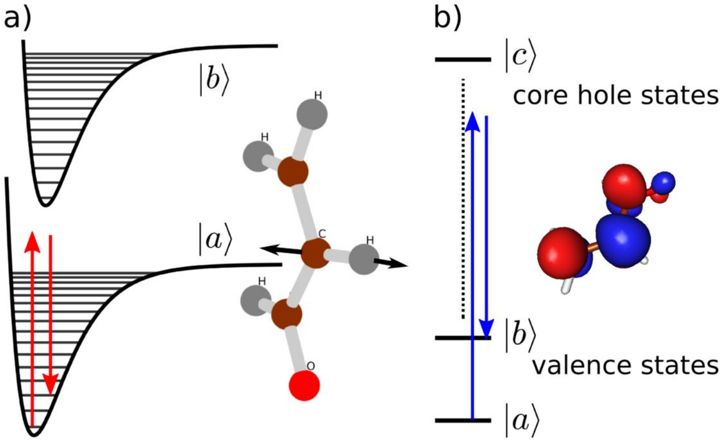
Ultrafast crash course

- Develop in order of the electric field
- Correllation functions
  e.g.:
  $\langle\Psi_0|U^\dagger(\tau_h+\tau_P)\alpha_{12}U(\tau_h)\mu_P U(\tau_P)|\Psi_0\rangle$
- Diagrams
  $\rightarrow$ represent correlation function
  $\rightarrow$ time flows:
  forward on the left (ket),
  backward on the right (bra)
  $\rightarrow$ arrows: interaction with field.
  excite/de-excite,
  resonant μ
  off-resoant α



Raman

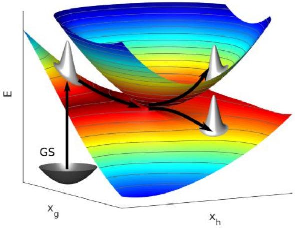
From the optical to X-rays



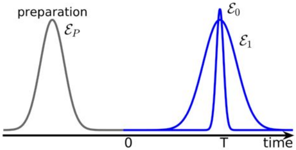
TRUECARS

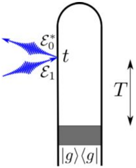
Transient Redistribution of Ultrafast Electronic Coherences Attosecond Raman Spectr.

- Linear Raman probe
- Homodyne detection
- Sensitive to coherences
- Off-resonant
- Hybrid probe



$$S(\omega, T) = 2\Im \int_{-\infty}^{+\infty} \mathrm{d}t \, e^{i\omega(t-T)} \mathcal{E}_0^*(\omega)\mathcal{E}_1(t-T) \times \langle\psi(t)|\hat{\alpha}|\psi(t)\rangle$$





M. Kowalewski, K. Bennett, K. E. Dorfman, and S. Mukamel, Phys. Rev. Lett., **115**, 193003 (2015).

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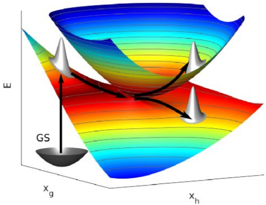
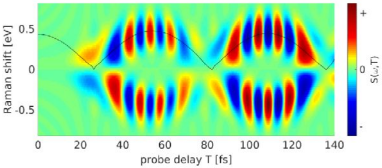
TRUECARS

Map of a conical intersection

- Sensitive to coherences
- Raman shift → energy separation

$$S(\omega, T) = 2\Im \int_{-\infty}^{+\infty} \mathrm{d}t\, e^{i\omega(t-T)} \mathcal{E}_0^*(\omega)\mathcal{E}_1(t - T) \times \langle \psi(t)|\hat{\alpha}|\psi(t)\rangle$$





M. Kowalewski, K. Bennett, K. E. Dorfman, and S. Mukamel, Phys. Rev. Lett., **115**, 193003 (2015).

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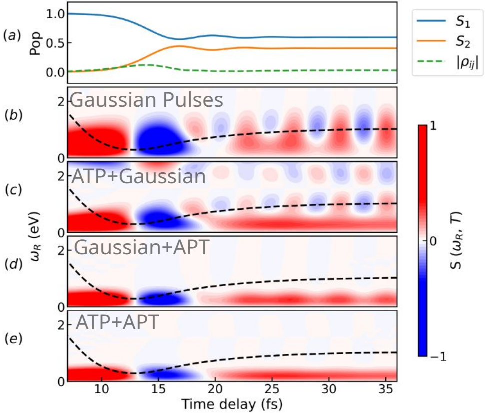
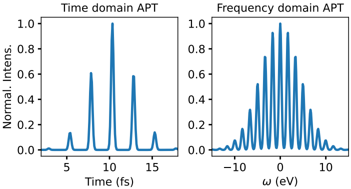
TRUECARS with attosecond pulse trains

An easier pulse source?

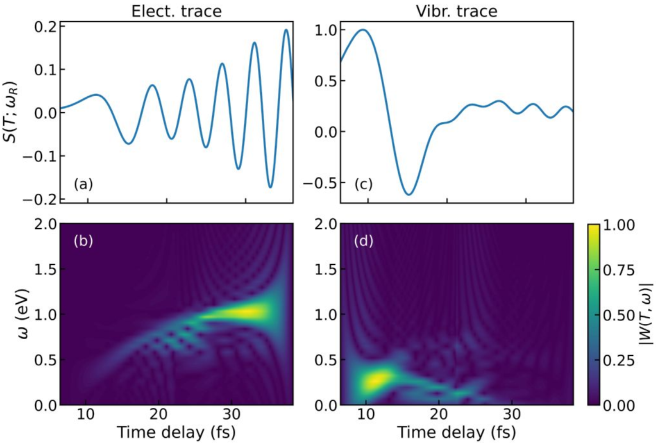




L. Restaino, D. Jadoun, M. Kowalewski, Struct. Dynam., **9**, 034101 (2022).

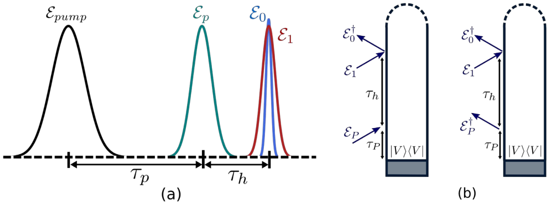
TRUECARS with attosecond pulse trains

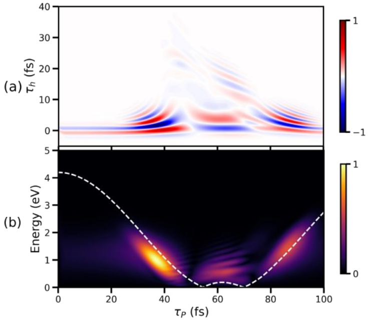
Extracting the energy gap – Wigner-Hilbert transform



Pumped Coherences, Raman Detected

TRUECARS extended





- Add IR/VIS/UV pump/dump
- Map region **before** CoIn
- Remove vibrational background
- Less dependent on gradients

D. Jadoun, M. Kowalewski, Ultrafast Science, **2022**, 0003 (2022)

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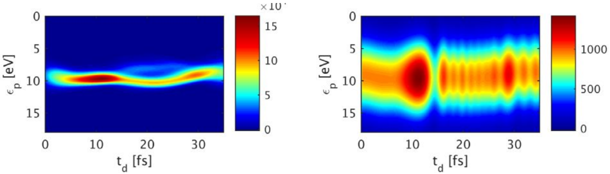
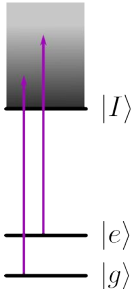
Time-Resolved Photoelectron Spectroscopy

Attosecond XUV pulses

- Linear probe
- Can track coherences
- Interference $\rightarrow$ oscillations
- Broadband pulse
- Fourier limited





$$S_e(\varepsilon_{\mathbf{p}}, t_d) = \int dt \int dt' \, \theta(t - t') E_x(t) E_x(t') \left(\langle \hat{\mu}_{\mathbf{p}}(t) \hat{\mu}^{\dagger}_{\mathbf{p}}(t') \rangle_0 + \langle \hat{\mu}_{\mathbf{p}}(t') \hat{\mu}^{\dagger}_{\mathbf{p}}(t) \rangle_0 \right)$$

K. Bennett, M. Kowalewski, and S. Mukamel, J. Chem. Theory Comput., **12**, 740 (2016).

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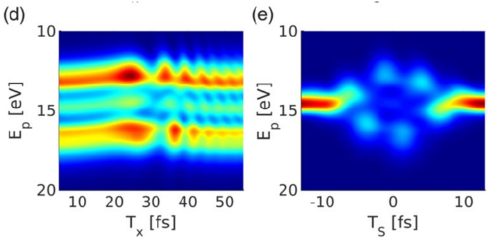
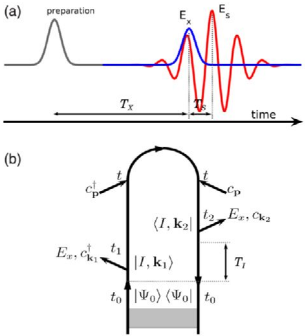
Streaking of Photoelectrons

Politely ask your photoelectrons for the molecular coherence

- IR streaking field
- 2D technique
- No sub-fs pulse needed





M. Kowalewksi, K. Bennett, J. R. Rouxel, and S. Mukamel , Phys. Rev. Lett., **117**, 043201 (2016).

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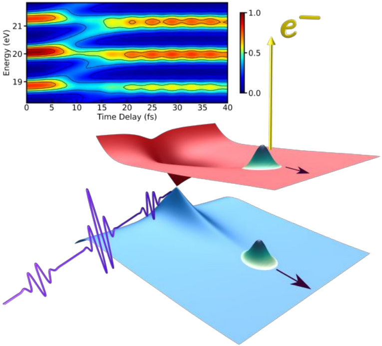
Photoelectron Spectroscopy with Attosecond Pulse Trains

Utilize Pulse Sources

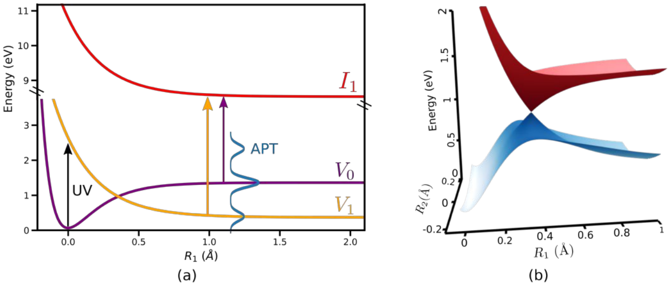


- Use attosecond pulse trains
- Create additional interference

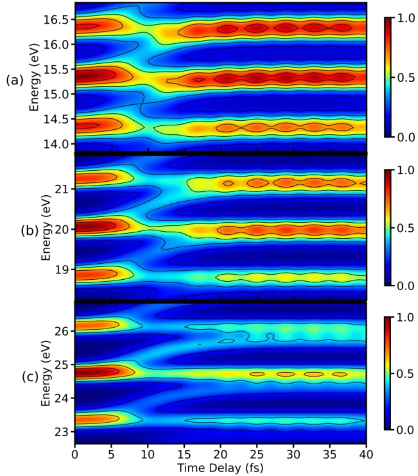
D. Jadoun, M. Kowalewski, J. Phys. Chem. Lett., **12**, 8103 (2021).

Photoelectron Spectroscopy with Attosecond Pulse Trains

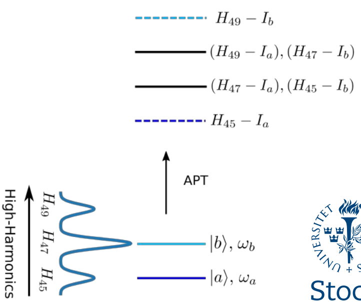
The scheme



- Use attosecond pulse train directly
- Match high-harmonic spacing to molecule
- Track coherence + resolve states



- Vary fundamental freq.: 0.5, 0.6, 0.7 eV
- Harmonics create overlapping replica



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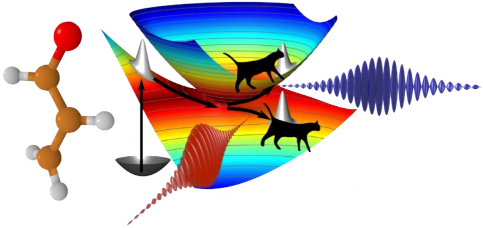
Summary

- Soft X-Rays and sub-femtosecond pulses are great for conical intersections
- Detect electronic coherences
- FELs and HHG sources allow for a broad range of different experiments



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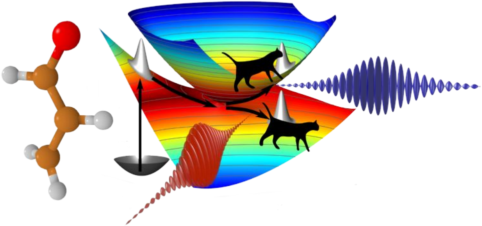
Outlook

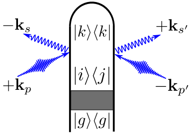
- Ultra-fast diffraction: Track transition densities?
- Non-linear probes?
- Entangled photons possible?

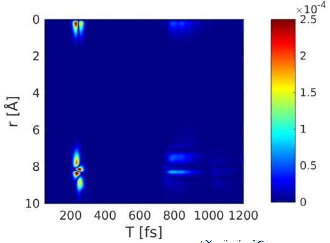


Time Resolved Diffraction

Going beyond spectroscopy: spatial information

- Single particle diffraction
- Transition charge densities σ_{ge}!
- Contribution of electronic coherences
- Can give spatial information about avoided crossing/CoIn
- Weak signal (10^{-3})





M. Kowalewski, K. Bennett, and S. Mukamel, Struct. Dynam., **4**, 054101 (2017).

K. Bennett, M. Kowalewski, et al., Proc. Natl. Acad. Soc. USA, **115**, 6538 (2018).

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Thank you for your attention!