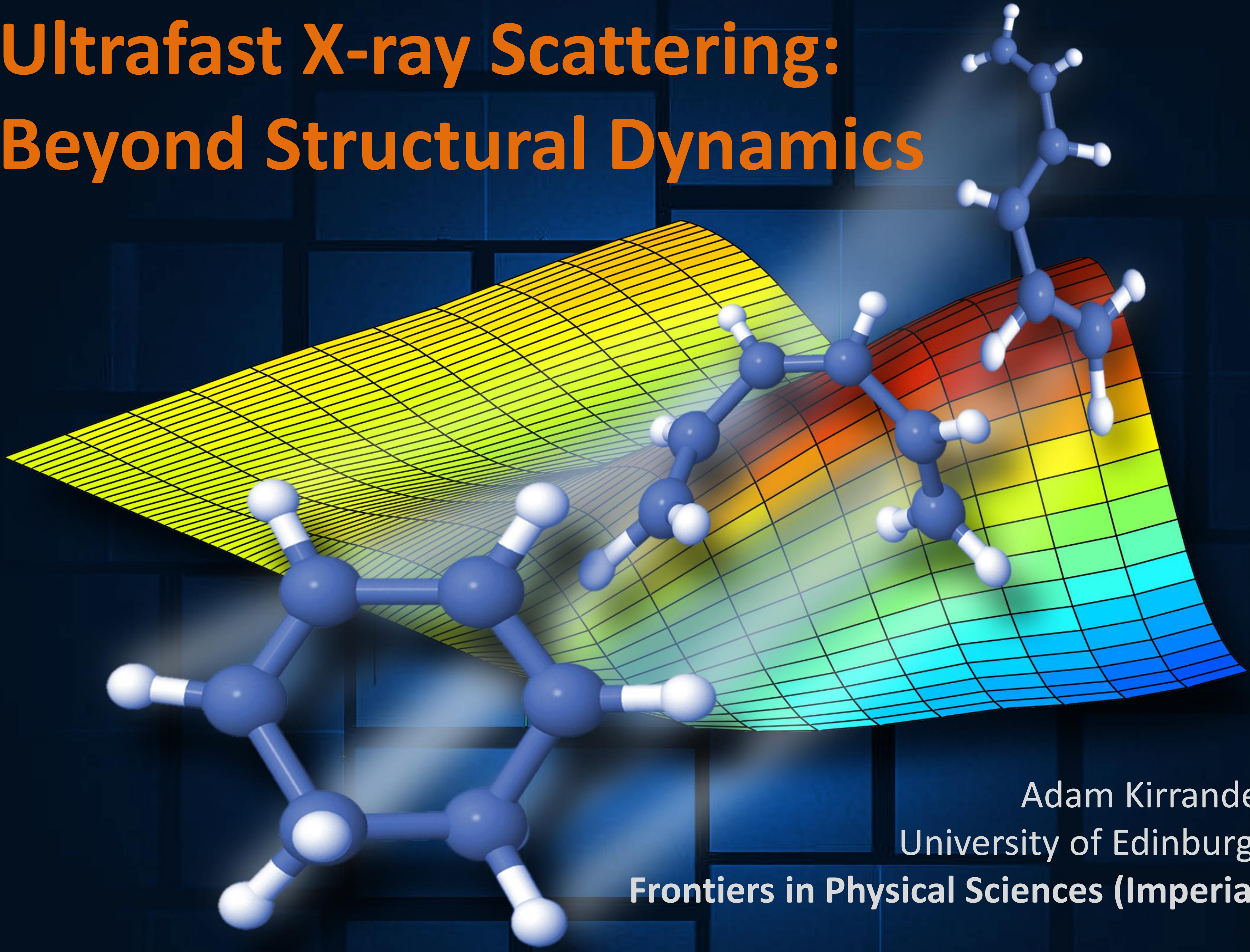
Ultrafast X-ray Scattering: Beyond Structural Dynamics

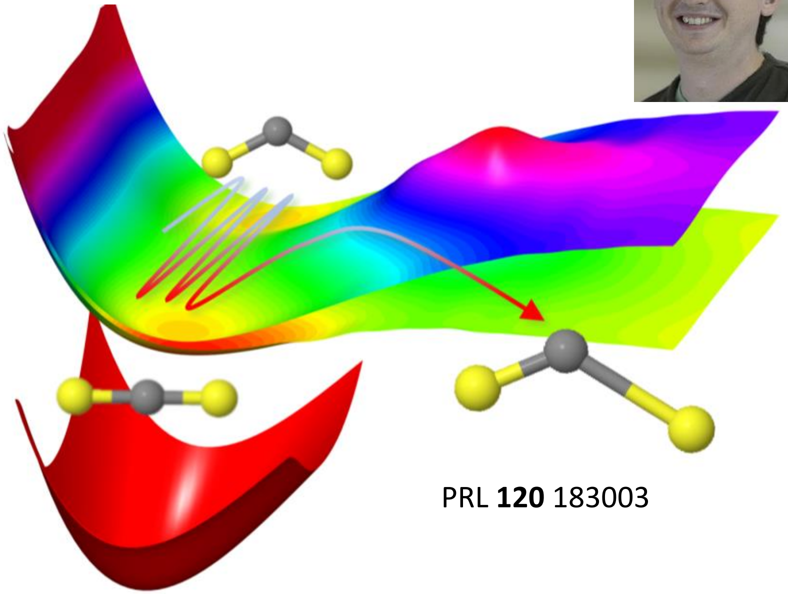


Adam Kirrander
University of Edinburgh
Frontiers in Physical Sciences (Imperial)

Vision: Map total wave packet

Complex processes

- ➢ Nuclear and electronic dynamics
- ➢ Internal conversion
- ➢ Intersystem crossing
- ➢ Multiple electronic states



PRL **120** 183003

Experiments

- ➢ Ultrafast spectroscopy
- ➢ Strong-field measurements
- ➢ Scattering

Theory

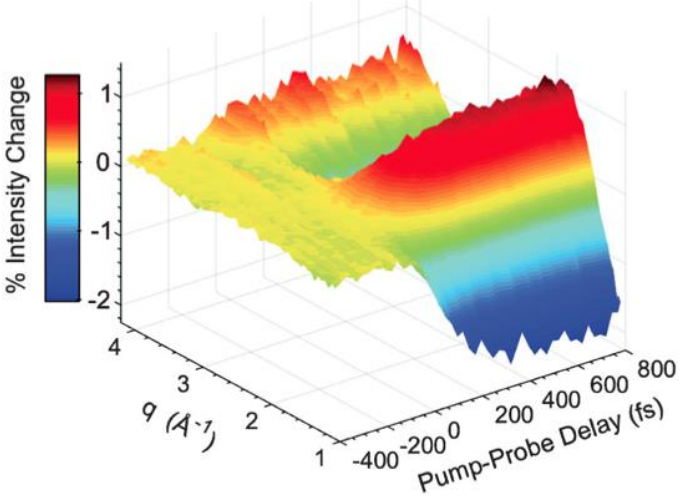
- ➢ Electronic structure
- ➢ Nuclear dynamics
- ➢ Observables

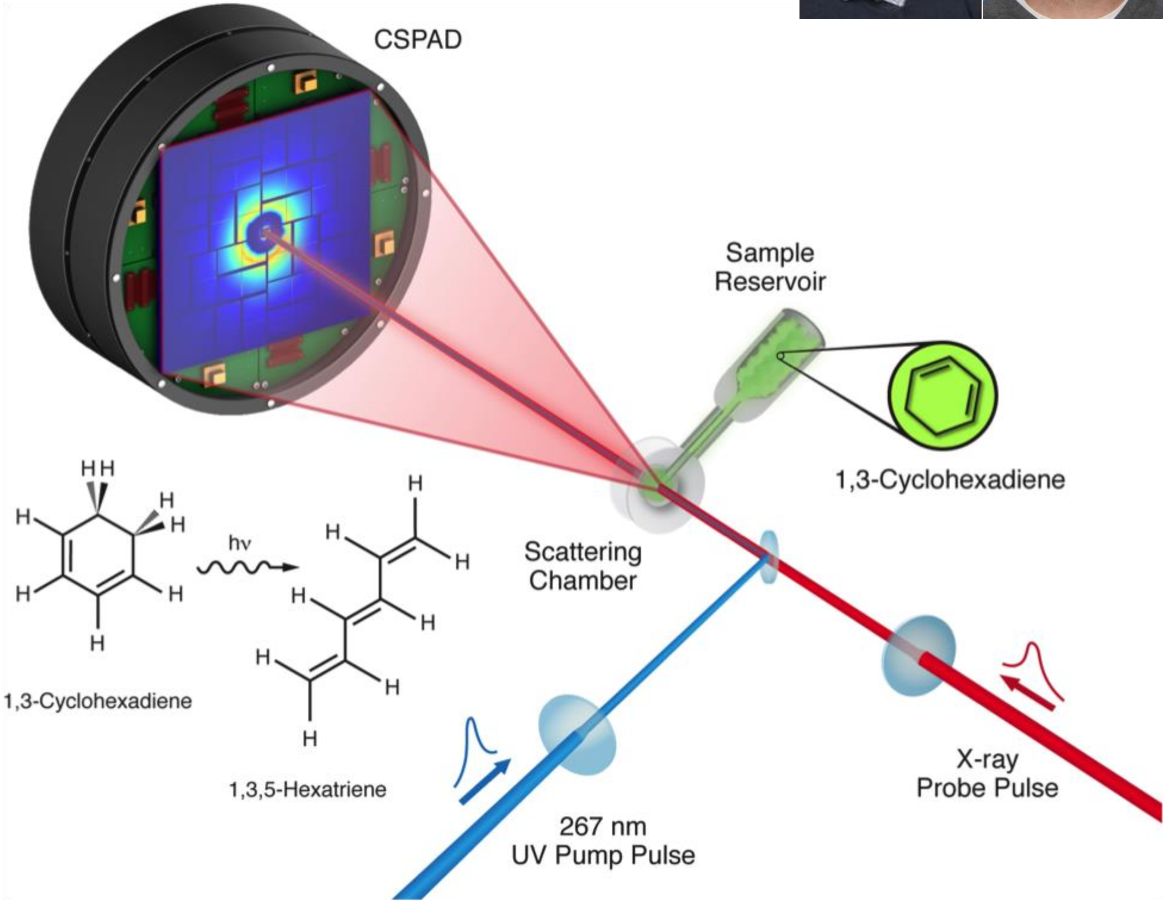
Ultrafast x-ray scattering is emerging as an important technique

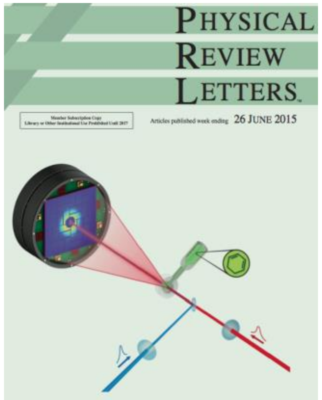
AMO physics, photochemistry, new technologies

TODAY

Example 1/2: STRUCTURAL DYNAMICS





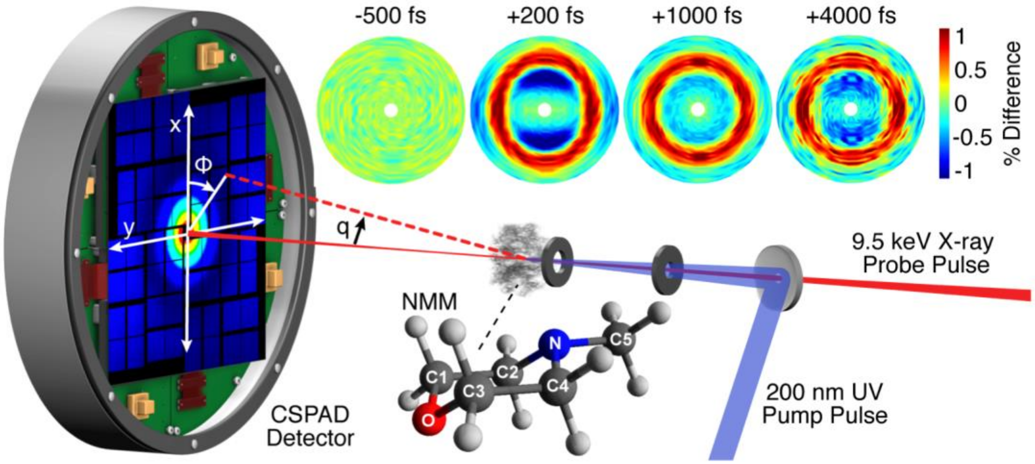

Physical Review Letters

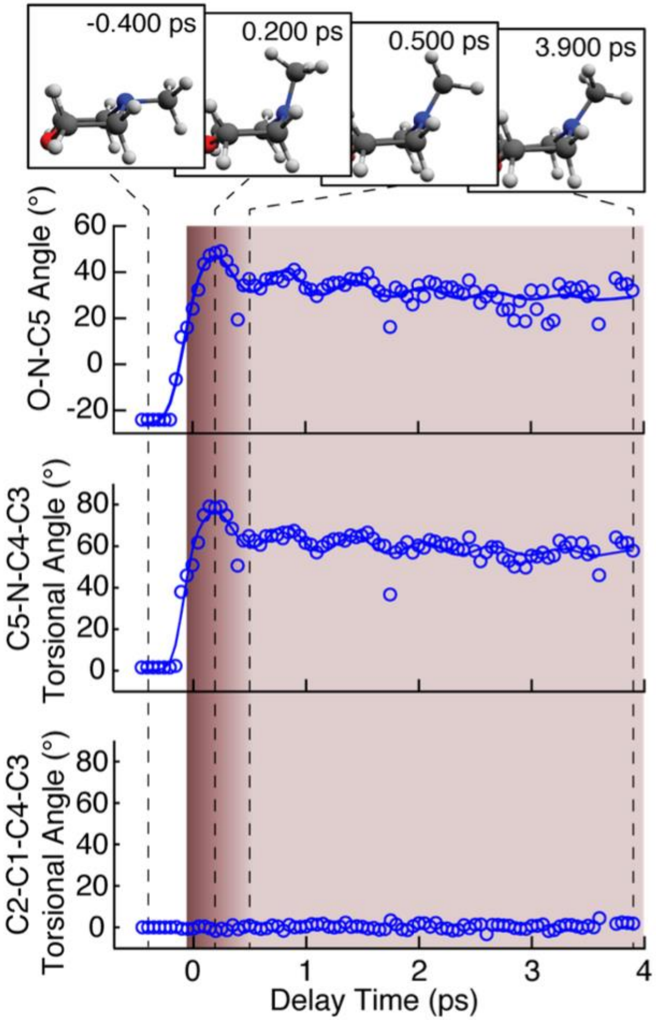
Articles published week ending 26 June 2015

Minitti *et al.* PRL **114** 255501 (2015) + Wolf *et al*. Nature Chem. **11** 504 (2019)

Example 2/2: Excited state structure (N-methyl morpholine)

$X \xrightarrow{200\,nm} 3p_z \xrightarrow{106\,fs} 3s$ (coherent vibration)





Stankus *et al*. Nature Chemistry (2019)

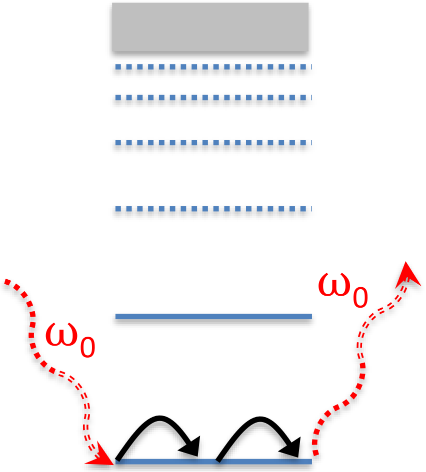
TOMORROW

Identify electronic states, analyse coherences

$$\frac{d\sigma}{d\Omega} \approx \left(\frac{d\sigma}{d\Omega}\right)_{\text{Th}} \sum_{i,j}^{N} \sum_{f}^{\infty} W_{fij}(\Delta\omega) \int I(t) \int \chi_i(\bar{\boldsymbol{R}},t)\chi_j^*(\bar{\boldsymbol{R}},t)\; L_{fi}(\tilde{\boldsymbol{q}},\bar{\boldsymbol{R}})L_{fj}^*(\tilde{\boldsymbol{q}},\bar{\boldsymbol{R}})d\bar{\boldsymbol{R}}dt$$

Elastic

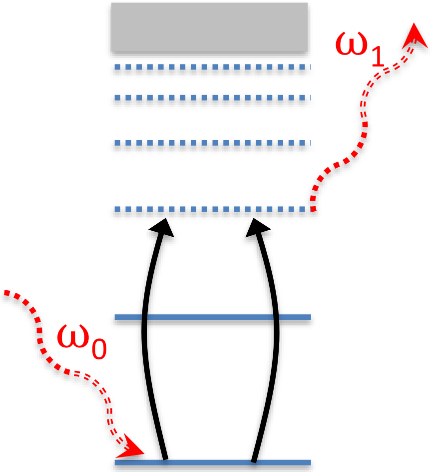
$i = j = f$



$$|L_{ii}|^2 = \left|\int \rho(r)e^{iqr}dr\right|^2$$

Inelastic

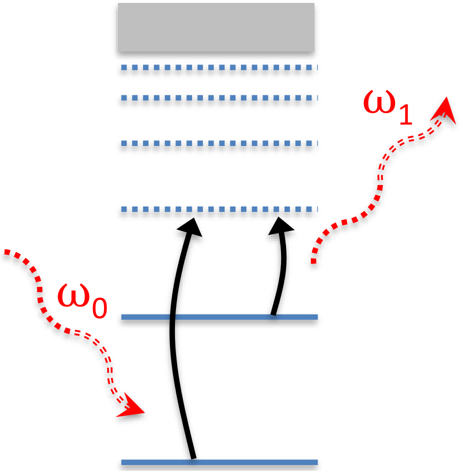
$i = j \neq f$



$$|L_{ij}|^2 = \left|\int \rho_{ij}(r)e^{iqr}dr\right|^2$$

Coherent Mixed[*]

$i \neq j$, any f



$$L_{fi}L_{fj}^*$$

[*] Simmermacher *et al.* PRL **122** 073003 (2019) and JCP **151** 174302 (2019)

Final thoughts

Full characterization of molecular wave packet
- Identify electronic state
- Nuclear + electronic dynamics (inversion problem) PRL **117** 153003
- Coherent mixed scattering*
  - Transient electronic dynamics
  - Degree of coherence
  - Signatures of conical intersections (Mukamel)

Experimental considerations
- *q*-range
- Signal/noise (repetition rate)
- Characterized/seeded x-ray pulses
- New detectors? Energy resolution?
- Optical laser systems @ LCLS
- Sample delivery (molecular alignment)

- **COMPUTATIONAL AND THEORETICAL GUIDANCE ESSENTIAL**

*Simmermacher *et al.* PRL **122** 073003 (2019) and JCP **151** 174302 (2019)

Colleagues & collaborators

University of Edinburgh:
Darren Bellshaw, **Nikola Zotev**,
Andrés Moreno, **Mats Simmermacher**,
Maria Tudorovskaya, Kyle Acheson,
Hai-Wang Yong (visitor from Brown)

Collaborations (theory):

Dmitry Shalashilin	Leeds
Niels Henriksen	DTU
Klaus Møller	DTU
Christian Jungen	UCL/CNRS
Martin Paterson	Heriot-Watt

Collaborations (experiment):

Peter Weber	Brown
Mike Minitti	SLAC
Russell Minns	Southampton

archer

MARIE CURIE ACTIONS

THE UNIVERSITY OF EDINBURGH

EPSRC
Engineering and Physical Sciences
Research Council

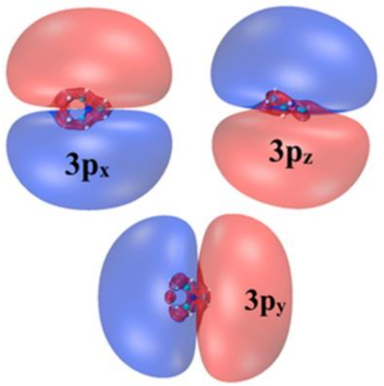
THE CARNEGIE TRUST
FOR THE UNIVERSITIES OF SCOTLAND

The Leverhulme Trust

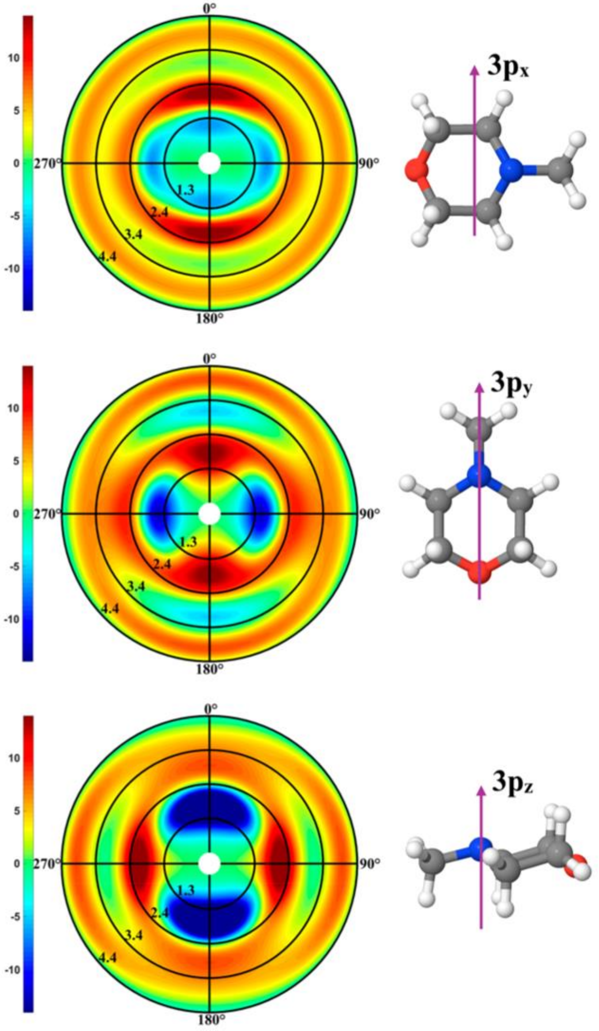
RSE
The Royal Society
of Edinburgh

Example 3: Confirm excited state (N-methyl morpholine)

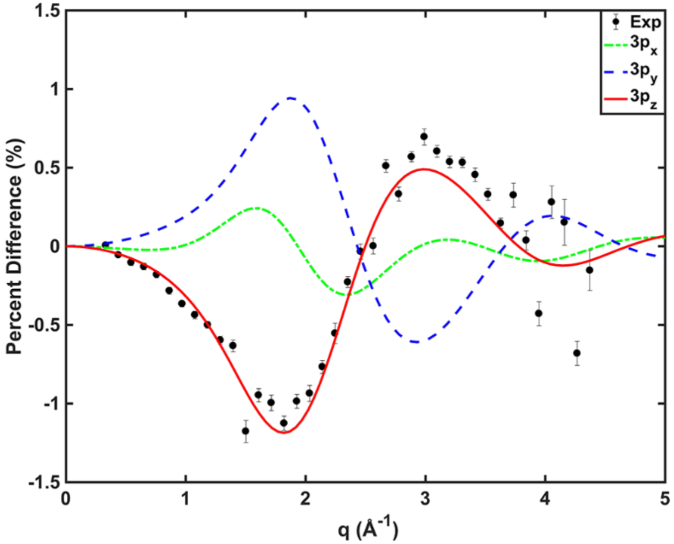
$$X \xrightarrow{200\ nm} \{3p_x, 3p_y, 3p_z\}$$



Use anisotropy of scattering



Anistropy confirms excitation to $3p_z$ state



Yong *et al*. J. Phys. Chem. Lett. (2018)

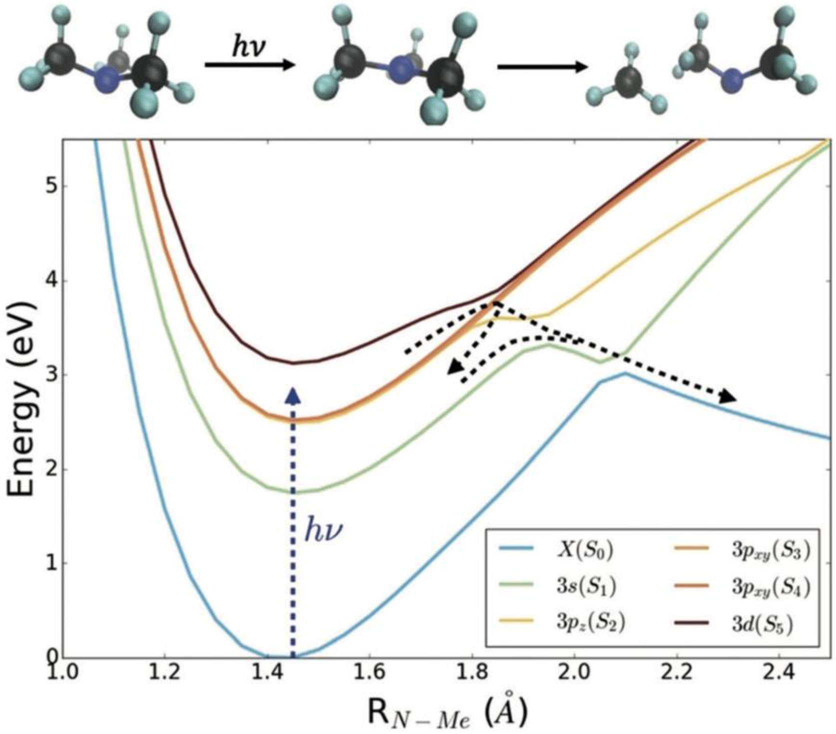
Example 4: Counting electrons during dissociation

Signal $q \to 0 \propto N_{elec}^2$

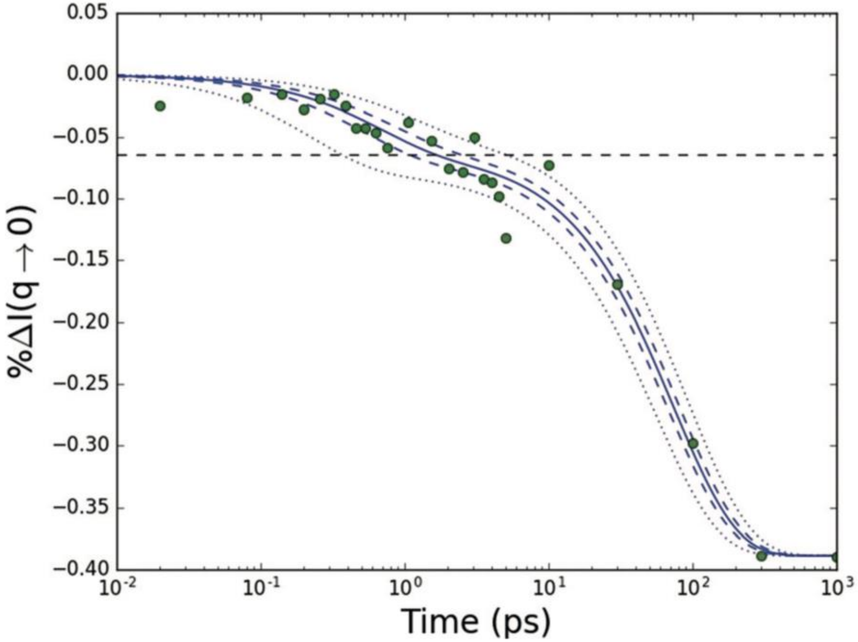
Photodissociation reaction $\mathrm{TMA} \longrightarrow \mathrm{DMA} + \mathrm{CH_3}$

Number electrons $N_{\mathrm{TMA}} = N_{\mathrm{DMA}} + N_{\mathrm{CH_3}}$

$$\left(N_{\mathrm{DMA}} + N_{\mathrm{CH_3}}\right)^2 > N_{\mathrm{DMA}}^2 + N_{\mathrm{CH_3}}^2$$



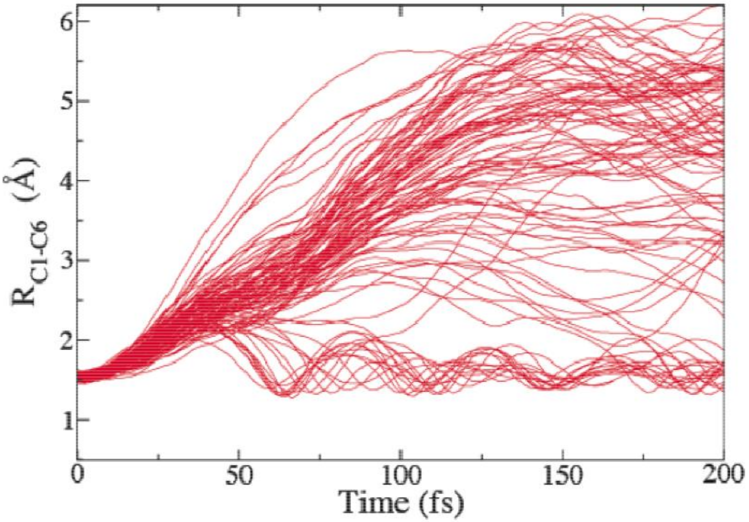
$q \to 0$ signal for TMA



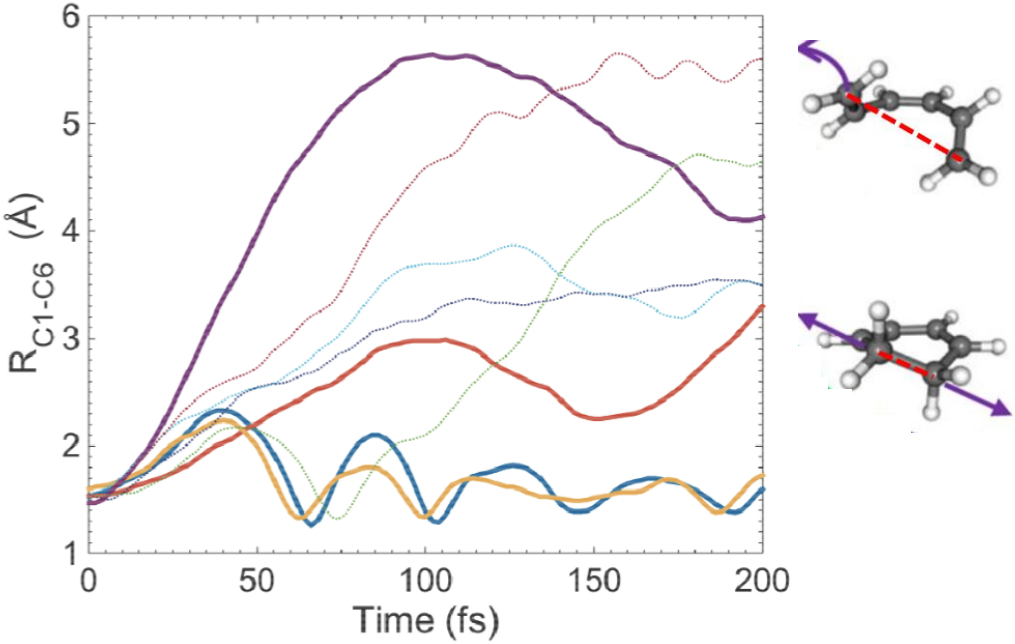
Ruddock *et al*. Angew. Chemie (2019)

Computational tools: reconstruct dynamics

Trajectories from QM simulations[§]

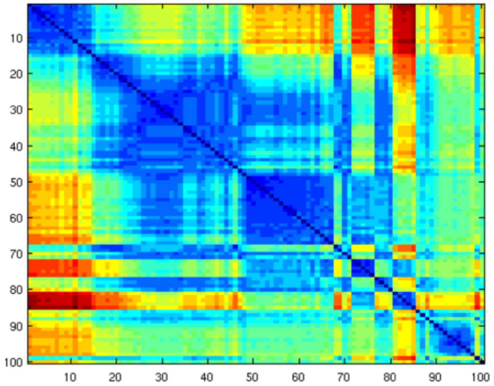


Weighted by experimental data*

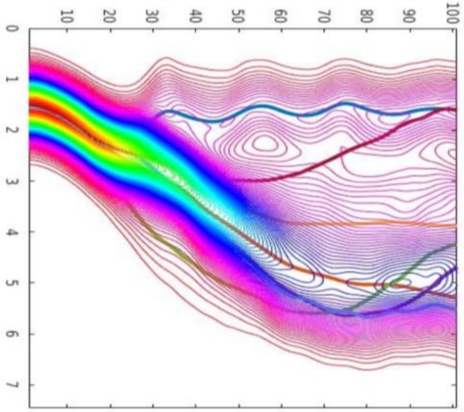


*Quantum yield close to recent CASPT2 simulations

- $\langle RMSD \rangle_t$ for all trj-pairs
- Clustering algorithm OPTICS (reachability plots)
- 7 clusters



Probability density plot for unweighted simulation



[§]AI-MCE/SA3-CASSCF(6,4)/cc-pVDZ

Consider **future experiments** that exploit **coherence** of x-rays

Original work by Cao+Wilson, Bratos, Møller+Henriksen, **Dixit+**Santra, **Mukamel**

Scattering of coherent x-rays

- Quantized x-ray field $\left(\hat{a},\hat{a}^{\dagger}\right)$
- Non-stationary molecular wavepacket $\Psi(\bar{\boldsymbol{r}},\bar{\boldsymbol{R}},t) = \sum_i^N \chi_i(\bar{\boldsymbol{R}},t)\ \varphi_i(\bar{\boldsymbol{r}};\bar{\boldsymbol{R}})$
- Scattering in 1st order perturbation theory $\hat{H}_{int} = \cancel{\vec{j}\vec{A}} + \boxed{\vec{A}^2}$

$$\frac{d\sigma}{d\Omega} \approx \underbrace{\left(\frac{d\sigma}{d\Omega}\right)_{\text{Th}}}_{\text{Thomson x-section}} \sum_{i,j}^{N}\sum_{f}^{\infty} \underbrace{W_{fij}(\Delta\omega)}_{\text{window fcn}} \int \underbrace{I(t)}_{\text{pulse profile}} \int \underbrace{\chi_i(\bar{\boldsymbol{R}},t)\chi_j^*(\bar{\boldsymbol{R}},t)}_{\text{nuclear wps}} \underbrace{L_{fi}(\tilde{\boldsymbol{q}},\bar{\boldsymbol{R}})L_{fj}^*(\tilde{\boldsymbol{q}},\bar{\boldsymbol{R}})}_{\text{scattering matrix elements}} d\bar{\boldsymbol{R}}dt$$

Simmermacher *et al.* PRL **122** 073003 (2019) and JCP **151** 174302 (2019)

Scattering of coherent x-rays

- Quantized x-ray field $\left(\hat{a}, \hat{a}^{\dagger}\right)$
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$$L_{fi}(\boldsymbol{q}, \bar{\boldsymbol{R}}) = \langle \varphi_f(\bar{\boldsymbol{R}}) | \hat{L} | \varphi_i(\bar{\boldsymbol{R}}) \rangle \qquad \hat{L} = \sum_n e^{\imath \boldsymbol{q}\boldsymbol{r}_n}$$

electronic states *f* and *i*

scattering operator

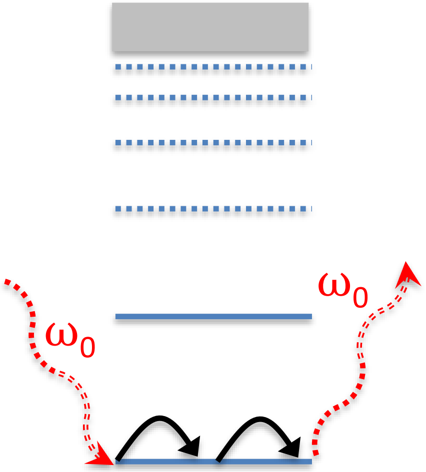
Simmermacher *et al.* PRL **122** 073003 (2019) and JCP **151** 174302 (2019)

3 distinct components

$$\frac{d\sigma}{d\Omega} \approx \left(\frac{d\sigma}{d\Omega}\right)_{\mathrm{Th}} \sum_{i,j}^{N}\sum_{f}^{\infty} W_{fij}(\Delta\omega)\int I(t)\int \chi_i(\bar{\mathbf{R}},t)\chi_j^*(\bar{\mathbf{R}},t)\,\boxed{L_{fi}(\tilde{\mathbf{q}},\bar{\mathbf{R}})L_{fj}^*(\tilde{\mathbf{q}},\bar{\mathbf{R}})}\,d\bar{\mathbf{R}}dt$$

1.Elastic

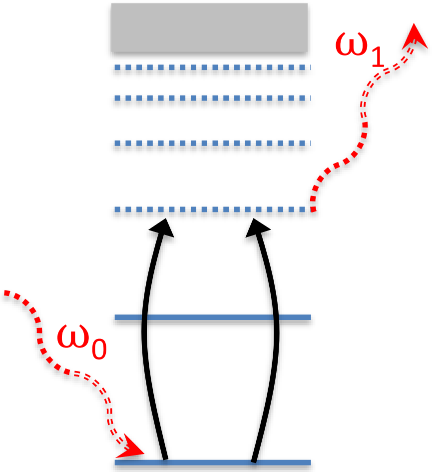
$i = j = f$



$$|L_{ii}|^2 = \left|\int \rho(r)e^{iqr}dr\right|^2$$

2.Inelastic

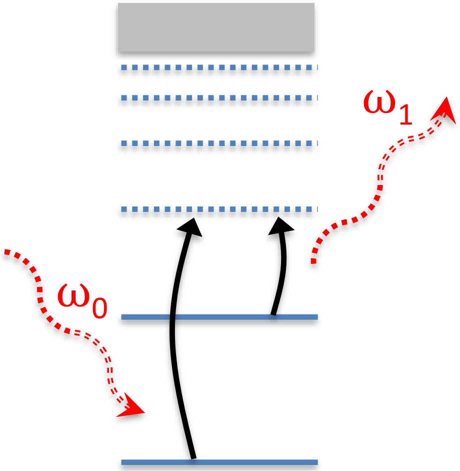
$i = j \neq f$



$$|L_{ij}|^2 = \left|\int \rho_{ij}(r)e^{iqr}dr\right|^2$$

3.Mixed

$i \neq j$, any f



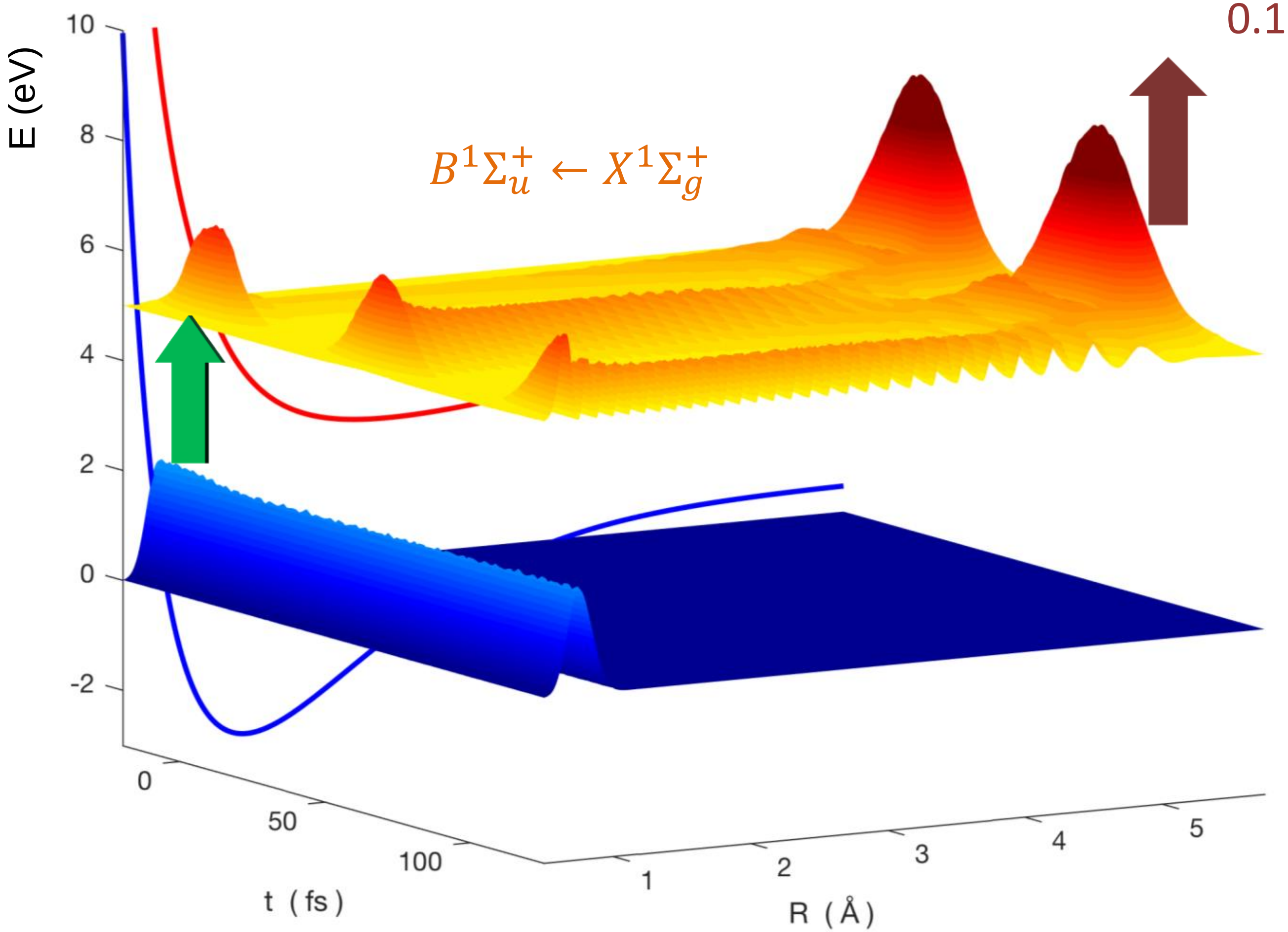
$$L_{fi}L_{fj}^*$$

Simmermacher *et al.* PRL **122** 073003 (2019) and JCP **151** 174302 (2019)

Simulation of experiment in H_2

Optical Pump
14.3 eV
25 fs^{FWHM}
10% excitation

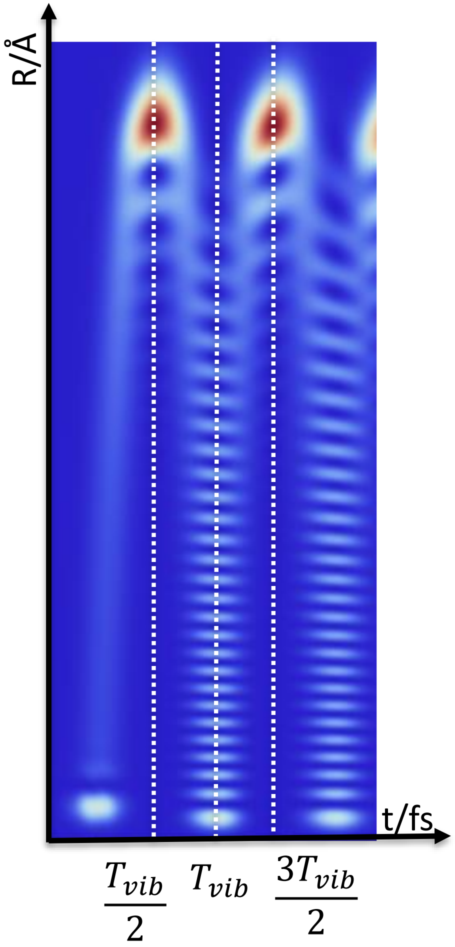
X-ray Probe
8.5 keV.
0.1 fs^{FWHM}



Simmermacher *et al.* PRL **122** 073003 (2019) and JCP **151** 174302 (2019)

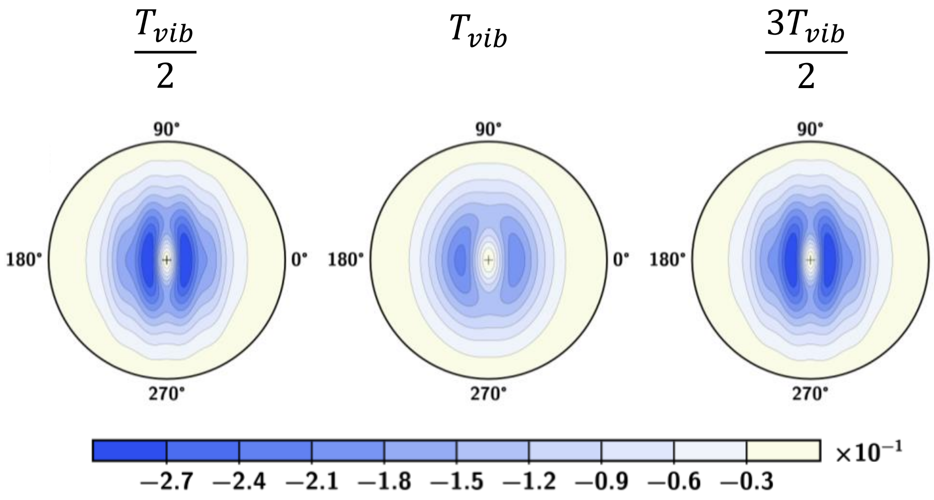
Difference Signal

Nuclear probability density on $B^1\Sigma_u^+$



ELASTIC

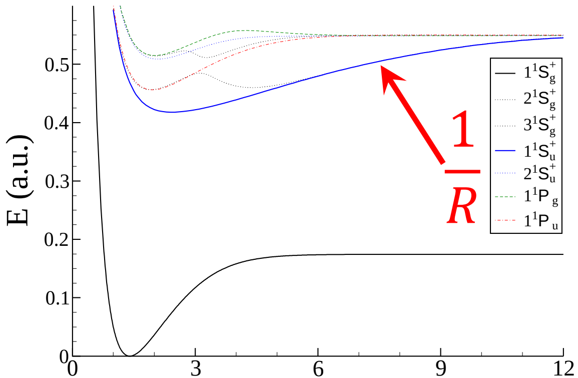
$$i = j = f$$



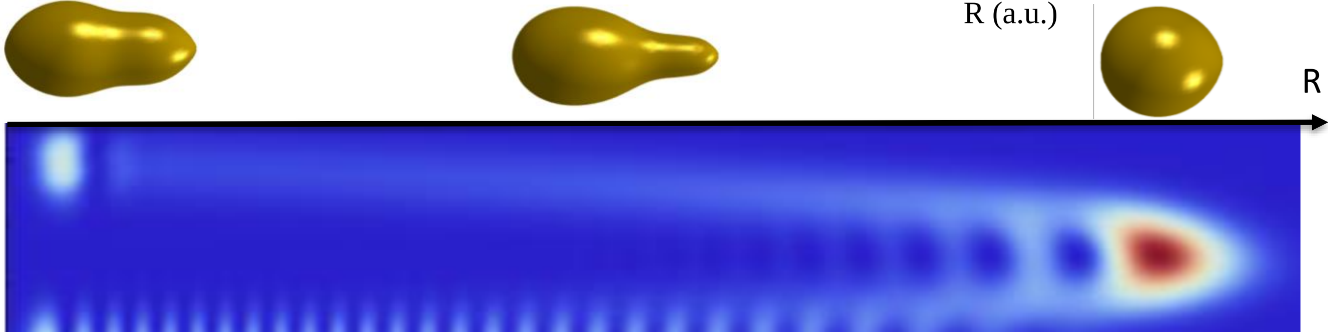
Signal < 0 at all times ⇒ expanded electron density compared to X-state

Changes in signal correspond to changes in e⁻ density

Electron transfer



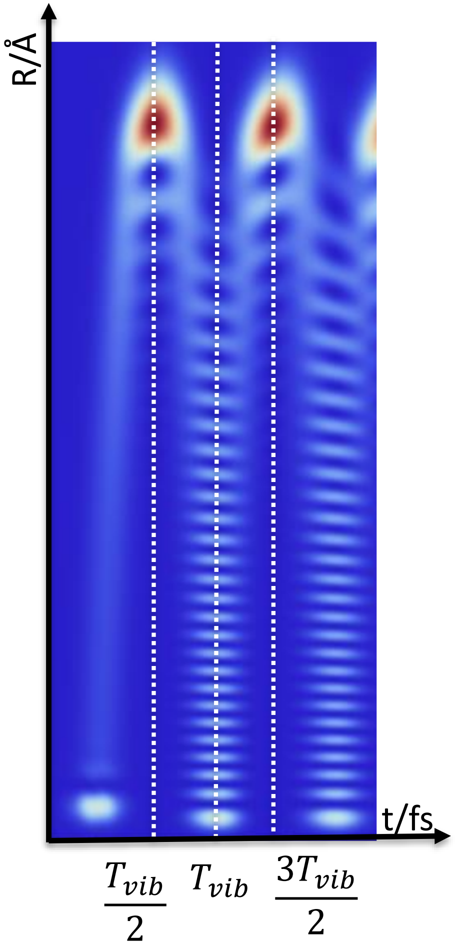
Electron-density iso-surfaces for wavepacket on $B^1\Sigma_u^+$ state



$T_{vib} = 62$ fs

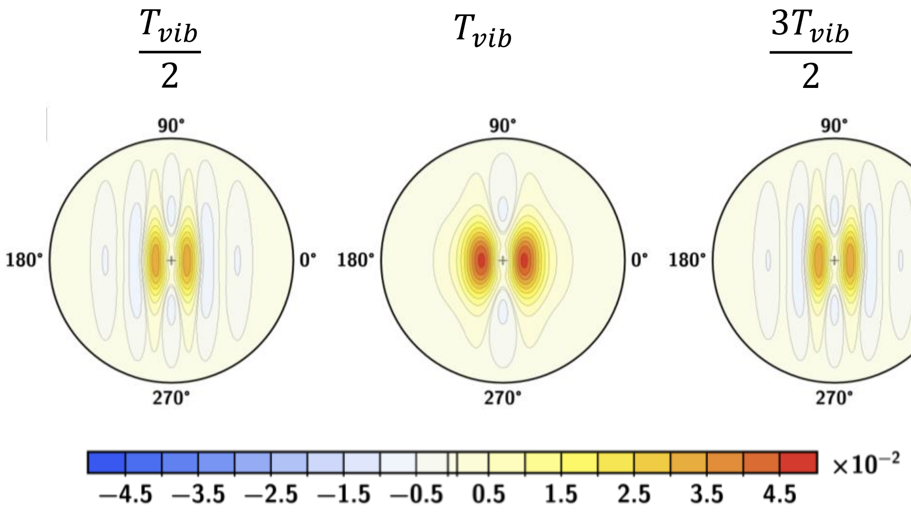
Difference Signal

Nuclear probability density on $B^1\Sigma_u^+$



INELASTIC

$\boldsymbol{i = j \neq f}$



Signal predominantly > 0 ⇒ inelastic transitions from B-state more likely

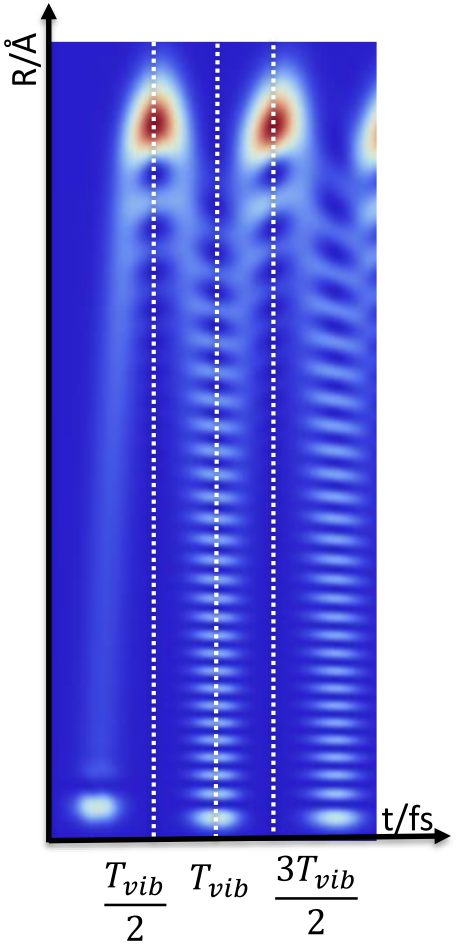
The inelastic component changes with geometry

⇒ in contrast to the Independent Atom Model (IAM)

$T_{vib} = 62$ fs

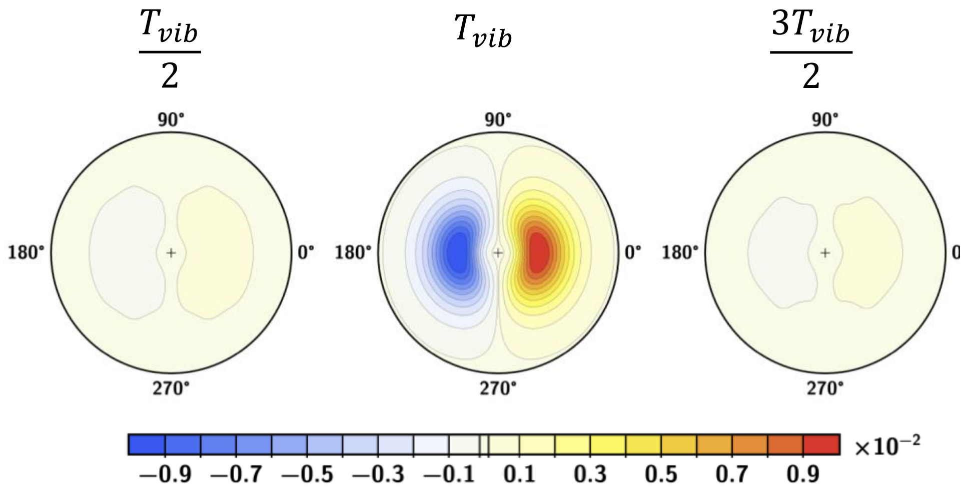
Difference Signal

Nuclear probability density on $B^1\Sigma_u^+$



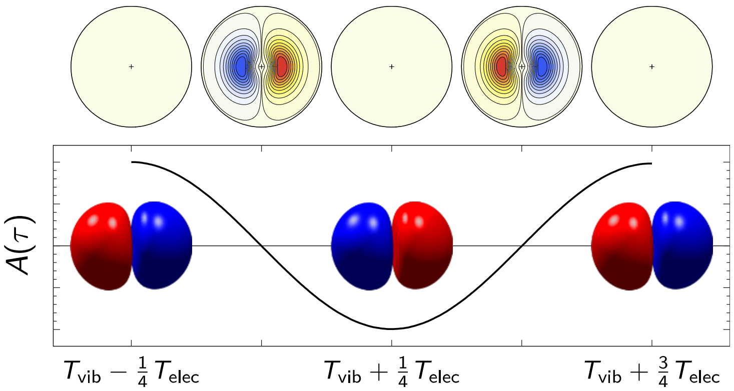
MIXED

i ≠ j*, any *f



Note that **not centrosymmetric** as two previous contributions

Appears at times nT_{vib} when nuclear overlap $|\chi_X(R)\chi_B^*(R)|$ maximal



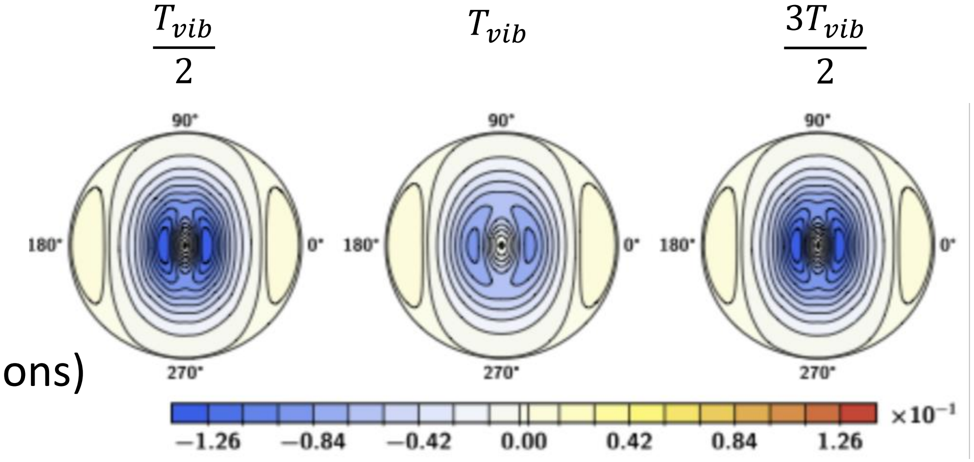
Transient beating between electronic X and B states with period $T_{elec} = 0.3$ fs

$T_{vib} = 62$ fs

DETECTION WINDOW

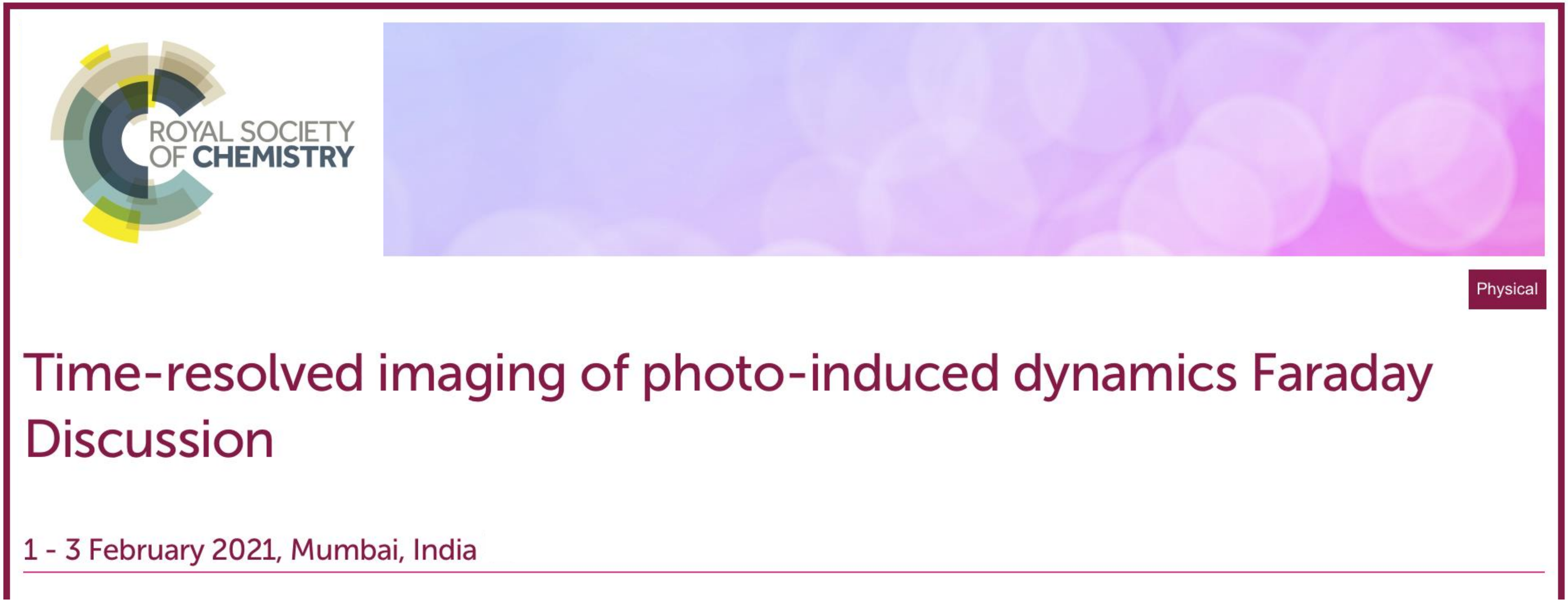
TOTAL SCATTERING

(all possible transitions)



Coherent mixed term vanishes for **LARGE DETECTION WINDOW** in present case (due to symmetry)

Simmermacher *et al.* JCP **151** 174302 (2019)


ROYAL SOCIETY OF CHEMISTRY

Physical

Time-resolved imaging of photo-induced dynamics Faraday Discussion

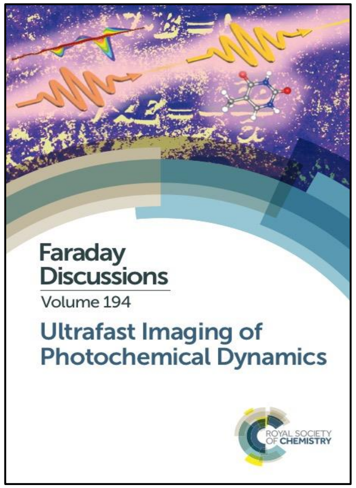
1 - 3 February 2021, Mumbai, India

A discussion meeting…

Recorded for posterity

High impact

Everyone can contribute


Faraday Discussions

Volume 194

Ultrafast Imaging of Photochemical Dynamics

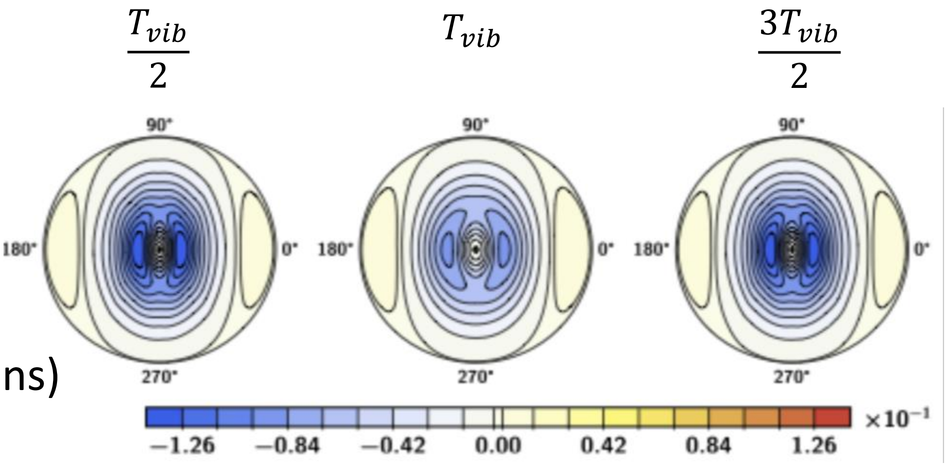
ROYAL SOCIETY OF CHEMISTRY

Chairs: **Gopal Dixit** and Adam Kirrander

DETECTION WINDOW

TOTAL SCATTERING

(all possible transitions)



Coherent mixed term vanishes for **LARGE DETECTION WINDOW** in present case (symmetry)

$$\Lambda_{ji}(\bar{\mathbf{q}},\bar{\mathbf{R}}) = \langle \varphi_j(\bar{\mathbf{R}}) | \hat{\bar{L}}^{\dagger} \hat{\bar{L}} | \varphi_i(\bar{\mathbf{R}}) \rangle$$

$$\frac{d\sigma}{d\Omega} = \left(\frac{d\sigma}{d\Omega}\right)_{\mathrm{Th}} W(\Delta\omega) \sum_{i,j}^{N} \int I(t) \, \langle \chi_j(t) | \, \Lambda_{ji}(\bar{\mathbf{q}},\bar{\mathbf{R}}) \, | \chi_i(t) \rangle \, dt,$$

$$\frac{d\sigma}{d\Omega} = \frac{d\sigma_{\mathrm{bg}}}{d\Omega} + \frac{d\sigma_{2\mathrm{e}}}{d\Omega} + \frac{d\sigma_{\mathrm{cm}}}{d\Omega}.$$

Simmermacher *et al.* JCP **151** 174302 (2019)