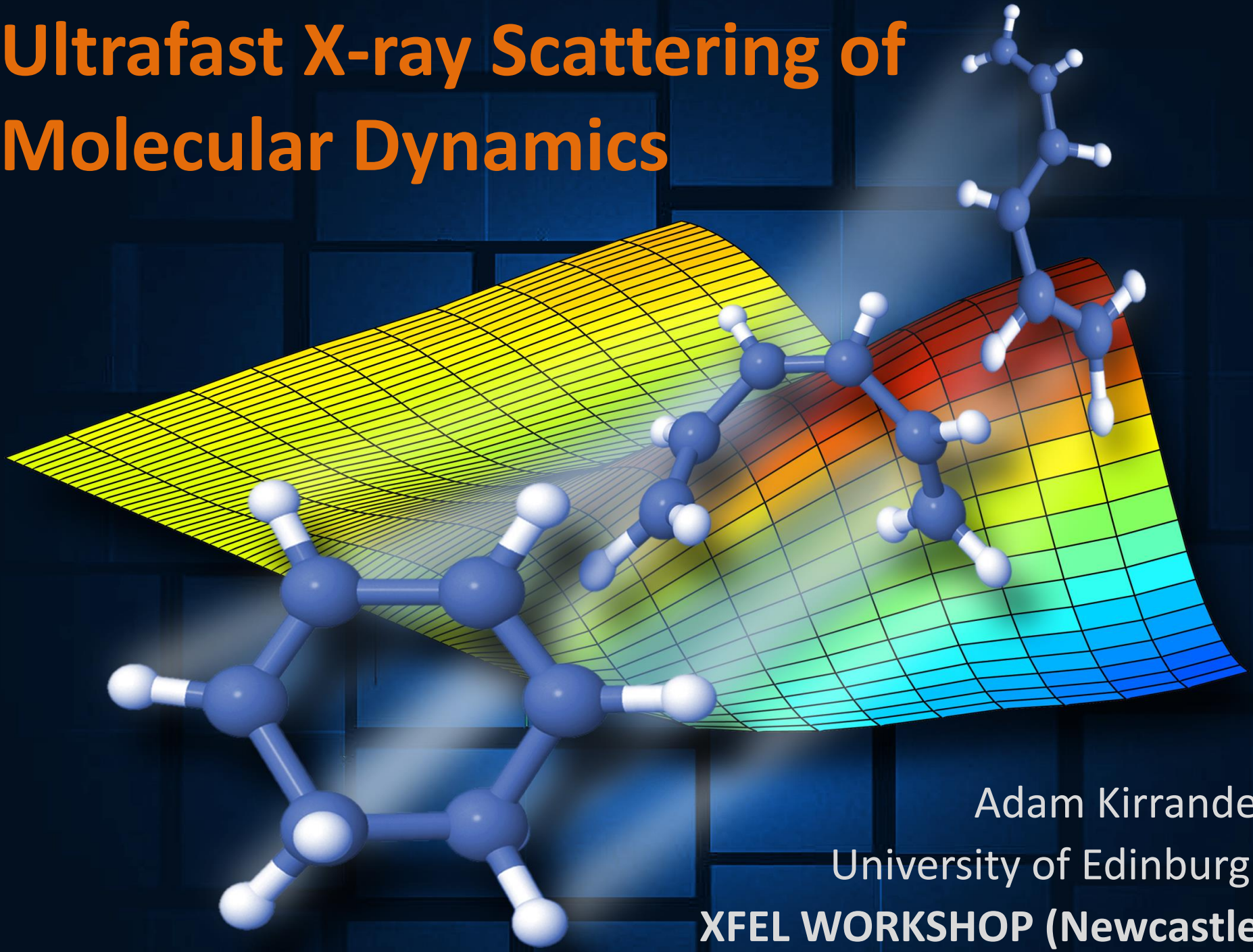
Ultrafast X-ray Scattering of Molecular Dynamics



Adam Kirrander
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XFEL WORKSHOP (Newcastle)

Colleagues & collaborators

University of Edinburgh:
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Collaborations (theory):

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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

EPSRC
Engineering and Physical Sciences Research Council

THE CARNEGIE TRUST
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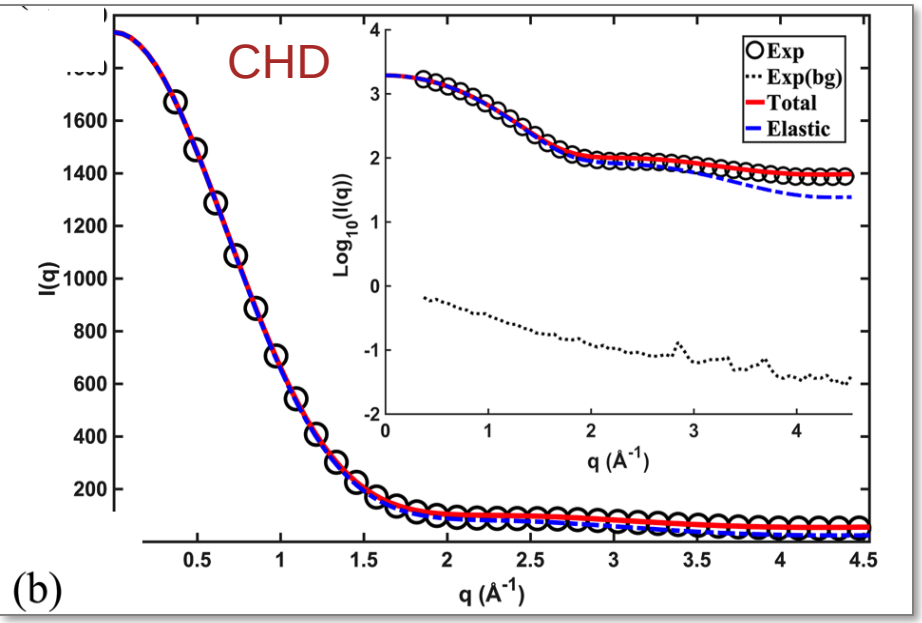
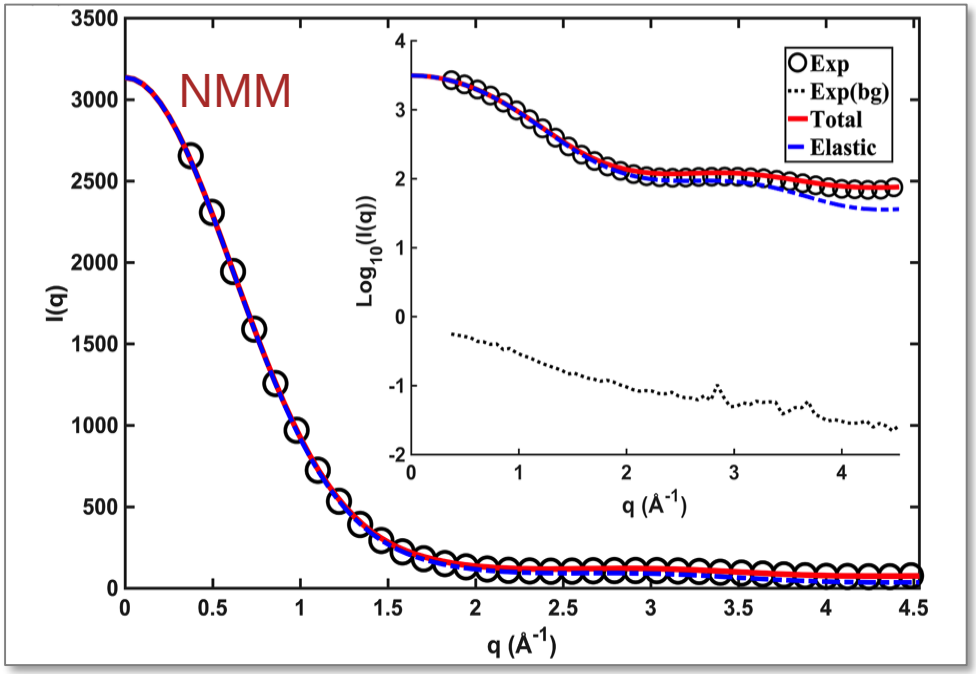
Experiment vs. Theory

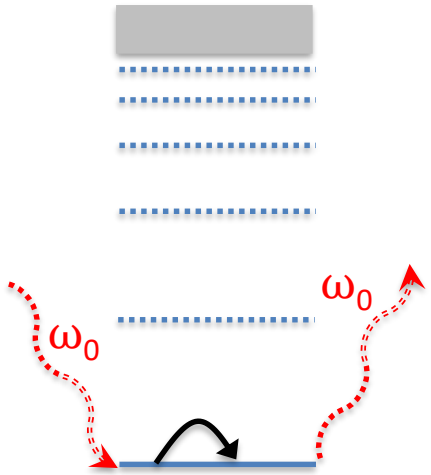


Excellent quantitative agreement!



Computational tools: scattering matrix elements from electronic structure calculations

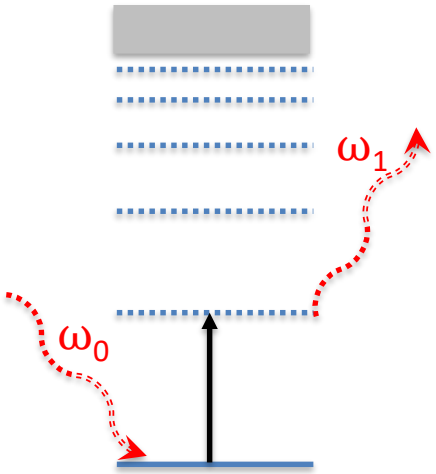
Elastic



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

Northey *et al*. JCTC **10** 4911 (2014)

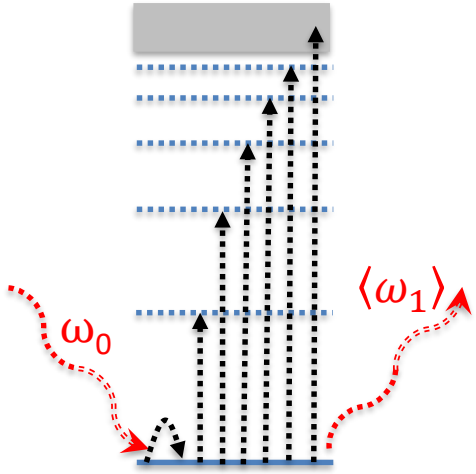
Inelastic



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

Moreno *et al*. PCCP **19** 19545 (2017)

Total

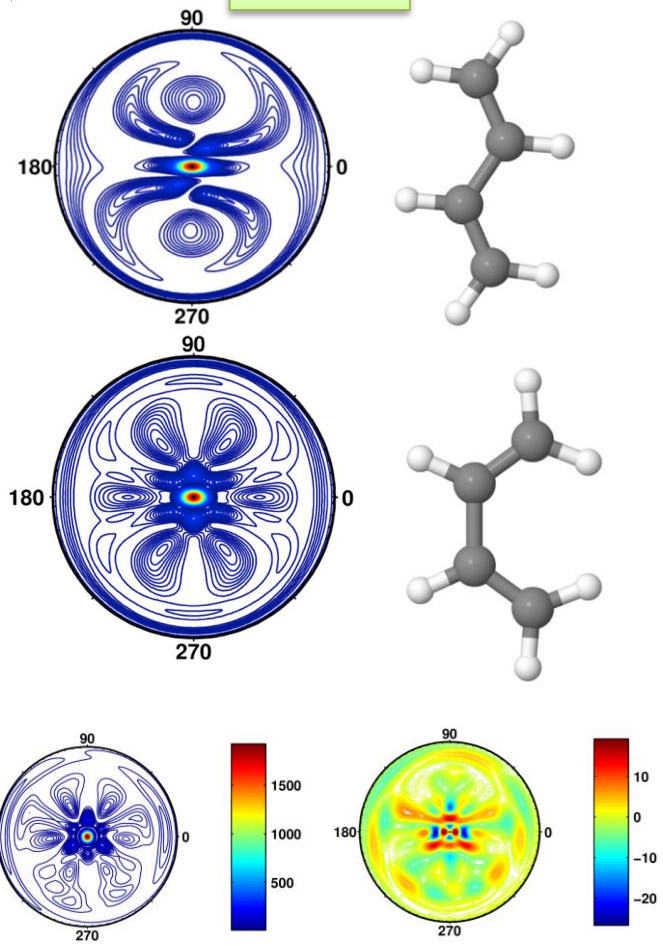


$$\langle L_{ii} \rangle = \iint \Gamma(r_1, r_2) e^{iq(r_2 - r_1)} dr_1 dr_2 + N$$

Moreno *et al*. JCTC **15** 2836 (2019)

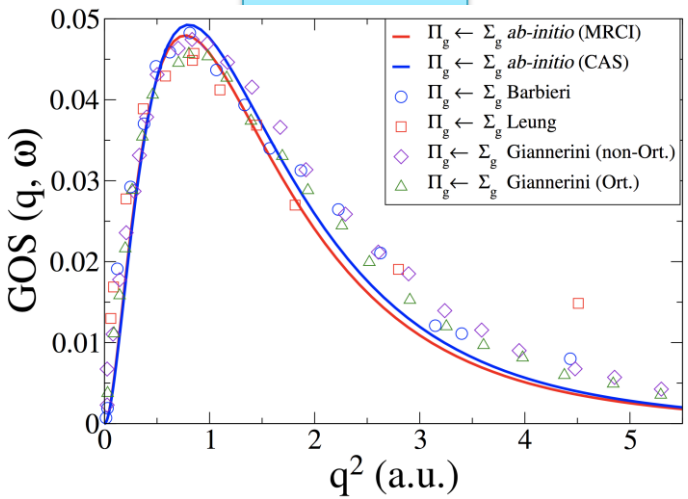
Elastic, inelastic, total X-ray scattering

Elastic



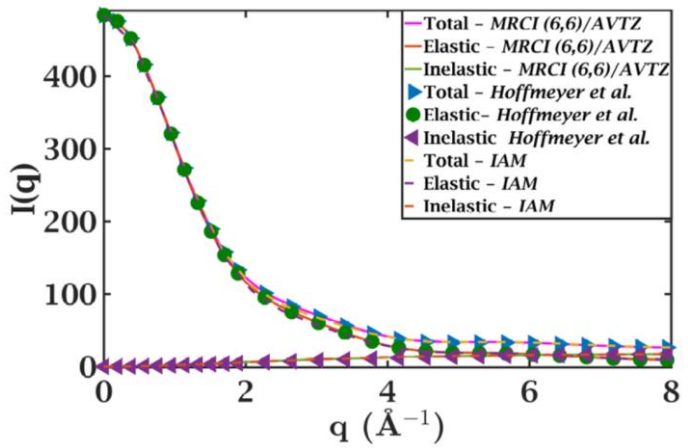
Northey *et al*. JCTC **10** 4911 (2014)

Inelastic



Moreno *et al*. PCCP **19** 19545 (2017)

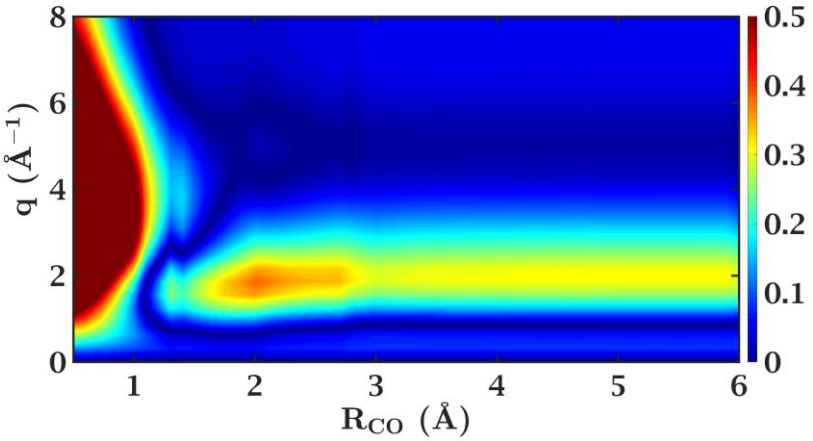
Total



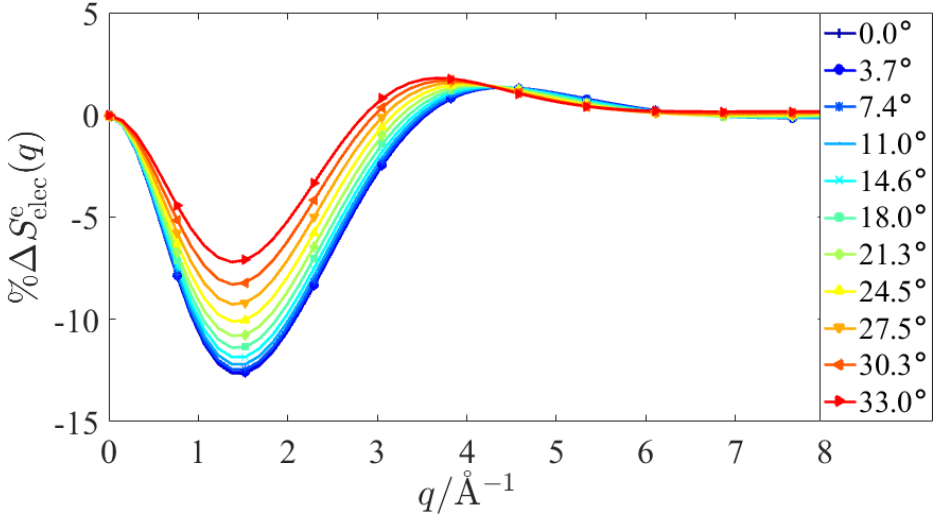
Moreno *et al*. JCTC **15** 2836 (2019)

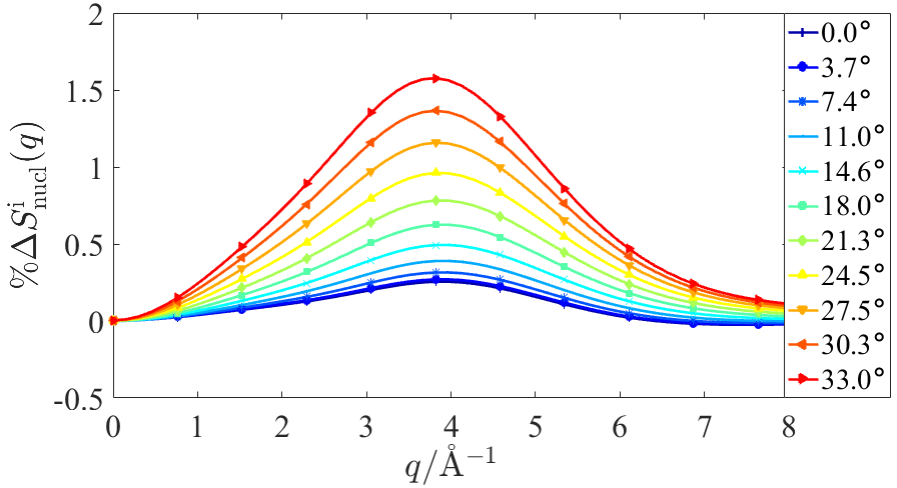
Inelastic scattering depends on **molecular geometry**

CO_2 inelastic changes as function of geometry (**ground state**)



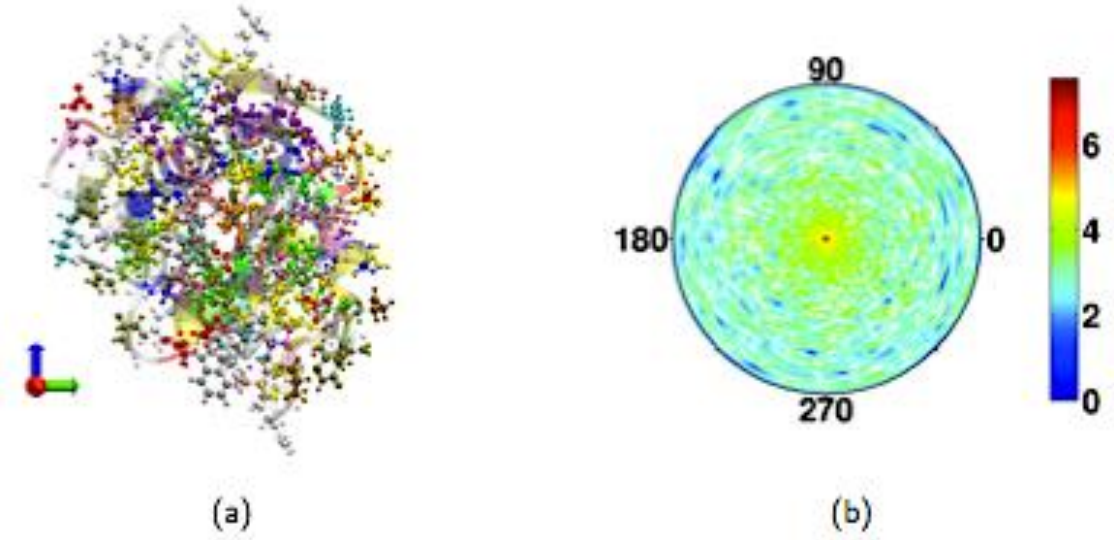
NH_3 (3p) inelastic changes as function of geometry (**excited state**)





Moreno *et al*. JCTC **15** 2836 (2019) + **Zotev** *et al.* JCTC (under review)

Going large: lysozyme (protein)



Independent Atom Model gives ~2% error compared to *Ab Initio*

Inversion of data yields *molecular movie*

- Phase-problem
- Insufficient q-range
- Less defined orientation than in crystal**

Diatomics (sine-transform)

I_2 wavepacket:
Yang *et al* PRL **117** 153002 (2016)
Glownia *et al* PRL **117** 153003 (2016)

Polyatomics → infer previous knowledge

1. ”*Unwrapping*” (exploit that the initial structure is known)*
2. Optimize weights of semiclassical trajectories in QMD simulation§
3. “Million structure” analysis⍰

Complementary data incredibly helpful

* Ishikawa Science **350** 6267 (2015)
§ Minitti PRL 255501 **114** (2015)
⍰ Stankus Nature Chem. **11** 716 (2019)

Küpper PRL **112 083002 2014

Scattering of coherent x-rays

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

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

Thomson x-section | window fcn | pulse profile | nuclear wps | scattering matrix elements

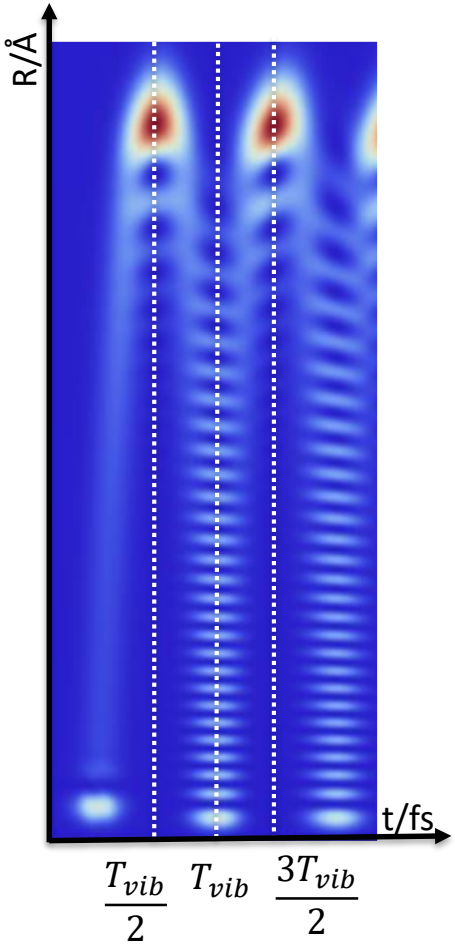
$$L_{fi}(\boldsymbol{q}, \bar{\boldsymbol{R}}) = \langle \varphi_f(\bar{\boldsymbol{R}}) | \hat{L} | \varphi_i(\bar{\boldsymbol{R}}) \rangle \qquad \hat{L} = \sum_n e^{\imath \boldsymbol{q} \boldsymbol{r}_n}$$

electronic states *f* and *i* | scattering operator

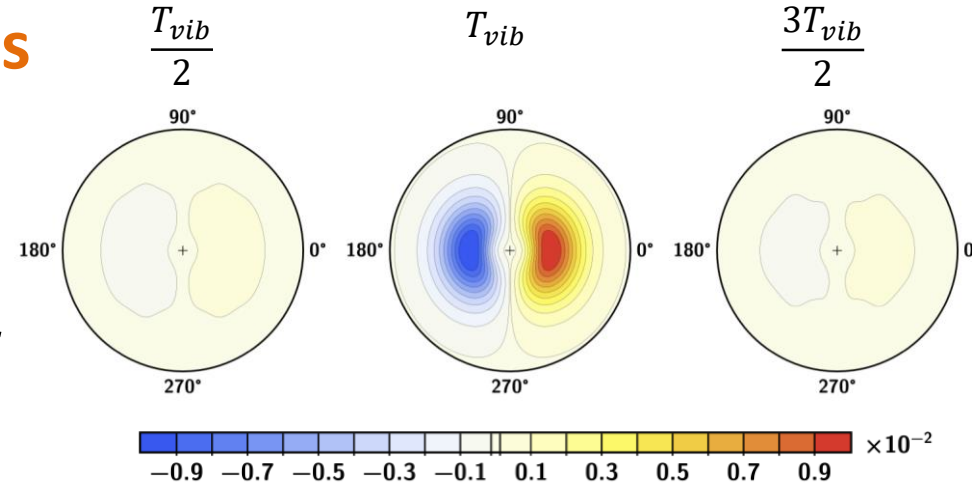
Simmermacher *et al.* PRL **122** 073003 (2019) and JCP **151** 174302 (2019)

Detecting electron dynamics

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

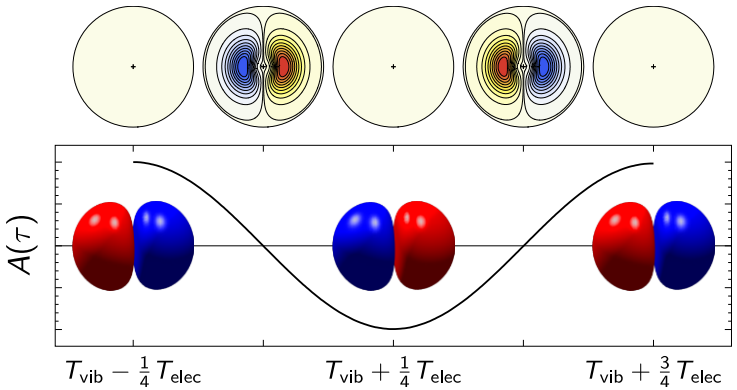


COHERENT
MIXED
$i \neq j$, any f



Not centrosymmetric as elastic and inelastic scattering

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

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

Conclusions

Status of current experiments

- Structural dynamics - **YES**
- Excited state structure -**YES**
- Many valuable ‘tricks’, *eg*:
  - Dipole transition moments (anisotropy)
  - Counting electrons (photodissociation kinetics)

Full characterization of molecular wave packet

- Measurement not easy, interpretation often harder

Coherent mixed scattering

- Electron dynamics, electronic transitions, and transient coherences – **intriguing opportunities**

Visit
Edinburgh!!

ROYAL SOCIETY OF CHEMISTRY

Physical

Time-resolved imaging of photo-induced dynamics Faraday Discussion

1 - 3 February 2021, Mumbai, India

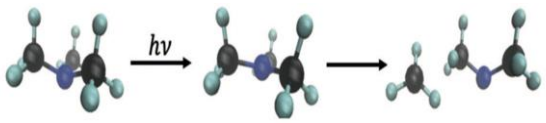
A discussion meeting…

Recorded for posterity

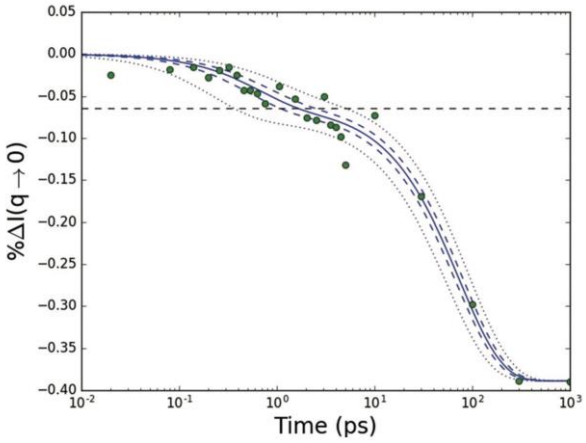
High impact publications

PLEASE SUBMIT ABSTRACT FOR PAPER - CALL WILL APPEAR IN JANUARY 2020

Counting electrons in photofragments

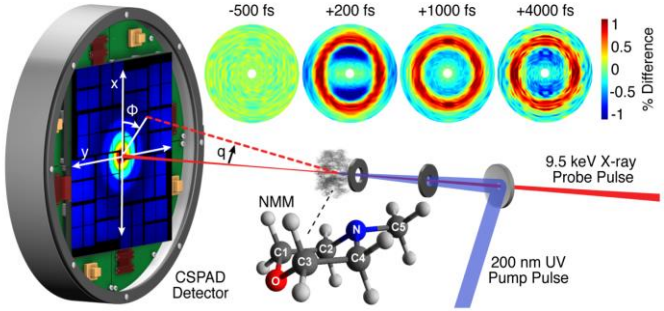


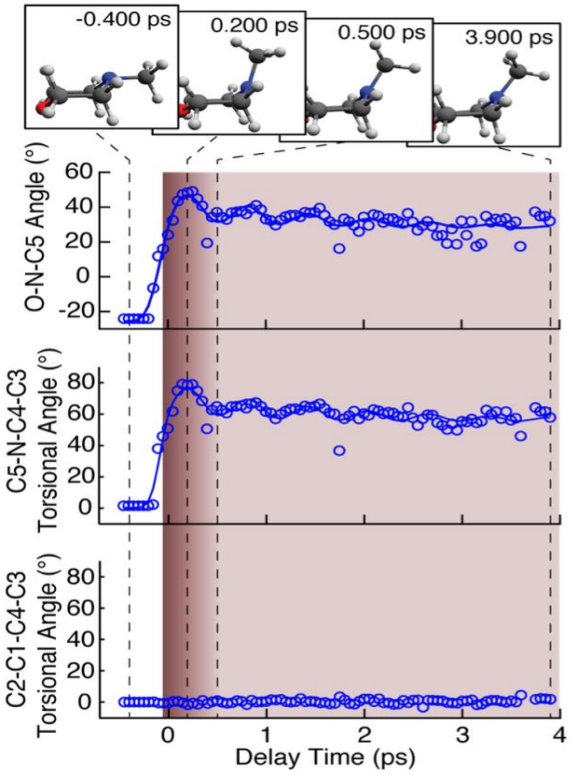
$q \rightarrow 0$ signal for TMA



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

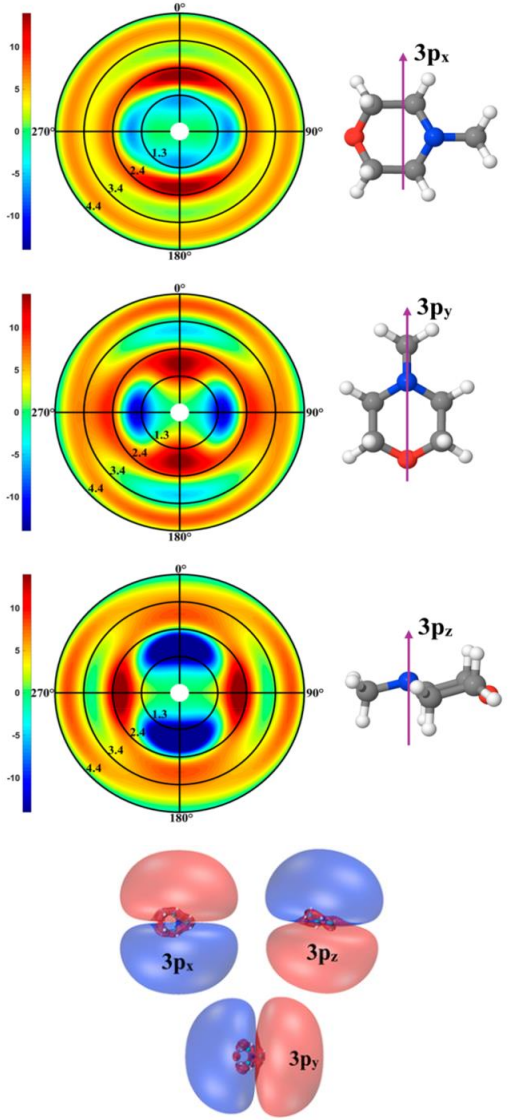
Structural dynamics in excited NMM





Stankus *et al*. Nature Chem. (2019)

Anistropy confirms excited state



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

Map total wave packet

Complex processes

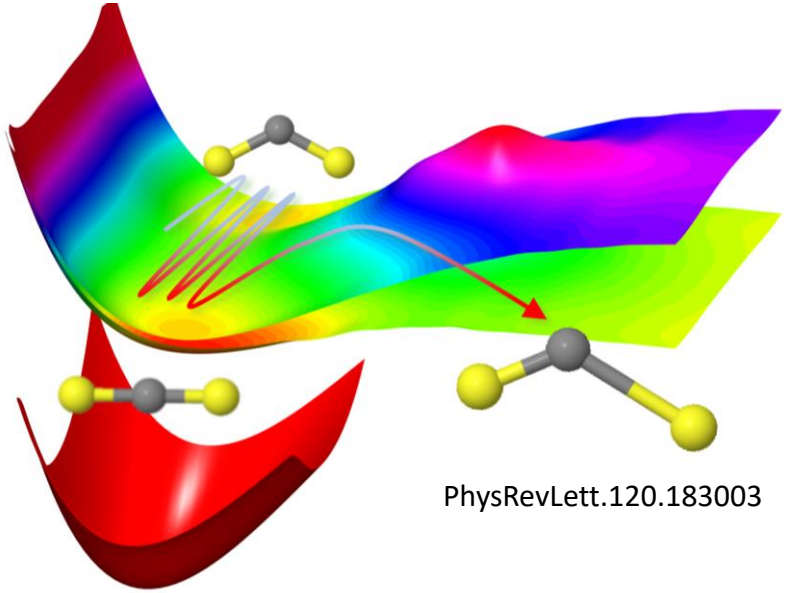
- Nuclear and electronic dynamics
- Nonadiabatic coupling (internal conversion)
- Spin-orbit coupling (intersystem crossing)
- Multiple electronic states

Experiments

- Vibrational spectroscopy
- Photoelectron spectroscopy
- Strong-field measurements
- Diffraction-based techniques, ***etc***.

Theory

- Electronic structure
- Nuclear dynamics
- Observables

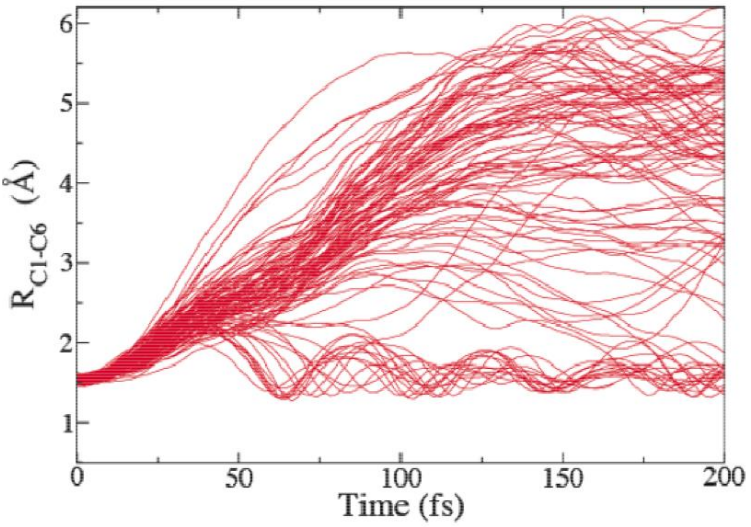


PhysRevLett.120.183003

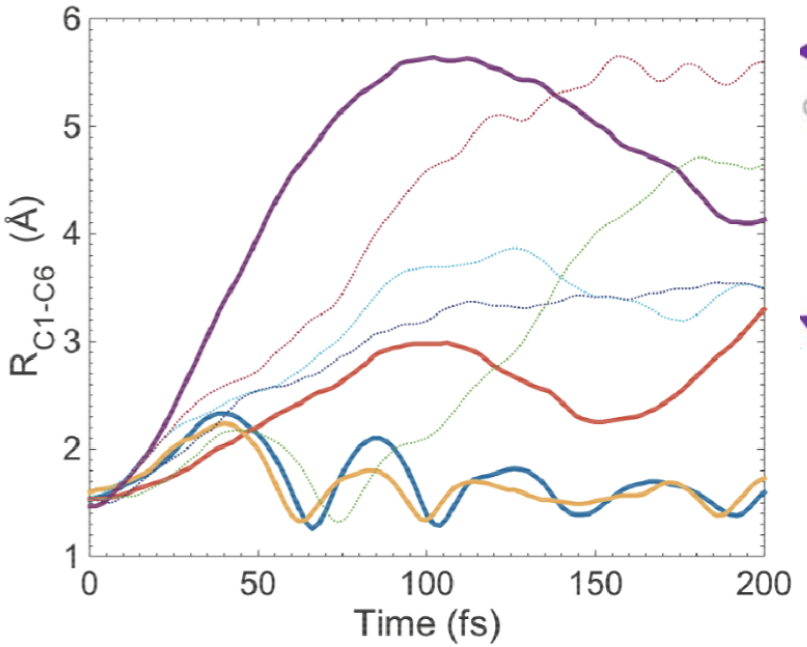
How useful is ultrafast x-ray scattering?

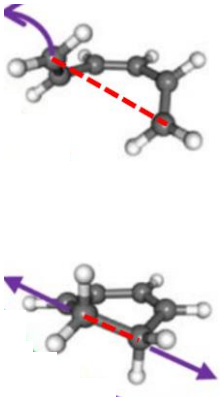
Computational tools: reconstruct dynamics

Trajectories from QM simulations[§]



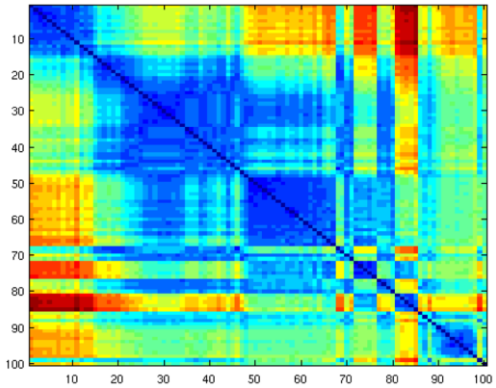
Weighted by experimental data*



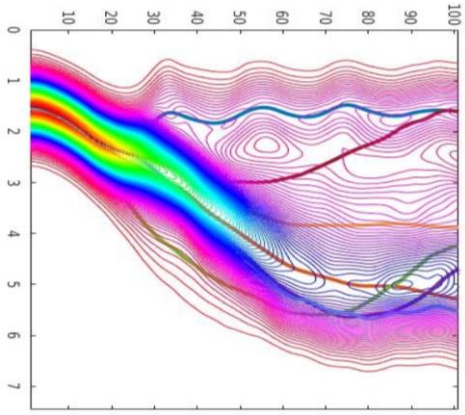


*Quantum yield close to recent CASPT2 simulations

- <RMSD>$_t$ for all trj-pairs
- Clustering algorithm OPTICS (reachability plots)
- 7 clusters



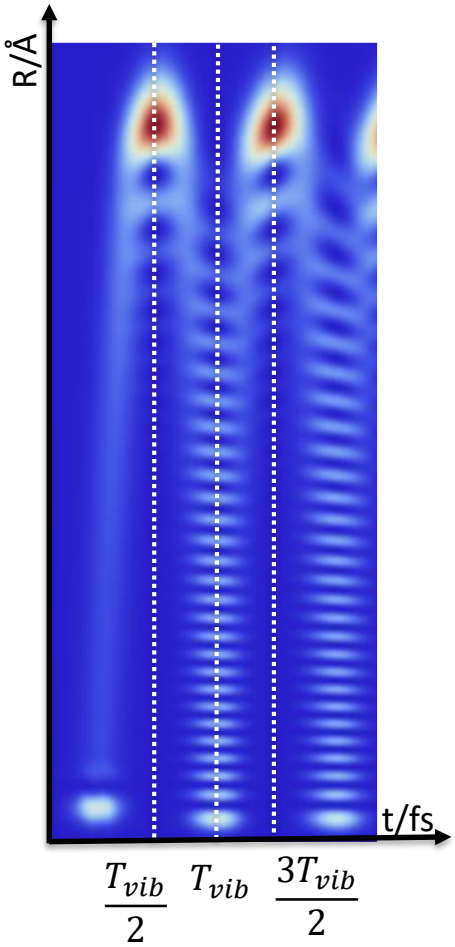
Probability density plot for unweighted simulation



[§]AI-MCE/SA3-CASSCF(6,4)/cc-pVDZ

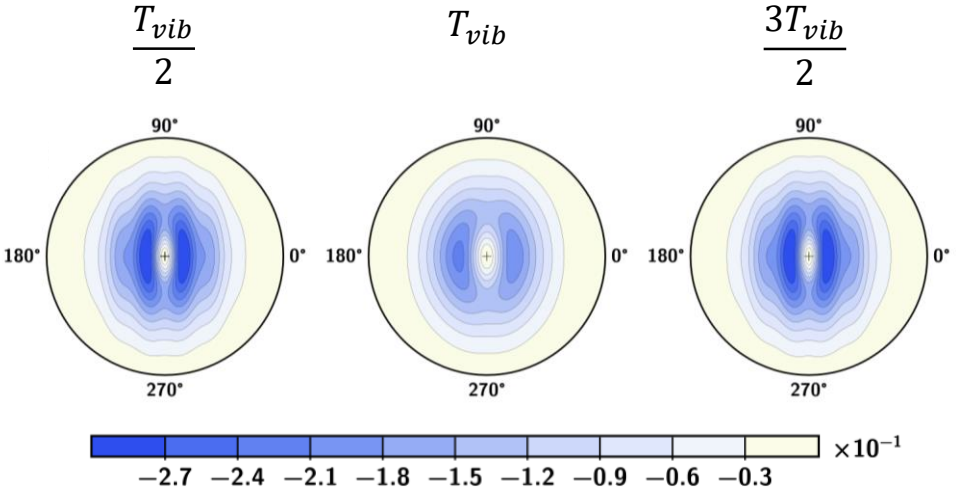
Difference Signal

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



ELASTIC

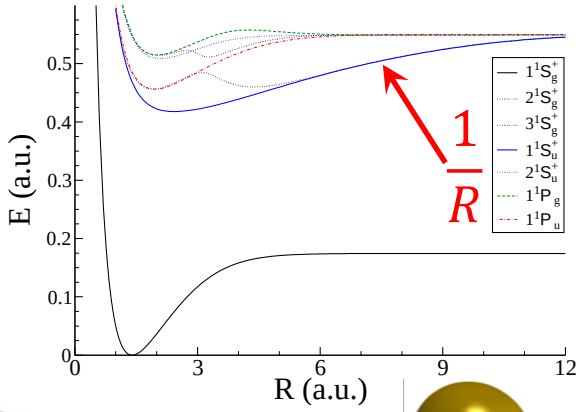
$i = j = f$



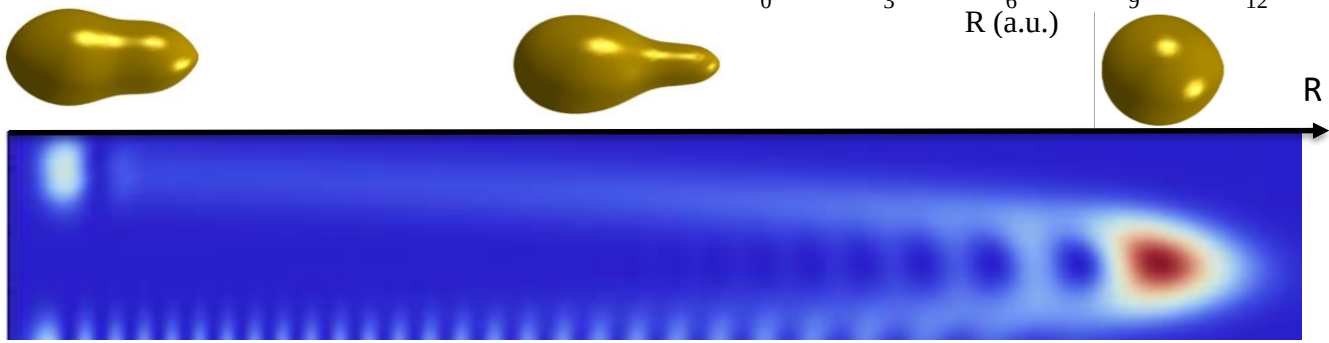
Signal < 0 at all times ⇒ expanded electron density compared to X-state

Changes in signal correspond to changes in e⁻ density

Electron transfer



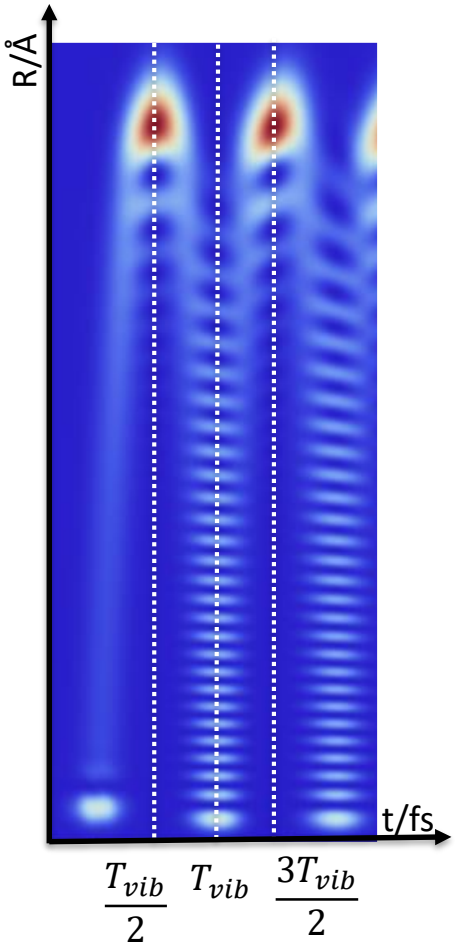
Electron-density iso-surfaces for wavepacket on $B^1\Sigma_u^+$ state



$T_{vib} = 62$ fs

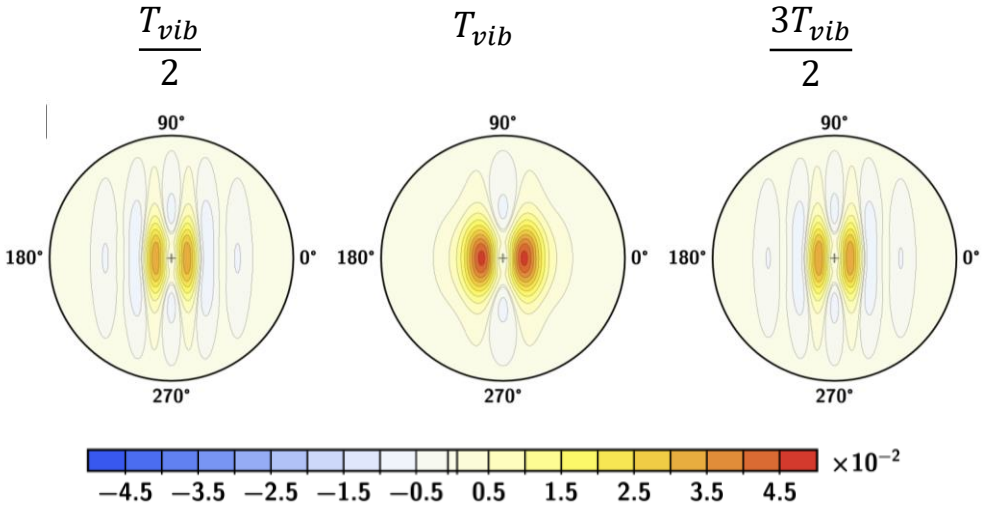
Difference Signal

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



INELASTIC

$$i = j \neq f$$



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

The inelastic component changes with geometry

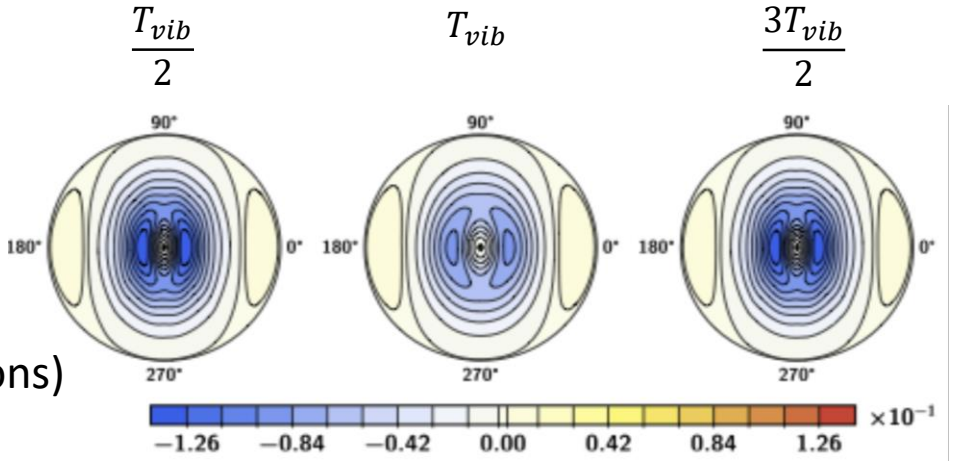
⇒ in contrast to the Independent Atom Model (IAM)

$T_{vib} = 62$ fs

DETECTION WINDOW

TOTAL SCATTERING

(all possible transitions)



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

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

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

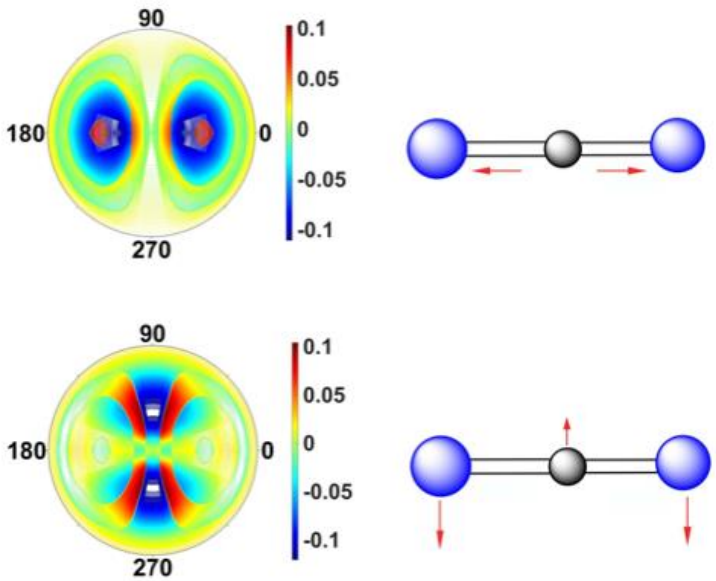
$$\frac{d\sigma}{d\Omega} = \frac{d\sigma_{\mathrm{bg}}}{d\Omega} + \frac{d\sigma_{2e}}{d\Omega} + \frac{d\sigma_{\mathrm{cm}}}{d\Omega}.$$

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

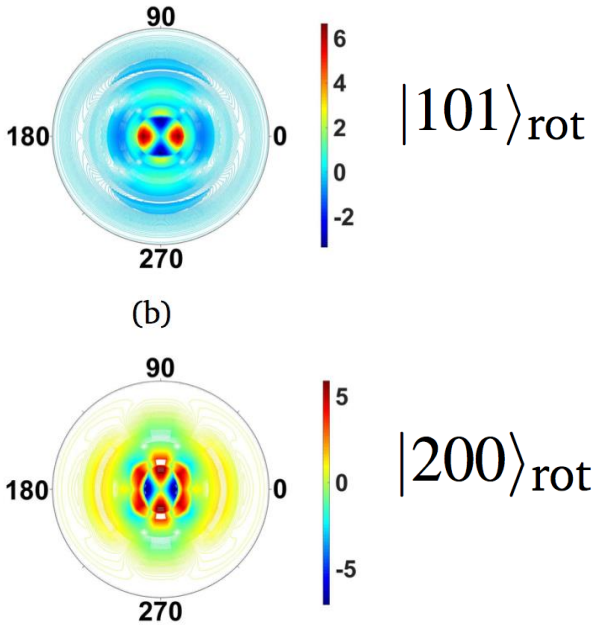
What can we measure?

Elastic scattering:

1. Structure
2. Dynamics
3. Electron density
4. Rotational and vibrational states



CS_2 vibrations



CS_2 rotations

Moreno, Northey, Kirrander PCCP 2017

Northey J. Chem. Phys. 2016

How to calculate matrix elements L_{ij}

1. Ab-initio electronic wfs
2. Matrix-elements analytic (Gaussian basis)

$$f^0(\mathbf{q};\,\bar{\mathbf{R}},\,\alpha) = \mathcal{F}_{\mathbf{r}}[\rho_{\mathrm{tot}}^{(N_{\mathrm{el}})}(\mathbf{r};\,\bar{\mathbf{R}},\,\alpha)](\mathbf{q})$$

Fourier Transform

$$g_s(\mathbf{r}) = \mathcal{N}_s(x-x_s)^{l_s}(y-y_s)^{m_s}(z-z_s)^{n_s}e^{-\gamma_s(\mathbf{r}-\mathbf{r}_s)^2}$$

GTO primitives

$$\mathcal{F}_x[xf(x)](q) = -\imath\frac{d}{dq}\mathcal{F}_x[f(x)](q)$$

Recurrence relation

$$\mathcal{F}_x[g(x;\,l)](q) = \frac{i^l\sqrt{\pi}\,\mathrm{e}^{-q^2/4\gamma}}{2^l\gamma^{(2l+1)/2}}\sum_{p=0}^{l/2}(-1)^p\frac{l!\gamma^p q^{l-2p}}{(l-2p)!p!}$$

Analytic

Northey JCTC 2014 and Moreno PCCP 2017