Ultrafast X-ray Scattering of Molecular Dynamics

Adam Kirrander
University of Edinburgh
XFEL WORKSHOP (Newcastle)
Colleagues & collaborators

University of Edinburgh:
Darren Bellshaw, Nikola Zotev,
Andrés Moreno, Mats Simmermacher,
Kyle Acheson, Gabriella Wallentin,
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
Experiment vs. Theory

Excellent quantitative agreement!
Computational tools: scattering matrix elements from electronic structure calculations

Elastic

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

Inelastic

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

Total

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

Northey et al. JCTC 10 4911 (2014)  
Moreno et al. PCCP 19 19545 (2017)  
Moreno et al. JCTC 15 2836 (2019)
Elastic, inelastic, total X-ray scattering

Moreno et al. PCCP 19 19545 (2017)

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)

\[ I_2 \text{ wavepacket:} \]
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※

* Ishikawa Science **350** 6267 (2015)
§ Minitti PRL **255**501 **114** (2015)

**Küpper PRL **112** 083002 2014**

Complementary data incredibly helpful
Scattering of coherent x-rays

- Quantized x-ray field ($\hat{a}, \hat{a}^\dagger$)
- Non-stationary molecular wavepacket
- Scattering in 1st order perturbation theory

$$\Psi(\vec{r}, \vec{R}, t) = \sum_i^N \chi_i(\vec{R}, t) \varphi_i(\vec{r}; \vec{R})$$

$$\hat{H}_{\text{int}} = \vec{f} \hat{A} + \hat{A}^2$$

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

$$L_{fi}(\vec{q}, \vec{R}) = \langle \varphi_f(\vec{R}) | \hat{L} | \varphi_i(\vec{R}) \rangle$$

$$\hat{L} = \sum_n e^{\text{i}qr_n}$$

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!!
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

Structural dynamics in excited NMM

Anisotropy confirms excited state

$q \rightarrow 0$ signal for TMA


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

How useful is ultrafast x-ray scattering?

PhysRevLett.120.183003
Computational tools: reconstruct dynamics

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

*Quantum yield close to recent CASPT2 simulations

Probability density plot for unweighted simulation

---

5 Al-MCE/SA3-CASSCF(6,4)/cc-pVDZ
Difference Signal

Nuclear probability density on $B^{1}\Sigma_{u}^{+}$

Signal $< 0$ at all times $\Rightarrow$ 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 $> 0 \Rightarrow$ inelastic transitions from B-state more likely

The inelastic component changes with geometry

$\Rightarrow$ in contrast to the Independent Atom Model (IAM)

$T_{vib} = 62\, \text{fs}$
DETECTION WINDOW

TOTAL SCATTERING

(all possible transitions)

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

\[
\Lambda_{ji}(\tilde{q}, \tilde{R}) = \langle \varphi_j(\tilde{R}) | \hat{L}^\dagger \hat{L} | \varphi_i(\tilde{R}) \rangle
\]

\[
\frac{d\sigma}{d\Omega} = \left( \frac{d\sigma}{d\Omega} \right)_\text{Th} W(\Delta \omega) \sum_{ij} \int I(t) \langle \chi_j(t) | \Lambda_{ji}(\tilde{q}, \tilde{R}) | \chi_i(t) \rangle dt,
\]

\[
\frac{d\sigma}{d\Omega} = \frac{d\sigma_{bg}}{d\Omega} + \frac{d\sigma_{2e}}{d\Omega} + \frac{d\sigma_{cm}}{d\Omega}.
\]

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
How to calculate matrix elements $L_{ij}$

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

\[ f^0(q; \overline{R}, \alpha) = \mathcal{F}_r[\rho_{tot}^{(N_{el})}(r; \overline{R}, \alpha)](q) \]

\[ g_s(r) = N_s(x - x_s)^l_s(y - y_s)^m_s(z - z_s)^n_se^{-\gamma_s(r-r_s)^2} \]

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

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