1m structure method: time-resolved x-ray scattering and photoelectron spectroscopy

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4 Oct 2022 group meeting

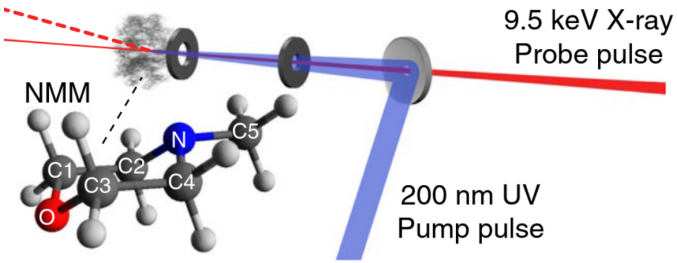

Figure: NMM geometry, and experimental setup.

- 107 surface hopping trajectories (1000 fs), $\sim 10^6$ molecular geometries

B. Stankus, et al. Nature Chem. 11.8 (2019): 716-721.

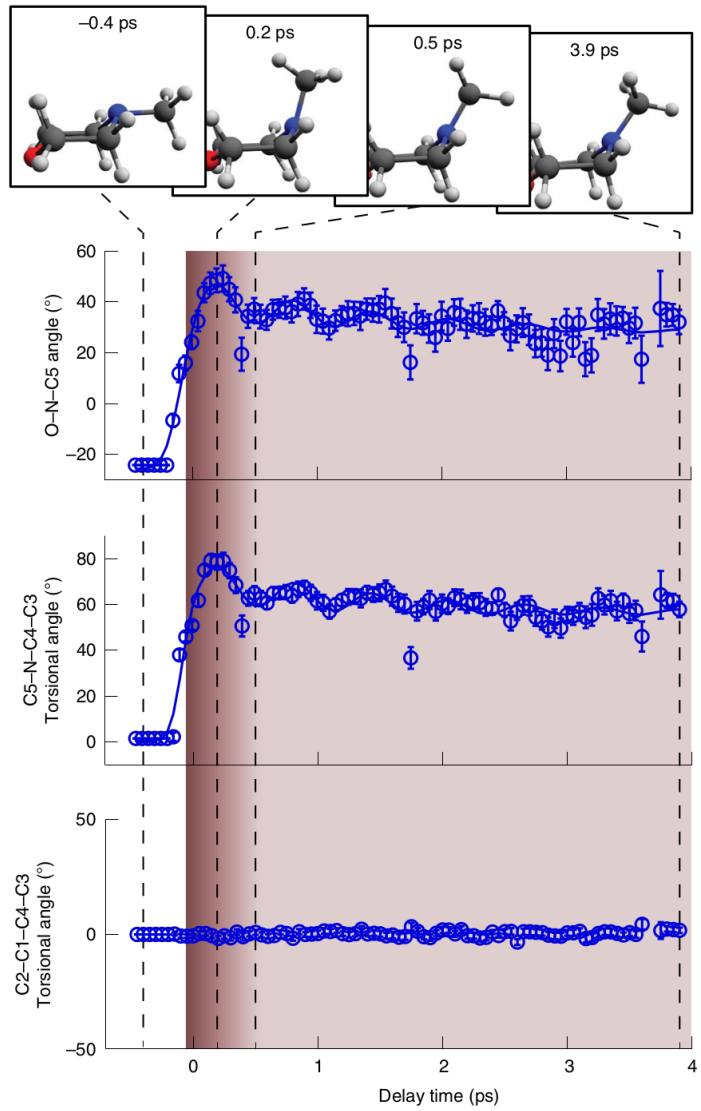

Figure: Time-dependent angle plots following Rydberg excitation.

- 107 surface hopping trajectories (1,000 fs), giving $\sim 10^6$ molecular geometries

Defining structure pool parameters

$$\mu \qquad \sigma_i$$

$$\rho$$

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$$\mu = 0, \text{ e.g. } \mathbf{R}_0$$

[picture of potential energy curve along a bond-distance, + bell curve vibrational distribution]
[and picture of $\mu \neq 0$ situation, shifted bell curve]

Defining structure pool parameters

$$\sigma = \begin{pmatrix} 0.4 \\ 0.2 \\ 0.2 \\ \vdots \\ 0.2 \end{pmatrix} \text{ Å}$$

- some displacements more important than others
- some could be irrelevant $\sigma_i = 0$ (i.e. don't displace at all)

Defining structure pool parameters

$$\rho \propto \text{accuracy} \;/\; \text{resolution}$$
$$\propto N$$
$$\propto 1/\sigma_i$$

NMM previous work

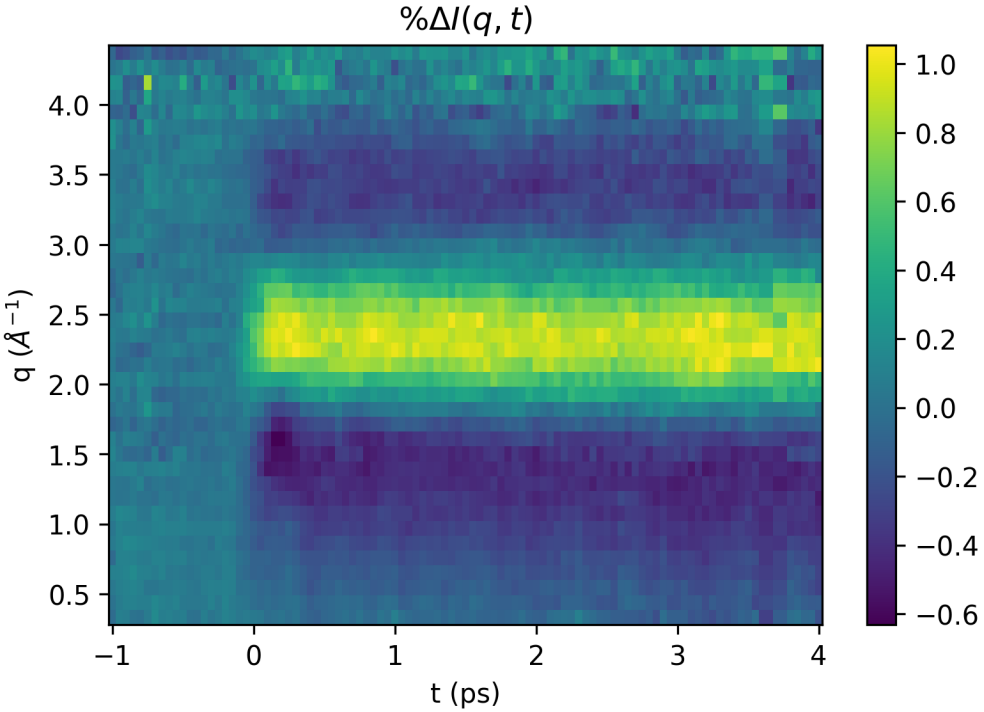

Figure: Time-resolved x-ray scattering percent difference signal for NMM.

- $q = [0.33, 4.37]$ Å^{-1}, (with 39 q-bins)
- Excitation percentage, 5.7%
- Maximum signal difference $\simeq 1\%$

NMM previous work

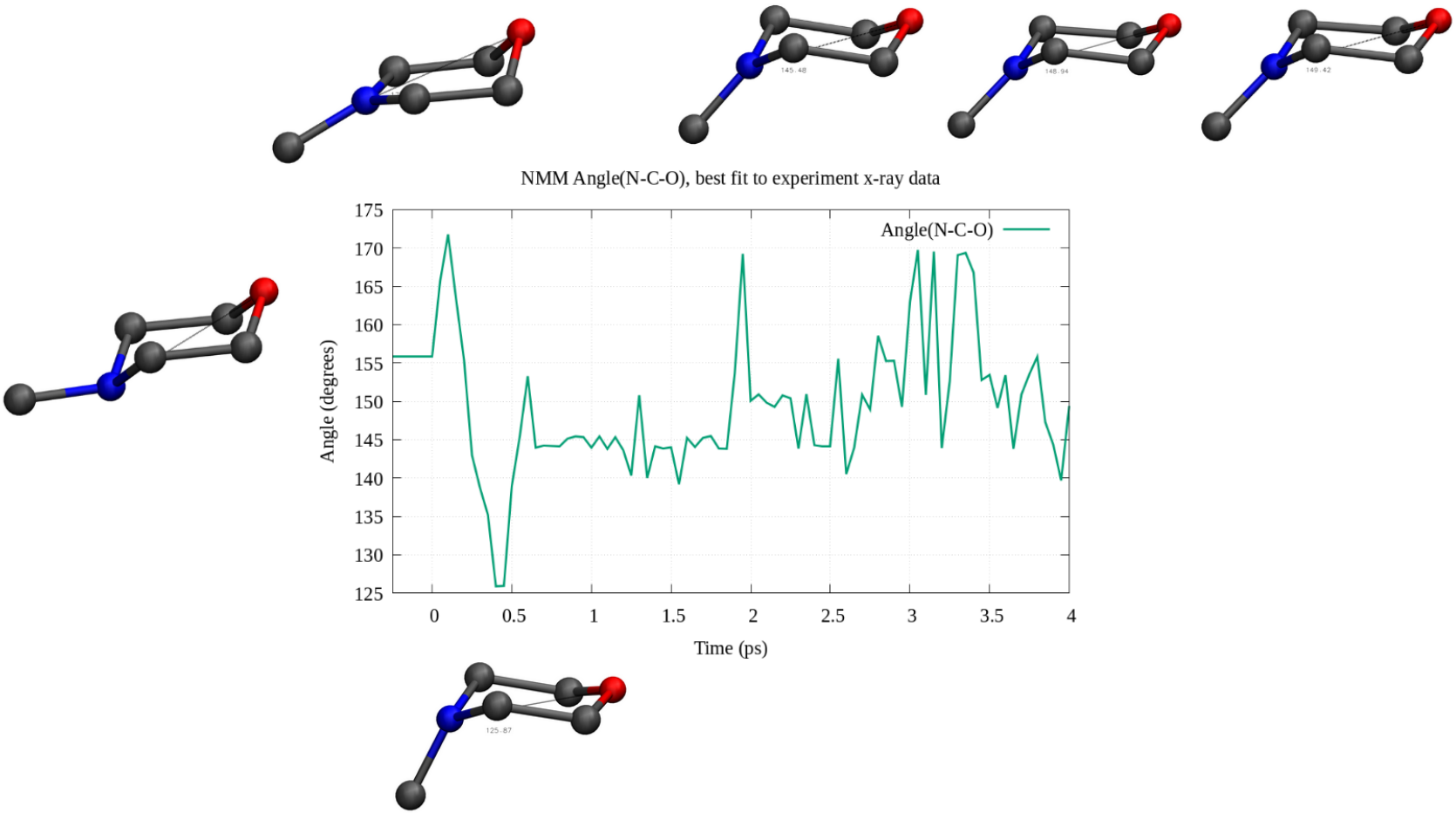

Figure: N-C-O angle, best fit to experiment x-ray data.

Sampling method

The sampling equation for generating the displaced molecular coordinates is,

$$\mathbf{R} = \mathbf{R}_0 + \sum_{i}^{\text{modes}} a_i \mathbf{d}_i \tag{1}$$

with starting geometry $\mathbf{R}_0$, and displacement unit vectors $\mathbf{d}_i$ for each normal mode are obtained from a frequency calculation. The factors a_i are randomly generated within a bell curve centered at $\mu = 0$, and chosen standard deviation, σ.