A general simulated annealing approach to extracting nuclear dynamics from ultrafast x-ray scattering data

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Abstract

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1 Introduction

1m structure method [6]

Some references [7, 6, 4, 5, 1, 3, 2]

2 Method

2.1 Simulated Annealing

The molecular coordinates move iteratively according to,

$$\mathbf{R}_{i+1} = \mathbf{R}_i + T_i \Delta s \sum_{k=0}^{\text{modes}} w_k a_k \hat{d}_k$$

for temperature T_i at iteration i, step-size Δs, displacement unit vectors $\hat{d}_k$, and wavenumbers ω_k for each normal mode. The factors a_k are obtained from a uniform random distribution with range $[-1, 1]$ to allow the molecule unconstrained movement along all its degrees of freedom. The motions are ω-damped by the factor,

$$w_k = \frac{\omega_0}{\omega_k}$$

or

$$w_k = \exp\left(\frac{\omega_0}{\omega_k}\right)$$

for mode wavenumbers $\{\omega_0, \omega_1, \ldots, \omega_n\}$, to avoid oversampling large motions of high frequency modes.

The temperature decreases linearly at iteration i as,

$$T_i = T_0(1 - i/N)$$

for starting temperature $T_0 \in (0, 1]$, and total iterations N.

After each iteration, if the error function χ^2 decreases the iteration is accepted

$$i \to i + 1$$

If not, the iteration can still be accepted with probability,

$$P = T_i$$

which allows the molecule to sometimes travel uphill on the χ^2 surface, thus escape local minima.

3 Algorithm

3.1 current testing version

Assumption: the next best fit is 'nearby' the previous step.

- Start at $\mathbf{R}(t_0)$, e.g. the optimised ground state geometry
  - Start at $\mathbf{R}(t_j)$ and search for $\mathbf{R}(t_{j+1})$
  - Perform N temperature cycles ($T = T_0$), to allow a large search space around $\mathbf{R}(t_j)$
    - Start at the end point of each cycle $\mathbf{R}_i$ to find the next cycle end point $\mathbf{R}_{i+1}$
    - Save $\mathbf{R}_{\text{best}}$, the geometry with the lowest value of χ^2

4 Results

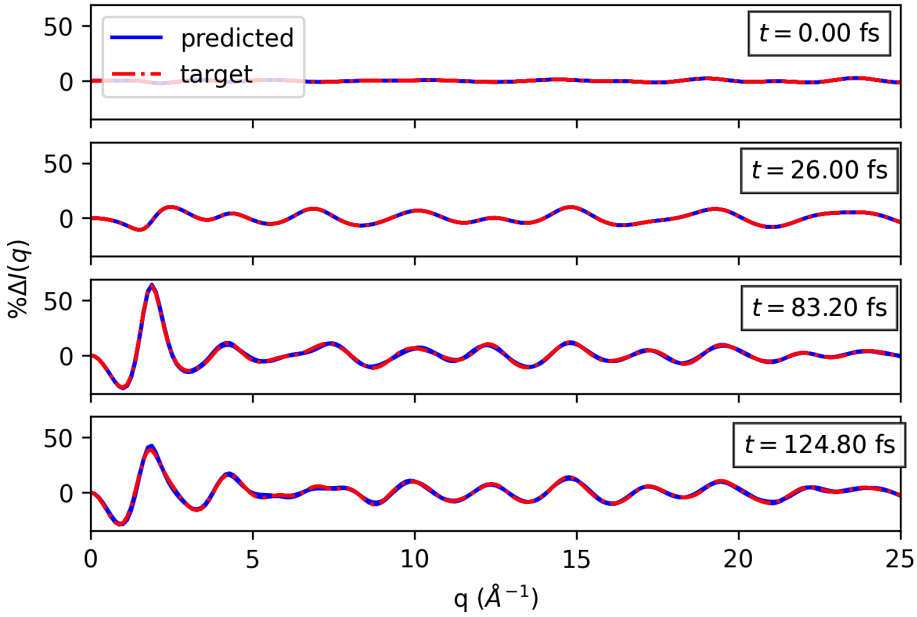
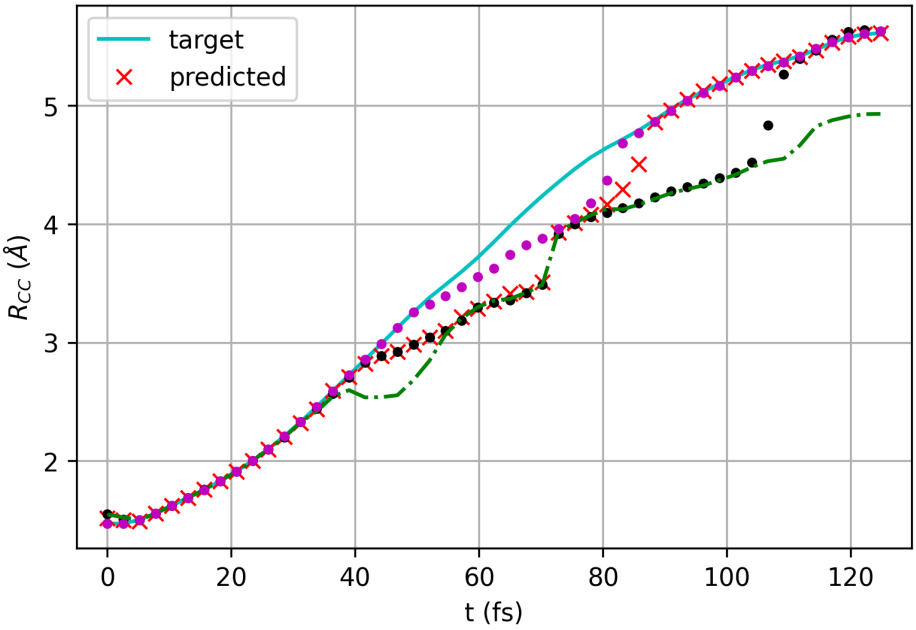
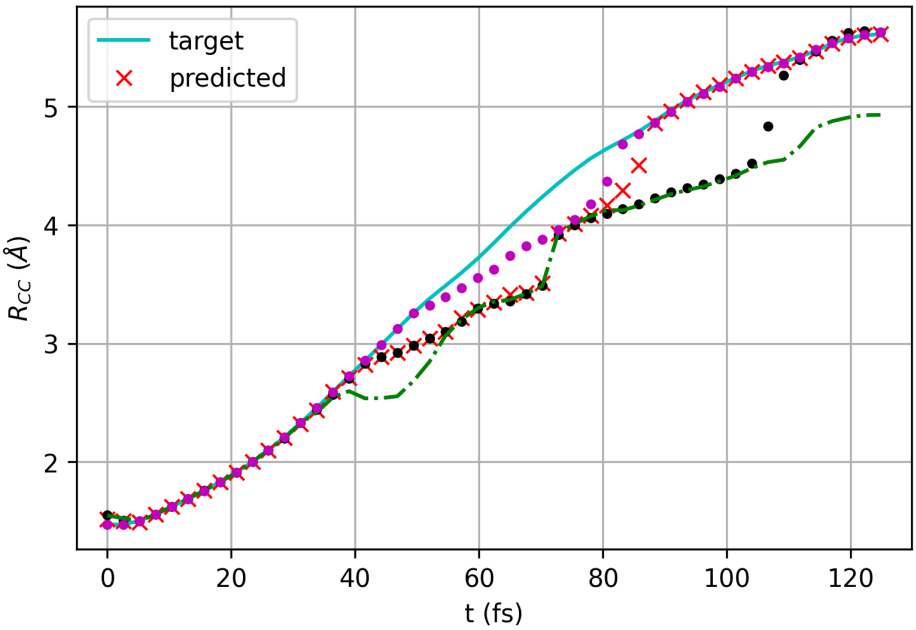


Figure 1: CHD x-ray scattering lineouts.

It seems like $\chi^2 \sim 0.001$ corresponds with R_{CC} matching the target.

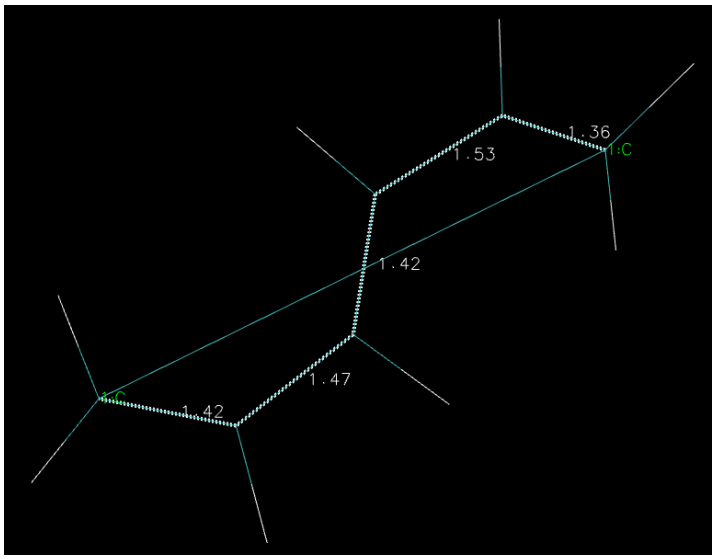


(a) Temperature cycle method: Do not restart from the starting geometry at each cycle, but start at the last geometry of the previous cycle.

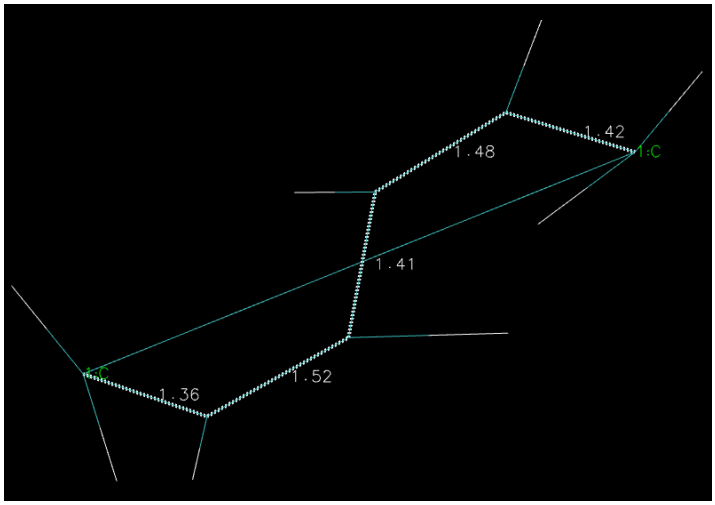


(b) Robust restart method: Restart from a slight perturbation of the starting geometry at each cycle, and use 5x the amount of steps per cycle.

Figure 2: CHD ring-opening C-C distance, R_{CC}. The target is from a surface hopping trajectory. Predictions are using $q_{\max} = 25.0$ Å^{-1}.



(a) Target.



(b) Predicted.

Figure 3: CHD target and predicted, showing all C-C bond-lengths.

References

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[4] Brian Stankus, Haiwang Yong, Nikola Zotev, Jennifer M Ruddock, Darren Bellshaw, Thomas J Lane, Mengning Liang, Sébastien Boutet, Sergio Carbajo, Joseph S Robinson, et al. Ultrafast x-ray

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[6] Haiwang Yong, Andrés Moreno Carrascosa, Lingyu Ma, Brian Stankus, Michael P Minitti, Adam Kirrander, and Peter M Weber. Determination of excited state molecular structures from time-resolved gas-phase x-ray scattering. *Faraday Discussions*, 228:104–122, 2021.

[7] Haiwang Yong, Jennifer M Ruddock, Brian Stankus, Lingyu Ma, Wenpeng Du, Nathan Goff, Yu Chang, Nikola Zotev, Darren Bellshaw, Sébastien Boutet, et al. Scattering off molecules far from equilibrium. *The Journal of Chemical Physics*, 151(8):084301, 2019.