Inversion of Ultrafast X-ray Scattering with Dynamics Constraints

Link:
[Link to publication record in Edinburgh Research Explorer](#)

Document Version:
Peer reviewed version

Inversion of Ultrafast X-ray Scattering with Dynamics Constraints

Martin Asenov[*]
School of Informatics,
University of Edinburgh, UK

Nikola Zotev[*]
EaStCHEM,
School of Chemistry,
University of Edinburgh, UK

Subramanian Ramamoorthy
School of Informatics,
University of Edinburgh, UK

Adam Kirrander
Centre for Science at Extreme
Conditions and EaStCHEM,
School of Chemistry,
University of Edinburgh, UK

Abstract

Studying molecular transformations on an ultrafast time-scale is vital for understanding chemical reactivity, but interpreting the relevant experiments is challenging because chemical dynamics need to be inferred from an indirect and often incomplete sequence of observations. We propose a method that uses a form of variational recurrent neural network to tackle the problem of inversion of time-resolved X-ray scattering from molecules recorded on a detector. By training our model with molecular trajectories, dynamic correlations and constraints associated with molecular motion can be learned. We show this leads to a more accurate inversion from a detector signal to atom-atom distances, compared to the traditional frame-by-frame approach.

1 Introduction

Understanding the rapid transformations in the molecular structure during a reaction has profound implications for our ability to control chemistry – from designing new materials and drugs to controlling reaction products and intermediates. Ultrafast X-ray Scattering (UXS) is one of the few techniques, which allows a direct time-resolved imaging of these structural changes. While the sequence of X-ray scattering images collected on a detector in a typical UXS experiment (Figure 1) bears naïve resemblance to motion pictures, "inverting" it to extract the molecular motion is not straightforward.

In this work, we focus on the important case of a dilute gas phase which is in a thermal equilibrium before triggering the molecular motion so that the scattering signal is free from intermolecular effects [1, 2]. We approach the isotropic component of the signal, which encodes the internal molecular motion via the full set of atom-atom distances [3, 4, 5]. Physically, the pattern on the detector at any given time is connected to the electron density of the molecule, and there exists a mathematical relation between the two based on the Fourier transform [6].

In theory, taking any individual detector snapshot and applying an inverse sine-transform gives direct access to the distribution of atom-atom distances in the molecule at this time. In practice, the finite size of the detector reduces the available data and renders the procedure impractical. To overcome
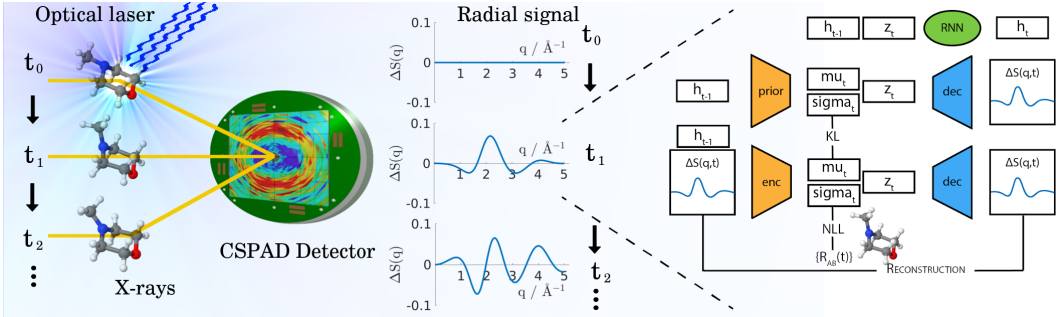
---

[*]Equal contribution

Figure 1: (Left) Schematic of a prototypical UXS experiment performed at an X-ray Free Electron Laser facility. After excitation with an optical laser, the molecular structure begins to evolve. Ultrashort X-ray pulses are used to probe the dynamics at a series of time points. The isotropic, radial, part of the signal is a function of the magnitude of the scattering vector, q, which measures the distance from the centre of the detector. Here, we represent the signal at time t as a fractional signal change, $\Delta S(q, t)$, with respect to the signal at t_0. (Right) Inference and generation process at a given time step, the same process applies for previous and future time steps. We aim to decode the atom-atom distances, $R_{AB}(t)$, from detector images, $\Delta S(q, t)$.

this issue, theoretical models are often fitted to the experimental signal to elucidate the dynamics. For example, the scattering patterns for a set of plausible molecular geometries is first calculated theoretically, and then fitted to the experimental data to determine the set of atom-atom distances that best reproduces the experimental signal on the detector at time t in a χ^2 sense [7, 8, 9].

Importantly, such methods are applied on a frame-by-frame basis and, thus, ignore the time-dependence of the experimental data. In this article, we propose a model based on [10], where the inference of the atom-atom distances from the detector signal can be learned from quantum molecular dynamics trajectories, so that the time-dependence is accounted for. We demonstrate that this outperforms the traditionally used frame-by-frame inversion on three different molecules.

2 Methods

2.1 Molecular dynamics and X-ray scattering simulations

We utilise simulated data to train, validate and test our model, which is done separately for each molecule. We use previously published full-dimensional quantum molecular dynamics (MD) simulations for three molecules – N-Methylmorpholine (NMM) [8], carbon disulfide (CS_2) [13], and ethene (C_2H_4) [14], which are are summarised in Table 1. When taken collectively, the full set of trajectories for a given molecule gives a statistical representation of the molecular wave packet. Here, we use

Table 1: Quantum molecular dynamics simulations used to train, validate and test our model. The table reports only the number of intermediate time steps used in our model. The numbers in brackets are the trajectories that do not show dissociation. All three simulations use CASSCF *ab initio* level of theory.

Molecule	NMM	CS_2	C_2H_4
Method	SHARC	SHARC [11]	AI-MCE [12]
Electronic states	X/3s/3p	S_0–S_3, T_1–T_4	S_0–S_2
Simulated time	1 ps	1 ps	150 fs
Time steps	201	201	151
# Train	85	753	800
# Val	11	94 (26)	100 (82)
# Test	11	95 (32)	100 (87)

them independently as if they represent different modes of motion that the molecule may exhibit. Thus, our approach ignores phenomena such as wave packet width, dispersion and bifurcation. Nonetheless, the trajectories obey the physical principles of propagation (energy conservation, continuity, *etc.*) and, thus, encode the relevant physics of molecular motion. This is crucial because, as detailed in the introduction, the inversion problem is under-determined – the simulated trajectories provide meaningful constraints on the type of motion. It should also be pointed out that complexity

2

of nuclear motion necessitates a case-by-case approach [15], which means that the network needs to be trained on the specific molecule under consideration, and the inversion of real-life data would only be as good as the simulated trajectories used to train the model.

We also use synthetic detector images calculated from these trajectories as follows.[2] To a first approximation, the electrons in the molecule can be considered to be bound to the atomic nuclei, the so called Independent Atom Model (IAM), in which case the elastic X-ray scattering recorded on the detector is proportional to the Debye scattering formula:

$$I(q,t) = \sum_A |f_A(q)|^2 + \sum_A \sum_{B \neq A} f_A(q) f_B(q) \frac{\sin(qR_{AB}(t))}{qR_{AB}(t)}, \qquad \Delta S(q,t) = \frac{I(q,t) - I(t,t_0)}{I(q,t_0)}. \tag{1}$$

In Eq. (1), the scattering intensity, $I(q,t)$, is function of the delay time between optical laser and the X-rays, t, and the magnitude of the scattering vector, q. $f_A(q)$ and $f_B(q)$ are tabulated quantities. $R_{AB}(t)$ denotes the interatomic distance between atoms A and B. In addition to the terms in Eq. (1), the intensity on the detector, $I(q,t)$, has a contribution from inelastic X-ray scattering, which to a first approximation is constant that does not evolve with time. To ensure that the approach is valid beyond the approximations implied in the IAM, our CS_2 data set used a more advanced method to calculate the scattering signal directly from the *ab initio* electron density of the molecule [16].

2.2 Inversion with dynamics constraints

We are interested in recovering all atomic distances as a function of time, $R_{AB}(t)$, from a sequence of detector images $\Delta S(q,t)$. Neural network based approaches have been explored in simulating molecular dynamics [17, 18] as well as inverse problems in challenging physics domains such as reservoir simulations [19], light scattering by nanoparticles [20], deblending galaxy images [21] and fluid flow prediction [22] and many more [23]. We use the vid2param method proposed in [10], where the parameters of a bouncing ball dynamics system are encoded from videos, using a variational recurrent neural network (VRNN) [24]. The VRNN model extends a standard variational autoencoder (VAE), by introducing an RNN encoding the dynamics of the latent space and conditioning the encoder and decoder part of the VAE on the hidden state of that RNN. An additional negative log-likelihood is used to enforce consistency between part of the latent space and the parameters of interest.

The model allows the detector image at each time step, together with the dynamics carried by the recurrent part of the model, to be encoded into a latent space. Part of that latent space is simultaneously trained to represent the different distances in the given trajectory. As such, the model can account for time dependencies of the detector images and atomic distances, unlike traditional frame-by-frame methods, while also interpolating between the training examples.

3 Results and Discussion

As two of the molecules exhibit dissociation of the molecule structure, in two of the simulations we explicitly separate out this hard-to-tackle phenomenon. Therefore, we perform a set of five experiments – all NMM, all CS_2, all C_2H_4, and separately with only the dissociation-free CS_2 and C_2H_4 trajectories. We use a frame-by-frame χ^2 structural fitting as a baseline. More specifically, at each time step, we compute the sum of squared residuals (SSR) between the current detector image and all the reference detector images from the training data. We then assign the atom-atom distances from that reference detector image that has the lowest SSR.

3.1 Nuclear geometry recovery

We evaluate how well we can recover the true underlying molecular geometry from a sequence of detector images by using a mass-weighted root-mean-square deviation (RMSD) from the ground truth. We observe that in all but one experiment the proposed method outperforms the baseline method (Figure 2a). Our model is able to *capture time dependencies and constraints associated with movements of atoms*. As exemplified in Figure 2c, the vid2param RMSD values for most individual

---

[2]Datasets, expanded results and source code can be seen at https://sites.google.com/view/mlscattering/
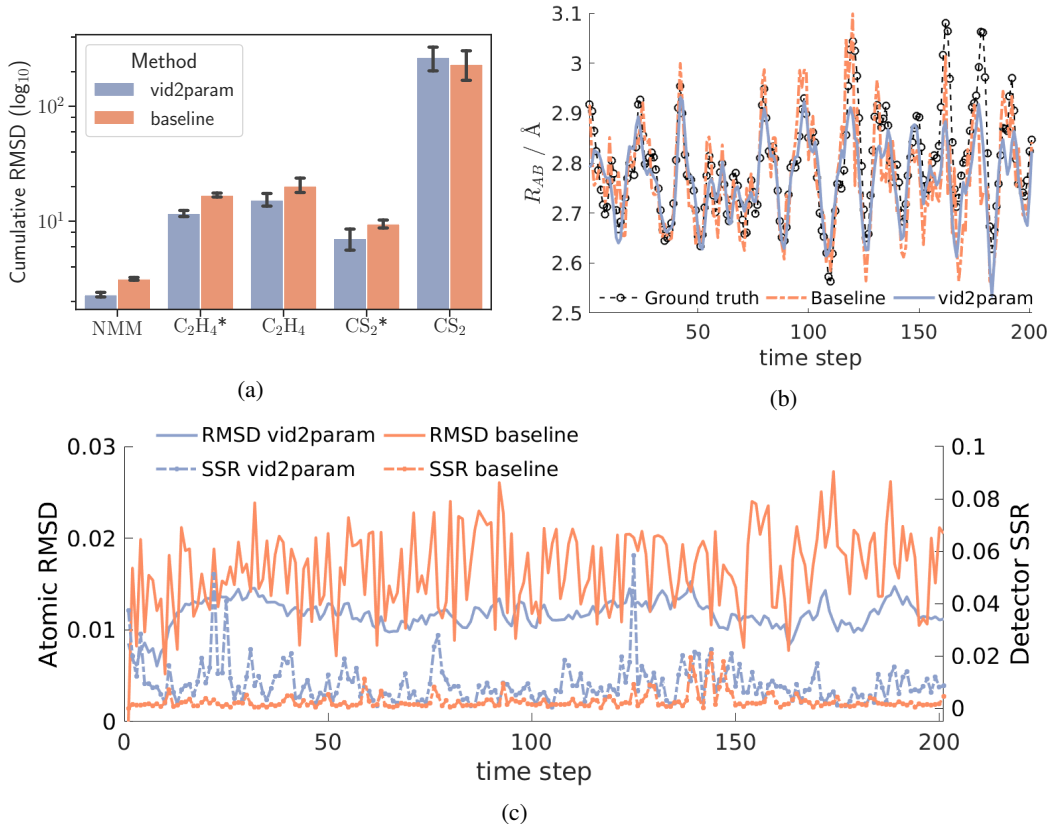
3

(a)

(b)

(c)

Figure 2: (2a) Sum of atomic RMSD values for all time steps and all trajectories in the test part of the five data sets. The asterisk (*) denotes the data sets where trajectories with dissociation has been filtered out. (2b) O−N distance in a single NMM trajectory. (2c) RMSD and sum of squared residuals (SSR) as a function of time step for the baseline and vid2param methods.

time points are indeed below the baseline. Importantly, the vid2param exhibits much smoother behaviour compared to the large variations with time seen in the baseline. This is a manifestation of the fact that different time points are correlated. The smooth changes in the RMSD imply that the evolution of the molecular structure is also smooth, as expected physically.

Beyond the RMSD metric, the quality of the inversion of individual atom-atom distances depends on two factors. Physically, X-ray scattering is dominated by atoms with many electrons, hence, the detector signal has vanishing contributions from light atoms such as Hydrogen. Accurate estimates of the distances between such atoms are not possible even with our model. However, we noticed that vid2param tends to infer the correct oscillation periods, presumably, because of the correlation with the motion of heavier atoms. The detector signal also has almost no contribution from atoms that are far away (see Eq. 1). While sometimes correlated motion can ensure that these distances are still adequately inferred, the process of dissociation possesses a challenge because coherence between the fragments is lost quickly. We believe this is the reason why our experiment with C_2H_4 where dissociation occurs fails against the baseline method. In the case, of relatively heavy atoms and no dissociation, both vid2param and the baseline method perform quite well as illustrated on Figure 2b.

3.2 Analytic reconstruction of detector images

In this set of experiments, we evaluate how well the detector image can be *analytically* reconstructed from the estimated set of atomic distances using Eq. (1). This gives us a second metric which is not based directly on the molecular geometry but on its scattering fingerprint. A typical SSR between the ground truth and the reconstructed detector is illustrated also on Figure 2c. It is important to note that we try to reconstruct only the *visible* part of the detector – the part of the signal that is not detected, i.e. at large values of q, still contains vital information.

4

We observe that the baseline outperforms the proposed model as seen in Figure 2c, which at first may seem counter-intuitive. However, given the limited information in the detector image, even an exact match of the visible part of the signal at any given time does not guarantee a perfect estimate for the molecular structure via the atomic separations. Unlike the baseline method, vid2param learns atomic distances and *motion* constraints from previous time points, hence, producing a better estimate for the molecular structure without producing a perfect fit for the visible part of the detector image. This again suggests that because of the limited information in a single detector image, it is useful to incorporate time dependencies in the process of inferring the atomic distances, to carry out constraints and information from previous time steps.

4   Conclusion

This paper presents a method for time-dependent inference of atom-atom distances in molecules from UXS data. We perform experiments with three molecules against a standard frame-by-frame structural fitting. We found that due to the limited information present in a single detector image, it is beneficial to include and reason about molecular motion from the entire time-series of collected images. In the future, it will be interesting to explore if similar methods are suitable for inferring electronic states and treating the motion fully quantum mechanically.

Broader Impact

In this article, we address the issue of how to unravel the evolution of molecular structure given a time-series of detector images generated by a novel experimental technique called Ultrafast X-ray Scattering (UXS). While still in its early days, UXS has shown enormous capacity to elucidate fundamental questions in chemistry such as how molecules move, how bonds between atoms are broken or formed, and even how electrons may change their position inside molecules. Nevertheless, there are still big gaps in our ability to analyse and interpret such experiments. We believe that the method presented here addresses a major limitation in the current way of extracting information from UXS data, thus improving our ability to unravel chemical dynamics.

Inverse problems are common beyond UXS. Recent advances in light and electron sources have opened the door for a plethora of experimental techniques for imaging ultrafast process in chemistry. While they are all based on different physics, the fundamental setting is similar – the output from the experiment is a series of images (spectra, diffraction patterns, etc.), and one aims to extract from it a given dynamic parameter that describes the changes that occurred in the molecule (bond lengths, transitional energies, fragment velocities, etc.). Given the similarity, we are confident that our method can find direct applications to such experimental techniques, which are currently at the forefront of experimental physical chemistry.

Acknowledgment

References

[1] Haiwang Yong, Nikola Zotev, Jennifer M. Ruddock, Brian Stankus, Mats Simmermacher, Andrés Moreno Carrascosa, Wenpeng Du, Nathan Goff, Yu Chang, Darren Bellshaw, Mengning Liang, Sergio Carbajo, Jason E. Koglin, Joseph S. Robinson, Sébastien Boutet, Michael P. Minitti, Adam Kirrander, and Peter M. Weber. Observation of the molecular response to light upon photoexcitation. *Nature Communications*, 11(1):1–6, May 2020.

[2] M. P. Minitti, J. M. Budarz, A. Kirrander, J. S. Robinson, D. Ratner, T. J. Lane, D. Zhu, J. M. Glownia, M. Kozina, H. T. Lemke, M. Sikorski, Y. Feng, S. Nelson, K. Saita, B. Stankus, T. Northey, J. B. Hastings, and P. M. Weber. Imaging Molecular Motion: Femtosecond X-Ray Scattering of an Electrocyclic Chemical Reaction. *Physical Review Letters*, 114(25), 2015.

[3] U Lorenz, K B Møller, and N E Henriksen. On the interpretation of time-resolved anisotropic diffraction patterns. *New Journal of Physics*, 12(11):113022, 2010.

[4] M. Ben-Nun, Jianshu Cao, and Kent R. Wilson. Ultrafast x-ray and electron diffraction: Theoretical considerations. *The Journal of Physical Chemistry A*, 101(47):8743, Nov 1997.

[5] J. Spencer Baskin and Ahmed H. Zewail. Oriented Ensembles in Ultrafast Electron Diffraction. *ChemPhysChem*, 7(7):1562–1574, 2006.

[6] Ulf Lorenz, Klaus B. Møller, and Niels E. Henriksen. Theory of time-resolved inelastic x-ray diffraction. *Physical Review A*, 81(2), 2010.

[7] Jie Yang, Xiaolei Zhu, J. Pedro F. Nunes, Jimmy K. Yu, Robert M. Parrish, Thomas J. A. Wolf, Martin Centurion, Markus Gühr, Renkai Li, Yusong Liu, Bryan Moore, Mario Niebuhr, Suji Park, Xiaozhe Shen, Stephen Weathersby, Thomas Weinacht, Todd J. Martinez, and Xijie Wang. Simultaneous observation of nuclear and electronic dynamics by ultrafast electron diffraction. *Science*, 368(6493):885–889, 2020.

[8] Brian Stankus, Haiwang Yong, Nikola Zotev, Jennifer M. Ruddock, Darren Bellshaw, Thomas J. Lane, Mengning Liang, Sébastien Boutet, Sergio Carbajo, Joseph S. Robinson, Wenpeng Du, Nathan Goff, Yu Chang, Jason E. Koglin, Michael P. Minitti, Adam Kirrander, and Peter M. Weber. Ultrafast X-ray scattering reveals vibrational coherence following Rydberg excitation. *Nature Chemistry*, 11(8):716–721, 2019.

[9] Tadahiko Ishikawa, Stuart A. Hayes, Sercan Keskin, Gastón Corthey, Masaki Hada, Kostyantyn Pichugin, Alexander Marx, Julian Hirscht, Kenta Shionuma, Ken Onda, Yoichi Okimoto, Shin-ya Koshihara, Takashi Yamamoto, Hengbo Cui, Mitsushiro Nomura, Yugo Oshima, Majed Abdel-Jawad, Reizo Kato, and R. J. Dwayne Miller. Direct observation of collective modes coupled to molecular orbital–driven charge transfer. *Science*, 350(6267):1501–1505, 2015.

[10] Martin Asenov, Michael Burke, Daniel Angelov, Todor Davchev, Kartic Subr, and Subramanian Ramamoorthy. Vid2param: Modeling of dynamics parameters from video. *IEEE Robotics and Automation Letters*, 5(2):414–421, 2019.

[11] Sebastian Mai, Philipp Marquetand, and Leticia González. Nonadiabatic dynamics: The SHARC approach. *WIREs Computational Molecular Science*, 8(6):e1370, 2018.

[12] Dmitrii V. Shalashilin. Multiconfigurational Ehrenfest approach to quantum coherent dynamics in large molecular systems. *Faraday Discussions*, 153(0):105–116, 2011.

[13] Darren Bellshaw, Daniel A. Horke, Adam D. Smith, Hannah M. Watts, Edward Jager, Emma Springate, Oliver Alexander, Cephise Cacho, Richard T. Chapman, Adam Kirrander, and Russell S. Minns. Ab-initio surface hopping and multiphoton ionisation study of the photodissociation dynamics of CS2. *Chemical Physics Letters*, 683:383–388, 2017.

[14] Adam Kirrander, Kenichiro Saita, and Dmitrii V. Shalashilin. Ultrafast X-ray Scattering from Molecules. *Journal of Chemical Theory and Computation*, 12(3):957–967, 2016.

[15] R. J. Dwayne Miller. Ultrafast imaging of photochemical dynamics: roadmap to a new conceptual basis for chemistry. *Faraday Discussions*, 194:777–828, 2016.

[16] Nikola Zotev, Andrés Moreno Carrascosa, Mats Simmermacher, and Adam Kirrander. Excited Electronic States in Total Isotropic Scattering from Molecules. *Journal of Chemical Theory and Computation*, 16(4):2594–2605, 2020.

[17] Sun-Ting Tsai, En-Jui Kuo, and Pratyush Tiwary. Learning molecular dynamics with simple language model built upon long short-term memory neural network. *arXiv preprint arXiv:2004.12360*, 2020.

[18] Samuel S Schoenholz and Ekin D Cubuk. End-to-end differentiable, hardware accelerated, molecular dynamics in pure python. *Machine Learning for Physical Sciences Workshop, Advances in Neural Information Processing Systems*, 2019.

[19] Vivek Sivaraman Narayanaswamy, Jayaraman J Thiagarajan, Rushil Anirudh, Fahim Forouzanfar, Peer-Timo Bremer, and Xiao-Hui Wu. Designing deep inverse models for history matching in reservoir simulations. In *Machine Learning for Physical Sciences Workshop, Advances in Neural Information Processing Systems*, 2019.

[20] John Peurifoy, Yichen Shen, Li Jing, Yi Yang, Fidel Cano-Renteria, Brendan G DeLacy, John D Joannopoulos, Max Tegmark, and Marin Soljačić. Nanophotonic particle simulation and inverse design using artificial neural networks. *Science advances*, 4(6):eaar4206, 2018.

[21] Francois Lanusse, Peter Melchior, and Fred Moolekamp. Hybrid physical-deep learning model for astronomical inverse problems. *Machine Learning for Physical Sciences Workshop, Advances in Neural Information Processing Systems*, 2019.

[22] N Benjamin Erichson, Michael Muehlebach, and Michael W Mahoney. Physics-informed autoencoders for lyapunov-stable fluid flow prediction. *Machine Learning for Physical Sciences Workshop, Advances in Neural Information Processing Systems*, 2019.

[23] Giuseppe Carleo, Ignacio Cirac, Kyle Cranmer, Laurent Daudet, Maria Schuld, Naftali Tishby, Leslie Vogt-Maranto, and Lenka Zdeborová. Machine learning and the physical sciences. *Reviews of Modern Physics*, 91(4):045002, 2019.

[24] Junyoung Chung, Kyle Kastner, Laurent Dinh, Kratarth Goel, Aaron C Courville, and Yoshua Bengio. A recurrent latent variable model for sequential data. In *Advances in Neural Information Processing Systems*, pages 2980–2988, 2015.