Electronic Supplementary Information for Imaging of femtosecond bond breaking and charge dynamics in ultracharged peptides

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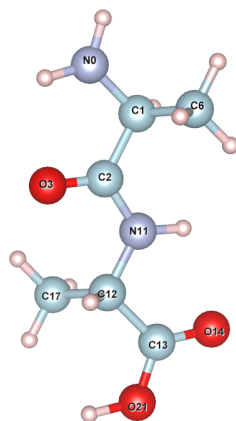
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Results of bond-integrity, Hirshfeld charge, diffraction simulations and the analysis.
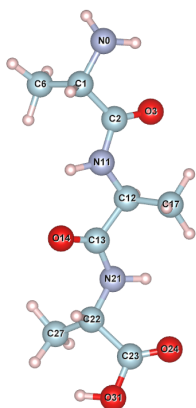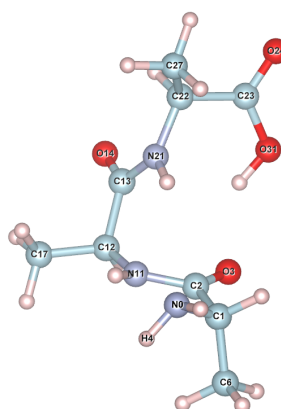
A. Bond-integrity
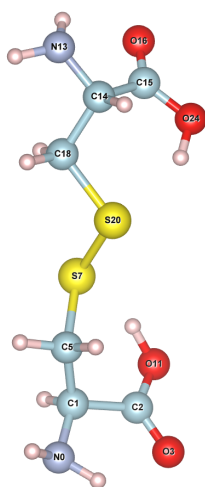
(a) Cystine.

(b) Dialanine.

(c) Trialanine.

(d) Alpha helix conformation of trialanine.

Figure 1: The four biomolecules studied. The numbering of the atoms is referenced throughout the entire document.
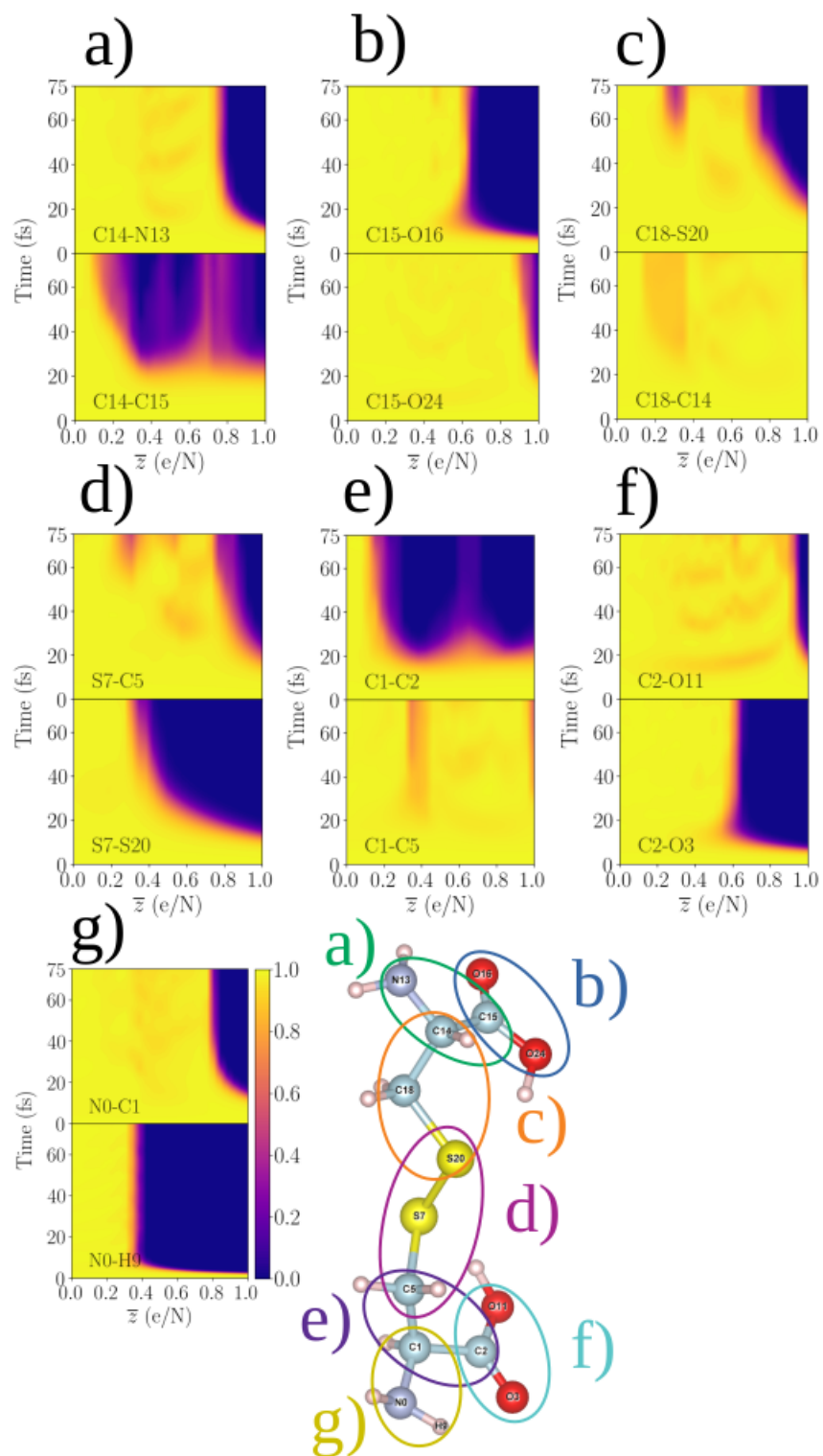
Figure 2: Bond integrity as a function of ionization $\bar{z}$, as described by equation (1) in the manuscript, for the majority of the bonds in cystine.
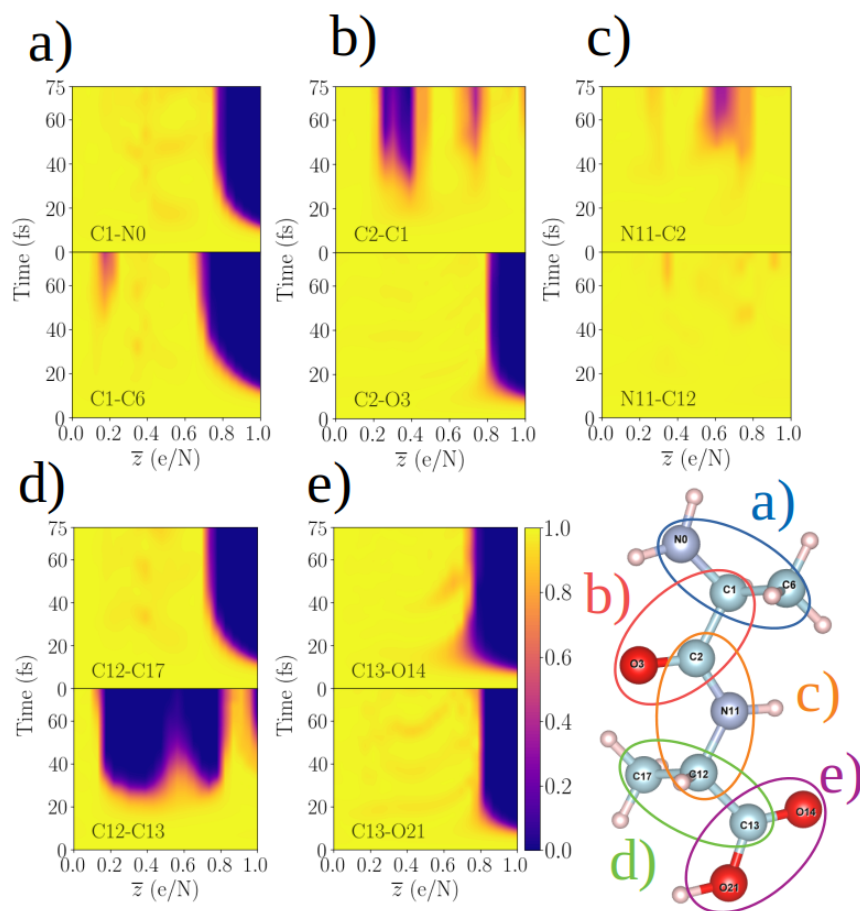
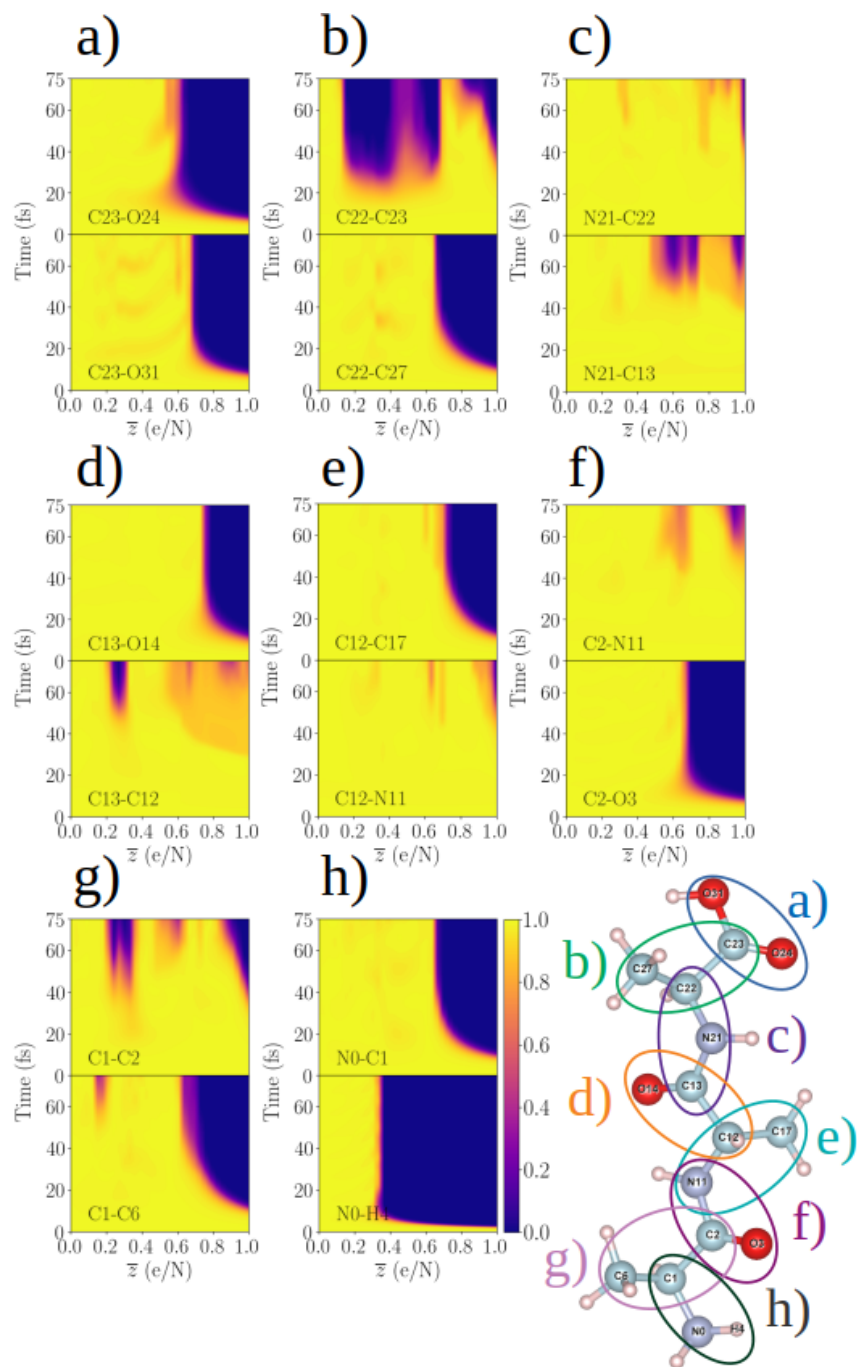Figure 3: Bond integrity for the majority of the bonds in dialanine.

Figure 4: Bond integrity for the majority of the bonds in trialanine.
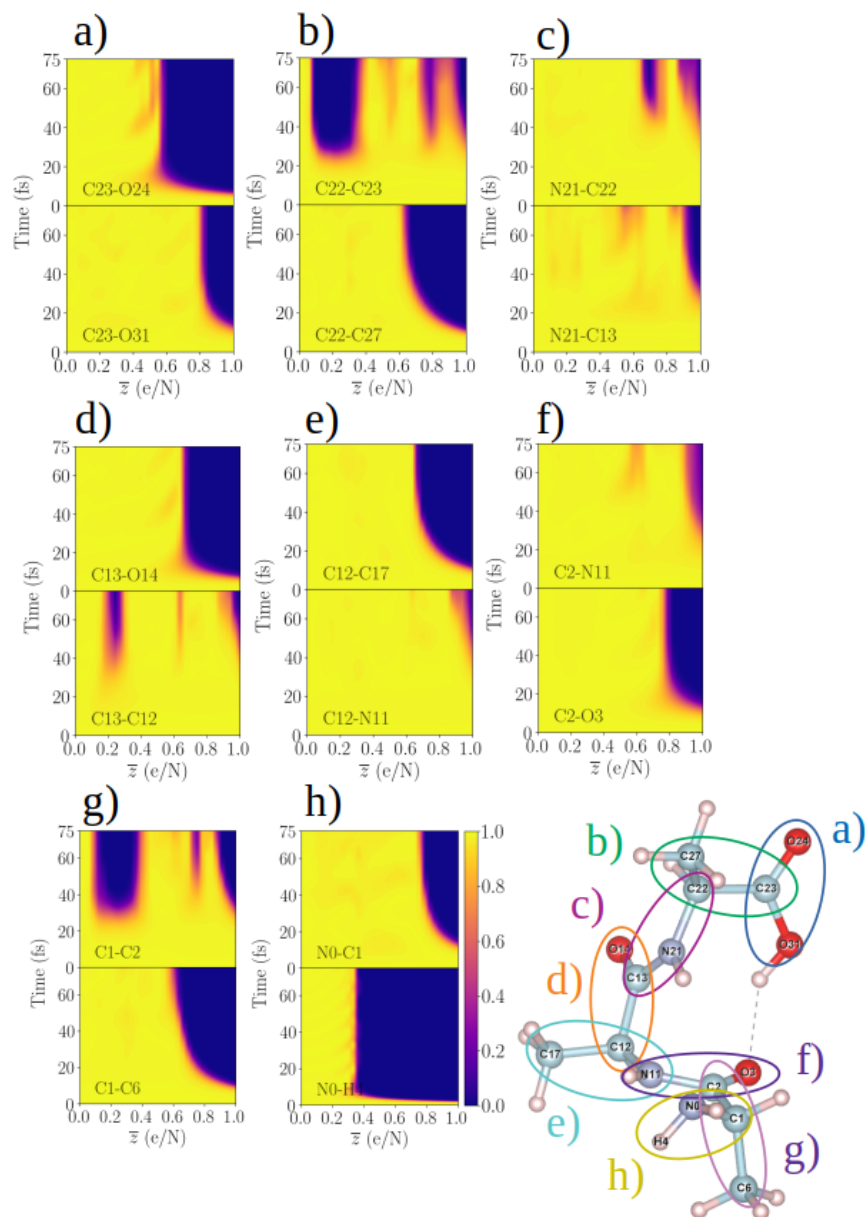
Figure 5: Bond integrity for the majority of the bonds in trialanine, in the alpha helix conformation.

B. Radius of gyration
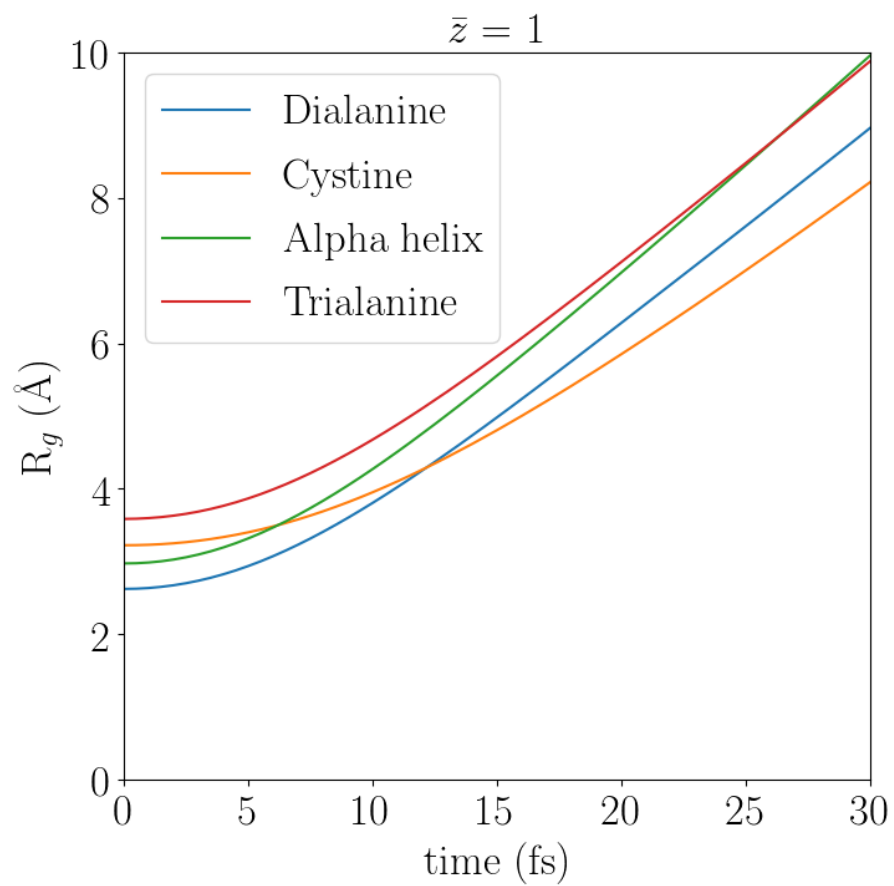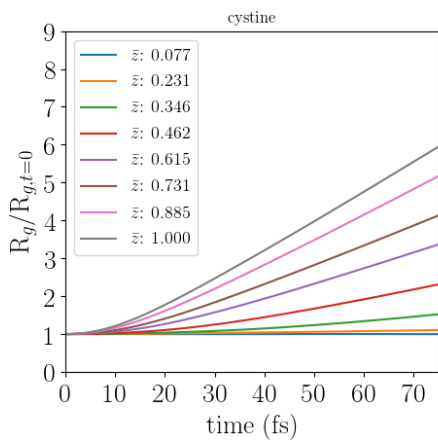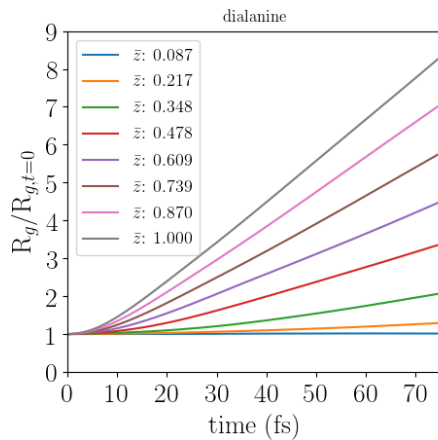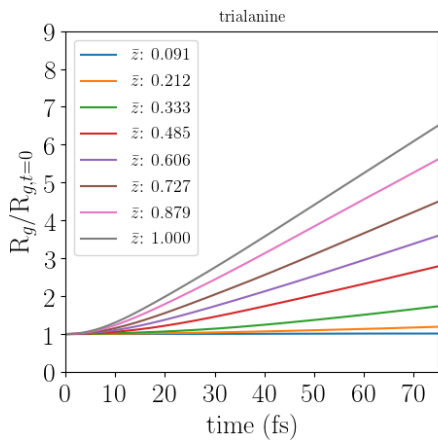

Figure 6: Radius of gyration of each molecule as a function of time. Shown only until 30 fs, in order to compare to the diffraction calculations.
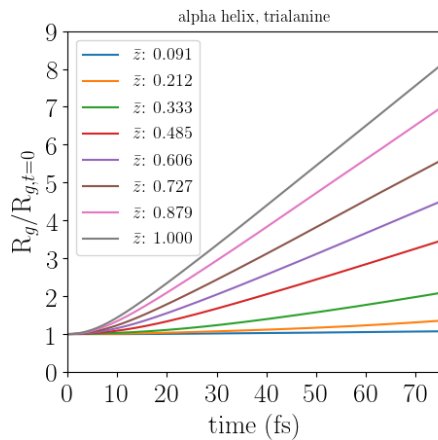
(a) Cystine.

(b) Dialanine.

(c) Trialanine.

(d) Alpha helix, Trialanine.

Figure 7: The relative radius of gyration R_g for a) cystine, b) dialanine, c) trialanine and d) the alpha helix over a wide range of ionization states ($\bar{z}$).

C. Coherent diffraction imaging with radiation damage

(a) Cystine at 0 fs.

(b) Cystine at 30 fs.

(c) Trialanine at 0 fs.

(d) Trialanine at 30 fs.

(e) Alpha helix at 0 fs.

(f) Alpha helix at 30 fs.
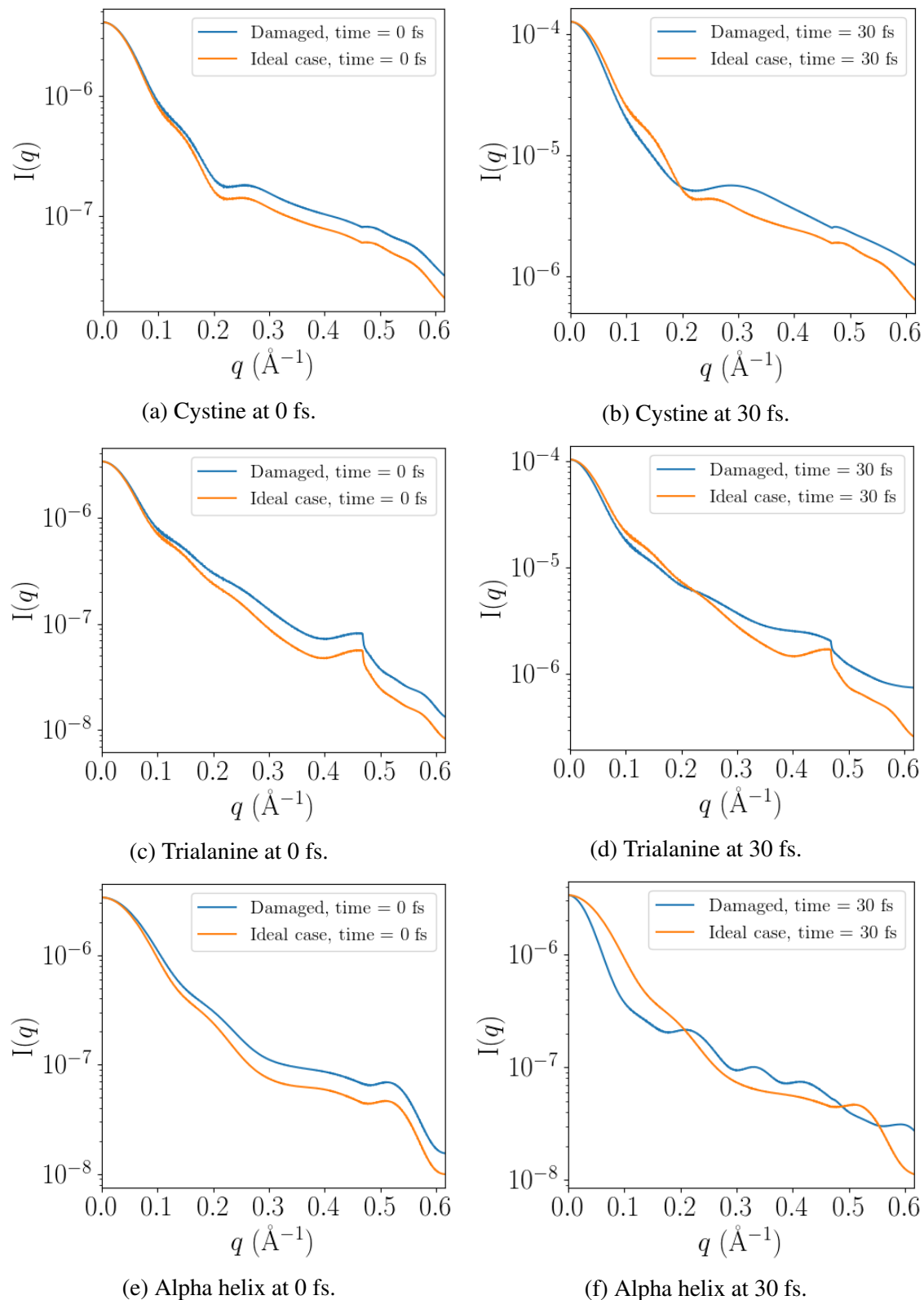
Figure 8: Comparison of the integrated intensity for the ideal undamaged case and the damaged case for cystine in **(a)**, **(b)**, trialanine in **(c)**, **(d)** and the alpha helix in **(e)**, **(f)** as a function of resolution $q = 1/d$ Å^{-1}. The intensity has been normalized such that they are equal at $q = 0$. At 30 fs, the coherent integrated intensity corresponds to the total accumulated signal during the molecular dynamics trajectory.
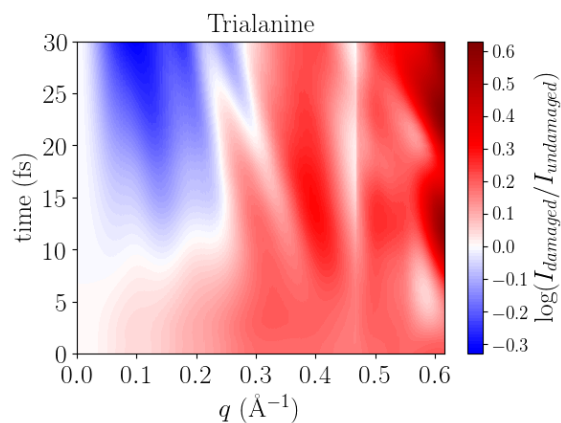
(a) Trialanine.
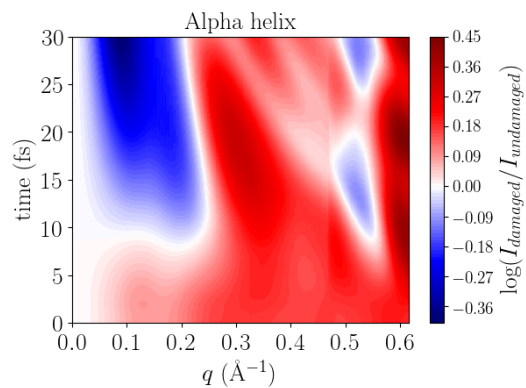
(b) Alpha helix.
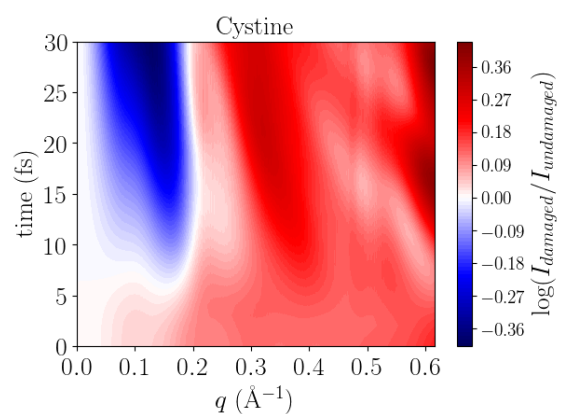
(c) Cystine.

Figure 9: In (**a**), (**b**) and (**c**) we compare damaged and undamaged time-resolved noiseless intensity of the molecules at ($\bar{z} = 1$), for the first 30 fs of the molecular dynamics trajectory. The figure depicts the logarithm of the ratio ($\frac{I_{damaged}}{I_{undamaged}}$), where the data has been normalized such that they are equal at $q = 0$.

I. Pseudo-potentials

In this section, we present information regarding the parameters used for the pseudopotentials in the simulations. For carbon (C) we had a cut-off 1.54 Bohr for the s, p, d and f orbitals. For nitrogen (N) we had 1.48 Bohr for the s, p, d and f orbitals. For oxygen (O) we had 1.47 Bohr for the s, p, d and f orbitals. For sulfur (S) we had for the s electrons 1.61 Bohr, p 1.76 Bohr, d 1.92 Bohr and f 1.92 Bohr.

II.   Comparison of PBE with PBE0

A.   Potential energy scan along the peptide bond C-N

We present a comparison of potential energy scans (PES) along a peptide bond (C-N) comparing the results from a calculation using pseudopotentials in SIESTA and semi-local PBE as exchange-correlation functional, with an all-electron calculation in Gaussian09 [3], using the hybrid functional PBE0 [1, 2]. The results are shown in figure (10).
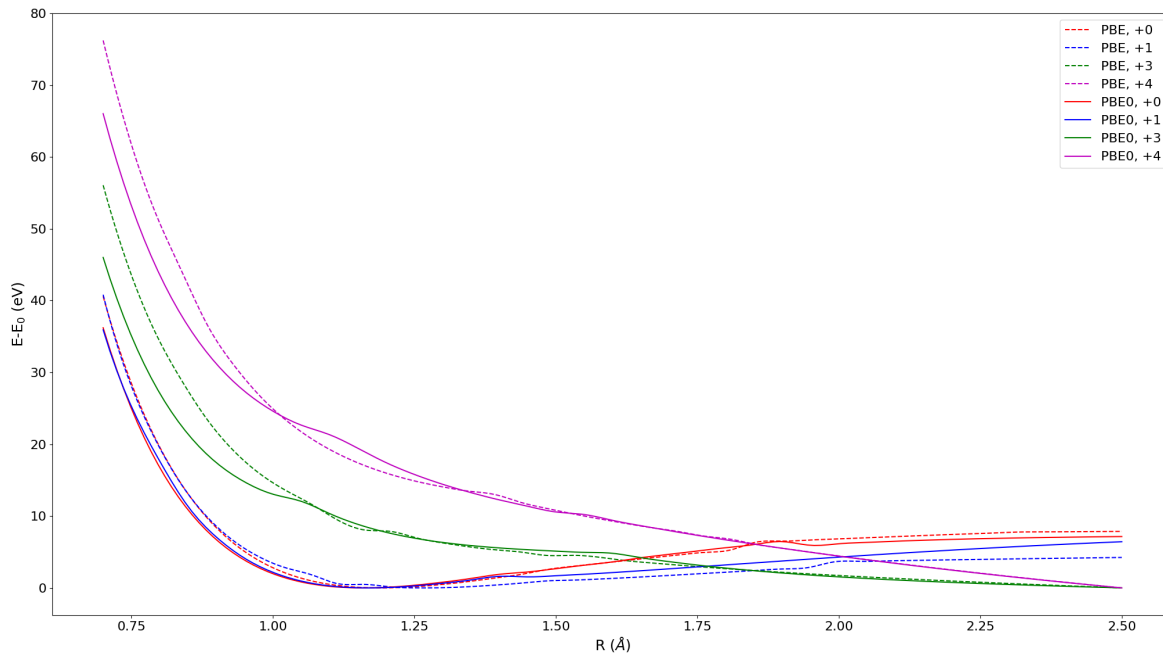

Figure 10: The potential energy scan along the peptide bond (C-N), for a range of different charge states.

The results are for a range of net charges $(+0, +1, +3, +4)$. We note that qualitatively, the shape of the PES are similar for all charge states. The differences in PES are not large enough to provide a change in the dynamics which would change our conclusions in the manuscript.

B. Hirshfeld charge scan along the peptide bond C-N

In figure (11), we show a comparison of the Hirshfeld charge as a function of the separation of the peptide bond (C-N). This is done for several charge states using the hybrid functional PBE0 in Gaussian09 and PBE in Siesta. The result shows that the Hirshfeld charges are qualitatively the same. They follow a similar behaviour, even though the values are not exactly the same for each coordinate.
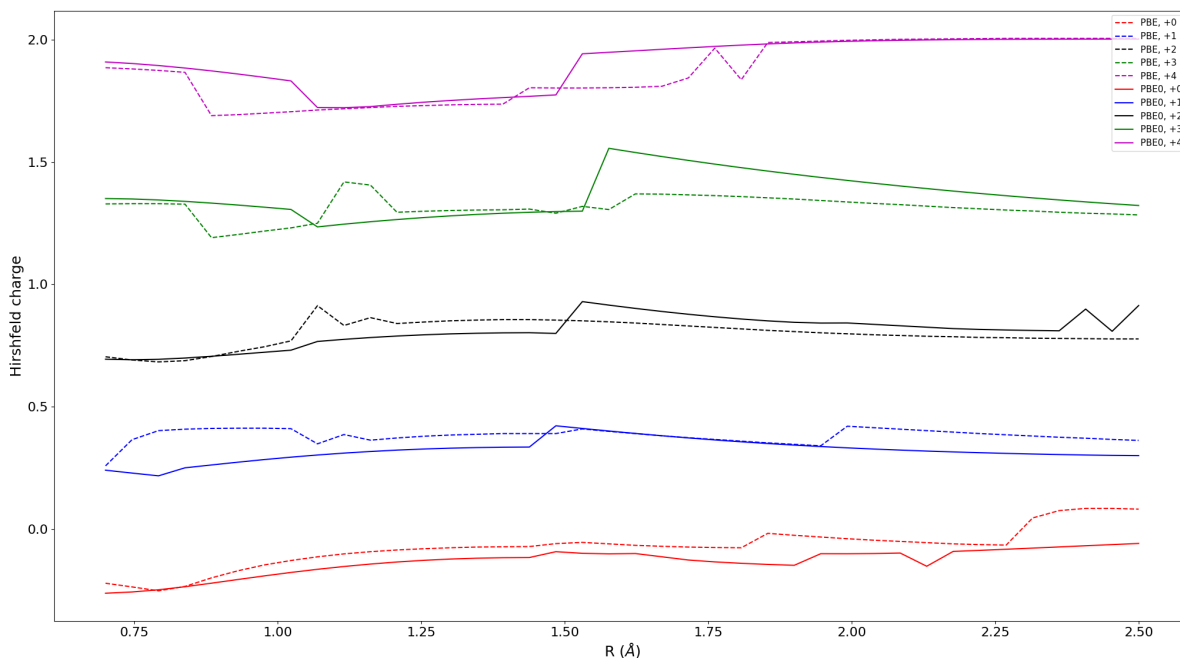

Figure 11: The Hirshfeld charge along the peptide bond (C-N), for a range of different charge states.

III. Spin contamination

The molecular dynamics simulations presented in the manuscript are in spin polarized mode, where the spin in the SIESTA runs are not fixed. Therefore, the spin moment can change or flip for each SCF calculation in the molecular dynamics trajectory. In our results as seen in figure (12), we note that the spin changes during the MD trajectory. We have compared an MD run with fixed
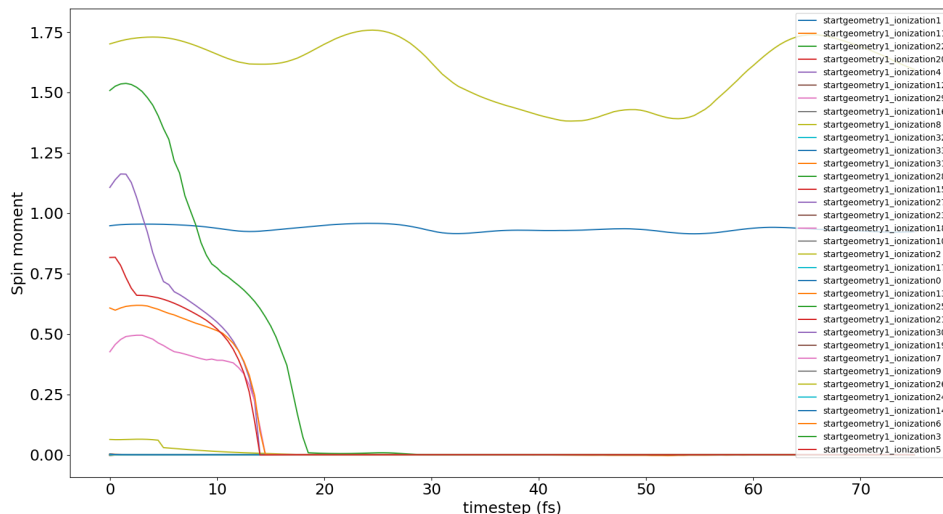

Figure 12: Evolution of the spin moment with time, for the alpha helix. The result is only from a single geometry. It can be seen that the spin moment in several trajectories is not constant.

spin with one where the spin can change for each SCF calculation. In the fix spin calculations, the spin was set to $s = \frac{1}{2}$ if the number of bound electrons in uneven, otherwise we put it to $s = 0$. We made a comparison of the bond-integrity between the (restricted) fixed-spin calculation and the unrestricted spin calculations. The result is seen in figure (13). From this result, we conclude that the runs presented in the manuscript would not change if we would have restricted the spin.
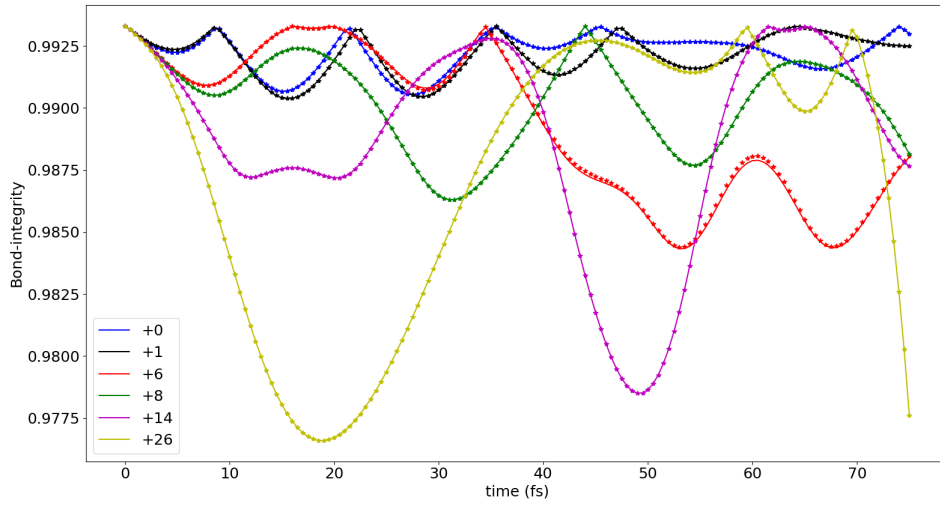
Figure 13: Comparison of the bond-integrity as a function of time for the simulations with restricted spin ($s = \frac{1}{2}$ or $s = 0$) or unrestricted spin. The restricted spin simulations correspond to the dotted lines.

IV. Energy and temperature

Since the simulations are done in NVE, the energy should be conserved but the temperature is not conserved. The total energy fluctuates only a few percent during the MD trajectory. Very few trajectories have slightly larger than a few percent changes. This will not affect our conclusions, since it is a very small fraction of the total number of trajectories. Following are figures of the fractional energy difference as a function of time. The difference is taken with respect to the mean energy for a trajectory

$$error = \left| \frac{E(t) - E_{mean}}{E_{mean}} \right| \tag{1}$$

where
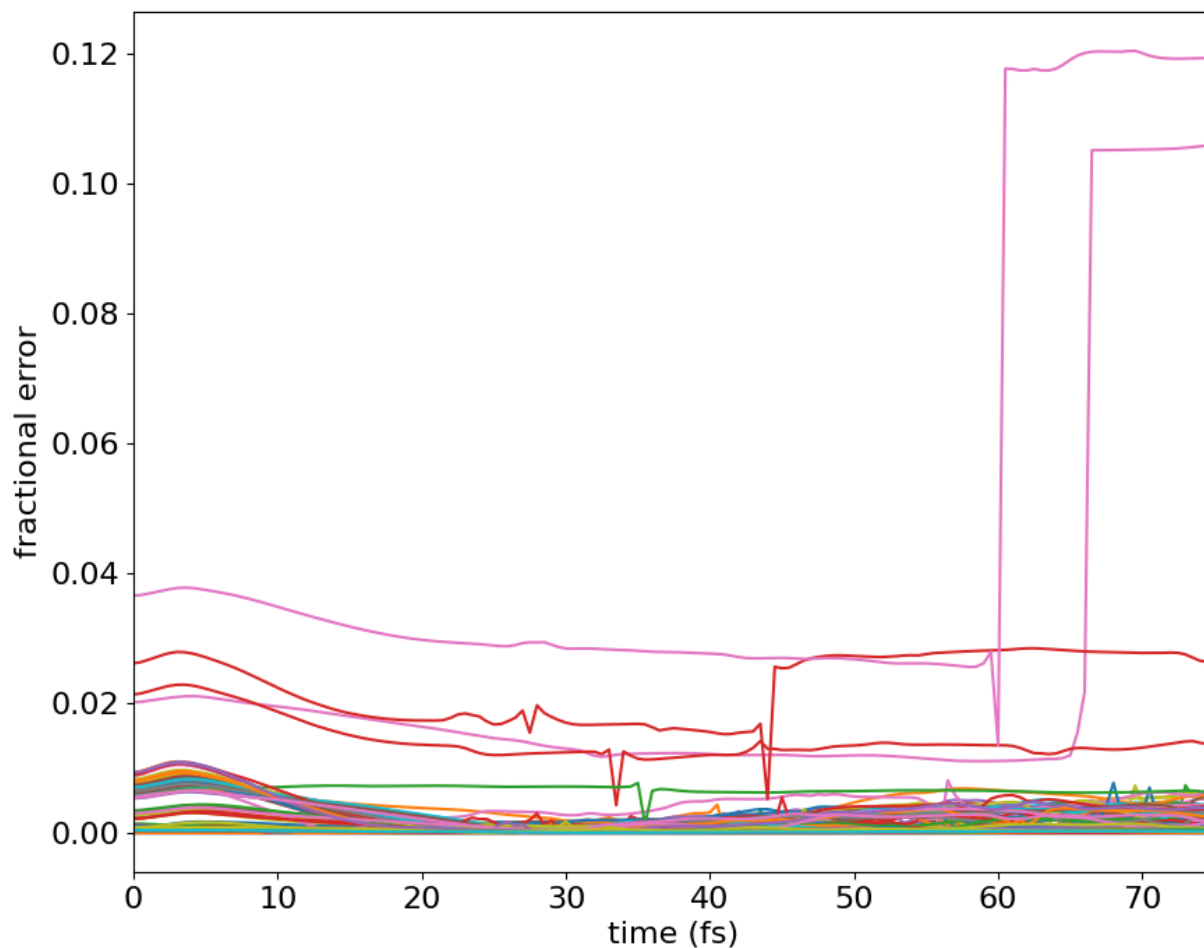
$$E_{mean} = \sum_t E(t) \tag{2}$$

Figure 14: Fractional energy difference as a function of time for dialanine. The total number of trajectories is 240.
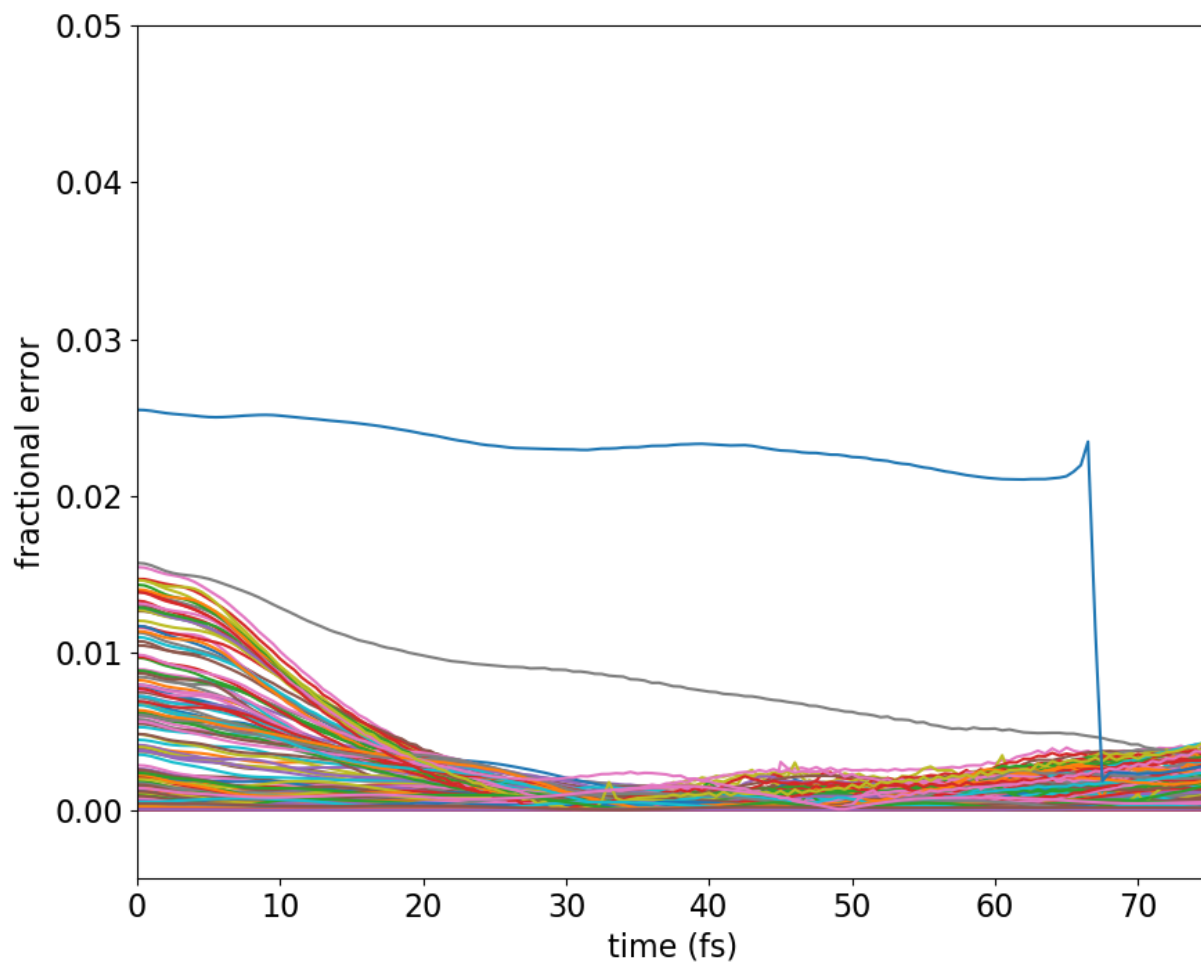
Figure 15: Fractional energy difference as a function of time for cystine. The total number of trajectories is 260.
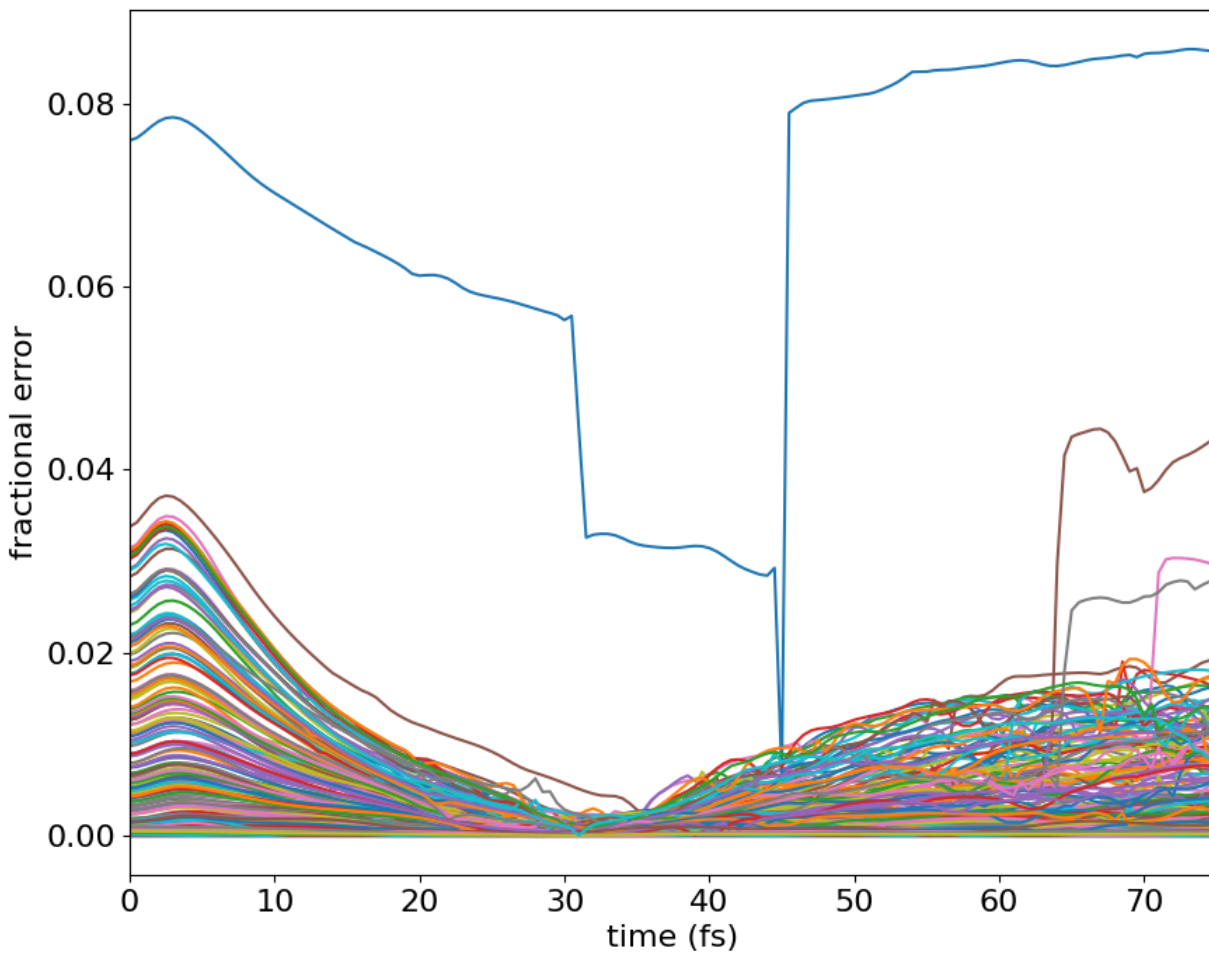
Figure 16: Fractional energy difference as a function of time for alpha helix. The total number of trajectories is 330.
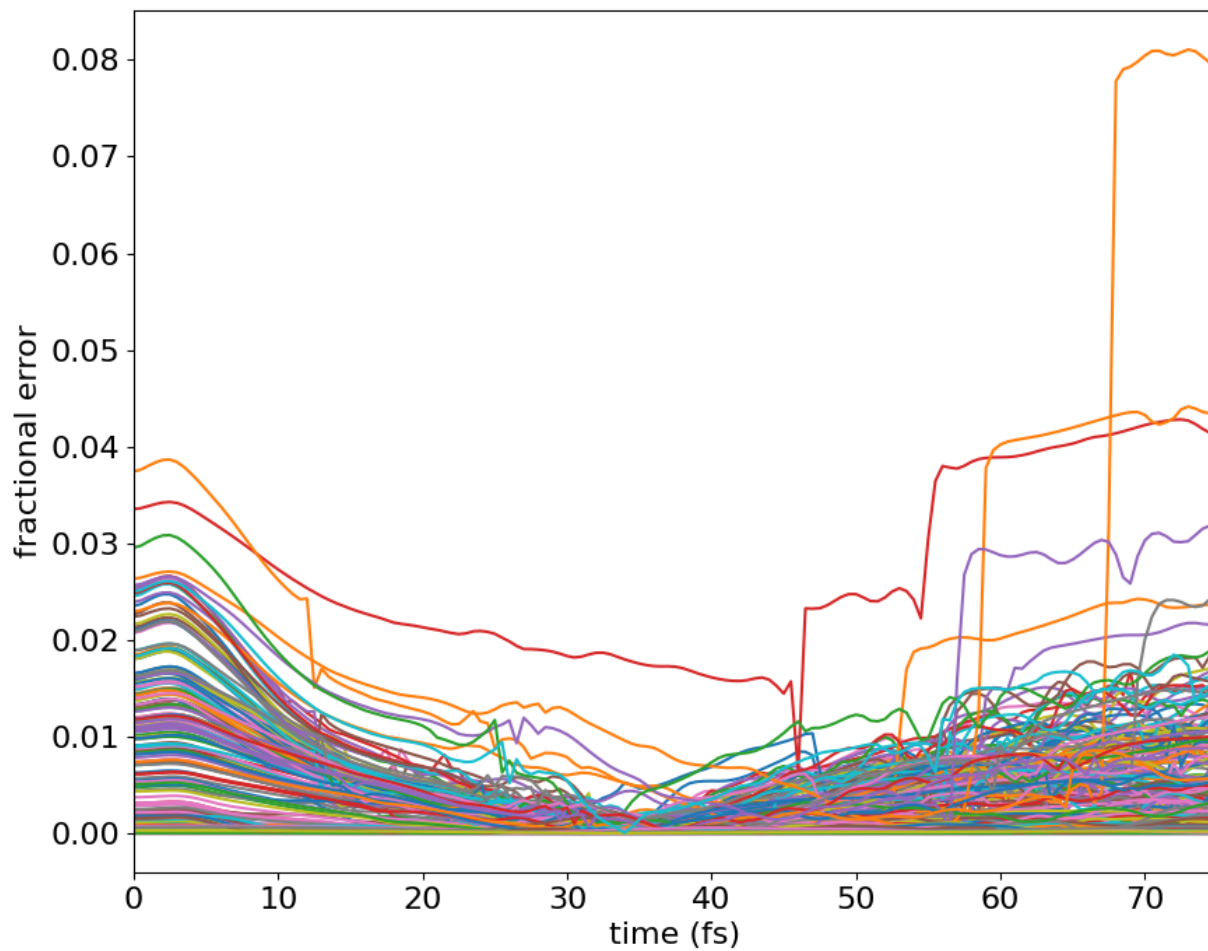
Figure 17: Fractional energy difference as a function of time for trialanine. The total number of trajectories is 330.

References

[1] Carlo Adamo and Vincenzo Barone. "Toward reliable density functional methods without adjustable parameters: The PBE0 model". In: *The Journal of Chemical Physics* 110.13 (1999), pp. 6158–6170. DOI: 10.1063/1.478522. URL: https://doi.org/10.1063/1.478522.

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[3] M. Frisch et al. "Gaussian 09 (Revision A02)". In: *Gaussian Inc. Wallingford CT* (Jan. 2009).