Tracking the Mechanism of Fibril Assembly by Simulated Two-Dimensional Ultraviolet Spectroscopy

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Figures Captions

- **Figure S1**. 1D and 2D spectra in the FUV regime for Configuration 2 at different simulation times. **Top**: Linear Absorption (1D) . **Middle**: The 2D non-chiral *xxxx* spectra. **Bottom**: The 2D non-chiral combination *xyxy-xyyx* signal. The non-chiral *xxxx* spectra have extended blue peaks at 52,000 cm^{-1}, while the non-chiral combination *xyxy-xyyx* spectra have broader and diffused blue peaks at 52,000 cm^{-1}. The 2D signal **S** in each spectrum of this study is normalized in a color scale to rank the weak (in blue) and strong (in red) peaks, and plotted on a nonlinear scale that interpolates between logarithmic, for small values, and linear for large values, of the signal intensity. The nonlinear scale is defined as $\operatorname{arcsinh}(c\boldsymbol{S}) = \ln\left(c\boldsymbol{S} + \sqrt{1 + (c\boldsymbol{S})^2}\right)$ with a fixed value for *c* defined by the user.

- **Figure S2**. 1D and 2D chiral signals in the FUV for Configuration 2 at different simulation times. **Top Row**: Representative snapshots (as in Rojas *et al.*[1]) of A $\beta_{(9\text{-}40)}$ monomer (red) interacting with the amyloid template (blue) at different simulation times. Aromatic residues, Tyr and Phe, are colored in orange and green, respectively. **Middle Panels**: circular dichroism. **Bottom Panels**: 2DFUV chiral *xxxy* spectra.

- **Figure S3**. Maps A to F show the average chirality factor $\langle CF(m,n)\rangle$ (defined in Zhuang *et al.* [2]) for $\pi\pi^*$ transitions for Configuration 2 at different simulation times, indicated at the left of each map. A representative snapshot (obtained from ref. 1) of the A $\beta_{(9\text{-}40)}$ monomer (red) interacting with the amyloid template (blue) for the corresponding time, is also shown at the left of each map. Axes in each map correspond to the amino-acid residue index. To highlight the contribution of a pair of amino-acid residues to the chirality factor, a similar normalization scale as in the 2D signals was used here.

- **Figure S4**. Components of the 2DFUV non-chiral *xxxx* signal dissection defined as $\boldsymbol{S}_{Complex} = \boldsymbol{S}_{Template} + \boldsymbol{S}_{Monomer} + \Delta\boldsymbol{S}$ for Configuration 1 at different simulation times. The signal S of each component was normalized using the equation described in the caption of Fig. S1. The constant factor *c* is displayed in the bottom row.

- **Figure S5**. Same as in Fig. S4 but for Configuration 2.

Figure S1:

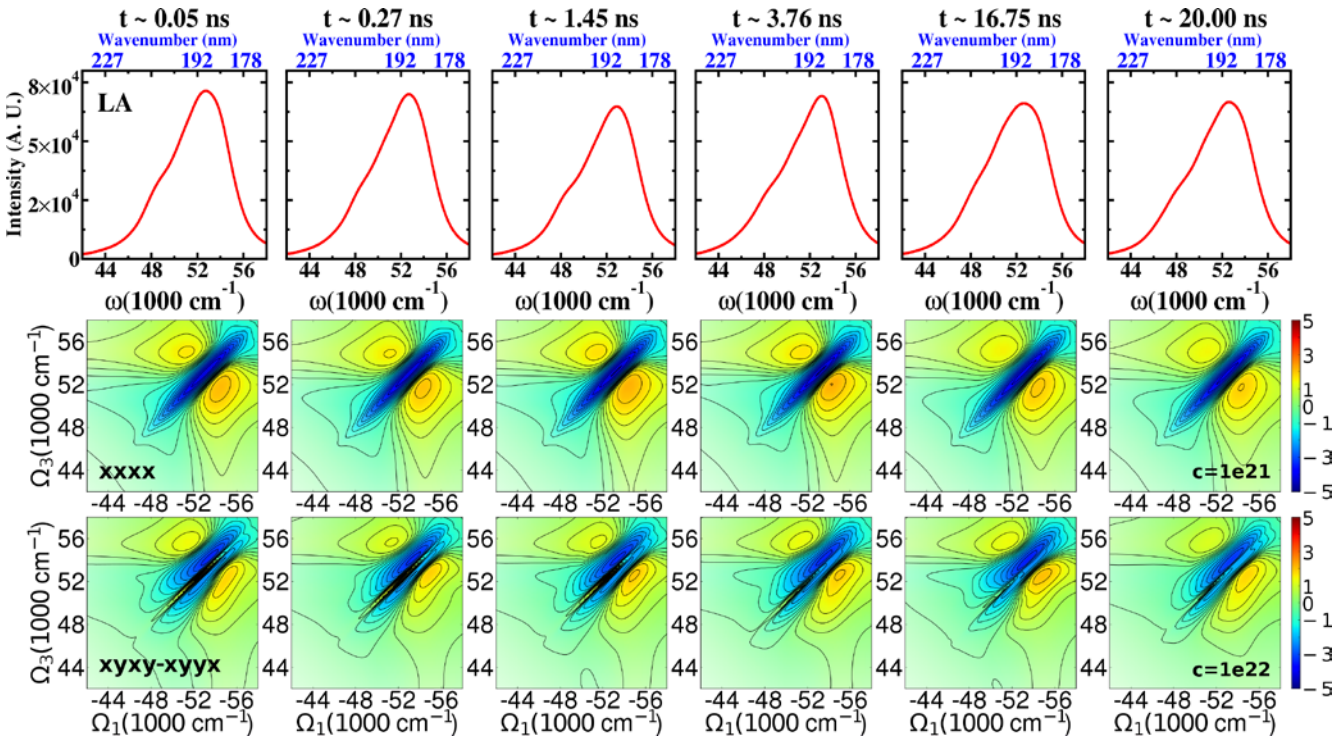

t ~ 0.05 ns
t ~ 0.27 ns
t ~ 1.45 ns
t ~ 3.76 ns
t ~ 16.75 ns
t ~ 20.00 ns
Wavenumber (nm)
227 192 178
Intensity (A. U.)
LA
ω(1000 cm-1)
Ω3(1000 cm-1)
Ω1(1000 cm-1)
xxxx
xyxy-xyyx
c=1e21
c=1e22

Figure S2:

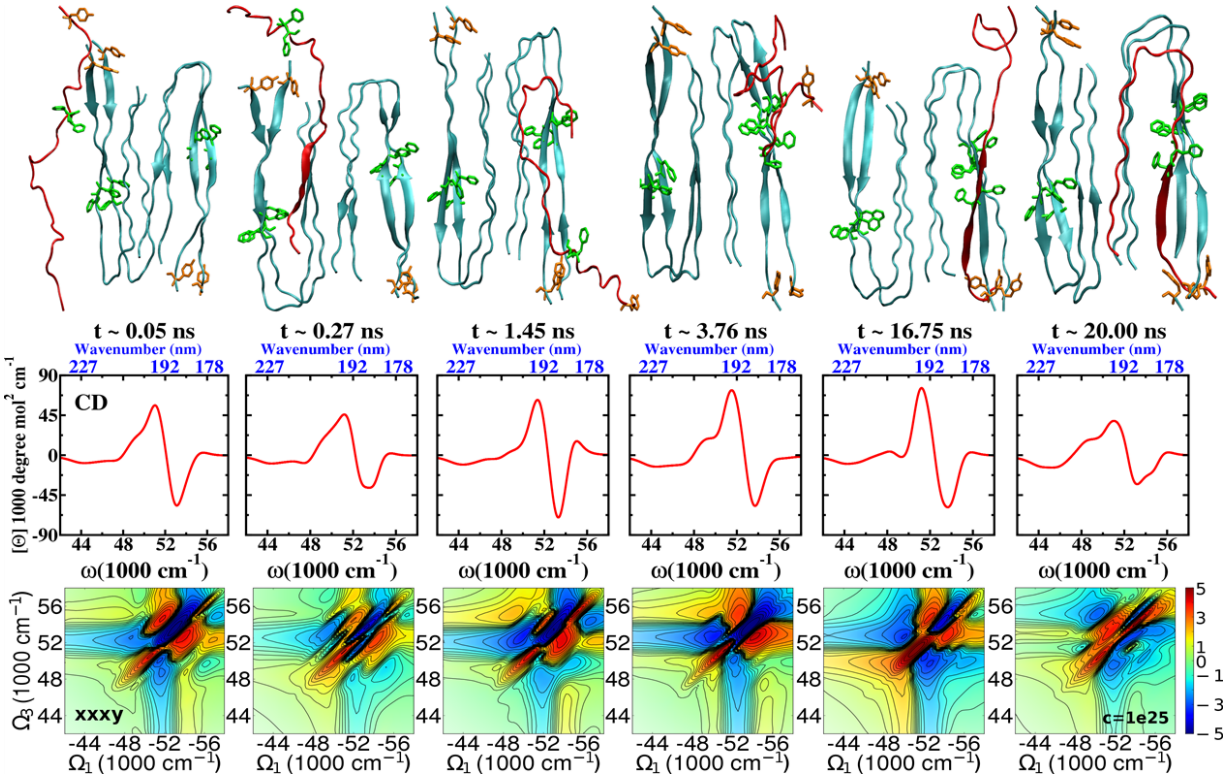

t ~ 0.05 ns
t ~ 0.27 ns
t ~ 1.45 ns
t ~ 3.76 ns
t ~ 16.75 ns
t ~ 20.00 ns
Wavenumber (nm)
227 192 178
CD
[Θ] 1000 degree mol^2 cm^{-1}
ω(1000 cm^{-1})
Ω$_3$ (1000 cm^{-1})
Ω$_1$ (1000 cm^{-1})
xxxy
c=1e25

Figure S3:

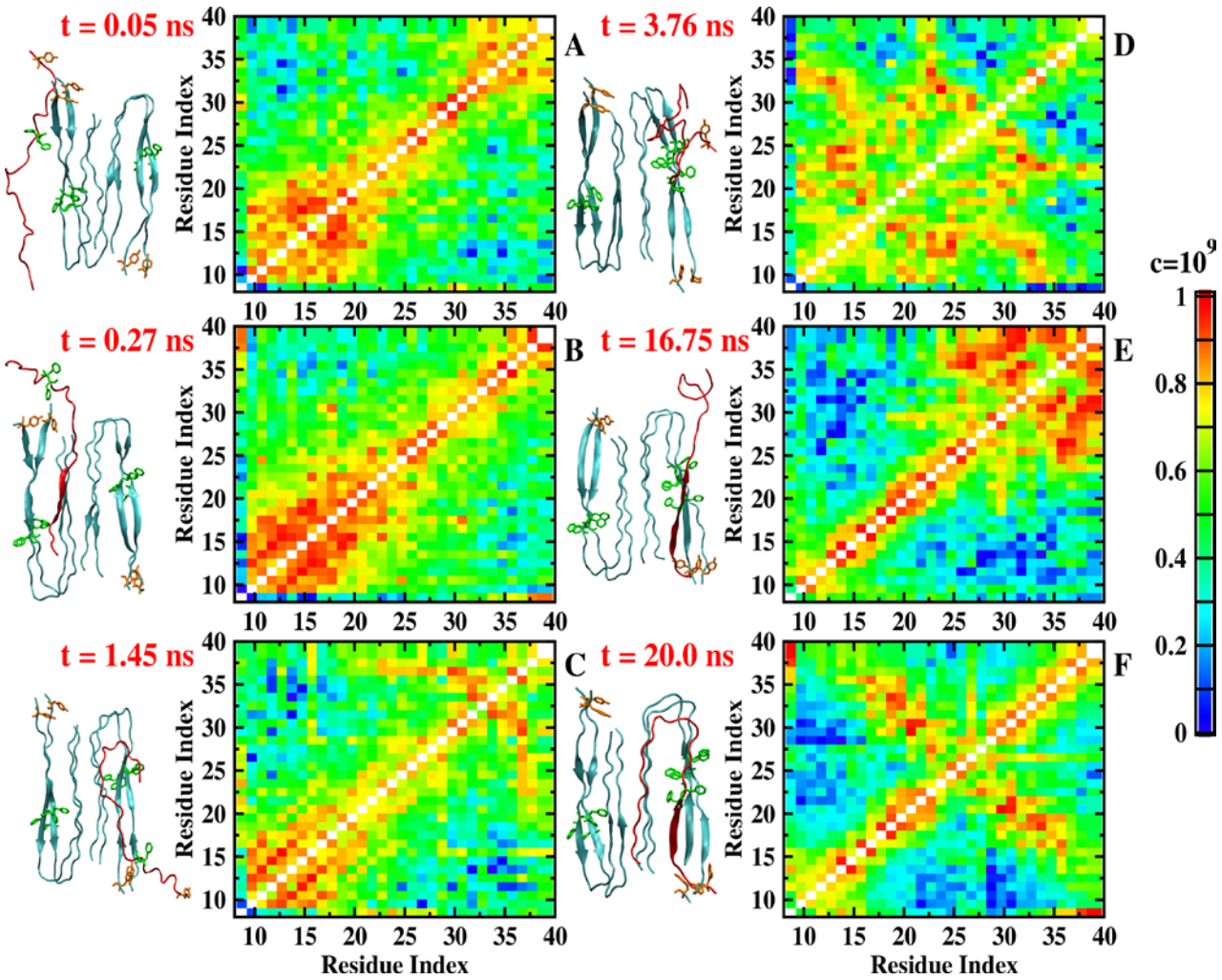

t = 0.05 ns
A
t = 3.76 ns
D
t = 0.27 ns
B
t = 16.75 ns
E
t = 1.45 ns
C
t = 20.0 ns
F
Residue Index
Residue Index
c=10^9
1
0.8
0.6
0.4
0.2
0

Figure S4:

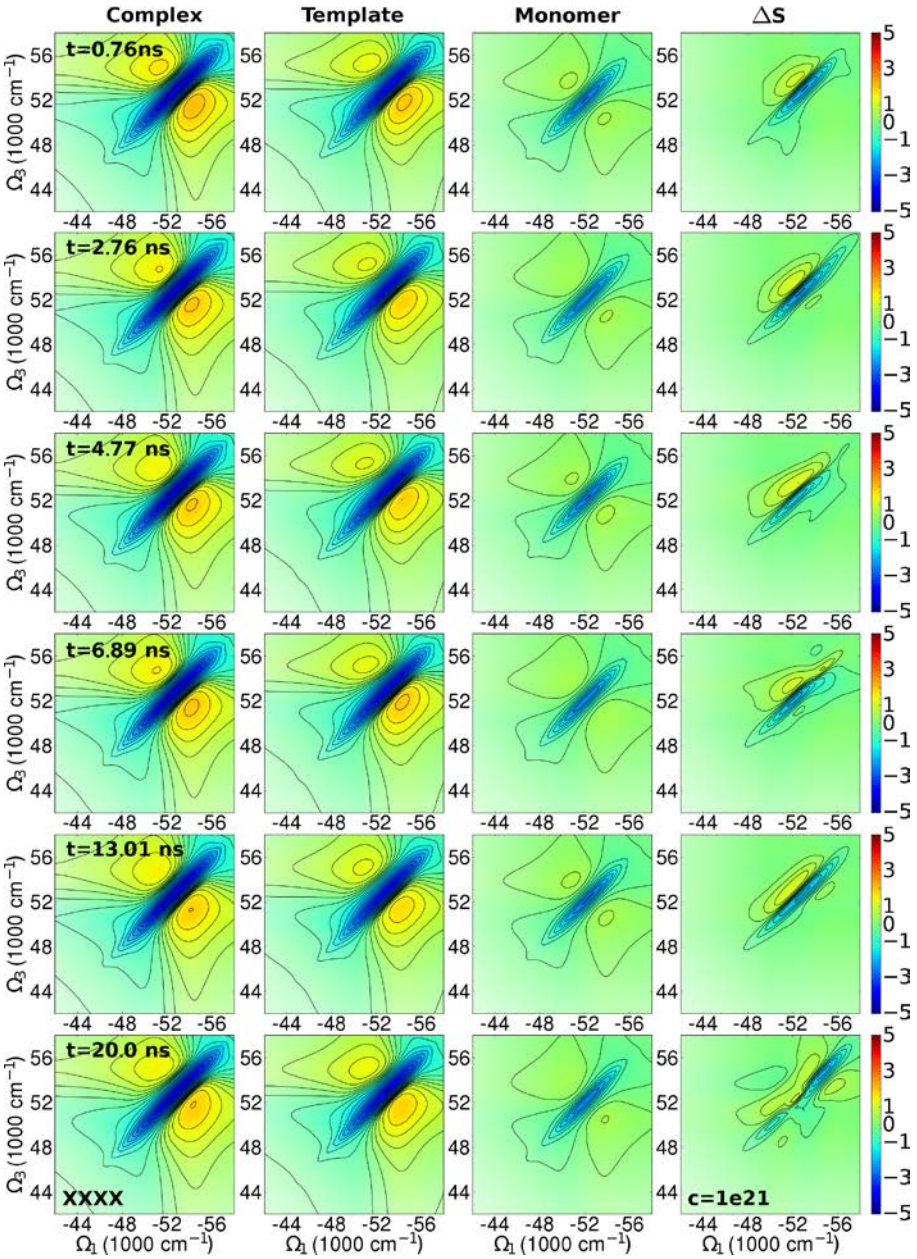
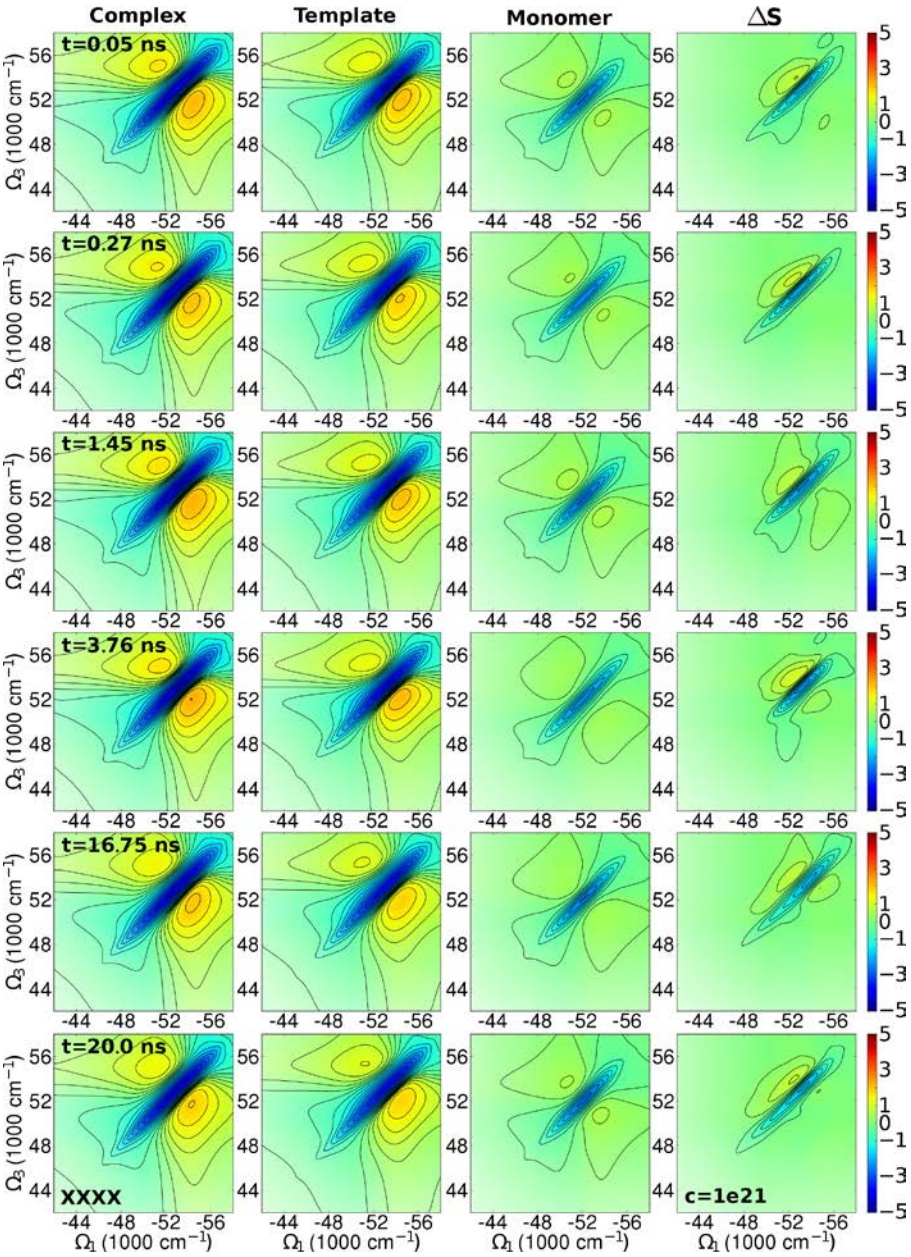

Complex
Template
Monomer
ΔS
t=0.76ns
t=2.76 ns
t=4.77 ns
t=6.89 ns
t=13.01 ns
t=20.0 ns
XXXX
c=1e21
Ω3 (1000 cm−1)
Ω1 (1000 cm−1)
56
52
48
44
-44 -48 -52 -56
5
3
1
0
−1
−3
−5

Figure S5:


Complex
Template
Monomer
ΔS
t=0.05 ns
t=0.27 ns
t=1.45 ns
t=3.76 ns
t=16.75 ns
t=20.0 ns
XXXX
c=1e21
Ω3 (1000 cm−1)
Ω1 (1000 cm−1)
56
52
48
44
-44
-48
-52
-56
5
3
1
0
−1
−3
−5

References

(1) Rojas, A.; Liwo, A.; Browne, D.; Scheraga, H. A. *J. Mol. Biol*. **2010**, *404*, 537-552
(2) Zhuang, W.; Sgourakis, N. K.; Zhenyu, L.; Garcia, A.; Mukamel, S. *Proc. Natl. Acad. Sci. USA* **2010**, *107*, 15687-15692.