Supplemental Figures

Figure S1. The 2D-IR spectrum of unlabeled amyloid fibrils at T=0 fs illustrating the potential for absorptions from groups in the peptide other than $^{13}C=^{18}O$. The black square (1500-1550 cm^{-1}) outlines the region where amide II' absorptions occur. The area within the red square (1550-1600 cm^{-1}) is scaled 20-fold in the inset, demonstrating the absence of absorption due to arginine side chains.

Figure S2. Comparison of ICLS (inverse of central line slope) and IS (inverse of the nodal line slope) calculations in 4-year old A30* fibrils at waiting times T = 0, 250 fs, and 1500 fs. (a) Central lines are identified by determining the value of ω_t where spectral intensity is maximal for values of ω_τ,[31] and are illustrated by black lines. Nodal lines are identified by determining the value of ω_t where spectral intensity is zero between the negative and positive transitions for values of ω_τ. (b) The decay of ICLS and IS values for the 1583 cm^{-1} transition of A30* exhibited time constants of 1.2 ± 0.3 ps and 1.3 ± 0.3 ps, respectively, indicating that the two methods yield similar results for the spectral diffusion rate of a single transition. In some 2D IR spectra, lineshape distortion may arise due to peak overlap. This overlap can cause uncertainty in the determination of the spectral diffusion rate using methods described here (see Kwak et al., J.Chem.Phys. 128 (20), 2008). This distortion is particularly severe at early waiting times when lineshapes are elongated along the diagonal, requiring cuatious measurement and interpretation. At longer waiting times, spectral diffusion improves peak resolution, and ICLS and IS may be applied directly. The two methods yielded similar results for the spectral diffusion rate in this study.

Figure S3. Off-diagonal crosspeaks in a 2D-IR photon echo experiment have possitive and negative components that correspond to the on-diagonal absorption peaks, with a negative crosspeak at low ω_t and a positive crosspeak at high ω_t. The biphasic character of L17*, V18*, G29* and A30* crosspeaks are clearly seen with an expanded scale. That character is not present in an expanded-scale spectrum from F19*. For G29*, the positive crosspeak is obscured by a negative crosspeak at higher ω_t. For V36*, crosspeak appears between the 1590 cm^{-1} transition and the weak transition at ~1580 cm^{-1} at longer waiting time (T = 3000 fs).

Figure S4. Electron micrographs of 4-year-old L17* (left) and V36* (right) fibrils, negatively stained with 1% aqueous uranyl nitrate.

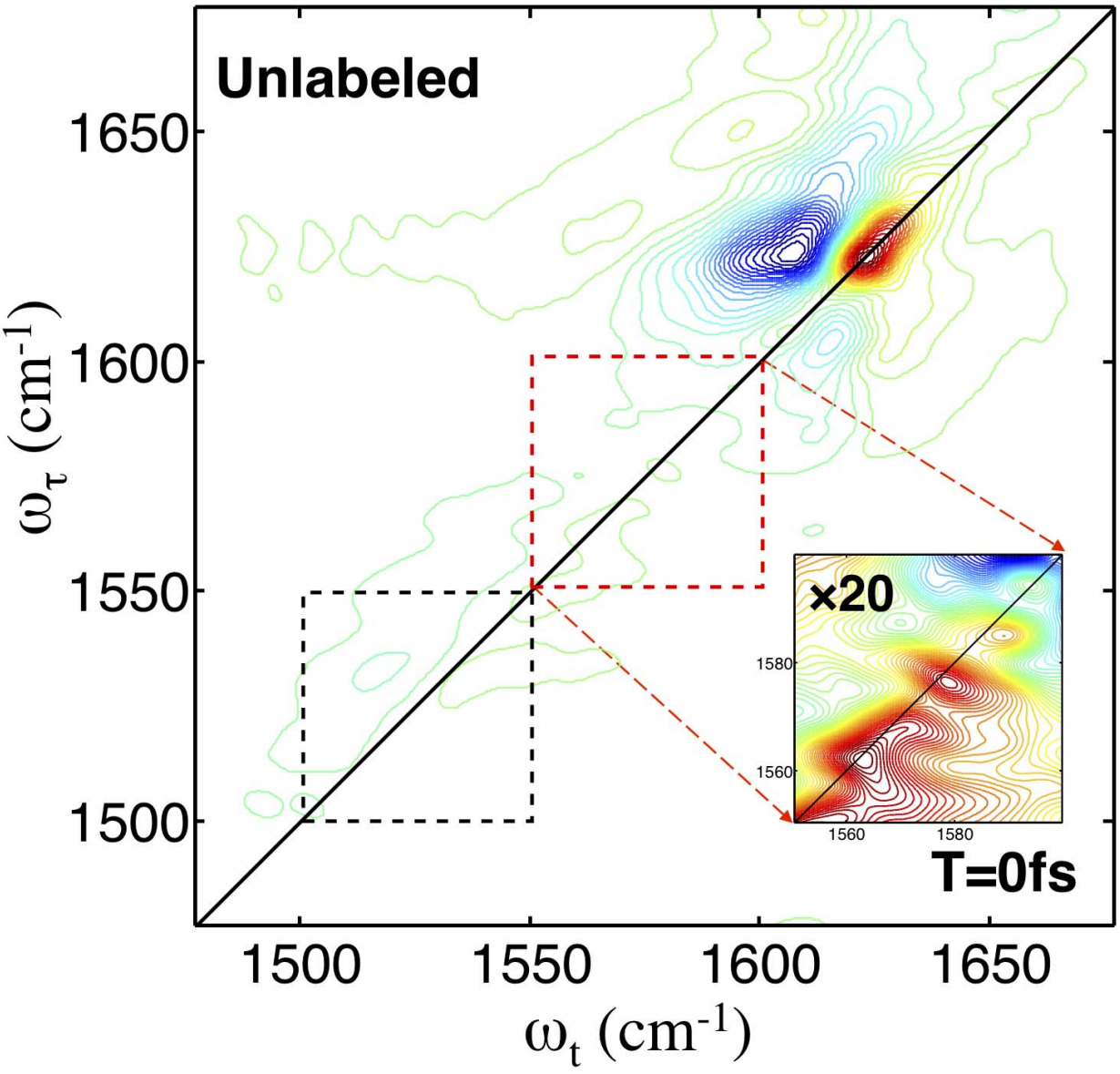
Unlabeled
1650
1600
1550
1500
ω_τ (cm^{-1})
1500
1550
1600
1650
ω_t (cm^{-1})
×20
1580
1560
1560
1580
T=0fs

Figure S1

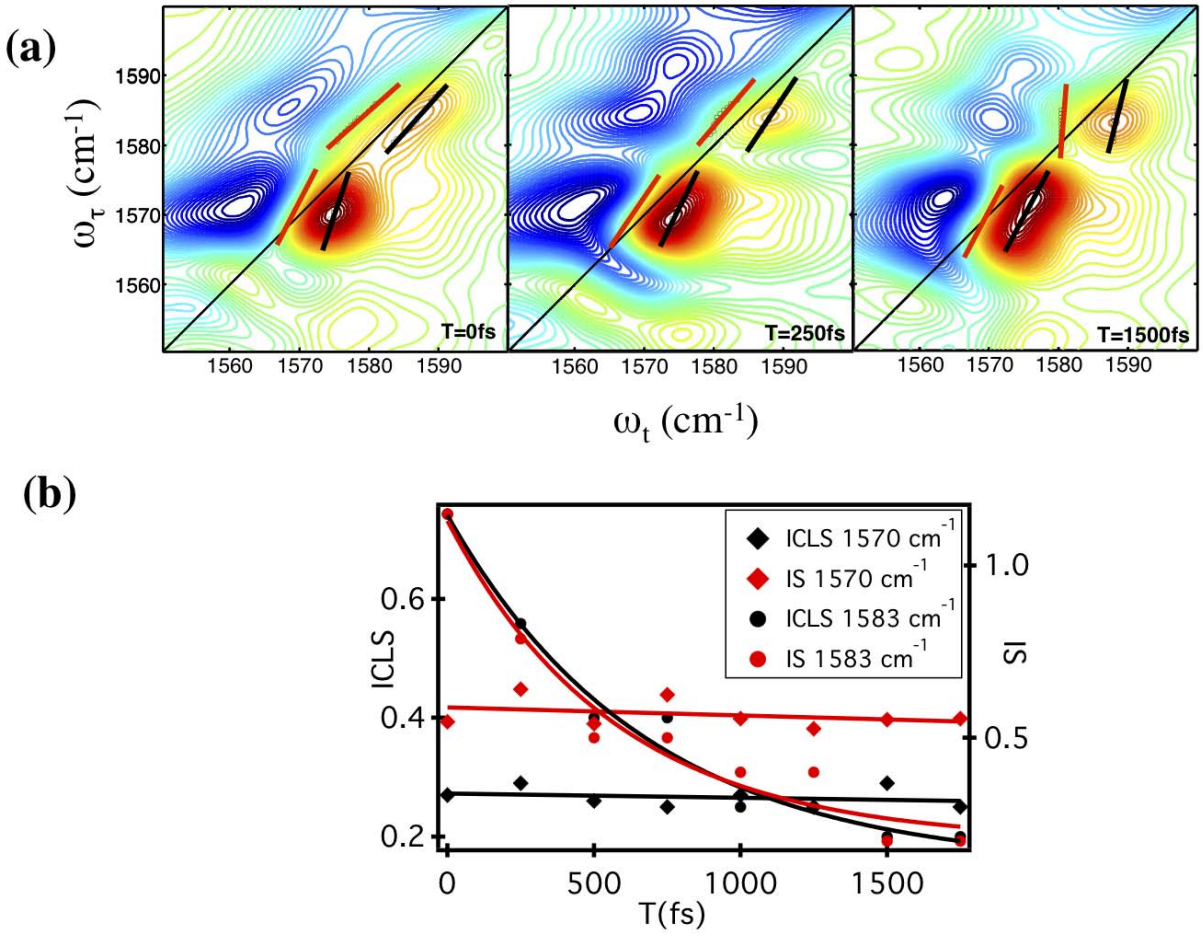
(a)
1590
1580
1570
1560
ω_τ (cm^{-1})
T=0fs
T=250fs
T=1500fs
1560 1570 1580 1590
ω_t (cm^{-1})
(b)
ICLS 1570 cm^{-1}
IS 1570 cm^{-1}
ICLS 1583 cm^{-1}
IS 1583 cm^{-1}
ICLS
SI
0.6
0.4
0.2
1.0
0.5
0
500
1000
1500
T(fs)

Figure S2

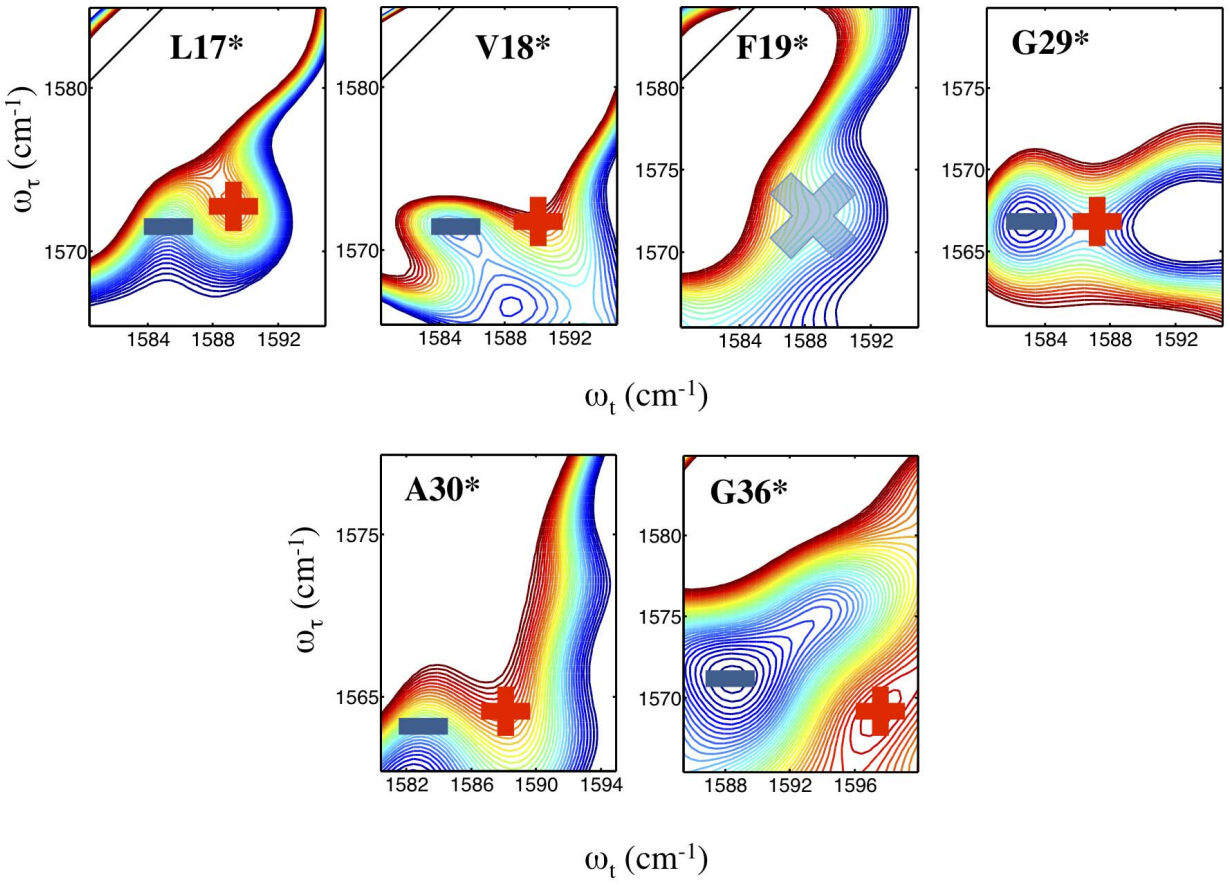
L17*
V18*
F19*
G29*
A30*
G36*
ω_τ (cm^-1)
ω_t (cm^-1)
1580
1570
1584
1588
1592
1575
1565
1582
1586
1590
1594
1596

Figure S3

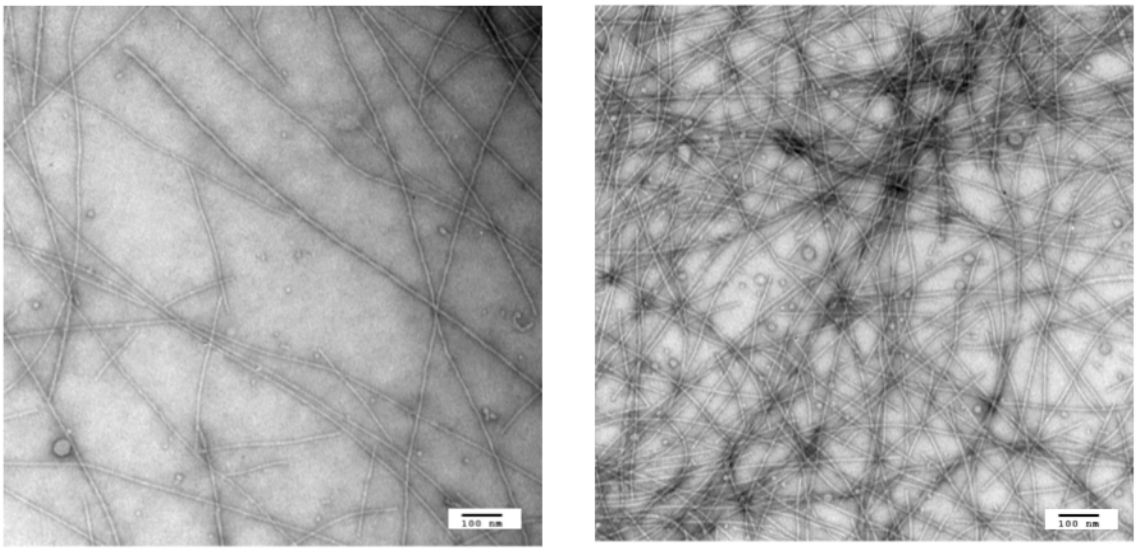

Figure S4