Identical Water Dynamics in Acrylamide Hydrogels, Polymers, and Monomers in Solution: Ultrafast IR Spectroscopy and Molecular Dynamics Simulations

Sean A. Roget[a], Zeke A. Piskulich[b], Ward H. Thompson[b]*, and Michael D. Fayer[a]*

[a]Department of Chemistry, Stanford University, Stanford, CA 94305
*Email: fayer@stanford.edu; Phone: (650) 723-4446
[b]Department of Chemistry, University of Kansas, Lawrence, KS 66045
*Email: wthompson@ku.edu; Phone: (785) 864-3980

A. Testing the Population dynamics in Acrylamide-based Systems

To test the idea that ODs H-bonded to acrylamide have a similar lifetime as ODs H-bonded to water, the following heuristic calculations were performed. The results are displayed in Fig. S1.
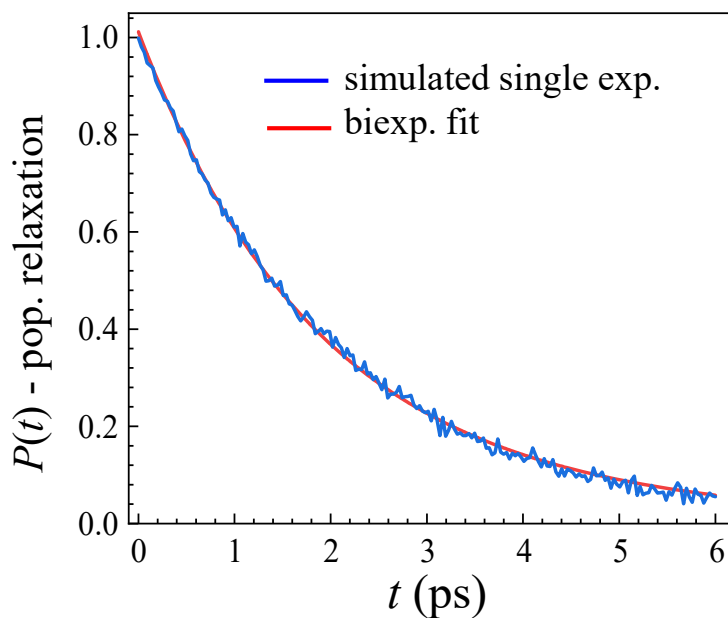

Figure S1. Simulated single exponential decay of $T = 25\%$ at 2572 cm^{-1} with 1% noise (blue) to simulate the population data and its biexponential fit (red).

For $T = 25\%$, the longest lifetime, which occurs at the highest frequency, is 2.03 ps. For this concentration, there are 12 water molecules (24 hydroxyls) per amide moiety. There are 24 hydroxyl donors for every 3 acrylamide acceptor sites. If three hydroxyls are bound to acrylamide, then 21 hydroxyls are bound to other water molecules, giving a ratio of 1:7. In the Fig. S1, the blue curve is a single exponential decay with a time constant of 2.03 ps and has 1% Gaussian noise added to simulate the experimental data. This simulated curve was fit with a biexponential decay in which one time constant was fixed at 1.8 ps, the water/water lifetime. The two coefficients of the biexponential were fixed at 0.875 for the 1.8 ps component, and 0.125 for the unknown water bound to acrylamide lifetime, modeling the 1:7 ratio. The resulting single parameter fit is the red curve. The fit is very good and yields a OD bound to acrylamide lifetime of 3.6 ps.

As a further test, the $T = 10\%$ data were treated in a similar manner. For $T = 10\%$, there are 36 water molecules per amide moiety. Then the coefficients of the 1.8 ps and 3.6 ps components should be 0.96 and 0.04, respectively. Again, a single exponential decay with 1% noise was simulated to model the slowest $T = 10\%$ decay and fit with a biexponential decay. This time, the time constants were fixed at 1.8 ps and 3.6 ps, and the coefficients were allowed to float. The resulting coefficients are 0.935 and 0.065, reasonably close to the values predicted by the simple model of hydroxyl H-bonding to water and acrylamide. The agreement is likely somewhat fortuitous, but the point is not to obtain quantitative agreement. The idea is to show that there could be two lifetimes, with the OD bound to acrylamide lifetime similar in decay constant and relatively low amplitude.
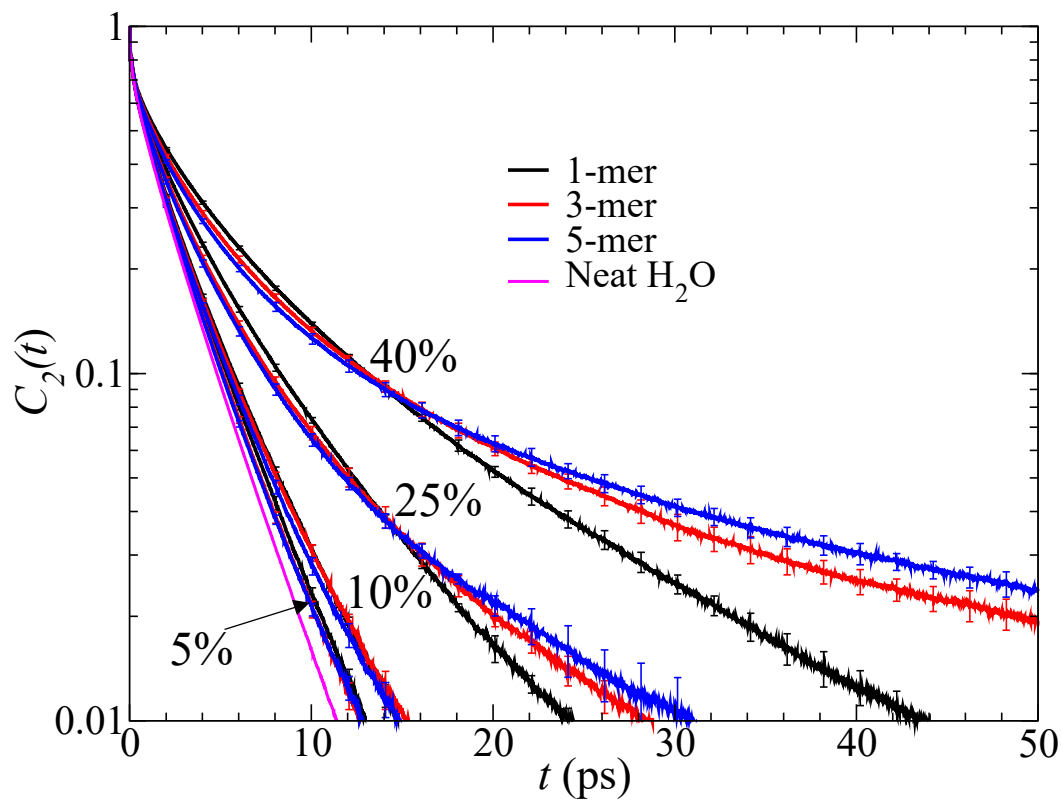
B. Simulated $C_2(t)$ to 50 ps

Figure S2. Simulated $C_2(t)$, for neat water and acrylamide 1-mer, 3-mer, and 5-mer, for $T = 5$ - 40% over the full simulated range of 50 ps.

Table S1. Molecular details of simulated systems.

	1-mer			3-mer			5-mer		
T	N_{PAAm}	N_w	L (Å)	N_{PAAm}	N_w	L (Å)	N_{PAAm}	N_w	L (Å)
5%	5	395	23.09	2	450	24.09	1	395	23.02
10%	11	396	23.46	4	432	24.05	2	353	22.47
25%	31	369	24.14	12	432	25.14	6	357	23.52
40%	57	343	25.11	22	396	24.09	12	361	24.92

C. Corrections to the Population Fractions used in the model

The effect of overlapping first solvation shells of the acrylamide molecules is addressed by a simple empirical model. The fraction of water molecules in the first solvation shell of an acrylamide molecule, f_{1st}, is shown as a function of concentration in Fig. S3A for the 1-mer, 3-mer, and 5-mer. At lower concentrations ($T = 5$ and 10%) the fraction is linear in $x = T/(100\%-T)$, which is expected if the acrylamide solvation shells do not overlap. However, at the higher concentrations f_{1st} rises more slowly and appears to plateau, indicative of water molecules that are simultaneously in two acrylamide solvation shells at once. This is account for in the model by expressing f_{1st} as an exponential rise function,

$$f_{1st} = \frac{f_{1st,0}}{b}\left[1 - e^{-b(s)x}\right]$$

where

$$f_{1st,0} = \frac{m_w}{2m_{Am,u}}\left[\frac{(n_{end}-n_{mid})}{s} - n_{mid}\right].$$

This expression recovers the linear behavior in x at small values (*i.e.,* low concentration). The fit to the fractions obtained from the MD simulations are shown in Fig. S3A and are in excellent agreement. The effect of overlapping solvation shells is chain length dependent, which is evident from the dependence of b on the number of acrylamide units, s. However, $b(s)$ appears to approach a constant value with increasing s and is well described by a single exponential decay, which is shown in Fig. S3B. The results of this model are compared to that assuming non-overlapping solvation shells in Fig. S4. The primary effect is to reduce the fraction of first solvation shell waters at higher concentrations (as more of them are shared by different acrylamide molecules). The agreement with the fractions obtained directly from the simulations is excellent.
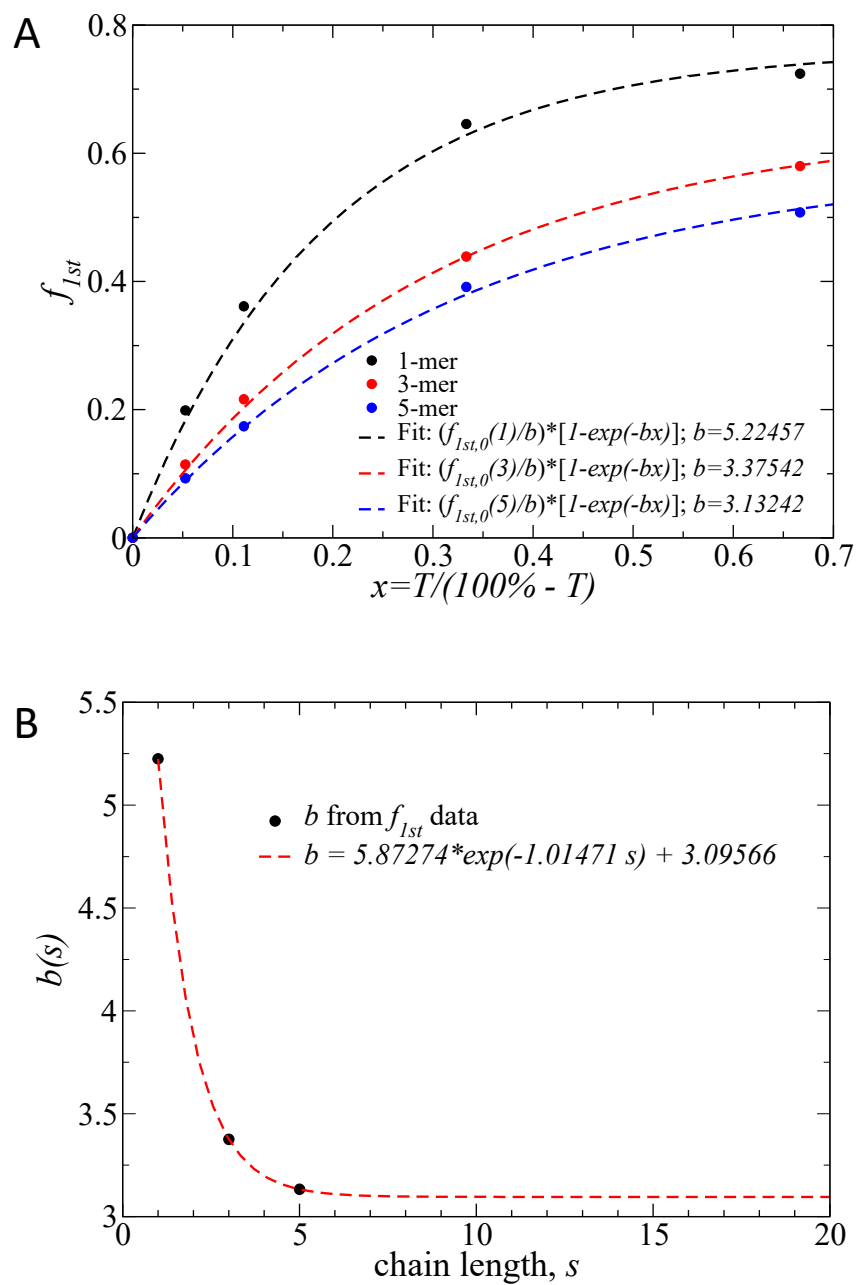
Figure S3. A) Fitting the fractions determined from the simulations to the first-order correction to the simple model used to describe the chemical system. **B)** Single exponential fit to the correction factor, $b(s)$, to use to describe its chain length dependence.
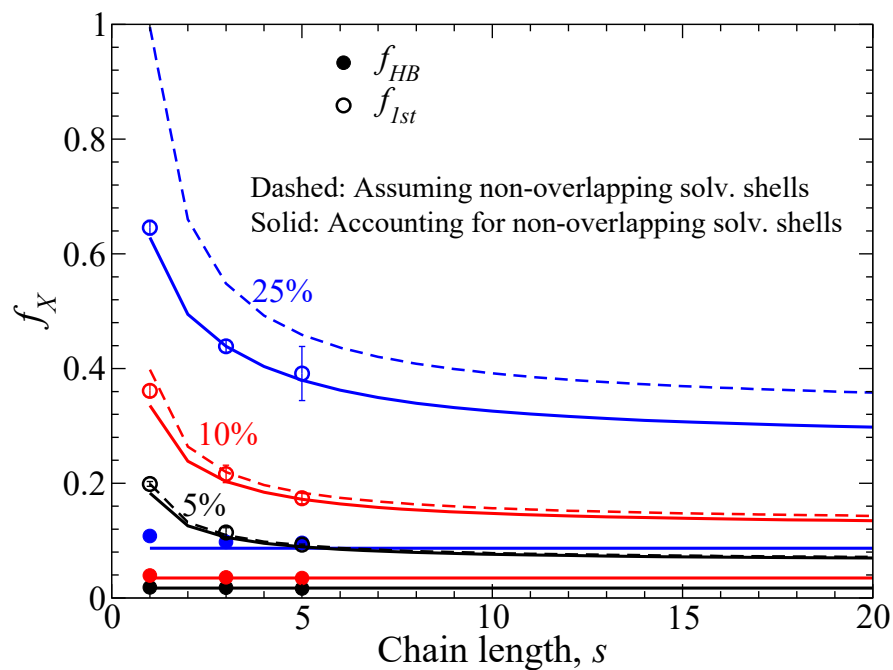
Figure S4. Comparison of the fractions of water molecules H-bonded to acrylamide, and those in the first solvation shell but not H-bonded calculated from the model, before (dashed line) and after (solid line) accounting for overlapping solvation shells. The fractions determined from the simulation are shown as points.
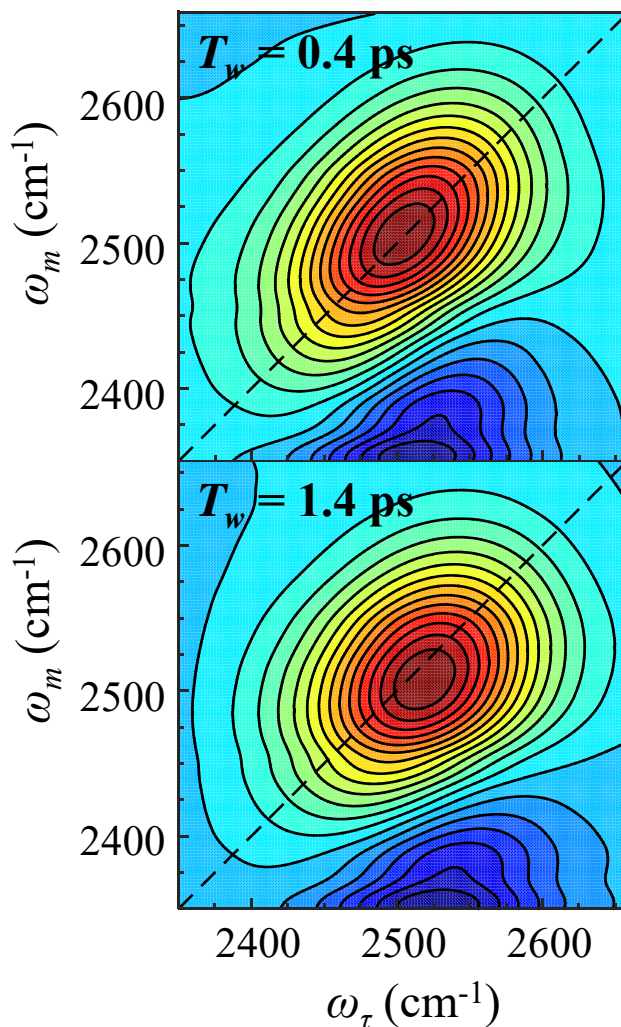
D. Representative 2D Spectra

Figure S5. Representative 2D spectra of the OD stretch of HOD in AAm at $T = 25\%$ at two waiting times, $T_w = 0.4$ ps and 1.4 ps.

The time dependence of the 2D line shape is illustrated in Fig. S5, which displays 2D spectra of the OD stretch of HOD in AAm with $T = 25\%$ at two times, T_w, 0.4 ps and 1.4 ps. The red band on the diagonal (dashed line) arises from the 0-1 vibrational transition while the blue band is a result of the 1-2 transition. The data analysis is performed on the 0-1 band. At 0.4 ps, the 2D spectrum is more elongated along the diagonal than the band at 1.4 ps.