

Weight Averaged Anharmonic Vibrational Analysis of Hydration Structures of Polyamide 6

Supporting Information

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S1 Force field parameters for polyamide 6

The force field used to model polyamide 6 (PA6) in this study are parameterized using the form of the CHARMM force field, *i.e.* based on bond lengths, angles, dihedral angles and pairs of non-bonding interactions. The parameters are assigned based on the atom types involved in a given interaction. The atom types in the repeating unit and the two capping groups of the PA6 chains are given in Figure S1. These types and the corresponding parameters in Table S1-S5 were assigned by similarity to parameters in the CHARMM 36 lipid force field,¹ the CHARMM 22 force field,² and the sphingomyelin force field.³ Parameters from the various force fields were used primarily for the carbon chains, the capping groups and the amide group in the repeating unit respectively. Water was in this study modeled using the TIP3P model.⁴

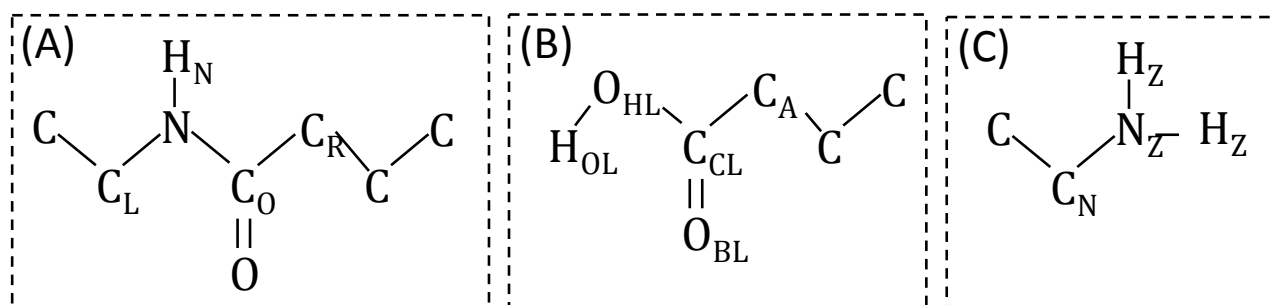


Figure S1: The topology of (A) the repeating unit of PA6, (B) the left terminal group and (C) the right terminal group. The carbon atoms C, C_L, C_A and C_{CN} are all bound two hydrogen atoms, which are left out for clarity. These hydrogen atoms have the same subscript as the carbon atom they are bound to, *i.e.* C_L is bound to two hydrogen atoms with the label H_L.

In the following the CHARMM force field form will briefly be described, this is done for completeness and understanding of how the parameters in S1-5 is used in the model presented in Figure 5. The CHARMM force field is divided into a set of bonded and non-bonded interactions,

$$V = V_{bonded} + V_{non-bonded}. \quad (S1)$$

The non-bonded term contains two contributions,

$$V_{non-bonded} = V_{elec} + V_{LJ}. \quad (S2)$$

Both of these terms are calculated as a set of pairwise interactions, with a given cutoff length and cutoff scaling function range as described in the main text. V_{elec} is the electrostatic interactions given as the standard columbic charge interaction,

$$V_{elec} = \frac{q_i q_j}{\epsilon r_{ij}}, \quad (S3)$$

where q_i is the charge of the given atom type, r_{ij} is the distance between the atoms and ϵ is the permittivity of vacuum. The charges for the individual atom types are given in Table S1.

Table S1 : Non-bonding parameters used for PA6 in this study.

Atom type	q_i (C)	ϵ_i (kcal/mol)	$R_{min}/_2$ (Å)	$\epsilon_i(1 - 4)$ (kcal/mol)	$R_{min}/_2 (1 - 4)$ (Å)
C	-0.18	-0.056	2.010	-0.01	1.90
H	0.09	-0.028	1.340	-	-
C _L	0.25	-0.056	2.010	-0.01	1.90
H _L	0.05	-0.028	1.340	-	-
N	-0.70	-0.200	1.850	-0.20	1.55
H _N	0.35	-0.046	0.2245	-	-
C _O	0.55	-0.110	2.000	-	-
O	-0.60	-0.120	1.700	-0.12	1.40
C _R	-0.07	-0.056	2.010	-0.01	1.90
H _R	0.06	-0.028	1.340	-	-
C _{CN}	0.13	-0.056	2.010	-0.01	1.90
H _{CN}	0.075	-0.028	1.340	-	-
N _Z	-0.96	-0.200	1.850	-	-
H _Z	0.34	-0.046	0.2245	-	-
H _{OL}	0.44	-0.046	0.2245	-	-
O _{HL}	-0.61	-0.1521	1.770	-	-
C _{CL}	0.75	-0.070	2.000	-	-
O _{BL}	-0.55	-0.120	1.700	-0.12	1.40
C _A	-0.21	-0.056	2.010	-0.01	1.90
H _A	0.09	-0.028	1.340	-	-

The second term in Eq. (2) is the Lenard-Jones potential, given as

$$V_{LJ} = \sqrt{\epsilon_i \epsilon_j} \left(\left(\frac{R_{min_i} + R_{min_j}}{2r_{ij}} \right)^{12} - 2 \left(\frac{R_{min_i} + R_{min_j}}{2r_{ij}} \right)^6 \right). \quad (S4)$$

r_{ij} is the distance between the two atoms, the two parameters ε_i and R_{min_i} are determined by the Van der Walls radius and the interaction strengths of a given atom. The fixed parameters for each atom type are given in Table S1. The non-bonding interactions are not calculated for bond neighbors or bond neighbors' neighbors. For interactions between atoms which are separated by three bonds the parameters are for some atoms changes slightly as seen for the atoms which has entries in the 1-4 column of Table S1.

Table S2 : The Bond force constants, K_{ij}^b , and equilibrium distances, b_{ij}^0 , for the PA6 force field. The C_L , C_R , C_A and C_{CN} atom types can here be substituted in place of C, as the bond parameters are similar for these five types of carbon. The same applies to the attached hydrogen H_L , H_R , H_A and H_{CN} , which can be substituted in place for H.

Bond type	K_{ij}^b (kcal/mol)	b_{ij}^0 (Å)
C-C	222.50	1.530
C-H	309.00	1.111
C_L -N	320.00	1.430
N- H_N	440.00	0.997
N- C_O	370.00	1.345
C_O -O	620.00	1.230
C_O - C_R	250.00	1.490
N_Z - H_Z	460.0	1.000
C_{CN} - N_Z	240.0	1.430
C- C_{CL}	200.0	1.522
C_{CL} - O_{BL}	750.0	1.220
C_{CL} - O_{HL}	230.0	1.400
O_{HL} - H_{OL}	545.0	0.960

The bonded interactions are composed of the following in terms in this study

$$V_{bonded} = V_{bond} + V_{ang} + V_{UB} + V_{dih} + V_{imp}. \quad (S5)$$

The contribution from the bonds between atom i and j are calculated as follows,

$$V_{bond}(b_{ij}) = K_{ij}^b(b_{ij} - b_{ij}^0)^2. \quad (S6)$$

Where b_{ij} is the distance between the two bonded atoms, b_{ij}^0 is the equilibrium distance and K_{ij}^b is the bonds force constant. The equilibrium distances and force constants used in this study are given in Table S2.

Table S3: Angle and Urey-Bradley parameters for the PA6 force field. The substitutions C to C, C_L, C_R, C_A or C_{CN}; and H to H, H_L, H_R, H_A or H_{CN} applies here as described in Table S2.

Angle type	K_{ijk}^θ ((kcal/mol)/Rad ²)	θ_{ijk}^0 (Degrees)	K_{ik}^{UB} ((kcal/mol)/Å ²)	S_{ik}^0 (Å)
C-C-C	58.350	113.60	11.16	2.561
H-C-C	26.500	110.10	22.53	2.179
H-C-H	35.500	109.00	5.40	1.8020
C _O -C-C	52.000	108.00	-	-
O-C _O -C	80.000	121.00	-	-
H-C-C _O	33.000	109.50	30.00	1.630
O-C _O -N	80.000	122.50	-	-
N-C _O -C	80.000	116.50	-	-
H _N -N-C	34.000	123.00	-	-
CO-N-C	50.000	120.00	-	-
HN-N-C	35.000	117.00	-	-
N-C-C	70.000	113.50	-	-
N-C-H	35.000	117.00	-	-
H _Z -N _Z -H _Z	39.000	106.5	-	-
H _Z -N _Z -C	50.000	111.0	-	-
C-C-N _Z	67.700	110.0	-	-
N _Z -C-H	38.000	109.5	50.00	2.1400
O _{BL} -C _{CL} -C	70.0	125.0	20.0	2.442
O _{HL} -C _{CL} -C	55.0	110.5	-	-
H _{OL} -O _{HL} -C _{CL}	55.0	115.0	-	-
O _{HL} -C _{CL} -O _{BL}	50.0	123.0	210.0	2.262

The bond angle is defined as another harmonic potential,

$$V_{ang}(\theta_{ijk}) = K_{ijk}^\theta (\theta_{ijk} - \theta_{ijk}^0)^2. \quad (S7)$$

Here K_θ is the force parameter and θ_{ijk}^0 is the equilibrium angle. The Urey-Bradley (UB) terms further alter the interactions defined over two bonds. Their argument is the distance, S_{ik} , between the first and third atom in the angle definition.

$$V_{UB}(S_{ik}) = K_{ik}^{UB} (S_{ik} - S_{ik}^0)^2, \quad (S8)$$

where K_{ik}^{UB} is the force constant and S_{ik}^0 is the equilibrium distance. The parameters for PA6 angle and UB terms are given in Table S3, where it should be noted that only a select number of interactions through two bonds have UB terms.

Table S4: Dihedral parameters for the PA6 force field. The X symbols are used to denote that any atom type can be at this position. The substitutions C to C, C_L, C_R, C_A or C_{CN}; and H to H, H_L, H_R, H_A or H_{CN} applies here as described in Table S2.

Dihedral type	K_{ijkl}^χ (kcal/mole)	n	χ_{ijkl}^0 (Degrees)
X-C-C-X	0.190	3	0.000
C-C-C-C	0.101	2	0.000
C-C-C-C	0.142	3	180.0
C-C-C-C	0.074	4	0.000
C-C-C-C	0.097	5	0.000
O-C ₀ -C-C	1.400	1	0.000
O-C ₀ -C-H	0.000	3	180.0
N-C ₀ -C-H	0.000	3	0.000
H _N -N-C ₀ -O	0.530	1	0.000
H _N -N-C ₀ -O	1.270	2	180.0
H _N -N-C ₀ -O	0.140	3	0.000
H _N -N-C ₀ -O	0.780	4	0.000
H _N -N-C ₀ -C	2.500	2	180.0
C-C-C ₀ -N	1.990	1	0.000
C-C-C ₀ -N	0.640	2	180.0
C-C-C ₀ -N	0.280	3	180.0
C-N-C ₀ -C	0.000	1	0.000
C ₀ -N-C-H	0.000	3	0.000
C ₀ -N-C-C	1.800	1	0.000
O-C ₀ -N-C	2.500	2	180.0
H _N -N-C-H	0.000	3	0.000
H _N -N-C-C	0.000	1	0.000
H _Z -N _Z -C-H	0.11000	3	0.0000
C-C-N _Z -H _Z	0.11000	3	0.0000
C-C-C-C _{CL}	0.000	5	180.0
C-C-C-C _{CL}	0.317	3	180.0
C-C-C-C _{CL}	0.557	2	0.000
C-C-C-C _{CL}	0.753	1	0.000
O _{BL} -C _{CL} -C _A -H _A	0.000	6	180.0
H _A -C _A -C _{CL} -O _{HL}	0.000	6	180.0
X-C _{CL} -O _{HL} -X	2.050	2	180.0

The final two bonded interactions of Eq. (S5) are the dihedral and improper terms. These are defined by the dihedral, χ_{ijkl} , and improper angles, ψ_{ijkl} , between atoms connected over three bonds. The dihedral term is given as

$$V_{dih}(\chi_{ijkl}) = K_{ijkl}^{\chi} (1 + \cos(n\chi_{ijkl} - \chi_{ijkl}^0)), \quad (S9)$$

with the force parameter K_{ijkl}^{χ} and equilibrium angle χ_{ijkl}^0 . The parameter n is an integer, which modulates the number of minima and maxima in the potential term. There can be several different terms with different n 's determining the total dihedral potential of a given angle. The improper angle terms are defined as a simple harmonic term

$$V_{imp}(\psi_{ijkl}) = K_{ijkl}^{\psi} (\psi_{ijkl} - \psi_{ijkl}^0)^2, \quad (S10)$$

with the force constant K_{ψ} and equilibrium angle ψ_0 . The dihedral parameters for PA6 are given in Table S4 and the improper parameters in Table S5.

Table S5: Improper parameters for the PA6 force field. The X symbols denote that any atom type can be placed in the given position.

Improper type	K_{ijkl}^{ψ} ((kcal/mol)/rad ²)	ψ_{ijkl}^0 (Degrees)
N-X-X-H _N	20.00	0.000
O-X-X-C _O	120.0	0.000

S2 Molecular Dynamics Movies

The movie of water dynamics, SIMovie.mov, in the PA6 membrane were created using VMD.⁵ The first 400 ns of the trajectories of the PA6 membrane containing 2.3 wt %, 4.5 wt %, 8.6 wt %, and 15.9 wt % water were used to generate the movie. Every 50th frame from the molecular dynamics (MD) production run were rendered and used in the encoding of the final movie, corresponding to 0.5 ns of MD simulation time between each frame used.

S3 H-Bond Strength in the NMA Clusters

The H-bond strength of bonds formed by water and amide can be described based on fragmentation energies. The H-bond strength is calculated by considering the electronic ground state energy of the cluster and those of the fragments created upon breaking the H-bond in question. For example, the H-bond energy of the $\text{N-H}\cdots\text{O}=\text{C}$ H-bond in the 1A-A-1A cluster is calculated as

$$E_{HB}(1A-A-1A) = E_0(1A-A-) - E_0(-A-) - E_0(1A-A-1A). \quad (\text{S11})$$

The resulting H-bond strengths are given in Figures S2 and S3 for the $\text{N-H}\cdots\text{X}$ and $\text{C}=\text{O}\cdots\text{H}$ H-bonds, respectively.

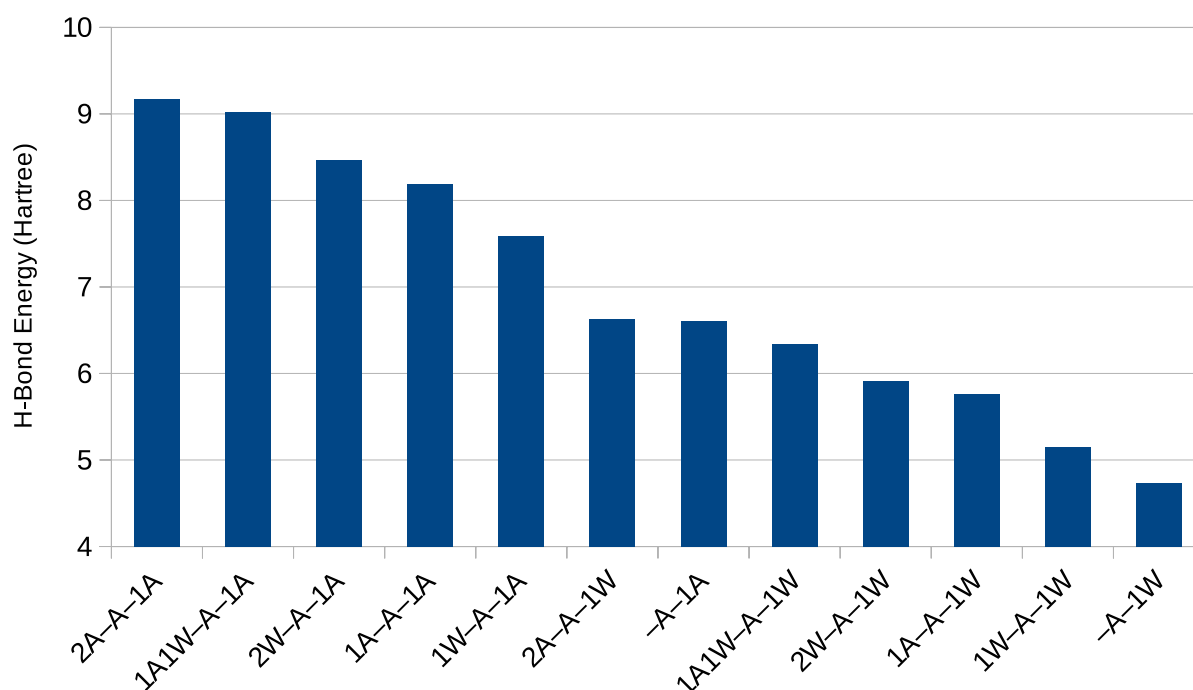


Figure S2: The H-bond strength of the $\text{N-H}\cdots\text{X}$ bonds in the amide clusters. The cluster types are sorted according to energy, *i.e.* the left most cluster has the strongest $\text{N-H}\cdots\text{X}$ H-bond.

We find that the H-bond strength of the $\text{N-H}\cdots\text{X}$ and $\text{C}=\text{O}\cdots\text{H}$ follows the trends in red shifts seen in amide A and I, respectively, whereas the blue shift of amide II follows the strength of the $\text{N-H}\cdots\text{X}$

X H-bond. This is because a stronger H-bond indicates a weakening of the N-H and C=O bonds participating in the H-bond. In the case of amide II, the bending motion of N-H becomes stiffer with a stronger H-bond acceptor, leading to a blue shift of the vibrational band.

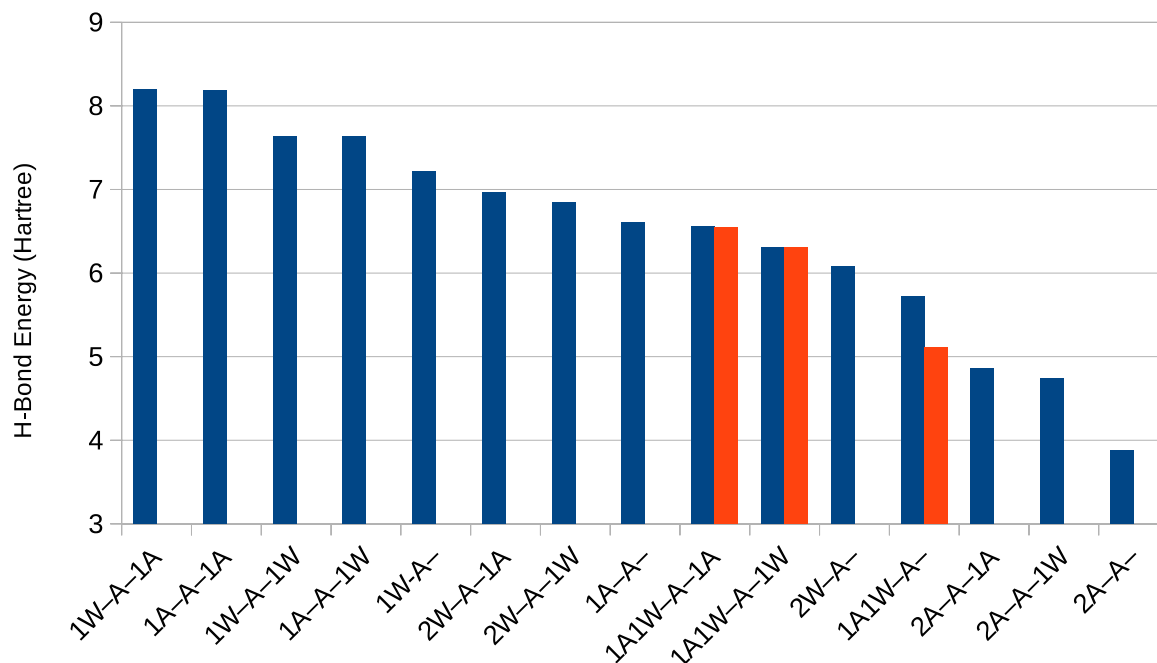


Figure S3: The H-bond strength of the C=O...H bonds in the amide clusters in blue. For the clusters 1A1W-A-1A, 1A1W-A-1W and 1A1W-A- the strength of the H-bond involving amide and C=O are given in red. The cluster types are sorted according to energy, *i.e.* the left most cluster has the strongest N-H...X H-bond.

S4 Anharmonic Vibrational Data

In the current study we use forty clusters to model the anharmonic vibrational spectrum of PA6. These clusters and their IR vibrational properties, as well as their concentrations in each MD simulation, are given in Table S6-12. The frequencies are given in cm^{-1} , the intensity is given in km/mol , and the concentrations in mol/L .

Table S6: Structures, concentrations and anharmonic vibrational data, see section C for details.

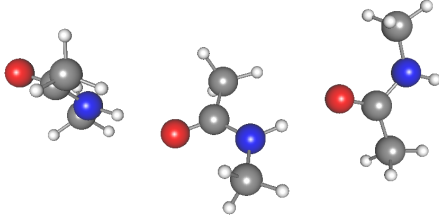
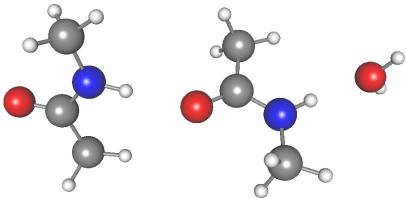
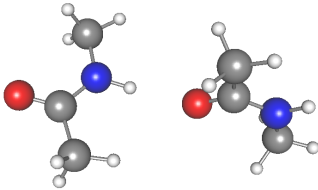
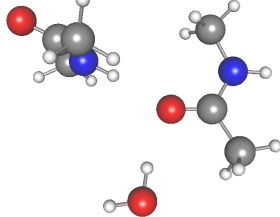
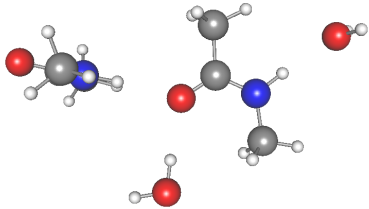
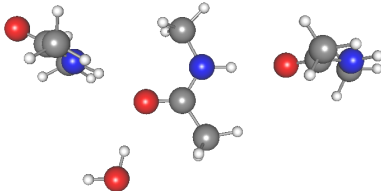
1A-A-1A						1A-A-1W					
											
Motion		Frequency		Intensity		Frequency		Intensity			
Amide III		1312		74		1296		70			
Amide II		1570		256		1552		256			
Amide I		1684		553		1692		508			
Amide A		3354		663		3408		349			
wt %	0	2.3	4.5	8.6	15.9	0	2.3	4.5	8.6	15.9	
Conc.	3.85	2.85	1.46	0.851	0.197	0	0.379	0.604	0.513	0.296	
1A-A-						1A1W-A-					
											
Motion		Frequency		Intensity		Frequency		Intensity			
Amide III		1259		57		1272		46			
Amide II		1519		271		1530		258			
Amide I		1701		466		1677		463			
Amide A		3505		31		3504		37			
wt %	0	2.3	4.5	8.6	15.9	0	2.3	4.5	8.6	15.9	
Conc.	1.70	1.18	1.01	0.576	0.207	0	0.120	0.248	0.329	0.335	
1A1W-A-1W						1A1W-A-1A					
											
Motion		Frequency		Intensity		Frequency		Intensity			
Amide III		1313		57		1329		68			
Amide II		1568		251		1583		258			
Amide I		1669		556		1661		542			
Amide A		3393		387		3323		733			
wt %	0	2.3	4.5	8.6	15.9	0	2.3	4.5	8.6	15.9	
Conc.	0	0.040	0.115	0.286	0.434	0	0.238	0.385	0.488	0.400	

Table S7: Structures, concentrations and anharmonic vibrational data, see section C for details.

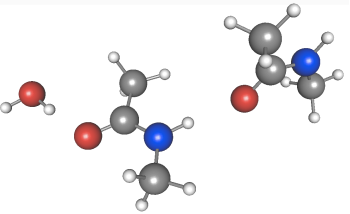
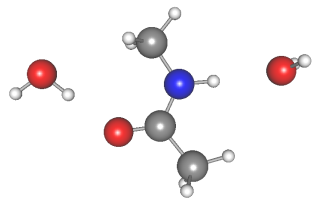
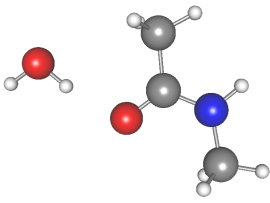
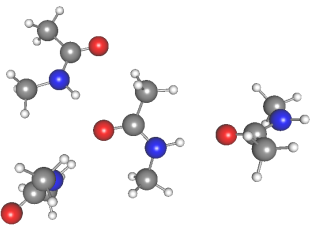
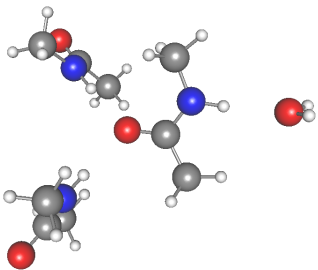
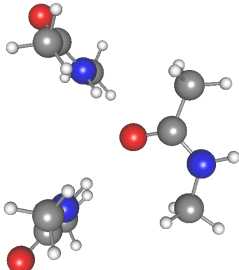
1W-A-1A						1W-A-1W					
											
Motion		Frequency		Intensity		Frequency		Intensity			
Amide III		1314		75		1296		73			
Amide II		1570		244		1553		230			
Amide I		1682		448		1695		406			
Amide A		3345		624		3413		311			
wt %	0	2.3	4.5	8.6	15.9	0	2.3	4.5	8.6	15.9	
Conc.	0	1.00	1.57	1.32	0.797	0	0.186	0.386	1.07	1.18	
1W-A-						2A-A-1A					
											
Motion		Frequency		Intensity		Frequency		Intensity			
Amide III		1260		57		1324		68			
Amide II		1519		270		1577		309			
Amide I		1696		370		1653		511			
Amide A		3507		28		3338		702			
wt %	0	2.3	4.5	8.6	15.9	0	2.3	4.5	8.6	15.9	
Conc.	0	0.460	0.952	1.07	1.02	0.243	0.283	0.200	0.068	0.083	
2A-A-1W						2A-A-					
											
Motion		Frequency		Intensity		Frequency		Intensity			
Amide III		1309		59		1271		47			
Amide II		1564		258		1530		264			
Amide I		1666		512		1678		485			
Amide A		3386		414		3501		39			
wt %	0	2.3	4.5	8.6	15.9	0	2.3	4.5	8.6	15.9	
Conc.	0	0.059	0.061	0.072	0.075	0.110	0.067	0.072	0.047	0.043	

Table S8: Structures, concentrations and anharmonic vibrational data, see section C for details.

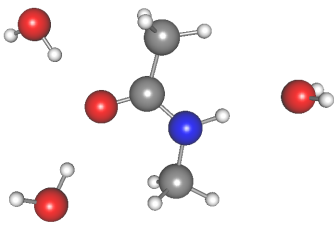
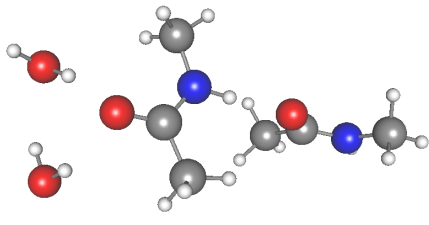
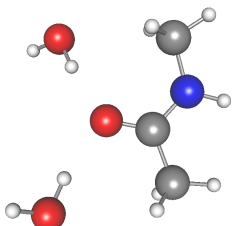
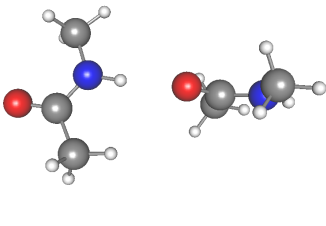
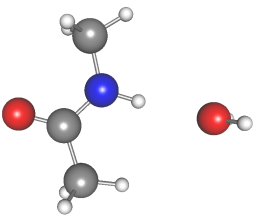
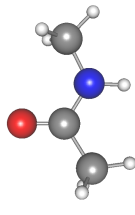
2W-A-1W 						2W-A-1A 					
Motion		Frequency		Intensity		Frequency		Intensity			
Amide III		1313		58		1327		70			
Amide II		1567		245		1583		242			
Amide I		1664		461		1667		474			
Amide A		3398		361		3310		641			
wt %	0	2.3	4.5	8.6	15.9	0	2.3	4.5	8.6	15.9	
Conc.	0	0.008	0.051	0.353	0.998	0	0.063	0.161	0.442	0.777	
2W-A- 						-A-1A 					
Motion		Frequency		Intensity		Frequency		Intensity			
Amide III		1276		43		1289		99			
Amide II		1535		257		1554		223			
Amide I		1671		423		1711		362			
Amide A		3502		33		3369		544			
wt %	0	2.3	4.5	8.6	15.9	0	2.3	4.5	8.6	15.9	
Conc.	0	0.037	0.075	0.300	0.883	2.05	1.16	0.689	0.291	0.047	
-A-1W 						-A- 					
Motion		Frequency		Intensity		Frequency		Intensity			
Amide III		1273		93		1240		77			
Amide II		1536		227		1504		244			
Amide I		1716		328		1726		302			
Amide A		3429		271		3506		21			
wt %	0	2.3	4.5	8.6	15.9	0	2.3	4.5	8.6	15.9	
Conc.	0	0.185	0.248	0.225	0.071	1.15	0.558	0.484	0.228	0.061	

Table S9: Structures, concentrations and anharmonic vibrational data, see section C for details.

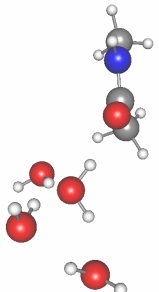
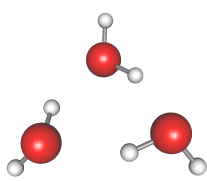
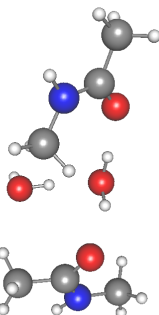
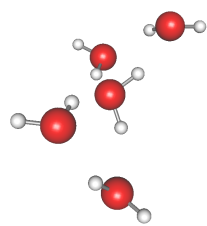
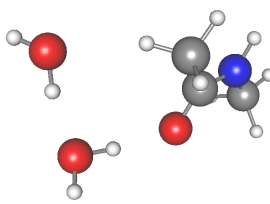
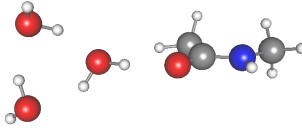
2W-W-1A1W 						1W-W-1W 				
Motion		Frequency		Intensity		Frequency		Intensity		
Bend		1594		36		1569		73		
H-Stretch		3214		797		3356		424		
H-Stretch		3431		564		3703		80		
wt %	0	2.3	4.5	8.6	15.9	0	2.3	4.5	8.6	15.9
Conc.	0	0.003	0.015	0.054	0.517	0	0.005	0.015	0.090	0.403
1W-W-2A 						2W-W-2W 				
Motion		Frequency		Intensity		Frequency		Intensity		
Bend		1615		88		1595		42		
H-Stretch		3390		659		3351		148		
H-Stretch		3449		581		3382		846		
wt %	0	2.3	4.5	8.6	15.9	0	2.3	4.5	8.6	15.9
Conc.	0	0.166	0.296	0.800	1.21	0	0.000	0.000	0.009	0.203
1W-W-1A 						1W-W-1A1W 				
Motion		Frequency		Intensity		Frequency		Intensity		
Bend		1596		54		1581		43		
H-Stretch		3228		621		3319		721		
H-Stretch		3708		81		3484		667		
wt %	0	2.3	4.5	8.6	15.9	0	2.3	4.5	8.6	15.9
Conc.	0	0.021	0.059	0.233	0.369	0	0.036	0.124	0.561	1.77

Table S10: Structures, concentrations and anharmonic vibrational data, see section C for details.

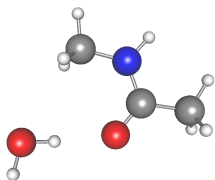
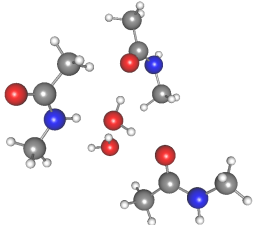
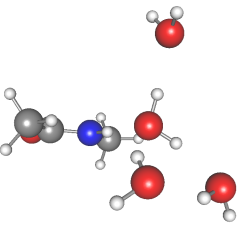
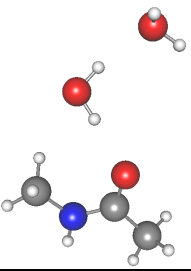
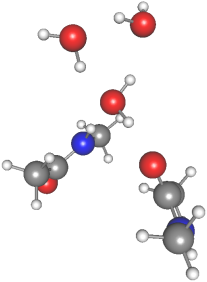
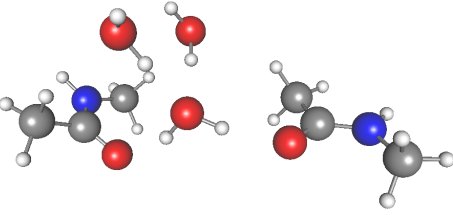
-W-1A 						1A1W-W-2A 				
Motion		Frequency		Intensity		Frequency		Intensity		
Bend		1587		62		1623		37		
H-Stretch		3398		642		3263		1202		
H-Stretch		3703		83		3308		677		
wt %	0	2.3	4.5	8.6	15.9	0	2.3	4.5	8.6	15.9
Conc.	0	0.042	0.108	0.093	0.080	0	0.047	0.075	0.160	0.204
1A1W-W-2W 						-W-1A1W 				
Motion		Frequency		Intensity		Frequency		Intensity		
Bend		1596		48		1613		82		
H-Stretch		3360		410		3471		364		
H-Stretch		3414		734		3565		442		
wt %	0	2.3	4.5	8.6	15.9	0	2.3	4.5	8.6	15.9
Conc.	0	0.000	0.000	0.029	0.141	0	0.040	0.117	0.249	0.320
1A1W-W-1A1W 						2W-W-2A 				
Motion		Frequency		Intensity		Frequency		Intensity		
Bend		1596		37		1573		55		
H-Stretch		3233		875		3248		825		
H-Stretch		3405		613		3382		1139		
wt %	0	2.3	4.5	8.6	15.9	0	2.3	4.5	8.6	15.9
Conc.	0	0.005	0.041	0.144	0.358	0	0.011	0.025	0.103	0.334

Table S11: Structures, concentrations and anharmonic vibrational data, see section C for details.

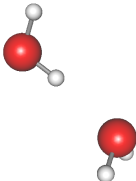
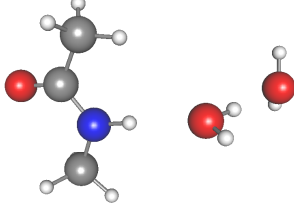
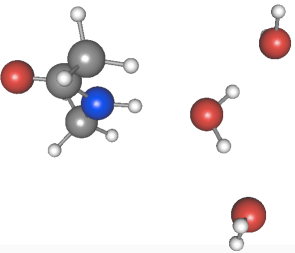
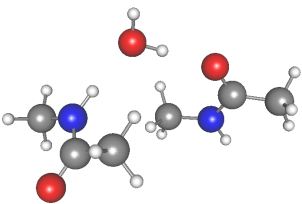
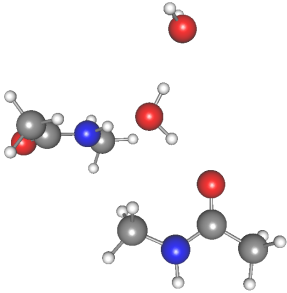
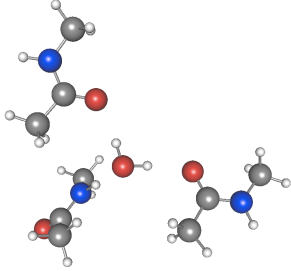
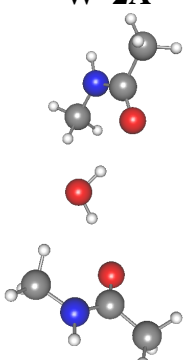
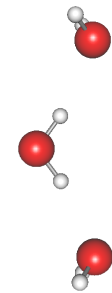
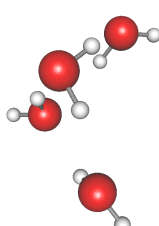
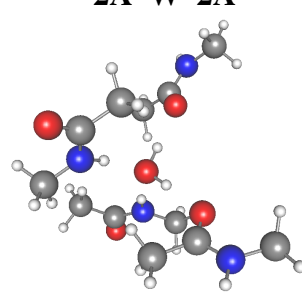
-W-1W 						1A-W-1W 					
Motion		Frequency		Intensity		Frequency		Intensity			
Bend		1565		59		1583		64			
H-Stretch		3485		363		3418		565			
H-Stretch		3697		89		3707		98			
wt %	0	2.3	4.5	8.6	15.9	0	2.3	4.5	8.6	15.9	
Conc.	0	0.010	0.017	0.056	0.095	0	0.025	0.025	0.086	0.149	
1A-W-2W 						1A-W-1A 					
Motion		Frequency		Intensity		Frequency		Intensity			
Bend		1588		40		1603		54			
H-Stretch		3465		257		3294		796			
H-Stretch		3507		775		3707		91			
wt %	0	2.3	4.5	8.6	15.9	0	2.3	4.5	8.6	15.9	
Conc.	0	0.028	0.023	0.132	0.350	0	0.058	0.135	0.156	0.122	
1A-W-1A1W 						1A-W-2A 					
Motion		Frequency		Intensity		Frequency		Intensity			
Bend		1599		36		1612		25			
H-Stretch		3392		661		3357		258			
H-Stretch		3505		714		3372		1676			
wt %	0	2.3	4.5	8.6	15.9	0	2.3	4.5	8.6	15.9	
Conc.	0	0.086	0.268	0.614	0.764	0	0.506	0.710	0.791	0.444	

Table S12: Structures, concentrations and anharmonic vibrational data, see section C for details.

<p>-W-2A</p> 						<p>-W-2W</p> 				
Motion		Frequency		Intensity		Frequency		Intensity		
Bend		1584		36		1573		39		
H-Stretch		3467		70		3509		92		
H-Stretch		3513		968		3562		597		
wt %	0	2.3	4.5	8.6	15.9	0	2.3	4.5	8.6	15.9
Conc.	0	0.223	0.467	0.263	0.206	0	0.014	0.006	0.042	0.154
<p>1W-W-2W</p> 						<p>2A-W-2A</p> 				
Motion		Frequency		Intensity		Frequency		Intensity		
Bend		1595		66		1620		20		
H-Stretch		3499		120		3263		1860		
H-Stretch		3560		265		3282		271		
wt %	0	2.3	4.5	8.6	15.9	0	2.3	4.5	8.6	15.9
Conc.	0	0.014	0.003	0.097	0.751	0	0.039	0.051	0.057	0.097

S5 Comparison of the amide vibrations

To compare the amide structures and vibrations of the amide chromophores of the clusters used to model the difference IR spectrum we measure the difference between them using a simple scheme.

For the structure we first align the central amide groups by translation of the entire cluster by the

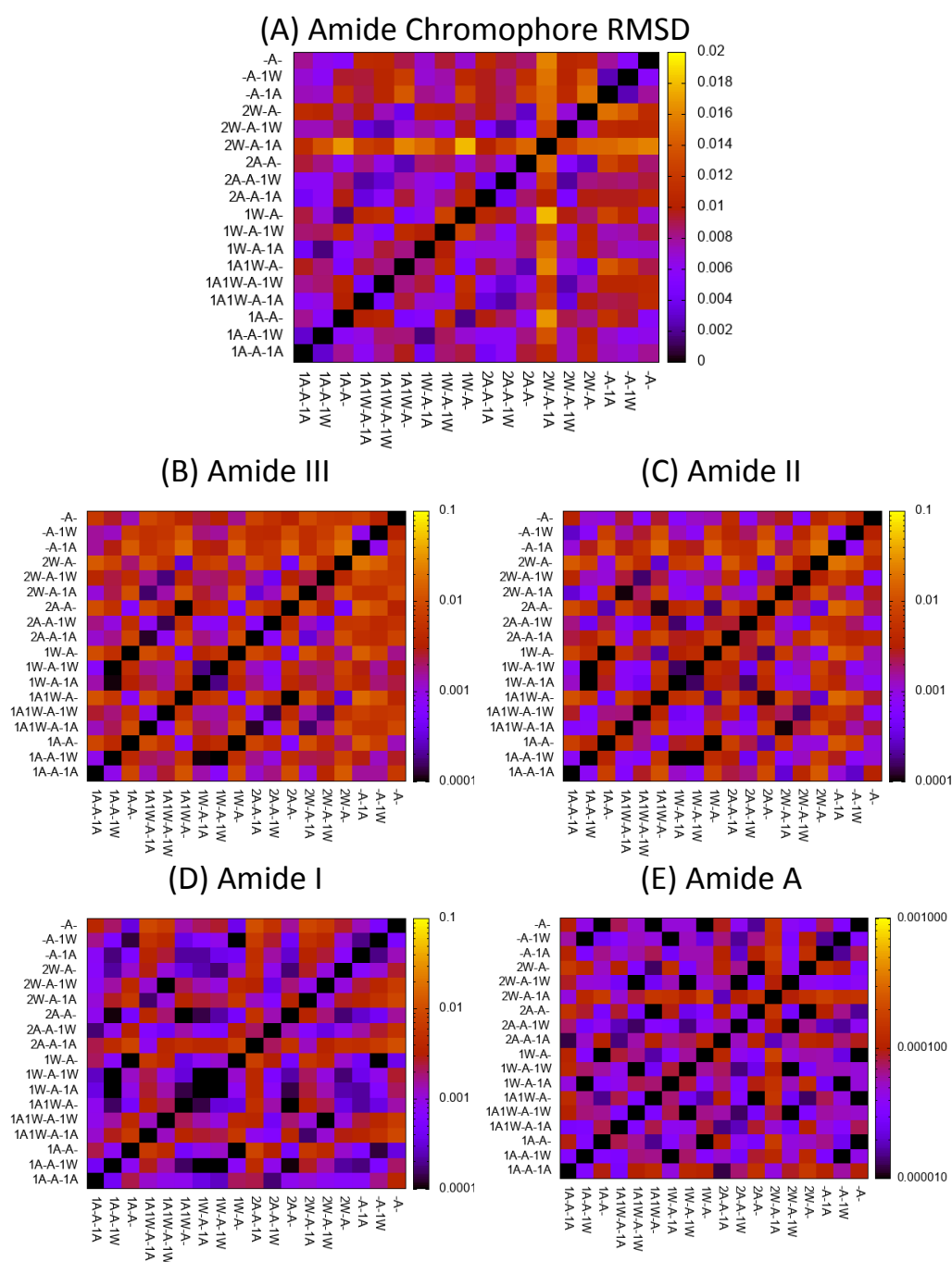


Figure S4: (A) The RMSD of aligned amide chromophores of the clusters used in this study. (B–E) σ_{jk}^i measure for the amide A, I, II and III of the clusters used in this study. In both cases a lower value signifies better agreement between the structures or vibrations, note the log scales on (B)–(E). centroid of the amide chromophore and then apply a fixed rotation for all coordinates of one cluster to minimize the difference between the chromophore coordinates of the two clusters.

The root mean squared deviation (RSMD) between the amide chromophores of the 18 investigated clusters is shown in a heat map representation in Figure S4A. The largest RSMD for the amide groups are 0.018, found between the clusters 2W–A–1A and 1W–A–. As can be seen in the figure the rotated structures are almost identical and we do therefore not expect any major contributions from the changes in internal geometry of the central amide in the vibrations of the cluster.

The rotation used to calculate the RSMD of the amide chromophore is also applied to the vibrational vectors to align the coordinate systems. We can then define the following measure,

$$\sigma_{jk}^i = 1 - v_j^i \cdot \tilde{v}_k. \quad (\text{S11})$$

Where v_j and \tilde{v}_k are the coordinate vector of the i th vibration of the j th cluster and k th rotated cluster respectively. A $\sigma_{jk}^i = 0$ means that the two vibrations are parallel and therefore equal, while $\sigma_{jk}^i = 1$ means that the vibrations are orthogonal.

Figure S2B-E display the σ_{jk}^i measure for the amide I, II, III and A vibrational vectors. The vectors in all cases very close to being parallel, suggesting that the vibrations generally happen in the same directions for all atoms in the amide group. This, coupled with the fact that the structures of the central amides are highly similar, suggests that a visualization of the vibrations of any one of the clusters would be equally valid for all clusters. We have therefore chosen to show the amide I, II, III and A motion of the –A– cluster in Figure S5A-D to clearly display the motions of an amide chromophore used in this study.

It should here be noted, that while the anharmonic description has vastly different band centers from the harmonic description, the VQDPT2 anharmonic description does not contain any significant mode mixing in any of the clusters investigated in the current study. We therefore expect that the motions of Figure S5 are a good representation of the anharmonic vibrations as well.

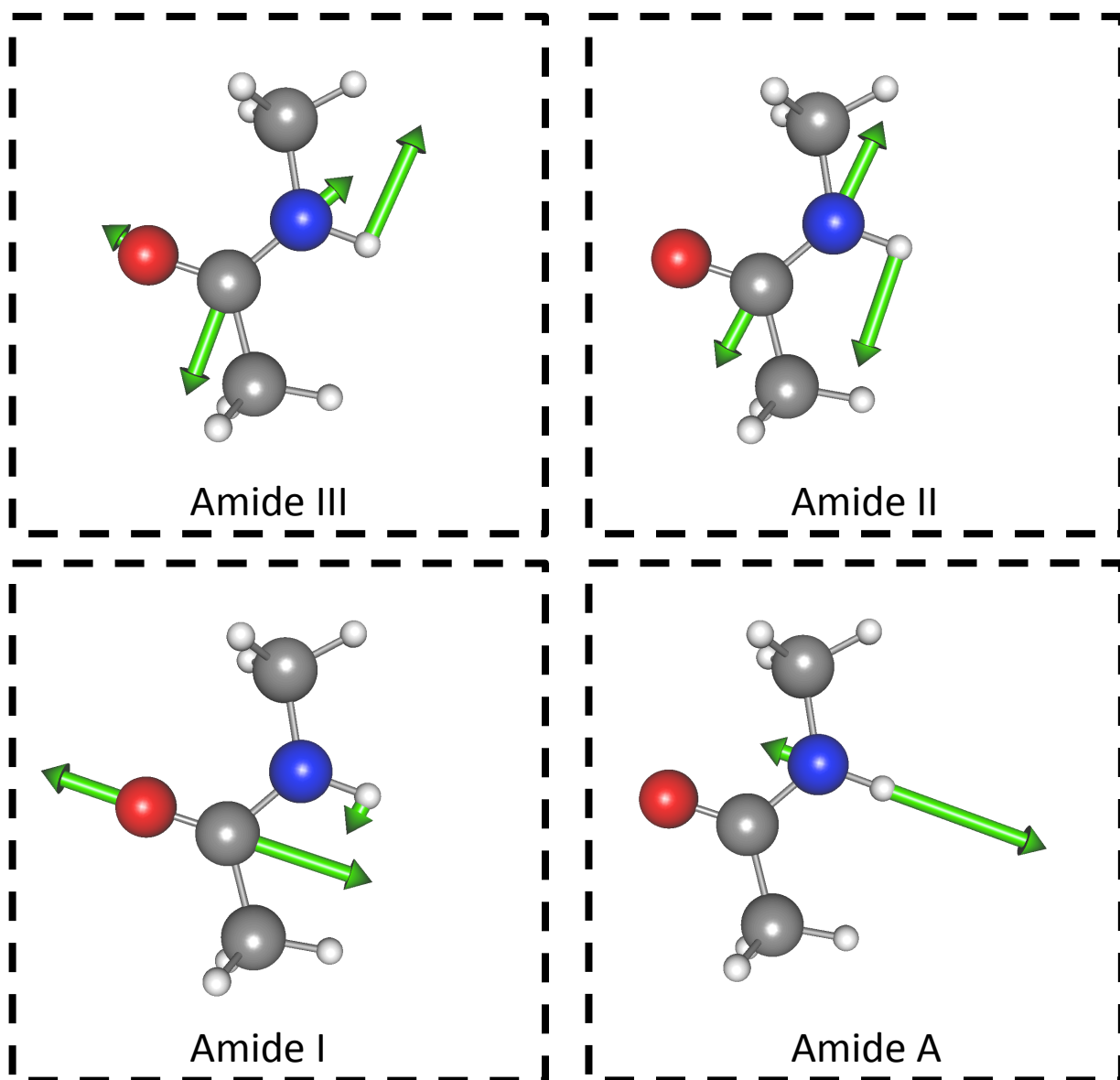


Figure S5: The normal coordinates of amide A, I, II and III of the $-A-$ cluster, corresponding to N-methyl acetamide (NMA). Note that only the Hessian of the central amide group were diagonalized to obtain these coordinates, as described in the main text.

S6 Infrared spectra of the five PA6 systems

The anharmonic IR spectrum of the PA6 systems containing 0.0 wt %, 2.3 wt %, 4.5 wt %, 8.62 wt % and 15.9 wt % have been calculated using the data in section C in Eq. (13) and plotted in

Figure S4. As is the case for the difference IR spectra in the main text a broadening factor, γ , of 40 cm^{-1} and 80 cm^{-1} have been used in the regions 3000 – 3800 cm^{-1} and 1400 – 1800 cm^{-1} respectively. These spectra are vastly different from the experimental spectra of hydrated PA6. This is because the statistic and models used in this study only captures the IR spectrum of the amorphous parts of PA6, where water can enter.

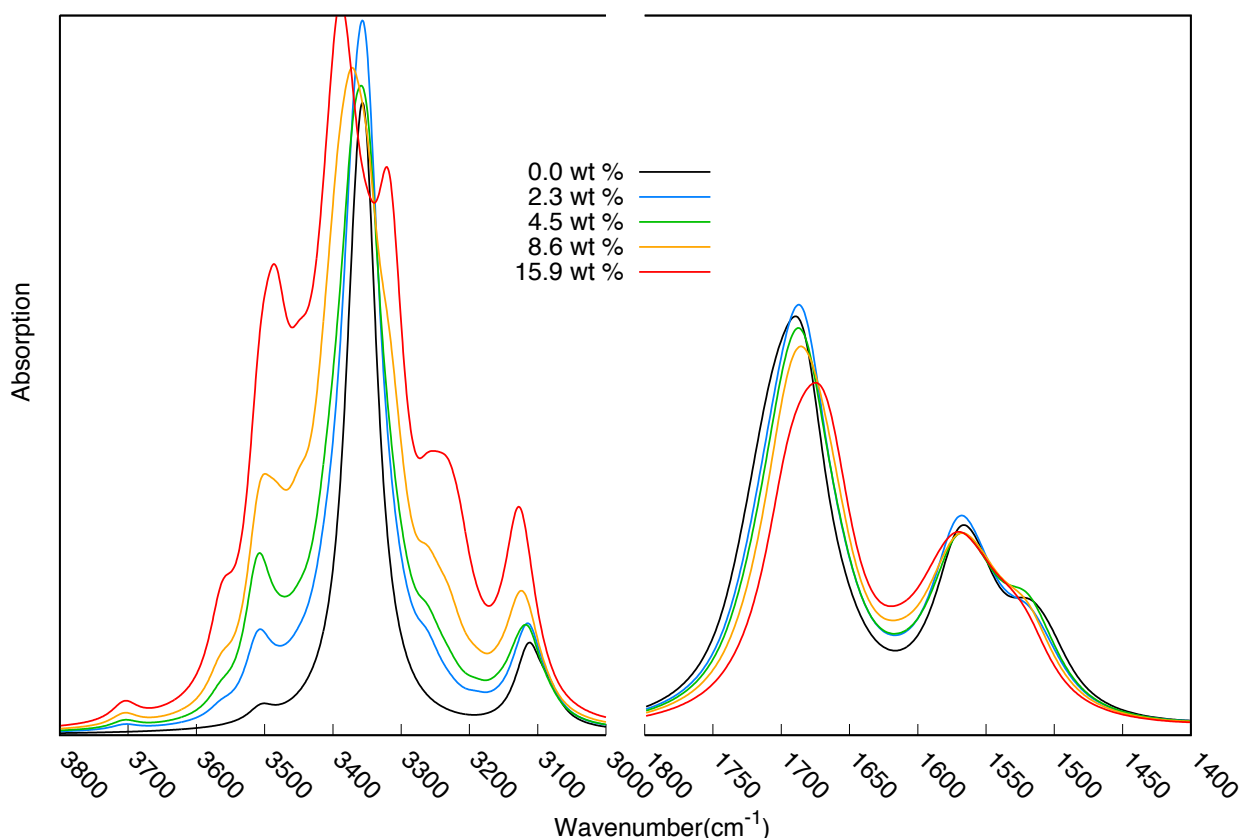


Figure S6: The anharmonic IR spectra of the five PA6 systems used in this study. They are calculated using the data presented in section C in Eq. (13) of the main text.

S7 Vibrational Shifts of The Amide I, II and A Vibrations

To help in identifying the patterns in the peak positions with respect to the H-bond acceptors and donors of the central amide chromophore three figures showing the vibrational shift when donors

and acceptors are added to the bare amide. The figures, Figure S7-9, are generated using the anharmonic frequencies given in Table S6-8.

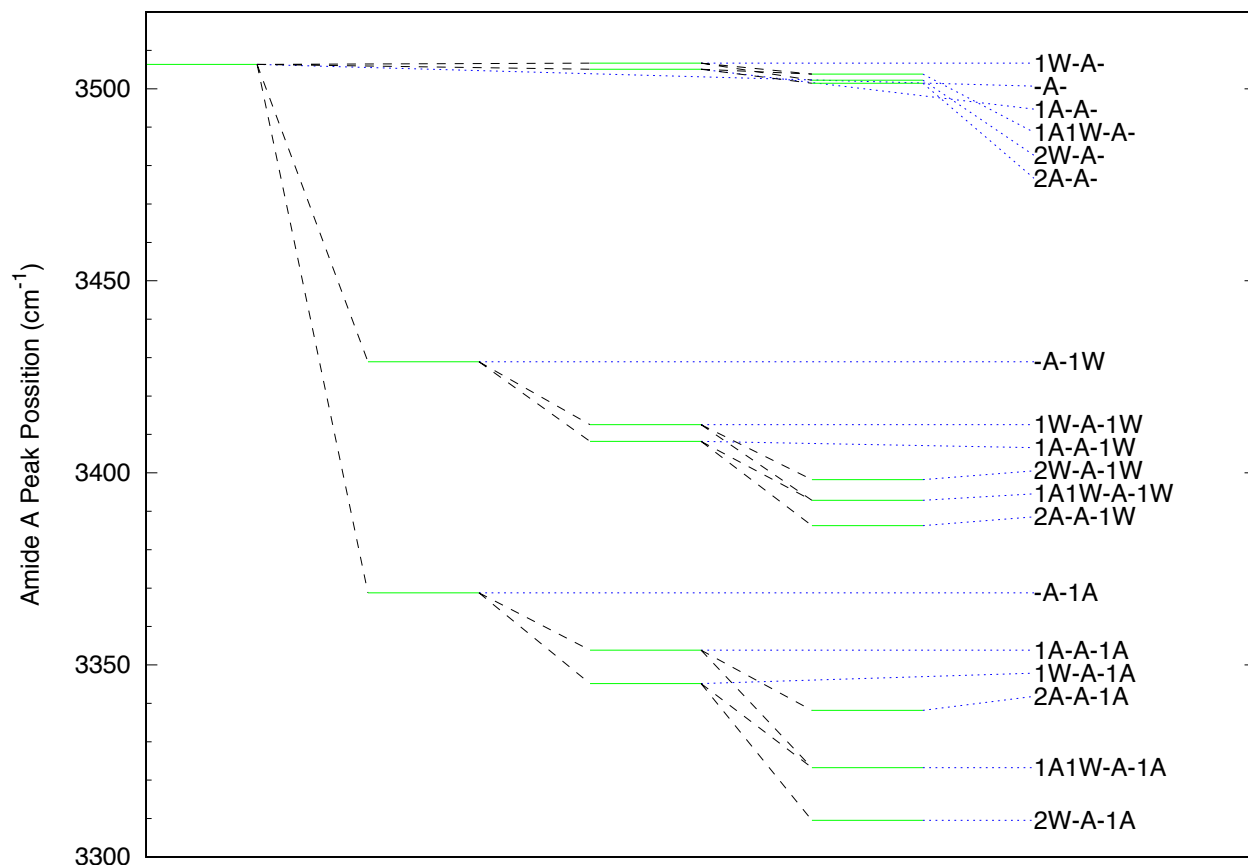


Figure S7: Shifts of the amide A vibrations categorized after H-bond acceptors and donors to the central amide chromophore. The first column corresponds to the bare amide chromophore, while the second adds a H-bond acceptor group. The third column adds the first H-bond donor to the chromophore and the fourth adds a second donor. The cluster names are given in descending order with respect to their amide A peak position.

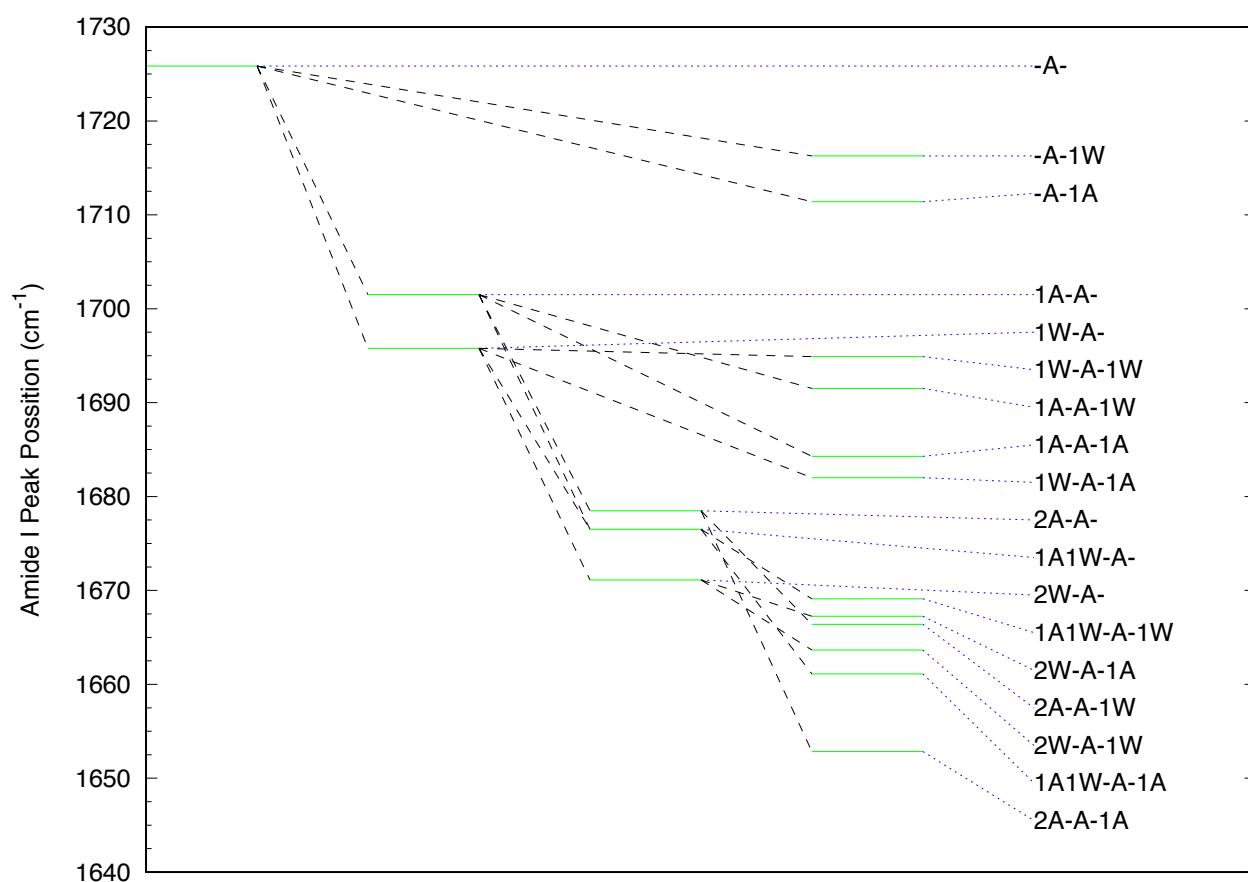


Figure S8: Shifts of the amide I vibrations categorized after H-bond acceptors and donors to the central amide chromophore. The first column corresponds to the bare amide chromophore, while the second and third column adds one or two H-bond donors respectively. The fourth column adds a H-bond acceptor to the central amide chromophore. The cluster names are given in descending order with respect to their amide I peak position.

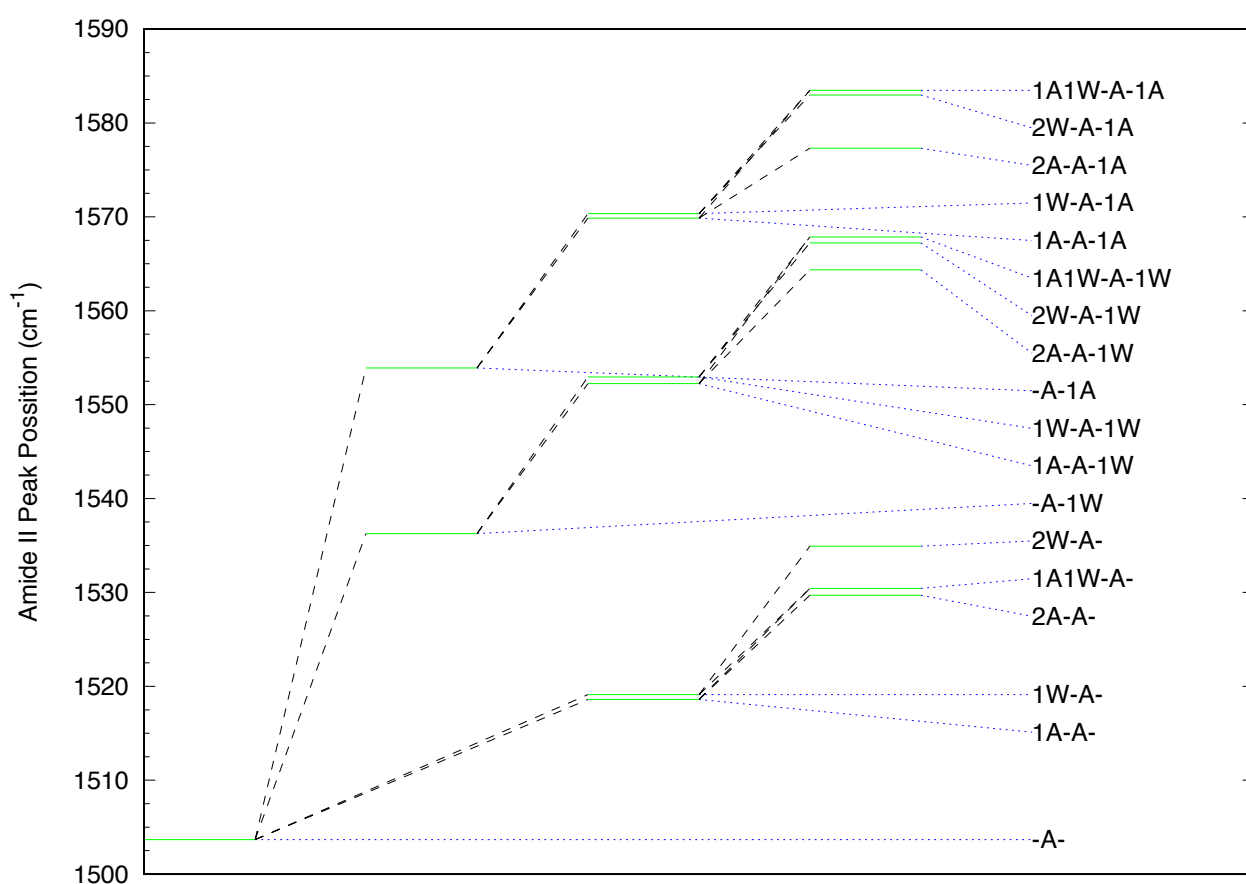


Figure S9: Shifts of the amide II vibrations categorized after H-bond acceptors and donors to the central amide chromophore. The first column corresponds to the bare amide chromophore, while the second adds a H-bond acceptor group. The third column adds the first H-bond donor to the chromophore and the fourth adds a second donor. The cluster names are given in descending order with respect to their amide II peak position.

S8 References

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