ELECTRONIC SUPPLEMENTARY INFORMATION

On the role of water in the hydrogen bond network in DES: An *ab-initio* molecular dynamics and quantum mechanical study on the urea–betaine system.

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I. SECOND ORDER PERTURBATION THEORY ENERGIES.

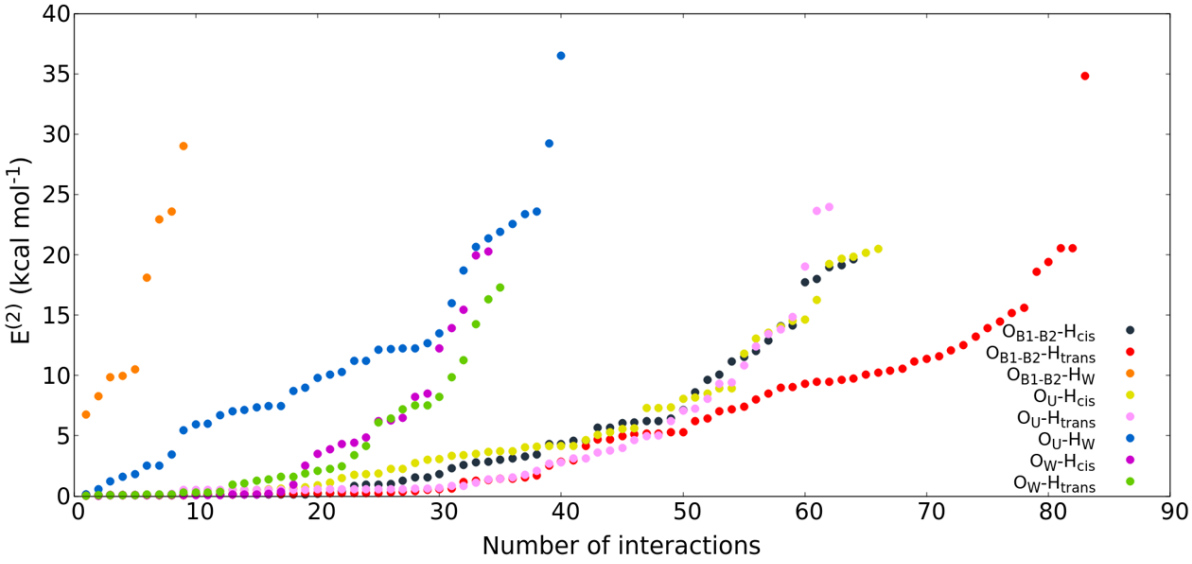


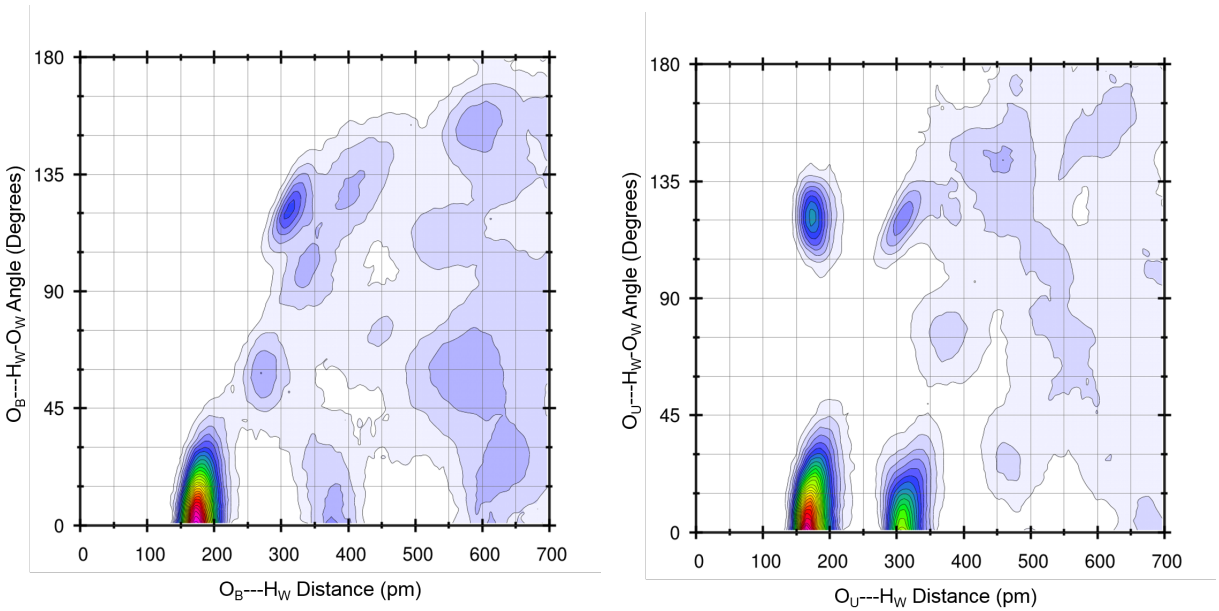
Figure S1. Summary of $E^{(2)}$ values obtained for different clusters obtained from the trajectory.

Table S1. Variation of $E^{(2)}$ for different clusters obtained from the trajectory. Data are summarized on Table S1. All values are presented in kcal mol^{-1}. See Figure 2 in the maintext for atom labelling. Data are presented as *electron donor – electron acceptor*.

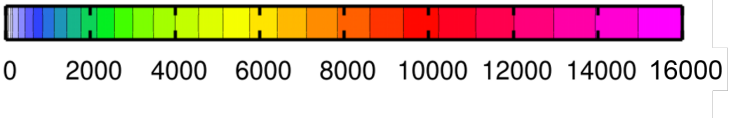
O_B–H_{cis}	O_B–H_{trans}	O_B–H_W	O_U–H_{cis}	O_U–H_{trans}	O_U–H_W	O_W–H_{cis}	O_B–H_{trans}
0.13	0.06	6.75	0.05	0.05	0.15	0.05	0.05
0.06	0.07	8.28	0.05	0.05	0.58	0.05	0.06
0.06	0.07	9.88	0.06	0.06	1.20	0.06	0.06
0.06	0.08	9.94	0.06	0.06	1.63	0.07	0.07
0.06	0.08	10.48	0.07	0.07	1.83	0.07	0.08
0.07	0.08	18.08	0.07	0.09	2.52	0.08	0.12
0.07	0.09	22.91	0.07	0.12	2.52	0.08	0.14
0.08	0.09	23.61	0.10	0.21	3.45	0.08	0.16
0.08	0.11	29.01	0.11	0.50	5.44	0.09	0.29
0.12	0.14		0.14	0.51	5.96	0.10	0.31
0.12	0.15		0.16	0.51	6.01	0.10	0.31
0.13	0.15		0.48	0.51	6.69	0.11	0.37
0.14	0.16		0.53	0.52	7.05	0.12	0.95
0.14	0.19		0.53	0.52	7.13	0.13	1.06
0.14	0.19		0.54	0.52	7.35	0.14	1.29
0.16	0.19		0.56	0.53	7.46	0.21	1.41
0.16	0.21		0.60	0.53	7.49	0.35	1.59
0.16	0.21		0.62	0.54	8.72	0.97	1.59
0.16	0.23		0.71	0.54	8.96	2.52	1.85
0.20	0.23		0.90	0.56	9.78	3.51	2.08
0.22	0.23		1.10	0.56	10.05	3.91	2.27
0.40	0.23		1.48	0.56	10.30	4.32	2.49
0.82	0.25		1.78	0.56	11.19	4.42	3.37
0.93	0.25		1.84	0.57	11.23	4.84	4.13
0.95	0.27		1.90	0.57	12.14	6.24	6.10
1.00	0.31		2.28	0.58	12.21	6.27	6.42
1.26	0.37		2.28	0.58	12.27	6.50	7.18
1.55	0.41		2.74	0.60	12.27	8.20	7.50
1.57	0.54		3.03	0.63	12.67	8.49	7.50
1.80	0.55		3.06	0.68	13.51	12.27	8.20
2.29	0.61		3.32	0.84	15.99	13.94	9.83
2.56	1.16		3.40	0.87	18.71	15.47	11.29
2.82	1.29		3.51	1.14	20.67	19.93	14.25
2.86	1.33		3.66	1.39	21.34	20.26	16.34
3.00	1.42		3.73	1.44	21.89		17.28
3.13	1.46		3.73	1.53	22.58		
3.31	1.54		4.05	1.78	23.35		
3.45	1.69		4.08	2.09	23.57		
4.31	2.50		4.15	2.67	29.24		
4.31	2.86		4.15	2.79	36.51		
4.58	2.97		4.16	3.12			
4.58	4.18		4.66	3.12			

Continued: Variation of $E^{(2)}$ for different clusters obtained from the trajectory. Data are summarized on Table S1. All values are presented in kcal mol^{-1}. See Figure 2 in the maintext for atom labelling. Data are presented as *electron donor – electron acceptor*.

O_B–H_{cis}	O_B–H_{trans}	O_B–H_W	O_U–H_{cis}	O_U–H_{trans}	O_U–H_W	O_W–H_{cis}	O_B–H_{trans}
5.68	4.69		5.10	3.62			
5.68	4.69		5.30	3.78			
6.08	4.95		5.54	4.00			
6.11	5.14		5.64	4.62			
6.24	5.17		7.32	4.96			
6.24	5.19		7.32	5.02			
6.41	5.28		7.37	6.21			
7.14	5.28		8.07	7.09			
8.61	6.22		8.15	7.27			
9.64	6.41		8.50	8.08			
10.07	7.04		8.92	9.33			
11.17	7.22		8.94	9.43			
11.55	7.43		11.83	10.81			
12.00	8.01		13.06	12.39			
12.91	8.50		13.56	13.42			
14.09	9.01		14.06	13.82			
14.17	9.04		14.51	14.87			
17.73	9.31		14.65	19.05			
17.98	9.45		16.25	23.64			
18.95	9.45		19.22	23.95			
19.11	9.63		19.70				
19.64	9.75		19.85				
	10.06		20.16				
	10.26		20.52				
	10.40						
	10.54						
	11.16						
	11.37						
	11.58						
	12.07						
	12.49						
	13.22						
	13.92						
	14.46						
	15.16						
	15.61						
	18.57						
	19.42						
	20.56						
	20.56						
	34.81						



(a) $O_B \cdots H_W$–O_W **(b)** $O_U \cdots H_W$–O_W



(c) Ocurrence

Figure S2. Combined Distribution Function (radial *vs.* angular distribution functions) obtained for the UBW sytem comparing the interaction of water with (a) betaine and (b) urea.

Table S2. Distance (Å), angle (Degree), and $E^{(2)}$ analysis (kcal mol^{-1}) from NBO, between *electron donor – electron acceptor* for $O_U \cdots H_W$–O_W interaction pairs.

Distance ($O_U \cdots H_W$)	Angle ($O_U \cdots H_W$–O_W)	$E^{(2)}$ analysis
3.12	41.35	0.15
2.47	133.13	0.58
1.85	163.41	1.20
1.64	172.34	5.44
1.88	175.05	5.96
1.96	139.79	6.01
1.94	163.74	7.49
1.82	145.89	8.96
1.56	161.13	9.78
1.81	160.52	10.30
1.80	175.80	11.23
1.67	170.44	12.14
1.59	163.75	12.21
1.50	167.82	21.89
1.54	159.87	22.58
1.54	159.87	23.35

Table S3. Distance (Å), angle (Degree), and $E^{(2)}$ analysis (kcal mol^{-1}) from NBO, between *electron donor – electron acceptor* for $O_B \cdots H_W$–O_W interaction pairs.

Distance ($O_B \cdots H_W$)	Angle ($O_B \cdots H_W$–O_W)	$E^{(2)}$ analysis
1.86	170.28	6.75
1.88	172.46	8.28
1.84	168.87	10.48
1.66	170.54	22.91
1.62	167.39	23.61

Table S4. Distance (Å), angle (Degree), and $E^{(2)}$ analysis (kcal mol^{-1}) from NBO, between *electron donor – electron acceptor* for $O_W \cdots H_{cis}$–N_U interaction pairs.

Distance ($O_W \cdots H_{cis}$)	Angle ($O_W \cdots H_{cis}$–N_U)	$E^{(2)}$ analysis
3.10	115.69	0.05
2.95	84.12	0.06
3.95	139.23	0.08
3.35	125.96	0.09
2.93	140.65	0.10
3.90	150.72	0.10
3.85	140.77	0.11
2.73	107.15	0.14
2.13	148.81	4.32
2.10	172.30	4.84
2.03	148.44	6.27
1.90	142.43	8.49
1.86	172.24	15.47
1.69	176.08	20.26

Table S5. Distance (Å), angle (Degree), and $E^{(2)}$ analysis (kcal mol^{-1}) from NBO, between *electron donor – electron acceptor* for $O_W \cdots H_{trans}$–N_U interaction pairs.

Distance ($O_W \cdots H_{trans}$)	Angle ($O_W \cdots H_{trans}$–N_U)	$E^{(2)}$ analysis
2.78	117.49	0.08
2.70	134.49	0.29
2.47	107.15	0.31
2.52	125.30	0.37
2.34	115.95	1.29
2.25	129.71	1.85
2.33	147.75	2.27
2.29	138.00	2.49
2.18	144.50	3.37
2.05	169.35	4.13
1.93	133.14	6.42
2.03	172.57	7.18
1.97	153.94	7.50
1.91	158.51	11.29
1.85	171.22	14.25
1.76	170.35	16.34
1.67	154.97	17.28

II. VIBRATIONAL ANALYSIS

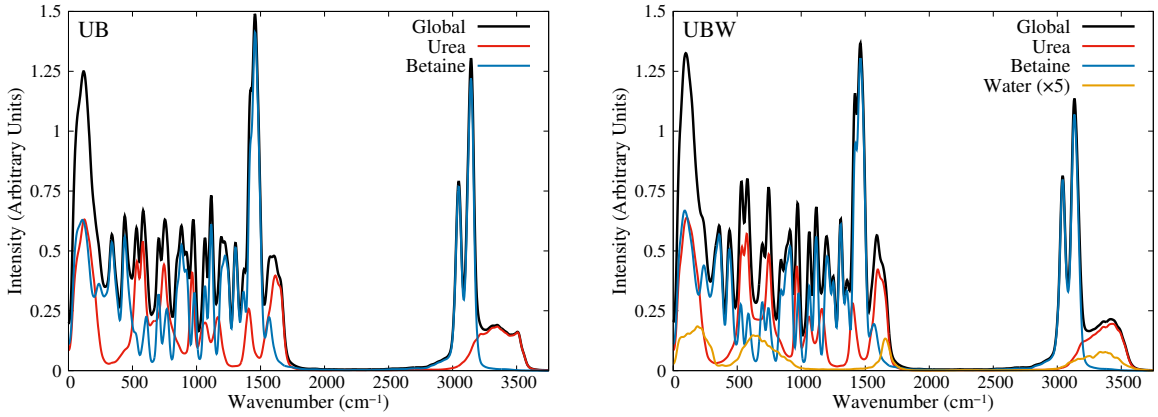
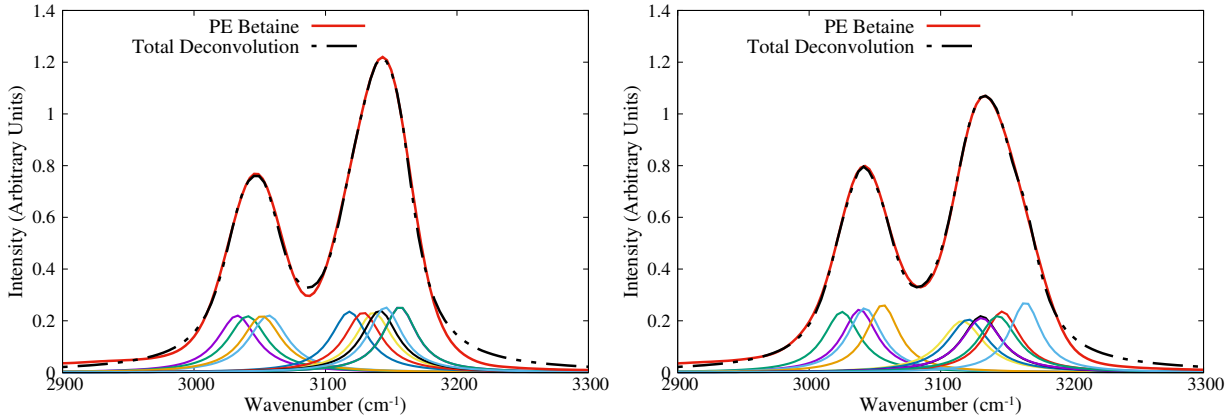
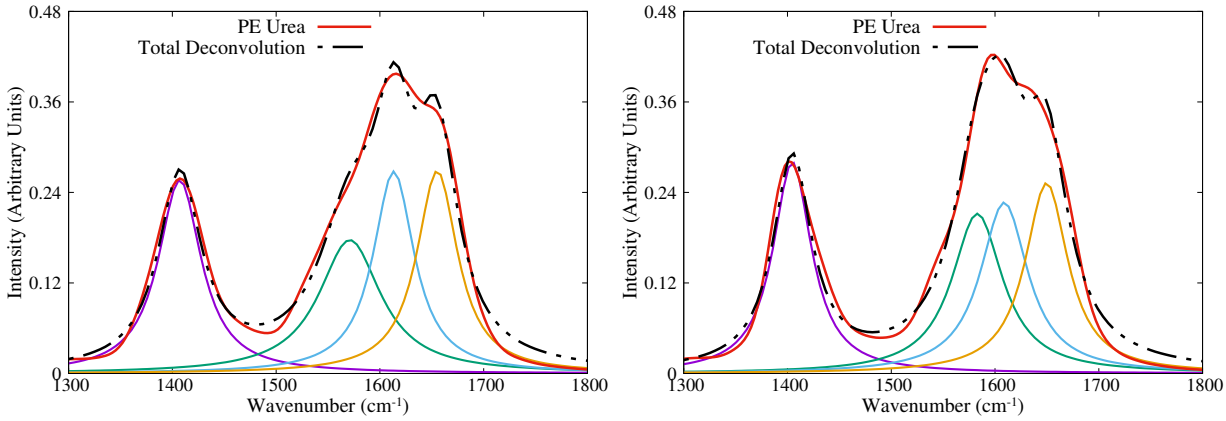


Figure S3. Full power spectra obtained from AIMD for UB and UBW mixtures, showing the global and molecule decomposed spectrum. Water plot in UBW was enhanced by a factor of 5, for better visualization.



(a) UB **(b)** UBW

Figure S4. Lorentzian deconvolution of betaine C–H stretching vibrational modes of decomposed power spectra (PE). Fit data, $\bar{\nu}[\sigma]$, for UB: 3033[18], 3041[18], 3057[18], 3052[18], 3137[17], 3118[17], 3129[17], 3141[17], 3157[16], 3157[16], and 3145[16]. For UBW: 3038[16], 3025[17], 3042[16], 3056[15], 3116[20], 3121[19], 3147[17], 3131[18], 3131[19], 3144[18], and 3164[15]. All quantities are presented in cm^{-1}.



(a) UB **(b)** UBW

Figure S5. Lorentzian deconvolution of Urea vibrational modes of decomposed power spectra (PE). Fit data, $\bar{\nu}[\sigma]$, for UB: 1407[25], 1571[36], 1613[24], and 1655[24]. For UBW: 1404[23], 1583[30], 1609[28], and 1650[25]. All quantities are presented in cm^{-1}.

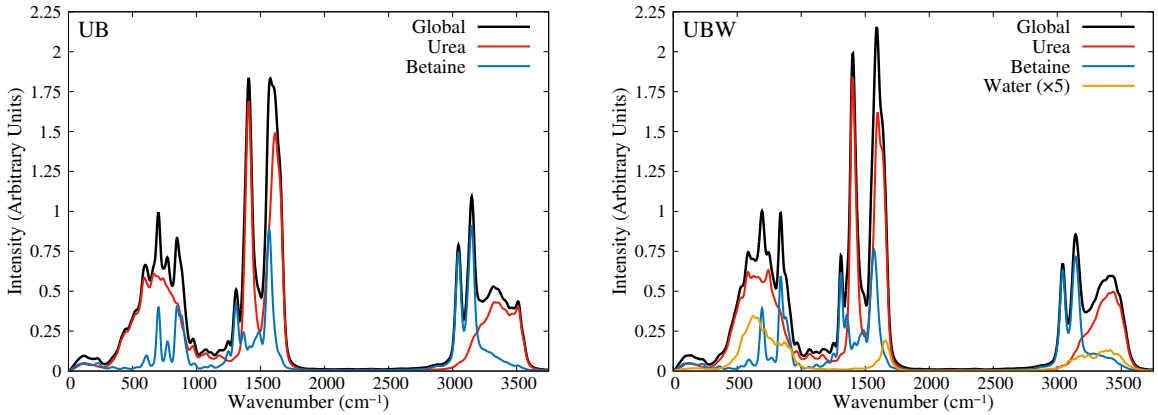


Figure S6. Full Infrared spectra obtained from AIMD for UB and UBW mixtures, using fluctuating Hirshfeld-I atomic partial charges, showing the global and molecule decomposed spectrum. Water plot in UBW was enhanced by a factor of 5, for a better visualization.