Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

p-Aminobenzoic Acid Protonation dynamics in an Evaporating Droplet by *Ab Initio* Molecular Dynamics

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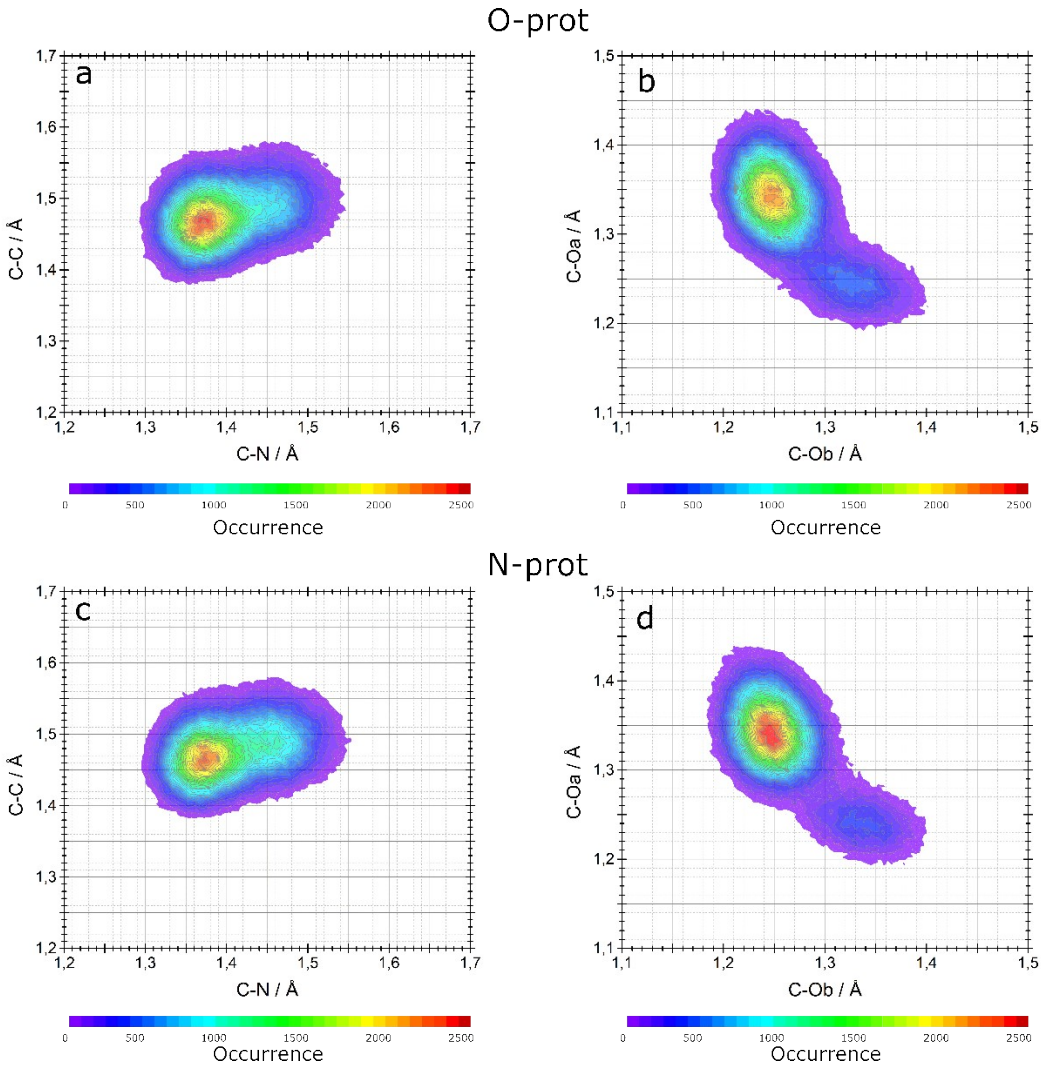

Figure S1. 2D occurrence plot observed for the O-protomer (a and b) and comparison to the 2D occurrence plot observed for the N-protomer (Figure 2c and d) in a 32 water droplet

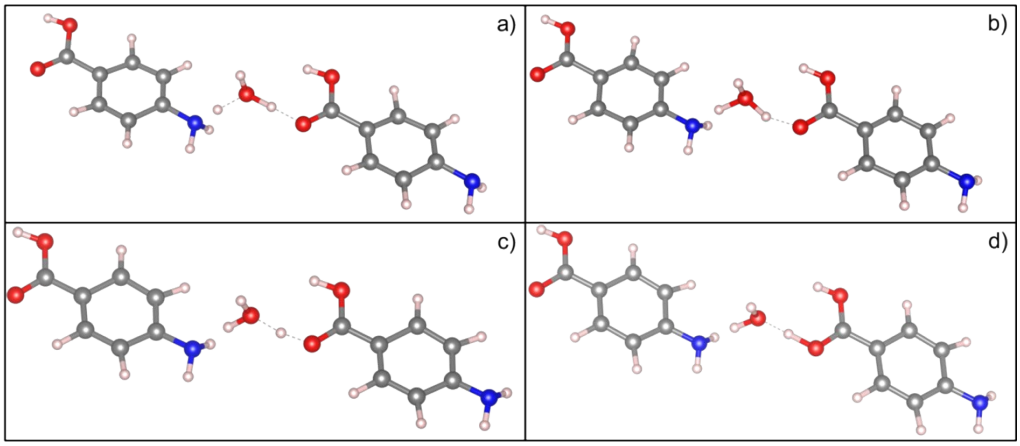

Figure S2. Proton water-bridge transfer (PWBT) between 2 PABA molecules represented by only one water molecule to better visualization showing a) the water molecule removing the proton from nitrogen atom; b) water molecule rearranges to transfer another proton to the PABA molecule; c) proton transfer from water to PABA; d) PABA protonated in the carboxyl group.

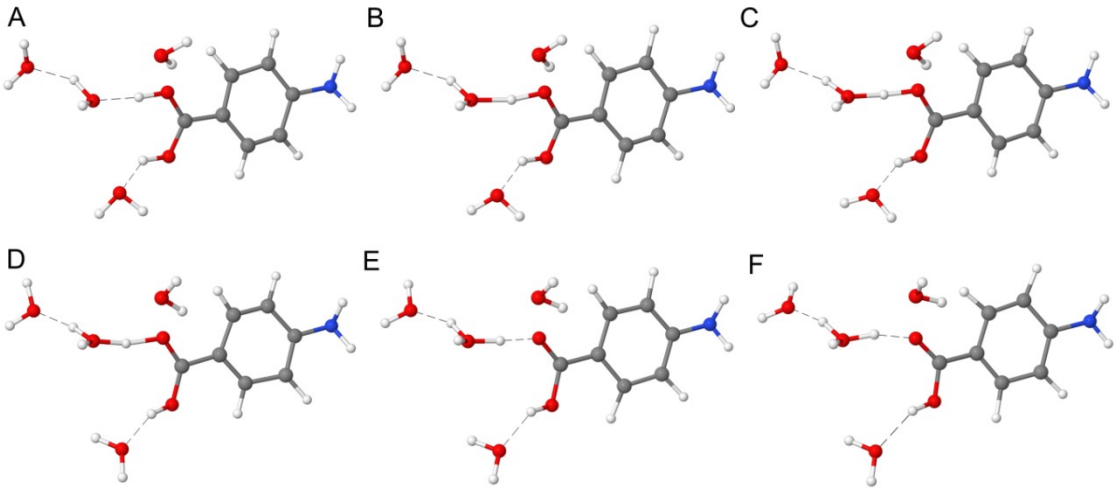

Figure S3. Snapshots representing the proton transfer mechanism for PABA+$H^+(H_2O)_4$ via the Grotthuss mechanism.

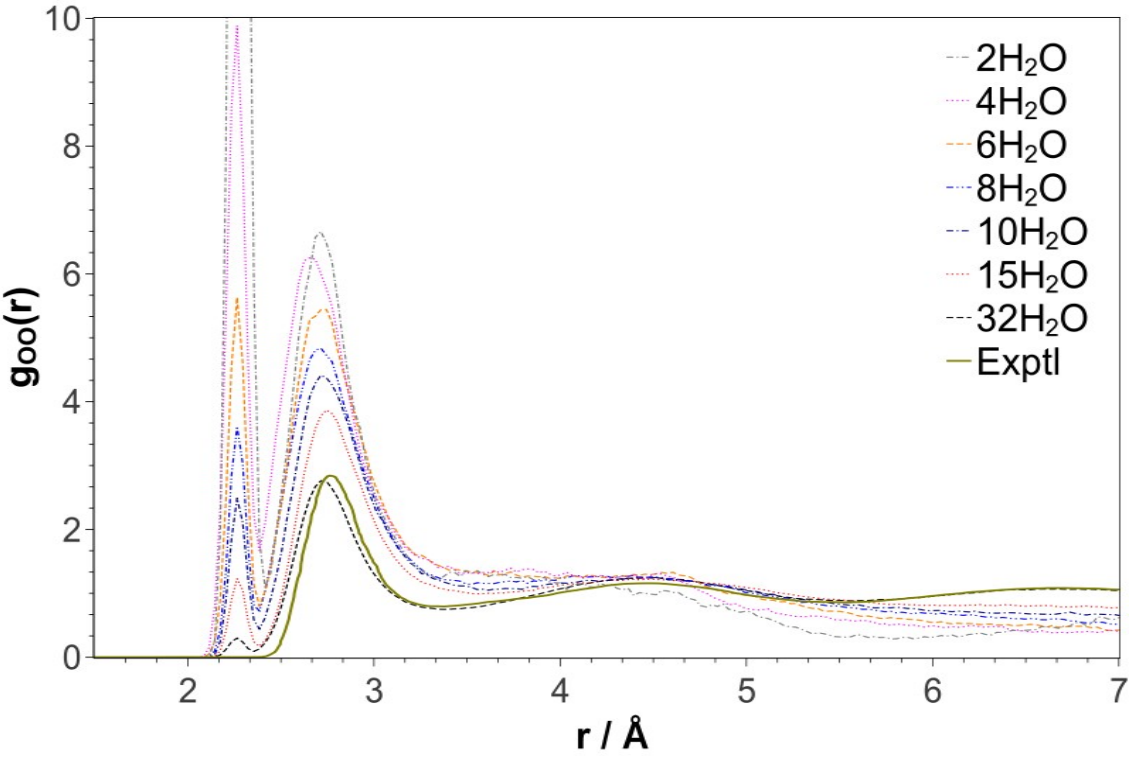

Figure S4. The RDFs for oxygen atoms (g(r)O-O) for bulk water and the evaluated clusters show that PABA+H+(H2O)32 is a good representation of bulk water as shown by comparison with the experimental work of Soper and Benmore [A. K. Soper and C. J. Benmore, Phys. Rev. Lett., 2008, 101, 065502 DOI: 10.1103/PhysRevLett.101.065502]

Annotation S1. Reliability of C-N, C-C and C-O bond lengths to depict proton transfer events

To validate the analysis of geometric parameters used to probe the proton transfer (PT), the radial distribution functions of pairs, g(r) were evaluated as well. The g(r) describes the variation of solvent atomic density with distance from a given atom in a system. It reveals regions in space with occurrence of solvent molecules and provides information on the structure of the solvation shell and also the specific intra- and intermolecular interactions. Through the integrals of g(r) the number of atom pairs observed within a given radius, *r*, is determined. In this way, it is possible to reliably show that the identified changes in the lengths of the C-N, C-O and C-C bonds, shown in Figures 4-6 of the main text, correspond to PT and not to simple atomic vibrational movements.

For instance, Figure S5 shows the initial molecular structure of PABA N-protomer and the plots of their evolution bond lengths of C-N, C-O and C-C solvated with 32 water molecules are shown in the Figure S6.

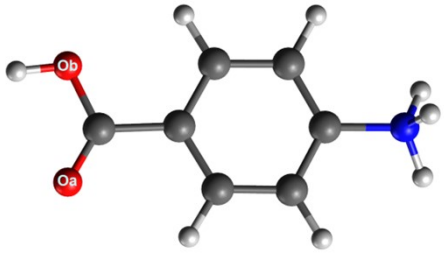

Figure S5. Molecular structure used in the simulation of the PABA N-protomer solvated with 32 water molecules.

In the Figure S6a, two main changes are observed, the first at 15 ps and the second at 80 ps. In Figures S6b and S6c the changes are observed at 81 ps and 30 ps, respectively. It is noteworthy that the identified changes, representing the PTs, differ from the “noises”, which are related to atomic vibrational movements. The changes in the lengths of the probed chemical bonds used to characterize the PTs are summarized below:

i) When the NH_3 group undergoes deprotonation, the length of the C-N bond decreases;

ii) The length of the C-C bond decreases when both oxygen atoms are protonated and/or when one is protonated and the other is interacting via a hydrogen bond with the hydronium ion or water molecules;

iii) The length of the C-O bond increases when oxygen is protonated and consequently decreases when oxygen is deprotonated, since the bond has a smaller *s*-character and is characterized as C=O.

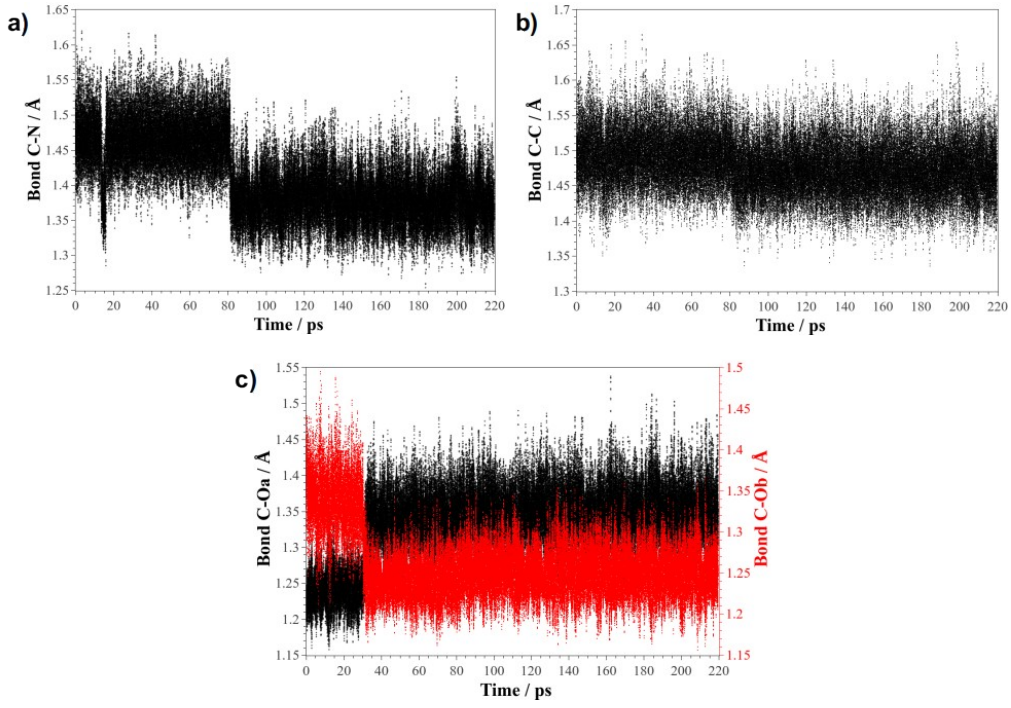

Figure S6. Evolution of (a) C-N, (b) C-C, and (c) C-O bond lengths from simulations of PABA N-protomer solvated with 32 water molecules.

The first peak of g(r)NH and g(r)OH in Figure S7a and c represents the hydrogen atoms bonded directly to the nitrogen and oxygen atoms, respectively. Thus, the integral of this peak affords the exact hydrogen count in the amino and carbonyl groups during the simulation. Furthermore, the center of the peaks represents the bond length between atoms observed in the g(r). The other peaks correspond to the N-H and O-H solute-solvent interactions.

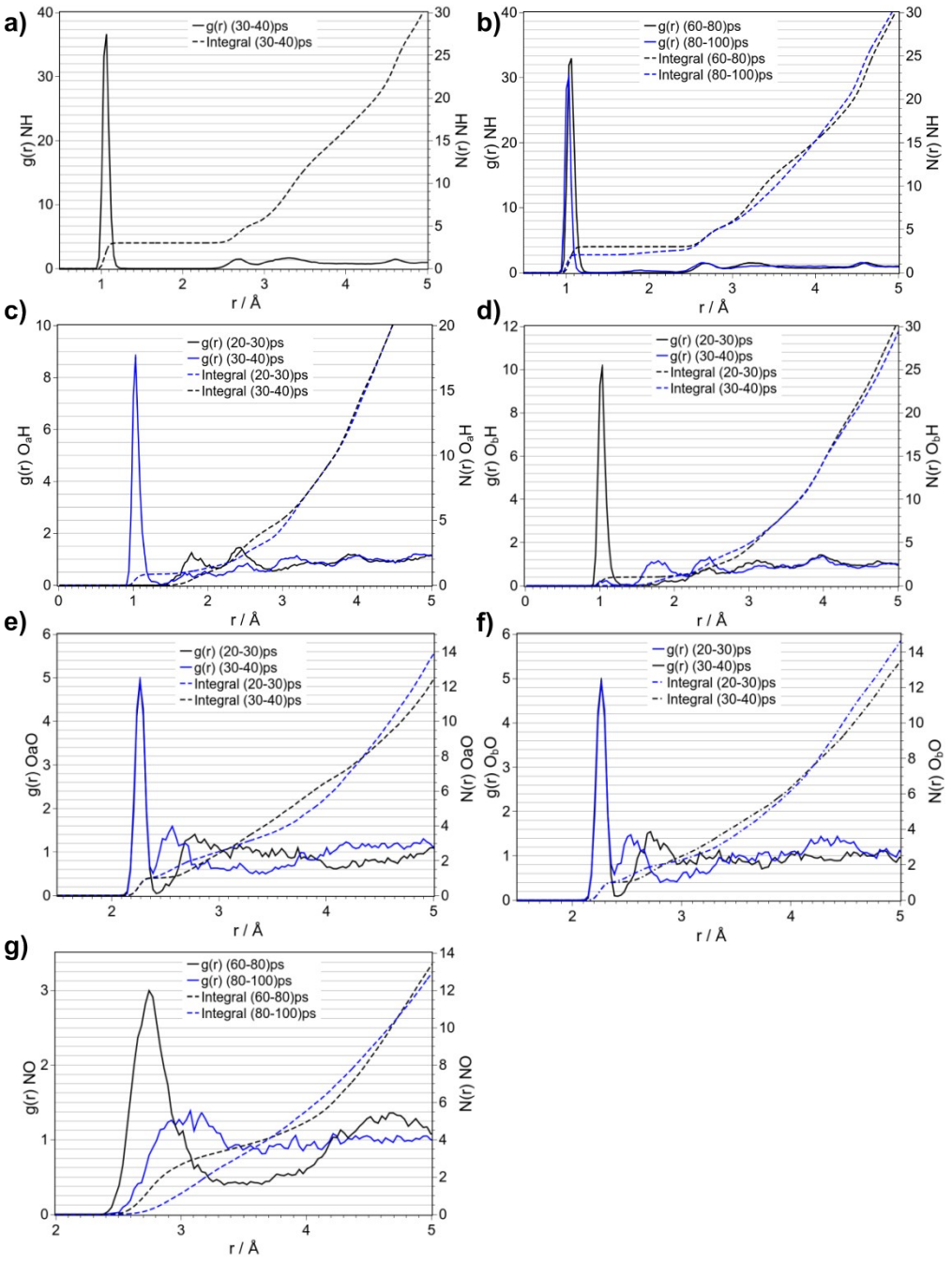

Figure S7. Radial distribution functions between PABA nitrogen/oxygen and water hydrogen/oxygen atoms (a,b) g(r)NH; (c) g(r)O_aH; (d) g(r)O_bH; (e) g(r)O_aO; (f) g(r)O_bO; g(r)NO; from N-protomer simulation solvated with 32 water molecules. The plots are related to regions of plots of Figure S5 that show the proton transfer.

Thus, the integral of g(r)NH, in the range of 30-40 ps (Figure S7a) shows that the N atom count 3 hydrogen atoms, thus corresponding to the NH_3 group. PABA remains protonated at the amino group up to 80 ps as shown by g(r)NH in the range of 60-80 ps (Figure S7b). After 80 ps the amino group undergoes a deprotonation, in agreement with

the C-N bond lenght decrease, seen in Figure S6a. Then, through the g(r)NH in the range of 80-100 ps, also in Figure S7b, it can be seen that the integral of the first peak decreases form 3 to 2, which represents the NH_2 amino group. Figure S6b shows that in approximately 85 ps the C-C bond length slightly decreases, meaning that the hydronium ion is now surrounding and interacting with the carbonyl group via hydrogen bonds.

In Figure S6c, the two alterations nearby to 30 ps represent the deprotonation of O_b (red line) and the protonation of O_a (black line) and this is evidenced by the integrals of g(r)O_aH (Figure S7c) and g(r)O_bH (Figure S7d). After 30 ps, O_b deprotonation and O_a protonation take place almost simultaneously. This indicates that the origin of O_a protonation consists of a fast PT from O_b to O_a mediated by neighboring water molecules.

The g(r)OO and g(r)NO (Figures S7e-S7g) describe the nearest solvent molecules surrounding the carbonyl and amino groups. Thus, through the first peak of g(r)NO, g(r)O_aO, and g(r)O_bO it is possible to determine the solvation distances of the water molecules, as well as the distance at which PT occurs (see Figure S8). The deprotonation of the amino and carbonyl groups takes place in the presence of a water molecule at a distance of 1.68 Å and 1.23 Å, respectively. The solvation of the amino group, via hydrogen bond, has a distance of 2.04 Å, while the carbonyl group is solvated at a distance equal to that of deprotonation.

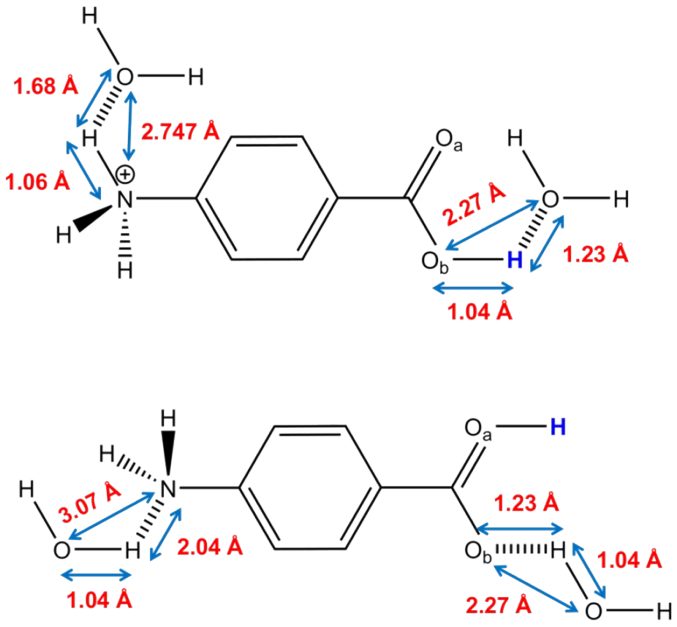

Figure S8. Average distances of solute-solvent interactions when the proton transfer takes place or when the amino and the carbonyl groups are solvated by water molecules.

Table S1. Geometric parameters used as a reference for probing the protonation site of the PABA for simulations with n=0 and n=32. All values given in Å.

Bond	Gas-phase (n = 0)		Solution (n = 32)		
	N-protomer	O-protomer	HB_{dn}	HB_{ac}	$HB_{dn/ac}$
C-N	1.51 ± 0.03	1.35 ± 0.03	1.47 ± 0.03	1.37 ± 0.03	-
C-C	1.51 ± 0.03	1.41 ± 0.03	-	1.46 ± 0.03	-
C-Oa	1.22 ± 0.03	1.33 ± 0.03	-	-	1.32 ± 0.03
C-Ob	1.36 ± 0.03	1.32 ± 0.03	-	-	1.32 ± 0.03

Table S2. Fraction of the simulation time spend by the system at each protonation state, considering N and O-protomers and the solvent network derived by the geometric parameters presented in Figure 2 for each starting configuration

	Initial protonation at NH_2			Initial protonation at COOH		
n	N-protomer	Solvent	O-protomer	N-protomer	Solvent	O-protomer
0	100	-	0	0	-	100
1	82	< 1	18	0	0	100
2	78	4	18	52	< 1	47
3	8	41	51	91	< 1	8
4	62	12	26	45	45	10
5	45	<1	54	4	95	< 1
6	74	23	3	42	56	2
7	59	40	< 1	0	99	< 1
8	61	39	< 1	27	72	< 1
9	32	68	< 1	91	9	< 1
10	73	27	< 1	76	23	< 1
15	86	13	< 1	42	57	< 1
32	36	64	< 1	29	71	< 1
Avg. 1-32	58	28	14	42	44	14
Avg. 6-32	60	39	0	44	55	0
Avg. 8-32	57	42	0	53	46	0

All values given in %.

Table S3. Average energies from snapshots protonated in each site.

Water molecules	NH_2	H_2O	COOH
0	-90.63390	Not observed	-90.64480
1	-108.06077	-107.95181	-108.05704
2	-125.46929	-125.47242	-125.46559
3	-142.87507	-142.87077	-142.87188
4	-160.28106	-160.27641	-160.27611
5	-177.68664	-177.67662	Not observed
6	-195.09400	-195.08920	-195.08353
7	-212.49460	-212.49586	-212.46371
8	-229.90604	-229.90111	Not observed
9	-247.31242	-247.30692	-247.25520
10	-264.71742	-264.71323	-264.65666
15	-351.75847	-351.75480	Not observed
32	-647.96191	-647.95345	Not observed

*Values in a.u. Results obtained from each kind of protonation site, using both starting configurations.