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

Supporting Information

Local electronic structure of histidine in aqueous solution

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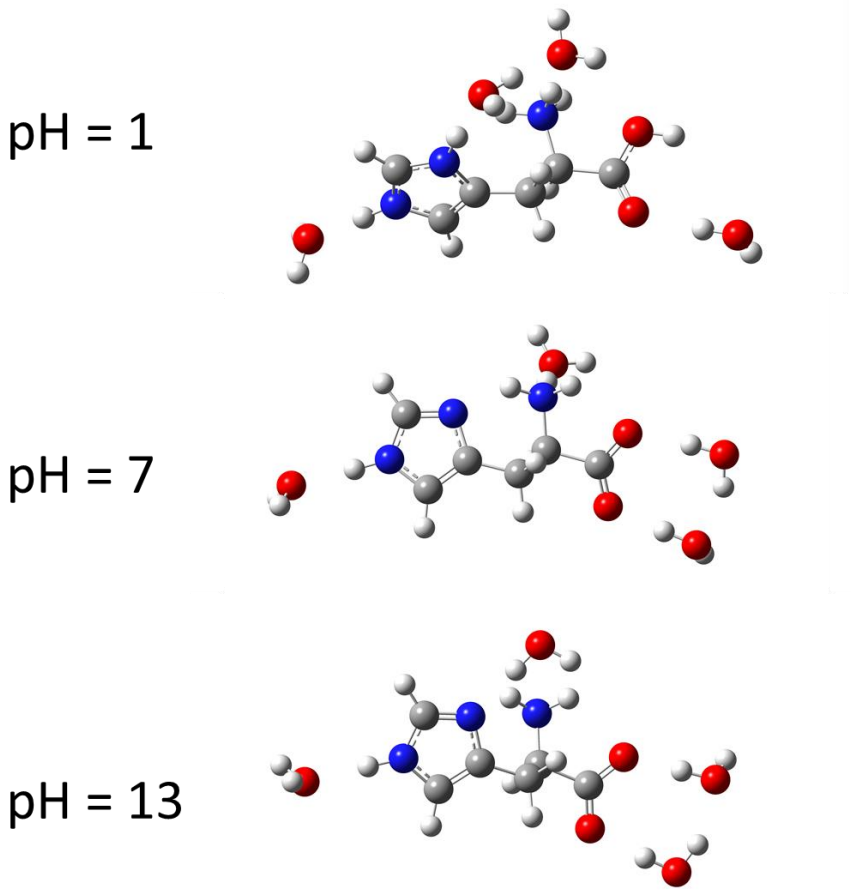

Figure S1. Structures of investigated histidine molecules in aqueous environment with different pH with explicitly included four water molecules.

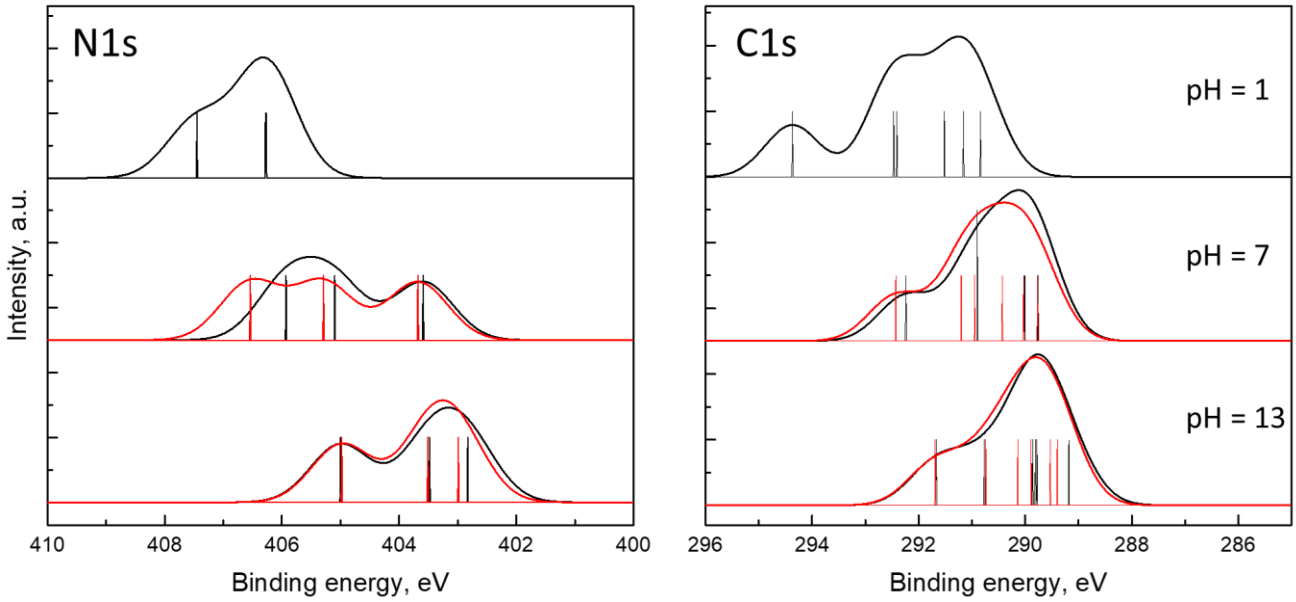

Figure S2. Theoretical N1s and C1s spectra of aqueous histidine tautomers calculated at pH = 1 (top), pH = 7 (middle), and pH = 13 (bottom). In black are shown spectra for π-tautomer of histidine, in red are shown spectra for τ-tautomer. The stick spectra, (black - π-tautomer, red - τ-tautomer) obtained in calculations are convoluted with Gaussian (FWHM = 1.2 eV) to correlate with the experimental photoelectron spectra.

NEXAFS spectroscopy

The VMI spectrometer also allows collection of NEXAFS spectra by scanning the photon energy as discussed in an earlier publication.[1]

The NEXAFS spectra collected using the same VMI apparatus at the C K-edge are shown in Fig. S3 for basic condition at pH = 13, and for the N K-edge at acidic (pH = 1) and basic (pH = 13) conditions. The C spectrum shows a π* resonance around 289 eV which arises from the C=O double bond of the carboxyl group. The second resonance at 285 eV arises from the C=C double bond in the aromatic ring. Finally, the peak at 287 eV arises from the π* resonance of the C=N bond. It is interesting to note that qualitatively (peak positions and shapes) our C NEXAFS spectra from an aqueous histidine aerosol agrees very well up to 293 eV with an earlier measurement performed on solid histidine.[2] For the N K-edge, we can directly compare our results to the NEXAFS spectra collected in a liquid jet using fluorescence yield spectroscopy (Fig. S3).[3] For a highly acidic solution (pH = 1), a π*resonance at 401.5 eV matches well with previous results. The peak consists from two unresolved resonances arising from the two nitrogen atoms in the imidazole group. For the basic solution at pH = 13, the peaks originating from the imidazole group are resolved: a π* resonance at 400 eV is arising from the deprotonated nitrogen, whereas another resonance at 401.8 eV is due to the protonated N. The basic features of the spectra agreeing very well with previous results reported from a liquid jet at pH = 10.[3]

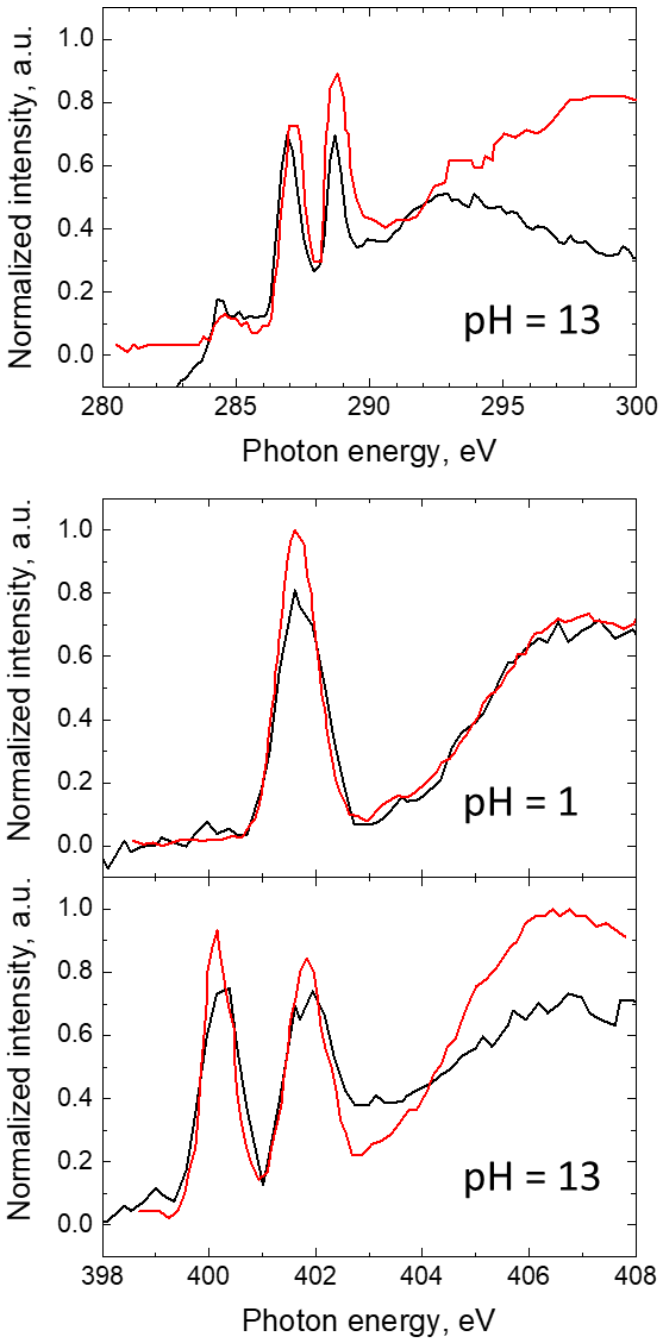

Figure S3. NEXAFS spectra at the carbon (top) and nitrogen (middle and bottom) edge of histidine in aqueous solution. The spectra are compared to the literature data shown in red.[2,3] Our NEXAFS spectra are blue shifted by 0.7 eV for C edge and by 0.9 eV for N edge to correlate with the literature data.

The relative fraction of each possible form of histidine under various pH conditions is shown in Figure S4.

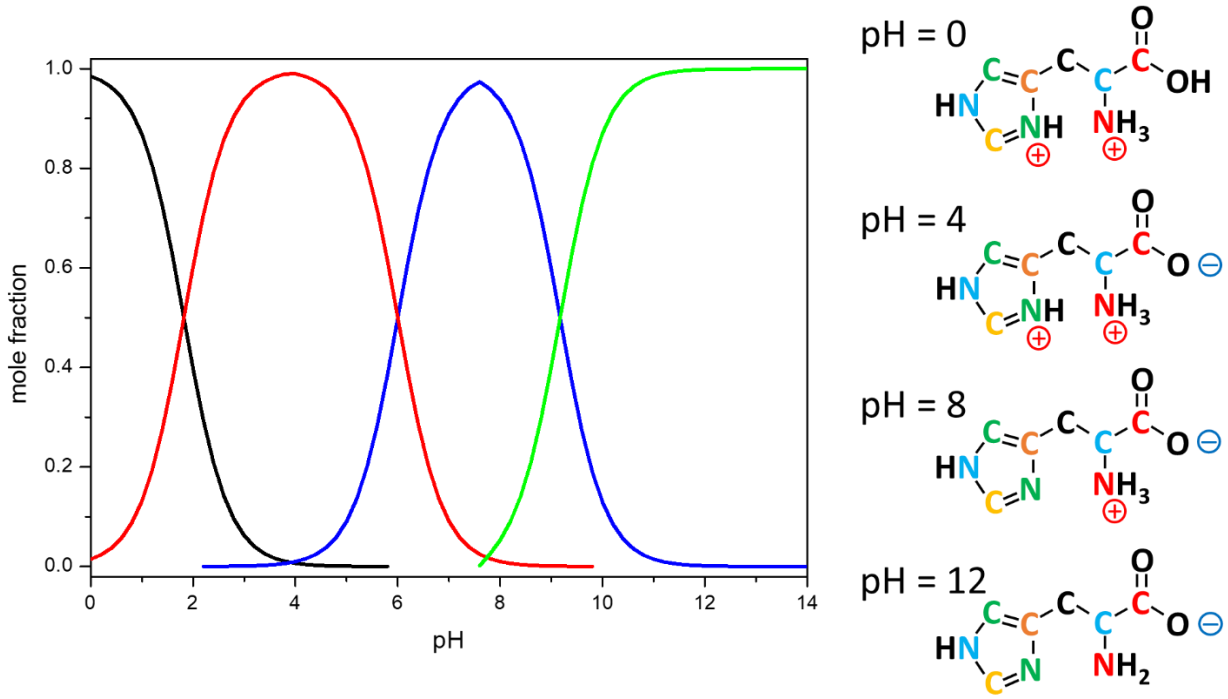

Figure S4: Histidine speciation in aqueous solution as a function of pH, calculated from p*K*a.

References

1 O. Kostko, B. Xu, M. I. Jacobs and M. Ahmed, Soft X-ray spectroscopy of nanoparticles by velocity map imaging, *J. Chem. Phys.*, 2017, **147**, 013931.

2 J. Boese, A. Osanna, C. Jacobsen and J. Kirz, Carbon edge XANES spectroscopy of amino acids and peptides, *J. Electron Spectrosc. Relat. Phenom.*, 1997, **85**, 9–15.

3 S. Eckert, J. Niskanen, R. M. Jay, P. S. Miedema, M. Fondell, B. Kennedy, W. Quevedo, M. Iannuzzi and A. Föhlisch, Valence orbitals and local bond dynamics around N atoms of histidine under X-ray irradiation, *Phys. Chem. Chem. Phys.*, 2017, **19**, 32091–32098.

Optimized Cartesian coordinates of histidine-water clusters shown in Fig. S1

pH = 1

C	-2.1690510	-0.9400830	-0.8874910
C	-1.5261420	-0.2447880	0.0914060
C	-3.5727860	0.5592090	-0.1010190
N	-3.4346040	-0.4195110	-0.9855480
H	-4.1741470	-0.7408720	-1.6350550
H	-1.8344320	-1.7529160	-1.5084670
H	-4.4604760	1.1474390	0.0552490
N	-2.4305820	0.6860240	0.5602280
H	-2.2398560	1.3747750	1.3164330
C	-0.1416520	-0.3646670	0.6415920
H	-0.0716690	0.1834930	1.5835650
H	0.0761880	-1.4087140	0.8661900
C	0.9442060	0.1165960	-0.3283760
H	0.8912210	-0.4532250	-1.2589290
C	2.3329360	-0.1280280	0.2483580
O	2.6290890	-1.1696850	0.7710060
O	3.1382790	0.9068160	0.0793510
H	4.0193650	0.7191730	0.4326200
N	0.7642080	1.5515380	-0.6934240
H	0.8062840	2.1870210	0.1356160
H	1.4872410	1.8569460	-1.3466670
H	-0.1360540	1.6926560	-1.1554690
O	5.0754610	-1.9725260	2.1218820
H	5.5746050	-2.5244510	1.5171750
H	4.2623360	-1.7561610	1.6476670
O	0.8152910	3.2837890	1.5171580
H	1.5378870	3.1430150	2.1374860
H	0.8702950	4.2091270	1.2572850
O	-5.4558090	-1.2409460	-2.6707170
H	-5.8603550	-2.0988250	-2.5192030
H	-5.3500080	-1.1659970	-3.6223560
O	-1.7269350	2.5116610	2.4628100
H	-1.7257610	2.2776950	3.3936840
H	-0.8441310	2.8671410	2.2666710

pH = 7

C	-2.7424790	-1.2284940	-0.1454710

C	-1.6345070	-0.7744010	0.5132940
C	-3.3181500	0.2848820	1.3338630
N	-3.8045570	-0.5471080	0.3930680
H	-4.7877990	-0.6493300	0.1276430
H	-2.8627820	-1.9596660	-0.9274910
H	-3.9469790	0.9437130	1.9123740
N	-2.0093500	0.1764640	1.4414380
C	-0.1974620	-1.1538460	0.3437100
H	0.1682300	-1.6583200	1.2456540
H	-0.0925920	-1.8562460	-0.4836790
C	0.7064410	0.0521330	0.0536850
H	0.3731900	0.5590120	-0.8520670
C	2.1742560	-0.3951050	-0.1110630
O	2.4409760	-0.9867640	-1.1769830
O	2.9354450	-0.1497550	0.8512620
N	0.6305990	1.0324910	1.1753730
H	-0.3193850	1.0188140	1.5918540
H	1.3448280	0.7672430	1.8605880
H	0.8544750	1.9873230	0.8418600
O	5.5914240	-0.9976650	0.7883570
H	5.5931670	-1.3900580	-0.0980980
H	4.6740600	-0.6753850	0.8689650
O	1.2461440	3.5222290	0.0131060
H	0.8622870	4.3350950	0.3510230
H	2.1754170	3.7165770	-0.1323480
O	-6.5559800	-0.8007160	-0.3124220
H	-6.9703510	-1.6639020	-0.2412210
H	-6.8520460	-0.4437060	-1.1531300
O	4.8847110	-1.9798240	-1.7794340
H	5.1846690	-1.5330740	-2.5728990
H	3.9913800	-1.6113950	-1.5879160

pH = 13

C	-1.1263060	3.2109880	1.5848300
C	0.1004650	2.9488190	1.0364090
C	-1.0396730	4.0160550	-0.4507920
N	-1.8365270	3.8889040	0.6262970
H	-2.7921880	4.2433220	0.7117500
H	-1.5425780	2.9813690	2.5517580
H	-1.3509900	4.5187960	-1.3534490
N	0.1390340	3.4612720	-0.2449560

C	1.2457520	2.1911220	1.6250190
H	2.1884090	2.6616820	1.3249970
H	1.1846410	2.2361960	2.7156850
C	1.2728090	0.7021580	1.1936920
H	0.3440850	0.2426630	1.5448560
C	2.4347210	0.0187920	1.9358800
O	2.2119820	-0.3598190	3.1094200
O	3.5303380	-0.0636080	1.3227120
N	1.3946390	0.4913690	-0.2444250
H	0.8598040	1.1906810	-0.7492030
H	2.3704820	0.6131450	-0.4980350
O	5.7958000	-1.1058480	2.2906150
H	6.0119090	-1.8572540	1.7360650
H	4.9575260	-0.7325060	1.9196880
O	4.2259760	-1.4629720	4.6322200
H	4.9397880	-1.4631580	3.9769130
H	3.4823700	-1.0746440	4.1253380
O	-4.5131970	4.8606950	0.8840920
H	-5.1825200	4.5105260	0.2914590
H	-4.6567520	5.8098720	0.8998140
O	2.4231530	3.5199290	-1.8868230
H	3.1353660	3.1962350	-1.3327900
H	1.6251870	3.4969230	-1.3129790