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Supporting Information

Fast Proton Exchange in Histidine: Measurement of Rate Constants through Indirect Detection by NMR Spectroscopy

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Table S1. Absolute values of one-bond scalar coupling constants for a) NH_3^+, b) $NH^{\varepsilon 2}$ and c) $NH^{\delta 1}$:

a) $\lvert {}^1J(NH_3^+)\rvert$ Hz				
Average pH	**272.6 K**	**278.0 K**	**283.5 K**	**292.5 K**
1.39	73.54	73.64	74.10	73.79
2.36	72.22	73.28	74.28	73.09
2.70	72.84	73.92	73.37	73.70
3.17	72.24	73.47	73.47	72.86
3.57	73.39	73.47	73.73	73.02
3.86	73.78	73.69	73.14	72.51
4.30	72.67	72.02	71.49	72.25
b) $\lvert {}^1J(NH^{\varepsilon 2})\rvert$ Hz				
1.39	100.34	100.20	99.90	99.16
2.36	100.25	100.16	97.99	97.36
2.70	99.24	98.51	97.49	97.09
3.17	98.93	98.34	98.10	98.11
3.57	97.97	97.90	98.07	96.50
3.86	99.51	99.07	99.42	99.48
4.30	98.82	95.79	100.71	94.81
c) $\lvert {}^1J(NH^{\delta 1})\rvert$ Hz				
1.39	96.71	97.29	101.25	95.06
2.36	93.61	92.27	93.58	102.39
2.70	93.13	92.66	100.91	98.19
3.17	93.31	96.51	97.80	91.99
3.57	92.67	94.38	93.77	97.33
3.86	98.54	103.49	100.86	105.40
4.30	92.08	111.99		

Table S2. Chemical shifts δ_H of a) NH_3^+ protons, b) $NH^{\varepsilon 2}$ proton and c) $NH^{\delta 1}$ proton:

a) δ_H (NH_3^+) ppm				
Average pH	**272.6 K**	**278.0 K**	**283.5 K**	**292.5 K**
1.39	8.174	8.134	8.113	8.109
2.36	8.120	8.113	8.114	8.075
2.70	8.086	8.057	8.077	8.032
3.17	8.052	8.034	8.027	8.007
3.57	8.045	8.046	8.032	8.009
3.86	8.036	8.033	8.019	8.021
4.30	8.071	8.095	8.045	7.972
b) δ_H ($NH^{\varepsilon 2}$) ppm				
1.39	13.777	13.703	13.659	13.677
2.36	13.793	13.697	13.608	13.599
2.70	13.665	13.714	13.702	13.664
3.17	13.704	13.768	13.647	13.628
3.57	13.713	13.686	13.660	13.574
3.86	13.712	13.712	13.662	13.615
4.30	13.760	13.657	13.524	13.898
c) δ_H ($NH^{\delta 1}$) ppm				
1.39	13.974	13.965	13.907	13.726
2.36	13.971	13.905	13.855	13.966
2.70	13.980	13.930	13.904	13.914
3.17	13.939	14.045	13.854	14.052
3.57	13.955	14.035	13.961	13.693
3.86	14.038	13.963	13.795	14.113
4.30	13.775	14.257		

Table S3. Exchange rate constants k_{ex} for a) NH_3^+ protons, b) $NH^{\varepsilon 2}$ proton and c) $NH^{\delta 1}$ proton:

a) k_{ex} (NH_3^+) s^{-1}				
Average pH	**272.6 K**	**278.0 K**	**283.5 K**	**292.5 K**
1.39	252.1±2.5	418.5±4.2	591.9±5.9	1204.9±12.1
2.36	223.8±2.2	366.7±3.7	542.0±5.4	1067.2±10.7
2.70	207.6±2.1	339.1±3.4	486.8±4.9	968.0±9.7
3.17	271.9±2.7	414.1±4.1	613.7±6.2	1257.5±12.6
3.57	377.1±3.8	575.9±5.8	889.5±8.9	1764.0±17.7
3.86	683.0±6.8	1052.0±10.6	1565.7±15.7	2921.2±29.5
4.30	3065.6±31.0	4107.9±41.8	5416.7±55.6	8397.4±88.6
4.88	17791.7±213.7	22581.6±296.7	27490.8±403.7	41970.8±939.3
b) k_{ex} ($NH^{\varepsilon 2}$) s^{-1}				
1.39	1058.6±10.6	1529.5±15.4	2235.7±22.5	3998.0±40.6
2.36	1100.2±11.0	1623.3±16.3	2353.9±23.7	4142.2±42.1
2.70	1103.1±11.0	1648.6±16.6	2427.6±24.4	4218.7±42.9
3.17	1442.4±14.5	2119.9±21.3	3071.7±31.1	5377.7±55.0
3.57	1876.7±18.9	2786.9±28.1	4025.3±40.9	6980.8±72.1
3.86	3627.1±36.8	5131.4±52.4	7080.9±73.2	11562.0±123.3
4.30	12692±136.6	15758±173.9	19474.1±227.7	27363.7±347.7
4.88	68380.8±2725.1	84882.9±5365.4		
c) k_{ex} ($NH^{\delta 1}$) s^{-1}				
1.39	11656.6±117.8	16099.1±163.5	22531.8±230.5	36719.8±388.6
2.36	12761.7±129.1	17909.5±182.2	24688.3±253.3	40844.1±440.8
2.70	12961.9±131.2	18316.4±186.5	25248.3±259.3	41681.8±451.7
3.17	13639.8±138.2	19072.6±194.3	26759.1±275.6	43864.4±481.7
3.57	14812.1±150.2	20631.6±210.6	28074.7±289.9	46728.2±523.9
3.86	16895.0±208.2	23141.6±236.9	31536.2±328.2	49126.8±561.3
4.30	32657.7±340.7	42538.6±457.0	52583.1±609.0	80903.8±1485.1