Supporting information for: "Structure of aqueous NaOH solutions: Insights from neural-network-based molecular dynamics simulations"

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1 Cartesian coordinates of typical polyhedra

These are the cartesian coordinates (in Å) of the coordination polyhedra shown in Figure 9 of the main text. The structures are given in .xyz format, that can be read by most molecular visualization programs, and the second line in each frame indicates which polyhedron the frame contains. The O atoms in hydroxido ligands (OH^-) are indicated by the placeholder element F, for an easy distinction from oxygen in water molecules.

```
12
See-saw
Na -0.2070 +0.3509 -0.1233
O -1.0334 -0.9588 -2.2444
H -0.9409 -1.9587 -1.9920
H -1.7831 -0.9940 -2.8989
O -0.0080 +0.7180 +2.1803
H -0.3317 +1.5495 +2.6344
H +0.7902 +0.4243 +2.8989
O +1.9528 -0.0994 -1.0305
H +2.6103 -0.6595 -0.5118
H +2.0831 +0.9068 -1.0527
F -1.8546 +1.9078 -0.8202
H -2.6103 +1.9587 -1.4410
13
Tetrahedron
Na -0.2124 -0.0207 -0.1006
O -1.7408 +1.4320 -0.9843
H -2.1157 +2.3117 -0.7940
H -2.4458 +0.8947 -1.4634
O -1.5505 -0.8159 +1.7189
H -2.4403 -1.1178 +1.4811
H -1.6233 -0.5797 +2.6825
O +1.6721 +1.4109 +0.6254
H +2.4458 +1.7918 +0.1888
H +1.2431 +2.0893 +1.1455
O +0.3416 -1.7451 -1.9156
H +0.2083 -2.3117 -2.6825
H +1.2907 -1.4711 -2.0436
13
Trigonal bipyramid
Na -0.2579 +0.0202 +0.1791
O +1.4903 -1.4947 +1.2764
H +2.3429 -1.4850 +0.7925
H +1.7379 -1.4828 +2.2803
O +0.6408 +2.4707 +1.3371
H +1.3973 +2.7646 +0.7390
H -0.1151 +3.0789 +1.1962
F -2.3429 +1.2329 +1.3433
H -1.8261 +2.0599 +1.3825
F +0.2697 +0.1537 -2.0332
H -0.6742 +0.3337 -2.2803
F -1.8026 -2.2948 -0.6437
```

H -2.1867 -3.0789 -1.0733
16
Square pyramid
Na +0.1138 -0.0704 -0.2453
O -1.7360 -0.8131 -1.9005
H -1.2349 -1.2991 -2.6523
H -2.4794 -0.1842 -2.2719
O +1.9802 +0.2029 -1.9456
H +2.0175 +1.0651 -2.4848
H +2.4794 -0.4421 -2.5126
O -1.3055 +2.1542 -0.7053
H -0.5030 +2.7081 -0.5463
H -2.0154 +2.7290 -0.3538
O +0.3155 +0.9712 +1.9950
H +0.8537 +1.7182 +2.3353
H +0.4180 +0.2883 +2.6523
O +0.8910 -1.9895 +0.5998
H +0.6774 -2.7290 -0.0106
H +0.6753 -2.4318 +1.4533
15
Flap pyramid
Na -0.2683 +0.2558 +0.1862
O -0.5656 -0.1452 -2.1071
H -1.5223 -0.2879 -2.5038
H -0.0770 -1.1059 -2.1176
O +1.6695 +1.3653 +0.0132
H +1.1011 +2.1553 +0.0770
H +2.0311 +1.3352 +1.0238
O -1.1939 -2.4744 +0.4825
H -1.1826 -3.4284 -0.0651
H -2.0311 -2.0369 +0.3557
O -0.3585 +3.4284 +0.2215
H -1.1293 +3.3428 -0.3598
H -0.8256 +3.3403 +1.1445
F -1.5710 +0.3660 +2.1071
H -1.5861 +1.2692 +2.5038
17
Octahedron
Na -0.4185 -0.3385 +0.1270
O -2.3659 +0.1140 +1.7799
H -2.2353 +1.0619 +2.0772
H -2.4862 -0.3358 +2.6135
O +0.6837 +2.1620 +0.5456
H +1.0931 +2.8909 +1.1545
H +0.7673 +2.6698 -0.2821
O +1.5707 -0.9384 +1.6623
H +2.4862 -1.3045 +1.3930
H +1.5649 -0.6339 +2.5993
O +0.9165 -0.6732 -1.8302
H +1.0529 -1.2596 -2.6135
H +1.2383 +0.2407 -2.1653
F -2.1950 +0.3943 -1.4000
H -1.3811 +0.5495 -1.9082
F -1.0893 -2.6483 +0.5188

H -1.6642 -2.8909 -0.1910
19
Flap octahedron
Na -0.1985 -0.6568 +0.2903
O -1.2180 +1.2342 -1.3383
H -1.0533 +1.0596 -2.3174
H -1.7920 +2.0403 -1.3702
O +2.4462 +0.6279 -0.1070
H +2.7731 +1.0519 -0.8859
H +3.0980 -0.0331 +0.1455
O +0.6389 -1.5730 -1.8283
H +0.8386 -0.9336 -2.4881
H +0.0448 -2.1787 -2.2405
O -2.1655 -2.0573 +0.3961
H -3.0980 -1.9634 +0.4839
H -2.0959 -2.7892 -0.2576
O -0.8835 +1.8488 +1.5180
H -0.9956 +2.7892 +1.6866
H -1.3196 +1.5717 +2.4186
O +1.2421 -1.9702 +1.6081
H +1.8604 -2.5073 +1.0868
H +1.6262 -2.1245 +2.4881
19
Double flap octahedron
Na +0.6573 -0.2989 +0.0055
O -0.5190 +2.2055 -0.1947
H -0.2800 +3.0791 +0.1585
H -0.9502 +2.4610 -1.0128
O +1.5191 +1.2531 +2.0988
H +1.9284 +2.0491 +2.4728
H +1.8566 +0.5030 +2.7170
O +0.1233 -0.6500 -2.1608
H +0.3054 -1.4498 -2.7170
H -0.7417 -0.2699 -2.3285
O -0.0081 -2.1030 +1.3661
H +0.0325 -3.0791 +0.9667
H +0.1631 -2.2422 +2.3390
O -2.4295 -0.0835 -0.0933
H -2.5579 +0.8604 -0.2664
H -3.2779 -0.3803 -0.3360
O +2.9353 -0.1705 -0.7056
H +3.2779 -0.7696 -0.0070
H +3.1114 -0.7376 -1.5104
19
Trigonal prism
Na -0.6879 +0.0602 +0.3980
O -2.6835 -0.4067 -0.7461
H -2.6823 +0.0312 -1.6623
H -3.2731 +0.1610 -0.2001
O -0.1958 +2.3415 +0.2797
H -1.0816 +2.7117 -0.0232
H -0.2185 +2.6298 +1.2913
O -0.1219 -2.0356 -1.8994
H -0.1857 -1.1792 -2.4206

H +0.0397 -2.7117 -2.5959
O +0.5492 -2.1172 +1.2318
H -0.3278 -2.4893 +0.9552
H +0.4418 -2.0556 +2.1713
O +2.3624 +0.4798 -0.2024
H +2.2177 +0.6693 +0.8503
H +3.2731 +0.7761 -0.3971
O -2.2063 +0.3731 +2.1551
H -2.9809 -0.1555 +2.5959
H -2.8324 +0.9801 +1.7031
20
Capped trigonal prism
Na +0.0534 +0.0823 -0.5482
O +0.7631 +2.4207 -0.7585
H +1.3609 +2.8428 -0.0838
H +1.2268 +2.6437 -1.6405
O -0.4990 -2.6115 -1.5949
H -0.8681 -2.3451 -0.7178
H +0.4002 -2.8428 -1.5234
O +1.9965 +0.1507 -2.1884
H +2.0194 -0.5332 -2.8915
H +1.7114 +0.9453 -2.6622
O +1.7799 -1.5930 +0.4054
H +1.3674 -2.4838 +0.6112
H +2.0740 -1.2834 +1.2833
O -0.0251 +1.4785 +1.9951
H +0.7228 +1.8406 +1.5907
H +0.1393 +1.0333 +2.8915
F -1.7454 -1.7429 +0.6739
H -1.0863 -1.7618 +1.3409
F -2.0740 +0.2807 -2.1083
H -1.8237 -0.5724 -2.4543
22
Capped octahedron
Na +0.8056 +0.1450 +0.1011
O -0.1061 -1.6408 +2.1204
H -0.4239 -2.5118 +2.4131
H -0.0754 -0.9786 +2.7659
O +2.3363 -1.7936 -0.4970
H +2.9533 -1.8749 +0.2524
H +2.9853 -1.9996 -1.1708
O +2.3215 +1.4318 -1.4174
H +2.1442 +0.8949 -2.2067
H +1.8549 +2.2255 -1.6468
O +2.1484 +0.7148 +1.8551
H +2.9819 +0.6787 +1.4395
H +2.2285 +1.2827 +2.6509
O -0.9181 +1.8493 +0.1656
H -0.9770 +2.5118 +0.9616
H -1.8700 +1.7527 -0.0128
O -0.6959 -0.4650 -2.0864
H -1.3018 -0.5596 -1.3191
H -1.1521 -0.9393 -2.7659
O -2.1248 -0.6718 +0.5059

H -2.9853 -1.1642 +0.3726
H -1.5874 -1.0453 +1.2614
21
Pentagonal bipyramid
Na -0.0770 -0.3790 +0.1006
O +0.4803 -0.1078 -2.1963
H -0.2616 -0.1139 -2.8495
H +1.2773 -0.3000 -2.7050
O +1.0125 -3.0145 -0.9142
H +1.2625 -3.4249 +0.0210
H +1.7087 -2.4061 -1.2455
O -2.0179 +1.4875 +0.3483
H -2.7273 +0.8219 +0.4384
H -1.9845 +1.6880 -0.6218
O +1.0756 +2.5007 +0.3821
H +1.8864 +1.9830 +0.5954
H +1.3875 +3.4249 +0.5103
O +0.1058 -1.5841 +2.2985
H -0.6967 -1.7389 +2.8495
H +0.6139 -2.4606 +2.2797
O -2.2405 -1.8558 -0.5811
H -2.8824 -1.1248 -0.2668
H -2.6258 -2.0621 -1.5408
F +2.8020 +0.2441 +0.5184
H +2.8824 +0.3290 -0.4426

2 The high-dimensional neural network potential

For our high-dimensional neural network potential of NaOH(aq) solutions, we use two types of symmetry functions (SFs), with radial (G^{rad}) or radial+angular (G^{ang}) dependencies, that for the atom i of element I (in the I-specific NN) are calculated as:

$$G_i^{\mathrm{rad},\ J} = \sum_{\substack{j\in J\\ j\neq i}} e^{-\eta(R_{ij}-R_{\mathrm{s}})^2}\cdot f_{\mathrm{c}}(R_{ij}) \tag{1}$$

$$G_i^{\mathrm{ang},\ J,\ K} = 2^{1-\zeta}\sum_{\substack{j\in J\\ j\neq i}}\sum_{\substack{k\in K\\ k\neq i,\ k\neq j}} (1+\lambda\cos\theta_{jik})^{\zeta}\cdot e^{-\eta(R_{ij}^2+R_{ik}^2+R_{jk}^2)}\cdot f_{\mathrm{c}}(R_{ij})\cdot f_{\mathrm{c}}(R_{ik})\cdot f_{\mathrm{c}}(R_{jk}) \tag{2}$$

where j and k are atoms, J and K are elements that can be the same as or different from I, and f_{c} is a smoothly decaying cutoff function, that reaches 0 at some cutoff distance R_{cut} (in our case $R_{\mathrm{cut}} = 12.00$ bohr for all SFs):

$$f_{\mathrm{c}}(R_{ij}) = \begin{cases} \tanh^3\left(1-\frac{R_{ij}}{R_{\mathrm{cut}}}\right) & R_{ij}\leq R_{\mathrm{cut}} \\ 0 & R_{ij} > R_{\mathrm{cut}} \end{cases} \tag{3}$$

By combining several SFs, with different values for the parameters R_{s}, η, λ, and ζ, and for different combinations of the elements J and K, the element-specific NN is able to distinguish

between different chemical environments. The sets of symmetry functions that we have used for the elements Na, O, and H are given in Tables S1–S6. There are in total 36 SFs in the Na-specific NN, 46 SFs in the O-specific NN, and 48 SFs in the H-specific NN.

The total energy E of a system with N_{Na} Na atoms, N_{O} O atoms, and N_{H} H atoms, is written as the sum over a set of atomic energies

$$E = \sum_{i=1}^{N} E_i = \sum_{i=1}^{N_{\mathrm{Na}}} E_{\mathrm{Na},i} + \sum_{i=1}^{N_{\mathrm{O}}} E_{\mathrm{O},i} + \sum_{i=1}^{N_{\mathrm{H}}} E_{\mathrm{H},i}. \tag{4}$$

where, e.g., the atomic energy $E_{\mathrm{Na},i}$ of atom i is calculated using the Na-specific NN. Each element-specific feed-forward NN contains 2 hidden layers, and each hidden layer contains 35 nodes. The atomic energies are calculated as

$$E_{\mathrm{Na},i} = b_1^3 + \sum_{l=1}^{35} a_{l1}^{23} \cdot f\left(b_l^2 + \sum_{k=1}^{35} a_{kl}^{12} \cdot f\left(b_k^1 + \sum_{j=1}^{36} a_{jk}^{01} \cdot G_{i,j}\right)\right) \tag{5}$$

$$E_{\mathrm{O},i} = b_1^3 + \sum_{l=1}^{35} a_{l1}^{23} \cdot f\left(b_l^2 + \sum_{k=1}^{35} a_{kl}^{12} \cdot f\left(b_k^1 + \sum_{j=1}^{46} a_{jk}^{01} \cdot G_{i,j}\right)\right) \tag{6}$$

$$E_{\mathrm{H},i} = b_1^3 + \sum_{l=1}^{35} a_{l1}^{23} \cdot f\left(b_l^2 + \sum_{k=1}^{35} a_{kl}^{12} \cdot f\left(b_k^1 + \sum_{j=1}^{48} a_{jk}^{01} \cdot G_{i,j}\right)\right) \tag{7}$$

where $G_{i,j}$ is the jth SF for the atom i, the indices k and l run over nodes in the first and second hidden layers, respectively, the activation function $f(x) = \tanh(x)$, and a_{jk}^{01}, b_k^1, a_{kl}^{12}, b_l^2, a_{l1}^{23} and b_1^3 are parameters that are fitted during the NN parameterization (the superscripts are labels and not exponents). Each element-specific NN contains its own set of these parameters, so that, for example, b_1^3 in the Na-specific NN is not necessarily the same as b_1^3 in the O-specific NN.

More information about the construction and applications of high-dimensional neural-network potentials can be found in Refs. S1, S2, S3, S4, S5.

Table S1: The 26 symmetry functions $G^{\mathrm{rad},\ J}$ for the element I = Na (i.e., for the Na-specific NN).

I	J	η (bohr^{-2})	R_{s} (bohr)	R_{cut} (bohr)
Na	H	0.001	0.0	12.00
Na	H	0.010	0.0	12.00
Na	H	0.030	0.0	12.00
Na	H	0.070	0.0	12.00
Na	H	0.150	0.0	12.00
Na	H	0.15	2.0	12.00
Na	H	0.30	2.0	12.00
Na	H	0.60	2.0	12.00
Na	H	1.50	2.0	12.00
Na	O	0.001	0.0	12.00
Na	O	0.010	0.0	12.00
Na	O	0.030	0.0	12.00
Na	O	0.070	0.0	12.00
Na	O	0.150	0.0	12.00
Na	O	0.15	3.5	12.00
Na	O	0.30	3.5	12.00
Na	O	0.60	3.5	12.00
Na	O	1.50	3.5	12.00
Na	Na	0.001	0.0	12.00
Na	Na	0.01	0.0	12.00
Na	Na	0.03	0.0	12.00
Na	Na	0.06	0.0	12.00
Na	Na	0.15	4.0	12.00
Na	Na	0.30	4.0	12.00
Na	Na	0.60	4.0	12.00
Na	Na	1.50	4.0	12.00

Table S2: The 10 symmetry functions $G^{\mathrm{ang},\ J,\ K}$ for the element I = Na (i.e., for the Na-specific NN).

I	J	K	η (bohr^{-2})	λ	ζ	R_{cut} (bohr)
Na	Na	Na	0.001	-1.0	1.0	12.00
Na	Na	Na	0.001	1.0	1.0	12.00
Na	O	H	0.001	-1.0	4.0	12.00
Na	O	H	0.001	1.0	4.0	12.00
Na	O	H	0.030	-1.0	1.0	12.00
Na	O	H	0.030	1.0	1.0	12.00
Na	O	O	0.001	-1.0	4.0	12.00
Na	O	O	0.001	1.0	4.0	12.00
Na	O	O	0.030	-1.0	1.0	12.00
Na	O	O	0.030	1.0	1.0	12.00

Table S3: The 25 symmetry functions $G^{\mathrm{rad},\ J}$ for the element I = O (i.e., for the O-specific NN).

I	J	η (bohr^{-2})	R_{s} (bohr)	R_{cut} (bohr)
O	H	0.001	0.0	12.00
O	H	0.01	0.0	12.00
O	H	0.03	0.0	12.00
O	H	0.06	0.0	12.00
O	H	0.15	0.9	12.00
O	H	0.30	0.9	12.00
O	H	0.60	0.9	12.00
O	H	1.50	0.9	12.00
O	O	0.001	0.0	12.00
O	O	0.01	0.0	12.00
O	O	0.03	0.0	12.00
O	O	0.06	0.0	12.00
O	O	0.15	4.0	12.00
O	O	0.30	4.0	12.00
O	O	0.60	4.0	12.00
O	O	1.50	4.0	12.00
O	Na	0.001	0.0	12.00
O	Na	0.010	0.0	12.00
O	Na	0.030	0.0	12.00
O	Na	0.070	0.0	12.00
O	Na	0.150	0.0	12.00
O	Na	0.15	3.5	12.00
O	Na	0.30	3.5	12.00
O	Na	0.60	3.5	12.00
O	Na	1.50	3.5	12.00

Table S4: The 21 symmetry functions $G^{\mathrm{ang},\ J,\ K}$ for the element I = O (i.e., for the O-specific NN).

I	J	K	η (bohr^{-2})	λ	ζ	R_{cut} (bohr)
O	H	H	0.07	1.0	1.0	12.00
O	H	H	0.07	-1.0	1.0	12.00
O	H	H	0.03	1.0	1.0	12.00
O	H	H	0.03	-1.0	1.0	12.00
O	H	H	0.01	1.0	4.0	12.00
O	H	H	0.01	-1.0	4.0	12.00
O	O	H	0.03	1.0	1.0	12.00
O	O	H	0.03	-1.0	1.0	12.00
O	O	H	0.001	1.0	4.0	12.00
O	O	H	0.001	-1.0	4.0	12.00
O	O	O	0.03	1.0	1.0	12.00
O	O	O	0.001	1.0	4.0	12.00
O	O	O	0.001	-1.0	4.0	12.00
O	Na	O	0.001	-1.0	4.0	12.00
O	Na	O	0.001	1.0	4.0	12.00
O	Na	O	0.030	-1.0	1.0	12.00
O	Na	O	0.030	1.0	1.0	12.00
O	Na	Na	0.001	-1.0	4.0	12.00
O	Na	Na	0.001	1.0	4.0	12.00
O	Na	Na	0.030	-1.0	1.0	12.00
O	Na	Na	0.030	1.0	1.0	12.00

Table S5: The 25 symmetry functions $G^{\mathrm{rad},\ J}$ for the element I = H (i.e., for the H-specific NN).

I	J	η (bohr^{-2})	R_{s} (bohr)	R_{cut} (bohr)
H	H	0.001	0.0	12.00
H	H	0.01	0.0	12.00
H	H	0.03	0.0	12.00
H	H	0.06	0.0	12.00
H	H	0.15	1.9	12.00
H	H	0.30	1.9	12.00
H	H	0.60	1.9	12.00
H	H	1.50	1.9	12.00
H	O	0.001	0.0	12.00
H	O	0.01	0.0	12.00
H	O	0.03	0.0	12.00
H	O	0.06	0.0	12.00
H	O	0.15	0.9	12.00
H	O	0.30	0.9	12.00
H	O	0.60	0.9	12.00
H	O	1.50	0.9	12.00
H	Na	0.001	0.0	12.00
H	Na	0.010	0.0	12.00
H	Na	0.030	0.0	12.00
H	Na	0.070	0.0	12.00
H	Na	0.150	0.0	12.00
H	Na	0.15	2.0	12.00
H	Na	0.30	2.0	12.00
H	Na	0.60	2.0	12.00
H	Na	1.50	2.0	12.00

Table S6: The 23 symmetry functions $G^{\mathrm{ang},\ J,\ K}$ for the element I = H (i.e., for the H-specific NN).

I	J	K	η (bohr^{-2})	λ	ζ	R_{cut} (bohr)
H	O	H	0.2	1.0	1.0	12.00
H	O	H	0.07	1.0	1.0	12.00
H	O	H	0.07	-1.0	1.0	12.00
H	O	H	0.03	1.0	1.0	12.00
H	O	H	0.03	-1.0	1.0	12.00
H	O	H	0.01	1.0	4.0	12.00
H	O	H	0.01	-1.0	4.0	12.00
H	O	O	0.03	1.0	1.0	12.00
H	O	O	0.03	-1.0	1.0	12.00
H	O	O	0.001	1.0	4.0	12.00
H	O	O	0.001	-1.0	4.0	12.00
H	Na	H	0.001	-1.0	4.0	12.00
H	Na	H	0.001	1.0	4.0	12.00
H	Na	H	0.030	-1.0	1.0	12.00
H	Na	H	0.030	1.0	1.0	12.00
H	Na	O	0.001	-1.0	4.0	12.00
H	Na	O	0.001	1.0	4.0	12.00
H	Na	O	0.030	-1.0	1.0	12.00
H	Na	O	0.030	1.0	1.0	12.00
H	Na	Na	0.001	-1.0	4.0	12.00
H	Na	Na	0.001	1.0	4.0	12.00
H	Na	Na	0.030	-1.0	1.0	12.00
H	Na	Na	0.030	1.0	1.0	12.00

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