

Supporting Information

Effect of Basicity on the Hydrolysis of the Bi(III) Aqua Ion in Solution: an Ab Initio Molecular Dynamics Study

Regla Ayala^{a,b}, José Manuel Martínez^c, Rafael R. Pappalardo^c, Keith Refson^{d,e} and Enrique Sánchez Marcos^{c,*}

^a Universidad de Sevilla, CSIC, ICMSE

^b Departamento Química Inorgánica, 41012 Seville, Spain

^c Universidad de Sevilla, Departamento Química Física, 41012 Seville, Spain

^d Royal Holloway University of London, Egham Hill, Egham, Surrey TW20 0EX, United Kingdom.

^e ISIS Facility, Science and Technology Facility Council, Harwell Science Campus, Didcot, OX11 0QX, UK

e-mail: sanchez@us.es

Supporting Information Available:

Bi-O RDF error analysis. O(OH)-O(H₂O) RDFs. Feff input files for EXAFS spectrum computations.

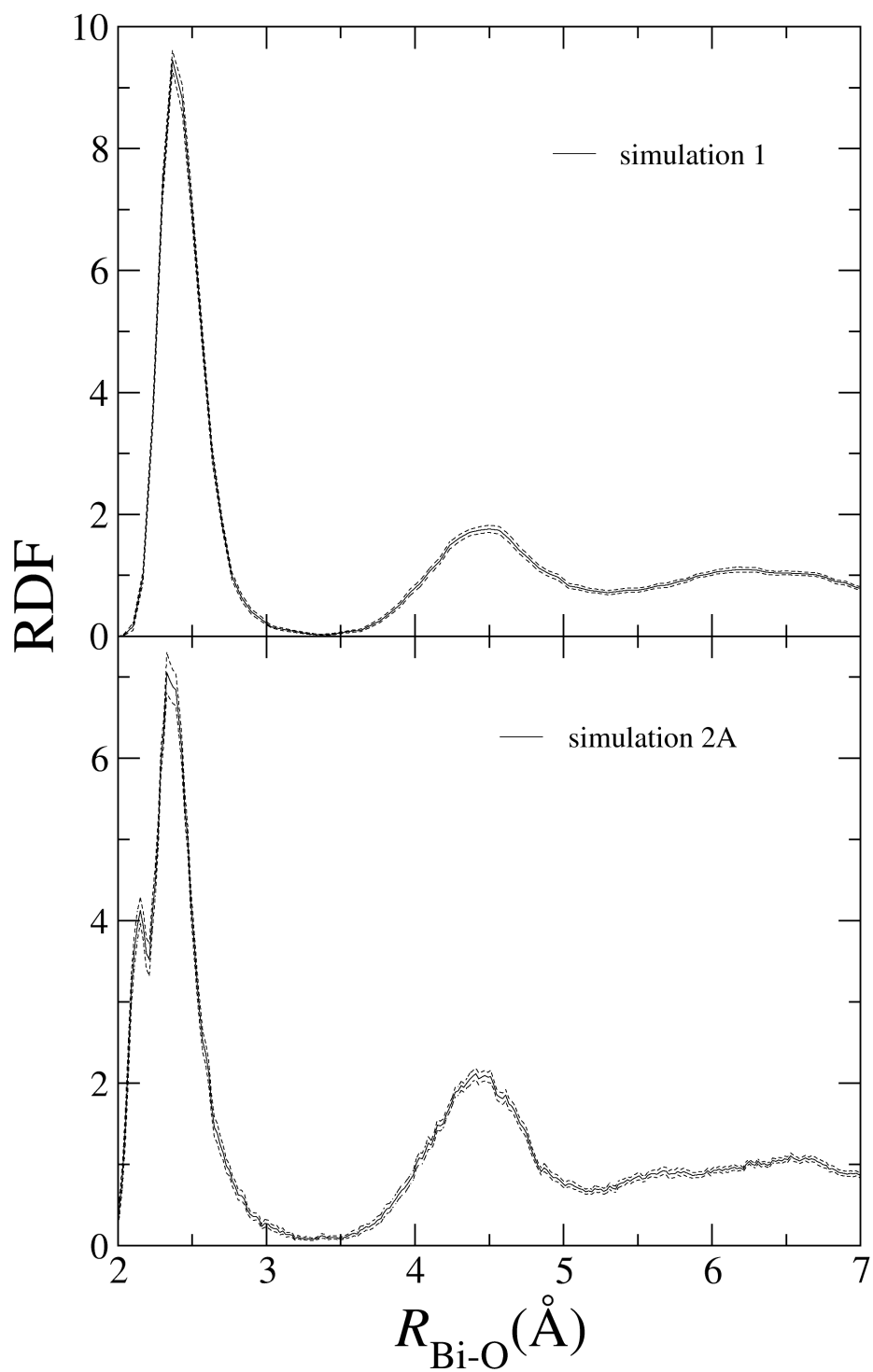


Figure S1: Bi-O RDFs (solid lines) for simulation **1**, $[\text{Bi}(\text{H}_2\text{O})_7]^{3+}$, and **2A**, $[\text{Bi}(\text{OH})(\text{H}_2\text{O})_5]^{2+}$, including the estimation of the standard error of the mean (SEM) whose corridor is defined by the dashed lines.

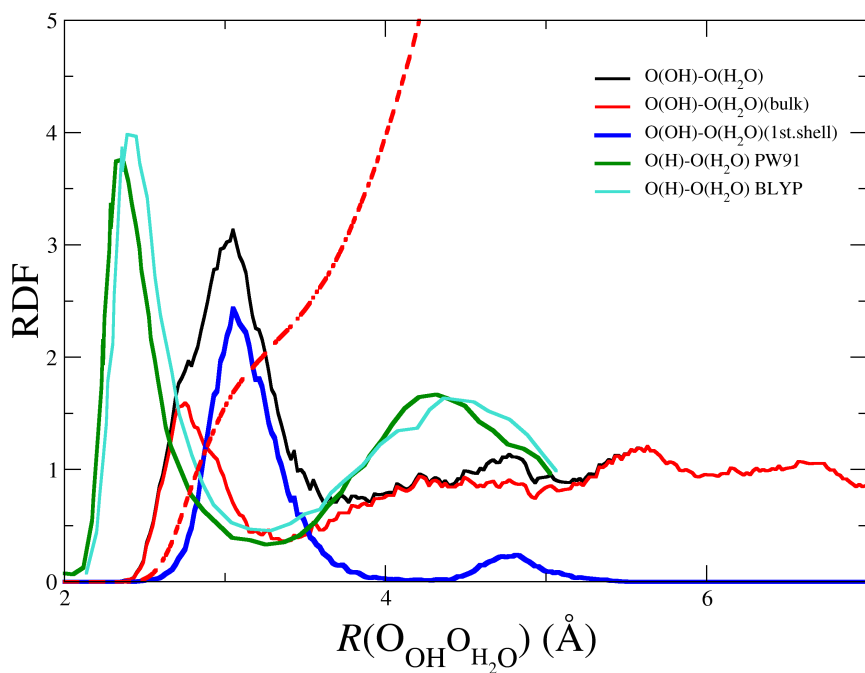


Figure S2: $\text{O}_{\text{OH}}-\text{O}_{\text{H}_2\text{O}}$ RDFs corresponding to ab initio MD simulations of OH^- in aqueous solution computed with PW91 (green) and BLYP (cyan) potentials (D. Marx et al., Chem.Rev. 110,2174 (2010)), and for simulation **2**, $[\text{Bi}(\text{OH})(\text{H}_2\text{O})_5]^{2+}$ (black). A decomposition of the last RDF in the contribution of first-shell oxygen atoms and that of bulk.

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TITLE FEFF input file for the EXAFS computation of a snapshot of the Bi(III) aqua ion taken from AIMD trajectory

* Bi L3 edge
EDGE L3

POTENTIALS
* ipot z label l
  0 83 Bi 3 3
  1 8 O 3 3
  2 1 H 2 2

* mphase, mpath, mfeff, mchi
CONTROL 1 1 1 1 1 1
PRINT 0 0 0 0 1

EXCHANGE 0 -22.5 0
SCF 6.0 1 20

CRITERIA 4.0 2.5

RPATH 6.0 ! ONLY for EXAFS
NLEG 4

SFCONV

S02 1.0
ATOMS
0.0000000 0.0000000 0.0000000 0 Bi 0.0000000 0
-1.8898700 -0.8186700 0.9596100 1 O 2.2721533 2
-1.4440500 -0.0154100 -1.8098300 1 O 2.3153839 2
0.7782900 -1.2097700 1.8276700 1 O 2.3258668 2
0.5166000 1.8572100 -1.6718800 1 O 2.5517224 2
0.1187700 -2.4988000 -0.6075000 1 O 2.5743279 2
2.3870600 -0.5105000 -0.9284000 1 O 2.6116264 2
1.3345500 1.5609300 1.7145900 1 O 2.6753215 2
-1.5818600 1.8201600 1.2174600 1 O 2.7013834 2
-1.0575500 0.3613000 -2.6388200 2 H 2.8657147 2
-1.8979200 -1.7822800 1.2066000 2 H 2.8695829 2
1.6721100 -1.6121100 1.8690300 2 H 2.9812956 2
0.4338600 -0.9510900 2.8041300 2 H 2.9926496 2
-1.0024700 2.6417800 1.0941000 2 H 3.0300169 3
-2.5563700 -0.4532900 1.6330500 2 H 3.0671406 3
-2.3405800 1.9574700 0.5995100 2 H 3.1095684 3
1.2019100 2.5738800 -1.3492900 2 H 3.1448417 3
-2.3841700 -0.6538600 -1.9487700 2 H 3.1479365 3
-0.3399900 -2.8211000 -1.4207200 2 H 3.1768921 3
-0.2220800 2.3045800 -2.1819900 2 H 3.1814287 3
2.5960200 -1.3106900 -1.4236300 2 H 3.2378929 3
3.0297700 0.2235600 -1.2017900 2 H 3.2670758 3
0.6176900 -3.2189300 -0.1391600 2 H 3.2806123 3
2.2843400 1.4075700 2.0187300 2 H 3.3577870 3
1.0380000 2.3955200 2.1198800 2 H 3.3630122 3
END

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TITLE FEFF input file for the EXAFS computation of a snapshot of a mono-hydrolyzed Bi(III) aqua ion taken from AIMD trajectory

* Bi L3 edge (    keV), s0^2=1.0
EDGE L3

POTENTIALS
*   ipot   z   label   l
      0    83   Bi      3   3
      1     8   O1      3   3
      2     8    O      3   3
      3     1    H      2   2

*           mphase, mpath, mfeff, mchi
CONTROL 1 1 1 1 1 1 1
PRINT   0      0      0      1

EXCHANGE 0 3.5 0
SCF 6.0 1 20

CRITERIA 4.0 2.5

RPATH 6.0 ! ONLY for EXAFS
NLEG 4

SFCONV

S02 1.0
ATOMS
  0.0000000 0.0000000 0.0000000 0 Bi 0.0000000
 -1.4833900 1.0016400 1.2631100 1 O1 2.1907020
  0.6383300 -1.2878300 1.7438400 2 O 2.2598560
 -0.9290800 1.4632800 -1.9161500 2 O 2.5837974
 -1.6123900 -1.6577200 -0.4938100 2 O 2.3646745
  1.7592200 -0.2840200 -2.4645200 2 O 3.0412795
  1.6258100 1.6976800 0.3694000 2 O 2.3794604
  1.4090100 -1.8999500 1.4463600 3 H 2.7725577
 -0.1052400 -1.7520900 2.3206800 3 H 2.9097166
 -1.6673800 1.8972300 0.9022600 3 H 2.6821094
 -1.3501300 2.1587000 -1.2768500 3 H 2.8483649
 -1.5512300 0.7286600 -2.3467700 3 H 2.9059576
 -2.0351700 -2.0455300 -1.2944000 3 H 3.1625277
 -2.2912200 -1.8334500 0.2233000 3 H 2.9429731
  1.7755800 -1.2688500 -2.4248500 3 H 3.2622940
  1.4152100 0.0113000 -3.3562200 3 H 3.6424113
  1.6827200 2.4263000 1.1172600 3 H 3.1570157
  2.1908900 2.0216100 -0.3856600 3 H 3.0059341
END

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