Electronic Supplementary Material (ESI) for Dalton Transactions.

The pathway for serial proton supply to the active site of nitrogenase: enhanced density functional modeling of the Grotthuss mechanism

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Supplementary material

1. Validation of the computational methodology

The density functional procedures used in this work have been evaluated by comparison of relevant test systems with experimental data and with high-level calculations.

Water dimer

The main test system is the water dimer, with the structure shown in Fig S1 (a). The water dimer is a benchmark species, and a very large number of quantum calculations of the water dimer exist in the literature, and have been extensively analysed and compared with some key experimental data.[1-7] [8-12] The experimental data and selected good calculated results are collected in Table S1. Corresponding results of calculations of this water dimer using the DMol/COSMO methodology of this paper are reported in Table S2.

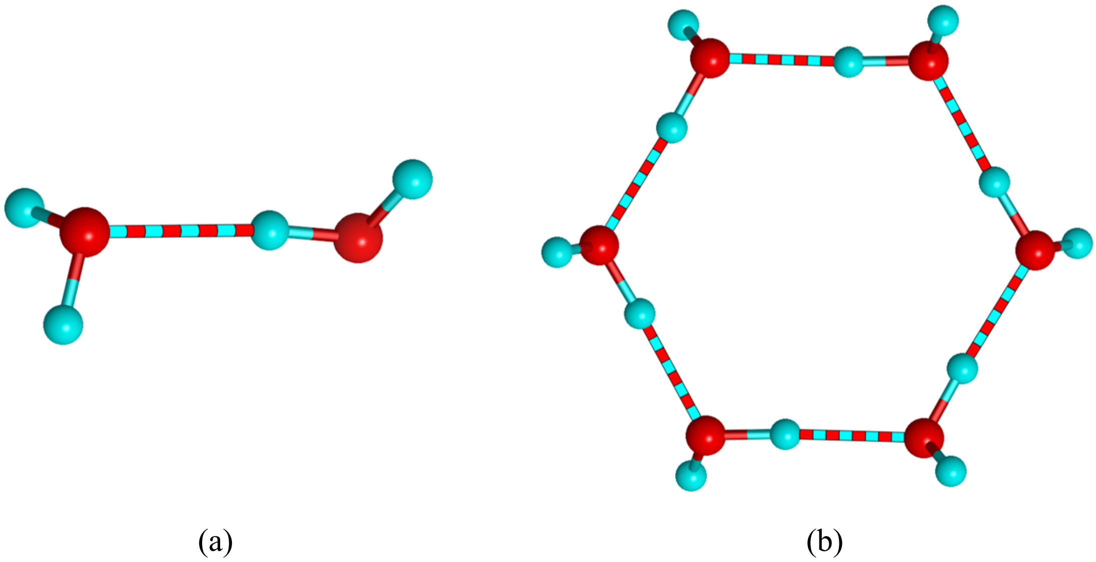
(a) (b)

Fig S1 (a). Structures of the water dimer and hexagonal hexamer.

Table S1. Experimental data and selected calculated results for the water dimer. In general the results for the best basis set reported in the cited reference is included here.

source	electronic dissociation energy, D_e kcal mol^{-1}	ΔH (375K, per dimer) kcal mol^{-1}	O-O distance Å	ref
expt (gas phase)	−5.44 ± 0.7	−3.59 ± 0.5		[2]
expt (gas phase)			2.98Å	[1]
CCSD(T)	−5.0		2.91Å	[5]
CCSD(T)/CBS	−5.02			[9]
CCSD(T)	−5.22		2.91	[12]
MP2	−5.26		2.92	[12]
X3LYP	−4.97	-2.77	2.91	[6]
MP2	−4.98			[11]
BLYP	−4.53			[11]
BLYP-D	−5.39			[11]
BLYP-D	−5.19		2.91	[8]

Table S2. The numerical basis set is dnp, real space cut-off (Atom_Rcut) = 4.76Å, ε is the dielectric constant in the continuum solvation model (COSMO).

calculation	electronic dissociation energy, D_e kcal mol^{-1}	ΔH (298K, per dimer) kcal mol^{-1}	O-O distance Å
BLYP COSMO off	-4.91	−3.19	2.96
BLYP COSMO, ε = 5	-3.47		2.89
BLYP COSMO, ε = 30	-2.95		2.87
B3LYP COSMO off	-4.68		2.97
B3LYP COSMO, ε = 5	-3.14		2.91

The conclusions from comparison of Table S2 with the experimental data (Table S1) are: (a) the O--O separation on the water dimer is accurately achieved by the BLYP and B3LYP without solvation (COSMO), with slight decrease (0.1Å) as the dielectric of the surrounding continuum increases; (b) the electronic dissociation energy is fairly well reproduced (-4.9 vs -5.4 kcal mol^{-1}) with the BLYP functional (no COSMO), but is progressively under-estimated as the dielectric increases; (c) the standard enthalpy of formation is calculated to be -3.19 (298K), slightly less than the experimental measurement (373K) of −3.59 ± 0.5 kcal mol^{-1}.

Water hexamer

Calculations of the hexagonal structure of $(H_2O)_6$ (see Fig S1 (b)) have been reported,[9] [10,11] with the general result that the total binding energy is approximately twice as large as 6 dimer binding energies. The same result is obtained with the DMol/BLYP methodology. Some values for the electronic binding energy (kcal mol^{-1}) of hexagonal $(H_2O)_6$ are -44.9 (MP2[11]) -50.4 (BLYP-D[11]) -44.6 (B3LYP[9]): my DMol calculation (BLYP, COSMO off) yields -46.1 kcal mol^{-1}, in the centre of the range of other calculated values.

Hydrated hydronium ion, $H_9O_4^+$, and the hydrated Zundel ion, $H_{13}O_6^+$

The structures of these two representative cations, as calculated by my DMol/BLYP method, without COSMO, are shown with key distances in Fig S2. These dimensions, including the short symmetrical O-H-O interaction in $H_{13}O_6^+$, are essentially the same as those obtained with various computational methods by Meraj and Chaudhar.[13]

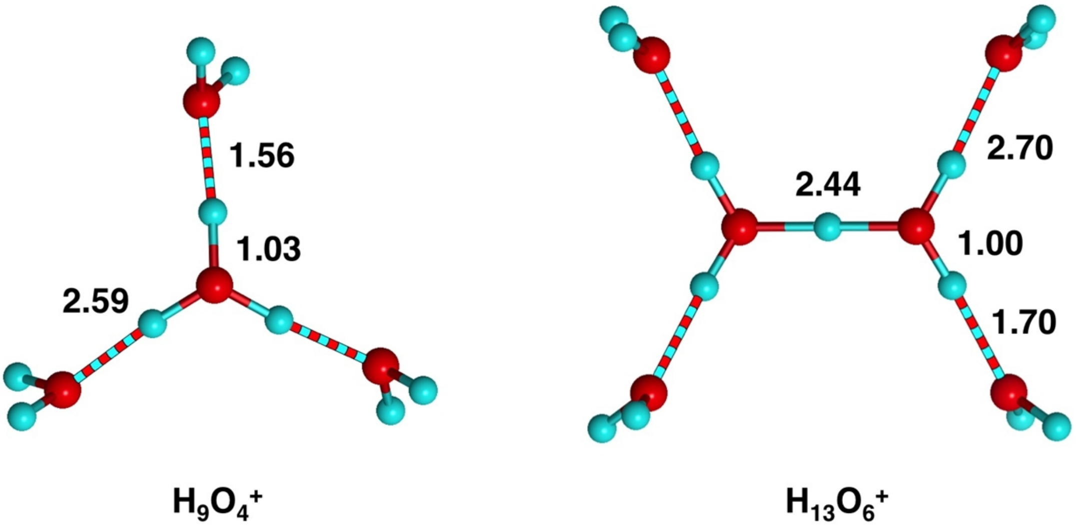

Fig S2. Structures of $H_9O_4^+$ and $H_{13}O_6^+$ with distances (Å) calculated with DMol/BLYP.

Acetic acid dimer

The DMol/BLYP calculated properties of the symmetrical acetic acid dimer (Fig S3), in comparison with experimental data and selected other calculations, are collected in Table S3. The DMol/BLYP method yield almost exact O--O geometry, and energies that just slightly less than reference values.

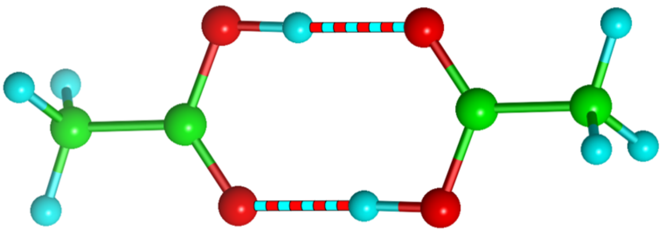

Fig S3.

Table S3. Experimental and calculated properties of the acetic acid dimer.

property	DMol/BLYP (this work)	expt	other calculations
O--O distance (Å)	2.69	2.68 [14]	2.65 [15]
electronic energy (kcal mol^{-1})	-14.8		-15.3 [15] -15.9 [16]
enthalpy (kcal mol^{-1})	-13.4	-15.0 [17]	

2. Comparison of calculated model A with experimental data

Table S4. Comparison of calculated and observed distances (Å) for model **A**. The 10 atoms fixed in the first optimisation were Cα of 94^{Ala}, 96^{Arg}, 231^{Ile}, 425^{Ile}, 442^{His}, 443^{Ser}, 446^{Tyr}, β'-522^{Val}, Cβ of 440^{Glu}, and Cδ of β-105^{Arg}.

distance	crystal	optimised with 10 fixed atoms	optimised without constraints
C^{c} --- Cα 231^{Ile}	9.46	9.6393	9.77
C^{c} --- Cα 442^{His}	6.74	7.12	7.13
C^{c} --- Cα 446^{Tyr}	15.30	15.68	15.83
C^{c} --- Cα β'-522^{Val}	17.61	18.07	18.21
C^{c} --- Cα 425^{Ile}	13.28	13.73	13.90
C^{c} --- Cβ 440^{Glu}	12.23	12.61	12.74
C^{c} --- Cα 96^{Arg}	9.68	9.96	10.04
C^{c} --- Cα 94^{Ala}	15.00	15.41	15.50
C^{c} --- Cα 443^{Ser}	9.60	10.00	9.94
C^{c} --- Cδ β-105^{Arg}	15.54	15.74	15.83
S3B--W1	4.05	4.19	
S5A -- NH_2 96^{Arg}	3.31	3.29	
CO 442^{His}-- W1	3.28	2.64	
N(H) 97^{Arg} -- W2	2.88	2.91	
CO 95^{Gly} -- W3	2.82	2.75	
NH_2 β-105^{Arg} -- W4	2.95	2.92	
Nε β-105^{Arg} -- W5	2.97	2.99	
OH 446^{Tyr} -- W5	2.67	3.00	
CO 95^{Gly} -- W6	2.73	2.73	
Ce1 446^{Tyr} -- W6	3.45	3.79	
CO β'-522^{Val} -- W7	2.86	2.63	
N(H) β'-522^{Val} -- W8	3.42	3.12	
CO Ala94^{Ala} -- W8	2.75	2.67	
O5 (hca) -- W1	2.81	2.57	
O6 (hca) -- W3	2.73	2.81	
O3 (hca) -- W4	2.87	2.86	
W1 -- W2	2.83	3.16	
W2 --W3	2.82	2.84	
W3 -- W4	2.80	2.81	
W4 -- W5	2.79	2.76	
W5 -- W6	2.73	2.80	
W6 -- W7	2.83	2.53	
W7 -- W8	2.73	2.56	

3. The Cε1-H group of 446^{Tyr}

Table S5. Distances (Å) and angles (°) involving the Cε1-H group of 446^{Tyr}, in relation to W6, W5 and W7, for six optimised intermediates.

intermediate	Cε1-H -- W6	Cε1-H -- W5	Cε1-H --W6 --W5	Cε1-H --W6 --W7
(i)	2.88	173	62	68
(ii)	2.86	171	62	69
(iii)	3.06	168	61	60
(iv)	2.73	164	60	80
(v)	2.87	177	67	66
(vi)	2.87	170	62	69

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