Supplementary Data

Orthovanadate Cofactor Chemistry of Marine Bromoperoxidases

Jens Hartung*

Fachbereich Chemie, Organische Chemie, Rheinland-Pfälzische Technische Universität Kaiserslautern-Landau,
Erwin-Schrödinger-Straße, D-67663 Kaiserslautern, Germany

Contents

1 General Remarks

1.1 References

The list of references (Section 8) refers exclusively to the *Supplementary data* and is therefore independent from the associated article.

1.2 Molecular graphics

Ball-and-stick graphics displayed in sections 3–7 were generated with thie ChemPlus add-on (Version 1.6) to HyperChem 4.5.[1] Atomic coordinates for the graphics are taken from B3LYP/6-311++G(d,p)-minimized energy functions archived in Gaussian03-logfiles.[2] Transforming Gaussian logfiles into HyperChem input was achieved by the Open-Babel-feeware.[3] The selected color code depicts vanadium in yellow, oxygen in red, and hydrogen in white.

2 Molecular Modelling

2.1 Electronic structure methods

Structures and energies were computed with the density functional/Hartree-Fock-hybrid model B3LYP in combination with the split valence triple-ζ basis set B3LYP/6-311++G(d,p) implemented in Gaussian03-suite of program (Revision E.01).[2] Supplemental energy function minimizations for predicting relative energies of isomers on the $H_4VO_4^+$-energy surface using a semiempiric hybrid density functional with perturbative second-order correlation (B2PLYP) combined with the split valence triple-ζ basis set B3LYP/6-311++G(d,p) were performed with the Gaussian09-suite of programm (Revision D.01)[4].

All energy functions were minimized without constraining symmetry or internal coordinates, using the Bernie-algorithm in combination with the tight-option and the ultrafine grid for integration. Minimum structures were identified as such from calculated vibrational spectra by the absence of imaginary vibrational modes.

2.2 Thermochemical model

Thermochemical analysis was performed from minimum structures on the associated potential energy surface, as secured by absence of negative normal modes in calculated vibrational spectra.

Gibbs free energies ($G°$) were calculated for temperature of 298.15 Kelvin and a pressure of 1 atmosphere, based on the thermochemical model implemented in the Gaussian-software and unscaled frequency calculations. Likewise obtained Gibbs free energies are corrected for zero-point vibrational energy, thermal contributions, and molecular entropy.

3 Orthovanadium Acid and Isoorthovanadium Acid

3.1 Orthovanadium Acid

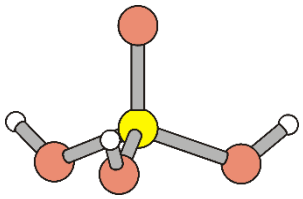

Figure S1. Calculated minimum structure of orthovanadium acid.

(*i*) B3LYP/6-311++G**//B3LYP/6-311++G**

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	23	0	0.000000	0.000000	0.027767
2	8	0	0.000000	0.000000	1.596654
3	8	0	0.000000	1.677284	-0.561099
4	8	0	1.452570	-0.838642	-0.561099
5	8	0	-1.452570	-0.838642	-0.561099
6	1	0	-0.000352	2.446734	0.018161
7	1	0	2.119110	-1.223062	0.018161
8	1	0	-2.118758	-1.223672	0.018161

Zero-point correction= 0.043521 (Hartree/Particle)
Thermal correction to Energy= 0.050709
Thermal correction to Enthalpy= 0.051653
Thermal correction to Gibbs Free Energy= 0.014104
Sum of electronic and zero-point Energies= -1246.940727
Sum of electronic and thermal Energies= -1246.933538
Sum of electronic and thermal Enthalpies= -1246.932594
Sum of electronic and thermal Free Energies= -1246.970143

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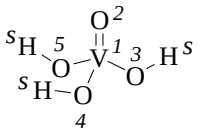
RMSF=1.363e-05\ PG=C03 [C3(V1O1),X(H3O3)]\NImag=0\\@.

(*ii*) NBO-analysis – B3LYP/6-31G*// B3LYP/6-311++G**

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=======================================================================
No. (Occupancy) Bond orbital/ Coefficients/ Hybrids
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 1. (1.92324) BD (1) V  1- O  2
    (28.98%) 0.5383* V  1  s(28.30%)   p(0.05%)    d(71.37%)   f(0.28%)
    (71.02%) 0.8427* O  2  s(11.63%)   p(88.18%)   d(0.19%)
 2. (1.98494) BD (2) V  1- O  2
    (22.62%) 0.4756* V  1  s(0.00%)    p(1.11%)    d(98.70%)   f(0.20%)
    (77.38%) 0.8796* O  2  s(0.00%)    p(99.89%)   d(0.11%)
 3. (1.98488) BD (3) V  1- O  2
    (22.62%) 0.4756* V  1  s(0.00%)    p(1.11%)    d(98.69%)   f(0.20%)
    (77.38%) 0.8797* O  2  s(0.00%)    p(99.89%)   d(0.11%)
 4. (1.97440) BD (1) V  1- O  3
    (19.02%) 0.4361* V  1  s(23.36%)   p(0.54%)    d(75.94%)   f(0.16%)
    (80.98%) 0.8999* O  3  s(14.67%)   p(85.25%)   d(0.08%)
 5. (1.97440) BD (1) V  1- O  4
    (19.01%) 0.4360* V  1  s(23.39%)   p(0.53%)    d(75.91%)   f(0.16%)
    (80.99%) 0.8999* O  4  s(14.67%)   p(85.25%)   d(0.08%)
 6. (1.97427) BD (1) V  1- O  5
    (19.10%) 0.4370* V  1  s(23.36%)   p(0.54%)    d(75.94%)   f(0.16%)
    (80.90%) 0.8995* O  5  s(14.59%)   p(85.33%)   d(0.08%)
23. (1.97474) LP (1) O  2  s(88.39%)   p(11.61%)   d(0.00%)
24. (1.95032) LP (1) O  3  s(59.64%)   p(40.30%)   d(0.06%)
25. (1.81299) LP (2) O  3  s(0.00%)    p(99.93%)   d(0.07%)
26. (1.95035) LP (1) O  4  s(59.64%)   p(40.30%)   d(0.06%)
27. (1.81352) LP (2) O  4  s(0.00%)    p(99.93%)   d(0.07%)
28. (1.95005) LP (1) O  5  s(59.75%)   p(40.19%)   d(0.06%)
29. (1.81161) LP (2) O  5  s(0.00%)    p(99.93%)   d(0.07%)
=======================================================================
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Second order perturbation theory analysis of Fock-matrix for *syn*/*syn*/*syn*-orthovanadium acid in NBO-basis(threshold for printing: 0.50 kcal/mol)

Donor NBO (i)	Acceptor NBO (j)	kcal/mol	a.u.	a.u.
23. LP (1) O 2	94. BD*(1) V 1- O 2	2.45	1.14	0.048
23. LP (1) O 2	97. BD*(1) V 1- O 3	1.65	1.06	0.039
23. LP (1) O 2	98. BD*(1) V 1- O 4	1.66	1.06	0.039
23. LP (1) O 2	99. BD*(1) V 1- O 5	1.65	1.06	0.039
24. LP (1) O 3	94. BD*(1) V 1- O 2	5.04	0.81	0.058
24. LP (1) O 3	96. BD*(3) V 1- O 2	9.20	0.62	0.069
24. LP (1) O 3	98. BD*(1) V 1- O 4	0.95	0.73	0.024
24. LP (1) O 3	99. BD*(1) V 1- O 5	0.95	0.73	0.024
25. LP (2) O 3	95. BD*(2) V 1- O 2	5.42	0.25	0.033
25. LP (2) O 3	98. BD*(1) V 1- O 4	9.42	0.36	0.052
25. LP (2) O 3	99. BD*(1) V 1- O 5	9.45	0.36	0.052
26. LP (1) O 4	94. BD*(1) V 1- O 2	5.04	0.81	0.058
26. LP (1) O 4	95. BD*(2) V 1- O 2	6.89	0.62	0.060
26. LP (1) O 4	96. BD*(3) V 1- O 2	2.30	0.62	0.034
26. LP (1) O 4	97. BD*(1) V 1- O 3	0.95	0.73	0.024
26. LP (1) O 4	99. BD*(1) V 1- O 5	0.94	0.73	0.024
27. LP (2) O 4	95. BD*(2) V 1- O 2	1.36	0.25	0.017
27. LP (2) O 4	96. BD*(3) V 1- O 2	4.05	0.25	0.029
27. LP (2) O 4	97. BD*(1) V 1- O 3	9.41	0.36	0.052
27. LP (2) O 4	99. BD*(1) V 1- O 5	9.43	0.36	0.052
28. LP (1) O 5	94. BD*(1) V 1- O 2	5.04	0.81	0.058
28. LP (1) O 5	95. BD*(2) V 1- O 2	6.93	0.62	0.060
28. LP (1) O 5	96. BD*(3) V 1- O 2	2.31	0.62	0.034
28. LP (1) O 5	97. BD*(1) V 1- O 3	0.95	0.73	0.024
28. LP (1) O 5	98. BD*(1) V 1- O 4	0.95	0.73	0.024
29. LP (2) O 5	95. BD*(2) V 1- O 2	1.36	0.25	0.017
29. LP (2) O 5	96. BD*(3) V 1- O 2	4.08	0.25	0.029
29. LP (2) O 5	97. BD*(1) V 1- O 3	9.44	0.36	0.052
29. LP (2) O 5	98. BD*(1) V 1- O 4	9.45	0.36	0.052

Natural bond orbital (NBO)-energies

NBO	Occupancy	Energy / a.u.
1. BD (1) V 1- O 2	1.92324	-0.60266
2. BD (2) V 1- O 2	1.98494	-0.37606
3. BD (3) V 1- O 2	1.98488	-0.37605
4. BD (1) V 1- O 3	1.97440	-0.54966
5. BD (1) V 1- O 4	1.97440	-0.54983
6. BD (1) V 1- O 5	1.97427	-0.54806

3.2 Isoorthovanadium Acid

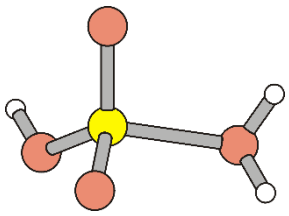

Figure S2. Calculated minimum structure of isorthovanadium acid.

(*i*) B3LYP/6-311++G**//B3LYP/6-311++G**

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	-0.098149	-0.775750	1.455103
2	23	0	-0.149966	-0.109804	0.000621
3	8	0	0.018815	-1.191444	-1.167499
4	8	0	-1.486321	1.069845	-0.272348
5	8	0	1.693194	0.861947	-0.061222
6	1	0	-2.041580	1.412243	0.435685
7	1	0	2.225375	0.761791	0.738502
8	1	0	2.245129	0.634677	-0.820730

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Zero-point correction=                          0.045039 (Hartree/Particle)
Thermal correction to Energy=                   0.052530
Thermal correction to Enthalpy=                 0.053474
Thermal correction to Gibbs Free Energy=        0.013661
Sum of electronic and zero-point Energies=          -1246.903014
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Sum of electronic and thermal Free Energies=        -1246.934392

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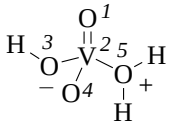
(*ii*) NBO-analysis – B3LYP/6-31G*// B3LYP/6-311++G**



No.	(Occupancy)	Bond orbital/ Coefficients/ Hybrids				
1.	(1.91863)	**BD (1) O 1- V 2**				
	(72.51%)	0.8515* O 1	s(10.45%)	p(89.37%)	d(0.18%)	
	(27.49%)	0.5243* V 2	s(13.23%)	p(3.13%)	d(82.62%)	f(1.02%)
2.	(1.89108)	**BD (2) O 1- V 2**				
	(89.06%)	0.9437* O 1	s(0.27%)	p(99.65%)	d(0.09%)	
	(10.94%)	0.3307* V 2	s(0.71%)	p(28.95%)	d(63.98%)	f(6.37%)
3.	(1.93964)	**BD (3) O 1- V 2**				
	(77.74%)	0.8817* O 1	s(0.02%)	p(99.87%)	d(0.11%)	
	(22.26%)	0.4718* V 2	s(6.53%)	p(8.03%)	d(84.42%)	f(1.02%)
4.	(1.91993)	**BD (1) V 2- O 4**				
	(28.10%)	0.5301* V 2	s(10.56%)	p(3.43%)	d(84.60%)	f(1.40%)
	(71.90%)	0.8479* O 4	s(10.17%)	p(89.65%)	d(0.18%)	
5.	(1.88747)	**BD (2) V 2- O 4**				
	(10.71%)	0.3273* V 2	s(1.96%)	p(26.89%)	d(64.42%)	f(6.74%)
	(89.29%)	0.9449* O 4	s(0.11%)	p(99.80%)	d(0.09%)	
6.	(1.92801)	**BD (3) V 2- O 4**				
	(22.17%)	0.4709* V 2	s(8.04%)	p(9.26%)	d(82.03%)	f(0.67%)
	(77.83%)	0.8822* O 4	s(0.02%)	p(99.87%)	d(0.11%)	
7.	(1.93450)	**BD (1) V 2- O 5**				
	(13.42%)	0.3664* V 2	s(42.50%)	p(5.87%)	d(51.23%)	f(0.40%)
	(86.58%)	0.9305* O 5	s(15.09%)	p(84.84%)	d(0.07%)	
24.	(1.97479)	**LP (1) O 1**	s(89.27%)	p(10.73%)	d(0.00%)	
25.	(1.98784)	**LP (1) O 3**	s(21.71%)	p(78.22%)	d(0.08%)	
26.	(1.88160)	**LP (2) O 3**	s(28.62%)	p(71.36%)	d(0.02%)	
27.	(1.97484)	**LP (1) O 4**	s(89.70%)	p(10.30%)	d(0.00%)	
28.	(1.96089)	**LP (1) O 5**	s(55.44%)	p(44.51%)	d(0.06%)	
29.	(1.81893)	**LP (2) O 5**	s(3.67%)	p(96.26%)	d(0.06%)	

Second order perturbation theory analysis of Fock-matrix for isoorthovanadium acid in NBO-basis(threshold for printing: 0.50 kcal/mol)

Donor NBO (i)	Acceptor NBO (j)	kcal/mol	a.u.	a.u.
within unit 1				
24. LP (1) O 1	95. BD*(3) O 1- V 2	1.30	0.98	0.032
24. LP (1) O 1	96. BD*(1) V 2- O 4	0.83	1.07	0.027
24. LP (1) O 1	97. BD*(2) V 2- O 4	6.23	1.21	0.082
24. LP (1) O 1	99. BD*(1) V 2- O 5	4.41	1.11	0.064
27. LP (1) O 4	93. BD*(1) O 1- V 2	1.08	1.06	0.031
27. LP (1) O 4	94. BD*(2) O 1- V 2	5.29	1.21	0.074
27. LP (1) O 4	98. BD*(3) V 2- O 4	1.74	0.97	0.037
27. LP (1) O 4	99. BD*(1) V 2- O 5	6.61	1.10	0.079
28. LP (1) O 5	93. BD*(1) O 1- V 2	4.43	0.74	0.052
28. LP (1) O 5	94. BD*(2) O 1- V 2	3.22	0.88	0.050
28. LP (1) O 5	95. BD*(3) O 1- V 2	0.81	0.65	0.021
28. LP (1) O 5	99. BD*(1) V 2- O 5	0.60	0.78	0.020
29. LP (2) O 5	93. BD*(1) O 1- V 2	3.37	0.43	0.034
29. LP (2) O 5	94. BD*(2) O 1- V 2	3.19	0.57	0.038
29. LP (2) O 5	96. BD*(1) V 2- O 4	6.35	0.43	0.047
29. LP (2) O 5	97. BD*(2) V 2- O 4	6.29	0.57	0.054
from unit 1 to unit 2				
None above threshold				
from unit 2 to unit 1				
25. LP (1) O 3	93. BD*(1) O 1- V 2	0.29	0.65	0.013
25. LP (1) O 3	95. BD*(3) O 1- V 2	1.43	0.56	0.026
25. LP (1) O 3	96. BD*(1) V 2- O 4	0.36	0.65	0.014
25. LP (1) O 3	98. BD*(3) V 2- O 4	1.82	0.56	0.029
26. LP (2) O 3	93. BD*(1) O 1- V 2	0.69	0.73	0.020
26. LP (2) O 3	94. BD*(2) O 1- V 2	0.41	0.87	0.017
26. LP (2) O 3	95. BD*(3) O 1- V 2	9.61	0.64	0.070
26. LP (2) O 3	96. BD*(1) V 2- O 4	0.92	0.72	0.023
26. LP (2) O 3	97. BD*(2) V 2- O 4	1.09	0.87	0.028
26. LP (2) O 3	98. BD*(3) V 2- O 4	10.39	0.63	0.073
26. LP (2) O 3	99. BD*(1) V 2- O 5	8.16	0.77	0.071
within unit 2				
None above threshold				

Natural bond orbital (NBO)-energies

NBO	Occupancy	Energy / a.u.
Molecular unit 1 (HO3V)		
1. BD (1) O 1- V 2	1.91863	-0.51506
2. BD (2) O 1- V 2	1.89108	-0.28241
3. BD (3) O 1- V 2	1.93964	-0.30974
4. BD (1) V 2- O 4	1.91993	-0.50426
5. BD (2) V 2- O 4	1.88747	-0.27440
6. BD (3) V 2- O 4	1.92801	-0.30343
7. BD (1) V 2- O 5	1.93450	-0.50290

4 Orthovanadium Acid with Hydron

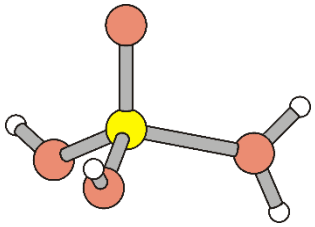


Figure S3. Calculated minimum structure of monoprotonated orthovanadium acid.

(*i*) B3LYP/6-311++G**//B3LYP/6-311++G**

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	0.189988	0.000007	1.590928
2	23	0	0.117926	-0.000000	0.044648
3	8	0	0.818159	-1.429341	-0.628856
4	8	0	-1.862659	0.000004	-0.305113
5	8	0	0.818174	1.429328	-0.628868
6	1	0	-2.540194	0.000036	0.388973
7	1	0	1.204502	2.225842	-0.232214
8	1	0	1.204475	-2.225858	-0.232195
9	1	0	-2.290377	-0.000007	-1.176197

```
Zero-point correction=                          0.055888 (Hartree/Particle)
Thermal correction to Energy=                   0.063688
Thermal correction to Enthalpy=                 0.064632
Thermal correction to Gibbs Free Energy=        0.024575
Sum of electronic and zero-point Energies=          -1247.237953
Sum of electronic and thermal Energies=             -1247.230154
Sum of electronic and thermal Enthalpies=           -1247.229209
Sum of electronic and thermal Free Energies=        -1247.269266

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(*ii*) B2PLYP/6-311++G//B2PLYP/6-311++G****

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	-0.182550	-0.000006	1.618744
2	23	0	-0.109251	-0.000000	0.020903
3	8	0	-0.850962	-1.452702	-0.612948
4	8	0	-0.850952	1.452711	-0.612938
5	8	0	1.895570	-0.000003	-0.307011
6	1	0	2.573384	-0.000021	0.383509
7	1	0	-1.240859	-2.233341	-0.189948
8	1	0	-1.240844	2.233351	-0.189934
9	1	0	2.332256	0.000012	-1.171174

Zero-point correction= 0.055234 (Hartree/Particle)
Thermal correction to Energy= 0.063255
Thermal correction to Enthalpy= 0.064200
Thermal correction to Gibbs Free Energy= 0.023560
Sum of electronic and zero-point Energies= -1246.751673
Sum of electronic and thermal Energies= -1246.743651
Sum of electronic and thermal Enthalpies= -1246.742707
Sum of electronic and thermal Free Energies= -1246.783347

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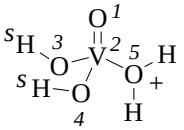
(*iii*) NBO-analysis – B3LYP/6-31G*// B3LYP/6-311++G**



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=======================================================================
No. (Occupancy) Bond orbital/ Coefficients/ Hybrids
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 1. (1.92556) BD (1) O  1- V  2
    (68.87%) 0.8299* O  1  s(10.11%)   p(89.67%)   d(0.23%)
    (31.13%) 0.5579* V  2  s(21.57%)   p(0.53%)    d(77.60%)   f(0.30%)
 2. (1.92302) BD (2) O  1- V  2
    (79.59%) 0.8921* O  1  s(0.00%)    p(99.87%)   d(0.13%)
    (20.41%) 0.4518* V  2  s(0.00%)    p(18.46%)   d(80.19%)   f(1.34%)
 3. (1.95832) BD (3) O  1- V  2
    (74.22%) 0.8615* O  1  s(0.03%)    p(99.82%)   d(0.15%)
    (25.78%) 0.5077* V  2  s(5.16%)    p(2.35%)    d(92.22%)   f(0.26%)
 4. (1.89809) BD (1) V  2- O  3
    (16.26%) 0.4032* V  2  s(27.85%)   p(13.76%)   d(57.21%)   f(1.18%)
    (83.74%) 0.9151* O  3  s(15.48%)   p(84.44%)   d(0.08%)
 5. (1.92759) BD (2) V  2- O  3
    (11.21%) 0.3348* V  2  s(3.70%)    p(22.34%)   d(72.08%)   f(1.87%)
    (88.79%) 0.9423* O  3  s(0.25%)    p(99.69%)   d(0.06%)
 6. (1.89809) BD (1) V  2- O  4
    (16.26%) 0.4032* V  2  s(27.85%)   p(13.76%)   d(57.21%)   f(1.18%)
    (83.74%) 0.9151* O  4  s(15.48%)   p(84.44%)   d(0.08%)
 7. (1.92759) BD (2) V  2- O  4
    (11.21%) 0.3348* V  2  s(3.70%)    p(22.34%)   d(72.08%)   f(1.87%)
    (88.79%) 0.9423* O  4  s(0.25%)    p(99.69%)   d(0.06%)
25. (1.97218) LP (1) O  1  s(89.88%)   p(10.12%)   d(0.00%)
26. (1.92922) LP (1) O  3  s(56.90%)   p(43.03%)   d(0.06%)
27. (1.92922) LP (1) O  4  s(56.90%)   p(43.03%)   d(0.06%)
28. (1.96568) LP (1) O  5  s(0.00%)    p(99.98%)   d(0.02%)
29. (1.86150) LP (1) O  5  s(52.00%)   p(47.99%)   d(0.01%)
=======================================================================
```

Second order perturbation theory analysis of Fock-matrix for *syn*/*syn*-orthovanadium acid with hydron in NBO-basis(threshold for printing: 0.50 kcal/mol)

Donor NBO (i)	Acceptor NBO (j)	kcal/mol	a.u.	a.u.
within unit 1				
25. LP (1) O 1	94. BD*(1) O 1- V 2	1.75	1.13	0.040
25. LP (1) O 1	96. BD*(3) O 1- V 2	0.66	0.98	0.023
25. LP (1) O 1	97. BD*(1) V 2- O 3	1.48	1.21	0.039
25. LP (1) O 1	99. BD*(1) V 2- O 4	1.48	1.21	0.039
26. LP (1) O 3	94. BD*(1) O 1- V 2	6.24	0.76	0.062
26. LP (1) O 3	95. BD*(2) O 1- V 2	10.18	0.75	0.079
26. LP (1) O 3	96. BD*(3) O 1- V 2	1.00	0.62	0.022
26. LP (1) O 3	97. BD*(1) V 2- O 3	0.69	0.85	0.022
26. LP (1) O 3	98. BD*(2) V 2- O 3	1.24	0.76	0.028
26. LP (1) O 3	99. BD*(1) V 2- O 4	1.11	0.85	0.028
27. LP (1) O 4	94. BD*(1) O 1- V 2	6.24	0.76	0.062
27. LP (1) O 4	95. BD*(2) O 1- V 2	10.18	0.75	0.079
27. LP (1) O 4	96. BD*(3) O 1- V 2	1.00	0.62	0.022
27. LP (1) O 4	97. BD*(1) V 2- O 3	1.11	0.85	0.028
27. LP (1) O 4	99. BD*(1) V 2- O 4	0.69	0.85	0.022
27. LP (1) O 4	100. BD*(2) V 2- O 4	1.24	0.76	0.028
from unit 1 to unit 2				
None above threshold				
from unit 2 to unit 1				
28. LP (1) O 5	97. BD*(1) V 2- O 3	0.75	0.58	0.019
28. LP (1) O 5	98. BD*(2) V 2- O 3	1.39	0.49	0.024
28. LP (1) O 5	99. BD*(1) V 2- O 4	0.75	0.58	0.019
28. LP (1) O 5	100. BD*(2) V 2- O 4	1.39	0.49	0.024
29. LP (2) O 5	96. BD*(3) O 1- V 2	13.50	0.69	0.087
29. LP (2) O 5	97. BD*(1) V 2- O 3	3.50	0.92	0.051
29. LP (2) O 5	98. BD*(2) V 2- O 3	10.46	0.84	0.084
29. LP (2) O 5	99. BD*(1) V 2- O 4	3.50	0.92	0.051
29. LP (2) O 5	100. BD*(2) V 2- O 4	10.46	0.84	0.084
within unit 2				
29. LP (2) O 5	103. BD*(1) O 5- H 6	0.50	1.16	0.022
29. LP (2) O 5	104. BD*(1) O 5- H 9	0.62	1.16	0.025

Natural bond orbital (NBO)-energies

NBO	Occupancy	Energy / a.u.
1. BD (1) O 1- V 2	1.92556	-0.80315
2. BD (2) O 1- V 2	1.92302	-0.54645
3. BD (3) O 1- V 2	1.95832	-0.57932
4. BD (1) V 2- O 3	1.89809	-0.73577
5. BD (2) V 2- O 3	1.92759	-0.53036
6. BD (1) V 2- O 4	1.89809	-0.73577
7. BD (2) V 2- O 4	1.92759	-0.53036

5 Hydrates of *cis*-Dioxidovanadium(V)

5.1 *cis*-Dioxidovanadium(V) dihydrate

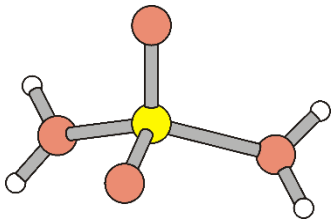

Figure S4. Calculated minimum structure of *cis*-dioxidovanadium(V) dihydrate.

(*i*) B3LYP/6-311++G**//B3LYP/6-311++G**

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	-0.000037	1.020701	-1.278666
2	23	0	-0.000006	0.108535	-0.000007
3	8	0	1.750136	-0.923131	-0.000403
4	8	0	0.000109	1.019392	1.279589
5	8	0	-1.750181	-0.923075	-0.000325
6	1	0	-2.310674	-1.011412	-0.787286
7	1	0	-2.310442	-1.012248	0.786707
8	1	0	2.310524	-1.011710	-0.787410
9	1	0	2.310506	-1.012039	0.786582

```
Zero-point correction=                          0.057362 (Hartree/Particle)
Thermal correction to Energy=                   0.065483
Thermal correction to Enthalpy=                 0.066428
Thermal correction to Gibbs Free Energy=        0.025237
Sum of electronic and zero-point Energies=          -1247.216041
Sum of electronic and thermal Energies=             -1247.207920
Sum of electronic and thermal Enthalpies=           -1247.206975
Sum of electronic and thermal Free Energies=        -1247.248166

Version=EM64L-G03RevE.01\State=1-A\HF=-1247.273403\RMSD=9.107e-10\
RMSF=1.409e-06 PG=C01 [X(H4O4V1)]\NImag=0\\@.
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(*ii*) B2PLYP/6-311++G//B2PLYP/6-311++G****

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	-0.000024	1.044213	-1.300751
2	23	0	-0.000000	0.074397	-0.000001
3	8	0	-1.808400	-0.905797	0.000019
4	8	0	1.808400	-0.905797	-0.000004
5	8	0	0.000024	1.044233	1.300736
6	1	0	-2.374368	-0.981455	-0.781149
7	1	0	-2.374340	-0.981507	0.781203
8	1	0	2.374328	-0.981541	-0.781194
9	1	0	2.374380	-0.981426	0.781159

Zero-point correction= 0.056567 (Hartree/Particle)
Thermal correction to Energy= 0.064943
Thermal correction to Enthalpy= 0.065887
Thermal correction to Gibbs Free Energy= 0.024040
Sum of electronic and zero-point Energies= -1246.746840
Sum of electronic and thermal Energies= -1246.738464
Sum of electronic and thermal Enthalpies= -1246.737520
Sum of electronic and thermal Free Energies= -1246.779367

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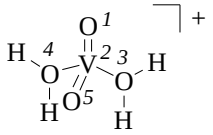
RMSD=3.929e-09\RMSF=7.021e-06 PG=C01 [X(H4O4V1)]\NImag=0\\@.

(*iii*) NBO-analysis – B3LYP/6-31G*// B3LYP/6-311++G**



```
=========================================================================
No. (Occupancy)         Bond orbital/ Coefficients/ Hybrids
=========================================================================
1. (1.91585) BD (1) O  1- V  2
    (69.86%)  0.8358* O  1  s(9.46%)   p(90.33%)  d(0.21%)
    (30.14%)  0.5490* V  2  s(3.95%)   p(4.73%)   d(89.79%)   f(1.53%)
2. (1.87616) BD (2) O  1- V  2
   (86.12%)   0.9280* O  1  s(0.05%)   p(99.84%)  d(0.11%)
   (13.88%)   0.3726* V  2  s(0.04%)   p(27.25%)  d(66.46%)   f(6.24%)
3. (1.98614) BD (3) O  1- V  2
   (72.77%)   0.8531* O  1  s(0.00%)   p(99.87%)  d(0.13%)
   (27.23%)   0.5218* V  2  s(0.00%)   p(1.11%)   d(98.71%)   f(0.18%)
4. (1.91589) BD (1) V  2- O  5
   (30.14%)   0.5490* V  2  s(3.95%)   p(4.72%)   d(89.80%)   f(1.53%)
   (69.86%)   0.8358* O  5  s(9.46%)   p(90.33%)  d(0.21%)
5. (1.87616) BD (2) V  2- O  5
   (13.88%)   0.3726* V  2  s(0.04%)   p(27.25%)  d(66.46%)   f(6.24%)
   (86.12%)   0.9280* O  5  s(0.05%)   p(99.84%)  d(0.11%)
6. (1.98614) BD (3) V  2- O  5
   (27.23%)   0.5218* V  2  s(0.00%)   p(1.11%)   d(98.71%)   f(0.18%)
   (72.77%)   0.8531* O  5  s(0.00%)   p(99.87%)  d(0.13%)
24.(1.97417) LP (1) O  1    s(90.52%)  p(9.48%)   d(0.00%)
25.(1.97066) LP (1) O  3    s(8.65%)   p(91.31%)  d(0.03%)
26.(1.87300) LP (2) O  3    s(41.66%)  p(58.34%)  d(0.00%)
27.(1.97067) LP (1) O  4    s(8.65%)   p(91.31%)  d(0.03%)
28.(1.87300) LP (2) O  4    s(41.66%)  p(58.34%)  d(0.00%)
29.(1.97417) LP (1) O  5    s(90.52%)  p(9.48%)   d(0.00%)
=========================================================================
```

Second order perturbation theory analysis of Fock-matrix for *cis*-dioxidovanadium(V) dihydrate acid in NBO-basis(threshold for printing: 0.50 kcal/mol)

Donor NBO (i)	Acceptor NBO (j)	kcal/mol	a.u.	a.u.
within unit 1				
24. LP (1) O 1	96. BD*(2) O 1- V 2	1.45	1.23	0.039
24. LP (1) O 1	99. BD*(2) V 2- O 5	4.68	1.23	0.070
29. LP (1) O 5	96. BD*(2) O 1- V 2	4.68	1.23	0.070
29. LP (1) O 5	99. BD*(2) V 2- O 5	1.45	1.23	0.039
from unit 1 to unit 2				
None above threshold				
from unit 1 to unit 3				
None above threshold				
from unit 2 to unit 1				
25. LP (1) O 3	95. BD*(1) O 1- V 2	0.62	0.51	0.016
25. LP (1) O 3	96. BD*(2) O 1- V 2	0.54	0.68	0.018
25. LP (1) O 3	97. BD*(3) O 1- V 2	1.27	0.40	0.020
25. LP (1) O 3	98. BD*(1) V 2- O 5	0.62	0.51	0.016
25. LP (1) O 3	99. BD*(2) V 2- O 5	0.54	0.68	0.018
25. LP (1) O 3	100. BD*(3) V 2- O 5	1.27	0.40	
26. LP (2) O 3	95. BD*(1) O 1- V 2	1.70	0.75	0.032
26. LP (2) O 3	96. BD*(2) O 1- V 2	0.12	0.91	0.010
26. LP (2) O 3	97. BD*(3) O 1- V 2	6.30	0.63	0.057
26. LP (2) O 3	98. BD*(1) V 2- O 5	1.70	0.75	0.032
26. LP (2) O 3	99. BD*(2) V 2- O 5	0.13	0.91	0.010
26. LP (2) O 3	100. BD*(3) V 2- O 5	6.29	0.63	0.057
within unit 2				
None above threshold				
from unit 2 to unit 3				
None above threshold				
from unit 3 to unit 1				
27. LP (1) O 4	95. BD*(1) O 1- V 2	0.62	0.51	0.016
27. LP (1) O 4	96. BD*(2) O 1- V 2	0.54	0.68	0.018
27. LP (1) O 4	97. BD*(3) O 1- V 2	1.27	0.40	0.020
27. LP (1) O 4	98. BD*(1) V 2- O 5	0.62	0.51	0.016
27. LP (1) O 4	99. BD*(2) V 2- O 5	0.54	0.68	0.018
27. LP (1) O 4	100. BD*(3) V 2- O 5	1.27	0.40	0.020
28. LP (2) O 4	95. BD*(1) O 1- V 2	1.70	0.75	0.032
28. LP (2) O 4	96. BD*(2) O 1- V 2	0.12	0.91	0.010
28. LP (2) O 4	97. BD*(3) O 1- V 2	6.30	0.63	0.057
28. LP (2) O 4	98. BD*(1) V 2- O 5	1.70	0.75	0.032
28. LP (2) O 4	99. BD*(2) V 2- O 5	0.12	0.91	0.010
28. LP (2) O 4	100. BD*(3) V 2- O 5	6.29	0.63	0.057
from unit 3 to unit 2				
None above threshold				
within unit 3				
None above threshold				

NBO	Occupancy	Energy / a.u.
Molecular unit 1 (O2V)		
1. BD (1) O 1- V 2	1.91585	-0.71351
2. BD (2) O 1- V 2	1.87616	-0.48381
3. BD (3) O 1- V 2	1.98614	-0.54369
4. BD (1) V 2- O 5	1.91589	-0.71354
5. BD (2) V 2- O 5	1.87616	-0.48381
6. BD (3) V 2- O 5	1.98614	-0.54369
Molecular unit 2 (H2O)		
Molecular unit 3 (H2O)		

5.2 *cis*-Dioxidovanadium(V) tetrahydrate

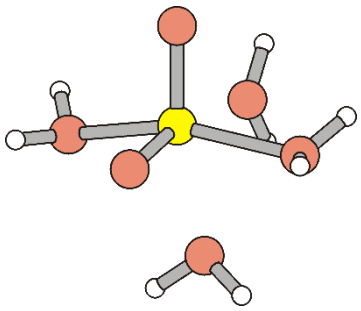


Figure S5 Calculated minimum structure of *cis*-dioxidovanadium(V) tetrahydrate.

B3LYP/6-311++G//B3LYP/6-311++G****

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	0.012929	-1.325915	-1.264705
2	23	0	0.002072	-0.385861	0.013552
3	8	0	0.004029	-1.325947	1.288440
4	8	0	2.077077	0.009112	-0.116878
5	8	0	-2.074742	-0.013828	-0.135938
6	8	0	-0.000192	1.611396	-1.238761
7	8	0	-0.021867	1.388838	1.420032
8	1	0	-2.546123	-0.694202	-0.638831
9	1	0	-2.574634	0.143005	0.677157
10	1	0	0.776912	1.776165	-1.788486
11	1	0	-0.767915	1.763168	-1.805187
12	1	0	-0.023057	2.319771	1.165041
13	1	0	-0.017331	1.321549	2.382939
14	1	0	2.556554	-0.662749	-0.623598
15	1	0	2.570064	0.158841	0.701760

```
Zero-point correction=                          0.108240 (Hartree/Particle)
Thermal correction to Energy=                   0.121725
Thermal correction to Enthalpy=                 0.122669
Thermal correction to Gibbs Free Energy=        0.070280
Sum of electronic and zero-point Energies=          -1400.148786
Sum of electronic and thermal Energies=             -1400.135301
Sum of electronic and thermal Enthalpies=           -1400.134357
Sum of electronic and thermal Free Energies=        -1400.186747

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6 Metavanadium Peroxoic Acid and its Conjugate Base

6.1 Metavanadium peroxoic acid – *end-on*-conformer

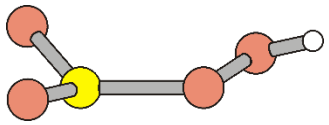

Figure S6. Calculated minimum structure of the *end-on*-conformer of metavanadium peroxoic acid.

(*i*) B3LYP/6-311++G**//B3LYP/6-311++G**

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	-1.658138	-1.006897	0.218141
2	23	0	-0.483514	-0.004797	-0.163018
3	8	0	1.200629	-0.676399	0.003492
4	8	0	2.308777	0.226638	0.039480
5	8	0	-0.834113	1.512587	0.151800
6	1	0	2.983578	-0.337115	0.446104

```
Zero-point correction=                          0.022997 (Hartree/Particle)
Thermal correction to Energy=                   0.029518
Thermal correction to Enthalpy=                 0.030462
Thermal correction to Gibbs Free Energy=       -0.008186
Sum of electronic and zero-point Energies=          -1245.557398
Sum of electronic and thermal Energies=             -1245.550877
Sum of electronic and thermal Enthalpies=           -1245.549932
Sum of electronic and thermal Free Energies=        -1245.588581

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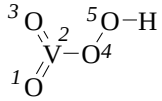
(*ii*) NBO-analysis – B3LYP/6-31G*// B3LYP/6-311++G**




```
=======================================================================
No. (Occupancy)          Bond orbital/ Coefficients/ Hybrids
=======================================================================
1. (1.91683) BD (1) O  1- V  2
   (78.31%)   0.8849* O  1  s(3.55%)   p(96.31%)  d(0.14%)
   (21.69%)   0.4658* V  2  s(1.96%)   p(8.66%)   d(88.21%)   f(1.17%)
2. (1.88120) BD (2) O  1- V  2
   (74.41%)   0.8626* O  1  s(4.81%)   p(95.02%)  d(0.17%)
   (25.59%)   0.5058* V  2  s(4.08%)   p(20.70%)  d(74.58%)   f(0.65%)
3. (1.92071) BD (1) V  2- O  3
   (19.37%)   0.4401* V  2  s(1.89%)   p(22.50%)  d(74.25%)   f(1.36%)
   (80.63%)   0.8979* O  3  s(0.78%)   p(99.11%)  d(0.11%)
4. (1.87618) BD (2) V  2- O  3
   (23.41%)   0.4838* V  2  s(17.34%)  p(13.10%)  d(68.67%)   f(0.88%)
   (76.59%)   0.8752* O  3  s(6.45%)   p(93.38%)  d(0.17%)
5. (1.87365) BD (3) V  2- O  3
   (18.16%)   0.4262* V  2  s(5.00%)   p(17.92%)  d(74.93%)   f(2.15%)
   (81.84%)   0.9046* O  3  s(1.24%)   p(98.63%)  d(0.12%)
6. (1.93607) BD (1) V  2- O  4
   (10.54%)   0.3247* V  2  s(5.15%)   p(34.05%)  d(60.14%)   f(0.65%)
   (89.46%)   0.9458* O  4  s(1.21%)   p(98.74%)  d(0.05%)
7. (1.95122) BD (2) V  2- O  4
   (11.04%)   0.3323* V  2  s(22.38%)  p(11.49%)  d(65.00%)   f(1.13%)
   (88.96%)   0.9432* O  4  s(13.45%)  p(86.48%)  d(0.07%)
8. (1.98882) BD (1) O  4- O  5
   (50.82%)   0.7129* O  4  s(14.19%)  p(85.65%)  d(0.16%)
   (49.18%)   0.7013* O  5  s(11.91%)  p(87.82%)  d(0.26%)
23.(1.97673) LP (1) O  1     s(91.54%)  p(8.46%)   d(0.00%)
24.(1.66110) LP (2) O  1     s(0.10%)   p(99.80%)  d(0.10%)
25.(1.97558) LP (1) O  3     s(91.52%)  p(8.48%)   d(0.00%)
26.(1.97878) LP (1) O  4     s(71.44%)  p(28.53%)  d(0.02%)
27.(1.99474) LP (1) O  5     s(65.69%)  p(34.28%)  d(0.04%)
28.(1.96041) LP (2) O  5     s(0.24%)   p(99.66%)  d(0.10%)
=======================================================================
```

Second order perturbation theory analysis of Fock-matrix for the end-on-conformer of metavanadium peroxoic acid in NBO-basis(threshold for printing: 0.50 kcal/mol)

Donor NBO (i)	Acceptor NBO (j)	kcal/mol	a.u.	a.u.
23. LP (1) O 1	92. BD*(1) V 2- O 3	2.68	1.04	0.049
23. LP (1) O 1	93. BD*(2) V 2- O 3	1.59	1.11	0.039
23. LP (1) O 1	94. BD*(3) V 2- O 3	7.54	1.04	0.082
23. LP (1) O 1	96. BD*(2) V 2- O 4	6.43	1.08	0.079
24. LP (2) O 1	90. BD*(1) O 1- V 2	3.06	0.27	0.027
24. LP (2) O 1	92. BD*(1) V 2- O 3	9.49	0.32	0.052
24. LP (2) O 1	93. BD*(2) V 2- O 3	8.95	0.39	0.056
24. LP (2) O 1	94. BD*(3) V 2- O 3	3.69	0.33	0.033
24. LP (2) O 1	96. BD*(2) V 2- O 4	28.00	0.36	0.093
25. LP (1) O 3	93. BD*(2) V 2- O 3	2.07	1.11	0.044
25. LP (1) O 3	96. BD*(2) V 2- O 4	2.09	1.08	0.045
26. LP (1) O 4	90. BD*(1) O 1- V 2	0.58	0.77	0.019
26. LP (1) O 4	93. BD*(2) V 2- O 3	0.78	0.89	0.024
26. LP (1) O 4	94. BD*(3) V 2- O 3	3.40	0.83	0.049
26. LP (1) O 4	95. BD*(1) V 2- O 4	0.56	0.80	0.020
28. LP (2) O 5	95. BD*(1) V 2- O 4	3.10	0.36	0.031

Natural bond orbital (NBO)-energies

NBO	Occupancy	Energy / a.u.
1. BD (1) O 1- V 2	1.91683	-0.40701
2. BD (2) O 1- V 2	1.88120	-0.43966
3. BD (1) V 2- O 3	1.92071	-0.35896
4. BD (2) V 2- O 3	1.87618	-0.47526
5. BD (3) V 2- O 3	1.87365	-0.35506
6. BD (1) V 2- O 4	1.93607	-0.37775
7. BD (2) V 2- O 4	1.95122	-0.53369
8. BD (1) O 4- O 5	1.98882	-0.78748
97.BD*(1) O 4- O 5	0.01578	0.07528

6.2 Metavanadium peroxoic acid – *side-on*-conformer

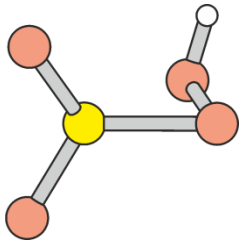


Figure S7. Calculated minimum structure of the *side-on*-conformer of metavanadium peroxoic acid.

(*i*) B3LYP/6-311++G**//B3LYP/6-311++G**

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	23	0	-0.310860	-0.006668	-0.015557
2	8	0	-1.049253	1.398843	0.060069
3	8	0	1.388137	-0.209705	0.812963
4	8	0	1.623300	-0.049098	-0.637394
5	8	0	-1.327240	-1.222392	-0.103175
6	1	0	2.070227	0.812170	-0.701900

```
Zero-point correction=                          0.023988 (Hartree/Particle)
Thermal correction to Energy=                   0.029717
Thermal correction to Enthalpy=                 0.030661
Thermal correction to Gibbs Free Energy=       -0.005874
Sum of electronic and zero-point Energies=          -1245.570244
Sum of electronic and thermal Energies=             -1245.564515
Sum of electronic and thermal Enthalpies=           -1245.563570
Sum of electronic and thermal Free Energies=        -1245.600106

Version=AM64L-G03RevE.01\State=1-A\HF=-1245.5942316\RMSD=7.995e-
09\RMSF=7.547e-07\PG=C01 [X(H1O4V1)]\\@.
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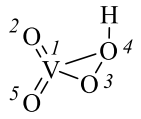
(*ii*) NBO-analysis – B3LYP/6-31G*// B3LYP/6-311++G**




```
=======================================================================
No. (Occupancy)         Bond orbital/ Coefficients/ Hybrids
=======================================================================
1. (1.97244) BD (1) V  1- O  2
   (30.49%)   0.5522* V  1  s(1.48%)   p(0.32%)   d(98.08%)   f(0.11%)
   (69.51%)   0.8337* O  2  s(6.74%)   p(93.06%)  d(0.20%)
2. (1.92555) BD (2) V  1- O  2
   (22.00%)   0.4690* V  1  s(3.42%)   p(19.25%)  d(76.78%)   f(0.55%)
   (78.00%)   0.8832* O  2  s(0.33%)   p(99.55%)  d(0.12%)
3. (1.92810) BD (1) V  1- O  3
   (12.96%)   0.3600* V  1  s(20.35%)  p(20.26%)  d(58.70%)   f(0.69%)
   (87.04%)   0.9329* O  3  s(6.73%)   p(93.14%)  d(0.13%)
4. (1.97773) BD (1) V  1- O  5
   (31.68%)   0.5628* V  1  s(2.45%)   p(0.47%)   d(96.93%)   f(0.14%)
   (68.32%)   0.8266* O  5  s(7.57%)   p(92.22%)  d(0.21%)
5. (1.98682) BD (2) V  1- O  5
   (19.86%)   0.4457* V  1  s(1.24%)   p(1.71%)   d(96.80%)   f(0.25%)
   (80.14%)   0.8952* O  5  s(0.84%)   p(99.06%)  d(0.10%)
6. (1.89080) BD ( 3) V  1- O  5
   (17.90%)   0.4231* V  1  s(7.85%)   p(26.16%)  d(65.10%)   f(0.90%)
   (82.10%)   0.9061* O  5  s(0.03%)   p(99.86%)  d(0.11%)
7. (1.97755) BD (1) O  3- O  4
   (41.57%)   0.6448* O  3  s(6.19%)   p(93.52%)  d(0.30%)
   (58.43%)   0.7644* O  4  s(12.73%)  p(87.06%)  d(0.21%)
22.(1.97116) LP (1) O  2    s(91.28%)  p(8.72%)   d(0.00%)
23.(1.69672) LP (2) O  2    s(1.64%)   p(98.26%)  d(0.10%)
24.(1.98593) LP (1) O  3    s(87.21%)  p(12.78%)  d(0.01%)
25.(1.93867) LP (2) O  3    s(0.10%)   p(99.82%)  d(0.08%)
26.(1.99022) LP (1) O  4    s(53.75%)  p(46.19%)  d(0.06%)
27.(1.84928) LP (2) O  4    s(10.78%)  p(89.14%)  d(0.08%)
28.(1.97008) LP (1) O  5    s(91.55%)  p(8.44%)   d(0.00%)
=======================================================================
```

Second order perturbation theory analysis of Fock-matrix for the *side-on*-conformer of metavanadium peroxoic acid in NBO-basis(threshold for printing: 0.50 kcal/mol)

Donor NBO (i)	Acceptor NBO (j)	kcal/mol	a.u.	a.u.
22. LP (1) O 2	92. BD*(2) V 1- O 2	0.83	1.00	0.026
22. LP (1) O 2	93. BD*(1) V 1- O 3	3.21	1.09	0.055
22. LP (1) O 2	95. BD*(2) V 1- O 5	5.35	0.95	0.068
22. LP (1) O 2	96. BD*(3) V 1- O 5	4.73	1.05	0.065
23. LP (2) O 2	93. BD*(1) V 1- O 3	3.70	0.39	0.035
23. LP (2) O 2	94. BD*(1) V 1- O 5	4.32	0.29	0.034
23. LP (2) O 2	95. BD*(2) V 1- O 5	62.25	0.25	0.112
23. LP (2) O 2	96. BD*(3) V 1- O 5	6.88	0.35	0.046
25. LP (2) O 3	91. BD*(1) V 1- O 2	6.26	0.31	0.039
25. LP (2) O 3	92. BD*(2) V 1- O 2	1.60	0.33	0.021
25. LP (2) O 3	94. BD*(1) V 1- O 5	4.62	0.32	0.035
25. LP (2) O 3	95. BD*(2) V 1- O 5	0.52	0.28	0.011
25. LP (2) O 3	96. BD*(3) V 1- O 5	1.07	0.37	0.018
25. LP (2) O 3	98. BD*(1) O 4- H 6	1.17	0.71	0.026
26. LP (1) O 4	91. BD*(1) V 1- O 2	1.27	0.69	0.027
26. LP (1) O 4	92. BD*(2) V 1- O 2	1.29	0.72	0.028
26. LP (1) O 4	95. BD*(2) V 1- O 5	0.58	0.67	0.019
27. LP (2) O 4	91. BD*(1) V 1- O 2	0.53	0.47	0.014
27. LP (2) O 4	92. BD*(2) V 1- O 2	5.81	0.50	0.049
27. LP (2) O 4	93. BD*(1) V 1- O 3	1.99	0.59	0.031
27. LP (2) O 4	94. BD*(1) V 1- O 5	2.61	0.49	0.032
27. LP (2) O 4	95. BD*(2) V 1- O 5	12.55	0.45	0.069
27. LP (2) O 4	96. BD*(3) V 1- O 5	1.29	0.54	0.024
28. LP (1) O 5	91. BD*(1) V 1- O 2	0.52	0.98	0.020
28. LP (1) O 5	93. BD*(1) V 1- O 3	2.87	1.09	0.052
28. LP (1) O 5	96. BD*(3) V 1- O 5	0.83	1.05	0.027

Natural bond orbital (NBO)-energies

NBO	Occupancy	Energy / a.u.
1. BD (1) V 1- O 2	1.97244	-0.52019
2. BD (2) V 1- O 2	1.92555	-0.35134
3. BD (1) V 1- O 3	1.92810	-0.46638
4. BD (1) V 1- O 5	1.97773	-0.53921
5. BD (2) V 1- O 5	1.98682	-0.37863
6. BD (3) V 1- O 5	1.89080	-0.33391
7. BD (1) O 3- O 4	1.97755	-0.75641
97.BD*(1) O 3- O 4	0.00416	0.00082

6.3 *iso*-Metavanadium peroxoic acid

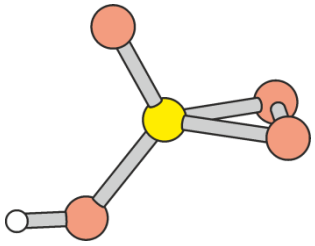


Figure S8. Calculated minimum structure of the *iso*-metavanadium peroxoic acid.

(*i*) B3LYP/6-311++G**//B3LYP/6-311++G**

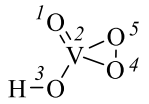
Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	23	0	-0.157616	0.080495	-0.000012
2	8	0	-0.575749	1.596072	0.000000
3	8	0	1.424671	-0.325595	0.726490
4	8	0	1.424691	-0.325628	-0.726468
5	8	0	-1.513275	-1.067005	0.000013
6	1	0	-2.457529	-0.874132	0.000001

```
Zero-point correction=                          0.022505 (Hartree/Particle)
Thermal correction to Energy=                   0.028358
Thermal correction to Enthalpy=                 0.029303
Thermal correction to Gibbs Free Energy=       -0.007133
Sum of electronic and zero-point Energies=          -1245.596667
Sum of electronic and thermal Energies=             -1245.590814
Sum of electronic and thermal Enthalpies=           -1245.589870
Sum of electronic and thermal Free Energies=        -1245.626305

Version=AM64L-G03RevE.01\State=1-A\HF=-1245.6191724\RMSD=4.475e-
09\RMSF=2.397e-06\PG=C01 [X(H1O4V1)]\\@.
```

(*ii*) NBO-analysis – B3LYP/6-31G*// B3LYP/6-311++G**




```
=======================================================================
No. (Occupancy)         Bond orbital/ Coefficients/ Hybrids
=======================================================================
1. (1.96961) BD (1) O  1- V  2
   (68.76%)   0.8292* O  1  s(8.83%)   p(90.94%)  d(0.23%)
   (31.24%)   0.5590* V  2  s(4.64%)   p(0.36%)   d(94.85%)   f(0.16%)
2. (1.91529) BD (2) O  1- V  2
   (81.67%)   0.9037* O  1  s(0.21%)   p(99.68%)  d(0.11%)
   (18.33%)   0.4281* V  2  s(9.64%)   p(8.54%)   d(81.16%)   f(0.67%)
3. (1.98330) BD (3) O  1- V  2
   (76.66%)   0.8755* O  1  s(0.00%)   p(99.88%)  d(0.12%)
   (23.34%)   0.4831* V  2  s(0.00%)   p(2.36%)   d(97.45%)   f(0.19%)
4. (1.96572) BD (1) V  2- O  3
   (16.09%)   0.4011* V  2  s(2.64%)   p(3.23%)   d(93.99%)   f(0.13%)
   (83.91%)   0.9160* O  3  s(15.41%)  p(84.52%)  d(0.07%)
5. (1.84650) BD ( 1) V  2- O  4
   (19.13%)   0.4373* V  2  s(33.50%)  p(5.72%)   d(60.35%)   f(0.43%)
   (80.87%)   0.8993* O  4  s(6.81%)   p(93.01%)  d(0.18%)
6. (1.84650) BD (1) V  2- O  5
   (19.12%)   0.4373* V  2  s(33.50%)  p(5.72%)   d(60.34%)   f(0.43%)
   (80.88%)   0.8993* O  5  s(6.81%)   p(93.01%)  d(0.18%)
7. (1.98495) BD (1) O  3- H  6
   (75.57%)   0.8693* O  3  s(26.98%)  p(72.89%)  d(0.13%)
   (24.43%)   0.4942* H  6  s(100.00%)
8. (1.93976) BD (1) O  4- O  5
   (50.00%)   0.7071* O  4  s(6.36%)   p(93.33%)  d(0.31%)
   (50.00%)   0.7071* O  5  s(6.36%)   p(93.33%)  d(0.31%)
22.(1.97008) LP (1) O  1    s(90.95%)  p(9.05%)   d(0.00%)
23.(1.94765) LP (1) O  3    s(57.65%)  p(42.29%)  d(0.06%)
24.(1.80872) LP (2) O  3    s(0.00%)   p(99.94%)  d(0.06%)
25.(1.97705) LP (1) O  4    s(86.54%)  p(13.46%)  d(0.01%)
26.(1.86005) LP (2) O  4    s(0.47%)   p(99.44%)  d(0.09%)
27.(1.97705) LP (1) O  5    s(86.54%)  p(13.46%)  d(0.01%)
28.(1.86006) LP (2) O  5    s(0.47%)   p(99.44%)  d(0.09%)
98.(0.04142) BD*(1) O  4- O  5
   (50.00%)   0.7071* O  4  s(6.36%)   p(93.33%)  d(0.31%)
   (50.00%)  -0.7071* O  5  s(6.36%)   p(93.33%)  d(0.31%)
=======================================================================
```

Second order perturbation theory analysis of Fock-matrix for *iso*-metavanadium peroxoic acid in NBO-basis(threshold for printing: 0.50 kcal/mol)

Donor NBO (i)	Acceptor NBO (j)	kcal/mol	a.u.	a.u.
22. LP (1) O 1	92. BD*(2) O 1- V 2	3.25	1.04	0.054
22. LP (1) O 1	95. BD*(1) V 2- O 4	4.69	1.11	0.067
22. LP (1) O 1	96. BD*(1) V 2- O 5	4.69	1.11	0.067
23. LP (1) O 3	91. BD*(1) O 1- V 2	1.76	0.69	0.031
23. LP (1) O 3	92. BD*(2) O 1- V 2	17.09	0.70	0.101
23. LP (1) O 3	95. BD*(1) V 2- O 4	1.65	0.77	0.033
23. LP (1) O 3	96. BD*(1) V 2- O 5	1.65	0.77	0.033
24. LP (2) O 3	93. BD*(3) O 1- V 2	9.04	0.25	0.043
24. LP (2) O 3	95. BD*(1) V 2- O 4	5.35	0.41	0.042
24. LP (2) O 3	96. BD*(1) V 2- O 5	5.35	0.41	0.042
25. LP (1) O 4	93. BD*(3) O 1- V 2	0.56	0.81	0.020
25. LP (1) O 4	94. BD*(1) V 2- O 3	1.52	0.85	0.033
25. LP (1) O 4	95. BD*(1) V 2- O 4	1.22	0.97	0.032
25. LP (1) O 4	98. BD*(1) O 4- O 5	0.62	0.95	0.022
26. LP (2) O 4	91. BD*(1) O 1- V 2	8.49	0.33	0.048
26. LP (2) O 4	92. BD*(2) O 1- V 2	0.84	0.34	0.015
26. LP (2) O 4	93. BD*(3) O 1- V 2	6.78	0.24	0.037
26. LP (2) O 4	94. BD*(1) V 2- O 3	7.82	0.29	0.043
27. LP (1) O 5	93. BD*(3) O 1- V 2	0.56	0.81	0.020
27. LP (1) O 5	94. BD*(1) V 2- O 3	1.52	0.85	0.033
27. LP (1) O 5	96. BD*(1) V 2- O 5	1.22	0.97	0.032
27. LP (1) O 5	98. BD*(1) O 4- O 5	0.62	0.95	0.022
28. LP (2) O 5	91. BD*(1) O 1- V 2	8.49	0.33	0.048
28. LP (2) O 5	92. BD*(2) O 1- V 2	0.84	0.34	0.015
28. LP (2) O 5	93. BD*(3) O 1- V 2	6.78	0.24	0.037
28. LP (2) O 5	94. BD*(1) V 2- O 3	7.82	0.29	0.043

Natural bond orbital (NBO)-energies

NBO	Occupancy	Energy / a.u.
1. BD (1) O 1- V 2	1.96961	-0.58755
2. BD (2) O 1- V 2	1.91529	-0.37318
3. BD (3) O 1- V 2	1.98330	-0.39109
4. BD (1) V 2- O 3	1.96572	-0.56766
5. BD (1) V 2- O 4	1.84650	-0.47849
6. BD (1) V 2- O 5	1.84650	-0.47848
7. BD (1) O 3- H 6	1.98495	-0.79730
8. BD (1) O 4- O 5	1.93976	-0.66900
98.BD*(1) O 4- O 5	0.04142	0.03991

6.4 Metavanadium peroxoic acid conjugate base

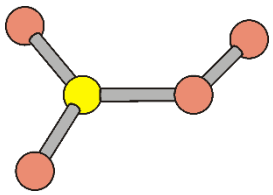


Figure S9. Calculated minimum structure of metavanadium peroxoic acid conjugate base.

(*i*) B3LYP/6-311++G**//B3LYP/6-311++G**

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	-1.597798	-1.121079	0.000068
2	23	0	-0.415339	0.007673	-0.000142
3	8	0	1.229243	-0.595703	0.000287
4	8	0	2.399356	0.113762	-0.000114
5	8	0	-0.836700	1.580961	0.000166

```
Zero-point correction=                          0.010677 (Hartree/Particle)
Thermal correction to Energy=                   0.016580
Thermal correction to Enthalpy=                 0.017524
Thermal correction to Gibbs Free Energy=       -0.019742
Sum of electronic and zero-point Energies=          -1245.032407
Sum of electronic and thermal Energies=             -1245.026504
Sum of electronic and thermal Enthalpies=           -1245.025560
Sum of electronic and thermal Free Energies=        -1245.062826

Version=EM64L-G09RevD.01\State=1-A\HF=-1245.0430835\RMSD=1.471e-09\
RMSF=4.054e-06\PG=C01 [X(O4V1)]\NImag=0\\@.
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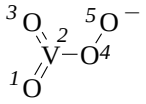
(*ii*) NBO-analysis – B3LYP/6-31G*// B3LYP/6-311++G**



No. (Occupancy)	Bond orbital/ Coefficients/ Hybrids				
1. (1.94008) **BD (1) O 1- V 2**					
(80.34%)	0.8963* O 1	s(0.00%)	p(99.91%)	d(0.09%)	
(19.66%)	0.4434* V 2	s(0.00%)	p(31.39%)	d(68.30%)	f(0.31%)
2. (1.99099) **BD (2) O 1- V 2**					
(72.46%)	0.8512* O 1	s(9.49%)	p(90.36%)	d(0.15%)	
(27.54%)	0.5248* V 2	s(2.69%)	p(0.55%)	d(96.63%)	f(0.13%)
3. (1.93125) **BD (1) V 2- O 3**					
(18.43%)	0.4293* V 2	s(0.00%)	p(35.32%)	d(64.30%)	f(0.38%)
(81.57%)	0.9032* O 3	s(0.00%)	p(99.91%)	d(0.09%)	
4. (1.99046) **BD (2) V 2- O 3**					
(28.10%)	0.5301* V 2	s(2.31%)	p(0.49%)	d(97.07%)	f(0.14%)
(71.90%)	0.8479* O 3	s(8.78%)	p(91.07%)	d(0.15%)	
5. (1.94164) **BD (1) V 2- O 4**					
(15.60%)	0.3950* V 2	s(0.00%)	p(32.52%)	d(67.19%)	f(0.30%)
(84.40%)	0.9187* O 4	s(0.00%)	p(99.95%)	d(0.05%)	
6. (1.99145) **BD (2) V 2- O 4**					
(19.77%)	0.4446* V 2	s(1.10%)	p(0.29%)	d(98.47%)	f(0.13%)
(80.23%)	0.8957* O 4	s(9.83%)	p(90.09%)	d(0.08%)	
7. (1.98178) **BD (1) O 4- O 5**					
(58.49%)	0.7648* O 4	s(20.10%)	p(79.77%)	d(0.13%)	
(41.51%)	0.6443* O 5	s(11.15%)	p(88.54%)	d(0.31%)	
21.(1.97648) **LP (1) O 1**		s(90.46%)	p(9.54%)	d(0.00%)	
22.(1.77910) **LP (2) O 1**		s(0.03%)	p(99.90%)	d(0.06%)	
23.(1.97340) **LP (1) O 3**		s(90.98%)	p(9.02%)	d(0.00%)	
24.(1.76586) **LP (2) O 3**		s(0.23%)	p(99.70%)	d(0.07%)	
25.(1.94575) **LP (1) O 4**		s(70.33%)	p(29.65%)	d(0.02%)	
26.(1.99302) **LP (1) O 5**		s(89.51%)	p(10.49%)	d(0.00%)	
27.(1.81985) **LP (2) O 5**		s(0.00%)	p(99.95%)	d(0.05%)	
28.(1.81552) **LP (3) O 5**		s(0.03%)	p(99.93%)	d(0.04%)	

Second order perturbation theory analysis of Fock-matrix for metavanadium peroxoic acid conjugate base in NBO-basis(threshold for printing: 0.50 kcal/mol)

Donor NBO (i)	Acceptor NBO (j)	kcal/mol	a.u.	a.u.
22. LP (2) O 1	91. BD*(2) O 1- V 2	0.83	0.27	0.014
22. LP (2) O 1	93. BD*(2) V 2- O 3	23.45	0.28	0.074
22. LP (2) O 1	95. BD*(2) V 2- O 4	35.15	0.24	0.083
24. LP (2) O 3	91. BD*(2) O 1- V 2	30.91	0.28	0.084
24. LP (2) O 3	95. BD*(2) V 2- O 4	30.51	0.24	0.078
25. LP (1) O 4	91. BD*(2) O 1- V 2	1.81	0.79	0.035
25. LP (1) O 4	93. BD*(2) V 2- O 3	4.86	0.79	0.057
27. LP (2) O 5	94. BD*(1) V 2- O 4	16.34	0.19	0.050
28. LP (3) O 5	95. BD*(2) V 2- O 4	13.42	0.21	0.049

Natural bond orbital (NBO)-energies

NBO	Occupancy	Energy / a.u.
1. BD (1) O 1- V 2	1.94008	-0.13369
2. BD (2) O 1- V 2	1.99099	-0.32951
3. BD (1) V 2- O 3	1.93125	-0.13380
4. BD (2) V 2- O 3	1.99046	-0.32447
5. BD (1) V 2- O 4	1.94164	-0.16673
6. BD (2) V 2- O 4	1.99145	-0.32494
7. BD (1) O 4- O 5	1.98178	-0.60774
96.BD*(1) O 4- O 5	0.01288	0.40574

6.5 *iso*-Metavanadium peroxoic acid conjugate base

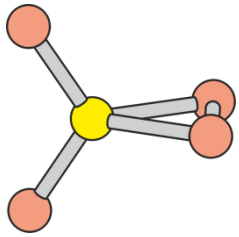


Figure S10. Calculated minimum structure of *iso*-metavanadium peroxoic acid conjugate base.

(*i*) B3LYP/6-311++G**//B3LYP/6-311++G**

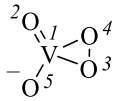
Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	23	0	-0.232429	-0.000004	-0.000001
2	8	0	-1.120797	-1.364629	0.000001
3	8	0	1.454892	-0.000010	-0.741514
4	8	0	1.454892	-0.000009	0.741515
5	8	0	-1.120753	1.364659	0.000001

Zero-point correction= 0.011594 (Hartree/Particle)
Thermal correction to Energy= 0.016816
Thermal correction to Enthalpy= 0.017760
Thermal correction to Gibbs Free Energy= -0.017492
Sum of electronic and zero-point Energies= -1245.094509
Sum of electronic and thermal Energies= -1245.089287
Sum of electronic and thermal Enthalpies= -1245.088343
Sum of electronic and thermal Free Energies= -1245.123595

Version=AM64L-G03RevE.01\State=1-A\HF=-1245.1061032\RMSD=5.110e-09\RMSF=3.836e-06\PG=C01 [X(O4V1)]\\@.

(*ii*) NBO-analysis – B3LYP/6-31G*// B3LYP/6-311++G**

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=======================================================================
No. (Occupancy)         Bond orbital/ Coefficients/ Hybrids
=======================================================================
1. (1.96453) BD (1) V  1- O  2
   (26.48%)   0.5146* V  1  s(1.06%)   p(0.73%)   d(98.11%)   f(0.10%)
   (73.52%)   0.8574* O  2  s(8.50%)   p(91.33%)  d(0.17%)
2. (1.91422) BD (2) V  1- O  2
   (17.19%)   0.4146* V  1  s(0.00%)   p(37.88%)  d(61.65%)   f(0.48%)
   (82.81%)   0.9100* O  2  s(0.00%)   p(99.92%)  d(0.08%)
3. (1.87527) BD (1) V  1- O  3
   (14.61%)   0.3822* V  1  s(36.53%)  p(13.23%)  d(49.80%)   f(0.45%)
   (85.39%)   0.9241* O  3  s(7.84%)   p(92.04%)  d(0.12%)
4. (1.87527) BD (1) V  1- O  4
   (14.61%)   0.3822* V  1  s(36.53%)  p(13.23%)  d(49.80%)   f(0.45%)
   (85.39%)   0.9241* O  4  s(7.84%)   p(92.04%)  d(0.12%)
5. (1.97200) BD (1) V  1- O  5
   (26.94%)   0.5190* V  1  s(1.63%)   p(1.10%)   d(97.13%)   f(0.14%)
   (73.06%)   0.8547* O  5  s(8.64%)   p(91.19%)  d(0.17%)
6. (1.94901) BD (2) V  1- O  5
   (13.48%)   0.3671* V  1  s(15.78%)  p(6.06%)   d(77.61%)   f(0.54%)
   (86.52%)   0.9302* O  5  s(1.40%)   p(98.53%)  d(0.07%)
7. (1.91421) BD (3) V  1- O  5
   (17.19%)   0.4146* V  1  s(0.00%)   p(37.88%)  d(61.65%)   f(0.48%)
   (82.81%)   0.9100* O  5  s(0.00%)   p(99.92%)  d(0.08%)
8. (1.94607) BD (1) O  3- O  4
   (50.00%)   0.7071* O  3  s(6.35%)   p(93.40%)  d(0.25%)
   (50.00%)   0.7071* O  4  s(6.35%)   p(93.40%)  d(0.25%)
22.(1.97237) LP (1) O  2    s(89.95%)  p(10.05%)  d(0.00%)
23.(1.72684) LP (2) O  2    s(1.53%)   p(98.39%)  d(0.08%)
24.(1.98099) LP (1) O  3    s(85.95%)  p(14.04%)  d(0.00%)
25.(1.91907) LP (2) O  3    s(0.00%)   p(99.94%)  d(0.06%)
26.(1.98099) LP (1) O  4    s(85.95%)  p(14.04%)  d(0.00%)
27.(1.91907) LP (2) O  4    s(0.00%)   p(99.94%)  d(0.06%)
28.(1.97237) LP (1) O  5    s(89.95%)  p(10.05%)  d(0.00%)
=======================================================================
```

Second order perturbation theory analysis of Fock-matrix for *iso*-metavanadium peroxoic acid conjugate base in NBO-basis(threshold for printing: 0.50 kcal/mol)

Donor NBO (i)	Acceptor NBO (j)	kcal/mol	a.u.	a.u.
22. LP (1) O 2	91. BD*(1) V 1- O 3	6.11	1.07	0.074
22. LP (1) O 2	92. BD*(1) V 1- O 4	6.11	1.07	0.074
22. LP (1) O 2	94. BD*(2) V 1- O 5	12.21	0.98	0.106
23. LP (2) O 2	91. BD*(1) V 1- O 3	1.21	0.39	0.020
23. LP (2) O 2	92. BD*(1) V 1- O 4	1.21	0.39	0.020
23. LP (2) O 2	93. BD*(1) V 1- O 5	2.85	0.29	0.027
23. LP (2) O 2	94. BD*(2) V 1- O 5	59.43	0.31	0.122
24. LP (1) O 3	90. BD*(2) V 1- O 2	0.69	0.88	0.023
24. LP (1) O 3	91. BD*(1) V 1- O 3	1.06	0.97	0.030
24. LP (1) O 3	92. BD*(1) V 1- O 4	0.66	0.97	0.023
24. LP (1) O 3	93. BD*(1) V 1- O 5	0.50	0.86	0.019
24. LP (1) O 3	95. BD*(3) V 1- O 5	0.69	0.88	0.023
25. LP (2) O 3	89. BD*(1) V 1- O 2	7.51	0.30	0.042
25. LP (2) O 3	90. BD*(2) V 1- O 2	1.72	0.32	0.021
25. LP (2) O 3	93. BD*(1) V 1- O 5	7.62	0.30	0.043
25. LP (2) O 3	95. BD*(3) V 1- O 5	1.72	0.32	0.021
26. LP (1) O 4	90. BD*(2) V 1- O 2	0.69	0.88	0.023
26. LP (1) O 4	91. BD*(1) V 1- O 3	0.66	0.97	0.023
26. LP (1) O 4	92. BD*(1) V 1- O 4	1.06	0.97	0.030
26. LP (1) O 4	93. BD*(1) V 1- O 5	0.50	0.86	0.019
26. LP (1) O 4	95. BD*(3) V 1- O 5	0.69	0.88	0.023
27. LP (2) O 4	89. BD*(1) V 1- O 2	7.51	0.30	0.042
27. LP (2) O 4	90. BD*(2) V 1- O 2	1.72	0.32	0.021
27. LP (2) O 4	93. BD*(1) V 1- O 5	7.62	0.30	0.043
27. LP (2) O 4	95. BD*(3) V 1- O 5	1.72	0.32	0.021
28. LP (1) O 5	91. BD*(1) V 1- O 3	5.72	1.07	0.072
28. LP (1) O 5	92. BD*(1) V 1- O 4	5.72	1.07	0.072
28. LP (1) O 5	94. BD*(2) V 1- O 5	3.46	0.98	0.056

Natural bond orbital (NBO)-energies

NBO	Occupancy	Energy / a.u.
1. BD (1) V 1- O 2	1.96453	-0.29678
2. BD (2) V 1- O 2	1.91422	-0.11641
3. BD (1) V 1- O 3	1.87527	-0.24901
4. BD (1) V 1- O 4	1.87527	-0.24901
5. BD (1) V 1- O 5	1.97200	-0.30283
6. BD (2) V 1- O 5	1.94901	-0.14716
7. BD (3) V 1- O 5	1.91421	-0.11640
8. BD (1) O 3- O 4	1.94607	-0.42145
96.BD*(1) O 3- O 4	0.03439	0.25587

7 Water Tetramer and Hydronium

7.1 Water tetramer

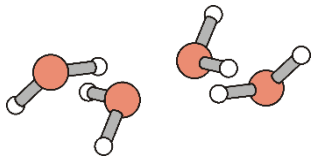

Figure S11. Calculated minimum structure of the water tetramer.

B3LYP/6-311++G//B3LYP/6-311++G****

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	1.475738	-1.259589	-0.090928
2	1	0	1.545602	-0.280438	-0.033546
3	8	0	1.269456	1.468206	0.087436
4	1	0	-0.291787	-1.563352	-0.079322
5	8	0	-1.269825	-1.468690	-0.085744
6	1	0	0.291490	1.563337	0.077172
7	8	0	-1.475596	1.259308	0.088885
8	1	0	-1.545609	0.280253	0.029501
9	1	0	2.114447	-1.613419	0.534071
10	1	0	-2.115704	1.614785	-0.533743
11	1	0	-1.605889	-2.077864	0.577553
12	1	0	1.609274	2.082824	-0.568874

```
Zero-point correction=                          0.098501 (Hartree/Particle)
Thermal correction to Energy=                   0.108340
Thermal correction to Enthalpy=                 0.109284
Thermal correction to Gibbs Free Energy=        0.064836
Sum of electronic and zero-point Energies=           -305.782999
Sum of electronic and thermal Energies=              -305.773160
Sum of electronic and thermal Enthalpies=            -305.772216
Sum of electronic and thermal Free Energies=         -305.816664

Version=AM64L-G03RevE.01\State=1-A\HF=-305.8815001\RMSD=1.268e-09\
RMSF=3.048e-05\PG=C01 [X(H8O4)]\NImag=0\\@.
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7.2 Hydronium

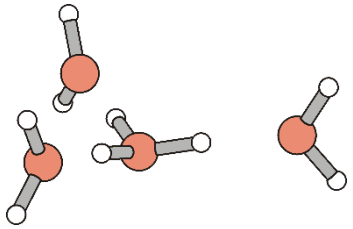

Figure S12. Calculated minimum structure of hydronium.

B3LYP/6-311++G//B3LYP/6-311++G****

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	-0.000269	0.000029	-0.370728
2	1	0	0.459282	0.872481	-0.142283
3	1	0	-0.985615	-0.038265	-0.142257
4	1	0	0.525586	-0.834096	-0.142200
5	8	0	1.336381	-2.132160	0.100016
6	8	0	-2.514934	-0.090942	0.100070
7	8	0	1.178833	2.223083	0.100008
8	1	0	1.680940	-2.689319	-0.607744
9	1	0	-3.169928	-0.110960	-0.607493
10	1	0	1.488770	2.800424	-0.607586
11	1	0	-2.989521	-0.126895	0.938291
12	1	0	1.605056	-2.525333	0.938099
13	1	0	1.385331	2.651881	0.938250

```
Zero-point correction=                          0.107579 (Hartree/Particle)
Thermal correction to Energy=                   0.119188
Thermal correction to Enthalpy=                 0.120133
Thermal correction to Gibbs Free Energy=        0.070256
Sum of electronic and zero-point Energies=           -306.129757
Sum of electronic and thermal Energies=              -306.118148
Sum of electronic and thermal Enthalpies=            -306.117204
Sum of electronic and thermal Free Energies=         -306.167081

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RMSF=1.348e-05\PG=C01 [X(H9O4)]\NImag=0\\@.
```

Chemistry started by saying
it would change baser metals into gold.
By doing so,
it has done much greater things.

– Ralph Waldo Emerson

8 References

(1) HyperChem(TM) Professional 7.51, Hypercube, Inc., 1115 NW 4th Street, Gainesville, Florida 32601, US.

(2) Gaussian 03, Revision E.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople, Gaussian, Inc., Wallingford CT, 2004.

(3) O'Boyle, N.M., Banck, M., James, C.A., Morley, C., Vandermeersch T., Hutchison, G.R. (2011) Open Babel: An open chemical toolbox. *J. Cheminform*. *3*, 33. DOI: 10.1186/1758-2946-3-33.

(4) Gaussian 09, Revision D.01,M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G.

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