Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Where does the Water go? A Computational Study on the Reactivity of a Ruthenium(V) Oxo Complex (bpc)(bpy)$Ru^{V}O$

*Ying Wang and Mårten S. G. Ahlquist**

Division of Theoretical Chemistry & Biology, School of Biotechnology, KTH Royal Institute of Technology, 106 91 Stockholm, Sweden.

Computational details

All Density Functional Theory (DFT) calculations were carried out with Jaguar 7.6 program package by Schrödinger LLC. For geometry optimisations, solvation energies, and frequency calculations, Becke's three-parameter hybrid functional and the LYP correlation functional (B3LYP)[i] was used with the LACVP** core potential and basis set, while single point energy corrections were performed with the M06[ii] functional using the LACV3P**++ basis set which, as suggested by Martin,[iii] was augmented with two f-polarisation functions on Ru. Frequency calculations were performed on the optimised geometries to verify that the geometries correspond to minima or first-order saddle points (transition states) on the potential energy surface (PES). The Gibbs free energies are calculated at standard state of 1 atm (g) and 1M(aq) and the G of each species is defined as the following equation G = E(M06/LACV3P**++ 2f on Ru) + G_{solv} + ZPE + H_{298} - TS_{298} + 1.9 kcal/mol (the 1.9 kcal/mol is a concentration correction to the free energy of solvation which by default is calculated at 1M(g) to 1M(aq) in Jaguar). Based on the gas-phase optimised structures, the effect of solvent was evaluated by single-point calculations using the Poisson-Boltzmann reactive field implemented in Jaguar 7.6 (PBF)[iv] with the standard settings for water. For the water molecule we used free energy of vaporisation of -2.05 kcal/mol, which is the free energy of transferring H_2O(g) at 1 atm and H_2O (liq) at 55.5 M at 298.15 K.[v] We have used the electron convention throughout the paper, meaning that the free energy of the electron was assumed to be zero. For activation strain analysis, the activation energy E_{act} is defined as the difference in single point energy E(M06/LACV3P**++ 2f on Ru) between the separated reactants and the transition state geometry in vacuum. The destabilising strain energy E_{strain} is defined as the difference in single point energy E(M06/LACV3P**++ 2f on Ru) between the separated reactants and corresponding geometrical parts in transition state in vacuum, respectively. For the proton we used the experimental free energy of solvation -264.0 kcal/mol at standard state conditions.

Our choice of M06 for the final energy corrections was based on previous studies that found M06 and PBE0 to be more reliable than other tested functionals (JCTC, 2013, 9, 1872). We also performed tests to validate M06, B3LYP and PBE0 for the specific system of the current study (Figure S2) and a four relevant transformations of water. M06 was the functional with the lowest error. Of special importance is the reduction potentials from III to IV and IV to V. Both B3LYP and PBE0 overestimates these potentials quite substantially, which we believe could cause artificially facile oxidations of other species, such as water. In almost all cases the larger basis set (LACV3P**++ 2f on Ru) improved the result compared to the smaller (LACVP**).

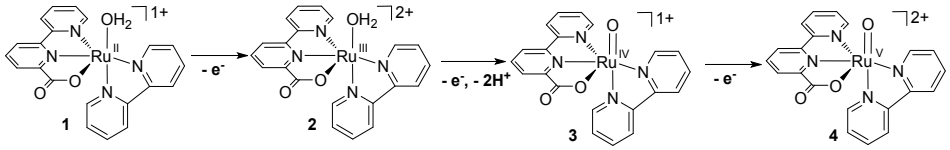

Figure S1. The oxidation steps of **1**.

	$Ru^{II/III}$	difference	$Ru^{III/IV}$	difference	$Ru^{IV/V}$	difference
Experimental data(V)	0.80		1.40		1.60	
M06/lacv3p**++(2f) (V)	0.83	0.03	1.52	0.12	1.77	0.17
b3lyp/lacv3p**++(2f) d3(V)	0.80	0.00	1.66	0.26	1.80	0.20
b3lyp/lacvp**(V)	0.68	-0.12	1.84	0.44	1.80	0.20
b3lyp/lacv3p**++(2f) (V)	0.80	0.00	1.78	0.38	1.84	0.24
M06/lacvp**(V)	0.69	-0.11	1.62	0.22	1.75	0.15
PBE0/lacv3p**++(V)	0.76	-0.04	1.76	0.36	1.81	0.21
PBE0/lacv3p**++ d3(V)	0.75	-0.05	1.67	0.27	1.79	0.19

Table S1. Calculated redox potentials for the oxidation steps of **1** (Figure S1) with different methods and basis set. All calculated potential values are referred to NHE.

	$H_2O(aq) \rightarrow$ $\bullet OH(g) + H^+(aq)$	difference	$2H_2O(aq) \rightarrow$ $\bullet OOH(g) + 3H^+(aq)$	difference	$2H_2O(aq) \rightarrow$ $O_2(g) + 4H^+(aq)$	difference	$H_2O(aq) \rightarrow OH^-(aq) + H^+(aq)$	difference
Experimental data (V)	2.81		1.64		1.23		19.0 kcal/mol	
M06/lacv3p**++(2f) (V)	2.70	-0.11	1.72	0.08	1.28	0.05	19.3 kcal/mol	0.3
b3lyp/lacv3p**++(2f) d3(V)	2.69	-0.12	1.72	0.08	1.30	0.07	17.7 kcal/mol	-1.3
b3lyp/lacvp**(V)	2.55	-0.26	1.51	-0.13	1.11	-0.12	57.9 kcal/mol	38.9
b3lyp/lacv3p**++(2f) (V)	2.68	-0.13	1.73	0.09	1.30	0.07	17.5 kcal/mol	-1.5
M06/lacvp**(V)	2.62	-0.19	1.56	-0.08	1.14	-0.09	57.2 kcal/mol	38.2
PBE0/lacv3p**++(V)	2.59	-0.22	1.61	-0.03	1.18	-0.05	20.8 kcal/mol	1.8
PBE0/lacv3p**++ d3(V)	2.60	-0.21	1.61	-0.03	1.18	-0.05	20.9 kcal/mol	1.9

Table S2. Calculated redox potentials for the oxidation of water with different methods and basis set. All calculated potential values are referred to NHE. The experimental values are from Hoare, J. P. In *Standard Potentials in Aqueous Solution*; Bard, A. J., Parsons, R., Jordan, J., Eds.; Marcel Dekker: New York, 1985; *Handbook of Chemistry and Physics*, 67th ed.; Weast, C. R., Ed.; CRC Press: Boca Raton, FL, 1986.

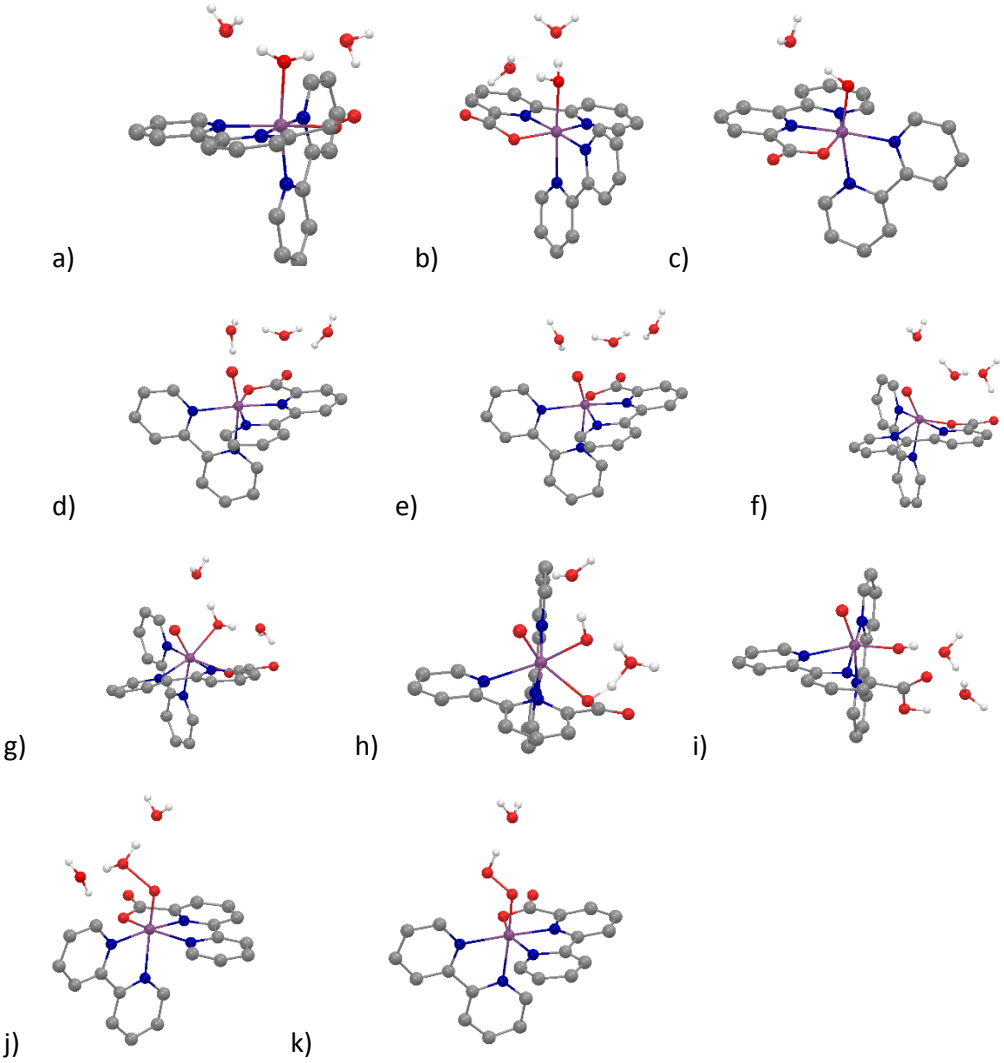

Figure S2. Optimised geometries of a) **1**; b) **2**; c) **2'**; d) **3**; e) **4**; f) **ts5**; g) **6**; h) **ts7**; i) **8**; j) **ts9**; k) **10**. Hydrogen atoms except the migrating H are omitted for clarity. (Purple = Fe; Red = O; Blue = N; Green = P; Yellow = S; Grey = C; White = H). The bond lengths are given in Å.

Cartesian coordinates in Å and energies in atomic units unless stated otherwise of the calculated geometries.

Figure S1a

E (M06/LACV3P++ 2f(Ru)) =**-1501.30367241688

ZPE (kcal mol^{-1}) = 251.959

G_{solv} = -0.0864438

DH_{298} (kcal mol^{-1})= 19.151

DS_{298} (cal K^{-1} mol^{-1})= 193.271

Cartesian coordinates

atom	x	y	z
Ru1	3.4570286793	5.9941720223	1.7118276224
N2	2.4764436111	5.0323675762	3.2577943631

C3	3.0536477240	4.5892031544	4.3922077288
H4	4.1135289868	4.7875979396	4.4942303503
C5	2.3493173324	3.9101451247	5.3772576996
H6	2.8642911353	3.5735665309	6.2704848957
C7	0.9884750546	3.6717294041	5.1867872515
H8	0.4076273014	3.1413242215	5.9342429554
C9	0.3852326402	4.1234511583	4.0181495735
H10	-0.6699883641	3.9459116849	3.8504565938
C11	1.1439266131	4.8036740913	3.0601522341
C12	0.5914009402	5.3203418283	1.7941831212
C13	-0.7433813401	5.1800682448	1.4018843739
H14	-1.4507995510	4.6603165374	2.0369010539
C15	-1.1604077424	5.7084081491	0.1844753368
H16	-2.1933555258	5.6023903612	-0.1306331591
C17	-0.2316746472	6.3692278478	-0.6215602818
H18	-0.5145729106	6.7919977531	-1.5792278608
C19	1.0815603536	6.4765738005	-0.1791462544
H20	1.8568599768	6.9669464682	-0.7577235832
N21	1.4873498101	5.9674918570	1.0003519180
N22	5.3143079709	5.9085891702	2.4411430071
C23	6.0792875493	4.8763104791	2.0448168593
C24	7.3899621467	4.7610325837	2.4967912657
H25	7.9971611347	3.9328243964	2.1493441833
C26	7.8755866069	5.7370908740	3.3742905699
H27	8.8890818277	5.6694001630	3.7571810744
C28	7.0721766904	6.8201264942	3.7420228133
H29	7.4648586908	7.5903555581	4.3960620766
C30	5.7679400494	6.8982207074	3.2422548519
C31	4.7706839581	7.9682041821	3.4589118213
C32	4.9982252813	9.0851625118	4.2648788824
H33	5.9462933268	9.1959547602	4.7792302104
C34	4.0068738114	10.0520050541	4.4057804057
H35	4.1754034279	10.9223296830	5.0318811623

C36	2.7990057490	9.8816317924	3.7299875551
H37	1.9987019950	10.6093972505	3.8096786946
C38	2.6264445565	8.7495666725	2.9407519956
H39	1.7055095152	8.5731172656	2.3960631080
N40	3.5759870835	7.8062870875	2.7992083030
C41	5.4053826291	3.9900857713	0.9998323251
O42	4.1311032417	4.1713928715	0.8482771284
O43	6.1212725476	3.2568313161	0.3104931464
O44	4.1746123335	6.8475801820	-0.1610863076
H45	4.8750773181	7.5340202452	-0.0782328151
H46	4.5635830693	6.1334006325	-0.7428712588
O54	6.2500649361	8.6125958443	0.0365759557
H55	6.9967311647	8.2312876762	-0.4453840669
H56	6.1156536853	9.4838351208	-0.3594671894
O50	5.3514635932	5.0456808456	-1.7946127094
H51	5.6780689449	4.2827189371	-1.2730081669
H52	4.7038069391	4.6611383273	-2.3993059294

Figure S1b

E (M06/LACV3P++ 2f(Ru)) =**-1500.97786853401

ZPE (kcal mol^{-1}) = 252.318

G_{solv} = -0.2281864

DH_{298} (kcal mol^{-1})= 19.088

DS_{298} (cal K^{-1} mol^{-1})= 191.916

Cartesian coordinates

atom	x	y	z
Ru1	3.4550806617	6.0162643348	1.7067174656
N2	2.4321953179	5.0953045818	3.2712167897
C3	2.9933697806	4.7040907638	4.4299994164
H4	4.0392786574	4.9507331048	4.5670607298
C5	2.2810495953	4.0123625143	5.4017048567
H6	2.7734819921	3.7138841979	6.3206814256
C7	0.9406292678	3.7114838253	5.1614608248
H8	0.3560582544	3.1676661747	5.8965230736

C9	0.3582940109	4.1145134886	3.9628069776
H10	-0.6809376884	3.8849698525	3.7628331849
C11	1.1228264740	4.8086817090	3.0212593472
C12	0.6028152522	5.2811143992	1.7247590009
C13	-0.7054335662	5.0845234156	1.2798905051
H14	-1.4211550382	4.5472643752	1.8901715839
C15	-1.0882297445	5.5808528765	0.0349633865
H16	-2.1025594679	5.4294324051	-0.3202518994
C17	-0.1575807564	6.2682315799	-0.7452638297
H18	-0.4200749317	6.6682761494	-1.7180825836
C19	1.1328482888	6.4306256736	-0.2540303118
H20	1.9068765527	6.9469622376	-0.8105242272
N21	1.5014583152	5.9502600975	0.9497189775
N22	5.3617056381	5.9426969350	2.4164052367
C23	6.0937091872	4.8914972817	2.0203141570
C24	7.4291190401	4.7797596759	2.3904177741
H25	8.0127263520	3.9300203289	2.0532951731
C26	7.9662694326	5.7899570836	3.1983409067
H27	9.0015236060	5.7326289742	3.5198623316
C28	7.1838620485	6.8804111622	3.5912235808
H29	7.6117038356	7.6614545153	4.2095108020
C30	5.8503818224	6.9454026374	3.1705132096
C31	4.8508078760	7.9988461842	3.4493178691
C32	5.1012057929	9.1312211519	4.2227333866
H33	6.0820199287	9.2883202549	4.6571355380
C34	4.0815852263	10.0583972022	4.4361976172
H35	4.2663768822	10.9428009417	5.0376664091
C36	2.8260840330	9.8322568330	3.8739387515
H37	2.0068327314	10.5275876457	4.0197091910
C38	2.6298514319	8.6823747282	3.1150083489
H39	1.6709799590	8.4597216987	2.6603678080
N40	3.6129271168	7.7902203310	2.8983078506
C41	5.3200701534	3.9561615597	1.1112292184

O42	4.0053080007	4.1714565108	1.1275333909
O43	5.8750221466	3.1369045004	0.4076668682
O44	4.2212151706	6.8722728014	-0.0968532428
H45	4.9862453301	7.5037218914	-0.0248277497
H46	4.4946594368	6.1614901058	-0.7566099940
O54	6.3040323125	8.5411825561	0.1189612529
H55	7.0880065499	8.2569082088	-0.3723920856
H56	6.1491775320	9.4529661323	-0.1659252274
O50	5.1329849963	5.0369559863	-1.7312923925
H51	5.3107664371	4.1471934517	-1.3821046299
H52	4.8974986024	4.9297515904	-2.6615698222

Figure S1c

E (M06/LACV3P++ 2f(Ru)) =**-1499.34855671183

ZPE (kcal mol^{-1}) = 230.426

G_{solv} = -0.0928285

DH_{298} (kcal mol^{-1})= 18.231

DS_{298} (cal K^{-1} mol^{-1})= 189.768

Cartesian coordinates

atom	x	y	z
Ru1	3.5029441430000	5.8674925740000	1.6472918943000
N2	2.3608745292000	5.1679326470000	3.3548920294000
C3	2.8686173943000	4.7955050448000	4.5412993056000
H4	3.9421151846000	4.9016731148000	4.6551348219000
C5	2.0800484597000	4.2937163244000	5.5692036930000
H6	2.5345811072000	4.0009974097000	6.5092570261000
C7	0.7072455350000	4.1741453234000	5.3532467607000
H8	0.0577344729000	3.7844178142000	6.1306569223000
C9	0.1762144866000	4.5566375438000	4.1256674040000
H10	-0.8874868204000	4.4646308713000	3.9454729253000
C11	1.0253827827000	5.0517269391000	3.1290911576000
C12	0.5540796135000	5.4726545932000	1.7907370611000
C13	-0.7774148915000	5.3957781735000	1.3722783948000
H14	-1.5433992747000	5.0139744617000	2.0362277034000
C15	-1.1150242250000	5.8047842474000	0.0848731763000

H16	-2.1453630657000	5.7450291055000	-0.2508049583000
C17	-0.1155352898000	6.2798668914000	-0.7638525814000
H18	-0.3371401673000	6.5979465463000	-1.7763685788000
C19	1.1922789470000	6.3338494518000	-0.2921843468000
H20	2.0314303506000	6.6758263621000	-0.8897645027000
N21	1.5119003140000	5.9483499318000	0.9546040461000
N22	5.3748068858000	5.6134100962000	2.3082065552000
C23	5.9249140837000	4.4183353988000	2.0466224811000
C24	7.2346234789000	4.1570543305000	2.4328879446000
H25	7.6619262171000	3.1843555814000	2.2158144090000
C26	7.9426948842000	5.1649254314000	3.0965233075000
H27	8.9665360866000	4.9913701654000	3.4125765396000
C28	7.3401257235000	6.3967610632000	3.3648157413000
H29	7.8910397689000	7.1714097556000	3.8862361574000
C30	6.0212358284000	6.6073888592000	2.9496727382000
C31	5.1846806692000	7.8107919257000	3.1447949543000
C32	5.6295028124000	8.9720195465000	3.7800313723000
H33	6.6454130792000	9.0315635199000	4.1531516082000
C34	4.7623726217000	10.0511163786000	3.9277943781000
H35	5.1000173639000	10.9580110445000	4.4192468070000
C36	3.4612262290000	9.9505541632000	3.4370231168000
H37	2.7563026948000	10.7690568841000	3.5301283725000
C38	3.0739565722000	8.7691097350000	2.8131805594000
H39	2.0768745652000	8.6398325317000	2.4075180707000
N40	3.9041394239000	7.7243420934000	2.6682515538000
C41	4.9825151531000	3.4331200087000	1.3572549393000
O42	3.7577567088000	3.8920362874000	1.1641359082000
O43	5.3830919205000	2.3225356407000	1.0645815231000
O44	4.0844260959000	6.6221030297000	-0.0333805660000
H46	5.0313331627000	6.8704585249000	-0.0712516109000
O50	6.8622249063000	7.1972835220000	-0.2718294386000
H51	7.1765595929000	6.4749668354000	-0.8323677538000
H52	7.0023292246000	7.9936497789000	-0.8012256460000

Figure S1d

E (M06/LACV3P++ 2f(Ru)) =**-1576.45417544406

ZPE (kcal mol^{-1}) = 253.363

G_{solv} = -0.0964913

DH_{298} (kcal mol^{-1})= 20.335

DS_{298} (cal K^{-1} mol^{-1})= 202.234

Cartesian coordinates

atom	x	y	z
Ru1	3.1242869367	6.0779903354	1.6666441832
N2	2.3670137598	4.9967068853	3.4835532560
C3	3.1228630502	4.4097933051	4.4234577472
H4	4.1969956578	4.4918871638	4.2933357634
C5	2.5813466182	3.7263722743	5.5061447069
H6	3.2330087515	3.2650976827	6.2398284568
C7	1.1935282797	3.6521989849	5.6122279173
H8	0.7281944892	3.1285057581	6.4413060475
C9	0.4055484422	4.2577630078	4.6387341870
H10	-0.6734912534	4.2057596621	4.7123810136
C11	1.0162264924	4.9275298670	3.5725794554
C12	0.2550219557	5.5913049684	2.4881919624
C13	-1.1401775863	5.5607689061	2.3996881804
H14	-1.7281696964	5.0383346220	3.1437446632
C15	-1.7747221697	6.1959342538	1.3356350331
H16	-2.8568261523	6.1722035122	1.2548364476
C17	-1.0031934581	6.8495754180	0.3766096493
H18	-1.4562302129	7.3476409302	-0.4733508322
C19	0.3805105752	6.8476297829	0.5165389556
H20	1.0412310881	7.3215274627	-0.2020575343
N21	0.9917534066	6.2398446140	1.5495765323
N22	5.0768156785	5.6673276389	1.8964064406
C23	5.5154636421	4.5480182571	1.3108257893
C24	6.8674374548	4.2129301476	1.3873198546
H25	7.2292279152	3.3241490405	0.8841294286
C26	7.7218342626	5.0887025303	2.0545694827
H27	8.7820234346	4.8645087518	2.1165560063
C28	7.2346708004	6.2645747337	2.6394333245
H29	7.9104563719	6.9412846005	3.1492159583
C30	5.8729155577	6.5450412672	2.5419884811
C31	5.1513720014	7.7198541428	3.0828926521
C32	5.7809877796	8.7599746238	3.7680464282
H33	6.8526197435	8.7366224716	3.9267426971
C34	5.0237945981	9.8328660669	4.2334542234

H35	5.5046004983	10.6502964891	4.7613357726
C36	3.6487721602	9.8452113731	4.0083119268
H37	3.0253417963	10.6644142361	4.3488715682
C38	3.0772520599	8.7777652523	3.3217629663
H39	2.0140615623	8.7413986209	3.1109182785
N40	3.7997801433	7.7423059423	2.8730374411
C41	4.4241945349	3.7217746260	0.6423758487
O42	3.2070995754	4.2240040116	0.7212064086
O43	4.6814521683	2.6448842830	0.1211004278
O44	3.3199461233	7.0492651650	0.1914252700
O45	5.5705747565	5.3747452919	-1.2961042273
H46	6.1129943362	4.6307532184	-1.6141982104
H47	4.7116647400	5.2861590518	-1.7524393280
O49	2.9141535063	4.6730315541	-2.0991201707
H50	2.7880769073	4.4107967111	-1.1705483320
H51	2.9325060656	3.8386483946	-2.5850204841
O51	6.9540537628	2.8719403956	-1.4679991827
H52	6.1616673092	2.5109240199	-1.0296253665
H53	7.1455259868	2.2874883273	-2.2112435746

Figure S1e

E (M06/LACV3P++ 2f(Ru)) =**-1576.102741342

ZPE (kcal mol^{-1}) = 253.165

G_{solv} = -0.2274867

DH_{298} (kcal mol^{-1})= 20.577

DS_{298} (cal K^{-1} mol^{-1})= 203.764

Cartesian coordinates

atom	x	y	z
Ru1	3.2003651395	6.0607005873	1.6121414792
N2	2.3950378053	5.1884780592	3.4782983160
C3	3.1437145287	4.7513727656	4.5058688747
H4	4.2152226100	4.8904660562	4.4200279270
C5	2.5877810533	4.1414633228	5.6227083918
H6	3.2282135193	3.7959660382	6.4266479358
C7	1.2026373524	3.9843112736	5.6723672111
H8	0.7299746726	3.5111635861	6.5273130773
C9	0.4277719690	4.4412276916	4.6103304083
H10	-0.6484828640	4.3261835422	4.6411907995

C11	1.0459741909	5.0443399952	3.5104435933
C12	0.3102880757	5.5565824034	2.3362078896
C13	-1.0738506640	5.4563279522	2.1851138778
H14	-1.6787352361	4.9828564400	2.9484135207
C15	-1.6785234694	5.9624294475	1.0360542398
H16	-2.7538862247	5.8868686050	0.9098253396
C17	-0.8866822148	6.5564398746	0.0559474594
H18	-1.3173361145	6.9584794288	-0.8543056436
C19	0.4883668321	6.6268062584	0.2558846853
H20	1.1556532264	7.0602412861	-0.4791078349
N21	1.0644406259	6.1487529831	1.3734629727
N22	5.1442054287	5.6184282129	1.9386907068
C23	5.5710576517	4.4899649318	1.3636785106
C24	6.9226894688	4.1645493103	1.3888440860
H25	7.2706745112	3.2708568731	0.8846940880
C26	7.7899384763	5.0577483189	2.0254674349
H27	8.8535364722	4.8428855204	2.0564459141
C28	7.3113919283	6.2285586574	2.6296240430
H29	7.9967772037	6.9075621862	3.1233659567
C30	5.9443909510	6.5025088144	2.5717457320
C31	5.2119582501	7.6486252974	3.1459022197
C32	5.8086671951	8.6764650274	3.8737073399
H33	6.8805785234	8.6794446566	4.0344659604
C34	5.0145017529	9.7021516133	4.3882335780
H35	5.4690994929	10.5114971858	4.9507279621
C36	3.6378620935	9.6772227981	4.1715778881
H37	2.9894307307	10.4589784891	4.5514882101
C38	3.0941126730	8.6262572420	3.4376125324
H39	2.0321500796	8.5676340103	3.2270290010
N40	3.8582632606	7.6425263351	2.9420942718
C41	4.4481997415	3.6741572082	0.7662117016
O42	3.2120818384	4.2147943993	0.9960753324
O43	4.5769967757	2.5970486981	0.2441593616
O44	3.3346798277	7.2104139368	0.3471969575
O45	5.0595599112	5.2794333031	-1.1363446223
H46	5.6723224769	4.6216651380	-1.5214042146
H47	4.2095653174	5.1832485578	-1.6073840983
O49	2.3921052590	4.8250201638	-1.9443648145

H50	2.2739710335	3.9067902890	-1.6644458727
H51	2.1539468323	4.8359701552	-2.8818418194
O51	6.7550180960	3.1032562667	-1.6053335173
H52	6.1770681903	2.3464266506	-1.4354026449
H53	7.2950175685	2.8642847547	-2.3702419041

Figure S1f

E (M06/LACV3P++ 2f(Ru)) =**-1576.09641357245

ZPE (kcal mol^{-1}) = 253.432

G_{solv} = -0.2297897

DH_{298} (kcal mol^{-1})= 19.836

DS_{298} (cal K^{-1} mol^{-1})= 196.632

Cartesian coordinates

atom	x	y	z
Ru1	3.5782105470	5.8977256399	1.5926420688
N2	2.4030957192	5.3235620521	3.3554154954
C3	2.9197319815	5.1054717033	4.5772368536
H4	3.9832835346	5.2765053626	4.6946176737
C5	2.1387700823	4.6740329351	5.6409786333
H6	2.5919384986	4.5031942510	6.6112240508
C7	0.7763154288	4.4640572625	5.4233895423
H8	0.1336355592	4.1261096509	6.2301669961
C9	0.2459834993	4.6909242309	4.1572469601
H10	-0.8101772239	4.5322075253	3.9782576244
C11	1.0824838160	5.1208851115	3.1216144616
C12	0.6191275992	5.3813233142	1.7440620485
C13	-0.6929178180	5.1812150039	1.3141021788
H14	-1.4478947521	4.8137443923	1.9980088752
C15	-1.0272389234	5.4477051706	-0.0125170465
H16	-2.0442853700	5.2921663307	-0.3579721404
C17	-0.0420601924	5.9058255118	-0.8837205966
H18	-0.2609579176	6.1175059723	-1.9242963171
C19	1.2525087629	6.0881895431	-0.4055282143
H20	2.0597172670	6.4227321355	-1.0517978787
N21	1.5625171448	5.8387536882	0.8803686034
N22	5.4318178800	5.6097176365	2.3746494992
C23	5.9667527964	4.4051764278	2.1521794474
C24	7.2859788925	4.1493931332	2.5055325261

H25	7.7163535114	3.1718941039	2.3179394929
C26	8.0046683331	5.1880920277	3.1106897998
H27	9.0392726478	5.0309086211	3.3994588228
C28	7.4001238765	6.4226511796	3.3779944414
H29	7.9586830082	7.2051840626	3.8790321051
C30	6.0698893316	6.6199089676	2.9974533329
C31	5.2001056505	7.7883175371	3.2445308199
C32	5.5983606619	8.9483009275	3.9057678339
H33	6.6210662963	9.0558066320	4.2485982163
C34	4.6716110670	9.9686309116	4.1222942388
H35	4.9740494833	10.8780524557	4.6318118427
C36	3.3603472232	9.8088420541	3.6778956979
H37	2.6134196122	10.5812001393	3.8247099221
C38	3.0151437139	8.6321949403	3.0175072825
H39	2.0164682449	8.4650233375	2.6306755787
N40	3.9085577074	7.6545629766	2.8150353233
C41	4.9659550948	3.4289030274	1.5784800620
O42	3.7158928722	3.9218208077	1.5396273655
O43	5.2502278733	2.3015136948	1.2506424208
O44	3.8887299190	7.0614218445	0.3488304567
O45	4.9407452506	4.8034454594	-0.7416872626
H46	4.6464368486	3.9265885334	-1.0830882093
H47	4.6657240179	5.4491841136	-1.4189286190
O49	3.6979121308	6.5197206272	-2.6511549353
H50	4.1342580255	7.3565841578	-2.8610537991
H51	3.5940579037	6.0731570058	-3.5029116846
O51	3.9905791677	2.3179893433	-1.3672160352
H52	4.2064901352	1.8666650586	-0.5357545009
H53	4.3704886662	1.7653453043	-2.0627847896

Figure S1g

E (M06/LACV3P++ 2f(Ru)) =**-1576.10281022977

ZPE (kcal mol^{-1}) = 254.164

G_{solv} = -0.2282873

DH_{298} (kcal mol^{-1})= 19.624

DS_{298} (cal K^{-1} mol^{-1})= 193.156

Cartesian coordinates

atom	x	y	z

Ru1	3.6311047570	5.8221773562	1.5451977002
N2	2.3492437146	5.1387938266	3.2162487695
C3	2.8499210477	4.7362206412	4.3952844930
H4	3.9261775848	4.7817974704	4.5074631136
C5	2.0315526632	4.2693751623	5.4158594235
H6	2.4685428987	3.9536060474	6.3568351068
C7	0.6550101838	4.2067701864	5.1924430531
H8	-0.0128151463	3.8390838867	5.9650468852
C9	0.1437231917	4.6154802362	3.9642856826
H10	-0.9213833629	4.5654981147	3.7765887246
C11	1.0193801650	5.0840011792	2.9783466920
C12	0.5989818367	5.5496943657	1.6443070090
C13	-0.7283513667	5.5818654454	1.2127700235
H14	-1.5250555171	5.2392615882	1.8616835045
C15	-1.0232417876	6.0581881191	-0.0626285266
H16	-2.0511610179	6.0860291176	-0.4099693102
C17	0.0172767484	6.4973709589	-0.8784757838
H18	-0.1677175904	6.8799115577	-1.8760284900
C19	1.3214042677	6.4405176759	-0.3977641596
H20	2.1604509031	6.7617451122	-1.0035993382
N21	1.6016750483	5.9761300711	0.8337329660
N22	5.5652641081	5.7056018850	2.2887605138
C23	6.2209405490	4.5520360444	2.1253694247
C24	7.5758494351	4.4573890530	2.4234295609
H25	8.0960914947	3.5176505040	2.2733360943
C26	8.2037954995	5.5933496898	2.9475803224
H27	9.2603987855	5.5636282574	3.1949714960
C28	7.4677366395	6.7533219767	3.2127520614
H29	7.9431823072	7.6027036230	3.6899087538
C30	6.1100469152	6.7855459473	2.8792361815
C31	5.1175553587	7.8254842275	3.2123214029
C32	5.4180873690	9.0387083057	3.8283569247
H33	6.4482505903	9.3009180111	4.0415188272
C34	4.3837512869	9.9118060939	4.1648400314
H35	4.6061084481	10.8619276875	4.6401452668
C36	3.0673871427	9.5507587645	3.8833391453
H37	2.2361535984	10.2015052210	4.1311474032
C38	2.8269554788	8.3306582347	3.2571369933

H39	1.8236039359	8.0149598116	2.9967089171
N40	3.8215355749	7.4917450658	2.9374466025
C41	5.2837999729	3.4285659046	1.7551429802
O42	4.0152758780	3.7661806603	1.9213148468
O43	5.6669635177	2.3234775368	1.4185199418
O44	4.0512605697	7.1240334027	0.4492358915
O45	3.9842108917	4.7211907315	-0.3086989236
H46	3.7204679924	3.7518657735	-0.4298816340
H47	3.9441005550	5.2349015991	-1.1553291790
O49	3.8196998075	6.1970311993	-2.5528435185
H50	4.5360869578	6.8392569865	-2.6522964045
H51	3.7527994434	5.7478562927	-3.4073706508
O51	3.7072429797	2.1843968667	-0.6692309615
H52	4.3508156287	1.8322764859	-0.0262949132
H53	2.9218710472	1.6277662901	-0.5971474939

Figure S1h

E (M06/LACV3P++ 2f(Ru)) =**-1576.07675468096

ZPE (kcal mol^{-1}) = 252.021

G_{solv} = -0.2274033

DH_{298} (kcal mol^{-1})= 18.932

DS_{298} (cal K^{-1} mol^{-1})= 187.966

Cartesian coordinates

atom	x	y	z
O42	0.0000000000000	0.0000000000000	0.0000000000000
H52	0.0000000000000	0.0000000000000	1.2192836561000
Ru1	2.2225475762649	0.0000000000000	-0.7179272024747
N2	1.5086992065542	-2.0543975751595	-0.6146302129536
C3	0.4768521507195	-2.4919783852345	-1.3587705319242
H4	-0.0010177694142	-1.7640858724367	-2.0007854408137
C5	0.0381747020334	-3.8072874062495	-1.2928551820512
H6	-0.7980190292918	-4.1270466747573	-1.9048312298328
C7	0.6867023355328	-4.6874416601932	-0.4243792902453
H8	0.3656498100998	-5.7213077943352	-0.3448083734910
C9	1.7511206939161	-4.2262296021278	0.3439617952684
H10	2.2610359353959	-4.8961380887162	1.0253359279744
C11	2.1535827999575	-2.8918136934298	0.2316516198024
C12	3.2682083614342	-2.2895613303870	0.9804116743176

C13	4.0626988300573	-2.9835809860827	1.8943086415255
H14	3.8750671407462	-4.0291467219981	2.1052614996774
C15	5.1045271614554	-2.3154966972609	2.5350045880452
H16	5.7330258633335	-2.8405943081362	3.2471765615753
C17	5.3259116072838	-0.9706139850293	2.2464951718751
H18	6.1277686848536	-0.4149306171851	2.7201404489128
C19	4.4989305107006	-0.3277572445275	1.3294353483262
H20	4.6337595922074	0.7202406836964	1.0851184071293
N21	3.4963780014551	-0.9786973265821	0.7118658822926
N22	0.9874676037100	0.8936915493484	-2.1801668613533
C23	-0.1284449455939	1.5244534951461	-1.7820149120880
C24	-0.8500300010666	2.3372210263148	-2.6467187204979
H25	-1.7412535400739	2.8404745386000	-2.2877126171299
C26	-0.4052956982652	2.4395348424114	-3.9681011647200
H27	-0.9395857688955	3.0639041216285	-4.6772498736541
C28	0.6937826713125	1.6918201593883	-4.3932861939569
H29	0.9915943055995	1.7111398813811	-5.4349544758487
C30	1.3862835676369	0.9001741986207	-3.4693794552867
C31	2.4764461918041	-0.0491672547657	-3.7847792093323
C32	3.0696167197539	-0.1643919140927	-5.0424042877245
H33	2.7826768374047	0.4977428099059	-5.8507479880619
C34	4.0457121641435	-1.1385524930215	-5.2496814069386
H35	4.5190659348660	-1.2370269278532	-6.2214526719680
C36	4.4044508792418	-1.9776418305135	-4.1967283993190
H37	5.1569517520255	-2.7489024819562	-4.3189829807184
C38	3.7800652394011	-1.8027747306319	-2.9633030894897
H39	4.0385823399164	-2.4209290937785	-2.1100442466260
N40	2.8397518517027	-0.8714971201383	-2.7655289295033
C41	-0.5807385980501	1.1544923562010	-0.4008239090484
O43	-1.4114423061719	1.7544360201209	0.2352143997897
O44	3.6025871124212	0.9522816494511	-1.1775365092274
O45	1.9145886935399	1.3720357866911	0.7631268697292
H46	1.1068813774304	0.8286389507591	2.0069637993888
H47	2.7251246000210	1.9203449477793	0.8674075326468
O49	4.2089088313622	2.9005007748031	1.0422199023629
H50	4.4806921075276	3.3744909466694	0.2447337882024
H51	4.2539182706255	3.5487116283728	1.7588621395824
O51	0.3532087631891	0.2269388450416	2.3449103207215

H53	-0.3103185861838	0.7666057399244	2.8045368172692

Figure S1i

E (M06/LACV3P++ 2f(Ru)) =**-1576.1125944554

ZPE (kcal mol^{-1}) = 255.136

G_{solv} = -0.2244191

DH_{298} (kcal mol^{-1})= 19.342

DS_{298} (cal K^{-1} mol^{-1})= 192.199

Cartesian coordinates

atom	x	y	z
O42	0.0000000000000	0.0000000000000	0.0000000000000
H52	0.0000000000000	0.0000000000000	0.9931053769000
Ru1	3.1938766838406	0.0000000000000	-1.7220862815942
N2	2.6522392785238	-2.0267490112695	-1.0719720574922
C3	1.4400797747469	-2.5848697047981	-1.2289438799393
H4	0.6916519323033	-1.9817051930974	-1.7267049516059
C5	1.1535774737960	-3.8600672562496	-0.7541295625660
H6	0.1642847681653	-4.2802525634034	-0.8971516788530
C7	2.1574269684401	-4.5677657266422	-0.0942125973042
H8	1.9693451916232	-5.5652146762701	0.2903823068241
C9	3.4108208792714	-3.9825486405657	0.0717364312844
H10	4.1946688700401	-4.5233901244767	0.5868306671682
C11	3.6406781801713	-2.6993552784953	-0.4286777320630
C12	4.9313532463341	-1.9883171556231	-0.3134506069873
C13	6.0585362511688	-2.5130503172463	0.3229192121687
H14	6.0241759524094	-3.4940737277527	0.7798879513595
C15	7.2324564921366	-1.7632331637965	0.3728213984386
H16	8.1121022086054	-2.1619903815540	0.8680654591833
C17	7.2631735056075	-0.5011229027212	-0.2187232551883
H18	8.1568079931571	0.1130866467491	-0.2038770215669
C19	6.1138097070736	-0.0262551196688	-0.8398790039405
H20	6.0756847423556	0.9450506086402	-1.3207816260657
N21	4.9827965066868	-0.7538796986198	-0.8841402165007
N22	1.2939323241584	0.6205945421385	-2.5473322068463
C23	0.3471146115513	1.3373629138533	-1.9045808265817
C24	-0.5868360891777	2.0996701619978	-2.6035492711569
H25	-1.3069475830100	2.6900974250595	-2.0481452153656

C26	-0.5810988532001	2.0661048261665	-3.9958220811424
H27	-1.2954449717973	2.6537908085338	-4.5635360578895
C28	0.3326289343130	1.2458067725312	-4.6532748164982
H29	0.3233364193980	1.1843905851832	-5.7340235657032
C30	1.2690759813149	0.5272633330855	-3.9067219475700
C31	2.2467424361721	-0.4056955901721	-4.5180033332196
C32	2.2257602066267	-0.7637388422820	-5.8687127923669
H33	1.4890746036442	-0.3438792546994	-6.5415140431054
C34	3.1609748924222	-1.6777366822348	-6.3509591954522
H35	3.1550498717515	-1.9579120890548	-7.3995376330787
C36	4.0980182088735	-2.2256914455565	-5.4760614711770
H37	4.8428312552723	-2.9370651695386	-5.8149645145811
C38	4.0684925657860	-1.8323569460768	-4.1427270770183
H39	4.7827526432643	-2.2148724939202	-3.4224450677208
N40	3.1660922358149	-0.9532868838896	-3.6817267583167
C41	0.2016062553730	1.2560709460806	-0.3983505716596
O43	0.1527994571869	2.2418641147355	0.3071922232458
O44	4.0797745571683	1.2452803300087	-2.5373635867177
O45	2.6678336621761	0.6558526680921	-0.0618896745964
H46	0.4029914608219	1.5223906817490	2.2511474059782
H47	3.0868267409356	0.3214726202938	0.7929241901541
O49	3.1918498825589	-0.1777611997295	2.3338675218264
H50	3.7777223009761	0.3065560338174	2.9312255135004
H51	2.2803255728876	0.0318991675285	2.6293396831718
O51	0.4979987286707	0.6115258054034	2.5917194741290
H53	-0.0839870718206	0.5396470655840	3.3621025203473

Figure S1j

E (M06/LACV3P++ 2f(Ru)) =**-1576.06966899183

ZPE (kcal mol^{-1}) = 252.82

G_{solv} = -0.2266143

DH_{298} (kcal mol^{-1})= 19.535

DS_{298} (cal K^{-1} mol^{-1})= 197.886

Cartesian coordinates

atom	x	y	z
Ru1	3.5702042631	6.1845748575	1.6660970984
N2	2.5739322566	5.0349647838	3.2267565071
C3	3.1443961181	4.5801219225	4.3573386770

H4	4.1684121378	4.8842991565	4.5389717762
C5	2.4746129428	3.7551265901	5.2515285644
H6	2.9750989095	3.4092672843	6.1491945599
C7	1.1624424816	3.3847039952	4.9584175020
H8	0.6083695886	2.7354919546	5.6289424170
C9	0.5664839649	3.8573385675	3.7922002430
H10	-0.4516815628	3.5747044297	3.5570687613
C11	1.2907717904	4.6897047758	2.9330313538
C12	0.7318142383	5.2540654444	1.6853004427
C13	-0.5772667811	5.0268511124	1.2555836070
H14	-1.2436151648	4.3960260568	1.8302976084
C15	-1.0296177756	5.6172180681	0.0777847274
H16	-2.0448789750	5.4422928097	-0.2633486153
C17	-0.1640334775	6.4314257512	-0.6486076996
H18	-0.4760795979	6.9132726800	-1.5683912504
C19	1.1314610627	6.6199536349	-0.1790552226
H20	1.8481113455	7.2320639314	-0.7129036736
N21	1.5675174797	6.0437367755	0.9573997729
N22	5.4049872724	6.0397076999	2.4955736630
C23	6.1608409348	5.0217469890	2.0629656039
C24	7.4582745168	4.8693436542	2.5392643473
H25	8.0693295696	4.0474158789	2.1826922749
C26	7.9215044021	5.8058112744	3.4719891869
H27	8.9286293200	5.7196450996	3.8680836209
C28	7.1049076451	6.8572266958	3.9040917612
H29	7.4810933751	7.5735062895	4.6255317515
C30	5.8085309311	6.9654412529	3.3882138824
C31	4.7776266904	7.9843917821	3.7062195315
C32	4.9771887949	9.0233993827	4.6135752688
H33	5.9268815904	9.1272921055	5.1259441006
C34	3.9468954974	9.9324066079	4.8574997527
H35	4.0941391178	10.7459172354	5.5607080982
C36	2.7345614377	9.7829337362	4.1888033241

H37	1.9108427990	10.4697904466	4.3488914967
C38	2.5909053753	8.7256878213	3.2923640518
H39	1.6704580423	8.5702951426	2.7406231247
N40	3.5782675311	7.8502988874	3.0564800903
C41	5.4760117293	4.1333291156	1.0373514465
O42	4.1882424687	4.4327120803	0.8084252126
O43	6.0688345832	3.2426016061	0.4747416826
O44	4.1997670510	7.3555220973	0.4368687587
O45	4.0353664636	7.0613571596	-1.3230418353
H46	3.9913560320	6.0418370052	-1.5102512744
O47	3.6725509690	4.6027721342	-1.8128740692
H48	4.0679059583	4.1116419508	-2.5451116161
H49	3.8371293132	4.1030236281	-0.9889914982
H50	4.9453189712	7.4296029064	-1.5769785246
O54	6.3834674465	8.0049797052	-1.9239220703
H55	6.8623745500	7.6709309397	-2.6950989646
H56	6.4447096211	8.9689147955	-1.9760297214

Figure S1k

E (M06/LACV3P++ 2f(Ru)) =**-1499.34855671183

ZPE (kcal mol^{-1}) = 230.426

G_{solv} =-0.0928285

DH_{298} (kcal mol^{-1})= 18.231

DS_{298} (cal K^{-1} mol^{-1})= 189.768

Cartesian coordinates

atom	x	y	z
Ru1	3.5672650734	6.2708299432	1.7355880684
N2	2.5486899503	4.9511652985	3.0855261458
C3	3.1081196035	4.3566293067	4.1532451395
H4	4.1250695893	4.6512831498	4.3852196190
C5	2.4402228317	3.4091456330	4.9184215371
H6	2.9354348219	2.9520105523	5.7678145448
C7	1.1378692220	3.0636939314	4.5598567107
H8	0.5852343179	2.3224752537	5.1280889082

C9	0.5525002034	3.6793416796	3.4588094968
H10	-0.4563515449	3.4164948495	3.1670367828
C11	1.2789400755	4.6261891151	2.7282601192
C12	0.7417427473	5.3327522169	1.5473274677
C13	-0.5573135164	5.1438871595	1.0663756934
H14	-1.2289526755	4.4481030375	1.5532493471
C15	-0.9853301459	5.8557049026	-0.0498976192
H16	-1.9903460912	5.7160443956	-0.4346724591
C17	-0.1020847822	6.7407571846	-0.6640779753
H18	-0.3902238980	7.3106372777	-1.5404729347
C19	1.1794590867	6.8843368589	-0.1426959019
H20	1.9210279280	7.5269039940	-0.6014904907
N21	1.5938691080	6.2021952196	0.9403672793
N22	5.4038783441	6.1027372947	2.5238878020
C23	6.1599074915	5.1196502411	2.0171043105
C24	7.4710365249	4.9611299312	2.4560591134
H25	8.0716167373	4.1612602020	2.0378182303
C26	7.9559083157	5.8505779127	3.4210903864
H27	8.9741846923	5.7532059248	3.7846687807
C28	7.1439003852	6.8729504520	3.9233771730
H29	7.5309136981	7.5616958178	4.6655847697
C30	5.8346169211	6.9885866719	3.4434080976
C31	4.8074952936	7.9868929785	3.8190142907
C32	5.0206020758	8.9916934914	4.7640965540
H33	5.9798135633	9.0727670647	5.2626336284
C34	3.9975042787	9.8887072623	5.0591467956
H35	4.1547063977	10.6749062257	5.7905644825
C36	2.7753825647	9.7619936249	4.4013209485
H37	1.9533752035	10.4411396423	4.5985510306
C38	2.6210839472	8.7396559962	3.4697494206
H39	1.6925418368	8.6026582714	2.9264652155
N40	3.6015150369	7.8699859187	3.1794084185
C41	5.4551785765	4.2496664680	0.9687953330

O42	4.2089642398	4.5851302226	0.7185027479
O43	6.0716048378	3.3277043333	0.4649828354
O44	4.3739628613	7.5194694309	0.4879977746
O45	4.0379875160	7.3137564222	-0.8648344844
H50	4.6993826960	7.9035113485	-1.3175132979
O54	5.9326929616	8.7419149352	-2.1133468830
H55	5.7058873215	9.3771451663	-2.8045687753
H56	6.5807962414	8.1459700282	-2.5114831260

([i]) a) A. D. Becke, *J. Chem. Phys.* **1993**, 98, 5648-5652; b) C. Lee, W.Yang, R. G. Parr, *Phys. Rev. B* 1988, **37**, 785-789.

([ii]) Y. Zhao, D. G. Truhlar, *Theor. Chem. Acc.***2006**, 120, 215-241.

([iii]) J.M.L. Martin and A. Sundermann, *J.Chem.Phys.*, **2001**, 114, 3408-3420

([iv]) B.Marten, K. Kim, C. Cortis, R. A. Friesner, R. B. Murphy,M. N. Ringnalda, D. Sitkoff and B. Honig, *J. Phys. Chem.*, **1996**, 100, 11775-11788.

([v])Donald D. Wagman, William H. Evans, Vivian B. Parker, Richard H. Schumm, Iva Halow, Sylvia M. Bailey, Kenneth L.Churney, and Ralph L. Nuttall, The NBS Tables of Chemical Thermodynamic Properties, *J. Phys. Chem. Ref. Data*, Vol. 11, Suppl. 2(1982).