Electronic Supplementary Material (ESI) for Chemical Science.

Electronic Supporting Information

Microhydration of PAH^+ Cations:
Evolution of Hydration Network in Naphthalene$^+$-$(H_2O)_n$ Clusters (n≤5)

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Cooperativity and Noncooperativity in Np^+-W_2 isomers

A further measure of the degree of cooperativity in Np^+-W_2(18) is provided by the NBO and NCI analyses. In the NBO model, the strength of the σ-type CH…O H-bond is correlated with the donor-acceptor charge transfer interaction from the lone pair of O to the antibonding σ* orbital of the C-H donor bond, which may be estimated by the second order perturbative energy $E^{(2)}$. While this energy for the bifurcated CH…O H-bonds (both bonds), is $E^{(2)}$=15.3 kJ/mol for the Np^+-W(18) dimer (n=1), it increases to 22.0 kJ/mol for the Np^+-W_2(18) trimer (n=2). A similar increase is observed for the OH…O H-bond in the W_2 unit. While for bare W_2 the donor-acceptor charge transfer interaction from the lone pair of the O atom of the W acceptor to the antibonding σ* orbital of the O-H donor bond is $E^{(2)}$=31.7 kJ/mol, it rises to 46.4 kJ/mol for W_2 in Np^+-W_2(18). The involved NBOs of the two H-bonds in Np^+-W_2(18) are visualized in Figure S1 in ESI. A further approach to quantify the cooperativity in the Np^+-W_2(18) is the NCI technique (Figure S2 and Table S1 in ESI). The strengths of the CH…O and OH…O H-bonds in Np^+-W_2(18) are described by values of –ρ=0.014 and 0.033 a.u., respectively, while the corresponding values of the individual isolated Np^+-W(18) and W-W dimers are significantly lower (–ρ=0.012 and 0.025 a.u.). Both the NBO and NCI indicators suggest that the neutral OH…O H-bond in Np^+-W_2(18) is stronger than the CH…O ionic H-bond! The final quantity of cooperativity considered here is the charge transfer from Np^+ to the solvent moiety (Figure S3 in ESI), which increases upon attachment of the second W ligand by 17% from Δq=12 me in Np^+-W(18) to 14 me in Np^+-W_2(18). Similar cooperative effects as found for the (18) structure of Np^+-W_2 are also observed for the (12) and (23) isomers, although both the OH…O and CH…O H-bonds are weaker in these less stable local minima as compared to the (18) isomer.

In the (18/45) isomer, the NBO energy per bifurcated CH…O H-bond decreases from $E^{(2)}$=15.3 to 15.1 kJ/mol upon attachment of the second W ligand (Figure S1 in ESI). Similarly, the NCI indicator for the H-bond strength decreases from –ρ=0.0116 to 0.0113 a.u. (Figure S2 and Table S1 in ESI). Along the same line, the charge transfer from Np^+ to each W ligand is reduced from 12.4 me for n=1 to 11.7 me for n=2 (Figure S3 in ESI).

Table S1. Electron density ρ* (=ρ•sign(λ_2) given in a.u.) for each s(ρ*) minimum in the NCI plot and assignment to the different intermolecular interactions (Figure S2). Only negative values corresponding to attractive H-bonds are listed.

	OH…O	CH…O [a]
W_2	-0.02529	
Np^+-W(18)		-0.01167
Np^+-W(12)		-0.01045 -0.00872
Np^+-W(23)		-0.00941
Bz^+-W(12)		-0.01141 -0.00999
Np^+-W_2(18)	-0.03263	-0.01424
Np^+-W_2(18/45)		-0.01132

[a] For symmetric bifurcated CH…O bonds, only one value is given.

Figure S1. Natural bond (NBO) orbitals of the H-bond interactions (CH…O, OH…O) in Np^+-W_2(18) and Np^+-W_2(18/45). The phases of the NBOs are indicated in blue and yellow.

Figure S2. NCI plots of the H-bonds in W_2, in the Np^+-W isomers (18), (12), and (23), in Bz^+-W(12), and in the Np^+-W_2 isomers (18) and (18/45). The NCI technique is based on the topological analysis of the electron density ρ and its reduced gradient $\sigma(r)$ in regions of weak electron density and small reduced gradient. The zones where $\sigma(r)$ is close to zero, i.e. close to minima of electron density, are characteristic of noncovalent interactions. The visualization is accomplished by plotting iso-surfaces of the reduced gradient and is based on a RGB color scheme to rank the interactions using the sign of the second eigenvalue, λ_2, of the Hessian matrix. Red iso-surfaces correspond to positive λ_2, i.e. repulsive regions, while blue iso-surfaces correspond to negative λ_2, i.e. regions corresponding to favorable interactions. Green iso-surfaces correspond to weak delocalized interactions, i.e. regions where λ_2 is almost zero (see also Table S1).

Figure S3. NBO charge distribution (in me) of the most stable isomers of Np^+-W_n calculated at the B3LYP-D3/aug-cc-pVTZ level.

Figure S4. Comparison of experimental IRPD spectrum of Np^+-W_2 to linear IR absorption spectra of the most stable isomers of Np^+-W_2 calculated at the B3LYP-D3/aug-cc-pVTZ level (Figure 4, Table 1).

Figure S5. Optimized structures of low-energy Np^+-W_3 local minima obtained at the B3LYP-D3/aug-cc-pVTZ level. Binding energies (D_0) and bond lengths are given in cm^{-1} and Å, respectively. Numbers in parenthesis correspond to relative energies and free energies (E_0, G).

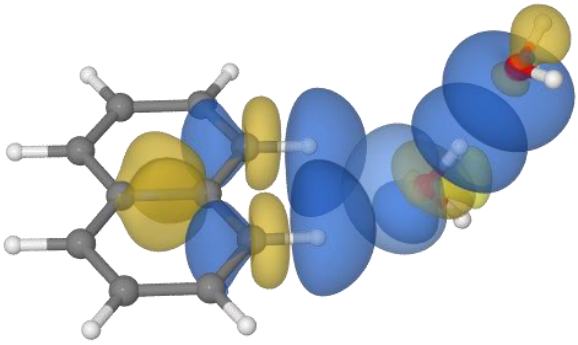
Figure S6. Optimized structures of W_n clusters obtained at the B3LYP-D3/aug-cc-pVTZ level. Binding energies (D_0) and bond lengths are given in cm^{-1} and Å, respectively.

Figure S7. Linear IR absorption spectra of the W_n clusters shown in Figure S6 obtained at B3LYP-D3/aug-cc-pVTZ level.

Figure S8. Comparison of experimental IRPD spectrum of Np^+-W_3 to linear IR absorption spectra of the most stable isomers of Np^+-W_3 calculated at the B3LYP-D3/aug-cc-pVTZ level (Figure 6 and S5, Table 1).

Figure S9. Most stable structures of Np^+-W_n (without proton transfer to the solvent) and most stable $C_{10}H_7$-H^+W_n structures for n=4 and 5 found at the B3LYP-D3/cc-pVTZ level. Relative energies (E_0) and bond lengths are given in cm^{-1} and Å, respectively.

Np^{+}-W_2(18)



Np^{+}-W_2(18/45)

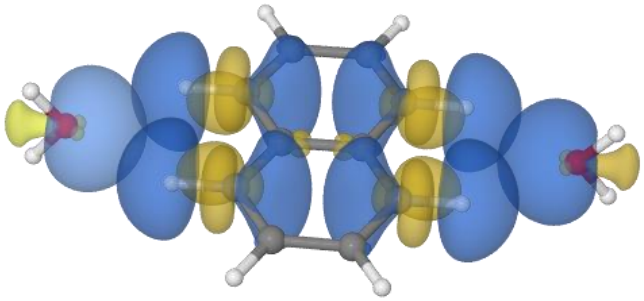
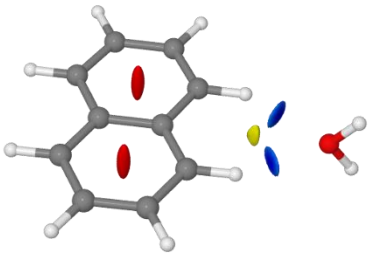
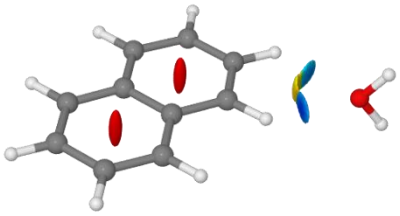


Figure S1

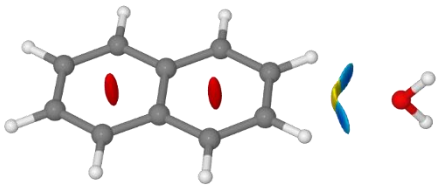
Np^+-W(18)



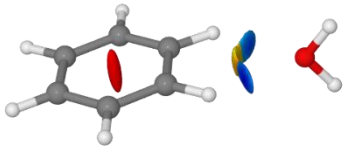
Np^+-W(12)



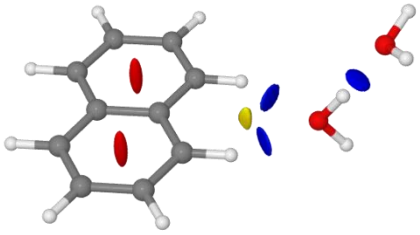
Np^+-W(23)



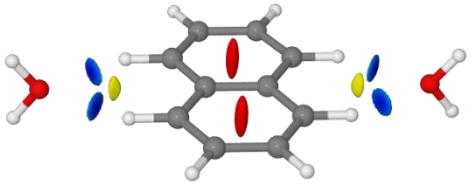
Bz^+-W(12)



Np^+-W_2(18)



Np^+-W_2(18/45)



W_2

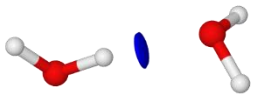


Figure S2

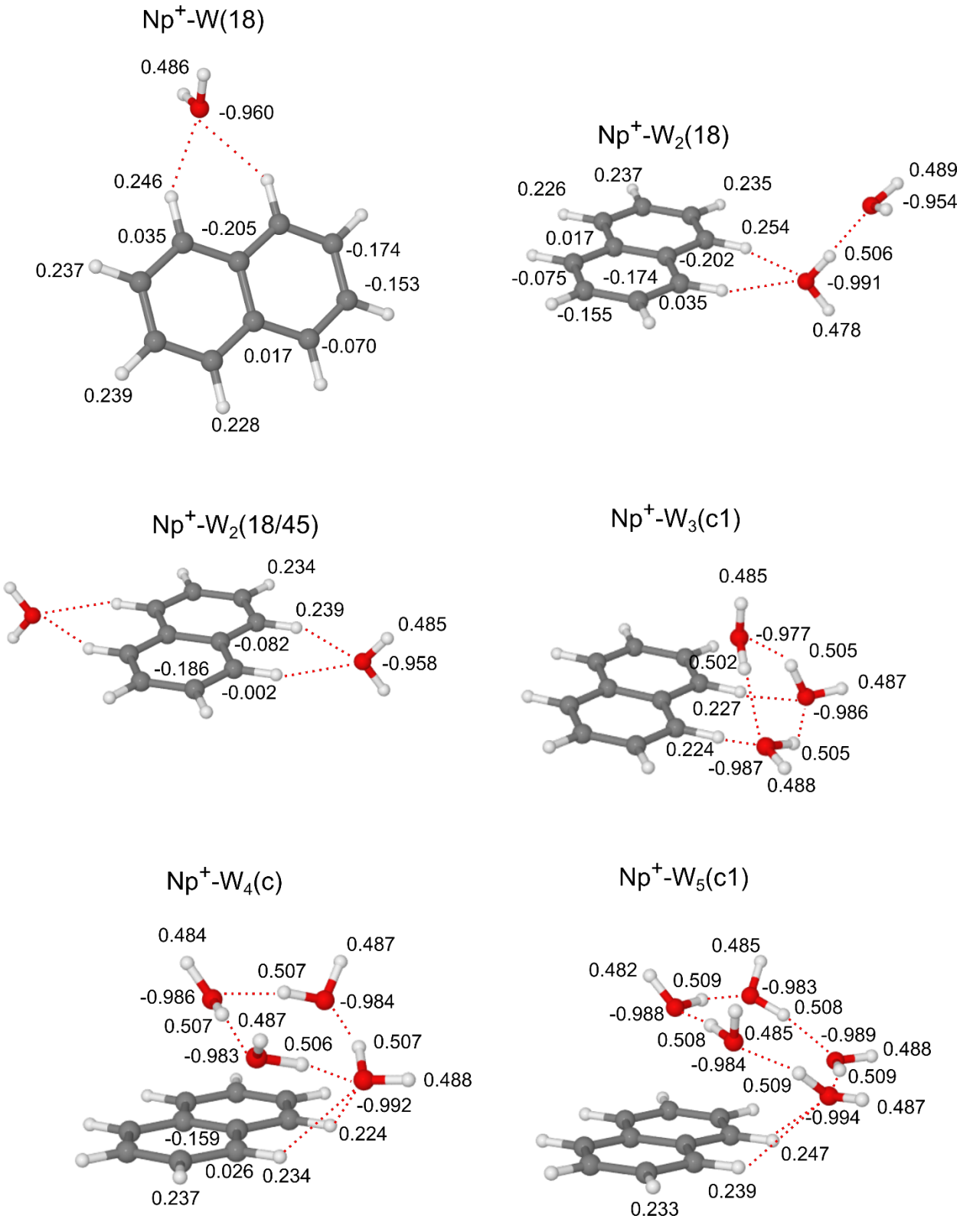

Np+-W(18)
0.486
-0.960
0.246
0.035
-0.205
-0.174
0.237
-0.153
0.017
-0.070
0.239
0.228
Np+-W2(18)
0.237
0.226
0.235
0.489
-0.954
0.017
0.254
-0.202
0.506
-0.075
-0.174
-0.991
0.035
-0.155
0.478
Np+-W2(18/45)
0.234
0.239
0.485
-0.082
-0.958
-0.186
-0.002
Np+-W3(c1)
0.485
-0.977
0.505
0.502
0.487
0.227
-0.986
0.224
0.505
-0.987
0.488
Np+-W4(c)
0.484
0.487
0.507
-0.986
-0.984
0.507
0.487
-0.983
0.506
0.507
0.488
-0.992
0.224
-0.159
0.026
0.234
0.237
Np+-W5(c1)
0.485
0.482
0.509
-0.983
-0.988
0.508
0.508
0.485
-0.989
0.488
-0.984
0.509
0.509
0.487
-0.994
0.247
0.239
0.233

Figure S3

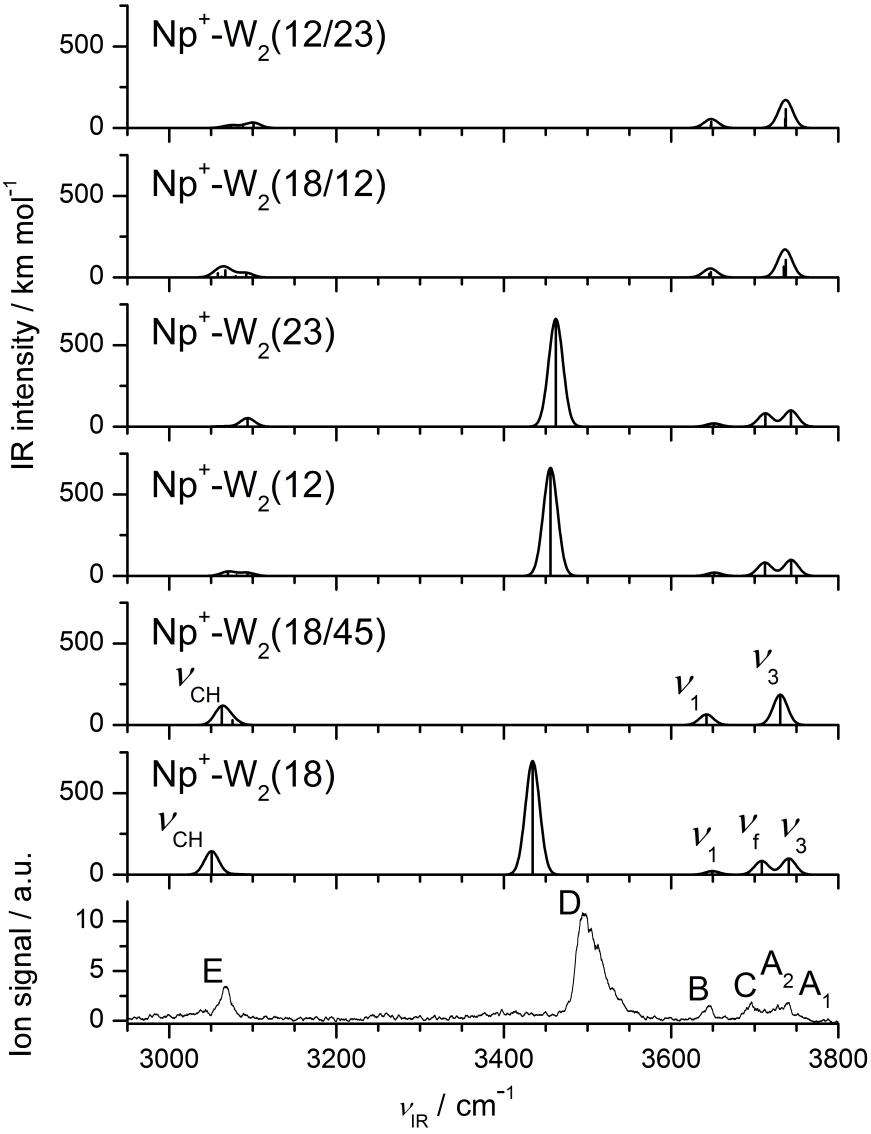

Np+-W2(12/23)
Np+-W2(18/12)
Np+-W2(23)
Np+-W2(12)
Np+-W2(18/45)
Np+-W2(18)
500
0
IR intensity / km mol-1
νCH
ν1
ν3
νf
10
5
Ion signal / a.u.
D
E
B
C
A2
A1
3000
3200
3400
3600
3800
νIR / cm-1

Figure S4

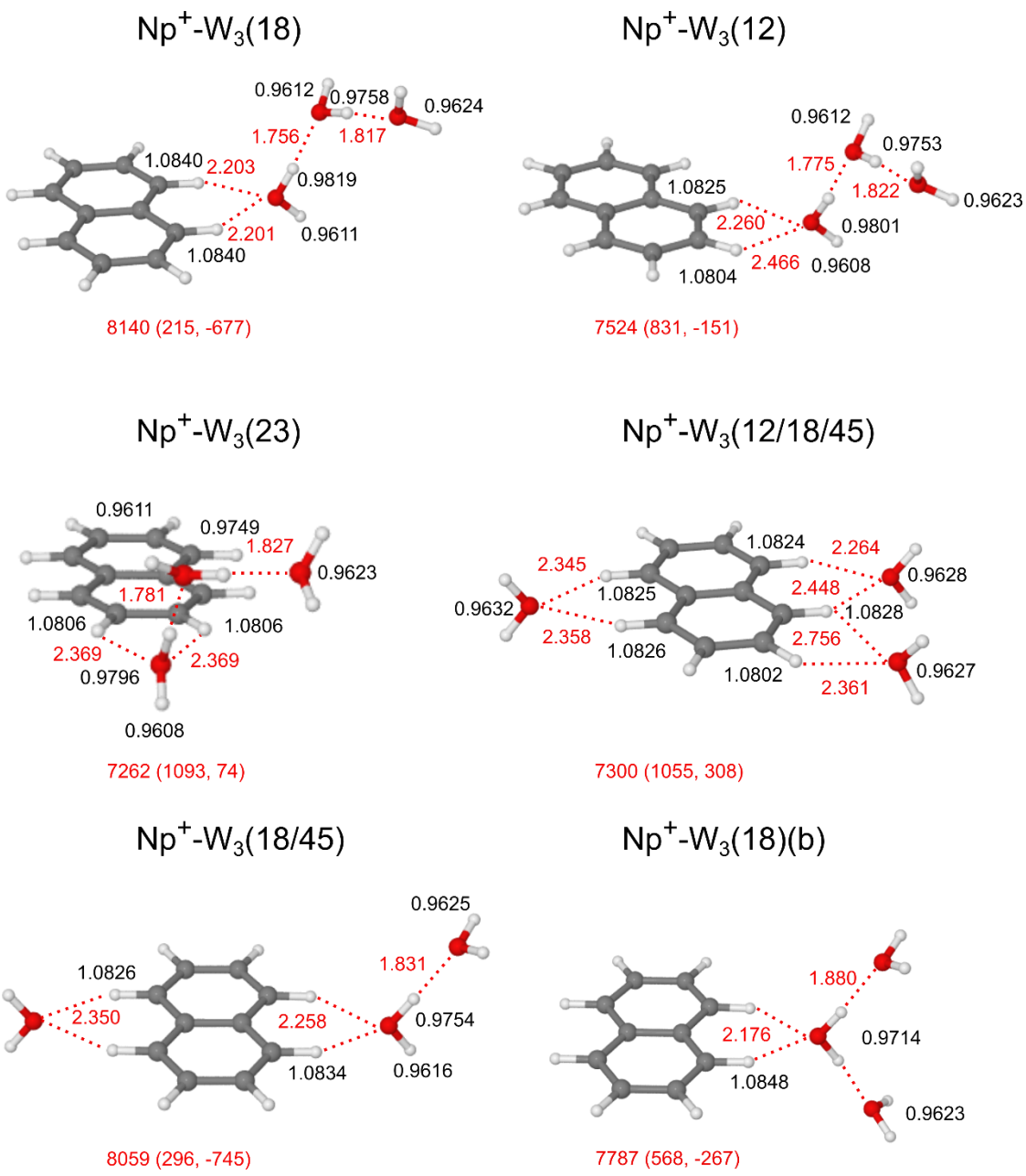

Np+-W3(18)
0.9612
0.9758
0.9624
1.756
1.817
1.0840
2.203
0.9819
2.201
0.9611
1.0840
8140 (215, -677)
Np+-W3(12)
0.9612
0.9753
1.775
1.822
0.9623
1.0825
2.260
0.9801
2.466
0.9608
1.0804
7524 (831, -151)
Np+-W3(23)
0.9611
0.9749
1.827
0.9623
1.781
1.0806
1.0806
2.369
2.369
0.9796
0.9608
7262 (1093, 74)
Np+-W3(12/18/45)
1.0824
2.264
2.345
0.9628
1.0825
2.448
0.9632
1.0828
2.358
1.0826
2.756
0.9627
1.0802
2.361
7300 (1055, 308)
Np+-W3(18/45)
0.9625
1.831
1.0826
2.350
2.258
0.9754
1.0834
0.9616
8059 (296, -745)
Np+-W3(18)(b)
1.880
2.176
0.9714
1.0848
0.9623
7787 (568, -267)

Figure S5

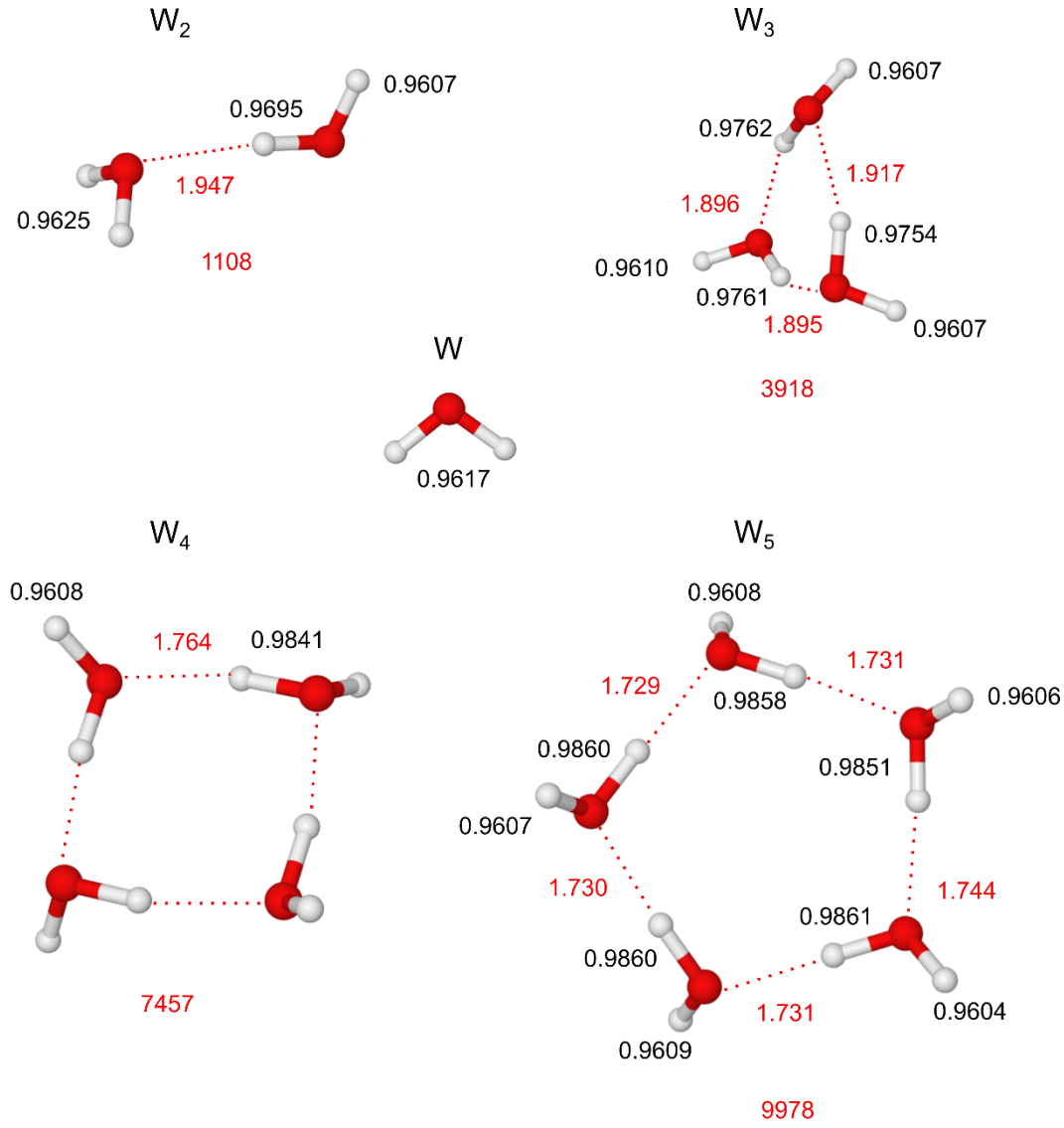

W2
0.9607
0.9695
1.947
0.9625
1108
W3
0.9607
0.9762
1.917
1.896
0.9754
0.9610
0.9761
1.895
0.9607
3918
W
0.9617
W4
0.9608
1.764
0.9841
7457
W5
0.9608
1.729
1.731
0.9858
0.9606
0.9860
0.9851
0.9607
1.730
1.744
0.9861
0.9860
1.731
0.9604
0.9609
9978

Figure S6

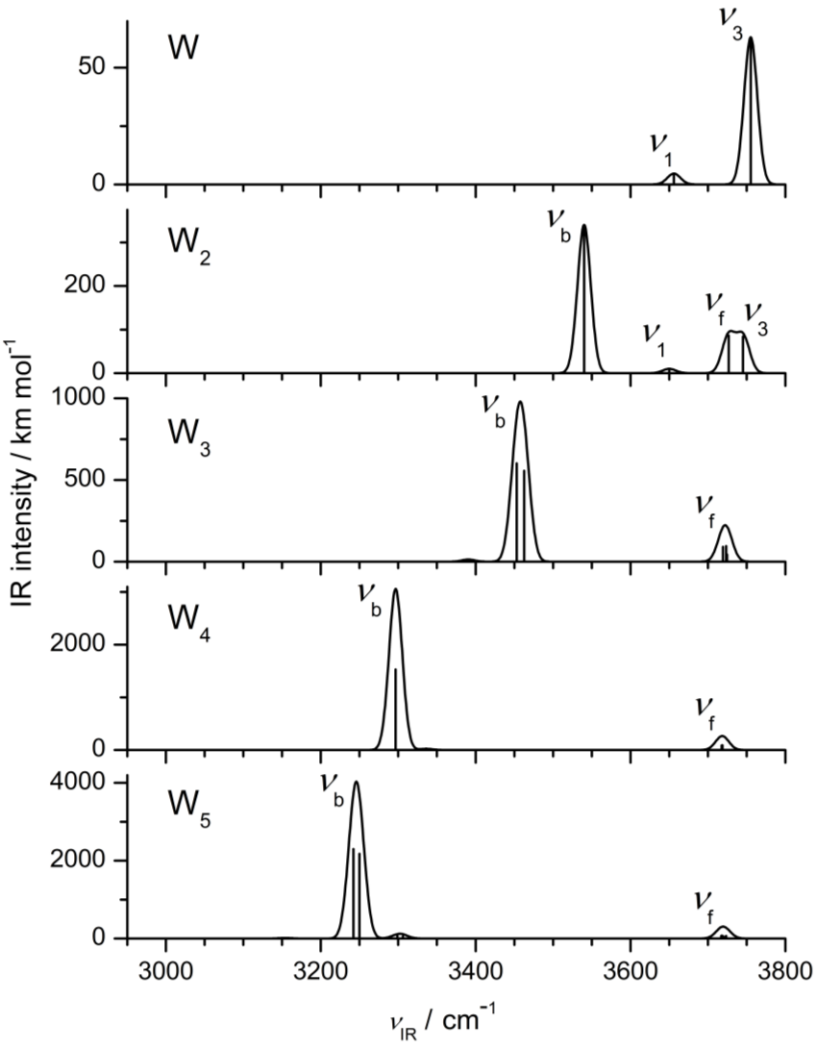

W
W2
W3
W4
W5
ν3
ν1
νb
νf
IR intensity / km mol-1
νIR / cm-1
0
50
200
1000
500
2000
4000
3000
3200
3400
3600
3800

Figure S7

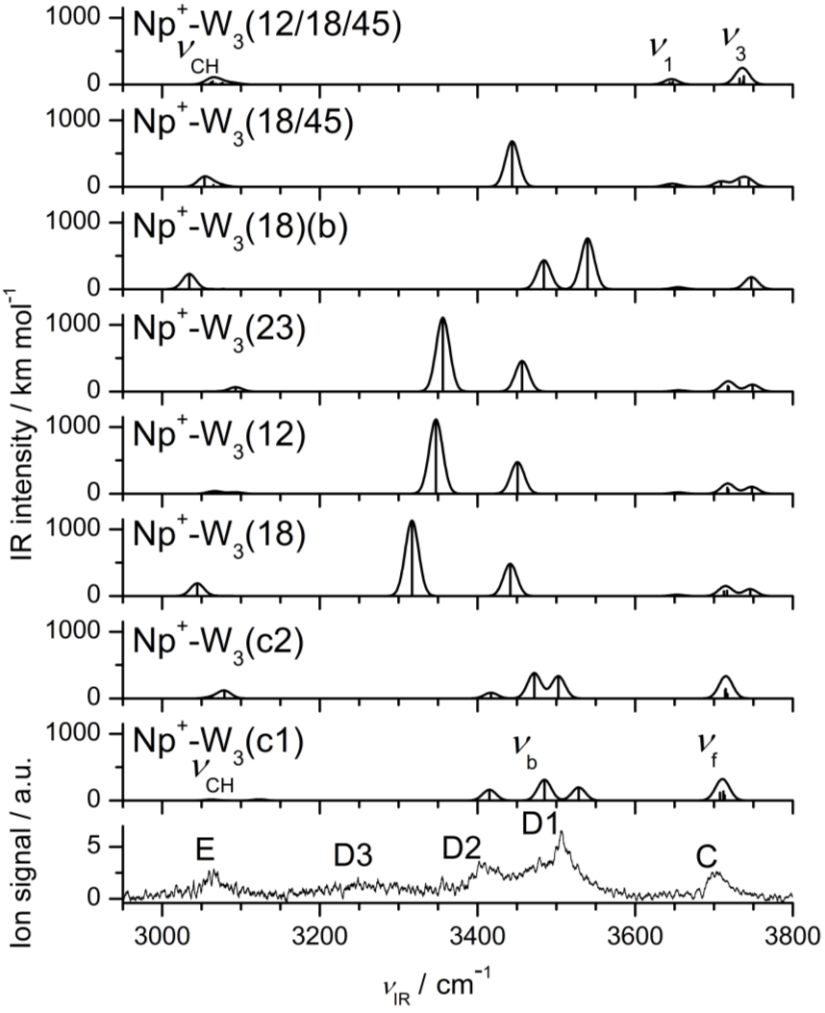

Np+-W3(12/18/45)
νCH
ν1
ν3
Np+-W3(18/45)
Np+-W3(18)(b)
Np+-W3(23)
Np+-W3(12)
Np+-W3(18)
Np+-W3(c2)
Np+-W3(c1)
νb
νf
E
D3
D2
D1
C
1000
0
5
IR intensity / km mol-1
Ion signal / a.u.
3000
3200
3400
3600
3800
νIR / cm-1

Figure S8

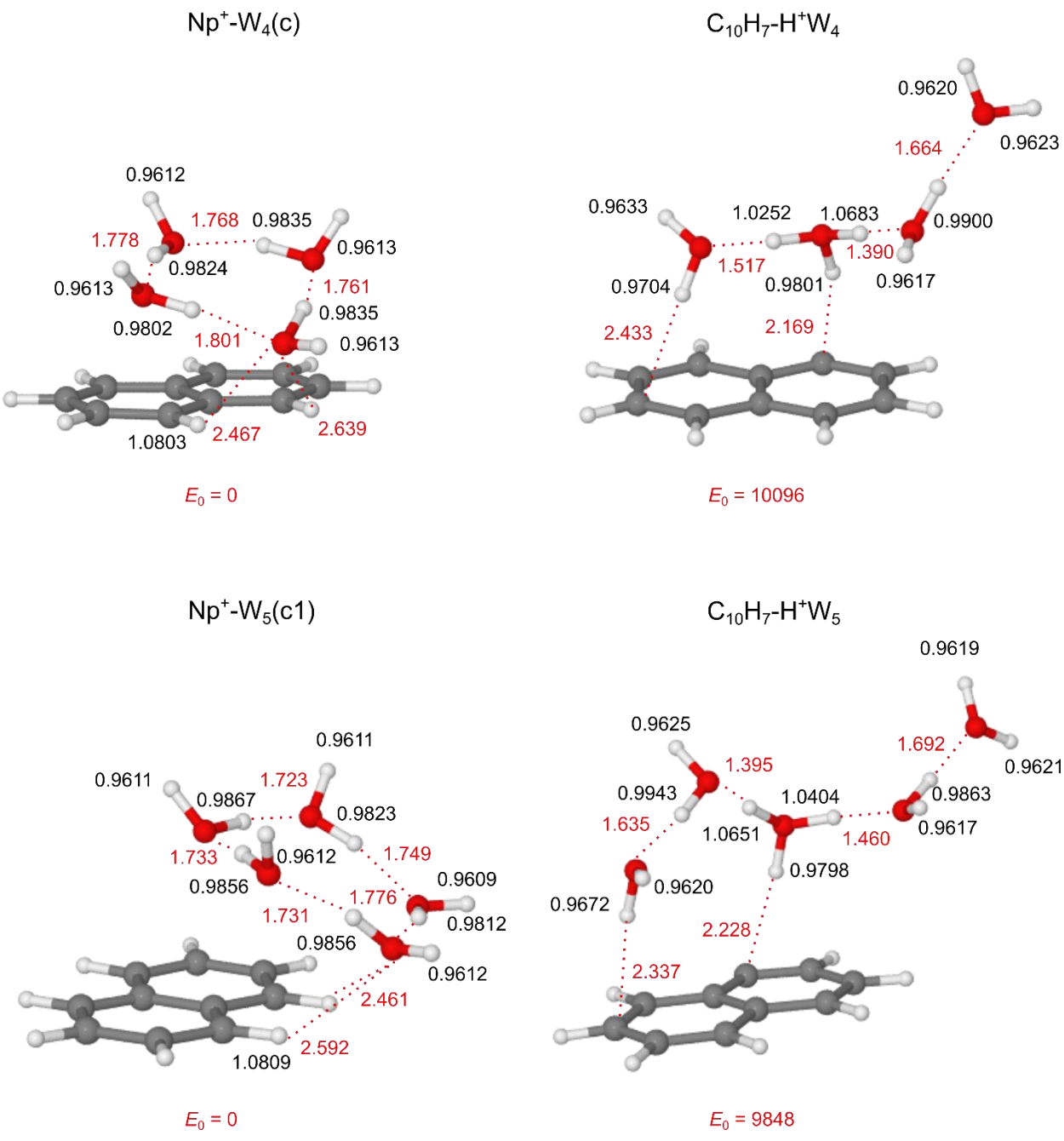

Np+-W4(c)
0.9612
1.768
0.9835
1.778
0.9613
0.9824
0.9613
1.761
0.9835
0.9802
1.801
0.9613
1.0803
2.467
2.639
E0 = 0
C10H7-H+W4
0.9620
1.664
0.9623
0.9633
1.0252
1.0683
0.9900
1.517
1.390
0.9704
0.9801
0.9617
2.433
2.169
E0 = 10096
Np+-W5(c1)
0.9611
0.9611
1.723
0.9867
0.9823
1.733
0.9612
1.749
0.9856
0.9609
1.776
1.731
0.9812
0.9856
0.9612
2.461
2.592
1.0809
E0 = 0
C10H7-H+W5
0.9619
0.9625
1.692
1.395
0.9621
0.9943
1.0404
0.9863
1.635
1.0651
1.460
0.9617
0.9798
0.9620
0.9672
2.228
2.337
E0 = 9848

Figure S9

W

O	0.00000000	0.00000000	0.11696500
H	0.00000000	0.76345100	-0.46786000
H	0.00000000	-0.76345100	-0.46786000

Zero-point correction=	0.021244 (Hartree/Particle)
Thermal correction to Energy=	0.024079
Thermal correction to Enthalpy=	0.025023
Thermal correction to Gibbs Free Energy=	0.003602
Sum of electronic and zero-point Energies=	-76.444961
Sum of electronic and thermal Energies=	-76.442126
Sum of electronic and thermal Enthalpies=	-76.441181
Sum of electronic and thermal Free Energies=	-76.462602

Np

C	0.00000000	2.42380900	0.70608000
C	0.00000000	1.24038200	1.39746300
C	0.00000000	0.00000000	0.71411700
C	0.00000000	0.00000000	-0.71411700
C	0.00000000	1.24038200	-1.39746300
C	0.00000000	2.42380900	-0.70608000
H	0.00000000	-1.23916500	2.48018400
H	0.00000000	3.36434700	1.24034800
H	0.00000000	1.23916500	2.48018400
C	0.00000000	-1.24038200	1.39746300
C	0.00000000	-1.24038200	-1.39746300
H	0.00000000	1.23916500	-2.48018400
H	0.00000000	3.36434700	-1.24034800
C	0.00000000	-2.42380900	-0.70608000
C	0.00000000	-2.42380900	0.70608000
H	0.00000000	-1.23916500	-2.48018400
H	0.00000000	-3.36434700	-1.24034800
H	0.00000000	-3.36434700	1.24034800

Zero-point correction=	0.147321 (Hartree/Particle)
Thermal correction to Energy=	0.154114
Thermal correction to Enthalpy=	0.155058
Thermal correction to Gibbs Free Energy=	0.117424
Sum of electronic and zero-point Energies=	-385.892955
Sum of electronic and thermal Energies=	-385.886162
Sum of electronic and thermal Enthalpies=	-385.885217
Sum of electronic and thermal Free Energies=	-385.922851

Np^+

C	0.00000000	2.44180000	0.69292400
C	0.00000000	1.23096000	1.39671200
C	0.00000000	0.00000000	0.71315400
C	0.00000000	0.00000000	-0.71315400
C	0.00000000	1.23096000	-1.39671200
C	0.00000000	2.44180000	-0.69292400
H	0.00000000	-1.23783100	2.47872900
H	0.00000000	3.37604400	1.23605900
H	0.00000000	1.23783100	2.47872900
C	0.00000000	-1.23096000	1.39671200
C	0.00000000	-1.23096000	-1.39671200
H	0.00000000	1.23783100	-2.47872900
H	0.00000000	3.37604400	-1.23605900
C	0.00000000	-2.44180000	-0.69292400
C	0.00000000	-2.44180000	0.69292400
H	0.00000000	-1.23783100	-2.47872900
H	0.00000000	-3.37604400	-1.23605900
H	0.00000000	-3.37604400	1.23605900

Zero-point correction=	0.146926 (Hartree/Particle)
Thermal correction to Energy=	0.153953
Thermal correction to Enthalpy=	0.154897
Thermal correction to Gibbs Free Energy=	0.116160
Sum of electronic and zero-point Energies=	-385.604269
Sum of electronic and thermal Energies=	-385.597242
Sum of electronic and thermal Enthalpies=	-385.596298
Sum of electronic and thermal Free Energies=	-385.635034

Np^{+}-W(18)

C	0.00000000	0.00000000	0.15285200
C	0.00000000	0.00000000	-1.27379600
C	0.00000000	1.22893900	0.84111800
C	0.00000000	1.23131500	-1.95631000
C	0.00000000	-1.22893900	0.84111800
C	0.00000000	-1.23131500	-1.95631000
C	0.00000000	2.43922000	0.13473400
C	0.00000000	2.44073000	-1.25130900
C	0.00000000	-2.43922000	0.13473400
C	0.00000000	-2.44073000	-1.25130900
H	0.00000000	1.22108700	1.92386200
H	0.00000000	1.23970000	-3.03843300
H	0.00000000	-1.22108700	1.92386200
H	0.00000000	-1.23970000	-3.03843300
H	0.00000000	3.37354400	0.67789500
H	0.00000000	3.37508600	-1.79434100
H	0.00000000	-3.37354400	0.67789500
H	0.00000000	-3.37508600	-1.79434100
O	0.00000000	0.00000000	3.90477500
H	-0.76375800	0.00000000	4.49192900
H	0.76375800	0.00000000	4.49192900

Zero-point correction=	0.170542 (Hartree/Particle)
Thermal correction to Energy=	0.181398
Thermal correction to Enthalpy=	0.182342
Thermal correction to Gibbs Free Energy=	0.133463
Sum of electronic and zero-point Energies=	-462.061863
Sum of electronic and thermal Energies=	-462.051007
Sum of electronic and thermal Enthalpies=	-462.050063
Sum of electronic and thermal Free Energies=	-462.098942

Np^{+}-H_2O(12)

C	-2.40796600	-1.84648500	0.00000000
C	-2.51091200	-0.45031100	0.00000000
C	-1.35911300	0.35592200	0.00000000
C	-0.07582400	-0.26841600	0.00000000
C	0.00000000	-1.67359700	0.00000000
C	-1.16154300	-2.45387400	0.00000000
H	-2.40305700	2.24332700	0.00000000
H	-3.30548300	-2.44840500	0.00000000
H	-3.48733900	0.01608500	0.00000000
C	-1.43286600	1.76379100	0.00000000
C	1.07768100	0.53878000	0.00000000
H	0.97072600	-2.15161700	0.00000000
H	-1.08253500	-3.53161000	0.00000000
C	0.97498200	1.93742400	0.00000000
C	-0.27073400	2.54413200	0.00000000
H	2.06355700	0.09321500	0.00000000
H	1.88503400	2.51949800	0.00000000
H	-0.35177900	3.62180200	0.00000000
O	4.11022300	1.35522500	0.00000000
H	4.69233100	1.43536700	0.76301600
H	4.69233100	1.43536700	-0.76301600

Zero-point correction=	0.170217 (Hartree/Particle)
Thermal correction to Energy=	0.181230
Thermal correction to Enthalpy=	0.182174
Thermal correction to Gibbs Free Energy=	0.131921
Sum of electronic and zero-point Energies=	-462.060428
Sum of electronic and thermal Energies=	-462.049415
Sum of electronic and thermal Enthalpies=	-462.048471
Sum of electronic and thermal Free Energies=	-462.098724

Np^{+}-H_2O(23)

C	0.00000000	0.71337300	-0.69142500
C	0.00000000	-0.71337300	-0.69142500
C	0.00000000	1.39600100	0.54187000
C	0.00000000	-1.39600100	0.54187000
C	0.00000000	1.39604000	-1.92107800
C	0.00000000	-1.39604000	-1.92107800
C	0.00000000	0.69329200	1.75283000
C	0.00000000	-0.69329200	1.75283000
C	0.00000000	0.69299500	-3.13186200
C	0.00000000	-0.69299500	-3.13186200
H	0.00000000	2.47829200	0.54776200
H	0.00000000	-2.47829200	0.54776200
H	0.00000000	2.47814700	-1.92816000
H	0.00000000	-2.47814700	-1.92816000
H	0.00000000	1.21725500	2.69756700
H	0.00000000	-1.21725500	2.69756700
H	0.00000000	1.23656800	-4.06581400
H	0.00000000	-1.23656800	-4.06581400
O	0.00000000	0.00000000	4.83870300
H	0.76291100	0.00000000	5.42634500
H	-0.76291100	0.00000000	5.42634500

Zero-point correction=	0.170186 (Hartree/Particle)
Thermal correction to Energy=	0.181201
Thermal correction to Enthalpy=	0.182145
Thermal correction to Gibbs Free Energy=	0.132647
Sum of electronic and zero-point Energies=	-462.059894
Sum of electronic and thermal Energies=	-462.048879
Sum of electronic and thermal Enthalpies=	-462.047935
Sum of electronic and thermal Free Energies=	-462.097433

Np^{+}-$H_2O(\pi)$

C	-2.33068200	-0.06321200	-0.61387100
C	-1.17435500	-0.63041600	-1.16109900
C	-0.01570800	-0.79301600	-0.38221300
C	-0.03049000	-0.37048400	0.97918000
C	-1.20360300	0.19722000	1.50573600
C	-2.34509800	0.34787400	0.71032200
H	1.18234600	-1.67178800	-1.94349900
H	-3.21246300	0.05189300	-1.22789100
H	-1.16860300	-0.94787900	-2.19551300
C	1.16173200	-1.35590500	-0.90886700
C	1.13262700	-0.52890200	1.75552200
H	-1.22086000	0.52139600	2.53795300
H	-3.23815100	0.78518500	1.13347800
C	2.28776400	-1.10183800	1.21013300
C	2.30207700	-1.51231800	-0.11176800
H	1.13027400	-0.20315100	2.78729200
H	3.16763100	-1.21934400	1.82638300
H	3.19322800	-1.95289600	-0.53545500
O	1.91707800	1.79503500	-0.43676300
H	1.47838400	2.61405000	-0.68988300
H	2.85633800	1.99826700	-0.49904000

Zero-point correction=	0.169801 (Hartree/Particle)
Thermal correction to Energy=	0.181111
Thermal correction to Enthalpy=	0.182055
Thermal correction to Gibbs Free Energy=	0.130087
Sum of electronic and zero-point Energies=	-462.058102
Sum of electronic and thermal Energies=	-462.046792
Sum of electronic and thermal Enthalpies=	-462.045847
Sum of electronic and thermal Free Energies=	-462.097816

Np^{+}-W_2(18)

C	-0.15960500	1.88648700	2.44017100
C	-0.32782300	2.57168100	1.23137600
C	-0.16612700	1.90872000	0.00000000
C	0.17231200	0.52285100	0.00000000
C	0.33663000	-0.14744900	1.22806900
C	0.16938700	0.54010500	2.43813500
H	-0.58500600	3.62279200	-1.23981700
H	-0.28764800	2.41394700	3.37471500
H	-0.58500600	3.62279200	1.23981700
C	-0.32782300	2.57168100	-1.23137600
C	0.33663000	-0.14744900	-1.22806900
H	0.59415600	-1.19992800	1.21451600
H	0.29921900	0.01275100	3.37252600
C	0.16938700	0.54010500	-2.43813500
C	-0.15960500	1.88648700	-2.44017100
H	0.59415600	-1.19992800	-1.21451600
H	0.29921900	0.01275100	-3.37252600
H	-0.28764800	2.41394700	-3.37471500
O	1.00357200	-3.03958800	0.00000000
H	0.33289200	-3.74851600	0.00000000
H	1.85275700	-3.49097000	0.00000000
O	-1.00882300	-4.98631000	0.00000000
H	-1.22262600	-5.52588400	-0.76811600
H	-1.22262600	-5.52588400	0.76811600

Zero-point correction=	0.194855 (Hartree/Particle)
Thermal correction to Energy=	0.209050
Thermal correction to Enthalpy=	0.209995
Thermal correction to Gibbs Free Energy=	0.150613
Sum of electronic and zero-point Energies=	-538.519383
Sum of electronic and thermal Energies=	-538.505187
Sum of electronic and thermal Enthalpies=	-538.504243
Sum of electronic and thermal Free Energies=	-538.563625

Np^{+}-W_2(12)

C	-3.54095900	-1.05349500	-0.26577200
C	-3.15255900	0.28821500	-0.35687100
C	-1.81484500	0.66425200	-0.14850800
C	-0.85120100	-0.34242600	0.15899200
C	-1.26742900	-1.68352000	0.24476700
C	-2.60530400	-2.03252600	0.03298600
H	-2.12006300	2.77608400	-0.46543100
H	-4.57472200	-1.32256400	-0.42948200
H	-3.88900100	1.04603100	-0.58991100
C	-1.39389700	2.00805800	-0.23289100
C	0.48917000	0.03379200	0.36884300
H	-0.53946300	-2.44923500	0.47798700
H	-2.90664500	-3.06790500	0.10305900
C	0.87937000	1.37898000	0.27894700
C	-0.05540200	2.35683800	-0.01982300
H	1.24697700	-0.70186600	0.60488000
H	1.91891400	1.61843100	0.45009100
H	0.24320100	3.39318300	-0.08904800
O	3.47452600	-0.23519700	0.99595500
H	3.92733200	-0.28538200	1.84257600
H	4.15378700	-0.44578100	0.32944600
O	5.35653400	-0.81434600	-1.01512500
H	5.73602000	-1.68731000	-1.15789800
H	6.03351200	-0.18634700	-1.28693000

Zero-point correction=	0.194580 (Hartree/Particle)
Thermal correction to Energy=	0.208896
Thermal correction to Enthalpy=	0.209841
Thermal correction to Gibbs Free Energy=	0.149963
Sum of electronic and zero-point Energies=	-538.517059
Sum of electronic and thermal Energies=	-538.502742
Sum of electronic and thermal Enthalpies=	-538.501798
Sum of electronic and thermal Free Energies=	-538.561676

Np^{+}-W_2(23)

C	-0.35887300	-3.87236100	0.69298500
C	-0.16229000	-2.67769300	1.39581900
C	0.03730000	-1.46512500	0.71332100
C	0.03730000	-1.46512500	-0.71332100
C	-0.16229000	-2.67769300	-1.39581900
C	-0.35887300	-3.87236100	-0.69298500
H	0.23943800	-0.24194300	2.47804700
H	-0.51035600	-4.79398400	1.23648700
H	-0.16323700	-2.68436900	2.47792200
C	0.23834700	-0.24715000	1.39569400
C	0.23834700	-0.24715000	-1.39569400
H	-0.16323700	-2.68436900	-2.47792200
H	-0.51035600	-4.79398400	-1.23648700
C	0.43596500	0.94757000	-0.69344700
C	0.43596500	0.94757000	0.69344700
H	0.23943800	-0.24194300	-2.47804700
H	0.59174300	1.88312400	-1.21106800
H	0.59174300	1.88312400	1.21106800
O	0.94088300	3.92520600	0.00000000
H	0.23957200	4.60155300	0.00000000
H	1.76652600	4.41767400	0.00000000
O	-1.16808600	5.79616500	0.00000000
H	-1.39451700	6.33062000	0.76784000
H	-1.39451700	6.33062000	-0.76784000

Zero-point correction=	0.194390 (Hartree/Particle)
Thermal correction to Energy=	0.208830
Thermal correction to Enthalpy=	0.209774
Thermal correction to Gibbs Free Energy=	0.149033
Sum of electronic and zero-point Energies=	-538.516292
Sum of electronic and thermal Energies=	-538.501853
Sum of electronic and thermal Enthalpies=	-538.500908
Sum of electronic and thermal Free Energies=	-538.561649

Np^{+}-W_2(18/45)

C	-0.69301600	2.43810900	0.00000000
C	-1.40097300	1.22910400	0.00000000
C	-0.71318000	0.00000000	0.00000000
C	0.71318000	0.00000000	0.00000000
C	1.40097300	1.22910400	0.00000000
C	0.69301600	2.43810900	0.00000000
H	-2.48359000	-1.22150300	0.00000000
H	-1.23569500	3.37281200	0.00000000
H	-2.48359000	1.22150300	0.00000000
C	-1.40097300	-1.22910400	0.00000000
C	1.40097300	-1.22910400	0.00000000
H	2.48359000	1.22150300	0.00000000
H	1.23569500	3.37281200	0.00000000
C	0.69301600	-2.43810900	0.00000000
C	-0.69301600	-2.43810900	0.00000000
H	2.48359000	-1.22150300	0.00000000
H	1.23569500	-3.37281200	0.00000000
H	-1.23569500	-3.37281200	0.00000000
O	-4.48073100	0.00000000	0.00000000
O	4.48073100	0.00000000	0.00000000
H	-5.06767200	0.00000000	0.76377600
H	-5.06767200	0.00000000	-0.76377600
H	5.06767200	0.00000000	0.76377600
H	5.06767200	0.00000000	-0.76377600

Zero-point correction=	0.193990 (Hartree/Particle)
Thermal correction to Energy=	0.208850
Thermal correction to Enthalpy=	0.209795
Thermal correction to Gibbs Free Energy=	0.151510
Sum of electronic and zero-point Energies=	-538.518771
Sum of electronic and thermal Energies=	-538.503910
Sum of electronic and thermal Enthalpies=	-538.502966
Sum of electronic and thermal Free Energies=	-538.561251

Np^{+}-W_2(18/12)

C	-2.17901900	-2.54885300	0.00000000
C	-2.78882300	-1.28896300	0.00000000
C	-2.01450800	-0.11516100	0.00000000
C	-0.59149300	-0.22292700	0.00000000
C	0.00000000	-1.50119700	0.00000000
C	-0.79692600	-2.65314100	0.00000000
H	-3.68146800	1.25361600	0.00000000
H	-2.79208300	-3.43886700	0.00000000
H	-3.86838200	-1.21415200	0.00000000
C	-2.60279500	1.16558500	0.00000000
C	0.18681000	0.95180900	0.00000000
H	1.07996700	-1.57707600	0.00000000
H	-0.32691400	-3.62634100	0.00000000
C	-0.42757600	2.21353600	0.00000000
C	-1.80954300	2.31765800	0.00000000
H	1.26747800	0.88179300	0.00000000
H	0.20210900	3.09122500	0.00000000
H	-2.28140100	3.28999400	0.00000000
O	2.55264800	3.25810400	0.00000000
H	3.01214400	3.62383500	0.76296400
H	3.01214400	3.62383500	-0.76296400
O	3.14289400	-0.71122400	0.00000000
H	3.72839600	-0.74262000	-0.76385000
H	3.72839600	-0.74262000	0.76385000

Zero-point correction=	0.193195 (Hartree/Particle)
Thermal correction to Energy=	0.207608
Thermal correction to Enthalpy=	0.208552
Thermal correction to Gibbs Free Energy=	0.149788
Sum of electronic and zero-point Energies=	-538.516141
Sum of electronic and thermal Energies=	-538.501728
Sum of electronic and thermal Enthalpies=	-538.500784
Sum of electronic and thermal Free Energies=	-538.559548

Np^{+}-W_2(12/23)

C	0.83761700	3.70315600	0.00000000
C	1.67046700	2.57826600	0.00000000
C	1.12790700	1.28227000	0.00000000
C	-0.28995800	1.12402900	0.00000000
C	-1.10470400	2.26975200	0.00000000
C	-0.54038100	3.55014900	0.00000000
H	3.01841200	0.24371500	0.00000000
H	1.27417500	4.69169900	0.00000000
H	2.74510000	2.70534600	0.00000000
C	1.94204700	0.12955300	0.00000000
C	-0.83387400	-0.17668500	0.00000000
H	-2.18058600	2.15450000	0.00000000
H	-1.18326000	4.41875100	0.00000000
C	0.00000000	-1.30400400	0.00000000
C	1.37775000	-1.15146100	0.00000000
H	-1.90572100	-0.32409800	0.00000000
H	-0.43667900	-2.29178200	0.00000000
H	2.00428200	-2.03145900	0.00000000
O	-3.09461300	-2.34591400	0.00000000
H	-3.55287000	-2.71310900	0.76305200
H	-3.55287000	-2.71310900	-0.76305200
O	1.17032400	-4.30111700	0.00000000
H	1.27016500	-4.87981400	-0.76298200
H	1.27016500	-4.87981400	0.76298200

Zero-point correction=	0.193237 (Hartree/Particle)
Thermal correction to Energy=	0.208458
Thermal correction to Enthalpy=	0.209402
Thermal correction to Gibbs Free Energy=	0.148078
Sum of electronic and zero-point Energies=	-538.514750
Sum of electronic and thermal Energies=	-538.499528
Sum of electronic and thermal Enthalpies=	-538.498584
Sum of electronic and thermal Free Energies=	-538.559908

W_2

O	-0.00039400	1.51531900	0.00000000
H	-0.09677300	0.55059500	0.00000000
H	-0.89669700	1.86124200	0.00000000
O	-0.00039400	-1.39367900	0.00000000
H	0.49988800	-1.69247900	0.76609500
H	0.49988800	-1.69247900	-0.76609500

Zero-point correction=	0.045887 (Hartree/Particle)
Thermal correction to Energy=	0.051724
Thermal correction to Enthalpy=	0.052668
Thermal correction to Gibbs Free Energy=	0.019591
Sum of electronic and zero-point Energies=	-152.894972
Sum of electronic and thermal Energies=	-152.889135
Sum of electronic and thermal Enthalpies=	-152.888191
Sum of electronic and thermal Free Energies=	-152.921267

Np^{+}-W_3(c1)

C	3.49972800	-0.89446900	0.12611700
C	3.34409300	0.49224600	0.23132200
C	2.10542500	1.09813400	-0.04510600
C	1.00829300	0.27719200	-0.43916600
C	1.18513000	-1.11510200	-0.53228800
C	2.42914700	-1.69175600	-0.25046000
H	2.73889700	3.12090000	0.35489000
H	4.45978000	-1.34129800	0.34200600
H	4.18380900	1.10686000	0.52815900
C	1.91144600	2.49048000	0.05646000
C	-0.23210600	0.87814400	-0.71835900
H	0.33867900	-1.73010800	-0.81073500
H	2.55203400	-2.76273300	-0.32668700
C	-0.39959400	2.26452600	-0.60362200
C	0.66469000	3.06402800	-0.22056400
H	-1.06211800	0.26150900	-1.02371300
H	-1.36923800	2.69227200	-0.81302800
H	0.53892900	4.13379200	-0.13275300
O	-2.10909100	-1.86311000	-0.51336700
H	-2.06664900	-1.58856500	0.42249600
H	-2.49939400	-2.74213600	-0.53070800
O	-2.00504900	-0.17239400	1.65761700
O	-3.45066000	0.66670400	-0.57073400
H	-3.34984200	-0.25603200	-0.85625500
H	-2.26975500	-0.18629300	2.58213600
H	-2.67642800	0.34448800	1.17859000
H	-4.34475400	0.93319400	-0.80525200

Zero-point correction=	0.220907 (Hartree/Particle)
Thermal correction to Energy=	0.237170
Thermal correction to Enthalpy=	0.238114
Thermal correction to Gibbs Free Energy=	0.174695
Sum of electronic and zero-point Energies=	-614.977221
Sum of electronic and thermal Energies=	-614.960958
Sum of electronic and thermal Enthalpies=	-614.960014
Sum of electronic and thermal Free Energies=	-615.023434

Np^{+}-W_3(c2)

C	4.06679500	0.72608700	0.26386300
C	2.85992900	1.40837300	0.07108300
C	1.65910300	0.70508300	-0.12604200
C	1.68349000	-0.72101600	-0.12724700
C	2.90750200	-1.38288300	0.06853600
C	4.09043200	-0.65976100	0.26259400
H	0.40394700	2.44742500	-0.32274100
H	4.97947100	1.28498700	0.41343500
H	2.84782100	2.49041900	0.07294500
C	0.42864600	1.36535100	-0.32342300
C	0.47586600	-1.42282100	-0.32517900
H	2.93266800	-2.46471000	0.06860400
H	5.02164600	-1.18748300	0.41124100
C	-0.73200600	-0.74259100	-0.51855500
C	-0.75570600	0.64440700	-0.51770200
H	0.48813800	-2.50512400	-0.32513600
H	-1.65162500	-1.29421700	-0.65841200
H	-1.69252100	1.16437000	-0.66406400
O	-3.90314800	-1.45955700	-0.31554800
H	-4.57067900	-2.15117400	-0.34059100
H	-3.81306900	-1.17947700	0.61489600
O	-3.94675200	1.30656900	-0.67774500
H	-4.17128300	0.37699500	-0.86421600
H	-4.63073100	1.84812100	-1.08188900
O	-3.27542300	0.19964700	1.79721500
H	-3.60990200	0.89614000	1.20638900
H	-3.63561300	0.37907700	2.67059100

Zero-point correction=	0.220825 (Hartree/Particle)
Thermal correction to Energy=	0.237106
Thermal correction to Enthalpy=	0.238051
Thermal correction to Gibbs Free Energy=	0.173622
Sum of electronic and zero-point Energies=	-614.974899
Sum of electronic and thermal Energies=	-614.958617
Sum of electronic and thermal Enthalpies=	-614.957673
Sum of electronic and thermal Free Energies=	-615.022101

Np^{+}-W_3(18)

C	-3.00453200	-2.03306200	-0.50727900
C	-3.36913000	-0.68807700	-0.63611500
C	-2.47639800	0.33748000	-0.27126100
C	-1.18952600	-0.01384300	0.23406900
C	-0.84254700	-1.37374200	0.35557700
C	-1.75352200	-2.37225900	-0.01639300
H	-3.78908200	1.97384600	-0.77118100
H	-3.70479700	-2.80517800	-0.79271700
H	-4.34768200	-0.43027800	-1.01964500
C	-2.81465500	1.69892500	-0.38907600
C	-0.28984600	1.00578000	0.60216200
H	0.13913100	-1.62479900	0.74069100
H	-1.47372500	-3.41147400	0.08254200
C	-0.65610200	2.35284700	0.47292400
C	-1.90603000	2.69636200	-0.01763000
H	0.68427200	0.72341800	0.98489700
H	0.04453700	3.12424100	0.75943800
H	-2.18552000	3.73574200	-0.11545600
O	2.09914400	-0.90006400	1.43907200
H	2.52123900	-1.09439700	2.28040100
H	2.81113500	-0.95465100	0.76512200
O	3.96316200	-1.01575300	-0.55923500
H	4.30211500	-1.85820400	-0.87429500
H	4.70631600	-0.38610400	-0.61815900
O	6.05474200	0.82733300	-0.71806200
H	6.35391300	1.20996300	-1.54892300
H	6.81550300	0.84327300	-0.12880300

Zero-point correction=	0.219346 (Hartree/Particle)
Thermal correction to Energy=	0.236701
Thermal correction to Enthalpy=	0.237645
Thermal correction to Gibbs Free Energy=	0.169068
Sum of electronic and zero-point Energies=	-614.976240
Sum of electronic and thermal Energies=	-614.958885
Sum of electronic and thermal Enthalpies=	-614.957941
Sum of electronic and thermal Free Energies=	-615.026518

W_3

O	-1.32286600	0.92136300	0.09544400
H	-1.21645700	-0.04614600	0.02070400
O	-0.14102900	-1.60154200	-0.11227800
H	0.64796000	-1.02969400	-0.05584100
H	-0.07386000	-2.22201000	0.61853600
O	1.46548300	0.67386600	0.08770200
H	0.58620800	1.09433100	0.04913100
H	-1.94579500	1.17784800	-0.58944300
H	1.98924600	1.07617400	-0.61002300

Zero-point correction=	0.072455 (Hartree/Particle)
Thermal correction to Energy=	0.079893
Thermal correction to Enthalpy=	0.080837
Thermal correction to Gibbs Free Energy=	0.043123
Sum of electronic and zero-point Energies=	-229.352733
Sum of electronic and thermal Energies=	-229.345295
Sum of electronic and thermal Enthalpies=	-229.344351
Sum of electronic and thermal Free Energies=	-229.382065

Np^{+}-W_4(c)

C	2.71814200	-1.67724400	0.16070100
C	2.78369400	-0.31825300	0.48845300
C	1.78981100	0.57570800	0.05282700
C	0.71010100	0.07827600	-0.73461900
C	0.66306700	-1.29198700	-1.04687600
C	1.66588600	-2.16063300	-0.59893700
H	2.64015200	2.32987100	0.97169900
H	3.49151800	-2.34792600	0.50698800
H	3.60681500	0.05178700	1.08557600
C	1.82369500	1.94528000	0.37459600
C	-0.29179100	0.96600700	-1.16280300
H	-0.16707400	-1.67046100	-1.62600500
H	1.60829400	-3.21134600	-0.84300100
C	-0.23552700	2.32362100	-0.82408800
C	0.81589200	2.80938200	-0.06466800
H	-1.12355400	0.58313000	-1.73634200
H	-1.02723600	2.98246600	-1.14773000
H	0.85899400	3.85695700	0.19709800
O	-2.76098300	-1.19111600	-1.12232200
H	-2.38635100	-1.75500400	-0.41005300
H	-3.45350300	-1.70060600	-1.55331500
O	-1.36165200	-2.29850700	0.93385200
O	-1.09620300	0.20064700	2.01680500
H	-1.82769800	0.65283200	1.54322500
H	-1.24058800	-1.48926600	1.47849200
O	-3.00470400	1.15743600	0.28909400
H	-3.13581900	0.35338600	-0.25573800
H	-3.87874600	1.49736900	0.50210400
H	-1.19696900	0.41742800	2.94822900
H	-1.63772200	-2.99923700	1.53181400

Zero-point correction=	0.246825 (Hartree/Particle)
Thermal correction to Energy=	0.265109
Thermal correction to Enthalpy=	0.266053
Thermal correction to Gibbs Free Energy=	0.198634
Sum of electronic and zero-point Energies=	-691.441329
Sum of electronic and thermal Energies=	-691.423044
Sum of electronic and thermal Enthalpies=	-691.422100
Sum of electronic and thermal Free Energies=	-691.489520

Np^{+}-W_4(l)

C	3.49603300	-1.24803900	-0.04226500
C	2.13261600	-1.22374600	0.27868100
C	1.42326100	-0.00728600	0.27333500
C	2.10263300	1.19822800	-0.07352700
C	3.47209900	1.14191800	-0.38931500
C	4.16022700	-0.07621300	-0.37057500
H	-0.45436300	-0.86710300	0.86974700
H	4.02789800	-2.18879700	-0.03522900
H	1.59789300	-2.13615800	0.51291100
C	0.05399300	0.04490600	0.59447500
C	1.37950400	2.40735900	-0.09141100
H	3.99634400	2.05219800	-0.64941000
H	5.21229600	-0.09824500	-0.61699800
C	0.01607900	2.43144600	0.22045700
C	-0.64359700	1.26104600	0.55919300
H	1.88852300	3.32557000	-0.35407500
H	-0.51958600	3.36974500	0.19419900
H	-1.69950800	1.25969500	0.78899800
O	-0.35039900	-3.16649900	0.46429500
H	-0.93875200	-2.83038500	-0.23840900
H	-0.63925300	-4.06143800	0.66140400
O	-1.86732200	-1.61264500	-1.24786000
H	-2.24543300	-1.81809000	-2.10719100
H	-2.57029100	-1.17876400	-0.72270800
O	-3.55823200	-0.33736800	0.53170900
O	-5.76902600	1.09670000	-0.33974800
H	-4.35241500	0.15305300	0.24018700
H	-3.85751100	-0.92104800	1.23577200
H	-6.24346200	1.74343200	0.19239300
H	-6.39963900	0.77713000	-0.99303900

Zero-point correction=	0.244391 (Hartree/Particle)
Thermal correction to Energy=	0.264587
Thermal correction to Enthalpy=	0.265531
Thermal correction to Gibbs Free Energy=	0.190708
Sum of electronic and zero-point Energies=	-691.434700
Sum of electronic and thermal Energies=	-691.414504
Sum of electronic and thermal Enthalpies=	-691.413560
Sum of electronic and thermal Free Energies=	-691.488383

W_4

O	-1.36651200	-1.36651200	0.00311600
H	-0.39180100	-1.50161500	0.01255800
O	1.36651200	1.36651200	0.00311600
H	0.39180100	1.50161500	0.01255800
O	-1.36651200	1.36651200	-0.00311600
H	-1.50161500	0.39180100	-0.01255800
O	1.36651200	-1.36651200	-0.00311600
H	1.50161500	-0.39180100	-0.01255800
H	1.86450600	-1.69879200	0.74839400
H	1.69879200	1.86450600	-0.74839400
H	-1.69879200	-1.86450600	-0.74839400
H	-1.86450600	1.69879200	0.74839400

Zero-point correction=	0.098203 (Hartree/Particle)
Thermal correction to Energy=	0.107833
Thermal correction to Enthalpy=	0.108777
Thermal correction to Gibbs Free Energy=	0.065747
Sum of electronic and zero-point Energies=	-305.813819
Sum of electronic and thermal Energies=	-305.804190
Sum of electronic and thermal Enthalpies=	-305.803246
Sum of electronic and thermal Free Energies=	-305.846276

Np^{+}-W_5(c1)

C	2.63589400	1.66954900	-0.39335700
C	1.37776000	1.30079200	-0.88500200
C	0.93648600	-0.03141100	-0.79542200
C	1.77918500	-1.00474600	-0.18441400
C	3.03788600	-0.60903400	0.29739000
C	3.46012400	0.72176300	0.18992400
H	-0.97338600	0.31594000	-1.72481500
H	2.95691000	2.69853500	-0.46638500
H	0.72377900	2.04074600	-1.32432500
C	-0.32784900	-0.42123000	-1.27063900
C	1.31593600	-2.32974800	-0.06863100
H	3.68539000	-1.34257400	0.75964300
H	4.43168500	1.00565500	0.56858300
C	0.05000700	-2.69023300	-0.53821700
C	-0.76698700	-1.74349100	-1.13405800
H	1.94882700	-3.07292700	0.39844600
H	-0.29234900	-3.70876500	-0.42597700
H	-1.75474500	-2.00681500	-1.48018800
O	-0.44036900	-0.24639500	2.19412200
O	-3.45172100	0.16191800	-0.89954700
O	-2.75740200	-1.32620600	1.28166200
H	-3.04660200	1.05559100	-0.89949900
H	-4.34384800	0.25772200	-1.24495800
H	-3.12614500	-0.78936400	0.54651400
H	-1.30006000	-0.66126700	1.94717700
H	-3.49443100	-1.54722700	1.85821400
O	-1.90327000	2.42429200	-0.89053300
H	-1.43083200	2.50315200	-0.03011000
H	-0.28509700	-0.47480600	3.11501700
O	-0.39162600	2.34319700	1.36011700
H	-0.41059600	1.43873600	1.75083700
H	-0.49258700	2.95926600	2.09155200
H	-2.23145900	3.30068500	-1.11174100

Zero-point correction=	0.271709 (Hartree/Particle)
Thermal correction to Energy=	0.292789
Thermal correction to Enthalpy=	0.293733
Thermal correction to Gibbs Free Energy=	0.219749
Sum of electronic and zero-point Energies=	-767.901645
Sum of electronic and thermal Energies=	-767.880565
Sum of electronic and thermal Enthalpies=	-767.879621
Sum of electronic and thermal Free Energies=	-767.953605

Np^{+}-W_5(c2)

C	-0.61559300	2.81492100	-0.59521300
C	-1.71495300	2.27794400	0.06660600
C	-1.97588500	0.89814900	0.01366600
C	-1.10170100	0.05605600	-0.73320100
C	-0.00169200	0.61973600	-1.39362100
C	0.23877200	1.98931600	-1.31974000
H	-3.75169300	0.95537700	1.23599900
H	-0.42754400	3.87813400	-0.54583000
H	-2.37877100	2.92330500	0.62653400
C	-3.08215900	0.31852200	0.67240600
C	-1.35467000	-1.33469300	-0.76782100
H	0.67080900	-0.02038000	-1.94562400
H	1.09682100	2.40585300	-1.82714700
C	-2.46996700	-1.87766300	-0.10326400
C	-3.32441100	-1.05551500	0.60735200
H	-0.71605100	-1.96771400	-1.36434300
H	-2.63949900	-2.94339400	-0.14187500
H	-4.17913900	-1.47330300	1.11965800
O	0.25186800	-2.21988200	1.01076900
H	0.91489700	-2.33665300	0.30483900
O	1.85615700	-2.24275200	-1.29389800
H	2.32894400	-3.01171200	-1.62552200
H	0.45237500	-1.35405800	1.41114400
H	2.49125400	-1.50000400	-1.29262000
O	3.31766700	0.11059200	-1.13884200
H	4.09678100	0.28840300	-1.67477400
H	3.55638400	0.33616700	-0.22443100
O	0.85239100	0.36637800	2.03536900
H	0.60663700	0.50406500	2.95545300
H	1.80809300	0.52704700	1.98999200
O	3.73531400	0.63146400	1.66849000
H	4.16170900	1.45358200	1.93730900
H	4.21437500	-0.07175200	2.12312200

Zero-point correction=	0.271022 (Hartree/Particle)
Thermal correction to Energy=	0.293048
Thermal correction to Enthalpy=	0.293992
Thermal correction to Gibbs Free Energy=	0.217961
Sum of electronic and zero-point Energies=	-767.889257
Sum of electronic and thermal Energies=	-767.867232
Sum of electronic and thermal Enthalpies=	-767.866288
Sum of electronic and thermal Free Energies=	-767.942319

W_5

O	-2.29940400	0.09685200	0.17257000
H	-1.72728600	0.88926600	0.04234800
O	1.91913800	1.29299100	0.06890700
H	1.94000700	0.30855800	0.04087700
O	-0.80846900	-2.15879800	-0.06459100
H	-1.38220000	-1.36424600	0.04370900
O	-0.62720000	2.20768500	-0.16281300
H	0.30885000	1.91016100	-0.07848400
O	1.80672900	-1.42589800	-0.07700800
H	0.86726800	-1.72540200	-0.08153200
H	2.40655100	1.55044800	0.85555200
H	-0.67554900	2.70015300	-0.98638500
H	-2.79403900	0.25504800	0.98081600
H	-1.13889700	-2.61627500	-0.84229300
H	2.26894200	-2.01037500	0.52887400

Zero-point correction=	0.122798 (Hartree/Particle)
Thermal correction to Energy=	0.135435
Thermal correction to Enthalpy=	0.136379
Thermal correction to Gibbs Free Energy=	0.083806
Sum of electronic and zero-point Energies=	-382.270268
Sum of electronic and thermal Energies=	-382.257632
Sum of electronic and thermal Enthalpies=	-382.256687
Sum of electronic and thermal Free Energies=	-382.309261