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Supporting Information:

Photodissociation and Theory to Investigate Uranium Oxide Cluster Cations

Joshua H. Marks,[1] Paula Kahn,[2] Monica Vasiliu,[2] David A Dixon,[2] Michael A. Duncan[1]*

[1]Department of Chemistry, University of Georgia, Athens, Georgia, U.S.A.

[1]Department of Chemistry & Biochemistry, University of Alabama, Tuscaloosa, Alabama, U.S.A.

*E-mail: maduncan@uga.edu

Full citations for Gaussian 16, reference 95, and MolPro, reference 106:

Reference 95: Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Petersson, G. A.; Nakatsuji, H.; Li, X.; Caricato, M.; Marenich, A. V.; Bloino, J.; Janesko, B. G.; Gomperts, R.; Mennucci, B.; Hratchian, H. P.; Ortiz, J. V.; Izmaylov, A. F.; Sonnenberg, J. L.; Williams-Young, D.; Ding, F.; Lipparini, F.; Egidi, F.; Goings, J.; Peng, B.; Petrone, A.; Henderson, T.; Ranasinghe, D.; Zakrzewski, V. G.; Gao, J.; Rega, N.; Zheng, G.; Liang, W.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Throssell, K.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M. J.; Heyd, J. J.; Brothers, E. N.; Kudin, K. N.; Staroverov, V. N.; Keith, T. A.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A. P.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Millam, J. M.; Klene, M.; Adamo, C.; Cammi, R.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Farkas, O.; Foresman, J. B.; Fox, D. J. Gaussian 16, Revision C.01, Gaussian, Inc., Wallingford CT, 2016.

Reference 106: Werner H.-J.; Knowles, P. J.; Knizia, G.; Manby, F. R.; Schütz, M.; Celani, P.; Györffy, W.; Kats, T.; Korona, T.; Lindh, R.; Mitrushenkov, A.; Rauhut, G.; Shamasundar K. R.; Adler, T. B.; Amos, R. D.; Bernhardsson, A.; Berning, A.; Cooper, D. L.; Deegan, M. J. O.; Dobbyn, A. J.; Eckert, F.; Goll, E.; Hampel, C.; Hesselmann, A.; Hetzer, G.; Hrenar, T.; Jansen, G.; Köppl, C.; Liu, Y.; Lloyd, A. W.; Mata, R. A.; May, A. J.; McNicholas, S. J.; Meyer, W.; Mura, M. E.; Nicklass, A.; O'Neill D. P.; Palmieri, P.; Peng, D.; Pflüger, K.; Pitzer, R.; Reiher, M.; Shiozaki, T.; Stoll, H.; Stone, A. J.; Tarroni, R.; Thorsteinsson, T.; Wang, M. MOLPRO, version 2018.1 a package of *ab initio* programs, See http://www.molpro.net.

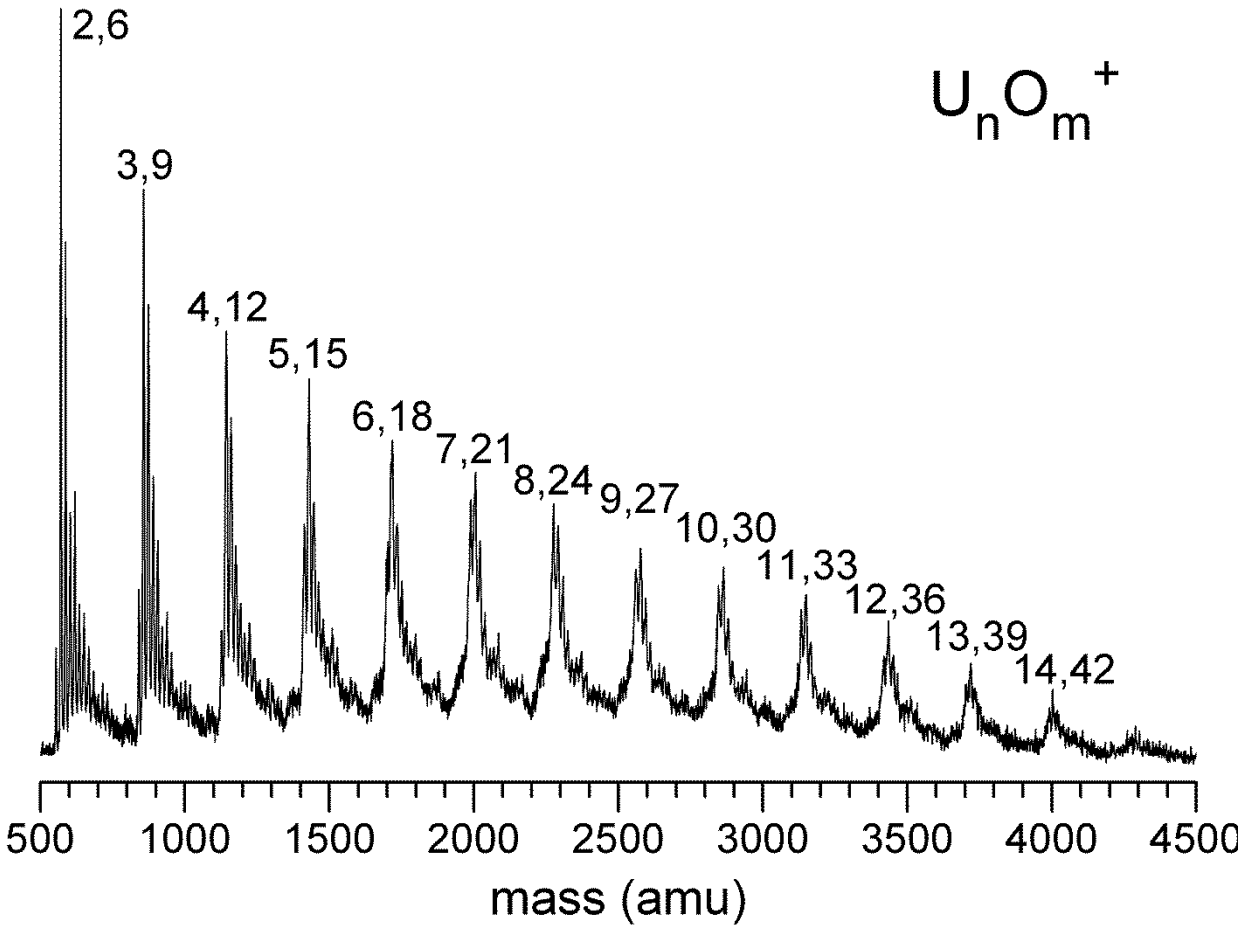
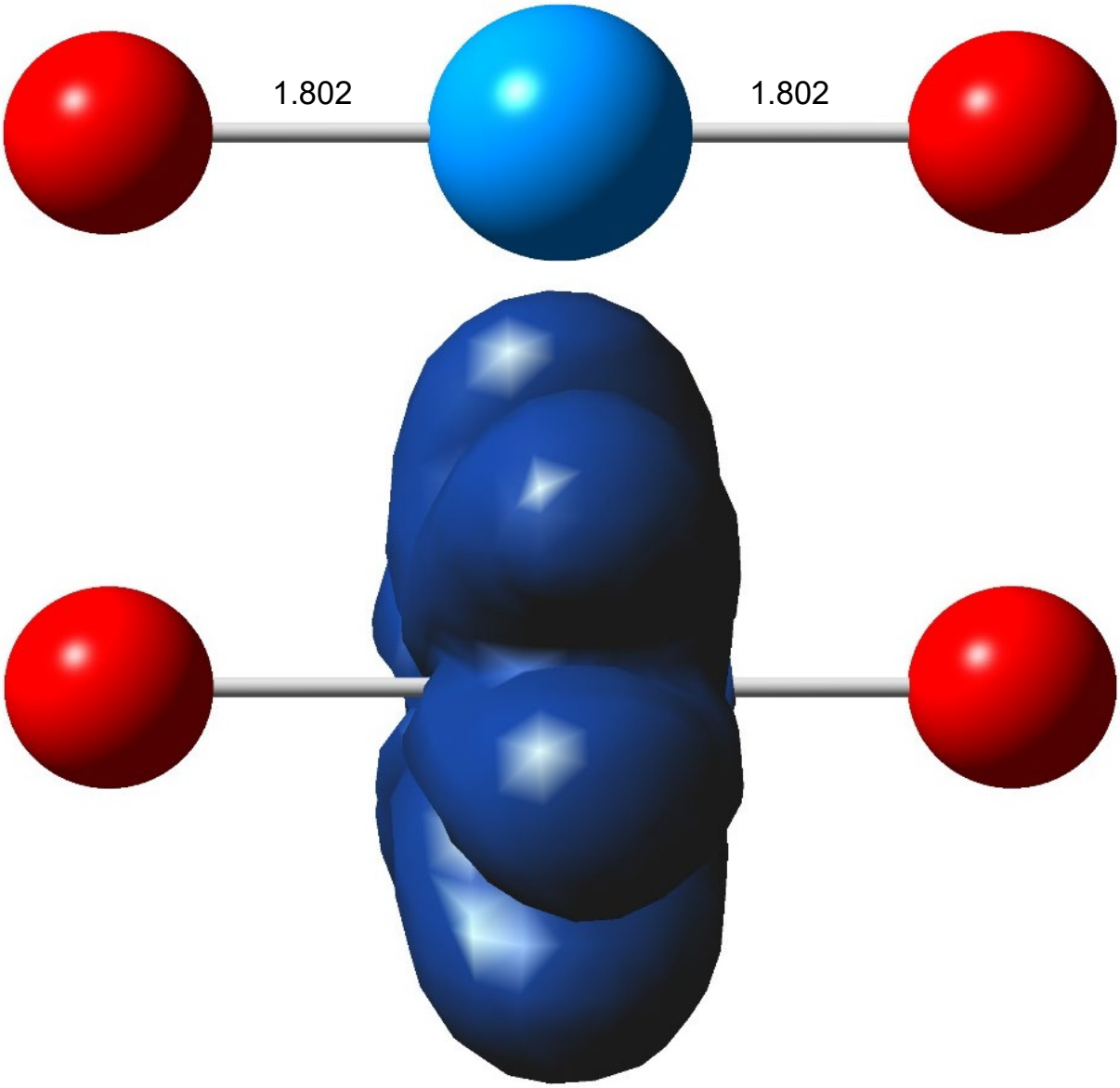


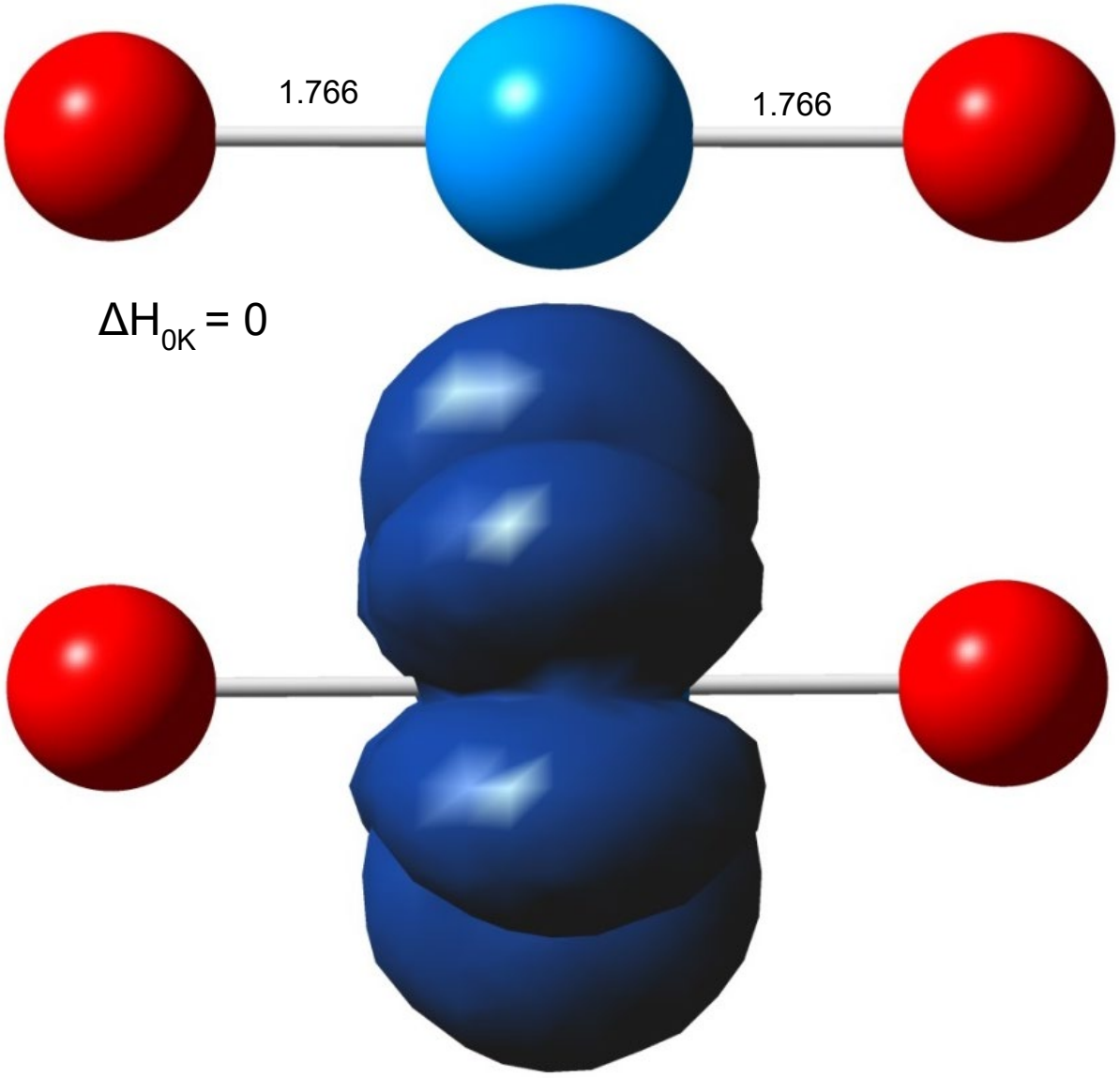
Figure S1. Mass spectrum of uranium oxide cluster cations recorded while the mass spectrometer is optimized to show high mass clusters.

Figure S2. Molecular parameters and singly occupied orbital of $^3UO_2$.



U	0.000000	0.000000	0.000000
O	0.000000	0.000000	1.802208
O	0.000000	0.000000	-1.802208

Figure S3. Molecular parameters and singly occupied orbital of $^2UO_2^+$.



U	0.000000	0.000000	0.000000
O	0.000000	0.000000	1.766097
O	0.000000	0.000000	-1.766097

Figure S4. Molecular parameters and singly occupied orbital of $^4UO_2^+$.

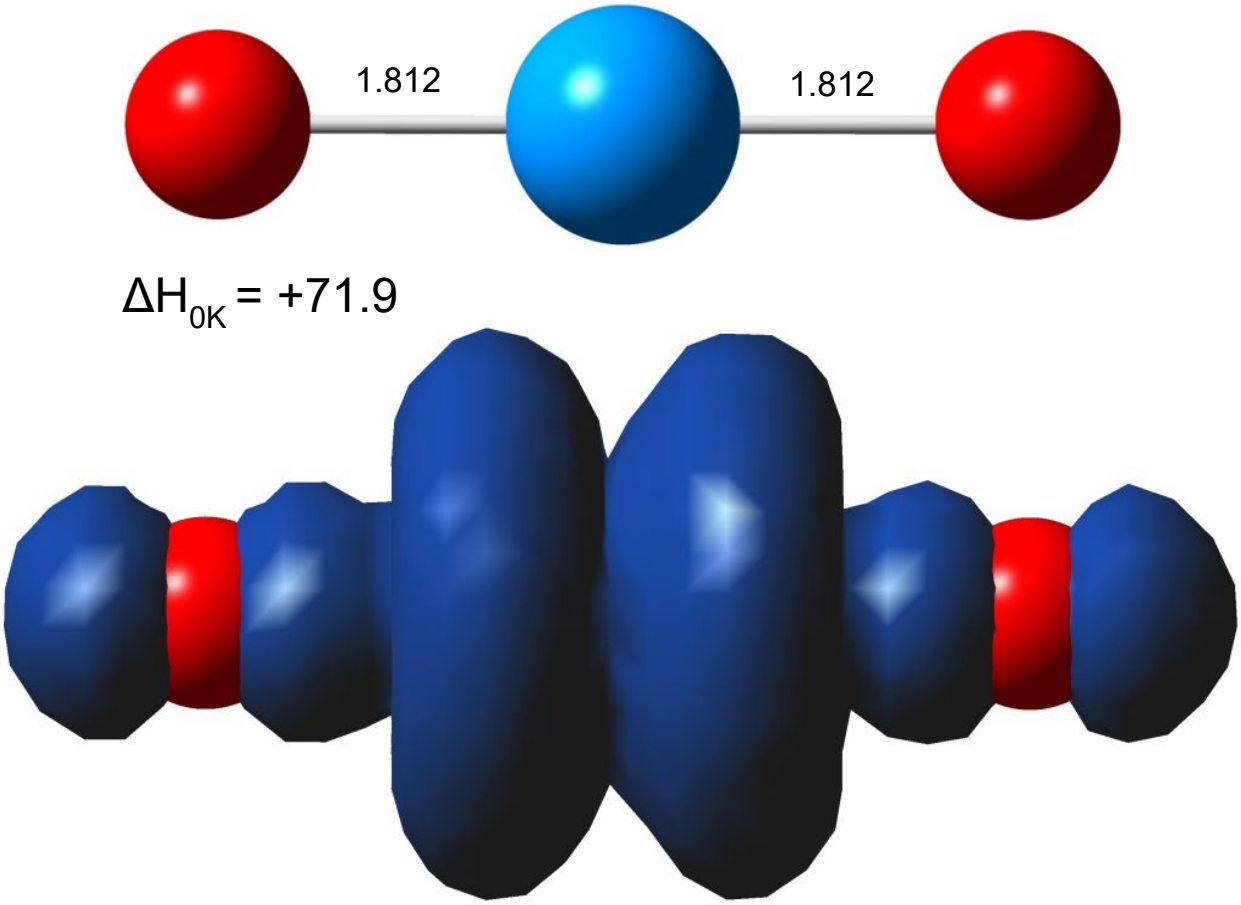
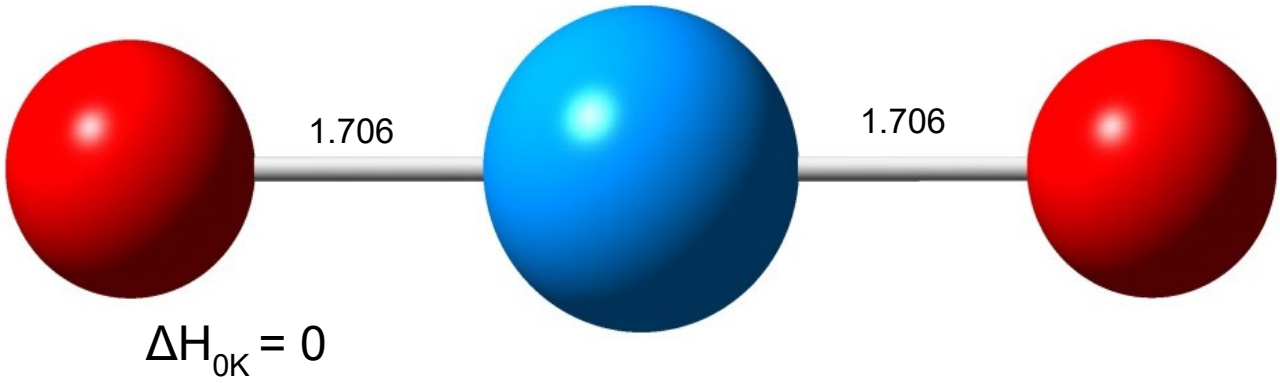


Figure S5. Molecular parameters of $^{1}UO_2^{2+}$.



U	0.000000	0.000000	0.000000
O	0.000000	0.000000	1.705516
O	0.000000	0.000000	-1.705516

Figure S6. Molecular parameters and singly occupied orbital of $^3UO_2^{2+}$.

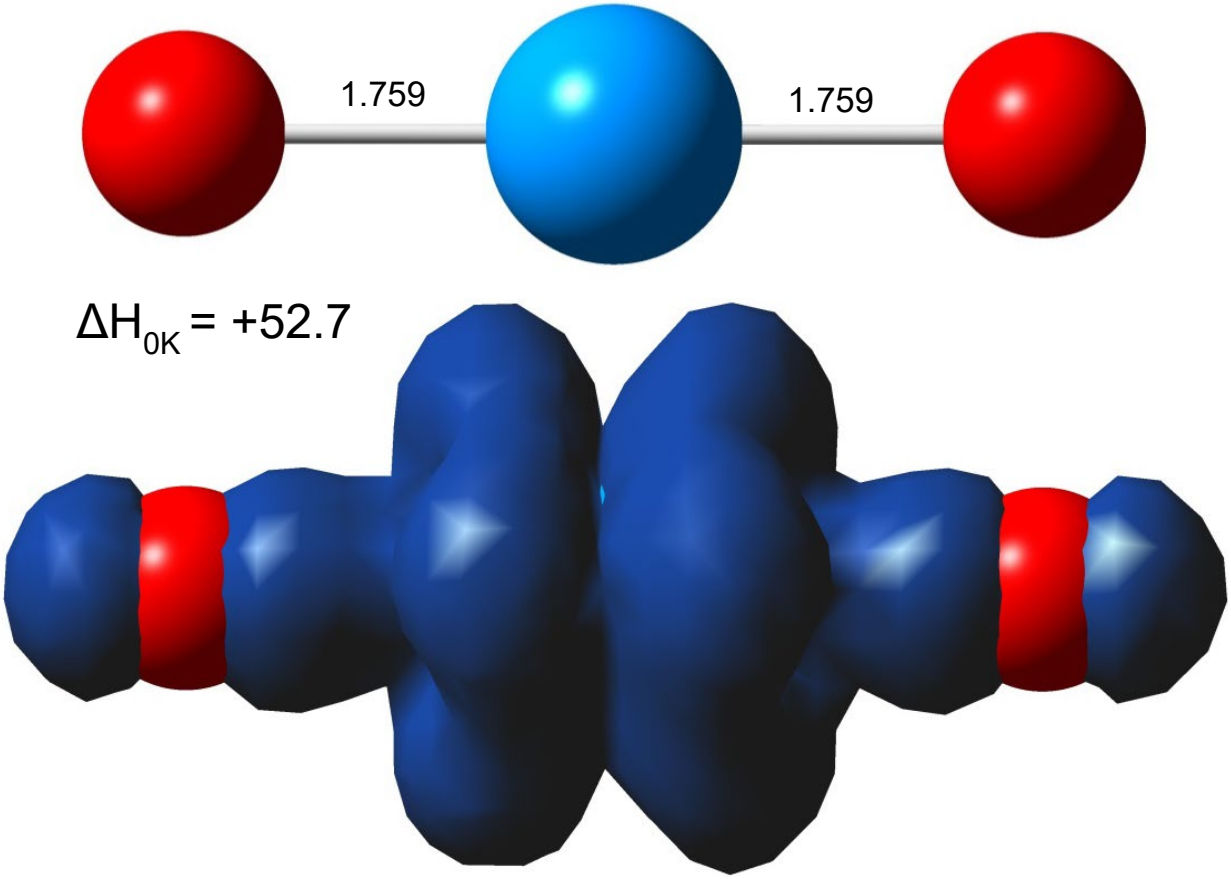
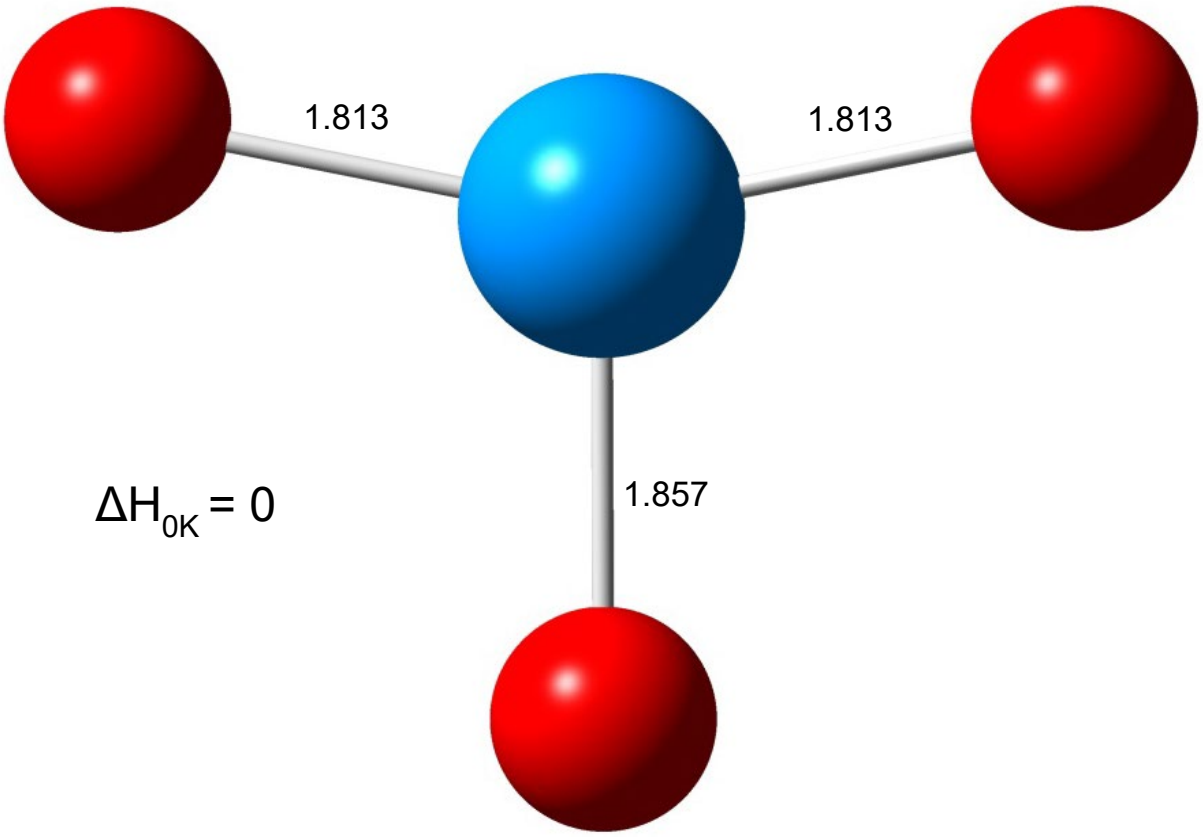


Figure S7. Molecular parameters of $^{1}UO_3$.



U	0.000000	0.000000	0.078944
O	0.000000	0.000000	-1.777942
O	0.000000	1.777504	0.435043
O	0.000000	-1.777504	0.435043

Figure S8. Molecular parameters and singly occupied orbital of $^3UO_3$.

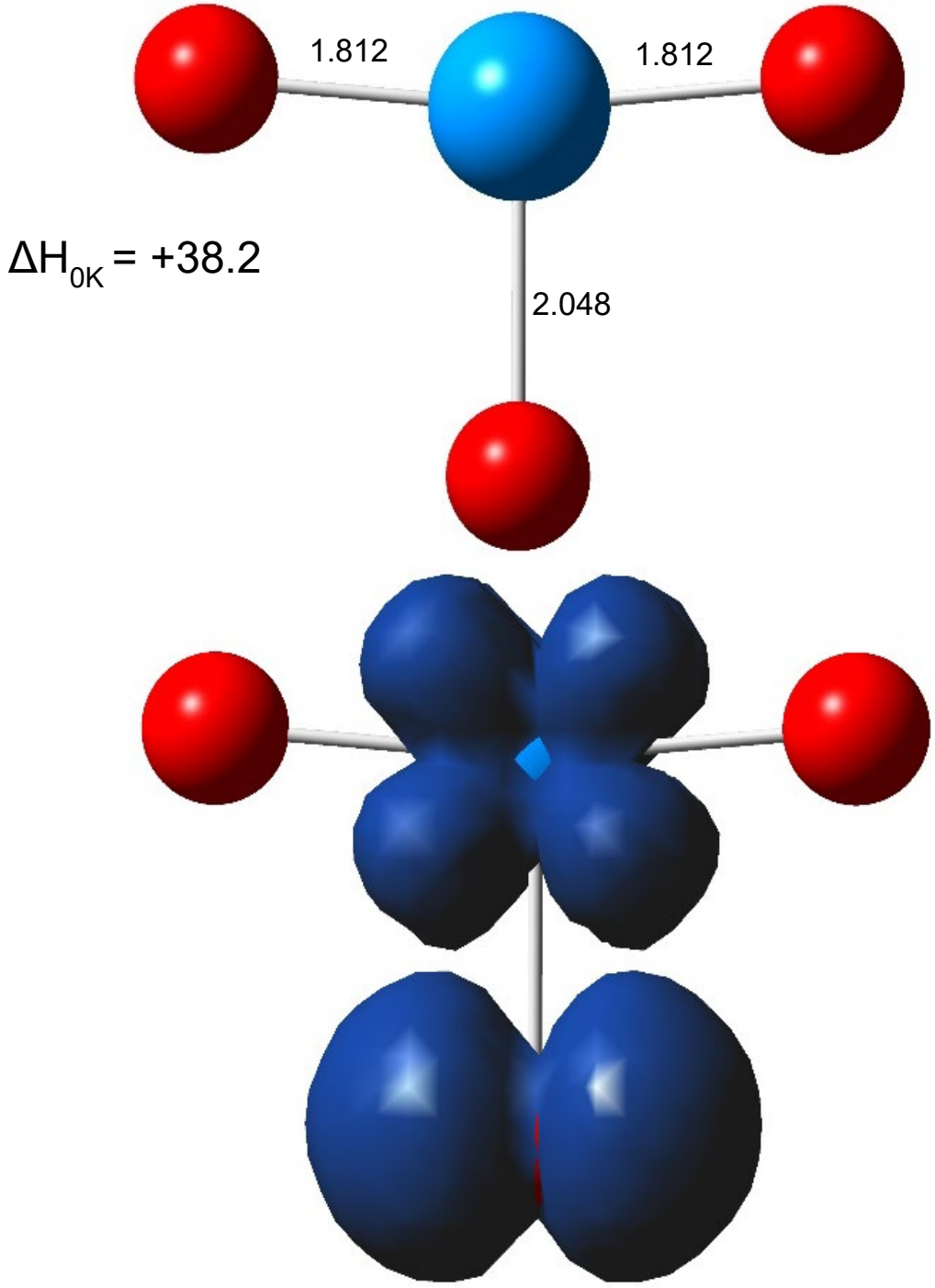
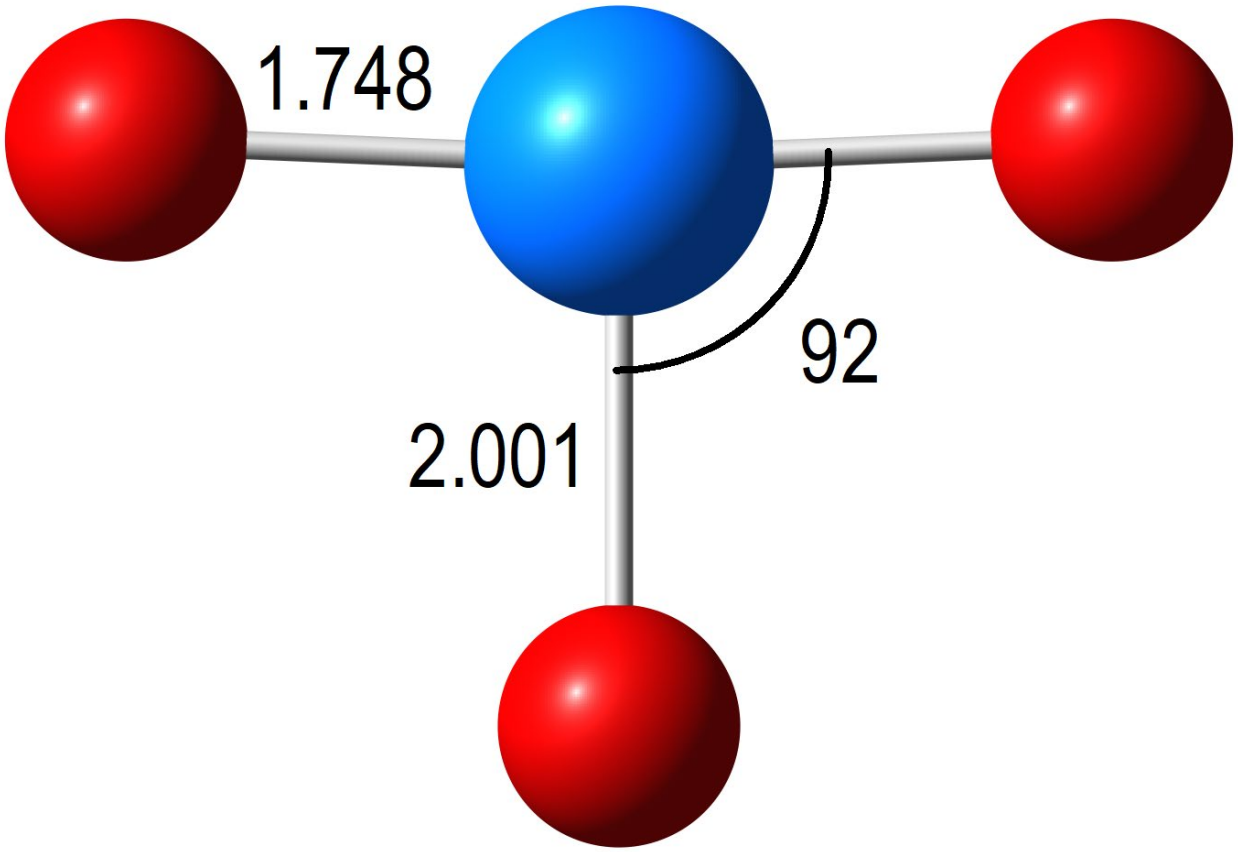
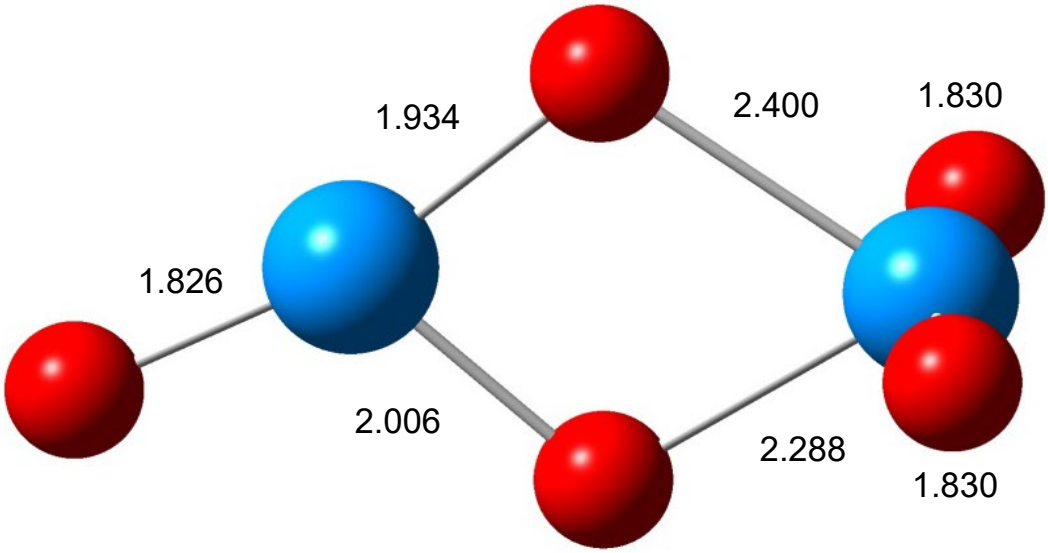


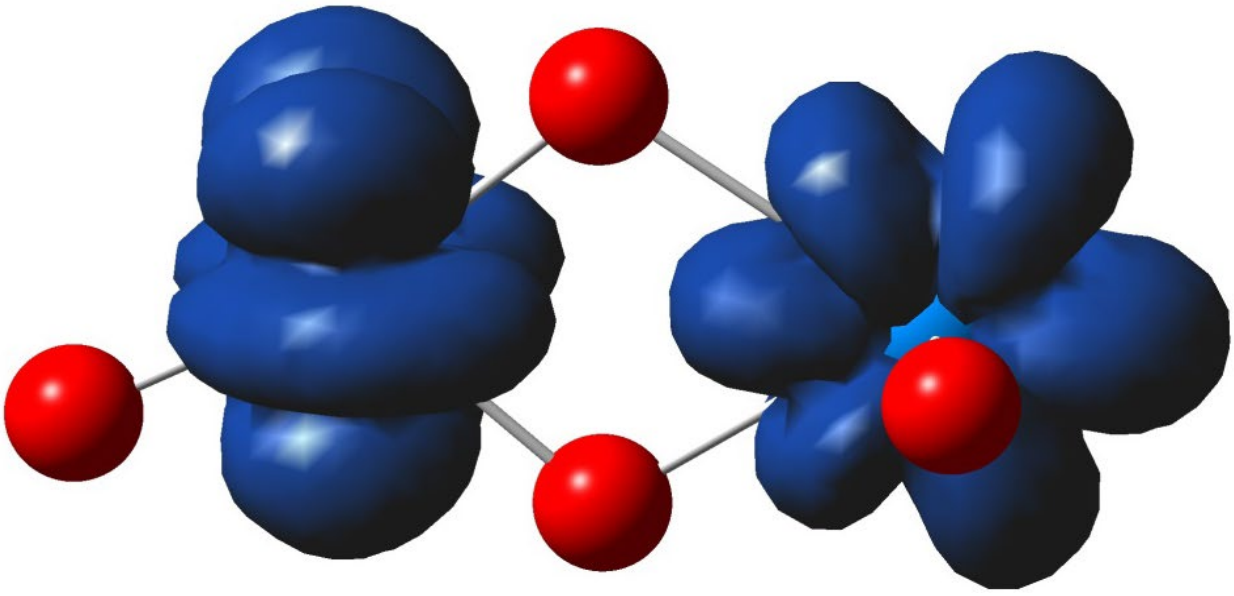
Figure S9. Molecular parameters and singly occupied orbital of $^{2}UO_3^{+}$.



U	0.000000	0.000000	0.127886
O	0.000000	0.000000	-1.873451
O	0.000000	1.746807	0.201379
O	0.000000	-1.746807	0.201379

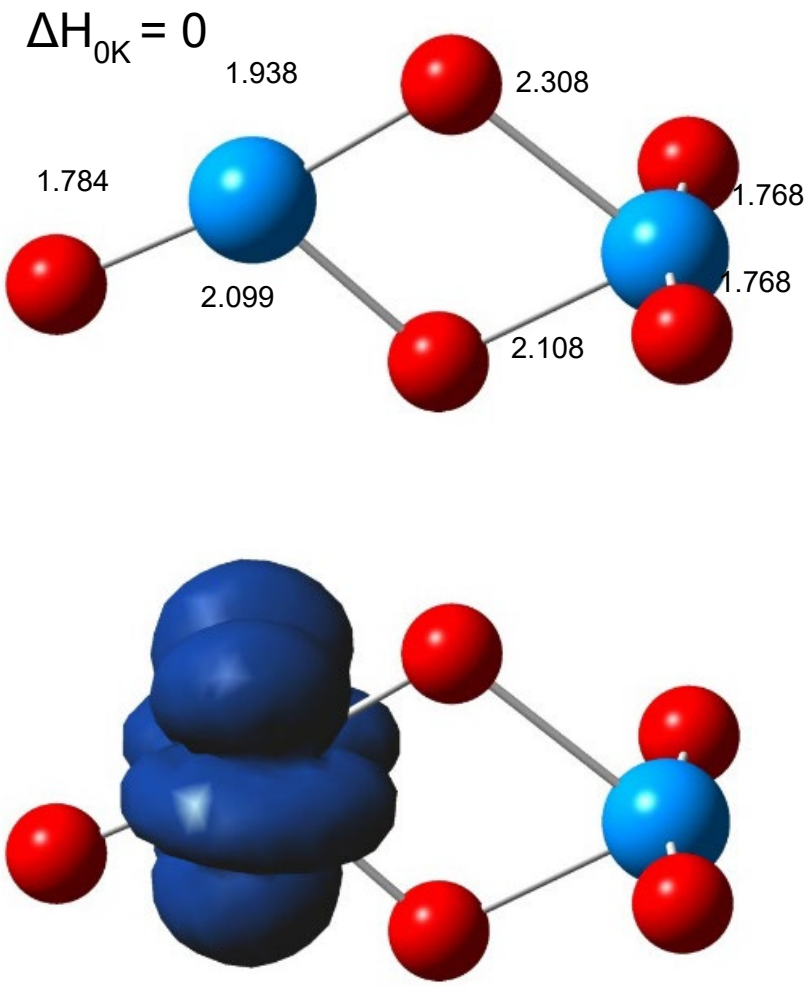
Figure S10. Molecular parameters and singly occupied orbital of $^3U_2O_5$.





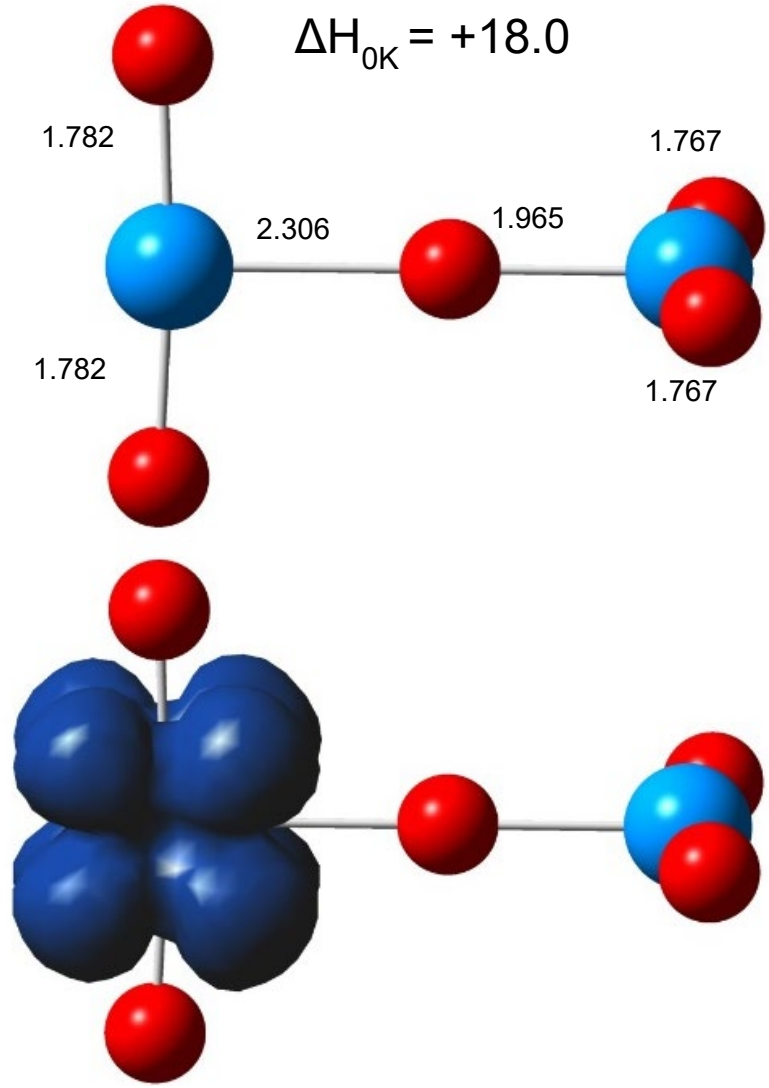
O	0.806139	3.345859	0.000000
O	-1.327204	0.284722	0.000000
O	1.242530	0.185844	0.000000
O	-0.040086	-1.919100	1.820038
O	-0.040086	-1.919100	-1.820038
U	-0.015679	-1.725697	0.000000
U	-0.040086	1.727590	0.000000

Figure S11. Molecular parameters and singly occupied orbital of the C_s isomer of $^2U_2O_5^+$.



O	-1.021151	3.190187	0.000000
O	-1.196705	-0.521338	0.000000
O	0.979963	0.683903	0.000000
O	0.979963	-1.578946	1.760130
O	0.979963	-1.578946	-1.760130
U	0.927709	-1.422979	0.000000
U	-0.990495	1.406034	0.000000

Figure S12. Molecular parameters and singly occupied orbital of the C_{2v} isomer of $^{2}U_2O_5^{+}$.



O	0.000000	1.756379	-2.310499
O	0.000000	-1.756379	-2.310499
O	0.000000	0.000000	-0.155773
O	-1.780424	0.000000	2.221908
O	1.780424	0.000000	2.221908
U	0.000000	0.000000	2.149945
U	0.000000	0.000000	-2.120993

Figure S13. Molecular parameters and singly occupied orbital of $^4U_2O_5^+$.

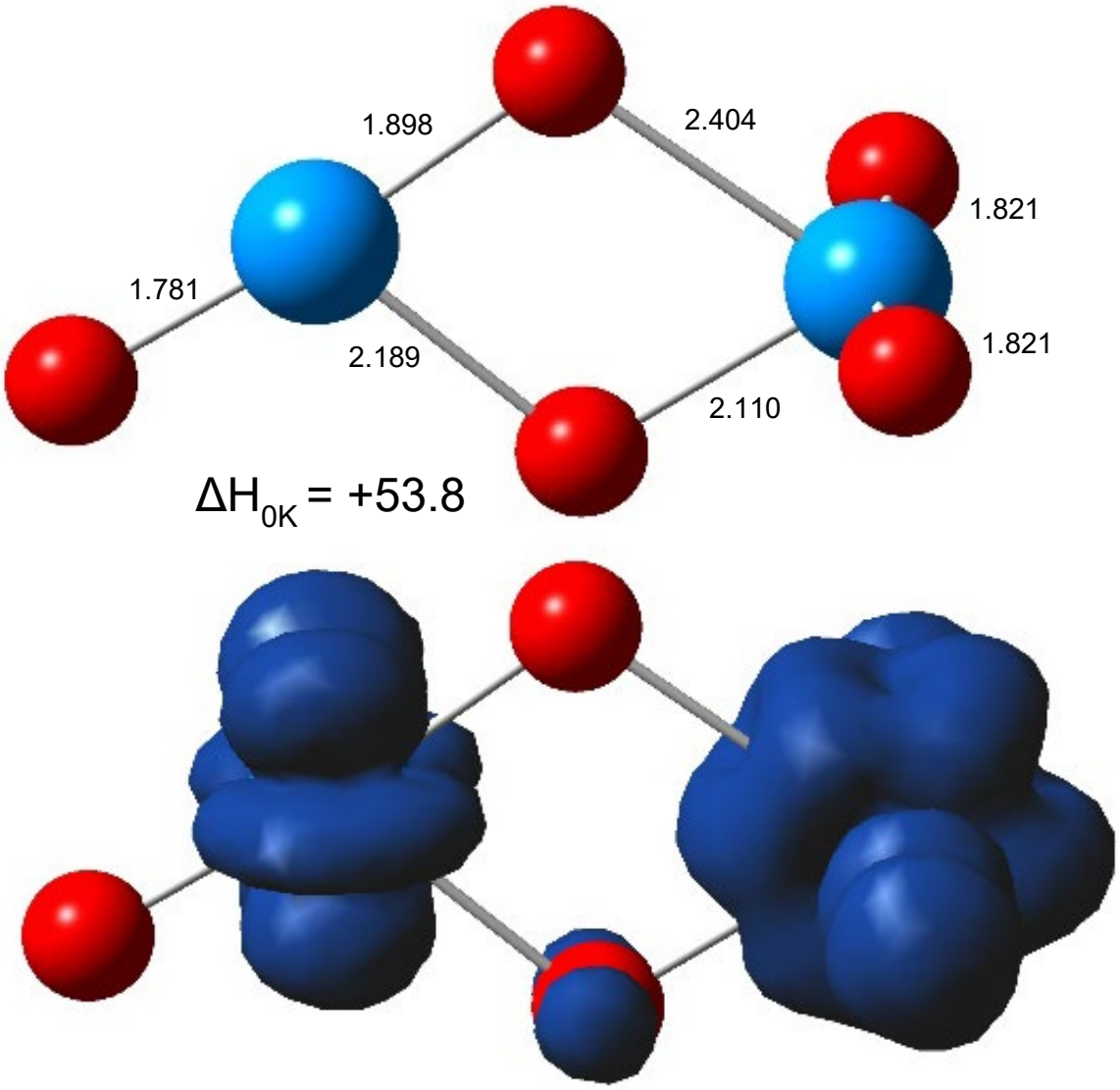
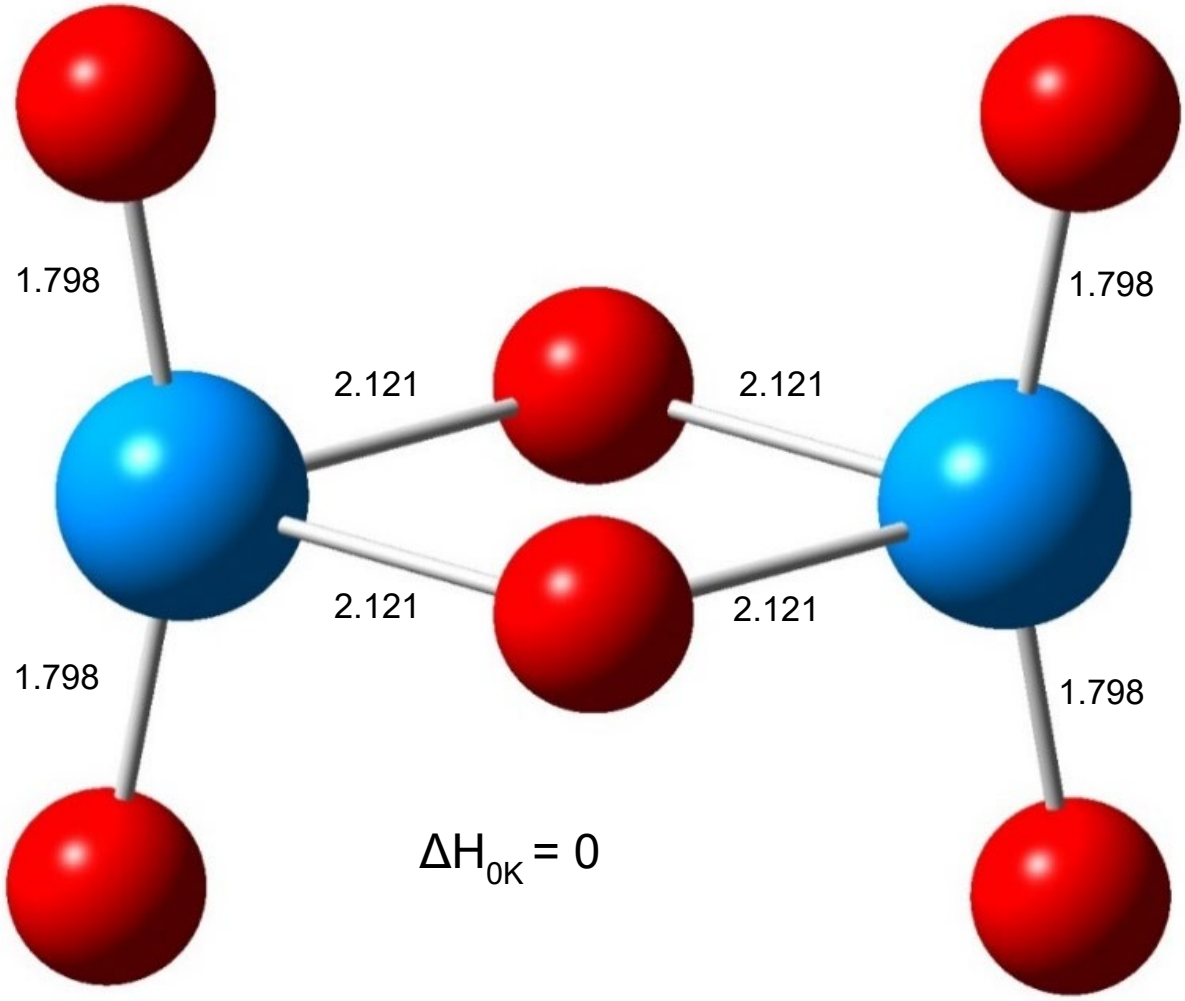


Figure S14. Molecular parameters of $^{1}U_2O_6$.



O	1.999222	1.773442	0.000000
O	1.999222	-1.773442	0.000000
O	0.000000	0.000000	1.262556
O	0.000000	0.000000	-1.262556
O	-1.999222	-1.773442	0.000000
O	-1.999222	1.773442	0.000000
U	-1.704321	0.000000	0.000000
U	1.704321	0.000000	0.000000

Figure S15. Molecular parameters and singly occupied orbital of $^3U_2O_6$.

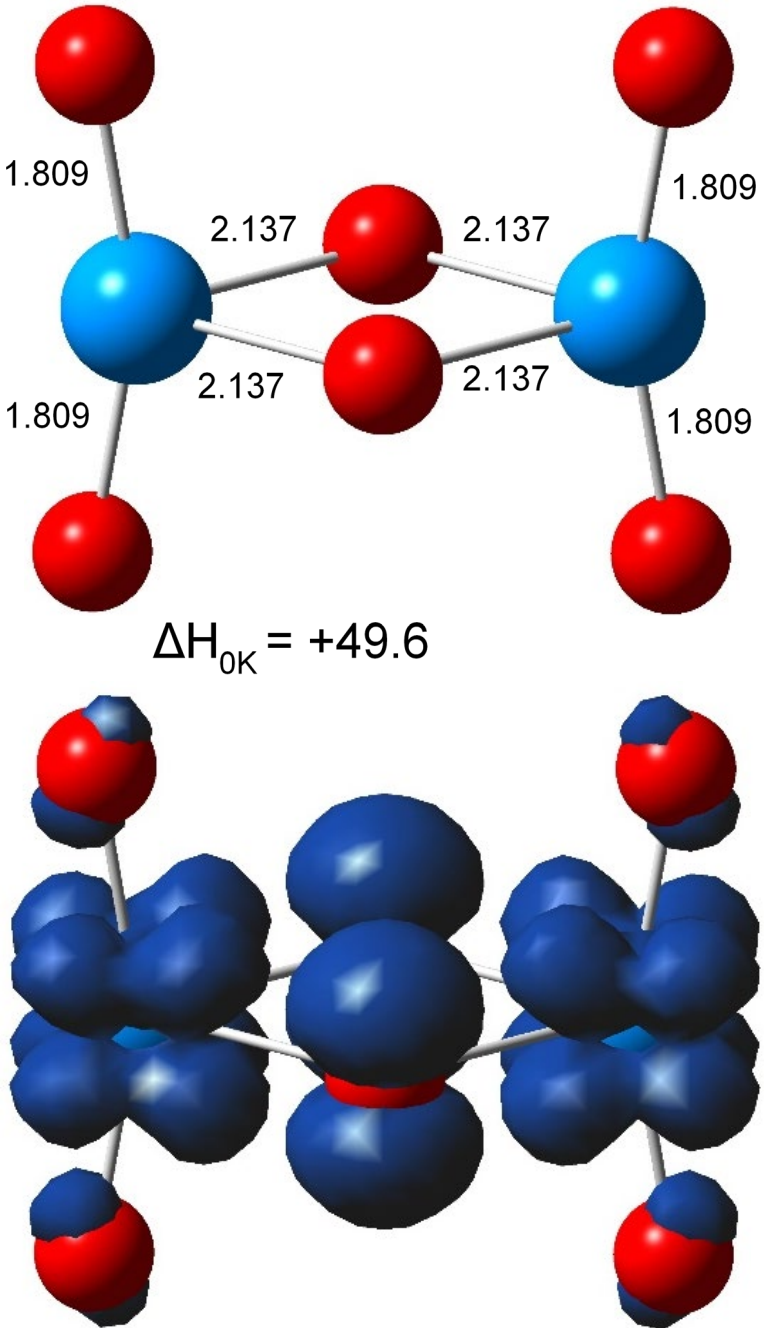
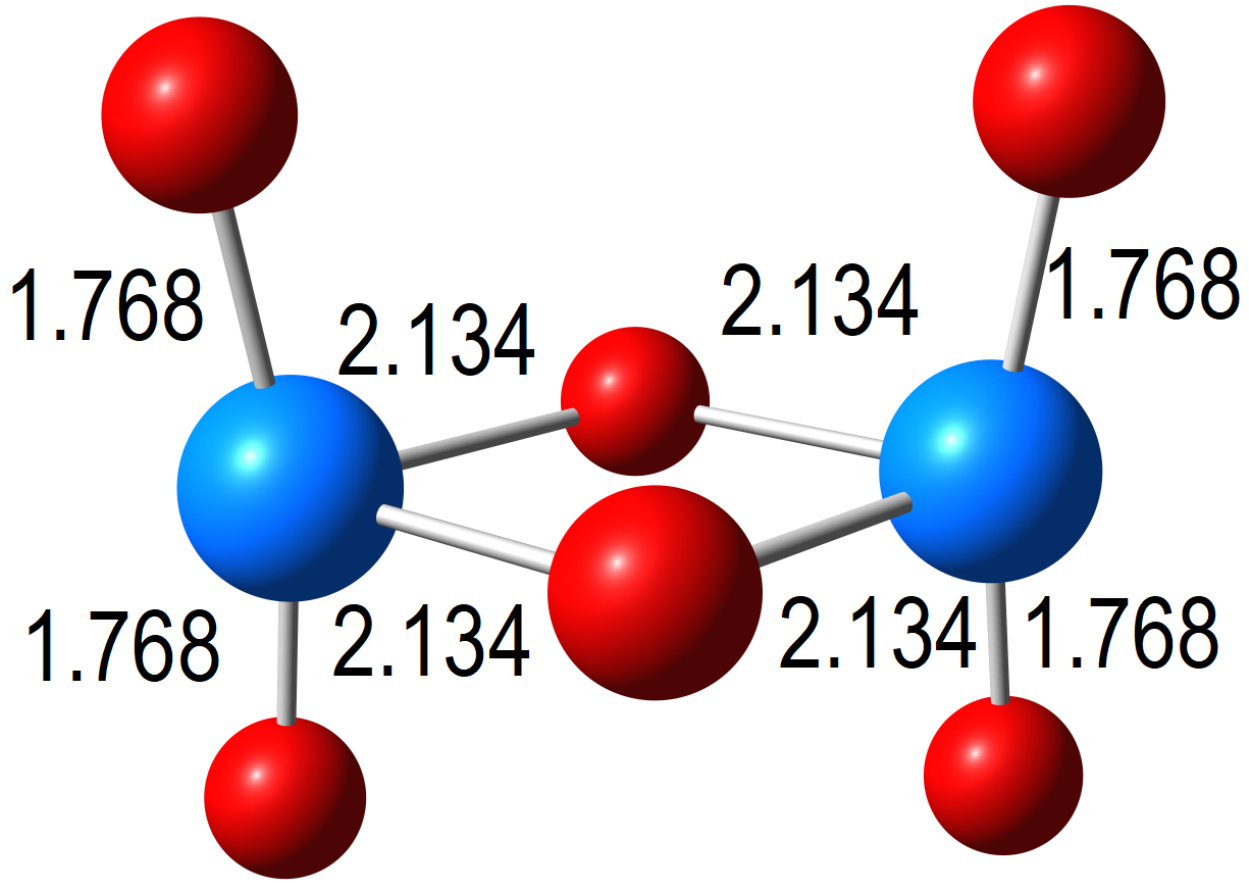
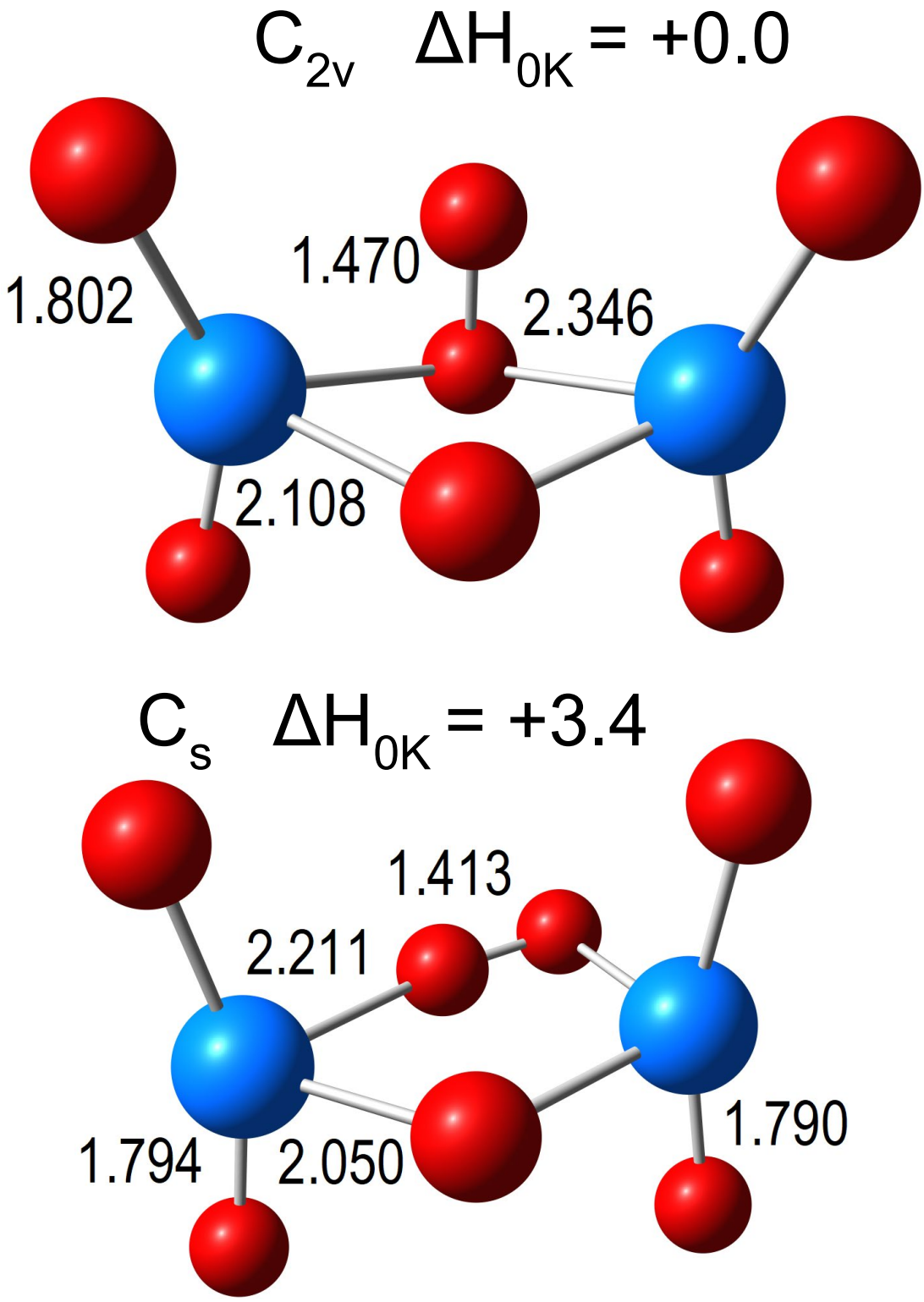


Figure S16. Molecular parameters and singly occupied orbital of $^{2}U_2O_6^{+}$.



O	1.923204	1.755496	0.000000
O	1.923204	-1.755496	0.000000
O	0.000000	0.000000	1.274031
O	0.000000	0.000000	-1.274031
O	-1.923204	-1.755496	0.000000
O	-1.923204	1.755496	0.000000
U	-1.712324	0.000000	0.000000
U	1.712324	0.000000	0.000000

Figure S17. Molecular parameters and singly occupied orbital of $^1U_2O_7$.



$^1U_2O_7$ (C_{2v})

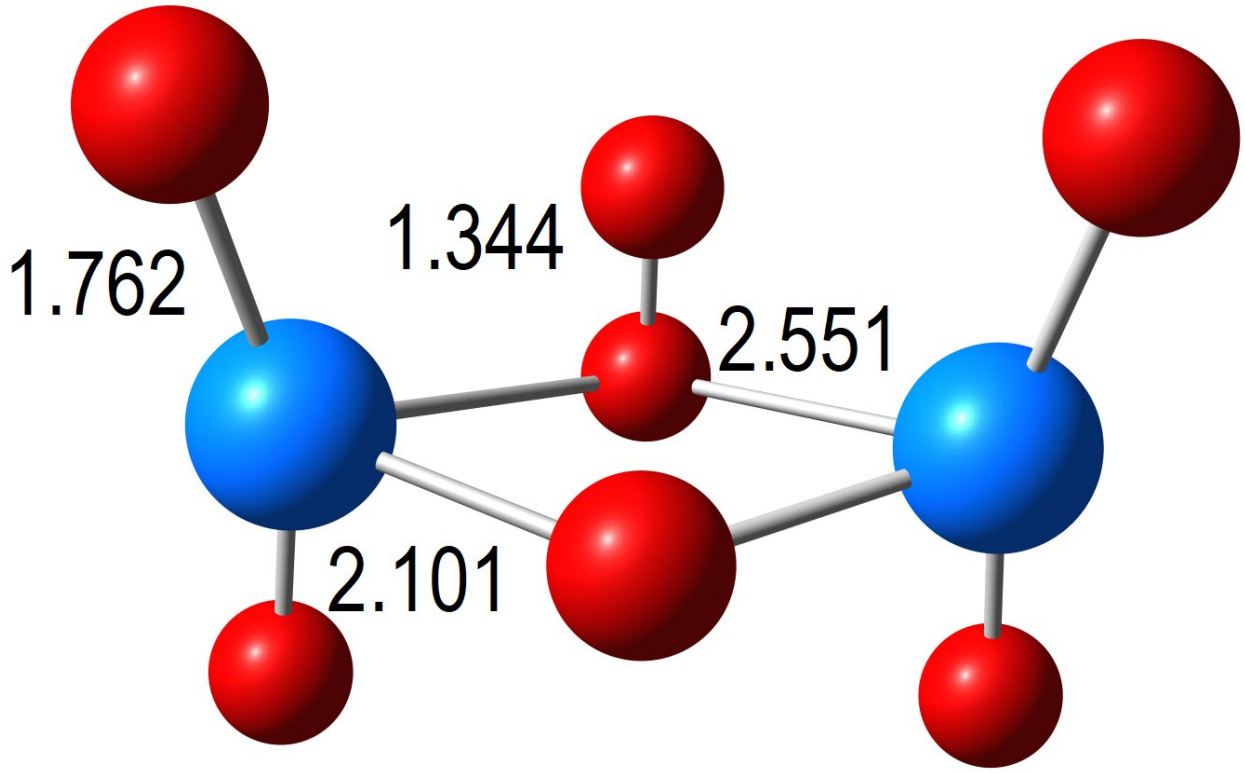
O	2.202091	1.731684	0.212054
O	-2.202091	-1.731684	0.212054

O	-2.202091	1.731684	0.212054
O	0.000000	0.000000	1.220833
O	2.202091	-1.731684	0.212054
O	0.000000	-0.735072	-1.364753
O	0.000000	0.735072	-1.364753
U	1.738267	0.000000	0.028716
U	-1.738267	0.000000	0.028716

$^{1}U_2O_7$ (C_s)

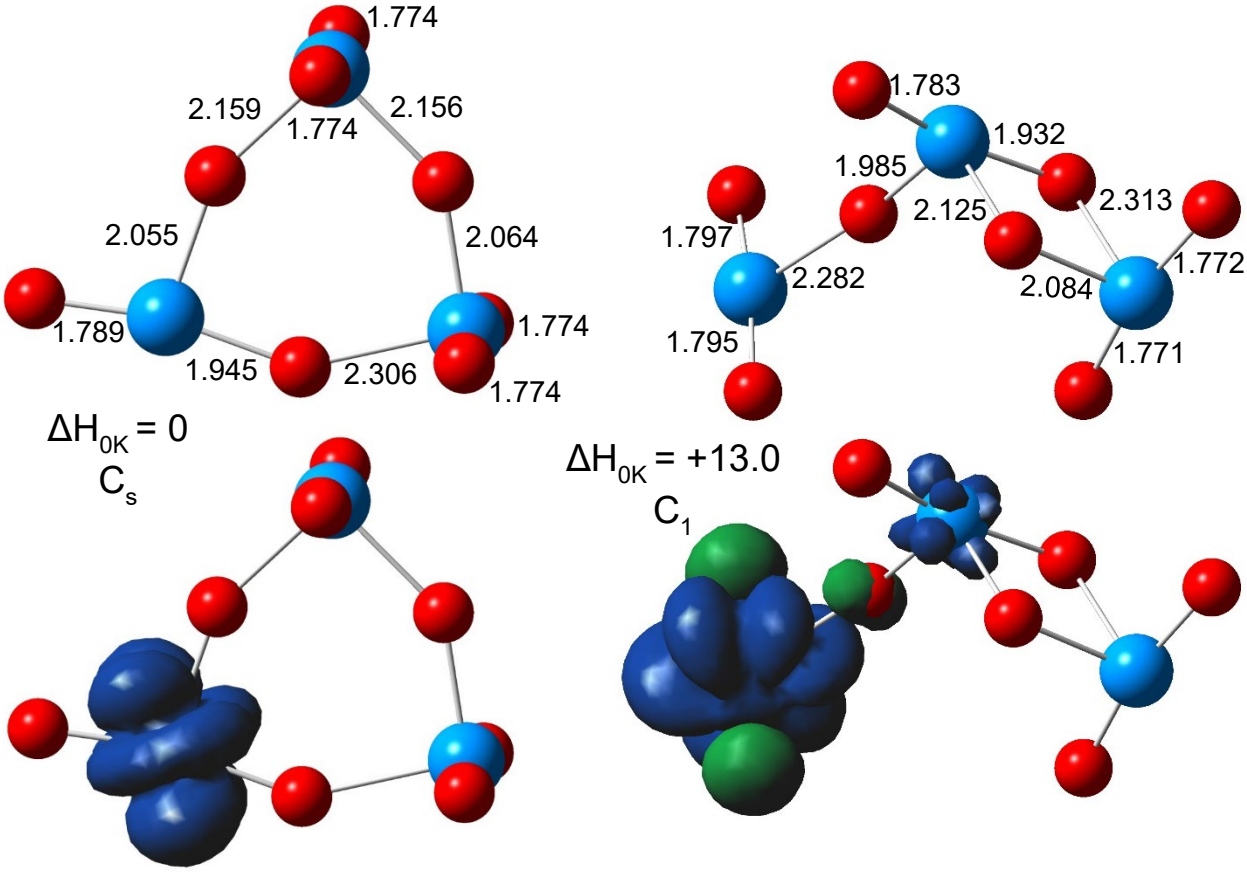
O	-0.135072	-1.966693	1.770929
O	-0.135072	2.101825	-1.763696
O	-0.135072	2.101825	1.763696
O	-1.279036	0.090642	0.000000
O	-0.135072	-1.966693	-1.770929
O	2.089933	-1.079182	0.000000
O	1.385518	0.145453	0.000000
U	-0.034715	-1.724897	0.000000
U	-0.109296	1.774708	0.000000

Figure S18. Molecular parameters and singly occupied orbital of $^{2}U_2O_7^{+}$.



O	2.112082	1.738763	0.151586
O	-2.112082	-1.738763	0.151586
O	-2.112082	1.738763	0.151586
O	0.000000	0.000000	1.072489
O	2.112082	-1.738763	0.151586
O	0.000000	-0.671792	-1.567571
O	0.000000	0.671792	-1.567571
U	1.842435	0.000000	0.063318
U	-1.842435	0.000000	0.063318

Figure S19. Molecular parameters and singly occupied orbital for ring and chain isomers of $^2U_3O_8^+$.



$^2U_3O_8^+$ (C_1)

1 1

O	1.384775	0.383550	-1.273107
O	1.741848	0.358706	1.194398
O	-1.265625	0.396295	-0.166080
O	-3.999478	0.377685	-1.348909
O	-2.830756	-1.680788	1.343163
O	4.198673	0.219469	-0.256341
O	-0.238373	2.676234	1.130962
O	1.752029	-2.293409	0.075805
U	2.850238	-0.908299	-0.034259
U	0.397334	1.471001	-0.018700
U	-3.312189	-0.600767	-0.007902

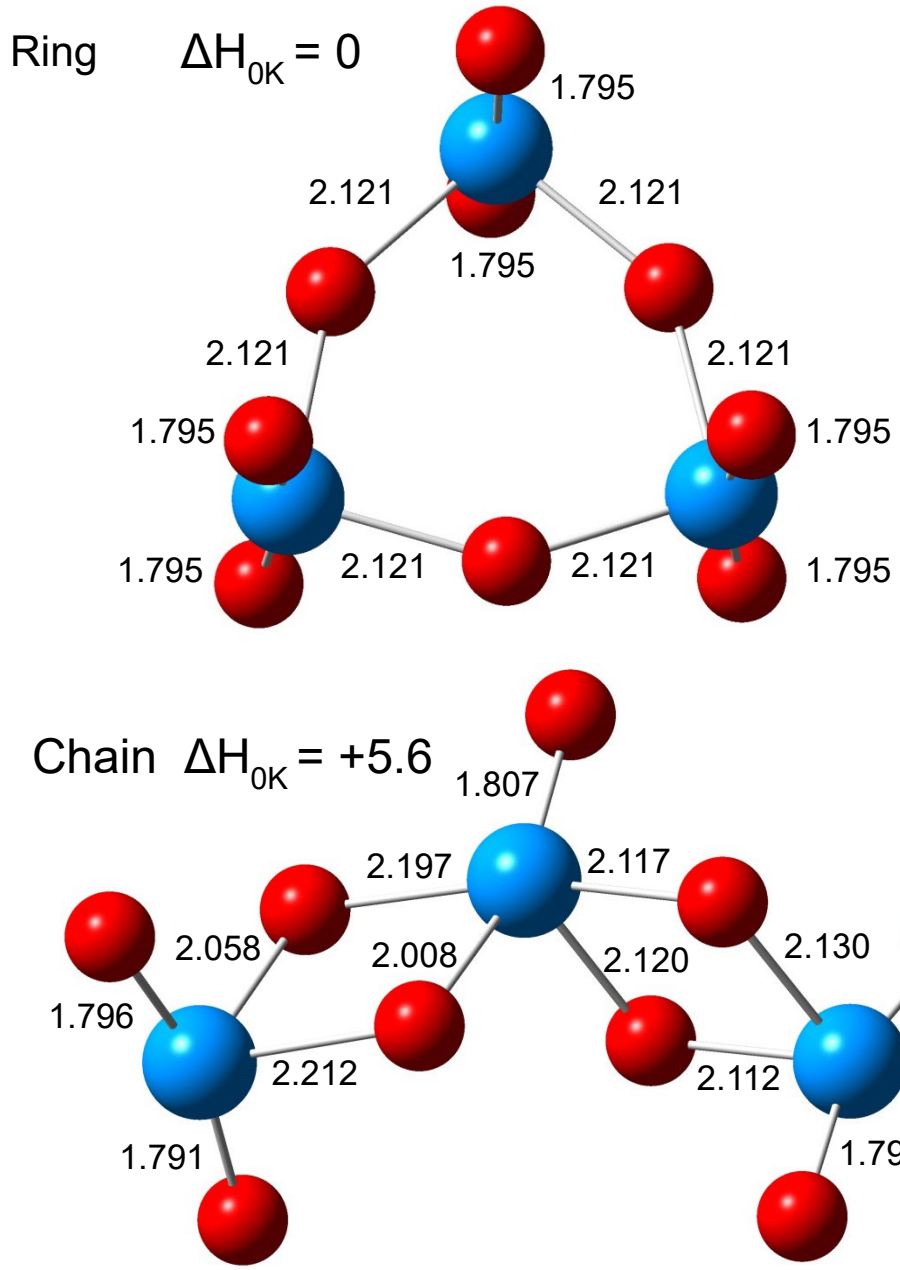
$^2U_3O_8^+$ (C_s)

1 1

O	1.205609	-2.172393	1.765009
O	1.205609	-2.172393	-1.765009
O	1.819032	0.043845	0.000000
O	-0.925062	-1.375490	0.000000

O	1.205609	2.201289	-1.763205
O	1.205609	2.201289	1.763205
O	-3.878136	-0.942576	0.000000
O	-1.054292	1.467948	0.000000
U	1.186989	2.008431	0.000000
U	-2.396166	0.059935	0.000000
U	1.141004	-2.003281	0.000000

Figure S20. Molecular parameters of ring and chain isomers of $^1U_3O_9$.

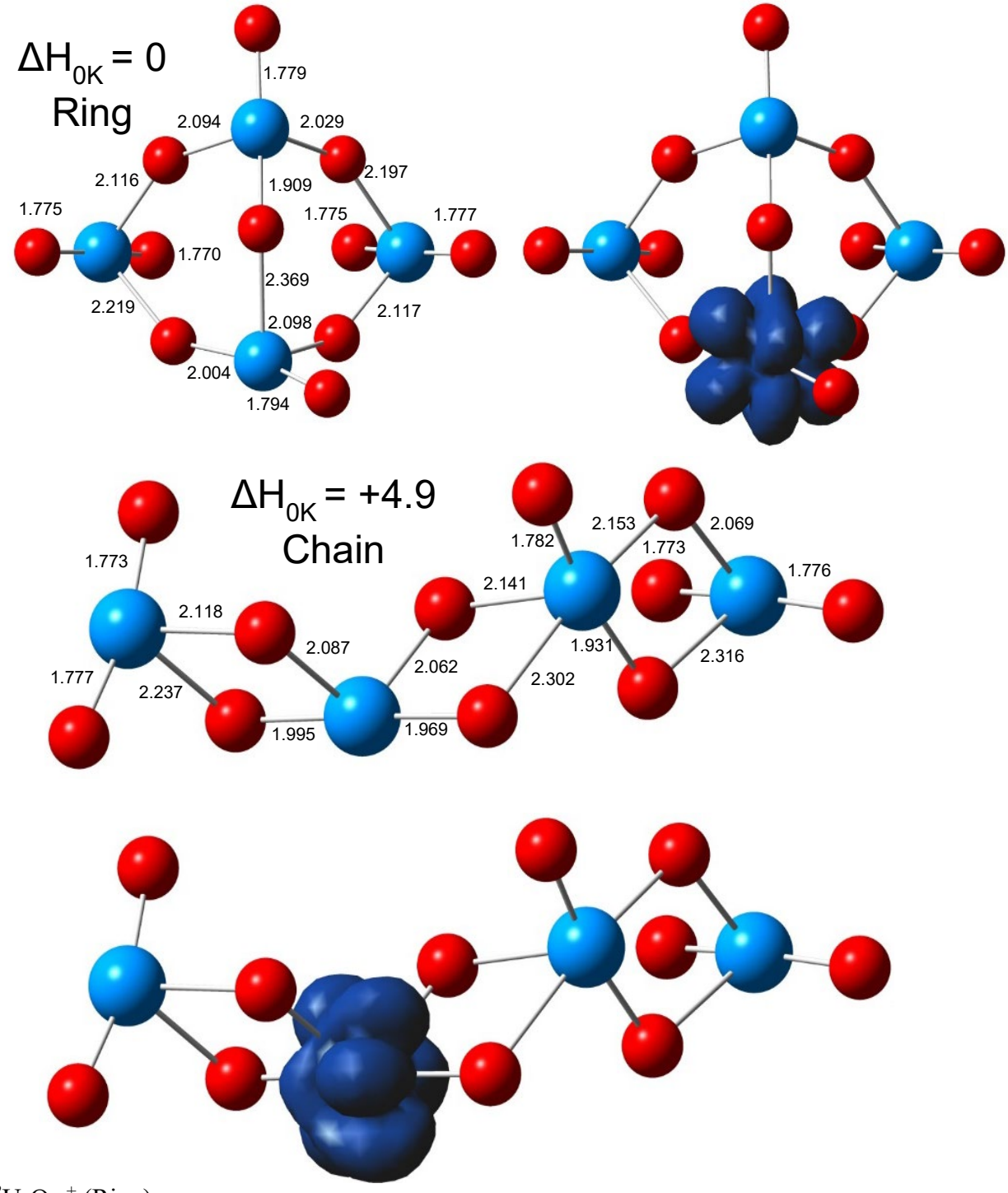


$^1U_3O_9$ (ring)

O	-1.774934	2.246330	-1.296577
O	1.774934	2.246330	-1.296577
O	0.000000	0.000000	-1.816743
O	0.000000	1.590856	0.916727
O	1.774934	-2.246330	-1.296577
O	-1.774934	-2.246330	-1.296577
O	-1.774701	0.000000	2.584738
O	0.000000	-1.590856	0.916727

O	1.774701	0.000000	2.584738
U	0.000000	-2.015737	-1.160814
U	0.000000	0.000000	2.321639
U	0.000000	2.015737	-1.160814

Figure S21. Molecular parameters for ring and chain isomers of $^2U_4O_{11}^+$.



$^2U_4O_{11}^+$ (Ring)

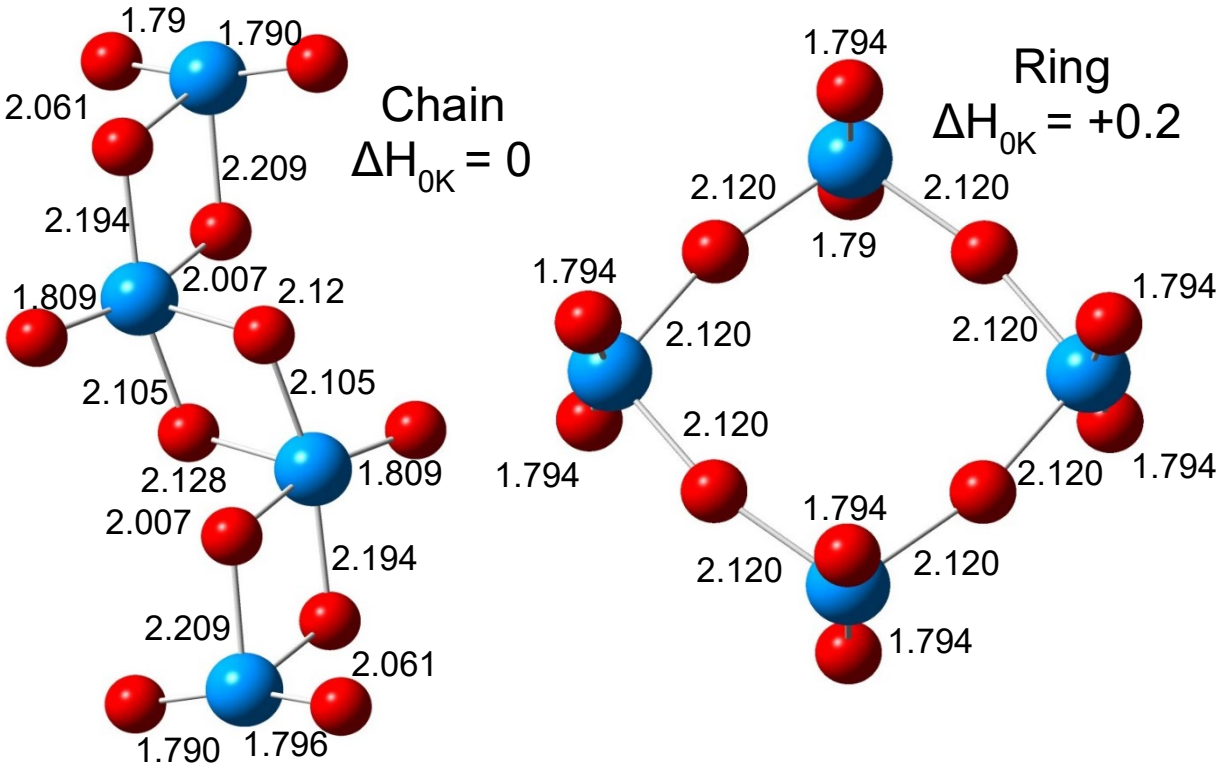
O	0.203876	3.698010	-0.976262
O	0.058033	0.138820	-1.839306
O	-1.466743	1.592395	0.039325
O	1.725532	1.445111	0.030172
O	-1.221494	-2.715502	-2.245091

O	1.804555	0.033882	2.532778
O	1.468908	-1.674114	0.177554
O	3.995611	-0.267388	-0.215518
O	-1.858598	0.329902	2.663335
O	-3.866867	0.021548	-0.223652
O	-1.492518	-1.476523	0.457865
U	-2.703923	0.130569	1.115138
U	-0.103886	-2.070232	-0.999041
U	2.760662	-0.094458	1.048222
U	0.103644	1.936196	-1.199205

$^{2}U_4O_{11}^{+}$ (Chain)

O	0.003871	0.464324	0.250182
O	-2.970433	-0.968142	0.339519
O	-2.878061	1.153905	-0.978878
O	-3.823777	1.365803	1.849428
O	-5.489955	-0.207726	-0.832096
O	3.208248	-0.058557	1.402540
O	2.575465	-0.260131	-1.007800
O	-0.126796	-1.699148	-0.998388
O	0.840893	-1.867695	1.836468
O	3.632367	2.407702	-0.023129
O	5.459330	-0.599013	-0.262535
U	4.395645	0.807496	-0.054453
U	1.539430	-1.015866	0.436053
U	-1.490488	-0.279832	-0.960973
U	-4.482079	0.511564	0.442390

Figure S22. Molecular parameters of ring and chain isomers of $^{1}U_4O_{12}$.



U_4O_{12} (Ring)

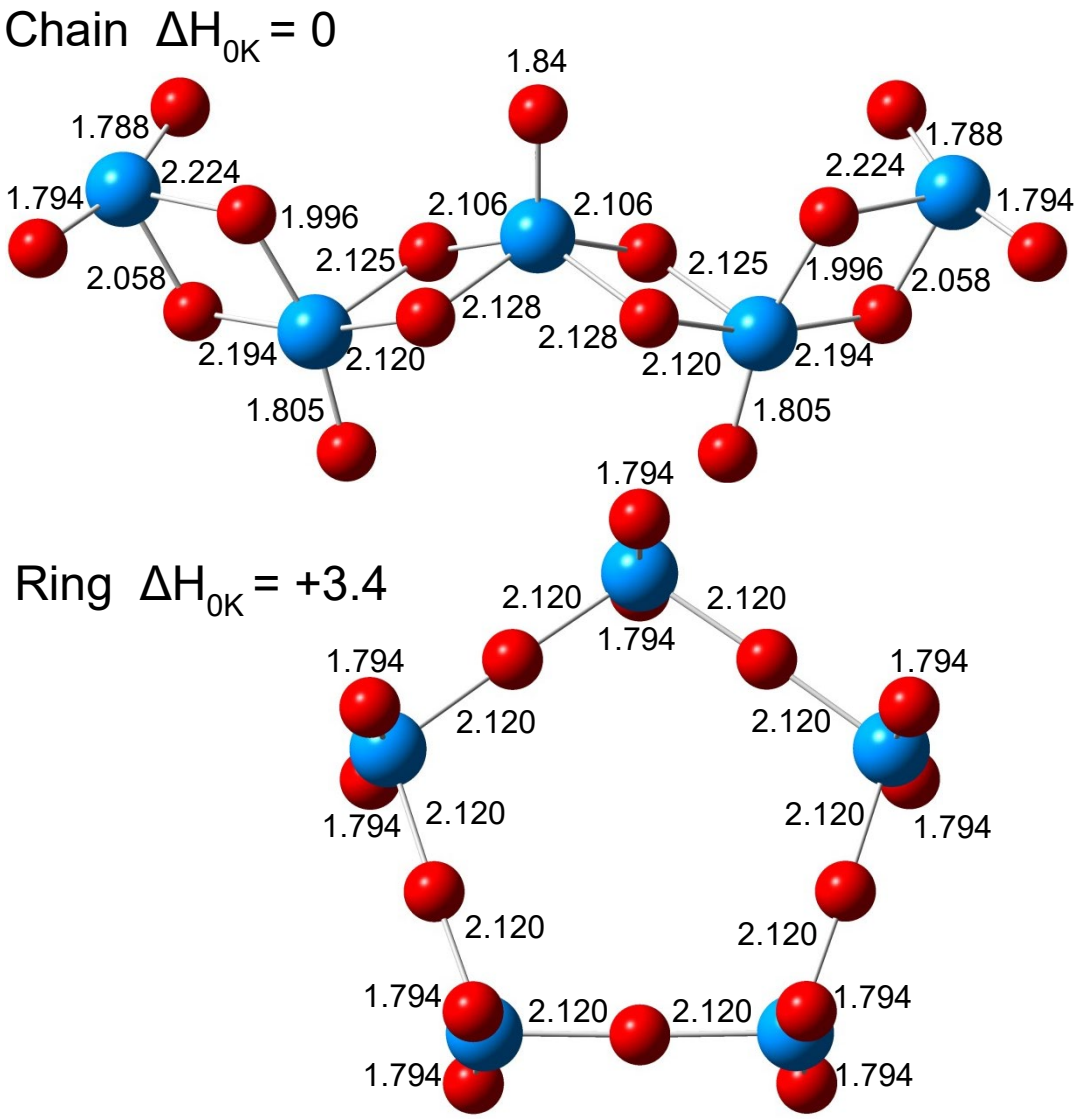
O	2.289816	2.289816	1.774790
O	2.289816	2.289816	-1.774790
O	0.000000	2.364613	0.000000
O	2.364613	0.000000	0.000000
O	-2.289816	-2.289816	-1.774790
O	-2.289816	-2.289816	1.774790
O	2.289816	-2.289816	1.774790
O	0.000000	-2.364613	0.000000
O	2.289816	-2.289816	-1.774790
O	-2.289816	2.289816	1.774790
O	-2.289816	2.289816	-1.774790
O	-2.364613	0.000000	0.000000
U	-2.103916	2.103916	0.000000
U	-2.103916	-2.103916	0.000000
U	2.103916	-2.103916	0.000000
U	2.103916	2.103916	0.000000

U_4O_{12} (Chain)

O	0.483972	0.339370	1.100944
O	-0.483972	-0.339370	-1.100944
O	-1.048312	3.350144	0.961985
O	0.318051	2.535711	-0.974534

O	1.713656	4.250819	1.098057
O	-0.806888	5.258230	-1.187538
O	1.048312	-3.350144	-0.961985
O	-0.318051	-2.535711	0.974534
O	-2.537593	0.742911	0.715968
O	2.537593	-0.742911	-0.715968
O	-1.713656	-4.250819	-1.098057
O	0.806888	-5.258230	1.187538
U	-0.336518	-4.524468	0.012349
U	1.006280	-1.380591	0.004590
U	-1.006280	1.380591	-0.004590
U	0.336518	4.524468	-0.012349

Figure S23. Molecular parameters of ring and chain isomers of $^{1}U_5O_{15}$.



$^{1}U_5O_{15}$ (Chain)

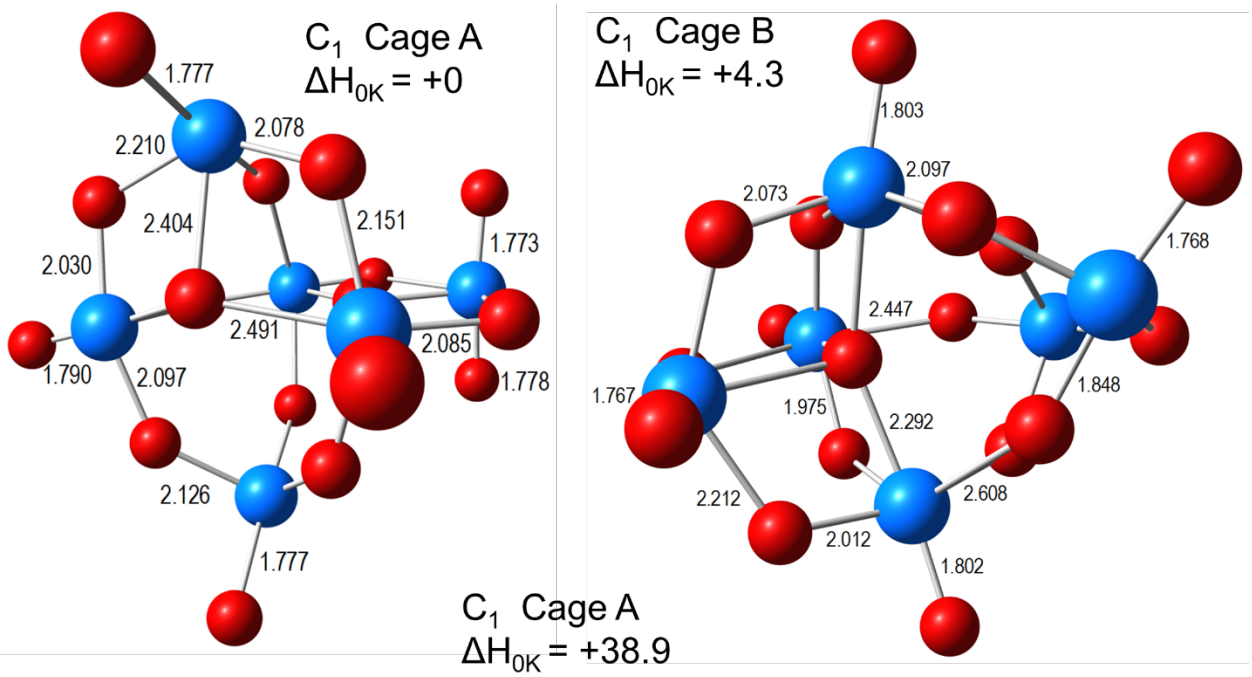
O	0.277647	-0.633889	1.529918
O	-1.284954	1.291860	1.563248
O	-0.383537	-1.336573	4.822682
O	0.315660	0.951746	4.074818
O	2.483010	-0.955508	5.011241
O	-0.056570	0.528342	6.991729
O	-1.284954	1.291860	-1.563248
O	0.277647	-0.633889	-1.529918
O	-2.488910	-1.134481	2.666287
O	1.472609	1.986511	0.000000
O	-2.488910	-1.134481	-2.666287
O	0.315660	0.951746	-4.074818
O	-0.383537	-1.336573	-4.822682
O	-0.056570	0.528342	-6.991729

O	2.483010	-0.955508	-5.011241
U	1.051369	-0.235921	-5.805309
U	-1.052321	-0.137380	-3.111717
U	0.071703	0.797949	0.000000
U	-1.052321	-0.137380	3.111717
U	1.051369	-0.235921	5.805309

$^{1}U_5O_{15}$ (Ring)

O	3.674655	-1.193968	1.775225
O	3.674655	-1.193968	-1.775225
O	0.000000	2.946370	0.000000
O	1.731833	-2.383663	0.000000
O	-3.674655	-1.193968	-1.775225
O	-3.674655	-1.193968	1.775225
O	0.000000	-3.863761	1.775225
O	-1.731833	-2.383663	0.000000
O	0.000000	-3.863761	-1.775225
O	-2.271062	3.125848	1.775225
O	-2.271062	3.125848	-1.775225
O	-2.802164	0.910478	0.000000
O	2.802164	0.910478	0.000000
O	2.271062	3.125848	1.775225
O	2.271062	3.125848	-1.775225
U	3.430074	-1.114499	0.000000
U	2.119902	2.917795	0.000000
U	-2.119902	2.917795	0.000000
U	-3.430074	-1.114499	0.000000
U	0.000000	-3.606593	0.000000

Figure S24. Molecular parameters for a predicted structure of $^2U_6O_{17}^+$.



$^2U_6O_{17}^+$ (Cage A)

O	1.499018	0.337916	-2.004288
O	1.462934	-0.462478	0.896976
O	-2.872852	-0.457526	1.714802
O	0.365691	-2.155731	-1.377337
O	-0.300594	-2.366568	1.380008
O	-0.520984	1.842507	1.615983
O	-0.381830	2.261769	-1.196099
O	-3.507989	-2.172239	-0.519979
O	2.150224	2.210253	0.165740
O	3.107056	-1.665106	-0.604943
O	-1.201268	-0.202341	-0.124153
O	4.439911	0.922563	-1.020726
O	-2.209572	-0.211314	-2.457800
O	-0.371598	-0.401938	3.668528
O	2.295401	-3.504071	1.443630
O	0.790365	4.405677	1.520990

O	-3.773026	1.349435	-0.345261
U	2.980369	0.316326	-0.179732
U	0.271295	3.191041	0.331900
U	1.335057	-2.745375	0.154935
U	-3.505594	-0.408719	-0.340002
U	-0.801624	-0.347469	1.928693
U	-0.363928	0.017603	-2.135452

$^{2}U_6O_{17}^{+}$ (Cage B)

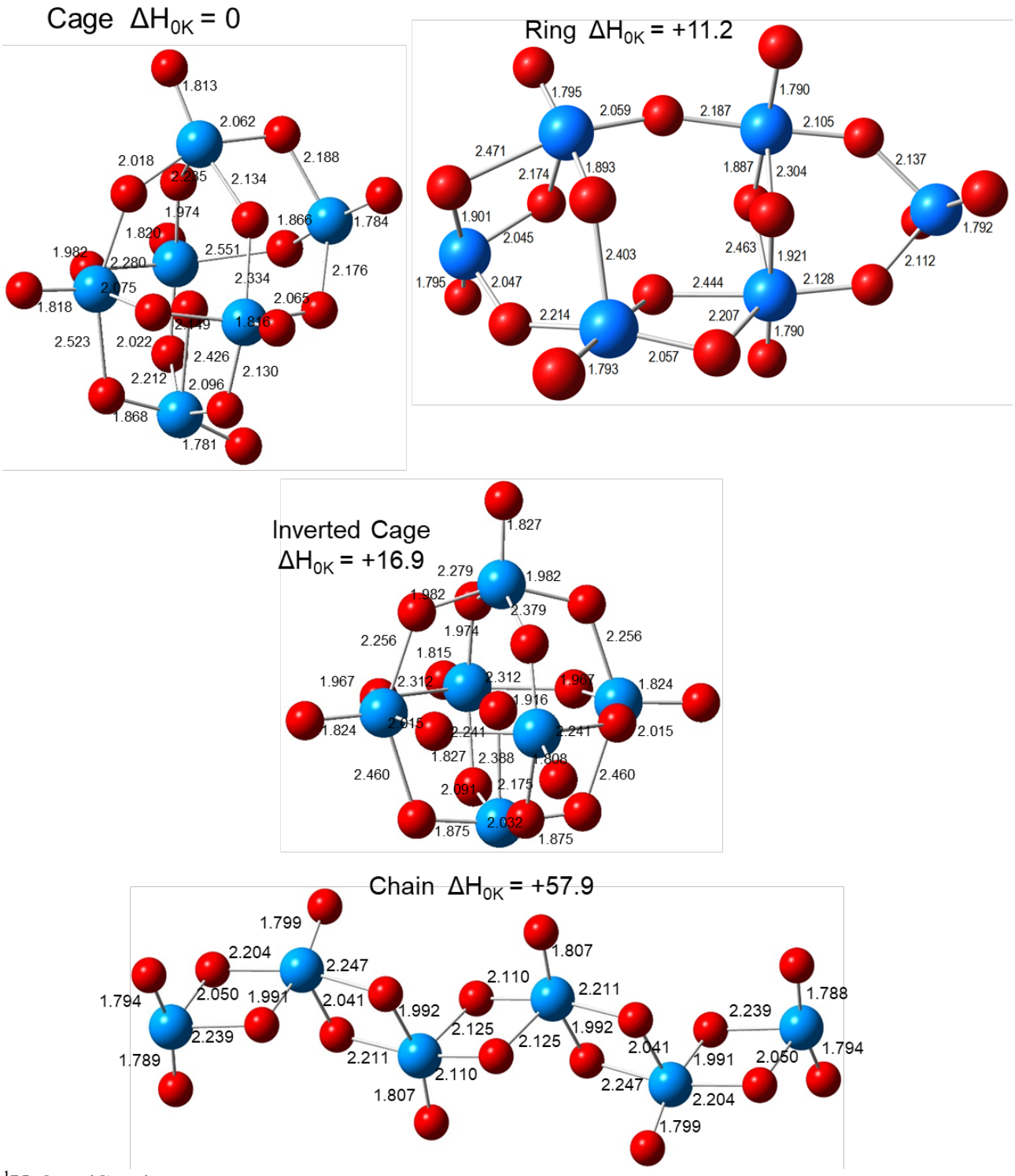
O	1.200871	-1.975914	1.198349
O	1.755759	0.327678	-0.980486
O	-1.886309	2.269562	-0.904724
O	1.452113	0.716459	1.987276
O	1.048062	2.591113	-0.019239
O	-0.983826	-0.084020	-2.529508
O	-1.496876	-2.374702	0.488530
O	-2.605233	2.608596	1.751267
O	-0.770089	0.106952	0.101561
O	0.792483	-2.327877	-1.542251
O	3.593681	-0.727319	0.443188
O	-2.145803	-0.080876	2.316517
O	-0.293714	-1.892127	3.634536
O	0.655017	2.456011	-3.031978
O	3.948724	2.243782	-0.118231
O	-2.377572	-2.766345	-2.438152
O	-3.384237	-0.175855	-0.417553
U	2.328767	-1.718468	-0.603416
U	-1.537722	-1.611710	-1.332675
U	2.653337	1.459606	0.795148
U	-2.865797	1.225105	0.683037
U	-0.019298	1.655666	-1.563497
U	-0.429118	-1.089773	2.026698

$^{2}U_6O_{17}^{+}$ (Chain)

O	3.605082	-1.624681	-0.528745
O	2.346807	-0.670044	1.415958
O	6.379852	0.272186	0.437155
O	4.143322	1.337252	0.118285
O	6.022414	1.252401	-2.252299
O	6.451341	3.123195	0.710762
O	-0.185248	-2.357211	0.290670
O	0.640007	-0.744451	-1.444937
O	4.917427	-1.680652	2.161572
O	-1.468140	-2.423342	-2.412426
O	-3.478757	-1.363525	-0.487713

O	-1.708189	0.314523	0.067027
O	-3.372026	-0.774896	2.378009
O	-6.035250	0.107330	1.238315
O	-4.604656	1.324544	-0.415562
O	-7.209241	0.101640	-1.391790
O	-6.878240	2.807686	0.848384
U	-6.898716	1.348474	-0.168146
U	-3.897143	0.114083	0.922369
U	-1.459758	-1.147496	-1.153763
U	1.693713	-1.938382	-0.119119
U	4.422956	-0.312143	1.114530
U	6.176644	2.022250	-0.659582

Figure S25. Molecular parameters for three predicted structures of $^{1}U_6O_{18}$.



$^{1}U_6O_{18}$ (Cage)

O	-1.337937	1.711891	1.370863
O	-1.693949	-0.431965	-1.015780
O	2.220948	-2.040963	-1.035356
O	-1.237468	-1.044441	1.964039

O	-0.694784	-2.696919	-0.241294
O	1.025109	0.260834	-2.549063
O	1.303142	2.427990	0.663758
O	2.965081	-2.485714	1.600120
O	0.823267	-0.092131	0.064206
O	-0.823306	2.214738	-1.362070
O	-3.526815	0.099395	0.627134
O	2.147298	0.090843	2.332096
O	-3.620438	2.905442	-0.534457
O	0.178934	1.580805	3.808903
O	-0.188937	-2.432488	-3.188739
O	-3.630198	-2.700911	-0.214539
O	2.145335	3.084734	-2.269841
O	3.391763	0.528245	-0.383496
U	-2.505131	1.476070	-0.519366
U	1.385723	1.812337	-1.216738
U	-2.416257	-1.785419	0.719451
U	3.001561	-1.004465	0.611686
U	0.251384	-1.538845	-1.670046
U	0.330803	0.955158	2.106623

$^{1}U_6O_{18}$ (Ring)

O	-5.535728	-0.022220	1.929845
O	-5.415594	-0.198236	-1.614717
O	-0.254674	-2.626477	-1.124085
O	-3.899682	1.573874	0.168026
O	1.763566	0.320444	-1.405964
O	2.915890	3.541663	-0.100686
O	-1.571170	0.626926	1.431602
O	-2.037157	3.086330	-1.262199
O	0.836262	-1.308245	0.710305
O	2.417704	-2.724233	-2.279258
O	3.683088	-1.698956	0.085017
O	-3.687304	-1.541590	0.244271
O	-1.551609	-0.145956	-0.997222
O	-1.540771	-2.853136	1.540389
O	3.026724	0.960877	1.255651
O	0.320465	2.323613	-0.021642
O	4.523729	0.933160	-0.765625
O	5.244862	-0.825619	2.374493
U	2.272246	1.925193	-0.540790
U	4.722227	-0.096295	0.819790
U	1.681517	-2.005925	-0.811140
U	-1.559901	-1.561377	0.301878
U	-5.228468	-0.099725	0.165019
U	-1.821413	1.888371	0.050617

$^{1}U_6O_{18}$ (Inverted Cage)

O	0.227331	0.000005	-0.163153
O	-1.917870	2.058053	0.070444
O	-1.917840	-2.058079	0.070446
O	1.912965	-2.201431	-0.250672
O	0.212970	1.915041	2.094314
O	0.212996	-1.915034	2.094315
O	-0.157722	-1.870123	-2.356795
O	-0.157750	1.870119	-2.356797
O	2.374849	0.000019	1.651314
O	1.902098	0.000011	-2.303472
O	-2.107030	-0.000015	-1.900607
O	-1.977609	-0.000013	1.896336
O	1.912936	2.201458	-0.250674
O	-4.510813	-0.000028	-0.403501
O	-0.153085	4.460478	-0.075013
O	-0.153023	-4.460483	-0.075009
O	0.334814	0.000005	4.419161
O	4.402324	0.000025	-0.637170
U	0.008266	-2.643918	-0.034398
U	-2.798176	-0.000018	0.170049
U	0.008231	2.643915	-0.034401
U	2.617416	0.000018	-0.308365
U	0.301668	0.000004	2.591980
U	-0.175714	-0.000002	-2.517341

$^{1}U_6O_{18}$ (Chain)

O	-3.428803	-1.218356	0.401858
O	-2.514531	0.889164	-0.586947
O	-6.516252	-0.926888	-0.920415
O	-5.407820	0.945385	0.333787
O	-7.234297	-0.907397	1.890499
O	-8.194593	1.392110	-0.630791
O	0.198521	1.047189	0.654377
O	-0.198521	-1.047189	-0.654377
O	-3.933107	-0.978167	-2.532472
O	-1.066076	-1.056556	2.283038
O	1.066076	1.056556	-2.283038
O	3.428803	1.218356	-0.401858
O	2.514531	-0.889164	0.586947
O	3.933107	0.978167	2.532472
O	6.516252	0.926888	0.920415
O	5.407820	-0.945385	-0.333787
O	7.234297	0.907397	-1.890499
O	8.194593	-1.392110	0.630791

U	7.506211	-0.176048	-0.494136
U	4.450295	0.159250	1.015980
U	1.515975	0.179268	-0.767317
U	-1.515975	-0.179268	0.767317
U	-4.450295	-0.159250	-1.015980
U	-7.506211	0.176048	0.494136

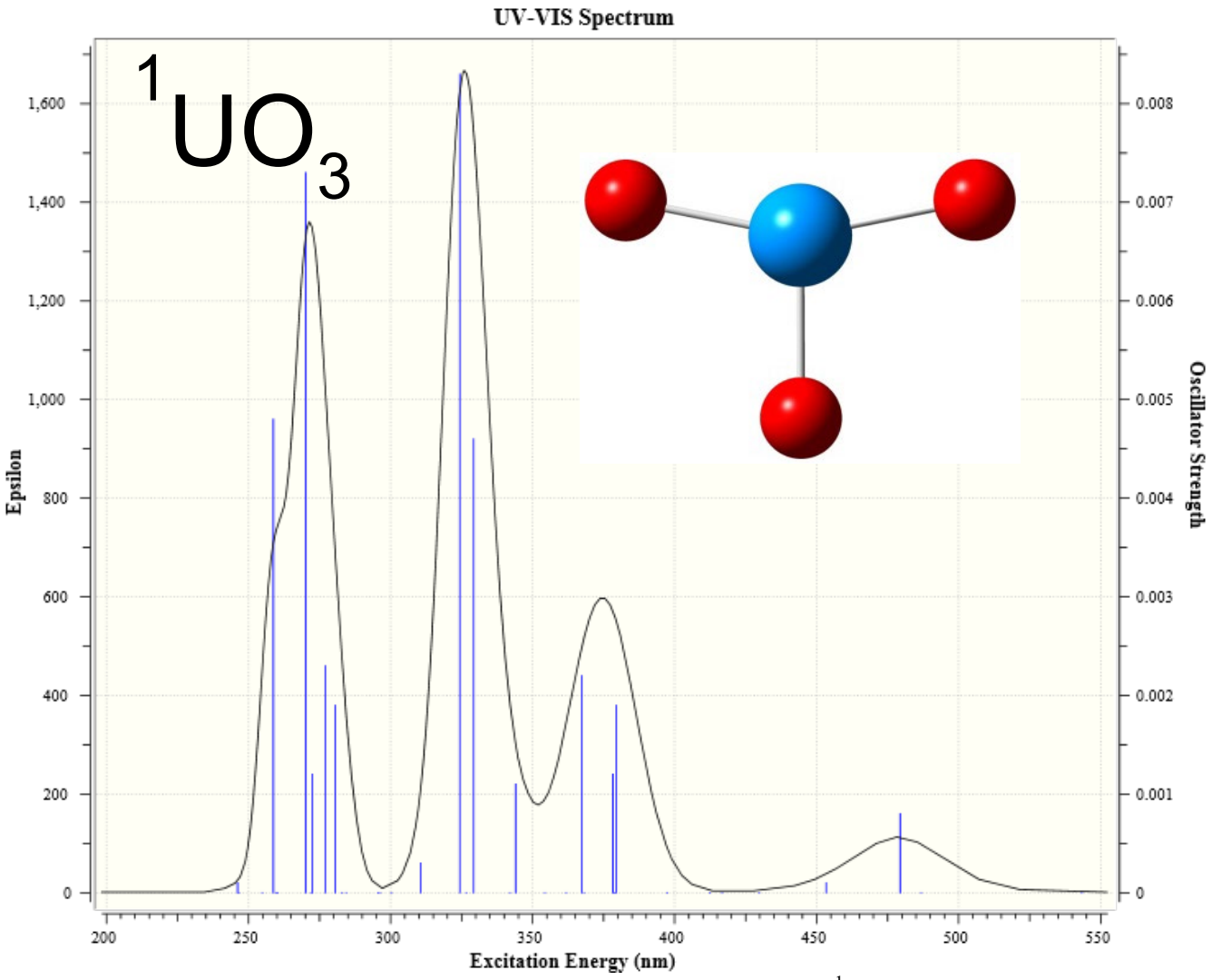


Figure S26. TDDFT B3LYP/aD/D-PP predicted electronic spectrum of $^{1}UO_3$.

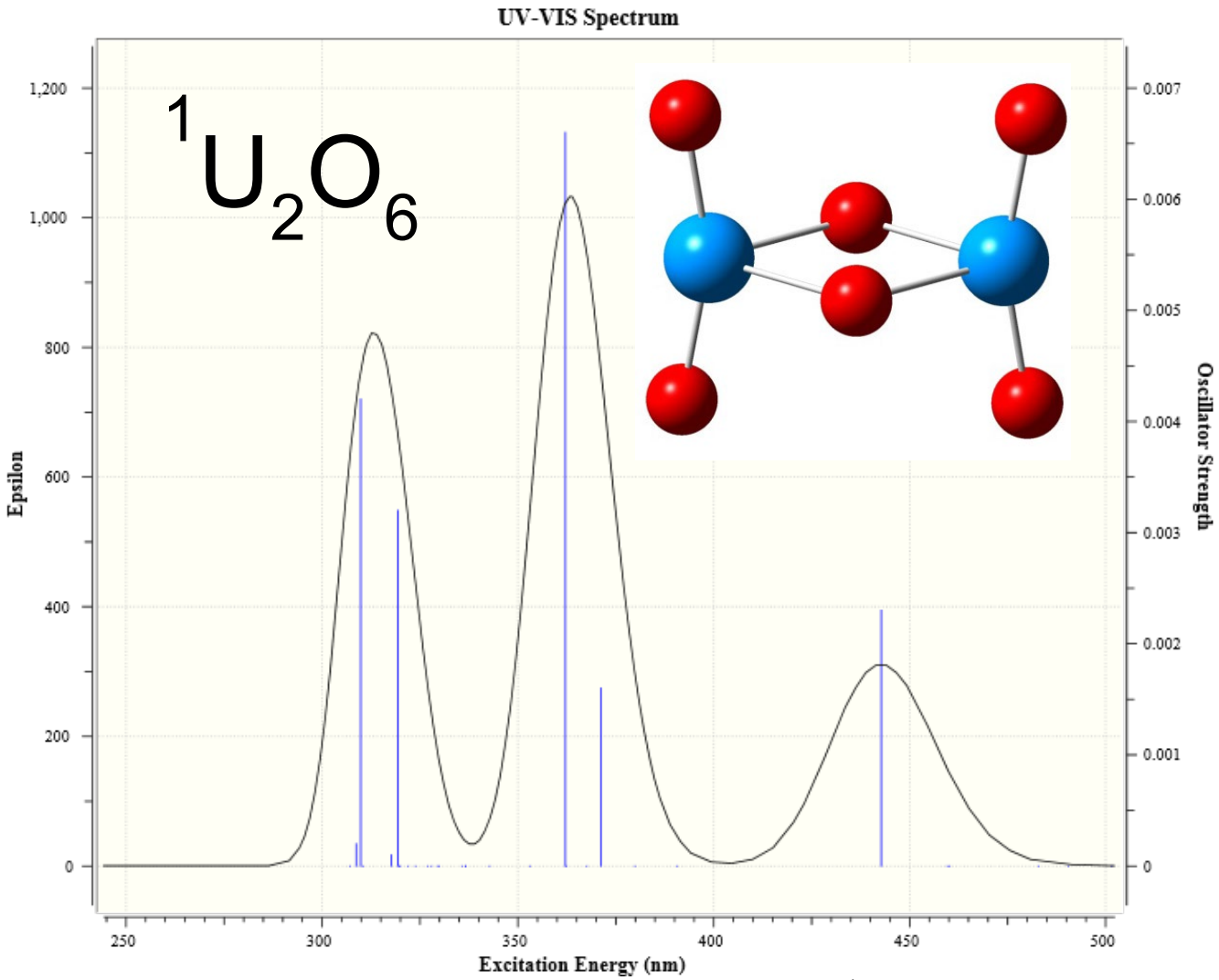


Figure S27. TDDFT B3LYP/aD/D-PP predicted electronic spectrum of $^1U_2O_6$.

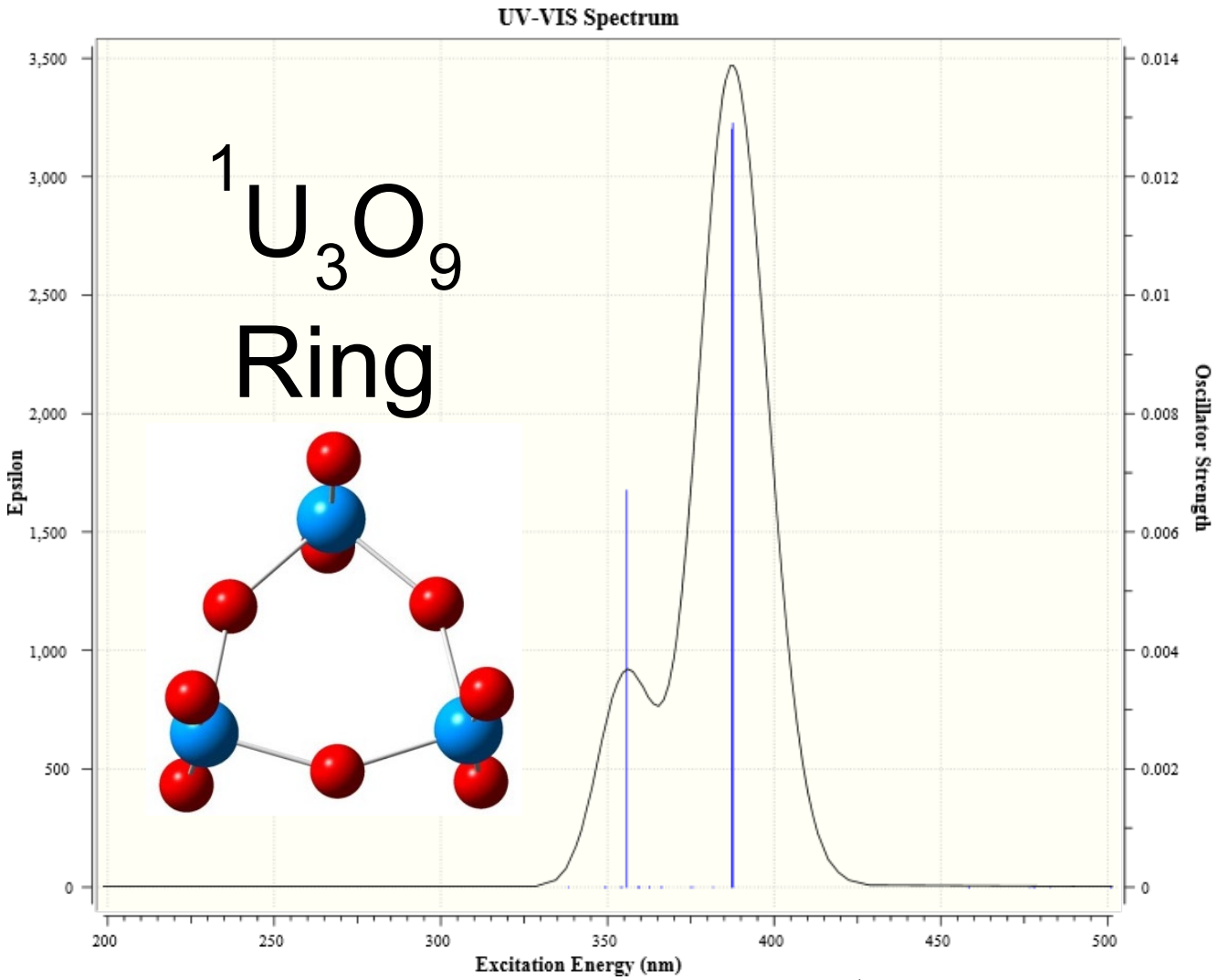


Figure S28. TDDFT B3LYP/aD/D-PP predicted electronic spectrum of $^1U_3O_9$ ring isomer.

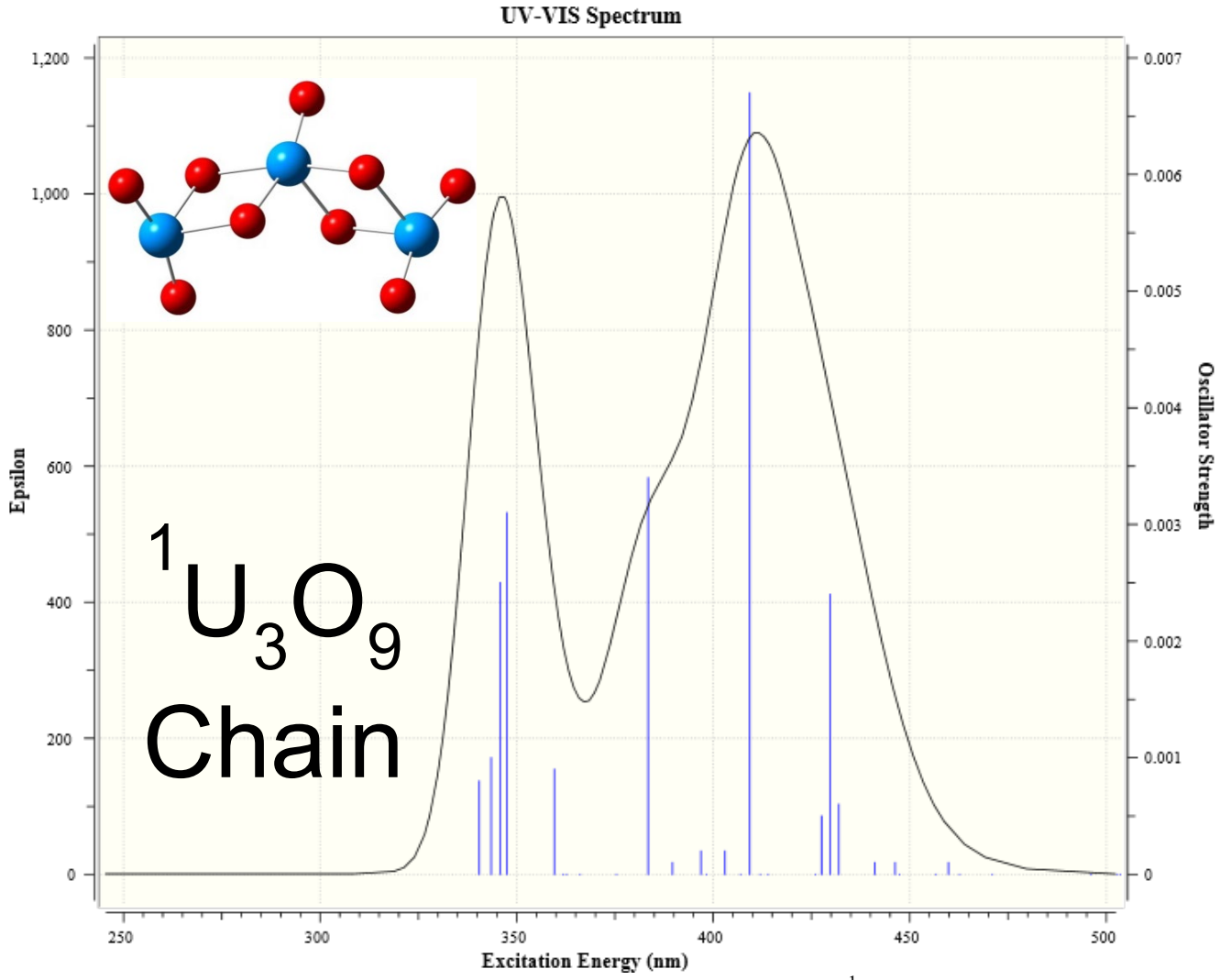


Figure S29. TDDFT B3LYP/aD/D-PP predicted electronic spectrum of $^{1}U_3O_9$ chain isomer.

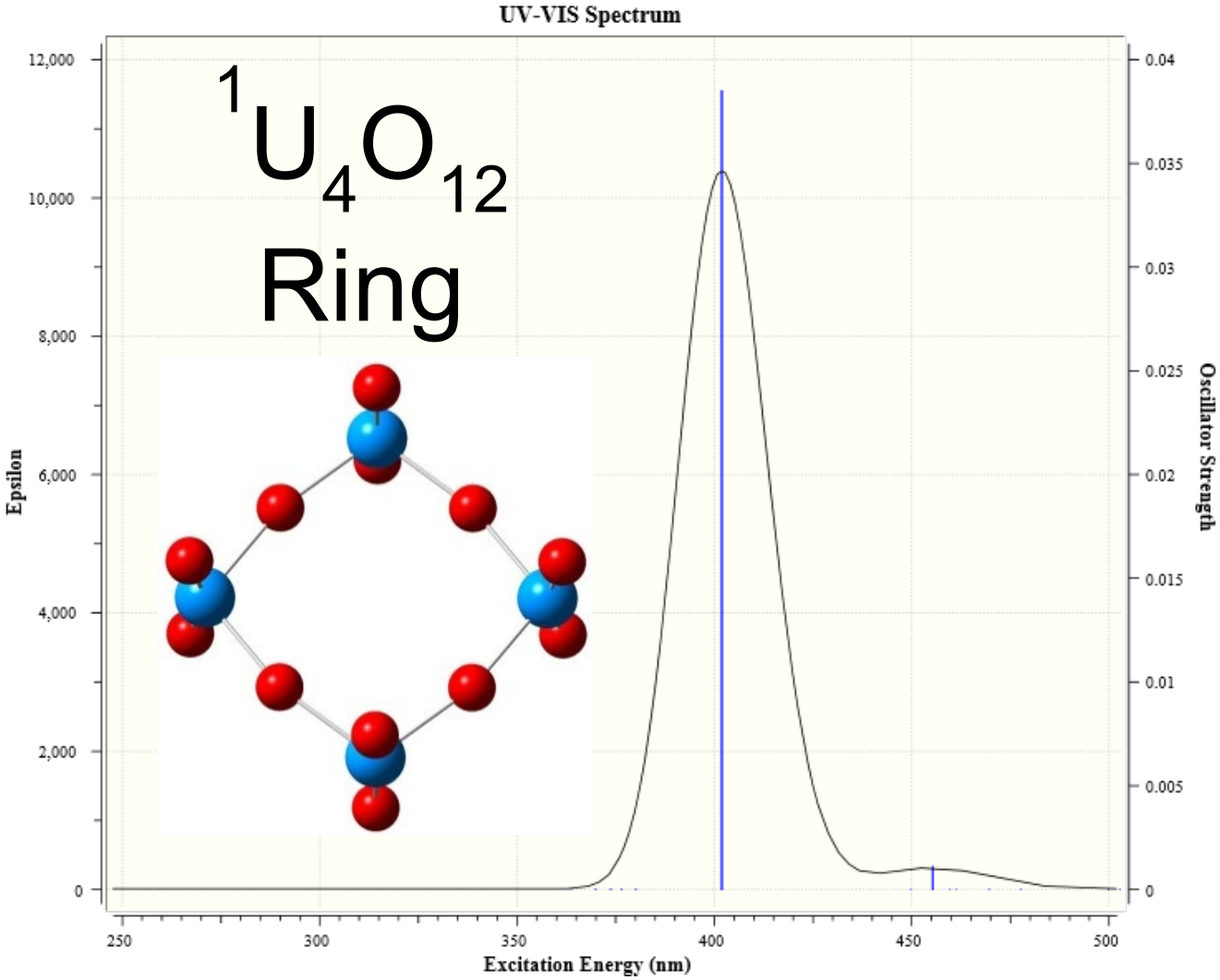


Figure S30. TDDFT B3LYP/aD/D-PP predicted electronic spectrum of $^1U_4O_{12}$ ring isomer.

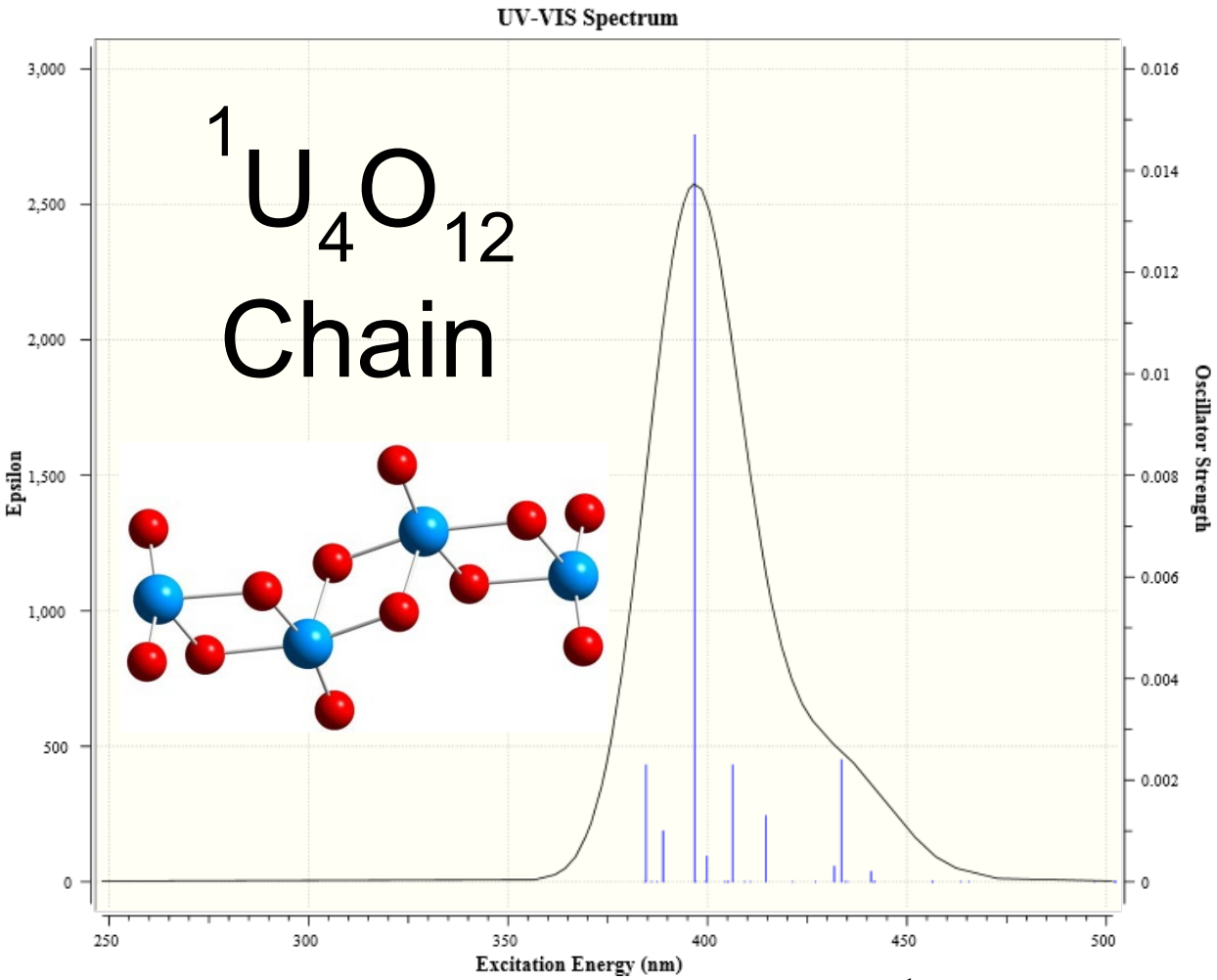


Figure S31. TDDFT B3LYP/aD/D-PP predicted electronic spectrum of $^1U_4O_{12}$ chain isomer.

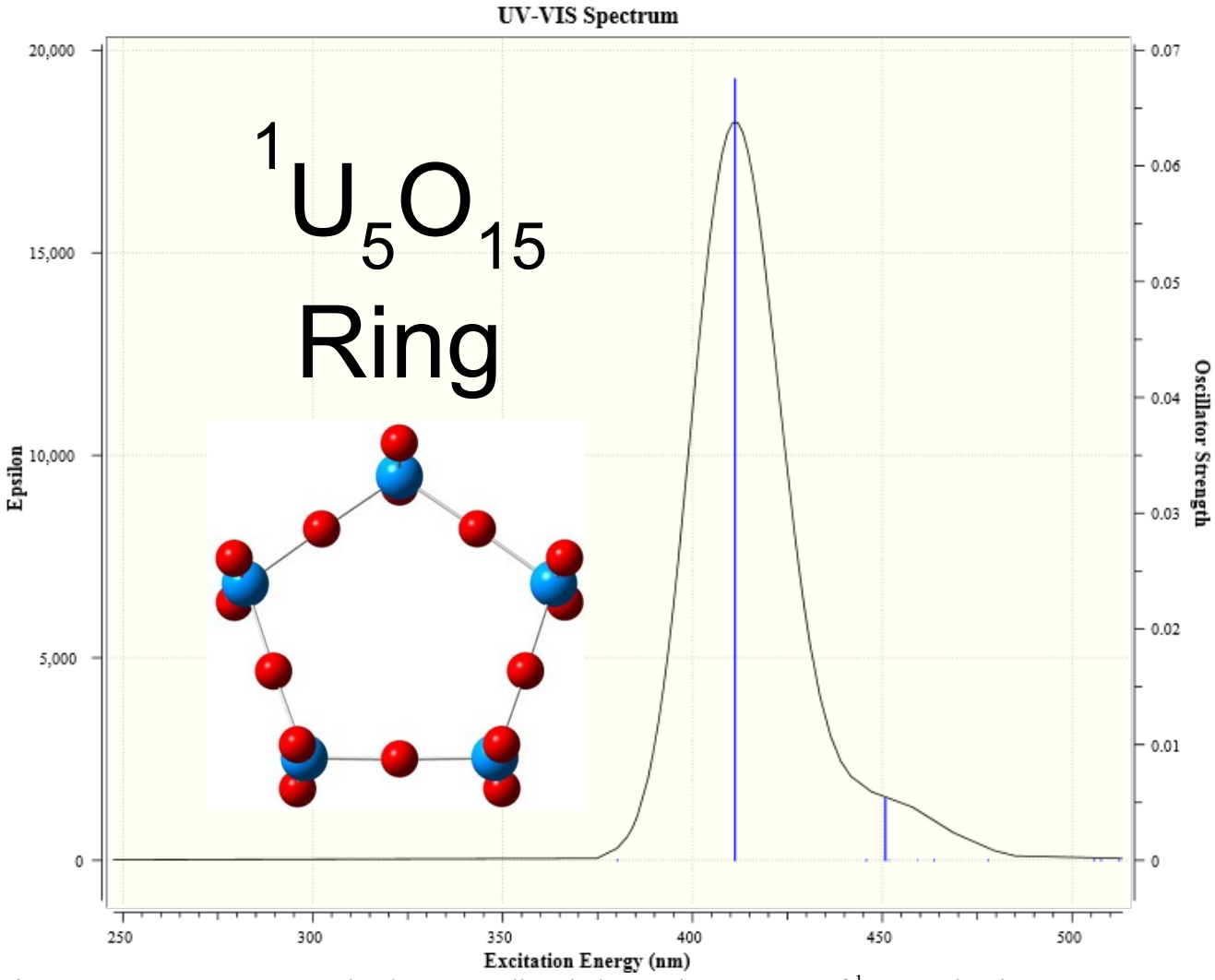


Figure S32. TDDFT B3LYP/aD/D-PP predicted electronic spectrum of $^1U_5O_{15}$ ring isomer.

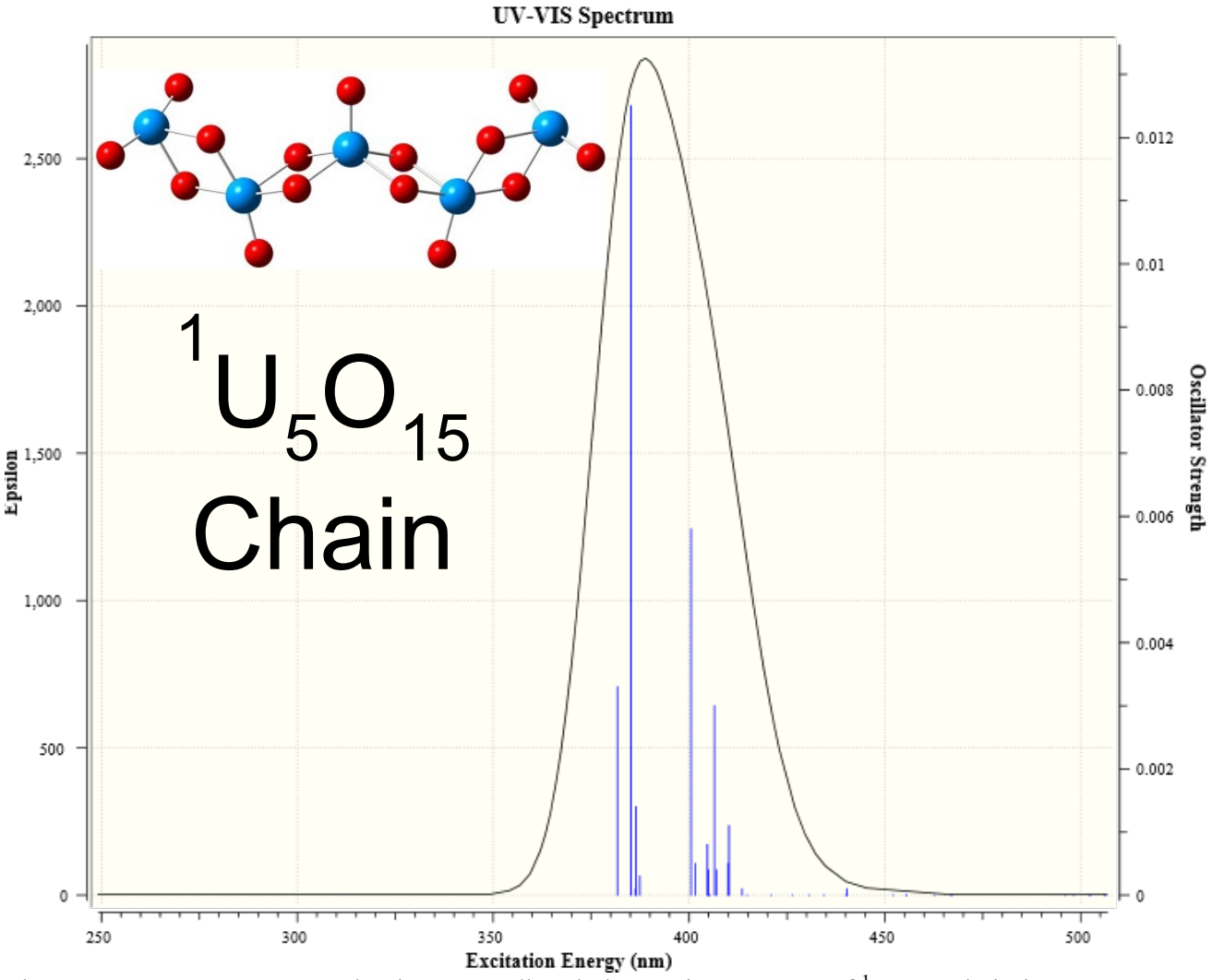


Figure S33. TDDFT B3LYP/aD/D-PP predicted electronic spectrum of $^1U_5O_{15}$ chain isomer.

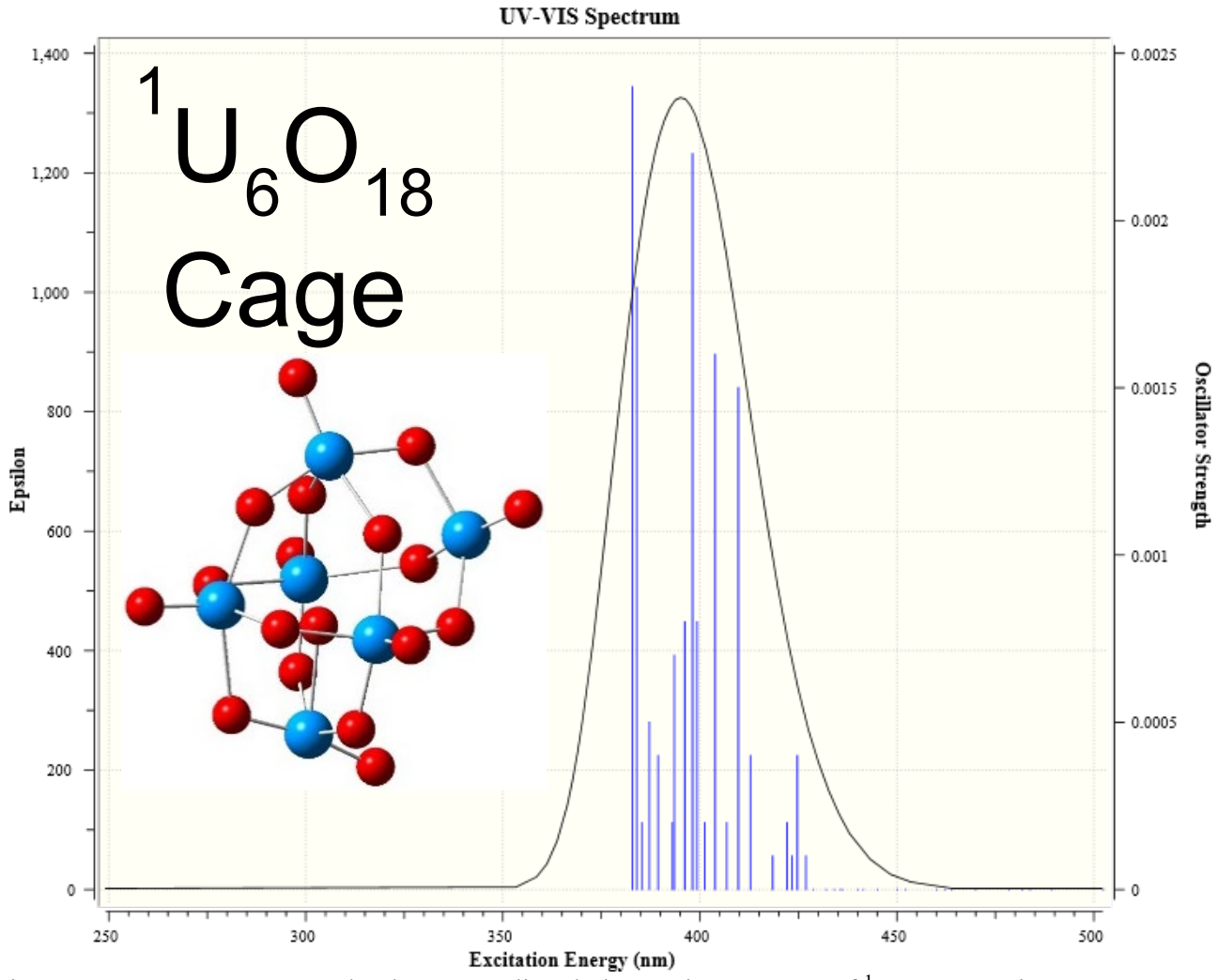


Figure S34. TDDFT B3LYP/aD/D-PP predicted electronic spectrum of $^1U_6O_{18}$ cage isomer.

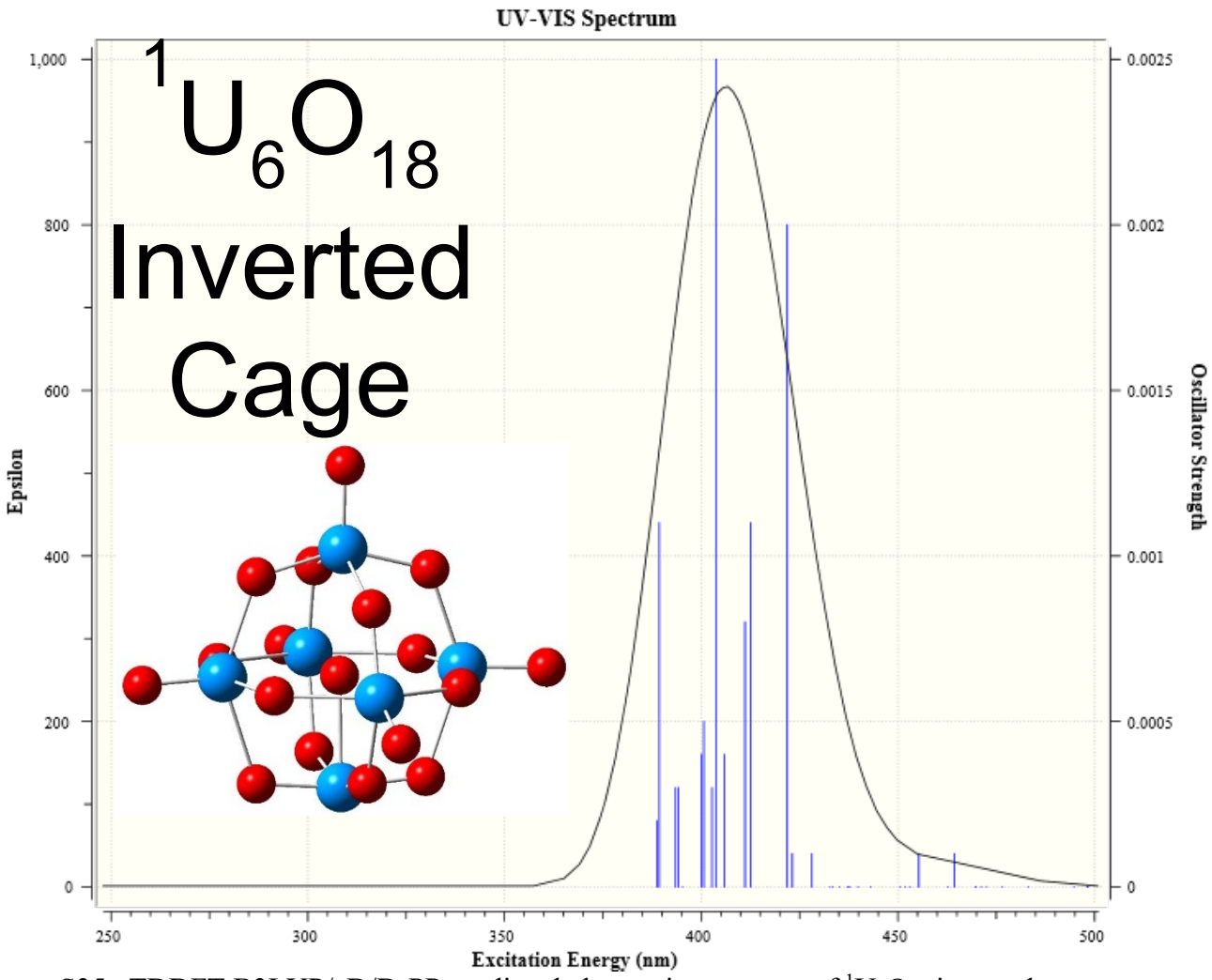


Figure S35. TDDFT B3LYP/aD/D-PP predicted electronic spectrum of $^1U_6O_{18}$ inverted cage isomer.

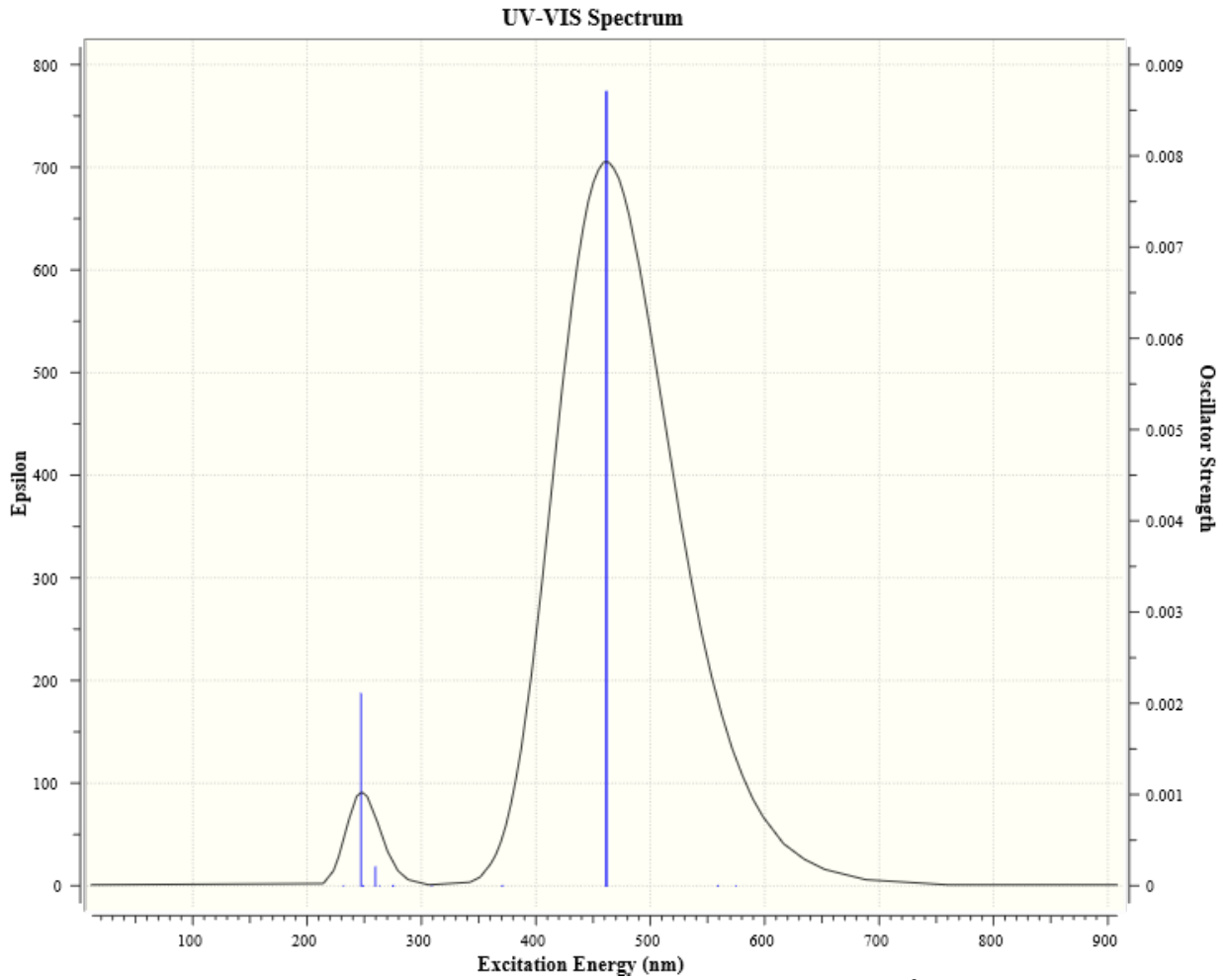


Figure S36. TDDFT B3LYP/aD/D-PP predicted electronic spectrum of $^{2}UO_{2}^{+}$

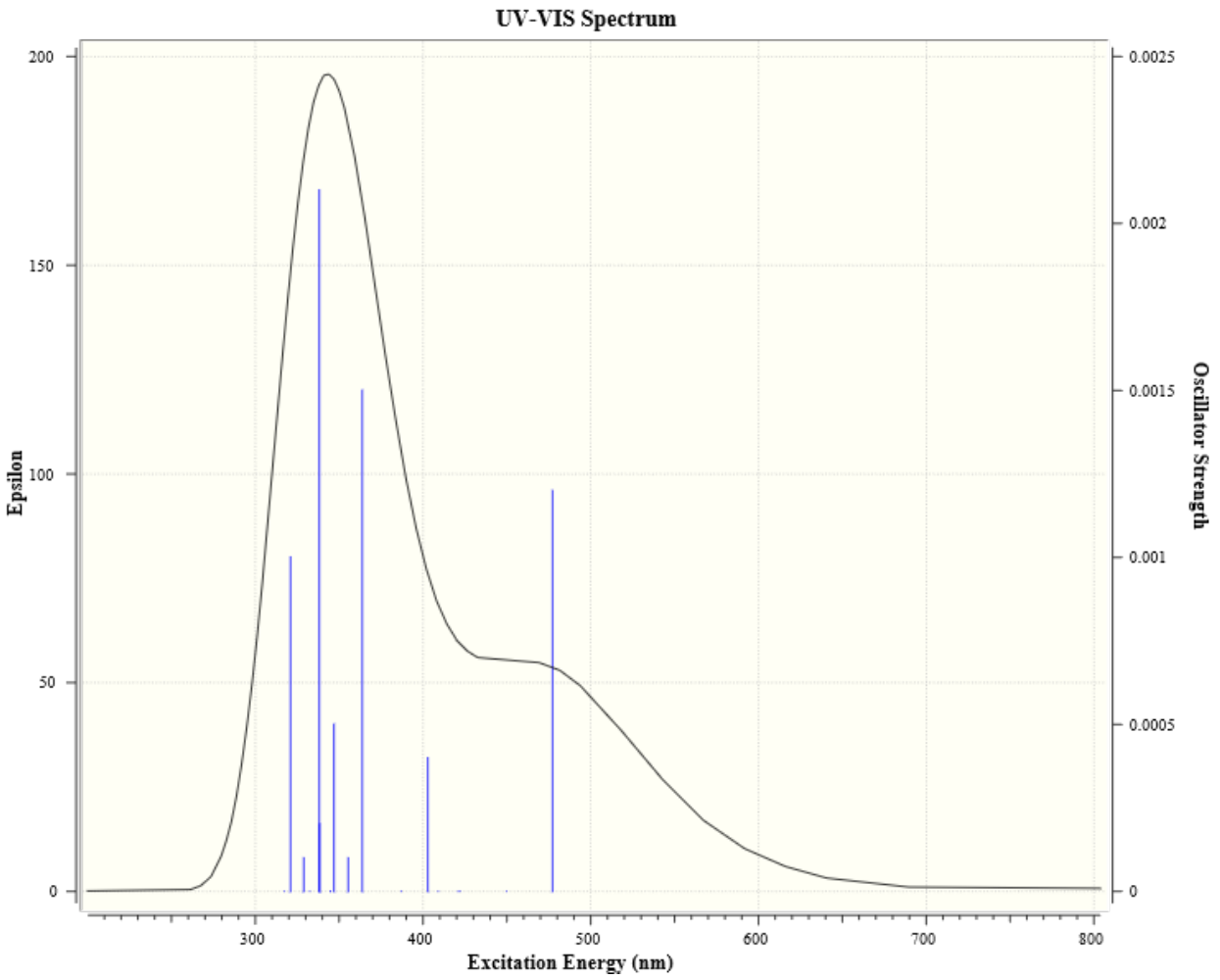


Figure S37. TDDFT B3LYP/aD/D-PP predicted electronic spectrum of $^{2}UO_{3}^{+}$

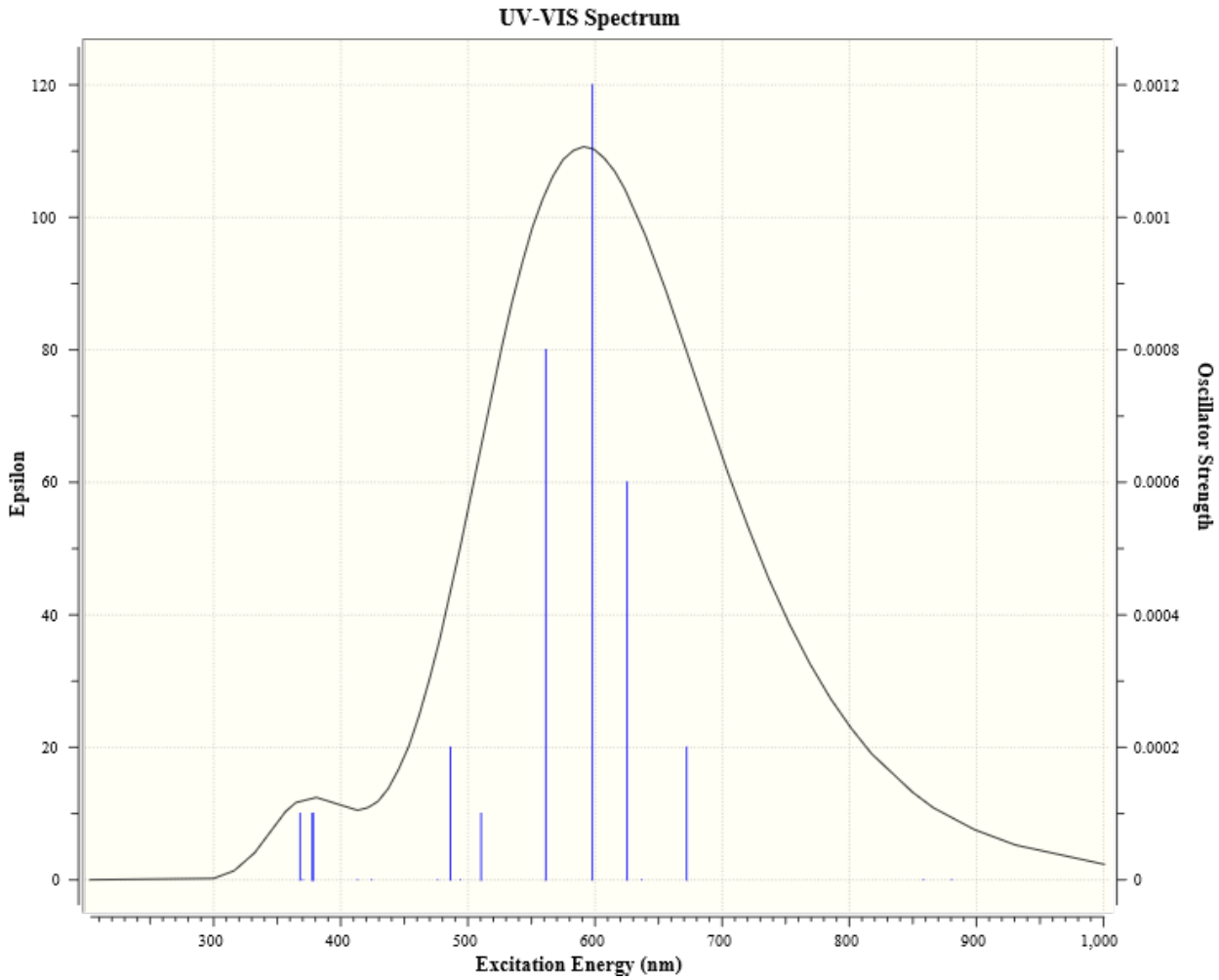


Figure S38. TDDFT B3LYP/aD/D-PP predicted electronic spectrum of $^{2}U_2O_5^{+}$

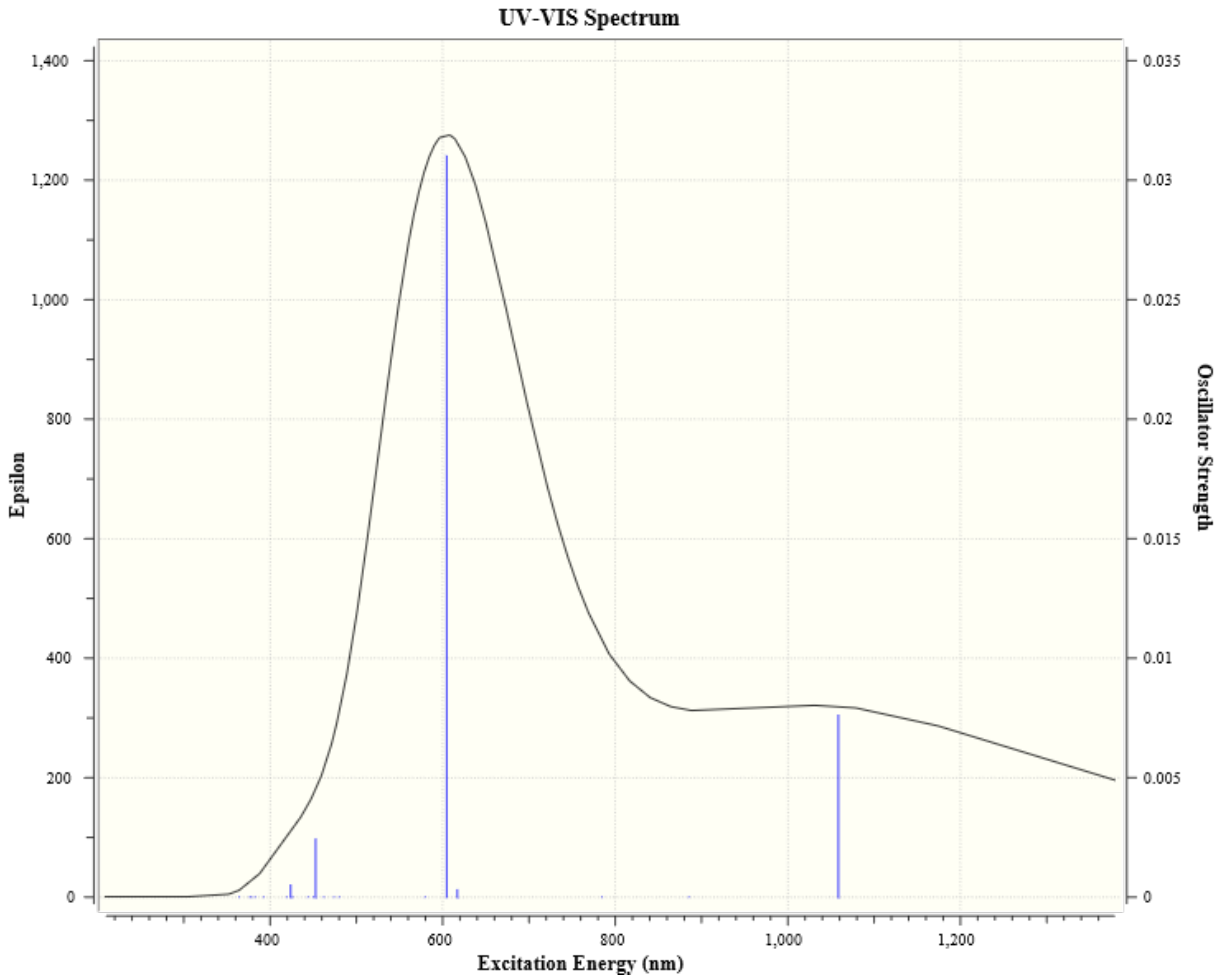


Figure S39. TDDFT B3LYP/aD/D-PP predicted electronic spectrum of $^{2}U_2O_6^{+}$

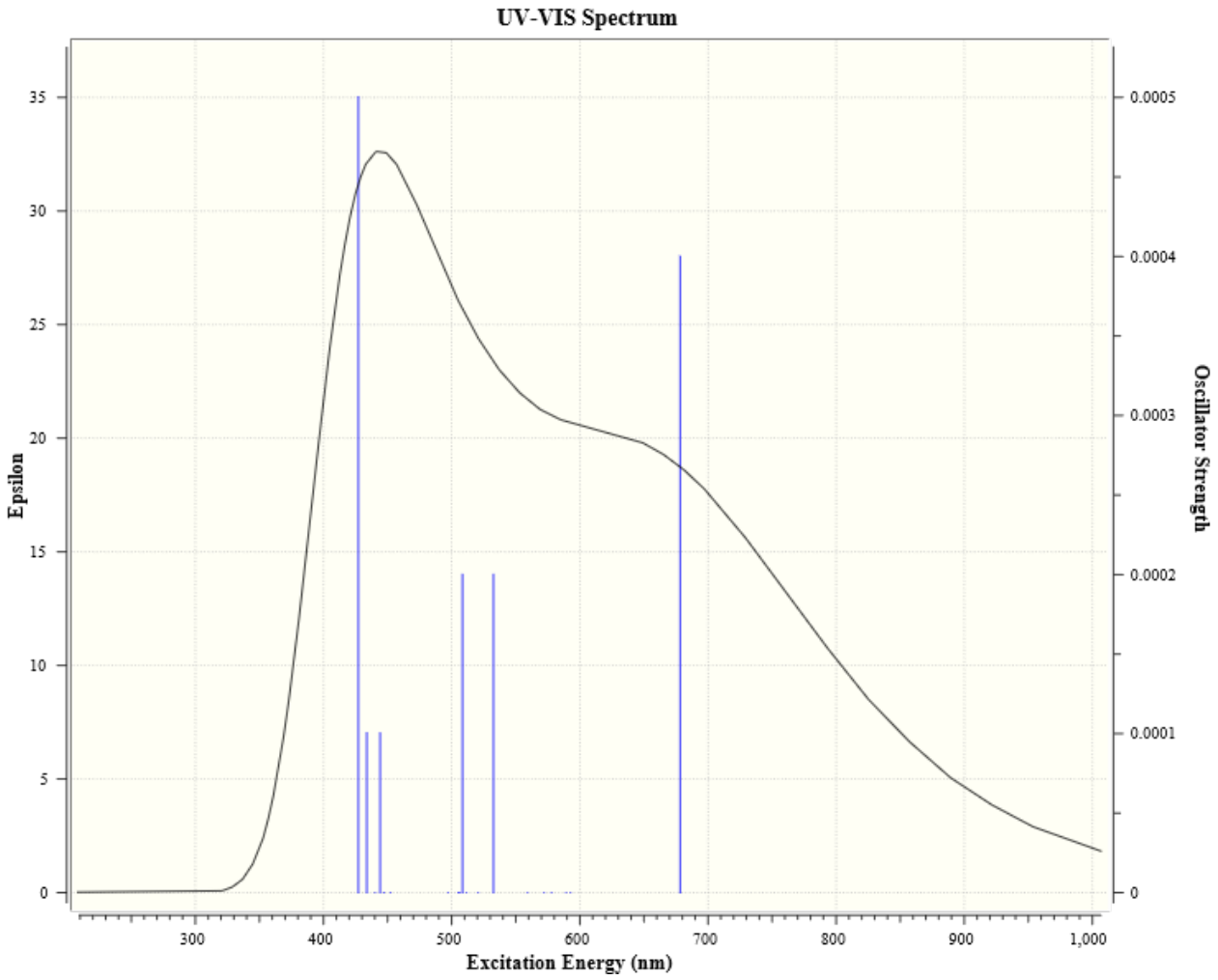


Figure S40. TDDFT B3LYP/aD/D-PP predicted electronic spectrum of $^{2}U_{2}O_{7}^{+}$

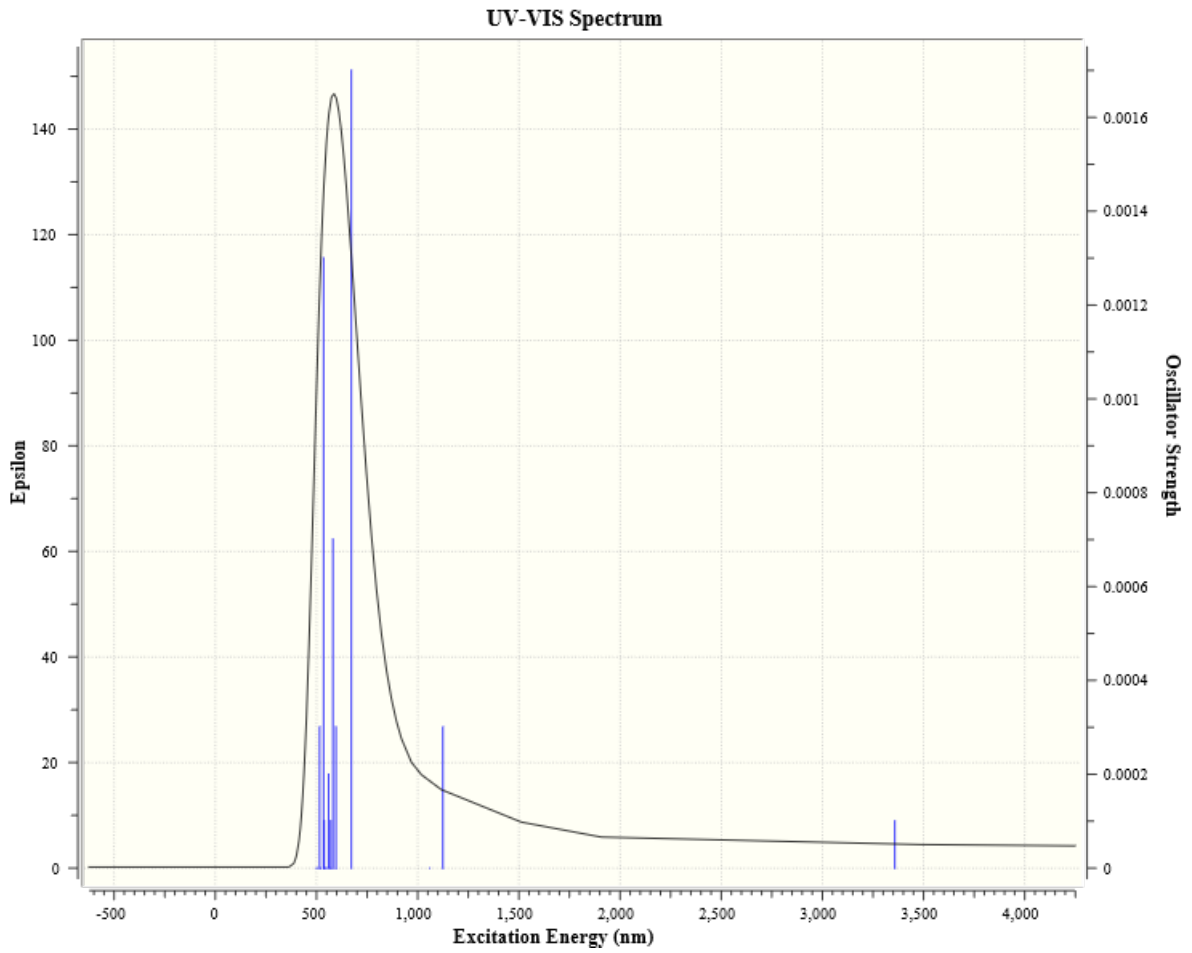


Figure S41. TDDFT B3LYP/aD/D-PP predicted electronic spectrum of $^{2}U_3O_8^{+}$

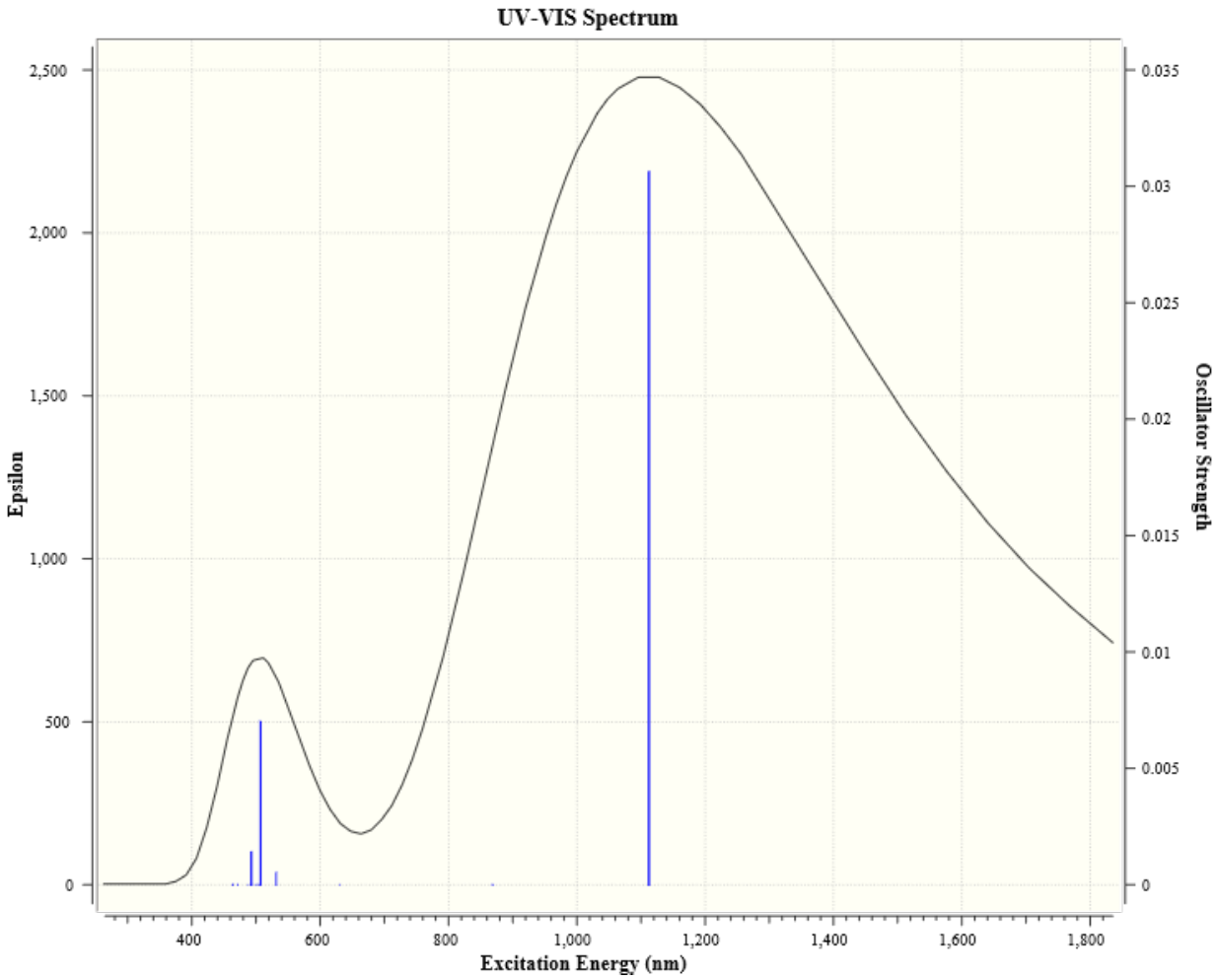


Figure S42. TDDFT B3LYP/aD/D-PP predicted electronic spectrum of $^{2}U_3O_9^{+}$

Table S1. Average U-O Bond Dissociation Energy in kcal/mol calculated using both the B3LYP functional and CCSD(T) method. Basis sets used in these calculations are either cc-pVDZ-PP or cc-pVTZ-PP with polarization basis function on oxygen, denoted aD/D-PP and aT/T-PP respectively. Complete basis set extrapolations were computed using the cc-pVNZ-PP and cc-pVNZ-dk3 families of basis sets. Binding energies for equatorial oxygen atoms were calculated assuming that the axial values are constant.

Molecule	U–O Position	Highest level	Average BDE
$^1UO_3 \rightarrow {}^3UO_2 + {}^3O$	Equatorial	CCSD(T)/CBS-PP	146.6
		CCSD(T)/CBS-dk3	147.7
		B3LYP/aD/D	135.1
	Axial	CCSD(T)/CBS-PP	174.7
		CCSD(T)/CBS-dk3	174.2
		B3LYP/aD/D-PP	180.5
$^3UO_2$ ($D_{\infty h}$)	Axial	CCSD(T)/CBS-PP	174.7
		CCSD(T)/CBS-dk3	174.2
		B3LYP/aD/D-PP	180.5
$^2UO_2^+$($D_{\infty h}$)	Axial	CCSD(T)/CBS-PP	173.5
		CCSD(T)/CBS- dk3	173.3
		B3LYP/aD/D-PP	182.0
$^3U_2O_5$(C_s)	Equatorial	CCSD(T)/aT/T-PP	102.2
		B3LYP/aD/D-PP	82.8
$^2U_2O_5^+$(C_{2v})	Equatorial	CCSD(T)/aT/T-PP	99.1
		B3LYP/aD/D-PP	90.0
$^2U_2O_5^+$(C_s)	Equatorial	CCSD(T)/aT/T-PP	101.9
		B3LYP/aD/D-PP	97.2
$^1U_2O_6$	Equatorial	CCSD(T)/CBS-PP	93.9
		B3LYP/aD/D-PP	85.3
$^2U_3O_8^+$(C_1)	Equatorial	B3LYP/aD/D-PP	90.9
$^2U_3O_8^+$(C_s)	Equatorial	B3LYP/aD/D-PP	93.1
$^1U_3O_9$(C_{2v})	Equatorial	CCSD(T)/aT/T-PP	98.7
$^2U_4O_{11}^+$(chain)	Equatorial	B3LYP/aD/D-PP	104.0

$^{2}U_4O_{11}^{+}$(ring)	Equatorial	B3LYP/aD/D-PP	104.6
		B3LYP/aD/D-PP	89.1
$^{1}U_4O_{12}(D_{4h})$	Equatorial	CCSD(T)/aD/D-PP	99.6
		B3LYP/aD/D-PP	89.5
$^{1}U_4O_{12}(C_i)$	Equatorial	CCSD(T)/aD/D-PP	100.8
		B3LYP/aD/D-PP	89.7
$^{1}U_5O_{15}(D_{5h})$	Equatorial	B3LYP/aD/D-PP	95.3
$^{1}U_5O_{15}(C_s)$	Equatorial	B3LYP/aD/D-PP	95.7
$^{2}U_6O_{17}^{+}$(cage)	Equatorial	B3LYP/aD/D-PP	96.2
$^{2}U_6O_{17}^{+}$(cage)	Equatorial	B3LYP/aD/D-PP	95.9
$^{2}U_6O_{17}^{+}$(chain)	Equatorial	B3LYP/aD/D-PP	92.9

Table S2. Isomer and spin state relative energies calculated with B3LYP/aD/D-PP

Name	**Molecule**	**Multiplicity**	**ΔHg,0K (kcal/mol)**
UO_2^+A	UO_2^+	doublet	0.0
UO_2^+B	UO_2^+	quartet	+71.9
UO_2^{2+}A	UO_2^{2+}	singlet	0.0
UO_2^{2+}B	UO_2^{2+}	triplet	+52.7
UO_3A	UO_3	singlet	0.0
UO_3B	UO_3	triplet	+38.2
U_2O_6A	U_2O_6	singlet	0.0
U_2O_6B	U_2O_6	triplet	+49.6
$U_2O_5^+$A	$U_2O_5^+$	doublet	0.0
$U_2O_5^+$B	$U_2O_5^+$	doublet	+18.0
$U_2O_5^+$C	$U_2O_5^+$	quartet	+53.8
U_3O_9A	U_3O_9	singlet	0.0
U_3O_9B	U_3O_9	singlet	+5.6
$U_3O_8^+$A	$U_3O_8^+$	doublet	0.0
$U_3O_8^+$B	$U_3O_8^+$	doublet	+13.0
U_4O_{12}A	U_4O_{12}	singlet	0.0
U_4O_{12}B	U_4O_{12}	singlet	+0.2
$U_4O_{11}^+$A	$U_4O_{11}^+$	doublet	0.0
$U_4O_{11}^+$B	$U_4O_{11}^+$	doublet	+4.9
U_5O_{15}A	U_5O_{15}	singlet	0.0
U_5O_{15}B	U_5O_{15}	singlet	+3.4
U_6O_{18}A	U_6O_{18}	singlet	0.0
U_6O_{18}B	U_6O_{18}	singlet	+16.9
U_6O_{18}C	U_6O_{18}	singlet	+57.9

Table S3. Normalized and Differential Clustering Energies (ΔH_{298K}) for Optimized Uranium Clusters U_nO_{3n} (kcal/mol)

Cluster	**Differential Clustering Energies (kcal/mol)**				
	B3LYP/ aD	CCSD(T)/ D/D	CCSD(T)/ aD/D	CCSD(T)/ T/T	CCSD(T)/ aT/T
$U_2O_6(D_{2h})$	-71.1	-87.3	-87.2	-85.2	-83.6
$U_3O_9(C_{2v})$	-57.8	-71.7	-69.2	-68.0	-
$U_4O_{12}(C_i)$	-47.9	-57.8	-63.6	-	-
$U_4O_{12}(D_{4h})$	-46.7	-58.2	-54.2	-	-
$U_5O_{15}(C_s)$	-46.7	-57.4	-59.7	-	-
$U_6O_{18}(C_1)$	-115.8				

Cluster	**Normalized Clustering Energies (kcal/mol)**				
	B3LYP/ aD	CCSD(T)/ D/D	CCSD(T)/ aD/D	CCSD(T)/ T/T	CCSD(T)/ aT/T
$U_2O_6(D_{2h})$	35.6	43.6	43.6	42.6	41.8
$U_3O_9(C_{2v})$	43.0	53.0	52.2	51.1	-
$U_4O_{12}(C_i)$	44.2	54.2	55.0	-	-
$U_5O_{15}(C_s)$	43.9	54.3	52.7	-	-
$U_5O_{15}(C_s)$	44.7	54.8	55.9		
$U_6O_{18}(C_1)$	56.6				

$\Delta E_{diff,n} = [E(U_{n-1}O_{3n-3}) + E(UO_3) - E(U_nO_{3n})]$
$\Delta E_{norm,n} = [E(cluster) - nE(UO_3)]/n$

Table S4. NBO Population Analysis

	q (nbo)	U 5f	U 5f α	U 5f β	U 6d	U 6d α	U 6d β
$^{3}UO_2^{0}$	1.61	2.73	1.90	0.83	0.96	0.56	0.40
$^{2}UO_2^{+}$	2.42	2.91	1.98	0.92	0.88	0.45	0.43
$^{3}U_2O_5^{0}(C_s)$	2.09	2.74	1.88	0.86	1.22	0.63	0.59
	2.18	2.70	1.87	0.82	1.21	0.63	0.58
$^{2}U_2O_5^{+}(C_s)$	2.26	2.50	1.25	1.25	1.39	0.70	0.70
	2.36	2.69	1.88	0.82	1.05	0.54	0.51
$^{2}U_2O_5^{+}(C_{2v})$	2.28	2.87	1.96	0.91	1.04	0.53	0.51
	2.34	2.55	1.28	1.28	1.35	0.68	0.68
$^{2}U_3O_8^{+}$(chain)	2.25	2.50	1.25	1.25	1.40	0.70	0.70
	2.23	2.38	1.21	1.17	1.49	0.74	0.74
	2.29	2.81	1.92	0.89	1.05	0.54	0.51
$^{2}U_3O_8^{+}$(ring)	2.27	2.48	1.24	1.24	1.42	0.71	0.71
	2.36	2.67	1.87	0.80	1.09	0.56	0.53
	2.27	2.46	1.23	1.23	1.43	0.71	0.71
$^{2}U_4O_{11}^{+}$(chain)	2.24	2.50	1.25	1.25	1.41	0.71	0.71
	2.17	2.38	1.19	1.19	1.46	0.73	0.73
	2.25	2.47	1.77	0.70	1.25	0.64	0.61
	2.24	2.48	1.24	1.24	1.42	0.71	0.71
$^{2}U_4O_{11}^{+}$(ring)	2.26	2.46	1.23	1.23	1.44	0.72	0.72
	2.30	2.59	1.83	0.76	1.15	0.59	0.56
	2.28	2.45	1.23	1.23	1.43	0.71	0.71
	2.27	2.37	1.18	1.18	1.47	0.74	0.74

Table S5. Summary of the Reaction energies (Rxn. en.) in kcal/mol using the calculated heats of formations from Table 1.

Reactant	Products	Rxn en to form O	Products	Rxn en to form UO_3^+	Products	Rxn en to form UO_3	Products	Rxn en to form UO_2^+
UO_3^+	$UO_2^+ + O$	59.5					$UO_2^+ + O$	59.5
UO_4^+	$UO_3^+ + O$	84.3	$UO_3^+ + O$	84.3			$UO_2^+ + O_2$	26.4
$U_2O_4^+$					$UO^+ + UO_3$	114.0	$UO_2^+ + UO_2$	81.2
$U_2O_5^+$	$U_2O_4^+ + O$	144.8	$UO_3^+ + UO_2$	166.5	$UO_2^+ + UO_3$	86.5	$UO_2^+ + UO_3$	86.5
$U_2O_6^+$	$U_2O_5^+ + O$	70.4	$UO_3^+ + UO_3$	97.4	$UO_3^+ + UO_3$	97.4		
$U_2O_7^+$	$U_2O_6^+ + O$	61.9			$UO_4^+ + UO_3$	64.0		
$U_3O_8^+$			$U_2O_5 + UO_3^+$	127.1	$U_2O_5^+ + UO_3$	58.7	$U_2O_6 + UO_2^+$	63.0
$U_3O_9^+$	$U_3O_8^+ + O$	90.2	$U_2O_6 + UO_3^+$	93.7	$U_2O_6^+ + UO_3$	78.5	$U_2O_7 + UO_2^+$	97.0
$U_4O_{11}^+$			$U_3O_8 + UO_3^+$	150.9	$U_3O_8^+ + UO_3$	82.5	$U_3O_9 + UO_2^+$	77.1
$U_4O_{12}^+$	$U_4O_{11}^+ + O$	77.3	$U_3O_9 + UO_3^+$	94.9	$U_3O_9^+ + UO_3$	69.6		
$U_5O_{15}^+$			$U_4O_{12} + UO_3^+$	88.9	$U_4O_{12}^+ + UO_3$	57.6		

Table S6. Electronic energies in Hartees at different levels of theory.

	B3LYP/aD/D-PP			**CCSD(T)**			
Molec.	$\Delta H_{g,0K}$	$\Delta H_{g,298K}$	$\Delta G_{g,298K}$	aD/D-PP	D/D-PP	aT/T-PP	T/T-PP
$^3UO_2$	-625.375494	-625.370751	-625.401931	-623.6261514	-623.613459	-623.864769	-623.847202
$^2UO_2^+$	-625.144887	-625.140181	-625.170872	-623.430988	-623.387538	-623.634947	-623.618756
$^2UO_2^+$	-625.030378	-625.025564	-625.057099				
$^1UO_3$	-700.666701	-700.660837	-700.696463	-698.7994101	-698.733508	-699.071199	-699.044931
$^3UO_3$	-700.605871	-700.599755	-700.636881				
$^2UO_3^+$	-700.314795	-700.308893	-700.345139	-698.4593267	-698.396100	-698.7235857	-698.700781
$^4UO_3^+$	-700.233695	-700.227557	-700.265594				
$^2UO_4^+$	-775.522764	-775.515975	-775.554417	-773.5077183	-773.423279	-773.8342514	-773.804519
$^1U_2O_6$	-1401.446016	-1401.435050	-1401.483785	-1397.740193	-1397.608424	-1398.278046	-1398.227919
$^1U_2O_6$	-1401.366942	-1401.355282	-1401.407236				
$^2U_2O_6^+$	-1401.117835	-1401.106711	-1401.156125				
$^3U_2O_5$	-1326.168106	-1326.157870	-1326.208285	-1322.593765	-1322.482302	-1323.069242	-1323.027153
$^2U_2O_5^+$	-1325.924998	-1325.915200	-1325.963748	-1322.372945	-1322.263831	-1322.845629	-1322.805521
$^2U_2O_5^+$	-1325.896297	-1325.885613	-1325.937926	-1322.351635	-1322.247048	-1322.828356	-1322.787468
$^4U_2O_5^+$	-1325.839243	-1325.828903	-1325.879804				
$^4U_2O_4^+$	-1250.625179	-1250.616053	-1250.664759	-1247.202830		-1247.611834	
$^1U_2O_7$	-1476.594007	-1476.581719	-1476.633621	-1472.731806	-1472.575263	-1473.328678	-1473.270090
$^2U_2O_7^+$	-1476.275094	-1476.261811	-1476.319810	-1472.418454	-1472.269443		-1472.956307
$^4U_2O_7^+$	-1476.257348	-1476.242728	-1476.307630				
$^1U_2O_8$	-1551.734267	-1551.720680	-1551.775629	-1547.710674	-1547.535711	-1548.371864	-1548.305929
$^1U_2O_8$	-1551.730303	-1551.717365	-1551.771504	-1547.703144	-1547.530344		-1548.301401
$^1U_2O_8$	-1551.720368	-1551.707644	-1551.760861	-1547.700304	-1547.518399	-1548.354542	-1548.287436
$^1U_3O_9$	-2102.205459	-2102.188047	-2102.255021	-2096.651826	-2096.458020		-2097.383144
$^1U_3O_9$	-2102.196608	-2102.179641	-2102.246117	-2096.646991	-2096.446881		

$^{2}U_3O_9^+$	-2101.893570	-2101.875812	-2101.942399				
$^{2}U_3O_9^+$	-2101.880230	-2101.863185	-2101.929820				
$^{3}U_3O_8$	-2026.918380	-2026.902398	-2026.968614				
$^{3}U_3O_8$	-2026.935302	-2026.919528	-2026.984382				
$^{2}U_3O_8^+$	-2026.692091	-2026.675652	-2026.743464		-2021.121551		
$^{1}U_4O_{12}$	-2802.947755	-2802.925222	-2803.005073	-2795.554418	-2795.285493		
$^{1}U_4O_{12}$	-2802.947434	-2802.923291	-2803.007199	-2795.539626	-2795.286231		
$^{2}U_4O_{12}^+$	-2802.645398	-2802.620439	-2802.708100				
$^{2}U_4O_{11}^+$	-2727.473107	-2727.451079	-2727.530245				
$^{1}U_5O_{15}$	-3503.688385	-3503.660426	-3503.754421				
$^{1}U_5O_{15}$	-3503.683044	-3503.654182	-3503.749646				
$^{1}U_6O_{18}$	-4204.539286	-4204.505874	-4204.605202				
$^{1}U_6O_{18}$	-4204.521426	-4204.487702	-4204.592268				
$^{1}U_6O_{18}$	-4204.512216	-4204.478179	-4204.579282				
$^{1}U_6O_{18}$	-4204.504993	-4204.470157	-4204.580707				
$^{1}U_6O_{18}$	-4204.501747	-4204.466712	-4204.577180				
$^{1}U_6O_{18}$	-4204.452256	-4204.416098	-4204.535453				
$^{1}U_6O_{18}$	-4204.446906	-4204.412397	-4204.524576				
$^{2}U_6O_{17}^+$	-4129.043275	-4129.011233	-4129.108991				
$^{2}U_6O_{17}^+$	-4129.036436	-4129.004485	-4129.102098				
$^{2}U_6O_{17}^+$	-4128.981262	-4128.948546	-4129.057733				