Supporting Information

Decomposition Pathways of Titanium Isopropoxide $Ti(O^iPr)_4$: New Insights from UV-Photodissociation Experiments and Quantum Chemical Calculations

Kirill S. Ershov,[a,b] Sergei A. Kochubei,[c] Vitaly G. Kiselev,[a,b,d] and Alexey V. Baklanov[a,b]**

[a] Novosibirsk State University, 2, Pirogova Str., 630090 Novosibirsk, Russia

[b] Institute of Chemical Kinetics and Combustion, 3, Institutskaya Str., 630090 Novosibirsk, Russia

[c] Institute of Semiconductor Physics, 13, Lavrentyeva Ave., 630090 Novosibirsk, Russia

[d] Semenov Institute of Chemical Physics RAS, 4, Kosygin Str., 119991 Moscow, Russia

Corresponding Authors
A.V.B.: E-mail: baklanov@kinetics.nsc.ru. V.G.K.: E-mail: kiselev@phys.nsu.ru

Contents

1. Raw computational data: optimized geometries, electronic energies, and thermal corrections to thermodynamic potentials of all compounds under study.

M06-2X/6-311++G(2df,p) geometries, electronic energies and thermal corrections to thermodynamic potentials. The data are grouped in accordance with the corresponding Figures from the manuscript, which are reproduced here for clarity.

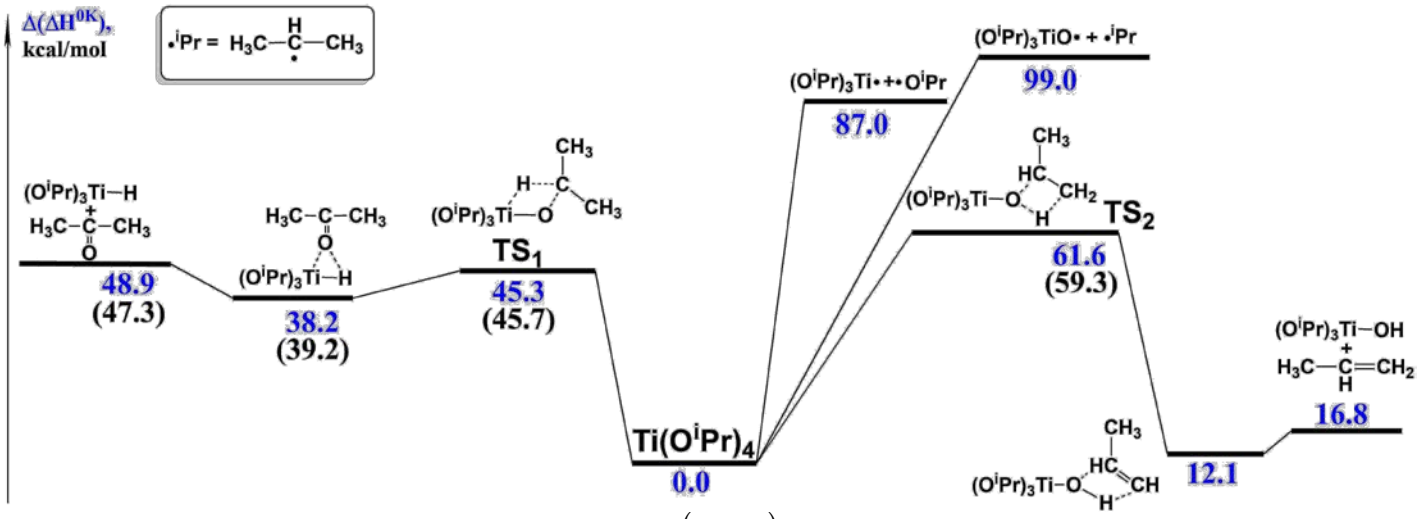


Figure 3. The relative enthalpies at 0 K ($\Delta(\Delta H^{0K})$) of the stationary points on the PES corresponding to thermal decomposition of TTIP. The TTIP was chosen as a reference compound for the calculations of the relative thermodynamic properties. All values are in kcal/mol and calculated at the M06-2X/6-311++G(2df,p) level of theory. For several PES points, the sums of DLPNO-CCSD(T)/aVTZ single-point electronic energies and M06-2X zero-point vibrational energies are given in parentheses.

Ti(O^{i}Pr)$_4$

Zero-point correction= 0.394704 (Hartree/Particle)
Thermal correction to Energy= 0.419547
Thermal correction to Enthalpy= 0.420491
Thermal correction to Gibbs Free Energy= 0.336452
Sum of electronic and zero-point Energies= -1624.184528

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	22	0	-0.125306	-0.057525	-0.628540
2	8	0	-0.569668	-0.839350	0.923908
3	8	0	-1.536110	-0.080687	-1.751255
4	8	0	0.302801	1.639284	-0.217235
5	8	0	1.280649	-0.874873	-1.373944
6	6	0	-0.775178	-0.588022	2.294648
7	6	0	0.381296	-1.169145	3.091362
8	6	0	-2.109854	-1.182222	2.714949
9	1	0	-0.802659	0.500785	2.442270
10	1	0	1.324107	-0.716894	2.780956
11	1	0	0.244090	-0.988756	4.159209

12	1	0	0.441722	-2.246493	2.922460
13	1	0	-2.924783	-0.747631	2.134748
14	1	0	-2.102454	-2.261087	2.545816
15	1	0	-2.299029	-0.994674	3.773415
16	6	0	-2.927088	0.123116	-1.653045
17	6	0	-3.225905	1.251918	-0.675836
18	6	0	-3.601283	-1.177256	-1.244580
19	1	0	-3.278706	0.413899	-2.649979
20	1	0	-2.698673	2.160517	-0.969235
21	1	0	-4.296447	1.461070	-0.635663
22	1	0	-2.892692	0.971601	0.328888
23	1	0	-3.376968	-1.962998	-1.966307
24	1	0	-3.228636	-1.490997	-0.266027
25	1	0	-4.684346	-1.052793	-1.185737
26	6	0	1.418805	2.437368	0.098793
27	6	0	2.145854	1.850305	1.299591
28	6	0	0.948354	3.859045	0.355704
29	1	0	2.096963	2.433355	-0.764471
30	1	0	2.464371	0.826857	1.085696
31	1	0	3.028329	2.440966	1.552652
32	1	0	1.477197	1.831763	2.164109
33	1	0	0.416778	4.244698	-0.514203
34	1	0	0.269192	3.874030	1.210833
35	1	0	1.795092	4.513973	0.569030
36	6	0	2.386320	-1.738727	-1.310607
37	6	0	2.448041	-2.417448	0.048369
38	6	0	3.650124	-0.949848	-1.614641
39	1	0	2.247966	-2.502363	-2.085537
40	1	0	1.511294	-2.933847	0.262077
41	1	0	3.266309	-3.139025	0.082697
42	1	0	2.610478	-1.671370	0.830845
43	1	0	3.567566	-0.460929	-2.585392
44	1	0	3.799733	-0.181956	-0.851460
45	1	0	4.522641	-1.605653	-1.623839

TS_1

Zero-point correction= 0.388943 (Hartree/Particle)
Thermal correction to Energy= 0.413374
Thermal correction to Enthalpy= 0.414318
Thermal correction to Gibbs Free Energy= 0.333024
Sum of electronic and zero-point Energies= -1624.112413

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	22	0	0.196291	0.001816	-0.407730
2	8	0	2.030434	-0.841495	0.491331
3	8	0	0.783111	1.595896	0.204862
4	8	0	-1.160839	0.543939	-1.444154
5	8	0	-0.653819	-1.198184	0.649342

6	6	0	2.647317	-1.103041	-0.550438
7	6	0	2.732710	-2.521508	-1.040748
8	6	0	3.600483	-0.100011	-1.138270
9	1	0	1.117371	-0.635046	-1.755751
10	1	0	1.869436	-3.087376	-0.697518
11	1	0	2.814703	-2.565281	-2.124862
12	1	0	3.639392	-2.958481	-0.608899
13	1	0	3.318253	0.903791	-0.828049
14	1	0	4.595249	-0.331351	-0.742220
15	1	0	3.638583	-0.175972	-2.223276
16	6	0	0.149498	2.859467	0.237944
17	6	0	1.210336	3.929665	0.432314
18	6	0	-0.887198	2.871842	1.351036
19	1	0	-0.358996	3.016385	-0.721935
20	1	0	1.946706	3.885933	-0.370948
21	1	0	0.758756	4.923503	0.436960
22	1	0	1.724508	3.773633	1.382865
23	1	0	-1.630346	2.089180	1.181188
24	1	0	-0.401164	2.686650	2.311790
25	1	0	-1.400145	3.834649	1.395972
26	6	0	-2.408439	0.128504	-1.947896
27	6	0	-3.464694	0.314371	-0.868888
28	6	0	-2.327057	-1.315774	-2.420117
29	1	0	-2.645272	0.773152	-2.802799
30	1	0	-3.511121	1.359607	-0.559899
31	1	0	-4.449107	0.014365	-1.233304
32	1	0	-3.204928	-0.297964	-0.001939
33	1	0	-1.536718	-1.425215	-3.164048
34	1	0	-2.102370	-1.964856	-1.569877
35	1	0	-3.272995	-1.632037	-2.863923
36	6	0	-0.474336	-1.792342	1.913378
37	6	0	-1.682540	-2.664058	2.215374
38	6	0	-0.267198	-0.714736	2.967085
39	1	0	0.426119	-2.418077	1.869503
40	1	0	-1.821464	-3.407494	1.429505
41	1	0	-1.558612	-3.181191	3.168790
42	1	0	-2.581766	-2.046118	2.268415
43	1	0	0.603790	-0.105249	2.717718
44	1	0	-1.146566	-0.066544	3.007907
45	1	0	-0.114093	-1.158086	3.952999

(^{i}PrO)$_3$Ti-H ···C$_3$H$_6$O

Zero-point correction= 0.389229 (Hartree/Particle)
Thermal correction to Energy= 0.414513
Thermal correction to Enthalpy= 0.415457
Thermal correction to Gibbs Free Energy= 0.332001
Sum of electronic and zero-point Energies= -1624.123694

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z

1	22	0	-0.114314	0.074723	-0.708107
2	8	0	1.789103	-1.149173	-0.516155
3	8	0	0.933203	1.256412	0.216489
4	8	0	-1.555904	1.097903	-1.004011
5	8	0	-0.834900	-1.411515	0.022399
6	6	0	2.948373	-0.895382	-0.783463
7	6	0	4.031373	-1.863280	-0.411495
8	6	0	3.347468	0.376122	-1.465525
9	1	0	0.328161	-0.128448	-2.341308
10	1	0	3.626588	-2.688203	0.168981
11	1	0	4.497170	-2.241241	-1.325126
12	1	0	4.810055	-1.343209	0.150688
13	1	0	3.338342	1.165093	-0.708228
14	1	0	4.339817	0.302883	-1.907080
15	1	0	2.598501	0.643675	-2.210774
16	6	0	0.582962	2.472526	0.841680
17	6	0	1.826367	3.340668	0.951747
18	6	0	-0.030949	2.181868	2.202926
19	1	0	-0.163156	2.984972	0.220863
20	1	0	2.245875	3.530877	-0.037472
21	1	0	1.592403	4.299908	1.417371
22	1	0	2.579832	2.834446	1.560587
23	1	0	-0.917937	1.554930	2.087507
24	1	0	0.688881	1.649472	2.829478
25	1	0	-0.321206	3.105217	2.708531
26	6	0	-2.959161	1.033904	-1.092997
27	6	0	-3.543044	0.938607	0.309072
28	6	0	-3.376808	-0.142801	-1.962666
29	1	0	-3.298163	1.965538	-1.562014
30	1	0	-3.236415	1.798172	0.907172
31	1	0	-4.633868	0.907103	0.276386
32	1	0	-3.177249	0.026989	0.789073
33	1	0	-2.912132	-0.066804	-2.946508
34	1	0	-3.053288	-1.075996	-1.495099
35	1	0	-4.461345	-0.166501	-2.086465
36	6	0	-0.573751	-2.426481	0.956246
37	6	0	-1.812843	-3.297034	1.093535
38	6	0	-0.158623	-1.808994	2.283909
39	1	0	0.255590	-3.035689	0.574575
40	1	0	-2.096636	-3.706262	0.123491
41	1	0	-1.633590	-4.123288	1.784325
42	1	0	-2.645150	-2.699391	1.472642
43	1	0	0.719387	-1.173981	2.145613
44	1	0	-0.972132	-1.191128	2.673427
45	1	0	0.076359	-2.580400	3.020138

(^{i}PrO)$_3$Ti-H

Zero-point correction= 0.302868 (Hartree/Particle)

Thermal correction to Energy= 0.322393

Thermal correction to Enthalpy= 0.323337
Thermal correction to Gibbs Free Energy= 0.248462
Sum of electronic and zero-point Energies= -1431.062364

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	22	0	-0.195310	0.095052	-0.737427
2	8	0	0.804173	-1.264445	-0.193046
3	8	0	-1.877377	0.075528	-0.168951
4	8	0	0.618052	1.673184	-0.601495
5	6	0	1.344664	-2.441189	0.347804
6	6	0	2.453954	-2.083151	1.323376
7	6	0	1.841984	-3.324840	-0.784545
8	1	0	0.545009	-2.963364	0.887358
9	1	0	2.073214	-1.436802	2.115304
10	1	0	2.870308	-2.983462	1.778590
11	1	0	3.252635	-1.555671	0.797566
12	1	0	1.030819	-3.546649	-1.478027
13	1	0	2.634191	-2.810797	-1.332529
14	1	0	2.237949	-4.263350	-0.392747
15	6	0	-3.148110	0.275693	0.389207
16	6	0	-3.304365	-0.604456	1.619165
17	6	0	-4.205099	-0.019236	-0.662836
18	1	0	-3.223623	1.328410	0.688242
19	1	0	-2.526432	-0.381695	2.350250
20	1	0	-4.277750	-0.443359	2.085736
21	1	0	-3.223155	-1.655372	1.333764
22	1	0	-4.055604	0.611841	-1.538845
23	1	0	-4.135899	-1.063730	-0.973023
24	1	0	-5.204282	0.163048	-0.263373
25	6	0	1.706863	2.500278	-0.277363
26	6	0	2.892260	1.651568	0.153702
27	6	0	1.285073	3.486240	0.799950
28	1	0	1.971654	3.054634	-1.185292
29	1	0	3.158147	0.941292	-0.630903
30	1	0	3.759584	2.278008	0.369443
31	1	0	2.635116	1.087217	1.053623
32	1	0	0.419537	4.061028	0.470538
33	1	0	1.017783	2.947424	1.711802
34	1	0	2.098610	4.176607	1.029515
35	1	0	-0.323120	-0.155982	-2.396434

C_3H_6O

Zero-point correction= 0.084031 (Hartree/Particle)
Thermal correction to Energy= 0.089477
Thermal correction to Enthalpy= 0.090422
Thermal correction to Gibbs Free Energy= 0.054391
Sum of electronic and zero-point Energies= -193.044222

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.000000	0.186555	0.000058
2	6	0	-1.283398	-0.610514	-0.000003
3	6	0	1.283398	-0.610514	-0.000004
4	1	0	-1.318235	-1.258824	0.878346
5	1	0	-2.138681	0.060360	0.000017
6	1	0	-1.318210	-1.258734	-0.878422
7	1	0	2.138682	0.060359	-0.000227
8	1	0	1.318336	-1.258616	0.878497
9	1	0	1.318106	-1.258943	-0.878271
10	8	0	0.000000	1.390155	-0.000031

TS_2

Zero-point correction= 0.387065 (Hartree/Particle)
Thermal correction to Energy= 0.411959
Thermal correction to Enthalpy= 0.412903
Thermal correction to Gibbs Free Energy= 0.329626
Sum of electronic and zero-point Energies= -1624.086363

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	22	0	-0.149897	-0.320187	-0.291617
2	8	0	-0.789433	1.163664	-0.901602
3	8	0	0.165679	0.099093	1.491107
4	8	0	-1.373640	-1.665671	-0.419339
5	8	0	1.407965	-0.820576	-1.088130
6	6	0	-1.031822	2.745816	0.592030
7	6	0	-2.078868	3.288960	-0.167955
8	6	0	0.346771	3.264748	0.563965
9	1	0	-1.236363	1.968042	1.321536
10	1	0	-1.729932	2.335960	-0.873809
11	1	0	-3.096882	3.093539	0.145729
12	1	0	-1.892875	4.211512	-0.705677
13	1	0	1.062944	2.477927	0.789420
14	1	0	0.573267	3.747517	-0.385750
15	1	0	0.400981	4.023588	1.356345
16	6	0	0.897905	-0.590143	2.478005
17	6	0	2.336467	-0.092163	2.476635
18	6	0	0.830747	-2.096298	2.257640
19	1	0	0.441993	-0.357158	3.449384
20	1	0	2.366721	0.986902	2.639533
21	1	0	2.925271	-0.577856	3.257516
22	1	0	2.791198	-0.311964	1.506960
23	1	0	-0.206970	-2.430734	2.218140
24	1	0	1.311314	-2.357268	1.308998
25	1	0	1.343911	-2.631354	3.059076
26	6	0	-2.771041	-1.782519	-0.388236

27	6	0	-3.351945	-1.412410	-1.745179
28	6	0	-3.350270	-0.914974	0.723547
29	1	0	-3.008408	-2.832335	-0.172661
30	1	0	-2.927856	-2.048160	-2.522776
31	1	0	-4.438204	-1.525358	-1.751990
32	1	0	-3.101881	-0.373192	-1.974566
33	1	0	-2.880979	-1.157817	1.678410
34	1	0	-3.155497	0.139112	0.499578
35	1	0	-4.429326	-1.055456	0.813778
36	6	0	2.469746	-0.359526	-1.878484
37	6	0	3.702084	-1.205462	-1.596393
38	6	0	2.722846	1.118874	-1.613025
39	1	0	2.192553	-0.483975	-2.933641
40	1	0	3.484570	-2.258599	-1.775328
41	1	0	4.536233	-0.904596	-2.233542
42	1	0	4.001844	-1.088508	-0.552137
43	1	0	1.813486	1.692348	-1.804451
44	1	0	3.011906	1.257827	-0.566580
45	1	0	3.524426	1.502674	-2.247492

(^{i}PrO)$_3$Ti-OH ···C$_3$H$_6$

Zero-point correction= 0.391174 (Hartree/Particle)
Thermal correction to Energy= 0.417277
Thermal correction to Enthalpy= 0.418222
Thermal correction to Gibbs Free Energy= 0.331908
Sum of electronic and zero-point Energies= -1624.165210

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	22	0	0.106819	-0.665962	-0.471731
2	8	0	-0.715212	0.091278	-1.896564
3	8	0	0.352860	0.626860	0.747611
4	8	0	-0.911461	-1.950992	0.262019
5	8	0	1.677249	-1.375315	-0.973507
6	6	0	-1.823395	2.721024	-0.467321
7	6	0	-2.891488	2.683453	-1.254122
8	6	0	-0.547866	3.432426	-0.788262
9	1	0	-1.847596	2.186095	0.479588
10	1	0	-3.788290	2.147064	-0.968346
11	1	0	-2.906819	3.199561	-2.208638
12	1	0	0.283087	2.722967	-0.809463
13	1	0	-0.608667	3.939962	-1.751474
14	1	0	-0.317719	4.174054	-0.018947
15	6	0	0.439672	1.007023	2.098325
16	6	0	1.581763	1.997097	2.259547
17	6	0	0.614727	-0.221649	2.977341
18	1	0	-0.502617	1.506904	2.364255
19	1	0	1.440456	2.851817	1.597123
20	1	0	1.640827	2.356051	3.288556

21	1	0	2.528060	1.514485	2.004534
22	1	0	-0.204467	-0.925672	2.821965
23	1	0	1.549496	-0.726857	2.720263
24	1	0	0.647134	0.056677	4.032137
25	6	0	-2.261538	-2.135781	0.622285
26	6	0	-2.991256	-2.843891	-0.507265
27	6	0	-2.906777	-0.797716	0.961746
28	1	0	-2.270114	-2.773032	1.514950
29	1	0	-2.505670	-3.792773	-0.734470
30	1	0	-4.031294	-3.036131	-0.237020
31	1	0	-2.969616	-2.220208	-1.404189
32	1	0	-2.342572	-0.285452	1.744659
33	1	0	-2.925114	-0.160416	0.071913
34	1	0	-3.933119	-0.935319	1.306607
35	6	0	2.993993	-0.948311	-1.238705
36	6	0	3.845812	-1.154479	0.003136
37	6	0	2.996244	0.504421	-1.694973
38	1	0	3.377335	-1.579535	-2.048714
39	1	0	3.808953	-2.196565	0.320885
40	1	0	4.885011	-0.879344	-0.186638
41	1	0	3.462690	-0.529950	0.814650
42	1	0	2.343180	0.632336	-2.559856
43	1	0	2.633313	1.145411	-0.885154
44	1	0	4.003596	0.826591	-1.964606
45	1	0	-1.326311	0.836089	-1.873363

(^{i}PrO)$_3$Ti-OH

Zero-point correction= 0.308843 (Hartree/Particle)
Thermal correction to Energy= 0.329968
Thermal correction to Enthalpy= 0.330912
Thermal correction to Gibbs Free Energy= 0.253641
Sum of electronic and zero-point Energies= -1506.360638

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	22	0	-0.011733	-0.139769	0.896897
2	8	0	0.127148	-0.317615	2.699453
3	8	0	0.542424	-1.624778	0.057443
4	8	0	-1.696488	0.165780	0.392526
5	8	0	1.058706	1.202446	0.394665
6	6	0	1.671446	-2.150654	-0.602189
7	6	0	2.874813	-2.108572	0.326707
8	6	0	1.919187	-1.377819	-1.888755
9	1	0	1.440387	-3.193776	-0.847973
10	1	0	2.659214	-2.643066	1.252219
11	1	0	3.747770	-2.561858	-0.146503
12	1	0	3.111743	-1.069881	0.573290
13	1	0	1.033110	-1.404921	-2.525065
14	1	0	2.150132	-0.336047	-1.650367

15	1	0	2.758620	-1.802709	-2.442274
16	6	0	-2.751915	-0.025632	-0.518128
17	6	0	-3.980115	-0.503670	0.238983
18	6	0	-2.336393	-0.999270	-1.608951
19	1	0	-2.969928	0.949958	-0.971361
20	1	0	-4.234199	0.198921	1.032632
21	1	0	-4.834099	-0.597242	-0.434084
22	1	0	-3.781712	-1.479392	0.687746
23	1	0	-1.462114	-0.624184	-2.143760
24	1	0	-2.075491	-1.963781	-1.168195
25	1	0	-3.148042	-1.143044	-2.324328
26	6	0	1.243683	2.268697	-0.504844
27	6	0	1.254022	3.577360	0.267785
28	6	0	0.165648	2.245703	-1.578502
29	1	0	2.223651	2.125770	-0.978430
30	1	0	2.016035	3.550969	1.046389
31	1	0	1.459328	4.416771	-0.398991
32	1	0	0.281944	3.734760	0.740010
33	1	0	0.181109	1.292871	-2.112620
34	1	0	-0.817269	2.368856	-1.116890
35	1	0	0.318938	3.050219	-2.299865
36	1	0	-0.417576	-0.757791	3.351353

C_3H_6

Zero-point correction= 0.079948 (Hartree/Particle)
Thermal correction to Energy= 0.084004
Thermal correction to Enthalpy= 0.084949
Thermal correction to Gibbs Free Energy= 0.054984
Sum of electronic and zero-point Energies= -117.797291

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.227284	-0.162202	0.000003
2	1	0	-1.164298	-1.250691	-0.000708
3	1	0	-1.798337	0.151043	-0.877352
4	6	0	0.134880	0.456436	-0.000030
5	1	0	0.171190	1.542987	-0.000019
6	6	0	1.271962	-0.221821	0.000015
7	1	0	1.280030	-1.306667	-0.000071
8	1	0	2.231777	0.278923	0.000056
9	1	0	-1.797711	0.149924	0.878168

$(^{i}PrO)_3Ti^{\bullet}$

Zero-point correction= 0.295297 (Hartree/Particle)
Thermal correction to Energy= 0.314691
Thermal correction to Enthalpy= 0.315636
Thermal correction to Gibbs Free Energy= 0.239815
Sum of electronic and zero-point Energies= -1430.486366

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	22	0	0.211267	-0.136404	-0.077264
2	8	0	-0.973494	-1.473729	-0.336570
3	8	0	1.985109	-0.480498	-0.031902
4	8	0	-0.407527	1.544205	0.136079
5	6	0	-2.089211	-2.306678	-0.462015
6	6	0	-3.360642	-1.483392	-0.318042
7	6	0	-2.013871	-3.419977	0.571687
8	1	0	-2.065129	-2.752685	-1.464478
9	1	0	-3.378008	-0.680589	-1.056834
10	1	0	-4.247776	-2.104548	-0.455066
11	1	0	-3.397876	-1.036938	0.678760
12	1	0	-1.086917	-3.982216	0.456880
13	1	0	-2.037823	-2.992375	1.576645
14	1	0	-2.856043	-4.106137	0.464928
15	6	0	3.368659	-0.672352	0.009873
16	6	0	3.917318	-0.151338	1.329762
17	6	0	4.015590	0.016821	-1.182265
18	1	0	3.565114	-1.750380	-0.054890
19	1	0	3.430448	-0.651536	2.167598
20	1	0	4.993131	-0.323151	1.397964
21	1	0	3.728914	0.921665	1.409296
22	1	0	3.597628	-0.364661	-2.114444
23	1	0	3.828893	1.091927	-1.132303
24	1	0	5.094269	-0.150286	-1.188978
25	6	0	-1.063318	2.771382	0.270553
26	6	0	-2.234399	2.620639	1.229763
27	6	0	-1.513028	3.259670	-1.098157
28	1	0	-0.350281	3.493299	0.688819
29	1	0	-1.888159	2.256269	2.197647
30	1	0	-2.742897	3.575202	1.377311
31	1	0	-2.950264	1.901766	0.824062
32	1	0	-0.659081	3.345046	-1.770848
33	1	0	-2.222974	2.548251	-1.526861
34	1	0	-1.998326	4.234486	-1.023211

^{i}PrO$^{\bullet}$

Zero-point correction= 0.094485 (Hartree/Particle)
Thermal correction to Energy= 0.099683
Thermal correction to Enthalpy= 0.100628
Thermal correction to Gibbs Free Energy= 0.066590
Sum of electronic and zero-point Energies= -193.559482

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	0.000001	1.415966	0.148749
2	6	0	0.000000	0.121895	-0.306186

3	6	0	-1.275516	-0.623483	0.079773
4	6	0	1.275515	-0.623484	0.079773
5	1	0	0.000000	0.267588	-1.405615
6	1	0	-2.153411	-0.057805	-0.229546
7	1	0	-1.303010	-1.609683	-0.385496
8	1	0	-1.310346	-0.754950	1.162774
9	1	0	2.153411	-0.057807	-0.229547
10	1	0	1.310346	-0.754949	1.162774
11	1	0	1.303008	-1.609685	-0.385496

(^{i}PrO)$_3$TiO$^{\bullet}$

Zero-point correction= 0.298384 (Hartree/Particle)
Thermal correction to Energy= 0.318643
Thermal correction to Enthalpy= 0.319587
Thermal correction to Gibbs Free Energy= 0.244321
Sum of electronic and zero-point Energies= -1505.675098

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	22	0	-0.010643	-0.132823	0.987110
2	8	0	-0.003726	1.617670	0.677561
3	8	0	1.530855	-0.842732	0.428482
4	8	0	-1.364528	-0.962088	0.180180
5	6	0	0.651496	2.740523	0.131836
6	6	0	-0.092531	3.195014	-1.112228
7	6	0	2.106965	2.411376	-0.157098
8	1	0	0.603499	3.530776	0.889542
9	1	0	-1.134948	3.411258	-0.877428
10	1	0	0.366734	4.093821	-1.527100
11	1	0	-0.063042	2.407460	-1.869519
12	1	0	2.606303	2.049260	0.742424
13	1	0	2.169991	1.630887	-0.919790
14	1	0	2.632763	3.296127	-0.519835
15	6	0	2.205788	-1.447959	-0.648272
16	6	0	1.362697	-1.360320	-1.912428
17	6	0	2.541569	-2.884604	-0.284796
18	1	0	3.137436	-0.887647	-0.797905
19	1	0	1.127637	-0.318004	-2.143519
20	1	0	1.892168	-1.791171	-2.763887
21	1	0	0.424366	-1.902421	-1.770101
22	1	0	3.121063	-2.915957	0.637587
23	1	0	1.620452	-3.452282	-0.135629
24	1	0	3.119416	-3.358403	-1.080288
25	6	0	-2.480125	-1.009288	-0.674922
26	6	0	-2.441537	0.170268	-1.632974
27	6	0	-3.750167	-1.032342	0.159122
28	1	0	-2.408565	-1.942385	-1.247318
29	1	0	-1.520074	0.154968	-2.218197
30	1	0	-3.289928	0.140761	-2.318806

31	1	0	-2.477417	1.104860	-1.068145
32	1	0	-3.731622	-1.869768	0.856310
33	1	0	-3.833451	-0.106553	0.732414
34	1	0	-4.628176	-1.127340	-0.482067
35	8	0	-0.178275	-0.303119	2.833202

$^{i}Pr^{\bullet}$

Zero-point correction= 0.088413 (Hartree/Particle)
Thermal correction to Energy= 0.093583
Thermal correction to Enthalpy= 0.094527
Thermal correction to Gibbs Free Energy= 0.061262
Sum of electronic and zero-point Energies= -118.351600

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.000000	0.541742	-0.052599
2	6	0	1.287150	-0.199691	0.004052
3	6	0	-1.287150	-0.199691	0.004052
4	1	0	0.000000	1.610015	0.118780
5	1	0	2.140479	0.443020	-0.212305
6	1	0	1.456511	-0.644729	0.995395
7	1	0	1.294709	-1.030380	-0.708998
8	1	0	-2.140478	0.443020	-0.212308
9	1	0	-1.294707	-1.030382	-0.708996
10	1	0	-1.456512	-0.644726	0.995396

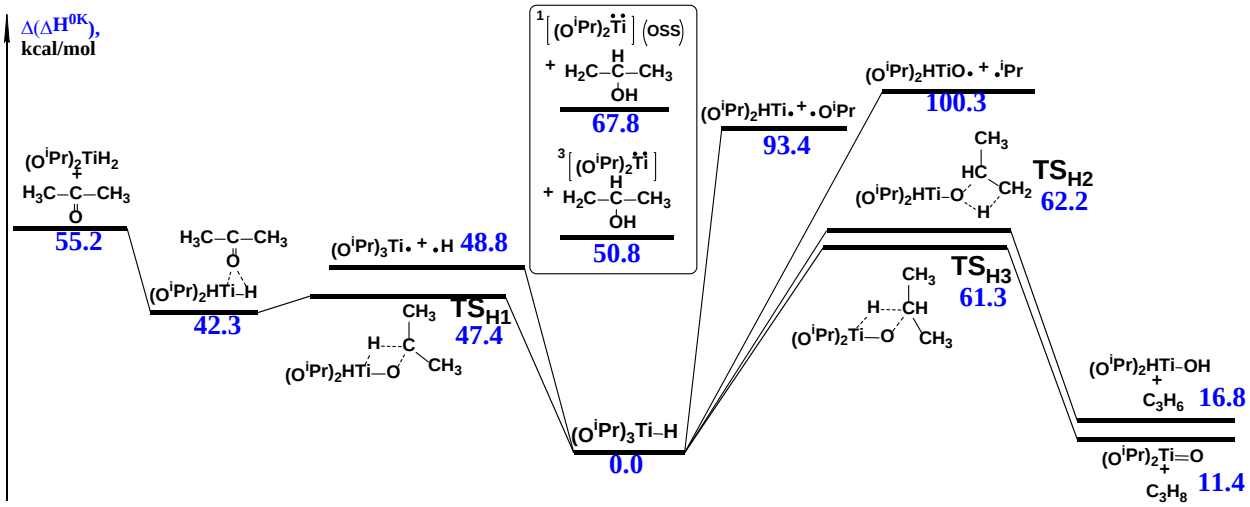


Figure 4. The relative enthalpies at 0 K ($\Delta(\Delta H^{0K})$) of the stationary points on the PES corresponding to thermal decomposition of the hydride intermediate $(^{i}PrO)_3Ti$-H. The latter species was chosen as a reference compound for the calculations of the relative thermodynamic

properties. Inset: relative enthalpies of the possible biradical intermediates. All values are in kcal/mol and calculated at the M06-2X/6-311++G(2df,p) level of theory.

TS_{H1}

Zero-point correction= 0.296812 (Hartree/Particle)
Thermal correction to Energy= 0.315875
Thermal correction to Enthalpy= 0.316819
Thermal correction to Gibbs Free Energy= 0.246857
Sum of electronic and zero-point Energies= -1430.986854

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	22	0	-0.238398	-0.278553	0.259356
2	8	0	-2.289347	-0.393804	1.052918
3	8	0	1.379461	-0.839583	-0.157835
4	8	0	-0.323952	1.465958	-0.115861
5	6	0	-2.994847	-0.723916	0.099820
6	6	0	-3.453029	0.284512	-0.911585
7	6	0	-3.588836	-2.098354	0.029867
8	1	0	-1.105957	-1.210418	-0.949835
9	1	0	-2.837605	1.179236	-0.854773
10	1	0	-3.429816	-0.137957	-1.915084
11	1	0	-4.492030	0.537593	-0.675422
12	1	0	-3.088572	-2.761792	0.730376
13	1	0	-4.648336	-2.022320	0.293734
14	1	0	-3.524807	-2.489796	-0.984415
15	6	0	2.707204	-1.269331	-0.254711
16	6	0	2.750247	-2.635525	-0.920221
17	6	0	3.334786	-1.280980	1.130045
18	1	0	3.241256	-0.545699	-0.885254
19	1	0	2.264090	-2.598062	-1.895221
20	1	0	3.781835	-2.966511	-1.052376
21	1	0	2.225627	-3.364600	-0.299150
22	1	0	3.269703	-0.291600	1.584562
23	1	0	2.799795	-1.984685	1.770748
24	1	0	4.383981	-1.577052	1.075099
25	6	0	0.424180	2.607903	-0.459203
26	6	0	1.839883	2.226978	-0.864895
27	6	0	0.410447	3.576322	0.713007
28	1	0	-0.076213	3.076375	-1.316000
29	1	0	1.824180	1.508345	-1.685709
30	1	0	2.396755	3.111650	-1.178983
31	1	0	2.357858	1.766911	-0.019259
32	1	0	-0.614466	3.821326	0.991647
33	1	0	0.900011	3.115791	1.573903
34	1	0	0.937301	4.498062	0.459146
35	1	0	-0.029323	-0.522852	1.919911

$(^{i}PrO)_2TiH_2 \cdots C_3H_6O$

Zero-point correction= 0.296988 (Hartree/Particle)
Thermal correction to Energy= 0.316894
Thermal correction to Enthalpy= 0.317838
Thermal correction to Gibbs Free Energy= 0.244679
Sum of electronic and zero-point Energies= -1430.994934

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	22	0	-0.008702	-0.586402	-0.170134
2	8	0	2.066715	-1.216190	-0.537560
3	8	0	-1.759109	-0.588703	0.055447
4	8	0	0.572279	1.098738	0.095493
5	6	0	3.122871	-0.952952	0.008476
6	6	0	3.194737	-0.024631	1.181082
7	6	0	4.392869	-1.569689	-0.490514
8	1	0	0.360220	-1.621402	1.151327
9	1	0	2.990735	0.988259	0.825774
10	1	0	2.392731	-0.275373	1.878028
11	1	0	4.166690	-0.061454	1.668799
12	1	0	4.206760	-2.164841	-1.380304
13	1	0	5.123229	-0.784573	-0.698657
14	1	0	4.815431	-2.194895	0.300331
15	6	0	-3.145466	-0.697303	0.190995
16	6	0	-3.481720	-1.947362	0.988554
17	6	0	-3.785586	-0.702476	-1.188425
18	1	0	-3.492939	0.186060	0.744229
19	1	0	-2.977217	-1.926274	1.954723
20	1	0	-4.558355	-2.023088	1.151606
21	1	0	-3.145990	-2.832401	0.443964
22	1	0	-3.513964	0.200689	-1.736179
23	1	0	-3.430216	-1.565615	-1.754759
24	1	0	-4.873052	-0.753676	-1.109237
25	6	0	0.165773	2.421909	0.339788
26	6	0	-1.305711	2.483375	0.721502
27	6	0	0.466839	3.268958	-0.887557
28	1	0	0.763524	2.795038	1.182958
29	1	0	-1.505554	1.842903	1.582055
30	1	0	-1.592588	3.507298	0.968274
31	1	0	-1.921748	2.134772	-0.110989
32	1	0	1.524255	3.203345	-1.146245
33	1	0	-0.116988	2.904813	-1.735720
34	1	0	0.213285	4.315601	-0.709045
35	1	0	-0.023513	-1.004072	-1.818440

(^{i}PrO)$_2$TiH$_2$

Zero-point correction= 0.210374 (Hartree/Particle)
Thermal correction to Energy= 0.224179
Thermal correction to Enthalpy= 0.225123

Thermal correction to Gibbs Free Energy= 0.167374
Sum of electronic and zero-point Energies= -1237.930201

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	22	0	0.000012	-1.366029	-0.000031
2	8	0	1.491811	-0.485623	-0.325145
3	8	0	-1.491796	-0.485648	0.325055
4	1	0	-0.291916	-2.379391	-1.324840
5	6	0	2.511657	0.473754	-0.461033
6	6	0	3.691655	0.070180	0.406718
7	6	0	1.971225	1.847093	-0.099767
8	1	0	2.818520	0.470554	-1.512838
9	1	0	4.040199	-0.926003	0.135210
10	1	0	4.514516	0.776225	0.283743
11	1	0	3.392826	0.058790	1.456815
12	1	0	1.116742	2.099848	-0.728682
13	1	0	1.651084	1.855305	0.944991
14	1	0	2.740132	2.609853	-0.232644
15	6	0	-2.511597	0.473758	0.461059
16	6	0	-3.691735	0.070179	-0.406506
17	6	0	-1.971222	1.847095	0.099680
18	1	0	-2.818307	0.470602	1.512907
19	1	0	-4.040315	-0.925958	-0.134878
20	1	0	-4.514537	0.776286	-0.283478
21	1	0	-3.393041	0.058692	-1.456639
22	1	0	-1.116700	2.099913	0.728516
23	1	0	-1.651169	1.855291	-0.945105
24	1	0	-2.740151	2.609827	0.232597
25	1	0	0.291837	-2.379389	1.324812

TS_{H2}
Zero-point correction= 0.294886 (Hartree/Particle)
Thermal correction to Energy= 0.314427
Thermal correction to Enthalpy= 0.315371
Thermal correction to Gibbs Free Energy= 0.243254
Sum of electronic and zero-point Energies= -1430.963215

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	22	0	0.208730	0.032018	-0.484965
2	8	0	-0.011737	-1.645282	-0.195075
3	8	0	-1.182382	0.874841	0.373592
4	8	0	1.873814	0.673210	-0.205963
5	6	0	-2.065577	-2.125627	0.456551
6	6	0	-1.632059	-3.411054	0.814857
7	6	0	-2.779995	-1.837091	-0.799541
8	1	0	-1.968982	-1.305985	1.161776

9	1	0	-0.598149	-2.931027	0.350293
10	1	0	-1.436039	-3.614750	1.860115
11	1	0	-1.947075	-4.243280	0.196063
12	1	0	-2.632275	-0.808313	-1.120286
13	1	0	-2.499033	-2.535972	-1.586029
14	1	0	-3.845867	-1.983794	-0.576004
15	6	0	-1.600791	2.195608	0.615824
16	6	0	-2.952256	2.410910	-0.049522
17	6	0	-0.564050	3.193207	0.118163
18	1	0	-1.716640	2.318632	1.700833
19	1	0	-3.676544	1.681313	0.316919
20	1	0	-3.335569	3.413031	0.152398
21	1	0	-2.849322	2.285943	-1.130367
22	1	0	0.403816	3.006402	0.586650
23	1	0	-0.445146	3.092973	-0.965156
24	1	0	-0.868347	4.218186	0.338300
25	6	0	3.212137	0.353999	0.069656
26	6	0	3.747512	-0.584671	-1.001610
27	6	0	3.318941	-0.256712	1.459412
28	1	0	3.785566	1.289155	0.045225
29	1	0	3.638794	-0.132765	-1.988026
30	1	0	4.801917	-0.811801	-0.832105
31	1	0	3.179822	-1.518928	-0.984222
32	1	0	2.919101	0.428939	2.207587
33	1	0	2.742177	-1.184639	1.493371
34	1	0	4.357951	-0.480221	1.709257
35	1	0	-0.142964	0.258949	-2.150519

(^{i}PrO)$_2$Ti(H)OH

Zero-point correction= 0.217115 (Hartree/Particle)
Thermal correction to Energy= 0.232564
Thermal correction to Enthalpy= 0.233508
Thermal correction to Gibbs Free Energy= 0.171088
Sum of electronic and zero-point Energies= -1313.238251

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	22	0	-0.025635	0.870488	-0.517699
2	8	0	0.338905	2.488492	0.173327
3	8	0	1.129265	-0.383216	-0.031123
4	8	0	-1.724781	0.364940	-0.426677
5	6	0	2.338757	-0.864544	0.505580
6	6	0	3.190865	0.300176	0.981106
7	6	0	3.043059	-1.704003	-0.547067
8	1	0	2.083505	-1.501078	1.361171
9	1	0	2.648585	0.898922	1.713827
10	1	0	4.115441	-0.059598	1.435697
11	1	0	3.444510	0.942721	0.134561
12	1	0	2.398485	-2.517930	-0.879051

13	1	0	3.288900	-1.082301	-1.410290
14	1	0	3.965042	-2.127163	-0.144727
15	6	0	-2.729840	-0.596505	-0.206243
16	6	0	-3.570193	-0.174469	0.987582
17	6	0	-2.104061	-1.968113	-0.014359
18	1	0	-3.360624	-0.608960	-1.102313
19	1	0	-3.983865	0.821396	0.828793
20	1	0	-4.392532	-0.874609	1.143938
21	1	0	-2.952958	-0.155997	1.888536
22	1	0	-1.496827	-2.236265	-0.880050
23	1	0	-1.459893	-1.963119	0.868216
24	1	0	-2.875999	-2.727605	0.120515
25	1	0	-0.072836	3.281062	0.513068
26	1	0	0.256388	1.042808	-2.166331

TS_{H3}

Zero-point correction= 0.300604 (Hartree/Particle)
Thermal correction to Energy= 0.319410
Thermal correction to Enthalpy= 0.320354
Thermal correction to Gibbs Free Energy= 0.251468
Sum of electronic and zero-point Energies= -1430.964659

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	22	0	-0.000022	-0.075156	-0.599087
2	8	0	0.000057	0.839593	0.805460
3	8	0	1.541361	-0.999225	-0.870302
4	8	0	-1.541437	-0.999235	-0.870091
5	6	0	0.000539	2.722971	-0.275106
6	6	0	1.291918	3.039830	0.389066
7	6	0	-1.290316	3.040731	0.389653
8	1	0	0.000394	3.009932	-1.317992
9	1	0	2.126579	2.548290	-0.108848
10	1	0	1.434243	4.123367	0.275702
11	1	0	1.284370	2.771515	1.441074
12	1	0	-2.125544	2.549774	-0.107883
13	1	0	-1.282483	2.772413	1.441658
14	1	0	-1.431931	4.124367	0.276346
15	6	0	2.745812	-1.375444	-0.258996
16	6	0	2.461209	-2.368664	0.859068
17	6	0	3.479924	-0.146433	0.258036
18	1	0	3.363624	-1.866565	-1.021308
19	1	0	1.910027	-3.225624	0.470563
20	1	0	3.387481	-2.723553	1.315193
21	1	0	1.855050	-1.885487	1.630466
22	1	0	3.678573	0.546099	-0.562528
23	1	0	2.860198	0.358267	1.004588
24	1	0	4.431526	-0.420006	0.718041
25	6	0	-2.746401	-1.374408	-0.259156

26	6	0	-3.479556	-0.144756	0.257725
27	6	0	-2.463039	-2.367949	0.858937
28	1	0	-3.364429	-1.864932	-1.021678
29	1	0	-3.677350	0.547979	-0.562878
30	1	0	-4.431534	-0.417475	0.717460
31	1	0	-2.859564	0.359359	1.004451
32	1	0	-1.912571	-3.225417	0.470543
33	1	0	-1.856643	-1.885383	1.630528
34	1	0	-3.389777	-2.721979	1.314784
35	1	0	-0.000134	1.294186	-1.664273

(^{i}PrO)$_2$Ti=O

Zero-point correction= 0.200181 (Hartree/Particle)
Thermal correction to Energy= 0.213504
Thermal correction to Enthalpy= 0.214448
Thermal correction to Gibbs Free Energy= 0.157380
Sum of electronic and zero-point Energies= -1312.043445

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	22	0	0.061306	-0.427783	-0.091649
2	8	0	1.547544	0.482919	0.435438
3	8	0	0.251377	-1.878285	-0.743816
4	8	0	-1.635625	0.198862	0.110000
5	6	0	2.952808	0.493077	0.530141
6	6	0	3.500841	1.599369	-0.357663
7	6	0	3.525571	-0.866844	0.166085
8	1	0	3.203878	0.722545	1.572848
9	1	0	3.051807	2.556708	-0.092910
10	1	0	4.584064	1.678158	-0.251657
11	1	0	3.271455	1.383816	-1.404052
12	1	0	3.115567	-1.645558	0.811162
13	1	0	3.271627	-1.117842	-0.866659
14	1	0	4.612165	-0.867787	0.268622
15	6	0	-3.013962	-0.033847	-0.064671
16	6	0	-3.568562	0.982258	-1.050341
17	6	0	-3.707087	0.053651	1.285589
18	1	0	-3.151650	-1.042711	-0.474559
19	1	0	-3.058310	0.903057	-2.011084
20	1	0	-4.635555	0.819461	-1.211577
21	1	0	-3.422863	1.991917	-0.661052
22	1	0	-3.292421	-0.679867	1.978033
23	1	0	-3.565465	1.049946	1.709241
24	1	0	-4.777062	-0.134577	1.182115

(^{i}PrO)$_3$Ti$^{\bullet}$

Zero-point correction= 0.295297 (Hartree/Particle)
Thermal correction to Energy= 0.314691
Thermal correction to Enthalpy= 0.315636

Thermal correction to Gibbs Free Energy= 0.239815
Sum of electronic and zero-point Energies= -1430.486366

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	22	0	0.211267	-0.136404	-0.077264
2	8	0	-0.973494	-1.473729	-0.336570
3	8	0	1.985109	-0.480498	-0.031902
4	8	0	-0.407527	1.544205	0.136079
5	6	0	-2.089211	-2.306678	-0.462015
6	6	0	-3.360642	-1.483392	-0.318042
7	6	0	-2.013871	-3.419977	0.571687
8	1	0	-2.065129	-2.752685	-1.464478
9	1	0	-3.378008	-0.680589	-1.056834
10	1	0	-4.247776	-2.104548	-0.455066
11	1	0	-3.397876	-1.036938	0.678760
12	1	0	-1.086917	-3.982216	0.456880
13	1	0	-2.037823	-2.992375	1.576645
14	1	0	-2.856043	-4.106137	0.464928
15	6	0	3.368659	-0.672352	0.009873
16	6	0	3.917318	-0.151338	1.329762
17	6	0	4.015590	0.016821	-1.182265
18	1	0	3.565114	-1.750380	-0.054890
19	1	0	3.430448	-0.651536	2.167598
20	1	0	4.993131	-0.323151	1.397964
21	1	0	3.728914	0.921665	1.409296
22	1	0	3.597628	-0.364661	-2.114444
23	1	0	3.828893	1.091927	-1.132303
24	1	0	5.094269	-0.150286	-1.188978
25	6	0	-1.063318	2.771382	0.270553
26	6	0	-2.234399	2.620639	1.229763
27	6	0	-1.513028	3.259670	-1.098157
28	1	0	-0.350281	3.493299	0.688819
29	1	0	-1.888159	2.256269	2.197647
30	1	0	-2.742897	3.575202	1.377311
31	1	0	-2.950264	1.901766	0.824062
32	1	0	-0.659081	3.345046	-1.770848
33	1	0	-2.222974	2.548251	-1.526861
34	1	0	-1.998326	4.234486	-1.023211

(^{i}PrO)$_2$HTi$^{\bullet}$

Zero-point correction= 0.202543 (Hartree/Particle)
Thermal correction to Energy= 0.216311
Thermal correction to Enthalpy= 0.217255
Thermal correction to Gibbs Free Energy= 0.157878
Sum of electronic and zero-point Energies= -1237.353966

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z

1	22	0	0.021241	-0.983385	-0.217145
2	8	0	1.704063	-0.366263	-0.313729
3	8	0	-1.514842	-0.079552	-0.014540
4	6	0	2.943734	0.288139	-0.319598
5	6	0	3.819579	-0.278971	0.786219
6	6	0	2.734797	1.787059	-0.170316
7	1	0	3.418308	0.088253	-1.287852
8	1	0	3.935443	-1.355946	0.664090
9	1	0	4.807596	0.184324	0.771359
10	1	0	3.359683	-0.086910	1.758209
11	1	0	2.093595	2.164834	-0.967549
12	1	0	2.258880	2.000620	0.789587
13	1	0	3.688352	2.316332	-0.210212
14	6	0	-2.688635	0.670006	0.148179
15	6	0	-3.382868	0.247787	1.433300
16	6	0	-3.580184	0.482183	-1.069060
17	1	0	-2.406174	1.727238	0.224870
18	1	0	-2.718824	0.381879	2.287776
19	1	0	-4.284932	0.839961	1.596510
20	1	0	-3.661993	-0.806135	1.372320
21	1	0	-3.054753	0.780426	-1.976826
22	1	0	-3.862696	-0.568638	-1.160454
23	1	0	-4.487526	1.081800	-0.978349
24	1	0	-0.144573	-2.724266	-0.332476

(^{i}PrO)$_2$HTiO$^{\bullet}$

Zero-point correction= 0.206400 (Hartree/Particle)
Thermal correction to Energy= 0.221138
Thermal correction to Enthalpy= 0.222082
Thermal correction to Gibbs Free Energy= 0.160562
Sum of electronic and zero-point Energies= -1312.550976

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	22	0	0.071237	1.248383	-0.298564
2	8	0	-1.502999	0.536655	0.050236
3	8	0	1.484565	0.200805	-0.436822
4	6	0	-2.616365	-0.310072	0.206372
5	6	0	-2.363311	-1.271875	1.354591
6	6	0	-2.886435	-1.030253	-1.103877
7	1	0	-3.470584	0.330733	0.450802
8	1	0	-2.142588	-0.724050	2.270864
9	1	0	-3.238455	-1.900756	1.525418
10	1	0	-1.513539	-1.916200	1.117770
11	1	0	-3.032550	-0.311881	-1.910480
12	1	0	-2.037449	-1.670058	-1.356438
13	1	0	-3.778118	-1.653634	-1.021176
14	6	0	2.303815	-0.944046	-0.441271

15	6	0	1.492393	-2.149345	0.003788
16	6	0	3.507960	-0.696067	0.451122
17	1	0	2.641326	-1.093058	-1.472682
18	1	0	0.619806	-2.279849	-0.638673
19	1	0	2.095332	-3.057656	-0.039881
20	1	0	1.152525	-2.006821	1.032410
21	1	0	4.053600	0.186327	0.117802
22	1	0	3.181109	-0.534745	1.480274
23	1	0	4.181192	-1.554462	0.428264
24	8	0	0.419119	2.665458	0.835853
25	1	0	-0.112630	1.908293	-1.834350

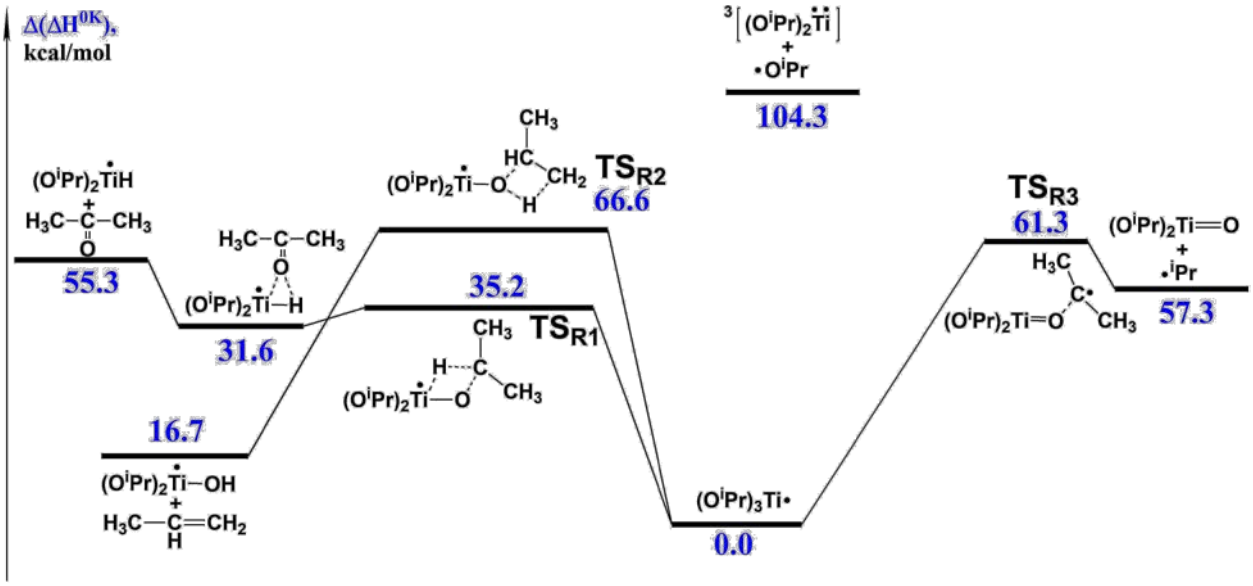


Figure 5. The relative enthalpies at 0 K ($\Delta(\Delta H^{0K})$) of the stationary points on the PES corresponding to thermal decomposition of the radical intermediate $(^{i}PrO)_3Ti\bullet$. The latter species was chosen as a reference compound for the calculations of the relative thermodynamic properties. All values are in kcal/mol and calculated at the M06-2X/6-311++G(2df,p) level of theory.

TS_{R1}•

Zero-point correction= 0.288234 (Hartree/Particle)
Thermal correction to Energy= 0.307566
Thermal correction to Enthalpy= 0.308510
Thermal correction to Gibbs Free Energy= 0.234603
Sum of electronic and zero-point Energies= -1430.430335

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	22	0	-0.158288	0.060161	0.162510
2	8	0	0.639560	1.642218	-1.044329
3	8	0	1.155808	-1.195677	0.292343

4	8	0	-1.929450	-0.150656	-0.186993
5	6	0	1.147825	2.523802	-0.355427
6	6	0	0.503990	3.866743	-0.241672
7	6	0	2.451741	2.309322	0.342877
8	1	0	0.011168	1.196215	1.513841
9	1	0	-0.274991	3.983564	-0.990482
10	1	0	0.057531	3.913327	0.755956
11	1	0	1.245129	4.663804	-0.311917
12	1	0	2.700774	1.250520	0.371608
13	1	0	3.221446	2.858919	-0.209522
14	1	0	2.405774	2.718300	1.352136
15	6	0	2.055212	-2.254977	0.397446
16	6	0	3.473245	-1.710939	0.506445
17	6	0	1.902056	-3.187559	-0.796074
18	1	0	1.825535	-2.815530	1.313342
19	1	0	3.556072	-1.045388	1.367212
20	1	0	4.197245	-2.519916	0.621483
21	1	0	3.722051	-1.149401	-0.397950
22	1	0	0.877110	-3.555029	-0.859456
23	1	0	2.133100	-2.647727	-1.717349
24	1	0	2.575697	-4.042803	-0.713835
25	6	0	-3.310728	-0.314199	-0.275811
26	6	0	-3.979874	0.296487	0.947667
27	6	0	-3.648866	-1.791236	-0.423304
28	1	0	-3.661623	0.216317	-1.171550
29	1	0	-3.712413	1.349782	1.038109
30	1	0	-5.066574	0.211849	0.882693
31	1	0	-3.640134	-0.220415	1.848020
32	1	0	-3.148352	-2.209404	-1.297409
33	1	0	-3.311809	-2.335657	0.461917
34	1	0	-4.725348	-1.936611	-0.533114

(^{i}PrO)$_2$TiH$^{\bullet\cdots}$C$_3$H$_6$O

Zero-point correction= 0.288449 (Hartree/Particle)
Thermal correction to Energy= 0.308520
Thermal correction to Enthalpy= 0.309464
Thermal correction to Gibbs Free Energy= 0.234643
Sum of electronic and zero-point Energies= -1430.435948

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	22	0	-0.234886	-0.133310	0.201382
2	8	0	0.180810	1.884487	-0.234551
3	8	0	-1.977560	-0.478779	-0.192962
4	8	0	1.322236	-0.977436	-0.265963
5	6	0	1.173946	2.566257	-0.021653
6	6	0	1.185888	4.009048	-0.408496
7	6	0	2.379179	1.974270	0.634626
8	1	0	-0.089949	0.242739	1.908392

9	1	0	2.035419	4.201570	-1.068014
10	1	0	0.254747	4.286840	-0.894726
11	1	0	1.339500	4.613583	0.489128
12	1	0	3.139140	2.720291	0.855579
13	1	0	2.048371	1.462843	1.544175
14	1	0	2.786902	1.199930	-0.020642
15	6	0	-3.350337	-0.697171	-0.293243
16	6	0	-4.061229	0.622173	-0.562476
17	6	0	-3.859700	-1.359605	0.979252
18	1	0	-3.532575	-1.372925	-1.140080
19	1	0	-3.668808	1.085868	-1.468407
20	1	0	-5.135622	0.470125	-0.683849
21	1	0	-3.896182	1.304090	0.274994
22	1	0	-3.336454	-2.300817	1.151580
23	1	0	-3.673535	-0.702936	1.832012
24	1	0	-4.931002	-1.560741	0.914349
25	6	0	2.464893	-1.762070	-0.399093
26	6	0	2.138662	-3.039465	-1.160160
27	6	0	3.047044	-2.059666	0.976518
28	1	0	3.209192	-1.195675	-0.980050
29	1	0	1.711518	-2.801351	-2.134834
30	1	0	3.033596	-3.647147	-1.307794
31	1	0	1.408314	-3.624878	-0.596879
32	1	0	3.262959	-1.131008	1.507241
33	1	0	2.321114	-2.623666	1.566284
34	1	0	3.966894	-2.642723	0.897281

(^{i}PrO)$_2$HTi$^{\bullet}$

Zero-point correction= 0.202543 (Hartree/Particle)
Thermal correction to Energy= 0.216311
Thermal correction to Enthalpy= 0.217255
Thermal correction to Gibbs Free Energy= 0.157878
Sum of electronic and zero-point Energies= -1237.353966

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	22	0	0.021241	-0.983385	-0.217145
2	8	0	1.704063	-0.366263	-0.313729
3	8	0	-1.514842	-0.079552	-0.014540
4	6	0	2.943734	0.288139	-0.319598
5	6	0	3.819579	-0.278971	0.786219
6	6	0	2.734797	1.787059	-0.170316
7	1	0	3.418308	0.088253	-1.287852
8	1	0	3.935443	-1.355946	0.664090
9	1	0	4.807596	0.184324	0.771359
10	1	0	3.359683	-0.086910	1.758209
11	1	0	2.093595	2.164834	-0.967549
12	1	0	2.258880	2.000620	0.789587
13	1	0	3.688352	2.316332	-0.210212

14	6	0	-2.688635	0.670006	0.148179
15	6	0	-3.382868	0.247787	1.433300
16	6	0	-3.580184	0.482183	-1.069060
17	1	0	-2.406174	1.727238	0.224870
18	1	0	-2.718824	0.381879	2.287776
19	1	0	-4.284932	0.839961	1.596510
20	1	0	-3.661993	-0.806135	1.372320
21	1	0	-3.054753	0.780426	-1.976826
22	1	0	-3.862696	-0.568638	-1.160454
23	1	0	-4.487526	1.081800	-0.978349
24	1	0	-0.144573	-2.724266	-0.332476

$TS_{R2}^{\bullet}$

Zero-point correction= 0.287217 (Hartree/Particle)
Thermal correction to Energy= 0.306642
Thermal correction to Enthalpy= 0.307586
Thermal correction to Gibbs Free Energy= 0.233457
Sum of electronic and zero-point Energies= -1430.380292

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	22	0	-0.042194	-0.354679	-0.176332
2	8	0	1.347265	-1.526526	-0.233002
3	8	0	0.405187	1.382354	-0.481768
4	8	0	-1.721297	-0.896710	0.219782
5	6	0	3.265877	-1.362349	-0.261133
6	6	0	3.458471	-2.690062	0.177194
7	6	0	3.475708	-0.196270	0.643971
8	1	0	3.293954	-1.155218	-1.324913
9	1	0	2.108819	-2.503283	0.126660
10	1	0	3.734221	-3.441060	-0.551141
11	1	0	3.800542	-2.841625	1.193934
12	1	0	2.911859	0.678013	0.322258
13	1	0	3.198829	-0.455845	1.666083
14	1	0	4.543323	0.046525	0.632794
15	6	0	0.256662	2.772780	-0.521409
16	6	0	1.455965	3.430945	0.144397
17	6	0	-1.051539	3.172023	0.145666
18	1	0	0.225883	3.080484	-1.574613
19	1	0	2.378759	3.137108	-0.357589
20	1	0	1.373641	4.518853	0.109715
21	1	0	1.514083	3.119027	1.190179
22	1	0	-1.891832	2.672775	-0.339653
23	1	0	-1.034066	2.872717	1.197064
24	1	0	-1.207963	4.251144	0.093565
25	6	0	-3.051155	-1.225309	0.495014
26	6	0	-3.550290	-2.235134	-0.527462
27	6	0	-3.900085	0.037287	0.505636
28	1	0	-3.086647	-1.684739	1.491186

29	1	0	-2.916376	-3.122140	-0.524799
30	1	0	-4.576175	-2.536096	-0.307088
31	1	0	-3.523410	-1.792986	-1.526045
32	1	0	-3.510209	0.750803	1.232902
33	1	0	-3.879098	0.503074	-0.482707
34	1	0	-4.936802	-0.191013	0.760151

(^{i}PrO)$_2$Ti(OH)$^{\bullet}$

Zero-point correction= 0.209352 (Hartree/Particle)
Thermal correction to Energy= 0.224928
Thermal correction to Enthalpy= 0.225872
Thermal correction to Gibbs Free Energy= 0.161284
Sum of electronic and zero-point Energies= -1312.662457

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	22	0	0.011215	0.917615	-0.051854
2	8	0	-1.666936	0.267522	0.035135
3	8	0	1.407234	-0.209360	0.114705
4	8	0	0.290783	2.688180	-0.311483
5	6	0	-2.962575	-0.258232	0.062463
6	6	0	-3.171991	-1.030082	1.356591
7	6	0	-3.182763	-1.134084	-1.161664
8	1	0	-3.669460	0.580785	0.030716
9	1	0	-2.994518	-0.384126	2.217122
10	1	0	-4.190436	-1.418335	1.415645
11	1	0	-2.474588	-1.869531	1.402951
12	1	0	-3.016561	-0.560871	-2.074523
13	1	0	-2.483150	-1.972942	-1.145739
14	1	0	-4.200376	-1.528629	-1.177856
15	6	0	2.519720	-1.048897	0.230556
16	6	0	3.602532	-0.353458	1.042039
17	6	0	3.010969	-1.435218	-1.156832
18	1	0	2.205008	-1.957223	0.760782
19	1	0	3.222164	-0.077286	2.026351
20	1	0	4.468083	-1.005567	1.172694
21	1	0	3.923287	0.555156	0.527179
22	1	0	2.213512	-1.919708	-1.721604
23	1	0	3.326731	-0.540516	-1.698615
24	1	0	3.858198	-2.120255	-1.090964
25	1	0	0.421382	3.620619	-0.449111

TS$_{R3}$$^{\bullet}$

Zero-point correction= 0.289776 (Hartree/Particle)
Thermal correction to Energy= 0.309347
Thermal correction to Enthalpy= 0.310291
Thermal correction to Gibbs Free Energy= 0.237713
Sum of electronic and zero-point Energies= -1430.388736

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	22	0	-0.173801	-0.560707	-0.336646
2	8	0	-1.676525	-1.356387	0.336773
3	8	0	-0.342536	0.897284	-1.071301
4	8	0	1.516853	-1.178233	-0.019367
5	6	0	-3.055324	-1.144575	0.506376
6	6	0	-3.780891	-1.426391	-0.801075
7	6	0	-3.308166	0.275938	0.992367
8	1	0	-3.407068	-1.851399	1.267912
9	1	0	-3.564817	-2.438738	-1.144218
10	1	0	-4.860746	-1.322091	-0.680174
11	1	0	-3.447972	-0.718475	-1.565227
12	1	0	-2.776642	0.455611	1.928969
13	1	0	-2.945367	0.987056	0.244215
14	1	0	-4.373000	0.451240	1.157311
15	6	0	-0.012157	2.966570	-0.363965
16	6	0	1.383996	3.046725	-0.848604
17	6	0	-0.266329	2.685076	1.054472
18	1	0	-0.814919	3.313833	-0.995875
19	1	0	1.437391	3.021563	-1.935583
20	1	0	1.872383	3.964514	-0.497148
21	1	0	1.960195	2.202540	-0.452921
22	1	0	-1.295492	2.873539	1.354371
23	1	0	-0.052608	1.610454	1.258657
24	1	0	0.411542	3.241562	1.709669
25	6	0	2.896098	-0.920433	-0.039543
26	6	0	3.646253	-2.217586	-0.299382
27	6	0	3.309025	-0.285668	1.280557
28	1	0	3.113827	-0.215357	-0.854183
29	1	0	3.326334	-2.659310	-1.243579
30	1	0	4.722774	-2.042060	-0.342959
31	1	0	3.438372	-2.929273	0.502221
32	1	0	2.753328	0.639254	1.449372
33	1	0	3.092403	-0.971741	2.102200
34	1	0	4.376338	-0.056408	1.287127

Triplet (^{i}PrO)$_2$Ti:

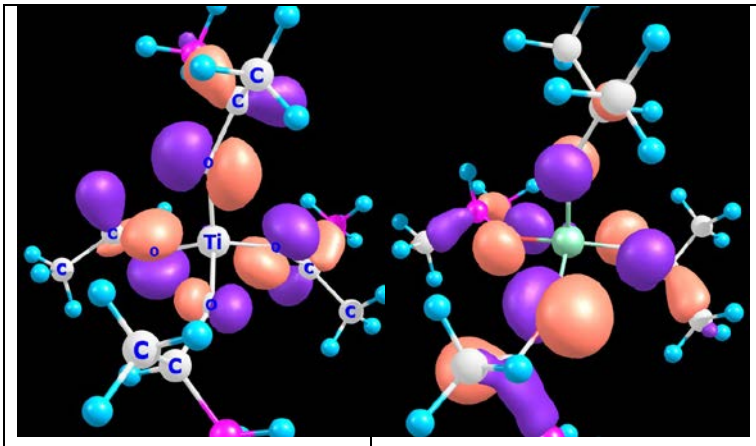
Zero-point correction= 0.196770 (Hartree/Particle)
Thermal correction to Energy= 0.209701
Thermal correction to Enthalpy= 0.210645
Thermal correction to Gibbs Free Energy= 0.153029
Sum of electronic and zero-point Energies= -1236.760730

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	22	0	-0.000008	-0.190764	-0.000247
2	8	0	-1.810834	-0.185861	-0.243358

3	8	0	1.810782	-0.185803	0.243123
4	6	0	-3.199847	-0.134156	-0.368992
5	6	0	-3.649290	1.313399	-0.505563
6	6	0	-3.848910	-0.815305	0.827139
7	1	0	-3.481815	-0.678117	-1.280175
8	1	0	-3.163132	1.782113	-1.361985
9	1	0	-4.730782	1.376296	-0.639801
10	1	0	-3.376569	1.869421	0.394586
11	1	0	-3.502792	-1.846187	0.910338
12	1	0	-3.579315	-0.284594	1.743369
13	1	0	-4.936454	-0.818011	0.733103
14	6	0	3.199756	-0.134058	0.369192
15	6	0	3.649129	1.313531	0.505653
16	6	0	3.849211	-0.815405	-0.826611
17	1	0	3.481442	-0.677859	1.280557
18	1	0	3.162705	1.782379	1.361852
19	1	0	4.730580	1.376484	0.640202
20	1	0	3.376660	1.869393	-0.394671
21	1	0	3.503143	-1.846309	-0.909739
22	1	0	3.579897	-0.284861	-1.743020
23	1	0	4.936724	-0.818069	-0.732219

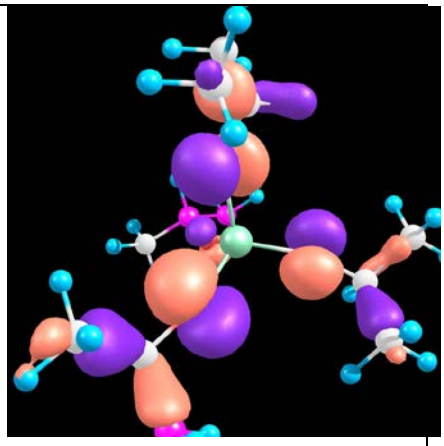
---

2. Theoretical UV-Vis spectrum of TTIP: molecular orbitals corresponding to the most important transitions, excitation energies, and oscillators strengths.

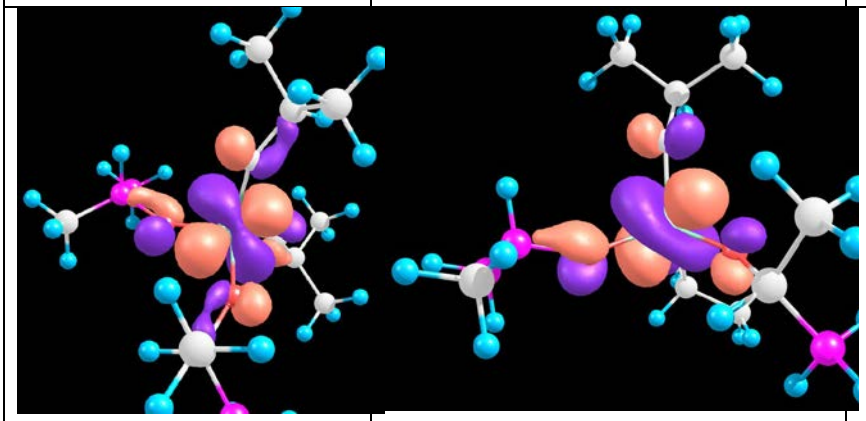


HOMO-2 (#75)

HOMO-1 (#76)



HOMO (#77)



LUMO (#78)

LUMO+1 (#79)

Excitation energies and oscillator strengths:

Excited State 1: Singlet-A 4.8948 eV 253.30 nm f=0.0020 <S**2>=0.000

77 -> 78 0.68473

Total Energy, E(TD-HF/TD-KS) = -1624.84323589

Excited State 2: Singlet-A 4.9932 eV 248.31 nm f=0.0037 <S**2>=0.000

75 -> 78 0.22029

76 -> 78 0.61555

76 -> 79 0.15572

77 -> 79 0.17510

Excited State 3: Singlet-A 5.1626 eV 240.16 nm f=0.0056 <S**2>=0.000

75 -> 78 0.39427

75 -> 79 -0.27789

76 -> 78 -0.11677

76 -> 79 0.38610

77 -> 79 -0.29304

Excited State 4: Singlet-A 5.2141 eV 237.79 nm f=0.0215 <S**2>=0.000

75 -> 78 0.38971
75 -> 79 0.11729
76 -> 78 -0.25910
77 -> 78 0.10875
77 -> 79 0.45683

Excited State 5: Singlet-A 5.2819 eV 234.73 nm f=0.0236 <S**2>=0.000
72 -> 78 0.13482
75 -> 78 -0.30727
76 -> 79 0.50334
77 -> 79 0.28553

Excited State 6: Singlet-A 5.3523 eV 231.65 nm f=0.0143 <S**2>=0.000
74 -> 78 0.18832
75 -> 79 0.59623
76 -> 79 0.14688
77 -> 79 -0.19571