

Supplementary Information for

**Account of chemical bonding and enhanced reactivity of  
vanadium-doped rhodium clusters toward C-H activation: a DFT  
investigation**

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# 1. Cartesian Coordinates, Energies, and Normal Modes of Vibration for Ground State

## Rh<sub>n</sub> Cluster [B3LYP(D3BJ)]

(Spin Multiplicities (M=2S+1) are included within parenthesis, energies are in kcal/mol)

Only first six normal vibrational modes are included

### Rh<sub>2</sub>(5)

Energy: -138760.9953341

Rh 0.00000 0.00000 1.10346

Rh 0.00000 0.00000 -1.10346

Frequencies -- 336.0842

### Rh<sub>3</sub>(6)

Energy: -208180.6595270

Rh -1.23813 0.72194 0.00000

Rh 0.00000 -1.42260 0.00000

Rh 1.23813 0.70066 0.00000

Frequencies -- 118.8831 151.5793 267.6398

### Rh<sub>4</sub>(7)

Energy: -277606.2186387

Rh -1.30281 0.01329 0.88079

Rh 0.01543 1.28566 -0.87909

Rh -0.01471 -1.28253 -0.88340

Rh 1.30210 -0.01642 0.88170

Frequencies -- 78.0693 114.4283 132.8905

Frequencies -- 153.9466 170.0035 273.7842

### Rh<sub>5</sub>(8)

Energy: -347021.1711523

Rh 0.00000 0.00000 1.53217

Rh 0.00000 1.32699 -0.76575

Rh -0.00000 -1.32699 -0.76575

Rh -2.00313 0.00000 -0.00034

Rh 2.00313 -0.00000 -0.00034

Frequencies -- 123.8375 124.0834 157.1070

Frequencies -- 183.9455 184.1865 194.4992

### Rh<sub>6</sub>(7)

Energy: -416462.7903353

Rh 0.00000 0.00000 1.81198

Rh -0.00000 1.81198 -0.00000

Rh 0.00000 -1.81198 0.00000

Rh -1.81198 -0.00000 -0.00000

Rh 1.81198 -0.00000 0.00000

Rh 0.00000 -0.00000 -1.81198

Frequencies -- 134.5269 134.5281 134.5293

Frequencies -- 141.1082 141.1082 180.4482

### Rh<sub>7</sub>(14)

Energy: -485892.0152305

Rh 1.89538 1.03787 0.00004

Rh 1.53470 -1.52022 -0.00076

Rh -0.91309 -1.92121 0.00099

Rh -2.16396 0.30408 -0.00067

Rh -0.34800 2.09849 0.00031

Rh -0.00231 0.00059 1.54237

Rh -0.00273 0.00041 -1.54228

Frequencies -- 45.9492 51.9125 59.3460

Frequencies -- 84.7627 101.4309 119.3011

**Rh<sub>8</sub>(13)**

**Energy: -555307.2017851**

Rh	0.00964	1.17236	1.72892
Rh	0.00268	1.23803	-0.75860
Rh	-0.01246	-1.16752	1.73218
Rh	-1.95795	0.01415	0.72758
Rh	1.95676	-0.01211	0.73081
Rh	-0.00145	-1.24015	-0.75514
Rh	-1.96086	0.00552	-1.70449
Rh	1.96364	-0.01028	-1.70126
Frequencies --	36.3313	52.5114	82.2821
Frequencies --	87.0303	106.5357	110.0020

**Rh<sub>9</sub>(18)**

**Energy: -624762.5756318**

Rh	0.74012	-1.30680	-1.32440
Rh	-1.50047	0.00156	-1.70715
Rh	-1.43821	-1.81574	0.02918
Rh	0.82870	1.30577	1.29266
Rh	-1.43900	1.81520	0.03220
Rh	-1.37158	-0.00163	1.78710
Rh	0.82885	-1.30793	1.29048
Rh	0.74022	1.30926	-1.32186
Rh	2.61138	0.00031	-0.07821
Frequencies --	39.5063	76.2880	89.6303
Frequencies --	98.1552	100.4714	106.0913

## 2. Cartesian Coordinates, Energies, and Normal Modes of Vibration for Ground State

### Rh<sub>m</sub>V Cluster

(Spin Multiplicities (M=2S+1) are included within parenthesis, energies are in kcal/mol)

Only first six normal vibrational modes are included

#### RhV(3)

Energy: -661748.7756679

Rh 0.00000 0.00000 0.65761

V 0.00000 0.00000 -1.28663

Frequencies -- 441.7509

#### Rh<sub>2</sub>V(4)

Energy: -731152.8475488

Rh 0.00000 1.26777 -0.36302

Rh -0.00000 -1.26777 -0.36302

V 0.00000 0.00000 1.42051

Frequencies -- 88.0103 173.4859 370.9549

#### Rh<sub>3</sub>V(1)

Energy: -800591.7238974

Rh -0.58771 -0.64052 1.47706

Rh -0.58771 -0.64052 -1.47706

Rh 1.47581 0.87110 0.00000

V -0.58771 0.80206 0.00000

Frequencies -- 80.7003 80.7424 141.6775

Frequencies -- 339.2791 339.3234 425.2359

#### Rh<sub>4</sub>V(2)

Energy: -870012.8370969

Rh 2.00190 -0.00000 0.43679

Rh 0.00000 1.31799 -0.75885

Rh -2.00190 -0.00000 0.43679

Rh -0.00000 -1.31799 -0.75885

V 0.00000 0.00001 1.26024

Frequencies -- 89.7390 96.2243 133.3895

Frequencies -- 158.3877 159.0405 187.0309

#### Rh<sub>5</sub>V(5)

Energy: -939439.6333108

Rh 0.06974 1.69555 -0.57213

Rh 0.84874 -1.67091 -0.53441

Rh 2.12245 0.33980 0.16128

Rh -0.10071 -0.05907 1.40609

Rh -2.54292 -0.18996 0.03705

V -0.77733 -0.22578 -0.97411

Frequencies -- 28.9528 60.0057 96.6591

Frequencies -- 114.7205 125.2924 138.2843

#### Rh<sub>6</sub>V(8)

Energy: -1008877.5575079

Rh 2.59264 -0.00117 -0.47316

Rh 0.66686 1.32546 0.82542

Rh -1.35938 -1.30065 -0.91441

Rh 0.66525 -1.32526 0.82596

Rh -1.35729 1.30068 -0.91576

Rh -1.51918 0.00116 1.29521

V 0.60866 -0.00045 -1.25852

Frequencies -- 67.0991 84.1874 117.4979

Frequencies -- 120.0222            127.1976            137.0229

**Rh<sub>7</sub>V(9)**

**Energy: -1078310.6361521**

Rh	0.59038	-1.89745	0.00456
Rh	1.69801	0.00089	1.52186
Rh	-2.09977	-1.37787	0.21300
Rh	2.08056	-0.00017	-1.02513
Rh	-0.49052	-0.00070	-1.44087
Rh	0.58973	1.89745	0.00305
Rh	-2.10030	1.37759	0.21309
V	-0.52453	0.00050	0.99869
Frequencies --	16.9835	76.6880	104.9019
Frequencies --	108.7667	114.6872	118.7792

**Rh<sub>8</sub>V(12)**

**Energy: -1147750.0134477**

Rh	0.07691	-1.64583	-1.38427
Rh	1.31817	0.83031	1.51637
Rh	-2.15270	-1.02628	-0.22262
Rh	-1.90194	1.49969	-1.06571
Rh	0.03414	-1.44057	1.24868
Rh	-1.34865	0.80060	1.50482
Rh	1.80653	1.58287	-1.02280
Rh	2.19197	-0.93053	-0.26406
V	-0.04779	0.64515	-0.60734
Frequencies --	34.6614	61.5811	69.3212
Frequencies --	94.8547	103.3156	107.3935

### 3. Cartesian Coordinates, Energies, and Normal Modes of Vibration for the Pre-Reaction Complexes (A) of the reaction $\text{CH}_4 + \text{Rh}_n$ Cluster [B3LYP(D3BJ)]

(Spin Multiplicities ( $M=2S+1$ ) are included within parenthesis, energies are in kcal/mol)

Only first six normal vibrational modes are included

**Rh<sub>3</sub>-CH<sub>4</sub>**  
**Energy: -233624.0103343**

Rh	-1.34499	-0.93853	-0.00270
Rh	1.08086	-0.46277	0.00519
Rh	-0.57648	1.39068	-0.00003
C	3.78181	0.04381	-0.01091
H	4.35543	0.96859	-0.03474
H	3.17047	0.05429	0.90217
H	3.16594	0.01050	-0.92054
H	4.44483	-0.81828	0.00812
Frequencies --	15.8782	38.1425	57.5491
Frequencies --	113.2754	138.6825	151.7570

**Rh<sub>4</sub>-CH<sub>4</sub>**  
**Energy: -303050.1123822**

Rh	-0.57548	-1.26659	-0.83728
Rh	1.26217	-0.17519	0.51270
Rh	-1.27019	0.12416	1.14494
Rh	-0.26818	1.31682	-0.84582
C	3.83105	0.00327	0.12036
H	3.33734	0.83881	0.63406
H	3.11469	-0.71630	-0.32447
H	4.40970	0.41769	-0.70317
H	4.47814	-0.52415	0.81759
Frequencies --	28.6687	45.2434	73.9444
Frequencies --	75.1911	91.5432	138.9218

**Rh<sub>5</sub>-CH<sub>4</sub>**  
**Energy: -372473.6440942**

Rh	0.18138	-1.18844	-0.95053
Rh	0.13974	-0.23063	1.53085
Rh	0.23180	1.47463	-0.50111
Rh	-1.81901	0.22480	-0.10095
Rh	2.19823	-0.13453	-0.00281
C	-4.19337	-0.65125	0.10906
H	-4.57914	-1.62264	0.41135
H	-3.56682	-0.81672	-0.78717
H	-5.00527	0.02612	-0.14407
H	-3.63477	-0.24183	0.97039
Frequencies --	16.9048	36.4996	57.6881
Frequencies --	90.8087	102.2754	124.0464

**Rh<sub>6</sub>-CH<sub>4</sub>**  
**Energy: -441907.1742842**

Rh	-1.58038	-0.60339	0.04610
Rh	-0.15390	1.00720	1.47112
Rh	0.45543	-1.00384	-1.46518
Rh	-0.34181	1.39276	-1.05110
Rh	0.64583	-1.38065	1.04130
Rh	1.87717	0.57474	-0.03981
C	-4.05946	0.05448	-0.00932
H	-3.53813	-0.05726	0.95415
H	-4.52032	1.04009	-0.01953
H	-3.37911	0.00924	-0.88254

H	-4.81072	-0.72577	-0.10517
Frequencies --	12.8344	51.1861	110.7785
Frequencies --	128.6672	131.5664	135.1797

**Rh<sub>7</sub>-CH<sub>4</sub>**

**Energy: -511335.4907822**

Rh	0.92371	1.88636	0.25024
Rh	-1.43776	1.51541	-0.46515
Rh	-1.75349	-1.01696	-0.65856
Rh	0.44040	-2.04801	-0.03166
Rh	2.20725	-0.29117	0.35964
Rh	0.45232	0.06921	-1.60299
Rh	-0.32833	-0.04821	1.42402
C	-2.26360	-0.30049	3.26218
H	-2.07145	0.57641	2.62065
H	-3.32646	-0.52028	3.18011
H	-1.71247	-1.19211	2.93878
H	-1.99274	-0.05945	4.28720
Frequencies --	27.9190	49.5539	53.2291
Frequencies --	81.0456	84.1090	93.7129

**Rh<sub>8</sub>-CH<sub>4</sub>**

**Energy: -580770.4058323**

Rh	2.03859	0.13686	-1.20318
Rh	-0.50159	0.57450	-1.55260
Rh	1.93893	-0.81185	1.18445
Rh	0.71115	1.41257	0.65166
Rh	0.33483	-1.73886	-0.62719
Rh	-0.61988	-0.66577	1.56183
Rh	-1.92434	1.28831	0.47856
Rh	-2.18761	-1.08946	-0.47238
C	0.94696	4.02176	-0.09231
H	0.66847	4.50832	-1.02512
H	0.03797	3.55955	0.32379
H	1.72011	3.27575	-0.31802
H	1.33857	4.74256	0.62149
Frequencies --	30.8921	47.2636	52.4767
Frequencies --	91.2875	99.1751	104.0716

**Rh<sub>9</sub>-CH<sub>4</sub>**

**Energy: -650207.4464389**

Rh	0.80381	1.18693	-1.29839
Rh	0.42413	-1.39954	-1.49754
Rh	2.29905	-0.55444	0.00159
Rh	-1.63238	0.22787	1.29913
Rh	-1.51384	-2.05720	-0.00115
Rh	0.42206	-1.39991	1.49800
Rh	0.80206	1.18659	1.30000
Rh	-1.63057	0.22822	-1.30093
Rh	-1.08817	2.41872	-0.00023
C	5.01315	0.73128	-0.00211
H	4.45322	0.46282	-0.90253
H	5.18452	1.80624	-0.00827
H	4.44693	0.47435	0.89781
H	5.95943	0.19310	0.00464
Frequencies --	9.9364	22.4101	45.6283
Frequencies --	78.3156	83.7597	84.0888



#### 4. Cartesian Coordinates, Energies, and Normal Modes of Vibration for the Transition States (T.S) of the reaction $\text{CH}_4 + \text{Rh}_n$ Cluster [B3LYP(D3BJ)]

(Spin Multiplicities ( $M=2S+1$ ) are included within parenthesis, energies are in kcal/mol)

Only first six normal vibrational modes are included

<b>Rh<sub>3</sub>-CH<sub>4</sub></b>			
<b>Energy: -233607.5750995</b>			
Rh	-1.30548	-1.01638	0.00490
Rh	1.31062	-0.27824	-0.02134
Rh	-0.75631	1.28603	0.00853
C	3.39605	-0.02664	0.08645
H	2.19017	0.82258	-0.68468
H	3.62226	0.49608	1.01678
H	3.56062	-1.10784	0.20653
H	4.05312	0.33533	-0.70161
Frequencies --	<b>-736.3081</b>	54.8111	79.1659
Frequencies --	87.6238	128.4428	137.4248

<b>Rh<sub>4</sub>-CH<sub>4</sub></b>			
<b>Energy: -303035.4233763</b>			
Rh	0.81349	1.28771	-0.64077
Rh	-1.39697	-0.00028	-0.28147
Rh	0.53299	0.00093	1.50934
Rh	0.81376	-1.28837	-0.63929
C	-3.45934	-0.00007	0.15585
H	-2.13193	0.00076	1.10144
H	-3.73495	0.90299	-0.39890
H	-3.73543	-0.90475	-0.39598
H	-3.98842	0.00166	1.10672
Frequencies --	<b>-821.8279</b>	67.0602	74.0226
Frequencies --	99.1172	110.2123	116.0154

<b>Rh<sub>5</sub>-CH<sub>4</sub></b>			
<b>Energy: -372461.4740582</b>			
Rh	-0.06578	-0.00415	1.52716
Rh	-0.22924	-1.44625	-0.66562
Rh	-0.23103	1.44796	-0.66023
Rh	1.83190	0.00159	-0.26438
Rh	-2.16106	0.00058	-0.00973
C	3.87227	0.00117	0.25216
H	4.37108	0.00605	1.21988
H	2.55232	0.00276	1.12555
H	4.16412	0.90273	-0.29595
H	4.16319	-0.90622	-0.28647
Frequencies --	<b>-862.3613</b>	32.2961	64.1113
Frequencies --	71.1023	88.0166	113.1522

<b>Rh<sub>6</sub>-CH<sub>4</sub></b>			
<b>Energy: -441892.9410316</b>			
Rh	1.65093	-0.53786	-0.00031
Rh	-0.13473	-0.00371	-1.79471
Rh	-0.13321	-0.00093	1.79475
Rh	0.39818	1.77576	-0.00158
Rh	-0.72646	-1.71610	0.00146
Rh	-1.87897	0.50736	0.00035
C	3.72676	-0.19059	0.00020
H	3.97948	-0.75521	-0.90289
H	4.30054	0.73468	-0.00049
H	2.47395	0.81286	-0.00189

H	3.97696	-0.75247	0.90566
Frequencies --	<b>-873.5985</b>	62.1945	73.2892
Frequencies --	119.4411	119.5278	124.0318

**Rh<sub>7</sub>-CH<sub>4</sub>**

**Energy: -511319.5383407**

Rh	1.70194	-1.28443	-0.38219
Rh	1.70184	1.28455	-0.38211
Rh	-0.69256	1.94032	0.06274
Rh	-2.27161	-0.00006	0.02119
Rh	-0.69247	-1.94034	0.06265
Rh	-0.20477	0.00003	-1.64835
Rh	0.23578	-0.00004	1.49584
C	0.91983	-0.00015	3.50202
H	1.69650	-0.00034	2.07402
H	1.94188	-0.00090	3.87421
H	0.41344	0.90161	3.85011
H	0.41208	-0.90109	3.85026
Frequencies --	<b>-844.1256</b>	62.8690	66.7456
Frequencies --	80.8443	89.1905	93.4867

**Rh<sub>8</sub>-CH<sub>4</sub>**

**Energy: -580755.5373380**

Rh	2.03496	-0.15892	-1.23668
Rh	-0.47767	0.44452	-1.62295
Rh	1.83966	-0.81859	1.24755
Rh	0.80856	1.47647	0.47259
Rh	0.15093	-1.80335	-0.42847
Rh	-0.70900	-0.44636	1.62925
Rh	-1.78958	1.52264	0.30337
Rh	-2.30264	-0.92170	-0.36127
C	1.97104	3.21199	0.04955
H	2.61834	3.45127	-0.79267
H	1.14746	3.92787	0.07017
H	1.86145	1.83695	-0.69459
H	2.56215	3.24932	0.96703
Frequencies --	<b>-930.0583</b>	55.0158	78.8680
Frequencies --	87.4719	94.6621	100.1935

**Rh<sub>9</sub>-CH<sub>4</sub>**

**Energy: -650182.8938759**

Rh	0.84362	1.21170	-1.22701
Rh	0.58707	-1.37022	-1.27973
Rh	2.56135	-0.25419	0.12209
Rh	-1.74971	0.14888	1.23825
Rh	-1.66429	-2.03890	-0.10002
Rh	0.41824	-1.42807	1.32056
Rh	0.68434	1.14215	1.37403
Rh	-1.55704	0.19754	-1.39430
Rh	-1.13949	2.36108	-0.00708
C	4.61139	0.06290	-0.16016
H	4.90360	0.15660	0.89122
H	4.86058	-0.92663	-0.55869
H	3.16413	0.92050	-0.73204
H	5.11950	0.82396	-0.74425
Frequencies --	<b>-631.1354</b>	47.8031	55.0720
Frequencies --	73.2841	78.7707	82.2643

## 5. Cartesian Coordinates, Energies, and Normal Modes of Vibration for the Post-Reaction Complexes (B) of the reaction $\text{CH}_4 + \text{Rh}_n$ Cluster [B3LYP(D3BJ)]

(Spin Multiplicities ( $M=2S+1$ ) are included within parenthesis, energies are in kcal/mol)

Only first six normal vibrational modes are included

**Rh<sub>3</sub>-CH<sub>4</sub>**  
**Energy: -233614.1929173**

Rh	-0.70165	1.30200	0.08193
Rh	1.33338	-0.10928	-0.40353
Rh	-1.16063	-1.08765	0.05999
C	2.49528	-0.34443	1.23739
H	0.68009	-1.56068	-0.18235
H	3.00201	0.61974	1.36945
H	1.91898	-0.59030	2.12708
H	3.22767	-1.13066	1.03418
Frequencies --	52.7208	74.1617	111.3929
Frequencies --	119.0163	143.9199	193.2081

**Rh<sub>4</sub>-CH<sub>4</sub>**  
**Energy: -303043.2302486**

Rh	0.76110	1.30171	-0.68089
Rh	-1.44013	0.00001	-0.18695
Rh	0.65683	-0.00004	1.47113
Rh	0.76110	-1.30168	-0.68096
C	-3.44324	-0.00002	0.21773
H	-1.19075	-0.00005	1.40184
H	-3.93158	0.00027	-0.76650
H	-3.73410	-0.89173	0.77659
H	-3.73411	0.89136	0.77712
Frequencies --	73.5575	78.6335	90.4633
Frequencies --	101.6753	120.7915	164.3619

**Rh<sub>5</sub>-CH<sub>4</sub>**  
**Energy: -372470.1203474**

Rh	0.15718	-0.19890	1.55623
Rh	0.23331	1.51495	-0.51670
Rh	0.15993	-1.42626	-0.77744
Rh	-1.83322	0.06456	-0.18704
Rh	2.11501	0.03406	-0.11687
C	-3.84988	0.06216	0.04856
H	-4.17516	0.89474	0.67484
H	-1.73739	-0.03496	1.39212
H	-4.18122	-0.88002	0.48942
H	-4.25616	0.16895	-0.96582
Frequencies --	50.7507	66.9718	71.5943
Frequencies --	79.7736	87.7874	118.3645

**Rh<sub>6</sub>-CH<sub>4</sub>**  
**Energy: -441899.0402517**

Rh	-1.70880	-0.42936	0.06126
Rh	0.19729	0.00560	1.78435
Rh	0.04458	-0.01616	-1.76905
Rh	-0.28482	1.84345	-0.00672
Rh	0.65896	-1.76030	-0.01039
Rh	1.90539	0.39605	-0.07120
C	-3.73249	-0.30678	0.01545
H	-4.06034	-0.83256	0.92060
H	-4.21037	0.66841	-0.03769
H	-1.91550	1.13284	0.42925

H	-3.98567	-0.89524	-0.87632
Frequencies --	34.3291	74.7497	97.3876
Frequencies --	99.5795	117.0823	122.4837

**Rh<sub>7</sub>-CH<sub>4</sub>**

**Energy: -511329.1951222**

Rh	-0.58962	-2.10971	-0.04168
Rh	1.86670	-1.14824	-0.03619
Rh	1.64499	1.37759	-0.12583
Rh	-0.78190	1.98682	-0.22166
Rh	-2.13961	-0.10785	-0.12837
Rh	0.04199	-0.10011	-1.61950
Rh	-0.02680	0.06660	1.43330
C	-0.14964	0.35021	3.45885
H	0.69277	-1.73273	1.16426
H	-0.05583	-0.61892	3.95061
H	0.66729	1.01365	3.74835
H	-1.11503	0.80760	3.68049
Frequencies --	38.3784	82.4939	83.3007
Frequencies --	90.3130	96.2374	100.2323

**Rh<sub>8</sub>-CH<sub>4</sub>**

**Energy: -580763.6291467**

Rh	2.09587	-0.34221	-1.21162
Rh	-0.44441	0.18366	-1.68258
Rh	1.82239	-0.54856	1.34972
Rh	0.79729	1.55186	0.21815
Rh	0.18939	-1.84502	-0.16760
Rh	-0.76413	-0.27985	1.68580
Rh	-1.76040	1.52652	0.08180
Rh	-2.27595	-0.99411	-0.27551
C	1.46236	3.47245	0.13176
H	2.54898	3.48379	0.23335
H	1.17832	3.94087	-0.81054
H	1.80505	1.39951	-1.10443
H	0.99153	3.98768	0.97392
Frequencies --	45.3995	55.2413	69.5116
Frequencies --	74.3981	88.6235	96.2326

**Rh<sub>9</sub>-CH<sub>4</sub>**

**Energy: -650184.5320584**

Rh	0.87999	1.00552	-1.32660
Rh	0.23622	-1.50204	-1.28711
Rh	2.57018	-0.56390	-0.08553
Rh	-1.55918	0.40867	1.35357
Rh	-1.98504	-1.79678	0.08711
Rh	0.33320	-1.46280	1.25934
Rh	0.97908	1.04987	1.27061
Rh	-1.65939	0.37254	-1.27918
Rh	-0.78346	2.48227	-0.01908
C	4.51690	-0.02297	0.25769
H	4.69720	-0.43461	1.25941
H	5.16260	-0.52053	-0.47124
H	2.80057	0.34562	-1.37851
H	4.71590	1.04649	0.25381
Frequencies --	42.4789	63.2288	65.5290
Frequencies --	74.5193	84.6139	87.7824

## 6. Cartesian Coordinates, Energies, and Normal Modes of Vibration for the Pre-Reaction Complexes (A) of the reaction $\text{CH}_4 + \text{Rh}_m\text{V}$ Cluster [B3LYP(D3BJ)]

(Spin Multiplicities ( $M=2S+1$ ) are included within parenthesis, energies are in kcal/mol)

Only first six normal vibrational modes are included

**Rh<sub>2</sub>V-CH<sub>4</sub>**  
**Energy: -756600.4720897**

Rh	-1.10204	-0.21402	-0.00005
Rh	1.58579	-0.47287	0.00002
V	0.70092	1.35781	0.00000
C	-3.78783	-0.03512	0.00011
H	-3.35269	-1.04076	-0.00030
H	-4.39413	0.08369	-0.89541
H	-4.39397	0.08305	0.89583
H	-3.02252	0.76531	0.00032
Frequencies --	37.8941	48.1557	69.2867
Frequencies --	126.3883	145.7481	185.8202

**Rh<sub>3</sub>V-CH<sub>4</sub>**  
**Energy: -826036.2469099**

Rh	1.22930	-1.39993	-0.11263
Rh	-1.49374	-0.13520	-0.28577
Rh	1.09267	1.49740	-0.14118
V	0.17325	0.01730	0.95184
C	-4.12475	0.12965	0.23681
H	-3.62541	-0.85092	0.19361
H	-4.58509	0.22491	1.21741
H	-3.42333	0.97050	0.10830
H	-4.87291	0.17744	-0.55121
Frequencies --	9.7427	37.8181	46.7904
Frequencies --	62.2641	89.2254	135.1716

**Rh<sub>4</sub>V-CH<sub>4</sub>**  
**Energy: -895455.8769029**

Rh	-1.59603	0.04003	-0.12094
Rh	0.43148	1.50141	-0.48847
Rh	1.64285	-0.69117	-0.72889
Rh	0.49448	0.03694	1.53324
V	-0.17675	-1.54141	-0.16326
C	-3.96759	-0.44315	-0.50411
H	-4.66470	0.38108	-0.38127
H	-4.49817	-1.37210	-0.69387
H	-3.32179	-0.24229	-1.37921
H	-3.42000	-0.57984	0.46180
Frequencies --	3.6842	48.2607	104.5048
Frequencies --	126.7238	131.1744	133.9607

**Rh<sub>5</sub>V-CH<sub>4</sub>**  
**Energy: -964885.5265279**

Rh	1.49187	1.10864	-0.06170
Rh	-0.67086	-1.40968	-0.93537
Rh	1.63517	-1.34572	0.11392
Rh	-0.28932	-0.27975	1.37137
Rh	-2.40353	0.83467	0.09086
V	-0.56743	0.70621	-0.84362
C	2.37258	3.28590	-0.66144
H	1.65763	3.16725	0.18429
H	2.45762	2.38905	-1.32378

H	1.99343	4.09449	-1.28402
H	3.35662	3.52428	-0.26317
Frequencies --	30.8476	48.4882	67.2109
Frequencies --	79.4271	119.8003	127.7355

**Rh<sub>6</sub>-CH<sub>4</sub>**

**Energy: -1034324.2565350**

Rh	2.52711	0.74865	-0.45296
Rh	0.50118	0.91081	1.29633
Rh	-1.02214	-1.27106	-1.32149
Rh	1.12285	-1.43968	0.23530
Rh	-1.65772	1.03925	-0.28271
Rh	-1.24467	-1.02134	1.20991
V	0.53181	0.52028	-1.14066
C	-2.24670	3.45015	-0.45571
H	-1.60227	4.32426	-0.51184
H	-3.29576	3.73283	-0.49240
H	-2.01275	2.81935	-1.33766
H	-2.03795	2.95778	0.51423
Frequencies --	35.1237	52.7291	75.2855
Frequencies --	84.8226	114.1890	115.8509

**Rh<sub>7</sub>-CH<sub>4</sub>**

**Energy: -1103756.6661474**

Rh	-0.59603	1.88456	-0.16561
Rh	-1.85751	-0.14458	1.08726
Rh	2.03312	1.45193	0.43565
Rh	-1.77361	-0.03689	-1.48245
Rh	0.81062	0.07139	-1.45238
Rh	-0.40540	-1.91978	-0.28681
Rh	2.15438	-1.33026	0.60340
V	0.43897	-0.04399	0.95723
C	-2.65833	0.20718	3.46854
H	-2.05688	-0.65717	3.11848
H	-2.15814	0.60054	4.35051
H	-2.72220	1.02898	2.73639
H	-3.65975	-0.14003	3.70949
Frequencies --	26.0031	41.3717	52.0110
Frequencies --	73.5301	89.0257	101.7104

**Rh<sub>8</sub>-CH<sub>4</sub>**

**Energy: -1173196.1375004**

Rh	-0.69761	-0.55039	-1.81837
Rh	1.80650	-0.31574	1.46233
Rh	-2.36654	-1.04884	0.08819
Rh	-1.81761	1.44989	-0.36876
Rh	0.06890	-1.93223	0.34474
Rh	-0.81880	0.13436	1.80041
Rh	2.20946	1.75403	-0.27867
Rh	1.89537	-0.82074	-1.17062
V	0.35017	0.81624	-0.16912
C	-2.06689	4.10521	0.12053
H	-1.38912	4.75377	0.67198
H	-2.42278	3.33084	0.81420
H	-2.91907	4.66378	-0.26068
H	-1.50603	3.68165	-0.72533
Frequencies --	14.2219	38.6532	52.5091
Frequencies --	76.9998	84.5936	90.0473

**7. Cartesian Coordinates, Energies, and Normal Modes of Vibration for the Transition States (T.S) of the reaction  $\text{CH}_4 + \text{Rh}_m\text{V}$  Cluster [B3LYP(D3BJ)]**  
 (Spin Multiplicities ( $M=2S+1$ ) are included within parenthesis, energies are in kcal/mol)  
 Only first six normal vibrational modes are included

**Rh<sub>2</sub>V-CH<sub>4</sub>**  
**Energy: -756586.6932869**

Rh	-1.16761	-0.20482	-0.18777
Rh	1.49751	-0.49859	0.08079
V	0.72362	1.36543	-0.00554
C	-3.16882	-0.04317	0.46099
H	-3.26286	-1.12928	0.59299
H	-1.91064	0.90245	0.63674
H	-3.73672	0.29714	-0.40824
H	-3.56553	0.43723	1.35388
Frequencies --	-856.7023	42.3892	88.8727
Frequencies --	104.5257	133.1932	182.8241

**Rh<sub>3</sub>V-CH<sub>4</sub>**  
**Energy: -826024.4818290**

Rh	1.20768	-1.33847	-0.08825
Rh	-1.59486	-0.32895	-0.27287
Rh	1.07624	1.48175	-0.18207
V	0.13088	0.07408	0.94610
C	-3.38358	0.72110	0.21776
H	-2.95139	1.70384	0.01431
H	-2.75971	-0.58786	0.75248
H	-3.90875	0.76643	1.17067
H	-4.09607	0.44253	-0.56087
Frequencies --	-880.8845	41.0179	53.2234
Frequencies --	74.0852	98.9240	123.1954

**Rh<sub>4</sub>V-CH<sub>4</sub>**  
**Energy: -895446.2982031**

Rh	-1.91687	0.15810	0.09237
Rh	0.17677	-1.11552	-1.01613
Rh	2.10525	-0.28781	0.63452
Rh	0.42560	1.44842	-0.53169
V	0.05216	-0.12565	1.19418
C	-3.69799	-0.55428	0.97538
H	-4.50495	-0.61107	0.24303
H	-3.79548	0.36471	1.57133
H	-3.76457	-1.40615	1.64894
H	-2.53058	-1.27541	0.15937
Frequencies --	-800.9858	65.9815	72.5367
Frequencies --	94.6478	106.5512	114.8858

**Rh<sub>5</sub>V-CH<sub>4</sub>**  
**Energy: -964874.6277678**

Rh	-0.82952	-1.61089	0.03760
Rh	-0.02284	1.62483	-1.06998
Rh	-2.01353	0.68316	0.23779
Rh	0.21891	0.57464	1.35807
Rh	2.52182	-0.32082	0.11120
V	0.76744	-0.36547	-0.90011
C	-1.15671	-3.47845	-0.91455
H	-0.25836	-3.90679	-0.45282
H	-1.11775	-3.67422	-1.98359
H	-2.05427	-3.93312	-0.49524

H	-1.64820	-2.00089	-1.23874
Frequencies --	-848.0368	31.5906	62.2766
Frequencies --	82.2665	93.1710	99.0822

**Rh<sub>6</sub>V-CH<sub>4</sub>**

**Energy: -1034310.4495571**

Rh	2.51668	0.62635	-0.52280
Rh	0.49756	1.14671	1.16056
Rh	-0.98053	-1.48751	-1.16367
Rh	1.08240	-1.38269	0.49763
Rh	-1.63237	1.05033	-0.52046
Rh	-1.29596	-0.77191	1.29545
V	0.54875	0.25046	-1.25182
C	-2.17328	3.09456	-0.52416
H	-3.12253	3.07603	0.01449
H	-2.32659	3.12825	-1.60989
H	-1.61644	3.98328	-0.23315
H	-0.96556	2.32696	0.16336
Frequencies --	-893.8228	41.5006	67.8114
Frequencies --	87.1801	96.2458	115.6889

**Rh<sub>7</sub>V-CH<sub>4</sub>**

**Energy: -1103741.3470348**

Rh	-0.55454	1.87875	0.27321
Rh	-1.87314	-0.30620	1.11687
Rh	2.09428	1.31044	0.64101
Rh	-1.79848	0.33549	-1.43032
Rh	0.76016	0.36728	-1.42490
Rh	-0.47624	-1.77826	-0.60984
Rh	2.14551	-1.49673	0.28034
V	0.53871	-0.25117	0.94027
C	-2.65578	-0.84093	3.00040
H	-1.17862	-0.30970	2.54143
H	-3.42030	-0.06792	3.11246
H	-3.08649	-1.79257	2.67462
H	-2.15997	-0.99121	3.95601
Frequencies --	-818.9992	46.5437	57.3253
Frequencies --	61.5699	88.5435	96.4583

**Rh<sub>8</sub>V-CH<sub>4</sub>**

**Energy: -1173180.1723731**

Rh	-0.64653	-0.53412	-1.80467
Rh	1.71383	-0.28426	1.51374
Rh	-2.40237	-1.01344	0.01337
Rh	-1.85183	1.51397	-0.42994
Rh	0.00734	-1.87679	0.37683
Rh	-0.90859	0.17310	1.76077
Rh	2.49686	1.59431	-0.26647
Rh	1.91692	-0.84808	-1.09943
V	0.45485	1.01455	-0.21613
C	-2.54041	3.42540	0.13193
H	-2.32445	4.00437	1.02766
H	-1.82031	2.23660	0.96265
H	-3.62174	3.31597	0.02929
H	-2.10593	3.94507	-0.72888
Frequencies --	-875.2599	41.4309	53.4191
Frequencies --	59.8400	81.9028	96.2957



## 8. Cartesian Coordinates, Energies, and Normal Modes of Vibration for the Post Reaction Complexes (B) of the reaction $\text{CH}_4 + \text{Rh}_m\text{V}$ Cluster [B3LYP(D3BJ)]

(Spin Multiplicities ( $M=2S+1$ ) are included within parenthesis, energies are in kcal/mol)

Only first six normal vibrational modes are included

**Rh<sub>2</sub>V-CH<sub>4</sub>**  
**Energy: -756598.410057**

Rh	-1.26439	-0.25166	-0.36569
Rh	1.44415	-0.48461	0.12576
V	0.65214	1.35814	-0.03840
C	-2.34697	0.06255	1.28392
H	-2.01342	0.89263	1.90712
H	-1.35174	1.27699	-0.77357
H	-2.25094	-0.87379	1.85142
H	-3.39063	0.22396	0.99159
Frequencies --	50.6779	72.6745	93.7369
Frequencies --	112.3240	194.2780	356.9713

**Rh<sub>3</sub>V-CH<sub>4</sub>**  
**Energy: -826035.2566497**

Rh	1.36133	-1.25292	-0.07153
Rh	-1.69095	-0.41300	-0.30333
Rh	0.98004	1.51243	-0.17805
V	0.10445	0.02634	0.89679
C	-3.17686	0.78741	0.36902
H	-2.92292	1.79847	0.03222
H	-2.26096	-1.46185	0.67348
H	-3.32474	0.78663	1.44834
H	-4.10173	0.45363	-0.11327
Frequencies --	42.8684	49.5970	55.2780
Frequencies --	115.8102	127.2337	140.0738

**Rh<sub>4</sub>V-CH<sub>4</sub>**  
**Energy: -895458.4481983**

Rh	-2.13180	0.39272	0.41674
Rh	-0.21292	0.08371	-1.48377
Rh	1.37414	-1.58837	0.20354
Rh	1.49215	1.44663	0.34815
V	0.18095	-0.04574	0.81730
C	-2.80852	-1.47491	0.60649
H	-3.76285	-1.55158	0.07673
H	-2.96626	-1.61168	1.68700
H	-2.11932	-2.23369	0.23733
H	-1.93315	0.23713	-1.24786
Frequencies --	32.5253	51.4148	66.6830
Frequencies --	99.9934	107.3728	117.7210

**Rh<sub>5</sub>V-CH<sub>4</sub>**  
**Energy: -964884.4960570**

Rh	-0.07597	1.80128	0.05916
Rh	0.84156	-1.53483	-1.08233
Rh	2.09261	0.23693	0.32959
Rh	0.01492	-0.73372	1.32059
Rh	-2.42879	-0.49774	0.10014
V	-0.74335	-0.03752	-0.93701
C	-0.45716	3.43819	-1.12066
H	-1.53906	3.60088	-1.11986
H	-0.09781	3.35536	-2.14523

H	0.04490	4.28081	-0.63379
H	1.43720	1.76074	-0.54761
Frequencies --	35.8737	58.9228	77.6635
Frequencies --	93.2059	101.3893	115.7102

**Rh<sub>6</sub>V\_CH<sub>4</sub>**

**Energy: -1034316.9118316**

Rh	2.46984	0.75318	-0.56624
Rh	0.43551	1.23711	1.12597
Rh	-0.81378	-1.59364	-1.12182
Rh	1.18417	-1.27213	0.58454
Rh	-1.74239	0.93884	-0.54083
Rh	-1.24585	-0.77200	1.30961
V	0.53622	0.19295	-1.29087
C	-2.68460	2.73994	-0.61184
H	-3.66041	2.53697	-0.15460
H	-2.80241	2.93561	-1.68548
H	-2.22138	3.60022	-0.13466
H	-0.47892	1.93918	-0.26928
Frequencies --	40.0061	63.1128	87.3373
Frequencies --	99.7349	109.6119	111.6370

**Rh<sub>7</sub>V\_CH<sub>4</sub>**

**Energy: -1103751.8599143**

Rh	-0.91420	1.91083	-0.20057
Rh	-1.44672	-0.25731	1.41224
Rh	1.67227	1.86509	0.35576
Rh	-1.89169	-0.22937	-1.25445
Rh	0.63862	0.15500	-1.49091
Rh	-0.34128	-2.00983	-0.27882
Rh	2.19127	-1.39722	0.22208
V	0.83376	0.02218	0.95003
C	-1.53238	-0.38022	3.46223
H	-1.07877	1.37797	1.48059
H	-2.46267	0.12042	3.74979
H	-1.60743	-1.45086	3.68304
H	-0.70533	0.05042	4.02292
Frequencies --	48.1835	53.8431	64.9210
Frequencies --	82.5731	89.5770	93.0932

**Rh<sub>8</sub>V\_CH<sub>4</sub>**

**Energy: -1173189.0483691**

Rh	-0.77358	0.08603	-1.81213
Rh	1.71589	-0.81397	1.30441
Rh	-2.48205	-0.89627	-0.11851
Rh	-1.78501	1.66648	0.10533
Rh	-0.15107	-1.88351	-0.15344
Rh	-0.85882	-0.28787	1.84301
Rh	2.60778	1.42873	0.11944
Rh	1.78342	-0.61614	-1.37547
V	0.54255	1.01356	0.06618
C	-1.55855	3.70498	0.09938
H	-0.55110	4.09426	0.23943
H	-0.97638	1.49092	1.56092
H	-2.20814	4.09247	0.89148
H	-1.93718	4.02417	-0.87925
Frequencies --	47.4868	61.0233	69.4520
Frequencies --	82.6962	90.2790	97.2459

## 9. Ionization Energies (eV) of $Rh_n$ and $Rh_mV$ Clusters

Pristine	I.E(eV)		Ground State (Neutral)	Ground State (Cation)
	B3LYP	TPSSh	M=2S+1	M=2S+1
Rh <sub>2</sub>	7.502235966	7.274289419	5	6
Rh <sub>3</sub>	7.04601634	6.891866025	6	7
Rh <sub>4</sub>	6.369741357	6.23050267	7	8
Rh <sub>5</sub>	5.737929148	5.804732153	8	9
Rh <sub>6</sub>	5.953195369	5.887018217	7	10
Rh <sub>7</sub>	6.010120781	5.879943357	14	11
Rh <sub>8</sub>	5.754990445	5.903263184	13	14
Rh <sub>9</sub>	6.318992842	6.192216793	18	15

Doped	IP		Ground State (Neutral)	Ground State (Cation)
	B3LYP	TPSSH	M=2S+1	M=2S+1
Rh <sub>1</sub> V	7.065390572	6.818097004	3	4
Rh <sub>2</sub> V	6.054365867	5.781385115	4	1
Rh <sub>3</sub> V	6.207890329	5.765330625	1	2
Rh <sub>4</sub> V	6.162964968	5.72573862	2	3
Rh <sub>5</sub> V	5.917276849	5.754908812	5	4
Rh <sub>6</sub> V	5.999671757	5.812895453	8	5
Rh <sub>7</sub> V	5.971481161	5.9265558	9	10
Rh <sub>8</sub> V	6.024705877	5.745684283	12	9

## 10. Table of Binding Energies per atom (eV) of Rh<sub>n</sub> and Rh<sub>m</sub>V Clusters

### Pristine Cluster (Rh<sub>n</sub>) B3LYP

<b>Rh2</b>					
	<b>E_Cluster</b>	<b>E_Rh</b>	<b>-Ebin</b>	<b>-E_bin(ev)</b>	<b>-E_bin(kcal/mol)</b>
E	-221.128958	-110.531751	-0.032728	-0.890561608	-20.53714728
U	-221.12622	-110.530335	-0.032775	-0.891840525	-20.56664025
H	-221.125276	-110.52939	-0.033248	-0.904711328	-20.86345248
G	-221.155148	-110.549611	-0.027963	-0.760901193	-17.54706213
<b>Rh3</b>					
E	-331.755775	-110.531751	-0.0535073333	-1.4559880473	-33.57638674
U	-331.751141	-110.530335	-0.0533786667	-1.4524868987	-33.49564712
H	-331.750196	-110.52939	-0.0540086667	-1.4696298287	-33.89097842
G	-331.789843	-110.549611	-0.0470033333	-1.2790077033	-29.4950617
<b>Rh4</b>					
E	-442.39157	-110.531751	-0.0661415	-1.7997763565	-41.504452665
U	-442.384879	-110.530335	-0.06588475	-1.7927899323	-41.3433394725
H	-442.383935	-110.52939	-0.06659375	-1.8120825312	-41.7882440625
G	-442.429296	-110.549611	-0.057713	-1.570428443	-36.21548463
<b>Rh5</b>					
E	-553.009463	-110.531751	-0.0701416	-1.9086230776	-44.014555416
U	-553.001447	-110.530335	-0.0699544	-1.9035291784	-43.897085544
H	-553.000503	-110.52939	-0.0707106	-1.9241061366	-44.371608606
G	-553.048066	-110.549611	-0.0600022	-1.6327198642	-37.651980522
<b>Rh6</b>					
E	-663.670938	-110.531751	-0.080072	-2.178839192	-50.24598072
U	-663.660852	-110.530335	-0.079807	-2.171628277	-50.07969057
H	-663.659908	-110.52939	-0.0805946667	-2.1930614747	-50.57395928
G	-663.709801	-110.549611	-0.0686891667	-1.8691009142	-43.103138975
<b>Rh7</b>					
E	-774.313418	-110.531751	-0.0844515714	-2.2980117101	-52.9942055871
U	-774.300585	-110.530335	-0.0840342857	-2.2866569486	-52.7323546286
H	-774.29964	-110.52939	-0.0848442857	-2.3086978586	-53.2406377286
G	-774.361683	-110.549611	-0.0734865714	-1.9996430951	-46.1135584371
<b>Rh8</b>					
E	-884.932302	-110.531751	-0.08478675	-2.3071322543	-53.2045334925

U	-884.917709	-110.530335	-0.084378625	-2.2960267649	-52.9484309737
H	-884.916765	-110.52939	-0.085205625	-2.3185302619	-53.4673817438
G	-884.982619	-110.549611	-0.073216375	-1.9922907801	-45.9440074763
<b>Rh9</b>					
E	-995.615213	-110.531751	-0.0921615556	-2.5078080882	-57.8322977267
U	-995.598868	-110.530335	-0.0917614444	-2.4969206648	-57.5812240033
H	-995.597923	-110.52939	-0.0926014444	-2.5197779048	-58.1083324033
G	-995.667597	-110.549611	-0.080122	-2.180199742	-50.27735622

## TPSSh

<b>Rh2</b>	<b>E_Cluster(a.u)</b>	<b>E_Rh(a.u)</b>	<b>-E_bin(a.u)</b>	<b>-E_bin(eV)</b>	<b>-E_bin(kcal/mol)</b>
E	-220.969194	-110.449211	-0.035386	-0.962888446	-22.20506886
U	-220.966459	-110.447794	-0.0354355	-0.9642353905	-22.236130605
H	-220.965515	-110.44685	-0.0359075	-0.9770789825	-22.532315325
G	-220.99538	-110.467071	-0.030619	-0.833173609	-19.21372869
<b>Rh3</b>					
E	-331.521778	-110.449211	-0.0580483333	-1.5795531983	-36.42590965
U	-331.517295	-110.447794	-0.057971	-1.577448881	-36.37738221
H	-331.51635	-110.44685	-0.0586	-1.5945646	-36.772086
G	-331.554839	-110.467071	-0.0512086667	-1.3934390287	-32.13395042
<b>Rh4</b>					
E	-442.0929	-110.449211	-0.074014	-2.013994954	-46.44452514
U	-442.086389	-110.447794	-0.07380325	-2.0082602357	-46.3122774075
H	-442.085445	-110.44685	-0.07451125	-2.0275256238	-46.7565544875
G	-442.130087	-110.467071	-0.06545075	-1.7809803582	-41.0710001325
<b>Rh5</b>					
E	-552.647614	-110.449211	-0.0803118	-2.1853643898	-50.396457618
U	-552.639683	-110.447794	-0.0801426	-2.1807602886	-50.290282926
H	-552.638739	-110.44685	-0.0808978	-2.2013100358	-50.764178478
G	-552.686007	-110.467071	-0.0701304	-1.9083183144	-44.007527304
<b>Rh6</b>					
E	-663.239871	-110.449211	-0.0907675	-2.4698744425	-56.957513925
U	-663.230054	-110.447794	-0.0905483333	-2.4639106983	-56.81998465
H	-663.22911	-110.44685	-0.091335	-2.485316685	-57.31362585
G	-663.278172	-110.467071	-0.079291	-2.157587401	-49.75589541
<b>Rh7</b>					
E	-773.808867	-110.449211	-0.0949128571	-2.5826737557	-59.5587669857

U	-773.796347	-110.447794	-0.0945412857	-2.5725629256	-59.3256021986
H	-773.795403	-110.44685	-0.0953504286	-2.5945805119	-59.8333474329
G	-773.856276	-110.467071	-0.0838255714	-2.2809776241	-52.6013843271
<b>Rh8</b>					
E	-884.35534	-110.449211	-0.0952065	-2.5906640715	-59.743030815
U	-884.341215	-110.447794	-0.094857875	-2.5811776366	-59.5242651413
H	-884.340271	-110.44685	-0.095683875	-2.6036539226	-60.0425884013
G	-884.403977	-110.467071	-0.083426125	-2.2701082874	-52.3507276988
<b>Rh9</b>					
E	-994.958061	-110.449211	-0.1016846667	-2.7669414647	-63.80814518
U	-994.94244	-110.447794	-0.101366	-2.758270226	-63.60817866
H	-994.941496	-110.44685	-0.1022051111	-2.7811032784	-64.1347292733
G	-995.007673	-110.467071	-0.0893371111	-2.4309521304	-56.0599305933

### Doped Cluster ( $Rh_mV$ ) B3LYP

<b>RhV</b>	<b>E_Cluster (a.u)</b>	<b>E_Rh (a.u)</b>	<b>E_V (a.u)</b>	<b>-E_bin (a.u)</b>	<b>-E_bin (eV)</b>	<b>-E_bin (kcal/mol)</b>
E	-1054.562802	-110.531751	-943.91194	-0.0595555	-1.6205647105	-37.371671805
U	-1054.560171	-110.530335	-943.910524	-0.059656	-1.623299416	-37.43473656
H	-1054.559227	-110.52939	-943.90958	-0.0601285	-1.6361566135	-37.731235035
G	-1054.588036	-110.549611	-943.928805	-0.05481	-1.49143491	-34.3938231
<b>Rh2V</b>						
E	-1165.164998	-110.531751	-943.91194	-0.0631853333	-1.7193361053	-39.64942852
U	-1165.161223	-110.530335	-943.910524	-0.063343	-1.723626373	-39.74836593
H	-1165.160279	-110.52939	-943.90958	-0.063973	-1.740769303	-40.14369723
G	-1165.196232	-110.549611	-943.928805	-0.0560683333	-1.5256754183	-35.18343985
<b>Rh3V</b>						
E	-1275.820927	-110.531751	-943.91194	-0.0784335	-2.1342539685	-49.217805585
U	-1275.81486	-110.530335	-943.910524	-0.07833275	-2.1315124602	-49.1545839525
H	-1275.813916	-110.52939	-943.90958	-0.0790415	-2.1507982565	-49.599331665
G	-1275.855776	-110.549611	-943.928805	-0.0695345	-1.8921032795	-43.633594095
<b>Rh4V</b>						
E	-1386.449928	-110.531751	-943.91194	-0.0821968	-2.2366571248	-51.579313968
U	-1386.441732	-110.530335	-943.910524	-0.0819736	-2.2305836296	-51.439253736
H	-1386.440788	-110.52939	-943.90958	-0.0827296	-2.2511551456	-51.913651296

G	-1386.488227	-110.549611	-943.928805	-0.0721956	-1.9645144716	-45.303460956
<b>Rh5V</b>						
E	-1497.087501	-110.531751	-943.91194	-0.0861343333	-2.3438013443	-54.05015551
U	-1497.077287	-110.530335	-943.910524	-0.085848	-2.336009928	-53.87047848
H	-1497.076343	-110.52939	-943.90958	-0.0866355	-2.3574385905	-54.364642605
G	-1497.130854	-110.549611	-943.928805	-0.0756656667	-2.0589384557	-47.48096249
<b>Rh6V</b>						
E	-1607.742843	-110.531751	-943.91194	-0.0914852857	-2.4894061096	-57.4079316386
U	-1607.730811	-110.530335	-943.910524	-0.0911824286	-2.4811650639	-57.2178857528
H	-1607.729867	-110.52939	-943.90958	-0.0919924286	-2.5032059739	-57.7261688529
G	-1607.787898	-110.549611	-943.928805	-0.0802038571	-2.1824271567	-50.3287223957
<b>Rh7V</b>						
E	-1718.390681	-110.531751	-943.91194	-0.0945605	-2.5730857655	-59.337659355
U	-1718.376522	-110.530335	-943.910524	-0.094206625	-2.5634564729	-59.1155992538
H	-1718.375578	-110.52939	-943.90958	-0.0950335	-2.5859565685	-59.634471585
G	-1718.439883	-110.549611	-943.928805	-0.082975125	-2.2578361264	-52.0677206888
<b>Rh8V</b>						
E	-1829.048398	-110.531751	-943.91194	-0.09805	-2.66803855	-61.5273555
U	-1829.032221	-110.530335	-943.910524	-0.0976685556	-2.6576590652	-61.2879952967
H	-1829.031276	-110.52939	-943.90958	-0.0985084444	-2.6805132818	-61.8150339733
G	-1829.100446	-110.549611	-943.928805	-0.0860836667	-2.3424226537	-54.01836167

## TPSSH

<b>RhV</b>	<b>E_Cluster (a.u)</b>	<b>E_Rh (a.u)</b>	<b>E_V (a.u)</b>	<b>-E_bin (a.u)</b>	<b>-E_bin (eV)</b>	<b>-E_bin (kcal/mol)</b>
E	-1054.480104	-110.449211	-943.895969	-0.067462	-1.835708482	-42.33307962
U	-1054.477469	-110.447794	-943.894553	-0.067561	-1.838402371	-42.39520311
H	-1054.476525	-110.44685	-943.893609	-0.068033	-1.851245963	-42.69138783
G	-1054.50534	-110.467071	-943.912834	-0.0627175	-1.7066058925	-39.355858425
<b>Rh2V</b>						
E	-1165.019409	-110.449211	-943.895969	-0.075006	-2.040988266	-47.06701506
U	-1165.014795	-110.447794	-943.894553	-0.0748846667	-2.0376866647	-46.99087718
H	-1165.013851	-110.44685	-943.893609	-0.075514	-2.054811454	-47.38579014
G	-1165.052994	-110.467071	-943.912834	-0.0686726667	-1.8686519327	-43.09278506
<b>Rh3V</b>						
E	-1275.605025	-110.449211	-943.895969	-0.09035575	-2.4586703132	-56.6991366825
U	-1275.599015	-110.447794	-943.894553	-0.09027	-2.45633697	-56.6453277
H	-1275.598071	-110.44685	-943.893609	-0.090978	-2.475602358	-57.08960478

G	-1275.639545	-110.467071	-943.912834	-0.0813745	-2.2142815195	-51.063312495
<b>Rh4V</b>						
E	-1386.164718	-110.449211	-943.895969	-0.094381	-2.568201391	-59.22502131
U	-1386.156688	-110.447794	-943.894553	-0.0941918	-2.5630530698	-59.106296418
H	-1386.155744	-110.44685	-943.893609	-0.094947	-2.583602817	-59.58019197
G	-1386.203488	-110.467071	-943.912834	-0.084474	-2.298622014	-53.00827974
<b>Rh5V</b>						
E	-1496.734883	-110.449211	-943.895969	-0.0988098333	-2.6887143748	-62.004158515
U	-1496.72493	-110.447794	-943.894553	-0.0985678333	-2.6821293128	-61.852301095
H	-1496.723986	-110.44685	-943.893609	-0.0993545	-2.7035352995	-62.345942295
G	-1496.777112	-110.467071	-943.912834	-0.0881538333	-2.3987539588	-55.317411955
<b>Rh6V</b>						
E	-1607.323089	-110.449211	-943.895969	-0.1045505714	-2.8449255991	-65.6065290771
U	-1607.311407	-110.447794	-943.894553	-0.1042985714	-2.8380684271	-65.4483965571
H	-1607.310463	-110.44685	-943.893609	-0.1051077143	-2.8600860134	-65.9561417914
G	-1607.367257	-110.467071	-943.912834	-0.0931424286	-2.5344986239	-58.4478053529
<b>Rh7V</b>						
E	-1717.911111	-110.449211	-943.895969	-0.108833125	-2.9614581644	-68.2938742687
U	-1717.897523	-110.447794	-943.894553	-0.1085515	-2.9537948665	-68.117151765
H	-1717.896579	-110.44685	-943.893609	-0.1093775	-2.9762711525	-68.635475025
G	-1717.958	-110.467071	-943.912834	-0.096958625	-2.6383411449	-60.8425067738
<b>Rh8V</b>						
E	-1828.487953	-110.449211	-943.895969	-0.1109217778	-3.0182924951	-69.6045247733
U	-1828.472122	-110.447794	-943.894553	-0.1105796667	-3.0089833097	-69.38984663
H	-1828.471178	-110.44685	-943.893609	-0.1114187778	-3.0318163621	-69.9163972433
G	-1828.539035	-110.467071	-943.912834	-0.0988481111	-2.6897559514	-62.0281782033

**11. Thermochemical Data**  
**Rh<sub>n</sub> Cluster**  
**B3LYP**



<b>Rh2</b>			<b>B3LYP/def2tzvp</b>	<b>D*H und</b>				
	<b>Cluster</b>	<b>CH4</b>	<b>P.R.C</b>	<b>TS</b>	<b>Po.R.C</b>	<b>Eb</b>	<b>Ea</b>	<b>Eh</b>
E	-221.128958	-40.494851	-261.6322	-261.608374	-261.631059	-5.26543641	14.95105326	0.71598891
U	-221.12622	-40.491983	-261.625007	-261.602341	-261.624665	-4.26957804	14.22314166	0.21460842
H	-221.125276	-40.491038	-261.624063	-261.601397	-261.623721	-4.86257499	14.22314166	0.21460842
G	-221.155148	-40.512165	-261.669433	-261.642495	-261.665236	-1.3303212	16.90386438	2.63365947
<b>Rh3</b>			<b>B3LYP/def2tzvp</b>	<b>6-A" Cs</b>				
	<b>Cluster</b>	<b>CH4</b>	<b>P.R.C</b>	<b>TS</b>	<b>Po.R.C</b>	<b>Eb</b>	<b>Ea</b>	<b>Eh</b>
E	-331.755775	-40.494851	-372.256928	-372.235654	-372.245421	-3.95456802	13.34964774	7.22075757
U	-331.751141	-40.491983	-372.247867	-372.227559	-372.237468	-2.97627993	12.74347308	6.52547649
H	-331.750196	-40.491038	-372.246923	-372.226615	-372.236524	-3.56990439	12.74347308	6.52547649
G	-331.789843	-40.512165	-372.298638	-372.274433	-372.28383	2.1147087	15.18887955	9.29216808
<b>Rh4</b>			<b>B3LYP/def2tzvp</b>	<b>7A C1</b>				
	<b>Cluster</b>	<b>CH4</b>	<b>P.R.C</b>	<b>TS</b>	<b>Po.R.C</b>	<b>Eb</b>	<b>Ea</b>	<b>Eh</b>
E	-442.39157	-40.494851	-482.89351	-482.874617	-482.886817	-4.44841839	11.85554643	4.19992443
U	-442.384879	-40.491983	-482.882662	-482.864829	-482.87693	-3.639558	11.19038583	3.59688732
H	-442.383935	-40.491038	-482.881718	-482.863885	-482.875985	-4.23255495	11.19038583	3.59751483
G	-442.429296	-40.512165	-482.937584	-482.915944	-482.928088	2.43285627	13.5793164	5.95883496
<b>Rh5</b>			<b>B3LYP/def2tzvp</b>	<b>8A1 C2V</b>				
	<b>Cluster</b>	<b>CH4</b>	<b>P.R.C</b>	<b>TS</b>	<b>Po.R.C</b>	<b>Eb</b>	<b>Ea</b>	<b>Eh</b>
E	-553.009463	-40.494851	-593.525803	-593.511114	-593.524685	-13.48456239	9.21749439	0.70155618
U	-553.001447	-40.491983	-593.513159	-593.499249	-593.512587	-12.38014479	8.7286641	0.3589357199
H	-553.000503	-40.491038	-593.512215	-593.498305	-593.511643	-12.97314174	8.7286641	0.3589357199
G	-553.048066	-40.512165	-593.573089	-593.556427	-593.569921	-8.06852358	10.45557162	1.98795168
<b>Rh6</b>			<b>B3LYP/def2tzvp</b>	<b>7-A1G Oh</b>				
	<b>Cluster</b>	<b>CH4</b>	<b>P.R.C</b>	<b>TS</b>	<b>Po.R.C</b>	<b>Eb</b>	<b>Ea</b>	<b>Eh</b>
E	-663.670938	-40.494851	-704.173654	-704.156107	-704.165447	-4.93536615	11.01091797	5.1499745701
U	-663.660852	-40.491983	-704.159474	-704.142573	-704.15164	-4.16603889	10.60554651	4.91591334
H	-663.659908	-40.491038	-704.15853	-704.141629	-704.150695	-4.75903584	10.60554651	4.91654085
G	-663.709801	-40.512165	-704.221988	-704.202369	-704.212618	-0.01380522	12.31111869	5.8797687
<b>Rh7</b>			<b>B3LYP/def2tzvp</b>	<b>14A C1</b>				
	<b>Cluster</b>	<b>CH4</b>	<b>P.R.C</b>	<b>TS</b>	<b>Po.R.C</b>	<b>Eb</b>	<b>Ea</b>	<b>Eh</b>
E	-774.313418	-40.494851	-814.814449	-814.793202	-814.810092	-3.8780118	13.33270497	2.7340610699
U	-774.300585	-40.491983	-814.797547	-814.777484	-814.794233	-3.12437229	12.58973313	2.07956814
H	-774.29964	-40.491038	-814.796603	-814.776539	-814.793289	-3.71799675	12.59036064	2.07956814
G	-774.361683	-40.512165	-814.867865	-814.843836	-814.860748	3.7543923299	15.07843779	4.4659886701
<b>Rh8</b>			<b>B3LYP/def2tzvp</b>	<b>13A C1</b>				
	<b>Cluster</b>	<b>CH4</b>	<b>P.R.C</b>	<b>TS</b>	<b>Po.R.C</b>	<b>Eb</b>	<b>Ea</b>	<b>Eh</b>

E	-884.932302	-40.494851	-925.464657	-925.445546	-925.458266	-23.5341350399	11.99234361	4.01041641
U	-884.917709	-40.491983	-925.446121	-925.4283	-925.440551	-22.85956179	11.1828557099	3.4952307
H	-884.916765	-40.491038	-925.445177	-925.427356	-925.439607	-23.4525587399	11.1828557099	3.4952307
G	-884.982619	-40.512165	-925.519562	-925.497623	-925.511754	-15.54844278	13.76694189	4.89959808
<b>Rh9</b>			<b>B3LYP/def2tzvp</b>	<b>18-A C1</b>				
	<b>Cluster</b>	<b>CH4</b>	<b>P.R.C</b>	<b>TS</b>	<b>Po.R.C</b>	<b>Eb</b>	<b>Ea</b>	<b>Eh</b>
E	-995.615213	-40.494851	-1036.118957	-1036.085016	-1036.087108	-5.58044643	21.2983169099	19.98556599
U	-995.598868	-40.491983	-1036.097865	-1036.065152	-1036.06712	-4.40135514	20.52773463	19.29279495
H	-995.597923	-40.491038	-1036.096921	-1036.064208	-1036.066176	-4.9949796001	20.52773463	19.29279495
G	-995.667597	-40.512165	-1036.180025	-1036.14179	-1036.144059	-0.1650351299	23.99284485	22.5690246599

## MN15

<b>Rh2</b>				<b>MN15 def2tzvp+sdd</b>				
	<b>Cluster</b>	<b>CH4</b>	<b>P.R.C</b>	<b>TS</b>	<b>Po.R.C</b>	<b>Eb</b>	<b>Ea</b>	<b>Eh</b>
E	-220.533159	-40.423087	-260.980954	-260.957064	-260.982326	-15.50451708	14.9912139	-0.86094372
U	-220.530459	-40.420216	-260.974131	-260.951163	-260.976047	-14.71887456	14.41264968	-1.20230916
H	-220.529515	-40.419272	-260.973187	-260.950219	-260.975103	-15.311244	14.41264968	-1.20230916
G	-220.559308	-40.440398	-261.018427	-260.990313	-261.015992	-11.74761471	17.64181614	1.52798685
<b>Rh3</b>	<b>Cluster</b>	<b>CH4</b>	<b>P.R.C</b>	<b>TS</b>	<b>Po.R.C</b>	<b>Eb</b>	<b>Ea</b>	<b>Eh</b>
E	-330.882326	-40.423087	-371.320026	-371.301983	-371.312309	-9.16980363	11.32216293	4.84249467
U	-330.87751	-40.420216	-371.311738	-371.294086	-371.304535	-8.79267012	11.07680652	4.51995453
H	-330.876566	-40.419272	-371.310794	-371.293142	-371.303591	-9.38503956	11.07680652	4.51995453
G	-330.917179	-40.440398	-371.359061	-371.340418	-371.350502	-0.93122484	11.69866893	5.37085809
<b>Rh4</b>	<b>Cluster</b>	<b>CH4</b>	<b>P.R.C</b>	<b>TS</b>	<b>Po.R.C</b>	<b>Eb</b>	<b>Ea</b>	<b>Eh</b>
E	-441.244286	-40.423087	-481.680884	-481.664945	-481.672836	-8.47828761	10.00188189	5.05020048
U	-441.237575	-40.420216	-481.670571	-481.65497	-481.663063	-8.0195778	9.78978351	4.71134508
H	-441.236631	-40.419272	-481.669627	-481.654026	-481.662119	-8.61194724	9.78978351	4.71134508
G	-441.282173	-40.440398	-481.723332	-481.707272	-481.713883	-0.47753511	10.0778106	5.92934199
<b>Rh5</b>	<b>Cluster</b>	<b>CH4</b>	<b>P.R.C</b>	<b>TS</b>	<b>Po.R.C</b>	<b>Eb</b>	<b>Ea</b>	<b>Eh</b>
E	-551.596669	-40.423087	-592.035951	-592.019879	-592.031896	-10.16252445	10.08534072	2.54455305
U	-551.588166	-40.420216	-592.023751	-592.008158	-592.020111	-9.64420119	9.78476343	2.2841363999
H	-551.587222	-40.419272	-592.022806	-592.007214	-592.019167	-10.23594312	9.78413592	2.2835088899
G	-551.637835	-40.440398	-592.081452	-592.064547	-592.076577	-2.01995469	10.60805655	3.05911125
<b>Rh6</b>	<b>Cluster</b>	<b>CH4</b>	<b>P.R.C</b>	<b>TS</b>	<b>Po.R.C</b>	<b>Eb</b>	<b>Ea</b>	<b>Eh</b>
E	-661.970523	-40.423087	-702.408466	-702.391891	-702.400211	-9.32228856	10.40097825	5.18009505
U	-661.960686	-40.420216	-702.394844	-702.378559	-702.386576	-8.74874442	10.21900035	5.18825268
H	-661.959742	-40.419272	-702.3939	-702.377614	-702.385631	-9.34111386	10.21962786	5.18888019
G	-662.01017	-40.440398	-702.454989	-702.4377	-702.446511	-2.77422171	10.84902039	5.32002978

<b>Rh7</b>	<b>Cluster</b>	<b>CH4</b>	<b>P.R.C</b>	<b>TS</b>	<b>Po.R.C</b>	<b>Eb</b>	<b>Ea</b>	<b>Eh</b>
E	-772.31383	-40.423087	-812.749514	-812.729227	-812.742966	-7.9047434699	12.73029537	4.10893548
U	-772.301655	-40.420216	-812.733409	-812.713801	-812.727416	-7.2402103801	12.30421608	3.7606674301
H	-772.300711	-40.419272	-812.732465	-812.712857	-812.726472	-7.8325798201	12.30421608	3.7606674301
G	-772.359721	-40.440398	-812.800864	-812.779047	-812.792921	-0.46749495	13.69038567	4.98431193
<b>Rh8</b>	<b>Cluster</b>	<b>CH4</b>	<b>P.R.C</b>	<b>TS</b>	<b>Po.R.C</b>	<b>Eb</b>	<b>Ea</b>	<b>Eh</b>
E	-882.690678	-40.423087	-923.126522	-923.108986	-923.11888	-8.00514507	11.00401536	4.79543142
U	-882.676946	-40.420216	-923.10878	-923.092038	-923.10151	-7.29041118	10.50577242	4.5619977
H	-882.676002	-40.419272	-923.107835	-923.091093	-923.100566	-7.88215311	10.50577242	4.56137019
G	-882.738183	-40.440398	-923.179612	-923.160396	-923.171611	-0.64696281	12.05823216	5.02070751
<b>Rh9</b>	<b>Cluster</b>	<b>CH4</b>	<b>P.R.C</b>	<b>TS</b>	<b>Po.R.C</b>	<b>Eb</b>	<b>Ea</b>	<b>Eh</b>
E	-993.044552	-40.423087	-1033.481706	-1033.453255	-1033.453999	-8.82718317	17.8532870101	17.38641957
U	-993.028695	-40.420216	-1033.461581	-1033.434106	-1033.434544	-7.9505517	17.2408372501	16.96598787
H	-993.027751	-40.419272	-1033.460636	-1033.433162	-1033.433599	-8.54229363	17.24020974	16.96598787
G	-993.095616	-40.440398	-1033.53932	-1033.50802	-1033.510089	-2.07454806	19.6410630001	18.34274481

## TPSSh

<b>Rh2</b>	<b>Cluster</b>	<b>CH4</b>	<b>P.R.C</b>	<b>TS</b>	<b>Po.R.C</b>	<b>Eb</b>	<b>Ea</b>	<b>Eh</b>
E	-220.969194	-40.492323	-261.465381	-261.448435	-261.462111	-2.42469864	10.63378446	2.0519577
U	-220.966459	-40.489456	-261.458407	-261.442264	-261.455772	-1.56375492	10.12989393	1.65348885
H	-220.965515	-40.488512	-261.457463	-261.44132	-261.454828	-2.15612436	10.12989393	1.65348885
G	-220.99538	-40.509639	-261.501301	-261.482687	-261.496751	2.33308218	11.68047114	2.8551705
<b>Rh3</b>	<b>Cluster</b>	<b>CH4</b>	<b>P.R.C</b>	<b>TS</b>	<b>Po.R.C</b>	<b>Eb</b>	<b>Ea</b>	<b>Eh</b>
E	-331.521778	-40.492323	-372.019629	-372.001015	-372.008069	-3.46887528	11.68047114	7.2540156
U	-331.517295	-40.489456	-372.010897	-371.993077	-371.999724	-2.60165646	11.1822282	7.01116923
H	-331.51635	-40.488512	-372.009952	-371.992133	-371.99878	-3.1940259	11.18160069	7.01054172
G	-331.554839	-40.509639	-372.060152	-372.039372	-372.046932	2.71460826	13.0396578	8.2956822
<b>Rh4</b>	<b>Cluster</b>	<b>CH4</b>	<b>P.R.C</b>	<b>TS</b>	<b>Po.R.C</b>	<b>Eb</b>	<b>Ea</b>	<b>Eh</b>
E	-442.0929	-40.492323	-482.590097	-482.575346	-482.588428	-3.05848374	9.25640001	1.04731419
U	-442.086389	-40.489456	-482.579586	-482.565718	-482.57866	-2.34751491	8.70230868	0.58107426
H	-442.085445	-40.488512	-482.578642	-482.564774	-482.577715	-2.93988435	8.70230868	0.58170177
G	-442.130087	-40.509639	-482.633156	-482.616213	-482.629351	4.1227407	10.63190193	2.38767555
<b>Rh5</b>	<b>Cluster</b>	<b>CH4</b>	<b>P.R.C</b>	<b>TS</b>	<b>Po.R.C</b>	<b>Eb</b>	<b>Ea</b>	<b>Eh</b>
E	-552.647614	-40.492323	-593.153687	-593.138461	-593.155254	-8.6282625	9.55446726	-0.98330817
U	-552.639683	-40.489456	-593.141477	-593.126772	-593.143363	-7.74221838	9.22753455	-1.18348386
H	-552.638739	-40.488512	-593.140533	-593.125828	-593.142419	-8.33458782	9.22753455	-1.18348386
G	-552.686007	-40.509639	-593.19907	-593.182936	-593.200438	-2.14859424	10.12424634	-0.85843368
<b>Rh6</b>	<b>Cluster</b>	<b>CH4</b>	<b>P.R.C</b>	<b>TS</b>	<b>Po.R.C</b>	<b>Eb</b>	<b>Ea</b>	<b>Eh</b>

E	-663.239871	-40.492323	-703.737499	-703.722624	-703.733191	-3.32894055	9.33421125	2.70331308
U	-663.230054	-40.489456	-703.723755	-703.70939	-703.720048	-2.66377995	9.01418115	2.32617957
H	-663.22911	-40.488512	-703.722811	-703.708446	-703.719104	-3.25614939	9.01418115	2.32617957
G	-663.278172	-40.509639	-703.784603	-703.76813	-703.778476	2.0130520801	10.3369722299	3.84475377
<b>Rh7</b>	<b>Cluster</b>	<b>CH4</b>	<b>P.R.C</b>	<b>TS</b>	<b>Po.R.C</b>	<b>Eb</b>	<b>Ea</b>	<b>Eh</b>
E	-773.808867	-40.492323	-814.303884	-814.286797	-814.308464	-1.6905119401	10.72226337	-2.8739957999
U	-773.796347	-40.489456	-814.287484	-814.27134	-814.293224	-1.05484431	10.13052144	-3.6019074
H	-773.795403	-40.488512	-814.28654	-814.270396	-814.29228	-1.64721375	10.13052144	-3.6019074
G	-773.856276	-40.509639	-814.355939	-814.336819	-814.357707	6.26003976	11.9979912	-1.10943768
<b>Rh8</b>	<b>Cluster</b>	<b>CH4</b>	<b>P.R.C</b>	<b>TS</b>	<b>Po.R.C</b>	<b>Eb</b>	<b>Ea</b>	<b>Eh</b>
E	-884.35534	-40.492323	-924.878153	-924.862827	-924.892187	-19.1327799	9.61721826	-8.80647534
U	-884.341215	-40.489456	-924.860129	-924.84585	-924.875688	-18.48518958	8.96021529	-9.76342809
H	-884.340271	-40.488512	-924.859185	-924.844906	-924.874744	-19.07755902	8.96021529	-9.76342809
G	-884.403977	-40.509639	-924.931667	-924.91445	-924.94207	-11.3271830099	10.80383967	-6.52798653
<b>Rh9</b>	<b>Cluster</b>	<b>CH4</b>	<b>P.R.C</b>	<b>TS</b>	<b>Po.R.C</b>	<b>Eb</b>	<b>Ea</b>	<b>Eh</b>
E	-994.958061	-40.492323	-1035.462379	-1035.433636	-1035.43912	-7.52698245	18.03651993	14.59525509
U	-994.94244	-40.489456	-1035.442081	-1035.414418	-1035.419858	-6.3911893499	17.3588091299	13.94515473
H	-994.941496	-40.488512	-1035.441137	-1035.413473	-1035.418914	-6.98355879	17.35943664	13.94515473
G	-995.007673	-40.509639	-1035.520251	-1035.488621	-1035.493739	-1.84425189	19.8481413	16.6365451199

## Rh<sub>m</sub>V Cluster B3LYP

<b>RhV</b>	<b>3-SG C*V</b>		<b>B3LYP/def2tzvp</b>					
	<b>Cluster</b>	<b>CH4</b>	<b>P.R.C</b>	<b>TS</b>	<b>Po.R.C</b>	<b>Eb</b>	<b>Ea</b>	<b>Eh</b>
E	-1054.562802	-40.494851	-1095.060159	-1095.018132	-1095.030896	-1.5725400602	26.3723627701	18.3628251301
U	-1054.560171	-40.491983	-1095.052767	-1095.012662	-1095.025127	-0.38466363	25.1662885499	17.3443763999
H	-1054.559227	-40.491038	-1095.051822	-1095.011717	-1095.024182	-0.97703307	25.1662885499	17.3443763999
G	-1054.588036	-40.512165	-1095.098901	-1095.049875	-1095.062727	0.8157630001	30.7643052601	22.69954674
<b>Rh2V</b>	<b>4-A2 C2V</b>							
	<b>Cluster</b>	<b>CH4</b>	<b>P.R.C</b>	<b>TS</b>	<b>Po.R.C</b>	<b>Eb</b>	<b>Ea</b>	<b>Eh</b>
E	-1165.164998	-40.494851	-1205.672277	-1205.655275	-1205.673244	-7.79869428	10.6689250199	-0.6068021701
U	-1165.161223	-40.491983	-1205.663743	-1205.647559	-1205.665535	-6.6120728701	10.15562184	-1.12449792
H	-1165.160279	-40.491038	-1205.662799	-1205.646615	-1205.664591	-7.2050698201	10.1556218399	-1.12449792
G	-1165.196232	-40.512165	-1205.711131	-1205.692397	-1205.71034	-1.7156123399	11.75577234	0.49636041
<b>Rh3V</b>	<b>Cs 1-A</b>							
	<b>Cluster</b>	<b>CH4</b>	<b>P.R.C</b>	<b>TS</b>	<b>Po.R.C</b>	<b>Eb</b>	<b>Ea</b>	<b>Eh</b>
E	-1275.820927	-40.494851	-1316.323959	-1316.308998	-1316.325234	-5.1336593101	9.3881771101	-0.8000752499
U	-1275.81486	-40.491983	-1316.313535	-1316.299885	-1316.315966	-4.1992969201	8.5655115001	-1.5254768099

H	-1275.813916	-40.491038	-1316.312591	-1316.298941	-1316.315022	-4.79229387	8.5655115001	-1.5254768099
G	-1275.855776	-40.512165	-1316.366864	-1316.348175	-1316.364595	0.6758282701	11.72753439	1.42382019
<b>Rh4V</b>	<b>C1 2-A</b>							
	<b>Cluster</b>	<b>CH4</b>	<b>P.R.C</b>	<b>TS</b>	<b>Po.R.C</b>	<b>Eb</b>	<b>Ea</b>	<b>Eh</b>
E	-1386.449928	-40.494851	-1426.950054	-1426.939354	-1426.958034	-3.31011525	6.7143569999	-5.0075298001
U	-1386.441732	-40.491983	-1426.93826	-1426.928118	-1426.946776	-2.85203295	6.3642064199	-5.3438751601
H	-1386.440788	-40.491038	-1426.937316	-1426.927174	-1426.945832	-3.4450299	6.3642064201	-5.3438751601
G	-1386.488227	-40.512165	-1426.994949	-1426.981339	-1427.001382	3.4155369302	8.5404111	-4.03677183
<b>Rh5V</b>	<b>C1 5-A</b>							
	<b>Cluster</b>	<b>CH4</b>	<b>P.R.C</b>	<b>TS</b>	<b>Po.R.C</b>	<b>Eb</b>	<b>Ea</b>	<b>Eh</b>
E	-1497.087501	-40.494851	-1537.591925	-1537.578968	-1537.59464	-6.00715323	8.1306470699	-1.7036896501
U	-1497.077287	-40.491983	-1537.578445	-1537.565874	-1537.581405	-5.7574042501	7.8884282101	-1.8574295999
H	-1497.076343	-40.491038	-1537.577501	-1537.56493	-1537.580461	-6.3504012001	7.88842821	-1.8574296
G	-1497.130854	-40.512165	-1537.638679	-1537.625407	-1537.64115	2.7233934001	8.3283127199	-1.55057721
<b>Rh6V</b>	<b>C1 8-A</b>							
	<b>Cluster</b>	<b>CH4</b>	<b>P.R.C</b>	<b>TS</b>	<b>Po.R.C</b>	<b>Eb</b>	<b>Ea</b>	<b>Eh</b>
E	-1607.742843	-40.494851	-1648.249083	-1648.232214	-1648.241542	-7.14671139	10.5854661899	4.73205291
U	-1607.730811	-40.491983	-1648.233221	-1648.216978	-1648.22634	-6.5430467701	10.19264493	4.31789631
H	-1607.729867	-40.491038	-1648.232277	-1648.216033	-1648.225396	-7.13604372	10.1932724401	4.31789631
G	-1607.787898	-40.512165	-1648.2992	-1648.281191	-1648.290586	0.5415411301	11.3008275899	5.4053711399
<b>Rh7V</b>	<b>C1 9-A</b>							
	<b>Cluster</b>	<b>CH4</b>	<b>P.R.C</b>	<b>TS</b>	<b>Po.R.C</b>	<b>Eb</b>	<b>Ea</b>	<b>Eh</b>
E	-1718.390681	-40.494851	-1758.895908	-1758.876333	-1758.892503	-6.51104376	12.28350825	2.13667155
U	-1718.376522	-40.491983	-1758.877776	-1758.858917	-1758.875209	-5.8176452101	11.83421109	1.61081817
H	-1718.375578	-40.491038	-1758.876832	-1758.857973	-1758.874264	-6.4106421601	11.83421109	1.6114456799
G	-1718.439883	-40.512165	-1758.950103	-1758.928803	-1758.94502	1.2205069501	13.3659629999	3.1896333299
<b>Rh8V</b>	<b>C1 12-A</b>							
	<b>Cluster</b>	<b>CH4</b>	<b>P.R.C</b>	<b>TS</b>	<b>Po.R.C</b>	<b>Eb</b>	<b>Ea</b>	<b>Eh</b>
E	-1829.048398	-40.494851	-1869.553735	-1869.533051	-1869.546772	-6.5800698601	12.97941684	4.36935213
U	-1829.032221	-40.491983	-1869.533388	-1869.51369	-1869.527604	-5.7630518401	12.36069198	3.62951784
H	-1829.031276	-40.491038	-1869.532444	-1869.512746	-1869.52666	-6.3566763001	12.3606919799	3.62951784
G	-1829.100446	-40.512165	-1869.611884	-1869.588463	-1869.601616	0.4561997701	14.6969117099	6.44327268

## MN15

				<b>MN15/def2tzvp+sdd</b>				
<b>RhV</b>	<b>Cluster</b>	<b>CH4</b>	<b>P.R.C</b>	<b>TS</b>	<b>Po.R.C</b>	<b>Eb</b>	<b>Ea</b>	<b>Eh</b>
E	-181.856963	-40.423087	-222.284571	-222.240555	-222.245072	-2.83697271	27.62048016	24.78601749
U	-181.854384	-40.420216	-222.2785	-222.235233	-222.239156	-2.447289	27.15047517	24.68875344

H	-181.85344	-40.419272	-222.277556	-222.234288	-222.238212	-3.03965844	27.15110268	24.68875344
G	-181.882132	-40.440398	-222.318003	-222.272056	-222.277329	2.84073777	28.83220197	25.52334174
<b>Rh2V</b>	<b>Cluster</b>	<b>CH4</b>	<b>P.R.C</b>	<b>TS</b>	<b>Po.R.C</b>	<b>Eb</b>	<b>Ea</b>	<b>Eh</b>
E	-292.157978	-40.423087	-332.613426	-332.602804	-332.616788	-20.30685111	6.66541122	-2.10968862
U	-292.154084	-40.420216	-332.605165	-332.595205	-332.609329	-19.36809615	6.2499996	-2.61295164
H	-292.15314	-40.419272	-332.604221	-332.594261	-332.608385	-19.96046559	6.2499996	-2.61295164
G	-292.189152	-40.440398	-332.651193	-332.639566	-332.652913	-13.58119893	7.29605877	-1.0793172
<b>Rh3V</b>	<b>Cluster</b>	<b>CH4</b>	<b>P.R.C</b>	<b>TS</b>	<b>Po.R.C</b>	<b>Eb</b>	<b>Ea</b>	<b>Eh</b>
E	-402.531894	-40.423087	-442.965623	-442.952588	-442.962517	-6.67796142	8.17959285	1.94904606
U	-402.525955	-40.420216	-442.955857	-442.94364	-442.953422	-6.07806186	7.66628967	1.52798685
H	-402.52501	-40.419272	-442.954913	-442.942696	-442.952478	-6.67105881	7.66628967	1.52798685
G	-402.566268	-40.440398	-443.005829	-442.991071	-443.000935	0.52522587	9.26079258	3.07103394
<b>Rh4V</b>	<b>Cluster</b>	<b>CH4</b>	<b>P.R.C</b>	<b>TS</b>	<b>Po.R.C</b>	<b>Eb</b>	<b>Ea</b>	<b>Eh</b>
E	-512.878643	-40.423087	-553.314955	-553.309661	-553.32105	-8.29881975	3.32203794	-3.82467345
U	-512.870582	-40.420216	-553.303174	-553.298557	-553.309794	-7.76606376	2.89721367	-4.1541162
H	-512.869637	-40.419272	-553.30223	-553.297613	-553.30885	-8.35906071	2.89721367	-4.1541162
G	-512.9165	-40.440398	-553.357749	-553.351093	-553.362612	-0.53401101	4.17670656	-3.05158113
<b>Rh5V</b>	<b>Cluster</b>	<b>CH4</b>	<b>P.R.C</b>	<b>TS</b>	<b>Po.R.C</b>	<b>Eb</b>	<b>Ea</b>	<b>Eh</b>
E	-623.228791	-40.423087	-663.66976	-663.66361	-663.665597	-11.22113382	3.8591865	2.61232413
U	-623.218811	-40.420216	-663.656401	-663.650438	-663.652518	-10.90235874	3.74184213	2.43662133
H	-623.217867	-40.419272	-663.655457	-663.649494	-663.651574	-11.49472818	3.74184213	2.43662133
G	-623.271571	-40.440398	-663.715717	-663.709138	-663.71181	-2.3519074801	4.12838829	2.45168157
<b>Rh6V</b>	<b>Cluster</b>	<b>CH4</b>	<b>P.R.C</b>	<b>TS</b>	<b>Po.R.C</b>	<b>Eb</b>	<b>Ea</b>	<b>Eh</b>
E	-733.603411	-40.423087	-774.045077	-774.028885	-774.032825	-11.65850829	10.16064192	7.68825252
U	-733.591664	-40.420216	-774.029777	-774.014014	-774.017818	-11.23054647	9.89144013	7.50439209
H	-733.590719	-40.419272	-774.028833	-774.01307	-774.016874	-11.82354342	9.89144013	7.50439209
G	-733.647856	-40.440398	-774.093937	-774.076772	-774.081387	-3.56613933	10.77120915	7.8752505
<b>Rh7V</b>	<b>Cluster</b>	<b>CH4</b>	<b>P.R.C</b>	<b>TS</b>	<b>Po.R.C</b>	<b>Eb</b>	<b>Ea</b>	<b>Eh</b>
E	-843.964425	-40.423087	-884.402242	-884.385148	-884.396704	-9.2432223	10.72665594	3.47515038
U	-843.950696	-40.420216	-884.384121	-884.36816	-884.379797	-8.28877959	10.01568711	2.71335324
H	-843.949752	-40.419272	-884.383177	-884.367216	-884.378852	-8.88114903	10.01568711	2.71398075
G	-844.011879	-40.440398	-884.456042	-884.436495	-884.448234	-2.36257515	12.26593797	4.89959808
<b>Rh8V</b>	<b>Cluster</b>	<b>CH4</b>	<b>P.R.C</b>	<b>TS</b>	<b>Po.R.C</b>	<b>Eb</b>	<b>Ea</b>	<b>Eh</b>
E	-954.32548	-40.423087	-994.777122	-994.761542	-994.771136	-17.91854805	9.7766058	3.75627486
U	-954.309619	-40.420216	-994.757703	-994.742362	-994.752218	-17.48744868	9.62663091	3.44189235
H	-954.308675	-40.419272	-994.756759	-994.741418	-994.751273	-18.07981812	9.62663091	3.44251986
G	-954.376901	-40.440398	-994.832334	-994.816275	-994.825593	-9.43461285	10.07718309	4.2300449099

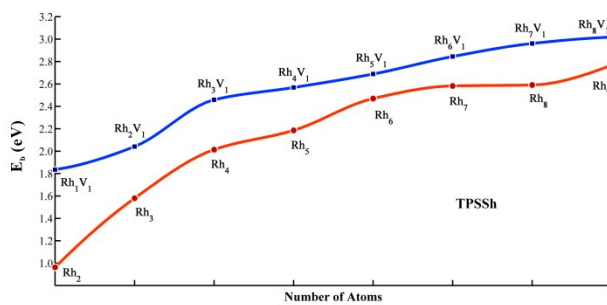
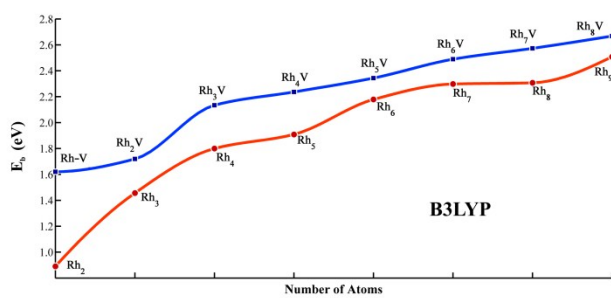
# TPSSh

				TPSSh/def2tzvp				
<b>RhV</b>	<b>Cluster</b>	<b>CH4</b>	<b>P.R.C</b>	<b>TS</b>	<b>Po.R.C</b>	<b>Eb</b>	<b>Ea</b>	<b>Eh</b>
E	-1054.480104	-40.492323	-1094.972521	-1094.936329	-1094.974918	-0.05898594	22.71084192	-1.50414147
U	-1054.477469	-40.489456	-1094.967623	-1094.930872	-1094.969362	-0.43800198	23.0616200101	-1.09123989
H	-1054.476525	-40.488512	-1094.966679	-1094.929928	-1094.968418	-1.0303714201	23.0616200101	-1.0912398899
G	-1054.50534	-40.509639	-1095.005679	-1094.968066	-1095.006513	5.835843	23.6025336301	-0.52334334
<b>Rh2V</b>	<b>Cluster</b>	<b>CH4</b>	<b>P.R.C</b>	<b>TS</b>	<b>Po.R.C</b>	<b>Eb</b>	<b>Ea</b>	<b>Eh</b>
E	-1165.019409	-40.492323	-1205.518133	-1205.5042	-1205.521292	-4.0166915101	8.74309683	-1.9823040899
U	-1165.014795	-40.489456	-1205.509854	-1205.496571	-1205.513602	-3.5159385299	8.33521533	-2.3519074801
H	-1165.013851	-40.488512	-1205.50891	-1205.495626	-1205.512658	-4.1083079701	8.3358428401	-2.3519074801
G	-1165.052994	-40.509639	-1205.555783	-1205.540767	-1205.558355	4.2984435	9.42269016	-1.6139557199
<b>Rh3V</b>	<b>Cluster</b>	<b>CH4</b>	<b>P.R.C</b>	<b>TS</b>	<b>Po.R.C</b>	<b>Eb</b>	<b>Ea</b>	<b>Eh</b>
E	-1275.605025	-40.492323	-1316.104934	-1316.093263	-1316.10837	-4.76029086	7.32366921	-2.15612436
U	-1275.599015	-40.489456	-1316.094906	-1316.084247	-1316.099245	-4.03802685	6.68862909	-2.72276589
H	-1275.598071	-40.488512	-1316.093961	-1316.083303	-1316.098301	-4.6297687802	6.6880015801	-2.7233934
G	-1275.639545	-40.509639	-1316.145625	-1316.131823	-1316.146733	2.23330809	8.6608930201	-0.69528108
<b>Rh4V</b>	<b>Cluster</b>	<b>CH4</b>	<b>P.R.C</b>	<b>TS</b>	<b>Po.R.C</b>	<b>Eb</b>	<b>Ea</b>	<b>Eh</b>
E	-1386.164718	-40.492323	-1426.660291	-1426.656773	-1426.671475	-2.0394075	2.20758018	-7.0180718401
U	-1386.156688	-40.489456	-1426.648531	-1426.645713	-1426.660229	-1.49786637	1.7683231801	-7.34061198
H	-1386.155744	-40.488512	-1426.647586	-1426.644769	-1426.659285	-2.0896083001	1.76769567	-7.3412394899
G	-1386.203488	-40.509639	-1426.702897	-1426.698294	-1426.713931	6.4194273002	2.8884285299	-6.9239453401
<b>Rh5V</b>	<b>Cluster</b>	<b>CH4</b>	<b>P.R.C</b>	<b>TS</b>	<b>Po.R.C</b>	<b>Eb</b>	<b>Ea</b>	<b>Eh</b>
E	-1496.734883	-40.492323	-1537.237416	-1537.227318	-1537.239759	-6.4068770999	6.33659598	-1.4702559301
U	-1496.72493	-40.489456	-1537.223761	-1537.214485	-1537.226723	-5.8829062499	5.82078276	-1.85868462
H	-1496.723986	-40.488512	-1537.222817	-1537.21354	-1537.225779	-6.4752756901	5.8214102701	-1.85868462
G	-1496.777112	-40.509639	-1537.284605	-1537.272322	-1537.285678	1.34663646	7.70770533	-0.6733182299
<b>Rh6V</b>	<b>Cluster</b>	<b>CH4</b>	<b>P.R.C</b>	<b>TS</b>	<b>Po.R.C</b>	<b>Eb</b>	<b>Ea</b>	<b>Eh</b>
E	-1607.323089	-40.492323	-1647.823892	-1647.81038	-1647.81945	-5.3212848	8.47891512	2.78739942
U	-1607.311407	-40.489456	-1647.808516	-1647.79546	-1647.804557	-4.8023340301	8.19277056	2.4843120901
H	-1607.310463	-40.488512	-1647.807572	-1647.794516	-1647.803613	-5.39470347	8.19277056	2.4843120899
G	-1607.367257	-40.509639	-1647.872772	-1647.858321	-1647.867679	2.5878512402	9.06814701	3.19590843
<b>Rh7V</b>	<b>Cluster</b>	<b>CH4</b>	<b>P.R.C</b>	<b>TS</b>	<b>Po.R.C</b>	<b>Eb</b>	<b>Ea</b>	<b>Eh</b>
E	-1717.911111	-40.492323	-1758.41059	-1758.393561	-1758.403586	-4.4904615601	10.6858677899	4.39508004
U	-1717.897523	-40.489456	-1758.39308	-1758.376505	-1758.386722	-3.82843851	10.4009782501	3.9897085801
H	-1717.896579	-40.488512	-1758.392136	-1758.375561	-1758.385778	-4.42080795	10.4009782499	3.9897085799
G	-1717.958	-40.509639	-1758.462839	-1758.445493	-1758.454704	3.0120480001	10.8847884601	5.10479385
<b>Rh8V</b>	<b>Cluster</b>	<b>CH4</b>	<b>P.R.C</b>	<b>TS</b>	<b>Po.R.C</b>	<b>Eb</b>	<b>Ea</b>	<b>Eh</b>

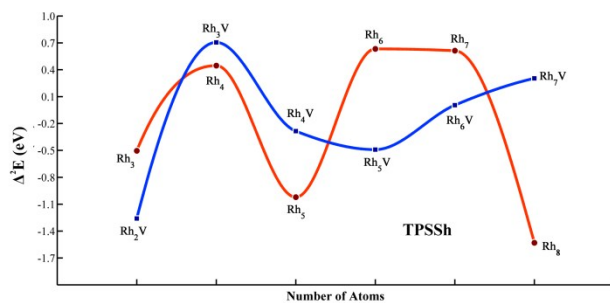
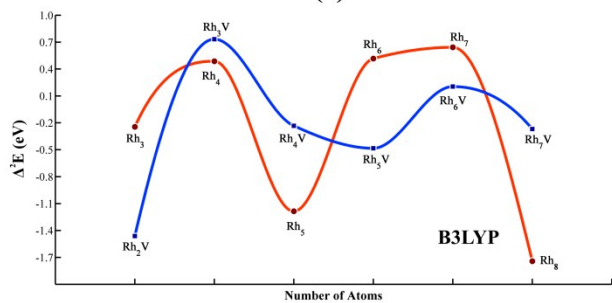
E	-1828.487953	-40.492323	-1868.984085	-1868.964142	-1868.977635	-2.39018559	12.51443193	4.0474395001
U	-1828.472122	-40.489456	-1868.96429	-1868.944993	-1868.958887	-1.70180712	12.1090604699	3.3904365299
H	-1828.471178	-40.488512	-1868.963346	-1868.944049	-1868.957943	-2.2941765601	12.10906047	3.3904365301
G	-1828.539035	-40.509639	-1869.040503	-1869.0195	-1869.031437	5.1273842101	13.1795925299	5.6890056599

## 12. Combined Plots of Properties with B3LYP and TPSSh functional

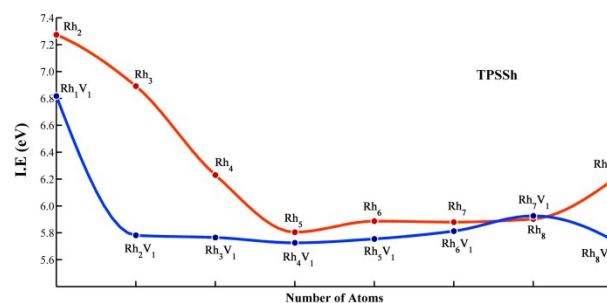
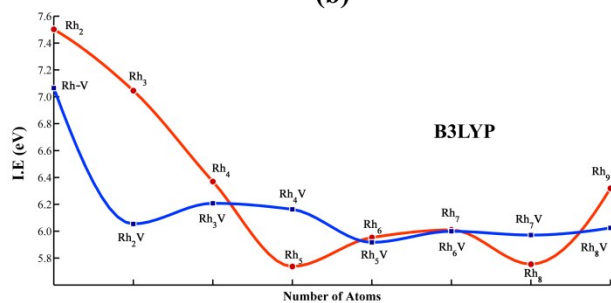




(a)



(b)

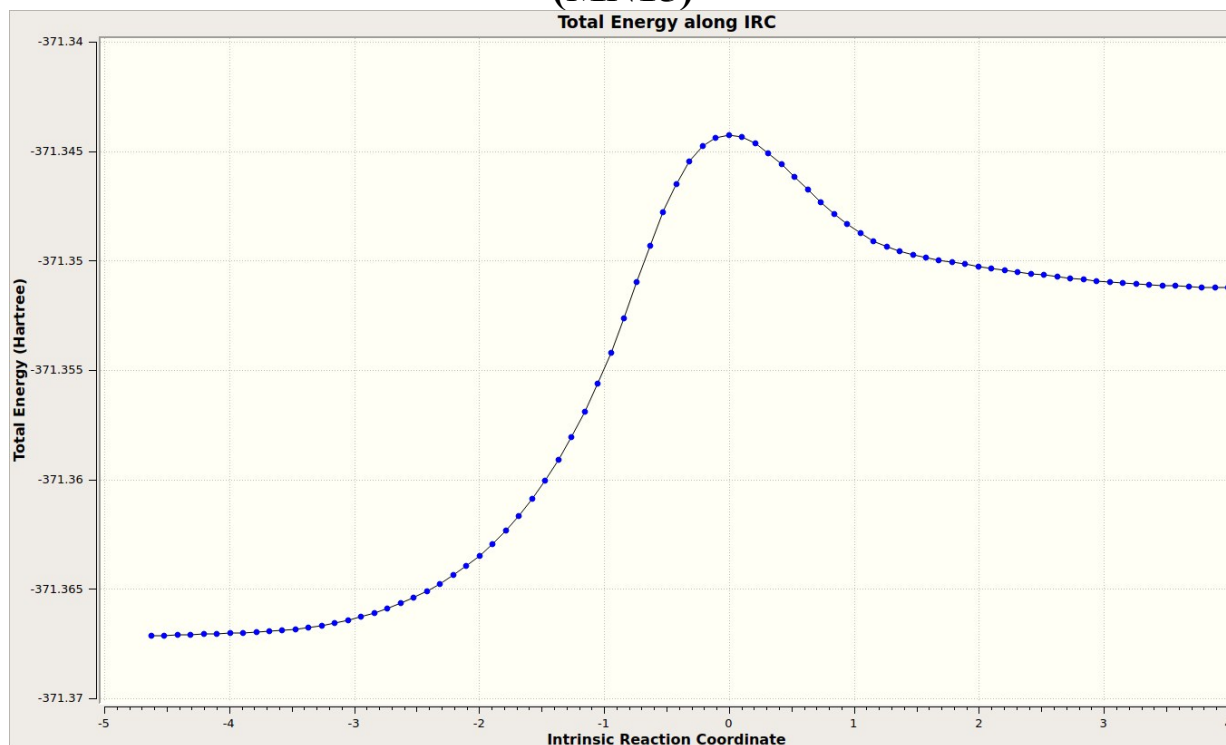


(c)

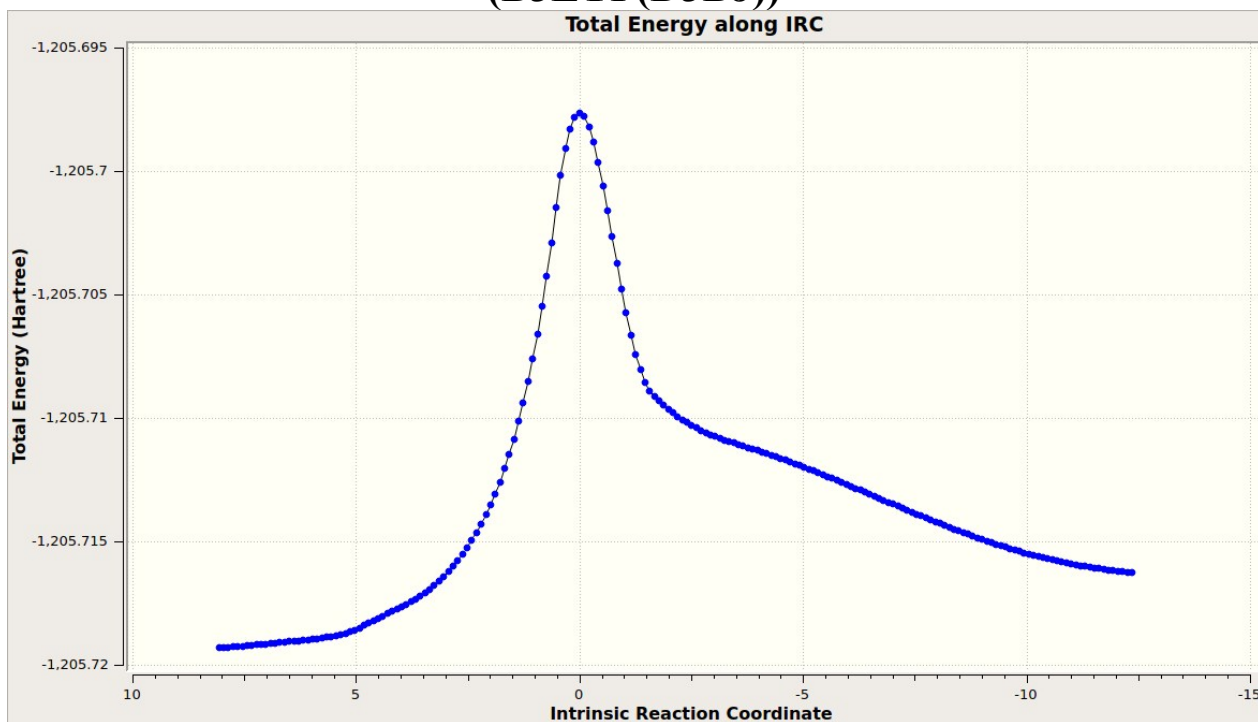
(Shape preserving interpolant was used for better visualization)

### 13. Sample IRC Plots

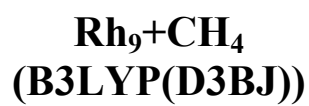
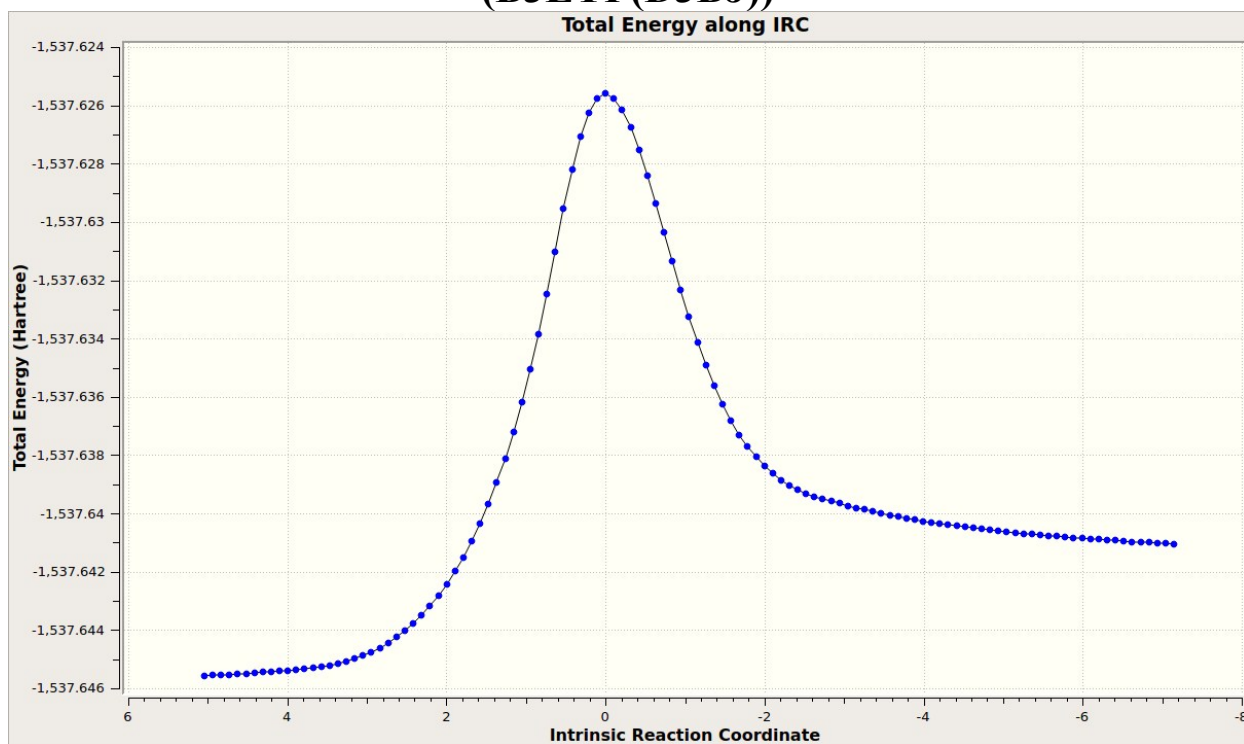
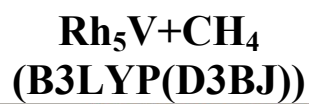
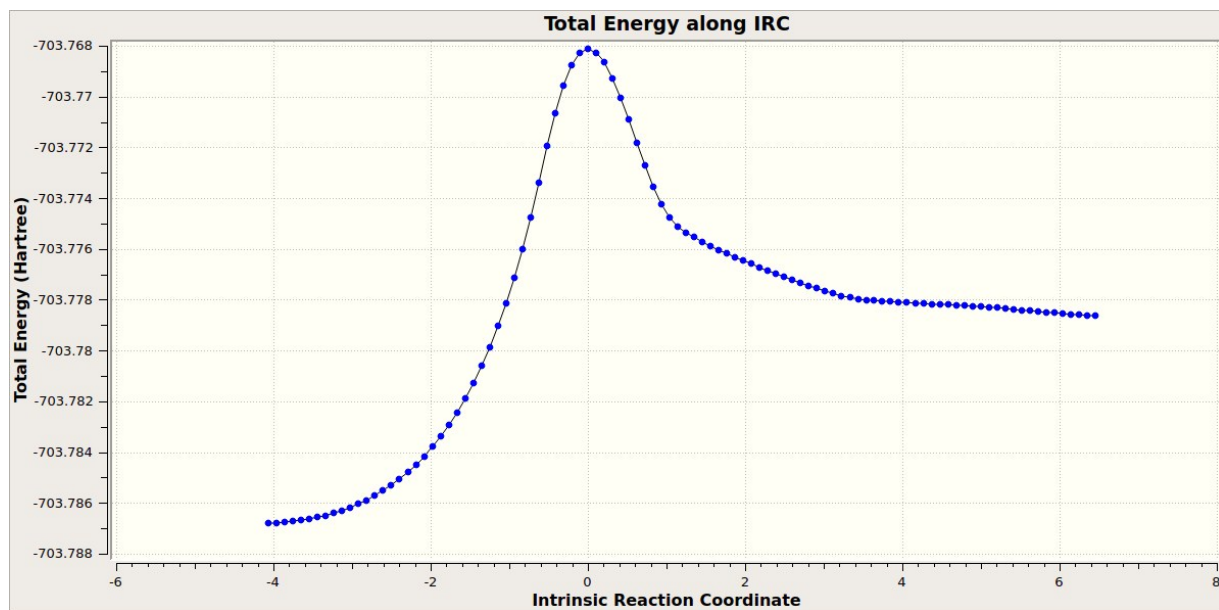
**Rh<sub>3</sub>+CH<sub>4</sub>**  
**(MN15)**

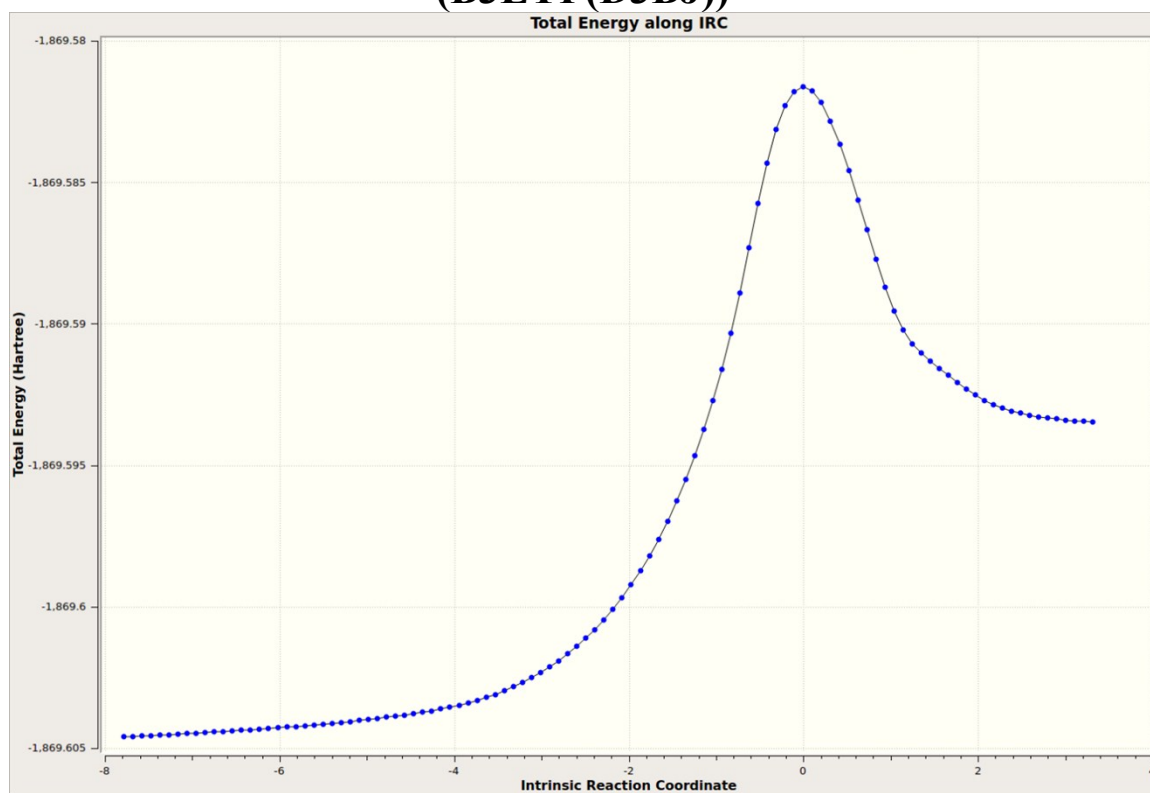
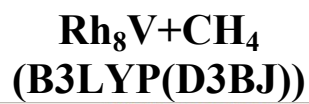
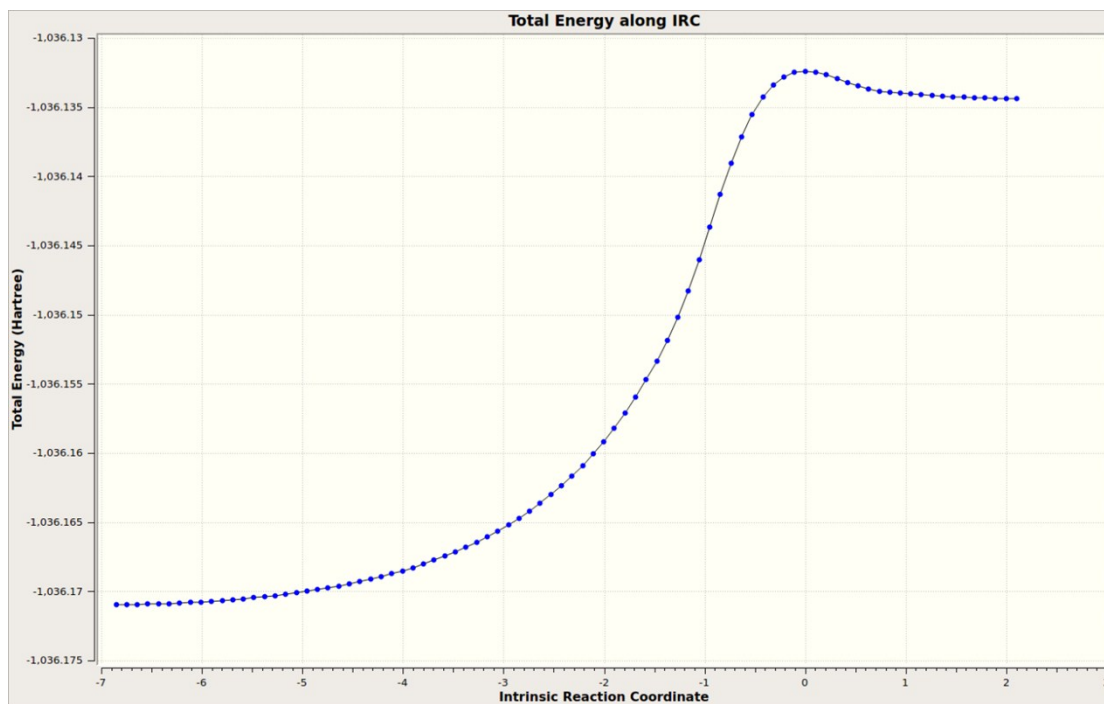


**Rh<sub>2</sub>V+CH<sub>4</sub>**  
**(B3LYP(D3BJ))**

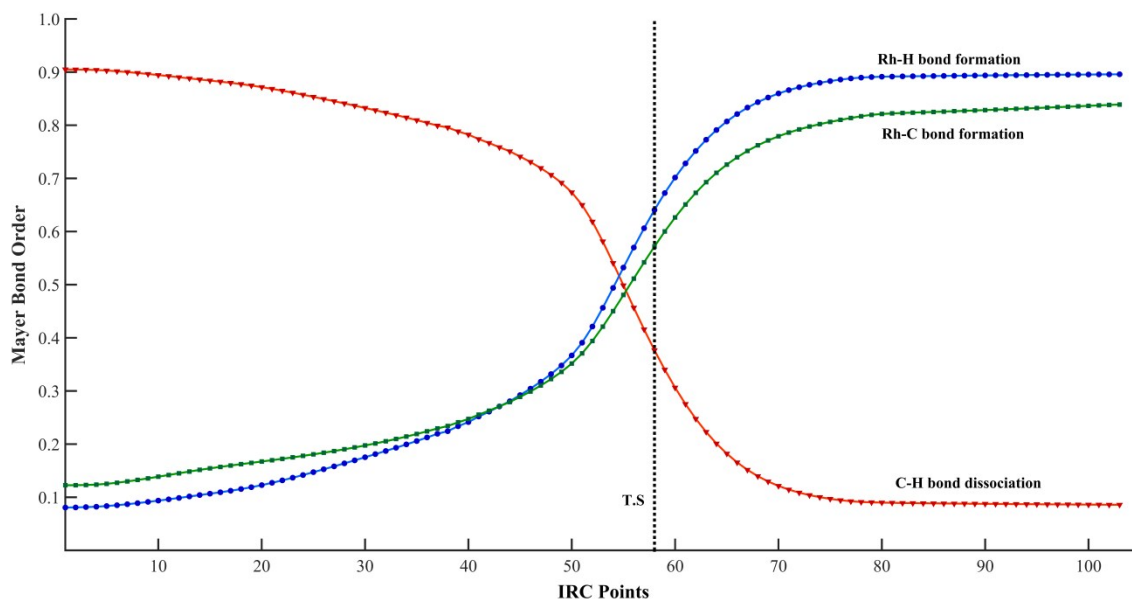


**Rh<sub>6</sub>+CH<sub>4</sub>**  
**(TPSSh)**





**14. Variation of Mayer Bond Order along the IRC of the Reaction Rh<sub>3</sub>V+CH<sub>4</sub>**



## 15. Bond Order Analysis

### a. Minimum spin $Rh_2$ and $RhV$ cluster

Cluster	Mayer Bond Order	WBO	WBON
$Rh_2$	2.981733	3.41253	3.0159
$RhV$	3.53960	4.12256	3.4071

### b. Ground State clusters

Cluster	Mayer Bond Order	WBO
$Rh_2$	1.25668	1.7538
$Rh_5$	0.674-0.106	0.852-0.308
$Rh_9$	0.618-0.05	0.73-0.104

Cluster	Mayer Bond Order		WBO	
	Rh-Rh	Rh-V	Rh-Rh	Rh-V
$RhV$		3.4086		3.9657
$Rh_4V$	0.51-0.25	1.49-0.80	0.79-0.36	1.84-1.03
$Rh_8V$	0.78-0.08	0.69-0.09	0.83-0.09	2.04-0.39

## 16. Energies of Selected Isomers of $Al_7V$ Cluster at Different Spin Multiplicities

## Isomer No:1

M=2S+1	Energy(Electronic+Thermal)
1	-1718.345984
3	-1718.355796
5	-1718.353193
7	-1718.365595
9	-1718.372178
11	-1718.357580
13	-1718.357285
15	-1718.337779
17	-1718.333348
19	-1718.287433

## Isomer No: 2

M=2S+1	Energy(Electronic+Thermal)
1	-1718.333732
3	-1718.362405
5	-1718.363776
7	-1718.375797 (N.D)
9	-1718.376522 (G.M)
11	-1718.368273
13	-1718.370150
15	-1718.358270
17	Not Converged
19	Not Converged

## Isomer No: 3

M=2S+1	Energy(Electronic+Thermal)
1	-1718.340156
3	-1718.352063
5	-1718.355950
7	-1718.355760
9	-1718.350127
11	-1718.361623
13	-1718.330580
15	-1718.358269
17	-1718.326444
19	-1718.286013

G.M=Global Minima

N.D= Near Degenerate structure to G.M

## 17. Energies of A, T.S., and B at Different Spin Multiplicities for Selected

# Pristine and V-Doped Rhodium Clusters [B3LYP(D3BJ)/def2-TZVP]

(Spin Multiplicities ( $M=2S+1$ ) of the clusters are included within parenthesis)

## Pristine Clusters

### **Rh<sub>4</sub> (M=7)**

<b>Energies (E+ZPE) in a.u</b>			
<b>M=2S+1</b>	<b>PRC (A)</b>	<b>TS</b>	<b>PoRC (B)</b>
1	-482.883117	-482.863057	-482.868662
3	-482.879639	-482.866102	-482.882572
5	-482.882132	-482.868671	-482.874883
<b>7</b>	<b>-482.89351</b>	<b>-482.874617</b>	<b>-482.886817</b>
9	-482.870105	-482.846787	-482.861203
11	-482.827564	-482.793927	-482.816461
<b>Relative Energy (kcal/mol)</b>			
1	6.52171143	7.2540156	11.39244405
3	8.70419121	5.34324765	2.66377995
5	7.13980878	3.73117446	7.48870434
<b>7</b>	<b>0</b>	<b>0</b>	<b>0</b>
9	14.68687155	17.4636033	16.07304114
11	41.38177446	50.6337819	44.14909356

### **Rh<sub>5</sub> (M=8)**

<b>Energies (E+ZPE) in a.u</b>			
<b>M=2S+1</b>	<b>PRC (A)</b>	<b>TS</b>	<b>PoRC (B)</b>
2	-593.50083	-593.490222	-593.502617
4	-593.50796	-593.494807	-593.511361
6	-593.513765	-593.501848	-593.52126
<b>8</b>	<b>-593.525803</b>	<b>-593.511114</b>	<b>-593.524685</b>
10	-593.512507	-593.485302	-593.511938
12	-593.485903	-593.444327	-593.484677

14	-593.442804	-593.38355	-593.411394
<b>Relative Energy (kcal/mol)</b>			
2	15.67080723	13.10993892	13.84789068
4	11.19666093	10.23280557	8.36094324
6	7.55396538	5.81450766	2.14922175
<b>8</b>	<b>0</b>	<b>0</b>	<b>0</b>
10	8.34337296	16.19728812	7.99886997
12	25.037649	41.90951037	25.10542008
14	52.08270249	80.04768564	71.09123541

## V-Doped Clusters

### **Rh<sub>3</sub>V (M=1)**

	<b>Energies (E+ZPE) in a.u</b>		
<b>M=2S+1</b>	<b>PRC (A)</b>	<b>TS</b>	<b>PoRC (B)</b>
<b>1</b>	<b>-1316.323959</b>	<b>-1316.308998</b>	<b>-1316.325234</b>
3	-1316.313883	-1316.299693	-1316.312164
5	-1316.302224	-1316.287796	-1316.294017
7	-1316.294254	-1316.282827	-1316.295411
9	-1316.268407	-1316.254517	-1316.288966
<b>Relative Energy (kcal/mol)</b>			
<b>1</b>	<b>0</b>	<b>0</b>	<b>0</b>
3	6.32279076	5.83898055	8.2015557
5	13.63892985	13.30446702	19.58897967
7	18.64018455	16.42256421	18.71423073
9	34.85943552	34.18737231	22.75853268

### **Rh<sub>4</sub>V (M=2)**



	<b>Energies (E+ZPE) in a.u</b>		
<b>M=2S+1</b>	<b>PRC (A)</b>	<b>TS</b>	<b>PoRC (B)</b>
<b>2</b>	<b>-1426.950054</b>	<b>-1426.939354</b>	<b>-1426.958034</b>
4	-1426.936728	-1426.936399	-1426.952155
6	-1426.93853	-1426.924659	-1426.945822
8	-1426.923831	-1426.917786	-1426.93622
10	-1426.912912	-1426.894425	-1426.931592
	<b>Relative Energy (kcal/mol)</b>		
<b>2</b>	<b>0</b>	<b>0</b>	<b>0</b>
4	8.36219826	1.85429205	3.68913129
6	7.23142524	9.22125945	7.66315212
8	16.45519473	13.53413568	13.68850314
10	23.30697642	28.19339679	16.59261942

### **Rh<sub>6</sub>V (M=8)**

	<b>Energies (E+ZPE) in a.u</b>		
<b>M=2S+1</b>	<b>PRC (A)</b>	<b>TS</b>	<b>PoRC (B)</b>
2	-1648.232437	-1648.216209	-1648.226538
4	-1648.234095	-1648.208335	-1648.230198
6	-1648.241961	-1648.226553	-1648.239531
<b>8</b>	<b>-1648.249083</b>	<b>-1648.232214</b>	<b>-1648.241542</b>
10	-1648.237173	-1648.219892	-1648.2359
12	-1648.221572	-1648.202381	-1648.223282
	<b>Relative Energy (kcal/mol)</b>		
2	10.44553146	10.04329755	9.41516004
4	9.40511988	14.98431129	7.11847344
6	4.46912622	3.55233411	1.26192261
<b>8</b>	<b>0</b>	<b>0</b>	<b>0</b>
10	7.4736441	7.73217822	3.54041142
12	17.26342761	18.72050583	11.4583326

## 18. Table of the Spin Contamination Values for Selected Complexes

Cluster	Spin Multiplicity	Number of unpaired electrons	$s(s+1)^\dagger$	Reported Values of $\langle S^2 \rangle$ from Gaussian16 Output (B3LYP-D3(BJ)/def2-TZVP)		
				A	T.S	B
Rh <sub>2</sub> V	4	3	3.75	3.7554	3.7559	3.7620
Rh <sub>6</sub> V	8	7	15.75	15.7551	15.7534	15.7533
Rh <sub>7</sub> V	9	8	20	20.0266	20.0283	20.0093
Rh <sub>8</sub> V	12	11	35.75	35.7598	35.7558	35.7570
Rh <sub>7</sub>	14	13	48.75	48.7526	48.7520	48.7515
Rh <sub>8</sub>	13	12	42	42.0071	42.0047	42.0048
Rh <sub>9</sub>	18	17	80.75	80.7521	80.7520	80.7521

<sup>†</sup>s equals 1/2 times the number of unpaired electrons.