Supporting Information

Gas-phase reactions of the bare Th^{2+} and U^{2+} ions with small alkanes, CH_4, C_2H_6 and C_3H_8: An experimental and theoretical study of elementary organoactinide chemistry.

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Scheme 1 : Lewis resonance structures for $UC_2H_2^{2+}$.

Complete citation for reference 69.

Gaussian 03, Revision C.02, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, Jr., J. A.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.;

Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; and Pople, J. A.; Gaussian, Inc., Wallingford CT, 2004.

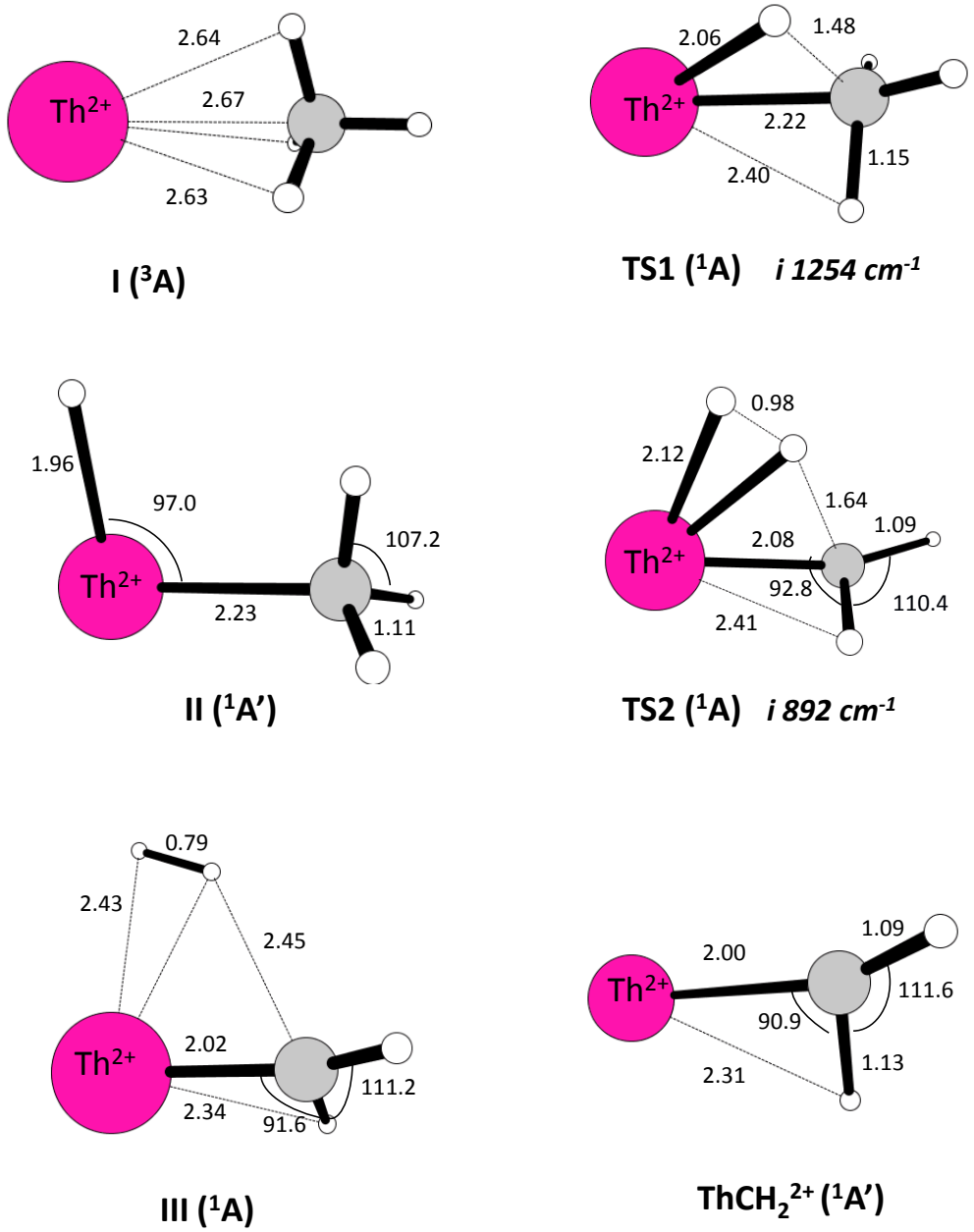

Th2+
2.64
2.67
2.63
I (3A)
Th2+
2.06
1.48
2.22
1.15
2.40
TS1 (1A) i 1254 cm-1
1.96
97.0
107.2
Th2+
2.23
1.11
II (1A')
0.98
2.12
1.64
1.09
Th2+
2.08
92.8
110.4
2.41
TS2 (1A) i 892 cm-1
0.79
2.43
2.45
Th2+
2.02
111.2
2.34
91.6
III (1A)
1.09
2.00
Th2+
111.6
90.9
1.13
2.31
ThCH2 2+ (1A')

Figure S1

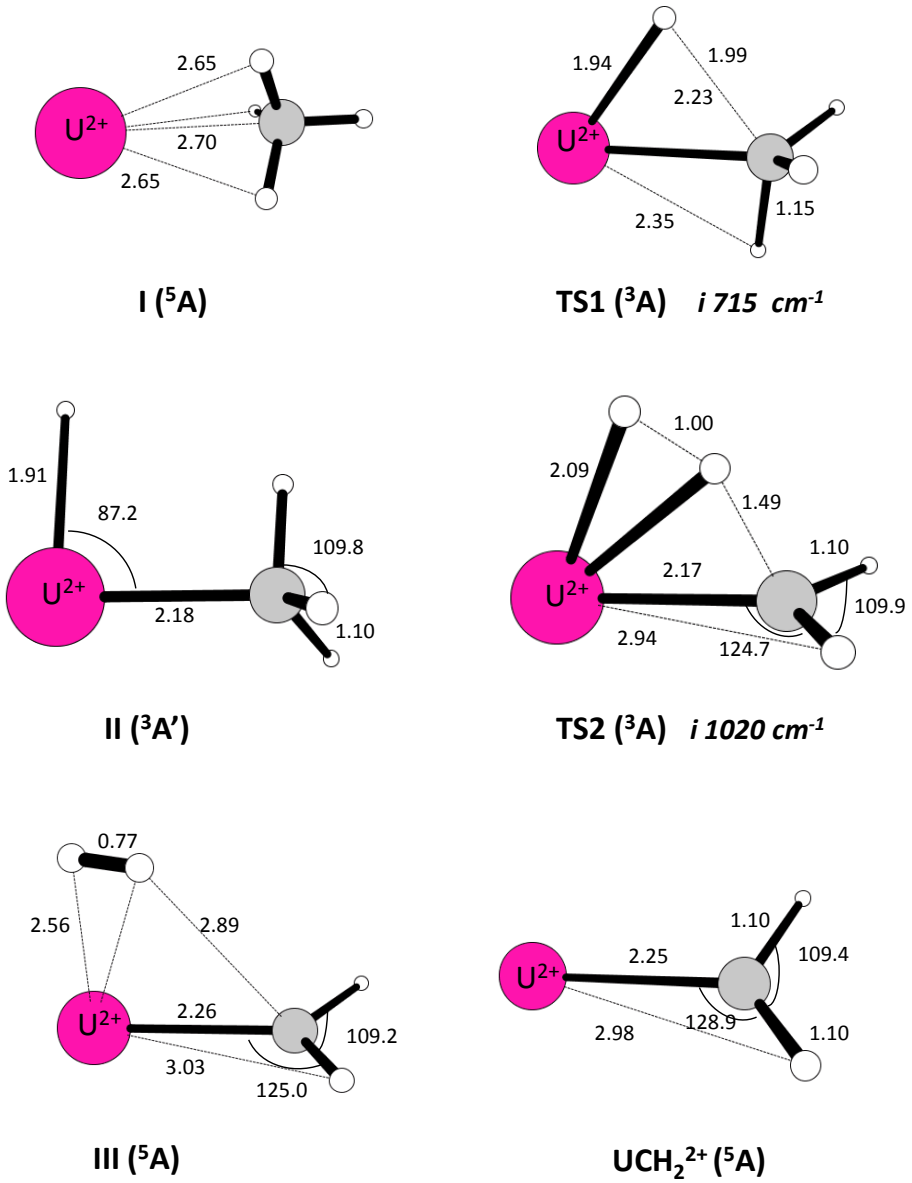

2.65
U2+
2.70
2.65
I (5A)
1.94
1.99
2.23
U2+
2.35
1.15
TS1 (3A) i 715 cm-1
1.91
87.2
109.8
U2+
2.18
1.10
II (3A')
1.00
2.09
1.49
1.10
2.17
U2+
109.9
2.94
124.7
TS2 (3A) i 1020 cm-1
0.77
2.56
2.89
U2+
2.26
109.2
3.03
125.0
III (5A)
1.10
2.25
109.4
U2+
128.9
2.98
1.10
UCH2 2+ (5A)

Figure S2

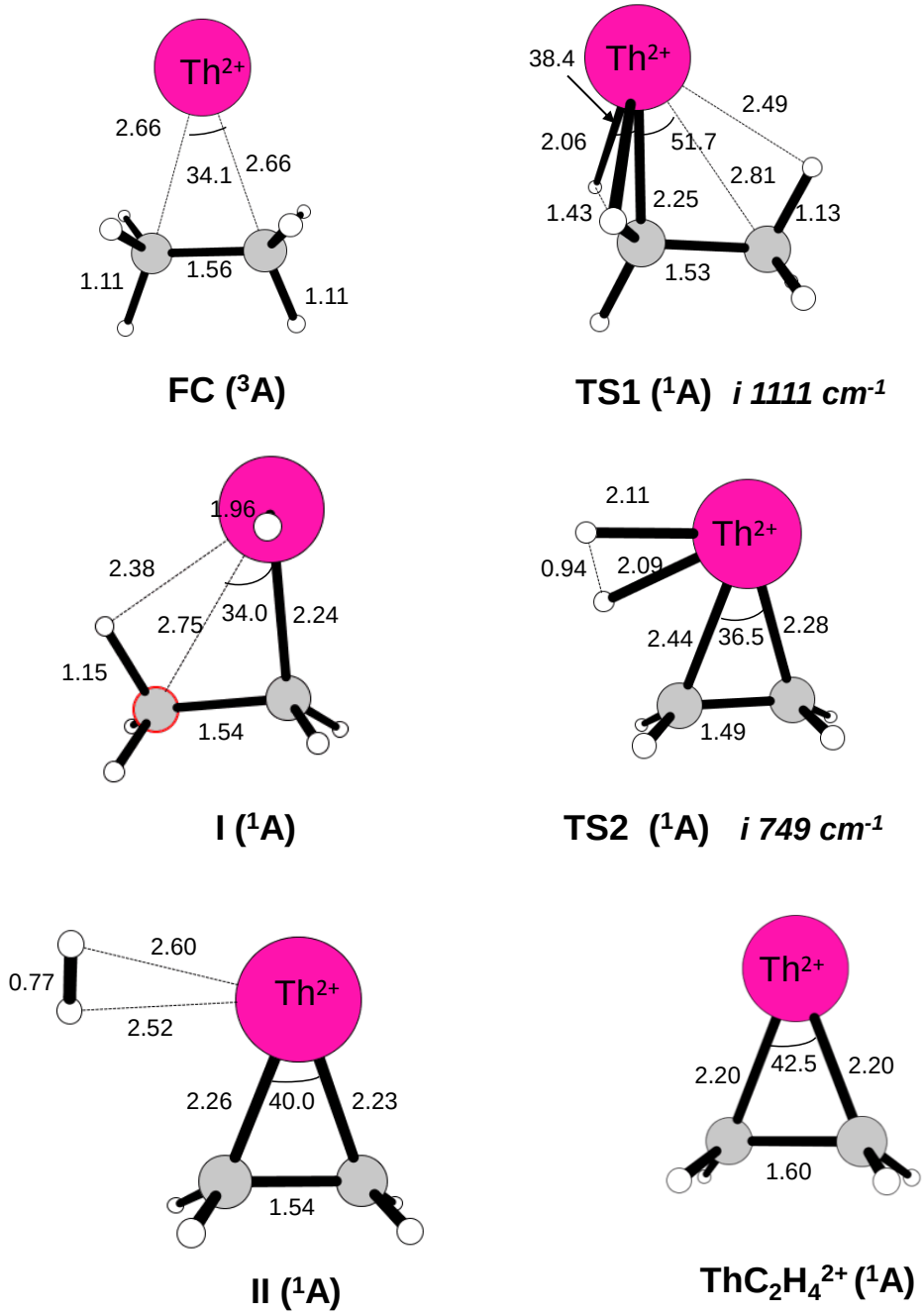

Th2+
2.66
34.1
2.66
1.11
1.56
1.11
FC (3A)
38.4
Th2+
2.49
2.06
51.7
2.81
1.43
2.25
1.13
1.53
TS1 (1A) i 1111 cm-1
1.96
2.38
2.75
34.0
2.24
1.15
1.54
I (1A)
2.11
Th2+
0.94
2.09
2.44
36.5
2.28
1.49
TS2 (1A) i 749 cm-1
2.60
0.77
Th2+
2.52
2.26
40.0
2.23
1.54
II (1A)
Th2+
2.20
42.5
2.20
1.60
ThC2H42+ (1A)

Figure S3

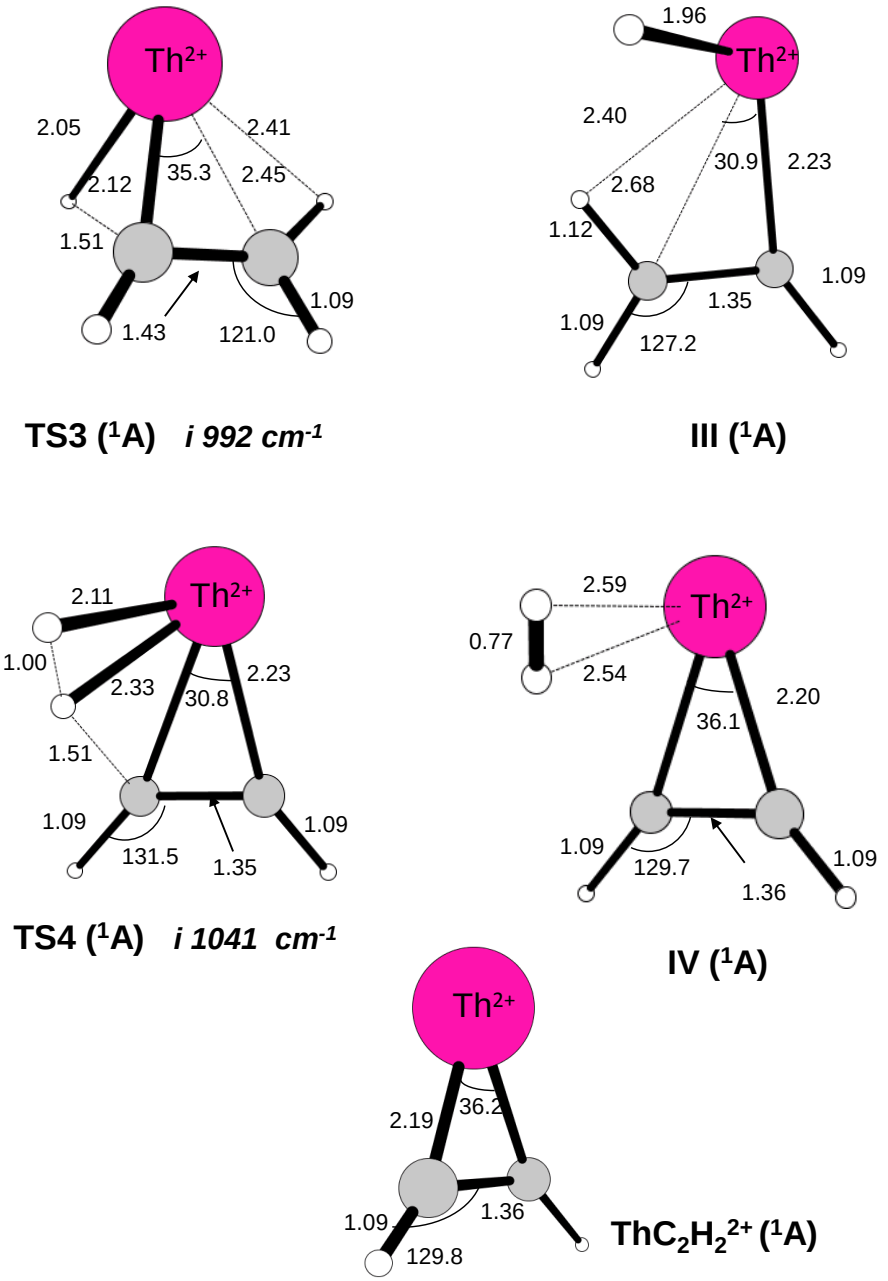

Th2+
2.05
2.41
2.12
35.3
2.45
1.51
1.09
1.43
121.0
TS3 (1A) i 992 cm-1
1.96
Th2+
2.40
30.9
2.23
2.68
1.12
1.09
1.35
1.09
127.2
III (1A)
2.11
Th2+
1.00
2.33
30.8
2.23
1.51
1.09
1.09
131.5
1.35
TS4 (1A) i 1041 cm-1
2.59
Th2+
0.77
2.54
2.20
36.1
1.09
129.7
1.09
1.36
IV (1A)
Th2+
2.19
36.2
1.09
1.36
129.8
ThC2H22+ (1A)

Figure S4

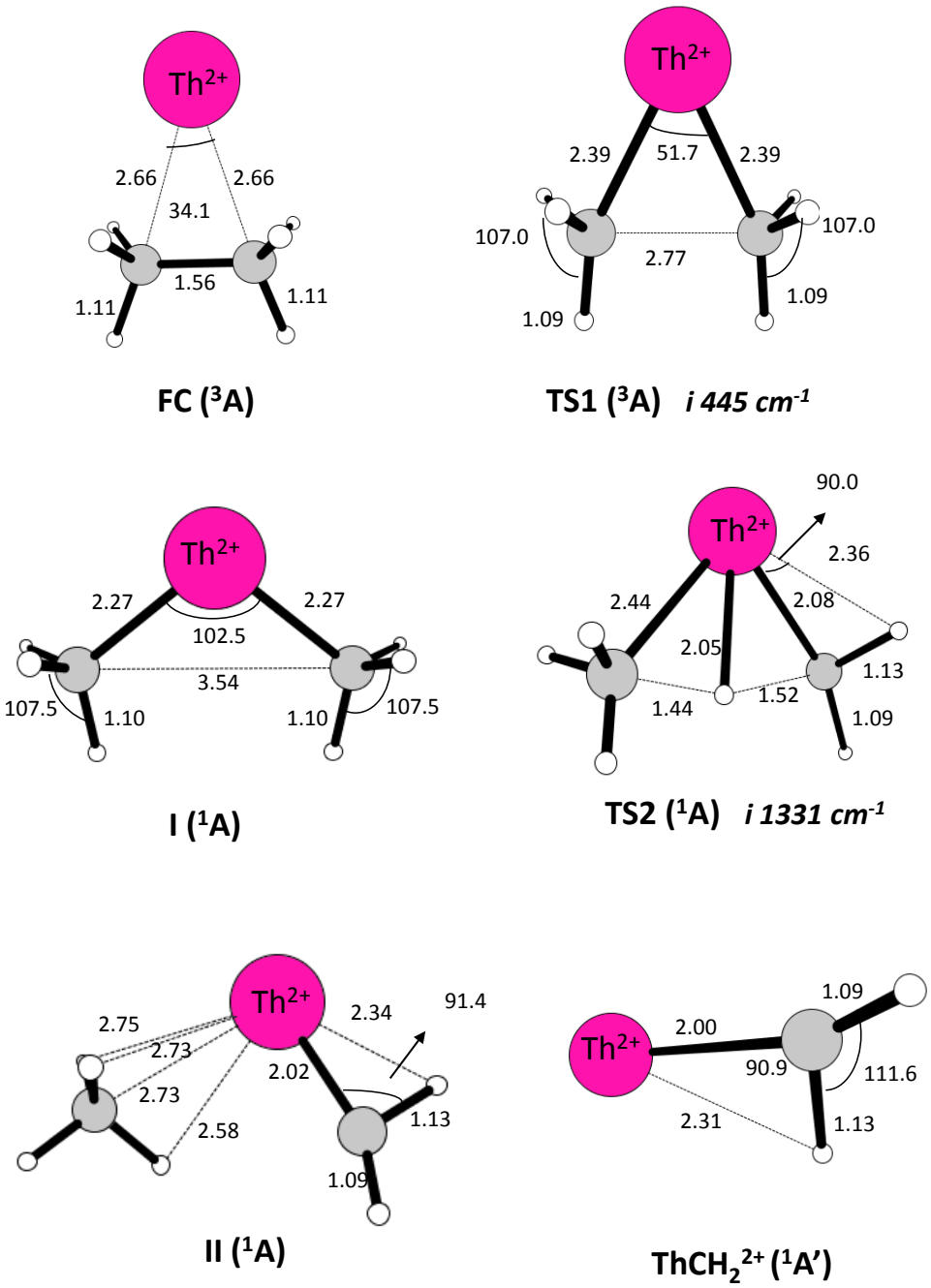

Th2+
2.66
2.66
34.1
1.56
1.11
1.11
FC (3A)
Th2+
2.39
51.7
2.39
107.0
107.0
2.77
1.09
1.09
TS1 (3A) i 445 cm-1
Th2+
2.27
2.27
102.5
3.54
107.5
1.10
1.10
107.5
I (1A)
90.0
Th2+
2.36
2.44
2.08
2.05
1.13
1.44
1.52
1.09
TS2 (1A) i 1331 cm-1
Th2+
2.75
2.73
2.73
2.58
2.02
2.34
91.4
1.13
1.09
II (1A)
1.09
Th2+
2.00
90.9
111.6
2.31
1.13
ThCH2 2+ (1A')

Figure S5

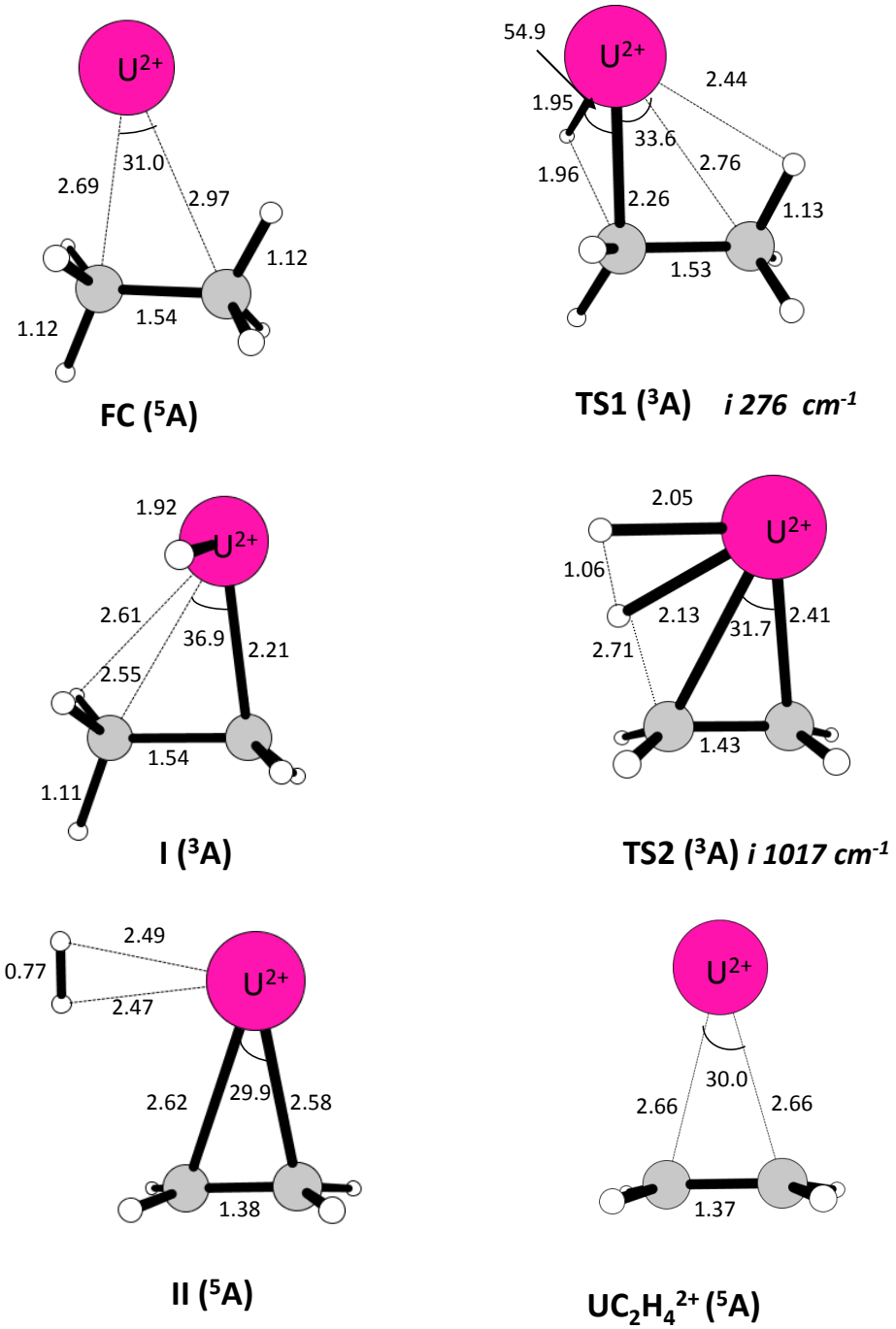
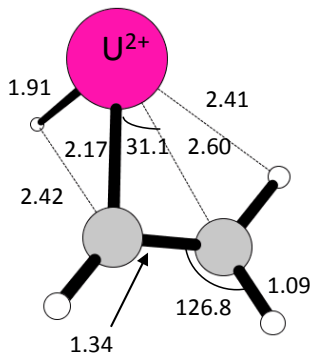
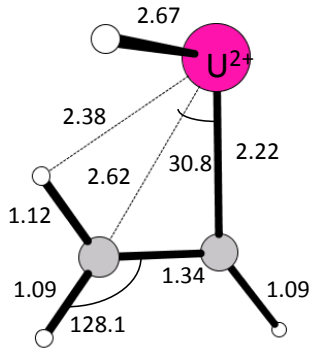

U2+
31.0
2.69
2.97
1.12
1.12
1.54
FC (5A)
54.9
U2+
2.44
1.95
33.6
2.76
1.96
2.26
1.13
1.53
TS1 (3A) i 276 cm-1
1.92
U2+
2.61
36.9
2.21
2.55
1.54
1.11
I (3A)
2.05
U2+
1.06
2.13
31.7
2.41
2.71
1.43
TS2 (3A) i 1017 cm-1
2.49
0.77
U2+
2.47
2.62
29.9
2.58
1.38
II (5A)
U2+
30.0
2.66
2.66
1.37
UC2H42+ (5A)

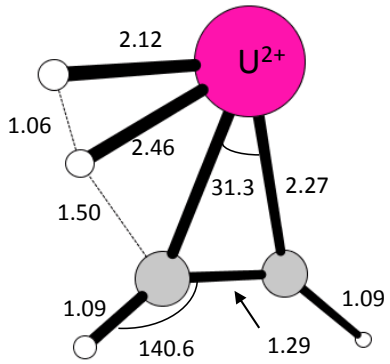
Figure S6



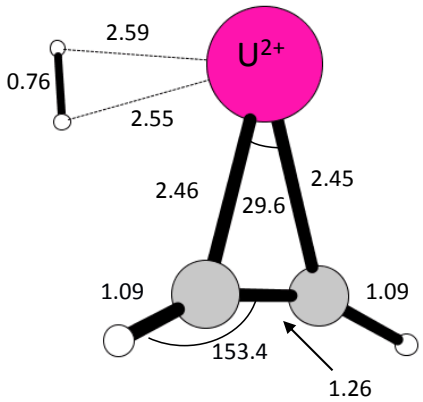
TS3 (^{3}A) *i 240 cm^{-1}*



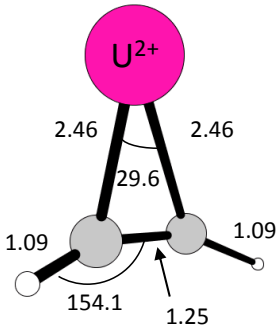
III (^{5}A)



TS4 (^{3}A) *i 947 cm^{-1}*



IV (^{5}A)



$UC_2H_2^{2+}$ (^{5}A)

Figure S7

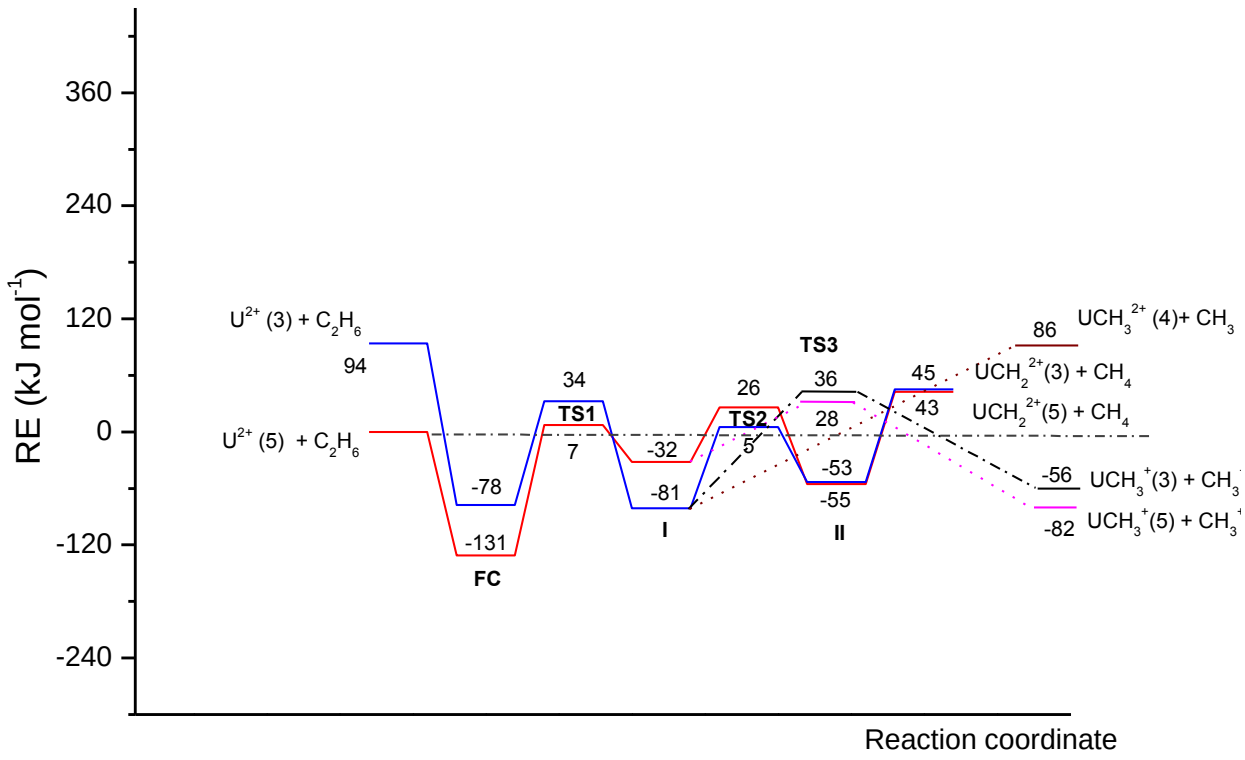
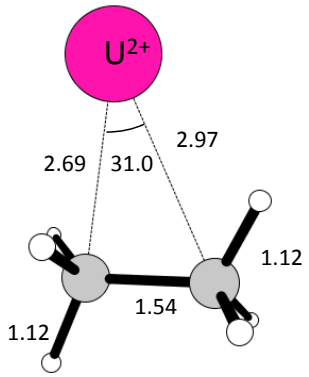
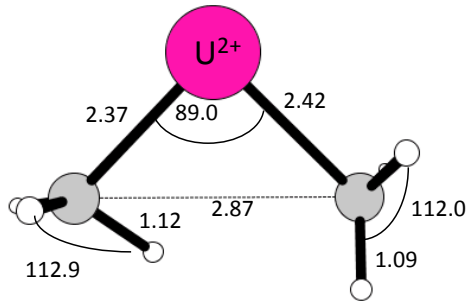

RE (kJ mol-1)
360
240
120
0
-120
-240
U2+ (3) + C2H6
94
U2+ (5) + C2H6
-78
-131
FC
34
TS1
7
-32
-81
I
26
TS2
5
TS3
36
28
-53
-55
II
45
43
86
UCH32+ (4)+ CH3
UCH22+(3) + CH4
UCH22+(5) + CH4
-56
UCH3+(3) + CH3
-82
UCH3+(5) + CH3
Reaction coordinate

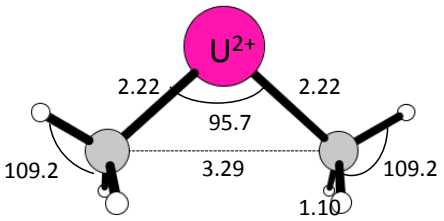
Figure S8



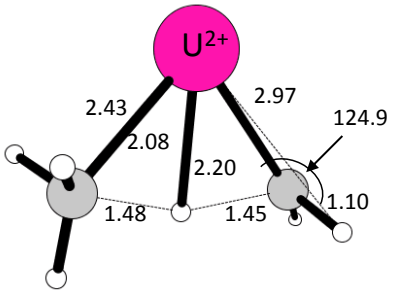
FC (^{5}A)



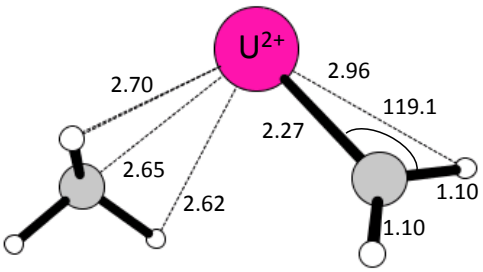
TS1 (^{5}A) ***i 696 cm^{-1}***



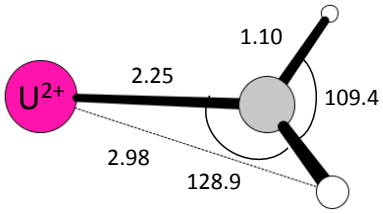
I (^{3}A)



TS2 (^{3}A) ***i 1359 cm^{-1}***



II (^{5}A)



UCH_2^{2+} (^{5}A)

Figure S9

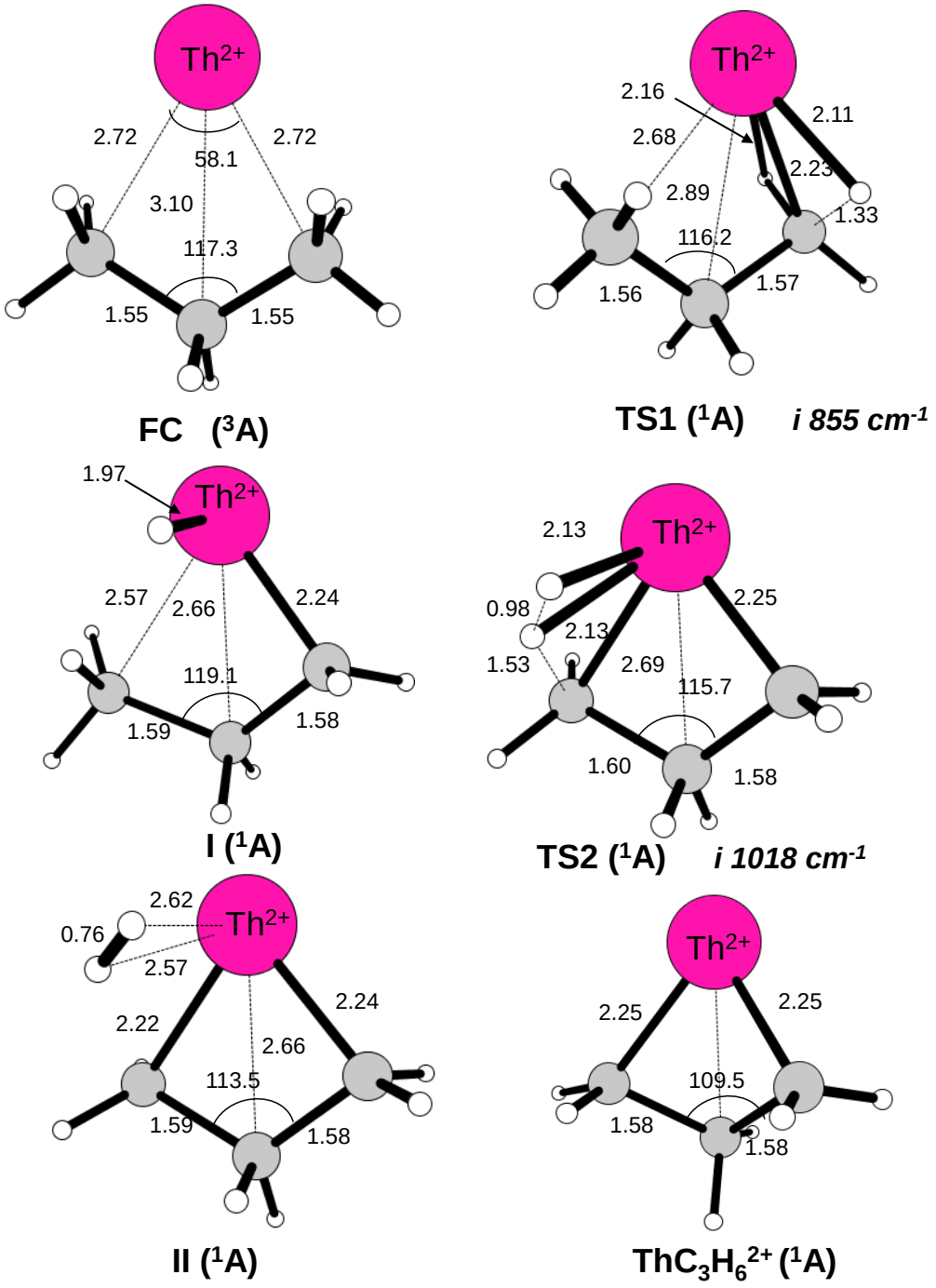
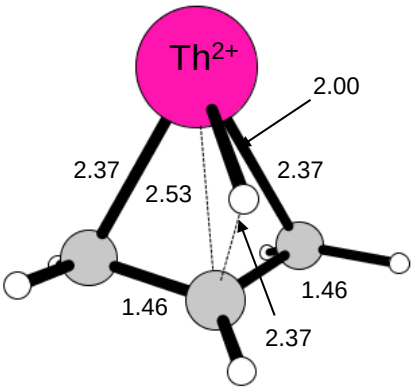
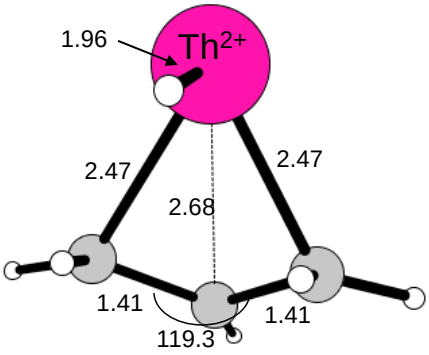

Th2+
2.72
2.72
58.1
3.10
117.3
1.55
1.55
FC (3A)
Th2+
2.16
2.11
2.68
2.23
2.89
1.33
116.2
1.56
1.57
TS1 (1A) i 855 cm-1
1.97
Th2+
2.57
2.66
2.24
119.1
1.59
1.58
I (1A)
2.13
Th2+
0.98
2.25
2.13
1.53
2.69
115.7
1.60
1.58
TS2 (1A) i 1018 cm-1
2.62
0.76
Th2+
2.57
2.24
2.22
2.66
113.5
1.59
1.58
II (1A)
Th2+
2.25
2.25
109.5
1.58
1.58
ThC3H62+ (1A)

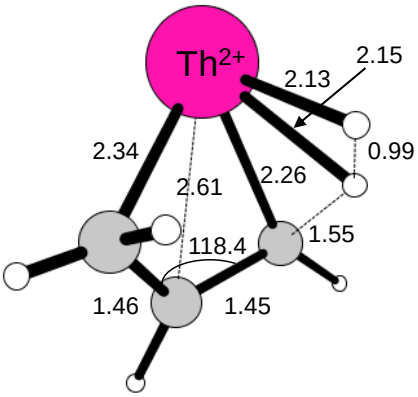
Figure S10 (a)



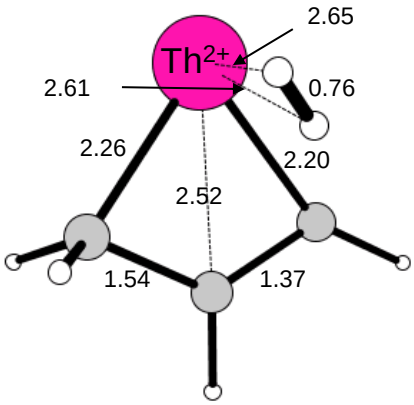
TS3 (^{1}A) ***i 833 cm^{-1}***



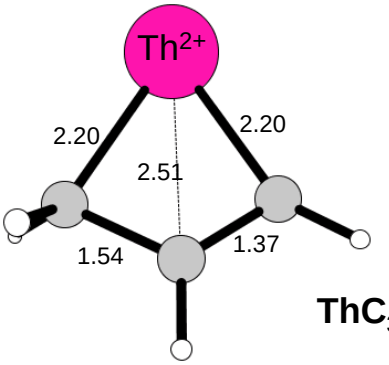
III (^{1}A)



TS4 (^{1}A) ***i 1075 cm^{-1}***



IV (^{1}A)



$ThC_3H_4^{2+}$ (^{1}A)

Figure S10 (b)

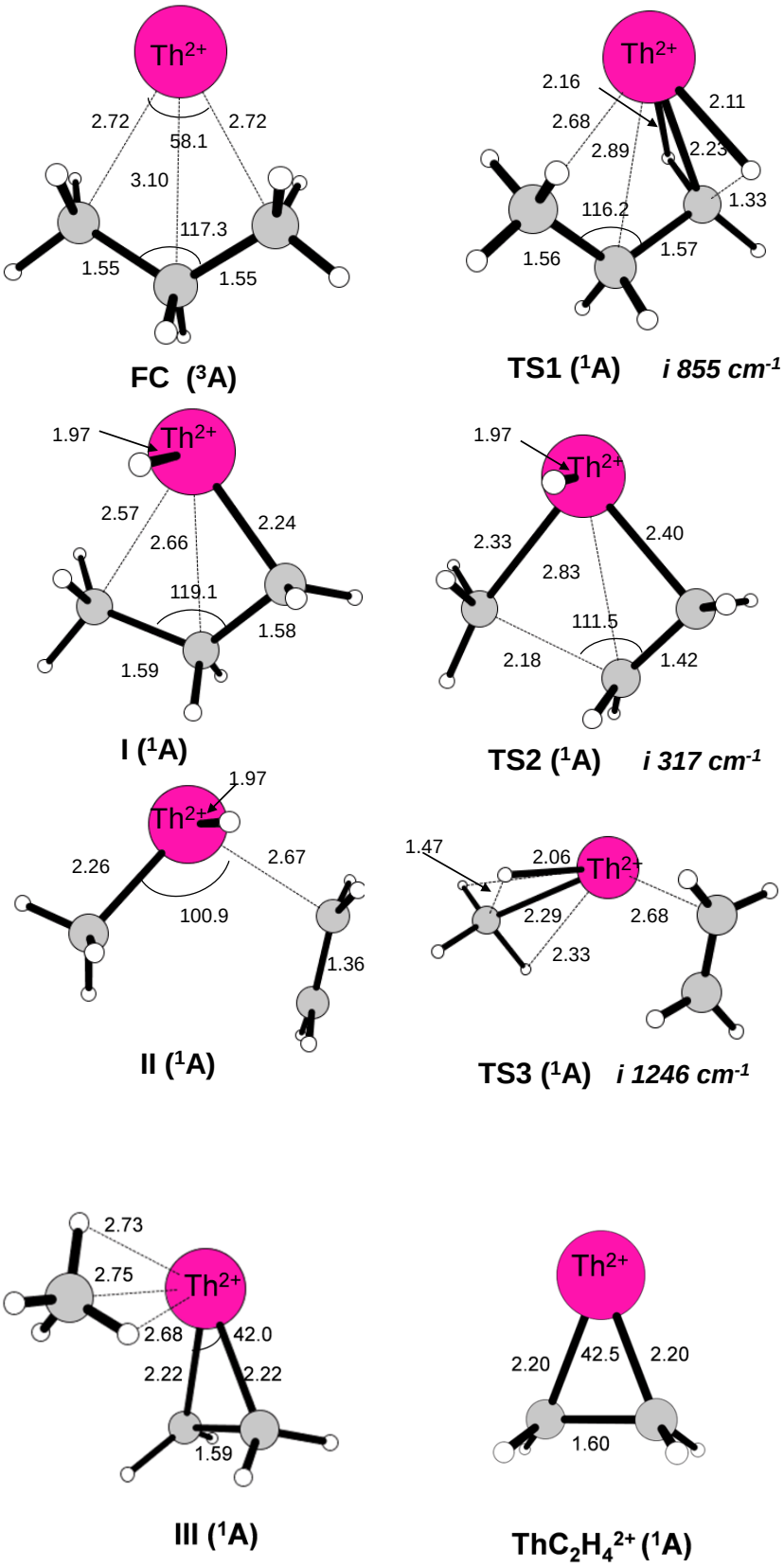
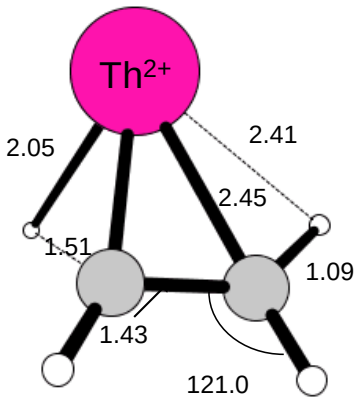
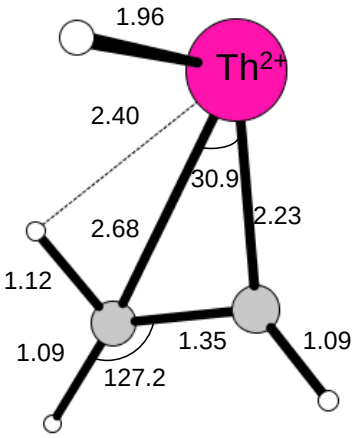

Th2+
2.72
2.72
58.1
3.10
117.3
1.55
1.55
FC (3A)
Th2+
2.16
2.11
2.68
2.89
2.23
1.33
116.2
1.56
1.57
TS1 (1A) i 855 cm-1
1.97
Th2+
2.57
2.24
2.66
119.1
1.58
1.59
I (1A)
1.97
Th2+
2.33
2.40
2.83
111.5
2.18
1.42
TS2 (1A) i 317 cm-1
1.97
Th2+
2.26
2.67
100.9
1.36
II (1A)
1.47
2.06
Th2+
2.29
2.68
2.33
TS3 (1A) i 1246 cm-1
2.73
2.75
Th2+
2.68
42.0
2.22
2.22
1.59
III (1A)
Th2+
2.20
42.5
2.20
1.60
ThC2H42+ (1A)

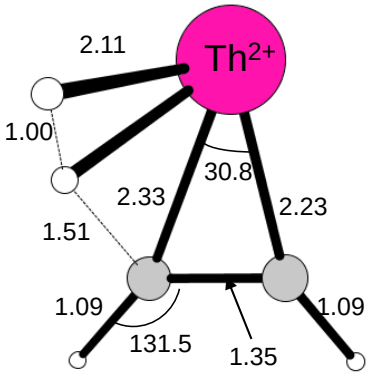
Figure S11 (a)



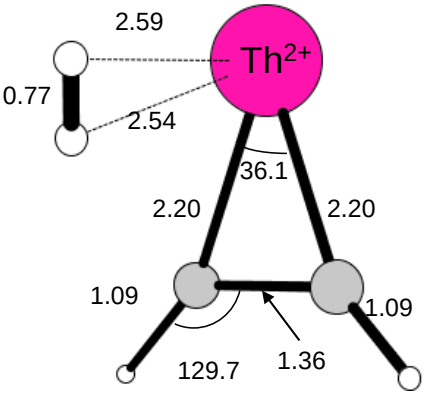
TS4 (^{1}A) ***i 992 cm^{-1}***



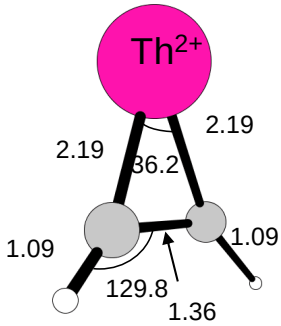
IV (^{1}A)



TS5 (^{1}A) ***i 1041cm^{-1}***



V (^{1}A)



$ThC_2H_2^{2+}$ (^{1}A)

Figure S11 (b)

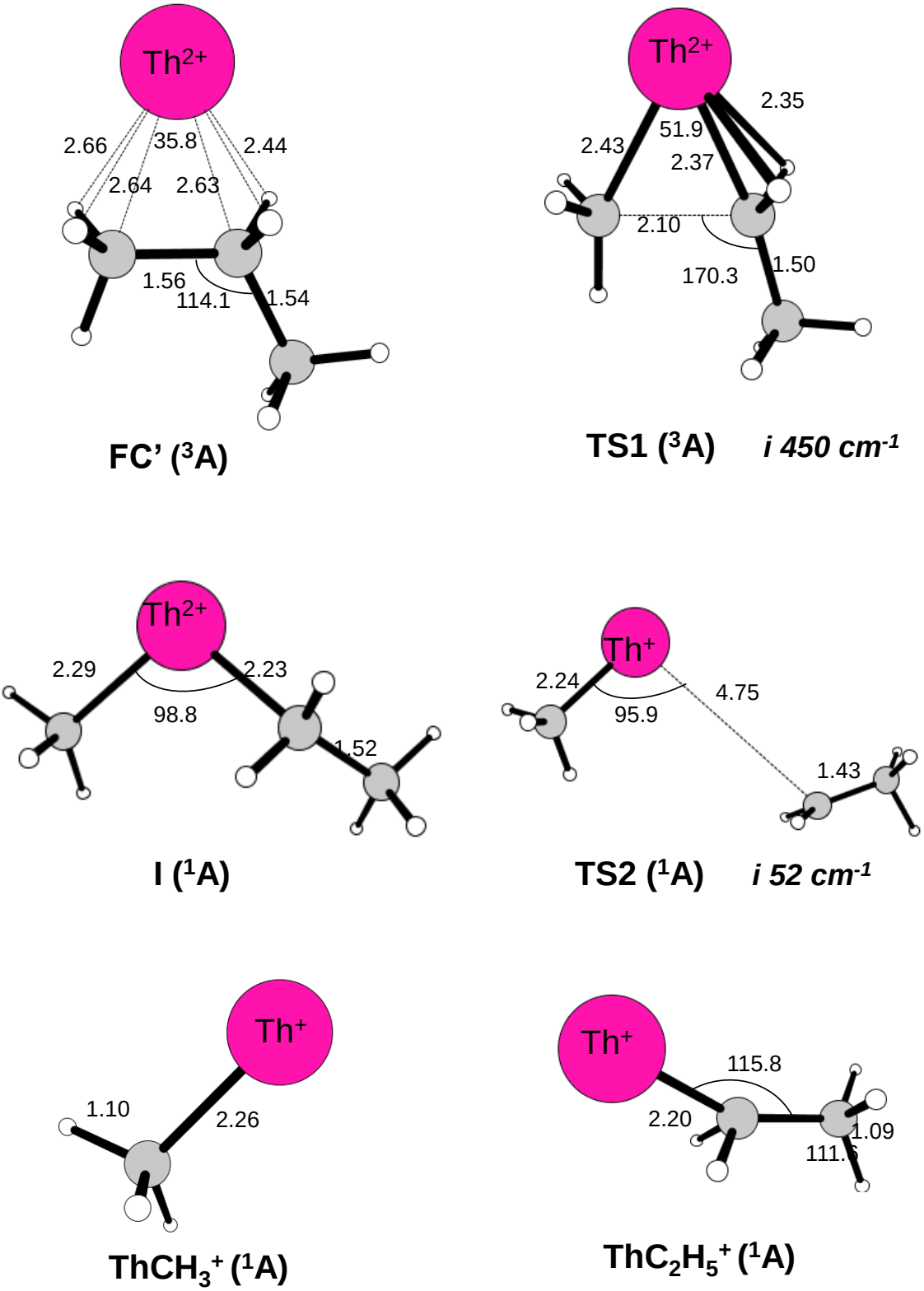

Th2+
2.66
35.8
2.44
2.64
2.63
1.56
114.1
1.54
FC' (3A)
Th2+
2.35
51.9
2.43
2.37
2.10
170.3
1.50
TS1 (3A) i 450 cm-1
Th2+
2.29
2.23
98.8
1.52
I (1A)
Th+
2.24
4.75
95.9
1.43
TS2 (1A) i 52 cm-1
Th+
1.10
2.26
ThCH3+ (1A)
Th+
115.8
2.20
1.09
ThC2H5+ (1A)

Figure S12

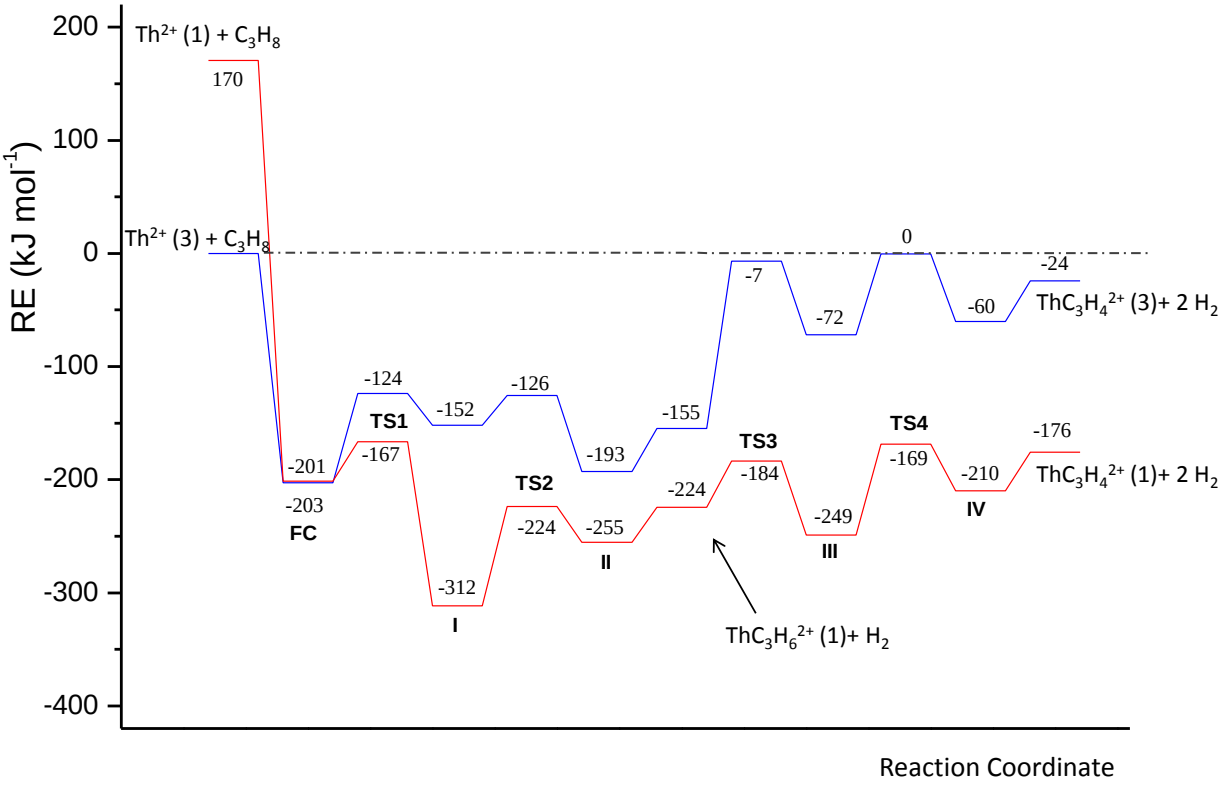

200
100
0
-100
-200
-300
-400
RE (kJ mol-1)
Th2+ (1) + C3H8
170
Th2+ (3) + C3H8
-201
-203
FC
-124
TS1
-167
-312
I
-152
-126
TS2
-224
-255
II
-193
-155
-224
TS3
-184
-249
III
-7
-72
0
TS4
-169
-210
IV
-60
-24
-176
ThC3H42+ (3)+ 2 H2
ThC3H42+ (1)+ 2 H2
ThC3H62+ (1)+ H2
Reaction Coordinate

Figure S13

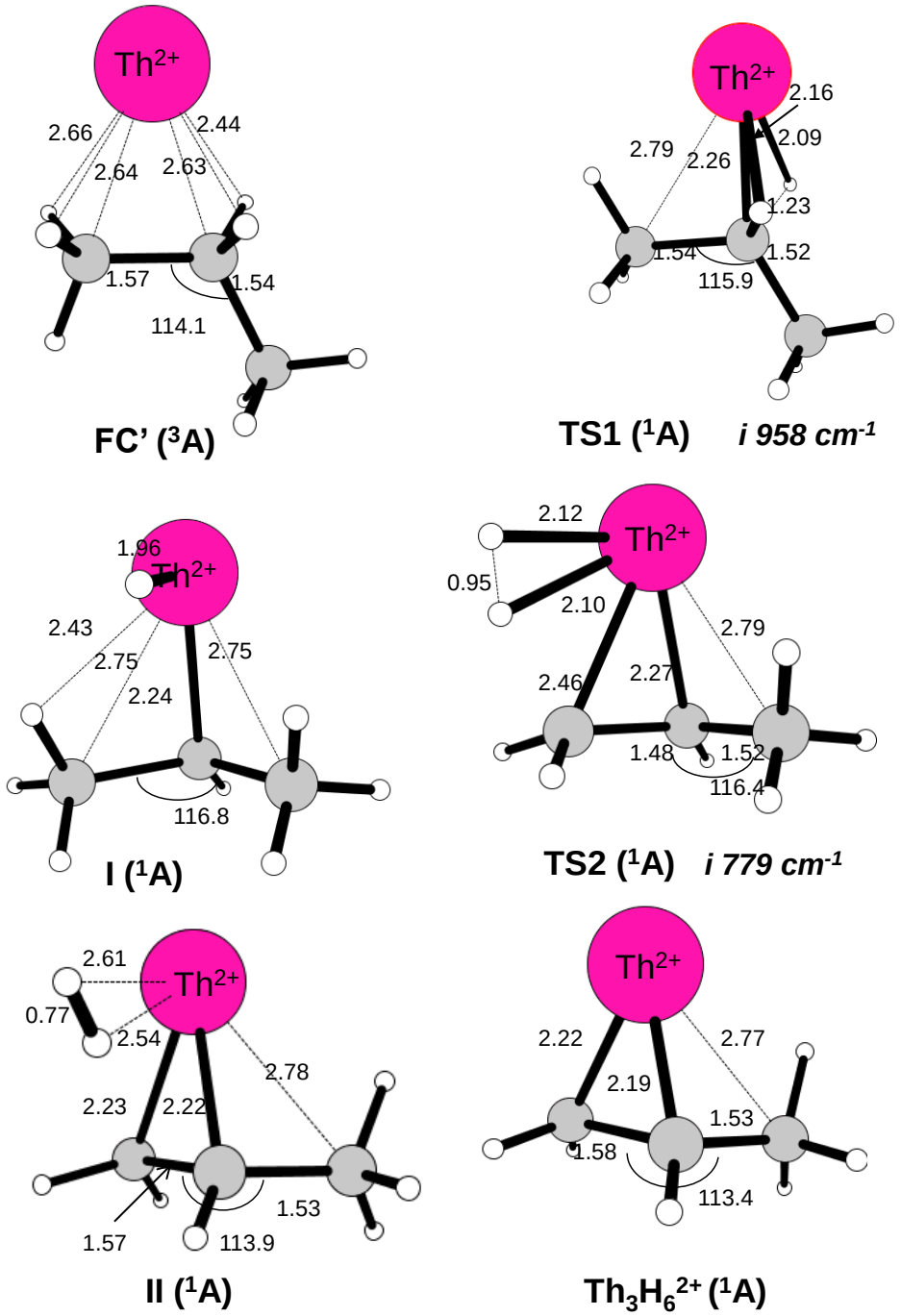
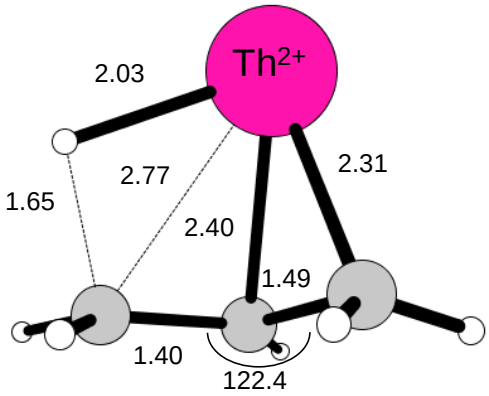
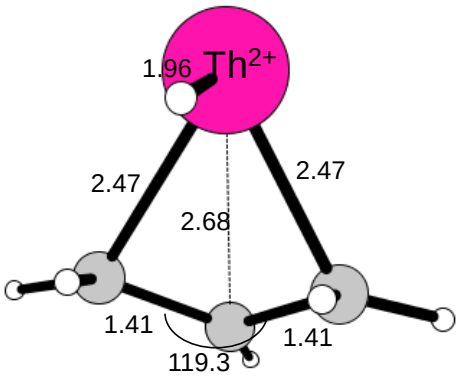

Th2+
2.66
2.44
2.64
2.63
1.57
1.54
114.1
FC' (3A)
Th2+
2.16
2.09
2.79
2.26
1.23
1.54
1.52
115.9
TS1 (1A) i 958 cm-1
1.96
Th2+
2.43
2.75
2.75
2.24
116.8
I (1A)
2.12
Th2+
0.95
2.10
2.79
2.46
2.27
1.48
1.52
116.4
TS2 (1A) i 779 cm-1
2.61
Th2+
0.77
2.54
2.78
2.23
2.22
1.53
1.57
113.9
II (1A)
Th2+
2.22
2.77
2.19
1.53
1.58
113.4
Th3H62+ (1A)

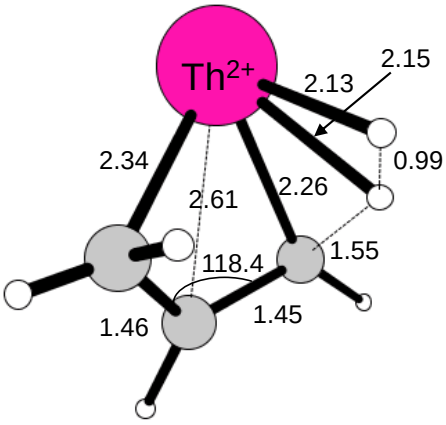
Figure S14 (a)



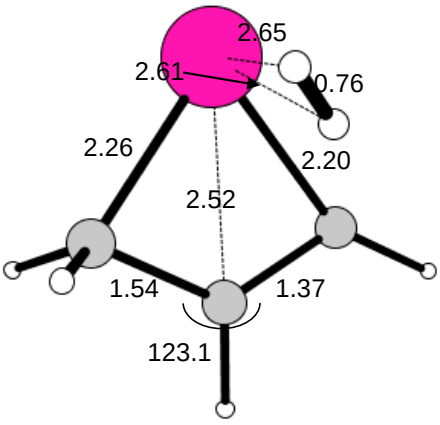
TS3 (^{1}A) ***i 743 cm^{-1}***



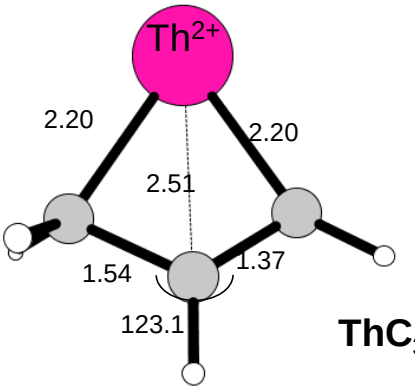
III (^{1}A)



TS4 (^{1}A) ***i 1075 cm^{-1}***



IV (^{1}A)



$ThC_3H_4^{2+}$ (^{1}A)

Figure S14 (b)

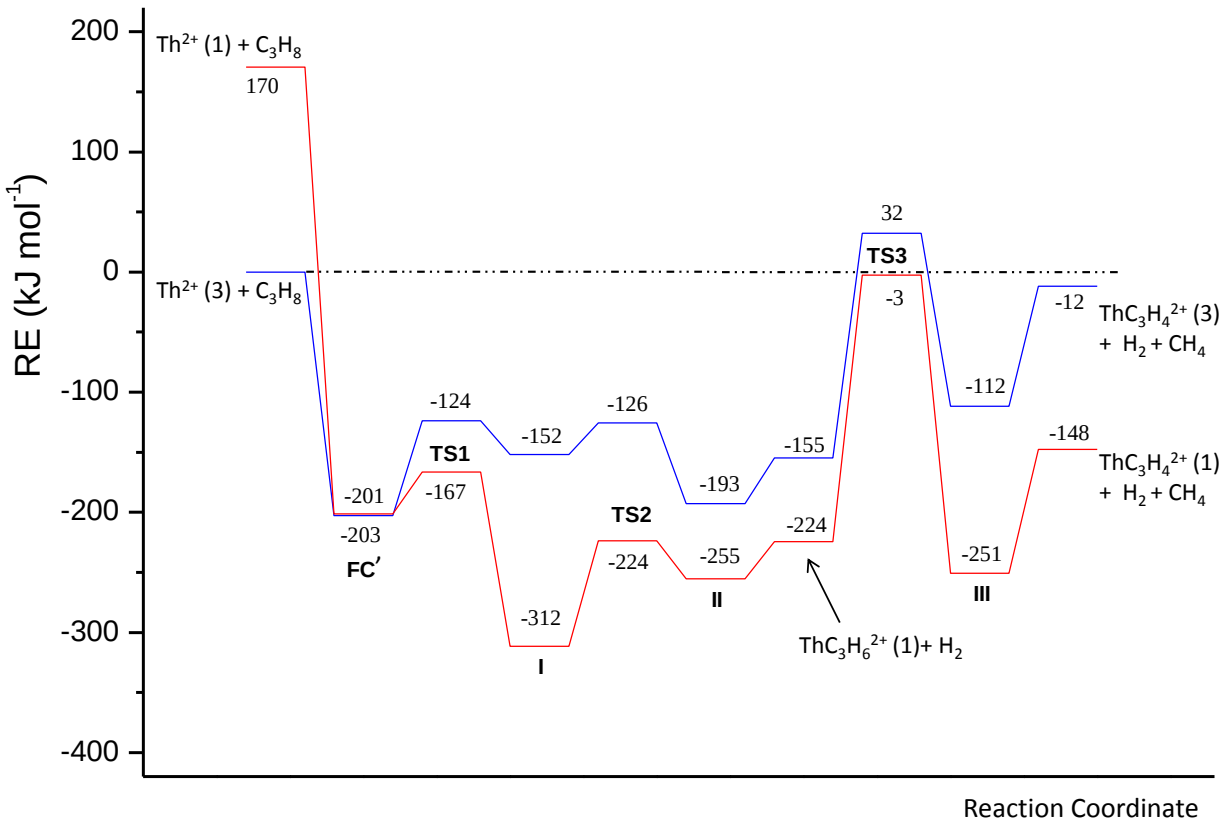

200
100
0
-100
-200
-300
-400
RE (kJ mol-1)
Th2+ (1) + C3H8
170
Th2+ (3) + C3H8
-201
-203
FC'
-124
TS1
-167
-152
-312
I
-126
TS2
-224
-193
-255
II
-155
-224
ThC3H62+ (1)+ H2
32
TS3
-3
-112
-251
III
-12
ThC3H42+ (3)
+ H2 + CH4
-148
ThC3H42+ (1)
+ H2 + CH4
Reaction Coordinate

Figure S15

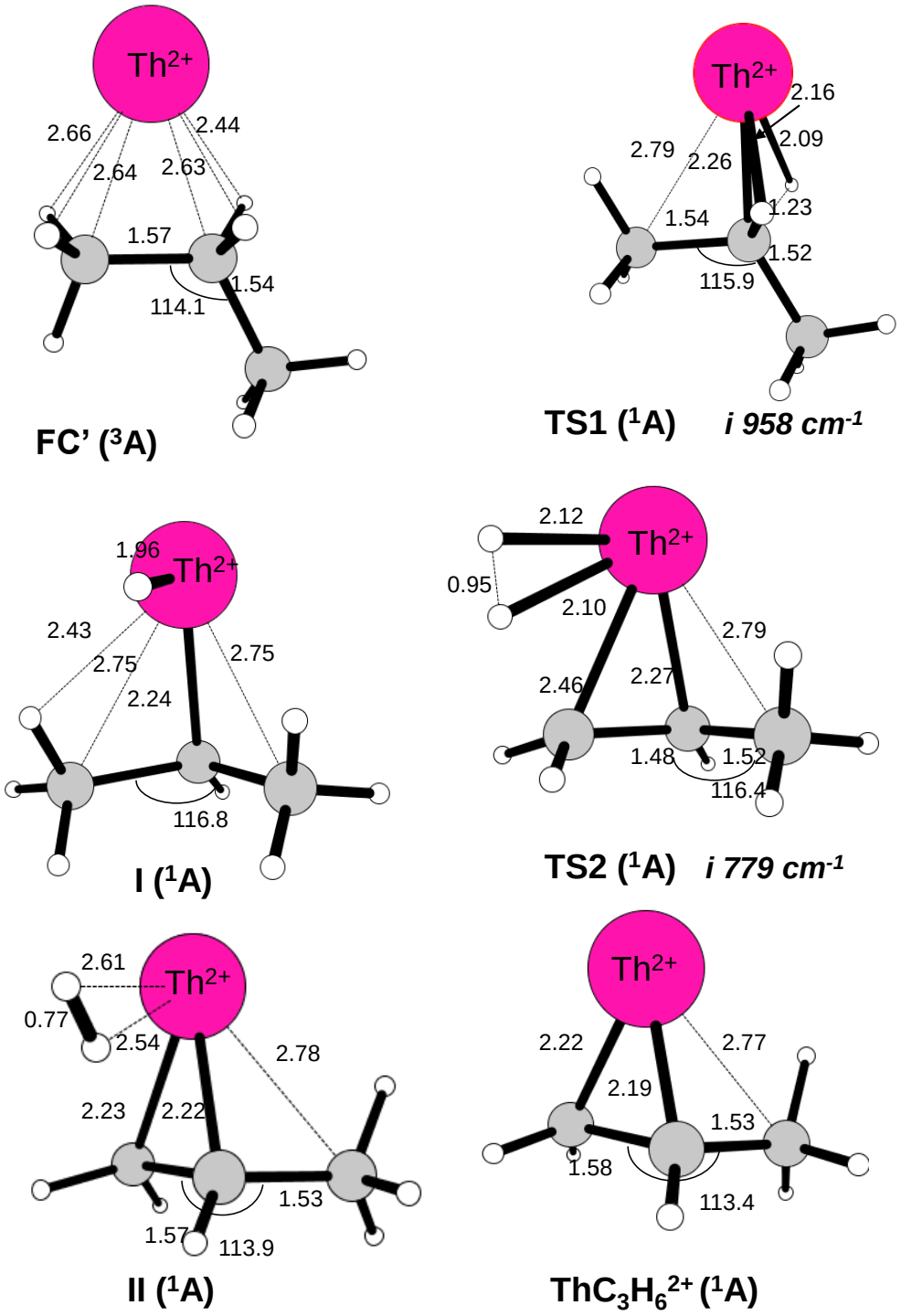
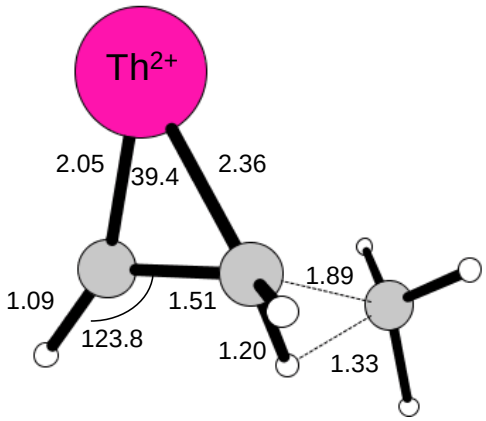
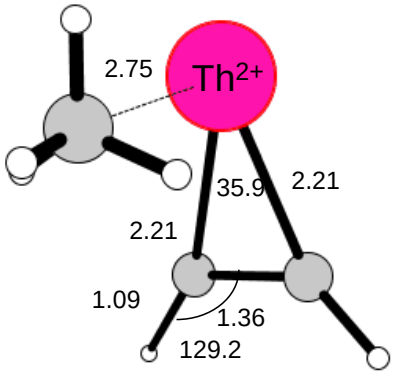

Th2+
2.66
2.44
2.64
2.63
1.57
1.54
114.1
FC' (3A)
Th2+
2.16
2.09
2.79
2.26
1.54
1.23
1.52
115.9
TS1 (1A) i 958 cm-1
1.96
Th2+
2.43
2.75
2.75
2.24
116.8
I (1A)
2.12
Th2+
0.95
2.10
2.79
2.46
2.27
1.48
1.52
116.4
TS2 (1A) i 779 cm-1
2.61
Th2+
0.77
2.54
2.78
2.23
2.22
1.53
1.57
113.9
II (1A)
Th2+
2.22
2.77
2.19
1.53
1.58
113.4
ThC3H62+ (1A)

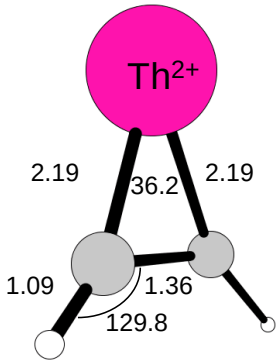
Figure S16 (a)



TS3 (^{1}A) ***i 726 cm^{-1}***



III (^{1}A)



$ThC_2H_2^{2+}$ (^{1}A)

Figure S16 (b)

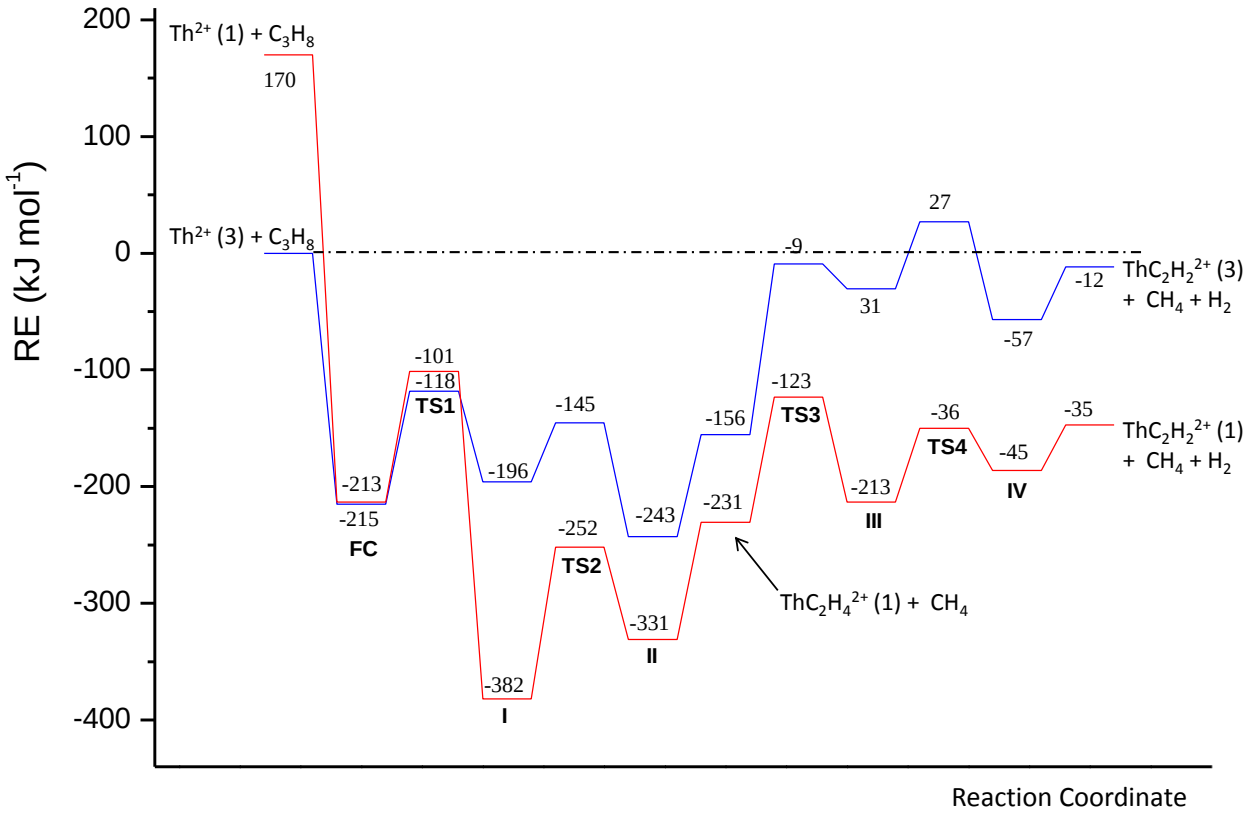
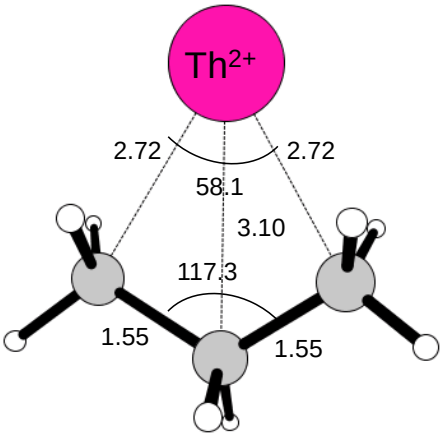
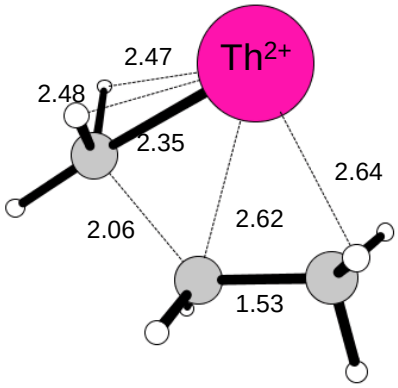

200
100
0
-100
-200
-300
-400
RE (kJ mol-1)
Th2+ (1) + C3H8
170
Th2+ (3) + C3H8
-213
-215
FC
-101
-118
TS1
-196
-382
I
-145
-252
TS2
-243
-331
II
-156
-231
-9
-123
TS3
31
-213
III
27
-36
TS4
-57
-45
IV
-12
-35
ThC2H22+ (3)
+ CH4 + H2
ThC2H22+ (1)
+ CH4 + H2
ThC2H42+ (1) + CH4
Reaction Coordinate

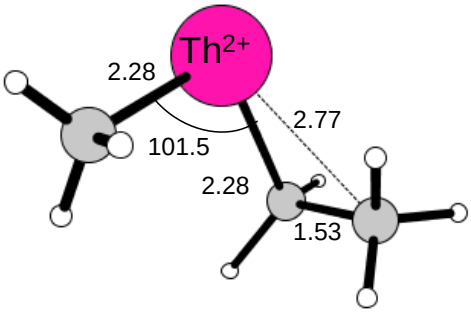
Figure S17



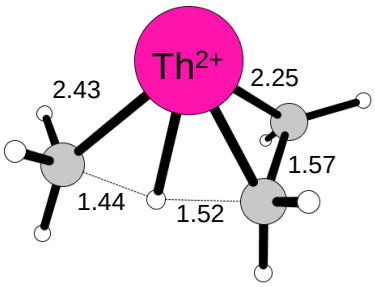
FC (^{3}A)



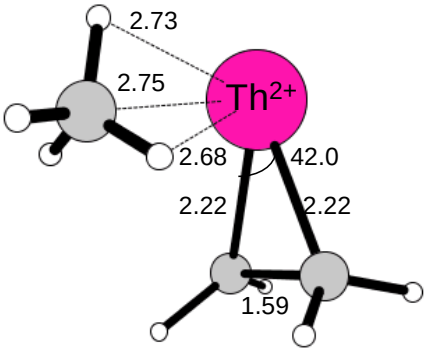
TS1 (^{3}A) ***i 485 cm^{-1}***



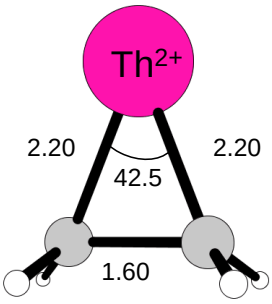
I (^{1}A)



TS2 (^{1}A) ***i 1366 cm^{-1}***



II (^{1}A)



$ThC_2H_4^{2+}$ (^{1}A)

Figure S18 (a)

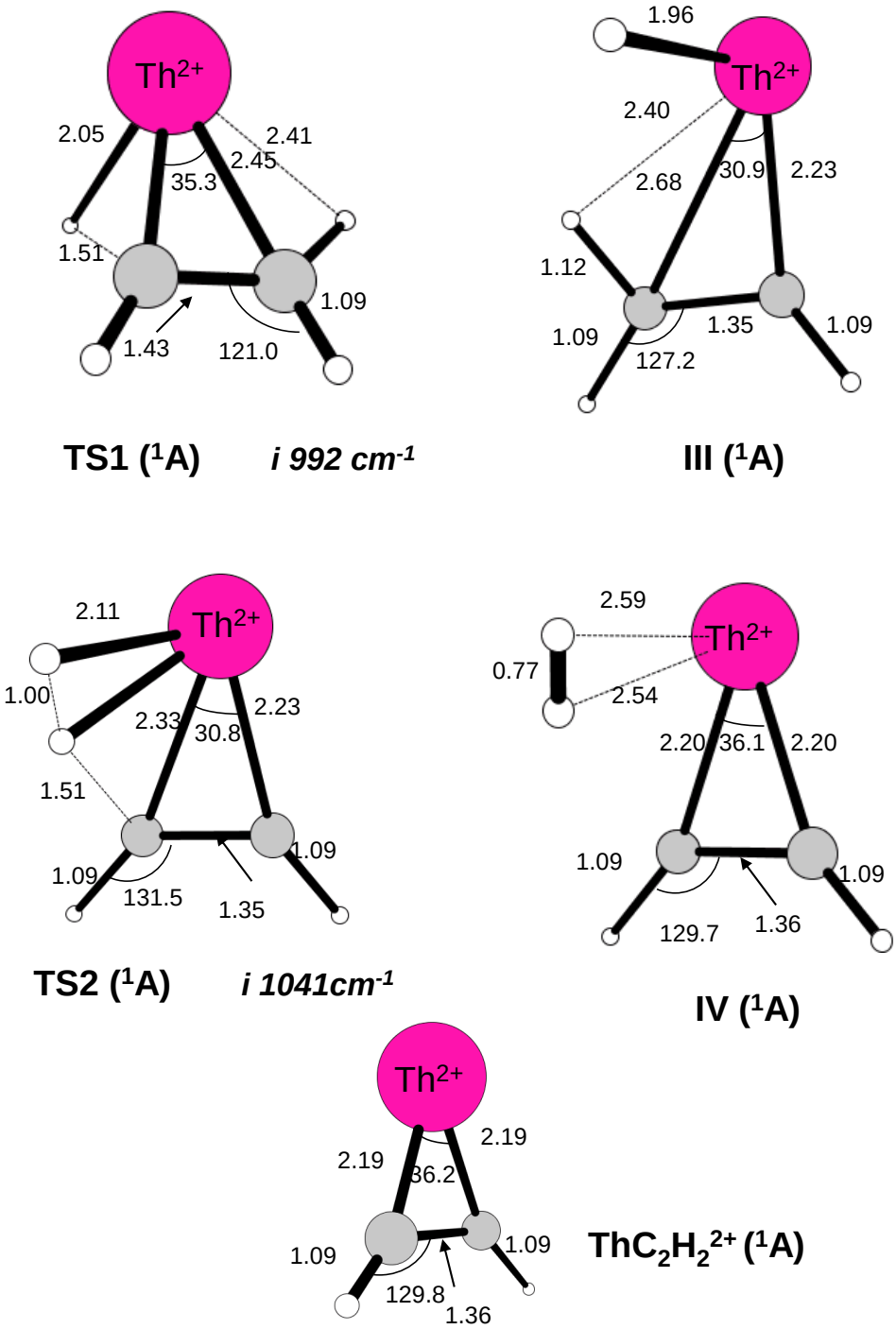

Th2+
2.05
2.41
2.45
35.3
1.51
1.09
1.43
121.0
TS1 (1A)
i 992 cm-1
1.96
Th2+
2.40
2.68
30.9
2.23
1.12
1.09
1.35
1.09
127.2
III (1A)
2.11
Th2+
1.00
2.33
30.8
2.23
1.51
1.09
1.09
131.5
1.35
TS2 (1A)
i 1041cm-1
2.59
Th2+
0.77
2.54
2.20
36.1
2.20
1.09
1.09
129.7
1.36
IV (1A)
Th2+
2.19
2.19
36.2
1.09
1.09
129.8
1.36
ThC2H22+ (1A)

Figure S18 (b)

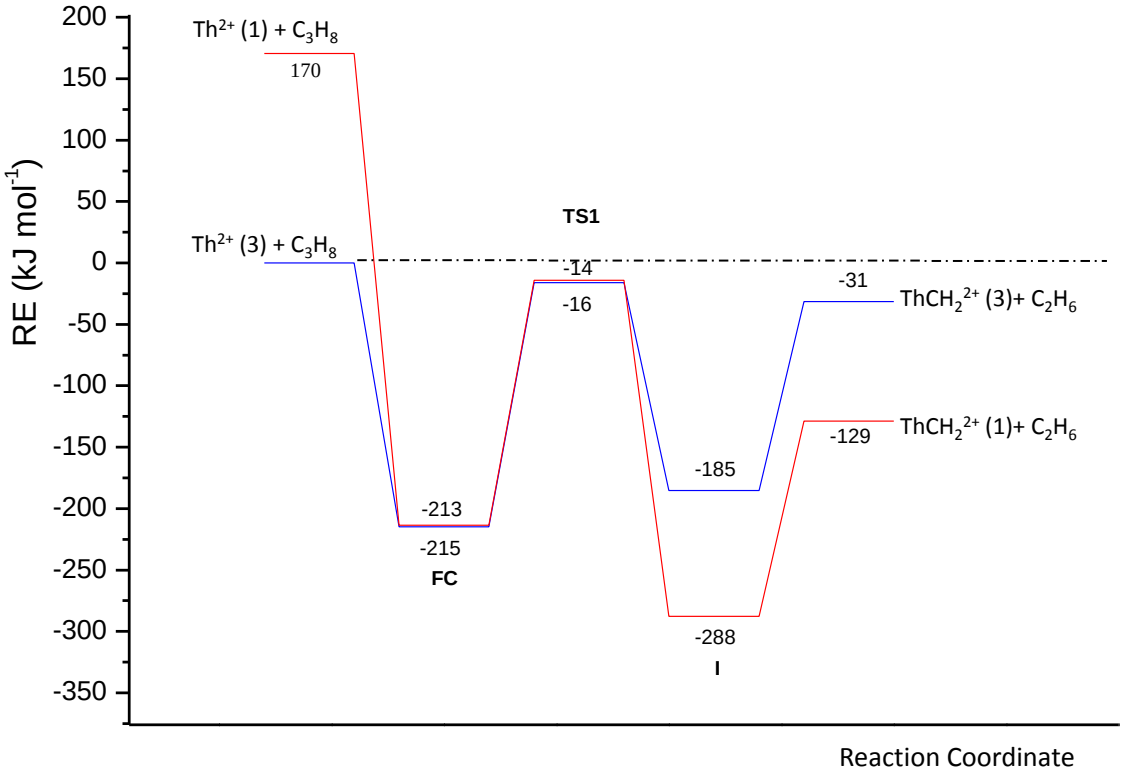
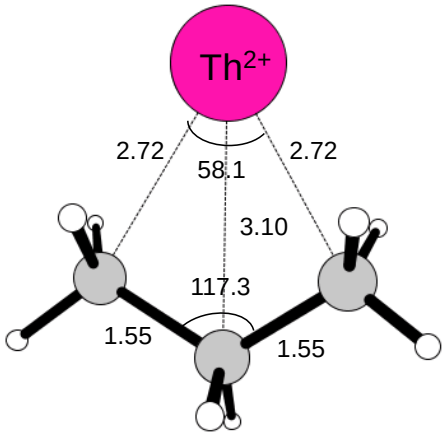
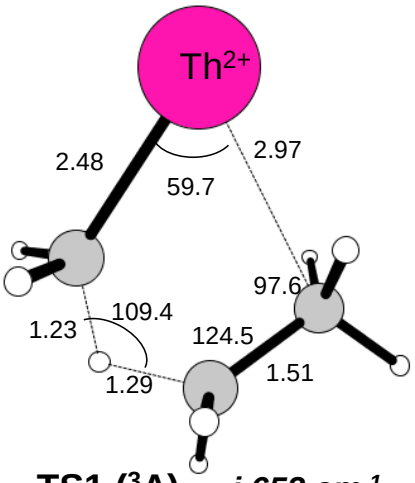

200
150
100
50
0
-50
-100
-150
-200
-250
-300
-350
RE (kJ mol-1)
Th2+ (1) + C3H8
170
Th2+ (3) + C3H8
TS1
-14
-16
-31
ThCH22+ (3)+ C2H6
ThCH22+ (1)+ C2H6
-129
-185
-213
-215
FC
-288
I
Reaction Coordinate

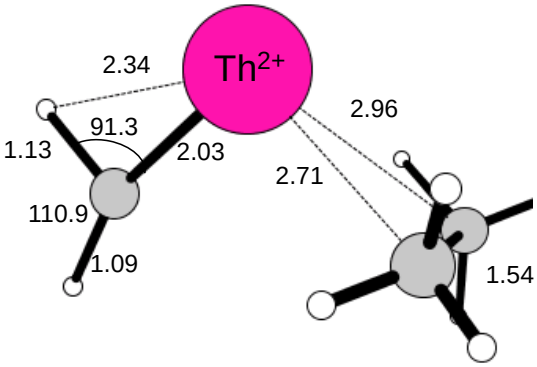
Figure S19



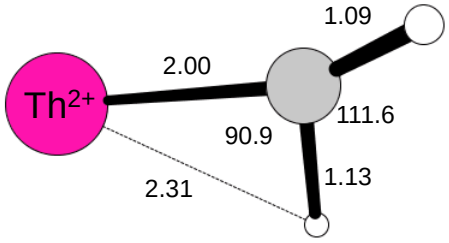
FC (^{3}A)



TS1 (^{3}A) ***i 653 cm^{-1}***



I (^{1}A)



$ThCH_2^{2+}$ (^{1}A')

Figure S20

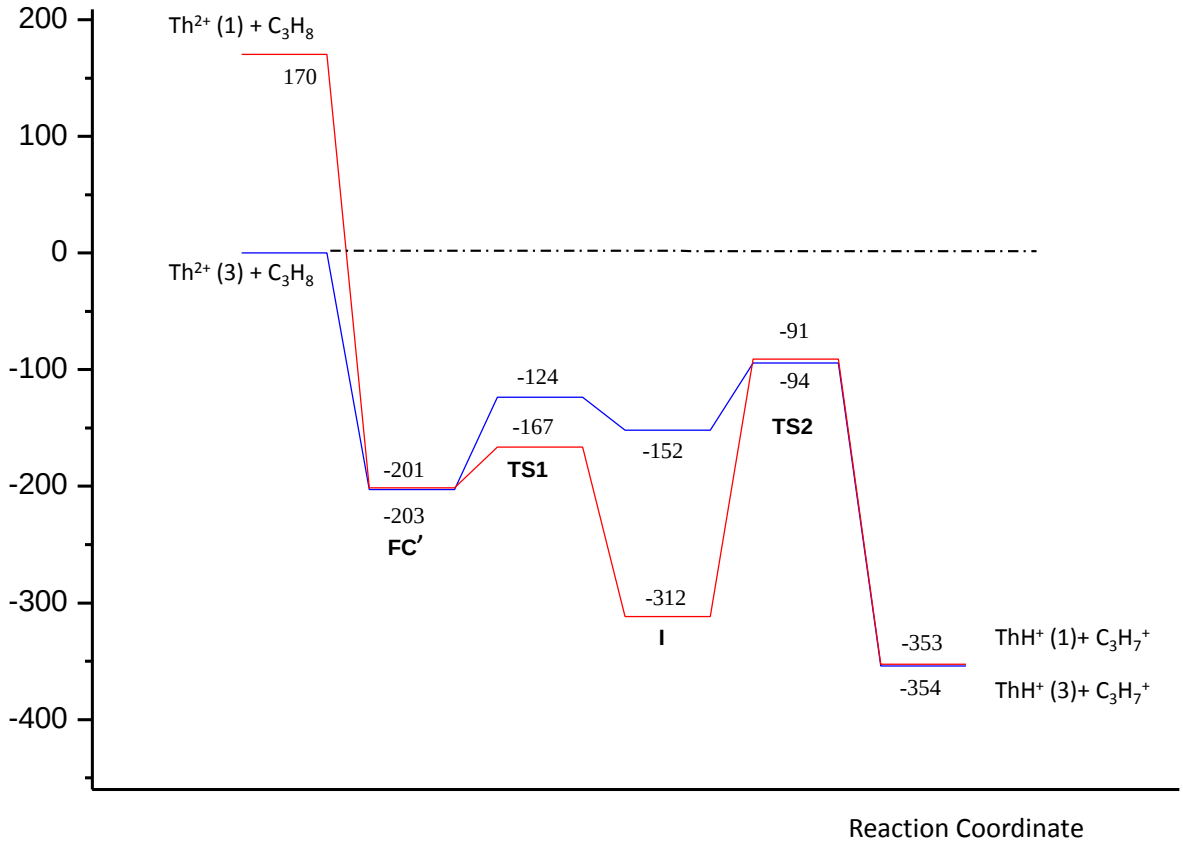

200
100
0
-100
-200
-300
-400
Th2+ (1) + C3H8
170
Th2+ (3) + C3H8
-201
-203
FC'
-124
-167
TS1
-152
-312
I
-91
-94
TS2
-353
-354
ThH+ (1)+ C3H7+
ThH+ (3)+ C3H7+
Reaction Coordinate

Figure S21

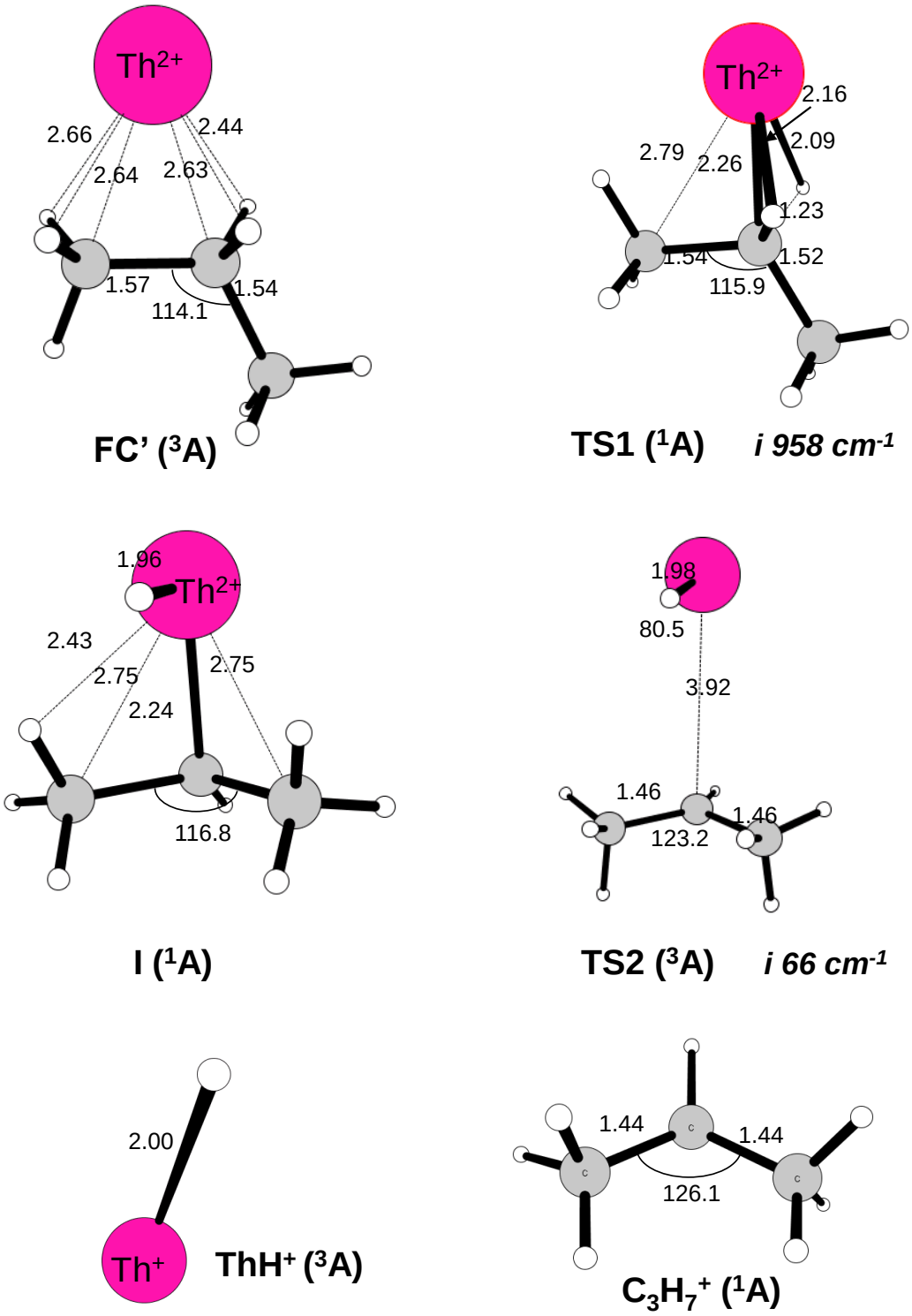

Th2+
2.66
2.44
2.64
2.63
1.57
1.54
114.1
FC' (3A)
Th2+
2.16
2.09
2.79
2.26
1.23
1.54
1.52
115.9
TS1 (1A) i 958 cm-1
1.96
Th2+
2.43
2.75
2.75
2.24
116.8
I (1A)
1.98
80.5
3.92
1.46
1.46
123.2
TS2 (3A) i 66 cm-1
2.00
Th+
ThH+ (3A)
1.44
1.44
126.1
C3H7+ (1A)

Figure S22

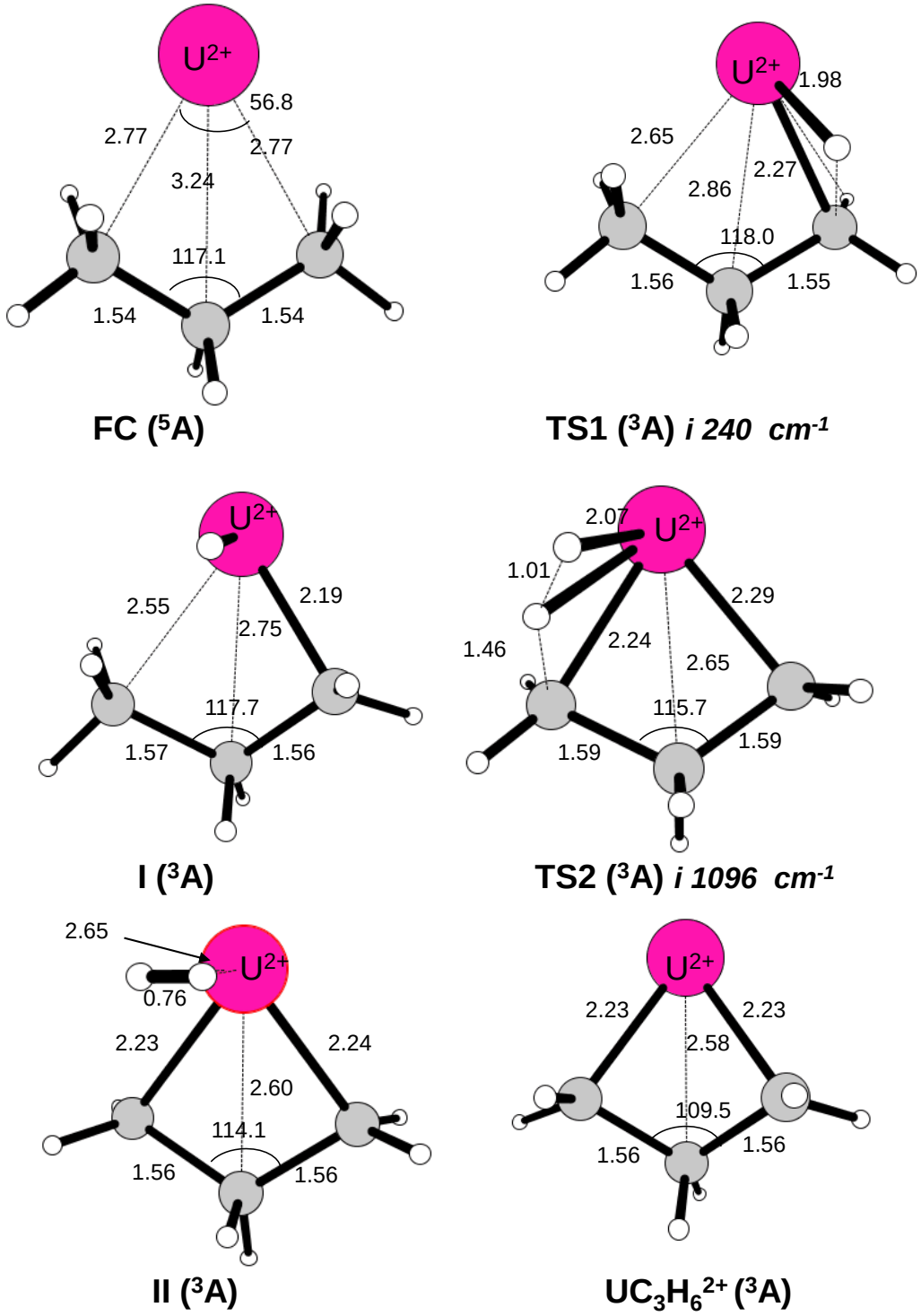

U2+
56.8
2.77
2.77
3.24
117.1
1.54
1.54
FC (5A)
U2+
1.98
2.65
2.27
2.86
118.0
1.56
1.55
TS1 (3A) i 240 cm-1
U2+
2.55
2.19
2.75
117.7
1.57
1.56
I (3A)
2.07
U2+
1.01
2.29
1.46
2.24
2.65
115.7
1.59
1.59
TS2 (3A) i 1096 cm-1
2.65
U2+
0.76
2.23
2.24
2.60
114.1
1.56
1.56
II (3A)
U2+
2.23
2.23
2.58
109.5
1.56
1.56
UC3H62+ (3A)

Figure S23 (a)

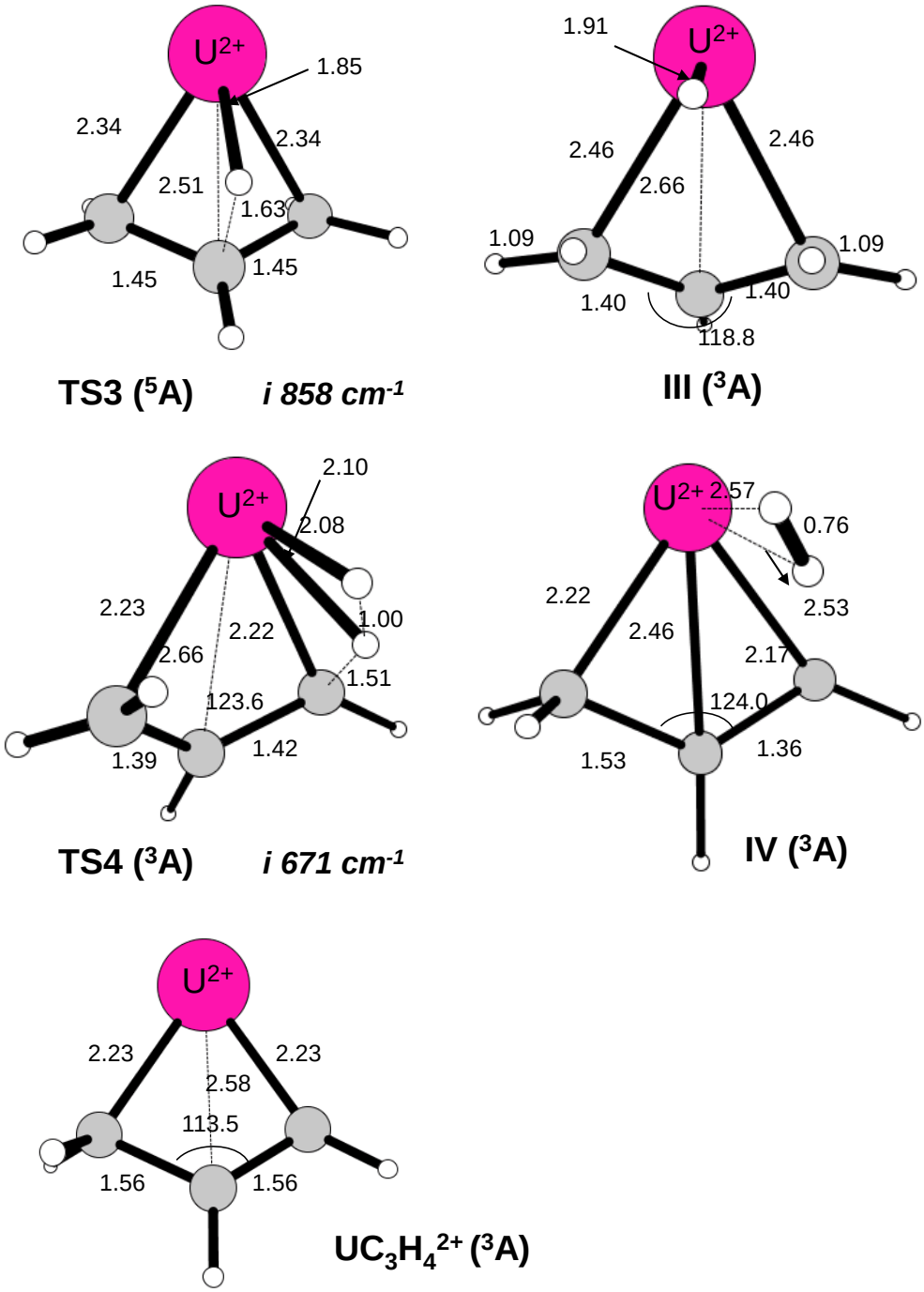
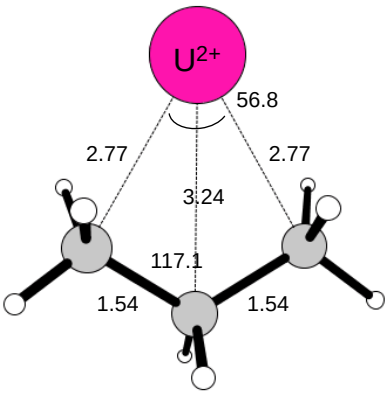
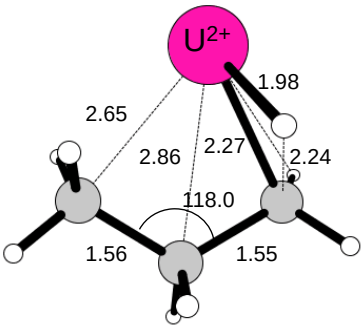

U2+
1.85
2.34
2.34
2.51
1.63
1.45
1.45
TS3 (5A)
i 858 cm-1
1.91
U2+
2.46
2.46
2.66
1.09
1.09
1.40
1.40
118.8
III (3A)
2.10
U2+
2.08
2.23
2.22
1.00
2.66
1.51
123.6
1.39
1.42
TS4 (3A)
i 671 cm-1
U2+ 2.57
0.76
2.22
2.53
2.46
2.17
124.0
1.53
1.36
IV (3A)
U2+
2.23
2.23
2.58
113.5
1.56
1.56
UC3H42+ (3A)

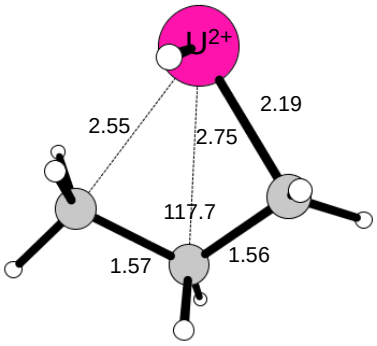
Figure S23 (b)



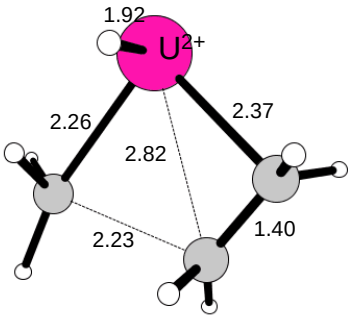
FC (^{5}A)



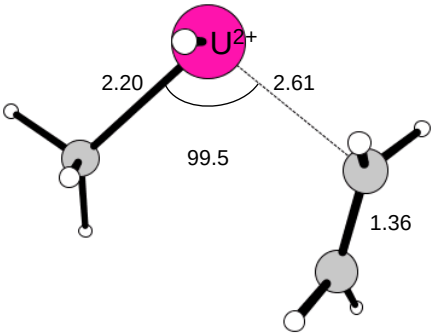
TS1 (^{3}A) ***i 240 cm^{-1}***



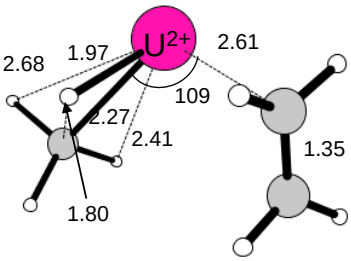
I (^{3}A)



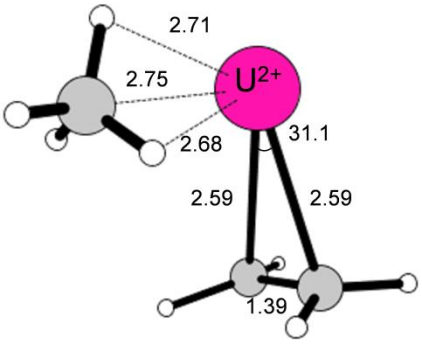
TS2 (^{3}A) ***i 295 cm^{-1}***



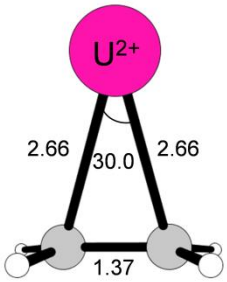
II (^{3}A)



TS3 (^{3}A) ***i 532 cm^{-1}***

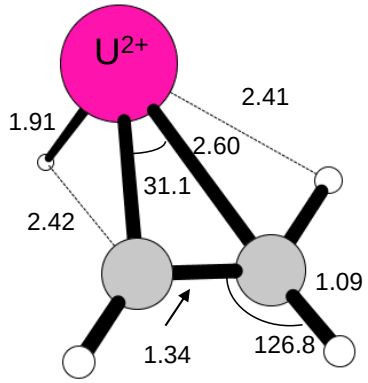


III (^{5}A)

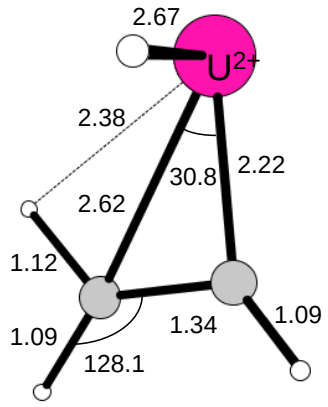


$UC_2H_4^{2+}$ (^{5}A)

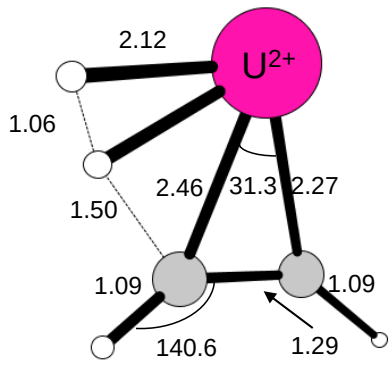
Figure S24 (a)



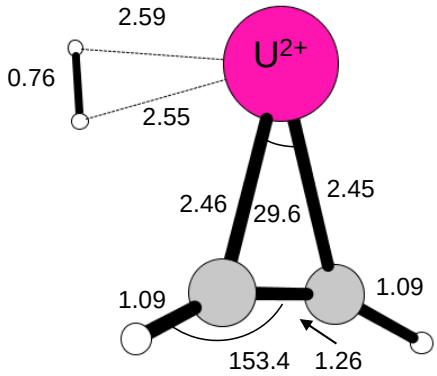
TS4 (^{3}A) ***i 240 cm^{-1}***



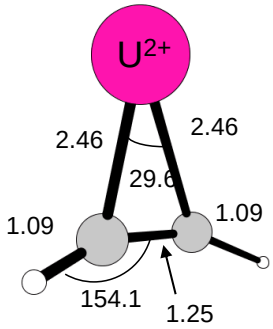
IV (^{5}A)



TS5 (^{3}A) ***i 947 cm^{-1}***



V (^{5}A)



$UC_2H_2^{2+}$ (^{5}A)

Figure S24 (b)

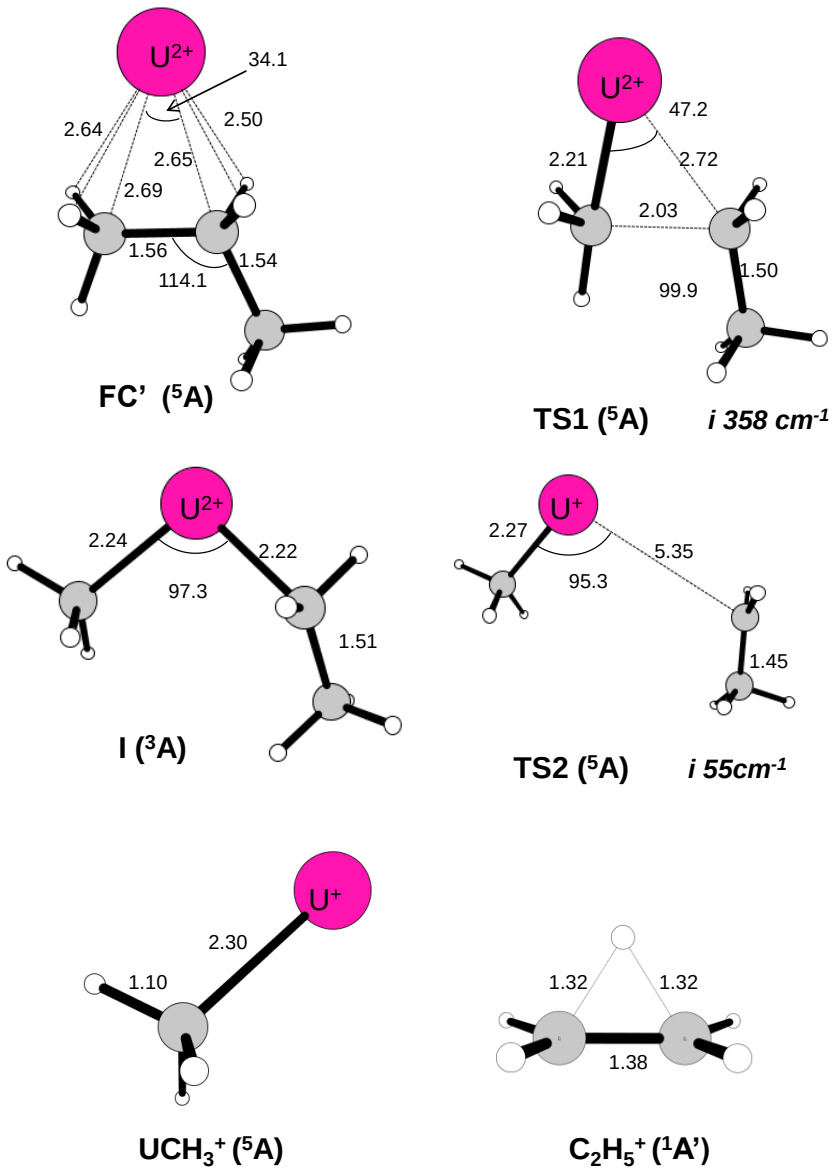

U2+
34.1
2.64
2.50
2.65
2.69
1.56
1.54
114.1
FC' (5A)
U2+
47.2
2.21
2.72
2.03
1.50
99.9
TS1 (5A)
i 358 cm-1
U2+
2.24
2.22
97.3
1.51
I (3A)
U+
2.27
5.35
95.3
1.45
TS2 (5A)
i 55cm-1
U+
2.30
1.10
UCH3+ (5A)
1.32
1.32
1.38
C2H5+ (1A')

Figure S25

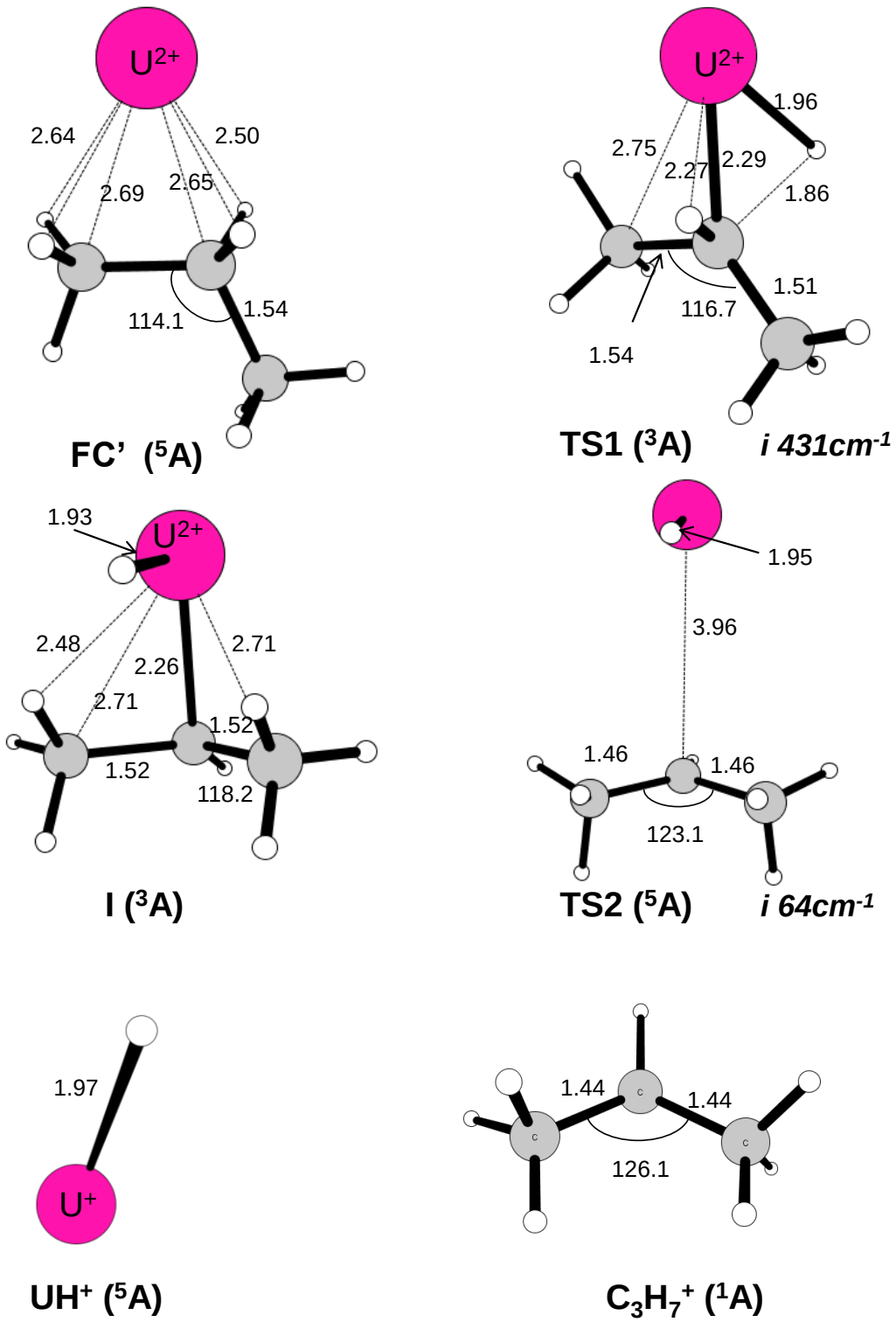

U2+
2.64
2.50
2.69
2.65
114.1
1.54
FC' (5A)
U2+
1.96
2.75
2.27
2.29
1.86
1.51
116.7
1.54
TS1 (3A)
i 431cm-1
1.93
U2+
2.48
2.26
2.71
2.71
1.52
1.52
118.2
I (3A)
1.95
3.96
1.46
1.46
123.1
TS2 (5A)
i 64cm-1
1.97
U+
UH+ (5A)
1.44
1.44
126.1
C3H7+ (1A)

Figure S26

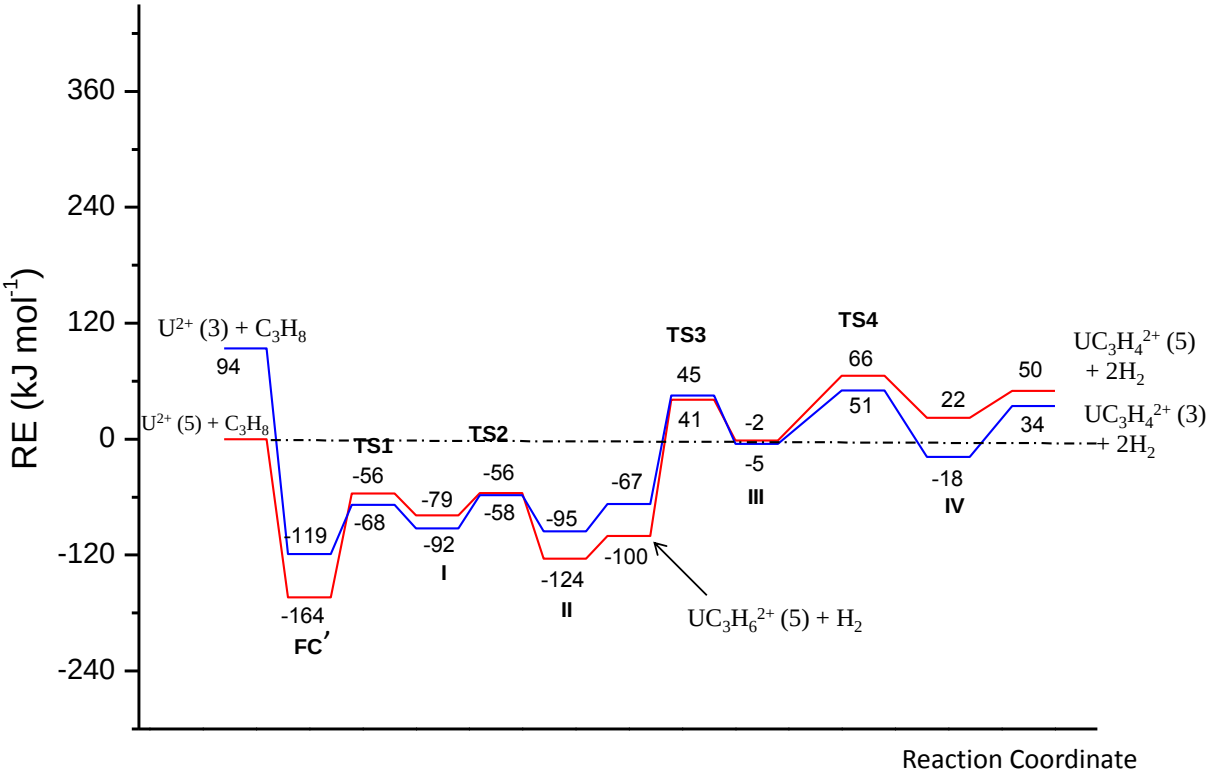

RE (kJ mol-1)
360
240
120
0
-120
-240
U2+ (3) + C3H8
94
U2+ (5) + C3H8
-119
-164
FC'
TS1
-56
-68
-79
-92
I
TS2
-56
-58
-95
-124
II
-67
-100
UC3H62+ (5) + H2
TS3
45
41
-2
-5
III
TS4
66
51
22
-18
IV
50
34
UC3H42+ (5)
+ 2H2
UC3H42+ (3)
+ 2H2
Reaction Coordinate

Figure S27

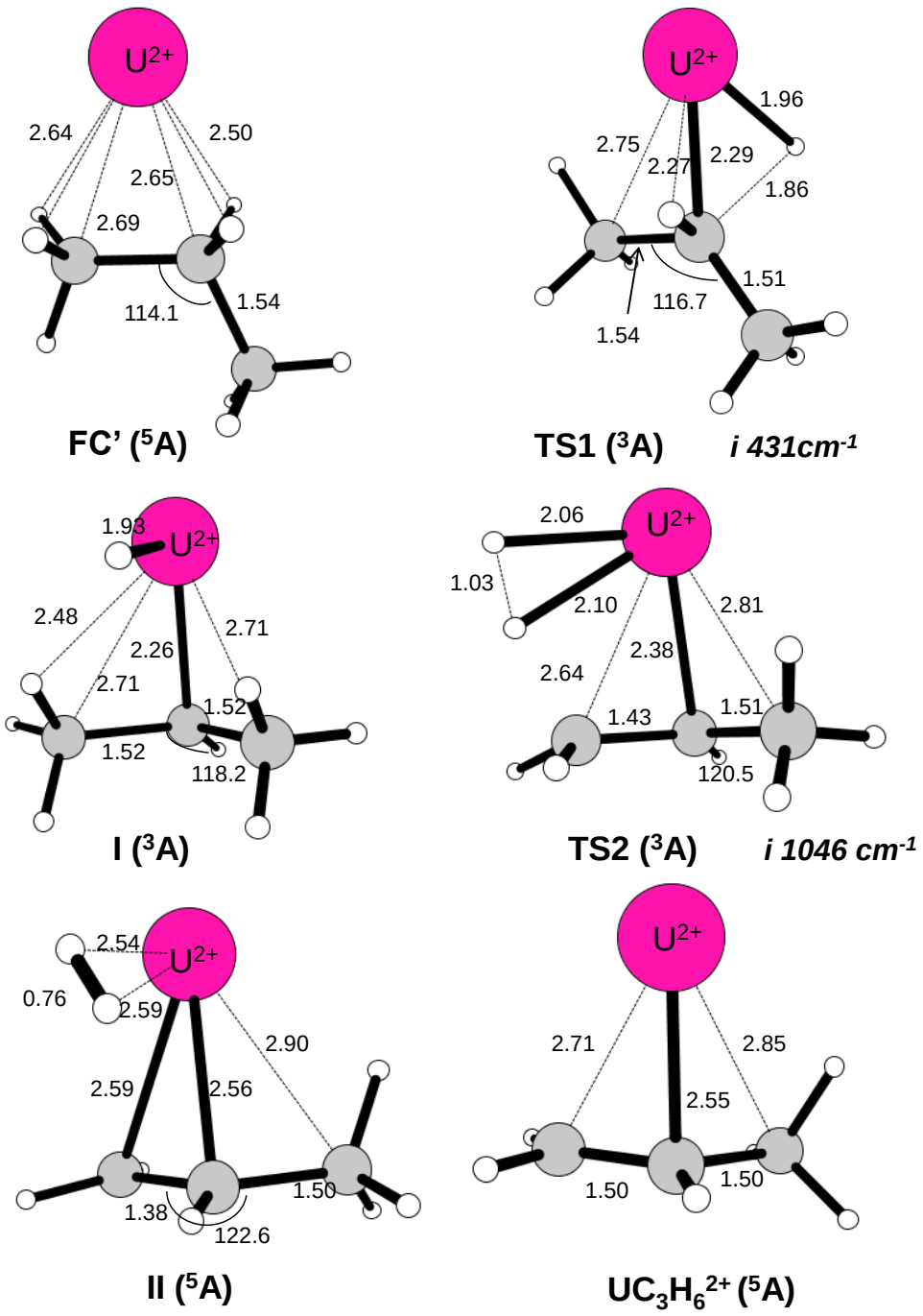
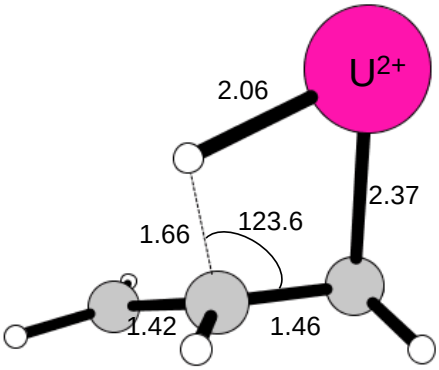
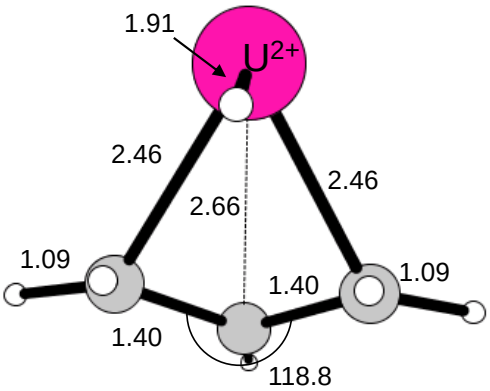

U2+
2.64
2.50
2.65
2.69
114.1
1.54
FC' (5A)
U2+
1.96
2.75
2.27
2.29
1.86
1.51
116.7
1.54
TS1 (3A)
i 431cm-1
1.93
U2+
2.48
2.71
2.26
2.71
1.52
1.52
118.2
I (3A)
2.06
U2+
1.03
2.10
2.81
2.38
2.64
1.43
1.51
120.5
TS2 (3A)
i 1046 cm-1
2.54
U2+
0.76
2.59
2.90
2.59
2.56
1.50
1.38
122.6
II (5A)
U2+
2.71
2.85
2.55
1.50
1.50
UC3H62+ (5A)

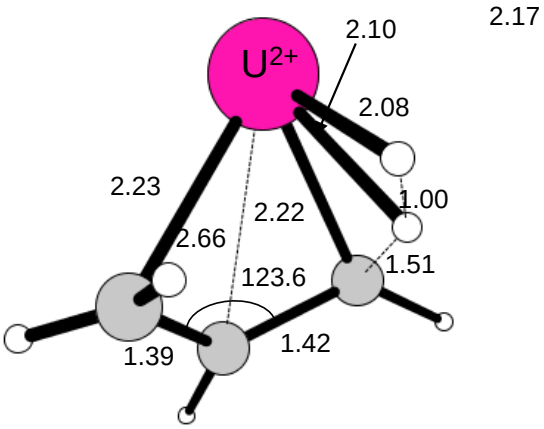
Figure S28 (a)



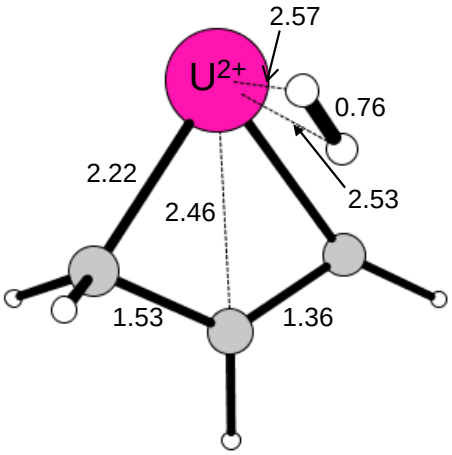
TS3 (^{5}A) ***i 671 cm^{-1}***



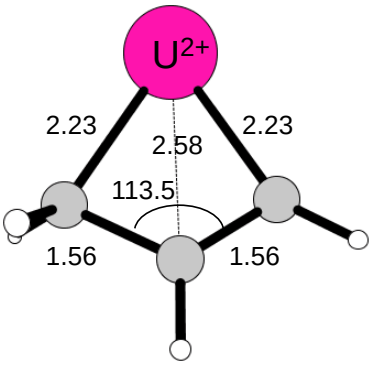
III (^{3}A)



TS4 (^{3}A) ***i 671 cm^{-1}***



IV (^{3}A)



$UC_3H_4^{2+}$ (^{3}A)

Figure S28 (b)

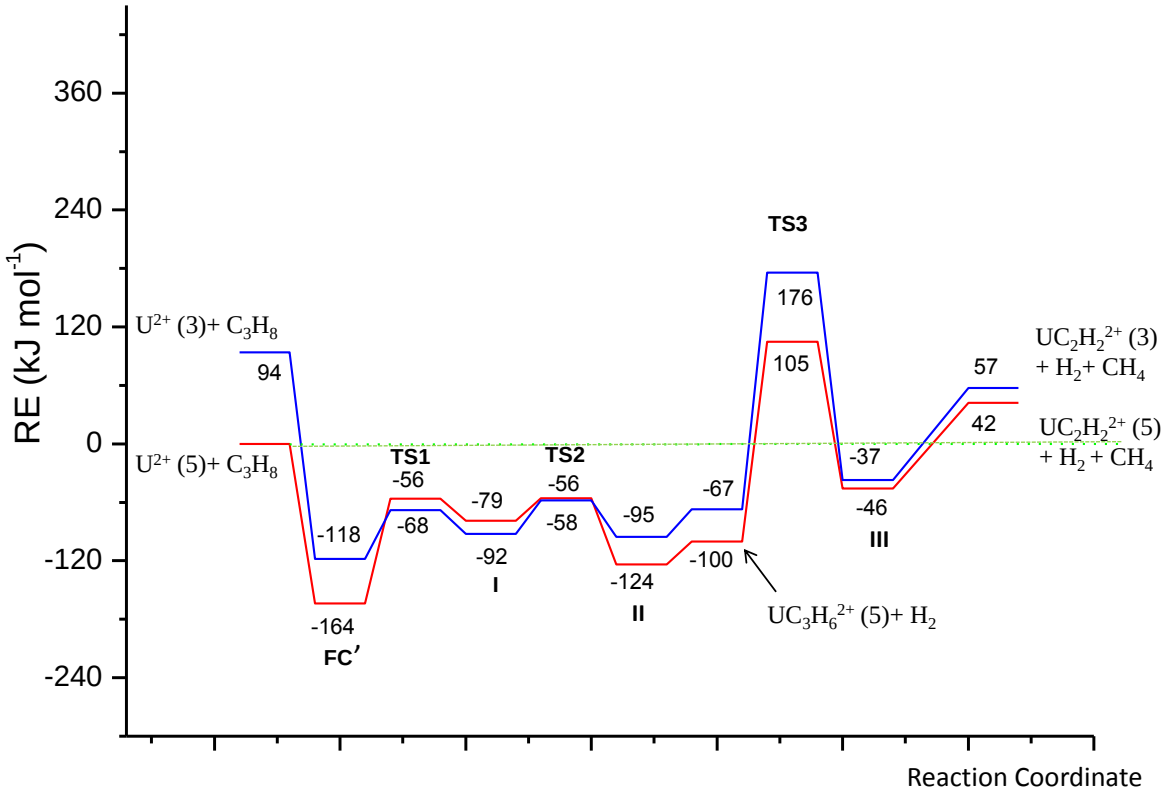

RE (kJ mol-1)
360
240
120
0
-120
-240
Reaction Coordinate
U2+ (3)+ C3H8
U2+ (5)+ C3H8
94
-118
-164
FC'
TS1
-56
-68
-79
-92
I
TS2
-56
-58
-95
-124
II
-67
-100
TS3
176
105
-37
-46
III
57
42
UC2H22+ (3)
+ H2+ CH4
UC2H22+ (5)
+ H2 + CH4
UC3H62+ (5)+ H2

Figure S29

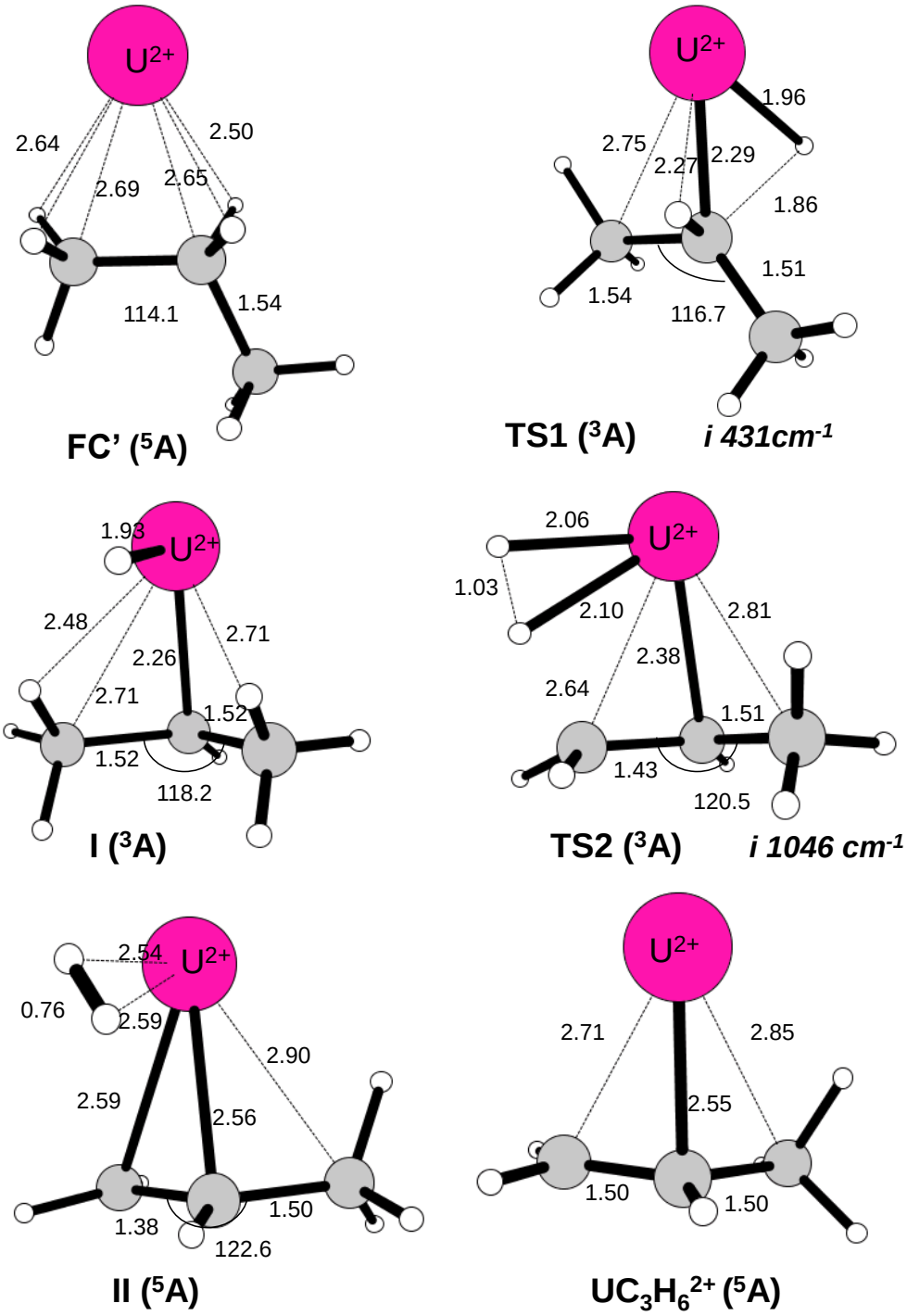
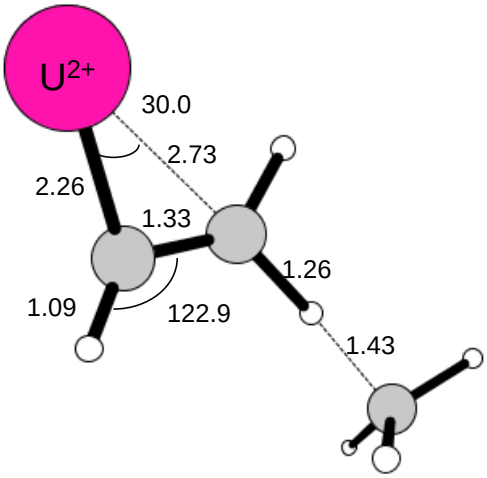
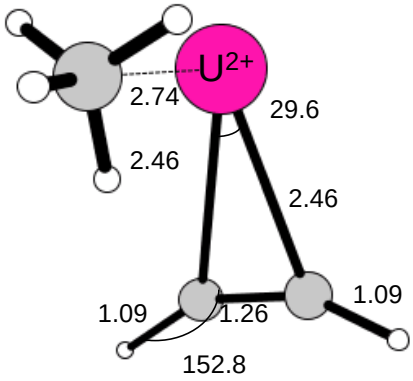

U2+
2.64
2.50
2.69
2.65
114.1
1.54
FC' (5A)
U2+
1.96
2.75
2.27
2.29
1.86
1.51
1.54
116.7
TS1 (3A)
i 431cm-1
1.93
U2+
2.48
2.71
2.26
2.71
1.52
1.52
118.2
I (3A)
2.06
U2+
1.03
2.10
2.81
2.38
2.64
1.51
1.43
120.5
TS2 (3A)
i 1046 cm-1
2.54
U2+
0.76
2.59
2.90
2.59
2.56
1.38
1.50
122.6
II (5A)
U2+
2.71
2.85
2.55
1.50
1.50
UC3H62+ (5A)

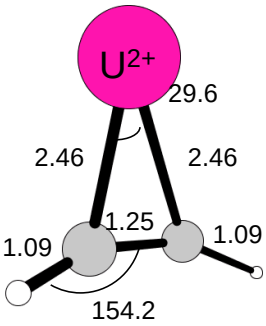
Figure S30 (a)



TS3 (^{5}A) ***i 693 cm^{-1}***



III (^{5}A)



$UC_2H_2^{2+}$ (^{5}A)

Figure S30 (b)

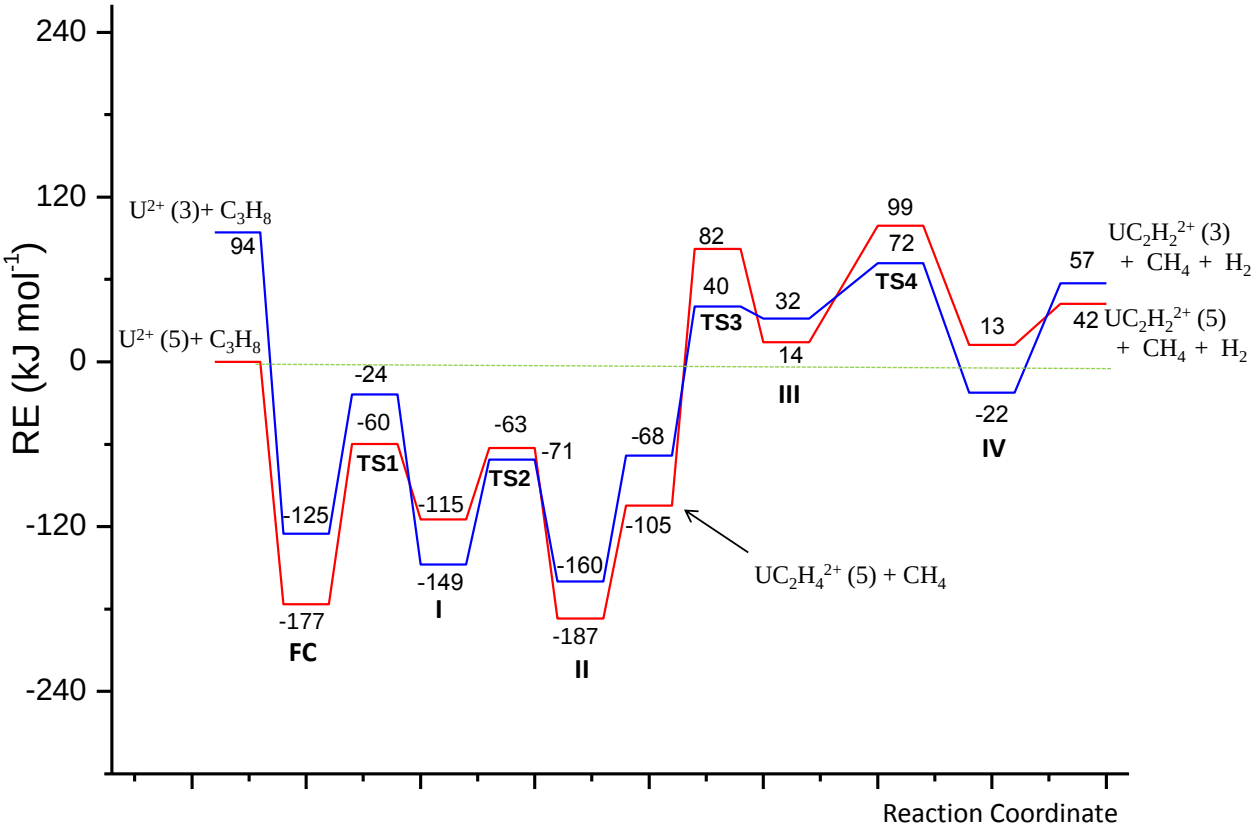

240
120
0
-120
-240
RE (kJ mol-1)
U2+ (3)+ C3H8
U2+ (5)+ C3H8
94
-125
-177
FC
-24
-60
TS1
-115
-149
I
-63
-71
TS2
-160
-187
II
-68
-105
82
40
TS3
32
14
III
99
72
TS4
13
-22
IV
57
42
UC2H22+ (3)
+ CH4 + H2
UC2H22+ (5)
+ CH4 + H2
UC2H42+ (5) + CH4
Reaction Coordinate

Figure S31

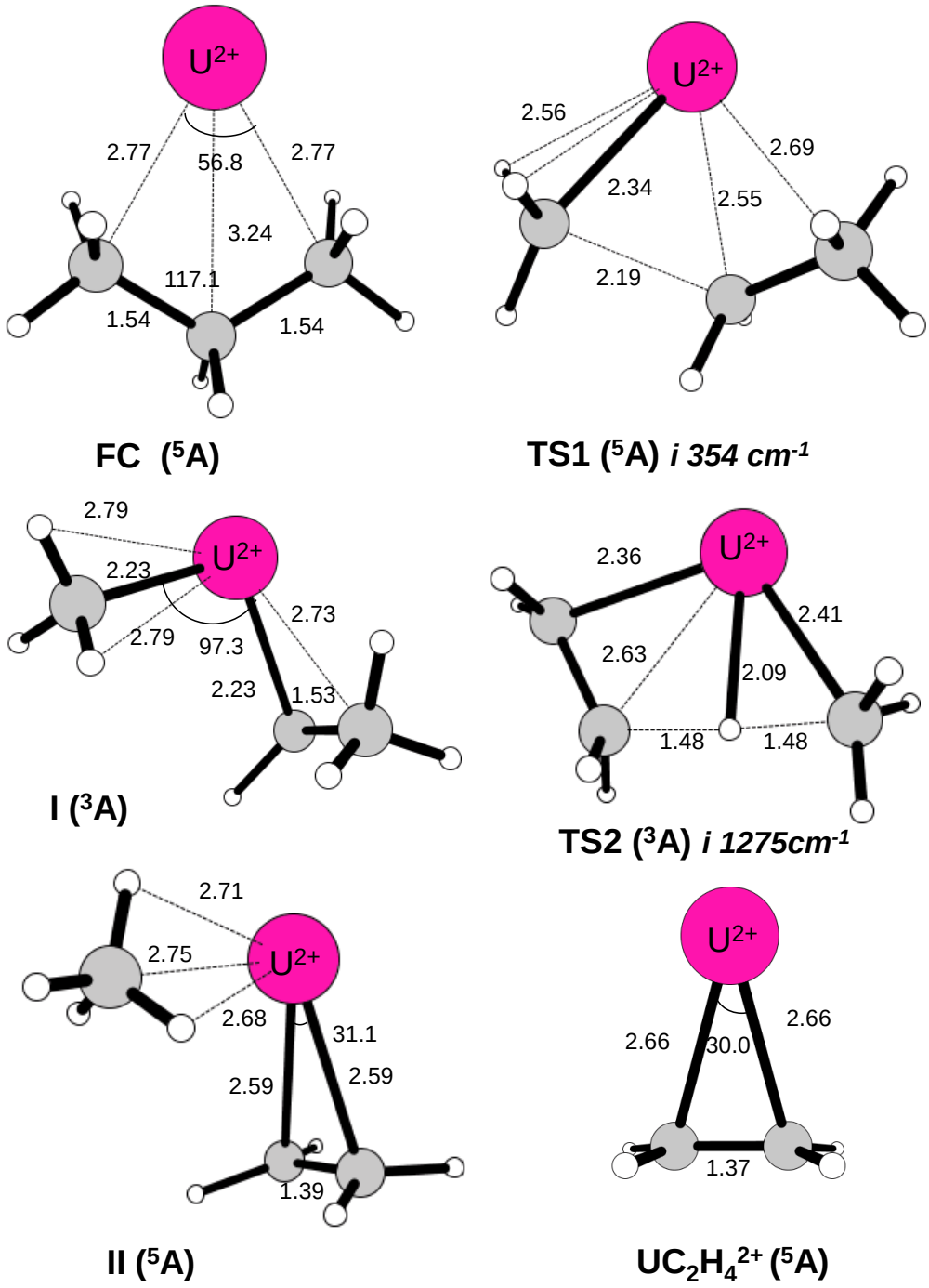
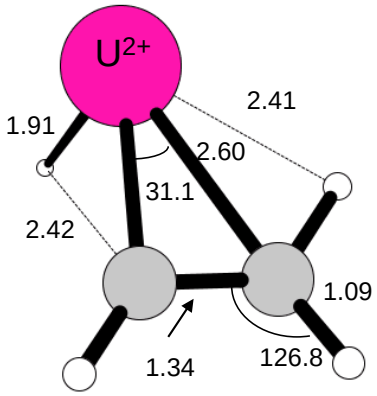
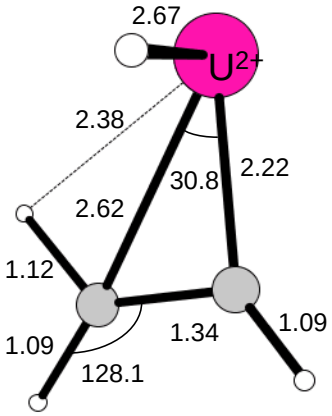

U2+
2.77
56.8
2.77
3.24
117.1
1.54
1.54
FC (5A)
U2+
2.56
2.69
2.34
2.55
2.19
TS1 (5A) i 354 cm-1
2.79
U2+
2.23
2.73
2.79
97.3
2.23
1.53
I (3A)
2.36
U2+
2.41
2.63
2.09
1.48
1.48
TS2 (3A) i 1275cm-1
2.71
2.75
U2+
2.68
31.1
2.59
2.59
1.39
II (5A)
U2+
2.66
2.66
30.0
1.37
UC2H42+ (5A)

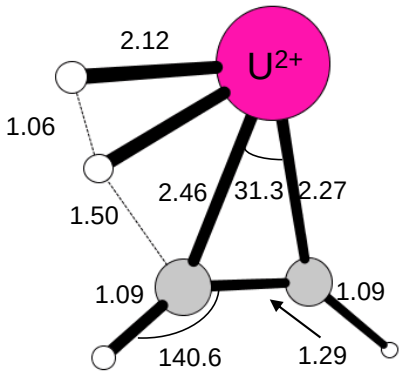
Figure S32 (a)



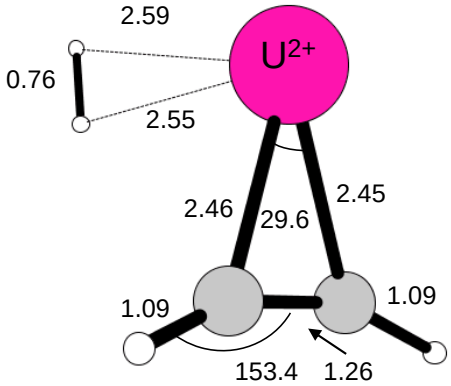
TS4 (^{3}A) ***i 240 cm^{-1}***



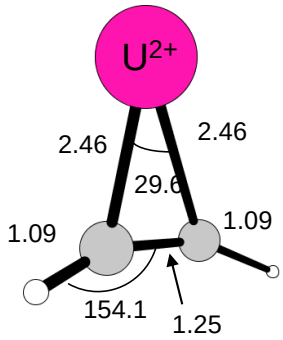
III (^{5}A)



TS5 (^{3}A) ***i 947 cm^{-1}***



IV (^{5}A)



$UC_2H_2^{2+}$ (^{5}A)

Figure S32 (b)

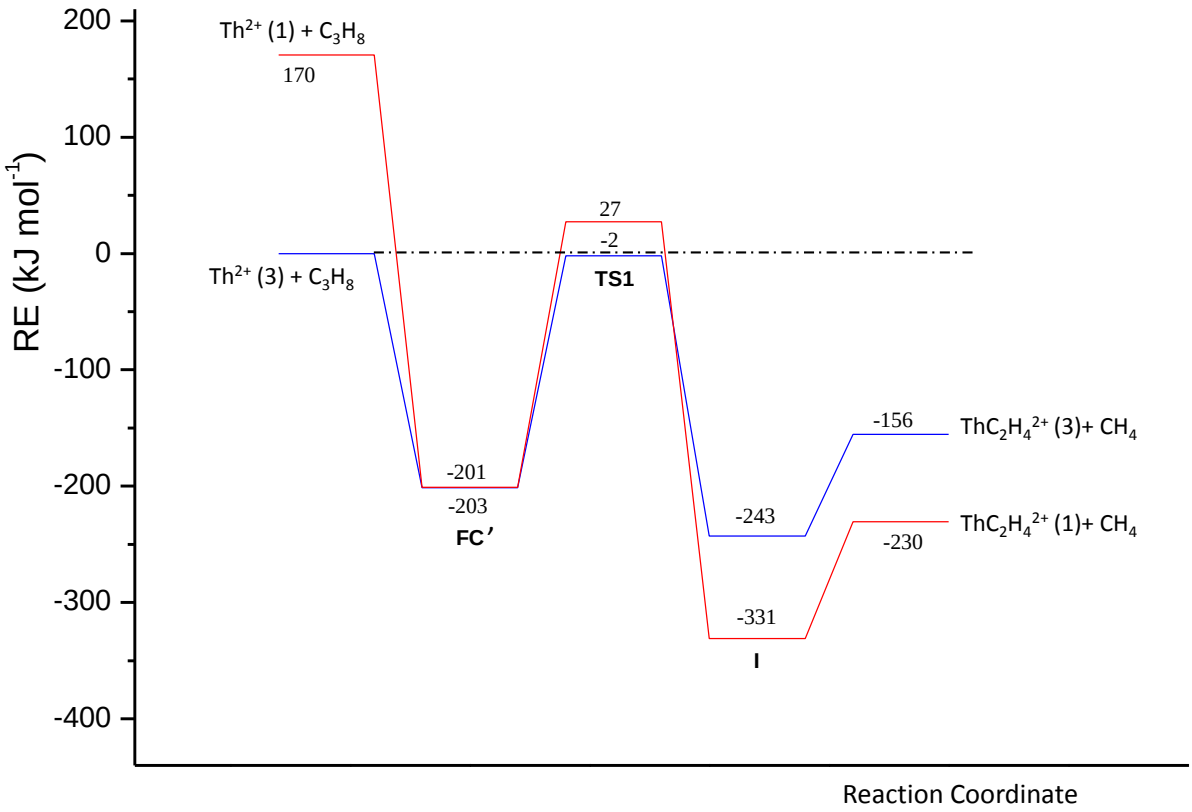
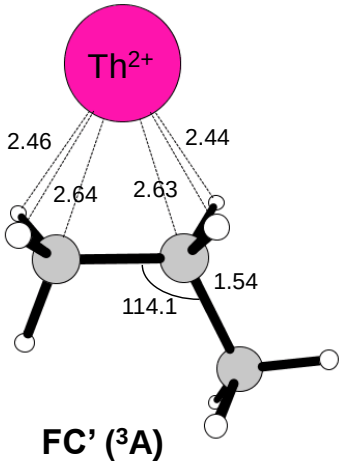
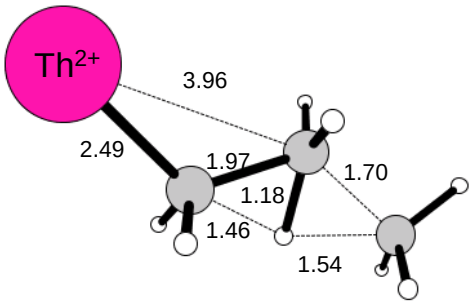

200
100
0
-100
-200
-300
-400
RE (kJ mol-1)
Th2+ (1) + C3H8
170
Th2+ (3) + C3H8
27
-2
TS1
-201
-203
FC'
-243
-331
I
-156
ThC2H42+ (3)+ CH4
-230
ThC2H42+ (1)+ CH4
Reaction Coordinate

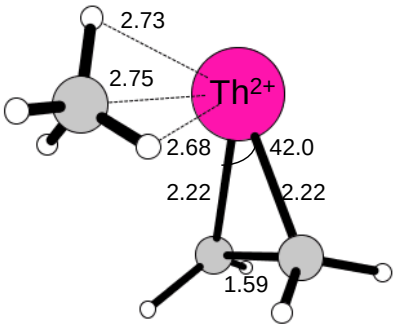
Figure S33



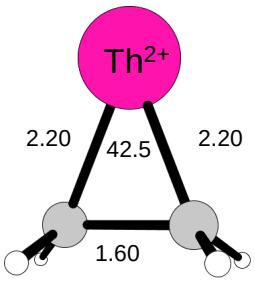
FC' (^{3}A)



TS1 (^{3}A) ***i 952 cm^{-1}***



I (^{1}A)



$ThC_2H_4^{2+}$ (^{1}A)

Figure S34

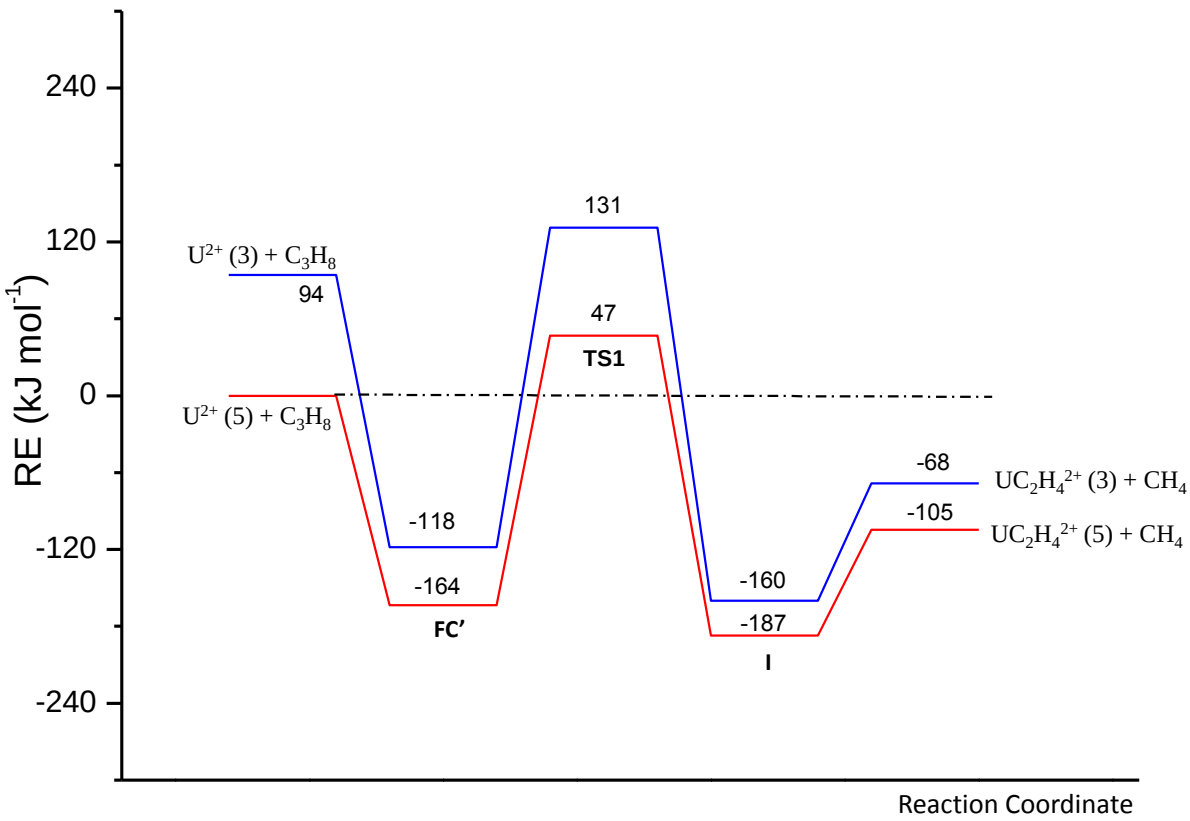

240
120
0
-120
-240
RE (kJ mol-1)
U2+ (3) + C3H8
94
U2+ (5) + C3H8
-118
-164
FC'
131
47
TS1
-160
-187
I
-68
-105
UC2H42+ (3) + CH4
UC2H42+ (5) + CH4
Reaction Coordinate

Figure S35

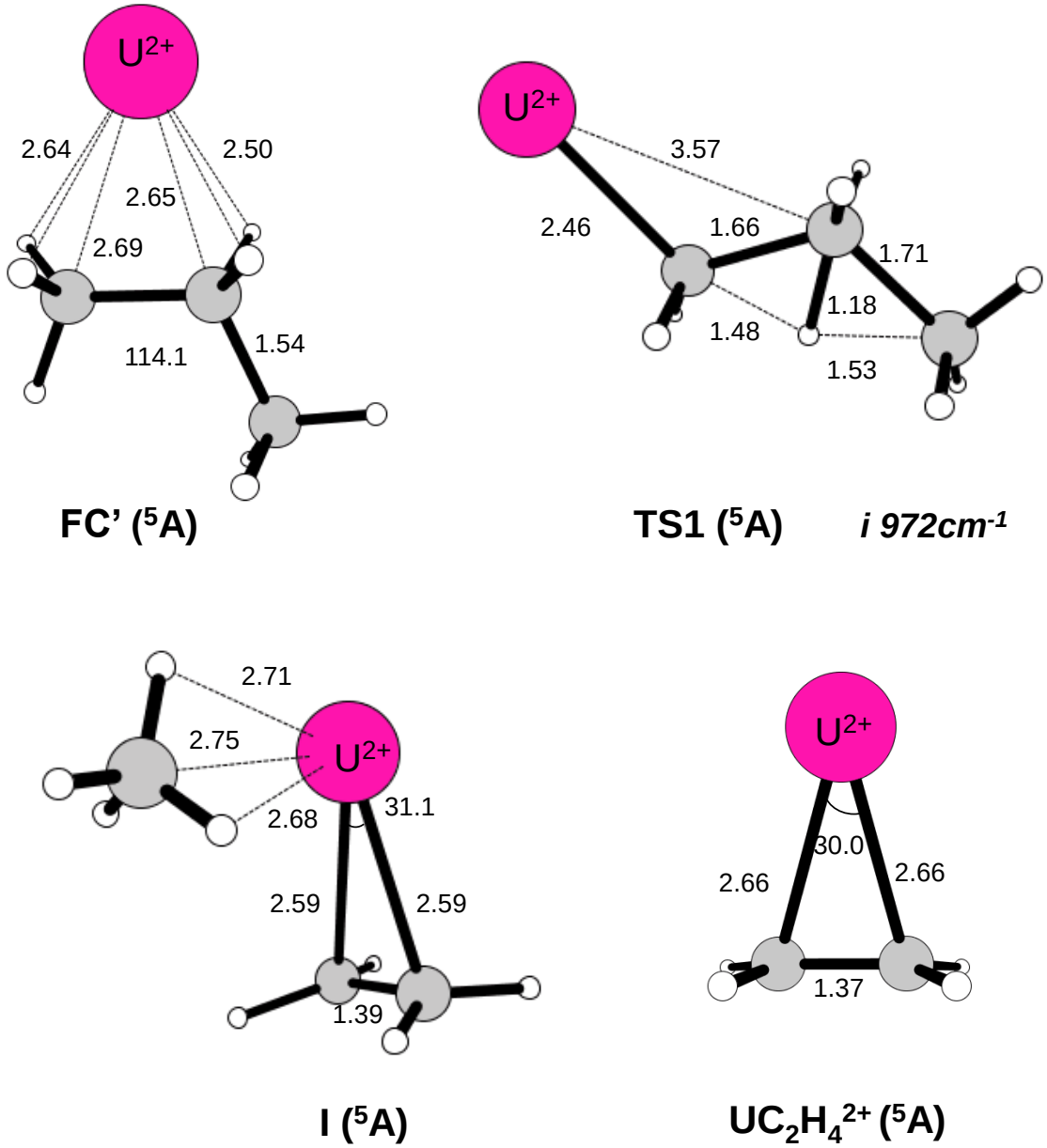

U2+
2.64
2.50
2.65
2.69
114.1
1.54
FC' (5A)
U2+
3.57
2.46
1.66
1.71
1.18
1.48
1.53
TS1 (5A)
i 972cm-1
2.71
2.75
U2+
2.68
31.1
2.59
2.59
1.39
I (5A)
U2+
30.0
2.66
2.66
1.37
UC2H42+ (5A)

Figure S36

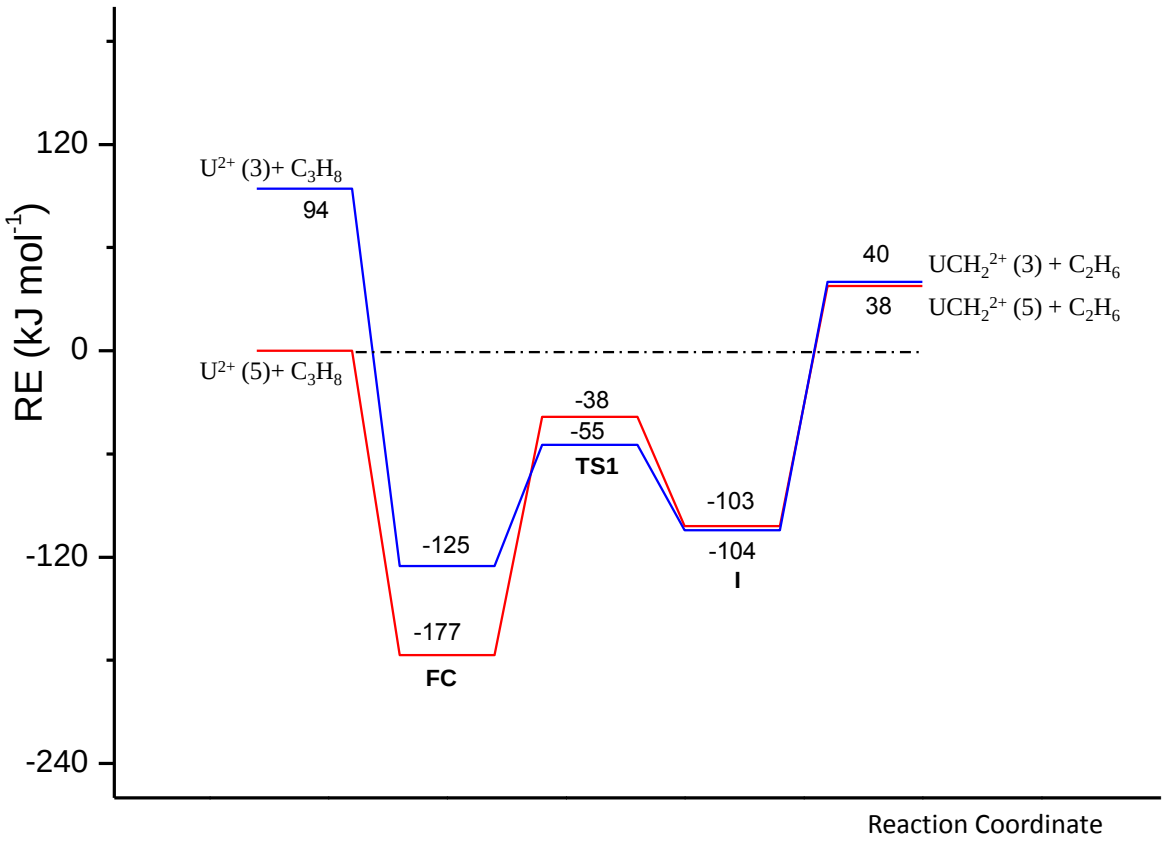

120
0
-120
-240
RE (kJ mol-1)
U2+ (3)+ C3H8
94
U2+ (5)+ C3H8
-125
-177
FC
-38
-55
TS1
-103
-104
I
40
38
UCH22+ (3) + C2H6
UCH22+ (5) + C2H6
Reaction Coordinate

Figure S37

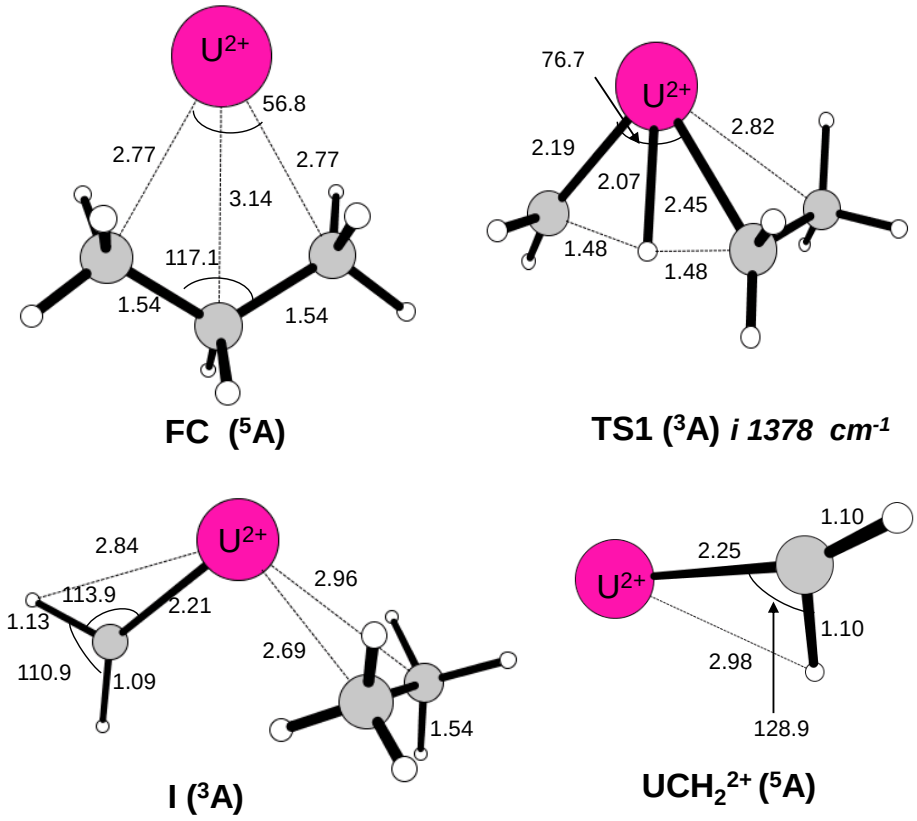
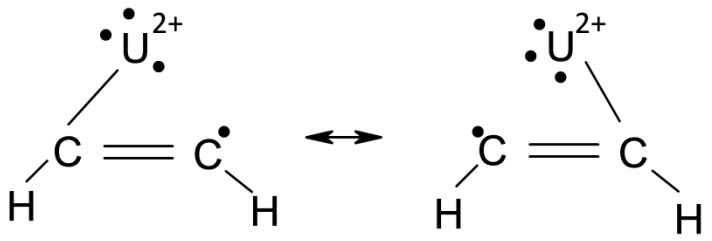

U2+
56.8
2.77
2.77
3.14
117.1
1.54
1.54
FC (5A)
76.7
U2+
2.82
2.19
2.07
2.45
1.48
1.48
TS1 (3A) i 1378 cm-1
2.84
U2+
2.96
113.9
2.21
1.13
2.69
110.9
1.09
1.54
I (3A)
1.10
2.25
U2+
1.10
2.98
128.9
UCH2 2+ (5A)

Figure S38



Scheme 1