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Electronic Supplementary Information

Quantum Chemical Calculations on NbO and its Reaction with Methane: Ground and Excited Electronic States

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Table S1: Optimal geometries (Cartesian coordinates in Å) of the reactants (R), their interacting complex (ICR), first transition state (TS1), intermediate (I), second transition state (TS2), interacting complex of the products (ICP), and products (P) of the NbO + CH_4 → Nb + CH_3OH reaction for the lowest doublet, quartet, and sextet states at the MN15 level theory.

	Doublet	**Quartet**	**Sextet**
R (NbO+CH_4)	Nb 0.0000000000 0.0000000000 0.2704490000 O 0.0000000000 0.0000000000 -1.3860520000 C 0.0000000000 0.0000000000 0.0000000000 H -0.6275790000 0.6275790000 -0.6275790000 H 0.6275790000 -0.6275790000 -0.6275790000 H -0.6275790000 -0.6275790000 0.6275790000 H 0.6275790000 0.6275790000 0.6275790000	Nb 0.0000000000 0.0000000000 0.2731080000 O 0.0000000000 0.0000000000 -1.3996790000 C 0.0000000000 0.0000000000 0.0000000000 H -0.6275790000 0.6275790000 -0.6275790000 H 0.6275790000 -0.6275790000 -0.6275790000 H -0.6275790000 -0.6275790000 0.6275790000 H 0.6275790000 0.6275790000 0.6275790000	Nb 0.0000000000 0.0000000000 0.3215720000 O 0.0000000000 0.0000000000 -1.6480560000 C 0.0000000000 0.0000000000 0.0000000000 H -0.6275790000 0.6275790000 -0.6275790000 H 0.6275790000 -0.6275790000 -0.6275790000 H -0.6275790000 -0.6275790000 0.6275790000 H 0.6275790000 0.6275790000 0.6275790000
ICR	Nb 0.3759490000 -0.0025810000 -0.0012330000 O 2.0367630000 0.0089980000 0.0042970000 C -3.1693070000 0.0033660000 0.0016930000 H -2.7983050000 0.4602320000 -0.9158390000 H -2.8250930000 0.5748740000 0.8634190000 H -2.8116680000 -1.0235350000 0.0735700000 H -4.2570920000 0.0020520000 -0.0151470000	Nb 0.2418260000 0.0647500000 -0.0001350000 O 1.9060010000 -0.2068560000 0.0004390000 C -2.5127710000 -0.0985880000 0.0001920000 H -2.0774460000 -0.6821280000 -0.8210360000 H -2.3105860000 0.9676540000 -0.1425930000 H -2.1103100000 -0.4366260000 0.9630530000 H -3.5879080000 -0.2572900000 0.0014640000	Nb -0.1682040000 0.0001640000 -0.0137870000 O -2.1602510000 -0.0004760000 0.0404180000 C 2.4130310000 -0.0003120000 0.0309290000 H 1.8301730000 0.9301310000 -0.1151410000 H 1.8302000000 -0.9294030000 -0.1238610000 H 2.8495300000 -0.0051340000 1.0248610000 H 3.1902960000 0.0033650000 -0.7295020000
TS1	Nb 0.3816470000 -0.2932190000 -0.0000030000 O 0.3674540000 1.4653070000 0.0000300000 C -1.8523600000 -0.0320750000 0.0000780000 H -2.3977290000 0.2691280000 -0.8939240000 H -1.8540930000 -1.1379270000 -0.0025490000 H -2.3956050000 0.2655530000 0.8965930000 H -0.8255650000 1.0952090000 -0.0007180000	Nb 0.4290530000 -0.2697090000 0.0000040000 O 0.1888640000 1.4971990000 -0.0002660000 C -1.8955760000 -0.1495050000 0.0002070000 H -2.4676240000 0.1071430000 -0.8909570000 H -1.8294290000 -1.2513000000 0.0003070000 H -2.4674110000 0.1073310000 0.8914540000 H -0.9641790000 1.0143120000 -0.0000780000	Nb -0.7416380000 -0.1361890000 -0.0000020000 O 0.6485780000 1.2127810000 0.0000120000 C 2.5437630000 -0.4377730000 0.0000390000 H 1.7438660000 0.4838120000 -0.0010460000 H 1.9661580000 -1.3605850000 -0.0045880000 H 3.1192920000 -0.3097950000 0.9106710000 H 3.1266330000 -0.3052760000 -0.9052910000
I	Nb 0.0180760000 -0.1952210000 0.0000000000 O 1.7945730000 0.3800310000 0.0000020000 C -1.8379640000 0.5030370000 -0.0000130000 H 2.3923970000 1.1305050000 -0.0000570000 H -1.8956130000 -0.1880420000 0.9101540000 H -2.6708370000 1.1911780000 0.0000900000 H -1.8958620000 -0.1880350000 -0.9101440000	Nb 0.0272960000 -0.1285910000 0.0000070000 O 1.8784870000 0.2414920000 0.0000170000 C -1.9800520000 0.3606020000 -0.0001060000 H 2.6035440000 0.8687120000 -0.0004720000 H -2.8627500000 0.9846010000 -0.0008910000 H -2.0039530000 -0.3394790000 -0.8833610000 H -2.0035500000 -0.3371510000 0.8849540000	Nb 0.7130680000 -0.2230200000 -0.0000130000 O -0.2135380000 1.4306730000 0.0000420000 C -2.9267620000 -0.4135460000 -0.0000800000 H -1.1794810000 1.4932910000 0.0009320000 H -2.4029690000 -0.5612290000 0.9305970000 H -2.4043360000 -0.5582890000 -0.9319730000 H -3.9801320000 -0.1940790000 0.0011170000
TS2	Nb -0.6756950000 -0.0656420000 -0.0037910000 O 1.0583660000 0.9272140000 0.1167620000 C 1.9291940000 -0.6206000000 -0.0130900000 H 1.3117390000 1.4618970000 -0.6543540000	Nb -0.7006710000 -0.0779720000 -0.0039680000 O 1.0096310000 0.9185630000 0.1181010000 C 2.1048600000 -0.5736110000 -0.0149550000 H 1.1828910000 1.4806320000 -0.6604770000	Nb -0.8235130000 -0.0682340000 -0.0052700000 O 1.0512150000 0.6655230000 0.1195440000 C 2.6212460000 -0.3889350000 -0.0215040000 H 1.2659200000 1.3457850000 -0.5346890000

	H 2.8853950000 -0.1186680000 -0.0741380000 H 1.7767220000 -1.1421680000 0.9226560000 H 1.6875610000 -1.2038340000 -0.8942870000	H 2.9787390000 0.0422790000 -0.1640700000 H 2.0051320000 -1.0054630000 0.9688110000 H 1.8545210000 -1.2274240000 -0.8366680000	H 3.3911900000 0.2908150000 0.3096060000 H 2.3363260000 -1.1590660000 0.6770580000 H 2.6334030000 -0.6704910000 -1.0632400000
ICP	Nb 0.8217940000 -0.0431970000 0.0000270000 O -1.2200750000 0.4874470000 -0.0006200000 C -2.4086560000 -0.3261440000 0.0001610000 H -1.4290610000 1.4317700000 0.0021470000 H -2.9937890000 -0.1198280000 -0.8935520000 H -2.0699840000 -1.3570190000 -0.0047240000 H -2.9881860000 -0.1265550000 0.8990270000	Nb 0.8117630000 -0.0452880000 0.0033250000 O -1.2445670000 0.5552100000 -0.0883890000 C -2.3477350000 -0.3655770000 0.0209630000 H -1.4268810000 1.4055180000 0.3384830000 H -3.2321180000 0.0787410000 -0.4305370000 H -2.0548720000 -1.2565260000 -0.5262430000 H -2.5254500000 -0.6191330000 1.0633100000	Nb 0.8218430000 -0.0437700000 0.0035370000 O -1.3303500000 0.6185390000 -0.1100210000 C -2.3134500000 -0.4123370000 0.0234090000 H -1.5273090000 1.3630430000 0.4708910000 H -3.2996070000 -0.0283010000 -0.2363420000 H -2.0301970000 -1.1961470000 -0.6745040000 H -2.3149480000 -0.8182970000 1.0346620000
P (Nb+ CH_3OH)	Nb 0.0000000000 0.0000000000 0.0000000000 O -0.7426320000 0.1225970000 0.0000000000 C 0.6615670000 -0.0209960000 0.0000000000 H -1.1571160000 -0.7440210000 0.0000000000 H 1.0863940000 0.9799760000 -0.0000010000 H 1.0211870000 -0.5453750000 0.8891790000 H 1.0211870000 -0.5453760000 -0.8891780000	Nb 0.0000000000 0.0000000000 0.0000000000 O -0.7426320000 0.1225970000 0.0000000000 C 0.6615670000 -0.0209960000 0.0000000000 H -1.1571160000 -0.7440210000 0.0000000000 H 1.0863940000 0.9799760000 -0.0000010000 H 1.0211870000 -0.5453750000 0.8891790000 H 1.0211870000 -0.5453760000 -0.8891780000	Nb 0.0000000000 0.0000000000 0.0000000000 O -0.7426320000 0.1225970000 0.0000000000 C 0.6615670000 -0.0209960000 0.0000000000 H -1.1571160000 -0.7440210000 0.0000000000 H 1.0863940000 0.9799760000 -0.0000010000 H 1.0211870000 -0.5453750000 0.8891790000 H 1.0211870000 -0.5453760000 -0.8891780000

Table S2: Harmonic vibrational frequencies (cm^{-1}) of the reactants (R), their interacting complex (ICR), first transition state (TS1), intermediate (I), second transition state (TS2), interacting complex of the products (ICP), and products (P) of the NbO + CH_4 → Nb + CH_3OH reaction for the lowest doublet, quartet, and sextet states at the MN15 level theory.

	R		ICR	TS1	I	TS2	ICP	P	
Doublet	NbO	CH_4	33	-1659	154	-877	51	Nb	CH_3OH
	1095	1325	33	135	201	143	201		285
		1325	40	253	475	206	348		1051
		1325	157	303	494	435	384		1115
		1546	162	523	504	535	1023		1169
		1546	1082	724	648	685	1064		1341
		3066	1309	934	725	761	1151		1471
		3183	1323	958	735	931	1330		1491
		3183	1324	1237	1108	1204	1450		1501
		3183	1537	1396	1413	1419	1484		3039
			1538	1441	1443	1425	1484		3091
			3037	2025	2568	3107	3087		3157
			3151	2946	2612	3232	3175		3909
			3153	3096	3246	3254	3201		
			3170	3146	3942	3735	3796		
Quartet	NbO	CH_4	14	-1706	130	-847	80	Nb	CH_3OH
	1051	1325	37	133	161	101	153		285
		1325	129	299	405	134	324		1051
		1325	300	479	445	542	359		1115
		1546	324	480	459	557	1019		1169
		1546	1022	651	522	678	1051		1341
		3066	1317	904	660	700	1157		1471
		3183	1320	1042	710	859	1306		1491
		3183	1321	1207	1123	1101	1448		1501
		3183	1531	1428	1402	1408	1476		3039
			1537	1445	1413	1422	1487		3091
			2971	1845	2744	3147	3090		3157
			3074	2960	2791	3284	3178		3909
			3097	3094	3237	3302	3196		
			3177	3151	3956	3662	3766		

Sextet	NbO	CH_4	59	-1307	36	-892	89	Nb	CH_3OH
	645	1325	74	53	55	74	128		285
		1325	188	91	114	118	317		1051
		1325	257	349	161	458	381		1115
		1546	617	433	205	468	1047		1169
		1546	655	667	278	679	1060		1341
		3066	1178	720	583	703	1161		1471
		3183	1347	1146	622	856	1316		1491
		3183	1369	1235	696	1019	1453		1501
		3183	1454	1287	1379	1413	1477		3039
			1595	1424	1384	1417	1485		3091
			2863	1428	3138	3138	3069		3157
			2971	3074	3305	3298	3146		3909
			3136	3191	3325	3302	3174		
			3194	3226	3796	3794	3844		

Table S3: Relative energies (kcal/mol) of the reactants (R), their interacting complex (ICR), first transition state (TS1), intermediate (I), second transition state (TS2), interacting complex of the products (ICP), and products (P) of the $NbO + CH_4 \rightarrow Nb + CH_3OH$ reaction for the lowest doublet, quartet, and sextet states at the MN15 level theory.

	Doublet	Quartet	Sextet
R	17.2	0.0	89.5
ICR	15.6	-4.5	77.4
TS1	43.9	43.4	92.0
I	8.0	-4.7	68.4
TS2	114.1	91.4	93.2
ICP	94.1	70.0	68.4
P	116.3	96.8	89.3

Table S4: T1 diagnostics obtained at the CCSD level for the reactants (R), their interacting complex (ICR), first transition state (TS1), intermediate (I), second transition state (TS2), interacting complex of the products (ICP), and products (P) of the $NbO + CH_4 \rightarrow Nb + CH_3OH$ reaction for the lowest doublet, quartet, and sextet states.

	Doublet	Quartet	Sextet
R	0.03603501	0.03719335	0.03324193
ICR	0.02726693	0.02806977	0.02024265
TS1	0.03304312	0.04217312	0.04048609
I	0.02288469	0.02150895	0.02630955
TS2	0.05607254	0.07290710	0.05987077
ICP	0.04323861	0.05051467	0.01997703
P	0.02446875	0.02253010	0.01015360

Table S5: Coefficients of the two most dominant configurations at the CASSCF level of theory for the reactants (R), their interacting complex (ICR), first transition state (TS1), intermediate (I), second transition state (TS2), interacting complex of the products (ICP), and products (P) of the $NbO + CH_4 \rightarrow Nb + CH_3OH$ reaction for the lowest doublet, quartet, and sextet states.

	Doublet	Quartet	Sextet
R	0.92 / -0.25	0.96 / -0.09	0.98 / -0.09
ICR	0.91 / -0.18	0.96 / -0.09	0.98 / -0.08
TS1	0.84 / -0.38	0.96 / -0.09	0.97 / -0.08
I	0.97 / 0.12	0.98 / 0.05	0.99 / -0.06
TS2	0.93 / -0.18	0.94 / -0.20	0.97 / -0.12
ICP	0.89 / -0.30	0.98 / 0.07	0.98 / -0.06
P	0.59 / -0.56	0.99 / 0.02	1.00 / 0.00

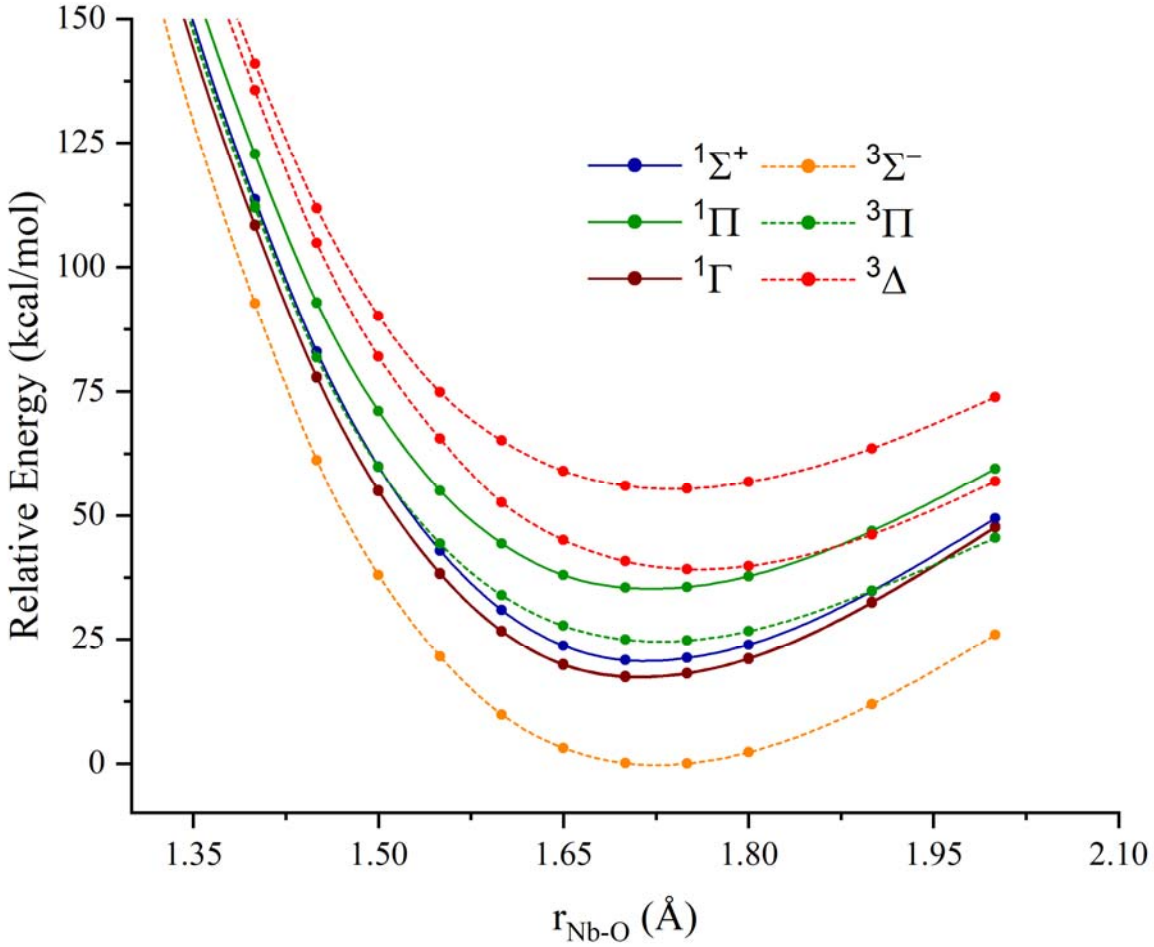

Figure S1: MRCI potential energy curves for ground state and lowest six excited electronic states of NbO^-.

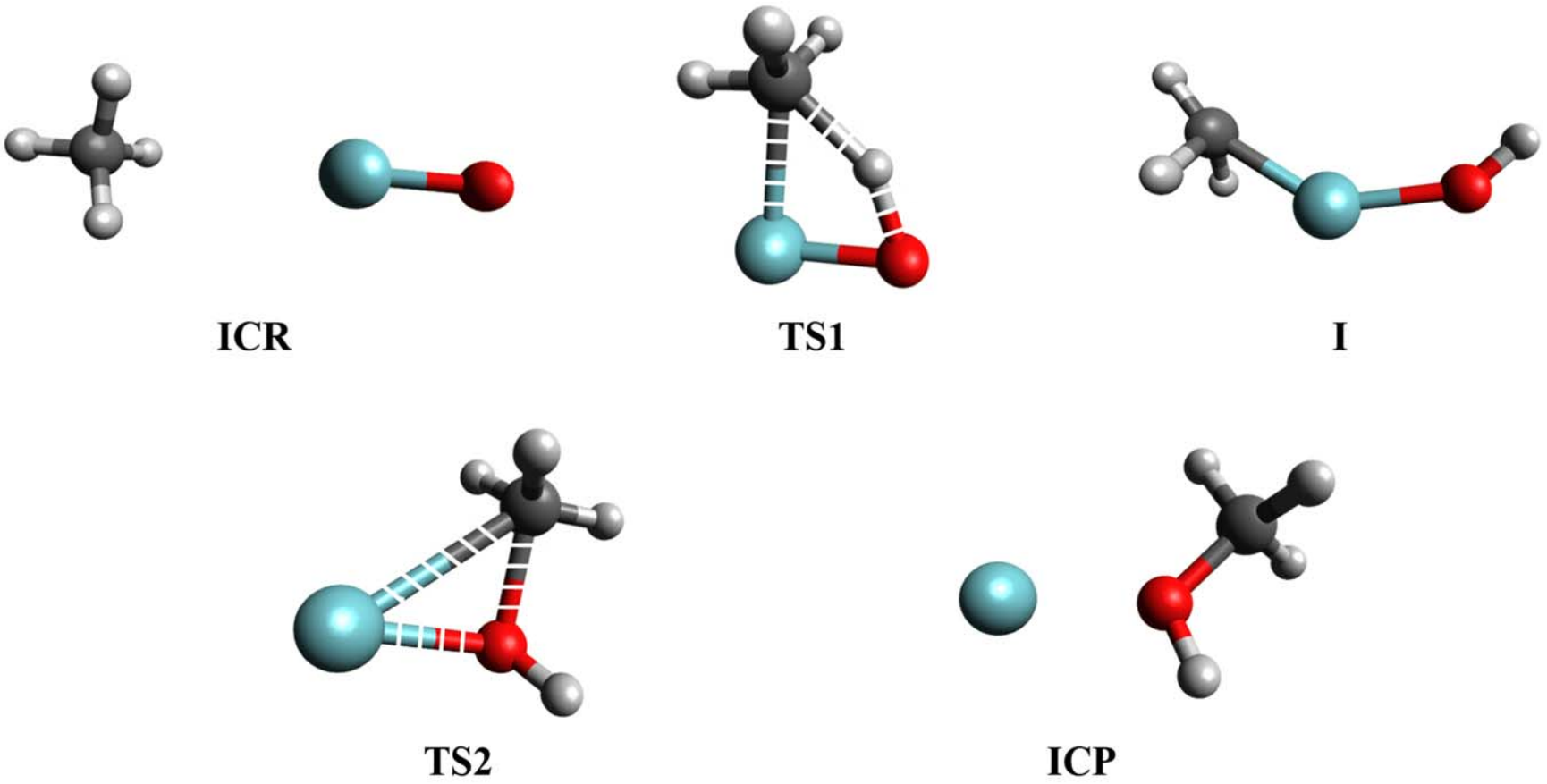

Figure S2: DFT/MN15 structures for intermediates and transition states of all steps along $NbO+CH_4 \rightarrow Nb+CH_3OH$ reaction pathway for the lowest doublet spin state. The [2+2] mechanism is followed in this case.

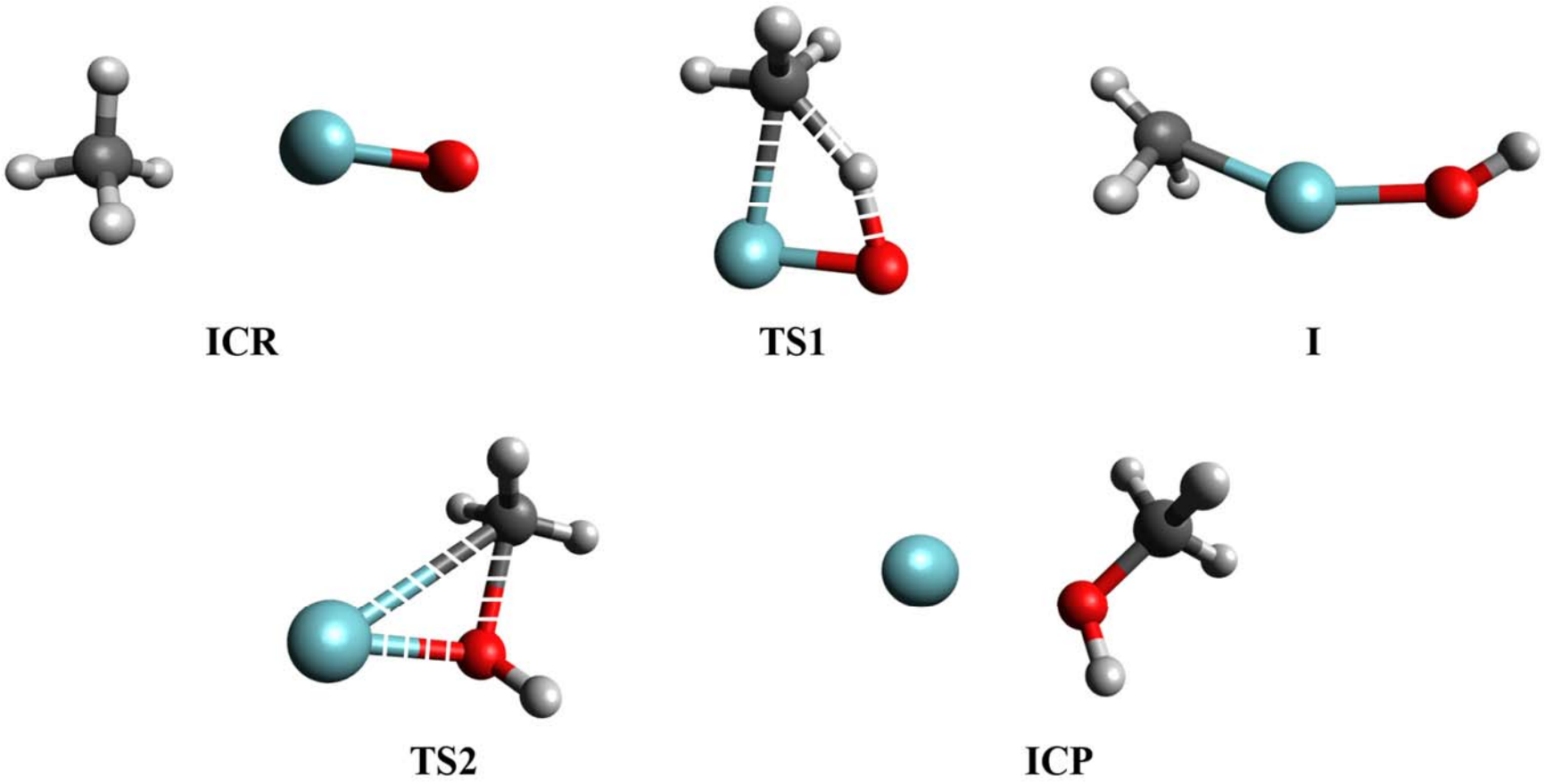

Figure S3: DFT/MN15 structures for intermediates and transition states of all steps along $NbO+CH_4 \rightarrow Nb+CH_3OH$ reaction pathway for the lowest quartet spin state. The [2+2] mechanism is followed in this case.

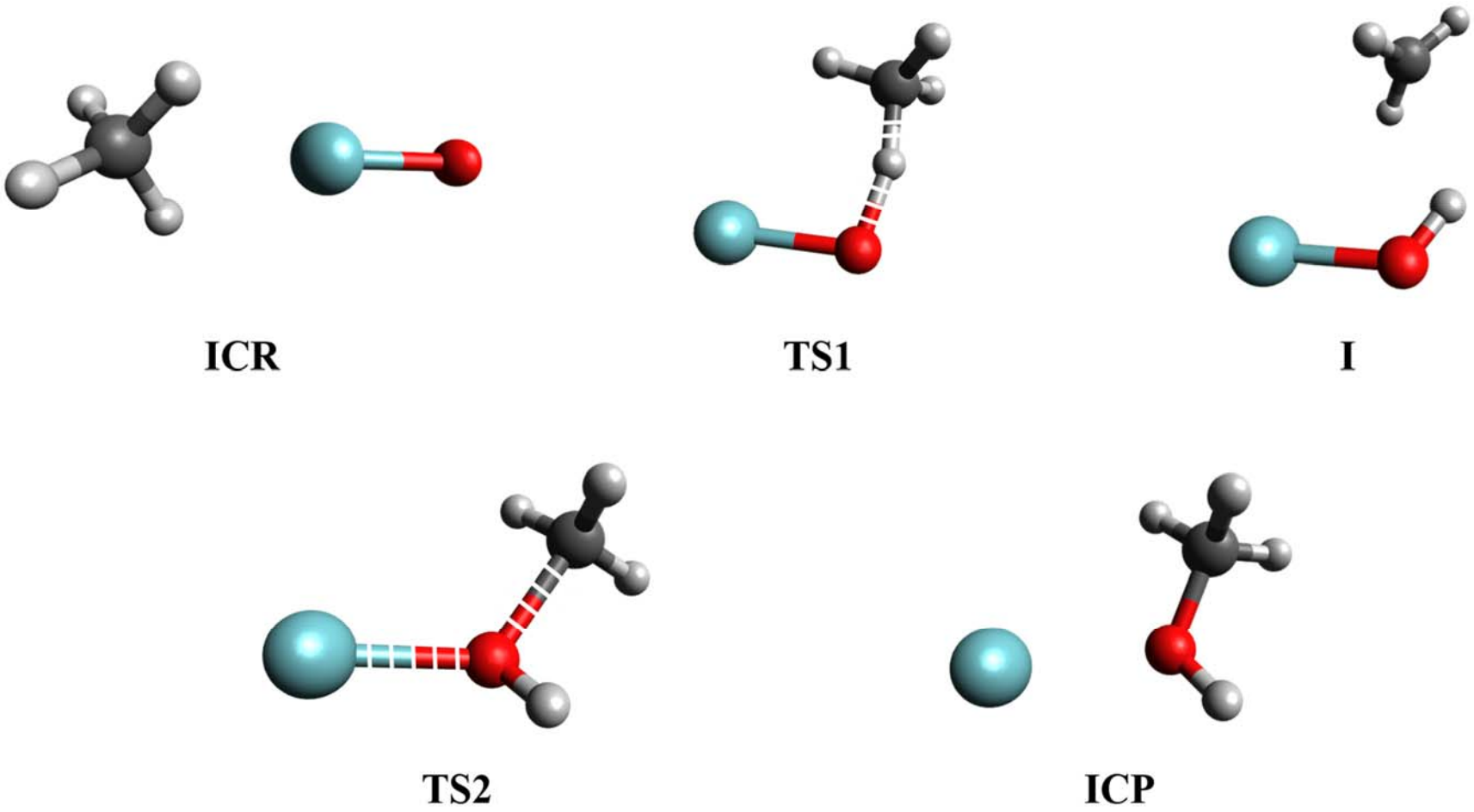

Figure S4: DFT/MN15 structures for intermediates and transition states of all steps along $NbO+CH_4 \rightarrow Nb+CH_3OH$ reaction pathway for the lowest sextet spin state. The radical mechanism is followed in this case.

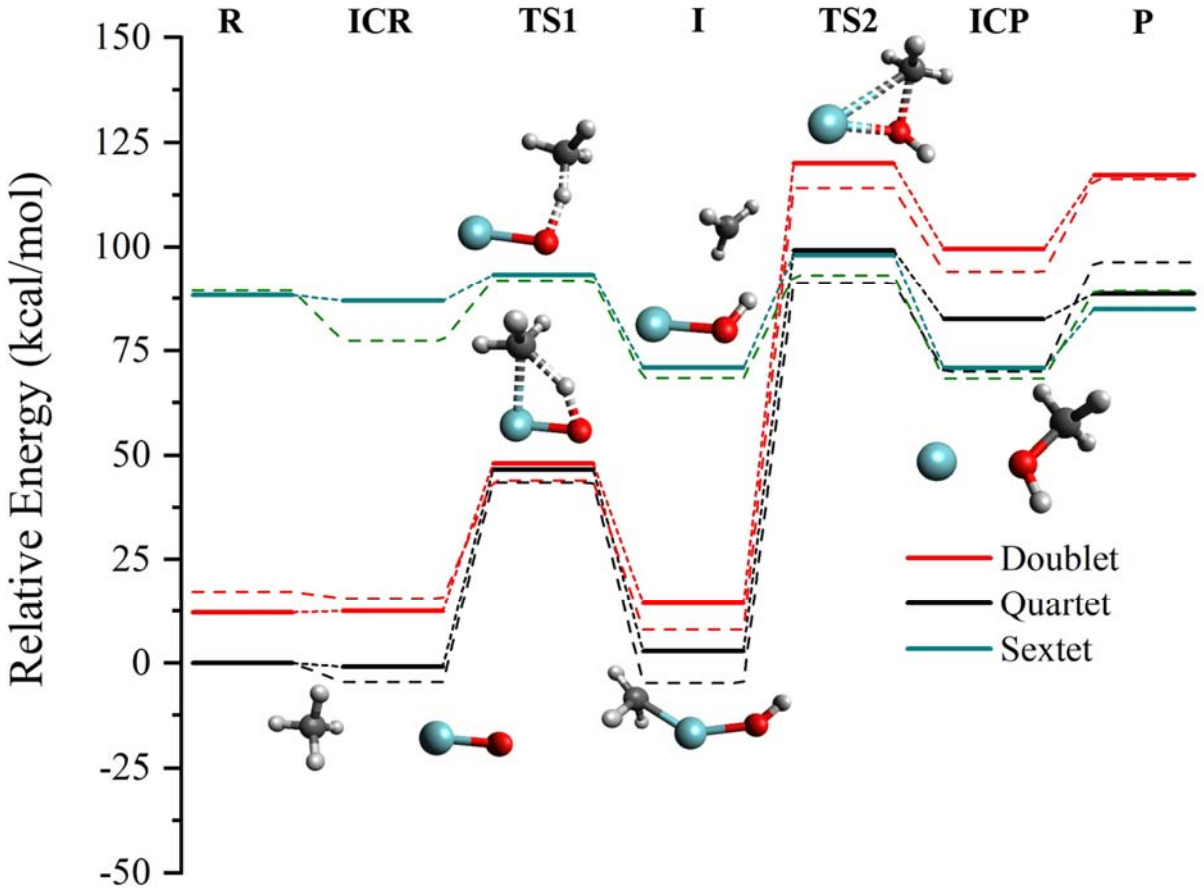

Figure S5: Comparison of the CCSD(T)//DFT/MN15 (solid and short-dashed lines) and MN15 (dashed-lines) potential energy diagrams for the $NbO+CH_4 \rightarrow Nb+CH_3OH$ reaction pathway for the lowest doublet, quartet, and sextet spin states.