

Insights into Facile Methane Activation by a Spin Forbidden Reaction with Ta⁺ Ions in the Gas Phase

Yang Liu,^a Milan Ončák,^{b,*} Tucker W. R. Lewis,^c Marcel Meta,^d Shaun G. Ard,^c Nicholas S.
Shuman,^{c,*} Jennifer Meyer,^d Albert A. Viggiano,^c and Hua Guo^{a,*}

^a*Department of Chemistry and Chemical Biology, Center for Computational Chemistry,
University of New Mexico, Albuquerque, New Mexico 87131, United States*

^b*Universität Innsbruck, Institut für Ionenphysik und Angewandte Physik, Technikerstraße 25,
6020 Innsbruck, Austria*

^c*Air Force Research Laboratory, Space Vehicles Directorate, Kirtland Air Force Base, New
Mexico 87117, United States*

^d*RPTU Kaiserslautern-Landau, Fachbereich Chemie und Forschungszentrum OPTIMAS, Erwin-
Schrödinger Str. 52, 67663 Kaiserslautern, Germany*

Supporting Information

*: corresponding authors: Milan.Oncak@uibk.ac.at, nicholas.shuman.1@spaceforce.mil, hguo@unm.edu

Table S1. ZPE-corrected energies (eV) and vibrational harmonic frequencies (cm⁻¹) of the stationary points along the reaction Ta⁺ + CH₄ → TaCH₂⁺ + H₂

Species	Method	<i>E</i>	Frequencies											
			1	2	3	4	5	6	7	8	9	10	11	12
⁵ Ta ⁺ + CH ₄	PES ^a	0	1308	1308	1308	1529	1529	3037	3143	3143	3143			
	DFT ^b	0	1303	1303	1303	1522	1522	3028	3144	3144	3144			
	DFT ^c	0												
	CC ^d	0												
	Expt. ^e	0												
³ Ta ⁺ + CH ₄	PES ^a	0.404	1308	1308	1308	1540	1540	3018	3230	3230	3230			
	DFT ^b	0.387	1303	1303	1303	1522	1522	3028	3144	3144	3144			
	DFT ^c	0.402												
	CC ^d	0.393												
	Expt. ^e	0.428												
¹ Ta ⁺ + CH ₄	PES ^a	0.593	1303	1303	1303	1513	1513	3077	3103	3103	3103			
	DFT ^b	0.584	1303	1303	1303	1522	1522	3028	3144	3144	3144			
	DFT ^c	1.900												
	CC ^d	1.328												
	Expt. ^e	1.216												
⁵ INT1	PES ^a	-0.634	144	209	238	1147	1313	1344	1451	1507	2838	2885	3110	3199
	DFT ^b	-0.611	71	209	491	1156	1289	1374	1454	1561	2670	3016	3107	3173
	DFT ^c	-0.561												
	CC ^d	-0.691												
³ INT1	PES ^a	-0.322	173	233	640	1046	1354	1397	1428	1521	2499	2625	3043	3129
	DFT ^b	-0.333	209	277	673	1094	1335	1341	1485	1552	2482	2671	3073	3149
	DFT ^c	-0.232												
	CC ^d	-0.417												
¹ INT1	PES ^a	-0.098	96	174	423	1045	1277	1398	1423	1523	2523	2636	2975	3062
	DFT ^b	-0.118	140	164	599	1103	1322	1362	1447	1571	2542	2804	3080	3158
	DFT ^c	0.840												
	CC ^d	-0.176												
⁵ INT2	PES ^a	0.743	133	153	269	380	449	966	1326	1343	1768	3004	3150	3170
	DFT ^b	0.530	177	224	281	331	425	913	1323	1349	1620	2973	3127	3173
	DFT ^c	0.631												
	CC ^d	0.642												
³ INT2	PES ^a	-1.805	251	366	349	521	621	1147	1318	1344	1890	2887	2998	3040
	DFT ^b	-1.802	260	261	340	554	612	1152	1314	1321	1951	2938	3028	3054
	DFT ^c	-1.637												
	CC ^d	-1.736												
¹ INT2	PES ^a	-1.619	288	299	379	527	645	1152	1317	1373	1929	2887	2968	3013
	DFT ^b	-1.612	262	271	321	536	639	1153	1304	1328	1964	2913	2992	3084
	DFT ^c	-1.440												
	CC ^d	-1.540												
⁵ INT3	PES ^a	1.829	124	168	393	462	530	635	662	809	1375	1661	3072	3082
	DFT ^b	1.826	101	172	405	584	629	658	723	991	1298	1509	3053	3155
	DFT ^c	2.037												
	CC ^d	2.083												
³ INT3	PES ^a	-0.738	125	350	385	594	673	716	806	1323	1946	2008	3036	3141
	DFT ^b	-0.731	151	311	325	597	647	727	808	1311	1949	1956	3041	3141

			-0.488											
	CC ^d		-0.595											
¹ INT3	PES ^a	-1.678	214	492	543	713	720	782	946	1314	1922	1939	2547	3157
	DFT ^b	-1.665	283	538	562	659	733	763	894	1341	1957	1973	2629	3213
	DFT ^c	1.420												
	CC ^d	-1.823												
⁵ INT4	PES ^a	0.269	197	331	394	556	633	782	913	1357	1422	3009	3099	3479
	DFT ^b	0.246	164	242	405	499	637	730	871	1310	1339	3038	3149	3413
	DFT ^c	0.401												
	CC ^d	0.293												
³ INT4	PES ^a	-0.511	<i>i</i> 160	319	412	685	825	869	996	1325	1595	2774	3517	3937
	DFT ^b	-0.571	228	309	398	565	655	734	863	1079	1358	2631	3218	3806
	CC ^d	-0.686												
³ INT5	PES ^a	-0.859	180	408	460	733	750	810	1085	1288	1704	2781	3002	3163
	DFT ^b	-0.861	188	318	519	702	735	837	1068	1272	1686	2748	3041	3138
	DFT ^c	-0.688												
	CC ^d	-0.901												
¹ INT4	PES ^a	-0.576	353	409	436	501	719	740	851	1339	1498	2622	3047	3241
	DFT ^b	-0.609	236	360	521	645	789	818	985	1301	1570	2725	3092	3213
	CC ^d	-0.748												
¹ INT5	PES ^a	-0.605	167	389	588	728	833	871	1034	1281	1727	2739	3070	3157
	DFT ^b	-0.614	174	321	546	736	738	843	1044	1269	1672	2777	3042	3140
	DFT ^c	0.168												
	CC ^d	-0.660												
⁵ SP1	PES ^a	0.735	<i>i</i> 221	<i>i</i> 111	227	383	424	1046	1362	1369	1935	3098	3246	3287
	DFT ^b	0.732	<i>i</i> 315	71	251	338	359	1016	1363	1376	1879	3041	3222	3237
	DFT ^c	0.832												
	CC ^d	0.779												
³ SP1	PES ^a	-0.362	<i>i</i> 787	366	420	912	1065	1246	1319	1389	1693	1886	3091	3171
	DFT ^b	-0.370	<i>i</i> 848	381	508	917	1020	1181	1366	1411	1747	1841	3043	3114
	DFT ^c	-0.190												
	CC ^d	-0.454												
¹ SP1	PES ^a	-0.164	<i>i</i> 627	273	381	1018	1066	1264	1285	1391	1638	1802	3048	3188
	DFT ^b	-0.161	<i>i</i> 692	346	425	954	1067	1219	1353	1389	1728	1827	3044	3116
	DFT ^c	1.361												
	CC ^d	-0.221												
⁵ SP2	PES ^a	2.093	<i>i</i> 834	98	168	326	652	677	732	840	1319	1688	3017	3212
	DFT ^b	2.090	<i>i</i> 854	345	351	443	539	626	698	849	1289	1673	3054	3154
	DFT ^c	2.300												
	CC ^d	2.128												
³ SP2	PES ^a	-0.601	<i>i</i> 482	313	341	474	686	747	823	1299	1903	1959	3021	3178
	DFT ^b	-0.597	<i>i</i> 497	304	387	452	666	691	803	1299	1871	1942	3046	3150
	DFT ^c	-0.227												
	CC ^d	-0.481												
¹ SP2	PES ^a	-0.872	<i>i</i> 759	366	632	705	739	847	1262	1344	1823	1991	1998	3171
	DFT ^b	-0.863	<i>i</i> 1018	410	672	725	740	852	1332	1367	1861	1968	1980	3219
	DFT ^c	-0.614												
	CC ^d	-1.064												
⁵ SP3	PES ^a	2.009	<i>i</i> 111	75	233	396	500	536	670	812	1298	1906	3064	3168

	DFT ^b	1.996	<i>i</i> 163	138	298	298	441	515	663	735	1256	1919	3042	3166
	DFT ^c	2.224												
	CC ^d	2.162												
³ SP3	PES ^a	0.141	<i>i</i> 1052	<i>i</i> 292	415	563	599	710	892	1440	1772	1925	3025	3180
	DFT ^b	0.145	<i>i</i> 1188	344	374	493	535	670	817	1324	1840	1895	2993	3152
	DFT ^c	0.027												
	CC ^d	0.323												
¹ SP3	PES ^a	-0.542	<i>i</i> 846	313	533	586	702	810	843	1335	1849	2084	2642	3298
	DFT ^b	-0.563	<i>i</i> 1024	358	523	539	715	819	870	1334	1809	2007	2613	3217
	DFT ^c	0.329												
	CC ^d	-0.701												
⁵ SP4	PES ^a	1.216	<i>i</i> 685	205	420	444	974	987	1216	1371	1523	1790	3038	3089
	DFT ^b	1.214	<i>i</i> 770	135	414	513	947	1037	1190	1343	1545	1789	3066	3173
	DFT ^c	1.431												
	CC ^d	1.233												
³ SP4	PES ^a	-0.888	<i>i</i> 573	240	562	734	846	922	1040	1289	1869	2099	3003	3148
	DFT ^b	-0.884	<i>i</i> 507	246	569	737	859	904	1049	1282	1865	2046	3042	3138
	DFT ^c	-0.686												
	CC ^d	-0.940												
¹ SP4	PES ^a	-0.632	<i>i</i> 607	231	646	724	896	993	1034	1292	1933	1974	3057	3141
	DFT ^b	-0.637	<i>i</i> 528	239	598	740	863	939	1035	1279	1867	2031	3041	3137
	DFT ^c	0.223												
	CC ^d	-0.701												
⁵ TaCH ₂ ⁺ + H ₂	PES ^a	0.764	398	642	701	1295	3104	3188		4360				
	DFT ^b	0.773	441	634	723	1306	3050	3129		4356				
	DFT ^c	0.854												
	CC ^d	0.819												
³ TaCH ₂ ⁺ + H ₂	PES ^a	-0.204	475	707	872	1327	2688	3219		4439				
	DFT ^b	-0.177	569	701	883	1345	2576	3215		4356				
	DFT ^c	0.253												
	CC ^d	-0.297												
	Expt. ^f	-0.10 ±0.02												
¹ TaCH ₂ ⁺ + H ₂	PES ^a	-0.171	531	729	902	1380	2537	3226		4403				
	DFT ^b	-0.162	562	723	896	1355	2571	3212		4356				
	CC ^d	-0.302												
⁵ HTaCH ⁺ + H ₂	PES ^a	1.869	496	542	599	751	1961	3162		4360				
	DFT ^b	1.941	389	506	507	731	1943	3172		4356				
	CC ^d	1.990												
³ HTaCH ⁺ + H ₂	PES ^a	0.860	495	634	656	913	2040	3272		4439				
	DFT ^b	0.864	595	685	707	909	1962	3188		4356				
	DFT ^c	0.969												
	CC ^d	0.793												
¹ HTaCH ⁺ + H ₂	PES ^a	0.282	621	770	799	1069	1963	3180		4403				
	DFT ^b	0.284	567	752	757	1020	1931	3188		4356				
	DFT ^c	0.398												
	CC ^d	0.017												

^a This work, PES. ^b This work, B3LYP/DZ. ^c B3LYP/HW+/6-311++G(3df,3p).¹ ^d CCSD(T)//B3LYP.² ^e Experimental values.³ ^f Experimental exothermicity.¹

Figure S1. Comparison of geometries in internal coordinates (distances in Å and angles in degrees) for the stationary points on the quintet state. The values correspond to PIP-NN PES, B3LYP/DZ, and B3LYP/HW+/6-311++G(3df,3p)¹ from top to bottom.

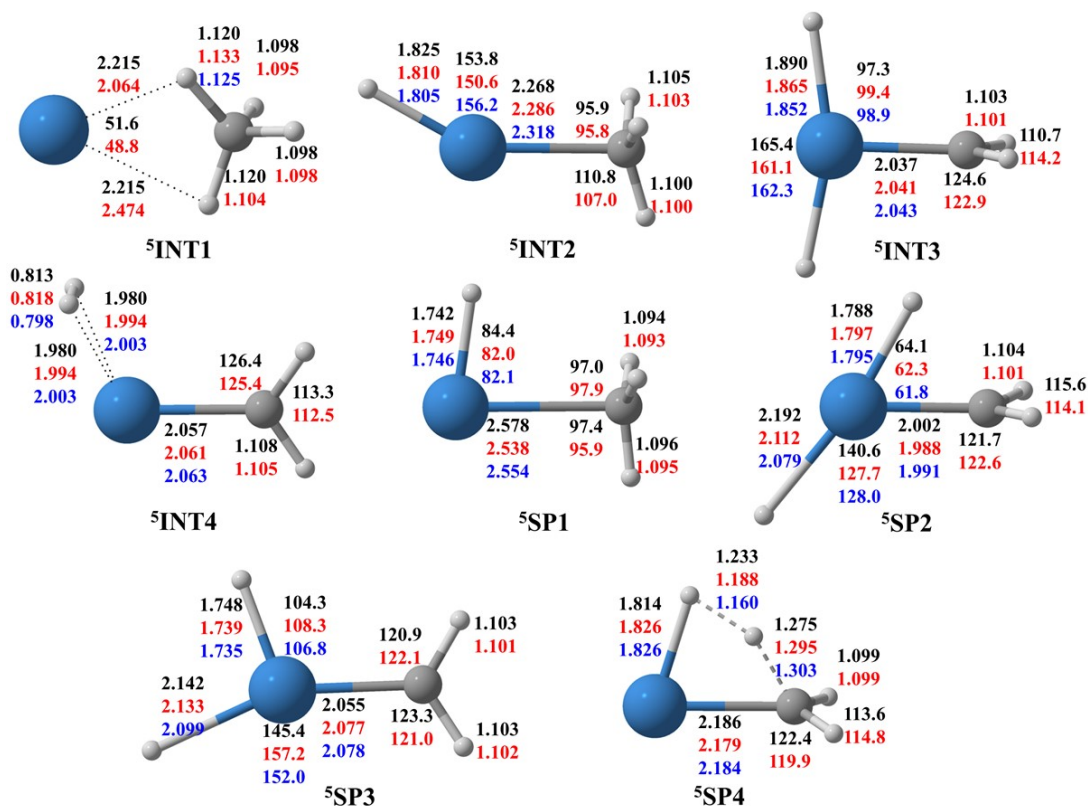


Figure S2. Similar to Figure S1 but for the triplet state.

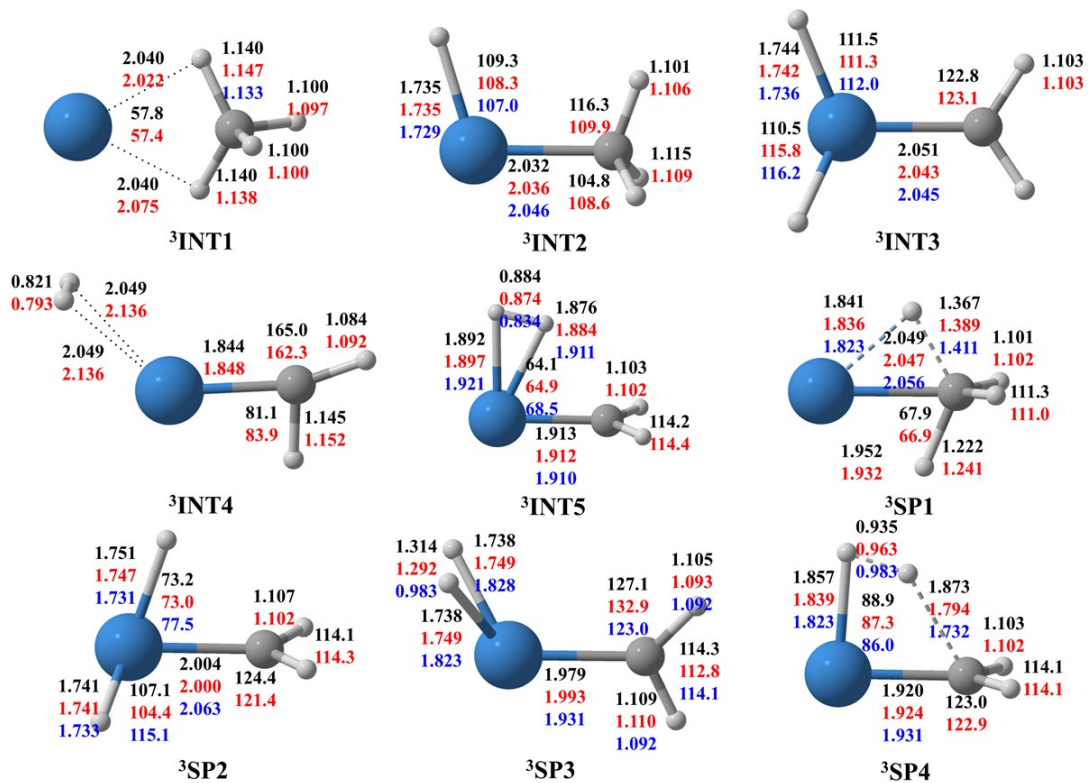


Figure S3. Similar to Figure S1 but for the singlet state.

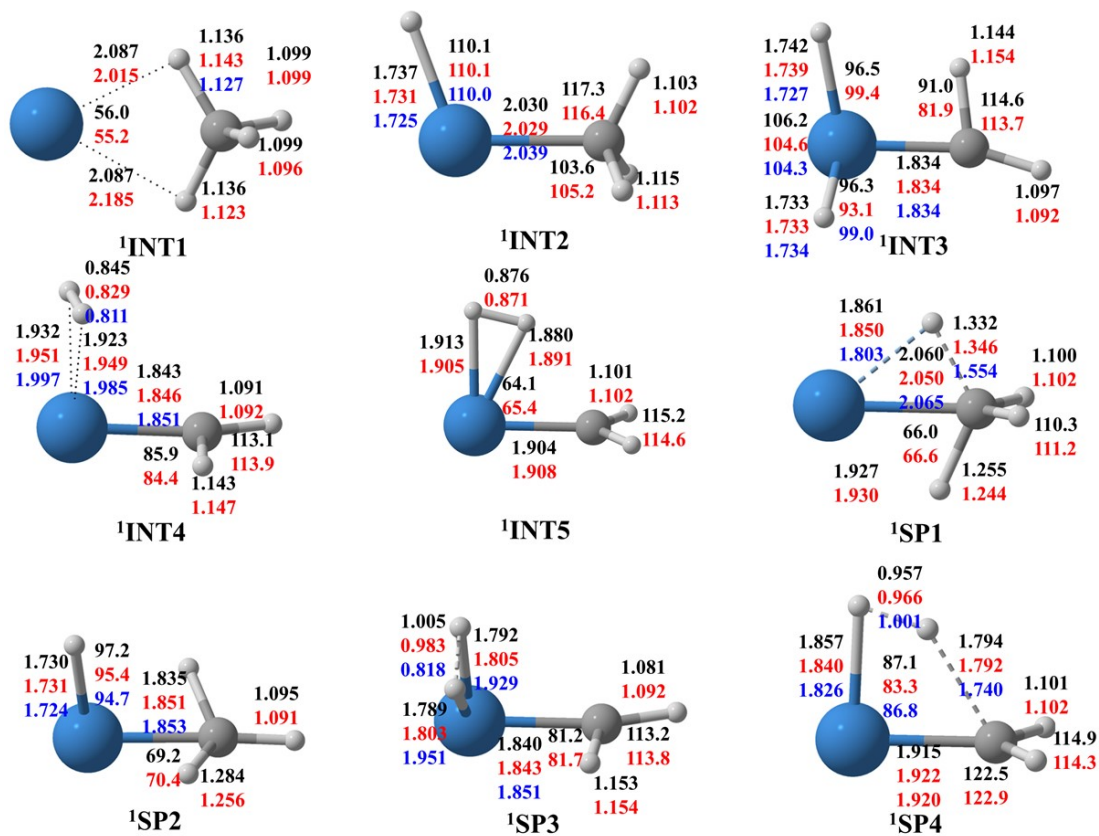


Figure S4. (a) Fitting error ($E_{\text{fit}} - E_{\text{target}}$, in eV) of the quintet, triplet, and singlet PESs as a function of the DFT energy (eV). (b) Distributions of the absolute fitting errors.

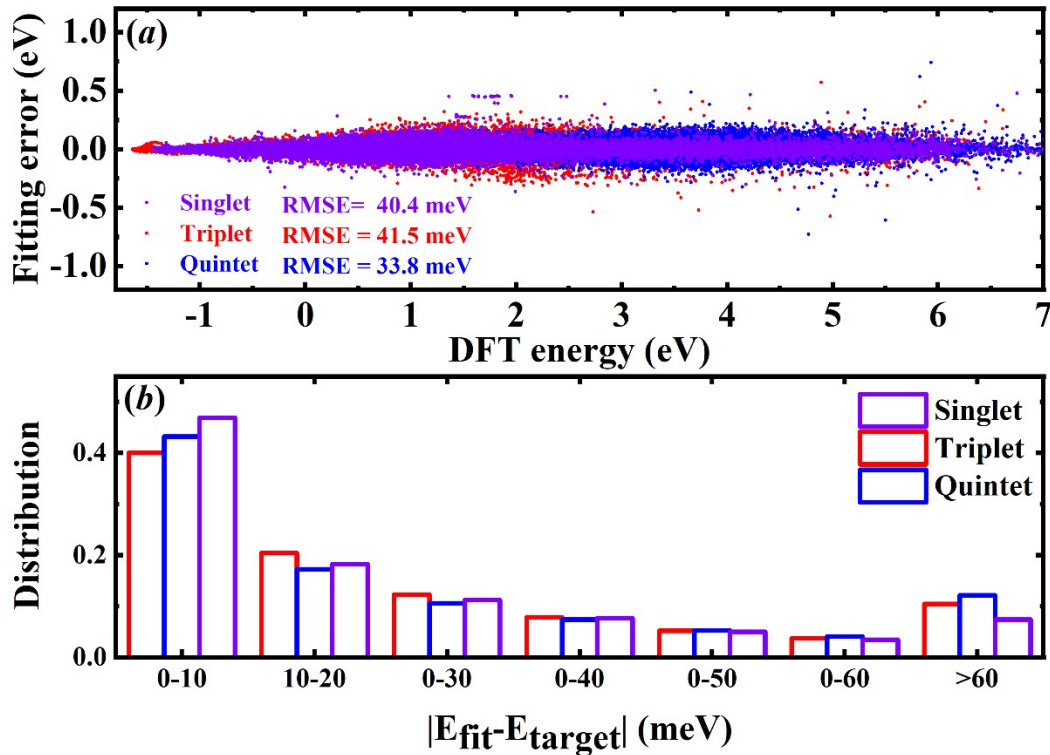


Figure S5. MEPs of the quintet state along (a) SP1, (b) SP2, (c) SP3, and (d) SP4.

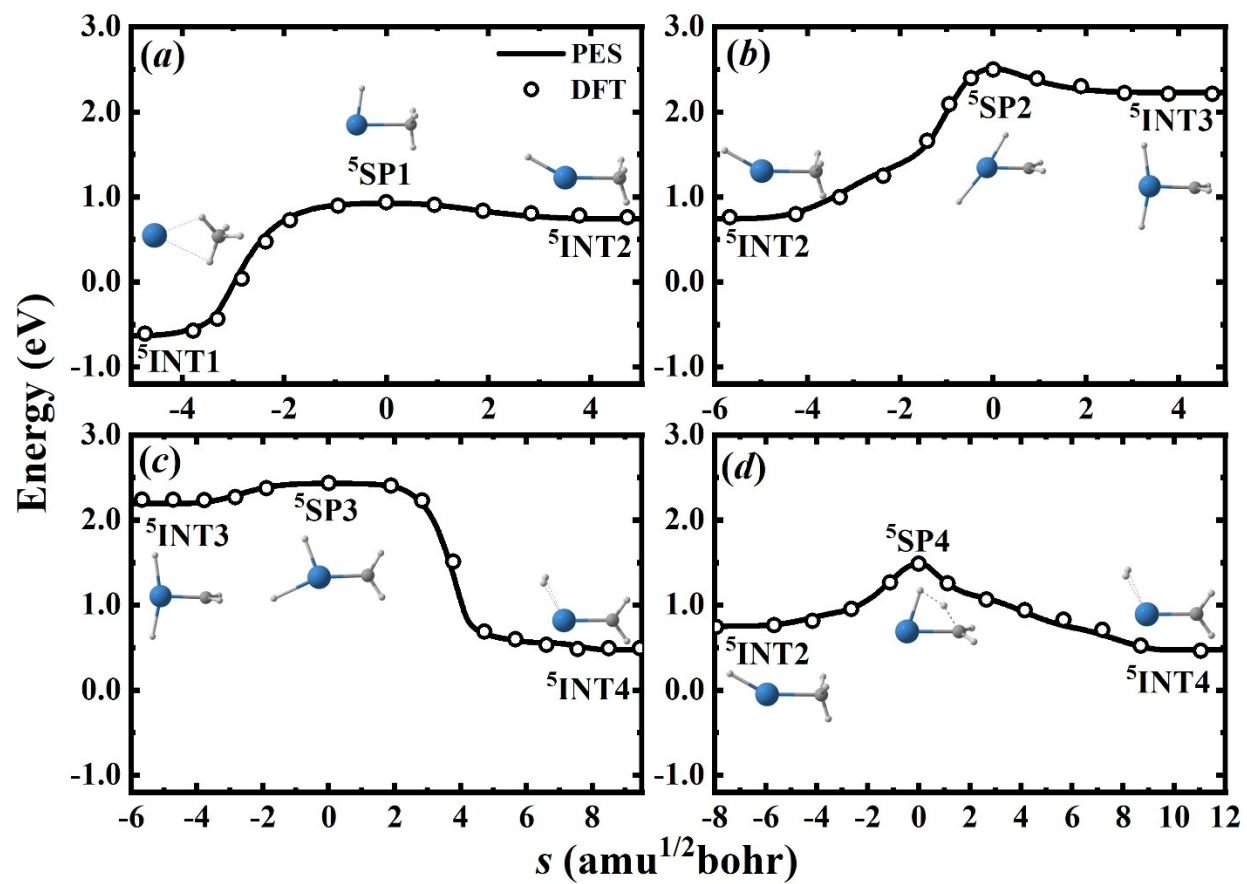


Figure S6. Similar to Figure S5 but for the triplet state.

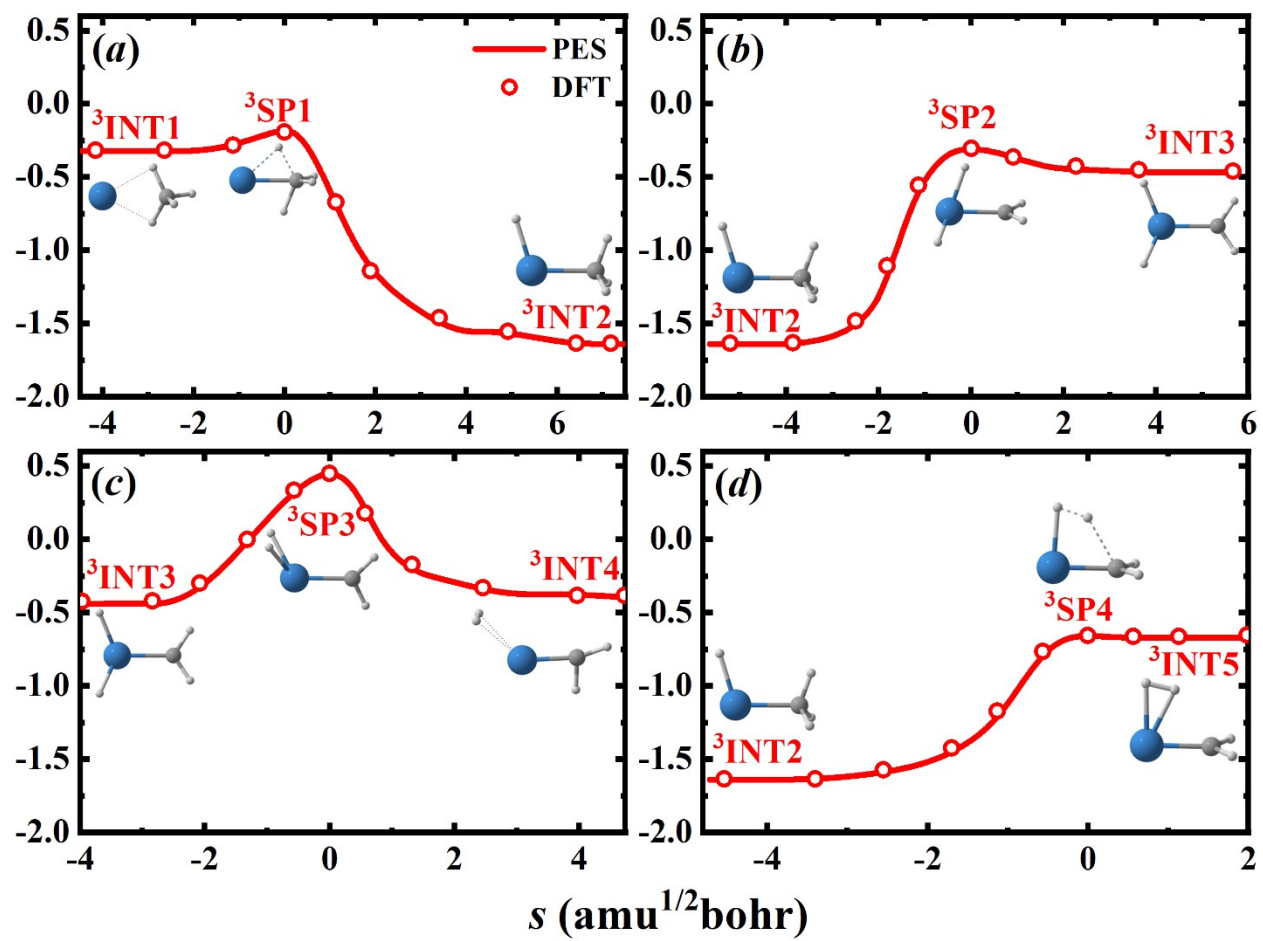


Figure S7. Similar to Figure S5 but for the singlet state.

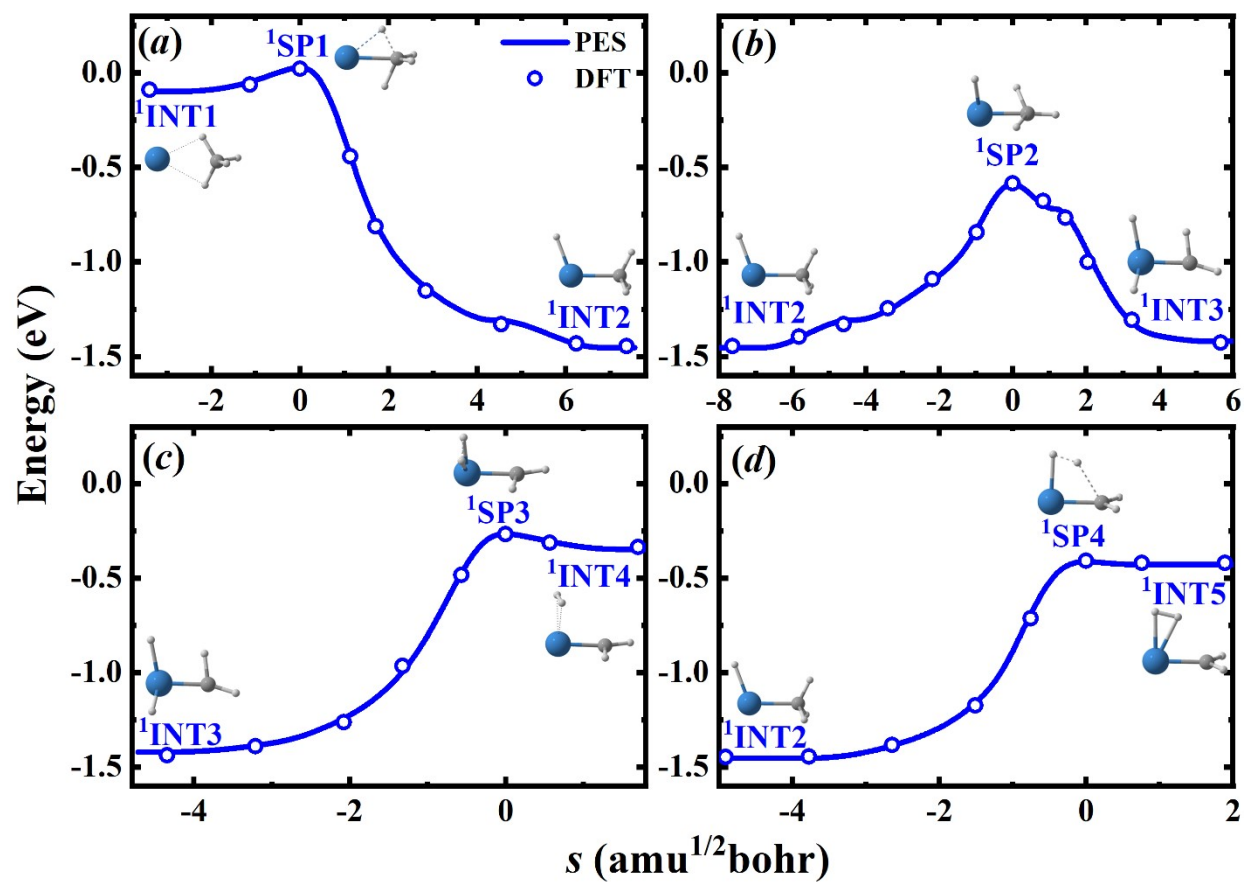


Figure S8. Comparison of geometries in internal coordinates (distances in Å and angles in degrees) for the MECP and $^3\text{SP1}$ at the B3LYP/DZ level.

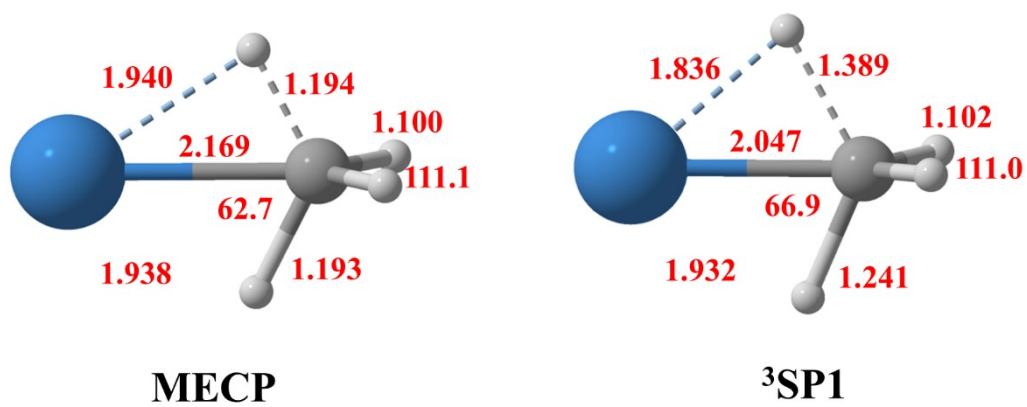


Figure S9. Correlation diagrams between the impact parameter and the scattering angle at different collision energies.

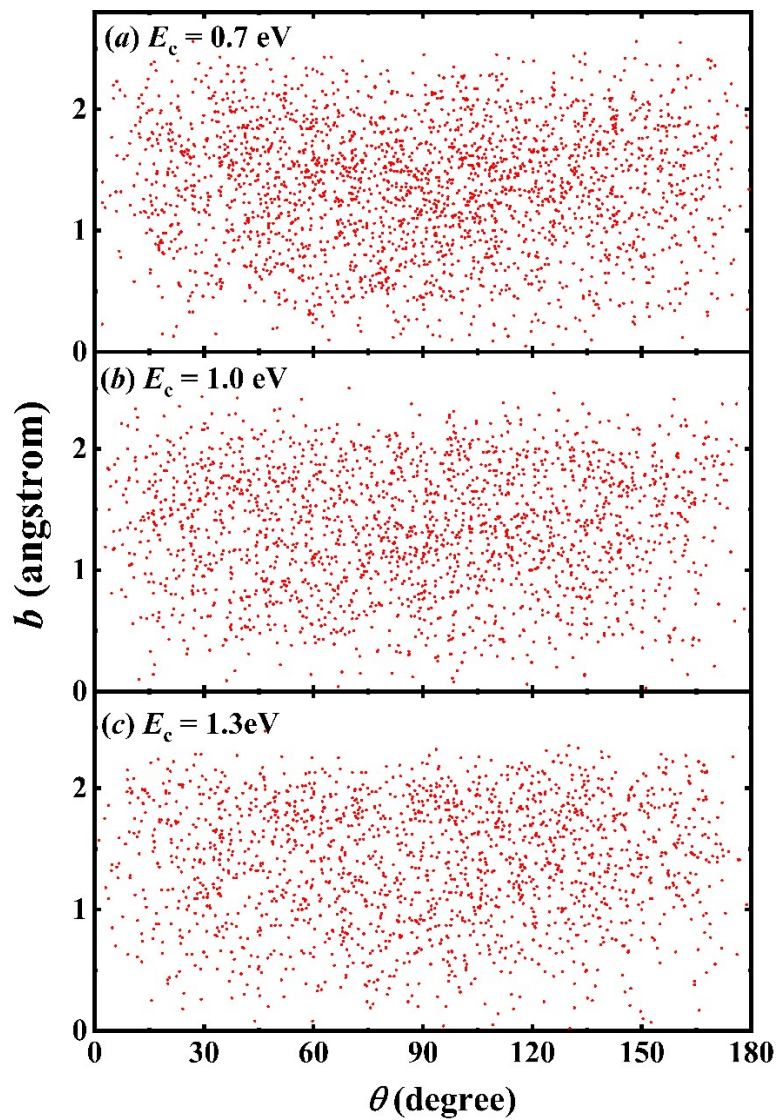


Figure S10. (a) Experimental velocity distributions of the TaCD_2^+ product ion at $E_c = 1.2$ eV. (b) Similar to (a) but for theoretical data. (c) Comparison of experimental integrated angular distributions between $\text{Ta}^+ + \text{CD}_4$ reaction at $E_c = 1.2$ eV and $\text{Ta}^+ + \text{CH}_4$ reaction at $E_c = 1.3$ eV. (d) Similar to (d) but for theoretical data. (e) Comparison of experimental distribution of the internal energy between $\text{Ta}^+ + \text{CD}_4$ reaction at $E_c = 1.2$ eV and $\text{Ta}^+ + \text{CH}_4$ reaction at $E_c = 1.3$ eV. (f) Similar to (e) but for theoretical data.

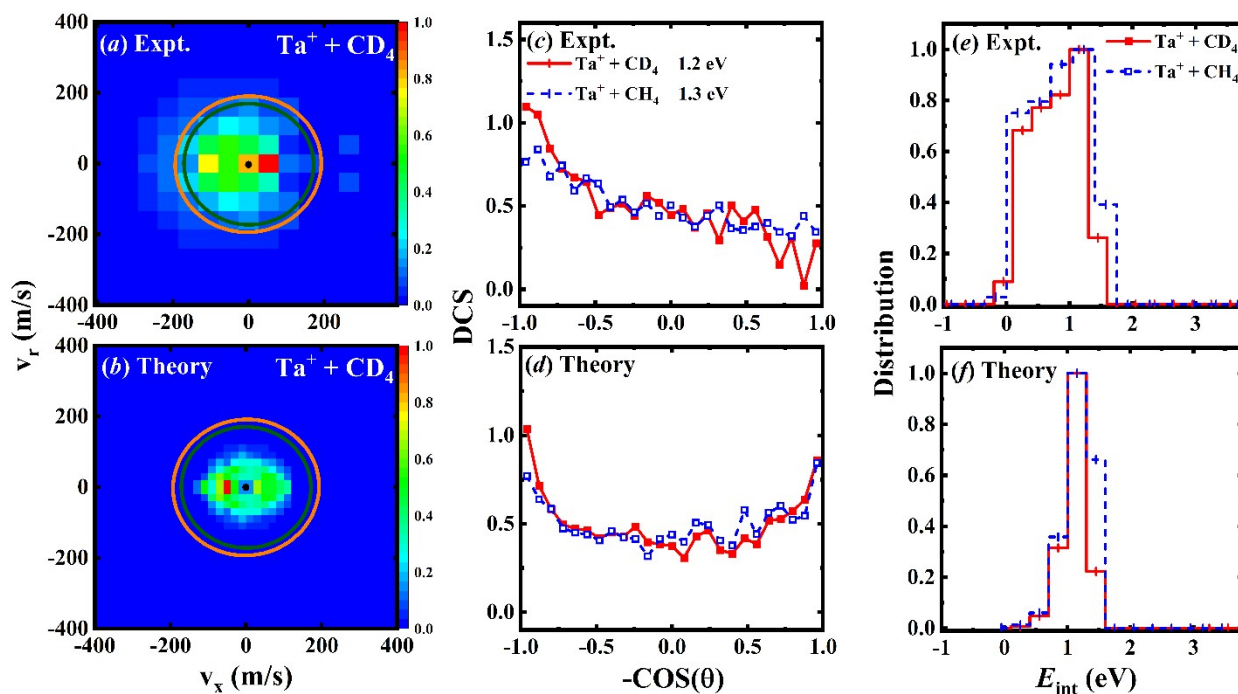


Figure S11. Spin-orbital couplings between quintet and triplet states at seven selected points along the minimum energy path.

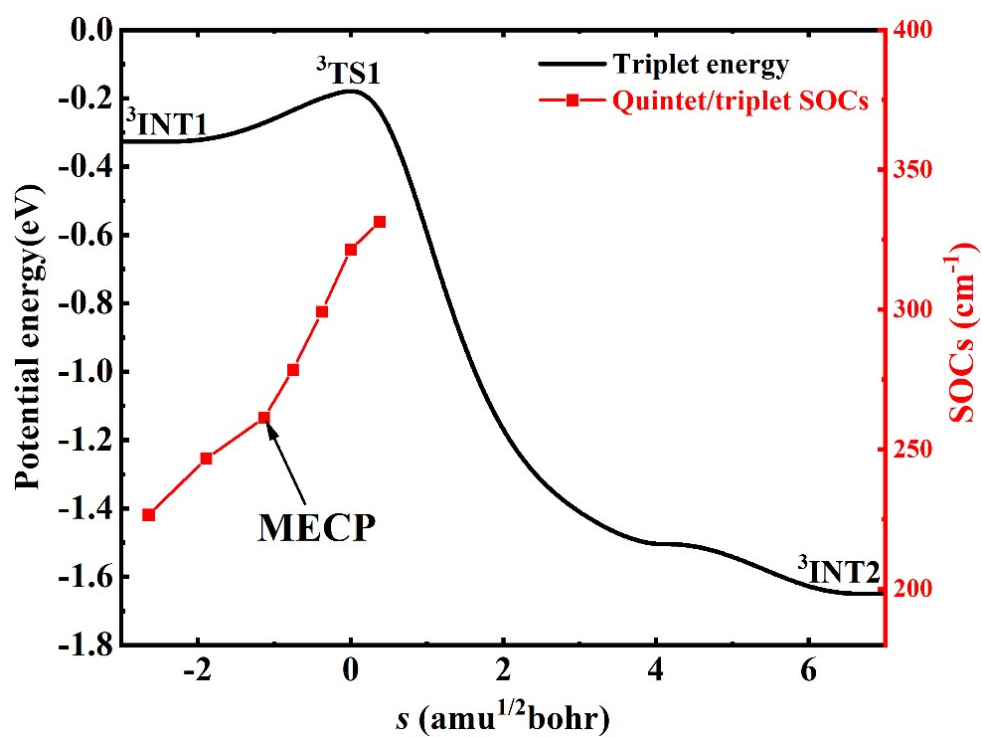
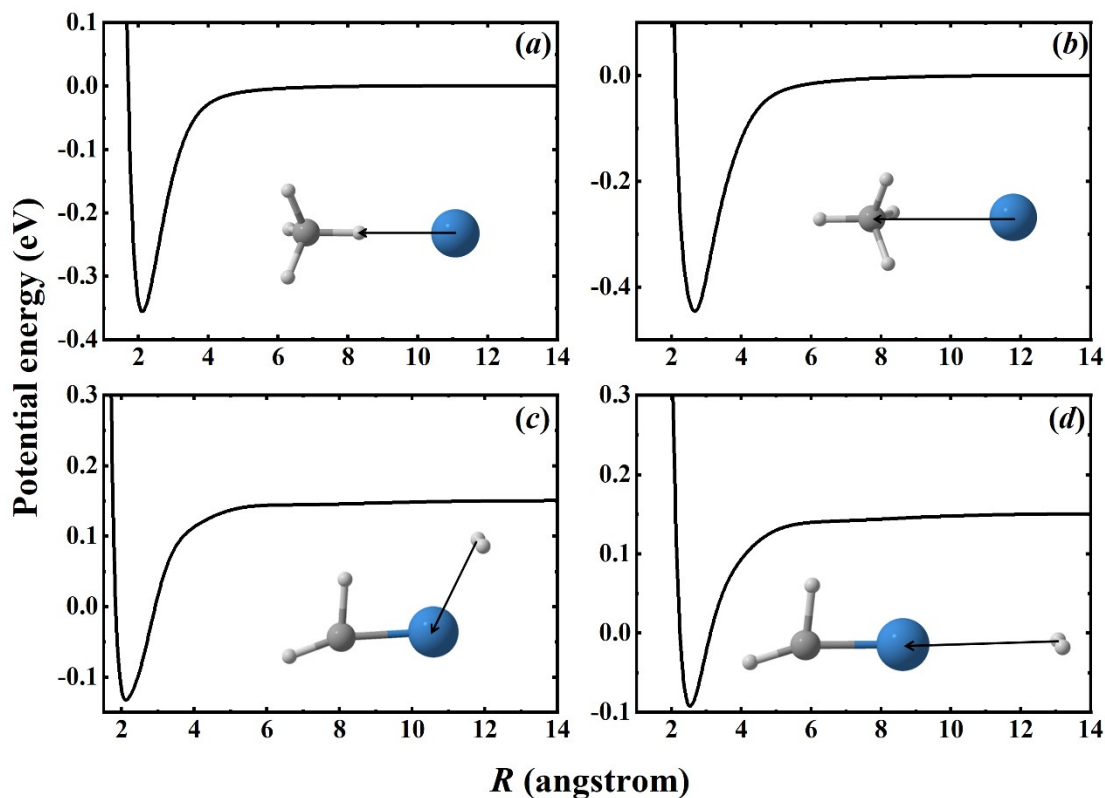


Figure S12. 1D cuts for the interaction potential energy surface between Ta^+ and CH_4 (top panels) and between TaCH_2^+ and H_2 (lower panels) with other coordinates fixed at their equilibrium values.



References:

1. L. G. Parke, C. S. Hinton and P. B. Armentrout, *J. Phys. Chem. C*, 2007, **111**, 17773-17787.
2. M. Meta, M. E. Huber, M. Birk, M. Wedele, M. Ončák and J. Meyer, *Faraday Disc.*, 2024, **251**, 587-603.
3. A. Kramida, Y. Ralchenko and J. Reader, NIST Atomic Spectra Database (ver. 5.8), Available: <https://physics.nist.gov/asd>. 2020.