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Dynamics of carbene formation in the reaction of methane with the tantalum cation in the gas phase

Supplementary Information

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- Figure S1: Reaction coordinate for $Ta^+ + CH_4$ including stationary points of lower importance
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- Cartesian coordinates and energies for optimized structures for $Ta^+ + CH_4$

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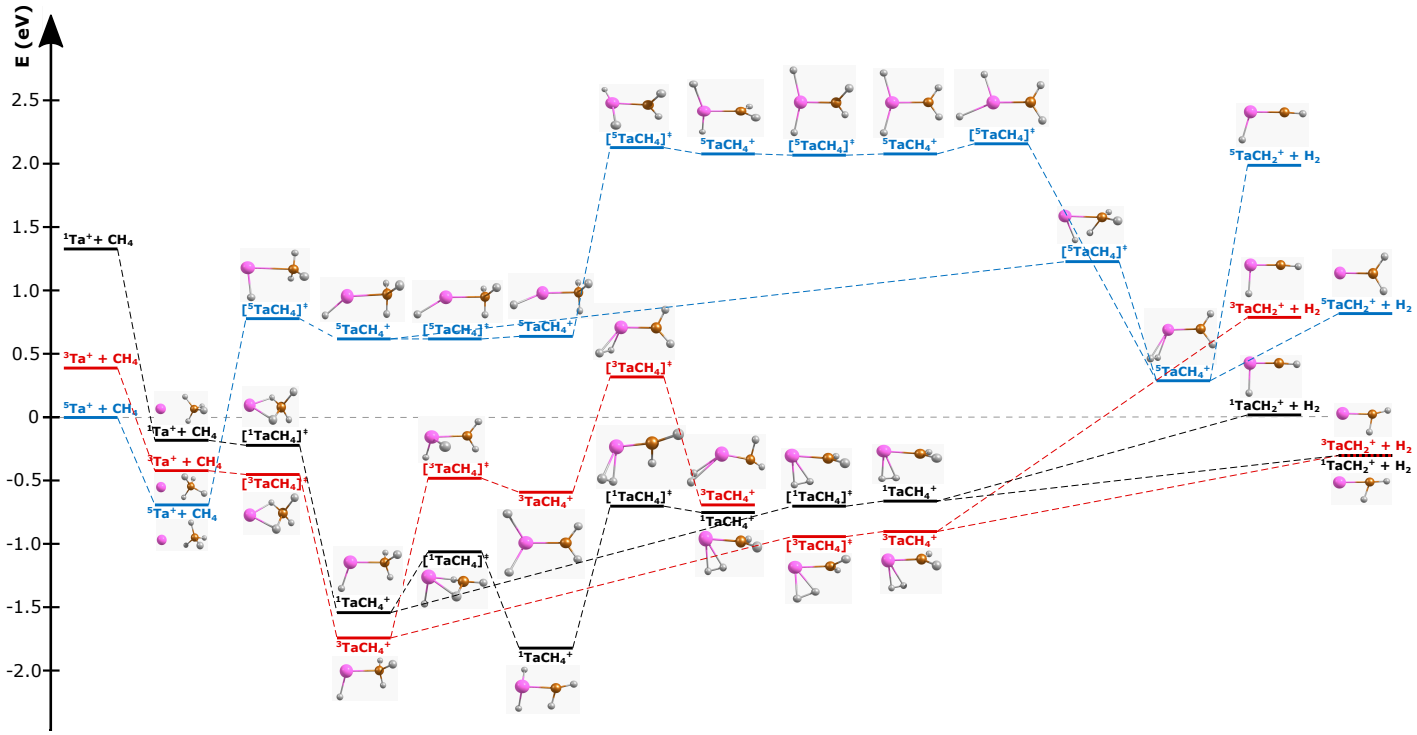

Fig. S1 Reaction pathway for $Ta^+ + CH_4 \longrightarrow TaCH_2^+ + H_2$ with structures of the stationary points along the reaction coordinate, i.e for the pre-reaction complex (entrance channel), intermediates, post-reaction complexes as well the transition states, for the quintet surface (blue), triplet (red) and singlet (black) are given (Ta = pink, carbon = orange, hydrogen = white, structural data can be found in the supplementary information). Details of hydrogen atom migration and subsequent rearrangement are shown in detail here, that have been omitted for clarity in figure 1 of the main manuscript. Energies are given in electron volts relative to the isolated ground state reactants $^5Ta^+ + CH_4$. Calculated at the CCSD(T)//B3LYP level (see methods section of the main manuscript for details). The energy of transition states below local minima is induced through the zero-point energy correction.

Table S1 Time-of-flight (tof) values for ions of interest calculated using the experimental time-of-flight constant $C_{exp} = 0.801$

	m/z	tof / μs
Ta^+	181	10.77
TaC^+	181+12	11.12
$TaCH_2^+$	181+14	11.18
$TaCD_2^+$ / TaO^+	181+16	11.24

Table S2 Relative energies (in eV) for three multiplicities in several structures of $[TaCH_4]^+$ optimized at the B3LYP level in a selected spin multiplicity and calculated at various levels of theory along with the aug-cc-pVDZ basis set. No zero-point correction is added. Energies shown in italics are too high, most probably due to the limited size of the active space in the MRCI calculation.

Method	Multiplicity	$[Ta \cdot CH_4]^+$ (M = 5)	$[HTaCH_3]^+$ (M = 1)	$[H_2TaCH_2]^+$ (M = 1)	$[H_2 \cdot TaCH_2]^+$ (M = 3)	$[H_2 \cdot TaCH_2]^+$ (M = 3)
B3LYP	1	0.53	0.19	0.00	0.14	0.24
	3	0.38	0.00	1.70	0.00	0.00
	5	0.00	3.30	5.60	1.45	2.33
CCSD	1	0.64	0.22	0.00	0.16	0.29
	3	0.48	0.00	1.70	0.00	0.00
	5	0.00	3.34	5.81	1.48	2.36
MRCI(6,7)	1	0.98	0.43	0.00	0.30	0.71
	3	0.54	0.00	1.50	0.00	0.00
	5	0.00	3.42	5.85	*3.74*	2.40
MRCI(8,8)	1	0.98	0.38	0.00	0.29	0.68
	3	0.49	0.00	1.74	0.00	0.00
	5	0.00	3.39	6.24	1.50	2.36
MRCI(6,8)	1	0.86	0.44	0.00	0.29	0.71
	3	0.42	0.00	1.70	0.00	0.00
	5	0.00	3.71	5.68	*3.75*	2.37

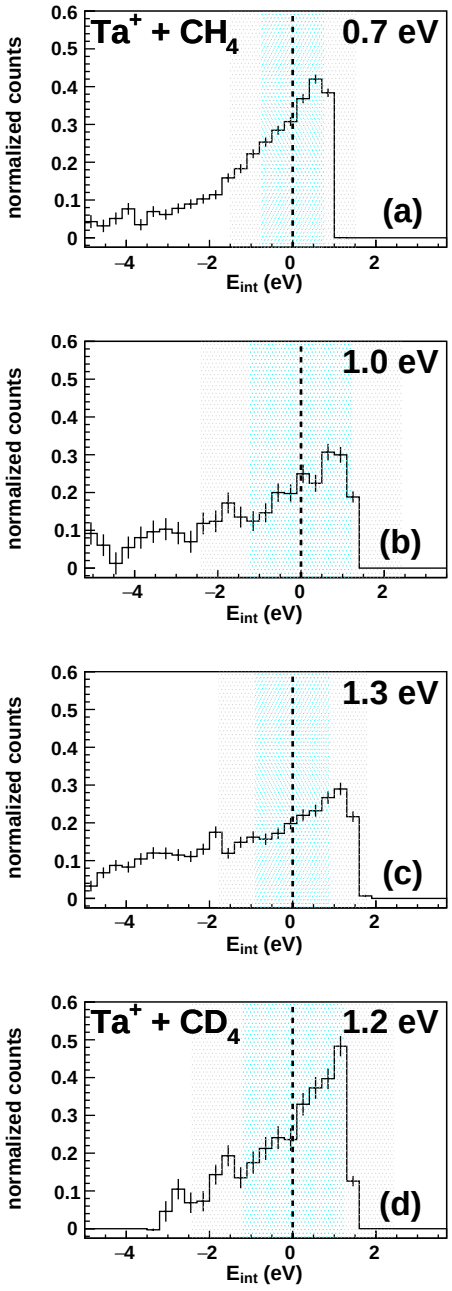

Fig. S2 Internal energy E_{int} distributions for $Ta^+ + CH_4 \longrightarrow TaCH_2{}^+ + H_2$ (a-c) and $Ta^+ + CD_4 \longrightarrow TaCD_2{}^+ + D_2$ (d). The internal energy is the difference between the total available energy to the reactive collision, i. e. relative collision energy and reaction exothermicity ($E_{\mathrm{rel}} + E_{\mathrm{exo}}$) and the amount of energy partitioned into product translation (E'_{rel}), i. e. into kinetic energy of $TaCH_2{}^+$ and H_2: $E_{\mathrm{int}} = E_{\mathrm{rel}} + E_{\mathrm{exo}} - E'_{\mathrm{rel}}$. The energy resolution was calculated using Gaussian error propagation [1]. The $\pm 1\sigma$-intervals are given by the dark gray area and the respective $\pm 2\sigma$ by light cyan area. The low energy tails extends beyond the energy defined by the 2σ-error (see also table 1 of the main manuscript). In words, this means that an unavailable amount of energy is converted into kinetic energy [2]. Possible explanations are missing contributions to the energy balance, for example electronically excited states of Ta^+ contributing or internal energy of CH_4. The unfavorable kinematics add to the effect [2]. A more detailed discussion can be found in the main manuscript.

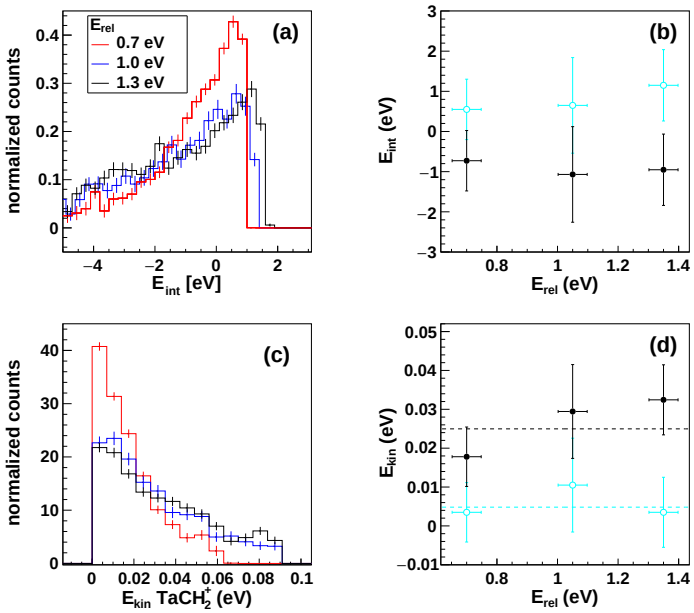

Fig. S3 Top row: internal energy. (a) Distributions of the internal energy for all three relative impact energies. (b) Plot of mean (black dots) and maximum (turquoise dots) for the distribution of the internal energy. Bottom row: kinetic energy. (c) Plot of the distribution of the kinetic energy of the product ion at the three different relative collision energies. (d) Plot of the mean values (black dots) and maxima (turquoise dots) for the kinetic energy distribution.

Table S3 Benchmarking of reaction energies (in eV) including Ta−H and Ta−C bonds as calculated at the B3LYP/aug-cc-pVTZ ('B3LYP'), CCSD/aug-cc-pVTZ//B3LYP/aug-cc-pVTZ ('CCSD'), CCSD(T)/aug-cc-pVTZ//B3LYP/aug-cc-pVTZ ('CCSD(T)'). Experimental values are taken from Ref.[3] (Armentrout *et al.*, J. Phys. Chem. C 2011) and references therein.

Reaction	B3LYP	CCSD	CCSD(T)	exp.
$TaH^+ \longrightarrow Ta^+ + H$	2.79	2.64	2.71	2.39±0.08
$TaCH^+ \longrightarrow Ta^+ + CH$	5.82	5.51	6.08	5.82±0.16
$TaCH_2^+ \longrightarrow Ta^+ + CH_2$	5.05	4.89	5.28	4.81±0.03
$TaCH_3^+ \longrightarrow Ta^+ + CH_3$	3.22	3.09	3.30	2.69±0.14

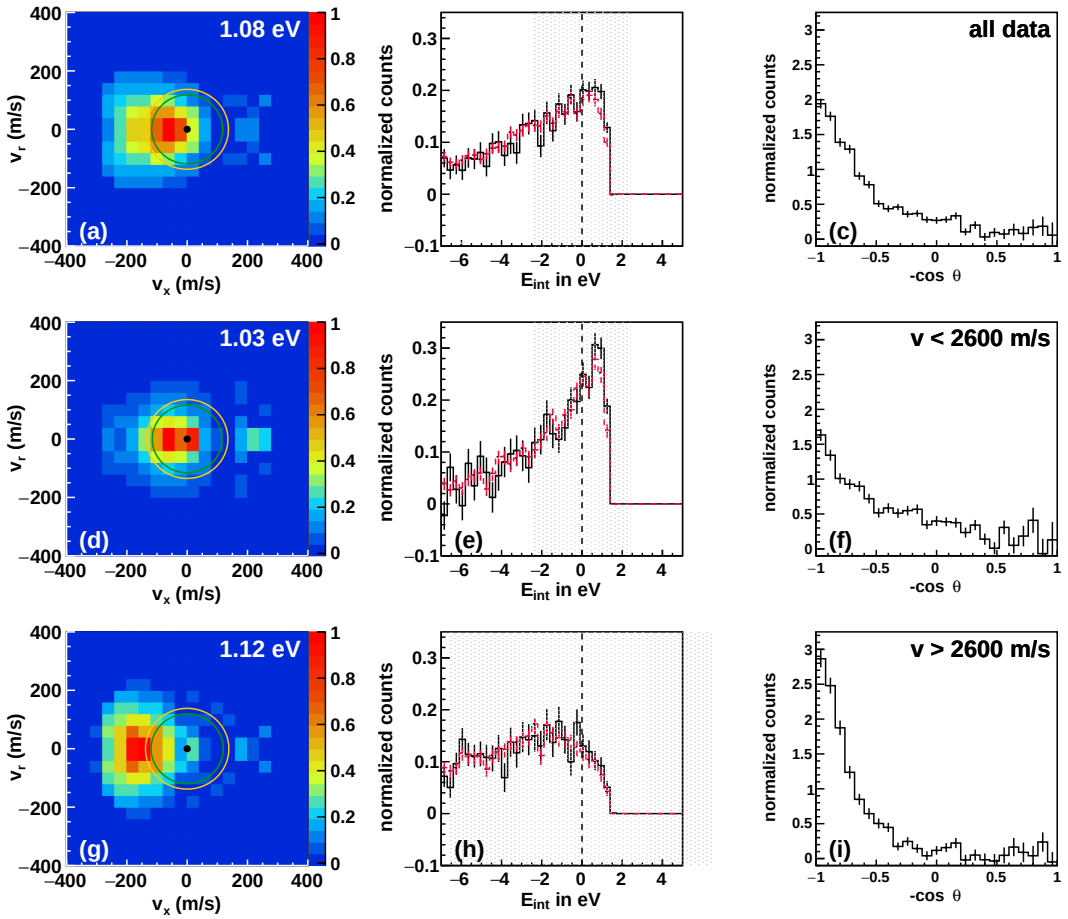

Fig. S4 Velocity distributions for $Ta^+ + CH_4 \longrightarrow TaCH_2^+ + H_2$ at 1.0 eV relative collision energy. The different rows show different sets of scattering files just for data analysis. The selection is based on the ion beam velocity and done prior to scattering analysis. Top row: Full data set without pre-selection, middle row: ion beam velocities $\leq$2,650 m/s, bottom row: ion beam velocities $\leq$2,650 m/s. The Left column (a,d,g) show the respective velocity distributions normalized to the bin of highest intensity. The superimposed rings indicate the kinematic cut-offs. The internal energy distributions for the full scattering range (black solid) and the forward hemisphere (pink, dashed) are shown in the second column (b,e,h) and the right column shows the integrated angular distributions (c,f,i). The gray area indicates the 2σ-error interval and the light blue area the 2σ-error interval. The pre-selected files are randomly distributed during the measurement campaign with one exception of several files all being recorded on a single day. It is obvious that careful preparation of the ion beam is key to a successful experiment. Although the 'deviations' seen for $v \geq 2,600$ m/s is also reproducible. We do not completely understand the origin of this but we think the huge mass difference combined with the large scattering angle in the laboratory frame makes the current experiment extremely sensitive to variations in source conditions.

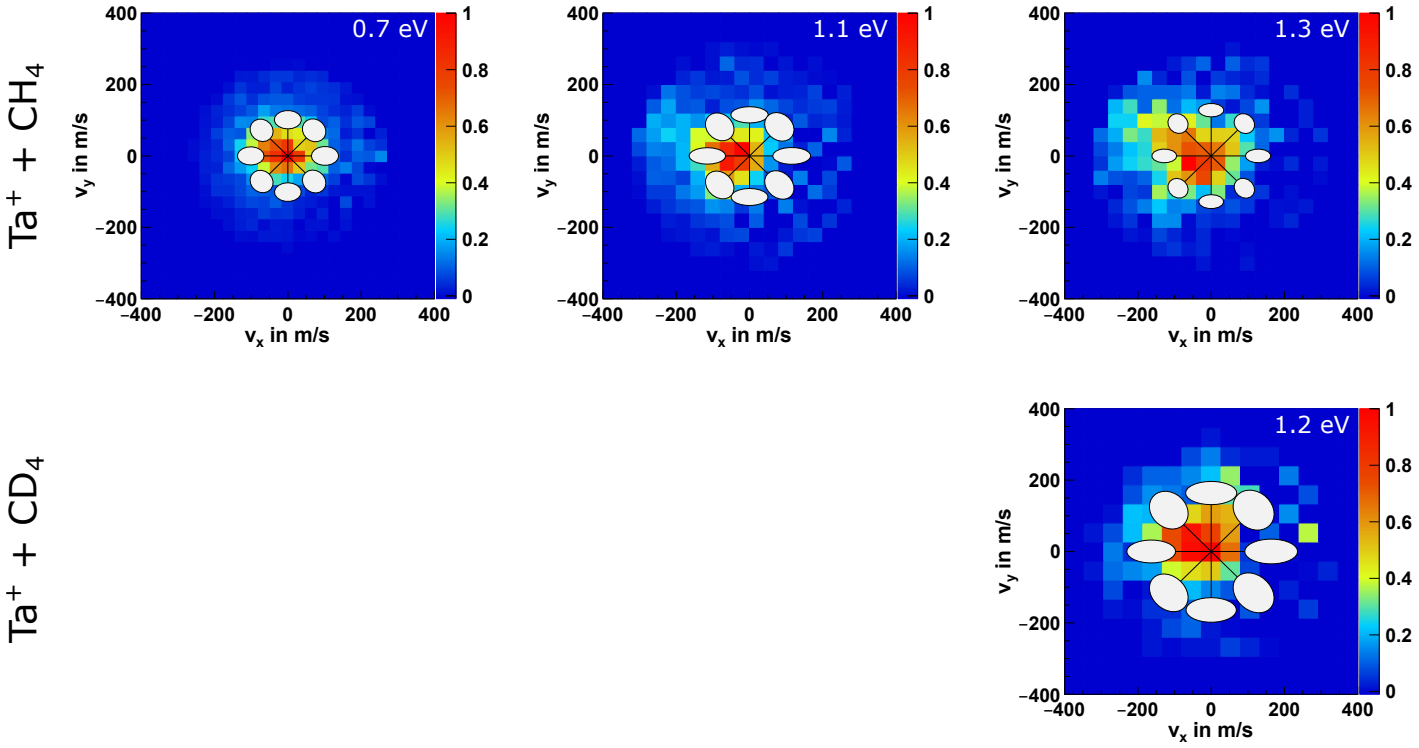

Fig. S5 Graphical error representation of product ion velocity distribution for $TaCH_2^+$ (upper panel) and $TaCD_2^+$(lower panel) displayed as 2D slice at the given relative collision energies. The ellipses are centred at the velocities of the kinematic cut-off which means that none of the available energy is partitioned into internal excitation of $TaCH_2^+/TaCD_2^+$ and/or H_2/D_2. They indicate the 1σ error and are the results of a Gaussian error propagation based on the mean velocity angular spread of the reactant beams. Details on the derivation can be found in ref. [1].

Cartesian coordinates B3LYP functional and the aug-cc-pVTZ basis set on C, H and ECP60MDF_AVTZ on Ta optimized structures (in Å) along with the electronic energy (in Hartrees)

Ta^+ (M=5)

$E = -57.0464675242$

Ta	0.000000	0.000000	0.000000

CH_4

$E = -40.493888$

C	0.000000	0.000000	0.000000
H	0.628319	0.628319	0.628319
H	-0.628319	-0.628319	0.628319
H	0.628319	-0.628319	-0.628319
H	-0.628319	0.628319	-0.628319

H_2

$E = -1.169960$

H	0.000000	0.000000	0.371432
H	0.000000	0.000000	-0.371432

LM1 (M=1)

$E = -97.542808$

C	-2.169961	0.009788	0.010542
H	-2.982130	-0.241901	-0.672569
H	-2.526181	0.101376	1.033650
H	-1.764831	0.972216	-0.350765
H	-1.513677	-0.907053	-0.080388
Ta	0.298720	0.000228	0.000093

LM2 (M=1)

$E = -97.596676$

Ta	-0.018149	-0.226618	0.000000
C	-0.018149	1.808780	0.000000
H	-0.574361	2.119726	0.900882
H	0.975452	2.267342	0.000000
H	-0.574361	2.119726	-0.900882
H	1.607072	-0.816377	0.000000

LM3 (M=1)

$E = -97.596503$

C	1.647478	-0.048107	-0.005302
Ta	-0.182207	-0.008538	-0.030286
H	-0.446891	1.467499	0.844862
H	2.679895	-0.371080	0.038158
H	1.504067	1.070231	0.197861
H	-0.320811	-1.254767	1.161839

LM4 (M=1)

$E = -97.559402$

H	-0.345153	1.902587	0.043301
H	0.464702	1.771728	0.026470
Ta	-0.197374	-0.043927	-0.004496
C	1.663037	-0.047593	-0.053872
H	1.656814	-0.159021	1.071400
H	2.653725	-0.023060	-0.489760

LM5 (M=1)

$E = -97.559524$

H	0.545699	1.707977	-0.000083
C	1.697432	-0.064901	0.000037
H	2.289488	-0.082071	0.918334
H	2.289593	-0.082141	-0.918189
Ta	-0.205927	-0.041528	-0.000005
H	-0.276670	1.877162	0.000106

TS1/2 (M=1)

$E = -97.542373$

H	1.152067	1.183390	-0.000000
C	1.802243	-0.010034	0.000000
Ta	-0.248299	-0.001136	0.000000
H	2.416461	0.048368	0.901566
H	1.327383	-1.136974	-0.000000
H	2.416461	0.048368	-0.901566

TS2/3 (M=1)

$E = -97.566116$

C	-1.649149	-0.030159	-0.000014
Ta	0.202057	-0.027884	-0.000002
H	-1.242576	0.314963	1.115493
H	0.358584	1.692259	0.000139
H	-1.242638	0.315187	-1.115444
H	-2.728633	-0.105945	0.000062

TS3/4 (M=1)

$E = -97.556415$

H	-0.401435	1.581772	-0.700552
H	-0.431119	1.699196	0.281858
Ta	-0.182061	-0.052614	0.002862
C	1.656322	-0.007769	-0.045961
H	1.489956	0.737625	0.807684
H	2.695110	-0.131181	-0.322184

TS2/5 (M=1)

$E = -97.559890$

H	-0.880485	1.431630	0.000000
C	-1.706028	-0.107102	-0.000000
H	-2.300117	-0.133391	-0.916600
H	-2.300117	-0.133392	0.916600
Ta	0.214940	-0.031631	0.000000
H	0.026244	1.786853	0.000000

$TaCH_2^+$ (M=1), iso1

$E = -96.375431$

Ta	0.010656	-0.190752	0.000000
C	0.010656	1.631330	0.000000
H	-1.125223	1.457914	0.000000
H	0.283369	2.678979	0.000000

$TaCH_2^+$ (M=1), iso2

$E = -96.358329$

Ta	0.022391	-0.163735	0.000000
C	0.022391	1.587852	0.000000
H	-0.056964	2.670010	0.000000
H	-1.711921	-0.244490	0.000000

LM1 (M=3)

$E = -97.550255$

C	-2.051701	-0.003858	-0.014092
H	-2.881174	0.107341	0.686562
H	-2.406399	-0.097876	-1.038675
H	-1.550723	-0.956472	0.318280
H	-1.494020	0.974404	0.132123
Ta	0.282774	-0.000058	-0.000188

LM2 (M=3)

$E = -97.603424$

Ta	-0.019738	-0.228295	0.000000
C	-0.019738	1.813161	0.000000
H	-0.544291	2.167151	0.900566
H	1.011432	2.188627	0.000000
H	-0.544291	2.167151	-0.900566
H	1.636480	-0.736377	0.000000

LM3 (M=3)

$E = -97.563049$

C	-0.016707	1.846441	-0.000000
Ta	-0.016707	-0.196066	0.000000
H	0.657388	-0.828701	1.473787
H	0.002550	2.445789	-0.913479
H	0.002550	2.445789	0.913479
H	0.657388	-0.828701	-1.473787

LM4 (M=3)

$E = -97.558412$

C	-0.028624	1.688690	0.000000
Ta	-0.028624	-0.155411	0.000000
H	1.564410	-1.537340	0.387982
H	-1.164369	1.567285	0.000000
H	0.296822	2.720222	0.000000
H	1.564410	-1.537340	-0.387982

LM5 (M=3)

$E = -97.568275$

H	0.553762	1.696589	-0.000017
C	1.700354	-0.065693	-0.000026
H	2.293464	-0.084158	0.917398
H	2.293486	-0.084038	-0.917435
Ta	-0.206485	-0.041155	0.000005
H	-0.269450	1.870095	-0.000150

TS1/2 (M=3)

$E = -97.549709$

H	-1.213766	1.112797	0.000000
C	0.002672	1.799755	0.000000
Ta	0.002672	-0.247530	-0.000000
H	-0.064041	2.415117	0.900074
H	-0.064041	2.415117	-0.900074
H	1.130739	1.328109	0.000000

TS2/3 (M=3)

$E = -97.557841$

H	-0.390022	-0.852271	1.393880
C	-1.787784	0.076402	-0.046696
Ta	0.207671	-0.019393	-0.018610
H	-2.432750	-0.687941	-0.486539
H	-2.329349	0.881742	0.454198
H	0.718828	1.615731	0.277168

TS3/4 (M=3)

$E = -97.530373$

H	1.142036	1.262006	0.639771
H	1.142058	1.261994	-0.639755
Ta	0.182714	-0.049851	0.000004
C	-1.801267	0.147364	-0.000033
H	-2.369333	-0.794092	-0.000034
H	-2.445254	1.025019	-0.000052

TS2/5 (M=3)

$E = -97.568696$

H	-0.878906	1.430684	0.000000
C	-1.708372	-0.106119	0.000000
H	-2.303315	-0.135058	-0.915758
H	-2.303315	-0.135058	0.915758
Ta	0.215217	-0.031632	0.000000
H	0.024925	1.785301	0.000000

$TaCH_2^+$ (M=3), iso1

$E = -96.375989$

Ta	0.010612	-0.191445	0.000000
C	0.010612	1.637953	0.000000
H	-1.124012	1.463230	0.000000
H	0.285667	2.684530	0.000000

$TaCH_2^+$ (M=3), iso2

$E = -96.336765$

Ta	0.022271	-0.172146	0.000000
C	0.022271	1.680121	0.000000
H	-0.057584	2.762765	0.000000
H	-1.701843	-0.276805	0.000000

LM1 (M=5)

$E = -97.560854$

H	-1.565784	0.851131	-0.032820
C	-2.281136	-0.017842	0.006823
Ta	0.314146	-0.000273	0.000018
H	-2.063453	-0.843007	-0.674939
H	-2.435665	-0.357801	1.027662
H	-3.180956	0.476662	-0.362134

LM2 (M=5)

$E = -97.517506$

H	-1.757656	0.921244	-0.000563
C	2.154281	0.066026	-0.000054
Ta	-0.248054	-0.022087	0.000026
H	2.411691	-0.431981	-0.931886
H	2.114086	1.157152	-0.000918
H	2.414108	-0.430243	0.931830

LM3 (M=5)

$E = -97.517979$

Ta	-0.011697	-0.238276	0.000000
C	-0.011697	2.071616	0.000000
H	0.545139	2.193875	0.932335
H	0.545139	2.193875	-0.932335
H	-1.056332	2.375403	0.000000
H	0.890078	-1.798700	0.000000

LM4 (M=5)

$E = -97.468369$

C	-0.000000	-0.000000	-1.837571
Ta	0.000000	0.000000	0.203613
H	-0.000000	1.837337	0.513187
H	-0.915262	0.000000	-2.432343
H	0.915262	-0.000000	-2.432343
H	-0.000000	-1.837337	0.513187

LM5 (M=5)

$E = -97.469067$

Ta	0.199941	-0.000002	0.000054
C	-1.838094	0.000039	-0.000408
H	0.651918	-1.810356	-0.000280
H	0.652194	1.810360	-0.000364
H	-2.435727	0.914132	-0.000326
H	-2.435524	-0.914195	-0.000492

LM6 (M=5)

$E = -97.528234$

C	-0.042801	1.866325	0.000000
Ta	-0.042801	-0.194371	0.000000
H	1.752622	-0.977447	0.400044
H	-0.969064	2.449048	0.000000
H	0.845061	2.496946	0.000000
H	1.752622	-0.977447	-0.400044

TS1/2 (M=5)

$E = -97.510842$

H	-0.014290	1.704158	0.000000
C	2.260789	-0.020917	-0.000000
Ta	-0.284312	-0.020665	0.000000
H	2.372054	-1.100986	-0.000003
H	2.416126	0.515450	-0.928845
H	2.416128	0.515445	0.928848

TS2/3 (M=5)

$E = -97.517852$

H	1.821212	0.825917	0.000210
Ta	0.244436	-0.020248	0.000058
C	-2.129423	0.062028	-0.000077
H	-2.115004	1.129601	-0.231806
H	-2.414778	-0.621764	-0.796237
H	-2.358706	-0.227805	1.024043

TS3/4 (M=5)

$E = -97.458347$

H	-1.586067	0.634451	0.000000
C	0.001081	1.787345	-0.000000
Ta	0.001081	-0.200142	0.000000
H	-0.082523	2.377036	-0.914860
H	-0.082523	2.377036	0.914860
H	1.665689	-1.502263	-0.000000

TS4/5 (M=5)

$E = -97.469183$

Ta	0.201224	0.000001	-0.000004
C	-1.837519	-0.000012	0.000006
H	0.601391	1.813101	0.186824
H	0.601511	-1.813082	-0.186572
H	-2.433567	-0.815277	0.415203
H	-2.433562	0.815254	-0.415201

TS5/6 (M=5)

$E = -97.462208$

H	2.177864	-0.767653	-0.000022
H	0.719078	1.644129	0.000015
Ta	0.183586	-0.007794	0.000000
C	-1.893984	-0.034306	-0.000001
H	-2.492567	0.877105	-0.000025
H	-2.442282	-0.978771	0.000019

TS2/6 (M=5)

$E = -97.491811$

H	-1.303087	1.041088	-0.002093
C	-1.922081	-0.098085	0.000132
H	-2.490242	-0.249808	-0.916692
H	-2.491391	-0.243036	0.917339
Ta	0.248790	-0.022819	0.000039
H	-0.344476	1.706045	-0.002186

$TaCH_2^+$ (M=5), iso1

$E = -96.341252$

Ta	0.216828	0.000000	-0.000036
C	-1.829600	0.000003	0.001964
H	-2.425378	-0.914302	-0.004563
H	-2.425452	0.914260	-0.004563

$TaCH_2^+$ (M=5), iso2

$E = -96.296703$

Ta	0.021384	-0.181332	0.000000
C	0.021384	1.827744	0.000000
H	-0.041085	2.912810	0.000000
H	-1.648268	-0.642006	0.000000

Structures used for benchmarking

LM1

H	-1.56002	0.864337	-0.0613158
C	-2.27421	-0.0126602	0.00863012
Ta	0.312789	-0.000268004	5.00005e-05
H	-1.92463	-0.985192	-0.379087
H	-2.62292	-0.104455	1.04243
H	-3.08077	0.320817	-0.6574859

LM2

H	0.89004	1.57092	0
C	-1.80241	0.0608408	0
Ta	0.224819	-0.0274854	0
H	-2.24966	1.06834	0
H	-2.11884	-0.498922	-0.908667
H	-2.11884	-0.498922	0.908667

LM3

C	1.65081	-0.0488887	-0.00492407
Ta	-0.182746	-0.00837712	-0.0303404
H	1.50965	1.08037	0.188539
H	-0.445183	1.46383	0.856769
H	-0.320928	-1.26331	1.15741
H	2.69201	-0.376022	0.0416986

LM4

H	1.56071	-1.52705	0.396415
H	1.56071	-1.52705	-0.396415
Ta	-0.0284284	-0.156146	0
C	-0.0284284	1.69173	0
H	-1.17365	1.56908	0
H	0.298058	2.73329	0

LM5

H	0.621756	1.6516	0
C	1.70318	-0.073705	0
H	2.29967	-0.0977214	0.926277
H	2.29967	-0.0977214	-0.926277
Ta	-0.208393	-0.0393405	0
H	-0.227478	1.85799	0

Notes and references

1 R. Wester, *Phys. Chem. Chem. Phys.*, 2014, **16**, 396–405

2 B. Bastian, T. Michaelsen, J. Meyer and R. Wester, *Astrophys. J.*, 2019, **878**, 162

3 L. G. Parke, C. S. Hinton and P. B. Armentrout, *J. Phys. Chem. C*, 2007, **111**, 17773–17787