Electronic Supplementary Information for

Infrared spectra of carbocations and CH_4^+ in helium

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Table S1. Cartesian coordinates for the global minimum structure of CH_3^+, along with the vibrational mode frequencies (v in cm^{-1}) and IR intensities (I in km.mol^{-1}) determined from harmonic and anharmonic (GVPT2) calculations at the MP2/aug-cc-pVTZ level of theory.

CH_3^+	X (Å)	Y (Å)	Z (Å)
C	-0.096	0.000	-0.137
H	-0.607	0.941	0.047
H	-0.607	-0.941	0.047
H	0.927	0.000	-0.503

Harmonic		Anharmonic	
v	I	v	I
3292.3	73.0	3158.8	76.2
3292.3	73.0	3158.8	76.2
3087.2	0.0	2988.3	0.0
1449.6	16.6	1413.4	18.3
1449.6	16.6	1413.4	18.3
1441.9	7.2	1427.3	10.3

Table S2. Cartesian coordinates for the global minimum structure of CH_5^+, in which the axis of the H_2 moiety eclipses a C-H bond in the CH_3 tripod. Also shown are vibrational mode frequencies (v in cm^{-1}) and IR intensities (I in km.mol^{-1}) obtained from harmonic and anharmonic (GVPT2) calculations at the MP2/aug-cc-pVTZ level of theory.

CH_5^+	X (Å)	Y (Å)	Z (Å)
C	-0.151	-0.023	0.027
H	-0.665	0.920	-0.129
H	-0.654	-0.955	-0.209
H	0.666	-0.054	0.881
H	0.812	0.006	-0.519
H	-0.253	-0.073	1.203

Harmonic		Anharmonic	
v	I	v	I
3266.2	77.4	3142.2	53.6
3165.2	72.3	3004.1	69.8
3029.2	108.8	2880.9	93.1
2714.9	34.7	2745.9	32.8
2515.9	64.4	2414.5	51.9
1582.9	14.1	1369.2	2.6
1501.8	0.2	1451.4	0.3
1472.4	0.2	1432.8	3.4
1301.7	52.2	1210.4	49.3
1288.5	35.6	1124.6	84.7
750.8	200.4	556.0	85.1
254.9	45.0	64.8	18.5

Table S3. Cartesian coordinates for the global minimum structure of $CH_5^+(CH_4)$, along with the vibrational mode frequencies (ν in cm^{-1}) and IR intensities (I in km.mol^{-1}) determined from harmonic calculations at the MP2/aug-cc-pVTZ level of theory.

$C_2H_9^+$	X (Å)	Y (Å)	Z (Å)
C	0.096	-0.101	-0.035
H	-0.474	0.424	-0.794
H	-0.410	-0.423	0.869
H	1.294	0.084	0.014
H	0.565	-0.986	-0.503
H	0.707	0.791	0.396
C	3.296	0.337	0.065
H	2.940	-0.496	0.679
H	4.368	0.196	-0.048
H	3.123	1.291	0.558
H	2.878	0.331	-0.945

ν	I
3267.5	55.9
3199.2	2.5
3168.6	70.4
3167.4	4.2
3138.4	2.0
3047.1	85.6
3018.4	48.1
2721.2	51.2
2194.5	721.6
1601.7	77.7
1588.1	1.4
1580.1	8.1
1507.0	0.0
1474.0	18.9
1384.6	8.0
1358.6	13.2
1327.3	28.9
1298.5	54.6
1291.9	42.4
725.2	155.2
464.4	22.1
287.6	44.7
236.0	1.0
213.2	68.3
168.1	0.3
141.2	34.6
98.3	1.1

Table S4. Cartesian coordinates for the global minimum structure of $C_2H_5^+$, also known as the non-classical structure, along with the vibrational mode frequencies (ν in cm^{-1}) and IR intensities (I in km.mol^{-1}) determined from harmonic and anharmonic (GVPT2) calculations at the MP2/aug-cc-pVTZ level of theory.

$C_2H_5^+$	X (Å)	Y (Å)	Z (Å)
C	-0.035	-0.016	-0.780
C	-0.033	-0.016	0.600
H	-0.036	0.918	-1.328
H	-0.037	-0.951	-1.328
H	-0.033	0.918	1.149
H	-0.034	-0.951	1.149
H	1.077	-0.017	-0.091

Harmonic		Anharmonic	
ν	I	ν	I
3296.4	67.8	3150.9	59.3
3279.4	0.0	3133.9	0.0
3171.2	0.4	3017.1	0.5
3168.2	34.3	3069.2	23.0
2215.6	52.0	2257.3	47.6
1585.5	7.7	1545.7	0.0
1488.7	20.8	1453.3	22.0
1369.8	7.0	1329.3	5.5
1293.1	9.6	1225.8	0.0
1261.5	0.0	1239.0	0.0
1148.1	40.5	1112.1	43.8
1102.6	20.8	1041.1	23.3
1099.1	0.0	1072.7	0.0
836.7	0.0	834.1	0.0
789.3	127.7	696.6	114.6

Table S5. Cartesian coordinates for the transition state structure of $C_2H_5^+$, alternatively known as the classical structure, along with the vibrational mode frequencies (ν in cm^{-1}) and IR intensities (I in km.mol^{-1}) determined from harmonic calculations at the MP2/aug-cc-pVTZ level of theory. The "-" symbol before the lowest frequency value indicates that the optimized geometry is a 1st order saddle point.

TS	X (Å)	Y (Å)	Z (Å)
C	0.662	-0.039	0.000
C	-0.745	-0.008	0.000
H	0.988	0.625	-0.830
H	1.144	-1.006	0.000
H	-1.267	0.945	0.000
H	-1.358	-0.906	0.000
H	0.988	0.625	0.830

ν	I
3272.1	44.6
3253.7	3.4
3155.1	3.9
2931.6	77.0
2925.9	186.2
1577.3	4.4
1470.9	17.1
1409.5	26.8
1281.7	47.5
1280.4	0.8
1191.9	10.4
1066.6	205.1
799.8	27.2
771.8	2.2
-398.6	44.6

Table S6. Cartesian coordinates for the global minimum structure of CH_4^+, along with the vibrational mode frequencies (ν in cm^{-1}) and IR intensities (I in km.mol^{-1}) determined from harmonic and anharmonic (GVPT2) calculations at the MP2/aug-cc-pVTZ level of theory.

CH_4^+	X (Å)	Y (Å)	Z (Å)
C	0.182	0.002	0.965
H	0.042	0.144	-0.096
H	1.132	-0.131	1.460
H	-0.719	-0.548	1.498
H	-0.637	0.533	1.632

Harmonic		Anharmonic	
ν	I	ν	I
3355.4	90.4	3198.7	101.3
3209.0	53.7	3089.1	53.2
2610.0	41.5	2475.5	22.7
2334.3	135.9	2211.5	135.9
1618.7	4.6	1504.7	1.6
1325.1	43.6	1279.7	33.1
1237.2	33.2	1150.0	31.4
906.3	91.5	850.0	107.0
485.9	0.0	397.7	0.0