

# Molecular Dynamics of Methylamine, Methanol and Methyl Fluoride Cations in 7 micron Laser Fields

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## Supporting Information

### Energetics

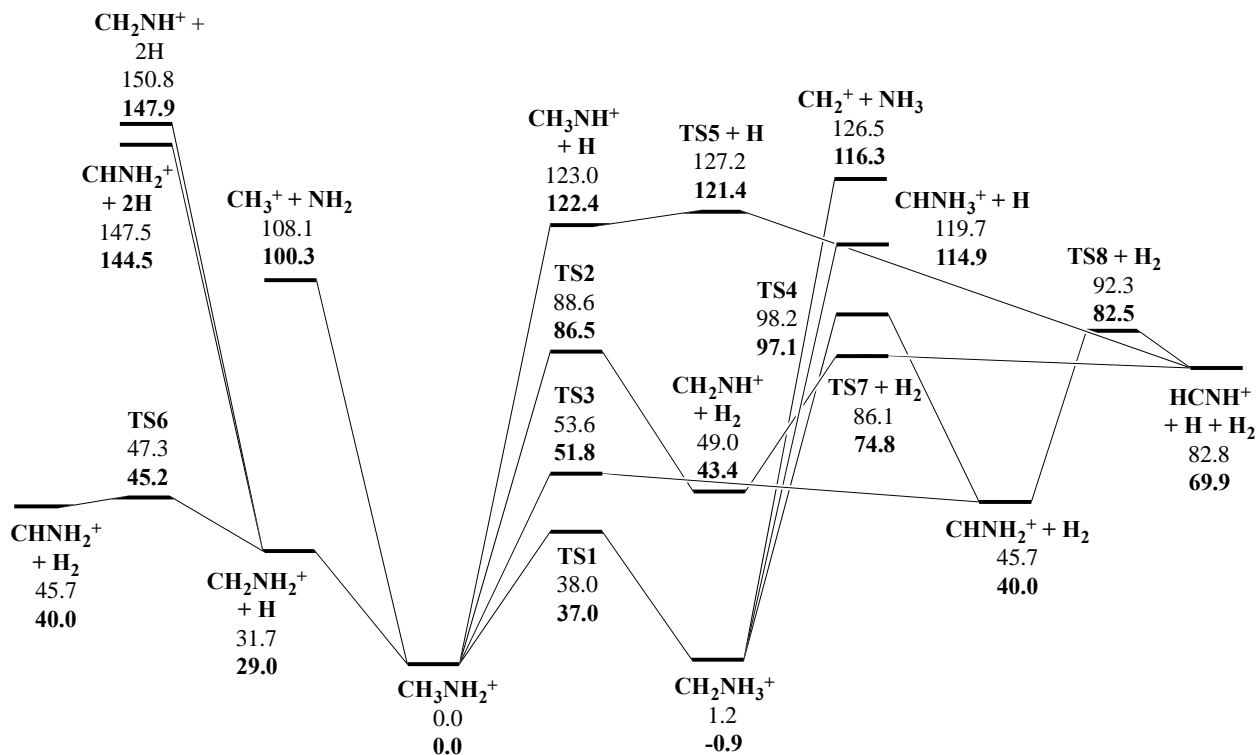


Figure S1. Relative energies at 0 K in kcal/mol for CH<sub>3</sub>NH<sub>2</sub><sup>+</sup> calculated at CAM-B3LYP/6-31G(d,p) and CBS-QB3 (bold) level of theory

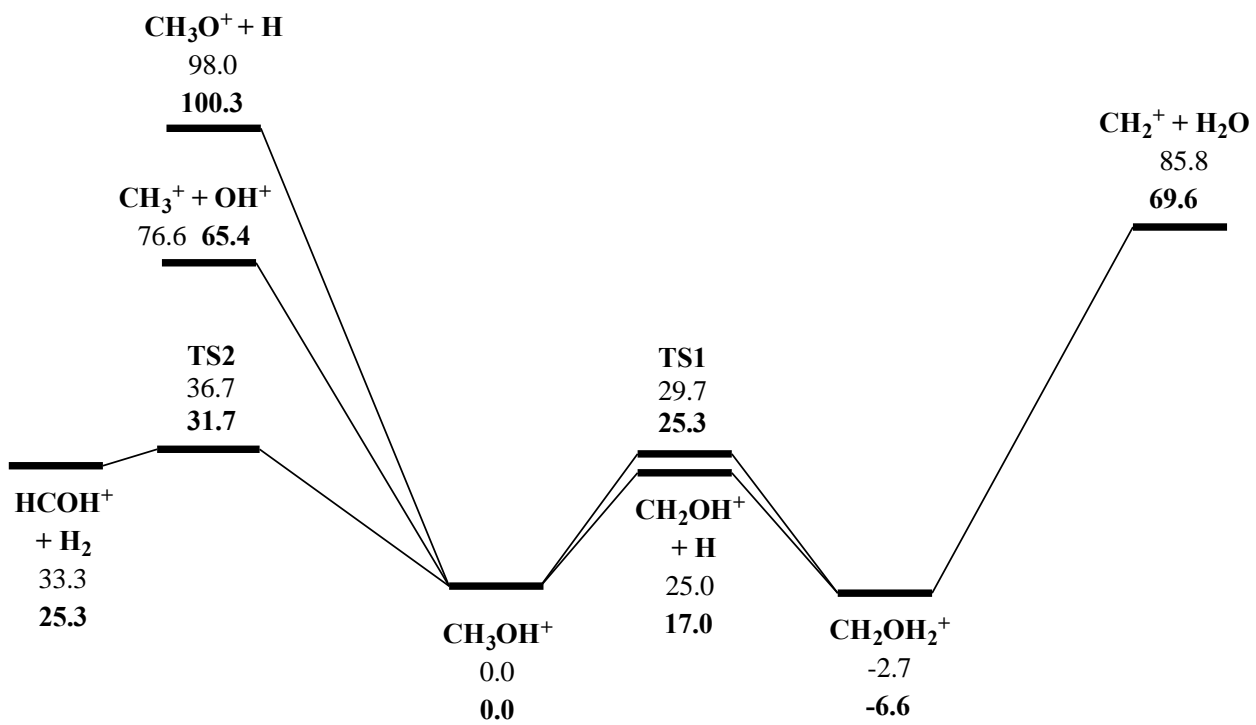


Figure S2. Relative energies at 0 K in kcal/mol for  $\text{CH}_3\text{OH}^+$  calculated at CAM-B3LYP/6-31G(d,p) and CBS-QB3 (bold) level of theory

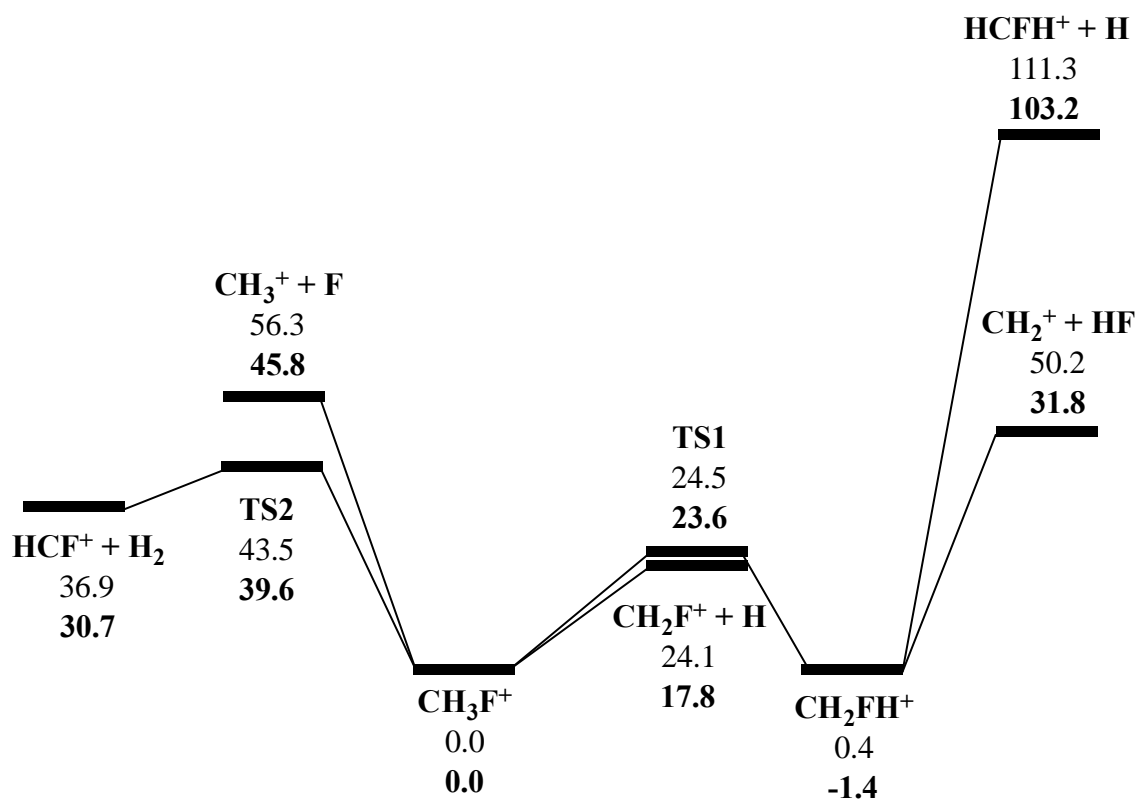


Figure S3. Relative energies at 0 K in kcal/mol for  $\text{CH}_3\text{F}^+$  calculated at CAM-B3LYP/6-31G(d,p) and CBS-QB3 (bold) level of theory

Table S1. Branching of the Reactive Trajectories for  $\text{CH}_3\text{X}^+$  (X=  $\text{NH}_2$ , OH and F)

molecular species	orientation	field strength and pulse shape	total trajectories	unreactive trajectories	reaction during pulse	reaction after pulse	$\text{CH}_2\text{X}^+ + \text{H}$	$\text{CH}_3^+ + \text{X}$	$\text{CH}_2\text{XH}^+$	$\text{CH}_2^+ + \text{HX}$	$\text{HCX}^+ + \text{H}_2$
$\text{CH}_3\text{NH}_2^+$	random	0.07 au, cosine sq	100	89	6	5	11	0	0	0	0
		0.05 au, trapezoid	200	172	3	25	26	0	1	0	1
		0.07au, trapezoid	183	81	14	88	93	1	2	0	6 <sup>c</sup>
	aligned	0.05 au, trapezoid	199	81	6	112	100	2	7	0	9
		0.07 au, trapezoid	161	7	18	136	97 <sup>a</sup>	5	1	0	51 <sup>d</sup>
$\text{CH}_3\text{OH}^+$	random	0.07 au, cosine sq	98	59	11	28	30	0	0	0	9
		0.05 au, trapezoid	199	129	9	61	58	0	3	0	9
		0.07 au, trapezoid	162	44	37	81	91 <sup>b</sup>	1	3	0	23 <sup>e</sup>
	aligned	0.05 au, trapezoid	198	55	9	134	102	0	12	0	29 <sup>f</sup>
		0.07 au, trapezoid	160	13	34	113	95	4	6	0	42 <sup>g</sup>
$\text{CH}_3\text{F}^+$	random	0.07 au, cosine sq	90	50	6	34	33	0	2	2	3
		0.05 au, trapezoid	194	128	10	56	50	1	5	0	10
		0.07 au, trapezoid	145	32	33	80	90	2	3	3	15
	aligned	0.05 au, trapezoid	199	61	0	138	100	6	10	1	21
		0.07 au, trapezoid	170	5	44	121	111	11	4	10	29

Trajectories with sequential dissociations have been classified according to the first dissociation event. <sup>a</sup>10 trajectories dissociated into  $\text{HCNH}^+ + \text{H} + \text{H}_2$ , which have been combined to H elimination, <sup>b</sup>2 trajectories dissociated into  $\text{CHO}^+ + \text{H} + \text{H}_2$  which have been combined to H elimination, <sup>c</sup>4 trajectories dissociated into  $\text{HCNH}^+ + \text{H}_2 + \text{H}$ , which have been combined to  $\text{H}_2$  elimination. <sup>d</sup>35 trajectories dissociated into  $\text{HCNH}^+ + \text{H}_2 + \text{H}$ , which have been combined to  $\text{H}_2$  elimination. <sup>e</sup>13 trajectories dissociated into  $\text{CHO}^+ + \text{H}_2 + \text{H}$  which have been combined to  $\text{H}_2$  elimination. <sup>f</sup>4 trajectories dissociated into  $\text{CHO}^+ + \text{H}_2 + \text{H}$  which have been combined to  $\text{H}_2$  elimination. <sup>g</sup>1 trajectory dissociated into  $\text{CHO}^+ + \text{H}_2 + \text{H}$  which has been combined to  $\text{H}_2$  elimination.

## Infra-Red Spectrum

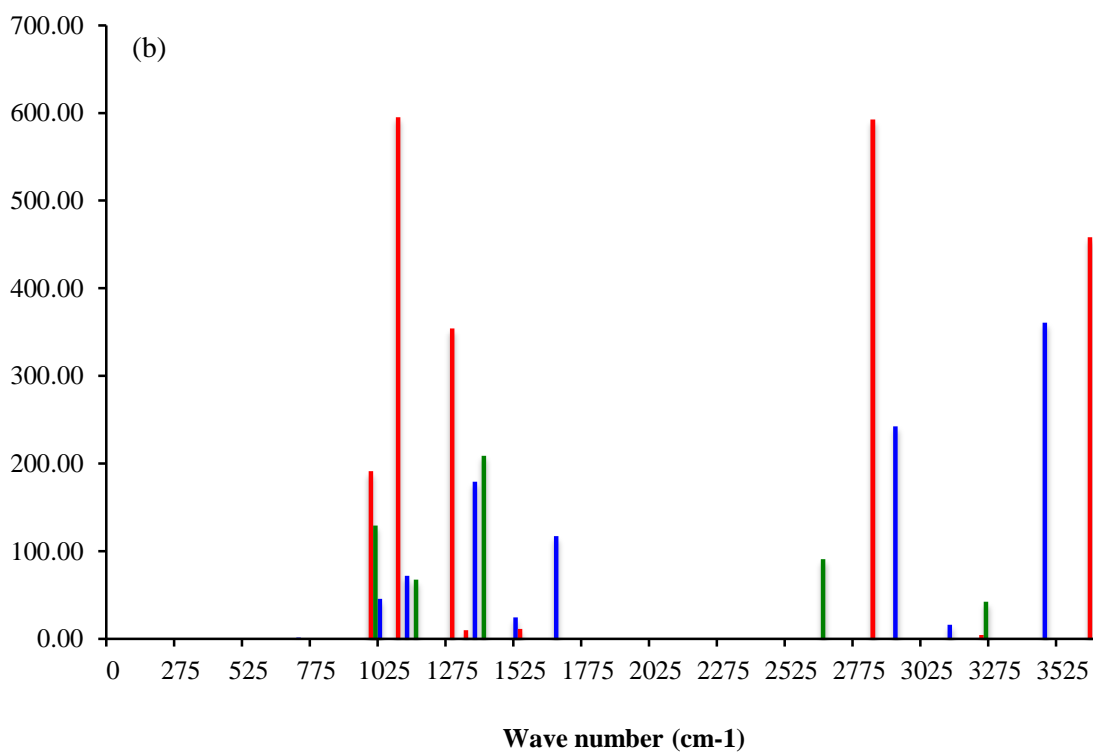
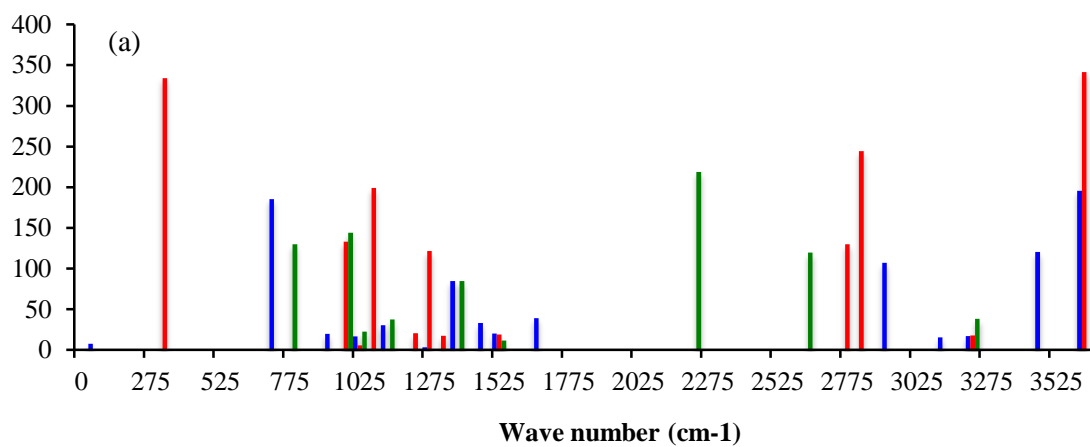
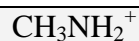


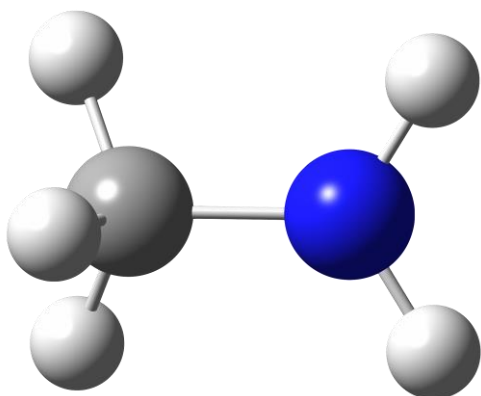
Figure 4. Infra-red (IR) intensities for  $\text{CH}_3\text{NH}_2^+$  (blue),  $\text{CH}_3\text{OH}^+$  (red) and  $\text{CH}_3\text{F}^+$  (green) (a) rotationally averaged and (b) with the C-X bond aligned with the laser polarization.

## GaussView Images of optimized geometries and Coordinates (CBS-QB3)

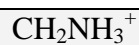
### Methylamine monocations surface



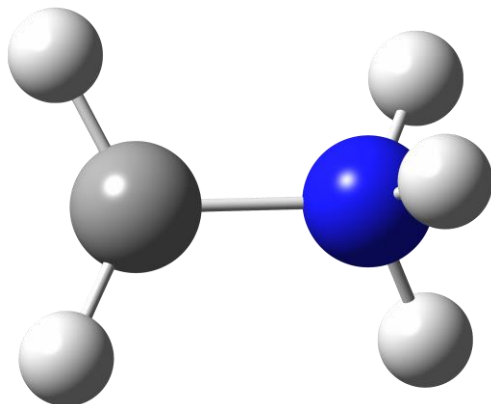
SCF energy: -94.968703 au



C	-0.70563300	0.00007300	-0.01500600
H	-1.09345500	0.91500900	-0.46780700
H	-1.04816700	-0.00164900	1.04702300
H	-1.09342000	-0.91371600	-0.47028900
N	0.71058100	0.00000200	-0.00844800
H	1.24746500	0.86950700	0.02016100
H	1.24730600	-0.86960500	0.02007800



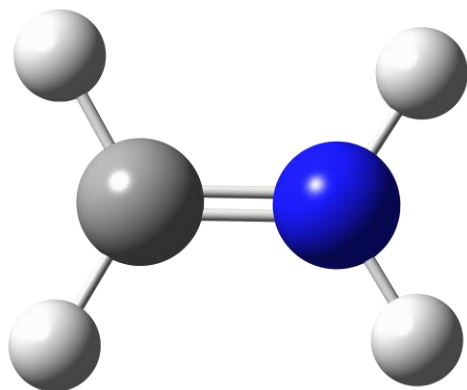
SCF energy: -94.970112 au



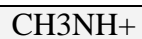
C	0.82644700	-0.00000100	-0.02752600
H	1.31128100	0.95933700	0.06194800
H	1.31124200	-0.95936100	0.06194100
N	-0.64319500	0.00000500	0.00191200
H	-1.03020100	0.82796100	-0.46740800
H	-1.03022700	-0.82729000	-0.46856900
H	-1.01841100	-0.00067600	0.96386100



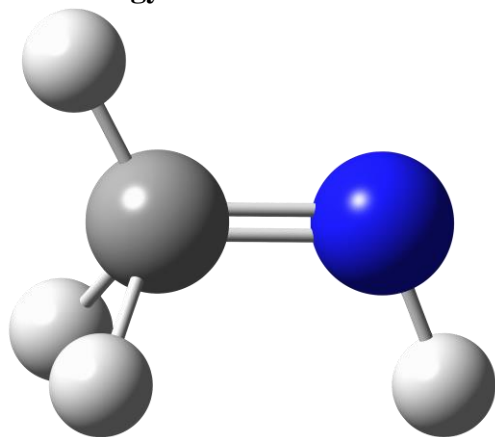
SCF energy: -94.793734 au



C	0.67492800	0.00000000	0.00032700
H	1.21370400	-0.94288200	-0.00023900
H	1.21370400	0.94288300	-0.00023900
N	-0.60010900	0.00000000	-0.00009000
H	-1.13810700	-0.86667900	-0.00042800
H	-1.13810700	0.86667900	-0.00042800



SCF energy: -94.252372 au



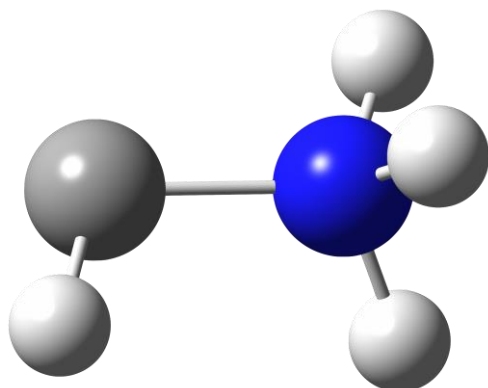
C	-0.57028100	-0.05208600	-0.00061000
H	-1.17342400	-0.95536300	0.00070300
H	-0.91870700	0.78608300	-0.70558500
H	-0.91399400	0.78440300	0.70926400
N	0.74389600	-0.15261300	0.00010400
H	1.22054300	0.76568400	-0.00144800

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**CHNH<sub>3</sub><sup>+</sup>**

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**SCF energy:** -94.302372 au



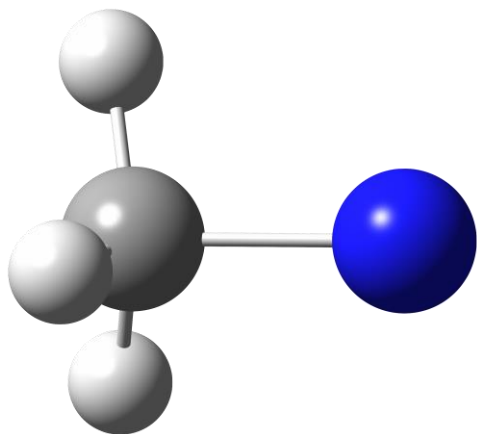
C	0.90211800	-0.18747500	-0.00002300
H	1.39735500	0.79389600	0.00002600
N	-0.56895500	0.01533100	-0.00002200
H	-0.88081000	0.55337900	0.82691300
H	-0.88093100	0.55487300	-0.82592400
H	-1.06563400	-0.88461400	-0.00072600

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**CH<sub>3</sub>N<sup>+</sup> (quartet)**

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**SCF energy:** -93.651687 au



C	0.65692400	0.00000400	0.00008700
H	0.86361500	0.93944100	0.52789400
H	0.86399500	-0.01227800	-1.07734500
H	0.86374300	-0.92711500	0.54918000
N	-0.93327100	-0.00001000	-0.00003600

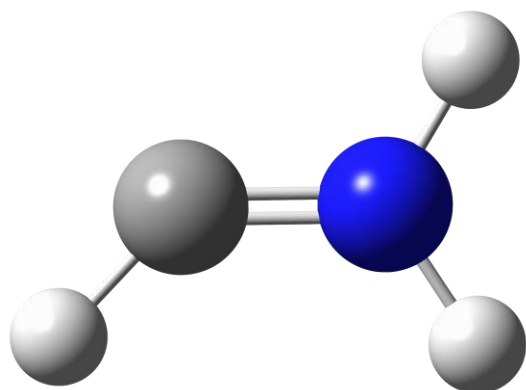


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**CHNH<sub>2</sub><sup>+</sup>**

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SCF energy: -93.760793 au



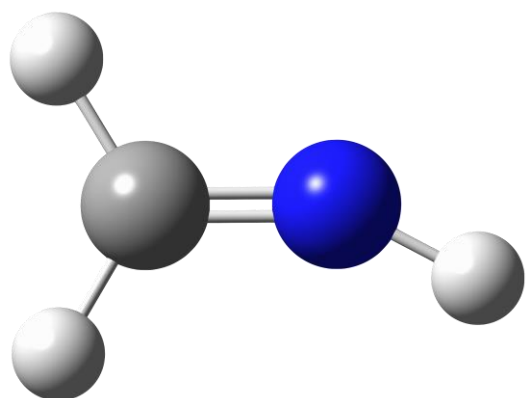
C	0.71055800	-0.15558400	0.00000000
H	1.57461200	0.50794500	-0.00017500
N	-0.52878200	0.03060100	0.00011800
H	-0.95111900	0.97031400	-0.00024800
H	-1.18536800	-0.75896200	-0.00040100

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**CH<sub>2</sub>NH<sup>+</sup>**

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SCF energy: -93.751589 au

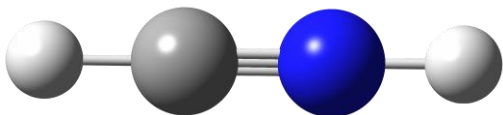


C	0.03041500	-0.60015800	0.00000000
H	-0.92253400	-1.16367300	0.00000000
H	0.97712800	-1.16268100	0.00000000
N	0.03041500	0.62803400	0.00000000
H	-0.44998700	1.53106700	0.00000000

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**HCNH<sup>+</sup>**

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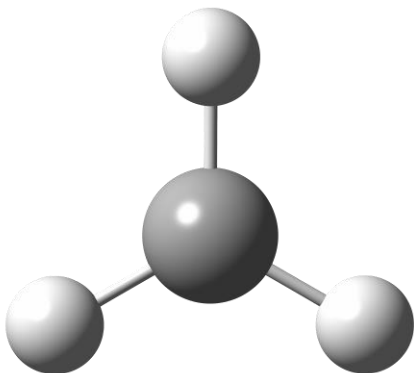
**SCF energy:** -93.193262 au

C	-0.00017700	0.59990000	0.00000000
H	-0.00034700	1.68076000	0.00000000
N	-0.00017700	-0.53281300	0.00000000
H	0.00264700	-1.55046900	0.00000000

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**CH<sub>3</sub><sup>+</sup>**

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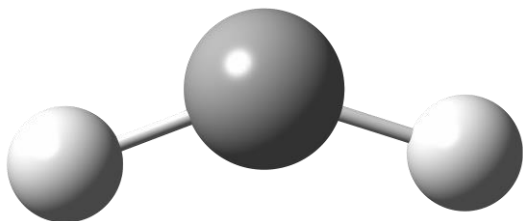
**SCF energy:** -39.246140 au

C	0.00000000	0.00000000	0.00000000
H	0.00000000	1.09349600	0.00000000
H	0.94699600	-0.54674800	0.00000000
H	-0.94699600	-0.54674800	0.00000000

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**CH<sub>2</sub><sup>+</sup>**

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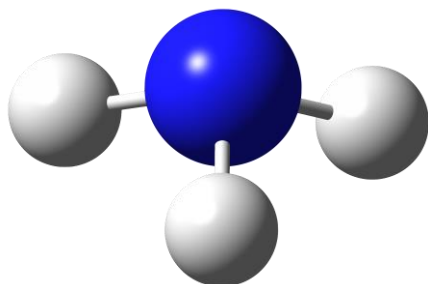
**SCF energy:** -38.579775 au

C	0.00000000	0.00000000	0.09067000
H	0.00000000	1.03726900	-0.27200900
H	0.00000000	-1.03726900	-0.27200900

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**NH<sub>3</sub>**

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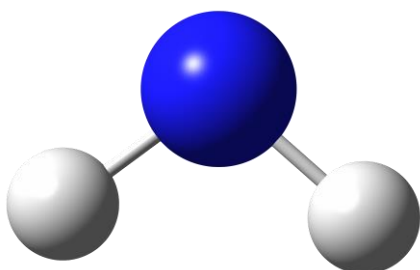
**SCF energy:** -56.217765 au

N	0.0000000	0.0000000	0.11602700
H	0.0000000	0.93895900	-0.27073000
H	-0.81316200	-0.46948000	-0.27073000
H	0.81316200	-0.46948000	-0.27073000

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**NH<sub>2</sub>**

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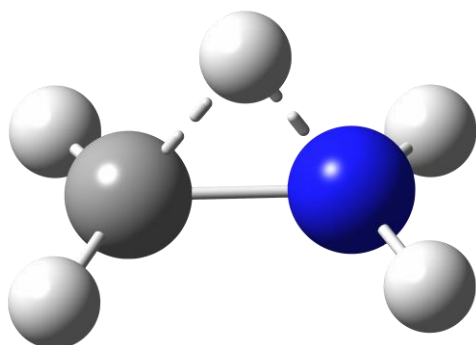
**SCF energy:** -55.791187 au

N	0.0000000	0.0000000	0.14391400
H	0.0000000	0.80193900	-0.50369900
H	0.0000000	-0.80193900	-0.50369900

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**TS1**

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**SCF energy:** -94.888621 au

C	0.77081200	0.00000000	-0.02025400
H	1.25422400	-0.95376900	-0.18145400
H	-0.02511600	0.00000000	1.04791700
H	1.25422400	0.95376900	-0.18145400
N	-0.67752100	0.00000000	-0.02582000
H	-1.18277600	-0.86982100	-0.19137400
H	-1.18277600	0.86982100	-0.19137400

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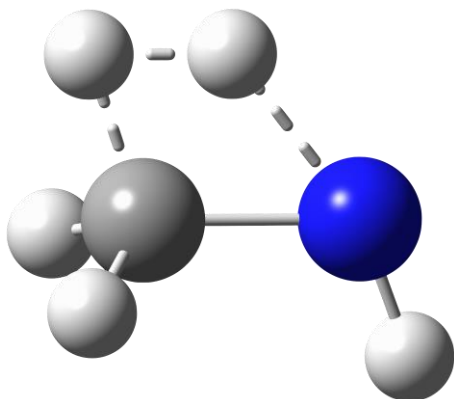
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TS2

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SCF energy: -94.816109 au



C	-0.61007600	-0.15007700	0.00004900
H	-1.22761900	0.90739900	-0.00006100
H	-1.00064200	-0.59500900	0.92384300
H	-1.00073000	-0.59525300	-0.92359100
N	0.82772900	0.12100800	-0.00005500
H	-0.27624000	1.08557800	-0.00013100
H	1.37158100	-0.74931100	0.00003200

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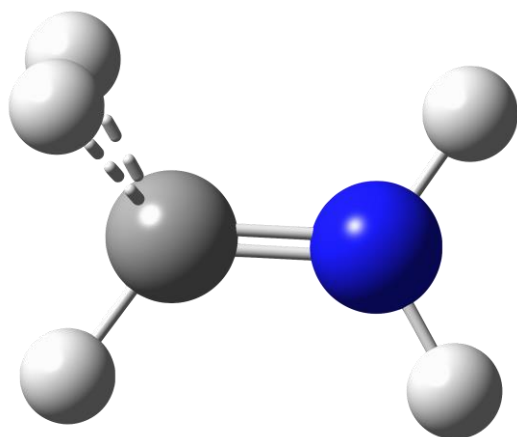
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TS3

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SCF energy: -94.861139 au



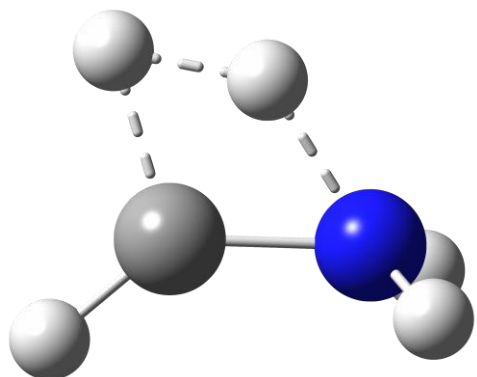
C	-0.52275400	-0.24098400	-0.17799000
H	-0.95648100	-1.18906100	0.12583300
H	-1.73538100	0.81750600	0.67120700
H	-1.50773200	0.80064200	-0.14781300
N	0.69955100	0.08494900	0.03014900
H	1.35014200	-0.54827300	0.49882100
H	1.08912100	0.97044800	-0.29114600

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**TS4**

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**SCF energy:** -94.776567 au



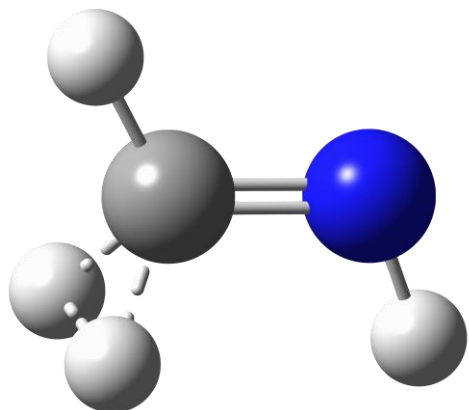
C	-0.66718000	-0.02846600	-0.02912100
H	-1.08203900	1.33817200	-0.28059500
H	-1.54914900	-0.78324400	-0.06708800
N	0.81855200	-0.07502800	-0.02408900
H	0.04825600	1.15209100	-0.06080300
H	1.24419300	-0.48561000	0.84558200
H	1.26705300	-0.40637200	-0.91953700

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**TS5**

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**SCF energy:** -94.248942 au



C	-0.55540600	-0.07222100	0.00001400
H	-1.17404100	-0.96476900	0.00002400
H	-0.95760800	0.81651800	0.63421100
H	-0.95764500	0.81653000	-0.63414200
N	0.74373700	-0.14415000	-0.00002200
H	1.21556700	0.77409800	-0.00002700

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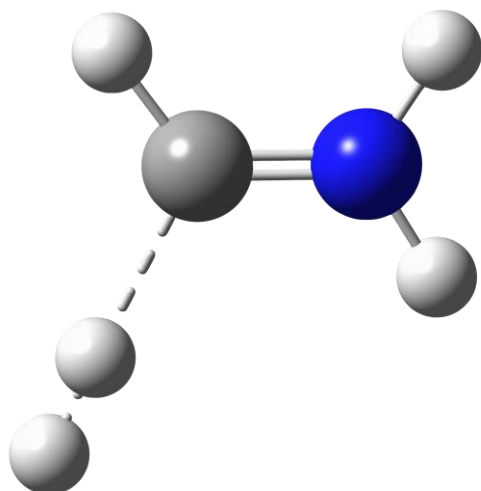
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TS6

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SCF energy: -94.874621 au



C	-0.40989400	0.40476600	0.00001500
H	-0.55138300	1.48475500	0.00002000
H	-1.76520800	-0.50952600	-0.00000300
N	0.69358100	-0.20868600	-0.00000800
H	1.59723100	0.27878700	-0.00002400
H	-2.41520200	-0.99053600	-0.00001500
H	0.73885700	-1.23127000	-0.00001100

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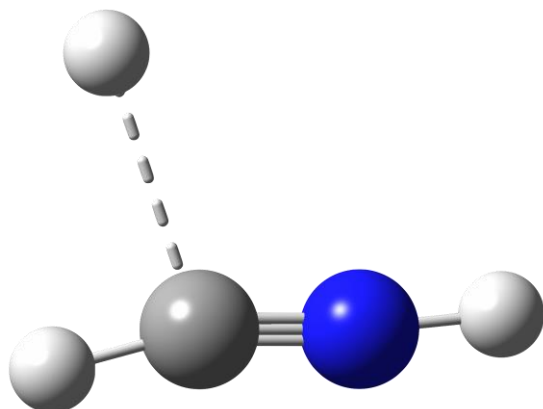
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TS7

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SCF energy: -93.682961 au



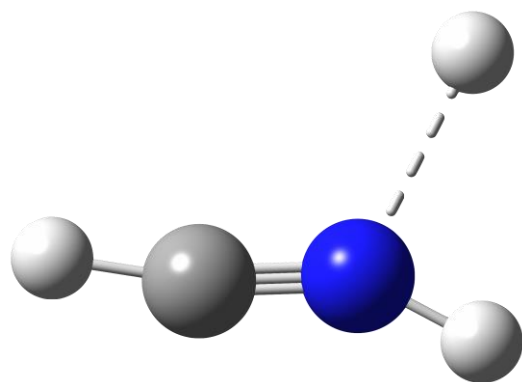
C	0.10926600	0.52483900	0.00000000
H	0.38622400	1.56925400	0.00000000
H	-1.81535800	1.22784100	0.00000000
N	0.10926600	-0.61696000	0.00000000
H	0.00867400	-1.62741200	0.00000000

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TS8

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SCF energy: -93.668433 au



C	0.08048900	0.69390000	0.00000000
H	-0.12147800	1.75452500	0.00000000
N	0.08048900	-0.46025000	0.00000000
H	-1.51337100	-1.35264600	0.00000000
H	0.58849600	-1.34352800	0.00000000

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## Methanol monocations surface

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GaussView images and coordinates of the geometries optimized at CBS-QB3 level of theory for methanol monocations are available in supporting information of our earlier publication (*J. Phys. Chem. A* **2014**, 118, 1769. ) for free of charge. (Copyright 2014 American Chemical Society)



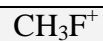
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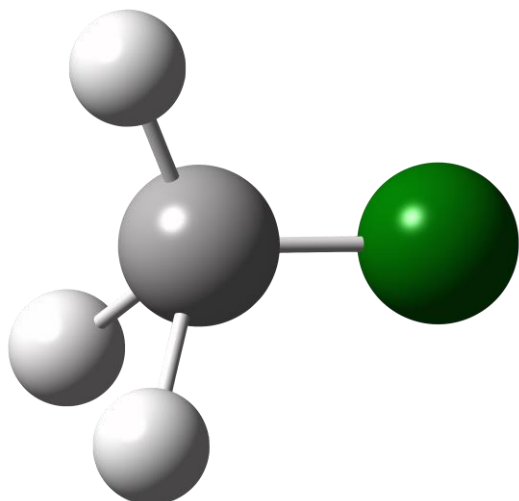
**Methyl fluoride monocations surface**

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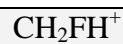
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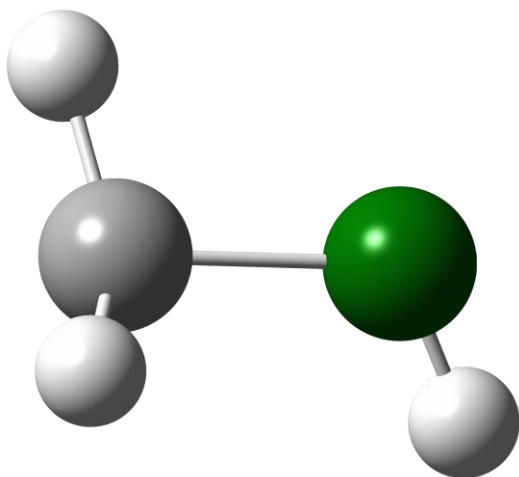
**SCF energy:** -138.649714 au



C	0.56930800	-0.08108000	0.00017100
H	1.03064900	0.70726600	-0.73005000
H	0.98119900	-1.08847400	0.00052900
H	1.02952700	0.70896600	0.72924900
F	-0.71746900	0.01763600	-0.00008400



**SCF energy:** -138.676835 au



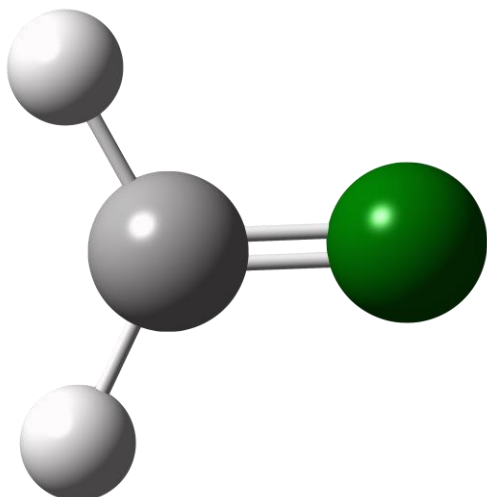
C	-0.85697100	0.03645100	0.09792000
H	-1.20238500	-0.98090000	-0.03779600
H	-1.14356300	0.98527400	-0.34184800
F	0.69653600	-0.08649100	-0.06816700
H	1.21895000	0.55533600	0.40563000

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**CH<sub>2</sub>F<sup>+</sup>**

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**SCF energy:** -138.145200 au



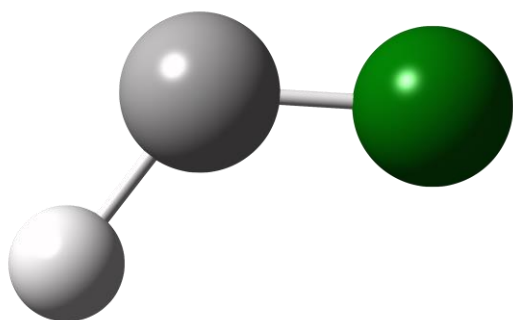
C	0.0000000	0.0000000	-0.5939670
H	0.0000000	0.9761110	-1.0929820
H	0.0000000	-0.9761110	-1.0929820
F	0.0000000	0.0000000	0.6388630

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**HCF<sup>+</sup>**

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**SCF energy:** -137.483149 au



C	0.0576310	0.6376150	0.0000000
H	-0.8644580	1.2676600	0.0000000
F	0.0576310	-0.5659280	0.0000000

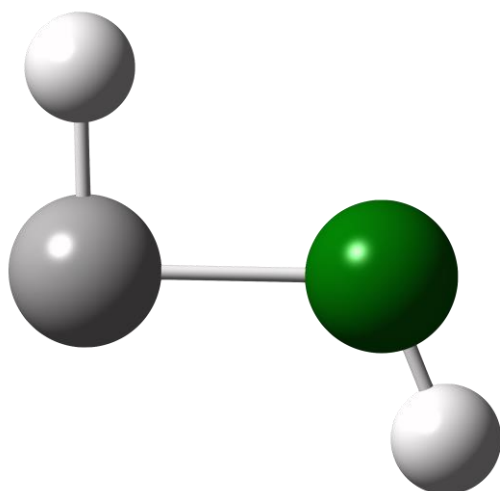
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HCFH<sup>+</sup>

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SCF energy: -138.003776 au



C	0.94033100	-0.20939700	0.00002200
H	1.21310900	0.87428500	-0.00017600
F	-0.63187100	0.11749300	0.00003000
H	-1.16825800	-0.67534400	-0.00022100

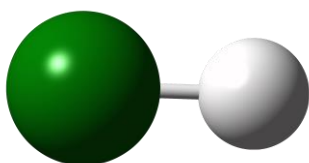
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HF

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SCF energy: -100.055623 au



F	0.00000000	0.00000000	0.09200900
H	0.00000000	0.00000000	-0.82808200

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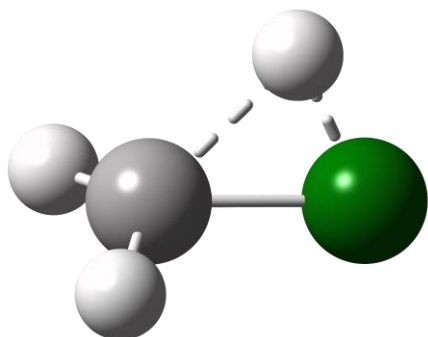
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TS1

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SCF energy: -138.610181 au



C	-0.73652000	-0.00000100	0.01829000
H	-1.14591300	0.98857800	-0.17211900
H	0.23760400	0.00007700	1.00102800
H	-1.14592200	-0.98859000	-0.17203400
F	0.71926100	-0.00000700	-0.08517900

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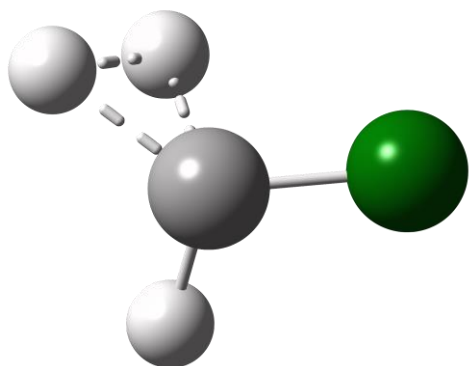
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TS2

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SCF energy: -138.576274 au



C	0.55995800	-0.19131200	-0.15224700
H	1.67714700	0.52754300	-0.32000100
H	1.00518900	0.96088200	0.58199300
H	0.81270000	-0.93197600	0.60939200
F	-0.76164200	0.06571400	0.00467800