Electronic Supplementary Material (ESI) for Faraday Discussions.

Supplementary Information

The FELion cryogenic ion trap beam line at the FELIX free-electron laser laboratory: Infrared signatures of primary alcohol cations

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NOTE: All structural parameters are given in units of Å and degrees. Vibrational wavenumbers are given in units of cm^{-1}. Harmonic/anharmonic wavenumbers are separated by a slash. If only one value is given, this refers to harmonic values. Intensities (in parantheses, km/mol) are given following the same format for selected species/ levels of theory.

1 Molecular structures – vibrational wavenumbers

1.1 Methanol radical cation CH_3OH^+ (1a)

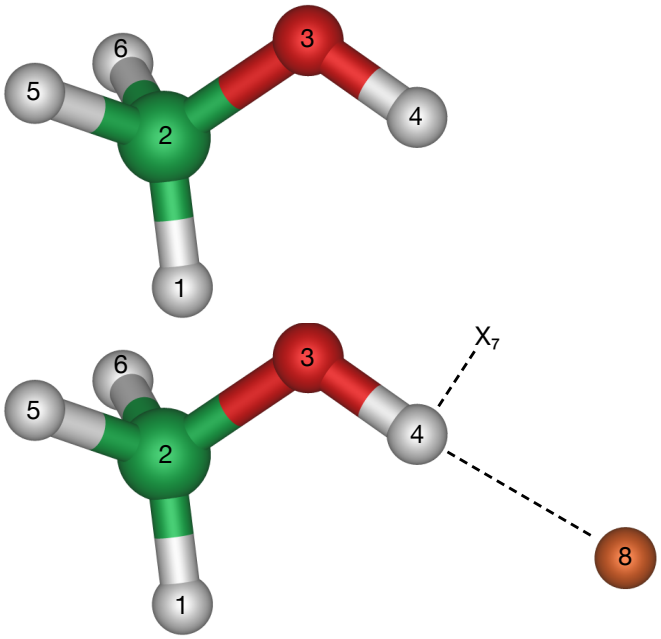

Figure S1: Molecular structures of CH_3OH^+ and CH_3OH^+–He (**1a**).

1.1.1 Structural parameters of CH_3OH^+

```
H
C 1 r1
O 2 r2 1 a1
H 3 r3 2 a2 1 d0
H 2 r4 3 a3 4 d1
H 2 r4 3 a3 4 md1

CCSD(T)/ANO1          B3LYP/aug-cc-pVTZ     B3LYP/aug-cc-pVTZ-GD3BJ
r1  =    1.084417     r1  =    1.0843       r1  =    1.0843
r2  =    1.373111     r2  =    1.3559       r2  =    1.3558
a1  =  115.463626     a1  =  116.7445       a1  =  116.7351
r3  =    0.986170     r3  =    0.9852       r3  =    0.9851
a2  =  113.601150     a2  =  114.5481       a2  =  114.5135
d0  =    0.000000     r4  =    1.1277       r4  =    1.1277
r4  =    1.119626     a3  =  106.6199       a3  =  106.6112
a3  =  105.412649     d1  =  130.3445       d1  =  130.3395
d1  =  128.745256     md1 = -130.3445       md1 = -130.3395
md1 = -128.745256     d0  =    0.0          d0  =    0.0
```

1.1.2 Structural parameters of CH_3OH^+–He

```
H
C 1 r1
O 2 r2 1 a1
H 3 r3 2 a2 1 d0
H 2 r4 3 a3 4 d1
H 2 r4 3 a3 4 md1
X 4 rd 3 a90 2 d180
HE 4 r5 7 a4 3 d180
```

B3LYP/aug-cc-pVTZ			B3LYP/aug-cc-pVTZ-GD3BJ		
r1	=	1.0844	r1	=	1.0844
r2	=	1.356	r2	=	1.356
a1	=	116.6575	a1	=	116.6283
r3	=	0.987	r3	=	0.9869
a2	=	114.5891	a2	=	114.4738
r4	=	1.127	r4	=	1.1269
a3	=	106.6413	a3	=	106.6398
d1	=	130.2044	d1	=	130.1865
md1	=	-130.2044	md1	=	-130.1865
r5	=	1.8079	r5	=	1.7899
a4	=	85.4499	a4	=	88.4457
d0	=	0.0	d0	=	0.0
rd	=	1.0	rd	=	1.0
a90	=	90.0	a90	=	90.0
d180	=	180.0	d180	=	180.0

Vibrational wavenumbers and IR intensities (harmonic/anharmonic; cm^{-1} and $km \cdot mol^{-1}$)

1.1.3 CH_3OH^+, B3LYP/aug-cc-pVTZ

$\nu_1(a') = 3547/3371(314/299)$, $\nu_2(a') = 3180/3019(15/14)$, $\nu_3(a') = 2744/2434(223/197)$, $\nu_4(a') = 1480/1457(18/3$
$\nu_5(a') = 1285/1272(25/10)$, $\nu_6(a') = 1234/1190(113/98)$, $\nu_7(a') = 1045/1016(161/160)$, $\nu_8(a') = 937/952(112/57)$,
$\nu_9(a'') = 2632/2411(115/89)$, $\nu_{10}(a'') = 1214/1141(14/11)$, $\nu_{11}(a'') = 973/939(5/3)$, $\nu_{12}(a'') = 303/196(285/247)$

1.1.4 CH_3OH^+, B3LYP/aug-cc-pVTZ-GD3BJ

$\nu_1(a') = 3547(314)$, $\nu_2(a') = 3180(15)$, $\nu_3(a') = 2743(223)$, $\nu_4(a') = 1480(18)$, $\nu_5(a') = 1286(24)$, $\nu_6(a') = 1235(113)$, $\nu_7(a') = 1045(161)$, $\nu_8(a') = 937(112)$, $\nu_9(a'') = 2632(115)$, $\nu_{10}(a'') = 1215(14)$, $\nu_{11}(a'') = 973(5)$, $\nu_{12}(a'') = 301(285)$

1.1.5 CH_3OH^+–He, B3LYP/aug-cc-pVTZ

$\nu_1(a') = 3511/3360(482/379)$, $\nu_2(a') = 3179/3020(14/12)$, $\nu_3(a') = 2748/2514(229/174)$, $\nu_4(a') = 1481/1464(18/2$
$\nu_5(a') = 1277(26/10)$, $\nu_6(a') = 1236/1194(113/119)$, $\nu_7(a') = 1053/1018(146/154)$, $\nu_8(a') = 938/957(123/56)$,
$\nu_9(a') = 158/89(7/4)$, $\nu_{10}(a') = 54/18(6/4)$, $\nu_{11}(a'') = 2640/2419(113/86)$, $\nu_{12}(a'') = 1220/1146(14/10)$,
$\nu_{13}(a'') = 977/938(6/2)$, $\nu_{14}(a'') = 339/224(279/241)$, $\nu_{15}(a'') = 81/45(1/0.3)$

1.1.6 CH_3OH^+–He, B3LYP/aug-cc-pVTZ-GD3BJ

$\nu_1(a') = 3511(487)$, $\nu_2(a') = 3179(14)$, $\nu_3(a') = 2748(229)$, $\nu_4(a') = 1481(19)$, $\nu_5(a') = 1294(26)$, $\nu_6(a') = 1237(112)$, $\nu_7(a') = 1054(144)$, $\nu_8(a') = 938(123)$, $\nu_9(a') = 168(8)$, $\nu_{10}(a') = 51(6)$, $\nu_{11}(a'') = 2641(113)$, $\nu_{12}(a'') = 1220(14)$, $\nu_{13}(a'') = 977(6)$, $\nu_{14}(a'') = 338(279)$, $\nu_{15}(a'') = 82(1)$

1.2 Methyl oxonym cation $CH_2OH_2^+$ (1b)

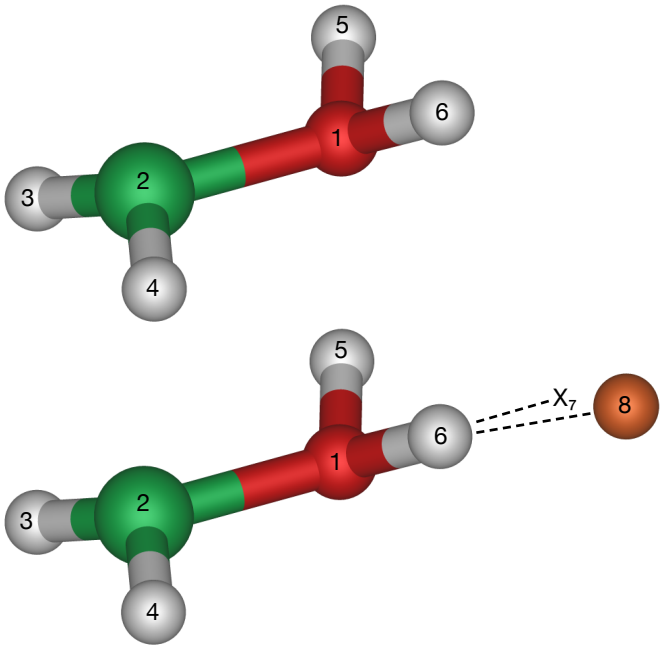

Figure S2: Molecular structures of $CH_2OH_2^+$ and $CH_2OH_2^+$–He (**1b**).

1.2.1 Structural parameters of $CH_2OH_2^+$

```
O
C 1 r1
H 2 r2 1 a1
H 2 r2 1 a1 3 d1
H 1 r3 2 a2 3 d2
H 1 r3 2 a2 4 md2

CCSD(T)/ANO1         B3LYP/aug-cc-pVTZ    B3LYP/aug-cc-pVTZ-GD3BJ
r1  =    1.457493    r1  =    1.4565      r1  =    1.4563
r2  =    1.078791    r2  =    1.0776      r2  =    1.0775
a1  = 110.932191     a1  = 111.35         a1  = 111.3342
d1  = 146.367075     d1  = 148.6307       d1  =
r3  =    0.975854    r3  =    0.9777      r3  =    0.9777
a2  = 114.429340     a2  = 115.5529       a2  = 115.5189
d2  =  42.207644     d2  =  39.2307       d2  =  39.2717
md2 = -42.207644     md2 = -39.2309       md2 = -39.2717
```

1.2.2 Structural parameters of $CH_2OH_2^+$–He

```
O
C 1 r1
H 2 r2 1 a1
H 2 r3 1 a2 3 d1
H 1 r4 2 a3 3 d2
H 1 r5 2 a4 4 d3
X 6 rd 1 a90 2 d180
HE 6 r6 7 a5 1 d4

B3LYP/aug-cc-pVTZ
r1   =   1.4542
r2   =   1.0775
```

```
r3   =   1.0775
a1   = 111.5047
a2   = 111.4283
d1   = 148.7735
r4   =   0.9772
r5   =   0.9799
a3   = 115.5249
a4   = 115.6796
d2   =  38.9411
d3   = -38.9528
r6   =   1.7662
a5   =  89.584
d4   = 176.3199
rd   =   1.0
a90  =  90.0
d180 =  180.0
```

Vibrational wavenumbers and IR intensities (harmonic/anharmonic; cm^{-1} and $km \cdot mol^{-1}$)

1.2.3 $CH_2OH_2^+$, CCSD(T)/ANO1, Harmonic/Anharmonic

$\nu_1(a') = 3641/3467$, $\nu_2(a') = 3175/3059$, $\nu_3(a') = 1692/1650$, $\nu_4(a') = 1438/1401$, $\nu_5(a') = 952/911$, $\nu_6(a') = 731/510$, $\nu_7(a') = 685/551$, $\nu_8(a'\prime) = 3729/3538$, $\nu_9(a'') = 3353/3222$, $\nu_{10}(a'') = 1296/1247$, $\nu_{11}(a'') = 933/901$, $\nu_{12}(a'') = 276/216$

1.2.4 $CH_2OH_2^+$, B3LYP/aug-cc-pVTZ

$\nu_1(a') = 3595/3422(239/209)$, $\nu_2(a') = 3160/3052(10/8)$, $\nu_3(a') = 1675/1625(133/113)$, $\nu_4(a') = 1428/1403(4/1)$, $\nu_5(a') = 926/884(47/71)$, $\nu_6(a') = 660/408(21/191)$, $\nu_7(a') = 637/461(350/299)$, $\nu_8(a'\prime) = 3671/3484(379/363)$, $\nu_9(a'') = 3338/3216(24/26)$, $\nu_{10}(a'') = 1281/1228(13/13)$, $\nu_{11}(a'') = 922/897(4/6)$, $\nu_{12}(a'') = 269/190(39/26)$

1.2.5 $CH_2OH_2^+$, B3LYP/aug-cc-pVTZ-GD3BJ

$\nu_1(a') = 3596(239)$, $\nu_2(a') = 3161(10)$, $\nu_3(a') = 1675(133)$, $\nu_4(a') = 1428(4)$, $\nu_5(a') = 927(47)$, $\nu_6(a') = 661(22)$, $\nu_7(a') = 638(349)$, $\nu_8(a'\prime) = 3672(379)$, $\nu_9(a'') = 3339(24)$, $\nu_{10}(a'') = 1282(13)$, $\nu_{11}(a'') = 923(4)$, $\nu_{12}(a'') = 269(39)$

1.2.6 $CH_2OH_2^+$–He, B3LYP/aug-cc-pVTZ

$\nu_1(a) = 3657/3477(414/375)$, $\nu_2(a) = 3567/3417(376/282)$, $\nu_3(a) = 3338/3216(23/23)$, $\nu_4(a) = 3162/3056(9/8)$, $\nu_5(a) = 1679/1628(122/105)$, $\nu_6(a) = 1429/1405(4/1)$, $\nu_7(a) = 1285/1232(11/12)$, $\nu_8(a) = 935/891(44/106)$, $\nu_9(a) = 932/902(7/13)$, $\nu_{10}(a) = 662/389(85/2389)$, $\nu_{11}(a) = 646/451(270/144)$, $\nu_{12}(a) = 300/230(45/25)$, $\nu_{13}(a) = 173/110(13/8)$, $\nu_{14}(a) = 106/83(2/2)$, $\nu_{15}(a) = 59/54(4/5)$

1.2.7 $CH_2OH_2^+$–He, B3LYP/aug-cc-pVTZ-GD3BJ

$\nu_1(a) = 3657(415)$, $\nu_2(a) = 3567(381)$, $\nu_3(a) = 3339(23)$, $\nu_4(a) = 3162(9)$, $\nu_5(a) = 1679(121)$, $\nu_6(a) = 1430(4)$, $\nu_7(a) = 1286(11)$, $\nu_8(a) = 936(44)$, $\nu_9(a) = 933(7)$, $\nu_{10}(a) = 664(103)$, $\nu_{11}(a) = 646(252)$, $\nu_{12}(a) = 302(46)$, $\nu_{13}(a) = 184(13)$, $\nu_{14}(a) = 107(2)$, $\nu_{15}(a) = 58(4)$

1.3 Protonated methanol $CH_3OH_2^+$ (2)

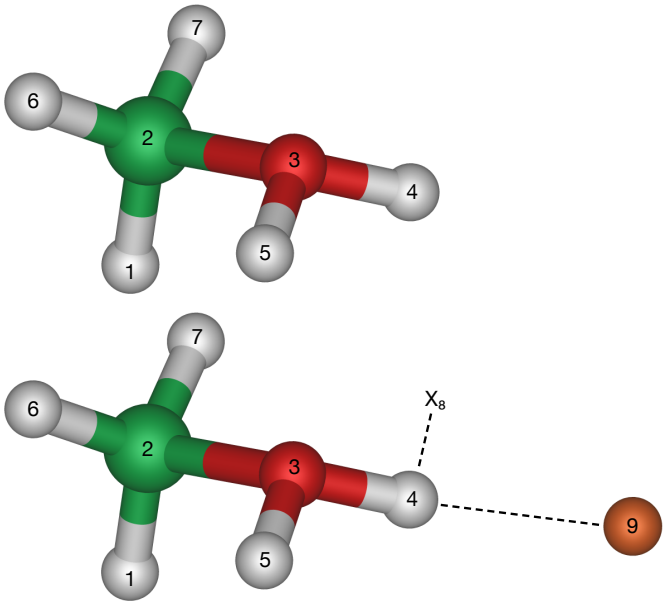

Figure S3: Molecular structures of $CH_3OH_2^+$ and $CH_3OH_2^+$–He (**2**).

1.3.1 Structural parameters of $CH_3OH_2^+$

```
CH3OH2+
H
C 1 r1
O 2 r2 1 a1
H 3 r3 2 a2 1 d1
H 3 r3 2 a2 1 md1
H 2 r4 3 a3 1 d2
H 2 r4 3 a3 1 md2

CCSD(T)/ANO1          B3LYP/aug-cc-pVTZ     B3LYP/aug-cc-pVTZ-GD3BJ
r1  =    1.085505     r1  =    1.0843       r1  =    1.0842
r2  =    1.513173     r2  =    1.522        r2  =    1.5216
a1  =  108.260510     a1  =  108.1088       a1  =  108.0936
r3  =    0.973644     r3  =    0.9751       r3  =    0.975
a2  =  113.730440     a2  =  114.5241       a2  =  114.4689
d1  =   63.070408     d1  =   64.3434       d1  =   64.2919
md1 =  -63.070408     md1 =  -64.3434       md1 =  -64.2919
r4  =    1.084510     r4  =    1.0835       r4  =    1.0834
a3  =  104.411941     a3  =  104.4062       a3  =  104.397
d2  =  121.138308     d2  =  121.1373       d2  =  121.1343
md2 = -121.138308     md2 = -121.1373       md2 = -121.1343
```

1.3.2 Structural parameters of $CH_3OH_2^+$–He

```
CH3OH2+-He
H
C 1 r1
O 2 r2 1 a1
H 3 r3 2 a2 1 d1
H 3 r4 2 a22 1 md1
H 2 r5 3 a3 1 d2
H 2 r6 3 a32 1 md2
X 4 rd 3 a90 5 d180
HE 4 r7 8 a4 3 d3
```

B3LYP/aug-cc-pVTZ			B3LYP/aug-cc-pVTZ-GD3BJ		
r1	=	1.0843	r1	=	1.0843
r2	=	1.5198	r2	=	1.5192
a1	=	108.1755	a1	=	108.1621
r3	=	0.9765	r3	=	0.9765
r4	=	0.9747	r4	=	0.9746
a2	=	114.5935	a2	=	114.4503
a22	=	114.4734	a22	=	114.4262
d1	=	64.5899	d1	=	64.5623
md1	=	-64.3166	md1	=	-64.1941
r5	=	1.0835	r5	=	1.0834
r6	=	1.0835	r6	=	1.0834
a3	=	104.517	a3	=	104.5256
a32	=	104.4702	a32	=	104.4559
d2	=	121.1558	d2	=	121.1618
md2	=	-121.1172	md2	=	121.1019
r7	=	1.8325	r7	=	1.8085
a4	=	86.9674	a4	=	84.7648
d3	=	183.7775	d3	=	181.7929
rd	=	1.0	rd	=	1.0
a90	=	90.0	a90	=	90.0
d180	=	180.0	d180	=	180.0

Vibrational wavenumbers and IR intensities (harmonic/anharmonic; cm^{-1} and $km \cdot mol^{-1}$)

1.3.3 $CH_3OH_2^+$, CCSD(T)/ANO1

$\nu_1(a') = 3671/3499$, $\nu_2(a') = 3230/3088$, $\nu_3(a') = 3098/2991$, $\nu_4(a') = 1694/1657$, $\nu_5(a') = 1486/1446$, $\nu_6(a') = 1470/1410$, $\nu_7(a') = 1181/1054$, $\nu_8(a') = 836/791$, $\nu_9(a') = 736/630$, $\nu_{10}(a'') = 3759/3571/$, $\nu_{11}(a'') = 3236/3093$, $\nu_{12}(a'') = 1491/1446$, $\nu_{13}(a'') = 1296/1246$, $\nu_{14}(a'') = 942/913$, $\nu_{15}(a'') = 247/203$

1.3.4 $CH_3OH_2^+$, B3LYP/aug-cc-pVTZ

$\nu_1(a') = 3631/3464(192/181)$, $\nu_2(a') = 3211/3076(4/3)$, $\nu_3(a') = 3090/2994(0.4/1)$, $\nu_4(a') = 1676/1630(109/84)$, $\nu_5(a') = 1478/1436(20/15)$, $\nu_6(a') = 1466/1435(2/4)$, $\nu_7(a') = 1166/1136(5/4)$, $\nu_8(a') = 794/745(36/64)$, $\nu_9(a') = 691/560(293/275)$, $\nu_{10}(a'') = 3707/3529(322/304)$, $\nu_{11}(a'') = 3215/3081(5/4)$, $\nu_{12}(a'') = 1482/1438(18/19$ $\nu_{13}(a'') = 1280/1229(1/1)$, $\nu_{14}(a'') = 928/899(7/11)$, $\nu_{15}(a'') = 229/173(37/29)$

1.3.5 $CH_3OH_2^+$, B3LYP/aug-cc-pVTZ-GD3BJ

$\nu_1(a') = 3632(192)$, $\nu_2(a') = 3211(4)$, $\nu_3(a') = 3090(0.5)$, $\nu_4(a') = 1676(109)$, $\nu_5(a') = 1478(20)$, $\nu_6(a') = 1467(2)$, $\nu_7(a') = 1167(5)$, $\nu_8(a') = 796(35)$, $\nu_9(a') = 693(293)$, $\nu_{10}(a'') = 3708(322)$, $\nu_{11}(a'') = 3216(5)$, $\nu_{12}(a'') = 1482(18)$, $\nu_{13}(a'') = 1280(1)$, $\nu_{14}(a'') = 929(7)$, $\nu_{15}(a'') = 230(37)$

1.3.6 $CH_3OH_2^+$–He, B3LYP/aug-cc-pVTZ

$\nu_1(a) = 3696/3523(364/77)$, $\nu_2(a) = 3615/3465(279/221)$, $\nu_3(a) = 3215/3084(5/39)$, $\nu_4(a) = 3210/3079(3/53)$, $\nu_5(a) = 3090/3001(0.4/1)$, $\nu_6(a) = 1680/1634(100/79)$, $\nu_7(a) = 1483/1440(18/165)$, $\nu_8(a) = 1479/1439(20/151)$, $\nu_9(a) = 1467/1436(1/3)$, $\nu_{10}(a) = 1282/1231(1/1)$, $\nu_{11}(a) = 1167/1107(5/4)$, $\nu_{12}(a) = 938/908(6/10)$, $\nu_{13}(a) = 801/754(35/56)$, $\nu_{14}(a) = 702/580(281/259)$, $\nu_{15}(a) = 261/221(46/32)$, $\nu_{16}(a) = 153/101(10/6)$, $\nu_{17}(a) = 80/83(6/6)$, $\nu_{18}(a) = 51/68(3/4)$

1.3.7 $CH_3OH_2^+$–He, B3LYP/aug-cc-pVTZ-GD3BJ

$\nu_1(a) = 3696(367)$, $\nu_2(a) = 3615(282)$, $\nu_3(a) = 3215(5)$, $\nu_4(a) = 3210(3)$, $\nu_5(a) = 3090(0.4)$, $\nu_6(a) = 1679(99)$, $\nu_7(a) = 1483(18)$, $\nu_8(a) = 1479(20)$, $\nu_9(a) = 1467(2)$, $\nu_{10}(a) = 1284(1)$, $\nu_{11}(a) = 1168(5)$, $\nu_{12}(a) = 939(7)$, $\nu_{13}(a) = 804(35)$, $\nu_{14}(a) = 705(281)$, $\nu_{15}(a) = 262(46)$, $\nu_{16}(a) = 165(10)$, $\nu_{17}(a) = 80(6)$, $\nu_{18}(a) = 48(3)$

1.4 Ethanol radical cation $C_2H_5OH^+$ (3a)

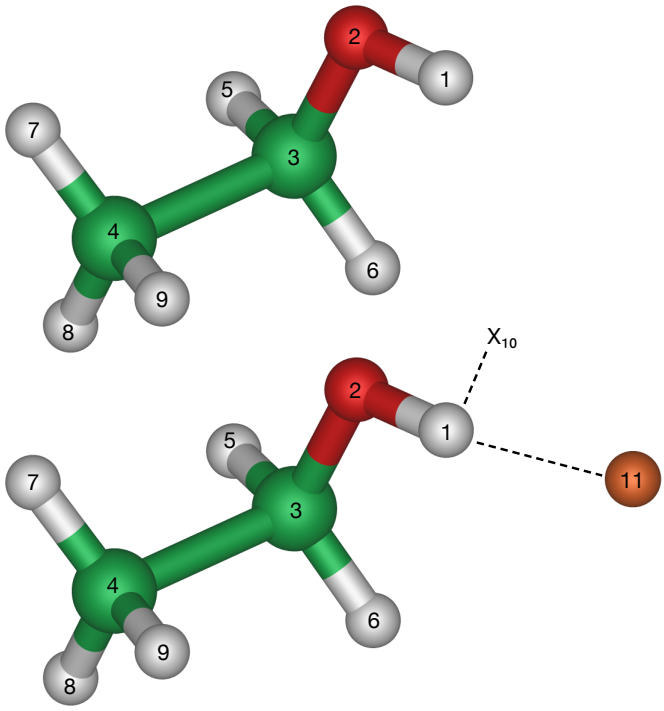

Figure S4: Molecular structure of $C_2H_5OH^+$ and $C_2H_5OH^+$–He (**3a**).

1.4.1 $C_2H_5OH^+$ (3a)

```
C2H5OH+ C1
H
O 1 r1
C 2 r2 1 a1
C 3 r3 2 a2 1 d1
H 3 r4 2 a3 4 d2
H 3 r5 2 a4 5 d3
H 4 r6 3 a5 2 d4
H 4 r7 3 a6 7 d5
H 4 r8 3 a7 8 d6
```

CCSD(T)/ANO1			B3LYP/aug-cc-pVTZ			B3LYP/aug-cc-pVTZ-GD3BJ		
r1	=	0.976643	r1	=	0.9774	r1	=	0.9773
r2	=	1.330173	r2	=	1.3319	r2	=	1.3321
a1	=	112.888965	a1	=	114.1209	a1	=	114.045
r3	=	1.763362	r3	=	1.7598	r3	=	1.757
a2	=	104.820447	a2	=	106.3657	a2	=	106.152
d1	=	92.472403	d1	=	94.4033	d1	=	93.9388
r4	=	1.088782	r4	=	1.0893	r4	=	1.089
a3	=	111.135659	a3	=	110.6442	a3	=	110.6641
d2	=	106.613018	d2	=	106.8332	d2	=	106.9831
r5	=	1.089409	r5	=	1.0884	r5	=	1.0883
a4	=	116.832211	a4	=	116.4545	a4	=	116.4448
d3	=	141.058895	d3	=	139.083	d3	=	139.1117
r6	=	1.085127	r6	=	1.0833	r6	=	1.0831
a5	=	104.551448	a5	=	105.0759	a5	=	105.0571
d4	=	57.074850	d4	=	56.6921	d4	=	56.7513
r7	=	1.088833	r7	=	1.0872	r7	=	1.0871
a6	=	98.837352	a6	=	99.4346	a6	=	99.388

```
d5   =      119.315627    d5   = 119.3345      d5 = 119.3374
r8   =        1.085801    r8   =   1.0842      r8 =   1.084
a7   =      104.969090    a7   = 104.8959      a7 = 104.9319
d6   =      119.038516    d6   = 119.0609      d6 = 119.0573

C2H5OH+ C1-He
H
O 1 r1
C 2 r2 1 a1
C 3 r3 2 a2 1 d1
H 3 r4 2 a3 4 d2
H 3 r5 2 a4 5 d3
H 4 r6 3 a5 2 d4
H 4 r7 3 a6 7 d5
H 4 r8 3 a7 8 d6
X 1 rd 2 a90 3 d180
HE 1 r10 10 a8 2 d7

B3LYP/aug-cc-pVTZ   B3LYP/aug-cc-pVTZ-GD3BJ
r1   =   0.9782     r1   =   0.978
r2   =   1.3321     r2   =   1.3323
a1   = 114.1611     a1   = 113.9872
r3   =   1.7559     r3   =   1.7528
a2   = 106.328      a2   = 106.0927
d1   =  94.5635     d1   =  93.9923
r4   =   1.0894     r4   =   1.0891
a3   = 110.6517     a3   = 110.6861
d2   = 106.9257     d2   = 107.1306
r5   =   1.0884     r5   =   1.0884
a4   = 116.3793     a4   = 116.3439
d3   = 138.8772     d3   = 138.8885
r6   =   1.0833     r6   =   1.0831
a5   = 105.1962     a5   = 105.1833
d4   =  56.7558     d4   =  56.8564
r7   =   1.0872     r7   =   1.0872
a6   =  99.5083     a6   =  99.4627
d5   = 119.3199     d5   = 119.3213
r8   =   1.0841     r8   =   1.084
a7   = 105.0056     a7   = 105.0623
d6   = 119.0523     d6   = 119.0467
r10  =   1.938      r10  =   1.9081
a8   =  83.0738     a8   =  89.2747
d7   = 177.0022     d7   = 177.7112
rd   =   1.0        rd   =   1.0
a90  =  90.0        a90  =  90.0
d180 =  180.0       d180 = 180.0
```

Vibrational wavenumbers and IR intensities (harmonic/anharmonic; cm^{-1} and $km \cdot mol^{-1}$)

1.4.2 $C_2H_5OH^+$ (3a), B3LYP/aug-cc-pVTZ

$\nu_1(a) = 3632/3445(282/7)$, $\nu_2(a) = 3223/3080(9/8)$, $\nu_3(a) = 3194/3054(12/9)$, $\nu_4(a) = 3152/2989(13/12)$, $\nu_5(a) = 3060/2949(15/16)$ $\nu_6(a) = 3043/2853(15/17)$, $\nu_7(a) = 1504/1467(1/2)$, $\nu_8(a) = 1445/1393(8/9)$, $\nu_9(a) = 1414/1365(11/11)$, $\nu_{10}(a) = 1362/1322(37/34)$, $\nu_{11}(a) = 1301/1262(39/23)$, $\nu_{12}(a) = 1262/1231(39/38)$, $\nu_{13}(a) = 1124/1095(96/40)$, $\nu_{14}(a) = 1104/1072(10/14)$, $\nu_{15}(a) = 933/894(38/40)$, $\nu_{16}(a) = 848/833(2/1)$, $\nu_{17}(a) = 830/810(0.4/1)$, $\nu_{18}(a) = 480/432(15/17)$, $\nu_{19}(a) = 391/325(128/109)$, $\nu_{20}(a) = 280/277(10/11)$, $\nu_{21}(a) = 212/195(2/2)$

1.4.3 $C_2H_5OH^+$ (3a), B3LYP/aug-cc-pVTZ-GD3BJ

$\nu_1(a) = 3633(281)$, $\nu_2(a) = 3224(9)$, $\nu_3(a) = 3194(12)$, $\nu_4(a) = 3154(13)$, $\nu_5(a) = 3061(14)$ $\nu_6(a) = 3045(15)$, $\nu_7(a) = 1505(1)$, $\nu_8(a) = 1446(8)$, $\nu_9(a) = 1414(11)$, $\nu_{10}(a) = 1363(37)$, $\nu_{11}(a) = 1301(38)$,

$\nu_{12}(a) = 1262(39)$, $\nu_{13}(a) = 1125(96)$, $\nu_{14}(a) = 1105(10)$, $\nu_{15}(a) = 934(38)$, $\nu_{16}(a) = 850(2)$, $\nu_{17}(a) = 833(0.4)$, $\nu_{18}(a) = 480(15)$, $\nu_{19}(a) = 393(128)$, $\nu_{20}(a) = 281(9)$, $\nu_{21}(a) = 214(2)$

1.4.4 $C_2H_5OH^+$ (3a), B3LYP/aug-cc-pVTZ

$\nu_1(a) = 3617(399)$, $\nu_2(a) = 3222(9)$, $\nu_3(a) = 3193(11)$, $\nu_4(a) = 3151(12)$, $\nu_5(a) = 3060(15)$ $\nu_6(a) = 3042(14)$, $\nu_7(a) = 1504(1)$, $\nu_8(a) = 1446(8)$, $\nu_9(a) = 1414(11)$, $\nu_{10}(a) = 1365(37)$, $\nu_{11}(a) = 1302(38)$, $\nu_{12}(a) = 1262(38)$, $\nu_{13}(a) = 1129(89)$, $\nu_{14}(a) = 1104(15)$, $\nu_{15}(a) = 940(37)$, $\nu_{16}(a) = 852(2)$, $\nu_{17}(a) = 833(0.5)$, $\nu_{18}(a) = 485(16)$, $\nu_{19}(a) = 407(121)$, $\nu_{20}(a) = 283(11)$, $\nu_{21}(a) = 214(2)$, $\nu_{22}(a) = 123(4)$, $\nu_{23}(a) = 42(4)$, $\nu_{24}(a) = 34(2)$

1.4.5 $C_2H_5OH^+$ (3a), B3LYP/aug-cc-pVTZ-GD3BJ

$\nu_1(a) = 3618(403)$, $\nu_2(a) = 3223(9)$, $\nu_3(a) = 3194(11)$, $\nu_4(a) = 3153(12)$, $\nu_5(a) = 3061(15)$ $\nu_6(a) = 3044(14)$, $\nu_7(a) = 1505(1)$, $\nu_8(a) = 1447(8)$, $\nu_9(a) = 1414(11)$, $\nu_{10}(a) = 1367(37)$, $\nu_{11}(a) = 1303(37)$, $\nu_{12}(a) = 1262(39)$, $\nu_{13}(a) = 1131(86)$, $\nu_{14}(a) = 1104(15)$, $\nu_{15}(a) = 942(36)$, $\nu_{16}(a) = 854(2)$, $\nu_{17}(a) = 836(0.6)$, $\nu_{18}(a) = 485(16)$, $\nu_{19}(a) = 411(121)$, $\nu_{20}(a) = 284(11)$, $\nu_{21}(a) = 216(2)$, $\nu_{22}(a) = 135(4)$, $\nu_{23}(a) = 40(4)$, $\nu_{24}(a) = 30(3)$

1.5 Ethanol radical cation $C_2H_5OH^+$ (3b)

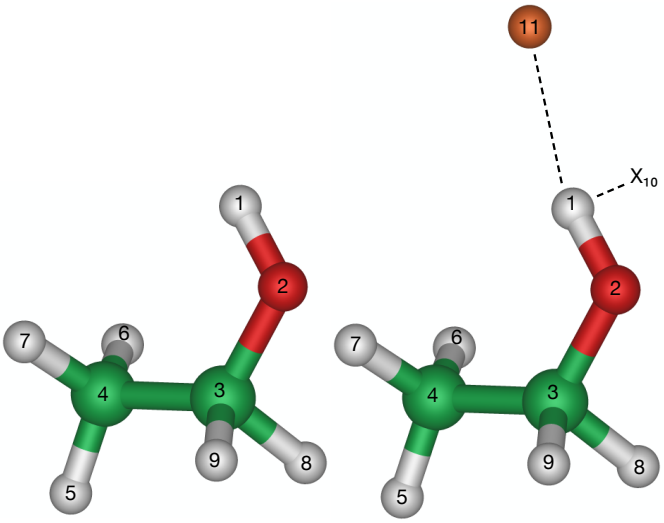

Figure S5: Molecular structure of $C_2H_5OH^+$ and $C_2H_5OH^+$–He (**3b**).

1.5.1 $C_2H_5OH^+$ (3b)

```
C2H5OH+ Cs, 3b
H
O 1 r1
C 2 r2 1 a1
C 3 r3 2 a2 1 d0
H 4 r4 3 a3 2 d180
H 4 r5 3 a4 2 d1
H 4 r5 3 a4 2 md1
H 3 r6 2 a5 1 d2
H 3 r6 2 a5 1 md2
```

CCSD(T)/ANO1			B3LYP/aug-cc-pVTZ			B3LYP/aug-cc-pVTZ-GD3BJ		
r1	=	0.983221	r1	=	0.9814	r1	=	0.9813
r2	=	1.358555	r2	=	1.3555	r2	=	1.3552
a1	=	112.775168	a1	=	114.0055	a1	=	113.8877
r3	=	1.494711	r3	=	1.4855	r3	=	1.4848
a2	=	119.618689	a2	=	121.0232	a2	=	120.9075
d0	=	0.000000	r4	=	1.0885	r4	=	1.0883
r4	=	1.089719	a3	=	109.7553	a3	=	109.7657
a3	=	109.313533	r5	=	1.095	r5	=	1.0949
d180	=	180.000000	a4	=	111.1662	a4	=	111.1055
r5	=	1.093195	d1	=	60.1149	d1	=	60.0933
a4	=	110.618914	md1	=	-60.1149	md1	=	-60.0933
d1	=	60.651760	r6	=	1.1368	r6	=	1.1366
md1	=	-60.651760	a5	=	104.5289	a5	=	104.5755
r6	=	1.134170	d2	=	133.2604	d2	=	133.2131
a5	=	103.829552	md2	=	-133.2604	md2	=	-133.2131
d2	=	132.823046	d180	=	180.0	d180	=	180.0
md2	=	-132.823046	d0	=	0.0	d0	=	0.0

1.5.2 $C_2H_5OH^+$–He (3b)

```
C2H5OH+-He Cs, 3b
H
O 1 r1
C 2 r2 1 a1
C 3 r3 2 a2 1 d0
H 4 r4 3 a3 2 d180
H 4 r5 3 a4 2 d1
H 4 r5 3 a4 2 md1
H 3 r6 2 a5 1 d2
H 3 r6 2 a5 1 md2
X 1 rd 2 a90 3 d180
HE 1 r7 10 a6 2 d3

B3LYP/aug-cc-pVTZ   B3LYP/aug-cc-pVTZ-GD3BJ
r1  =    0.9823     r1   =    0.9822
r2  =    1.3553     r2   =    1.355
a1  =  114.2321     a1   =  114.0318
r3  =    1.486      r3   =    1.4853
a2  =  121.0309     a2   =  120.8776
r4  =    1.0885     r4   =    1.0883
a3  =  109.7169     a3   =  109.7357
r5  =    1.0948     r5   =    1.0946
a4  =  111.1762     a4   =  111.1092
d1  =   60.1362     d1   =   60.1093
md1 =  -60.1362     md1  =  -60.1093
r6  =    1.1365     r6   =    1.1362
a5  =  104.5292     a5   =  104.5875
d2  =  133.2045     d2   =  133.1461
md2 = -133.2045     md2  = -133.1461
r7  =    1.9368     r7   =    1.8994
a6  =   73.4955     a6   =   78.3794
d3  =   180.0       d3   =  180.0
d180 =  180.0       d180 =  180.0
d0  =    0.0        d0   =    0.0
rd  =    1.0        rd   =    1.0
a90 =   90.0        a90  =   90.0
```

Vibrational wavenumbers and IR intensities (harmonic/anharmonic; cm^{-1} and $km \cdot mol^{-1}$)

1.5.3 $C_2H_5OH^+$ (3b), B3LYP/aug-cc-pVTZ

$\nu_1(a') = 3581(245)$, $\nu_2(a') = 3126(3)$, $\nu_3(a') = 2999(66)$, $\nu_4(a') = 2687(153)$, $\nu_5(a') = 1458(4)$, $\nu_6(a') = 1414(57)$, $\nu_7(a') = 1340(47)$, $\nu_8(a') = 1297(31)$, $\nu_9(a') = 1157(199)$, $\nu_{10}(a') = 1044(113)$, $\nu_{11}(a') = 1000(39)$, $\nu_{12}(a') = 888(38)$, $\nu_{13}(a') = 433(5)$, $\nu_{14}(a'') = 3051(5)$, $\nu_{15}(a'') = 2509(75)$ $\nu_{16}(a'') = 1440(13)$ $\nu_{17}(a'') = 1055(0.3)$ $\nu_{18}(a'') = 1015(18)$ $\nu_{19}(a'') = 637(5)$ $\nu_{20}(a'') = 357(200)$ $\nu_{21}(a'') = 113(6)$

1.5.4 $C_2H_5OH^+$ (3b), B3LYP/aug-cc-pVTZ-GD3BJ

$\nu_1(a') = 3581(243)$, $\nu_2(a') = 3127(3)$, $\nu_3(a') = 3000(66)$, $\nu_4(a') = 2688(153)$, $\nu_5(a') = 1458(4)$, $\nu_6(a') = 1414(57)$, $\nu_7(a') = 1341(47)$, $\nu_8(a') = 1298(31)$, $\nu_9(a') = 1158(198)$, $\nu_{10}(a') = 1046(114)$, $\nu_{11}(a') = 1001(38)$, $\nu_{12}(a') = 889(38)$, $\nu_{13}(a') = 434(5)$, $\nu_{14}(a'') = 3052(5)$, $\nu_{15}(a'') = 2511(75)$ $\nu_{16}(a'') = 1441(13)$ $\nu_{17}(a'') = 1055(0.4)$ $\nu_{18}(a'') = 1016(18)$ $\nu_{19}(a'') = 637(5)$ $\nu_{20}(a'') = 355(200)$ $\nu_{21}(a'') = 115(6)$

1.5.5 $C_2H_5OH^+$–He (3b), B3LYP/aug-cc-pVTZ

$\nu_1(a') = 3564(350)$, $\nu_2(a') = 3126(2)$, $\nu_3(a') = 3001(64)$, $\nu_4(a') = 2689(157)$, $\nu_5(a') = 1459(4)$, $\nu_6(a') = 1415(55)$, $\nu_7(a') = 1341(51)$, $\nu_8(a') = 1298(27)$, $\nu_9(a') = 1160(197)$, $\nu_{10}(a') = 1047(113)$, $\nu_{11}(a') = 1001(44)$, $\nu_{12}(a') = 887(41)$, $\nu_{13}(a') = 435(6)$, $\nu_{14}(a') = 124(5)$, $\nu_{15}(a') = 41(1)$, $\nu_{16}(a'') = 3054(4)$,

$\nu_{17}(a'') = 2514(74)$, $\nu_{18}(a'') = 1442(13)$, $\nu_{19}(a'') = 1058(0.3)$, $\nu_{20}(a'') = 1018(18)$, $\nu_{21}(a'') = 642(6)$, $\nu_{22}(a'') = 375(192)$, $\nu_{23}(a'') = 127(2)$, $\nu_{23}(a'') = 49(0.3)$

1.5.6 $C_2H_5OH^+$–He (3b), B3LYP/aug-cc-pVTZ-GD3BJ

$\nu_1(a') = 3563(359)$, $\nu_2(a') = 3127(2)$, $\nu_3(a') = 3002(63)$, $\nu_4(a') = 2690(158)$, $\nu_5(a') = 1459(4)$, $\nu_6(a') = 1416(55)$, $\nu_7(a') = 1342(50)$, $\nu_8(a') = 1301(28)$, $\nu_9(a') = 1161(194)$, $\nu_{10}(a') = 1049(110)$, $\nu_{11}(a') = 1002(44)$, $\nu_{12}(a') = 889(42)$, $\nu_{13}(a') = 436(5)$, $\nu_{14}(a') = 137(5)$, $\nu_{15}(a') = 40(1)$, $\nu_{16}(a'') = 3055(4)$, $\nu_{17}(a'') = 2516(74)$, $\nu_{18}(a'') = 1443(13)$, $\nu_{19}(a'') = 1058(0.4)$, $\nu_{20}(a'') = 1018(18)$, $\nu_{21}(a'') = 643(7)$, $\nu_{22}(a'') = 374(191)$, $\nu_{23}(a'') = 129(3)$, $\nu_{23}(a'') = 49(0.3)$

1.6 Protonated ethanol $C_2H_5OH_2^+$-*gauche* (4a)

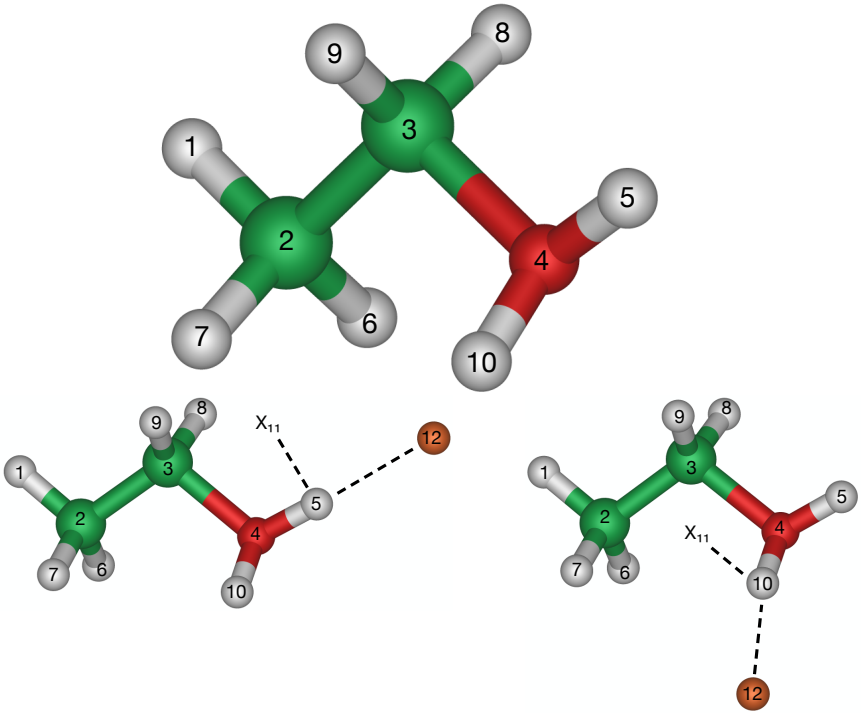

Figure S6: Molecular structures of $C_2H_5OH_2^+$, $C_2H_5OH_2^+$−He(a) (**4a**, bottom left) and $C_2H_5OH_2^+$−He(g) (**4a'**, bottom right).

1.6.1 Structural parameters of $C_2H_5OH_2^+$-*gauche* (4a)

```
C2H5OH2+ gauche
H
C 1 r1
C 2 r2 1 a1
O 3 r3 2 a2 1 d1
H 4 r4 3 a3 2 d2
H 2 r5 3 a4 1 d3
H 2 r6 3 a5 1 d4
H 3 r7 2 a6 6 d5
H 3 r8 2 a7 7 d6
H 4 r9 3 a8 5 d7

CCSD(T)/ANO1         B3LYP/aug-cc-pVTZ    B3LYP/aug-cc-pVTZ-GD3BJ
r1 =     1.092390    r1 =     1.0927      r1 =     1.0924
r2 =     1.500239    r2 =     1.4939      r2 =     1.4932
a1 =   107.131590    a1 =   106.859       a1 =   106.9314
r3 =     1.546106    r3 =     1.5702      r3 =     1.5684
a2 =   106.872105    a2 =   107.4967      a2 =   107.3179
d1 = -178.451094     d1 = -178.4855       d1 = -178.4815
r4 =     0.973377    r4 =     0.9744      r4 =     0.9743
d2 = -177.983603     d2 = -179.0934       d2 = -178.0746
r5 =     1.089230    r5 =     1.0882      r5 =     1.088
a4 =   111.527462    a4 =   112.0321      a4 =   111.956
d3 =   118.439095    d3 =   118.0188      d3 =   118.0814
r6 =     1.091797    r6 =     1.0907      r6 =     1.0906
a5 =   111.859582    a5 =   112.3566      a5 =   112.267
d4 = -117.416012     d4 = -117.0361       d4 = -117.0819
```

```
r7 =    1.086372    r7 =    1.0851      r7 =    1.0849
a6 =  114.403311    a6 =  114.6768      a6 =  114.6953
d5 =   51.878331    d5 =   51.1487      d5 =   51.2074
r8 =    1.087513    r8 =    1.086       r8 =    1.0858
a7 =  114.812203    a7 =  115.118       a7 =  115.0981
d6 =  -52.585745    d6 =  -51.8483      d6 =  -51.8258
r9 =    0.973603    r9 =    0.9745      r9 =    0.9744
a8 =  112.580013    a8 =  113.411       a8 =  113.2412
d7 =  125.019226    d7 =  127.1281      d7 =  127.0566
```

1.6.2 Structural parameters of $C_2H_5OH_2^+$–He(a) (4a)

```
C2H5OH2+ gauche, He at H5
H
C 1 r1
C 2 r2 1 a1
O 3 r3 2 a2 1 d1
H 4 r4 3 a3 2 d2
H 2 r5 3 a4 1 d3
H 2 r6 3 a5 1 d4
H 3 r7 2 a6 6 d5
H 3 r8 2 a7 7 d6
H 4 r9 3 a8 5 d7
X 5 rd 4 a90 3 d0
HE 5 r10 11 a9 4 d8

B3LYP/aug-cc-pVTZ   B3LYP/aug-cc-pVTZ-GD3BJ
r1 =    1.0925      r1 =    1.0922
r2 =    1.4944      r2 =    1.4937
a1 =  106.9294      a1 =  107.0078
r3 =    1.5669      r3 =    1.5648
a2 =  107.5642      a2 =  107.402
d1 = -178.5052      d1 = -178.4942
r4 =    0.9754      r4 =    0.9753
a3 =  114.539       a3 =  114.4518
d2 = -179.208       d2 = -178.213
r5 =    1.0882      r5 =    1.0881
a4 =  112.0059      a4 =  111.9258
d3 =  118.0689      d3 =  118.1353
r6 =    1.0907      r6 =    1.0906
a5 =  112.3277      a5 =  112.2352
d4 = -117.0835      d4 = -117.1354
r7 =    1.0851      r7 =    1.0849
a6 =  114.6053      a6 =  114.6205
d5 =   51.3088      d5 =   51.3856
r8 =    1.086       r8 =    1.0858
a7 =  115.0433      a7 =  115.0214
d6 =  -52.0394      d6 =  -52.0288
r9 =    0.9742      r9 =    0.9741
a8 =  113.3724      a8 =  113.2142
d7 =  127.329       d7 =  127.2103
r10=    1.8895      r10=    1.8595
a9 =   91.7425      a9 =   88.4025
d8 =  175.3107      d8 =  174.9381
rd =    1.0         rd =    1.0
a90=   90.0         a90=   90.0
d0 =    0.0         d0 =    0.0
```

1.6.3 Structural parameters of $C_2H_5OH_2^+$–He(g) (4a')

```
C2H5OH2+ gauche, He at H10
H
C 1 r1
C 2 r2 1 a1
O 3 r3 2 a2 1 d1
H 4 r4 3 a3 2 d2
H 2 r5 3 a4 1 d3
H 2 r6 3 a5 1 d4
H 3 r7 2 a6 6 d5
H 3 r8 2 a7 7 d6
H 4 r9 3 a8 5 d7
X 10 rd 4 a90 3 d0
HE 10 r10 11 a9 4 d8
```

B3LYP/aug-cc-pVTZ		B3LYP/aug-cc-pVTZ-GD3BJ	
r1 =	1.0926	r1 =	1.0922
r2 =	1.4942	r2 =	1.4937
a1 =	106.8736	a1 =	106.9588
r3 =	1.5677	r3 =	1.5656
a2 =	107.594	a2 =	107.3945
d1 =	-178.3365	d1 =	-178.3229
r4 =	0.9741	r4 =	0.974
a3 =	114.3313	a3 =	114.3553
d2 =	-180.5398	d2 =	-179.2865
r5 =	1.0882	r5 =	1.088
a4 =	111.9982	a4 =	111.916
d3 =	118.021	d3 =	118.0873
r6 =	1.0904	r6 =	1.0903
a5 =	112.3645	a5 =	112.2692
d4 =	-117.1053	d4 =	-117.1635
r7 =	1.0851	r7 =	1.0849
a6 =	114.5878	a6 =	114.6079
d5 =	51.4168	d5 =	51.5113
r8 =	1.086	r8 =	1.0858
a7 =	115.0815	a7 =	115.0504
d6 =	-51.9035	d6 =	-51.8741
r9 =	0.9754	r9 =	0.9754
a8 =	113.6797	a8 =	113.4258
d7 =	127.2449	d7 =	127.154
r10=	1.9281	r10=	1.8873
a9 =	100.4928	a9 =	96.612
d8 =	179.9294	d8 =	180.9937
rd =	1.0	rd =	1.0
a90=	90.0	a90=	90.0
d0 =	0.0	d0 =	0.0

Vibrational wavenumbers and IR intensities (harmonic/anharmonic; cm^{-1} and $km \cdot mol^{-1}$)

1.6.4 $C_2H_5OH_2^+$-*gauche*, B3LYP/aug-cc-pVTZ

$\nu_1(a) = 3719(265)$, $\nu_2(a) = 3634(167)$, $\nu_3(a) = 3183(0.4)$, $\nu_4(a) = 3129(1)$, $\nu_5(a) = 3108(2)$, $\nu_6(a) = 3095(2)$, $\nu_7(a) = 3038(8)$, $\nu_8(a) = 1654(128)$, $\nu_9(a) = 1504(7)$, $\nu_{10}(a) = 1496(4)$, $\nu_{11}(a) = 1475(11)$, $\nu_{12}(a) = 1420(26)$, $\nu_{13}(a) = 1399(12)$, $\nu_{14}(a) = 1287(3)$, $\nu_{15}(a) = 1197(9)$, $\nu_{16}(a) = 1140(16)$, $\nu_{17}(a) = 953(28)$, $\nu_{18}(a) = 915(7)$, $\nu_{19}(a) = 823(1)$, $\nu_{20}(a) = 695(193)$, $\nu_{21}(a) = 632(111)$, $\nu_{22}(a) = 365(4)$, $\nu_{23}(a) = 257(3)$, $\nu_{24}(a) = 185(47)$

1.6.5 $C_2H_5OH_2^+$-*gauche*, B3LYP/aug-cc-pVTZ, GD3BJ

$\nu_1(a) = 3720(265)$, $\nu_2(a) = 3634(165)$, $\nu_3(a) = 3185(0.4)$, $\nu_4(a) = 3130(1)$, $\nu_5(a) = 3109(2)$, $\nu_6(a) = 3097(2)$, $\nu_7(a) = 3039(8)$, $\nu_8(a) = 1654(129)$, $\nu_9(a) = 1505(7)$, $\nu_{10}(a) = 1496(4)$, $\nu_{11}(a) = 1476(11)$,

$\nu_{12}(a) = 1421(26)$, $\nu_{13}(a) = 1400(11)$, $\nu_{14}(a) = 1287(2)$, $\nu_{15}(a) = 1198(9)$, $\nu_{16}(a) = 1142(16)$, $\nu_{17}(a) = 955(27)$, $\nu_{18}(a) = 917(8)$, $\nu_{19}(a) = 824(1)$, $\nu_{20}(a) = 697(189)$, $\nu_{21}(a) = 635(115)$, $\nu_{22}(a) = 366(4)$, $\nu_{23}(a) = 258(3)$, $\nu_{24}(a) = 187(47)$

1.6.6 $C_2H_5OH_2^+$-*gauche*-He(a) (4a), B3LYP/aug-cc-pVTZ

$\nu_1(a) = 3708(309)$, $\nu_2(a) = 3624(239)$, $\nu_3(a) = 3182(0.3)$, $\nu_4(a) = 3129(1)$, $\nu_5(a) = 3108(2)$, $\nu_6(a) = 3096(2)$, $\nu_7(a) = 3039(7)$, $\nu_8(a) = 1658(120)$, $\nu_9(a) = 1505(7)$, $\nu_{10}(a) = 1496(4)$, $\nu_{11}(a) = 1476(11)$, $\nu_{12}(a) = 1421(26)$, $\nu_{13}(a) = 1401(12)$, $\nu_{14}(a) = 1288(3)$, $\nu_{15}(a) = 1200(8)$, $\nu_{16}(a) = 1141(15)$, $\nu_{17}(a) = 954(27)$, $\nu_{18}(a) = 923(8)$, $\nu_{19}(a) = 824(1)$, $\nu_{20}(a) = 706(183)$, $\nu_{21}(a) = 640(113)$, $\nu_{22}(a) = 370(2)$, $\nu_{23}(a) = 258(6)$, $\nu_{24}(a) = 223(48)$ $\nu_{25}(a) = 133(5)$ $\nu_{26}(a) = 41(3)$ $\nu_{27}(a) = 38(4)$

1.6.7 $C_2H_5OH_2^+$-*gauche*-He(a) (4a), B3LYP/aug-cc-pVTZ-GD3BJ

$\nu_1(a) = 3709(315)$, $\nu_2(a) = 3625(241)$, $\nu_3(a) = 3184(0.3)$, $\nu_4(a) = 3130(1)$, $\nu_5(a) = 3109(2)$, $\nu_6(a) = 3098(2)$, $\nu_7(a) = 3040(7)$, $\nu_8(a) = 1657(119)$, $\nu_9(a) = 1505(7)$, $\nu_{10}(a) = 1496(4)$, $\nu_{11}(a) = 1477(11)$, $\nu_{12}(a) = 1422(26)$, $\nu_{13}(a) = 1401(11)$, $\nu_{14}(a) = 1289(3)$, $\nu_{15}(a) = 1201(8)$, $\nu_{16}(a) = 1143(15)$, $\nu_{17}(a) = 957(26)$, $\nu_{18}(a) = 926(9)$, $\nu_{19}(a) = 825(1)$, $\nu_{20}(a) = 709(178)$, $\nu_{21}(a) = 643(116)$, $\nu_{22}(a) = 372(2)$, $\nu_{23}(a) = 259(6)$, $\nu_{24}(a) = 226(49)$ $\nu_{25}(a) = 145(5)$ $\nu_{26}(a) = 40(3)$ $\nu_{27}(a) = 37(4)$

1.6.8 $C_2H_5OH_2^+$-*gauche*-He(g) (4a'), B3LYP/aug-cc-pVTZ

$\nu_1(a) = 3711(301)$, $\nu_2(a) = 3625(218)$, $\nu_3(a) = 3182(0.3)$, $\nu_4(a) = 3130(1)$, $\nu_5(a) = 3108(2)$, $\nu_6(a) = 3097(2)$, $\nu_7(a) = 3040(7)$, $\nu_8(a) = 1658(125)$, $\nu_9(a) = 1504(7)$, $\nu_{10}(a) = 1497(4)$, $\nu_{11}(a) = 1476(11)$, $\nu_{12}(a) = 1421(26)$, $\nu_{13}(a) = 1400(12)$, $\nu_{14}(a) = 1288(3)$, $\nu_{15}(a) = 1200(8)$, $\nu_{16}(a) = 1140(16)$, $\nu_{17}(a) = 954(27)$, $\nu_{18}(a) = 921(7)$, $\nu_{19}(a) = 823(1)$, $\nu_{20}(a) = 706(187)$, $\nu_{21}(a) = 638(106)$, $\nu_{22}(a) = 367(4)$, $\nu_{23}(a) = 257(3)$, $\nu_{24}(a) = 219(48)$ $\nu_{25}(a) = 127(6)$ $\nu_{26}(a) = 47(3)$ $\nu_{27}(a) = 41(2)$

1.6.9 $C_2H_5OH_2^+$-*gauche*-He(g) (4a'), B3LYP/aug-cc-pVTZ-GD/3BJ

$\nu_1(a) = 3712(307)$, $\nu_2(a) = 3626(221)$, $\nu_3(a) = 3184(0.2)$, $\nu_4(a) = 3131(1)$, $\nu_5(a) = 3109(2)$, $\nu_6(a) = 3099(2)$, $\nu_7(a) = 3041(7)$, $\nu_8(a) = 1658(124)$, $\nu_9(a) = 1505(7)$, $\nu_{10}(a) = 1497(4)$, $\nu_{11}(a) = 1477(11)$, $\nu_{12}(a) = 1422(26)$, $\nu_{13}(a) = 1401(11)$, $\nu_{14}(a) = 1289(2)$, $\nu_{15}(a) = 1201(9)$, $\nu_{16}(a) = 1142(16)$, $\nu_{17}(a) = 957(26)$, $\nu_{18}(a) = 924(8)$, $\nu_{19}(a) = 824(1)$, $\nu_{20}(a) = 709(183)$, $\nu_{21}(a) = 643(109)$, $\nu_{22}(a) = 369(4)$, $\nu_{23}(a) = 258(3)$, $\nu_{24}(a) = 222(49)$ $\nu_{25}(a) = 141(6)$ $\nu_{26}(a) = 47(3)$ $\nu_{27}(a) = 42(2)$

1.7 $C_2H_5OH_2^+$-*anti* (4b)

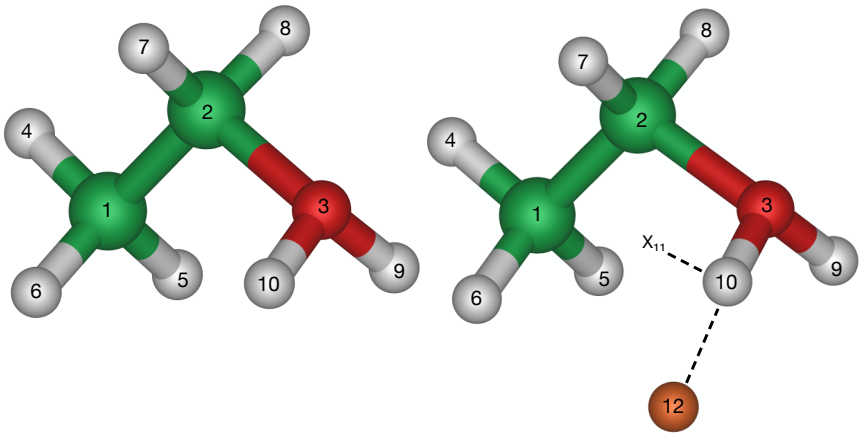

Figure S7: Molecular structure of $C_2H_5OH_2^+$ (*anti*) and $C_2H_5OH_2^+$–He **4b**.

1.7.1 Structural parameters of $C_2H_5OH_2^+$-*anti*

```
C2H5OH2+
C
C 1 r1
O 2 r2 1 a1
H 1 r3 2 a2 3 d180
H 1 r4 2 a3 4 d1
H 1 r4 2 a3 4 md1
H 2 r5 1 a4 4 d2
H 2 r5 1 a4 4 md2
H 3 r6 2 a5 1 d3
H 3 r6 2 a5 1 md3
```

CCSD(T)/ANO1		B3LYP/aug-cc-pVTZ		B3LYP/aug-cc-pVTZ-GD3BJ	
r1	1.501281	r1	1.4949	r1	1.4942
r2	1.544505	r2	1.5681	r2	1.5664
a1	110.801843	a1	111.2695	a1	111.0468
r3	1.092989	r3	1.0932	r3	1.0929
a2	107.089219	a2	106.8116	a2	106.9034
d180	180.000000	r4	1.0898	r4	1.0896
r4	1.090956	a3	112.4873	a3	112.3939
a3	112.026908	d1	117.4347	d1	117.507
d1	117.810144	md1	-117.4347	md1	-117.507
md1	-117.810144	r5	1.0853	r5	1.0851
r5	1.086555	a4	115.4515	a4	115.4619
a4	115.155944	d2	65.5544	d2	65.5983
d2	65.230970	md2	-65.5544	md2	-65.5983
md2	-65.230970	r6	0.9744	r6	0.9744
r6	0.973587	a5	113.6093	a5	113.3882
a5	112.720907	d3	62.8805	d3	62.6501
d3	61.676365	md3	-62.8805	md3	-62.6501
md3	-61.676365	d180	180.0	d180	180.0

1.7.2 Structural parameters of $C_2H_5OH_2^+$-*anti*-He (4b)

```
C2H5OH2+-He
C
C 1 r1
O 2 r2 1 a1
H 1 r3 2 a2 3 d5
H 1 r4 2 a3 4 d1
H 1 r5 2 a4 4 md1
H 2 r6 1 a5 4 d2
H 2 r7 1 a6 4 md2
H 3 r8 2 a7 1 d3
H 3 r9 2 a8 1 md3
X 10 rd 3 a90 2 d0
HE 10 r10 11 a9 3 d4
```

B3LYP/aug-cc-pVTZ			B3LYP/aug-cc-pVTZ-GD3BJ		
r1	=	1.4954	r1	=	1.4948
r2	=	1.5651	r2	=	1.5631
a1	=	111.3175	a1	=	111.0805
r3	=	1.0931	r3	=	1.0928
a2	=	106.8606	a2	=	106.9654
a3	=	112.4405	a3	=	112.3447
a4	=	112.4919	a4	=	112.3883
r4	=	1.0898	r4	=	1.0897
a5	=	115.3942	a5	=	115.3949
a6	=	115.3656	a6	=	115.3807
d1	=	117.4148	d1	=	117.4993
md1	=	-117.5383	md1	=	-117.6156
r5	=	1.0896	r5	=	1.0895
a7	=	113.5732	a7	=	113.3567
a8	=	113.8228	a8	=	113.4719
d2	=	65.5825	d2	=	65.6112
md2	=	-65.2829	md2	=	-65.3307
r6	=	1.0853	r6	=	1.0851
d3	=	61.3944	d3	=	61.3395
md3	=	-64.7257	md3	=	-64.2371
r7	=	1.0852	r7	=	1.085
r8	=	0.9742	r8	=	0.9741
r9	=	0.9754	r9	=	0.9753
r10	=	1.9032	r10	=	1.868
a9	=	94.9268	a9	=	90.1848
d4	=	172.369	d4	=	172.2502
d5	=	180.1597	d5	=	180.1233
a90	=	90.0	a90	=	90.0
d0	=	0.0	d0	=	0.0
rd	=	1.0	rd	=	1.0

Vibrational wavenumbers and IR intensities (harmonic/anharmonic; cm^{-1} and $km \cdot mol^{-1}$)

1.7.3 $C_2H_5OH_2^+$-*anti*, CCSD(T)/ANO1, Harmonic/Anharmonic

$\nu_1(a') = 3669/3496$, $\nu_2(a') = 3135/3006$, $\nu_3(a') = 3126/2992$, $\nu_4(a') = 3047/2946$, $\nu_5(a') = 1687/1651$, $\nu_6(a') = 1507/1467$, $\nu_7(a') = 1496/1416$, $\nu_8(a') = 1423/1391$, $\nu_9(a') = 1389/1351$, $\nu_{10}(a') = 1128/1138$, $\nu_{11}(a') = 967/935$, $\nu_{12}(a') = 760/667$, $\nu_{13}(a') = 707/651$, $\nu_{14}(a') = 370/365$, $\nu_{15}(a'') = 3760/3572$ $\nu_{16}(a'') = 3208/3065$ $\nu_{17}(a'') = 3141/2997$ $\nu_{18}(a'') = 1486/1442$ $\nu_{19}(a'') = 1333/1297$ $\nu_{20}(a'') = 1234/1195$ $\nu_{21}(a'') = 935/885$ $\nu_{22}(a'') = 796/790$ $\nu_{23}(a'') = 267/259$ $\nu_{24}(a'') = 188/151$

1.7.4 $C_2H_5OH_2^+$-*anti*, B3LYP/aug-cc-pVTZ

$\nu_1(a') = 3636(157)$, $\nu_2(a') = 3118(1)$, $\nu_3(a') = 3095(2)$, $\nu_4(a') = 3035(8)$, $\nu_5(a') = 1666(103)$, $\nu_6(a') = 1502(10)$, $\nu_7(a') = 1493(1)$, $\nu_8(a') = 1421(16)$, $\nu_9(a') = 1380(14)$, $\nu_{10}(a') = 1117(20)$, $\nu_{11}(a') = 947(31)$,

$\nu_{12}(a') = 713(186)$, $\nu_{13}(a') = 636(177)$, $\nu_{14}(a') = 364(10)$, $\nu_{15}(a'') = 3717(258)$, $\nu_{16}(a'') = 3186(1)$, $\nu_{17}(a'') = 3118(2)$, $\nu_{18}(a'') = 1478(14)$, $\nu_{19}(a'') = 1313(4)$, $\nu_{20}(a'') = 1223(4)$, $\nu_{21}(a'') = 913(0.1)$, $\nu_{22}(a'') = 796(6)$, $\nu_{23}(a'') = 262(0.4)$, $\nu_{24}(a'') = 167(54)$

1.7.5 $C_2H_5OH_2^+$-*anti*, B3LYP/aug-cc-pVTZ-GD3BJ

$\nu_1(a') = 3636(156)$, $\nu_2(a') = 3120(1)$, $\nu_3(a') = 3097(2)$, $\nu_4(a') = 3036(8)$, $\nu_5(a') = 1667(103)$, $\nu_6(a') = 1503(10)$, $\nu_7(a') = 1493(1)$, $\nu_8(a') = 1422(16)$, $\nu_9(a') = 1381(14)$, $\nu_{10}(a') = 1119(20)$, $\nu_{11}(a') = 949(30)$, $\nu_{12}(a') = 721(189)$, $\nu_{13}(a') = 640(174)$, $\nu_{14}(a') = 367(11)$, $\nu_{15}(a'') = 3717(257)$, $\nu_{16}(a'') = 3187(1)$, $\nu_{17}(a'') = 3119(2)$, $\nu_{18}(a'') = 1479(14)$, $\nu_{19}(a'') = 1314(4)$, $\nu_{20}(a'') = 1224(4)$, $\nu_{21}(a'') = 915(0.1)$, $\nu_{22}(a'') = 798(5)$, $\nu_{23}(a'') = 263(0.3)$, $\nu_{24}(a'') = 168(55)$

1.7.6 $C_2H_5OH_2^+$-*anti*-He (4b), B3LYP/aug-cc-pVTZ

$\nu_1(a) = 3709(300)$, $\nu_2(a) = 3627(213)$, $\nu_3(a) = 3185(0.5)$, $\nu_4(a) = 3118(1)$, $\nu_5(a) = 3118(1)$, $\nu_6(a) = 3096(2)$, $\nu_7(a) = 3036(8)$, $\nu_8(a) = 1669(97)$, $\nu_9(a) = 1503(10)$, $\nu_{10}(a) = 1493(1)$, $\nu_{11}(a) = 1479(14)$, $\nu_{12}(a) = 1422(16)$, $\nu_{13}(a) = 1381(14)$, $\nu_{14}(a) = 1315(4)$, $\nu_{15}(a) = 1224(3)$, $\nu_{16}(a) = 1117(19)$, $\nu_{17}(a) = 948(31)$, $\nu_{18}(a) = 921(0)$, $\nu_{19}(a) = 797(5)$, $\nu_{20}(a) = 719(178)$, $\nu_{21}(a) = 643(175)$, $\nu_{22}(a) = 367(9)$, $\nu_{23}(a) = 262(0.4)$ $\nu_{24}(a) = 208(58)$ $\nu_{25}(a) = 134(7)$ $\nu_{26}(a) = 44(2)$ $\nu_{27}(a) = 40(2)$

1.7.7 $C_2H_5OH_2^+$-*anti*-He (4b), B3LYP/aug-cc-pVTZ-GD3BJ

$\nu_1(a) = 3708(304)$, $\nu_2(a) = 3627(214)$, $\nu_3(a) = 3187(0.5)$, $\nu_4(a) = 3120(1)$, $\nu_5(a) = 3119(2)$, $\nu_6(a) = 3097(2)$, $\nu_7(a) = 3037(7)$, $\nu_8(a) = 1670(95)$, $\nu_9(a) = 1503(10)$, $\nu_{10}(a) = 1494(1)$, $\nu_{11}(a) = 1480(14)$, $\nu_{12}(a) = 1422(16)$, $\nu_{13}(a) = 1382(13)$, $\nu_{14}(a) = 1316(4)$, $\nu_{15}(a) = 1226(3)$, $\nu_{16}(a) = 1119(20)$, $\nu_{17}(a) = 951(30)$, $\nu_{18}(a) = 924(0)$, $\nu_{19}(a) = 799(5)$, $\nu_{20}(a) = 729(182)$, $\nu_{21}(a) = 648(171)$, $\nu_{22}(a) = 370(9)$, $\nu_{23}(a) = 263(0.4)$ $\nu_{24}(a) = 211(60)$ $\nu_{25}(a) = 147(7)$ $\nu_{26}(a) = 43(1)$ $\nu_{27}(a) = 39(2)$

2 Molecular structures

2.1 Energetics

Absolute energies, relative energies, harmonic zero-point vibrational energies (ZPE) and He binding energies (E_b) in units of hartree unless noted otherwise.

Table S1: B3LYP/aug-cc-pVT level of theory.

Id.	Ion	Ion-He	ZPE(I)	ZPE(I-He)	He-atom	E_b	E_b [a]
1a	−115.383480	−118.299484	0.046869	0.047630	−2.914694	0.000549	120.6
1b	−115.387709	−118.303927	0.049126	0.049961	−2.914694	0.000689	151.2
2	−116.074455	−118.990368	0.063890	0.064626	−2.914694	0.000484	106.1
3a	−154.736549	−157.652063	0.076990	0.077513	−2.914694	0.000298	65.4
3b	−154.733362	−157.648883	0.074270	0.074872	−2.914694	0.000225	49.4
4a	−155.417676	−158.333356	0.091820	0.092450	−2.914694	0.000356	78.2
4a'	−155.417676	−158.333238	0.091820	0.092440	−2.914694	0.000248	54.4
4b	−155.417240	−158.332871	0.091807	0.092436	−2.914694	0.000308	67.7

Note: [a] – in cm^{-1}.

Table S2: B3LYP/aug-cc-pVTZ-GD3BJ level of theory.

Id.	Ion	Ion-He	ZPE(I)	ZPE(I-He)	He-atom	E_b	E_b [a]
1a	−115.386574	−118.302902	0.046874	0.047660	−2.914694	0.000848	186.2
1b	−115.391013	−118.307597	0.049141	0.050006	−2.914694	0.001024	224.8
2	−116.078458	−118.994724	0.063914	0.064681	−2.914694	0.000806	176.8
3a	−154.743600	−157.659443	0.077036	0.077587	−2.914694	0.000598	131.2
3b	−154.740465	−157.656341	0.074307	0.074950	−2.914694	0.000538	118.2
4a	−155.425817	−158.341843	0.091886	0.092549	−2.914694	0.000669	146.9
4a'	−155.425817	−158.341763	0.091886	0.092556	−2.914694	0.000582	127.7
4b	−155.425459	−158.341469	0.091889	0.092559	−2.914694	0.000646	141.8

Note: [a] – in cm^{-1}.

Table S3: CCSD(T)/aug-cc-pVTZ level of theory.

Id.	Ion	Ion-He	ZPE(I)	ZPE(I-He)	He-atom	E_b	E_b [a]
2	−115.860892	−118.762867	0.064544	0.065225	−2.900598	0.000696	152.7

Note: [a] – in cm^{-1}.

Table S4: Relative energies of ion isomeric pairs (bare ions) at CCSD(T)/ANO1 (except for ZPE for 3a/3b calculated at the B3LYP/aug-ccpVTZ level).

Id.	Ion	ZPE(Ion)	E_{rel}	E_{rel} (kcal/mol)
1a	−115.168175	0.046818	0.010938	6.9
1b	−115.182191	0.049897	0.0	0.0
3a	−154.436055	0.076990	0.0	0.0
3b	−154.429421	0.074270	0.003913	2.5
4a'	−155.124827	0.092856	0.000443	0.3
4a	−155.125299	0.092885	0.0	0.0

2.2 Influence of the He tag

Table S5: Band position shift induced by the He tag at B3LYP/aug-cc-pVTZ level of theory for selected ions. Unscaled.

Methanol radical			Protonated methanol			Ethanol radical			Protonated ethanol		
1a			2			3a			4a		
I.	+He	Δ	I.	+He	Δ	I.	+He	Δ	I.	+He	Δ
3547	3511	36	3707	3696	11	3632	3617	15	3719	3708	11
3180	3179	1	3631	3615	16	3223	3222	1	3634	3624	10
2744	2748	−4	3215	3215	0	3194	3193	1	3183	3182	1
2632	2640	−8	3211	3210	1	3152	3151	1	3129	3129	0
1480	1481	−1	3090	3090	0	3060	3060	0	3108	3108	0
1285	1292	−7	1676	1680	−4	3043	3042	1	3095	3096	−1
1234	1236	−2	1482	1483	−1	1504	1504	0	3038	3039	−1
1214	1220	−6	1478	1479	−1	1445	1446	−1	1654	1658	−4
1045	1053	−8	1466	1467	−1	1414	1414	0	1504	1505	−1
937	977	−40	1280	1282	−2	1362	1365	−3	1496	1496	0
973	938	35	1166	1167	−1	1301	1302	−1	1475	1476	−1
303	339	−36	928	938	−10	1262	1262	0	1420	1421	−1
			794	801	−7	1124	1129	−5	1399	1401	−2
			691	702	−11	1104	1104	0	1287	1288	−1
			229	261	−32	933	940	−7	1197	1200	−3
						848	852	−4	1140	1141	−1
						830	833	−3	953	954	−1
						480	485	−5	915	923	−8
						391	407	−16	823	824	−1
						280	283	−3	695	706	−11
						212	214	−2	632	640	−8
									365	370	−5
									257	258	−1
									185	223	−38

3 Comparison of different computational methods

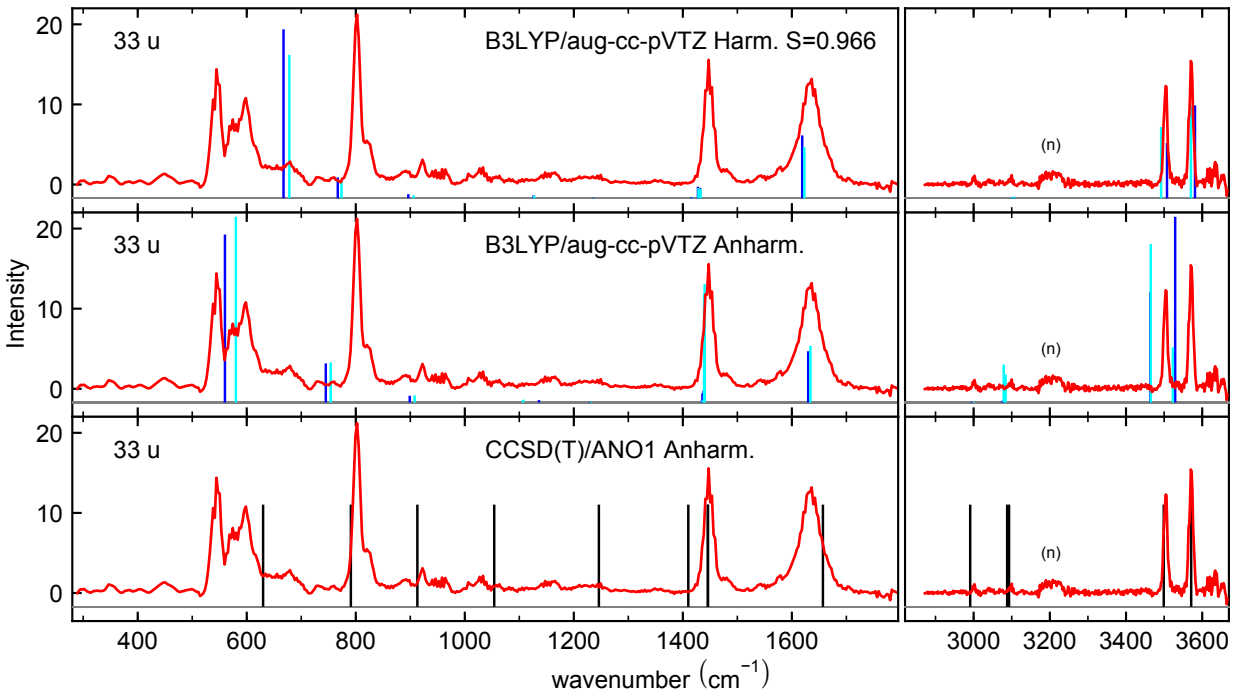

Figure S8: Comparison of the calculated spectra of protonated methanol ($33u$), obtained by the different methods with experimental data recorded using IR-PD (He). In first and second panel blue colour corresponds to the bare ion, whereas cyan colour corresponds to the ion·He complex. Black colour in the last panel corresponds to the bare ion.

4 Experimental

4.1 Line profiles

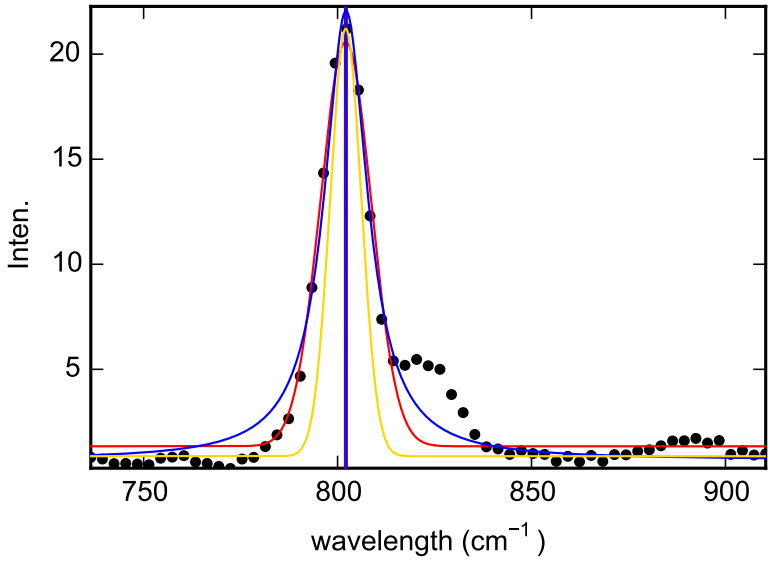

Figure S9: He IR-PD band around 802 cm^{-1} of protonated methanol (black points). Solid lines: least-square fit of a Doppler (red) and Lorentz (blue) broadened line shape. The line FWHM is approx 15 cm^{-1} (from Doppler fit). Yellow line represents the approximate spectral width of FELIX laser at the given wavelength ($\sigma = 0.5\%\lambda$).

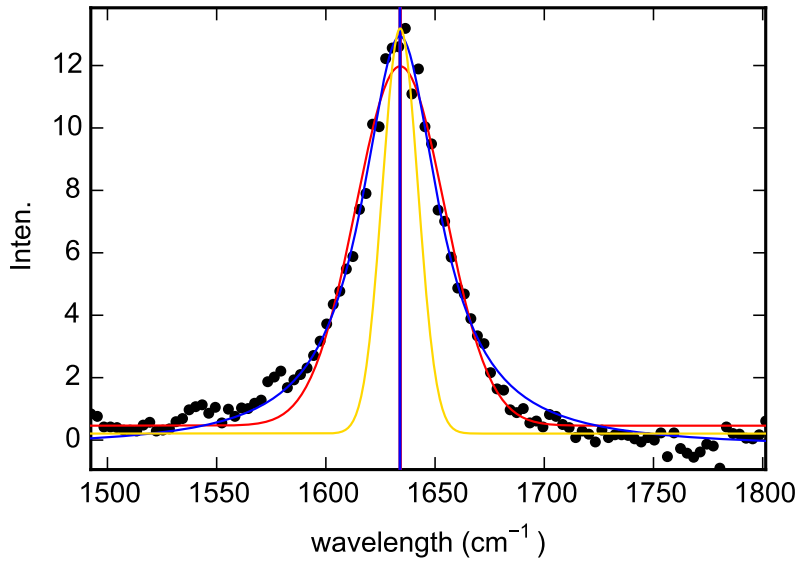

Figure S10: He IR-PD band around 1636 cm^{-1} of protonated methanol (black points). Solid lines: least-square fit of a Doppler (red) and Lorentz (blue) broadened line shape. The line FWHM is approx 43 cm^{-1} (from Lorentz fit). Yellow line represents the approximate spectral width of FELIX laser at the given wavelength ($\sigma = 0.5\%\lambda$).