Supplementary Information for

A Closer Examination of the coupling between Ionic Hydrogen Bond (IHB) Stretch and Flanking Group motions in $(CH_3OH)_2H^+$: The Strong Isotope Effects

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A. Normal modes considered in this study for $(CH_3OH)_2H^+$ and its isotopologues

Table S1. Key normal modes for MA conformer of $(CH_3OH)_2H^+$ obtained from MP2/aug-cc-pVDZ

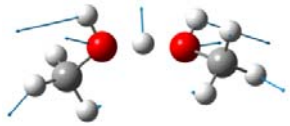
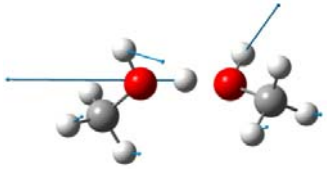
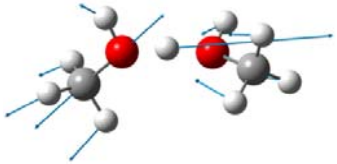
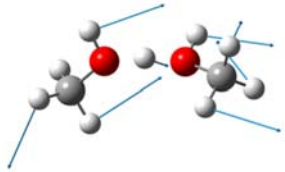
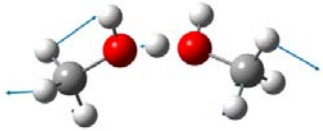
Mode Label in this paper	Mode # in G09 Output	Frequency (cm^{-1}) [Intensity] ($km\ mol^{-1}$)	Normal Mode Demonstration	Description
ν_1	8	577.49 [2.40]		O-O stretch coupled to CH_3 rock and H^+ bend
ν_2	9	701.67 [2502.82]		O-H^+-O stretch parallel to the O-O axis coupled to out-of-phase COH deformation and CH_3 rock.
ν_3	10	960.50 [94.92]		Out-of-phase C-O stretch coupled to IHB stretch and CH_3 wag
ν_4	13	1091.51 [227.36]		Out-of-phase in-plane CH_3 rock coupled to COH deformation and O-H^+-O stretch/bend hybrid
ν_4^*	15	1175.20 [80.95]		Out-of-phase out-plane CH_3 rock coupled to COH deformation and O-H^+-O stretch/bend hybrid

Table S2. Key normal modes for MA conformer of $(CD_3OH)_2H^+$ obtained from MP2/aug-cc-pVDZ

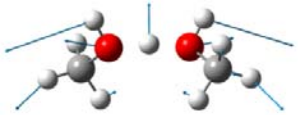
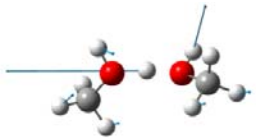
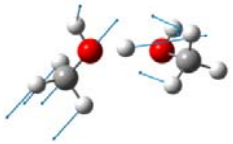
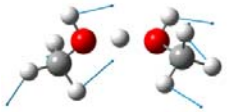
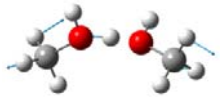
Mode Label in this paper	Mode # in G09 Output	Frequency (cm^{-1}) [Intensity] (km mol^{-1})	Normal Mode Demonstration	Description
ν_1	8	558.17 [2.80]		O-O stretch coupled to CD_3 rock and H^+ bend
ν_2	9	682.73 [2238.78]		O-H^+-O stretch parallel to the O-O axis coupled to out-of-phase COH deformation and CD_3 rock
ν_3	14	922.34 [43.53]		Out-of-phase C-O stretch coupled to O-H^+-O bend/stretch
ν_4	11	865.68 [20.43]		Out-of-phase in-plane CD_3 rock coupled to COH deformation and O-H^+-O bend
ν_4^*	13	912.83 [248.21]		Out-of-phase out-plane CD_3 rock coupled to COH deformation and O-H^+-O stretch

Table S3. Key normal modes for MA conformer of $(CH_3OD)_2D^+$ obtained from MP2/aug-cc-pVDZ

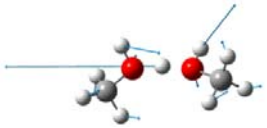
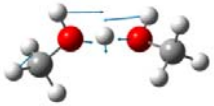
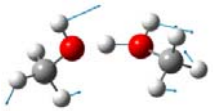
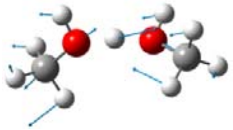
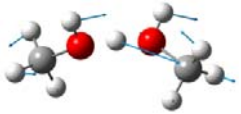
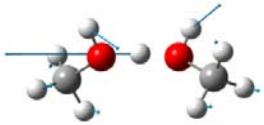
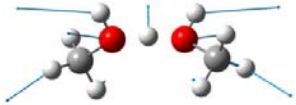
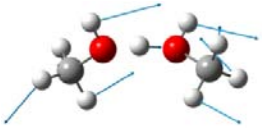
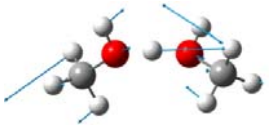
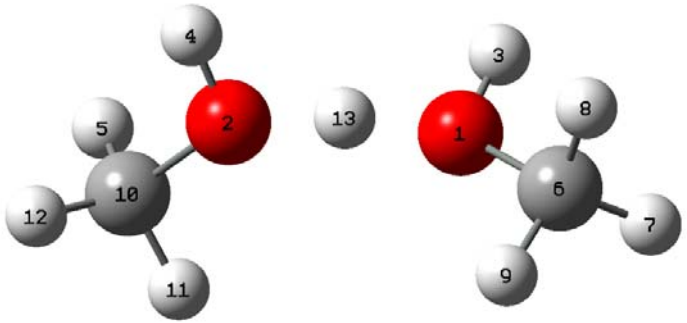
Mode Label in this paper	**Mode # in G09 Output**	**Frequency (cm^{-1}) [Intensity] (km mol^{-1})**	**Normal Mode Demonstration**	**Description**
ν_2	8	524.39 [1238.47]		O-D^+-O stretch parallel to the O-O axis coupled to out-of-phase COD deformation and CD_3 rock
ν_1	9	544.49 [0.00]		O-O stretch coupled to CH_3 rock and D^+ bend
ν_4	11	911.89 [368.66]		Out-of-phase in-plane CH_3 rock coupled to COD deformation and O-D^+-O stretch
ν_3	12	927.50 [121.72]		Out-of-phase C-O stretch coupled to O-D^+-O bend/stretch
ν_4^*	14	1083.81 [172.73]		Out-of-phase out-plane CH_3 rock coupled to COD deformation and O-D^+-O bend

Table S4. Key normal modes for MA conformer of $(CD_3OD)_2D^+$ obtained from MP2/aug-cc-pVDZ

Mode Label in this paper	**Mode # in G09 Output**	**Frequency (cm^{-1}) [Intensity] (km mol^{-1})**	**Normal Mode Demonstration**	**Description**
ν_2	8	515.27 [1206.88]		O-D^+-O stretch parallel to the O-O axis coupled to out-of-phase COD deformation and CD_3 rock
ν_1	9	530.66 [0.00]		O-O stretch coupled to CD_3 rock and D^+ bend
ν_4	11	795.87 [154.12]		Out-of-phase in-plane CD_3 rock coupled to COD deformation and O-D^+-O bend
ν_3	12	887.05 [37.85]		Out-of-phase C-O stretch coupled to O-D^+-O bend/stretch
ν_4^*	14	908.41 [68.82]		Out-of-phase out-plane CD_3 rock coupled to COD deformation and O-D^+-O bend

B. Potential energy distribution in internal coordinates for key normal modes of $(CH_3OH)_2H^+$ and its isotopologues.

Table S5. Potential energy distribution in internal coordinates of ν_1 for MA isotopologues obtained at MP2/aug-cc-pVDZ.



ν_1		$(CH_3OH)_2H^+$		$(CD_3OH)_2H^+$		$(CH_3OD)_2D^+$		$(CD_3OD)_2D^+$	
Name	Definition	Value	Weight (%)	Value	Weight (%)	Value	Weight (%)	Value	Weight (%)
R2	R(1,6)	0.0706	2.4	0.064	2	-0.0885	2.6	0.0881	2.9
R3	R(1,13)	0.2702	9.1	0.2472	7.6	-0.3205	9.6	0.3146	10.2
R5	R(2,10)	0.0706	2.4	0.064	2	-0.0885	2.6	0.0881	2.9
R6	R(2,13)	0.2702	9.1	0.2472	7.6	-0.3205	9.6	0.3146	10.2
A1	A(3,1,6)	---	---	---	---	0.1025	3.1	-0.079	2.6
A2	A(3,1,13)	0.0992	3.3	0.1018	3.1	-0.0464	1.4	0.0449	1.5
A3	A(6,1,13)	-0.0823	2.8	-0.0668	2	0.1168	3.5	-0.1116	3.6
A4	A(4,2,10)			---	---	0.1025	3.1	-0.079	2.6
A5	A(4,2,13)	0.0992	3.3	0.1018	3.1	-0.0464	1.4	0.0449	1.5
A6	A(10,2,13)	-0.0823	2.8	-0.0668	2	0.1168	3.5	-0.1116	3.6
A7	A(1,6,7)	---	---	0.0565	1.7	---	---	0.0507	1.6
A9	A(1,6,9)	---	---	-0.047	1.4	---	---	---	---
A14	A(2,10,11)	---	---	-0.047	1.4	---	---	---	---

A15	A(2,10,12)	---	---	0.0565	1.7	---	---	0.0507	1.6
A19	L(1,13,2,9,-1)	-0.1076	3.6	-0.0957	2.9	0.095	2.8	-0.0773	2.5
A20	L(1,13,2,9,-2)	0.0988	3.3	0.0871	2.7	-0.092	2.7	0.0735	2.4
D1	D(3,1,2,4)	-0.1039	3.5	-0.1917	5.9	-0.3764	11.2	0.3205	10.4
D2	D(3,1,2,10)	-0.0542	1.8	-0.0971	3	-0.1634	4.9	0.142	4.6
D3	D(6,1,2,4)	-0.0542	1.8	-0.0971	3	-0.1634	4.9	0.142	4.6
D4	D(6,1,2,10)	---	---	---	---	0.0497	1.5	---	---
D5	D(3,1,6,7)	0.139	4.7	0.1604	4.9	0.0694	2.1	-0.0572	1.9
D6	D(3,1,6,8)	0.1543	5.2	0.1924	5.9	0.0654	2	-0.0402	1.3
D7	D(3,1,6,9)	0.1392	4.7	0.1624	5	0.0791	2.4	-0.0705	2.3
D8	D(13,1,6,7)	0.0766	2.6	0.0606	1.9	-0.0833	2.5	0.0684	2.2
D9	D(13,1,6,8)	0.0919	3.1	0.0926	2.8	-0.0873	2.6	0.0855	2.8
D10	D(13,1,6,9)	0.0768	2.6	0.0627	1.9	-0.0736	2.2	0.0551	1.8
D11	D(4,2,10,5)	0.1543	5.2	0.1924	5.9	0.0654	2	-0.0402	1.3
D12	D(4,2,10,11)	0.1392	4.7	0.1624	5	0.0791	2.4	-0.0705	2.3
D13	D(4,2,10,12)	0.139	4.7	0.1604	4.9	0.0694	2.1	-0.0572	1.9
D14	D(13,2,10,5)	0.0919	3.1	0.0926	2.8	-0.0873	2.6	0.0855	2.8
D15	D(13,2,10,11)	0.0768	2.6	0.0627	1.9	-0.0736	2.2	0.0551	1.8
D16	D(13,2,10,12)	0.0766	2.6	0.0606	1.9	-0.0833	2.5	0.0684	2.2

Table S6. Potential energy distribution in internal coordinates of ν_2 for MA isotopologues obtained at MP2/aug-cc-pVDZ.

ν_2		$(CH_3OH)_2H^+$		$(CD_3OH)_2H^+$		$(CH_3OD)_2D^+$		$(CD_3OD)_2D^+$	
Name	Definition	Value	Weight (%)	Value	Weight (%)	Value	Weight (%)	Value	Weight (%)
R2	R(1,6)	-0.0621	1.3	-0.0536	1.2	-0.0387	0.8	-0.0377	0.8
R3	R(1,13)	0.7512	16.1	0.7289	15.7	0.7483	15.1	0.7454	15.4
R5	R(2,10)	0.0621	1.3	0.0536	1.2	0.0387	0.8	0.0377	0.8
R6	R(2,13)	-0.7512	16.1	-0.7289	15.7	-0.7483	15.1	-0.7454	15.4

A1	A(3,1,6)	-0.1755	3.8	-0.1686	3.6	-0.1921	3.9	-0.1886	3.9
A2	A(3,1,13)	---	---	---	---	-0.0426	0.9	-0.0342	0.7
A4	A(4,2,10)	0.1755	3.8	0.1686	3.6	0.1921	3.9	0.1886	3.9
A5	A(4,2,13)	---	---	---	---	0.0426	0.9	0.0342	0.7
A7	A(1,6,7)	0.0685	1.5	0.0945	2	0.054	1.1	0.0659	1.4
A9	A(1,6,9)	0.0489	1	0.0634	1.4	0.0434	0.9	0.0524	1.1
A10	A(7,6,8)	-0.0445	1	-0.0529	1.1	-0.0378	0.8	-0.0432	0.9
A11	A(7,6,9)	-0.0322	0.7	-0.0331	0.7	---	---	---	---
A12	A(8,6,9)	-0.0439	0.9	-0.0492	1.1	-0.036	0.7	-0.0382	0.8
A14	A(2,10,11)	-0.0489	1	-0.0634	1.4	-0.0434	0.9	-0.0524	1.1
A15	A(2,10,12)	-0.0685	1.5	-0.0945	2	-0.054	1.1	-0.0659	1.4
A16	A(5,10,11)	0.0439	0.9	0.0492	1.1	0.036	0.7	0.0382	0.8
A17	A(5,10,12)	0.0445	1	0.0529	1.1	0.0378	0.8	0.0432	0.9
A18	A(11,10,12)	0.0322	0.7	0.0331	0.7	---	---	---	---
D2	D(3,1,2,10)	0.3287	7.1	0.3096	6.7	0.3782	7.6	0.3633	7.5
D3	D(6,1,2,4)	-0.3287	7.1	-0.3096	6.7	-0.3782	7.6	-0.3633	7.5
D5	D(3,1,6,7)	-0.2183	4.7	-0.1998	4.3	-0.251	5.1	-0.2327	4.8
D6	D(3,1,6,8)	-0.2219	4.8	-0.2116	4.6	-0.2565	5.2	-0.2446	5.1
D7	D(3,1,6,9)	-0.2386	5.1	-0.2389	5.2	-0.2682	5.4	-0.26	5.4
D10	D(13,1,6,9)	---	---	-0.0313	0.7	---	---	---	---
D11	D(4,2,10,5)	0.2219	4.8	0.2116	4.6	0.2565	5.2	0.2446	5.1
D12	D(4,2,10,11)	0.2386	5.1	0.2389	5.2	0.2682	5.4	0.26	5.4
D13	D(4,2,10,12)	0.2183	4.7	0.1998	4.3	0.251	5.1	0.2327	4.8
D15	D(13,2,10,11)	---	---	0.0313	0.7	---	---	---	---

Table S7. Potential energy distribution in internal coordinates of ν_3 for MA isotopologues obtained at MP2/aug-cc-pVDZ.

ν_3		$(CH_3OH)_2H^+$		$(CD_3OH)_2H^+$		$(CH_3OD)_2D^+$		$(CD_3OD)_2D^+$	
Name	Definition	Value	Weight (%)	Value	Weight (%)	Value	Weight (%)	Value	Weight (%)
R2	R(1,6)	-0.5455	13	-0.4772	16.1	-0.4346	8.9	-0.299	8.1
R3	R(1,13)	-0.4494	10.7	-0.2318	7.8	---	---	-0.1909	5.2
R5	R(2,10)	0.5455	13	0.4772	16.1	0.4346	8.9	0.299	8.1
R6	R(2,13)	0.4494	10.7	0.2318	7.8	---	---	0.1909	5.2
A1	A(3,1,6)	0.1456	3.5	0.0605	2	0.1724	3.5	---	---
A2	A(3,1,13)	-0.1711	4.1	-0.1137	3.8	-0.1086	2.2	0.0586	1.6
A3	A(6,1,13)	---	---	---	---	-0.195	4	-0.0869	2.4
A4	A(4,2,10)	-0.1456	3.5	-0.0605	2	-0.1724	3.5	---	---
A5	A(4,2,13)	0.1711	4.1	0.1137	3.8	0.1086	2.2	-0.0586	1.6
A6	A(10,2,13)	---	---	---	---	0.195	4	0.0869	2.4
A7	A(1,6,7)	0.0486	1.2	-0.0308	1	0.1616	3.3	0.1556	4.2
A8	A(1,6,8)	0.0722	1.7	-0.0449	1.5	0.069	1.4	-0.2199	6
A9	A(1,6,9)	---	---	-0.0336	1.1	---	---	---	---
A10	A(7,6,8)	-0.0323	0.8	0.0484	1.6	---	---	---	---
A11	A(7,6,9)	-0.0529	1.3	0.024	0.8	-0.0635	1.3	---	---
A12	A(8,6,9)	-0.0485	1.2	0.0287	1	-0.0758	1.6	---	---
A13	A(2,10,5)	-0.0722	1.7	0.0449	1.5	-0.069	1.4	0.2199	6
A14	A(2,10,11)	---	---	0.0336	1.1	---	---	---	---
A15	A(2,10,12)	-0.0486	1.2	0.0308	1	-0.1616	3.3	-0.1556	4.2
A16	A(5,10,11)	0.0485	1.2	-0.0287	1	0.0758	1.6	---	---
A17	A(5,10,12)	0.0323	0.8	-0.0484	1.6	---	---	---	---
A18	A(11,10,12)	0.0529	1.3	-0.024	0.8	0.0635	1.3	---	---
A19	L(1,13,2,9,-1)	0.0591	1.4	0.0321	1.1	0.2883	5.9	0.1743	4.7
A20	L(1,13,2,9,-2)	0.0744	1.8	0.0414	1.4	0.3754	7.7	0.2248	6.1
D2	D(3,1,2,10)	-0.0677	1.6	---	---	-0.0907	1.9	-0.0697	1.9

D3	D(6,1,2,4)	0.0677	1.6	---	---	0.0907	1.9	0.0697	1.9
D5	D(3,1,6,7)	-0.0499	1.2	-0.0369	1.2	-0.0719	1.5	0.1185	3.2
D6	D(3,1,6,8)	---	---	-0.0239	0.8	---	---	0.1052	2.9
D7	D(3,1,6,9)	---	---	-0.0328	1.1	---	---	---	---
D8	D(13,1,6,7)	0.0691	1.6	0.0677	2.3	0.1054	2.2	0.1169	3.2
D9	D(13,1,6,8)	0.1032	2.5	0.0807	2.7	0.2055	4.2	0.1036	2.8
D10	D(13,1,6,9)	0.096	2.3	0.0718	2.4	0.1249	2.6	---	---
D11	D(4,2,10,5)	---	---	0.0239	0.8	---	---	-0.1052	2.9
D12	D(4,2,10,11)	---	---	0.0328	1.1	---	---	---	---
D13	D(4,2,10,12)	0.0499	1.2	0.0369	1.2	0.0719	1.5	-0.1185	3.2
D14	D(13,2,10,5)	-0.1032	2.5	-0.0807	2.7	-0.2055	4.2	-0.1036	2.8
D15	D(13,2,10,11)	-0.096	2.3	-0.0718	2.4	-0.1249	2.6	---	---
D16	D(13,2,10,12)	-0.0691	1.6	-0.0677	2.3	-0.1054	2.2	-0.1169	3.2

Table S8. Potential energy distribution in internal coordinates of ν_4 for MA isotopologues obtained at MP2/aug-cc-pVDZ.

ν_4		$(CH_3OH)_2H^+$		$(CD_3OH)_2H^+$		$(CH_3OD)_2D^+$		$(CD_3OD)_2D^+$	
Name	Definition	Value	Weight (%)	Value	Weight (%)	Value	Weight (%)	Value	Weight (%)
R2	R(1,6)	---	---	---	---	-0.1067	2.8	---	---
R3	R(1,13)	-0.1816	4.8	-0.0466	1.4	-0.3726	9.6	-0.2231	5.8
R5	R(2,10)	---	---	---	---	0.1067	2.8	---	---
R6	R(2,13)	0.1816	4.8	0.0466	1.4	0.3726	9.6	0.2231	5.8
A1	A(3,1,6)	-0.1596	4.2	-0.1096	3.2	-0.2544	6.6	-0.184	4.8
A2	A(3,1,13)	0.138	3.6	0.1431	4.2	0.1825	4.7	0.1621	4.2
A3	A(6,1,13)	0.0572	1.5	0.0265	0.8	0.081	2.1	0.0712	1.9
A4	A(4,2,10)	0.1596	4.2	0.1096	3.2	0.2544	6.6	0.184	4.8
A5	A(4,2,13)	-0.138	3.6	-0.1431	4.2	-0.1825	4.7	-0.1621	4.2
A6	A(10,2,13)	-0.0572	1.5	-0.0265	0.8	-0.081	2.1	-0.0712	1.9

A7	A(1,6,7)	-0.1897	5	-0.2227	6.5	-0.1089	2.8	-0.2013	5.2
A8	A(1,6,8)	-0.0575	1.5	-0.0572	1.7	---	---	-0.0533	1.4
A9	A(1,6,9)	0.2234	5.9	0.2731	8	0.1402	3.6	0.2051	5.3
A10	A(7,6,8)	-0.0511	1.3	-0.0308	0.9	---	---	---	---
A12	A(8,6,9)	0.0565	1.5	0.0309	0.9	---	---	---	---
A13	A(2,10,5)	0.0575	1.5	0.0572	1.7	---	---	0.0533	1.4
A14	A(2,10,11)	-0.2234	5.9	-0.2731	8	-0.1402	3.6	-0.2051	5.3
A15	A(2,10,12)	0.1897	5	0.2227	6.5	0.1089	2.8	0.2013	5.2
A16	A(5,10,11)	-0.0565	1.5	-0.0309	0.9	---	---	---	---
A17	A(5,10,12)	0.0511	1.3	0.0308	0.9	---	---	---	---
A19	L(1,13,2,9,-1)	-0.1079	2.8	-0.1132	3.3	-0.0864	2.2	-0.1348	3.5
A20	L(1,13,2,9,-2)	-0.1416	3.7	-0.1487	4.4	-0.1143	2.9	-0.1775	4.6
D2	D(3,1,2,10)	0.0921	2.4	0.05	1.5	0.1464	3.8	0.102	2.7
D3	D(6,1,2,4)	-0.0921	2.4	-0.05	1.5	-0.1464	3.8	-0.102	2.7
D5	D(3,1,6,7)	0.1372	3.6	0.1405	4.1	0.1241	3.2	0.1314	3.4
D6	D(3,1,6,8)	-0.0779	2.1	-0.0701	2.1	---	---	---	---
D7	D(3,1,6,9)	0.0876	2.3	0.0939	2.7	0.0956	2.5	0.0948	2.5
D9	D(13,1,6,8)	-0.1754	4.6	-0.1962	5.7	-0.0818	2.1	-0.1639	4.3
D10	D(13,1,6,9)	---	---	-0.0322	0.9	---	---	---	---
D11	D(4,2,10,5)	0.0779	2.1	0.0701	2.1	---	---	---	---
D12	D(4,2,10,11)	-0.0876	2.3	-0.0939	2.7	-0.0956	2.5	-0.0948	2.5
D13	D(4,2,10,12)	-0.1372	3.6	-0.1405	4.1	-0.1241	3.2	-0.1314	3.4
D14	D(13,2,10,5)	0.1754	4.6	0.1962	5.7	0.0818	2.1	0.1639	4.3
D15	D(13,2,10,11)	---	---	0.0322	0.9	---	---	---	---

Table S9. Potential energy distribution in internal coordinates of ν_4^* for MA isotopologues obtained at MP2/aug-cc-pVDZ.

ν_4^*		$(CH_3OH)_2H^+$		$(CD_3OH)_2H^+$		$(CH_3OD)_2D^+$		$(CD_3OD)_2D^+$	
Name	Definition	Value	Weight (%)	Value	Weight (%)	Value	Weight (%)	Value	Weight (%)
R2	R(1,6)	---	---	---	---	-0.1684	3	-0.231	5.6
R3	R(1,13)	0.1363	3.7	0.3268	7.5	0.0827	1.5	0.0924	2.3
R5	R(2,10)	---	---	---	---	0.1684	3	0.231	5.6
R6	R(2,13)	-0.1363	3.7	-0.3268	7.5	-0.0827	1.5	-0.0924	2.3
A1	A(3,1,6)	---	---	-0.0735	1.7	0.1648	3	-0.0314	0.8
A2	A(3,1,13)	---	---	-0.0646	1.5	-0.3028	5.5	-0.0831	2
A3	A(6,1,13)	---	---	---	---	0.3734	6.7	---	---
A4	A(4,2,10)	---	---	0.0735	1.7	-0.1648	3	0.0314	0.8
A5	A(4,2,13)	---	---	0.0646	1.5	0.3028	5.5	0.0831	2
A6	A(10,2,13)	---	---	---	---	-0.3734	6.7	---	---
A7	A(1,6,7)	-0.2047	5.6	-0.1884	4.3	---	---	-0.187	4.6
A8	A(1,6,8)	0.3119	8.5	0.3635	8.4	0.1287	2.3	0.3287	8
A9	A(1,6,9)	-0.088	2.4	-0.0802	1.8	---	---	-0.1411	3.4
A11	A(7,6,9)	-0.1117	3.1	-0.0728	1.7	---	---	-0.0492	1.2
A12	A(8,6,9)	0.0595	1.6	---	---	---	---	---	---
A13	A(2,10,5)	-0.3119	8.5	-0.3635	8.4	-0.1287	2.3	-0.3287	8
A14	A(2,10,11)	0.088	2.4	0.0802	1.8	---	---	0.1411	3.4
A15	A(2,10,12)	0.2047	5.6	0.1884	4.3	---	---	0.187	4.6
A16	A(5,10,11)	-0.0595	1.6	---	---	---	---	---	---
A18	A(11,10,12)	0.1117	3.1	0.0728	1.7	---	---	0.0492	1.2
A19	L(1,13,2,9,-1)	-0.0495	1.4	---	---	-0.5258	9.5	---	---
A20	L(1,13,2,9,-2)	-0.061	1.7	---	---	-0.6794	12.3	0.0335	0.8
D2	D(3,1,2,10)	0.0901	2.5	0.2162	5	---	---	0.1537	3.8
D3	D(6,1,2,4)	-0.0901	2.5	-0.2162	5	---	---	-0.1537	3.8
D5	D(3,1,6,7)	-0.1798	4.9	-0.2344	5.4	-0.1163	2.1	-0.197	4.8

D6	D(3,1,6,8)	-0.0924	2.5	-0.1593	3.7	-0.0916	1.7	-0.0946	2.3
D7	D(3,1,6,9)	0.0914	2.5	---	---	---	---	---	---
D8	D(13,1,6,7)	-0.1089	3	-0.0554	1.3	-0.2069	3.7	---	---
D9	D(13,1,6,8)	---	---	---	---	-0.1822	3.3	0.0847	2.1
D10	D(13,1,6,9)	0.1623	4.4	0.1591	3.7	-0.1198	2.2	0.1996	4.9
D11	D(4,2,10,5)	0.0924	2.5	0.1593	3.7	0.0916	1.7	0.0946	2.3
D12	D(4,2,10,11)	-0.0914	2.5	---	---	---	---	---	---
D13	D(4,2,10,12)	0.1798	4.9	0.2344	5.4	0.1163	2.1	0.197	4.8
D14	D(13,2,10,5)	---	---	---	---	0.1822	3.3	-0.0847	2.1
D15	D(13,2,10,11)	-0.1623	4.4	-0.1591	3.7	0.1198	2.2	-0.1996	4.9
D16	D(13,2,10,12)	0.1089	3	0.0554	1.3	0.2069	3.7	---	---

C. Comparison of vibrational calculations using 7^4 versus 9^4 DVR grid points

Table S10. RDAV-4D calculations using 7^4=2401 and 9^4=6561 shows that the frequencies agreed within 2 cm^{-1}.

	MP2/aug-cc-pVDZ			
	7x7x7x7 DVR Grids		9x9x9x9 DVR Grids	
State	Frequency (cm^{-1})	Intensity (km mol^{-1})	Frequency (cm^{-1})	Intensity (km mol^{-1})
0	0.0	N/A	0.0	N/A
1	563.5	2.4	562.8	2.4
2	896.1	1158.8	896.9	1126.9
3	1006.6	728.1	1007.8	739.4
4	1114.5	471.3	1114.7	478.5
5	1124.5	0.0	1123.6	0.0

D. Comparison of the RDAV-4D vibrational calculations using MP2 and CCSD(T) at aug-cc-pVDZ and aug-cc-pVTZ basis sets for $(CH_3OH)_2H^+$

Table S11. Frequencies and intensities for $(CH_3OH)_2H^+$ obtained by a RDAV-4D calculation using MP2/aug-cc-pVDZ and CCSD(T)/aug-cc-pVDZ//MP2/aug-ccpVDZ. The entries highlighted in green are the three major bands centered around 1000 cm^{-1}. The orange highlighted entries refer to the combination bands around 1500 cm^{-1}.

	MP2				CCSD(T)			
	aug-cc-pVDZ		aug-cc-pVTZ		aug-cc-pVDZ		aug-cc-pVTZ	
State	Frequency (cm^{-1})	Intensity (km mol^{-1})	Frequency (cm^{-1})	Intensity (km mol^{-1})	Frequency (cm^{-1})	Intensity (km mol^{-1})	Frequency (cm^{-1})	Intensity (km mol^{-1})
0	0	0	0	0	0	0	0	0
1	563	2	567	2	559	3	564	2
2	896	1159	944	724	865	1733	924	1299
3	1007	728	1052	697	992	515	1036	699
4	1115	471	1131	0	1096	327	1123	0
5	1125	0	1151	1115	1115	0	1126	747
6	1455	146	1506	127	1415	221	1479	238
7	1561	102	1613	187	1541	64	1588	155
8	1673	14	1698	0	1652	7	1680	30
9	1685	0	1702	66	1669	0	1686	0
10	1813	0	1894	0	1767	0	1858	0

E. Hamiltonian matrix elements for MP2 and CCSD(T) at aug-cc-pVDZ and aug-cc-pVTZ obtained from RDAV-4D vibrational calculations of $(CH_3OH)_2H^+$.

Table S12. Hamiltonian matrix elements (cm^{-1}) for the RDAV-4D vibrational calculation at MP2 and CCSD(T) with aug-cc-pVDZ and aug-cc-pVTZ as basis.

	MP2				
aug-cc-pVDZ	$< n_1, n_2, n_3, n_4\|$	|0,1,0,0 >	|1,1,0,0 >	|0,0,1,0 >	|0,0,0,1 >
	< 0,1,0,0|	1092	303	-101	-71
	< 1,1,0,0|	303	1693	-67	-56
	< 0,0,1,0|	-101	-67	1003	24
	< 0,0,0,1|	-71	-56	24	1124
aug-cc-pVTZ	$< n_1, n_2, n_3, n_4\|$	|0,1,0,0 >	|1,1,0,0 >	|0,0,1,0 >	|0,0,0,1 >
	< 0,1,0,0|	1218	339	-124	-112
	< 1,1,0,0|	339	1823	-77	-80
	< 0,0,1,0|	-124	-77	1038	41
	< 0,0,0,1|	-112	-80	41	1160

CCSD(T)				
$< n_1, n_2, n_3, n_4\|$	|0,1,0,0 >	|1,1,0,0 >	|0,0,1,0 >	|0,0,0,1 >
< 0,1,0,0|	1052	307	-96	-61
< 1,1,0,0|	307	1651	-68	-58
< 0,0,1,0|	-96	-68	1003	22
< 0,0,0,1|	-61	-58	22	1110
$< n_1, n_2, n_3, n_4\|$	|0,1,0,0 >	|1,1,0,0 >	|0,0,1,0 >	|0,0,0,1 >
< 0,1,0,0|	1180	346	-121	-102
< 1,1,0,0|	346	1785	-79	-83
< 0,0,1,0|	-121	-79	1040	39
< 0,0,0,1|	-102	-83	39	1149

F. Comparison of RDAV-4D and RDAV-5D vibrational calculations for $(CH_3OH)_2H^+$ at MP2/aug-cc-pVDZ

Table S13. Comparison between RDAV-4D and RDAV-5D vibrational calculations reveals that peak positions does not shift significantly (<50 cm^{-1}) upon inclusion of the out-of-phase out-plane CH_3 rock (ν_4^*). The frequency in red is corresponds to ν_4^*, which is not included in the RDAV-4D calculation.

	MP2/aug-cc-pVDZ			
	RDAV-4D calculation		RDAV-5D calculation	
State	Frequency (cm^{-1})	Intensity (km mol^{-1})	Frequency (cm^{-1})	Intensity (km mol^{-1})
0	0	0	0	0
1	563	2	563	2
2	896	1159	896	1138
3	1007	728	1006	678
4	1115	471	1116	401
5	1125	0	1124	0
6	1455	146	**1189**	181
7	1561	102	1457	162
8	1673	14	1561	112
9	1685	0	1676	15
10	1813	0	1685	0

G. Calculated RDAV-5D vibrational frequencies and intensities for $(CH_3OH)_2H^+$ and its isotopologues.

Table S14. Calculated RDAV- 5D vibrational frequencies and intensities for the $(CH_3OH)_2H^+$ and its isotopologues. In all calculations, seven DVR grids were used.

	MP2/aug-cc-pVDZ							
State	$(CH_3OH)_2H^+$		$(CD_3OH)_2H^+$		$(CH_3OD)_2D^+$		$(CD_3OD)_2D^+$	
	cm^{-1}	km mol^{-1}	cm^{-1}	km mol^{-1}	cm^{-1}	km mol^{-1}	cm^{-1}	km mol^{-1}
0	0	0	0	0	0	0	0	0
1	563	2	549	3	530	0	519	0
2	896	1138	857	700	653	991	644	967
3	1006	678	873	43	927	50	809	205
4	1116	401	920	106	929	394	891	51
5	1124	0	979	1341	1057	0	912	90
6	1189	181	1097	0	1071	203	1036	0
7	1457	162	1405	87	1186	156	1156	76
8	1561	112	1425	2	1388	0	1326	4
9	1676	15	1468	2	1445	10	1368	0
10	1685	0	1517	103	1455	0	1407	1
11	1748	5	1645	0	1571	0	1430	1
12	1813	0	1729	0	1580	0	1475	0
13	1951	0	1734	0	1597	1	1538	0
14	2013	0	1750	0	1633	0	1550	0

H. Comparison of the stick spectrum for RDAV-4D and RDAV-5D calculations using MP2/aug-cc-pVDZ.

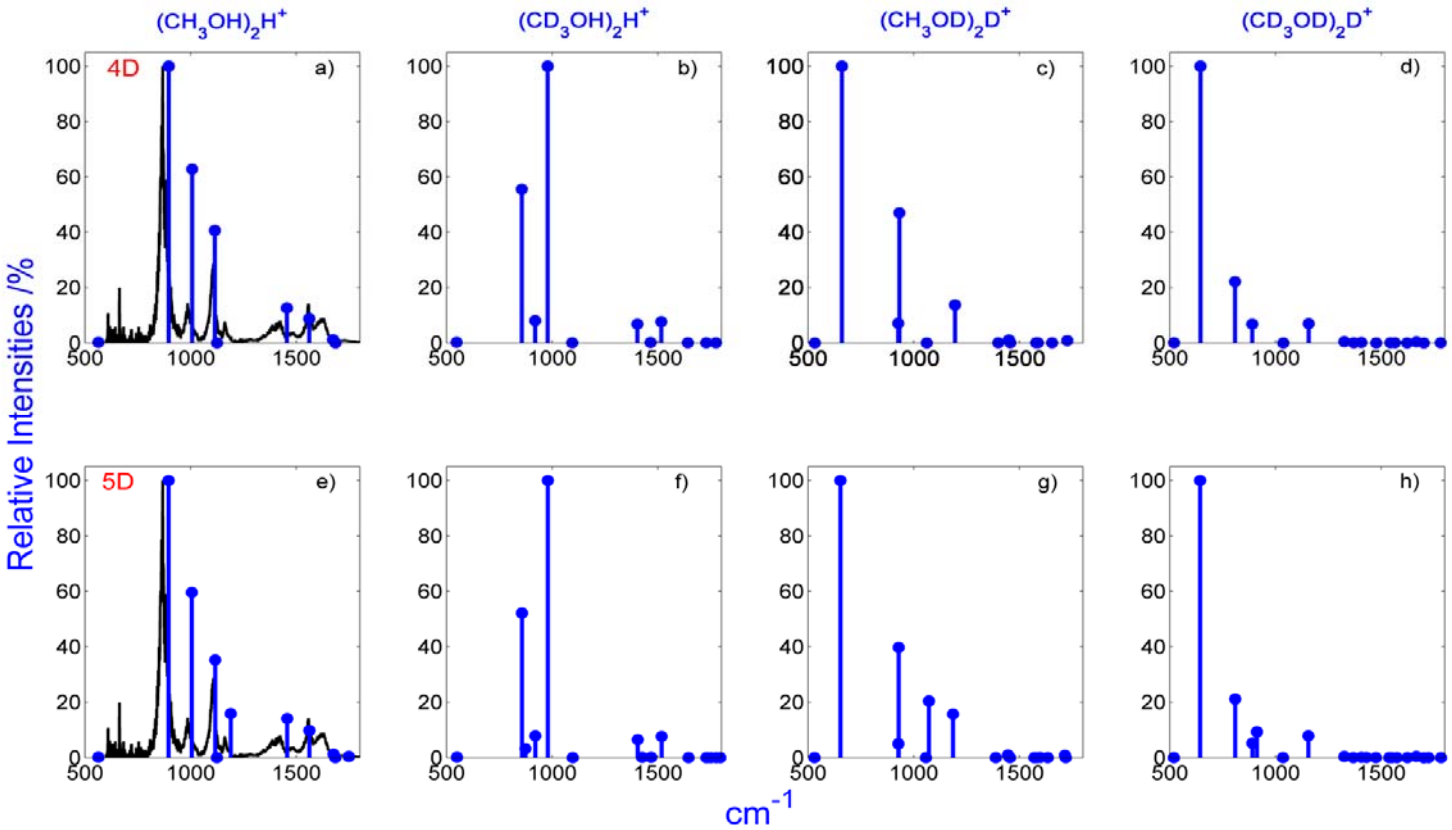


Figure S1. A comparison of the RDAV-4D (a-d) and RDAV-5D (e-h) calculations at MP2 aug-cc-pVDZ as basis, note that there are no significant differences between the peak positions of the RDAV-5D stick spectrum.

I. Comparison of 4D vibrational spectrum for $(CH_3OH)_2H^+$ and its isotopologues at MP2/aug-cc-pVDZ and CCSD(T)/aug-cc-pVDZ//MP2/aug-cc-pVDZ.

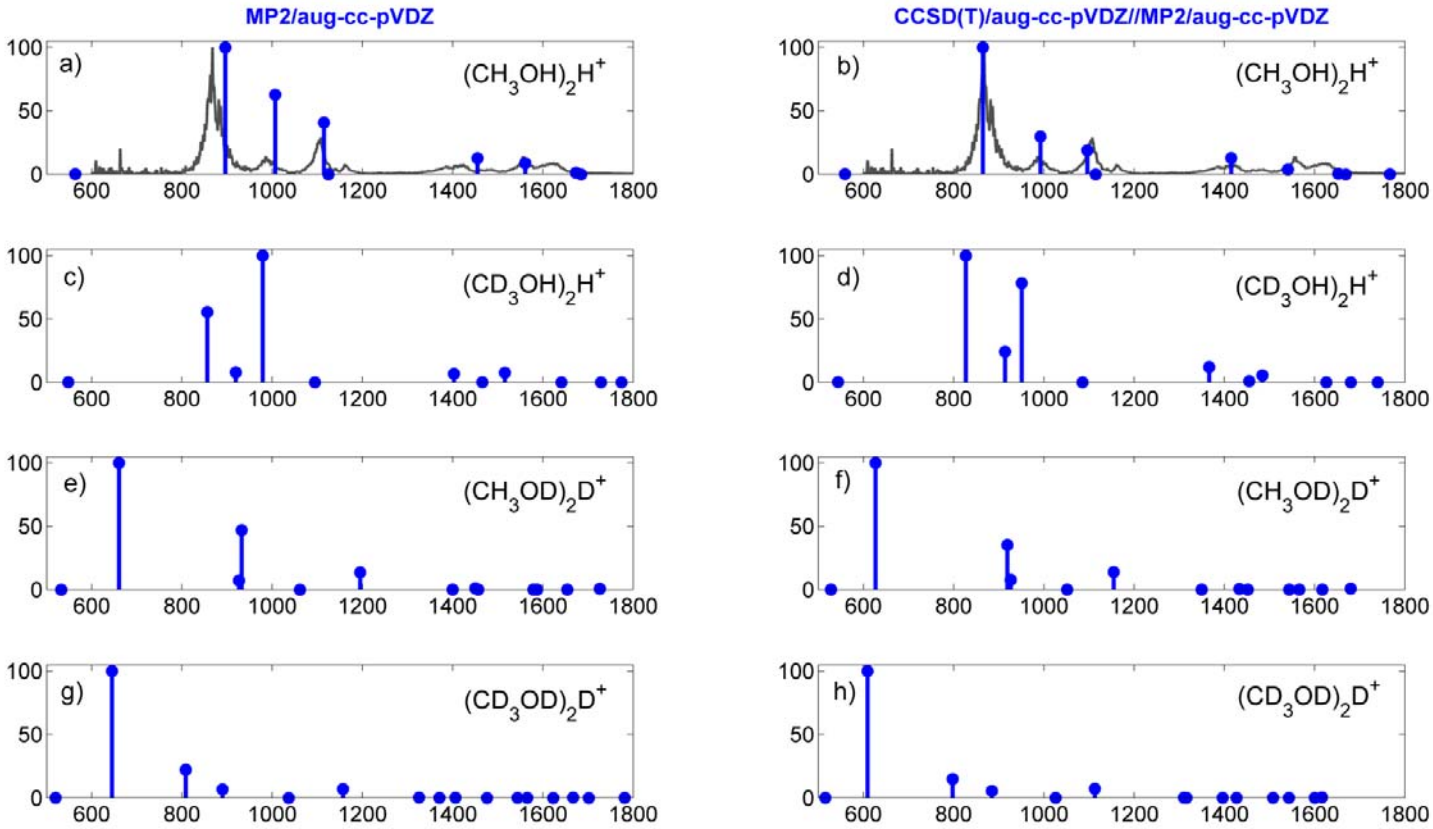


Figure S2. Comparison of RDAV-4D vibrational spectrum for $(CH_3OH)_2H^+$ and its isotopologues at MP2/aug-cc-pVDZ and CCSD(T)/aug-cc-pVDZ//MP2/aug-cc-pVDZ.

J. Hamiltonian matrix elements for 4D vibrational calculations of $(CH_3OH)_2H^+$ and its isotopologues performed at MP2/aug-cc-pVDZ.

Table S15. Hamiltonian matrix elements (cm^{-1}) for the 4D vibrational calculation at MP2 with aug-cc-pVDZ as basis set.

$(CH_3OH)_2H^+$				
$< m_1, m_2, m_3, m_4\|$	|0,1,0,0 >	|1,1,0,0 >	|0,0,1,0 >	|0,0,0,1 >
< 0,1,0,0|	1092	303	-101	-71
< 1,1,0,0|	303	1693	-67	-56
< 0,0,1,0|	-101	-67	1003	24
< 0,0,0,1|	-71	-56	24	1124
$(CD_3OH)_2H^+$				
$< m_1, m_2, m_3, m_4^*\|$	|0,1,0,0 >	|1,1,0,0 >	|0,0,0,1 >	|0,0,1,0 >
< 0,1,0,0|	1034	274	98	-49
< 1,1,0,0|	274	1615	68	-32
< 0,0,0,1|	98	68	953	-18
< 0,0,1,0|	-49	-32	-18	937

$(CH_3OD)_2D^+$				
$< m_1, m_2, m_3, m_4\|$	|0,1,0,0 >	|1,1,0,0 >	|0,0,0,1 >	|0,0,1,0 >
< 0,1,0,0|	753	-217	-84	1
< 1,1,0,0|	-217	1314	81	-10
< 0,0,0,1|	-84	81	967	-3
< 0,0,1,0|	1	-10	-3	930
$(CD_3OD)_2D^+$				
$< m_1, m_2, m_3, m_4\|$	|0,1,0,0 >	|1,1,0,0 >	|0,0,1,0 >	|0,0,0,1 >
< 0,1,0,0|	724	198	-44	-33
< 1,1,0,0|	198	1270	-46	-26
< 0,0,1,0|	-44	-46	817	12
< 0,0,0,1|	-33	-26	12	895

K. Hamiltonian matrix elements for 4D vibrational calculations of $(CH_3OH)_2H^+$ and its isotopologues performed at CCSD(T)/aug-cc-pVDZ.

Table S16. Hamiltonian matrix elements (cm^{-1}) for the 4D vibrational calculation at CCSD(T) with aug-cc-pVDZ as basis set.

$(CH_3OH)_2H^+$				
$< m_1, m_2, m_3, m_4\|$	|0,1,0,0 >	|1,1,0,0 >	|0,0,1,0 >	|0,0,0,1 >
< 0,1,0,0|	1052	307	-96	-61
< 1,1,0,0|	307	1651	-68	-58
< 0,0,1,0|	-96	-68	1003	22
< 0,0,0,1|	-61	-58	22	1110
$(CD_3OH)_2H^+$				
$< m_1, m_2, m_3, m_4^*\|$	|0,1,0,0 >	|1,1,0,0 >	|0,0,0,1 >	|0,0,1,0 >
< 0,1,0,0|	995	279	90	-48
< 1,1,0,0|	279	1574	70	-32
< 0,0,0,1|	90	70	939	-17
< 0,0,1,0|	-48	-32	-17	936

$(CH_3OD)_2D^+$				
$< m_1, m_2, m_3, m_4\|$	|0,1,0,0 >	|1,1,0,0 >	|0,0,0,1 >	|0,0,1,0 >
< 0,1,0,0|	722	-222	70	6
< 1,1,0,0|	-222	1283	-83	11
< 0,0,0,1|	70	-83	960	0
< 0,0,1,0|	6	11	0	929
$(CD_3OD)_2D^+$				
$< m_1, m_2, m_3, m_4\|$	|0,1,0,0 >	|1,1,0,0 >	|0,0,0,1 >	|0,0,1,0 >
< 0,1,0,0|	692	203	-34	-33
< 1,1,0,0|	203	1235	-47	-26
< 0,0,0,1|	-34	-47	808	11
< 0,0,1,0|	-33	-26	11	891