Electronic supplementary information for

How Many Methanol Molecules Effectively Solvate an Excess Proton in the Gas Phase?: Infrared Spectroscopy of $H^+(Methanol)_n$-Benzene Clusters

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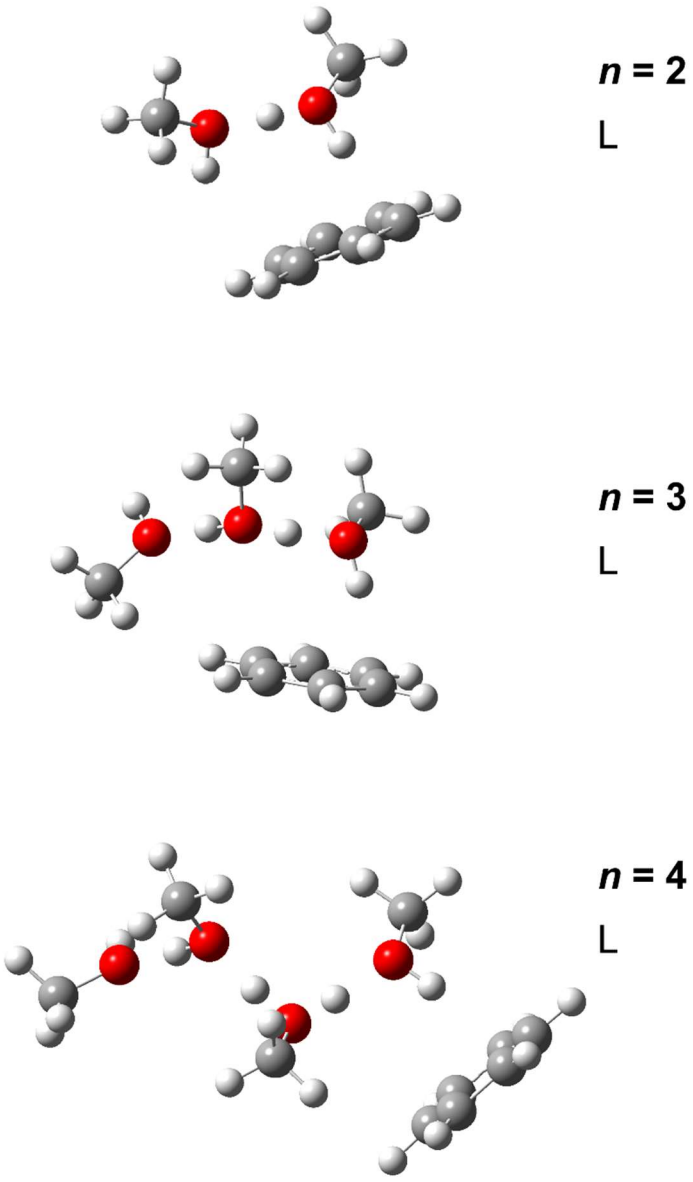

1. **Figure S1.** Schematic structures of energy-optimized isomers of $H^+(MeOH)_n$-Bz (n = 2 -4). All the computations were performed at ωB97X-D/6-31+G(d).

2. Coordinates of the energy optimized structures of $H^+(MeOH)_n$-Bz (n = 2 - 7) shown in Figure S1 (n = 2 -4) and Figure 3 (n = 5 – 7) in the main text

All the computations were performed at the ωB97X-D/6-31+G(d)level.

***n* = 2**

L

C	-0.8597300	2.5345810	-0.2559790
H	-1.9002110	2.8290490	-0.3752090
H	-0.3064940	3.2968800	0.2892420
H	-0.3950470	2.3070340	-1.2157970
O	-0.8713080	1.3341020	0.5787520
H	0.0486090	1.0167380	0.7616190
C	2.1341850	0.5933700	0.6218040
C	2.0733900	0.5431210	-0.7756700
C	1.4909600	-0.5550650	-1.4080020
C	0.9780710	-1.6082800	-0.6453480
C	1.0327680	-1.5598970	0.7483320
C	1.6101730	-0.4571560	1.3846710
H	2.6213820	1.4300510	1.1154060
H	2.5046450	1.3461550	-1.3662050
H	1.4679200	-0.6075010	-2.4925290
H	0.5782390	-2.4899140	-1.1418330
H	0.6586310	-2.3905560	1.3396330
H	1.6805770	-0.4286990	2.4680780
H	-1.4334770	0.5270700	0.1313150
C	-3.2763830	-1.0405220	0.2351010
O	-2.1748720	-0.4471660	-0.4909270
H	-2.9048710	-1.6488920	1.0629460
H	-1.6030190	-1.1312900	-0.8695570
H	-3.8741780	-0.2128350	0.6138780
H	-3.8738790	-1.6396950	-0.4530490

***n* = 3**

L

C	-0.6945610	2.2648020	1.4546870
H	0.0967410	2.9753640	1.6949870
H	-1.6638320	2.7532720	1.5682290
H	-0.6343260	1.3871240	2.1038130
O	-0.5103230	1.8886230	0.0794110
H	-1.2583950	1.3371400	-0.2203230
C	-2.9216490	-0.0983740	-0.7880640
C	-2.9129920	-0.3840060	0.5806150
C	-1.8769550	-1.1412810	1.1282850
C	-0.8502110	-1.6132860	0.3096810
C	-0.8601810	-1.3332280	-1.0570830
C	-1.8949320	-0.5756840	-1.6078990
H	-3.7381980	0.4739290	-1.2187200
H	-3.7225290	-0.0311750	1.2129220
H	-1.8801960	-1.3782330	2.1882810
H	-0.0549590	-2.2166840	0.7378870
H	-0.0753900	-1.7183550	-1.7021780
H	-1.9122180	-0.3700400	-2.6740290
H	0.6880660	1.3062060	-0.2788240
C	2.5770070	2.0041520	-0.9344760
O	1.6380470	0.9398200	-0.6290340
H	3.4363280	1.5494370	-1.4247760
H	2.0334810	0.2315670	-0.0218440
H	2.0680780	2.6825690	-1.6167530
H	2.8728270	2.5205250	-0.0194390
O	2.6654170	-0.9244040	0.8176480
H	3.2129910	-0.7886240	1.6008960
C	2.9579310	-2.1939500	0.2114080
H	2.3120490	-2.2732240	-0.6633190
H	2.7295430	-3.0047090	0.9074960
H	4.0040850	-2.2432810	-0.1014370

***n* = 4**

L

C	0.9579660	2.2751680	-0.8388880
H	-0.0736190	2.6290540	-0.8298310
H	1.6346470	3.1284290	-0.7548010
H	1.1569460	1.7234700	-1.7620960
O	1.1123590	1.4211220	0.3041790
H	2.0323630	1.1026230	0.3475000
C	3.2751710	-1.1657810	0.9980680
C	4.0438540	-0.0158280	0.7990740
C	4.1755270	0.5206590	-0.4846370
C	3.5365360	-0.0909380	-1.5660760
C	2.7626200	-1.2330060	-1.3640310
C	2.6339430	-1.7714010	-0.0826620
H	3.2003860	-1.5985170	1.9920950
H	4.5562560	0.4479890	1.6368090
H	4.7914250	1.4012000	-0.6434400
H	3.6554090	0.3160430	-2.5660760
H	2.2755360	-1.7152360	-2.2063800
H	2.0520350	-2.6769640	0.0661530
H	0.1387050	0.3249950	0.4110500
C	-0.5238740	-0.9504740	1.8932340
O	-0.6077780	-0.3880850	0.5610150
H	-1.3199410	-1.6882710	1.9821060
H	-1.5497590	0.0595590	0.3852010
H	0.4484570	-1.4333610	1.9769410
H	-0.6310520	-0.1632880	2.6424150
O	-2.7717440	0.7363070	0.1417110
H	-3.4731180	0.2749370	-0.3821090
C	-3.3617660	1.5645470	1.1478320
H	-4.0413990	2.2826570	0.6833160
H	-2.5520710	2.1064160	1.6398480
H	-3.9026950	0.9621590	1.8843460
O	-4.7390480	-0.4541520	-1.2179230
H	-4.9823270	-0.1715380	-2.1074890
C	-5.7378650	-1.3284250	-0.6863570
H	-5.8343200	-2.2267110	-1.3030810
H	-6.7032560	-0.8193030	-0.6085800

H	-5.4015950	-1.6150060	0.3109060

***n* = 5**

L

C	2.4448210	-2.1533440	1.2574330
H	1.5502930	-2.6225340	1.6697270
H	3.1380600	-2.9321210	0.9266330
H	2.9215150	-1.5327820	2.0228480
O	2.0216770	-1.3601610	0.1464640
H	2.8042480	-0.9883980	-0.2928820
C	3.8157790	1.5423520	-0.9545730
C	4.2556410	0.4366040	-1.6839500
C	5.0167800	-0.5538200	-1.0572800
C	5.3359640	-0.4359570	0.2970530
C	4.8910180	0.6675530	1.0253200
C	4.1311800	1.6558680	0.3997230
H	3.2452780	2.3243440	-1.4481860
H	4.0238530	0.3536650	-2.7418990
H	5.3732120	-1.4065200	-1.6279690
H	5.9398930	-1.1985930	0.7801210
H	5.1485480	0.7641430	2.0759800
H	3.8031440	2.5242170	0.9643920
H	0.8263050	-0.2904870	0.4333440
C	0.2213220	1.5560190	-0.0837270
O	0.0158450	0.2857760	0.5402690
H	-0.7175480	2.1089080	-0.0184690
H	-1.1188150	-0.3921360	0.2086090
H	1.0005920	2.1025660	0.4518080
H	0.5085500	1.4352750	-1.1334490
O	-2.0172730	-0.9394910	-0.0504350
H	-2.8622950	-0.4151730	0.2614480
C	-2.0696400	-1.2297090	-1.4655290
H	-2.9304830	-1.8742110	-1.6397810
H	-1.1507410	-1.7571280	-1.7195290
H	-2.1580630	-0.3037880	-2.0387150

O	-4.0196890	0.3980760	0.6512000
H	-4.8852700	0.0938970	0.2862860
C	-4.1622080	0.7176850	2.0386010
H	-4.4537990	-0.1643520	2.6173890
H	-4.9059920	1.5088620	2.1624630
H	-3.1946260	1.0793640	2.3899330
O	-6.3545970	-0.4007440	-0.4144450
C	-7.2092830	0.5431000	-1.0679830
H	-7.9620580	0.9364520	-0.3778450
H	-7.6959860	0.0863140	-1.9345730
H	-6.5685580	1.3585360	-1.4051370
H	-6.8752100	-1.1440750	-0.0875020

C

C	3.4834130	0.3602870	-1.9456650
H	3.5151680	1.2401530	-2.5859720
H	4.4061740	-0.2095930	-2.0437590
H	2.6099050	-0.2569410	-2.1658820
O	3.4166700	0.8307680	-0.5727090
H	3.2888290	0.0206470	0.0893610
H	2.5926040	1.4620280	-0.4420520
C	0.0767710	-2.7801210	-0.8710200
H	-0.5044310	-3.1901400	-0.0378210
H	-0.5810930	-2.6094130	-1.7290220
H	0.8496860	-3.4960360	-1.1552330
O	0.7370790	-1.5745380	-0.4963160
H	0.0904660	-0.9037150	-0.1987350
C	1.4357900	3.5268910	0.3435070
H	1.5818700	3.4046970	1.4214010
H	2.2801010	4.0716920	-0.0794030
H	0.5162440	4.0843930	0.1486810
O	1.3799120	2.2560410	-0.3142840
H	0.6250770	1.7227680	0.0268730
C	3.8238280	-2.0616100	1.3771160
H	4.6636650	-1.5403150	1.8370000

H	3.3517110	-2.7082270	2.1207860
H	4.1793730	-2.6605030	0.5326490
O	2.8931200	-1.0641610	0.9436280
H	2.1013440	-1.4634730	0.5019840
C	-0.5244620	0.3784400	2.0742170
H	0.5184120	0.2165200	2.3517850
H	-0.9177030	1.2503710	2.6048700
H	-1.1147670	-0.5064210	2.3279080
O	-0.5436890	0.5977940	0.6568040
H	-1.4579850	0.7739360	0.3700190
C	-3.2847810	-1.4599530	-0.4329050
C	-3.7350650	-0.9528240	0.7863220
C	-3.9114500	0.4219840	0.9474000
C	-3.6360400	1.2898940	-0.1128060
C	-3.1838880	0.7807440	-1.3336830
C	-3.0082360	-0.5948090	-1.4919980
H	-3.1705220	-2.5322480	-0.5635850
H	-3.9671780	-1.6288490	1.6041440
H	-4.2799970	0.8166310	1.8898230
H	-3.7943800	2.3582000	0.0047030
H	-2.9862110	1.4538220	-2.1627980
H	-2.6763830	-0.9907460	-2.4476090

C_vdW

C	-3.7448430	1.5201770	-0.6350810
H	-3.7953180	2.6079360	-0.6286440
H	-4.3332880	1.1250390	-1.4619550
H	-4.0846070	1.1129610	0.3195300
O	-2.3655140	1.1470240	-0.8758900
H	-2.2289660	0.0677470	-0.8805120
H	-1.7450430	1.5614370	-0.1619940
C	0.0081000	-3.0190270	1.5505850
H	0.9938550	-2.8290550	1.1116310
H	0.1151010	-3.3000430	2.6029620
H	-0.4711670	-3.8404650	1.0157980

O	-0.8393250	-1.8785600	1.4211310
H	-0.4210140	-1.1129580	1.8589250
C	-0.0772130	3.2771430	0.6738620
H	0.8788520	2.9194400	0.2797130
H	-0.5656220	3.9049400	-0.0723560
H	0.0804050	3.8617780	1.5842420
O	-0.9556020	2.1796960	0.9459990
H	-0.5213610	1.5536190	1.5637750
C	-3.1275320	-2.1440030	-1.1093340
H	-3.5897250	-1.8149400	-2.0407820
H	-2.7677220	-3.1675920	-1.2340570
H	-3.8535210	-2.1008350	-0.2917120
O	-2.0158030	-1.2757850	-0.8539750
H	-1.5481510	-1.5409830	-0.0121260
C	1.7880640	0.4061170	2.1763900
H	1.8143440	0.3315380	1.0896580
H	2.2544050	1.3420660	2.4956340
H	2.3135180	-0.4466500	2.6140380
O	0.3943940	0.3838160	2.5480110
H	0.3090900	0.4737380	3.5066890
C	3.6398440	-0.4474090	-0.9031800
C	3.3220580	0.8634060	-1.2592820
C	2.0232940	1.1818450	-1.6573780
C	1.0404010	0.1921100	-1.6907430
C	1.3585970	-1.1186850	-1.3344350
C	2.6590130	-1.4386420	-0.9442890
H	4.6552900	-0.6996690	-0.6119320
H	4.0906290	1.6308110	-1.2470270
H	1.7856710	2.1952200	-1.9697940
H	0.0375870	0.4323550	-2.0330920
H	0.5972000	-1.8912100	-1.3898000
H	2.9156790	-2.4639450	-0.6916980

***n* = 6**

L

C	-3.3498250	2.5263880	-0.3639960
H	-2.4568730	3.1447320	-0.2606230
H	-3.9808650	2.9377270	-1.1575520
H	-3.9023490	2.5178500	0.5811070
O	-2.9059470	1.2138510	-0.7096980
H	-3.6799920	0.6524610	-0.8781060
C	-4.8362980	-1.6878840	0.1669830
C	-5.1442020	-1.3223520	-1.1442960
C	-5.8750260	-0.1568570	-1.3897780
C	-6.2963360	0.6398600	-0.3233140
C	-5.9838000	0.2748520	0.9863000
C	-5.2537770	-0.8880670	1.2310680
H	-4.2875270	-2.6057890	0.3588240
H	-4.8320790	-1.9509680	-1.9733330
H	-6.1277840	0.1205830	-2.4090600
H	-6.8759540	1.5384770	-0.5136830
H	-6.3201190	0.8896970	1.8160250
H	-5.0273030	-1.1796600	2.2528570
H	-1.7681770	0.5478300	0.2823160
C	-1.3235810	-1.1578050	1.2385730
O	-1.0122320	0.1665240	0.8072360
H	-0.4498690	-1.5444190	1.7665590
H	0.2477370	0.3985320	0.2006850
H	-2.1752870	-1.1324570	1.9229010
H	-1.5560350	-1.8056670	0.3862920
O	1.1870970	0.5713350	-0.2560830
H	1.9810300	0.2630320	0.3845230
C	1.2766390	-0.0947280	-1.5362130
H	2.2857150	0.0630700	-1.9158250
H	0.5437260	0.3668710	-2.1968880
H	1.0769380	-1.1628020	-1.4202700
O	3.0493560	-0.2184010	1.1605580
H	3.7870950	-0.4922940	0.5469690
C	3.5574240	0.6683810	2.1621790

H	4.0161160	1.5520020	1.7067390
H	4.2898750	0.1422220	2.7795820
H	2.7169220	0.9726580	2.7872740
O	4.8655360	-0.8363340	-0.6360090
C	5.4152660	-2.1460430	-0.7483730
H	6.1846460	-2.3214850	0.0120440
H	5.8430520	-2.2998400	-1.7442040
H	4.5999620	-2.8559980	-0.5984820
H	5.5825350	-0.1754720	-0.7519820
O	6.9190120	0.9507730	-0.7993300
H	7.1889250	1.3915430	-1.6135730
C	8.0372950	0.8257940	0.0796940
H	8.4298610	1.8099560	0.3535650
H	8.8302650	0.2188670	-0.3694890
H	7.6705670	0.3275180	0.9784520

C

C	-3.1486360	1.3920840	1.5079300
H	-3.0531260	2.4167420	1.8743220
H	-4.0947570	0.9774190	1.8595760
H	-2.3128620	0.7799960	1.8623680
O	-3.1938330	1.4049440	0.0749560
H	-3.4051070	0.2059630	-0.5043700
H	-2.3631850	1.8294010	-0.2785500
C	-1.0617750	-3.1756370	-0.8700490
H	-0.4061990	-2.6267400	-1.5548460
H	-0.4716390	-3.8632700	-0.2572830
H	-1.7851960	-3.7518910	-1.4483160
O	-1.7936820	-2.2820820	-0.0333830
H	-1.1724590	-1.7327000	0.5086120
C	-0.7724230	3.7321110	-1.3562240
H	-0.0274330	3.7153480	-2.1584400
H	-1.7351040	4.0290320	-1.7747550
H	-0.4763150	4.4581790	-0.5909770
O	-0.9388030	2.4324910	-0.7973940

H	-0.1019440	2.1181170	-0.4019800
C	-4.9108000	-1.2713270	-0.6960420
H	-5.6102340	-0.4922480	-0.9964140
H	-5.0580340	-2.1609310	-1.3072000
H	-5.0238890	-1.5089350	0.3640640
O	-3.5793640	-0.7721860	-0.9583970
H	-2.8470920	-1.4247500	-0.6220950
C	1.9431750	2.0933730	1.4877670
H	1.1474890	2.4872240	2.1219780
H	2.5848560	1.4261620	2.0710070
H	2.5355440	2.9224450	1.0900760
O	1.3060070	1.3721630	0.4272380
H	1.9840150	1.0317540	-0.1821670
C	0.3275900	-1.1364940	2.6555180
H	1.3024090	-1.6011640	2.4699350
H	0.4455450	-0.3118600	3.3671860
H	-0.3474920	-1.8786660	3.0849870
O	-0.2616240	-0.6778610	1.4431150
H	0.3314130	-0.0229120	1.0205750
C	3.2561300	0.0291720	-1.8398450
C	2.4437980	-1.0755650	-1.5727110
C	2.5996130	-1.7828950	-0.3808810
C	3.5692980	-1.3910320	0.5426000
C	4.3808320	-0.2879530	0.2783820
C	4.2238870	0.4243560	-0.9121640
H	3.1469050	0.5706310	-2.7750670
H	1.7033220	-1.3883980	-2.3033430
H	1.9776920	-2.6499610	-0.1772750
H	3.7071920	-1.9562570	1.4600470
H	5.1455540	0.0080070	0.9905130
H	4.8663910	1.2733420	-1.1269390

Ct (5+1)

C	2.5830240	1.2309870	-2.2269900
H	1.8718330	1.8936750	-2.7178550

H	3.5367280	1.2498750	-2.7527420
H	2.1923850	0.2126940	-2.1608870
O	2.8171520	1.7555110	-0.8962070
H	3.4310590	1.0821070	-0.3312050
H	1.9135490	1.8810570	-0.3940710
C	2.1909340	-3.1061650	0.2697130
H	2.4095730	-3.3484290	1.3157050
H	1.2197420	-3.5301910	-0.0071660
H	2.9623210	-3.5400730	-0.3682000
O	2.2023890	-1.6954690	0.0536170
H	1.4392040	-1.2921700	0.5221830
C	0.3277990	3.0702970	1.1243650
H	0.7813940	2.8858220	2.1033160
H	0.7644420	3.9683060	0.6858880
H	-0.7505650	3.2173520	1.2341270
O	0.5845910	1.9884350	0.2257160
H	0.2785580	1.1309800	0.6120870
C	5.4767680	-0.1693280	0.1659860
H	6.0120570	0.7786210	0.2249070
H	5.8554050	-0.8441250	0.9370100
H	5.6178620	-0.6143730	-0.8241270
O	4.0937210	0.1095530	0.4109880
H	3.5338350	-0.7082450	0.3454170
C	-0.2619350	-0.7359500	2.5395200
H	0.5595120	-0.3172800	3.1234580
H	-1.2026790	-0.2655460	2.8419430
H	-0.3214140	-1.8140360	2.7172040
O	0.0120560	-0.4711970	1.1614460
H	-0.6796200	-0.9127220	0.5987080
C	-1.0911160	-1.8562940	-1.7831520
H	-1.6016170	-2.6192450	-2.3788600
H	-1.2336630	-0.8716080	-2.2427320
H	-0.0244730	-2.0880380	-1.7437910
O	-1.5641600	-1.8666680	-0.4385470
H	-2.5039690	-1.6238700	-0.4284950
C	-4.4213920	-0.2528320	-1.1506450

C	-3.5301890	0.7753280	-1.4634900
C	-2.8326630	1.4267590	-0.4472060
C	-3.0332430	1.0562940	0.8824490
C	-3.9239160	0.0313980	1.1989580
C	-4.6172950	-0.6267060	0.1810860
H	-4.9751050	-0.7517370	-1.9408060
H	-3.3905520	1.0747620	-2.4982790
H	-2.1405850	2.2274480	-0.6924690
H	-2.5091630	1.5786720	1.6788440
H	-4.0912660	-0.2472100	2.2354640
H	-5.3214260	-1.4165170	0.4257660

C_vdW

C	2.0190890	2.8670160	1.2425630
H	1.6051260	3.8639250	1.4145630
H	2.9333370	2.7603640	1.8286770
H	2.2424100	2.7343570	0.1784890
O	1.1018830	1.8720220	1.7012460
H	1.5998670	0.5173800	1.7424530
H	0.2184080	2.0035830	1.2758800
C	0.0356330	-2.9074410	2.9079750
H	-0.5870330	-2.3001280	3.5716370
H	-0.4474340	-3.8696210	2.7213040
H	1.0083390	-3.0767040	3.3714950
O	0.2677150	-2.2338030	1.6656410
H	-0.5951190	-2.0676300	1.2100740
C	-1.9404050	3.5527840	1.1430580
H	-2.4681480	3.2711770	2.0609320
H	-1.1811410	4.2973590	1.3869450
H	-2.6437950	3.9911530	0.4273790
O	-1.2665790	2.4347540	0.5683870
H	-1.9238260	1.7617500	0.3096220
C	3.1054310	-0.6371940	0.8758440
H	3.9884460	-0.2032610	1.3439900
H	3.2375770	-1.7092950	0.7387860

H	2.8812610	-0.1578520	-0.0784570
O	2.0000020	-0.4516710	1.7951640
H	1.2436940	-1.1724140	1.6913070
C	-3.2870580	0.6262050	-1.7262590
H	-2.2828190	0.4336110	-2.1047270
H	-3.9761470	-0.1339150	-2.1045980
H	-3.6114150	1.6212150	-2.0426540
O	-3.1989860	0.5571350	-0.2897480
H	-4.0734880	0.7161020	0.0899490
C	-2.4604710	-2.8378350	-0.5617550
H	-3.5394980	-3.0240190	-0.5733090
H	-2.1373040	-2.4560630	-1.5376220
H	-1.9444960	-3.7782270	-0.3603230
O	-2.1149050	-1.9346020	0.4852140
H	-2.5228810	-1.0672580	0.3052660
C	0.7681880	1.0222780	-1.6780160
C	1.7857880	0.9696960	-2.6304430
C	2.2976140	-0.2631000	-3.0370370
C	1.7906530	-1.4441980	-2.4954930
C	0.7776970	-1.3931310	-1.5383810
C	0.2716360	-0.1599740	-1.1290610
H	0.3536160	1.9768580	-1.3647610
H	2.1736780	1.8873460	-3.0633980
H	3.0857140	-0.3031790	-3.7831000
H	2.1848170	-2.4030360	-2.8192150
H	0.3936110	-2.3122630	-1.1052950
H	-0.5111570	-0.1226410	-0.3764740

Ct (5+1)_vdW

C	-1.1738880	-3.6543450	1.6724360
H	-0.8078980	-3.7592350	2.6927270
H	-2.1488790	-4.1302860	1.5757890
H	-0.4589650	-4.0761080	0.9625850
O	-1.3580940	-2.2412980	1.4172090
H	-1.6995890	-2.0592420	0.4091870

H	-0.4684830	-1.7199630	1.5761580
C	-0.1644170	0.0726020	-3.2572890
H	-0.3770750	1.0785490	-2.8781400
H	0.7408560	0.0914660	-3.8728890
H	-1.0001290	-0.2621040	-3.8743730
O	-0.0229330	-0.8594410	-2.1888850
H	0.6858530	-0.5520940	-1.5848690
C	1.0109240	-0.2080900	2.8964310
H	0.6055360	0.7795220	2.6558630
H	0.4713540	-0.6256500	3.7476840
H	2.0717330	-0.1303060	3.1506650
O	0.8411520	-1.1079400	1.7975540
H	1.2545870	-0.7211610	0.9869910
C	-2.7175110	-2.8541250	-1.6271460
H	-3.5375250	-3.2416750	-1.0210180
H	-3.1241000	-2.4541590	-2.5588620
H	-2.0022420	-3.6528650	-1.8475110
O	-2.0964720	-1.7994550	-0.8841870
H	-1.3392600	-1.4053810	-1.4058180
C	1.6630620	1.5038100	-0.2596930
H	0.6215400	1.6647340	0.0212340
H	2.3203500	1.9053920	0.5177440
H	1.8662450	2.0101200	-1.2078120
O	1.8496120	0.0873870	-0.3957480
H	2.7918860	-0.0931710	-0.6242190
C	-1.2924610	3.7540790	-0.0114480
C	-1.2548600	3.3946690	1.3358100
C	-1.6899130	2.1296200	1.7316970
C	-2.1528800	1.2206860	0.7799570
C	-2.1896270	1.5802970	-0.5672600
C	-1.7633360	2.8482420	-0.9619680
H	-0.9706060	4.7450970	-0.3179820
H	-0.9059860	4.1068360	2.0780900
H	-1.6934970	1.8627840	2.7852260
H	-2.5203520	0.2464240	1.0899210
H	-2.5741750	0.8779580	-1.3010680

H	-1.8136430	3.1389460	-2.0078770
C	5.4824910	-0.3017990	0.0539440
H	5.0015360	-0.0552550	1.0016690
H	5.8988100	-1.3120800	0.1151680
H	6.2792990	0.4221380	-0.1413520
O	4.4677980	-0.2242290	-0.9486750
H	4.8388170	-0.4332910	-1.8138690

***n* = 7**

L

C	4.2128640	-2.4499400	0.6565670
H	3.3070090	-2.9621350	0.9845420
H	4.8352140	-3.1496740	0.0903370
H	4.7655980	-2.0869840	1.5293150
O	3.7969190	-1.3663260	-0.1740600
H	4.5824140	-0.9277260	-0.5384900
C	5.7992680	1.5941060	-0.4816140
C	6.1075150	0.7370780	-1.5391210
C	6.8131380	-0.4442650	-1.2960090
C	7.2091570	-0.7652920	0.0037660
C	6.8966380	0.0908490	1.0598470
C	6.1915930	1.2694590	0.8171670
H	5.2687100	2.5225680	-0.6736680
H	5.8141170	0.9943300	-2.5528140
H	7.0652960	-1.1050820	-2.1203570
H	7.7686090	-1.6773420	0.1905610
H	7.2128040	-0.1548150	2.0694550
H	5.9640780	1.9428610	1.6388040
H	2.6619190	-0.3404610	0.4773790
C	2.2720980	1.6065270	0.7293800
O	1.9179160	0.2279990	0.8110570
H	1.4078970	2.1871660	1.0579030
H	0.6155140	-0.1899860	0.3266960
H	3.1162260	1.8140630	1.3924460
H	2.5341310	1.8873670	-0.2968500

O	-0.3226130	-0.4840010	-0.0299750
H	-1.1149640	0.0945390	0.4392910
C	-0.3884840	-0.3685580	-1.4691540
H	-1.4204180	-0.5591210	-1.7635360
H	0.2759900	-1.1213230	-1.8920940
H	-0.0862690	0.6342570	-1.7811480
O	-2.1328910	0.8455740	0.9354340
H	-2.8256770	0.9127050	0.2134680
C	-2.7459890	0.3284460	2.1244020
H	-3.2911300	-0.5955420	1.9087950
H	-3.4278450	1.0778810	2.5331220
H	-1.9508430	0.1339760	2.8453160
O	-3.8605530	0.7242260	-1.0127800
C	-4.5601160	1.8436050	-1.5452330
H	-5.2680360	2.2535910	-0.8153140
H	-5.0965890	1.5624010	-2.4577180
H	-3.8208950	2.6077690	-1.7922600
H	-4.5150620	0.0373170	-0.7319030
O	-7.8633200	0.0592860	0.9291490
H	-8.2685670	-0.1424710	1.7805550
C	-8.8664330	0.4515640	-0.0064930
H	-9.3794580	1.3591790	0.3271500
H	-9.5948120	-0.3498260	-0.1698650
H	-8.3492780	0.6609320	-0.9443370
O	-5.5722930	-1.0869930	-0.0466860
C	-5.9474350	-2.2673840	-0.7452540
H	-6.6881280	-2.0533940	-1.5250350
H	-6.3514430	-3.0162470	-0.0555080
H	-5.0467950	-2.6690230	-1.2134880
H	-6.3675190	-0.6970270	0.3726320

C

O	-1.5539950	0.7767850	1.2164010
H	-2.5100960	0.6276510	1.1304680
O	1.2314410	-2.2321480	-0.8484050

H	0.6732640	-1.9915580	-0.0605800
O	-0.1243490	-1.5840190	1.3148680
H	-0.6547860	-0.7613130	1.3021410
O	-0.0481380	1.3792420	-1.0076140
H	-0.7687600	1.1498880	-0.3868290
O	1.9330980	2.0637180	0.6988330
H	1.2443020	1.8514930	0.0274260
O	3.6216910	-1.6959750	-0.5286710
H	2.5873980	-1.8752940	-0.6834630
O	4.0944700	0.5859480	0.3083960
H	3.7927510	-0.7072510	-0.1896790
H	3.2873120	1.1319370	0.5150490
C	5.0081890	1.3671040	-0.4649820
H	4.5389580	1.7194500	-1.3896430
H	5.3567160	2.2188350	0.1250140
H	5.8603350	0.7314790	-0.7097380
C	2.0445820	3.4744990	0.8389190
H	1.0807040	3.9147860	1.1198100
H	2.7633530	3.6689080	1.6369570
H	2.3990180	3.9442720	-0.0864900
C	-1.2939540	1.7557440	2.2283400
H	-1.6726460	1.4198440	3.1982520
H	-0.2095000	1.8656090	2.2777970
H	-1.7517530	2.7138340	1.9623680
C	0.5674340	-1.8663350	-2.0603570
H	0.2974150	-0.8056430	-2.0448540
H	1.2566720	-2.0657350	-2.8825810
H	-0.3249020	-2.4861770	-2.1895820
C	4.1810270	-2.6688890	0.3851780
H	5.2542820	-2.4906600	0.4347290
H	3.7259510	-2.5617540	1.3719740
H	3.9813120	-3.6552650	-0.0310920
C	-0.5284220	2.2364640	-2.0349290
H	-1.0889400	3.0836880	-1.6232850
H	0.3412920	2.6148920	-2.5754160
H	-1.1662430	1.6868150	-2.7363490

C	-0.7657440	-2.5627130	2.1224580
H	-0.1332900	-3.4521080	2.1195830
H	-0.8717140	-2.2068480	3.1527670
H	-1.7517870	-2.8262060	1.7228180
C	-3.7778580	0.7444250	-1.4243650
C	-3.0741430	-0.4501690	-1.5762660
C	-3.2009390	-1.4623560	-0.6251210
C	-4.0345040	-1.2808400	0.4786280
C	-4.7328580	-0.0812100	0.6372490
C	-4.6039430	0.9322750	-0.3156570
H	-3.6959960	1.5251920	-2.1750080
H	-2.4378900	-0.5985850	-2.4444320
H	-2.6626710	-2.3977260	-0.7502170
H	-4.1530100	-2.0748960	1.2103640
H	-5.3926750	0.0545430	1.4893400
H	-5.1613220	1.8574950	-0.2026480

Ct (6+1)

C	-4.5339910	-0.1932890	0.1615790
H	-5.2016170	0.6622790	0.0352890
H	-5.1358670	-1.0958270	0.2808570
H	-3.8908060	-0.0495420	1.0357520
O	-3.7461280	-0.3607680	-1.0246860
H	-2.9176950	-1.4583640	-1.0367650
H	-3.2248180	0.4700130	-1.1960130
C	0.5964950	-2.1692780	0.8164740
H	0.9556640	-1.2239910	0.3983200
H	1.0751490	-2.3570130	1.7820730
H	0.8364880	-2.9889030	0.1366400
O	-0.8255830	-2.1520510	0.9802130
H	-1.0931840	-1.3391280	1.4838380
C	-2.5931020	2.9330770	-2.1547740
H	-1.6872530	3.4245050	-2.5260520
H	-3.1785790	2.5824130	-3.0059220
H	-3.1907290	3.6487840	-1.5795110

O	-2.2597830	1.7910170	-1.3718670
H	-1.7163910	2.0516250	-0.5985570
C	-3.0247720	-3.5582590	-1.0553930
H	-3.7065760	-3.5082460	-1.9034810
H	-2.3162800	-4.3742290	-1.1920920
H	-3.5752810	-3.6808510	-0.1199590
O	-2.2729250	-2.3236680	-1.0361620
H	-1.6339670	-2.2651330	-0.2029800
C	-0.2590230	3.4843890	1.2995270
H	-1.1886660	3.8853310	1.7063880
H	0.4774550	3.3954630	2.1045500
H	0.1199170	4.1637460	0.5293990
O	-0.5560310	2.2035370	0.7414870
H	0.2543470	1.8155820	0.3298650
C	-1.6850390	0.2797820	3.5484620
H	-0.6834600	0.4485620	3.9600100
H	-2.3356530	1.1209220	3.8102480
H	-2.0976120	-0.6335020	3.9801510
O	-1.6398860	0.0983810	2.1358380
H	-1.2545470	0.8947980	1.7109000
C	1.1470370	0.6250060	-1.9243720
H	0.0831760	0.7967930	-2.1018470
H	1.7349180	1.2782220	-2.5775370
H	1.3913150	-0.4207310	-2.1400240
O	1.3889530	0.9211380	-0.5502030
H	2.3407530	0.8758040	-0.3653780
C	4.6920700	0.9570700	-0.3287980
C	4.4169310	0.4815500	0.9561250
C	4.0607880	-0.8545550	1.1430680
C	3.9788620	-1.7139390	0.0476110
C	4.2514020	-1.2400960	-1.2355420
C	4.6091570	0.0950350	-1.4246850
H	4.9881070	1.9922710	-0.4731120
H	4.4985200	1.1478450	1.8101120
H	3.8639960	-1.2278320	2.1440240
H	3.7202300	-2.7588240	0.1958740

H	4.2013200	-1.9135540	-2.0862750
H	4.8378090	0.4610580	-2.4214320

Ct (5+2)

C	4.3693270	-0.9629630	-2.0589360
H	4.6935840	-0.2155460	-2.7811870
H	4.8959940	-1.9014840	-2.2264390
H	3.2868070	-1.1036750	-2.0937110
O	4.7565770	-0.4844990	-0.7436650
H	4.3703440	-1.1213440	0.0032880
H	4.3785910	0.4812370	-0.5855840
C	0.0623710	-1.7180460	-0.3368720
H	-0.5055600	-1.6672750	0.5992360
H	-0.4544300	-1.1307160	-1.1030940
H	0.1319530	-2.7576510	-0.6629180
O	1.3920890	-1.2374390	-0.1582300
H	1.3490860	-0.2849310	0.0753470
C	4.5204840	2.8723480	0.1083800
H	4.5896520	2.7578080	1.1948850
H	5.5211220	2.8506810	-0.3244290
H	4.0433600	3.8239990	-0.1390170
O	3.7819600	1.7953020	-0.4750730
H	2.8573140	1.7732250	-0.1267670
C	4.0814640	-3.2485770	1.2843100
H	5.1357420	-3.2050830	1.5591140
H	3.5048670	-3.6239810	2.1333370
H	3.9521620	-3.9117360	0.4226410
O	3.6702940	-1.9149040	0.9734290
H	2.7232430	-1.8775640	0.6872980
C	1.0328690	1.5708880	1.8948600
H	1.8986950	1.1889310	2.4392510
H	0.8781670	2.6235220	2.1526150
H	0.1476430	0.9865130	2.1667820
O	1.3076530	1.4299740	0.4983110
H	0.4869890	1.6637330	-0.0151660

C	-1.7164720	2.7215450	-1.2811530
H	-1.0319510	3.2322020	-1.9606470
H	-2.5832850	2.3691720	-1.8505980
H	-2.0507210	3.4281070	-0.5119480
O	-1.0138050	1.6257620	-0.7114130
H	-1.5869850	1.1591890	-0.0613840
C	-3.0001910	1.2844420	2.1942590
H	-2.2881250	2.0476570	2.5152680
H	-3.8314540	1.7634410	1.6651820
H	-3.3808510	0.7590250	3.0759890
O	-2.2911360	0.3927930	1.3374140
H	-2.8944570	-0.3108120	1.0497180
C	-3.4652190	-1.7336150	-1.0869000
C	-3.7572580	-0.5242320	-1.7174240
C	-4.7505240	0.3081940	-1.2014090
C	-5.4477880	-0.0642260	-0.0522350
C	-5.1496440	-1.2694290	0.5853420
C	-4.1584810	-2.1063430	0.0663430
H	-2.7091970	-2.3944270	-1.5014510
H	-3.2194720	-0.2378170	-2.6167300
H	-4.9938290	1.2406850	-1.7029040
H	-6.2306180	0.5778670	0.3409920
H	-5.6992470	-1.5653050	1.4742210
H	-3.9398150	-3.0534700	0.5512400

bC_vdW

O	1.0667980	-1.4626250	-1.0424650
O	-1.1285500	0.2193890	2.2841790
O	-0.2763270	-1.9055280	1.2874450
O	3.3458760	1.3349610	0.1596220
O	1.0059190	1.2539000	-1.3487460
O	-0.2628950	2.1214550	0.9054170
O	3.3771800	-1.3820670	0.1931320
H	3.5260550	-0.4119230	0.2590640
H	1.0057410	0.2684840	-1.3340250

H	0.1295510	-1.7716500	0.3990290
H	1.9923700	-1.5541240	-0.6791180
H	2.6583440	1.5231310	-0.5055450
H	0.1303180	1.8237440	0.0520620
H	-0.8020260	-0.6758100	1.8460050
H	-0.7923320	1.0189910	1.6995930
C	4.6057830	-2.0496200	-0.0785010
H	5.3143100	-1.9009040	0.7425410
H	4.3857330	-3.1151690	-0.1640490
H	5.0519790	-1.6983840	-1.0159920
C	4.3813390	2.3103900	0.1002920
H	3.9874920	3.3118620	0.3080220
H	5.1086950	2.0528250	0.8714890
H	4.8786300	2.3086630	-0.8761660
C	0.6485680	1.7140150	-2.6557940
H	0.5928740	2.8024420	-2.6116560
H	1.4081250	1.4218780	-3.3874660
H	-0.3262460	1.3149710	-2.9553070
C	0.6581010	2.9903460	1.5780740
H	0.2153350	3.2443390	2.5419200
H	1.6216210	2.4938290	1.7279550
H	0.7904970	3.9063160	0.9956230
C	-2.5615100	0.2536580	2.5199310
H	-3.0934610	0.3671390	1.5756020
H	-2.8256050	-0.6839160	3.0062800
H	-2.7524890	1.0930410	3.1868200
C	0.6409700	-2.6347610	2.1164870
H	0.6936640	-3.6727970	1.7776430
H	1.6351790	-2.1793150	2.0894420
H	0.2467690	-2.6107670	3.1331620
C	0.8661650	-2.3573350	-2.1413680
H	-0.1504250	-2.2020270	-2.5079320
H	1.5773750	-2.1457030	-2.9456810
H	0.9769270	-3.3963480	-1.8165500
C	-2.9528390	-1.3419580	-0.7142070
C	-4.3267520	-1.2200480	-0.5099130

C	-4.9355560	0.0322560	-0.5953690
C	-4.1722890	1.1640210	-0.8828410
C	-2.7980630	1.0429350	-1.0874100
C	-2.1916750	-0.2098280	-1.0033810
H	-2.4771500	-2.3159430	-0.6419320
H	-4.9235330	-2.1002170	-0.2896880
H	-6.0067040	0.1256800	-0.4427850
H	-4.6483010	2.1376250	-0.9519510
H	-2.2044130	1.9264140	-1.3055460
H	-1.1223580	-0.3066860	-1.1655130

3. Table S1. Observed and calculated OH frequencies and some geometric factors of $H^+(MeOH)_n$-Bz (n = 2- 7). All the computations were performed at the ωB97X-D/6-31+G(d)level. The calculated frequencies were scaled by a scaling factor of 0.951. The shortest OH---C distance is distance between the π-bonded hydrogen atom and the nearest neighbor carbon atom of the benzene moiety. The isomer types highlighted in red are those observed in the present study.

size	Free OH frequency (cm^{-1})		π-hydrogen bonded OH frequency (cm^{-1})		Isomer type	O-H (free) bond length (Å)	O-H (π-hydrogen-bonded) bond length (Å)	Minimum OH---C distance (Å)
	Obs.	Calc.	Obs.	Calc.				
n = 2	3660	3624	3180	3250	**L**	0.9687	0.9902	2.1327
n = 3	3670	3670	3410	3486	**L**	0.9653	0.9765	2.2692
n = 4	3675	3676	3500	3514	**L**	0.9646	0.9745	2.3454
n = 5	3675	3676	3535	3565	**L**	0.9646	0.9714	2.3809
			3505	3521	**C**		0.9743	2.2898
n = 6	N.A.	3677	N.A.	3575	**L**	0.9644	0.9709	2.3948
			3520	3539	**C**		0.9731	2.3176
			3555	3578	**Ct**(5+1)		0.9707	2.4150
n = 7	N.A.	3677	N.A.	3581	**L**	0.9643	0.9707	2.4049
			3565	3563	**C**		0.9715	2.3846
				3575	**Ct**(6+1)		0.9706	2.3530
				3582	**Ct**(5+2)		0.9705	2.4060

4. Gibbs free energies of the energy-optimized structures of $H^+(MeOH)_n$-Bz (*n* = 5-7).

All the computations were performed at the ωB97X-D/6-31+G(d)level. Free energies are in kJ/mol with zero point energy corrections. Calculated temperature was set to 298.15 K.

***n* = 5**

L	0
C	6.09
C_vdW	24.28

***n* = 6**

L	0
C	7.15
Ct (5+1)	17.17
C_vdW	20.54
Ct (5+1)_vdW	18.99

***n* = 7**

L	2.13
C	2.56
Ct (6+1)	0
Ct (5+2)	7.68
bC_vdW	8.68