Electronic Supplementary MAterial for PCCP

Supporting Information

The Structure of Protonated Acetone and its Dimer: Infrared Photodissociation Spectroscopy from 800 to 4000 cm^{-1}

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Note: All computations were done at the MP2(fc) 6-311++G(d,p) level with GAMESS. Tabulated frequencies are scaled by a factor of 0.96 and have units cm^{-1}(km/mol). All X,Y,Z geometrical parameters are given for the optimized geometries in Angstroms. Images were generated and normal modes were visualized with ChemCraft (v1.5).

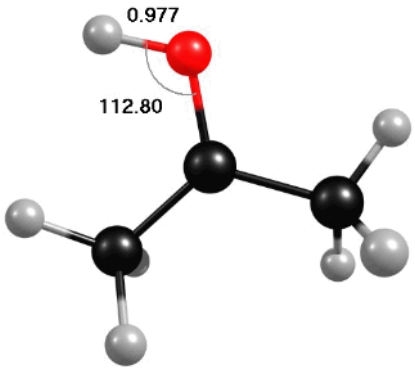

Figure S1. The structure of the $H^+(C_3H_6O)$ cation, calculated at the MP2(fc) 6-311++G(d,p) level of theory using GAMESS.

ATOM	CHARGE	X	Y	Z
C	6.0	-0.0015142729	-0.0104907179	-0.0003436820
C	6.0	-1.3051263617	0.6821212779	-0.0041823311
H	1.0	-1.4625268351	1.0638833079	1.0150967057
H	1.0	-1.2595559176	1.5525419268	-0.6635417697
H	1.0	-2.1369612452	0.0301877777	-0.2769739137
O	8.0	0.0822761404	-1.2824361607	0.0022789671
C	6.0	1.2769195010	0.7173880151	0.0069532965
H	1.0	1.4432180348	1.0671307587	-1.0230831661
H	1.0	1.2003859100	1.6080695693	0.6348574330
H	1.0	2.1039469614	0.0747495757	0.3057566847
H	1.0	-0.7905020038	-1.7194148989	-0.0357402298

The normal mode frequencies (scaled) and intensities of the $H^+(C_3H_6O)$ cation, calculated at the MP2(fc) 6-311++G(d,p) level of theory using GAMESS, are:

108.7(1.6), 138.1(0.7), 376.8(0), 459.1(2.9), 491.5(15.1), 705.5(86.2), 812.9(10.8), 908.6(23.1), 921.9(20.5), 1048.8(0.6), 1060.7(25.6), 1131.3(103.8), 1322.9(22.3), 1339.5(62.2), 1378.6(68.4), 1395.8(47.4), 1410.4(44.7), 1427.2(50), 1453.7(94.1), 1570.9(123.3), 2931.4(49.3), 2938.1(23.1), 3022(4.4), 3027.7(16.1), 3071.8(4.4), 3094.2(7.1), 3545.6(216.2)

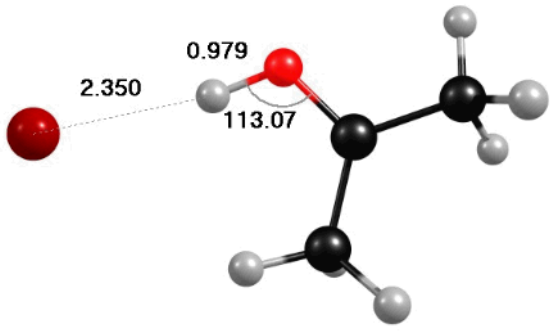

Figure S2. The structure of the $H^+(C_3H_6O)Ar$ cation, calculated at the MP2(fc) 6-311++G(d,p) level of theory using GAMESS.

ATOM	CHARGE	X	Y	Z
C	6.0	1.6592514224	0.0038545496	0.0060712505
C	6.0	1.3494319436	1.4482355609	0.0010920539
H	1.0	1.5502089399	1.8170071511	1.0174104565
H	1.0	2.0371060137	1.9725901587	-0.6669662764
H	1.0	0.3121642787	1.6618749329	-0.2606747205
O	8.0	0.7413739337	-0.8776005247	0.0366857305
C	6.0	3.0407522467	-0.5028969752	-0.0154016764
H	1.0	3.3976775099	-0.3990305570	-1.0509568834
H	1.0	3.6828418906	0.1274841703	0.6044448835
H	1.0	3.0888138320	-1.5504368080	0.2787122181
H	1.0	-0.1596060614	-0.4941675776	0.0176031872
Ar	18.0	-2.4507064988	0.0272860241	-0.0192393240

The counterpoise corrected binding energy of Ar to protonated acetone is 475 cm^{-1}.

The normal mode frequencies (scaled) and intensities of the $H^+(C_3H_6O)Ar$ cation, calculated at the MP2(fc) 6-311++G(d,p) level of theory using GAMESS, are:

42.6(4.3), 43(0.8), 71.2(10.9), 108.4(1.3), 138(0.6), 376.4(0.2), 459.5(1.4), 495.8(9.7), 739.2(52.1), 816.6(11.8), 917(6.3), 931.6(40.8), 1049.4(0.7), 1062.3(23.4), 1142.1(115.7), 1323.8(28.4), 1340.8(59.5), 1381(65), 1397.2(46.1), 1411(38.1), 1427.1(46.1), 1453.1(82.3), 1577.6(134.3), 2932.8(46.5), 2939.5(22.6), 3023.5(0.8), 3027.8(17.7), 3076.9(4.3), 3093.9(6.6), 3486.9(563.6)

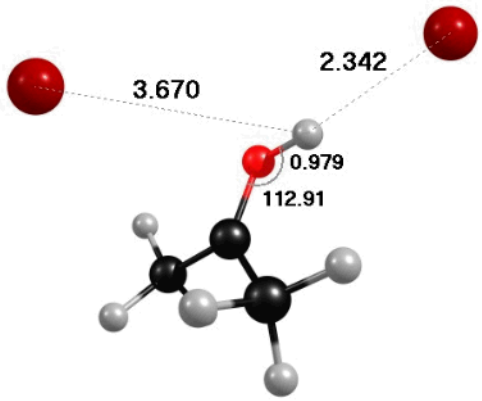

Figure S3. The structure of the $H^+(C_3H_6O)Ar_2$ cation, calculated at the MP2(fc) 6-311++G(d,p) level of theory using GAMESS.

ATOM	CHARGE	X	Y	Z
C	6.0	1.8289428995	0.1353692874	-0.0433878454
C	6.0	1.6045040418	0.5341420298	-1.4474832465
H	1.0	1.3424345180	1.6009211299	-1.4403995069
H	1.0	2.5409937832	0.4433733875	-2.0049952509
H	1.0	0.8085665957	-0.0331007513	-1.9316971035
O	8.0	1.0053490804	-0.6030465829	0.5853601226
C	6.0	3.0225279184	0.5556657160	0.7083355056
H	1.0	3.8434634954	-0.1026925395	0.3863789589
H	1.0	3.3041708755	1.5747606359	0.4345972147
H	1.0	2.8779586123	0.4453481786	1.7822913197
H	1.0	0.2439966768	-0.8792340853	0.0351177951
Ar	18.0	-0.1313977589	2.5452553823	1.3011442631
Ar	18.0	-1.6758169093	-1.7806900179	-0.9585590852

The normal mode frequencies (scaled) and intensities of the $H^+(C_3H_6O)Ar_2$ cation, calculated at the MP2(fc) 6-311++G(d,p) level of theory using GAMESS, are:

14.4(2), 44(3.7), 47.3(1.1), 52.7(5.9), 66.3(3), 74.9(9.9), 100.8(1.8), 141.6(0.8), 377.6(0.2), 455.7(0.7), 496.1(9), 744(54.6), 817.5(12.5), 913.4(9), 935.2(42.9), 1049.8(0.5), 1060(26.5), 1145.8(110), 1323.1(16.6), 1340.6(69.9), 1381.8(77.9), 1399.7(37.1), 1412.1(37.2), 1425.3(41.1), 1454.2(82.6), 1580.1(127.2), 2933.3(41.7), 2943.8(22.8), 3023.8(4.1), 3029.6(14.1), 3075.4(4.1), 3094.1(6), 3489.1(556.6)

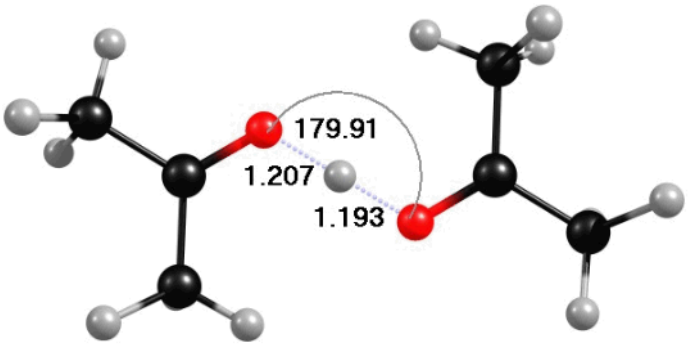

Figure S4. The structure of the $H^+(C_3H_6O)_2$ cation, calculated at the MP2(fc) 6-311++G(d,p) level of theory using GAMESS.

ATOM	CHARGE	X	Y	Z
C	6.0	2.1082100918	-0.0002961147	0.0268605050
C	6.0	2.1616560519	-1.4921424664	0.0403592624
H	1.0	2.4706975476	-1.8193570257	-0.9601214082
H	1.0	2.9343411408	-1.8273809640	0.7362809639
H	1.0	1.2015581788	-1.9452940438	0.2854461774
O	8.0	1.0281869286	0.6272854515	0.0016754663
C	6.0	3.3784147015	0.7736795209	0.0386607543
H	1.0	3.7983822191	0.7111752836	1.0502925145
H	1.0	4.1053584189	0.3164245473	-0.6373269613
H	1.0	3.2033885989	1.8174212781	-0.2176836409
H	1.0	0.0077437321	0.0086654137	0.0222477738
O	8.0	-1.0234899486	-0.6181942153	0.0418241595
C	6.0	-2.1077805235	0.0009668957	0.0288525569
C	6.0	-3.3739874900	-0.7803764548	0.0155517889
H	1.0	-3.8029458244	-0.7054874298	-0.9912865132
H	1.0	-4.0979021659	-0.3375392608	0.7042479427
H	1.0	-3.1907868492	-1.8266421897	0.2549848397
H	1.0	-2.9524753494	1.8306157767	-0.6547261822
C	6.0	-2.1722338536	1.4930302061	0.0315715246
H	1.0	-2.4746228662	1.8081891552	1.0379489494
H	1.0	-1.2172823308	1.9553364536	-0.2168292411

The normal mode frequencies (scaled) and ithe $H^+(C_3H_6O)_2$ cation, calculated at the MP2(fc) 6-311++G(d,p) levntensities of el of theory using GAMESS, are:

22.7(14.9), 24.9(80.2), 53.6(3.6), 99.1(0), 112.5(3.1), 121(0), 124.5(0.6), 142.2(0.3), 157(0), 305.1(128.6), 332.5(1183), 404.3(5.7), 451.2(1104.6), 468.7(202.6), 470.6(12.3), 626.2(3420), 680.9(148.3), 813.6(4.6), 836.5(1032.4), 857.3(264), 868(6.1), 912.6(19), 913.7(32.1), 1064.7(171.1), 1066.3(73.3), 1076.6(1), 1076.8(51.2), 1249.3(166.5), 1269.5(0), 1301.1(70.6), 1352.5(107.2), 1353(0.9), 1364.6(136.7), 1371.2(0), 1405.1(73.3), 1406.7(1.1), 1414.5(14.4),

1414.9(1), 1429.3(13.4), 1430.4(0), 1442.6(0), 1444.6(53.6), 1617.7(176.3), 1652.9(4.4), 1662.5(171.3), 2950(10.1), 2950.3(9.8), 2954.7(2.4), 2954.9(6.2), 3031.2(0.3), 3031.6(0.2), 3036.2(3.8), 3036.3(2.1), 3083.3(1.2), 3084.2(1), 3090.3(1.2), 3090.8(1.2)

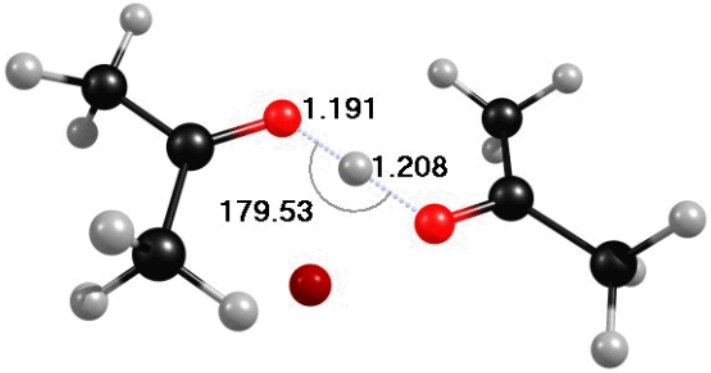

Figure S5. The structure (top view) of the $H^+(C_3H_6O)_2Ar$ cation, calculated at the MP2(fc) 6-311++G(d,p) level of theory using GAMESS.

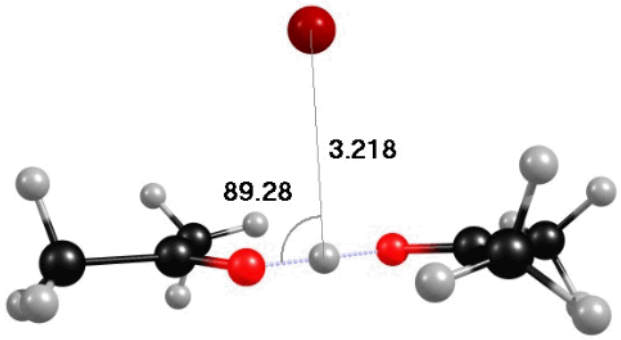

Figure S6. The structure (side view) of the $H^+(C_3H_6O)_2Ar$ cation, calculated at the MP2(fc) 6-311++G(d,p) level of theory using GAMESS.

ATOM	CHARGE	X	Y	Z
C	6.0	-2.0610153112	-0.8511959790	0.0075804794
C	6.0	-2.1114694666	-0.7968230237	-1.4830512870
H	1.0	-2.4534192444	-1.7771553567	-1.8372665920
H	1.0	-2.8602316539	-0.0662502712	-1.7993427007
H	1.0	-1.1432067077	-0.5712210737	-1.9288212416
O	8.0	-0.9830105507	-0.9109042085	0.6354192379
C	6.0	-3.3314467709	-0.8322873738	0.7807377938
H	1.0	-3.7200108126	0.1935601352	0.7563379588
H	1.0	-4.0778306729	-1.4692171336	0.2999100632
H	1.0	-3.1644521771	-1.1312133344	1.8145041176
H	1.0	0.0332236916	-0.8804475861	0.0144084087

O	8.0	1.0626213867	-0.8397886280	-0.6164304583
C	6.0	2.1414052239	-0.7395035190	0.0032514931
C	6.0	3.4103788792	-0.7282337027	-0.7737794077
H	1.0	3.8938957921	-1.7035471660	-0.6379920727
H	1.0	4.0930231714	0.0257385167	-0.3741676858
H	1.0	3.2183652308	-0.5644509408	-1.8330701148
H	1.0	2.9987206767	-1.2678653503	1.8757220635
C	6.0	2.1973638908	-0.6316878578	1.4914835681
H	1.0	2.4661292422	0.4024965601	1.7393872204
H	1.0	1.2496286872	-0.8822711651	1.9673627451
Ar	18.0	-0.1308560579	2.3327418680	-0.0194295654

The counterpoise corrected binding energy of Ar to the protonated acetone dimer is 175 cm^{-1}.

The normal mode frequencies (scaled) and intensities of the $H^+(C_3H_6O)_2Ar$ cation, calculated at the MP2(fc) 6-311++G(d,p) level of theory using GAMESS, are:

18.1(3.9), 24.9(5.4), 28.7(7.7), 34.8(62.4), 43(2), 65.4(0.5), 99.9(0.2), 112(3.1), 118.6(0.1), 124.2(0.5), 144.6(0.4), 156.4(2), 305(122.4), 337.2(987.4), 404(6.2), 453.6(723.9), 465.9(10.7), 466.3(479), 631.3(3304.6), 684(238.9), 814(3.9), 837.5(934), 856.5(393.4), 867.5(18.2), 911.9(19.1), 914.1(42.7), 1065.3(133.2), 1066.7(115.8), 1073.2(51.7), 1074.1(3.7), 1249.4(169.4), 1255.1(66.2), 1271.9(12.3), 1352.1(95.1), 1352.9(20), 1364.5(135.7), 1371.3(0.5), 1405(70), 1406.5(2.3), 1414.2(12.5), 1414.9(2.7), 1429.7(11.3), 1430.9(0.4), 1442(1.9), 1444(52.1), 1619.7(165.1), 1654.9(5.5), 1664.3(156.9), 2949.5(10.1), 2950.2(9.1), 2954.2(3.2), 2954.9(5.1), 3031.1(0.3), 3031.1(0.3), 3035.7(3.2), 3035.9(2.1), 3082.4(1.3), 3084(1.1), 3090(0.9), 3090.5(1.2)

Table S1. Detailed assignments of the proton bound acetone dimer spectrum. There is no change in the interpretation of the normal modes upon addition of Ar to the dimer complex. Calculated frequencies are scaled by 0.96, and were determined at the MP2 / 6-311++g(2d,2p) level of theory. Notation: ip (in plane), oop (out of plane), iph (in phase), ooph (out of phase), str (stretch), bn (bend). $\nu_{sp}(//,\perp)$ corresponds to the shared proton motion either parallel or perpendicular to the OH^+O axis. The plane of the dimer is defined as the COH^+OC plane.

$H^+(C_3H_6O)_2$ MP2	$H^+(C_3H_6O)_2Ar$ MP2	$H^+(C_3H_6O)_2Ar$ IRPD	Assignment
3090.8(1.2)	3090.5(1.2)		Methyl str
3090.3(1.2)	3090.0(0.9)		
3084.2(1)	3084.0(1.1)	3086	
3083.3(1.2)	3082.4(1.3)		
3036.3(2.1)	3035.9(2.1)	3025	
3036.2(3.8)	3035.7(3.2)		
3031.6(0.2)	3031.1(0.3)		
3031.2(0.3)	3031.1(0.3)		
2954.9(6.2)	2954.9(5.1)		
2954.7(2.4)	2954.2(3.2)		
2950.3(9.8)	2950.2(9.1)		
2950.0(10.1)	2949.5(10.1)	2930	
1662.5(171.3)	1664.3(156.9)		ooph CO str, COH bn [CO contracted as COH angle opens] some $\nu_{sp}(\perp)$ip

1652.9(4.4)	1654.9(5.5)		Same as 1662.5 but no proton motion
1617.7(176.3)	1619.7(165.1)	1625	ooph CO str, COH bn [CO extended as COH angle opens] some $\nu_{sp}(\perp)$ip
1444.6(53.6)	1444.0(52.1)	1478	Sym/Asym/iph/ooph methyl bending
1442.6(0)	1442.0(1.9)		
1430.4(0)	1430.9(0.4)		
1429.3(13.4)	1429.7(11.3)		
1414.9(1)	1414.9(2.7)		
1414.5(14.4)	1414.2(12.5)		
1406.7(1.1)	1406.5(2.3)		
1405.1(73.3)	1405.0(70)	1415	
1371.2(0)	1371.3(0.5)		Double (on both acetones) ooph methyl umbrella
1364.6(136.7)	1364.5(135.7)	1380	Single ooph methyl umbrella with a small amount of $\nu_{sp}(\perp)$ip
1353(0.9)	1352.9(20)		Double iph methyl umbrella with a small amount of $\nu_{sp}(\perp)$ip
1352.5(107.2)	1352.1(95.1)	1367	Double ooph methyl umbrella with a small amount of $\nu_{sp}(\perp)$ip
1301.1(70.6)	1255.1(66.2)		$\nu_{sp}(\perp)$oop with some methyl bending
1269.5(0)	1271.9(12.3)		Ooph CCC asymmetric str
1249.3(166.5)	1249.4(169.4)	1260	Iph CCC asymmetric str with $\nu_{sp}(\perp)$ip
1076.8(51.2)	1073.2(51.7)		Ooph/op CCC wag, methyl bn/twist
1076.6(1)	1074.1(3.7)		Ooph/op CCC wag, methyl bn/twist
1066.3(73.3)	1066.7(115.8)	1097	Methyl bending, iph on one acetone and ooph on the other; small amount of $\nu_{sp}(//)$
1064.7(171.1)	1065.3(133.2)	1058	Methyl bending, iph on one acetone and ooph on the other; small amount of $\nu_{sp}(//)$
913.7(32.1)	914.1(42.7)	1000	Methyl bending, iph on one acetone and ooph on the other; small amount of $\nu_{sp}(//)$
912.6(19)	911.9(19.1)	984	Methyl bending, iph on one acetone and ooph on the other; small amount of $\nu_{sp}(//)$
868.0(6.1)	867.5(18.2)	953	iph methyl rock (closest to proton), iph symmetric CCC str.
857.3(264) 836.5(1032.4)	856.5(393.4) 837.5(934)	930 900	$\nu_{sp}(\perp)$oop, ooph methyl rocking $\nu_{sp}(//)$, ooph methyl rock (closest to proton), ooph symmetric CCC str.
813.6(4.6)	814.0(3.9)		iph methyl rock (furthest from proton), iph symmetric CCC str.
680.9(148.3)	684.0(238.9)		CO bends, symmetric OH^+O str, asymmetric CCC str.
626.2(3420)	631.3(3304.6)	1180 (overtone)	$\nu_{sp}(//)$, ooph methyl rock (furthest from proton), ooph symmetric CCC str.
451.2(1104.6)	453.6(723.9)		$\nu_{sp}(//)$, ooph CCC ip bend, angle closes as proton approaches oxygen.
332.5(1183)	337.2(987.4)		$\nu_{sp}(//)$, ooph CCC ip bend angle opens as proton approaches oxygen.

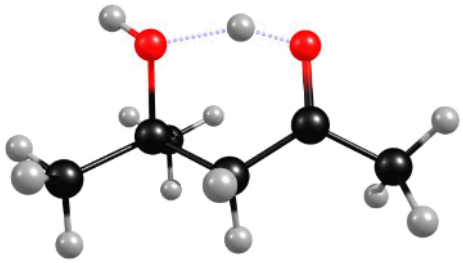

Figure S7. The structure of the $H^+(C_6H_{12}O_2)$ protonated diacetone alcohol cation, calculated at the MP2(fc) 6-31++G(d,p) level of theory using GAMESS.

ATOM	CHARGE	X	Y	Z
C	0.0	0.000820	-0.041755	0.022079
H	1.0	-0.086894	-0.111050	1.105027
H	1.0	1.055282	-0.061720	-0.253917
H	1.0	-0.477594	-0.912586	-0.426751
C	6.0	-0.649472	1.230576	-0.485928
C	6.0	-0.014357	2.468710	0.168854
H	1.0	1.009666	2.604542	-0.180070
H	1.0	0.037824	2.319231	1.256085
C	6.0	-0.779512	3.742362	-0.018567
C	6.0	-0.111654	5.056919	-0.063435
H	1.0	0.444034	5.119232	-1.003801
H	1.0	-0.833651	5.865585	-0.004300
H	1.0	0.621659	5.122799	0.741398
C	6.0	-0.637556	1.319639	-2.005400
H	1.0	-1.135827	2.219776	-2.367632
H	1.0	0.389354	1.318165	-2.370672
H	1.0	-1.141615	0.454067	-2.436127
O	8.0	-2.039907	1.286136	0.004619
H	1.0	-2.585653	0.603362	-0.420872
O	8.0	-2.043534	3.702710	-0.117682
H	1.0	-2.326881	2.681551	-0.085292

The normal mode frequencies (scaled) and intensities of the $H^+(C_6H_{12}O_2)$ protonated diacetone alcohol cation, calculated at the MP2(fc) 6-31++G(d,p) level of theory using GAMESS, are:

91.3(0.4), 109.7(2.1), 135.1(0.2), 220.8(11.5), 229.3(0.2), 275.8(1.7), 309.3(10.6), 319.5(4), 377.4(43.9), 394.7(24.9), 420(29.1), 446.4(16.6), 471.7(20.9), 510.7(48.3), 593.2(45.5), 749.6(8.1), 793.8(16), 866(6.5), 889.9(17.4), 930.6(1.3), 949.7(7.3), 981.7(2.3), 983.7(4.7), 1021.7(1.7), 1098(77.7), 1134.9(17.3), 1174.2(13.7), 1177.8(46.1), 1235.9(70.2), 1271.2(13), 1307.6(26.4), 1358.5(29.3), 1378.2(31.3), 1395.8(28.6), 1407.5(15.2), 1416.6(22.8), 1424.3(20.4), 1441.1(20.3), 1457.5(0.7), 1465.5(4.5), 1483(40.1), 1487.2(7.3), 1556.7(592.9), 1610.3(146.3), 2203.7(1399.6), 2968.2(13.7), 2988.7(15.2), 2993.7(4.7), 2999.3(0.7), 3070.7(0.8), 3073.6(4.6), 3087.6(8.7), 3092.1(3.3), 3097(6), 3107.5(3.8), 3139.9(4.3), 3652.6(107.6)

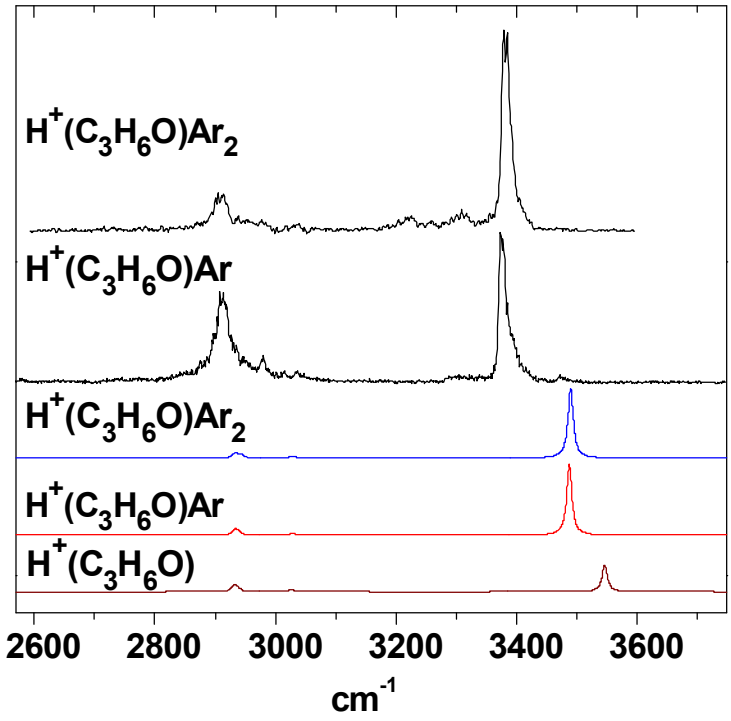

Figure S8. Infrared photodissociation spectra of protonated acetone in the C-H and O-H stretching region with one and two attached argons. The 59 cm^{-1} red shifted OH stretch (ab initio) of $H^+(C_3H_6O)Ar$ shifts 6 cm^{-1} back to the blue upon addition of the second Ar.

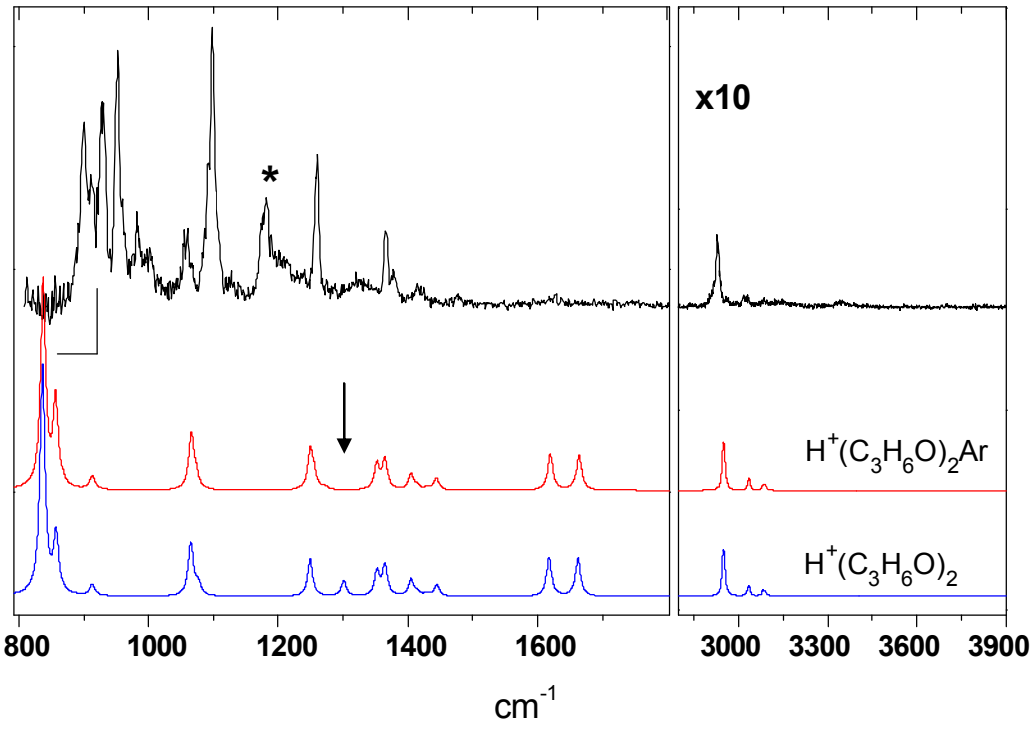

Figure S9. Comparison of the predicted proton bound acetone dimer spectra with (red) and without (blue) argon. The arrow indicates the only qualitative change in the spectrum, corresponding to a 46 cm^{-1} red shift of the out of plane $\nu_{sp}(\perp)$ transition at 1300 cm^{-1} in the bare dimer.