Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

A Microwave Spectroscopic and *ab initio* Study of Keto-enol Tautomerism and Isomerism in the Cyclohexanone-Water Complex

Electronic Supporting Information

Jiao Gao, Nathan A. Seifert, and Wolfgang Jäger*

Department of Chemistry, University of Alberta, Edmonton, AB T6G 2G2, Canada

* Corresponding Author, e-mail: wolfgang.jaeger@ualberta.ca. Fax: 1-780-492-8231.

Table of Contents

Table S1 Cartesian coordinates for the predicted structure of Keto chair in Table 1 at the B3LYP-D3/aVTZ level of theory.

Atom	X	Y	Z
C1	-1.080	0.000	-0.095
O2	-2.215	0.000	0.326
C3	-0.315	-1.279	-0.372
H4	-0.192	-1.358	-1.457
H5	-0.915	-2.124	-0.040
C6	1.075	-1.260	0.287
H7	1.627	-2.155	-0.001
H8	0.954	-1.301	1.373
C9	1.855	0.000	-0.086
H10	2.054	0.000	-1.162
H11	2.826	0.000	0.412
C12	1.075	1.260	0.287
H13	1.627	2.155	-0.001
H14	0.954	1.301	1.373
C15	-0.315	1.279	-0.372
H16	-0.915	2.124	-0.040
H17	-0.192	1.358	-1.457

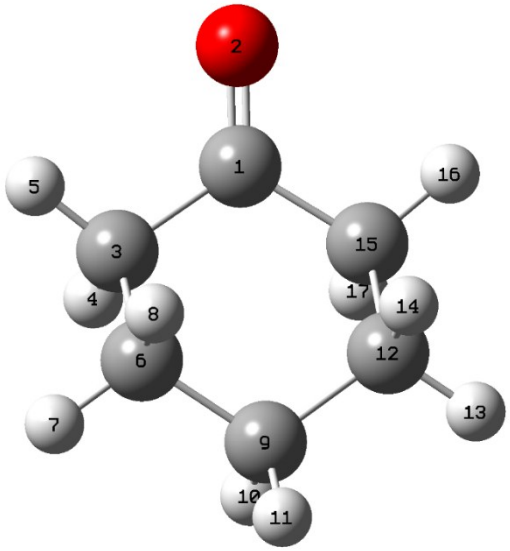

Table S2 Cartesian coordinates for the predicted structure of Keto boat in Table 1 at the B3LYP-D3/aVTZ level of theory.

Atom	X	Y	Z
C1	-1.068	1.230	-0.364
C2	-1.923	0.000	0.000
C3	-1.068	-1.230	0.364
C4	0.282	-1.229	-0.355
C5	1.099	0.000	0.000
C6	0.282	1.229	0.355
H7	-2.577	-0.239	-0.839
H8	-2.577	0.239	0.839
H9	-0.883	-0.243	1.440
H10	-1.611	-2.147	0.140
H11	0.877	-2.114	-0.134
H12	0.131	-1.212	-1.440
H13	0.131	1.212	1.440
H14	0.877	2.114	0.134
H15	-0.883	1.243	-1.440
H16	-1.611	2.147	-0.140
O17	2.309	0.000	0.000

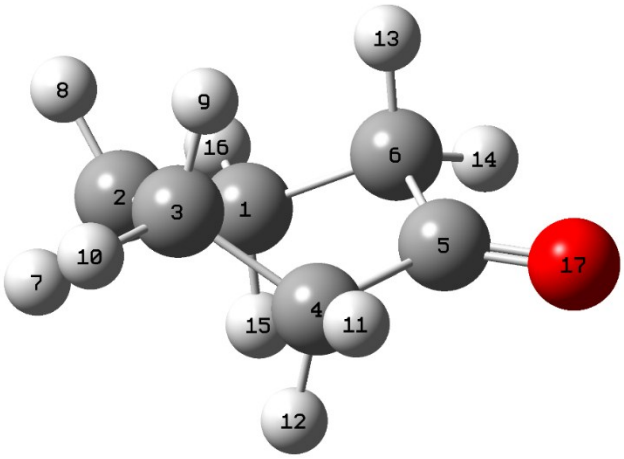

Table S3 Cartesian coordinates for the predicted structure of Keto skew in Table 1 at the B3LYP-D3/aVTZ level of theory.

Atom	X	Y	Z
C1	-1.711	-0.017	-0.524
C2	-1.077	1.330	-0.120
C3	1.070	-0.023	0.047
C4	0.315	-1.344	0.091
C5	-1.187	-1.168	0.335
H6	-0.967	1.961	-1.001
H7	-1.739	1.864	0.563
H8	-1.380	-0.962	1.391
H9	-1.472	-0.236	-1.568
H10	0.783	-1.960	0.864
H11	0.501	-1.850	-0.858
H12	-1.712	-2.095	0.102
H13	-2.798	0.050	-0.464
C14	0.301	1.170	0.564
H15	0.148	0.994	1.634
H16	0.912	2.064	0.463
O17	2.205	0.050	-0.367

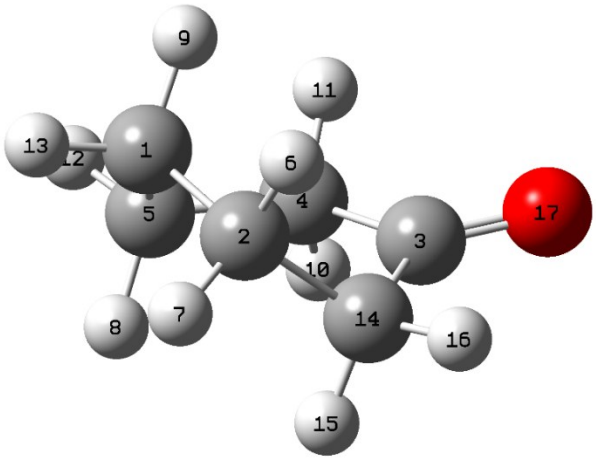

Table S4 Cartesian coordinates for the predicted structure of Enol 1(cis) in Table 1 at the B3LYP-D3/aVTZ level of theory.

Atom	X	Y	Z
C1	-0.965	0.075	-0.006
C2	-0.325	-1.275	-0.077
H3	-0.447	-1.668	-1.092
H4	-0.875	-1.955	0.576
C5	1.154	-1.224	0.305
H6	1.642	-2.157	0.024
H7	1.241	-1.134	1.392
C8	1.844	-0.030	-0.351
H9	1.748	-0.116	-1.437
H10	2.912	-0.032	-0.124
C11	1.211	1.284	0.108
H12	1.551	2.102	-0.531
H13	1.565	1.530	1.116
C14	-0.291	1.220	0.092
H15	-0.838	2.155	0.165
O16	-2.335	-0.012	-0.056
H17	-2.712	0.874	-0.053

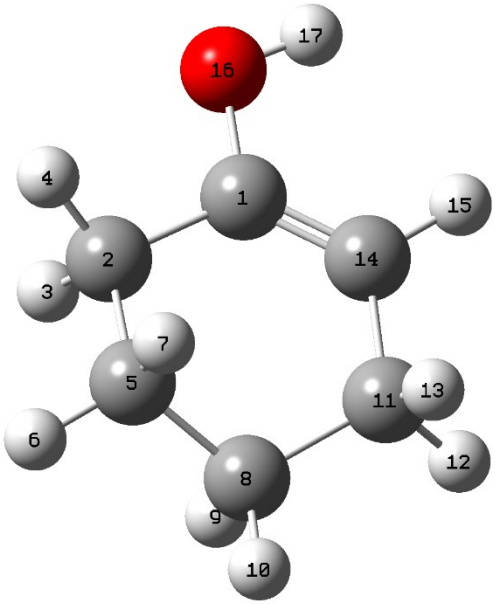

Table S5 Cartesian coordinates for the predicted structure of Enol 2(trans) in Table 1 at the B3LYP-D3/aVTZ level of theory.

Atom	X	Y	Z
C1	0.966	0.077	0.001
C2	0.323	-1.275	0.073
H3	0.447	-1.677	1.085
H4	0.855	-1.960	-0.596
C5	-1.159	-1.226	-0.303
H6	-1.645	-2.160	-0.018
H7	-1.249	-1.138	-1.388
C8	-1.844	-0.031	0.355
H9	-1.743	-0.116	1.441
H10	-2.912	-0.034	0.133
C11	-1.210	1.280	-0.108
H12	-1.547	2.100	0.531
H13	-1.569	1.526	-1.115
C14	0.291	1.219	-0.099
H15	0.849	2.144	-0.168
O16	2.342	0.100	0.064
H17	2.678	-0.799	0.038

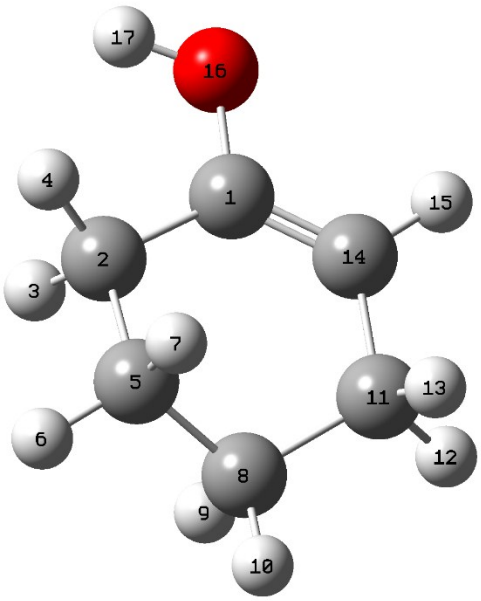

Table S6 Cartesian coordinates for the predicted structure of Keto chair-H_2O in Table 1 at the B3LYP-D3/aVTZ level of theory.

Atom	X	Y	Z
C1	0.258	-0.649	0.240
C2	0.216	0.811	0.625
C3	-0.877	1.559	-0.158
C4	-2.232	0.862	-0.043
C5	-2.145	-0.591	-0.508
C6	-1.070	-1.369	0.270
O7	1.284	-1.215	-0.089
H8	-1.376	-1.446	1.318
H9	-0.933	-2.377	-0.116
H10	-3.107	-1.092	-0.395
H11	-1.901	-0.617	-1.573
H12	-2.570	0.892	0.997
H13	-2.979	1.398	-0.631
H14	-0.938	2.586	0.203
H15	-0.584	1.614	-1.209
H16	1.197	1.256	0.481
H17	-0.022	0.855	1.694
O18	3.487	0.555	-0.234
H19	4.314	0.155	-0.512
H20	2.835	-0.169	-0.213

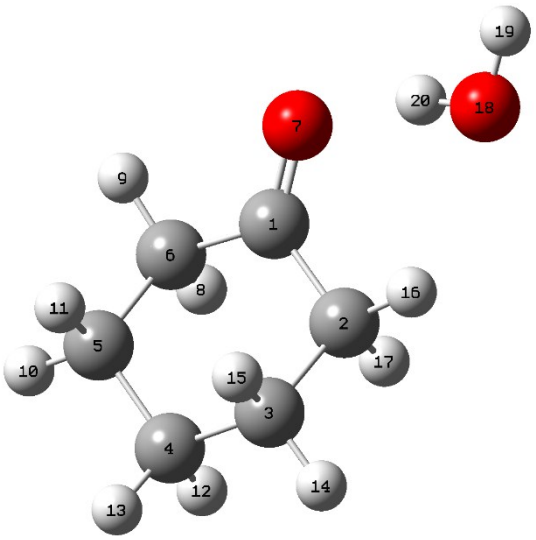

Table S7 Cartesian coordinates for the predicted structure of Keto boat-H_2O in Table 1 at the B3LYP-D3/aVTZ level of theory.

Atom	X	Y	Z
C1	-1.052	1.470	-0.433
C2	-2.348	0.803	0.068
C3	-2.134	-0.665	0.486
C4	-1.000	-1.329	-0.298
C5	0.311	-0.609	-0.079
C6	0.200	0.870	0.209
H7	-3.103	0.859	-0.715
H8	-2.746	1.359	0.918
H9	-1.890	-0.714	1.549
H10	-3.056	-1.232	0.361
H11	-0.868	-2.379	-0.043
H12	-1.211	-1.287	-1.373
H13	0.153	0.974	1.299
H14	1.116	1.366	-0.106
H15	-0.972	1.352	-1.516
H16	-1.083	2.544	-0.249
O17	1.377	-1.192	-0.129
O18	3.541	0.601	0.157
H19	4.400	0.229	-0.062
H20	2.905	-0.129	0.059

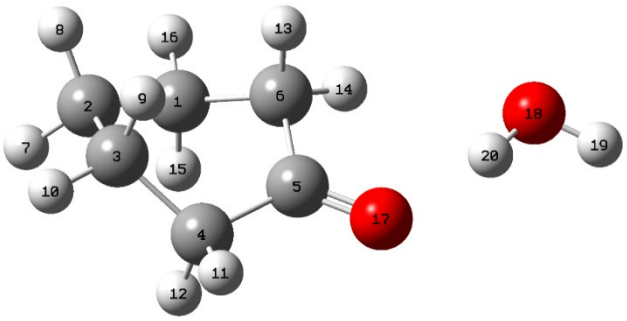

Table S8 Cartesian coordinates for the predicted structure of Keto skew-H_2O I in Table 1 at the B3LYP-D3/aVTZ level of theory.

Atom	X	Y	Z
C1	-1.953	-0.874	-0.664
C2	-2.147	0.648	-0.505
C3	0.267	0.625	0.267
C4	0.260	-0.872	0.494
C5	-1.151	-1.465	0.495
H6	-2.137	1.124	-1.485
H7	-3.124	0.858	-0.068
H8	-1.654	-1.254	1.442
H9	-1.411	-1.080	-1.590
H10	0.785	-1.061	1.434
H11	0.879	-1.323	-0.282
H12	-1.093	-2.550	0.412
H13	-2.921	-1.365	-0.757
C14	-1.069	1.306	0.387
H15	-0.957	2.367	0.178
H16	-1.367	1.204	1.435
O17	1.289	1.236	0.013
O18	3.432	-0.568	-0.358
H19	4.242	-0.166	-0.681
H20	2.804	0.166	-0.236

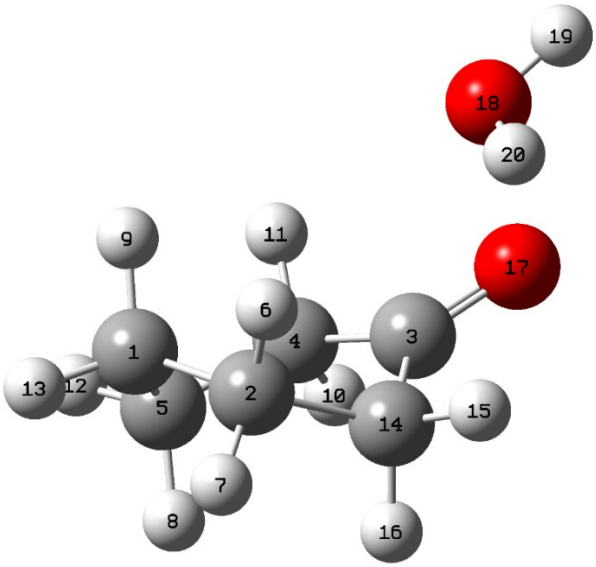

Table S9 Cartesian coordinates for the predicted structure of Keto skew-H_2O II in Table 1 at the B3LYP-D3/aVTZ level of theory.

Atom	X	Y	Z
C1	-2.057	0.831	-0.575
C2	-0.832	1.611	-0.053
C3	0.244	-0.675	0.118
C4	-1.089	-1.391	0.025
C5	-2.285	-0.455	0.218
H6	-0.331	2.109	-0.883
H7	-1.152	2.396	0.631
H8	-2.417	-0.220	1.278
H9	-1.901	0.561	-1.622
H10	-1.077	-2.196	0.764
H11	-1.124	-1.876	-0.952
H12	-3.200	-0.952	-0.103
H13	-2.942	1.465	-0.549
C14	0.191	0.718	0.685
H15	1.184	1.159	0.693
H16	-0.129	0.602	1.726
O17	1.273	-1.215	-0.239
O18	3.474	0.544	-0.101
H19	2.823	-0.174	-0.188
H20	4.315	0.171	-0.378

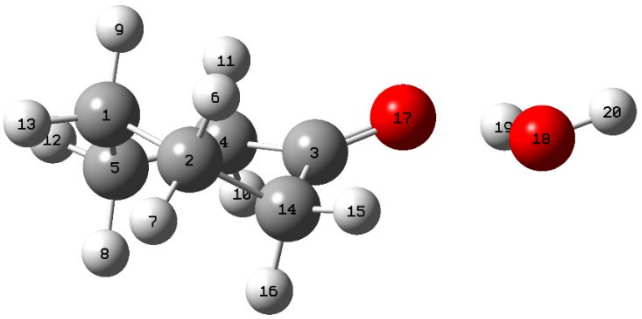

Table S10 Cartesian coordinates for the predicted structure of (cis)Enol I-H_2O I in Table 1 at the B3LYP-D3/aVTZ level of theory.

Atom	X	Y	Z
C1	0.223	0.563	-0.314
C2	0.124	-0.918	-0.487
H3	0.686	-1.404	0.315
H4	0.626	-1.195	-1.417
C5	-1.332	-1.385	-0.495
H6	-1.372	-2.469	-0.378
H7	-1.780	-1.153	-1.465
C8	-2.134	-0.692	0.604
H9	-1.681	-0.919	1.573
H10	-3.155	-1.073	0.632
C11	-2.145	0.823	0.396
H12	-2.518	1.319	1.296
H13	-2.852	1.083	-0.399
C14	-0.777	1.353	0.060
H15	-0.614	2.423	0.137
O16	1.497	1.026	-0.591
H17	1.539	1.974	-0.419
O18	3.537	-0.550	0.741
H19	4.185	-0.858	0.102
H20	2.913	-0.009	0.233

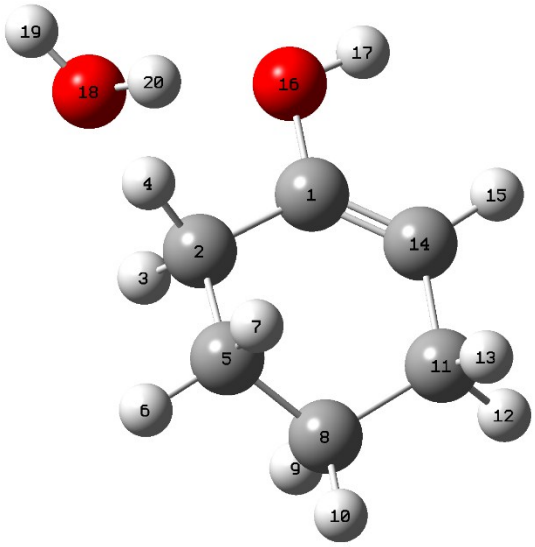

Table S11 Cartesian coordinates for the predicted structure of (cis)Enol I-H_2O II in Table 1 at the B3LYP-D3/aVTZ level of theory.

Atom	X	Y	Z
C1	0.237	-0.463	0.004
C2	-0.936	-1.392	0.083
H3	-0.998	-1.793	1.100
H4	-0.742	-2.248	-0.565
C5	-2.244	-0.699	-0.300
H6	-3.093	-1.324	-0.017
H7	-2.284	-0.583	-1.387
C8	-2.340	0.677	0.351
H9	-2.288	0.561	1.438
H10	-3.301	1.143	0.126
C11	-1.194	1.577	-0.114
H12	-1.141	2.465	0.521
H13	-1.410	1.950	-1.123
C14	0.130	0.862	-0.099
H15	1.031	1.460	-0.176
O16	1.423	-1.142	0.051
H17	2.168	-0.518	0.031
O18	3.765	0.498	-0.002
H19	4.274	0.434	0.811
H20	4.366	0.238	-0.707

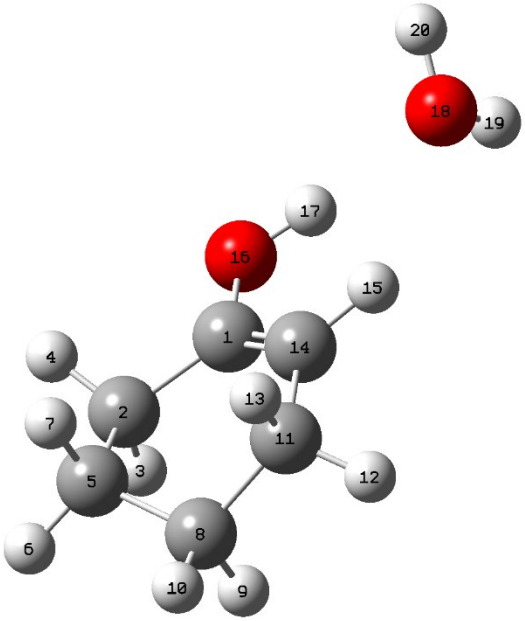

Table S12 Cartesian coordinates for the predicted structure of (trans)Enol II-H_2O I in Table 1 at the B3LYP-D3/aVTZ level of theory.

Atom	X	Y	Z
C1	-0.237	-0.459	-0.044
C2	0.939	-1.386	-0.051
H3	1.051	-1.819	-1.051
H4	0.744	-2.223	0.627
C5	2.226	-0.668	0.365
H6	3.090	-1.290	0.127
H7	2.222	-0.528	1.449
C8	2.331	0.693	-0.316
H9	2.328	0.552	-1.401
H10	3.275	1.175	-0.061
C11	1.156	1.591	0.076
H12	1.115	2.460	-0.584
H13	1.320	1.995	1.082
C14	-0.157	0.863	0.028
H15	-1.072	1.442	0.040
O16	-1.481	-1.065	-0.133
H17	-1.382	-2.020	-0.143
O18	-3.890	0.553	-0.025
H19	-3.121	-0.033	-0.062
H20	-4.151	0.567	0.899

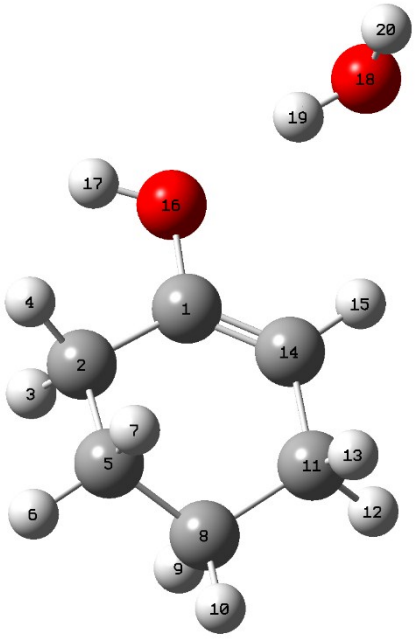

Table S13 Cartesian coordinates for the predicted structure of (cis)Enol II-H_2O II in Table 1 at the B3LYP-D3/aVTZ level of theory.

Atom	X	Y	Z
C1	-0.179	-0.605	0.003
C2	-0.165	0.896	0.065
H3	-0.446	1.212	1.076
H4	-0.940	1.290	-0.597
C5	1.199	1.475	-0.312
H6	1.244	2.530	-0.035
H7	1.321	1.425	-1.397
C8	2.326	0.688	0.353
H9	2.196	0.728	1.438
H10	3.293	1.142	0.130
C11	2.307	-0.771	-0.103
H12	2.961	-1.366	0.538
H13	2.737	-0.844	-1.110
C14	0.920	-1.350	-0.089
H15	0.808	-2.426	-0.149
O16	-1.410	-1.202	0.067
H17	-2.116	-0.538	0.044
O18	-3.715	0.486	-0.014
H19	-4.200	0.446	0.815
H20	-4.309	0.125	-0.680

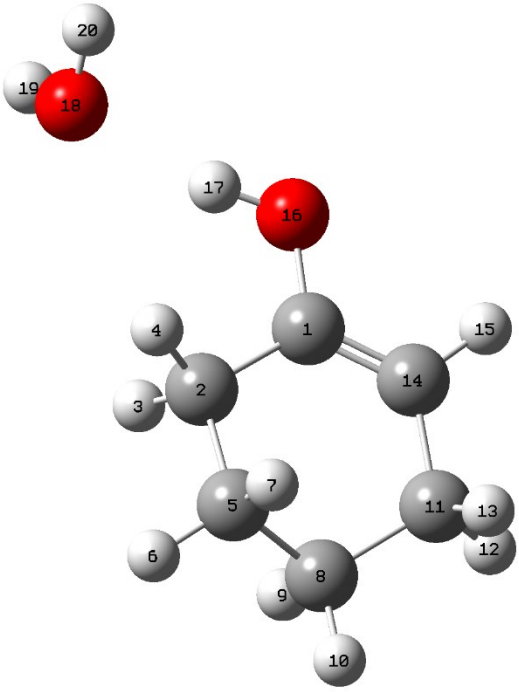

Table S14 Measured and assigned transition frequencies (MHz) of cyclohexanone-water complex and its ^{13}C isotopologues.

J'	Ka'	Kc'	J''	Ka''	Kc''	Parent species	o-c [a]	$^{13}C1$	o-c	$^{13}C2$	o-c	$^{13}C3$	o-c
4	1	4	3	1	3	7653.4669	-0.0014	7648.4162	0.0004	7616.9535	-0.0023	7582.5818	-0.0002
4	0	4	3	0	3	7966.8746	-0.0001	7961.7640	-0.0004	7930.1009	-0.0026	7892.0374	-0.0004
4	2	3	3	2	2	8105.8421	0.0015	8101.9076	0.0004			8026.0685	-0.0004
4	3	1	3	3	0	8151.5101	0.0059						
4	3	2	3	3	1	8147.3348	-0.0092						
4	2	2	3	2	1	8256.6417	0.0012	8253.9858	-0.0011	8229.0496	0.0035	8171.4966	0.0006
4	1	3	3	1	2	8519.7005	0.0002	8516.5409	0.0004	8490.1650	-0.0043	8432.4521	0.0001
5	1	5	4	1	4	9541.9745	-0.0001	9535.4694	0.0008	9495.6188	-0.0002	9454.2051	0.0011
5	0	5	4	0	4	9857.5866	0.0002	9850.4869	-0.0006	9808.9700	-0.0023	9767.2686	-0.0009
5	2	4	4	2	3	10112.7261	0.0023	10107.6361	-0.0012	10071.5926	-0.0098	10013.7249	0.0011
5	3	3	4	3	2	10194.0923	0.0030						
5	3	2	4	3	1	10208.5433	-0.0015						
5	2	3	4	2	2	10401.8661	-0.0011	10399.0891	0.0004	10369.3599	-0.0066	10292.9389	-0.0017
5	1	4	4	1	3	10615.4494	0.0020	10611.1653	0.0003	10577.2781	-0.0002	10507.7230	0.0009
6	1	6	5	1	5	11417.2271	-0.0025	11409.1916	0.0006	11360.7386	0.0046	11312.9647	0.0003
6	0	6	5	0	5	11702.4169	-0.0011	11693.2252	-0.0004	11641.5896	-0.0003	11597.5194	-0.0005
6	2	5	5	2	4	12106.7479	0.0024	12100.3976	0.0009	12056.4676	-0.0048	11988.9800	-0.0002
3	1	2	2	0	2	9028.3536	0.0007	9017.0353	0.0001				
2	2	0	1	1	0	10810.3779	-0.0006						
2	2	1	1	1	1	11012.4566	0.0003						
4	1	3	3	0	3	11521.3266	-0.0007						
6	2	4	5	2	3	12579.4457	-0.0035	12576.5300	-0.0000	12541.9568	0.0020	12446.3464	0.0001
6	1	5	5	1	4	12684.6070	0.0008	12678.9231	-0.0003	12636.7553	0.0056	12557.4922	0.0002
7	1	7	6	1	6	13279.3988	0.0001	13269.7679	-0.0002				
7	0	7	6	0	6	13513.9845	0.0011	13502.8208	-0.0001				

[a] observed - calculated

Table S14 (continued)

J’	Ka’	Kc’	J’’	Ka’’	Kc’’	^{13}C4	o-c [a]	^{13}C5	o-c	^{13}C6	o-c
4	1	4	3	1	3	7574.5005	-0.0001	7617.1697	-0.0011	7644.9030	0.0014
4	0	4	3	0	3	7884.8118	0.0019	7930.9659	-0.0003	7957.1899	0.0000
4	2	3	3	2	2	8020.2680	-0.0022	8076.7644	0.0003	8097.3671	-0.0026
4	3	1	3	3	0						
4	3	2	3	3	1						
4	2	2	3	2	1	8167.2506	0.0016	8235.0237	-0.0001	8249.4938	-0.0015
4	1	3	3	1	2	8428.5224	0.0003	8495.8662	0.0005	8510.9652	-0.0004
5	1	5	4	1	4	9443.8626	-0.0009	9495.4873	0.0032	9531.0759	0.0015
5	0	5	4	0	4	9757.3152	-0.0003	9808.5389	-0.0021	9844.8003	0.0010
5	2	4	4	2	3	10006.2699	0.0008	10075.3792	0.0006	10101.9580	0.0010
5	3	3	4	3	2						
5	3	2	4	3	1						
5	2	3	4	2	2	10288.3390	0.0000	10377.9834	-0.0015	10393.4354	-0.0002
5	1	4	4	1	3	10502.4178	-0.0018	10583.7110	0.0009	10604.1693	0.0005
6	1	6	5	1	5	11300.2564	0.0002	11360.0767	0.0013	11403.9288	0.0042
6	0	6	5	0	5	11584.6077	-0.0001	11639.5866	-0.0027	11686.5223	-0.0071
6	2	5	5	2	4	11979.7365	0.0003	12060.4897	0.0007	12093.5701	0.0012
3	1	2	2	0	2						
2	2	0	1	1	0						
2	2	1	1	1	1						
4	1	3	3	0	3						
6	2	4	5	2	3	12441.4757	-0.0003	12553.2338	-0.0016	12569.6020	-0.0001
6	1	5	5	1	4	12550.4986	0.0007	12643.3443	0.0019	12670.4755	0.0004
7	1	7	6	1	6						
7	0	7	6	0	6						

[a] observed – calculated

Table S15 Measured and assigned transition frequencies (MHz) of cyclohexanone-water complex and its deuterium isotopologues.

J'	Ka'	Kc'	J''	Ka''	Kc''	D_2O	o-c [a]	DOH(D1)	o-c	HOD(D2)	o-c
4	1	4	3	1	3	7296.6310	-0.0002	7402.5886	-0.0012	7538.3193	0.0013
4	0	4	3	0	3	7591.5310	-0.0004	7702.8872	-0.0005	7846.2262	0.0002
4	2	3	3	2	2	7703.4802	-0.0069	7822.5315	0.0014	7975.8315	-0.0025
4	2	2	3	2	1			7952.2881	0.0019	8116.4520	-0.0005
4	1	3	3	1	2	8079.5313	0.0020	8209.4646	0.0012	8377.5305	0.0016
5	1	5	4	1	4	9100.5082	0.0015	9231.6430	0.0005	9399.6161	0.0004
5	0	5	4	0	4	9406.1798	0.0008	9540.2448	-0.0005	9712.8163	-0.0020
5	2	4	4	2	3	9613.6802	0.0019	9761.3717	-0.0015	9951.5784	0.0018
5	2	3	4	2	2	9848.3957	-0.0007	10011.6262	-0.0039	10221.9882	-0.0016
5	1	4	4	1	3	10072.5027	0.0020	10232.8715	0.0014	10440.2929	0.0010
6	1	6	5	1	5	10893.2658	0.0009	11048.9561	-0.0002	11248.3846	0.0012
6	0	6	5	0	5	11179.9637	-0.0017	11335.1898	-0.0008	11535.0647	-0.0027
6	2	5	5	2	4	11513.5416	0.0057	11689.1650	0.0031	11915.3410	0.0027
3	1	2	2	0	2	8704.2522	0.0001	8795.1668	-0.0000	8927.9227	0.0003
2	2	0	1	1	0	10747.3514	-0.0030	10752.7578	-0.0001	10803.2995	-0.0001
2	2	1	1	1	1	10931.4029	0.0028				
6	2	4	5	2	3	11901.9789	-0.0029	12101.8222	-0.0019	12359.3091	-0.0023
6	1	5	5	1	4	12044.8057	-0.0010	12233.9507	0.0012	12478.5632	0.0013
7	1	7	6	1	6	12764.7708	-0.0016				

[a] observed – calculated

Table S16 Spectroscopic parameters of ^{13}C and deuterium isotopologues of cyclohexanone-water.

Rotational constant	^{13}C-C1	^{13}C-C2	^{13}C-C3	^{13}C-C4	^{13}C-C5	^{13}C-C6
A/MHz	3285.9316(25)	3255.551(71)	3283.8142(59)	3280.540(25)	3244.814(11)	3273.634(11)
B/MHz	1123.32189(21)	1120.4620(13)	1111.45482(28)	1111.27360(47)	1121.60512(58)	1122.4991(10)
C/MHz	905.21272(13)	901.0346(11)	897.98257(25)	896.74560(38)	900.77576(32)	904.90316(78)
Δ_K/kHz	17.23(17)	21(18)	24.87234771	18.0(67)	24.87234771	17.4(73)
Δ_{JK}/kHz	-7.7041(16)	-7.63(13)	-7.474(23)	-7.62(4)	-7.467(49)	-7.601(69)
Δ_J/kHz	1.0469(16)	1.038(12)	1.0182(15)	1.0294(42)	1.0483(33)	1.042(7)
δ_J/kHz	0.1704(13)	0.17(1)	0.161(2)	0.1700(35)	0.1715(42)	0.1583(73)
N	18	14	15	15	15	15
σ/kHz	0.57	3.0	0.72	1.0	1.5	2.5

Rotational constant	[a]DOH(D1)	[b]HOD(D2)	D_2O
A/MHz	3287.2880(41)	3298.6954(42)	3289.7280(63)
B/MHz	1080.39298(61)	1103.76562(61)	1062.38808(90)
C/MHz	877.82359(50)	893.01318(50)	865.90822(54)
Δ_K/kHz	25.5(9)	25.61(91)	19.3(13)
Δ_{JK}/kHz	-7.290(45)	-7.089(46)	-6.706(71)
Δ_J/kHz	0.9803(35)	0.970(35)	0.9099(58)
δ_J/kHz	0.1500(45)	0.01564(45)	0.1402(52)
N	17	17	18
σ/kHz	1.6	1.6	2.7

[a] D1 is the free proton of water.

[b] D2 is the proton of water hydrogen bonded to the carbonyl oxygen of cyclohexanone.

Table S17 Cartesian coordinates for the fitted $r_{m\_}^{(1)}$ geometry of the cyclohexanone-water complex.

Atom	X	Y	Z
C1	0.202	0.648	-0.263
C2	0.170	-0.792	-0.667
C3	-0.912	-1.561	0.162
C4	-2.259	-0.860	0.044
C5	-2.174	0.574	0.551
C6	-1.105	1.372	-0.267
O7	1.341	1.237	0.084
H8	-0.952	2.379	0.120
H9	-1.440	1.450	-1.309
H10	1.167	-1.214	-0.540
H11	-0.093	-0.843	-1.731
H12	-1.920	0.565	1.617
H13	-3.140	1.074	0.459
H14	-0.628	-1.621	1.219
H15	-0.979	-2.590	-0.197
H16	-3.000	-1.419	0.621
H17	-2.601	-0.858	-0.998
H18	2.889	0.070	0.298
O19	3.615	-0.577	0.242
H20	4.409	-0.102	0.502

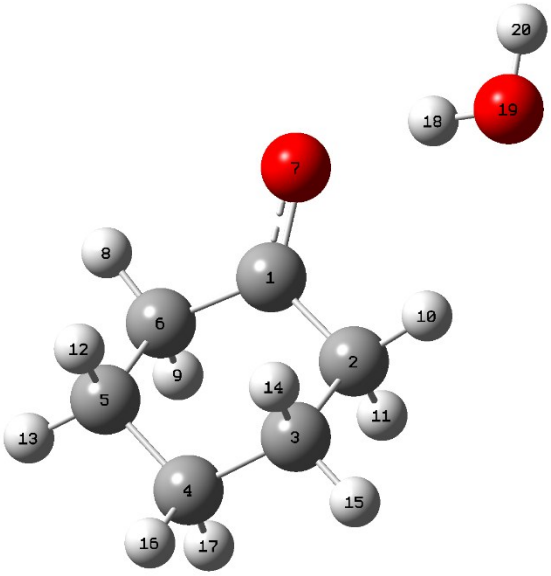

Table S18 BSSE corrected interaction energy analysis for a selection of ketone-water complexes at the MP2/6-311++g(2d,p) level of theory.

Species	Cyclohexanone	Cyclopentanone	Cyclobutanone	Acetone	Formaldehyde
$\Delta E_{binding}$(kcal mol^{-1})	-5.60	-5.35	-4.52	-5.43	-3.75