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Aqueous Microsolvation of 4-hydroxy-2-butanone: Competition between intra- and inter-Molecular hydrogen bonds

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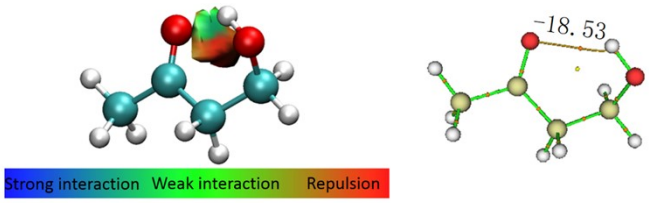
1. **Figure Fig.1** The NCI and QTAIM analyses for conformer I of 4H2B.
2. **Tables S1-S6** The measured transition frequencies v of the six isotopologues of the 4H2B monomer with quantum numbers and difference to calculated frequencies $\triangle v$ in the fit
3. **Table S7** The SE rotational constants of the six isotopologues of the 4H2B monomer.
4. **Table S8** The r_s, r^{SE}, r_e coordinates of the six isotopologues of the 4H2B monomer
5. **Table S9** The r_s, r^{SE} and r_e structural parameters of conformer I of the 4H2B monomer
6. **Table S10** Geometries of conformer I of the 4H2B monomer calculated at B3LYP-(GD3BJ)/6-311++G(d,p).
7. **Tables S11-S15** The measured transition frequencies v of the five isotopologues of the 4H2B-H_2O complex with quantum numbers and difference to calculated frequencies $\triangle v$ in the fit.
8. **Table S16** Geometries of isomer I of the 4H2B-H_2O complex calculated at B3LYP-(GD3BJ)/6-311++G(d,p).

1. The NCI analysis for conformer I of 4H2B. (Fig. 1)



(a) (b)

Fig. 1 (a)The NCI plots for conformer I of 4H2B. Blue and green color signify the strong and weak attractive interaction respectively, while red color indicates repulsive interaction. (b)QTAIM analysis (kJ mol^{-1}). Orange dots show the BCPs and brown lines show the bond paths.

2. The measured transition frequencies *v* of the six isotopologues of the 4H2B monomer with quantum numbers and difference to calculated frequencies △*v* in the fit. (Tables S1-S6)

Table S1 The measured transition frequencies *v* of the 4H2B monomer with quantum numbers and difference to calculated frequencies △*v* in the fit.

J''(*ka*' *kc*')-*J*''(*ka*'' *kc*'')	state	*v*/MHz	△*v*/kHz
2_{02}-1_{01}	*A*	8407.8704	0.8
	E	8407.0600	1.6
2_{12}-1_{11}	*A*	8067.0262	0.4
	E	8149.2585	1.8
2_{11}-1_{10}	*A*	8786.0263	0.1
	E	8703.0646	2.1
3_{03}-2_{02}	*A*	12565.4711	1.1
	E	12564.0487	0.1
3_{13}-2_{12}	*A*	12089.1348	0.6
	E	12120.0668	1.3
3_{12}-2_{11}	*A*	13167.0277	0.1
	E	13134.8924	0.1
4_{04}-3_{03}	*A*	16669.3607	1.9
	E	16667.0637	2.1
4_{14}-3_{13}	*A*	16098.3881	2.6
	E	16111.2410	1.7
4_{13}-3_{12}	*A*	17532.7520	3.7
	E	17518.1412	2.5
4_{23}-3_{22}	*A*	16838.4501	13.1
	E	16916.6241	2.8
4_{22}-3_{21}	*A*	17021.9901	1.5
	E	16942.8191	5.1
5_{15}-4_{14}	*A*	20091.8333	5.4
	E	20097.9983	4.6
1_{10}-1_{01}	*A*	5371.7791	0.6
	E	5499.1779	4.6
1_{11}-0_{00}	*A*	9225.5430	5.9
	E	9055.6248	0.0
2_{11}-2_{02}	*A*	5749.9390	4.4
	E	5795.1864	0.1
2_{21}-2_{12}	*A*	16115.0579	9.4
	E	15579.7518	5.9
2_{20}-2_{11}	*A*	15055.2186	1.9
	E	15463.0197	4.1
2_{12}-1_{01}	*A*	13079.3045	2.0
	E	12991.9834	0.6
3_{12}-3_{03}	*A*	6351.4953	5.3
	E	6366.0311	1.0
3_{22}-3_{13}	*A*	16665.7099	10.7
	E	16135.2659	2.7
3_{21}-3_{12}	*A*	14602.2321	4.7
	E	15005.4243	0.9
3_{03}-2_{12}	*A*	7894.0355	1.4
	E	7979.1246	1.5
3_{13}-2_{02}	*A*	16760.5708	1.3
	E	16704.9911	2.6
4_{13}-4_{04}	*A*	7214.8882	5.1
	E	7217.1113	3.3
4_{23}-4_{14}	*A*	17405.7601	9.4
	E	16940.6549	4.3
4_{22}-4_{13}	*A*	14091.4705	2.2
	E	14430.1015	7.7
4_{04}-3_{13}	*A*	12474.2612	4.2
	E	12526.1209	0.1
5_{14}-5_{05}	*A*	8384.2558	2.4
	E	8381.4725	1.8
5_{24}-5_{15}	*A*	18338.5890	22.0
	E	17980.6984	4.9
5_{23}-5_{14}	*A*	13598.0718	5.8
	E	13830.9260	7.7
5_{05}-4_{14}	*A*	17083.1691	7.8

	E	17118.6582	6.3
6_{15}-6_{06}	*A*	9899.9524	21.2
	E	9895.9727	4.5
6_{24}-6_{15}	*A*	13205.6515	19.5
	E	13334.8381	12.9
1_{11}-0_{00}	*A*	9585.0509	2.3
	E	9712.0814	2.2
2_{12}-1_{01}	*A*	14157.8102	4.4
	E	14202.2444	0.5
3_{22}-3_{12}	*A*	14509.3114	4.9
	E	13910.1777	5.8
3_{12}-2_{02}	*A*	18916.9670	4.8
	E	18930.0776	1.1

Table S2 The measured transition frequencies ν for ^{13}C4 of the 4H2B monomer with quantum numbers and difference to calculated frequencies $\triangle\nu$ in the fit.

$J''(ka'\ kc')$-$J''(ka''\ kc'')$	state	ν/MHz	$\triangle\nu$/kHz
2_{02}-1_{01}	*A*	8321.6214	0.8
	E	8320.8245	1.9
2_{12}-1_{11}	*A*	7986.6812	0.6
	E	8068.4975	1.5
2_{11}-1_{10}	*A*	8692.7211	1.4
	E	8610.1886	1.3
3_{03}-2_{02}	*A*	12437.5174	0.1
	E	12436.1257	2.4
3_{13}-2_{12}	*A*	11968.9633	1.3
	E	11999.9177	0.2
3_{12}-2_{11}	*A*	13027.4437	1.4
	E	12995.3124	8.9
4_{04}-3_{03}	*A*	16501.3027	0.2
	E	16499.0634	5.1
4_{14}-3_{13}	*A*	15938.7700	4.9
	E	15951.6586	3.1
4_{13}-3_{12}	*A*	17347.3789	1.0
	E	17332.7702	9.4
1_{10}-1_{01}	*A*	5342.5426	10.3
1_{11}-0_{00}	*A*	9159.3790	0.8
	E	8990.1027	4.2
2_{12}-1_{01}	*A*	12976.2038	4.3
	E	12889.1053	4.6
3_{03}-2_{12}	*A*	7782.9350	2.4
	E	7867.8449	5.1
3_{13}-2_{02}	*A*	16623.5457	3.3
	E	16568.1985	6.3
4_{13}-4_{04}	*A*	7149.6450	4.8
4_{22}-4_{13}	*A*	14036.2767	3.5
4_{04}-3_{13}	*A*	12315.2744	0.6
	E	12366.9906	6.2
5_{05}-4_{14}	*A*	16877.4680	2.3
	E	16912.8763	11.5

Table S3 The measured transition frequencies ν for ^{13}C3 of the 4H2B monomer with quantum numbers and difference to calculated frequencies $\triangle\nu$ in the fit.

$J''(ka'\ kc')$-$J''(ka''\ kc'')$	state	ν/MHz	$\triangle\nu$/kHz
2_{02}-1_{01}	*A*	8391.3815	2.6
	E	8390.5573	0.2
2_{12}-1_{11}	*A*	8044.2160	5.1
	E	8124.5068	0.3
2_{11}-1_{10}	*A*	8778.2181	4.1
	E	8697.1993	2.7
3_{03}-2_{02}	*A*	12537.8373	1.9
	E	12536.3848	2.0
3_{13}-2_{12}	*A*	12054.2107	1.4
	E	12083.8513	3.8
3_{12}-2_{11}	*A*	13154.5429	0.8
	E	13123.6984	0.2
4_{04}-3_{03}	*A*	16627.3858	0.4
	E	16625.0272	3.3
4_{14}-3_{13}	*A*	16050.5888	1.1
	E	16062.8352	3.3
4_{13}-3_{12}	*A*	17514.5743	2.2
	E	17500.5607	0.0
1_{10}-1_{01}	*A*	5272.0340	1.9
1_{11}-0_{00}	*A*	9110.6472	2.6
	E	8946.1668	1.2
2_{11}-2_{02}	*A*	5658.8707	7.9
2_{12}-1_{01}	*A*	12949.2489	8.9
	E	12865.4307	0.9
3_{12}-3_{03}	*A*	6275.5762	4.2
	E	6289.1686	7.5
3_{03}-2_{12}	*A*	7979.9699	1.9
	E	8061.5115	6.7
3_{13}-2_{02}	*A*	16612.0781	1.7
	E	16558.7246	3.7
4_{13}-4_{04}	*A*	7162.7648	2.0
4_{04}-3_{13}	*A*	12553.1450	3.7
	E	12602.6874	0.6
5_{05}-4_{14}	*A*	17150.0792	1.2
	E	17183.7488	6.1

Table S4 The measured transition frequencies ν for ^{13}C2 of the 4H2B monomer with quantum numbers and difference to calculated frequencies $\triangle\nu$ in the fit.

$J''(ka'\ kc')$-$J''(ka''\ kc'')$	state	ν/MHz	$\triangle\nu$/kHz
2_{02}-1_{01}	*A*	8378.9924	1.0
	E	8378.1874	0.6
2_{12}-1_{11}	*A*	8040.3373	5.0
	E	8122.5398	3.4
2_{11}-1_{10}	*A*	8754.4001	2.4
	E	8671.4724	2.7
3_{03}-2_{02}	*A*	12522.8411	1.5
	E	12521.4330	1.9
3_{13}-2_{12}	*A*	12049.2680	4.8
	E	12080.2782	0.5
3_{12}-2_{11}	*A*	13119.7702	0.2
	E	13087.5677	1.6
4_{04}-3_{03}	*A*	16613.7464	1.0
	E	16611.4775	3.5
4_{14}-3_{13}	*A*	16045.5249	1.6
	E	16058.4223	3.3
4_{13}-3_{12}	*A*	17470.1050	0.1
	E	17455.4636	5.3
1_{10}-1_{01}	*A*	5377.3125	2.3
1_{11}-0_{00}	*A*	9218.9712	5.8
	E	9048.9378	1.1
2_{11}-2_{02}	*A*	5752.7201	1.2
	E	5798.1863	7.0
2_{12}-1_{01}	*A*	13060.6183	2.3
	E	12973.1521	1.3
3_{12}-3_{03}	*A*	6349.6492	6.7
	E	6364.3210	5.5
3_{03}-2_{12}	*A*	7841.2152	5.4
	E	7926.4683	2.0
4_{13}-4_{04}	*A*	7206.0079	2.6
	E	7208.3071	3.4
4_{04}-3_{13}	*A*	12405.6937	1.9
	E	12457.6676	6.7
5_{05}-4_{14}	*A*	16999.7221	0.4
	E	17035.3310	6.2

Table S5 The measured transition frequencies ν for ^{13}C1 the 4H2B monomer with quantum numbers and difference to calculated frequencies $\triangle\nu$ in the fit.

$J''(ka'\ kc')$-$J''(ka''\ kc'')$	state	ν/MHz	$\triangle\nu$/kHz
2_{02}-1_{01}	*A*	8218.6984	2.2
	E	8217.9484	0.5
2_{12}-1_{11}	*A*	7891.8667	1.4
	E	7974.8051	3.7
2_{11}-1_{10}	*A*	8579.4524	2.1
	E	8495.8332	1.5
3_{03}-2_{02}	*A*	12285.8892	2.7
	E	12284.5794	0.3
3_{13}-2_{12}	*A*	11827.4146	0.0
	E	11859.3682	0.8
3_{12}-2_{11}	*A*	12858.2696	2.3
	E	12825.1981	2.5
4_{04}-3_{03}	*A*	16304.0495	0.7
	E	16301.9436	1.9
4_{14}-3_{13}	*A*	15751.2189	5.5
	E	15764.6083	6.3
4_{13}-3_{12}	*A*	17123.2536	0.5
	E	17108.2283	8.3
1_{10}-1_{01}	*A*	5394.9391	6.7
1_{11}-0_{00}	*A*	9168.9817	6.8
	E	8996.1106	1.7
2_{12}-1_{01}	*A*	5755.6931	1.4
	E	12943.0129	5.5
3_{12}-3_{03}	*A*	12853.4202	1.3
	E	6328.0734	5.7
3_{03}-2_{12}	*A*	6343.9002	0.3
	E	7561.5747	1.0
	E	7649.1075	3.3
4_{04}-3_{13}	*A*	12038.2096	1.4
	E	12091.6828	1.4
4_{13}-4_{04}	*A*	7147.2775	3.6
	E	7150.1850	3.6
5_{05}-4_{14}	*A*	16548.5261	3.5
	E	16585.3981	0.6

Table S6 The measured transition frequencies ν for ^{18}O6 of the 4H2B monomer with quantum numbers and difference to calculated frequencies $\triangle\nu$ in the fit.

$J''(ka'\ kc')$-$J''(ka''\ kc'')$	state	ν/MHz	$\triangle\nu$/kHz
2_{02}-1_{01}	*A*	8331.9008	4.2
	E	8331.0486	5.0
2_{12}-1_{11}	*A*	7976.5511	2.6
	E	8051.2733	4.7
2_{11}-1_{10}	*A*	8730.8005	6.0
	E	8655.3297	2.4
3_{03}-2_{02}	*A*	12443.8641	1.4
	E	12442.3667	5.5
3_{13}-2_{12}	*A*	11951.5550	12.5
	E	11978.0607	8.7
3_{12}-2_{11}	*A*	13082.1419	0.1
	E	13054.3882	7.5
4_{04}-3_{03}	*A*	16493.7520	12.4
	E	16491.3256	9.2
1_{11}-0_{00}	*A*	8882.1240	0.7
	E	8731.5940	0.3
2_{12}-1_{01}	*A*	12681.8315	2.8
	E	12606.4090	7.8
3_{03}-2_{12}	*A*	8093.9334	12.4
	E	8167.0063	5.2
4_{13}-4_{04}	*A*	7041.3255	0.8
5_{05}-4_{14}	*A*	12636.1305	3.5
	E	12680.2712	1.1

3. The SE rotational constants of the six isotopologues of the 4H2B monomer. (Table S7)

Table S7 The SE rotational constants of the six isotopologues of the 4H2B monomer.

parameter	*A*/MHz	*B*/MHz	*C*/MHz
Parent	7360.694(3)[a]	2318.887(7)	1942.6359(5)
C1	7343.606(1)	2261.8911(2)	1902.0689(2)
C2	7359.329(1)	2310.1589(2)	1936.5533(2)
C3	7250.679(1)	2318.4206(2)	1934.4113(2)
C4	7309.146(1)	2293.1344(3)	1923.5726(3)
O6	7042.384(4)	2309.273(1)	1914.9297(9)

[a]Constain's errors expressed in parentheses in units of the last digit.

4. The r_s, r^{SE}, r_e coordinates of the six isotopologues of the 4H2B monomer. (Table S8)

Table S8 The r_s, r^{SE} and r_e, coordinates of the five isotopologues of the 4H2B monomer.

parameter	*a*/Å			*b*/Å			*c*/Å		
	r_s	r^{SE}	r_e	r_s	r^{SE}	r_e	r_s	r^{SE}	r_e
C1	±2.341(6)[a]	±2.340(6)	2.360	±0.318(5)	±0.336(4)	-0.316	±0.254(6)	±0.231(6)	-0.191
C2	±0.909(2)	±0.956(2)	0.919	±0.08(2)	±0.06(3)	0.087	±0.09(2)	±0.10(2)	0.026
C3	±0.070(2)	±0.233(6)	-0.118	±1.019(1)	±1.030(1)	-1.020	±0.05(3)	0.00[b]	-0.045
C4	±1.507(1)	±1.511(1)	-1.497	±0.532(3)	±0.559(3)	-0.567	±0.427(4)	±0.426(4)	0.421
O6	±0.614(3)	±0.626(2)	0.600	±1.233(1)	±1.235(1)	1.247	±0.296(5)	±0.260(6)	0.253

[a] Constain's errors expressed in parentheses in units of the last digit. [b] Imaginary values, fixed at zero.

5. The r_s, r^{SE} and r_e structural parameters of conformer I of the 4H2B monomer. (Table S9)

Table S9 The r_s, r^{SE} and r_e structural parameters of conformer I of the 4H2B monomer.

	r_s	r^{SE}	r_e[b]
RC1C2	1.51(1)	1.524(8)	1.513
RC2C3	1.45(3)	1.58(2)	1.521
RC3C4	1.59(2)[a]	1.427(6)	1.529
RC2O6	1.25(3)	1.22(3)	1.216
∠C1C2C3	116(2)	119(1)	116.8
∠C2C3C4	111(2)	114(1)	113.5
∠C1C2O6	120(2)	120(2)	121.6
∠O6C2C3	123(3)	120(2)	121.6

[a] Numbers in parentheses are 1σ uncertainties in the last significant digit. [b] B3LYP-(GD3BJ)/6-311++G(d,p) level of theory.

6. Geometries of conformer I of the 4H2B monomer calculated at B3LYP-(GD3BJ)/6-311++G(d,p). (Table S10)

Table S10 Ggeometries of conformer I of the 4H2B monomer calculated at B3LYP-(GD3BJ)/6-311++G(d,p).

Bond lengths/Å		Valence angles/°		Dihedral Angles/°	
C1C2	1.51(1)[a]	C1C2C3	116(2)	C1C2C3C4	170.6
C2C3	1.45(3)[a]	C2C3C4	111(2)	O6C2C3C4	-9.4
C3C4	1.59(2)[a]	C1C2O6	120(2)	C2C3C4O5	64.9
C2O6	1.25(3)[a]	C2C3O6	123(3)		
C4O5	1.420	C3C4O5	112.5		
O6H7	2.219	O5H7O6	125.8		

[a] Values of partial r_0 structure with errors expressed in parentheses in units of the last digit.

7. The measured transition frequencies *v* of the five isotopologues of the 4H2B-H_2O complex with quantum numbers and difference to calculated frequencies △*v* in the fit. (Tables S11-S15)

Table S11 The measured transition frequencies *v* of the 4H2B-H_2O complex with quantum numbers and difference to calculated frequencies △*v* in the fit.

J''(*ka*' *kc*')-*J*''(*ka*'' *kc*'')	state	*v*/MHz	△*v*/kHz
2_{02}-1_{01}	*A*	5641.9787	2.3
	E	5641.8853	2.6
2_{12}-1_{11}	*A*	5273.1612	5.9
	E	5274.9867	2.7
2_{11}-1_{10}	*A*	6213.8507	1.9
	E	6212.1946	6.0
3_{03}-2_{02}	*A*	8236.8981	1.7
	E	8236.5136	1.4
3_{13}-2_{12}	*A*	7851.8627	0.9
	E	7852.5245	2.5
3_{12}-2_{11}	*A*	9248.7993	3.4
	E	9248.3801	9.8
3_{22}-2_{21}	*A*	8615.2344	1.2
	E	8641.1444	6.8
3_{21}-2_{20}	*A*	8993.5592	3.3
	E	8968.1224	3.9
4_{04}-3_{03}	*A*	10669.7431	0.4
	E	10668.7579	6.1
4_{14}-3_{13}	*A*	10378.5453	2.2
	E	10379.3829	5.3
4_{13}-3_{12}	*A*	12178.1161	5.5
	E	12177.7931	1.9
4_{23}-3_{22}	*A*	11407.0399	0.3
	E	11413.2385	2.8
4_{22}-3_{21}	*A*	12222.5850	0.1
	E	12216.9720	1.9
4_{32}-3_{31}	*A*	11654.6253	0.3
	E	11686.5909	1.9
4_{31}-3_{30}	*A*	11736.3978	4.6
	E	11705.0175	2.4
5_{05}-4_{04}	*A*	13030.8428	0.6
	E	13028.3398	3.9
5_{15}-4_{14}	*A*	12858.1690	2.8
	E	12860.3966	7.2
5_{14}-4_{13}	*A*	14943.6601	1.4
	E	14943.0882	8.4
5_{24}-4_{23}	*A*	14133.8616	4.3
	E	14135.6993	5.6
5_{23}-4_{22}	*A*	15448.9023	0.5
	E	15447.5348	0.6
5_{33}-4_{32}	*A*	14585.9709	7.4
	E	14625.8236	2.5
5_{32}-4_{31}	*A*	14851.9588	7.7
	E	14813.0012	2.4
6_{06}-5_{05}	*A*	15390.1228	3.7
	E	15383.6832	4.0
6_{16}-5_{15}	*A*	15302.9224	1.6
	E	15309.0982	7.5
6_{15}-5_{14}	*A*	17505.8430	3.3
	E	17504.7907	3.8
6_{25}-5_{24}	*A*	16787.4848	6.7
	E	16788.2226	7.6
6_{24}-5_{23}	*A*	18572.7020	2.8
	E	18572.1687	1.0
7_{07}-6_{06}	*A*	17765.7447	5.7
	E	17754.5605	0.2
7_{17}-6_{16}	*A*	17725.8361	4.2
	E	17736.8111	3.8
2_{20}-1_{11}	*A*	10906.8370	1.3
	E	10940.9496	1.8
3_{13}-2_{02}	*A*	8856.7476	0.2

	E	8855.5663	5.5
3_{22}-2_{11}	*A*	12736.3485	2.5
	E	12722.6499	3.1
4_{04}-3_{13}	*A*	10049.8936	9.6
	E	10049.7051	9.0
4_{14}-3_{03}	*A*	10998.3947	8.7
	E	10998.4356	3.4
5_{05}-4_{14}	*A*	12702.1911	7.8
	E	12698.6620	8.4
5_{15}-4_{04}	*A*	13186.8206	3.8
	E	13190.0743	3.6

Table S12 The measured transition frequencies ν for the 4H2B-HOD complex with quantum numbers and difference to calculated frequencies $\triangle\nu$ in the fit.

$J''(ka'\ kc')$-$J''(ka''\ kc'')$	state	ν/MHz	$\triangle\nu$/kHz
2_{02}-1_{01}	*A*	5495.2795	3.0
	E	5495.1776	2.3
2_{11}-1_{10}	*A*	6055.0623	13.1
	E	6053.4261	1.6
3_{03}-2_{02}	*A*	8021.5611	4.7
	E	8021.1692	3.5
3_{13}-2_{12}	*A*	7644.8351	10.4
	E	7645.4682	0.3
3_{12}-2_{11}	*A*	9012.1039	0.9
	E	9011.6773	7.7
4_{04}-3_{03}	*A*	10389.2190	6.8
	E	10388.2314	13.7
4_{14}-3_{13}	*A*	10104.3992	6.3
	E	10105.2025	8.5
4_{13}-3_{12}	*A*	11865.6893	2.7
4_{23}-3_{22}	*A*	11111.0891	5.2
	E	11117.1472	6.8
4_{22}-3_{21}	*A*	11909.5838	5.5
	E	11904.0508	5.6
5_{05}-4_{04}	*A*	12686.7291	1.0
	E	12684.2382	4.7
5_{15}-4_{14}	*A*	12517.9001	1.4
5_{14}-4_{13}	*A*	14558.8812	0.2
	E	14558.3008	7.0
5_{24}-4_{23}	*A*	13766.5158	4.2
	E	13768.2928	1.4
6_{06}-5_{05}	*A*	14982.5065	1.8
	E	14976.1301	3.6

Table S13 The measured transition frequencies ν for the 4H2B-DOH complex with quantum numbers and difference to calculated frequencies $\triangle\nu$ in the fit.

$J''(ka'\ kc')$-$J''(ka''\ kc'')$	state	ν/MHz	$\triangle\nu$/kHz
2_{02}-1_{01}	*A*	5593.1598	0.7
	E	5593.0566	2.8
2_{11}-1_{10}	*A*	6167.8097	0.8
	E	6166.1189	9.4
3_{03}-2_{02}	*A*	8160.0874	1.2
	E	8159.6797	2.9
3_{13}-2_{12}	*A*	7779.4718	1.1
	E	7780.1448	3.0
3_{12}-2_{11}	*A*	9178.1120	0.5
	E	9177.6741	1.0
3_{22}-2_{21}	*A*	8545.0443	0.8
4_{04}-3_{03}	*A*	10565.1007	2.7
	E	10564.0603	0.8
4_{14}-3_{13}	*A*	10280.6701	5.3
	E	10281.5438	0.4
4_{13}-3_{12}	*A*	12080.1258	8.9
	E	12079.7782	6.5
4_{23}-3_{22}	*A*	11311.8308	3.9
	E	11318.0146	2.0
4_{22}-3_{21}	*A*	12138.3399	1.9
5_{05}-4_{04}	*A*	12901.0165	1.0
	E	12898.3477	2.7
5_{15}-4_{14}	*A*	12734.6120	2.6
	E	12736.9872	0.6
5_{14}-4_{13}	*A*	14814.4994	5.5
	E	14813.8888	0.1
6_{06}-5_{05}	*A*	15236.8464	1.8
	E	15230.0114	0.6
6_{16}-5_{15}	*A*	15153.9068	2.2

Table S14 The measured transition frequencies v for the 4H2B-$H_2{}^{18}O$ complex with quantum numbers and difference to calculated frequencies $\triangle v$ in the fit.

$J''(ka'\ kc')$-$J'''(ka''\ kc'')$	state	v/MHz	$\triangle v$/kHz
2_{02}-1_{01}	*A*	5450.8193	5.0
	E	5450.7276	7.7
2_{11}-1_{10}	*A*	5995.9460	4.7
	E	5994.3068	3.0
3_{03}-2_{02}	*A*	7965.2087	4.6
	E	7964.8577	5.0
3_{13}-2_{12}	*A*	7587.0197	9.5
	E	7587.6324	2.4
3_{12}-2_{11}	*A*	8927.5350	2.0
	E	8927.1119	1.9
3_{22}-2_{21}	*A*	8317.3353	1.9
4_{04}-3_{03}	*A*	10323.6789	10.4
	E	10322.7970	3.1
4_{14}-3_{13}	*A*	10031.3065	10.4
	E	10032.0354	7.6
4_{13}-3_{12}	*A*	11762.1600	5.1
	E	11761.8495	6.7
4_{23}-3_{22}	*A*	11015.7512	1.2
	E	11022.0099	2.1
4_{22}-3_{21}	*A*	11780.3834	4.5
	E	11774.6082	2.8
4_{32}-3_{31}	*A*	11246.0769	2.3
	E	11275.3642	1.4
4_{31}-3_{30}	*A*	11319.3457	0.2
	E	11290.5238	9.6
5_{05}-4_{04}	*A*	12608.4795	8.1
	E	12606.2934	0.7
5_{15}-4_{14}	*A*	12430.7300	8.9
	E	12432.6233	10.4
5_{14}-4_{13}	*A*	14446.1118	5.1
	E	14445.5976	11.4
5_{24}-4_{23}	*A*	13653.7726	4.5
	E	13655.6140	6.7
5_{23}-4_{22}	*A*	14896.4007	4.9
	E	14894.9484	1.7
5_{33}-4_{32}	*A*	14075.9155	3.9
	E	14114.8988	4.0
5_{32}-4_{31}	*A*	14315.5145	1.1
	E	14277.2539	0.4
6_{06}-5_{05}	*A*	14888.2415	3.2
	E	14882.6269	1.7
6_{16}-5_{15}	*A*	14796.2605	2.2
6_{15}-5_{14}	*A*	16939.4738	6.0
	E	16938.5428	4.9
6_{25}-5_{24}	*A*	16223.2990	9.6
	E	16224.0136	15.2
7_{07}-6_{06}	*A*	17183.1561	9.7
	E	17172.7402	6.7
4_{04}-3_{13}	*A*	9686.1650	2.1
	E	9686.0554	5.6

Table S15 The measured transition frequencies ν for the 4H2B-D_2O complex with quantum numbers and difference to calculated frequencies $\triangle\nu$ in the fit.

$J''(ka'\ kc')$-$J''(ka''\ kc'')$	state	ν/MHz	$\triangle\nu$/kHz
2_{02}-1_{01}	*A*	5450.1649	1.7
	E	5450.0561	5.7
3_{03}-2_{02}	*A*	7951.2776	5.7
	E	7950.8683	2.8
3_{13}-2_{12}	*A*	7578.4895	9.6
	E	7579.1332	1.7
3_{12}-2_{11}	*A*	8945.6065	8.4
	E	8945.1678	14.5
4_{04}-3_{03}	*A*	10294.0636	5.1
	E	10293.0315	16.7
4_{14}-3_{13}	*A*	10014.9561	3.8
	E	10015.7925	9.1
4_{13}-3_{12}	*A*	11774.2131	10.2
	E	11773.8618	9.3
4_{23}-3_{22}	*A*	11022.6591	3.2
	E	11028.7002	1.8
5_{05}-4_{04}	*A*	12568.8878	6.1
	E	12566.2584	6.8
5_{15}-4_{14}	*A*	12405.2513	1.6
5_{14}-4_{13}	*A*	14439.5214	0.5
	E	14438.9140	4.9
5_{24}-4_{23}	*A*	13654.1978	14.0
	E	13655.9651	2.1
6_{06}-5_{05}	*A*	14843.3657	6.5
	E	14836.6563	3.1
6_{16}-5_{15}	*A*	14761.6375	0.8
	E	14768.0173	2.0

8. Geometries of isomer I of the 4H2B-H_2O complex calculated at B3LYP-GD3(BJ)/6-311++G(d,p). (Table S16)

Table S16 Geometries of isomer I of the 4H2B-H_2O complex calculated at B3LYP-GD3(BJ)/6-311++G(d,p).

Bond lengths/Å		Valence angles/°		Dihedral Angles/°	
C1C2	1.511	C1C2C3	116.3	C1C2C3C4	-163.4
C2C3	1.517	C2C3C4	115.4	C2C3C4O5	69.7
C3C4	1.524	C3C4O5	111.0	C4O5O15O6	54.8(7)
C2O6	1.218	O5O15O6	70.6	O6C2C3C4	17.1
C4O5	1.419	O5H7O6	94.0		
O5O15	2.827(4)[a]				
O6O15	3.02(2)[a]				
O6H7	3.019				

[a] Values of partial r_0 structure with errors expressed in parentheses in units of the last digit.