Water Induces the Same Crown Shapes as Li^+ or Na^+ in 15-Crown-5 Ether: a Broadband Rotational Study

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15-crown-5 ether (15C5) and its complexes with water have been studied using broadband Fourier transform microwave spectroscopy in a supersonic jet. A new conformer of 15C5 has been observed and established as the new global minimum out of a total of nine isolated structures. In addition, two 15C5-H_2O and two 15C5-$(H_2O)_2$ clusters have been observed. The cluster structures have been unambiguously identified through the observation of water ^{18}O isotopologue spectra. In all the clusters, at least one water molecule, located close to the axis of the 15C5 ring, interacts through two simultaneous hydrogen bonds to the endocyclic oxygen atoms. This interaction reshapes the 15C5 ring to reduce its rich conformational landscape to only two open structures, related to those found in complexes with Li^+ or Na^+ ions. In the most abundant 15C5-$(H_2O)_2$ form, the two water molecules repeat the same interaction scheme while binding to opposite sides of the ring. In the second most abundant dihydrated form the two water molecules lie on the same side of the ring. This finding is exceptionally rare because water-water interactions typically prevail over the formation of additional solute-water contacts, and it showcases the particular binding features of crown ethers.

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IDENTIFICATION OF THE OBSERVED CONFORMERS OF THE 15-CROWN-5 ETHER-WATER ADDUCTS WITH THE HELP OF AB INITIO COMPUTATIONS.

The identification of the observed rotamers as the structures shown in Figure 3 of the main text was achieved with the help of ab initio computations as described herein. A summary of the most relevant results is given in Tables S5 and S6 and Figures S3 and S4. In those tables the conformers are labeled as 15C5-w-*n* or 15C5-w$_2$-*n* (*n* = 1, 2, 3,…) where *n* refers to the order of increasing energy. For the 1:1 complexes (see Table S5 and Figure S3) the different forms were first investigated using the low energy 15C5 structures optimized for the monomer including observed and non-observed forms. In each case different possible interactions with water were allowed. The most stable form 15C5-w-1, which can be identified as 15C5-w-B, was found directly from the non-observed 15C5-VII monomer with C_2 symmetry (see Figures S1 and S2). However, using the 15C5 low energy conformers it was not possible to obtain any 1:1 complex with a value of the C rotational constant as low as that found for the observed rotamer 15C5-w-C. At this point we decided to broaden our search to high energy open ring forms as 15C5-XX (see Table S2), found in the structures of cation complexes,[24,34,35] that has a value of the *C* rotational constant close to 282 MHz. 15C5-XX leads to the conformers 15C5-w-3 and 15C5-w-7 (see Table S3) depending on the side of the ring where water is located. Complex 15C5-w-3 is predicted to be only 93 cm^{-1} above the most stable form and could be identified as 15C5-w-C. No spectrum identifiable as form 15C5-w-2, 44 cm^{-1} above the global minimum structure, was observed.

The structure for the 1:2 complex 15C5-w$_2$-1 (see Table S6 and Figure 3), identifiable as 15C5-w$_2$-D, was optimized from 15C5-w-3 by locating a second water molecule on the opposite side of the ring. It should be noted that 15C5-w$_2$-2, obtained from 15C5-w-1 with two water molecules in opposite sides of the ring, has almost the same energy as

15C5-w_2-1 but it has an electric dipole moment close to zero and is thus invisible to rotational spectroscopy. The species with the weakest spectrum labeled 15C5-w_2-E could be tentatively assigned to a complex of 15C5 with two water molecules, one of which is close to the *c* inertial axis as found for the other observed complexes. The ab initio search for the structure of this rotamer started from the previously optimized 1:1 species. A series of conformers with energies of about 10-13 kJ/mol above the global minimum 15C5-w_2-1 was obtained. The form 15C5-w_2-6 (see Table S6, Figure S4) shown in Figure 3, derived from the 1:1 complex form 15C5-w-7, has a set of rotational constants similar to those of rotamer 15C5-w_2-E. The rotational constants resulting from subtracting the inertial contribution of the water molecule in the center of the ring of the optimized form 15C5-w_2-6 are in good agreement with the experimental result for 15C5-w_2-E as shown in Table 3.

Table S1. Rotational parameters obtained from the analysis of the spectrum of the observed rotamers of 15-crown-5 ether

Param.[a]	A/0[b]	I[c]	II[c]	III[c]	IV[c]	V[c]	VI[c]	VIII[c]	IX[c]
A/MHz	599.41652(16)[d]	806.82516(10)	595.89856(53)	710.44964(23)	675.53367(23)	616.3436(12)	600.2136(11)	774.81960(74)	753.07281(73)
B/MHz	554.06562(19)	417.162756(78)	560.83118(25)	434.54713(20)	452.972754(97)	493.0203(33)	493.5517(11)	413.55113(19)	412.42611(16)
C/MHz	339.94984(20)	303.779900(38)	342.00696(14)	287.05316(10)	289.871259(79)	295.03807(21)	285.719595(96)	287.02341(10)	279.824036(75)
κ	0.65	-0.55	0.72	-0.30	-0.15	0.23	0.32	-0.48	-0.43
P_{aa}/uÅ^2	777.81918(71)	1124.36142(26)	765.35782(88)	1106.11352(69)	1055.51806(48)	959.0162(48)	975.3794(22)	1165.2762(90)	1180.17580(80)
P_{bb}/uÅ^2	708.80899(59)	539.27402(22)	712.32851(50)	654.46284(57	687.94216(36)	753.9119(40)	793.4143(14)	595.4827(59)	625.88424(48)
P_{cc}/uÅ^2	134.30926(44)	87.10581(10)	135.76720(30)	56.8880(31)	60.17600(24)	66.05116(61)	48.58430(30)	56.7711(31)	45.20493(24)
Δ_J /kHz	0.0458(14)	0.00951(25)	0.01421(60)	0.01098(34)	0.00490(30)	0.00895(58)	0.092(11)	0.00187(36)	0.00213(41)
Δ_{JK} /kHz	[0.][e]	0.0581(11)	[0.]	0.0425(16)	0.1338(33)	-0.088(11)	-0.221(34)	[0.]	[0.]
Δ_K /kHz	[0.]	0. 1183(18)	0.225(11)	0.0682(19)	[0.]	[0.]	[0.]	0.002139(12)	[0.]
δ_J /kHz	0.01830(74)	0.00091(12)	[0.]	0.00379(17)	[0.]	[0.]	0.0437(58)	[0.]	[0.]
δ_k /kHz	0.0590(44)	0.0604(15)	[0.]	0.0458(13)	0.0547(29)	[0.]	0.080(10)	[0.]	[0.]
σ/kHz	5.1	6.0	5.8	6.7	5.9	6.3	4.3	6.1	5.6
n	98	333	102	238	200	52	53	47	41

[a] Analysis of the spectra have been done with the A-reduced semirigid rotor Hamiltonian of Watson[27] in the I^r representation; A, B and C are the rotational constants; κ is the Ray's asymmetry parameter ($-1 < \kappa = (2B - A - C)/(A - C) < 1$); $P_{\alpha\alpha}$ ($\alpha = a$, b or c) are the planar moments of inertia derived from the inertial moments I_α ($P_{cc} = (I_a + I_b - I_c)/2$); Δ_J, Δ_{JK}, Δ_K, δ_J and δ_K are the quartic centrifugal distortion constants; σ is the rms deviations of the fit; n is the number of lines fitted. [b] From the analysis of the spectrum measured in this work. [c] Constants for conformers I-IX from the spectra measured in this and previous works.[16,17] [d] Standard errors are given in parentheses in units of the last digit. [e] Values in square brackets were kept fixed in the fit.

Table S2. Rotational parameters, electric dipole moment components and energies for the most stable 15-crown-5 ether conformers obtained from ab initio MP2/6-311++G(d,p) optimizations.

Param.[a]	0[b]	I[c]	II[c]	III[c]	IV[c]	V[c]	VI[c]	VII[c]	VIII[c]	IX[c]	XX[b]
A/MHz	606.5	828.5	602.9	725.2	692.8	618.3	607.4	728.2	791.9	789.6	566.8
B/MHz	556.8	416.9	565.6	433.3	451.5	499.5	494.5	444.9	412.3	431.9	507.4
C/MHz	344.4	307.7	347.9	289.2	293.8	298.4	288.4	303.0	288.6	308.5	282.2
κ	0.6	-0.6	0.7	-0.3	-0.2	0.3	0.3	-0.3	-0.5	-0.5	0.6
P_{aa}/uÅ^2	771.0	1122.4	753.9	1108.6	1055.0	944.1	971.2	1054.9	1169.3	1084.1	947.6
P_{bb}/uÅ^2	696.5	520.0	698.7	639.1	665.2	749.8	781.3	613.0	581.7	554.1	843.3
P_{cc}/uÅ^2	136.7	89.9	139.6	57.8	64.3	67.6	50.8	81.0	56.5	86.0	48.3
μ_a/D	0.4	0.9	3.7	0.1	0.7	2.4	0.6	0.0	0.5	1.6	-0.1
μ_b/D	0.2	2.3	0.1	4.2	3.4	0.8	2.9	2.1	3.7	3.1	0.0
μ_c/D	1.2	0.6	0.8	1.6	1.3	0.3	1.2	0.0	2.1	0.8	1.4
μ_T/D	1.3	2.6	3.8	4.5	3.7	2.6	3.2	2.1	4.2	3.6	1.4
ΔE/kJmol^{-1}	0.0	0.3	2.6	3.3	4.5	4.8	6.7	6.6	4.4	7.5	16.2
ΔG_{298}/kJmol^{-1}	0.0	0.1	1.2	1.7	1.7	1.8	2.0	2.9	2.9	4.0	10.7

[a] *A*, *B* and *C* are the rotational constants. κ is the Ray's asymmetry parameter ($-1 < \kappa = (2B - A - C)/(A - C) < 1$); $P_{\alpha\alpha}$ ($\alpha = a$, b or c) are the planar moments of inertia derived from the inertial moments I_α ($P_{cc} = (I_a + I_b - I_c)/2$). μ_T, μ_a , μ_b *and* μ_c are the electric dipole moment (in Debye) and its components along the principal inertial axes; ΔE are the calculated electronic energies relative to the global minimum; ΔG_{298} are the standard relative Gibbs energies estimated at 298 K from the harmonic approximation. [b] From this work. [c] From previous works. [16,17]

Table S3. Rotational parameters obtained from the analysis of the spectrum of the observed species of 15-crown-5 ether–water complexes.

	ab initio	Experimental		ab initio	Experimental	
Param.[a]	15C5-w-1	15c5-w-B	$H_2{}^{18}O$	15C5-w-3	15c5-w-C	$H_2{}^{18}O$
A/MHz	561.3	550.48306(17)	545.36314(38)	516.8	506.27482(12)[b]	502.07837(22)
B/MHz	452.3	450.93827(12)	447.52271(30)	480.5	478.08872(15)	474.29760(24)
C/MHz	290.0	287.15720(11)	287.18397(44)	281.9	279.72069(12)	279.65737(25)
κ	0.20	0.24	0.24	0.69	0.75	0.75
P_a/uÅ^2	979.5	981.30079(63)	981.1861(20)	933.7	932.78939(67)	933.0469(29)
P_b/uÅ^2	763.3	778.63770(49)	778.5883(17)	859.7	873.93792(55)	874.0894(22)
P_c/uÅ^2	137.0	139.42690(34)	148.0951(13)	118.2	124.29267(39)	132.4845(17)
Δ_J /kHz		0.03298(72)	[0.03298]		0.02546(80)	[0.02546]
Δ_{JK} /kHz		-0.0552(27)	[-0.0552]		[0.][c]	[0.]
Δ_K /kHz		0.1267(37)	[0.1267]		[0.]	[0.]
δ_J /kHz		0.01531(33)	[0.01531]		0.01154(42)	[0.01154]
δ_k /kHz		0.0287(18)	[0.0287]		0.0344(20)	[0.0344]
μ_a/D	0.7	weak		0.2	No	
μ_b/D	1.0	weak		-0.6	weak	
μ_c/D	2.9	intense		1.5	intense	
σ/kHz		5.2	7.6		4.9	7.0
n		67	43		164	43
E/Hartree	-843.545929			-843.545504		
ΔE/kJmol^{-1}	0.			1.11		

[a] Analysis of the spectra have been done with the A-reduced semirigid rotor Hamiltonian of Watson[27] in the I^r representation; *A*, *B* and *C* are the rotational constants; κ is the Ray's asymmetry parameter ($-1 < \kappa = (2B - A - C)/(A - C) < 1$); $P_{\alpha\alpha}$ ($\alpha = a$, *b* or *c*) are the planar moments of inertia derived from the inertial moments I_α ($P_{cc} = (I_a + I_b - I_c)/2$); Δ_J, Δ_{JK}, Δ_K, δ_J and δ_K are the quartic centrifugal distortion constants; σ is the rms deviations of the fit; n is the number of lines fitted; *E* are the calculated electronic energies and ΔE the energies relative to the global minimum. [b] Standard errors are given in parentheses in units of the last digit. [c] Values in square brackets were kept fixed in the fit.

Table S4. Rotational parameters obtained from the analysis of the spectrum of the observed species of the 15-crown-5 ether-w_2 complexes.

	Experimental	ab initio			Experimental	ab initio	
Param.[a]	15c5-w_2-D	15C5-w_2-1	$(H_2{}^{18}O)_a$	$(H_2{}^{18}O)_b$	15c5-w_2-E	15C5-w_2-6	$(H_2{}^{18}O)_a$
A/MHz	468.67292(21)[b]	474.1	464.35724(18)	464.24965(19)	411.00203(38)	417.9	408.97667(96)
B/MHz	428.35788(10)	434.8	424.72604(19)	424.61040(23)	406.94503(37)	410.9	405.00427(92)
C/MHz	278.01562(11)	280.0	278.00530(94)	278.00134(68)	260.63832(19)	262.3	260.61(20)
κ	0.58	0.60	0.57	0.57	0.94	0.91	0.94
P_a/uÅ^2	959.64716(74)	950.7	959.7143(36)	959.7632(28)	975.6318(18)	973.7	975.66(45)
P_b/uÅ^2	858.16080(50)	854.4	858.1612(33)	858.1382(25)	963.3732(13)	953.1	963.54(45
P_c/uÅ^2	220.15840(36)	211.6	230.1798(31)	230.4550(22)	266.25337(71)	256.1	272.17(45)
Δ_J /kHz	[0.][c]		[0.]	[0.]	0.0329(10)		
Δ_{JK} /kHz	0.0445(25)		[0.0445]	[0.0445]	-0.0303(11)		
Δ_K /kHz	[0.]		[0.]	[0.]	[0.]		
δ_J /kHz	[0.]		[0.]	[0.]	-0.0455(21)		
δ_k /kHz	-0.0030(18)		[-0.0030]	[-0.0030]	[0.]		
μ_a/D	no	0.3			very weak	-0.8	
μ_b/D	no	0.2			weak	2.4	
μ_c/D	intense	1.3			moderate	2.9	
σ/kHz	5.4		6.5	7.1	7.0		8.2
n	134		41	42	156		28
E/Hartree		-919.844021				-919.8392755	
ΔE/kJmol^{-1}		0.				12.5	

[a] Analysis of the spectra have been done with the A-reduced semirigid rotor Hamiltonian of Watson[27] in the I^r representation; *A*, *B* and *C* are the rotational constants; κ is the Ray's asymmetry parameter ($-1 < \kappa = (2B - A - C)/(A - C) < 1$); $P_{\alpha\alpha}$ ($\alpha = a$, *b* or *c*) are the planar moments of inertia derived from the inertial moments I_α ($P_{cc} = (I_a + I_b - I_c)/2$); Δ_J, Δ_{JK}, Δ_K, δ_J and δ_K are the quartic centrifugal distortion constants; σ is the rms deviations of the fit; n is the number of lines fitted; *E* are the calculated electronic energies and ΔE the energies relative to the global minimum. [b] Standard errors are given in parentheses in units of the last digit. [c] Values in square brackets were kept fixed in the fit.

Table S5. Rotational parameters, electric dipole moment components and energies for the most stable 15-crown-5 ether - water conformers obtained from ab initio MP2/6-311++G(d,p) calculations.

conformer	15C5-w-1	15C5-w-2	15C5-w-3	15C5-w-4	15C5-w-5	15C5-w-6	15C5-w-7	15C5-w-8	15C5-w-9
	15C5-w-B		15C5-w-C						
A/MHz[a]	561.3	572.5	516.8	562.8	658.8	580.1	534.9	535.6	569.5
B/MHz	452.3	465.5	480.5	471.5	395.5	435.4	460.5	447.7	441.1
C/MHz	290.0	300.7	281.9	327.5	287.6	300.1	281.7	287.9	285.9
κ	0.20	0.2	0.7	0.2	-0.4	0.0	0.4	0.3	0.1
P_{aa}/uÅ^2	979.5	941.8	933.5	858.6	1134.1	986.6	973.4	970.4	1013.1
P_{bb}/uÅ^2	763.3	738.8	859.5	684.6	623.3	697.3	820.9	785.3	754.8
P_{cc}/uÅ^2	137.0	143.9	118.4	213.3	143.8	174.0	124.0	158.4	132.6
μ_a/D	0.7	-0.6	0.2	-1.5	-0.9	0.3	-0.2	0.4	-1.7
μ_b/D	1.0	2.8	-0.6	-0.7	2.5	1.6	0.0	2.2	2.1
μ_c/D	2.9	-2.9	-1.5	-4.1	-3.9	-2.3	-4.0	3.6	-1.1
μ_T/D	3	4.1	1.6	4.4	4.8	2.8	4.0	4.2	2.9
E/Hartree	-843.545929	-843.545724	-843.545504	-843.545413	-843.544986	-843.544870	-843.544678	-843.544434	-843.5443045
ΔE/kJmol^{-1}	0.0	0.5	1.1	1.3	2.5	2.8	3.3	3.9	4.3

[a] A, B and C are the rotational constants. κ is the Ray's asymmetry parameter ($-1 < \kappa = (2B - A - C)/(A - C) < 1$). $P_{\alpha\alpha}$ ($\alpha = a$, b or c) are the planar moments of inertia derived from the inertial moments I_α ($P_{cc} = (I_a + I_b - I_c)/2$); μ_T, μ_a , μ_b *and* μ_c are the electric dipole moment (in Debye) and its components along the principal inertial axes; ΔE are the calculated electronic energies relative to the global minimum.

Table S6. Rotational parameters, electric dipole moment components and energies for the most stable 15-crown-5 ether – water$_2$ conformers obtained from ab initio MP2/6-311++G(d,p) calculations.

	15C5-w$_2$-1	15C5-w$_2$-2	15C5-w$_2$-3	15C5-w$_2$-4	15C5-w$_2$-5	15C5-w$_2$-6	15C5-w$_2$-7	15C5-w$_2$-8
	15c5-w$_2$-D					15c5-w$_2$-E		
A/MHz[a]	474.1	477.0	440.4	431.8	452.0	417.9	458.0	430.9
B/MHz	434.7	446.6	406.9	392.9	388.6	410.9	363.6	409.5
C/MHz	279.9	280.4	288.3	267.8	266.3	262.3	271.4	268.2
κ	0.6	0.7	0.6	0.5	0.3	0.9	0.0	0.7
P_{aa}/uÅ^2	950.9	937.2	923.8	1001.8	1040.0	973.7	1074.2	972.8
P_{bb}/uÅ^2	854.4	865.1	829.3	885.7	857.6	953.1	787.7	911.5
P_{cc}/uÅ^2	211.6	194.4	318.2	284.7	260.4	256.1	315.9	261.3
μ_a/D	0.3	0.0	-0.7	-2.4	1.8	-0.8	1.6	0.7
μ_b/D	0.2	0.1	1.2	1.5	2.1	2.4	-1.3	2.7
μ_c/D	1.3	0.0	-1.5	-3.0	-6.0	-2.9	-2.6	-6.1
μ_T/D	1.3	0.1	2.1	4.1	6.6	3.8	3.3	6.7
E/Hartree	-919.8440207	-919.8440167	-919.8399194	-919.8395035	-919.8393076	-919.8392755	-919.8391265	-919.8391204
ΔE/kJmol^{-1}	0.0	0.0	10.8	11.9	12.4	12.5	12.8	12.9

[a] A, B and C are the rotational constants. κ is the Ray's asymmetry parameter ($-1<\kappa=(2B-A-C)/(A-C)<1$); $P_{\alpha\alpha}$ (α= a, b or c) are the planar moments of inertia derived from the inertial moments I_α ($P_{cc}=(I_a+I_b-I_c)/2$); μ_T μ_a , μ_b *and* μ_c are the electric dipole moment (in Debye) and its components along the principal inertial axes: E are the calculated electronic energies and ΔE the energies relative to the global minimum.

Table S7. Comparison of the r_s determined coordinates (Å) for the oxygen atom of water (O36) of the 15c5-w-B conformer with the ab initio coordinates and the complete ab initio structure of the 15C5−w−1 form. In the figure the r_s position of water oxygen and the ab initio structure are compared.

O36	a	b	c
$\|r_s\|$	0.239i(6)	0.156i(9)	2.08816 (73)
ab	0.036	-0.013	-2.047

ab initio MP2/6-311++G(d,p)

	a	b	c		a	b	c
C1	-2.762	1.038	0.529	H20	-2.482	-2.057	-1.752
C2	-3.361	-0.288	0.104	H21	-1.328	-0.722	-1.427
O3	-2.441	-1.365	0.205	H22	-0.236	-2.937	-1.715
C4	-1.774	-1.636	-1.020	H23	-1.078	-3.530	-0.251
C5	-0.676	-2.638	-0.752	H24	1.639	-3.506	0.585
O6	0.299	-2.001	0.052	H25	1.833	-2.831	-1.062
C7	1.586	-2.586	-0.018	H26	3.579	-2.024	0.557
C8	2.578	-1.568	0.499	H27	2.273	-1.236	1.499
O9	2.561	-0.479	-0.407	H28	4.192	0.780	-0.124
C10	3.116	0.720	0.098	H29	2.974	0.787	1.185
C11	2.385	1.870	-0.562	H30	2.927	2.814	-0.397
O12	1.090	1.939	0.010	H31	2.316	1.680	-1.642
C13	0.192	2.765	-0.711	H32	0.533	3.812	-0.688
C14	-1.166	2.658	-0.054	H33	0.126	2.435	-1.758
O15	-1.727	1.398	-0.375	H34	-1.042	2.757	1.033
H16	-3.559	1.801	0.524	H35	-1.818	3.470	-0.412
H17	-2.348	0.948	1.542	O36	0.080	0.149	2.031
H18	-4.194	-0.517	0.779	H37	0.402	0.693	1.299
H19	-3.756	-0.214	-0.919	H38	-0.204	-0.645	1.560

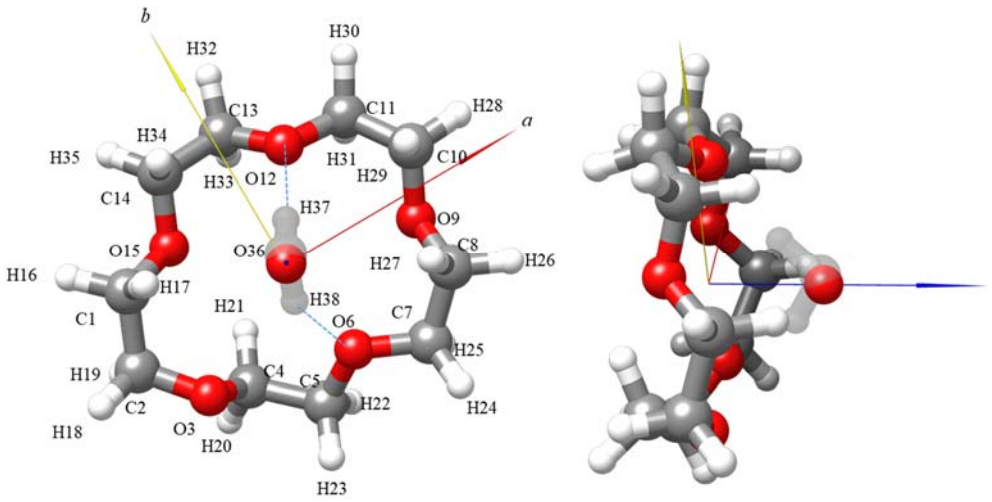

Table S8. Comparison of the r_s determined coordinates (Å) for the oxygen atom of water (O36) of the 15c5-w-C conformer and the complete ab initio structure of the 15C5−w−3 form. In the figure the r_s position of water oxygen and the ab initio structure are compared.

O36	a	b	c
$\|r_s\|$	0.3455(50)	0.2568(68)	2.03291(85)
ab	-0.208	0.128	1.967

ab initio MP2/6-311++G(d,p)

	a	b	c		a	b	c
C1	2.870	1.250	-0.035	H20	1.970	-2.745	-1.558
C2	2.978	-0.236	0.225	H21	3.024	-2.709	-0.122
O3	2.270	-0.898	-0.806	H22	0.954	-2.098	1.260
C4	2.113	-2.288	-0.575	H23	0.933	-3.715	0.492
C5	0.919	-2.629	0.298	H24	-1.654	-3.697	0.148
O6	-0.255	-2.264	-0.406	H25	-1.337	-2.420	1.359
C7	-1.435	-2.625	0.284	H26	-3.538	-2.204	0.018
C8	-2.563	-1.790	-0.280	H27	-2.492	-1.789	-1.375
O9	-2.412	-0.471	0.224	H28	-4.100	0.538	-0.450
C10	-3.006	0.537	-0.574	H29	-2.765	0.373	-1.633
C11	-2.435	1.868	-0.136	H30	-3.011	2.688	-0.595
O12	-1.084	1.906	-0.551	H31	-2.505	1.954	0.958
C13	-0.366	2.991	0.002	H32	-0.722	3.949	-0.409
C14	1.092	2.804	-0.355	H33	-0.479	3.010	1.095
O15	1.571	1.672	0.350	H34	1.185	2.640	-1.437
H16	3.632	1.799	0.537	H35	1.659	3.706	-0.077
H17	3.028	1.429	-1.107	O36	-0.208	0.128	1.967
H18	4.038	-0.539	0.216	H37	-0.920	-0.080	1.347
H19	2.558	-0.459	1.215	H38	0.403	0.617	1.398

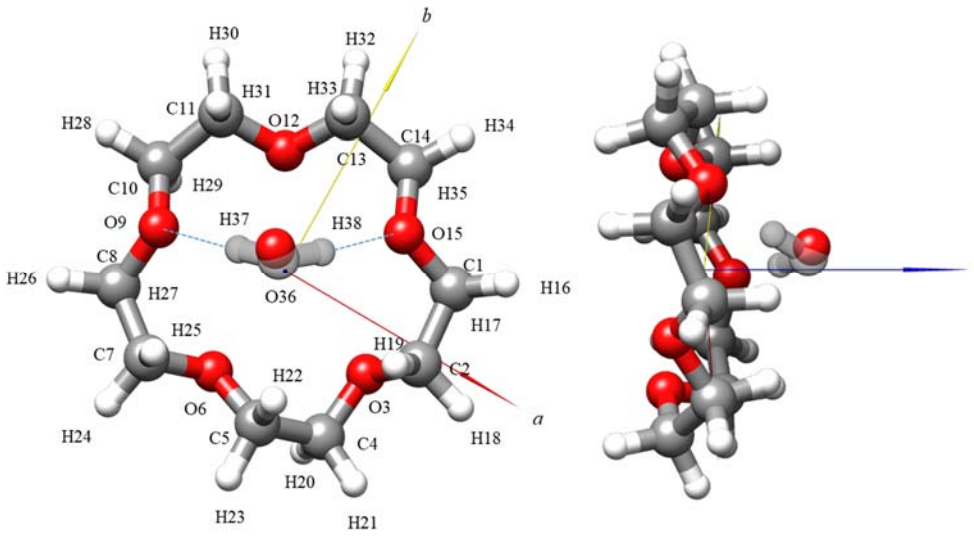

Table S9. Comparison of the r_s determined coordinates (Å) for the oxygen atoms of water (O36 and O39) of the 15c5-w_2-D conformer and the complete ab initio structure of 15C5−w_2−1 form. In the figure the r_s position of water oxygen and the ab initio structure are compared.

O36	a	b	c	O39	a	b	c
$\|r_s\|$	0.1825(90)	0.019(86)	2.24482(73)	$\|r_s\|$	0.2475(64)	0.087i(18)	2.27481(70)
ab	-0.291	0.061	-2.162	ab	0.042	-0.442	2.261

ab initio MP2/6-311++G(d,p)

	a	b	c		a	b	c
C1	1.859	-2.376	-0.054	H22	1.840	1.439	-1.492
C2	2.738	-1.188	-0.378	H23	2.573	2.889	-0.740
O3	2.522	-0.198	0.616	H24	0.328	4.032	-0.097
C4	3.062	1.073	0.277	H25	-0.060	2.867	-1.397
C5	2.097	1.915	-0.536	H26	-2.020	3.577	0.133
O6	0.930	2.076	0.249	H27	-1.214	2.591	1.398
C7	0.013	2.998	-0.308	H28	-3.861	1.538	0.267
C8	-1.339	2.732	0.317	H29	-2.717	0.934	1.506
O9	-1.854	1.547	-0.275	H30	-4.034	-0.886	0.303
C10	-2.937	0.964	0.430	H31	-3.150	-0.431	-1.188
C11	-3.105	-0.447	-0.091	H32	-2.577	-3.145	-0.022
O12	-1.976	-1.187	0.342	H33	-1.849	-2.279	-1.411
C13	-1.801	-2.426	-0.324	H34	-0.301	-3.963	-0.362
C14	-0.438	-2.958	0.066	H35	-0.356	-3.012	1.159
O15	0.533	-2.059	-0.445	O36	-0.291	0.061	-2.162
H16	2.213	-3.265	-0.599	H37	-0.804	0.581	-1.528
H17	1.899	-2.572	1.025	H38	0.041	-0.652	-1.599
H18	3.795	-1.496	-0.374	O39	0.042	-0.442	2.261
H19	2.483	-0.813	-1.378	H40	0.820	-0.159	1.763
H20	3.262	1.577	1.227	H41	-0.607	-0.564	1.557
H21	4.011	0.958	-0.267				

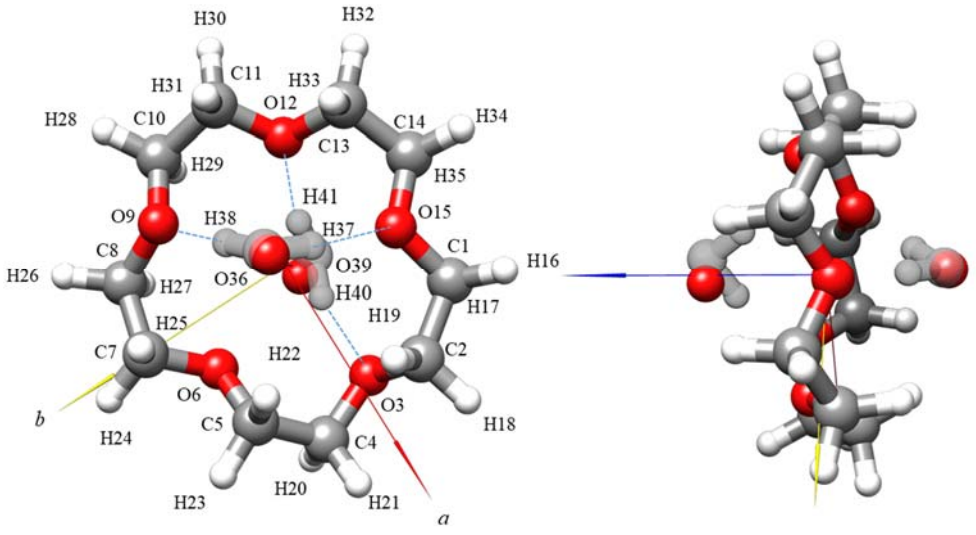

Table S10. Comparison of the r_s determined coordinates (Å) for the oxygen atom of water (O36) of the 15C5-w_2-E rotamer with the ab initio coordinates (O36 and O39) and the complete ab initio structure of the form 15C5−w_2−6. In the figure the r_s position of water oxygen and the ab initio structure are compared.

O36	a	b	c	O39	a	b	c
$\|r_s\|$	0.1825(90)	0.019(86)	2.24482(73)				
ab	-0.291	0.061	-2.162	ab	0.042	-0.442	2.261

ab initio MP2/6-311++G(d,p)

	a	b	c		a	b	c
C1	-1.322	2.423	-0.720	H22	-2.129	-1.479	-1.587
C2	-2.437	1.415	-0.889	H23	-3.169	-2.633	-0.716
O3	-2.454	0.533	0.229	H24	-1.044	-4.123	0.090
C4	-3.256	-0.628	0.063	H25	-0.487	-3.143	-1.290
C5	-2.494	-1.770	-0.592	H26	1.310	-3.996	0.378
O6	-1.405	-2.090	0.252	H27	0.676	-2.736	1.477
C7	-0.590	-3.163	-0.197	H28	3.476	-2.440	0.229
C8	0.785	-3.029	0.425	H29	2.573	-1.399	1.365
O9	1.502	-2.038	-0.294	H30	4.246	-0.175	-0.132
C10	2.722	-1.639	0.304	H31	3.194	-0.600	-1.509
C11	3.212	-0.406	-0.428	H32	3.184	2.343	-1.027
O12	2.350	0.676	-0.106	H33	2.189	1.296	-2.077
C13	2.278	1.721	-1.068	H34	1.065	2.897	0.272
C14	1.059	2.570	-0.775	H35	1.084	3.464	-1.419
O15	-0.094	1.787	-1.051	O36	0.197	0.198	1.670
H16	-1.500	3.273	-1.397	H37	0.845	0.301	0.952
H17	-1.305	2.794	0.312	H38	-0.615	-0.064	1.210
H18	-3.403	1.938	-0.956	O39	-0.078	2.833	2.397
H19	-2.276	0.863	-1.825	H40	-0.003	1.863	2.244
H20	-3.557	-0.934	1.068	H41	-0.095	2.942	3.351
H21	-4.164	-0.403	-0.515				

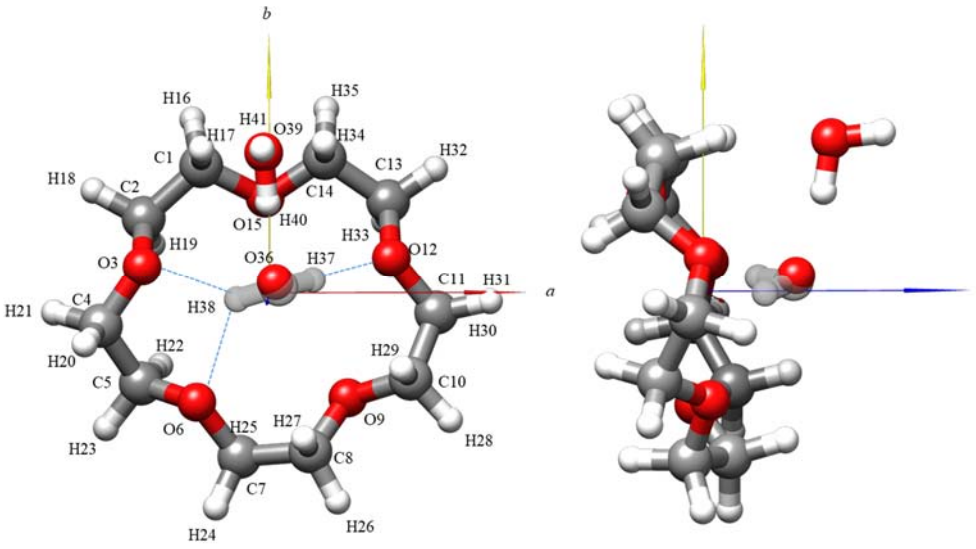

Table S11. Observed frequencies (MHz) for 15C5 crown ether form 0.

J	K_a	K_c	←	J	K_a	K_c	obs.	o-c	J	K_a	K_c	←	J	K_a	K_c	obs.	o-c
2	1	1		1	0	1	2261.6140	0.0031	5	4	2		4	3	2	5781.7337	0.0060
3	1	3		2	1	2	2272.6985	0.0008	6	3	3		5	3	2	5810.0237	0.0023
2	2	0		1	1	0	2313.4336	0.0016	5	5	1		4	4	0	5819.2047	-0.0040
2	2	1		1	1	1	2352.3104	-0.0031	5	5	0		4	4	0	5869.7256	0.0032
4	0	4		3	0	3	2955.6552	-0.0063	5	5	1		4	4	1	5903.6647	-0.0045
3	2	1		2	1	1	3396.7885	0.0016	7	2	5		6	3	4	5938.3850	-0.0086
4	1	3		3	2	2	3410.7491	-0.0133	7	3	5		6	3	4	5938.5837	-0.0012
4	2	3		3	2	2	3414.8065	0.0040	7	2	5		6	2	4	5940.3162	0.0007
4	1	3		3	1	2	3442.2840	-0.0002	7	3	5		6	2	4	5940.5130	0.0061
4	2	3		3	1	2	3446.3225	-0.0016	5	5	0		4	4	1	5954.1823	-0.0005
3	3	0		2	2	0	3485.4949	0.0038	6	5	1		5	5	0	6137.3814	-0.0004
3	3	1		2	2	1	3532.2592	0.0013	8	2	7		7	2	6	6146.4396	-0.0019
5	1	5		4	1	4	3635.2230	0.0010	6	4	2		5	4	1	6203.1968	-0.0052
4	2	2		3	2	1	3950.7277	-0.0028	9	0	9		8	1	8	6354.7803	-0.0018
5	2	4		4	2	3	4105.6150	-0.0004	7	3	4		6	4	3	6392.2373	-0.0053
5	1	4		4	1	3	4109.2657	-0.0001	7	4	4		6	4	3	6399.1372	0.0007
4	3	1		3	3	0	4138.0387	-0.0037	7	3	4		6	3	3	6437.6062	-0.0032
4	3	1		3	2	1	4538.0375	0.0033	7	4	4		6	3	3	6444.5108	0.0074
5	3	3		4	3	2	4546.4197	-0.0041	6	5	2		5	4	1	6544.8570	-0.0010
4	2	2		3	1	2	4560.9429	-0.0010	8	3	6		7	3	5	6618.5773	0.0089
4	4	1		3	3	0	4587.5170	-0.0028	7	5	3		6	5	2	6764.0576	-0.0087
4	3	2		3	2	2	4618.9739	0.0047	6	4	2		5	3	2	6799.4284	0.0021
5	2	3		4	2	2	4620.1906	0.0018	9	2	8		8	2	7	6826.2817	-0.0036
4	4	0		3	3	0	4671.9815	0.0009	6	5	1		5	4	1	6852.3970	0.0048
4	4	1		3	3	1	4715.9863	-0.0004	6	3	3		5	2	3	6869.5617	-0.0002
6	1	5		5	1	4	4787.0920	0.0046	6	2	4		5	1	4	6897.7936	0.0019
4	4	0		3	3	1	4800.4308	-0.0165	6	4	3		5	3	3	6899.1449	-0.0019
5	3	2		4	3	1	5092.4256	0.0000	6	3	4		5	2	4	6899.3186	-0.0053
5	4	1		4	4	0	5154.7075	-0.0044	6	1	5		5	0	5	6904.5354	0.0025
6	3	4		5	3	3	5254.3414	-0.0075	6	2	5		5	1	5	6904.5354	0.0025
6	2	4		5	2	3	5268.2106	0.0015	6	5	2		5	4	2	6949.5425	0.0053
6	3	4		5	2	3	5270.1365	0.0055	7	4	3		6	4	2	6999.9873	0.0044
5	4	2		4	3	1	5283.9717	0.0008	10	0	10		9	1	9	7034.6770	0.0074
7	1	6		6	2	5	5466.6257	0.0091	6	6	0		5	5	0	7072.4661	-0.0139
6	4	3		5	4	2	5663.8370	-0.0061	8	4	5		7	4	4	7090.6392	0.0001
8	0	8		7	1	7	5674.8913	-0.0025	6	6	1		5	5	1	7094.8883	-0.0117
5	3	2		4	2	2	5679.7291	-0.0002	8	3	5		7	3	4	7096.7148	-0.0011
5	4	1		4	3	1	5688.6555	0.0055	7	5	2		6	5	1	7277.3287	0.0009
5	2	3		4	1	3	5738.8527	0.0042	9	2	7		8	2	6	7298.2130	-0.0038
5	3	3		4	2	3	5750.5937	0.0032	9	2	7		8	3	6	7298.2126	0.0060
5	1	4		4	0	4	5752.7010	0.0074	9	3	7		8	3	6	7298.2126	0.0060
5	2	4		4	1	4	5753.0445	0.0048	9	3	7		8	2	6	7298.2126	0.0060
8	3	5		7	3	4	7096.7148	-0.0011	7	6	2		6	5	1	7815.3835	-0.0019

Table S11. (Continued).

J	K_a	K_c	←	J	K_a	K_c	obs.	o-c	J	K_a	K_c	←	J	K_a	K_c	obs.	o-c
7	5	2		6	5	1	7277.3287	0.0009	8	6	3		7	6	2	7845.1605	0.0077
9	2	7		8	2	6	7298.2130	-0.0038	7	5	2		6	4	2	7926.5264	0.0085
9	2	7		8	3	6	7298.2126	0.0060	10	3	8		9	3	7	7977.9003	-0.0051
9	3	7		8	3	6	7298.2126	0.0060	7	4	3		6	3	3	7989.3837	-0.0041
9	3	7		8	2	6	7298.2126	0.0060	5	3	3		4	2	2	4635.9761	0.0052
10	1	9		9	1	8	7506.1461	0.0020	6	2	5		5	2	4	4786.7291	-0.0008
8	5	4		7	5	3	7536.7927	-0.0088	6	1	5		5	1	4	4787.0920	0.0046
11	0	11		10	1	10	7714.5510	-0.0043	5	4	1		4	4	0	5154.7075	-0.0044
9	4	6		8	4	5	7771.2673	0.0046	7	5	3		6	4	2	7105.7227	0.0003

Table S12. New observed frequencies (MHz) for 15C5 crown ether form I.

J	K_a	K_c	←	J	K_a	K_c	obs.	o-c	J	K_a	K_c	←	J	K_a	K_c	obs.	o-c
3	1	3		2	0	2	2278.089	-0.002	8	4	5		8	3	6	3212.536	-0.001
2	2	1		1	1	0	2724.253	0.001	8	1	7		8	0	8	3311.773	0.009
4	1	4		3	0	3	2817.003	0.003	9	5	4		9	4	5	3677.041	0.008
5	1	5		4	0	4	3362.986	0.001	10	3	8		10	2	9	3772.549	-0.002
4	2	3		3	1	2	3880.796	0.014	11	4	8		11	3	9	3797.895	0.001
6	1	6		5	0	5	3929.180	0.004	10	4	7		10	3	8	3538.169	0.000
5	2	4		4	1	3	4378.778	0.009	10	5	5		10	4	6	3469.602	0.006
3	3	1		2	2	0	4385.529	0.003	7	5	2		7	4	3	3900.822	0.000
7	1	7		6	0	6	4513.624	0.008	9	2	8		9	1	9	3900.974	0.004
6	2	5		5	1	4	4843.201	0.006	9	5	5		9	4	6	3914.045	-0.002
4	3	2		3	2	1	5061.736	0.005	8	5	4		8	4	5	3920.477	0.002
8	1	8		7	0	7	5109.588	0.006	10	5	6		10	4	7	3932.321	0.015
7	2	6		6	1	5	5301.597	0.007	7	5	3		7	4	4	3938.246	0.002
5	3	3		4	2	2	5670.848	0.004	6	5	1		6	4	2	3946.875	0.000
9	1	9		8	0	8	5711.678	0.005	6	5	2		6	4	3	3957.672	0.003
8	2	7		7	1	6	5782.505	0.005	11	3	9		11	2	10	4198.188	0.001
4	4	1		3	3	0	6010.112	0.006	10	6	4		10	5	5	4700.808	-0.003
6	3	4		5	2	3	6201.526	0.006	11	6	6		11	5	7	4723.383	0.004
9	2	8		8	1	7	6300.886	0.007	9	6	3		9	5	4	4770.978	-0.002
10	1	10		9	0	9	6316.738	0.007	9	6	4		9	5	5	4790.995	-0.011
7	3	5		6	2	4	6660.629	0.003	8	6	2		8	5	3	4814.554	0.000
5	4	2		4	3	1	6727.236	0.008	8	6	3		8	5	4	4820.581	0.002
10	2	9		9	1	8	6854.303	0.004	11	1	10		11	0	11	4827.906	-0.001
11	1	11		10	0	10	6923.164	0.010	7	6	1		7	5	2	4841.850	0.005
8	3	6		7	2	5	7065.586	0.007	7	6	2		7	5	3	4843.284	-0.004
6	4	3		5	3	2	7417.715	0.008	11	2	10		11	1	11	4844.076	-0.002
11	2	10		10	1	9	7432.147	0.002	6	6	0		6	5	1	4858.926	0.010
9	3	7		8	2	6	7441.373	0.003	6	6	1		6	5	2	4859.172	0.009
12	1	12		11	0	11	7530.192	0.004	13	2	11		13	1	12	5054.076	-0.010
5	5	1		4	4	0	7625.147	0.001	13	3	11		13	2	12	5117.558	-0.020
5	5	0		4	4	1	7625.435	0.011	12	2	11		12	1	12	5322.070	-0.006
10	3	8		9	2	7	7819.876	0.009	11	7	4		11	6	5	5636.334	0.003
5	3	3		5	2	4	2394.705	0.001	11	7	5		11	6	6	5646.590	0.009
6	3	4		6	2	5	2548.732	0.003	10	7	3		10	6	4	5679.388	0.005
7	4	3		7	3	4	2760.227	0.004	9	7	2		9	6	3	5709.550	0.007
7	3	5		7	2	6	2765.451	0.003	9	7	3		9	6	4	5710.362	-0.003
6	4	2		6	3	3	2923.114	0.003	8	7	1		8	6	2	5730.681	0.008
5	4	1		5	3	2	3024.448	0.009	8	7	2		8	6	3	5730.848	0.005
4	4	0		4	3	1	3075.492	-0.004	9	8	1		9	7	2	6617.945	0.008
5	4	2		5	3	3	3089.570	0.007	8	8	0		8	7	1	6631.124	0.002
6	4	3		6	3	4	3099.182	0.005	3	0	3		2	0	2	2082.015	0.001
7	4	4		7	3	5	3135.246	0.000	3	1	2		2	1	1	2318.050	0.003
4	1	4		3	1	3	2620.919	-0.004	8	2	6		7	2	5	6125.175	0.006

Table S12. (Continued 1).

J	K_a	K_c	←	J	K_a	K_c	obs.	o-c	J	K_a	K_c	←	J	K_a	K_c	obs.	o-c
4	0	4		3	0	3	2704.401	0.007	9	1	8		8	1	7	6229.195	0.001
4	2	2		3	2	1	3046.138	0.001	10	1	10		9	1	9	6314.351	0.008
4	1	3		3	1	2	3059.432	0.001	10	0	10		9	0	9	6315.737	0.009
5	1	5		4	1	4	3250.383	0.004	9	3	7		8	3	6	6500.964	0.003
5	2	4		4	2	3	3557.410	-0.008	9	7	3		8	7	2	6575.936	0.011
5	3	3		4	3	2	3655.254	0.002	9	7	2		8	7	1	6575.936	-0.005
5	1	4		4	1	3	3767.472	0.004	9	6	4		8	6	3	6596.408	0.006
5	2	3		4	2	2	3855.250	0.007	9	5	5		8	5	4	6625.979	0.003
6	1	6		5	1	5	3871.075	0.007	9	4	6		8	4	5	6632.403	0.000
6	0	6		5	0	5	3901.335	0.001	9	5	4		8	5	3	6640.657	0.013
6	2	5		5	2	4	4231.892	-0.001	9	4	5		8	4	4	6780.853	-0.005
6	3	4		5	3	3	4385.921	0.003	10	2	9		9	2	8	6782.614	-0.001
6	4	3		5	4	2	4395.535	0.004	9	2	7		8	2	6	6792.190	0.004
6	4	2		5	4	1	4404.325	0.014	10	1	9		9	1	8	6819.152	0.008
6	1	5		5	1	4	4431.422	0.006	11	1	11		10	1	10	6922.163	0.010
7	1	7		6	1	6	4485.777	0.002	11	0	11		10	0	10	6922.750	0.009
7	0	7		6	0	6	4500.937	0.005	9	3	6		8	3	5	6983.622	0.006
6	3	3		5	3	2	4505.646	0.008	10	3	8		9	3	7	7170.687	0.003
6	2	4		5	2	3	4647.426	0.001	10	6	4		9	6	3	7351.309	0.004
7	2	6		6	2	5	4889.812	0.001	10	4	7		9	4	6	7364.882	0.008
7	1	6		6	1	5	5051.432	0.006	10	5	6		9	5	5	7383.140	0.008
8	1	8		7	1	7	5096.903	0.004	10	2	8		9	2	7	7409.816	0.007
8	0	8		7	0	7	5104.008	0.002	11	1	10		10	1	9	7415.567	0.006
7	3	5		6	3	4	5106.531	0.001	12	1	12		11	1	11	7529.784	0.010
7	5	3		6	5	2	5123.176	0.001	12	0	12		11	0	11	7530.022	0.003
7	5	2		6	5	1	5124.389	-0.005	10	4	6		9	4	5	7628.915	0.005
7	4	4		6	4	3	5142.607	0.007	10	3	7		9	3	6	7761.284	0.007
7	4	3		6	4	2	5170.457	0.009	11	3	9		10	3	8	7822.636	0.011
7	3	4		6	3	3	5333.342	0.006	11	2	9		10	2	8	7994.191	0.014
7	2	5		6	2	4	5407.599	0.005	4	2	2		3	1	2	4162.066	0.005
8	2	7		7	2	6	5532.340	0.004	5	2	3		4	1	3	4957.882	0.010
8	1	7		7	1	6	5643.765	0.005	4	3	2		3	2	2	5163.890	0.000
9	1	9		8	1	8	5706.104	0.008	5	3	2		4	2	2	5738.242	0.009
9	0	9		8	0	8	5709.291	0.006	6	2	4		5	1	4	5837.834	0.005
8	7	2		7	7	1	5834.973	0.008	5	3	3		4	2	3	5952.127	0.004
8	6	3		7	6	2	5849.367	0.007	4	4	0		3	3	0	6010.362	0.001
8	6	2		7	6	1	5849.498	-0.008	4	4	1		3	3	1	6012.677	0.005
8	5	4		7	5	3	5872.074	0.005	6	1	5		5	0	5	6122.867	0.017
8	5	3		7	5	2	5876.798	0.001	6	3	3		5	2	3	6388.633	0.005
8	4	5		7	4	4	5889.838	0.000	6	2	5		5	1	5	6476.531	0.010
8	4	4		7	4	3	5960.378	0.005	5	4	1		4	3	1	6729.500	0.009
9	2	8		8	2	7	6162.146	0.008	5	4	2		4	3	2	6744.827	0.012
8	3	5		7	3	4	6168.014	0.001	6	3	4		5	2	4	6780.621	-0.002

Table S12. (Continued 2).

J	K_a	K_c	←	J	K_a	K_c	obs.	o-c	J	K_a	K_c	←	J	K_a	K_c	obs.	o-c
6	4	2		5	3	2	7428.761	0.011	11	4	7		10	5	6	5074.910	0.000
6	4	3		5	3	3	7485.095	0.000	7	6	2		6	6	1	5107.299	-0.001
8	3	5		7	2	5	7834.967	0.009	15	4	12		15	3	13	5363.401	-0.016
8	2	6		7	1	6	7887.757	0.007	8	1	7		7	2	6	5393.600	0.005
9	4	5		9	3	6	2349.818	-0.006	13	7	6		13	6	7	5481.602	-0.009
4	0	4		3	1	3	2508.324	0.007	14	7	8		14	6	9	5504.855	-0.010
9	4	6		8	5	3	2705.739	0.007	10	2	8		9	3	6	5508.606	0.015
13	4	9		13	3	10	2714.515	-0.004	18	6	13		18	5	14	5506.426	0.003
13	5	8		13	4	9	2762.977	0.000	12	7	5		12	6	6	5573.950	0.005
6	2	4		5	3	3	2831.818	-0.006	12	7	6		12	6	7	5602.801	0.001
2	2	0		1	1	1	2858.988	0.007	10	3	7		9	4	6	5669.339	0.007
5	1	4		4	2	3	2946.127	0.009	10	7	3		10	6	4	5679.388	0.005
12	5	7		12	4	8	2952.122	0.002	10	7	4		10	6	5	5682.551	0.002
7	2	6		7	1	7	3009.486	-0.004	9	0	9		8	1	8	5703.714	0.006
5	0	5		4	1	4	3192.275	0.004	7	7	1		7	6	2	5745.236	-0.001
11	5	6		11	4	7	3211.142	0.004	7	7	0		7	6	2	5745.236	-0.001
9	4	6		9	3	7	3343.972	-0.007	9	2	7		8	3	6	5851.783	0.005
9	3	7		9	2	8	3384.472	-0.010	4	4	0		3	3	1	6012.933	0.006
8	3	5		7	4	4	3446.687	0.007	5	3	2		4	2	3	6019.514	0.003
8	5	3		8	4	4	3817.240	-0.006	9	1	8		8	2	7	6090.462	0.008
6	0	6		5	1	5	3843.229	0.003	15	5	11		14	6	8	6152.494	0.000
7	2	5		6	3	4	3853.503	0.004	12	4	8		11	5	7	6256.952	-0.006
5	2	3		4	2	2	3855.250	0.007	14	1	13		14	1	14	6279.605	-0.007
5	5	0		5	4	1	3971.167	-0.007	10	0	10		9	1	9	6313.349	0.008
5	5	1		5	4	2	3973.411	-0.003	14	8	6		14	7	7	6440.130	0.000
11	5	7		11	4	8	3990.182	0.004	14	8	7		14	7	8	6454.538	0.005
11	4	8		10	5	5	4090.853	0.014	13	8	5		13	7	6	6498.613	-0.003
3	3	0		2	2	0	4388.105	0.013	13	8	6		13	7	7	6503.701	-0.006
3	3	0		2	2	1	4409.441	0.004	12	8	4		12	7	5	6542.238	0.008
12	6	6		12	5	7	4414.459	-0.004	12	8	5		12	7	6	6543.812	-0.018
7	0	7		6	1	6	4473.091	0.001	11	8	4		11	7	5	6575.496	0.001
12	2	10		12	1	11	4527.736	0.000	11	8	3		11	7	5	6575.496	-0.011
11	6	5		11	5	6	4588.253	0.002	9	6	3		8	6	2	6597.079	0.008
14	3	11		14	2	12	4590.878	0.007	9	6	3		8	6	2	6597.079	0.008
7	1	6		6	2	5	4639.649	0.001	10	8	3		10	7	3	6599.693	-0.003
12	3	10		12	2	11	4649.780	0.000	10	8	2		10	7	3	6599.693	-0.005
12	6	7		12	5	8	4700.476	-0.005	10	8	3		10	7	4	6599.808	0.010
13	6	8		13	5	9	4701.208	-0.001	10	8	2		10	7	4	6599.808	0.009
14	6	9		14	5	10	4740.533	-0.004	5	4	1		4	3	2	6747.087	0.009
10	6	5		10	5	6	4756.762	0.012	10	1	9		9	2	8	6747.469	0.010
4	2	2		3	1	3	4839.797	0.007	10	2	8		9	3	7	6760.627	0.002
8	2	6		7	3	5	4872.146	0.007	11	3	8		10	4	7	6793.910	0.001
14	4	11		14	3	12	4914.373	0.004	11	0	11		10	1	10	6921.749	0.010

Table S12. (Continued 3).

J	K_a	K_c	←	J	K_a	K_c	obs.	o-c	J	K_a	K_c	←	J	K_a	K_c	obs.	o-c
17	3	15		17	2	16	7042.572	0.002	9	9	0		9	8	1	7516.857	0.009
9	4	5		9	1	8	7058.035	0.009	9	9	0		9	8	2	7516.857	0.009
15	9	7		15	8	8	7361.540	0.001	9	9	1		9	8	2	7516.857	0.009
11	1	10		10	2	9	7380.410	0.005	18	3	16		18	2	17	7525.926	0.016
11	2	10		10	2	9	7396.987	-0.002	12	0	12		11	1	11	7529.607	0.001
10	5	5		9	5	4	7421.473	-0.001	11	2	9		10	3	8	7584.128	0.008
6	4	2		5	3	3	7496.141	0.003	7	3	5		6	2	5	7655.250	-0.010
9	9	1		9	8	1	7516.857	0.009	12	3	9		11	4	8	7872.611	0.011

Table S13. New observed frequencies (MHz) for 15C5 crown ether form II.

J	K_a	K_c	←	J	K_a	K_c	obs.	o-c	J	K_a	K_c	←	J	K_a	K_c	obs.	o-c
4	2	3		3	2	2	3435.804	0.014	8	3	5		7	3	4	7125.841	0.004
4	1	3		3	1	2	3453.028	-0.001	9	3	7		8	3	6	7334.986	0.010
5	1	5		4	1	4	3655.799	0.011	9	2	7		8	2	6	7334.986	0.007
5	0	5		4	0	4	3655.799	-0.004	7	5	2		6	5	1	7381.529	-0.003
4	3	2		3	3	1	3813.370	0.005	10	2	9		9	2	8	7547.253	0.011
4	2	2		3	2	1	3968.090	0.005	10	1	9		9	1	8	7547.253	0.011
5	2	4		4	2	3	4126.810	0.007	8	5	4		7	5	3	7583.112	0.013
5	1	4		4	1	3	4128.546	-0.003	8	4	4		7	4	3	7627.884	0.007
4	3	1		3	3	0	4207.325	0.008	11	1	11		10	1	10	7759.791	0.006
6	1	6		5	1	5	4339.801	0.008	11	0	11		10	0	10	7759.791	0.006
6	0	6		5	0	5	4339.801	0.008	9	4	6		8	4	5	7807.475	0.013
5	3	3		4	3	2	4578.736	0.008	9	3	6		8	3	5	7807.684	0.010
5	2	3		4	2	2	4626.692	0.004	8	6	3		7	6	2	7941.325	-0.005
6	2	5		5	2	4	4811.375	0.009	3	3	0		2	1	1	3778.265	0.008
6	1	5		5	1	4	4811.496	-0.001	5	5	0		4	3	1	6305.967	0.008
5	4	2		4	4	1	4901.564	0.000	5	4	1		4	2	2	6313.232	-0.012
7	1	7		6	1	6	5023.782	-0.011									
7	0	7		6	0	6	5023.782	-0.011									
5	3	2		4	3	1	5128.525	0.002									
6	3	4		5	3	3	5281.228	0.003									
6	2	4		5	2	3	5287.967	0.002									
7	2	6		6	2	5	5495.345	0.013									
7	1	6		6	1	5	5495.345	0.004									
8	1	8		7	1	7	5707.801	0.007									
8	0	8		7	0	7	5707.801	0.007									
6	4	3		5	4	2	5712.189	0.005									
6	3	3		5	3	2	5812.213	0.001									
7	3	5		6	3	4	5967.261	0.006									
7	2	5		6	2	4	5967.903	0.004									
8	2	7		7	2	6	6179.299	0.009									
8	1	7		7	1	6	6179.299	0.008									
6	4	2		5	4	1	6268.114	0.010									
9	1	9		8	1	8	6391.802	0.008									
9	0	9		8	0	8	6391.802	0.008									
7	4	4		6	4	3	6433.912	0.012									
7	3	4		6	3	3	6453.136	0.001									
8	3	6		7	3	5	6651.175	0.023									
8	2	6		7	2	5	6651.175	-0.027									
7	5	3		6	5	2	6833.703	0.002									
9	2	8		8	2	7	6863.271	0.009									
9	1	8		8	1	7	6863.271	0.009									
7	4	3		6	4	2	7005.441	0.005									
8	4	5		7	4	4	7123.550	0.006									

Table S14. New observed frequencies (MHz) for 15C5 crown ether form III.

J	K_a	K_c	←	J	K_a	K_c	obs.	o-c	J	K_a	K_c	←	J	K_a	K_c	obs.	o-c
4	1	4		3	0	3	2607.826	-0.001	5	1	4		4	0	4	5145.402	0.001
3	2	2		2	1	1	2992.490	-0.014	5	3	2		4	2	2	5267.812	0.008
5	1	5		4	0	4	3146.264	0.005	4	4	1		3	3	1	5344.919	-0.001
4	2	3		3	1	2	3491.033	0.005	5	2	4		4	1	4	5353.222	0.007
6	1	6		5	0	5	3704.387	0.010	5	3	3		4	2	3	5570.864	0.009
3	3	1		2	2	0	3892.827	0.002	6	2	4		5	1	4	5942.076	0.005
5	2	4		4	1	3	3938.594	0.003	6	3	3		5	2	3	6013.478	-0.004
7	1	7		6	0	6	4272.326	0.004	5	4	2		4	3	2	6096.712	0.002
6	2	5		5	1	4	4381.466	0.005	6	1	5		5	0	5	6277.298	0.007
4	3	2		3	2	1	4525.397	0.009	6	2	5		5	1	5	6380.601	-0.002
8	1	8		7	0	7	4844.216	0.011	6	3	4		5	2	4	6470.641	0.003
7	2	6		6	1	5	4860.945	0.007	6	4	2		5	3	2	6721.861	0.009
5	3	3		4	2	2	5054.782	0.007	5	5	0		4	4	0	6761.674	0.005
4	4	1		3	3	0	5335.769	0.010	5	5	1		4	4	1	6762.973	0.006
8	2	7		7	1	6	5383.733	0.007	7	3	4		6	2	4	6865.863	0.009
9	1	9		8	0	8	5417.522	0.006	6	4	3		5	3	3	6873.488	0.006
6	3	4		5	2	3	5491.503	0.014	7	2	5		6	1	5	7064.620	0.008
7	3	5		6	2	4	5867.034	0.010	7	4	3		6	3	3	7367.235	0.011
9	2	8		8	1	7	5934.559	0.007	7	1	6		6	0	6	7389.327	0.009
5	4	2		4	3	1	6036.400	0.002	7	3	5		6	2	5	7427.637	0.002
8	3	6		7	2	5	6229.660	0.000	7	2	6		6	1	6	7433.855	0.003
10	2	9		9	1	8	6498.999	0.011	6	5	1		5	4	1	7491.367	0.009
9	3	7		8	2	6	6631.914	0.007	6	5	2		5	4	2	7502.126	0.006
6	4	3		5	3	2	6660.462	0.008	7	4	4		6	3	4	7690.946	0.012
5	5	1		4	4	0	6761.447	0.008	8	3	5		7	2	5	7844.397	0.011
11	2	10		10	1	9	7069.177	0.014	6	0	6		5	1	5	3686.900	0.004
10	3	8		9	2	7	7097.956	0.009	5	0	5		4	1	4	3097.868	0.002
12	1	12		11	0	11	7139.338	-0.002	3	1	3		2	0	2	2092.176	-0.006
7	4	4		6	3	3	7168.949	0.008	10	5	5		10	4	6	2126.472	0.000
6	5	2		5	4	1	7488.916	0.007	7	2	5		7	1	6	2252.690	0.016
8	4	5		7	3	4	7562.470	0.010	9	5	4		9	4	5	2342.991	0.010
11	3	9		10	2	8	7616.141	0.008	4	4	1		4	3	2	2389.116	0.015
12	2	11		11	1	10	7641.618	0.013	4	0	4		3	1	3	2486.611	-0.001
13	1	13		12	0	12	7713.414	0.011	7	5	2		7	4	3	2837.752	0.005
9	4	6		8	3	5	7874.732	0.012	8	2	6		8	1	7	2861.267	0.003
3	1	2		2	0	2	2967.995	0.013	8	3	6		7	4	3	2956.363	0.002
3	2	1		2	1	1	3196.164	0.000	6	5	1		6	4	2	2974.166	-0.013
3	3	0		2	2	0	3901.978	-0.009	7	5	3		7	4	4	3022.050	-0.007
4	2	2		3	1	2	4007.109	0.003	9	5	5		9	4	6	3127.155	0.008
4	1	3		3	0	3	4022.453	0.003	12	4	8		12	3	9	3233.310	-0.010
4	3	1		3	2	1	4585.713	0.012	10	6	4		10	5	5	3243.503	-0.001
4	3	2		3	2	2	4729.039	-0.009	5	1	4		4	2	3	3265.186	0.001
5	2	3		4	1	3	4917.748	0.007	14	5	9		14	4	10	3343.728	0.002

Table S14. (Continued 1).

J	K_a	K_c	←	J	K_a	K_c	obs.	o-c	J	K_a	K_c	←	J	K_a	K_c	obs.	o-c
9	2	7		9	1	8	3445.443	0.001	11	8	3		11	7	4	4974.538	0.002
9	6	3		9	5	4	3474.216	0.006	11	8	4		11	7	5	4985.336	0.001
10	4	7		10	3	8	3493.885	-0.005	10	8	2		10	7	3	5034.473	-0.013
8	6	2		8	5	3	3614.444	0.005	10	8	3		10	7	4	5037.078	-0.003
7	3	4		6	4	3	3628.772	-0.002	12	2	10		12	1	11	5038.777	-0.001
9	6	4		9	5	5	3633.871	0.006	9	8	2		9	7	2	5076.156	0.013
6	2	4		5	3	3	3636.395	-0.006	9	8	2		9	7	3	5076.646	0.009
11	6	6		11	5	7	3663.007	0.004	8	8	0		8	7	1	5105.354	-0.008
8	6	3		8	5	4	3667.579	-0.003	8	8	1		8	7	2	5105.427	0.001
7	6	1		7	5	2	3691.863	0.000	4	4	0		3	3	1	5346.448	0.001
7	6	2		7	5	3	3705.428	0.002	9	0	9		8	1	8	5416.914	0.004
11	3	8		11	2	9	3712.553	-0.002	8	2	6		7	3	5	5494.041	0.008
6	6	0		6	5	1	3734.244	0.007	13	2	11		13	1	12	5548.214	0.012
6	6	1		6	5	2	3736.660	0.006	13	3	11		13	2	12	5550.878	0.001
12	6	7		12	5	8	3775.622	-0.006	11	9	3		11	8	3	5726.114	0.014
10	5	6		9	6	3	3873.962	0.010	11	9	3		11	8	4	5726.606	0.001
12	5	8		12	4	9	3882.926	-0.005	16	4	12		16	3	13	5717.964	0.006
3	3	0		2	2	1	3947.187	-0.002	12	9	4		12	8	5	5679.165	-0.001
6	1	5		5	2	4	4021.948	0.004	12	9	3		12	8	4	5676.866	0.008
12	7	6		12	6	7	4205.813	-0.001	5	3	2		4	2	3	5783.891	0.008
13	7	7		13	6	8	4206.488	-0.006	9	3	6		8	4	5	5879.000	0.005
11	7	5		11	6	6	4243.725	0.009	9	1	8		8	2	7	5908.713	-0.014
10	7	3		10	6	4	4251.370	-0.007	10	0	10		9	1	9	5991.146	0.009
7	0	7		6	1	6	4266.382	-0.013	14	2	12		14	1	13	6054.603	0.007
14	7	8		14	6	9	4271.708	-0.003	14	3	12		14	2	13	6055.553	0.015
13	5	9		13	4	10	4294.090	0.007	5	4	1		4	3	2	6109.929	0.008
10	7	4		10	6	5	4296.542	0.000	8	3	6		7	2	5	6229.660	0.000
12	3	9		12	2	10	4305.539	-0.020	9	2	7		8	3	6	6255.566	0.006
9	7	2		9	6	3	4335.479	0.005	10	1	9		9	2	8	6489.704	0.010
9	7	3		9	6	4	4347.996	0.006	14	1	13		14	0	14	6662.711	0.002
8	7	1		8	6	2	4387.388	0.004	5	5	0		4	4	1	6763.202	0.006
12	4	9		12	3	10	4408.683	0.001	12	5	7		11	6	6	6803.929	0.007
7	7	0		7	6	1	4420.532	0.002	7	3	4		6	2	4	6865.863	0.009
7	7	1		7	6	2	4420.936	0.000	10	3	7		9	4	6	6890.184	0.009
11	2	9		11	1	10	4523.351	0.001	10	2	8		9	3	7	6926.868	0.001
8	3	5		7	4	3	4571.088	0.001	6	4	2		5	3	3	6934.886	0.006
9	4	5		8	5	4	4590.497	0.003	6	3	3		5	2	4	6992.641	0.010
7	2	5		6	3	4	4615.913	-0.005	11	4	7		10	5	6	7051.948	-0.004
7	1	6		6	2	5	4695.613	0.002	11	1	10		10	2	9	7065.956	0.005
4	3	1		3	2	2	4789.363	0.003	11	2	10		10	1	9	7069.177	0.014
8	0	8		7	1	7	4842.288	0.008	12	0	12		11	1	11	7139.338	0.015
13	4	10		13	3	11	4905.565	0.006	7	4	4		6	3	3	7168.949	0.007
12	8	4		12	7	5	4885.268	-0.006	5	3	3		4	0	4	7451.059	-0.013

Table S14. (Continued 2).

J	K_a	K_c	←	J	K_a	K_c	obs.	o-c	J	K_a	K_c	←	J	K_a	K_c	obs.	o-c
11	2	9		10	3	8	7544.906	0.004	13	1	13		12	0	12	7713.414	0.011
12	1	11		11	2	10	7640.542	0.014	11	3	8		10	4	7	7763.574	0.007
13	0	13		12	1	12	7713.414	0.016	7	4	3		6	3	4	7889.223	0.006

Table S15. New observed frequencies (MHz) for 15C5 crown ether form IV

J	K_a	K_c	←	J	K_a	K_c	obs.	o-c	J	K_a	K_c	←	J	K_a	K_c	obs.	o-c
4	0	4		3	1	3	2537.964	-0.002	9	3	7		8	2	6	6556.670	0.004
5	0	5		4	1	4	3139.776	0.006	11	1	11		10	0	10	6628.095	0.006
6	0	6		5	1	5	3726.723	0.003	10	3	8		9	2	7	7088.473	-0.003
7	0	7		6	1	6	4308.545	0.002	11	2	10		10	1	9	7131.510	0.013
7	1	6		6	2	5	4784.819	0.001	6	5	2		5	4	1	7204.425	0.001
8	0	8		7	1	7	4888.808	0.002	12	1	12		11	0	11	7207.798	0.005
9	0	9		8	1	8	5468.648	0.007	9	4	6		8	3	5	7518.358	0.006
9	0	9		8	1	8	5468.648	0.007	11	3	9		10	2	8	7648.534	0.013
9	1	8		8	2	7	5969.731	0.006	12	2	11		11	1	10	7710.682	0.009
10	1	9		9	2	8	6551.020	0.006	7	5	3		6	4	2	7889.855	0.001
11	0	11		10	1	10	6628.095	0.014	5	4	1		4	3	1	5832.393	0.003
10	2	8		9	3	7	7040.407	0.009	5	5	0		4	4	0	6460.393	0.004
11	1	10		10	2	9	7130.944	0.008	5	5	1		4	4	1	6463.213	0.007
12	0	12		11	1	11	7207.798	0.007	6	4	2		5	3	2	6523.689	0.006
11	2	9		10	3	8	7632.370	0.014	6	4	3		5	3	3	6732.191	0.003
13	0	13		12	1	12	7787.523	0.017	6	5	1		5	4	1	7211.462	0.008
3	1	3		2	0	2	2071.997	0.003	7	4	3		6	3	3	7233.493	-0.002
4	1	4		3	0	3	2604.429	-0.003	6	5	2		5	4	2	7233.785	-0.007
5	1	5		4	0	4	3161.524	0.000	7	5	2		6	4	2	7928.552	0.003
4	2	3		3	1	2	3394.113	0.010	3	1	3		2	0	2	2071.997	0.003
3	3	1		2	2	0	3720.431	0.008	6	4	3		6	3	4	2200.165	0.001
6	1	6		5	0	5	3733.167	0.001	4	0	4		3	1	3	2537.964	-0.002
5	2	4		4	1	3	3850.965	-0.004	4	1	4		3	0	3	2604.429	-0.003
7	1	7		6	0	6	4310.342	0.004	8	5	4		8	4	5	2685.735	-0.004
6	2	5		5	1	4	4327.122	0.006	7	6	1		7	5	2	3116.035	-0.005
4	3	2		3	2	1	4347.467	0.006	8	6	3		8	5	4	3117.273	0.002
7	2	6		6	1	5	4849.788	0.007	8	3	6		8	2	7	3132.226	-0.012
5	3	3		4	2	2	4859.743	0.002	5	0	5		4	1	4	3139.775	0.005
8	1	8		7	0	7	4889.289	0.003	7	6	2		7	5	3	3153.219	-0.003
4	4	1		3	3	0	5100.431	0.009	5	1	5		4	0	4	3161.523	-0.001
6	3	4		5	2	3	5282.584	-0.002	4	2	3		3	1	2	3394.114	0.010
8	2	7		7	1	6	5405.564	0.008	5	1	4		4	2	3	3451.079	0.004
9	1	9		8	0	8	5468.767	0.003	11	7	5		11	6	6	3599.300	0.003
7	3	5		6	2	4	5666.748	-0.002	10	7	4		10	6	5	3629.436	0.001
5	4	2		4	3	1	5803.025	0.003	9	7	3		9	6	4	3682.391	0.003
9	2	8		8	1	7	5976.453	0.008	3	3	1		2	2	0	3720.431	0.008
10	1	10		9	0	9	6048.400	-0.002	8	7	1		8	6	2	3725.723	0.005
8	3	6		7	2	5	6078.847	0.007	6	0	6		5	1	5	3726.722	0.002
6	4	3		5	3	2	6394.347	0.001	6	1	6		5	0	5	3733.167	0.001
5	5	1		4	4	0	6459.721	0.004	3	3	1		2	2	1	3782.836	0.009
10	2	9		9	1	8	6553.002	0.009	3	3	0		2	2	1	3799.119	0.002
4	0	4		3	1	3	2537.964	-0.002	5	2	4		4	1	3	3850.964	-0.005
5	0	5		4	1	4	3139.776	0.006	6	1	5		5	2	4	4152.389	0.006

Table S15. (Continued 1).

J	K_a	K_c	←	J	K_a	K_c	obs.	o-c	J	K_a	K_c	←	J	K_a	K_c	obs.	o-c
6	1	5		5	2	4	4152.389	0.006	5	5	1		4	4	0	6459.720	0.003
7	0	7		6	1	6	4308.545	0.001	5	5	0		4	4	1	6463.884	0.005
7	1	7		6	0	6	4310.342	0.004	9	3	6		8	4	5	6488.980	-0.002
6	2	5		5	1	4	4327.121	0.005	6	4	2		5	3	2	6523.689	0.006
4	3	2		3	2	1	4347.467	0.006	10	1	9		9	2	8	6551.019	0.006
4	3	1		3	2	1	4450.377	-0.002	10	1	9		9	1	8	6552.553	-0.001
4	3	2		3	2	2	4616.141	-0.004	10	2	9		9	1	8	6553.002	0.009
11	3	9		11	2	10	4627.618	0.003	9	3	7		8	2	6	6556.669	0.003
4	3	1		3	2	2	4719.068	0.004	8	4	4		7	4	3	6602.518	0.006
7	1	6		6	2	5	4784.818	0.000	11	0	11		10	1	10	6628.094	0.013
7	2	6		6	1	5	4849.787	0.006	11	1	11		10	0	10	6628.094	0.005
5	3	3		4	2	2	4859.743	0.002	6	4	3		5	3	3	6732.191	0.003
8	0	8		7	1	7	4888.807	0.001	7	4	4		6	3	3	6852.148	-0.001
8	1	8		7	0	7	4889.288	0.003	7	3	4		6	2	4	7011.991	0.001
7	2	5		6	3	4	4981.351	0.012	10	2	8		9	3	7	7040.406	0.008
5	2	3		4	1	3	5031.676	0.001	10	3	8		9	2	7	7088.472	-0.003
4	4	1		3	3	0	5100.430	0.008	11	1	10		10	2	9	7130.943	0.007
4	4	1		3	3	1	5116.711	-0.001	11	2	10		10	1	9	7131.509	0.012
4	4	0		3	3	1	5120.200	-0.001	6	5	2		5	4	1	7204.425	0.001
12	3	10		12	2	11	5133.543	0.000	8	4	5		7	3	4	7206.947	-0.001
5	3	2		4	2	2	5197.581	-0.001	12	0	12		11	1	11	7207.798	0.006
6	3	4		5	2	3	5282.583	-0.002	12	1	12		11	0	11	7207.798	0.004
5	2	4		4	1	4	5379.074	0.010	6	5	1		5	4	1	7211.462	0.008
8	1	7		7	2	6	5383.898	0.009	6	3	3		5	2	4	7222.867	-0.012
8	2	7		7	1	6	5405.564	0.008	7	4	3		6	3	3	7233.493	-0.002
9	0	9		8	1	8	5468.647	0.006	6	5	2		5	4	2	7233.785	-0.007
9	1	9		8	0	8	5468.767	0.003	6	5	1		5	4	2	7240.823	0.002
8	3	5		7	4	4	5479.989	-0.002	7	2	5		6	1	5	7292.255	0.007
5	3	3		4	2	3	5508.606	0.005	10	3	7		9	4	6	7339.675	0.003
9	4	5		8	5	4	5627.407	-0.002	9	4	5		8	4	4	7479.982	-0.002
7	3	5		6	2	4	5666.747	-0.003	9	4	6		8	3	5	7518.357	0.005
8	2	6		7	3	5	5753.517	0.013	7	4	4		6	3	4	7611.740	0.004
5	4	2		4	3	1	5803.025	0.002	11	2	9		10	3	8	7632.369	0.014
5	4	1		4	3	1	5832.393	0.002	11	3	9		10	2	8	7648.533	0.012
5	3	2		4	2	3	5846.449	0.006	12	2	11		11	1	10	7710.681	0.008
5	4	1		4	3	2	5935.314	0.005	6	6	0		5	5	0	7812.760	0.009
9	1	8		8	2	7	5969.731	0.006	6	6	0		5	5	1	7813.432	0.009
9	2	8		8	1	7	5976.452	0.008	10	4	7		9	3	6	7860.823	0.005
6	3	3		5	2	3	6042.180	0.007	7	5	3		6	4	2	7889.855	0.001
8	3	6		7	2	5	6078.846	0.007	7	4	3		6	3	4	7993.086	0.005
6	2	4		5	1	4	6133.049	0.008									
6	4	3		5	3	2	6394.347	0.000									
9	2	7		8	3	6	6424.404	0.014									

Table S16. New observed frequencies (MHz) for 15C5 crown ether form V.

J	K_a	K_c	←	J	K_a	K_c	obs.	o-c	J	K_a	K_c	←	J	K_a	K_c	obs.	o-c
6	0	6		5	0	5	3792.980	-0.014	11	1	11		10	1	10	6743.063	0.003
8	1	8		7	1	7	4972.908	0.007	11	0	11		10	0	10	6743.063	0.003
8	0	8		7	0	7	4972.908	0.000	11	2	10		10	2	9	7247.967	0.012
9	1	9		8	1	8	5562.956	0.005	11	2	10		10	2	9	7247.967	0.012
9	2	8		8	2	7	6068.123	0.000	11	1	10		10	1	9	7247.967	0.010
9	1	8		8	1	7	6068.202	-0.012	12	1	12		11	1	11	7333.123	0.006
10	1	10		9	1	9	6153.011	0.007	12	2	11		11	2	10	7837.939	0.013
10	0	10		9	0	9	6153.011	0.006	12	1	11		11	1	10	7837.939	0.012
8	3	5		7	3	4	6591.426	0.007	13	1	13		12	1	12	7923.188	0.016
10	1	9		9	1	8	6658.037	0.002	13	0	13		12	0	12	7923.188	0.016

Table S17. New observed frequencies (MHz) for 15C5 crown ether form VI

J	K_a	K_c	←	J	K_a	K_c	obs.	o-c	J	K_a	K_c	←	J	K_a	K_c	obs.	o-c
6	2	4		6	1	5	2230.856	-0.008	7	4	4		6	3	3	6057.016	-0.003
8	5	4		8	4	5	2273.200	-0.004	11	1	10		10	2	9	7053.145	0.007
6	3	3		5	4	2	4615.161	0.000	11	2	10		10	2	9	7053.145	0.007
8	0	8		7	1	7	4827.238	0.006	11	1	10		10	1	9	7053.145	0.007
8	1	8		7	1	7	4827.238	0.006	11	2	10		10	1	9	7053.145	0.006
8	0	8		7	0	7	4827.238	0.003	12	0	12		11	0	11	7112.937	0.007
8	1	8		7	0	7	4827.238	0.003	12	0	12		11	1	11	7112.937	0.007
8	1	7		7	2	6	5339.199	-0.001	12	1	12		11	0	11	7112.937	0.007
9	0	9		8	1	8	5398.657	0.005	12	1	12		11	1	11	7112.937	0.007
9	1	9		8	1	8	5398.657	0.005	10	4	7		9	3	6	7518.541	0.004
9	0	9		8	0	8	5398.657	0.004	7	3	5		6	2	5	7541.726	0.008
9	1	9		8	0	8	5398.657	0.004	12	1	11		11	2	10	7624.510	0.010
10	0	10		9	1	9	5970.085	0.008	12	2	11		11	2	10	7624.510	0.010
10	0	10		9	0	9	5970.085	0.008	12	1	11		11	1	10	7624.510	0.010
10	1	10		9	0	9	5970.085	0.008	12	2	11		11	1	10	7624.510	0.010
10	1	10		9	1	9	5970.085	0.008	9	5	5		8	4	4	7710.682	0.001

Table S18. New observed frequencies (MHz) for 15C5 crown ether form VIII.

J	K_a	K_c	←	J	K_a	K_c	obs.	o-c	J	K_a	K_c	←	J	K_a	K_c	obs.	o-c
4	1	4		3	0	3	2663.811	-0.004	5	3	3		4	2	2	5417.429	0.008
5	1	5		4	0	4	3182.128	-0.004	8	2	7		7	1	6	5473.861	-0.001
10	3	8		9	4	5	3190.520	-0.001	5	3	2		4	2	2	5518.219	-0.013
10	4	7		9	5	4	3411.784	-0.012	9	1	8		8	2	7	5860.232	-0.013
6	0	6		5	1	5	3666.275	0.006	6	3	4		5	2	3	5892.493	0.008
6	1	6		5	0	5	3722.851	0.000	9	2	8		8	1	7	5982.024	-0.004
11	4	8		11	3	9	3891.343	0.003	10	0	10		9	1	9	5988.638	0.006
3	3	0		2	2	1	4244.018	-0.001	10	1	9		9	2	8	6464.738	0.010
7	0	7		6	1	6	4255.942	0.007	5	4	2		4	3	2	6496.058	-0.010
7	1	7		6	0	6	4280.237	0.007	10	2	9		9	1	8	6520.712	0.003
13	3	10		13	2	11	4425.925	0.010	11	0	11		10	1	10	6563.049	0.007
7	1	6		6	2	5	4537.258	-0.002	11	1	11		10	0	10	6563.638	0.009
8	0	8		7	1	7	4836.746	0.005	11	1	10		10	2	9	7052.685	0.007
8	1	8		7	0	7	4846.726	0.008	11	2	10		10	1	9	7077.295	0.009
8	1	7		7	2	6	5224.612	-0.007	12	0	12		11	1	11	7137.198	0.008
9	0	9		8	1	8	5413.540	0.004									

Table S19. New observed frequencies (MHz) for 15C5 crown ether form IX.

J	K_a	K_c	←	J	K_a	K_c	obs.	o-c	J	K_a	K_c	←	J	K_a	K_c	obs.	o-c
12	2	10		11	3	9	7927.023	0.010	9	1	9		8	0	8	5289.200	-0.003
13	0	13		12	1	12	7526.115	-0.012	6	3	3		5	2	4	6821.290	0.006
6	1	6		5	0	5	3631.697	0.009	8	1	7		7	2	6	5146.453	-0.007
9	1	9		8	0	8	5289.200	-0.003	10	1	9		9	2	8	6335.426	0.009
10	2	9		9	1	8	6372.519	-0.003	11	0	11		10	1	10	6406.820	0.013
6	1	6		5	0	5	3631.697	0.009	11	1	11		10	0	10	6407.142	-0.004
8	3	5		7	4	4	3831.360	0.012	11	2	9		10	3	8	7306.109	0.014
8	1	7		7	2	6	5146.466	0.006	9	1	9		8	0	8	5289.200	-0.003

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Table S20. Observed frequencies (MHz) for the parent species of 15C5-w-B complex

J	K_a	K_c	←	J	K_a	K_c	obs.	o-c	J	K_a	K_c	←	J	K_a	K_c	obs.	o-c
3	2	1		2	1	1	2912.649	0.000	8	7	1		7	6	1	7837.531	0.004
3	2	2		2	1	2	2953.091	0.004	8	4	4		7	3	4	7853.488	-0.002
3	3	0		2	2	0	2964.089	0.000	8	5	4		7	4	4	7856.332	-0.001
3	3	1		2	2	1	2997.038	0.003	8	6	3		7	5	3	7859.239	-0.002
4	3	1		3	2	1	3887.213	-0.001	8	3	5		7	2	5	7861.042	-0.003
4	2	2		3	1	2	3913.190	-0.003	8	4	5		7	3	5	7861.132	-0.004
4	1	3		3	0	3	3931.314	0.010	8	2	6		7	1	6	7864.263	-0.004
4	3	2		3	2	2	3939.625	0.001	8	3	6		7	2	6	7864.263	-0.006
4	4	0		3	3	0	3963.887	0.002	8	2	7		7	1	7	7866.142	-0.003
4	4	1		3	3	1	3998.924	0.002	8	1	7		7	0	7	7866.142	-0.003
5	4	1		4	3	1	4865.460	0.000	8	7	2		7	6	2	7907.930	0.007
5	4	1		4	3	1	4865.460	0.000	5	0	5		4	1	4	3009.218	0.004
5	3	2		4	2	2	4878.912	-0.002	6	0	6		5	1	5	3568.651	0.001
5	2	3		4	1	3	4910.302	-0.001	5	2	3		4	3	2	3837.835	-0.004
5	3	3		4	2	3	4913.889	0.001	7	0	7		6	1	6	4128.085	-0.001
5	4	2		4	3	2	4928.003	0.000	7	1	6		6	2	5	4552.165	0.001
5	5	0		4	4	0	4970.961	0.001	8	1	7		7	2	6	5111.568	-0.002
5	5	1		4	4	1	5002.814	0.004	9	0	9		8	1	8	5246.968	0.006
6	4	2		5	3	2	5841.749	-0.003	7	3	4		6	4	3	5396.190	0.002
6	5	1		5	4	1	5848.899	0.002	8	2	6		7	3	5	5535.888	0.007
6	3	3		5	2	3	5885.861	0.003	9	1	8		8	2	7	5670.986	-0.001
6	4	3		5	3	3	5895.176	0.001	10	0	10		9	1	9	5806.396	-0.003
6	2	4		5	1	4	5896.435	0.002	8	3	5		7	4	4	5960.586	-0.008
6	3	4		5	2	4	5896.753	0.000	9	2	7		8	3	6	6095.198	0.008
6	1	5		5	0	5	5899.146	0.003	8	4	5		7	3	4	5962.172	0.004
6	5	2		5	4	2	5918.639	0.002	10	1	9		9	2	8	6230.408	-0.005
6	6	0		5	5	0	5983.352	-0.002	11	0	11		10	1	10	6365.839	0.002
6	6	1		5	5	1	6008.701	-0.001	10	2	8		9	3	7	6654.548	0.001
7	5	2		6	4	2	6805.132	0.002	11	1	10		10	2	9	6789.840	-0.001
7	6	1		6	5	1	6839.164	0.003	12	0	12		11	1	11	6925.273	-0.001
7	4	3		6	3	3	6856.689	-0.001	12	1	11		11	2	10	7349.268	-0.003
7	3	4		6	2	4	6875.925	-0.002	13	0	13		12	1	12	7484.707	-0.003
7	5	3		6	4	3	6876.738	-0.002	11	3	8		10	4	7	7638.276	-0.006
7	4	4		6	3	4	6876.980	-0.001	12	3	10		11	3	9	7773.339	0.005
7	2	5		6	1	5	6880.537	0.010	13	1	12		12	2	11	7908.717	0.015
7	3	5		6	2	5	6880.537	-0.013	5	1	5		4	1	4	3009.218	0.004
7	1	6		6	0	6	6882.660	-0.001	5	0	5		4	0	4	3009.218	-0.005
7	2	6		6	1	6	6882.660	-0.001	6	1	6		5	1	5	3568.651	0.001
7	6	2		6	5	2	6911.866	0.001	6	0	6		5	0	5	3568.651	0.000
7	7	0		6	6	0	6998.276	-0.008	7	1	7		6	1	6	4128.085	-0.001
7	7	1		6	6	1	7016.398	-0.008	7	0	7		6	0	6	4128.085	-0.001
8	6	2		7	5	2	7771.952	0.006	7	2	6		6	2	5	4552.165	0.001
8	5	3		7	4	3	7821.909	0.006	7	1	6		6	1	5	4552.165	-0.004

Table S20. (Continued 1).

J	K_a	K_c	←	J	K_a	K_c	obs.	o-c	J	K_a	K_c	←	J	K_a	K_c	obs.	o-c
8	2	7		7	2	6	5111.568	-0.002	6	2	4		5	3	3	4415.432	-0.004
8	1	7		7	1	6	5111.568	-0.002	6	3	4		5	3	3	4415.834	-0.004
9	1	9		8	1	8	5246.968	0.006	6	2	4		5	2	3	4420.236	0.001
9	0	9		8	0	8	5246.968	0.006	6	3	4		5	2	3	4420.626	-0.010
9	1	8		8	1	7	5670.986	-0.002	5	4	2		4	3	1	4425.757	0.008
9	2	8		8	2	7	5670.986	-0.001	5	4	1		4	4	0	4479.807	-0.007
10	0	10		9	0	9	5806.396	-0.003	7	1	6		6	2	5	4552.165	0.001
10	1	10		9	1	9	5806.396	-0.003	6	3	3		5	4	2	4795.689	-0.004
9	3	7		8	3	6	6095.198	0.008	6	4	2		5	5	1	4894.728	0.008
9	2	7		8	2	6	6095.198	0.007	5	2	3		4	1	3	4910.302	-0.001
10	2	9		9	2	8	6230.408	-0.005	7	2	5		6	3	4	4976.537	0.007
10	1	9		9	1	8	6230.408	-0.005	7	3	5		6	3	4	4976.537	-0.021
11	1	11		10	1	10	6365.839	0.002	7	2	5		6	2	4	4976.945	0.014
11	0	11		10	0	10	6365.839	0.002	7	3	5		6	2	4	4976.945	-0.013
10	3	8		9	3	7	6654.548	0.001	5	5	0		4	4	1	5075.953	0.000
10	2	8		9	2	7	6654.548	0.001	7	4	4		6	4	3	5397.653	0.009
11	2	10		10	2	9	6789.840	-0.001	7	3	4		6	3	3	5410.297	-0.007
11	1	10		10	1	9	6789.840	-0.001	6	5	2		5	4	1	5478.937	0.011
12	1	12		11	1	11	6925.273	-0.001	8	4	5		7	4	4	5960.719	0.007
12	0	12		11	0	11	6925.273	-0.001	8	3	5		7	3	4	5962.037	-0.012
12	2	11		11	2	10	7349.268	-0.003	6	6	0		5	5	1	6056.491	-0.005
12	1	11		11	1	10	7349.268	-0.003	8	4	4		7	5	3	6372.949	0.011
13	0	13		12	0	12	7484.707	-0.003	8	6	3		7	6	2	6715.277	-0.012
13	1	13		12	1	12	7484.707	-0.003	6	6	1		5	4	2	6866.416	0.000
11	4	8		10	4	7	7638.276	-0.007	7	7	1		6	6	0	6968.605	-0.008
11	3	8		10	3	7	7638.276	-0.007	6	5	2		5	3	3	7004.007	0.004
12	3	10		11	3	9	7773.339	0.005	10	3	7		9	4	6	7079.061	-0.003
12	2	10		11	2	9	7773.339	0.005	10	4	7		9	4	6	7079.061	-0.003
4	2	3		3	1	2	2882.171	0.001	10	3	7		9	3	6	7079.061	-0.011
4	3	2		3	3	1	3216.025	0.010	10	4	7		9	3	6	7079.061	-0.012
5	1	4		4	2	3	3432.896	0.004	7	6	1		6	5	2	7209.127	-0.004
5	2	4		4	1	3	3434.177	-0.009	11	2	9		10	2	8	7213.938	0.006
5	3	3		4	3	2	3842.636	-0.001	11	2	9		10	3	8	7213.938	0.006
4	4	1		3	3	0	3858.896	0.005	11	3	9		10	2	8	7213.938	0.006
6	1	5		5	2	4	3992.798	0.042	11	3	9		10	3	8	7213.938	0.006
6	2	5		5	2	4	3992.798	0.038	9	6	4		8	6	3	7352.998	0.001
6	1	5		5	1	4	3992.798	-0.039	7	6	1		6	4	2	7375.332	-0.001
6	2	5		5	1	4	3992.798	-0.043	13	0	13		12	0	12	7484.707	-0.003
4	4	0		3	3	1	4103.923	0.007	10	5	6		9	4	5	7504.999	0.005

Table S21. Observed frequencies (MHz) for the $H_2{}^{18}O$ isotopologue of 15C5-w-B complex.

J	K_a	K_c	←	J	K_a	K_c	obs.	o-c	J	K_a	K_c	←	J	K_a	K_c	obs.	o-c
3	2	1		2	1	1	2889.274	-0.002	7	5	2		6	4	2	6750.326	0.001
4	3	1		3	2	1	3856.012	-0.001	7	6	1		6	5	1	6784.215	-0.001
4	3	2		3	2	2	3907.651	0.000	7	4	3		6	3	3	6801.089	0.000
4	4	0		3	3	0	3931.657	0.007	7	5	3		6	4	3	6820.994	-0.007
4	4	1		3	3	1	3966.110	0.003	7	1	6		6	0	6	6826.819	-0.010
5	4	1		4	3	1	4826.404	0.006	7	2	6		6	1	6	6826.819	-0.010
5	3	2		4	2	2	4839.463	0.000	7	6	2		6	5	2	6855.733	0.003
5	4	2		4	3	2	4888.003	0.001	7	7	0		6	6	0	6941.042	0.005
5	5	0		4	4	0	4930.476	0.004	7	7	1		6	6	1	6958.763	0.000
5	5	1		4	4	1	4961.747	0.003	11	2	9		10	2	8	7192.901	-0.008
6	4	2		5	3	2	5794.599	-0.008	11	2	9		10	3	8	7192.903	-0.006
6	5	1		5	4	1	5801.938	0.012	11	3	9		10	2	8	7192.903	-0.006
6	3	3		5	2	3	5838.114	-0.008	11	3	9		10	3	8	7192.903	-0.006
6	4	3		5	3	3	5847.378	0.000	8	6	2		7	5	2	7709.482	0.008
6	2	4		5	1	4	5848.602	-0.003	8	5	3		7	4	3	7758.495	-0.005
6	5	2		5	4	2	5870.594	0.012	8	6	3		7	5	3	7795.558	0.000
6	6	0		5	5	0	5934.527	0.010	8	2	6		7	1	6	7800.486	0.011
6	6	1		5	5	1	5959.361	0.000	8	3	6		7	2	6	7800.486	0.009
10	2	8		9	3	7	6633.665	0.016	8	7	2		7	6	2	7843.679	0.005
10	3	8		9	3	7	6633.665	0.016	8	8	0		7	7	0	7947.962	-0.008
10	2	8		9	2	7	6633.665	0.015	8	8	1		7	7	1	7959.624	-0.017
10	3	8		9	2	7	6633.665	0.015									

Table S22. Observed frequencies (MHz) for the parent species of 15C5-w-C complex.

J	K_a	K_c	←	J	K_a	K_c	obs.	o-c	J	K_a	K_c	←	J	K_a	K_c	obs.	o-c
3	2	1		2	1	1	2880.823	-0.001	7	0	7		6	0	6	4227.970	-0.015
2	2	0		1	1	0	2036.324	-0.005	7	0	7		6	0	6	4227.970	-0.015
3	1	2		2	1	1	2364.642	-0.006	7	1	7		6	0	6	4227.970	-0.021
4	0	4		3	1	3	2500.973	-0.002	4	4	0		3	3	1	4272.072	0.005
4	1	4		3	1	3	2502.367	-0.002	6	2	4		5	3	3	4384.669	0.002
4	0	4		3	0	3	2508.508	-0.004	8	4	5		7	5	3	4394.506	0.011
4	1	3		3	2	2	2820.400	-0.008	6	3	4		5	3	3	4439.134	-0.002
4	2	3		3	2	2	2869.306	0.002	6	2	4		5	2	3	4552.722	-0.006
3	2	1		2	1	1	2880.823	-0.001	6	3	4		5	2	3	4607.194	-0.003
3	1	2		2	0	2	2889.472	-0.006	7	1	6		6	2	5	4643.192	0.006
4	1	3		3	1	2	2968.685	0.007	7	2	6		6	2	5	4643.643	0.001
3	3	1		2	2	0	3074.204	0.008	7	1	6		6	1	5	4645.649	0.004
5	0	5		4	1	4	3078.690	-0.001	7	2	6		6	1	5	4646.104	0.002
5	1	5		4	1	4	3078.925	0.003	7	4	3		6	5	1	4711.674	0.006
5	1	5		4	0	4	3080.319	0.002	5	3	2		4	2	2	4762.041	0.002
3	3	0		2	2	0	3119.037	-0.001	8	0	8		7	1	7	4802.255	0.005
3	3	1		2	2	1	3171.920	0.000	8	1	8		7	1	7	4802.255	0.004
3	3	0		2	2	1	3216.757	-0.004	8	0	8		7	0	7	4802.255	-0.001
4	2	2		3	2	1	3296.118	0.001	8	1	8		7	0	7	4802.255	-0.001
5	2	3		4	3	1	3383.546	-0.003	5	2	3		4	1	3	4829.249	-0.001
5	1	4		4	2	3	3468.430	0.001	5	4	2		4	3	1	4847.100	-0.008
5	2	4		4	2	3	3480.370	0.001	5	1	4		4	0	4	4922.868	0.000
5	1	4		4	1	3	3517.331	0.005	5	2	4		4	1	4	4933.417	0.002
5	2	4		4	1	3	3529.265	-0.001	5	3	3		4	2	3	4948.416	0.002
6	0	6		5	1	5	3653.568	-0.008	6	4	2		5	4	1	4949.049	-0.009
6	0	6		5	0	5	3653.800	-0.008	6	3	3		5	3	2	4951.538	-0.002
6	1	6		5	0	5	3653.850	0.006	5	4	1		4	3	1	4969.268	0.000
6	2	4		5	3	2	3776.330	0.005	7	3	5		6	3	4	5048.273	0.000
5	3	3		4	3	2	3785.259	0.001	5	4	2		4	3	2	5080.761	0.005
4	2	2		3	1	2	3812.294	0.001	7	2	5		6	2	4	5088.886	0.004
4	3	1		3	2	1	3898.203	0.000	7	3	5		6	2	4	5102.743	0.002
4	2	3		3	1	3	3955.411	-0.003	9	3	6		8	4	4	5138.872	-0.001
5	2	3		4	2	2	3985.639	0.004	7	3	4		6	4	3	5197.831	-0.007
4	3	2		3	2	2	4032.462	0.001	5	4	1		4	3	2	5202.916	0.000
6	1	5		5	2	4	4064.160	0.000	8	1	7		7	2	6	5218.172	-0.015
6	2	5		5	2	4	4066.617	-0.003	8	2	7		7	2	6	5218.265	-0.001
6	1	5		5	1	4	4076.096	-0.005	8	1	7		7	1	6	5218.641	-0.002
6	2	5		5	1	4	4078.564	0.004	8	2	7		7	1	6	5218.717	-0.006
5	3	3		4	2	2	4153.698	0.002	5	5	1		4	4	0	5330.534	-0.004
4	4	1		3	3	0	4210.169	-0.007	5	5	0		4	4	0	5336.323	-0.006
4	4	0		3	3	0	4227.223	-0.002	5	5	1		4	4	1	5347.583	-0.004
7	0	7		6	1	6	4227.970	0.021	6	4	3		5	3	2	5349.424	0.003
7	1	7		6	1	6	4227.970	0.015	5	5	0		4	4	1	5353.379	0.000

Table S22. (Continued 1).

J	K_a	K_c	←	J	K_a	K_c	obs.	o-c	J	K_a	K_c	←	J	K_a	K_c	obs.	o-c
7	4	4		6	4	3	5368.089	0.003	6	4	2		5	3	3	6366.707	-0.009
9	0	9		8	1	8	5376.548	0.002	5	4	1		4	1	3	6414.965	-0.004
9	1	9		8	1	8	5376.548	0.002	6	6	1		5	5	0	6439.401	-0.012
9	0	9		8	0	8	5376.548	0.001	6	6	0		5	5	0	6441.245	-0.005
9	1	9		8	0	8	5376.548	0.001	6	6	1		5	5	1	6445.206	0.001
7	5	3		6	5	2	5502.468	0.013	6	6	0		5	5	1	6447.048	0.007
5	4	1		4	2	2	5571.348	-0.006	11	6	6		10	7	4	6474.022	0.010
7	3	4		6	3	3	5595.719	0.001	11	0	11		10	0	10	6525.153	0.006
8	4	4		7	5	2	5626.692	0.006	11	0	11		10	1	10	6525.153	0.006
8	2	6		7	3	5	5630.381	0.006	11	1	11		10	0	10	6525.153	0.006
8	3	6		7	3	5	5633.425	0.005	11	1	11		10	1	10	6525.153	0.006
8	2	6		7	2	5	5644.235	0.000	7	5	3		6	4	2	6579.840	-0.001
8	3	6		7	2	5	5647.282	0.002	9	3	6		8	4	5	6605.356	0.001
6	3	3		5	2	3	5727.946	0.003	9	4	6		8	4	5	6619.515	0.004
6	4	2		5	3	2	5758.379	0.006	8	5	3		7	5	2	6649.446	0.015
7	4	4		6	3	3	5765.968	0.001	7	4	3		6	3	3	6649.446	0.002
7	4	3		6	4	2	5842.608	-0.004	9	3	6		8	3	5	6659.641	0.000
6	2	4		5	1	4	5864.652	-0.001	9	4	6		8	3	5	6673.795	-0.003
6	3	4		5	2	4	5907.184	0.003	10	6	4		9	7	2	6689.353	0.001
6	2	5		5	1	5	5921.114	0.002	7	3	4		6	2	4	6770.936	0.002
10	0	10		9	1	9	5950.849	0.003	10	2	8		9	2	7	6784.384	0.002
10	1	10		9	1	9	5950.849	0.003	10	3	8		9	2	7	6784.497	0.002
10	0	10		9	0	9	5950.849	0.003	9	4	5		8	5	4	6794.695	0.001
10	1	10		9	0	9	5950.849	0.003	7	5	2		6	4	2	6814.132	0.000
6	4	3		5	3	3	5957.766	0.001	7	2	5		6	1	5	6877.433	-0.002
8	3	5		7	4	4	5960.923	0.008	7	4	4		6	3	4	6886.711	-0.002
8	4	5		7	4	4	6015.200	-0.001	7	3	5		6	2	5	6888.834	0.000
6	5	2		5	4	1	6026.438	-0.005	7	1	6		6	0	6	6910.724	0.002
6	5	1		5	4	1	6080.001	0.000	7	2	6		6	1	6	6911.140	-0.003
8	3	5		7	3	4	6131.163	0.000	11	1	10		10	2	9	6940.829	0.004
6	5	2		5	4	2	6148.599	-0.003	11	2	10		10	2	9	6940.829	0.004
9	4	5		8	5	3	6171.169	0.003	11	1	10		10	1	9	6940.829	0.002
6	5	1		5	4	2	6202.162	0.002	11	2	10		10	1	9	6940.829	0.001
9	2	7		8	3	6	6209.161	-0.001	9	5	5		8	5	4	6956.556	-0.004
9	3	7		8	3	6	6209.770	0.001	7	5	3		6	4	3	6988.792	0.000
9	2	7		8	2	6	6212.193	-0.014	9	8	1		8	8	0	7047.229	-0.006
9	5	4		8	6	2	6250.461	-0.004	10	5	5		9	6	3	7098.221	-0.002
8	5	4		7	5	3	6260.196	0.001	12	0	12		11	0	11	7099.451	-0.001
10	4	6		9	5	4	6353.219	0.000	12	0	12		11	1	11	7099.451	-0.001
10	1	9		9	2	8	6366.631	0.009	12	1	12		11	0	11	7099.451	-0.001
10	2	9		9	2	8	6366.631	0.007	12	1	12		11	1	11	7099.451	-0.001
10	1	9		9	1	8	6366.631	-0.004	9	7	3		8	7	2	7104.450	0.002
10	2	9		9	1	8	6366.631	-0.006	9	6	4		8	6	3	7114.278	-0.003

Table S22. (Continued 2).

J	K_a	K_c	←	J	K_a	K_c	obs.	o-c	J	K_a	K_c	←	J	K_a	K_c	obs.	o-c
9	7	2		8	7	1	7145.730	0.004	13	0	13		12	1	12	7673.755	-0.002
7	6	2		6	5	1	7178.249	-0.002	13	1	13		12	0	12	7673.755	-0.002
9	4	5		8	4	4	7193.926	0.015	13	1	13		12	1	12	7673.755	-0.002
7	6	1		6	5	1	7198.963	0.002	10	4	6		9	4	5	7705.380	0.002
10	4	7		9	4	6	7202.158	-0.004	10	5	6		9	4	5	7756.256	-0.001
10	3	7		9	3	6	7213.041	-0.030	7	4	3		6	3	4	7770.180	-0.011
10	4	7		9	3	6	7216.313	-0.005	11	3	8		10	4	7	7776.531	0.000
7	5	2		6	4	3	7223.088	0.005	11	4	8		10	4	7	7777.212	0.000
7	6	2		6	5	2	7231.808	-0.003	11	3	8		10	3	7	7779.774	-0.004
7	6	1		6	5	2	7252.517	-0.003	11	4	8		10	3	7	7780.462	0.002
9	5	5		8	4	4	7355.781	0.004	11	6	5		10	7	3	7795.538	0.008
9	6	3		8	6	2	7384.035	0.000	8	6	3		7	5	2	7808.283	0.005
6	4	3		5	1	4	7437.757	0.008	8	3	5		7	2	5	7813.214	-0.001
10	5	5		9	6	4	7481.977	-0.013	10	9	2		9	9	1	7821.133	0.004
12	1	11		11	2	10	7515.060	0.003	7	4	3		6	2	4	7824.655	-0.004
12	2	11		11	2	10	7515.060	0.003	6	4	2		5	1	4	7846.716	0.015
12	1	11		11	1	10	7515.060	0.003	8	4	5		7	3	5	7853.642	0.000
12	2	11		11	1	10	7515.060	0.003	10	6	5		9	6	4	7863.340	-0.012
7	7	1		6	6	0	7543.160	0.002	8	2	6		7	1	6	7876.027	0.002
10	4	6		9	5	5	7543.507	-0.005	8	3	6		7	2	6	7878.613	0.001
7	7	0		6	6	0	7543.718	0.004	8	5	4		7	4	4	7880.901	0.001
7	7	1		6	6	1	7545.002	0.008	10	8	3		9	8	2	7885.051	-0.003
7	7	0		6	6	1	7545.551	0.001	8	2	7		7	1	7	7901.456	0.001
10	5	6		9	5	5	7594.395	0.004	8	6	2		7	5	2	7922.299	0.007
8	5	3		7	4	3	7620.953	0.002	12	2	10		11	3	9	7931.599	0.015
7	5	2		6	3	3	7620.953	-0.011	12	2	10		11	2	9	7931.599	-0.005
8	4	4		7	3	4	7651.931	0.000	12	3	10		11	2	9	7931.599	-0.008
6	5	1		5	2	3	7665.723	0.003	10	7	4		9	7	3	7935.198	0.000
13	0	13		12	0	12	7673.755	-0.002									

Table S23. Observed frequencies (MHz) for the $H_2{}^{18}O$ isotopologue of 15C5-w-C complex.

J	K_a	K_c	←	J	K_a	K_c	obs.	o-c	J	K_a	K_c	←	J	K_a	K_c	obs.	o-c
2	2	0		1	1	0	2018.779	0.001	6	5	1		5	4	2	6147.349	0.016
3	2	1		2	1	1	2857.412	-0.009	6	6	0		5	5	0	6382.844	-0.006
3	3	0		2	2	0	3091.699	-0.003	6	6	1		5	5	1	6386.685	-0.006
3	3	1		2	2	1	3143.492	0.003	7	4	3		6	3	3	6595.674	-0.007
4	2	2		3	1	2	3781.270	-0.002	7	3	4		6	2	4	6714.376	0.003
4	3	1		3	2	1	3866.214	-0.013	10	2	8		9	3	7	6763.217	0.003
4	3	2		3	2	2	3997.943	0.004	7	4	4		6	3	4	6828.920	-0.004
4	4	0		3	3	0	4189.582	0.011	7	3	5		6	2	5	6830.835	0.012
4	4	1		3	3	1	4216.717	0.007	7	5	3		6	4	3	6929.683	-0.005
5	3	2		4	2	2	4723.588	-0.009	7	6	1		6	5	1	7136.761	-0.004
5	2	3		4	1	3	4789.075	0.007	7	6	2		6	5	2	7168.715	0.000
5	3	3		4	2	3	4906.688	-0.003	10	5	5		9	6	4	7441.586	-0.007
5	4	1		4	3	1	4927.877	-0.014	8	4	4		7	3	4	7588.800	0.010
5	4	2		4	3	2	5037.023	0.005	13	0	13		12	0	12	7670.236	-0.004
5	5	0		4	4	0	5288.283	0.016	13	0	13		12	1	12	7670.236	-0.004
5	5	1		4	4	1	5299.235	0.006	13	1	13		12	0	12	7670.236	-0.004
10	5	6		9	6	4	5654.830	0.009	13	1	13		12	1	12	7670.236	-0.004
6	3	3		5	2	3	5680.995	-0.001	8	4	5		7	3	5	7787.695	0.003
6	3	4		5	2	4	5857.491	0.006	8	5	4		7	4	4	7814.874	0.000
6	4	3		5	3	3	5907.502	-0.001	8	1	7		7	0	7	7834.639	-0.001
6	5	1		5	4	1	6028.373	-0.016	8	6	3		7	5	3	7974.249	-0.009
6	5	2		5	4	2	6095.331	0.003									

Table S24. Observed frequencies (MHz) for the parent species of 15C5-w2-D complex.

J	K_a	K_c	←	J	K_a	K_c	obs.	o-c	J	K_a	K_c	←	J	K_a	K_c	obs.	o-c
3	2	1		2	1	1	2635.507	0.005	9	1	9		8	0	8	5173.591	0.000
4	1	3		3	2	2	2714.001	-0.002	9	1	9		8	1	8	5173.591	0.000
3	3	0		2	2	0	2718.063	0.002	6	4	2		5	3	2	5268.806	0.000
3	3	1		2	2	1	2755.657	0.002	6	3	3		5	2	3	5323.348	0.005
5	2	4		4	1	3	3292.039	-0.004	6	5	1		5	4	1	5338.029	-0.006
6	0	6		5	1	5	3505.520	0.004	6	2	4		5	1	4	5356.359	0.002
6	1	6		5	1	5	3505.520	0.004	6	3	4		5	2	4	5358.890	0.001
6	0	6		5	0	5	3505.520	-0.002	6	4	3		5	3	3	5361.197	0.003
6	1	6		5	0	5	3505.520	-0.003	6	5	2		5	4	2	5413.340	0.001
4	3	1		3	2	1	3524.228	0.002	9	1	8		8	2	7	5512.313	0.005
4	2	2		3	1	2	3533.130	0.005	9	2	8		8	2	7	5512.313	0.005
4	1	3		3	0	3	3571.395	0.010	9	1	8		8	1	7	5512.313	0.004
4	2	3		3	1	3	3576.042	0.013	9	2	8		8	1	7	5512.313	0.004
4	3	2		3	2	2	3593.665	0.001	6	6	1		5	5	0	5516.527	-0.006
4	4	1		3	3	0	3601.325	0.000	6	6	0		5	5	0	5529.228	-0.003
4	4	0		3	3	0	3648.726	-0.003	6	6	1		5	5	1	5541.993	-0.002
4	4	1		3	3	1	3680.833	-0.002	6	6	0		5	5	1	5554.684	-0.009
5	3	2		4	3	1	3978.070	0.008	10	0	10		9	0	9	5729.625	0.006
7	0	7		6	1	6	4061.541	0.001	10	0	10		9	1	9	5729.625	0.006
7	1	7		6	1	6	4061.541	0.001	10	1	10		9	0	9	5729.625	0.006
7	0	7		6	0	6	4061.541	0.001	10	1	10		9	1	9	5729.625	0.006
7	1	7		6	0	6	4061.541	0.001	10	1	9		9	2	8	6068.300	-0.003
5	3	2		4	2	2	4398.654	0.006	10	2	9		9	2	8	6068.300	-0.003
5	4	1		4	3	1	4423.802	0.002	10	1	9		9	1	8	6068.300	-0.003
5	2	3		4	1	3	4452.435	-0.002	10	2	9		9	1	8	6068.300	-0.003
5	3	3		4	2	3	4467.957	0.003	7	5	2		6	4	2	6149.087	-0.005
5	1	4		4	0	4	4468.897	0.009	7	6	2		6	5	1	6157.848	0.000
5	2	4		4	1	4	4469.470	0.005	7	4	3		6	3	3	6184.201	-0.002
5	4	2		4	3	2	4500.827	0.002	7	3	4		6	2	4	6238.862	-0.002
5	5	0		4	4	0	4587.897	-0.001	7	4	4		6	3	4	6246.952	0.000
5	5	1		4	4	1	4609.826	-0.013	7	2	5		6	1	5	6253.505	0.005
8	0	8		7	0	7	4617.568	0.003	7	3	5		6	2	5	6253.828	0.002
8	0	8		7	1	7	4617.568	0.003	7	5	3		6	4	3	6257.511	0.000
8	1	8		7	1	7	4617.568	0.003	7	1	6		6	0	6	6259.107	0.010
8	1	8		7	0	7	4617.568	0.003	7	2	6		6	1	6	6259.107	0.004
6	4	2		5	4	1	4823.070	0.002	7	6	1		6	5	1	6267.842	-0.002
8	1	7		7	2	6	4956.332	0.003	11	0	11		10	0	10	6285.642	-0.005
8	2	7		7	2	6	4956.332	0.002	11	0	11		10	1	10	6285.642	-0.005
8	1	7		7	1	6	4956.332	-0.003	11	1	11		10	0	10	6285.642	-0.005
8	2	7		7	1	6	4956.332	-0.004	11	1	11		10	1	10	6285.642	-0.005
9	0	9		8	0	8	5173.591	0.000	7	6	2		6	5	2	6331.514	-0.003
9	0	9		8	1	8	5173.591	0.000	10	2	8		9	3	7	6407.310	-0.005
3	2	1		2	1	1	2635.507	0.005	9	1	9		8	0	8	5173.591	0.000

Table S24. (Continued 1).

J	K_a	K_c	←	J	K_a	K_c	obs.	o-c	J	K_a	K_c	←	J	K_a	K_c	obs.	o-c
10	2	8		9	3	7	6407.310	-0.005	8	2	7		7	1	7	7153.903	0.010
10	3	8		9	3	7	6407.310	-0.006	8	6	3		7	5	3	7158.484	-0.002
10	2	8		9	2	7	6407.310	-0.010	12	1	11		11	1	10	7180.326	0.006
10	3	8		9	2	7	6407.310	-0.010	12	1	11		11	2	10	7180.326	0.006
7	6	1		6	5	2	6441.513	-0.002	12	2	11		11	1	10	7180.326	0.006
7	7	1		6	6	0	6463.693	0.007	12	2	11		11	2	10	7180.326	0.006
7	7	0		6	6	0	6469.702	-0.002	8	7	1		7	6	1	7208.862	-0.002
7	7	1		6	6	1	6476.385	0.001	10	6	4		9	7	2	7213.938	-0.014
11	1	10		10	1	9	6624.315	0.006	8	7	2		7	6	2	7255.108	0.002
11	1	10		10	2	9	6624.315	0.006	10	5	5		9	6	4	7398.975	0.003
11	2	10		10	1	9	6624.315	0.006	8	8	1		7	7	0	7406.165	0.013
11	2	10		10	2	9	6624.315	0.006	8	8	0		7	7	0	7408.907	0.004
12	0	12		11	0	11	6841.677	0.001	8	8	1		7	7	1	7412.175	0.004
12	0	12		11	1	11	6841.677	0.001	7	6	1		6	3	3	7459.553	-0.008
12	1	12		11	0	11	6841.677	0.001	12	2	10		11	3	9	7519.153	0.003
12	1	12		11	1	11	6841.677	0.001	12	3	10		11	3	9	7519.153	0.003
8	5	3		7	4	3	7040.580	-0.010	10	2	8		9	3	7	6407.310	-0.005
8	5	3		7	4	3	7040.580	-0.010	12	2	10		11	2	9	7519.153	0.003
8	6	2		7	5	2	7043.173	-0.012	12	3	10		11	2	9	7519.153	0.003
10	4	6		9	5	5	7087.479	-0.008	10	9	1		9	9	0	7702.767	0.006
8	4	4		7	3	4	7113.882	-0.004	13	1	12		12	1	11	7736.328	-0.007
8	5	4		7	4	4	7134.629	-0.003	13	1	12		12	2	11	7736.328	-0.007
8	3	5		7	2	5	7140.250	0.000	13	2	12		12	1	11	7736.328	-0.007
8	4	5		7	3	5	7141.521	0.000	13	2	12		12	2	11	7736.328	-0.007
8	2	6		7	1	6	7149.103	0.005	9	5	4		8	4	4	7978.847	-0.009
8	1	7		7	0	7	7153.903	0.011									

Table S25. Observed frequencies (MHz) for the $H_2{}^{18}O$-a isotopologue of 15C5-w2-D complex.

J	K_a	K_c	←	J	K_a	K_c	obs.	o-c	J	K_a	K_c	←	J	K_a	K_c	obs.	o-c
3	3	1		2	2	1	2730.741	0.001	7	4	3		6	3	3	6129.579	0.007
4	3	1		3	2	1	3493.645	0.005	7	4	4		6	3	4	6191.700	-0.001
4	2	2		3	1	2	3502.034	0.007	7	5	3		6	4	3	6202.268	-0.003
4	3	2		3	2	2	3561.814	-0.001	7	6	1		6	5	1	6213.236	-0.003
4	4	0		3	3	0	3616.186	-0.002	7	6	2		6	5	2	6275.294	0.003
4	4	1		3	3	1	3647.533	-0.003	7	7	0		6	6	0	6411.159	0.005
5	3	2		4	2	2	4360.153	0.011	7	7	1		6	6	1	6417.600	0.001
5	4	1		4	3	1	4385.397	0.001	8	5	3		7	4	3	6978.685	-0.007
5	3	3		4	2	3	4428.452	0.012	8	6	2		7	5	2	6982.321	-0.013
5	4	2		4	3	2	4460.922	0.003	8	4	4		7	3	4	7050.847	0.006
5	5	0		4	4	0	4546.758	-0.002	8	5	4		7	4	4	7071.590	0.003
5	5	1		4	4	1	4568.096	-0.002	8	6	3		7	5	3	7095.343	-0.002
6	4	2		5	3	2	5222.935	0.000	8	7	1		7	6	1	7145.728	-0.007
6	3	3		5	2	3	5276.221	0.007	8	7	2		7	6	2	7190.599	0.003
6	5	1		5	4	1	5291.652	-0.003	8	8	0		7	7	0	7341.676	0.012
6	4	3		5	3	3	5313.835	0.013	8	8	1		7	7	1	7344.803	-0.001
6	5	2		5	4	2	5365.312	0.001	9	7	2		8	6	2	7885.467	-0.019
6	6	0		5	5	0	5479.395	0.002	9	5	4		8	4	4	7908.117	-0.001
6	6	1		5	5	1	5491.750	-0.004	9	6	4		8	5	4	7952.594	-0.014
8	5	4		7	4	3	6036.034	0.004	9	7	3		8	6	3	7994.159	0.000
7	5	2		6	4	2	6095.793	0.001									

Table S26. Observed frequencies (MHz) for the $H_2{}^{18}O$-b isotopologue of 15C5-w2-D complex.

J	K_a	K_c	←	J	K_a	K_c	obs.	o-c	J	K_a	K_c	←	J	K_a	K_c	obs.	o-c
3	2	1		2	1	1	2611.974	0.014	7	5	2		6	4	2	6094.219	-0.001
3	3	0		2	2	0	2693.270	0.002	7	4	3		6	3	3	6127.903	-0.006
4	3	1		3	2	1	3492.753	0.003	7	5	3		6	4	3	6200.702	-0.005
4	2	2		3	1	2	3501.088	-0.004	7	6	1		6	5	1	6211.790	0.005
4	3	2		3	2	2	3560.925	-0.002	7	6	2		6	5	2	6273.780	0.003
4	4	0		3	3	0	3615.342	-0.002	7	7	0		6	6	0	6409.672	0.001
4	4	1		3	3	1	3646.667	-0.002	7	7	1		6	6	1	6416.103	0.001
5	3	2		4	2	2	4358.976	-0.002	8	6	2		7	5	2	6980.574	-0.012
5	4	1		4	3	1	4384.309	0.002	8	4	4		7	3	4	7048.975	0.002
5	3	3		4	2	3	4427.301	-0.010	8	5	4		7	4	4	7069.763	-0.007
5	4	2		4	3	2	4459.815	-0.003	8	1	7		7	0	7	7088.755	0.015
5	5	1		4	4	0	4521.192	0.002	8	2	7		7	1	7	7088.755	0.015
5	5	0		4	4	0	4545.704	-0.006	8	6	3		7	5	3	7093.569	-0.004
5	5	1		4	4	1	4567.021	-0.001	8	7	1		7	6	1	7144.090	0.002
6	4	2		5	3	2	5221.553	-0.005	8	7	2		7	6	2	7188.878	-0.002
6	3	3		5	2	3	5274.802	-0.002	8	8	1		7	7	1	7343.098	0.004
6	5	1		5	4	1	5290.379	-0.002	9	7	2		8	6	2	7883.567	-0.010
6	5	2		5	4	2	5364.000	-0.002	11	5	6		10	6	5	7937.178	0.001
6	6	0		5	5	0	5478.126	-0.002	9	5	5		8	4	5	7954.350	0.004
6	6	1		5	5	1	5490.464	-0.004	9	1	8		8	0	8	7975.366	0.031
6	6	0		5	5	1	5502.648	-0.001	9	7	3		8	6	3	7992.184	-0.003

Table S27. Observed frequencies (MHz) for the parent species of 15C5-w2-E complex.

J	K_a	K_c	←	J	K_a	K_c	obs.	o-c	J	K_a	K_c	←	J	K_a	K_c	obs.	o-c
5	1	4		4	2	3	3051.359	0.012	8	4	5		7	3	4	5208.483	0.002
5	2	4		4	2	3	3051.359	0.012	10	0	10		9	1	9	5361.066	-0.003
5	2	4		4	1	3	3051.359	0.004	10	1	10		9	0	9	5361.066	-0.003
4	2	2		3	1	2	3271.022	0.005	9	2	7		8	3	6	5433.062	-0.003
4	3	2		3	2	2	3271.847	0.001	9	3	7		8	2	6	5433.062	-0.003
6	0	6		5	1	5	3275.973	-0.003	7	7	1		6	6	0	5630.381	0.008
6	1	6		5	0	5	3275.973	-0.003	10	1	9		9	2	8	5657.696	-0.001
5	3	3		4	3	2	3347.494	-0.001	10	2	9		9	1	8	5657.696	-0.001
5	3	3		4	2	2	3348.727	-0.012	7	6	1		6	5	1	5712.600	-0.001
6	1	5		5	2	4	3572.603	-0.015	7	5	2		6	4	2	5721.722	0.011
6	2	5		5	1	4	3572.603	-0.015	7	4	3		6	3	3	5724.836	0.003
7	0	7		6	1	6	3797.251	0.000	7	5	3		6	4	3	5724.963	-0.003
7	1	7		6	0	6	3797.251	0.000	7	3	4		6	2	4	5725.180	0.001
6	2	4		5	3	3	3869.294	0.017	7	4	4		6	3	4	5725.180	-0.001
6	3	4		5	2	3	3869.293	-0.014	7	2	5		6	1	5	5725.302	0.000
5	3	2		4	2	2	4088.263	0.006	7	3	5		6	2	5	5725.302	0.000
5	2	3		4	1	3	4089.436	0.011	7	1	6		6	0	6	5725.376	0.008
5	3	3		4	2	3	4089.436	-0.012	7	2	6		6	1	6	5725.376	0.008
5	1	4		4	0	4	4089.533	-0.006	7	6	2		6	5	2	5726.224	-0.004
5	2	4		4	1	4	4089.533	-0.006	9	3	6		8	4	5	5729.723	0.001
7	1	6		6	2	5	4093.884	-0.004	9	4	6		8	3	5	5729.723	0.001
7	2	6		6	1	5	4093.884	-0.004	7	7	0		6	6	1	5840.472	0.000
6	3	3		5	4	2	4164.746	0.013	11	0	11		10	1	10	5882.341	0.000
6	4	3		5	4	2	4164.820	-0.003	11	1	11		10	0	10	5882.341	0.000
6	4	3		5	3	2	4167.719	0.005	10	2	8		9	3	7	5954.328	-0.001
8	0	8		7	1	7	4318.525	0.001	10	3	8		9	2	7	5954.328	-0.001
8	1	8		7	0	7	4318.525	0.001	9	4	5		8	5	4	6026.438	-0.003
7	2	5		6	3	4	4390.544	0.003	9	5	5		8	4	4	6026.438	-0.008
7	3	5		6	3	4	4390.544	0.003	8	6	2		7	6	1	6138.078	0.005
7	3	5		6	2	4	4390.544	0.002	8	7	2		7	6	1	6155.005	0.009
6	4	2		5	3	2	4905.177	0.009	11	1	10		10	2	9	6178.965	0.001
6	3	3		5	2	3	4907.176	0.005	11	2	10		10	1	9	6178.965	0.001
6	2	4		5	1	4	4907.378	0.000	10	3	7		9	4	6	6250.975	0.001
6	3	4		5	2	4	4907.378	0.000	10	4	7		9	3	6	6250.975	0.001
6	1	5		5	0	5	4907.458	0.002	12	0	12		11	1	11	6403.609	-0.003
6	1	5		5	0	5	4907.458	0.002	12	1	12		11	0	11	6403.609	-0.003
6	2	5		5	1	5	4907.458	0.002	11	2	9		10	3	8	6475.595	0.003
6	5	2		5	4	2	4908.020	-0.008	11	3	9		10	2	8	6475.595	0.003
7	4	3		6	5	2	4981.531	-0.007	8	7	1		7	6	1	6529.157	-0.003
9	1	8		8	2	7	5136.429	0.001	8	6	2		7	5	2	6537.877	0.012
9	2	8		8	1	7	5136.429	0.001	8	5	3		7	4	3	6542.389	0.000
8	3	5		7	4	4	5208.483	0.004	8	6	3		7	5	3	6542.652	-0.001
8	3	5		7	3	4	5208.483	0.002	8	4	4		7	3	4	6542.936	0.001

Table S27 (Continued 1).

J	K_a	K_c	←	J	K_a	K_c	obs.	o-c	J	K_a	K_c	←	J	K_a	K_c	obs.	o-c
8	5	4		7	4	4	6542.936	-0.003	9	6	4		8	5	4	7360.643	-0.007
8	3	5		7	2	5	6543.117	-0.001	9	4	5		8	3	5	7360.899	-0.002
8	4	5		7	3	5	6543.117	-0.001	9	5	5		8	4	5	7360.899	-0.002
8	2	6		7	1	6	6543.214	-0.001	9	3	6		8	2	6	7361.036	-0.001
8	3	6		7	2	6	6543.214	-0.001	9	4	6		8	3	6	7361.036	-0.001
8	1	7		7	0	7	6543.266	-0.009	9	2	7		8	1	7	7361.128	0.006
8	2	7		7	1	7	6543.266	-0.009	9	3	7		8	2	7	7361.128	0.006
8	7	2		7	6	2	6544.510	-0.009	9	8	2		8	7	2	7362.909	0.001
10	4	6		9	5	5	6547.657	0.003	11	5	6		10	6	5	7365.606	0.002
10	5	6		9	4	5	6547.657	0.002	11	5	6		10	5	5	7365.606	0.002
8	8	0		7	7	0	6550.146	-0.021	11	6	6		10	5	5	7365.606	0.002
8	8	1		7	7	1	6561.151	-0.015	9	9	0		8	8	0	7370.697	-0.009
9	7	3		8	7	2	6613.971	0.011	10	7	3		9	8	2	7427.168	0.008
12	1	11		11	2	10	6700.234	0.004	10	8	3		9	8	2	7428.964	0.019
12	2	11		11	1	10	6700.234	0.004	14	0	14		13	1	13	7446.149	0.000
11	3	8		10	4	7	6772.229	0.000	14	1	14		13	0	13	7446.149	0.000
11	4	8		10	3	7	6772.229	0.000	13	2	11		12	3	10	7518.115	0.000
10	5	5		9	6	4	6844.446	0.008	13	3	11		12	2	10	7518.115	0.000
10	6	5		9	5	4	6844.446	-0.007	12	4	8		11	5	7	7590.132	0.003
13	0	13		12	1	12	6924.882	0.001	12	5	8		11	4	7	7590.132	0.003
13	1	13		12	0	12	6924.882	0.001	14	1	13		13	2	12	7742.759	-0.001
12	2	10		11	3	9	6996.855	0.001	14	2	13		13	1	12	7742.759	-0.001
12	3	10		11	2	9	6996.855	0.001	13	3	10		12	4	9	7814.746	0.008
11	4	7		10	5	6	7068.889	0.002	13	4	10		12	3	9	7814.746	0.008
11	5	7		10	4	6	7068.889	0.002	8	4	4		7	3	5	7877.585	0.013
10	6	4		9	7	3	7141.178	0.000	8	5	4		7	2	5	7877.585	0.008
10	7	4		9	6	3	7142.177	-0.002	12	5	7		11	6	6	7886.810	0.000
13	1	12		12	2	11	7221.493	-0.003	12	6	7		11	5	6	7886.810	0.000
13	2	12		12	1	11	7221.493	-0.003	11	7	4		10	8	3	7959.143	-0.013
12	3	9		11	4	8	7293.488	0.004	11	7	4		10	7	3	7960.940	-0.001
12	4	9		11	3	8	7293.488	0.004	11	8	4		10	7	3	7961.006	-0.006
9	7	2		8	6	2	7353.639	0.000	15	0	15		14	1	14	7967.413	-0.004
9	6	3		8	5	3	7359.811	-0.002	15	1	15		14	0	14	7967.413	-0.004
9	7	3		8	6	3	7360.290	-0.004	9	8	1		8	7	1	7345.905	-0.024
9	5	4		8	4	4	7360.643	0.001	9	9	1		8	8	1	7381.709	0.014

Table S28. Observed frequencies (MHz) for the $H_2{}^{18}O$-a isotopologue of 15C5-w2-E complex.

J	K_a	K_c	←	J	K_a	K_c	obs.	o-c	J	K_a	K_c	←	J	K_a	K_c	obs.	o-c
4	3	1		3	2	1	3248.158	0.011	7	2	6		6	1	6	5697.620	0.009
4	4	0		3	3	0	3256.720	0.000	8	7	1		7	6	1	6497.715	-0.002
4	4	1		3	3	1	3263.993	-0.014	8	6	3		7	5	3	6510.945	-0.002
5	2	3		4	1	3	4069.618	0.015	8	4	4		7	3	4	6511.231	0.008
5	3	3		4	2	3	4069.618	-0.006	8	5	4		7	4	4	6511.231	0.005
5	1	4		4	0	4	4069.711	-0.003	8	3	5		7	2	5	6511.407	0.007
6	6	0		5	5	0	4886.621	-0.015	8	4	5		7	3	5	6511.407	0.007
7	6	1		6	5	1	5685.103	0.003	8	8	0		7	7	0	6518.240	-0.011
7	5	2		6	4	2	5694.047	-0.010	8	8	1		7	7	1	6529.068	0.013
7	3	4		6	2	4	5697.431	0.003	9	7	2		8	6	2	7318.148	-0.011
7	4	4		6	3	4	5697.431	0.002	9	2	7		8	1	7	7325.447	0.011
7	2	5		6	1	5	5697.541	-0.005	9	3	7		8	2	7	7325.447	0.011
7	3	5		6	2	5	5697.541	-0.005	9	8	2		8	7	2	7327.171	0.001
7	1	6		6	0	6	5697.620	0.009	9	9	0		8	8	0	7334.751	-0.001

Figure S1. CP-FTMW spectrum (upper trace in black) of 15-crown-5 ether (without the addition of water) and its comparison with that simulated (lower trace in blue) from the rotational constants of the eight conformers found in previous works.[16,17] From this comparison it can be seen that there are many unassigned strong lines left as shown in the zoom window.

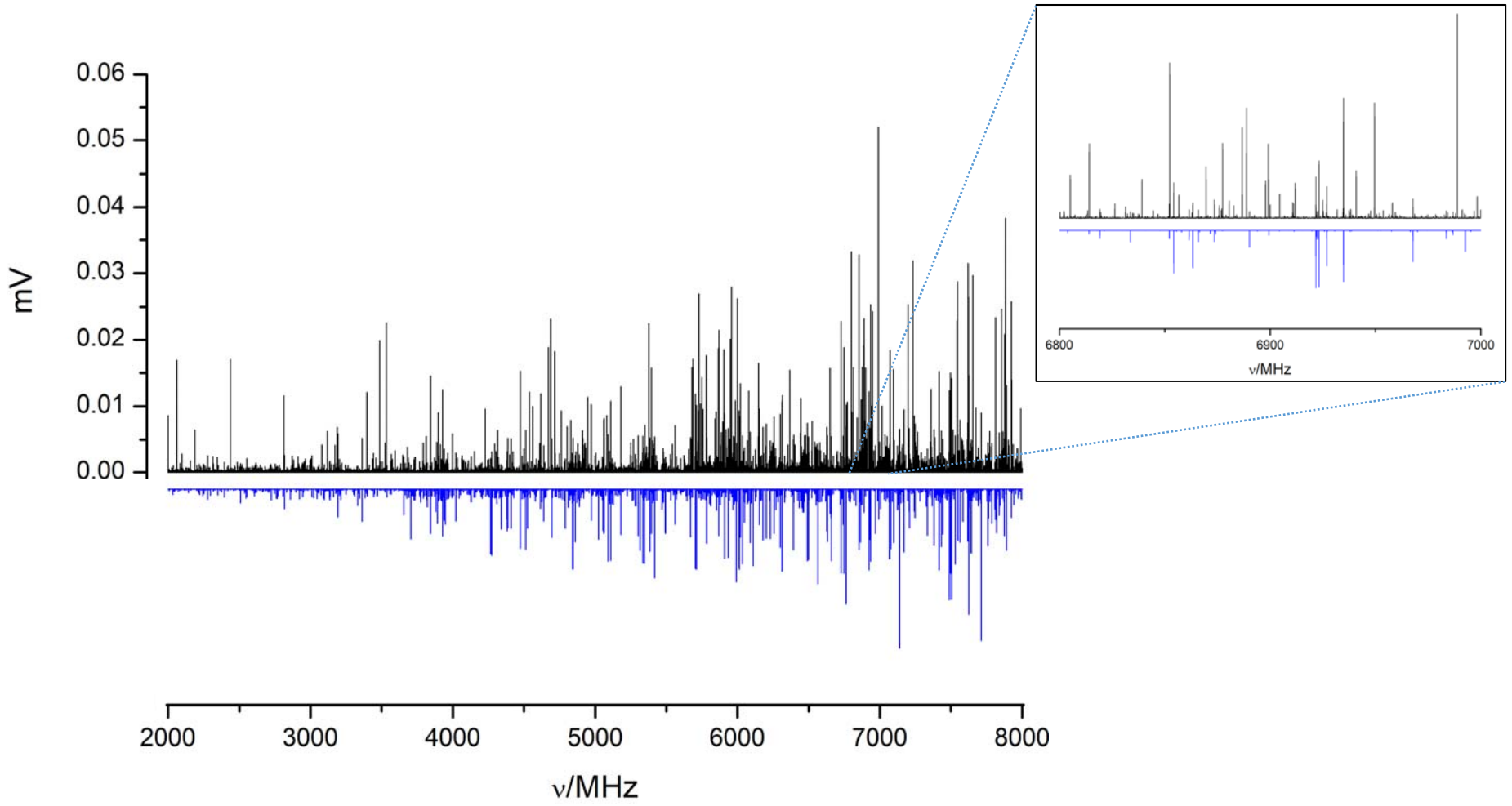

Figure S2a. Structures, relative Gibbs energies and calculated populations for the most stable 15-crown-5 ether conformers obtained from ab initio MP2/6-311++G(d,p) optimizations. The global minimum, form 0, has been observed for the first time in this work. Forms I-VI and VIII-IX were previously observed. Form VII has not been observed. Form XX is calculated by subtracting water from the microsolvated complexes observed in this work (15C5-w-B and 15C5-w_2-C).

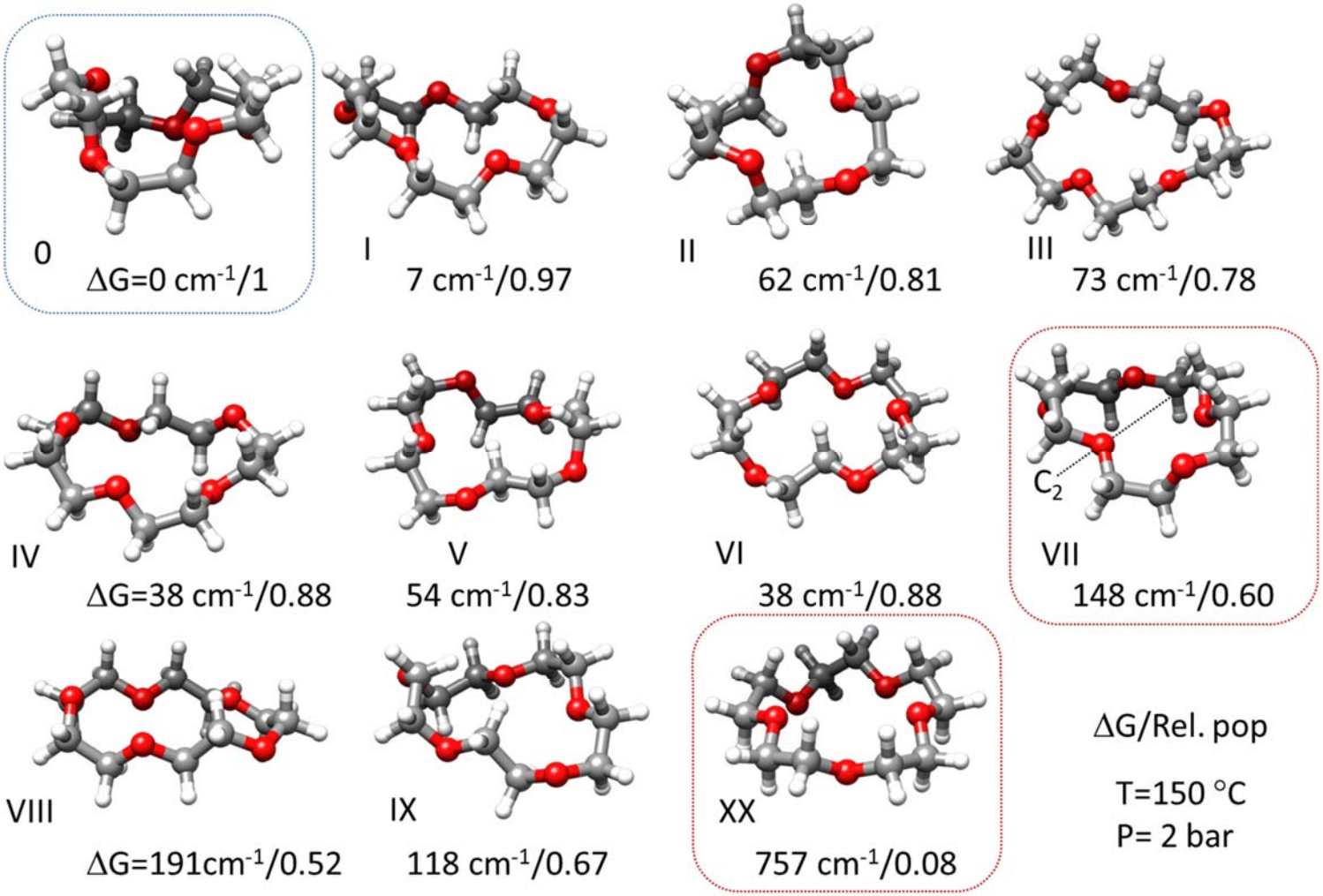

Figure S2b. Different perspectives of the conformers shown in fig S2a.

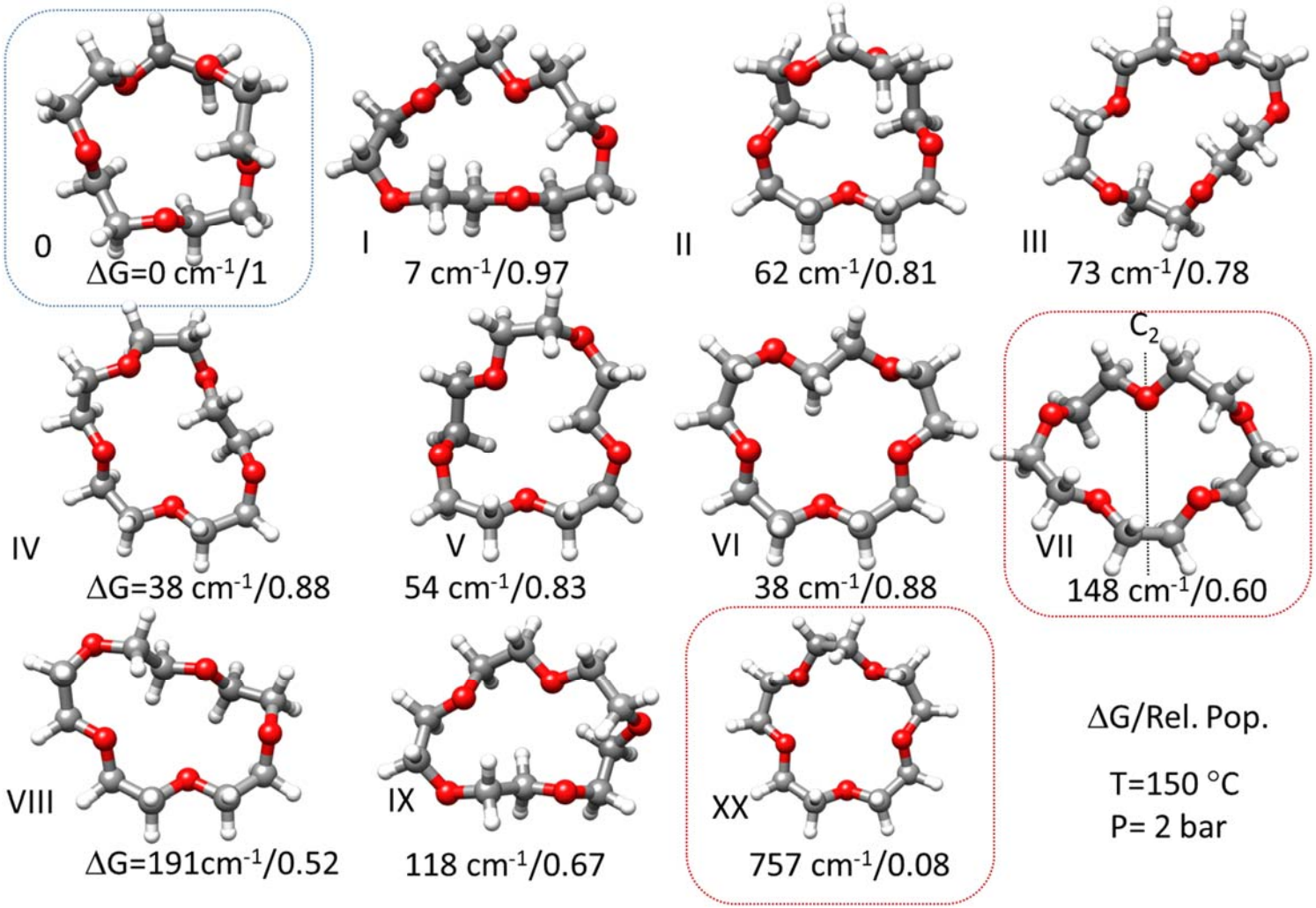

Figure S3. Sections of the spectrum of 15-crown-5 ether-H_2O-B (left) and 15-crown-5 ether-$(H_2O)_2$-E (right) species showing examples of recognizable spectral patterns which were very useful for the assignment of the spectra.

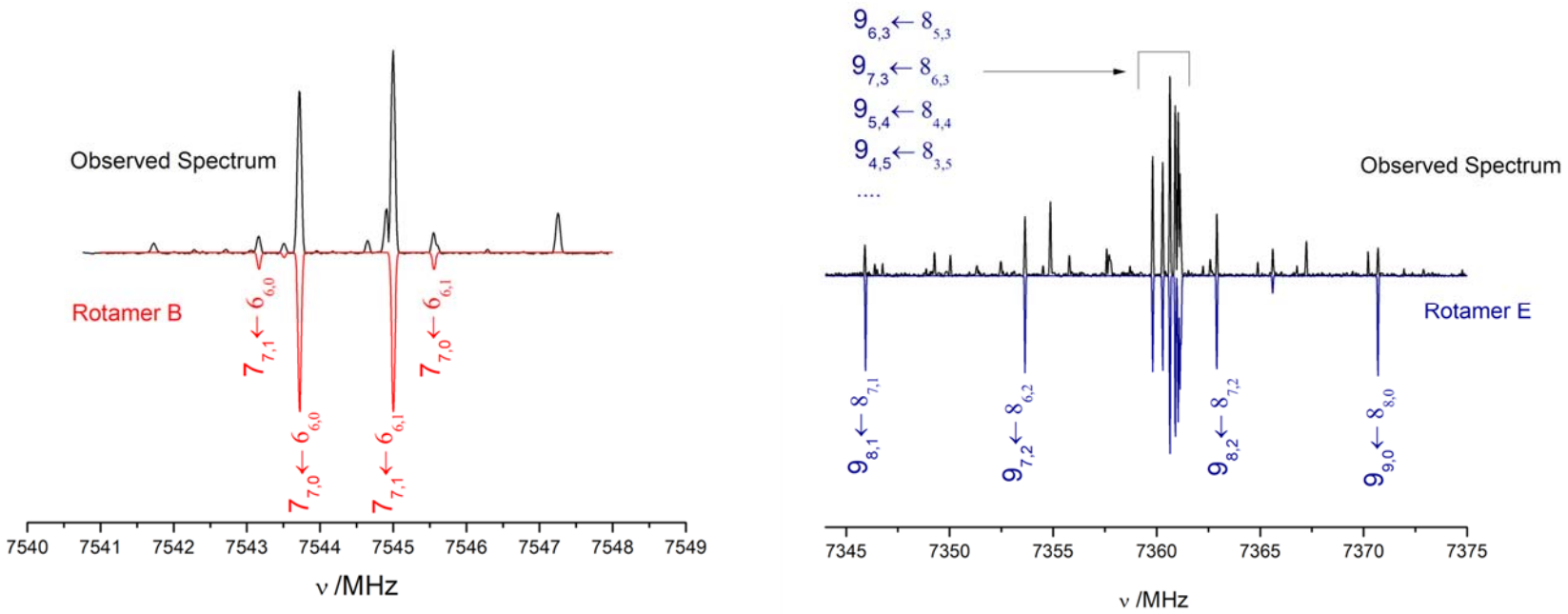

Figure S4. Structures of the most stable 15-crown-5 ether – H_2O (1:1) conformers obtained from ab initio MP2/6-311++G(d,p) calculations and relative energies. Only forms 15C5-w-1 and 15C5−w−3 have been observed. Note that as depicted, in all the conformers the lower part of the 15C5 ring has approximately the same structure. In the three low energy forms 15C5-w-1, 15C5-w-2 and 15C5-w-3 the structure of the ring shows many similarities and can be traced back to the monomer forms 15C5-VII, 15C5-II and 15C5-XX, respectively. The conversion Conformers 15C5-w-3 and 15C5-w-7 have the same 15C5 crown ether structure with water interacting on opposite sides of the ring plane.

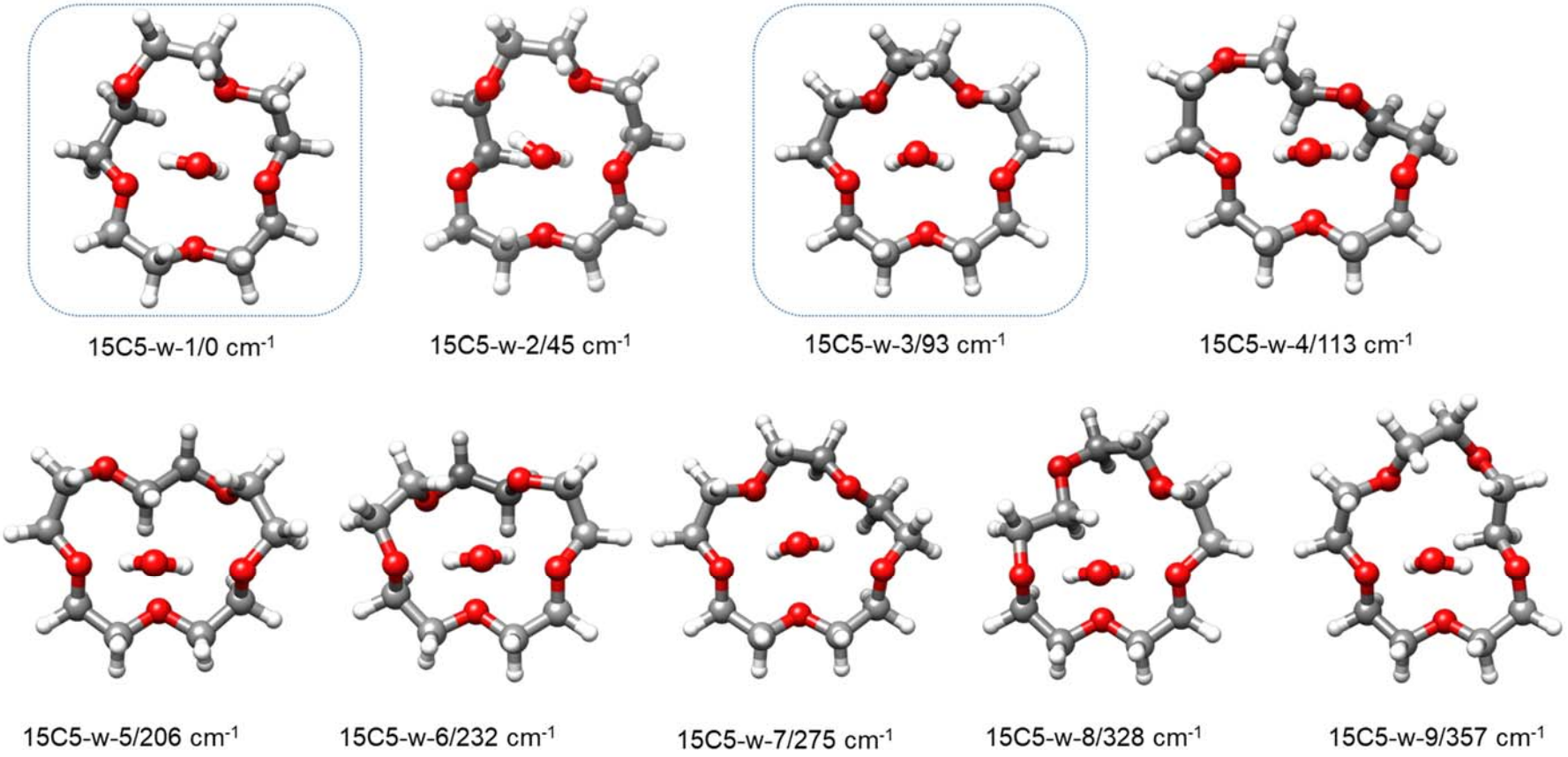

Figure S5. Structures of the most stable 15-crown-5 ether – $(H_2O)_2$ (1:2) conformers obtained from ab initio MP2/6-311++G(d,p) calculations and relative energies. Only forms 15C5-w_2-1 and 15C5-w_2-6 have been observed. 15C5-w_2-2, which derives from 15C5-VII and 15C5-w-1 (see figure S5), has almost the same energy as 15C5-w_2-1 but has no dipole moment and is thus unobservable by rotational spectroscopy.

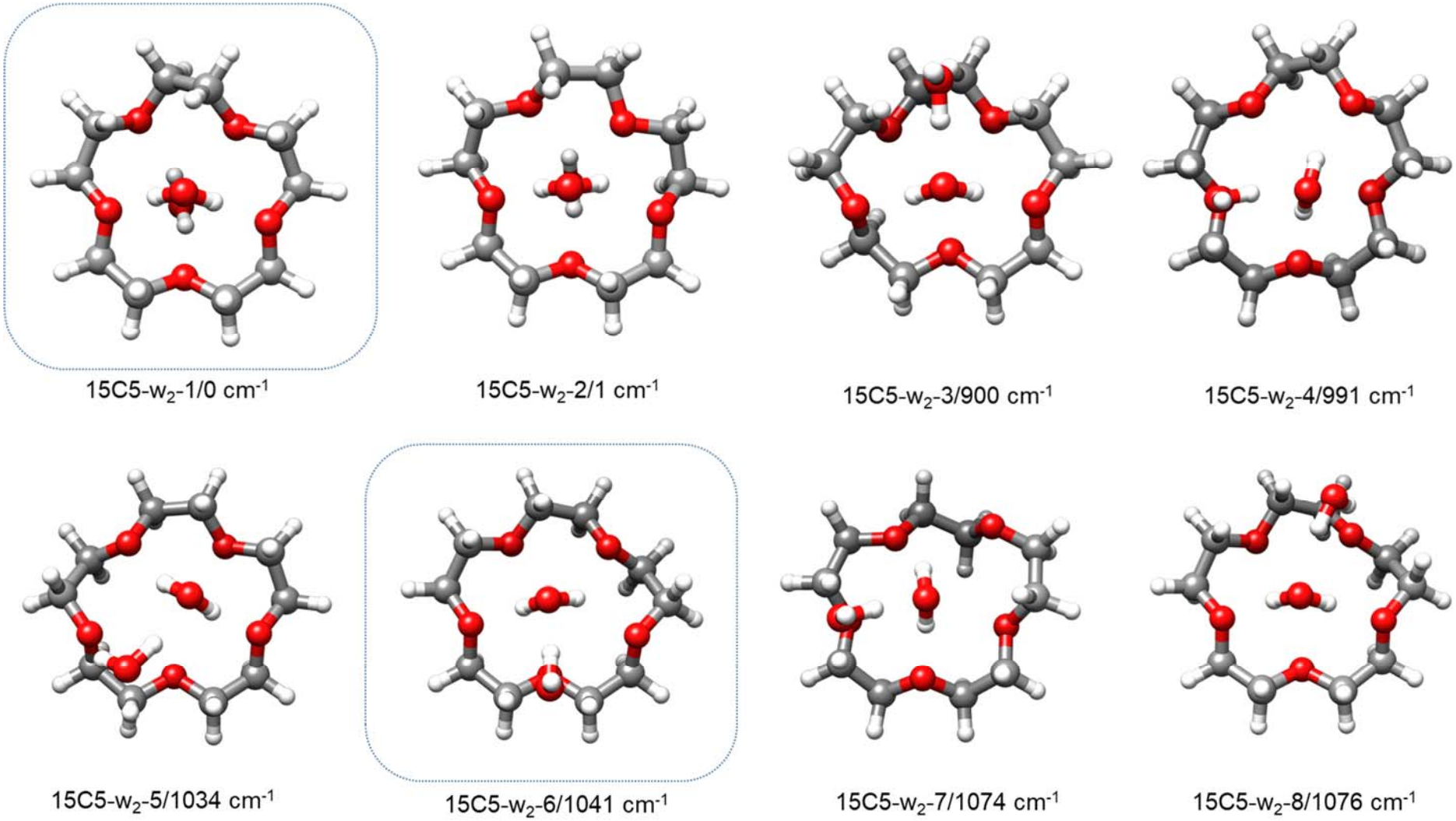

Figure S6. Monomer 15C5-VII (C_2 symmetry), not observed in the supersonic jet, is at the origin of the observed water complex 15C5-w-1 by allowing it to interact with a water molecule on any of the two faces of the ring. The complex has been identified as the observed rotamer 15C5-w-B. When adding a second water molecule on the opposite face the complex 15C5-w_2-2 (C_2 symmetry) is obtained. This three-body complex has no dipole moment and is thus not observable by microwave spectroscopy. However it is expected to have the same population than the observed rotamer 15C5-w_2-D, assigned to the 15C5-w_2-1 predicted form. Ab initio computations show that optimization of the 15C5 crown ether by starting from its structure in either 15C5-w-1 or 15C5-w_2-2 yields conformer 15C5-VII again. In the figure the three species are depicted showing the same orientation in order to show the changes in the 15C5-VII ring structure upon complexation.