Supplementary information for:

Microsolvation of Ethyl Carbamate Conformers: Effect of Carrier Gas on the Formation of Complexes.

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Abstract

Microsolvated complexes of ethyl carbamate with up to three water molecules formed in a supersonic expansion have been characterized by high-resolution microwave spectroscopy. Both chirped-pulse and cavity Fourier transform microwave spectrometers covering the 2-13 GHz frequency range have been used. The structures of the complexes have been characterized and show water molecules closing sequential cycles through hydrogen bonding with the amide group. As happen in the monomer, the ethyl carbamate-water complexes exhibit a conformational equilibrium between two conformers close in energy. The interconversion barrier between both forms has been studied analyzing the spectra obtained using different carrier gas in the expansion. Complexation of ethyl carbamate with water molecules seems apparently not to alter substantially the potential energy function for the interconversion between the two conformations of ethyl carbamate.

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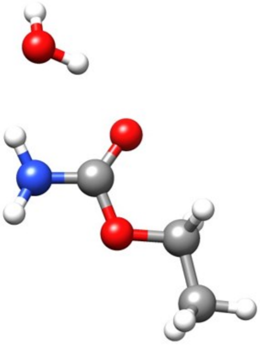
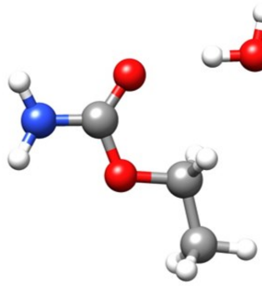
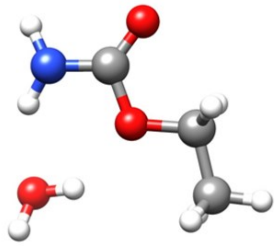
Figure S1. Conformers predicted for ethyl carbamate I (ecb-I) and ethyl carbamate II (ecb-II) complexes with one molecule of water. ΔE is the stabilization energy relative to the most stable complex (ecb-I-w-a) calculated at the B3LYP-GD3/6-311++G(d,p) level of theory including ZPE correction. The corresponding parameters are given in Table S1. Since, only the most stable conformer has been detected, the nomenclature for this complex will be ecb-I-w in the manuscript.



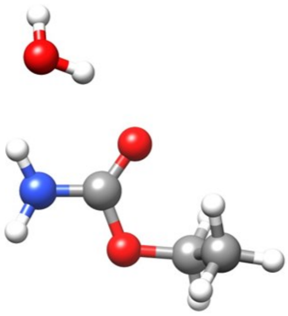
Ecb-I-w-a
$\Delta E = 0$ cm^{-1}



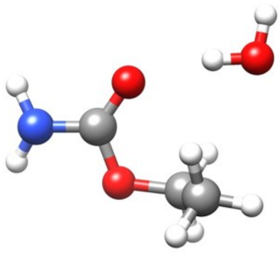
Ecb-I-w-b
$\Delta E = 723$ cm^{-1}



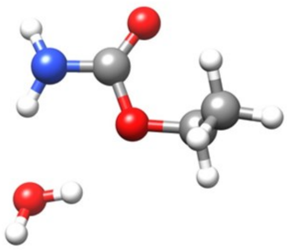
Ecb-I-w-c
$\Delta E = 741$ cm^{-1}



Ecb-II-w-a
$\Delta E = 23$ cm^{-1}



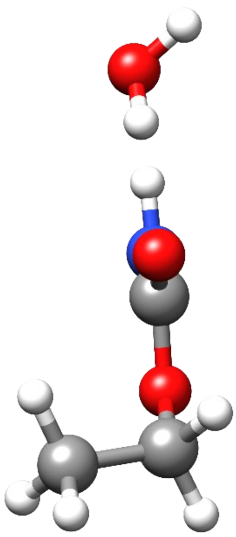
Ecb-II-w-b
$\Delta E = 728$ cm^{-1}

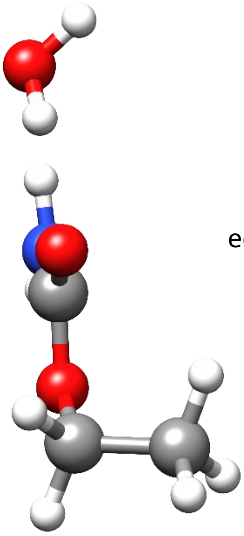


Ecb-II-w-c
$\Delta E = 825$ cm^{-1}

Figure S2. Nomenclature of ethyl carbamate-II water complexes. The projection in which the carbamate disposition present the ethyl chain in the front side and the ethyl chain has and clock angle (*ca*. 80 degree) the conformers are labeled as G+, if the angle has anti-clock orientation are labelled G-.

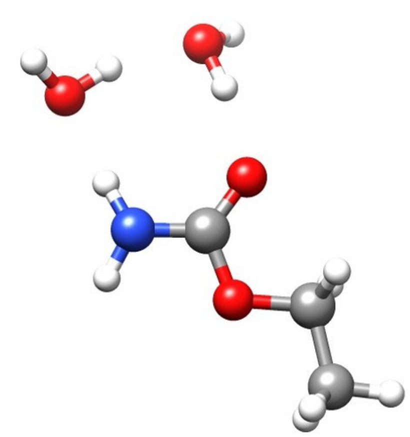
ecb-II-w_n-G-



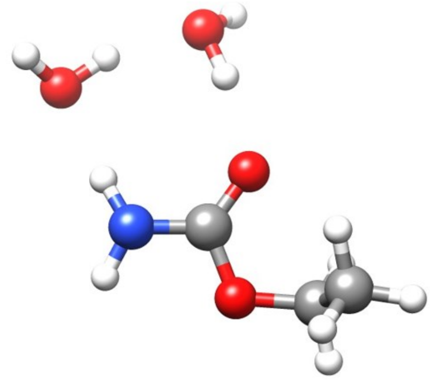


ecb-II-w_n-G+

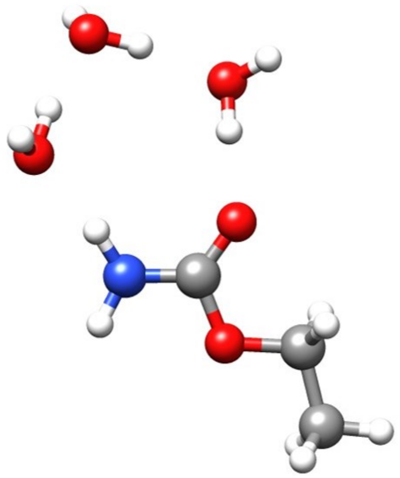
Figure S3. Conformers predicted for ethyl carbamate I (ecb-I) and ethyl carbamate II (ecb-II) complexes with two and three molecules of water. ΔE is the stabilization energy relative to the most stable complex (ecb-I-w_2 and ecb-I-w_3) calculated at the B3LYP-GD3/6-311++G(d,p) level of theory including ZPE correction. The corresponding parameters are given in Table S2.



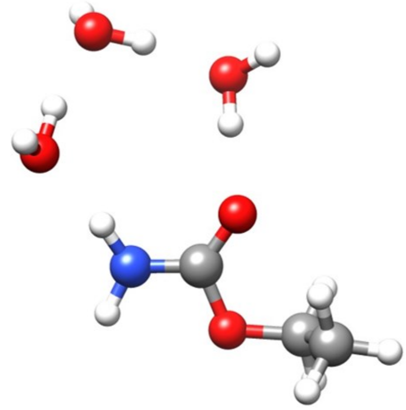
Ecb-I-w_2
$\Delta E = 0$ cm^{-1}



Ecb-II-w_2
$\Delta E = 10$ cm^{-1}



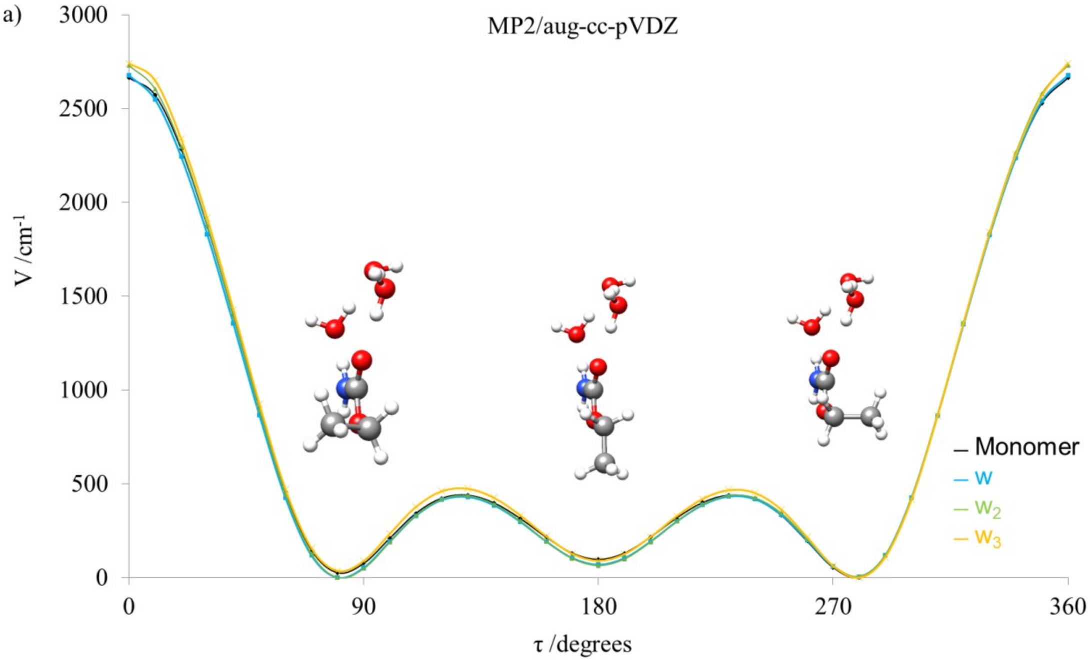
Ecb-I-w_3
$\Delta E = 0$ cm^{-1}



Ecb-II-w_3
$\Delta E = 26$ cm^{-1}

Figure S4. Overlap of Potential Energy function for the interconversion of ethyl carbamate monomeric forms and water complexes at the a) MP2/aug-cc-pVDZ and b) B3LYP-GD3/6-311++G(d,p) levels of theory.

a)



b)

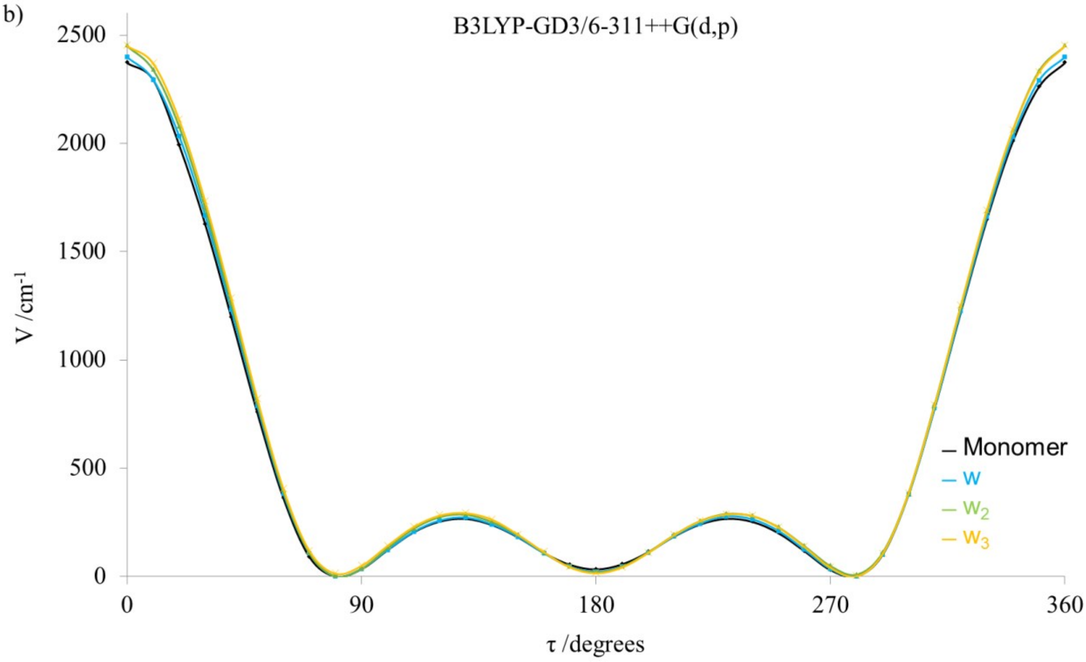
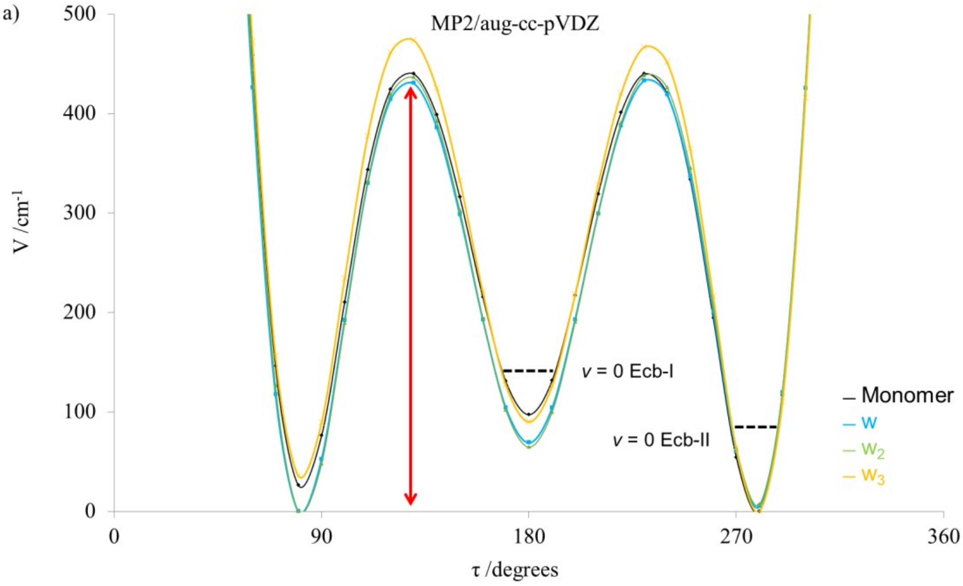


Figure S5. Zoom-in into the lower part of the of potential energy function for the interconversion of ethyl carbamates monomeric forms and water complexes at the a) MP2/aug-cc-pVDZ and b) B3LYP-GD3/6-311++G(d,p) levels of theory.

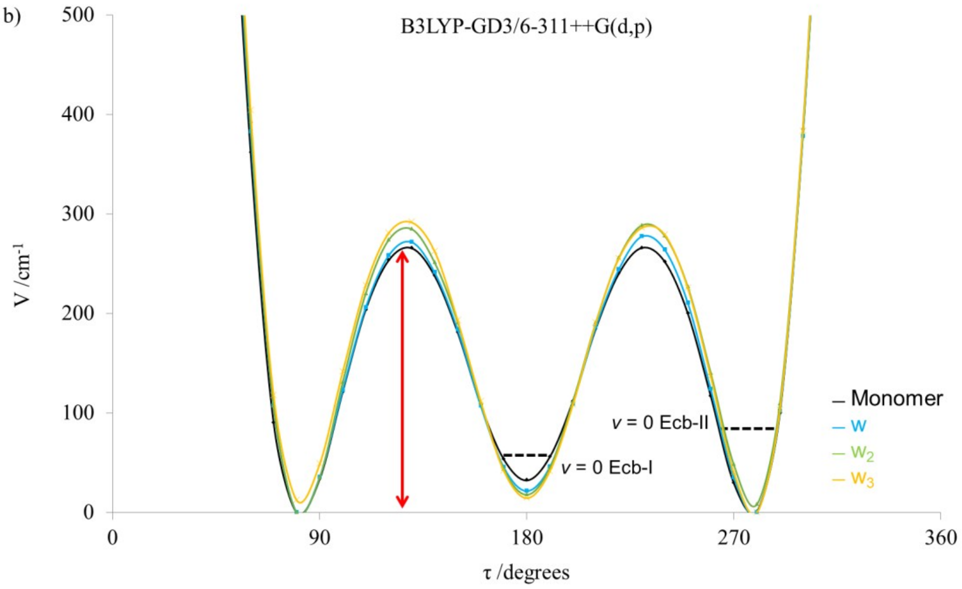
a)



	Monomer	-w	-w_2	-w_3
$\Delta E_{II\text{-}I}$ v = 0 (ZPE, cm^{-1})	-50	-35[a]	-22	-16
$\Delta E_{II\text{-}I}$ (no ZPE, cm^{-1})	-97	-69/-64[b]	-65/-58	-54/-90
$Barrier_{II\text{-}I}$ (no ZPE, cm^{-1})	440	430/420	436/426	474/466

[a] Only values for G+ available · [b] Values for G-/G+ separated by slash

b)



	Monomer	-w	-w_2	-w_3
$\Delta E_{II\text{-}I}$ v = 0 (ZPE, cm^{-1})	19	23/49[a]	10/42	26/0
$\Delta E_{II\text{-}I}$ (no ZPE, cm^{-1})	-31	-22/-22	-20/-10	-3/-12
$Barrier_{II\text{-}I}$ (no ZPE, cm^{-1})	265	277/	280/	286/

[a] Values for G-/G+ separated by slash

Table S1. Theoretical rotational parameters calculated at B3LYP-GD3/6-311++G(d,p) level of theory for the ethyl carbamate I (ecb-I) and ethyl carbamate II (ecb-II) complexes with one molecule of water.

Parameter[a]	Ecb-I-w-a	Ecb-I-w-b	Ecb-I-w-c	Ecb-II-w-a G-	Ecb-II-w-a G+	Ecb-II-w-b	Ecb-II-w-c
A /MHz	7689.84	2257.73	2338.56	5109.80	5298.30	3052.59	2874.51
B /MHz	1031.44	1922.35	2091.43	1220.31	1203.98	1722.13	1752.29
C /MHz	921.95	1052.07	1123.12	1067.74	1058.60	1210.17	1184.88
P_a /uÅ^2	486.21	259.71	237.76	394.28	400.89	272.76	269.56
P_b /uÅ^2	61.96	220.66	212.22	79.04	76.52	144.85	156.96
P_c /uÅ^2	3.76	3.19	3.89	19.86	18.87	20.70	18.85
μ_a /D	1.56	3.05	1.59	1.16	1.43	3.13	0.62
μ_b /D	0.89	1.04	2.22	1.15	0.66	0.28	2.53
μ_c /D	0.89	0.31	1.07	0.65	1.02	0.29	1.01
^{14}N χ_{aa} /MHz	1.81	2.77	2.68	1.80	1.74	2.76	2.29
^{14}N χ_{bb} /MHz	2.72	2.10	1.91	1.87	2.35	1.70	1.94
^{14}N χ_{cc} /MHz	-4.53	-4.88	-4.59	-3.67	-4.10	-4.45	-4.24
ΔE /cm^{-1}	22	863	818	0	0	814	842
ΔE_{ZPE} /cm^{-1}	0	723	741	23	49	728	825
ΔE /kJmol^{-1}	0.3	10.3	9.8	0.0	0.0	9.7	10.1
ΔE_{ZPE} /kJmol^{-1}	0.0	8.7	8.9	0.3	0.6	8.7	9.9

[a] A, B and C are the rotational constants. P_α (α= a, b or c) are the planar moments of inertia, these are derived from the moments of inertia I_α as for example $P_c = (I_a+I_b-I_c)/2$. μ_α (α = a, b or c) are the electric dipole moment components, 1 D = 3.33·10^{-30} C·m. χ_{aa}, χ_{bb}, and χ_{cc}, are the quadrupole coupling tensor diagonal elements for ^{14}N atom. ΔE is the energy relative to the most stable conformer. ΔE_{ZPE} is the energy relative to the most stable conformer including zero point energy correction.

Table S2. Theoretical rotational parameters calculated at B3LYP-GD3/6-311++G(d,p) level of theory for the ethyl carbamate I (ecb-I) and ethyl carbamate II (ecb-II) complexes with two and three molecules of water.

Parameter[a]	Ecb-I-w_2	Ecb-II-w_2 G-	Ecb-II-w_2 G+	Ecb-I-w_3	Ecb-II-w_3 G-	Ecb-II-w_3 G+
A /MHz	3793.57	3060.95	3025.03	2260.09	2017.15	1899.24
B /MHz	704.09	802.41	810.67	493.14	543.22	568.28
C /MHz	599.88	676.37	678.06	413.03	452.44	462.15
P_a /uÅ^2	713.51	605.96	600.84	1012.40	898.40	858.38
P_b /uÅ^2	128.96	141.24	144.49	211.19	218.60	235.16
P_c /uÅ^2	4.26	23.87	22.57	12.42	31.94	30.93
μ_a /D	1.62	1.42	1.42	1.68	1.60	1.46
μ_b /D	0.47	0.50	0.48	0.08	0.11	0.05
μ_c /D	0.16	0.09	0.20	0.47	0.49	0.43
^{14}N χ_{aa} /MHz	1.45	1.42	1.48	1.25	1.09	1.37
^{14}N χ_{bb} /MHz	2.79	2.68	2.43	2.53	2.62	1.99
^{14}N χ_{cc} /MHz	-4.24	-4.10	-3.92	-3.78	-3.71	-3.36
ΔE /cm^{-1}	20	0	10	15	12	0
ΔE_{ZPE} /cm^{-1}	0	10	42	0	26	0
ΔE /kJmol^{-1}	0.2	0.0	0.1	0.2	0.1	0.0
ΔE_{ZPE} /kJmol^{-1}	0.0	0.1	0.5	0.0	26	0.0

[a] See table S1 for definitions.

Table S3. Observed rotational parameters obtained for the ecb-I-w complex for the parent and the $^{18}O_w$ isotopologue compared to B3LYP-GD3/6-311++G(d,p) values.

Fitted Parameters[a]	ecb-I-w	ecb-I-w $^{18}O_w$	theoretical
A /MHz	7659.94791(44)[b]	7632.97(37)	7689.84
B /MHz	1034.10646(11)	986.93854(11)	1031.44
C /MHz	923.276293(93)	885.14275(12)	921.95
Δ_J /kHz	0.1124(13)	[0.1124][c]	0.098
Δ_{JK} /kHz	0.088(13)	[0.088]	-0.193
Δ_K /kHz	[0.]	[0.]	22.061
δ_J /kHz	0.01594(58)	[0.01594]	0.011
δ_K /kHz	[0.]	[0.]	0.321
^{14}N 3/2(χ_{aa}) /MHz	2.4588(18)	[2.4588]	2.72
^{14}N ¼(χ_{bb}-χ_{cc}) /MHz	1.60147(59)	[1.60147]	1.81
n	138/37	25/9	
σ /kHz	2.4	1.6	
Derived Parameters			
P_a /uÅ^2	485.05484(52)	508.4074(32)	486.21
P_b /uÅ^2	62.32085(52)	62.5501(32)	61.96
P_c /uÅ^2	3.65596(52)	3.6598(32)	3.76
^{14}N χ_{aa}/MHz	1.6392(12)	[1.6392]	1.81
^{14}N χ_{bb}/MHz	2.3833(18)	[2.3833]	2.72
^{14}N χ_{cc}/MHz	-4.0225(18)	[-4.0225]	-4.53

[a] A, B and C are the rotational constants. Δ_J, Δ_{JK}, Δ_K, δ_J and δ_K are the quartic centrifugal distortion constants. χ_{aa}, χ_{bb} and χ_{cc} are the quadrupole coupling tensor diagonal elements for ^{14}N atom. n is the number of quadrupole hyperfine components/rotational transitions fitted. σ is the rms deviation of the fit. P_α (α = a, b or c) are the planar moments of inertia, these are derived from the moments of inertia I_α as for example $P_c = (I_a+I_b-I_c)/2$. [b] Standard errors are given in parentheses in units of the last digits. [c] Parameters in square brackets were kept fixed to those given for the parent species in the fit.

Table S4. Observed rotational parameters obtained for the ecb-I-w_2 complex for the parent the $^{18}O_{w1}$ and the $^{18}O_{w2}$ isotopologues compared to B3LYP-GD3/6-311++G(d,p) values.

Fitted Parameters[a]	ecb-I-w_2	ecb-I-w_2 $^{18}O_{w1}$	ecb-I-w_2 $^{18}O_{w2}$	theoretical
A /MHz	3734.1586(72)	3599.386(31)	3675.093(47)	3793.57
B /MHz	701.90967(10)	686.889435(79)	680.60559(11)	704.09
C /MHz	597.04077(10)	582.706572(84)	580.11263(11)	599.88
Δ_J /kHz	0.05569(31)	[0.05569]	[0.05569]	0.042
Δ_{JK} /kHz	0.2351(29)	[0.2351]	[0.2351]	0.161
Δ_K /kHz	[0.]	[0.]	[0.]	4.566
δ_J /kHz	0.01043(24)	[0.01043]	[0.01043]	0.007
δ_K /kHz	0.291(33)	[0.291]	[0.291]	0.264
^{14}N $3/2(\chi_{aa})$ /MHz	2.0278(58)	[2.0278]	[2.0278]	2.18
^{14}N $¼(\chi_{bb}-\chi_{cc})$ /MHz	1.5582(57)	[1.5582]	[1.5582]	1.76
n	153/53	25/9	25/9	
σ /kHz	1.4	1.5	2.1	
Derived Parameters				
P_a /uÅ^2	715.56974(31)	731.3195(23)	738.1010(18)	713.51
P_b /uÅ^2	130.90344(31)	135.9763(23)	133.0728(18)	128.96
P_c /uÅ^2	4.43601(31)	4.4306(23)	4.4417(18)	4.26
^{14}N χ_{aa}/MHz	1.3519(39)	[1.3519]	[1.3519]	1.45
^{14}N χ_{bb}/MHz	2.440(13)	[2.440]	[2.440]	2.79
^{14}N χ_{cc}/MHz	-3.792(13)	[-3.792]	[-3.792]	-4.24

[a] See table S3 for definitions.

Table S5. Observed rotational parameters obtained for the ecb-I-w_3 complex compared to B3LYP-GD3/6-311++G(d,p) values.

Fitted Parameters[a]	ecb-I-w_3		theoretical
	v=0	v=1	
A /MHz	2254.4370(61)	2254.4248(61)	2260.09
B /MHz	486.842445(98)	486.843300(98)	493.14
C /MHz	410.026213(87)	410.027428(87)	413.03
Δ_J /kHz	0.08650(18)		0.062
Δ_{JK} /kHz	-1.104(10)		-0.595
Δ_K /kHz	[0.]		6.594
δ_J /kHz	0.01445(21)		0.010
δ_K /kHz	[0.]		0.217
^{14}N 3/2(χ_{aa}) /MHz	1.734(36)		1.79
^{14}N ¼(χ_{bb}-χ_{cc}) /MHz	1.4378(63)		1.38
n	180/30/30		
σ /kHz	2.0/1.7/2.2		
Derived Parameters			
P_{a0} /uÅ^2	1023.22858(69)	1023.22523(69)	1012.40
P_{b0} /uÅ^2	209.32433(69)	209.32402(69)	211.19
P_{c0} /uÅ^2	14.84648(69)	14.84801(69)	12.42
^{14}N χ_{aa}/MHz	1.156(24)		1.19
^{14}N χ_{bb}/MHz	2.298(25)		2.17
^{14}N χ_{cc}/MHz	-3.454(25)		-3.36

[a] See table S3 for definitions.

Table S6. Observed rotational parameters obtained for the ecb-II-w complex compared to B3LYP-GD3/6-311++G(d,p) values.

Fitted Parameters[a]	ecb-II-w	theoretical – G-	theoretical – G+
A /MHz	5196.3808(28)	5109.80	5298.30
B /MHz	1212.1730(10)	1220.31	1203.98
C /MHz	1063.34957(89)	1067.74	1058.60
Δ_J /kHz	0.471(34)	0.392	0.337
Δ_{JK} /kHz	-2.35(14)	-3.545	-2.120
Δ_K /kHz	[0.]	33.579	25.081
δ_J /kHz	0.076(13)	0.082	0.074
δ_K /kHz	[0.]	0.149	0.427
^{14}N 3/2(χ_{aa}) /MHz	2.3891(81)	2.70	2.62
^{14}N ¼(χ_{bb}-χ_{cc}) /MHz	1.2977(28)	1.38	1.61
N	54/16		
σ /kHz	6.6		
Derived Parameters			
P_a /uÅ^2	397.46735(26)	394.28	400.89
P_b /uÅ^2	77.80345(26)	79.04	76.52
P_c /uÅ^2	19.45251(26)	19.86	18.87
^{14}N χ_{aa}/MHz	1.5927(54)	1.80	1.74
^{14}N χ_{bb}/MHz	1.799(16)	1.87	2.35
^{14}N χ_{cc}/MHz	-3.392(16)	-3.67	-4.10

[a] See table S3 for definitions.

Table S7. Observed rotational parameters obtained for the ecb-II-w_2 complex compared to B3LYP-GD3/6-311++G(d,p) values.

Fitted Parameters[a]	ecb-II-w_2	theoretical – *G*-	theoretical – G+
A /MHz	3023.593(94)	3060.95	3025.03
B /MHz	797.6169(12)	802.41	810.67
C /MHz	672.6464(11)	676.37	678.06
Δ_J /kHz	0.168(11)	0.132	0.136
Δ_{JK} /kHz	-0.942(62)	-0.561	-0.590
Δ_K /kHz	[0.]	6.122	5.664
δ_J /kHz	0.064(16)	0.028	0.031
δ_K /kHz	[0.]	0.219	0.253
^{14}N 3/2(χ_{aa}) /MHz	2.001(12)	2.13	2.23
^{14}N ¼(χ_{bb}-χ_{cc}) /MHz	1.503(13)	1.69	1.59
N	51/18		
σ /kHz	5.5		
Derived Parameters			
P_a /uÅ^2	608.8977(27)	605.96	600.84
P_b /uÅ^2	142.4317(27)	141.24	144.49
P_c /uÅ^2	24.7135(27)	23.87	22.57
^{14}N χ_{aa}/MHz	1.3340(80)	1.42	1.48
^{14}N χ_{bb}/MHz	2.339(30)	2.68	2.43
^{14}N χ_{cc}/MHz	-3.673(30)	-4.10	-3.92

[a] See table S3 for definitions.

Table S8. Observed rotational parameters obtained for the ecb-II-w_3 complex compared to B3LYP-GD3/6-311++G(d,p) values.

Fitted Parameters[a]	ecb-II-w_3	theoretical – G-	theoretical – G+
A /MHz	1885.263(24)	2017.15	1899.24
B /MHz	557.96382(68)	543.22	568.28
C /MHz	458.15647(59)	452.44	462.15
Δ_J /kHz	0.2207(32)	0.080	0.184
Δ_{JK} /kHz	-1.619(33)	-0.342	-1.146
Δ_K /kHz	[0.]	3.816	5.477
δ_J /kHz	0.0392(37)	0.016	0.042
δ_K /kHz	[0.]	0.180	0.305
^{14}N 3/2(χ_{aa}) /MHz	1.900(50)	1.64	2.05
^{14}N ¼(χ_{bb}-χ_{cc}) /MHz	1.281(22)	1.58	1.34
N	76/27		
σ /kHz	6.0		
Derived Parameters			
P_a /uÅ^2	870.3792(19)	898.41	858.38
P_b /uÅ^2	232.6915(19)	218.60	235.16
P_c /uÅ^2	35.3766(19)	31.95	30.93
^{14}N χ_{aa}/MHz	1.267(33)	1.09	1.37
^{14}N χ_{bb}/MHz	1.929(61)	2.62	1.99
^{14}N χ_{cc}/MHz	-3.195(61)	-3.71	-3.36

[a] See table S3 for definitions.

Table S9. r_0 structure obtained by the fitting of the rotational constants for all the available isotopologues for the ecb-I-w complex and comparison with the r_e (B3LYP-GD3/6-311++G(d,p)) structure. Four parameters of ecb-I-w were fitted to six rotational constants (three from the parent and three from the $^{18}O_{w1}$ species) achieving a final deviation of the fit of 0.012 uÅ^2. Geometrical parameters for water fixed to the r_0 values [R. L. Cook, F. C. DeLucia, P. Helminger, *J. Mol. Spectrosc.* **1974**, *53*, 62-76]. The rest of the parameters were fixed to the r_e values, the uncertainties given in parenthesis were obtained from the coordinates uncertainties resulting from the r_0 fitting.

Fitted parameter	r_0	r_e	Derived parameter	r_0	r_e
$r(O_{w1}\cdots H_1)$ /Å	2.0958(6)	2.079	$r(O_{w1}–H_{w1-1})$ /Å	1.02(1)	0.975
$r(H_{w1-1}\cdots O_1)$ /Å	1.83(1)	1.913	$\angle(O_1–C_1–N)$ /°	125.100(8)	125.1
$\angle(O_{w1}\cdots H_1–N)$ /°	137.66(3)	138.2	$\angle(H_1\cdots O_{w1}–H_{w1-1})$ /°	80.3(4)	81.5
$\angle(H_{w1-1}\cdots O_1–C_1–N)$ /°	-181.5(1)	-175.2	$\angle(O_{w1}–H_{w1-1}\cdots O_1)$ /°	148.4(4)	148.5

Fixed parameter	r_0	r_e	Fixed parameter	r_0	r_e
$r(O_1–C_1)$ /Å	[1.224]	1.224	$\angle(O_1–C_1–O_2–C_2)$ /°	[0.0]	0.0
$r(N–C_1)$ /Å	[1.352]	1.352	$\angle(C_1–O_2–C_2–C_3)$ /°	[180.0]	179.8
$r(O_2–C_1)$ /Å	[1.351]	1.351	$\angle(N–C_1–O_2–C_2)$ /°	[180.0]	179.4
$r(O_2–C_2)$ /Å	[1.448]	1.448	$\angle(H_1–N–C_1–O_2)$ /°	[180.0]	175.7
$r(C_2–C_3)$ /Å	[1.515]	1.515	$\angle(H_2–N–C_1–O_2)$ /°	[0.0]	5.7
$r(N–H_1)$ /Å	[1.013]	1.013	$\angle(C_1–O_2–C_2–H_3)$ /°	[60.0]	58.4
$r(N–H_2)$ /Å	[1.005]	1.005	$\angle(C_1–O_2–C_2–H_4)$ /°	[-60.0]	-58.8
$r(O_{w1}–H_{w1-2})$ /Å	[0.965]	0.965	$\angle(O_2–C_2–C_3–H_5)$ /°	[60.0]	60.3
$r(C_2–H_3)$ /Å	[1.092]	1.092	$\angle(O_2–C_2–C_3–H_6)$ /°	[-60.0]	-60.3
$r(C_2–H_4)$ /Å	[1.092]	1.092	$\angle(O_2–C_2–C_3–H_7)$ /°	[180.0]	180.0
$r(C_3–H_5)$ /Å	[1.092]	1.092	$\angle(O_{w1}\cdots H_1–N–C_1)$ /°	[0.0]	-0.8
$r(C_3–H_6)$ /Å	[1.092]	1.092			
$r(C_3–H_7)$ /Å	[1.093]	1.093			
$\angle(O_1–C_1–O_2)$ /°	[123.4]	123.4			
$\angle(O_2–C_1–N)$ /°	[111.5]	111.5			
$\angle(C_1–O_2–C_2)$ /°	[116.1]	116.1			
$\angle(C_1–N–H_1)$ /°	[117.8]	117.8			
$\angle(C_1–N–H_2)$ /°	[120.1]	120.1			
$\angle(O_2–C_2–C_3)$ /°	[107.1]	107.1			
$\angle(O_2–C_2–H_3)$ /°	[108.8]	108.8			
$\angle(O_2–C_2–H_4)$ /°	[108.8]	108.8			
$\angle(C_2–C_3–H_5)$ /°	[110.9]	110.9			
$\angle(C_2–C_3–H_6)$ /°	[110.9]	110.9			
$\angle(C_2–C_3–H_7)$ /°	[109.7]	109.7			
$\angle(H_{w1-2}–O_{w1}–H_{w1-1})$ /°	[104.8]	106.4			
$\angle(H_{w1-1}\cdots O_1–C_1)$ /°	[108.5]	108.5			

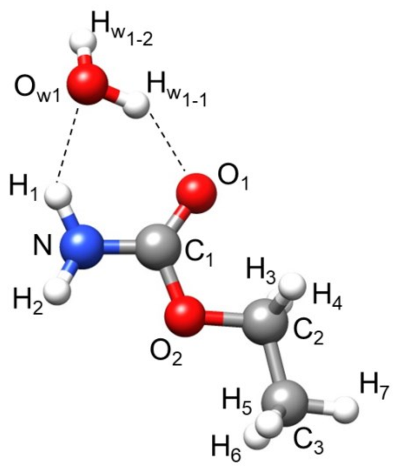


Table S10. r_0 structure obtained by the fitting of the rotational constants for all the available isotopologues for the ecb-I-w_2 complex and comparison with the r_e (B3LYP-GD3/6-311++G(d,p)) structure. Five parameters of ecb-I-w_2 were fitted to nine rotational constants (three from the parent, three from the $^{18}O_{w1}$ and three from the $^{18}O_{w2}$ species) achieving a final deviation of the fit of 0.025 uÅ^2. Geometrical parameters for water fixed to the r_0 values [R. L. Cook, F. C. DeLucia, P. Helminger, *J. Mol. Spectrosc.* **1974**, *53*, 62-76]. The rest of the parameters were fixed to the r_e values, the uncertainties given in parenthesis were obtained from the coordinates uncertainties resulting from the r_0 fitting.

Fitted parameter	r_0	r_e	Derived parameter	r_0	r_e
$r(O_{w2}\cdots H_1)$ /Å	1.887(7)	1.876	$r(H_{w1\text{-}1}\cdots O_{w1})$ /Å	1.836(5)	1.775
$r(H_{w1\text{-}1}\cdots O_1)$ /Å	1.778(1)	1.767	$r(O_{w2}\cdots O_{w1})$ /Å	2.763(5)	2.722
∠$(O_{w2}\cdots H_1–N)$ /°	175.0(6)	174.1	∠$(O_{w2}–H_{w1\text{-}1}\cdots O_{w1})$ /°	160.3(5)	161.0
∠$(H_{w1\text{-}1}\cdots O_1–C_1)$ /°	129.5(3)	129.4	∠$(H_{w1\text{-}1}\cdots O_{w1}–H_{w1\text{-}1})$ /°	98.6(2)	98.9
∠$(H_{w1\text{-}1}\cdots O_1–C_1–O_2)$ /°	174.0(2)	176.5			

Fixed parameter	r_0	r_e	Fixed parameter	r_0	r_e
$r(O_1–C_1)$ /Å	[1.227]	1.227	∠$(O_1–C_1–O_2–C_2)$ /°	[0.0]	0.2
$r(N–C_1)$ /Å	[1.345]	1.345	∠$(N–C_1–O_2–C_2)$ /°	[-180.0]	-179.6
$r(O_2–C_1)$ /Å	[1.352]	1.352	∠$(C_1–O_2–C_2–C_3)$ /°	[180.0]	179.5
$r(O_2–C_2)$ /Å	[1.447]	1.447	∠$(H_1–N–C_1–O_2)$ /°	[-180.0]	-178.0
$r(C_2–C_3)$ /Å	[1.515]	1.515	∠$(H_2–N–C_1–O_2)$ /°	[0.0]	-2.8
$r(N–H_1)$ /Å	[1.021]	1.021	∠$(C_1–O_2–C_2–H_3)$ /°	[60.0]	58.2
$r(N–H_2)$ /Å	[1.006]	1.006	∠$(C_1–O_2–C_2–H_4)$ /°	[-60.0]	-59.1
$r(C_2–H_3)$ /Å	[1.092]	1.092	∠$(O_2–C_2–C_3–H_5)$ /°	[-60.0]	-60.4
$r(C_2–H_4)$ /Å	[1.092]	1.092	∠$(O_2–C_2–C_3–H_6)$ /°	[60.0]	60.2
$r(C_3–H_5)$ /Å	[1.092]	1.092	∠$(O_2–C_2–C_3–H_7)$ /°	[180.0]	179.9
$r(C_3–H_6)$ /Å	[1.092]	1.092	∠$(O_{w2}\cdots H_1–N–C_1)$ /°	[16.0]	16.0
$r(C_3–H_7)$ /Å	[1.093]	1.093	∠$(H_{w2\text{-}1}–O_{w2}\cdots H_1–N)$ /°	[[-14.5]	-14.5
$r(O_{w2}–H_{w2\text{-}1})$ /Å	[0.965]	0.982	∠$(H_{w2\text{-}2}–O_{w2}–H_{w2\text{-}1}\cdots N)$ /°	[130.0]	130.0
$r(O_{w2}–H_{w2\text{-}2})$ /Å	[0.965]	0.961	∠$(O_{w1}–H_{w1\text{-}1}\cdots O_1–C_1)$ /°	[-10.2]	-10.2
$r(O_{w1}–H_{w1\text{-}1})$ /Å	[0.965]	0.982	∠$(H_{w1\text{-}2}–O_{w1}–H_{w1\text{-}1}\cdots O_1)$ /°	[-117.7]	-117.7
$r(O_{w1}–H_{w1\text{-}2})$ /Å	[0.965]	0.961			
∠$(O_1–C_1–O_2)$ /°	[122.5]	122.5			
∠$(O_2–C_1–N)$ /°	[111.6]	111.6			
∠$(C_1–O_2–C_2)$ /°	[116.3]	116.3			
∠$(O_2–C_2–C_3)$ /°	[107.1]	107.1			
∠$(C_1–N–H_1)$ /°	[120.5]	120.5			
∠$(C_1–N–H_2)$ /°	[119.1]	119.1			
∠$(O_2–C_2–H_3)$ /°	[108.5]	108.5			
∠$(O_2–C_2–H_4)$ /°	[108.5]	108.5			
∠$(C_2–C_3–H_5)$ /°	[110.8]	110.8			
∠$(C_2–C_3–H_6)$ /°	[110.8]	110.8			
∠$(C_2–C_3–H_7)$ /°	[109.7]	109.7			
∠$(H_{w2\text{-}1}–O_{w2}\cdots H_1)$ /°	[99.2]	99.2			
∠$(H_{w2\text{-}2}–O_{w2}–H_{w2\text{-}1})$ /°	[104.8]	105.9			
∠$(O_{w1}–H_{w1\text{-}1}\cdots O_1)$ /°	[170.3]	170.3			
∠$(H_{w1\text{-}2}–O_{w1}–H_{w1\text{-}1})$ /°	[104.8]	106.2			

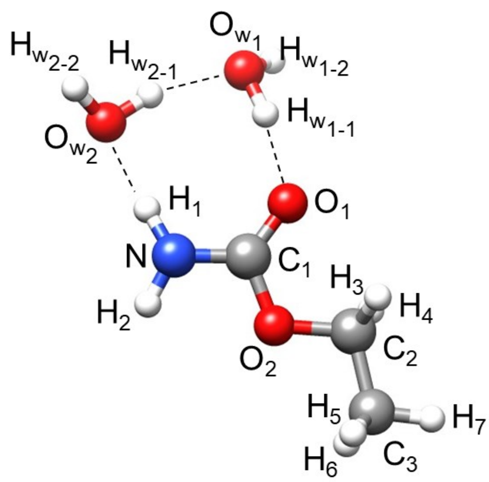


Table S11. Experimental and theoretical (B3LYP-GD3/6-311++G(d,p)) nuclear quadrupole coupling constants for the ^{14}N atom of the observed complexes with up to three water molecules for the rotamer ecb-I and values reported for the monomer [reference 11], together with the values of the unbalanced 2p_z electronic charge ($(U_p)_z$) both calculated from χ_{cc} and from the natural atomic orbital populations obtained by a Natural Bond Orbital Analysis [reference 47]. The plots represent the correlations between a) experimental values of χ_{cc}/eQq_{210} *vs.* -$(U_p)_z$. b) Theoretical values of χ_{cc}/eQq_{210} *vs.* -$(U_p)_z$. c) Theoretical *r*(C–N) *vs*. experimental χ_{cc}/eQq_{210}. d) Theoretical *r*(C=O) *vs*. experimental χ_{cc}/eQq_{210}.

The electric field gradient giving rise to nuclear quadrupole coupling of most molecules has been attributed primarily to the unequal filling of the p orbitals of the valence shell of the coupling atoms. According to this, the ^{14}N χ_{zz} constants can be related to the unbalanced 2p_z electronic charge $(U_p)_z = [(n_x + n_y)/2 - n_z]$ by:

$$\chi_{zz}/eQq_{210} = -(U_p)_z \quad (1)$$

Where n_α are the p_α orbital occupation numbers and q_{210} the electric field gradient associated to a 2p electron in an isolated atom (eQq_{210}≈-10 MHz for N). This definition of $(U_p)_z$ is such that its positive or negative values correspond respectively to electron deficit or excess along the *z* reference axis (W. Gordy, R. L. Cook, *Microwave Molecular Spectra*, Wiley, New York, **1984**).

Experimental	Ecb-I	Ecb-I-w	Ecb-I-w_2	Ecb-I-w_3
χ_{aa} /MHz	2.1151(14)	1.6392(12)	1.3519(39)	1.156(24)
χ_{bb} /MHz	2.1667(15)	2.3833(18)	2.440(13)	2.298(25)
χ_{cc} /MHz	-4.2818(15)	-4.0225(18)	-3.792(13)	-3.454(25)
χ_{cc}/eQq_{210}	0.42818	0.40225	0.3792	0.3454

Theoretical	Ecb-I	Ecb-I-w	Ecb-I-w_2	Ecb-I-w_3
χ_{aa} /MHz	2.39	1.81	1.45	1.25
χ_{bb} /MHz	2.47	2.72	2.79	2.53
χ_{cc} /MHz	-4.86	-4.53	-4.24	-3.78
χ_{ab} /MHz	0.30	0.37	0.36	0.43
χ_{ac} /MHz	0.44	-0.07	0.12	0.62
χ_{bc} /MHz	0.56	0.43	-0.40	-1.41
χ_{xx} /MHz	2.13	1.69	1.37	1.29
χ_{yy} /MHz	2.80	2.87	2.90	2.88
χ_{zz} /MHz	-4.93	-4.56	-4.27	-4.17
χ_{zz}/eQq_{210}	0.49	0.46	0.43	0.42
-$(U_p)_z$ NBO	0.43	0.39	0.36	0.32

Table S11. Continued.

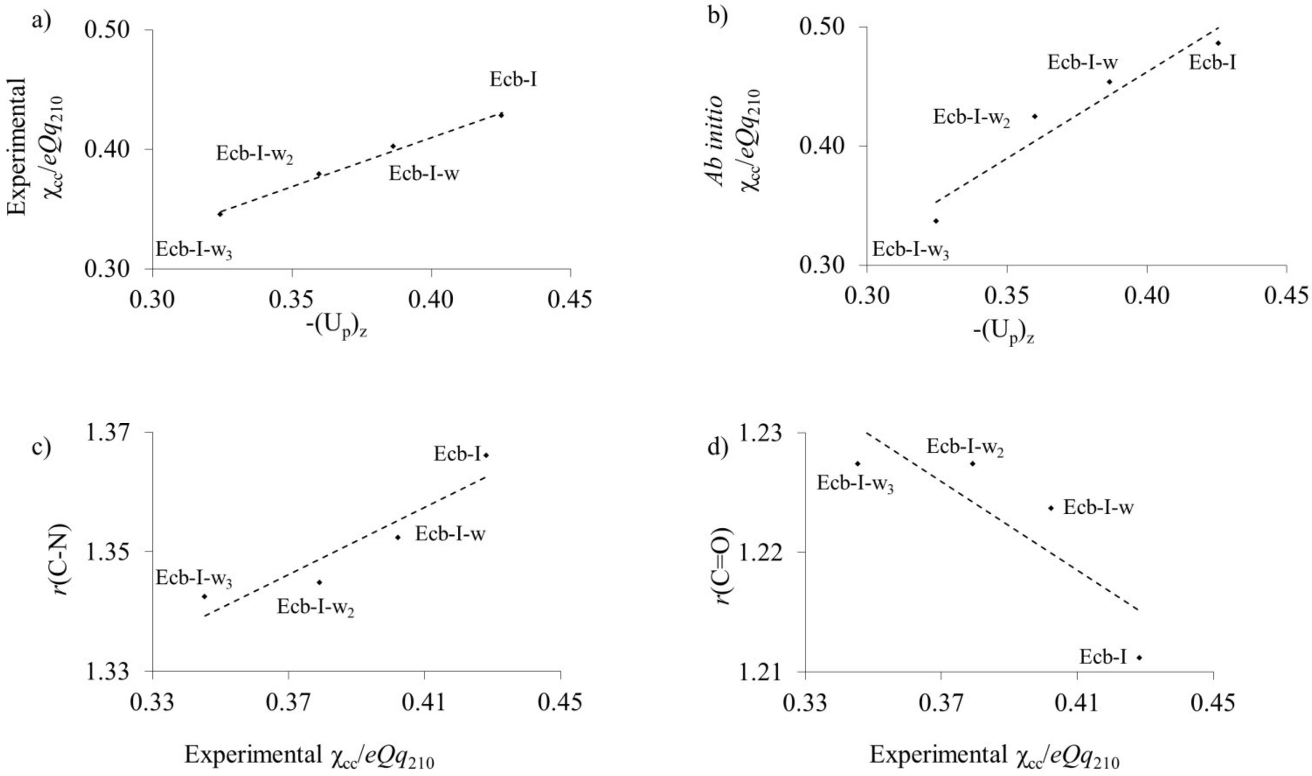


Table S12. Experimental and theoretical (B3LYP-GD3/6-311++G(d,p)) nuclear quadrupole coupling constants for the ^{14}N atom of the observed complexes with up to three water molecules for the rotamer ecb-II and values reported for the monomer [reference 11], together with the values of the unbalanced 2p_z electronic charge (-$(U_p)_z$) both calculated from χ_{cc} and from the natural atomic orbital populations obtained by a Natural Bond Orbital Analysis [reference 47]. The plots represent the correlations between a) experimental values of χ_{cc}/eQq_{210} *vs.* -$(U_p)_z$. b) Theoretical values of χ_{cc}/eQq_{210} *vs.* -$(U_p)_z$.

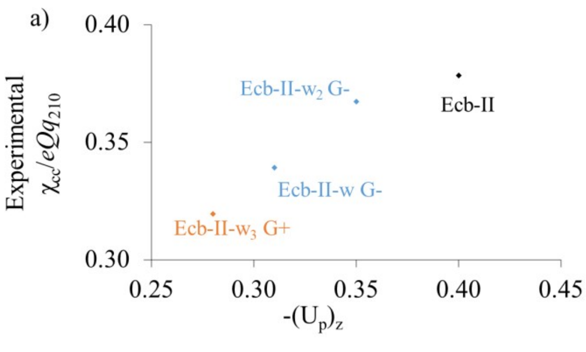
The electric field gradient giving rise to nuclear quadrupole coupling of most molecules has been attributed primarily to the unequal filling of the p orbitals of the valence shell of the coupling atoms. According to this, the ^{14}N χ_{zz} constants can be related to the unbalanced 2p_z electronic charge $(U_p)_z = [(n_x + n_y)/2 - n_z]$ by:

$$\chi_{zz}/eQq_{210} = -(U_p)_z \quad (1)$$

Where n_α are the p_α orbital occupation numbers and q_{210} the electric field gradient associated to a 2p electron in an isolated atom (eQq_{210}≈-10 MHz for N). This definition of $(U_p)_z$ is such that its positive or negative values correspond respectively to electron deficit or excess along the *z* reference axis (W. Gordy, R. L. Cook, *Microwave Molecular Spectra*, Wiley, New York, **1984**).

Experimental	Ecb-II	Ecb-II-w	Ecb-II-w_2	Ecb-II-w_3
χ_{aa} /MHz	1.8923(11)	1.5927(54)	1.3340(80)	1.267(33)
χ_{bb} /MHz	1.8918(11)	1.799(16)	2.339(30)	1.929(61)
χ_{cc} /MHz	-3.7841(11)	-3.392(16)	-3.673(30)	-3.195(61)
χ_{cc}/eQq_{210}	0.37841	0.3392	0.3673	0.3195

Theoretical	Ecb-II	Ecb-II-w G-	Ecb-II-w G+	Ecb-II-w_2 G-	Ecb-II-w_2 G+	Ecb-II-w_3 G-	Ecb-II-w_3 G+
χ_{aa} /MHz	2.37	1.80	1.74	1.42	1.48	1.09	1.37
χ_{bb} /MHz	2.26	1.86	2.35	2.67	2.43	2.61	1.99
χ_{cc} /MHz	-4.62	-3.66	-4.10	-4.09	-3.92	-3.70	-3.36
χ_{ab} /MHz	-0.21	-0.16	-0.28	-0.42	-0.36	0.58	-0.47
χ_{ac} /MHz	-1.35	-0.96	-1.09	-0.82	0.60	-1.17	-0.14
χ_{bc} /MHz	0.41	2.20	1.31	0.48	-1.36	0.96	-2.16
χ_{xx} /MHz	2.11	1.69	1.66	1.36	1.36	1.28	1.28
χ_{yy} /MHz	2.77	2.86	2.84	2.87	2.87	2.86	2.86
χ_{zz} /MHz	-4.89	-4.55	-4.52	-4.23	-4.25	-4.14	-4.14
χ_{zz}/eQq_{210}	0.49	0.46	0.45	0.42	0.45	0.41	0.41
-$(U_p)_z$ NBO	0.40	0.31	0.34	0.35	0.33	0.32	0.28



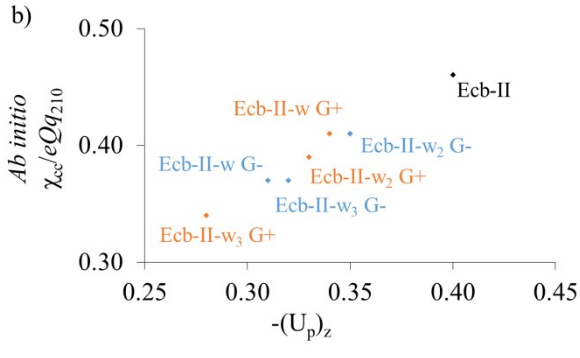


Table S13. Observed rotational frequencies and residuals (all the values in MHz) for the parent species of the ecb-I-w complex for $J^{'}K^{'}_{-1}K^{'}_{+1}F^{'} \leftarrow J^{''}K^{''}_{-1}K^{''}_{+1}F^{''}$ transitions.

$J^{'}K^{'}_{-1}K^{'}_{+1}$	$J^{''}K^{''}_{-1}K^{''}_{+1}$	$F^{'}$	$F^{''}$	**Obs.**	**Res.**
$2_{1,2}$	$1_{1,1}$	1	1	3802.3333	0.0023
		3	2	3803.7650	0.0012
		3	2	3803.7679	0.0041
		1	0	3804.1166	-0.0013
		2	1	3804.3415	-0.0005
		2	2	3805.0564	-0.0002
$2_{0,2}$	$1_{0,1}$	1	1	3912.5532	0.0028
		3	2	3913.3455	0.0012
		1	0	3913.7768	-0.0029
		2	2	3913.8908	0.0026
$2_{1,1}$	$1_{1,0}$	1	0	4024.1759	-0.0003
		2	2	4024.7951	0.0006
		3	2	4025.5631	0.0027
		2	1	4025.9963	-0.0047
$3_{1,3}$	$2_{1,2}$	2	2	5703.1407	0.0002
		4	3	5704.9527	0.0004
		3	2	5705.1417	-0.0005
		3	3	5706.4341	-0.0010
$3_{0,3}$	$2_{0,2}$	2	2	5865.8462	0.0009
		4	3	5866.5970	0.0012
		3	2	5866.6425	0.0001
		2	1	5866.6896	-0.0015
		3	3	5867.1804	-0.0058
$3_{2,2}$	$2_{2,1}$	2	1	5871.7186	-0.0056
		4	3	5872.0251	0.0080
		3	2	5872.5435	-0.0004
$3_{2,1}$	$2_{2,0}$	2	1	5877.2441	-0.0069
		4	3	5877.5437	0.0058
		3	2	5878.0376	0.0000
$3_{1,2}$	$2_{1,1}$	3	3	6036.8519	-0.0007
		2	1	6037.3084	0.0011
		4	3	6037.5042	-0.0005
		3	2	6037.6177	-0.0008
		2	2	6038.5035	0.0040
$4_{1,4}$	$3_{1,3}$	3	3	7603.1792	-0.0003
		5	4	7605.0696	0.0007
		4	3	7605.1672	0.0002
		3	2	7605.1837	0.0023
$4_{0,4}$	$3_{0,3}$	3	3	7814.9492	-0.0004
		5	4	7815.7057	0.0010
		3	2	7815.7452	-0.0015
		4	3	7815.7545	0.0004
		4	4	7816.3482	0.0036
$4_{2,3}$	$3_{2,2}$	3	2	7828.3103	0.0025
		5	4	7828.3684	0.0020
		4	3	7828.5951	0.0010
$4_{2,2}$	$3_{2,1}$	3	2	7842.0987	0.0004
		5	4	7842.1520	0.0005
		4	3	7842.3427	0.0004
$4_{1,3}$	$3_{1,2}$	4	4	8047.7605	-0.0026
		3	2	8048.2898	-0.0022
		5	4	8048.3646	-0.0008
		4	3	8048.4152	0.0000
		3	3	8049.1730	0.0002
$5_{1,5}$	$4_{1,4}$	4	4	9501.9174	-0.0005
		6	5	9503.8341	0.0003
		5	4	9503.8966	-0.0007
		4	3	9503.9061	0.0008
		5	5	9505.4761	-0.0020
$5_{0,5}$	$4_{0,4}$	4	4	9758.5413	-0.0022
		6	5	9759.3250	0.0000
		4	3	9759.3491	0.0011
		5	4	9759.3802	-0.0002
		5	5	9760.0151	-0.0052
$5_{2,4}$	$4_{2,3}$	4	3	9783.7370	-0.0033
		6	5	9783.7546	0.0011
		5	4	9783.8771	0.0000
$5_{2,3}$	$4_{2,2}$	4	3	9811.2663	-0.0026
		6	5	9811.2780	0.0011
		5	4	9811.3535	-0.0002
$5_{1,4}$	$4_{1,3}$	4	3	10057.7367	-0.0017
		6	5	10057.7772	0.0002
		5	4	10057.8047	-0.0029
$6_{1,6}$	$5_{1,5}$	7	6	11400.9629	0.0003
		5	4	11401.0115	-0.0003
		6	5	11401.0115	0.0012
$6_{0,6}$	$5_{0,5}$	7	6	11696.1573	0.0011
		5	4	11696.1704	0.0005
		6	5	11696.2198	0.0010
$6_{2,5}$	$5_{2,4}$	5	4	11737.9656	-0.0001
		7	6	11737.9656	-0.0010
		6	5	11738.0467	0.0018
$6_{2,4}$	$5_{2,3}$	7	6	11786.0006	-0.0003
		5	4	11786.0070	0.0018

Table S13. Continued.

$J'K'_{-1}K'_{+1}$	$J''K''_{-1}K''_{+1}$	F'	F''	**Obs.**	**Res.**
		6	5	11786.0217	-0.0013
$6_{1,5}$	$5_{1,4}$	5	4	12065.3149	-0.0011
		7	6	12065.3397	-0.0005
		6	5	12065.3648	0.0000
$5_{0,5}$	$4_{1,4}$	6	5	3615.3815	0.0007
		5	4	3614.4999	0.0048
		4	3	3615.6521	0.0065
$6_{0,6}$	$5_{1,5}$	6	5	5806.8166	0.0001
		7	6	5807.7022	-0.0008
		5	4	5807.9098	-0.0002
$7_{0,7}$	$6_{1,6}$	7	6	8030.8655	0.0027
		8	7	8031.7255	-0.0016
		6	5	8031.8938	0.0005
$1_{1,1}$	$0_{0,0}$	0	1	8582.0311	-0.0010
		2	1	8583.1034	-0.0010
		1	1	8583.8154	-0.0037
$2_{1,2}$	$1_{0,1}$	1	1	10428.3625	0.0045
		3	2	10429.5686	0.0006
		2	1	10430.3705	0.0014
		2	2	10430.8616	0.0008
$3_{1,3}$	$2_{0,2}$	2	1	12220.9587	-0.0003
		4	3	12221.1769	0.0009
		3	2	12222.1135	-0.0013
$1_{1,0}$	$1_{0,1}$	1	1	6735.2560	0.0000
		1	2	6735.7494	0.0015
		2	1	6736.4614	-0.0012
		1	0	6736.4872	0.0018
		2	2	6736.9621	0.0076
		0	1	6738.2750	0.0020

$J'K'_{-1}K'_{+1}$	$J''K''_{-1}K''_{+1}$	F'	F''	**Obs.**	**Res.**
$2_{1,1}$	$2_{0,2}$	2	2	6847.8602	0.0005
		3	2	6848.6264	0.0002
		2	1	6848.7075	0.0008
		1	2	6849.0505	0.0023
		3	3	6849.1659	0.0046
$3_{1,2}$	$3_{0,3}$	3	3	7018.8366	0.0003
		3	2	7019.6376	0.0035
		2	3	7019.7153	0.0025
		4	4	7020.0793	0.0003
		2	2	7020.5131	0.0017
$4_{1,3}$	$4_{0,4}$	4	4	7251.4967	0.0014
		5	5	7252.7394	0.0011
		3	3	7253.0624	0.0022
$5_{1,4}$	$5_{0,5}$	5	5	7549.9246	0.0007
		6	6	7551.1927	0.0003
		4	4	7551.4503	0.0003
$6_{1,5}$	$6_{0,6}$	6	6	7919.0695	0.0019
		7	7	7920.3780	0.0014
		5	5	7920.5957	0.0013
$7_{1,6}$	$7_{0,7}$	7	7	8364.6679	0.0032
		8	8	8366.0198	0.0031
		6	6	8366.2107	0.0011
$8_{1,7}$	$8_{0,8}$	8	8	8893.0279	0.0047
		9	9	8894.4365	0.0015
		7	7	8894.6194	0.0043

Table S14. Observed rotational frequencies and residuals (all the values in MHz) for the [18]O_w species of the ecb-I-w complex for $J^{'}K^{'}_{-1}K^{'}_{+1}F^{'} \leftarrow J^{''}K^{''}_{-1}K^{''}_{+1}F^{''}$ transitions.

$J^{'}K^{'}_{-1}K^{'}_{+1}$	$J^{''}K^{''}_{-1}K^{''}_{+1}$	$F^{'}$	$F^{''}$	**Obs.**	**Res.**
$3_{1,3}$	$2_{1,2}$	4	3	5462.7346	-0.0002
		3	2	5462.9225	-0.0018
$3_{0,3}$	$2_{0,2}$	4	3	5611.5641	-0.0007
		3	2	5611.6109	0.0016
$3_{1,2}$	$2_{1,1}$	4	3	5768.1891	0.0023
		3	2	5768.2966	-0.0033
		2	1	5767.9907	0.0014
$4_{1,4}$	$3_{1,3}$	5	4	7282.3609	-0.0004
		4	3	7282.4586	0.0000
		3	2	7282.4774	0.0034
$4_{0,4}$	$3_{0,3}$	5	4	7476.6779	-0.0012
		4	3	7476.7259	0.0003
		3	2	7476.7259	0.0041
$4_{1,3}$	$3_{1,2}$	3	2	7689.4615	-0.0003
		5	4	7689.5353	0.0001
		4	3	7689.5844	0.0002
$5_{1,5}$	$4_{1,4}$	6	5	9100.8424	0.0000
		5	4	9100.9014	-0.0035
		4	3	9100.9159	0.0019
$5_{0,5}$	$4_{0,4}$	6	5	9337.1655	-0.0010
		4	3	9337.1898	-0.0001
		5	4	9337.2189	0.0008
$5_{1,4}$	$4_{1,3}$	4	3	9609.6272	0.0003
		6	5	9609.6653	0.0001
		5	4	9609.6937	-0.0011

Table S15. Observed rotational frequencies and residuals (all the values in MHz) for the parent species of the ecb-I-w$_2$ complex for $J'K'_{-1}K'_{+1}F' \leftarrow J''K''_{-1}K''_{+1}F''$ transitions.

$J'K'_{-1}K'_{+1}$	$J''K''_{-1}K''_{+1}$	F'	F''	Obs.	Res.
$2_{1,2}$	$1_{1,1}$	3	2	2492.8792	-0.0027
		2	1	2493.3695	0.0004
$2_{0,2}$	$1_{0,1}$	3	2	2595.1920	0.0025
$2_{1,1}$	$1_{1,0}$	3	2	2702.7495	-0.0007
$3_{1,3}$	$2_{1,2}$	4	3	3737.8195	0.0019
		3	2	3737.9842	-0.0020
$3_{0,3}$	$2_{0,2}$	4	3	3886.1355	0.0017
		3	2	3886.2050	0.0014
		2	1	3886.2050	-0.0004
$3_{1,2}$	$2_{1,1}$	2	1	4052.2538	-0.0014
		4	3	4052.4502	0.0001
		3	2	4052.5465	0.0017
$4_{1,4}$	$3_{1,3}$	5	4	4980.7878	0.0035
		4	3	4980.8800	0.0017
		3	2	4980.8800	-0.0089
$4_{0,4}$	$3_{0,3}$	5	4	5169.1287	-0.0003
		3	2	5169.1587	0.0011
		4	3	5169.2117	-0.0006
$4_{2,3}$	$3_{2,2}$	3	2	5193.6018	0.0019
		5	4	5193.6486	-0.0008
		4	3	5193.8436	0.0013
$4_{2,2}$	$3_{2,1}$	3	2	5220.2625	0.0043
		5	4	5220.2965	-0.0004
		4	3	5220.4180	0.0012
$4_{1,3}$	$3_{1,2}$	3	2	5399.9646	0.0000
		5	4	5400.0405	-0.0006
		4	3	5400.0886	-0.0007
$5_{1,5}$	$4_{1,4}$	6	5	6221.2680	0.0000
		5	4	6221.3337	-0.0013
		4	3	6221.3337	0.0001
$5_{0,5}$	$4_{0,4}$	6	5	6441.7459	-0.0003
		4	3	6441.7585	-0.0007
		5	4	6441.8434	-0.0010
$5_{2,4}$	$4_{2,3}$	4	3	6488.7288	-0.0024
		6	5	6488.7433	0.0000
		5	4	6488.8538	0.0005
$5_{3,3}$	$4_{3,2}$	4	3	6503.3554	0.0046
		6	5	6503.4025	0.0022
		5	4	6503.5973	0.0033
$5_{3,2}$	$4_{3,2}$	4	3	6504.2457	0.0001
		6	5	6504.2927	-0.0019
		5	4	6504.4836	-0.0017
$5_{2,3}$	$4_{2,2}$	6	5	6541.7089	-0.0009
		4	3	6541.7089	0.0012
		5	4	6541.7293	0.0006
$5_{1,4}$	$4_{1,3}$	4	3	6744.6914	-0.0011
		6	5	6744.7336	-0.0009
		5	4	6744.7721	0.0001
$6_{1,6}$	$5_{1,5}$	7	6	7458.8127	0.0000
		5	4	7458.8539	-0.0033
		6	5	7458.8685	0.0004
$6_{0,6}$	$5_{0,5}$	7	6	7701.9213	-0.0005
		5	4	7701.9294	0.0012
		6	5	7702.0339	-0.0002
$6_{2,5}$	$5_{2,4}$	7	6	7781.5970	-0.0011
		5	4	7781.5970	0.0009
		6	5	7781.6729	0.0000
$6_{3,4}$	$5_{3,3}$	5	4	7807.1168	0.0026
		7	6	7807.1314	-0.0009
		6	5	7807.2413	0.0006
$6_{3,3}$	$5_{3,2}$	5	4	7809.4936	-0.0018
		7	6	7809.5118	-0.0010
		6	5	7809.6151	-0.0002
$6_{2,4}$	$5_{2,3}$	6	5	7873.2717	-0.0013
		7	6	7873.3039	-0.0014
		5	4	7873.3133	0.0007
$6_{1,5}$	$5_{1,4}$	5	4	8085.6172	0.0001
		7	6	8085.6435	-0.0009
		6	5	8085.6814	0.0000
$7_{1,7}$	$6_{1,6}$	8	7	8693.0521	0.0007
		6	5	8693.0831	-0.0005
		7	6	8693.1008	-0.0004
$7_{0,7}$	$6_{0,6}$	8	7	8948.2324	0.0013
		6	5	8948.2324	-0.0011
		7	6	8948.3550	0.0000
$7_{2,6}$	$6_{2,5}$	6	5	9071.7807	-0.0011
		8	7	9071.7807	-0.0002
		7	6	9071.8391	0.0000
$7_{3,5}$	$6_{3,4}$	6	5	9112.1299	-0.0024
		8	7	9112.1394	0.0005
		7	6	9112.2030	-0.0001
$7_{3,4}$	$6_{3,3}$	6	5	9117.4715	-0.0026
		8	7	9117.4797	0.0000
		7	6	9117.5337	-0.0009

Table S15. Continued.

$J'K'_{-1}K'_{+1}$	$J''K''_{-1}K''_{+1}$	F'	F''	**Obs.**	**Res.**
$7_{2,5}$	$6_{2,4}$	7	6	9215.9928	-0.0005
		8	7	9216.0547	-0.0002
		6	5	9216.0660	0.0017
$7_{1,6}$	$6_{1,5}$	6	5	9421.7534	-0.0006
		8	7	9421.7740	0.0000
		7	6	9421.8134	-0.0014
$8_{1,8}$	$7_{1,7}$	9	8	9923.7200	-0.0007
		7	6	9923.7458	0.0006
		8	7	9923.7682	0.0002
$8_{0,8}$	$7_{0,7}$	7	6	10180.1704	0.0000
		9	8	10180.1704	0.0008
		8	7	10180.3011	0.0000
$8_{2,7}$	$7_{2,6}$	7	6	10358.8643	-0.0009
		9	8	10358.8643	0.0006
		8	7	10358.9186	0.0047
$8_{3,6}$	$7_{3,5}$	7	6	10418.3499	-0.0005
		9	8	10418.3499	-0.0023
		8	7	10418.3936	0.0016
$8_{3,5}$	$7_{3,4}$	7	6	10428.9876	-0.0010
		9	8	10428.9876	-0.0012
		8	7	10429.0138	-0.0006
$8_{2,6}$	$7_{2,5}$	8	7	10569.9180	0.0010
		9	8	10569.9947	-0.0002
		7	6	10570.0056	0.0016
$8_{1,7}$	$7_{1,6}$	7	6	10751.9801	-0.0005
		9	8	10751.9971	0.0008
		8	7	10752.0441	0.0010
$9_{1,9}$	$8_{1,8}$	10	9	11150.6694	0.0013
		8	7	11150.6857	-0.0013
		9	8	11150.7153	0.0015
$9_{0,9}$	$8_{0,8}$	10	9	11398.3373	0.0003
		8	7	11398.3373	0.0001
		9	8	11398.4710	-0.0002
$9_{2,8}$	$8_{2,7}$	10	9	11642.4313	0.0006
		8	7	11642.4313	-0.0005
		9	8	11642.4776	0.0005
$9_{3,7}$	$8_{3,6}$	10	9	11725.5909	-0.0006
		8	7	11725.5909	-0.0009
		9	8	11725.6165	-0.0002
$9_{3,6}$	$8_{3,5}$	10	9	11744.9736	0.0000
		8	7	11744.9736	-0.0020
		9	8	11744.9796	0.0011
$9_{2,7}$	$8_{2,6}$	9	8	11933.9528	-0.0003
		10	9	11934.0363	-0.0016
		8	7	11934.0469	0.0011
$9_{1,8}$	$8_{1,7}$	8	7	12075.0301	0.0013
		10	9	12075.0432	0.0015
		9	8	12075.0953	-0.0006
$10_{1,10}$	$9_{1,9}$	11	10	12373.8510	0.0005
		9	8	12373.8644	-0.0013
		10	9	12373.8953	0.0000
$10_{0,10}$	$9_{0,9}$	9	8	12604.4093	0.0003
		11	10	12604.4093	0.0001
		10	9	12604.5408	0.0000
$10_{2,9}$	$9_{2,8}$	11	10	12922.0819	0.0006
		9	8	12922.0819	-0.0023
		10	9	12922.1243	-0.0012
$10_{3,8}$	$9_{3,7}$	9	8	13033.5654	0.0001
		11	10	13033.5654	0.0013
		10	9	13033.5805	0.0000
$10_{3,7}$	$9_{3,6}$	10	9	13066.4950	-0.0007
		11	10	13066.5102	0.0031
		9	8	13066.5102	-0.0001
$10_{2,8}$	$9_{2,7}$	10	9	13305.9092	0.0001
		11	10	13305.9915	-0.0016
		9	8	13306.0004	0.0011
$10_{1,9}$	$9_{1,8}$	9	8	13389.4862	-0.0006
		11	10	13389.4971	-0.0006
		10	9	13389.5607	0.0002

Table S16. Observed rotational frequencies and residuals (all the values in MHz) for the $^{18}O_{w1}$ species of the ecb-I-w$_2$ complex for $J'K'_{-1}K'_{+1}F' \leftarrow J''K''_{-1}K''_{+1}F''$ transitions.

$J'K'_{-1}K'_{+1}$	$J''K''_{-1}K''_{+1}$	F'	F''	**Obs.**	**Res.**
$5_{1,5}$	$4_{1,4}$	6	5	6075.9230	0.0003
		5	4	6075.9885	-0.0018
		4	3	6075.9885	0.0004
$5_{0,5}$	$4_{0,4}$	6	5	6293.5834	-0.0001
		4	3	6293.5951	-0.0012
		5	4	6293.6845	-0.0001
$5_{1,4}$	$4_{1,3}$	4	3	6595.8623	0.0003
		6	5	6595.9021	-0.0019
		5	4	6595.9412	-0.0010
$6_{1,6}$	$5_{1,5}$	7	6	7284.2396	0.0006
		5	4	7284.2826	-0.0009
		6	5	7284.2940	-0.0011
$6_{0,6}$	$5_{0,5}$	7	6	7523.4512	-0.0008
		5	4	7523.4512	-0.0068
$6_{1,5}$	$5_{1,4}$	5	4	7906.7799	-0.0011
		7	6	7906.8082	-0.0003
		6	5	7906.8473	0.0005
$7_{1,7}$	$6_{1,6}$	8	7	8489.1857	0.0018
		7	6	8489.2354	0.0008
$7_{0,7}$	$6_{0,6}$	8	7	8739.2213	0.0016
		6	5	8739.2213	-0.0007
		7	6	8739.3483	0.0015
$7_{1,6}$	$6_{1,5}$	6	5	9212.7619	0.0042
		8	7	9212.7777	0.0000
		7	6	9212.8197	-0.0002

Table S17. Observed rotational frequencies and residuals (all the values in MHz) for the $^{18}O_{w2}$ species of the ecb-I-w$_2$ complex for $J' K'_{-1} K'_{+1} F' \leftarrow J'' K''_{-1} K''_{+1} F''$ transitions.

$J' K'_{-1} K'_{+1}$	$J'' K''_{-1} K''_{+1}$	F'	F''	**Obs.**	**Res.**
$5_{1.5}$	$4_{1.4}$	5	4	6041.8857	0.0000
		4	3	6041.8857	0.0009
$5_{0.5}$	$4_{0.4}$	6	5	6254.2467	0.0002
		4	3	6254.2593	-0.0005
		5	4	6254.3413	-0.0008
$5_{1.4}$	$4_{1.3}$	4	3	6543.4492	-0.0015
		6	5	6543.4898	-0.0027
		5	4	6543.5274	-0.0018
$6_{1.6}$	$5_{1.5}$	7	6	7243.9250	0.0002
		5	4	7243.9679	-0.0015
		6	5	7243.9796	0.0001
$6_{0.6}$	$5_{0.5}$	7	6	7478.8206	0.0005
		5	4	7478.8206	-0.0059
		6	5	7478.9293	-0.0003
$6_{1.5}$	$5_{1.4}$	7	6	7844.7338	0.0028
		6	5	7844.7743	0.0072
$7_{1.7}$	$6_{1.6}$	8	7	8442.9348	-0.0008
		6	5	8442.9688	0.0008
		7	6	8442.9861	0.0012
$7_{0.7}$	$6_{0.6}$	8	7	8690.3887	0.0026
		6	5	8690.3887	0.0000
		7	6	8690.5080	0.0008
$7_{1.6}$	$6_{1.5}$	6	5	9141.5214	-0.0009
		8	7	9141.5405	-0.0016
		7	6	9141.5806	-0.0011

Table S18. Observed rotational frequencies and residuals (all the values in MHz) for the parent species of the ecb-I-w$_3$ complex in the *v = 0* and *v = 1* vibrational states for $J'K'_{-1}K'_{+1}v'F' \leftarrow J''K''_{-1}K''_{+1}v''F''$ transitions.

$J'K'_{-1}K'_{+1}$	$J''K''_{-1}K''_{+1}$	v	F'	F''	**Obs.**	**Res.**
$6_{1,6}$	$5_{1,5}$	*0*	7	6	5132.4223	0.0008
		0	5	4	5132.4673	0.0058
		0	6	5	5132.4761	-0.0003
		1	7	6	5132.4350	0.0000
		1	5	4	5132.4761	0.0011
		1	6	5	5132.4917	0.0017
$6_{0,6}$	$5_{0,5}$	*0*	7	6	5297.9925	-0.0008
		0	5	4	5297.9925	-0.0037
		0	6	5	5298.1181	0.0005
		1	7	6	5298.0066	0.0006
		1	5	4	5298.0066	-0.0022
		1	6	5	5298.1304	0.0002
$6_{2,5}$	$5_{2,4}$	*0*	5	4	5370.1514	-0.0001
		0	7	6	5370.1514	-0.0027
		0	6	5	5370.2223	-0.0010
		1	5	4	5370.1645	0.0004
		1	7	6	5370.1645	-0.0020
		1	6	5	5370.2352	-0.0005
$6_{2,4}$	$5_{2,3}$	*0*	6	5	5453.2147	0.0008
		0	7	6	5453.2607	-0.0037
		0	5	4	5453.2729	0.0007
		1	6	5	5453.2323	0.0061
		1	7	6	5453.2813	0.0046
		1	5	4	5453.2874	0.0030
$6_{1,5}$	$5_{1,4}$	*0*	5	4	5590.5654	0.0017
		0	7	6	5590.5918	0.0011
		0	6	5	5590.6293	-0.0022
		1	5	4	5590.5773	0.0022
		1	7	6	5590.6039	0.0019
		1	6	5	5590.6424	-0.0005
$7_{1,7}$	$6_{1,6}$	*0*	8	7	5979.9326	0.0000
		0	6	5	5979.9615	0.0002
		0	7	6	5979.9861	0.0030
		1	8	7	5979.9470	-0.0013
		1	6	5	5979.9705	-0.0065
		1	7	6	5980.0002	0.0013
$7_{0,7}$	$6_{0,6}$	*0*	8	7	6148.2422	-0.0008
		0	6	5	6148.2422	-0.0013
		0	7	6	6148.3776	0.0002
		1	8	7	6148.2574	-0.0004
		1	6	5	6148.2574	-0.0009
		1	7	6	6148.3912	-0.0009
$7_{2,6}$	$6_{2,5}$	*0*	6	5	6258.9883	-0.0008
		0	8	7	6258.9883	-0.0010
		0	7	6	6259.0437	-0.0018
		1	6	5	6259.0031	-0.0006
		1	8	7	6259.0031	-0.0008
		1	7	6	6259.0590	-0.0011
$7_{2,5}$	$6_{2,4}$	*0*	7	6	6388.5315	-0.0016
		0	8	7	6388.6058	-0.0019
		0	6	5	6388.6168	0.0001
		1	7	6	6388.5456	-0.0017
		1	8	7	6388.6191	-0.0028
		1	6	5	6388.6311	0.0001
$7_{1,6}$	$6_{1,5}$	*0*	6	5	6511.4976	-0.0004
		0	8	7	6511.5190	0.0010
		0	7	6	6511.5623	-0.0026
		1	6	5	6511.5190	0.0076
		1	8	7	6511.5324	0.0011
		1	7	6	6511.5772	-0.0010
$8_{1,8}$	$7_{1,7}$	*0*	9	8	6824.4004	0.0015
		0	7	6	6824.4184	-0.0021
		0	8	7	6824.4487	0.0014
		1	9	8	6824.4184	0.0014
		1	7	6	6824.4372	-0.0014
		1	8	7	6824.4666	0.0012
$8_{0,8}$	$7_{0,7}$	*0*	9	8	6987.0686	-0.0014
		0	7	6	6987.0686	-0.0009
		0	8	7	6987.2067	-0.0014
		1	9	8	6987.0856	-0.0015
		1	7	6	6987.0856	-0.0009
		1	8	7	6987.2268	0.0016
$8_{2,7}$	$7_{2,6}$	*0*	9	8	7144.9923	0.0014
		0	7	6	7144.9923	-0.0014
		0	8	7	7145.0406	0.0005
		1	9	8	7145.0073	-0.0001
		1	7	6	7145.0073	-0.0030
		1	8	7	7145.0553	-0.0014
$8_{2,6}$	$7_{2,5}$	*0*	8	7	7332.3411	-0.0005
		0	9	8	7332.4272	0.0006
		0	7	6	7332.4373	0.0027
		1	8	7	7332.3552	-0.0026
		1	9	8	7332.4455	0.0027
		1	7	6	7332.4507	0.0000

Table S18. Continued.

$J'K'_{-1}K'_{+1}$	$J''K''_{-1}K''_{+1}$	v	F'	F''	**Obs.**	**Res.**
$8_{1,7}$	$7_{1,6}$	*0*	7	6	7426.7362	0.0000
		0	9	8	7426.7515	-0.0003
		0	8	7	7426.8072	0.0001
		1	7	6	7426.7515	0.0000
		1	9	8	7426.7671	0.0000
		1	8	7	7426.8216	-0.0006
$9_{1,9}$	$8_{1,8}$	*0*	10	9	7665.7711	0.0011
		0	8	7	7665.7848	-0.0020
		0	9	8	7665.8185	0.0015
		1	10	9	7665.7923	0.0019
		1	8	7	7665.8052	-0.0020
		1	9	8	7665.8395	0.0021
$9_{0,9}$	$8_{0,8}$	*0*	10	9	7815.8974	-0.0010
		0	8	7	7815.8974	-0.0041
		0	9	8	7816.0356	-0.0007
		1	10	9	7815.9161	-0.0016
		1	8	7	7815.9161	-0.0047
		1	9	8	7816.0551	-0.0005
$9_{2,8}$	$8_{2,7}$	*0*	10	9	8027.8006	0.0010
		0	8	7	8027.8006	0.0013
		0	9	8	8027.8499	0.0020
		1	10	9	8027.8180	-0.0002
		1	8	7	8027.8180	0.0000
		1	9	8	8027.8669	0.0003
$9_{2,7}$	$8_{2,6}$	*0*	9	8	8282.7422	-0.0009
		0	10	9	8282.8250	-0.0028
		0	8	7	8282.8331	-0.0008
		1	9	8	8282.7565	-0.0046
		1	10	9	8282.8414	-0.0044
		1	8	7	8282.8511	-0.0008
$9_{1,8}$	$8_{1,7}$	*0*	8	7	8334.9995	-0.0003
		0	10	9	8335.0154	0.0020
		0	9	8	8335.0799	0.0016
		1	8	7	8335.0154	-0.0016
		1	10	9	8335.0284	-0.0021
		1	9	8	8335.0952	-0.0001
$10_{1,10}$	$9_{1,9}$	*0*	11	10	8504.1014	-0.0007
		0	9	8	8504.1164	0.0004
		0	10	9	8504.1508	0.0028
		1	11	10	8504.1285	0.0036
		1	9	8	8504.1361	-0.0025
		1	10	9	8504.1716	0.0009
$10_{0,10}$	$9_{0,9}$	*0*	11	10	8636.9773	-0.0016
		0	9	8	8636.9773	-0.0009
		0	10	9	8637.1052	-0.0002
		1	11	10	8636.9996	-0.0010
		1	9	8	8636.9996	-0.0002
		1	10	9	8637.1264	-0.0007
$10_{2,9}$	$9_{2,8}$	*0*	11	10	8907.0669	0.0019
		0	9	8	8907.0669	0.0013
		0	10	9	8907.1136	0.0012
		1	11	10	8907.0876	0.0018
		1	9	8	8907.0876	0.0012
		1	10	9	8907.1344	0.0012
$10_{2,8}$	$9_{2,7}$	*0*	10	9	9236.9771	0.0004
		0	11	10	9237.0517	-0.0013
		0	9	8	9237.0562	-0.0009
		1	10	9	9236.9988	0.0022
		1	11	10	9237.0719	-0.0010
		1	9	8	9237.0778	0.0008
$10_{1,9}$	$9_{1,8}$	*0*	9	8	9234.8897	0.0029
		0	11	10	9234.8973	-0.0012
		0	10	9	9234.9760	0.0017
		1	9	8	9234.9089	0.0030
		1	11	10	9234.9159	-0.0017
		1	10	9	9234.9943	0.0009
$11_{1,11}$	$10_{1,10}$	*0*	12	11	9339.5438	-0.0010
		0	10	9	9339.5571	0.0012
		0	11	10	9339.5904	0.0010
		1	12	11	9339.5701	0.0002
		1	10	9	9339.5831	0.0022
		1	11	10	9339.6165	0.0021
$11_{0,11}$	$10_{0,10}$	*0*	12	11	9452.8708	-0.0028
		0	10	9	9452.8708	-0.0045
		0	11	10	9452.9855	-0.0037
		1	12	11	9452.8965	-0.0012
		1	10	9	9452.8965	-0.0028
		1	11	10	9453.0127	-0.0005
$11_{2,10}$	$10_{2,9}$	*0*	12	11	9782.4917	0.0038
		0	10	9	9782.4917	0.0033
		0	11	10	9782.5347	-0.0011
		1	12	11	9782.5139	0.0030
		1	10	9	9782.5139	0.0025
		1	11	10	9782.5556	-0.0031

Table S18. Continued.

$J'K'_{-1}K'_{+1}$	$J''K''_{-1}K''_{+1}$	v	F'	F''	**Obs.**	**Res.**
$11_{2,9}$	$10_{2,8}$	*0*	11	10	10191.9160	-0.0005
		0	12	11	10191.9798	0.0006
		0	10	9	10191.9798	-0.0014
		1	11	10	10191.9399	0.0017
		1	12	11	10191.9988	-0.0020
		1	10	9	10191.9988	-0.0041
$11_{1,10}$	$10_{1,9}$	*0*	10	9	10124.9342	0.0013
		0	12	11	10124.9442	0.0007
		0	11	10	10125.0316	0.0007
		1	10	9	10124.9556	0.0017
		1	12	11	10124.9639	-0.0006
		1	11	10	10125.0516	-0.0002

Table S19. Observed rotational frequencies and residuals (all the values in MHz) for the parent species of the ecb-II-w complex for $J'K'_{-1}K'_{+1}F' \leftarrow J''K''_{-1}K''_{+1}F''$ transitions.

$J'K'_{-1}K'_{+1}$	$J''K''_{-1}K''_{+1}$	F'	F''	Obs.	Res.	$J'K'_{-1}K'_{+1}$	$J''K''_{-1}K''_{+1}$	F'	F''	Obs.	Res.
$1_{0,1}$	$0_{0,0}$	0	1	2274.7162	-0.0081	$3_{1,2}$	$2_{1,1}$	2	1	7046.9842	-0.0044
		2	1	2275.4418	0.0007			4	3	7047.1497	-0.0004
		1	1	2275.9202	0.0013			3	2	7047.2693	-0.0021
$2_{1,2}$	$1_{1,1}$	3	2	4402.0643	-0.0018	$3_{0,3}$	$2_{1,2}$	2	2	2969.4752	0.0105
		1	0	4402.2719	0.0018			3	2	2970.2884	0.0011
		2	1	4402.6252	0.0083			4	3	2970.7689	0.0008
		2	2	4403.1645	0.0082			2	1	2971.1647	0.0043
$2_{0,2}$	$1_{0,1}$	1	1	4546.1221	0.0036			3	3	2971.3706	-0.0068
		3	2	4546.8944	-0.0031	$4_{0,4}$	$3_{1,3}$	4	3	5430.6961	0.0086
		2	1	4546.9538	-0.0080			5	4	5431.2809	0.0071
		1	0	4547.3124	-0.0005			3	2	5431.5264	-0.0161
		2	2	4547.4337	-0.0060	$1_{1,0}$	$1_{0,1}$	1	2	4132.2702	0.0027
$2_{1,1}$	$1_{1,0}$	1	0	4698.6173	0.0026			1	0	4132.9751	-0.0090
		3	2	4699.8205	0.0012			2	2	4133.2929	0.0080
		2	1	4700.2554	-0.0032			0	1	4134.3325	-0.0009
		1	1	4701.1592	0.0007	$2_{1,1}$	$2_{0,2}$	2	2	4285.0857	-0.0006
$3_{1,3}$	$2_{1,2}$	4	3	6600.7096	0.0044			3	3	4286.2095	0.0027
		2	1	6600.8481	-0.0170			1	1	4286.8369	0.0073
		3	2	6600.9004	0.0125	$4_{1,3}$	$4_{0,4}$	4	4	4852.1304	-0.0026
$3_{0,3}$	$2_{0,2}$	4	3	6810.1419	0.0025			5	5	4853.2172	0.0004
		3	2	6810.2021	-0.0042			3	3	4853.4934	-0.0022
$3_{2,2}$	$2_{2,1}$	2	1	6826.1683	-0.0067	$3_{1,2}$	$3_{0,3}$	3	3	4522.1508	-0.0006
		4	3	6826.4673	0.0078			4	4	4523.2179	0.0002
		3	2	6826.9866	0.0151			2	2	4523.5927	0.0017
$3_{2,1}$	$2_{2,0}$	2	1	6842.5486	0.0044	$5_{1,4}$	$5_{0,5}$	5	5	5286.4076	0.0002
		4	3	6842.7994	-0.0185			6	6	5287.5396	0.0018
		3	2	6843.2785	-0.0034			4	4	5287.7685	0.0003

Table S20. Observed rotational frequencies and residuals (all the values in MHz) for the parent species of the ecb-II-w$_2$ complex for $J'K'_{-1}K'_{+1}F' \leftarrow J''K''_{-1}K''_{+1}F''$ transitions.

$J'K'_{-1}K'_{+1}$	$J''K''_{-1}K''_{+1}$	F'	F''	**Obs.**	**Res.**
$2_{1,2}$	$1_{1,1}$	3	2	2815.4147	0.0035
		1	0	2815.8066	-0.0014
		2	1	2815.8873	-0.0030
$2_{0,2}$	$1_{0,1}$	3	2	2935.3681	0.0024
		2	1	2935.4486	0.0021
		1	0	2935.6898	-0.0088
$2_{1,1}$	$1_{1,0}$	3	2	3065.4751	-0.0017
		2	1	3065.8301	0.0031
$3_{1,3}$	$2_{1,2}$	4	3	4220.1222	0.0033
		3	2	4220.2974	0.0071
		2	1	4220.2974	-0.0041
$3_{0,3}$	$2_{0,2}$	4	3	4390.3320	0.0023
		3	2	4390.4276	-0.0006
$3_{2,2}$	$2_{2,1}$	2	1	4410.4490	-0.0118
		4	3	4410.6933	-0.0057
		3	2	4411.1322	0.0043
$3_{2,1}$	$2_{2,0}$	2	1	4430.9087	0.0036
		4	3	4431.1210	-0.0041
		3	2	4431.4684	-0.0029
$3_{1,2}$	$2_{1,1}$	2	1	4594.7673	0.0006
		4	3	4594.9567	-0.0001
		3	2	4595.0571	-0.0004
$4_{1,4}$	$3_{1,3}$	5	4	5621.1989	0.0034
		3	2	5621.2964	0.0014
		4	3	5621.2964	0.0001
$4_{0,4}$	$3_{0,3}$	5	4	5830.3222	-0.0054
		3	2	5830.3623	0.0119
		4	3	5830.4501	0.0015
$4_{2,3}$	$3_{2,2}$	3	2	5876.9458	-0.0122
		5	4	5877.0026	-0.0057
		4	3	5877.1982	-0.0050
$4_{3,2}$	$3_{3,1}$	3	2	5890.6978	0.0099
		5	4	5890.8419	0.0052
		4	3	5891.2132	0.0050
$4_{2,2}$	$3_{2,1}$	5	4	5927.6798	0.0019
		4	3	5927.7573	-0.0045
$4_{1,3}$	$3_{1,2}$	3	2	6120.2303	0.0017
		5	4	6120.3095	0.0052
		4	3	6120.3670	0.0040
$5_{1,5}$	$4_{1,4}$	6	5	7017.7618	-0.0058
		4	3	7017.8462	0.0164
		5	4	7017.8462	0.0022
$5_{0,5}$	$4_{0,4}$	6	5	7251.3879	0.0000
		4	3	7251.3879	-0.0084
		5	4	7251.5342	0.0044
$5_{2,4}$	$4_{2,3}$	6	5	7339.8609	-0.0105
		4	3	7339.8609	0.0030
		5	4	7339.9759	-0.0116
$5_{2,3}$	$4_{2,2}$	6	5	7439.6854	-0.0009
		5	4	7439.6854	0.0179
		4	3	7439.6854	-0.0020

Table S21. Observed rotational frequencies and residuals (all the values in MHz) for the parent species of the ecb-II-w$_3$ complex for $J^{'}K^{'}_{-1}K^{'}_{+1}F^{'} \leftarrow J^{''}K^{''}_{-1}K^{''}_{+1}F^{''}$ transitions.

$J^{'}K^{'}_{-1}K^{'}_{+1}$	$J^{''}K^{''}_{-1}K^{''}_{+1}$	$F^{'}$	$F^{''}$	Obs.	Res.
$3_{1,3}$	$2_{1,2}$	4	3	2895.2719	0.0005
		3	2	2895.4329	-0.0003
		2	1	2895.4329	0.0072
$3_{0,3}$	$2_{0,2}$	4	3	3026.7290	0.0030
		3	2	3026.8270	-0.0064
$3_{1,2}$	$2_{1,1}$	2	1	3194.3978	0.0000
		4	3	3194.5675	0.0062
		3	2	3194.6643	0.0007
$4_{1,4}$	$3_{1,3}$	5	4	3854.4749	-0.0059
		3	2	3854.5731	0.0068
		4	3	3854.5731	-0.0051
$4_{0,4}$	$3_{0,3}$	3	2	4011.1289	-0.0180
		5	4	4011.1289	0.0012
		4	3	4011.2535	-0.0058
$4_{2,3}$	$3_{2,2}$	3	2	4060.1557	-0.0047
		5	4	4060.2139	0.0050
$4_{1,3}$	$3_{1,2}$	3	2	4252.5545	-0.0054
		5	4	4252.6289	0.0044
		4	3	4252.6931	0.0050
$5_{1,5}$	$4_{1,4}$	6	5	4809.1184	-0.0041
		4	3	4809.2011	0.0252
		5	4	4809.2011	0.0034
$5_{0,5}$	$4_{0,4}$	4	3	4976.5887	-0.0042
		6	5	4976.5887	0.0023
		5	4	4976.7378	0.0004
$5_{2,4}$	$4_{2,3}$	6	5	5068.4788	-0.0039
		4	3	5068.4788	0.0083
		5	4	5068.5976	0.0017

$J^{'}K^{'}_{-1}K^{'}_{+1}$	$J^{''}K^{''}_{-1}K^{''}_{+1}$	$F^{'}$	$F^{''}$	Obs.	Res.
$5_{2,3}$	$4_{2,2}$	5	4	5172.2936	-0.0159
		4	3	5172.3452	0.0034
		6	5	5172.3452	0.0050
$5_{1,4}$	$4_{1,3}$	4	3	5304.2547	-0.0071
		6	5	5304.3040	0.0057
		5	4	5304.3602	0.0025
$6_{1,6}$	$5_{1,5}$	7	6	5758.6793	0.0029
		6	5	5758.7482	0.0062
$6_{0,6}$	$5_{0,5}$	7	6	5922.2588	0.0011
		5	4	5922.2588	-0.0031
		6	5	5922.4146	-0.0041
$6_{2,5}$	$5_{2,4}$	7	6	6072.2460	-0.0048
		5	4	6072.2460	-0.0006
		6	5	6072.3368	0.0016
$6_{3,4}$	$5_{3,3}$	5	4	6121.5727	0.0185
		7	6	6121.5727	0.0015
		6	5	6121.6624	-0.0040
$6_{3,3}$	$5_{3,2}$	5	4	6131.7295	-0.0111
		7	6	6131.7623	0.0075
		6	5	6131.8277	-0.0019
$6_{2,4}$	$5_{2,3}$	6	5	6246.2693	0.0076
		7	6	6246.3340	0.0015
		5	4	6246.3340	-0.0063
$6_{1,5}$	$5_{1,4}$	5	4	6347.2507	-0.0117
		7	6	6347.2964	0.0089
		6	5	6347.3562	0.0023
$7_{1,7}$	$6_{1,6}$	8	7	6702.9396	-0.0088
		7	6	6703.0117	0.0026

$J^{'}K^{'}_{-1}K^{'}_{+1}$	$J^{''}K^{''}_{-1}K^{''}_{+1}$	$F^{'}$	$F^{''}$	Obs.	Res.
$7_{0,7}$	$6_{0,6}$	8	7	6850.4824	0.0044
		6	5	6850.4824	0.0028
		7	6	6850.6327	-0.0018
$7_{2,6}$	$6_{2,5}$	6	5	7070.6842	0.0032
		8	7	7070.6842	0.0023
		7	6	7070.7539	0.0009
$7_{3,5}$	$6_{3,4}$	8	7	7146.9228	-0.0090
		6	5	7146.9228	-0.0025
$7_{3,4}$	$6_{3,3}$	6	5	7169.5455	-0.0080
		6	7	7169.5455	-0.0026
		7	6	7169.5899	0.0094
$7_{2,5}$	$6_{2,4}$	7	6	7332.0412	0.0016
		6	5	7332.1190	-0.0082
		8	7	7332.1190	-0.0012
$7_{1,6}$	$6_{1,5}$	8	7	7378.8746	-0.0011
		6	5	7378.8746	0.0183
		7	6	7378.9481	-0.0063
$8_{0,8}$	$7_{0,7}$	9	8	7766.0969	0.0082
		7	6	7766.0969	0.0048
		8	7	7766.2247	-0.0070