Electronic Supplementary Tables for:

Corannulene and its complex with water: A tiny cup of water

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Table of Contents

Table S1: Measured rotational transition frequencies (MHz) for the parent species of corannulene and obs.-calc. differences (MHz) resulting from a weighted symmetric rotor fit.

J'	K_a'	←	J''	K_a''	ν_{obs}	$\nu_{\mathrm{obs}} - \nu_{\mathrm{calc}}$	$\delta\nu^a$
This work							
3	0		2	0	3059.0565	0.0008	0.005
4	0		3	0	4078.7407	0.0002	0.005
5	0		4	0	5098.4307	0.0060	0.005
6	0		5	0	6118.1125	0.0040	0.005
7	0		6	0	7137.7998	0.0081	0.005
F.J.Lovas, et al., *JACS* **127**, 4345-4349 (2005)							
5	0		4	0	5098.4246	−0.0001	0.001
6	0		5	0	6118.1081	−0.0003	0.001
7	0		6	0	7137.7916	0.0000	0.001
8	0		7	0	8157.4739	−0.0001	0.001
9	0		8	0	9177.1560	0.0003	0.002
10	0		9	0	10196.8380	0.0016	0.002
11	0		10	0	11216.5170	0.0010	0.002
12	0		11	0	12236.1970	0.0026	0.002
13	0		12	0	13255.8720	0.0004	0.002
14	0		13	0	14275.5490	0.0016	0.002
15	0		14	0	15295.2220	0.0002	0.002
16	0		15	0	16314.8940	−0.0005	0.002
17	0		16	0	17334.5640	−0.0016	0.002
18	0		17	0	18354.2340	−0.0009	0.002
19	0		18	0	19373.9030	0.0005	0.002
							rms = 2.62 kHz

[a]Estimated frequency measurement uncertainty (MHz).

Table S2: Measured rotational transition frequencies for the $^{13}C_o$ (substituted outer carbon atom) species of corannulene and obs.-calc. differences (all in MHz) resulting from an asymmetric rotor fit.

J'	K'_a	K'_c	←	J''	K''_a	K''_c	ν_{obs}	$\nu_{obs} - \nu_{calc}$
2	2	0		1	1	0	2028.5398	−0.0043
3	2	1		2	1	1	3034.6531	−0.0004
3	3	0		2	2	0	3043.0340	−0.0052
3	3	1		2	2	1	3050.8199	−0.0019
4	3	1		3	2	1	4046.3067	−0.0037
4	2	2		3	1	2	4056.0839	−0.0013
4	2	3		3	1	3	4056.7267 [a]	−0.0002 [a]
4	1	3		3	0	3	4056.7267 [a]	−0.0002 [a]
4	3	2		3	2	2	4056.9790	0.0020
4	4	0		3	3	0	4057.7997	−0.0010
4	4	1		3	3	1	4067.8639	−0.0001
5	4	1		4	3	1	5058.0625	0.0013
5	3	2		4	2	2	5069.5514	−0.0017
5	2	3		4	1	3	5070.8374 [a]	0.0134 [a]
5	3	3		4	2	3	5070.8374 [a]	0.0134 [a]
5	2	4		4	1	4	5070.9433 [a]	0.0140 [a]
5	1	4		4	0	4	5070.9433 [a]	0.0140 [a]
5	4	2		4	3	2	5071.3269	−0.0051
5	5	0		4	4	0	5072.9132	−0.0011
6	5	1		5	4	1	6069.9335	0.0011
6	4	2		5	3	2	6082.6614	−0.0005
6	3	3		5	2	3	6084.8367	−0.0021
6	5	2		5	4	2	6085.7627	0.0017
6	6	0		5	5	0	6088.4667	0.0060
6	6	1		5	5	1	6102.2172	−0.0018
7	6	1		6	5	1	7081.9498	−0.0034
7	5	2		6	4	2	7095.3566	0.0003
7	4	3		6	3	3	7098.7848	0.0055
7	5	3		6	4	3	7098.8970	0.0013
7	3	4		6	2	4	7099.1378 [a]	0.0065 [a]
7	4	4		6	3	4	7099.1378 [a]	0.0065 [a]
7	3	5		6	2	5	7099.2452 [a]	−0.0079 [a]
7	2	5		6	1	5	7099.2452 [a]	−0.0079 [a]
7	6	2		6	5	2	7100.2801	0.0017
7	7	0		6	6	0	7104.5082	−0.0014
7	7	1		6	6	1	7119.5640	−0.0012

rms = 4.69 kHz

[a] Blended line, fitted to the average of the calculated frequencies.

Table S3: Measured rotational transition frequencies (MHz) for the $^{13}C_m$ (substituted middle carbon atom) species of corannulene and obs.-calc. differences (all in MHz) resulting from an asymmetric rotor fit.

J'	K'_a	K'_c	←	J''	K''_a	K''_c	ν_{obs}	$\nu_{obs} - \nu_{calc}$
4	3	1		3	2	1	4060.0011	−0.0119
4	3	1		3	2	1	4060.0011	−0.0118
4	2	2		3	1	2	4065.9526 [a]	−0.0020
4	2	2		3	1	2	4065.9526 [a]	−0.0020
4	4	0		3	3	0	4066.5345 [a]	−0.0016
4	4	0		3	3	0	4066.5345 [a]	−0.0016
4	4	1		3	3	1	4072.5629	−0.0122
5	4	1		4	3	1	5075.0670	−0.0063
5	3	2		4	2	2	5082.2557	0.0016
5	3	3		4	2	3	5082.6980 [a]	−0.0030
5	2	3		4	1	3	5082.6980 [a]	−0.0030
5	1	4		4	0	4	5082.6980 [a]	−0.0030
5	2	4		4	1	4	5082.6980 [a]	−0.0030
5	4	2		4	3	2	5082.8569	−0.0015
5	5	0		4	4	0	5083.3988	0.0031
5	5	1		4	4	1	5090.7709	−0.0027
6	5	1		5	4	1	6090.1823	0.0092
6	4	2		5	3	2	6098.4379	0.0095
6	3	3		5	2	3	6099.1854 [a]	0.0036
6	4	3		5	3	3	6099.1854 [a]	0.0036
6	2	4		5	1	4	6099.2520 [a]	0.0066
6	3	4		5	2	4	6099.2520 [a]	0.0066
6	5	2		5	4	2	6099.4823	−0.0021
6	6	0		5	5	0	6100.4048	0.0004
6	6	1		5	5	1	6109.0035	−0.0042
7	6	1		6	5	1	7105.3131	−0.0074
7	5	2		6	4	2	7114.4540	−0.0006
7	4	3		6	3	3	7115.6640 [a]	0.0109
7	5	3		6	4	3	7115.6640 [a]	0.0109
7	3	5		6	2	5	7115.7734 [a]	0.0000
7	3	4		6	2	4	7115.7734 [a]	0.0000
7	4	4		6	3	4	7115.7734 [a]	0.0000
7	2	5		6	1	5	7115.7734 [a]	0.0000
7	4	4		6	3	4	7115.7753 [a]	0.0019
7	2	5		6	1	5	7115.7753 [a]	0.0019
7	3	4		6	2	4	7115.7753 [a]	0.0019
7	3	5		6	2	5	7115.7753 [a]	0.0019
7	7	0		6	6	0	7117.5995	0.0092
7	7	1		6	6	1	7127.2788	−0.0046

rms = 6.50 kHz

[a] Blended line, fitted to the average of the calculated frequencies.

Table S4: Measured rotational transition frequencies for the $^{13}C_m$ (substituted inner carbon atom) species of corannulene and obs.-calc. differences (all in MHz) resulting from an asymmetric rotor fit.

J'	K'_a	K'_c	←	J''	K''_a	K''_c	ν_{obs}	$\nu_{obs} - \nu_{calc}$
3	2	1		2	1	1	3054.5538	−0.0208
3	3	1		2	2	1	3056.8174	0.0008
4	3	1		3	2	1	4072.7556	−0.0121
4	2	2		3	1	2	4074.2557 [a]	−0.0039 [a]
4	4	0		3	3	0	4074.2557 [a]	−0.0039 [a]
4	3	2		3	2	2	4074.2557 [a]	−0.0039 [a]
4	1	3		3	0	3	4074.2557 [a]	−0.0039 [a]
4	2	3		3	1	3	4074.2557 [a]	−0.0039 [a]
4	4	1		3	3	1	4075.7528	−0.0041
5	4	1		4	3	1	5090.9785	0.0164
5	2	3		4	1	3	5092.8346 [a]	0.0144 [a]
5	4	2		4	3	2	5092.8346 [a]	0.0144 [a]
5	1	4		4	0	4	5092.8346 [a]	0.0144 [a]
5	3	3		4	2	3	5092.8346 [a]	0.0144 [a]
5	2	4		4	1	4	5092.8346 [a]	0.0144 [a]
5	5	1		4	4	1	5094.7024	0.0038
6	3	4		5	2	4	6111.3716 [a]	−0.0105 [a]
6	4	3		5	3	3	6111.3716 [a]	−0.0105 [a]
6	2	4		5	1	4	6111.3716 [a]	−0.0105 [a]
6	3	3		5	2	3	6111.3716 [a]	−0.0105 [a]
6	2	5		5	1	5	6111.3716 [a]	−0.0105 [a]
6	1	5		5	0	5	6111.3716 [a]	−0.0105 [a]
6	5	2		5	4	2	6111.3716 [a]	−0.0105 [a]
6	6	1		5	5	1	6113.6387	−0.0030
7	6	1		6	5	1	7127.3620	0.0058
7	1	6		6	0	6	7129.9408 [a]	−0.0023 [a]
7	3	4		6	2	4	7129.9408 [a]	−0.0023 [a]
7	4	4		6	3	4	7129.9408 [a]	−0.0023 [a]
7	2	5		6	1	5	7129.9408 [a]	−0.0023 [a]
7	5	3		6	4	3	7129.9408 [a]	−0.0023 [a]
7	2	6		6	1	6	7129.9408 [a]	−0.0023 [a]
7	6	2		6	5	2	7129.9408 [a]	−0.0023 [a]
7	3	5		6	2	5	7129.9408 [a]	−0.0023 [a]
7	4	3		6	3	3	7129.9408 [a]	−0.0023 [a]
7	7	1		6	6	1	7132.5903	0.0034

rms = 9.92 kHz

[a] Blended line, fitted to the average of the calculated frequencies.

Table S5: The abbreviated results of fitting the r_0 geometry of corannulene with the STRFIT program.

```
corannulene set up from the MP2/6-311++G(d,p) calculation
```

```
!
!  centrosymmetric declaration, using six parameters to define the complete
!  carbon skeleton:
!  r                  for the inner carbon atom Ci
!  r+theta            for the middle carbon atom Cm
!  r+theta+dihedral   for the outer carbon atom Co
!
!  CH geometry is specified with three unique parameters (CoH distance,
!  HCoCo angle, HCoCoCm dihedral), their starting values are all
!  assumed at the ab initio result
!
!  Dummy atoms 1,2 define the b-inertial axis, 2,3 define the c-inertial axis,
!  and 3 is positioned in the centre of the central five membered ring.
!
```

NUMBER OF ATOMS = 33 (including 3 dummy atoms)

NO	NA	NB	NC	NO.NA	NO.NA.NB	NO.NA.NB.NC	MASS
1	0	0	0	0.000000	0.000000	0.000000	0.0000000
2	1	0	0	0.800000	0.000000	0.000000	0.0000000
3	2	1	0	2.000000	90.000000	0.000000	0.0000000
4	3	2	1	1.207000	90.000000	0.000000	12.0000000
5	3	2	1	1.207000	90.000000	-72.000000	12.0000000
6	3	2	1	1.207000	90.000000	72.000000	12.0000000
7	3	2	1	1.207000	90.000000	-144.000000	12.0000000
8	3	2	1	1.207000	90.000000	144.000000	12.0000000
9	3	2	1	2.546300	102.080000	0.000000	12.0000000
10	3	2	1	2.546300	102.080000	-72.000000	12.0000000
11	3	2	1	2.546300	102.080000	72.000000	12.0000000
12	3	2	1	2.546300	102.080000	-144.000000	12.0000000
13	3	2	1	2.546300	102.080000	144.000000	12.0000000
14	3	2	1	3.386100	106.100000	-23.591000	12.0000000
15	3	2	1	3.386100	106.100000	23.591000	12.0000000
16	3	2	1	3.386100	106.100000	48.409000	12.0000000
17	3	2	1	3.386100	106.100000	-48.409000	12.0000000
18	3	2	1	3.386100	106.100000	120.409000	12.0000000
19	3	2	1	3.386100	106.100000	-120.409000	12.0000000
20	3	2	1	3.386100	106.100000	-95.591000	12.0000000
21	3	2	1	3.386100	106.100000	95.591000	12.0000000
22	3	2	1	3.386100	106.100000	-167.591000	12.0000000
23	3	2	1	3.386100	106.100000	167.591000	12.0000000
24	14	17	10	1.089200	118.316000	174.023000	1.0078250
25	15	16	11	1.089200	118.316000	-174.023000	1.0078250
26	16	15	9	1.089200	118.316000	174.023000	1.0078250
27	17	14	9	1.089200	118.316000	-174.023000	1.0078250
28	18	21	11	1.089200	118.316000	174.023000	1.0078250
29	19	20	10	1.089200	118.316000	-174.023000	1.0078250
30	20	19	12	1.089200	118.316000	174.023000	1.0078250
31	21	18	13	1.089200	118.316000	-174.023000	1.0078250

```
  32  22  23  13     1.089200   118.316000   174.023000      1.0078250
  33  23  22  12     1.089200   118.316000  -174.023000      1.0078250
!
!
!------------------------
! Parameters of fit
!------------------------
!

   TOTAL NUMBER OF PARAMETERS:     9

      Parameters to be fitted:
      --------
          R( 4, 3) =     1.250000
                          , and at 4 more atom(s):   5  6  7  8
          R( 9, 3) =     2.546300
                          , and at 4 more atom(s):  10 11 12 13
          R(14, 3) =     3.386100
                          , and at 9 more atom(s):  15 16 17 18 19 20 21 22 23
       A( 9, 3, 2) =   102.080000
                          , and at 4 more atom(s):  10 11 12 13
       A(14, 3, 2) =   106.100000
                          , and at 9 more atom(s):  15 16 17 18 19 20 21 22 23
          R(24,14) =     1.100000
                          , and at 9 more atom(s):  25 26 27 28 29 30 31 32 33

             Fixed parameters:
             ------
    D(14, 3, 2, 1) =   -23.660000
                          , also at atom  -15 =     23.660  (difference =      0.000 )
                          , also at atom   16 =     48.340  (difference =     72.000 )
                          , also at atom  -17 =    -48.340  (difference =    -72.000 )
                          , also at atom   18 =    120.340  (difference =    144.000 )
                          , also at atom  -19 =   -120.340  (difference =   -144.000 )
                          , also at atom   20 =    -95.660  (difference =    -72.000 )
                          , also at atom  -21 =     95.660  (difference =     72.000 )
                          , also at atom   22 =   -167.660  (difference =   -144.000 )
                          , also at atom  -23 =    167.660  (difference =    144.000 )
       A(24,14,17) =   118.450000
                          , and at 9 more atom(s):  25 26 27 28 29 30 31 32 33
    D(24,14,17,10) =   174.130000
                          , also at atom  -25 =   -174.130  (difference =      0.000 )
                          , also at atom   26 =    174.130  (difference =      0.000 )
                          , also at atom  -27 =   -174.130  (difference =      0.000 )
                          , also at atom   28 =    174.130  (difference =      0.000 )
                          , also at atom  -29 =   -174.130  (difference =      0.000 )
                          , also at atom   30 =    174.130  (difference =      0.000 )
                          , also at atom  -31 =   -174.130  (difference =      0.000 )
                          , also at atom   32 =    174.130  (difference =      0.000 )
                          , also at atom  -33 =   -174.130  (difference =      0.000 )
!
!------------------------
! spectroscopic constants:
!
! A,B and Pb specified directly
!
! A,B,C from 13C1 =13Co used to evaluate Pb, which is assumed to be invariant
! on isotopic sunbstitution and using A,B for each species leads
```

```
! to evaluation of C via:
!
! Ic = 2Pb - Ia + Ib
!
!------------------------
!

     NO OF CONSTANTS IN INPUT:    12
                         A  =   509.84269
                         B  =   509.84269
                        P.b =   529.32016
Isotopic species  2:     A  =   509.80864
                         B  =   504.41888
                         C  =   263.20000
Isotopic species  3:     A  =   509.65615
                         B  =   508.90885
                        P.b =   529.32016
Isotopic species  4:     A  =   509.84975
                         B  =   506.70892
                        P.b =   529.32016

!
!------------------------
! declaration of isotopic species
!------------------------
!
!  13C1  = C outer
!
ISOTOPIC SPECIES  2,  changes from parent species:
atom no.,parameter no.,value    14  4       13.0033544
!
!  13C2  = C inner
!
ISOTOPIC SPECIES  3,  changes from parent species:
atom no.,parameter no.,value     4  4       13.0033544
!
!  13C3  = C middle
!
ISOTOPIC SPECIES  4,  changes from parent species:
atom no.,parameter no.,value     9  4       13.0033544

!------------------------
after:   7 iterations,  ALAMDA=  0.10E-09

FINAL RESULTS OF LEAST SQUARES FIT:

          R( 4, 3) =     1.205593 +-  0.003767      and at atom  5  6  7  8
          R( 9, 3) =     2.538494 +-  0.004251      and at atom 10 11 12 13
          R(14, 3) =     3.375698 +-  0.001422      and at atom 15 16 17 18 19 20 21 22 23
       A( 9, 3, 2) =   102.562326 +-  0.364661      and at atom 10 11 12 13
       A(14, 3, 2) =   105.362596 +-  0.051748      and at atom 15 16 17 18 19 20 21 22 23
    D(14, 3, 2, 1) = [ -23.660000 ]    FIXED        and at atom-15 16-17 18-19 20-21 22-23
          R(24,14) =     1.101218 +-  0.013837      and at atom 25 26 27 28 29 30 31 32 33
       A(24,14,17) = [ 118.450000 ]    FIXED        and at atom 25 26 27 28 29 30 31 32 33
    D(24,14,17,10) = [ 174.130000 ]    FIXED        and at atom-25 26-27 28-29 30-31 32-33

              Chi-squared =        0.0002516993
         Deviation of fit =        0.006477
```

Translation table to notation for centrosymmetric parameters defined in Fig.2:

R(4, 3) =	1.205593	+- 0.003767	r_i
R(9, 3) =	2.538494	+- 0.004251	r_m
R(14, 3) =	3.375698	+- 0.001422	r_o
A(9, 3, 2) =	102.562326	+- 0.364661	θ_m
A(14, 3, 2) =	105.362596	+- 0.051748	θ_o
D(14, 3, 2, 1) =	[-23.660000]	FIXED	Θ_o
R(24,14) =	1.101218	+- 0.013837	$r(HC_o)$
A(24,14,17) =	[118.450000]	FIXED	$\theta(HC_oC_o)$
D(24,14,17,10) =	[174.130000]	FIXED	$\Theta(HC_oC_oC_m)$

Ni	Axis	Iobs	Icalc	Io-c	Bobs	Bcalc	Bo-c
1	a	991.24499	991.23658	0.00841	509.8427	509.8470	-0.0043
1	b	991.24499	991.23659	0.00840	509.8427	509.8470	-0.0043
1	P.b	954.77000	954.77101	-0.00101	529.3202	529.3196	0.0006
2	a	991.31119	991.31514	-0.00395	509.8086	509.8066	0.0020
2	b	1001.90344	1001.90465	-0.00121	504.4189	504.4183	0.0006
2	c	1920.13302	1920.13152	0.00149	263.2000	263.2002	-0.0002
3	a	991.60779	991.61069	-0.00290	509.6562	509.6547	0.0015
3	b	993.06391	993.06379	0.00012	508.9088	508.9089	-0.0001
3	P.b	954.77000	954.77101	-0.00101	529.3202	529.3196	0.0006
4	a	991.23126	991.24018	-0.00892	509.8497	509.8452	0.0046
4	b	997.37540	997.37530	0.00010	506.7089	506.7090	-0.0001
4	P.b	954.77000	954.77101	-0.00101	529.3202	529.3196	0.0006

Correlation coefficients:

		1	2	3	4	5	6
1:	R(4, 3)	1.000					
2:	R(9, 3)	-0.560	1.000				
3:	R(14, 3)	-0.356	0.724	1.000			
4:	A(9, 3, 2)	-0.638	0.938	0.715	1.000		
5:	A(14, 3, 2)	-0.554	0.963	0.785	0.987	1.000	
6:	R(24,14)	-0.256	-0.394	-0.747	-0.220	-0.366	1.000

!------------------------

Final principal coordinates of parent:

ATOM NO.	A	B	C	MASS
1	0.362122	-0.713349	-2.612327	0.0000000
2	0.000000	0.000000	-2.612327	0.0000000
3	0.000000	0.000000	-0.612327	0.0000000
4	0.545715	-1.075012	-0.612327	12.0000000
5	1.191032	0.186809	-0.612327	12.0000000
6	-0.853762	-0.851203	-0.612327	12.0000000
7	0.190383	1.190466	-0.612327	12.0000000
8	-1.073369	0.548939	-0.612327	12.0000000
9	1.121548	-2.209353	-0.060201	12.0000000
10	2.447797	0.383928	-0.060201	12.0000000
11	-1.754642	-1.749383	-0.060201	12.0000000
12	0.391274	2.446634	-0.060201	12.0000000
13	-2.205977	1.128175	-0.060201	12.0000000

14	2.514372	-2.067239	0.281985	12.0000000
15	0.184767	-3.249831	0.281985	12.0000000
16	-1.189077	-3.030122	0.281985	12.0000000
17	3.147869	-0.828529	0.281985	12.0000000
18	-3.249262	0.194521	0.281985	12.0000000
19	1.760723	2.737772	0.281985	12.0000000
20	2.743045	1.752498	0.281985	12.0000000
21	-3.033677	-1.179977	0.281985	12.0000000
22	-0.819077	3.150342	0.281985	12.0000000
23	-2.059683	2.520565	0.281985	12.0000000
24	3.074192	-2.942777	0.646288	1.0078250
25	0.561132	-4.218497	0.646288	1.0078250
26	-1.848769	-3.833098	0.646288	1.0078250
27	4.185429	-0.769919	0.646288	1.0078250
28	-4.216794	0.573792	0.646288	1.0078250
29	2.025605	3.742661	0.646288	1.0078250
30	3.748724	2.014362	0.646288	1.0078250
31	-3.838630	-1.837256	0.646288	1.0078250
32	-0.757353	4.187721	0.646288	1.0078250
33	-2.933536	3.083011	0.646288	1.0078250

Table S6: Observed rotational transition frequencies (MHz) for the two tunneling components, m=0 and m=1, of the corannulene-water complex $C_{20}H_{10}$-H_2O.

	$m = 0$			$m = 1$		
$J + 1 - J$	obs.	o.-c.[a]	o.-c.[b]	obs.	o.-c.[a]	o.-c.[b]
3 - 2	3644.7713	0.0001	0.0001	3610.3152	0.0003	0.0003
4 - 3	4555.9607	0.0003	0.0003	4512.8899	0.0006	0.0005
5 - 4	5467.1468	−0.0003	−0.0003	5415.4591	−0.0007	−0.0006
6 - 5	6378.3307	−0.0003	−0.0002	6318.0267	0.0006	0.0005
7 - 6	7289.5117	0.0002	0.0002	7220.5876	−0.0002	−0.0002

[a]Values from a global fit of transitions in m=0 and m=1 substates.
[b]Values from separate fits of transitions in each of m=0 and m=1 substates.

Table S7: Spectroscopic and molecular parameters obtained from a global analysis (including both tunneling components) of the spectrum of the observed corannulene-water cluster, $C_{20}H_{10}$-H_2O-in and comparison with quantum chemistry calculations.

Parameter	exp.		RI-MP2-F12/cc-pVTZ-F12// RI-MP2/aug-cc-pVDZ		RI-MP2-F12/cc-pVTZ-F12// RI-MP2/aug-cc-pVTZ		M062x/ 6-311++G(d,p)	
			in	out	in	out	in	out
A (MHz)			459.1	406.6	465.8	410.6	466.1	411.4
B (MHz)	455.597043(55)		458.4	406.4	465.1	410.5	465.0	411.1
C (MHz)	264.66		262.1	260.6	266.9	265.3	268.0	265.8
D_J (kHz)	0.02013(57)							
D_{Jm} (MHz)	4.306704(78)							
H_{Jm} (kHz)	0.00801(81)							
$\lvert\mu_a\rvert$ (D)			0.11	0.10	0.15	0.11	0.40	0.03
$\lvert\mu_b\rvert$ (D)			0.01	0.01	0.01	0.08	0.02	0.01
$\lvert\mu_c\rvert$ (D)			0.37	4.88	0.30	4.77	0.37	4.99
μ_{tot} (D)			0.39	4.88	0.34	4.77	0.55	4.99
	Pseudoatomic model							
μ (u) [a]	16.806							
R_{cm} (Å) [b]	2.640		2.38	3.75	2.41	3.79	2.45	3.79
	in	out						
R_{Ox} (Å)	3.318	2.094	3.10	3.20	3.05	3.25	3.16	3.24
R_{OC_i} (Å)	3.531	2.416	3.32	3.43	3.33	3.46	3.38	3.46
k_σ (N m^{-1}) [c]	2.19							
ν_σ (cm^{-1}) [d]	47							
E_d (kJ mol^{-1}) [e]	−12.0		−21.4	−12.3	−25.6	−12.3	−28.0	−13.2
ΔE (kJ/mol)			0	+15.6		+14.2		+14.0

[a] Reduced mass, $\mu = M_c M_w/(M_c + M_w)$, where M_c and M_w are molecular masses of corannulene and water, respectively.
[b] Separation between centres of mass of corannulene and water monomers, Eq.17 in D.J.Millen, Canad.J.Chem. 7 (1985) 1477-1479.
[c] Intermolecular stretching force constant, Eq.12=Eq.16 in D.J.Millen, Canad.J.Chem. 7 (1985) 1477-1479.
[d] Wavenumber of the intermolecular stretching mode, Eq.15 in T.J.Balle, et al., J. Chem.Phys. 72 (1980) 922-932, using the k_σ above.
[e] Computed dimerisation energy (counterpoise-corrected) or -ve of Lennard-Jones well depth from the pseudodiatomic model, Eq.19 in T.J.Balle, et al., J. Chem.Phys. 72 (1980) 922-932.

Table S8: Spectroscopic and molecular parameters obtained when the two tunneling components $m = 0$ and $m = 1$ are fit separately, including results using the pseudo-diatomic model.

	$m = 0$	$m = 1$
Fitted parameter		
B (MHz)	455.597040(55)	451.290340(55)
D_J (kHz)	0.02010(57)	0.02810(57)
Pseudo-diatomic model		
μ (u)	16.806	16.806
R_{cm} (Å)	2.640	2.757
R_{Ox} (Å)	3.318	3.435
$R_{\mathrm{OC_i}}$ (Å)	3.531	3.641
k_σ (N m^{-1})	2.19	1.64
ν_σ (cm^{-1})	47	41
E_d (kJ mol^{-1})	12.1	9.1

Table S9: MP2/6-311++G(d,p) optimized Cartesian coordinates for H_2O, $C_{20}H_{10}$, $C_{20}H_{10}$-H_2O-in and $C_{20}H_{10}$-H_2O-out.

3			
H_2O			
O	0.000000	0.000000	0.118850
H	0.000000	-0.753360	-0.475380
H	0.000000	0.753360	-0.475380
30			
$C_{20}H_{10}$			
C	0.151120	-3.249510	-0.274080
C	1.501030	-2.886030	-0.273980
C	1.931330	-1.559920	0.100650
C	0.938960	-0.758450	0.666610
C	3.137500	-0.860400	-0.273440
C	3.208850	0.535710	-0.273310
C	2.080370	1.354560	0.100650
C	1.011470	0.658650	0.666810
C	1.787850	2.717650	-0.273910
C	0.482110	3.217040	-0.274100
C	-0.645500	2.397230	0.100680
C	-0.313830	1.165470	0.666660
C	-2.032360	2.540120	-0.273800
C	-2.910830	1.452650	-0.273570
C	-2.479260	0.126920	0.100660
C	-1.205500	0.061720	0.666900
C	-3.043950	-1.147840	-0.273460
C	-2.281210	-2.319380	-0.273730
C	-0.886940	-2.318820	0.100600
C	-0.431220	-1.127380	0.666510
H	-0.120040	-4.231370	-0.659840
H	3.987470	-1.421770	-0.659130
H	2.584320	3.352400	-0.660060
H	-2.390020	3.493880	-0.659570
H	-4.061470	-1.193170	-0.659460
H	-2.734440	-3.231620	-0.659430
H	2.228560	-3.598940	-0.659800
H	4.111600	1.007410	-0.659220
H	0.312550	4.221380	-0.660010
H	-3.918380	1.601700	-0.659570

33			
$C_{20}H_{10}$-H_2O-in			
C	-2.425040	2.168930	0.109670
C	-1.292000	2.985790	0.109500
C	0.005150	2.482570	-0.271360
C	0.000610	1.211090	-0.848810
C	1.306290	2.973990	0.111780
C	2.435400	2.149130	0.110830
C	2.359610	0.759750	-0.273810
C	1.146130	0.372340	-0.848580
C	3.232170	-0.327650	0.101770
C	2.795550	-1.655520	0.099000
C	1.449170	-2.010870	-0.279480
C	0.702930	-0.976420	-0.848710
C	0.686370	-3.175040	0.101360
C	-0.711700	-3.169310	0.105090
C	-1.468080	-1.998460	-0.271800
C	-0.716780	-0.970320	-0.847490
C	-2.810500	-1.631150	0.111660
C	-3.235890	-0.299390	0.111770
C	-2.357930	0.779290	-0.271170
C	-1.150260	0.381440	-0.848140
H	-3.354610	2.573070	0.507770
H	1.403890	3.982670	0.510740
H	4.224620	-0.109730	0.493900
H	1.201170	-4.051190	0.492990
H	-3.483880	-2.390430	0.506950
H	-4.223900	-0.072750	0.509960
H	-1.381420	3.995500	0.507480
H	3.368570	2.547610	0.506620
H	3.464430	-2.420970	0.489720
H	-1.231780	-4.041540	0.498810
O	0.000710	0.004730	2.330530
H	-0.425590	-0.659340	1.778410
H	0.725680	0.308150	1.773840

33			
$C_{20}H_{10}$-H_2O-out			
C	1.817040	-2.695850	-0.551990
C	2.782290	-1.683360	-0.550430
C	2.461900	-0.326280	-0.177500

C	1.195660	-0.158690	0.385820
C	3.127460	0.900910	-0.543960
C	2.461620	2.131130	-0.539870
C	1.072080	2.244030	-0.165560
C	0.520290	1.089060	0.389040
C	0.111140	3.257710	-0.531280
C	-1.264540	3.005690	-0.528770
C	-1.801940	1.716670	-0.162600
C	-0.874520	0.833530	0.391930
C	-3.061990	1.117090	-0.531000
C	-3.247260	-0.269740	-0.533600
C	-2.188310	-1.179880	-0.168950
C	-1.062140	-0.573020	0.388930
C	-2.008260	-2.563300	-0.540510
C	-0.746670	-3.166880	-0.546080
C	0.446400	-2.442570	-0.176610
C	0.216970	-1.185670	0.383190
H	2.097540	-3.675620	-0.936190
H	4.145910	0.866590	-0.928490
H	0.459540	4.217890	-0.909250
H	-3.866730	1.745860	-0.909610
H	-2.854990	-3.133040	-0.920860
H	-0.662270	-4.183160	-0.928520
H	3.774220	-1.915570	-0.935670
H	2.989440	3.004840	-0.919700
H	-1.931860	3.779270	-0.906230
H	-4.188470	-0.663970	-0.914310
O	0.030680	-0.033850	3.627860
H	0.770700	-0.086180	3.014820
H	-0.721960	0.010420	3.029770

Table S10: RI-MP2/6-311++G(d,p) optimized Cartesian coordinates for H_2O, $C_{20}H_{10}$, $C_{20}H_{10}$-H_2O-in and $C_{20}H_{10}$-H_2O-out.

3			
H_2O			
O	0.029449	0.002643	2.198459
H	-0.725691	0.103493	1.599155
H	0.788844	0.087373	1.602053
30			
$C_{20}H_{10}$			
C	-0.70368	-0.99282	-0.87857
C	0.72001	-0.99544	-0.88725
C	1.16251	0.35771	-0.87575
C	0.01233	1.19662	-0.86013
C	-1.14104	0.36193	-0.86171
C	2.3923	0.7479	-0.3269
C	2.4684	2.14454	0.05322
C	1.33135	2.9739	0.06864
C	0.01812	2.47956	-0.29455
C	-1.45985	-2.03984	-0.33285
C	-0.69425	-3.22009	0.01596
C	0.71317	-3.22266	0.00745
C	1.47884	-2.04523	-0.35064
C	-2.36266	0.75667	-0.29808
C	-2.42899	2.15357	0.08289
C	-1.28878	2.97871	0.08453
C	-3.2434	-0.3368	0.0618
C	-2.81103	-1.67611	0.04509
C	2.83581	-1.6865	0.01098
C	3.27328	-0.3488	0.02239
H	3.41146	2.55293	0.43441
H	1.439	3.99159	0.46127
H	-1.21066	-4.11071	0.39223
H	1.23083	-4.11517	0.37748
H	-3.36585	2.56545	0.47546
H	-1.38789	3.99678	0.47844
H	-4.24455	-0.12154	0.45273
H	-3.49452	-2.44479	0.42381
H	3.52096	-2.45771	0.38146
H	4.27985	-0.13723	0.4012

33			
$C_{20}H_{10}$-H_2O-in			
C	-0.704551	-0.994168	-0.906806
C	0.719652	-0.99671	-0.915237
C	1.162174	0.357939	-0.901113
C	0.011736	1.198682	-0.888288
C	-1.141881	0.362133	-0.887213
C	2.387825	0.747584	-0.335497
C	2.462717	2.141486	0.054658
C	1.32649	2.970757	0.06591
C	0.017535	2.477499	-0.309404
C	-1.457029	-2.038109	-0.34599
C	-0.694098	-3.216322	0.010987
C	0.711926	-3.218822	0.002775
C	1.474845	-2.043351	-0.363195
C	-2.359221	0.756117	-0.306787
C	-2.424262	2.150214	0.084455
C	-1.284963	2.975387	0.081926
C	-3.235089	-0.335846	0.068785
C	-2.802338	-1.674992	0.048866
C	2.82598	-1.685094	0.01589
C	3.263932	-0.347522	0.030245
H	3.401963	2.543169	0.451926
H	1.428104	3.98305	0.47347
H	-1.211947	-4.09968	0.401721
H	1.231163	-4.104035	0.387422
H	-3.357113	2.555216	0.493245
H	-1.377928	3.987956	0.490867
H	-4.227795	-0.117671	0.479045
H	-3.476359	-2.442585	0.446163
H	3.501776	-2.455077	0.405486
H	4.262194	-0.132934	0.42876
O	0.029449	0.002643	2.198459
H	-0.725691	0.103493	1.599155
H	0.788844	0.087373	1.602053

33			
$C_{20}H_{10}$-H_2O-out			
C	-0.911804	0.826748	0.279664
C	0.482	1.115847	0.279076
C	1.187534	-0.12075	0.292986

C	0.229603	-1.173283	0.300509
C	-1.067423	-0.588518	0.292563
C	2.472734	-0.266039	-0.249732
C	2.827186	-1.626733	-0.601129
C	1.878969	-2.667611	-0.595494
C	0.492986	-2.44071	-0.236993
C	-1.866234	1.691275	-0.275371
C	-1.353529	2.995142	-0.647538
C	0.025032	3.280836	-0.648094
C	1.013748	2.288146	-0.276077
C	-2.187972	-1.232575	-0.251803
C	-1.971779	-2.622047	-0.603662
C	-0.688171	-3.200212	-0.596808
C	-3.271127	-0.344927	-0.624444
C	-3.117375	1.055058	-0.635527
C	2.415231	2.202244	-0.63481
C	3.113634	0.979323	-0.622095
H	3.833327	-1.846193	-0.976583
H	2.18958	-3.651033	-0.966906
H	-2.039357	3.758292	-1.033065
H	0.350913	4.253713	-1.033758
H	-2.807479	-3.223333	-0.979775
H	-0.581704	-4.226097	-0.967953
H	-4.210569	-0.764013	-1.003116
H	-3.944	1.662392	-1.021986
H	2.93236	3.088348	-1.020694
H	4.142868	0.968625	-0.999083
O	-0.018885	0.314357	3.476884
H	-0.776212	0.331112	2.874335
H	0.729565	0.392273	2.868099

Table S11: RI-MP2/aug-cc-pVDZ optimized Cartesian coordinates for H_2O, $C_{20}H_{10}$, $C_{20}H_{10}$-H_2O-in and $C_{20}H_{10}$-H_2O-out.

3			
H_2O			
O	0.029469	0.003615	2.192197
H	-0.728837	0.103041	1.602281
H	0.79197	0.086853	1.605189
30			
$C_{20}H_{10}$			
C	-0.70368	-0.99282	-0.87857
C	0.72001	-0.99544	-0.88725
C	1.16251	0.35771	-0.87575
C	0.01233	1.19662	-0.86013
C	-1.14104	0.36193	-0.86171
C	2.3923	0.7479	-0.3269
C	2.4684	2.14454	0.05322
C	1.33135	2.9739	0.06864
C	0.01812	2.47956	-0.29455
C	-1.45985	-2.03984	-0.33285
C	-0.69425	-3.22009	0.01596
C	0.71317	-3.22266	0.00745
C	1.47884	-2.04523	-0.35064
C	-2.36266	0.75667	-0.29808
C	-2.42899	2.15357	0.08289
C	-1.28878	2.97871	0.08453
C	-3.2434	-0.3368	0.0618
C	-2.81103	-1.67611	0.04509
C	2.83581	-1.6865	0.01098
C	3.27328	-0.3488	0.02239
H	3.41146	2.55293	0.43441
H	1.439	3.99159	0.46127
H	-1.21066	-4.11071	0.39223
H	1.23083	-4.11517	0.37748
H	-3.36585	2.56545	0.47546
H	-1.38789	3.99678	0.47844
H	-4.24455	-0.12154	0.45273
H	-3.49452	-2.44479	0.42381
H	3.52096	-2.45771	0.38146
H	4.27985	-0.13723	0.4012

33			
$C_{20}H_{10}$-H_2O-in			
C	-0.704502	-0.994233	-0.90684
C	0.719692	-0.996743	-0.915195
C	1.162279	0.357891	-0.901336
C	0.011801	1.198569	-0.888083
C	-1.14186	0.362077	-0.887329
C	2.387866	0.747504	-0.335513
C	2.462803	2.141417	0.054598
C	1.326584	2.97069	0.06591
C	0.01761	2.477505	-0.309469
C	-1.456985	-2.038207	-0.346069
C	-0.694024	-3.21642	0.010863
C	0.712005	-3.218905	0.002614
C	1.474941	-2.043436	-0.363389
C	-2.359097	0.756023	-0.306635
C	-2.424174	2.150136	0.084549
C	-1.284885	2.975321	0.081993
C	-3.235004	-0.335932	0.068859
C	-2.802269	-1.675086	0.048878
C	2.826074	-1.685159	0.015736
C	3.26403	-0.347584	0.0301
H	3.402048	2.543058	0.451911
H	1.428231	3.982991	0.47344
H	-1.211845	-4.099797	0.401591
H	1.231241	-4.104149	0.387196
H	-3.357006	2.555099	0.49342
H	-1.377862	3.987904	0.490894
H	-4.227685	-0.117755	0.479176
H	-3.476297	-2.442693	0.446138
H	3.501895	-2.455157	0.405261
H	4.262281	-0.132999	0.428648
O	0.028469	0.004128	2.19896
H	-0.726412	0.104237	1.5992
H	0.788098	0.087483	1.602662

33			
$C_{20}H_{10}$-H_2O-out			
C	-0.911942	0.826797	0.279451
C	0.481849	1.115909	0.2789
C	1.187392	-0.120673	0.292902

C	0.229455	-1.173185	0.300405
C	-1.06759	-0.588455	0.292604
C	2.472626	-0.265987	-0.249707
C	2.827149	-1.626714	-0.60093
C	1.878911	-2.667573	-0.595301
C	0.492891	-2.440675	-0.236892
C	-1.866351	1.691332	-0.275587
C	-1.353619	2.995206	-0.647733
C	0.024932	3.280949	-0.648196
C	1.013617	2.28821	-0.276209
C	-2.188086	-1.232524	-0.251908
C	-1.971866	-2.622008	-0.603678
C	-0.688255	-3.200172	-0.596745
C	-3.271216	-0.344895	-0.624642
C	-3.117456	1.05509	-0.635805
C	2.415124	2.202296	-0.634837
C	3.113534	0.979371	-0.622051
H	3.833374	-1.846209	-0.976198
H	2.189542	-3.651026	-0.966618
H	-2.039444	3.758352	-1.033274
H	0.350847	4.253914	-1.033685
H	-2.80753	-3.223303	-0.979856
H	-0.581774	-4.22607	-0.967846
H	-4.210629	-0.763992	-1.003375
H	-3.944052	1.662404	-1.022362
H	2.932284	3.088392	-1.020691
H	4.142802	0.968683	-0.998945
O	-0.017984	0.313621	3.477248
H	-0.775333	0.330699	2.874713
H	0.730445	0.391895	2.868469

Table S12: RI-MP2/aug-cc-pVTZ optimized Cartesian coordinates for H_2O, $C_{20}H_{10}$, $C_{20}H_{10}$-H_2O-in and $C_{20}H_{10}$-H_2O-out.

3			
H_2O			
O	0.02948	0.004072	2.189254
H	-0.726485	0.102787	1.603756
H	0.789607	0.08665	1.606656

30			
$C_{20}H_{10}$			
C	-0.697568	-0.98458	-0.87089
C	0.713994	-0.98718	-0.879432
C	1.152748	0.35444	-0.868021
C	0.012355	1.186209	-0.85243
C	-1.131206	0.358652	-0.854202
C	2.371925	0.741309	-0.326762
C	2.446126	2.126058	0.05154
C	1.32056	2.947014	0.066923
C	0.018079	2.458139	-0.294588
C	-1.447254	-2.022526	-0.332684
C	-0.687096	-3.191986	0.014711
C	0.706114	-3.19455	0.006277
C	1.46631	-2.027892	-0.35032
C	-2.342312	0.750003	-0.298238
C	-2.406816	2.135015	0.080894
C	-1.278122	2.951808	0.082643
C	-3.214565	-0.334919	0.059907
C	-2.786569	-1.660684	0.043434
C	2.811404	-1.671003	0.009557
C	3.244448	-0.346824	0.020828
H	3.378556	2.529448	0.432113
H	1.4267	3.953073	0.4588
H	-1.197835	-4.072264	0.390529
H	1.218124	-4.07671	0.375903
H	-3.333078	2.541844	0.4727
H	-1.3758	3.958241	0.475758
H	-4.204184	-0.121832	0.450076
H	-3.461996	-2.420841	0.421513
H	3.488544	-2.433656	0.379457
H	4.239485	-0.137386	0.399013

33			
$C_{20}H_{10}$-H_2O-in			
C	-0.697679	-0.986619	-0.901891
C	0.714285	-0.989224	-0.910465
C	1.153157	0.353682	-0.896431
C	0.012442	1.187035	-0.882521
C	-1.13139	0.357873	-0.882574
C	2.367832	0.739556	-0.337902
C	2.441174	2.12141	0.050612
C	1.316504	2.942225	0.062272
C	0.018305	2.454906	-0.311628
C	-1.443298	-2.021645	-0.348837
C	-0.685949	-3.189149	0.0061
C	0.7056	-3.191742	-0.002406
C	1.462843	-2.027004	-0.36655
C	-2.337679	0.748183	-0.309178
C	-2.401139	2.130252	0.080405
C	-1.273384	2.946945	0.078241
C	-3.20496	-0.335106	0.064595
C	-2.776333	-1.660497	0.044725
C	2.801952	-1.670732	0.010569
C	3.235662	-0.346927	0.025165
H	3.369833	2.517942	0.446835
H	1.416737	3.942843	0.468721
H	-1.198312	-4.062295	0.395424
H	1.21945	-4.066793	0.380629
H	-3.323413	2.530208	0.48796
H	-1.364968	3.947888	0.485936
H	-4.18643	-0.119239	0.473068
H	-3.442207	-2.419684	0.440801
H	3.469843	-2.432349	0.398497
H	4.222795	-0.134741	0.421724
O	0.026913	-0.002981	2.221874
H	-0.736255	0.122867	1.644687
H	0.776111	0.110688	1.624278

33			
$C_{20}H_{10}$-H_2O-out			
C	-0.907113	0.827532	0.265815
C	0.474927	1.11429	0.265712

C	1.174718	-0.111704	0.283425
C	0.225067	-1.155752	0.292652
C	-1.061246	-0.575818	0.282385
C	2.449239	-0.257506	-0.250909
C	2.799754	-1.607978	-0.595848
C	1.861384	-2.638486	-0.587772
C	0.486668	-2.413854	-0.233448
C	-1.852388	1.682339	-0.287185
C	-1.342688	2.973339	-0.66126
C	0.021792	3.256326	-0.660822
C	1.002547	2.274343	-0.286385
C	-2.171332	-1.216336	-0.254229
C	-1.955268	-2.594849	-0.599382
C	-0.684692	-3.167143	-0.58949
C	-3.243973	-0.336688	-0.629185
C	-3.091689	1.049005	-0.64486
C	2.392345	2.186894	-0.641474
C	3.083878	0.976615	-0.624393
H	3.794686	-1.825973	-0.969171
H	2.168808	-3.61168	-0.955443
H	-2.020332	3.726115	-1.049706
H	0.344455	4.216525	-1.048958
H	-2.781009	-3.190478	-0.97374
H	-0.579019	-4.182399	-0.956722
H	-4.17189	-0.75241	-1.007312
H	-3.908007	1.647971	-1.03429
H	2.903483	3.061562	-1.02939
H	4.101488	0.964766	-1.000092
O	-0.00365	0.289611	3.515592
H	-0.755243	0.271341	2.913194
H	0.747947	0.330138	2.914315

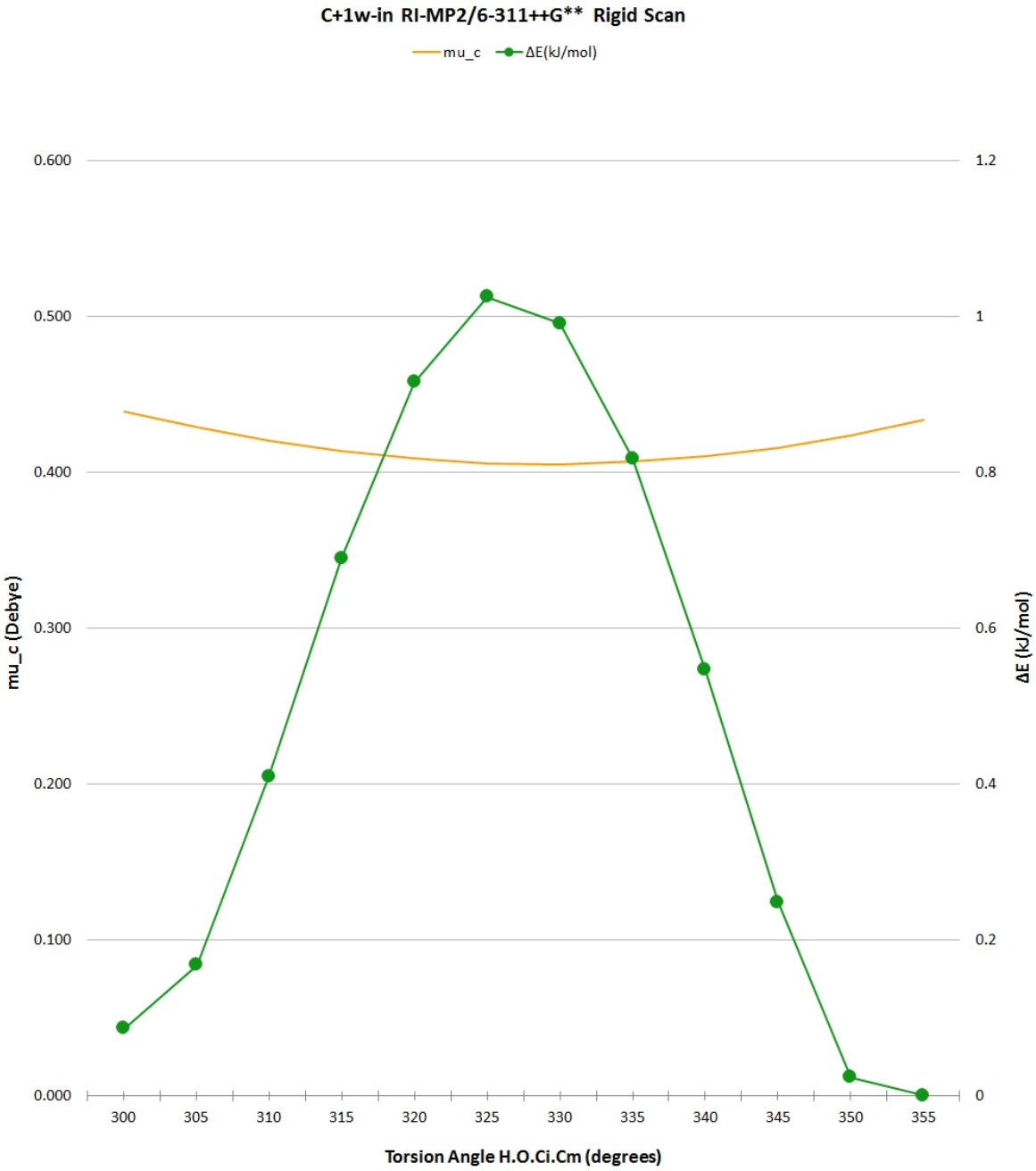

Figure S1: The variation of binding energy and of main dipole moment component for $C_{20}H_{10}$-H_2O-in on rotation of the water molecule around its C_2 axis, which is nearly coincident with the C_5 axis of corannulene. This rigid geometry scan covers one of the five identical barriers to rotation, and these are estimated to be significantly lower on allowance for full coordinate relaxation.