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

Electronic Supplementary Information for: Rotational spectra and semi-experimental structures of furonitrile and its water cluster

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1 Isotopologues of 2- and 3-furonitrile

Table S1: Experimental ground state rotational constants of the ^{13}C, ^{15}N, and ^{18}O-substituted isotopologues of 2- and 3-furonitrile.

				2-furonitrile			
Parameter	^{13}C7	^{13}C9	^{13}C4	^{13}C3	^{13}C2	^{15}N	^{18}O
A	9137.5856(6)	9154.0081(6)	8991.4613(6)	9218.5138(8)	9220.0281(6)	9220.2631(5)	8866.490(1)
B	2004.8248(1)	2000.4705(1)	2026.6066(1)	2028.7908(1)	2006.6066(1)	1966.4099(1)	2026.3543(2)
C	1643.5398(1)	1641.1426(1)	1653.2629(1)	1662.2688(1)	1647.3915(1)	1620.1953(1)	1648.8163(1)
Lines	56	56	56	50	56	17	47
rms	1.6	1.7	1.6	1.3	1.5	0.6	1.3
				3-furonitrile			
Parameter	^{13}C7	^{13}C4	^{13}C3	^{13}C5	^{13}C2	^{15}N	^{18}O
A	9218.0154(8)	9068.0384(8)	9296.84(3)	9106.2285(8)	9296.5039(8)	9296.561(2)	9149.64(4)
B	1916.7287(1)	1938.2414(1)	1939.5560(1)	1938.5122(1)	1917.8572(1)	1880.0222(2)	1894.4775(1)
C	1586.1899(1)	1596.29798(9)	1604.1607(1)	1597.66410(9)	1589.27546(9)	1563.1955(2)	1568.9249(1)
No. of lines	77	77	66	77	76	18	54
rms error	2.6	1.9	1.4	2.2	1.9	1.1	2.4

Notes: Rotational constants are given in MHz, while the rms error is expressed in kHz. Values in parentheses are one times the standard error in unit of the last quoted digits. Centrifugal distortion terms and nuclear quadrupole coupling constants used in the fit were kept fixed to the values obtained for the corresponding main species (see Table 1 of the main text).

2 Furonitrile-water complexes

2.1 Conformers found within 1000 cm^{-1}

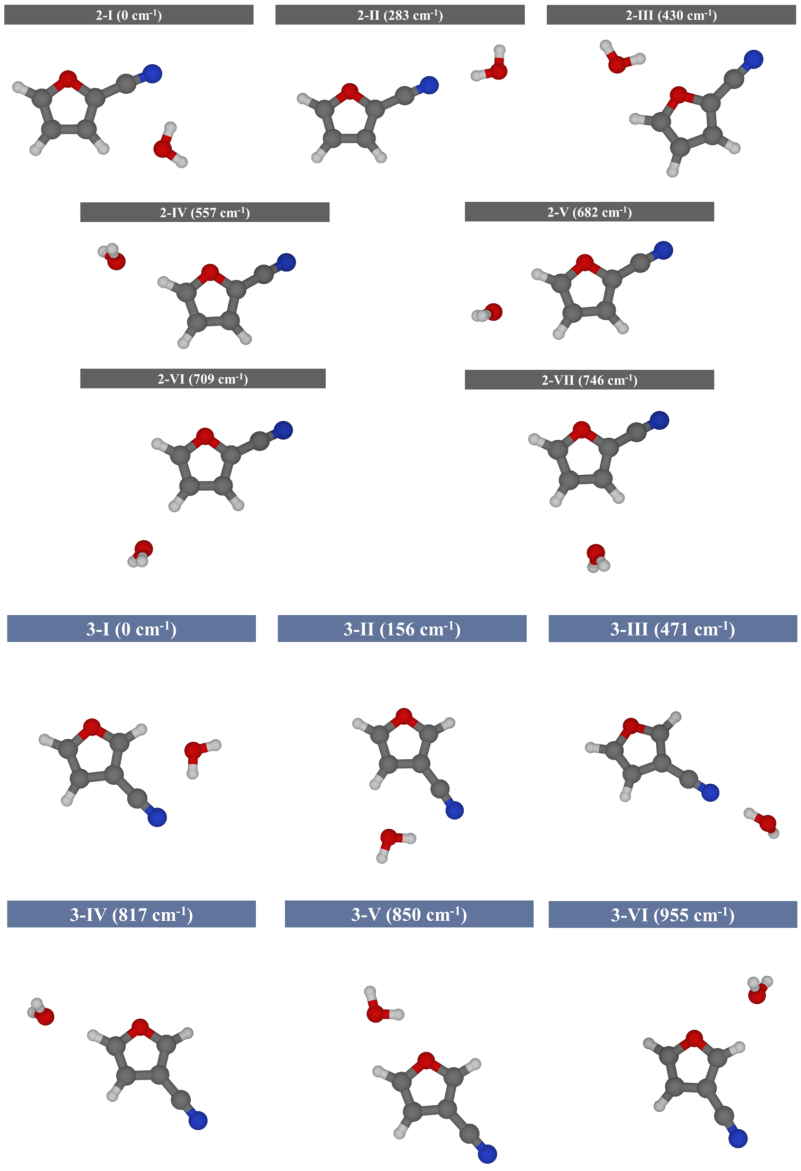

Figure S1: Geometry of the thirteen isomers of the furonitrile-water complex lying within 1000 cm^{-1}. Energies are calculated at the B3LYP-D3BJ/6-311G++(d,p) level of theory.

2.2 Results of the spectral analysis

Table S2: Spectroscopic constants derived for several isotopologues of conformer **2-I**.

Parameter	Unit	$H_2{}^{18}O$		D_2O	HDO	DOH
		0	1			
A	MHz	3383.6060(4)	3383.1436(4)	3408.163(2)	3399.5116(5)	3473.019(3)
B	MHz	1267.72874(9)	1267.68371(9)	1248.1882(2)	1277.6849(2)	1289.8220(4)
C	MHz	922.38944(7)	922.39917(7)	914.0152(3)	929.0429(2)	940.8077(2)
D_J	kHz	0.5603		0.537(3)	0.549(2)	0.5603
D_{JK}	kHz	-1.409		-1.409	-1.409	-1.409
D_K	kHz	13.27		13.27	13.27	13.27
d_1	kHz	-0.1957		-0.1957	-0.1957	-0.1957
d_2	kHz	-0.0204		-0.0204	-0.0204	-0.0204
$3/2 \times \chi_{aa}$	MHz	-3.12(1)		-3.52(8)	-3.21(2)	-2.7(1)
$(\chi_{bb} - \chi_{cc})/4$	MHz	-0.243(2)		-0.238(7)	-0.235(3)	-0.1975
No. of lines		155		45	67	25
rms error	kHz	3.1		3.6	3.3	3.9

Notes: Numbers in parentheses represent the standard error in unit of the last quoted digit. Parameters without error are kept fixed to the corresponding parent species values.

Table S3: Spectroscopic constants derived for several isotopologues of conformer **2-II**.

Parameter	Unit	$H_2{}^{18}O$		D_2O	HDO	DOH
		0	1			
A	MHz	9013.(1)	9004.4(9)	8892.(1)	8509(55)	9021.6(5)
B	MHz	620.8781(2)	620.9090(2)	625.5731(2)	637.32(1)	647.0573(1)
C	MHz	580.9773(2)	581.0107(2)	584.9619(2)	595.17(1)	603.9141(1)
D_J	kHz	0.139(1)		0.1257(8)	0.1482	0.1314(5)
D_{JK}	kHz	9.22(2)		8.03(4)	10.185	9.61(2)
d_1	kHz	-0.0169		-0.0169	-0.0169	-0.0169
d_2	kHz	-0.0069		-0.0069	-0.0069	-0.0069
$3/2 \times \chi_{aa}$	MHz	-5.98		-5.98	-5.98	-5.98
$(\chi_{bb} - \chi_{cc})/4$	MHz	0.26		0.26	0.26	0.26
No. of lines		78		51	31	57
rms error	kHz	3.4		3.1	318	2.7

Notes: Numbers in parentheses represent the standard error in unit of the last quoted digit. Parameters without error are kept fixed to the corresponding parent species values.

Table S4: Spectroscopic constants derived for several isotopologues of conformer **3-I**.

Parameter	Unit	$H_2{}^{18}O$		D_2O		HDO	DOH
		0	1	0	1		
A	MHz	3299.1586(3)	3298.9285(3)	3318.730(2)	3318.691(2)	3313.237(2)	3392.638(2)
B	MHz	1286.9907(1)	1286.9760(1)	1267.0764(3)	1267.0768(3)	1295.8606(2)	1306.1382(4)
C	MHz	925.96986(7)	925.97432(7)	917.3233(2)	917.3234(2)	931.8422(1)	943.2819(2)
D_J	kHz	0.419		0.409(3)		0.419	0.419
D_{JK}	kHz	-0.54		-0.54		-0.54	-0.54
D_K	kHz	9.97		9.97		9.97	9.97
d_1	kHz	-0.144		-0.144		-0.144	-0.144
d_2	kHz	-0.016		-0.016		-0.016	-0.016
$3/2 \times \chi_{aa}$	MHz	-3.824(9)		-4.01(3)		-3.96(2)	-4.00(5)
$(\chi_{bb} - \chi_{cc})/4$	MHz	-0.208(1)		-0.165		-0.172(8)	-0.165
$\lvert\chi_{ab}\rvert$	MHz	2.1		2.1		2.1	2.1
No. of lines		116		98		58	47
rms error	kHz	2.8		4.8		5.0	5.0

Notes: Numbers in parentheses represent the standard error in unit of the last quoted digit. Parameters without error are kept fixed to the corresponding parent species values.

Table S5: Spectroscopic constants derived for several isotopologues of conformer **3-II**.

Parameter	Unit	$H_2{}^{18}O$		D_2O	HDO	DOH
		0	1			
A	MHz	3392.98(2)	3392.92(2)	3416.689(3)	3409.8389(6)	3485.958(4)
B	MHz	1231.8853(4)	1231.8641(4)	1213.7438(4)	1241.2381(3)	1252.6256(4)
C	MHz	904.0070(3)	904.0130(3)	896.0291(3)	910.4031(1)	921.8110(2)
D_J	kHz	0.494		0.494	0.494	0.494
D_{JK}	kHz	-1.10		-1.10	-1.10	-1.10
D_K	kHz	11.79		11.79	11.79	9.8(8)
d_1	kHz	-0.169		-0.169	-0.169	-0.169
d_2	kHz	-0.015		-0.015	-0.015	-0.015
$3/2 \times \chi_{aa}$	MHz	-3.68(4)		-3.940	-3.86(3)	-3.940
$(\chi_{bb} - \chi_{cc})/4$	MHz	-0.204		-0.204	-0.204	-0.204
$\lvert\chi_{ab}\rvert$	MHz	2.6		2.6	2.6	2.6
No. of lines		53		37	46	34
rms error	kHz	4.5		6.1	4.6	4.5

Notes: Numbers in parentheses represent the standard error in unit of the last quoted digit. Parameters without error are kept fixed to the corresponding parent species values.

2.3 Calculations relevant for the structure determination

Table S6: revDSD equilibrium structures for 2- and 3-furonitrile.

2-furonitrile		**3-furonitrile**	
Parameter	revDSD	Parameter	revDSD
r(N1C2)	1.16333	r(N1C2)	1.16284
r(C2C3)	1.41801	r(C2C3)	1.42190
r(C3C4)	1.3656	r(C3C4)	1.43927
r(C3O5)	1.36492	r(C3C5)	1.36568
r(H6C4)	1.07754	r(C4H6)	1.07700
r(C7O5)	1.35786	r(C4C7)	1.35553
r(H8C7)	1.0765	r(C7H8)	1.07600
r(C9C7)	1.36158	r(C7O9)	1.36588
r(C9H10)	1.07732	r(H10C5)	1.07636
∠(C3C2N1)	181.40185	∠(N1C2C3)	179.30149
∠(C4C2C2)	131.80329	∠(C4C3C2)	127.4006
∠(O5C3C2)	110.69814	∠(C5C3C2)	126.27422
∠(H6C4C3)	125.88758	∠(H6C4C3)	127.0532
∠(C7O5C3)	106.11755	∠(C7C4C3)	105.57092
∠(H8C7O5)	115.52447	∠(H8C7C4)	133.4647
∠(C9C7O5)	111.09916	∠(O9C7C4)	110.70528
∠(H10C9C4)	127.49681	∠(H10C5O9)	117.03

Notes: Bond lengths are given in Å, angles in degrees.

Table S7: revDSD equilibrium structures for the **2-I** and **2-II** complexes togheter with the templated sturctures.

	2-I			**2-II**	
Parameter	revDSD	revDSD+TM	Parameter	revDSD	revDSD+TM
r(N1C2)	1.16384	1.15917	r(N1C2)	1.16174	1.15707
r(C2C3)	1.41672	1.41598	r(C2C3)	1.41685	1.41685
$\angle$(C3C2N1)	183.49949	182.38603	$\angle$(C3C2N1)	181.5222	181.5222
r(C3C4)	1.36548	1.36214	r(C3C4)	1.36583	1.36583
$\angle$(C4C3C2)	130.83427	130.09349	$\angle$(C4C3C2)	131.67932	131.67932
r(C3O5)	1.36533	1.35946	r(C3O5)	1.36441	1.36441
$\angle$(O5C3C4)	111.11122	111.34571	$\angle$(O5C3C4)	110.81174	110.81174
r(H6C4)	1.07814	1.07526	r(H6C4)	1.07761	1.07761
$\angle$(H6C4C3)	125.00262	125.04152	$\angle$(H6C4C3)	125.93699	125.93699
r(C7O5)	1.35819	1.35479	r(C7O5)	1.35756	1.35756
$\angle$(C7O5C3)	106.04441	106.16774	$\angle$(C7O5C3)	106.25678	106.25678
r(H8C7)	1.07657	1.07380	r(H8C7)	1.07654	1.07654
$\angle$(H8C7O5)	115.55416	115.68143	$\angle$(H8C7O5)	115.58702	115.58702
r(C9C7)	1.36221	1.35779	r(C9C7)	1.36193	1.36193
$\angle$(C9C7O5)	110.99726	110.96812	$\angle$(C9C7O5)	110.98042	110.98042
r(C9H10)	1.07742	1.07449	r(C9H10)	1.07727	1.07727
$\angle$(H10C9C4)	127.39163	127.36443	$\angle$(H10C9C4)	127.41562	127.41562
$r(\mathrm{H}_a \cdots \mathrm{N})$	2.36168	2.36168	$r(\mathrm{H}_a \cdots \mathrm{N1})$	2.08165	2.08165
$r(\mathrm{OH}_a)$	0.96423	0.96423	$r(\mathrm{OH}_a)$	0.96657	0.96657
$r(\mathrm{H}_b\mathrm{O})$	0.96071	0.95693	$r(\mathrm{H}_b\mathrm{O})$	0.96019	0.95641
$\angle(\mathrm{CN}\cdots\mathrm{H})$	87.32051	87.32051	$\angle(\mathrm{C2N1}\cdots\mathrm{H}_a)$	171.00147	171.00147
$\angle(\mathrm{OH}_a \cdots \mathrm{N})$	142.84843	142.84843	$\angle(\mathrm{OH}_a \cdots \mathrm{N1})$	176.78183	176.78183
$\angle(\mathrm{H}_a\mathrm{OH}_b)$	104.9118	104.98389	$\angle(\mathrm{H}_a\mathrm{OH}_b)$	104.35183	104.42392
			$\theta(\mathrm{OH}_a \cdots \mathrm{N1C2})$	4.604	4.604
			$\theta(\mathrm{H}_b\mathrm{OH}_a \cdots \mathrm{N1})$	173.839	173.839

Notes: Bond lengths are given in Å, angles in degrees. If not otherwise stated, all dihedral angles are fixed to 0° or 180°.

Table S8: RevDSD equilibrium structures for the **3-I** and **3-II** complexes together with the templated structures.

	3-I			**3-II**	
Parameter	revDSD	revDSD+TM	Parameter	revDSD	revDSD+TM
r(C5O9)	1.34996	1.34712	r(C5O9)	1.34926	1.34642
r(O9C7)	1.36645	1.36342	r(O9C7)	1.36881	1.36578
$\angle$(C7O9C5)	107.43189	107.32463	$\angle$(C7O9C5)	107.22199	107.11473
r(C5C3)	1.36685	1.36196	r(C5C3)	1.36577	1.36088
$\angle$(C3C5O9)	109.84406	109.90552	$\angle$(C3C5O9)	109.99146	110.05292
r(C7C4)	1.35561	1.35166	r(C7C4)	1.35494	1.35100
$\angle$(C4C7O9)	110.71156	110.81807	$\angle$(C4C7O9)	110.86218	110.96869
r(C5H10)	1.07692	1.07425	r(C5H10)	1.07643	1.07376
$\angle$(H10C5O9)	118.28938	118.36613	$\angle$(H10C5O9)	117.06306	117.13981
r(H8C7)	1.07598	1.07315	r(H8C7)	1.07597	1.07314
$\angle$(H8C7O9)	115.86981	115.87887	$\angle$(H8C7O9)	115.64906	115.65812
r(H6C4)	1.07701	1.07416	r(H6C4)	1.07766	1.07481
$\angle$(H6C4C7)	127.33004	127.39629	$\angle$(H6C4C7)	128.74889	128.81514
r(C2C3)	1.41990	1.41904	r(C2C3)	1.42009	1.41923
$\angle$(C3C2C5)	125.12271	125.08344	$\angle$(C3C2C5)	126.92883	126.88956
r(N1C2)	1.16350	1.15879	r(N1C2)	1.16337	1.06696
$\angle$(N1C2C3)	178.42084	178.30470	$\angle$(N1C2C3)	182.76276	182.87889
r(N1C2)	1.16350	1.15879	r(N1C2)	1.16337	1.06696
r($H_a \cdots$ N1)	2.33705	2.33705	r($H_a \cdots$N1)	2.31366	2.31366
$\angle$(C2N1$\cdots H_a$)	86.08448	86.08448	$\angle$(C2N1$\cdots H_a$)	0.96474	0.96474
r(OH_a)	0.96479	0.96479	r(OH_a)	0.96064	0.96064
$\angle$($OH_a \cdots$N1)	144.10859	144.10859	$\angle$($OH_a \cdots$N1)	88.15559	88.15559
r(H_bO)	0.96062	0.95683	r(H_bO)	145.64094	145.63715
$\angle$(H_aOH_b)	105.04544	105.11753	$\angle$(H_aOH_b)	104.94176	105.01385

Notes: Bond lengths are given in Å, angles in degrees. If not otherwise stated, all dihedral angles are fixed to 0° or 180°.