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

Supplementary Information for

Modulation of π character upon complexation captured by molecular rotation spectra

Yang Zheng,[a,b] Qin Yang,[b] Sven Herbers,[c] Wanying Cheng,[a] Zhongming Jiang,[b] Hao Wang,[a] Xuefang Xu,[a] Julien Bloino*[b] and Qian Gou*[a,d]

[a] *School of Chemistry and Chemical Engineering, Chongqing University, 401331 Chongqing, China*

[b] *Scuola Normale Superiore di Pisa, Piazza dei Cavalieri 7, 56125 Pisa, Italy*

[c] *Institute for Molecules and Materials, Radboud University, Heijendaalseweg 135, NL-6525 AJ Nijmegen, Netherlands*

[d] *Chongqing Key Laboratory of Theoretical and Computational Chemistry, Chongqing University, 401331 Chongqing, China*

* Julien Bloino: julien.bloino@sns.it

* Qian Gou: qian.gou@cqu.edu.cn;

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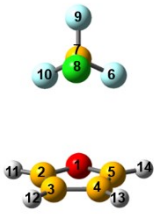
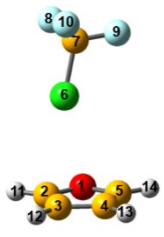
1. Table S1. Equilibrium spectroscopic parameters of the nine isomers of furan–CF_3Cl calculated at the rDSD-PBEP86-D3(BJ)/jun-cc-pVTZ level of theory.

	I	II	III	IV	V
A_e, B_e, C_e [MHz]	2241, 642, 618	2083, 659, 620	2511, 465, 463	2553, 448, 447	2099, 656, 601
χ_{aa} [MHz]	8.68	9.69	-65.06	-64.61	36.02
$(\chi_{bb}-\chi_{cc})$ [MHz]	-81.76	-82.90	-9.01	-9.34	-105.62
$\lvert\chi_{ab}\rvert$ [MHz]	48.74	48.28	30.49	31.10	10.25
$\lvert\mu_a\rvert$, $\lvert\mu_b\rvert$, $\lvert\mu_c\rvert$ [D]	0.8, 0.8, 0.0	0.2, 0.3, 0.0	0.9, 0.5, 0.5	0.9, 0.6, 0.0	0.5, 0.1, 0.4
ΔE, ΔE_0 [kJ mol^{-1}]	0, 0	0.28, 0.17	0.76, 0.40	1.80, 1.26	1.63, 1.53

	VI	VII	VIII	IX
A_e, B_e, C_e [MHz]	1966, 672, 617	1985, 663, 615	2710, 546, 541	2524, 556, 553
χ_{aa} [MHz]	37.16	34.25	-63.48	-63.50
$(\chi_{bb}-\chi_{cc})$ [MHz]	-109.82	-106.69	9.50	-8.60
$\lvert\chi_{ab}\rvert$ [MHz]	1.16	17.13	0.0	30.19
$\lvert\mu_a\rvert$, $\lvert\mu_b\rvert$, $\lvert\mu_c\rvert$ [D]	0.0, 1.0, 0.2	0.0, 0.3, 0.6	0.1, 0.0, 0.7	0.3, 0.4, 0.4
ΔE, ΔE_0 [kJ mol^{-1}]	1.77, 1.58	1.88, 1.72	2.71, 2.47	2.92, 2.64

2. Table S2. Equilibrium geometries of the two observed isomers of furan–CF_3Cl.

Isomers	Cartesian coordinates (Å)				
I 	1	O	1.584038	1.071822	-0.000080
	2	C	2.111918	0.453411	-1.093408
	3	C	2.961299	-0.538373	-0.717583
	4	C	2.961182	-0.538336	0.717730
	5	C	2.111825	0.453540	1.093366
	6	F	-1.393831	0.867135	1.078213
	7	C	-1.688612	0.153587	0.000000
	8	Cl	-0.790872	-1.358641	-0.000010
	9	F	-2.994966	-0.087901	0.000040
	10	F	-1.393891	0.867115	-1.078241
	11	H	1.786899	0.830310	-2.047880
	12	H	3.516722	-1.186447	-1.375585
	13	H	3.516503	-1.186373	1.375856
	14	H	1.786722	0.830549	2.047765
III 	1	O	-2.703414	-0.821666	-0.843165
	2	C	-2.756387	0.532503	-0.977699
	3	C	-2.880740	1.129139	0.237952
	4	C	-2.907276	0.065307	1.200965
	5	C	-2.795823	-1.087354	0.489904
	6	Cl	0.474079	0.446666	-0.030024
	7	C	2.158057	-0.054090	0.013918
	8	F	2.638448	-0.176821	-1.217808
	9	F	2.277626	-1.223945	0.630651
	10	F	2.892009	0.841277	0.664426
	11	H	-2.696964	0.907518	-1.985016
	12	H	-2.947057	2.188481	0.425173
	13	H	-2.993445	0.149359	2.271822
	14	H	-2.765510	-2.127718	0.764263

3. Table S3. Relative intensity measurements in arbitrary units of the two observed isomers of furan–CF_3Cl in Helium.

Transitions	Isomers	Frequencies/MHz	Intensities
$8_{1\,7}\leftarrow7_{1\,6}$	I	9964.837	0.013
	III	7258.676	0.008
$8_{1\,8}\leftarrow7_{1\,7}$	I	9782.272	0.019
	III	7243.972	0.0063
$9_{1\,8}\leftarrow8_{1\,7}$	I	11208.52	0.0089
	III	8165.74	0.0048
$9_{1\,9}\leftarrow8_{1\,8}$	I	11003.39	0.0058
	III	8149.219	0.0049
$10_{1\,9}\leftarrow9_{1\,8}$	I	12451.46	0.0048
	III	9072.751	0.0055
$10_{1\,10}\leftarrow9_{1\,9}$	I	12223.97	0.0031
	III	9054.416	0.0041
$11_{1\,10}\leftarrow10_{1\,9}$	I	13693.55	0.0052
	III	9979.705	0.0053
$11_{1\,11}\leftarrow10_{1\,10}$	I	13443.98	0.0031
	III	9959.578	0.0028
$12_{1\,12}\leftarrow11_{1\,11}$	I	14663.39	0.0031
	III	10864.67	0.0021
$12_{1\,11}\leftarrow11_{1\,10}$	I	14934.67	0.0015
	III	10886.58	0.0028

The measured intensities were used to evaluate the experimental ratio of relative abundance of the two observed isomers according to the following expression:

$$\frac{N_1}{N_2} = (I_I \mu_{a,III} \gamma_{III} \nu_{III}^2 \omega_{III})/(I_{III} \mu_{a,I} \gamma_I \nu_I^2 \omega_I)$$

where I denotes the experimental peak intensity, μ_a denotes the value of dipole moment along principal a-axis, γ represents the predicted line strength, ν represents the frequency of the corresponding transition, and ω is the conformational degeneracy.

4. Table S4. Experimental spectroscopic parameters of the two observed isomers of furan–CF_3Cl.

	Isomer I					Isomer III
	^{35}Cl	^{37}Cl	Cα	Cβ	C_{CF3Cl}	^{35}Cl
A [MHz]	2248.91(1)[a]	2213.61(1)	2235.4(1)	2241.1(2)	2248.7(2)	[2447][b]
B [MHz]	628.91(1)	627.92(1)	624.48(1)	621.70(1)	626.64(1)	454.14(1)
C [MHz]	606.00(1)	602.48(1)	602.59(1)	599.45(1)	603.88(1)	452.29(1)
χ_{aa} [MHz]	9.66(1)	7.91(1)	[9.663][c]	[9.663]	[9.663]	-71.5 (5)
$(\chi_{bb}-\chi_{cc})$ [MHz]	-86.06(1)	-68.14(1)	[-86.056]	[-86.056]	[-86.056]	--
$\lvert\chi_{ab}\rvert$ [MHz]	50.89(3)	39.93(2)	[50.89]	[50.89]	[50.89]	--
D_J [kHz]	0.44(1)	[0.4393]	[0.4393]	[0.4393]	[0.4393]	0.27(1)
D_{JK} [kHz]	-0.18(1)	[-0.190]	[-0.190]	[-0.190]	[-0.190]	-15.2(1)
D_K [kHz]	1.94(1)	[1.92]	[1.92]	[1.92]	[1.92]	--
d_1 [kHz]	-0.031(1)	[-0.0312]	[-0.0312]	[-0.0312]	[-0.0312]	-0.019(1)
d_2 [kHz]	0.0037(1)	[0.0035]	[0.0035]	[0.0035]	[0.0035]	--
σ[d] [kHz]	3.5	3.9	2.0	3.7	3.3	6.0
$N_{transitions}/N_{lines}$[e]	88/350	54/215	11/43	11/43	9/28	25/100

[a] Uncertainties (in parentheses) are 1σ uncertainties expressed in units of the last digit. [b] The value of rotational constant A for isomer III was fixed at the calculated value which is based on the deviation pattern (0.7%) of isomer I (see the main text). [c] Values fixed at the normal species. [d] Root mean square deviation of the fit. [e] Number of transitions/lines in the fit.

5. Measured transition frequencies of the observed isomers of furan–CF_3Cl.

Table S5. Experimental transition frequencies (ν_{obs}, MHz) and observed minus calculated values ($\Delta\nu$, kHz) of isomer I of furan–$CF_3{}^{35}Cl$ and furan–$CF_3{}^{37}Cl$.

								Isomer I ^{35}Cl		Isomer I ^{37}Cl	
J'	K_a'	K_c'	J''	K_a''	K_c''	F'+1/2	F''+1/2	ν_{obs}/MHz	$\Delta\nu$/kHz	ν_{obs}/MHz	$\Delta\nu$/kHz
5	0	5	4	0	4	7	6	6169.5998	0.0		
						6	5	6169.1352	3.3		
						5	4	6169.4301	0.8		
						4	3	6169.6831	-3.3		
5	1	5	4	1	4	7	6	6116.1842	0.9		
						6	5	6116.8971	-4.6		
						5	4	6115.7712	-3.6		
						4	3	6116.8451	0.0		
5	2	4	4	2	3	7	6	6173.4664	2.9		
						6	5	6173.9923	4.5		
						5	4	6173.7761	1.6		
						4	3	6173.5130	-0.4		
5	2	3	4	2	2	7	6	6178.2695	0.3		
						6	5	6179.0428	-1.6		
						5	4	6178.9746	10.6		
						4	3	6178.1182	3.9		
6	0	6	5	0	5	8	7	7400.7985	-0.9	7371.5427	-3.3
						7	6	7400.4997	1.8	7371.2622	0.9
						6	5	7400.5342	-1.3	7371.2994	-1.4
						5	4	7401.1788	-1.0		
6	1	6	5	1	5	8	7	7338.6130	-2.1	7303.4398	-7.2
						7	6	7338.5497	0.1	7303.3872	-4.9
						6	5	7338.1795	0.4	7303.0862	-10.3
						5	4	7338.1795	-3.0	7303.1250	8.6
6	1	5	5	1	4	8	7	7475.6081	-1.2	7455.6363	-1.1
						7	6	7475.5370	-2.9	7455.5740	-2.0
						6	5	7476.1490	-3.9	7456.0602	-0.9
						5	4	7476.1703	1.9	7456.0887	-2.8
6	2	5	5	2	4	8	7	7407.9024	-0.3	7380.5474	-3.8
						7	6	7408.0250	-3.5	7380.6445	-13.8
						6	5	7408.1356	4.7	7380.7264	-3.3
						5	4	7407.8114	-3.3	7380.4839	-7.6
6	2	4	5	2	3	8	7	7416.0962	0.6	7390.9410	1.2
						7	6	7416.6921	-1.2	7391.4565	-3.3
						6	5	7416.7028	1.2	7391.4565	-4.4
						5	4	7415.9665	-9.2	7390.8468	5.9
6	3	4	5	3	3	8	7	7409.8817	-3.9		
						7	6	7410.7283	-4.6		
						6	5	7410.3563	-2.8		
						5	4	7409.9194	-2.7		
6	3	3	5	3	2	8	7	7409.9795	3.4		
						7	6	7410.8328	4.7		
						6	5	7410.4453	-13.1		

						5	4	7410.0052	-0.2		
7	0	7	6	0	6	9	8	8630.5227	1.2	8595.4747	-2.1
						8	7	8629.9724	0.2	8594.9958	-1.2
						7	6	8630.1313	-0.4	8595.1216	-3.3
						6	5	8630.6102	-1.2	8595.5655	-1.5
7	1	7	6	1	6	9	8	8560.6645	0.9	8519.4231	-4.1
						8	7	8560.5712	-0.9	8519.3454	-0.4
						7	6	8560.2989	-1.7	8519.1348	-0.1
						6	5	8560.3714	0.8	8519.2018	-1.1
7	1	6	6	1	5	9	8	8720.5083	3.3	8696.9289	-0.4
						8	7	8720.3931	-4.4	8696.8298	-2.0
						7	6	8720.8392	-1.6	8697.1807	-4.4
						6	5	8720.9215	-0.1	8697.2652	-1.2
7	2	6	6	2	5	9	8	8641.8198	0.7	8609.7497	-4.3
						8	7	8642.0825	-1.2	8609.9179	-4.4
						7	6	8641.9593	1.2	8609.8532	-4.9
						6	5	8642.1032	9.8	8609.9179	-5.5
7	2	5	6	2	4	9	8	8655.0059	2.9	8626.3997	-0.6
						8	7	8655.7874	-0.6	8627.0333	-1.2
						7	6	8655.6009	0.2	8626.9144	-0.9
						6	5	8655.2223	0.7	8626.5215	-0.6
7	3	5	6	3	4	9	8	8645.5509	4.0	8614.4161	-5.1
						8	7	8645.9121	1.0	8614.7473	-6.6
						7	6	8645.9730	1.6	8614.7579	-4.4
						6	5	8645.3835	-9.1	8614.3241	-3.6
7	3	4	6	3	3	9	8	8645.7325	-0.4	8614.6933	-2.7
						8	7	8646.1201	0.2	8615.0448	-3.4
						7	6	8646.1690	0.3	8615.0448	-4.6
						6	5	8645.5837	0.0	8614.6009	-2.8
7	4	4	6	4	3	9	8	8644.6887	0.9		
						8	7	8645.3950	-7.3		
						7	6	8645.2764	2.4		
						6	5	8644.5144	3.6		
7	4	3	6	4	2	9	8	8644.6887	0.0		
						8	7	8645.3950	-8.5		
						7	6	8645.2766	1.5		
						6	5	8644.5144	2.6		
8	0	8	7	0	7	10	9	9858.5553	-1.8	9817.3342	2.1
						9	8	9857.9599	-1.9	9816.8014	-4.1
						8	7	9858.0823	-1.2	9816.9056	-1.4
						7	6	9858.6505	-5.7	9817.4202	0.0
8	1	8	7	1	7	10	9	9782.2799	8.4	9734.8767	1.9
						9	8	9782.1623	8.0	9734.7694	-1.2
						8	7	9781.9530	-4.4	9734.6174	0.4
						7	6	9782.0541	-5.9	9734.7115	-0.5
8	1	7	7	1	6	10	9	9964.8364	-1.1	9937.5333	-0.1
						9	8	9964.6942	-0.4	9937.4061	2.4
						8	7	9965.0323	-4.7	9937.6779	0.7
						7	6	9965.1640	5.0	9937.7918	-1.5
8	2	7	7	2	6	10	9	9875.3864	4.1	9838.5211	-4.3

						9	8	9875.3117	3.4	9838.4823	-7.4
						8	7	9875.4377	8.4	9838.5574	-1.9
						7	6	9875.2974	-0.2	9838.5064	5.4
8	2	6	7	2	5	10	9	9895.1547	3.6	9863.4194	-1.1
						9	8	9895.6732	1.1	9863.9130	2.9
						8	7	9895.7299	2.8	9863.9307	5.3
						7	6	9895.0164	-6.7	9863.3550	1.7
8	3	6	7	3	5	10	9	9880.9339	3.6	9845.5089	-2.3
						9	8	9881.2197	2.0	9845.7506	-4.7
						8	7	9881.2370	-3.8	9845.7664	-2.2
						7	6	9880.8637	-0.8	9845.4594	-3.2
8	3	5	7	3	4	10	9	9881.3149	0.3	9846.0639	-1.8
						9	8	9881.6333	2.0	9846.3367	-2.3
						8	7	9881.6481	3.7	9846.3367	-6.0
						7	6	9881.2528	1.7	9846.0160	-2.8
8	4	5	7	4	4	10	9	9880.0201	1.7	9844.5353	-5.7
						9	8	9880.3754	6.3	9844.6561	-6.1
						8	7	9880.4856	4.7	9844.9540	-5.3
						7	6	9879.7806	4.9	9844.1652	-0.3
8	4	4	7	4	3	10	9	9880.0201	-1.9	9844.5468	-5.4
						9	8	9880.3754	3.3	9844.6630	-4.6
						8	7	9880.4856	0.7	9844.9664	-5.2
						7	6	9879.7806	2.2	9844.1652	-4.8
9	0	9	8	0	8	11	10	11084.7259	0.0	11036.9126	3.7
						10	9	11084.0749	0.6	11036.3373	3.4
						9	8	11084.1763	-1.4	11036.4240	3.2
						8	7	11084.8194	2.8	11036.9919	3.9
9	1	9	8	1	8	11	10	11003.3909	2.6	10949.7380	5.1
						10	9	11003.2467	-2.5	10949.6149	4.8
						9	8	11003.1004	0.2	10949.4984	4.5
						8	7	11003.2259	-0.0	10949.6149	6.7
9	1	8	8	1	7	11	10	11208.5184	-2.2	11177.3389	2.1
						10	9	11208.3396	-1.6	11177.1737	0.0
						9	8	11208.6196	0.0	11177.3959	-1.0
						8	7	11208.7668	-4.3	11177.5395	0.6
9	2	8	8	2	7	11	10	11108.5358	0.9	11066.8015	-2.6
						10	9	11108.4823	-2.5	11066.7571	-2.1
						9	8	11108.5434	1.2	11066.8015	-0.7
						8	7	11108.5544	5.2	11066.8209	-1.9
9	2	7	8	2	6	11	10	11136.6648	-1.5	11102.1424	5.2
						10	9	11137.2648	0.3	11102.6701	5.2
						9	8	11137.2648	-0.3	11102.6630	3.6
						8	7	11136.6316	0.9	11102.1168	5.4
9	3	7	8	3	6	11	10	11116.6374	-1.5	11076.6263	-1.4
						10	9	11116.5272	-3.3	11076.6224	-0.9
						9	8	11116.8918	-1.7	11076.7899	-1.1
						8	7	11116.2348	3.2	11076.3484	0.0
9	3	6	8	3	5	11	10	11117.1594	-0.9	11077.7605	0.0
						10	9	11117.2850	9.7	11077.6823	-1.1
						9	8	11117.4360	1.9	11077.9858	-0.3

						8	7	11116.9452	1.4	11077.3647	0.0
10	0	10	9	0	9	12	11	12308.8868	0.5	12254.0738	8.7
						11	10	12308.1824	-0.9	12253.4568	8.2
						10	9	12308.2736	-0.3	12253.5327	8.2
						9	8	12308.9702	2.2	12254.1449	9.3
10	1	10	9	1	9	12	11	12223.9722	2.2	12163.9645	11.1
						11	10	12223.8060	-3.8	12163.8245	11.4
						10	9	12223.6986	1.7	12163.7363	11.3
						9	8	12223.8380	0.8	12163.8614	9.7
10	1	9	9	1	8	12	11	12451.4552	-2.7	12416.2159	1.7
						11	10	12451.0548	1.5	12416.1307	0.9
						10	9	12451.4749	3.2	12416.2159	3.9
						9	8	12451.4552	-1.4	12416.5224	3.5
10	2	9	9	2	8	12	11	12341.2257	-2.9	12294.5319	-0.4
						11	10	12341.1506	-2.5	12294.4616	-1.3
						10	9	12341.2009	4.6	12294.4970	-0.3
						9	8	12341.2582	7.6	12294.5530	-1.1
11	0	11	10	0	10	13	12	13530.9462	-1.3		
						12	11	13530.1988	-3.1		
						11	10	13530.2831	0.8		
						10	9	13531.0194	-1.3		
11	1	11	10	1	10	13	12	13443.9783	-0.9		
						12	11	13443.7540	-1.0		
						11	10	13443.7104	-3.2		
						10	9	13443.8079	-1.2		
11	1	10	10	1	9	13	12	13693.5423	-2.2		
						12	11	13693.5470	-3.9		
						11	10	13693.5113	4.3		
						10	9	13693.9855	2.1		
12	0	12	11	0	11	14	13	14750.8818	2.4		
						13	12	14750.0974	0.8		
						12	11	14750.1676	-5.6		
						11	10	14750.9381	-0.7		
12	1	12	11	1	11	14	13	14663.3860	0.9		
						13	12	14663.3036	1.6		
						12	11	14663.1248	-3.8		
						11	10	14663.4249	3.9		
12	1	11	11	1	10	14	13	14934.6679	0.8		
						13	12	14934.3933	-0.8		
						12	11	14934.5619	-1.8		
						11	10	14934.8084	-0.7		
2	2	1	1	1	0	4	3	7355.4259	3.0	7245.4282	2.1
						3	2	7343.5467	-0.3	7235.9759	2.3
						2	1	7362.5335	0.0	7250.9800	-2.5
						3	3	7353.0220	-6.5	7243.4616	1.3
2	2	0	1	1	1	4	3	7374.1421	2.6	7267.6716	2.5
						3	2	7383.7850	-1.3	7275.3003	2.4
						2	1	7363.8500	-1.7	7259.4981	2.5
						2	2	7385.4323	-1.1	7276.6330	-1.7
3	2	2	2	1	1	5	4	8568.7851	3.4	8454.1690	-1.3

						4	3	8556.3224	-4.2	8442.9344	-5.3
						3	2	8565.9899	-0.9	8442.7343	-3.4
						2	1	8576.6548	9.4	8457.7209	0.2
3	3	0	2	2	1	5	4	11862.2674	2.0	11683.5147	3.4
						4	3	11861.7047	-1.8	11683.0576	-0.4
						3	2	11861.3289	-6.4	11682.7540	-3.3
						2	1	11861.9354	14.6		
3	3	1	2	2	0	4	3	11861.3555	2.3	11682.6555	2.4
						3	2	11861.0938	-1.8	11682.4500	-2.5
						5	4	11862.0701	2.4	11683.2485	3.6
						2	1	11861.8265	3.2	11683.0576	2.3
4	1	4	3	0	3	6	5	6460.9075	6.3		
						5	4	6449.3787	3.1		
						4	3	6453.9094	5.9		
						3	2	6463.6946	1.7		
4	2	3	3	1	2	6	5	9769.0217	1.6		
						5	4	9757.3817	-1.0		
						4	3	9763.0165	-1.5		
						3	2	9774.4975	0.8		
5	1	5	4	0	4	7	6	7639.9369	0.3	7565.0222	-2.7
						6	5	7629.4570	1.2	7556.7544	-8.0
						5	4	7632.5107	0.2	7559.1677	-6.7
						4	3	7643.0925	-2.8	7567.4983	-2.6
5	2	4	4	1	3	7	6	10958.0820	1.8	10822.9045	-1.1
						6	5	10946.4667	-0.4	10813.8055	-3.8
						5	4	10950.7238	2.5	10817.1027	-6.1
						4	3	10961.6122	-3.0	10825.9242	-5.9
5	3	3	4	2	2	7	6	14330.0338	-1.1	14141.6510	0.0
						6	5	14328.7456	-1.4	14140.5705	-1.0
						5	4	14329.3325	-2.7	14141.0486	-0.4
						4	3	14330.3641	-3.6	14141.9547	2.5
5	3	2	4	2	3	7	6	14333.5504	3.8	14145.9596	-0.4
						6	5	14333.3613	0.8.	14145.5739	2.6
						5	4	14333.0609	-1.3	14145.7205	1.8
						4	3	14332.8400	0.7	14146.1312	0.1
6	0	6	5	1	5	8	7	5930.4612	-1.5		
						7	6	5937.4550	-0.6		
						6	5	5937.4550	0.7		
						5	4	5927.7699	-1.0		
6	1	6	5	0	5	8	7	8808.9507	-1.1		
						7	6	8798.8741	0.7	8722.6790	-6.4
						6	5	8801.2614	1.1	8714.7855	-3.8
						5	4	8811.58970	-1.7	8716.6460	-2.6
6	2	5	5	1	4	8	7	12135.7577	-0.3	8724.7648	-2.8
						7	6	12124.5095	-1.5		
						6	5	12127.8106	-1.5		
						5	4	12138.8337	-3.3		
6	3	4	5	2	3	8	7	15561.6531	1.5		
						7	6	15560.4345	-1.1		
						6	5	15560.7297	-0.8		

						5	4	15562.1773	1.6		
7	0	7	6	1	6	9	8	7222.3705	1.4	7244.3356	-1.8
						8	7	7231.5955	-1.1	7251.4700	0.9
						7	6	7229.4054	-1.6	7249.7778	0.6
						6	5	7220.1992	-0.6	7242.6522	-4.8
7	1	7	6	0	6	9	8	9968.8150	-0.9	9870.5649	-1.7
						8	7	9958.9438	-3.8	9862.8745	0.6
						7	6	9961.0226	-2.7	9864.4804	-2.3
						6	5	9970.7800	-2.1	9872.1080	-4.9
7	2	6	6	1	5	9	8	13301.9669	-0.8		
						8	7	13291.0510	-3.8		
						7	6	13293.6177	0.3		
						6	5	13304.7619	-0.1		
7	3	4	6	2	5	9	8	16807.7066	3.2		
						8	7	16807.7690	-1.8		
						7	6	16807.7865	2.4		
						6	5	16807.8126	5.1		
8	0	8	7	1	7	10	9	8520.2611	-1.5	8542.2434	1.1
						9	8	8528.9850	-1.3	8548.9297	0.9
						8	7	8527.1857	-4.3	8547.5507	1.4
						7	6	8518.4868	1.2	8540.8750	0.6
8	1	8	7	0	7	10	9	11120.5665	0.6	11009.9659	1.4
						9	8	11111.1291	-0.6	11002.6480	0.6
						8	7	11112.8495	-1.5	11003.9736	-1.1
						7	6	11122.2306	0.0	11011.2586	0.7
9	0	9	8	1	8	11	10	9822.7158	-1.3	9844.2813	4.9
						10	9	9830.9049	-1.4	9850.4960	4.0
						9	8	9829.4083	-2.0	9849.3563	3.2
						8	7	9821.2433	1.2	9843.1564	6.0
9	1	9	8	0	8	11	10	12265.3694	-0.6	12142.3725	7.1
						10	9	12256.4185	1.3	12135.4567	4.7
						9	8	12257.8658	-1.7	12136.5658	4.3
						8	7	12266.8041	3.6	12143.4482	2.4
7	3	4	7	2	5	8	8	8134.2187	-1.0	7963.7253	-3.5
						7	7	8134.7432	-3.4	7964.1478	-2.4
						9	9	8136.4206	1.4	7965.5998	-1.7
						6	6	8136.6804	-4.0	7965.8866	-3.2
6	3	3	6	2	4	7	7	8143.8850	-2.3	7975.7140	-1.1
						6	6	8144.1764	-0.8	7976.0179	1.7
						8	8	8145.6891	-0.1	7977.3066	0.7
						5	5	8146.3214	-0.8	7977.8067	-1.4
5	3	2	5	2	3	6	6	8149.7513	-1.3	7983.1260	2.5
						5	5	8150.4192	-1.1	7983.6801	2.2
						7	7	8151.8087	0.0	7984.8649	3.5
						4	4	8152.2900	-2.5	7985.2842	3.0
3	2	1	2	1	2	5	4	8631.4498	2.6	8523.6542	2.3
						4	4	8632.0631	0.4	8524.0914	0.7
						3	2	8634.0745	0.3	8525.8607	0.1
						2	2	8634.2543	-0.8	8528.7366	0.2
						3	3	8640.9512	-1.0	8531.2748	1.8

						4	3	8641.5817	-2.4	8531.6018	1.4
4	2	2	3	1	3	3	2	9897.8533	-0.6	9790.8797	0.2
						6	5	9902.5603	1.2	9794.6303	2.9
						4	3	9908.3630	-1.7	9799.2678	-0.7
						4	4	9912.6011	-3.3		
						5	4	9913.2066	-1.8		
5	2	3	4	1	4	4	3	11184.8061	0.0	11072.7498	-1.8
						7	6	11187.3991	2.5	11081.3247	2.3
						5	4	11195.0008	-0.1	11088.7862	-0.8
						6	5	11199.2679	-0.2	11093.5241	-0.2
8	4	4	8	3	5	9	9	11415.8355	-0.4		
						8	8	11416.2217	-0.1		
						7	7	11416.8960	-2.1		
9	4	6	9	3	7	8	8	11416.3760	1.4		
8	4	5	8	3	6	9	9	11416.5984	-0.3		
						7	7	11417.5928	-1.2		
						10	10	11417.6150	3.3		
7	4	3	7	3	4	8	8	11417.0933	-1.8		
						7	7	11417.3776	-3.6		
						9	9	11418.2066	0.8		
						6	6	11418.3710	0.1		
7	4	4	7	3	5	8	8	11417.4470	-0.3		
						7	7	11417.7281	2.7		
						9	9	11418.5219	-1.6		
						6	6	11418.6793	-3.6		
4	4	0	4	3	1	5	5	11417.7688	8.6		
						4	4	11418.6497	10.0		
						6	6	11420.3567	-1.9		
						3	3	11421.3002	0.3		
4	4	1	4	3	2	5	5	11417.7765	1.1		
						4	4	11418.6497	-1.9		
						6	6	11420.3750	3.2		
						3	3	11421.3098	0.9		
6	4	2	6	3	3	7	7	11417.8058	-5.7		
						6	6	11418.2737	-1.1		
						8	8	11419.2492	-0.6		
						5	5	11419.4411	-1.7		
6	4	3	6	3	4	7	7	11417.9528	-3.2		
						6	6	11418.4160	-6.7		
						8	8	11419.3802	-2.4		
						5	5	11419.5620	-2.8		
5	4	1	5	3	2	6	6	11418.0254	-1.0		
						5	5	11418.4423	18.0		
						7	7	11419.7499	-0.7		
						4	4	11420.3237	0.1		
5	4	2	5	3	3	6	6	11418.0840	7.6		
						5	5	11418.4921	17.9		
						7	7	11419.7888	-4.6		
						4	4	11420.3567	-5.8		
5	4	2	4	3	1	7	6	17594.5399	-1.8		

						6	5	17593.9088	-7.9	
						5	4	17594.0187	-4.5	
						4	3	17594.6752	-1.7	
5	4	1	4	3	2	7	6	17594.5544	-0.5	
						6	5	17593.9287	-3.2	
						5	4	17594.0347	-0.6	
						4	3	17594.6856	-0.4	

Table S6. Experimental transition frequencies (ν_{obs}, MHz) and observed minus calculated values ($\Delta\nu$, kHz) of the α ^{13}C isotopologue of isomer I of furan–CF_3Cl.

								Furan–CF_3Cl Cα	
J'	K_a'	K_c'	J''	K_a''	K_c''	F'+1/2	F''+1/2	ν_{obs}/MHz	$\Delta\nu$/kHz
6	0	6	5	0	5	8	7	7354.4540	-2.1
						7	6	7354.1693	-2.5
						6	5	7354.2055	-1.6
						5	4	7354.8358	1.0
6	1	6	5	1	5	8	7	7294.7935	-1.2
						7	6	7294.7317	-1.4
						6	5	7294.3608	-1.3
						5	4	7294.3608	-0.7
6	1	5	5	1	4	8	7	7425.7004	-3.1
						7	6	7425.6363	-2.3
						6	5	7426.2498	-1.4
						5	4	7426.2618	0.2
6	2	5	5	2	4	8	7	7360.9695	-2.3
						7	6	7361.0988	-1.6
						6	5	7361.2031	0.4
						5	4	7360.8794	-3.8
7	0	7	6	0	6	9	8	8576.7428	-1.0
						8	7	8576.2113	-2.3
						7	6	8576.3703	-1.2
						6	5	8576.8326	1.2
7	1	7	6	1	6	9	8	8509.6084	-0.2
						8	7	8509.5225	0.7
						7	6	8509.2500	0.2
						6	5	8509.3155	0.4
7	1	6	6	1	5	9	8	8662.3626	1.2
						8	7	8662.2603	0.6
						7	6	8662.7041	1.8
						6	5	8662.7758	-1.4
7	2	6	6	2	5	9	8	8587.1198	4.1
						8	7	8587.3797	-5.5
						7	6	8587.2571	-0.6
						6	5	8587.3920	0.4
8	0	8	7	0	7	10	9	9797.4718	0.6
						9	8	9796.8965	-0.6
						8	7	9797.0191	2.0
8	1	8	7	1	7	10	9	9724.0132	1.9
						9	8	9723.8992	0.1
						8	7	9723.7039	2.1
						7	6	9723.8025	3.2
8	1	7	7	1	6	10	9	9898.4982	2.3
						9	8	9898.3626	2.9
						8	7	9898.7026	1.2
						7	6	9898.8190	2.5

Table S7. Experimental transition frequencies (ν_{obs}, MHz) and observed minus calculated values ($\Delta\nu$, kHz) of the β ^{13}C isotopologue of isomer I of furan–CF_3Cl.

								Furan–CF_3Cl Cβ	
J'	K_a'	K_c'	J''	K_a''	K_c''	F'+1/2	F''+1/2	ν_{obs}/MHz	$\Delta\nu$/kHz
6	0	6	5	0	5	8	7	7318.7343	-2.7
						7	6	7318.4327	-4.1
						6	5	7318.4768	-5.1
						5	4	7319.0901	-9.3
6	1	6	5	1	5	8	7	7258.1484	-1.4
						7	6	7258.0820	-3.0
						6	5	7257.7155	-5.1
						5	4	7257.7155	-1.2
6	1	5	5	1	4	8	7	7391.2396	-1.4
						7	6	7391.1720	-1.8
						6	5	7391.7814	-6.4
						5	4	7391.7996	1.7
6	2	5	5	2	4	8	7	7325.4462	2.5
						7	6	7325.5689	-4.9
						6	5	7325.6684	-7.6
7	0	7	6	0	6	9	8	8534.9796	0.1
						8	7	8534.4420	1.7
						7	6	8534.6007	-1.1
						6	5	8535.0578	-4.6
7	1	7	6	1	6	9	8	8466.8355	1.3
						8	7	8466.7452	-0.4
						7	6	8466.4692	-0.1
						6	5	8466.5369	-0.4
7	1	6	6	1	5	9	8	8622.1306	0.7
						8	7	8622.0267	0.3
						7	6	8622.4655	-3.4
						6	5	8622.5432	-2.1
7	2	6	6	2	5	9	8	8545.6486	2.2
						8	7	8545.9338	-0.2
						7	6	8545.7858	-3.4
						6	5	8545.9539	6.1
8	0	8	7	0	7	10	9	9749.6237	2.5
						9	8	9749.0420	1.4
						8	7	9749.1642	2.6
						7	6	9749.7152	-2.8
8	1	8	7	1	7	10	9	9675.1031	5.1
						9	8	9674.9882	3.8
						8	7	9674.7901	2.9
						7	6	9674.8896	3.5
8	1	7	7	1	6	10	9	9852.4889	6.1
						9	8	9852.3515	6.7
						8	7	9852.6892	2.5
						7	6	9852.8073	3.6

Table S8. Experimental transition frequencies (ν_{obs}, MHz) and observed minus calculated values ($\Delta\nu$, kHz) of the ^{13}C isotopologue in CF_3Cl fragment of isomer I of furan–$^{13}CF_3Cl$.

								Furan–$^{13}CF_3Cl$	
J'	K_a'	K_c'	J''	K_a''	K_c''	F'+1/2	F''+1/2	ν_{obs}/MHz	$\Delta\nu$/kHz
6	0	6	5	0	5	8	7	7374.5960	-1.0
						7	6	7374.2927	-0.2
						6	5	7374.9671	-1.2
6	1	6	5	1	5	8	7	7312.7647	0.5
						7	6	7312.6946	-3.9
						6	5	7312.3285	-1.6
						5	4	7312.3285	-2.6
6	1	5	5	1	4	8	7	7448.8759	-1.6
						7	6	7448.8077	-0.8
						6	5	7449.4208	-1.2
7	0	7	6	0	6	9	8	8599.9979	-3.5
						8	7	8599.4547	0.3
						7	6	8599.6147	-0.3
						6	5	8600.0883	-0.5
7	1	7	6	1	6	9	8	8530.5157	-0.1
						8	7	8530.4391	13.9
						7	6	8530.1490	-3.2
						6	5	8530.2202	-1.4
7	1	6	6	1	5	9	8	8689.3332	1.6
						8	7	8689.2235	-1.7
						7	6	8689.6674	-0.8
8	0	8	7	0	7	10	9	9823.7440	3.0
						9	8	9823.1479	-1.6
						8	7	9823.2722	1.0
8	1	8	7	1	7	10	9	9747.8301	-1.7
						9	8	9747.7151	-0.6
						8	7	9929.2336	4.2
						7	6	9929.0887	0.8

Table S9. Experimental transition frequencies (ν, MHz) and observed minus calculated values ($\Delta\nu$, kHz) of isomer III of furan–$CF_3{}^{35}Cl$.

								Isomer III	
J'	K_a'	K_c'	J''	K_a''	K_c''	F'+1/2	F''+1/2	ν_{obs}/MHz	$\Delta\nu$/kHz
7	1	6	6	1	5	9	8	6351.5825	2.4
						8	7	6351.2528	-5.2
						7	6	6351.7722	-4.9
						6	5	6351.0966	1.5
8	0	8	7	0	7	10	9	7250.9242	7.8
						9	8	7250.9242	8.5
						8	7	7250.4854	14.8
						7	6	7250.4854	13.3
8	1	8	7	1	7	10	9	7243.9718	3.1
						9	8	7243.7529	-1.2
						8	7	7243.3733	0.7
						7	6	7243.5675	-8.2
8	1	7	7	1	6	10	9	7258.6770	1.7
						9	8	7258.4560	-4.6
						8	7	7258.0780	-1.0
						7	6	7258.2878	-3.4
9	0	9	8	0	8	11	10	8157.0146	-15.0
						10	9	8157.0146	-14.5
						9	8	8156.6874	-2.8
						8	7	8156.6874	-3.8
9	1	9	8	1	8	11	10	8419.2241	7.8
						10	9	8149.0665	0.3
						9	8	8148.7592	1.6
						8	7	8148.9088	2.5
9	1	8	8	1	7	11	10	8165.7392	0.9
						10	9	8165.5862	-1.9
						9	8	8165.2818	2.2
						8	7	8165.4288	0.5
10	0	10	9	0	9	12	11	9063.0893	7.9
						11	10	9063.0893	8.3
						10	9	9062.7912	-10.2
						9	8	9062.7912	-10.9
10	1	10	9	1	9	12	11	9054.4195	-2.9
						11	10	9054.3128	-0.4
						10	9	9054.0617	2.3
						9	8	9054.1686	1.0
10	1	9	9	1	8	12	11	9072.7522	0.3
						11	10	9072.6508	2.0
						10	9	9072.3951	6.3
						9	8	9072.5087	11.7
11	0	11	10	0	10	13	12	9969.0509	-10.4
						12	11	9969.0509	-10.1
						11	10	9968.8280	-3.3
						10	9	9968.8280	-3.8

11	1	11	10	1	10	13	12	9959.5795	4.3
						12	11	9959.4941	0.7
						11	10	9959.2830	1.9
						10	9	9959.3672	4.9
11	1	10	10	1	9	13	12	9979.7051	2.0
						12	11	9979.6141	-7.1
						11	10	9979.4107	1.8
						10	9	9979.4896	-0.4
12	0	12	11	0	11	14	13	10874.9414	-18.8
						13	12	10874.9414	-18.6
						12	11	10874.7567	-11.1
						11	10	10874.7567	-11.5
12	1	12	11	1	11	14	13	10864.6663	1.4
						13	12	10864.6033	1.4
						12	11	10864.4188	-3.1
						11	10	10864.4848	0.3
12	1	11	11	1	10	14	13	10886.5868	5.6
						13	12	10886.5167	-1.5
						12	11	10886.3407	2.4
						11	10	10886.3987	-2.0
13	0	13	12	0	12	15	14	11780.7648	-4.6
						14	13	11780.7648	-4.4
						13	12	11780.6035	-2.5
						12	11	11780.6035	-2.8
13	1	13	12	1	12	15	14	11769.6773	-5.5
						14	13	11769.6386	5.1
						13	12	11769.4792	0.0
						12	11	11769.5248	-3.4
13	1	12	12	1	11	15	14	11793.3787	1.8
						14	13	11793.3258	-1.6
						13	12	11793.1738	0.6
						12	11	11793.2270	4.7
14	0	14	13	0	13	16	15	12686.4987	17.8
						15	14	12686.4984	18.0
						14	13	12686.3551	15.0
						13	12	12686.3551	14.8
14	1	14	13	1	13	16	15	12674.6201	-1.6
						15	14	12674.5849	2.7
						14	13	12674.4488	0.3
						13	12	12674.4806	-7.1
14	1	13	13	1	12	16	15	12700.0801	-1.4
						15	14	12700.0457	3.6
						14	13	12699.9099	1.6
						13	12	12699.9494	1.8
15	0	15	14	0	14	17	16	13592.0969	11.3
						16	15	13592.0969	11.4
						15	14	13591.9628	-0.7
						14	13	13591.9628	-0.8
15	1	15	14	1	14	17	16	13579.4748	0.7
						16	15	13579.4353	-6.6

						15	14	13579.3254	0.4
						14	13	13579.3571	0.2
15	1	14	14	1	13	17	16	13606.6742	-12.9
						16	15	13606.6500	-5.0
						15	14	13606.5389	0.9
						14	13	13606.5684	-1.5

6. Table S10. NBO results calculated at the B3LYP-D3(BJ)/aug-cc-pVTZ level of isomers I and III in kJ·mol^{-1}.

Isomer I			Isomer III		
Donor NBO	Acceptor NBO	E(2)	Donor NBO	Acceptor NBO	E(2)
From furan to CF_3Cl			From furan to CF_3Cl		
LP(2) O1	**BD*(1) C7 – F9**	**0.33**	**BD(2) C2 – C3**	**BD*(1) Cl 6 – C7**	**3.26**
			BD(2) C2 – C3	RY (1) Cl 6	0.75
From CF_3Cl to furan				From CF_3Cl to furan	
LP(3) Cl 6	**BD*(2) C2 – C3**	**0.38**	**LP(3) Cl 6**	**BD*(2) C2 – C3**	**0.92**
LP(3) Cl 6	**BD*(2) C4 – C5**	**0.38**	LP(3) Cl 6	BD*(2) C4 – C5	0.21
LP(3) Cl 6	**BD*(1) O1 – C2**	**0.25**			
LP(3) Cl 6	**BD*(1) O1– C5**	**0.25**			
LP(3) Cl 6	RY (8) O1	0.21