Electronic Supplementary Material (ESI) for RSC Advances.

On the formation of 2- and 3-cyanofurans and their protonation in interstellar medium conditions: quantum chemical evidences.

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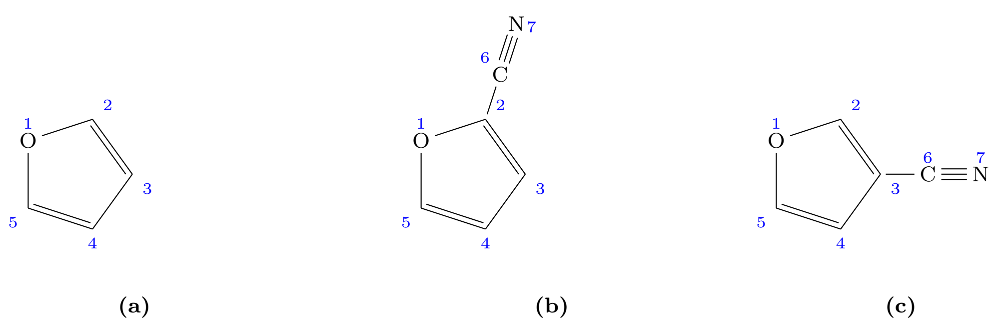
Supplementary Informafion (SI)



Scheme S1 – Chemical structures of **(a)** furan, **(b)** 2-cyanofuran (2 CF),**(c)** 3-cyanofuran (3 CF).

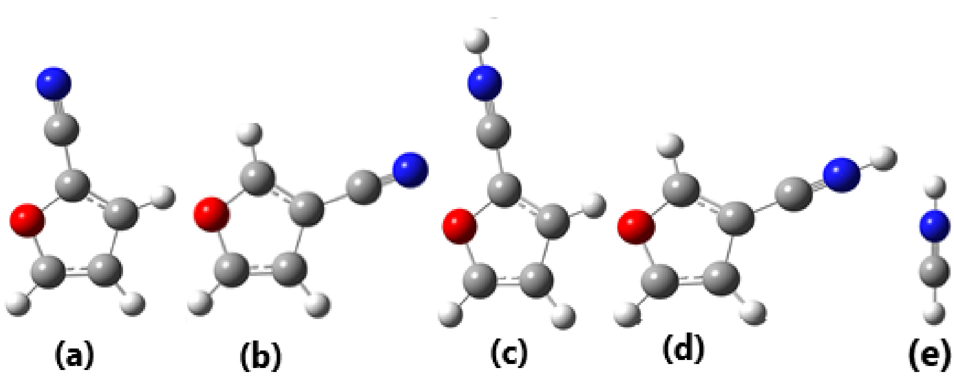
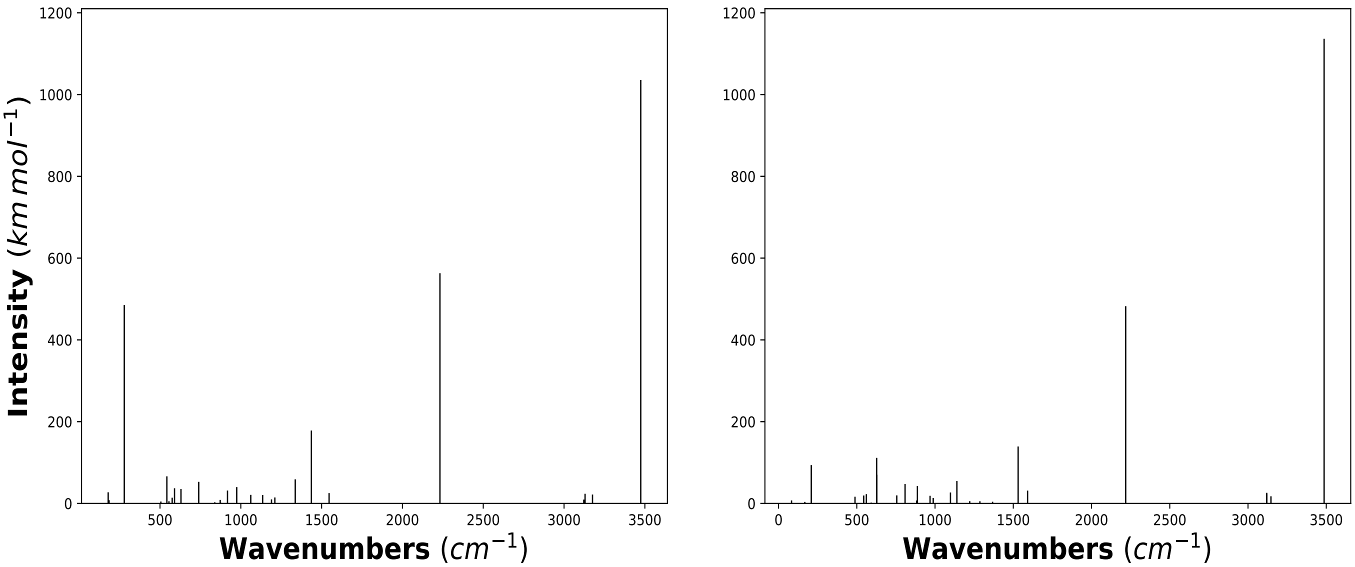
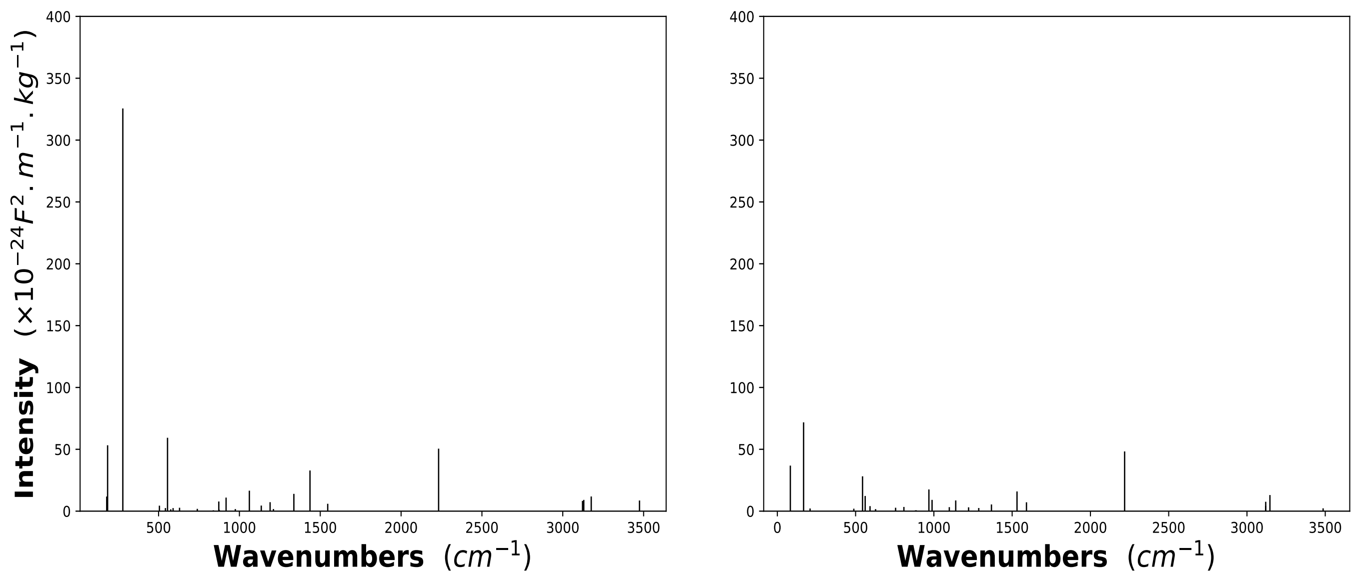


Figure S1 – B3LYP/6-31G(d,p) optimized 3D geometries for: (a) 2 CF, (b) 3 CF, (c) 2 CFH^+, (d) 3 CFH^+ and (e) $HCNH^+$(red=O, gray=C, blue=N and light gray=H).



(a) **(b)**

Figure S2 – Simulated IR spectra for (a) 2 CFH^+ and (b) 3 CFH^+.



(a) **(b)**

Figure S3 – Simulated Raman spectra for (a) 2 CFH^+ and (b) 3 CFH^+.

Table S1 – Experimental and calculated bond lengths (in Å), bond angles (in °) and rotational constants (in MHz) at different levels of theory.

Paramètres Géométriques	HF Basis[1]	MP2 Basis[2]	MP3 Basis[3]	M062X Basis[2]	M062X Basis[4]	B3LYP Basis[1]	B3LYP Basis[2]	B3LYP Basis[4]	B3LYP Basis[5]	Basis[6]	Basis[7]	Exp.
Bond lengths (in Å)												
O1-C5/O1-C2	1.3438	1.3653	1.3566	1.3542	1.3530	1.3643	1.3641	1.3621	1.3628	1.3656	1.3513	1.362
C2=C3/C4=C5	1.3391	1.3664	1.3607	1.3563	1.3511	1.3607	1.3606	1.3546	1.3553	1.3627	1.3506	1.361
C3-C4	1.4410	1.4273	1.4419	1.4341	1.4331	1.4357	1.4355	1.4327	1.4332	1.4371	1.4324	1.431
C2-H6/C5-H9	1.0681	1.0752	1.0786	1.0782	1.0744	1.0793	1.0787	1.0744	1.0742	1.0794	1.075	1.075
C3-H7/C4-H8	1.0702	1.0764	1.0798	1.0791	1.0751	1.0811	1.0803	1.0758	1.0757	1.0816	1.077	1.077
Bond angles (in °)												
C5-O1-C2	107.1	106.6	106.8	107.7	106.9	106.8	106.9	106.7	106.5	107.0	107.0	-
O1-C2=C3/O1-C5=C4	110.8	110.5	110.9	110.6	110.7	110.5	110.5	110.5	110.4	110.4	110.6	110.7
C5=C4-C3/C2=C3-C4	105.6	106.2	105.7	105.9	105.9	106.1	106.1	106.1	106.2	106.1	105.9	106.0
O1-C2-H6/O1-C5-H9	116.4	115.7	115.9	115.9	116.1	115.6	115.8	116.0	116.0	115.7	116.1	115.9
C3-C2-H6/C4-C5-H9	133.05	133.8	133.2	133.6	133.3	133.8	133.7	133.5	133.5	133.9	133.3	-
C3-C4-H8/C4-C3-H7	127.6	127.6	127.7	127.5	127.7	127.3	127.2	127.4	127.5	127.4	127.6	127.9
Rotationnal constants												
A(MHZ)	9605.1	9492.0	9499.1	9529.5	9559.9	9459.7	9460.5	9500.6	9484.5	9428.7	9569.4	9446.9
B(MHZ)	9535.3	9201.9	9258.7	9335.2	9385.4	9247.9	9252.7	9317.9	9318.0	9237.5	9400.5	9246.6
C(MHZ)	4785.1	4672.4	4688.7	4715.7	4735.9	4676.3	4677.7	4704.1	4700.3	4666.1	4742.1	4670.8
Δ A (MHZ)	158.2	45.1	52.2	82.6	113	12.8	13.6	53.7	37.6	-18.2	122.5	0.0
Δ B (MHZ)	358.5	-44.7	12.1	88.6	138.8	1.3	6.1	71.3	71.4	-9.1	153.9	0.0
Δ C (MHZ)	114.3	1.6	17.9	44.9	65.1	5.5	6.9	33.3	29.5	-4.7	71.3	0.0

[1]**Basis set**: 6-31G(d); [2]**Basis set**: 6-31G(d,p); [3]**Basis set**: 6-311G(d); [4]**Basis set**: 6-311G(2d,2p); [5]**Basis set**: 6-311+G(2d,2p); [6]**Basis set**: 6-31+G(d); [7]**Basis set**: 6-311g(2df,2p).

Table S2 – Experimental and B3LYP/6-31G(d,p) optimized geometrical parameters (including empirical corrections) for Furan, 2 CF, 3CF, 2 CFH$^+$ and 3CFH$^+$ (bond lengths in Å, bond angles in ^{o} and rotational constants in MHz [(1)].

	Furan		2 CF		3CF	2CFH$^+$	3CFH$^+$	HCNH$^+$	
	Calc	Exp[a]	Calc	Exp[b]	Calc	Calc	Calc	Calc	Exp[c]
Bond length									
O-C2	1.3584	1.362	1.3589	-	1.3422	1.3722	1.3212		
O-C5	1.3584	1.362	1.350	-	1.3605	1.3503	1.3796		
C2=C3	1.3622	1.361	1.3679	-	1.3746	1.3726	1.3909		
C3-C4	1.4520	1.431	1.4462	-	1.44106	1.4423	1.4514		
C4=C5	1.3622	1.361	1.3730	-	1.3478	1.3663	1.3519		
C2/C3-C6	-	-	1.099	-	1.4163	1.4099	1.3856		
C ≡ N	-	-	1.1717	-	1.1655	1.1716	1.1571	1.1397	1.1368
N-H	-	-	-	-	-	1.0113	1.0069	1.0171	1.0091
Bond angle									
C5-O-C2	107.13	106.5	105.42	-	107.35	105.60	108.77		
O-C2=C3	110.814	110.7	111.29	-	110.41	111.64	108.63		
O-C5=C4	110.814	110.7	113.28	-	110.85	111.99	111.09		
C5=C4-C3	105.622	106.0	103.52	-	105.96	105.89	104.04		
C2=C3-C4	105.622	106.0	105.66	-	105.43	104.87	107.48		
C2/C3-C6≡N	-	-	-		179.54	175.05	179.34		
C6≡N-H	-	-		-		155.00	179.87		

[(1)]Numbering scheme used is that of Scheme S1.; [a]Experimental data from Bak et al. (1962). [b]Experimental data from Engelbrecht & Sutter (1976). [c]Experimental data from Amano and Keiichi (1986).

Table S3 – G2MP2 and G3 Proton Affinity (PA in kJ/mol) of 2-cyanofuran (2 CF) and 3-cyanofuran (3 CF) at different sites for T = 298 K and 10 K.

	T = 298 K				T = 10 K			
	2 CF		3 CF		2 CF		3 CF	
Site[(1)]	G2MP2	G3	G2MP2	G3	G2MP2	G3	G2MP2	G3
1	643.39	642.18	636.48	635.54	635,93	634.71	631.33	630.39
2	732.07	727.39	753.58	751.89	726.97	722.29	748.65	746.96
3	702.78	701.18	677.78	672.71	698.23	696.65	672.97	667.90
4	709.78	707.45	709.00	706.34	705.07	702.76	704.26	701.60
5	747.83	746.38	747.75	745.32	742.97	735.37	742.78	740.35
N	795.14	796.35	801.47	802.75	790.48	791.69	796.57	797.85

[(1)]Numbering scheme used is that of Scheme S1; [a]Experimental data from Bak et al. (1962) [b]Experimental data from Engelbrecht & Sutter (1967)

Table S4 – G2MP2 and G3 Proton Affinity (PA in kJ/mol) of 2-cyanofuran (2 CF) and 3-cyanofuran (3 CF) at different sites for T = 298 K and 10 K.

	T = 150 K				T = 5 K			
	2 CF		3 CF		2 CF		3 CF	
Site	G2MP2	G3	G2MP2	G3	G2MP2	G3	G2MP2	G3
1	647.21	645.99	634.11	633.18	638.19	636.98	631.23	630.29
2	735.89	731.20	751.27	749.58	726.87	722.19	748.55	746.86
3	707.15	699.20	675.47	670.41	698.13	696.55	672.87	667.80
4	707.68	705.36	706.88	704.22	704.97	702.65	686.37	701.50
5	745.57	744.11	745.42	743.00	742.87	741.43	725.12	740.24
N	793.15	794.35	799.32	800.60	790.38	791.59	778.84	797.75

Table S5 – Gase phase G2MP2 and G3 calculated enthalpy, entropy and Gibbs free energy variations ($\Delta_r H$, $\Delta_r S$ and $\Delta_r G$ in $kJ\ mol^{-1}$) of reaction producing cyanofurans and their protonated forms ($T = 150\,K$ and $T = 5\,K$ for $P = 10^{-5}$ atm).

Equation of the reaction		T = 150 K			T = 5 K			level of theory
		$\Delta_r H$	$\Delta_r G$	$\Delta_r S$	$\Delta_r H$	$\Delta_r G$	$\Delta_r S$	
$C_4H_3O^+ + CN^- \longrightarrow 2\,CF + H$	**(1)**	-566.33	-557.82	-0.056	-533.38	-533.20	-0.036	G2MP2
		-569.11	-560.59	-0.056	-568.94	-568.75	-0.038	G3
$C_4H_3O^+ + CN^- \longrightarrow 3\,CF + H$	**(2)**	-573.21	-564.72	-0.056	-540.24	-540.06	-0.036	G2MP2
		-575.26	-566.76	-0.056	-575.08	-574.88	-0.038	G3
$C_4H_3OCN + {H_3}^+ \longrightarrow 2\,CF\text{-}H^+ + H_2$	**(3)**	-379.19	-345.81	-0.222	-375.23	-374.58	-0.128	G2MP2
		-376.34	-373.42	-0.019	-375.98	-375.95	-0.007	G3
$C_4H_3OCN + {H_3}^+ \longrightarrow 3\,CF\text{-}H^+ + H_2$	**(4)**	-385.36	-351.86	-0.223	-381.32	-380.68	-0.128	G2MP2
		-382.60	-379.54	-0.020	-382.15	-382.12	-0.007	G3

Table S6 – Potential energy distribution of fundamental vibrational modes of $2\,CFH^+$

Frequency (cm^{-1})	PED (%)	Mode	Atoms[1] h	k	l	m	PED (%)	Mode	Atoms[1] h	k	l	m
In - plane modes												
3475	97%	ν_{NH}	7	11	0	0						
3176	97%	ν_{CH}	5	10	0	0						
3130	61%	ν_{CH}	3	8	0	0	37%	ν_{CH}	4	9	0	0
3122	60%	ν_{CH}	4	9	0	0	38%	ν_{CH}	5	10	0	0
2232	85%	$\nu_{C\equiv N}$	6	7	0	0	12%	ν_{CC}	3	6	0	0
1546	36%	$\nu_{C=C}$	2	3	0	0	23%	$\nu_{C=C}$	4	5	0	0
	7%	ν_{CC}	3	6	0	0	7%	δ_{CH}	4	3	8	0
	6%	δ_{CH}	3	4	9	0						
1437	29%	$\nu_{C=C}$	4	5	0	0	25%	$\nu_{C=C}$	2	3	0	0
	13%	δ_{CH}	1	5	10	0	7%	δ_{OC}	2	1	5	0
	7%	δ_{CH}	4	5	10	0	6%	ν_{CC}	3	6	0	0
1337	19%	ν_{CC}	3	4	0	0	17%	δCH	3	4	9	0
	11%	δ_{CH}	4	5	10	0	9%	δ_{CH}	4	5	10	0
	9%	ν_{OC}	1	5	0	0	5%	δ_{CH}	2	3	8	0
1211	38%	ν_{OC}	1	2	0	0	23%	ν_{CC}	3	6	0	0
	5%	δ_{CC}	1	2	3	0						
1190	26%	δ_{CH}	2	3	8	0	23%	δ_{CH}	4	3	8	0
	14%	ν_{CC}	3	4	0	0	13%	δ_{CH}	1	5	10	0
	8%	δ_{CH}	4	5	10	0	5%	ν_{CH}	3	6	0	0
1135	39%	ν_{OC}	1	5	0	0	20%	δ_{CH}	1	5	10	0
	12%	$\nu_{C=C}$	4	5	0	0	11%	δ_{CH}	4	5	10	0
1062	28%	ν_{OC}	1	5	0	0	19%	δ_{CH}	3	4	9	0
	17%	δ_{CH}	5	4	9	0	8%	$\nu_{C=C}$	4	5	0	0
	6%	ν_{CC}	3	4	0	0	5%	δ_{CH}	4	5	10	0
975	33%	ν_{CC}	3	4	0	0	21%	δ_{CH}	4	3	8	0
	12%	δ_{CH}	3	4	9	0	11%	δ_{CC}	2	3	8	0
	10%	$\delta_{C=C}$	5	4	9	0						
918	29%	ν_{OC}	1	2	0	0	16%	δ_{OC}	2	1	5	0
	11%	δ_{CH}	4	5	10	0	8%	$\nu_{C=C}$	2	3	0	0
	6%	δ_{CH}	5	4	9	0						
872	25%	δ_{CC}	3	4	5	0	24%	δ_{OC}	4	5	1	0
	121%	δ_{CC}	2	3	4	0	9%	δ_{OC}	2	1	5	0
	9%	δ_{CH}	2	3	8	0	7%	δ_{CH}	3	4	9	0
590	39%	δ_{CN}	2	6	7	0	15%	δ_{CNH}	6	7	11	0

(Continued)

Table S6 – *(Continued)*

Frequency (cm^{-1})	PED (%)	Mode	Atoms[1] h	k	l	m	PED (%)	Mode	Atoms[1] h	k	l	m
	12%	δ_{CN}	2	6	7	0	9%	ν_{CC}	1	2	6	0
575	24%	ν_{CN}	2	6	7	0	20%	δ_{CNH}	6	7	11	0
	10%	δ_{CC}	1	2	6	0	9%	δ_{CC}	3	2	6	0
555	47%	ν_{CC}	2	6	0	0	11%	δ_{CC}	1	2	3	0
	8%	$\nu_{C\equiv N}$	6	7	0	0	6%	δ_{OC}	2	1	5	0
	5%	δ_{CC}	2	3	4	0						
279	62%	δ_{CNH}	2	6	7	0	15%	$\nu_{C\equiv N}$	6	7	0	0
	11%	δ_{CN}	2	6	7	0						
185	48%	δ_{CN}	2	6	7	0	23%	δ_{CC}	1	2	6	0
	22%	δ_{CC}	3	2	6	0						
Out-of-plane modes												
875	31%	γ_{HCCH}	8	3	4	9	24%	γ_{HCCH}	9	4	5	10
	9%	γ_{OCCH}	1	5	4	9	8%	γ_{CCCH}	6	2	3	8
	7%	γ_{CCCH}	2	3	4	9	7%	γ_{OCCH}	1	2	3	8
839	28%	γ_{HCCH}	9	4	5	10	23%	γ_{CCCH}	3	4	5	10
	10%	γ_{CCCH}	6	2	3	8	10%	γ_{COCH}	2	1	5	10
	9%	γ_{CCCH}	5	4	3	8	8%	γ_{OCCH}	1	2	3	8
740	30%	γ_{OCCH}	1	5	4	9	22%	γ_{CCCH}	2	3	4	9
	11%	γ_{OCCH}	1	2	3	8	10%	γ_{CCCH}	6	2	3	8
	9%	γ_{CCCH}	3	4	5	10	6%	γ_{CCCH}	5	4	3	8
630	23%	γ_{CCNH}	2	6	7	11	22%	γ_{CCN}	0	2	6	7
	11%	γ_{CCN}	3	6	7	9	7%	γ_{COCC}	5	1	2	3
	7%	γ_{OCCC}	1	2	3	4	6%	γ_{CCCH}	6	2	3	8
542	78%	γ_{CCNH}	2	6	7	11						
505	85%	γ_{CCN}	0	2	6	7						
179	38%	γ_{CCCC}	4	3	2	6	23%	γ_{CCCH}	6	2	3	8
	21%	γ_{COCC}	5	1	2	6	11%	γ_{CCN}	0	2	6	7

[a]Only contributions greater than 5% were taken into account; [b]See Scheme S1 for atom numbering;
[c]ν: stretching; δ: in-plane bending modes; γ: out-of-plane bending modes.

Table S7 – Potential energy distribution of fundamental vibrational modes of 3 CFH^+

Frequency (cm^{-1})	PED (%)	Mode	Atoms[1] h	k	l	m	PED (%)	Mode	Atoms[1] h	k	l	m
In - plane modes												
3486	97%	ν_{NH}	7	11	0	0						
3147	82%	ν_{CH}	5	10	0	0	16%	ν_{CH}	4	9	0	0
3120	90%	ν_{CH}	2	8	0	0	9%	ν_{CH}	4	9	0	0
3120	90%	ν_{CH}	4	9	0	0	17%	ν_{CH}	5	10	0	0
	8%	ν_{CH}	2	8	0	0						
2218	79%	$\nu_{C\equiv N}$	6	7	0	0	18%	ν_{CC}	2	6	0	0
1591	54%	$\nu_{C=C}$	4	5	0	0	10%	$\nu_{C=C}$	2	3	0	0
	8%	δ_{CH}	3	4	9	0						
1531	35%	$\nu_{C=C}$	2	3	0	0	15%	$\nu_{C=C}$	3	6	0	0
	13%	$\nu_{C=C}$	4	5	0	0	8%	δ_{CH}	1	2	8	0
	7%	δ_{CH}	3	2	8	0						
1368	40%	ν_{CC}	3	4	0	0	15%	νC=C	2	3	0	0
	6%	δ_{CH}	5	4	9	0	6%	δ_{CH}	4	5	10	0

(Continued)

Table S7 – *(Continued)*

Frequency	PED	Mode	Atoms[1]				PED	Mode	Atoms[1]			
(cm^{-1})	(%)		h	k	l	m	(%)		h	k	l	m
1287	23%	ν_{CC}	3	6	0	0	19%	ν_{OC}	1	2	0	0
	18%	δ_{CH}	1	2	8	0	13%	δ_{CH}	3	2	8	0
	6%	$\nu_{C\equiv N}$	6	7	0	0						
1222	19%	δ_{CH}	4	5	10	0	18%	δ_{CH}	1	5	10	0
	16%	δ_{CH}	3	2	8	0	13%	δ_{CH}	1	2	8	0
	11%	δ_{CH}	5	4	9	0	6%	δ_{CH}	3	4	9	0
1140	51%	ν_{OC}	1	2	0	0	21%	δ_{CH}	1	2	8	0
	7%	δ_{CC}	1	2	8	0	6%	δ_{CH}	3	2	8	0
1099	28%	δ_{CH}	5	4	9	0	19%	δ_{CH}	1	5	10	0
	18%	δ_{CH}	3	4	9	0	10%	δ_{CH}	4	5	10	0
	7%	$\nu_{C=C}$	4	5	0	0	7%	ν_{OC}	1	5	0	0
988	18%	δ_{CH}	3	4	9	0	14%	δ_{CC}	3	4	5	0
	12%	δ_{CC}	1	5	4	0	12%	ν_{CC}	3	4	0	0
	9%	$\nu_{C=C}$	2	3	0	0	6%	ν_{OC}	1	5	0	0
968	53%	ν_{OC}	1	5	0	0	10%	ν_{CC}	3	4	1	0
	6%	ν_{OC}	1	2	0	0	5%	δ_{CH}	4	5	10	0
	5%	δ_{CH}	3	4	9	0						
755	36%	δ_{OC}	2	1	5	0	23%	ν_{OC}	1	5	0	0
	12%	δ_{CC}	1	5	4	0	6%	δ_{CC}	1	2	3	0
	6%	δ_{CH}	3	2	8	0						
592	59%	δ_{CNH}	6	7	11	0	14%	δ_{CC}	4	3	6	0
	11%	δ_{CC}	2	3	6	0	6%	ν_{CC}	3	4	0	0
544	42%	ν_{CC}	3	6	0	0	11%	δ_{CC}	2	3	4	0
	8%	δ_{CC}	1	2	3	0	6%	$\nu_{C\equiv N}$	6	7	8	0
	6%	$\nu_{C=C}$	2	3	0	0						
168	47%	δ_{CNH}	1	2	0	0	25%	δ_{CC}	2	3	6	0
	25%	δ_{CC}	4	3	6	0						
Out-of-plane modes												
887	33%	γ_{CCCH}	6	3	2	8	29%	γ_{CCCH}	4	3	2	8
	14%	γ_{COCH}	5	1	2	8	11%	γ_{CCCH}	3	4	5	10
	7%	γ_{HCCH}	9	4	5	10						
882	36%	γ_{HCCH}	9	4	5	10	16%	γ_{CCCH}	6	3	4	9
	12%	γ_{OCCH}	1	5	4	9	10%	γ_{CCCH}	2	3	4	9
	9%	γ_{CCCH}	3	4	5	10	5%	γ_{COCH}	2	1	5	10
808	20%	γ_{CCCH}	3	4	5	10	19%	γ_{OCCH}	1	5	4	9
	17%	γ_{CCCH}	2	3	4	9	15%	γ_{CCCH}	6	3	4	9
	10%	γ_{COCH}	2	1	5	10	8%	γ_{CCCH}	6	3	2	8
628	35%	γ_{CNH}	3	6	7	11	9%	γ_{CCCC}	1	2	3	4
	8%	γ_{CCCH}	6	3	4	9	7%	γ_{CCCC}	5	4	3	6
	6%	γ_{CCCC}	2	3	4	5	5%	γ_{CCCH}	4	3	2	8
627	91%	γ_{CNH}	3	6	7	11						
561	26%	γ_{COCC}	2	1	5	4	25%	γ_{OCCC}	1	5	4	3
	12%	γ_{CCCC}	2	3	4	5	7%	γ_{CCCC}	5	4	3	6
	7%	γ_{COCC}	5	1	2	3						
489	21%	γ_{CCNH}	3	6	7	11	15%	γ_{OCCC}	1	2	3	6
	10%	γ_{COCC}	5	1	2	3	9%	γ_{CCN}	0	3	6	7
	8%	γ_{OCCC}	1	2	3	4	6%	γ_{COCH}	2	1	5	10
209	68%	γ_{CCNH}	3	6	7	11	10%	γ_{CCCC}	5	4	3	6
	9%	γ_{OCCC}	1	2	3	6						
83	75%	γ_{CCN}	0	3	6	7	18%	γ_{CCNH}	3	6	7	11

[a]Only contributions greater than 5% were taken into account; [b]See Scheme S1 for atom numbering;
[c]ν: stretching; δ: in-plane bending modes; γ: out-of-plane bending modes.

Table S8 – M06-2X/6-31G(d,p) calculated frequencies (cm^{-1}), infrared intensities ($km.mol^{-1}$) and Raman activities ($Å^4/amu$) and Raman intensities ($\times 10^{-24} F^2.m^{-1}.kg^{-1}$) for compounds 2 CFH^+ and 3 CFH^+.

2 CFH^+					3 CFH^+				
Non scaled frequencies	Scaled	IR int.	Ram. Activ	Ram. Int.	Non scaled frequencies	Scaled	IR int.	Ram. Activ	Rama. Int
3684	3475	1033.74	113.26	8.01	3746	3486	1134.57	23.84	1.67
3368	3176	19.90	119.64	11.27	3318	3147	15.69	128.17	12.42
3319	3130	21.83	86.36	8.50	3291	3120	24.18	70.30	6.99
3311	3122	7.58	77.56	7.69	3291	3120	20.80	36.99	3.68
2241	2232	561.27	211.70	49.92	2355	2218	480.58	199.51	47.69
1603	1546	23.47	10.91	5.35	1585	1591	29.48	14.08	6.56
1493	1437	176.46	57.80	32.29	1540	1531	137.49	30.70	15.34
1390	1337	57.17	21.18	13.37	1372	1368	2.30	7.93	4.82
1259	1211	12.82	1.50	1.11	1344	1287	3.52	2.89	1.94
1244	1190	8.04	8.70	6.65	1268	1222	3.67	3.41	2.49
1186	1135	18.92	4.76	3.92	1228	1140	53.21	9.86	8.06
1105	1062	19.17	17.46	15.95	1135	1099	24.88	3.03	2.63
1018	975	38.12	1.04	1.08	1033	988	11.48	8.35	8.51
945	918	29.65	9.10	10.36	979	968	16.86	16.13	16.95
925	875	0.15	0.38	0.46	887	887	40.90	0.07	0.09
892	872	6.83	5.88	7.21	881	882	5.32	0.04	0.05
878	839	1.05	0.08	0.10	851	808	45.84	2.03	2.79
786	740	51.01	0.80	1.25	770	755	17.87	1.42	2.15
655	630	33.48	1.09	2.15	620	628	68.39	0.52	1.02
616	590	35.25	0.87	1.88	608	627	109.67	0.27	0.53
596	575	12.19	0.38	0.86	593	592	0.19	1.61	3.46
569	555	3.54	24.90	58.72	579	561	20.80	5.03	11.68
561	542	64.50	0.78	1.89	569	544	17.59	11.35	27.57
518	505	2.84	1.41	3.82	521	489	14.57	0.48	1.38
294	279	483.37	48.59	324.98	192	209	91.94	0.15	1.56
192	185	6.11	3.99	52.66	166	168	1.96	4.58	71.21
186	179	25.45	0.81	11.21	149	83	5.48	0.66	36.22

Table S9 – 2 CNFH$^+$ selected strongest line transitions and the corresponding hyperfine splitting components for $T = 10\,K$.

$J''_{K_{-1}K_{+1}} \leftarrow J'_{K_{-1}K_{+1}}$	$F'' \leftarrow F'$	ν_{cal}	Est.Err[1]	Int.[2]	Transition		ν_{cal}	Est.Err[1]	Int.[2]
$14_{0\,14} \leftarrow 13_{0\,13}$	14 ← 14	46200.9476	0.0000	0.0301	$14_{1\,13} \leftarrow 13_{1\,12}$	13 ← 13	49774.2835	0.0000	0.0300
	12 ← 12	46479.1077	0.0000	0.0354		13 ← 14	49774.4687	0.0000	0.0000
	12 ← 13	46479.2314	0.0000	0.0001		13 ← 12	49774.4829	0.0001	5.4319
	12 ← 11	46479.2418	0.0001	5.5056		15 ← 14	49774.4865	0.0001	6.2711
	14 ← 13	46479.2457	0.0001	6.4277		14 ← 13	49774.5525	0.0001	5.8367
	13 ← 12	46479.3072	0.0001	5.9490		14 ← 14	49774.7377	0.0000	0.0299
	13 ← 13	46479.4309	0.0000	0.0354					
$12_{1\,11} \leftarrow 11_{1\,10}$	11 ← 11	43124.9010	0.0000	0.0409	$14_{1\,14} \leftarrow 13_{1\,13}$	13 ← 13	45981.5151	0.0000	0.0297
	11 ← 12	43124.9687	0.0000	0.0001		13 ← 14	45982.5892	0.0000	0.0000
	11 ← 10	43124.9749	0.0001	5.3817		15 ← 14	45982.6676	0.0002	6.2278
	13 ← 12	43124.9791	0.0001	6.3658		13 ← 12	45982.6721	0.0002	5.3944
	12 ← 11	43125.0350	0.0001	5.8534		14 ← 13	45982.6887	0.0002	5.7963
	12 ← 12	43125.1028	0.0000	0.0409		14 ← 14	45983.7628	0.0000	0.0297
$13_{0\,13} \leftarrow 12_{0\,12}$	12 ← 12	43053.1158	0.0000	0.0349	$13_{1\,13} \leftarrow 12_{1\,12}$	12 ← 12	42771.2954	0.0000	0.0342
	12 ← 13	43054.0900	0.0000	0.0001		12 ← 13	42772.3472	0.0000	0.0001
	14 ← 13	43054.1685	0.0002	6.3332		14 ← 13	42772.4301	0.0002	6.2150
	12 ← 11	43054.1714	0.0002	5.4248		12 ← 11	42772.4352	0.0002	5.3234
	13 ← 12	43054.2122	0.0002	5.8616		13 ← 12	42772.4524	0.0002	5.7521
	13 ← 13	43055.1863	0.0000	0.0349		13 ← 13	42773.5042	0.0000	0.0342
$14_{0\,14} \leftarrow 13_{0\,13}$	13 ← 13	46198.7991	0.0000	0.0301	$12_{0\,12} \leftarrow 11_{0\,11}$	11 ← 11	39909.9233	0.0000	0.0396
	13 ← 14	46199.8170	0.0000	0.0000		11 ← 12	39910.8463	0.0000	0.0001
	15 ← 14	46199.8925	0.0002	6.3131		13 ← 12	39910.9278	0.0001	6.1607
	13 ← 12	46199.8955	0.0002	5.4683		11 ← 10	39910.9305	0.0001	5.2083
	14 ← 13	46199.9297	0.0002	5.8756		12 ← 11	39910.9789	0.0001	5.6647
	14 ← 14	46200.9476	0.0000	0.0301		12 ← 12	39911.9019	0.0000	0.0396
$14_{1\,13} \leftarrow 13_{1\,12}$	13 ← 13	49774.2835	0.0000	0.0300	$15_{0\,15} \leftarrow 14_{0\,14}$	14 ← 14	49348.9706	0.0000	0.0255
	13 ← 14	49774.4687	0.0000	0.0000		14 ← 15	49350.0256	0.0000	0.0000
	13 ← 12	49774.4829	0.0001	5.4319		16 ← 15	49350.0982	0.0002	6.1149
	15 ← 14	49774.4865	0.0001	6.2711		14 ← 13	49350.1012	0.0002	5.3481
	14 ← 13	49774.5525	0.0001	5.8367		15 ← 14	49350.1298	0.0002	5.7188
	14 ← 14	49774.7377	0.0000	0.0299		15 ← 15	49351.1848	0.0000	0.0255

Est.Err[1]: Estimated error (in MHz) for calculated frequency from observed one; Int.[2]: intensity of the line (in $\times 10^{-3} nm^2$MHz).

Table S10 – 3 $CNFH^+$ selected strongest line transitions and the corresponding hyperfine splitting components for T = 10 K.

$J''_{K_{-1}K_{+1}} \leftarrow J'_{K_{-1}K_{+1}}$	$F'' \leftarrow F'$	ν_{cal}	Est.Err[1]	Int.[2]	Transition		ν_{cal}	Est.Err[1]	Int.[2]
$13_{1\,12} \leftarrow 12_{1\,11}$	12 ← 12	45437.7268	0.0001	0.2606	$14_{1\,13} \leftarrow 13_{1\,12}$	13 ← 13	48678.7108	0.0001	0.2216
	12 ← 13	45437.9860	0.0000	0.0004		13 ← 14	48679.0118	0.0000	0.0003
	12 ← 11	45438.0077	0.0001	40.5230		13 ← 12	48679.0350	0.0001	40.2290
	14 ← 13	45438.0092	0.0001	47.3090		15 ← 14	48679.0365	0.0001	46.4430
	13 ← 12	45438.0510	0.0001	43.7860		14 ← 13	48679.0813	0.0001	43.2250
	13 ← 13	45438.3102	0.0001	0.2606		14 ← 14	48679.3823	0.0001	0.2217
$12_{1\,11} \leftarrow 11_{1\,10}$	11 ← 11	42141.7955	0.0001	0.2996	$14_{1\,14} \leftarrow 13_{1\,13}$	13 ← 13	44979.7173	0.0002	0.2189
	11 ← 12	42142.0166	0.0000	0.0005		13 ← 14	44980.6577	0.0000	0.0003
	11 ← 10	42142.0368	0.0001	39.3890		15 ← 14	44980.7261	0.0002	45.8610
	13 ← 12	42142.0383	0.0001	46.5910		13 ← 12	44980.7302	0.0002	39.7240
	12 ← 11	42142.0764	0.0001	42.8400		14 ← 13	44980.7416	0.0002	42.6830
	12 ← 12	42142.2975	0.0001	0.2996		14 ← 14	44981.6820	0.0002	0.2189
$14_{0\,14} \leftarrow 13_{0\,13}$	13 ← 13	45215.0458	0.0002	0.2222	$13_{1\,13} \leftarrow 12_{1\,12}$	12 ← 12	41836.9572	0.0002	0.2509
	13 ← 14	45215.9426	0.0000	0.0003		12 ← 13	41837.8811	0.0000	0.0004
	15 ← 14	45216.0088	0.0002	46.5580		14 ← 13	41837.9536	0.0002	45.5510
	13 ← 12	45216.0118	0.0002	40.3280		12 ← 11	41837.9583	0.0002	39.0160
	14 ← 13	45216.0363	0.0002	43.3320		13 ← 12	41837.9701	0.0002	42.1580
	14 ← 14	45216.9331	0.0002	0.2222		13 ← 13	41838.8940	0.0002	0.2509
$13_{0\,13} \leftarrow 12_{0\,12}$	12 ← 12	42137.9563	0.0002	0.2562	$15_{0\,15} \leftarrow 14_{0\,14}$	14 ← 14	48295.8382	0.0002	0.1892
	12 ← 13	42138.8210	0.0000	0.0004		14 ← 15	48296.7626	0.0000	0.0002
	14 ← 13	42138.8901	0.0002	46.5040		16 ← 15	48296.8259	0.0002	45.3120
	12 ← 11	42138.8933	0.0002	39.8330		14 ← 13	48296.8287	0.0002	39.6310
	13 ← 12	42138.9223	0.0002	43.0400		15 ← 14	48296.8494	0.0002	42.3770
	13 ← 13	42139.7869	0.0002	0.2562		15 ← 15	48297.7737	0.0002	0.1892
$14_{1\,13} \leftarrow 13_{1\,12}$	13 ← 13	48678.7108	0.0001	0.2216	$12_{0\,12} \leftarrow 11_{0\,11}$	11 ← 11	39062.1142	0.0001	0.2897
	13 ← 14	48679.0118	0.0000	0.0003		11 ← 12	39062.9416	0.0000	0.0005
	13 ← 12	48679.0350	0.0001	40.2290		13 ← 12	39063.0139	0.0001	45.0510
	15 ← 14	48679.0365	0.0001	46.4430		11 ← 10	39063.0171	0.0001	38.0870
	14 ← 13	48679.0813	0.0001	43.2250		12 ← 11	39063.0511	0.0001	41.4250
	14 ← 14	48679.3823	0.0001	0.2217		12 ← 12	39063.8785	0.0001	0.2897

Est.Err[1]: Estimated error (in MHz) for calculated frequency from observed one; Int.[2]: intensity of the line (in $\times 10^{-3} nm^2$MHz).