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

Table S1. Newly measured frequencies of CF_3CN-Ar, MHz[a]

$J'_{Ka\,Kc}$	$J''_{Ka\,Kc}$	F'	F''	Frequency	o-c[b]
9_{09}	8_{18}	9	9	16198.916	0
		8	7	16199.500	1
		10	9	16199.533	2
		9	8	16199.718	3
3_{31}	2_{20}	3	3	16228.826	-6
		3	2	16229.314	-8
		2	1	16229.518	5
		4	3	16229.534	-4
		2	2	16230.266	-8
3_{30}	2_{21}	3	3	16236.540	-4
		3	2	16237.103	-2
		2	1	16237.180	-2
		4	3	16237.246	-1
		2	2	16238.055	0
10_{19}	9_{28}	9	8	16316.511	3
		11	10	16316.584	2
		10	9	16317.357	0
9_{19}	8_{18}	9	8	16597.408	3
		8	7	16597.447	-4
		10	9	16597.457	0
9_{09}	8_{08}	9	8	16750.433	1
		10	9	16750.583	-1
		8	7	16750.598	3
6_{25}	5_{14}	5	5	16781.283	0
		6	5	16781.696	1
		7	6	16782.880	1
		5	4	16783.133	1
		6	6	16783.233	2
5_{23}	4_{14}	4	3	16902.890	-2
		6	5	16903.226	-1
		4	4	16903.700	-4
		5	5	16904.057	-3
		5	4	16904.703	-3
9_{19}	8_{08}	9	8	17148.120	-1
		10	9	17148.509	-1
		8	7	17148.547	0
9_{28}	8_{27}	9	8	17278.758	-4
		10	9	17278.792	-5
		8	7	17278.807	1
9_{18}	8_{17}	9	8	17789.337	0

		10	9	17789.457	0
		8	7	17789.489	0
9_{27}	8_{26}	10	9	17935.136	-6
		8	7	17935.146	-3
		9	8	17935.254	-3
10_{010}	9_{19}	9	8	18127.267	-2
		11	10	18127.292	3
		10	9	18127.399	0
4_{32}	3_{21}	4	3	18148.040	1
		4	4	18148.229	4
		3	3	18148.229	-1
		5	4	18148.379	2
		3	2	18148.479	-2
4_{31}	3_{21}	4	3	18187.161	0
		4	4	18187.161	0
		5	4	18187.308	3
		3	3	18187.340	-2
		3	2	18187.340	-2
7_{26}	6_{15}	6	6	18291.128	-3
		7	6	18291.542	0
		8	7	18292.687	1
		6	5	18292.884	0
10_{110}	9_{19}	10	9	18407.777	0
		9	8	18407.824	0
		11	10	18407.824	-4
10_{010}	9_{09}	10	9	18525.086	-2
		11	10	18525.218	3
		9	8	18525.218	-3

[a] Previously measured transitions can be found in reference 14.
[b] Observed minus calculated frequencies in kHz.

Table S2. Spectroscopic constants of CF_3CN-Ar.

	Lin *et al*[14]	This work
A /MHz	3053.0903(2)	3053.0897(2)
B /MHz	1039.9570(2)	1039.95688(9)
C /MHz	895.5788(1)	895.57932(9)
Δ_J/kHz	2.687(1)	2.6889(6)
Δ_{JK}/kHz	15.904(8)	15.928(4)
Δ_K/kHz	-12.38(2)	-12.45(2)
δ_J/kHz	0.4258(8)	0.4260(2)
δ_K/kHz	7.05(5)	6.93(3)
χ_{aa}/MHz	1.746(1)	1.747(1)
χ_{bb} - χ_{cc} /MHz	-6.426(2)	-6.425(3)
N	133	201
σ/kHz	2	2

Table S3. Measured frequencies of CF_3CN-H_2O in MHz

				A state		B state	
J'$_{Ka\,Kc}$	J"$_{Ka\,Kc}$	F'	F"	Frequency	o-c[a]	Frequency	o-c[a]
				a-type			
5_{15}	4_{14}	5	5	16314.234	-1	16312.886	-2
		5	4	16315.175	3	16313.827	1
		4	3	16315.239	1	16313.892	1
		6	5	16315.270	2	16313.923	1
		4	4	16316.415	0	16315.070	0
5_{05}	4_{04}	5	5	16462.732	-1	16461.031	-1
		5	4	16463.479	1	16461.779	0
		6	5	16463.684	2	16461.984	1
		4	4	16464.621	0	16462.922	-1
3_{21}	2_{02}	2	1	16837.243	3	16826.515	5
		4	3	16837.517	-0	16826.785	-3
		3	2	16838.218	-3	16827.491	-2
5_{24}	4_{23}	5	4	17472.657	0	17470.278	0
		6	5	17472.734	3	17470.356	4
		4	3			17470.356	-1
5_{41}	5_{40}	4	3	17903.411	0	17900.986	0
		6	5	17903.450	-2	17901.021	-4
		5	4	17903.633	0	17901.205	2
5_{32}	4_{31}	4	4			18140.961	2
		4	3	18143.687	2	18141.255	4
		6	5	18143.720	-1	18141.285	-2
		5	4	18143.958	-1	18141.524	1
		5	5			18141.750	-6
5_{14}	4_{13}	4	4	18195.072	-1	18191.730	-1
		5	4	18195.613	0	18192.266	0
		6	5	18195.841	0	18192.492	-1
		4	3	18195.924	1	18192.574	2
		5	5	18196.28	-3	18192.934	-2
				b-type			
5_{05}	4_{14}	5	5			16183.365	-2
		4	3	16185.199	0	16184.270	3
		6	5	16185.248	-6	16184.313	-4
		4	4	16186.378	0	16185.448	0
5_{15}	4_{04}	5	5	16592.668	-2	16590.552	-2
		5	4	16593.416	1	16591.301	0
		6	5	16593.705	2	16591.591	3
		4	3	16593.719	-3		
		4	4	16594.658	0	16592.544	0

6_{24}	5_{33}	5	4	17025.087	2	17031.469	3
		7	6	17025.199	-2	17031.580	-1
		6	5	17025.927	0	17031.302	-2
4_{23}	3_{12}	4	3	17123.737	0	17116.114	-1
		4	4			17116.114	-1
		5	4	17124.576	0	17116.952	1
		3	2	17124.867	0	17117.241	0
3_{31}	2_{20}	3	2	17678.709	-3	17665.846	1
		4	3	17678.907	-2	17666.042	1
		2	1	17679.013	4	17666.140	-1
3_{30}	2_{21}	2	1	17786.786	0	17773.905	0
		4	3	17786.830	2	17773.950	3
		3	2	17786.894	-2	17774.013	-3

[a] Observed minus calculated frequencies in kHz.