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Electronic Supplementary Information for

Direct evidence for a radiation-induced synthesis of acetonitrile and isoacetonitrile from a 1:1 CH_4···HCN complex at cryogenic temperatures: is it a missing link between inorganic and prebiotic astrochemistry?

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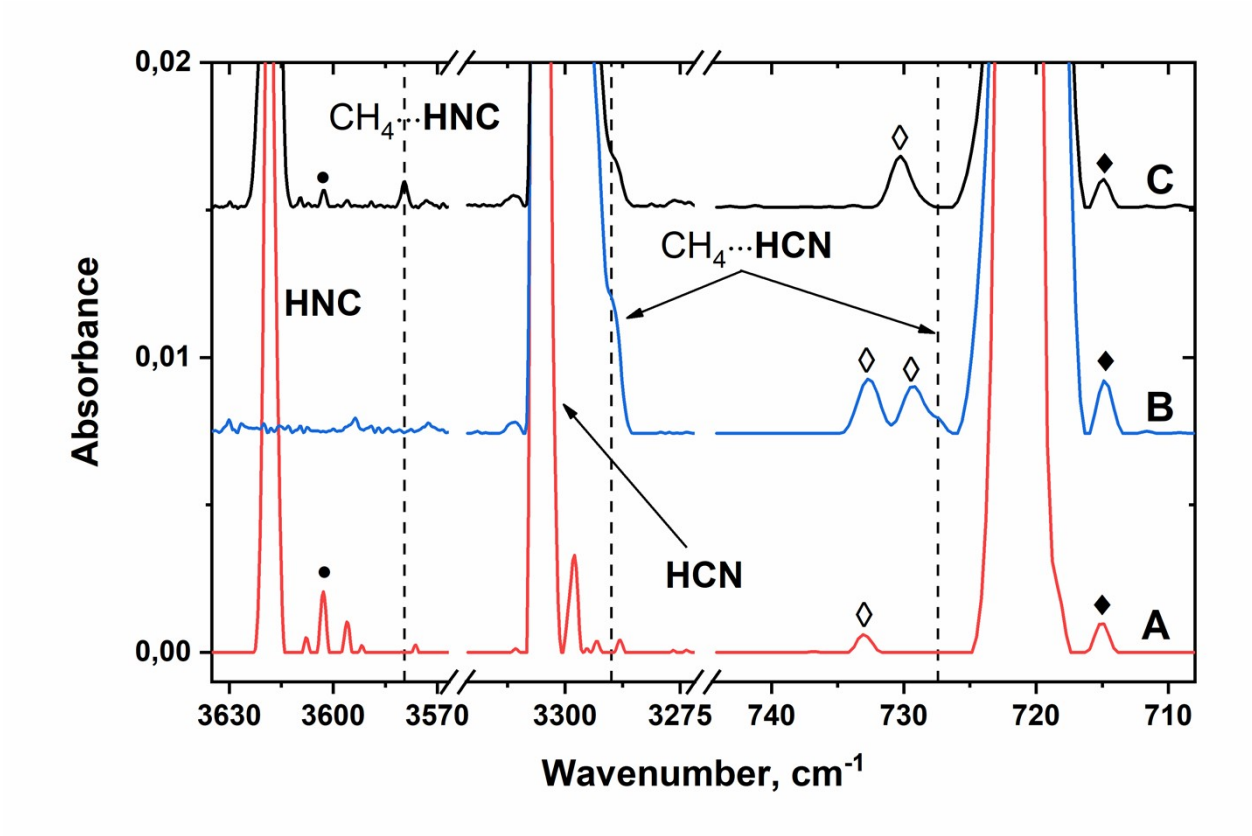

Fig. S1 Fragments of FTIR spectra of the matrix samples: (A) HCN/Ar (1:1000) sample after X-ray irradiation (absorbed dose 110 kGy); (B and C) HCN/CH_4/Ar (1:3:1000) sample before and after X-ray irradiation (absorbed dose 70 kGy), respectively. Absorptions of HCN···H_2O are marked with empty diamonds, absorptions of HCN dimers are marked with filled diamonds, and absorptions of HNC···H_2O are marked with filled circles.

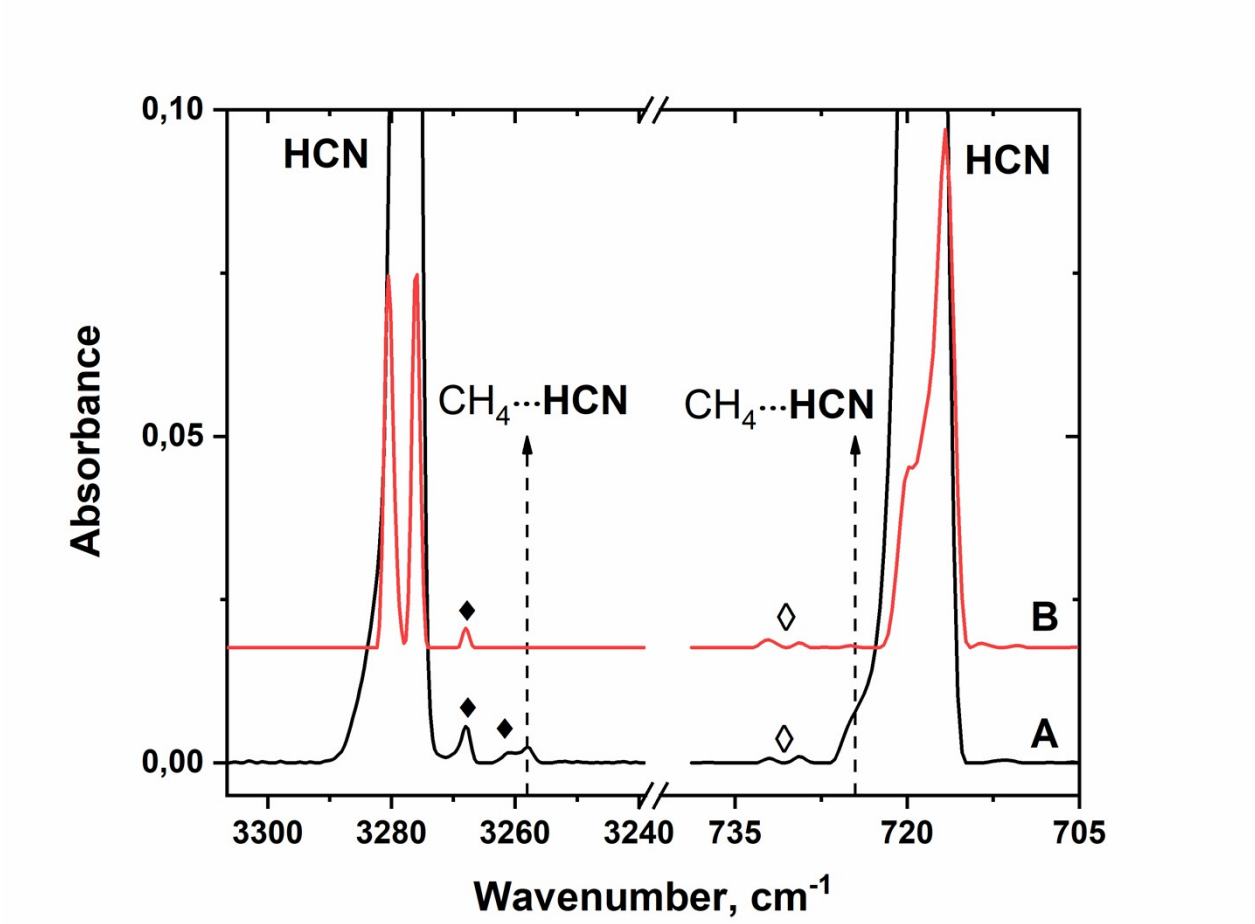

Fig. S2 Fragments of FTIR spectra of the matrix samples: (A) HCN/CH_4/Xe (1:3:1000) and (B) (A) HCN/Xe (1:1000) samples before X-ray irradiation, respectively. Absorptions of HCN···H_2O are marked with empty diamonds, absorptions of HCN dimers are marked with filled diamonds.

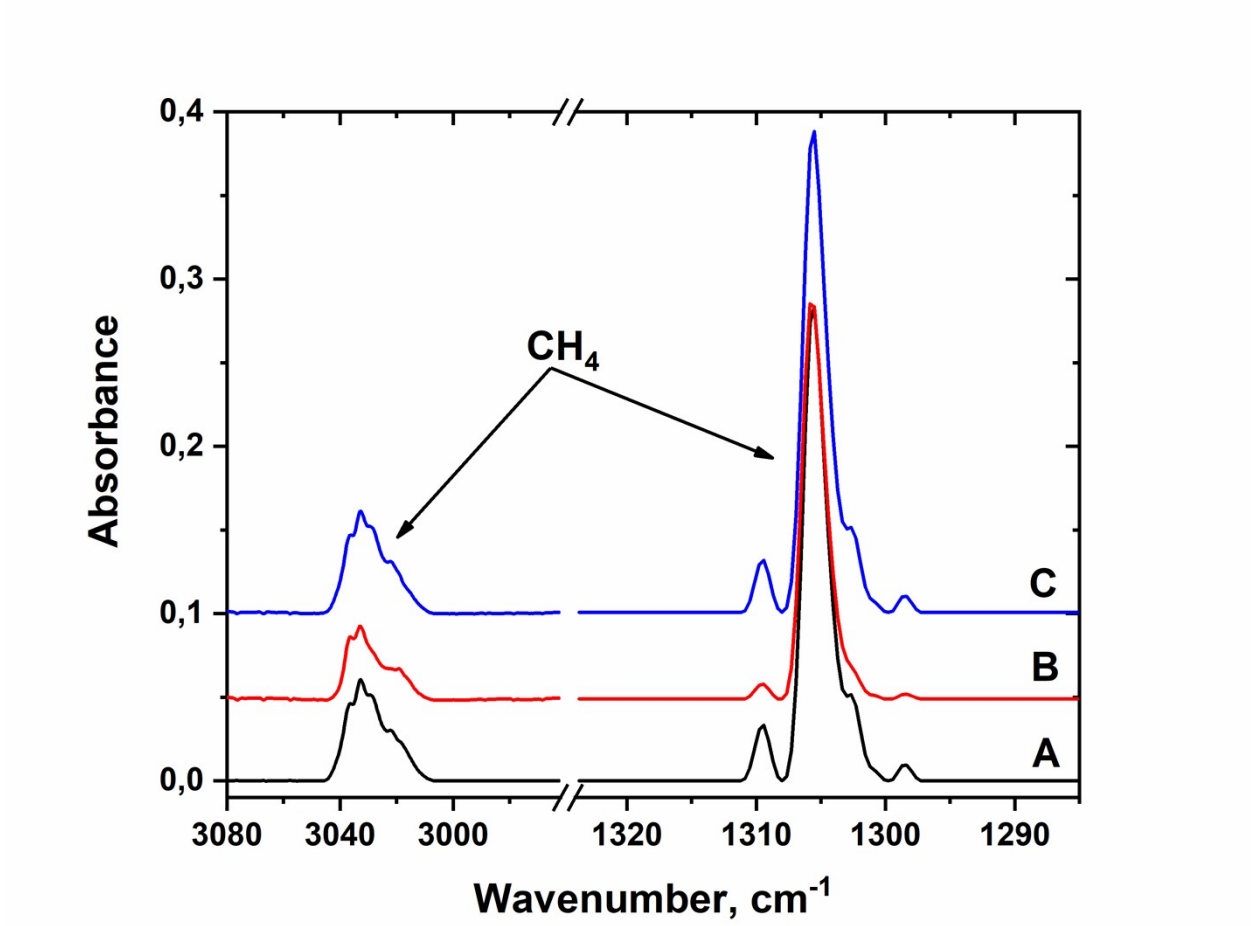

Fig. S3 Fragments of FTIR spectra of the matrix samples illustrating the regions of the CH_4 absorptions: (A) CH_4/Ar (3:1000) sample before X-ray irradiation; (B and C) HCN/CH_4/Ar (1:3:1000) sample after (absorbed dose 230 kGy) and before X-ray irradiation, respectively.

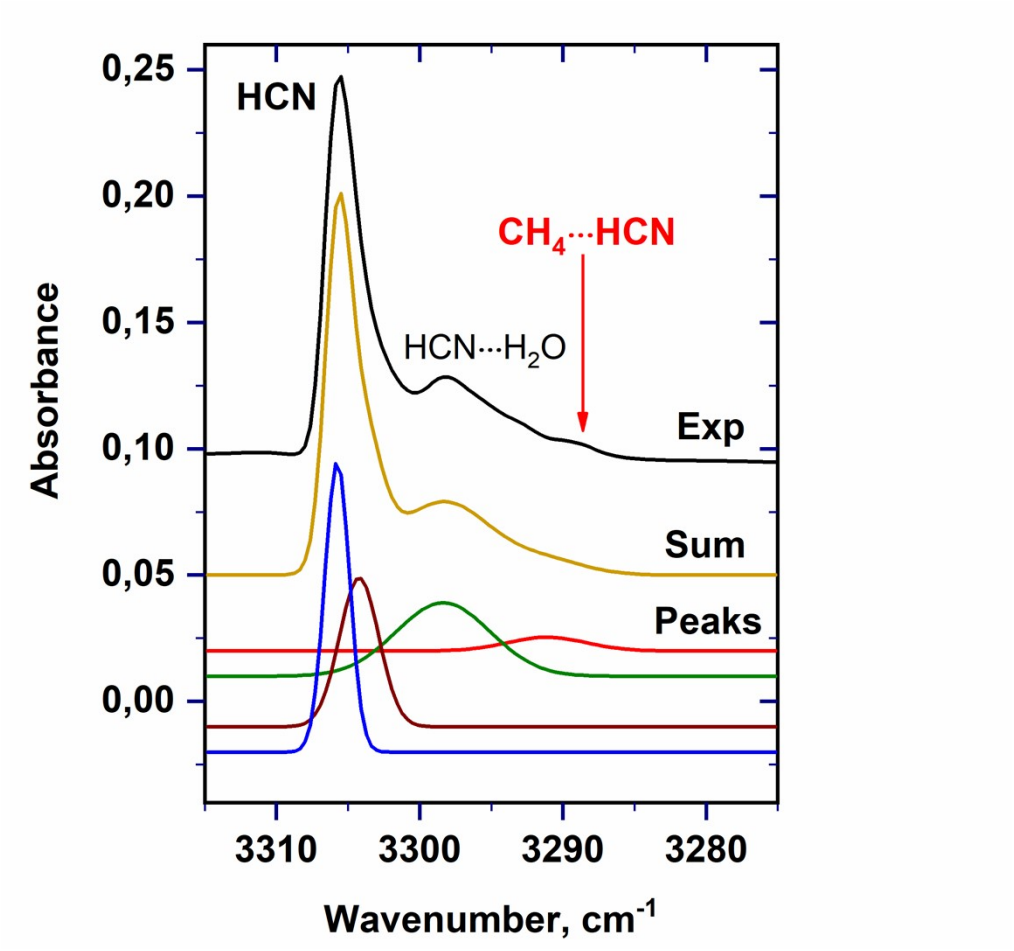

Fig. S4 Deconvoluted fragment of the FTIR spectrum of the deposited HCN/CH_4/Ar sample illustrating the components of the HCN CH stretching absorption band.

Table S1 Optimized molecular geometries (in Angstroms) for the CH_4, HCN, and HNC monomers; CH_4···HCN and CH_4···HNC complexes obtained via MP2/L4a_3 calculations. Symmetry groups are provided in parentheses.

Element	Cartesian coordinates, Å		
	x	y	z
	CH_4 (T_d)		
C	−0.00000048	−0.00000097	0.00000093
H	−1.02719963	0.02441586	0.34540260
H	0.66885911	0.06469421	0.85057660
H	0.17790985	0.83804485	−0.66412629
H	0.18043115	−0.92715395	−0.53185385
	HCN ($C_{\infty v}$)		
C	0.00000000	0.00000000	0.00000000
N	−1.16279490	0.00000000	0.00000000
H	1.06409427	0.00000000	0.00000000
	HNC ($C_{\infty v}$)		
C	0.00000000	0.00000000	0.00000000
N	1.17263600	0.00000000	0.00000000
H	2.16897334	0.00000000	0.00000000
	CH_4···HCN (C_{3v})		
C	−0.41667790	0.82359006	−1.03563258
H	−1.28593719	0.35642401	−0.58461354
H	0.10683703	1.42209367	−0.29739163
H	−0.74212853	1.46695943	−1.84463105
H	0.24711283	0.06349531	−1.43427081
H	0.36717777	−0.72574776	0.91253609
C	0.68715136	−1.35819188	1.70787219
N	1.03646463	−2.04862284	2.57613133
	CH_4···HNC (C_{3v})		
C	−0.37262762	0.63413896	−1.04884712
H	−1.22349605	0.53301769	−0.38213928
H	0.41899572	1.19722331	−0.56410991
H	−0.68782768	1.17057691	−1.93584910
H	−0.00935699	−0.34524234	−1.34472953
H	0.31733371	−0.54003284	0.89318760
C	0.94904371	−1.61509558	2.67132493
N	0.60793521	−1.03458611	1.71116240

Table S2 Optimized molecular geometries (in Angstroms), energies, and zero-point vibrational energies (ZPVE) for the CH_4, HCN, and HNC monomers; CH_4···HCN and CH_4···HNC complexes obtained via L19-PBE96-VV10/L3a_3 calculations. Symmetry groups are provided in parentheses.

Element	Cartesian coordinates, Å			Energy [ZPVE], a.u.
	x	y	z	
			CH_4 (T_d)	
C	0.00000000	0.00000000	0.00000000	−40.46682648 [0.044607]
H	0.62927447	0.62927447	0.62927447	
H	−0.62927447	−0.62927447	0.62927447	
H	0.62927447	−0.62927447	−0.62927447	
H	−0.62927447	0.62927447	−0.62927447	
			HCN ($C_{\infty v}$)	
C	0.00000000	0.00000000	−0.02449369	−93.33300936 [0.016412]
N	0.00000000	0.00000000	1.11992989	
H	0.00000000	0.00000000	−1.09543620	
			HNC ($C_{\infty v}$)	
C	0.00000000	0.00000000	1.10830107	−93.31124792 [0.015852]
N	0.00000000	0.00000000	−0.05427530	
H	0.00000000	0.00000000	−1.05402577	
			CH_4···HCN (C_{3v})	
C	0.00000000	0.00000000	−1.40935679	−133.80130413 [0.061893]
H	1.03190544	0.00000000	−1.05534506	
H	−0.51595272	−0.89365633	−1.05534506	
H	0.00000000	0.00000000	−2.49872528	
H	−0.51595272	0.89365633	−1.05534506	
H	0.00000000	0.00000000	1.26175458	
C	0.00000000	0.00000000	2.33388574	
N	0.00000000	0.00000000	3.47847692	
			CH_4···HNC (C_{3v})	
C	0.00000000	0.00000000	−1.30015706	−133.78040320 [0.061597]
H	1.03406561	0.00000000	−0.95072582	
H	−0.51703280	−0.89552708	−0.95072582	
H	0.00000000	0.00000000	−2.38933416	
H	−0.51703280	0.89552708	−0.95072582	
H	0.00000000	0.00000000	1.12476353	
C	0.00000000	0.00000000	3.28962620	
N	0.00000000	0.00000000	2.12727896	

Table S3 Computed energies (in Hartrees) of the CH_4, HCN, and HNC monomers; CH_4···HCN and CH_4···HNC complexes. E_4^{HF} is HF/L4a_3 energy, $E_{\infty c}^{MP2}$, E_{3c}^{MP2}, and E_{4c}^{MP2} are MP2 correlation energies: extrapolated to the CBS limit, computed using L3a_3, and L4a_3 basis sets, respectively. E_{∞}^{MP2} is extrapolated to the CBS energy. ZPVE is zero-point vibration energy computed at the MP2/L4a_3 level.

Species	E_4^{HF}	E_{3c}^{MP2}	E_{4c}^{MP2}	$E_{\infty c}^{MP2}$	E_{∞}^{MP2}	ZPVE
CH_4	−40.21709709	−0.211989020	−0.215166487	−0.219014283	−40.4361114	0.045416
HCN	−92.91416972	−0.374579629	−0.380486119	−0.387638662	−93.3018084	0.015871
HNC	−92.89987067	−0.360331577	−0.366336168	−0.373607508	−93.2734782	0.015572
CH_4···HCN	−133.1311506	−0.588466710	−0.597494001	−0.608425719	−133.739576	0.062169
CH_4···HNC	−133.1167708	−0.575398877	−0.584511517	−0.595546590	−133.712317	0.062088

Table S4 Harmonic vibrational frequencies (cm^{-1}) and IR intensities ($km\ mol^{-1}$) of the CH_4, HCN, and HNC monomers; CH_4···HCN and CH_4···HNC complexes computed at the MP2/L4a_3 level. IR intensity values are provided including the degeneracy of the vibrational modes.

Mode number	Mode type	**CH_4**		**HCN**		**HNC**		**CH_4···HCN**		**CH_4···HNC**	
		Frequency	Symmetry	Frequency	Symmetry	Frequency	Symmetry	Frequency	Symmetry	Frequency	Symmetry
1, 2	Intermolecular							38.8 (49)	E	60.6 (47)	E
3	Intermolecular							80.0 (0)	A_1	106.0 (1)	A_1
4, 5	Intermolecular							117.4 (2)	E	121.4 (1)	E
6, 7	HCN (HNC) bending			729.8 (71)	Π	492.2 (247)	Π	743.2 (53)	E	532.4 (185)	E
8	degenerate deformation	1349.7 (12)	T_2					1349.8 (22)	A_1	1352.0 (24)	A_1
9, 10	degenerate deformation	1349.8 (23)	T_2					1352.8 (25)	E	1353.7 (25)	E
11, 12	degenerate deformation	1584.9 (0)	E					1587.8 (0)	E	1591.0 (0)	E
13	CN stretching			2038.1 (0)	$\sum^+$	2029.3 (35)	$\sum^+$	2037.2 (1)	A_1	2028.6 (22)	A_1
14	symmetrical stretching	3075.1 (0)	A_1					3067.7 (3)	A_1	3062.8 (6)	A_1
15, 16	degenerate stretching	3213.6 (30)	T_2					3204.3 (21)	E	3198.8 (16)	E
17	degenerate stretching	3213.7 (15)	T_2					3214.1 (14)	A_1	3214.8 (11)	A_1
18	CH (NH) stretching			3468.6 (78)	$\sum^+$	3821.4 (263)	$\sum^+$	3452.0 (160)	A_1	3770.0 (561)	A_1

Table S5 Harmonic vibrational frequencies (cm^{-1}) and IR intensities ($km\ mol^{-1}$) of the CH_4, HCN, and HNC monomers; CH_4···HCN and CH_4···HNC complexes computed at the L19-PBE96-VV10/L3a_3 level. IR intensity values are provided including the degeneracy of the vibrational modes.

Mode number	Mode type	**CH_4**		**HCN**		**HNC**		**CH_4···HCN**		**CH_4···HNC**	
		Frequency	Symmetry	Frequency	Symmetry	Frequency	Symmetry	Frequency	Symmetry	Frequency	Symmetry
1, 2	Intermolecular							40.3 (51)	E	63.1 (42)	E
3	Intermolecular							69.8 (0)	A_1	92.6 (1)	A_1
4, 5	Intermolecular							114.0 (3)	E	127.0 (2)	E
6, 7	HCN (HNC) bending			769.4 (69)	Π	504.9 (253)	Π	783.1 (52)	E	547.2 (191)	E
8	degenerate deformation	1318.1 (16)	T_2					1318.7 (27)	A_1	1321.1 (32)	A_1
9, 10	degenerate deformation	1318.2 (32)	T_2					1322.5 (34)	E	1323.6 (34)	E
11, 12	degenerate deformation	1541.6 (0)	E					1545.2 (0)	E	1547.9 (0)	E
13	CN stretching			2231.4 (2)	$\sum^+$	2136.9 (69)	$\sum^+$	2229.6 (9)	A_1	2138.6 (53)	A_1
14	symmetrical stretching	3041.2 (0)	A_1					3034.6 (3)	A_1	3030.6 (6)	A_1
15, 16	degenerate stretching	3167.1 (32)	T_2					3158.6 (23)	E	3154.3 (18)	E
17	degenerate stretching	3167.2 (16)	T_2					3170.2 (15)	A_1	3170.9 (13)	A_1
18	CH (NH) stretching			3434.0 (69)	$\sum^+$	3811.6 (276)	$\sum^+$	3417.5 (143)	A_1	3758.0 (573)	A_1