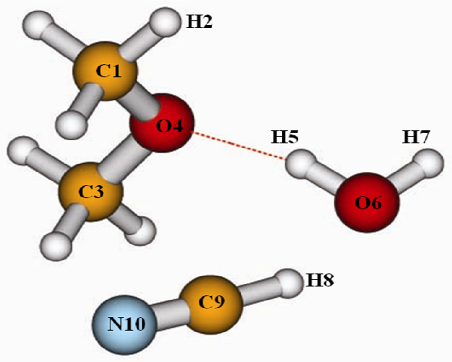
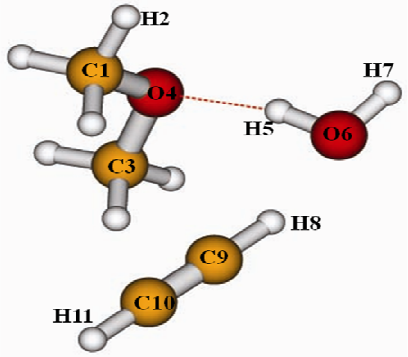
SUPPORTING INFORMATION



1a. HCN-H_2O-DME



1b. H_2C_2-H_2O-DME

Figure S1. Ternary complexes of a) HCN…H_2O…DME b) H_2C_2-H_2O-DME optimized at MP2/aug-cc-pvDZ level of theory.

Table S1. The total energies (a.u), bond lengths (Å), harmonic frequencies (cm^{-1}) and intensities (km/mol) of the clusters given in the main text (Figs. 2a-f) and above (Fig.1a-b) optimized by B3LYP and MP2 levels with aug-cc-pvDZ basis sets. The labeling of atoms in the Table is represented in Fig. 2a-f in the main text and in Fig 1a-b shown above.

System	method	Total Energy (a.u.)	Bond lengths (Å)	Freqs (cm^{-1}) (intensity, km/mol)
H_2O	B3LYP	-76.44464	0.964 O-H	3904 (60) (O-H) asym 3794 (4) (O-H) sym
	MP2	-76.26090	0.965 O-H	3937 (67) (O-H) asym 3803 (4) (O-H) sym
DME	B3LYP	-155.04602	1.415 C1-O4 2.354 C1-C3 1.096 C1-H2	3017 (130) (C-H) asym 2976 (66) (C-H) sym 1184 (102) (C-O) asym 934 (35) (C-O) sym
	MP2	-154.59160	1.423 C1-O4 2.341 C1-C3 1.097 C1-H2	3084 (108) (C-H) asym 3020 (58) (C-H) sym 1188 (96) (C-O) asym 939 (34) (C-O) sym
EO	B3LYP	-153.80949	1.438 C1-O4 1.470 C1-C3 1.092 C1-H2	3196 (40) (C-H) asym 3093 (35) (C-H) sym 831 (10) (C-O) asym 880 (71) (C-O) sym
	MP2	-153.37498	1.453 C1-O4 1.475 C1-C3 1.093 C1-H2	3266 (27) (C-H) asym 3148 (25) (C-H) sym 809 (7) (C-O) asym 879 (68) (C-O) sym
TMO	B3LYP	-193.13115	1.453 C1-O4 2.086 C1-C3 1.070 C1-H2	3070 (68) (C-H) asym 3023 (159) (C-H) sym 1020 (95) (C-O) asym 918 (32) (C-O) sym
	MP2	-192.56496	1.465 C1-O4 2.073 C1-C3 1.100 C1-H2	3145 (32) (C-H) asym 3064 (105) (C-H) sym 1004 (72) (C-O) asym 915 (26) (C-O) sym
THF	B3LYP	-232.47891	1.428 C1-O4 2.279 C1-C3 1.105 C1-H2	3123 (68) (C-H) asym 2980 (103) (C-H) sym 1092 (79) (C-O) asym 933 (28) (C-O) sym

	MP2	-231.78541	1.438 C1-O4 2.271 C1-C3 1.106 C1-H2	3173 (54) (C-H) asym 3034 (66) (C-H) sym 1094 (71) (C-O) asym 932 (22) (C-O) sym
HCN	B3LYP	-93.43705	1.156 C1-N3 1.074 C1-H2	2186 (1.5) (C-N) 3450 (67) (C-H)
	MP2	-93.18365	1.182 C1-N3 1.077 C1-H2	1990 (0.5) (C-N) 3456 (74) (C-H)
C_2H_2 (acetylene)	B3LYP	-77.33850	1.209 C1-C3 1.070 C1-H2	2062 (0) (C-C) sym 3417 (95) (C-H) asym 3521 (0) (C-H) sym
	MP2	-77.09299	1.231 C1-C3 1.075 C1-H2	1946 (0) (C-C) sym 3431 (93) (C-H) asym 3518 (0) (C-H) sym
DME…H_2O	B3LYP	-231.49887	1.422 C1-O4 2.368 C1-C3 1.095 C1-H2 1.892 O4…H5 0.975 O6-H5 0.963 O6-H7	3871 (87) (O-H) asym 3624 (479) (O-H) sym 3047 (96) (C-H) asym 2996 (64) (C-H) sym 1175 (83) (C-O) asym 923 (49) (C-O) sym
	MP2	-230.86344	1.432 C1-O4 2.354 C1-C3 1.097 C1-H2 1.872 O4…H5 0.976 O6-H5 0.964 O6-H7	3895 (104) (O-H) asym 3626 (395) (O-H) sym 3113 (74) (C-H) asym 3037 (47) (C-H) sym 1175 (74) (C-O) asym 923 (39) (C-O) sym
EO…H_2O	B3LYP	-230.26272	1.446 C1-O4 1.469 C1-C3 1.091 C1-H2 1.905 O4…H5 0.974 O6-H5 0.963 O6-H7	3876 (88) (O-H) asym 3626 (383) (O-H) sym 3217 (19) (C-H) asym 3108 (22) (C-H) sym 814 (11) (C-O) asym 874 (83) (C-O) sym
	MP2	-229.64741	1.463 C1-O4 1.474 C1-C3 1.092 C1-H2 1.888 O4…H5 0.976 O6-H5 0.964 O6-H7	3898 (102) (O-H) asym 3631 (325) (O-H) sym 3281 (11) (C-H) asym 3158 (15) (C-H) sym 793 (8) (C-O) asym 871 (76) (C-O) sym
TMO…H_2O	B3LYP	-269.58551	1.462 C1-O4 2.094 C1-C3 1.098 C1-H2 1.848 O4…H5 0.977 O6-H5 0.963 O6-H7	3871 (78) (O-H) asym 3572 (548) (O-H) sym 3097 (36) (C-H) asym 3089 (26) (C-H) sym 1002 (87) (C-O) asym 913 (45) (C-O) sym
	MP2	-268.83863	1.475 C1-O4 2.084 C1-C3 1.102 C1-H2 1.828 O4…H5 0.979 O6-H5 0.964 O6-H7	3893 (93) (O-H) asym 3572 (470) (O-H) sym 3199 (24) (C-H) asym 3083 (76) (C-H) sym 990 (48) (C-O) asym 908 (31) (C-O) sym
THF-H_2O	B3LYP	-308.93221	1.437 C1-O4 2.292 C1-C3 1.103 C1-H2 1.889 O4…H5 0.975 O6-H5 0.963 O6-H7	3871 (90) (O-H) asym 3611 (566) (O-H) sym 3129 (57) (C-H) asym 3008 (58) (C-H) sym 1077 (76) (C-O) asym 921 (47) (C-O) sym
	MP2	-308.05966	1.460 C1-O4 2.362 C1-C3 1.101 C1-H2	3890 (91) (O-H) asym 3572 (446) (O-H) sym 3170 (34) (C-H) asym

			1.830 O4…H5 0.978 O6-H5 0.964 O6-H7	3052 (63) (C-H) sym 1069 (85) (C-O) asym 892 (23) (C-O) sym
HCN-H_2O (HCN is proton donor)	B3LYP	-169.88980	1.157 C1-N3 1.083 C1-H2 0.964 O4-H5 2.035 O4…H2	3904 (85) (O-H) asym 3797 (14) (O-H) sym 2172 (39) (C-N) 3322 (376) (C-H)
	MP2	-169.45358	1.183 C1-N3 1.085 C1-H2 0.965 O4-H5 2.049 O4…H2	3933 (91) (O-H) asym 3802 (13) (O-H) sym 1989 (9) (C-N) 3352 (362) (C-H)
C_2H_2-H_2O (C_2H_2 is proton donor)	B3LYP	-153.78765	1.070 C1-H2 1.210 C1-C3 1.076 C3-H4 0.964 O5-H6 2.191 O5…H4	3906 (73) (O-H) asym 3798 (9) (O-H) sym 2051 (11) (C-C) 3371 (273) (C-H) asym 3498 (1.4) (C-H) sym
	MP2	-153.35965	1.074 C1-H2 1.232 C1-C3 1.080 C3-H4 0.965 O5-H6 2.173 O5…H4	3935 (80) (O-H) asym 3802 (9) (O-H) sym 1938 (8) (C-C) 3390 (262) (C-H) asym 3497 (1.0) (C-H) sym
HCN-H_2O-DME	B3LYP	-324.94735	1.425 C1-O4 2.374 C1-C3 1.095 C1-H2 1.803 O4…H5 0.979 O6-H5 0.962 O6-H7 1.939 O6…H8 1.089 C9-H8 1.157 C9-N10	3874 (92) (O-H) free 3527 (751) (O-H) bound 3057 (87) (C-H) asym 3003 (60) (C-H) sym 1097 (60) (C-O) asym 920 (51) (C-O) sym 2162 (71) (C-N) 3242 (558) (C-H) of HCN
	MP2	-324.06105	1.433 C1-O4 2.362 C1-C3 1.097 C1-H2 1.800 O4…H5 0.980 O6-H5 0.964 O6-H7 1.994 O6…H8 1.087 C9-H8 1.183 C9-N10	3898 (108) (O-H) free 3552 (580) (O-H) bound 3121 (56) (C-H) asym 3042 (47) (C-H) sym 1101 (56) (C-O) asym 924 (43) (C-O) sym 1985 (8) (C-N) 3317 (274) (C-H) of HCN
C_2H_2-H_2O-DME	B3LYP	-308.84361	1.424 C1-O4 2.371 C1-C3 1.095 C1-H2 1.843 O4…H5 0.977 O6-H5 0.962 O6-H7 2.106 O6…H8 1.079 C9-H8 1.211 C9-C10 1.070 C10-H11	3877 (88) (O-H) free 3570 (602) (O-H) bound 3054 (93) (C-H) asym 3001 (58) (C-H) sym 1098 (58) (C-O) asym 921 (47) (C-O) sym 2045 (18) (C-C) of H_2C_2 3336 (346) (C-H) asym of H_2C_2 3490 (1.9) (C-H) sym of H_2C_2
	MP2	-307.96657	1.434 C1-O4 2.359 C1-C3 1.097 C1-H2 1.812 O4…H5 0.980 O6-H5 0.964 O6-H7 2.088 O6…H8 1.082 C9-H8 1.233 C9-C10 1.074 C10-H11	3894 (99) (O-H) free 3553 (543) (O-H) bound 3119 (56) (C-H) asym 3040 (48) (C-H) sym 1175 (65) (C-O) asym 921 (39) (C-O) sym 1930 (7) (C-C) of H_2C_2 3353 (253) (C-H) asym of H_2C_2 3488(5.6) (C-H) sym of H_2C_2

Table S2. Comparison of classical and nonclassical infrared-band frequencies for CHs of ethers with HCN, SO_2 and C_2H_2 as sc guests.

CH type	Ether lc	Guest sc	Classical sc (cm^{-1})	Non-Classical sc (cm^{-1})	Classical lc (cm^{-1})	Non-Classical lc (cm^{-1})
s-II	THF				1073 cm^{-1}	1054 cm^{-1}
		HCN	2093 cm^{-1}	2085 cm^{-1}		
	THF				1072	1055
"		SO_2	1348	1338		
			1153	?		
"	THF				1073	?
		C_2H_2	3278	3254		
	THF				1073	1054
"		HCN &	2093	2085		
		CO_2	2346	2345		
s-I	TMO				~985	~975
		HCN	2091	2086		
s-II	TMO				988	974
		HCN	2093	2086		
s-II	DME					918
					1096	1090
					1170	1166
					2808	2826
		HCN	~2092	2083		
	DME				929	~918: broad
"					1096	broadened
					1170	broadened
					2808	~2826: broad
		H_2S	2603/2614	?		
	DME				928	~918: broad
"					1096	broadened
					1170	broadened
					2808	~2826: broad
		CO_2	2346 (H_20)			
"	DME				928	918
					1096	1090
					1170	1165
					2808	2824
		C_2H_2	3280	~3253		
s-II	Acetone				1720	1705
		HCN	2092	2085		
s-I	EO		1281		872	864
					1268	broadened
		HCN	2093	~2085		