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

Electronic Supporting Information

Infrared Spectroscopic Study of Trifluoromethoxybenzene···Methanol Complexes Formed in Superfluid Helium Nanodroplets

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1. Mass spectra

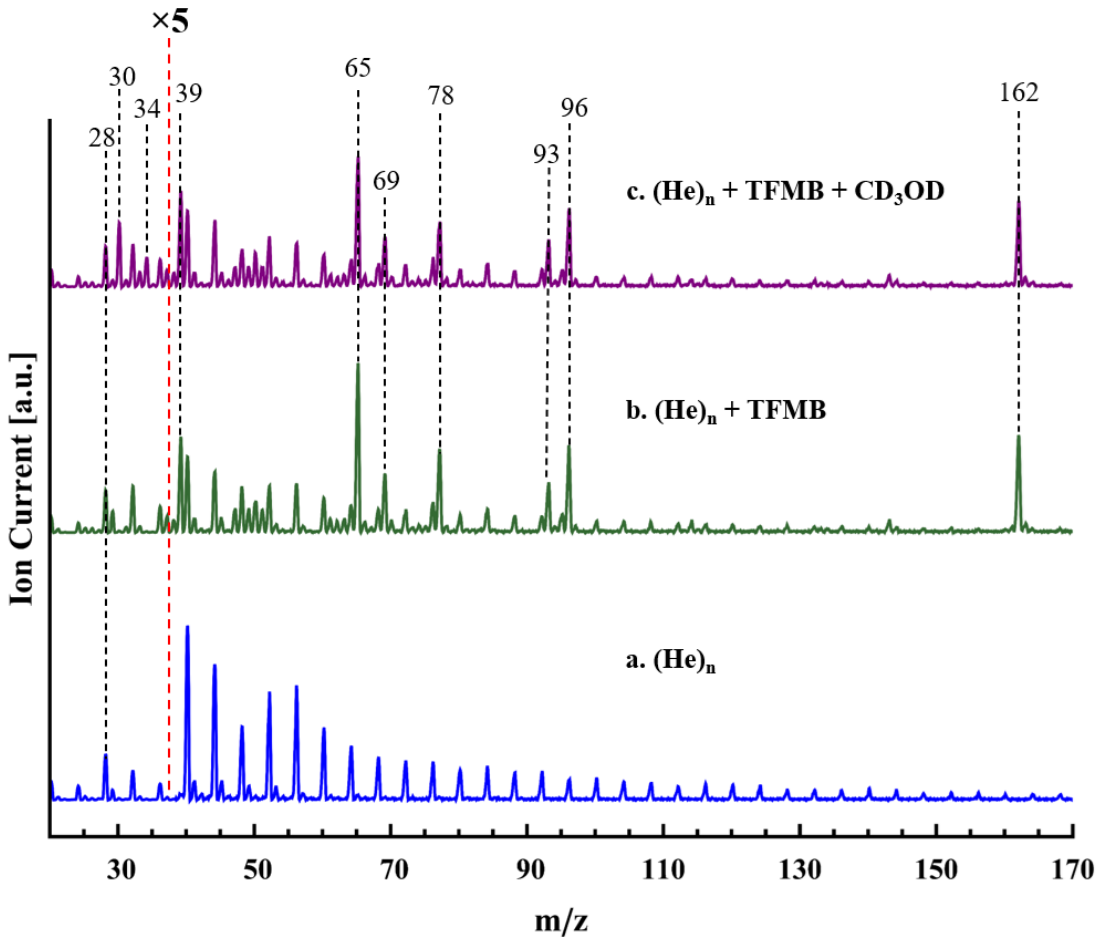


Fig. S1: Mass spectra of a) pure helium cluster beam b) the droplet beam doped with TFMB and c) the droplet beam doped with TFMB and methanol.

The observed mass spectra of neat helium droplet beam, droplets doped with TFMB, and droplets doped with TFMB, and methanol molecules are shown in Fig. S1. The mass spectrum of pure helium droplet beam reveals that the emerging peaks are separated by m/z=4, attributing to the formation of helium clusters, $(He)_n^+$, Fig S1. a. The peak at m/z= 28 corresponds to the He_7^+ cluster and residual nitrogen in the experimental setup.

The addition of TFMB in the first pickup chamber causes additional peaks at m/z= 39 $(C_3H_3)^+$, 65 $(C_5H_5)^+$, 69 $(C_5H_9)^+$, 78 $(C_6H_6)^+$, 93 $(C_6H_5O)^+$, 96 $(C_6H_7O)^+$ and 162 $(C_6H_5OCF_3)^+$ correspond to the fragments obtained from TFMB moleucle or clusters (Fig S1.b).

The addition of the CD_3OD in the second pickup chamber leads to the pickup of the CD_3OD molecule in TFMB dropped droplets. Thus, the mass spectrum obtained for TFMB and CD_3OD doped droplets exhibits the peaks that correspond to the mass fragments of TFMB and CD_3OD (Fig S1. c). The resulting mass spectrum shows new peaks at m/z = 30 and 34 which are attributed to the $(DCO)^+$ and $(CD_3O)^+$ fragments, respectively.

2. IR spectra of TFMB

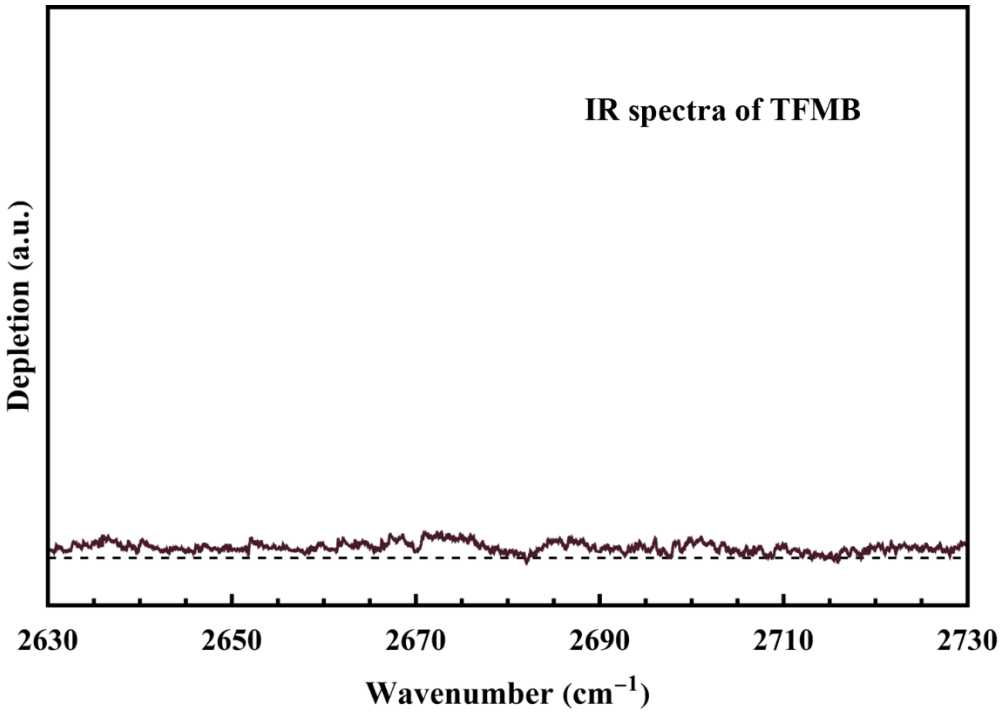


Fig. S2: Depletion IR spectra of pure TFMB measured at m/z ≥ 22 in the O-D stretch range.

3. Molecular electrostatic potential (MEP) surfaces of anisole and TFMB

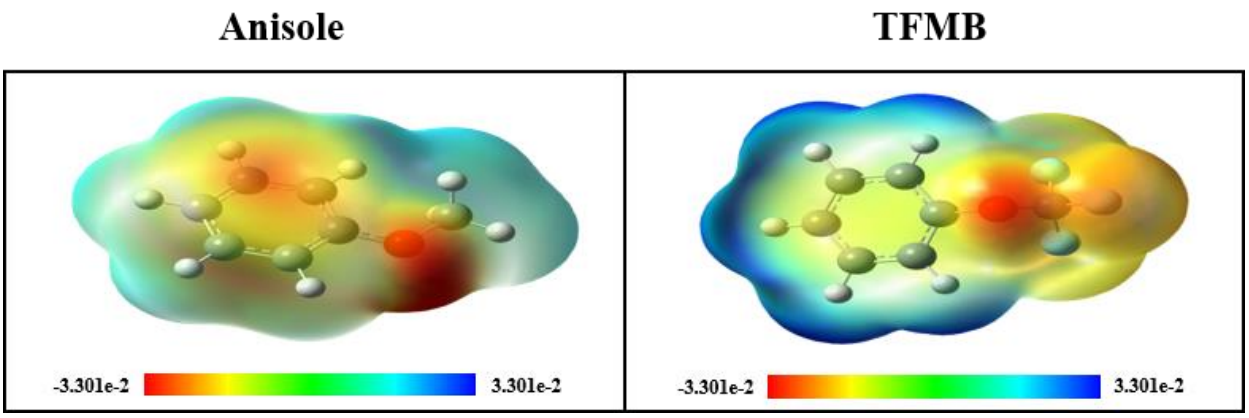


Fig. S3 Molecular electrostatic potential (MEP) surfaces of anisole and TFMB calculated at MP2/6-311++G (d,p) level of theory. The color bar at the bottom describes the magnitude of the MEPs in the atomic unit. The blue and red shades around the molecules suggest the electropositive and electronegative regions, respectively.

4. Natural bond orbital (NBO) analysis

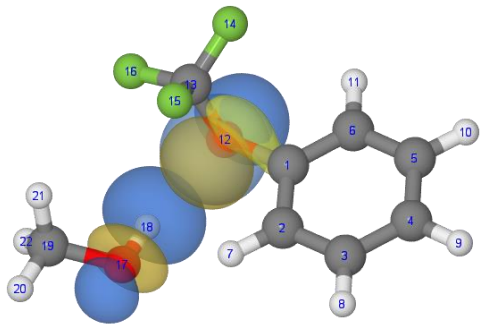
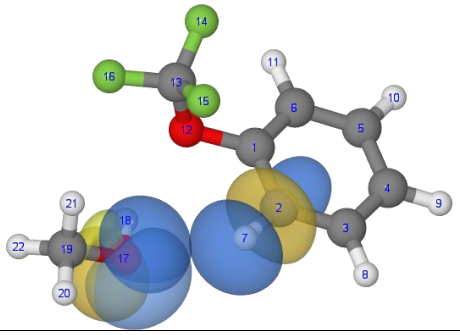
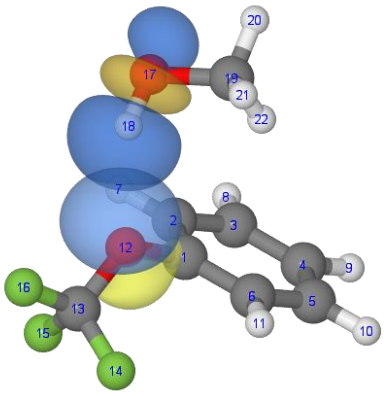
Table S1 Occupancy of the oxygen lone pair of electrons (n-type and p-type) of anisole and TFMB obtained by NBO analysis.

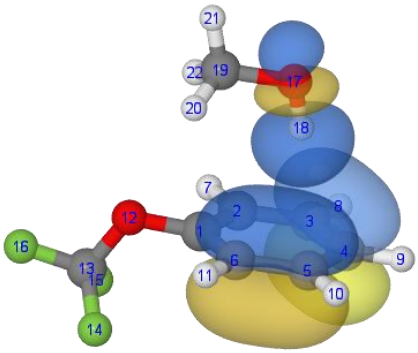
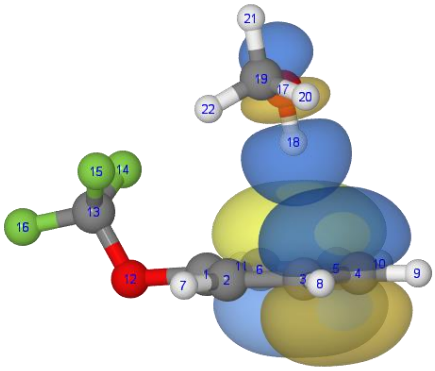
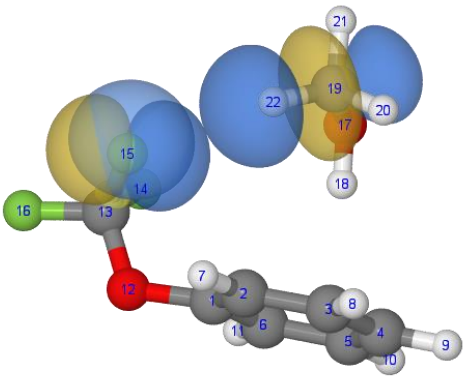
	Lone pair on ether oxygen	Occupancy of lone pair orbital
Anisole	O_{12} (n_σ)	1.97178
	O_{12} (n_p)	1.89406
TFMB	O_{12} (n_σ)	1.94748
	O_{12} (n_p)	1.91830

Table S2. Second-order perturbation energy $\boldsymbol{E_{i\rightarrow j^*}}$ values for different type interactions in TFMB-methanol complexes calculated at the MP2/6-311++G (d,p) level of theory

Conformer	**Interaction**	**Donor (i)**	**Acceptor(j*)**	**$E^2_{i\rightarrow j^*}$ (Kcal/mol)**
Structure I	O-H···O	O_{12} (n_σ)	O_{17}-H_{18} (σ^*)	0.92
		O_{12} (n_p)	O_{17}-H_{18} (σ^*)	0.76
	C–H···O	O_{17} (n_σ)	C_2-H_7(σ^*)	0.60
		O_{17} (n_p)	C_2-H_7(σ^*)	0.64
Structure II	O-H···O	O_{12} (n_σ)	O_{17}-H_{18} (σ^*)	2.01
Structure III	O–H···π	C_3=C_4	O_{17}-H_{18} (σ^*)	0.31
		C_5=C_6	O_{17}-H_{18} (σ^*)	0.09
Structure IV	O–H···π	C_5=C_6	O_{17}-H_{18} (σ^*)	0.43
		C_3=C_4	O_{17}-H_{18} (σ^*)	0.20
	C–H···F	F_{15} (n_σ)	C_{19}-H_{22}(σ^*)	0.28

Table S3: NBO view showing the overlaps between donor and acceptor orbital of different H-bond in TFMB-methanol complexes. The Second-order perturbation energy $\boldsymbol{E_{i\rightarrow j*}}$ values also provided for different intermolecular interactions.

Structure I	**O-H···O H-bonding** O_{12} (n_σ) → O_{17}-H_{18} (σ^*) O_{12} (n_p) → O_{17}-H_{18} (σ^*) $E^2_{i\rightarrow j^*}$ = 7.02 kJ/mol	
	C-H···O H-bonding O_{17} (n_σ) → C_2-H_7 (σ^*) O_{17} (n_p) → C_2-H_7 (σ^*) $E^2_{i\rightarrow j^*}$ = 5.18 kJ/mol	
Structure II	**O-H···O H-bonding** O_{12} (n_σ) → O_{17}-H_{18} (σ^*) $E^2_{i\rightarrow j^*}$ = 8.40 kJ/mol	

Structure III	**O-H··· π H-bonding** $C_3=C_4 \rightarrow O_{17}\text{-}H_{18}$ (σ*) $C_5=C_6 \rightarrow O_{17}\text{-}H_{18}$ (σ*) $E^2_{i \rightarrow j^*}$ = 1.67 kJ/mol	
Structure IV	**O-H··· π H-bonding** $C_5=C_6 \rightarrow O_{17}\text{-}H_{18}$ (σ*) $C_3=C_4 \rightarrow O_{17}\text{-}H_{18}$ (σ*) $E^2_{i \rightarrow j^*}$ = 2.63 kJ/mol	
	C-H···F H-bonding F_{15} (n_σ) → $C_{19}\text{-}H_{22}$ (σ*) $E^2_{i \rightarrow j^*}$ = 1.17 kJ/mol	

5. Optimized structurs with intramolecular C-H···F distences

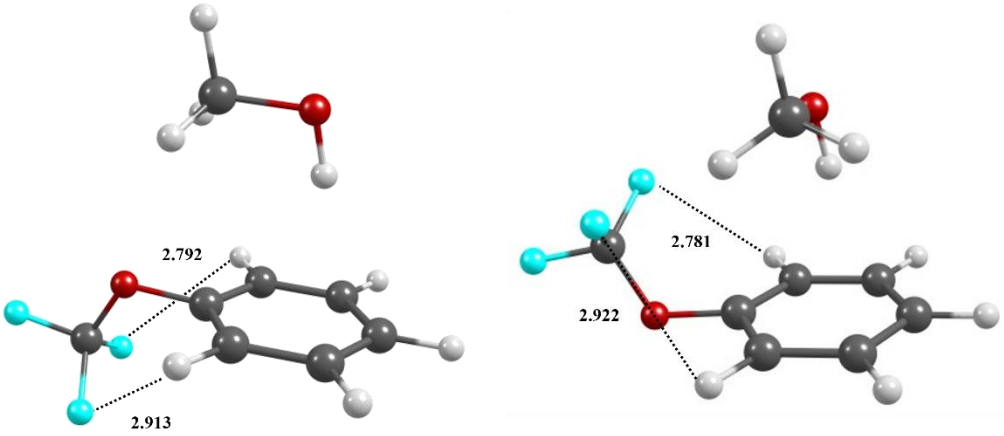
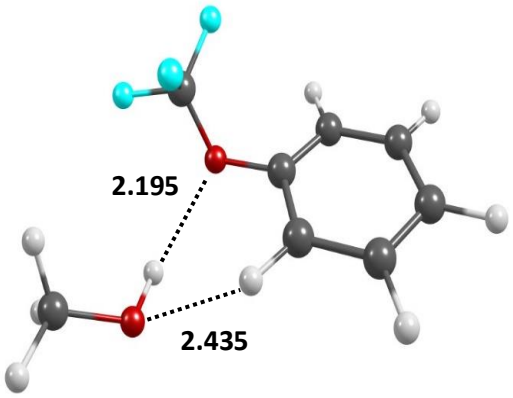


Fig. S4: Optimized structure of Structure III and Structure IV calculated at MP2/6-311++G(d,p) level of theory. The C-H···F intramolecular interactions are shown by dotted lines and the corresponding distances are given in Å.

6. Cartesian coordinates for the optimized molecular geometries

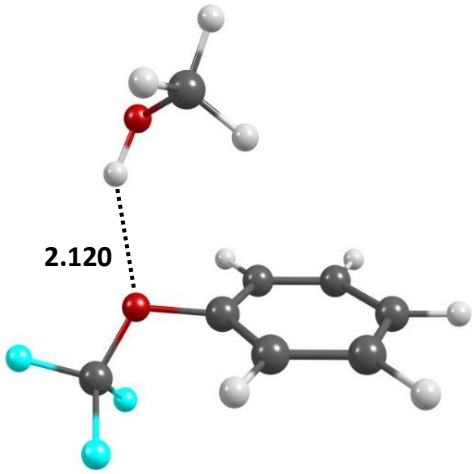
Structure I

Atom label	Atom	x (Å)	y (Å)	z (Å)
1	C	-0.90428	0.01331	-0.34645
2	C	-1.03743	1.24982	0.28248
3	C	-2.32783	1.70650	0.57420
4	C	-3.44774	0.94289	0.22237
5	C	-3.28216	-0.28945	-0.42154
6	C	-1.99976	-0.76090	-0.72518
7	H	-0.15017	1.82518	0.52883
8	H	-2.45492	2.66743	1.06443
9	H	-4.44589	1.30549	0.45048
10	H	-4.14949	-0.87907	-0.70427
11	H	-1.84671	-1.70714	-1.23350
12	O	0.39691	-0.41820	-0.69220
13	C	0.95916	-1.30579	0.16167
14	F	0.32052	-2.48436	0.17622
15	F	0.99303	-0.85871	1.42238
16	F	2.20931	-1.51092	-0.24846
17	O	2.07189	2.07439	-0.43686
18	H	1.75776	1.29219	-0.90041
19	C	3.44230	1.85630	-0.12087
20	H	3.79410	2.75144	0.39282
21	H	3.57569	0.99515	0.54342
22	H	4.04968	1.70941	-1.02102



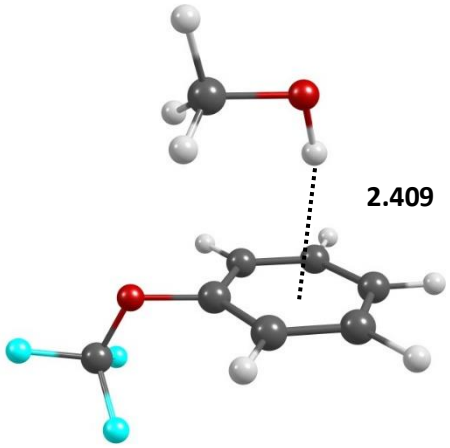
Structure II

Atom label	Atom	x (Å)	y (Å)	z (Å)
1	C	-0.35952	0.31019	-0.01759
2	C	-1.07639	0.27623	-1.21115
3	C	-2.34118	0.87317	-1.24607
4	C	-2.86631	1.48233	-0.09943
5	C	-2.12578	1.49690	1.08901
6	C	-0.86309	0.89529	1.14334
7	H	-0.65154	-0.21998	-2.07781
8	H	-2.91638	0.85483	-2.16722
9	H	-3.84920	1.94350	-0.13154
10	H	-2.53442	1.96293	1.98108
11	H	-0.28110	0.87821	2.05880
12	O	0.86744	-0.38510	0.02621
13	C	1.98834	0.37619	-0.02562
14	F	2.11923	1.17033	1.04786
15	F	2.01676	1.16539	-1.10579
16	F	3.02781	-0.44737	-0.06673
17	O	-0.38175	-3.06225	-0.39967
18	H	0.30678	-2.41281	-0.23015
19	C	-1.31004	-2.96774	0.67215
20	H	-2.06293	-3.74019	0.50901
21	H	-0.83609	-3.14630	1.64485
22	H	-1.81115	-1.99220	0.69451



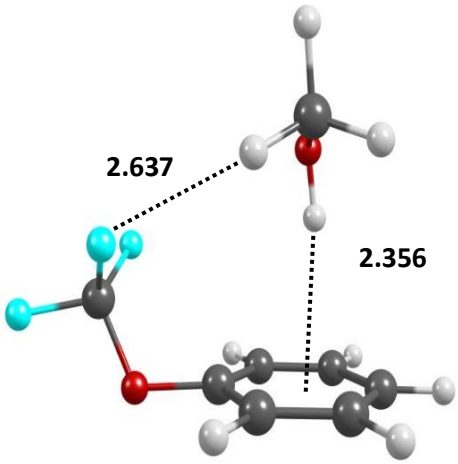
Structure III

Atom label	Atom	x (Å)	y (Å)	z (Å)
1	C	-0.05668	-0.20670	-0.02093
2	C	-0.58934	-0.59299	1.20907
3	C	-1.70618	-1.43741	1.22059
4	C	-2.28046	-1.86707	0.01663
5	C	-1.73398	-1.45560	-1.20649
6	C	-0.61673	-0.61228	-1.23211
7	H	-0.13361	-0.23952	2.12843
8	H	-2.13265	-1.74841	2.16981
9	H	-3.15094	-2.51628	0.03154
10	H	-2.18138	-1.78125	-2.14105
11	H	-0.17880	-0.27395	-2.16589
12	O	1.01041	0.70673	-0.04634
13	C	2.24584	0.15555	-0.00104
14	F	2.47274	-0.67750	-1.02797
15	F	2.45447	-0.54559	1.12436
16	F	3.12924	1.14319	-0.05295
17	O	-3.09345	1.66765	0.01768
18	H	-2.75272	0.76885	0.01606
19	C	-1.97185	2.54040	-0.01036
20	H	-1.36642	2.40416	-0.91440
21	H	-2.36533	3.55778	-0.00428
22	H	-1.32574	2.40908	0.86573



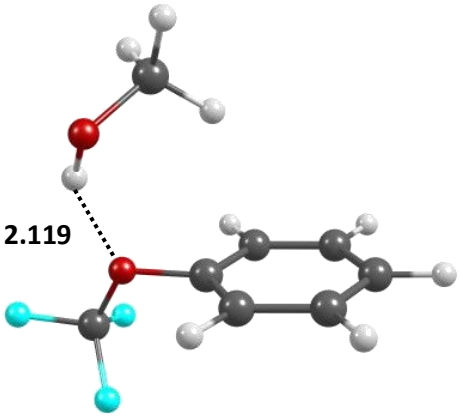
Structure IV

Atom label	Atom	x (Å)	y (Å)	z (Å)
1	C	0.05594	-1.05346	0.23445
2	C	0.80515	-0.69489	1.35505
3	C	2.20015	-0.64720	1.24550
4	C	2.82492	-0.97277	0.03437
5	C	2.05204	-1.34285	-1.07519
6	C	0.65600	-1.39442	-0.97846
7	H	0.29777	-0.45710	2.28472
8	H	2.79656	-0.36920	2.10991
9	H	3.90748	-0.93762	-0.04587
10	H	2.53367	-1.60135	-2.01377
11	H	0.03804	-1.68176	-1.82282
12	O	-1.33668	-1.16513	0.36479
13	C	-2.04169	-0.06262	0.01165
14	F	-1.86918	0.26752	-1.27391
15	F	-1.70522	1.01117	0.74414
16	F	-3.32604	-0.32678	0.21476
17	O	1.30408	2.05805	-0.99676
18	H	1.49399	1.13297	-0.81884
19	C	1.33014	2.73474	0.25207
20	H	2.30079	2.63289	0.75323
21	H	1.15836	3.79132	0.04167
22	H	0.54196	2.37991	0.92542



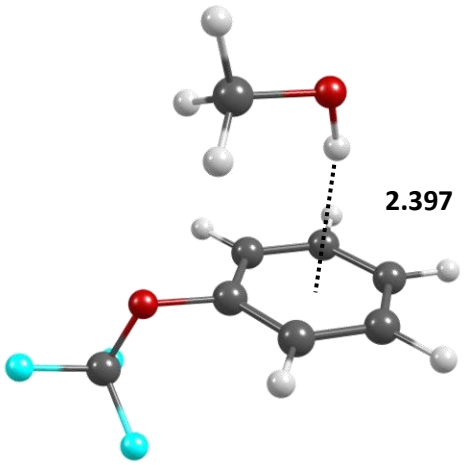
Structure IIA

Atom label	Atom	x (Å)	y (Å)	z (Å)
1	C	-0.35951	-0.31021	-0.01724
2	C	-0.86327	-0.89545	1.143523
3	C	-2.12596	-1.49705	1.088883
4	C	-2.86623	-1.48232	-0.09974
5	C	-2.34087	-0.87306	-1.24623
6	C	-1.0761	-0.2761	-1.21099
7	H	-0.28141	-0.8785	2.059069
8	H	-2.53478	-1.96319	1.9808
9	H	-3.84912	-1.94348	-0.13209
10	H	-2.9159	-0.85464	-2.16749
11	H	-0.65106	0.220207	-2.07749
12	O	0.867446	0.385117	0.026947
13	C	1.988299	-0.37617	-0.02561
14	F	2.016712	-1.16431	-1.10653
15	F	2.119087	-1.17137	1.047129
16	F	3.027822	0.44737	-0.06588
17	O	-0.38194	3.062081	-0.39985
18	H	0.306625	2.412675	-0.23031
19	C	-1.30993	2.967845	0.672271
20	H	-2.06297	3.740131	0.509071
21	H	-1.8109	1.992242	0.695124
22	H	-0.83573	3.146813	1.644774



Structure IIIA

Atom label	Atom	x (Å)	y (Å)	z (Å)
1	C	-0.05726	0.206583	0.007657
2	C	-0.61816	0.560553	-1.21936
3	C	-1.73475	1.405797	-1.22795
4	C	-2.27991	1.868309	-0.02245
5	C	-1.7048	1.489182	1.19777
6	C	-0.58848	0.645012	1.22045
7	H	-0.18223	0.182906	-2.13888
8	H	-2.1815	1.693937	-2.17516
9	H	-3.14984	2.518341	-0.03427
10	H	-2.13126	1.838704	2.133435
11	H	-0.1311	0.33014	2.152982
12	O	1.009558	-0.70744	0.024912
13	C	2.245161	-0.15556	-0.00277
14	F	2.473908	0.643111	1.051089
15	F	2.452551	0.58223	-1.10443
16	F	3.128239	-1.14471	0.016482
17	O	-3.09175	-1.66841	0.031425
18	H	-2.75665	-0.77734	-0.10188
19	C	-1.97015	-2.54164	0.035081
20	H	-1.29979	-2.34668	0.880479
21	H	-2.3617	-3.55564	0.127012
22	H	-1.39065	-2.47269	-0.89326



Methanol dimer

Atom label	Atom	x (Å)	y (Å)	z (Å)
1	C	-2.16539	-0.38606	-0.24840
2	H	-1.63125	-1.01398	-0.96047
3	H	-2.47473	-1.00212	0.60120
4	H	-3.04778	0.03715	-0.73744
5	O	-1.25240	0.63929	0.15090
6	H	-1.69121	1.18938	0.80464
7	C	2.22812	0.20272	-0.32682
8	H	3.18297	-0.32517	-0.30760
9	H	1.89777	0.28108	-1.37027
10	H	2.38703	1.21540	0.06483
11	O	1.31874	-0.53956	0.46581
12	H	0.47006	-0.07962	0.42262