

The X-C●●●Y (X=O/F, Y=O/S/F/Cl/Br/N/P) 'carbon bond' and hydrophobic interactions.

Devendra Mani and E. Arunan,

**Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore, India-
560012**

Supplementary Information.

S1. Coordinates of the optimized structures

CH₃OH

MP2/6-311+G(3df,2p)				MP2/Aug-cc-pVTZ			
Atom	x(Å)	y(Å)	z(Å)	Atom	x(Å)	y(Å)	z(Å)
C	-0.0464	0.6631	0.0000	C	-0.0467	0.6657	0.0000
O	-0.0464	-0.7546	0.0000	O	-0.0467	-0.7576	0.0000
H	-1.0867	0.9723	0.0000	H	-1.0878	0.9751	0.0000
H	0.4367	1.0722	0.8886	H	0.4373	1.0731	0.8893
H	0.4367	1.0722	-0.8886	H	0.4373	1.0731	-0.8893
H	0.8629	-1.0584	0.0000	H	0.8675	-1.0546	0.0000

H₂O...CH₃OH

MP2/6-311+G(3df,2p)				MP2/Aug-cc-pVTZ			
Atom	x(Å)	y(Å)	z(Å)	Atom	x(Å)	y(Å)	z(Å)
C	0.7430	0.0028	0.0014	C	0.7417	0.0028	0.0024
H	0.3494	-0.0253	1.0115	H	0.3484	-0.0254	1.0132
H	0.3676	-0.8666	-0.5386	H	0.3669	-0.8671	-0.5377
H	0.3735	0.9047	-0.4868	H	0.3728	0.9053	-0.4858
O	2.1605	-0.0051	0.1096	O	2.1640	-0.0051	0.1113
H	2.5297	0.0199	-0.7746	H	2.5279	0.0200	-0.7778
O	-2.4241	0.0015	-0.0448	O	-2.4251	0.0015	-0.0476
H	-2.9961	0.7475	0.1459	H	-2.9999	0.7478	0.1467
H	-2.9733	-0.7682	0.1164	H	-2.9770	-0.7687	0.1173

H₂S...CH₃OH

MP2/6-311+G(3df,2p)				MP2/Aug-cc-pVTZ			
Atom	x(Å)	y(Å)	z(Å)	Atom	x(Å)	y(Å)	z(Å)
C	-1.5435	0.0076	0.0054	C	-1.5317	0.0077	0.0055
H	-1.1555	0.9623	0.3452	H	-1.1445	0.9749	0.3109
H	-1.1673	-0.1781	-1.0016	H	-1.1559	-0.2146	-0.9945
H	-1.1701	-0.7719	0.6709	H	-1.1600	-0.7475	0.6998
O	-2.9595	0.1048	0.0373	O	-2.9529	0.1067	0.0330
H	-3.3266	-0.7288	-0.2620	H	-3.3139	-0.7425	-0.2359
S	2.1674	-0.0966	-0.0393	S	2.1585	-0.0985	-0.0358
H	2.5688	0.3221	1.1614	H	2.5546	0.3700	1.1515
H	2.5094	1.0564	-0.6154	H	2.4971	1.0359	-0.6559

HF•••CH₃OH

MP2/6-311+G(3df,2p)				MP2/Aug-cc-pVTZ			
Atom	x(Å)	y(Å)	z(Å)	Atom	x(Å)	y(Å)	z(Å)
C	0.7208	0.0392	-0.0002	C	-0.7068	0.0195	0.0002
H	0.3757	1.0680	-0.0019	H	-0.3415	1.0415	0.0008
H	0.3243	-0.4546	0.8877	H	-0.3245	-0.4842	-0.8881
H	0.3270	-0.4581	-0.8869	H	-0.3250	-0.4851	0.8882
O	2.1409	0.0827	0.0000	O	-2.1311	0.0937	-0.0001
H	2.4699	-0.8175	0.0026	H	-2.4737	-0.8041	-0.0004
H	-3.2655	0.2755	0.0042	H	3.3023	0.0596	-0.0020
F	-2.4092	-0.0567	-0.0005	F	2.3835	-0.0216	0.0002

HCl•••CH₃OH

MP2/6-311+G(3df,2p)				MP2/Aug-cc-pVTZ			
Atom	x(Å)	y(Å)	z(Å)	Atom	x(Å)	y(Å)	z(Å)
C	1.4630	0.0025	-0.0206	C	1.4584	0.0004	-0.0157
H	1.0878	0.7917	-0.6642	H	1.0784	0.7774	-0.6721
H	1.0609	0.1525	0.9822	H	1.0637	0.1690	0.9873
H	1.1057	-0.9539	-0.4056	H	1.1021	-0.9645	-0.3807
O	2.8793	0.0914	-0.0472	O	2.8793	0.0923	-0.0528
H	3.2363	-0.5969	0.5166	H	3.2359	-0.5886	0.5241
H	-2.5267	1.0895	0.2906	H	-2.5254	1.0912	0.2925
Cl	-2.1045	-0.0723	-0.0128	Cl	-2.1023	-0.0721	-0.0138

HBr•••CH₃OH

MP2/6-311+G(3df,2p)				MP2/Aug-cc-pVTZ			
Atom	x(Å)	y(Å)	z(Å)	Atom	x(Å)	y(Å)	z(Å)
C	-2.2944	-0.0145	-0.0257	C	-2.1885	-0.0146	-0.0120
H	-1.9143	0.6955	-0.7535	H	-1.7982	0.5934	-0.8225
H	-1.9515	-1.0115	-0.3070	H	-1.8434	-1.0404	-0.1531
H	-1.8828	0.2379	0.9526	H	-1.7926	0.3663	0.9306
O	-3.7091	0.0907	-0.0531	O	-3.6083	0.0834	-0.0736
H	-4.0712	-0.5304	0.5811	H	-3.9740	-0.4515	0.6361
H	1.6094	1.3487	0.2418	H	1.6433	1.3287	0.2382
Br	1.4757	-0.0394	-0.0039	Br	1.4218	-0.0393	-0.0048

ClF•••CH₃OH

MP2/6-311+G(3df,2p)				MP2/Aug-cc-pVTZ			
Atom	x(Å)	y(Å)	z(Å)	Atom	x(Å)	y(Å)	z(Å)
C	-1.7844	0.1418	-0.0165	C	-1.7506	0.1433	-0.0191
H	-1.7031	1.2222	-0.0808	H	-1.6619	1.2227	-0.0944
H	-1.2833	-0.2945	-0.8820	H	-1.2539	-0.3067	-0.8805
H	-1.2782	-0.1889	0.8917	H	-1.2484	-0.1832	0.8931
O	-3.1699	-0.1626	0.0057	O	-3.1440	-0.1512	0.0064
H	-3.2708	-1.1139	0.0656	H	-3.2441	-1.1046	0.0767
Cl	1.9240	-0.4769	-0.0017	Cl	1.8768	-0.4949	-0.0019
F	1.2103	0.9924	0.0099	F	1.2398	1.0149	0.0112

LiF•••CH₃OH

MP2/6-311+G(3df,2p)				MP2/Aug-cc-pVTZ			
Atom	x(Å)	y(Å)	z(Å)	Atom	x(Å)	y(Å)	z(Å)
C	0.9443	0.0321	0.0064	C	0.9426	0.0322	0.0064
H	0.5690	-0.4879	0.8858	H	0.5684	-0.4884	0.8864
H	0.5539	-0.4601	-0.8823	H	0.5531	-0.4605	-0.8829
H	0.5670	1.0480	0.0255	H	0.5661	1.0490	0.0255
O	2.3693	0.1180	-0.0044	O	2.3724	0.1186	-0.0044
H	2.7183	-0.7742	-0.0219	H	2.7161	-0.7785	-0.0218
Li	-3.5705	0.2860	-0.0123	Li	-3.5736	0.2865	-0.0122
F	-2.0352	-0.1467	0.0030	F	-2.0352	-0.1470	0.0029

LiCl•••CH₃OH

MP2/6-311+G(3df,2p)				MP2/Aug-cc-pVTZ			
Atom	x(Å)	y(Å)	z(Å)	Atom	x(Å)	y(Å)	z(Å)
C	1.6385	0.0584	0.0082	C	1.6376	0.0590	0.0081
H	1.2657	-0.4488	0.8976	H	1.2654	-0.4486	0.8980
H	1.2472	-0.4466	-0.8743	H	1.2468	-0.4463	-0.8750
H	1.2633	1.0761	0.0131	H	1.2635	1.0777	0.0131
O	3.0608	0.1414	-0.0065	O	3.0648	0.1419	-0.0066
H	3.4097	-0.7512	-0.0133	H	3.4078	-0.7557	-0.0131
Li	-3.6965	0.5837	-0.0047	Li	-3.7024	0.5855	-0.0046
Cl	-1.7890	-0.1566	-0.0003	Cl	-1.7894	-0.1572	-0.0003

LiBr•••CH₃OH

MP2/6-311+G(3df,2p)				MP2/Aug-cc-pVTZ			
Atom	x(Å)	y(Å)	z(Å)	Atom	x(Å)	y(Å)	z(Å)
C	2.3323	0.0854	0.0003	C	-2.2677	0.1103	0.0004
H	1.9553	-0.4229	0.8875	H	-1.8741	-0.3890	-0.8850
H	1.9547	-0.4255	-0.8853	H	-1.8750	-0.3853	0.8882
H	1.9476	1.0999	-0.0011	H	-1.9176	1.1377	-0.0016
O	3.7525	0.1837	-0.0004	O	-3.6962	0.1603	-0.0005
H	4.1120	-0.7049	0.0009	H	-4.0189	-0.7447	0.0011
Li	-2.6491	1.5755	0.0001	Li	3.0829	1.0752	0.0002
Br	-1.3153	-0.1787	0.0000	Br	1.2461	-0.1368	-0.0001

NH₃ •••CH₃OH

MP2/6-311+G(3df,2p)				MP2/Aug-cc-pVTZ			
Atom	x(Å)	y(Å)	z(Å)	Atom	x(Å)	y(Å)	z(Å)
C	0.8174	0.0078	0.0055	C	-0.8181	0.0173	0.0004
H	0.4390	0.5229	-0.8772	H	-0.4531	0.5355	0.8872
H	0.4513	0.5210	0.8945	H	-0.4538	0.5365	-0.8862
H	0.4213	-1.0021	0.0069	H	-0.4120	-0.9891	-0.0003
N	-2.5598	0.0254	-0.0022	N	2.5655	0.0275	-0.0011
H	-2.8235	-0.5135	-0.8164	H	2.8036	-0.5234	0.8145
H	-3.1481	0.8480	0.0081	H	3.1969	0.8191	-0.0090
H	-2.8111	-0.5250	0.8082	H	2.7998	-0.5364	-0.8089
O	2.2348	-0.1066	-0.0043	O	-2.2393	-0.1136	0.0009
H	2.6073	0.7765	-0.0073	H	-2.6166	0.7701	0.0017

PH₃•••CH₃OH

MP2/6-311+G(3df,2p)				MP2/Aug-cc-pVTZ			
Atom	x(Å)	y(Å)	z(Å)	Atom	x(Å)	y(Å)	z(Å)
C	1.6276	-0.0244	-0.0079	C	1.5044	-0.0649	-0.1210
H	1.2114	0.9781	0.0074	H	1.0162	0.8956	0.0200
H	1.2597	-0.5641	0.8659	H	1.0772	-0.7800	0.5843
H	1.2755	-0.5300	-0.9081	H	1.3074	-0.4096	-1.1374
O	3.0396	0.1200	0.0077	O	2.8926	0.1500	0.1121
H	3.4328	-0.7541	-0.0066	H	3.3464	-0.6888	-0.0070
P	-2.1758	-0.0450	-0.0053	P	-2.0962	-0.0828	-0.0363
H	-3.0097	-0.2345	1.1146	H	-1.9987	0.1809	1.3481
H	-2.4294	1.3392	-0.0774	H	-1.9656	1.2771	-0.3956
H	-3.1858	-0.3735	-0.9311	H	-3.5079	-0.0435	-0.0382

CH₃F

MP2/6-311+G(3df,2p)				MP2/Aug-cc-pVTZ			
Atom	x(Å)	y(Å)	z(Å)	Atom	x(Å)	y(Å)	z(Å)
C	0.0000	0.6331	0.0000	C	0.0000	-0.6360	0.0000
F	0.0000	-0.7496	0.0000	F	0.0000	0.7522	0.0000
H	-1.0290	0.9827	0.0000	H	1.0297	-0.9848	0.0000
H	0.5145	0.9827	0.8911	H	-0.5148	-0.9847	0.8918
H	0.5145	0.9827	-0.8911	H	-0.5148	-0.9847	-0.8918

H₂O••• CH₃F

MP2/6-311+G(3df,2p)				MP2/Aug-cc-pVTZ			
Atom	x(Å)	y(Å)	z(Å)	Atom	x(Å)	y(Å)	z(Å)
C	0.7213	0.0083	-0.0067	C	0.7198	0.0084	-0.0068
H	0.3680	-0.7915	-0.6501	H	0.3668	-0.7919	-0.6506
H	0.3842	0.9666	-0.3897	H	0.3831	0.9673	-0.3897
H	0.3577	-0.1373	1.0055	H	0.3566	-0.1377	1.0059
O	-2.3244	0.0012	-0.0015	O	-2.3257	0.0012	-0.0016
H	-2.8836	-0.7780	0.0141	H	-2.8883	-0.7787	0.0145
H	-2.9393	0.7373	0.0161	H	-2.9434	0.7382	0.0167
F	2.1090	-0.0063	0.0063	F	2.1124	-0.0063	0.0063

H₂S••• CH₃F

MP2/6-311+G(3df,2p)				MP2/Aug-cc-pVTZ			
Atom	x(Å)	y(Å)	z(Å)	Atom	x(Å)	y(Å)	z(Å)
C	1.5164	0.0010	-0.0086	C	1.5092	0.0019	-0.0177
F	2.9015	-0.0013	0.0211	F	2.8996	-0.0016	0.0263
H	1.1774	-0.8179	-0.6368	H	1.1693	1.0053	-0.2604
H	1.1423	-0.1254	1.0032	H	1.1819	-0.6986	-0.7815
H	1.1757	0.9486	-0.4164	H	1.1271	-0.2976	0.9542
S	-2.1078	-0.0022	-0.0983	S	-2.1132	0.0002	-0.0998
H	-2.4742	0.9796	0.7265	H	-2.4134	0.9585	0.7820
H	-2.5071	-0.9439	0.7574	H	-2.4060	-0.9685	0.7731

HF••• CH₃F

MP2/6-311+G(3df,2p)				MP2/Aug-cc-pVTZ			
Atom	x(Å)	y(Å)	z(Å)	Atom	x(Å)	y(Å)	z(Å)
C	0.6914	0.0319	0.0000	C	0.6900	0.0316	0.0000
F	2.0765	-0.0210	0.0000	F	2.0799	-0.0206	0.0000
H	0.3208	-0.4689	-0.8894	H	0.3206	-0.4701	-0.8899
H	0.3209	-0.4670	0.8905	H	0.3207	-0.4682	0.8911
H	0.3808	1.0725	-0.0011	H	0.3794	1.0727	-0.0011
H	-3.1878	0.1874	-0.0001	H	-3.1935	0.1879	-0.0001
F	-2.2968	-0.0363	0.0000	F	-2.2984	-0.0362	0.0000

HCl••• CH₃F

MP2/6-311+G(3df,2p)				MP2/Aug-cc-pVTZ			
Atom	x(Å)	y(Å)	z(Å)	Atom	x(Å)	y(Å)	z(Å)
C	1.4454	0.0110	-0.0115	C	1.4437	0.0112	-0.0116
F	2.8297	0.0048	0.0099	F	2.8328	0.0047	0.0100
H	1.0785	0.0627	1.0097	H	1.0770	0.0634	1.0102
H	1.1073	0.8763	-0.5748	H	1.1058	0.8769	-0.5755
H	1.0984	-0.9018	-0.4882	H	1.0967	-0.9022	-0.4882
H	-2.5686	1.0901	0.0025	H	-2.5700	1.0921	0.0024
Cl	-2.0503	-0.0727	0.0018	Cl	-2.0510	-0.0729	0.0018

HBr••• CH₃F

MP2/6-311+G(3df,2p)				MP2/Aug-cc-pVTZ			
Atom	x(Å)	y(Å)	z(Å)	Atom	x(Å)	y(Å)	z(Å)
C	-2.2581	0.0196	0.0038	C	-2.1648	0.0238	0.0023
F	-3.6422	-0.0049	-0.0032	F	-3.5539	-0.0078	-0.0019
H	-1.8934	-0.5190	-0.8666	H	-1.7996	-0.5141	-0.8688
H	-1.9256	1.0535	-0.0317	H	-1.8379	1.0598	-0.0351
H	-1.9034	-0.4550	0.9145	H	-1.8064	-0.4482	0.9134
H	1.8159	1.3218	-0.0009	H	1.7792	1.3099	-0.0006
Br	1.4353	-0.0421	-0.0003	Br	1.3897	-0.0423	-0.0002

ClF••• CH₃F

MP2/6-311+G(3df,2p)				MP2/Aug-cc-pVTZ			
Atom	x(Å)	y(Å)	z(Å)	Atom	x(Å)	y(Å)	z(Å)
C	-1.7791	0.1474	0.0009	C	-1.7775	0.1485	0.0008
H	-1.7737	1.2338	0.0016	H	-1.7740	1.2354	0.0016
H	-1.2832	-0.2282	-0.8899	H	-1.2815	-0.2275	-0.8904
H	-1.2847	-0.2295	0.8920	H	-1.2830	-0.2288	0.8924
F	-3.0912	-0.2935	-0.0007	F	-3.0940	-0.2948	-0.0007
Cl	1.9182	-0.4594	0.0000	Cl	1.9191	-0.4610	0.0000
F	1.1364	0.9767	-0.0003	F	1.1361	0.9800	-0.0003

LiF••• CH₃F

MP2/6-311+G(3df,2p)				MP2/Aug-cc-pVTZ			
Atom	x(Å)	y(Å)	z(Å)	Atom	x(Å)	y(Å)	z(Å)
C	-0.9105	-0.0050	0.0002	C	-0.9088	-0.0049	0.0001
F	-2.3058	0.0094	-0.0004	F	-2.3093	0.0092	-0.0001
H	-0.5486	0.8974	-0.4789	H	-0.5485	0.9162	-0.4445
H	-0.5597	-0.0462	1.0250	H	-0.5586	-0.0857	1.0232
H	-0.5675	-0.8773	-0.5443	H	-0.5662	-0.8557	-0.5784
Li	3.5213	0.0397	-0.0016	Li	3.5255	0.0394	-0.0001
F	1.9252	-0.0164	0.0006	F	1.9259	-0.0163	0.0000

LiCl••• CH₃F

MP2/6-311+G(3df,2p)				MP2/Aug-cc-pVTZ			
Atom	x(Å)	y(Å)	z(Å)	Atom	x(Å)	y(Å)	z(Å)
C	-1.6043	0.0054	0.0000	C	-1.6038	0.0052	0.0000
F	-2.9959	0.0344	0.0000	F	-2.9999	0.0346	0.0000
H	-1.2321	1.0193	-0.1058	H	-1.2314	1.0197	-0.1058
H	-1.2622	-0.4210	0.9375	H	-1.2614	-0.4214	0.9379
H	-1.2660	-0.6041	-0.8317	H	-1.2652	-0.6047	-0.8321
Li	3.7377	0.2496	0.0000	Li	3.7446	0.2495	0.0000
Cl	1.7139	-0.0638	0.0000	Cl	1.7145	-0.0638	0.0000

LiBr••• CH₃F

MP2/6-311+G(3df,2p)				MP2/Aug-cc-pVTZ			
Atom	x(Å)	y(Å)	z(Å)	Atom	x(Å)	y(Å)	z(Å)
C	2.2908	0.0252	0.0012	C	2.2269	0.0232	0.0012
F	3.6807	0.0563	-0.0010	F	3.6222	0.0562	-0.0010
H	1.9467	-0.2381	0.9966	H	1.8836	-0.2350	0.9985
H	1.9547	-0.7162	-0.7170	H	1.8924	-0.7231	-0.7132
H	1.9170	1.0064	-0.2745	H	1.8525	1.0029	-0.2802
Li	-3.3530	0.4909	0.0001	Li	-3.3273	0.4691	0.0000
Br	-1.2180	-0.0624	-0.0001	Br	-1.1888	-0.0599	-0.0001

H₃N••• CH₃F

MP2/6-311+G(3df,2p)				MP2/Aug-cc-pVTZ			
Atom	x(Å)	y(Å)	z(Å)	Atom	x(Å)	y(Å)	z(Å)
C	-0.7861	0.0001	0.0000	C	-0.7845	0.0001	0.0000
H	-0.4340	-0.3232	0.9743	H	-0.4333	-0.2266	1.0021
H	-0.4343	1.0057	-0.2073	H	-0.4334	0.9813	-0.3049
H	-0.4341	-0.6821	-0.7673	H	-0.4333	-0.7545	-0.6974
N	2.4451	0.0000	0.0000	N	2.4457	0.0000	0.0000
H	2.8255	-0.9162	0.1979	H	2.8306	-0.8919	0.2864
H	2.8255	0.6296	0.6944	H	2.8306	0.6940	0.6291
H	2.8249	0.2867	-0.8926	H	2.8302	0.1979	-0.9157
F	-2.1748	-0.0001	0.0001	F	-2.1783	0.0000	0.0000



MP2/6-311+G(3df,2p)				MP2/Aug-cc-pVTZ			
Atom	x(Å)	y(Å)	z(Å)	Atom	x(Å)	y(Å)	z(Å)
C	-1.6143	0.0171	0.0005	C	-1.5912	0.0104	0.0005
H	-1.2492	-0.5626	-0.8426	H	-1.2351	-0.3452	-0.9628
H	-1.2538	-0.4115	0.9313	H	-1.2320	-0.6391	0.7944
H	-1.2859	1.0490	-0.0867	H	-1.2542	1.0296	0.1704
F	-2.9993	-0.0143	-0.0004	F	-2.9815	-0.0085	-0.0003
P	2.1225	0.0009	0.0003	P	2.1016	0.0014	0.0009
H	2.8450	-1.0955	-0.5098	H	2.8304	-0.9316	-0.7685
H	2.9031	0.9565	-0.6791	H	2.8833	1.1008	-0.4160
H	2.8832	0.0770	1.1834	H	2.8638	-0.2210	1.1684

S2. Table: Population on bonded carbon, N_C , its energy E_C , dipolar polarization M_C , and volume V_C in different complexes and monomers calculated from AIM analysis. Δ represents the change in the properties on complex formation. All the properties are given in atomic units.

	N_C	E_C	$ M_C $	V_C	ΔN_C	ΔE_C	$\Delta M_C $	ΔV_C
CH ₃ OH complexes								
CH ₃ OH	5.426	-37.5259	0.109	69.10	-	-	-	-
H ₂ O...CH ₃ OH	5.428	-37.5529	0.079	65.65	0.002	-0.0270	-0.030	-3.44
H ₂ S...CH ₃ OH	5.222	-37.2936	0.098	60.30	-0.204	0.2323	-0.011	-8.79
HF...CH ₃ OH	5.222	-37.3213	0.115	60.01	-0.204	0.2323	0.006	-9.09
HCl...CH ₃ OH	5.222	-37.2889	0.112	60.87	-0.204	0.2046	0.004	-8.22
HBr...CH ₃ OH	5.222	-37.9601	0.109	60.53	-0.205	0.2370	0.000	-8.56
ClF...CH ₃ OH	5.221	-37.3010	0.126	59.20	-0.205	0.2249	0.018	-9.89
LiF...CH ₃ OH	5.233	-37.3339	0.063	59.36	-0.193	0.1919	-0.046	-9.74
LiCl...CH ₃ OH	5.236	-37.9774	0.069	60.09	-0.190	-0.4515	-0.040	-9.00
LiBr...CH ₃ OH	5.233	-37.3000	0.071	59.93	-0.193	0.2259	-0.038	-9.16
H ₃ N...CH ₃ OH	5.223	-37.3322	0.089	59.86	-0.203	0.1937	-0.020	-9.24
H ₃ P...CH ₃ OH	5.224	-37.2934	0.105	61.52	-0.202	0.2325	-0.004	-7.57
CH ₃ F complexes								
CH ₃ F	5.376	-37.5134	0.055	69.53	-	-	-	-
H ₂ O...CH ₃ F	5.213	-37.3229	0.030	60.62	-0.163	0.1906	-0.025	-8.92
H ₂ S...CH ₃ F	5.213	-37.2826	0.026	61.58	-0.163	0.2309	-0.029	-7.96
HF...CH ₃ F	5.212	-37.3108	0.049	60.92	-0.164	0.2026	-0.006	-8.62
HCl...CH ₃ F	5.212	-37.2768	0.046	61.50	-0.164	0.2366	-0.009	-8.04
HBr...CH ₃ F	5.213	-37.2856	0.042	61.94	-0.163	0.2279	-0.013	-7.59
ClF...CH ₃ F	5.208	-37.2832	0.062	60.16	-0.168	0.2303	0.007	-9.37
LiF...CH ₃ F	5.225	-37.3269	0.019	60.13	-0.168	0.1866	-0.036	-9.41
LiCl...CH ₃ F	5.229	-37.2979	0.005	61.18	-0.151	0.2156	-0.050	-8.35
LiBr...CH ₃ F	5.228	-37.2951	0.001	61.42	-0.148	0.2184	-0.054	-8.11
H ₃ N...CH ₃ F	5.214	-37.3286	0.012	60.90	-0.162	0.1848	-0.043	-8.64
H ₃ P...CH ₃ F	5.214	-37.2819	0.022	61.98	-0.162	0.2315	-0.033	-7.56

S3. Table : Natural charges on atoms (q), charge transferred (ΔQ , e) and second order interaction energy for the corresponding donor-acceptor interaction, E^2 (l.p. $\longrightarrow$ C-O anti-bonding) in kJ.mol^{-1} , for CH_3OH complexes.

at MP2/6-311+G(3df,2p)								
Complex	q(C)	q(H)	q(H)	q(H)	q(O)	q(H)	ΔQ	$E^2[\text{l.p.} \longrightarrow (\sigma^* (\text{C-O}))]$
CH_3OH	-0.091	0.1492	0.1283	0.1283	-0.7728	0.4581	-	-
$\text{H}_2\text{O} \cdots \text{CH}_3\text{OH}$	-0.087	0.1505	0.1297	0.1299	-0.7797	0.4551	-0.0014	2.6
$\text{H}_2\text{S} \cdots \text{CH}_3\text{OH}$	-0.089	0.1496	0.1288	0.1292	-0.7766	0.4568	-0.0011	2.4
$\text{HF} \cdots \text{CH}_3\text{OH}$	-0.0893	0.1482	0.1307	0.1307	-0.7775	0.4562	-0.001	1.5
$\text{HCl} \cdots \text{CH}_3\text{OH}$	-0.0904	0.1494	0.1297	0.1286	-0.7752	0.4573	-0.0007	2
$\text{HBr} \cdots \text{CH}_3\text{OH}$	-0.0907	0.149	0.1293	0.1292	-0.7749	0.4575	-0.0007	2
$\text{ClF} \cdots \text{CH}_3\text{OH}$	-0.0912	0.1518	0.1271	0.1275	-0.7739	0.457	-0.0018	2.3
$\text{LiF} \cdots \text{CH}_3\text{OH}$	-0.0847	0.1359	0.1365	0.1469	-0.7883	0.4514	-0.0022	3.6
$\text{LiCl} \cdots \text{CH}_3\text{OH}$	-0.0913	0.1344	0.1351	0.1495	-0.7832	0.4534	-0.0021	3
$\text{LiBr} \cdots \text{CH}_3\text{OH}$	-0.0907	0.1352	0.1353	0.1455	-0.7822	0.455	-0.0019	2.9
$\text{H}_3\text{N} \cdots \text{CH}_3\text{OH}$	-0.0861	0.1316	0.131	0.147	-0.7803	0.4551	-0.0017	3
$\text{H}_3\text{P} \cdots \text{CH}_3\text{OH}$	-0.0899	0.147	0.1303	0.1309	-0.7762	0.4571	-0.0009	1.9
at MP2/Aug-cc-pVTZ								
CH_3OH	-0.1115	0.152	0.1309	0.1309	-0.758	0.4558	-	-
$\text{H}_2\text{O} \cdots \text{CH}_3\text{OH}$	-0.1067	0.1529	0.1319	0.132	-0.7652	0.453	-0.0021	2.8
$\text{H}_2\text{S} \cdots \text{CH}_3\text{OH}$	-0.1094	0.1521	0.1314	0.1318	-0.7621	0.4545	-0.0016	3
$\text{HF} \cdots \text{CH}_3\text{OH}$	-0.1094	0.1523	0.1325	0.1325	-0.7631	0.4536	-0.0016	1.6
$\text{HCl} \cdots \text{CH}_3\text{OH}$	-0.1105	0.1521	0.1321	0.131	-0.7609	0.455	-0.0013	2.3
$\text{HBr} \cdots \text{CH}_3\text{OH}$	-0.1112	0.1525	0.1312	0.1316	-0.761	0.455	-0.0018	3.3
$\text{ClF} \cdots \text{CH}_3\text{OH}$	-0.1113	0.1547	0.129	0.1294	-0.7592	0.4546	-0.0027	2.2
$\text{LiF} \cdots \text{CH}_3\text{OH}$	-0.1034	0.1382	0.1388	0.1492	-0.7747	0.4492	-0.0027	3.6
$\text{LiCl} \cdots \text{CH}_3\text{OH}$	-0.1108	0.1366	0.1372	0.1516	-0.7693	0.4511	-0.0036	3.1
$\text{LiBr} \cdots \text{CH}_3\text{OH}$	-0.1119	0.1371	0.1371	0.1504	-0.7686	0.4518	-0.004	3.9
$\text{H}_3\text{N} \cdots \text{CH}_3\text{OH}$	-0.1059	0.134	0.134	0.149	-0.766	0.453	-0.0019	2.8
$\text{H}_3\text{P} \cdots \text{CH}_3\text{OH}$	-0.1137	0.1474	0.1333	0.1356	-0.7591	0.4559	-0.0006	1.8

S4. Table: Natural charges on different atoms (q), charge transferred (ΔQ , e) and second order interaction energy for the corresponding donor-acceptor interaction, E^2 (l.p. $\rightarrow$ C-F anti-bonding) in kJ.mol^{-1} , for CH_3F complexes.

at MP2/6-311+G(3df,2p)							
Complex	q(C)	q(F)	q(H)	q(H)	q(H)	ΔQ	$E^2[\text{l.p.} \rightarrow \sigma^*(\text{C-F})]$
CH_3F	0.0428	-0.4371	0.1314	0.1314	0.1314	-	-
$\text{H}_2\text{O} \cdots \text{CH}_3\text{F}$	0.0463	-0.4471	0.1323	0.1318	0.1347	-0.002	3.6
$\text{H}_2\text{S} \cdots \text{CH}_3\text{F}$	0.0441	-0.4424	0.1323	0.1327	0.1316	-0.0017	3.3
$\text{HF} \cdots \text{CH}_3\text{F}$	0.0441	-0.4438	0.1336	0.1336	0.1311	-0.0014	2.3
$\text{HCl} \cdots \text{CH}_3\text{F}$	0.0428	-0.4404	0.1335	0.1315	0.1318	-0.0009	2.8
$\text{HBr} \cdots \text{CH}_3\text{F}$	0.0427	-0.4401	0.1329	0.1306	0.1329	-0.001	2.5
$\text{ClF} \cdots \text{CH}_3\text{F}$	0.0425	-0.4396	0.134	0.1306	0.1306	-0.002	3.3
$\text{LiF} \cdots \text{CH}_3\text{F}$	0.0502	-0.4601	0.1354	0.1355	0.1356	-0.0035	5.9
$\text{LiCl} \cdots \text{CH}_3\text{F}$	0.0418	-0.4523	0.1353	0.1361	0.1362	-0.0029	4.1
$\text{LiBr} \cdots \text{CH}_3\text{F}$	0.0404	-0.4499	0.1355	0.1358	0.1349	-0.0033	3.6
$\text{H}_3\text{N} \cdots \text{CH}_3\text{F}$	0.048	-0.4485	0.1326	0.1326	0.1326	-0.0027	5.1
$\text{H}_3\text{P} \cdots \text{CH}_3\text{F}$	0.0445	-0.4426	0.1322	0.1322	0.1321	-0.0016	2.8
at MP2/Aug-cc-pVTZ							
CH_3F	0.0194	-0.4249	0.1352	0.1352	0.1352	-	-
$\text{H}_2\text{O} \cdots \text{CH}_3\text{F}$	0.0243	-0.4353	0.1354	0.135	0.138	-0.0026	3.6
$\text{H}_2\text{S} \cdots \text{CH}_3\text{F}$	0.0208	-0.4308	0.1357	0.1366	0.1355	-0.0023	4
$\text{HF} \cdots \text{CH}_3\text{F}$	0.0218	-0.4318	0.1368	0.1368	0.1346	-0.0018	2.5
$\text{HCl} \cdots \text{CH}_3\text{F}$	0.0195	-0.4284	0.1371	0.1351	0.1352	-0.0015	3.1
$\text{HBr} \cdots \text{CH}_3\text{F}$	0.0185	-0.4287	0.1368	0.1343	0.1369	-0.0022	4.1
$\text{ClF} \cdots \text{CH}_3\text{F}$	0.0201	-0.4277	0.1376	0.1337	0.1337	-0.0026	2.9
$\text{LiF} \cdots \text{CH}_3\text{F}$	0.0294	-0.4493	0.1386	0.1387	0.1388	-0.0038	5.6
$\text{LiCl} \cdots \text{CH}_3\text{F}$	0.0411	-0.4536	0.136	0.1368	0.1369	-0.0029	4.1
$\text{LiBr} \cdots \text{CH}_3\text{F}$	0.0178	-0.4396	0.1391	0.1393	0.1384	-0.005	4.9
$\text{H}_3\text{N} \cdots \text{CH}_3\text{F}$	0.0256	-0.4369	0.1361	0.1361	0.1361	-0.0029	4.9
$\text{H}_3\text{P} \cdots \text{CH}_3\text{F}$	0.0211	-0.4309	0.1359	0.1359	0.136	-0.002	3.5

