Electronic Supporting Information

Competition between hydrogen bond and halogen bond in [CH_3OH-CCl_4] complex: A matrix isolation IR spectroscopy and computational study†

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Table S1 The selected experimental IR transitions and FWHM values for the CH_3OH and CCl_4 in N_2 and Ar matrix at 8K.

N_2-matrix		**Ar-matrix**		**Assignment**
Transitions	**FWHM(cm^{-1})**	**Transitions**	**FWHM(cm^{-1})**	
3664	3	3666	7	ν_{OHstr} (CH_3OH)
3003	3	3004	9	
2995	7	2962	3	
2914	3	2955	3	ν_{CH3str} (CH_3OH)
2844	3	2930	4	
		2848	3	
2054	2	2054	3	$2\nu_{CO}$ (CH_3OH)
1035	2	1034	2	ν_{COstr} (CH_3OH)
		1027	4	Secondary monomeric site
789	8	788	6	$\nu_{3(C-Cl)str}$ (CCl_4)
767	9	767	10	$\nu_1 + \nu_4$ (CCl_4)

Table S2 Uncorrected stabilization energy (ΔE), zero-point energy (ΔZPE), counterpoise uncorrected stabilization energy (ΔE'), Basis Set Superposition Error (BSSE), counterpoise corrected stabilization energy (D_0) of complexes obtained at the MP2 level of theory using aug-cc-pVDZ basis set. Values in parentheses are obtained at MP2 level using def2-TZVPP basis set. All energy values are in kcal mol^{-1}.

Conformers	**ΔE**	**ΔZPE**	**ΔE'**	**BSSE**	**D_0**
C1	-3.72(-2.76)	0.61(0.49)	-3.11(-2.27)	1.21(0.65)	1.90(1.62)
C2	-4.72(-2.96)	0.66(0.46)	-4.06(-2.50)	2.43(1.09)	1.63(1.41)
C3	-4.31(-2.72)	0.57(0.46)	-3.74(-2.26)	2.34(1.15)	1.40(1.11)
C4	-3.56(-)	0.50(-)	-3.06(-)	2.25(-)	0.81(-)
C5	-3.39(-1.68)	0.59(0.30)	-2.80(-1.38)	2.16(0.64)	0.64(0.74)

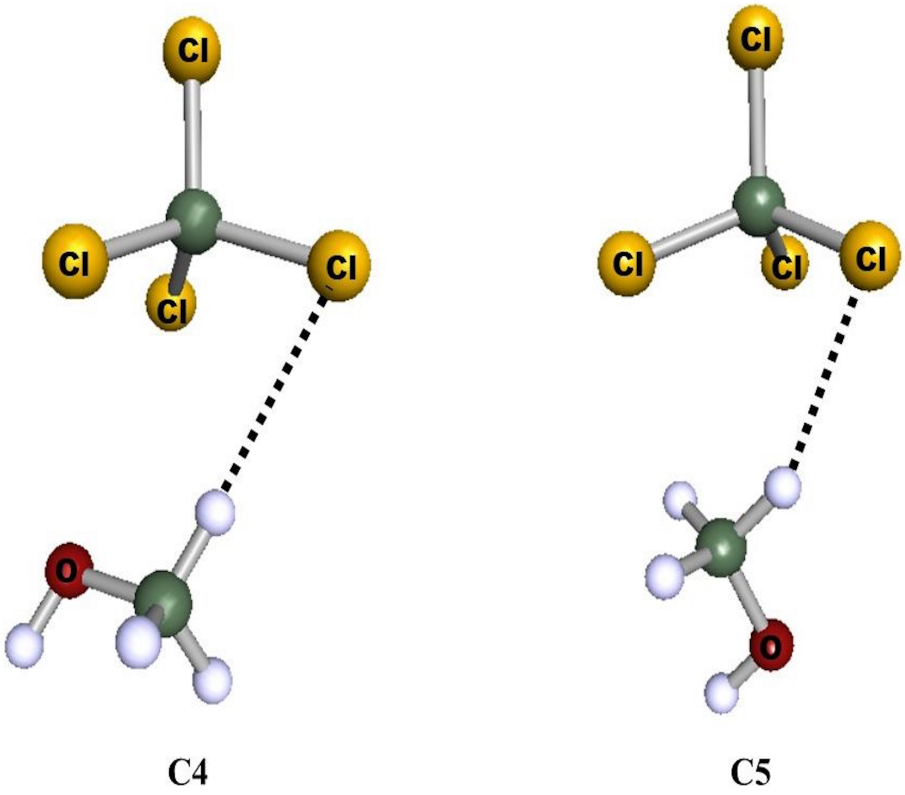

Figure S1: Optimized geometry of the less stable local minima for [CH_3OH-CCl_4] obtained at MP2 level using aug-cc-pVDZ basis set. C4 and C5 conformers are stabilised by C-H$\cdots$Cl interactions although the relative orientation of individual monomers are different. Minimum corresponding to C4 conformer is not identified at the MP2/def2-TZVPP level of calculation whereas C5 is a minimum at the same level of theory.

Table S3 Important energetic, geometrical, and vibrational parameters for the two less stable minima C4 and C5. All the parameters are obtained at the MP2 level using aug-cc-pVDZ (def2-TZVPP) basis set.

	C4	**C5**
D_0	0.81	0.64
(kcal mol^{-1})		(0.74)
D_0'	0.96	1.00
(kcal mol^{-1})		(0.83)
R	2.860	2.867
($\AA$)		(3.179)
r_{CCl}	1.787	1.783
($\AA$)		(1.763)
Δr_{CCl}	6.0	2.0
(m$\AA$)		(2.0)
r_{CO}	1.434	1.434
($\AA$)		(1.419)
Δr_{CO}	1.0	1.0
(m$\AA$)		(1.0)
r_{OH}	0.966	0.965
($\AA$)		(0.958)
Δr_{OH}	1.0	0.0
(m$\AA$)		(0.0)
$\nu_{CCl,1}$	778	782
(cm^{-1})		(783)
$\Delta\nu_{CCl,1}$	-9	-5
(cm^{-1})		(-4)
$\nu_{CCl,2}$	785	786
(cm^{-1})		(786)
$\Delta\nu_{CCl,2}$	-2	-1
(cm^{-1})		(-1)
$\nu_{CCl,3}$	791	787
(cm^{-1})		(787)
$\Delta\nu_{CCl,3}$	+4	0
(cm^{-1})		(0)
$\nu_{CO,1}$	1033	1038
(cm^{-1})		(1032)
$\Delta\nu_{CO,1}$	0	+5
(cm^{-1})		(-1)
$\nu_{OH,1}$	3661	3665
(cm^{-1})		(3664)
$\Delta\nu_{OH,1}$	-5	-1
(cm^{-1})		(-2)

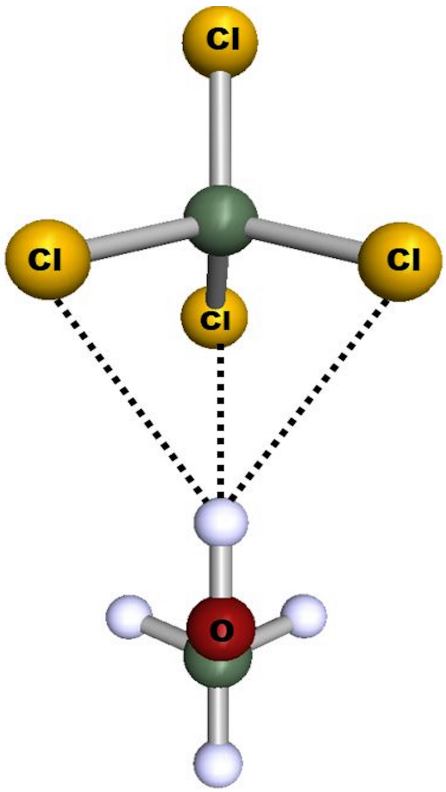

Figure S2: Initial geometry of trifurcated hydrogen bonded conformer used for optimisation at the MP2 level using aug-cc-pVDZ and def2-TZVPP basis set

Table S4 Total charge transfer at MP2 level, total charge transfer at M06-2X level and charge transfer energy obtained at the M06-2X level of theory using aug-cc-pVDZ basis set. Values in parentheses are obtained using def2-TZVPP basis set. Total charge transfer are in me and charge transfer energy are in kcal mol^{-1}.

Conformers	**Charge transfer (MP2)**	**Charge transfer (M06-2X)**	**Charge transfer energy (M06-2X)**
C1	4.28(4.46)	7.83(7.66)	2.11(2.38)
C2	8.63(2.32)	10.53(4.12)	2.83(0.83)
C3	9.95(2.70)	11.66(4.21)	3.08(0.81)

Table S5 Energy Decomposition analysis into different components for the complexes obtained at SAPT2 level of theory using aug-cc-pVDZ basis set. Values in parentheses are obtained at SAPT2 level using def2-TZVPP basis set. All the energy components are in kcal mol^{-1}.

Conformers	**Electrostatics**	**Induction**	**Dispersion**	**Exchange**	**Total energy**
C1	-4.33(-3.77)	-1.51(-1.07)	-2.80(-2.51)	6.19(5.06)	-2.45(-2.28)
C2	-2.88(-1.99)	-1.09(-0.66)	-4.31(-3.58)	6.22(4.34)	-2.06(-1.89)
C3	-2.09(-1.85)	-1.34(-0.79)	-3.96(-3.47)	5.54(4.49)	-1.84(-1.62)

Table S6 Electron density at bond critical point (ρ), Laplacian of electron density at the bond critical point ($\nabla^2\rho$), kinetic energy density ($G(r_c)$), potential energy density ($V(r_c)$), total energy density ($H(r_c)$), Lambda parameters (λ_1, λ_3), ratio of potential and kinetic energy density ($|V|$:G) and ratio of the Lambda parameters (λ_1:λ_3) at all the bond paths between CH_3OH and CCl_4 for the complexes C1, C2 and C3.

Conf	**Bond path**	ρ	$\nabla^2\rho$	$\mathbf{G(r}_c\mathbf{)}$	$\mathbf{V(r}_c\mathbf{)}$	$\mathbf{H(r}_c\mathbf{)}$	λ_1	λ_3	$\|V\|$:**G**	λ_1:λ_3
C1	Cl$\cdots$O	0.0139	0.0128	0.0116	0.0103	0.0219	-0.0110	0.0730	0.89	0.15
C2	H$\cdots$Cl[a]	0.0083	0.0069	0.0059	0.0049	0.0108	-0.0068	0.0404	0.83	0.17
	H$\cdots$Cl[a]	0.0083	0.0069	0.0059	0.0049	0.0108	-0.0068	0.0406	0.83	0.17
	H$\cdots$Cl[b]	0.0057	0.0052	0.0041	0.0031	0.0072	-0.0041	0.0274	0.76	0.15
	H$\cdots$Cl[b]	0.0057	0.0052	0.0041	0.0031	0.0072	-0.0041	0.0273	0.76	0.15
	C$\cdots$Cl[c]	0.0042	0.0040	0.0031	0.0021	0.0052	-0.0026	0.0189	0.68	0.14
C3	H$\cdots$Cl[d]	0.0097	0.0071	0.0065	0.0059	0.0124	-0.0081	0.0444	0.91	0.18
	H$\cdots$Cl[d]	0.0065	0.0055	0.0049	0.0042	0.0091	-0.0048	0.0299	0.86	0.16
	H$\cdots$Cl[e]	0.0052	0.0044	0.0036	0.0028	0.0064	-0.0037	0.0249	0.78	0.15
	C$\cdots$Cl[f]	0.0054	0.0048	0.0038	0.0027	0.0065	-0.0025	0.0227	0.71	0.11

[a] bond path between O-H$\cdots$Cl; [b] bond path between C-H$\cdots$Cl; [c] bond path between C$\cdots$Cl
[d] bond path between O-H$\cdots$Cl; [e] bond path between C-H$\cdots$Cl; [f] bond path between C$\cdots$Cl

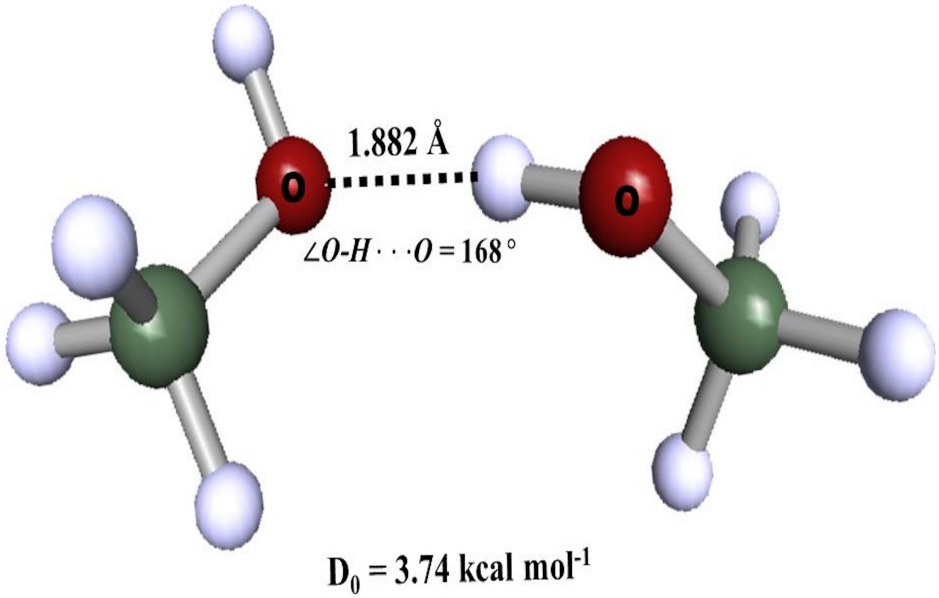

Figure S3: Optimized geometry of the dimer of methanol obtained at the MP2 level using aug-cc-pVDZ basis set. The relevant geometrical parameters are mentioned in the figure.

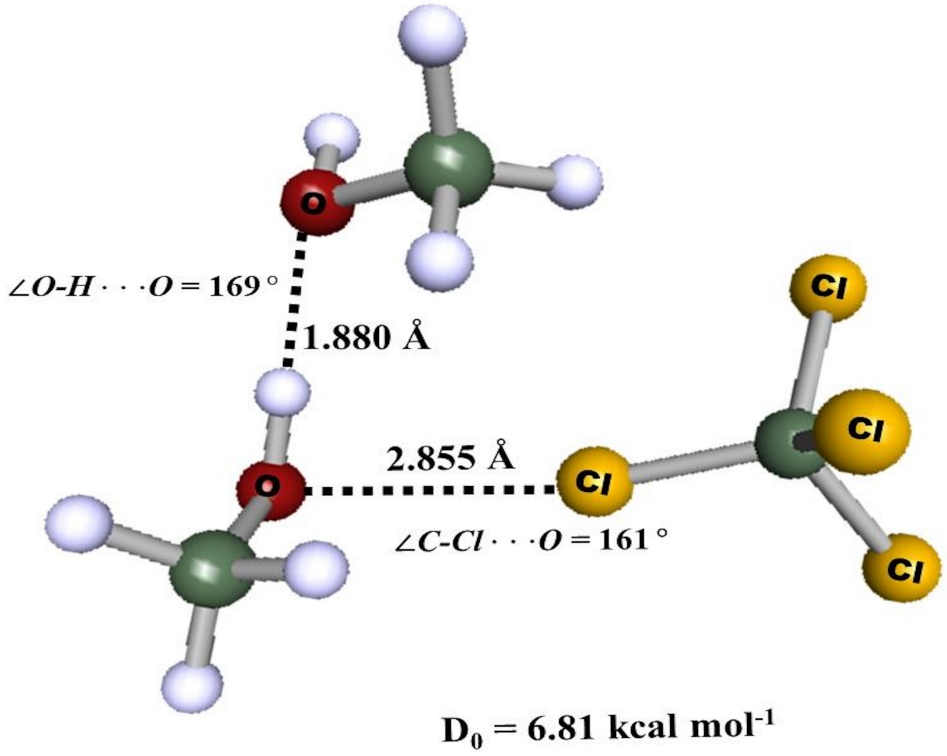

Figure S4: Optimized geometry of the trimer obtained at the MP2 level using aug-cc-pVDZ basis set. The structure represents halogen bonded interaction between CCl_4 and CH_3OH and the hydrogen bond interaction between two CH_3OH The relevant geometrical parameters are mentioned in the figure.

Cartesian co-ordinates of the optimized geometries of the complexes of [CH_3OH-CCl_4] obtained at the MP2 level using aug-cc-pVDZ basis set.

C1

Atom	**X**	**Y**	**Z**
C	-0.630033	-1.683114	1.939888
Cl	0.226807	-1.223823	3.436490
Cl	-0.659493	-3.460458	1.801500
Cl	-2.305617	-1.070996	2.012933
Cl	0.198622	-0.982787	0.535488
O	1.186403	0.522445	-1.715289
H	2.054354	0.938486	-1.634523
C	0.190236	1.552306	-1.612128
H	0.299992	2.304688	-2.408540
H	-0.779509	1.053766	-1.726472
H	0.218240	2.049485	-0.629349

C2

Atom	**X**	**Y**	**Z**
C	1.806471	-0.734475	0.512548
Cl	1.890902	0.894008	-0.212122
Cl	3.452416	-1.371100	0.733112
Cl	0.985034	-0.642463	2.088472
Cl	0.891978	-1.814397	-0.574603
O	-1.362592	0.705634	-1.516283
H	-0.456112	0.379832	-1.591967
C	-1.717202	0.650627	-0.129885
H	-1.063280	1.289414	0.485912
H	-2.746486	1.021969	-0.056888
H	-1.681129	-0.379048	0.261704

C3

Atom	X	Y	Z
C	1.968925	-0.720538	0.321413
Cl	1.979092	1.027247	-0.007386
Cl	3.534441	-1.215439	1.002595
Cl	0.666028	-1.100035	1.480609
Cl	1.672450	-1.608172	-1.198859
O	-1.398454	0.154078	-1.244751
H	-0.671791	-0.432351	-0.996365
C	-1.838984	0.831645	-0.063102
H	-1.027946	1.417671	0.398367
H	-2.637557	1.514715	-0.376993
H	-2.246205	0.131179	0.684472

C4

Atom	X	Y	Z
C	-2.143983	0.486871	-0.031051
C	1.581807	-0.704710	0.007087
H	0.529996	-0.838186	0.280710
H	2.195042	-1.388710	0.615848
H	1.701732	-0.957846	-1.058851
O	1.897479	0.669298	0.268412
H	2.827874	0.805578	0.048771
Cl	-1.295630	1.095358	1.406412
Cl	-2.285959	-1.291620	0.069495
Cl	-3.776091	1.199164	-0.111683
Cl	-1.232269	0.924803	-1.495150

C5

Atom	X	Y	Z
C	-2.274037	0.164006	-0.207437
C	1.546729	-0.031144	0.201884
H	0.804258	0.126271	-0.588012
H	1.680954	0.915676	0.750370
H	1.164608	-0.799628	0.893009
O	2.752777	-0.447974	-0.451336
H	3.424211	-0.589260	0.227633
Cl	-1.578501	0.791076	1.310234
Cl	-1.782965	-1.532513	-0.432385
Cl	-4.050288	0.262836	-0.126663
Cl	-1.687746	1.140653	-1.577297

Cartesian co-ordinates of the optimized geometries of the complexes of [CH_3OH-CCl_4] obtained at the MP2 level using def2-TZVPP basis set.

C1

Atom	X	Y	Z
C	-0.622254	-1.707601	1.995059
Cl	0.351477	-1.502484	3.451710
Cl	-0.832272	-3.428103	1.673522
Cl	-2.203778	-0.965808	2.245824
Cl	0.179310	-0.942562	0.634006
O	1.236575	0.599272	-1.602817
H	2.043284	1.081380	-1.413233
C	0.181746	1.543910	-1.719829
H	0.355105	2.245337	-2.533175
H	-0.716680	0.979202	-1.935516
H	0.027487	2.097458	-0.795552

C2

Atom	X	Y	Z
C	1.885265	-0.765464	0.526739
Cl	1.946114	0.850538	-0.177911
Cl	3.518392	-1.391327	0.702331
Cl	1.106674	-0.689203	2.102454
Cl	0.959031	-1.825840	-0.536066
O	-1.376400	0.710110	-1.511648
H	-0.476353	0.380467	-1.540072
C	-1.792636	0.682089	-0.157038
H	-1.175582	1.320179	0.473792
H	-2.809281	1.055407	-0.134974
H	-1.785223	-0.326956	0.252393

C3

Atom	X	Y	Z
C	2.065897	-0.718669	0.266672
Cl	1.988005	1.027355	0.086822
Cl	3.618669	-1.176313	0.955491
Cl	0.772862	-1.255882	1.349224
Cl	1.863669	-1.487389	-1.302205
O	-1.370702	0.044019	-1.101113
H	-0.918330	-0.682138	-0.667700
C	-1.894011	0.884455	-0.086707
H	-1.108434	1.308316	0.536664
H	-2.411236	1.693867	-0.587420
H	-2.606389	0.362380	0.550272

C5

Atom	X	Y	Z
C	-2.387133	0.197546	-0.142361
C	1.634475	-0.108803	0.084043
H	1.009045	-0.157886	-0.798595
H	1.556722	0.892773	0.503964
H	1.256549	-0.826434	0.810331
O	2.955666	-0.413853	-0.333019
H	3.521069	-0.376387	0.439558
Cl	-1.672908	0.663838	1.400344
Cl	-1.961551	-1.471836	-0.504913
Cl	-4.137878	0.350694	-0.045721
Cl	-1.774057	1.250350	-1.413631

Cartesian co-ordinates of the optimized geometry of CH_3OH dimer obtained at the MP2 level using aug-cc-pVDZ basis set.

$(CH_3OH)_2$ dimer

Atom	X	Y	Z
C	-1.477660	0.017043	-1.406089
H	-0.810423	0.871011	-1.567630
H	-2.477790	0.261420	-1.793498
H	-1.072561	-0.856899	-1.937849
C	1.839230	0.321385	1.253755
H	2.927733	0.183992	1.222161
H	1.503283	0.210864	2.298851
H	1.605776	1.345038	0.913930
O	-1.510757	-0.200962	0.019277
H	-2.093229	-0.951481	0.195008
O	1.265137	-0.668566	0.400059
H	0.301261	-0.532846	0.402025

Cartesian co-ordinates of the optimized geometry of [CH_3OH-CCl_4] trimer obtained at the MP2 level using aug-cc-pVDZ basis set.

[$(CH_3OH)_2$-CCl_4] trimer

Atom	X	Y	Z
C	-2.807724	-0.075629	-0.521545
Cl	-2.881028	0.296055	1.226459
Cl	-3.005317	-1.839498	-0.747603
Cl	-4.132884	0.772448	-1.357183
Cl	-1.241490	0.437255	-1.172298
O	1.552948	0.987836	-1.361695
H	1.597491	0.117869	-0.923967
C	1.671355	1.968896	-0.329398
H	2.602648	1.846040	0.247685
H	1.686033	2.952502	-0.815825
H	0.812908	1.937536	0.365360
C	0.454245	-1.442447	1.159874
H	0.341765	-0.422375	1.544262
H	-0.495454	-1.756334	0.704028
H	0.710697	-2.114506	1.992682
O	1.519634	-1.393981	0.190495
H	1.614174	-2.271667	-0.201331

Cartesian co-ordinates of the initial geometry of the trifurcated hydrogen bonded complex of [CH_3OH-CCl_4].

Atom	**X**	**Y**	**Z**
C	-0.660851	0.004526	0.014786
Cl	0.265534	0.031705	1.542711
Cl	-0.235334	1.439222	-0.950877
Cl	-2.400978	0.012830	0.373687
Cl	-0.238147	-1.465631	-0.897356
C	3.765216	-0.004072	0.580632
H	4.842597	-0.008384	0.375792
H	3.513615	-0.900106	1.171594
H	3.520095	0.896389	1.167587
O	3.108664	-0.004509	-0.691977
H	2.158288	-0.002035	-0.520804