Acta Cryst

B

STRUCTURAL SCIENCE
CRYSTAL ENGINEERING
MATERIALS

Volume 73 (2017)

Supporting information for article:

Taking the halogen bonding-hydrogen bonding competition one step further: Complexes of difluoroiodomethane with trimethyl-phosphine, dimethyl sulfide and chloromethane

Yannick Geboes, Frank De Proft and Wouter A. Herrebout

Table S1.1: Cartesian coordinates of the MP2/aug-cc-pVDZ-PP optimized geometry of difluoroiodomethane.

	X	Y	Z
CHF$_2$I			
C	0.461801	-1.276126	0.000000
H	1.552810	-1.382611	0.000000
F	-0.060896	-1.882815	1.101579
F	-0.060896	-1.882815	-1.101579
I	-0.060896	0.810001	0.000000

Table S1.2: Cartesian coordinates of the MP2/aug-cc-pVDZ optimized geometry of trimethylphosphine.

	X	Y	Z
TMP			
P	0.000000	0.000000	0.618978
C	0.000000	1.626598	-0.285498
H	-0.889964	2.208825	-0.001487
H	0.889964	2.208825	-0.001487
H	0.000000	1.481355	-1.378927
C	-1.408675	-0.813299	-0.285498
H	-1.467917	-1.875144	-0.001487
H	-2.357881	-0.333681	-0.001487
H	-1.282891	-0.740678	-1.378927
C	1.408675	-0.813299	-0.285498
H	2.357881	-0.333681	-0.001487
H	1.467917	-1.875144	-0.001487
H	1.282891	-0.740678	-1.378927

Table S1.3: Cartesian coordinates of the MP2/aug-cc-pVDZ optimized geometry of dimethyl sulfide.

	X	Y	Z
DMS			
S	0.000000	0.674247	0.000000
C	-1.370330	-0.522675	0.000000
H	-2.309643	0.047454	0.000000
H	-1.334542	-1.152689	-0.900834
H	-1.334542	-1.152688	0.900834
C	1.370330	-0.522675	0.000000
H	1.334542	-1.152689	-0.900834
H	2.309643	0.047454	0.000000
H	1.334542	-1.152689	0.900834

Table S1.4: Cartesian coordinates of the MP2/aug-cc-pVDZ optimized geometry of chloromethane.

CH$_3$Cl	X	Y	Z

	X	Y	Z
CH₃Cl			
C	0.000000	0.000000	-1.134242
H	0.000000	1.040001	-1.477217
H	-0.900667	-0.520001	-1.477217
H	0.900667	-0.520001	-1.477217
Cl	0.000000	0.000000	0.661006

Table S2.1: Cartesian coordinates of the MP2/aug-cc-pVDZ-PP optimized geometry of the hydrogen bonded complex between CHF₂I and trimethylphosphine.

	X	Y	Z
CHF₂I			
C	-1.216105	1.353406	-0.000007
H	-0.132928	1.531390	-0.000019
F	-1.797300	1.906772	-1.100901
F	-1.797275	1.906778	1.100897
I	-1.556091	-0.778530	0.000002
TMP			
P	2.433219	0.310927	-0.000005
C	2.626429	-0.879781	-1.413081
H	1.740677	-1.530608	-1.468765
H	2.700723	-0.323563	-2.360047
H	3.527461	-1.503794	-1.290861
C	4.140404	1.046128	-0.000009
H	4.271464	1.679600	-0.890422
H	4.271460	1.679624	0.890387
H	4.915127	0.261437	0.000003
C	2.626421	-0.879749	1.413099
H	2.700709	-0.323510	2.360052
H	1.740667	-1.530573	1.468791
H	3.527452	-1.503766	1.290898

Table S2.2: Cartesian coordinates of the MP2/aug-cc-pVDZ-PP optimized geometry of the halogen bonded complex between CHF₂I and trimethylphosphine.

	X	Y	Z
CHF₂I			
C	3.039329	0.000074	-0.120817
H	3.521408	0.000128	-1.106167
F	3.443285	-1.103496	0.579305
F	3.443117	1.103684	0.579340
I	0.894182	-0.000089	-0.330647
TMP			
P	-2.597960	-0.000069	-0.084146
C	-2.962250	1.415033	1.061597

H	-2.183466	1.468763	1.837625
H	-2.946416	2.360742	0.498785
H	-3.946593	1.299233	1.545139
C	-4.168149	-0.000761	-1.076796
H	-4.197578	0.889428	-1.723114
H	-4.197437	-0.891692	-1.722098
H	-5.055548	-0.000457	-0.422101
C	-2.962026	-1.413920	1.063213
H	-2.946027	-2.360269	0.501483
H	-2.183240	-1.466632	1.839308
H	-3.946393	-1.297731	1.546613

Table S2.3: Cartesian coordinates of the MP2/aug-cc-pVDZ-PP optimized geometry of the hydrogen bonded complex between CHF_2I and dimethyl sulfide.

	X	Y	Z
CHF_2I			
C	-0.785959	1.258032	-0.381791
H	0.079193	1.257115	-1.054250
F	-0.488219	1.947842	0.756259
F	-1.860138	1.858460	-0.964421
I	-1.281284	-0.778912	0.124298
DMS			
S	2.745384	0.432273	-0.507237
C	2.637149	0.518652	1.308262
H	2.514127	1.574865	1.584687
H	1.767347	-0.049505	1.669318
H	3.559797	0.130779	1.763817
C	2.888789	-1.375358	-0.664189
H	2.002971	-1.868460	-0.238243
H	2.953370	-1.612667	-1.735166
H	3.800441	-1.730811	-0.162384

Table S2.4: Cartesian coordinates of the MP2/aug-cc-pVDZ-PP optimized geometry of the halogen bonded complex between CHF_2I and dimethyl sulfide.

	X	Y	Z
CHF_2I			
C	-2.639583	0.000071	-0.002747
H	-3.199738	0.000218	-0.945700
F	-2.982435	-1.103272	0.727881
F	-2.982301	1.103281	0.728144
I	-0.520886	-0.000012	-0.388345
DMS			
S	2.929895	-0.000077	-0.424875
C	2.967183	1.372335	0.770366
H	2.930865	2.310712	0.199858
H	2.094133	1.323466	1.437999
H	3.896366	1.343011	1.357619
C	2.967139	-1.372225	0.770669
H	2.094094	-1.323176	1.438295
H	2.930784	-2.310727	0.200369
H	3.896326	-1.342805	1.357911

Table S2.5: Cartesian coordinates of the MP2/aug-cc-pVDZ-PP optimized geometry of the hydrogen bonded complex with a secondary C-H···F between CHF_2I and chloromethane.

	X	Y	Z
CHF_2I			
C	-0.341590	1.277646	-0.128791
H	0.442884	1.290430	-0.893239
F	-1.301935	2.198920	-0.414227
F	0.193498	1.594957	1.086312
I	-1.222580	-0.684963	-0.035059
CH_3Cl			
C	2.847452	-0.704367	0.946920
H	2.382405	0.045316	1.595374
H	3.855860	-0.952773	1.294024
H	2.222981	-1.601401	0.880877
Cl	2.990197	-0.003711	-0.704497

Table S2.6: Cartesian coordinates of the MP2/aug-cc-pVDZ-PP optimized geometry of the hydrogen bonded complex with a secondary C-H···I between CHF_2I and chloromethane.

	X	Y	Z
CHF_2I			
C	-0.676612	1.305798	-0.000004
H	0.402006	1.498825	-0.000030
F	-1.257116	1.857254	-1.101066
F	-1.257061	1.857249	1.101089
I	-1.011921	-0.824659	0.000000
CH_3Cl			
C	3.096877	-1.100970	0.000022
H	2.582231	-1.451300	-0.900496
H	2.582225	-1.451256	0.900554
H	4.146207	-1.414069	0.000033
Cl	3.060303	0.697955	-0.000023

Table S2.7: Cartesian coordinates of the MP2/aug-cc-pVDZ-PP optimized geometry of the halogen bonded complex between CHF_2I and chloromethane.

	X	Y	Z
CHF_2I			
C	2.439103	-0.010448	-0.000231
H	2.987805	-0.959635	-0.001505
F	2.782525	0.717958	-1.101619
F	2.782955	0.715250	1.102809
I	0.322673	-0.385166	-0.000280
CH_3Cl			
C	-3.173743	1.461749	0.000851

H		-4.185999	1.879482	0.001089			
H		-2.627700	1.761309	-0.899947			
H		-2.627660	1.760383	0.901930			
Cl		-3.313505	-0.331435	-0.000066			

Table S3A: MP2/aug-cc-pVDZ-PP vibrational frequencies, in cm^{-1}, infrared intensities, in km mol^{-1}, and Raman intensities, in Å^4 amu^{-1}, for the hydrogen bonded complex of CHF$_2$I and trimethylphosphine and both monomers, as well as the complexation shift Δv.

	Monomer			Hydrogen bonded complex			
	Frequency	IR intensity	Raman intensity	Frequency	Δv	IR intensity	Raman intensity
CHF$_2$I							
v_1 (A')	3192.4	3.6	94.4	3172.8	-19.6	18.9	210.1
v_2 (A')	1279.7	99.2	7.5	1280.3	0.6	129.6	31.5
v_3 (A')	1074.1	300.4	3.2	1070.1	-3.9	309.6	3.5
v_4 (A')	652.5	81.8	18.4	651.0	-1.5	72.8	10.9
v_5 (A')	549.4	2.9	1.8	551.0	1.6	5.3	2.0
v_6 (A')	276.0	0.2	6.6	272.7	-3.3	0.01	6.2
v_7 (A")	1346.0	4.1	2.7	1369.5	23.5	8.9	1.0
v_8 (A")	1096.9	186.9	1.9	1092.7	-4.2	164.9	1.5
v_9 (A")	277.0	0.0004	1.2	275.5	-1.5	0.002	0.9
TMP							
v_1 (A$_1$)	3148.5	33.6	160.8	3151.3	2.7	28.5	148.6
v_2 (A$_1$)	3043.5	29.4	528.4	3045.9	2.3	30.0	526.0
v_3 (A$_1$)	1469.0	9.2	1.5	1468.7	-0.3	8.0	0.9
v_4 (A$_1$)	1314.7	5.1	7.3	1315.6	1.0	9.0	5.5
v_5 (A$_1$)	957.8	20.1	5.0	959.4	1.5	34.9	4.2
v_6 (A$_1$)	660.9	0.5	26.5	662.8	1.9	0.9	28.0
v_7 (A$_1$)	287.5	1.0	1.5	287.8	0.3	0.9	1.4
v_8 (A$_2$)	3168.1	0.0	0.0	3170.5	2.4	0.2	3.3
v_9 (A$_2$)	1440.1	0.0	0.0	1439.3	-0.8	0.2	0.3
v_{10} (A$_2$)	776.6	0.0	0.0	779.5	2.9	0.0001	0.03
v_{11} (A$_2$)	164.1	0.0	0.0	164.5	0.4	0.007	0.01
v_{12} (E)	3167.9	11.5	95.9	3170.2	2.3	8.6	78.4
v_{13} (E)	3149.3	3.0	18.4	3152.4	3.1	2.6	23.2
v_{14} (E)	3046.9	16.7	4.2	3049.3	2.4	14.1	14.8
v_{15} (E)	1456.7	8.7	3.0	1456.0	-0.7	6.8	3.9
v_{16} (E)	1446.2	3.1	9.5	1445.9	-0.3	2.6	8.4
v_{17} (E)	1290.0	2.3	0.7	1290.6	0.7	2.4	0.7
v_{18} (E)	946.6	16.5	0.5	948.9	2.3	16.4	0.9
v_{19} (E)	831.0	0.2	0.3	833.2	2.2	0.2	0.4
v_{20} (E)	718.3	11.6	11.8	722.8	4.5	9.4	13.0

v_{21} (E)	249.8	0.2	2.8	248.2	-1.6	0.2	2.3
v_{22} (E)	207.4	0.0009	0.6	207.3	-0.1	0.003	0.4

Van der Waals vibrations: 6.3 cm^{-1}, 0.07 km mol^{-1}, 0.1 Å^4 amu^{-1}, 27.1 cm^{-1}, 0.2 km mol^{-1}, 0.06 Å^4 amu^{-1}, 33.3 cm^{-1}, 0.2 km mol^{-1}, 0.5 Å^4 amu^{-1}, 46.7 cm^{-1}, 0.8 km mol^{-1}, 0.5 Å^4 amu^{-1}, 50.3 cm^{-1}, 0.8 km mol^{-1}, 0.2 Å^4 amu^{-1}, 65.4 cm^{-1}, 0.2 km mol^{-1}, 0.7 Å^4 amu^{-1}.

Table S3B: MP2/aug-cc-pVDZ-PP vibrational frequencies, in cm^{-1}, infrared intensities, in $km\ mol^{-1}$, and Raman intensities, in $Å^4\ amu^{-1}$, for the hydrogen bonded complex of CHF_2I and trimethylphosphine-d_9 and both monomers, as well as the complexation shift Δv.

	Monomer			Hydrogen bonded complex			
	Frequency	IR intensity	Raman intensity	Frequency	Δv	IR intensity	Raman intensity
CHF_2I							
v_1 (A')	3192.4	3.6	94.4	3172.8	-19.6	17.5	200.9
v_2 (A')	1279.7	99.2	7.5	1280.6	0.9	129.8	28.9
v_3 (A')	1074.1	300.4	3.2	1070.2	-3.9	307.3	3.7
v_4 (A')	652.5	81.8	18.4	651.2	-1.3	74.5	13.3
v_5 (A')	549.4	2.9	1.8	551.0	1.6	5.3	2.0
v_6 (A')	276.0	0.2	6.6	272.8	-3.2	0.008	6.5
v_7 (A")	1346.0	4.1	2.7	1369.5	23.5	8.7	1.0
v_8 (A")	1096.9	186.9	1.9	1092.7	-4.2	164.2	1.4
v_9 (A")	277.0	0.0004	1.2	275.5	-1.5	0.002	0.9
TMP-d_9							
v_1 (A$_1$)	2330.8	15.5	84.8	2333.2	2.4	13.1	87.2
v_2 (A$_1$)	2184.5	10.3	254.0	2186.0	1.5	10.6	250.2
v_3 (A$_1$)	1058.7	8.5	0.9	1058.4	-0.4	7.1	0.6
v_4 (A$_1$)	1021.8	3.7	15.4	1022.0	0.2	6.6	16.3
v_5 (A$_1$)	779.8	14.3	2.3	781.3	1.5	22.5	1.7
v_6 (A$_1$)	597.0	0.0	20.0	598.6	1.6	0.2	18.6
v_7 (A$_1$)	246.1	0.5	1.1	246.9	0.8	0.4	0.8
v_8 (A$_2$)	2344.5	0.0	0.0	2346.4	1.9	0.001	0.2
v_9 (A$_2$)	1041.0	0.0	0.0	1040.1	-0.9	0.002	0.2
v_{10} (A$_2$)	582.2	0.0	0.0	584.4	2.3	0.002	0.02
v_{11} (A$_2$)	116.8	0.0	0.0	117.2	0.4	0.003	0.006
v_{12} (E)	2345.4	3.7	50.1	2347.3	1.9	2.9	43.6
v_{13} (E)	2332.7	1.4	11.4	2335.1	2.4	1.0	12.2
v_{14} (E)	2186.9	6.7	0.7	2188.5	1.5	5.5	5.3
v_{15} (E)	1052.1	4.8	1.2	1051.3	-0.8	5.4	1.5
v_{16} (E)	1044.7	0.2	4.5	1044.4	-0.4	0.2	3.9
v_{17} (E)	1009.0	8.5	3.5	1009.7	0.7	8.9	3.5
v_{18} (E)	760.6	15.4	1.8	762.9	2.3	15.1	2.7
v_{19} (E)	652.0	3.6	6.9	655.9	3.9	1.9	7.7
v_{20} (E)	625.1	0.5	0.7	626.6	1.5	0.2	0.8
v_{21} (E)	208.8	0.1	2.3	207.9	-0.8	0.09	1.8
v_{22} (E)	150.6	0.01	0.1	150.3	-0.2	0.01	0.1

Van der Waals vibrations: 5.9 cm^{-1}, 0.08 $km\ mol^{-1}$, 0.1 $Å^4\ amu^{-1}$, 25.3 cm^{-1}, 0.1 $km\ mol^{-1}$, 0.04 $Å^4\ amu^{-1}$, 32.2 cm^{-1}, 0.2 $km\ mol^{-1}$, 0.4 $Å^4\ amu^{-1}$, 43.5 cm^{-1}, 0.7 $km\ mol^{-1}$, 0.5 $Å^4\ amu^{-1}$, 45.3 cm^{-1}, 0.6 $km\ mol^{-}$

[1],
0.2 Å^4 amu^{-1}, 63.6 cm^{-1}, 0.2 km mol^{-1}, 0.7 Å^4 amu^{-1}.

Table S4A: MP2/aug-cc-pVDZ-PP vibrational frequencies, in cm^{-1}, infrared intensities, in $km\ mol^{-1}$, and Raman intensities, in $Å^4\ amu^{-1}$, for the halogen bonded complex of CHF_2I and trimethylphosphine and both monomers, as well as the complexation shift Δv.

	Monomer			Halogen bonded complex			
	Frequency	IR intensity	Raman intensity	Frequency	Δv	IR intensity	Raman intensity
CHF$_2$I							
v_1 (A')	3192.4	3.6	94.4	3180.3	-12.1	8.7	168.9
v_2 (A')	1279.7	99.2	7.5	1278.5	-1.2	147.4	9.0
v_3 (A')	1074.1	300.4	3.2	1068.1	-6.0	349.6	4.6
v_4 (A')	652.5	81.8	18.4	647.5	-5.0	45.4	95.4
v_5 (A')	549.4	2.9	1.8	544.7	-4.7	2.7	6.1
v_6 (A')	276.0	0.2	6.6	272.0	-4.0	4.5	31.1
v_7 (A")	1346.0	4.1	2.7	1343.7	-2.3	4.2	3.6
v_8 (A")	1096.9	186.9	1.9	1079.6	-17.2	183.7	1.7
v_9 (A")	277.0	0.0004	1.2	278.6	1.6	0.04	1.5
TMP							
v_1 (A$_1$)	3148.5	33.6	160.8	3151.6	3.1	31.3	188.2
v_2 (A$_1$)	3043.5	29.4	528.4	3046.0	2.5	35.6	563.3
v_3 (A$_1$)	1469.0	9.2	1.5	1467.7	-1.3	7.4	1.6
v_4 (A$_1$)	1314.7	5.1	7.3	1315.4	0.7	3.9	17.1
v_5 (A$_1$)	957.8	20.1	5.0	957.6	-0.3	72.2	22.1
v_6 (A$_1$)	660.9	0.5	26.5	662.3	1.4	0.9	26.5
v_7 (A$_1$)	287.5	1.0	1.5	286.2	-1.4	0.7	2.3
v_8 (A$_2$)	3168.1	0.0	0.0	3170.0	1.9	3.9	32.9
v_9 (A$_2$)	1440.1	0.0	0.0	1439.0	-1.1	0.01	0.05
v_{10} (A$_2$)	776.6	0.0	0.0	779.1	2.6	0.0	0.01
v_{11} (A$_2$)	164.1	0.0	0.0	163.9	-0.2	0.0008	0.002
v_{12} (E)	3167.9	11.5	95.9	3170.9	3.0	6.2	65.4
v_{13} (E)	3149.3	3.0	18.4	3152.8	3.5	2.3	29.9
v_{14} (E)	3046.9	16.7	4.2	3049.4	2.5	13.4	18.5
v_{15} (E)	1456.7	8.7	3.0	1455.5	-1.2	9.2	4.2
v_{16} (E)	1446.2	3.1	9.5	1445.0	-1.2	2.2	8.5
v_{17} (E)	1290.0	2.3	0.7	1290.9	0.9	4.0	1.2
v_{18} (E)	946.6	16.5	0.5	948.9	2.3	16.0	0.8
v_{19} (E)	831.0	0.2	0.3	832.1	1.2	0.8	0.6
v_{20} (E)	718.3	11.6	11.8	724.7	6.4	8.7	16.0
v_{21} (E)	249.8	0.2	2.8	245.3	-4.5	0.2	2.8
v_{22} (E)	207.4	0.0009	0.6	207.0	-0.3	0.02	0.4

Van der Waals vibrations: 3.7 cm^{-1}, 1.0 $km\ mol^{-1}$, 0.009 $Å^4\ amu^{-1}$, 12.0 cm^{-1}, 0.7 $km\ mol^{-1}$, 0.6 $Å^4\ amu^{-1}$, 12.4 cm^{-1}, 1.5 $km\ mol^{-1}$, 0.5 $Å^4\ amu^{-1}$, 52.0 cm^{-1}, 2.4 $km\ mol^{-1}$, 3.7 $Å^4\ amu^{-1}$, 52.9 cm^{-1}, 0.004 km

mol^{-1},
0.2 Å^4 amu^{-1}, 57.7 cm^{-1}, 0.8 km mol^{-1}, 0.4 Å^4 amu^{-1}.

Table S4B: MP2/aug-cc-pVDZ-PP vibrational frequencies, in cm^{-1}, infrared intensities, in km mol^{-1}, and Raman intensities, in Å^4 amu^{-1}, for the halogen bonded complex of CHF$_2$I and trimethylphosphine-d$_9$ and both monomers, as well as the complexation shift $\Delta\nu$.

	Monomer			Halogen bonded complex			
	Frequency	IR intensity	Raman intensity	Frequency	$\Delta\nu$	IR intensity	Raman intensity
CHF$_2$I							
ν_1 (A')	3192.4	3.6	94.4	3180.3	-12.1	8.7	168.6
ν_2 (A')	1279.7	99.2	7.5	1278.6	-1.1	150.6	9.4
ν_3 (A')	1074.1	300.4	3.2	1067.9	-6.1	359.8	3.8
ν_4 (A')	652.5	81.8	18.4	647.2	-5.4	43.9	100.5
ν_5 (A')	549.4	2.9	1.8	544.7	-4.7	2.7	6.1
ν_6 (A')	276.0	0.2	6.6	272.2	-3.8	4.0	32.0
ν_7 (A")	1346.0	4.1	2.7	1343.7	-2.3	4.2	3.6
ν_8 (A")	1096.9	186.9	1.9	1079.6	-17.2	184.0	1.7
ν_9 (A")	277.0	0.0004	1.2	278.5	1.6	0.04	1.4
TMP-d$_9$							
ν_1 (A$_1$)	2330.8	15.5	84.8	2333.6	2.7	12.5	127.0
ν_2 (A$_1$)	2184.5	10.3	254.0	2186.1	1.6	12.7	263.2
ν_3 (A$_1$)	1058.7	8.5	0.9	1057.6	-1.1	9.3	0.7
ν_4 (A$_1$)	1021.8	3.7	15.4	1022.1	0.3	3.7	20.8
ν_5 (A$_1$)	779.8	14.3	2.3	780.1	0.2	46.1	10.8
ν_6 (A$_1$)	597.0	0.0	20.0	598.2	1.2	0.0	21.2
ν_7 (A$_1$)	246.1	0.5	1.1	245.7	-0.4	0.5	1.3
ν_8 (A$_2$)	2344.5	0.0	0.0	2346.3	1.8	0.5	6.4
ν_9 (A$_2$)	1041.0	0.0	0.0	1040.0	-1.0	0.0001	0.04
ν_{10} (A$_2$)	582.2	0.0	0.0	584.3	2.1	0.0003	0.008
ν_{11} (A$_2$)	116.8	0.0	0.0	116.7	-0.1	0.0004	0.001
ν_{12} (E)	2345.4	3.7	50.1	2347.7	2.3	2.2	39.4
ν_{13} (E)	2332.7	1.4	11.4	2335.4	2.8	0.7	14.5
ν_{14} (E)	2186.9	6.7	0.7	2188.5	1.6	5.1	6.1
ν_{15} (E)	1052.1	4.8	1.2	1051.0	-1.1	4.5	1.8
ν_{16} (E)	1044.7	0.2	4.5	1043.7	-1.0	0.2	4.0
ν_{17} (E)	1009.0	8.5	3.5	1010.1	1.1	8.0	5.0
ν_{18} (E)	760.6	15.4	1.8	763.7	3.0	13.5	3.3
ν_{19} (E)	652.0	3.6	6.9	657.7	5.7	3.6	5.7
ν_{20} (E)	625.1	0.5	0.7	625.6	0.5	0.3	1.6
ν_{21} (E)	208.8	0.1	2.3	206.0	-2.7	0.1	2.2
ν_{22} (E)	150.6	0.01	0.1	149.8	-0.8	0.04	0.1

Van der Waals vibrations: 3.6 cm^{-1}, 1.0 km mol^{-1}, 0.007 Å^4 amu^{-1}, 11.0 cm^{-1}, 0.6 km mol^{-1}, 0.6 Å^4 amu^{-1}, 11.4 cm^{-1}, 1.2 km mol^{-1}, 0.5 Å^4 amu^{-1}, 50.2 cm^{-1}, 2.5 km mol^{-1}, 3.5 Å^4 amu^{-1}, 50.8 cm^{-1}, 0.02 km mol^{-}

[1],
0.1 Å^4 amu^{-1}, 54.9 cm^{-1}, 0.4 km mol^{-1}, 0.3 Å^4 amu^{-1}.

Table S5A: MP2/aug-cc-pVDZ-PP vibrational frequencies, in cm^{-1}, infrared intensities, in km mol^{-1}, and Raman intensities, in Å^4 amu^{-1}, for the hydrogen bonded complex of CHF$_2$I and dimethyl sulfide and both monomers, as well as the complexation shift Δv.

	Monomer			Hydrogen bonded complex			
	Frequency	IR intensity	Raman intensity	Frequency	Δv	IR intensity	Raman intensity
CHF$_2$I							
v_1 (A')	3192.4	3.6	94.4	3202.1	9.7	3.0	99.6
v_2 (A')	1279.7	99.2	7.5	1276.8	-2.9	100.4	17.0
v_3 (A')	1074.1	300.4	3.2	1068.2	-5.9	269.8	3.3
v_4 (A')	652.5	81.8	18.4	650.5	-2.0	72.7	14.0
v_5 (A')	549.4	2.9	1.8	550.1	0.7	4.0	1.5
v_6 (A')	276.0	0.2	6.6	273.5	-2.5	0.03	5.9
v_7 (A")	1346.0	4.1	2.7	1344.4	-1.6	6.7	5.2
v_8 (A")	1096.9	186.9	1.9	1092.9	-4.0	209.0	3.1
v_9 (A")	277.0	0.0004	1.2	277.6	0.7	0.09	1.0
DMS							
v_1 (A$_1$)	3186.3	9.8	92.1	3187.8	1.4	5.8	74.2
v_2 (A$_1$)	3062.2	31.8	338.0	3063.7	1.5	24.5	329.7
v_3 (A$_1$)	1473.5	0.3	7.6	1472.7	-0.8	2.1	7.8
v_4 (A$_1$)	1352.5	0.8	0.9	1353.1	0.6	1.2	1.0
v_5 (A$_1$)	1046.4	8.6	0.4	1047.9	1.5	8.0	0.3
v_6 (A$_1$)	713.3	2.8	22.1	710.9	-2.4	2.8	19.3
v_7 (A$_1$)	260.8	0.03	3.0	260.6	-0.2	0.05	2.4
v_8 (A$_2$)	3168.0	0.0	16.5	3172.0	4.0	0.2	12.1
v_9 (A$_2$)	1450.1	0.0	10.3	1448.3	-1.8	0.4	9.3
v_{10} (A$_2$)	945.6	0.0	0.1	948.8	3.2	0.01	0.5
v_{11} (A$_2$)	171.2	0.0	0.1	174.2	3.0	0.04	0.06
v_{12} (B$_1$)	3159.9	21.3	119.4	3165.0	5.1	17.2	99.4
v_{13} (B$_1$)	1462.5	12.9	0.02	1460.7	-1.8	10.7	0.5
v_{14} (B$_1$)	982.7	4.1	0.006	985.7	3.0	10.9	0.4
v_{15} (B$_1$)	187.1	0.8	0.09	188.5	1.4	1.1	0.1
v_{16} (B$_2$)	3187.4	3.4	42.0	3190.0	2.6	2.7	43.4
v_{17} (B$_2$)	3066.9	26.3	2.8	3068.0	1.1	20.5	6.1
v_{18} (B$_2$)	1464.2	13.6	0.03	1462.9	-1.2	8.0	0.2
v_{19} (B$_2$)	1326.0	6.5	0.1	1325.9	-0.1	4.2	0.1
v_{20} (B$_2$)	912.7	0.2	0.2	915.2	2.5	0.1	0.1
v_{21} (B$_2$)	765.1	0.1	8.5	762.7	-2.3	0.4	7.0

Van der Waals vibrations: 24.5 cm^{-1}, 0.6 km mol^{-1}, 0.5 Å^4 amu^{-1}, 31.4 cm^{-1}, 0.3 km mol^{-1}, 0.4 Å^4 amu^{-1}, 36.8 cm^{-1}, 1.1 km mol^{-1}, 0.2 Å^4 amu^{-1}, 61.8 cm^{-1}, 0.04 km mol^{-1}, 1.2 Å^4 amu^{-1}, 72.7 cm^{-1}, 0.3 km mol^{-1}

[1],
0.5 Å^4 amu^{-1}, 91.6 cm^{-1}, 7.3 km mol^{-1}, 0.2 Å^4 amu^{-1}.

Table S5B: MP2/aug-cc-pVDZ-PP vibrational frequencies, in cm^{-1}, infrared intensities, in km mol^{-1}, and Raman intensities, in Å^4 amu^{-1}, for the hydrogen bonded complex of CHF$_2$I and dimethyl sulfide-d$_6$ and both monomers, as well as the complexation shift Δv.

	Monomer			Hydrogen bonded complex			
	Frequency	IR intensity	Raman intensity	Frequency	Δv	IR intensity	Raman intensity
CHF$_2$I							
v_1 (A')	3192.4	3.6	94.4	3202.1	9.7	2.9	99.6
v_2 (A')	1279.7	99.2	7.5	1277.1	-2.6	101.4	16.0
v_3 (A')	1074.1	300.4	3.2	1069.4	-4.6	254.4	3.3
v_4 (A')	652.5	81.8	18.4	650.4	-2.1	73.4	13.1
v_5 (A')	549.4	2.9	1.8	550.1	0.7	4.0	1.5
v_6 (A')	276.0	0.2	6.6	273.5	-2.5	0.03	5.9
v_7 (A")	1346.0	4.1	2.7	1344.9	-1.1	6.1	4.9
v_8 (A")	1096.9	186.9	1.9	1093.5	-3.4	201.8	3.2
v_9 (A")	277.0	0.0004	1.2	277.6	0.6	0.09	1.1
DMS-d$_6$							
v_1 (A$_1$)	2361.4	4.6	45.5	2363.7	2.3	2.1	35.0
v_2 (A$_1$)	2194.1	16.7	162.8	2195.0	0.8	12.9	158.2
v_3 (A$_1$)	1064.3	0.5	3.0	1063.2	-1.1	13.1	3.4
v_4 (A$_1$)	1037.4	1.2	5.6	1036.0	-1.4	0.3	5.5
v_5 (A$_1$)	837.1	3.9	1.7	837.4	0.2	3.0	1.3
v_6 (A$_1$)	655.7	2.7	17.4	654.5	-1.2	2.2	16.3
v_7 (A$_1$)	223.6	0.0	2.2	223.7	0.1	0.05	1.8
v_8 (A$_2$)	2350.5	0.0	8.5	2353.5	3.0	0.08	6.2
v_9 (A$_2$)	1046.5	0.0	4.3	1044.4	-2.1	7.6	3.7
v_{10} (A$_2$)	708.3	0.0	0.4	710.6	2.3	0.008	0.7
v_{11} (A$_2$)	122.8	0.0	0.1	126.3	3.5	0.04	0.09
v_{12} (B$_1$)	2344.4	10.8	63.9	2348.2	3.9	8.6	53.5
v_{13} (B$_1$)	1056.3	7.2	0.0	1054.2	-2.1	17.7	0.4
v_{14} (B$_1$)	751.1	0.9	0.1	753.2	2.1	2.8	0.4
v_{15} (B$_1$)	136.8	0.8	0.1	139.4	2.6	1.9	0.1
v_{16} (B$_2$)	2360.9	1.2	22.7	2362.1	1.2	1.6	25.8
v_{17} (B$_2$)	2197.7	15.2	0.5	2198.2	0.5	11.8	2.4
v_{18} (B$_2$)	1060.2	7.9	0.1	1058.7	-1.5	0.7	0.2
v_{19} (B$_2$)	1017.4	2.5	0.6	1016.0	-1.4	0.9	0.5
v_{20} (B$_2$)	720.2	0.0	7.3	718.8	-1.3	0.1	6.0
v_{21} (B$_2$)	686.0	0.0	0.1	687.8	1.8	0.003	0.05

Van der Waals vibrations: 22.5 cm^{-1}, 0.5 km mol^{-1}, 0.4 Å^4 amu^{-1}, 31.0 cm^{-1}, 0.3 km mol^{-1}, 0.4 Å^4 amu^{-1}, 36.2 cm^{-1}, 1.0 km mol^{-1}, 0.2 Å^4 amu^{-1}, 54.5 cm^{-1}, 0.07 km mol^{-1}, 0.9 Å^4 amu^{-1}, 67.1 cm^{-1}, 0.9 km mol^{-}

0.5 Å^4 amu^{-1}, 83.8 cm^{-1}, 4.6 km mol^{-1}, 0.1 Å^4 amu^{-1}.

Table S6A: MP2/aug-cc-pVDZ-PP vibrational frequencies, in cm^{-1}, infrared intensities, in km mol^{-1}, and Raman intensities, in Å^4 amu^{-1}, for the halogen bonded complex of CHF$_2$I and dimethyl sulfide and both monomers, as well as the complexation shift Δv.

	Monomer			Halogen bonded complex			
	Frequency	IR intensity	Raman intensity	Frequency	Δv	IR intensity	Raman intensity
CHF$_2$I							
v_1 (A')	3192.4	3.6	94.4	3183.2	-9.3	7.2	148.4
v_2 (A')	1279.7	99.2	7.5	1279.5	-0.2	135.6	8.0
v_3 (A')	1074.1	300.4	3.2	1069.0	-5.0	327.5	2.8
v_4 (A')	652.5	81.8	18.4	650.5	-2.0	54.0	58.5
v_5 (A')	549.4	2.9	1.8	545.6	-3.8	2.6	4.0
v_6 (A')	276.0	0.2	6.6	274.1	-1.9	3.1	20.1
v_7 (A")	1346.0	4.1	2.7	1344.2	-1.8	3.8	3.2
v_8 (A")	1096.9	186.9	1.9	1082.2	-14.6	181.7	1.7
v_9 (A")	277.0	0.0004	1.2	279.3	2.3	0.01	1.5
DMS							
v_1 (A$_1$)	3186.3	9.8	92.1	3188.3	1.9	6.6	89.9
v_2 (A$_1$)	3062.2	31.8	338.0	3062.3	0.1	24.3	311.5
v_3 (A$_1$)	1473.5	0.3	7.6	1471.5	-2.0	2.8	9.7
v_4 (A$_1$)	1352.5	0.8	0.9	1352.2	-0.3	0.2	7.5
v_5 (A$_1$)	1046.4	8.6	0.4	1047.4	1.1	6.5	0.6
v_6 (A$_1$)	713.3	2.8	22.1	710.5	-2.8	3.3	19.0
v_7 (A$_1$)	260.8	0.03	3.0	261.1	0.3	0.03	2.5
v_8 (A$_2$)	3168.0	0.0	16.5	3170.6	2.6	0.4	14.5
v_9 (A$_2$)	1450.1	0.0	10.3	1448.3	-1.8	0.3	8.6
v_{10} (A$_2$)	945.6	0.0	0.1	948.9	3.3	0.003	0.4
v_{11} (A$_2$)	171.2	0.0	0.1	173.6	2.4	0.02	0.09
v_{12} (B$_1$)	3159.9	21.3	119.4	3163.6	3.7	16.3	113.3
v_{13} (B$_1$)	1462.5	12.9	0.02	1461.2	-1.4	13.6	0.5
v_{14} (B$_1$)	982.7	4.1	0.006	984.9	2.3	13.6	0.7
v_{15} (B$_1$)	187.1	0.8	0.09	188.0	0.9	1.8	0.4
v_{16} (B$_2$)	3187.4	3.4	42.0	3189.3	1.9	1.7	32.6
v_{17} (B$_2$)	3066.9	26.3	2.8	3066.7	-0.2	18.7	7.5
v_{18} (B$_2$)	1464.2	13.6	0.03	1461.5	-2.6	8.0	0.4
v_{19} (B$_2$)	1326.0	6.5	0.1	1326.0	0.1	3.5	0.09
v_{20} (B$_2$)	912.7	0.2	0.2	914.9	2.2	0.2	0.2
v_{21} (B$_2$)	765.1	0.1	8.5	762.3	-2.8	0.4	7.2

Van der Waals vibrations: 6.3 cm^{-1}, 2.5 km mol^{-1}, 0.05 Å^4 amu^{-1}, 32.2 cm^{-1}, 0.0002 km mol^{-1}, 1.0 Å^4 amu^{-1}, 32.5 cm^{-1}, 2.0 km mol^{-1}, 0.6 Å^4 amu^{-1}, 63.9 cm^{-1}, 1.5 km mol^{-1}, 1.8 Å^4 amu^{-1}, 67.2 cm^{-1}, 0.007 km mol^{-1}, 0.8 Å^4 amu^{-1}, 106.5 cm^{-1}, 12.3 km mol^{-1}, 2.9 Å^4 amu^{-1}.

Table S6B: MP2/aug-cc-pVDZ-PP vibrational frequencies, in cm^{-1}, infrared intensities, in km mol^{-1}, and Raman intensities, in Å^4 amu^{-1}, for the halogen bonded complex of CHF_2I and dimethyl sulfide-d$_6$ and both monomers, as well as the complexation shift Δv.

	Monomer			Halogen bonded complex			
	Frequency	IR intensity	Raman intensity				
CHF$_2$I							
v_1 (A')	3192.4	3.6	94.4	3183.2	-9.3	7.2	148.8
v_2 (A')	1279.7	99.2	7.5	1279.5	-0.2	136.1	7.9
v_3 (A')	1074.1	300.4	3.2	1069.4	-4.7	311.5	2.1
v_4 (A')	652.5	81.8	18.4	650.4	-2.1	52.9	60.6
v_5 (A')	549.4	2.9	1.8	545.6	-3.8	2.6	4.0
v_6 (A')	276.0	0.2	6.6	274.0	-1.9	3.1	20.0
v_7 (A'')	1346.0	4.1	2.7	1344.2	-1.8	3.9	3.2
v_8 (A'')	1096.9	186.9	1.9	1082.2	-14.6	181.4	1.7
v_9 (A'')	277.0	0.0004	1.2	279.3	2.3	0.01	1.5
DMS-d$_6$							
v_1 (A$_1$)	2361.4	4.6	45.5	2363.2	1.9	2.9	46.5
v_2 (A$_1$)	2194.1	16.7	162.8	2194.0	-0.2	13.0	148.8
v_3 (A$_1$)	1064.3	0.5	3.0	1062.0	-2.4	20.4	5.5
v_4 (A$_1$)	1037.4	1.2	5.6	1036.0	-1.4	0.6	9.2
v_5 (A$_1$)	837.1	3.9	1.7	836.9	-0.3	2.6	1.5
v_6 (A$_1$)	655.7	2.7	17.4	654.3	-1.4	4.6	13.0
v_7 (A$_1$)	223.6	0.0	2.2	224.3	0.7	0.05	1.9
v_8 (A$_2$)	2350.5	0.0	8.5	2352.4	1.9	0.2	7.2
v_9 (A$_2$)	1046.5	0.0	4.3	1045.1	-1.4	0.2	3.6
v_{10} (A$_2$)	708.3	0.0	0.4	710.9	2.6	0.004	0.8
v_{11} (A$_2$)	122.8	0.0	0.1	126.4	3.6	0.01	0.1
v_{12} (B$_1$)	2344.4	10.8	63.9	2347.2	2.8	7.8	58.6
v_{13} (B$_1$)	1056.3	7.2	0.0	1055.1	-1.2	8.8	0.1
v_{14} (B$_1$)	751.1	0.9	0.1	753.1	2.1	2.2	0.9
v_{15} (B$_1$)	136.8	0.8	0.1	140.3	3.5	4.3	1.1
v_{16} (B$_2$)	2360.9	1.2	22.7	2362.6	1.7	0.6	17.5
v_{17} (B$_2$)	2197.7	15.2	0.5	2197.3	-0.3	10.9	3.0
v_{18} (B$_2$)	1060.2	7.9	0.1	1057.9	-2.3	4.7	0.2
v_{19} (B$_2$)	1017.4	2.5	0.6	1016.1	-1.3	1.7	0.5
v_{20} (B$_2$)	720.2	0.0	7.3	718.5	-1.6	0.1	5.9
v_{21} (B$_2$)	686.0	0.0	0.1	687.8	1.8	0.0008	0.1

Van der Waals vibrations: 6.0 cm^{-1}, 2.2 km mol^{-1}, 0.03 Å^4 amu^{-1}, 30.2 cm^{-1}, 0.002 km mol^{-1}, 1.0 Å^4 amu^{-1}, 31.4 cm^{-1}, 1.9 km mol^{-1}, 0.6 Å^4 amu^{-1}, 61.0 cm^{-1}, 0.009 km mol^{-1}, 0.5 Å^4 amu^{-1}, 61.3 cm^{-1}, 1.3

km $\quad$ mol^{-1},
1.6 Å^4 amu^{-1}, 94.9 cm^{-1}, 8.4 km mol^{-1}, 2.2 Å^4 amu^{-1}.

Table S7: MP2/aug-cc-pVDZ-PP vibrational frequencies, in cm^{-1}, infrared intensities, in $km\ mol^{-1}$, and Raman intensities, in $Å^4\ amu^{-1}$, for the hydrogen bonded complex with a secondary C-H$\cdots$F interaction of CHF_2I and chloromethane and both monomers, as well as the complexation shift Δv.

	Monomer			Hydrogen bonded complex (C-H$\cdots$Cl + F$\cdots$H-C)			
	Frequency	IR intensity	Raman intensity	Frequency	Δv	IR intensity	Raman intensity
CHF_2I							
v_1 (A')	3192.4	3.6	94.4	3208.2	15.7	0.8	82.7
v_2 (A')	1279.7	99.2	7.5	1280.8	1.1	101.4	8.9
v_3 (A')	1074.1	300.4	3.2	1067.8	-6.3	266.0	3.0
v_4 (A')	652.5	81.8	18.4	650.1	-2.5	75.2	15.9
v_5 (A')	549.4	2.9	1.8	549.6	0.2	3.4	1.5
v_6 (A')	276.0	0.2	6.6	275.0	-1.0	0.09	6.0
v_7 (A'')	1346.0	4.1	2.7	1342.8	-3.2	0.7	5.1
v_8 (A'')	1096.9	186.9	1.9	1093.8	-3.1	216.3	2.6
v_9 (A'')	277.0	0.0004	1.2	278.2	1.2	0.07	1.1
CH_3Cl							
v_1 (A)	3109.9	24.4	147.2	3111.6	1.7	17.0	139.7
v_2 (A)	1369.8	13.2	0.006	1370.0	0.3	11.1	0.1
v_3 (A)	750.4	25.3	17.9	741.4	-8.9	23.8	14.7
v_4 (E)	3230.5	3.6	48.9	3235.5	5.0	2.6	40.3
v_5 (E)	1474.7	5.0	4.0	1472.3	-2.5	9.6	3.7
v_6 (E)	1031.9	2.1	0.6	1034.2	2.2	3.5	0.6

Van der Waals vibrations: 22.8 cm^{-1}, 2.2 $km\ mol^{-1}$, 0.9 $Å^4\ amu^{-1}$, 26.6 cm^{-1}, 0.8 $km\ mol^{-1}$, 0.5 $Å^4\ amu^{-1}$, 41.9 cm^{-1}, 1.3 $km\ mol^{-1}$, 0.2 $Å^4\ amu^{-1}$, 56.6 cm^{-1}, 0.3 $km\ mol^{-1}$, 0.2 $Å^4\ amu^{-1}$, 70.2 cm^{-1}, 0.7 $km\ mol^{-1}$, 0.3 $Å^4\ amu^{-1}$, 80.7 cm^{-1}, 7.3 $km\ mol^{-1}$, 1.0 $Å^4\ amu^{-1}$.

Table S8: MP2/aug-cc-pVDZ-PP vibrational frequencies, in cm^{-1}, infrared intensities, in km mol^{-1}, and Raman intensities, in Å^4 amu^{-1}, for the hydrogen bonded complex with a secondary C-H···I interaction of CHF$_2$I and chloromethane and both monomers, as well as the complexation shift Δv.

	Monomer			Hydrogen bonded complex (C-H···Cl + I···H-C)			
	Frequency	IR intensity	Raman intensity	Frequency	Δv	IR intensity	Raman intensity
CHF$_2$I							
v_1 (A')	3192.4	3.6	94.4	3205.2	12.7	1.6	115.7
v_2 (A')	1279.7	99.2	7.5	1279.1	-0.6	104.5	13.2
v_3 (A')	1074.1	300.4	3.2	1073.0	-1.1	309.9	3.3
v_4 (A')	652.5	81.8	18.4	650.2	-2.3	75.8	15.9
v_5 (A')	549.4	2.9	1.8	550.8	1.4	4.5	1.8
v_6 (A')	276.0	0.2	6.6	273.9	-2.1	0.04	6.3
v_7 (A")	1346.0	4.1	2.7	1354.6	8.7	6.5	1.6
v_8 (A")	1096.9	186.9	1.9	1097.2	0.4	176.1	1.8
v_9 (A")	277.0	0.0004	1.2	276.2	-0.8	0.0	1.0
CH$_3$Cl							
v_1 (A)	3109.9	24.4	147.2	3111.9	2.0	16.4	142.6
v_2 (A)	1369.8	13.2	0.006	1369.9	0.2	12.0	0.1
v_3 (A)	750.4	25.3	17.9	741.9	-8.5	24.1	14.5
v_4 (E)	3230.5	3.6	48.9	3236.0	5.5	3.3	42.6
v_5 (E)	1474.7	5.0	4.0	1470.6	-4.2	11.1	3.5
v_6 (E)	1031.9	2.1	0.6	1033.6	1.6	3.1	0.6

Van der Waals vibrations: 5.7 cm^{-1}, 0.6 km mol^{-1}, 0.6 Å^4 amu^{-1}, 18.5 cm^{-1}, 3.7 km mol^{-1}, 0.1 Å^4 amu^{-1}, 28.5 cm^{-1}, 0.2 km mol^{-1}, 0.6 Å^4 amu^{-1}, 57.2 cm^{-1}, 0.04 km mol^{-1}, 0.03 Å^4 amu^{-1}, 61.1 cm^{-1}, 0.04 km mol^{-1},
0.4 Å^4 amu^{-1}, 72.2 cm^{-1}, 6.2 km mol^{-1}, 0.7 Å^4 amu^{-1}.

Table S9: MP2/aug-cc-pVDZ-PP vibrational frequencies, in cm^{-1}, infrared intensities, in km mol^{-1}, and Raman intensities, in Å^4 amu^{-1}, for the halogen bonded complex of CHF_2I and chloromethane and both monomers, as well as the complexation shift Δv.

	Monomer			Halogen bonded complex			
	Frequency	IR intensity	Raman intensity	Frequency	Δv	IR intensity	Raman intensity
CHF_2I							
v_1 (A')	3192.4	3.6	94.4	3189.4	-3.0	4.6	113.8
v_2 (A')	1279.7	99.2	7.5	1281.2	1.5	119.1	6.8
v_3 (A')	1074.1	300.4	3.2	1071.6	-2.5	312.1	2.8
v_4 (A')	652.5	81.8	18.4	654.5	2.0	72.8	26.5
v_5 (A')	549.4	2.9	1.8	548.0	-1.4	2.8	2.1
v_6 (A')	276.0	0.2	6.6	276.9	1.0	0.8	8.9
v_7 (A")	1346.0	4.1	2.7	1345.1	-0.9	4.1	2.8
v_8 (A")	1096.9	186.9	1.9	1089.6	-7.3	185.1	1.8
v_9 (A")	277.0	0.0004	1.2	278.7	1.7	0.01	1.4
CH_3Cl							
v_1 (A)	3109.9	24.4	147.2	3109.6	-0.3	17.3	144.7
v_2 (A)	1369.8	13.2	0.006	1369.3	-0.4	8.2	0.7
v_3 (A)	750.4	25.3	17.9	743.2	-7.2	23.6	15.4
v_4 (E)	3230.5	3.6	48.9	3232.7	2.2	3.3	46.1
v_5 (E)	1474.7	5.0	4.0	1471.7	-3.0	9.2	3.5
v_6 (E)	1031.9	2.1	0.6	1032.7	0.7	4.1	0.8

Van der Waals vibrations: 5.0 cm^{-1}, 4.6 km mol^{-1}, 0.7 Å^4 amu^{-1}, 22.5 cm^{-1}, 2.1 km mol^{-1}, 0.8 Å^4 amu^{-1}, 26.5 cm^{-1}, 0.6 km mol^{-1}, 0.3 Å^4 amu^{-1}, 43.6 cm^{-1}, 0.02 km mol^{-1}, 0.05 Å^4 amu^{-1}, 51.2 cm^{-1}, 0.1 km mol^{-1},

0.5 Å^4 amu^{-1}, 69.5 cm^{-1}, 7.3 km mol^{-1}, 1.1 Å^4 amu^{-1}.

Table S10: Experimental vibrational frequencies for the monomer and complexes, as well as experimental complexation shifts ($\Delta\nu_{exp}$) and MP2/aug-cc-pVDZ-PP calculated complexation shifts ($\Delta\nu_{calc}$), in cm^{-1}, for the halogen bonded complex (XB) and hydrogen bonded complex (HB) of difluoroiodomethane (CHF$_2$I) with trimethylphosphine (TMP) dissolved in LKr at 130 K.

	Assignment	$\nu_{monomer}$	$\nu_{complex,XB}$	$\Delta\nu_{exp,XB}$	$\Delta\nu_{calc,XB}$	$\nu_{complex,HB}$	$\Delta\nu_{exp,HB}$	$\Delta\nu_{calc,HB}$
CHF$_2$I	ν_1	3003.3	2989.9[a]	-13.4	-12.1	2989.9[a]	-13.4	-19.6
	$\nu_5 + \nu_7 + \nu_8$	2993.9			-24.3			21.0
	$\nu_3 + \nu_8$	2171.2	2145.2	-26.0	-23.2	2160.6	-10.6	-8.1
	$2\nu_3$	2144.1	2129.0	-15.1	-11.9	2133.9	-10.2	-7.9
	ν_7	1337.2	1335.5	-1.7	-2.3			23.5
	ν_2	1247.6	1244.0	-3.6	-1.2	1247.8	0.8	0.6
	ν_8	1107.6	1087.7	-19.9	-17.2	1101.8	-5.8	-4.2
	ν_3	1077.1	1070.7	-6.4	-6.0	1072.5	-4.6	-3.9
	ν_4	633.6	628.5	-5.1	-5.0	663.1	-0.5	-1.5
	ν_5	567.8	563.2	-4.6	-4.7	568.3	0.5	-1.6
	$2\nu_6$	536.8						
TMP	ν_{12}	2971.9	2974.6	2.7	3.0	2974.6	2.7	2.3
	ν_1	2957.7	2961.0	2.3	3.1	2961.0	2.3	2.7
	ν_{13}	2957.7	2961.0	2.3	3.5	2961.0	2.3	3.1
	ν_2	2897.2	2899.2	2.0	2.5	2899.2	2.0	2.3
	ν_{14}	2897.2	2899.2	2.0	2.5	2899.2	2.0	2.4
	ν_3	1436.6	1436.2	-0.4	-1.3	1436.2	-0.4	-0.3
	ν_{15}	1426.9	1426.1	-0.8	-1.2	1426.1	-0.8	-0.7
	ν_{16}	1418.3	1417.9	-0.4	-1.2	1417.9	-0.4	-0.3
	$\nu_{6 + \nu_{20}}$	1359.4	1366.9	7.5	7.8	1366.9	7.5	6.4
	$2\nu_6$	1310.9	1314.5	3.6	2.7	1314.5	3.6	3.8
	ν_4	1295.1	1297.7	2.6	0.7	1297.7	2.6	1.0
	ν_{17}	1278.7	1280.8	2.1	0.9	1280.8	2.1	0.7
	ν_5	949.0	948.8	-0.2	-0.3	950.5	1.5	1.5
	ν_{18}	937.6	939.8	2.2	2.3	939.8	2.2	2.3
	ν_{19}	825.3	827.2	1.9	1.2	827.2	1.9	2.2
	ν_{20}	708.7	715.0	6.3	6.4	713.1	4.4	4.5
	ν_6	654.1	656.0	1.9	1.4	656.0	1.9	1.9

[a] Shoulder of TMP complex band

Table S11: Experimental vibrational frequencies for the monomer and complexes, as well as experimental complexation shifts ($\Delta\nu_{exp}$) and MP2/aug-cc-pVDZ-PP calculated complexation shifts ($\Delta\nu_{calc}$), in cm^{-1}, for the halogen bonded complex (XB) and hydrogen bonded complex (HB) of difluoroiodomethane (CHF$_2$I) with dimethyl sulfide (DMS) dissolved in LKr at 130 K.

	Assignment	$\nu_{monomer}$	$\nu_{complex,XB}$	$\Delta\nu_{exp,XB}$	$\Delta\nu_{calc,XB}$	$\nu_{complex,HB}$	$\Delta\nu_{exp,HB}$	$\Delta\nu_{calc,HB}$
CHF$_2$I	ν_1	3003.3	2994.5	-8.8	-9.3	2994.5	-8.8	9.7
	$\nu_{5+}\nu_{7+}\nu_8$	2993.9			-20.3			-4.9
	$\nu_{3+}\nu_8$	2170.7	2150.9	-19.8	-19.7	2163.0	-7.7	-9.9
	$2\nu_3$	2143.7	2132.7	-11.0	-10.1	2132.7	-11.0	-11.7
	ν_7	1337.3	1336.2	-1.1	-1.8	1336.2	-1.1	-1.6
	ν_2	1247.6	1247.9	0.3	-0.2	1247.9	0.3	-2.9
	ν_8	1107.3	1092.7	-14.6	-14.6	1103.6	-3.7	-4.0
	ν_3	1077.1	1072.5	-4.6	-5.0	1072.5	-4.6	-5.9
	ν_4	633.6	632.3	-1.3	-2.0	663.3	-1.3	-2.0
	ν_5	567.7	564.3	-3.4	-3.8	568.0	0.3	0.7
	$2\nu_6$	536.3	533.0	-3.3	-3.8	533.0	-3.3	-5.0
DMS	ν_1	2992.0	2994.4	2.4	1.9	2994.4	2.4	1.4
	ν_{16}	2992.0	2994.4	2.4	1.9	2994.4	2.4	2.6
	ν_{12}	2965.5	2970.3	4.8	3.7	2970.3	4.8	5.1
	ν_{17}	2920.4	2921.9	1.5	-0.2	2921.9	1.5	1.1
	ν_2	2917.3	2918.9	1.6	0.1	2918.9	1.6	1.5
		2883.8						
		2864.6	2862.4	-2.2		2862.4	-2.2	
		2856.5	2855.3	-1.2		2855.3	-1.2	
	$2\nu_9$	2838.4	2836.3	-2.1	-3.5	2836.3	-2.1	-3.7
	ν_3	1444.4	1442.8	-1.6	-2.0	1444.4	0.0	-0.8
	ν_{18}	1438.9	1437.2	-1.7	-2.6	1437.2	-1.7	-1.2
	ν_{13}	1432.8	1432.2	-0.6	-1.4	1432.2	-0.6	-1.8
	ν_4 (vw)	1331.8			-0.3			0.6
	ν_{19}	1310.4	1311.5	1.1	0.1	1311.5	1.1	-0.1
	ν_5	1030.8	1032.0	1.2	1.1	1032.0	1.2	1.5
	ν_{14}	973.3	975.3	2.0	2.3	975.3	2.0	3.0
	ν_{20}	901.8	904.0	2.2	2.2	904.0	2.2	2.5
	ν_6	696.2	694.0	-2.2	-2.8	696.2	-2.2	-2.4

Table S13: Overview of the different van 't Hoff plots constructed for the halogen bonded complex between CHF$_2$I and TMP or TMP-d$_9$ in LKr in the 120-156 K temperature interval, showing the estimated mole fractions of each monomer, range of the integrated monomer and complex bands and complex enthalpies $\Delta H°$ (LKr).

x_{CHF_2I}	x_{TMP}	Integrated CHF$_2$I band (cm^{-1})	Integrated TMP band (cm^{-1})	Integrated Complex band (cm^{-1})	$\Delta H°$ (LKr) [a]
1.1×10^{-4}	1.9×10^{-3}	1128-1093	3000-2930	1095-1080	-15.6(2)
6.1×10^{-5}	9.4×10^{-4}	646-622	834.4-819.5	1095-1080	-15.6(3)
1.9×10^{-4}	1.9×10^{-3} [b]	1128-1093	2263-2185	1095-1080	-15.0(1)

[a] Values are given with the standard deviation of the linear regression in parentheses.

[b] Measurement involving TMP-d$_9$, rather than TMP.

Table S14: Overview of the different van 't Hoff plots constructed for the hydrogen bonded complex between CHF_2I and TMP or TMP-d_9 in LKr in the 120-156 K temperature interval, showing the estimated mole fractions of each monomer, range of the integrated monomer and complex bands and complex enthalpies $\Delta H°$ (LKr).

x_{CHF_2I}	x_{TMP}	Integrated CHF_2I band (cm^{-1})	Integrated TMP band (cm^{-1})	Integrated Complex band (cm^{-1})	$\Delta H°$ (LKr) [a]
1.1×10^{-4}	1.9×10^{-3}	1128-1093	3000-2930	1110-1095	-10.40(5)
6.1×10^{-5}	9.4×10^{-4}	646-622	834.4-819.5	1109-1095	-10.3(1)
1.9×10^{-4}	1.9×10^{-3} [b]	1128-1093	2263-2185	1110-1095	-10.8(1)

[a] Values are given with the standard deviation of the linear regression in parentheses.

[b] Measurement involving TMP-d_9, rather than TMP.

Table S15: Overview of the different van 't Hoff plots constructed for the halogen bonded complex between CHF_2I and DMS or DMS-d_6 in LKr in the 120-156 K temperature interval, showing the estimated mole fractions of each monomer, range of the integrated monomer and complex bands and complex enthalpies $\Delta H°$ (LKr).

x_{CHF_2I}	x_{DMS}	Integrated CHF_2I band (cm^{-1})	Integrated DMS band (cm^{-1})	Integrated Complex band (cm^{-1})	$\Delta H°$ (LKr) [a]
3.8×10^{-5}	1.9×10^{-3}	1263-1234	997-955	CHF_2I ν_8 (1092.6)	-12.0(2)
1.1×10^{-4}	1.9×10^{-3} [b]	1263-1232	2275-2195	CHF_2I ν_8 (1092.6) [c]	-11.3(3)
1.9×10^{-4}	1.9×10^{-3}	1262-1238	1322-1302	CHF_2I ν_8 (1092.6) [c]	-10.8(2)
1.9×10^{-4}	1.9×10^{-3} [b]	1262.5-1235	2280-2185	CHF_2I ν_8 (1092.6) [c]	-11.1(1)

[a] Values are given with the standard deviation of the linear regression in parentheses.

[b] Measurement involving DMS-d_6, rather than DMS.

[c] Intensity obtained from a band fit analysis.

Table S16: Overview of the different van 't Hoff plots constructed for the hydrogen bonded complex between CHF_2I and DMS or DMS-d_6 in LKr in the 120-156 K temperature interval, showing the estimated mole fractions of each monomer, range of the integrated monomer and complex bands and complex enthalpies $\Delta H°$ (LKr).

x_{CHF_2I}	x_{DMS}	Integrated CHF_2I band (cm^{-1})	Integrated DMS band (cm^{-1})	Integrated Complex band (cm^{-1})	$\Delta H°$ (LKr) [a]
3.8×10^{-5}	1.9×10^{-3}	1263-1234	997-955	1114-1090	-8.0(2)
1.1×10^{-4}	1.9×10^{-3} [b]	1124-1093	2275-2195	1118-1090	-7.1(3)
1.9×10^{-4}	1.9×10^{-3}	1262.1238	1322-1302	1116-1091	-7.4(1)
1.9×10^{-4}	1.9×10^{-3} [b]	1262.5-1235	2280-2185	1114-1089	-8.3(2)

[a] Values are given with the standard deviation of the linear regression in parentheses.

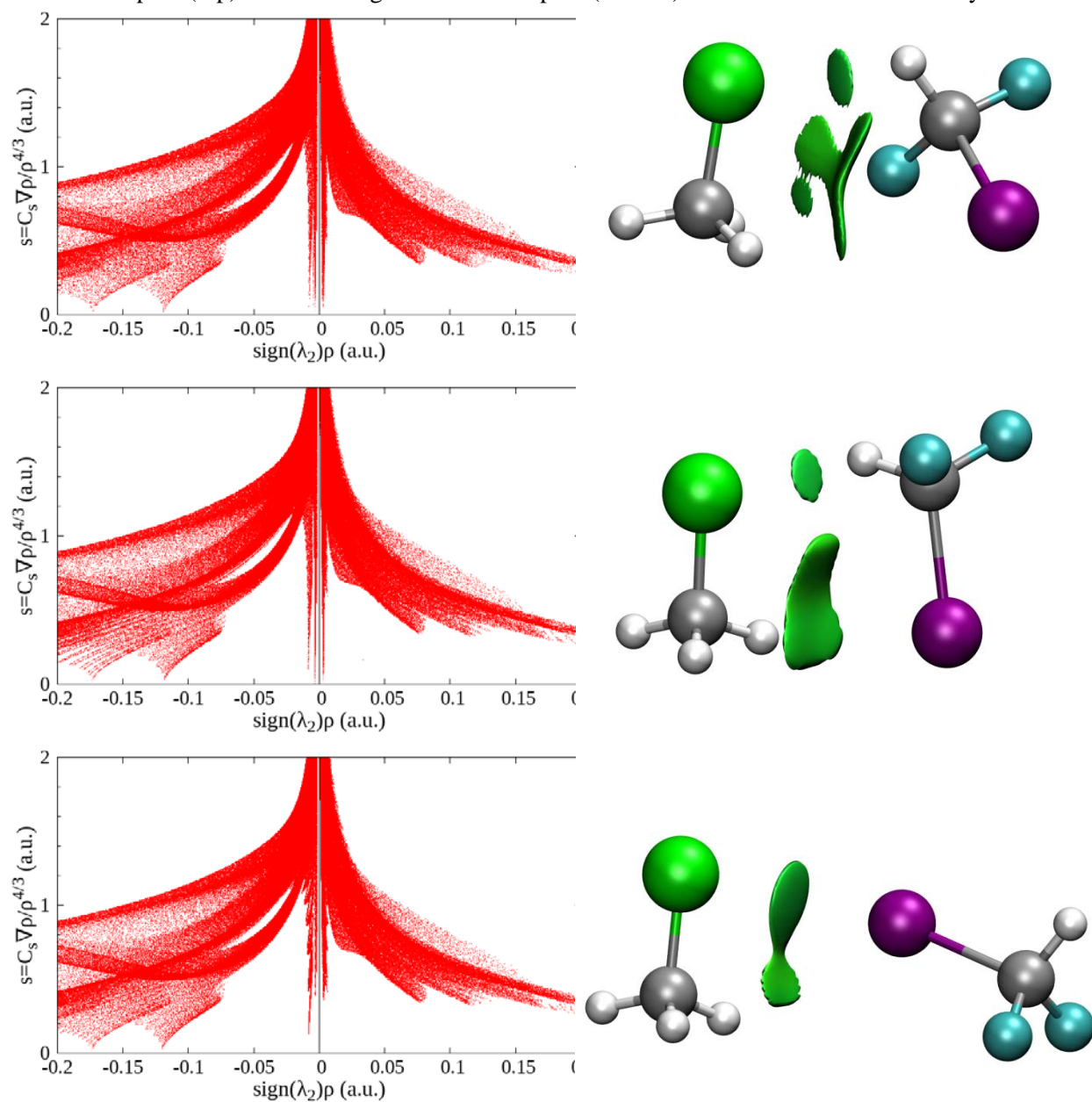[b] Measurement involving DMS-d_6, rather than DMS.
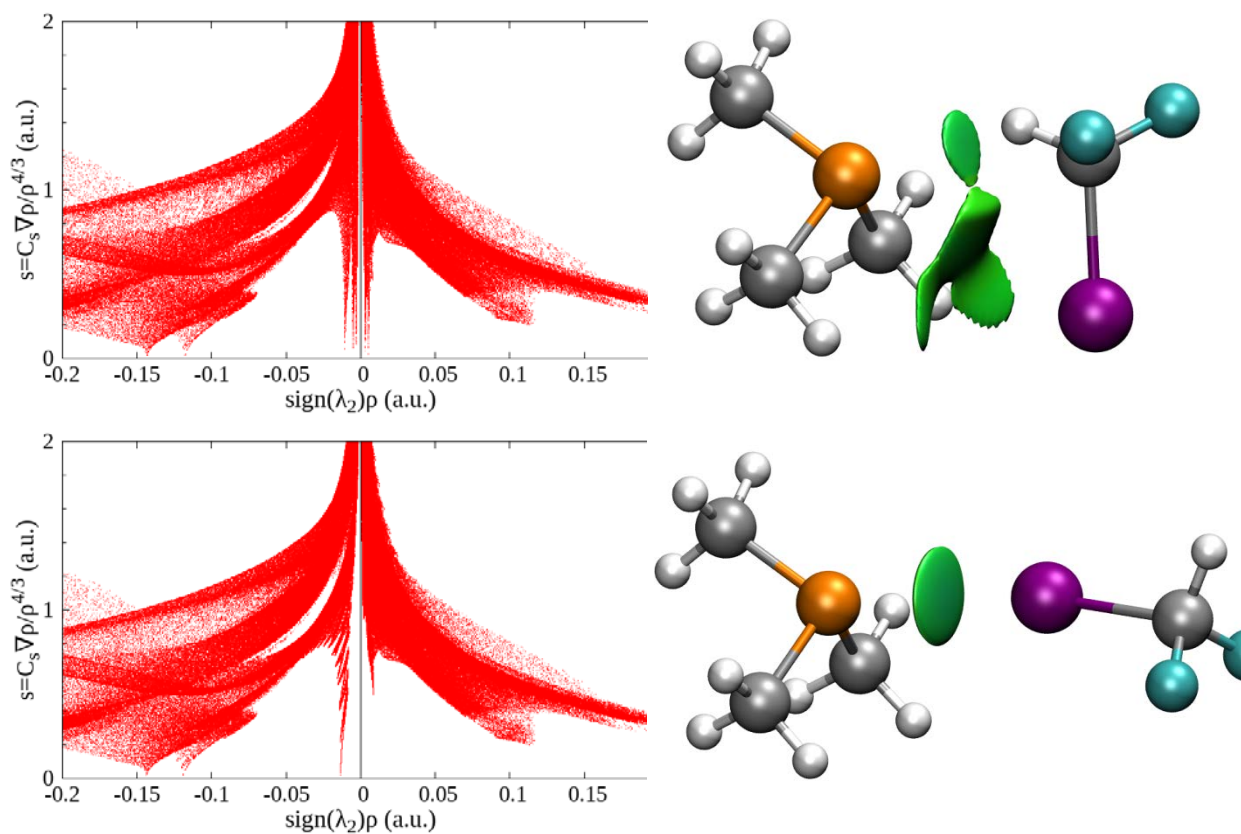
Figure S1: Plots of the reduced density gradient versus the electron density multiplied by the sign of the second Hessian eigenvalue (left) and gradient isosurfaces (s = 0.5 a.u., right) for the hydrogen bonded complex (top) and the halogen bonded complex (bottom) between CHF$_2$I and trimethylphosphine.
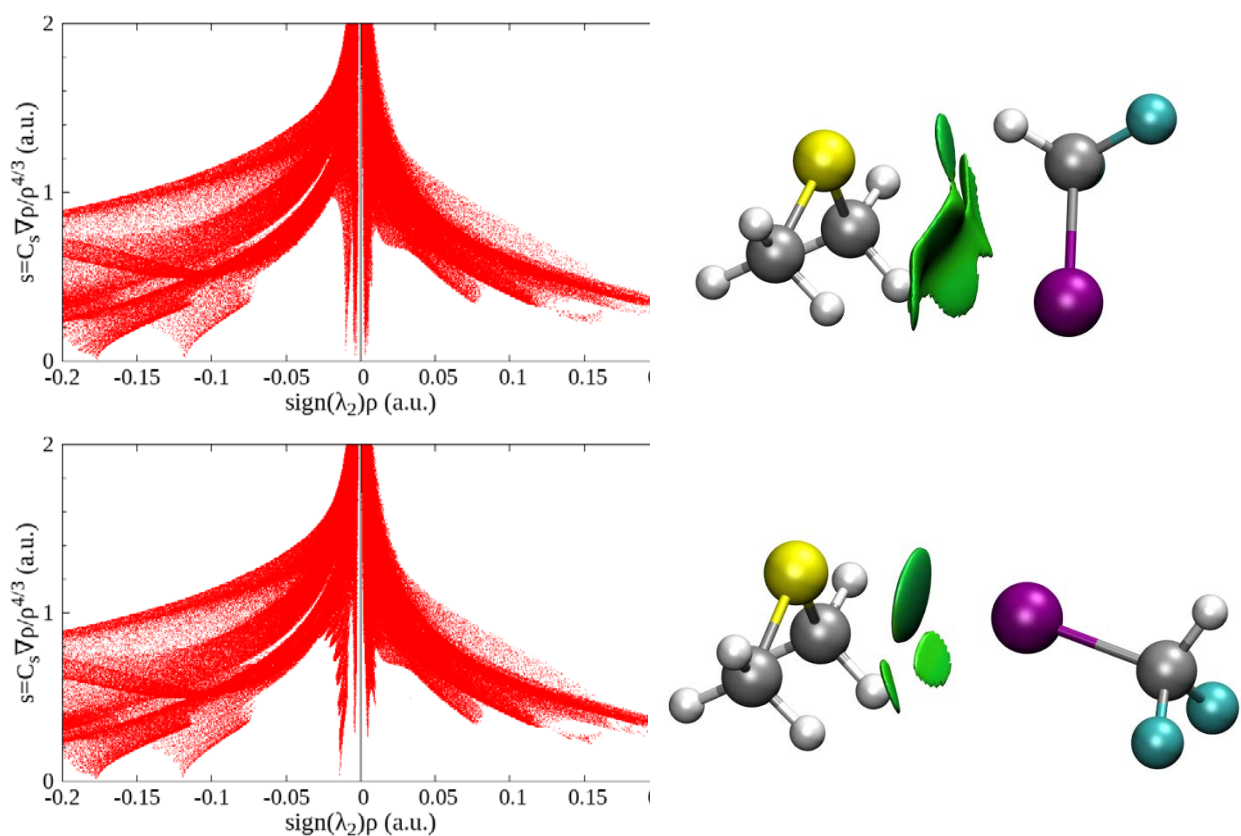
Figure S2: Plots of the reduced density gradient versus the electron density multiplied by the sign of the second Hessian eigenvalue (left) and gradient isosurfaces (s = 0.5 a.u., right) for the hydrogen bonded complex (top) and the halogen bonded complex (bottom) between CHF_2I and dimethyl sulfide.

Figure S3: Plots of the reduced density gradient versus the electron density multiplied by the sign of the second Hessian eigenvalue (left) and gradient isosurfaces (s = 0.5 a.u., right) for the hydrogen bonded complexes with a secondary C-H···F (top) or C-H···I interaction (middle) and the halogen bonded complex (bottom) between CHF_2I and CH_3Cl.
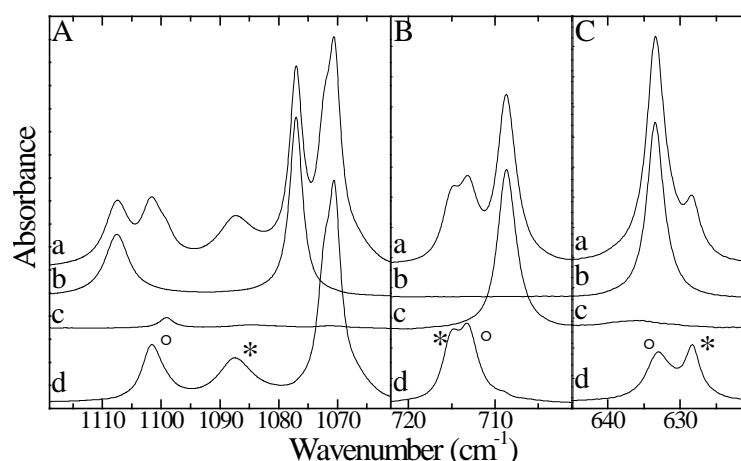
Figure S4: Infrared spectra of selected spectral regions for the mixtures of difluoroiodomethane with trimethylphosphine dissolved in LKr at 130 K. In each panel, trace *a* represents the mixed solution, while traces *b* and *c* show the rescaled spectra of the solutions containing only difluoroiodomethane or trimethylphosphine, respectively. Trace *d* represents the spectrum of the complex which is obtained by subtracting the rescaled traces *b* and *c* from trace *a*. Bands due to the halogen and hydrogen bonded complexes observed in traces *d* are marked with an asterisk (*) or open circle (°), respectively. Estimated mole fractions of the solutions of the mixtures are 5.6×10^{-5} for CHF_2I and 3.8×10^{-3} for TMP in panel A, 9.4×10^{-4} for CHF_2I and 9.4×10^{-4} for TMP in panel B and 5.6×10^{-5} for CHF_2I and 2.4×10^{-3} for TMP-d9 in panel C.
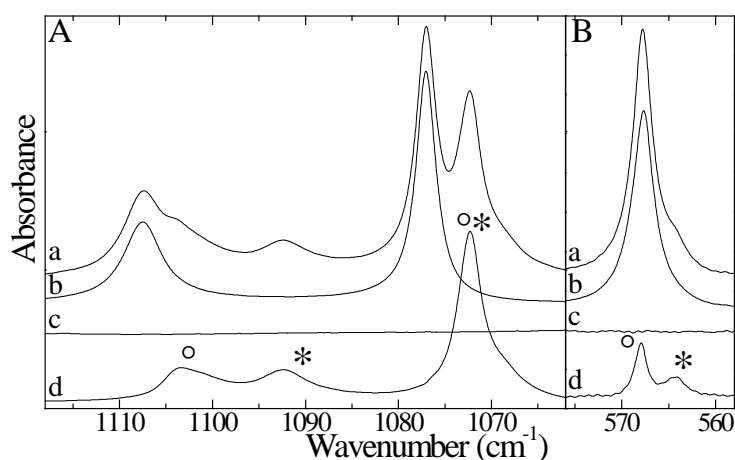
Figure S5: Infrared spectra of selected spectral regions for the mixtures of difluoroiodomethane with dimethyl sulfide dissolved in LKr at 130 K. In each panel, trace *a* represents the mixed solution, while traces *b* and *c* show the rescaled spectra of the solutions containing only difluoroiodomethane or dimethyl sulfide, respectively. Trace *d* represents the spectrum of the complex which is obtained by subtracting the rescaled traces *b* and *c* from trace *a*. Bands due to the halogen and hydrogen bonded complexes observed in traces *d* are marked with an asterisk (*) or open circle (°), respectively. Estimated mole fractions of the solutions of the mixtures are 5.6×10^{-5} for CHF_2I and 3.8×10^{-3} for DMS in panel A and 9.4×10^{-4} for CHF_2I and 1.9×10^{-3} for DMS in panel B.
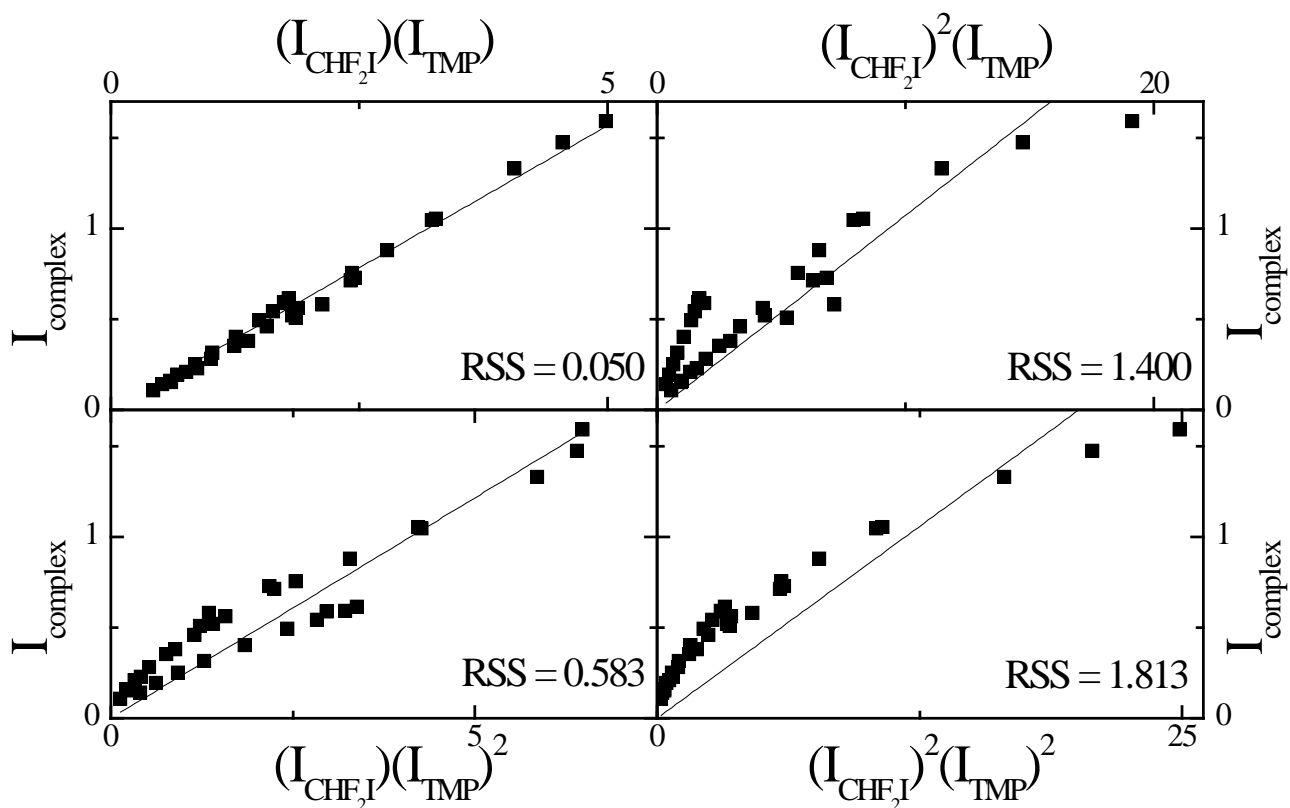
Figure S6: Concentration study plots of the $CHF_2I \cdot TMP$ halogen bonded complex at 130 K in LKr. Integrated intensity of the complex is plotted against the product of monomer intensities $\left(I_{CHF_2I}\right)^m (TMP)^n$. Top left: $m = 1, n = 1$, top right: $m = 2, n = 1$, bottom left $m = 1, n = 2$ and bottom right $m = 2, n = 2$. Additionally, residual sum of square values (RSS) have been included.
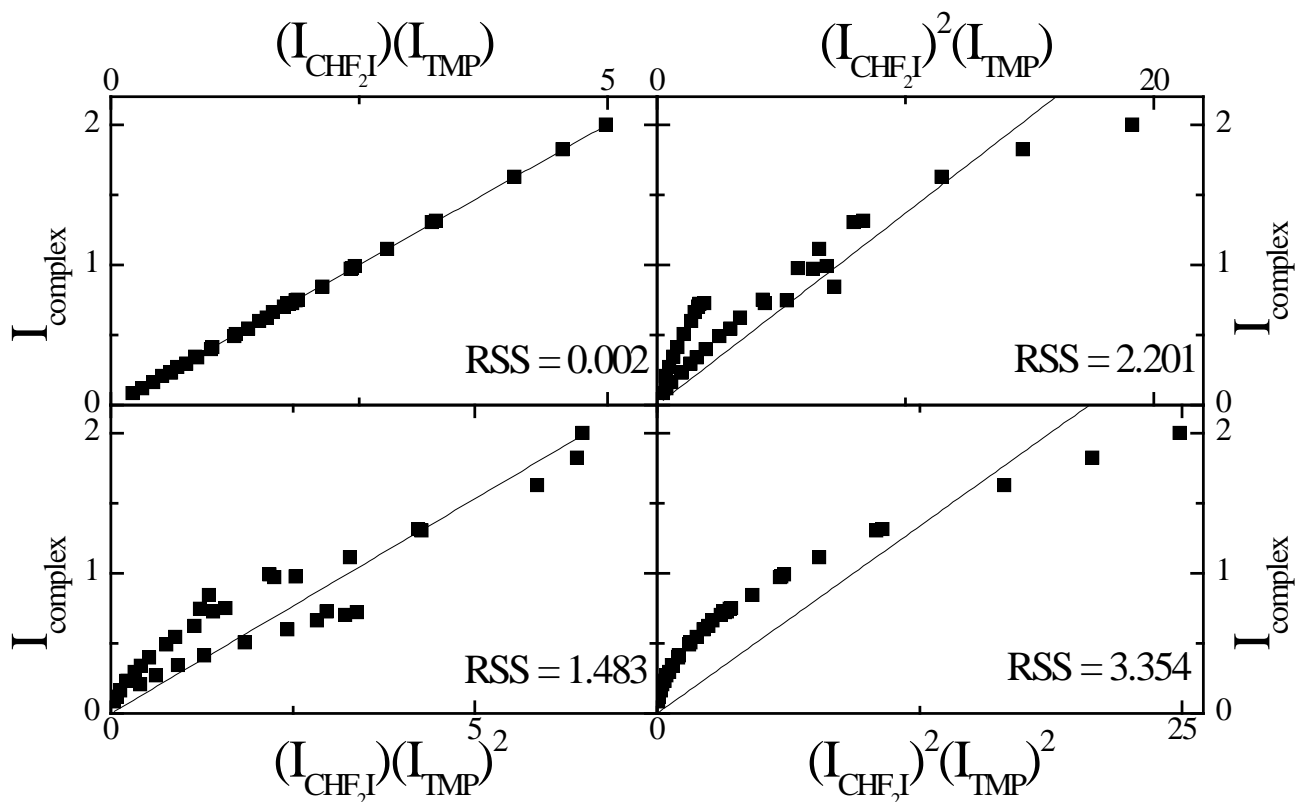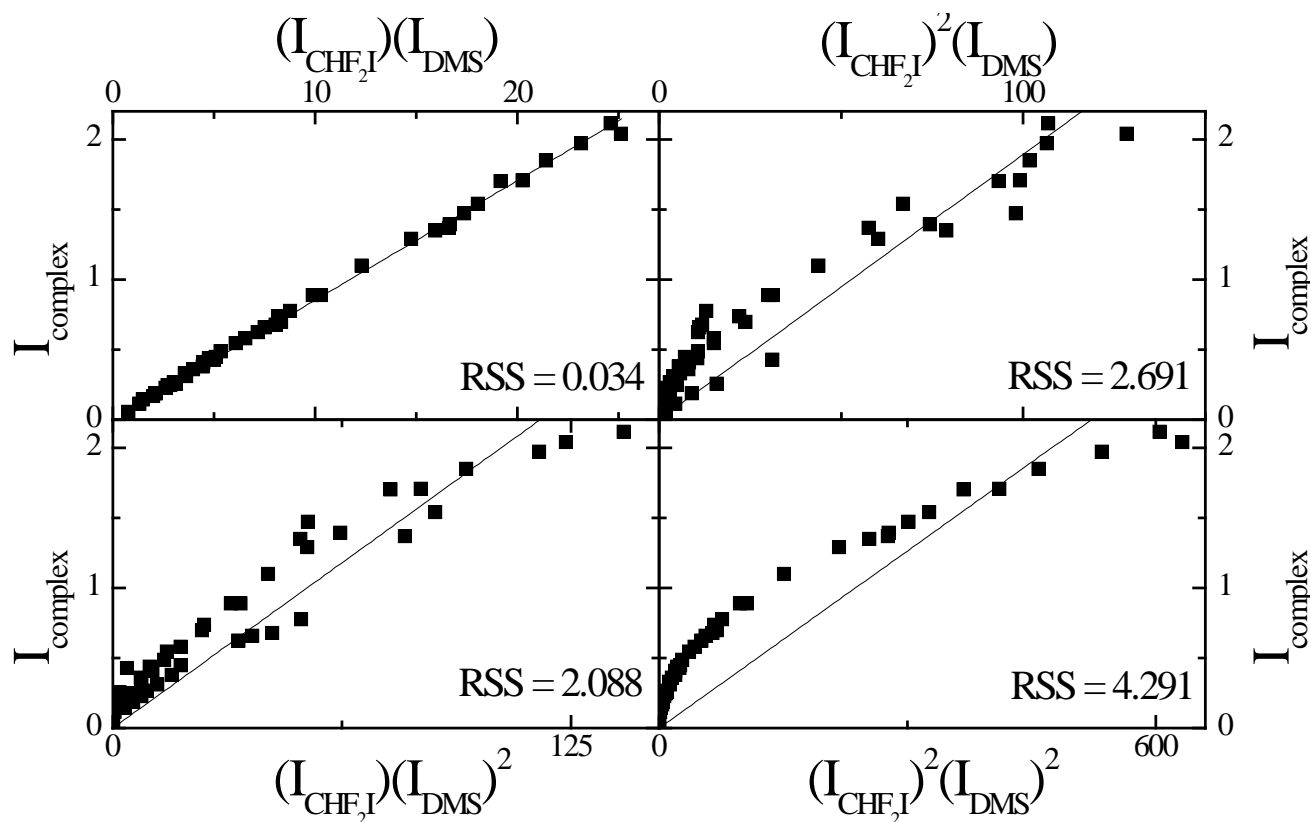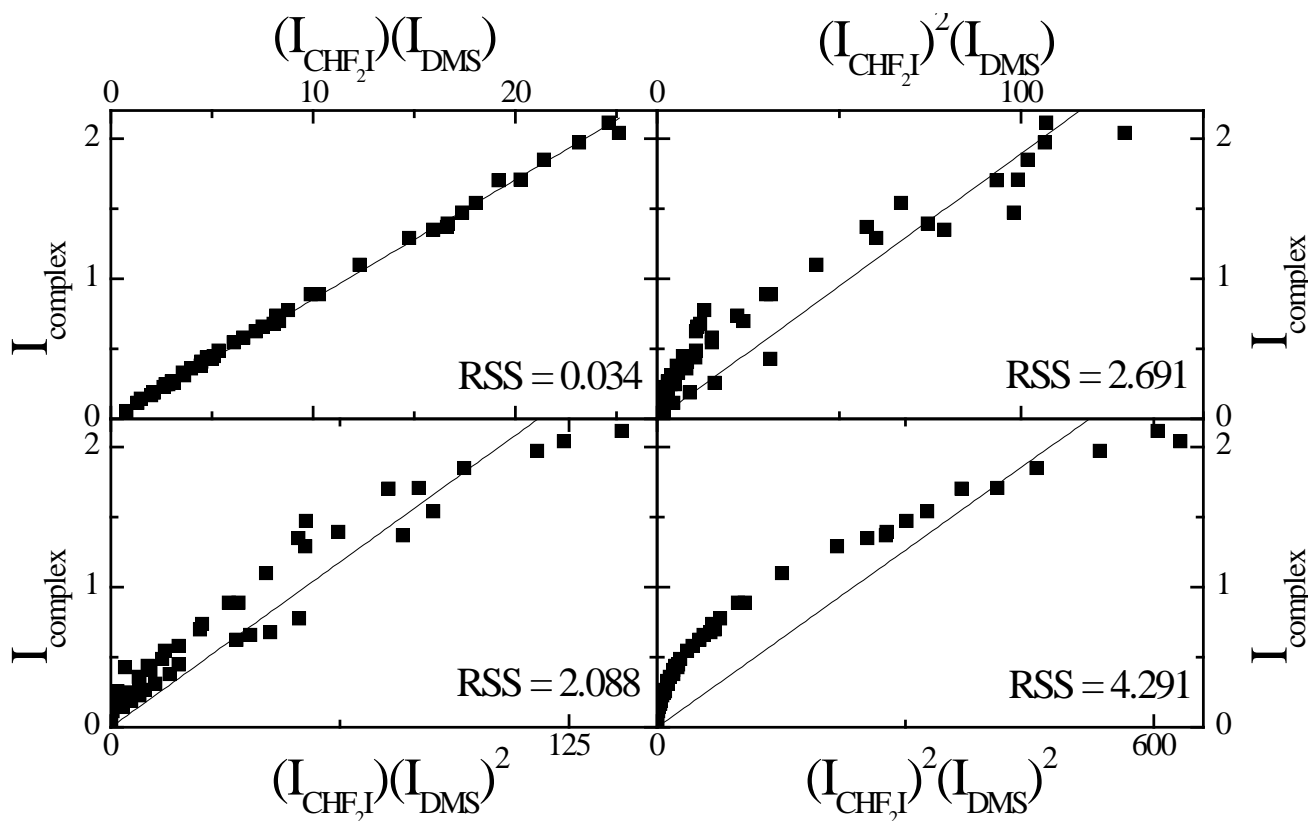
Figure S7: Concentration study plots of the CHF$_2$I·TMP hydrogen bonded complex at 130 K in LKr. Integrated intensity of the complex is plotted against the product of monomer intensities $\left(I_{CHF_2I}\right)^m (TMP)^n$. Top left: $m = 1, n = 1$, top right: $m = 2, n = 1$, bottom left $m = 1, n = 2$ and bottom right $m = 2, n = 2$. Additionally, residual sum of square values (RSS) have been included.


Figure S8: Concentration study plots of the CHF$_2$I·DMS halogen bonded complex at 130 K in LKr. Integrated intensity of the complex is plotted against the product of monomer intensities $\left(I_{CHF_2I}\right)^m (DMS)^n$. Top left: $m = 1, n = 1$, top right: $m = 2, n = 1$, bottom left $m = 1, n = 2$ and bottom right $m = 2, n = 2$. Additionally, residual sum of square values (RSS) have been included.

Figure S9: Concentration study plots of the $CHF_2I \cdot DMS$ hydrogen bonded complex at 130 K in LKr. Integrated intensity of the complex is plotted against the product of monomer intensities $(I_{CHF_2I})^m (DMS)^n$. Top left: $m = 1, n = 1$, top right: $m = 2, n = 1$, bottom left $m = 1, n = 2$ and bottom right $m = 2, n = 2$. Additionally, residual sum of square values (RSS) have been included.
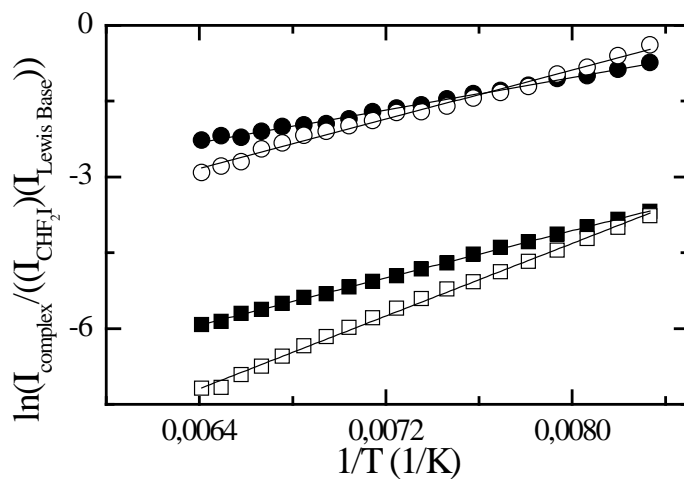
Figure S10: Typical van 't Hoff plots of the hydrogen bonded complexes (filled) and halogen bonded complexes (hollow) of CHF_2I with dimethyl sulfide (round) and trimethylphosphine (square) in LKr.
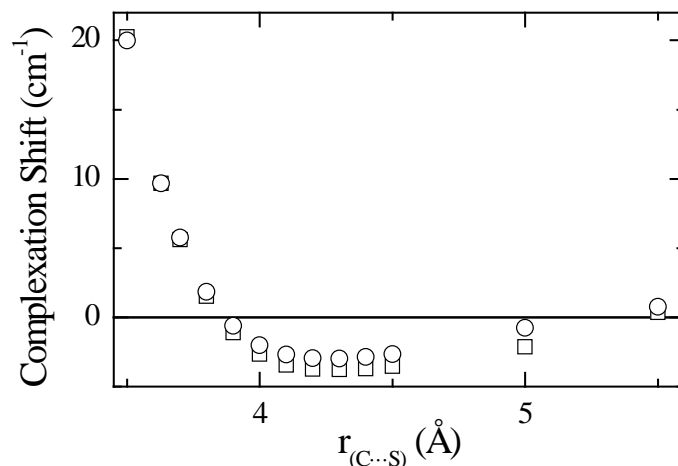
Figure S11: Complexation shifts (in cm^{-1}) of the CHF$_2$I ν_1 mode plotted against the C$\cdots$S distance (in Å) for the partially optimized hydrogen bonded complex with the C-H$\cdots$S angle (□) and C-H$\cdots$S angle and C-H$\cdots$S-C dihedral angle (○) from the equilibrium geometry.
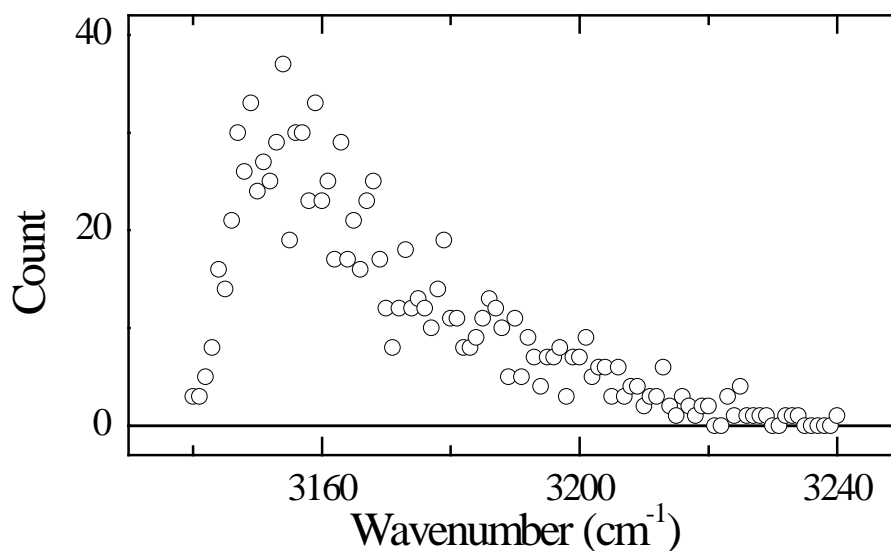

Figure S12: Distribution of MP2/aug-cc-pVDZ-PP *ab initio* frequencies for the CH stretching mode of the hydrogen bonded complex between CHF$_2$I and DMS-d$_6$ at 130 K, obtained from a Monte Carlo sample of the internal coordinates describing the relative orientation of both molecules. Division of the frequencies was made using a bin-width of 1 wavenumber.
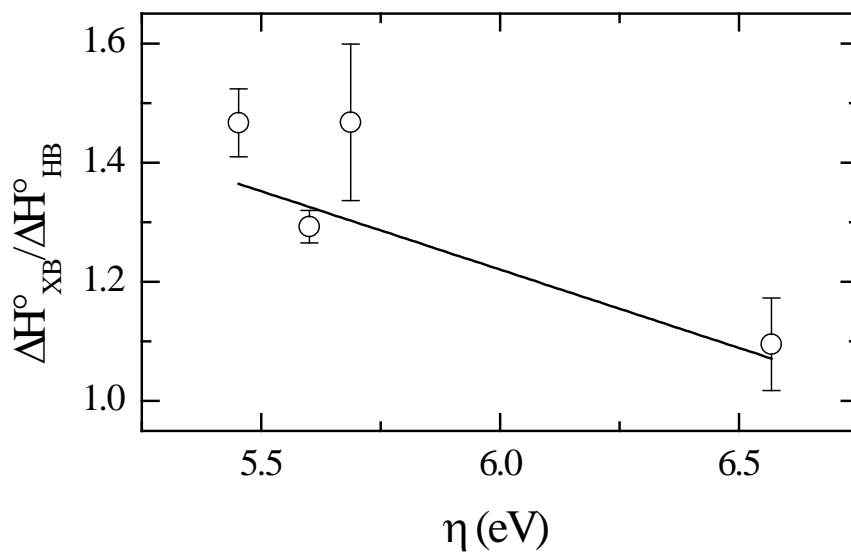
Figure S13: Plot of the enthalpy ratio of $\frac{\Delta H°_{XB}}{\Delta H°_{HB}}$ versus chemical hardness η (in eV), as calculated using the method of Tozer et al. for the complexes formed between difluoroiodomethane and the Lewis bases trimethylamine, dimethyl ether, trimethylphosphine and dimethyl sulfide.