Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

Supporting Information

for:

C–X···π Halogen and C–H···π hydrogen bonding: interactions of CF_3X (X = Cl, Br, I, H) with ethene and propene †

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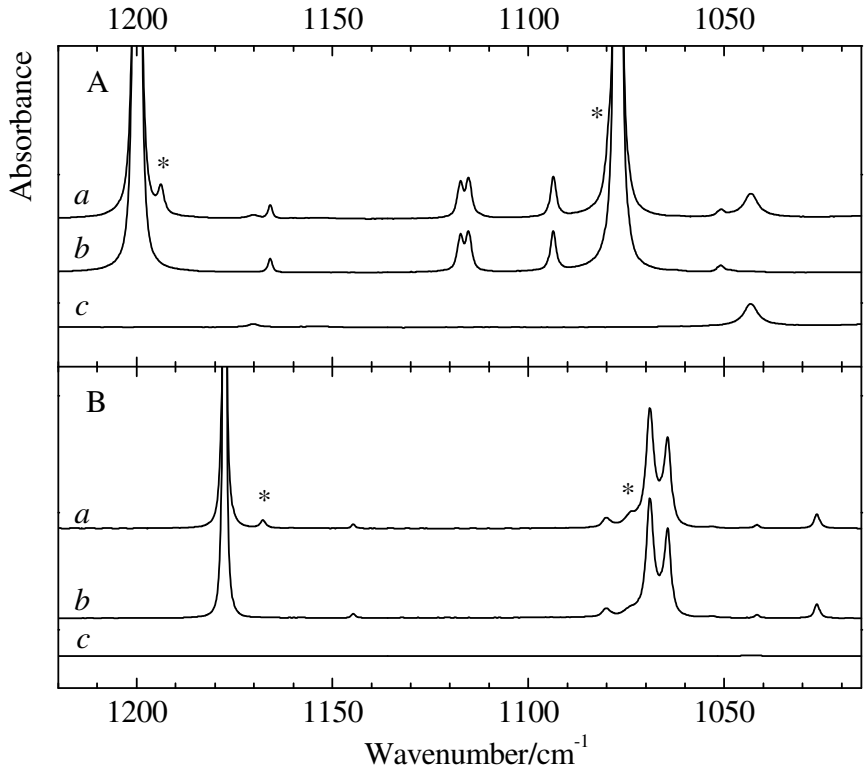

Fig. S1. Infrared spectra in the 1220 – 1010 cm^{-1} region for solutions in liquid argon of mixtures of CF_3Br (panel A) or CF_3I (panel B) with propene. In each panel the spectrum of the mixed solution is give as trace *a*, while those of the solutions containing only propene and CF_3X are shown as traces *b* and *c*, respectively. New bands appearing in the spectra of the mixture are marked with an asterisk (*) and are assigned to the 1:1 complex. All spectra were recorded at 93 K

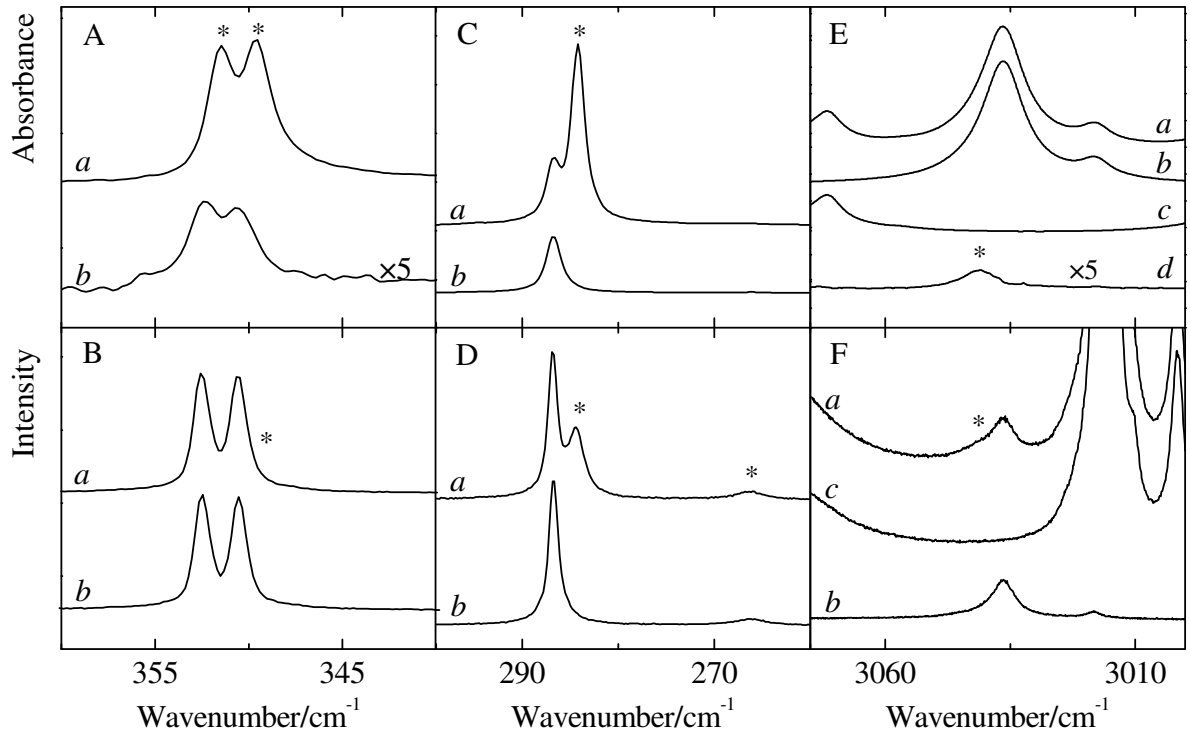

Fig. S2. Infrared (panels A, C and E) and Raman (panels B, D and F) spectra of the C–X stretching region for solutions in liquid argon of mixtures of CF_3Br (panels A and B), CF_3I (panels C and D) or CF_3H (panels E and F) with ethene. Trace *a* gives the spectrum of the mixed solution, while traces *b* and *c*, where shown, are the spectra of the monomer CF_3X and ethene solution, respectively. Trace *d*, where shown, is the spectrum of the 1:1 complex, obtained by subtracting traces *b* and *c* from trace *a*. New bands appearing in the spectra of the mixture are marked with an asterisk (*) and are assigned to the 1:1 complex. All spectra were recorded at 93 K.

Table S1. MP2/aug-cc-pVDZ vibrational frequencies, in cm^{-1}, and infrared intensities, in km mol^{-1}, for CF_3Cl·ethene.

Mode	$\nu_{monomer}$	IR Intensity	$\nu_{complex}$	IR Intensity	$\Delta\nu$
CF_3Cl					
ν_1 (a_1)	1096.4	496.6	1099.4	502.4	3.0
ν_2 (a_1)	764.7	24.8	762.9	21.8	-1.8
ν_3 (a_1)	479.9	0.1	479.0	1.1	-1.0
ν_4 (e)	1192.5	564.4	1186.5	556.7	-6.0
ν_5 (e)	545.9	2.8	545.9	3.1	-0.1
ν_6 (e)	347.1	0.004	348.6	0.01	1.5
Ethene					
ν_1 (a_g)	3198.3	0.0	3196.9	0.01	-1.4
ν_2 (a_g)	1671.2	0.0	1667.7	0.2	-3.5
ν_3 (a_g)	1372.4	0.0	1371.3	0.07	-1.1
ν_4 (a_u)	1048.9	0.0	1050.0	0.0	1.1
ν_5 (b_{1g})	3275.2	0.0	3275.3	0.0	0.1
ν_6 (b_{1g})	1229.7	0.0	1229.3	0.0	-0.3
ν_7 (b_{1u})	980.9	95.0	984.1	136.0	3.2
ν_8 (b_{2g})	954.8	0.0	956.1	0.01	1.3
ν_9 (b_{2u})	3303.3	17.1	3303.2	12.3	-0.1
ν_{10} (b_{2u})	820.6	0.0	820.6	0.0	-0.2
ν_{11} (b_{3u})	3180.6	11.2	3179.8	8.0	-0.8
ν_{12} (b_{3u})	1468.3	7.7	1467.5	7.7	-0.7

Van der Waals vibrations: 71.1 cm^{-1}, 0.05 km mol^{-1}; 55.7 cm^{-1}, 0.1 km mol^{-1}; 48.2 cm^{-1}, 0.02 km mol^{-1}; 26.0 cm^{-1}, 0.03 km mol^{-1}; 23.9 cm^{-1}, 0.05 km mol^{-1}; 0.6 cm^{-1}, 0.0 km mol^{-1}.

Table S2. MP2/aug-cc-pVDZ-PP vibrational frequencies, in cm^{-1}, and infrared intensities, in km mol^{-1}, for CF_3Br•ethene.

Mode	$\nu_{monomer}$	IR Intensity	$\nu_{complex}$	IR Intensity	$\Delta\nu$
CF_3Br					
ν_1 (a_1)	1078.3	496.2	1081.8	520.9	3.6
ν_2 (a_1)	739.5	30.4	736.6	26.1	-2.9
ν_3 (a_1)	360.9	0.03	357.8	1.3	-3.1
ν_4 (e)	1180.2	509.7	1172.7	509.3	-7.5
ν_5 (e)	531.4	1.8	530.7	2.1	-0.7
ν_6 (e)	305.5	0.02	306.6	0.01	1.1
Ethene					
ν_1 (a_g)	3198.3	0.0	3196.1	0.01	-2.1
ν_2 (a_g)	1671.2	0.0	1665.4	0.8	-5.8
ν_3 (a_g)	1372.4	0.0	1370.7	0.3	-1.7
ν_4 (a_u)	1048.9	0.0	1050.4	0.0	1.5
ν_5 (b_{1g})	3275.2	0.0	3275.4	0.0	0.2
ν_6 (b_{1g})	1229.7	0.0	1229.2	0.0	-0.4
ν_7 (b_{1u})	980.9	95.0	987.1	152.3	6.1
ν_8 (b_{2g})	954.8	0.0	958.2	0.0	3.4
ν_9 (b_{2u})	3303.3	17.1	3303.1	10.0	-0.2
ν_{10} (b_{2u})	820.6	0.0	820.8	03.0	-0.1
ν_{11} (b_{3u})	3180.6	11.2	3179.5	6.5	-1.1
ν_{12} (b_{3u})	1468.3	7.7	1467.5	7.8	-0.8

Van der Waals vibrations: 100.4 cm^{-1}, 0.1 km mol^{-1}; 64.8 cm^{-1}, 0.5 km mol^{-1}; 63.5 cm^{-1}, 0.07 km mol^{-1}; 30.4 cm^{-1}, 0.01 km mol^{-1}; 28.6 cm^{-1}, 0.02 km mol^{-1}; 5.8 cm^{-1}, 0.0 km mol^{-1}.

Table S3. MP2/aug-cc-pVDZ-PP vibrational frequencies, in cm^{-1}, and infrared intensities, in km mol^{-1}, for CF_3I·ethene.

Mode	$\nu_{monomer}$	IR Intensity	$\nu_{complex}$	IR Intensity	$\Delta\nu$
CF_3I					
ν_1 (a_1)	1059.6	547.3	1066.1	556.8	6.5
ν_2 (a_1)	722.3	34.7	719.4	27.9	-2.9
ν_3 (a_1)	294.9	0.3	291.0	3.2	-3.9
ν_4 (e)	1162.6	455.5	1153.5	458.8	-9.1
ν_5 (e)	518.8	1.1	517.9	1.4	-0.9
ν_6 (e)	269.1	0.1	269.6	0.003	0.6
Ethene					
ν_1 (a_g)	3198.3	0.0	3195.4	0.03	-2.9
ν_2 (a_g)	1671.2	0.0	1662.8	2.1	-8.4
ν_3 (a_g)	1372.4	0.0	1370.0	0.8	-2.4
ν_4 (a_u)	1048.9	0.0	1050.6	0.0	1.7
ν_5 (b_{1g})	3275.2	0.0	3276.6	0.0	1.4
ν_6 (b_{1g})	1229.7	0.0	1229.1	0.0	-0.5
ν_7 (b_{1u})	980.9	95.0	990.4	177.9	9.4
ν_8 (b_{2g})	954.8	0.0	960.4	0.0	5.5
ν_9 (b_{2u})	3303.3	17.1	3303.1	7.5	-0.2
ν_{10} (b_{2u})	820.6	0.0	820.9	0.0	0.1
ν_{11} (b_{3u})	3180.6	11.2	3179.2	4.8	-1.4
ν_{12} (b_{3u})	1468.3	7.7	1467.4	7.9	-0.9

Van der Waals vibrations: 129.0 cm^{-1}, 0.2 km mol^{-1}; 77.9 cm^{-1}, 0.1 km mol^{-1}; 70.6 cm^{-1}, 1.6 km mol^{-1}; 33.2 cm^{-1}, 0.01 km mol^{-1}; 31.8 cm^{-1}, 0.02 km mol^{-1}; 1.1 cm^{-1}, 0.0 km mol^{-1}.

Table S4. MP2/aug-cc-pVDZ vibrational frequencies, in cm^{-1}, and infrared intensities, in km mol^{-1}, for CF_3H·ethene.

Mode	$\nu_{monomer}$	IR Intensity	$\nu_{complex}$	IR Intensity	$\Delta\nu$
CF_3H					
ν_1 (a_1)	3226.1	20.7	3239.5	12.8	13.4
ν_2 (a_1)	1121.2	94.0	1117.3	99.9	-3.9
ν_3 (a_1)	677.5	12.7	676.0	14.0	-1.6
ν_4 (e)	1382.5	80.2	1383.9	63.2	1.4
ν_5 (e)	1144.0	597.9	1138.4	560.2	-5.5
ν_6 (e)	490.7	4.6	490.6	4.6	-0.1
Ethene					
ν_1 (a_g)	3198.3	0.0	3195.8	0.08	-2.5
ν_2 (a_g)	1671.2	0.0	1667.7	0.03	-3.5
ν_3 (a_g)	1372.4	0.0	1372.2	0.02	-0.2
ν_4 (a_u)	1048.9	0.0	1053.8	1.3	4.9
ν_5 (b_{1g})	3275.2	0.0	3274.9	0.2	-0.3
ν_6 (b_{1g})	1229.7	0.0	1230.9	0.05	1.2
ν_7 (b_{1u})	980.9	95.0	989.6	111.8	8.7
ν_8 (b_{2g})	954.8	0.0	961.1	0.1	6.3
ν_9 (b_{2u})	3303.3	17.1	3302.5	12.1	-0.8
ν_{10} (b_{2u})	820.6	0.0	822.2	0.0	1.4
ν_{11} (b_{3u})	3180.6	11.2	3179.1	7.1	-1.5
ν_{12} (b_{3u})	1468.3	7.7	1469.1	7.8	0.8

Van der Waals vibrations: 93.5 cm^{-1}, 0.03 km mol^{-1}; 66.8 cm^{-1}, 0.6 km mol^{-1}; 60.9 cm^{-1}, 0.0 km mol^{-1}; 36.3 cm^{-1}, 0.9 km mol^{-1}; 32.8 cm^{-1}, 2.4 km mol^{-1}; 3.8 cm^{-1}, 0.02 km mol^{-1}.

Table S5. MP2/aug-cc-pVDZ vibrational frequencies, in cm^{-1}, and infrared intensities, in km mol^{-1}, for CF_3Cl·propene.

Mode	$\nu_{monomer}$	IR Intensity	$\nu_{complex}$	IR Intensity	$\Delta\nu$
CF_3Cl					
ν_1 (a_1)	1096.4	496.6	1098.9	520.6	2.5
ν_2 (a_1)	764.7	24.8	762.5	21.7	-2.2
ν_3 (a_1)	479.9	0.1	478.7	1.3	-1.2
ν_4 (e)	1192.5	564.4	1186.1	545.4	-6.5
ν_5 (e)	545.9	2.8	545.8	3.0	-0.1
ν_6 (e)	347.1	0.004	348.8	0.01	1.7
Propene					
ν_1 (a')	3283.3	13.9	3282.3	10.7	-1.0
ν_2 (a')	3193.8	13.7	3192.8	11.8	-1.1
ν_3 (a')	3177.3	13.0	3175.7	9.5	-1.7
ν_4 (a')	3161.1	9.4	3160.9	8.1	-0.2
ν_5 (a')	3059.4	21.2	3058.7	17.2	-0.7
ν_6 (a')	1696.3	10.7	1692.0	8.9	-4.3
ν_7 (a')	1486.3	13.2	1485.4	15.4	-0.9
ν_8 (a')	1446.8	0.8	1446.0	1.2	-0.9
ν_9 (a')	1389.0	1.5	1389.2	2.0	0.2
ν_{10} (a')	1316.8	0.1	1316.1	0.1	-0.7
ν_{11} (a')	1188.3	0.2	1188.4	1.8	0.1
ν_{12} (a')	941.4	2.8	940.8	3.9	-0.6
ν_{13} (a')	934.4	2.4	934.1	20.7	-0.3
ν_{14} (a')	419.1	0.9	419.2	0.7	0.0
ν_{15} (a")	3139.6	14.7	3139.4	16.6	-0.2
ν_{16} (a")	1469.0	6.3	1467.6	7.4	-1.4
ν_{17} (a")	1056.4	4.4	1056.3	3.7	-0.1
ν_{18} (a")	1011.3	16.5	1013.1	28.1	1.8
ν_{19} (a")	932.1	38.8	934.8	33.4	2.6
ν_{20} (a")	582.4	11.8	586.1	14.0	3.6
ν_{21} (a")	204.8	0.5	209.8	0.8	5.0

Van der Waals vibrations: 65.0 cm^{-1}, 0.4 km mol^{-1}; 58.8 cm^{-1}, 0.02 km mol^{-1}; 52.3 cm^{-1}, 0.04 km mol^{-1}; 28.8 cm^{-1}, 0.06 km mol^{-1}; 23.8 cm^{-1}, 0.09 km mol^{-1}; 4.3 cm^{-1}, 0.02 km mol^{-1}.

Table S6. MP2/aug-cc-pVDZ-PP vibrational frequencies, in cm^{-1}, and infrared intensities, in km mol^{-1}, for CF_3Br·propene.

Mode	$\nu_{monomer}$	IR Intensity	$\nu_{complex}$	IR Intensity	$\Delta\nu$
CF_3Br					
ν_1 (a_1)	1078.3	496.2	1081.7	541.2	3.4
ν_2 (a_1)	739.5	30.4	736.1	25.5	-3.4
ν_3 (a_1)	360.9	0.03	356.9	1.7	-4.0
ν_4 (e)	1180.2	509.7	1171.8	502.4	-8.3
ν_5 (e)	531.4	1.8	530.5	2.1	-0.9
ν_6 (e)	305.5	0.02	306.6	0.01	1.1
Propene					
ν_1 (a')	3283.3	13.9	3282.1	8.7	-1.2
ν_2 (a')	3193.8	13.7	3192.4	10.9	-1.4
ν_3 (a')	3177.3	13.0	3175.2	7.9	-2.1
ν_4 (a')	3161.1	9.4	3161.8	7.4	0.7
ν_5 (a')	3059.4	21.2	3059.2	15.7	-0.2
ν_6 (a')	1696.3	10.7	1688.9	10.0	-7.3
ν_7 (a')	1486.3	13.2	1485.2	15.6	-1.1
ν_8 (a')	1446.8	0.8	1445.7	1.6	-1.2
ν_9 (a')	1389.0	1.5	1389.3	2.4	0.3
ν_{10} (a')	1316.8	0.1	1315.8	0.2	-1.0
ν_{11} (a')	1188.3	0.2	1188.7	0.05	0.4
ν_{12} (a')	941.4	2.8	940.6	10.0	-0.7
ν_{13} (a')	934.4	2.4	934.4	5.2	0.0
ν_{14} (a')	419.1	0.9	418.9	0.7	-0.2
ν_{15} (a")	3139.6	14.7	3140.3	15.3	0.6
ν_{16} (a")	1469.0	6.3	1467.4	7.4	-1.6
ν_{17} (a")	1056.4	4.4	1056.5	6.3	0.1
ν_{18} (a")	1011.3	16.5	1014.0	32.4	2.7
ν_{19} (a")	932.1	38.8	936.6	49.9	4.5
ν_{20} (a")	582.4	11.8	589.2	15.9	6.8
ν_{21} (a")	204.8	0.5	209.9	0.9	5.1

Van der Waals vibrations: 74.5 cm^{-1}, 1.2 km mol^{-1}; 70.9 cm^{-1}, 0.06 km mol^{-1}; 55.5 cm^{-1}, 0.04 km mol^{-1}; 32.9 cm^{-1}, 0.04 km mol^{-1}; 26.9 cm^{-1}, 0.08 km mol^{-1}; 3.4 cm^{-1}, 0.02 km mol^{-1}.

Table S7. MP2/aug-cc-pVDZ-PP vibrational frequencies, in cm^{-1}, and infrared intensities, in km mol^{-1}, for CF_3I·propene.

Mode	$\nu_{monomer}$	IR Intensity	$\nu_{complex}$	IR Intensity	$\Delta\nu$
CF_3I					
ν_1 (a_1)	1059.6	547.3	1066.3	571.1	6.7
ν_2 (a_1)	722.3	34.7	718.7	26.6	-3.6
ν_3 (a_1)	294.9	0.3	289.7	4.1	-5.2
ν_4 (e)	1162.6	455.5	1152.0	453.9	-10.6
ν_5 (e)	518.8	1.1	517.6	1.3	-1.2
ν_6 (e)	269.1	0.1	269.4	0.006	0.3
Propene					
ν_1 (a')	3283.3	13.9	3281.9	6.6	-1.5
ν_2 (a')	3193.8	13.7	3192.1	9.8	-1.7
ν_3 (a')	3177.3	13.0	3174.7	6.1	-2.7
ν_4 (a')	3161.1	9.4	3162.8	6.7	1.7
ν_5 (a')	3059.4	21.2	3059.7	13.8	0.3
ν_6 (a')	1696.3	10.7	1685.1	13.1	-11.2
ν_7 (a')	1486.3	13.2	1484.9	16.4	-1.4
ν_8 (a')	1446.8	0.8	1445.2	2.2	-1.7
ν_9 (a')	1389.0	1.5	1389.4	2.9	0.4
ν_{10} (a')	1316.8	0.1	1315.5	0.3	-1.3
ν_{11} (a')	1188.3	0.2	1189.2	0.05	0.9
ν_{12} (a')	941.4	2.8	937.9	28.1	-3.4
ν_{13} (a')	934.4	2.4	934.6	4.3	0.2
ν_{14} (a')	419.1	0.9	418.7	0.7	-0.4
ν_{15} (a")	3139.6	14.7	3141.2	14.1	1.5
ν_{16} (a")	1469.0	6.3	1466.9	7.8	-2.1
ν_{17} (a")	1056.4	4.4	1056.3	20.6	-0.1
ν_{18} (a")	1011.3	16.5	1015.0	39.2	3.7
ν_{19} (a")	932.1	38.8	941.8	43.3	9.7
ν_{20} (a")	582.4	11.8	593.6	18.3	11.2
ν_{21} (a")	204.8	0.5	211.5	1.0	6.7

Van der Waals vibrations: 87.5 cm^{-1}, 0.1 km mol^{-1}; 84.6 cm^{-1}, 3.1 km mol^{-1}; 59.6 cm^{-1}, 0.3 km mol^{-1}; 35.9 cm^{-1}, 0.0. km mol^{-1}; 29.6 cm^{-1}, 0.07 km mol^{-1}; 2.3 cm^{-1}, 0.01 km mol^{-1}.

Table S8. MP2/aug-cc-pVDZ vibrational frequencies, in cm^{-1}, and infrared intensities, in km mol^{-1}, for CF_3H·propene.

Mode	$\nu_{monomer}$	IR Intensity	$\nu_{complex}$	IR Intensity	$\Delta\nu$
CF_3H					
ν_1 (a_1)	3226.1	20.7	3236.8	8.5	10.7
ν_2 (a_1)	1121.2	94.0	1115.6	98.5	-5.6
ν_3 (a_1)	677.5	12.7	675.5	13.8	-2.1
ν_4 (e)	1382.5	80.2	1384.9	38.7	2.4
ν_5 (e)	1144.0	597.9	1136.3	567.7	-7.6
ν_6 (e)	490.7	4.6	490.2	4.8	-0.5
Propene					
ν_1 (a')	3283.3	13.9	3279.9	10.8	-3.4
ν_2 (a')	3193.8	13.7	3192.2	12.7	-1.6
ν_3 (a')	3177.3	13.0	3173.6	9.6	-3.8
ν_4 (a')	3161.1	9.4	3164.3	5.1	3.2
ν_5 (a')	3059.4	21.2	3061.8	14.3	2.4
ν_6 (a')	1696.3	10.7	1691.3	10.3	-5.0
ν_7 (a')	1486.3	13.2	1486.9	14.3	0.5
ν_8 (a')	1446.8	0.8	1446.1	1.0	-0.8
ν_9 (a')	1389.0	1.5	1392.4	24.8	3.4
ν_{10} (a')	1316.8	0.1	1316.6	0.1	-0.2
ν_{11} (a')	1188.3	0.2	1189.6	0.8	1.3
ν_{12} (a')	941.4	2.8	940.5	4.9	-0.9
ν_{13} (a')	934.4	2.4	934.7	22.8	0.4
ν_{14} (a')	419.1	0.9	418.9	0.7	-0.2
ν_{15} (a")	3139.6	14.7	3143.2	11.9	3.6
ν_{16} (a")	1469.0	6.3	1467.7	7.2	-1.3
ν_{17} (a")	1056.4	4.4	1058.4	3.5	2.0
ν_{18} (a")	1011.3	16.5	1017.3	20.6	6.0
ν_{19} (a")	932.1	38.8	935.4	22.2	3.3
ν_{20} (a")	582.4	11.8	589.6	13.1	7.2
ν_{21} (a")	204.8	0.5	213.6	0.7	8.8

Van der Waals vibrations: 71.2 cm^{-1}, 1.1 km mol^{-1}; 62.7 cm^{-1}, 0.3 km mol^{-1}; 59.9 cm^{-1}, 0.08 km mol^{-1}; 29.1 cm^{-1}, 0.1 km mol^{-1}; 17.9 cm^{-1}, 1.9 km mol^{-1}; 8.2 cm^{-1}, 1.3 km mol^{-1}.

Table S9. MP2/aug-cc-pVDZ(-PP) complexation enthalpies, in vapour phase (vap) and corresponding liquid argon (LAr)[a], and experimental complexation enthalpies for the complexes of CF_3Cl, CF_3Br and CF_3I with ethene and propene. All data are in kJ mol^{-1}.

	Ethene			Propene		
	CF_3Cl	CF_3Br	CF_3I	CF_3Cl	CF_3Br	CF_3I
$\Delta H°$(vap,calc)	-5.6	-8.8	-11.4	-8.1	-11.6	-15.0
$\Delta H°$(LAr,calc)[b]	-0.6(4)	-3.1(4)	-5.0(4)	-2.5(5)	-5.6(5)	-8.5(5)
Experimental						
$\Delta H°$(LAr)[b]		-5.3(2)	-7.5(2)		-5.6(1)	-8.8(1)

[a] The temperature at which the transformation was calculated is 113 K.

[b] Uncertainties are 2σ.