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The Effect of Fluorination on the Competition of Halogen Bonding and Hydrogen Bonding: Complexes of Fluoroiodomethane with Dimethyl Ether and Trimethylamine

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Abstract

To further rationalize the competition between halogen and hydrogen bonding, a combined experimental and theoretical study on the weakly bound molecular complexes formed between the combined halogen bond / hydrogen bond donor fluoroiodomethane and the Lewis bases dimethyl ether and trimethylamine (in standard and fully deuterated form) is presented. The experimental data are obtained by recording infrared and Raman spectra of mixtures of the compounds in liquid krypton, at temperatures between 120 K and 156 K. The experiments are supported by *ab initio* calculations at the MP2/aug-cc-pVDZ-PP level, statistical thermodynamics and Monte Carlo Free Energy Perturbation calculations. For the mixtures containing fluoroiodomethane and dimethyl ether a hydrogen bonded complex with an experimental complexation enthalpy of $-7.0(2)$ kJ mol⁻¹ is identified. Only a single weak spectral feature is observed which can be tentatively assigned to the halogen bonded complex. For the mixtures involving trimethylamine, both halogen and hydrogen bonded complexes are observed, the experimental complexation enthalpies being $-12.5(1)$ and $-9.6(2)$ kJ mol⁻¹ respectively. To evaluate the influence of fluorination on the competition between halogen and hydrogen bonding, the results obtained for fluoroiodomethane are compared with those of a previous study involving difluoroiodomethane.

1. Introduction

Halogen bonds, the noncovalent interactions between covalently bonded halogen atoms and electron rich sites in the same or in another molecule, have been widely studied as a consequence of their applicability in, amongst other, the fields of rational drug design, molecular recognition, supramolecular chemistry and crystal engineering. One of the main aspects studied in this field is the relationship between this noncovalent interaction and the ubiquitous hydrogen bonding. It has been demonstrated that both noncovalent interactions can coexist¹⁻³, compete⁴⁻¹⁰ or cooperate¹¹ with each other in multiple theoretical and experimental studies.

To be able to rationalize the competition between halogen bonding and hydrogen bonding, we have recently pursued a combined experimental and computational study on the weakly bound bimolecular complexes formed between difluoroiodomethane (CHF_2I), which can simultaneously act as a halogen and hydrogen bond donor, and several Lewis bases including dimethyl ether (DME), trimethylamine (TMA), dimethyl sulfide (DMS) and trimethylphosphine (TMP).¹²⁻¹³ The cornerstones of these studies were the infrared and Raman measurements of liquefied noble gas solutions containing mixtures of CHF_2I and one of the Lewis bases, thereby exploiting the advantage that the weakly bonded complexes can be studied at thermodynamic equilibrium with the monomers. It was found that for some Lewis bases the halogen bonded complex was stronger than the hydrogen bonded one, while for other electron donors the hydrogen bonded complex prevailed over the halogen bonded isomer. Rationalization of the results, supported by DFT calculations, suggested that iodine halogen bonding is generally preferred by the softer Lewis bases, while harder Lewis bases tend to favor hydrogen bonded complexes.

To get a more general view of the competition between both types of bonding, it is of interest to understand whether the tendencies observed for CHF_2I hold up when the nature of the combined donor molecule is altered by substituting the electron withdrawing groups present. Such information can, for example, be deduced by comparing data for fluoroiodomethane (CH_2FI) and CHF_2I .

Figure 1: Electrostatic potential on the molecular surface of fluoroiodomethane (CH_2FI , left) and difluoroiodomethane (CHF_2I , right), defined by the 0.001 electrons Bohr^{-3} contour of the electron density. Positive, neutral and negative regions are shown in blue, green and red, respectively.

The molecular electrostatic potentials of both species are presented in Figure 1. It can be seen that, upon additional fluorination, the size of the σ -hole on the iodine atom increases significantly. The

increase for the σ -hole, influencing the halogen bond capabilities of both species, is also illustrated by the maximum values for the electrostatic potential mapped on the 0.001 electrons Bohr⁻³ electron density isosurface, the values being 0.0292 a.u. for CH₂FI and 0.0377 a.u. for CHF₂I. Also for the hydrogen atom(-s) an increase of the maximal potential is observed upon additional fluorination, the values for the maxima localized near the hydrogen atoms in CH₂FI being 0.0424 a.u. and that for the remaining hydrogen atom in CHF₂I being 0.0547 a.u.

To further investigate the effect of fluorination on the strength of these noncovalent interactions and their competition, experimental data for the complexes between CH₂FI and the Lewis bases DME and TMA are obtained in this study using FTIR on solutions in liquid krypton. The interpretation of the data is supported by *ab initio* and statistical thermodynamics calculations, and Monte Carlo Free Energy Perturbation simulations. The results reported and tendencies observed will be compared with the data recently reported for the complexes with CHF₂I.

2. Methods

The sample of fluoriodomethane (CH₂FI, 99%) was purchased from ABCR and was transferred into a glass sample tube and degassed using a freeze-thaw cycle procedure. Dimethyl ether (DME, 99+%) and dimethyl ether-d₆ (DME-d₆, 98+% d), trimethylamine (TMA, 99%) and fully deuterated trimethylamine (TMA-d₉, +99% d) were purchased from Sigma-Aldrich and were used without further purification. The solvent gas krypton was supplied by Air Liquide and had a stated purity of 99.9995%. When referring to (measurements or results of) both undeuterated and fully deuterated Lewis bases, the notations DME(-d₆) or TMA(-d₉) are used in the remainder of this paper.

The infrared spectra were recorded on a Bruker 66v FTIR spectrometer, equipped with a global source, a Ge/KBr beam splitter and MCT detector, cooled with liquid nitrogen. Measurements were performed using liquid cells equipped with Si windows and with a path length of 10 mm. All interferograms were averaged over 500 scans, Blackman-Harris 3-term apodized and Fourier transformed with a zero filling factor of 8 to yield spectra between 6500 cm⁻¹ and 450 cm⁻¹ with a resolution of 0.5 cm⁻¹.

Estimated mole fractions of the components in solution varied between 7.5×10^{-5} and 1.9×10^{-3} for CH₂FI, 1.3×10^{-4} and 4.9×10^{-3} for DME(-d₆) and 2.8×10^{-4} and 1.9×10^{-3} for TMA(-d₉). As the experimental setup does not allow for verification of full solubility of the compounds, or verification of the fluid level in the filling tube, only approximate concentrations are known.¹⁴

Experimental complexation enthalpies were determined by using the van 't Hoff isochore, based on measurements performed in the 120-156 K temperature interval. Using a subtraction procedure in

which spectra of monomer solutions, recorded at identical temperatures and similar concentrations, are rescaled and subtracted from the spectrum of the mixture, a spectrum containing solely complex bands is obtained in the first phase of the actual analysis.¹⁴ Subsequently band intensities of monomers and complexes are integrated numerically, or, for cases for which both complex bands are not fully resolved, are obtained from band fit analyses. Thermal expansion of the solvent gas during temperature studies was accounted for using the method published by van der Veken.¹⁵

To support the experimental measurements, *ab initio* MP2 calculations were performed using Dunning's augmented correlation consistent basis set of double (aug-cc-pVDZ) zeta quality in Gaussian09.¹⁶ The standard aug-cc-pVDZ basis set was used for hydrogen, carbon, nitrogen, fluorine and chlorine, while the aug-cc-pVDZ-PP basis set including a small-core energy-consistent relativistic pseudopotential (PP) were used for iodine.¹⁷⁻¹⁸ The counterpoise technique as proposed by Boys and Bernardi¹⁹ was used during all *ab initio* calculations to account for basis set superposition error. Energies at the basis set limit were calculated with Molpro²⁰ using the extrapolation scheme of Truhlar²¹ in which the effect of electron correlation is obtained from MP2 calculations.

$$E_{CBS}^{HF} = \frac{3^\alpha}{3^\alpha - 2^\alpha} E_3^{HF} - \frac{2^\alpha}{3^\alpha - 2^\alpha} E_2^{HF} \quad (1)$$

$$E_{CBS}^{cor,MP2} = \frac{3^\beta}{3^\beta - 2^\beta} E_3^{cor,MP2} - \frac{2^\beta}{3^\beta - 2^\beta} E_2^{cor,MP2} \quad (2)$$

In these calculations $\alpha = 3.4$ and $\beta = 2.2$,²¹ while energies with subscript 2 and 3 are calculated using the aug-cc-pVDZ(-PP) and aug-cc-pVTZ(-PP) basis sets respectively.

Furthermore, a correction for higher order correlation effects is made using the method of Jurečka and Hobza²², yielding results of $E_{CBS}^{CCSD(T)}$ quality.

$$\Delta E^{CCSD(T)} = |E^{CCSD(T)} - E^{MP2}|_{aug-cc-pVDZ(-PP)} \quad (3)$$

$$E_{CBS}^{CCSD(T)} = E_{CBS}^{HF} + E_{CBS}^{cor,MP2} + \Delta E^{CCSD(T)} \quad (4)$$

Complexation enthalpies in the vapor phase $\Delta H^\circ(\text{vap,calc})$ were obtained from the calculated complexation energies $\Delta E(\text{CCSD(T)})$ by applying a zero-point energy correction and a correction for thermal effects, calculated at the MP2/aug-cc-pVDZ(-PP) level of theory. Correction of these calculated enthalpy values with solvent effects for liquid krypton yields complexation enthalpies in solution $\Delta H^\circ(\text{LKr,calc})$, which can be compared with the experimental complexation enthalpies $\Delta H^\circ(\text{LKr})$. Corrections for thermal effects and zero-point vibrational contributions were obtained using statistical thermodynamics, whereas effects of solvation were accounted for using the Monte Carlo Free Energy Perturbation (MC-FEP) approach as implemented in an in-house modified version of BOSS 4.0.²³

3. Results

3.1 *Ab initio* calculations

Ab initio calculations at the MP2/aug-cc-pVDZ-PP level of theory yielded two stable complex geometries between CH₂FI and each of the Lewis bases DME and TMA. The equilibrium geometries of the complexes are shown in Figure 2. Cartesian coordinates of monomers and complexes are given in Tables S1 and S2 of the ESI. The intermolecular parameters defined in Figure 2 and energetics for all complexes are summarized in Table 1. The halogen bonded complexes, formed through the interaction between iodine and the lone pair on the oxygen or nitrogen atom, are both characterized by a C_s symmetry. The hydrogen bonded complexes, in which one of the hydrogen atoms of CH₂FI interacts the oxygen or nitrogen atom have C₁ symmetry.

Figure 2: MP2/aug-cc-pVDZ-PP equilibrium geometries for the halogen bonded and hydrogen bonded complexes of CH₂FI with DME and TMA.

Table 1: Intermolecular distance R_{eq} (Å), bond angles ($^{\circ}$), MP2/aug-cc-pVDZ-PP $\Delta E(DZ)$ and CCSD(T)/CBS extrapolated complexation energies $\Delta E(CCSD(T))$, calculated vapor phase complexation enthalpies ΔH° (vap,calc), the calculated complexation enthalpies in liquid krypton (ΔH° (LKr,calc)) and the corresponding experimentally obtained complexation enthalpies (ΔH° (LKr)) (kJ mol^{-1}) for the complexes of CH_2FI with DME and TMA. For comparison, calculated (ΔH° (CHF_2I , LKr, calc)) and experimental (ΔH° (CHF_2I , LKr))¹² complexation enthalpies for the complexes with CHF_2I are also given (kJ mol^{-1}).

	DME		TMA	
	XB	HB	XB	HB
$R_{eq}=R_{X\dots Y}^a$	3.10	2.29	2.99	2.31
$\varphi_{C-X\dots Y}^a$	174.70	143.40	179.20	156.04
$\psi_{C-Y\dots X}^a$	106.52	104.99/122.98	107.50/109.13/109.13	96.23/114.40/115.78
$\Delta E(DZ)$	-14.5	-17.4	-23.6	-20.8
$\Delta E(CCSD(T))$	-15.4	-19.0	-22.8	-21.9
ΔH° (vap,calc)	-13.0	-16.1	-20.4	-19.0
ΔH° (LKr,calc)	-9.4	-10.1	-16.4	-12.7
Experimental				
ΔH° (LKr)		-7.0(2)	-12.5(1)	-9.6(2)
ΔH° (CHF_2I , LKr, calc)	-12.4	-12.0	-23.4	-16.6
ΔH° (CHF_2I , LKr) ^b	-11.5(6)	-10.5(5)	-19.0(3)	-14.7(2)

^a X = I, H; Y = O, N

^b Values from Nagels et al.¹²

For both halogen bonded complexes, nearly linear geometries are obtained, the C-I $\cdots$ Y angles being 174.7 $^{\circ}$ for DME and 179.2 $^{\circ}$ for TMA. For the hydrogen bonded complexes, the C-H $\cdots$ Y angles are reduced to 143.4 $^{\circ}$ and 156.0 $^{\circ}$ for DME and TMA, respectively. In agreement with tendencies observed and described in previous publications¹²⁻¹³, these deviations from linearity enable the formation of secondary interaction between the halogen atoms of CH_2FI and the methyl groups of the Lewis bases in the hydrogen bonded complexes. To aid characterization of such interactions, in this study, additional information supporting their role was obtained using the noncovalent interactions (NCI) index visualized using NCIPLOT²⁴⁻²⁵. Plots of the reduced density gradient versus the electron density multiplied by the sign of the second Hessian eigenvalue and figures showing the gradient isosurfaces are given in Figures S1 and S2 of the ESI. For both halogen bonded complexes, a single isosurface is observed between the iodine atom and the lone pair carrying atom of the Lewis base. Inspection of the result for the hydrogen bonded complex with DME in Figure S1 reveals the presence of isosurfaces between iodine and a hydrogen atom of both methyl groups, as well as an isosurface between fluorine and a hydrogen atom in addition to the isosurface between the CH_2FI hydrogen atom and the oxygen

atom. Similar secondary interactions are also observed in the hydrogen bonded complex with TMA, shown in Figure S2.

3.2 Infrared spectroscopy

The assignment of the vibrational modes of DME(-d₆) and TMA(-d₉) observed in liquefied noble gases has been discussed in detail in previous publications^{12,26-30} and is not repeated here. The assignment of the vibrational modes of CH₂FI given is based on *ab initio* calculations and the Raman study reported by Feller et al.³¹ In order to assess the presence of halogen and/or hydrogen bonded complex, the complexation shifts of the bands in the subtracted spectra are compared to those obtained from *ab initio* calculations, given in Tables S3 to S6 of the ESI. Due to the limited solubility of CH₂FI, a comprehensive study over a wide concentration interval was not feasible. As a result, some complex bands of the vibrational modes with the lowest IR intensities could not be observed.

3.2.1 CH₂FI-DME infrared spectra

The *ab initio* calculations suggest that a distinction between the halogen and hydrogen bonded complex between CH₂FI and DME can be made in the ν_5 , ν_7 , ν_8 and ν_3 spectral regions of CH₂FI, whereas no DME modes are suitable for distinction between both dimer geometries.

An overview of experimentally observed monomer bands, complex bands, complexation shifts and the corresponding calculated shifts is given in Table 2 for the complexes with DME and Table S7 for the complexes with DME-d₆. Selected spectral regions for the mixtures between CH₂FI and DME or DME-d₆ are given in Figures 3 and S3 of the ESI, respectively.

Figure 3: Infrared spectra of selected spectral regions for the mixtures of CH₂FI with DME 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 CH₂FI or DME, respectively. Trace *d* represents the spectrum of the complex which is obtained by subtracting the rescaled traces *b* and *c* from trace *a*.

Estimated mole fractions of the solutions of the mixtures are 1.2×10^{-4} for CH₂FI and 4.9×10^{-3} for DME in panel A, 1.3×10^{-4} for CH₂FI and 4.7×10^{-3} for DME in panel B and 1.2×10^{-4} for CH₂FI and 4.9×10^{-3} for DME in panel C.

Table 2: Experimental infrared frequencies for the monomers and complexes, as well as experimental complexation shifts (Δv_{exp}) and MP2/aug-cc-pVDZ-PP calculated complexation shifts (Δv_{calc}), in cm⁻¹, for the halogen bonded complex (XB) and hydrogen bonded complex (HB) of CH₂FI with DME dissolved in LKr at 130 K.

Assignment	v_{monomer}	$v_{\text{complex,HB}}$	$\Delta v_{\text{exp,HB}}$	$\Delta v_{\text{calc,HB}}$	$\Delta v_{\text{calc,XB}}$
CH₂FI					
v_7	3043.0	^a		7.1	-8.0
v_1	2981.5	^a		-3.0	-5.0
	2975.7	-			
$2v_2$	2877.3	^a		-1.6 ^b	-2.1
$2v_4$	2070.0	2057.0	-13.0	-21.3	-21.1
v_2	1448.1	-		-0.8 ^b	-1.0
v_3	1268.0	1274.5	6.5	8.0	-0.7
v_8	1219.8	1225.1	5.3	13.5	-0.8
$2v_5$	1130.1	1124.4	-5.7	-7.0	5.8
v_4	1043.2	1036.7	-6.5	-10.7	-10.5
v_4 (¹³ C)	1020.6	1014.4	-6.2	-10.7	-10.5
v_9	855.1	-			
v_5	566.7	563.9	-2.8	-3.5	2.9
DME					
v_1	2990.0	2991.7	1.7	1.2	2.0
v_{16}	2990.0	2991.7	1.7	-0.6	2.0
$2v_3$	2950.6	-		-3.1	-4.8
$v_3 + v_{18}$	2932.8	2931.2	-1.6	-2.9	-4.6
$v_3 + v_{13}$	2929.5	2931.2	1.7	-2.6	-3.3
v_{12}	2916.5	2919.2	2.7	11.9	11.1
$v_3 + v_{19}$	2905.5	-		-1.1	-3.1
$v_4 + v_{19}$	2880.5	2885.4	4.9	3.8	-1.6
	2866.8	2868.6	1.8		
v_2	2811.6	2816.6	5.0	6.1	5.6
$v_6 + v_{20}$	2092.6	2084.5	-8.1	-15.1	-17.7
$v_6 + v_{21}$	2020.4	2012.6	-7.8	-10.7	-15.0
v_3	1474.9	1474.8	-0.1	-1.6	-2.4
v_{18}	1457.4	1457.8	0.4	-1.4	-2.2
v_{13}	1455.1	1455.0	-0.1	-1.1	-0.9
v_{19}	1426.2	-		0.4	-0.7
v_5	1244.9	1246.5	1.6	1.6	-0.4
v_{20}	1172.2	1168.4	-3.8	-7.6	-8.0
v_{21}	1099.1	1096.8	-2.3	-3.1	-5.3
v_6	929.3	924.2	-5.1	-7.6	-9.7

^a Modes could not be assigned due to overlap with DME modes

^b Vibrational mode is degenerate with DME modes in *ab initio* calculations

For the ν_5 mode of CH_2FI , shown in Panel C of Figure 3, a -2.8 cm^{-1} redshifted band corresponding to the hydrogen bonded complex with a calculated value of -3.5 cm^{-1} is observed. No blueshifted band corresponding to the halogen bonded complex, with a calculated shift of 2.9 cm^{-1} , is observed.

Further evidence for the presence of a hydrogen bonded complex is found for CH_2FI ν_7 mode, which, due to overlap with the C-H stretches of DME and its low IR intensity, is shown for a mixture with DME- d_6 in Panel S3A of the ESI. For this spectral region, a 7.4 cm^{-1} blueshifted band corresponding to the calculated value of 7.1 cm^{-1} is observed. As before, no band corresponding to the -8.0 cm^{-1} redshifted halogen bonded complex was observed.

It is worth noting that the complex bands of the ν_7 mode and ν_1 mode (shown on the right hand side in the same Panel) have similar intensities, whereas the intensity of the ν_1 mode of the monomer is far more intense than the ν_7 mode (trace *b*). This can be explained by the increase of intensity of the ν_7 mode upon hydrogen bond formation, as predicted in the calculations given in Table S4B, where an intensity of 0.5 km mol^{-1} is calculated for this mode in the monomer and 7.8 km mol^{-1} for the same mode in the hydrogen bonded complex. For the halogen bonded complex, a less pronounced intensity enhancement to 1.4 km mol^{-1} is predicted, as seen in Table S3B. To explore whether the low infrared intensity might be a reason for the absence of a halogen bonded complex band in the spectra studied, Raman experiments were also initiated. Unfortunately, due to the low solubility and the larger bandwidth of the ν_7 mode, no complex bands were observed for this mode.

For the ν_8 mode of CH_2FI a very weak 5.3 cm^{-1} blueshifted band is observed, corresponding to the 13.5 cm^{-1} blueshift calculated for the hydrogen bonded complex, whereas no trace of a redshifted band for the halogen bonded complex ($\Delta\nu_{\text{calc}} = -0.8\text{ cm}^{-1}$) was observed.

Up to this point, all complex bands observed corresponded well to the hydrogen bonded complex, whereas no bands corresponding to the halogen bonded complex were detected. For the CH_2FI ν_3 mode, shown in Panel 3A, a clear 6.5 cm^{-1} blueshifted band is observed, which is again in excellent correspondence with the calculated value of 8.0 cm^{-1} for the hydrogen bonded complex. However, apart from this band, a weaker spectral feature with a blueshift of 1.3 cm^{-1} is also observed. To evaluate whether this feature originates from the Lewis base involved, mixtures involving DME- d_6 were also investigated. As shown in Panel B of Figure S3 of the ESI, this spectral feature is also present when using the fully deuterated Lewis base. It must therefore be considered that this spectral feature can come from the presence of a small amount of halogen bonded complex ($\Delta\nu_{\text{calc}} = -0.7\text{ cm}^{-1}$) in the solution.

3.2.2 CH₂FI·DME van 't Hoff plots and experimental complexation enthalpies

By performing measurements of CH₂FI·DME(-d₆) mixtures within the 120 K - 156 K temperature interval, 4 van 't Hoff plots were constructed, yielding an average complexation enthalpy of -7.0(2) kJ mol⁻¹. An overview of the concentrations and integration intervals used, as well as the resulting complexation enthalpies, is given in Table S9 of the ESI. An example of a typical van 't Hoff plot for this complex is given in Figure S6 of the ESI. It should be noted that for the van 't Hoff plots constructed using the complex band intensities of the ν_3 mode of CH₂FI, the small additional band intensity was integrated separately and subtracted from the total intensity. Apart from the complex intensities of the ν_3 mode of CH₂FI, the integrated intensities of the complex band of the CH₂FI ν_4 mode, shown in Panel 3B, were also used for the construction of a van 't Hoff plot.

3.2.3 CH₂FI·TMA infrared spectra

As TMA vibrational modes are found in the same regions as the CH₂FI ν_3 and ν_4 modes, the mixtures involving the fully deuterated TMA-d₉ will be discussed here, while spectra and assignments for the mixtures involving TMA are given in the ESI.

An overview of experimentally observed monomer bands, complex bands, complexation shifts and the corresponding calculated shifts is given in Table 3 for the complexes with TMA-d₉ and Table S8 for the complexes with TMA, while selected spectral regions of CH₂FI·TMA mixtures are shown in Figure S4. In order to avoid saturation of the detector in the spectral regions where vibrational modes of CHF₂I and TMA overlap, the spectra shown in panels S4A and S4B were obtained using reduced concentrations of both monomers.

Table 3: Experimental infrared frequencies for the monomers and complexes, as well as experimental complexation shifts (Δv_{exp}) and MP2/aug-cc-pVDZ-PP calculated complexation shifts (Δv_{calc}), in cm^{-1} , for the halogen bonded complex (XB) and hydrogen bonded complex (HB) of CH_2FI with TMA- d_9 dissolved in LKr at 130 K.

Assignment	v_{monomer}	$v_{\text{complex,HB}}$	$\Delta v_{\text{exp,HB}}$	$\Delta v_{\text{calc,HB}}$	$v_{\text{complex,XB}}$	$\Delta v_{\text{exp,XB}}$	$\Delta v_{\text{calc,XB}}$
CH_2FI							
v_7	3043.0	3031.5	-11.5	-17.1	3031.5	-11.5	-16.0
v_1	2981.5	2965.8	-15.7	-41.1	2975.5	-6.0	-11.7
	2975.7	-			-		
$2v_2$	2877.3	2885.3	8.0	25.3	2872.7	-4.6	-5.9
$2v_4$	2070.0	^a		-27.0	^a		-37.0
v_2	1448.1	1455.9	7.8	12.6	1446.3	-1.8	-3.0
v_3	1268.0	1280.8	12.8	24.2	1264.8	-3.2	-6.4
v_8	1219.8	-		18.6	1217.8 ^b	-2.0	-2.7
$2v_5$	1130.1	1126.9	-3.2	-11.8	1126.9	-3.2	-10.7
v_4	1043.2	1033.3	-9.9	-13.5	1026.5	-16.7	-18.5
v_4 (^{13}C)	1020.6	-		-13.5	-		-18.5
v_5	566.7	562.6	-4.1	-5.9	565.3	-1.4	-5.4
TMA-d_9							
v_{12}	2232.7	2234.0	1.3	0.5	2234.0	1.3	1.3
v_1	2181.9	2186.6	4.7	2.6	2186.6	4.7	5.8
v_{13}	2181.9	2186.6	4.7	4.2	2186.6	4.7	6.2
v_2	2029.4	2036.7	7.3	6.5	2036.7	7.3	9.9
v_{14}	2029.4	2036.7	7.3	7.6	2036.7	7.3	10.9
$v_{19} + v_{21}$	1226.3	1225.2	-1.1	-1.4	1225.2	-1.1	-1.0
v_{15}	1220.8	1217.8	-3.0	-7.3	1217.8	-3.0	-2.7
v_3	1138.7 ^c	1136.4 ^d	-2.3	-2.3	1136.4 ^d	-2.3	-3.1
v_4	1063.1	1063.2	0.1	1.1	1063.2	0.1	0.0
v_{16}	1062.4	1061.7	-0.7	-0.6	1061.7	-0.7	-1.7
v_{18}	1047.8	1048.6	0.8	0.4	1048.6	0.8	-1.0
v_5	1003.7	1011.2	7.5	7.5	1011.2	7.5	9.9
v_{19}	873.8	873.6	-0.2	-0.4	873.6	-0.2	0.1
v_6	741.0	738.6	-2.4	-2.3	738.6	-2.4	-3.6

^a Band could not be assigned due to overlap with TMA- d_9 modes

^b Overlap with the complex bands of the TMA- d_9 v_{15} mode.

^c Obtained from a Raman measurement at 130 K in LKr

^d Tentatively assigned from IR measurements

In several of the spectral regions discussed for the CH_2FI -DME mixtures, two distinct complex bands are observed for CH_2FI -TMA- d_9 mixtures. In the CH_2FI v_3 region near 1268 cm^{-1} , a broad band with a 12.8 cm^{-1} blueshift as well as a narrower band with a -3.2 cm^{-1} redshift are observed upon subtraction, as shown in Panel A of Figure 4. These complex bands can be assigned to the hydrogen bonded complex and halogen bonded complex with calculated shifts of 24.2 cm^{-1} and -6.4 cm^{-1} respectively.

In the CH_2FI v_5 spectral region, shown in Panel 4C, two overlapping redshifted bands are observed, the experimental complexation shifts being -4.1 cm^{-1} and -1.4 cm^{-1} . Although redshifts were calculated

for both complex geometries (-5.9 cm^{-1} for the hydrogen bonded and -5.4 cm^{-1} for the halogen bonded complex), the difference between experimental complexation shifts of -1.4 cm^{-1} and -4.1 cm^{-1} is noticeably larger than predicted. The assignment of the band with the largest redshift to the hydrogen bonded complex and the band with the smallest redshift to the halogen bonded complex, given in Tables 3 and S8 of the ESI, should therefore be interpreted with the necessary prudence.

Also in the spectral region of the $\text{CH}_2\text{FI } \nu_4$ mode shown in panel 4B, two partially overlapping redshifted bands are observed with experimental complexation shifts of -16.7 cm^{-1} and -9.9 cm^{-1} corresponding to the halogen bonded complex ($\Delta\nu_{\text{calc}} = -18.5\text{ cm}^{-1}$) and hydrogen bonded complex ($\Delta\nu_{\text{calc}} = -13.5\text{ cm}^{-1}$) respectively.

Figure 4: Infrared spectra of selected spectral regions for the mixtures of CH_2FI with TMA-d_9 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 CH_2FI or TMA-d_9 , 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 1.3×10^{-4} for CH_2FI and 1.9×10^{-3} for TMA-d_9 in panel A, 7.1×10^{-5} for CH_2FI and 1.9×10^{-3} for TMA-d_9 in panel B and 1.3×10^{-4} for CH_2FI and 1.9×10^{-3} for TMA-d_9 in panel C.

Another interesting spectral feature is the presence of a sharp complex band at 1136.4 cm^{-1} in the spectra of $\text{CH}_2\text{FI-TMA-d}_9$ mixtures, shown in Panel B of Figure 5, which is absent in the spectra of $\text{CH}_2\text{FI-TMA}$ mixtures, shown in Panel A of the same Figure. Even though no vibrational modes with appreciable infrared intensities are present for the TMA-d_9 monomer in this spectral region, as shown in trace *c* in Figure 5B, Raman measurements have revealed the presence of the ν_3 mode of TMA-d_9 at 1138.7 cm^{-1} . Investigation of the *ab initio* calculated IR intensities for the $\text{CH}_2\text{FI-TMA-d}_9$ complexes, given in Tables S5B and S6B, shows that for the halogen bonded complex the calculated IR intensity for the ν_3 mode of TMA-d_9 rises from 0.2 km mol^{-1} to 5.8 km mol^{-1} . For the hydrogen bonded complex a rise of the infrared intensity is also observed for this vibrational mode, albeit less noticeable to a value of 0.7 km mol^{-1} . For both complexes redshifts are calculated (-2.3 cm^{-1} for the hydrogen bonded complex and -3.1 cm^{-1} for the halogen bonded complex), which are in excellent agreement with the experimental shift of -2.3 cm^{-1} when taking into account the monomer band frequency from the

Raman measurements. Therefore, this additional complex band is assigned to the TMA-d₉ ν_3 mode in the halogen and hydrogen bonded complexes.

Figure 5: Infrared spectra for the mixtures of CH₂FI with TMA (left) or TMA-d₉ (right) 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 CH₂FI or TMA(-d₉), respectively. Trace *d* represents the spectrum of the complex which is obtained by subtracting the rescaled traces *b* and *c* from trace *a*. Estimated mole fractions of the solutions of the mixtures are 9.4×10^{-5} for CH₂FI and 1.9×10^{-3} for TMA in panel A and 1.3×10^{-4} for CH₂FI and 1.9×10^{-3} for TMA-d₉ in panel B.

Furthermore, when studying the C-H stretching region for solutions containing CH₂FI, apart from the antisymmetric C-H stretch ν_7 and the symmetric C-H stretch ν_1 , a third band is found at 2877.3 cm⁻¹. Inspection of the CH₂FI·TMA-d₉ mixtures shows the existence of two complex bands, with a broad 8.0 cm⁻¹ blueshifted band and a narrow -4.6 cm⁻¹ redshifted band as shown in Figure S5 of the ESI. The presence of these two complex bands is consistent with the *ab initio* calculated shifts of -5.9 cm⁻¹ for the halogen bonded complex and 25.3 cm⁻¹ for the hydrogen bonded complex for the first overtone of ν_2 , an assignment previously made by Feller et al.³¹

3.2.4 CH₂FI·TMA van 't Hoff plots and experimental complexation enthalpies

Due to the band overlaps of CH₂FI and TMA in the regions of interest, solutions with reduced concentrations of both species had to be used for the CHF₂I·TMA mixtures to avoid saturation of the detector. As a consequence, only limited amounts of the complexes are observed in the CHF₂I·TMA solutions. Therefore, all experimental enthalpies are determined from measurements involving TMA-d₉, recorded in the 120 - 156 K temperature interval. Furthermore, as the complex bands of the CH₂FI ν_4 mode had a significant overlap, which inhibits the use of direct numerical integrations to obtain the intensities needed in the van 't Hoff plots, the band intensities for these complex bands were obtained using least-squares bandfitting.

Average experimental complexation enthalpies of -12.5(1) kJ mol⁻¹ for the halogen bonded complex and -9.6(2) kJ mol⁻¹ for the hydrogen bonded complex were obtained from four van 't Hoff plots for

each complex, the details of which are given in Tables S10 and S11 of the ESI. Typical van 't Hoff plots obtained for both complexes are given in Figure S6 of the ESI.

4. Discussion

Despite calculations indicating that the complexation enthalpies of the halogen and hydrogen bonded complex between CH₂FI and DME(-d₆) are separated by a mere 0.7 kJ mol⁻¹, the hydrogen bonded complex being slightly stronger, from the cryosolutions experiments only clear indications were found for the presence of a hydrogen bonded complex. Especially the absence of the blueshifted band of the ν_5 CH₂FI mode near 567 cm⁻¹ and the redshifted band for the ν_3 CH₂FI mode near 1268 cm⁻¹, which are calculated for the halogen bonded complex, is noteworthy. The absence of halogen bonded complex is remarkable, as complexes with differences in relative stability of up to -7.5(7) kJ mol⁻¹ were found simultaneously in liquefied noble gas solutions in previous studies.¹² The weak blueshifted feature in the ν_3 spectral region might indicate the presence of a limited amount of halogen bonded complex, but the band is found to be too weak for further analysis.

For the mixtures involving the Lewis base TMA(-d₉), both hydrogen bonded and halogen bonded complexes are observed, with clearly resolved complex bands occurring in several spectral regions. Consistent with a strong increase of IR intensity predicted upon complexation, a complex band is also observed for the ν_3 mode of TMA-d₉, while this mode is too weak to be observed in IR in the monomer.

As expected from the electrostatic potentials shown in Figure 1, reduction of the number electron withdrawing fluorine atoms decreased the binding strength of both the halogen and hydrogen bonded complex with both Lewis bases. For the hydrogen bonded complex with DME the complexation enthalpy is reduced from -10.5(5) to -7.0(2) kJ mol⁻¹ when going from CHF₂I to CH₂FI, while no halogen bonded complex could be assigned decisively. For TMA the complexation energy of the hydrogen bonded complex is reduced from -14.7(2) kJ mol⁻¹ to -9.6(2) kJ mol⁻¹ when going from CHF₂I to CH₂FI, while the complexation enthalpy of the halogen bonded complex diminishes from -19.0(3) to -12.5(1) kJ mol⁻¹. Closer inspection of these values reveals that the ratio of the halogen and hydrogen bond complexation enthalpies of 1.29(2) for CHF₂I and 1.30(2) for CH₂FI remains constant for the complexes with TMA. This indicates that enhancing the noncovalent interactions by addition of electron withdrawing fluorine atoms does not promote the formation of halogen bonded complexes over hydrogen bonded complexes or *vice versa*. Increasing fluorination of the bond donor molecule is therefore most likely not a suitable method to influence the bond strength order of both noncovalent interactions when interacting with a nitrogen electron donor. It should also be noted that despite the HB site having the greater electrostatic potential, the largest complexation

energies and enthalpies are predicted for the XB complexes when TMA is used as a Lewis base. Furthermore, the order of the complexation strengths is also not upheld when switching to DME as a Lewis base, as the CHF₂I-DME halogen bonded complex has a slightly higher theoretical and experimental complexation enthalpy than the CHF₂I-DME hydrogen bonded complex, while the CH₂FI-DME hydrogen bonded complex has a higher calculated complexation enthalpy than the CH₂FI-DME halogen bonded complex.

These observations confirm that, even though the electrostatic potentials on the donor molecules give a good indication of the complexes that might be formed in solution, they do not tell the full story, as the Lewis base involved in the interaction also plays a significant role through its chemical hardness and ability to form secondary interactions.

To further rationalize these results, the different contributions to the interaction energy were analysed using a Ziegler-Rauk-type energy decomposition analysis³²⁻³⁴ on the complexes of CH₂FI and CHF₂I with DME and TMA, were performed to assess the contributions of the different forces at play to the strength of the noncovalent interactions. An overview of the results of this analysis is given in Table 4, which for comparison also includes the results of the complexes of DME and TMA with CHF₂I.

Table 4: Interaction energy (ΔE_{int}) and its components, ΔE_{Pauli} , ΔV_{elst} , ΔE_{oi} and dispersion (E_{disp}), strain energy ΔE_{strain} and complexation energy (ΔE^{DFT}) obtained at PBE/TZ2P level in kJ mol⁻¹ for the complexes of CH₂FI and CHF₂I with DME or TMA.^a

	CH ₂ FI				CHF ₂ I			
	DME		TMA		DME		TMA	
	HB	XB	HB	XB	HB	XB	HB	XB
ΔE_{Pauli}	16.0	24.0	23.9	61.6	19.0	29.1	30.8	75.4
ΔV_{elst}^b	-19.4 (68)	-22.6 (65)	-26.1 (65)	-52.2 (64)	-23.0 (68)	-27.5 (65)	-33.5 (64)	-63.4 (63)
ΔE_{oi}^b	-9.0 (32)	-12.2 (35)	-13.8 (35)	-29.7 (36)	-10.8 (32)	-15.0 (35)	-18.6 (36)	-37.1 (37)
E_{disp}	-8.7	-5.8	-9.9	-8.3	-8.7	-5.8	-9.5	-8.5
ΔE_{int}	-21.1	-16.6	-25.9	-28.6	-23.5	-19.1	-30.8	-33.7
ΔE_{strain}	0.4	0.6	0.3	0.4	0.3	0.8	0.3	0.6
ΔE^{DFT}	-20.7	-16.0	-25.6	-28.2	-23.2	-18.4	-30.7	-33.1

^a Single point PBE/TZ2P calculations were performed based on MP2/aug-cc-pVDZ-PP optimized geometries

^b The relative contributions of the electrostatic and orbital interaction energies to the stabilization energy are indicated in brackets in percentages.

From this analysis it becomes clear that both the stabilizing electrostatic and orbital interaction contributions and the destabilizing Pauli repulsion increase between 19 and 35 % when changing the donor molecule CH₂FI to the more fluorinated CHF₂I. This implies that a purely electrostatic description, i.e. based on the electrostatic potential, will give an incomplete picture of the effect of the addition of fluorine atoms on the bond donor on the noncovalent interactions formed. It should, however, also be noted that, when comparing the equivalent complexes formed with both bond

donors, the relative contributions of both stabilizing forces remain remarkably similar, differing at most 1 %. Furthermore, the absolute contributions of the dispersion energies remain stable when going from CH₂FI to CHF₂I. The increased stability of the complexes formed with the more fluorinated donor is therefore not the consequence of one single contribution, but of the combination of both the stabilizing ΔV_{elst} and ΔE_{oi} and repulsive ΔE_{Pauli} contributions. From this analysis it is therefore clear that, although fluorination of the bond donor increases the strength of the noncovalent interactions formed, it does not change the nature of the interactions themselves, as the relative contributions of ΔV_{elst} and ΔE_{oi} and the absolute contributions of E_{disp} remain constant.

Reviewing the relative contributions of ΔV_{elst} and ΔE_{oi} (which contains the stabilization caused by interactions between the occupied molecular orbitals on one fragment and the unoccupied molecular orbitals of the other fragment) shows that the former dominates over the latter for both types of noncovalent interactions between all donor-acceptor pairs studied. Moreover, the relative contributions of ΔV_{elst} and ΔE_{oi} for the HB and XB complexes are very similar. This is somewhat different from the previous studies performed by Shaik and coworkers where, based on a different decomposition, Charge Transfer (CT) was found to be the dominant contribution for XBs, while its role in HBs was minor.³⁵⁻³⁶ Not only is such dominance in XB complexes not observed in the current study, but the difference in energetic contributions between XB and HB complexes is also absent.

Within these results also no indication is found as to the reason why no halogen bonded complex is observed in the infrared spectra of the CH₂FI-DME mixtures, despite the small difference in calculated complexation enthalpy. As the concentration ratio of the halogen and hydrogen bonded complexes in the liquid noble gas solutions is linked to the free energy of both complexes through the equilibrium constant, the low relative concentration of halogen bonded complex most probably must be ascribed to a more unfavorable entropic contribution to this complex compared to the hydrogen bonded complex. The reason for this is not understood but might be correlated with the fact that in the solutions studied, all complexes are extremely non-rigid and are thus characterized by several strongly anharmonic large amplitude intramolecular motions. Unfortunately, a reliable approach allowing the thermodynamic contributions of these motions to be correctly estimated encounters large difficulties as the intramolecular motions cannot be reduced to a set of (an-)harmonic motions and internal rotations.³⁷⁻³⁸ This limitation, obviously, limits the use of the rigid rotor harmonic oscillator approximation often used in statistical thermodynamics. The floppy character of the molecules further limits the use of anharmonic corrections based on perturbation theory based approaches³⁹⁻⁴² as harmonic frequencies and corrections for anharmonicity in these types of calculations are obtained for specific, well defined equilibrium geometries only.

5. Conclusions

The competition between halogen and hydrogen bonding was assessed using infrared spectroscopy on solutions in liquid krypton containing mixtures of the Lewis bases DME or TMA (including their fully deuterated counterparts) and CH₂FI.

Despite calculations on the CH₂FI·DME dimers indicating that both the halogen and hydrogen bonded complex would have very similar complexation enthalpy, the hydrogen bonded complex being stronger by a mere -0.7 kJ mol⁻¹, only clear complex bands assigned to the hydrogen bonded complex were observed. An experimental complexation enthalpy in solution $\Delta H^\circ(\text{LKr})$ for this hydrogen bonded complex was obtained of -7.0(2) kJ mol⁻¹ using the van 't Hoff isochore. Additionally, a single, weak spectral feature was also observed in the CH₂FI ν_4 spectral region, which can be tentatively assigned to a small amount of halogen bonded complex.

For the solutions in liquid krypton containing CH₂FI and TMA(-d₉) both the halogen and hydrogen bonded complex were observed in several spectral regions. As complex bands due to both complexes were sufficiently resolved, complexation enthalpies could be determined of -12.5(1) kJ mol⁻¹ for the halogen bonded complex and -9.6(2) kJ mol⁻¹ for the hydrogen bonded complex. As suggested by the *ab initio* calculations, the halogen bonded complex is indeed found to be more stable than its hydrogen bonded counterpart.

Comparison of these results with the results from a previous study on the complexes of DME and TMA with CHF₂I, using a Ziegler-Rauk-type energy-decomposition analysis, also shows that although fluorination of the bond donor enhances the stability of the noncovalent interactions formed, the nature of the interactions formed is not altered, as the different contributions to the interaction energy remain similar.

Supporting Information Available:

MP2/aug-cc-pVDZ(-PP) cartesian coordinates, vibrational frequencies, IR and Raman intensities of all monomers and complexes, experimental frequencies of CH₂FI, DME-d₆, TMA and observed complexes in LKr, overview of parameters used in van 't Hoff plots, NCI plots for all calculated complex geometries and IR spectra of the regions of interest for mixtures involving DME-d₆, TMA or TMA-d₉ and a typical van 't Hoff for each of the three observed complexes.

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TOC Graphic

The Effect of Fluorination on the Competition of Halogen Bonding and Hydrogen Bonding: Complexes of Fluoroiodomethane with Dimethyl Ether and Trimethylamine

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Electronic supplementary information

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

C _s	X	Y	Z
CH ₂ FI			
C	-0.536137	-1.469079	0.000000
H	-1.106997	-1.662637	0.914403
H	-1.106997	-1.662637	-0.914403
F	0.603424	-2.258519	0.000000
I	0.000000	0.612574	0.000000

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

C _{2v}	X	Y	Z
DME			
O	0.000000	0.000000	0.607066
C	0.000000	1.169581	-0.202099
H	0.000000	2.032636	0.474896
H	0.898418	1.208635	-0.845282
H	-0.898418	1.208635	-0.845282
C	0.000000	-1.169581	-0.202099
H	0.898418	-1.208635	-0.845282
H	0.000000	-2.032636	0.474896
H	-0.898418	-1.208635	-0.845282

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

C _{3v}	X	Y	Z
TMA			
N	0.000000	0.000000	0.410619
C	0.000000	1.379959	-0.066347
H	-0.892330	1.901918	0.309142
H	0.892330	1.901918	0.309142
H	0.000000	1.440847	-1.178318
C	1.195079	-0.689979	-0.066347
H	2.093274	-0.178178	0.309142
H	1.200944	-1.723740	0.309142
H	1.247810	-0.720423	-1.178318
C	-1.195079	-0.689979	-0.066347
H	-1.200944	-1.723740	0.309142
H	-2.093274	-0.178178	0.309142
H	-1.247810	-0.720423	-1.178318

Table S2.1: Cartesian coordinates of the MP2/aug-cc-pVDZ-PP optimized geometry of the halogen bonded complex between fluoroiodomethane and dimethyl ether.

C _s	X	Y	Z
CH ₂ FI			
C	-0.460142	2.602075	0.000000
H	-0.978026	2.918326	0.912224
H	-0.978026	2.918326	-0.912224
F	0.820697	3.147717	0.000000
I	-0.360534	0.455758	0.000000
DME			
O	0.068618	-2.615536	0.000000
C	0.820697	-2.919865	-1.173111
H	1.074674	-3.994444	-1.208687
H	0.192801	-2.663019	-2.035116
H	1.753329	-2.328069	-1.208842
C	0.820697	-2.919865	1.173111
H	1.753329	-2.328069	1.208842
H	0.192801	-2.663019	2.035116
H	1.074674	-3.994444	1.208687

Table S2.2: Cartesian coordinates of the MP2/aug-cc-pVDZ-PP optimized geometry of the hydrogen bonded complex between fluoroiodomethane and dimethyl ether.

	X	Y	Z
CH ₂ FI			
C	-0.386073	1.271767	0.839189
H	0.623038	0.985344	1.154151
H	-1.055746	1.566405	1.654190
F	-0.301447	2.315680	-0.074435
I	-1.249640	-0.460203	-0.104708
DME			
O	2.594135	0.087985	0.412919
C	2.737780	0.566208	-0.923945
H	2.056972	0.029684	-1.608956
H	2.479426	1.632414	-0.917347
H	3.777488	0.439950	-1.275825
C	2.886379	-1.305453	0.481092
H	3.927070	-1.505087	0.167711
H	2.755389	-1.614275	1.525691
H	2.198684	-1.883810	-0.161570

Table S2.3: Cartesian coordinates of the MP2/aug-cc-pVDZ-PP optimized geometry of the halogen bonded complex between fluoroiodomethane and trimethylamine.

C _s	X	Y	Z
CH ₂ FI			
C	0.441539	2.832276	0.000000
H	0.978372	3.120143	0.911327
H	0.978372	3.120143	-0.911327
F	-0.803977	3.462466	0.000000
I	0.200057	0.689365	0.000000
TMA			
N	-0.176394	-2.278145	0.000000
C	0.441539	-2.839479	-1.200143
H	-0.012258	-2.386518	-2.093844
H	1.517493	-2.610897	-1.201599
H	0.313669	-3.942478	-1.257974
C	0.441539	-2.839479	1.200143
H	1.517493	-2.610897	1.201599
H	-0.012258	-2.386518	2.093844
H	0.313669	-3.942478	1.257974
C	-1.615150	-2.538870	0.000000
H	-2.071343	-2.085621	0.892334
H	-2.071343	-2.085621	-0.892334
H	-1.841147	-3.627483	0.000000

Table S2.4: Cartesian coordinates of the MP2/aug-cc-pVDZ-PP optimized geometry of the hydrogen bonded complex between fluoroiodomethane and trimethylamine.

	X	Y	Z
CH ₂ FI			
C	-0.467376	1.248030	-0.698891
H	0.554484	0.858317	-0.803737
H	-0.925692	1.603616	-1.628250
F	-0.473856	2.282721	0.230022
I	-1.675291	-0.387617	0.017001
TMA			
N	2.510889	-0.139132	-0.102619
C	2.547100	-1.590665	-0.281552
H	1.609777	-2.031192	0.088190
H	2.648029	-1.829732	-1.350554
H	3.397384	-2.056388	0.264224
C	3.745910	0.456329	-0.610694
H	3.855323	0.227383	-1.681033
H	3.708413	1.548891	-0.488057
H	4.644184	0.074625	-0.076862
C	2.352931	0.181493	1.316974

H	2.298378	1.272525	1.447094
H	1.418761	-0.260306	1.693960
H	3.198494	-0.205727	1.927099

Table S3A: MP2/aug-cc-pVDZ-PP vibrational frequencies, in cm^{-1} , infrared intensities, in km mol^{-1} , and Raman intensities, in $\text{\AA}^4 \text{amu}^{-1}$, for the halogen bonded complex between fluoroiodomethane and dimethyl ether 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
CHF₂I							
$\nu_1 (\text{A}')$	3144.9	8.6	115.8	3139.9	-5.0	12.5	135.3
$\nu_2 (\text{A}')$	1469.3	0.4	6.4	1468.3	-1.0	0.3	7.0
$\nu_3 (\text{A}')$	1307.7	54.8	6.8	1307.0	-0.7	62.9	7.1
$\nu_4 (\text{A}')$	1042.6	191.1	3.1	1032.1	-10.5	189.0	3.2
$\nu_5 (\text{A}')$	591.6	38.5	25.5	594.5	2.9	24.6	38.9
$\nu_6 (\text{A}')$	271.2	0.8	4.3	274.8	3.6	5.3	5.8
$\nu_7 (\text{A}'')$	3243.7	0.5	51.7	3235.7	-8.0	1.4	58.2
$\nu_8 (\text{A}'')$	1233.0	2.3	1.7	1232.2	-0.8	2.2	1.7
$\nu_9 (\text{A}'')$	874.7	0.7	0.4	871.2	-3.5	0.2	0.6
DME							
$\nu_1 (\text{A}_1)$	3188.7	20.1	87.6	3190.7	2.0	17.7	62.7
$\nu_2 (\text{A}_1)$	3024.8	58.6	320.3	3030.4	5.6	57.2	312.4
$\nu_3 (\text{A}_1)$	1505.9	2.9	5.6	1503.5	-2.4	7.1	5.7
$\nu_4 (\text{A}_1)$	1473.5	0.0	2.2	1472.6	-0.9	0.4	3.3
$\nu_5 (\text{A}_1)$	1261.1	6.6	0.5	1260.7	-0.4	6.5	0.4
$\nu_6 (\text{A}_1)$	942.4	34.7	9.8	932.7	-9.7	51.4	11.2
$\nu_7 (\text{A}_1)$	416.8	2.3	1.0	416.3	-0.5	2.8	0.9
$\nu_8 (\text{A}_2)$	3096.2	0.0	14.7	3106.8	10.6	0.4	14.4
$\nu_9 (\text{A}_2)$	1474.8	0.0	11.4	1472.9	-1.9	0.6	9.1
$\nu_{10} (\text{A}_2)$	1157.2	0.0	1.5	1155.9	-1.3	0.03	1.6
$\nu_{11} (\text{A}_2)$	195.2	0.0	0.2	191.9	-3.3	0.003	0.1
$\nu_{12} (\text{B}_1)$	3089.5	107.8	94.2	3100.6	11.1	99.4	117.2
$\nu_{13} (\text{B}_1)$	1489.2	13.0	0.0	1488.3	-0.9	17.3	0.1
$\nu_{14} (\text{B}_1)$	1187.2	7.2	0.0	1187.6	0.5	5.5	0.2
$\nu_{15} (\text{B}_1)$	260.2	5.1	0.0	264.6	4.3	9.7	0.08
$\nu_{16} (\text{B}_2)$	3187.3	24.6	59.2	3189.3	2.0	15.2	41.1
$\nu_{17} (\text{B}_2)$	3018.4	55.2	0.6	3025.0	6.7	43.3	3.9
$\nu_{18} (\text{B}_2)$	1490.1	10.3	1.0	1487.8	-2.2	8.1	0.6
$\nu_{19} (\text{B}_2)$	1441.5	2.5	1.3	1440.8	-0.7	0.5	1.4
$\nu_{20} (\text{B}_2)$	1191.9	98.1	0.7	1183.9	-8.0	77.3	0.4
$\nu_{21} (\text{B}_2)$	1113.8	35.0	1.6	1108.5	-5.3	38.7	2.0

Van der Waals vibrations: 6.6 cm⁻¹, 4.5 km mol⁻¹, 0.4 Å⁴ amu⁻¹, 30.1 cm⁻¹, 3.4 km mol⁻¹, 0.3 Å⁴ amu⁻¹, 44.9 cm⁻¹, 3.8 km mol⁻¹, 1.7 Å⁴ amu⁻¹, 63.7 cm⁻¹, 0.1 km mol⁻¹, 0.5 Å⁴ amu⁻¹, 82.6 cm⁻¹, 0.7 km mol⁻¹, 0.1 Å⁴ amu⁻¹, 95.3 cm⁻¹, 12.4 km mol⁻¹, 0.5 Å⁴ amu⁻¹.

Table S3B: MP2/aug-cc-pVDZ-PP vibrational frequencies, in cm^{-1} , infrared intensities, in km mol^{-1} , and Raman intensities, in $\text{\AA}^4 \text{amu}^{-1}$, for the halogen bonded complex between fluoroiodomethane and dimethyl ether- d_6 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
CHF₂I							
$\nu_1 (\text{A}')$	3144.9	8.6	115.8	3139.9	-5.0	12.6	134.9
$\nu_2 (\text{A}')$	1469.3	0.4	6.4	1468.3	-1.0	0.3	6.9
$\nu_3 (\text{A}')$	1307.7	54.8	6.8	1307.0	-0.7	62.3	7.3
$\nu_4 (\text{A}')$	1042.6	191.1	3.1	1031.8	-10.8	189.2	2.9
$\nu_5 (\text{A}')$	591.6	38.5	25.5	594.5	2.9	24.6	38.9
$\nu_6 (\text{A}')$	271.2	0.8	4.3	274.4	3.2	3.2	5.8
$\nu_7 (\text{A}'')$	3243.7	0.5	51.7	3235.7	-8.0	1.4	58.3
$\nu_8 (\text{A}'')$	1233.0	2.3	1.7	1232.2	-0.8	2.2	1.7
$\nu_9 (\text{A}'')$	874.7	0.7	0.4	871.0	-3.7	0.2	1.0
DME-d_6							
$\nu_1 (\text{A}_1)$	2364.1	17.0	37.1	2366.3	2.2	14.3	29.0
$\nu_2 (\text{A}_1)$	2171.1	32.1	166.2	2174.4	3.3	33.0	157.3
$\nu_3 (\text{A}_1)$	1153.5	5.3	2.6	1148.3	-5.2	9.0	5.1
$\nu_4 (\text{A}_1)$	1085.9	0.09	2.5	1083.9	-1.9	1.2	2.3
$\nu_5 (\text{A}_1)$	1058.5	17.5	1.8	1057.8	-0.7	23.2	1.9
$\nu_6 (\text{A}_1)$	834.8	16.9	7.7	829.4	-5.3	25.8	8.2
$\nu_7 (\text{A}_1)$	351.5	1.5	0.7	351.6	0.1	2.0	0.6
$\nu_8 (\text{A}_2)$	2297.2	0.0	7.5	2305.5	8.2	0.2	7.3
$\nu_9 (\text{A}_2)$	1065.8	0.0	4.2	1064.2	-1.6	0.4	3.3
$\nu_{10} (\text{A}_2)$	877.6	0.0	2.2	876.8	-0.8	0.0	1.6
$\nu_{11} (\text{A}_2)$	139.5	0.0	0.1	137.4	-2.1	0.0009	0.09
$\nu_{12} (\text{B}_1)$	2290.4	65.1	51.2	2299.1	8.8	58.9	63.1
$\nu_{13} (\text{B}_1)$	1077.4	4.3	0.003	1076.4	-1.0	5.6	0.08
$\nu_{14} (\text{B}_1)$	937.8	9.9	0.1	938.6	0.8	11.8	0.2
$\nu_{15} (\text{B}_1)$	200.5	4.6	0.0	208.7	8.2	12.3	0.2
$\nu_{16} (\text{B}_2)$	2360.7	10.6	31.7	2362.9	2.2	6.4	22.6
$\nu_{17} (\text{B}_2)$	2164.0	44.9	0.03	2168.2	4.3	35.2	1.2
$\nu_{18} (\text{B}_2)$	1170.3	134.3	0.9	1158.6	-11.8	113.7	0.9
$\nu_{19} (\text{B}_2)$	1077.4	0.5	0.2	1075.6	-1.8	0.4	0.07
$\nu_{20} (\text{B}_2)$	1066.1	1.6	1.1	1065.4	-0.7	3.1	1.0
$\nu_{21} (\text{B}_2)$	860.9	0.08	0.9	859.6	-1.3	0.2	1.0

Van der Waals vibrations: 6.3 cm^{-1} , 4.1 km mol^{-1} , $0.3 \text{ \AA}^4 \text{amu}^{-1}$, 28.2 cm^{-1} , 3.1 km mol^{-1} , $0.3 \text{ \AA}^4 \text{amu}^{-1}$, 41.8 cm^{-1} , 3.5 km mol^{-1} , $1.5 \text{ \AA}^4 \text{amu}^{-1}$, 59.2 cm^{-1} , 0.07 km mol^{-1} , $0.5 \text{ \AA}^4 \text{amu}^{-1}$, 77.3 cm^{-1} , 1.1 km mol^{-1} , $0.2 \text{ \AA}^4 \text{amu}^{-1}$, 82.9 cm^{-1} , 7.4 km mol^{-1} , $0.4 \text{ \AA}^4 \text{amu}^{-1}$.

Table S4A: MP2/aug-cc-pVDZ-PP vibrational frequencies, in cm^{-1} , infrared intensities, in km mol^{-1} , and Raman intensities, in $\text{\AA}^4 \text{amu}^{-1}$, for the hydrogen bonded complex between fluoroiodomethane and dimethyl ether and both monomers, as well as the complexation shift $\Delta\nu$.

	Monomer			Hydrogen bonded complex			
	Frequency	IR intensity	Raman intensity	Frequency	$\Delta\nu$	IR intensity	Raman intensity
CHF₂I							
$\nu_1 (\text{A}')$	3144.9	8.6	115.8	3141.9	-3.0	18.6	139.4
$\nu_2 (\text{A}')$	1469.3	0.4	6.4	1468.5	-0.8	2.6	5.9
$\nu_3 (\text{A}')$	1307.7	54.8	6.8	1315.7	8.0	54.5	8.0
$\nu_4 (\text{A}')$	1042.6	191.1	3.1	1032.0	-10.7	166.1	2.8
$\nu_5 (\text{A}')$	591.6	38.5	25.5	588.1	-3.5	37.6	22.5
$\nu_6 (\text{A}')$	271.2	0.8	4.3	269.8	-1.4	0.7	3.8
$\nu_7 (\text{A}'')$	3243.7	0.5	51.7	3250.8	7.1	7.8	49.5
$\nu_8 (\text{A}'')$	1233.0	2.3	1.7	1246.5	13.5	4.1	1.7
$\nu_9 (\text{A}'')$	874.7	0.7	0.4	889.2	14.4	3.9	0.6
DME							
$\nu_1 (\text{A}_1)$	3188.7	20.1	87.6	3189.9	1.2	13.6	51.4
$\nu_2 (\text{A}_1)$	3024.8	58.6	320.3	3030.9	6.1	49.3	313.8
$\nu_3 (\text{A}_1)$	1505.9	2.9	5.6	1504.3	-1.6	9.1	5.7
$\nu_4 (\text{A}_1)$	1473.5	0.0	2.2	1476.9	3.4	0.9	2.8
$\nu_5 (\text{A}_1)$	1261.1	6.6	0.5	1262.7	1.6	5.4	0.4
$\nu_6 (\text{A}_1)$	942.4	34.7	9.8	934.8	-7.6	34.3	9.5
$\nu_7 (\text{A}_1)$	416.8	2.3	1.0	417.8	1.0	2.3	0.8
$\nu_8 (\text{A}_2)$	3096.2	0.0	14.7	3107.8	11.6	1.1	12.1
$\nu_9 (\text{A}_2)$	1474.8	0.0	11.4	1473.3	-1.6	0.5	9.4
$\nu_{10} (\text{A}_2)$	1157.2	0.0	1.5	1156.5	-0.8	0.0004	1.9
$\nu_{11} (\text{A}_2)$	195.2	0.0	0.2	191.4	-3.8	0.01	0.07
$\nu_{12} (\text{B}_1)$	3089.5	107.8	94.2	3101.4	11.9	100.2	81.6
$\nu_{13} (\text{B}_1)$	1489.2	13.0	0.0	1488.2	-1.1	15.7	0.4
$\nu_{14} (\text{B}_1)$	1187.2	7.2	0.0	1187.6	0.5	5.6	0.4
$\nu_{15} (\text{B}_1)$	260.2	5.1	0.0	262.8	2.6	10.4	0.05
$\nu_{16} (\text{B}_2)$	3187.3	24.6	59.2	3186.7	-0.6	18.3	53.4
$\nu_{17} (\text{B}_2)$	3018.4	55.2	0.6	3025.6	7.2	43.8	5.1
$\nu_{18} (\text{B}_2)$	1490.1	10.3	1.0	1488.7	-1.4	6.9	0.5
$\nu_{19} (\text{B}_2)$	1441.5	2.5	1.3	1441.9	0.4	0.9	1.0
$\nu_{20} (\text{B}_2)$	1191.9	98.1	0.7	1184.3	-7.6	78.4	0.5
$\nu_{21} (\text{B}_2)$	1113.8	35.0	1.6	1110.7	-3.1	40.5	1.7

Van der Waals vibrations: 24.6 cm^{-1} , 1.4 km mol^{-1} , $0.6 \text{ \AA}^4 \text{amu}^{-1}$, 33.3 cm^{-1} , 0.03 km mol^{-1} , $0.5 \text{ \AA}^4 \text{amu}^{-1}$, 46.4 cm^{-1} , 2.4 km mol^{-1} , $0.2 \text{ \AA}^4 \text{amu}^{-1}$, 58.5 cm^{-1} , 0.5 km mol^{-1} , $0.3 \text{ \AA}^4 \text{amu}^{-1}$, 73.9 cm^{-1} , 5.4 km mol^{-1} , $0.1 \text{ \AA}^4 \text{amu}^{-1}$, 147.3 cm^{-1} , 18.1 km mol^{-1} , $1.2 \text{ \AA}^4 \text{amu}^{-1}$.

Table S4B: MP2/aug-cc-pVDZ-PP vibrational frequencies, in cm^{-1} , infrared intensities, in km mol^{-1} , and Raman intensities, in $\text{\AA}^4 \text{amu}^{-1}$, for the hydrogen bonded complex between fluoroiodomethane and dimethyl ether- d_6 and both monomers, as well as the complexation shift $\Delta\nu$.

	Monomer			Hydrogen bonded complex			
	Frequency	IR intensity	Raman intensity	Frequency	$\Delta\nu$	IR intensity	Raman intensity
CHF₂I							
$\nu_1 (\text{A}')$	3144.9	8.6	115.8	3141.9	-3.0	19.1	135.0
$\nu_2 (\text{A}')$	1469.3	0.4	6.4	1470.8	1.5	4.5	6.0
$\nu_3 (\text{A}')$	1307.7	54.8	6.8	1315.9	8.2	53.3	7.8
$\nu_4 (\text{A}')$	1042.6	191.1	3.1	1031.5	-11.1	167.9	2.8
$\nu_5 (\text{A}')$	591.6	38.5	25.5	588.1	-3.5	37.5	22.5
$\nu_6 (\text{A}')$	271.2	0.8	4.3	269.8	-1.4	0.7	3.8
$\nu_7 (\text{A}'')$	3243.7	0.5	51.7	3250.8	7.1	7.8	49.3
$\nu_8 (\text{A}'')$	1233.0	2.3	1.7	1246.5	13.5	3.9	1.6
$\nu_9 (\text{A}'')$	874.7	0.7	0.4	889.3	14.5	2.9	0.5
DME-d_6							
$\nu_1 (\text{A}_1)$	2364.1	17.0	37.1	2365.4	1.3	11.7	27.4
$\nu_2 (\text{A}_1)$	2171.1	32.1	166.2	2174.8	3.7	26.6	160.4
$\nu_3 (\text{A}_1)$	1153.5	5.3	2.6	1149.4	-4.1	5.2	2.8
$\nu_4 (\text{A}_1)$	1085.9	0.09	2.5	1084.7	-1.2	1.4	2.4
$\nu_5 (\text{A}_1)$	1058.5	17.5	1.8	1059.8	1.3	19.6	1.6
$\nu_6 (\text{A}_1)$	834.8	16.9	7.7	830.8	-3.9	18.1	7.4
$\nu_7 (\text{A}_1)$	351.5	1.5	0.7	353.0	1.4	1.7	0.6
$\nu_8 (\text{A}_2)$	2297.2	0.0	7.5	2306.1	8.9	0.5	6.2
$\nu_9 (\text{A}_2)$	1065.8	0.0	4.2	1064.2	-1.6	1.2	3.0
$\nu_{10} (\text{A}_2)$	877.6	0.0	2.2	876.8	-0.8	0.02	2.3
$\nu_{11} (\text{A}_2)$	139.5	0.0	0.1	137.4	-2.2	0.002	0.06
$\nu_{12} (\text{B}_1)$	2290.4	65.1	51.2	2299.7	9.3	60.9	45.6
$\nu_{13} (\text{B}_1)$	1077.4	4.3	0.003	1076.3	-1.0	4.6	0.1
$\nu_{14} (\text{B}_1)$	937.8	9.9	0.1	937.8	0.0	9.4	0.4
$\nu_{15} (\text{B}_1)$	200.5	4.6	0.0	207.6	7.1	12.9	0.07
$\nu_{16} (\text{B}_2)$	2360.7	10.6	31.7	2361.4	0.7	8.4	24.2
$\nu_{17} (\text{B}_2)$	2164.0	44.9	0.03	2168.6	4.6	35.2	1.8
$\nu_{18} (\text{B}_2)$	1170.3	134.3	0.9	1159.2	-11.2	115.5	1.0
$\nu_{19} (\text{B}_2)$	1077.4	0.5	0.2	1076.6	-0.8	0.5	0.09
$\nu_{20} (\text{B}_2)$	1066.1	1.6	1.1	1066.4	0.3	1.4	1.6
$\nu_{21} (\text{B}_2)$	860.9	0.08	0.9	861.1	0.3	0.2	0.8

Van der Waals vibrations: 22.3 cm^{-1} , 1.2 km mol^{-1} , $0.5 \text{ \AA}^4 \text{amu}^{-1}$, 31.9 cm^{-1} , $0.004 \text{ km mol}^{-1}$, $0.4 \text{ \AA}^4 \text{amu}^{-1}$, 44.5 cm^{-1} , 2.3 km mol^{-1} , $0.1 \text{ \AA}^4 \text{amu}^{-1}$, 52.8 cm^{-1} , 0.9 km mol^{-1} , $0.3 \text{ \AA}^4 \text{amu}^{-1}$, 60.4 cm^{-1} , 3.2 km mol^{-1} , $0.08 \text{ \AA}^4 \text{amu}^{-1}$, 142.8 cm^{-1} , 13.8 km mol^{-1} , $1.2 \text{ \AA}^4 \text{amu}^{-1}$.

Table S5A: MP2/aug-cc-pVDZ-PP vibrational frequencies, in cm^{-1} , infrared intensities, in km mol^{-1} , and Raman intensities, in $\text{\AA}^4 \text{amu}^{-1}$, for the halogen bonded complex between fluoroiodomethane and trimethylamine 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
CHF₂I							
$\nu_1 (\text{A}')$	3144.9	8.6	115.8	3133.2	-11.7	17.6	163.8
$\nu_2 (\text{A}')$	1469.3	0.4	6.4	1466.5	-2.8	0.3	12.3
$\nu_3 (\text{A}')$	1307.7	54.8	6.8	1301.1	-6.6	61.9	11.4
$\nu_4 (\text{A}')$	1042.6	191.1	3.1	1026.0	-16.6	197.8	3.2
$\nu_5 (\text{A}')$	591.6	38.5	25.5	586.3	-5.3	10.5	88.0
$\nu_6 (\text{A}')$	271.2	0.8	4.3	272.6	1.3	5.6	12.6
$\nu_7 (\text{A}'')$	3243.7	0.5	51.7	3227.7	-16.0	2.7	66.5
$\nu_8 (\text{A}'')$	1233.0	2.3	1.7	1230.3	-2.7	1.8	1.7
$\nu_9 (\text{A}'')$	874.7	0.7	0.4	860.5	-14.3	0.2	0.8
TMA							
$\nu_1 (\text{A}_1)$	3111.8	42.4	235.1	3115.4	3.6	28.9	109.9
$\nu_2 (\text{A}_1)$	2962.3	167.2	390.2	2979.5	17.2	222.5	508.2
$\nu_3 (\text{A}_1)$	1499.0	23.4	0.4	1498.7	-0.4	26.2	1.3
$\nu_4 (\text{A}_1)$	1464.0	1.6	2.3	1463.7	-0.3	0.1	16.5
$\nu_5 (\text{A}_1)$	1204.0	24.9	5.6	1210.7	6.8	20.3	20.9
$\nu_6 (\text{A}_1)$	853.0	22.9	12.0	847.7	-5.3	68.4	11.7
$\nu_7 (\text{A}_1)$	383.8	7.6	1.1	397.0	13.3	30.2	1.3
$\nu_8 (\text{A}_2)$	3163.7	0.0	0.0	3165.1	1.5	0.2	0.4
$\nu_9 (\text{A}_2)$	1477.7	0.0	0.0	1476.1	-1.7	0.001	0.003
$\nu_{10} (\text{A}_2)$	1057.3	0.0	0.0	1059.0	1.7	0.0003	0.0004
$\nu_{11} (\text{A}_2)$	243.9	0.0	0.0	236.4	-7.5	0.0	0.0
$\nu_{12} (\text{E})$	3166.8	34.6	87.1	3168.3	1.5	23.7	58.1
$\nu_{13} (\text{E})$	3111.1	26.1	27.8	3114.5	3.5	18.8	50.7
$\nu_{14} (\text{E})$	2955.2	44.4	18.3	2974.2	19.0	39.0	34.6
$\nu_{15} (\text{E})$	1500.8	9.8	5.5	1500.4	-0.4	13.8	5.9
$\nu_{16} (\text{E})$	1475.1	5.7	8.8	1473.5	-1.5	1.9	7.7
$\nu_{17} (\text{E})$	1421.1	0.7	1.6	1421.3	0.3	0.003	1.7
$\nu_{18} (\text{E})$	1303.4	14.9	1.7	1302.7	-0.7	14.8	1.7
$\nu_{19} (\text{E})$	1115.9	9.1	0.4	1114.1	-1.8	7.6	0.7
$\nu_{20} (\text{E})$	1066.2	13.6	2.7	1063.9	-2.3	12.7	2.7
$\nu_{21} (\text{E})$	423.6	0.006	0.7	421.7	-2.0	0.01	0.7
$\nu_{22} (\text{E})$	290.9	0.4	0.6	283.9	-7.0	0.4	0.8

Van der Waals vibrations: 4.1 cm^{-1} , 2.3 km mol^{-1} , 0.1 $\text{\AA}^4 \text{amu}^{-1}$, 34.8 cm^{-1} , 0.6 km mol^{-1} , 0.4 $\text{\AA}^4 \text{amu}^{-1}$, 44.5 cm^{-1} , 2.8 km mol^{-1} , 1.4 $\text{\AA}^4 \text{amu}^{-1}$, 75.3 cm^{-1} , 4.1 km mol^{-1} , 1.7 $\text{\AA}^4 \text{amu}^{-1}$, 88.7 cm^{-1} , 0.9 km mol^{-1} , 0.2 $\text{\AA}^4 \text{amu}^{-1}$, 102.4 cm^{-1} , 2.0 km mol^{-1} , 0.3 $\text{\AA}^4 \text{amu}^{-1}$.

Table S5B: MP2/aug-cc-pVDZ-PP vibrational frequencies, in cm^{-1} , infrared intensities, in km mol^{-1} , and Raman intensities, in $\text{\AA}^4 \text{amu}^{-1}$, for the halogen bonded complex between fluoroiodomethane and trimethylamine- 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
CHF₂I							
$\nu_1 (\text{A}')$	3144.9	8.6	115.8	3133.2	-11.7	17.5	161.8
$\nu_2 (\text{A}')$	1469.3	0.4	6.4	1466.4	-3.0	0.4	8.3
$\nu_3 (\text{A}')$	1307.7	54.8	6.8	1301.3	-6.4	66.2	13.0
$\nu_4 (\text{A}')$	1042.6	191.1	3.1	1024.1	-18.5	213.1	9.7
$\nu_5 (\text{A}')$	591.6	38.5	25.5	586.2	-5.4	10.3	88.1
$\nu_6 (\text{A}')$	271.2	0.8	4.3	272.5	1.3	5.6	12.8
$\nu_7 (\text{A}'')$	3243.7	0.5	51.7	3227.7	-16.0	2.7	66.5
$\nu_8 (\text{A}'')$	1233.0	2.3	1.7	1230.3	-2.7	1.5	1.6
$\nu_9 (\text{A}'')$	874.7	0.7	0.4	860.6	-14.2	0.1	0.7
TMA-d_9							
$\nu_1 (\text{A}_1)$	2286.9	51.7	81.2	2292.7	5.8	46.6	90.7
$\nu_2 (\text{A}_1)$	2142.3	72.7	232.7	2152.1	9.9	100.3	260.9
$\nu_3 (\text{A}_1)$	1151.7	0.2	5.9	1148.7	-3.1	5.8	17.1
$\nu_4 (\text{A}_1)$	1079.2	12.6	0.2	1079.2	0.0	18.4	0.5
$\nu_5 (\text{A}_1)$	1018.9	33.5	3.4	1028.8	9.9	31.9	4.6
$\nu_6 (\text{A}_1)$	756.9	12.4	9.6	753.3	-3.6	38.2	9.3
$\nu_7 (\text{A}_1)$	323.0	4.6	0.8	335.5	12.6	22.1	1.4
$\nu_8 (\text{A}_2)$	2345.4	0.0	0.0	2346.6	1.1	0.04	0.1
$\nu_9 (\text{A}_2)$	1067.7	0.0	0.0	1065.9	-1.8	0.0001	0.0002
$\nu_{10} (\text{A}_2)$	801.3	0.0	0.0	802.9	1.6	0.0	0.0001
$\nu_{11} (\text{A}_2)$	173.1	0.0	0.0	167.7	-5.4	0.0	0.0
$\nu_{12} (\text{E})$	2349.0	17.4	46.2	2350.2	1.3	11.8	30.8
$\nu_{13} (\text{E})$	2287.5	8.1	21.2	2293.7	6.2	5.2	20.4
$\nu_{14} (\text{E})$	2135.6	36.1	4.2	2146.5	10.9	29.7	10.9
$\nu_{15} (\text{E})$	1252.4	33.4	1.0	1249.6	-2.7	29.5	0.8
$\nu_{16} (\text{E})$	1078.6	2.1	2.4	1076.9	-1.7	3.6	2.5
$\nu_{17} (\text{E})$	1073.1	0.2	0.4	1073.5	0.4	0.3	0.4
$\nu_{18} (\text{E})$	1063.4	1.6	3.7	1062.5	-1.0	0.3	3.1
$\nu_{19} (\text{E})$	886.2	7.4	2.6	886.3	0.1	6.6	2.4
$\nu_{20} (\text{E})$	839.0	0.03	1.0	837.2	-1.8	0.005	1.4
$\nu_{21} (\text{E})$	352.0	0.007	0.5	350.9	-1.1	0.02	0.6
$\nu_{22} (\text{E})$	210.6	0.2	0.3	205.8	-4.7	0.2	0.4

Van der Waals vibrations: 4.0 cm^{-1} , 2.4 km mol^{-1} , $0.09 \text{ \AA}^4 \text{amu}^{-1}$, 32.5 cm^{-1} , 0.5 km mol^{-1} , $0.5 \text{ \AA}^4 \text{amu}^{-1}$, 40.6 cm^{-1} , 2.3 km mol^{-1} , $1.3 \text{ \AA}^4 \text{amu}^{-1}$, 71.0 cm^{-1} , 3.3 km mol^{-1} , $1.4 \text{ \AA}^4 \text{amu}^{-1}$, 81.6 cm^{-1} , 1.2 km mol^{-1}

¹,
0.2 Å⁴ amu⁻¹, 97.0 cm⁻¹, 2.4 km mol⁻¹, 0.5 Å⁴ amu⁻¹.

Table S6A: MP2/aug-cc-pVDZ-PP vibrational frequencies, in cm^{-1} , infrared intensities, in km mol^{-1} , and Raman intensities, in $\text{\AA}^4 \text{amu}^{-1}$, for the hydrogen bonded complex between fluoroiodomethane and trimethylamine and both monomers, as well as the complexation shift $\Delta\nu$.

	Monomer			Hydrogen bonded complex			
	Frequency	IR intensity	Raman intensity	Frequency	$\Delta\nu$	IR intensity	Raman intensity
CHF₂I							
$\nu_1 (\text{A}')$	3144.9	8.6	115.8	3103.9	-41.0	60.8	235.6
$\nu_2 (\text{A}')$	1469.3	0.4	6.4	1482.7	13.4	3.9	5.5
$\nu_3 (\text{A}')$	1307.7	54.8	6.8	1331.7	24.0	65.6	10.0
$\nu_4 (\text{A}')$	1042.6	191.1	3.1	1029.5	-13.1	165.2	3.0
$\nu_5 (\text{A}')$	591.6	38.5	25.5	585.7	-5.9	37.4	22.4
$\nu_6 (\text{A}')$	271.2	0.8	4.3	268.9	-2.3	0.6	3.8
$\nu_7 (\text{A}'')$	3243.7	0.5	51.7	3226.7	-17.1	23.0	74.3
$\nu_8 (\text{A}'')$	1233.0	2.3	1.7	1251.3	18.2	5.1	1.5
$\nu_9 (\text{A}'')$	874.7	0.7	0.4	907.1	32.3	1.9	0.2
TMA							
$\nu_1 (\text{A}_1)$	3111.8	42.4	235.1	3114.0	2.2	35.1	125.4
$\nu_2 (\text{A}_1)$	2962.3	167.2	390.2	2973.8	11.5	175.6	419.4
$\nu_3 (\text{A}_1)$	1499.0	23.4	0.4	1500.0	1.0	23.6	1.1
$\nu_4 (\text{A}_1)$	1464.0	1.6	2.3	1464.1	0.09	1.3	5.0
$\nu_5 (\text{A}_1)$	1204.0	24.9	5.6	1210.2	6.3	23.3	5.3
$\nu_6 (\text{A}_1)$	853.0	22.9	12.0	849.3	-3.7	33.3	11.2
$\nu_7 (\text{A}_1)$	383.8	7.6	1.1	397.5	13.7	14.8	0.9
$\nu_8 (\text{A}_2)$	3163.7	0.0	0.0	3163.7	0.1	4.3	12.7
$\nu_9 (\text{A}_2)$	1477.7	0.0	0.0	1477.8	0.0	0.06	0.1
$\nu_{10} (\text{A}_2)$	1057.3	0.0	0.0	1057.7	0.4	0.3	0.06
$\nu_{11} (\text{A}_2)$	243.9	0.0	0.0	241.2	-2.7	0.007	0.04
$\nu_{12} (\text{E})$	3166.8	34.6	87.1	3167.3	0.4	24.4	64.0
$\nu_{13} (\text{E})$	3111.1	26.1	27.8	3112.5	1.4	21.2	49.9
$\nu_{14} (\text{E})$	2955.2	44.4	18.3	2968.2	13.0	42.3	30.0
$\nu_{15} (\text{E})$	1500.8	9.8	5.5	1501.5	0.8	13.1	6.2
$\nu_{16} (\text{E})$	1475.1	5.7	8.8	1475.0	-0.1	4.2	7.9
$\nu_{17} (\text{E})$	1421.1	0.7	1.6	1421.8	0.7	0.4	1.6
$\nu_{18} (\text{E})$	1303.4	14.9	1.7	1299.1	-4.3	13.9	1.4
$\nu_{19} (\text{E})$	1115.9	9.1	0.4	1115.6	-0.4	7.8	0.6
$\nu_{20} (\text{E})$	1066.2	13.6	2.7	1062.8	-3.4	14.6	2.5
$\nu_{21} (\text{E})$	423.6	0.006	0.7	421.8	-1.8	0.1	0.6
$\nu_{22} (\text{E})$	290.9	0.4	0.6	291.2	0.3	0.3	0.4

Van der Waals vibrations: 20.1 cm^{-1} , 0.4 km mol^{-1} , 0.2 $\text{\AA}^4 \text{amu}^{-1}$, 30.1 cm^{-1} , 0.2 km mol^{-1} , 0.4 $\text{\AA}^4 \text{amu}^{-1}$, 40.4 cm^{-1} , 0.4 km mol^{-1} , 0.2 $\text{\AA}^4 \text{amu}^{-1}$, 52.4 cm^{-1} , 2.5 km mol^{-1} , 0.2 $\text{\AA}^4 \text{amu}^{-1}$, 64.8 cm^{-1} , 0.2 km mol^{-1}

¹,
0.2 Å⁴ amu⁻¹, 145.9 cm⁻¹, 17.6 km mol⁻¹, 2.4 Å⁴ amu⁻¹.

Table S6B: MP2/aug-cc-pVDZ-PP vibrational frequencies, in cm^{-1} , infrared intensities, in km mol^{-1} , and Raman intensities, in $\text{\AA}^4 \text{amu}^{-1}$, for the hydrogen bonded complex between fluoroiodomethane and trimethylamine- d_9 and both monomers, as well as the complexation shift $\Delta\nu$.

	Monomer			Hydrogen bonded complex			
	Frequency	IR intensity	Raman intensity	Frequency	$\Delta\nu$	IR intensity	Raman intensity
CHF₂I							
$\nu_1 (\text{A}')$	3144.9	8.6	115.8	3103.8	-41.1	68.6	221.9
$\nu_2 (\text{A}')$	1469.3	0.4	6.4	1482.0	12.6	6.2	5.8
$\nu_3 (\text{A}')$	1307.7	54.8	6.8	1331.9	24.2	65.8	9.6
$\nu_4 (\text{A}')$	1042.6	191.1	3.1	1029.1	-13.5	165.4	2.7
$\nu_5 (\text{A}')$	591.6	38.5	25.5	585.7	-5.9	37.4	22.5
$\nu_6 (\text{A}')$	271.2	0.8	4.3	268.9	-2.3	0.6	3.8
$\nu_7 (\text{A}'')$	3243.7	0.5	51.7	3226.6	-17.1	23.3	73.6
$\nu_8 (\text{A}'')$	1233.0	2.3	1.7	1251.6	18.6	8.6	1.8
$\nu_9 (\text{A}'')$	874.7	0.7	0.4	907.2	32.5	2.0	0.2
TMA-d_9							
$\nu_1 (\text{A}_1)$	2286.9	51.7	81.2	2289.6	2.6	30.0	49.7
$\nu_2 (\text{A}_1)$	2142.3	72.7	232.7	2148.8	6.5	75.6	250.5
$\nu_3 (\text{A}_1)$	1151.7	0.2	5.9	1149.5	-2.3	0.7	6.8
$\nu_4 (\text{A}_1)$	1079.2	12.6	0.2	1080.3	1.1	16.4	0.4
$\nu_5 (\text{A}_1)$	1018.9	33.5	3.4	1026.4	7.5	37.4	3.4
$\nu_6 (\text{A}_1)$	756.9	12.4	9.6	754.6	-2.3	19.2	8.9
$\nu_7 (\text{A}_1)$	323.0	4.6	0.8	335.3	12.3	10.4	0.6
$\nu_8 (\text{A}_2)$	2345.4	0.0	0.0	2345.6	0.2	0.9	3.5
$\nu_9 (\text{A}_2)$	1067.7	0.0	0.0	1067.0	-0.7	0.02	0.01
$\nu_{10} (\text{A}_2)$	801.3	0.0	0.0	801.8	0.5	0.002	0.01
$\nu_{11} (\text{A}_2)$	173.1	0.0	0.0	171.3	-1.8	0.006	0.02
$\nu_{12} (\text{E})$	2349.0	17.4	46.2	2349.4	0.5	13.0	35.4
$\nu_{13} (\text{E})$	2287.5	8.1	21.2	2291.7	4.2	15.5	26.3
$\nu_{14} (\text{E})$	2135.6	36.1	4.2	2143.1	7.6	30.9	7.5
$\nu_{15} (\text{E})$	1252.4	33.4	1.0	1245.1	-7.3	29.2	0.9
$\nu_{16} (\text{E})$	1078.6	2.1	2.4	1077.9	-0.6	1.7	2.8
$\nu_{17} (\text{E})$	1073.1	0.2	0.4	1073.2	0.1	0.2	0.5
$\nu_{18} (\text{E})$	1063.4	1.6	3.7	1063.8	0.4	1.8	3.4
$\nu_{19} (\text{E})$	886.2	7.4	2.6	885.8	-0.4	6.9	2.4
$\nu_{20} (\text{E})$	839.0	0.03	1.0	838.3	-0.7	0.002	1.1
$\nu_{21} (\text{E})$	352.0	0.007	0.5	351.0	-1.0	0.1	0.4
$\nu_{22} (\text{E})$	210.6	0.2	0.3	210.8	0.3	0.2	0.2

Van der Waals vibrations: 18.4 cm^{-1} , 0.4 km mol^{-1} , $0.2 \text{ \AA}^4 \text{amu}^{-1}$, 28.8 cm^{-1} , 0.2 km mol^{-1} , $0.3 \text{ \AA}^4 \text{amu}^{-1}$, 36.6 cm^{-1} , 0.2 km mol^{-1} , $0.2 \text{ \AA}^4 \text{amu}^{-1}$, 47.1 cm^{-1} , 2.1 km mol^{-1} , $0.1 \text{ \AA}^4 \text{amu}^{-1}$, 59.6 cm^{-1} , 0.3 km mol^{-1}

¹,
0.2 Å⁴ amu⁻¹, 144.1 cm⁻¹, 17.5 km mol⁻¹, 2.4 Å⁴ amu⁻¹.

Table S7: Experimental vibrational frequencies for the monomers and hydrogen bonded complex ($\nu_{\text{complex,HB}}$), as well as experimental complexation shifts ($\Delta\nu_{\text{exp,HB}}$) and MP2/aug-cc-pVDZ-PP calculated complexation shifts, in cm^{-1} , for the hydrogen bonded complex ($\Delta\nu_{\text{calc,HB}}$) and halogen bonded complex ($\Delta\nu_{\text{calc,XB}}$) of fluoroiodomethane (CH_2FI) with dimethyl ether- d_6 (DME-d_6) dissolved in LKr at 130 K.

Assignment	ν_{monomer}	$\nu_{\text{complex,HB}}$	$\Delta\nu_{\text{exp,HB}}$	$\Delta\nu_{\text{calc,HB}}$	$\Delta\nu_{\text{calc,XB}}$
CH_2FI					
ν_7	3043.0	3050.4	7.4	7.1	-8.0
ν_1	2981.5	2978.9	-2.6	-3.0	-5.0
	2975.7	2962.2	-13.5		
$2\nu_2$	2877.3	-		3.0	-2.0
$2\nu_4$	2070.0	^a		-22.3	-21.5
ν_2	1448.1	-		1.5	-1.0
ν_3	1268.0	1274.9	6.9	8.2	-0.7
ν_8	1219.8	-		13.5	-0.8
$2\nu_5$	1130.1	1123.8	-6.3	-7.0	5.8
ν_4	1043.2	1036.4	-6.8	-11.1	-10.8
ν_4 (^{13}C)	1020.6	1014.2	-6.4	-11.1	-10.8
ν_9	855.1	-			
ν_5	566.7	563.9	-2.8	-3.5	2.9
DME-d_6					
ν_1	2243.4	2245.4	2.0	1.3	2.2
ν_{16}	2243.4	2245.4	2.0	0.7	2.2
ν_{12}	2179.9	2186.5	6.6	9.3	8.8
ν_2	2054.4	2057.1	2.7	3.7	3.3
ν_{17}	2049.6	2053.0	3.4	4.6	4.3
ν_{18}	1153.5	1146.9	-6.6	-11.2	-11.8
ν_3	1144.7	-		-4.1	-5.2
ν_{13}	1060.9	1061.2	0.3	-1.0	-1.0
ν_{19}	1057.7	1058.3	0.6	-0.8	-1.8
ν_{20}	1057.7	1058.3	0.6	0.3	-0.7
ν_5	1050.6	1051.7	1.1	1.3	-0.7
ν_{14}	929.0	928.9	-0.1	0.0	0.8
ν_{21}	857.8	-		0.3	-1.3
ν_6	826.3	823.9	-2.4	-3.9	-5.3

^a modes could not be assigned due to overlap with DME-d_6 modes

Table S8: Experimental vibrational frequencies for the monomers and complexes, as well as experimental complexation shifts (Δv_{exp}) and MP2/aug-cc-pVDZ-PP calculated complexation shifts (Δv_{calc}), in cm^{-1} , for the halogen bonded complex (XB) and hydrogen bonded complex (HB) of fluoroiodomethane (CH_2FI) with trimethylamine (TMA) dissolved in LKr at 130 K.

Assignment	v_{monomer}	$v_{\text{complex,HB}}$	$\Delta v_{\text{exp,HB}}$	$\Delta v_{\text{calc,HB}}$	$v_{\text{complex,XB}}$	$\Delta v_{\text{exp,XB}}$	$\Delta v_{\text{calc,XB}}$
CH_2FI							
v_7	3043.0	-		-17.1	-		-16.0
v_1	2981.5	^a		-41.0	^a		-11.7
	2975.7	-		-41.0	-		-11.7
$2v_2$	2877.3	^a		26.9	^a		-5.6
$2v_4$	2070.0	2050.9	-19.1	-26.2	2035.8	-34.2	-33.3
v_2	1448.1	overlap		13.4	1446.3	-1.8	-2.8
v_3	1268.0	1280.8	12.8	24.0	1264.8	-3.2	-6.6
v_8	1219.8	-		18.2	1218.7	-1.1	-2.7
$2v_5$	1130.1	1127.1	-3.0	-11.8	1127.1	-3.0	-10.6
v_4	1043.2	1033.8	-9.4	-13.1	1026.4	-16.8	-16.6
v_4 (^{13}C)	1020.6	-		-13.1	1004.1	-16.5	-16.6
v_5	566.7	562.7	-4.0	-5.9	565.5	-1.2	-5.3
TMA							
v_{12}	2976.6	2979.2	2.6	0.4	2979.2	2.6	1.5
v_1	2944.2	2945.9	1.7	2.2	2945.9	1.7	3.6
v_{13}	2944.2	2945.9	1.7	1.4	2945.9	1.7	3.5
$2v_4$	2818.3	2825.6	7.3	0.2	2818.3	0.0	-0.7
v_2	2768.6	2776.6	8.0	11.5	2776.6	8.0	17.2
v_{14}	2768.6	2776.6	8.0	13.0	2776.6	8.0	19.0
$v_{20}^+ v_{21}$	1474.7	1472.7	-2.0	-5.2	1472.7	-2.0	-4.3
v_{15}	1467.5	1467.5	0.0	0.8	1467.5	0.0	-0.4
v_3	1454.7	1453.3	-1.4	1.0	1453.3	-1.4	-0.4
v_4	1438.8	1439.4	0.6	0.1	1439.4	0.6	-0.3
v_{16}	1438.8	1439.4	0.6	-0.1	1439.4	0.6	-1.5
v_{18}	1273.2	1269.5	-3.7	-4.3	1269.5	-3.7	-0.7
v_5	1184.1	1189.6	5.5	6.3	1190.9	6.8	6.8
v_{19}	1098.4	1098.6	0.2	-0.4	1098.6	0.2	-1.8
v_{20}	1041.4	1038.1	-3.3	-3.4	1038.1	-3.3	-2.3
v_6	827.9	825.1	-2.8	-3.7	825.1	-2.8	-5.3

^a modes could not be assigned due to overlap with TMA modes

Table S9: Overview of the different van 't Hoff plots constructed for the hydrogen bonded complex between fluoroiodomethane and dimethyl ether 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 ΔH° (LKr).

x_{CH_2FI}	x_{DME}	Integrated CH_2FI band (cm^{-1})	Integrated DME band (cm^{-1})	Integrated Complex band (cm^{-1})	ΔH° (LKr) ^a
1.1×10^{-3}	4.9×10^{-3}	1283 - 1253	2125 - 2068	1292 - 1258 ^c	-7.1(2)
1.9×10^{-3}	4.7×10^{-3}	1283 - 1253	2125 - 2068	1290 - 1260 ^c	-7.2(1)
3.8×10^{-4}	4.7×10^{-3}	1288 - 1252	2127 - 2065	1056 - 1020	-6.9(2)
3.8×10^{-4}	4.7×10^{-3} ^b	1291 - 1252	968 - 889 ^b	1293 - 1254 ^c	-7.0(1)

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

^b Measurement involving DME-d₆

^c Intensity of the additional band was integrated numerically and deducted from the intensity of the band assigned to the hydrogen bonded complex

Table S10: Overview of the different van 't Hoff plots constructed for the halogen bonded complex between fluoroiodomethane and trimethylamine-d₉ 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 ΔH° (LKr).

x_{CH_2FI}	x_{TMA-d_9}	Integrated CH_2FI band (cm^{-1})	Integrated TMA-d ₉ band (cm^{-1})	Integrated Complex band (cm^{-1})	ΔH° (LKr) ^a
5.6×10^{-4}	1.9×10^{-3}	1290 - 1248	1974 - 1948	1270-1259	-12.56(3)
5.6×10^{-4}	1.9×10^{-3}	1290 - 1248	1974 - 1948	ν_4 (1026.4) ^b	-12.39(3)
2.3×10^{-4}	1.9×10^{-3}	1290 - 1248	1974 - 1948	1269 - 1259	-12.57(2)
2.3×10^{-4}	1.9×10^{-3}	1290 - 1248	1974 - 1948	ν_4 (1026.4) ^b	-12.44(1)

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

^b Due to overlap between both complex bands, the intensity used is obtained from a band fit analysis

Table S11: Overview of the different van 't Hoff plots constructed for the hydrogen bonded complex between fluoroiodomethane and trimethylamine-d₉ 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 ΔH° (LKr).

x_{CH_2FI}	x_{TMA-d_9}	Integrated CH_2FI band (cm^{-1})	Integrated TMA-d ₉ band (cm^{-1})	Integrated Complex band (cm^{-1})	ΔH° (LKr) ^a
5.6×10^{-4}	1.9×10^{-3}	1290 - 1248	1974 - 1948	1292 - 1270	-9.80(7)
5.6×10^{-4}	1.9×10^{-3}	1290 - 1248	1974 - 1948	ν_4 (1033.8) ^b	-9.57(3)
2.3×10^{-4}	1.9×10^{-3}	1290 - 1248	1974 - 1948	1292 - 1269	-9.5(1)
2.3×10^{-4}	1.9×10^{-3}	1290 - 1248	1974 - 1948	ν_4 (1033.8) ^b	-9.33(5)

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

^b Due to overlap between both complex bands, the intensity used is obtained from a band fit analysis

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 halogen bonded complex (top) and the hydrogen bonded complex (bottom) between CH₂FI and dimethyl ether.

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 halogen bonded complex (top) and the hydrogen bonded complex (bottom) between CH_2FI and trimethylamine.

Figure S3: Infrared spectra of selected spectral regions for the mixtures of fluoroiodomethane with dimethyl ether- d_6 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 fluoroiodomethane or dimethyl ether- d_6 , respectively. Trace *d* represents the spectrum of the complex which is obtained by subtracting the rescaled traces *b* and *c* from trace *a*. Estimated mole fractions of the solutions of the mixtures are 1.9×10^{-4} for CH_2FI and 4.7×10^{-3} for DME- d_6 in panel A, 9.4×10^{-5} for CH_2FI and 4.7×10^{-3} for DME- d_6 in panel B, 6.8×10^{-5} for CH_2FI and 2.8×10^{-3} for DME- d_6 in panel C and 1.9×10^{-4} for CH_2FI and 4.7×10^{-3} for DME- d_6 in panel D.

Figure S4: Infrared spectra of selected spectral regions for the mixtures of fluoroiodomethane with trimethylamine 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 fluoroiodomethane or

trimethylamine, respectively. Trace *d* represents the spectrum of the complex which is obtained by subtracting the rescaled traces *b* and *c* from trace *a*. For clarity, trace *d* has been multiplied by a factor of 4 in Panels A and B. 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 2.9×10^{-4} for CH₂FI and 3.8×10^{-4} for TMA in panel A, 4.7×10^{-5} for CH₂FI and 3.8×10^{-4} for TMA in panel B and 9.4×10^{-5} for CH₂FI and 1.9×10^{-3} for TMA in panel C.

Figure S5: Infrared spectra of the $2\nu_2$ spectral region for the mixtures of fluoriodomethane with trimethylamine- d_9 dissolved in LKr at 130 K. Trace *a* represents the mixed solution, while traces *b* and *c* show the rescaled spectra of the solutions containing only fluoriodomethane or trimethylamine- d_9 , 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 trace *d* are marked with an asterisk (*) or open circle (°), respectively. Estimated mole fractions of the solution of the mixture is 1.3×10^{-4} for CH_2FI and 1.9×10^{-3} for TMA- d_9 .

Figure S6: Typical van 't Hoff plots of the hydrogen bonded complexes (squares) and halogen bonded complex (circles) between fluoriodomethane and dimethyl ether (filled) and trimethylamine (open) in LKr in the 120-156 K temperature interval.