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Lone pair $\cdots\pi$ interactions involving carbonyl π -systems: Experimental and theoretical study of the complexes of COF₂ and COFCl with dimethyl ether.

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Abstract

In this theoretical and experimental study, the ability of carbonyl fluoride (COF₂) and carbonyl chloride fluoride (COFCl) to form noncovalent interactions with the Lewis base dimethyl ether (DME) is assessed. From *ab initio* calculations, two stable complexes are found for COF₂·DME, both formed through a lone pair $\cdots\pi$ interaction. FTIR measurements on liquefied noble gas solutions, supported by *ab initio* calculations, statistical thermodynamical calculations and Monte Carlo Free Energy Perturbation calculations, show that a 1:1 lone pair $\cdots\pi$ bonded complex is found in solution, with an experimental complexation enthalpy of -14.5(3) kJ mol⁻¹. For COFCl·DME three lone pair $\cdots\pi$ complexes, as well as a Cl $\cdots$ O halogen bonded complex, are found from *ab initio* calculations. Experimentally, clear complex bands for 1:1 lone pair $\cdots\pi$ complexes are observed, with an experimental complexation enthalpy of -11.4(2) kJ mol⁻¹. Furthermore, indications of the presence of a small amount of the halogen bonded complex are also observed.

1. Introduction

The existence of an attractive noncovalent interaction between the lone pair of a Lewis base and an electron deficient π -system, called a lone pair $\cdots\pi$ interaction (lp $\cdots\pi$), has been demonstrated both theoretically and experimentally in recent years for aromatic and non-aromatic π systems.¹⁻³ The best studied lp $\cdots\pi$ complex is undoubtedly the one between hexafluorobenzene, an ideal model compound for aromatic electron deficient compounds, and water, because of its biological importance.⁴⁻⁸

During many of these studies, research was focused on homoatomic π -systems, such as ethylene or benzene containing moieties. However, the first descriptions of $lp \cdots \pi$ interactions involved the π -hole of carbonyl groups.⁹⁻¹⁰ As electron withdrawing groups near the π -system greatly enhance the strength of the noncovalent interaction,¹⁰ phosgene-like compounds are ideal candidates for the study of $lp \cdots \pi$ interactions involving carbonyl groups. Indeed, attractive intermolecular interactions between carbonyl fluoride (COF₂) and Ar,¹¹⁻¹² N₂,¹² Cl₂,¹³ IF¹⁴ and BrF¹⁵ have already been described experimentally. Here, the complexes with Ar and N₂ are of the $lp \cdots \pi$ type, the Cl₂ complex is halogen bonded (XB) and in the cases of IF and BrF the $lp \cdots \pi$ complex is an intermediary state to the formation of a halogen bonded complex between iodine/bromine and oxygen. Even though the $lp \cdots \pi$ interactions with HCN¹⁶ and H₂O¹⁷ have also been described theoretically, experimental studies involving phosgene-like compounds and traditional Lewis bases capable of forming stronger intermolecular interaction have not been described.

2. Experimental and computational section

Dimethyl ether (DME, 99+%) and dimethyl ether-d₆ (DME-d₆, 98+% d) were purchased from Aldrich, while carbonyl fluoride (COF₂, 97%) and carbonyl chloride fluoride (COFCl, 97%) were purchased from ABCR. The solvent gas krypton was supplied by Air Liquide and had a stated purity of 99.9995%. All products were used without further purification steps.

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. A specialized cell with 1 cm path length equipped with wedged silicon windows, a PID controlled heating element and top mounted LN₂ cryostat enabled the measurements of LKr solutions up to 12 bar at different temperatures. To avoid condensation of CO₂ and H₂O on the Si windows, the cell is placed in a vacuum chamber. A detailed description of the experimental setup is given in a recent review.¹⁸ 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 with a resolution of 0.5 cm⁻¹. Thermal expansion of the solvent gas during temperature studies was accounted for using the method published by van der Veken.¹⁹ The numbering of the fundamental vibrational modes of COF₂, COFCl, DME and DME-d₆ follows the numbering scheme of Herzberg.²⁰⁻²² To aid assignments and avoid spectral congestion, measurements are performed using both undeuterated and fully deuterated Lewis base.

Complexation stoichiometries were determined by performing an isothermal concentration study in which the concentrations of the solutes are systematically varied. By combining the Lambert-Beer law with the equilibrium constant for the formation of the complex A_mB_n

$$mA + nB \rightleftharpoons A_mB_n \quad (1)$$

it can be shown that the integrated intensity of a complex band is linearly related to the product of the m th power of the monomer intensity I_A and the n th power of monomer intensity I_B .¹⁸

$$I_{A_mB_n} = C(I_A)^m(I_B)^n \quad (2)$$

where C is a constant related to the equilibrium constant. When plotting the integrated intensity of the complex $I_{A_mB_n}$ against the product of the integrated monomer intensities $(I_A)^x(I_B)^y$ a linear relationship will thus only be found when $x=m$ and $y=n$.¹⁸ By preparing a series of plots for various integer values of x and y and evaluating their linearity, the complex stoichiometry can be established experimentally.

Estimated mole fractions of the solutions varied between 5.6×10^{-5} and 5.6×10^{-4} for COF_2 , 5.6×10^{-5} and 1.9×10^{-3} for COFCl and 1.5×10^{-4} and 4.7×10^{-3} for DME and DME- d_6 . 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, exact concentrations are not known. An overview of the estimated mole fractions used in the van 't Hoff plots is given in Tables S11 and S12 of the ESI.

To support the experimental measurements, *ab initio* MP2 calculations were performed using Dunning's augmented correlation consistent basis sets of double zeta quality (aug-cc-pVDZ) in Gaussian09.²³ The counterpoise technique as proposed by Boys and Bernardi was used during all *ab initio* calculations to account for the basis set superposition error.²⁴ Energies at the basis set limit were calculated with Molpro²⁵ using the extrapolation scheme of Truhlar, in which the effect of electron correlation is obtained from MP2 calculations.²⁶

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

$$E_{CBS}^{cor,MP2} = \frac{3^\beta}{3^\beta - 2^\beta} E_3^{cor,MP2} - \frac{2^\beta}{3^\beta - 2^\beta} E_2^{cor,MP2} \quad (4)$$

In these calculations $\alpha = 3.4$ and $\beta = 2.2$,²⁶ while energies with subscript 2 and 3 are calculated using the aug-cc-pVDZ and aug-cc-pVTZ basis sets respectively.

Furthermore, a correction for higher order correlation effects is made using Hobza's method,²⁷ yielding results of $E_{CBS}^{CCSD(T)}$ quality.

$$\Delta E^{CCSD(T)} = |E^{CCSD(T)} - E^{MP2}|_{aug-cc-pVDZ} \quad (5)$$

$$E_{CBS}^{CCSD(T)} = E_{CBS}^{HF} + E_{CBS}^{cor,MP2} + \Delta E^{CCSD(T)} \quad (6)$$

Complexation enthalpies in the gas phase $\Delta H^\circ(\text{vap,calc})$ were obtained from the calculated complexation energies $\Delta E(\text{CCSD(T)/CBS})$ by applying a zero-point energy correction and a correction for thermal effects, obtained from statistical thermodynamics at MP2/aug-cc-pVDZ level of theory, calculated at 138 K, the center of the experimental temperature interval of 120 K to 156 K. By correcting these calculated enthalpy values with solvent effects, obtained from the Monte Carlo Free Energy Perturbation (MC-FEP) approach using an in-house modified version of BOSS 4.0²⁸, complexation enthalpies in solution $\Delta H^\circ(\text{LKr,calc})$ are obtained which can be compared with the

experimental complexation enthalpies $\Delta H^\circ(\text{LKr})$. A full description of the computational methods used has been summarized before.¹⁸

3. Results and discussion

Ab initio calculations at the MP2/aug-cc-pVDZ level yield an attractive interaction between COF_2 and DME in which the oxygen atom of the DME moiety faces towards the carbon atom of COF_2 , thus forming a $\text{lp} \cdots \pi$ complex with C_s symmetry. Apart from this global minimum, a local minimum is also found when the DME molecule is rotated above the COF_2 molecular plane, located only 0.8 kJ mol^{-1} higher in energy. The result of the relaxed potential energy scan in which the DME molecule rotates above the COF_2 molecular plane and solely the dihedral angle between the $\text{C}=\text{O}$ axis and the DME bisector is fixed during optimization is shown in Figure 1. The geometries of the global and local minima are also shown in Figure 2 while major geometrical intermolecular parameters and complexation energies and enthalpies are summarized Table 1. Cartesian coordinates of all monomers and complexes are given in Tables S1 and S2 of the ESI.

Figure 1 MP2/aug-cc-pVDZ calculated complexation energies for the $\text{COF}_2 \cdot \text{DME}$ complex, obtained from a relaxed potential energy scan, plotted against the dihedral angle between the $\text{C}=\text{O}$ axis and the bisector of DME. The geometries of the global and local minima are also shown above the graph.

Figure 2: MP2/aug-cc-pVDZ equilibrium geometries for the $O\cdots\pi$ complex between COF_2 and DME on the left (global minimum) and middle (local minimum) and the XB complex between $COFCl$ and DME on the right, including the designation of the binding distances and angles given in Table 1.

Table 1: Intermolecular distance R_{eq} (Å), bond angles and dihedrals ($^\circ$), calculated complexation energies at different levels of theory as well as theoretical and experimental complexation enthalpies ($kJ\ mol^{-1}$) for the complexes of COF_2 and $COFCl$ with DME.

	COF ₂ ·DME			COFCl·DME		
	O $\cdots\pi_{global}$	O $\cdots\pi_{local}$	O $\cdots\pi_1$	O $\cdots\pi_2$	O $\cdots\pi_3$	XB
Symmetry	C _s	C ₁	C ₁	C ₁	C ₁	C _s
R_{eq} ^a	2.64	2.63	2.74	2.75	2.72	2.94
θ	96.0	96.6	94.6	92.9	94.2	174.7
γ ^b	33.9	46.6	34.9	26.9	44.8	
τ ^c	0.0	(-)92.4 ^j	156.2	66.3	-45.6	
ΔE (DZ) ^d	-20.6	-19.9	-18.3	-19.0	-18.2	-11.3
ΔE (TZ) ^e	-22.7	-21.6	-19.9	-21.0	-20.1	-12.0
ΔE (CCSD(T)) ^f	-23.8	-22.6	-20.2	-21.3	-20.2	-12.4
ΔH° (vap,calc) ^g	-20.8	-19.7	-17.5	-18.5	-17.5	-9.9
ΔH° (LKr,calc) ^g	-16.2	-15.4	-11.5	-12.4	-12.0	-7.4
Experimental ^h						
ΔH° (LKr)	-14.5(3)	-14.5(3)	-11.4(2)	-11.4(2)	-11.4(2)	

^a $R_{eq} = R_{C\cdots O}$ for $lp\cdots\pi$ complexes and $R_{eq} = R_{Cl\cdots O}$ for the XB complex ^b Angle between the approximate COFX (X = F, Cl) molecular plane defined by the atoms C, O and F and the DME bisector ^c τ dihedral angle between the O=C bond and DME bisector ^d MP2/aug-cc-pVDZ energies, ^e MP2/aug-cc-pVDZ//MP2/aug-cc-pVTZ energies ^f CCSD(T)/CBS extrapolated energies, ^g Values based on CCSD(T) energies, ^h Values determined in the 120 K – 156 K temperature interval, given with one standard uncertainty in parentheses. ^j Depending on the local minimum observed this value can be either 92.4° or -92.4°.

For $COFCl\cdot DME$, *ab initio* calculations yielded a $Cl\cdots O$ halogen bonded (XB) complex as well as three $lp\cdots\pi$ bonded complex geometries, in which the DME oxygen directly faces towards the $COFCl$ carbon atom. The geometries of the $lp\cdots\pi$ complexes are shown in Figure 3, while the XB complex is shown in Figure 2. Major geometrical intermolecular parameters and complexation energies and enthalpies can be found in Table 1. The different stable $lp\cdots\pi$ bonded complex geometries are again the consequence of the rotation of the DME moiety above the $COFCl$ molecular plane. The relaxed potential energy scan in which the DME molecule rotates above the $COFCl$ molecular plane and

solely the dihedral angle between the C=O axis and the DME bisector is fixed during optimization is given in Figure 3.

Figure 3: MP2/aug-cc-pVDZ calculated complexation energies for the COFCl·DME complex, obtained from a relaxed potential energy scan, plotted against the dihedral angle between the C=O axis and the bisector of DME.

Even though optimizations were initiated from a structure in which the DME molecular plane is nearly perpendicular to the COFX (X = F, Cl) molecular plane, the C-O-C plane of the DME molecule is tilted towards the COFX (X = F, Cl) molecular plane during optimization in all $lp\cdots\pi$ complexes, as can be seen on the left side of Figure 2 for the global minimum of the complex with COF_2 , as well as Table 1. This is consistent with the rabbit-ear like configuration of the lone pairs on oxygen and furthermore enables the formation of secondary interactions. As the COFX (X = F, Cl) molecules lose their planarity upon complexation, the plane used to assess the angle between the approximate molecular plane of COFX (X = F, Cl) and the DME bisector is defined by the atoms in the carbonyl bond as well as the first fluorine atom, as given in the cartesian coordinates in Tables S2 of the ESI. Slightly different angles will be obtained when using the other halogen atom (F or Cl) to define the molecular plane.

In an attempt to rationalize the differences in observed stability, the topology of the electron density was examined for all complexes studied using the Atom in Molecules approach.²⁹ For all complexes, a single bond path due to the intermolecular interaction was found. The values for the electron density at the corresponding bond critical points and the extrapolated CCSD(T)/CBS complexation energies have been plotted in Figure S1 of the ESI. From the data given it is clear that in general a high degree of linearity between both properties is observed. However, subtle differences in complexation energies

and electron densities are observed when comparing the different $lp \cdots \pi$ complexes, making further use of the AIM approach less straightforward. The reason for the small discrepancies can most presumably be ascribed to weak secondary effects that escape detection in the AIM approach. To further investigate the effect of secondary interactions on the complexation energy, these secondary interactions have been studied using the noncovalent interactions index visualized using NCIPLOT³⁰⁻³¹, as shown in Figure S2 for the $COF_2 \cdot DME$ complexes and Figure S3 for the $COFCl \cdot DME$ complexes. For the global minimum of the $COF_2 \cdot DME$ complex two smaller isosurfaces between the oxygen atom of COF_2 and the hydrogens of the methyl groups of DME are observed, apart from the isosurface caused by the $O \cdots \pi$ interaction, whereas only one small isosurface due to a secondary hydrogen bond is found for the local minimum. For each of the $O \cdots \pi$ complexes between $COFCl$ and DME several isosurfaces caused by secondary weak hydrogen bonds are found, apart from the central isosurface caused by the $O \cdots \pi$ interaction, whereas, due to its linearity, a single isosurface is obtained for the $Cl \cdots O$ halogen bonded complex. The absence of additional isosurfaces for the highly directional halogen bond is consistent with previous observations for XB complexes.^{1, 32}

The spectra of DME and DME- d_6 and their assignments have been discussed in detail in previous publications.^{1, 32} The assignment of the vibrational modes of COF_2 was aided by the assignments found in the literature,^{13, 22, 33} as well as the performed *ab initio* calculations. The assignment of the complex bands was aided by the *ab initio* calculations performed at the MP2/aug-cc-pVDZ level of theory, of which the results are reported in tables S3 and S4 of the ESI.

Upon investigation of spectra of $COF_2 \cdot DME$, shown in Figure 4, clearly resolved complex bands are observed. Most noticeably, complex bands are found in the COF_2 ν_6 spectral range (Panel 4D) with a -20.8 cm^{-1} red shifted complex band ($\Delta v_{calc, O \cdots \pi, global} = -30.0$ cm^{-1}), the COF_2 ν_1 spectral region (Panel 4A) with a -4.0 cm^{-1} red shift ($\Delta v_{calc, O \cdots \pi, global} = -6.4$ cm^{-1}) and COF_2 ν_2 / DME ν_6 spectral range (Panel 4C), with complex shifts of -2.1 cm^{-1} and -3.5 cm^{-1} respectively (corresponding to calculated values of $\Delta v_{calc, O \cdots \pi, global} = -2.4$ cm^{-1} and $\Delta v_{calc, O \cdots \pi, global} = -7.3$ cm^{-1}). These shifts are all in good agreement with the MP2/aug-cc-pVDZ calculated complex shifts for the $lp \cdots \pi$ complex at the global minimum. An overview of the experimental complexation shifts and corresponding calculated values is given in Table 2. Inspection of the spectra and comparison with the calculated shifts given in Table 2 also shows some differences between the calculated and experimental complexation shifts. The difference between the experimental shift of 0.4 cm^{-1} of the ν_4 mode of COF_2 , shown in Panel 4B, and the calculated shifts of 5.7 cm^{-1} and -3.9 cm^{-1} for the global and local minimum respectively can be explained by a mechanical coupling with the asymmetric O-CH₃ stretching mode ν_{20} mode of DME (ν_{18} in case of DME- d_6) in the calculations. The overestimation of the calculated shift of the ν_{12} mode of DME can be ascribed to the presence of multiple overtones and combination bands in the DME C-H stretching region, which causes resonant effects and greatly complicates the assignment of these modes. As in our previous study on $lp \cdots \pi$ interactions,¹ small experimental blueshifts are found for the

DME modes ν_3 and ν_{18} as opposed to the calculated redshifts. As the solutions are at thermodynamic equilibrium, the different calculated geometries are expected to occur in the solution in a Boltzmann-weighted ratio. Nevertheless only a single complex band is found for each vibrational mode, which can be explained by a nearly free rotation between the global and local minimum, the rotational barrier being similar to the RT at 120 K, as shown in Figure 1, which leads to an averaged structure being observed experimentally. Spectra of multiple spectral ranges for $\text{COF}_2 \cdot \text{DME-d}_6$ mixtures are given in Figure S4 of the ESI. A full assignment of the monomers and corresponding complex bands, including the calculated complexation shifts, is given in Table 2 for $\text{COF}_2 \cdot \text{DME}$ and in Table S8 for $\text{COF}_2 \cdot \text{DME-d}_6$.

Figure 4: Infrared spectra of selected spectral regions of mixtures of COF_2 and DME dissolved in LKr at 120 K. In each panel, trace *a* represents the mixed solution, while traces *b* and *c* show the solution containing only COF_2 or DME, respectively. Trace *d* represents the spectrum of the complex and is obtained by subtracting the rescaled traces *b* and *c* from trace *a*. Estimated mole fractions of the solutions of the mixtures are 5.6×10^{-5} for COF_2 and 5.6×10^{-4} for DME in panels A and D and 5.6×10^{-4} for COF_2 and 1.9×10^{-4} for DME in panels B and C.

Table 2: Experimental infrared frequencies for the monomer and complex, as well as experimental complexation shifts ($\Delta\nu_{\text{exp}}$) and MP2/aug-cc-pVDZ calculated complexation shifts for the global ($\Delta\nu_{\text{calc, O}\cdots\pi \text{ global}}$) and local minimum ($\Delta\nu_{\text{calc, O}\cdots\pi \text{ local}}$), in cm^{-1} , of the $\text{O}\cdots\pi$ bonded complex of COF_2 with DME dissolved in LKr at 120 K.

	Assignment	Symmetry	ν_{monomer}	ν_{complex}	$\Delta\nu_{\text{exp}}$	$\Delta\nu_{\text{calc, O}\cdots\pi \text{ global}}$	$\Delta\nu_{\text{calc, O}\cdots\pi \text{ local}}$
COF_2	ν_1	A_1	1934.6	1930.6	-4.0	-6.4	0.3
	$2\nu_2$	A_1	1905.4	1901.3	-4.1	-4.8	-10.4
	ν_4	B_1	1232.7	1233.1	0.4	5.7	-3.9
	ν_2	A_1	960.1	958.0	-2.1	-2.4	-5.2
	ν_6	B_2	769.0	748.2	-20.8	-30.0	-29.2
	ν_5	B_1	662.7	662.6	-0.1	1.4	-0.5
	ν_3	A_1	580.5	580.7	0.2	-1.2	-0.2
DME	ν_1	A_1	2990.0	2995.8	5.8	4.0	6.8
	ν_{16}	B_2	2990.0	2995.8	5.8	4.0	2.4
	ν_{12}	B_1	2916.2	2921.3	5.1	17.7	15.0
	ν_2	A_1	2811.5	2820.0	8.5	10.3	8.8
	ν_3	A_1	1474.7	1475.1	0.4	-1.4	-0.9

ν_{18}	B_2	1457.4	1457.8	0.4	-1.1	-1.2
ν_{13}	B_1	1454.7	1456.1	1.4	1.8	0.8
ν_{19}	B_2	1426.1	1428.3	2.2	0.2	0.6
ν_5	A_1	1244.9	1248.5	3.6	1.4	2.5
ν_{20}	B_2	1172.0	1168.8	-3.2	-10.4	-6.2
ν_{21}	B_2	1099.1	1096.8	-2.3	-5.9	-2.8
ν_6	A_1	929.4	925.9	-3.5	-7.3	-5.6

By measuring mixtures with different concentrations of each of the monomers at a constant temperature of 120 K, the 1:1 complex stoichiometry was determined experimentally by plotting the integrated intensity of the complex band against the product of the integrated intensities of the monomers at different ratios. The procedure has been described in more detail in the recent review by Herrebout.¹⁸ The results of this concentration study can be found in Figure 5.

Figure 5: Concentration study plots of the $\text{COF}_2\cdot\text{DME}$ $\text{O}\cdots\pi$ complex at 120 K in LKr. Integrated intensity of the complex is plotted against the product of monomer intensities $(I_{\text{COF}_2})^m(\text{DME})^n$. 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.

By constructing van ‘t Hoff plots from measurements between 120 K and 156 K, 13 experimental complexation enthalpies between -14.1 and -15.0 kJ mol^{-1} have been determined for the $\text{lp}\cdots\pi$ complex of COF_2 with DME and DME- d_6 , the average being -14.5(3) kJ mol^{-1} . An example of a van ‘t Hoff plot for the $\text{COF}_2\cdot\text{DME}$ and $\text{COFCl}\cdot\text{DME}$ complexes is shown in Figure 6 while an overview of all performed temperature studies for the $\text{COF}_2\cdot\text{DME}$ complex can be found in Table S11 of the ESI.

Figure 6: Typical van 't Hoff plots of the lp $\cdots\pi$ complexes between of COF₂ and dimethyl ether (square) and COFCl and dimethyl ether (round) in LKr.

Upon initial spectroscopic evaluation of the COFCl sample, it was clear that this sample also contained a considerable amount of CO₂, which can, as published in a previous article by van Ginderen et al.³⁴, form a lp $\cdots\pi$ complex with DME in liquefied noble gas solutions. To account for CO₂ and its complex with DME and enable their subtraction from the COFCl-DME spectra, spectra of CO₂ and CO₂-DME mixtures were measured and studied separately. A more complete description of the performed subtraction procedure has been included in the ESI. Assignment of the vibrational modes of the COFCl monomer was aided by assignments found in the literature,^{13, 33} as well as the *ab initio* calculations reported in Tables S5 to S8 of the ESI. A full assignment of the CO₂-DME complex can be found in the article of van Ginderen et al.³⁴

Upon first inspection of the spectra of COFCl-DME mixtures, two complex bands can be seen near the ν_6 vibrational mode of COFCl, one blue shifted, and a more intense one with a large red shift. The shifts of these bands are in good agreement with the calculated values of the XB complex and lp $\cdots\pi$ complexes of COFCl-DME. However, these complex shifts also correspond well to the calculated complex shifts of the degenerate π_u mode of CO₂. Subtraction of the CO₂ monomer and CO₂-DME complex spectra was performed using a rescaling factor determined for the σ_u^+ mode near 2340 cm⁻¹, as shown in panel A of Figure 7. Upon subtraction of the rescaled CO₂ and CO₂-DME spectra, most of the redshifted band in the COFCl ν_6 spectral region is retained, whereas only a very small amount of blue shifted band is retained, as can be seen in Panel D of Figure 7. With experimental shifts of -13.8 cm⁻¹ and 4.4 cm⁻¹ these bands correspond well to the calculated values given in Table 3 for the lp $\cdots\pi$ complexes (between -20.8 and -21.9 cm⁻¹) and XB complex (5.3 cm⁻¹) respectively. The retention of a small blue shifted band indicates the presence of a small amount of XB complex. Also in other spectral ranges, such as the ν_1 and ν_3 spectral ranges of COFCl, which are shown in Panels B and C of Figure 7, small complex bands are retained apart from those assigned to the lone pair $\cdots\pi$ complexes. With experimental shifts of -7.4 cm⁻¹ and 2.3 cm⁻¹, these values correspond well to the calculated shifts of -10.3 cm⁻¹ and 2.2 cm⁻¹ for the ¹²COFCl-DME XB complex. Additional spectra of interesting

spectral regions of the COFCl·DME complex are given in Figures S5 and S6 of the ESI. The spectral regions discussed above for mixtures containing DME-d₆ are shown in Figure S7 of the ESI.

Figure 7: Infrared spectra of selected spectral regions of mixtures of COFCl and DME dissolved in LKr at 120 K. In each panel, trace *a* represents the mixed solution of COFCl with DME, while traces *b* and *c* show the solution containing only COFCl or DME, respectively. Trace *d* shows the rescaled spectrum of CO₂, whereas trace *e* shows the spectrum of the rescaled CO₂·DME complex, which has obtained from a separate measurement. Finally, trace *f* shows the spectrum of the COFCl·DME complex, obtained by subtracting traces *b-e* from trace *a*. Bands due to the lp··· π complex and XB complex observed in trace *f* are marked with an open circle (°) or asterisk (*), respectively. Estimated mole fractions of the solutions of the mixtures are 1.9×10^{-4} for COFCl and 4.7×10^{-3} for DME in panels A, B and D and 5.6×10^{-5} for COFCl and 4.7×10^{-3} for DME in panel C.

In order to aid assignment of the other vibrational modes and help identify the lp··· π complex or complexes present in solution, behaviour of the complexation shifts upon rotation of DME above the COFCl molecular plane was evaluated. The dependence of the complexation shifts upon rotation and the corresponding complexation energies are given in Figure 8. The complexation shift of the ν_6 mode remains stable at around -21 cm^{-1} , which is consistent with the assignment of the -13.8 cm^{-1} redshifted band to the lp··· π complex. The overestimation of the calculated complexation shifts for the lp··· π complexes is believed to be a consequence of the harmonic approximation which has been used in all frequency calculations. Upon further inspection of Figure 8, it becomes clear that the ν_1 , ν_2 and ν_3 modes of COFCl show a large dependence on the C=O···C-O-C bisector angle, all having both blueshifts and redshifts at different dihedral angles. Comparison of these calculated shifts with the experimental shifts, given in Table 3, shows that no exact match is found for either of the three calculated energy minima. A mean absolute deviations (MAD) analysis, in which the average of the absolute deviation between the experimental and calculated shifts is calculated, yielded the lowest value of 2.3 cm^{-1} for the O··· π_2 complex when looking at the 7 assigned COFCl modes, whereas values of 7.4 and 3.5 cm^{-1} were found for O··· π_1 and O··· π_3 , respectively. These values indicate a clear preference for a major contribution of the O··· π_2 complex, as can expected from the calculated complexation energies. However, when including the shifts for the assigned DME modes, values of

4.8, 2.7 and 2.6 cm^{-1} are obtained for $\text{O}\cdots\pi_1$, $\text{O}\cdots\pi_2$ and $\text{O}\cdots\pi_3$ respectively and the preference of $\text{O}\cdots\pi_2$ over $\text{O}\cdots\pi_3$ diminishes.

To assess whether the discrepancies between experimental and calculated shifts of the $\text{O}\cdots\pi$ complexes can be ascribed to the method used, calculations of these complexes were also performed using MP2 with the aug-cc-pVTZ basis set and B3LYP (including a GD3 correction for dispersion) with the aug-cc-pVDZ and aug-cc-pVTZ basis set. Results of the MAD analysis of these calculations are given in Table S13 of the ESI. From this analysis it becomes clear that MAD values increase when going from MP2 to B3LYP and, for both methods, when going from the aug-cc-pVDZ to the aug-cc-pVTZ basis set, while the relative values of the different $\text{O}\cdots\pi$ complexes stay similar throughout the used methods. Hence, the best correspondence between experimental and calculated shifts is obtained for the MP2/aug-cc-pVDZ calculated values.

Again, as the rotational barrier between the different calculated minima, shown in Figures 6 and 8, is similar to the RT value at 120 K, nearly free rotation between the three complex geometries is expected and an average structure is observed experimentally, rather than three individual structures with individual complex bands.

Figure 8: MP2/aug-cc-pVDZ calculated complexation shifts for the ν_1 , ν_2 , ν_3 and ν_6 modes of COFCl and complexation energy for the COFCl·DME complex, obtained from a relaxed potential energy scan, plotted against the dihedral angle between the C=O axis and the bisector of DME.

A full experimental assignment of all observed vibrational modes for the monomers and corresponding complex bands, including the calculated complexation shifts, can be found in Table 3 for COFCl·DME and Table S10 for COFCl·DME- d_6 .

Table 3: Experimental infrared frequencies for the monomer and complex, as well as experimental complexation shifts (Δv_{exp}) and MP2/aug-cc-pVDZ calculated complexation shifts (Δv_{calc}), in cm^{-1} , for the $\text{lp} \cdots \pi$ bonded complexes and XB complex of COFCl with DME dissolved in LKr at 120 K.

Assignment	Sym	v_{monomer}	v_{complex}	$\Delta v_{\text{exp}, \text{O} \cdots \pi}$	$\Delta v_{\text{calc}, \text{O} \cdots \pi 1}$	$\Delta v_{\text{calc}, \text{O} \cdots \pi 2}$	$\Delta v_{\text{calc}, \text{O} \cdots \pi 3}$	v_{complex}	$\Delta v_{\text{exp}, \text{XB}}$	$\Delta v_{\text{calc}, \text{XB}}$
COFCl										
$2\nu_2$	A'	2158.0	2161.4	3.4	-15.5	5.2	4.0			-7.3
ν_1	A'	1863.8	1864.5	0.7	2.6	-3.4	5.7	1856.4	-7.4	-10.3
$\nu_2 + \nu_3$	A'	1832.1	1832.9	0.8	-9.2	2.9	-2.8	1832.9	0.8	-1.4
		1823.2	1823.9	0.7						
ν_2	A'	1083.9	1085.2	1.3	-7.7	2.6	2.0	1081.1	-2.8	-3.7
ν_2 (^{13}C)	A'	1056.4	1057.9	1.5	-8.0	2.4	2.4	1052.9	-3.5	-4.5
ν_3 (^{35}Cl)	A'	761.8	761.4	-0.4	-1.4	0.4	-4.8	764.1	2.3	2.2
ν_3 (^{37}Cl)	A'	759.8	759.6	-0.2	-1.4	0.4	-4.6	761.4	1.6	2.1
ν_6	A''	663.6	649.8	-13.8	-21.8	-20.8	-21.9	668.0	4.4	5.3
DME										
ν_1	A ₁	2990.0	2992.2	2.2	4.7	3.8	2.4	2992.2	2.2	0.3
ν_{16}	B ₂	2990.0	2992.2	2.2	-0.8	0.1	0.9	2992.2	2.2	-0.5
ν_{12}	B ₁	2916.2	2919.1	2.9	12.0	13.2	9.7	2919.1	2.9	8.8
ν_2	A ₁	2811.5	2817.5	6.0	6.7	7.3	4.8	2817.5	6.0	5.1
ν_3	A ₁	1474.7	1474.6	-0.1	-1.6	-1.5	-1.8	1474.6	-0.1	0.0
ν_{18}	B ₂	1457.4	1457.5	0.1	-1.8	-1.4	-1.9	1457.5	0.1	0.1
ν_{13}	B ₁	1454.7	1455.5	0.8	-0.3	-0.3	0.7	1455.5	0.8	-0.3
ν_{19}	B ₂	1426.1			-0.2	-0.5	-0.5			0.8
ν_5	A ₁	1244.9	1247.5	2.6	1.2	0.6	1.3	1247.5	2.6	1.6
ν_{20}	B ₂	1172.0	1169.3	-2.7	-6.7	-8.3	-5.5	1169.3	-2.7	-3.3
ν_{21}	B ₂	1099.1	1097.6	-1.5	-3.1	-5.0	-2.8	1097.6	-1.5	-1.1
ν_6	A ₁	929.4	925.8	-3.6	-6.4	-7.0	-5.6	925.8	-3.6	-4.3

The construction of van 't Hoff plots from temperature studies yielded 10 experimental complexation enthalpies, varying between -11.0 and -11.7 kJ mol⁻¹, with an average of -11.4(2) kJ mol⁻¹. An example of a van 't Hoff plot is given in Figure 5, while an overview of the parameters used in the van 't Hoff plots is given in Table S12 of the ESI. Furthermore the 1:1 complex stoichiometry of the lp $\cdots\pi$ bonded complex was confirmed experimentally by a concentration study of which the results can be found in Figure 9.

Figure 9: Concentration study plots of the COFCl·DME O $\cdots\pi$ complex at 120 K in LKr. Integrated intensity of the complex is plotted against the product of monomer intensities $(I_{\text{COFCl}})^m(\text{DME})^n$. 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.

4. Conclusions

Ab initio calculations at the MP2/aug-cc-pVDZ level of theory yielded two stable complexes between COF₂ and DME formed through a lp $\cdots\pi$ interaction, the difference in energy being a mere 0.8 kJ mol⁻¹. The existence and stoichiometry of a 1:1 lp $\cdots\pi$ bonded complex was verified experimentally by means of FTIR measurements on liquefied krypton solutions, the assignment was aided by the complexation shifts of the *ab initio* calculations. As the rotational barrier between the global and local minimum is comparable to the RT value at 120 K, an averaged structure is observed in the spectra. Furthermore, a complexation enthalpy of -14.5(3) kJ mol⁻¹ was determined experimentally by means of a temperature study, which corresponds well with the CCSD(T)/CBS extrapolated values after correction for thermal and solvent effects of -16.2 kJ mol⁻¹ and -15.4 kJ mol⁻¹ for the lp $\cdots\pi$ complex at the global and local minima, respectively.

For the combination of COFCl with DME, *ab initio* calculations yielded a XB complex geometry, as well as 3 complex geometries bonded by a lp $\cdots\pi$ interaction. These latter three complexes are the result of a rotation of DME above the COFCl molecular plane, with a rotational barrier comparable to the RT value at 120 K, impeding experimental differentiation between the different lp $\cdots\pi$ geometries. Despite the presence of CO₂ in the COFCl sample, the formation of a 1:1 lp $\cdots\pi$ complex with a complexation enthalpy of -11.4(2) kJ mol⁻¹ between COFCl and DME or DME-d₆ were demonstrated experimentally. Furthermore, clear indications for the formation of XB complex between COFCl and DME or DME-d₆ were also observed. Unfortunately, due to the low intensity of the bands belonging to the XB complex, neither the complexation enthalpy nor the complexation stoichiometry could be verified experimentally.

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Supporting Information Available:

MP2/aug-cc-pVDZ cartesian coordinates, vibrational frequencies, IR and raman intensities of all monomers and complexes, experimental frequencies of COF₂, COFCl and DME-d₆ and observed complex bands in LKr, overview of parameters used in van 't Hoff plots, results of MAD analysis and of the AIM study, NCI plots for all complexes, additional IR spectra of the regions of interest for COF₂ and COFCl mixtures involving DME and DME-d₆ and a detailed description of the used subtraction procedure for COFCl·DME and COFCl·DME-d₆ mixtures including spectra. This material is available free of charge via www.sciencedirect.com.

Graphical Abstract

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Lone pair $\cdots\pi$ interactions involving carbonyl π -systems: Experimental and theoretical study of the complexes of COF₂ and COFCl with dimethyl ether(-d₆).

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Electronic supplementary information

Table S1.1: Cartesian coordinates of the MP2/aug-cc-pVDZ optimized geometry of COF₂.

C _{2v}	X	Y	Z
COF ₂			
C	0.000000	0.000000	0.148815
O	0.000000	0.000000	1.334592
F	0.000000	1.073442	-0.642757
F	0.000000	-1.073442	-0.642757

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

C _s	X	Y	Z
COFCl			
C	0.000000	0.503758	0.000000
O	-0.794527	1.388686	0.000000
F	1.338047	0.690833	0.000000
Cl	-0.334483	-1.197031	0.000000

Table S1.3: 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 S2.1: Cartesian coordinates of the MP2/aug-cc-pVDZ optimized geometry of the global minimum lone pair... π complex between COF₂ and dimethyl ether.

C _s	X	Y	Z
COF ₂			
C	0.446473	-1.238034	0.000000
O	1.556787	-0.816310	0.000000
F	-0.274213	-1.556818	1.075014
F	-0.274213	-1.556818	-1.075014
DME			
O	-0.744237	1.117259	0.000000
C	-0.274213	1.781064	-1.173003
H	0.829959	1.776852	-1.210974
H	-0.673110	1.233581	-2.035715
H	-0.633274	2.824855	-1.201338
C	-0.274213	1.781064	1.173003
H	-0.673110	1.233581	2.035715
H	0.829959	1.776852	1.210974
H	-0.633274	2.824855	1.201338

Table S2.2: Cartesian coordinates of the MP2/aug-cc-pVDZ optimized geometry of the local minimum lone pair $\cdots\pi$ complex between COF₂ and dimethyl ether.

C ₁	X	Y	Z
COF ₂			
C	1.379102	0.129643	0.029753
O	1.485532	1.303606	-0.104794
F	1.161372	-0.513938	1.181268
F	1.536864	-0.795169	-0.915657
DME			
O	-1.213082	0.005821	-0.413785
C	-1.838516	1.202125	0.047884
H	-1.864391	1.232097	1.152144
H	-1.241832	2.042704	-0.32628
H	-2.870196	1.277419	-0.338535
C	-1.912084	-1.146429	0.051165
H	-1.381459	-2.024873	-0.33643
H	-1.925004	-1.181311	1.155439
H	-2.951856	-1.151514	-0.321002

Table S2.3: Cartesian coordinates of the MP2/aug-cc-pVDZ optimized geometry of the lone pair $\cdots\pi$ complex between COFCl and dimethyl ether, indicated with the label O $\cdots\pi_1$ in the remainder of this document and the accompanying manuscript.

C ₁	X	Y	Z
COFCl			
C	-1.070520	0.581881	0.200504
O	-0.954142	1.649502	-0.310715
F	-0.704564	0.314446	1.475958
Cl	-1.791808	-0.833167	-0.491408
DME			
O	1.449063	-0.258228	-0.46932
C	2.270913	0.906590	-0.427406
H	1.801327	1.656596	-1.075343
H	2.340058	1.303102	0.601833
H	3.287868	0.682358	-0.795604
C	1.980406	-1.283056	0.366430
H	1.301283	-2.142055	0.296494
H	2.988528	-1.583464	0.029060
H	2.038577	-0.945386	1.416994

Table S2.4: Cartesian coordinates of the MP2/aug-cc-pVDZ optimized geometry of the lone pair $\cdots\pi$ complex between COFCl and dimethyl ether, indicated with the label O $\cdots\pi_2$ in the remainder of this document and the accompanying manuscript.

C ₁	X	Y	Z
COFCl			
C	-1.003116	-0.496266	0.369164
O	-0.630887	-0.576025	1.497330
F	-0.921327	-1.506302	-0.522740
Cl	-1.795602	0.856134	-0.369183
DME			
O	1.474235	0.290897	-0.538929
C	1.851764	1.344480	0.345252
H	1.202771	2.201006	0.123852
H	1.715749	1.042017	1.399382
H	2.906159	1.632118	0.185257
C	2.282469	-0.863117	-0.314550
H	1.955724	-1.630170	-1.027130
H	3.349495	-0.633259	-0.483792
H	2.153802	-1.238837	0.716796

Table S2.5: Cartesian coordinates of the MP2/aug-cc-pVDZ optimized geometry of the lone pair $\cdots\pi$ complex between COFCl and dimethyl ether, indicated with the label O $\cdots\pi_3$ in the remainder of this document and the accompanying manuscript.

C ₁	X	Y	Z
COFCl			
C	-1.204666	-0.466259	-0.211942
O	-1.187745	-1.594426	0.163311
F	-1.209093	-0.093866	-1.506906
Cl	-1.321430	0.953929	0.786777
DME			
O	1.503240	-0.258655	-0.337441
C	2.093013	1.007677	-0.617732
H	1.630430	1.382699	-1.539162
H	1.905747	1.721632	0.205189
H	3.183320	0.910394	-0.766328
C	2.041656	-0.816697	0.858915
H	1.536538	-1.776674	1.022296
H	3.129219	-0.982541	0.760428
H	1.856923	-0.151191	1.722119

Table S2.6: Cartesian coordinates of the MP2/aug-cc-pVDZ optimized geometry of the halogen bonded complex between COFCl and dimethyl ether.

C _s	X	Y	Z
COFCl			
C	2.361484	0.121929	0.000009
O	2.991185	1.133056	0.000069
F	2.932724	-1.108456	-0.000064
Cl	0.642334	-0.043677	0.000001
DME			
O	-2.30152	-0.056092	-0.000018
C	-2.923349	1.225458	-0.000055
H	-2.121764	1.974637	-0.000112
H	-3.551703	1.360165	-0.898959
H	-3.551648	1.360243	0.898877
C	-3.277358	-1.093371	0.000061
H	-2.736144	-2.047533	0.000086
H	-3.917429	-1.034314	0.898879
H	-3.917487	-1.034395	-0.898721

Table S3A: MP2/aug-cc-pVDZ vibrational frequencies, in cm^{-1} , infrared intensities, in km mol^{-1} , and Raman intensities, in $\text{\AA}^4 \text{amu}^{-1}$, for the global minimum lone pair $\cdots\pi$ complex of COF_2 and dimethyl ether and both monomers, as well as the complexation shift $\Delta\nu$.

	Monomer			Lone pair $\cdots\pi$ complex			
	Frequency	IR intensity	Raman intensity	Frequency	$\Delta\nu$	IR intensity	Raman intensity
COF₂							
ν_1 (A ₁)	1932.2	422.4	12.8	1925.8	-6.4	356.9	11.5
ν_2 (A ₁)	934.1	66.3	9.1	931.7	-2.4	56.3	9.1
ν_3 (A ₁)	563.4	6.0	1.1	562.2	-1.2	4.1	0.8
ν_4 (B ₁)	1201.6	417.7	1.4	1207.3	5.7	410.4	1.4
ν_5 (B ₁)	600.2	5.7	2.0	601.6	1.4	4.1	1.5
ν_6 (B ₂)	768.0	32.7	0.4	738.1	-30.0	91.4	3.8
DME							
ν_1 (A ₁)	3188.7	20.1	87.6	3192.6	4.0	16.0	68.6
ν_2 (A ₁)	3024.8	58.6	320.3	3035.1	10.3	46.2	289.0
ν_3 (A ₁)	1505.9	2.9	5.6	1504.5	-1.4	8.6	5.7
ν_4 (A ₁)	1473.5	0.0008	2.2	1474.1	0.6	0.1	1.9
ν_5 (A ₁)	1261.1	6.6	0.5	1262.5	1.4	6.1	0.4
ν_6 (A ₁)	942.4	34.7	9.8	935.1	-7.3	30.4	8.9
ν_7 (A ₁)	416.8	2.3	1.0	418.8	2.0	2.6	0.9
ν_8 (A ₂)	3096.2	0.0	14.7	3113.0	16.8	0.2	12.1
ν_9 (A ₂)	1474.8	0.0	11.4	1475.7	0.9	0.02	10.3
ν_{10} (A ₂)	1157.2	0.0	1.5	1157.3	0.1	0.1	1.6
ν_{11} (A ₂)	195.2	0.0	0.2	191.7	-3.5	0.0	0.1
ν_{12} (B ₁)	3089.5	107.8	94.2	3107.2	17.7	83.3	87.7
ν_{13} (B ₁)	1489.2	13.0	0.04	1491.0	1.8	16.5	0.2
ν_{14} (B ₁)	1187.2	7.2	0.04	1190.5	3.4	5.9	0.3
ν_{15} (B ₁)	260.2	5.1	0.002	272.2	11.9	9.9	0.03
ν_{16} (B ₂)	3187.3	24.6	59.2	3191.3	4.0	16.6	44.3
ν_{17} (B ₂)	3018.4	55.2	0.6	3029.8	11.5	44.2	1.3
ν_{18} (B ₂)	1490.1	10.3	1.0	1488.9	-1.1	8.4	0.7
ν_{19} (B ₂)	1441.5	2.5	1.3	1441.7	0.2	2.1	1.2
ν_{20} (B ₂)	1191.9	98.1	0.7	1181.5	-10.4	16.5	0.1
ν_{21} (B ₂)	1113.8	35.0	1.6	1107.9	-5.9	35.7	1.8

Van der Waals vibrations: 23.6 cm^{-1} , 1.1 km mol^{-1} , 0.4 $\text{\AA}^4 \text{amu}^{-1}$, 79.0 cm^{-1} , 0.2 km mol^{-1} , 0.01 $\text{\AA}^4 \text{amu}^{-1}$, 81.7 cm^{-1} , 3.8 km mol^{-1} , 0.4 $\text{\AA}^4 \text{amu}^{-1}$, 95.7 cm^{-1} , 4.8 km mol^{-1} , 0.6 $\text{\AA}^4 \text{amu}^{-1}$, 121.9 cm^{-1} , 0.03 km mol^{-1} , 0.6 $\text{\AA}^4 \text{amu}^{-1}$, 147.0 cm^{-1} , 2.2 km mol^{-1} , 0.4 $\text{\AA}^4 \text{amu}^{-1}$.

Table S3B: MP2/aug-cc-pVDZ vibrational frequencies, in cm^{-1} , infrared intensities, in km mol^{-1} , and Raman intensities, in $\text{\AA}^4 \text{amu}^{-1}$, for the global minimum lone pair $\cdots\pi$ complex of COF_2 and dimethyl ether- d_6 and both monomers, as well as the complexation shift $\Delta\nu$.

	Monomer			Lone pair $\cdots\pi$ complex			
	Frequency	IR intensity	Raman intensity	Frequency	$\Delta\nu$	IR intensity	Raman intensity
COF_2							
$\nu_1 (\text{A}_1)$	1932.2	422.4	12.8	1925.7	-6.6	356.9	11.1
$\nu_2 (\text{A}_1)$	934.1	66.3	9.1	931.5	-2.6	52.3	8.6
$\nu_3 (\text{A}_1)$	563.4	6.0	1.1	562.2	-1.2	4.0	0.8
$\nu_4 (\text{B}_1)$	1201.6	417.7	1.4	1207.7	6.1	395.4	1.4
$\nu_5 (\text{B}_1)$	600.2	5.7	2.0	601.6	1.4	4.1	1.5
$\nu_6 (\text{B}_2)$	768.0	32.7	0.4	737.8	-30.3	92.9	3.9
DME-d_6							
$\nu_1 (\text{A}_1)$	2364.1	17.0	37.1	2368.0	4.0	13.5	30.5
$\nu_2 (\text{A}_1)$	2171.1	32.1	166.2	2177.7	6.6	27.1	148.5
$\nu_3 (\text{A}_1)$	1153.5	5.3	2.6	1149.2	-4.3	4.0	2.4
$\nu_4 (\text{A}_1)$	1085.9	0.09	2.5	1085.2	-0.7	1.0	2.3
$\nu_5 (\text{A}_1)$	1058.5	17.5	1.8	1059.5	1.0	19.4	1.6
$\nu_6 (\text{A}_1)$	834.8	16.9	7.7	831.3	-3.5	13.7	7.3
$\nu_7 (\text{A}_1)$	351.5	1.5	0.7	353.9	2.4	1.9	0.6
$\nu_8 (\text{A}_2)$	2297.2	0.0	7.5	2310.2	13.0	0.06	6.1
$\nu_9 (\text{A}_2)$	1065.8	0.0	4.2	1066.1	0.3	5.0	2.7
$\nu_{10} (\text{A}_2)$	877.6	0.0	2.2	877.6	-0.1	0.03	2.1
$\nu_{11} (\text{A}_2)$	139.5	0.0	0.1	137.7	-1.8	0.002	0.1
$\nu_{12} (\text{B}_1)$	2290.4	65.1	51.2	2304.3	13.9	51.2	47.0
$\nu_{13} (\text{B}_1)$	1077.4	4.3	0.003	1077.9	0.6	5.6	0.2
$\nu_{14} (\text{B}_1)$	937.8	9.9	0.1	941.4	3.6	12.9	0.5
$\nu_{15} (\text{B}_1)$	200.5	4.6	0.0	220.7	20.2	9.8	0.07
$\nu_{16} (\text{B}_2)$	2360.7	10.6	31.7	2364.6	3.9	7.4	24.0
$\nu_{17} (\text{B}_2)$	2164.0	44.9	0.03	2171.6	7.6	36.4	0.3
$\nu_{18} (\text{B}_2)$	1170.3	134.3	0.9	1155.1	-15.3	62.7	0.6
$\nu_{19} (\text{B}_2)$	1077.4	0.5	0.2	1076.6	-0.8	0.9	0.09
$\nu_{20} (\text{B}_2)$	1066.1	1.6	1.1	1065.0	-1.1	1.1	2.0
$\nu_{21} (\text{B}_2)$	860.9	0.08	0.9	860.3	-0.6	0.3	0.9

Van der Waals vibrations: 21.8 cm^{-1} , 0.9 km mol^{-1} , $0.3 \text{ \AA}^4 \text{amu}^{-1}$, 71.5 cm^{-1} , 3.5 km mol^{-1} , $0.3 \text{ \AA}^4 \text{amu}^{-1}$, 72.5 cm^{-1} , 0.1 km mol^{-1} , $0.01 \text{ \AA}^4 \text{amu}^{-1}$, 92.4 cm^{-1} , 3.5 km mol^{-1} , $0.4 \text{ \AA}^4 \text{amu}^{-1}$, 117.2 cm^{-1} , 0.06 km mol^{-1} , $0.5 \text{ \AA}^4 \text{amu}^{-1}$, 131.7 cm^{-1} , 0.1 km mol^{-1} , $0.5 \text{ \AA}^4 \text{amu}^{-1}$.

Table S4A: MP2/aug-cc-pVDZ vibrational frequencies, in cm^{-1} , infrared intensities, in km mol^{-1} , and Raman intensities, in $\text{\AA}^4 \text{amu}^{-1}$, for the local minimum lone pair $\cdots\pi$ complex of COF_2 and dimethyl ether and both monomers, as well as the complexation shift $\Delta\nu$.

	Monomer			Lone pair $\cdots\pi$ complex			
	Frequency	IR intensity	Raman intensity	Frequency	$\Delta\nu$	IR intensity	Raman intensity
COF₂							
$\nu_1 (\text{A}_1)$	1932.2	422.4	12.8	1932.5	0.3	368.3	13.2
$\nu_2 (\text{A}_1)$	934.1	66.3	9.1	928.9	-5.2	50.5	11.0
$\nu_3 (\text{A}_1)$	563.4	6.0	1.1	563.2	-0.2	4.1	0.9
$\nu_4 (\text{B}_1)$	1201.6	417.7	1.4	1197.7	-3.9	358.8	1.1
$\nu_5 (\text{B}_1)$	600.2	5.7	2.0	599.7	-0.5	4.2	1.5
$\nu_6 (\text{B}_2)$	768.0	32.7	0.4	738.9	-29.2	90.5	4.7
DME							
$\nu_1 (\text{A}_1)$	3188.7	20.1	87.6	3195.5	6.8	13.2	52.1
$\nu_2 (\text{A}_1)$	3024.8	58.6	320.3	3033.6	8.8	55.4	298.6
$\nu_3 (\text{A}_1)$	1505.9	2.9	5.6	1505.0	-0.9	3.2	5.9
$\nu_4 (\text{A}_1)$	1473.5	0.0008	2.2	1473.9	0.4	0.4	4.5
$\nu_5 (\text{A}_1)$	1261.1	6.6	0.5	1263.5	2.5	5.9	0.5
$\nu_6 (\text{A}_1)$	942.4	34.7	9.8	936.8	-5.6	39.0	6.9
$\nu_7 (\text{A}_1)$	416.8	2.3	1.0	418.0	1.2	3.4	0.9
$\nu_8 (\text{A}_2)$	3096.2	0.0	14.7	3110.7	14.5	0.6	14.0
$\nu_9 (\text{A}_2)$	1474.8	0.0	11.4	1475.0	0.2	0.2	8.0
$\nu_{10} (\text{A}_2)$	1157.2	0.0	1.5	1157.1	-0.1	0.003	1.5
$\nu_{11} (\text{A}_2)$	195.2	0.0	0.2	190.1	-5.1	0.01	0.2
$\nu_{12} (\text{B}_1)$	3089.5	107.8	94.2	3104.6	15.0	88.7	98.0
$\nu_{13} (\text{B}_1)$	1489.2	13.0	0.04	1490.0	0.8	15.4	0.09
$\nu_{14} (\text{B}_1)$	1187.2	7.2	0.04	1189.3	2.2	6.3	0.1
$\nu_{15} (\text{B}_1)$	260.2	5.1	0.002	265.3	5.1	7.2	0.009
$\nu_{16} (\text{B}_2)$	3187.3	24.6	59.2	3189.7	2.4	17.3	54.6
$\nu_{17} (\text{B}_2)$	3018.4	55.2	0.6	3028.2	9.9	44.6	2.2
$\nu_{18} (\text{B}_2)$	1490.1	10.3	1.0	1488.8	-1.2	10.7	0.9
$\nu_{19} (\text{B}_2)$	1441.5	2.5	1.3	1442.1	0.6	0.3	1.4
$\nu_{20} (\text{B}_2)$	1191.9	98.1	0.7	1185.7	-6.2	76.4	0.3
$\nu_{21} (\text{B}_2)$	1113.8	35.0	1.6	1110.9	-2.8	40.3	2.0

Van der Waals vibrations: 16.5 cm^{-1} , 0.5 km mol^{-1} , 0.2 $\text{\AA}^4 \text{amu}^{-1}$, 44.8 cm^{-1} , 2.5 km mol^{-1} , 0.1 $\text{\AA}^4 \text{amu}^{-1}$, 70.3 cm^{-1} , 1.5 km mol^{-1} , 0.04 $\text{\AA}^4 \text{amu}^{-1}$, 98.8 cm^{-1} , 1.0 km mol^{-1} , 0.2 $\text{\AA}^4 \text{amu}^{-1}$, 123.8 cm^{-1} , 1.3 km mol^{-1} , 0.4 $\text{\AA}^4 \text{amu}^{-1}$, 131.7 cm^{-1} , 1.3 km mol^{-1} , 1.0 $\text{\AA}^4 \text{amu}^{-1}$.

Table S4B: MP2/aug-cc-pVDZ vibrational frequencies, in cm^{-1} , infrared intensities, in km mol^{-1} , and Raman intensities, in $\text{\AA}^4 \text{amu}^{-1}$, for the local minimum lone pair $\cdots\pi$ complex of COF_2 and dimethyl ether- d_6 and both monomers, as well as the complexation shift $\Delta\nu$.

	Monomer			Lone pair $\cdots\pi$ complex			
	Frequency	IR intensity	Raman intensity	Frequency	$\Delta\nu$	IR intensity	Raman intensity
COF_2							
$\nu_1 (\text{A}_1)$	1932.2	422.4	12.8	1932.4	0.2	366.8	13.2
$\nu_2 (\text{A}_1)$	934.1	66.3	9.1	929.0	-5.1	51.7	8.6
$\nu_3 (\text{A}_1)$	563.4	6.0	1.1	563.2	-0.2	4.1	0.9
$\nu_4 (\text{B}_1)$	1201.6	417.7	1.4	1198.1	-3.5	351.9	1.1
$\nu_5 (\text{B}_1)$	600.2	5.7	2.0	599.7	-0.5	4.2	1.5
$\nu_6 (\text{B}_2)$	768.0	32.7	0.4	738.5	-29.5	92.0	4.8
DME-d_6							
$\nu_1 (\text{A}_1)$	2364.1	17.0	37.1	2369.3	5.2	11.6	25.7
$\nu_2 (\text{A}_1)$	2171.1	32.1	166.2	2176.8	5.7	31.6	153.2
$\nu_3 (\text{A}_1)$	1153.5	5.3	2.6	1150.5	-3.0	5.2	2.4
$\nu_4 (\text{A}_1)$	1085.9	0.09	2.5	1084.1	-1.8	2.1	2.7
$\nu_5 (\text{A}_1)$	1058.5	17.5	1.8	1060.6	2.0	21.9	1.9
$\nu_6 (\text{A}_1)$	834.8	16.9	7.7	832.3	-2.4	15.3	7.2
$\nu_7 (\text{A}_1)$	351.5	1.5	0.7	353.5	2.0	2.5	0.6
$\nu_8 (\text{A}_2)$	2297.2	0.0	7.5	2308.3	11.1	0.2	7.0
$\nu_9 (\text{A}_2)$	1065.8	0.0	4.2	1065.6	-0.2	0.02	3.6
$\nu_{10} (\text{A}_2)$	877.6	0.0	2.2	877.4	-0.3	0.06	2.1
$\nu_{11} (\text{A}_2)$	139.5	0.0	0.1	135.8	-3.7	0.01	0.1
$\nu_{12} (\text{B}_1)$	2290.4	65.1	51.2	2302.1	11.8	54.0	52.7
$\nu_{13} (\text{B}_1)$	1077.4	4.3	0.003	1077.6	0.3	4.7	0.02
$\nu_{14} (\text{B}_1)$	937.8	9.9	0.1	940.0	2.2	10.3	0.2
$\nu_{15} (\text{B}_1)$	200.5	4.6	0.0	211.4	10.8	7.0	0.03
$\nu_{16} (\text{B}_2)$	2360.7	10.6	31.7	2364.0	3.3	8.6	25.7
$\nu_{17} (\text{B}_2)$	2164.0	44.9	0.03	2170.6	6.6	37.7	0.5
$\nu_{18} (\text{B}_2)$	1170.3	134.3	0.9	1161.0	-9.3	118.6	0.8
$\nu_{19} (\text{B}_2)$	1077.4	0.5	0.2	1075.7	-1.7	0.7	0.2
$\nu_{20} (\text{B}_2)$	1066.1	1.6	1.1	1067.0	0.9	3.1	1.2
$\nu_{21} (\text{B}_2)$	860.9	0.08	0.9	861.2	0.3	0.2	1.1

Van der Waals vibrations: 15.1 cm^{-1} , 0.4 km mol^{-1} , $0.09 \text{ \AA}^4 \text{amu}^{-1}$, 38.7 cm^{-1} , 1.7 km mol^{-1} , $0.08 \text{ \AA}^4 \text{amu}^{-1}$, 64.3 cm^{-1} , 1.1 km mol^{-1} , $0.03 \text{ \AA}^4 \text{amu}^{-1}$, 95.1 cm^{-1} , 1.0 km mol^{-1} , $0.2 \text{ \AA}^4 \text{amu}^{-1}$, 115.3 cm^{-1} , 0.4 km mol^{-1} , $0.3 \text{ \AA}^4 \text{amu}^{-1}$, 127.6 cm^{-1} , 0.6 km mol^{-1} , $1.0 \text{ \AA}^4 \text{amu}^{-1}$.

Table S5A: MP2/aug-cc-pVDZ vibrational frequencies, in cm^{-1} , infrared intensities, in km mol^{-1} , and Raman intensities, in $\text{\AA}^4 \text{amu}^{-1}$, for the lone pair $\cdots\pi$ complex of COFCl and dimethyl ether ($\text{O}\cdots\pi_1$) and both monomers, as well as the complexation shift $\Delta\nu$.

Monomer				Lone pair $\cdots\pi$ complex ($\text{O}\cdots\pi_1$)			
	Frequency	IR intensity	Raman intensity	Frequency	$\Delta\nu$	IR intensity	Raman intensity
COFCl							
$\nu_1 (\text{A}')$	1863.0	345.9	16.5	1865.6	2.6	304.1	14.8
$\nu_2 (\text{A}')$	1058.0	425.3	2.2	1050.3	-7.7	377.9	1.6
$\nu_3 (\text{A}')$	749.9	74.2	11.0	748.5	-1.4	61.1	10.4
$\nu_4 (\text{A}')$	499.1	0.3	5.6	498.0	-1.1	0.2	4.9
$\nu_5 (\text{A}')$	410.4	0.6	1.8	411.2	0.8	0.3	1.3
$\nu_6 (\text{A}'')$	662.8	13.5	0.1	641.0	-21.8	42.4	3.2
DME							
$\nu_1 (\text{A}_1)$	3188.7	20.1	87.6	3193.4	4.7	14.2	50.2
$\nu_2 (\text{A}_1)$	3024.8	58.6	320.3	3031.5	6.7	57.2	297.2
$\nu_3 (\text{A}_1)$	1505.9	2.9	5.6	1504.3	-1.6	3.7	6.0
$\nu_4 (\text{A}_1)$	1473.5	0.0008	2.2	1473.4	-0.2	0.5	5.7
$\nu_5 (\text{A}_1)$	1261.1	6.6	0.5	1262.2	1.2	6.4	0.5
$\nu_6 (\text{A}_1)$	942.4	34.7	9.8	936.0	-6.4	41.6	9.1
$\nu_7 (\text{A}_1)$	416.8	2.3	1.0	417.8	1.0	2.8	0.9
$\nu_8 (\text{A}_2)$	3096.2	0.0	14.7	3107.7	11.5	0.6	14.3
$\nu_9 (\text{A}_2)$	1474.8	0.0	11.4	1473.9	-0.9	0.4	6.5
$\nu_{10} (\text{A}_2)$	1157.2	0.0	1.5	1156.5	-0.8	0.1	1.5
$\nu_{11} (\text{A}_2)$	195.2	0.0	0.2	190.6	-4.7	0.03	0.2
$\nu_{12} (\text{B}_1)$	3089.5	107.8	94.2	3101.5	12.0	89.9	101.0
$\nu_{13} (\text{B}_1)$	1489.2	13.0	0.04	1488.9	-0.3	14.8	0.1
$\nu_{14} (\text{B}_1)$	1187.2	7.2	0.04	1188.5	1.4	6.7	0.1
$\nu_{15} (\text{B}_1)$	260.2	5.1	0.002	264.9	4.7	7.2	0.01
$\nu_{16} (\text{B}_2)$	3187.3	24.6	59.2	3186.5	-0.8	18.1	47.1
$\nu_{17} (\text{B}_2)$	3018.4	55.2	0.6	3025.9	7.5	44.7	2.9
$\nu_{18} (\text{B}_2)$	1490.1	10.3	1.0	1488.2	-1.8	10.1	0.9
$\nu_{19} (\text{B}_2)$	1441.5	2.5	1.3	1441.3	-0.2	0.2	1.4
$\nu_{20} (\text{B}_2)$	1191.9	98.1	0.7	1185.2	-6.7	77.5	0.3
$\nu_{21} (\text{B}_2)$	1113.8	35.0	1.6	1110.7	-3.1	37.3	2.1

Van der Waals vibrations: 17.8 cm^{-1} , 0.8 km mol^{-1} , $0.3 \text{ \AA}^4 \text{amu}^{-1}$, 54.5 cm^{-1} , 4.0 km mol^{-1} , $0.4 \text{ \AA}^4 \text{amu}^{-1}$, 64.3 cm^{-1} , 0.6 km mol^{-1} , $0.2 \text{ \AA}^4 \text{amu}^{-1}$, 87.0 cm^{-1} , 0.2 km mol^{-1} , $0.1 \text{ \AA}^4 \text{amu}^{-1}$, 105.7 cm^{-1} , 0.7 km mol^{-1} , $1.2 \text{ \AA}^4 \text{amu}^{-1}$, 117.3 cm^{-1} , 2.5 km mol^{-1} , $0.6 \text{ \AA}^4 \text{amu}^{-1}$.

Table S5B: MP2/aug-cc-pVDZ vibrational frequencies, in cm^{-1} , infrared intensities, in km mol^{-1} , and Raman intensities, in $\text{\AA}^4 \text{amu}^{-1}$, for the lone pair $\cdots\pi$ complex of COFCl and dimethyl ether- d_6 ($\text{O}\cdots\pi_1$) and both monomers, as well as the complexation shift $\Delta\nu$.

Monomer				Lone pair $\cdots\pi$ complex ($\text{O}\cdots\pi_1$)			
	Frequency	IR intensity	Raman intensity	Frequency	$\Delta\nu$	IR intensity	Raman intensity
COFCl							
ν_1 (A')	1863.0	345.9	16.5	1865.5	2.5	303.2	14.8
ν_2 (A')	1058.0	425.3	2.2	1049.1	-8.9	383.3	1.7
ν_3 (A')	749.9	74.2	11.0	748.4	-1.5	61.2	10.5
ν_4 (A')	499.1	0.3	5.6	498.0	-1.1	0.2	4.9
ν_5 (A')	410.4	0.6	1.8	411.3	0.9	0.3	1.4
ν_6 (A'')	662.8	13.5	0.1	640.9	-21.9	42.6	3.3
DME- d_6							
ν_1 (A_1)	2364.1	17.0	37.1	2367.6	3.5	12.2	24.5
ν_2 (A_1)	2171.1	32.1	166.2	2175.3	4.2	32.4	151.8
ν_3 (A_1)	1153.5	5.3	2.6	1150.2	-3.4	7.6	2.6
ν_4 (A_1)	1085.9	0.09	2.5	1085.1	-0.8	6.1	2.8
ν_5 (A_1)	1058.5	17.5	1.8	1059.5	1.0	6.6	1.8
ν_6 (A_1)	834.8	16.9	7.7	831.6	-3.2	20.4	7.0
ν_7 (A_1)	351.5	1.5	0.7	353.0	1.5	2.0	0.6
ν_8 (A_2)	2297.2	0.0	7.5	2306.1	8.9	0.2	7.2
ν_9 (A_2)	1065.8	0.0	4.2	1064.8	-1.0	1.0	3.2
ν_{10} (A_2)	877.6	0.0	2.2	877.0	-0.6	0.003	2.0
ν_{11} (A_2)	139.5	0.0	0.1	136.3	-3.2	0.02	0.1
ν_{12} (B_1)	2290.4	65.1	51.2	2299.8	9.4	54.5	54.5
ν_{13} (B_1)	1077.4	4.3	0.003	1076.8	-0.5	4.8	0.04
ν_{14} (B_1)	937.8	9.9	0.1	939.3	1.5	8.8	0.2
ν_{15} (B_1)	200.5	4.6	0.0	210.1	9.6	7.1	0.03
ν_{16} (B_2)	2360.7	10.6	31.7	2361.5	0.9	9.0	22.8
ν_{17} (B_2)	2164.0	44.9	0.03	2168.8	4.9	37.0	0.7
ν_{18} (B_2)	1170.3	134.3	0.9	1160.9	-9.4	112.5	0.8
ν_{19} (B_2)	1077.4	0.5	0.2	1075.5	-1.8	1.4	0.2
ν_{20} (B_2)	1066.1	1.6	1.1	1066.3	0.1	3.7	1.2
ν_{21} (B_2)	860.9	0.08	0.9	860.6	-0.3	0.2	1.1

Van der Waals vibrations: 16.2 cm^{-1} , 0.7 km mol^{-1} , $0.2 \text{ \AA}^4 \text{amu}^{-1}$, 47.3 cm^{-1} , 2.8 km mol^{-1} , $0.2 \text{ \AA}^4 \text{amu}^{-1}$, 60.2 cm^{-1} , 0.7 km mol^{-1} , $0.2 \text{ \AA}^4 \text{amu}^{-1}$, 81.5 cm^{-1} , 0.2 km mol^{-1} , $0.2 \text{ \AA}^4 \text{amu}^{-1}$, 99.6 cm^{-1} , 0.5 km mol^{-1} , $1.0 \text{ \AA}^4 \text{amu}^{-1}$, 111.1 cm^{-1} , 0.9 km mol^{-1} , $0.9 \text{ \AA}^4 \text{amu}^{-1}$.

Table S6A: MP2/aug-cc-pVDZ vibrational frequencies, in cm^{-1} , infrared intensities, in km mol^{-1} , and Raman intensities, in $\text{\AA}^4 \text{amu}^{-1}$, for the lone pair $\cdots\pi$ complex of COFCl and dimethyl ether ($\text{O}\cdots\pi_2$) and both monomers, as well as the complexation shift $\Delta\nu$.

Monomer				Lone pair $\cdots\pi$ complex ($\text{O}\cdots\pi_2$)			
	Frequency	IR intensity	Raman intensity	Frequency	$\Delta\nu$	IR intensity	Raman intensity
COFCl							
$\nu_1 (\text{A}')$	1863.0	345.9	16.5	1859.6	-3.4	298.4	13.4
$\nu_2 (\text{A}')$	1058.0	425.3	2.2	1060.6	2.6	334.1	1.5
$\nu_3 (\text{A}')$	749.9	74.2	11.0	750.3	0.4	64.0	10.2
$\nu_4 (\text{A}')$	499.1	0.3	5.6	498.8	-0.3	0.2	5.0
$\nu_5 (\text{A}')$	410.4	0.6	1.8	411.2	0.8	0.1	1.1
$\nu_6 (\text{A}'')$	662.8	13.5	0.1	642.0	-20.8	42.4	2.7
DME							
$\nu_1 (\text{A}_1)$	3188.7	20.1	87.6	3192.5	3.8	15.9	57.6
$\nu_2 (\text{A}_1)$	3024.8	58.6	320.3	3032.1	7.3	48.5	291.3
$\nu_3 (\text{A}_1)$	1505.9	2.9	5.6	1504.4	-1.5	9.5	5.6
$\nu_4 (\text{A}_1)$	1473.5	0.0008	2.2	1473.5	0.0	0.06	2.1
$\nu_5 (\text{A}_1)$	1261.1	6.6	0.5	1261.7	0.6	5.7	0.4
$\nu_6 (\text{A}_1)$	942.4	34.7	9.8	935.4	-7.0	37.5	9.1
$\nu_7 (\text{A}_1)$	416.8	2.3	1.0	419.0	2.2	2.5	1.0
$\nu_8 (\text{A}_2)$	3096.2	0.0	14.7	3108.7	12.5	0.4	12.7
$\nu_9 (\text{A}_2)$	1474.8	0.0	11.4	1474.7	-0.2	0.3	9.9
$\nu_{10} (\text{A}_2)$	1157.2	0.0	1.5	1157.1	-0.2	0.2	1.6
$\nu_{11} (\text{A}_2)$	195.2	0.0	0.2	192.8	-2.4	0.003	0.1
$\nu_{12} (\text{B}_1)$	3089.5	107.8	94.2	3102.7	13.2	86.9	90.1
$\nu_{13} (\text{B}_1)$	1489.2	13.0	0.04	1490.0	0.7	16.5	0.3
$\nu_{14} (\text{B}_1)$	1187.2	7.2	0.04	1189.6	2.5	5.8	0.3
$\nu_{15} (\text{B}_1)$	260.2	5.1	0.002	269.9	9.7	9.0	0.04
$\nu_{16} (\text{B}_2)$	3187.3	24.6	59.2	3187.4	0.1	17.9	45.1
$\nu_{17} (\text{B}_2)$	3018.4	55.2	0.6	3026.5	8.2	44.7	2.4
$\nu_{18} (\text{B}_2)$	1490.1	10.3	1.0	1488.7	-1.4	8.4	0.7
$\nu_{19} (\text{B}_2)$	1441.5	2.5	1.3	1441.0	-0.5	1.2	1.3
$\nu_{20} (\text{B}_2)$	1191.9	98.1	0.7	1183.6	-8.3	91.7	0.5
$\nu_{21} (\text{B}_2)$	1113.8	35.0	1.6	1108.8	-5.0	57.0	2.0

Van der Waals vibrations: 23.8 cm^{-1} , 1.1 km mol^{-1} , $0.5 \text{ \AA}^4 \text{amu}^{-1}$, 68.3 cm^{-1} , 2.0 km mol^{-1} , $0.5 \text{ \AA}^4 \text{amu}^{-1}$, 84.1 cm^{-1} , 0.4 km mol^{-1} , $0.3 \text{ \AA}^4 \text{amu}^{-1}$, 87.2 cm^{-1} , 5.1 km mol^{-1} , $0.7 \text{ \AA}^4 \text{amu}^{-1}$, 100.8 cm^{-1} , 0.3 km mol^{-1} , $0.7 \text{ \AA}^4 \text{amu}^{-1}$, 132.0 cm^{-1} , 2.7 km mol^{-1} , $0.5 \text{ \AA}^4 \text{amu}^{-1}$.

Table S6B: MP2/aug-cc-pVDZ vibrational frequencies, in cm^{-1} , infrared intensities, in km mol^{-1} , and Raman intensities, in $\text{\AA}^4 \text{amu}^{-1}$, for the lone pair $\cdots\pi$ complex of COFCl and dimethyl ether- d_6 ($\text{O}\cdots\pi_2$) and both monomers, as well as the complexation shift $\Delta\nu$.

	Monomer			Lone pair $\cdots\pi$ complex ($\text{O}\cdots\pi_2$)			
	Frequency	IR intensity	Raman intensity	Frequency	$\Delta\nu$	IR intensity	Raman intensity
COFCl							
$\nu_1 (\text{A}')$	1863.0	345.9	16.5	1859.5	-3.5	299.4	13.1
$\nu_2 (\text{A}')$	1058.0	425.3	2.2	1056.3	-1.7	250.1	1.7
$\nu_3 (\text{A}')$	749.9	74.2	11.0	750.2	0.3	64.0	10.2
$\nu_4 (\text{A}')$	499.1	0.3	5.6	498.8	-0.3	0.2	5.0
$\nu_5 (\text{A}')$	410.4	0.6	1.8	411.4	1.0	0.3	1.3
$\nu_6 (\text{A}'')$	662.8	13.5	0.1	641.9	-20.8	42.7	2.7
DME- d_6							
$\nu_1 (\text{A}_1)$	2364.1	17.0	37.1	2367.0	2.9	12.7	28.1
$\nu_2 (\text{A}_1)$	2171.1	32.1	166.2	2175.8	4.6	27.8	149.0
$\nu_3 (\text{A}_1)$	1153.5	5.3	2.6	1149.3	-4.3	4.6	2.5
$\nu_4 (\text{A}_1)$	1085.9	0.09	2.5	1084.9	-0.9	1.2	2.2
$\nu_5 (\text{A}_1)$	1058.5	17.5	1.8	1059.0	0.5	19.4	1.5
$\nu_6 (\text{A}_1)$	834.8	16.9	7.7	831.0	-3.8	18.5	7.2
$\nu_7 (\text{A}_1)$	351.5	1.5	0.7	353.7	2.2	1.6	0.6
$\nu_8 (\text{A}_2)$	2297.2	0.0	7.5	2306.8	9.6	0.1	6.4
$\nu_9 (\text{A}_2)$	1065.8	0.0	4.2	1069.7	3.9	80.1	3.0
$\nu_{10} (\text{A}_2)$	877.6	0.0	2.2	877.4	-0.2	0.04	2.0
$\nu_{11} (\text{A}_2)$	139.5	0.0	0.1	138.4	-1.1	0.0009	0.1
$\nu_{12} (\text{B}_1)$	2290.4	65.1	51.2	2300.8	10.4	52.7	48.6
$\nu_{13} (\text{B}_1)$	1077.4	4.3	0.003	1077.4	0.0	10.7	0.3
$\nu_{14} (\text{B}_1)$	937.8	9.9	0.1	940.2	2.4	9.8	0.3
$\nu_{15} (\text{B}_1)$	200.5	4.6	0.0	216.0	15.5	8.9	0.06
$\nu_{16} (\text{B}_2)$	2360.7	10.6	31.7	2362.1	1.4	8.7	21.9
$\nu_{17} (\text{B}_2)$	2164.0	44.9	0.03	2169.3	5.3	36.5	0.5
$\nu_{18} (\text{B}_2)$	1170.3	134.3	0.9	1158.2	-12.1	146.1	0.9
$\nu_{19} (\text{B}_2)$	1077.4	0.5	0.2	1076.5	-0.9	0.1	0.1
$\nu_{20} (\text{B}_2)$	1066.1	1.6	1.1	1064.8	-1.3	4.4	1.6
$\nu_{21} (\text{B}_2)$	860.9	0.08	0.9	860.1	-0.8	0.3	0.9

Van der Waals vibrations: 21.6 cm^{-1} , 0.9 km mol^{-1} , 0.4 $\text{\AA}^4 \text{amu}^{-1}$, 64.9 cm^{-1} , 2.2 km mol^{-1} , 0.5 $\text{\AA}^4 \text{amu}^{-1}$, 75.1 cm^{-1} , 1.8 km mol^{-1} , 0.3 $\text{\AA}^4 \text{amu}^{-1}$, 81.7 cm^{-1} , 2.2 km mol^{-1} , 0.3 $\text{\AA}^4 \text{amu}^{-1}$, 94.0 cm^{-1} , 0.3 km mol^{-1} , 0.7 $\text{\AA}^4 \text{amu}^{-1}$, 119.1 cm^{-1} , 0.3 km mol^{-1} , 0.8 $\text{\AA}^4 \text{amu}^{-1}$.

Table S7A: MP2/aug-cc-pVDZ vibrational frequencies, in cm^{-1} , infrared intensities, in km mol^{-1} , and Raman intensities, in $\text{\AA}^4 \text{amu}^{-1}$, for the lone pair $\cdots\pi$ complex of COFCl and dimethyl ether ($\text{O}\cdots\pi_3$) and both monomers, as well as the complexation shift $\Delta\nu$.

Monomer				Lone pair $\cdots\pi$ complex ($\text{O}\cdots\pi_3$)			
	Frequency	IR intensity	Raman intensity	Frequency	$\Delta\nu$	IR intensity	Raman intensity
COFCl							
$\nu_1 (\text{A}')$	1863.0	345.9	16.5	1868.7	5.7	300.1	15.1
$\nu_2 (\text{A}')$	1058.0	425.3	2.2	1060.0	2.0	363.2	1.8
$\nu_3 (\text{A}')$	749.9	74.2	11.0	745.1	-4.8	68.4	10.0
$\nu_4 (\text{A}')$	499.1	0.3	5.6	494.4	-4.7	0.2	5.2
$\nu_5 (\text{A}')$	410.4	0.6	1.8	410.8	0.4	0.3	1.4
$\nu_6 (\text{A}'')$	662.8	13.5	0.1	640.9	-21.9	43.0	3.0
DME							
$\nu_1 (\text{A}_1)$	3188.7	20.1	87.6	3191.1	2.4	13.3	51.1
$\nu_2 (\text{A}_1)$	3024.8	58.6	320.3	3029.6	4.8	53.2	289.2
$\nu_3 (\text{A}_1)$	1505.9	2.9	5.6	1504.1	-1.8	5.7	5.6
$\nu_4 (\text{A}_1)$	1473.5	0.0008	2.2	1472.8	-0.7	0.2	2.6
$\nu_5 (\text{A}_1)$	1261.1	6.6	0.5	1262.4	1.3	5.9	0.4
$\nu_6 (\text{A}_1)$	942.4	34.7	9.8	936.8	-5.6	35.9	8.8
$\nu_7 (\text{A}_1)$	416.8	2.3	1.0	417.2	0.4	2.6	0.8
$\nu_8 (\text{A}_2)$	3096.2	0.0	14.7	3105.4	9.2	1.3	14.3
$\nu_9 (\text{A}_2)$	1474.8	0.0	11.4	1474.2	-0.6	0.5	9.4
$\nu_{10} (\text{A}_2)$	1157.2	0.0	1.5	1156.3	-0.9	0.05	1.6
$\nu_{11} (\text{A}_2)$	195.2	0.0	0.2	192.8	-2.4	0.01	0.2
$\nu_{12} (\text{B}_1)$	3089.5	107.8	94.2	3099.2	9.7	95.8	98.1
$\nu_{13} (\text{B}_1)$	1489.2	13.0	0.04	1489.4	0.1	15.6	0.2
$\nu_{14} (\text{B}_1)$	1187.2	7.2	0.04	1188.2	1.0	6.9	0.2
$\nu_{15} (\text{B}_1)$	260.2	5.1	0.002	264.5	4.3	8.0	0.01
$\nu_{16} (\text{B}_2)$	3187.3	24.6	59.2	3188.2	0.9	16.0	49.5
$\nu_{17} (\text{B}_2)$	3018.4	55.2	0.6	3023.9	5.5	43.6	2.7
$\nu_{18} (\text{B}_2)$	1490.1	10.3	1.0	1488.1	-1.9	9.8	0.9
$\nu_{19} (\text{B}_2)$	1441.5	2.5	1.3	1440.9	-0.5	0.3	1.3
$\nu_{20} (\text{B}_2)$	1191.9	98.1	0.7	1186.4	-5.5	80.5	0.3
$\nu_{21} (\text{B}_2)$	1113.8	35.0	1.6	1111.0	-2.8	38.1	1.9

Van der Waals vibrations: 21.6 cm^{-1} , 0.3 km mol^{-1} , $0.6 \text{ \AA}^4 \text{amu}^{-1}$, 57.3 cm^{-1} , 1.5 km mol^{-1} , $0.5 \text{ \AA}^4 \text{amu}^{-1}$, 64.0 cm^{-1} , 0.5 km mol^{-1} , $0.07 \text{ \AA}^4 \text{amu}^{-1}$, 89.5 cm^{-1} , 0.08 km mol^{-1} , $0.7 \text{ \AA}^4 \text{amu}^{-1}$, 109.1 cm^{-1} , 5.7 km mol^{-1} , $0.2 \text{ \AA}^4 \text{amu}^{-1}$, 115.8 cm^{-1} , 0.2 km mol^{-1} , $1.1 \text{ \AA}^4 \text{amu}^{-1}$.

Table S7B: MP2/aug-cc-pVDZ vibrational frequencies, in cm^{-1} , infrared intensities, in km mol^{-1} , and Raman intensities, in $\text{\AA}^4 \text{amu}^{-1}$, for the lone pair $\cdots\pi$ complex of COFCl and dimethyl ether- d_6 ($\text{O}\cdots\pi_3$) and both monomers, as well as the complexation shift $\Delta\nu$.

	Monomer			Lone pair $\cdots\pi$ complex ($\text{O}\cdots\pi_1$)			
	Frequency	IR intensity	Raman intensity	Frequency	$\Delta\nu$	IR intensity	Raman intensity
COFCl							
ν_1 (A')	1863.0	345.9	16.5	1868.6	5.6	299.7	15.0
ν_2 (A')	1058.0	425.3	2.2	1057.9	-0.1	288.6	1.8
ν_3 (A')	749.9	74.2	11.0	745.0	-4.9	67.9	10.1
ν_4 (A')	499.1	0.3	5.6	494.4	-4.7	0.2	5.2
ν_5 (A')	410.4	0.6	1.8	410.8	0.4	0.3	1.4
ν_6 (A'')	662.8	13.5	0.1	640.9	-21.9	43.1	3.0
DME- d_6							
ν_1 (A_1)	2364.1	17.0	37.1	2366.3	2.2	12.2	25.6
ν_2 (A_1)	2171.1	32.1	166.2	2174.1	3.0	30.5	149.2
ν_3 (A_1)	1153.5	5.3	2.6	1150.2	-3.4	7.1	2.4
ν_4 (A_1)	1085.9	0.09	2.5	1084.6	-1.3	8.4	2.6
ν_5 (A_1)	1058.5	17.5	1.8	1060.3	1.8	65.5	1.2
ν_6 (A_1)	834.8	16.9	7.7	832.1	-2.6	18.5	6.7
ν_7 (A_1)	351.5	1.5	0.7	352.5	1.0	1.8	0.6
ν_8 (A_2)	2297.2	0.0	7.5	2304.2	6.9	0.4	7.0
ν_9 (A_2)	1065.8	0.0	4.2	1065.4	-0.4	4.9	3.6
ν_{10} (A_2)	877.6	0.0	2.2	876.8	-0.8	0.02	2.1
ν_{11} (A_2)	139.5	0.0	0.1	138.2	-1.3	0.007	0.1
ν_{12} (B_1)	2290.4	65.1	51.2	2297.8	7.4	57.8	51.5
ν_{13} (B_1)	1077.4	4.3	0.003	1077.2	-0.1	7.1	0.06
ν_{14} (B_1)	937.8	9.9	0.1	939.1	1.3	9.6	0.2
ν_{15} (B_1)	200.5	4.6	0.0	209.8	9.3	8.0	0.02
ν_{16} (B_2)	2360.7	10.6	31.7	2362.3	1.7	6.9	23.3
ν_{17} (B_2)	2164.0	44.9	0.03	2167.5	3.5	36.0	0.7
ν_{18} (B_2)	1170.3	134.3	0.9	1162.1	-8.2	116.4	0.8
ν_{19} (B_2)	1077.4	0.5	0.2	1075.5	-1.9	4.4	0.3
ν_{20} (B_2)	1066.1	1.6	1.1	1066.4	0.2	11.2	1.1
ν_{21} (B_2)	860.9	0.08	0.9	860.8	-0.1	0.2	1.0

Van der Waals vibrations: 19.6 cm^{-1} , 0.2 km mol^{-1} , $0.5 \text{ \AA}^4 \text{amu}^{-1}$, 50.9 cm^{-1} , 1.2 km mol^{-1} , $0.4 \text{ \AA}^4 \text{amu}^{-1}$, 58.5 cm^{-1} , 0.4 km mol^{-1} , $0.05 \text{ \AA}^4 \text{amu}^{-1}$, 86.5 cm^{-1} , 0.09 km mol^{-1} , $0.7 \text{ \AA}^4 \text{amu}^{-1}$, 96.8 cm^{-1} , 2.9 km mol^{-1} , $0.2 \text{ \AA}^4 \text{amu}^{-1}$, 112.6 cm^{-1} , 0.3 km mol^{-1} , $1.1 \text{ \AA}^4 \text{amu}^{-1}$.

Table S8A: MP2/aug-cc-pVDZ 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 of COFCl 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
COFCl							
$\nu_1 (\text{A}')$	1863.0	345.9	16.5	1852.6	-10.3	364.3	18.3
$\nu_2 (\text{A}')$	1058.0	425.3	2.2	1054.3	-3.7	450.1	2.2
$\nu_3 (\text{A}')$	749.9	74.2	11.0	752.1	2.2	59.7	14.8
$\nu_4 (\text{A}')$	499.1	0.3	5.6	501.8	2.7	2.3	9.1
$\nu_5 (\text{A}')$	410.4	0.6	1.8	416.2	5.8	0.6	1.7
$\nu_6 (\text{A}'')$	662.8	13.5	0.1	668.1	5.3	13.9	0.1
DME							
$\nu_1 (\text{A}_1)$	3188.7	20.1	87.6	3189.0	0.3	20.2	65.8
$\nu_2 (\text{A}_1)$	3024.8	58.6	320.3	3029.9	5.1	69.0	326.9
$\nu_3 (\text{A}_1)$	1505.9	2.9	5.6	1505.9	0.0	1.5	6.7
$\nu_4 (\text{A}_1)$	1473.5	0.0008	2.2	1474.3	0.8	0.1	3.8
$\nu_5 (\text{A}_1)$	1261.1	6.6	0.5	1262.7	1.6	6.6	1.3
$\nu_6 (\text{A}_1)$	942.4	34.7	9.8	938.1	-4.3	70.5	11.5
$\nu_7 (\text{A}_1)$	416.8	2.3	1.0	417.7	0.9	4.8	1.0
$\nu_8 (\text{A}_2)$	3096.2	0.0	14.7	3104.9	8.7	0.07	13.8
$\nu_9 (\text{A}_2)$	1474.8	0.0	11.4	1474.4	-0.4	0.004	10.2
$\nu_{10} (\text{A}_2)$	1157.2	0.0	1.5	1157.0	-0.2	0.0	1.5
$\nu_{11} (\text{A}_2)$	195.2	0.0	0.2	193.7	-1.6	0.0	0.2
$\nu_{12} (\text{B}_1)$	3089.5	107.8	94.2	3098.3	8.8	91.8	109.4
$\nu_{13} (\text{B}_1)$	1489.2	13.0	0.04	1488.9	-0.3	12.4	0.2
$\nu_{14} (\text{B}_1)$	1187.2	7.2	0.04	1187.3	0.1	7.4	0.02
$\nu_{15} (\text{B}_1)$	260.2	5.1	0.002	258.1	-2.2	4.5	0.002
$\nu_{16} (\text{B}_2)$	3187.3	24.6	59.2	3186.8	-0.5	19.3	50.7
$\nu_{17} (\text{B}_2)$	3018.4	55.2	0.6	3024.3	6.0	50.4	2.0
$\nu_{18} (\text{B}_2)$	1490.1	10.3	1.0	1490.1	0.1	11.1	0.9
$\nu_{19} (\text{B}_2)$	1441.5	2.5	1.3	1442.3	0.8	1.2	1.6
$\nu_{20} (\text{B}_2)$	1191.9	98.1	0.7	1188.6	-3.3	90.1	0.7
$\nu_{21} (\text{B}_2)$	1113.8	35.0	1.6	1112.7	-1.1	38.3	2.3

Van der Waals vibrations: 11.8 cm^{-1} , 3.1 km mol^{-1} , $0.01 \text{ \AA}^4 \text{amu}^{-1}$, 12.6 cm^{-1} , 1.1 km mol^{-1} , $0.02 \text{ \AA}^4 \text{amu}^{-1}$, 14.7 cm^{-1} , 0.4 km mol^{-1} , $0.3 \text{ \AA}^4 \text{amu}^{-1}$, 43.1 cm^{-1} , 1.6 km mol^{-1} , $1.0 \text{ \AA}^4 \text{amu}^{-1}$, 62.7 cm^{-1} , 0.6 km mol^{-1} , $0.2 \text{ \AA}^4 \text{amu}^{-1}$, 69.0 cm^{-1} , 0.8 km mol^{-1} , $0.2 \text{ \AA}^4 \text{amu}^{-1}$.

Table S8B: MP2/aug-cc-pVDZ 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 of COFCl 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
COFCl							
$\nu_1 (\text{A}')$	1863.0	345.9	16.5	1852.6	-10.4	364.5	18.2
$\nu_2 (\text{A}')$	1058.0	425.3	2.2	1053.9	-4.1	481.0	2.1
$\nu_3 (\text{A}')$	749.9	74.2	11.0	752.1	2.2	60.5	14.6
$\nu_4 (\text{A}')$	499.1	0.3	5.6	501.8	2.7	2.2	9.1
$\nu_5 (\text{A}')$	410.4	0.6	1.8	416.3	5.9	1.0	1.9
$\nu_6 (\text{A}'')$	662.8	13.5	0.1	668.1	5.3	13.9	0.1
DME-d_6							
$\nu_1 (\text{A}_1)$	2364.1	17.0	37.1	2364.8	0.7	16.7	29.6
$\nu_2 (\text{A}_1)$	2171.1	32.1	166.2	2174.2	3.1	38.3	166.7
$\nu_3 (\text{A}_1)$	1153.5	5.3	2.6	1151.7	-1.9	7.0	4.2
$\nu_4 (\text{A}_1)$	1085.9	0.09	2.5	1085.7	-0.2	0.8	3.1
$\nu_5 (\text{A}_1)$	1058.5	17.5	1.8	1060.7	2.2	3.7	3.8
$\nu_6 (\text{A}_1)$	834.8	16.9	7.7	832.5	-2.3	32.0	8.3
$\nu_7 (\text{A}_1)$	351.5	1.5	0.7	352.9	1.4	3.3	0.6
$\nu_8 (\text{A}_2)$	2297.2	0.0	7.5	2303.9	6.7	0.03	7.0
$\nu_9 (\text{A}_2)$	1065.8	0.0	4.2	1065.3	-0.5	0.002	3.7
$\nu_{10} (\text{A}_2)$	877.6	0.0	2.2	877.3	-0.4	0.0002	2.0
$\nu_{11} (\text{A}_2)$	139.5	0.0	0.1	138.4	-1.1	0.0005	0.1
$\nu_{12} (\text{B}_1)$	2290.4	65.1	51.2	2297.3	6.9	56.2	59.2
$\nu_{13} (\text{B}_1)$	1077.4	4.3	0.003	1076.9	-0.4	4.0	0.01
$\nu_{14} (\text{B}_1)$	937.8	9.9	0.1	937.4	-0.4	9.8	0.2
$\nu_{15} (\text{B}_1)$	200.5	4.6	0.0	198.7	-1.8	4.1	0.005
$\nu_{16} (\text{B}_2)$	2360.7	10.6	31.7	2361.2	0.5	8.1	26.2
$\nu_{17} (\text{B}_2)$	2164.0	44.9	0.03	2167.8	3.8	40.9	0.2
$\nu_{18} (\text{B}_2)$	1170.3	134.3	0.9	1165.5	-4.8	128.3	1.2
$\nu_{19} (\text{B}_2)$	1077.4	0.5	0.2	1077.2	-0.2	0.6	0.2
$\nu_{20} (\text{B}_2)$	1066.1	1.6	1.1	1066.8	0.7	2.5	1.3
$\nu_{21} (\text{B}_2)$	860.9	0.08	0.9	861.1	0.3	0.1	1.1

Van der Waals vibrations: 9.9 cm^{-1} , 2.4 km mol^{-1} , $0.02 \text{ \AA}^4 \text{amu}^{-1}$, 11.7 cm^{-1} , 0.4 km mol^{-1} , $0.09 \text{ \AA}^4 \text{amu}^{-1}$, 13.5 cm^{-1} , 0.3 km mol^{-1} , $0.3 \text{ \AA}^4 \text{amu}^{-1}$, 42.5 cm^{-1} , 1.2 km mol^{-1} , $1.0 \text{ \AA}^4 \text{amu}^{-1}$, 60.3 cm^{-1} , 0.5 km mol^{-1} , $0.2 \text{ \AA}^4 \text{amu}^{-1}$, 66.2 cm^{-1} , 0.7 km mol^{-1} , $0.2 \text{ \AA}^4 \text{amu}^{-1}$.

Table S9 : Experimental infrared frequencies for the monomer and complex, as well as experimental complexation shifts (Δv_{exp}) and MP2/aug-cc-pVDZ calculated complexation shifts for the global ($\Delta v_{\text{calc, O}\cdots\pi \text{ global}}$) and local minimum ($\Delta v_{\text{calc, O}\cdots\pi \text{ local}}$), in cm^{-1} , of the $\text{O}\cdots\pi$ bonded complex of COF_2 with DME- d_6 dissolved in LKr at 120 K.

	Assignment	Symmetry	v_{monomer}	v_{complex}	Δv_{exp}	$\Delta v_{\text{calc,}}$	$\Delta v_{\text{calc,}}$
						O $\cdots\pi$ global	O $\cdots\pi$ local
COF ₂	ν_1	A ₁	1934.6	1930.5	-4.1	-6.6	0.2
	$2\nu_2$	A ₁	1905.4	1901.2	-4.2	-5.2	-10.1
	ν_4	B ₁	1232.7	1233.4	0.7	6.1	-3.5
	ν_2	A ₁	960.1	958.0	-2.1	-2.6	-5.1
	ν_6	B ₂	769.0	747.3	-21.7	-30.3	-29.5
	ν_5	B ₁	662.7	662.6	-0.1	1.4	-0.5
	ν_3	A ₁	580.5	580.5	0.0	-1.2	-0.2
DME- d_6	ν_1	A ₁	2243.3	2249.3	6.0	4.0	5.2
	ν_{16}	B ₂	2243.3	2249.3	6.0	3.9	3.3
	ν_{12}	B ₁	2179.8	2190.3	10.5	13.9	11.8
	ν_2	A ₁	2054.3	2059.7	5.4	6.6	5.7
	ν_{17}	B ₂	2049.5	2055.7	6.2	7.6	6.6
	ν_{18}	B ₂	1153.4	1146.1	-7.3	-15.3	-9.3
	ν_3	A ₁	1144.7	1143.2	-1.5	-4.3	-3.0
	ν_{13}	B ₁	1060.5	1061.7	1.2	0.6	0.3
	ν_{20}	B ₂	1057.7	1058.5	0.8	-1.1	0.9
	ν_{19}	B ₂	1057.7	1058.5	0.8	-0.8	-1.7
	ν_5	A ₁	1050.7	1053.6	2.9	1.0	2.0
	ν_{14}	B ₁	929.0	930.2	1.2	3.6	2.2
	ν_6	A ₁	826.3	825.5	-0.8	-3.5	-2.4

Table S10 Experimental infrared frequencies for the monomer and complex, as well as experimental complexation shifts (Δv_{exp}) and MP2/aug-cc-pVDZ calculated complexation shifts (Δv_{calc}), in cm^{-1} , for the $\text{O} \cdots \pi$ bonded complexes and halogen bonded complex of COFCl with DME- d_6 dissolved in LKr at 120 K.

	Assignment	Sym	ν_{monomer}	ν_{complex}	Δv_{exp}	$\Delta v_{\text{calc, O} \cdots \pi 1}$	$\Delta v_{\text{calc, O} \cdots \pi 2}$	$\Delta v_{\text{calc, O} \cdots \pi 3}$	ν_{complex}	Δv_{exp}	$\Delta v_{\text{calc, XB}}$
COFCl	$2\nu_2$	A'	2158.0	2164.2 ^b	6.2	-17.7	-3.5 ^a	-0.3 ^a			-8.2
	ν_1	A'	1863.8	1864.4	0.6	2.5	-3.5	5.6	1856.2	-7.6	-10.4
	$\nu_2 + \nu_3$	A'	1832.1	1834.4	2.3	-10.3	-1.4 ^a	-5.0 ^a	1834.4	2.3	-1.9
			1823.2	1824.3	1.1						
	ν_2	A'	1083.9	1086.6	2.7	-8.9	-1.7 ^a	-0.1 ^a	1081.0	-2.9	-4.1
	ν_2 (^{13}C)	A'	1056.4	1058.4 ^b	2.0	-8.5	1.4	1.9	1052.3 ^b	-4.1	-4.8
	ν_3 (^{35}Cl)	A'	761.8	761.4	-0.4	-1.5	0.3	-4.9	764.1	2.3	2.2
	ν_3 (^{37}Cl)	A'	759.8	759.6	-0.2	-1.4	0.4	-4.7	761.8	2.0	2.1
	ν_6	A''	663.6	649.6	-14.0	-21.9	-20.8	-21.9	668.2	4.6	5.3
DME- d_6	ν_1	A_1	2243.3	2248.2	4.9	3.5	2.9	2.2	2248.2	4.9	0.7
	ν_{16}	B_2	2243.3	2244.8	1.5	0.9	1.4	1.7	2244.8	1.5	0.5
	ν_{12}	B_1	2179.8	2187.2	7.4	9.4	10.4	7.4	2187.2	7.4	6.9
	ν_2	A_1	2054.3	2057.9	3.6	4.2	4.6	3.0	2057.9	3.6	3.1
	ν_{17}	B_2	2049.5	2053.6	4.1	4.9	5.3	3.5	2053.6	4.1	3.8
	ν_{18}	B_2	1153.4	1147.8	-5.6	-9.4	-12.1	-8.2	1147.8	-5.6	-4.8
	ν_3	A_1	1144.7			-3.4	-4.3	-3.4			-1.9
	ν_{13}	B_1	1060.5	1060.7	0.2	-0.5	0.0	-0.1	1060.7	0.2	-0.4
	ν_{19}	B_2	1057.7	1058.4	0.7	-1.8	-0.9	-1.9	1058.4	0.7	-0.2
	ν_{20}	B_2	1057.7	1058.4	0.7	0.1	-1.3	0.2	1058.4	0.7	0.7
	ν_5	A_1	1050.7	1052.3	1.6	1.0	0.5	1.8	1052.3	1.6	2.2
	ν_{14}	B_1	929.0	929.8	0.8	1.5	2.4	1.3	929.8	0.8	-0.4
	ν_{21}	B_2	857.8			-0.3	-0.8	-0.1			0.3
	ν_6	A_1	826.3	825.0	-1.3	-3.2	-3.8	-2.6	825.0	-1.3	-2.3

^a mechanical coupling between COFCl ν_2 mode and DME- d_6 modes causes deviating calculated shifts as compared to the nondeuterated species.

^b overlap with DME- d_6 bands.

Table S11: Overview of the different van 't Hoff plots constructed for the lone pair $\cdots\pi$ complex between COF₂ and DME or DME-d₆ 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_{COF_2}	x_{DME}	Integrated COF ₂ band (cm ⁻¹)	Integrated DME band (cm ⁻¹)	Integrated Complex band (cm ⁻¹)	ΔH° (LKr) ^a
9.4×10^{-5}	1.9×10^{-3}	1269.4 - 1202.9	2117 - 2070	1960 - 1880	-14.1(1)
9.4×10^{-5}	1.9×10^{-3}	1965 - 1886	2040 - 2006	971 - 947	-14.50(8)
5.6×10^{-5}	5.6×10^{-4}	2000 - 1820	3050 - 2770	1950 - 1891	-14.9(2)
5.6×10^{-5}	5.6×10^{-4}	1296 - 1180.5	970 - 900	1255 - 1210	-14.2(2)
9.4×10^{-5}	9.4×10^{-4}	1970 - 1880	3035 - 2965	1975 - 1876	-14.4(1)
5.6×10^{-4}	5.6×10^{-4}	1000 - 930	3050 - 2760	764 - 728	-15.00(5)
5.6×10^{-4}	5.6×10^{-4}	797 - 748	980 - 890	937 - 912	-14.83(9)
5.6×10^{-4}	1.9×10^{-4}	1000 - 930	1215 - 1140	972 - 946	-14.5(1)
5.6×10^{-4}	1.9×10^{-4}	794 - 750	3050 - 2760	1113 - 1076	-15.0(2)
5.6×10^{-4}	1.9×10^{-4b}	1000 - 930	2273 - 2222	971 - 947	-14.3(1)
5.6×10^{-4}	1.9×10^{-4b}	797 - 784	2085 - 2025	2215 - 2171	-14.37(7)
5.6×10^{-5}	5.6×10^{-4b}	1980 - 1880	855 - 805	1950 - 1915	-14.7(1)
5.6×10^{-5}	5.6×10^{-4b}	1300 - 1177	2272 - 2222	1255 - 1210	-14.3(1)

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

^b Measurement involving DME-d₆, rather than DME.

Table S12: Overview of the different van 't Hoff plots constructed for the lone pair $\cdots\pi$ complex between COFCl and DME or DME-d₆ 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_{COF_2}	x_{DME}	Integrated COF ₂ band (cm ⁻¹)	Integrated DME band (cm ⁻¹)	Integrated Complex band (cm ⁻¹)	ΔH° (LKr) ^a
9.4×10^{-5}	4.7×10^{-3}	1920 - 1801	2130 - 2065	1885 - 1847	-11.4(2)
9.4×10^{-5}	4.7×10^{-3}	1130 - 1045	2053 - 1993	1885 - 1847	-11.3(2)
1.9×10^{-4}	1.9×10^{-3}	682 - 652	2050 - 1990	1845 - 1819	-11.5(2)
1.9×10^{-4}	1.9×10^{-3}	778 - 748	2050 - 1990	767 - 754	-11.4(2)
9.4×10^{-4}	4.7×10^{-3}	686 - 648	2130 - 2065	662 - 637	-11.23(7)
9.4×10^{-4}	4.7×10^{-3}	2190 - 2130	2053 - 1993	662 - 637	-11.35(7)
9.4×10^{-5}	4.7×10^{-3b}	1920 - 1801	2315 - 2275	1885 - 1847	-11.7(2)
9.4×10^{-5}	4.7×10^{-3b}	1130 - 1045	1985 - 1958	1847 - 1818	-11.7(3)
9.4×10^{-4}	4.7×10^{-3b}	2190 - 2130	2315 - 2275	661 - 640	-11.0(1)
1.9×10^{-4}	4.7×10^{-3b}	683 - 652	1986 - 1958	1846.5 - 1818	-11.5(2)

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

^b Measurement involving DME-d₆, rather than DME.

Table S13: Overview of the MAD analysis of the different O $\cdots\pi$ complexes between COFCl and dimethyl ether, calculated using MP2 and B3LYP (with GD3 dispersion) at the aug-cc-pVDZ and aug-cc-pVTZ levels of theory. Values are given for the 7 assigned COFCl modes with and without the 11 assigned DME modes in cm⁻¹.

MAD values in cm ⁻¹	Assigned modes	O $\cdots\pi_1$	O $\cdots\pi_2$	O $\cdots\pi_3$
MP2/aug-cc-pVDZ	COFCl	7.4	2.3	3.5
	COFCl+DME	4.8	2.7	2.6
MP2/aug-cc-pVTZ	COFCl	8.1	3.3	4.7
	COFCl+DME	5.1	3.1	3.2
B3LYP/aug-cc-pVDZ	COFCl	7.9	3.0	4.2
	COFCl+DME	5.6	3.9	3.9
B3LYP/aug-cc-pVTZ	COFCl	6.9	3.7	4.6
	COFCl+DME	5.2	4.2	4.1

	CCSD(T)/CBS extrapolated energy (kJ mol^{-1})	Electron density in (3,-1) intermolecular bond critical point (10^{-2} a.u.)
$\text{COF}_2 \cdot \text{DME O} \cdots \pi$ local minimum	-23.8	1.45
$\text{COF}_2 \cdot \text{DME O} \cdots \pi$ global minimum	-22.6	1.40
$\text{COFCI} \cdot \text{DME O} \cdots \pi_1$	-20.2	1.20
$\text{COFCI} \cdot \text{DME O} \cdots \pi_2$	-21.3	1.22
$\text{COFCI} \cdot \text{DME O} \cdots \pi_3$	-20.2	1.25
$\text{COFCI} \cdot \text{DME XB}$	-12.4	1.04

Figure S1: Overview of the electron densities in the (3,-1) bond critical point due to the formation of an intermolecular interaction and the corresponding extrapolated CCSD(T)/CBS complexation energies for all complexes studied.

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 lone pair $\cdots\pi$ complexes between COF₂ and dimethyl ether. The global minimum is shown on top, the local minimum on the bottom.

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 lone pair $\cdots\pi$ complexes (from top to second to last: $\text{O}\cdots\pi_1$, $\text{O}\cdots\pi_2$ and $\text{O}\cdots\pi_3$) and the halogen bonded complex (bottom) between COFCl and dimethyl ether.

Figure S4: Infrared spectra of selected spectral regions of mixtures of COF_2 and DME-d_6 dissolved in LKr at 120 K. In each panel, trace *a* represents the mixed solution, while traces *b* and *c* show the solution containing only COF_2 or DME-d_6 , respectively. Trace *d* represents the spectrum of the complex and is obtained by subtracting the rescaled traces *b* and *c* from trace *a*. Estimated mole fractions of the solutions of the mixtures are 5.6×10^{-5} for COF_2 and 5.6×10^{-4} for DME-d_6 in panels A and D and 5.6×10^{-4} for COF_2 and 1.9×10^{-4} for DME-d_6 in panels B and C.

Figure S5: Infrared spectra of selected spectral regions of mixtures of COFCl and DME dissolved in LKr at 120 K. In each panel, trace *a* represents the mixed solution of COFCl with DME , while traces *b* and *c* show the solution containing only COFCl or DME , respectively. Trace *d* shows the rescaled spectrum of CO_2 , whereas trace *e* shows the spectrum of the rescaled $\text{CO}_2\cdot\text{DME}$ complex, which has been obtained from a separate measurement. Finally, trace *f* shows the spectrum of the $\text{COFCl}\cdot\text{DME}$ complex, obtained by subtracting traces *b-e* from trace *a*. Bands due to the lone pair $\cdots\pi$ complex and halogen bonded complex observed in trace *f* are marked with an open circle ($^\circ$) or asterisk (*), respectively. Estimated mole fractions of the solutions of the mixtures are 5.6×10^{-5} for COFCl and

4.7×10^{-3} for DME in panel A, 5.6×10^{-4} for COFCl and 4.7×10^{-3} for DME in panel B and 6.6×10^{-4} for COFCl and 1.5×10^{-4} for DME in panel C.

Figure S6: Infrared spectra of the C-H stretching region for mixtures of COFCl and DME dissolved in LKr at 120 K. Trace *a* represents the mixed solution of COFCl with DME, while traces *b* and *c* show the solution containing only COFCl or DME, respectively. Trace *d* shows the rescaled spectrum of CO₂, whereas trace *e* shows the spectrum of the rescaled CO₂·DME complex, which has been obtained from a separate measurement. Finally, trace *f* shows the spectrum of the COFCl·DME complex, obtained by subtracting traces *b-e* from trace *a*. For reasons of clarity, trace *f* has been multiplied by a factor of 10. Estimated mole fractions of the solution of the mixture are 6.6×10^{-4} for COFCl and 1.5×10^{-4} for DME in panel C.

Figure S7: Infrared spectra of selected spectral regions of mixtures of COFCl and DME-d₆ dissolved in LKr at 120 K. In each panel, trace *a* represents the mixed solution of COFCl with DME-d₆, while traces *b* and *c* show the solution containing only COFCl or DME-d₆, respectively. Trace *d* shows the rescaled spectrum of CO₂, whereas trace *e* shows the spectrum of the rescaled CO₂·DME-d₆ complex, which has been obtained from a separate measurement. Finally, trace *f* shows the spectrum of the COFCl·DME-d₆ complex, obtained by subtracting traces *b-e* from trace *a*. Bands due to the lone pair... π complex and halogen bonded complex observed in trace *f* are marked with an open circle (°) or asterisk (*), respectively. Estimated mole fractions of the solutions of the mixtures are 1.9×10^{-4} for

COFCl and 4.7×10^{-3} for DME-d₆ in panels A, C and D and 5.6×10^{-5} for COFCl and 4.7×10^{-3} for DME-d₆ in panel D.

Addendum: Description of the subtraction procedure for COFCl·DME(-d₆) spectra:

In order to obtain spectra of the COFCl·DME(-d₆) complex bands, spectra of both COFCl and DME(-d₆) have to be rescaled and subtracted from the spectrum of the mixture. As the COFCl sample contains an appreciable amount of CO₂, which is also able to form complexes with DME and whose π_u mode overlaps with the ν_6 mode of COFCl, bands caused by CO₂ and CO₂·DME(-d₆) complex also have to be subtracted from the spectrum of the COFCl·DME(-d₆) mixture to obtain a spectrum containing solely bands due to the COFCl·DME complexes. An example of the used subtraction procedure is given here.

As many bands of DME(-d₆) are well isolated from the CO₂ and COFCl modes, these spectral regions will only contain DME(-d₆) monomer bands and accompanying complex bands from the interactions with COFCl and CO₂. The region used to determine the subtraction factor is chosen based on *ab initio* calculated complexation shifts, so that overlap with complex bands is avoided. An example of this subtraction for DME is given in Figure S8.

Figure S8: Subtraction of DME from the COFCl·DME mixture in LKr at 120 K which also contains CO₂ and its accompanying complex with DME. Trace *a* shows the spectrum of the mixture, while trace *b* shows the rescaled DME spectrum. Trace *c* shows the spectrum resulting from the subtraction procedure.

In order to perform a subtraction of the COFCl monomer in its ν_6 spectral region, CO₂ and CO₂·DME(-d₆) complex also have to be accounted for. These latter two components can be dealt with before the COFCl subtraction, if the CO₂ σ_u^+ mode around 2340 cm⁻¹ is in-scale, or have to be subtracted simultaneous in the COFCl ν_6 region if the σ_u^+ mode of CO₂ is out-of-scale. To subtract CO₂ and the CO₂·DME(-d₆) complex in the σ_u^+ spectral region of CO₂, a spectrum containing solely the CO₂·DME(-d₆) complex must be obtained. To this end, CO₂·DME(-d₆) mixtures were measured separately and subtracted beforehand.

Figure S9: Subtraction of CO₂ and DME from the CO₂·DME mixture, measured at 120 K in LKr. Trace *a* shows the CO₂·DME mixture, while traces *b* and *c* show the rescaled CO₂ and DME spectra, respectively. Trace *d* shows the spectrum resulting from the subtraction procedure, containing solely CO₂·DME complex.

Figure S10: Subtraction of CO₂ and CO₂·DME complex from the spectrum obtained in Figure S8. Trace *a* shows the spectrum obtained in Figure S7, trace *b* shows the rescaled CO₂ spectrum and trace *c* shows the rescaled CO₂·DME complex spectrum, obtained in Figure S9. The resulting spectrum is shown in trace *d*. All measurements were performed at 120 K in LKr.

Before COFCl can be subtracted from the spectrum obtained in Figure S10, CO₂ has to be subtracted from the monomer spectrum. As CO₂ and COFCl don't form any (appreciable amount of) complex, subtraction in the σ_u^+ spectral region (near 2340 cm⁻¹) of CO₂ is straightforward.

Figure S11: Subtraction of CO₂ from the COFCl monomer spectra. Trace *a* shows the COFCl spectrum also containing CO₂, trace *b* shows the rescaled CO₂ spectrum and trace *c* shows the resulting spectrum containing only COFCl bands. All measurements were performed at 120 K in LKr.

Finally, the CO₂ subtracted spectrum of COFCl can be subtracted from the spectrum obtained in Figure S10 to obtain a spectrum containing solely bands due to the COFCl·DME(-d₆) complex.

Figure S12: Subtraction of COFCl from the spectrum obtained in Figure S10, yielding a spectrum containing solely COFCl·DME complex bands. Trace *a* shows the spectrum obtained in Figure S10, trace *b* shows the COFCl spectrum, corrected for CO₂, obtained in Figure S11. The spectrum resulting from the subtraction procedure containing only COFCl·DME complex bands is shown in trace *c*.