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Exploiting the σ -hole Concept: an Infrared and Raman based characterization of the S...O Chalcogen Bond between 2,2,4,4-Tetrafluoro-1,3-dithiethane and Dimethyl Ether

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Abstract

In the last decade halogen bonds, noncovalent interactions formed between positive regions in the electrostatic potential on halogen atoms, often referred to as σ -holes, and electron rich sites, have gained a lot of interest. Recently this interest has been expanded towards interactions with group V and group VI elements, giving rise to pnictogen and chalcogen bonds. Although chalcogen bonds have already shown some promising results for applications in crystallography and catalysis, experimental results characterizing these noncovalent interactions remain scarce. In this combined experimental and

theoretical study, original data allowing the characterization of S...O chalcogen bonds is obtained by studying the 1:1 molecular complexes between 2,2,4,4-tetrafluoro-1,3-dithiethane (C₂F₄S₂) and dimethyl ether (DME).

Ab initio calculations of the C₂F₄S₂·DME dimer yield two stable chalcogen bonded isomers, the difference being the presence or absence of secondary F...H interactions. Liquid krypton solutions containing C₂F₄S₂ and DME were studied using FTIR and Raman spectroscopy. Upon subtraction of rescaled monomer spectra, clear complex bands are observed. The observed complexation shifts agree favourably with the *ab initio* calculated shifts of the chalcogen bonded complexes. The 1:1 stoichiometry of the complex is confirmed and a complexation enthalpy of -13.5(1) kJ mol⁻¹ is found, which is in good agreement with the calculated values. A Ziegler-Rauk energy decomposition analysis revealed that electrostatic interactions prominently dominate over orbital interactions. Nevertheless, significant charge transfer occurs from the oxygen in DME to one of the sulfur atoms in C₂F₄S₂ and the carbon along the extension of the chalcogen bond.

1. Introduction

For many years, noncovalent interactions formed through σ -holes,^[1] positive regions in the electrostatic potential opposite to a covalent bond, have been studied theoretically and experimentally. Heretofore most attention has focused on interactions formed through the σ -hole on a halogen atom, the so-called halogen bonds, proving the value of these noncovalent interactions in the fields of, amongst others, crystal engineering,^[2] supramolecular chemistry^[3] and rational drug design.^[4] Nevertheless, substantial evidence for the existence of interactions between electron rich sites and the σ -holes on Group VI and Group V elements, giving rise to chalcogen bonds and pnictogen bonds respectively, has been found in theoretical and crystallographical studies.^[5] In a recent study by Garrett et al.^[6] the existence of tellurium based chalcogen bonds has also been described in solution for the first time using UV-VIS, ¹H and ¹⁹F NMR experiments. Furthermore, chalcogen bonds may also be of interest in the field of catalysis^[7] and anion recognition,^[8] as they, just as halogen bonds, are more directional and hydrophobic than hydrogen bonds.

Because of the presence of oxygen and sulfur in proteins, several studies concerning chalcogen bonds have focused specifically on S...O chalcogen bonds, suggesting that these interactions might play a role in controlling protein structures^[9] and in the enzymatic activity of sulfur-containing compounds.^[10] As chalcogen bonding can affect binding of possible drug molecules, the principle of chalcogen bonding is of interest to researchers developing new pharmaceuticals.^[11] Motivated by the biochemical importance of this kind of interaction, most of the previous studies have focused on the interactions formed with an sp²-hybridized carbonyl oxygen atom.^[5b, 12]

Although S...O chalcogen bonds involving neutral species have already shown some promising results for applications, experimental results characterizing these noncovalent interactions remain scarce. Therefore, within this combined experimental and theoretical study, the moderately strong S...O chalcogen bond formed between 2,2,4,4-tetrafluoro-1,3-dithiethane ($C_2F_4S_2$) and dimethyl ether (DME) is investigated. The experimental study involves an IR and Raman spectroscopic study of the formation of S...O bonded $C_2S_2F_4$ -DME dimers in liquid krypton. The basis for this study is the observation that, in general, cryospectroscopy forms an excellent technique to study weak noncovalent interactions, as the measurements are performed at moderately low temperatures in a solution where the solvent is only weakly interacting with the solutes, thereby creating a pseudo-gas phase experiment in which the 1:1 (or higher) adducts formed are only weakly distorted by solvent interactions. Furthermore, by working at thermodynamic equilibrium and by measuring spectra at various temperatures, thermodynamic properties of the noncovalent interactions, such as the complexation enthalpy, can be determined.

To assign the complex bands observed in the spectra, the measurements are supported by *ab initio* calculations. By performing Monte Carlo-Free Energy Perturbation (MC-FEP) simulations and using statistical thermodynamics, calculated complexation enthalpies are obtained which can be compared with the experimental values. The chalcogen bond energy is qualitatively analyzed via the Ziegler-Rauk Energy Decomposition Analysis (EDA) by decomposing it into its different components: orbital interactions, electrostatic interactions, Pauli repulsion (often associated with steric repulsion) and dispersion interaction. The orbital interactions are further scrutinized by a Natural Orbital for Chemical Valence (NOCV) analysis allowing the quantification and visualization of the charge density reorganization upon chalcogen bond formation. In addition, a noncovalent interaction (NCI) analysis is performed, revealing which types of weak interactions are present to stabilize the complex.

The choice for $C_2F_4S_2$ as a chalcogen bond donor was based on the observation that, in order to obtain complexes with an appreciable strength, a highly fluorinated molecule is preferred, a strategy that has been followed extensively in studies involving halogen bonding^[13] and has also been proven to work for chalcogen bonding.^[14] The choice for $C_2F_4S_2$ was further motivated by the fact that high purity (>97 %) samples are commercially available, and by the observation that $C_2F_4S_2$ is a rigid molecule with D_{2h} symmetry. This rigidity reduces complexity due to internal rotations or large amplitude motions, while the use of a high symmetry molecule allows to apply the principles of mutual exclusivity and thus allows the complementarity of IR and Raman spectroscopy to be exploited. As a Lewis base the choice was made for DME, which has been used extensively as an oxygen donor in previous cryospectroscopic studies.^[15] DME has proven to possess no self-associating properties, a phenomenon which is known to limit a thorough analysis^[16] of the data and, in contrast to acetone and ethylene oxide, is known to have a substantial solubility in liquid noble gases.

Inspection of the electrostatic potential of $C_2F_4S_2$, shown in Figure 1, reveals the presence of four equivalent σ -holes, two on both sulfur atoms. The presence of multiple σ -holes implies the ability of this molecule to simultaneously undergo interactions with multiple Lewis bases, giving rise to complexes of higher stoichiometric ratio's. Therefore, special interest will be given to the experimental determination of the complexation stoichiometry within this study.

Figure 1: Electrostatic potential of $C_2F_4S_2$ on the molecular surface defined by the 0.001 electrons Bohr^{-3} contour of the electron density, calculated at the MP2/aug-cc-pVDZ level, with positive, neutral and negative regions shown in blue, green and red, respectively.

2. Experimental

The sample of 2,2,4,4-tetrafluoro-1,3-dithiethane ($C_2F_4S_2$, 97%), purchased from Alfa Aesar, was transferred into a glass sample tube and degassed using a freeze-thaw cycle procedure. Dimethyl ether (DME, 99+%) was purchased Sigma-Aldrich and was used without further purification. The solvent gas krypton was supplied by Air Liquide and had a stated purity of 99.9995%.

The IR spectra were recorded on a Bruker 66v FTIR spectrometer, equipped with a global source, a Ge/KBr beam splitter and MCT detector. Measurements were conducted in cells equipped with Si windows and a path length of 10 mm to obtain spectra between 6500 cm^{-1} and 450 cm^{-1} . All interferograms were averaged over 500 scans, Blackman-Harris 3-term apodized and Fourier transformed to yield spectra with a resolution of 0.5 cm^{-1} .

Raman spectra were recorded using a Trivista 557 spectrometer equipped with a $f=70\text{ cm}$ spectrograph with a $1800\text{ lines mm}^{-1}$ grating and a CCD detector. The 514.5 nm line of an argon ion laser was used for Raman excitation, and the power of the incident laser beam was set to 0.8 W . Frequencies were calibrated using Ne emission lines, and are expected to be accurate to 0.5 cm^{-1} . The experimental setup, which includes a liquid cell equipped with four quartz windows at right angles has been described by Herrebout.^[17]

Estimated mole fractions of the solutions varied between 2.8×10^{-5} and 9.4×10^{-4} for $C_2F_4S_2$ and 2.6×10^{-4} and 7.5×10^{-4} for DME. As the experimental setups do 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.

Complexation stoichiometries were determined by performing isothermal concentration studies in which the concentrations of the solutes are systematically varied.^[17] By combining the Lambert-Beer law with the equilibrium constant for the formation of the complex A_mB_n

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 .

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

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 $y=n$. By preparing a series of plots for various integer values of x and y and evaluating their linearity, the complex stoichiometry can be established.

Complexation enthalpies were determined using van 't Hoff plots, based on measurements performed in the 120-156 K temperature interval. The approach typically involves 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, to obtain a spectrum that solely contains bands due to the complexes present.^[17] Subsequently, band intensities for monomers and complexes are integrated numerically. Thermal expansion of the solvent gas during temperature studies was accounted for using the method published by van der Veken.^[18]

To support the experimental measurements, MP2/aug-cc-pVDZ calculations were performed using Gaussian09.^[19] During all *ab initio* calculations, the counterpoise technique^[20] was used to account for basis set superposition error. Energies at the basis set limit were calculated with Molpro^[21] using the extrapolation scheme of Truhlar^[22]

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

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

In these expressions $\alpha = 3.4$ and $\beta = 2.2$,^[22] while energies with subscript 2 and 3 are calculated using the aug-cc-pVDZ and aug-cc-pVTZ basis sets respectively.

An additional correction for higher order correlation effects yielding results of $E_{CBS}^{CCSD(T)}$ quality is made using the method of Jurečka and Hobza^[23]

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

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

Complexation enthalpies in the vapour phase $\Delta H^\circ(\text{vap,calc})$ were obtained from the complexation energies $\Delta E(\text{CCSD(T)})$ by applying a zero-point energy correction and a correction for thermal effects. Correction of the calculated enthalpy values with solvent effects of the liquid noble gas (LN_g) yields complexation enthalpies in solution $\Delta H^\circ(\text{LN}_g, \text{calc})$, which can be compared with the experimental values $\Delta H^\circ(\text{LN}_g)$. Corrections for thermal effects and zero-point vibrational contributions were obtained using statistical thermodynamics, using MP2/aug-cc-pVDZ data. Effects of solvation were accounted for using a Monte Carlo-Free Energy Perturbation^[17, 24]

To further rationalize the nature of the complex present, conceptual quantum chemical calculations are performed. Secondary interactions are analyzed using the noncovalent interactions (NCI) index based on MP2 electron densities, which is visualized using NCIPLOT.^[25] A Ziegler-Rauk-type energy decomposition analysis (EDA)^[26] and Natural Orbital for Chemical Valence (NOCV)^[27] analyses were performed on the MP2/aug-cc-pVDZ optimized geometries, as implemented in ADF2013^[28], using the gradient-corrected PBE functional and the TZ2P basis set^[29] in combination with dispersion correction through Grimme's D3 method.^[30] Relativistic effects were considered by using the zeroth-order regular approximation (ZORA).^[31] This particular EDA was chosen since it is rooted in Density Functional Theory and allows to decompose interactions into charge transfer and electrostatic components, in analogy with the perturbation expansions from conceptual DFT,^[32] where the interaction energy between two chemical species is written as contributions from their changes in number of electrons and external potentials.

3. Results

3.1. *Ab initio* calculations

Ab initio calculations yielded two stable isomers for the C₂F₄S₂ complex with DME, both of which are formed through a S...O chalcogen bond. Both complexes have a C_s symmetry and were optimized without imposing symmetry restrictions. The complex geometries are shown in Figure 2, while the main intermolecular parameters and energetics are summarized in Table 1. Cartesian coordinates of the monomers and complexes are given in Tables S1 and S2 of the ESI. In the first complex the methyl groups are facing towards the fluorine atoms of C₂F₄S₂, while in the other complex an interaction is formed with the other oxygen lone pair, resulting in a complex geometry where the

methyl groups are facing away from the fluorine atoms. When the methyl groups are facing towards the electronegative fluorine atoms, which have a negative electrostatic potential, the formation of secondary $F\cdots H$ can be expected even though at 2.92 Å the $F\cdots H$ distance is still larger than the sum of van der Waal radii of 2.55 Å. The presence of secondary interactions was confirmed using the NCI approach.^[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 Figure S1 of the ESI. When comparing the gradient isosurfaces of the complex geometries where the methyl groups are facing toward (top) and away from (bottom) the fluorine atoms, two extensions of the gradient isosurface are clearly visible between the hydrogen atoms of the methyl groups and the fluorine atoms in the top image, thus revealing the presence of these secondary interactions.

Figure 2: MP2/aug-cc-pVDZ geometries for the chalcogen bonded complexes between $C_2F_4S_2$ and DME. The complex geometry with secondary $C-F\cdots H-C$ interactions is given at the top, while the complex geometry without the secondary interactions is given at the bottom.

Table 1: Intermolecular distance R_{eq} (Å) and bond angles ($^\circ$) from the MP2/aug-cc-pVDZ optimized geometries, MP2/aug-cc-pVDZ $\Delta E(DZ)$ and CCSD(T)/CBS extrapolated complexation energies $\Delta E(CCSD(T))$, calculated vapour phase complexation enthalpies ΔH° (vap,calc), the calculated complexation enthalpies in liquid krypton (ΔH° (LKr,calc)) and the corresponding experimentally obtained complexation enthalpy (ΔH° (LKr)) (kJ mol^{-1}) of the chalcogen bonded complexes between $C_2F_4S_2$ and DME.

	Chalcogen bonded complexes	
	With secondary interactions	Without secondary interactions
Symmetry	C_s	C_s
$R_{eq}=R_{S\cdots O}$	2.81	2.80
$R_{eq}/\Sigma r_{vdW}$	0.864	0.862
$\varphi_{C-S\cdots O}$	80.0	77.6
$\psi_{C-O\cdots S}$	121.6	106.5
ΔE (DZ)	-23.4	-22.2
ΔE (CCSD(T))	-25.0	-23.5
ΔH° (vap,calc)	-22.1	-20.8

ΔH° (LKr,calc)	-16.6	-15.2
Experimental ΔH° (LKr)	-13.5(1)	

Even though the complex without secondary F...H interactions has a slightly smaller intermolecular distance, the complexation energies reveal that the complex with the secondary F...H interactions is indeed the most stable geometry, the energy difference at the CCSD(T)/CBS level of theory being 1.5 kJ mol⁻¹.

A transition state search ^[33] between both complex geometries yielded a transition state with an imaginary frequency of -42 cm⁻¹, merely 0.7 kJ mol⁻¹ higher in energy at the MP2/aug-cc-pVDZ level than the complex geometry without secondary interactions. Consequently, rapid interconversion between both complex geometries is expected during the experimental measurements. An energy diagram of both minima and the transition state is given in Figure S2 of the ESI, the Cartesian coordinates of the transition state are given in Table S2.3 of the ESI.

Table 2: Complexation energies (ΔE_{int}) at the PBE/TZ2P level, together with the Ziegler-Rauk energy decomposition components (ΔE_{Pauli} , ΔV_{elst} , ΔE_{oi} , E_{disp}) for the chalcogen bonded complexes with and without secondary F...H interactions. For comparison, the EDA analysis for the halogen-bonded complex CF₃I...DME, taken from a previous study ^[34], has been included. All values are in kJ mol⁻¹. The relative contributions of the stabilizing interactions are indicated in parentheses.

Complex	ΔE_{int}	ΔE_{Pauli}	ΔV_{elst}	ΔE_{oi}	E_{disp}
With F...H	-24.1	36.1	-32.5 (54%)	-17.7 (29%)	-9.9 (17%)
Without F...H	-23.9	40.5	-33.7 (52%)	-21.3 (33%)	-9.4 (15%)
CF ₃ I...DME	-24.0	38.0	-35.9 (58%)	-20.3 (33%)	-5.7 (9%)

An energy decomposition analysis (EDA) of the interaction energy between C₂F₄S₂ and DME was carried out to evaluate the relative importance of electrostatic and orbital interactions, steric effects, and dispersion interactions. The results are given in Table 2. The PBE/TZ2P interaction energies agree well with the MP2/aug-cc-pVDZ and the CCSD(T)/CBS extrapolated complexation energies in Table 1. However, the energy difference between the complex with and without secondary interactions is now negligible. In both complexes, the electrostatic interactions (ΔV_{elst}) clearly dominate the orbital interactions (ΔE_{oi}). The larger electrostatic and particularly orbital interaction energy values observed for the complex without secondary interactions are compensated by a larger destabilizing Pauli repulsion term (ΔE_{Pauli}). The orbital interaction energy (ΔE_{oi}) represents the stabilization originating from all interactions of occupied and unoccupied molecular orbitals between the two fragments as well as the stabilizing orbital interactions within one single fragment upon complex formation. The Natural Orbital for Chemical Valence (NOCV) analysis provides a special means for further decomposing and

visualizing the components (so-called NOCV orbitals) of the charge density reorganization resulting from the interacting orbitals of the two fragments. Only one significant NOCV determines the charge distribution rearrangement upon chalcogen-bond formation, shown in Figure 3. A significant charge transfer of 0.20 to 0.24 e takes place, being slightly more pronounced for the complex without secondary interactions, in accordance with the EDA results. The values of the charge transfer are also nearly identical to the charge transfer of 0.22 e for the relevant NOCV of the $\text{CF}_3\text{I}\cdot\text{DME}$ complex ($\Delta E_{\text{NOCV}} = -16.6 \text{ kJ mol}^{-1}$) described by Pinter et al.^[34] The associated stabilization energy ranges from -12.7 to -16.4 kJ mol^{-1} , which corresponds to 72-77% of the total orbital interaction energy. It is clearly observed that electron donation takes place from DME to $\text{C}_2\text{F}_4\text{S}_2$. The electron density does not solely accumulate on the chalcogen atom, but further delocalizes into $\text{C}_2\text{F}_4\text{S}_2$, accumulating mostly on the carbon atoms adjacent to the chalcogen, and quantitatively considerably more on the carbon along the extension of the chalcogen bond. The build-up of electron density in the internuclear region strongly implies a characteristic charge transfer character for the investigated chalcogen interaction.

Figure 3: Relevant NOCVs with the corresponding orbital energy interaction and density change for the complex with secondary interactions (a) and without secondary interactions (b). Electron depletion is indicated by the red-colored regions, while electron accumulation is represented by the blue-colored regions.

3.2. Vibrational Spectra

Assignment of the vibrational modes of DME is based on previous publications^[15] while the assignment of the bands of $\text{C}_2\text{F}_4\text{S}_2$ is based on the *ab initio* calculations, including anharmonic frequency calculations using Gaussian09, and assignments found in the literature.^[35] An overview of the *ab initio* calculated frequencies of the monomers and complexes and the numbering of the vibrational modes are given in Tables S3 and S4 of the ESI. As solubility problems occurred at lower temperatures for mixtures with increased concentrations, Raman measurements were performed at 147

K. The IR concentration study was performed at 130 K, whereas IR spectra and assignments given are based on measurements performed at 120 K.

3.2.1. IR spectroscopy

Upon subtraction of the IR spectra of $C_2F_4S_2$ -DME mixtures, complex bands are observed in multiple spectral regions, of which a selection is shown in Figure 4. For the $C_2F_4S_2$ ν_{16} mode, shown in Panel 4B, a -2.4 cm^{-1} redshifted complex band is observed, corresponding well to the -4.3 cm^{-1} and -1.3 cm^{-1} complex shifts for the chalcogen bonded complexes with and without secondary $F\cdots H$ interactions. A 1.3 cm^{-1} blueshifted band is observed in the $C_2F_4S_2$ ν_{13} spectral range, shown on the left side of Panel 4C, whereas only a 0.3 cm^{-1} blueshift is predicted by the *ab initio* calculations for the complex with secondary interactions. Due to a degeneracy with a DME vibrational mode in the calculations, a -1.8 cm^{-1} redshift is predicted for this vibrational mode in the complex without secondary interactions. Also for the ν_{17} $C_2F_4S_2$ mode, shown in Panel 4E, and the ν_8 $C_2F_4S_2$ mode redshifted complex bands were observed with shifts of -0.5 cm^{-1} and -4.3 cm^{-1} , corresponding to the calculated shifts of -1.1 and -11.2 cm^{-1} for the most stable chalcogen bonded complex. Also noteworthy is the presence of a complex band at 836.2 cm^{-1} , corresponding to the ν_6 mode of $C_2F_4S_2$ with B_{1g} symmetry in the monomer. This band is forbidden for the monomer, but becomes IR active upon complexation. The assignment of this band is confirmed by the Raman measurements in which both the monomer and complex band are visible (*vide infra*). A similar effect is calculated for the $C_2F_4S_2$ ν_{11} vibrational mode with B_{2g} symmetry, as seen in Tables S3 and S4 of the ESI. Due to the nearby presence of the $\nu_2 + \nu_9$ and $\nu_7 + \nu_{17}$ combination bands of $C_2F_4S_2$ and the ν_{22} mode of DME, the appearance of this band is not clear at first sight. By combining this data with the data from Raman measurements with the data from additional IR measurements involving fully deuterated DME ($[D_6]DME$), the band at 1087.5 cm^{-1} can be reliably assigned to the complex band of the $C_2F_4S_2$ ν_{11} mode. Also for the DME modes, complex bands with shifts corresponding well to the calculated shifts of the chalcogen bonded complexes are observed, the best resolved bands being the 7.7 cm^{-1} blueshifted band for ν_2 ($\Delta\nu_{calc, F\cdots H} = 10.5\text{ cm}^{-1}$) shown in Panel 4A and the -8.0 cm^{-1} redshifted band for ν_6 ($\Delta\nu_{calc, F\cdots H} = -10.5\text{ cm}^{-1}$), shown in Panel 4C. An overview of the assignments and the differences with previous assignments of the IR spectra is given in Table S5.

Figure 4: IR spectra of selected spectral regions for the mixtures of $\text{C}_2\text{F}_4\text{S}_2$ with DME dissolved in LKr at 120 K. In each panel, trace *a* represents the mixed solution, while traces *b* and *c* show the rescaled spectra of the solutions containing only $\text{C}_2\text{F}_4\text{S}_2$ 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 1.9×10^{-4} for $\text{C}_2\text{F}_4\text{S}_2$ and 4.7×10^{-4} for DME in panels A and E, 2.8×10^{-5} for $\text{C}_2\text{F}_4\text{S}_2$ and 7.5×10^{-4} for DME in panel B, 1.3×10^{-4} for $\text{C}_2\text{F}_4\text{S}_2$ and 7.5×10^{-4} for DME in panel C and 9.4×10^{-4} for $\text{C}_2\text{F}_4\text{S}_2$ and 2.6×10^{-4} for DME in panel D.

Apart from the bands assigned in Table 3, an additional shoulder at the high frequency side of the complex band of the $\text{C}_2\text{F}_4\text{S}_2$ ν_{13} mode (Panel 4C) is observed for the lowest temperatures. This band is tentatively assigned to a 1:2 complex involving two DME molecules.

3.2.2. Raman spectroscopy

Due to the D_{2h} symmetry of $\text{C}_2\text{F}_4\text{S}_2$, Raman measurements yield data which is highly complementary to the IR measurements, as all but one *ungerade* vibrational modes are IR active and all *gerade* vibrational modes have an appreciable Raman intensity.

In the $\text{C}_2\text{F}_4\text{S}_2$ ν_3 spectral region, shown in Panel 5C, a 1.8 cm^{-1} blueshifted band is observed, corresponding well to the calculated blueshifts of 1.0 cm^{-1} . Also for the $\text{C}_2\text{F}_4\text{S}_2$ ν_7 mode, shown in Panel 5D, a blueshifted complex band is observed for which the shift of 2.8 cm^{-1} is in good agreement with the calculated shifts of 3.0 cm^{-1} and 3.1 cm^{-1} for the complex with and without the additional $\text{F}\cdots\text{H}$ interactions, respectively. For the ν_6 mode of $\text{C}_2\text{F}_4\text{S}_2$, shown in Panel 5B, an experimental shift of 0.4 cm^{-1} is found, which lies in the middle of the calculated shifts for the complex with ($\Delta\nu_{\text{calc}} = 1.4 \text{ cm}^{-1}$) and without secondary interactions ($\Delta\nu_{\text{calc}} = -1.7 \text{ cm}^{-1}$).

An overview of all bands assigned using Raman spectroscopy is given in Table S6.

Figure 5: Raman spectra of selected spectral regions for the mixtures of $\text{C}_2\text{F}_4\text{S}_2$ with DME dissolved in LKr at 147 K. In each panel, trace *a* represents the mixed solution, while traces *b* and *c* show the rescaled spectra of the solutions containing only $\text{C}_2\text{F}_4\text{S}_2$ 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 mixtures are 1.1×10^{-3} for $\text{C}_2\text{F}_4\text{S}_2$ and 1.1×10^{-3} for DME in all panels.

3.2.3. Complex stoichiometry and experimental complexation enthalpy

Assignment of the complex bands present in the solutions and analysis of the complexation shifts of the mixtures shows that the bands are in good agreement with the calculated complexes with a 1:1 stoichiometry. To confirm the stoichiometry, a concentration study was performed, for which the results are given in Figure S3 of the ESI.

it was noted above that at the high frequency side for the $\text{C}_2\text{F}_4\text{S}_2$ ν_{13} complex band a small shoulder due to a complex with higher stoichiometry was observed to emerge at the lowest temperatures,. Unfortunately, as the observed feature largely overlaps with the 1:1 complex band and is too small to reliably determine its integrated intensity, a robust statistical analysis allowing the stoichiometry to be confirmed was not possible.

Analyses of the different temperature studies performed, for which details are summarized in Table S7 and Figure S4 of the ESI, yielded, an average experimental complexation enthalpy of $-13.5(1) \text{ kJ mol}^{-1}$.

4. Discussion

Apart from the spectral features assigned to the monomers involved, in the IR spectra of the LKr solutions containing mixtures of $\text{C}_2\text{F}_4\text{S}_2$ and DME, separate features due to 1:1 complexes are observed. Hence, direct spectroscopic evidence for the co-existence of monomer and complexes, each with a separate spectrum, is found. This result differs from the studies reported by Garrett and co-workers in which evidence for the existence of 1:1 $\text{Te} \cdots \text{N}$ bonded adducts with benzatelluradiazoles

were obtained indirectly by analyzing shifts of the λ_{max} in the UV-vis spectra and of the magnetic shielding in the NMR spectra during titration experiments of the benzatelluradiazoles with $Bu_4N^+Cl^-$ in THF.^[6] It should also be noted that observations of Garret et al. focused on the experimental observations of the stronger tellurium chalcogen bond in solution, while up to now, evidence for the sulfur based chalcogen bonding between neutral species in solution is, to the best of our knowledge, still non-existing. The study of the binary complexes between $C_2F_4S_2$ and DME reported here, therefore, clearly is one of the first, and probably the most convincing, study reporting the existence of such interactions in solution.

Ab initio calculations yielded two stable chalcogen bonded complex isomers, which are distinguished by the presence or absence of secondary $F\cdots H$ interactions. As expected from the low energy barrier between both geometries, a single band due to a single species is found for each of the vibrational modes and no distinction between both calculated geometries could be found. A concentration study at 130 K confirmed the 1:1 complex stoichiometry.

As both complex geometries are based on an $S\cdots O$ chalcogen bond, they are inherently very similar as reflected by the nearly identical calculated shifts for both complex geometries. The only vibrational mode for which shifts are calculated in opposite directions is the ν_6 mode of $C_2F_4S_2$, as observed in Raman spectroscopy. Here, the experimentally observed shift of 0.4 cm^{-1} is found to lie in between the blueshift calculated for the complex geometry with the secondary interactions and the redshift calculated for the geometry without secondary interactions.

To evaluate the correspondence between the experimental results and the *ab initio* calculations, the calculated shifts for both complexes are compared with the experimental shifts assigned to the fundamental vibrational modes. An overview of this analysis can be found in Table S of the ESI, while a plot of the experimental shifts against the calculated shifts can be found in Figure 6.

Figure 6: Plot of the experimental complexation shifts of the fundamental modes determined using IR (full circles) and Raman spectroscopy (open circles) against the MP2/aug-cc-pVDZ calculated complexation shifts for the complex with secondary $F\cdots H$ interactions (left) and without secondary

F...H interactions (right). Residual sum of square values (RSS) and the adjusted R^2 values are also given.

The good correlation between the calculated and experimental values reported in Table S8 of the ESI, the slope of the linear fit being close to 1 with an intercept close to 0, confirms the assignment of the complex bands to a chalcogen bonded complex. The largest discrepancy is found for the DME ν_{12} mode in IR and Raman, where an experimental shift is found of 2.4 cm^{-1} in IR and 1.3 cm^{-1} in Raman, while the calculated shifts are 18.1 cm^{-1} for the chalcogen bonded complex with F...H interactions and 13.5 cm^{-1} for the complex without secondary interactions. While the exact nature of this discrepancy is unknown, it probably is due to resonance effects in the C-H stretching region not accounted for in the harmonic force field calculations.^[15b, 15c, 36] Omitting these values decreases the residual sum of squares (RSS) values to 130 for the complex with and 80 for the complex without secondary interactions. The better correlation for the complex without secondary interactions can be ascribed to the general overestimation of the complexation shifts, consistent with the overestimation of the complexation energy at the MP2/aug-cc-pVDZ level, which is more pronounced for the more stable complex with secondary interactions.

The average experimental complexation enthalpy of $-13.5(1)\text{ kJ mol}^{-1}$ derived from the temperature studies is in good agreement with the calculated values of -16.6 and -15.2 kJ mol^{-1} for the chalcogen bonded complexes with and without the F...H interactions.

Comparison with the previously studied halogen bonded complexes between DME and a series of trifluorohalomethanes (CF_3X)^[15a] shows that this complexation enthalpy lies between the values of the halogen bonded complex formed with bromotrifluoromethane ($\Delta H^\circ(\text{LAr}) = -10.2(1)\text{ kJ mol}^{-1}$) and the complex formed with trifluoriodomethane ($\Delta H^\circ(\text{LAr}) = -15.5(1)\text{ kJ mol}^{-1}$). Since $\text{CF}_3\text{I}\cdot\text{DME}$ and $\text{C}_2\text{F}_4\text{S}_2\cdot\text{DME}$ have similar interaction energies and similar acceptor...donor distances, the EDA interaction energy components can be compared quantitatively. The EDA results for the halogen-bonded complex were taken from a previous study^[34] and are listed in Table 2. Except for a slightly larger dispersion interaction in the chalcogen-bonded complex, nearly the same energy contributions are obtained, emphasizing the similarities between both types of noncovalent interactions. Analogously, the size of the charge transfer and associated energy for the relevant NOCVs of the $\text{C}_2\text{F}_4\text{S}_2\cdot\text{DME}$ complexes are nearly identical to the values obtained for the $\text{CF}_3\text{I}\cdot\text{DME}$ complex.^[34]

From the above, it is clear that sulfur chalcogen bonds can be comparable in strength with bromine and iodine halogen bonds when the interaction involves an sp^3 hybridized oxygen atom. Further studies are needed to assess whether this relation holds up when other Lewis bases are used. Comparison of actual results with the complexation enthalpy of the chlorotrifluoromethane·DME halogen bonded complex ($\Delta H^\circ(\text{LAr}) = -6.8(3)\text{ kJ mol}^{-1}$) also implies that sulfur chalcogen bonding can be stronger than chlorine halogen bonding. Chalcogen bonds therefore hold great potential to form

stronger noncovalent interactions than halogen bonds involving halogens from the same period of the periodic table. An important aspect in this regard is the lower electronegativity of chalcogens compared to same-period halogens, which might enhance the effect of electron withdrawing moieties on the covalently bonded group, giving rise to larger σ -holes on the chalcogen atom and stronger chalcogen bonds. The fact that divalent chalcogens form two covalent bonds yields additional possibilities to enhance the electron depletion of the chalcogen atom.

Even though chalcogen bonding involving non-charged oxygen donors have been reported to play an important role in, amongst others, the folding and interactions of biomolecules, a more thorough understanding of the chalcogen bonding concept with $\text{C}_2\text{F}_4\text{S}_2$ as a bond donor might benefit from complementary studies involving other Lewis bases including, amongst others, nitrogen bases such as ammonia or trimethylamine (TMA). Experimental studies of complexes with $\text{C}_2\text{F}_4\text{S}_2$ and ammonia and TMA similar to those reported above were initiated but so far failed completely: due to the low solubility of ammonia in cryogenic liquids no results could be obtained for ammonia, while experiments with TMA failed due to the formation of a white, yet unknown, precipitate appearing after condensing the TMA and $\text{C}_2\text{F}_4\text{S}_2$ gases. The appearance of such a solid is not surprising as it is in line with observations suggesting that particularly the tellurium-bearing congeners are prone to self-association in the solid state through $\text{N}\cdots\text{chalcogen}$ interactions^[37] and by the observations that co-crystallization with Lewis basic solvents and anions can appear. The appearance of a solid precipitate stable at room temperature, hampers the preparation of cryosolutions, as these experiments typically involve the subsequent condensation of the compounds under study and the solvent gas into the liquid cell used.

5. Conclusions

MP2/aug-cc-pVDZ calculations yielded two stable $\text{S}\cdots\text{O}$ chalcogen bonded complexes between $\text{C}_2\text{F}_4\text{S}_2$ and DME. Analysis of the bonding in the complexes with NCIPLOT revealed that the difference between both isomers is the presence or absence of secondary $\text{F}\cdots\text{H}$ interactions, the complex with the secondary interactions being 1.5 kJ mol^{-1} more stable at the CCSD(T)/CBS level. Due to the low energy barrier between both complexes, rapid interconversion between them is expected.

By studying the IR and Raman spectra of solutions in LKr containing $\text{C}_2\text{F}_4\text{S}_2$ and DME, the presence of complex bands is revealed, the shifts being consistent with those of the *ab initio* calculations.. The proposed 1:1 stoichiometry is confirmed by performing a concentration study. Analysis of various temperature runs, yielded an average experimental complex enthalpy of $-13.5(1) \text{ kJ mol}^{-1}$. This value agrees favorably with the calculated complexation enthalpy values of -16.6 and $-15.2 \text{ kJ mol}^{-1}$ for the chalcogen bonded complex with and without secondary $\text{F}\cdots\text{H}$ interactions.

This study does not only show that oxygen based chalcogen bonding between neutral species can exist in solution at thermodynamic equilibrium, but also that, when using a highly fluorinated chalcogen bond donor, the strength of the interaction formed is of the same order as that of halogen bonded complexes formed through bromine and iodine.

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TOC Text

Sulfur chalcogen bonding: a σ -hole interaction with an oxygen electron donor.

The electrostatic potential on the molecular surface of 2,2,4,4-Tetrafluoro-1,3-dithiethane shows two positive regions (shown in blue), so called σ -holes, on either sulfur atom. Through these regions a noncovalent interaction with an electron rich site can be formed, giving rise to chalcogen bonded complexes. For the dimer with dimethyl ether, *ab initio* calculations yield a chalcogen bonded complex with and without secondary $F\cdots H$ interactions.

Graphical abstract