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## Dimers or trimers? A characterization of the halogen bonded complexes of $\text{CF}_3\text{X}$ ( $\text{X} = \text{I}$ or $\text{Br}$ ) with dimethyl ether and acetone in cryosolutions



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### ABSTRACT

Acetone molecules dissolved in liquid krypton are inclined to self-associate into dimers. This behavior affects its use as a prototype Lewis base in studies of weak intermolecular interactions. In this study infrared spectra of mixed solutions of dimethyl ether and  $\text{CF}_3\text{X}$  and of acetone and  $\text{CF}_3\text{X}$  (with  $\text{X} = \text{I}$  or  $\text{Br}$ ) dissolved in liquid argon and liquid krypton are recorded at constant temperature. The dataset for dimethyl ether is used to validate a numerical method based on least-squares fitting of a model including contributions of both monomers and a heterodimer with 1:1 stoichiometry. The resulting monomer and dimer spectra show excellent agreement with previous studies found in literature. The analysis of the dataset for acetone requires an extension of the model with contributions for the acetone homodimer and for  $(\text{acetone})_2 \cdot \text{CF}_3\text{X}$  and acetone  $\cdot (\text{CF}_3\text{X})_2$  trimers. The results show that many signals for acetone  $\cdot \text{CF}_3\text{I}$  and  $(\text{acetone})_2 \cdot \text{CF}_3\text{I}$  are observed, while only a few bands due to acetone  $\cdot (\text{CF}_3\text{I})_2$  occur. The use of numerical approaches adjusted to the specificities of a mixture of two compounds allows to reliably resolve overlapping spectra of monomers and heterocomplexes and characterizing heterocomplex features that could not be deduced using earlier methods. To support the assignments made, ab initio calculations predicting geometries, relative stabilities and harmonic vibrational frequencies for the species envisaged are performed.

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### 1. Introduction

Solutions in liquefied inert gases have proven to be an ideal medium to study molecular complexes held together by weak and medium-strong interactions [1]. They create a weakly interacting environment that, combined with the low temperatures used, leads to small bandwidths and thus facilitates the detection of complex bands only slightly shifted from the monomer modes. This advantage makes it possible to thoroughly investigate heterocomplexes involving an electron rich Lewis base and an electron deficient region related to a hydrogen bond, a halogen bond or a lone pair- $\pi$  acceptor under equilibrium conditions [2]. In addition, experimental data can be derived for homocomplexes where two or more identical molecules associate [3–5].

For heterocomplexes, experimental evidence for the formation on complexes is typically obtained [1] by carefully comparing spectra of monomers and mixtures and by the observation of new bands appearing upon mixing. Moreover, more accurate data is obtained using so-called subtraction procedures in which spectra of the monomers recorded under identical circumstances are multiplied by a scaling factor and subsequently subtracted from the spectrum of the mixture. The value of this scaling factor is such that, after subtraction, no features due to the monomers are withheld and that the remaining spectrum thus solely contains bands assigned to the complexes formed. For

homocomplexes, experimental evidence is typically found by carefully analyzing spectral changes occurring while changing temperature and/or concentration of the solute. Because in many cases, including much diluted solutions, both monomers and homocomplexes are present simultaneously, the traditional subtraction procedure discussed above cannot be used, and thus more sophisticated numerical methods must be applied. A typical example of such a method involves the fitting of measured absorbances, for each wavenumber, to monomer absorbances determined at one or more reference wavenumbers. This method was successfully validated and applied to prototypes of hydrogen bonding such as HCl and pyrrole clusters [3,4]. A similar approach was recently used to analyze the spectra of solutions of acetone in liquid krypton [5]. The results lead to the conclusion that at the temperature studied a large fraction of the acetone molecules present are involved in dimer formation, and yield a spectrum that is quite similar to and only slightly shifted from that of the monomers.

The observation of a large fraction of acetone molecules being involved in dimer formation obviously affects its use as a prototype Lewis base in studies of heterocomplexes. Results obtained from mixed solutions containing acetone and typical hydrogen and halogen bonding donors therefore should not be tackled using the routine approaches but require a dedicated approach in which the contributions of monomer acetone, dimer acetone and their complexes with the acceptor molecule are separated using numerical approaches. In the following paragraphs we report on the development and validation of an extended least-squares model, based on the experience gathered while

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studying the prototypes for hydrogen bonding and the acetone dimer formation in solutions, allowing such analysis to be performed on a routine basis.

The first part of the study involves the development of the model and the applications towards the study of halogen bonded complexes formed between dimethyl ether and the trifluoromethyl halides CF<sub>3</sub>Br and CF<sub>3</sub>I. The spectral properties of these complexes have been described in detail before [6] and are considered to be excellent test cases involving two monomers and a single complex with a 1:1 stoichiometry. The second part of the study involves the application of the model towards the complexes formed between acetone and the same halogen bond donors. Such complexes have not been reported before but are considered ideal test cases for more complex solutions containing possibly six different species, i.e. acetone, CF<sub>3</sub>X, (acetone)<sub>2</sub>, acetone·CF<sub>3</sub>X, (acetone)<sub>2</sub>·CF<sub>3</sub>X and acetone·(CF<sub>3</sub>X)<sub>2</sub>. To rationalize the results obtained, and to support the idea of different complexes species present, standard ab initio methods are used to predict the spectroscopic properties of the species studied.

## 2. Experimental section

The samples of trifluoromethyl iodide (CF<sub>3</sub>I, 99%), dimethyl ether (DME, 99%) and acetone (AC, 99.5%) were purchased from Sigma Aldrich. The sample of trifluorobromide (CF<sub>3</sub>Br, 99%) was purchased from Pfaltz & Bauer. All samples were used without further purification. The cryosolvents argon and krypton had stated purities of 99.9999% and 99.9995% respectively and were supplied by Air Liquide.

Infrared spectra were recorded on a Bruker IFS 66v Fourier transform spectrometer. A Globar source was used in combination with a Ge/KBr beamsplitter and a LN<sub>2</sub>-cooled broad band MCT detector. All interferograms were averaged over 500 scans, Blackman-Harris 3-term apodized and Fourier transformed with a zero filling factor of 4 to yield spectra with a resolution of 0.5 cm<sup>-1</sup>. The experimental set-up used to investigate the solutions in liquid noble gases has been described before [1]. In the actual cryostat, a liquid cell with 1 cm path length and equipped with wedged Si windows was mounted below a LN<sub>2</sub> Dewar. The temperature of the cell body is measured using a Pt-100 thermoresistor. The SunRod electric minicartridge heater is controlled using a Eurotherm 3504 PID controller. The temperatures of the argon and krypton solutions were stabilized at 103 K and 138 K respectively. The temperature variation during a typical run is <0.05 K. Spectra were obtained and pre-analyzed using OPUS 6.5. Further calculations were performed using Matlab [7].

The data sets recorded consist of 328 spectra for mixtures of CF<sub>3</sub>I and DME in liquid argon (LAr), 200 spectra for mixtures of CF<sub>3</sub>Br and DME in LAr and, 274 spectra for mixtures of CF<sub>3</sub>I and acetone in liquid krypton. For each set, spectra were measured for a series of different concentrations and concentration ratios. The mole fractions of the species used are difficult to accurately quantify [1], but are estimated to vary between 1.1 × 10<sup>-4</sup> to 2.9 × 10<sup>-3</sup> for CF<sub>3</sub>X, between 9.6 × 10<sup>-5</sup> for 3.1 × 10<sup>-3</sup> for DME and between 1.1 × 10<sup>-4</sup> for 4.3 × 10<sup>-4</sup> for acetone. To maximize the amount of species dissolved, the temperature of the solution in liquid argon was increased to 111 K after filling the cell at 103 K and was subsequently stabilized at 103 K. For the solutions in liquid krypton, solutions were prepared at 123 K, heated to 160 K, and stabilized at 138 K. The concentrations and concentration ratios used are chosen so that the region between minimum and maximum absorbance for both monomers is uniformly covered.

## 3. Results and discussion

### 3.1. General methodology

Recently we developed and validated a robust numerical approach that enables the investigation of spectra in which spectral features due to monomers and homocomplexes are present simultaneously, and in

which monomer absorbances cannot be accurately determined using traditional subtraction procedures [3]. In this method the monomeric and different oligomeric contributions are obtained by fitting the measured absorbances, for each wavenumber, to monomer absorbances using a higher order polynomial. The new approach is based on the fact that, with some exceptions, cryosolutions are known to be in thermodynamical equilibrium [1]. For the formation of homocomplexes the equilibrium reaction and the equilibrium constant  $K_p$  can be written as.



with the equilibrium concentrations  $C$  and  $p$  the number of molecules in the complex.

The spectra of the mixtures of species in cryosolutions can be seen as a superposition of monomer spectra and spectra of possible complexes, so that the measured absorbance at a wavenumber  $\nu_{\sim i}$ ,  $A_{exp}(\nu_{\sim i})$  equals the sum of individual contributions related to the monomer,  $A_1$  or to one of the oligomers, e.g. dimer  $A_2$ , trimer  $A_3$ , tetramer  $A_4$ , etc., i.e.

$$A_{exp}(\nu_{\sim i}) = A_1(\nu_{\sim i}) + A_2(\nu_{\sim i}) + A_3(\nu_{\sim i}) + A_4(\nu_{\sim i}) + \dots \quad (2)$$

The experimental absorbances for each wavenumber  $\nu_{\sim i}$  originating from all contributing species in the solution are then expressed as a function of the absorbance of a chosen monomer wavenumber  $\nu_{\sim m}$  with the polynomial degree  $p$  equal to 1, 2, 3, 4 or 5 with intercept equal to zero.

$$A_{exp}(\nu_{\sim i}) = \sum_{p=1}^n a_p(\nu_{\sim i}, \nu_{\sim m}) [A_{mon}(\nu_{\sim m})]^p \quad (3)$$

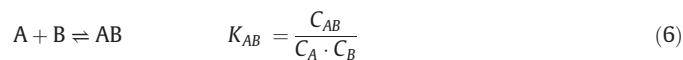
The coefficient  $a_p(\tilde{\nu}_i, \tilde{\nu}_m)$  being a constant related to the equilibrium constant  $K_p$  of the oligomerization reaction

$$p = 1 : a_1(\nu_{\sim i}, \nu_{\sim m}) = \frac{A_1(\nu_{\sim i})}{A_1(\nu_{\sim m})} = \frac{\varepsilon_1(\nu_{\sim i})}{\varepsilon_1(\nu_{\sim m})} \quad (4)$$

$$p > 1 : a_p(\nu_{\sim i}, \nu_{\sim m}) = a_1(\nu_{\sim i}, \nu_{\sim m})^p \frac{\varepsilon_p(\nu_{\sim i})}{\varepsilon_1(\nu_{\sim m})^p} \frac{1}{d^{p-1}} K_p \quad (5)$$

with  $\varepsilon$  as the molar attenuation coefficients of the monomeric species and of the associations formed,  $d$  as the path length of the cell.

These equations can be adjusted so they can also be used to analyze spectra of two or more species to investigate the formation of heterocomplexes. For a mixed solution in which two species A and B are in equilibrium with a complex with 1:1 stoichiometry,



A similar expression can be easily derived in which, for each arbitrary wavenumber  $\nu_{\sim i}$  the measured absorbance  $A_{exp}$  can be written as a sum of absorbance contributions related to the monomers A and B  $A_A$  and  $A_B$  and to the heterocomplexes, e.g. the dimer  $A_{AB}$ ,

$$A_{exp}(\nu_{\sim i}) = A_A(\nu_{\sim i}) + A_B(\nu_{\sim i}) + A_{AB}(\nu_{\sim i}) \quad (7)$$

Hence, by choosing appropriate reference wavenumbers  $\nu_{\sim m}$  (A) and  $\nu_{\sim m}$  (B) for which the measured absorbances are due to monomer A or monomer B only, i.e.

$$\begin{aligned} A_{exp}(\tilde{\nu}_{mA}) &= A_A(\tilde{\nu}_{mA}) \text{ and } A_{AB}(\tilde{\nu}_{mA}) = A_B(\tilde{\nu}_{mB}) = 0 \\ A_{exp}(\tilde{\nu}_{mB}) &= A_B(\tilde{\nu}_{mB}) \text{ and } A_{AB}(\tilde{\nu}_{mB}) = A_A(\tilde{\nu}_{mA}) = 0 \end{aligned} \quad (8)$$

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