



# Exploring the limits of cryospectroscopy: Least-squares based approaches for analyzing the self-association of HCl



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## ABSTRACT

To rationalize the concentration dependent behavior observed for a large spectral data set of HCl recorded in liquid argon, least-squares based numerical methods are developed and validated. In these methods, for each wavenumber a polynomial is used to mimic the relation between monomer concentrations and measured absorbances. Least-squares fitting of higher degree polynomials tends to overfit and thus leads to compensation effects where a contribution due to one species is compensated for by a negative contribution of another. The compensation effects are corrected for by carefully analyzing, using *AIC* and *BIC* information criteria, the differences observed between consecutive fittings when the degree of the polynomial model is systematically increased, and by introducing constraints prohibiting negative absorbances to occur for the monomer or for one of the oligomers. The method developed should allow other, more complicated self-associating systems to be analyzed with a much higher accuracy than before.

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## 1. Introduction

Hydrogen chloride is a textbook example of a simple hydrogen-bonding molecule. The self-association of HCl into molecular clusters is used as a model in the study of intermolecular interactions. Using different spectroscopic techniques, HCl dimers up to hexamers have been studied in the gas phase through jet-cooled spectroscopy [1–5], in helium nanodroplets [6] and in solid matrices [7,8]. In 1992, van der Veken and De Munck [9] reported a systematic study of HCl dissolved in liquefied noble gases and this work was expanded in 2001 by Herrebout, Van Gils and van der Veken [10]. Inspection of the data available showed that at sufficiently low concentrations, the spectrum is dominated by contributions of the monomeric species, while at higher concentrations, additional bands due to oligomeric species of HCl can be observed at wavenumbers well below that of the monomer.

To be able to rationalize the features observed, in the original paper [9] the phenomenon was firstly analyzed by subjecting it to a factor analysis [11], but because of unsatisfying results this methodology was abandoned and a band profile analysis was performed instead. In this method, the contributions of the monomer and the oligomeric species were approximated by subtracting the spectra of solutions containing larger amounts of HCl and a rescaled spectrum of a highly diluted solution recorded under similar circumstances. Subsequently, the difference spectra were least-squares fitted using a series of Gauss–Lorentz sum profiles. The analysis of the data obtained in isothermal concentration

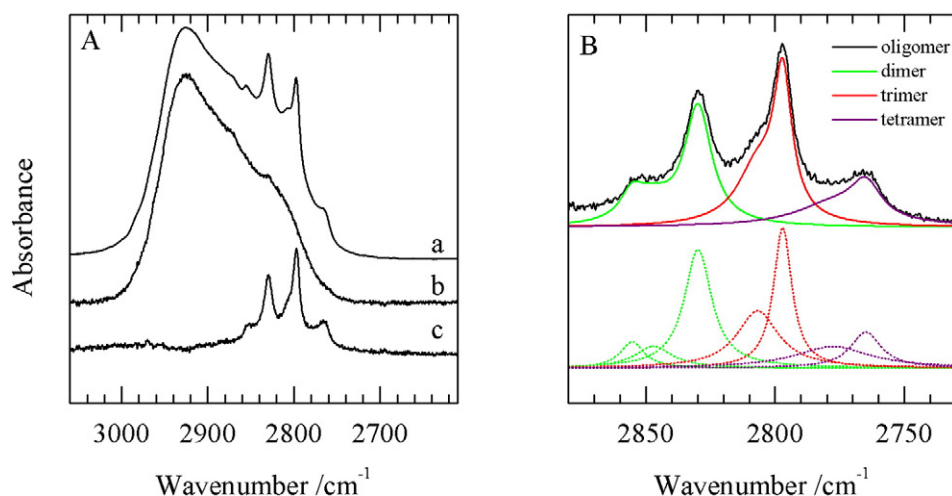
studies allowed assigning the different band features to dimers, trimers, and tetramers. The study of the temperature behavior yielded approximate values for the enthalpies of complexation in the cryosolutions [9, 12].

Based on the results obtained during ongoing research projects involving, amongst others, the studies of more complex systems such as C–H···Y hydrogen [13–21], C–X···Y halogen [13,18,22–28] and lone pair··· $\pi$  [29] interactions, and based on new technological developments made in recent years, we started to realize that the analysis performed [9,12] had several drawbacks and could thus be improved. These ideas originated from the current availability of liquid cells with a smaller optical path allowing more concentrated solutions to be studied without saturating the detector used, and the integration of new, proportional-integral-derivative (PID) controlled setups allowing spectra to be recorded with a much higher temperature stability than that used in the original studies [9]. Apart from these technological developments, we were also triggered by the observation that results of least-squares band fitting procedures depend strongly on the initial parameters chosen and thus can be severely biased by the end-user.

In this paper, we report on the development of more robust numerical methods in which the concentration dependent behavior observed for a large spectral data set recorded at a constant temperature is scrutinized. The new method allows the contributions due to monomers and due to different types of self-association to be separated directly, thereby avoiding the requirement that at the lowest concentrations studied the contribution of complex species should be negligibly small. It will be shown that due to overfitting simpler approaches such as regular least-squares fitting of absorbances versus monomer

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**Fig. 1.** (A) Subtraction procedure involving an original spectrum of a concentrated solution of HCl in liquid argon (a) and a rescaled spectrum of a highly diluted solution recorded under the same conditions (b). The result of the subtraction showing the summed contributions of the different oligomers present is given in the bottom trace (c). (B) Results from a least-squares band profile analysis in which the spectrum of the complex species obtained in panel (A) is fitted using Gauss-Lorentz sum profiles (dotted line). The calculated contributions for the dimer, trimer and tetramer, obtained by summing the different Gauss/Lorentz sum profiles involved, are also given (solid line). As the outcome of the least-squares band profile analysis is often biased by the choice of the initial parameters, in the current study these parameters were optimized to achieve the best agreement with the outcome of the original studies [9,12].

concentrations fail to accurately determine the different contributions. These drawbacks are corrected for by carefully analyzing, using the statistically acknowledged selection *AIC* and *BIC* criteria, the differences between consecutive fittings when the degree of the polynomial is systematically increased, and by introducing constraints prohibiting negative absorbances to occur for the monomer or for one of the complexes. The models and approaches developed, and the Matlab based software packages used for their implementation should allow other, more complex systems [30,31] to be analyzed with a much higher accuracy than before, thereby avoiding the bias originating from the empirical selection of the initial parameters to be used in traditional least-squares band profile analyses.

## 2. Experimental section

HCl (99%) was purchased from Sigma-Aldrich and was used without further purification. The argon used as a cryosolvent had a stated purity of 99.9995% and was supplied by Air Liquide.

Infrared spectra were recorded on a Bruker IFS 66v Fourier transform spectrometer. For the mid-infrared spectra, 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 [32]. 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 temperature variation during a typical experiment is less than 0.05 K.

Spectra were obtained and pre-analyzed using OPUS 6.5. Further calculations were performed using Matlab [33].

## 3. Results and discussion

In the following paragraphs, the general methodology used in this study will be described. Subsequently, results obtained using a fixed-degree polynomial approximation, and results based on the A and B information criteria used to select the appropriate polynomial degree and to avoid overfitting and/or negative absorbances are discussed in detail.

### 3.1. General concept

The general concept of the method used is based on the fact that, with some exceptions [34,35], cryosolutions are known to be in thermodynamical equilibrium. The spectra for cryosolutions of self-associating species therefore are a superposition of monomer spectra and spectra of the different complexes, with the relative absorbances determined by the equilibrium concentrations *C* and the molar attenuation coefficients  $\epsilon$  of the monomeric species and of the associations formed. The latter, are determined by the equilibrium constants *K* involved.

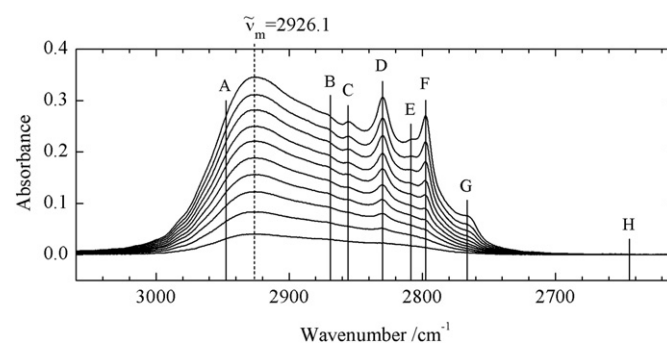
$$2 \text{ monomer} \rightleftharpoons \text{dimer} \quad K_2 = \frac{C_{\text{dimer}}}{C_{\text{monomer}}^2} = \frac{C_{\text{di}}}{C_{\text{mono}}^2} \quad (1)$$

$$3 \text{ monomer} \rightleftharpoons \text{trimer} \quad K_3 = \frac{C_{\text{trimer}}}{C_{\text{monomer}}^3} = \frac{C_{\text{tri}}}{C_{\text{mono}}^3} \quad (2)$$

$$4 \text{ monomer} \rightleftharpoons \text{tetramer} \quad K_4 = \frac{C_{\text{tetramer}}}{C_{\text{monomer}}^4} = \frac{C_{\text{tetra}}}{C_{\text{mono}}^4} \quad (3)$$

Starting from these assumptions, each arbitrary wavenumber  $\tilde{\nu}_i$  the measured absorbance  $A_{\text{exp}}$  can be written as a sum of contributions;

$$A_{\text{exp}}(\tilde{\nu}_i) = A_{\text{mono}}(\tilde{\nu}_i) + A_{\text{di}}(\tilde{\nu}_i) + A_{\text{tri}}(\tilde{\nu}_i) + A_{\text{tetra}}(\tilde{\nu}_i) \quad (4)$$



**Fig. 2.** Infrared spectra of solutions in liquid argon, at 103 K. From top to bottom, the mole fraction of HCl decreases from approximately  $5.0 \times 10^{-3}$  to  $2.0 \times 10^{-5}$ . The 10 spectra shown represent a small fraction of the spectral database used in the fitting procedures.

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