The self-associating behavior of pyrrole in liquid xenon

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ABSTRACT

The self-associating behavior of pyrrole in liquid xenon was investigated by analyzing a data set of 185 −113 infrared spectra obtained for different concentrations recorded at a constant temperature of 203 K. Analysis of the data using a recently developed least-squares approach allows the vibrational spectra of the monomer and of the different oligomers to be isolated. Apart from the monomer transitions, intense absorption bands originating from pyrrole trimers are observed in almost every spectral region including regions for which no data have yet been reported. Apart from these bands, weak features proving the presence of pyrrole dimer and pyrrole tetramer in the solutions are also reported. The weak character of the dimer bands observed and the low concentrations of these species deduced are explained by the fact that the cryosolutions studied are in chemical equilibrium and by the fact that due to strong cooperative effect present in the trimer, the complexation equilibria are strongly shifted towards the latter species, thereby strongly reducing the equilibrium concentrations of dimer and tetramer.

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1. Introduction

Solutions in liquefied inert gases have become an ideal medium to investigate weakly bound molecular complexes. They create a weakly interacting environment which, 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. The complexes studied so far mainly involve heterocomplexes involving, amongst others, a hydrogen or halogen bond interaction. [1-10] In addition, it has been possible to observe aggregates due to self-associating of molecules that simultaneously provide a hydrogen bond donor and acceptor group within their structure.

Whereas the analysis of spectra obtained for mixed solutions can be based on robust subtraction procedures in which spectra of the mixed solution are compared with spectra of the non-interacting monomers, the analysis of spectra of solutions containing self-associating species is more complicated. The reason for this is due to the fact that even for much diluted solutions, the spectra obtained often are determined by non-interacting monomers and by homocomplexes, thereby limiting the possibilities to accurately determine the spectra caused by the monomers only.

To overcome the limitation of the standard subtraction procedures used for heterodimers, we have recently developed least-squares fitting based methods in which, for each wavenumber studied, contributions due to monomers and the homocomplexes are isolated by analyzing the observed absorbances in an isothermal concentration series, and by fitting the data with a higher-degree polynomial mimicking the relations between monomer concentrations and measured absorbances. Validation experiments involving solutions of HCl in liquid argon [11] showed that by analyzing the differences between consecutive fittings and by introducing nonnegative constraints, the contributions due to monomers and self-associated species could be accurately resolved with a much higher accuracy than before. To further rationalize the possibilities and, eventually, limitations, of the methods developed, more testing involving other self-associating species is required. Therefore, in the current study, we expand the data set towards the self-associating model system, pyrrole (C_4H_4NH). The structure thus provides a compact donor N−H group and acceptor π-system in one molecule which can lead to self-association trough one or more N−H ⋯ π hydrogen bonds. The choice of pyrrole as a third model systems is ideal because i) the pyrrole molecule is often considered a basic building block for a large family of important biomolecules [12] and ii) the self-association of the pyrrole monomers is well documented experimentally, in the gas phase [13-16], in traditional or less-traditional solvents including, e.g., CCl_4 and CCl_3F [17-19], and in solid matrices [20]. The different homocomplexes also have been thoroughly studied by density function theory calculations. [17,20].

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It is worth noting that in most of the studies reported, the study of the vibrational spectra of pyrrole and its oligomers strongly focusses on the N−H stretch and the N−H out-of-plane bend [13,17-19,21], thereby limiting the analysis of data available in other spectral regions. An exception to these studies is the work of Gómez-Zavaglia et al. [20] These authors reported on the complete mid infrared spectrum of pyrrole trapped in solid argon and xenon matrices. Besides the assignment of the absorption bands of the pyrrole monomer, they successfully assigned a large number of absorption features related to pyrrole clusters up to tetramer. In the following paragraphs, experimental details on the self-associating behavior of pyrrole in solutions in liquid xenon at 183 K are reported. Inspection of the data shows that by using the recently developed polynomial regression based methods, spectral data due to monomer pyrrole and due to dimer and trimer species can be accurately resolved. The results support and expand the data on the solid matrices reported by Gómez-Zavaglia et al. Apart from further validating the least-squares fitting approach, the analysis therefore also leads to a more complete characterization of the self-association in pyrrole and their effects on the vibrational spectra obtained.

2. Experimental section

Pyrrole (99,99%) was purchased from TCI Europe and was purified with a cold vacuum bulb to bulb distillation. The solvent gas, xenon, had a stated purity of 99.999% and was supplied by Linde.

A data set of 212 mid-infrared spectra of pyrrole in liquid xenon was recorded on a Bruker IFS 66v Fourier transform spectrometer. A Globar source was used in combination with a Ge/KBr beamsplitter and a LN_2-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^{-1}. The experimental set-up used to investigate the solutions in liquid noble gases has been described before. [22] For all experiments, a liquid cell with 1 cm path length and equipped with wedged Si windows was mounted below a LN_2 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 of the solutions was stabilized at 203 K, the temperature variation during a typical run being less than 0.05 K. Spectra were obtained and pre-analyzed using OPUS 6.5. Further calculations were performed using Matlab. [23]

The mole fractions of pyrrole used for the data sets are difficult to accurately quantify [24,25], but are estimated to vary between approximately 9.4×10^{-5} and 2.8×10^{-4}. The concentrations used are chosen so that the region between minimum and maximum absorbance is uniformly covered. Fig. 1 shows different spectra of the gathered data set for the five spectra regions that were investigated. As the outcome of the used fitting procedures can largely depend on baseline artifacts, during all experiments, baseline corrections were performed using spectra of pure liquid xenon recorded at exactly the same conditions. Moreover, special attention was paid to remove spectral features by small water particles suspended in the solution, or condensation of water vapors onto the cold windows of the cryostat and the detector.

3. Results and discussion

3.1. Vibrational spectra

The pyrrole molecule has a C_{2v} symmetry point group that spans 24 fundamental vibrations. In the C_{2v} symmetry the z-axis is the axis of symmetry, but the choice of the x- and y-axes, hence the
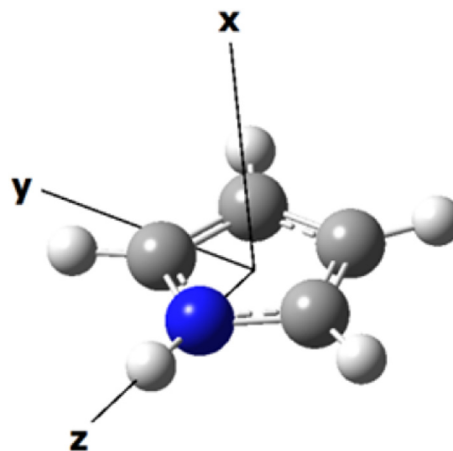

Fig. 1. Illustration of the xyz-frame used to characterize the symmetry elements and irreducible representations of the pyrrole structure.

identification of the two planes in Table 1, is somewhat arbitrary. The lack of solid guidelines has manifested itself in literature two different numbering schemes and different use of symmetry labels B_1 and B_2 [14,20,26−29]. To avoid confusion, we followed the recommendations of Mulliken [30] and defined the x- and y-axes as stated in Fig. 1. Using these conventions, also used by Herman and co-workers [28], the fundamental modes span the $9A_1 + 3A_2 + 4B_1 + 8B_2$ symmetries with all but three A_2 modes being active in the infrared. The modes are numbered according to descending degree of wavenumber in each symmetry block.

Since all fundamental bands occur at wavenumbers above 450 cm^{-1} [20], all 21 infrared active modes could be observed under the experimental conditions used in this study. The typical spectral regions of the recorded data set of pyrrole, for which the assignments of monomer and oligomer absorption bands will be discussed in the following paragraphs, are given in Fig. 2. In this Fig. it can easily be observed that upon increasing the solute concentration, new bands due to self-association emerge in every spectral region of the vibrational spectrum. The complete assignment, largely based on the results reported for the gas phase and solid state [20,26,28], can be found in Table 2.

3.2. Least-squares fitting method

Recently, a polynomial regression approach to isolate overlapping absorption bands of monomeric and oligomeric species observed in the spectra of cryosolutions was developed and validated. [11] The method is based on the assumptions that the measured absorbance at a wavenumber $\tilde{\nu}_i$, $A_{exp}(\tilde{\nu}_i)$ is the sum of individual contributions related to the monomer, A_{mono} or to one of the oligomers, e.g. dimer A_{di}, trimer A_{tri}, tetramer A_{tetra}, etc., i.e.

$$A_{exp}(\tilde{\nu}_i) = A_{mono}(\tilde{\nu}_i) + A_{di}(\tilde{\nu}_i) + A_{tri}(\tilde{\nu}_i) + A_{tetra}(\tilde{\nu}_i) + \ldots \quad (1)$$

The experimental absorbances for each wavenumber $\tilde{\nu}_i$

Table 1
Character Table of the C_{2v} symmetry point group with the defined planes of symmetry (the xyz-frame is defined in Fig. 1).

C_{2v}	E	$C_2(z)$	$\sigma_v(xz)$	$\sigma_v(yz)$
A_1	1	1	1	1
A_2	1	1	−1	−1
B_1	1	−1	1	−1
B_2	1	−1	−1	1