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Infrared spectra and relative stability of the F_3CH/NH_3 H-bonded complex in liquefied Xe

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Dedicated to Professor Dr. James R. Durig, mentor, colleague and friend, on the occasion of his 70th birthday.

Abstract

FTIR spectra of mixtures of fluoroform (F_3CH) and ammonia (NH_3), have been studied in liquid xenon between 5400 and 500 cm^{-1}. Spectroscopic evidence for the formation of a hydrogen bonded complex has been found and the complexation enthalpy $\Delta_{\mathrm{LXe}}H^\circ$ in the temperature interval between 173 and 215 K, was determined to be 14.4 (7) kJ mol^{-1}. The parallel fundamentals ν_1 and ν_2 of ammonia reveal a strong narrowing effect upon complex formation, whereas the perpendicular fundamentals ν_3 and ν_4 show a modest decrease of their width. CP corrected ab initio calculations at the MP2(FULL)/6-311++G(3df,2pd) level predict a linear geometry for the complex, characterized by a small red shift of the CH stretch frequency of fluoroform. The ab initio interaction energy was found to be compatible with the isolated molecule complexation energy extrapolated from the experimental $\Delta_{\mathrm{LXe}}H^\circ$.

Keywords: Hydrogen bond; CH···B interactions; Fluoroform; Ammonia; Relative stability; Cryosolutions; Liquid xenon

1. Introduction

Ammonia is a simple, convenient model system, which features the electron donor nitrogen atom. The strengths of hydrogen bonded complexes formed by ammonia range from very strong, with phenomena of proton transfer [1–3], to very weak, as found in C–H·B type complexes [4–10]. It is well-known that ammonia can self-associate even in the gas phase, and that liquid ammonia forms a highly associated substance, in which practically no monomer NH_3 molecules are present [5,6]. Dimers and higher associates of ammonia, as well as, other simple complexes have been intensively studied [1–15]. Preliminary infrared experiments in cryosolutions focusing on the C–H stretching region have shown that fluoroform forms a H-bonded complex with ammonia, which can be categorized as a red shifted system despite the observed small blue shift of the $\nu_1(A_1)$ CH stretch vibration of fluoroform [16]. The goal of the present work is a more extensive study of the IR spectra of the F_3CH/NH_3 system in cryosolution, using liquid xenon (LXe), as the solvent. In the spectra, we have identified and characterized a series of transitions due to the complex. The complexation enthalpy $\Delta_{\mathrm{LXe}}H^\circ$, measuring the stability of the complex in liquid xenon, was evaluated from the temperature dependence of the infrared intensities of bands due to monomers and complex, and this quantity was extrapolated to a complexation energy for the isolated complex using Monte Carlo simulations of the solvent influences. Also, ab initio calculations were performed to determine the optimized geometry and the spectroscopic parameters of the complex.

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2. Experimental and computational methods

NH_3 and F_3CH were obtained from Praxair with a stated purity of >99.9% and were used without further purification. The xenon used was supplied by Air Liquide and had a stated purity of 99.995%.

The infrared spectra were recorded using a Bruker IFS 66v Fourier transform spectrometer, equipped with a Globar source, a Ge/KBr beamsplitter and a LN2-cooled broad band MCT detector. All interferograms were averaged over 250 scans, Blackman-Harris 3-term apodized and Fourier transformed with a zero filling factor of 4, to yield spectra at a resolution of $0.5\,\mathrm{cm}^{-1}$. The experimental setup consists of a pressure manifold needed for filling and evacuating the cell and for monitoring the amount of gas used in a particular experiment and the actual cell. The cells used have a path lengths of 1 and 10 mm and are equipped with wedged Si windows.

The geometry of the 1:1 complex and its harmonic vibrational frequencies were calculated using the CP-corrected gradient techniques of Simon et al. [17], as included in Gaussian 03 [18]. Geometry optimizations and frequency calculations were performed at the MP2(FULL)/6-311++G(3df,2pd) level. Additional information on the complexation energy was obtained by carrying out single point energy calculations at the MP2 and the MP4(SDTQ) level, using the 6-311++G(3df,2pd) and the aug-cc-PVXZ (X = D, T or Q) basis sets.

Solvation Gibbs energies of monomers and complexes were obtained from Monte–Carlo perturbation calculations, using a modified version of BOSS 4.1 [19]. All simulations were run in the NPT ensemble, using periodic boundary conditions. The system consisted of one solute molecule surrounded by 256 solvent atoms. Preferential Metropolis sampling was used as described before [20]. An attempt to move the solute molecule was made on every 50th configuration and a change in volume was tried on every 600th configuration. The ranges for the attempted moves were the same in each calculation, and provided a ∼40% acceptance probability for new configurations. The quantity calculated is the Gibbs energy $\Delta_{\mathrm{sol}}G$ for the process of introducing one solute into the box with solvent atoms via a coupling parameter λ. The path for $\lambda = 0$ (pure xenon) to $\lambda = 1$ (a solution with one solute molecule) was completed in 50 equidistant steps. Each step consisted of an equilibrium phase for 25.0×10^6 configurations, followed by a production phase of 75.0×10^6 configurations. The Gibbs energy changes between the perturbed and reference systems were always small enough (≈kT) to guarantee reliable results by the statistical pertubation theory.

The enthalpy of solvation $\Delta_{\mathrm{sol}}H$ and the entropy of solvation $\Delta_{\mathrm{sol}}S$ in LXe were extracted from the Gibbs energies of solvation $\Delta_{\mathrm{sol}}G$, using a method similar to that described by Levy and Gallicchio [21]. To this end, for each species, the Gibbs energies of solvation were calculated at 10 different temperatures between 231 and 166 K, and at a pressure of 26 bar, i.e. the vapor pressure of LXe at 231 K.

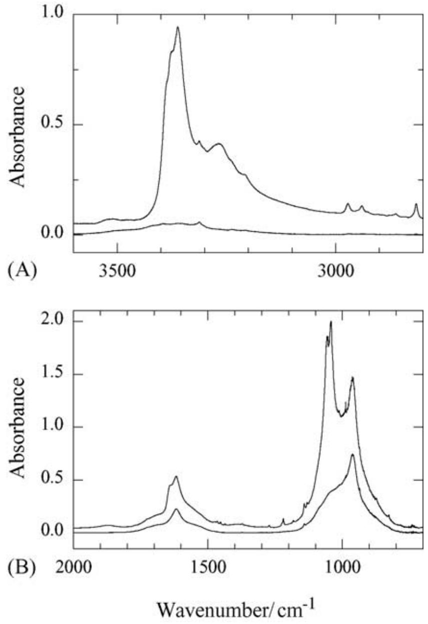

Fig. 1. Infrared spectra of ammonia in liquid xenon. The top trace was recorded from a solution containing a mole fraction of $\sim 6 \times 10^{-4}$, for the lower trace the mole fraction was $\sim 1.5 \times 10^{-4}$. The spectra were recorded at 178 K.

3. Results and discussion

3.1. Vibrational spectra

Fig. 1 presents details of the IR spectrum of ammonia dissolved in liquefied ammonia measured at 178 K. The transitions observed at lower concentrations, bottom traces of Fig. 1A and B, originate in monomeric ammonia. Fig. 1B shows the rotational PQR structure of $\nu_2(A_1)$ and $\nu_4(E)$. Their widths are due to the large values of the rotational constants ($A \sim 6.2\,\mathrm{cm}^{-1}$, $B \sim 10\,\mathrm{cm}^{-1}$) of monomer ammonia. The weak, broad absorption in the N–H stretching region, Fig. 1A, which ranges from approximately 3600 to $3100\,\mathrm{cm}^{-1}$, is caused by the overlapping $\nu_3(E)$, $\nu_1(A_1)$ and $2\nu_4(A_1, E)$ monomer bands.

With increasing concentration of ammonia, the spectrum becomes more complicated as a consequence of the emergence of new bands due to self-associated species. It can be seen in the top traces of Fig. 1A and B that these eventually grow to dominate the spectrum.

Even for dilute solutions, decreasing the temperature below ∼175 K results in the appearance of bands due to self-associated species. Therefore, the majority of our measurments were made at temperatures higher than 175 K.

It is worthwhile comparing the experimental second spectral moments μ_2 of ν_2 and ν_4 with theoretical values. The former were calculated as follows:

$$\mu_2 = \mu_0^{-1} \int_{\mathrm{band}} \mathrm{d}\nu (\nu - \mu_1)^2 \Phi(\nu) \qquad (1)$$