

# **SUPERCRITICAL AMMONIA: A MOLECULAR DYNAMICS SIMULATION AND VIBRATIONAL SPECTROSCOPIC INVESTIGATION**

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## **I - INTRODUCTION**

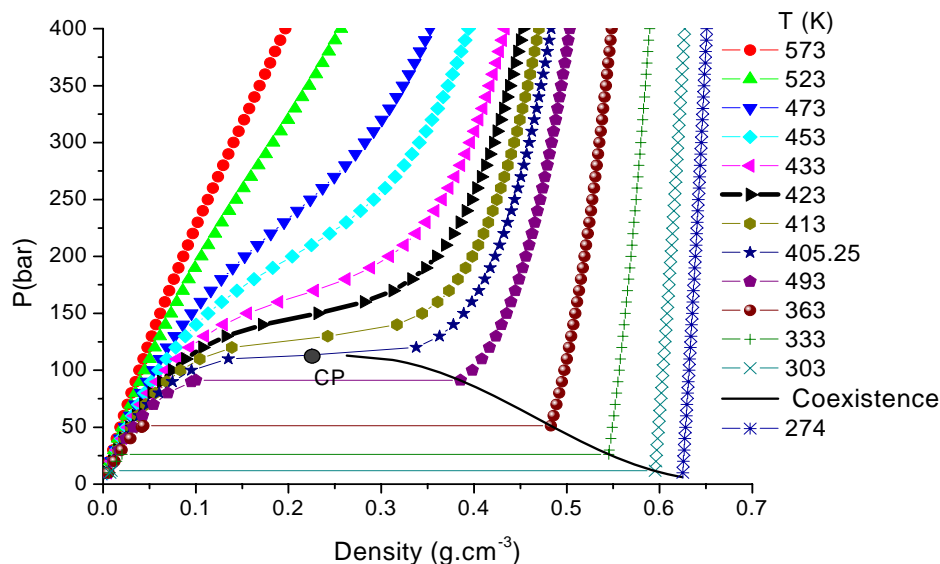
Ammonia or NH<sub>3</sub> has widespread use in many industrial sectors and is one of the most highly produced chemicals in the world. Main uses are in industrial refrigeration systems, as well as in fertilizer, explosives, chemicals production and more recently in the CO<sub>2</sub> capture technology. By the same token, supercritical ammonia has been shown to provide advanced technological processes with less energy consumption and high efficiency, in particular in chemicals production.[1,2] Although liquid ammonia has been the subject of numerous investigations both using experimental X-rays [3-5], neutron scattering [6-8], infrared [9], Raman scattering [10-12], non linear transient spectroscopy [13] and theoretical simulations [14-21], a detailed understanding of the molecular structure of supercritical ammonia is still lacking. Nevertheless, we believe that some special features of supercritical ammonia are relevant to the understanding of supercritical phenomena. Indeed, NH<sub>3</sub> is a simple molecule where a subtle balance between hydrogen bonding and dipole-dipole interactions is expected to provide some peculiarities of its structure and dynamics in the supercritical domain. These considerations prompt us to investigate the structural and dynamical properties of ammonia from the liquid state up to the supercritical fluid by means of molecular dynamics simulations and infrared absorption spectroscopy. In particular, a strongly anharmonic potential developed by Spirko[19] has been used in our simulations in order to get accurate insights of the evolution of the system up to high temperatures and to have access to vibrational properties.

## **II - EXPERIMENTAL DETAILS AND MOLECULAR DYNAMICS**

### **II-1 Thermodynamics States.**

The phase diagram of ammonia obtained from thermodynamics data [22] reported in the literature is displayed on figure 1. The critical point of ammonia is found at  $T_C=405.23\text{M}$ ,

$P_C=11.33$  MPa and  $\rho_C=0.225$  g.cm<sup>-3</sup>. We have performed measurements in the supercritical domain under isothermal conditions, at a temperature of 423K and for densities ranging between 0.02 and 0.36 g.cm<sup>-3</sup>.



**Figure 1:** Phase diagram of ammonia

## II-2 Mid-infrared spectroscopy

The measurements were performed on a Biorad interferometer (type FTS-60A) equipped with a globar source, a KBr beam splitter and a DTGS detector. Single beam spectra recorded in the spectral range 400-6000 cm<sup>-1</sup> with a 2 cm<sup>-1</sup> resolution were obtained by the Fourier transformation of 50 accumulated interferograms. Because of the strong absorption of ammonia in the mid infrared region, we have used a special stainless steel cell designed in our laboratory, in order to obtain a thin film of supercritical ammonia at temperatures reaching 200 °C and under pressures varying up to 20 MPa. The cell was equipped with silicon windows and a teflon spacer ensuring a path length of about 30 μm. The sealing of the cell was ensured with Teflon rings. The heating of the cell was performed using cartridge heaters disposed around the cell. Two thermocouples were used, the first one located close to one cartridge is used for the temperature regulation and the second one was kept close to the sample area in order to measure the temperature of the sample with an accuracy of about 2 °C. The cell was filled with liquid ammonia at room temperature and under a pressure of 10 MPa and then slowly heated up to the working temperature. During the increase of temperature the pressure in the cell was limited by a valve to the highest pressure desired for a set of experiments. Then, the whole set of experiment was performed by decreasing increments of pressure. A Bourdon-tube gauge was used to measure the pressure with an uncertainty of about ± 0.3 MPa.

## II-3 Molecular Dynamics simulations details

We have carried out six simulations in the NEV ensemble on systems consisting in 1015 ammonia molecules under the thermodynamic conditions listed in the table displayed below.

| MD simulation | T (K) | P (bar) | $\rho$ (g.cm <sup>-3</sup> ) |
|---------------|-------|---------|------------------------------|
| A01           | 220   | 1       | 0,710                        |
| A02           | 303   | 11,7    | 0,595                        |
| B14           | 423   | 140     | 0,172                        |
| B15           | 423   | 150     | 0,232                        |
| B16           | 423   | 160     | 0,282                        |
| B25           | 423   | 250     | 0,397                        |

The NH<sub>3</sub> molecules were described using a flexible four sites model initially proposed by Hannongbua et al. [19,23] Periodic boundary conditions were used and a cutoff corresponding to half of the edge of the simulation box have been applied for all the interactions. Each simulation consisted of a 100 ps run using a 0.1 femtosecond time step after an appropriate equilibration period. The vibrational density of states was calculated by Fourier transformation of the hydrogen velocity autocorrelation functions.

### III- RESULTS AND DISCUSSION

#### III-1 Infrared absorption

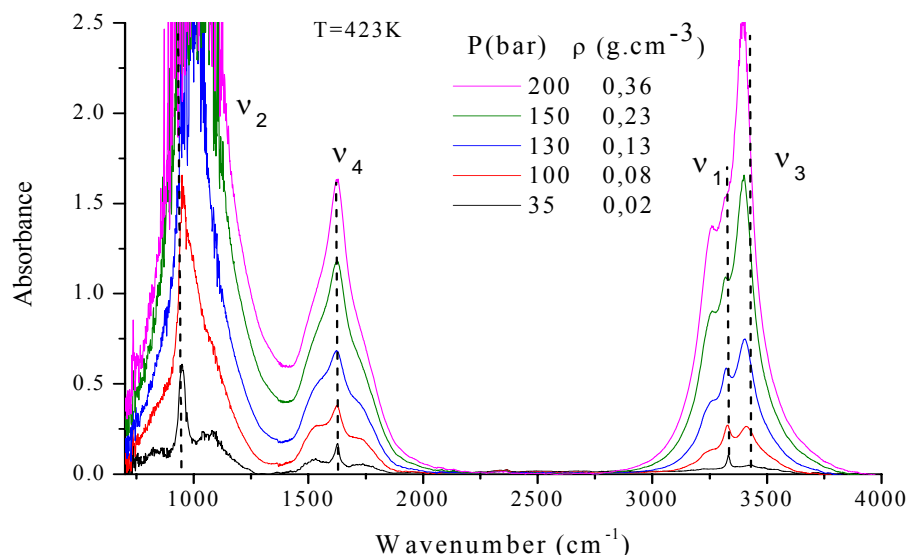
We have reported on figure 2 the infrared spectra of ammonia in the supercritical state at T=423 K and for pressure (density) ranging from 3 to 20 MPa (0.02 to 0.36 g.cm<sup>-3</sup>). The profile observed in the spectral range 3000-4000 cm<sup>-1</sup> relates to the fundamental NH stretching vibrations, namely, the anti-symmetric  $\nu_3$  (E type) and symmetric  $\nu_1$  (A<sub>1</sub> type) stretching vibrations whereas the bands observed around 1600 and 1000 cm<sup>-1</sup> are associated with the asymmetric  $\nu_4$  (E type) and symmetric  $\nu_2$  (A<sub>1</sub> type) NH bending modes, respectively. At the lowest density, we observe for each profile a remnant of the complicated rovibrational structure of the stretching and bending modes that qualitatively indicates that under these conditions, NH<sub>3</sub> molecules rotate almost freely.

Concerning the NH stretching region, the  $\nu_1$  mode exhibits a PQR structure centred at 3330 cm<sup>-1</sup>, whereas the contribution of the  $\nu_3$  mode is barely detected at 3430 cm<sup>-1</sup> (figure 2). For both  $\nu_2$  and  $\nu_4$  bending modes, we also observe at the lowest density a well defined PQR structure, the Q branch being centred at 950 and 1625 cm<sup>-1</sup>, respectively.

As the density increases from  $\rho=0.02$  up to  $\rho=0.36$  g.cm<sup>-3</sup>, we observe an enhancement of the intensity of the whole spectrum which is essentially related to the increase of the concentration (density) of the fluid. However, the shapes of the profiles associated with both the NH stretching and the bending modes are significantly perturbed. In the NH stretching region, upon a density increase, the peak associated with the anti-symmetric  $\nu_3$  mode centred at about 3410 cm<sup>-1</sup> for the density  $\rho=0.08$  g.cm<sup>-3</sup>, is clearly enhanced and shifted towards lower frequencies, pointing at about 3395 cm<sup>-1</sup> at the highest density  $\rho=0.36$  g.cm<sup>-3</sup>. Concomitantly, the peak (Q branch) associated to the symmetric  $\nu_1$  mode centred at 3330 cm<sup>-1</sup> for  $\rho=0.08$  g.cm<sup>-3</sup>, progressively disappears and shifts towards lower frequencies to give a weak peak centred at about 3315 cm<sup>-1</sup> at the highest density  $\rho=0.36$  g.cm<sup>-3</sup>. The shoulder at 3260 cm<sup>-1</sup>

clearly observed at higher densities is associated to the overtone of the asymmetric  $\nu_4$  mode.[10]

In the  $\nu_4$  mode region, the PR structure is progressively smeared out to give wings superimposed over a broadened Q branch centred at about  $1625\text{ cm}^{-1}$ . The band center frequency is independent on the density variation.



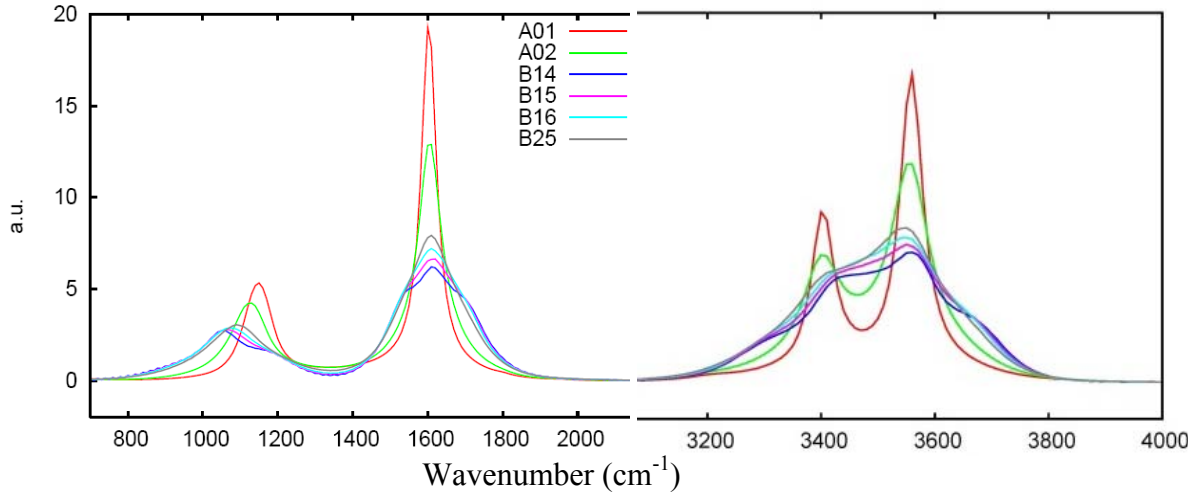
**Figure 2:** Infrared absorption spectra of supercritical ammonia

Finally, in the  $\nu_2$  mode region, the spectra measured under our experimental conditions are reliable only for pressures below 100 bar because of the very strong absorption of the infrared signal in this spectral range. However, although it is not possible to discuss the evolution of the shape of this band, we observe a shift towards higher frequencies upon the density increase. In order to provide a molecular scale understanding of the evolution of the shape of the IR spectra as a function of density, we have performed MD simulations.

### III-2 Molecular Dynamics simulations

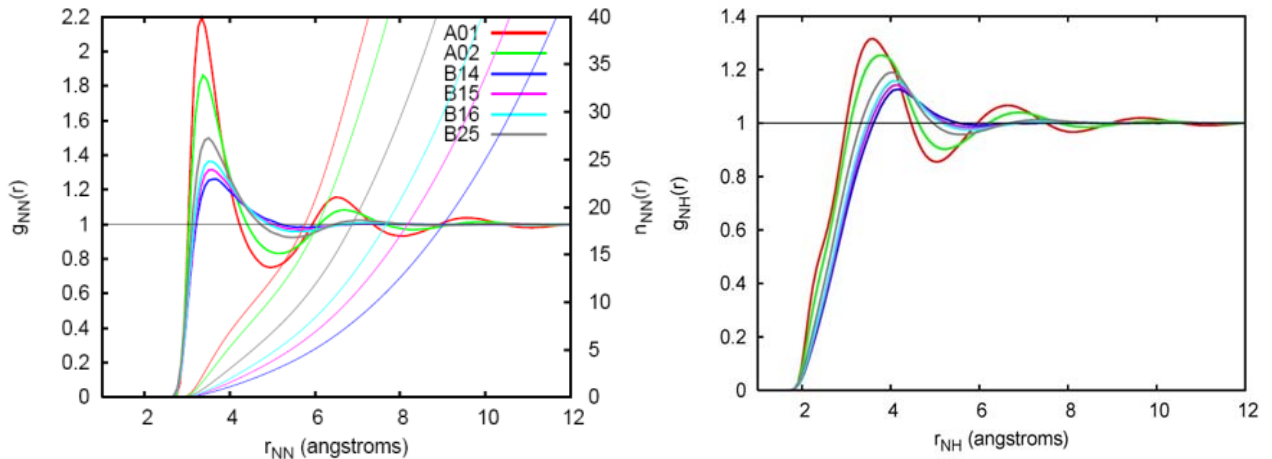
The calculated vibrational spectra of supercritical ammonia are reported on figure 3. For comparison, the results obtained for liquid ammonia under two different thermodynamic conditions are reported. Although our method of calculation does not allow to discuss the relative intensity of each vibrational modes, the shape and their evolution as a function of density can be qualitatively compared with the experimental spectra. In the NH stretching region, the spectra of liquid ammonia display two well separated contributions centred at about  $3400$  and  $3600\text{ cm}^{-1}$ . However, a more complicated profile is observed for supercritical ammonia. Indeed, we observe a broad profile which results from the superposition of the remnant of the two well defined peaks observed in the liquid phase flanked with two shoulders on both sides of the two main components. The overall shape of the NH stretching region is in qualitative agreement with the experimental spectra. In particular, the density effect is well reproduced as we observe a shift to lower frequencies of the two main components upon a density increase. Concerning the  $\nu_4$  mode region, the evolution of the shape and band centre frequency of the band is in a very good agreement with the

experimental one. In particular, we notice no frequency shift as a function of density as reported for the experimental spectra. Finally, the position of the maximum of the peak associated with the  $\nu_2$  mode is found to shift strongly to higher frequencies upon the density increase, a result qualitatively observed in the experimental spectra. Thus, our molecular dynamics simulations are able to reproduce the main features of our experimental findings which provide support for the validity of the proposed potential to describe the structural and dynamic properties of supercritical ammonia.



**Figure 3:** Simulated Infrared spectra of liquid and supercritical ammonia

In order to discuss in detail the evolution of the local order in ammonia as a function of temperature and pressure, we have reported on figure 4 the atom-atom radial distribution function (rdf)  $g_{NN}(r)$  and  $g_{NH}(r)$  of liquid and supercritical ammonia. In particular, we observe that the three first peaks on  $g_{NN}(r)$  respectively situated at about 4, 7 and 10 Å for liquid ammonia and which are characteristic of three well defined shells of neighbouring molecules disappear in the supercritical fluid and lead to a broad single peak at about 4 Å whatever the density is. The same conclusions can be inferred from the other rdf  $g_{NH}(r)$  for which the first shoulder situated at about 2.3 Å characteristic of intermolecular N--H bonds progressively vanishes upon heating and completely disappears in the supercritical domain. These findings indicate that the orientational and translational order which is well defined in liquid ammonia, is drastically affected on going towards the supercritical domain.



**Figure 4:** Radial distribution function  $g_{NN}(r)$  and  $g_{NH}(r)$  of liquid and supercritical ammonia

## IV- CONCLUSION

The evolution of the molecular structure of supercritical ammonia has been investigated combining infrared absorption spectroscopy and molecular dynamics simulations. A good agreement between our experimental and calculated spectra has been obtained hence validating the intermolecular potential used in this study to simulate supercritical ammonia. In particular, we found that the well defined local order in liquid ammonia that is mainly governed by intermolecular hydrogen bonds is strongly attenuated in the supercritical domain. Detailed analysis of the MD simulation results are still in progress to provide more quantitative insights of the relative importance of hydrogen bonding versus non-hydrogen-bonded interactions that governs the structure of supercritical ammonia.

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