Interactions in the ammonia-deuterium system under pressure

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Abstract. We have investigated the NH\textsubscript{3}-D\textsubscript{2} mixture to 50 GPa using micro-Raman spectroscopy. Proton exchange was observed in the mixture, resulting in the formation of deuterated isotopes of ammonia and the formation of HD and H\textsubscript{2}. We report the changes in the vibrational spectra of the various components of the mixture, which include blueshifts and splitting in the vibration modes of hydrogen. These frequency shifts in the mixture are compared to frequency shifts in mixtures composed of the hydrogen isotopes. The changes not accounted for by interactions between the hydrogen molecules suggest repulsive interactions between the hydrogen and ammonia. The bond length of the hydrogen molecules is calculated using a Morse potential, revealing a bond length shorter than in pure hydrogen. Additionally, a change in slope of the bond length as a function of pressure was observed around ~10-18 GPa, which is attributed to the reordering Phase IV to V transition in ammonia.

1. Introduction

The behavior of simple binary mixtures under pressure are of interest because of the fundamental properties exhibited by these systems as well as the applications that these systems have to planetary science and fuel cell applications. A key concept in mixtures is to provide different environments for the molecules, which can alter the properties of molecules relative to what they would be in a bulk sample. In particular, it is of interest to examine the changes that take place to the hydrogen bonding in this system. The resulting changes manifest themselves often by affecting the vibrational properties of the molecules, which appear with the frequencies shifted upwards or downwards relative to the frequency in bulk or in the splitting of peaks. In particular, molecules that exhibit hydrogen bonds, such as water, can form cage structures at low pressures, known as clathrates. Smaller atoms or molecules can end up trapped within the cages [1]. Since ammonia forms hydrogen bonds, the nature and strength of its interactions with smaller atoms or molecules are of interest. It is these properties that generate interest for applications in fuel cell technology. Furthermore, the behaviors of these molecules under pressure are also relevant for planetary science as these simple molecules are found within the interiors of the Jovian planets [2].

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2. Experimental
The high-pressure experiments were performed using diamond anvil cells with pairs of either 300 µm or 500 µm diamonds. Rhenium was used as the gasket material with the 300 µm diamonds, and for the 500 µm stainless steel was used. The gasket was first pre-indented to a thickness of 30 to 40 µm, and then a hole for the sample chamber of 150 µm to 250 µm was drilled in the gasket using an electrical discharge machine. Ammonia was loaded into the diamond anvil cell by first condensing the gas using liquid nitrogen. A small air bubble was then introduced in the sample chamber, which was later replaced by deuterium using a high-pressure loader designed and built at Washington State University. The pressure was determined from the shift of the R1 line of ruby [3] measured from small ruby chips that were placed in the sample chamber. The Raman spectra were collected using a confocal micro-Raman spectroscopy setup using the 514.5 nm line from a cw Ar+ laser. The spectral resolution of the spectrograph is 0.7 cm⁻¹.

3. Results and Discussion
The sample is divided into two distinct regions, one will be referred to as the ammonia-rich and the other will be referred to as the hydrogen-rich (this designation is preferable to deuterium-rich since three isotopes of hydrogen are present, as will be shown below). Initially, at low pressure, the sample is in a fluid phase with hydrogen dissolved in the ammonia-rich region (figure 1). Proton exchange rapidly takes place between the NH₃ and the D₂ leading the formation of HD and H₂, as well as the formation of deuterated forms of ammonia, evidenced by the appearance of a mode around 2400 cm⁻¹ in figure 2. The sample that started only containing molecules of D₂ changes to a ratio of 80% D₂ and 20% HD after 30 minutes to a ratio of 22% D₂, 49% HD, and 29% H₂ after 21 hours. These ratios are estimated from the ratios of the integrated intensities of the vibrational modes. The results of the proton exchange are manifested in the Raman spectra, as these molecules have various Raman active modes, those that are related to the N-D vibrations appearing around 2500 cm⁻¹, which overlap with the diamond two-phonon line, and those related to the N-H vibrations appearing around 3300 cm⁻¹. The vibrational modes of hydrogen appear around their normal frequencies, with D₂ at 3000 cm⁻¹, HD at 3600 cm⁻¹, and H₂ at 4100 cm⁻¹.

3.1 Hydrogen Vibrational Modes
In the fluid phase, the vibrational frequency of the hydrogen isotopes were shifted to lower frequencies with respect to the frequencies in the pure [4], which represents an attractive interaction between the hydrogen molecules and the ammonia molecules. This is the origin of the “splitting” in the vibrational modes that are occurring at 0.6 and 0.8 GPa in the boundary region (see figure 2), where the higher frequency mode agrees with the frequency of the mode seen in the hydrogen-rich part of the sample.
and the lower frequency mode corresponds to the mode seen in the ammonia-rich side. This can be associated with the attractive interaction experienced by the hydrogen isotopes dissolved in the fluid ammonia.

![Image](image)

**Figure 2.** Spectra of the NH$_3$-D$_2$ mixture to 50 GPa in the boundary region between the ammonia-rich region showing the formation of HD and H$_2$ that take place very quickly after the sample is loaded. The HD quickly became the most intense vibrational mode. Notice the appearance of an N-D band (the peak to the left of the two-phonon diamond line shown with the arrow) at 0.8 GPa. The N-H and N-D bands contain many overlapping modes from the various N-H and N-D modes from the various deuterated isotopes of ammonia. Also, notice the asymmetry on the high frequency side the hydrogen peaks and the clear shoulder on the D$_2$ vibron at high pressures.

As the pressure increases, the hydrogen vibrational modes shift to higher frequencies with respect to the pure frequencies [4]. Nevertheless, it has been observed that the vibrational frequencies of hydrogen isotopes shift to higher frequencies when they are mixed together [5]. These shifts are very sensitive to the concentration of the hydrogen isotopes, with the shift in frequency being greater the more dilute the species. For example, a given hydrogen isotope will have a higher frequency at a concentration of 10% than at a concentration of 20%. Figure 3 shows the peak shift of the hydrogen isotopes compared to comparable ratios in mixtures of H$_2$, HD and D$_2$. It will be noticed that they are very similar, but the difference between these data emerging in the appearance of a shoulder on the high-frequency side of the hydrogen vibrational modes, which is particularly pronounced in the case of H$_2$ in Run 1 and in the case of D$_2$ (figures 2 and 3). This asymmetry on the high-frequency side of the HD and H$_2$ vibrons begins to appear around 12 GPa, although it is not pronounced until around 20 GPa. The splitting observed at higher pressure is observed everywhere in the hydrogen-rich and consequently has a different origin than “splitting” observed at lower pressure. Additionally, this splitting is to the higher frequency side of the vibron, rather than the red-shifting observed in the fluid. Brown and Daniels, while observing splitting at higher pressures, did not provide many details, aside from mentioning that they were particularly prominent at high pressures in “very low minority-concentration mixtures” and that these were observed in some spectra [5]. The splitting that was observed in the present NH$_3$-D$_2$ study occurred in a sample that was not dilute, with a clear shoulder being observed in a sample with a composition ratio of H$_2$:HD:D$_2$ of 35:48:17.

### 3.2 Hydrogen bond length

The phenomenological, three-parameter Morse potential for diatomic molecules can be used to generate a semi-empirical determination of the bond length of the hydrogen molecules [6-8]. The depth of the Morse potential and the range parameter can be calculated using the frequencies of two vibrational modes from two different isotopes. With these parameters and the frequency of a hydrogen rotational mode, an expression can be obtained which is a sixth-order polynomial in the bond length $r_c$. 

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as described elsewhere [6-8]. The hydrogen bond length calculated for the present NH$_3$-D$_2$ mixtures and the bond length calculated from data for bulk hydrogen [7] are plotted in figure 4. We cannot compare with the bond length in the mixture of hydrogen isotopes since Brown and Daniels did not publish any rotational data, although it is probable that hydrogen-hydrogen interaction contributes significantly to the shortening, especially at lower pressures before the splitting becomes apparent. As the pressure increases, the rotational modes broaden, increasing the uncertainty of its peak position, and causing more scattering in the results and making them more unreliable with increasing pressure. Nevertheless, here we see a clear difference in the pressure-dependent bond length between pure hydrogen and the present mixture. Until 5.5 GPa, the difference in bond length can be attributed (at least partially) to the difference in phase between the fluid hydrogen in the present study and the solid hydrogen in Loubeyre et al. [7]. The increased intermolecular interactions in the solid will tend to lengthen the molecular bond consistent with figure 4. The shortening of the bond suggests the internal pressure that the molecules are sensing due to repulsive interactions in this system. Additionally, in figure 4, it is clear that the bond length is very consistent for the two runs until around 10 GPa after which the data from the two runs begins to diverge. Then after 18 GPa, the bond length does not exhibit significant changes. The pressures at which these changes occur coincide with the appearance of the asymmetry in the hydrogen vibron (~12 GPa) as well as the Phase IV to V transition in ammonia (12 GPa in NH$_3$ and 18 GPa in ND$_3$). This transition exhibits an isostructural reorientation of the N-D bonds [9], which would affect the hydrogen bonding in the ammonia and the hydrogen molecules would certainly be affected by this change in the ammonia lattice.

Figure 3. The shifts of the various modes of hydrogen with pressure. The H$_2$:HD:D$_2$ composition of Run 1 the mixture was of 60:36:4, while for Run 2 it was 35:48:17. These compositions are compared to the relevant ratios from the Brown and Daniels [5]. The frequencies of the D$_2$ vibrational mode for 5% concentration were not shown in the paper. While the shift to higher frequencies may be accounted for by the presence of the mixtures of isotopes, it is not clear that the splitting originates from this hydrogen-hydrogen interaction, and it is possible that it finds its origin in ammonia-hydrogen interaction. The solid triangles show the shift to lower frequencies of the hydrogen isotopes in the ammonia-rich region. The pure frequencies are from Moshary et al. [4].

3.3 Ammonia Vibrational Modes
The ammonia peaks were observed in the boundary region and the ammonia-rich region as seen in figure 2. No ammonia peaks were observed in the hydrogen-rich region. As the pressure is increased above 1 GPa, the sample solidifies, and this transition is observed visually, with hydrogen-rich bubbles emerging out of the ammonia-rich region. After this point, the vibrational modes of the hydrogen isotopes were no longer observed in the ammonia-rich region. Around 4 GPa, another phase transition is observed in the Raman spectra of the ammonia, which is especially pronounced in the N-
D modes around the diamond two-phonon line, as these modes become very sharp. The pressures at which these changes take place are similar to those in pure ammonia [10, 12, 13]. This is consistent with the Phase IV of ammonia being more ordered than Phase III. The frequencies of the peaks in the bands around 2500 cm⁻¹ and 3300 cm⁻¹ are complicated in pure NH₃ and pure ND₃ samples due to the presence of many overlapping modes, including fundamentals and mixing of fundamentals with overtones [10, 12, 13]. In addition, in the present sample, there can be additional vibrational frequencies due to the presence of the deuterated isotopes of ammonia such as NH₂D, NHD₂ and ND₃. Thus, as expected, the modes occurred at different frequencies in the present study than where they occurred in the pure samples of NH₃ and ND₃ and previous study of NH₃-H₂ [11].

![Figure 4. The bond length of the hydrogen molecules in the NH₃-D₂ system. Note that is consistently shorter than the bond in bulk hydrogen. The data taken from Loubeyre was taken from low temperature experiments (6 K) [7], so the line represents data from solid samples, while the scattered data represents the data from the present studies. The ammonia phase IV to V transition is shown at ~15 GPa since it occurs at 12 GPa in NH₃ and 18 GPa in ND₃. Note the divergence between the two runs at ~10 GPa and the change in slope in Run 2 at ~18 GPa.](image)

4. Conclusions
This study provides a rich amount of information about the vibrational structure of the hydrogen and ammonia as various isotopes are present in the sample. The significant attractive interaction between hydrogen and ammonia is demonstrated in the fluid based up the rapid proton exchange and the lower vibrational frequencies of hydrogen in the fluid. This is consistent with the fact that ammonia exhibits hydrogen bonding and thus by the same mechanism attracts the atoms in the molecules of the hydrogen isotopes. With increasing pressure, understanding the interactions becomes more complicated due to the fact that interactions have been observed between H₂, HD, and D₂, which are manifested by shifts in the vibrational frequencies. Although the shift of the most intense vibrational mode can be accounted for by the presence of other isotopes, the splitting could be interpreted as due to interaction with ammonia molecules. This interpretation is plausible because the splitting occurs in mixtures in which the hydrogen isotopes are not dilute, which was the condition under which Brown and Daniels reported having seen splitting. The calculation using the bond length from the Morse potential shows a shorter bond length that in pure hydrogen, but it is not certain how much of this might be attributed to the interaction between the hydrogen isotopes. Additionally, changes in the calculated bond length of hydrogen between 10-18 GPa coincide with the appearance of the shoulder on the hydrogen vibron and the phase IV to V transition in ammonia [9]. The attraction between the ammonia and the hydrogen in the fluid is clearly displayed in this study, and the evidence suggests a weak, repulsive interaction between the ammonia and hydrogen in the solid.

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