EFFECTS OF HYDROGEN-BONDING IN HYDROGEN-RICH MIXTURES UNDER PRESSURE: A SYSTEMATIC STUDY OF THE DEUTERIUM-WATER, DEUTERIUM-AMMONIA, AND DEUTERIUM-METHANE MIXTURES

By
GUSTAV MICHAEL BORSTAD

A dissertation submitted in partial fulfillment of the requirements for the degree of DOCTOR OF PHILOSOPHY

WASHINGTON STATE UNIVERSITY Department of Physics and Astronomy

MAY 2014
To the Faculty of Washington State University:

The members of the Committee appointed to examine the dissertation of GUSTAV MICHAEL BORSTAD find it satisfactory and recommend that it be accepted.

Choong-Shik Yoo, Ph.D., Chair

Christian Mailhiot, Ph.D.

Gary S. Collins, Ph.D.

Matthew D. McCluskey, Ph.D.
ACKNOWLEDGMENTS

It is a pleasure to be able to mention the many people who have been important to me during the process that my time as a doctoral student has been. I want to first of all acknowledge my advisor, Prof. Choong-Shik Yoo, for all that he has done for me. In particular, for all the encouragement, the support, the knowledge and the insight he has shared with me over the years. He provided insight into the nature of performing scientific research and necessary perspective during moments of uncertainty and doubt. He also helped me immeasurably in the area of presentation of scientific results, showing me the art of telling an interesting story both in writing journal articles and oral conference presentations. I also want to thank my committee members, Professors Gary Collins, Christian Mailhiot, and Matthew McCluskey for their willingness to take time to examine my work, their interest in my progress and their dedication to helping me improve and achieve my goals.

I would like to acknowledge the help received from the engineering staff at the Institute for Shock Physics, and in particular thank Kurt Zimmerman for patience as he tirelessly answered questions and assisted with the maintenance of equipment. I would also like to thank Sabreen Dodson of the office at the Department of Physics and Astronomy for her expertise and her assistance. I would also like to thank the administrative staff of the Institute for Shock Physics: Sheila Heyns, Kristina Peterson, Karly Gomez, and Serena Bruns for all the help they provided.

I would also like to recognize the steady encouragement of my wonderful wife, Delia Marisol Aguilar Borstad, and all the work that she did and does to enable me to have the time to read and work in the laboratory, her patience during all the late nights
and my moments of doubt and sense of fatigue during this process. The delicious and nutritious meals were no small part of what enabled me to continue forward towards the goal.

I want to acknowledge all the group members (past and present) from who I have learned much and am fortunate to call them friends. The past and present postdoctoral members of the group are Drs. Jing-Yin Chen, Mathew Debessai, Minseob Kim, Amartya Sengupta, Haoyan Wei, Alistair Davidson, and Hong-Young Chang. I also want to acknowledge by name the past and present graduate students: Dr. Ranga Dias, Mihindra Dunuwille, Dane Tomasino, Young-Jay Ryu, Sakun Duwal, Nikolay Frik, Seth Wall, and William Bott. I have learned much from all of these individuals, and they have all been an important part of what I have attempted and achieved as a graduate student. I want to particularly acknowledge the assistance and friendship of Ranga Dias during my time as a graduate student.

I also want to thank my parents, Michael and Sheryl, for their constant encouragement, and all that they have provided me with over the years, a loving and stable home and guidance throughout my childhood, adolescence and young adulthood. I would also like to recognize my in-laws, Alejandro and Alcira Aguilar, for their interest in my work and life, and all the times that they have offered me wisdom and encouragement.

I would also like to thank my older sister, Breta, and her husband, Andrew, without whose wisdom, encouragement and help at maintaining a proper perspective, this would never have been possible. I also want to acknowledge my brothers because they have always had a way of cheering me up when I needed it, and they have always been
very supportive of me in my endeavors. I also want to mention the encouragement that I have received from my brothers-in-law, Alejandro and Ricardo and their families, who have always been encouraging and kind to me.

Finally, I would like to also thank my extended family—my grandparents and my uncle and aunts and cousins—for the support that they have provided for so many years during my high school and undergraduate years as well as the past years as a doctoral student.

Most importantly, I recognize the sovereign grace of God, which has granted me my very life and the opportunity to pursue the doctorate in physics. God blessed me with the necessary strength and knowledge. “For from him [God] and through him and to him are all things. To him be glory forever. Amen.” (Romans 11:36).

This research was made in support of the NSF-DMR (Grant No. 0854618 and 1203834) and DTRA (HDTRA1-12-01-0020), and I am also grateful for receiving the ISP Graduate Student Scholarship in support of DOE-NNSA (Grant no. DE-NA0000970).
EFFECTS OF HYDROGEN-BONDING IN HYDROGEN-RICH MIXTURES UNDER PRESSURE: A SYSTEMATIC STUDY OF THE DEUTERIUM-WATER, DEUTERIUM-AMMONIA, AND DEUTERIUM-AMMONIA MIXTURES

Abstract

By Gustav Michael Borstad, Ph.D.
Washington State University
May 2014

Chair: Choong-Shik Yoo

We have investigated the D\textsubscript{2}-H\textsubscript{2}O, D\textsubscript{2}-NH\textsubscript{3}, and D\textsubscript{2}-CH\textsubscript{4} mixtures under pressure using confocal micro-Raman spectroscopy. The D\textsubscript{2}-H\textsubscript{2}O mixture was studied to 64 GPa. The spectral data indicate the presence of deuterated isotopes of water and hydrogen due to proton exchange reactions, which were observed over a wide pressure range. The Raman spectra show significant differences between the mixture and pure hydrogen or water samples. The hydrogen vibrational modes shift to higher frequencies without a frequency turnover and split into two bands, with each band containing additional modes. These changes suggest that the proton-ordering transition in the ice lattice occurs over a large pressure range between 28 and 50 GPa, which is lower than that of pure ice (40–80 GPa). All these changes indicate the presence of high internal pressure due to the repulsive interactions.
The D$_2$-NH$_3$ mixture was investigated to 50 GPa. The spectral data indicate that proton exchange reactions also occur in the D$_2$-NH$_3$ mixture, producing deuterated isotopes of hydrogen and ammonia. An assignment is given for the vibrational stretching modes of NH$_2$D and NHD$_2$. The vibrational modes of hydrogen isotopes in D$_2$-NH$_3$ are blue shifted with respect to those of the pure hydrogen isotopes and they exhibit asymmetries and splittings beginning at ~10 GPa. Similarly, the stretching vibrational modes indicate less attractive interactions in the mixtures relative to pure ammonia. This suggests the presence of repulsion and internal pressure in the D$_2$-NH$_3$ mixture.

Finally, the D$_2$-CH$_4$ mixture was investigated to 30 GPa. Somewhat surprisingly, proton exchange processes in the D$_2$-CH$_4$ mixture are highly limited, with no evidence of deuterated methane or hydrogen. The vibrational modes of D$_2$-CH$_4$ show overall agreement with those in pure D$_2$ and CH$_4$.

The bond length of the hydrogen molecules was calculated for the three mixtures using the spectral data. The above results suggest that the strength of repulsive interaction or the magnitude of internal pressure in the mixtures is proportional to the strength of hydrogen bonding in H$_2$O, NH$_3$, and CH$_4$ in decreasing order. Hence, we suggest that the proton exchange is assisted by hydrogen bonding in these molecules.
# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>ACKNOWLEDGMENTS</th>
<th>vii</th>
</tr>
</thead>
<tbody>
<tr>
<td>ABSTRACT</td>
<td>vi</td>
</tr>
<tr>
<td>LIST OF TABLES</td>
<td>xii</td>
</tr>
<tr>
<td>LIST OF FIGURES</td>
<td>xiii</td>
</tr>
</tbody>
</table>

## CHAPTER

1. INTRODUCTION

1.1 Simple Dense Solids

1.2 Dense Hydrogen Mixtures

1.3 Implications for the Jovian Planets

1.4 Outline of the Dissertation

2. SCIENTIFIC BACKGROUND

2.1 Hydrogen

2.1.1 Isotopes of Hydrogen

2.1.2 Basic Properties of Molecular Hydrogen

2.1.3 Nuclear Statistics in Hydrogen

2.1.4 Rotational States in Hydrogen

2.1.5 Vibrational Structure of Hydrogen

2.1.6 Vibron Turnover in Pure Hydrogen

2.1.7 High-Pressure Hydrogen Phases III and IV

2.1.8 Vibron Frequency and its Turnover in Mixtures

2.2 Water

2.2.1 Water and the Hydrogen Bond

2.2.2 Vibrational Modes of the Water Molecule

2.2.3 Hydrogen-Water Mixture and Clathrates

2.2.4 Spectral Features of the H\textsubscript{2}-H\textsubscript{2}O Mixture

2.3 Ammonia

2.3.1 Ammonia and the Hydrogen Bond

2.3.2 Vibrational Modes of the Ammonia Molecule
B.3 Comments Regarding the Calculation .......................... 132

BIBLIOGRAPHY .............................................................. 134
LIST OF TABLES

2.1 The frequencies of the symmetric stretching vibrations of the normal and deuterated forms of water, ammonia, and methane. In the harmonic approximation, the square of the frequencies of the normal form is expected to be twice that of the deuterated form. The differences reflect the large anharmonicities in potentials with hydrogen. Data from Herzberg (1945). .............................................. 9

2.2 The nuclear states of H$_2$ and D$_2$. The left-hand side gives the wave function in terms of total spin for the molecular system. The right-hand side provides the wave function in terms of the spin on the individual atoms. The symmetry of the exchange is evident from the right hand side wave functions. Note that the ortho-para ratio is 3:1 for H$_2$ and 2:1 for D$_2$. ......................................................... 13

5.1 Classification of the stretching modes of the different isotopes of ammonia as discussed in Chapter 2. ................................................................. 94

A.1 Illustrating the superposition of isotopic molecules to use the sum rule. .......... 127

A.2 The frequencies of the vibrational modes for the different isotopes of ammonia (data from Reding & Horning, 1951; 1955). .............................. 128
LIST OF FIGURES

1.1 Models of the planets Jupiter, Saturn, Uranus, and Neptune, showing the pressures and temperatures and the proposed components that form each layer of the interior. Figure from Guillot (1999). ......................................................... 6

2.1 Equilibrium concentrations of ortho-$H_2$ and para-$D_2$ as a function of the temperature in K. The limiting percentages are 75% for ortho-$H_2$ and 33% for para-$D_2$. Figure from Silvera (1980). ......................................................... 12

2.2 (a) Raman rotational spectra of $H_2$ at 77 K. The intensity variations of the $S_1(0))$ (which is $S_0(1)$ in the notation used above) and the $E_{2g}$ phonon showed no temperature dependence in spectra measured at 77 and 295 K. (b) The peaks shift of the rotational Raman modes of $H_2$. Note the hybridization of the $S_1(0)$ and the $E_{2g}$ phonon mode. Figures from Hemley, et al. (1990). ......................... 16

2.3 The Raman frequencies of the $H_2$, HD, and $D_2$ scaled by the reduced mass (the frequency of $H_2$ is divided by $\sqrt{2}$ and the frequency of HD divided by $\sqrt{3/2}$). It is evident that the scaled frequency of $H_2$ is lower than the scaled frequency of HD, which in turn is lower than that of $D_2$. If the diatomic potential were harmonic, the frequencies would scale as the reduced masses and the frequencies for the different isotopes should all lie on top of each other. This demonstrates the effect of the anharmonicity in the potential. This effect is more pronounced in the lighter isotopes than in the heavier. Data from Moshary et al. (1993a). ....................... 18

2.4 This figure shows the Raman frequency and the IR frequency. Additionally, the difference between the IR and the Raman frequencies are shown at the bottom of the figure. The horizontal axis is given in terms of the density, $\rho$, and $\rho_0$ is the density at 4 K and ambient pressure. Figure from Hanfland et al. (1992). ............ 20
2.5 Comparison of the Raman frequencies of the isotopes of hydrogen in pure, compared with the frequencies of mixtures for (a) H₂, (b) D₂, and (c) HD. Notice that the impurity frequencies are much higher than those in pure, and that they often coincide with the IR frequencies. Figure from Moshary et al. (1993a).

2.6 Representative Raman and peak shift of the ice phase VII of (a) H₂O and (b) D₂O. Notice that all the modes redshift indicating the strength of the intermolecular bonds. The strength of the attractive interaction increases with increasing pressure, due to the strengthening of the hydrogen bond as the intermolecular distances decrease. Note the increased number of modes due to the crystal effects (see text). Figures from Pruzan, Chervin, & Gauthier (1990).

2.7 (a) Comparison of the spectral features of the C₁ and C₂ H₂-H₂O mixtures. (b) The peak shift for the frequency of the ν₁ modes C₂ clathrate redshift at about twice the rate as those in the phase VII of H₂O. The bottom axis corresponds to the square figures and the top axis corresponds to the lines. Also, the top pressure scale increases faster by a factor of two. Figure (a) from Vos et al. (1993), and Figure (b) modified from Vos et al. (1996).

2.8 (a) Representative Raman spectra of solid ammonia. Phase III is disordered with very broad modes. The peaks of Phase IV are sharper, indicating with the ordered structured. Phase V shows similar Raman features to Phase V, apart from the shift of the frequency modes. (b) The shift of the vibrational modes with pressure. Figure from Gauthier et al. (1988).

2.9 Summary of the H₂-NH₃ mixture to 15 GPa. The normal ammonia phase progressions are observed at the same pressure as in pure ammonia (a) and (b), and hydrogen freezes at 5.5 GPa, the same pressure as in pure (c). The hydrogen dissolved in the ammonia is redshifted with respect to the frequency in bulk hydrogen ((a) at 0.88 GPa). Figure from Chidester and Strobel (1988).
2.10 Representative vibrational Raman spectra of (a) CH₄ and (b) CD₄. The two dominant modes are the two stretching modes: \( v_1 \) (symmetric) and the \( v_3 \) (antisymmetric). The double degenerate bending mode, \( v_2 \), and the triply degenerate bending mode, \( v_4 \), are both weak. The \( v_4 \) lines are not observed in either CH₄ or CD₄, although in CH₄ it overlaps with the strong first-order diamond line at \( \sim 1330 \) cm\(^{-1}\). The asterisks indicate plasma lines. Figures from Wu et al. (1995).

2.11 Peak shift of the vibrational modes of CH₄ and CD₄. Notice the spectral changes that coincide with the phase transitions. Also, the vibrational stretching modes (including symmetric \( v_1 \)) blueshift in contrast to the \( v_1 \) modes of ammonia and all the vibrational stretching modes of water. Figures from Wu et al. (1995).

2.12 The phase diagram of the H₂-CH₄ mixture exhibiting the solidification line as a function of hydrogen composition at room temperature. Additionally, the regions of stabilities of the different stoichiometric compounds are shown. (b) Microphotographs of the samples and representative Raman spectra of the H₂ vibrational modes are shown. These allow the different stoichiometric compounds to be identified. Note that the vibrational frequency is different from the frequency of pure H₂. Figure from Somayazulu et al. (1996).

3.1 Schematic showing the diamond anvil cell. The culets of the two press the sample, which is confined by a metal gasket. A ruby is placed in the sample chamber to serve as a pressure marker. The diamonds are transparent to a wide range of electromagnetic radiation, which allow the sample to be observed visually and probed by spectroscopy or by diffraction. On the upper left hand, a microphotograph shows the two diamonds with the gasket between them.

3.2 The diamond anvil cell, showing the cylinder side (on the far left) and the piston in the middle. The diamonds are joined to the tungsten carbide seats with epoxy, and the diamonds can be aligned with setscrews through the sides of the cell. On the far right, the diamond anvil cell is shown closed, with the screws for applying pressure.
The screws should be tightened in a criss-crossing fashion (ABCD, etc.).  

3.3 Schematic of the high-pressure gas loader. The LP Vent and HP Vent close off the system. It is equipped with a vacuum pump to evacuate the lines to remove air and any source of impurities. On the low-pressure side are lecture bottles for generating mixtures of gases. The LP Fill 2 valve closes the circuit so that pressure can build up on the high-pressure side.  

3.4 A schematic of the Raman effect. In Stokes scattering, a photon of energy $h\nu$ collides with a molecule, which absorbs energy $\Delta E$ equal to the difference between a higher energy state and its current state, and a photon is emitted at a frequency $\Delta E/h$ less than the incident frequency. The reverse process occurs when after the collision, the molecule gives up an energy equal to the difference between its current state and a lower energy state, yielding a photon of frequency $\Delta E/h$ less than the incident frequency $\nu$. Figure adapted from Herzberg (1950).  

3.5 Schematic of the micro-Raman system with a backscattering geometry. The laser source is a 514.5 nm Ar$^+$ laser and the beam is expanded five times. Then it is directed by the holographic bandpass filter toward the diamond anvil cell. The 20x infinity-corrected objective focuses the beam on the sample, and then it is scattered backwards. After being transmitted through the holographic bandpass filter and passing through the confocal arrangement, the Rayleigh line is removed at the notch filter. Finally the Raman scattered light is focused on the monochromator with a lens.  

4.1 Microphotographs of the D$_2$-H$_2$O mixture. It shows the fluid D$_2$-H$_2$O mixture at 0.2 GPa separated into two phases—the hydrogen-rich and the water-rich. There appear to be small bubbles dissolved in the water-rich region at 2.6 GPa. The boundary stays clearly distinguished to the highest pressure, and the hydrogen-rich region does not show much volume collapse from about 2.6 GPa until the highest pressures measured relatively to the H$_2$O-rich region. This is in contrast to the
large, typical volume collapse in hydrogen, suggesting the inclusion of H$_2$O in the hydrogen-rich region. ................................................................. 63

4.2 Rotational spectrum of the hydrogen isotopes at 0.2 GPa after 15 h, exhibiting evidence for proton exchange. The assignments of the rotational modes are indicated in the energy level diagram in the inset. The HD rotons are much broader than the D$_2$ and H$_2$ modes, quite likely due to lifetime broadening. ............... 64

4.3 (a) Low-frequency Raman spectra of D$_2$-H$_2$O mixtures taken from the water-rich region, showing the pressure-induced spectral changes. (b) High-frequency Raman spectra of the D$_2$-H$_2$O mixtures in the water-rich region, showing the spectral signatures for O-H, O-D, D$_2$, HD, and H$_2$. ........................................... 65

4.4 (a) Low-frequency Raman spectra of the mixtures taken from the deuterium-rich region at high pressures, showing the spectral evidences for the rotational modes of the hydrogen isotopes. (b) High-frequency Raman spectra of the mixtures in the deuterium-rich region at high pressures, showing the pressure-induced vibron splittings of the hydrogen isotopes. ............................................ 69

4.5 (a) The pressure-induced shifts of the rotational modes of the hydrogen isotopes of the D$_2$-H$_2$O mixtures (solid symbols), showing an overall agreement with those of pure hydrogen isotopes (solid lines) (Hemley et al., 1990; Hemley et al., 1993; Moshary et al. 1993b). (b) The pressure-induced shifts of the vibrational modes of the hydrogen isotopes of the mixtures, showing contrasting behaviors with those of pure hydrogen isotopes (Moshary, Chen, & Silvera, 1993a) and spectral evidences for the proton-ordering transition between around 28 GPa and 50 GPa (see the text). .............................................................. 70

4.6 (a) The pressure-induced peak shift of $v_1$ OH stretching mode in comparison with those in pure H$_2$O (blue from Pruzan et al., 2003) and H$_2$-H$_2$O (red from Vos et al., 1996). The pressure-induced peak shift of $v_1$ OD stretching mode in comparison
with those in pure D₂O (blue from Pruzan et al., 2003), H₂-D₂O (red from Vos et al., 1996). Note that the slope of H₂-D₂O is about twice that observed in D₂-H₂O.

4.7 (a) Low-frequency Raman spectra of D₂ in the hydrogen-rich region at 0.2 GPa, showing the evolution of hydrogen isotopes with the proton exchange reaction in the D₂-H₂O mixtures. (b) High-frequency Raman spectra in the D₂-rich region at 0.2 GPa, showing the spectral changes associated with the proton exchanges and the rotational-vibrational modes (three from the S₁ branch and one from the O₁ branch) of D₂ – but not of H₂ or HD.

4.8 Time-dependent Raman spectral changes measured at the boundary at 2 GPa, showing the rotational modes of D₂ and H₂ and the translational modes (labeled ν₁) of the water (Vos et al., 1993) in (a) and the evidences for which the water has solidified into a phase similar to the C₁ clathrate in (b).

4.9 Time-dependent Raman spectral change measured at the ice-rich region, showing the intensity enhancements of the H₂ S₀(1) and H₂ S₀(0) rotons (a) and of the HD and H₂ vibrons in (b). Note the gradual increase in the intensity of the rotational modes of H₂, as well as the appearance of O-D vibrational mode ~2400 cm⁻¹.

4.10 The normalized Raman intensity changes of hydrogen isotopes plotted as a function of time, showing the kinetics associated with the proton exchange reactions between water and fluid D₂ at 0.2 GPa. The data was fit to Eqs. (4.5) – (4.7) as described in the text.

4.11 The normalized Raman intensity changes of hydrogen isotopes plotted as a function of time, showing the kinetics associated with the proton exchange reactions between ice and fluid D₂ at 2 and 4 GPa. These time-dependent intensity changes
are fitted to the phenomenological Eq. (4.8) to yield the rate constants marked on the plots.

4.12 The normalized Raman intensity changes of hydrogen isotopes plotted as a function of time, showing the kinetics associated with the proton exchange reactions between ice and solid D\textsubscript{2} at 8 GPa. These time-dependent intensity changes are fitted to Avrami’s equation (Eq. 4.10) (solid curves, see the text) to yield the rate constants marked on the plots.

4.13 The D\textsubscript{2} vibrons of the D\textsubscript{2}-H\textsubscript{2}O mixtures (black lines) plotted with those of pure D\textsubscript{2} (blue lines) at several pressures, to illustrate the attractive nature of water-D\textsubscript{2} interaction and the repulsive interaction of ice-D\textsubscript{2} interactions, which increases with pressure.

4.14 The integrated intensity ratio of two vibrons, $v_{S}^{H}$ at higher frequency and $v_{S}^{L}$ at lower frequency, of the hydrogen isotopes after split above 28 GPa, showing evidence for the proton-ordering transition of the mixtures between 28 and 50 GPa. This transition is likely associated with the proton-ordering transition of ice VII occurring over a large pressure range between 40 and 80 GPa.

5.1 Microphotographs for D\textsubscript{2}-NH\textsubscript{3} mixtures showing the changes with pressure. At 0.6 GPa, it appears phase separated into hydrogen-rich (the upper left) and ammonia-rich (the right) regions. Upon the solidification at ~1 GPa, it forms hydrogen-rich bubbles in the ammonia-rich region, which remains to 42 GPa.

5.2 Vibrational spectra of D\textsubscript{2}-NH\textsubscript{3} mixtures from the boundary region, showing a rapid proton exchange to form HD. Note that ammonia vibrons appear in two broad spectral regions: one at ~2500 cm\textsuperscript{-1} which overlaps with the diamond second-order diamond modes and the other at ~3300 cm\textsuperscript{-1}. The H\textsubscript{2} vibron exhibits an asymmetric spectral shape above 12 GPa, whereas D\textsubscript{2} vibron develops a shoulder at ~26 GPa,
which remains to the highest pressure studied.

5.3 (a) External vibrational modes of D₂-NH₃ mixtures, which first appear weakly at ~5 GPa upon the transition to phase IV of ammonia, but get stronger as pressure increases. (b) The pressure dependent shifts of the lattice modes lying in between the frequencies observed in pure NH₃ and ND₃, consistent with the expected presence of NH₂D and NHD₂.

5.4 (a) Spectral profile fittings of the N-D band. (b) Pressure-induced peak shifts of de-convoluted N-D modes in comparison with those of pure ND₃ (red lines reproduced from Pruzan et al., 1990). The sum rule of Wilson and Decius were used in assigning of the modes (see text).

5.5 (a) Spectral profile fittings of the N-H band. Note that the highest frequency peak appears to have a shoulder at 6.2 GPa and 10 GPa. (b) Pressure-induced peak shifts of de-convoluted N-H modes in comparison with those of pure NH₃ (gold lines reproduced from Gauthier et al., 1988) and of NH₃-H₂ mixture (open circles reproduced from Strobel and Chidester, 2011). Again, the sum rule of Wilson and Decius were used in assigning the modes (see text).

5.6 (a) Raman spectra of hydrogen isotopes in the hydrogen-rich region, showing the asymmetric spectral shape arising from the presence of shoulders and peak splittings. In Run 1 it is particularly evident for the peak splitting of H₂ vibron and the shoulder of HD vibron, while in Run 2 the presence of a shoulder is evident for D₂ vibron at 50 GPa. (b) The pressure-induced Raman shifts of hydrogen isotopes, showing the composition dependence. The composition dependence is compared to the previous results at similar compositions (solid and dashed lines reproduced from Brown and Daniels, 1992) and pure hydrogen (dotted lines from Moshary et al., 1993).
5.7 Micrographs of the D$_2$-CH$_4$ mixture. Note that the mixture forms a homogeneous fluid up to 6.4 GPa, above which it solidifies and separates into two distinct regions. Then, upon a small increase in pressure, it further divides into three regions at 6.6 GPa. Finally, at higher pressures, the boundaries disappear and the sample appears homogeneous.

5.8 (a) Raman spectra of D$_2$-CH$_4$ mixtures in the region of methane modes. A weak peak is observed on the high-pressure side of D$_2$ vibron at 12 GPa and a small peak attributed to HD was observed at 26 GPa. (b) The pressure-dependent peak shifts, showing that D$_2$ vibron follows that of pure D$_2$ and CH$_4$ peaks also roughly follow those of pure CH$_4$ (Wu et al., 1995; Chen et al., 2011) up until about 20 GPa. The discrepancies below 6 GPa between the present study and the previous studies for the v$_3^{CH}$ vibrational modes of methane are most likely due to the fact that methane did not solidify until around 6 GPa, whereas pure methane solidifies at 1.7 GPa. The HD peak lies slightly above the 8% composition line from Brown and Daniels (1992). This is reasonable considering that the HD vibron in the present study is about 200 times weaker than the D$_2$ mode.

5.9 Raman spectra of D$_2$-CH$_4$ obtained in different regions of the sample (see the insets), showing strong intensity variation between the D$_2$ and C-H modes. The appearance of doublet in both the D$_2$ and C-H modes is likely due to the formation of CH$_4$(D$_2$)$_4$ as previously observed in Somayazulu et al. (1996). Note that this stoichiometric compound is stable only within a narrow region of pressure between 6.5 and 7 GPa.

5.10 Raman spectra of rotational modes of hydrogen isotopes in (a) D$_2$-NH$_3$, and (b) D$_2$-CH$_4$ mixtures. Note the presence of the H$_2$ and D$_2$ isotopes in the case of D$_2$-NH$_3$ due to the proton exchange (similar to the D$_2$-H$_2$O mixture), but that only the D$_2$ isotopes are present in the D$_2$-CH$_4$ mixture.
5.11 The pressure-dependent peak shifts of hydrogen vibrons in the mixtures in excellent agreement with those of pure hydrogen isotopes (Hemley, Mao, & Shu, 1990; Hemley et al., 1993; Moshary et al., 1993b). The most important differences are between the D$_2$ S$_0$(2) and the H$_2$ S$_0$(1) modes, the latter, which deviates in the pure due to coupling with the E$_{2g}$ lattice mode of the hcp lattice (Hemley, Mao, & Shu, 1990). Their absence suggests that hydrogen has a different lattice than what it assumes in its pure form.

5.12 Raman spectra exhibiting slow proton exchange in fluid D$_2$-solid NH$_3$ at 2 GPa (upper panel), in contrast to negligible proton exchange in D$_2$-CH$_4$ mixture (lower panel).

6.1 Hydrogen bond length calculated from the present spectral data using the Morse potential. It shows the bond length of hydrogen in D$_2$-NH$_3$ (red circles) is shorter than that in D$_2$-H$_2$O (blue squares). The calculated bond length of hydrogen in the D$_2$-CH$_4$ mixture (closed green diamonds) is longer than in either mixture. Nevertheless, more representative values may be indicated by the open green diamonds as explained in the text and Appendix B.

6.2 The pressure-induced peak shifts of hydrogen isotopes in D$_2$-H$_2$O (blue squares), D$_2$-NH$_3$ (red circles), and D$_2$-CH$_4$ (green diamonds) mixtures, showing in comparison with those of pure hydrogen isotopes (solid lines). Note that both the degree of peak shifts and splitting increases with the strength of hydrogen bonding in these mixtures.
Dedication

This dissertation is dedicated to my beautiful wife, Delia Marisol Aguilar, who faithfully and patiently supported me throughout the entire process.
Chapter 1

Introduction

1.1 Simple Dense Solids

High-pressure studies of the fundamental properties of simple molecules occupy an important place in chemistry and physics. In the present work, the simple molecules of interest are H₂, H₂O, NH₃, and CH₄. The prominent position of simple molecules is amply justified by their fundamental importance, great abundance, variety and significance to a wide range of important applications, among other reasons. Nevertheless, their simplicity can be deceptive. The idea has been expressed well by Arthur Ruoff: “Hydrogen is the simplest atom, the simplest molecule and perhaps the most complicated elemental solid” (cited in Amato, 2012, p. 175). Hydrogen, a mere proton and electron, is the only atom for which an exact solution to Schrödinger’s equation exists. Similarly, with only two electrons, it is the (neutral) molecule with the most simple electronic structure. Nevertheless, in the solid, the protons, with large zero-point motions, vibrate about the lattice points with large amplitude even at low temperatures. Additionally, dense hydrogen is expected to exhibit metallic (Huntington & Wigner, 1935) and high-temperature superconducting (Ashcroft, 1968) behaviors under high pressure. Despite these exciting and intriguing possibilities, these predicted states have remained quite elusive despite the persistent efforts of many scientists over many decades (see, for example, Mao, Hemley, & Hanfland, 1990; Loubeyre, Occelli, & LeToullec 2002; Eremets & Troyan, 2011).

The molecules H₂, H₂O, NH₃, and CH₄ form molecular crystals. Molecular
crystals are characterized by weak van der Waals bonds, mostly quadrupole-quadrupole interactions between neighboring molecules (English, & Venables, 1974) and strong covalent bonds within the molecules. This makes molecular solids relatively soft and they form relatively “open” structures at least at low pressures. The complexity, however, increases for molecules like H₂O and NH₃, which contain relatively strong hydrogen bonds, resulting in dipolar interaction between molecules. The electric quadrupole-quadrupole interaction varies as \( R^{-6} \), where \( R \) is the intermolecular separation. The dipole interaction varies as \( R^{-2} \), albeit with dependence on the geometric arrangement. The stronger dipolar interaction in hydrogen-bonded H₂O, for example, gives rise to a large number of polymorphs at relatively low pressures; more than 15 ordered phases and many more disordered ones below 5 GPa.

At 1 Mbar, the intermolecular interactions of molecular solids become substantially stronger than those of van der Waals or hydrogen bonding. Thus molecular solids undergo further physical and chemical transformations to extended structures and chemical bondings. For example, a symmetrizing transition is reported in solid H₂O (Polian & Grimsditch, 1984; Aoki, Yamawaki, Sakashita, & Fujihisa, 1996) at \(~45-70\) GPa, and is expected in solid NH₃ (Gauthier, Pruzan, Chervin, & Besson, 1988). These transitions occur when the proton of the hydrogen atom lies exactly midway between two neighboring oxygen (nitrogen) atoms in the H₂O (NH₃) lattice. This also results in a change from a molecular to an extended non-molecular phase. This is because the distinction between the covalent bond and the hydrogen bond disappears (consequently, individual H₂O molecules can no longer be distinguished). At even higher temperatures and pressures, H₂O and NH₃ are expected to undergo transitions to ionic or superionic
states (Cavazzoni, Chiarotti, Scandolo, Tosatti, Bernasconi, & Parrinello, 1999). The ionic state occurs when H$_2$O (NH$_3$) molecules ionize to form OH$^-$ and OH$_3^+$ (NH$_2^-$ and NH$_4^+$). Evidence for this ionization in ammonia was recently reported above ~150 GPa by Ninet et al. (2014). The superionic state refers to the formation of oxygen (nitrogen) anions and hydrogen cations (protons). The protons flow freely through the oxygen (nitrogen) lattice. These transitions have been reported above 1500 K and 50 GPa in H$_2$O (Schwegler, Sharma, Gygi, & Galli, 2008) and above 700 K and 57 GPa in NH$_3$ (Ninet, Datchi, & Saitta, 2012) with significant rates of proton diffusion.

### 1.2 Dense Hydrogen Mixtures

Studying dense hydrogen mixtures with H$_2$O, NH$_3$, and CH$_4$, known as the planetary “ices”, provides opportunities to gain insights into the nature of the intermolecular interactions. Adding molecules like H$_2$ into these “ices” can strongly modify intermolecular interactions, for example, by perturbing the hydrogen bondings. Furthermore, filling small hydrogen molecules in the interstitial sites can enhance the local electron density and create a large internal (or chemical) pressure in the host lattice (i.e., P ~ dE/dV). First-principles calculations, for example, predict that methane—a mixture of hydrogen and carbon—metallizes at substantially lower pressures than pure H$_2$ (Ashcroft, 2004). It is also predicted that adding a little lithium to hydrogen will generate a stable metal (Li$_x$H$_2$) at $\frac{1}{4}$ the pressure required to metallize pure H$_2$ (Zurek, Hoffmann, Ashcroft, Oganov, & Lyakhov 2009). In fact, the concept of such internal chemical pressure is not new but has been used for decades to make novel functional materials at ambient conditions; for example, the Mott transition in MnO occurring above 100 GPa (Yoo, Maddox, Klepeis, Iota, Evans, McMahan et al., 2005) can occur in Sr-
doped manganite at ambient pressure (Okuda, Asamitsu, Tomioka, Kimura, Taguchi, & Tokura, 1998). This, in turn, provides the opportunity of tuning materials properties, as the properties of mixtures are sensitive to the composition (see, for example, Somayazulu, Finger, Hemley, & Mao, 1996). Furthermore, the mixtures of H₂ and CH₄ with hydrogen-bonded H₂O and probably NH₃ form clathrate hydrates and stable molecular alloys such as (CH₄)(H₂)₄—novel energy and hydrogen-storage materials. Clathrate hydrates are inclusion compounds in which host H₂O molecules form a network of hydrogen-bonded cages containing atoms or molecules such as CH₄, N₂, and Ar among others (Struzhkin, Militzer, Mao, Mao, & Hemley, 2007). This illustrates the potential of simple mixtures to generate structures that tune the hydrogen bond by the structure and the chemical environment.

Dense mixtures offer a way of studying solid-solid interfaces. Repulsive or attractive interactions of varying strength can exist at the interface, depending on the degree of miscibility. Immiscible components will exhibit a clear boundary, with no change in the properties compared to the pure components. On the other hand, miscible components may exhibit somewhat blurred boundaries and often clear changes in the properties due to the altered interactions. The degree of miscibility and interactions are dependent on the crystal structure of the phase. Hydrogen-containing compounds can exhibit proton-exchanging reactions (which can be traced by using different isotopes of hydrogen). These reactions (or their absence) provide additional evidence regarding the bonding nature of the intermolecular interactions.

1.3 Implications for the Jovian Planets

Hydrogen is the most abundant, and carbon, nitrogen, and oxygen are also among
the ten most abundant elements in the solar system (Lodders, 2003). These elements are present mostly in the molecular forms \( \text{H}_2, \text{H}_2\text{O}, \text{NH}_3, \) and \( \text{CH}_4, \) in the interiors of the Jovian gas planets (Guillot, 1999). Therefore, the high-pressure properties and transformations of \( \text{H}_2, \text{H}_2\text{O}, \text{NH}_3, \) and \( \text{CH}_4 \) provide critical constraints for modeling the composition, internal structure, and dynamo of Jovian planets. Furthermore, the aspects concerning the miscibility of the components in the mixtures furnish important information to understand the behavior in the interior of the Jovian planets. Models of the Jovian planets, shown in Fig. 1.1, propose an atmosphere and outer layer composed of molecular hydrogen and helium atoms, followed by a layer of metallic hydrogen. An inhomogeneous region may separate these two layers. Further in the interior, a layer is formed of the planetary ices (\( \text{H}_2\text{O}, \text{NH}_3, \) and \( \text{CH}_4 \)), and finally the rocky, iron-rich core. The magnetic fields of the Jovian planets also provide insight into their interior structures (Ness, Acuna, Behannon, Burlaga, Connerney, Lepping et al., 1986). For example, the large magnetic field of Uranus, generated by the dynamo mechanism, requires conductivity in the ice layers in order to be maintained (Cavazzoni et al., 1999).

In order to model the structure, composition, and the dynamics of the Jovian planets, it is important to understand the properties of simple molecules at the relevant extreme pressures (~0.1 Mbar to 3 Mbar) and temperatures (100 K to 5000 K). The equations of state and the physical and chemical transformations of the planetary ices provide useful constraints for planetary models. For instance, metallic hydrogen and/or the superionic phases of the \( \text{H}_2\text{O} \) and \( \text{NH}_3 \) may satisfy the conductivity required in the planetary ices (Cavazzoni, 1999).
Figure 1.1: Models of the planets Jupiter, Saturn, Uranus, and Neptune, showing the pressures and temperatures and the proposed components that form each layer of the interior. Figure from Guillot (1999).

The study of mixtures yields further information applicable to planetary science. The outer layers are composed of mixtures of hydrogen and helium, and the layer of the planetary ices or mixtures of H$_2$O, NH$_3$, and CH$_4$. The degree of miscibility between the components in solid phases at different pressures and temperatures will help determine the sharpness of the interfacial boundaries. Combining two miscible components would result in regions of mixed components between the layers. For example, a high degree of miscibility between H$_2$ and H$_2$O, would suggest that an H$_2$-H$_2$O mixed phase exists between the H$_2$ layer and the ice layer. Studying mixtures of miscible components would reveal the potential properties of these multi-component layers. Thus, in addition to the behavior of the pure components, examining the behaviors of the mixtures is essential to further test and constrain the planetary models.

To summarize, high-pressure behaviors of simple binary mixtures of hydrogen
with hydrogen-bonded molecules such as water, ammonia, and methane are fundamental to the understanding of intermolecular interactions, hydrogen bonding, proton exchange reactions, and miscibility. In nature, these mixtures are found in the giant planets such as Uranus and Neptune at pressures of ~100 GPa and temperatures of ~1000 K—a condition readily accessible by high-pressure studies. Investigations on hydrogen mixtures with planetary ices—water, ammonia, and methane—have important implications for understanding interlayer mixing, internal structure, chemical composition, and dynamics of these planets.

1.4 Outline of the Dissertation

The present work is aimed at understanding intermolecular interactions in three deuterium mixtures—D$_2$-H$_2$O, D$_2$-NH$_3$, and D$_2$-CH$_4$—probed by the spectral changes in vibrational Raman spectra at high pressures. The main findings in this research relate to the interactions between deuterium mixed with these ten-electron molecules. The systematic study reveals the effect of hydrogen bonding on the intermolecular interactions, miscibility, proton exchange, phase transitions, and molecular structures. These results and the relevant background will be reported in the following five chapters and two appendices.

Following this introductory chapter, background on the relevant previous studies on hydrogen, water, ammonia, and methane will be presented in Chapter 2. The experimental techniques, apparatus, and materials used in this work will be reviewed in Chapter 3. Then the results and discussions on the D$_2$-H$_2$O mixture will be presented in Chapter 4. Further results and discussion on the D$_2$-NH$_3$ and D$_2$-CH$_4$ mixtures will appear in Chapter 5. Finally, in Chapter 6, the properties of the mixtures will be compared and
the significance and conclusions will be presented. Two appendices have been included: Appendix A, which discusses the sum rule of Decius and Wilson and Appendix B, in which the determination of the bond length of a diatomic molecule by means of the Morse potential is outlined. The major findings of the present work have been published in:


Chapter 2

Scientific Background

2.1 Hydrogen

2.1.1 Isotopes of Hydrogen

The vast majority of hydrogen (> 99.9%) in the universe is composed of a one-proton nucleus and an electron (\(^1\)H). The only other naturally occurring isotope of hydrogen is deuterium (\(^2\)H or simply D), which was discovered by Urey, Brickwedde, and Murphy (1932). The nucleus of deuterium (called a deuteron) consists of a proton and a neutron, and has a mass twice that of the \(^1\)H isotope. In this work, hydrogen will be used to refer to both H and D, with the latter two symbols used to distinguish when necessary. This is the largest percent mass difference between isotopes of the same element. The electronic structure of the H and D atoms are essentially identical, and thus a D atom can easily replace H atom in chemical compounds (Halverson, 1947). This difference in mass has been used to great benefit in spectroscopy, as this allows large frequency differences between the hydrogen- and deuterium-containing bonds, and thus provides aid in the assignment of spectroscopic modes. For example, as evident in Table 2.1.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>H(_2)O</th>
<th>D(_2)O</th>
<th>NH(_3)</th>
<th>ND(_3)</th>
<th>CH(_4)</th>
<th>CD(_4)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Raman Frequency of (v_1) (cm(^{-1}))</td>
<td>3650.0</td>
<td>2666</td>
<td>3342.5</td>
<td>2420.0</td>
<td>2914.2</td>
<td>2084.7</td>
</tr>
<tr>
<td>((v_1^H/v_1^D)^2)</td>
<td>1.874</td>
<td>1.908</td>
<td>1.954</td>
<td>1.954</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 2.1: The frequencies of the symmetric stretching vibrations of the normal and deuterated forms of water, ammonia, and methane. In the harmonic approximation, the square of the frequencies of the normal form is expected to be twice that of the deuterated form. The differences reflect the large anharmonicities in potentials with hydrogen. Data from Herzberg (1945).
2.1, the square of the frequencies of the symmetric stretching modes of water, ammonia, and methane all scale as approximately two.

Also, at a given temperature, H atoms have an average velocity greater than that of D atoms by a factor of $\sqrt{2}$ at a given temperature. This can be significant in hydrogen diffusion, for instance. Another important property of hydrogen arises from its light mass, which leads to large quantum effects. As a result, even in crystals, the hydrogen nuclei contain large kinetic energies and large displacements in the lattice even at low temperatures. Since the mass enters through the uncertainty principle (in the momentum), comparisons between hydrogen and deuterium can be significant in understanding these effects. Besides the differences in mass, the spins of the nuclei also distinguish the two isotopes, with $^1\text{H}$ nucleus (a proton) being a fermion and the $^2\text{H}$ nucleus being a boson. This has important implications for the rotational states that will be discussed below.

2.1.2 Basic Properties of Molecular Hydrogen

Hydrogen forms a simple diatomic molecule. Despite having the simplest electronic structure of all elements and the simplest covalent bond, the properties of hydrogen contain many subtleties. Quantum effects, as mentioned above for the hydrogen atom, are also very important in the behavior of the hydrogen molecule. This arises due to its light mass, which provides a very large uncertainty in both its position and velocity in accordance with the uncertainty principle even at low temperatures. Thus the hydrogen has very large anharmonicities in its potential and very high compressibility (Silvera 1980; van Kranendonk, 1983). This makes it a very interesting case to study the effects of increasing density, because an enormous increase in density (by a factor of two) is achieved over the relatively modest pressure range from ambient pressure to 1 GPa.
As hydrogen is a diatomic molecule, it has one vibrational degree of freedom and two degenerate rotational degrees of freedom and three translational degrees of freedom. The vibrational and rotational structure of the hydrogen molecule can be understood from the model of the vibrating rotor. The energy levels (in units of wavenumbers) of a diatomic molecule in terms of the vibrational quantum number \( v \), and the rotational quantum number \( J \) are described well by Eq. (2.1),

\[
\frac{E_{ej}}{\hbar c} = \tilde{v}_e \left( v + \frac{1}{2} \right) - x_e \tilde{v}_e \left( v + \frac{1}{2} \right)^2 + J(J + 1)B_e - D_e J^2 (J + 1)^2 - \alpha_e \left( v + \frac{1}{2} \right) J(J + 1)
\]

(2.1)

where \( \tilde{v}_e \) is the equilibrium vibrational constant, \( B_e \) is the equilibrium rotational constant, \( \alpha_e \) is the vibrational-rotational constant, \( x_e \) is an anharmonic correction constant, and \( D_e \) is the second-order rotational constant (Wilson & Pauling, 1935). The values of these constants can be determined from experimental data (Herzberg, 1950).

### 2.1.3 Nuclear Statistics in Hydrogen

The behavior of the rotational modes is affected by the nuclear statistics in the case of the homonuclear species (H\(_2\) and D\(_2\)) and to this we now turn our attention. Hydrogen (H\(_2\)) and deuterium (D\(_2\)) molecules each have identical nuclei unlike the case of hydrogen deuteride (HD). The symmetry of the total wave functions of H\(_2\) and D\(_2\) under exchange depends on the total spin of the individual nuclei. Each nuclei of H\(_2\) has spin \( \frac{1}{2} \) and should obey Fermi-Dirac statistics (that is, the total wave function should be anti-symmetric under exchange of the nuclei). The electronic ground state of H\(_2\) belongs to the \( ^1\Sigma_g^+ \) representation, which is symmetric about the reflection plane that bisects the molecular bond (Herzberg, 1950). Additionally, the vibrational wave function is also
symmetric about this same reflection plane. The rotational wave functions are symmetric for even $J$ rotational quantum numbers, and anti-symmetric of odd $J$ rotational quantum numbers (Herzberg, 1950). Finally, the total spin, $I$, of the $H_2$ molecules can be either 0 or 1, with the anti-symmetric state corresponding to spin 0 and the symmetric states corresponding to spin 1 (Herzberg, 1950; Silvera, 1980; van Kranendonk, 1983). Thus, it is evident that the symmetry of the total wave function (which must be anti-symmetric) depends only on the rotational and nuclear wave functions. This requirement can be satisfied in two ways: (1) the rotational wave function must be symmetric and the nuclear wave function anti-symmetric ($J$ even and $I = 0$), or (2) the rotational wave function must be anti-symmetric and the nuclear wave function must be symmetric ($J$ odd and $I = 1$). The states with even $J$ are referred to as $para$-$H_2$ and the states with odd $J$ are referred to as $ortho$-$H_2$. This nomenclature arises since the designation “$ortho$” is used to refer to the specie with the largest spin degeneracy (Silvera, 1980). The equilibrium $ortho$-to-$para$ ratio for $H_2$ is 3:1 at sufficiently high temperatures (~200 K) after a few weeks for the transfer to take place. Fig. 2.1 shows the temperature dependence and a summary of the
orth and para states is provided in Table 2.2.

<table>
<thead>
<tr>
<th><strong>H₂ Molecule</strong></th>
<th><strong>D₂ Molecule</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Symmetric Triplet States</strong> ( (I = 1) )</td>
<td><strong>Symmetric Quintuplet States</strong> ( (I = 2) )</td>
</tr>
<tr>
<td>( J ) must be odd, Ortho-H₂</td>
<td>( J ) must be even, Ortho-D₂</td>
</tr>
<tr>
<td>(</td>
<td>l = 1, M_I = 1\rangle =</td>
</tr>
<tr>
<td>(</td>
<td>l = 1, M_I = 0\rangle = \frac{1}{\sqrt{2}}</td>
</tr>
<tr>
<td>(</td>
<td>l = 1, M_I = -1\rangle =</td>
</tr>
</tbody>
</table>

| **Anti-Symmetric Singlet State** \( (I = 0) \) | **Anti-symmetric Triplet States** \( (I = 1) \) |
| \( J \) must be even, Para-H₂ | \( J \) must be odd, Para-D₂ |
| \( |l = 0, M_I = 0\rangle = \frac{1}{\sqrt{2}}|+\rangle - \frac{1}{\sqrt{2}}|\rightarrow\rangle \) | \( |l = 1, M_I = 1\rangle = \frac{1}{\sqrt{2}}|1,0\rangle - \frac{1}{\sqrt{2}}|0,1\rangle \) |
| \( |l = 1, M_I = -1\rangle = \frac{1}{\sqrt{2}}|0, -1\rangle - \frac{1}{\sqrt{2}}|-1,1\rangle \) | \( |l = 1, M_I = 0\rangle = \frac{1}{\sqrt{2}}|0, -1\rangle - \frac{1}{\sqrt{2}}|-1,0\rangle \) |

| **Symmetric Singlet State** \( (I = 0) \) | **Symmetric Quintuplet States** \( (I = 2) \) |
| \( J \) must be even, Ortho-D₂ | \( J \) must be odd, Ortho-D₂ |
| \( |l = 0, M_I = 0\rangle = \frac{1}{\sqrt{6}}|1, -1\rangle - \frac{2}{\sqrt{6}}|0,0\rangle + \frac{1}{\sqrt{6}}|-1,1\rangle \) |

**Table 2.2:** The nuclear states of H₂ and D₂. The left-hand side gives the wave function in terms total spin for the molecular system. The right-hand side provides the wave function in terms of the spin on the individual atoms. The symmetry of the exchange is evident from the right hand side wave functions. Note that the ortho-para ratio is 3:1 for H₂ and 2:1 for D₂.

The same principles hold for the deuterium molecule. The only difference arises from the fact that the nuclei are bosons, each with spin 1. This imposes the requirement that Bose-Einstein statistics be satisfied and that the total molecular wave function be symmetric. As in the case of hydrogen, both the molecular electronic wave function and the vibrational wave functions are symmetric with respect to reflection about the plane that bisects the bond. Additionally, as before, the rotational wave function is symmetric for even \( J \), and anti-symmetric for odd \( J \). Thus the overall symmetry of the total wave function will depend on the symmetry of the rotational and the nuclear states. The
possible spin states for the molecule are $I = 0, 1, \text{ and } 2$. The states with total spin 0 and 2 are symmetric under particle exchange, while the total spin state 1 is anti-symmetric under particle exchange, as can be seen in Table 2.2. Thus, for the total wave function to be symmetric, it is necessary to combine the symmetric states $I = 0, 2$ with the rotational states with even $J$ and the anti-symmetric state $I = 1$ with the rotational states with odd $J$. Thus the $(I = 0, 2, J \text{ even})$ are ortho-deuterium (since this is the specie with the largest spin degeneracy), and the $I = 1, J \text{ odd}$ are para-deuterium, and we obtain a ratio of ortho-to-para of 2:1 at sufficiently high temperatures (~100 K) given sufficient time. This process takes weeks, although the conversion time can be decreased by catalysts or the application of pressure to days or even hours (Silvera, 1980, 1998; Pravica & Silvera, 1998; Silvera & Pravica, 1998). The ortho and para states for both H$_2$ and D$_2$ are given in Table 2.2, and the temperature dependence is provided in Fig. 2.1.

From the above discussion, we observe that there is a difference in the temperature behavior between H$_2$ and D$_2$ as shown in Fig. 2.1. In the ground state H$_2$ is entirely para-H$_2$ in equilibrium, but with increasing temperature, the ortho-H$_2$ comes to dominate with an equilibrium ratio of 3:1. On the other hand, ortho-D$_2$ forms the ground state of D$_2$ in equilibrium and it also dominates at higher temperatures with an equilibrium ratio of 2:1. The ortho and para distinction remain valid even at high pressures. However, the distinction can disappear when a hydrogen atom can exchange with a hydrogen atom on another molecule. Then the symmetry of the wave function no longer depends solely on the exchange of two atoms within a given molecule (Silvera, 1998; Silvera and Pravica, 1998).
2.1.4 Rotational States in Hydrogen

The Raman rotational selection rule for diatomic molecules is $\Delta J = 0, \pm 2$. The band corresponding to $\Delta J = 2$ is referred to as the $S_{\Delta v}(J)$ band, where $\Delta v$ gives the change in the vibrational quantum number, and $J$ gives the initial rotational state (Silvera, 1980). Thus, $S_0(J)$ gives the pure rotational state with $(v = 0, J \rightarrow J+2)$. The nuclear statistics of hydrogen influence the intensities of the rotational band of homonuclear isotopes of hydrogen, causing the intensities to vary in the rotational modes. In the case of $H_2$, the sum of the intensities of all the rotational modes $S_0(\text{odd})$ is approximately three times larger than those of $S_0(\text{even})$. For $D_2$, on the other hand, the intensities of the rotational modes $S_0(\text{even})$ are about twice as large as those for $S_0(\text{odd})$. Thus the Raman selection rule and the requirement of the nuclear statistics both coincide to give the same restriction on the transitions. That is, the selection $\Delta J = \pm 1$, is not allowed for the homonuclear species. On the other hand, $\Delta J = \pm 1$ is allowed for HD.

The intensities of the rotational modes will be influenced by three factors: (a) the degeneracy of the modes, (b) the population of the states, and (c) the line strength. For (a) the rotational modes have a degeneracy factor $(2J + 1)$. Regarding (b), the Boltzmann factor $\exp(-E_J/k_BT)$ will give the ratio of the states in the case of heteronuclear HD. In the case of homonuclear $H_2$ and $D_2$, the ortho-para ratios (3:1 for $H_2$ and 2:1 for $D_2$) must be taken into account. Finally, for (c), the intensity also depends on a line strength factor, $S_J$, which is given by

$$S_J = \frac{3(J + 1)(J + 2)}{2(2J + 3)}$$

for the case $\Delta J = 2$ (Herzberg, 1950).

Figure 2.2 shows the rotational modes of hydrogen and the peak shift (Hemley,
Mao, & Shu, 1990). Note that the transverse optical E\textsubscript{2g} phonon couples with the S\textsubscript{1}(0) rotational mode. Similar coupling was observed between the E\textsubscript{2g} phonon and the S\textsubscript{0}(0) rotational mode in H\textsubscript{2} (Lagendijk, Wijngaarden, & Silvera, 1985). This was also observed in D\textsubscript{2}, between the E\textsubscript{2g} and both the S\textsubscript{0}(0) and S\textsubscript{0}(1) rotational modes (Lagendijk, A., Wijngaarden, R. J., & Silvera, 1985; Hemley, Eggert, & Mao, 1993).

![Figure 2.2](image)

**Figure 2.2:** (a) Raman rotational spectra of H\textsubscript{2} at 77 K. The intensity variations of the S\textsubscript{1}(0) (which is S\textsubscript{0}(1) in the notation used above) and the E\textsubscript{2g} phonon showed no temperature dependence in spectra measured at 77 and 295 K. (b) The peaks shift of the rotational Raman modes of H\textsubscript{2}. Note the hybridization of the S\textsubscript{1}(0) and the E\textsubscript{2g} phonon mode. Figures from Hemley, *et al.* (1990).

The transverse optical E\textsubscript{2g} phonon arises as a result of the hcp structure of phase I of hydrogen. It is important because it provides evidence of the stability of the structure into regions where x-ray diffraction is difficult due to the weak x-ray scattering of hydrogen.

### 2.1.5 Vibrational Structure of Hydrogen

The Raman vibrational selection rule is \( \Delta \nu = \pm 1 \). The \( \nu = 0 \) to 1 vibration of hydrogen can exhibit three different branches, the Q-branch (\( \Delta J = 0 \)), the R branch (\( \Delta J = -2 \)) and the S branch (\( \Delta J = 2 \)). The Q-branch includes several modes arising from
different initial $J$ states, which results in slightly different frequencies, which follows from the term involving $\alpha_e$ in Eq. (2.1). The frequency spacing of these terms are of order $\alpha_e$ which is $\sim 3 \text{ cm}^{-1}$ for $\text{H}_2$ and $\sim 1 \text{ cm}^{-1}$ for $\text{D}_2$ (Herzberg, 1950). The other two branches involve a change in the rotational quantum number and the frequency spacing on the order of $B_e$, which is $\sim 60 \text{ cm}^{-1}$ for $\text{H}_2$ and $\sim 30 \text{ cm}^{-1}$ for $\text{D}_2$ for (Herzberg, 1950).

Because of the light mass of the hydrogen atom, the anharmonicities in the diatomic potential become significant, and this leads to clear deviations from the behavior that would be observed in a harmonic potential. In the harmonic potential the modes of the different molecules would scales exactly as the inverses of the square roots of the reduced masses. For diatomic molecules, the reduced mass is defined as

$$\mu = \frac{m_A m_B}{m_A + m_B}$$  \hspace{1cm} (2.2)

where $m_A$ and $m_B$ are the masses of the two atoms in the diatomic molecule. On the other hand, the vibrational energies of the lighter isotopes of hydrogen are observed to be lower than what they would be in a harmonic potential as can be seen in Fig. 2.3 (also see Table 2.1). This is particularly important in the case of the isotopes of hydrogen as the vibrational energies are very high due to the light masses of the nuclei, and also can exhibit significant differences between the different isotopic forms since the reduced masses change by large percentages, for example, with $\text{D}_2$ having double that of $\text{H}_2$.

The change from fluid to solid has important effects on the vibrational and rotational modes (as already encountered in the discussion of the $E_{2g}$ transverse optical phonon). This phonon arises from the $hcp$ structure of hydrogen (space group $P6_3/mmc$) determined by x-ray crystallography (Hemley, Mao, Finger, Jephcoat, Hazen, & Zha,
Figure 2.3: The Raman frequencies of the H$_2$, HD, and D$_2$ scaled by the reduced mass (the frequency of H$_2$ is divided by $\sqrt{2}$ and the frequency of HD divided by $\sqrt{3/2}$). It is evident that the scaled frequency of H$_2$ is lower than the scaled frequency of HD, which in turn is lower than that of D$_2$. If the diatomic potential were harmonic, the frequencies would scale as the reduced masses and the frequencies for the different isotopes should all lie on top of each other. This demonstrates the effect of the anharmonicity in the potential. This effect is more pronounced in the lighter isotopes than in the heavier. Data from Moshary et al. (1993a).

1990). The hydrogen molecules are freely rotating in this structure. The fluid-solid transition takes place at 5.5 GPa at room temperature (Mao & Bell, 1979). This is accompanied by a slight redshift (shift to lower frequencies) in the frequency in the solid with respect to the frequency in the fluid at the freezing pressure (Sharma, Mao, & Bell, 1980b). Additionally, the vibron peak becomes sharper in the solid until 17.5 GPa after which it begins to broaden again. Another related and important experimental fact of hydrogen relates to the appearance of the infrared stretching band the hydrogen crystal (Hanfland, Hemley, Mao, & Williams, 1992). In a homonuclear diatomic molecule, the infrared vibrational mode is symmetry forbidden since there is no permanent dipole. The presence of the infrared mode arises from the fluctuating dipole moments due to intermolecular interactions in the crystal (Hanfland et al., 1992). This will be discussed further in the next section.
2.1.6 Vibron Turnover in Pure Hydrogen

The vibrational modes of hydrogen exhibit an increase in frequency with increasing pressure until a maximum is reached after which the frequency of the vibrational mode decreases with pressure. The pressure at which the turnover in the vibrational mode occurs depends on the isotope of hydrogen, occurring at \( \sim 30 \) GPa for \( \text{H}_2 \) (Sharma, 1980b), \( \sim 40 \) GPa for HD (Moshary, 1993) and \( \sim 50 \) GPa for \( \text{D}_2 \) (Sharma, 1980a; Mao & Hemley, 1994). The turnover pressure is largely unaffected by temperature (Mao & Hemley, 1994).

The initial increase in frequency with pressure is expected and is understood as being due to the compression of the molecular bond. The turnover in the frequency, however, was surprising. For instance, it was not possible to account for based upon the Dunham’s rotating vibrator (Dunham, 1932) and van Kranendonk and Karl’s potential for solid hydrogen (Wijngaarden, Lagendijk, & Silvera, 1982).

It was suggested that it indicated a weakening of the molecular bonds. Thus, it was seen as providing evidence of a transition from molecular to metallic, atomic hydrogen (Sharma et al., 1980b) consistent with the prediction of Wigner and Huntington (1935). This interpretation suggested a weakened bond due to charge transfer from the bond region. The difference between the pressures at which the turnover between the different isotopes was taken as a suggestion that \( \text{H}_2 \) would metallize at a lower pressure than \( \text{D}_2 \) (Sharma et al., 1980a).

Progress was made towards understanding this phenomena by synchrotron experiments performed on the IR vibrons on hydrogen (Hanfland et al., 1992) and
deuterium (Silvera et al., 1992), which did not show the turnover at the pressures of ~30-

50 GPa as had been observed in the case of the Raman vibron. The interpretation of the IR and the Raman vibrons was guided by van Kranendonk’s theory for the vibrational band structure of solid hydrogen with hcp structure (van Kranendonk, 1983; Mao & Hemley, 1994). The IR vibron probes the intramolecular potential in solid hydrogen to a much greater degree than does the Raman vibron (Silvera et al., 1992). Thus the increase in IR frequency suggested that the bond between the hydrogen atoms was not weakening, and that charge transfer was not taking place from the bond. More precisely, in the crystal the vibron forms a band of frequencies due to the intermolecular interactions. The Raman vibron mode probed in the in-phase vibrations, and the IR vibron mode probed the out-

Figure 2.4: This figure shows the Raman frequency and the IR frequency. Additionally, the difference between the IR and the Raman frequencies are shown at the bottom of the figure. The horizontal axis is given in terms of the density, \( \rho \), and \( \rho_0 \) is the density at 4 K and ambient pressure. Figure from Hanfland et al. (1992).
of-phase vibrations. The difference between the IR and the Raman vibrons indicated the degree of the intermolecular coupling. This coupling becomes apparent by the divergence of the IR vibron to higher frequencies (see Fig. 2.4), and the difference only increases as the Raman frequency begins to slow its rate of increase to higher frequencies and turns over (Mao & Hemley, 1994). This behavior of increasing intermolecular interaction is in agreement with the expected physical behavior with increasing compression. The IR vibrational mode did indeed show turnover at much higher pressures (Hanfland, 1992). This turnover may provide evidence of the weakening in the intermolecular bond.

Ashcroft argued that the crossing of the Raman $q = 0$ vibron and the zone-boundary phonon mode yielded a pressure at which dynamical instabilities would be present in the system, quite likely affecting the intramolecular bond (Ashcroft, 1990). He also observed that the different turnover pressures between H$_2$ and D$_2$, which difference is likely accounted for by the anharmonicities in the vibrational potential. He used the Morse potential (Morse, 1929) to attempt to examine the effective charge in the bond and demonstrated a progressive weakening of the bond supporting charge transfer out the hydrogen bond. The hydrogen molecular bond was shortened with increasing pressure consistent with Quantum Monte Carlo studies (Ceperley & Adler, 1987). Nevertheless, the intramolecular bond length is increasing relative to the lattice parameter (which naturally decreases upon compression).

### 2.1.7 High-Pressure Hydrogen Phases III and IV

As already mentioned, phase I of hydrogen has a hcp structure (space group P6$_3$/mmc). The c/a ratio begins at the ideal value of 1.633, but it decreases with pressure due to increased anisotropy in the crystal (Mao, Jephcoat, Hemley, Finger, Zha, Hazen, et al., 1992).
This structure is stable starting from the solidification at 5.5 GPa at 300 K, although the x-ray diffraction experiment becomes difficult with increasing pressure. This phase has a large stability field down to the lowest temperatures measured at ambient pressure. It has been argued that this structure is stable up until ~26-110 GPa below 135 K (this transition is heavily dependent on temperature, pressure, and ortho-para state), where a discontinuity is observed in the Raman and IR vibrons as well as in the low-frequency modes. This is known as phase II, and has been identified as an ordered phase. Then, around ~155 GPa, at 77 K, a discontinuity of about 100 cm\(^{-1}\) is observed, which has been identified as corresponding to a phase III. This discontinuity decreases with increasing temperature and is continuous at room temperature (although a change in slope at 143 GPa was reported in D\(_2\) by Baer, Evans, and Yoo (2007)). This suggests the existence of a critical point, below which the transition is discontinuous and above which the transition is continuous. Thus this implies that the structure must be one that can be reached continuous from Phase I (Mao & Hemley, 1994).

Recently, a new phase of hydrogen has been proposed at 220 GPa at room temperature, and is referred to as Phase IV (Troyan & Eremets, 2011; Howie, Guillaume, Scheler, Goncharov, & Gregoryanz, 2012). This phase was identified by the appearance of a new vibron mode and changes to the low-frequency region of the spectrum. The structures of both phase III and phase IV are unknown, although there have been numerous theoretical predictions (see, for example, Pickard & Needs, 2007).

2.1.8 Vibron Frequency and its Turnover in Mixtures

In contrast to the behavior of the hydrogen isotopes seen in pure hydrogen, in mixtures the vibron frequencies are commonly blueshifted (shift to higher wavenumbers).
Mixtures that have been studied include H$_2$-He, H$_2$-Ne, H$_2$-Ar, and H$_2$-D$_2$, (Loubeyre, Le Toullec, & Pinceaux, 1992; Brown, & Daniels, 1993), and N$_2$-D$_2$ (Kim & Yoo, 2011). It is interesting to note that the frequency of hydrogen isotopes in the mixture (labeled as impurity Raman in Fig. 2.5) is often very similar to the IR frequencies. The blueshift in the case of helium and neon gases (a change of ~250 cm$^{-1}$ by 12 GPa in helium) is stronger than that of dilute H$_2$ in D$_2$ (Loubeyre et al., 1992). The blueshift in N$_2$-D$_2$ is comparable to that of the hydrogen in the noble gases. Additionally, a definite trend is observed with greater frequency shifts being measured the more dilute the concentration of the hydrogen isotope (Loubeyre, Le Toullec, & Pinceaux, 1992; Brown and Daniels, 1992). This holds both in hydrogen-noble gas mixtures as well as in mixtures of hydrogen isotopes.

![Figure 2.5](image-url)

**Figure 2.5:** Comparison of the Raman frequencies of the isotopes of hydrogen in pure, compared with the frequencies of mixtures for (a) H$_2$, (b) D$_2$, and (c) HD. Notice that the impurity frequencies are much higher than those in pure, and that they often coincide with the IR frequencies. Figure from Moshary et al. (1993a).
These blueshifts reveal important information about the effect of the chemical environment on the vibrational frequency of hydrogen. Loubeyre et al. (1992) determined that the effect of the crystal compression and of vibration-phonon coupling on the vibron frequency should be very small. Thus, the shift should be attributed to vibrational coupling. This is particularly interesting in the case of dilute H\textsubscript{2} mixed with D\textsubscript{2}, since the intermolecular potentials between H\textsubscript{2}-H\textsubscript{2} and H\textsubscript{2}-D\textsubscript{2} should be essentially the same. The difference in vibron shift has been attributed the charge-transfer out of the hydrogen covalent bond.

Having discussed the properties of hydrogen in its molecular form, we now turn to discuss three chemical compounds—water, ammonia, and methane. The hydrogen plays a significant role in the properties of these ten-electron compounds.

2.2 Water

2.2.1 Water and the Hydrogen Bond

As already mentioned in the introduction, the hydrogen bond is responsible for many of the unique properties of water. These are a consequence of the strong intermolecular attraction between water molecules. The hydrogen bond is responsible for the ice rules that characterize solid water (Bernal and Fowler, 1935). Four protons are associated with each oxygen atom, of which in an average sense two “belong” to it through the covalent bonds, and two “belong” to other oxygen atoms, but still have a strong attractive interaction. This is responsible for the high boiling and melting points of water compared to ammonia and methane and other light molecules.
2.2.2 Vibrational Modes of the Water Molecule

The H$_2$O and D$_2$O molecules both belong to the point group C$_{2v}$, which has normal modes that transform as 2A$_1$+B$_2$ (where the molecule is taken to lie in the yz-plane) of which all are Raman and infrared active. In particular the stretching modes transform as the A$_1$ and B$_2$ representations of the C$_{2v}$ point group. The other A$_1$ mode corresponds to the bending mode. In the HDO molecule belongs to the C$_s$ point group and its the normal modes all transform as the A' representation. Thus the two stretching modes and the bending mode are all Raman and infrared active.

![Graph showing Raman and peak shift of ice phase VII for H$_2$O and D$_2$O.](image)

**Figure 2.6:** Representative Raman and peak shift of the ice phase VII of (a) H$_2$O and (b) D$_2$O. Notice that all the modes redshift indicating the strength of the intermolecular bonds. The strength of the attractive interaction increases with increasing pressure, due to the strengthening of the hydrogen bond as the intermolecular distances decrease. Note the increased number of modes due to the crystal effects (see text). Figures from Pruzan, Chervin, & Gauthier (1990).

At room temperature, H$_2$O solidifies at 0.9 GPa to form tetragonal phase VI (space group $P4_2/nmc$) (Kamb, 1965). Then at 2 GPa, phase VI transforms into phase
cubic VII (space group *Pn3m*). Ice VII consists of two interpenetrating, but not interconnected, diamond lattices with the oxygen atoms occupying the *Td* sites, and the hydrogen atoms are disordered (occupying one set of the *D3d* sites in an average fashion) (Kamb & Davis, 1964). Representative spectra are given in Fig. 2.6 for phase VII of H\(_2\)O and D\(_2\)O, as well as the peak shift. Note the strong redshift with pressure, indicating the strength of the hydrogen bond in water. The shift is \(\sim -25 \text{ cm}^{-1}/\text{GPa}\) for H\(_2\)O and \(\sim -19 \text{ cm}^{-1}/\text{GPa}\) for D\(_2\)O.

As will be seen below ice VII has a more important relationship with hydrogen and water mixtures than does ice VI. At lower temperature (278 K at 2.1 GPa for instance) the proton disordered ice VII orders to form ice tetragonal VIII (space group *I4_1/amd*). The two interpenetrated lattices have opposite dipole moments, leading to an antiferroelectric structure. The tetragonal distortion is weak, with the sublattices displaced by 0.2 Å (Pruzan et al., 2003).

Upon the solidification of a sample, two significant changes in the behavior are reflected. First, lattice modes appear in low-frequency region of the spectrum due to the collective vibrations of the molecules in the crystal. In ice VI, broad lattice modes are present (Chou, Blank, Goncharov, Mao, & Hemley, 1998). In phase VII, the lattice modes are weak and broad, whereas in the proton-ordered phase VIII, the lattice modes are strong and sharp (Pruzan et al., 2003).

Secondly, the relatively simple vibrational behavior of molecules is modified in crystals. This is due to the coupling of the vibrational motions of molecules in the cell, giving rise to in-phase and out-of-phase vibrations. As shown in Fig. 2.6, instead of the two stretching modes predicted for the water molecule, in ice VII three modes are
observed in the stretching region, \(v_1(A_{1g})\), \(v_1(B_{1g})\) and \(v_3(E_g)\) (Pruzan, Chervin, Wolanin, Canny, Gauthier, & Hanfland, 2003). The first two modes are symmetric stretching modes (\(A_{1g}\) corresponds to the in-phase and \(B_{1g}\) to the out-of-phase) while the third is the doubly degenerate antisymmetric stretching. These modes are not predicted from correlation with the \(Pn3m\) space group due to the disordered nature of the hydrogen atoms in the crystal. The correlation is with the \(I4_1/amd\) space group of ice VIII, justified by the spectroscopic similarity between these two phases and understood as arising from the partial proton ordering (Pruzan et al., 2003). The bending mode, \(v_2\), is weak and not reported in Raman spectra of ice VII. It has been reported in infrared spectra of ice VII (Holzapfel, Seiler, & Nicol, 1984) and Raman of ice VIII (Pruzan et al., 2003).

One more complication, however, must be considered. These couplings are not expected in crystals of mixed isotopes (Reding & Horning, 1955) since there no longer exists an identical unit cell repeated throughout the crystal. The case of H\(_2\)O, HDO, and D\(_2\)O, is somewhat exceptional due to the strong hydrogen bond. Even though there is not an identical unit cell throughout the crystal, there is still a strong intermolecular interaction that can give rise to intermolecular coupling (Haas & Hornig, 1960).

Finally, with increasing pressure, H\(_2\)O is expected to undergo a phase transition to a symmetric ice, referred as phase X, with the protons (or deuterons) of the hydrogen nuclei occupying a midpoint between the oxygen atoms of the ice sublattice (Polian & Grimsditch, 1984). This symmetrizing transition is believed to take place over a pressure range since the proton can occupy two positions along the line connecting the two oxygen atoms corresponding to a double well potential. As the distance between the oxygen atoms decreases, the potential barrier is expected to decrease and this will cause the
proton to delocalize, tunneling through the barrier between the two stable equilibria to occur more frequently, until eventually the proton will spend equal time in either well (Loubeyre, LeToullec, Wolanin, Hanfland, & Hausermann, 1996; Pruzan et al., 2003; Benoit, Marx, & Parrinello, 1998). This leads to symmetrization in a statistical sense, although physically, it still resides closer to one oxygen atom at any one instant. Finally, with increasing pressure, the double well potential may collapse into a single well, with the proton localized in the minimum of the well lying exactly halfway between the two oxygen atoms.

In addition to the room temperature phases of H$_2$O already mentioned and the low-temperature phase VIII, there is one other phase relevant to room temperature H$_2$-H$_2$O mixtures. Ice II is rhombohedral (space group $R\overline{3}$) and is significant because it is similar to the structure assumed by the oxygen atoms in mixtures with He and H$_2$ as will be discussed in the next section.

### 2.2.3 Hydrogen-Water Mixtures and Clathrates

We now turn our attention to H$_2$-H$_2$O mixtures. H$_2$O forms inclusion compounds known as the clathrate hydrates. The H$_2$O molecules form cages that can trap other molecules such as CH$_4$, N$_2$, Ar, Xe among others (Loveday, Nelmes, Klug, Tse, & Desgreniers, 2003). There are three clathrate structures formed of polyhedral cages, known as structures I, II, and H (Mao, Koh, & Sloan, 2007). However, these structures cannot trap smaller atoms and molecules such as H$_2$ and He. It was found that a structure similar to phase II of H$_2$O could trap He (Londono, Kuhs, & Finney, 1988) and H$_2$ (Vos, Finger, Hemley, & Mao, 1993). This H$_2$-H$_2$O clathrate (referred to as C$_1$) was stable between 0.75 and 3.1 GPa at room temperature (which is above the temperature and
pressure stability field of ice II for pure H\textsubscript{2}O). At higher pressures (above 3 GPa), these
cages become unstable, and x-ray data shows that the structure of this H\textsubscript{2}-H\textsubscript{2}O compound
becomes fcc, belonging to the space group Fd3m, with the oxygen atoms occupying the
positions of the carbon atoms in the diamond lattice (Vos, Finger, Hemley, & Mao, 1993;
1996). This is related to ice VII, which has two of these interpenetrating lattices, and it is
supposed that the hydrogen molecules are occupying the positions of the other lattice as
well as perhaps interstitials in the lattice.

2.2.4  Spectral Features of H\textsubscript{2}-H\textsubscript{2}O Mixture

Figure 2.7 shows Raman spectra of the C\textsubscript{1} and C\textsubscript{2} phases of H\textsubscript{2}-H\textsubscript{2}O mixtures. The
Q\textsubscript{1} vibrational mode of hydrogen and the rotational modes of hydrogen are evident and
quite similar in both. The main differences concern the five lattice modes in the low-
pressure clathrate C\textsubscript{1} compared with three that were observed in C\textsubscript{2}. Additionally, the
features of the O-H stretching vibrational band are better resolved in C\textsubscript{2} compared to C\textsubscript{1}. There is also a clear resemblance between the O-H stretching vibrational bands in ice VII.

Figure 2.7: (a) Comparison of the spectral features of the C\textsubscript{1} and C\textsubscript{2} H\textsubscript{2}-H\textsubscript{2}O mixtures. (b) The peak shift
for the frequency of the v\textsubscript{1} modes C\textsubscript{2} clathrate redshift at about twice the rate as those in the phase VII of
H\textsubscript{2}O. The bottom axis corresponds to the square figures and the top axis corresponds to the lines. Also, the
top pressure scale increases faster by a factor of two. Figure (a) from Vos et al. (1993), and Figure (b)
modified from Vos et al. (1996).
and C₂, which is due to the similarity between these structures. Finally, the rate of redshift for both the v₁ vibrational modes of O-H and O-D in C₂ is about twice that in ice VII (Vos et al., 1996). This was attributed to the fact that one of the two interpenetrating lattices of ice VII is absent in the C₂ clathrate. Thus the ice lattice was, in a sense, supporting twice the load at a given pressure in C₂ compared to ice VII.

2.3 Ammonia

2.3.1 Ammonia and the Hydrogen Bond

Ammonia, as mentioned in the introduction, also exhibits hydrogen bonding. This is due to its pyramidal shape, with the unpaired electrons of the nitrogen atom exposed and able to attract the hydrogen atoms of an adjacent ammonia molecule. This then suggests that ammonia may exhibit similar behavior to water mixed with other molecules. In particular, this justifies the search for analogues to clathrates. Nevertheless, since there is only one lone pair of electrons (as opposed to the two of H₂O), it should be expected that the effects of hydrogen bonding will be less pronounced in ammonia.

2.3.2 Vibrational Modes of the Ammonia Molecule

The normal ammonia (NH₃) and triply-deuterated ammonia (ND₃) molecules belong to the point group C₃v. They have four fundamental vibrational modes that transform as 2A₁ + 2E. All these modes are both infrared and Raman active. These are classified as the symmetric stretching mode v₁(A₁), the symmetric bending mode v₂(A₁), the doubly-degenerate antisymmetric stretching mode v₃(E) and the doubly-degenerate antisymmetric bending mode v₄(E). The singly-deuterated (NH₂D) and doubly-deuterated (NHD₂) ammonia molecules belong to the point group Cₛ. There are six fundamental vibrational modes that transform as 4A'+2A". Once again, all these modes are both
infrared and Raman active. For NH$_2$D, there is one N-D stretching mode $\nu_1^{\text{ND}}(A')$, and two modes correspond to stretching vibrations of the two N-H bonds: the symmetric $\nu_3^{\text{NH}}(A')$ and the antisymmetric $\nu_3^{\text{nNH}}(A'\prime \prime)$. Also, there is the bending mode of the N-D bond $\nu_2^{\text{ND}}(A')$ and the bending modes involving the two N-H bonds: symmetric $\nu_4^{\text{NH}}(A')$ and the antisymmetric $\nu_4^{\text{nNH}}(A'\prime \prime)$.

Similarly for NHD$_2$, there is one N-H stretching mode $\nu_1^{\text{NH}}(A')$, and the two modes correspond to stretching vibrations of the two N-D bonds: the symmetric $\nu_3^{\text{ND}}(A')$ and the antisymmetric $\nu_3^{\text{nND}}(A'\prime \prime)$. Finally, there is the bending mode of the N-H bond $\nu_2^{\text{NH}}(A')$ and the bending modes involving the two N-D bonds: symmetric $\nu_4^{\text{ND}}(A')$ and the antisymmetric $\nu_4^{\text{nND}}(A'\prime \prime)$.

**Figure 2.8:** (a) Representative Raman spectra of solid ammonia. Phase III is disordered with very broad modes. The peaks of Phase IV are sharper, indicating with the ordered structured. Phase V shows similar Raman features to Phase V, apart from the shift of the frequency modes. (b) The shift of the vibrational modes with pressure. Figure from Gauthier et al. (1988).
Ammonia and its triply-deuterated form, ND₃, have been the subject of Raman, x-ray, neutron and x-ray studies under high pressure (Gauthier, Pruzan, Chervin, & Besson, 1988; Pruzan Chervin, J. C., & Gauthier, 1990; Datchi, Ninet, Gauthier, Saitta, Canny, & Decremps 2006; Ninet, Datchi, Saitta, Lazzeri, & Canny 2006; Ninet, Datchi, Klotz, Hamel, Loveday, & Nelmes, 2009).

Figure 2.8 shows representative Raman spectra and the peak shift of the vibrational modes with pressure. The ν₂ and ν₄ bending modes are weak and are not observed in room temperature Raman (Ninet et al., 2006). Ammonia undergoes a transition from liquid to fcc phase III, (space group Fm3m) at 1 GPa. The vibrational spectrum of liquid ammonia is very similar to that of phase III. Both appear to have three broad peaks, and phase III has no lattice modes. The phase III to orthorhombic phase IV (P2₁2₁2₁) occurs at 4 GPa. This transition to Phase IV is indicated by the appearance of lattice modes and sharper peaks in the vibrational region of the spectrum. This is consistent with the ordering of Phase IV. Additionally, a discontinuity is observed in the ν₁ mode at this transition. Finally ammonia undergoes an isostructural transition to an orthorhombic phase V at 12 GPa in NH₃, and 18 GPa in ND₃ (Datchi et al., 2006). This phase transition involved significant changes in the lengths and orientations of the hydrogen bonds in solid ND₃ (Ninet et al., 2009).

The stretching vibrational spectra of the ammonia isotopes are complicated. (Ninet et al., 2006). This is due to the presence of many broad, overlapping features, especially in the frequency ranges of the N-D (~2300-2500 cm⁻¹) and N-H (~3200-3400 cm⁻¹) stretching modes. Fermi resonances have been suggested due to the closeness of the frequencies of the ν₁ and 2ν₄ modes in both NH₃ and ND₃. Further complications arise in
the crystal, leading to splitting of the peaks. As previously mentioned on the discussion of water, the vibrational modes will split due to the coupling between molecules in unit cell and will result in Davydov splitting. This results, for instance in phase IV, in the $v_1$ stretching mode splitting into four modes, and the degenerate stretching $v_3$ modes splitting into eight modes.

Note that within each phase the $v_1$ modes redshifts (Fig. 2.8). This symmetric stretching mode probes the hydrogen bond, the attractive interaction between hydrogen atoms on a molecule and the nitrogen atom on a neighboring molecule. This shift to lower frequency reveals the increasing strength of the hydrogen bond. Nevertheless, notice that the redshift is much weaker than that observed in water ($\sim -3 \text{ cm}^{-1}/\text{GPa}$ compared to $\sim -20 \text{ cm}^{-1}/\text{GPa}$). The $v_1$ mode of ND$_3$ exhibits a much weaker redshift (Pruzan, Gauthier, & Chervin, 1990).

There have been no previous high-pressure studies of NH$_2$D and NHD$_2$. NH$_3$ and ND$_3$ have been mixed and these have led to mixtures of NH$_3$, NH$_2$D, NHD$_2$, and ND$_3$. These samples were then studied with low-temperature (between 18 and 190 K) Raman and infrared spectroscopy. These correspond to the stability region of Phases I and II of ammonia (Reding & Hornig, 1951; 1954; 1955; Rollar, & Wolff, 1971; Binbrek & Anderson, 1972). The modes observed in the infrared and the Raman spectra were assigned to the modes described above. There exist relationships between the products and sums of the squares of the vibrational frequencies of isotopic molecules (Wilson, Decius, & Cross, 1980). This will be described further in Appendix A.

In the crystal composed of mixed isotopes, the splitting in the vibrational modes does not occur. There is no unit cell with identical molecules repeating throughout the
lattice due to the presence of different isotopes. This eliminates the intermolecular coupling and the observed frequencies are similar to the molecular frequencies (Reding & Horning, 1955).

2.3.3 Hydrogen-Ammonia Mixture

Chidester and Strobel (2011) studied H₂-NH₃ up to 15 GPa, observing the phase transitions taking place at the same pressures as were observed in pure NH₃ (Chidester & Strobel, 2011). Interactions were observed in the fluid between the NH₃ and the H₂, but it was claimed that the H₂ and NH₃ were immiscible upon solidification of NH₃. The attractive interaction between the fluid NH₃ and the H₂ dissolved in the NH₃ is clearly observed from the lower vibrational frequency, and was also observed under 4 GPa in one of four experimental runs.

![Figure 2.9: Summary of the H₂-NH₃ mixture to 15 GPa. The normal ammonia phase progressions are observed at the same pressure as in pure ammonia (a) and (b), and hydrogen freezes at 5.5 GPa, the same pressure as in pure (c). The hydrogen dissolved in the ammonia is redshifted with respect to the frequency in bulk hydrogen ((a) at 0.88 GPa). Figure from Chidester and Strobel (1988).](image-url)
2.4 Methane

2.4.1 Absence of Hydrogen Bonding in Methane

Methane is the simplest saturated hydrocarbon. The molecular has a tetrahedral structure, resulting in a nonpolar molecule. As a result, hydrogen bonding is absent in methane, in contrast to water and ammonia, as mentioned in the introduction. Consequently, intermolecular interactions are expected to be weak for methane. Its behavior has been compared to that of a bad noble gas (Hebert, Polian, Loubeyre, & Le Toullec, 1987).

2.4.2 Vibrational Modes of Methane Molecule

Unlike H$_2$O and NH$_3$, CH$_4$ does not have lattice modes. CH$_4$ belongs to the point group T$_d$, and has four fundamental vibrational modes that transform as A$_1$ + E + 2T$_2$ (T$_2$ is sometimes labelled as F$_2$ in the literature as in the present reference). The modes are classified as the symmetric stretching mode $v_1$(A$_1$), the doubly degenerate bending mode $v_2$(E), the triply degenerate stretching mode $v_3$(T$_2$), and the triply degenerate bending mode $v_4$(T$_2$).

Methane and its quadruply-deuterated form, have been studied under pressure by Raman and x-ray studies (Hebert et al., 1987; Wu, Sasaki & Shimizu 1995; Hirai, Konagi, Kawamura, Yamamoto, & Yagi, 2008; Chen, Zha, Chen, Shu, Hemley, & Mao, 2011). It solidifies at around 1.7 GPa at room temperature in Phase I with an fcc structure (space group Fm3m), and solid-solid phase transitions have been reported at 5.2 GPa (to phase A), 12 GPa (to phase a), 13 GPa (to Phase B), and various ill-characterized, high-pressure phases have been reported at 25 GPa and higher pressures (Bini, Ulivi, Jodl, & Salvi, 1997; H. Hirai et al. 2008; Chen et al., 2011). These studies have indicated that the
transitions to the high-pressure phases are sluggish with a relaxation period of at least 12 hours being required for them to form.

**Figure 2.10:** Representative vibrational Raman spectra of (a) CH$_4$ and (b) CD$_4$. The two dominant modes are the two stretching modes: $v_1$ (symmetric) and the $v_3$ (antisymmetric). The double degenerate bending mode, $v_2$, and the triply degenerate bending mode, $v_4$, are both weak. The $v_4$ lines are not observed in either CH$_4$ or CD$_4$, although in CH$_4$ it overlaps with the strong first-order diamond line at $\sim$1330 cm$^{-1}$. The asterisks indicate plasma lines. Figures from Wu et al. (1995).

Figure 2.10 shows representative Raman spectra of CH$_4$ (a) and CD$_4$ (b). The dominant mode is the $v_1$ vibrational mode in both CH$_4$ and CD$_4$, with the intensity of $v_3$ mode increasing with pressures in both molecules. The $v_2$ mode is weak in both cases, and the $v_4$ was not observed in either sample. In addition, the $v_4$ mode in CH$_4$ overlaps with the very intense first-order diamond line, which would conceal it even if it were intense enough to be observed.

Figure 2.11 presents the pressure dependence of the vibrational modes of methane that indicates the phase transitions. The discontinuities of the $v_3$ vibron at 1.7 GPa in both CH$_4$ and CD$_4$ indicate the solidification of methane, and the presence of a new peak on the side of $v_1$ vibron coincides with the transition to Phase VII at 5.7 GPa. Notice that
unlike water and ammonia, all the vibrational modes exhibit blueshift with pressure.

![Graph showing peak shift of vibrational modes of CH₄ and CD₄](image)

**Figure 2.11**: Peak shift of the vibrational modes of CH₄ and CD₄. Notice the spectral changes that coincide with the phase transitions. Also, the vibrational stretching modes (including symmetric $\nu_1$) blueshift in contrast to the $\nu_1$ modes of ammonia and all the vibrational stretching modes of water. Figures from Wu et al. (1995).

### 2.4.3 Hydrogen-Methane Mixtures

Hydrogen-methane mixtures have been studied under pressure (Somayazulu, Finger, Hemley & Mao 1996; Mao & Mao, 2004; Struzkhin, Militzer, Mao, Mao & Hemley, 2007), although the papers by Mao and Mao and Struzkhin et al. the mixtures were studied at very low pressures on the order of 0.1 GPa. Somayazulu et al. found that the freezing pressure of the H₂-CH₄ mixtures is dependent on the composition. It ranges from 1.7 for pure methane, up to 7 GPa in hydrogen-rich mixtures. The freezing pressure is around 5 GPa for a D₂:CH₄ ratio of 1:1, significantly higher than that observed in pure CH₄ samples. (Somayazulu et al., 1996). H₂-CH₄ mixtures were studied using both x-ray and Raman spectroscopy up to 30 GPa. The pressure was increased on the fluid sample until it crossed the liquidus line, then the sample was heated until it melted. Finally the sample was allowed to cool and thus recrystallize. This generated two regions in the
sample, one with the crystal and the other only with a fluid. The following four different stoichiometric molecular compounds were found and characterized: CH₄H₂, CH₄(H₂)₂, (CH₄)₂H₂, and CH₄(H₂)₄.

Figure 2.12: (a) The phase diagram of the H₂–CH₄ mixture exhibiting the solidification line as a function of hydrogen composition at room temperature. Additionally, the regions of stabilities of the different stoichiometric compounds are shown. (b) Microphotographs of the samples and representative Raman spectra of the H₂ vibrational modes are shown. These allow the different stoichiometric compounds to be identified. Note that the vibrational frequency is different from the frequency of pure H₂. Figure from Somayazulu et al. (1996).

2.5 Proton Exchange Reactions

Soon after the discovery of deuterium (Urey et al., 1932), proton exchange reactions were observed between water and deuterium (Oliphant, 1933). Nevertheless, these reactions took months to occur unless a catalyst was used (Horiuti & Polanyi, 1933). Deuterium was mixed with many hydrogen-containing chemical compounds to examine whether proton exchange would take place (Urey & Teal, 1935). For instance, it was observed that the hydrogen of the –OH of sucrose would exchange, but the H of –CH
in this molecule did not exchange. Rapid exchange was also observed for the hydrogen of the –NH$_2$ group with water, but not for the hydrogen of the –CHO group exchanged slowly. Additionally, it was observed that there was a dependence on the acidity of the solutions, with the exchange taking place rapidly in alkaline solutions, more slowly in acidic solutions, and very slowly in neutral solutions.

More recently, proton exchange was reported in mixtures of H$_2$ and D$_2$ to form HD (Bell, 1981). Within the fluid hydrogen mixtures the rate of proton exchange was observed to increase with pressure. This was also observed in dilute mixtures of H$_2$ (4 mol%) in D$_2$ because about half the H$_2$ molecules would react with D$_2$ to form HD (Loubeyre, Le Toullec & Pinceaux, 1992). More details were provided in another study, which examined the degree of completion of the reaction and the dependence of the frequency shift with the composition of the isotopes (Brown & Daniels, 1992). As previously mentioned, it was found that the more dilute the isotopic species, the greater the frequency blue shift at a given pressure.
Chapter 3

Experimental Methods

3.1 Static High Pressure Techniques: The Diamond Anvil Cell

Pressure is defined as the force applied over a given area. The key idea in generating high pressures comes directly from this definition, since for a given applied force, merely reducing the area over which it acts will increase the pressure. The fact that high-pressure research began in 1909 with Percy Bridgman, after classical mechanics and thermodynamics were well-developed and temperature was a standard experimental variable (helium was liquefied around the same time) illustrates the magnitude of the experimental challenges (Jayaraman, 1983). Bridgman’s techniques allowed for high-pressure studies of materials, but only with limited techniques, such as transport measurements and compressibility studies. This was because his anvils were opaque to substantial regions of the electromagnetic spectrum. As a result, diamond, the hardest known material, presented the possibility of a considerable advance. Diamond is transparent to a large energy range of the electromagnetic spectrum including x-ray (greater than 10 keV), infrared, visible and near-ultraviolet (less than 5 eV) (Dunstan & Spain, 1989). An attempt to exploit these properties was first made by Lawson and Tang. They performed x-ray diffraction measurements using a drilled single-crystal diamond with a miniature piston (Lawson & Tang, 1950). Nevertheless, with the invention of the diamond anvil cell in 1959, a tool was found that made possible application of static high-pressure techniques to a wide range of problems in physics and chemistry. The diamond anvil cell was invented independently for absorption measurements (Weir,
3.1.1 The Diamonds, Bases, and Cell

The diamonds are gem-quality and usually cut so that the (100) or (110) plane of the diamond is parallel to the surface used as the anvil (Jayaraman, 1983). The diamonds used in experiments must exhibit very low fluorescence to prevent interference with the signal from the sample. A hard material supports the diamond in order to transfer the load from the cell and prevent the diamonds from indenting the cell. Also, it is necessary to ensure that the faces of the two diamonds culets are parallel to each other. Furthermore, it must be possible to adjust the position of the diamonds in order to align the culets directly over each other. In the present work, this was achieved by mounting each diamond on a tungsten carbide base using a Stycast epoxy (2850 FT Black), which would set in 24 hours at ambient temperature or 3-4 hours at 65° C. The tungsten carbide bases each have an aperture in the center providing optical access to the diamond culet. The bases are lapped until flat, and then polished successively with 15-, 9- and 3-μm diamond grit to make a smooth, shiny surface to provide for even contact between the base and the
diamond surface, thereby helping distribute the stresses evenly. The diamond culet must be placed so that the center of the anvil is aligned with the center of hole in the base. The tungsten carbide bases in turn, are placed in the cell, one on the piston side, and the other on the cylinder side. The piston and the anvil of the diamond anvil cell were machined to fit very tightly together, and the area of the cell on which tungsten carbide bases sit are machined so that they are parallel. Then, the bases can be adjusted with setscrews until the two diamond culets are aligned in the cell.

Figure 3.1: Schematic showing the diamond anvil cell. The culets of the two press the sample, which is confined by a metal gasket. A ruby is placed in the sample chamber to serve as a pressure marker. The diamonds are transparent to a wide range of electromagnetic radiation, which allow the sample to be observed visually and probed by spectroscopy or by diffraction. On the upper left hand, a microphotograph shows the two diamonds with the gasket between them.

Different sizes of diamond culets can be used, and as would be expected, the smaller the culet size, the higher the pressure that can be achieved. There are two different types of diamond, flats and beveled. Typical diameters for flat diamonds are 500 and 300 μm. Both 500 and 300 μm diameter anvils were used, with the 300 μm being the most commonly used in these experiments. The 500-μm flats were used up to 30 GPa in
these experiments and the 300 μm flats were used up to 65 GPa. For higher pressures beveled diamonds with 180 μm or 100 μm are used.

![Figure 3.2: The diamond anvil cell, showing the cylinder side (on the far left) and the piston in the middle. The diamonds are joined to the tungsten carbide seats with epoxy, and the diamonds can be aligned with setscrews through the sides of the cell. On the far right, the diamond anvil cell is shown closed, with the screws for applying pressure. The screws should be tightened in a criss-crossing fashion (ABCD, etc.).](image)

The cells used in the present work, designed by Professor Choong-Shik Yoo and shown in Fig. 3.2, are made out of hardened stainless steel, with cylinder and piston sides. The cell diameter is 2" inches, and the cell height is about 1.9" (the height will vary slightly once the cell is assembled).

It is necessary to apply a load to the diamond anvil cells in order to increase the pressure. One of the features of using the small area of the diamonds is that high pressures can be reached by applying moderate forces to the cell. The pressure can be adjusted by using two different methods in our laboratory. The first method is simply by adjusting four screws on the diamond anvil cell. Hex screws (5/32” head size) with Belleville spring lock serrated washers placed along their shanks are tightened to increase the pressure in the diamond anvil cell. These should be tightened (and released) in a criss-crossed pattern ABCD (as shown from the screws labeled in Fig. 3.2).
The other method of increasing the pressure is utilizing the membrane that is pressed against the back of piston end of the diamond anvil cell. It is held in place by a metal cap that is screwed onto threads on the outside edge of the cylinder of the diamond anvil cell. Helium gas is directed through a tube and into the membrane, thereby applying force to the back of the piston, while the cylinder cannot move away to release the pressure because it is held fixed by the cap. A membrane controller controls the flow of helium. The membrane controller is advantageous because it allows for the uniform application of force. It also allows the pressure to be increased when the diamond anvil cell cannot be easily touched or accessed in the case of high- or low-temperature experiments.

3.1.2 Gasket Materials

A metal gasket is a standard component of diamond anvil cells (Dunstan, 1989). Stainless steel and spring steel are used for low-pressure experiments (< 40 GPa), and rhenium and tungsten are used for megabar pressures. The gasket is a thin metal plate, normally around 200 μm in thickness, which is first pre-indentated to a final thickness of 30 – 40 μm using the diamond anvil cell. The pre-indentation creates a depressed area, with the surrounding region raised up that fits the facets of diamond exactly. Then a hole is drilled in the middle using an electric discharge machine (EDM), which will become the sample chamber. The EDM allows the hole to be drilled in the center of the pre-indentated area so that the sample chamber remains stable as pressure is applied and is situated in the region of maximum pressure. This is particularly important in highly compressible molecules such as H₂ or He, because the volume collapse of the sample must be compensated for a corresponding shrinking of the sample chamber. This collapse
can lead to instabilities that will often result in the sample drifting from the center of the pre-indented area. This will prevent the experiment from reaching the highest possible pressures for the diamond anvil culet area, and also increases the risk of breaking the diamonds. The metal gasket serves two purposes, allowing the formation of a cylindrically shaped sample chamber that permits the use of a pressure medium, and furthermore, the diamond-shaped depressed region provides support and guides the two diamonds together (Jayaraman, 1983).

An ideal material for a gasket would have high yield strength and high ductility. The yield strength allows it to withstand the high stresses and the greater the strength the higher pressures that can be achieved. The important of the ductility, while not quite so obvious, is because it allows the gasket to assume the shape of the diamond, extruding around it without fracturing. While both of these properties are important, the general relationship requires that trade-offs be made as the yield strength of a material tends to decrease with increasing ductility (Moss, Hallquist, Reichlin, Goettel, & Martin, 1986). Also importantly, the gasket must not react with the chemicals loaded into the sample chamber. This is especially important when working with highly reactive materials, and also when working with small atoms and molecules, like hydrogen and helium, that can enter the lattice of the metal, and embrittle it, causing the gasket to weaken and fail. It has been observed that under pressure and at high temperature hydrogen will diffuse into the gasket and diamond (see for example, Datchi, Loubeyre, & LeToullec, 2000; Gregoryanz, Goncharov, Matsuishi, Mao, & Hemley, 2003; Deemyad & Silvera, 2008).
3.1.3 Pressure Calibrant-Ruby

There are many pressure calibrants in use, such as ruby, copper, and diamond among others. The most commonly used method for determining the pressure of samples in the diamond anvil cell is ruby luminescence. Ruby is chromium-doped aluminum oxide (α-Al₂O₃). The Cr³⁺ replaces aluminum atoms and due to the size of the Cr³⁺ ions, they increase the lattice size (Syassen, 2008). The emission lines of ruby exhibit a pressure-dependence. The line that is used, R₁, has a wavelength of ~694.3 nm at ambient temperature and pressure. Additionally, there is another nearby line, referred to as R₂. These two lines arise from the splitting in the trigonal crystal field of the ²E and ⁴A₂ energy levels of the Cr³⁺ ion. The energy difference between these two excited states and the ground state decreases as the crystal is strained, leading to a frequency redshift (Syassen, 2008). This shift has been determined by shock wave experiments, since these allow for the pressure to be determined mechanically.

Ruby is useful for determining the pressure in the diamond anvil cell due to its strong luminescence, and the sharpness of the R₁ line. Thus this signal can be collected quickly and the wavelength can be determined accurately. Additionally, the wavelengths of the R-lines are far from the frequency ranges of interest for most high-pressure experiments (in particular if laser frequencies between 488 and 532 nm are used). Finally, ruby is also useful since it is stable and does not react with most samples.

The most commonly used formula for the ruby line is given by

\[
    P(\lambda) = \frac{A}{B} \left[ \left( \frac{\lambda}{\lambda_0} \right)^B - 1 \right]
\]

where \( A = 1904 \text{ GPa}, B = 7.665 \), and \( \lambda_0 \) is the wavelength corresponding to the R₁ line at ambient pressure (Mao, Xu, & Bell, 1986; Syassen, 2008). Although, there have been
more recent works on the pressure-dependence of the R-lines, these have not led significant differences under 50 GPa (Syassen, 2008).

3.2 High-Pressure Gas Loader

It is necessary to obtain highly compressed gases for loading into the diamond anvil cell. The density of gases at room temperature and atmospheric pressure is too low to obtain a sufficient quantity of sample after they condense into fluid or solid phases. The higher density will provide enough molecules to reduce the collapsing of the sample chamber as the pressure increases and provide a large enough sample to study. While it is possible to load gas samples cryogenically, another very useful way of achieving these high densities is by means of a high-pressure gas loader. In practice, pressures of 0.1-0.2 GPa (15,000 to 30,000 psi) are needed to achieve adequate densities.

3.2.1 Principles and Operation of High-Pressure Gas Loader

The high-pressure gas loader used in the present work was designed by Professor Choong-Shik Yoo at Washington State University and uses a 30,000-psi two-stage compressor from Newport Scientific. The first stage requires pressures greater than 200 psi to function, and the second stage requires pressure of 7,600 psi. Each head has two chambers, one for oil and the other for gas, separated by a metal diaphragm, which is a round, thin piece of 302 Stainless steel (9 cm diameter by 200 μm thick). The two sides of each heads are held together by 8 nuts and bolts, with the first stage nuts being tightened to 150 ft-lbs, and the second stage being tightened to 350 ft-lbs. The low-pressure head used one diaphragm, while the high-pressure head has two diaphragms to withstand the higher pressures. The compressor forces oil into the chamber, which then exerts pressure on the metal diaphragm. Then the oil pressure is transmitted to the gas on
the other side of the diaphragm. The gas chambers on both heads have gas check valves. Each head has an inlet check valve that only allows flow into the chamber, and an outlet check valve that only allows flow out of the chamber.

![Figure 3.3: Schematic of the high-pressure gas loader. The LP Vent and HP Vent close off the system. It is equipped with a vacuum pump to evacuate the lines to remove air and any source of impurities. On the low-pressure side are lecture bottles for generating mixtures of gases. The LP Fill 2 valve closes the circuit so that pressure can build up on the high-pressure side.](image)

**Figure 3.3**: Schematic of the high-pressure gas loader. The “LP Vent” and “HP Vent” on the upper right hand side allow the system to be closed and also allow the gas to be vented after loading. Two sizes of tubing are used. The ¼" tubing is rated for maximum pressures of 30,000 psi, and the ½" tubing is rated for pressures of 60,000 psi.

The diamond anvil cell is placed into a cell holder. This cell holder is a cylinder with outer diameter 2.51" and an inner diameter of 2.01", and the cylinder is about 3
inches long. The cell fits inside it, and there are holes in the cylinder cover to allow the gas to reach the cell and the screws of the diamond anvil cell to be accessed. The cell holder is then placed inside a cell chamber in the high-pressure loader. The cell chamber is a large cylinder (made of an A286 alloy), with an inner diameter of about 2.5", and an outer diameter of about 7.5". The wall thickness of the cell chamber is 2.5". The cell chamber is sealed with a metal ring and O-ring, and then a heavy metal cap is screwed on.

The high-pressure loader is also equipped with a vacuum pump (Varian) to remove the air from the tubing before loading. Also it can be used to remove all the air from the lecture bottles before they are filled with gas, thereby removing a source of impurities.

Large gas tanks (~200 cubic feet) are connected to the high-pressure gas loader. With the tank open, the gas can flow into the high-pressure loader by opening the upper left needle valve (all valves are from High Pressure Equipment) labeled “Gas from Tanks”. Before this needle valve there is a one-way valve, which prevents backflow and contamination of the large gas tanks. The two valves on the left labeled “Gas 1” and “Gas 2” allow for gas to be stored in lecture bottles in order to save and reuse expensive gases and also to produce gas mixtures for experiments. When mixing gases caution must be exercised so that the gases do not mix on other side of the “Gas from Tanks” valve, where under the current design three tanks can be connected. The LP Fill 1 allows for the gases to be mixed by allowing the compressor to increase the pressure on the side of the lecture bottles above that of the pressure of the large gas tank. The “Inlet Pressure” digital pressure gauge (Design Concepts, Inc.) can be used to read the pressure in any given
tank. When the LP Fill 1 valve is closed, the “Inlet Pressure” gauge will give the pressure in lecture bottle(s) assuming the appropriate valves are opened. A relief valve (labeled “1.8k psi Limit”) prevents the pressure at the lecture bottles from exceeding 1800 psi for safety. The LP Fill 2 valve closes the circuit and allowing the pressure to build up on the cell side of the compressor. There is also a line filter before the compressor to prevent the passage of dust particles into the compressor. On the high-pressure side, there is also a 40,000 psi rupture disc for safety (labeled “30k psi Limit”). There is also a digital pressure gauge (labeled “Cell Pressure”).

Once the compressor has been used to compress the gas to the desired pressure, the HP fill valve can be closed to maintain the highest possible pressure at the cell. Two screws of the diamond anvil cell, on opposite sides (for example, A and B, as labeled in Fig. 3.2), can be accessed to open and close the cell.

Nevertheless, there are significant dangers involved in compressing gases, such as dangers of ruptures, with metal tubing and parts being forced outward at high velocities. Additionally, any rupture would likely be accompanied by a very loud sound, possibly damaging to the operators’ and any bystanders’ hearing. To provide protection against this danger, the entire system (the compressor, vacuum pump, and all the tubing) is surrounded by a polycarbonate layer, which then has aluminum surrounding it. Finally, while leaks are always to be avoided, when loading toxic gases their prevention is even more important as they pose a considerable hazard. The present work does not use any toxic gases.

The high-pressure gas loader can be used with inert noble gases (helium and neon) as well as with simple diatomic gases such as hydrogen, deuterium, nitrogen, and
polyatomic gases such as methane. Notably, oxygen gas cannot be loaded with the high-pressure loader, due to the danger of explosion because of the oils used in the high-pressure loader.

3.2.2 Sample Loading Procedure

We will now describe the loading procedure, with a special emphasis on mixtures. When loading a gas into a liquid already loaded in the cell, it is critical to open the cell enough to allow the gas to enter, but not so much that the liquid can escape the cell. After having loaded the ruby chips and any other solid or liquid sample, the diamond anvil cell should be closed. In the case of liquids it will be necessary to create a bubble to give the gas room to fill. In order to do this, we first gently tighten all four screws until they exert an even pressure on the pre-indented area, sealing the cell. It is important that the tops of the screws be even with the top of the cell. A metal cap is screwed onto the top of the diamond anvil cell. This is necessary so that when the screws are loosened, they will exert pressure on the cap, and force the cell to open. Only one set of two screws can be accessed while the cell is inside the high-pressure gas loader. These two screws (for example, A and B with reference to Fig. 3.2) should be loosened slowly until they exert a slight pressure on the cap. If a bubble does not form at this point, the A and B should be returned to their initial tightness. Then the other two screws (C and D) should be loosened 5-10°, and A and B should once again be loosened until a bubble forms. In the event that loosening A and B again exert a slight pressure on the cap without a bubble forming, the process should be repeated until a bubble forms.

Once the bubble forms, the screws should be tightened until the cell is sealed to prevent the liquid from evaporating out of the cell. The amount that was closed this final
time should be noted and that is how much the cell should be opened in the high-pressure loader. The result of this procedure is to ensure that the cell opens in the high-pressure loader, but not so much as to allow the liquid previously loaded to escape. Of course, these problems are not present when loading a gas into a cell with a solid sample. After the gas has been loaded into the cell, the two screws are closed again before venting (or recollecting) the gas and removing the cell.

The loading of the actual samples studied in this work will now be described. For all the samples, the gasket was pre-indentated to 40 µm. A hole of 100 to 150 µm for 300-µm diamonds or 200 to 300 µm for 500-µm diamonds was drilled using the electrical discharge machine. Then a few particles of ruby crystals for pressure measurements were placed in the sample chamber. For the D₂-H₂O sample, de-ionized water was loaded into the diamond anvil cell, and an air bubble was captured in the sample chamber. Then D₂ (Advanced Specialty Gases, 99.999% purity) was loaded using the high-pressure gas loader as described above. For the D₂-NH₃ mixture, after the ruby was loaded, NH₃ (Sigma Aldrich, purity >99.99%) gas was liquefied into the diamond anvil cell at −50° C. Once again the air bubble was allowed to form in the sample chamber, and then D₂ was loaded using the high-pressure gas loader as before. For the D₂-CH₄ mixture, after loading the ruby, a mixture of D₂ and CH₄ (Advanced Specialty Gases, 99.999% purity) was prepared in a lecture bottle as described above. Then it was loaded into in an empty diamond anvil cell using the high-pressure gas loader in a single step.
3.3 Raman Spectroscopy

3.3.1 Principles of Raman Spectroscopy

Raman spectroscopy exploits the Raman effect, which A. Smekal predicted (Smekal, 1923) and was discovered by Raman and Krishnan, in liquid solutions (Raman, 1928; Raman & Krishnan, 1928), for which Raman was awarded the Nobel Prize in Physics in 1930. G. Landsberg and L. Mandelstamm also observed the effect in solids (Landsberg and Mandelstamm, 1928). The Raman effect, which is quite weak, involves inelastically scattered light. The majority of the scattered light is scattered elastically (with the same energy as the incident light). This is known as Rayleigh scattering. A small percentage of the light is scattered inelastically, and this is referred to as Raman scattering. The Raman scattered light emerges with definite frequencies, which are frequency differences from the incoming radiation. These frequencies are located symmetrically both above (anti-Stokes) and below (Stokes) the incident frequency. As will be explained in detail below, the Stokes line tends to be more intense. The scattered frequencies are characteristic of the bonds in the sample, and are independent of the exciting wavelength. The effect can be understood both classically and quantum-mechanically, and these ideas will be briefly sketched out below.

3.3.2 Classical Explanation of the Raman Effect

The classical explanation of the Raman effect considers the induced dipole moment by both the polarizability of the molecule under rotation or vibration and electric field of incident photon (Herzberg, 1945, 1950). The induced dipole moment, $P$, is related to the polarizability $\alpha$ and electric field by

$$ P = \alpha |E|. \quad (3.2) $$
In general, it is necessary to take into account the directions of \( \mathbf{P} \) and \( \mathbf{E} \), and all the components of the tensor \( \alpha \). Nevertheless, what follows is sufficient to show how the classical argument accounts for some of the essential features of the Raman effect. The electric field of the incident light is given by

\[
\mathbf{E} = E_0 \sin(\omega_i t)
\]

(3.3)

where \( \omega_i = 2\pi \nu_i \), where \( \nu_i \) is the frequency of incident radiation. The change in the polarizability tensor to first-order due to vibration or rotation can be approximated as:

\[
\alpha = \alpha_0 + \alpha_1 \sin(\omega_{\text{mol}} t)
\]

(3.4)

where \( \omega_{\text{mol}} = 2\pi \nu_{\text{vib}} \) for general vibrational modes, and \( \omega_{\text{mol}} = 2\pi 2\nu_{\text{rot}} \) for diatomic rotational modes. The factor of two in the rotational modes is due to the fact that for rotation, the polarizability will be the same after a rotation of 180°. Thus, the polarizability rotates with twice the frequency of a diatomic molecule. Then, the polarizability, to first order can be expressed as

\[
|\mathbf{P}| = \alpha_0 |E_0| \sin(\omega_i t) + \alpha_1 |E_0| \sin(\omega_i t) \sin(\omega_{\text{mol}} t)
\]

(3.5)

The first term describes scattered light with the same frequency as the incident light. This accounts for the Rayleigh line from a stationary molecule. Using the cosine sum and difference formulae, the second term can be rewritten as

\[
\alpha|\mathbf{E}| = \frac{1}{2} \alpha_1 |E_0| \cos[(\omega_i - \omega_{\text{mol}}) t] - \frac{1}{2} \alpha_1 |E_0| \cos[(\omega_i + \omega_{\text{mol}}) t]
\]

(3.6)

Thus frequency of the scattered light will depend upon the frequencies of the rotational and vibrational motions of the molecule.

The classical explanation successfully accounts for the emission of frequencies above or below the exciting wavelength. Nevertheless, there are three discrepancies with
experiment. First, the predicted shift in the rotational frequency is twice as great as that experimentally observed for diatomic molecules. Additionally, the rotational lines are not quantized classically, thus a band is predicted rather than the discrete lines observed experimentally. Finally, the classical theory predicts the same intensities for the Stokes and anti-Stokes lines, in disagreement with experiment.

**Figure 3.4:** A schematic of the Raman effect. In Stokes scattering, a photon of energy $h\nu$ collides with a molecule, which absorbs energy $\Delta E$ equal to the difference between a higher energy state and its current state, and a photon is emitted at a frequency $\Delta E/h$ less than the incident frequency. The reverse process occurs when after the collision, the molecule gives up an energy equal to the difference between its current state and a lower energy state, yielding a photon of frequency $\Delta E/h$ less than the incident frequency $\nu$. Figure adapted from Herzberg (1950).

### 3.3.3 Quantum Theoretical Explanation of the Raman Effect

The explanation of the Raman effect based on quantum theory is more straightforward (Herzberg, 1945, 1950). An incident photon with energy $h\nu$ strikes a molecule in a given rotational and vibrational state. If the photon is scattered elastically (Rayleigh scattering), neither the energy of the photon or of the molecule is altered from
this interaction. If, on the other hand, inelastic scattering occurs, then the only changes in energy that are possible are those that are those equal to the differences between stationary states of the system. Figure 3.4 shows the relevant energy levels of the molecule and the virtual states of the photon. Thus, the molecule can absorb an amount of energy from the photon equal to the difference of a higher state and it current state, and emit a photon with energy $hv - \Delta E$, which is known as Stokes scattering. The process is reversed if the molecule gives up an amount of energy equal to the difference between its current state and a lower state. As a result a photon of energy $hv + \Delta E$ is emitted, which is known as anti-Stokes scattering. The quantum explanation can account for those features of the Raman effect that classically could not be explained. The rotational energies of molecules are discrete (even if so close together in some cases that they may appear as unresolved bands). Thus, the only energies that can appear in these processes are those of differences of the stationary states of the molecule. This accounts the actual rotational frequencies being observed, rather than a band around a frequency double of that of the rotational frequency.

Additionally, the empirical difference between the intensities of the Stokes and the anti-Stokes lines is accounted by the Boltzmann distribution of rotational and vibrational population levels. Thus, whenever there are significant differences in the populations of different energy levels, there will be a significant difference in intensity between the Stokes and the anti-Stokes lines. The excited vibrational levels of most molecules are at high energies relative to $k_B T$ at room temperature. As a result, the vibrational ground state will have a much greater population than the first excited state leading to the Stokes vibrational spectrum to be much more intense than the population-
limited anti-Stokes for this transition. Nevertheless, for the rotational levels and molecules with smaller vibrational energies, many energy levels may be populated even at room temperature. In these cases (or at sufficiently high temperatures) the intensities of the Stokes and anti-Stokes lines may be similar.

Raman spectroscopy is useful to detect what chemical bonds may be present in a sample, as many types of bonds have characteristic frequency ranges. It is also very sensitive to changes in the local environment, which can cause the vibrational frequencies of a given bond to split, shift, or appear or disappear, based on changes in the structure. Liquid and different solid phases usually exhibit clear differences in the Raman spectrum. Raman spectroscopy also is sensitive to the composition of a sample, with the integrated peak intensity being directly proportional to the amount of the molecule present. It is often difficult (or impossible) to compare the peak intensities directly since all molecules have different Raman cross-sections depending on how well they scatter light. Nevertheless, there are cases, such as for different isotopic forms of the same molecule, where such comparisons are possible.

3.3.4 Micro-Raman Experimental System

The micro-Raman experimental setup allows Raman spectroscopy to be performed using diamond anvil cells. It is referred to as a micro-Raman system due to the small sample size, which, as previously mentioned in the section on the diamond anvil cell, and range from 50 to 300 μm.

Raman scattering is a very weak effect. Thus it is first necessary to maximize the number of photons that reach the sample, and then the number of scattered photons that reach the detector. This is achieved by obtaining a good alignment, so that the most
intense part of the beam (that is, the center of the beam) reaches the sample. Then it is necessary to ensure that the scattered light goes directly into the monochromator. The schematic of the micro-Raman system is given in Fig. 3.5.

**Figure 3.5:** Schematic of the micro-Raman system with a backscattering geometry. The laser source is a 514.5 nm Ar\(^+\) laser and the beam is expanded five times. Then it is directed by the holographic bandpass filter toward the diamond anvil cell. The 20x infinity-corrected objective focuses the beam on the sample, and then it is scattered backwards. After being transmitted through the holographic bandpass filter and passing through the confocal arrangement, the Rayleigh line is removed at the notch filter. Finally the Raman scattered light is focused on the monochromator with a lens.

In principle, Raman spectroscopy can be performed with any wavelength. The intensity of Raman scattering, like that of Rayleigh scattering, increases as the fourth power of the frequency of the source (see, for example, Sakurai, 1967). Thus, all else equal, a more intense Raman signal will be achieved with a shorter wavelength. Nevertheless, using higher energy photons (shorter wavelengths) increases the risk of damaging the diamonds. As a result, it is common to use blue and green light sources,
with 488.0, 514.5 and 532 nm being commonly used. In the present work, the excitation laser line used is the 514.5 nm line of a cw Ar⁺ laser.

The laser beam diameter is 1.5 mm (Coherent Laser Group). After the light leaves the laser, it passes through quarter-wave plate (Melles Griot). This is important because the polarization of the light is crucial for the holographic bandpass filter and will be discussed below. The periscope raises the laser light from the height of the laser to the height of the monochromator entrance slit. Then the light passes through a beam expander, which increases the beam diameter by a factor of five (or to ~8 mm diameter or ~4 mm radius). The purpose of the beam expander is to increase the spot size of the beam thereby allowing it to be focused more tightly. This will be discussed in detail in connection with the objective.

The holographic bandpass filter (Kaiser Optical Systems) is an important component of the micro-Raman system and permits the use of a backscattering geometry. This means that the Raman scattering will be scattered back along the path of the incident light. The holographic bandpass filter is extremely sensitive to the polarization of the light, reflecting about 90% incoming s-polarized light and transmitting p-polarized light (Tedesco, Owen, Pallister, & Morris, 1993). The s-polarization (vertical, in this case) corresponds to the light perpendicular plane of incidence (the plane defined by the normal of the reflecting plane and the direction of propagation). Thus, the polarization of the light at the plane of the holographic bandpass filter can be controlled by adjusting the quarter-wave plate. In this way the s-polarization component is maximized (reflecting most of the light to the sample) and minimize the p-polarization component (which is
transmitted and lost). The holographic band pass filter then transmits about 75-80% of the Raman scattered light.

The 20x apochromatic, infinity-corrected objective (Edmund Optics) has an effective focal length of 100 mm, and a working distance of 30.5 mm. The spot size achievable by focusing a Gaussian beam through a lens is (to leading order) directly proportional to the wavelength of the light and the focal length of the lens, and inversely proportional to the beam waist before focusing (Yariv, 1989). The relationship is given by Eq.(3.6)

\[ w(f) = \frac{f\lambda}{\pi w_0} \]  

where \( w(f) \) is the beam waist (radius) at \( f \), \( f \) is the focal length, \( \lambda \) is the wavelength of the laser, and \( w_0 \) is the beam waist at the lens.\(^1\) Using the values, \( f = 100 \text{ mm} \), \( \lambda = 514.5 \text{ nm} \), \( w_0 = 4 \text{ mm} \), a value of 4.1 \( \mu \text{m} \) for \( w(f) \) is achieved (beam diameter of \( \sim 8 \mu \text{m} \)).

The confocal arrangement uses two lenses (Edmund Optics) with 100 mm focal lengths, and they are located 200 mm apart. A rectangular aperture (Ealing Optics) is placed halfway between the lenses (at their focal lengths). The rectangular aperture is closed so that only the light scattering from the point of interest on the sample passes. This allows spatially-resolution of the sample, and eliminates stray beams that would tend to increase the noise.

The purpose of the notch filter (Kaiser Optical) is to reject the elastically scattered Rayleigh line (as well as the quasi-elastically scattered light at nearby frequencies) that would overwhelm the weak Raman signal. Ideally, notch filter would remove the light in

\(^1\) The derivation of the beam waist in Yariv (1989) is for the case with lens placed right at the minimum beam waist. Since the beam is very slowly divergent the difference is not significant. Indeed the divergence of the beam is slower for larger the beam waists. Thus, although there are small differences, the general principle of being able to be focus a wider beam waist more tightly to a smaller spot size remains valid.
a very narrow frequency range centered on the Rayleigh line. In practice, the notch filter blocks about 100 cm\(^{-1}\) on either side of the Rayleigh line. The light is then focused onto the monochromator slit using a 100-mm focal length lens (Edmund Optics).

The slit of the monochromator (Acton SpectraPro, Princeton Instruments) is opened to 100 \(\mu\)m. The 500-mm focal length monochromator is used with 1800 lines/mm grating and is equipped with liquid nitrogen cooled CCD (SPEC-10, Princeton Instruments). The CCDs used in this work had either 1340 or 2048 pixels yielding spectral resolutions of \~0.8 cm\(^{-1}\) or \~0.5 cm\(^{-1}\), respectively.

The CCD is calibrated using pencil style calibration lamps (Oriel Instruments). Two lamps are mostly used: neon and krypton. The emission lines of the neon lamp provide sufficient coverage for most of the spectral range of interest. In a few regions, the krypton lamp is necessary to fill in some gaps. It is necessary to have at least two emission lines to calibrate, with one line on either side of the center wavelength of the range. It is preferable to have three or more emission lines, once again with lines on either side of the central wavelength. With two emission lines, a linear fit was performed, and with three or more, a quadratic fit was performed. These fittings are performed automatically with the WinSpec software (Princeton Instruments), which is also used to acquire the spectra.

Finally, the micro-Raman systems feature imaging capabilities. The system is equipped with a camera (Marlin, Allied Vision Technologies) and lamps to illuminate the sample from the front and back. These allow the sample to be located, and the laser positioned on the sample at the point of interest. Also, this allows images and videos of the sample to be captured for further analysis and presentation.
Chapter 4

Deuterium-Water Mixture

4.1 Overview of Results

The D₂-H₂O mixture was loaded as described in Chapter 3, and the results of the D₂-H₂O mixture will now be presented. These include the visual appearance of the sample and the Raman spectra. The modes that were observed in the Raman spectra include the rotational and vibrational modes of hydrogen, and the lattice and stretching vibrational modes of water (the ν₂ bending mode was not observed). The details of the Raman spectra provide evidence for proton exchange, and substantial mixing and interaction between the hydrogen and the water. These results provide information on the ordering of high-pressure ices and hydrogen diffusion.

4.2 Visual Appearance

Figure 4.1 shows microphotographs of the mixture at various pressures. At 0.2 GPa, both components of the mixture are fluid. There is a clear boundary. Nevertheless, the formation of bubbles at 2.6 GPa suggests that hydrogen was dissolved in the fluid water. This is confirmed by Raman spectra, as will be seen below. This is the pressure range where the C₁ clathrate is transforming into the C₂ clathrate with a hydrogen-filled ice VII-like structure (Vos et al., 1993), and these bubbles could be a result of this transition. The boundary remains clearly marked, but interestingly the hydrogen-rich region does not show a large change in area relative to the water-rich region even up to the highest pressure. Pure hydrogen decreases in volume by a factor of ~4 from 1 GPa to 60 GPa (for example, Tkacz & Litwiniuk, 2002) compared to the decrease by a factor of
~2 for water (for example, Loubeyre et al., 1999) over the same pressure range.

![Figure 4.1: Microphotographs of the D₂-H₂O mixture. It shows the fluid D₂-H₂O mixture at 0.2 GPa separated into two phases—the hydrogen-rich and the water-rich. There appear to be small bubbles dissolved in the water-rich region at 2.6 GPa. The boundary stays clearly distinguished to the highest pressure, and the hydrogen-rich region does not show much volume collapse from about 2.6 GPa until the highest pressures measured relatively to the H₂O-rich region. This is in contrast to the large, typical volume collapse in hydrogen, suggesting the inclusion of H₂O in the hydrogen-rich region.](image)

**4.3 Raman Spectroscopy**

As discussed in Chapter 2, the hydrogen molecule has Raman active rotational modes (ΔJ = 0, ±2) and Raman active vibrational modes (Δν = ±1). Figure 4.2 shows a Raman spectrum of the rotational modes of the three different isotopes at 0.2 GPa, measured ~15 h after the D₂ first came into contact with the water. At this pressure, the hydrogen isotopes are in a supercritical fluid phase, which hereafter will simply be referred to as fluid phase, and the water is in the liquid phase. The rotons of the homonuclear species are sharp, with full-widths at half-maximum (FWHM) of ~5 cm⁻¹, while those of HD are ~40 cm⁻¹.
Figure 4.2: Rotational spectrum of the hydrogen isotopes at 0.2 GPa after 15 h, exhibiting evidence for proton exchange. The assignments of the rotational modes are indicated in the energy level diagram in the inset. The HD rotons are much broader than the D₂ and H₂ modes, quite likely due to lifetime broadening.

As already discussed in Chapter 2, the symmetry requirements of the total wave function of H₂ and D₂ limit the allowed rotational transition to $\Delta J = 0, \pm 2$. While the Raman selection rule is the same ($\Delta J = 0, \pm 2$), the nuclear statistics account for the fact $S_0$(even) for D₂ and the $S_0$(odd) for H₂ are more intense. For the heteronuclear molecule HD, there are no such symmetry restrictions, and hence the $\Delta J = \pm 1$ transition is allowed, although Raman-inactive. A previous study explained the broadness of the HD rotational modes relative to the homonuclear species as being due to lifetime broadening, and the mechanism being due to the $\Delta J = \pm 1$ transitions in a two-phonon process (McTague, Silvera, & Hardy, 1971). To compare the previous observed HD rotational broadening (McTague et al., 1971; Kozioziemski & Collins, 2003) with the present result, it is
important to note that the previous measurements were performed on low-temperature, solid samples. The present study, on the other hand, represents broadening of HD rotational modes in the fluid phase, and so would be subject to other broadening mechanisms such as thermal Doppler and pressure broadenings. In this regard, our data complement these previous results.

**Figure 4.3:** (a) Low-frequency Raman spectra of D$_2$-H$_2$O mixtures taken from the water-rich region, showing the pressure-induced spectral changes. (b) High-frequency Raman spectra of the D$_2$-H$_2$O mixtures in the water-rich region, showing the spectral signatures for O-H, O-D, D$_2$, HD, and H$_2$.

The pressure-induced spectral changes will be examined in two different regions of the samples. Figure 4.3 shows spectra from the water-rich region with (a) showing broadening and disappearing of the rotational modes in the low-frequency range in the water-rich region and (b) showing vibrational modes of the hydrogen isotopes and the water peaks with their pressure shifts in the water-rich region. Figure 4.4 displays spectra from the deuterium-rich region with (a) showing the broadening and disappearing of the
rotational modes in the low-frequency range in the deuterium-rich region; and (b) showing the blue shifts and splittings of the vibrational modes in the high-frequency range also in the deuterium-rich region.

Figure 4.3(a) exhibits the low-frequency data in the water-rich region. In this case, we see that initially there is a broad peak corresponding to the $S_0(2) D_2$ mode, which is consistent with the presence of $D_2$ dissolved in the water, and also consistent with the broadness of the $D_2$ vibrational peak observed in Fig. 4.3(b). The sample solidifies at $\sim 1.8$ GPa, and this change is clearly indicated by the appearance of translational modes in water as well as by the increasing intensities of the rotational modes in Fig. 4.3(a). This is accompanied by sharpenings of the O–H vibrational modes and the hydrogen isotopes vibrons in Fig. 4.3(b). These spectral features, seen in the spectra at 2.6 GPa, closely resemble those of the C$_1$ phase of water clathrate previously reported by Vos et al. (1993) from Raman and x-ray studies. Five lattice modes were observed in the low-pressure C$_1$ clathrate and three were observed in the present D$_2$-H$_2$O mixture (Borstad & Yoo, 2011), possibly with other concealed under the rotational modes of the three isotopes of hydrogen. The C$_1$ clathrate possesses an ice lattice similar to ice II that forms small cages. It was claimed that this clathrate was stable between 0.75 GPa and 3.1 GPa at room temperature. In the present study, we did not observe formation at such a low pressure, which was previously detected by x-ray (Vos, et al., 1993). Nevertheless, we see the features resembling to C$_1$ phase in our Raman data in the range between 1.8 and 3.5 GPa.

The Raman spectra in Figs. 4.3(a) and (b) indicate a structural change at $\sim 3.5$ GPa. This is the C$_1$ to C$_2$ clathrate transition. The structure of the water molecules in the
C\textsubscript{2} clathrate is similar to that of ice VII; however, of the two interpenetrated sublattices in ice VII only one is present with the other one being replaced by hydrogen molecules. This phase was reported to be stable from 2 GPa up until at least 60 GPa. We did not see evidence for the C\textsubscript{2} phase in the Raman data until around 3.5 GPa, however, as in the case of the C\textsubscript{1} phase, the x-ray data provided more information for determining the onset of the different phases. The peaks in the low-pressure range vanish and the lineshape of the O–H vibrational modes change. In the C\textsubscript{2} clathrate, three broad and weak lattice modes were observed, but none were observed in the present study. The two lattice modes observed in the phase VII of ice (Pruzan \textit{et al.}, 2003) were also broad and weak, and in the present study the lattice modes might be covered by the stronger rotational modes of the three hydrogen isotopes. The rotational modes continue to broaden and weaken, disappearing in the water-rich region above around 36 GPa.

Figure 4.3(b) shows the vibron changes associated with the phase transitions to the C\textsubscript{1} phase at \textasciitilde2 GPa and the C\textsubscript{2} at \textasciitilde3.5 GPa, as well as the appearance of new O–D vibron at around 2400 cm\textsuperscript{-1} above \textasciitilde2 GPa. By comparing the spectra at 0.2 GPa and 1.1 GPa, it is obvious that when the water is still in the liquid phase, the intensity of the D\textsubscript{2} vibration mode increases and an HD vibrational mode emerges. These changes should not be interpreted, however, solely or even primarily to be pressure-induced, because there is a time-dependent aspect to the diffusion and exchange reaction of D\textsubscript{2} into the water, as we will show later in this chapter. By 2.6 GPa, it is clear that in addition to the O–H vibrational mode around \textasciitilde3150 cm\textsuperscript{-1}, there is an additional peak from the O–D vibration alongside the diamond Raman overtone at \textasciitilde2420 cm\textsuperscript{-1}, which redshifts with increasing pressure. In the vibrational region there is also evidence of the transition to the
ice-VII-like $C_2$ structure at 3.5 GPa (a representative spectrum is shown at 8.2 GPa), which appears to be stable to at least 60 GPa. In this ice-VII like structure, we see three peaks: (1) the O-H band around 3200 cm$^{-1}$ at 8.2 GPa with a prominent feature on the lower frequency side and broader features at higher frequencies, (2) a weak broad peak around 2900 cm$^{-1}$, and (3) the O-D mode at 2400 cm$^{-1}$ at 8.2 GPa. The O–D band is clearly resolved until ~50 GPa, after which it becomes broad and weak (although it is still detectable until 64 GPa, the highest pressure measured). On the other hand, the O–H vibrational peak collides with the diamond second harmonic around 20 GPa and becomes unresolvable. The redshift in the vibrational frequencies of both the O–H and the O–D is attributed to hydrogen bonding, where a hydrogen atom belonging to one water molecule is attracted to an oxygen atom on a different water molecule. Around 24 GPa, the hydrogen isotopes begin to show splitting. At higher pressures the intensity of the deuterium vibron decreases relative to those of the HD and H$\_2$ vibrons, which is likely a combined effect of time and pressure as mentioned before.

The Raman spectra in Fig. 4.4 taken in the hydrogen-rich region, which initially appeared as a bubble, do not show any O–H vibrational modes. Nevertheless, there are evidences for the presence of water in this region; for example, the hydrogen peaks are blueshifted with respect to the frequencies of the hydrogen isotopes in pure samples and also split into several peaks unlike the pure samples. Therefore, it is likely that the sample is mixed (probably not homogeneously) and the absence of water Raman features is due to relatively weak Raman signals of water with respect to those of the hydrogen isotopes. This is also consistent with the similar volume reduction of the hydrogen-rich and water-rich regions.
Figure 4.4: (a) Low-frequency Raman spectra of the mixtures taken from the deuterium-rich region at high pressures, showing the spectral evidences for the rotational modes of the hydrogen isotopes. (b) High-frequency Raman spectra of the mixtures in the deuterium-rich region at high pressures, showing the pressure-induced vibron splittings of the hydrogen isotopes.

4.3.1 Rotational and Vibrational Raman Spectra of H₂, HD, and D₂

Figure 4.5 summarizes the pressure-dependence of the Raman spectra to 64 GPa of the rotational (a) and vibrational modes (b). The black, red, and blue solid symbols (squares in (a) and circles in (b)), respectively, correspond to the present D₂, HD, and H₂ data taken from the deuterium-rich region of the present D₂-H₂O mixture. The solid lines in (a) correspond to the rotational modes in pure samples, which include only the lowest energy modes as these measurements were performed at low temperatures (Hemley, Mao, & Shu, 1990; Hemley, Eggert, & Mao 1993; Moshary, Chen, & Silvera, 1993b). The solid lines in (b) represent vibron frequencies in pure samples reproduced from Moshary et al. (1993) for comparison.
Figure 4.5: (a) The pressure-induced shifts of the rotational modes of the hydrogen isotopes of the D$_2$-H$_2$O mixtures (solid symbols), showing an overall agreement with those of pure hydrogen isotopes (solid lines) (Hemley et al., 1990; Hemley et al., 1993; Moshary et al. 1993b). (b) The pressure-induced shifts of the vibrational modes of the hydrogen isotopes of the mixtures, showing contrasting behaviors with those of pure hydrogen isotopes (Moshary, Chen, & Silvera, 1993a) and spectral evidences for the proton-ordering transition between around 28 GPa and 50 GPa (see the text).

Note that the rotational modes in Fig. 4.5(a) quickly disappear with increasing pressure, with the exceptions of the $S_0(0)$ mode of HD at $\sim$250 cm$^{-1}$, $S_0(2)$ mode of D$_2$ at $\sim$425 cm$^{-1}$, and the $S_0(0)$, $S_0(1)$, and $S_0(2)$ of H$_2$ at $\sim$350, $\sim$610, and $\sim$850 cm$^{-1}$, respectively. However, these peaks are very broad ($\sim$100 cm$^{-1}$ FWHM) at pressures above 10 GPa and disappear by $\sim$45 GPa. The rotons measured in the present study follow the corresponding pure rotons quite well, as far as they can be traced, except for the $S_0(2)$ mode for D$_2$. In the case of the $S_0(2)$, Hemley et al. observed an increase in the frequency of this mode relative to what would be expected for a freely rotating molecule based on the comparisons with the frequency observed for the $S_0(0)$ mode (1993). Thus, the observed frequency of the $S_0(2)$ mode suggests that the hydrogen molecules are less
constrained in this mixture with the water than in a low-temperature, pure sample even at 10 GPa. The steep increase of ~45 GPa for the pure S₀(1) mode for H₂ is due to a hybridization with an E₂g phonon (Hemley, Mao, & Shu, 1990); however, in the present study, the peak shift of the S₀(1) shows no evidence of any such perturbation nor is any evidence of such a phonon mode observed. This also provides further evidence that hydrogen is perturbed by the presence of the water in the deuterium-rich region, and does not form its usual hcp structure where this phonon mode is observed (Hemley, Eggert, & Mao, 1993). The S₀(0) mode of the HD is observed and its peak position in the solid is significantly redshifted from the value measured in the fluid phase, in agreement with the previously observed measurements. The other HD rotational modes, even those corresponding to the more populated levels than the S₀(0) mode, overlap with the stronger D₂ and H₂ modes and hence are not resolved.

Like the rotational modes, the vibrons of the hydrogen isotopes in the mixture (shown in Fig. 4.5(b)) exhibit several interesting pressure-dependent spectral changes from those characteristics of the pure isotopes. First, the vibron frequencies of the mixtures are similar to those of pure isotopes at low pressures in the fluid phase. Nevertheless, they shift upwards to higher frequencies more rapidly with increasing pressure relative to the pure isotopes. Second, while the pure samples exhibit a frequency turnover in the vibron frequencies at ~30 GPa for H₂, ~40 GPa for HD, and ~50 GPa for D₂; there is no signature of such turnover in the mixture at least to 64 GPa. Third, the vibrons of the mixtures split into two groups, a strong singlet following the same pressure-dependent shift of the main vibrons and a relatively weak doublet in equal intensities newly formed at the low-frequency tails of the main peak at ~28 GPa, then the
main peak further splits into several poorly resolved peaks on the high-frequency side (see Fig. 4.4(b)). The splitting at 28 GPa occurs at a somewhat lower pressure of \(~23\) GPa in the water-rich region, which likely represents a variation in the composition as previously recognized in \(H_2-D_2\) mixtures (Brown & Daniels, 1992) and \(H_2-Ne\) mixtures (Loubeyre, LeToullec, & Pinceaux, 1992). On release, the splitting remains to 12 GPa in the deuterium-rich and until around 17 GPa in the water-rich region, showing a relatively large pressure-hysteresis. Finally, the pressure-dependent behaviors of \(D_2\), HD, and \(H_2\) vibrons mirror each other quite closely in terms of the peak splittings, and spectral lineshapes.

**4.3.2 O-H and O-D Raman Modes and Hydrogen Bonding**

We now compare the behavior of the O-H and the O-D bonds between the different isotopes of \(H_2O\), HDO, and \(D_2O\). The weak peak at 8.2 GPa (in Fig. 4.3(b)) should be identified with the symmetric stretching \((v^\text{OH}_1)\) of \(H_2O\) in the mixture, as it red shifts at about twice as fast as in pure: \(-52\) to \(-59\) \(\text{cm}^{-1}/\text{GPa}\) in the mixture compared to \(-25\) \(\text{cm}^{-1}/\text{GPa}\) in pure as shown in Fig. 4.6(a). A similar behavior has been reported for the O-D mode \((-36\) \(\text{cm}^{-1}/\text{GPa}\) compared to \(-19\) \(\text{cm}^{-1}/\text{GPa}\) as shown in Fig. 4.6(b). There are two, non-mutually exclusive, interpretations for the dominant mode \(~3150\) \(\text{cm}^{-1}\): (a) that it corresponds to the O-H stretching vibration in \(H_2O\) in bulk (ice VII) and (b) that it corresponds to at least some HDO (possibly an overlap of O-H vibrations of both HDO and \(H_2O\) ice VII). It is quite likely that the O-D stretching \((v^\text{OD})\) and O-H stretching \((v^\text{OH})\) of HDO feature prominently in the bands around \(2400\) \(\text{cm}^{-1}\) and \(3150\) \(\text{cm}^{-1}\), respectively, at 8.2 GPa. It is likely that a substantial amount of HDO was formed from the degree of proton exchange observed in the hydrogen isotopes, and for there to be a O-D band, even
if it is from D₂O, it would have been necessary for there to have been the prior formation of HDO. It also seems reasonable to conclude that the HDO and the D₂O molecules are at least as likely to be located in a region of hydrogen filled ice as any H₂O molecule, since the D₂ molecule had to be present for the HDO or D₂O to form. Additionally, the frequency of the ν^{OH} should be greater than the dominant ν₁ of H₂O, and the frequency of ν^{OD} should be greater than the ν₁ mode of D₂O. That is, the ν^{OH} would be expected between the ν₁ and ν₃ stretching modes of H₂O, and similarly for ν^{OD} with respect to the ν₁ and ν₃ stretching modes of D₂O (Herzberg, 1945; Benedict, Gailar, & Plyler, 1953a, 1953b).

**Figure 4.6:** (a) The pressure-induced peak shift of ν₁ OH stretching mode in comparison with those in pure H₂O (blue from Pruzan et al., 2003) and H₂-H₂O (red from Vos et al., 1996). The pressure-induced peak shift of ν₁ OD stretching mode in comparison with those in pure D₂O (blue from Pruzan et al., 2003), H₂-D₂O (red from Vos et al., 1996). Note that the slope of H₂-D₂O is about twice that observed in D₂-H₂O.

In contrast, option (a) above would imply that the modes of HDO are much weaker than those of H₂O and D₂O, and thus these bands could be O-H and O-D modes in bulk ice VII (that is, correspond to a region of the sample without the hydrogen filled ice). However, this interpretation seems unlikely because of the presence of hydrogen vibrational modes throughout the entire sample. Furthermore, since the O-D mode does not behave as the previously observed O-D in H₂-D₂O mixture (Vos et al., 1996) as
shown in red in Fig. 8(c), it seems reasonable to assign it to the HDO molecule, suggesting that there should be a corresponding O-H mode for HDO.

Thus, it seems very probably that at least some of the modes in the dominant O-H band and the O-D band are due to HDO. Furthermore, given the strong hydrogen-bonding present in water, it is possible a degree of coupling is taking place in the crystal, even without an identical unit cell repeated throughout the crystal. It is also possible that the sample is mixed with regions of ice VII and C\textsubscript{2} given the compatibility of these structures.

If the assignment of O-H and O-D to HDO given in Figs. 4.6(a) and 4.6(b) is correct, then we see that the O-H and O-D modes of HDO red shift at a slower rate in the mixture than the modes of \(v_1\) of H\textsubscript{2}O and D\textsubscript{2}O, respectively. This seems somewhat surprising, because it is more natural for those modes to shift at a similar rate to the O-H of H\textsubscript{2}O and O-D of D\textsubscript{2}O. The lack of high-pressure data of bulk HDO makes the analysis at this point challenging. Nevertheless, the difference in frequency shift between the modes of HDO and those of H\textsubscript{2}O and D\textsubscript{2}O may be understood in terms of an alteration in in the intermolecular interaction between the water molecules due to the presence of more than one isotope. In conclusion, the redshift of the vibrational modes in the mixture indicate hydrogen bonding at least as strong in the mixture as in pure water.

### 4.4 Proton Exchange Reactions in the D\textsubscript{2}-H\textsubscript{2}O Mixtures

The spectral characteristics of the isotope mixtures are strongly altered with time, evident by the proton exchange reactions as illustrated in Figs 4.7 through 4.9. In the water-fluid mixture at 0.2 GPa in Fig. 4.7(b), we observed the splitting of vibrons in both D\textsubscript{2} and H\textsubscript{2} (not in HD), arising from the Q branch of vibrons in different \(J\) states. The
most intense peak corresponds to the $Q_1(2)$ in $D_2$ and to the $Q_1(1)$ in $H_2$. The absence of the corresponding modes in HD is likely due to the broadness of the rotational modes of HD and based on the intensity distribution of the rotational modes of HD, the strongest (central) vibrational mode in HD would correspond to $Q_1(1)$. In addition, for $D_2$ we also observed the peaks from the S and O branches, located at intervals of about $\sim 200 \text{ cm}^{-1}$ away from the $D_2$ Q branch. These, as are the Q branch splitting, are seen only at very low pressures when the hydrogen isotopes are in the fluid phase.

Figure 4.7: (a) Low-frequency Raman spectra of $D_2$ in the hydrogen-rich region at 0.2 GPa, showing the evolution of hydrogen isotopes with the proton exchange reaction in the $D_2$-$H_2O$ mixtures. (b) High-frequency Raman spectra in the $D_2$-rich region at 0.2 GPa, showing the spectral changes associated with the proton exchanges and the rotational-vibrational modes (three from the $S_1$ branch and one from the $O_1$ branch) of $D_2$ – but not of $H_2$ or HD.

In the ice-fluid $D_2$ mixture at 2 GPa in Figs. 4.8(a) and (b), we observed the emergence of the rotons corresponding to different isotopes of $D_2$ and $H_2$. The HD $S_0(0)$ perhaps appears as a shoulder on the $D_2$ $S_0(1)$ mode. Clearly, the rotational modes are much broader than at lower pressures. The O–H vibrational modes also appear in a broad
band centered at $\sim 3170$ cm$^{-1}$, which resembles the Raman spectrum of the previously observed ice II-like clathrate structure (Vos et al., 1993). Additionally, by comparing the diamond second-order modes at eight days with that seen in the other two spectra, it becomes apparent that there is a peak just to the left of the diamond second-order modes that suggests the formation of O–D (compare to the spectrum at 2.6 GPa in Fig. 4.3(b)).

**Figure 4.8:** Time-dependent Raman spectral changes measured at the boundary at 2 GPa, showing the rotational modes of D$_2$ and H$_2$ and the translational modes (labeled $\nu_T$) of the water (Vos et al., 1993) in (a) and the evidences for which the water has solidified into a phase similar to the C$_1$ clathrate in (b).

In the solid mixtures at 8 GPa, we observed the rotational modes further broadened in Fig. 4.9(a), as well as the clear appearance of the O–D vibrational mode around $\sim 2420$ cm$^{-1}$ in Fig. 4.9(b). The O–H peaks at $\sim 3150$ cm$^{-1}$ clearly represent a different phase of ice than that at 2 GPa in Fig. 4.8(b), which is very similar to the Raman spectrum of ice VII. Furthermore, we observed a new peak near 2930 cm$^{-1}$ at the lower
frequency sideband of the D\textsubscript{2} and O–H peaks and the H\textsubscript{2} vibron is much stronger relative to the other isotopes than it was at 2 GPa.

**Figure 4.9**: Time-dependent Raman spectral change measured at the ice-rich region, showing the intensity enhancements of the H\textsubscript{2} S\textsubscript{0}(1) and H\textsubscript{2} S\textsubscript{0}(0) rotons (a) and of the HD and H\textsubscript{2} vibrons in (b). Note the gradual increase in the intensity of the rotational modes of H\textsubscript{2}, as well as the appearance of O-D vibrational mode ~2400 cm\textsuperscript{-1}.

The present spectral data offer the detailed information regarding the rates and extents of the exchange reactions in different phases and different isotopes as demonstrated in Figs. 4.10 through 4.12. The observed Raman intensity is proportional to the Raman scattering cross section and the number of molecules sampled. To determine the concentrations of each isotope, we assume the scattering cross sections to be equal in all three isotopes. In this way, the ratio of the integrated Raman intensities can be equated to the ratio of the concentrations of each isotope. This is a reasonable approximation, considering the similar polarizability changes associated with the relevant transitions. For example, the difference in the isotropic polarizability between the vibrational ground
state and the first excited state is about 8% in $\text{H}_2$, 7% in HD, and 6% in $\text{D}_2$, while that of the anisotropic polarizability is 21% for $\text{H}_2$, 18% HD, and 15% $\text{D}_2$ (Kolos & Wolniewicz, 1967). A similar approximation was previously employed to determine the concentrations of hydrogen isotopes using the relative intensities of the vibrons (Brown & Daniels, 1992) and of the rotons (Koziol & Collins, 2003).

4.4.1 Proton Exchange Kinetics in Fluid $\text{D}_2$-Water Mixtures

The time-dependent changes of the normalized Raman intensities of isotope mixtures will be described in three different phases. Figure 4.10 shows the fluid $\text{D}_2$-water, Fig. 4.11 the fluid $\text{D}_2$-ice II-like clathrate, and Fig. 4.12 the solid $\text{D}_2$-ice VII. The time zero signifies when the $\text{D}_2$ and $\text{H}_2\text{O}$ molecules first came into contact. We first describe the proton exchange reactions in the deuterium fluid and water mixture at 0.2 GPa (Fig. 4.1) in terms of two consecutive elementary gas-phase reactions (see, for example, Atkins, 1997),

$$
\text{D}_2 \xrightarrow{k_1} \text{HD} \xrightarrow{k_2} \text{H}_2
$$

where $k_1$ and $k_2$ are the rates of reactions. The following set of differential equations (Eqs. 4.2-4.4) can be used to describe these reactions:

$$
\frac{d}{dt}[\text{D}_2](t) = -k_1[\text{D}_2](t) \quad (4.2)
$$

$$
\frac{d}{dt}[\text{HD}](t) = k_1[\text{D}_2](t) - k_2[\text{HD}](t) \quad (4.3)
$$

$$
\frac{d}{dt}[\text{H}_2](t) = k_2[\text{HD}](t) \quad (4.4)
$$

From these equations, we derive the following equations with the initial condition that initially there are only water and deuterium present

$$
[D_2](t) = [D_{2\text{f}}] + \{1 - [D_{2\text{f}}]\} e^{-k_1t} \quad (4.5)
$$

$$
[\text{HD}](t) = [\text{HD}_\text{f}][1 - e^{-k_2t}] + \left[\frac{k_1}{k_2 - k_1}\right][1 - [D_{2\text{f}}]] \quad (4.6)
$$
\[
[H_2](t) = 1 - [D_{2f}] - [HD_f][1 - e^{-k_2t}] - \frac{1 - [D_{2f}]}{k_2 - k_1}(k_2 e^{-k_1t} - k_1 e^{-k_2t})
\]  
(4.7)

where \([X](t)\) is the concentration of isotope \(X\) as a function of time \(t\), and \([X_f]\) is the final concentration of isotope \(X\) after it has reached chemical equilibrium. Fitting the normalized Raman intensity data of \(D_2\) to Eq. (4.5) yields the parameters \(k_1\) and \([D_{2f}]\); then, fitting the HD data to Eq. (4.6) yields the values of \(k_2\) and \([HD_f]\). Equation (4.7) can be used independently to check any or all of these values for consistency. Clearly, the agreement between the spectral data and the calculated curves are excellent as shown in Fig. 4.10.

Figure 4.10: The normalized Raman intensity changes of hydrogen isotopes plotted as a function of time, showing the kinetics associated with the proton exchange reactions between water and fluid \(D_2\) at 0.2 GPa. The data was fit to Eqs. (4.5) – (4.7) as described in the text.

In this reaction, after 70 h, the reaction had reached equilibrium, and \(D_2\) had almost completely disappeared. Water was still present, and so the HD could have continued to react with the water, but it reached equilibrium as well. The rates of reaction \(k_1\) and \(k_2\) are nearly equal, which is a reasonable result since the proton exchange should occur regardless of whether it involves initially a \(D_2\) or an HD molecule.
Throughout the entire period of this experiment, the sample remained separated between a bubble composed of hydrogen fluid isotopes without any spectral signature for water being present in the hydrogen-rich region. In the water-rich region, some dissolved hydrogen isotopes were observed. This suggests that the reaction is limited by the exchange rate of deuterium with water (i.e., $k_1$). Once the exchange occurs, the fluid HD or H$_2$ molecules will diffuse quickly into the deuterium-rich region. While the reaction equations adequately accounts for the data, in reality the water must be involved in further reactions such as,

$$
\begin{align*}
    &H_2O + D_2 \rightarrow HDO + HD \\
    &HDO + D_2 \rightarrow D_2O + HD \\
    &H_2O + HD \rightarrow HDO + H_2 \\
    &HDO + HD \rightarrow D_2O + H_2
\end{align*}
\quad (4.8)
$$

Although there is no spectral evidence of the O–D vibration, this may be because it is broad and may not be resolvable under the strong diamond Raman feature.

### 4.4.2 Proton Exchange Kinetics in Fluid D$_2$ and Ice Mixtures

Proton exchange reactions also occurred between fluid deuterium and ice mixtures. However, the extent of reaction is less and the reaction rates are substantially slower. Figure 4.11 shows the time-dependent changes of the normalized Raman intensities of fluid deuterium isotopes mixed with an ice II-like clathrate at 2 GPa (open squares) or ice VII at 4 GPa (closed squares). We found that the previously derived gas-phase rate equations, as expected, did not describe these fluid-ice mixtures. Therefore, we used a phenomenological kinetic model given by

$$
A + Be^{-kt}
\quad (4.9)
$$

with an exponential dependence similar to the previous equations. The fitted results in Fig. 4.11 describe the spectral kinetic data reasonably well. Note that the reaction rates at
2 GPa are an order of magnitude greater than those at 4 GPa, but ~2.5 times slower than those of the fluid-liquid mixtures. This is in partial contrast to a previous study of fluid H₂-D₂ mixtures (Bell, Mao, & Sharma, 1980). In this study faster reaction rates were observed in the H₂-D₂ mixtures as the pressure increased. However, the important difference is that one of the reactants (H₂O) in the present study is in a solid phase. Hence, even if the reaction rate in fluid hydrogen increases with pressure, it could be offset by a much slower reaction rate resulting when the H₂O forms a solid and thereby reduces the freedom for exchange reactions to take place.

![Figure 4.11](image)

**Figure 4.11:** The normalized Raman intensity changes of hydrogen isotopes plotted as a function of time, showing the kinetics associated with the proton exchange reactions between ice and fluid D₂ at 2 and 4 GPa. These time-dependent intensity changes are fitted to the phenomenological Eq. (4.8) to yield the rate constants marked on the plots.

### 4.4.3 Proton Exchange Kinetics in Solid D₂ and Ice Mixtures

As expected, the proton exchange reaction in the solid-solid phase proceeds more slowly as evident in Fig. 4.11. Note that the shapes of the curves are different, and the concentration of H₂ tracks very closely with that of HD, and eventually overtakes it. To describe the spectral kinetic data, we used Avrami’s equation (Avrami, 1939; 1940; 1941)
\[ x = 1 - \exp(-bt^n) \]  

(4.10)

where \( x \) is the degree of completion of the reaction at time \( t \), and \( b \) and \( n \) are the parameters relating to the rate of reaction and the processes that characterize the reaction. The reaction rate \( k \) is equal to \( b^{1/n} \). We obtained the best fit with the Avrami parameters of \( n_H = n_D = 2 \), and \( n_{HD} = 1.6 \), which indicate diffusion-controlled processes (Hulbert, 1969). That is, the composition at the point-sampled is influenced by the following two effects: the rate of diffusion of the different molecules into and through that region (which will probably be fastest for \( H_2 \) and slowest for \( D_2 \)) and the rate at which a deuteron nuclei in a \( D_2 \) or and HD molecule will exchange with a proton in the ice. Nevertheless, the hydrogen diffusion process is probably the slower of the two factors listed above, and hence is likely the rate-determining step of the reaction in the solid mixtures. Notice also that the value of the \( n \) parameter in the Avrami equation is the same for the two homonuclear species, while the heteronuclear specie has a different value.

**Figure 4.12:** The normalized Raman intensity changes of hydrogen isotopes plotted as a function of time, showing the kinetics associated with the proton exchange reactions between ice and solid \( D_2 \) at 8 GPa. These time-dependent intensity changes are fitted to Avrami’s equation (Eq. 4.10) (solid curves, see the text) to yield the rate constants marked on the plots.
This difference in the $n$ values is most likely due to the fact that the heteronuclear HD is an intermediate in these reactions.

### 4.5 Hydrogen Bonding and Repulsive Hydrogen-Ice Interactions

The present spectral data indicate the hydrogen isotopes experience a repulsive interaction with ice—unlike the attractive interaction with water. Fig. 4.13 clearly indicates that the change of the interactions felt by the hydrogen molecules compared to what they experience in pure samples. After observing an initially attractive interaction due to hydrogen-bonding with the liquid water, after the ice solidifies, the interaction becomes increasingly repulsive with increasing pressure. In this case, we observe similar behavior to other binary mixtures of hydrogen with D$_2$, He, Ne, Ar, and N$_2$ (Loubeyre, LeToullec, & Pinceaux, 1985; 1992; Kim & Yoo, 2011) where the hydrogen vibrational

![Figure 4.13](image)

**Figure 4.13:** The D$_2$ vibrons of the D$_2$-H$_2$O mixtures (black lines) plotted with those of pure D$_2$ (blue lines) at several pressures, to illustrate the attractive nature of water-D$_2$ interaction and the repulsive interaction of ice-D$_2$ interactions, which increases with pressure.

83
frequencies are blueshifted. This is unlike the behavior that was observed in SiH₄-H₂ (Strobel, Somayazulu, & Hemley, 2009) where the observed frequency was redshifted with respect to the bulk hydrogen. The repulsive interaction then decreases the effective area of the proton exchange reaction and thus the reaction rate, as we observed.

4.6 Evidence for Ordering and Symmetrization

Recall that the hydrogen vibrational modes split into two different branches Figs. 4.3-4.5, which exhibit remarkably similar spectral lineshapes and intensities. This suggests that the origin of this splitting should be sought in the ice structure. Thus, the hydrogen molecules are located at, at least, two non-equivalent sites within the ice lattice. Taking the ratio of intensity of the higher frequency branch to the lower frequency branch

![Figure 4.14: The integrated intensity ratio of two vibrons, $\nu^H_s$ at higher frequency and $\nu^L_s$ at lower frequency, of the hydrogen isotopes after split above 28 GPa, showing evidence for the proton-ordering transition of the mixtures between 28 and 50 GPa. This transition is likely associated with the proton-ordering transition of ice VII occurring over a large pressure range between 40 and 80 GPa.](image)

84
in the water-rich region, we obtain different values in two different ranges as indicated in Fig. 4.14; a ratio of ~1.5 between 28 GPa and 50 GPa and a ratio of 1 above 50 GPa at least to 64 GPa—highest pressure measured.

A plausible explanation of the splitting is due to the proton ordering transition of ice VII occurring over a large pressure range between 40 and 70 GPa (Polian & Grimsditch, 1984; Goncharov, Struzhkin, Mao, & Hemley, 1999). Below 28 GPa, the mixtures may exist either in C\textsubscript{2} phase (Vos, et al., 1993, 1996) or in the phase where hydrogen isotopes exclusively occupy the octahedral (O\textsubscript{h}, D\textsubscript{2h}) sites of bcc-like ice-VII lattice. (Recall, that based upon the O-H and O-D vibrational bands, the presence of some ice VII cannot be ruled out). This stems from the larger (and unperturbed) O\textsubscript{h} site than the tetrahedral (T\textsubscript{d}, D\textsubscript{3d}) sites. Note that half of the T\textsubscript{d} sites are occupied (or perturbed) by hydrogen atoms in the hydrogen bonding of ice VII. Above 28 GPa, the proton-ordering process starts (albeit some internal pressure arising from the repulsive interaction) and/or the C\textsubscript{2} phase converts to ice VII, the hydrogen isotope molecules redistribute themselves into the O\textsubscript{h} and T\textsubscript{d} sites in this bcc-like ice VII lattice. This would eventually result in the observed intensity ratio of 3:2, as the hydrogen isotopes fill all the six O\textsubscript{h} and four empty T\textsubscript{d} sites. Note that the molecules located at the O\textsubscript{h} sites are at the higher vibron frequency relative to those located at the T\textsubscript{d} sites, experiencing a stronger repulsive potential. The frequency of the molecules at the T\textsubscript{d} sites is about ~50 cm\textsuperscript{-1} higher than those in the pure hydrogen, so while this represents a slightly repulsive potential relative to the bulk samples, it is a position much more conducive to proton exchange and thus hydrogen-bonding than the higher frequency O\textsubscript{h} site. This conjecture is further supported by further splittings of the low frequency ν\textsubscript{L} mode from the T\textsubscript{d} sites in this pressure range of 28–50
GPa, while the high frequency \( v_s^H \) mode from the \( O_h \) sites remains singlet (see Figs. 4.4(b) and 4.5(b)). This model, in turn, suggests that the proton ordering process is completed at around 50 GPa in the mixture—substantially lower than 60-70 GPa in pure ice VII—confirming the presence of large internal pressure (or repulsive interaction). This is consistent with what was previously observed by (Vos et al., 1996) in their \( C_2 \) phase, which was more compressible than ice phase VII since one of the two interpenetrating ice lattices was replaced by hydrogen molecules. Having achieved a symmetrized ice lattice in the mixture above 50 GPa, the disparity of hydrogen molecules in the \( T_d \) sites disappears, merging all \( v_s^L \), modes into one. Yet, the larger \( O_h \) site might become more prone to structural distortion upon further compression, splitting the \( v_s^H \) mode. These are consistent with the spectral changes observed in the spectrum at 61 GPa in Fig. 4.4(b) and the decrease in the intensity ratio to 1:1 in Fig. 4.14 (compare to Fig. 4.3(b)).

4.7 Hydrogen Diffusion

The present kinetic data in Fig. 4.12 clearly indicate that the proton exchange reaction occurs in solid mixtures. In fact, the exchange is evident even at pressures above 20 GPa (see Fig. 4.3(b)). This is in contrast to the previous reports (Bell, et al., 1980; Brown & Daniels, 1992), where the proton exchange was observed only in the fluid phase. The proton exchange in solids under high pressure, on the other hand, demonstrates the extremely high mobility of hydrogen arising from the quantum nature of hydrogen. Catalytic effects have been shown to play a role in these proton exchange reactions in pure hydrogen isotope mixtures with platinum black (Oliphant, 1933; Horiuti & Polanyi, 1933) and Be-Cu gasket (Bell et al., 1980) – not in the ice-D\(_2\) mixtures.
Furthermore, note that the D₂ samples (typically in bubble shapes) are well isolated by the ice layers from the gasket. As such, the catalytic effect of the present mixture may be present by diffusion through the surrounding ice layer, but is expected to be substantially smaller. In fact, the experiments performed using a stainless steel gasket do show the proton exchange in the solid mixtures at a somewhat reduced rate of \( \sim 6 \times 10^{-5} \text{ h}^{-1} \) at 6 GPa.

We estimate the order of magnitude of the diffusion coefficient, \( D \), based on the observed proton exchange rate and the following relation:

\[
D \sim \frac{V}{d} \times k
\]  

(4.11)

where \( V \) is the volume of the unit cell, \( d \) is the distance between the tetrahedral sites, and \( k \) is the reaction rate. This yields a diffusion coefficient on the order of \( 10^{-21} \) or \( 10^{-22} \) cm²/s for \( d \approx 1 \text{ Å} \), \( V \approx 10^{-23} \text{ cm}^3 \), and \( k \approx 10^{-6} \text{ s}^{-1} \). This value is then compared with the diffusion coefficient of H₂ or D₂ into niobium (bcc, like ice VII) of an order of \( 10^{-13} \) cm²/s at room temperature and ambient pressure (Mehrer, 2007). Extrapolating it to solid H₂ at 14 K and ambient pressure based on theoretically calculated values by Kaneko (1995) and taking into account the pressure-temperature effect, we estimate the diffusion coefficient of H₂ into Nb to be on the order of \( 10^{-26} \) cm²/s—considerably smaller than the estimated diffusion rate in the ice-D₂ mixtures. Recall that ice VII has a bcc structure, while C₂ has an fcc diamond structure. The C₂ has one oxygen lattice compared to the two that ice VII has, so the hydrogen diffusion in C₂ should be at least as fast as in ice VII. This difference might be due to a substantially smaller lattice of Nb (1.18 Å between

---

\(^{1}\) As the diffusion coefficient was given as a function of temperature, it was necessary to approximately correlate the pressure-dependent data from the present study to the temperature-dependent values from the calculation. For purposes of comparison, the freezing pressure of H₂ (\(~6\) GPa) was approximated to the freezing temperature of H₂ (\(~14\) K).
two adjacent Td sites) than ice VII (1.6 Å at 6 GPa), yet confirms that the proton exchange reaction is largely governed by the diffusion of H2 into the ice (not by the gasket).
Chapter 5

The Deuterium-Ammonia and Deuterium-Methane Mixtures

5.1 Overview of Results

In this chapter, the visual appearance and the Raman spectra are examined for the D$_2$-NH$_3$ mixture. In addition, the proton exchange in the D$_2$-NH$_3$ is examined, and an assignment is suggested for the vibrational modes of the isotopes of ammonia—NH$_3$, NH$_2$D, NHD$_2$, and ND$_3$. The behavior of the ammonia lattice and vibrational modes in the mixture and in pure are compared and contrasted. Similarly, the rotational and vibrational modes of hydrogen in the mixtures are compared to that in bulk hydrogen and H$_2$-D$_2$ mixtures. The visual appearance and the Raman spectra of the D$_2$-CH$_4$ mixture are presented. Once again, the modes of both methane and hydrogen will be compared to the behaviors in pure samples. The absence of both significant vibrational differences and significant proton exchange will be examined.

5.2 Visual Appearance of D$_2$-NH$_3$ Mixture

Figure 5.1 shows the visual appearance of D$_2$-NH$_3$ mixtures at high pressures. It shows several interesting features associated with the formation of two distinct regions, a large deuterium-rich solid surrounded by an ammonia-rich fluid mixture and the appearance of bubbles in the ammonia-rich region upon solidification, as noted previously in H$_2$-NH$_3$ mixtures (Chidester & Strobel, 2011). This clearly indicates that, although the fluid phases appear to be phase separated, there is indeed hydrogen dissolved in the fluid, as also confirmed by the Raman spectra below in Figs. 5.2-5.5. It
also demonstrates a lower solubility in the solid than in the fluid. The regions where the bubbles formed remained separated and trapped in the ammonia-rich region. Nevertheless, the boundaries between the different regions of the sample are increasingly blurred, which can be due to the decrease of the index of refraction difference between the two phases or, more likely, the diffusion of hydrogen between the two phases giving rise to a gradual structural modification at the interfacial region. In fact, the Raman spectra obtained in the boundary region in Fig. 5.2 show the vibrational modes from both ammonia and hydrogen, whereas no hydrogen modes were observed in solid NH$_3$ and no ammonia modes were observed in the hydrogen-rich region.

![Figure 5.1: Microphotographs for D$_2$-NH$_3$ mixtures showing the changes with pressure. At 0.6 GPa, it appears phase separated into hydrogen-rich (the upper left) and ammonia-rich (the right) regions. Upon the solidification at ~1 GPa, it forms hydrogen-rich bubbles in the ammonia-rich region, which remains to 42 GPa.](image)

**Figure 5.1:** Microphotographs for D$_2$-NH$_3$ mixtures showing the changes with pressure. At 0.6 GPa, it appears phase separated into hydrogen-rich (the upper left) and ammonia-rich (the right) regions. Upon the solidification at ~1 GPa, it forms hydrogen-rich bubbles in the ammonia-rich region, which remains to 42 GPa.

### 5.3 Raman Spectroscopy of D$_2$-NH$_3$ Mixture

Figure 5.2 shows two broad vibrational bands from ammonia: the N-D stretching modes (labeled as $v_{s}^{ND}$) centered at 2400 cm$^{-1}$ and the N-H stretching modes (labeled as
Figure 5.2: Vibrational spectra of D$_2$-NH$_3$ mixtures from the boundary region, showing a rapid proton exchange to form HD. Note that ammonia vibrons appear in two broad spectral regions: one at ~2500 cm$^{-1}$ which overlaps with the diamond second-order modes and the other at ~3300 cm$^{-1}$. The H$_2$ vibron exhibits an asymmetric spectral shape above 12 GPa, whereas D$_2$ vibron develops a shoulder at ~26 GPa, which remains to the highest pressure studied.

$v_{s}^{\text{NH}}$ mode at 3300 cm$^{-1}$. This assignment follows from a simple reduced mass argument, since the N-D to N-H frequency ratio is ~0.73, which is in good agreement with the calculated reduced mass ratio of $(\mu_{\text{NH}}^{\text{ND}}/\mu_{\text{ND}}^{\text{ND}})^{1/2} \sim (8/15)^{1/2} \sim 0.73$. Also, the stretching modes of hydrogen isotopes $v_{s}^{\text{HH}}$, $v_{s}^{\text{HD}}$, and $v_{s}^{\text{DD}}$ were observed with the intensity ratio of roughly 1:2:1. The lower frequency $v_{s}^{\text{ND}}$ band overlaps with the diamond second-order modes, which was subtracted using the reference data for further analysis. Note that the phase III-to-IV transition is evident from the emergence of several sharp vibrational peaks above 5 GPa in Fig. 5.2, as well as the appearance of strong lattice modes in Fig. 5.3(a). Phase III with its broad peaks in the mixture shows the stability in the same pressure range as in pure NH$_3$, whereas phase IV shows much sharper features representing an enhanced crystal order. The bending modes $v_2$ and $v_4$ of ammonia were
not observed in this study. These modes are very weak and in high-pressure studies have only been observed in single-crystal low-temperature work (Ninet et al., 2006).

### 5.3.1 Ammonia Lattice Modes in D₂-NH₃ Mixture

Upon the transition to phase IV, several lattice modes appear in the ammonia-rich region above 4 GPa as seen in Fig. 5.3(a) in agreement with the transition pressure in pure NH₃. Group theory predicts 21 lattice modes for phase IV in orthorhombic $P2_12_12_1$, (Ninet et al., 2006) many of which are not observed even in low-temperature studies. At high pressures, there are three prominent peaks in the low-frequency range and several other broad features that emerge in the high frequency side. The broad features can be compared with the one previously observed in pure NH₃; for example, five lattice modes were observed for NH₃ in phase IV (Gauthier et al., 1988) and six for ND₃ in phase IV.

![Figure 5.3: (a) External vibrational modes of D₂-NH₃ mixtures, which first appear weakly at ~5 GPa upon the transition to phase IV of ammonia, but get stronger as pressure increases. (b) The pressure dependent shifts of the lattice modes lying in between the frequencies observed in pure NH₃ and ND₃, consistent with the expected presence of NH₃D and NHD₂.](image-url)
The modes observed in the present study seem to be only in approximate agreement with the modes observed in pure NH$_3$ and ND$_3$, but fall somewhere in between the two. Nevertheless, this is reasonable since NH$_2$D and NHD$_2$ isotopes are present in the present mixture as will be discussed below. This suggests that the overall structure of ammonia is similar to pure phase IV, which is the pressure region in which these peaks are observed and to which they are compared. As the comparison between pure NH$_3$ and ND$_3$ demonstrates, the lattice modes exhibit similar behavior, with the modes in NH$_3$ at slightly higher frequencies in all cases except one. This seems to indicate that hydrogen atoms in pure ammonia play a role, although the dominant effect is due to nitrogen atoms. The presence of different hydrogen isotopes in ammonia, for example, may decrease the long-range order relative to pure NH$_3$, resulting in weakening of the hydrogen bonding and thereby softening of the lattice modes as observed in the mixture.

5.3.2 The Stretching Vibrational Modes of Ammonia

The vibrational modes of ammonia are difficult to interpret, particularly in the stretching frequency region of $v_{s,\text{ND}}^{\text{ND}}$ at $\sim2400$ cm$^{-1}$, $v_{s,\text{NH}}^{\text{NH}}$ at $\sim3300$ cm$^{-1}$, where many broad and overlapping features emerge. The vibrational modes of ammonia and its isotopes have already been described in Chapter 2. These stretching vibrational modes and the notation used in the present work are summarized in Table 5.1.

All the modes of all these isotopic forms of ammonia are Raman and IR active. The bands are deconvoluted as shown in Fig. 5.4(a) (for the N-D band) and Fig. 5.5(a) (for the N-H band) with the pressure dependence of the modes plotted in Figs. 5.4(b) and 5.5(d). In what follows we attempt to correlate these modes between N-H bands and N-D
bands.

**Figure 5.4:** (a) Spectral profile fittings of the N-D band. (b) Pressure-induced peak shifts of de-convoluted N-D modes in comparison with those of pure ND$_3$ (red lines reproduced from Pruzan et al., 1990). The sum rule of Wilson and Decius were used in assigning of the modes (see text).

First, it is apparent in Fig. 5.2 that the N-D modes are sharper than the N-H modes, although these modes follow roughly the same pressure dependence.

Unfortunately, Teller-Redlich product isotopic rules (Decius, Wilson, & Cross, 1980)

---

### Stretching modes of Ammonia Isotopes

<table>
<thead>
<tr>
<th>Mode</th>
<th>Symmetry</th>
<th>Classification</th>
</tr>
</thead>
<tbody>
<tr>
<td>$v_1$</td>
<td>$A_1$</td>
<td>Totally symmetric stretching</td>
</tr>
<tr>
<td>$v_3$</td>
<td>$E$</td>
<td>Doubly degenerate anti-symmetric stretching</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Mode</th>
<th>Symmetry</th>
<th>Classification</th>
</tr>
</thead>
<tbody>
<tr>
<td>$v_1^{\text{NH}} / v_1^{\text{ND}}$</td>
<td>$A'$</td>
<td>N-H (N-D) stretching</td>
</tr>
<tr>
<td>$v_3^{\text{nND}} / v_3^{\text{nNH}}$</td>
<td>$A'$</td>
<td>Symmetric N-D (N-H) stretching</td>
</tr>
<tr>
<td>$v_3^{\text{nND}}$</td>
<td>$A''$</td>
<td>Antisymmetric N-D (N-H) stretching</td>
</tr>
</tbody>
</table>

**Table 5.1:** Classification of the stretching modes of the different isotopes of ammonia as discussed in Chapter 2.
cannot be applied, as insufficient modes were observed. For instance, the symmetric bending \( \nu_2 \) mode and the anti-symmetric bending \( \nu_4 \) mode were absent. Nevertheless, the sum rule of Wilson and Decius can be applied (Decius et al., 1980). The sum rule states that if several isotopic molecules are superimposed (by addition or subtraction as appropriate) such that the masses of the isotopic atoms cancel at each position, the resulting linear combination of the sums of the squares of the frequencies will vanish (see Appendix A). This is because the sum of the square of the frequencies is, assuming unchanged force constants among the isotopic molecules, equal to linear functions of the reciprocal masses of the atoms in the molecule. The sum of the squares of the frequencies of all the normal modes for isotope \( X \), \( \sigma(X) \), is defined as follows:

\[
\sigma(X) = \sum_k \lambda_k = 4\pi^2 c^2 \sum \nu_k^2
\]  
(5.1)

Thus, the superposition of three \( \text{NH}_2\text{D} \) and three \( \text{NHD}_2 \) molecules, positioned so there are three H atoms and three D atoms at each hydrogen position, can be cancelled by three \( \text{NH}_3 \) molecule and three \( \text{ND}_3 \) molecules. This gives us the following relationship:

\[
3\sigma(\text{NH}_2\text{D}) + 3\sigma(\text{NHD}_2) - 3\sigma(\text{NH}_3) - 3\sigma(\text{ND}_3) = 0
\]  
(5.2)

Given that the bending modes and the stretching modes are well separated in energy, assume that the stretching and the bending frequencies are independent and we can use relation (2) for just the stretching modes of the different isotopes, which results in

\[
\begin{align*}
\lambda_{1\text{ND}}^{\text{NH}_2\text{D}} + \lambda_{3\text{NH}}^{\text{NH}_2\text{D}} + \lambda_{1\text{NH}}^{\text{NHD}_2} + \lambda_{3\text{ND}}^{\text{NHD}_2} &= \lambda_{1\text{NH}}^{\text{NH}_3} + 2\lambda_{3\text{HD}}^{\text{NH}_3} + \lambda_{1\text{ND}}^{\text{ND}_3} + 2\lambda_{3\text{ND}}^{\text{ND}_3}
\end{align*}
\]  
(5.3)

where the subscripts and superscripts correspond to the modes as defined above. That is, in the \( \text{NH}_2\text{D} \) bracket, \( \lambda_{1\text{ND}}^{\text{NH}_2\text{D}} \) corresponds to the ND stretching, and \( \lambda_{1\text{NH}}^{\text{NH}_2\text{D}} \) and \( \lambda_{1\text{NH}}^{\text{NH}_2\text{D}} \) correspond to the symmetric and antisymmetric NH modes, respectively, and analogously.
for NHD$_2$ bracket. In NH$_3$ and ND$_3$ brackets, $\lambda_1$ refers to the symmetric stretching mode while $\lambda_3$ refers to the antisymmetric stretching modes.

**Figure 5.5:** (a) Spectral profile fittings of the N-H band. Note that the highest frequency peak appears to have a shoulder at 6.2 GPa and 10 GPa. (b) Pressure-induced peak shifts of de-convoluted N-H modes in comparison with those of pure NH$_3$ (gold lines reproduced from Gauthier *et al.*, 1988) and of NH$_3$-H$_2$ mixture (open circles reproduced from Strobel and Chidester, 2011). Again, the sum rule of Wilson and Decius were used in assigning the modes (see text).

We now proceed to present an assignment for the modes present in the N-D and N-H bands in phase IV of ammonia based upon the sum of the squares relationship derived above. The starting point of the assignment will be based on the frequencies of the previous low-temperature Raman and infrared data (Reding & Hornig, 1951; 1954; 1955; Wolff *et al.*, 1971; Binbrek and Anderson, 1972). Based on the Raman and infrared data, we expect the order of the N-D modes, from lowest frequency to highest, to be as follows: the symmetric stretching ($v_1$) of ND$_3$, the symmetric N-D stretching ($v_3^{\text{ND}}$) of NHD$_2$, the N-D stretching ($v_1^{\text{ND}}$) of NH$_2$D, the antisymmetric N-D stretching ($v_3^{\text{mND}}$) of NHD$_2$, and the antisymmetric stretching ($v_3$) of ND$_3$, although these last two modes
(ν₃^{ND} of NHD₂ and ν₃ of ND₃) occur at very similar frequencies (Reding & Hornig, 1951; 1954; Wolff et al., 1971). Similarly, we expect the order of the N-H modes, from lowest to highest, to be the symmetric stretching (ν₁) of NH₃, the symmetric N-H stretching (ν₃^{NH}) of NH₂D, the N-H stretching (ν₁^{NH}) of NHD₂, the antisymmetric stretching (ν₃^{NH}) of NH₂D, and finally, the antisymmetric stretching (ν₃) of NH₃. As in the ND band, the ν₃^{NH} of NH₂D and ν₃ of NH₃ occur at nearly the same frequencies (Reding & Hornig, 1951; 1954; Wolff et al., 1971).

Following the above relationship, the mode observed at around 2350 cm⁻¹ (in red) in Fig. 5.4(b), is assigned to the symmetric stretching mode (ν₁) of ND₃, which is about 20 cm⁻¹ higher than the frequency reported in Pruzan et al. (1990). The highest frequency mode with a frequency ranging from 2510 to 2560 cm⁻¹ over the pressure range (in red) is assigned to the antisymmetric degenerate stretching (ν₃) of ND₃. This ν₃ mode is in good agreement with the frequency ν₃ (E₁g) mode (Pruzan et al., 1990). The mode observed around 2400 cm⁻¹ in Fig. 5.4(b) is assigned to the symmetric N-D stretching (ν₃^{ND}) of NHD₂, while the mode around 2505 cm⁻¹ is assigned to the antisymmetric N-D stretching (ν₃^{ND}) of NHD₂. These assignments are based on the fact that the ν₃^{ND} of NHD₂ is expected to be above the ν₁ of ND₃, while the ν₃^{ND} of the NHD₂ has a frequency very similar to that of the ν₃ of ND₃. The mode with a frequency of about 2470 cm⁻¹ (in blue at a higher frequency) has been assigned to the ν₁' of NH₂D, although it is possible that the mode at a lower frequency (also in blue) may correspond to this mode. The agreement between both sides in Eq. (5.2) was better with the ν₁' of NH₂D assigned to the higher frequency mode. Finally, regarding the mode around 2400 cm⁻¹ at 5 GPa may be explained by either a Fermi resonance or a combination of a lattice mode and an internal
vibration. A Fermi resonance could occur between the totally symmetric stretching mode of ND₃ and the first overtone of v₄ bending mode of ND₃, since both modes are totally symmetric and have similar frequencies (from Ninet et al. (2006) for ND₃ at 6.3 GPa and 80 K the v₁ mode is at 2325 cm⁻¹ and v₄ is at ~1170 cm⁻¹ or ~2340 cm⁻¹ for 2v₄). A similar Fermi resonance has been observed in NH₃ (Gauthier et al., 1988). On the other hand, it is also possible that the mode might be assigned to a combination of a lattice mode and an internal vibration, similar to the assignment in an infrared study of a low-temperature mixed crystal of NH₃, NH₂D, NHD₂, and ND₃ (Reding & Hornig, 1955).

It is possible to switch the assignment of the v₃ mode of ND₃ and v₃'' mode of NHD₂ in Fig. 5.4(b) since the frequencies of the v₃ of ND₃ and v₃'' of NHD₂ are very similar. Both have been reported as 2500 cm⁻¹ in low-temperature infrared studies (Reding & Hornig, 1954; 1955) or differing by 5–6 cm⁻¹ in another study (Wolff et al., 1971). Indeed, the assignment with the v₃ of ND₃ at the higher frequency gave an agreement between both sides of Eq. (3) within 0.49% over the pressure range, while with the v₃'' of NHD₂ at the higher frequency yielded an agreement between both sides of Eq. (5.3) within 0.06% over the pressure range. Additionally, a calculation of the frequencies of these molecules obtained a slightly higher value for the v₃''ND of NHD₂ than the v₃ of the ND₃ (Zeng & Anderson, 1990). Nevertheless, since both assignments lead to reasonable agreement with Eq. (5.3), the highest frequency was assigned to the v₃ of ND₃ given the agreement with the observed v₃ frequency in pure ND₃ (Pruzan et al., 1990), and this assignment also finds support from the assignment given in an infrared study of low-temperature mixed crystal of NH₃, NH₂D, NHD₂, and ND₃.¹⁵

Similarly, Fig. 5.5 illustrates the analysis of N-H stretching modes and signifies
the presence of NH$_3$, NH$_2$D, and NHD$_2$. A total of five peaks are used to fit the broad, unresolved three groups of NH bands: two for fitting the high-frequency feature, one for the middle, and two for the low frequency feature, as shown in Fig. 5.5(a). Note that this three-grouped spectral shape is largely maintained throughout all the pressures, although the exact location of peaks and relative intensities are changed. Following the procedure that was used above for the N-D band, we assign the lowest frequency mode around 3200 cm$^{-1}$ (shown in gold) to the symmetric stretching ($v_1$) of NH$_3$. We also assign the highest frequency mode (shown in gold ranging from 3375 to 3450 cm$^{-1}$ over the pressure range) to the degenerate antisymmetric stretching ($v_3$) of NH$_3$. These assignments find support as they are in approximate agreement with the previous measurements of pure NH$_3$ (Gauthier, Pruzan, Chervin, and Besson, 1988) and NH$_3$-H$_2$ mixtures (Chidester & Strobel, 2011). The mode at ~3275 cm$^{-1}$ (shown in blue) is assigned to the symmetric N-H stretching ($v_3^{\text{NH}}$) of NH$_2$D and the mode at around 3360 cm$^{-1}$ (shown in blue) is assigned to the antisymmetric N-H stretching ($v_3^{\text{nNH}}$) of NH$_2$D. Both of these modes are assigned in this way because we expect the $v_3^{\text{NH}}$ of NH$_2$D to be at a higher frequency than the $v_1$ of NH$_3$ and the $v_3^{\text{nNH}}$ of NH$_2$D to be at a lower frequency than the $v_3$ of NH$_3$. We assign the mode with a frequency that varies 3310–3360 cm$^{-1}$ to the N-H stretching ($v_1^{\text{NH}}$) of NHD$_2$. The vibrational modes associated with NH$_3$, NH$_2$D, NHD$_2$, and ND$_3$ in Figs. 5.4(b) and 5.5(b), therefore, indicate that the proton exchange reactions occur between NH$_3$ and D$_2$ in solid NH$_3$-rich region.

Having completed the assignment of the modes as described above, one can make the following observations. In pure NH$_3$ (or ND$_3$) samples, the $v_1$ mode splits into four Davydyov components and the degenerate $v_3$ mode splits into eight Davydyov components.
(due to the in-phase and out-of-phase couplings, Kume, Sasaki, & Shimizu, 2001; Ninet et al., 2006) which are evident from the \( v_3(E_{2g}) \) (the red line in Fig. 5.4(b), reproduced from Pruzan et al., 1990) and the \( v_1(F) \) and \( v_3(F) \) (the gold lines from Gauthier et al., 1988). No modes in the present study were observed that corresponded to these Davydov components. It is, however, expected because the presence of different isotopes does not permit the existence of an identical unit cell repeated throughout the entire crystal. As a result, the coupling between the internal modes of the ammonia molecules is decreased in the mixture. Nevertheless, note that the crystal does have lattice modes as mentioned before (Fig. 5.3(a)), and there is still sufficient order in the crystal to give rise to the sharp stretching vibrational modes in Fig. 5.4(b) after 5 GPa.

As can be seen in Figs. 5.4(b) and 5.5(b), all the antisymmetric modes (\( v_3 \) for \( \text{NH}_3 \) and \( \text{ND}_3 \) and \( v_3'' \) for \( \text{NH}_2\text{D} \) and \( \text{NHD}_2 \)) blue shift with increasing pressure. The symmetric stretching mode of \( \text{NH}_3 \) shows a strong red shift with pressure decreasing by about 65 cm\(^{-1}\) from 5 to 50 GPa, although less than that observed in pure \( \text{NH}_3 \) by Gauthier et al. (1988). The symmetric \( v_3^{\text{NH}} \) of \( \text{NH}_2\text{D} \), also shows a strong red shift by about 65 cm\(^{-1}\) over the pressure range. The \( v_3^{\text{ND}} \) of \( \text{NHD}_2 \) shows only a slight net red shift of about 10 cm\(^{-1}\) from 5 to 50 GPa, while the \( v_1 \) of \( \text{ND}_3 \) shows a moderate blue shift to even higher frequencies by about 15 cm\(^{-1}\) over the same pressure range. This contrasts with the behavior seen in Fig. 5.4(b) for the \( v_1 \) of \( \text{ND}_3 \), showing a net red shift over the 5-to-40 GPa range. As the symmetric stretching modes probe the strength of hydrogen bonding, which gains in strength at the expense of the N-H or N-D covalent bond (the bonds in ammonia), the present observations of the mode softening indicate greater hydrogen bond strength for the bonds involving hydrogen than those involving deuterium, showing
considerable strength in NH\textsubscript{3} and NH\textsubscript{2}D, and being much weaker in NHD\textsubscript{2}, and perhaps absent in ND\textsubscript{3}. Furthermore, the \(v\textsubscript{1}\) of NH\textsubscript{3} in the mixture shifts to lower frequencies at about half the rate of the \(v\textsubscript{1}\) in pure NH\textsubscript{3}; that is, \(-1.5\) cm\(^{-1}\)/GPa in the mixture compared to \(-2.7\) cm\(^{-1}\)/GPa in the pure. This difference may be due to the reduced coupling caused by the presence of the different isotopes of ammonia or by the presence of hydrogen molecules that also attract the lone pair electrons of the nitrogen atom, and thereby reduce the extent of hydrogen bonding between ammonia molecules.

5.3.3 The Raman Modes of Hydrogen

The rotational and vibrational modes of hydrogen provide structural information about the hydrogen molecules and crystal. The rotational modes will be discussed in more detail below together with the rotational modes in the CH\textsubscript{4}-D\textsubscript{2} mixture. The vibrational spectra of the different isotopes of hydrogen provide a sensitive probe to the chemical environment in the mixture. The peak position is sensitive to the composition, as it shifts to higher frequencies in dilute hydrogen mixtures with different hydrogen isotopes (Brown & Daniels, 1992; Loubeyre et al., 1992) water, nitrogen (Kim & Yoo, 2011), and noble gas solids (Loubeyre et al., 1992). Given the presence of different isotopes of hydrogen, we consider this effect in the present mixtures. Figure 5.6, for example, shows (a) the spectral evidence of the proton exchange occurring in D\textsubscript{2}-NH\textsubscript{3} mixtures and (b) the peak positions of hydrogen vibrational modes in the mixtures, which occur at substantially higher frequencies than those in pure hydrogen (Moshary et al., 1993).

The Raman spectra of D\textsubscript{2}-NH\textsubscript{3} mixture in Fig. 5.6(a) are evidence for the presence of all three hydrogen isotopes after the proton exchange occurred rapidly in the fluid.
Note that there are two different peak positions at 0.6 GPa in Fig. 5.2: one at the high frequency is from the hydrogen-rich region and the other at the low frequency is from the ammonia-rich region where deuterium is dissolved in ammonia. The latter peak gives an evidence of attractive interactions between the fluid ammonia and deuterium as expected from the hydrogen bonding between them, as also observed in the D$_2$-H$_2$O mixture (Borstad and Yoo, 2011 and Chapter 4). All the modes gradually diverge from the frequencies observed in pure bulk samples by 10 GPa. At around 12 GPa, the modes begin to show splitting (see Fig. 5.6(a)) and the shoulder on the D$_2$ becomes quite clear by 18 GPa.

**Figure 5.6:** (a) Raman spectra of hydrogen isotopes in the hydrogen-rich region, showing the asymmetric spectral shape arising from the presence of shoulders and peak splittings. In Run 1 it is particularly evident for the peak splitting of H$_2$ vibron and the shoulder of HD vibron, while in Run 2 the presence of a shoulder is evident for D$_2$ vibron at 50 GPa. (b) The pressure-induced Raman shifts of hydrogen isotopes, showing the composition dependence. The composition dependence is compared to the previous results at similar compositions (solid and dashed lines reproduced from Brown and Daniels, 1992) and pure hydrogen (dotted lines from Moshary et al., 1993).

Figure 5.6(b) shows the peak shift of hydrogen vibrons in two different D$_2$-NH$_3$...
mixtures: one in open symbols with a $\text{H}_2:\text{HD}:\text{D}_2$ ratio of 60:36:4 and the other in solid symbols with a ratio of 35:48:17. The lines show the frequencies in mixtures of $\text{H}_2$, $\text{HD}$, and $\text{D}_2$ with appropriate ratios from Brown and Daniels (1992). The compositions of hydrogen isotopes were determined by dividing the integrated intensity of the vibrational modes of each isotope by the sum of integrated intensities of all three isotopes vibrational modes. As mentioned when discussing the $\text{D}_2$-$\text{H}_2\text{O}$ mixture, this should yield a reasonable estimate with an estimated error within ~5%, since the polarizabilities of three isotopes vary only by small amounts (Kolos & Wolniewicz, 1967). A similar approach has been applied to vibrons (Brown & Daniels, 1992) and rotons (Kozioziemski & Collins, 2003). The lower frequency mode follows the frequency observed in the mixtures consistent with the results of Brown and Daniels (1992) but a higher frequency shoulder emerges. This is particularly clear if two different runs are examined, with different compositions. In Fig. 5.6(a) the higher frequency shoulder is very clear for the HD vibron, while the splitting occurs for the $\text{H}_2$ vibron in Run 1 and for the $\text{D}_2$ vibron in Run 2. Thus, while the effects of the different isotopes of hydrogen may be a contributing factor to the blue shift, it appears that the splitting that was observed as a shoulder on the high-frequency side is not entirely accounted by it. As such, it seems to point to the presence of ammonia in the deuterium-rich region. In fact, Brown and Daniels (1992) did mention “in very low minority-concentration mixtures where line splitting in some of the spectra was observed at higher pressures” (p. 6435). Nevertheless, the splitting occurs in the 35:48:17 mixture, hardly a dilute mixture for any of the hydrogen isotopes, yet we see similar behavior in both runs independent of the mixing ratio. In this regard, the $\text{D}_2$ vibron was very weak in Run 1, which may account for the reason why it appears as only
a singlet, as the shoulder or any higher frequency minor peaks may have been too weak to be observed. Thus, the hydrogen isotopes appear to exhibit a slightly repulsive interaction with ammonia, while the symmetric vibrational modes of ammonia, especially N-H, exhibit attractive interactions.

Based on the previous neutron study (Ninet et al., 2009), it is known that hydrogen bonds in phase IV undergo a series of reorientation to phase V at ~18 GPa accompanying the changes in covalent bond angles and hydrogen bond angles in ND₃. The pressure at which this transition takes place in NH₃ is ~12 GPa, which corresponds to the onset of the asymmetric vibron changes observed in the present study.

**5.4 Visual Appearance of D₂-CH₄ Mixtures**

Figure 5.7 shows the microphotographs of D₂-CH₄ mixtures at different pressures, exhibiting a single fluid phase below 6 GPa, the formation of two and three phase regions.

![Figure 5.7: Micrographs of the D₂-CH₄ mixture. Note that the mixture forms a homogeneous fluid up to 6.4 GPa, above which it solidifies and separates into two distinct regions. Then, upon a small increase in pressure, it further divides into three regions at 6.6 GPa. Finally, at higher pressures, the boundaries disappear and the sample appears homogenous.](image)
at 6.4–12.0 GPa, and the continuous blurring of phase boundaries above 12 GPa. Note that the two-phase image at 6.4 GPa quickly develops a third phase region within a small pressure range; the sample image at 6.6 GPa clearly shows the three phase boundaries. Upon further increasing pressures, however, the boundaries tend to blur as seen at 12 GPa in Fig. 5.7 and the visual distinctions between the regions continue to decrease as seen at 26 GPa.

5.5 Raman Vibrational Spectra in the D$_2$-CH$_4$ Mixture

Raman spectroscopy was, again, employed to characterize the phases in the different regions of D$_2$-CH$_4$ mixtures, as shown in Figs. 5.8 and 5.9. Unlike the D$_2$ mixtures of H$_2$O and NH$_3$, D$_2$-CH$_4$ mixtures show no apparent lattice modes below 1000 cm$^{-1}$. The only modes present in this region of the spectrum are the rotational modes of deuterium (see Fig. 7). This is not surprising, as pure methane does not have lattice modes either.

As already mentioned in Chapter 2, methane has four Raman active vibrational modes, which transform as $A_1 + E + 2T_2$. The most distinctive Raman features of the mixtures are the internal Raman modes: the totally symmetric stretching mode ($v_1$ with $A_1$ symmetry) and the antisymmetric mode ($v_3$ with $T_2$ symmetry) for CH$_4$ and the $v_5$ for D$_2$, all of which appear in the similar spectral range (~2900–3100 cm$^{-1}$ depending on pressures) as noted in Fig. 5.8. The doubly degenerate bending mode $v_2$(E) and the triply degenerate bending mode $v_4$ ($T_2$) of CH$_4$, however, were not observed, as the former is very weak and the latter overlaps with the first-order diamond line around 1330 cm$^{-1}$.

Notice the appearance of the $v_3$ mode of CH$_4$ as a minor peak at 12 GPa (also shown magnified) and 21 GPa in Fig. 5.8(a). Additionally, there are two weak features, a
Figure 5.8: (a) Raman spectra of D₂-CH₄ mixtures in the region of methane modes. A weak peak is observed on the high-pressure side of D₂ vibron at 12 GPa and a small peak attributed to HD was observed at 26 GPa. (b) The pressure-dependent peak shifts, showing that D₂ vibron follows that of pure D₂ and CH₄ peaks also roughly follow those of pure CH₄ (Wu et al., 1995; Chen et al., 2011) up until about 20 GPa. The discrepancies below 6 GPa between the present study and the previous studies for the v₁(CH) vibrational modes of methane are most likely due to the fact that methane did not solidify until around 6 GPa, whereas pure methane solidifies at 1.7 GPa. The HD peak lies slightly above the 8% composition line from Brown and Daniels (1992). This is reasonable considering that the HD vibron in the present study is about 200 times weaker than the D₂ mode.

peak on the high frequency side of the hydrogen vibron, which appears after 12 GPa (shown in the magnification at 12 GPa in Fig. 5.8(a)), and a peak due to HD, possibly resulting from an HD impurity already present in the deuterium sample. The integrated intensity of the higher frequency D₂ peak is about 90 times weaker than the main D₂ mode, while the integrated intensity of the HD peak is about 200 times weaker than the main D₂ mode. The pressure-induced shifts of these Raman modes observed in the present mixture are presented in Fig. 5.8(b), in comparison with those of pure CH₄ (Wu, Sasaki, & Shimizu, 1995; Chen, et al., 2011) and D₂ (Moshary, N. H. Chen, and I. F. Silvera, 1993). Apparently, the pressure-dependence of CH₄ in the mixture exhibits a
reasonable agreement with that of pure CH$_4$ to 20 GPa, above which they show considerable divergence. Also note that all the methane stretching vibrational modes shift to higher frequencies with pressure in contrast to the D$_2$-H$_2$O and D$_2$-NH$_3$ mixtures. The HD mode is strongly blue shifted with respect to the pure which is expected due to its low concentration (Brown & Daniels, 1992), where it is slightly above the frequency observed in a sample with a H$_2$:HD:D$_2$ ratio of 91:8:1 as expected. Important to note is that unlike D$_2$-H$_2$O and D$_2$-NH$_3$ mixtures, the D$_2$-CH$_4$ mixture shows no vibrational modes that could be accounted for deuterated methane. This demonstrates at most a very limited proton exchange in D$_2$-CH$_4$ mixtures, which will be discussed in detail below.

Figure 5.9: Raman spectra of D$_2$-CH$_4$ obtained in different regions of the sample (see the insets), showing strong intensity variation between the D$_2$ and C-H modes. The appearance of doublet in both the D$_2$ and C-H modes is likely due to the formation of CH$_4$(D$_2$)$_4$ as previously observed in Somayazulu et al. (1996). Note that this stoichiometric compound is stable only within a narrow region of pressure between 6.5 and 7 GPa.

The behavior of the dominant D$_2$ vibron in the present D$_2$-CH$_4$ mixture above 7.4 GPa follows the frequency of pure D$_2$ unlike the behavior observed in the previous study by Somayazulu et al. (1996). In that study, two stoichiometric compounds (CH$_4$H$_2$ or CH$_4$(H$_2$)$_2$) were reported to form above 7 GPa: methane-rich CH$_4$H$_2$ and hydrogen-rich
CH₄(H₂)₂ in the composition range of 30%–50% methane. In both compounds, the hydrogen mode occurs at a higher frequency than in pure bulk H₂. The higher frequency D₂ mode shown in Figs. 5.8(a) and 5.8(b) may be accounted for by the formation of a small amount of the previously reported stoichiometric compounds. Perhaps, the difference is due to the fact that the previous sample was allowed sufficient time and heating-cooling cycles for recrystallization, whereas the present mixture was neither heated nor allowed time for recrystallization. As a result, the previous sample formed the stoichiometric compounds over larger areas upon cooling, while the present sample is separated into essentially many regions of pure deuterium or methane, leaving small boundary areas to form the stoichiometric compounds.

Figure 5.9 shows the Raman spectra corresponding to the different regions at 6.6 and 7.4 GPa: (a) the deuterium-rich region, showing a very strong D₂ band (νₓDD), together with no C-H modes at 6.6 GPa or a weak C-H stretching mode (ν₁CH) at 7.4 GPa, (b) the CH₄-D₂ mixture region near (a), showing both the νₓDD and ν₁CH peaks in considerable intensities with a weak feature from ν₃CH, and (c) the mixture region far from (a), exhibiting a more complex Raman band at 6.6 GPa. At 6.6 GPa, both the ν₁CH and νₓDD modes seem to split or, more likely, develop new peaks on the low frequency sides of the peaks. This stems from the peak positions of higher frequency modes exactly corresponding to those of (b) at the same pressure. Thus, the new peaks emerge at ~7 cm⁻¹ below the νₓDD and ~12 cm⁻¹ below the ν₁CH. The spectral shapes and peak positions of these features are similar to the stoichiometric compound of CH₄(H₂)₄ in H₂-CH₄ mixture (24% CH₄ starting composition) at 5.4 GPa (Somayazulu, et al. 1996), showing the splitting of hydrogen vibron (νₓHH) in a way that one peak aligns with the
frequency at that pressure and the other peak shifts to \( \sim 10 \, \text{cm}^{-1} \) lower. Hence, we attribute the new features in Fig. 5.9(c) at 6.6 GPa to a \( \text{CH}_4(\text{D}_2)_4 \) compound. Nevertheless, we note that at higher pressures the sample appears quite similar in the different regions (see the images in Fig. 5.8(a)), suggesting a narrow stability region of \( \text{CH}_4(\text{D}_2)_4 \).

![Raman spectra](image)

**Figure 5.10:** Raman spectra of rotational modes of hydrogen isotopes in (a) \( \text{D}_2-\text{NH}_3 \), and (b) \( \text{D}_2-\text{CH}_4 \) mixtures. Note the presence of the \( \text{H}_2 \) and \( \text{D}_2 \) isotopes in the case of \( \text{D}_2-\text{NH}_3 \) due to the proton exchange (similar to the \( \text{D}_2-\text{H}_2\text{O} \) mixture), but that only the \( \text{D}_2 \) isotopes are present in the \( \text{D}_2-\text{CH}_4 \) mixture.

### 5.6 Hydrogen Rotational Modes in the \( \text{D}_2-\text{NH}_3 \) and \( \text{D}_2-\text{CH}_4 \) Mixtures

Figure 5.10 shows the rotational Raman spectra of hydrogen isotopes observed in (a) \( \text{NH}_3-\text{D}_2 \), and (b) \( \text{CH}_4-\text{D}_2 \), and Fig. 5.11 shows the pressure-dependent shifts of all mixtures. Clearly, all rotational modes of hydrogen in the mixtures show quite similar spectral characteristics and pressure shifts to that in pure (Hemley, Mao, & Shu, 1990;
Figure 5.11: The pressure-dependent peak shifts of hydrogen vibrons in the mixtures in excellent agreement with those of pure hydrogen isotopes (Hemley, Mao, & Shu, 1990; Hemley et al., 1993; Moshary et al., 1993b). The most important differences are between the D\_2 S\_0(2) and the H\_2 S\_0(1) modes, the latter, which deviates in the pure due to coupling with the E\_2\_g lattice mode of the hcp lattice (Hemley, Mao, & Shu, 1990). Their absence suggests that hydrogen has a different lattice than what it assumes in its pure form. Hemley, et al., 1993; Moshary et al., 1993b), except that different isotopes are present in the mixtures with H\_2O and NH\_3. They show a similar progression, beginning quite sharp at low pressures (<1 GPa), and they proceed to broaden with increasing pressure. The rotational modes of the homonuclear species H\_2 and D\_2 dominate, while HD modes are much broader than the H\_2 and D\_2 modes and consequently disappear much more quickly as shown in Chapter 4. Figure 5.11 shows that all the rotational modes follow a similar behavior and they also follow the low-temperature pure modes quite well (Hemley, Mao, & Shu, 1990; Hemley et al., 1993; Moshary et al., 1993b). They track quite well with the pure, with some differences seen in H\_2 S\_0(1) and D\_2 S\_0(2). The former case is interesting since the discontinuous change in the slope of the frequency with pressure of the S\_0(1)
rotational mode of hydrogen is associated with the crossing of the E\textsubscript{2g} lattice mode from the hcp structure of hydrogen (Hemley, Mao, & Shu, 1990). Its absence suggests that hydrogen has not assumed its stable hcp structure in this range, which is consistent with the presence of other molecules, particularly H\textsubscript{2}O and NH\textsubscript{3}, along with hydrogen. Across all three mixtures, the rotational modes show the same frequency shift with pressure.

5.7 Proton Exchange Reactions in the D\textsubscript{2}-NH\textsubscript{3} and D\textsubscript{2}-CH\textsubscript{4} Mixtures

Our studies have shown the spectral evidences for significant proton exchange reactions in D\textsubscript{2}-H\textsubscript{2}O and D\textsubscript{2}-NH\textsubscript{3} mixtures, but not in D\textsubscript{2}-CH\textsubscript{4}. The appearance of the rotational and vibrational modes of HD and H\textsubscript{2}, for example, is due to the proton exchange reactions, as well as the bands corresponding to O-D and N-D for D\textsubscript{2}-H\textsubscript{2}O and the D\textsubscript{2}-NH\textsubscript{3} mixtures, respectively. For D\textsubscript{2}-H\textsubscript{2}O mixtures, similar proton exchanges have been observed in fluid D\textsubscript{2}-water mixtures, fluid D\textsubscript{2}-ice mixtures, and solid D\textsubscript{2}-ice mixtures (see Chapter 4). Similar proton exchange reactions were also observed in D\textsubscript{2}-NH\textsubscript{3}, in both fluid-fluid and solid-fluid mixtures at 2 GPa (as shown in red in the upper panel of Fig. 5.12) above the solidification pressure (~1 GPa) of NH\textsubscript{3} in the D\textsubscript{2}-NH\textsubscript{3} mixture. The proton exchange occurs very rapidly in the fluid phase for both D\textsubscript{2}-H\textsubscript{2}O and D\textsubscript{2}-NH\textsubscript{3} of these mixtures (see Figs. 4.3(b) and 5.2).

We observe a clear difference between D\textsubscript{2}-H\textsubscript{2}O and D\textsubscript{2}-NH\textsubscript{3} mixtures in that the vibrational modes of hydrogen isotopes are observed in the water-rich region and absent in the ammonia-rich region. This suggests that the solubility of hydrogen in solid ammonia is very low, as also indicated by the appearance of hydrogen-rich bubbles that form inside the ammonia-rich region when it solidifies. Nevertheless, ammonia and hydrogen still exhibit attractive interactions even after the solidification of ammonia,
which can be traced by the proton exchange reactions (see Fig. 5.12). Furthermore, note that in D$_2$-H$_2$O mixture, the intensity of D$_2$ isotope continues to decrease even at high pressures with respect to the intensity of the isotopes between 13 GPa and 24 GPa and even higher pressure in Fig. 4.3(b). This is in contrast with the case of D$_2$-NH$_3$, where at high pressures the ratio of the isotopes does not change appreciably (see Figs. 5.2 and 5.6(a)). This may be due to the solidification of the hydrogen, the transition to ammonia IV or both.

![Figure 5.12: Raman spectra exhibiting slow proton exchange in fluid D$_2$-solid NH$_3$ at 2 GPa (upper panel), in contrast to negligible proton exchange in D$_2$-CH$_4$ mixture (lower panel).](image)

In the case of D$_2$-CH$_4$ mixtures, no HD or H$_2$ peaks are observed in the fluid phase as shown in the lower panel (in green) of Fig. 5.12 in methane-rich D$_2$-CH$_4$ mixtures and a very weak HD vibrational mode appear above 7 GPa. This does not necessarily imply the occurrence of proton exchange in the solid, because the peaks tend to sharpen upon solidification and thereby the weak HD mode to be detected. The
concentration of HD is estimated to be only \( \sim 0.3\%-0.7\% \), which is very small compared to those observed in D\(_2\)-H\(_2\)O and D\(_2\)-NH\(_3\) mixtures, and may be due to HD impurity already present in the deuterium sample. While methane and hydrogen form the stoichiometric compounds such as (CH\(_4\))(H\(_2\))\(_4\) within a limited composition range between 50\% and 70\% H\(_2\) at pressures between 5 and 6 GPa, their interactions are generally weak of a non-bonded type, especially in fluids as evident from its complete miscibility and an elevated solidification pressure of methane in the mixture.

In this regard, the absence of proton exchange is unexpected, underscoring the significance of hydrogen bonding in the proton exchange reactions observed in D\(_2\)-H\(_2\)O and D\(_2\)-NH\(_3\). This difference can be attributed to the stronger covalent C-H bonds in CH\(_4\) molecules owing to the lacking of attractive hydrogen bonding, which is unlike the cases of D\(_2\)-H\(_2\)O and D\(_2\)-NH\(_3\). Although it is possible for proton exchange to occur without the formation of hydrogen bonding, as in the case of H\(_2\)-D\(_2\) mixtures (Brown & Daniels, 1992; Loubeyre et al., 1992) the mechanism in that case is likely collisions aided by much larger reaction area and higher diffusion rates of small diatomic molecules relative to those of substantially massive methane molecules. The absence of proton exchange in D\(_2\)-CH\(_4\) mixtures despite the fact that the two components are well mixed in fluids, compared to D\(_2\)-H\(_2\)O and D\(_2\)-NH\(_3\) mixtures clearly showing visual appearances of the phase separations, further supports the conclusion that the presence of hydrogen bonding assists, if not induces the proton exchange reactions in the H\(_2\)O and NH\(_3\) mixtures.
Chapter 6

Comparisons of the Mixtures and Conclusions

6.1 Overview

In this chapter, the three mixtures—D$_2$-H$_2$O, D$_2$-NH$_3$, and D$_2$-CH$_4$—will be compared. In particular, the degree of mixing in the different phases of the different mixtures will be discussed. Also, the features of the vibrational modes of hydrogen will be compared in the different mixtures. Furthermore, the bond lengths of the hydrogen molecules obtained from the spectral data and Morse potential will be presented and compared for each of the mixtures. Finally, the main conclusions of this work will be presented.

6.2 Mixing of the Components

6.2.1 Mixing in the Fluid Phases

These three mixtures exhibit interesting behavior in the fluid states. The D$_2$-H$_2$O and D$_2$-NH$_3$ mixtures both appear to be phase separated in the fluid. Hydrogen-rich and water- or ammonia-rich regions can be easily distinguished with a clear boundary. Nevertheless, despite the appearance of a perfect phase separation, two facts indicate that there is indeed mixing. First, upon solidification, bubbles appear in both the water- and ammonia-rich regions in the D$_2$-H$_2$O and D$_2$-NH$_3$ mixtures, respectively. Secondly, a weak hydrogen vibron was apparent in the water- and the ammonia-rich regions in the fluid. Additionally, the frequency of the hydrogen vibrational mode was at a lower frequency in the water- and ammonia-rich regions compared to the hydrogen rich regions at a given pressure. This is due to the strong attraction between the protons in the hydrogen
molecules and the oxygen in water or nitrogen in ammonia. Additionally, the behavior of the hydrogen vibrational modes, which will be summarized below, is different than either in pure hydrogen or in mixtures of hydrogen isotopes. This fact suggests that water and ammonia are present in the D$_2$-H$_2$O and D$_2$-NH$_3$ mixtures, respectively.

The case of the D$_2$-CH$_4$ mixture is quite different. In this case, the fluid mixture exhibits complete miscibility. No boundaries or separate regions are observed, and the Raman signatures of both D$_2$ and CH$_4$ were observed throughout the entire sample chamber. The interactions were of a weak, nonbonding type leading to an elevated solidification pressure of methane in the mixture. Upon the solidification of the D$_2$-CH$_4$ mixture, the sample divided into different regions. The Raman spectrum from one of these regions indicated the formation of a CH$_4$(D$_2$)$_4$ stoichiometric compound—a deuterated form of the previously reported CH$_4$(H$_2$)$_4$ (Somayazulu et al., 1996).

### 6.2.2 Mixing in the Fluid Hydrogen-Solid Ice and Solid-Solid Phases

As the pressure increases, the vibrational modes of the hydrogen isotopes are still present in the water-rich region in the D$_2$-H$_2$O mixture. Thus from ambient pressure to 65 GPa, there is evidence of hydrogen in the water-rich region. In contrast, there is no evidence of hydrogen vibrational modes in the ammonia-rich region indicating a negligible solubility of hydrogen in solid ammonia. For the case of the methane and the hydrogen, immediately upon the solidification (observed at ~6 GPa in a 1:1 mixture) boundaries in the sample begin to form. Additionally, the Raman spectra indicate that the deuterium and the methane are mixed, albeit inhomogenously. As the pressure increases, the phase boundaries disappear. One side of the sample exhibits deuterium peaks and a weak methane signature. On the other side, a deuterium peak is present with a more
intense methane signature (Fig. 5.9).

6.3 Vibrational Modes of Water, Ammonia, and Methane in Mixtures

In summary, all O-D and O-H stretching modes in the D$_2$-H$_2$O mixture exhibit a strong redshift (between ~25 to 50 cm$^{-1}$/GPa). Some modes redshift at the same rate as that observed in pure water, and others redshift at twice that rate. This suggests that the attractive hydrogen bonding is at least as strong in the mixture as in pure water. As discussed above and shown in Figs. 5.4(b) and 5.5(b), the symmetric N-H modes of NH$_3$ ($v_1$) and NH$_2$D ($v_3^{NH}$) in the D$_2$-NH$_3$ mixture show red shifts. The symmetric N-D mode of NHD$_2$ ($v_3^{ND}$) shows a weak red shift while that of ND$_3$ ($v_1$) exhibits a slight blue shift. The $v_1$ of NH$_3$ red shifts twice as fast in pure as it does in the mixture. The $v_1$ of ND$_3$ blueshifts in the mixture compared to the red shift observed in the pure. All the other N-H and N-D modes shift toward the blue with pressure. Furthermore, the rate of the red shift in the ammonia mixture is an order of magnitude lower than that observed in water mixture (~3 cm$^{-1}$/GPa in D$_2$-NH$_3$ compared to order of ~20 cm$^{-1}$/GPa in D$_2$-H$_2$O). Thus, the trend in the D$_2$-NH$_3$ mixture is towards reducing the strength of the attractive interaction relative to the pure ammonia.

Finally, in the case of C-H modes in the D$_2$-CH$_4$ mixture, all shift to higher frequencies with increasing pressure, exhibiting the essentially repulsive interactions in this mixture. Thus, this shows the dominant attractive interactions between H$_2$O molecules in the D$_2$-H$_2$O mixture (at least equal to those in pure water), weaker hydrogen bonding between NH$_3$ molecules in the D$_2$-NH$_3$ (at appears to be weaker than pure ammonia), and the lack of attractive hydrogen bonding in CH$_4$ molecules in the case of D$_2$-CH$_4$. The strong hydrogen bonding, on the other hand, weakens the covalent O-H and
N-H bonds of H$_2$O and NH$_3$, subjected to the proton exchange of these molecules in the mixtures with D$_2$.

### 6.4 Hydrogen Bond Length from the Morse Potential

The present spectral data can reveal insights of the potential landscape in dense mixtures as well as be used to calculate the bond length of dense hydrogen as previously demonstrated (Ashcroft, 1990; Loubeyre, Jean-Louis, & Silvera, 1991). The calculation employs the Morse potential, as an approximation to the true diatomic molecular potential, and the measured vibrational frequency of two isotopes of hydrogen and the rotational frequency of one of the isotopes. The Morse potential is a three-parameter, semi-quantitative model for the potential curve of diatomic models. This three-parameter potential has the advantage of possessing an exact solution (Morse, 1929), and being simple enough that it requires only three experimental data points:

$$\phi(r) = D\left[e^{-2a(r-r_e)} - e^{-a(r-r_e)}\right]$$

(6.1)

where $D$ is the depth of the potential, $a$ is the range parameter, and $r_e$ is the equilibrium bond length. The mathematical details have been described in Ashcroft (1990) and Loubeyre et al. (1991) and are summarized in Appendix B.

Figure 6.1 shows the comparison of hydrogen bond lengths as determined by using the above procedure in D$_2$-H$_2$O (blue squares), D$_2$-NH$_3$ mixtures (red circles), and D$_2$-CH$_4$ (green diamonds). The calculated bond length of hydrogen molecules in D$_2$-H$_2$O (calculated from the main continuous vibrons of D$_2$ and H$_2$ shown in Fig. 6.2) is more similar to the bond length in pure hydrogen than that in D$_2$-NH$_3$. The calculated bond lengths are clearly longer in D$_2$-H$_2$O mixtures than in the D$_2$-NH$_3$ mixtures. The calculated bond length for D$_2$-NH$_3$ shows good agreement between the two runs until
around 12 GPa, above which there is an apparent increase in the bond length. Also noted is a clear change in the slope of the bond length at around 18 GPa.

The bond length in D$_2$-CH$_4$ was calculated from the weak, higher frequency D$_2$ and HD modes shown in Fig. 6.2, because the dominant D$_2$ vibron cannot be used except for the two lower pressure data points. The bond length is similar to pure hydrogen until 12 GPa (Fig. 6.1 in the closed green diamonds), above which it becomes longer than that of pure H$_2$ and even in D$_2$-H$_2$O mixtures. However, it is important to note that this bond length was calculated from two weak vibrons (both at higher frequencies). As such, the frequency of dominant D$_2$ vibron did not enter into the calculation above 11 GPa and, therefore, it does not represent the vast majority (~99%) of the deuterium molecules in the mixture above 12 GPa.

Figure 6.1: Hydrogen bond length calculated from the present spectral data using the Morse potential. It shows the bond length of hydrogen in D$_2$-NH$_3$ (red circles) is shorter than that in D$_2$-H$_2$O (blue squares). The calculated bond length of hydrogen in the D$_2$-CH$_4$ mixture (closed green diamonds) is longer than in either mixture. Nevertheless, more representative values may be indicated by the open green diamonds as explained in the text and Appendix B.

In order to examine the bond length in D$_2$-CH$_4$ mixtures using the dominant D$_2$ vibron, we use the vibron frequency of pure HD from Moshary et al. (1993a), together
with a $S_0(2)$ rotational mode of D$_2$ as observed in the D$_2$-CH$_4$ mixture. This is a reasonable approximation, considering that the D$_2$ frequency of the D$_2$-CH$_4$ mixture follows that of pure D$_2$ (see Fig. 6.2). This analysis then results in a shorter bond length of hydrogen in the mixture than that of pure H$_2$, following the trend of the other two mixtures until ~4–7 GPa as illustrated in Fig. 6.1. Above this pressure, it gradually approaches closer to the bond length of pure hydrogen than either of the other mixtures, consistent with much weaker interactions observed in the D$_2$-CH$_4$ mixture.

It is interesting to note that the bond length change observed at 18 GPa in the D$_2$-NH$_3$ mixture coincides with the onset of the isosymmetric phase IV-V transition in ammonia and the structural change in ND$_3$ observed in the previous neutron diffraction studies (Ninet et al., 2009). It is found that three ND bonds and three DND bond angles of pure ND$_3$ are no longer equivalent in phase IV. The N-D bond lengths differ by about 5% with respect to each other over the pressure range of 5 to 25 GPa with one bond even elongating with increasing pressure. The three N⋯D hydrogen bondings shorten over the entire pressure range. Clearly, the elongation of N-D is a manifestation of the strengthening of hydrogen bonding between nearby ND$_3$ molecules. The bond angles in ammonia are also all different over a range of 100° to 120°, with two of the angles exhibiting nearly no pressure-induced change, but the third one shows a drastic change from decreasing to sharply increasing at ~18 GPa. This change is correlated with a dramatic change in one of the hydrogen bond angle N⋯D-N, which changes from about 166° at 15 GPa until almost 180° at 24 GPa. It is likely that any structural changes in ammonia would affect the potential sensed by hydrogen vibrons and thereby manifested in the spectral and bond length changes.
6.5 Comparison of Hydrogen Vibrons

The spectral changes are more dramatic in the D$_2$-H$_2$O mixture showing relatively large peak splitting and shifts toward higher frequencies. In the D$_2$-NH$_3$ mixture, slight changes appear, such as small shoulders and subtle splitting on the high frequency side of the vibron. In contrast, D$_2$-CH$_4$ mixture shows no apparent spectral changes, nor any significant level of the proton exchange with the exception of the formation of a stoichiometric compound within a small pressure range. Figure 6.2 summarizes the pressure dependent spectral changes of hydrogen vibrons in D$_2$-H$_2$O, D$_2$-NH$_3$, and D$_2$-CH$_4$ mixtures. In the D$_2$-H$_2$O mixture, all three isotopes were observed after the proton exchange occurred rapidly in the fluid at pressures under 1 GPa. In this case, the frequencies of hydrogen vibrons dissolved in water also gave a lower frequency suggesting an attractive interaction as seen in Fig. 6.1 (in blue squares). With increasing pressures, all the modes showed a shift to higher frequency relative to the frequency observed in pure from very low pressures and to frequencies higher than those that would be expected due to the mixture of H$_2$:HD:D$_2$, clearly demonstrating that the interaction with water is responsible for much of this shift. Notice the difference between the attractive interaction sensed by the O-H and O-D bonds (Fig. 4.6), and the repulsive interaction sensed by the D$_2$, HD, and H$_2$ vibrational modes. Two bands of hydrogen peaks were observed. The lower frequency band shows multiplets that roughly follow the composition dependence. These two peaks have been interpreted as coming from two different sites of the ice lattice, and their initial splitting at 25 GPa as an onset of the proton ordering process that completes at around 50–60 GPa. This splitting in the
vibrational modes at 25 GPa is anticipated by the change in the slope of the pressure dependence of the hydrogen bond length at 20 GPa (Fig. 6.1).

Figure 6.2: The pressure-induced peak shifts of hydrogen isotopes in D₂-H₂O (blue squares), D₂-NH₃ (red circles), and D₂-CH₄ (green diamonds) mixtures, showing in comparison with those of pure hydrogen isotopes (solid lines). Note that both the degree of peak shifts and splitting increases with the strength of hydrogen bonding in these mixtures.

Figure 6.2 suggests that hydrogen molecules experience strong repulsive interaction with water molecules in the D₂-H₂O mixture, resulting in the presence of strong internal pressure, while the O-H and O-D modes reveal attractive hydrogen bonding. In the D₂-ND₃ mixture, both the repulsive interaction shown by the vibrons of hydrogen isotopes and the attractive interaction in N-H and N-D are still apparent but weaker than those in the D₂-H₂O. In the D₂-CH₄ mixture, on the other hand, deuterium molecules experience little interaction with carbon atoms at least above 7 GPa at room temperature. These results then correlate well with the expected strength of repulsive interaction of deuterium with H₂O, NH₃, and CH₄ as in order of the number of unpaired
electrons. The presence of strong repulsive interaction between D₂ and H₂O (or NH₃) is probably responsible for the proton ordering transition of H₂O that occurs at a substantially lower pressure (25–50 GPa) in D₂-H₂O than in pure H₂O (40–80 GPa) and the proton exchange reactions between D₂ and H₂O (or NH₃) – both mediated through the hydrogen bonding network of H₂O (or NH₃) molecules.

6.6 Conclusions

The main findings can be understood as being related to the strength of the hydrogen bond. The stronger the hydrogen bond in these molecules, the greater the change in the behavior of the mixture compared to the pure components. The main findings are as follows:

The D₂-H₂O and the D₂-NH₃ mixtures appear to be phase-separated in the fluid, but both are actually mixed as seen by the formation of bubbles and rapid proton exchange. D₂-CH₄ is well-mixed in the fluid, but the absence of proton exchange suggests weak, non-bonding interactions.

After the solidification of H₂O, hydrogen was still present in the H₂O-rich region. Also proton exchange was observed fluid D₂-ice and solid D₂-ice mixture. Evidence of the exchange was seen up to pressures on the order of at least ~30 GPa.

Proton exchange was observed in the fluid D₂-NH₃ and the fluid D₂-solid NH₃ (Phase III) mixture. The hydrogen isotope ratio appeared to be unchanging above 5 GPa, indicating no high-pressure proton exchange. This may be due to the solidification of hydrogen, the characteristics of ammonia IV or both. The mixing in solid D₂-NH₃ appears to be less than in the D₂-H₂O.

With the exception of the narrow pressure range of 6-7.5 GPa, clear boundaries
were not observed in the D₂-CH₄ mixture. Both molecules were observed mixed in many regions of the sample. Yet no significant proton exchange was observed in the D₂-CH₄ mixture in any phases. The HD peak observed was weak (0.5%), and may be due to HD impurity already present in the deuterium.

The proton exchange in the D₂-H₂O and D₂-NH₃ mixtures naturally leads to the formation of HD and H₂, as well as HDO, D₂O, NH₂D, NHD₂, and ND₃.

The behavior of the vibrational modes agrees well with the above observations. The vibrational modes of H₂O, HDO, and D₂O all redshift with pressure at least as fast as in pure, and some redshift at twice the rate. The hydrogen vibrational modes show a large blueshift, and the modes of each isotope split into two bands, each with multiplets.

In comparison to pure, the vibrational modes of NH₃ and ND₃ tend to exhibit less redshift with pressure (for the pure modes that redshift) or greater blueshift with pressure (for the pure modes that blueshift). Thus, the intermolecular attractions appear to be weakened in the mixture. This is the first high-pressure Raman assignment proposed for the stretching modes of NH₂D and NHD₂. The hydrogen vibrons show small splitting and asymmetry in the case of the D₂-NH₃ mixture.

The frequencies in the D₂-CH₄ mixture are essentially the same as the frequencies in blue D₂ and bulk CH₄, and all the stretching modes blueshift with increasing pressure.

Finally, in the D₂-H₂O and D₂-NH₃ mixtures, the hydrogen vibron peak shifts and bond lengths exhibit behavior that suggests changes in the underlying H₂O or NH₃ ice lattice. The initial splitting in the hydrogen vibrons in the D₂-H₂O mixture at ~25 GPa suggests the onset of the ordering transition, which may be completed by 50 GPa. These pressures are highlighted by the change of ratio between the vibron bands from 3:2 to 1:1.
at 50 GPa. The changes in hydrogen vibrational spectra (appearance of shoulders) and bond length (change in slope) in D₂-NH₃ mixture at ~12-18 GPa may be due to the isosymmetric Phase IV-Phase V ammonia transition.

The above results suggest a trend that corresponds to the strength of the hydrogen bond in these mixtures. The most dramatic changes are those in the D₂-H₂O mixture, with much more subtle changes taking place in the D₂-NH₃, and finally the least changes taking place in the D₂-CH₄ mixture. These differences highlight the systematic trends of these simple mixtures of deuterium with H₂O, NH₃, and CH₄, in which hydrogen bonding plays a significant role to govern the proton exchange and the nature of intermolecular interaction in these mixtures. Finally, the present result of proton exchange reactions observed between D₂ and H₂O and NH₃ may have some implications for understanding the miscibility between the upper H₂/He layer and the middle “ice” layer of the giant planets.
Appendix A

**Sum Rule**

### A.1 Introduction

The sum rule (Decius & Wilson, 1951; Wilson, Decius, & Cross, 1980) gives expressions relating the sum of the squares of frequencies of isotopic molecules. The essence of the sum rule is that if the several isotopic molecules are superimposed (by addition or subtraction as appropriate) such that the masses of the atoms cancel at each position, the resulting weighted linear combination of the sums of the squares will vanish. The weighted linear combination of the sum of squares is based upon the number of times the molecule appears in order to cancel the other molecules. We will now justify this statement, and then provide some examples.

### A.2 Justification of the Sum Rule

It is assumed in what follows that the isotopic substitution does not change the geometry of the molecule (angles or bond lengths) nor its potential function. This is a good approximation, provided that potential is nearly harmonic. Wilson (1939) introduced a symmetric matrix, which only depends on the inverse mass of the atoms, \( \mu \), and the displacement coordinates of the atoms. This can be written in the form for a molecule with \( N \) atoms

\[
G_{mn} = \sum_{\alpha}^{N} \mu_{\alpha} s_{m\alpha} \cdot s_{n\alpha} \equiv \sum_{\alpha}^{N} \mu_{\alpha} H_{mn}^{(\alpha)}
\]

(A.1)
where $\mu_a$ is the inverse mass of the $a$th atom, and $s_{ma}$ is a displacement vector associated with the $a$th atom. Specifically, $s_{ma}$ gives the direction in which a displacement of atom $a$ will yield the maximum increase in the $m$th internal coordinate (total of $3N - 6$ coordinates, or $3N - 5$ for linear molecules). Thus, the $s_{ma}$ and $H_m^{(\alpha)}$ are the same for all isotopic species.

Also, a matrix can be defined that provides the force constants, expressed in the internal coordinates. We assume this matrix, $F$, will be the same for all isotopic species. Then, the squares of the normal frequencies of the molecule are given by

$$\det(F G - E\lambda) = 0$$

(A.2)

where $\lambda_m = 4\pi^2\nu^2$ ($c$ is the speed of light and $\nu$ is the vibrational frequency) and $E$ is the $(k \times k)$ identity matrix, where $k$ corresponds to number of modes. Then, we define the sum of the squares of all the modes for isotope $X$ as follows:

$$\sigma^{(X)} = \sum_m \lambda_m^{(X)}$$

(A.3)

But from eq. (A.2), it follows that

$$\sigma^{(X)} = \sum_m \lambda_m^{(X)} = \sum_{mn} F_{mn}G_{mn} = \sum_{mn} F_{mn}G_{mn} = \sum_{mn} \sum_{\alpha} H_m^{(\alpha)} \mu_{\alpha}$$

(A.4)

Then, if $n^{(X)}$ is the coefficient for isotope $X$ (number of times isotope $X$ appears in the superposition), we have the following

$$\sum_X n^{(X)} \sigma^{(X)} = \sum_X n^{(X)} \sum_{mn} \sum_{\alpha} H_m^{(\alpha)} \mu_{\alpha}^{(X)} = \sum_{\alpha} \sum_{mn} \sum_X n^{(X)} H_m^{(\alpha)} \mu_{\alpha}^{(X)}$$

(A.5)

The final factor, $\sum_X n^{(X)} \mu_{\alpha}^{(X)} = 0$, by the hypothesis above, and thus,

$$\sum_X n^{(X)} \sigma^{(X)} = 0.$$  

(A.6)
Thus, the sum of the square of the frequencies can be written in the linear combinations that cause all the masses to cancel.

### A.3 Examples of the Sum Rule

#### A.3.1 Isotopes of Hydrogen

The case of a diatomic is trivial and hence illustrates the idea very clearly. The $F$ matrix is simply the force constant $k$ between the molecules, and the $G$ matrix is simple the reduced mass $(\mu_1 + \mu_2)$. Thus, for three diatomic molecules, AA, AB, and BB, we have

- $\lambda^{(AA)} = k(2\mu_A)$
- $\lambda^{(AB)} = k(\mu_A + \mu_B)$
- $\lambda^{(BB)} = k(2\mu_B)$

Thus, the required superposition is shown in Table A.1:

<table>
<thead>
<tr>
<th>Coefficient</th>
<th>Atom at Position 1</th>
<th>Atom at Position 2</th>
<th>Molecule</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>A</td>
<td>A</td>
<td>AA</td>
</tr>
<tr>
<td>1</td>
<td>B</td>
<td>B</td>
<td>BB</td>
</tr>
<tr>
<td>-1</td>
<td>A</td>
<td>A</td>
<td>AB</td>
</tr>
<tr>
<td>-1</td>
<td>B</td>
<td>B</td>
<td>AB</td>
</tr>
</tbody>
</table>

| Table A.1: Illustrating the superposition of isotopic molecules to use the sum rule. |

This results in the following relationship

$$\sigma^{(AA)} + \sigma^{(BB)} = 2\sigma^{(AB)}$$

For the isotopes of hydrogen, using the ambient pressure values of $\nu_{HH} = 4162$ cm$^{-1}$, $\nu_{HD} = 3633$ cm$^{-1}$, and $\nu_{DD} = 2994$ cm$^{-1}$, the difference between the two sides is $\sim 6\%$. Most of this error is due to the large anharmonicities characteristic of the hydrogen diatomic potential.
A.3.2 Isotopes of Ammonia

We will now consider the case of the ammonia isotopes. As mentioned in Chapter 5, three NH\textsubscript{3} and three ND\textsubscript{3} molecules are needed to cancel three NH\textsubscript{2}D and three NHD\textsubscript{2} molecules. This is easy to verify, since there will be three H atom and three D atoms on each site from the NH\textsubscript{3} and ND\textsubscript{3}, that will be exactly cancelled by the other two isotopes. That is,

\[ \sigma^{(NH_3)} + \sigma^{(ND_3)} = \sigma^{(NH_2D)} + \sigma^{(NHD_2)} \]  \hspace{1cm} (A.11)

Consider the low-temperature infrared data for ammonia and its isotopes (Reding & Horning, 1951; 1955). Table A.2 gives the frequencies of vibrational modes for ammonia.

<table>
<thead>
<tr>
<th>(\text{NH}_3)</th>
<th>(\text{ND}_3)</th>
<th>(\text{NH}_2\text{D})</th>
<th>(\text{NHD}_2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1060 cm\textsuperscript{-1}</td>
<td>815 cm\textsuperscript{-1}</td>
<td>994 cm\textsuperscript{-1}</td>
<td>905 cm\textsuperscript{-1}</td>
</tr>
<tr>
<td>1646 cm\textsuperscript{-1}</td>
<td>1196 cm\textsuperscript{-1}</td>
<td>1393 cm\textsuperscript{-1}</td>
<td>1255 cm\textsuperscript{-1}</td>
</tr>
<tr>
<td>1646 cm\textsuperscript{-1}</td>
<td>1196 cm\textsuperscript{-1}</td>
<td>1609 cm\textsuperscript{-1}</td>
<td>1476 cm\textsuperscript{-1}</td>
</tr>
<tr>
<td>3223 cm\textsuperscript{-1}</td>
<td>2318 cm\textsuperscript{-1}</td>
<td>2444 cm\textsuperscript{-1}</td>
<td>2389 cm\textsuperscript{-1}</td>
</tr>
<tr>
<td>3378 cm\textsuperscript{-1}</td>
<td>2500 cm\textsuperscript{-1}</td>
<td>3307 cm\textsuperscript{-1}</td>
<td>2500 cm\textsuperscript{-1}</td>
</tr>
<tr>
<td>3378 cm\textsuperscript{-1}</td>
<td>2500 cm\textsuperscript{-1}</td>
<td>3378 cm\textsuperscript{-1}</td>
<td>3338 cm\textsuperscript{-1}</td>
</tr>
</tbody>
</table>

Table A.2: The frequencies of the vibrational modes for the different isotopes of ammonia (data from Reding & Horning, 1951; 1955).

The difference between the both sides is of eq. A.11 is 0.59%. If the bending modes are not observed as happened in the present case with ammonia (Chapter 5), the sum rule can still be used to provide information just using the stretching modes. The stretching modes of one isotope can practically be expressed as linear combinations of the stretching modes of another, and the sum rule takes into account to mass differences. For example, in the case of the stretching modes only, this yields a difference between both sides of Eq. A.11 of 0.66%. This is only slightly greater than the difference obtained using the both
the bending and stretching modes. The difference using only the bending modes is 0.23%, which is better than either of the above.
Appendix B

Bond Length from Morse Potential

B.1 Introduction

The Morse potential is a three-parameter, semi-quantitative model for the potential curve of diatomic molecules (Morse, 1929). This three-parameter potential has the advantage of possessing an exact solution and being simple enough that it requires only three experimental data points:

$$
\phi(r) = D[e^{-2a(r-r_e)} - e^{-a(r-r_e)}]
$$

(B.1)

where $D$ is the depth of the potential, $a$ is the range parameter, and $r_e$ is the equilibrium bond length. It was proposed by Ashcroft (1990) that this potential be used to calculate the bond length of the hydrogen molecules. This is done using the frequencies of two vibrational modes of hydrogen (from two different isotopes), and the frequency of a rotational mode.

B.2 Determination of Bond Length

Solving the Schrödinger equation for this potential yield the following expression:

$$
\tilde{\nu}_{vJ} = \tilde{\nu}_e \left( v + \frac{1}{2} \right) - x_e \tilde{\nu}_e \left( v + \frac{1}{2} \right)^2 + J(J+1)B_e - D_eJ^2(J+1)^2
- \alpha_e \left( v + \frac{1}{2} \right)J(J+1)
$$

(B.2)

where

$$
\tilde{\nu}_e = \frac{a}{2\pi c} \sqrt{\frac{2D}{\mu}},
$$

(B.3)

$$
x_e = \frac{\pi\hbar\tilde{\nu}_e c}{2D},
$$

(B.4)
In these expressions, \( \mu \) is the reduced mass of the molecule, and \( c \) is the speed of light (Wilson & Pauling, 1935).

For \( \Delta J = J = 0 \) and \( \Delta \nu = 1 \), the expression reduces to

\[
\Delta \bar{\nu} = \bar{\nu}_{10} - \bar{\nu}_{00} = \bar{\nu}_e - 2x_e \bar{\nu}_e = \frac{a}{2\pi c} \sqrt{\frac{2D}{\mu}} - \frac{h a^2}{2\pi \mu c}.
\]  

(B.8)

Thus, the vibrational frequency depends on the range parameter \( a \) and the potential depth, \( D \), but not on the bond length \( r_e \). Thus taking two vibrational frequencies, \( \bar{\nu}_1 \) and \( \bar{\nu}_2 \) substituting them into Eq. (B.3), yields two equations in two unknowns. Inverting these equations yields the following expressions for the range parameter and potential depth:

\[
a^2 = \frac{2\pi c \sqrt{\mu_1 \mu_2}}{h (\sqrt{\mu_1} - \sqrt{\mu_2})} (\sqrt{\mu_1} \bar{\nu}_1 - \sqrt{\mu_2} \bar{\nu}_2)
\]  

(B.9)

\[
D = \frac{\pi h c}{\sqrt{\mu_1 \mu_2} (\sqrt{\mu_1} - \sqrt{\mu_2}) (\sqrt{\mu_1} \bar{\nu}_1 - \sqrt{\mu_2} \bar{\nu}_2)^2}.
\]  

(B.10)

where \( \mu_i \) and \( \bar{\nu}_i \) correspond to the reduced mass and the measured vibrational frequencies of a hydrogen isotope, respectively. Then evaluating Eq. (B.2) for \( \Delta J = 2 \) and \( \Delta \nu = \nu = 0 \), we obtain

\[
\Delta \bar{\nu} = \bar{\nu}_{0(J+2)} - \bar{\nu}_{0J} = 2(2J + 3)B_e - (2J + 3)\alpha_e - 4D_e (2J + 3)(J^2 + 3J + 3)
\]  

(B.11)

This expression is a sixth order polynomial in \( r_e \), thereby allowing the bond length to be determined.
B.3 Comments Regarding the Calculation

The calculation, as noted above, is derived for $\Delta J = 0$, $\Delta \nu = 1$, $J = 0$, which implies that the $Q_1(0)$ vibron of each mode should be used. Nevertheless, due to the thermal populations of the rotational levels, we measure the $Q_1(1)$ vibron for H$_2$ and HD, and the $Q_1(2)$ vibron for D$_2$. This yields a small difference ($6a_e$ for D$_2$ and $2a_e$ for H$_2$), which at ambient pressure is $\sim 6$ cm$^{-1}$ for both D$_2$ and H$_2$. Judging from the broadening of the peaks, it would increase by a factor 2 or 3 by 30 GPa, resulting in an uncertainty of $\sim 20$ cm$^{-1}$ or $\sim 0.7\%$.

First, the Morse potential is anharmonic and precisely such a potential is necessary as to model the hydrogen molecule. The H$_2$, HD and D$_2$ molecules have substantial anharmonicities due to their light masses. One consequence of the anharmonicity is that the frequencies of the isotopes do not scale as the respective reduced masses. Indeed, if they scaled perfectly were the case, the range parameter $a$ would vanish, and while the potential depth $D$ would become infinite, as can be seen by examining Eqs. (B.4) and (B.5). However, the manner in which the vibrational modes scale with reduced mass causes them to fall into the mathematical stability range of Eqs. (B.4) and (B.5) derived from the Morse potential, thereby yielding results for the three parameters that are neither negative nor imaginary. In other words, because the following inequalities $\mu_{DD}\tilde{\nu}_{DD}^2 > \mu_{HD}\tilde{\nu}_{HD}^2$ and $\mu_{HD}\tilde{\nu}_{HD}^2 > \mu_{HH}\tilde{\nu}_{HH}^2$ hold, physical values for the Morse potential parameters are obtained.

This was important in the case of the D$_2$-CH$_4$ mixture. The HD vibrational frequency was much higher than in pure, while the D$_2$ frequency was essentially identical to that in pure. This is because the Morse parameter $a$ depends on
where \( \mu_{DD} \) and \( \mu_{HD} \) are the reduced masses of \( \text{D}_2 \) and \( \text{HD} \) and, \( \tilde{\nu}_{DD} \) and \( \tilde{\nu}_{HD} \) are the vibrational frequencies of \( \text{D}_2 \) and \( \text{HD} \), respectively. Thus, if \( \mu_{DD}^{1/2} \tilde{\nu}_{DD} < \mu_{HD}^{1/2} \tilde{\nu}_{HD} \), then \( a \) becomes imaginary since \( \mu_{DD} > \mu_{HD} \). These imaginary values of \( a \) occur if the dominant, lower frequency \( \text{D}_2 \) is used to determine the bond length in the \( \text{D}_2\text{-CH}_4 \) mixture, except for the data points at 6.6 and 7.4 GPa. As a result, it is only possible to get real, physical values for the bond length if the weak, higher frequency mode is used.


Mao, H. K., & Bell, P. M. (1979). Observations of hydrogen at room temperature (25 C) and high pressure (to 500 kilobars). *Science, 203*(4384), 1004-1006.


