

Trapping and Matrix Isolation of Chemical Species in Solid Hydrogen

J. Sirak^a, J. Graham^b, N. Heston^b, G. Ihas^b, and G. Labbe^b

^a*Department of Physics, Rutgers University, Piscataway, NJ 08901*

^b*Department of Physics, University of Florida, Gainesville, FL 32611*

Abstract

A novel cryostat was designed and built such that elemental boron could be laser ablated and allowed to form within a solid hydrogen matrix. This cryostat was attached to an infrared spectrometer and absorption spectra determined. The first task, however, was to remove the impurities from the hydrogen that was going to become a solid at the cryogenic temperatures. In order to do this, a gas handling system was created using a charcoal, liquid nitrogen cold trap to remove the water and carbon-dioxide impurities. While the cleaned gaseous hydrogen was sprayed on the sample cold finger of the cryostat, a boron lump mounted in the cryostat can be ablated using a Neodymium-YAG (yttrium-aluminum-garnet) laser. The gaseous boron and hydrogen are then allowed to mix; thus forming a variety of different matrix-isolated species that deposit upon the aluminum cold finger. The bonding states of these species are then analyzed by studying the infrared absorption spectra produced.

Introduction

In the recent past, matrix isolation experiments were done by mixing a sample vapor, in our case boron, with an inert gas such as argon or neon. The use of an inert gas proves beneficial because it reduces the number of reactions occurring between this embedded impurity (in our case a proposed rocket propellant) and the inert solid matrix. The unreactive nature of the two gases and the low temperatures at which the solid is formed ensures maximum embedding and hence maximum possible release energy upon warming. Even though the inert gases have proved successful, they do have substantial flaws. The inert gases do not burn and they have a relatively high atomic mass. In particular, the atomic weight of neon and argon are 20.18 amu and 39.95 amu respectively; whereas the atomic weight of hydrogen is a mere 1.01 amu. This drastic difference in weights gives the solid hydrogen matrix a volumetric advantage. More particularly, the result would be more energetic outputs and a higher specific impulse of the propellant system. In other words, the increased density of propellant atoms embedded within this low density hydrogen matrix increases the number of possible chemical reactions taking place within the engine [1].

The benefits of having a low mass matrix could further be described by the relation between specific impulse and specific enthalpy. First, the specific enthalpy of a system is defined by the following equation:

$$h_{sp} = u + Pv \quad (1)$$

In Eq. (1), h_{sp} is the specific enthalpy, u is specific internal energy of the system, P is the pressure of the system, and v is the specific volume. This specific enthalpy can be found to be proportional to the specific impulse by the following [2]:

$$I_{sp} \propto \sqrt{\frac{\Delta h_{sp}}{m}} \quad (2)$$

Above, I_{sp} is simply the specific impulse, Δh_{sp} is the change in specific enthalpy, and m is the mean molecular mass of the expelled gas. It is obvious from Eq. (2) that the lower molecular mass of the solid matrix results in a higher specific impulse. Therefore, this proportionality equation proves that a solid hydrogen matrix would be more effective than the heavier inert gas matrices [3].

In order to use this lighter, more combustible, molecule as a rocket fuel storage device, and prevent the recombination of the atomic propellant, the hydrogen must be formed and held at cryogenic temperatures. These sorts of temperatures are easily achieved in the laboratory setting by constantly inputting liquid helium into the cryostat chamber. At these cold temperatures, the hydrogen serves as a barrier to isolate the boron atoms, stabilize the atoms, and prevent vibrational motion. However, upon warming, the atom stability weakens, recombination occurs, and high thrust and acceleration is achieved. This process, in turn, warms the surrounding air and thus presents a problem in keeping the rest of the solid unreactive [2].

To combat this problem, fuel injection systems are being researched, tested, and developed. More information on the fuel injection designs can be found in [4] and [5]. With each of these designs, the fuel

system must compensate for all species formed within the solid matrix. This makes it necessary to use spectroscopic techniques to study those molecules.

An advantage of the solid hydrogen matrix is the innate softness of the atom. This property reduces the number of trapping sites for impurities, thereby allowing more space for the propellant atoms. The reduction of trapped impurities makes infrared spectroscopic outputs easier to analyze because the sharp bands displayed are only of the boron-hydrogen molecules. Since many of the impurities, particularly water and carbon dioxide, found within hydrogen are infrared active, the reduction is both necessary and beneficial.

Four types of spectroscopy can be used to analyze chemical species. These species can be detected in a solid hydrogen matrix by Raman, electron-spin resonance (ESR), Ultra-Violet/Visible (UV/Vis), and particularly, infrared (IR) spectroscopy [1]. Infrared spectroscopy recognizes the vibrating bonds of the species and thus displays an infrared spectrum particular to that certain molecule. In the mid-infrared region, the spectrum, or characteristic fingerprint, is caused by a permanent dipole in the molecule. If there is no permanent dipole, the species is rendered infrared inactive. The information gathered from these studies is later implemented into the design and construction of the fuel injection systems of rockets.

Background

In order to determine the spectrum of a variety of molecules, infrared spectroscopy is used. This method passes laser radiation through a sample and observes, via a detector, the fraction of radiation absorbed at a given frequency. Absorption of radiation is due to the vibrational frequencies of the molecule itself. In the mid-infrared region of the spectrum, the vibrational modes commonly observed are rotational and translational. If the molecules' vibrational frequency matches the radiations' frequency, the radiation is absorbed and is shown as a sharp peak on the spectrum output.

As discussed above, the frequency of vibrational modes gives rise to the molecule's absorption spectrum. However, the complexities of these spectra are explained by the coupling of vibrations over the large parts of the molecule. Also known as skeletal vibrations, these types form the pattern, the infrared spectrum, of the species [3]. While molecular vibrations establish the peaks of the spectrum, the molecular symmetry determines whether or not the molecule will be infrared active. Species of an asymmetric geometry will produce larger dipole moments and hence a sharper, more intense band than a symmetric molecule. Even though vibrations and symmetry are important, the masses of the atoms cannot be overlooked. The concept of reduced mass is of particular interest and can be described by the following equation:

$$\mu = \frac{m_1 m_2}{m_1 + m_2} \quad (3)$$

In Eq. (3), μ is the reduced mass, and m_1 and m_2 are the masses of the atoms respectively. Since this is a generalized formula, it provides only the reduced mass, μ , of two atoms of the molecule under study. Even

so, the reduced mass of the molecule allows for the frequency of the vibrational modes to be calculated. In particular, this frequency can be found using the formula:

$$\nu = \frac{1}{2\pi} \sqrt{k/\mu}, \quad (4)$$

where the frequency of absorption is represented as ν , k is a predetermined force constant, and μ is the reduced mass as calculated from Eq. (3). These absorption frequencies provide us with an idea of where a sharp band could be expected on the infrared spectrum output. As would be expected, the theoretical numbers are only a rough estimate as to where the bands will actually lie when experimentally determined using a spectrometer [3].

Infrared Spectrometer

In our experiment, a Fourier-transform infrared spectrometer (Bruker Model 113) was used to analyze the chemical species in solid hydrogen. This particular type of spectrometer uses a Michelson interferometer in order to collect and analyze the absorption spectra of the sample. The Michelson interferometer utilizes two perpendicular plane mirrors and a semi-reflecting film beamsplitter which bisects the plane of these two mirrors. The beamsplitter material chosen is one that is infrared inactive. A most common substance used when studying the mid-infrared region is germanium coated with a cesium iodide (CsI) substrate [3,6].

As can be gathered from the name, the beamsplitter splits the incoming monochromatic radiation beam into two beams of equal energy, typically half the energy of the initial. Each of these 50% beams is directed to one of the two perpendicular mirrors. However, one of the beams is subjected to an optical delay caused by a movable mirror within the interferometer. After one beam passes through the sample, and some radiation is absorbed, the two beams reflect back to the beamsplitter and recombine either with constructive or destructive interference. If the two beams are to recombine as constructive interference, then the optical delay is either zero or an integral number of wavelengths; otherwise, the delay is destructive. Ultimately, this transmitted beam emerges as a 90° angle and is detected [6]. The path of the beam, including its reflections to and from the sample, is shown below in Fig. 1.

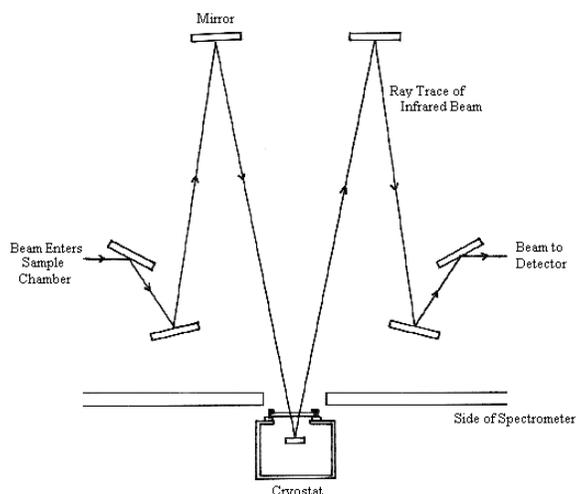


FIGURE 1: The path of the infrared beam (helium-neon laser), of a Globar spectrometer, is shown. Notice the number of reflections that the beam must take to get from the source, to the sample, and ultimately to the detector.

Typically two sorts of detectors are used to find the spectrum of a species trapped in a hydrogen matrix, either a DTGS (deuterium tryglycine sulphate) or an MCT (mercury cadmium telluride). The DGTS is a detector that works at room temperatures, but is far less sensitive than the MCT. However, for the MCT to work properly it must be cooled to liquid nitrogen temperatures.

At the detector, an interferogram is created which reads in analogue signal only. To be useful for data analysis, a Fourier transform occurs which converts the analogue signal into a digital signal. However, in order for this conversion to occur, a reference is needed. The reference comes from the data points collected when laser radiation passed through an interferometer and was subject to the same optical delay as the light being analyzed. The data collected from this reference laser is recorded and stored as an interferogram and is compared to the sample interferogram. So, for every two data points that are collected from the sample interferogram one cycle of the reference interferogram is needed. After a reference is established, the analogue signal is converted to a digital signal via an analogue to digital converter. Finally, a spectrogram is computed and could be displayed for visual reference.

Gas Handling System

A simple gas handling system was made in order to regulate the flow of hydrogen from the cylinder into the cryostat. Its also serves to eliminate some of the common impurities found in hydrogen, e.g. water and carbon dioxide. This device makes use of a 500ml volume to store small amounts of hydrogen at any time and a pressure gauge for safety purposes. Impurities are frozen out by a liquid nitrogen cooled, charcoal cold trap. Valves allow the user to control the flow of hydrogen into the cryostat. The general schematic of the gas handling system is shown below in Fig. 2.

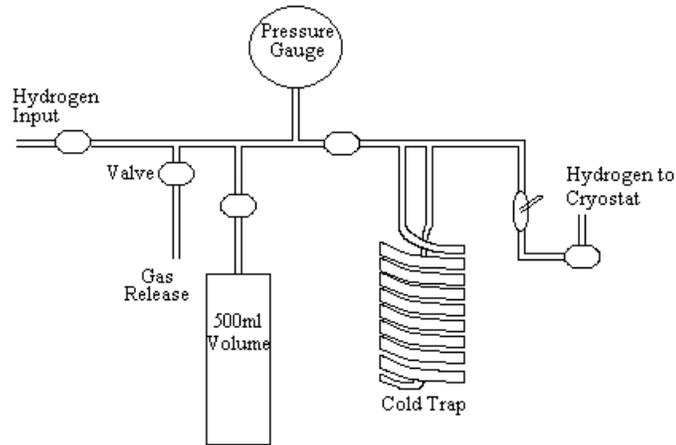


FIGURE 2: Schematic of the gas handling system designed and implemented in the experiment.

Cryostat

The cryostat that was developed for the experiment involves the use of both high vacuum technologies and cryogenics. According to Green et al. [7] “a high vacuum is required around the cold surfaces because all gases, except helium, will be condensed at the temperature” required to solidify hydrogen (pp.11). The cold surface which is supplied in the cryostat design is a polished aluminum plate. Upon this plate, the once gaseous hydrogen will solidify to form a solid hydrogen matrix. This matrix serves to isolate species, including impurities and the atomic propellants being studied, and prevent recombination of the atoms. A high vacuum, typically about 10^{-5} torr or better, upon the cryostat is a necessary feature because it eliminates the unnecessary gases that would simply contaminate the solid hydrogen matrix created.

The cryostat’s vacuum connection is attached to a rotatable cold finger as shown in Fig. 3. In other words, a length of metal extends down the center of the cryostat, upon which an aluminum plate is mounted. This novel idea allows for the aluminum plate to be rotated at any point during the experiment, even while under high vacuum. This deviance from original designs allows for the direct deposition of hydrogen and the ability to record a spectrum without moving the entire cryostat.

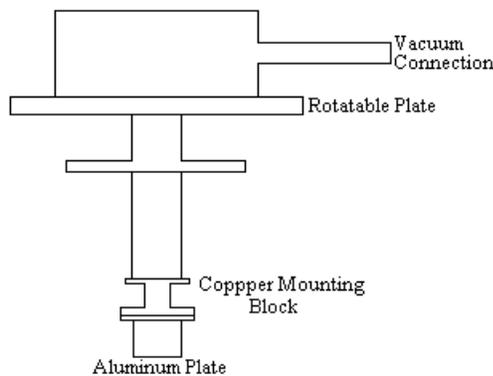


FIGURE 3: The cryostat interior with an aluminum plate extending into the cryostat chamber.

Even though the rotatable cold finger is an improvement to previous designs, the windows chosen to be mounted upon the evacuated shroud are just as important. The four windows in this design each serve different purposes, none of which is more vital than the other. Fig. 4 shows the cryostat chamber with the different windows.

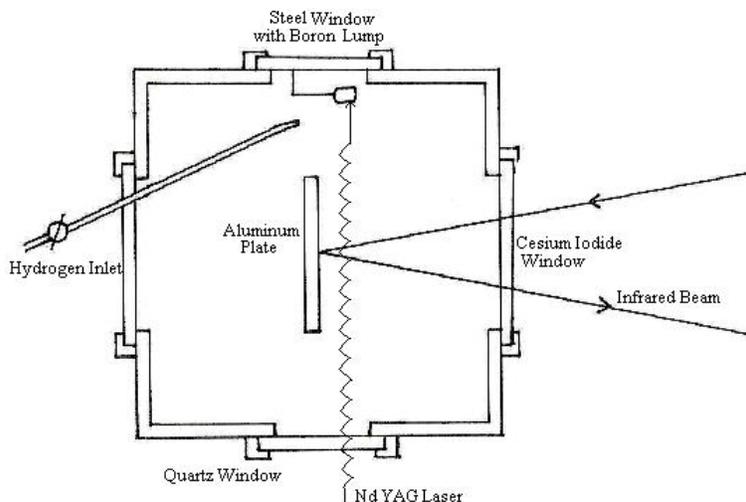


FIGURE 4: The cryostat chamber with each of the four windows labeled by the purpose they serve.

A cesium iodide window is used because it allows the infrared beam to pass through it unaffected. This substance is infrared inactive and therefore will have no effect on the spectrum of the sample. Cesium Iodide windows must be handled with care because the salt is very soluble and the slightest moisture could affect the window's performance. The steel window serves only one purpose, and that is to hold the boron sample in place while it is laser ablated with an NdYAG laser. The quartz window is utilized because it allows for the ablating laser beam to pass through relatively unaffected. Once the laser hits the boron, the boron will evaporate, mix with the gaseous hydrogen, and then settle upon the aluminum plate as a hydrogen matrix with trapped chemical species. The only other window of interest is the one in which a hydrogen gas inlet line is mounted. The windows' sole purpose is to hold the inlet line in place [7,8].

When all of these instruments, the spectrometer, cryostat, and gas handling system, work together the chamber is evacuated and cooled down to liquid helium temperatures. Purified hydrogen deposition may commence when the cryostat reaches cryogenic temperatures. After this process, the laser is used and evaporates a small portion of the boron lump within the chamber. The hydrogen and gaseous boron mix and deposit upon the aluminum cold finger. This matrix is then analyzed using the infrared spectrometer that was discussed above. Each of these instruments serves a different purpose, but each contributes an important factor to the overall success of the experiment.

Procedural Methods

As with any experiment, the set-up and procedure is just as important as the results acquired. In order to obtain a solid hydrogen matrix, the cryostat must be assembled with all of the windows in their correct places as mentioned and shown in Fig. 4. The cryostat must be arranged such that the cesium iodide window faces the spectrometer and that the boron lump and quartz window are opposite each other. The gas handling system could then be connected to the cryostat, via the hydrogen inlet line, with copper tubing. Once the windows are installed and the gas handling system connected, the apparatus could be tested for air leaks.

In this case, the best way to test for air leaks is to connect a vacuum pump to the cryostat and start pumping it down. If there is a leak within the system, the pressure will not decrease further than a certain value. If the cryostat seems to be leak proof, a diffusion pump could be used. The diffusion pump will allow for the system to reach the high vacuum needed. This sort of pump will certainly bring the cryostat pressure down to approximately 6.0×10^{-6} torr. Once the cryostat has reached the lowest pressure it is going to attain, liquid helium transfer could commence.

By transferring liquid helium to the cryostat, the temperature will be lowered to about 4.4 Kelvin. The temperature can be determined by a simple thermocoupler installed on the cold finger of the cryostat. Once the temperature has reached a minimum, as will be shown via the thermocouple output, a cold background spectrum could be taken and the hydrogen could be transferred into the cryostat. By taking a cold background spectrum, the spectrometers control software, OPUS, will eliminate any spectra identical to it when actually taking a sample spectrum. In other words, unnecessary frequency bands will be reduced dramatically, thus making sample spectra easier to analyze. If desired, a sample spectrum could be taken to verify that there is indeed nothing present on the aluminum plate or cesium iodide window that could affect the hydrogen matrix spectrum.

After the desired spectra have been taken, the hydrogen should be transferred into the cryostat. To assure that the hydrogen deposits upon the cold aluminum plate, the cryostat could be rotated to directly face the hydrogen injection line. Once the hydrogen has been deposited, the plate is rotated towards the infrared beam to verify that it is indeed aligned correctly. The OPUS align mode is used to check for maximum alignment. If desired, a spectrum could be taken of the hydrogen matrix, and the impurities caught within it, typically water and carbon dioxide, could be seen through the spectrum output.

A NdYAG laser could then be set up to go through the quartz window and should be aimed directly at the boron lump. Once the laser is turned on, the boron will be ablated and will mix with the gaseous hydrogen. In the process, the two species will interact and deposit upon the aluminum cold finger. Again, using the spectrometer, the species formed could be analyzed via the spectra obtained.

Data Analysis and Results

A major concern in the experiment was whether or not solid hydrogen could be formed in the cryostat. The cryostat, vacuum apparatus, and gas handling system were connected and the experiment was started. Once the apparatus was under high vacuum and the cryostat had been cooled with liquid helium, hydrogen was transferred into the system. The major difference from the procedure used in the laboratory and the one described above is that the cold trap was not used.

Allowing impurities to remain in the hydrogen made it much easier to determine whether or not hydrogen solidified and deposited upon the aluminum plate. If the hydrogen had not deposited, then the spectra of both carbon dioxide and water would be minimal. However, we observed just the opposite results. Table I shows the pressure of hydrogen injected into the cryostat during different time intervals for a multitude of trials.

TABLE I. Pressures of hydrogen injected with their corresponding time intervals.

Trial Number	Pressure Injected (psi)	Time Interval (minutes)	Trial Number	Pressure Injected (psi)	Time Interval (minutes)
1	14	5	8	13	9
2	13.2	10	9	12.25	10
3	12	15	10	10	11
4	9.2	7	11	11.25	10
5	8	4	12	10.5	8
6	12	8	13	8	7
7	13	8			

With a simple application of the ideal gas law, it can be shown that similar quantities of hydrogen were injected into the cryostat during each trial. After each deposition of hydrogen, a spectrum was taken. In most cases, the impurities of carbon dioxide and water were readily visible on the output. Since the spectra are graphed in terms of absorbance units versus wavenumber, measured in units of cm^{-1} , bands will be expressed in terms of wavenumber. For the common impurities, two bands are found and are due to different vibrational modes within the molecule.

However, one of the first dominant features seen in the spectrum of the solid hydrogen matrix, with impurities, was the drastic drop of water vapor within the cryostat. This water vapor is shown in Fig.5 as the cluster of downward lines around both 3600 cm^{-1} and 1600 cm^{-1} . One of the more obvious impurities found in the spectrum shown in Fig. 5 was the trapped water molecule bands. Published wavenumbers for water molecules are 1630 cm^{-1} and 3765 cm^{-1} and thus correspond well with the spectrum achieved [8]. The water bands, on the spectrum, are the upward lines at those approximate values. These water bands can be identified rather easily in all the spectra taken.

Another common impurity found within the solid hydrogen matrix is carbon dioxide. In the attached Fig. 6, two carbon dioxide bands are readily visible very near the published wavenumbers of 667 cm^{-1} and 2349 cm^{-1} [8]. The sharpness of these bands, especially the one occurring at 2349 cm^{-1} , is due to the amount of hydrogen that was deposited upon the aluminum. The more hydrogen that was deposited, the more carbon dioxide impurity observed.

Fig. 7, which not only shows short bands of the water and carbon dioxide molecules, but also displays an overall downward trend. This trend in the spectrum is because of the increased thickness of hydrogen solid upon the cold finger. As the thickness increases, the slope of this line becomes steeper because the infrared beam has to burrow further, taking more time, before reflecting back to the detector. Fig. 8, shows carbon dioxide and water bands, but it also shows a small carbon 13 band just on the right shoulder of the carbon dioxide band at 2349 cm^{-1} . The height of this band is small because it is band is due to the small natural abundance of carbon 13 in the environment. Another feature present on this spectrum is a large humplike line at approximately wavenumber 3400. This hump is due to the presence of ice forming on the aluminum plate. Published data verify this estimated number as indeed ice.

Finally, as shown in Fig. 9, all features discussed are shown, except for the downward slope. Both of the water and carbon dioxide bands are present, as would be expected. A small, but noticeable band reveals that some carbon 13 is trapped within the hydrogen matrix. This spectrum even shows the formation of ice due to the extreme temperatures within the cryostat.

Solid hydrogen formed upon the cold aluminum plate even when the impurities were not removed. This simply made it easier to determine that trapping species within a solid hydrogen matrix is possible at 4 Kelvin. Time constraints and equipment failure did not allow for much analysis of boron to take place. The boron chunk was mounted within the cryostat and was prepared to be laser ablated. Once the laser evaporated a small portion of the boron, the boron and the hydrogen would theoretically mix and deposit upon the cold finger. During this process, boron-hydrogen molecules would be formed and trapped in the solid hydrogen matrix along with individual boron atoms.

Even though the analysis of boron species never was fully studied in our laboratory, at this point it has been found that a multitude of molecules can be trapped within the solid hydrogen matrix. The molecules that have formed between boron and hydrogen at high temperatures and studied using infrared spectroscopy studies include BH, BH₃, BH₄, and B₂H₆. Other species include ones in which the boron reacted with an impurity such as nitrogen or oxygen. Once again, other experiments show that common impurity molecules formed include BO, HBO, HOBO, OBOB, BO₂, and B₂N [8]. Table II shows possible boron species formed and trapped within a solid hydrogen matrix and their corresponding wavenumber bands.

TABLE II. Boron species and corresponding wavenumbers.

Boron Species	Wavenumber	Boron Species	Wavenumber
BH	2259	HBO	1822 and 757
BH ₃	1129	HOBO	2023
BH ₄	2115 and 2168	OBOB	2048
B ₂ H ₆	1598 and 2608	BO ₂	1247
BO	1854	B ₂ N	882

An interesting process occurs when the boron atom is isolated within the solid hydrogen matrix and does not form any molecule. When this process occurs, it means that upon warming the boron atoms will be allowed to recombine and produce energy. This sort of experiment can be done using the techniques described above and comparing the bands of the species trapped within the matrix. However, we expect that most molecular forms of boron and hydrogen will be inhibited at low temperatures.

Conclusion

A solid hydrogen matrix could be used to trap a variety of chemical species. It was shown that solid hydrogen was achieved at temperatures of 4.4 Kelvin within the cryostat. The water and carbon dioxide spectra were observed using infrared technology. This simply proves that a layer of hydrogen had isolated a chemical species. Since chemical species' isolation is possible, further isolation studies could commence. These studies include laser ablating a boron lump, allowing it to mix with gaseous hydrogen, and depositing it upon a cold finger. The variety of molecules formed and trapped in a solid hydrogen matrix need to be measured.

Infrared spectrometry allows these species to be individually analyzed. From the spectra, the relative amounts of each species trapped can be determined. If there is enough atomic boron isolated, then storage of atomic propellants for rockets can be improved using the cryogenic technologies. When and if there is enough isolated boron, warming of the sample will cause recombination and hence a large amount energy. This sort of storage not only decreases the amount of space necessary, but also allows for higher specific impulses. Further studies could be carried out to determine just how much the specific impulse increases and the benefits it holds for future densified propellants.

Acknowledgements

First, I would like to thank the University of Florida and the National Science Foundation for funding the research done this summer. Without them, this project would have never been. I would also like to thank Dr. Kevin Ingersent and Dr. Alan Dorsey for their support and recognition of the REU physics program. I thank various members of the Ihas Research Group and the Physic Department Shops for their support. This includes both Nathan Heston and Greg Labbe. Finally, I would like to thank my mentor Dr. Gary Ihas and the post-doctoral associate John Graham for their continued help and involvement throughout this entire project.

References

- [1] J. T. Graham (private communication).
- [2] M.E. Fajardo, S.Tam, T.L. Thompson, and M.E. Cordonnier, "Spectroscopy and Reactive Dynamics of Atoms Trapped in Molecular Hydrogen Matrices" *Chemical Physics*. **189**, 351-365 (1994).
- [3] B. Stuart, in *Modern Infrared Spectroscopy*, edited by David J. Ando (University of Greenwich, London, England, 1996), pp. 1-13, 24-28.
- [4] B. Palaszewski, presented for NASA, Lewis Research Center, Cleveland, Ohio, 1998 (unpublished).
- [5] B. Palaszewski, L.S. Ianovski, and P.C. Carrick, "Propellant Technologies: Far-reaching Benefits for Aeronautical and Space-Vehicle Propulsion," *Journal of Propulsion and Power*. **14**, 641-647 (1998).
- [6] Patrick Hendra, in *Fourier Transform Raman Spectroscopy*, edited by Catherine Jones and Gavin Warnes, (University of South Hampton, England, 1991), pp. 21, 29, 80-86.
- [7] D.W. Green and G.T. Reedy, in *Fourier Transform Infrared Spectroscopy*, (Academic Press, Inc., New York, 1978), Vol. 1, Chap. 1, pp. 11-14, 19-20.
- [8] Thomas J. Tague. Jr. and Lester Andrews, "Reactions of Pulsed-Laser Evaporated Boron Atoms with Hydrogen. Infrared Spectra of Boron Hydride Intermediate Species in Solid Argon," *J. Am. Chem. Soc.* **116**, 4970-4976 (1994).

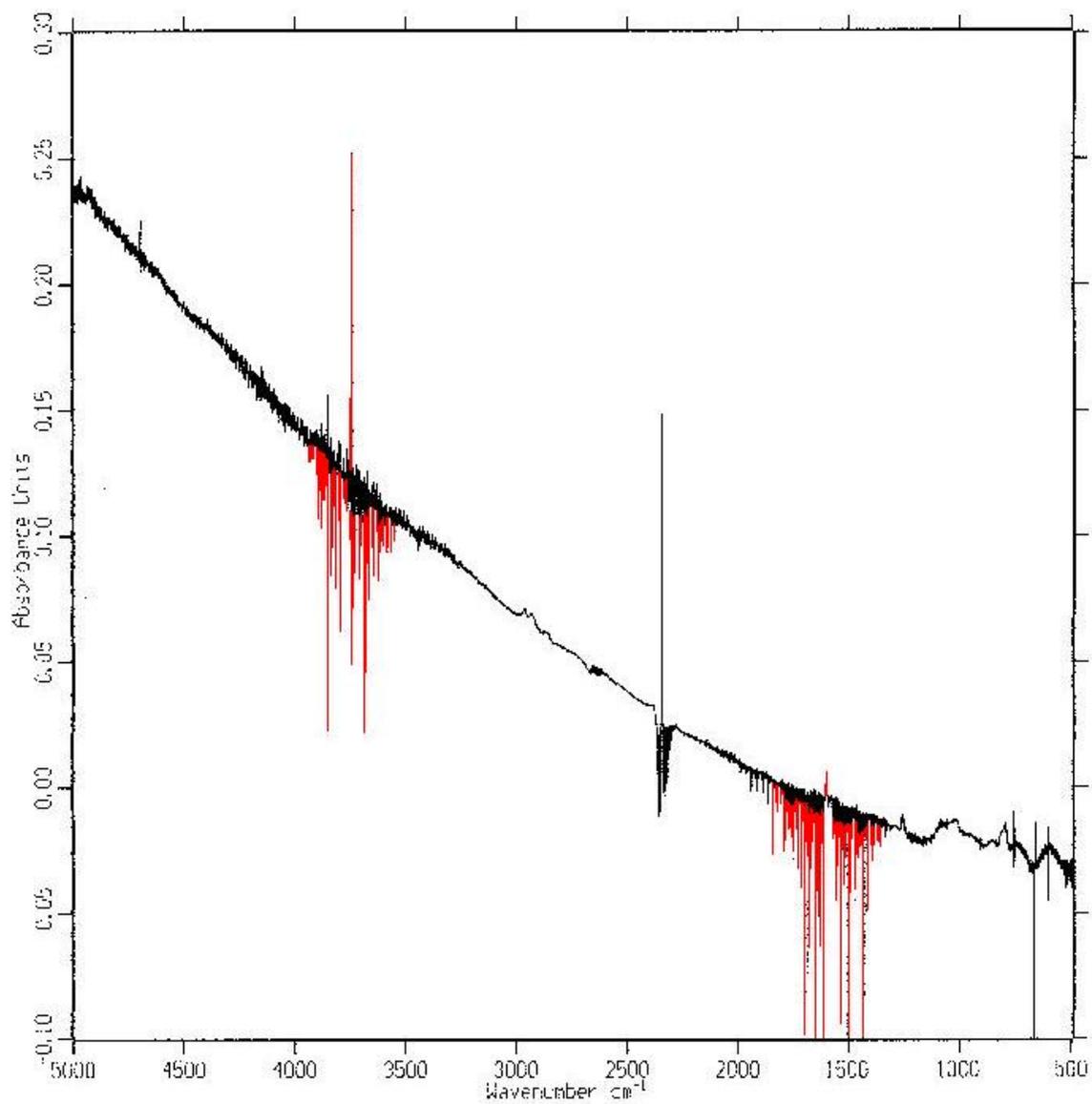


Figure 5: Shows the dropping of water vapor within the cryostat and the two bands associated with trapped water molecules.

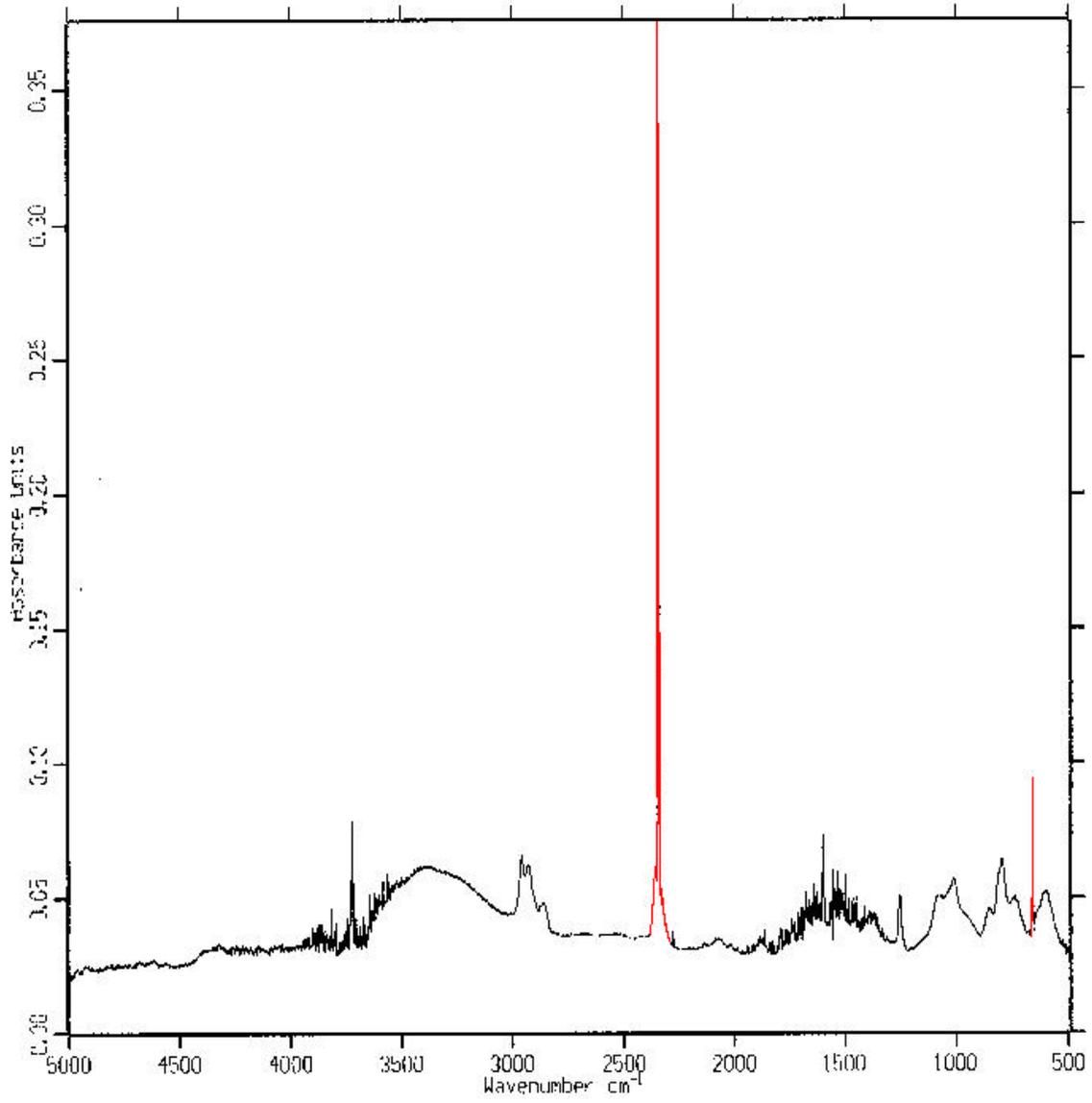


Figure 6: The bands of the carbon dioxide trapped in a solid hydrogen matrix.

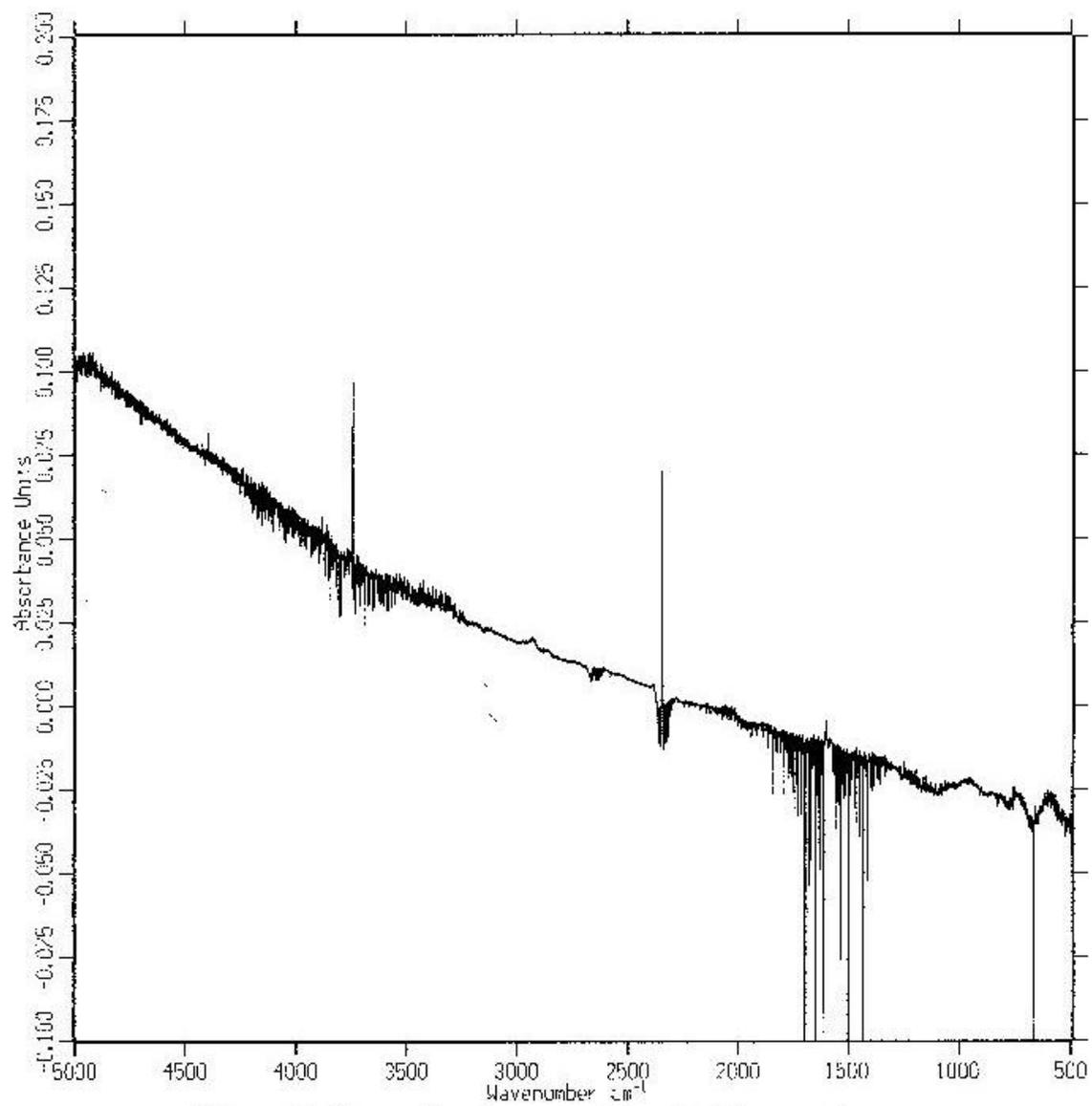


Figure 7: Shows the downward trend of the spectrum as more solid is deposited.

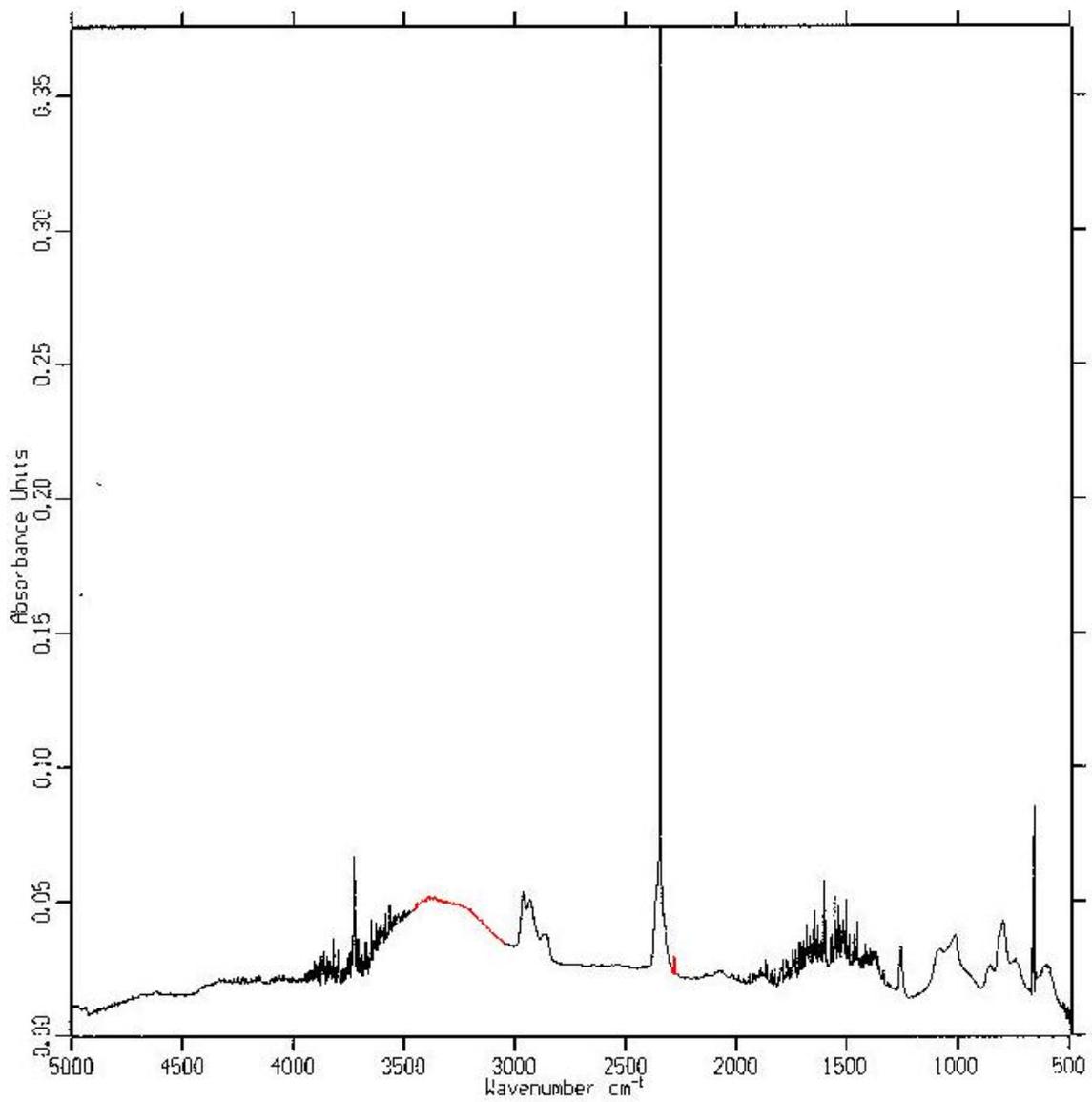


Figure 8: This spectrum shows a C13 band and ice formation.

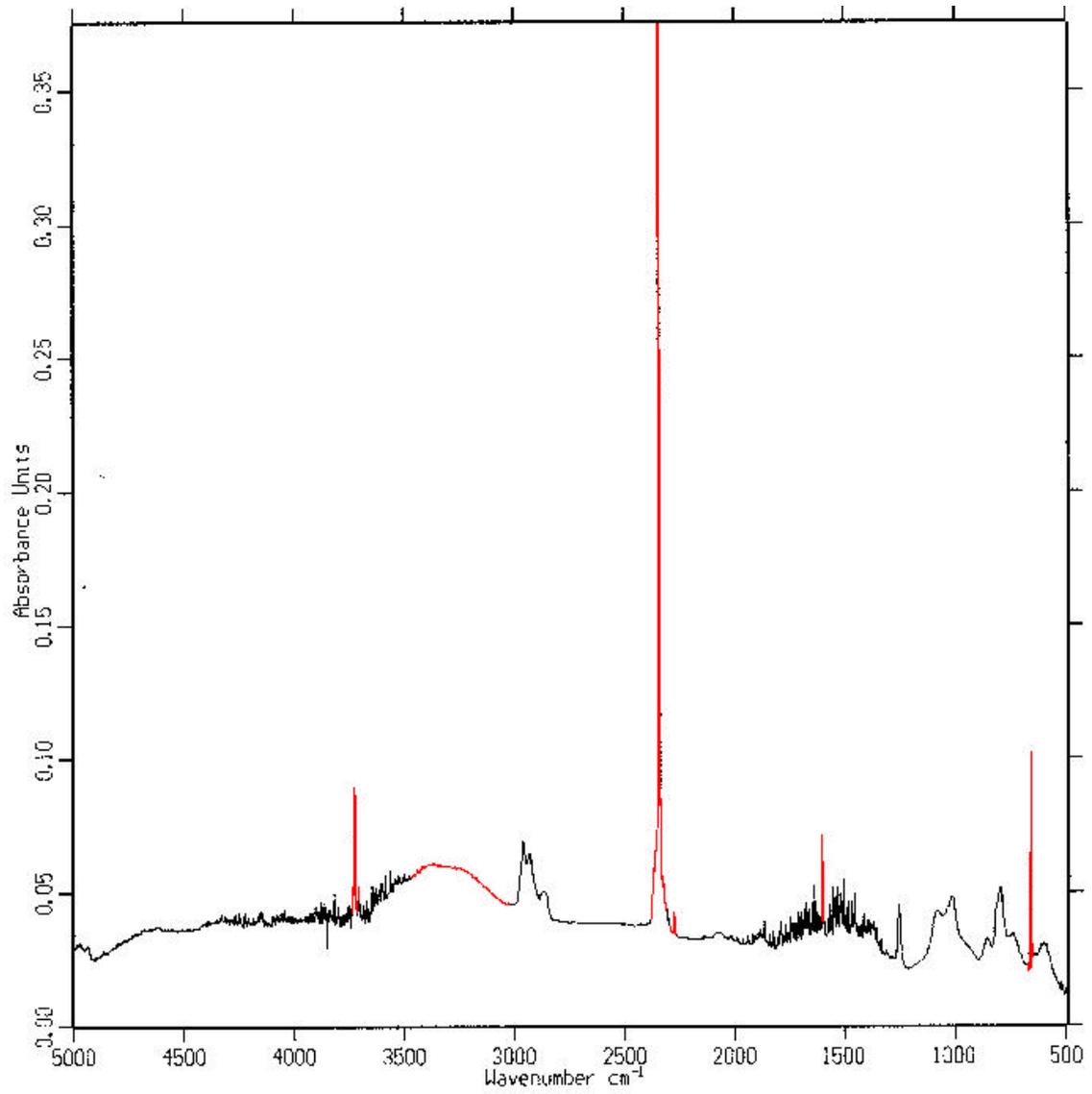


Figure 9: Shows both carbon dioxide bands, both water bands, a C13 band, and ice formation.