

Surface-Atmosphere Interactions with Ultraviolet Light on Mars

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A senior thesis submitted to the faculty of
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Bachelor of Science

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ABSTRACT

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The Labeled Release experiment of the Viking landers led to the hypothesis that martian soil is highly oxidized. Hydrogen peroxide has been suggested as the primary oxidant, but no definitive theory exists as to how it forms in the martian environment. We propose that ultraviolet radiation interacts with carbon dioxide, water, and other trace substances in the martian atmosphere to form this hydrogen peroxide. We tested this theory by constructing a Mars-like atmosphere within a vacuum system and then exposing it to ultraviolet radiation from a UV lamp. The resulting products were then collected into a cold trap and analyzed by a mass spectrometer. Initial results do seem to indicate that hydrogen peroxide was generated by the interaction, as well as other substances. If correct, this data further expands our knowledge of the martian environment and explains why no martian organics have been discovered thus far.

Keywords: Mars, Peroxide, Carbon Dioxide, Ultraviolet, Photolysis

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Chapter 1

Introduction

1.1 Introduction

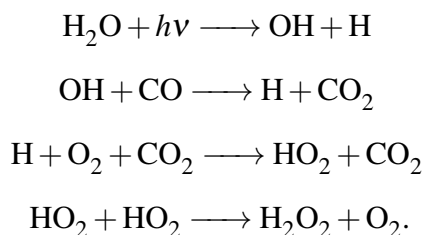
Compared to Earth, the planet Mars is hostile: its surface temperature is 60 K lower than that of Earth's, and its atmosphere (comprised mainly of unbreathable carbon dioxide) is approximately one-one hundredth the density of our planet's, leaving the martian surface extremely vulnerable to cosmic radiation (Encrenaz et al. 2012). Much of what we know about Mars came from the Viking lander mission, which touched down on the martian surface in 1976, but the mission also raised many questions, some of which are still unanswered. Specifically, the Viking Landers' Labeled Release (LR) Experiment indicated that the martian soil was highly reactive; one hypothesis posits that it was oxidized by hydrogen peroxide, but there isn't a consensus as to how martian hydrogen peroxide might be formed. We propose that hydrogen peroxide is formed through the photolysis of carbon dioxide and water vapor, caused by solar radiation.

1.2 The Labeled Release Experiment

The Labeled Release Experiment was one of four experiments included on the Viking Landers to fulfill their objective to search for life on Mars. It was the only test to return a positive result, which is one reason why its results are still being discussed to this day. In the experiment, water was filled with nutrients that were tagged with radioactive ^{14}C , and this mixture was then added to a sample of martian soil. A radiation detector was placed in the sample chamber to look for released ^{14}C . The proposed hypothesis posited that, if there were organisms in the soil, they would metabolize the nutrients and then expel radioactive carbon dioxide, which would be registered by the detector.

1.3 UV oxidation

When the LR experiment was originally performed, it returned a positive result, which suggested organic life might have been present in the sample. When the results from the other three tests came back negative, though, this theory was largely abandoned, and scientists looked for new theories to explain the LR positive. One prevailing theory is that the soil was oxidized by some agent, which caused a violent reaction in which the nutrients and water were ripped apart and then recombined into radioactive CO_2 . For this hypothesis to be valid, an oxidizer is required; many researchers have suggested hydrogen peroxide as this primary oxidizer. There are numerous explanations as to how hydrogen peroxide may be formed on Mars (as can be seen in the Literature Review); we are concerned with H_2O_2 production through photolysis. T. Encrenaz et al. (2004) supported this theory with the following chemical model:



In short, ultraviolet radiation breaks apart water vapor, and the resulting products combine with carbon dioxide and carbon monoxide to eventually form hydrogen peroxide. Our research aims to recreate this process by means of a vacuum system; though our results are preliminary, we saw that some hydrogen peroxide does appear to be produced by these interactions.

1.4 Literature Review

As noted above, other explanations have been proposed for the LR results and/or for how hydrogen peroxide is formed on Mars. Ponnampetuma et al. (1977) hypothesized that the release of the labeled CO_2 in the LR experiment was due to the formation of H_2O_2 from irradiated hematite (Fe_2O_3). Though the presence of martian hydrogen peroxide had not yet been confirmed, they noted that "the possibility of H_2O_2 on the surface of Mars should not be discounted." The presence of H_2O_2 on Mars was not confirmed until it was detected by Clancy, Sandor and Moriarty-Schieven in 2004 (Clancy et al. 2004). Taking a slightly different approach, Atreya et al. propose that H_2O_2 (and other oxidants) may be formed by electrostatic fields emerging from dust devils on the surface (Atreya et al. 2006).

(Here we should note that hydrogen peroxide is not universally accepted as the primary surface oxidant; Bullock et al. (1994) argue that HO_2 is too unstable to have undergone the thermal processes of the LR experiment and produced the same results.)

1.5 Previous Research at BYU

Though others have conducted Mars-related research at BYU (especially in association with the University Rover Competition Capstone team from the College of Engineering), this project is the first of its kind and has no antecedent here at the university. Dr. David Allred came up with the idea for this project through his ongoing interest and personal research into martian astrobiology and through conversations with Dr. P. Douglas Archer, a BYU alumnus currently conducting Mars research in the Astromaterials Research and Exploration Science (ARES) Division of NASA.

1.6 Thesis Overview

The aim of this thesis is to determine if hydrogen peroxide is formed by exposing a simulated martian atmosphere to ultraviolet radiation. To do so, the experimental apparatus is described, as well as the process of conducting the experiment and collecting and analyzing the results. The results (a noticeable increase in hydrogen peroxide and other products) are presented and discussed, and we conclude that this model could be representative of what happens on Mars. Further research to be done is then described for future group members to carry out.

Chapter 2

Methods

2.1 Overview

The overall aim of the experiment is to create a Mars-like atmosphere in which we can study the interaction between UV light and other substances. This was achieved by means of a vacuum system; we pumped the system down to low pressures, introduced certain elements to create the analog environment, exposed these elements to ultraviolet radiation, and collected the products for later analysis with a mass spectrometer.

2.2 Apparatus

In order to clearly outline the construction and operation of the apparatus, we refer to its four "branches," corresponding to the cardinal directions (North, South, East, and West) (See Fig. 2.1). The reference point is a four-way VCR junction where the four branches meet; each branch is described starting with the "outer" extremity and then moving in to this central reference point.

The West branch is used for pumping the system down to low pressure and for storing and

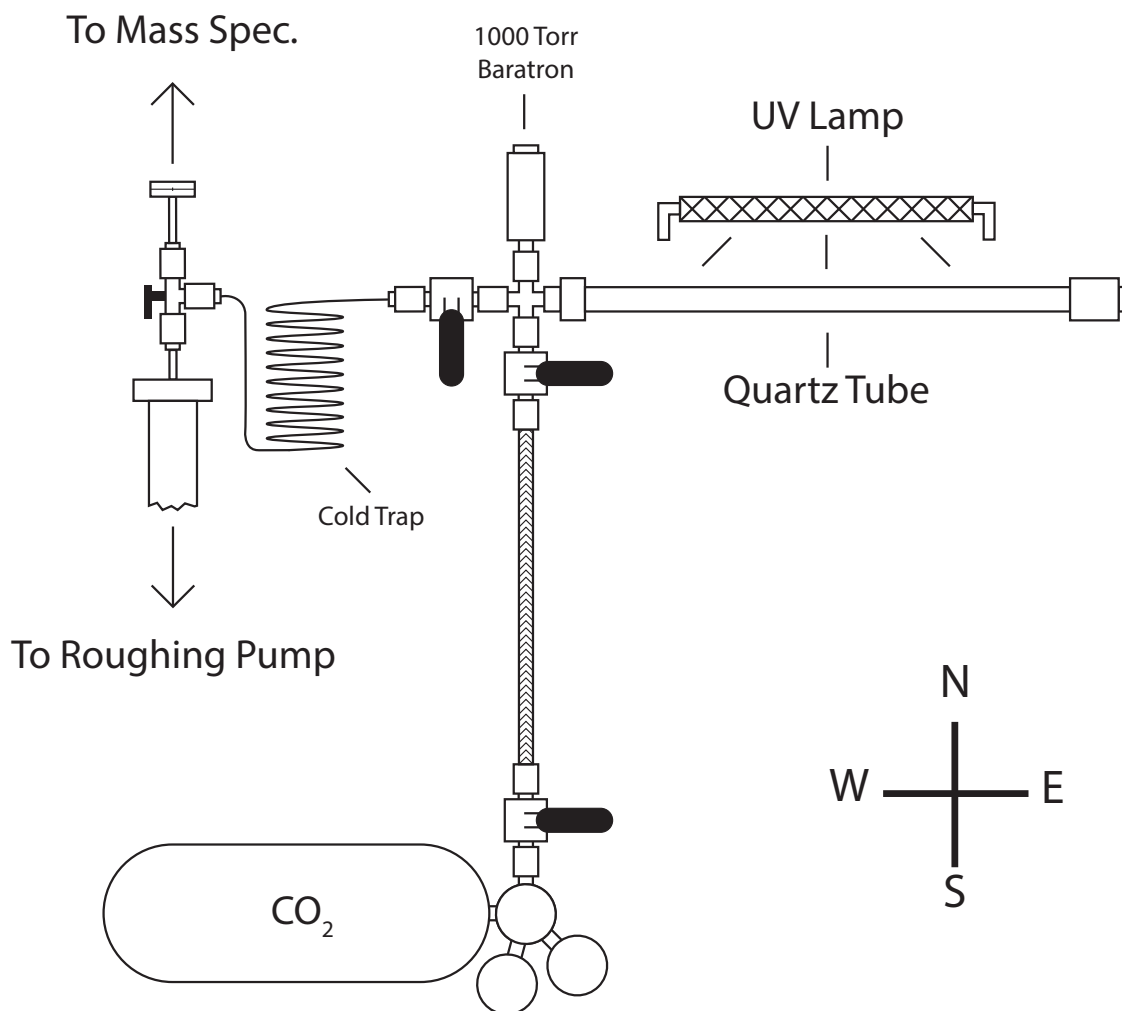


Figure 2.1 A schematic of the experimental apparatus used to replicate the martian atmosphere, simplified in order to highlight the most important features. A compass rose is included in order to demarcate the different "branches" of the apparatus in respect to the central four-way VCR junction.

analyzing the final products of the experiment. It begins with an adjustable three-way VCR junction ("T-valve") that can be used to connect the rest of the system to the roughing pump or the mass spectrometer, or to isolate the system from either. The common arm of the junction leads to a length of steel tubing wrapped into a coil; in conjunction with a dewar of liquid nitrogen, this tubing functions as the cold trap where the products of the experiment are collected. A cutoff valve connects the cold trap to the apparatus's central junction.

The North branch of the apparatus is solely used to measure the pressure inside the system, and so its design is the simplest; it consists solely of a 1000 Torr baratron that connects directly to the central junction, used to monitor the overall pressure of the system.

The East branch is where the simulated martian environment is created, and thus where most of the experiment takes place. It begins with a two-way compression union, plugged on one end with a steel plug. The other end is affixed to the end of a supracil quartz tube that runs through the plastic casing of an excimer UV lamp; for our purposes, this quartz tube represents the martian atmosphere. The other end of the tube is connected to the central junction with a compression-VCR union.

The role of the South branch is to deliver carbon dioxide to the rest of the system. The branch begins with a canister of CO₂ gas and a regulator. The regulator connects to a system of two check valves, with a flexible gas line in between (the two valves allow for greater control when introducing the carbon dioxide to the system at large). The second of these valves connects to the central junction.

2.3 Procedure

The first step in the experimental procedure is to create an environment similar to the martian atmosphere within the vacuum system. All valves are moved to their "open" position and the T-valve

is positioned so that the roughing pump is connected to the system. The roughing pump is then activated and allowed to run until the pressure readout from the baratron is 0.0 ± 0.1 Torr. Once this threshold is reached, the T-valve is moved into its middle position, sealing the system off from the pump while maintaining the vacuum. At this point, atmosphere begins to leak in, but the leakup rate is slow enough (approximately 0.25 Torr/minute) that it generally does not contaminate our results. In fact, it is preferable to have some water vapor enter the system through leakup, as we have not yet devised a way to add water to our gas mixture.

With most of the normal atmosphere removed, we now attempt to re-create the martian atmosphere, which is approximately one one-hundredth as dense as Earth's and comprised almost entirely (~95%) of carbon dioxide. The cutoff valve on the West branch is moved to its closed position, as is the valve closest to the CO₂ regulator. The regulator is briefly opened to allow some carbon dioxide to enter the line, then the canister is sealed off again. Carbon dioxide is introduced into the system gradually by slowly opening the valve closest to the regulator; the valve remains open until the pressure measured by the baratron is in the range of 10-25 Torr, at which point both valves in the South branch are closed to prevent more CO₂ from increasing the pressure.

With the substitute atmosphere in place, the next step is to simulate interactions between the atmosphere and ultraviolet radiation from the sun. This is achieved by running a constant air supply through our excimer lamp (to prevent overheating) and then switching the lamp on and allowing it to run for approximately thirty minutes. When that time elapses, the lamp and the air supply are turned off. The cold trap is then prepared by immersing the steel tubing in a dewar of liquid nitrogen. When the trap is in place, the West branch cutoff valve is re-opened, allowing the radiation-exposed gases to flood into the cold trap and condense on its walls. After waiting a few minutes, the cutoff valve is closed again and the T-valve is repositioned so that the cold trap is connected to the roughing pump once more. After pumping out excess gas, the T-valve is re-closed and the roughing pump shut off, leaving the condensed products of the experiment contained in the cold trap.

2.4 Acquisition

The first step in the acquisition phase is to disconnect the cold trap from the rest of the system. Unfortunately, with the current iteration of our system design, disconnecting the cold trap involves dismantling a large section of the apparatus. To free the cold trap, the T-valve is disconnected from the KF-50 coupling that attaches it to the roughing pump, and the VCR coupling that attaches the West branch valve to the central junction is undone, taking care not to accidentally move the valve into the "open" position and release the product into the open air. Since the VCR system uses disposable gaskets between joints, the system must be resealed and checked for leaks and the systems' new leakup rate must be measured every time new data is collected.

With the cold trap decoupled from the system, it is then attached to the mass spectrometer using a non-rotatable conflat flange fitting. With the trap in place, the mass spectrometer is prepared by pumping out the spectrometer chamber and activating the filament. With the mass spectrometer prepped, the next step is to introduce the products and read in data. The mass spectrometer connects to a computer, which interfaces with the equipment and reads out the results.

The computer software can characterize the results in a variety of ways; of primary concern are its bar graph and line graph functions (see Fig. 3.1 and Fig. 3.3 for examples of the bar graph and line graph, respectively). For the bar graph, the software analyzes the interior of the mass spectrometer for one complete cycle before introducing any of the products are introduced; this provides a baseline measurement for the pressures of the substances present in the spectrometer, which are captured via screenshot. After the baseline is obtained, the T-valve is opened (briefly) to the mass spectrometer, letting a small portion of the products enter. The bar graph on screen changes slowly as the spectrometer sweeps over different molecular masses, and another screenshot is captured to show the change from the baseline once the spectrometer has completed one whole sweep. For the line graph, a baseline is established more quickly; the spectrometer only needs to analyze the "empty" chamber for a few seconds before the products can be introduced. The line

graph then traces out the pressure of each molecular weight over time, providing more information as to how the pressure of each compound changes over time. The drawback of using the line graph is that it can only track a handful of molecular weights at a time, whereas the bar graph shows us the full range (from mass 1 to mass 50).

Chapter 3

Results and Conclusions

3.1 Results

Preliminary results appear to indicate that hydrogen peroxide has been created by our process. As seen on the bar graphs (See Fig. 3.1 and Fig. 3.2), hydrogen peroxide (mass 34 on the graph's scale) increases in pressure by approximately 1.5×10^{-10} Torr. We see a similar bump in our line graph (Fig. 3.3) when we introduce the experimental products at approximately T=30 seconds; the average pressure increases from approximately 3.0×10^{-10} Torr to approximately 6.0×10^{-10} Torr. The discrepancy in pressure changes (between the line graphs and the bar graphs) is due to differences in how long the T-valve was kept open when exposing the products in the cold trap to the mass spectrometer.

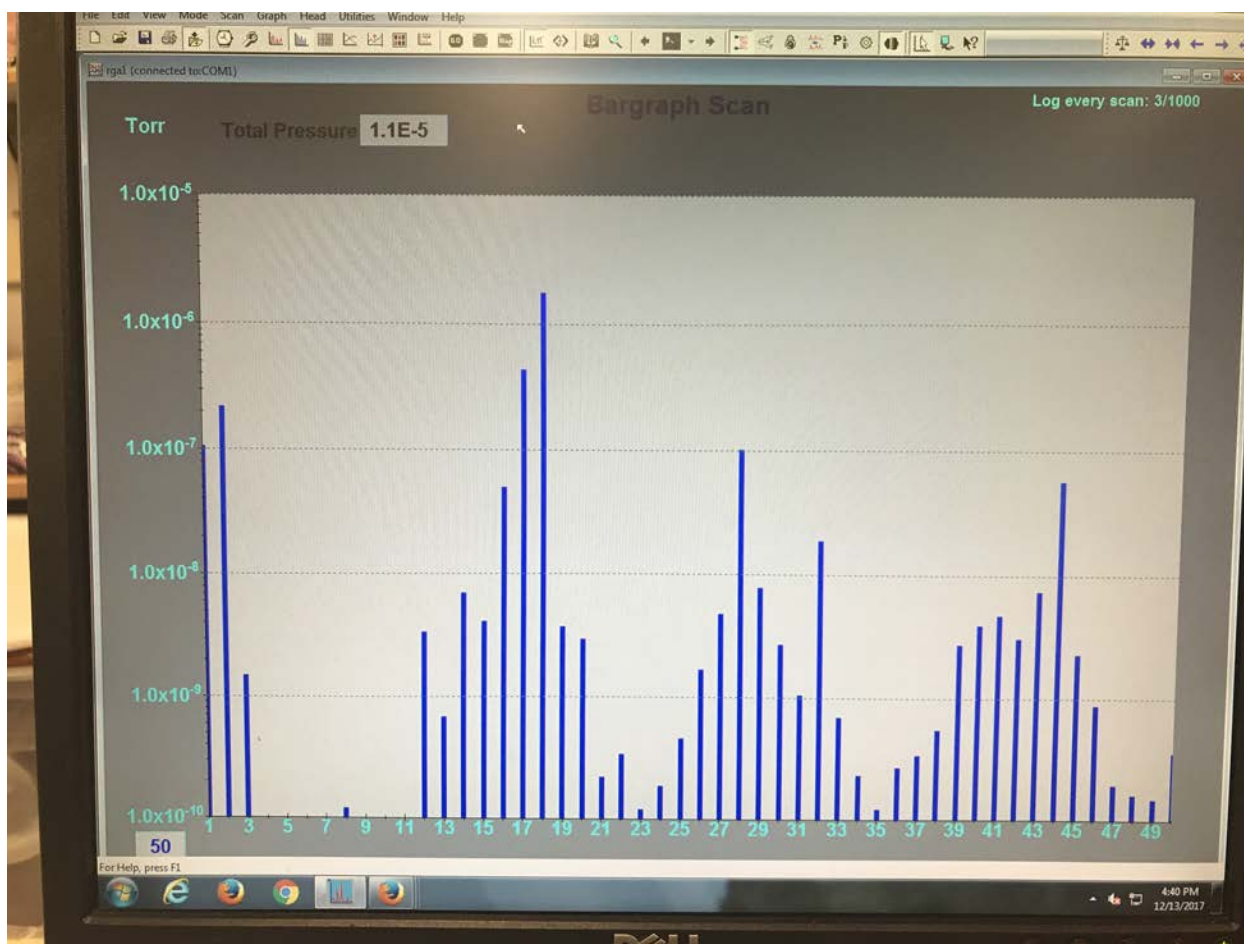


Figure 3.1 A bar graph of the pressures different molecular compositions inside the mass spectrometer prior to the introduction of our experimental products. Note that the pressure scale on the left is logarithmic. The pressure of hydrogen peroxide (mass 34) is approximately 1.5×10^{-10} Torr.

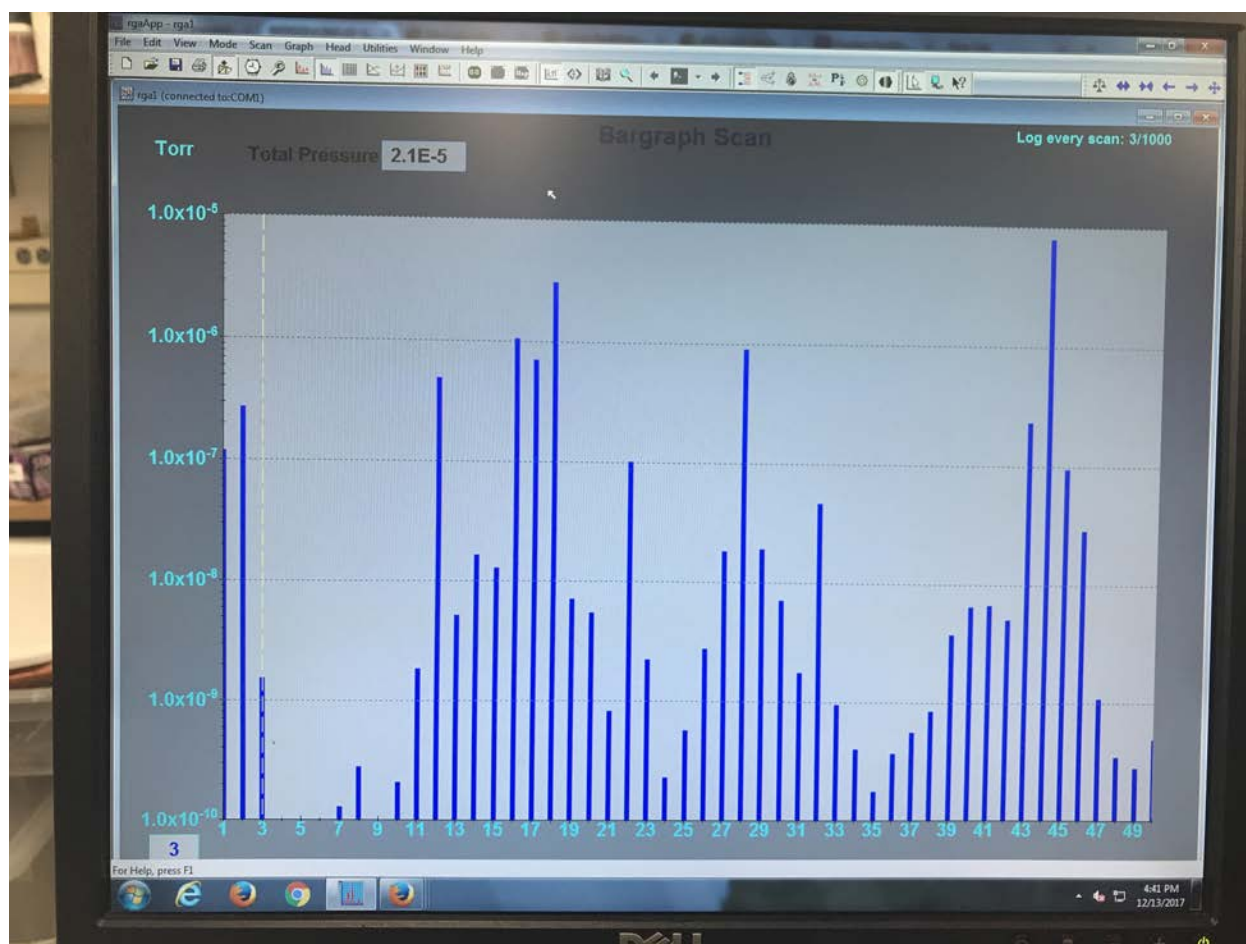


Figure 3.2 A bar graph of the pressures different molecular compositions inside the mass spectrometer after the introduction of our experimental products. The pressure of most compositions is increased; in particular, the pressure of hydrogen peroxide is now approximately 3.0×10^{-10} Torr.

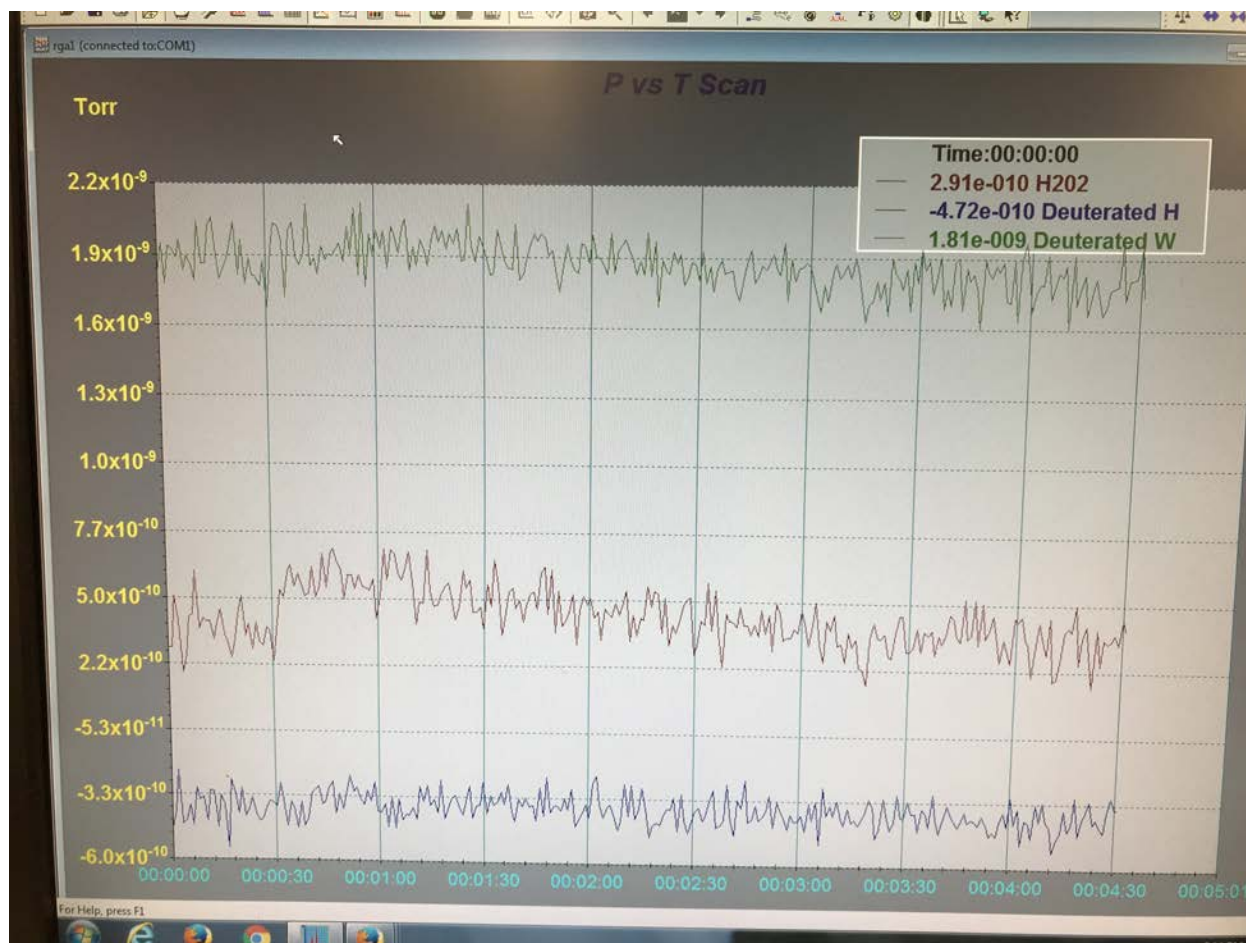


Figure 3.3 A line graph depicting the changes in the molecular pressures of hydrogen peroxide (H_2O_2), deuterated hydrogen (^2H), and deuterated water ($^2\text{H}_2\text{O}$). The experimental products were introduced into the mass spectrometer at approximately $T=30$ seconds.

3.2 Discussion

As can be seen from the graphs, the change in pressure of the various molecular compositions in the spectrometer differs from mass to mass. As noted, by looking at the bar graphs (Fig. 3.1 and Fig. 3.2), we see an increase in hydrogen peroxide pressure of approximately 3.0×10^{-10} Torr. This is a small change compared to that seen in mass 28 and mass 44; the former increases by an order of magnitude (ten times the original pressure), while the latter nearly achieves an increase of two orders of magnitude (one hundred times the original pressure). On the other end, mass 2 (which we believe to be deuterated hydrogen, ^2H) doesn't seem to experience any change at all between Figure 3.1 and Figure 3.2; this is confirmed by the line graph in Figure 3.3, which shows no apparent change in the average pressure after the products are introduced at $T=30$ seconds.

3.3 Conclusions

Based on the results, we can conclude that our experiment produced some amount of hydrogen peroxide (unfortunately, the data acquisition program crashed when we tried to extract the exact numbers, so our results aren't exactly quantifiable). As other molecular compositions experienced changes in different orders of magnitude from hydrogen peroxide, we can conclude that they were also created by the experiment (and that the increase in hydrogen peroxide isn't merely a trivial increase in pressure from just exposing the mass spectrometer to our carbon dioxide/air mix). Though we don't know the exact molecular compositions associated with some of these masses (such as mass 12), we may be able to deduce them through further research.

As exposing a Mars-like atmosphere to ultraviolet radiation has produced hydrogen peroxide, we conclude that this model is at least viable in describing how martian hydrogen peroxide could

exist (and, by extension, how the martian soil became reactive).

3.4 Further Research

Now that we have successfully built our apparatus and carried out the experiment, our future research will focus on increasing the fidelity of our process, taking steps to improve the emulation of the martian atmosphere. The first goal will be to introduce non-trace amounts of water into the system before activating the excimer lamp. If we have created hydrogen peroxide through water photolysis, then increasing the amount of initial water should increase the amount of hydrogen peroxide in the product we collect in the cold trap. We could add this water in by installing a leakup valve near the glass tube and letting water evaporate into it.

After introducing water to the system, the next step will be to introduce a stand-in for the martian soil. We could then run the experiment in full and see if the interactions between ultraviolet radiation and our "martian atmosphere" actually produce enough hydrogen peroxide to oxidize the soil. We have a sample of martian regolith simulant, which is earthly soil that has similar characteristics as that of Mars. Inserting it into the apparatus poses more of a problem, however, as the simulant could easily damage the system's roughing pump and tamper with the vacuum in general. As a result, incorporating this aspect of the research may require us to redesign and rebuild substantial sections of our current apparatus.

Moving past our proposed hypothesis, future efforts far down the line may incorporate other theories concerning how the martian soil is oxidized. For example, as mentioned previously, Atreya et al. (2006) have suggested that hydrogen peroxide may be formed by dust devils on the surface of Mars. They propose that these dust devils may contain charged particles, which could create electrostatic fields when they move at high speeds. These electric fields then interact with elements in the atmosphere to form the hydrogen peroxide. At this point, we don't have any concrete plans

as to how we would put this hypothesis to the test, but it does represent a possible future avenue, which is why we include it here.

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