

THE PENNSYLVANIA STATE UNIVERSITY  
SCHREYER HONORS COLLEGE

DEPARTMENT OF CHEMISTRY

THE CHARACTERIZATION OF SILANE FRAGMENTS IN AN ARGON MATRIX USING  
MATRIX ISOLATION INFRARED SPECTROSCOPY

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Spring 2013

A thesis  
submitted in partial fulfillment  
of the requirements  
for a baccalaureate degree  
in Chemistry  
with honors in Chemistry

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## Abstract

Performing matrix isolation vacuum ultraviolet photolysis and microwave discharge experiments on samples of  $\text{SiH}_4$  in an Ar matrix at 12 K produced the reactive transient molecules  $\text{SiH}$  and  $\text{SiH}_2$ . Infrared spectroscopy of these intermediates showed absorption bands at  $1953.6\text{ cm}^{-1}$  for  $\text{SiH}$  and  $1997.6$ ,  $1992.8$ ,  $1973.2$ ,  $1964.4\text{ cm}^{-1}$ ,  $1008.4\text{ cm}^{-1}$ , and  $994.8\text{ cm}^{-1}$  for  $\text{SiH}_2$ . Analogous experiments with  $\text{SiD}_4$  produced absorption peaks at  $1443.8$ ,  $1438.9$ , and  $1436.9\text{ cm}^{-1}$  attributed to  $\text{SiD}_2$  and at  $1420.5\text{ cm}^{-1}$  attributed to  $\text{SiD}$ . These observations show that these species were produced by VUV photolysis of  $\text{SiH}_4$  in an argon matrix. It was also observed that a microwave discharge energy source produces a significantly smaller amount of these species than a hydrogen resonance lamp energy source based on the relative intensities of the peaks observed in each experiment.

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## 1. Introduction

In order for most chemical reactions to take place, an energy barrier called the activation energy must be overcome. This energy barrier is the result of the formation of an intermediate molecule or molecules, referred to as the transition state, that are higher in energy than both the reactants and the products. Transition state molecules are often unstable species that possess a very short lifetime. Reaction intermediates are species proposed in a reaction mechanism that are formed in one step of the reaction and used up in a subsequent step, and are therefore not observed in the final products of the reaction. An understanding of the structure of the transition states and the intermediates of a reaction is critical to determining the mechanism of a reaction, which in turn can potentially open new synthetic pathways that could not be dreamed of without the understanding of the reaction mechanism. Characterizing transient molecules is difficult to do because they do not last long due to the inherent instability and reactivity of existing in a high-energy state; therefore, the intermediates must be quickly isolated once formed if they are to be studied. One technique that does this effectively is the matrix isolation technique.

In a matrix isolation experiment, the sample is made up by mixing a relatively small amount of the species of interest with a relatively large amount of an inert material (the “matrix”). The matrix is usually made up of  $N_2$  molecules or rare gas atoms such as Ar. This mixture is deposited onto a surface called the “matrix window” at low temperatures (10-20 Kelvin, K). The basic idea behind the technique is that the molecules of the species of interest will be separated from each other by the vastly more numerous atoms or molecules of the matrix, and because the matrix is made up of an inert atom or molecule, no reactions will take place between the species of interest and the matrix molecules. The reason for depositing at low temperature is to minimize the molecular motion and molecular internal energy of the species of

interest, which in turn minimizes the probability of the molecules of the sample of interest colliding and reacting with one another while on the matrix window. These aspects make matrix isolation an appealing technique to use when examining transient species of a reaction that, under normal conditions, are extremely short-lived. Transient molecules are typically produced by subjecting stable molecules to energy – which could be in the form of heat, light, electrical discharge, etc. – to cause fragmentation and/or reactions.

In 1970, Dolphus E. Milligan and Marilyn E. Jacox were the first to perform an experiment that attempted to identify the infrared absorption bands of the reactive species formed when SiH<sub>4</sub> undergoes 121-nm vacuum ultraviolet (VUV) photolysis in a low-temperature argon matrix in order to assign infrared absorption bands to the possible transient species SiH<sub>x</sub> (x = 1, 2, 3).<sup>1</sup> Matrix isolation experiments were performed on samples of SiH<sub>4</sub> and SiD<sub>4</sub> (D stands for deuterium, <sup>2</sup>H) in an Ar matrix with mole ratios (Ar:SiH<sub>4</sub>) ranging from 200 – 2000 at temperatures of 14 K and 4 K. Infrared spectra were taken of the range 400 – 3000 cm<sup>-1</sup>. The assignments of peaks to SiH<sub>2</sub>, SiH<sub>3</sub>, and SiD<sub>2</sub> by Milligan and Jacox are summarized below in Table 1.

**TABLE 1: Infrared Absorptions (cm<sup>-1</sup>) Assigned to Silicon Hydride Species Observed by Milligan and Jacox<sup>1</sup>**

Species	Infrared Absorptions
SiH <sub>2</sub>	2032(s), 2022(s), 1008(b)
SiH <sub>3</sub>	1999(s), 1955(s), 996(b), 925(b)
SiD <sub>2</sub>	1468(s), 1472(s), 729(b)

The letters in parenthesis indicate vibrational modes: s = stretching, b = bending

Several peaks were observed in the spectral regions where Si – H stretching vibrations and H – Si – H bending vibrations would be expected to occur. Assignments were made for SiH<sub>3</sub> and SiH<sub>2</sub> but an absorption peak for SiH was unable to be assigned. The authors also observed

$\text{Si}_2\text{H}_6$  in their spectra, which led them to believe that  $\text{SiH}_3$  was forming in the matrices. However, due to inconsistencies in the collected spectra, the authors were quite uncertain of the  $\text{SiH}_3$  peak assignments. Additionally, the quantum chemical calculations at the time of the experiments were not as refined as they are today, nor as straightforward to perform, and this often led to a lack of confidence in spectral assignments.

In 1985, John L. Margrave and co-workers performed a different experiment to produce  $\text{SiH}_2$  using an alternative method to see if the previous absorption band assignments by Milligan and Jacox were correct.<sup>2</sup> Specifically, these experiments focused on characterizing the vibrational modes of the silylene species  $\text{SiH}_2$  and  $\text{SiD}_2$ . To synthesize  $\text{SiH}_2$  and  $\text{SiD}_2$  in this experiment, solid Si was vaporized in a graphite crucible at temperatures between 1725 K and 1975 K. The gaseous Si atoms were then deposited at 10 K with either a mixture of  $\text{H}_2/\text{Ar}$  or  $\text{D}_2/\text{Ar}$ , depending on the species examined and the infrared spectra were obtained. The reaction occurring with  $\text{H}_2$  during the deposition is shown below in equation 1.



The vibrational peaks observed by Margrave and co-workers for the  $\text{SiH}_2$  and  $\text{SiD}_2$  species are shown below in Table 2. The experiment also produced molecules of  $\text{SiH}_4$  and  $\text{Si}_2\text{H}_6$ , but the focus of the assignment was on the  $\text{SiH}_2$  species. Margrave's assignment for  $\text{SiH}_2$  disagreed significantly with the earlier assignment of  $\text{SiH}_2$  by Milligan and Jacox and also cast doubt on their assignment of  $\text{SiH}_3$ .

**TABLE 2: Infrared Absorptions ( $\text{cm}^{-1}$ ) for the Silylene Species Observed in the Matrix Isolation Experiments Performed by Margrave and Co-Workers<sup>2</sup>**

Species	Infrared Absorptions
$\text{SiH}_2$	1992.8(2xb), 1973.3(s), 1964.4(s), 994.8(b)
$\text{SiD}_2$	1444.6(2xb), 1439.1(s), 1426.9(s), 719.8(b)

The letters in parenthesis indicate vibrational modes: s = stretching, b = bending, 2xb = second harmonic of bending

In 2002, Lester Andrews and Xuefeng Wang investigated the intermediates formed during the gaseous reaction of silicon and hydrogen to produce silicon hydrides of the form  $\text{Si}_x\text{H}_y$ ;  $x = 1, y = 1, 2, 3, 4$  or  $x = 2, y = 2, 4, 6$  in solid neon (Ne), argon (Ar), and deuterium ( $\text{D}_2$ ) matrices.<sup>3</sup> In these experiments, a solid silicon target was hit with a focused laser beam, causing the silicon to vaporize into the gas phase and atomize. The silicon atoms were then reacted with  $\text{H}_2$  or  $\text{D}_2$  gas in excess neon, argon, or pure  $\text{D}_2$  at a temperature of 3.5 K, so that condensation occurred in concert with the reaction. The resulting matrix and trapped transient molecules were then analyzed via infrared spectroscopy. The samples were annealed and exposed to a mercury arc lamp, and more spectra were recorded to help identify the peaks of the transient  $\text{Si}_x\text{H}_y$  species. The difference between this experiment by Andrews and Wang and the earlier experiment performed by Margrave and co-workers is that the laser ablation experiment results in gaseous Si atoms with much higher energies to react with the  $\text{H}_2$  molecules, resulting in a greater number of observed species. Andrews and Wang also performed quantum chemical calculations for the  $\text{Si}_x\text{H}_y$  species to obtain optimized structures and theoretical vibrational frequencies and the comparison of the experimental and theoretical frequencies also aided in the peak assignments. The results of this experiment were the assignment of infrared peaks to the



various  $\text{Si}_x\text{H}_y$  compounds, and the peaks assigned in the argon matrix by Andrews and Wang are summarized in Table 3 below.

**TABLE 3: Infrared Absorption Peak Assignments ( $\text{cm}^{-1}$ ) of Species Observed in Andrews and Wang Experiments in Argon Matrix<sup>3</sup>**

Species	Infrared Absorptions
SiH; SiD	1953.4(s); 1420.4(s)
SiH <sub>2</sub> ; SiD <sub>2</sub>	1992.8(2xb), 1976.2(s), 1972.8(s), 1964.9(s), 1007.6(b), 994.6(b); 1443.6(2xb), 1438.9(s), 1435.9(s), 728.7(b), 718.6(b)
SiH <sub>3</sub> ; SiD <sub>3</sub>	727.2(b), 724.9(b); 547.2(b), 545.4(b)
Si <sub>2</sub> H <sub>2</sub> ; Si <sub>2</sub> D <sub>2</sub>	1093.3(s); 815.0(s)
Si <sub>2</sub> H <sub>4</sub> ; Si <sub>2</sub> D <sub>4</sub>	2150.5(s), 2145.5(s), 857.3(b); 630.7(b)

The letters in parenthesis indicate vibrational modes: s = stretching, b = bending, 2xb = second harmonic of bending

The laser ablation experiments produced significantly different results from the original VUV photolysis experiment performed by Milligan and Jacox; specifically, the correction of peak assignments which were either incorrectly assigned or not assigned at all by Milligan and Jacox. The SiH absorption observed at  $1953.4 \text{ cm}^{-1}$  by Andrews and Wang is close to the absorption peak at  $1955 \text{ cm}^{-1}$  reported and assigned to SiH<sub>3</sub> by Milligan and Jacox. The stretching peaks of SiH<sub>2</sub> at 1976.2, 1972.8, and  $1964.9 \text{ cm}^{-1}$  assigned by Andrews and Wang were observed by Milligan and Jacox ( $1974$  and  $1967 \text{ cm}^{-1}$ ) but not assigned as such. The bending peak is a point of agreement in the two experiments ( $1007.6 \text{ cm}^{-1}$  for Andrews and Wang and  $1008 \text{ cm}^{-1}$  for Milligan and Jacox). The SiD<sub>2</sub> stretching bands differ as well; for Andrews and Wang, these bands occurred around  $1440 \text{ cm}^{-1}$  but Milligan and Jacox observed these bands around  $1470 \text{ cm}^{-1}$ . Also, the experiments by Andrews and Wang produced an additional bending band at  $718.6 \text{ cm}^{-1}$ . The bending bands for SiH<sub>3</sub> observed by Andrews and

Wang differ significantly from those observed by Milligan and Jacox; no stretching bands for  $\text{SiH}_3$  were reported by Andrews and Wang. Finally, Andrews and Wang also assigned peaks to transient species  $\text{Si}_2\text{H}_4$  and  $\text{Si}_2\text{H}_2$  that were not observed by Milligan and Jacox.  $\text{SiH}_4$  and  $\text{Si}_2\text{H}_6$  were also observed by Andrews and Wang, but the focus of their experiments was the transient  $\text{Si}_x\text{H}_y$  species. These results show the need for further experiments in order to determine whether the differences in peak assignments between the experiments by Andrews and Wang and the experiments by Milligan and Jacox are due to the different experimental methods used by each group, different species produced by the different techniques, or simply that the initial assignments made by Milligan and Jacox were incorrect.

In 2008, the research group led by Dr. Jay C. Amicangelo at Penn State Erie, the Behrend College investigated the infrared absorption bands of the reactive intermediates formed by the 121 nm vacuum ultraviolet photolysis of  $\text{SiH}_4$  in a  $\text{N}_2$  matrix at 12K using matrix isolation infrared spectroscopy.<sup>4</sup> These experiments were analogous to those performed by Milligan and Jacox, except that an  $\text{N}_2$  matrix was used rather than an Ar matrix. The focus of this experiment was in characterizing transient species of the form  $\text{SiH}_x\text{N}_2$ . Isotopic substitution was used to examine both the effect of substituting  $\text{SiD}_4$  for  $\text{SiH}_4$  as well as substituting  $^{15}\text{N}_2$  for  $^{14}\text{N}_2$ . The peak assignments by Amicangelo and co-workers for each of the  $\text{SiH}_x\text{N}_2$  species observed are summarized below in Table 4. Additionally, an attempt was made to observe absorption bands that were due to  $\text{SiH}_3$  or  $\text{SiH}_3\text{N}_2$  using the assignments of the previous experiments by Andrews and Wang (referred to above) as starting points, but these species were not observed in the spectra.

**TABLE 4: Infrared Absorptions ( $\text{cm}^{-1}$ ) for the  $\text{SiH}_x(^{14}\text{N}_2)_y$  ( $x = 0, 1, 2$ ;  $y = 1, 2$ ) Species Observed in the VUV Photolysis of  $\text{SiH}_4$  in Nitrogen Matrices at  $12 \text{ K}^4$**

Species	Infrared Absorptions
$\text{SiH}_2\text{N}_2$ ; $\text{SiD}_2\text{N}_2$	2274.2(s), 2013.6(s), 2009.4(s); 2274.4(s), 1466.2(s), 1460.4(s)
$\text{SiHN}_2$ ; $\text{SiDN}_2$	2023.9(s), 2006.6(s), 813.7(b); 2023.5(s), 1458.9(s)
$\text{Si}(\text{N}_2)_2$	2044.5(s), 1913.0(s)
$\text{SiN}_2$	1754.5(s)

The letters in parenthesis indicate vibrational modes: s = stretching, b = bending

The thesis presented here describes a project whose goal was to repeat the experiments of Milligan and Jacox in order to determine what  $\text{SiH}_x$  species are actually produced from the VUV photolysis of  $\text{SiH}_4$  in an Ar matrix, as well as to examine the  $\text{SiH}_x$  species produced using a microwave plasma discharge source. This work will also help with future experiments in the Amicangelo lab on VUV photolysis experiments of  $\text{GeH}_4$  in Ar.

## 2. Experimental Method

The experiments described here used silane ( $\text{SiH}_4$ ) gas as the species of interest, also referred to as the “parent molecule” when discussing fragmentation, argon (Ar) gas as the matrix, and cesium iodide (CsI) as the matrix window. The  $\text{SiH}_4$ :Ar “concentrations” were indicated by the ratio of the individual pressures of each of the gases in the sample. Samples were prepared by allowing a small amount of  $\text{SiH}_4$  gas to flow from the available supply tank through a length of flexible metal tubing into the evacuated sample canister. The amount of pressure (in units of inches of mercury) of  $\text{SiH}_4$  that flowed into the canister was calculated by subtracting the pressure reading of the evacuated canister from the pressure reading after flowing  $\text{SiH}_4$  into the canister. The amount of pressure (inches of mercury) of Ar that were required to reach the desired pressure ratio (concentration) was then calculated and that amount of Ar was flowed from the Ar tank into the sample canister, which was then labeled with the concentration ratio, for example 1:100  $\text{SiH}_4$ :Ar.

Through the course of this research, two primary matrix isolation experiments were performed, along with two secondary experiments. The primary experiments were direct microwave discharge and hydrogen lamp vacuum-ultraviolet (VUV) photolysis (121 nm) of the  $\text{SiH}_4$ :Ar mixtures with simultaneous deposition on the CsI matrix window. The secondary experiments were annealing (warming and re-cooling of the deposited matrices) and ultraviolet-visible (UV-vis) photolysis (200-800 nm) of the deposited matrices. All experiments were performed at a matrix window temperature of 12 K unless otherwise noted. The details of each experiment are discussed below. Each of these secondary experiments helps in the identification of the infrared peaks that are due to transient molecules.

In one of the primary experiments, direct microwave discharge, the SiH<sub>4</sub>/Ar gas mixture was flowed through the tubes from the sample canister to the matrix window. However, before being deposited on the matrix window, the gas was passed through a quartz tube which was surrounded by a microwave discharge cavity. In this cavity, microwave energy creates a high energy plasma, which is made up of excited argon atoms (Ar\*), argon ions (Ar<sup>+</sup>), and high-energy electrons. A power level of 50W was used on the microwave power supply. In this cavity, two tuning stubs were used to direct the power – one metal and one ceramic. The possibility of arcing (sparks between the stubs) meant that the reflected power level and the tube itself had to be carefully watched. The silane molecules pass through this plasma region directly and experience collisions with the energetic Ar\* atoms and Ar<sup>+</sup> ions, and electrons, and are also possibly exposed to high energy radiation from the plasma. This causes fragmentation of the SiH<sub>4</sub>\* (excited parent molecule) by the reaction shown below in equation 2.



Possible fragments resulting from this process are of the form SiH<sub>x</sub> where x = 0, 1, 2, or 3. This deposition was performed for approximately four hours after the ignition of the plasma, during which time a pressure reading was regularly taken and the flow rate of gas was maintained at approximately 1.5 inches of mercury per hour, which corresponds to approximately 4.0 – 4.5 mmols of Ar/hour (the silane molecules are not taken into account for this calculation because the number of moles of silane is negligible in comparison to the number of moles of argon). At the end of the deposition, an infrared spectrum was obtained by moving the matrix isolation head into the infrared spectrometer and adjusting its position to obtain maximum absorbance. This is a key step, as the peaks of interest tended to be very small in comparison to the absorption peaks of the parent molecule.

In the other primary experiment, hydrogen lamp VUV photolysis, the microwave cavity was used in the same manner as the direct discharge experiment, but on a tube containing a mixture of hydrogen and argon gases, which was L-shaped and closed at both ends with a magnesium fluoride ( $\text{MgF}_2$ ) window facing the matrix window. The microwave cavity is used to create a plasma inside the  $\text{H}_2/\text{Ar}$  mixture, which produces excited hydrogen atoms ( $\text{H}^*$ ), that emit vacuum-ultraviolet radiation with a wavelength of 121 nm. The  $\text{SiH}_4/\text{Ar}$  sample mixture was flowed through the tubing and onto the window, with fragmentation caused by the absorption of the 121 nm radiation given off by the  $\text{H}^*$  atoms during deposition instead of collisions with excited Ar atoms as in the direct discharge experiment. Three different levels of power – 50W, 100W, and 150W – were used on the power supply with the idea that higher power levels would cause more fragmentation, thereby making the fragment peaks easier to observe. This different mode of fragmentation will produce some of the same fragments as the direct discharge experiments, except that  $\text{SiH}_3$  should not be produced in this process due to the fact that it would violate the laws of quantum mechanics in this case, because the fragmentation of  $\text{SiH}_4$  into  $\text{SiH}_3 + \text{H}$  is spin forbidden.<sup>5</sup> This deposition was performed for approximately four hours after the ignition of the plasma, during which time a pressure reading was regularly taken and the flow rate of gas was maintained at approximately 1.5 inches of mercury per hour, which corresponds to approximately 4.0 – 4.5 mmol Ar/hour. At the end of the deposition, an infrared spectrum was obtained in the same manner as described above.

The secondary experiments were performed at the end of each primary experiment after the deposition spectrum was obtained. In the annealing experiment, the matrix isolation head was left in the infrared spectrometer and the matrix window temperature was ramped up from 12 K to 25 K at a rate of 1.5 K/min using the temperature controller. The matrix window was allowed to

sit at 25 K for approximately 30 minutes before being brought back down to 12 K and obtaining an infrared spectrum. This process was repeated with the final temperature changing to 35 K instead of 25 K. The UV-vis photolysis secondary experiment was slightly more complicated. In this experiment, the matrix isolation head needed to be taken out of the infrared spectrometer, and the matrix window was then exposed to a mercury-xenon (Hg-Xe) lamp which produces radiation in the 200-800 nm range. Because the UV-vis radiation caused the matrix window temperature to increase as the source was brought near the matrix window, this was done slowly in order to maintain a window temperature of around 12 K. The matrix window was first exposed to the lamp with a long-pass (LP) filter, which blocked wavelengths below 400 nm, between the source and the window for approximately 30 minutes. At the end of this time, the lamp was removed from the window, the matrix isolation head was realigned in the infrared spectrometer, and an infrared spectrum was obtained. After the filtered photolysis, this process was repeated, but instead without the filter, again for 30 minutes. The purpose of these secondary experiments was to provide different energy sources (heat versus light) that would theoretically allow some of the fragments trapped in the matrix to recombine with other fragments, lowering the infrared absorption peaks that were due to the fragments themselves and possibly causing new peaks to form due to the different recombination of fragments. This would help with the identification of the  $\text{SiH}_x$  fragment peaks.

In addition to the primary experiments listed here, background depositions were performed in which the  $\text{SiH}_4/\text{Ar}$  mixture was allowed to flow directly onto the matrix window without being exposed to either the direct discharge or VUV excitation energies. The secondary experiments were still performed on the matrix after these background depositions. These depositions were performed to provide control spectra with which to compare to the spectra

obtained in the direct discharge and VUV experiments in order to help identify any peaks that appear, grow, or shrink in those experiments that were due to a transient species of interest and not due to the parent  $\text{SiH}_4$  molecule, the matrix window, or the matrix itself.

Another way in which the  $\text{SiH}_x$  peaks were identified was the use of isotopic substitution experiments with deuterium ( $^2\text{H}$ , or D). The experiments were run in exactly the same manner as described above, however deuterated silane ( $\text{SiD}_4$ ) was used as the parent molecule in place of  $\text{SiH}_4$ . Since  $\text{SiD}_4$  is commercially available, the  $\text{SiD}_4$  tank was connected for the isotopic substitution experiments. The reason for substituting deuterium for hydrogen is that deuterium atoms are heavier than hydrogen atoms, and thus the infrared transition will occur at lower energies (and therefore lower frequencies) in the infrared spectrum. The typical shift in frequencies is known for  $\text{Si} - \text{H}$  to  $\text{Si} - \text{D}$ , and the shift in the fragment peaks was determined by comparing the infrared spectra obtained from experiments with silane to those spectra obtained from experiments with deuterated silane. The peaks will also exhibit a different peak pattern depending on the number of deuterium atoms within the fragment, which helps with the assignment of multiple peaks due to the same fragment.<sup>4</sup>

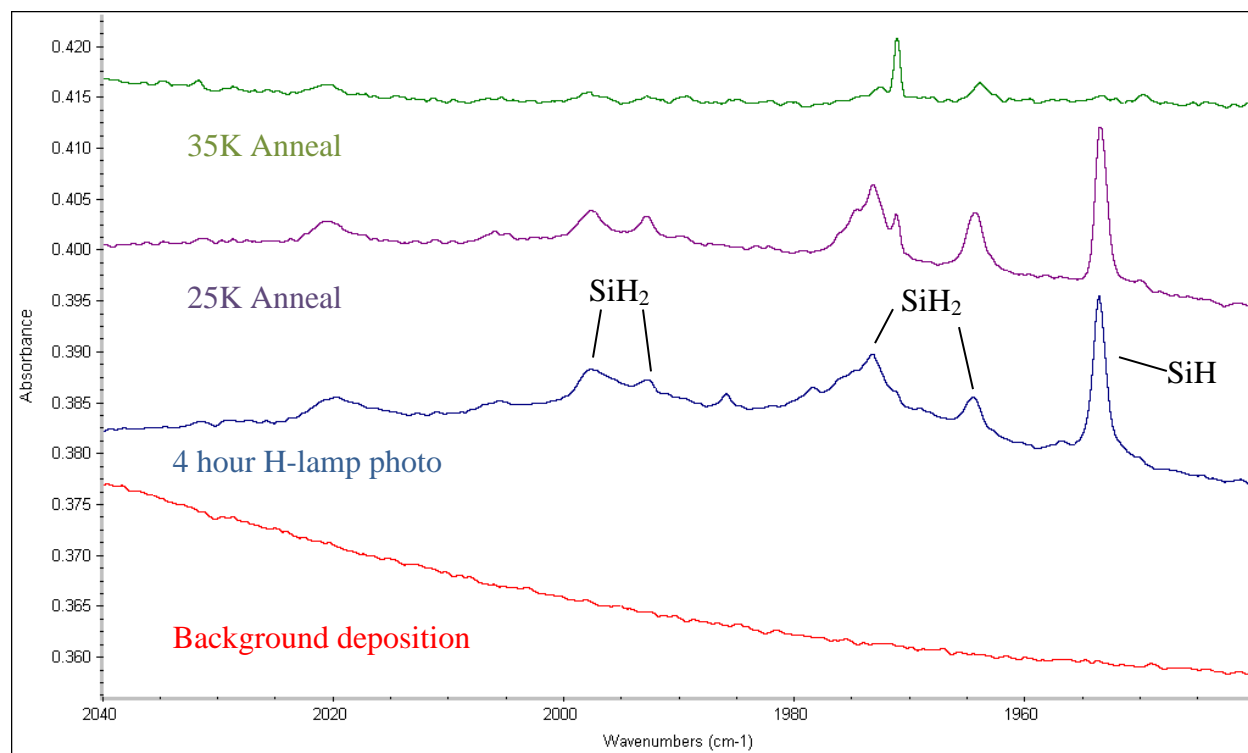


### 3. Results and Discussion

In order to optimize the intensity of the absorption peaks of the  $\text{SiH}_x$  species, several initial experiments were performed with the  $\text{SiH}_4$ :Ar concentration between 1:100 – 1:400. However, because this analysis is qualitative and not quantitative in nature, these differences are of no real consequence in terms of the peak positions. Shown below in Figures 1 through 9 are representative spectra obtained from the hydrogen lamp and microwave discharge experiments.

#### 3.1. Hydrogen Resonance Lamp Experiments

In the hydrogen lamp VUV photolysis experiments, the microwave cavity was used to create a plasma inside the  $\text{H}_2$ /Ar mixture, which produced excited hydrogen atoms ( $\text{H}^*$ ) that emitted vacuum-ultraviolet radiation with a wavelength of 121 nm. The  $\text{SiH}_4$ /Ar sample mixture was flowed through the tubing and onto the matrix window at 12 K, with fragmentation caused by the absorption of the 121 nm radiation given off by the  $\text{H}^*$  atoms during deposition. Shown in Figure 1 are the high-frequency range (Si – H stretching region) spectra obtained from the hydrogen lamp VUV photolysis primary experiment with the annealing secondary experiment for  $\text{SiH}_4$ /Ar.

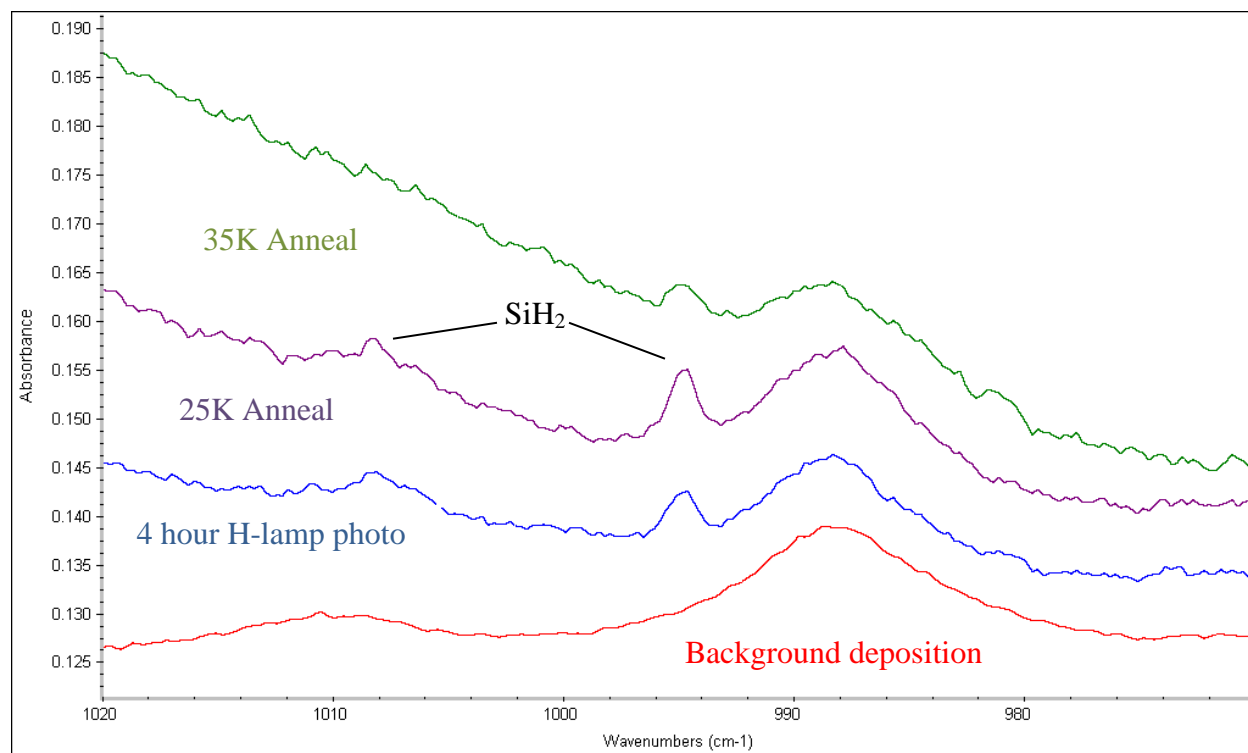


**Figure 1.** Infrared Spectra in the 2040-1940  $\text{cm}^{-1}$  region for deposition of 1:400  $\text{SiH}_4$ :Ar at 12 K for 4 h (red) and 1:400  $\text{SiH}_4$ :Ar at 12 K for 4 h with simultaneous photolysis by a 121.6-nm hydrogen resonance lamp (blue) followed by annealing to 25 K (purple) and 35 K (green).

In this experiment, the SiH stretching absorption band was observed at  $1953.6 \text{ cm}^{-1}$ . This band is observed in nearly the exact same position as observed by Andrews and Wang at  $1953.4 \text{ cm}^{-1}$ . The  $\text{SiH}_2$  stretching absorption bands were observed at  $1973.2$  and  $1964.4 \text{ cm}^{-1}$ . The bands at  $1997.6$  and  $1992.8 \text{ cm}^{-1}$  are site peaks of the second harmonic of the bending mode, and are most likely the  $2000 \text{ cm}^{-1}$  band observed by Milligan and Jacox.<sup>1</sup> The band at  $1992.8 \text{ cm}^{-1}$  is identical to a band observed at the same wavelength by Margrave<sup>2</sup>, as well as Andrews and Wang.<sup>3</sup> The bands at  $1973.2$  and  $1964.4 \text{ cm}^{-1}$  are close to the bands observed by Andrews and Wang at  $1972.8$  and  $1964.9 \text{ cm}^{-1}$ .<sup>3</sup> These peaks do not appear in the background deposition spectrum, and their disappearance with the annealing experiments is consistent with the behavior of highly reactive intermediate species: warming the matrix window allows some of the

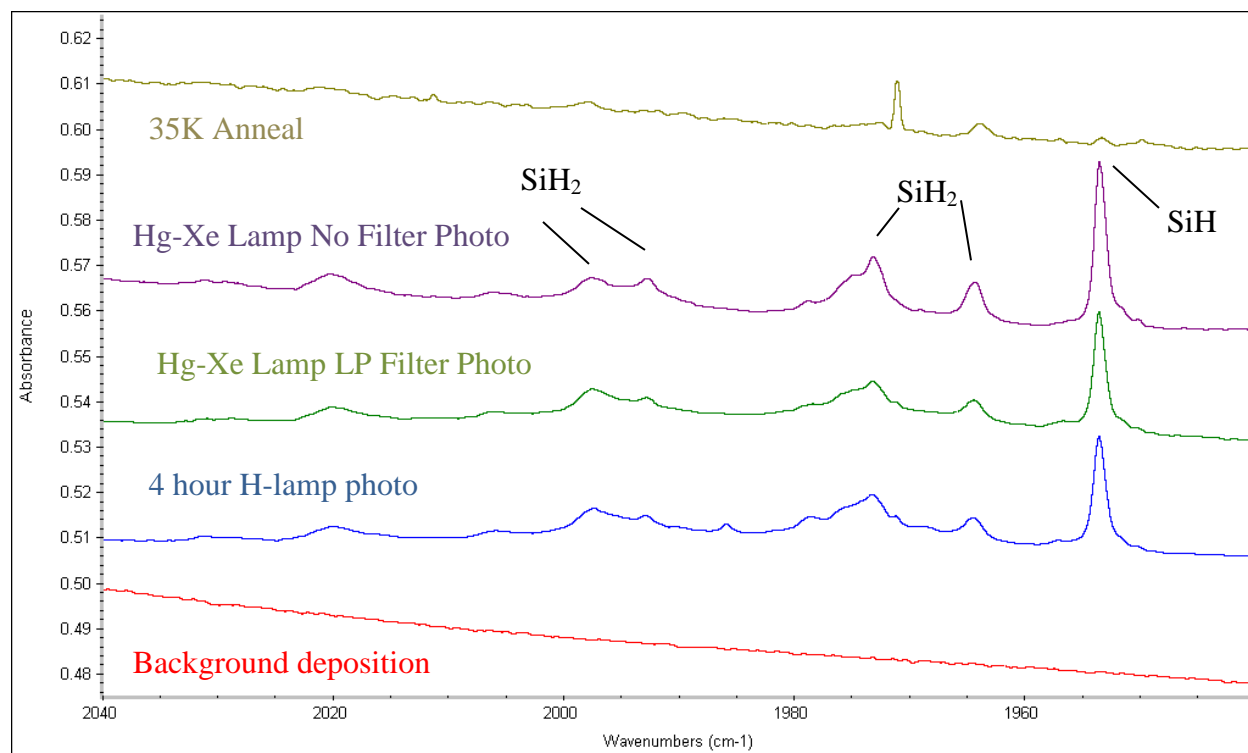
molecules to free themselves from the matrix and react with other molecules, thus lowering the concentration (and therefore intensity of the absorption bands) due to those species.

Shown in Figure 2 are the low-frequency range (H – Si – H bending region) spectra obtained from the hydrogen lamp VUV photolysis primary experiment with the annealing secondary experiment for SiH<sub>4</sub>/Ar. The absorption peaks visible in this region are due to SiH<sub>2</sub> at 1008.4 cm<sup>-1</sup> which corresponds to the band observed by Andrews and Wang<sup>3</sup> at 1007.6 cm<sup>-1</sup> and another band at 994.8 cm<sup>-1</sup> which corresponds to the band observed by Milligan and Jacox<sup>1</sup> at 996 cm<sup>-1</sup> (assigned to SiH<sub>3</sub>) and observed by Margrave<sup>2</sup> at 994.8 cm<sup>-1</sup> and by Andrews and Wang<sup>3</sup> at 994.6 cm<sup>-1</sup> (assigned to SiH<sub>2</sub>). These peaks do not appear in the background deposition spectrum and their disappearance with the annealing experiments is consistent with the behavior of highly reactive intermediate species.



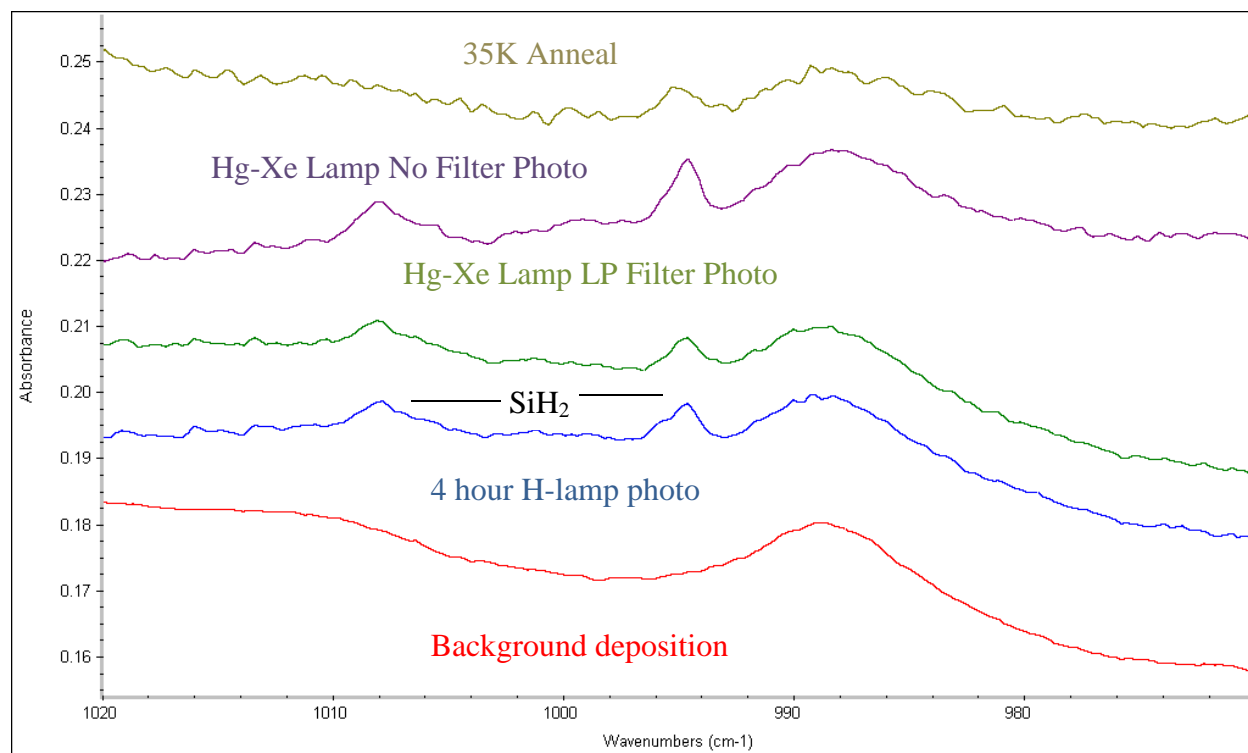
**Figure 2.** Infrared Spectra in the 1020-970  $\text{cm}^{-1}$  region for deposition of 1:400  $\text{SiH}_4$ :Ar at 12 K for 4 h (red) and deposition of 1:400  $\text{SiH}_4$ :Ar at 12 K for 4 h with simultaneous photolysis by a 121.6-nm hydrogen resonance lamp (blue) followed by annealing to 25 K (purple) and 35 K (green).

Shown in Figure 3 are the high-frequency range (Si – H stretching range) spectra obtained from the hydrogen lamp VUV photolysis primary experiment with the Hg-Xe lamp photolysis secondary experiment for  $\text{SiH}_4$ /Ar. In this experiment, the SiH stretching absorption band and the  $\text{SiH}_2$  stretching absorption bands were found at the same positions as in Figure 1. When exposed to the filtered Hg-Xe lamp radiation, no change was observed in peak intensity. When exposed to the Hg-Xe lamp without the filter, the peaks grew in intensity, indicating that more of these molecules were being produced. The peaks disappeared with annealing to 35 K.



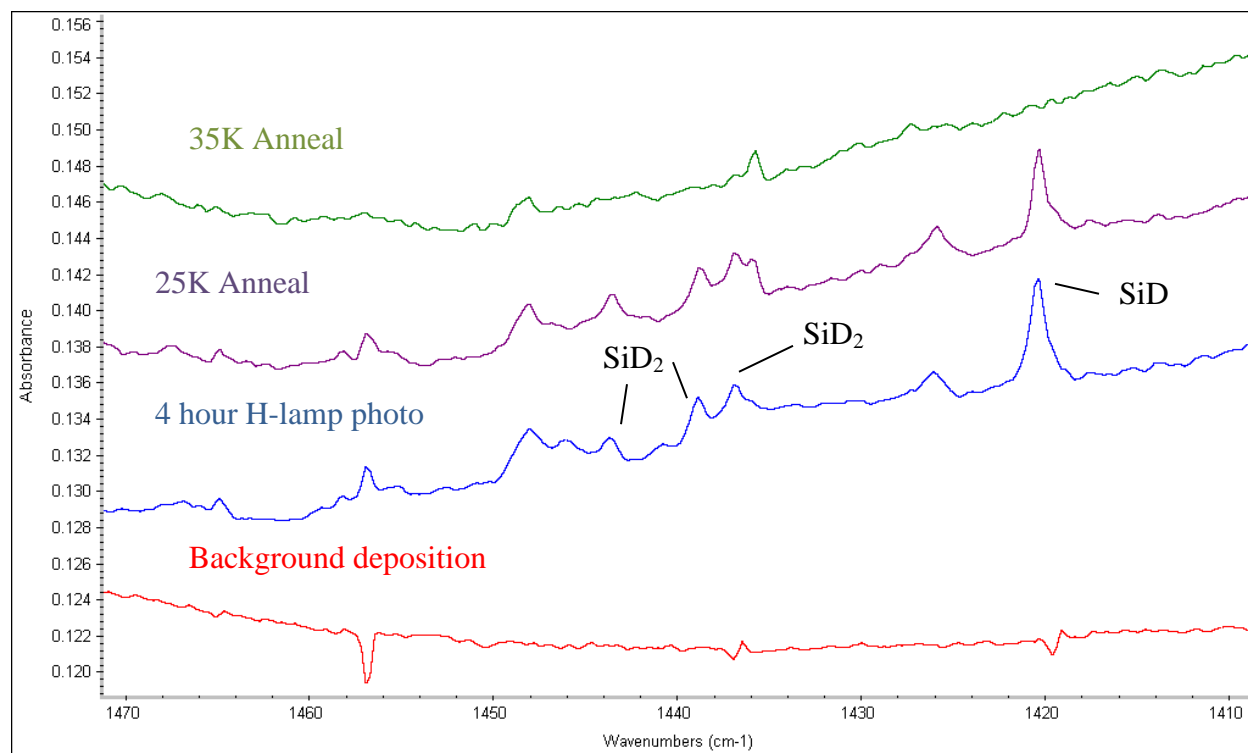
**Figure 3.** Infrared Spectra in the 2040-1940  $\text{cm}^{-1}$  region for deposition of 1:400  $\text{SiH}_4$ :Ar at 12 K for 4 h (red) and deposition of 1:400  $\text{SiH}_4$ :Ar at 12 K for 4 h with simultaneous photolysis by a 121.6-nm hydrogen resonance lamp (blue), after 400 – 900-nm irradiation for 30 min (green), after 200 – 900-nm irradiation for 30 min (purple) and after annealing to 35 K for 30 min (gold).

Shown in Figure 4 are the low-frequency range (H – Si – H bending region) spectra obtained from the hydrogen lamp VUV photolysis primary experiment with the Hg-Xe lamp photolysis secondary experiment for  $\text{SiH}_4$ /Ar. The absorption peaks visible in this region are in the same position as those in Figure 2, and behave similarly to the peaks in Figure 3 during the course of Hg-Xe lamp photolysis. Using the reported peaks of Andrews and Wang as a guideline, absorption peaks for  $\text{SiH}_3$  were not observed in the hydrogen lamp experiments.



**Figure 4.** Infrared Spectra in the 1020-970  $\text{cm}^{-1}$  region for deposition of 1:400  $\text{SiH}_4$ :Ar at 12 K for 4 h (red) and deposition of 1:400  $\text{SiH}_4$ :Ar at 12 K for 4 h with simultaneous photolysis by a 121.6-nm hydrogen resonance lamp (blue), after 400 – 900-nm irradiation for 30 min (green), after 200 – 900-nm irradiation for 30 min (purple) and after annealing to 35 K for 30 min (gold).

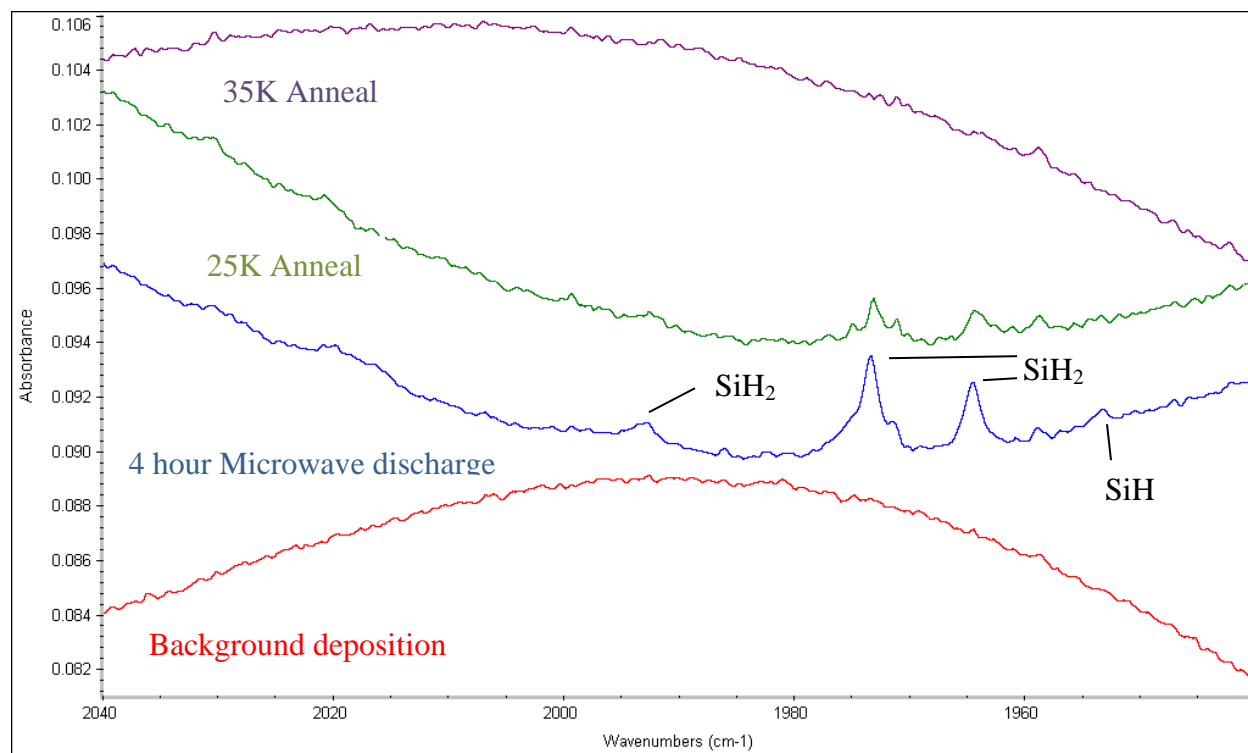
Shown in Figure 5 are the high-frequency range (Si – D stretching region) spectra obtained from the hydrogen lamp VUV photolysis primary experiment with the annealing secondary experiment for  $\text{SiD}_4$ /Ar. The stretching absorption peak for SiD was observed at  $1420.5 \text{ cm}^{-1}$ , which is in excellent agreement with the peak reported by Andrews and Wang for SiD at  $1420.4 \text{ cm}^{-1}$ . The stretching peaks for  $\text{SiD}_2$  were observed at  $1438.9$  and  $1436.9 \text{ cm}^{-1}$ . The stretching peaks at  $1438.9$  and  $1436.9 \text{ cm}^{-1}$  are in good agreement with the assignments by Andrews and Wang at  $1438.9$  and  $1435.9 \text{ cm}^{-1}$ , respectively. The peak at  $1443.8 \text{ cm}^{-1}$  is the second harmonic of the bending mode of  $\text{SiD}_2$  and was reported by Andrews and Wang at  $1443.6 \text{ cm}^{-1}$ . These peaks behave in a similar manner to those in Figure 1 during the course of the annealing secondary experiment.



**Figure 5.** Infrared Spectra in the 1470-1410  $\text{cm}^{-1}$  region for deposition of 1:400  $\text{SiD}_4$ :Ar at 12 K for 4 h (red) and deposition of 1:400  $\text{SiD}_4$ :Ar at 12 K for 4 h with simultaneous photolysis by a 121.6-nm hydrogen resonance lamp (blue) followed by annealing to 25 K (purple) and 35 K (green).

### 3.2. Microwave Discharge Experiments

In the direct microwave discharge experiments, the  $\text{SiH}_4$ /Ar gas mixture was flowed through the tubes from the sample canister to the matrix window. However, before being deposited on the matrix window, the gas was passed through a quartz tube which was surrounded by a microwave discharge cavity. In this cavity, microwave energy creates a high energy plasma, which is made up of excited argon atoms ( $\text{Ar}^*$ ), argon ions ( $\text{Ar}^+$ ), and high-energy electrons. A power level of 50W was used on the microwave power supply. Shown in Figure 6 are the high-frequency range (Si – H stretching region) spectra obtained from the microwave discharge primary experiment and the annealing secondary experiment with  $\text{SiH}_4$ /Ar.

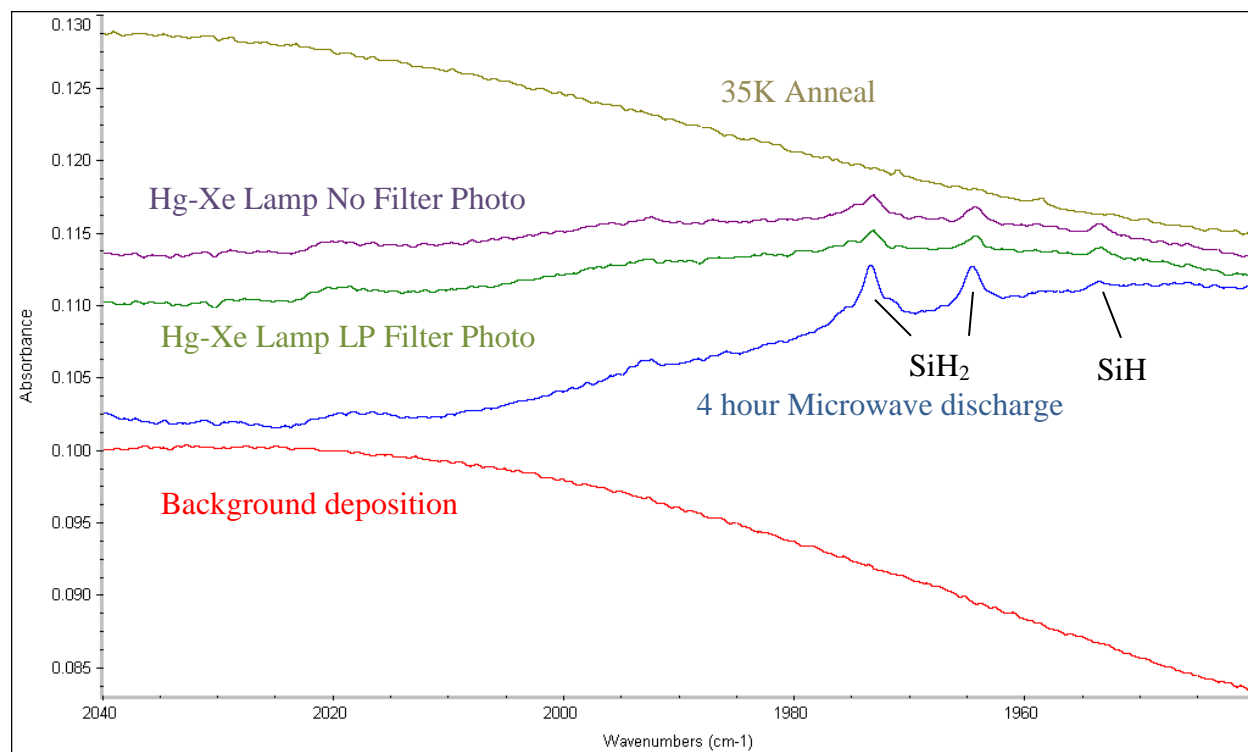


**Figure 6.** Infrared Spectra in the 2040-1940  $\text{cm}^{-1}$  region for deposition of 1:100  $\text{SiH}_4$ :Ar at 12 K for 4 h (red) and deposition of 1:100  $\text{SiH}_4$  in argon at 12 K for 4 h with simultaneous passage through a microwave discharge cavity (blue) followed by annealing to 25 K (green) and 35 K (purple).

The peaks observed for  $\text{SiH}_2$  and  $\text{SiH}$  in this experiment occur at the same positions as in Figure 1 (hydrogen lamp experiment), and behave in a similar manner with annealing. However, when comparing the absolute intensities of the  $\text{SiH}_2$  and  $\text{SiH}$  peaks in Figure 6 to Figure 1, it can be seen that the intensities in Figure 6 are much lower. This indicates that much less  $\text{SiH}_2$  and  $\text{SiH}$  are being trapped in the Ar matrix in the microwave discharge experiments. In addition, when the relative intensities of the  $\text{SiH}_2$  to the  $\text{SiH}$  peaks in Figure 6 are compared to the relative intensities in Figure 1, it is found that the intensity of  $\text{SiH}$  is much smaller than  $\text{SiH}_2$  in Figure 6, while the intensity of  $\text{SiH}$  is much larger than  $\text{SiH}_2$  in Figure 1. This indicates that much less  $\text{SiH}$  is being formed and trapped in the Ar matrix in the microwave discharge experiments as compared to the hydrogen lamp experiments.

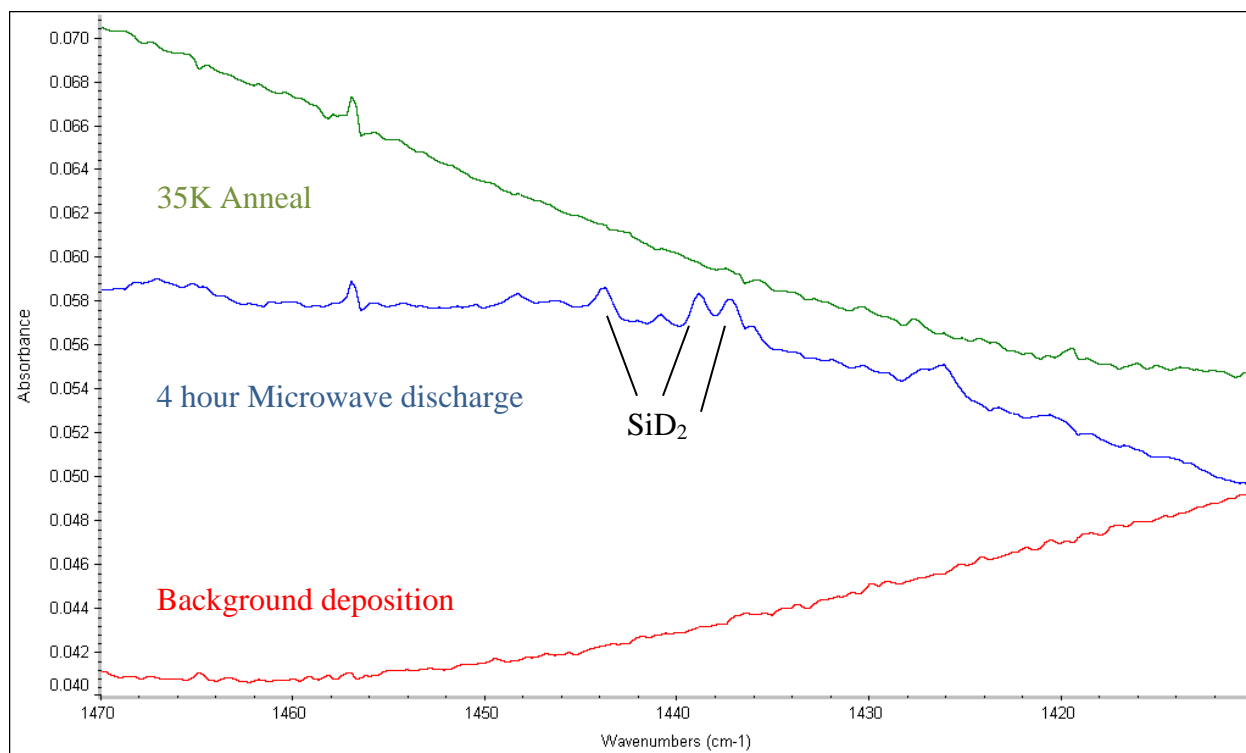


Shown in Figure 7 are the high-frequency range (Si – H stretching region) spectra obtained from the microwave discharge primary experiment and the Hg-Xe lamp photolysis secondary experiment with SiH<sub>4</sub>/Ar. The peaks observed in this experiment occur at the same positions as Figure 1, and behave in a slightly different manner than described in Figure 3, in that they were observed to decrease in intensity with photolysis by the filtered Hg-Xe lamp. Using the reported peaks of Andrews and Wang as a guideline, absorption peaks for SiH<sub>3</sub> were not observed in the microwave discharge experiments.



**Figure 7.** Infrared Spectra in the 2040-1970 cm<sup>-1</sup> region for deposition of 1:100 SiH<sub>4</sub>:Ar at 12 K for 4 h (red) and deposition of 1:100 SiH<sub>4</sub> in argon at 12 K for 4 h with simultaneous passage through a microwave discharge cavity (blue), after 400 – 900-nm irradiation for 30 min (green), after 200 – 900-nm irradiation for 30 min (purple) and after annealing to 35 K for 30 min (gold).

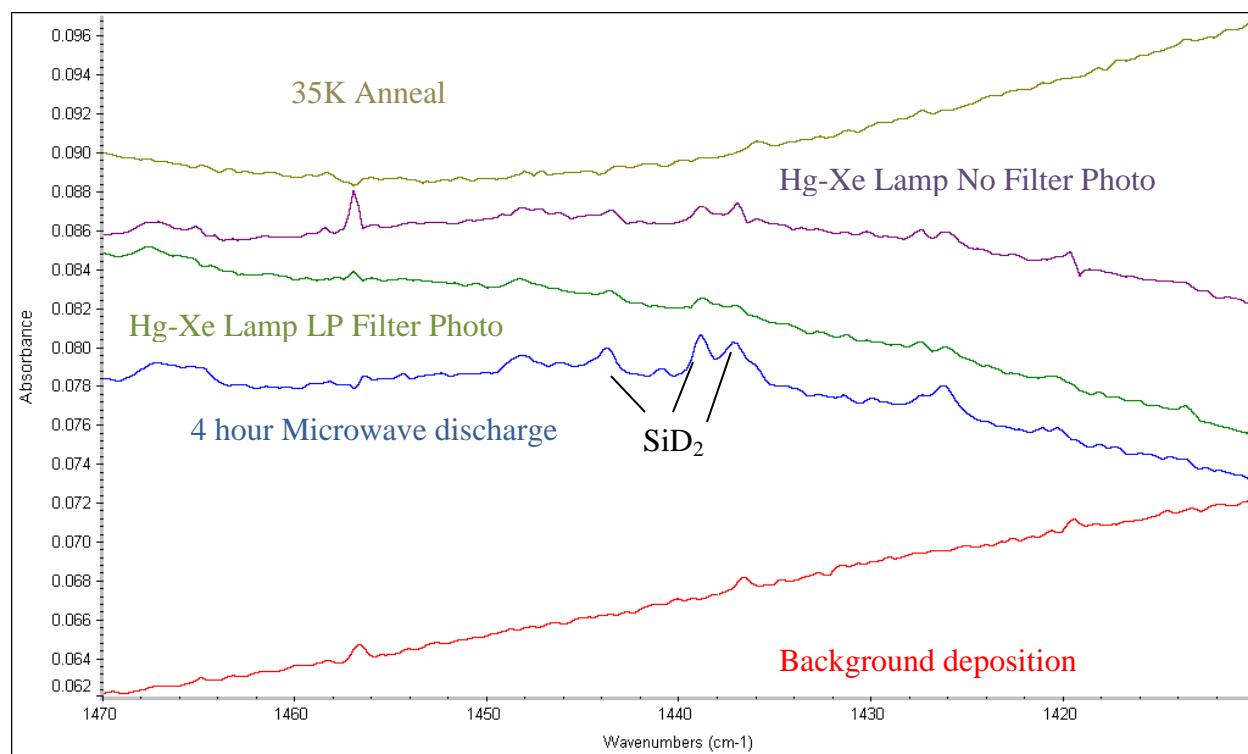
Shown in Figure 8 are the high-frequency range (Si – D stretching region) spectra obtained from the microwave discharge primary experiment and the annealing secondary experiment with SiD<sub>4</sub>/Ar. The peaks observed in this experiment are only due to SiD<sub>2</sub>, occur at the same positions as described in Figure 5, and behave in the same manner as described in Figure 1, except that the absolute intensities are again lower and the peak for SiD was not observable above the noise.



**Figure 8.** Infrared Spectra in the 1470-1410 cm<sup>-1</sup> region for deposition of 1:100 SiD<sub>4</sub>:Ar at 12 K for 4 h (red) and deposition of 1:100 SiD<sub>4</sub> in argon at 12 K for 4 h with simultaneous photolysis by a microwave discharge cavity (blue) followed by annealing to 35 K (green).

Shown in Figure 9 are the high-frequency range (Si – D stretching region) infrared spectra from the microwave discharge primary experiment and the Hg-Xe lamp photolysis secondary experiment with SiD<sub>4</sub>/Ar. The peaks observed in this experiment are the same as those in Figure 8. With filtered photolysis by the Hg-Xe lamp, the peaks were observed to decrease in

intensity, but rose in intensity with unfiltered photolysis by the Hg-Xe lamp, and finally disappearing when annealed to 35 K. For the microwave discharge experiments with  $\text{SiH}_4$  and experiments with  $\text{SiD}_4$ , the low range peaks were too weak to be resolved from the noise, and are thus not presented here.



**Figure 9.** Infrared Spectra in the  $1470\text{-}1410\text{ cm}^{-1}$  region for deposition of  $1:100\text{ SiD}_4:\text{Ar}$  at  $12\text{ K}$  for  $4\text{ h}$  (red) and deposition of  $1:100\text{ SiD}_4$  in argon at  $12\text{ K}$  for  $4\text{ h}$  with simultaneous passage through a microwave discharge cavity (blue), after  $400\text{ - }900\text{-nm}$  irradiation for  $30\text{ min}$  (green), after  $200\text{ - }900\text{-nm}$  irradiation for  $30\text{ min}$  (purple) and after annealing to  $35\text{ K}$  for  $30\text{ min}$  (gold).

#### 4. Conclusions

Performing matrix isolation vacuum ultraviolet photolysis and microwave discharge experiments on gaseous samples of  $\text{SiH}_4$  in an Ar matrix at 12 K produced the reactive transient molecules  $\text{SiH}$  and  $\text{SiH}_2$ . Infrared spectroscopy of these intermediates showed absorption bands at  $1953.6\text{ cm}^{-1}$  for  $\text{SiH}$  and  $1997.6$ ,  $1992.8$ ,  $1973.2$ ,  $1964.4\text{ cm}^{-1}$ ,  $1008.4\text{ cm}^{-1}$ , and  $994.8\text{ cm}^{-1}$  for  $\text{SiH}_2$ . These peaks were in good agreement with the assignments made by Andrews and Wang. These observations show that the Milligan and Jacox reported observation of  $\text{SiH}_3$  was incorrect; this molecule is not formed by VUV photolysis. The assignments of Milligan and Jacox in general were also incorrect; most of the observed peaks were due to  $\text{SiH}_2$ , not  $\text{SiH}_3$ . Analogous experiments with  $\text{SiD}_4$  produced absorption peaks at  $1443.8$ ,  $1438.9$ , and  $1436.9\text{ cm}^{-1}$  attributed to  $\text{SiD}_2$  and at  $1420.5\text{ cm}^{-1}$  attributed to  $\text{SiD}$ . These peaks were generally in good agreement with the assignments made by Andrews and Wang. It was also observed that the yields of  $\text{SiH}$  and  $\text{SiH}_2$  molecules were much larger in the VUV photolysis experiments as compared to the microwave discharge experiments.

## **5. Acknowledgements**

I would like to thank Dr. Jay Amicangelo and Dr. Jason Bennett for all of their support, guidance, and advice throughout the course of this project. I would also like to thank the members of the Amicangelo Group, past and present, for their assistance at various stages; namely, Madelyn Hoover for orienting me on the project and Jennifer Pezdek and Christopher Bailey for their assistance in running the experiments (a day-long project for each experiment). Thanks to the Penn State Behrend Undergraduate Research Fund for summer funding.

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### **Research Experience**

*Penn State Department of Chemistry, Erie, PA* 2011-2013

- Investigated vibrational modes of reactive intermediates produced by photolysis of SiH<sub>4</sub> gas in Ar matrix.
- Performed matrix isolation experiments with SiH<sub>4</sub>:Ar and SiD<sub>4</sub>:Ar
- Used infrared spectroscopy to assign absorption peaks

### **Work Experience**

*LORD Corporation*

- Analytical Chemistry Intern October 2012-March 2013
  - Worked in routine analytical services laboratory. Duties included cleaning/restocking glassware, general sample preparation, and operation of instruments as trained with them.
  - Gained experience in chemical industry, and further expanded laboratory techniques.

*Penn State Erie, the Behrend College*

- Learning Resource Center Tutor Fall 2011 – May 2013
  - Worked with students to improve their understanding of General and Organic Chemistry, Physics (Mechanics), and Calculus at weekly appointments.
  - My time with the LRC helped me to develop effective communication skills: specifically, the clear explanation of an idea using examples to another person so that they can understand it.

### **Awards and Recognition**

- Academic Excellence in Chemistry Spring 2013
- Dean's List Fall/Spring 2009, Fall 2011-Spring 2013