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Computer Modeling of Molecular Vibration Frequencies and its Application to the Modeling of Silane Compounds

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**Computer Modeling of Molecular
Vibrational Frequencies and its
Application to the Modeling of Silane
Compounds**

Ryan T. Merrell

**Computer Modeling of Molecular Vibrational
Frequencies and its Application to the
Modeling of Silane Molecules**

by

Ryan Merrell

**Submitted in Joint Fulfillment of the Honors Program Senior
Project and Chemistry 493**

at

The University of Alabama in Huntsville

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Introduction:

Silane molecules are a unique class of chemical compounds that are used as coupling agents to bond organic coatings to inorganic substrates. This unique capability for bonding two chemically dissimilar substrates lies in the chemical structure of silane compounds. The general structural formula for a silane molecule is X_nSiR_{4-n} , where R is an organofunctional group and X is a hydrolyzable group that is an intermediate for adhesion promotion to a metal substrate. The functionality of the silane molecule is determined by n. If $n=1$, then $4-1=3$, which would give a tri-functional silane molecule. An example of a tri-functional silane molecule can be seen in Figure 1. In a silane molecule, the silicon atom is able to bond oxy groups and straight chain hydrocarbon groups. This gives the silane molecule its two fold bonding capability.

Silanes have been used since the 1950's to enhance the bonding of epoxy resins to glass and are commonly used today in many paints to enhance their adhesion to metal surfaces. Silane modified surfaces have been found suitable for enzyme and protein immobilization and cell adhesion. The bonding of silanes on metal surfaces is the underlying motivation for the studies presented here.

Computer molecular modeling is an excellent method for gaining insight into the bonding nature of silanes to metal surfaces. The data for vibrational frequency values from the computer models is an excellent tool for determining the accuracy of experimental vibrational frequency data. The thrust of my project is to develop a cookbook procedure for how to take data values for vibrational frequencies from computer models and overlay them onto experimental data for vibrational frequencies.

The Chemistry Department at the University of Alabama in Huntsville recently acquired a Silicon Graphics computer. This computer is valuable in modeling chemical compounds and making associated calculations on them. Data gleaned from calculations on the SGI computer is practical in making comparisons between what theory predicts and what data is obtained experimentally in the laboratory. What is needed is a methodology for how to map the theoretical data obtained through SGI software calculations onto experimental data that is logged into another computer. This mapping serves as a useful indicator of just how much theory differs from what is observed in the laboratory.

My specific problem involves modeling the vibrational frequencies of silanes through Spartan software on the SGI computer and overlaying this data onto experimental data obtained through Fourier Transform Infrared Spectroscopy. This data overlay will reveal the deviation between experimental results and what theory predicts. This will give an indication of the experimental error. The recipe I develop will serve as a useful procedure for future students to use in related studies. Any application of the modeling process to silane molecules is secondary to the goal of the project.

Theoretical Section:

The nature of the bonding of silanes to metals is not as well characterized as their bonding to glass. Hence, the chemist turns to analytical techniques to uncover the nature of the bonding of silanes to metal surfaces. One such technique that is a useful indicator of the nature of bonding in molecules is the study of molecular vibrational frequencies.

Vibrational frequencies are commonly used in chemistry as useful qualitative analytical indicators of chemical structures. For example, infrared spectroscopy makes use of vibrational frequencies in elucidating the structure of unknown organic molecules. Vibrational frequencies have their basis in the chemical nature of bonds in molecules. Most structural drawings of chemical compounds give a very static image of chemical bonds. Atoms are not bonded at a fixed distance from one another. Rather, they are moving about one another at assignable rates or vibrational frequencies. There are two general types of frequencies, stretching and bending. Stretching involves a change in the interatomic distance along the axis of the atoms, while bending involves a change in the angle between bonds and falls into four types: scissoring, rocking, wagging and twisting. The general rule in chemistry is that the number of different types of vibrational frequencies in a nonlinear molecule follows the $3n-6$ rule, where n is the number of atoms in the molecule. Water is a simple molecule which demonstrates the $3n-6$ rule. With three atoms, water would have three different vibrational frequencies. Figure 2 demonstrates the three different vibrational frequencies in water. Obviously, more complicated molecules such as silane molecules would have many more vibrational frequencies. Additionally, more complicated molecules have vibrational interactions between a multitude of vibrational

centers. These vibrational frequencies have finite values which can be assigned to them through IR spectroscopy.

Infrared spectroscopy is the analytical technique by which vibrational frequencies can be assigned for bonds in molecules. The bonds in molecules vibrate at frequencies that correspond in energy to the energy of infrared light or radiation. Frequencies can be likened to energy just as light radiation can be likened to energy according to the equation:

$$E=hv$$

Here, E is energy, h is Planck's constant, and v is frequency. In order for a bond in a molecule to absorb infrared radiation, the molecule must undergo a net change in dipole moment as a consequence of its vibrational or rotational motion. The fluctuation of a dipole moment in a molecule creates an electrical field which can interact with the electrical field associated with incident radiation. If the frequency of the incident radiation exactly matches the frequency of a natural vibrational frequency in a molecule, a net transfer of energy takes place that results in a change in the amplitude of the molecular vibration. The consequence is absorption of radiation.

Figure 3 shows a diagram of an IR spectrometer. The three main components of the instrument are the radiation source, the monochromator, and the detector. The infrared source consists of an inert solid that has been heated to a temperature of 1500-2200 K. The radiation from the source is sent via a series of mirrors to the monochromator. The monochromator acts as a frequency selector, allowing only one frequency of radiation to pass on to the sample in a given amount of time. If a frequency of radiation matches that of a natural vibrational frequency in the sample, it will be absorbed. The detector detects the amount of light transmitted through the sample. Thus a sharp spike would represent a bond that absorbed radiation in a plot of frequency versus percent transmittance.

It has been mentioned already that IR spectroscopy is useful in identifying the structural configurations in unknown molecules such as organic compounds. IR spectroscopy also can give insight into the bonding in molecules through vibrational frequency data. The masses of the atoms involved in the bonds and the strength of the bonds go into determining the various vibrational frequencies associated with the bonds. When a silane molecule bonds to a surface, the observed vibrational frequencies change from those in the free standing molecule. These changes in the vibrational frequencies gives the chemist insight into the nature of the bonding on the surface.

Literature values for the vibrational frequencies of silanes bonded to metal surfaces are often ambiguous or not confirmed enough by experiment. Hence, determining the accuracy of experimental values for the vibrational frequencies of silanes bonded to metal surfaces is often impossible. The peaks for the vibrational frequencies of compounds bonded to surfaces are often broad. Therefore, it is difficult to assign specific values for a particular vibrational frequency. Also, it is often difficult to determine which peak corresponds to a particular vibrational mode for a spectrum.

Because of these uncertainties in comparing experimental values for vibrational frequencies to accepted values, the chemist must turn to another method of verifying his results. This is where the modeling process comes into play. Through the use of Spartan software, one can model any compound one desires. The software is capable of making calculations on the vibrational frequencies for every bond in the generated compound. These calculations are largely based on Newtonian mechanics and some quantum mechanics. The software generates a vibrational sequence for the molecule with a list of frequencies that correspond to different vibrational modes in the molecule. It is up to the chemist to determine which of the modes he is interested in and which are of lesser

significance. What is needed is an efficient means of transferring the modeled vibrational frequency data from the Silicon Graphics computer to another computer where it can be overlaid onto experimental data. This is the core of this experiment.

Experimental Section:

Spartan software on an Indy R 5000 Silicon Graphics 150 Megahertz workstation was used to model various silane molecules. The ab initio calculations of the software were used to generate a vibrational sequence which could be exported to another computer. The compounds modeled were the mono, di, and tri functional ethoxy silane molecules. Igor software was used to create a histogram, which was used to overlay the modeled vibrational frequencies for a particular molecule onto the experimentally determined vibrational frequencies for that molecule.

Results and Discussion:

The following two pages give results from the vibrational frequencies data transfer from the SGI computer to the computer in the downstairs Surface Science Preparations lab. For the recipe on how to most efficiently make this data transfer, see Appendix A.

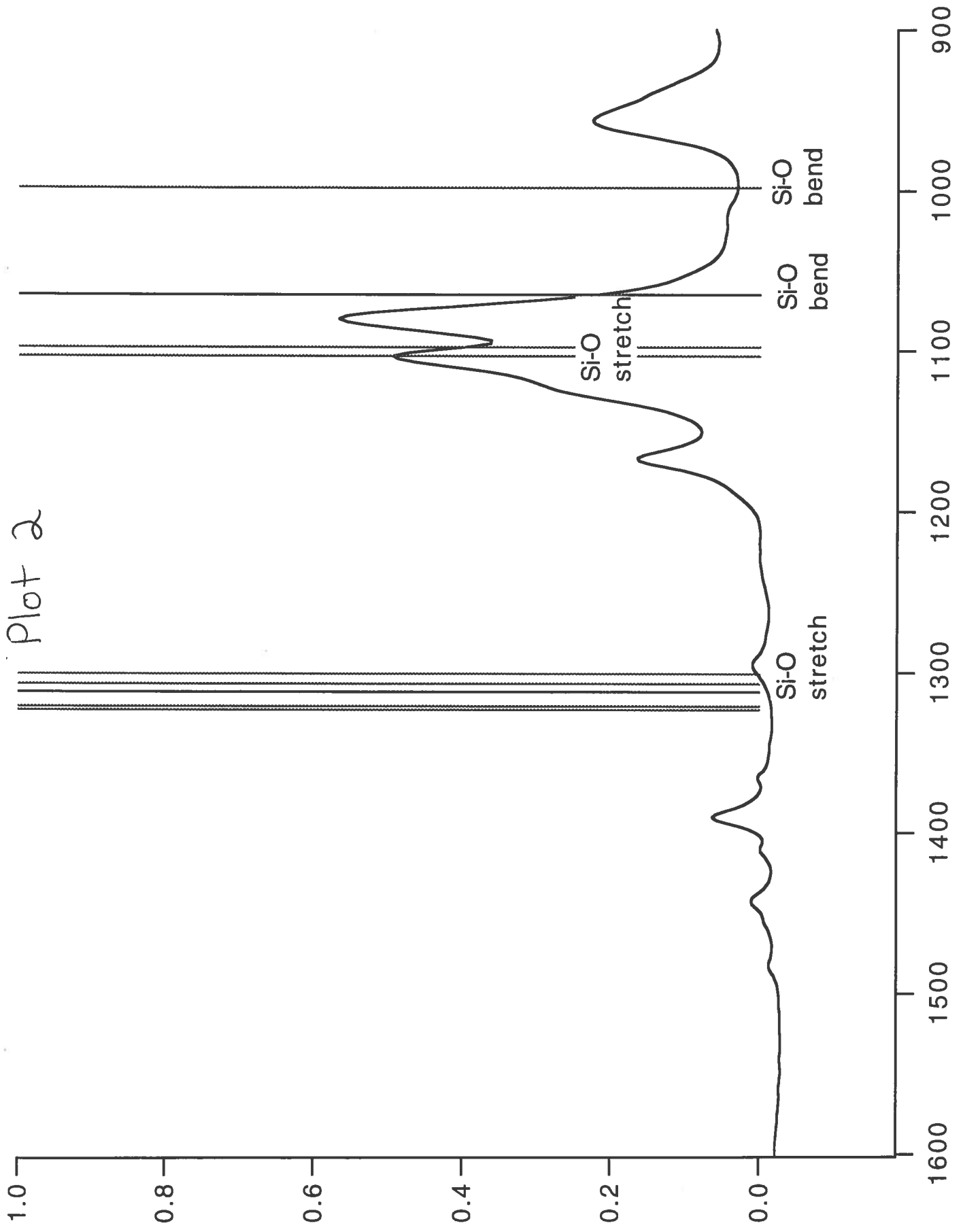
Plot 1 represents the vibrational frequency data along with modes assigned to each frequency for the tri ethoxy substituted silane molecule(Figure 1). For this molecule, the modes corresponding to Si-O stretches were exported from the SGI computer, and the other non Si-O frequencies were deleted. The modes assigned in the plot are not entirely accurate, as knowledge of vibrational modes limits this author. Plot 1 represents the data that has been formatted in a way such that it can be imported into Igor and made into a histogram.

Plot 2 shows a histogram where the data from Plot 1 has been overlaid onto experimental data for the same tri ethoxy substituted silane molecule. The plot is labeled to show the modes for the Si-O frequencies from the modeled data. The Igor program that allows one to make such an overlay is shown in Appendix B.

From this histogram overlay sample, the goals of the project are fully achieved. The overlay allows the chemist to make a good comparison between the vibrational frequency data modeled on the SGI computer with the vibrational frequency data obtained through IR spectrosocopy experiments.

Plot 1

Si-O bend	998.15
Si-O bend	1065.04
Si-O stretch	1097.73
Si-O scissor	1103.28
Si-O stretch	1300.81
Si-O stretch	1307.15
Si-O wag	1312.26
Si-O rocking	1321.05
Si-O stretch	1323.43
Si-O stretch	1385.02
Si-O stretch	1395.36
Si-O rocking	1399.70



References

1. Miser, Sourabh, Fundamental Investigation of Silane Adhesion Promoters on Metal Surfaces. In fulfillment of the Ph.D. Degree in the Joint Material Science Department at the University of Alabama in Huntsville, March, 1997.
2. Skoog, Douglas, Principles of Instrumental Analysis. Harcourt Brace College Publishers, 1992.
3. Wade, L.G., Organic Chemistry. Prentice Hall Publishers, 1991.

Figure 1

Tri ethoxy substituted silane

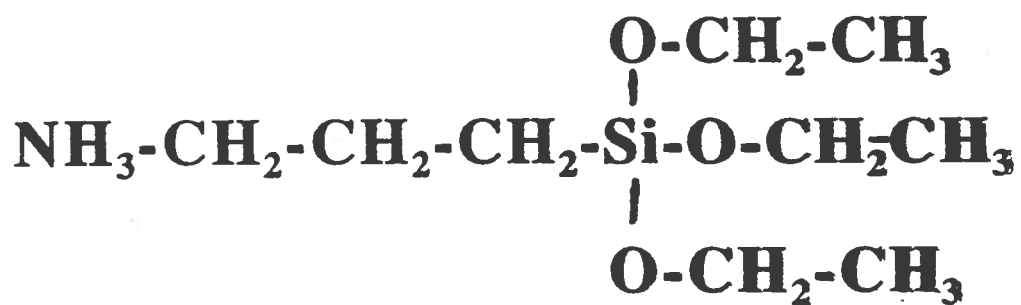
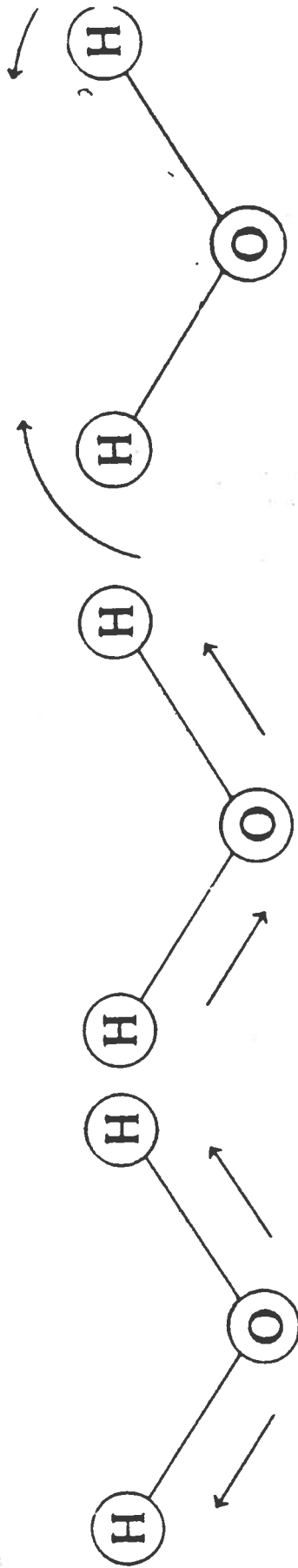


Figure 2

Vibrational modes in Water



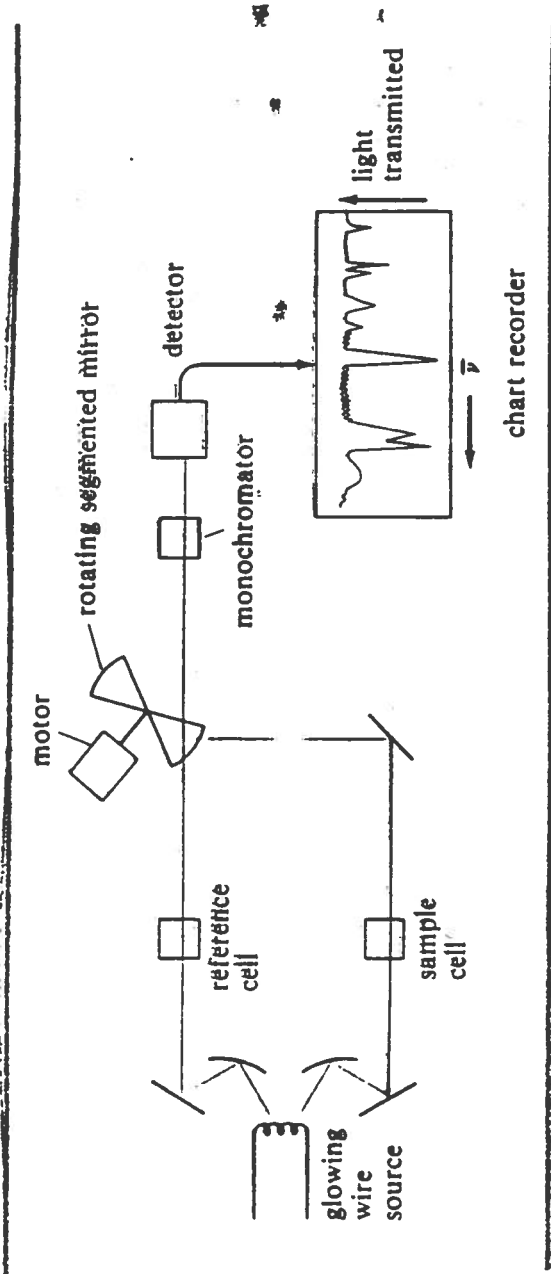
symmetric stretching

antisymmetric stretching

bending (scissoring)

Figure 3

IR Spectrometer



Appendix A

Recipe for Efficient Data Transfer

The first step I took in attacking the problem was familiarizing myself with the Spartan software on the SGI computer. I went through the tutorial in the Spartan manual, which allows one to build increasingly complicated molecules by following the step by step instructions. After completing this tutorial, I was ready to begin building my own molecules. I started with the mono ethoxy substituted silane and worked my way up to the tri ethoxy substituted silane.

Next, I generated a vibrational sequence for each molecule by initiating the ab initio calculations feature of the software. This generated a series of vibrational frequencies corresponding to specific bonds in the molecule. The computer generates a visual display of each frequency upon selection of that frequency. It is up to the individual to select which frequencies are useful for his purposes. For example, in the vibrational sequence of any substituted silane molecule, I am only interested in the frequencies corresponding to the Si-O stretch. All other frequencies can be discarded. Using the UNIX jot path command, one can pull up a window containing the frequency data output file while viewing the visual vibrational sequence in Spartan. Thus, one can delete the irrelevant frequencies and keep the ones of interest. Once, the relevant frequencies are determined and the irrelevant frequencies are discarded, the remaining frequencies must be formatted in such a way that they can be imported into the Igor software. The best way for formatting purposes is to paste all frequencies into one column and enter the text values for the vibration involved in a column to the left of them. The frequency values must be tabbed one tab length over from the text values, and all other spaces must be deleted.

The next step in the process is to export the data off of the SGI computer and import it onto another computer. This can be done via Fetch software. From the computer downstairs in the Surface Science Preparation lab, one can fetch the appropriate file into a text file which can be stored on the computer downstairs. Then, the file can be imported into Igor. There, a program can be written to convert the data output into a convenient histogram which displays an array of the frequencies(see example program in Appendix B).

Appendix B

Igor Program For Histogram

1

```
!#include <Concatenate Waves>
```

```
macro LoadWaves()
```

```
    DoAlert 0 "Load IR experiment data"
```

```
    LoadWave/T
```

```
    DoAlert 0 "Load SGI generated data as textwave and irfreq"
```

```
    LoadWave/J
```

```
end
```

```
macro ShowWaves()
```

```
    Silent 1
```

```
    killwaves/Z textwave
```

```
    Sort irfreq, irfreq
```

```
    duplicate/o irfreq unitywave
```

```
    unitywave=1
```

```
    Graph0()
```

```
end
```

```
macro EndofThis()
```

```
    Silent 1; PauseUpdate
```

```
    DoWindow/K Graph0
```

```
    killwaves/A/Z
```

```
End
```

```
Window Graph0() : Graph
```

```
    PauseUpdate; Silent 1
```

```
    display apts
```

```
    SetAxis/R bottom 1600,400
```

```
    appendtograph unitywave vs irfreq
```

```
    ModifyGraph mode(unitywave)=1
```

```
    ModifyGraph rgb(apts)=(0,0,0)
```

```
EndMacro
```

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