

# **FTIR Interferometers and Conjugated Polymers**

Levica Chapman  
East Central University

with

Maria Nikolou and David B. Tanner  
Department of Physics, University of Florida

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## **Abstract**

Fourier transform infrared (FTIR) spectrometers are used for optical spectroscopy measurements. They have an interferometer that operates similarly to a Michelson interferometer. The two interferometers used in the lab are Bruker 113V interferometers. Both are mostly used for measuring the reflectance and transmittance of samples. Due to recent experiments by a visiting scientist, it was believed that the response of the detectors of one of the Brukers was not linear. Two to three weeks were spent taking spectra of several beam splitters while changing filters, scanner velocities, and apertures. These spectra were then to be compared and used to determine if the detectors' response is linear or not. Another group made some nanotube films on plastic. These were taken to the Chemistry Dept. to perform electrochemical polymerization on. Polymerization was also performed on ITO (indium tin oxide) coated glass slides to use as a standard for comparison.

## Introduction

Chemists and physicists have been studying conjugated polymers extensively in recent years because of their interesting properties. Conjugated polymers are great electrochromic materials, meaning their optical properties change when a voltage is applied. Known as electrochromism, this ability is a change in the absorbance spectra of the polymers due to electronic excitations in the polymer chain caused by a change in dopant level. The properties of the polymers will allow them to be used in a number of ways such as flat-panel displays, optical switches, electrically tinted window and mirrors, etc. More work is needed to find the best polymer for each application and the best way to assemble the material for widespread production.

I worked under Dr. David Tanner with graduate student Maria Nikolou on a project involving polymers. Maria had some electrodes with nanotubes made by Professor Rinzler's group on which to deposit the polymer poly(3,4-ethylenedioxythiophene) (PEDOT). In order to perform the polymer deposition, we used the Reynolds Polymer lab in the Chemistry building. Before depositing the polymer on the electrodes, we first deposited the polymer onto ITO (indium tin oxide) coated glass slides. We did this because the properties of PEDOT on ITO are well known, and thus we can use it as a standard to compare to the results of the nanotubes as electrodes. If the PEDOT on nanotubes give similar results to those of the PEDOT on ITO, then that means the nanotubes are good electrodes and can be used.

Before depositing the PEDOT in the ITO/glass, we first cleaned the glass slides using the following procedure: we placed the slides in a beaker of acetone, sonicated them for 5-10 minutes using a Branson ultrasonic cleaner, sonicated them with deionized water,

then dried them. Then we put copper tape on one end of the slides to serve as an electrical lead during the polymerization. After attaching the copper tape, we placed the slides and a beaker of the EDOT monomer solution inside the glove box. The monomer-electrolyte solution was composed of the monomer EDOT and an electrolyte TBAP (tetrabutylammonium perchlorate)[1], with ACN (acetonitrile) as the solvent. The glove box is needed to perform the polymerization under an argon environment to keep the samples from coming in contact with air.

We looked at the spectrum of the polymer film in the near infrared (NIR) and visible and ultra violet (VIS-UV) range as we ran a varying voltage (+1.0V: -0.6V) through the polymer. We placed the samples in a monomer-free solution to perform the transmittance measurements. The electric current caused it to become doped (oxidized or reduced), and as it is doped and un-doped we could see the changes in the spectrum as the absorbance of the film increased and decreased. I took the spectra data we obtained while running the voltage through the PEDOT, and graphed the data in Excel. The graph of the spectra in the VIS-UV region is shown in Figure 1, and the graph for the spectra in the NIR region is shown in Figure 2.

Maria will transfer the samples to our lab in a desiccator under vacuum, so as to not expose them to air. Then she will look at the films in the FIR-UV spectrum more with our equipment in the doped and un-doped states. To look at the different states, we have to cause each sample to be in a different state. We can't change the state of the sample unless it's in the solution, so positive voltage is applied to one film to cause it to be p-doped (oxidized), then zero voltage is applied to another polymer film making it neutral. The p-doped state is the most stable state, because if it's exposed to air for a very short time, it

won't be readily affected because it's already oxidized. Three different spectrometers are used for the transmittance measurements: Zeiss 800 MPM microscope photometer, modified Perkin-Elmer 16U monochromator, and Bruker 113V interferometer. The MPM microscope (Figure 3) and Perkin-Elmer both measure from the NIR to VIS-UV, while the Bruker measures in the far infrared (FIR) and mid-infrared (MIR). I used the second Bruker interferometer to check for the detectors' response to see if they're linear or not.

### **Instruments and Experiment**

On the interferometers, we use OPUS, a commercial spectroscopic software program, to take measurements and graph the resulting spectra. Also with OPUS we can change several different parameters in the interferometer electronically, which is very useful when performing measurements under vacuum. I performed measurements on the Bruker, changing such parameters as beam splitters, apertures, velocity of the scanning mirror, and filters on the filter wheel. I changed each of these parameters one at a time, and took the spectrum after each run. I scanned every run with a screen in the filter wheel and without the screen. After collecting all the spectra, I then had to change each spectrum file to a data file. I then transferred the data files by FTP to my office computer. Using a .hpp program, I graphed four similar spectra at a time to compare the change due to certain parameters. I then converted the .hpp plot files to .eps format using 4DOS program and a land2eps command. In the .eps format I was then able to plot the spectra using a program called GSview. Figures 4-6 are some of the spectra that I plotted. The spectra I got are used to check the response of the detectors in the interferometer, MCT and DTGS, and the bolometer to see if the response is linear or not.

The interferometer is divided into mainly four chambers: the source, interferometer, sample, and detector chambers. During measurements, the entire system is under vacuum to avoid H<sub>2</sub>O and CO<sub>2</sub> absorption. The principle of the interferometer is similar to that of the Michelson interferometer. The sources for radiation are the mercury-arc lamp for FIR (20-700 cm<sup>-1</sup>) and the globar (silicon carbide) for the MIR (400-5000 cm<sup>-1</sup>) [3,4]. Light from the source lamp passes through a circular aperture, is focused onto the beam splitter by a collimating mirror, and is then divided into two beams: one reflected and the other transmitted. Both beams are sent to a two-sided mirror, which reflects them back to be recombined at the beam splitter site. Part of the recombined light from the two beams returns to the source, while the other part of the recombined beam is sent into the sample chamber and then goes to the detector. The position of the mirror at time  $t$  is the path difference  $x = 4vt$  [2,3]. “The calibration of the position of the two-sided moving mirror is monitored by an HeNe laser reference interferometer and white-light interferometer”[3]. Figure 7 shows a schematic diagram of the Bruker FTIR and the paths of the light beams.

The bolometer is a detector consisting of three main parts: the detector which has four filters for four different spectrum regions, a liquid helium dewar with a liquid nitrogen dewar around it, and a preamplifier [2]. A schematic diagram of the bolometer is shown in Figure 8. We first filled both dewars in the bolometer with liquid nitrogen, after vacuuming it out, to pre-cool it to 77 K. After the nitrogen cools then helium chamber, we took out the nitrogen. Then we filled the helium dewar with liquid helium that is at 4 K [2,3,4]. This was done so we wouldn't use a large amount of liquid helium, which is much more expensive than liquid nitrogen. After filling it with helium, we kept nitrogen dewar

filled to keep the helium dewar cool. The bolometer then stayed cool for about 22-24 hours. The bolometer on the other Bruker will stay cool 14. If the bolometer starts getting warm before we refill it, we have to let it completely warm up to room temperature and repeat the whole cooling procedure.

## **Conjugated Polymer Theory**

Conjugated polymers, sometimes called  $\pi$ -conjugated polymers, in their neutral state are insulators or semiconductors, but when doped, they can have metallic electrical conductivity. As electrochromic materials conjugated polymers are very interesting to study. Redox electroactive conducting polymers are of particular interest because they are easily electrochemically deposited, spin-coated, or spray-coated as thin films. Prof. Reynolds' group has found that the most promising conducting polymers for use in electrochemical devices (ECDs) are poly(3,4-ethylenedioxythiophene) (PEDOT) and its derivatives. These polymers exhibit a high contrast in the visible spectrum, fast switching times, stability at elevated temperatures and an excellent stability towards electrochemical cycling [5].

Theoretical modeling of conjugated polymers is difficult and several models have been used to explain the many characteristics of them. The chemical units of the monomers and their complexity can change dramatically. Theorists' conjugated polymer models are infinite, defect-free, and isolated one-dimensional chains. But real polymers are limited in length, can have defects and impurities, subtle solid-state interchain effects, and direct interchain chemical bonding. These factors make polymer study quite difficult.

The backbone of conjugated polymers contains carbon (C) atoms. The electronic configuration of the carbon atom is  $1s^2 2s^2 2p^2$ . It has four valence electrons so that a

carbon atom can form four nearest neighbor bonds. Carbon atoms in conjugated polymers have  $sp^2p_z$  hybridization. “Each of the  $sp^2$  C-atoms has three identical  $\sigma$ -bonds, and one remaining  $p_z$  atomic orbital which makes  $\pi$ -overlap with the  $p_z$ -orbitals of the nearest neighbor  $sp^2$  hybridized C atoms. Because of the  $\pi$ -overlap of the atomic  $p_z$ -orbitals,  $\pi$ -states are delocalized along the polymer chain [2].” Conjugated polymers have small band gaps, which cause them to act like semiconductors; they’re easily doped; and when they’re in the doped state, the charge carriers move fairly freely along the polymer chain.

Based on whether or not their ground states are degenerated or not, conjugated polymers can be separated into two groups: degenerate ground state polymers (DGSPs) or non-degenerate ground state polymers (NDGSPs). Some polymers have interchanging single and double bonds along their backbones that gives no energy differences. These are degenerate ground state polymers. Non-degenerate polymers have interchanging single and double bonds along their backbones that give two different energy states; “i.e., there is no degeneracy in the ground state energy for the single-double bond interchange transformation” [2].

Conjugational defects, which cause the cause the interesting EC properties when voltage is applied, can be solitons, polarons, or bipolarons. A soliton is simply a lone charge, either an electron or a positive charge. A polaron is a soliton-antisoliton pair (one charged and one neutral). Bipolarons results from adding an electron to an electron polaron. Solitons and antisolitons are stable in DGSPs that are heavily doped. Polarons are stable in NDGSPs that are slightly doped. And bipolarons are stable in heavily doped NDGSP systems [2].

## Results and Discussion

After plotting the spectra in GSview to print them, I then needed to analyze the plots and determine if the detectors' response for each parameter set was linear or not. I looked at the plots I had made for obvious distortions. I did this because non-linearity causes distortions in the Fourier Transform spectra. I then needed to take ratios of similar parameter sets that were the same, except whether or not the filter wheel was open or if the screen was in. To calculate the ratio I used the command CMP (compare) in the 4DOS program and divided screen by no screen. I graphed the ratio of these versus the frequency. Figures 9-12 show some of these ratio plots. Figure 9 is a ratio of screen to no screen taken with the DTGS detector with parameters: Beam Splitter Mylar 6, Aperture 10mm, Scanning Velocity 12.5 KHz. In the regions  $\sim 300\text{-}700\text{ cm}^{-1}$  and  $\sim 750\text{-}1000\text{ cm}^{-1}$ , because the ratio line is fairly straight around 20%, these regions can be used for this parameter set. It starts to drop off around  $300\text{ cm}^{-1}$ , which is due to the wavelength approaching the size of the slits in the screen. The ratio in Figure 10 is of the two spectra taken with the Bolometer detector, Filter 1, and parameters: Beam Splitter Mylar 12.5, Aperture 10mm, Scanning Velocity 21.022 KHz. There are two small regions in which the ratio line is partially straight:  $\sim 300\text{-}400\text{ cm}^{-1}$  and  $550\text{-}650\text{ cm}^{-1}$ . In these regions, the detector's response is partially linear for this parameter set and this set is okay. Figure 11 is a ratio of screen to no screen taken with the MCT detector with parameters: Beam Splitter-Germanium (Ge), Aperture-10mm, Scanning Velocity - 35.356 KHz. In the frequency range of  $600\text{-}4800\text{ cm}^{-1}$  the ratio has been condensed up to 30%, but since we were expecting 20% for this ratio, then this is non-linear and this parameter set can't be used. The ratio in Figure 12 is bad as well. The spectra for it were taken with the

Bolometer detector, Filter 4, and parameters: Beam Splitter Mylar 50, Aperture 10mm, Scanning Velocity 4.41 KHz. It has no regions in which the ratio line is straight, thus the detector's response for this parameter set is very non-linear and this set is also useless.

I collected a complete set of data from the Bruker, but due to time constraints, I was unable to plot and analyze all the spectra. Someone else will finish the project to determine the optimization of the detectors. Some of the spectra may need to be taken again to check that the first ones were correct, due to possibility of human error. And more analysis should be done on the spectra ratios that have been plotted to check to see if my analysis is correct.

## References

- [1] M. C. Morvant, J. R. Reynolds, *Synthetic Metals* **92**, 57-61 (1998).
- [2] J. Hwang, Ph.D. Thesis, University of Florida (2001).
- [3] Nacira Tache, Ph.D. Thesis, University of Florida (1997).
- [4] F. Gao, Ph.D. Thesis, University of Florida (1992).
- [5] I. Schwendeman, J. Hwang, D. M. Welsh, D. B. Tanner, and J. R. Reynolds, *Adv. Mater.*, **13**, 634 (2001).

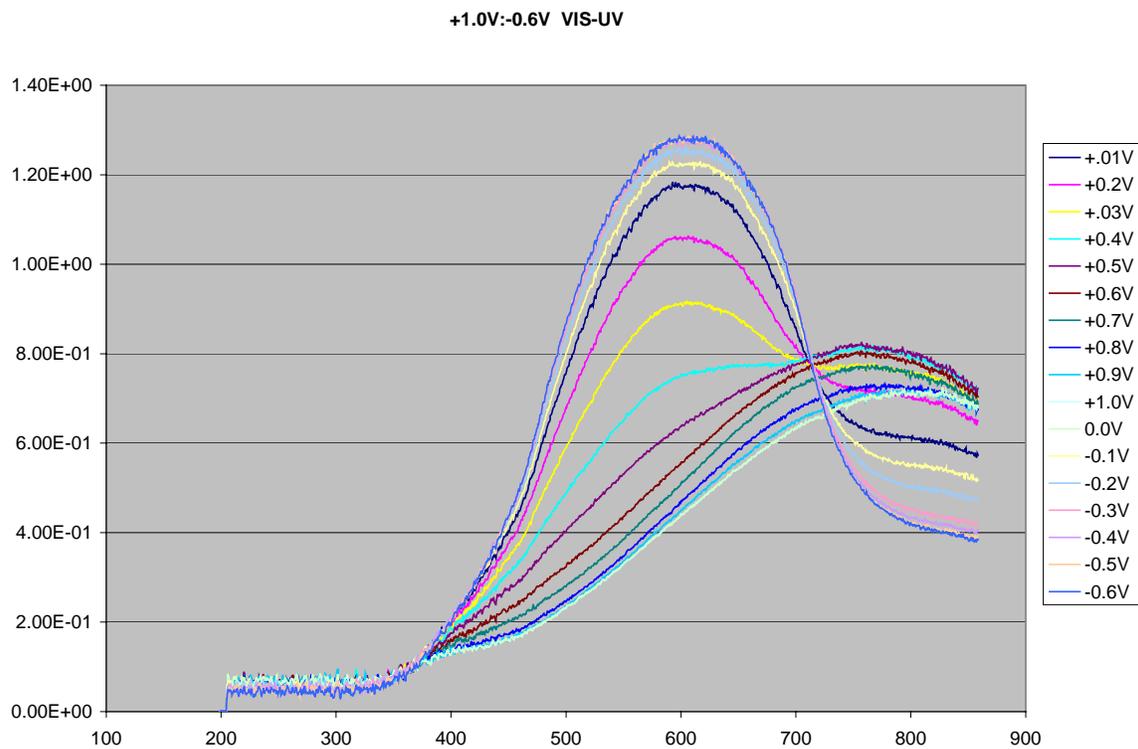


FIGURE 1: Spectra of PEDOT on ITO in the VIS-UV region when voltage of +1.0V to -0.6V is applied.

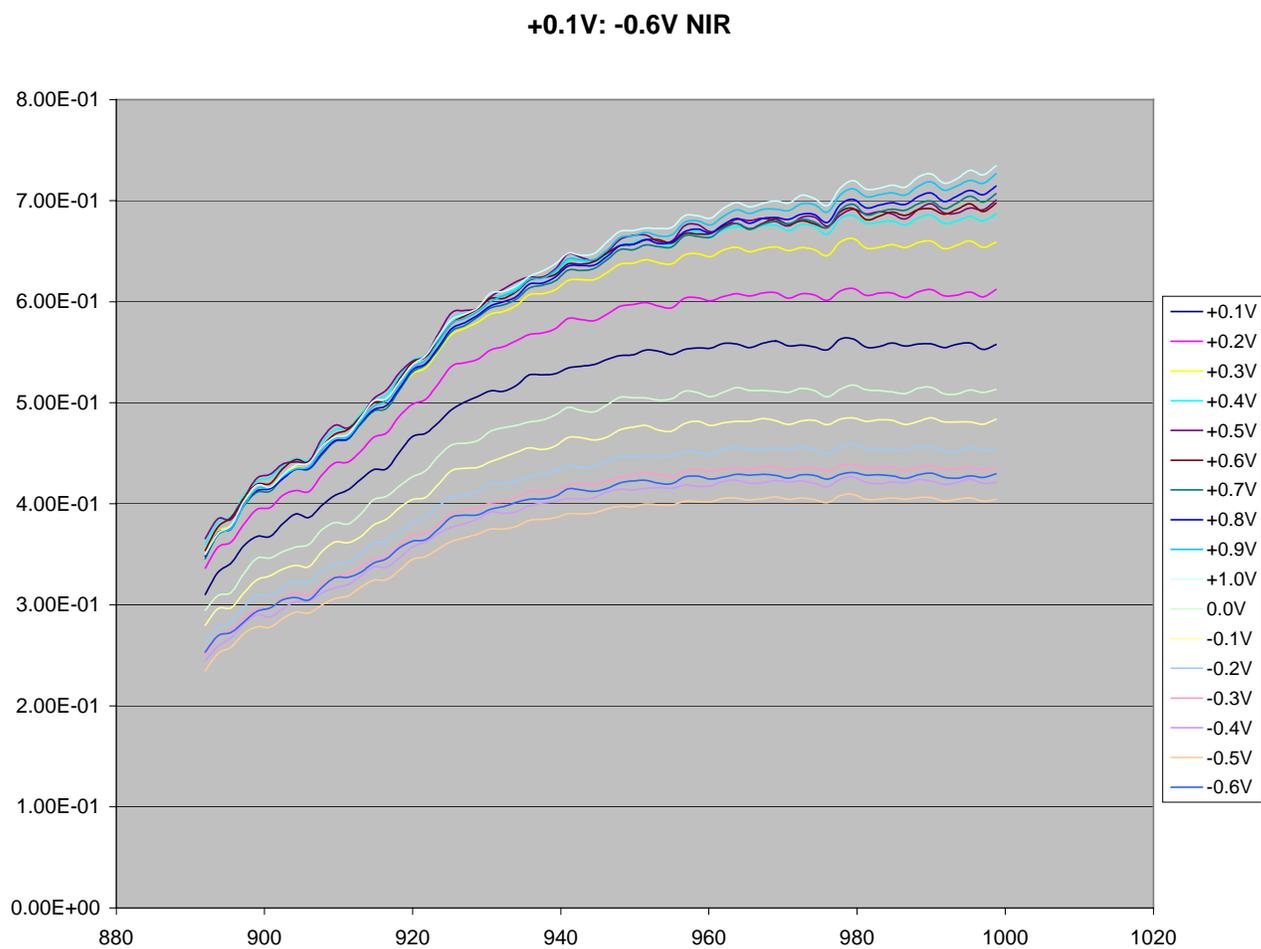
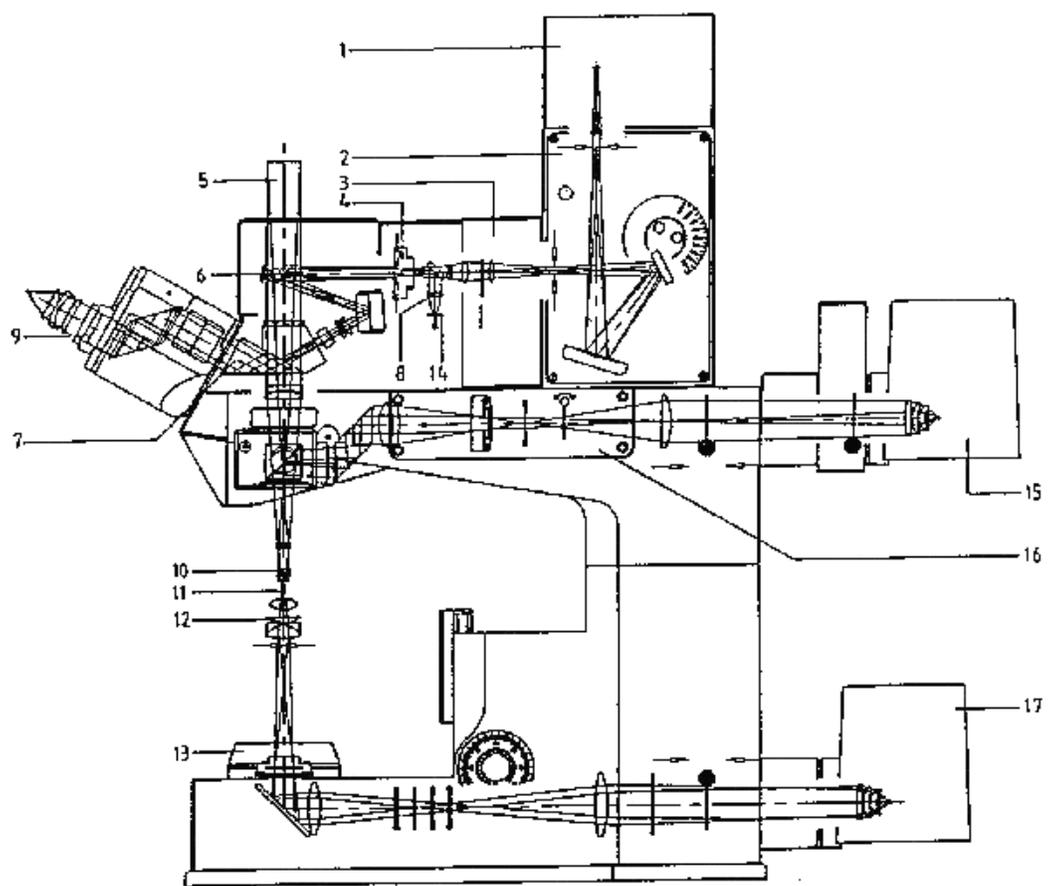


FIGURE 2: Spectra of PEDOT on ITO in the NIR region when voltage of +1.0V to -0.6V is applied.



- |   |   |
|---|---|
| 1 Detector unit PMT with/without PbS cell           | 10 Objective  |
| 2 Grating monochromator                             | 11 Specimen   |
| 3 Motorized filter changer                          | 12 Condenser  |
| 4 Intermediate image plane with measuring diaphragm | 13 Luminous field diaphragm for transmitted light             |
| 5 TV/photo port                                     | 14 Pilot lamp   |
| 6 Switching mirror TV/measurement                   | 15 HBO illuminator with fast shutter                          |
| 7 Beam splitter in photometer tube                  | 16 Aperture and luminous field diaphragms for reflected light |
| 8 Image-forming beam path of measuring diaphragms   | 17 Halogen illuminator with light shutter                     |
| 9 Intermediate image plane in eyepiece              |   |

FIGURE 3: Schematic drawing of the beam paths of MPM 800 microscope photometer for transmitted and reflected light.

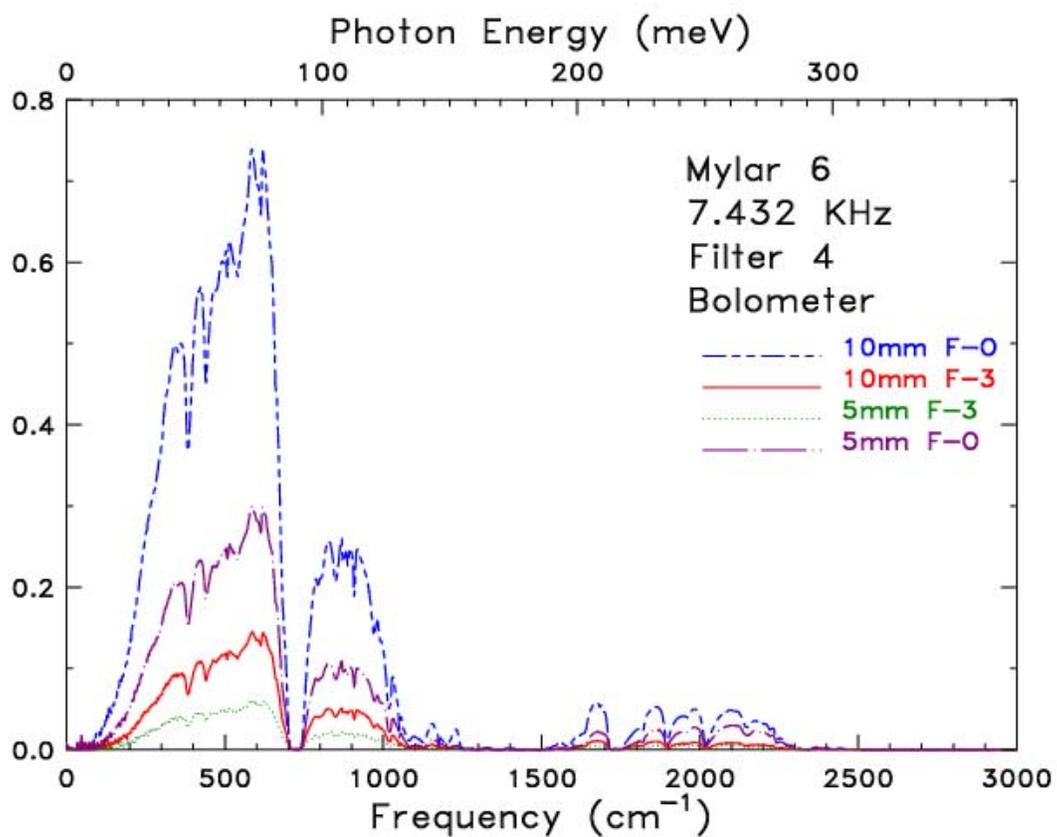


FIGURE 4: Plot of four spectra taken with the Bolometer Filter 4, parameters: Beam Splitter- Mylar 6, Scanning Velocity-7.432 KHz, Aperture-10mm, 5mm, Filter (F)-Open, Screen (3).

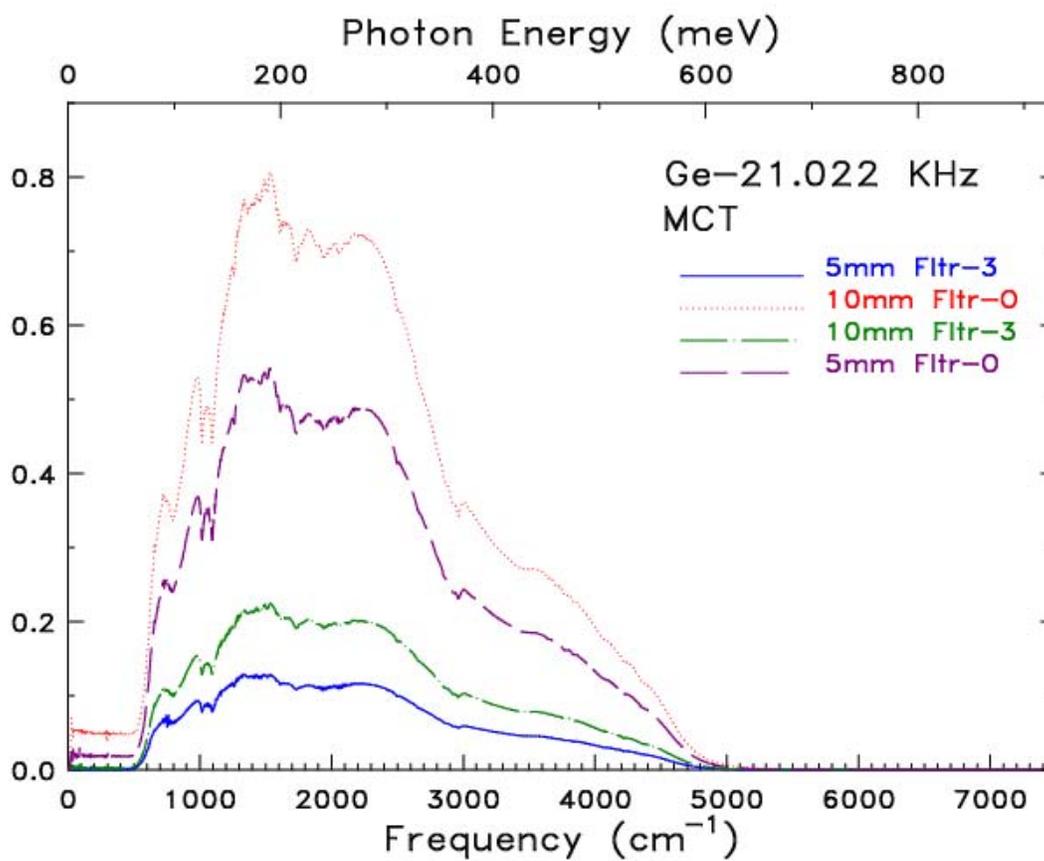


FIGURE 5: Plot of four spectra taken with the MCT detector, parameters: Beam Splitter-Ge, Scanning Velocity-21.022 KHz, Aperture-10mm, 5mm, Filter (F)-Open, Screen (3).

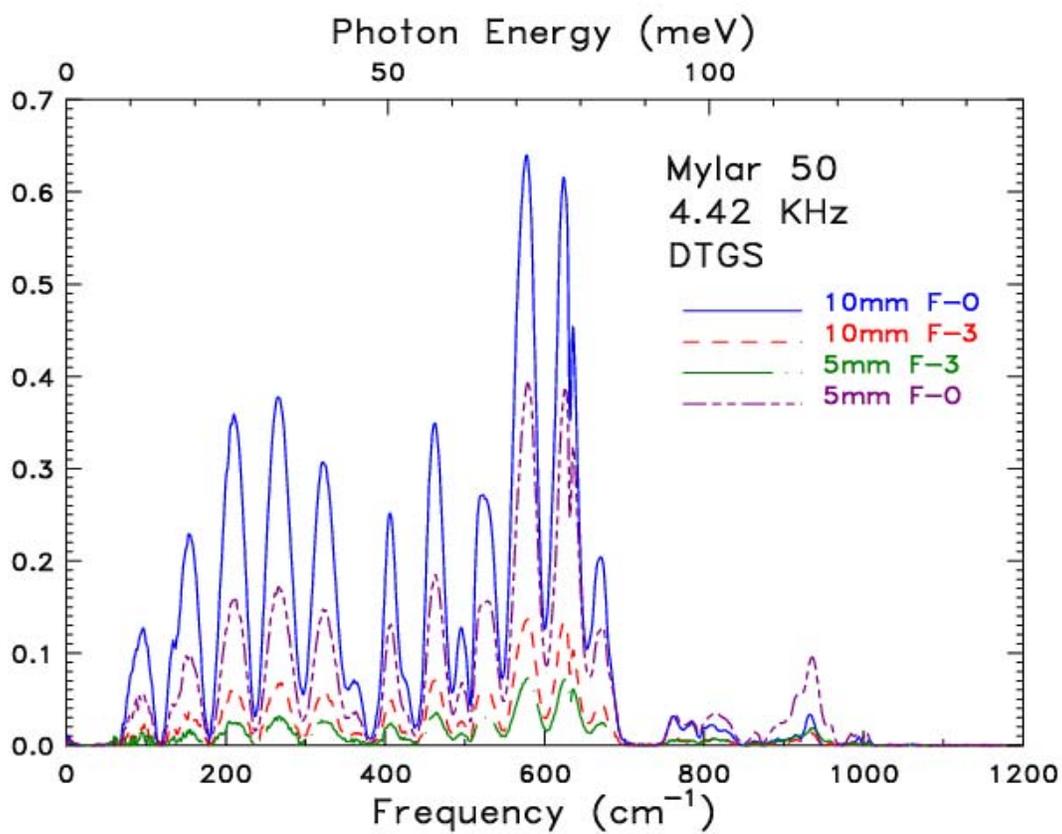


FIGURE 6: Plot of four spectra taken with the DTGS detector, parameters: Beam Splitter- Mylar 50, Scanning Velocity- 4.41 KHz, Aperture-10mm, 5mm, Filter (F)-Open, Screen (3).

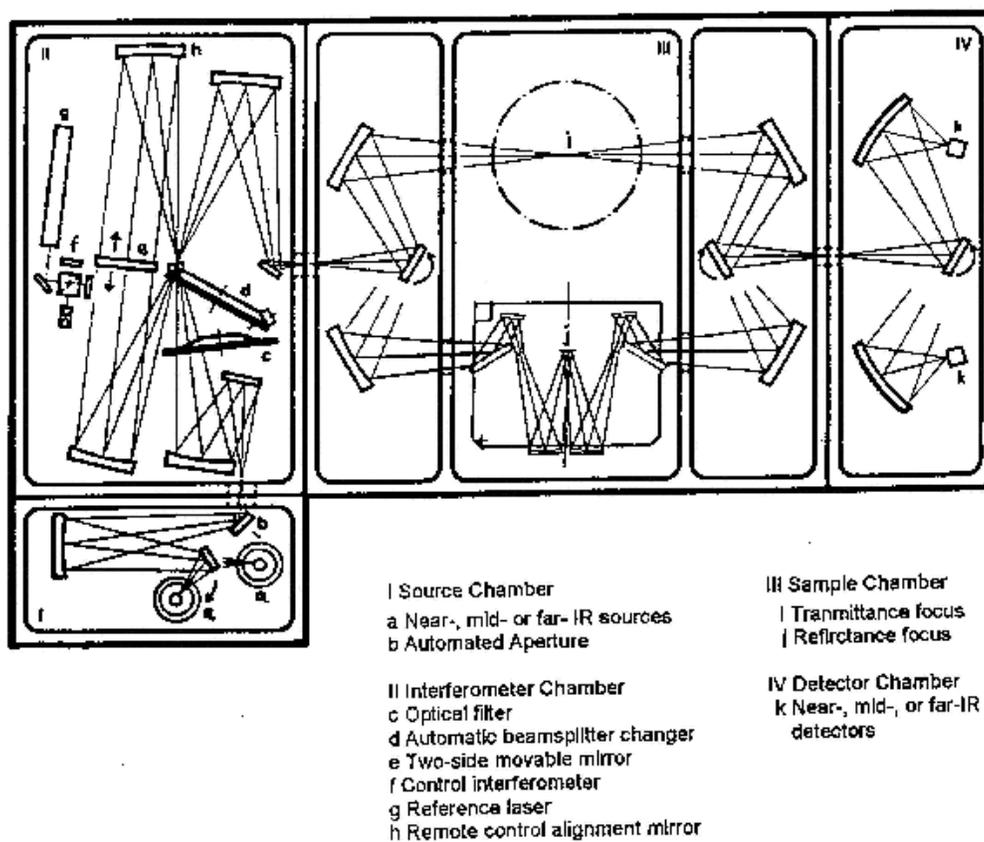


FIGURE 7: Schematic drawing of Bruker 113v FTIR spectrometer.

## DEWAR, MODEL HD-3 OUTLINE SKETCH

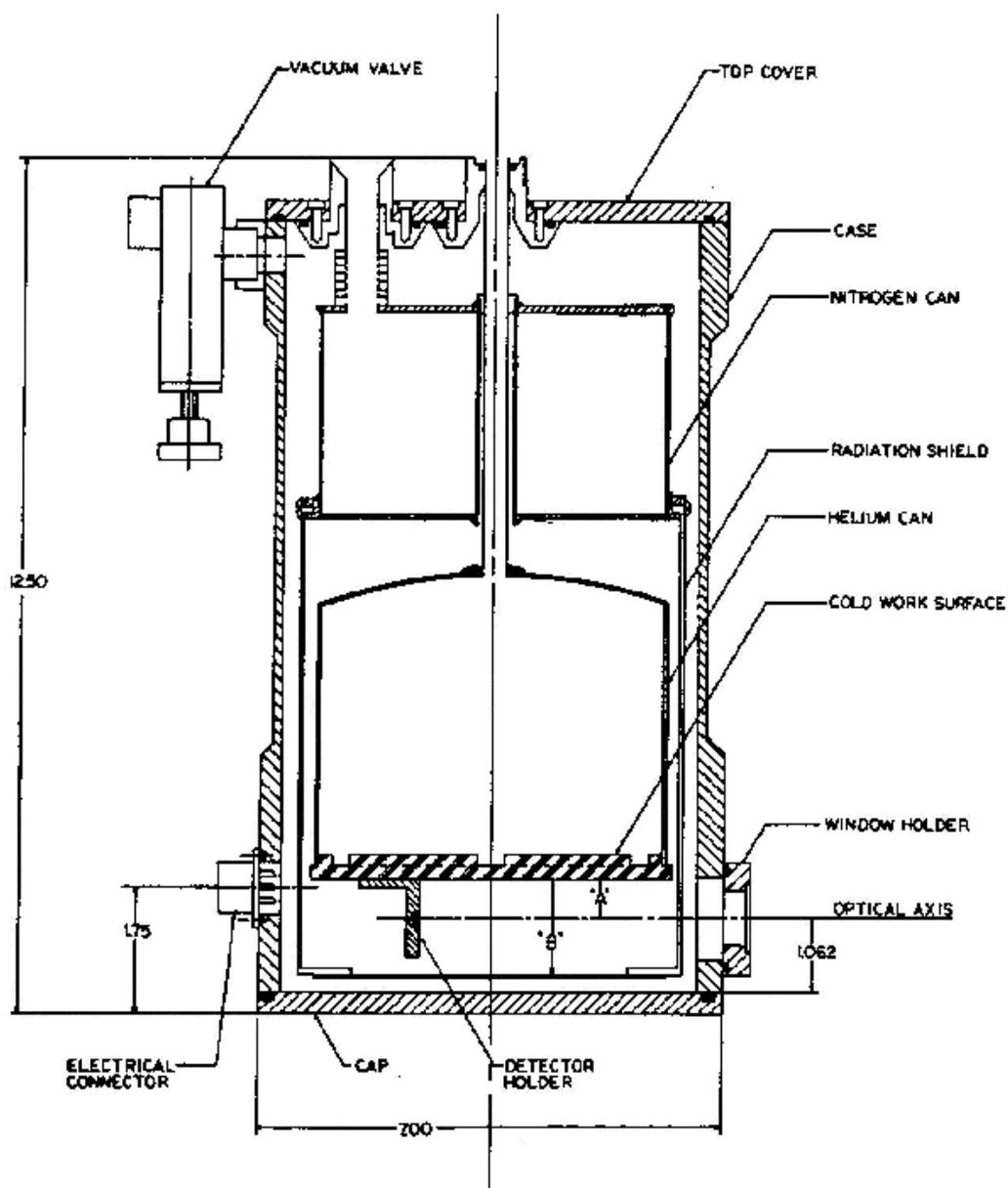


FIGURE 8: Schematic diagram of the bolometer. Dimensions are in inches.

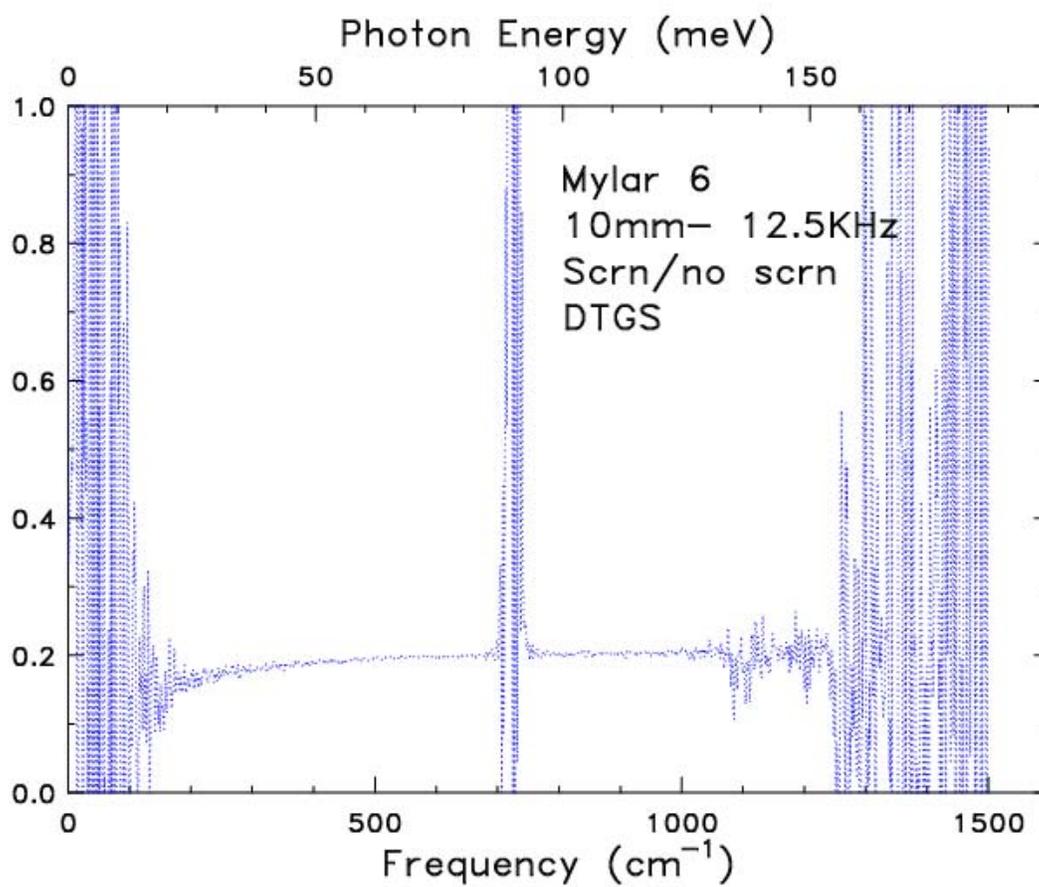


FIGURE 9: Graph of Ratio of Screen to No Screen taken with DTGS detector, parameters: Beam Splitter Mylar 6, Aperture 10mm, Scanning Velocity 12.5 KHz.

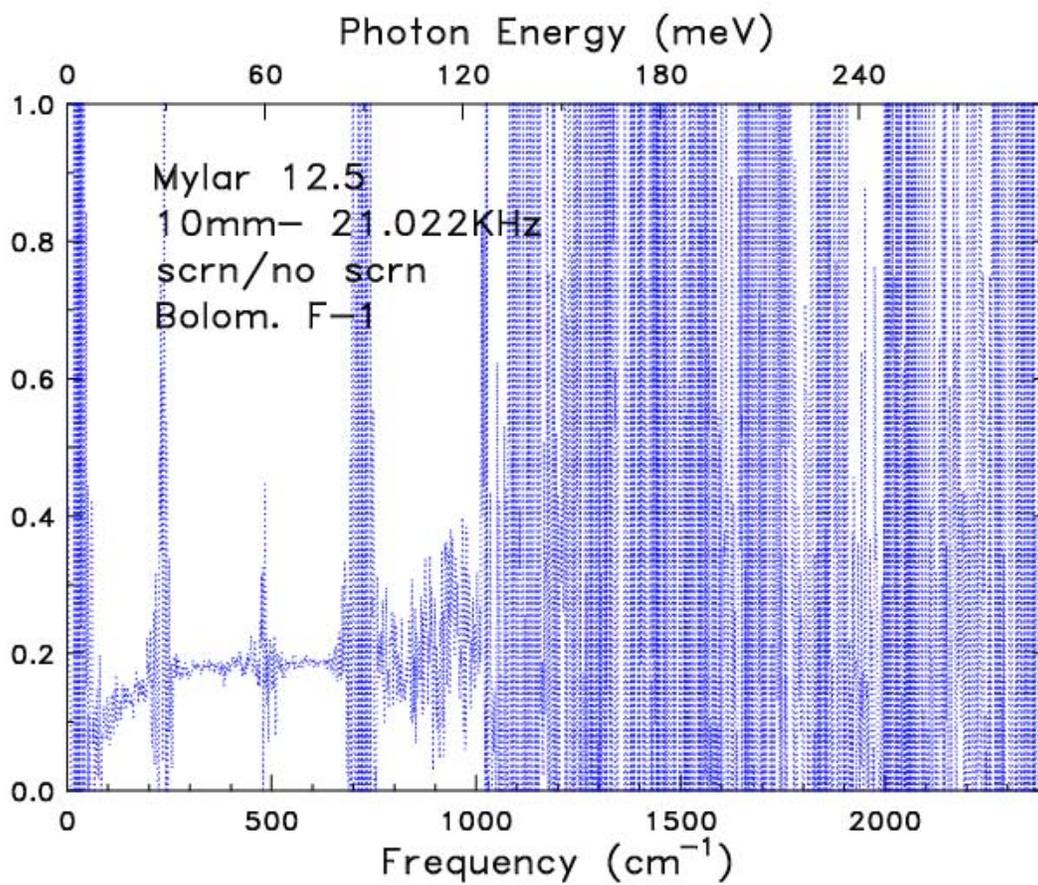


FIGURE 10: Graph of Ratio of Screen to No Screen taken with Bolometer detector, Filter 1, parameters: Beam Splitter Mylar 12.5, Aperture 10mm, Scanning Velocity 21.022 KHz.

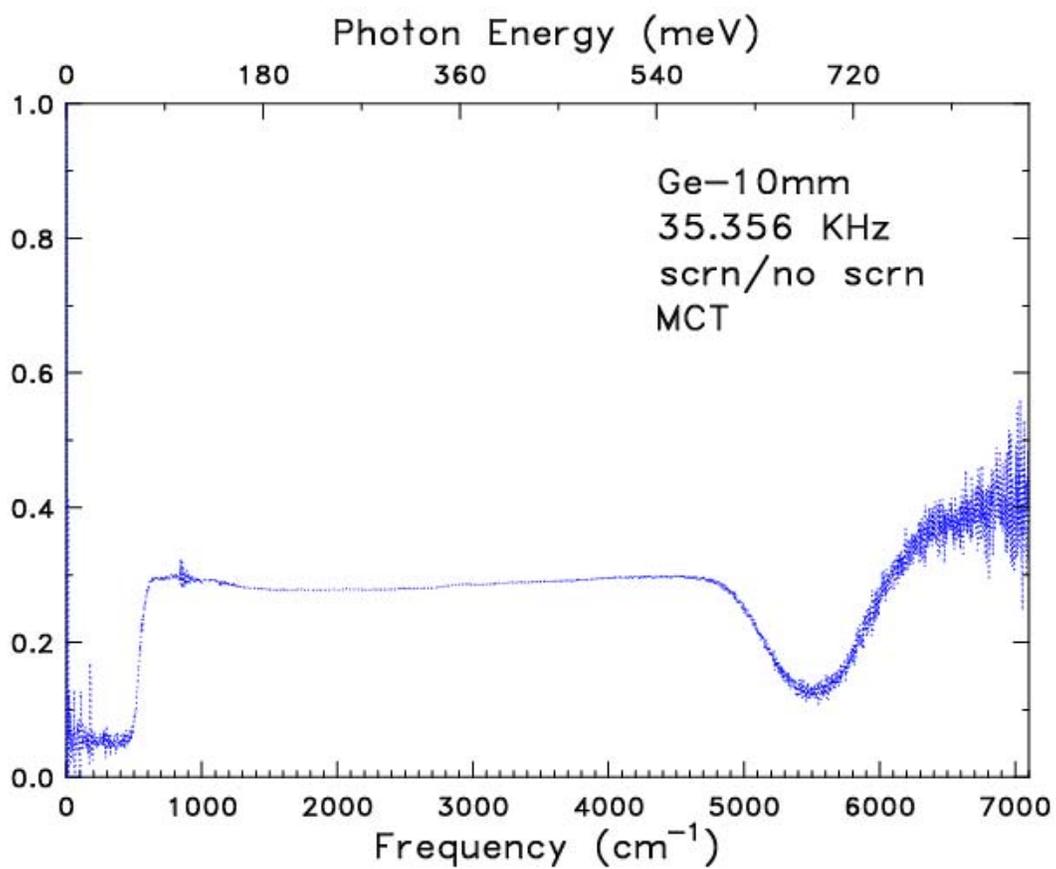


FIGURE 11: Graph of Ratio of Screen to No Screen taken with MCT detector, parameters: Beam Splitter Ge, Aperture 10mm, Scanning Velocity 35.356 KHz.

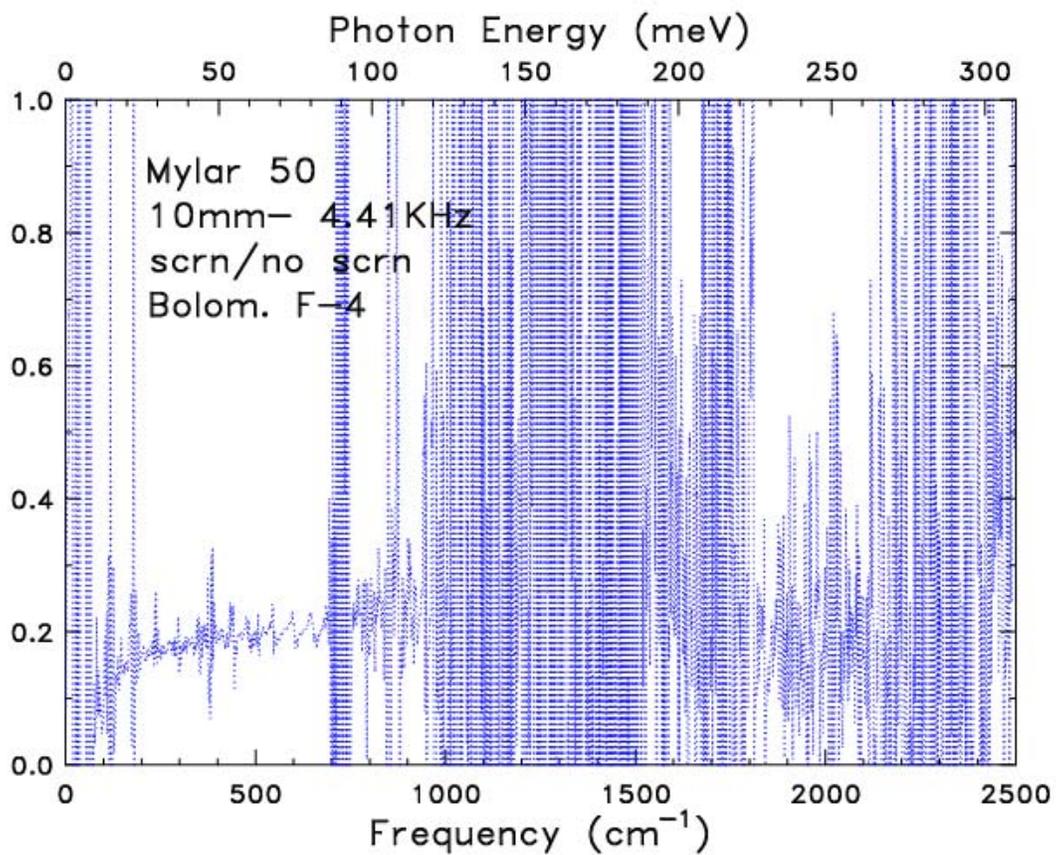


FIGURE 12: Graph of Ratio of Screen to No Screen taken with Bolometer detector, Filter 4, parameters: Beam Splitter Mylar 50, Aperture 10mm, Scanning Velocity 4.41 KHz.