

The Cryogenic Buffer Gas Beam and the Spectroscopy of Carbon Clusters

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Thesis directed by Prof. Heather Lewandowski

Abstract

Cryogenic buffer gas beams are a useful source of cold molecules to be used in cold chemical experiments. The goal of this experiment is to create a functional buffer gas beam that can be adapted to source a variety of molecules. The apparatus is explained. Carbon clusters are useful initial molecules to study while the beam is in its preliminary phases. This thesis includes a literature review on previous experiments involving carbon clusters in order to gather the necessary information to identify spectral peaks and create a comparison benchmark for the products of our buffer gas beam.

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Chapter 1

Cold Chemistry

1.1 Introduction

Cold chemistry reduces the complexity usually present in room temperature experiments. Cooling chemical reactions to the kelvin regime allows the study of aspects of reactions that normally occur too quickly to be observed, such as the existence of reaction intermediates.² One of the core struggles of cold chemistry is creating a cold source of the desired molecules. Creating cold molecules is more challenging than simply cooling atoms because, instead of solely translational kinetic energy, molecules have internal degrees of freedom and thus rotational and vibrational kinetic energy. It is possible, but difficult, to cool the molecules directly by laser cooling or by assembling the molecules with already cooled atoms.³ Incredibly low temperatures can be reached through these methods, but only for limited types of molecules. A more versatile approach is instead to focus on cooling molecules via thermalization with a cold, chemically inert medium, such as a noble gas, and then trap the desired molecules inside. These types of methods can only reach temperatures of a few kelvin compared to the microkelvin of other experiments, but they have the distinct advantage of being able to cool most any molecule through collisions with the medium.

1.2 Supersonic Expansion Beam

Supersonic expansion is a method of cooling a gas by forcing it from a high-pressure region through a nozzle into a vacuum. As the gas expands into the low-pressure environment, it cools through constant enthalpy expansion. Seeding the gas with molecules of interest results in a source of cold molecules traveling at high velocities, typically 300-600 m/s.¹ The gas continues to expand until there are no longer any collisions in the beam, so the window of time for the gas to cool the molecules is limited to a few microseconds²³. The high exit velocity is also difficult to work with. Spectroscopically probing the beam is challenging because of how briefly an individual molecule is in the line of sight of the spectrometer, and trapping the molecules while preserving their temperature is nearly impossible.⁴ These apparatuses are still quite popular because they are relatively easy to create because most of their operation can occur at room temperature.

1.3 Buffer Gas Beam

A cryogenic buffer gas beam source achieves a lower exit velocity at the cost of a more technically involved apparatus. In this more intuitive method, a buffer gas flows through a cell that is held by a cryocooler at a temperature very near to the gas's freezing point. The gas cools inside the cell to the kelvin regime and is seeded with the molecule of interest through any convenient method of insertion. This thesis will focus on the method of laser ablation. These molecules enter the buffer gas hot, typically between 300 and 10,000 K,¹ but the gas to molecule ratio is kept such that the molecules become entrained in the gas beam and quickly thermalize

with the surrounding gas without significantly heating it. This strategy allows the seeded molecules to interact with the buffer gas for longer, on the order of several milliseconds, thus they efficiently cool to the temperature of the gas¹. The temperature is limited mostly by the capabilities of the cryocooler itself.

Chapter 2

Cryogenic Buffer Gas Beam Source

2.1 Motivations

The purpose of this project is to create and investigate the properties of a buffer gas beam with the goal of creating a source of cold vanadium oxide, VO, or perhaps the radical methylidyne, CH. VO, like many transition metal oxides, is a useful catalyst,²⁴ and CH is a molecule abundant in the interstellar medium (ISM)¹⁶ and significant to simple combustion reactions,¹⁸ so both molecules warrant close study. In its current stage, we cannot be certain of the density or composition of the beam's products without observing the beam directly, and need a method to evaluate the quality of the apparatus. This is achieved by freezing the beam on a deposition window and probing the resulting crystal with IR spectroscopy. The crystals spectrum reveals which molecules are trapped in the crystal, and thus which molecules are being produced and cooled by the CBGB. The molecules of interest that are being investigated for this thesis are small carbon clusters. This study will help us characterize the beam, and may result in some insight into carbon cluster chemistry.

2.1.1 Motivation for Studying Carbon Clusters

Carbon clusters were chosen as the initial study molecule because they are convenient molecules to research while the details of the apparatus are being

perfected. For instance, they are very easy to produce. The ablation precursor, graphite, is a commonplace substance that is cheap, solid at room temperature, and safe to work with. Creating clusters through ablation requires little energy per pulse of the laser to yield a large number of molecules. They are also easy to detect. It's easy to induce a dipole moment in long, floppy molecules (that is, they have a relatively high absorption cross section or IR intensity), so the long chains of carbon atoms create a very strong signal in IR spectroscopy⁵. Additionally, their spectrum exists in a region that is relatively free of noise caused by CO₂, H₂O, or hydrocarbons in the air or in the system. These factors make carbon clusters a reliable, easy to work with source of signal.

2.2 Apparatus

Our apparatus employs neon as the buffer gas, and laser-ablated carbon as the molecules of interest. Ablation is the process of irradiating a solid with a pulsed laser in order to remove material by evaporating or sublimating it. The ablation frees some distribution of carbon clusters from the graphite target, which are then entrained in the neon flowing through the cell, which is held at ~40K. The neon exits the cell and freezes to a CaF₂ window held at ~5K with the carbon clusters trapped inside. The window is visible to the beam of an IR spectrometer, which measures the IR vibrational spectrum, the unique fingerprints of the molecules contained within.

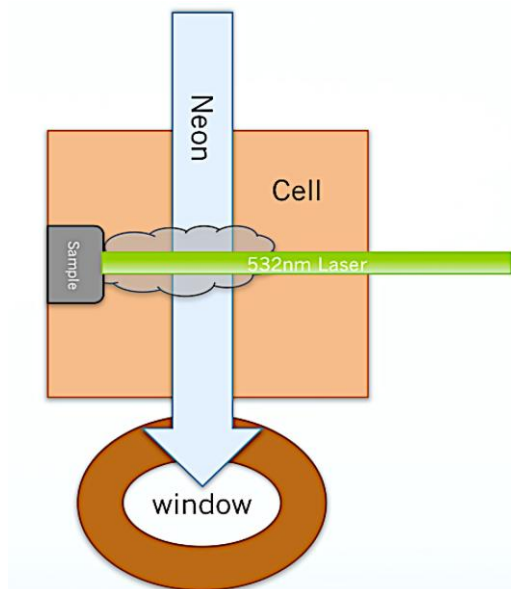


Fig 2.2: cartoon of a CBGB

2.3 Thermalization

The apparatus is cooled by a Sumitomo SRDK series two-stage cryocooler, which has the capacity to cool the first stage to 40K and the second stage to 4K. The cryocooler works by using gaseous helium to cool the apparatus in much the same way a standard refrigerator uses tetrafluoroethane. The neon gas is initially cooled by coupling its piping to the first stage of the cold head. It then flows into the cell where it cools further by colliding with the walls. The carbon is then introduced to the beam and allowed to thermalize. When the carbon is ablated, the molecules leave the surface of the graphite on the order of 1000K, but quickly cool to the temperature of the neon through a few collisions with the gas atoms. The ratio of neon to carbon is kept low enough that the introduction of the superheated molecules does not significantly heat the neon.

2.4 Spectroscopy, Matrix Isolation, and Annealing

In order to probe the contents of the beam, it is frozen onto a window then spectroscopically analyzed. The neon is aimed at a CaF_2 window held at $\sim 5\text{K}$, well below neon's freezing point at 24.56K . CaF_2 was chosen because it has a high transmission in the IR region. The neon freezes, and all of the entrained carbon clusters become trapped inside the solid neon matrix. The window is situated such that it intersects the neon beam coming from the cell and the IR beam of a Nicolet iS50 FTIR spectrometer as illustrated below in figure 2.3.

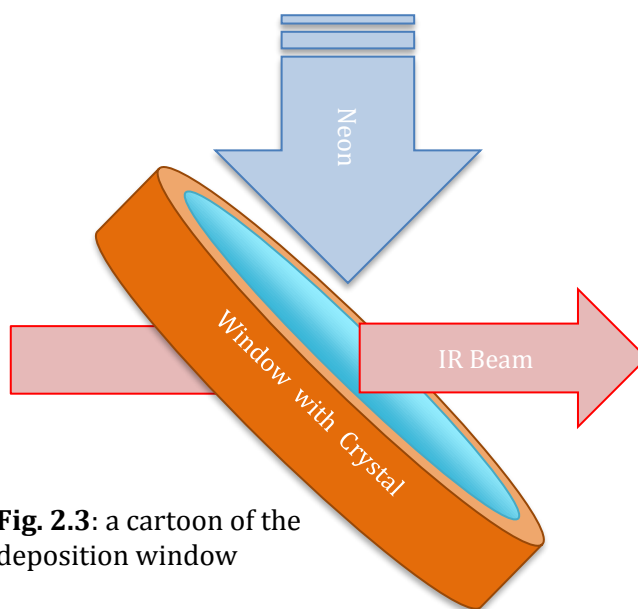


Fig. 2.3: a cartoon of the deposition window

The spectrographic properties of matrix isolation will be detailed later in Section 3.4. In short, the spectrum of a molecule trapped in rare gas matrix varies by a small amount from its gas-phase spectrum, so the molecules within can still be identified.² The crystal can be sublimated by heating the window with an attached resistor. The resistor can also be used to anneal the crystal, that is heat the crystal to near its sublimation point. This doesn't sublime the crystal, but instead causes the

domains to recrystallize, and during this process some of the isolated molecules migrate and react with one another. Evidence for these reactions can be observed in the changing set of peaks in the spectrum. This mechanism can be used to study the dynamics of carbon clusters reacting in matrix, and will later be used to study the reactions of co-deposited molecules, such as CH deposited together with O₂.

2.5 Ablation

The ablation process is achieved by a focused Nd:YAG laser. The laser outputs 2mJ, 532nm pulses at 30Hz, which is then chopped to 10Hz by blocking two out of three pulses. This mechanism is adjustable to chop the laser to any frequency $\frac{30\text{Hz}}{n}$, where n is an integer in the range 3-10. The beam is focused onto the graphite target by a 1" diameter lens with focal length of 20cm. The beam of the laser scans across the sample every 25 seconds in order to avoid depleting a particular point on the graphite.

2.5.1 Laser Scanning Motivation

Early experiments without a scanning mechanism showed an asymptotic growth of the peak heights with time as show in figure 2.5.1a, which suggested that we were reaching a maximum quantity of carbon tapped in the crystal.

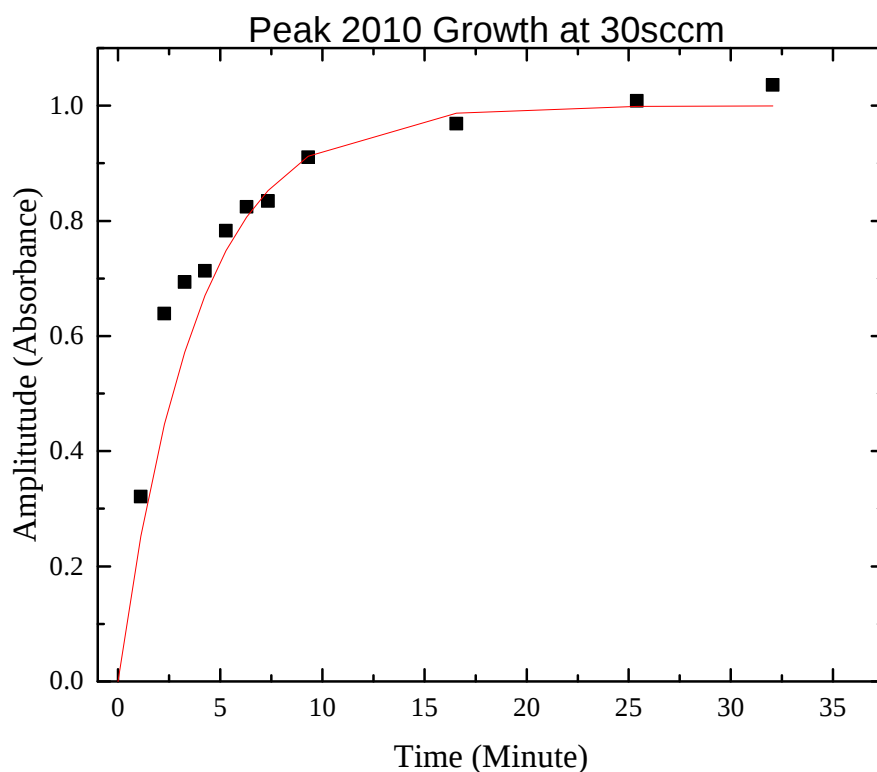


Fig. 2.5.1a: A plot of the growth of the ν_6 C₉ peak at 2010 cm^{-1} with respect to deposition time.

This was either caused by approaching a maximum crystal thickness on the window, or by somehow depleting the point on the graphite disk such that it was no longer producing carbon clusters. Moving the laser to a different point on the target during deposition and observing the resulting spectra easily tested which of these hypotheses was more likely true. Evident in figure 2.5.1b, moving the laser resulted in a significant increase in peak height past the asymptote the peak was approaching before the adjustment. This suggests that the graphite was indeed being depleted.

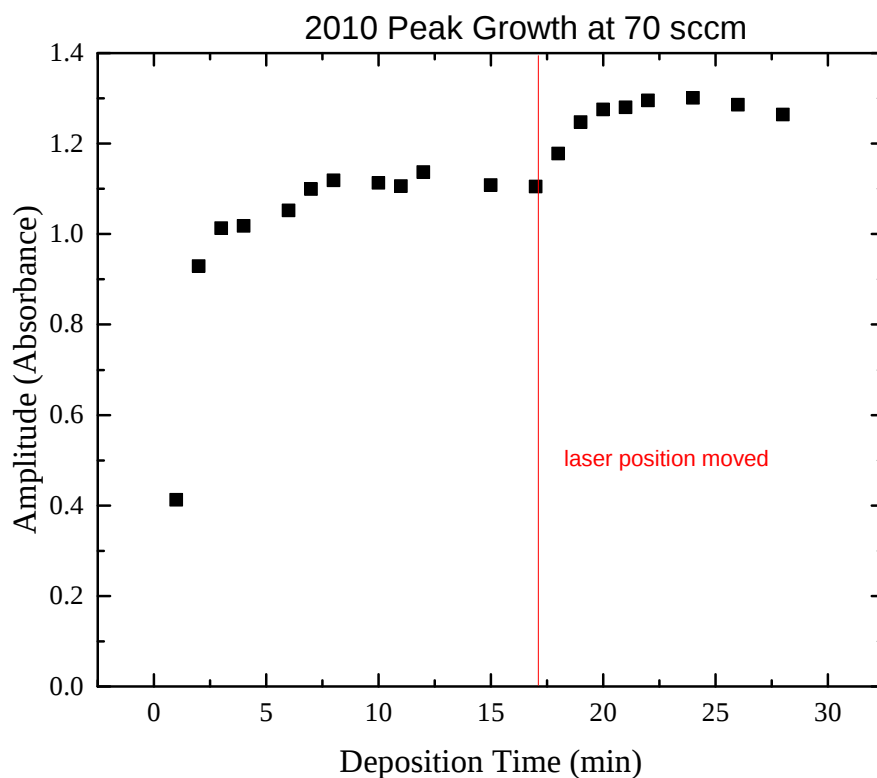


Fig. 2.5.1b: Another plot of the growth of the ν_6 C₉ peak, this time with the laser moved mid-deposition.

The scanning mechanism was proposed to solve the depletion problem by constantly moving the laser across the graphite target, thus taking advantage of as much “fresh” graphite as possible.

2.5.2 Mechanism

It is rather difficult to put moving parts inside of a vacuum chamber and maintain the temperatures and pressure desired, so the mechanics of the scanning all must occur outside the chamber. This was achieved by coupling the fine-

adjustment screws of final mirror before the chamber to a pair of Arduino-controlled stepper motors as shown in figure 2.5.2. The two motors control the horizontal and vertical position of the laser beam on the target, so by cycling them through a preetermined sequence of adjustments, the laser scans a two-dimensional path across the target.

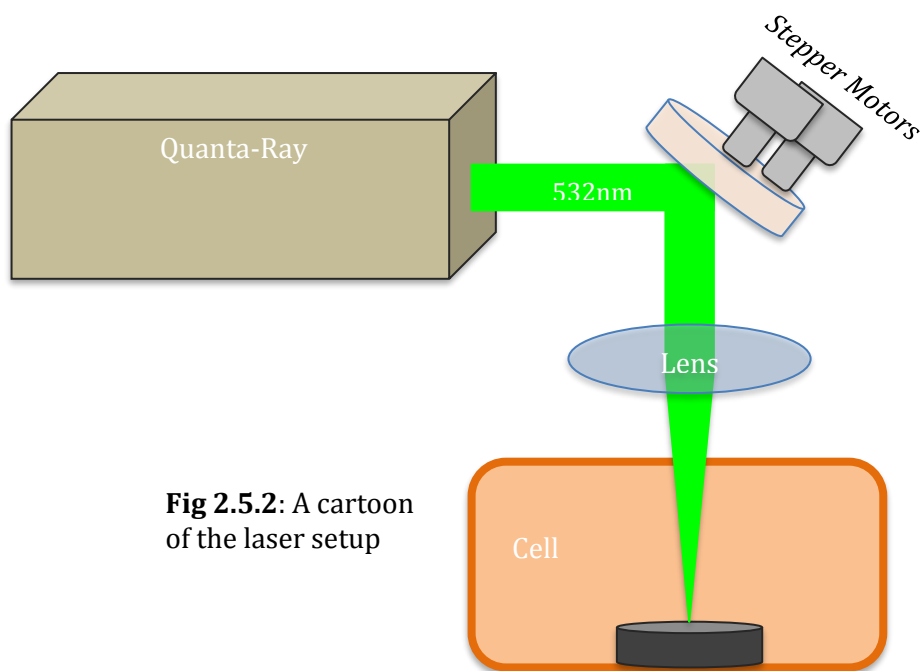


Fig 2.5.2: A cartoon of the laser setup

2.5.3 Calculation

The goal of the scanning mechanism is to move the laser in a pattern across the graphite target with an arbitrary number of scans as illustrated in the figure 2.5.3a.

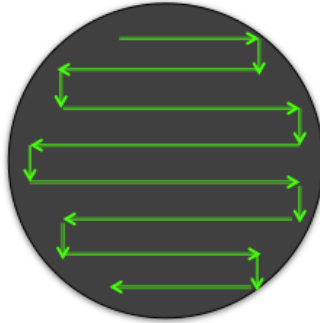


Fig. 2.5.3a: A cartoon of the laser scanning across the graphite

In order to do this in a predictable, one must derive the function that translates Cartesian coordinates on the disk to a rotation on a knob of the mirror. This function is determined by the trigonometry of the mirror mount, and mirror setup.



Fig. 2.5.3b: An image of a mirror in a fine-adjustment kinematic mirror mount

The mirror mount is pictured above. The angle of the mirror is adjusted by turning the screws, which changes how much they protrude past the base. The two screws and the mirror define a triangle as show in figure 2.5.3c.

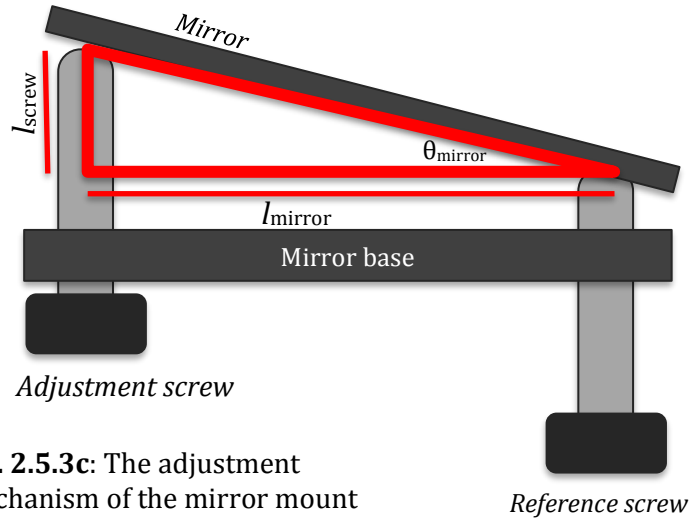


Fig. 2.5.3c: The adjustment mechanism of the mirror mount

From this triangle it's clear that

$$\theta_{mirror} = \tan^{-1} \left[\frac{l_{screw}}{l_{mirror}} \right] \quad \text{Eqn(1)}$$

Where l_{screw} is the difference in lengths that the adjustment and reference screw protrude. The relation of the length that each screw protrudes is proportional to the angle the screw has been rotated through multiplied by the pitch. That is

$$g \phi_{screw} = l_{screw} \quad \text{Eqn(2)}$$

where g is the pitch in mm/rad and ϕ_{screw} is the angle of the adjustment screw measured from when it protrudes the same amount as the reference screw. Any adjustment of the θ_{mirror} will change the angle of the beam by twice as much. θ_{beam} is defined as the angle between the path to the center of the graphite disk and the path the laser is taking as shown below.

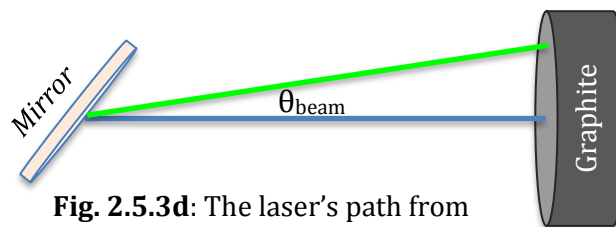


Fig. 2.5.3d: The laser's path from the mirror to the target, no lens

Upon striking the mirror the beam gets reflected through twice the angle it makes with the mirror's normal vector as shown in figure 2.5.3e

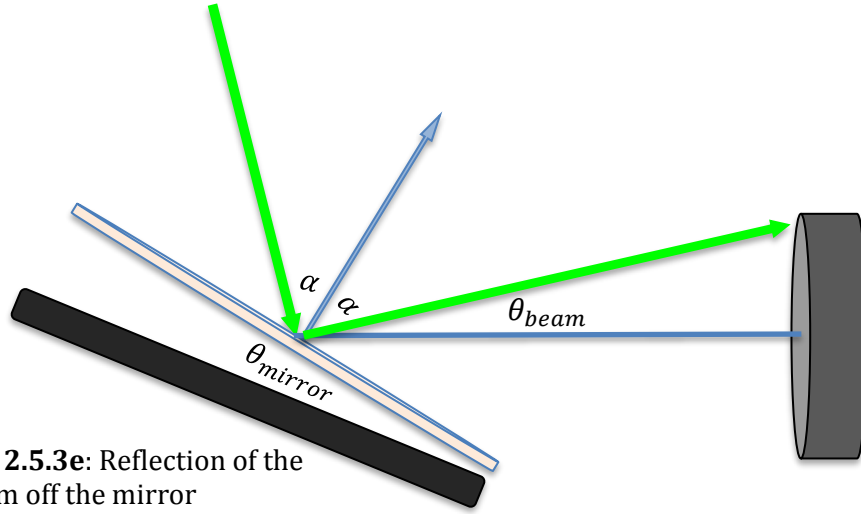


Fig. 2.5.3e: Reflection of the beam off the mirror

θ_{beam} can be expressed in terms of θ_{mirror}

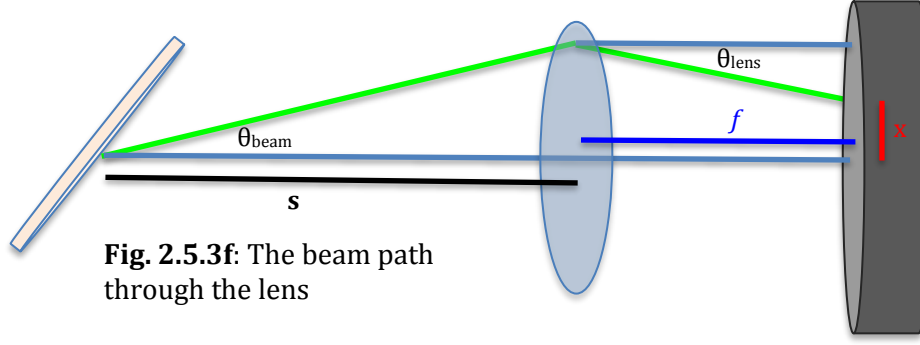
$$\theta_{beam} = 2(\theta_{mirror} - \theta_{0-mirror}) \quad \text{Eqn(3)}$$

where $\theta_{0-mirror}$ is the angle of the mirror required to center the beam on the disk.

$l_{0-screw}$ and $\phi_{0-screw}$ are the associated lengths and angle of the screw respectively.

$$\theta_{0-mirror} = \tan^{-1} \frac{l_{0-screw}}{l_{mirror}} = \tan^{-1} \frac{g \phi_{0-screw}}{l_{mirror}} \quad \text{Eqn(4)}$$

We have yet to take into account the lens. Its purpose is to focus the beam on the graphite, but it will also refract the beam towards the centerline of the lens as shown in figure 2.5.3f.



From this figure it's clear that $x = s \tan \theta_{beam} - \tan \theta_{lens}$. Using Snell's law, which assumes the small angle approximation $\tan \theta \approx \theta$, the relation $\theta_{lens} = \frac{\theta_{beam}}{M}$ arises, where M is the magnification of the lens given by $M = \frac{f}{s-f}$, f being the focal length of the lens. This leads to the result Eqn(5) below

$$x = s \theta_{beam} - \frac{f}{M} \theta_{beam} = \left(s - \frac{f}{M} \right) \theta_{beam} = \left(s - \frac{f}{\frac{f}{s-f}} \right) \theta_{beam} = f \theta_{beam}$$

assuming the small angle approximation, $\tan[\varphi] \approx \varphi$. This approximation is accurate to 1% error provided the angle is less than 10° . In our case that means the approximation is valid for θ_{beam} as long as the distance from the final mirror is more six times the radius of the lens. The lens is 1" in diameter and the distance between it and the mirror is ~ 8 " so the approximation holds.

We now have enough information to completely determine the position of the laser based off of the angle of the screws combining Eqn 1, 2, 3, 4, & 5 yields the equation

$$x = 2f \left(\tan^{-1} \left[\frac{g \phi_{screw}}{l_{mirror}} \right] - \tan^{-1} \frac{g \phi_{0-screw}}{l_{mirror}} \right)$$

which, upon solving for ϕ_{screw} , yields

$$\phi_{screw} = \frac{l_{mirror}}{g} \tan\left[\frac{x}{2f} + \tan^{-1} \frac{g \phi_{0-screw}}{l_{mirror}}\right]$$

The derivation for y is identical. Now, provided the dimensions of the mirror mount, the pitch of the screws, and the focal length of the lens, any desired position on the target can be mapped to a position of the two adjustment screws.

We can now return to the desired path. The goal is that each successive scan to be as close to the previous scan as possible without overlapping, so we need to know the diameter of the beam as it strikes the target. The beam passes through a lens with the target positioned at the focal length, but the beam does not focus down to an infinitesimal point, as classic ray tracing would have us believe. The laser is best approximated as a Gaussian beam i.e. a beam that has a Gaussian intensity profile, $E = E_0 \text{Exp}(-\frac{r^2}{r_0^2})$, where E_0 is the max strength of the electric field on its axis, r is the distance from the center from the beam, and r_0 is the radius where the amplitude is 1/e its value on axis. These beams have a hyperbolic wave front when focused as illustrated in figure 2.5.3g.

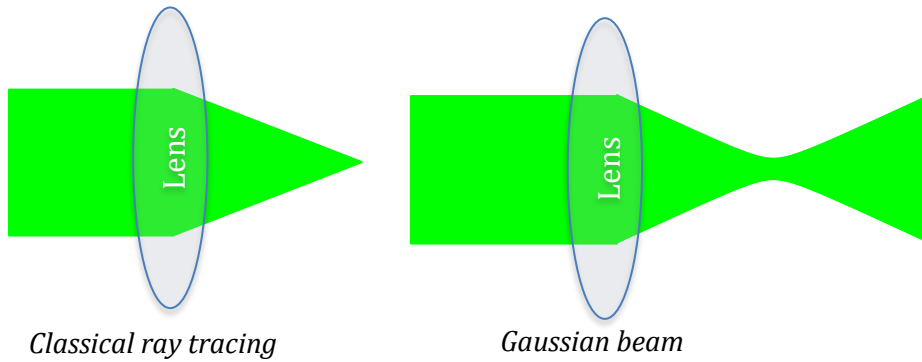


Fig. 2.5.3g: A cartoon of a focused Gaussian beam compared to ray tracing a collimated beam.

We need to determine the diameter of the beam at the waist of the hyperbola.

According to the optics of Gaussian beams,¹¹ and several parameters of the laser and

lens such as the wavelength and the distance between them, the diameter of the beam will be about 15 nm as it strikes to target. This small spot size allows us to space the scans of the beam as close together as the apparatus will allow. The beam scans the target 65 times in the space of 5 mm.

Chapter 3

Spectroscopy & Matrix Isolation

3.1 Overview

Spectroscopy is the study of how matter interacts with light. Atoms and molecules interact with light by either emitting or absorbing individual photons upon changing their energy. Due to the quantum nature of atoms and molecules, they can only exist on a finite set of discrete energies. This fact and the conservation of energy requires that the energy of the photons emitted or absorbed reflect the differences in energy required to transition from one state to another. Observing the absorption or emission spectra of a known atom or molecule reveals its unique energetic structure. Observing the spectra of an unknown substance results in a plethora of spectral bands, each corresponding to a particular transition in energy level. These can then be compared to the transition energies of known atoms and molecules in order to deduce which are present in the sample.

3.2 Rovibrational Spectroscopy

Whereas atoms can only be spectroscopically detected through electronic transitions, molecules can be detected through transitions of rovibrational energies. This is because molecules are linkages of atoms with internal degrees of freedom and thus have additional sets of energies (rotation and vibration). Classically, molecules can be thought of as systems of masses and springs. Their dynamics are

described by coupled systems of differential equations that give rise to a set of normal modes as shown in figure 3.2b for a three-body system. Each of these modes has an associated frequency. Classically the modes can vibrate with any of a continuous range of energies, but in the quantum version, each normal mode has its own set of discrete energy values. To first approximation, the normal modes can be thought of as simple harmonic motion. Quantum harmonic oscillators have equally spaced energy levels as depicted in figure 3.2a thus each can absorb or emit photons with energy any multiple of $h\nu$, where ν is the frequency of the vibration and h is Planck's constant.

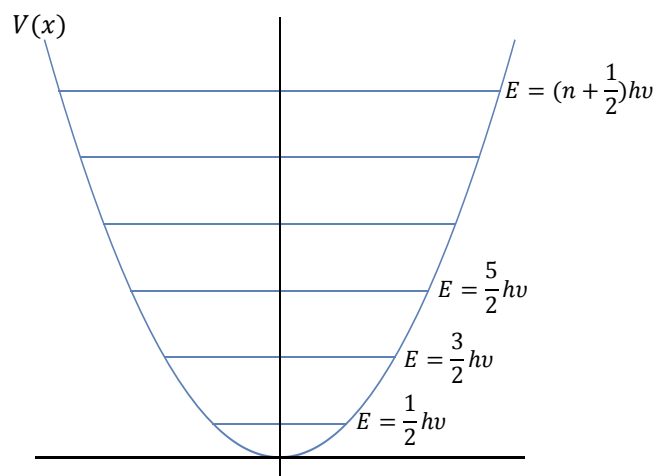


Fig. 3.2a: Quantum harmonic oscillator

In reality, the energies of the modes are slightly anharmonic, so the energy levels will not be exactly equally spaced as pictured, but the approximation holds at low energy. In an absorption spectrum, the most likely transition to be detected is that of exciting a ground state vibrational mode to its first excited state. Every vibrational mode has its own unique frequency, so this first excitation will result in a spectral

band for each normal mode of a molecule. These bands constitute a characteristic signature for every molecule.

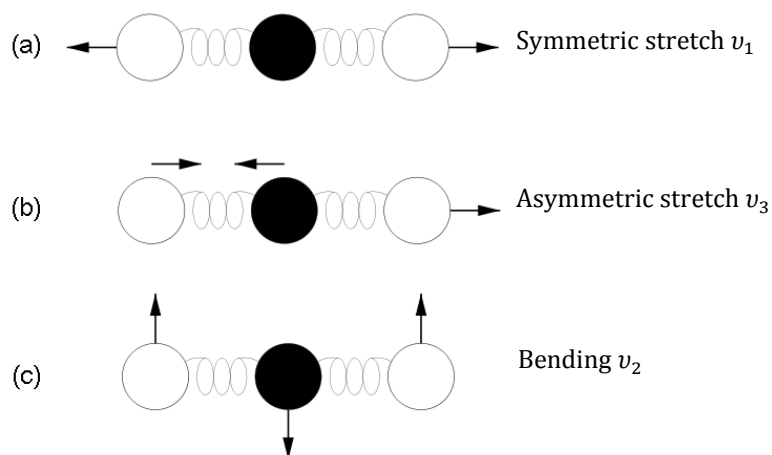


Fig. 3.2b: Normal modes of a simple coupled three-mass system

Vibrational modes are lower energy than electronic transitions, thus are likely to appear in the infrared region instead of the visible. Only modes that have an oscillating dipole moment can be detected by infrared spectroscopy. For example, in the figure above, which can be thought of as the vibrational modes of a CO_2 molecule, (b) and (c) would be sensitive to IR, but (a) would not. This is because the wavelength of the light is much greater than the scale of the molecule, that is about an μm (10^{-6} m) compared to an $\text{\AA}$ (10^{-10} m), so the molecule to first order “sees” a spatially uniform oscillating electric field. This field can induce a dipole moment in the molecule, but has no way of inducing other vibrations without higher order effects.

3.3 Spectral Peaks and Absorbance Units

An example of typical spectral bands is shown in figure 3.3. Each of these peaks is due to a different carbon cluster absorbing photons resonant with one of its normal modes.

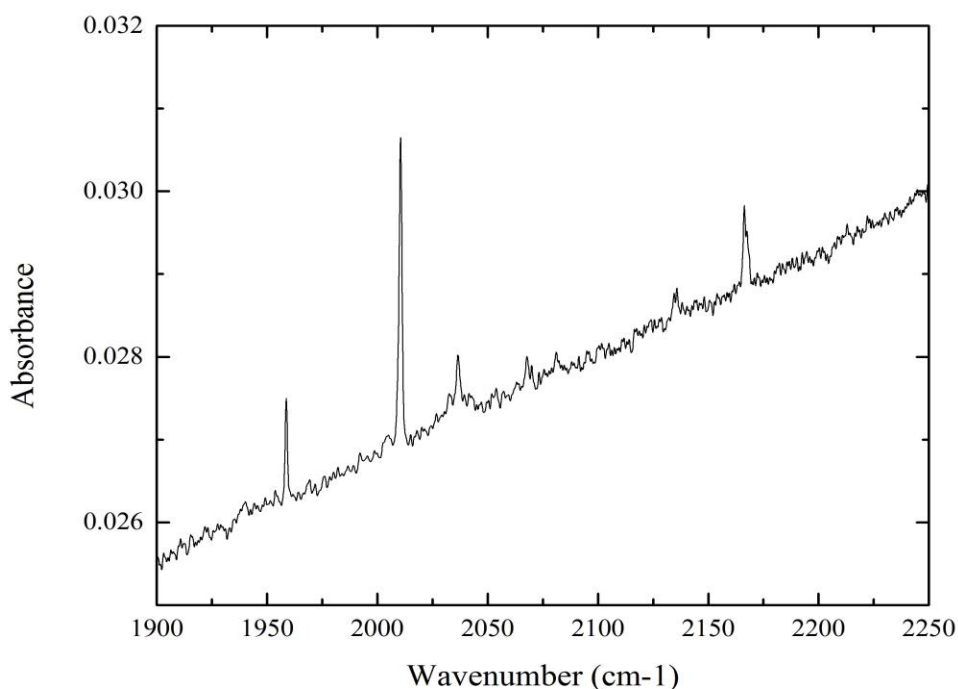


Figure 3.3: Several spectral peaks due to carbon clusters

This is a plot of spectral absorbance per wavenumber. Wavenumber is the number of wavelengths that occur in a cm and is simply proportional to frequency.

Absorbance is a bit more complicated. The spectrometer calculates the spectral flux, the power per unit frequency, transmitted by the sample, and compares it to the spectral flux incident on the sample. This ratio is the sample's transmittance.

Absorbance is the negative decadic logarithm of the transmittance.

$$A = -\log_{10} \frac{\Phi_t}{\Phi_i} = -\log_{10} T = \frac{\tau}{\ln 10}$$

A is the absorbance, Φ_i and Φ_t are the incident and transmitted spectral flux respectively, T is the transmittance, and τ is the optical depth. Absorbance is a useful unit because it is proportional to the optical depth but in decimal instead of using a natural logarithm. The optical depth is useful because it is proportional to how many absorbers are in the beam's path according to the Beer-Lambert law

$$\tau = \sigma n l$$

Where n is the number density, l is the path length of the beam through the sample, and σ is the absorption cross-section. This means that the size of a peak can give us an notion of how much of the corresponding molecule is present in a sample, but we cannot compare the relative abundance of molecules by the sizes of their peaks because each peak has a different absorption cross section dependent of the characteristics of the molecule.

3.4 Matrix Isolation

Matrix isolation is a technique used to study transient, highly reactive molecules. In order to prevent them from reacting with surrounding material, these molecules are trapped in the matrix of a solid inert substance such as a frozen noble gas. The molecules will become fixed at or between lattice sites in the crystal.¹⁵ The molecules and rare gas are deposited at about a 1:1000 ratio in a typical experiment,¹⁵ which ensures that the rare gas surrounds most every molecule and isolates them from reacting with one another. This isolation is crucial to avoid band

broadening caused by interactions between molecules. The matrix constrains the molecules from rotating or translating, but they can still vibrate with nearly the same frequencies they would in the gas phase.² This means that the vibrational spectrum of a molecule trapped in rare gas matrix varies only by a small amount from its gas-phase counterpart.

3.5 FTIR

Absorption spectroscopy works by shining a source of light through a sample into a detector and comparing the light detected to the light emitted in order to extract information about the sample. In the case of diffuse atoms or molecules, the absorption will be due to the electronic or rovibrational transitions described in the previous two sections. The most logical strategy to use absorption spectroscopy to identify molecules is to shine a tunable monochromatic laser at a source and measure the amount of light that is absorbed for each wavelength. Vibrational modes that are resonant with the frequency of incoming photons will absorb them and become excited, so it is easy to identify spectral peaks by observing the absorbance vs. frequency measurements. The problem with this approach is that this sort of tunable laser is very difficult to create in the IR; most lasers are only equipped either to output narrow bandwidth centered on a single frequency or a very narrow range compared with the spacing of different vibrational transitions. A less intuitive but more pragmatic solution is to use a more attainable light source, say a hot piece of metal acting as an IR filament, to shine a wide range of frequencies through the sample. Fourier Transform Infrared Spectroscopy, or FTIR is a

spectroscopic technique that uses a broadband IR source of light, a Michelson interferometer, and a fast Fourier transform algorithm to measure IR absorption spectra.¹⁴ The spectrometer repeatedly measures the total absorbance of the sample over all frequencies present in the beam. Between each measurement, it slightly alters the frequency composition of the probe beam using the interferometer. These repeated measurements yield a relation of absorbance to the parameter it uses to vary the frequency composition, called an interferogram. The absorbance per individual wavelength can be backed out of this information with an algorithm. The frequency composition of the light source is not altered by physically adjusting the filament itself, but instead by sending the beam through an interferometer before it passes through the sample. A system of mirrors splits the beam, has it travel two distances, and recombines it as shown in figure 3.5a.

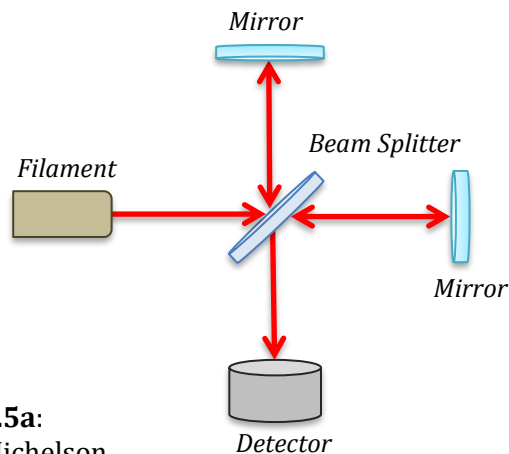


Fig. 3.5a:
The Michelson
Interferometer

If the two arms of the arms are not quite equal length the two travelling waves of light recombine out of phase with each other and constructively or destructively interfere in a known pattern. The spectrometer varies the length of one of the paths by moving one of the mirrors, which parameterizes the frequency composition.

Consider a monochromatic beam running through the interferometer. At equal path lengths the beam splits then recombines with no phase shift as shown in *A* in figure 3.5b. At a path length difference of half the wavelength, the peaks and troughs of the wave align and the wave cancels itself out upon recombination as shown in *C* in the figure. At a path difference equal to the wavelength the waves line up again to full constructive interference.

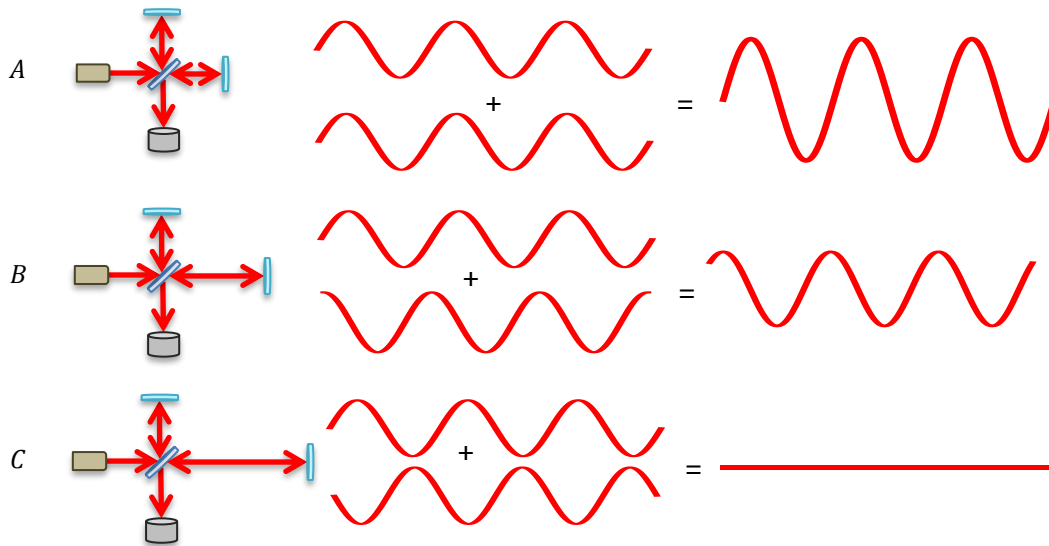


Fig. 3.5b: *A* is equal path lengths, *B* is a shift of a quarter wavelength, an *C* is a half wavelength shift

This behavior is sinusoidal as the path length changes. The amplitude of the wave will be proportional to $\cos^2[2\pi \frac{l}{\lambda}]$, or equivalently $\cos^2[2\pi l \nu/c]$, where l is the displacement of the moving mirror from equal path lengths, λ is the wavelength and ν is the frequency. This process is happening for each frequency of light present in the probe beam, and the detector measures the total power of all of them. Summing all of them up, the full interferogram function will look like $\int f(\nu)\cos^2[2\pi l \nu/c]d\nu$,

where $f(\nu)$ is the Planck distribution of frequencies emitted through black body radiation by the filament. This beam will pass through the sample, and particular frequencies will get absorbed so the new function will look like $\int g(\nu) \cos^2[2\pi l \nu / c] d\nu$ where $g(\nu)$ is $f(\nu)$ with the absorption spectrum subtracted out. This looks quiet a bit like the Fourier Transform of $g(\nu)$, so it's understandable that an inverse Fourier transform of this function will recover $g(\nu)$, which, when compared to $f(\nu)$, yields the absorption spectrum. An example background spectrum and the corresponding interferogram are shown below.

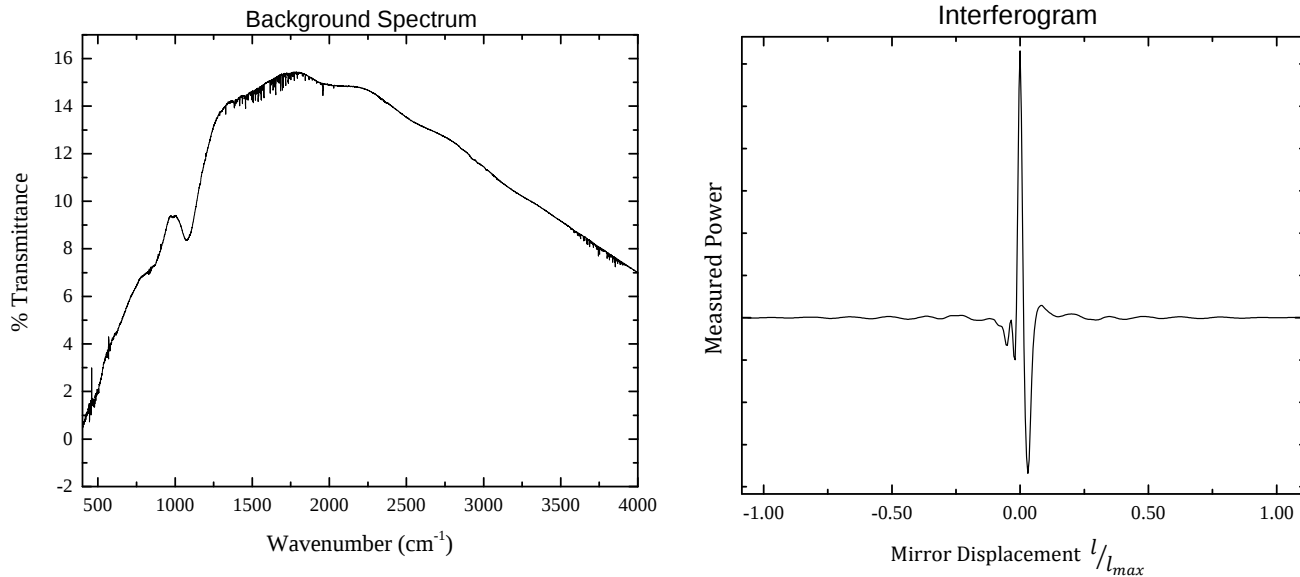


Fig 3.5c: An example background spectrum and the corresponding interferogram

The bands in the background spectrum are mostly due to CO₂ and H₂O, and its shape is determined by the frequency dependent transmittance of air and the materials in the spectrometer. The interferogram has the feature of a large spike at zero displacement because all wavelengths pass through the interferometer with no interference at equal path lengths. As the mirror advances the amount of power the

detector measures settles to an average value across all wavelengths. This method is less technically challenging to construct than a laser spectrometer. It also has the benefit of scanning the whole frequency range simultaneously, so any time-dependent information about the spectrum will be captured.

Chapter 4

Carbon Clusters

4.1 Identification

Carbon is arguably the most important element in chemistry. Pure carbon clusters show up in variety of systems. In astronomy, their spectrographic signal is present in carbon stars, comets, and the interstellar medium.¹³ They are also produced by combustion of fossil fuels,¹⁷ so they've been studied rather thoroughly. Since carbon can form single, double and triple bonds with itself, it forms a variety of structures from the spherical buckminsterfullerene, to rings, to simple chains of atoms⁵. Though all of these molecules are interesting, we'll focus on the ones relevant to our CBGB apparatus, namely those produced by laser ablation of graphite, i.e. small, predominantly linear clusters. Some of these clusters are pictured in figure 4.1a.

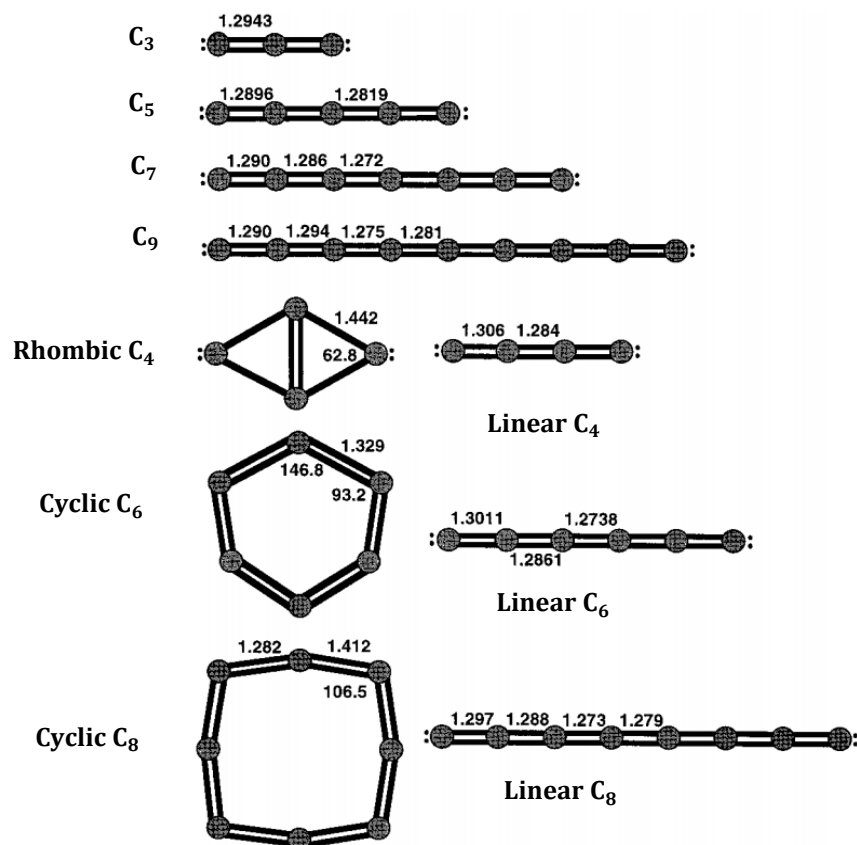


Fig. 4.1a: Illustration of carbon clusters taken from reference 5. Calculated bond lengths are shown in angstroms and angles in degrees.

Many experiments involving these molecules detect them through vibrational spectroscopy.⁵ Each cluster has a unique set of vibrational spectral bands corresponding to its vibrational modes used to identify them. The normal modes of C₄ and C₅ are shown below for example. In order to tell which species are present in a spectrum, one must know where those species' signature bands occur based on previous experiments or theoretical calculations. For carbon clusters, a wealth of research has been conducted, so the most prominent peaks of many clusters are known.⁵ There are several strategies for identifying previously unknown peaks detailed in the following sections.

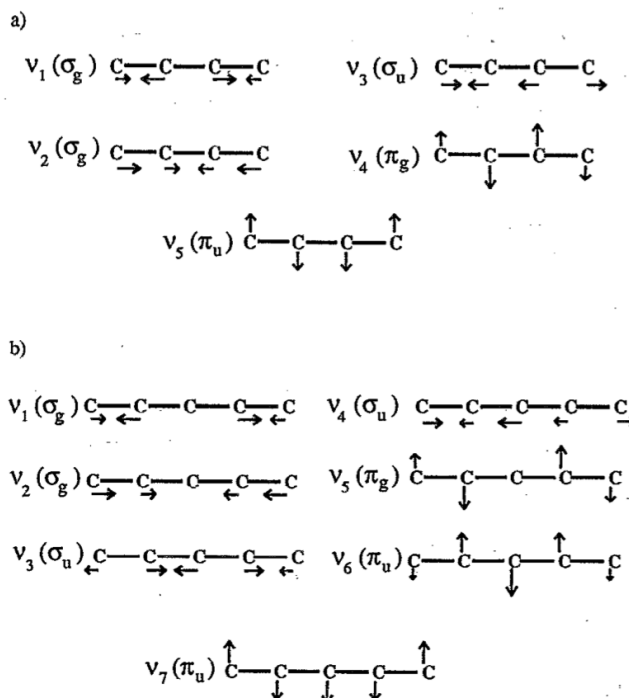


Fig 4.1b: the normal modes of the linear C_4 and C_5 molecules. Taken from reference 21.

4.1.1 *Ab Initio* Calculations

Ab initio calculations use approximations of quantum mechanics in order to predict vibrational behaviors of molecules. Density Functional Theory (DFT) is a computational method that drastically simplifies the many-body problem of the electrons in a molecule.¹² The theory approximates the system as a non-interacting electrons in an effective potential, which reduces the many-body problem of N electrons requiring $3N$ coordinates (three spacial coordinates for each electron) with a 3 coordinate electron density. This electron density is found by minimizing an energy functional, and the properties of the system can be calculated through

other functionals of the density.¹² These calculations are used as a first approximation to be measured with much higher accuracy by physical experiments.

4.1.2 Mass selection

Mass selection studies typically use a quadrupole mass spectrometer to filter a particular species of ionized carbon cluster (anions) from a source, neutralize the molecules with UV radiation, and then spectroscopically analyse the result.⁵ The mass spectrometer selects particular charge to mass ratio with high accuracy, so the resulting spectral peaks can be assigned to a single carbon cluster with confidence.

4.1.3 Isotopomer Studies

An isotopomer is a molecule that has one or more of its constituent atoms replaced with a different isotope than normal. In rovibrational spectroscopy, isotopomers have slightly different spectra than the normal version of the molecule because the increased or decreased mass changes the frequency of oscillation, much like attaching a heavier weight on the end of a spring. Changing these frequencies changes the wavelength of light required to excite them, thus shifting each peak a small amount.¹⁹ In carbon cluster studies, this strategy involves carbon clusters produced from ^{13}C -enriched sources in order to create a distribution of every possible ^{13}C substitution.²⁰ When compared to the spectrum of pure ^{12}C molecules, the spectrum of the isotopomers have the effect of splitting all the peaks in a predictable way. By observing this splitting, it's possible to deduce which peaks in the pure spectrum belong to which vibrational modes of a particular molecule.

4.1.4 Annealing Studies

These studies track the behavior of individual peaks of matrix isolated carbon clusters with respect to temperature in order to correlate the peaks together.⁶ Annealing the matrix allows for the clusters to migrate and react. As the concentration of a species increases or decreases in the reaction, all the peaks corresponding to the vibrational modes of a particular molecule will grow or shrink proportionally. If the most prominent peak of a molecule is known, this technique allows researchers to find peaks corresponding to other vibrational modes of the molecule.

4.1.5 Identification Table

Using these strategies or combinations of multiple strategies, studies have over the course of decades identified several peaks of many carbon cluster in the gas phase and trapped in several noble gas matrices. Synthesizing the results of these studies yields the following identification table:

Cluster	Vibrational Mode	Gas Phase	Ne Matrix	Ar Matrix	Kr Matrix	Calculated (DFT)
C₃	ν_1	1124.5	1226 ^[13]	1214 ^[14]	1215.8 ^[14]	1224
	ν_2	63.42	75 ^[4]	83 ^[4]		84.5
	ν_3	2040.02	2036.4 ^[4]	2038.9 ^[14]	2033.3 ^[1]	2039
C₄	ν_3	1548.94	1547.2 ^[4]	1543.4 ^[9]	1539.5 ^[1]	1532
	ν_5	160		172.4 ^[6]		259
C₅	ν_2	779 ^[16]		775.8 ^[1]		776
	ν_3	2169.44	2166.4 ^[4]	2164.1 ^[7]	2157.0 ^[1]	2216
	ν_4		1444.3 ^[4]	1446.6 ^[5]	1443.2 ^[1]	1440
C₆	ν_1	2061		2050.3 ^[1]		2123
	ν_2	1322		1665.8 ^[1]		1676
	ν_3	489		627.3 ^[1]		645
	ν_4	1959.86	1958.7 ^[4]	1952.6 ^[8]	1951.2 ^[1]	1972
	ν_5		1199.4 ^[4]	1197.2 ^[8]	1197.0 ^[1]	1176
C₇	ν_3	548		581.7 ^[1]		586
	ν_4	2138.32	2134.6 ^[4]	2127.7 ^[3]	2120.4 ^[1]	2216
	ν_5	1898.38	1897.5 ^[4]	1894.3 ^[3]	1889.3 ^[1]	1917
C₈	ν_5	2068	2067.8 ^[2]	2071 ^[1]		2109
	ν_6		1707.3 ^[1,2]	1710.5 ^[1]		1703
C₉	ν_3	1258 ^[16]	◀			1247
	ν_4	484 ^[16]	◀	447.6 ^[1]		458
	ν_5	2079.67	2081.1 ^[2]	2078.1 ^[1]		2182
	ν_6	2014.28	2010.0 ^[4]	1998 ^[10]	1994.2 ^[1]	2073
	ν_7		1602.8 ^[1]	1601.0 ^[11]	1600.8 ^[1]	1624
C₁₀	ν_6	2074	2074.5 ^[2]			
			1915.4 ^[2]			
C₁₁	ν_7		1938.6 ^[2]			
	ν_8		1853.4 ^[2]			
C₁₂	ν_8		2003.9 ^[2]	1997.2 ^[12]		
	ν_9			1818.0 ^[12]		
C₁₃	ν_8	1808.96 ^[15]				

Table 1: All values are given in wavenumber measured in cm⁻¹. A separate bibliography is given for this information

4.2 Comparison

We're interested in comparing the products of our buffer-gas beam to those that other experiments have produced. Our apparatus creates a large distribution of carbon clusters, so we need to compare to other studies that also create a distribution instead of focusing on one cluster. For this comparison, five studies were selected that investigated several carbon sources and the behavior of carbon clusters in matrix. They are summarized in the following sections.

1 The Kinetics and Formation of Small Carbon Clusters in an Argon

Matrix⁶ by Jan Szczepanski, Robert Pellow, and Martin Vala is an annealing study.

They investigate the temperature dependence of the prominent bands of C_3 , C_5 , C_6 , and C_9 trapped in argon matrix. They propose a kinetic model based on pairwise interactions of clusters to fit the annealing data. They use laser ablation of a rotating graphite rod as their source of clusters. An example of some of their spectra is shown in figure 4.2.1.

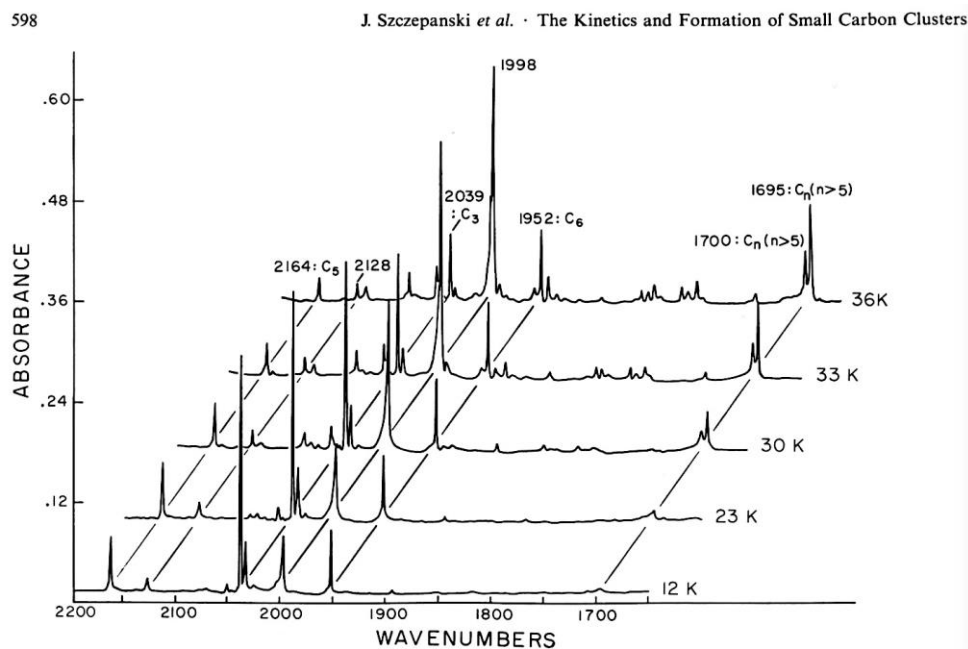


Fig 4.2.1 from reference 6. Carbon clusters trapped in Ar annealed to various temperatures

2 Rare Gas Matrix Studies of Absorption and Fluorescence of Reactive Intermediates Formed in Discharges through Acetylene⁷ is a study involving a novel technique of producing a carbon cluster beam. They use the discharge of acetylene, C_2H_2 , to seed a supersonic expansion beam of either neon or argon gas, which is then frozen to a matrix isolation window. An example spectrum for each buffer gas is shown in figure 4.2.2.

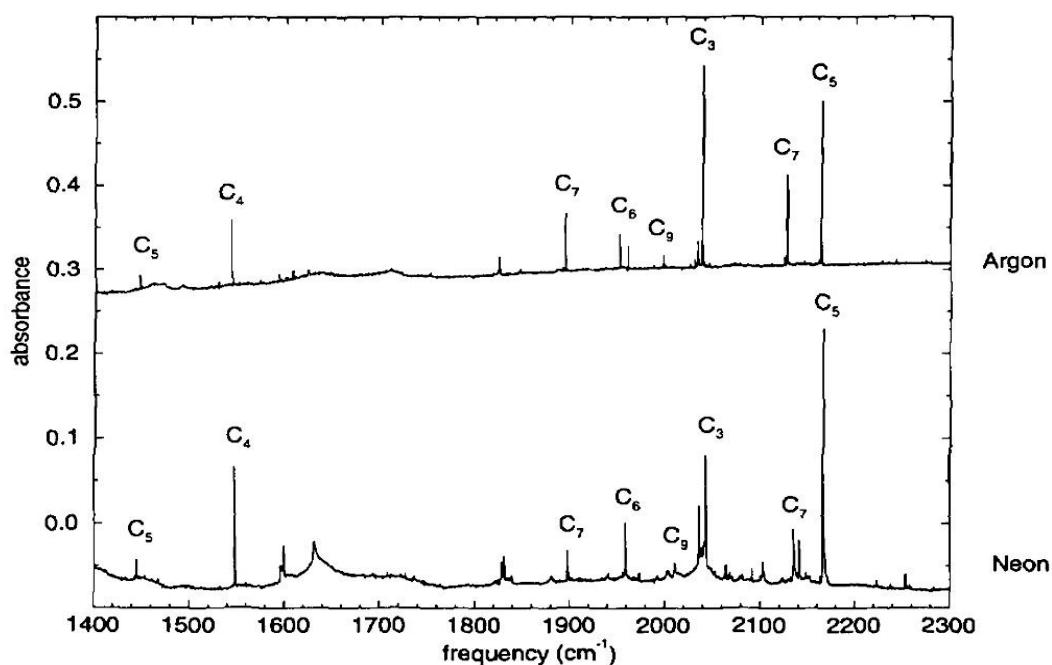


Fig 4.2.2 from reference 7. Carbon clusters trapped in neon and argon held at 5K and 11K respectively

3 Infrared Spectroscopy of Matrix-Isolated Carbon Clusters, With

Emphasis on C_8 and C_9 ,⁸ by the same group as the first paper studies is an annealing study with the goal of identifying new peaks. The apparatus employs laser ablated graphite tapped in Ne, Ar, or Kr deposited on a window. By observing annealing behavior and comparing with DFT calculations they identify new bands of C_8 and C_9 .

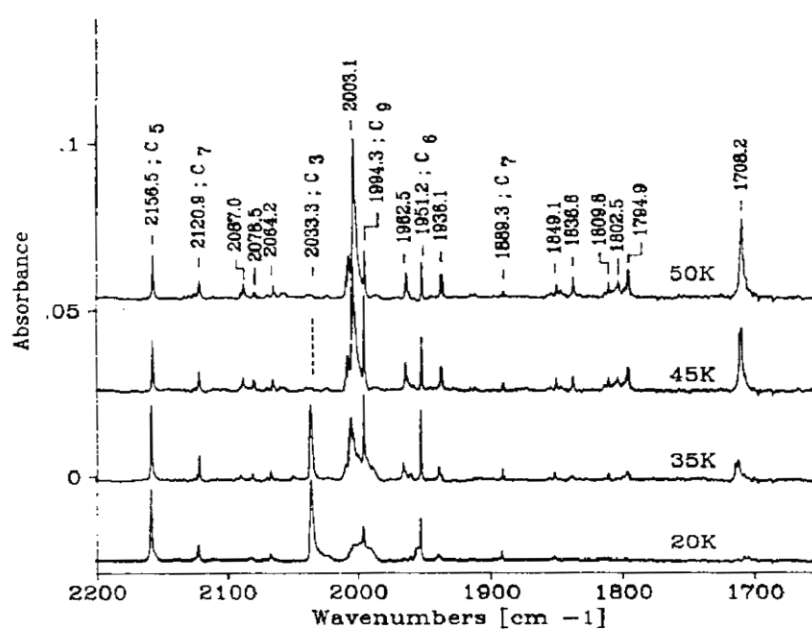


Fig 4.2.3 from reference 8. Carbon clusters in Kr matrix annealed to various temperatures.

4 Spectroscopy of Carbon Molecules. IV. C₄, C₅, C₆ (and C₉),⁹ by W. Weltner

Jr., K. R. Thompson, and R. L. DeKock is an isotopomer study. They use isotopic substitution in order to identify previously unknown spectral peaks and investigate which species form with diffusion. The experiment employs a tantalum carbide oven cluster source, a tantalum tube packed with carbon powder heated by passing a few hundred amperes through it. The oven can be loaded with can be pure ¹²C powder or some mix of ¹³C and ¹²C in order to create isotopically substituted clusters. They also calculated the stretching force constants of the bonds of several clusters.

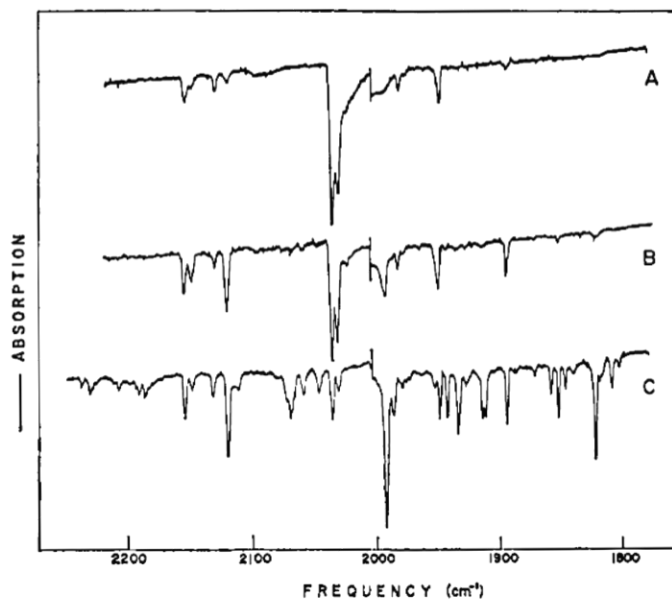


Fig 4.2.4 from reference 9. Carbon clusters trapped in Ar matrix. A is the original spectrum. B and C are the spectra after annealing at 15K and 30K respectively.

5 Diffusion of Mass-Selected Carbon Atoms and Molecules on Argon and

Neon Matrices⁹, by Michel Grutter et al. is a different sort annealing study that seeks to explain the mechanism of reactions in annealing. The carbon source instead of being a random distribution of clusters is a mass selected beam of carbon anions in neon or argon that are neutralized by UV radiation as they're being deposited in matrix. They deposited first C⁻ ions and observed their behavior upon annealing. The resulting spectra are shown in figure 4.2.5. The first spectrum is nearly featureless because monatomic C is invisible to IR spectroscopy. The second is full of peaks, demonstrating the readiness that carbon atoms aggregate into clusters provided the chance to migrate. In another test they repeated the same procedure with C₂. In this case the pre and post annealing spectra are similarly blank, suggesting no aggregation occurred. Gutter et al. draw the conclusion that it is only monatomic carbon that is capable of diffusing within the matrix during annealing, though this result is contested in other studies.

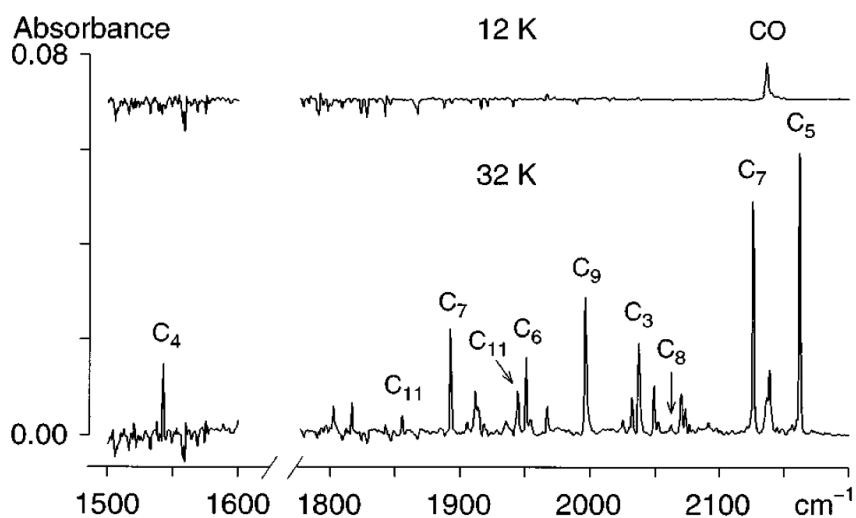


Fig 4.2.5 from reference 10. Mass-selected carbon atoms in Ar matrix. The bottom trace is post annealing

Comparison Table

Taking data from these studies and identifying the peaks yielded the following table. The number assigned to each paper corresponds to the numbering of the preceding 5 sections. The three numbers following each cluster are the wavenumbers (cm^{-1}) of that peak in neon, argon, and krypton respectively. The values listed in the table are the ratios of that peak's absorbance value to the absorbance of a common peak, in this case the ν_3 mode of C_3 , in order to factor out differences in total cluster production. This table combined with information from the experimental setup of each of these experiments gives us a reference for what distribution of carbon clusters have been produced under what conditions.

Paper	1			2			3			4			5	This Experiment
Temperature	12K	36K	5K	11K	20K	50K	20K	36K	5K	30K	32K	5K		
Buffer Gas	Argon	Argon	Neon	Argon	Krypton	Krypton	Argon	Argon	Argon	Argon	Argon	Neon		
C5 (2166, 2164, 2157)	2.71512276	1.20947283	5.35497715	1.80055668	4.87612443	2.53341655	3.7538217	1.41835296		0	0	1.21282564	1.441541708	
C7 (2134, 2127, 2120)		1	1	1	1	1	1	1	1	1	1	1	1	1
C9(2081, 2078, _)	0	1.39912174		0	0	0	0.34678714	0.72364693	2.00954979	0	0	0.09291698	0.098253962	
C10(2075, _)	0	0	0	0	0	0	0	0.43384226		0	0	0	0.087530183	
C8(2068, 2071, _)	0	0	0.27744075		0	0.44833781	0.62644396	0.41766079		0	0	2.03309099	0.15709563	0.242837287
C6 (_ 2050, _)	0.79459116	1.63325434		0	0	0	0	0	0	0	1.077697	0.19931982	0.880968082	
C3 (2036, 2039, 2033)	10.1714463	2.77739532	1.354876	2.20206794	5.56826959		0	1.72353263	9.18348954	10.0423206	2.1331848	0.38427185	1.676019114	
C9(2010, 1998, 1994)	2.75465236	8.78080143	0.12903581		0	2.18295511	2.63997702	6.9077196	9.06348264	2.27682721	7.29969512	0.59456686	1.097414423	
C12(2004, 1998, _)	0	0	0	0	0	0	0	0	0	0	0	0	0.299537873	
C6 (1959, 1953, 1951)	3.02257066	2.90237617	0.12905726	0.37119266	2.835827	2.13319067	5.91888111	5.57912435	2.25510273	2.2108349	0.31924753	0.500233346		
C11(1939, _)	0	0.60748624		0	0	0	0	0.4492991		0	2.65574578	0.18749538	0.143018384	
C10(1915, _)	0	0.43102325		0	0	0	0	0	0	0	2.51097561	0.1663706	0.062427713	
C7 (1898, 1894, 1889)	0.56266763	0.49460999	0.63224187	0.63131054	0.69366501	0.37343716	0.45285378	0.39322344	0.48975749		0	0.45184313	0.555724083	
C11(1853, _)	0	0.68167578	0.54195683	0.18181818		0	1.11987557	0	0.38663805		0	2.22216229	0.07855401	0.082530994
C12(_ 1818, _)	0	0.84627445		0	0	0	0	0.25864347	0.82089016		0	0.46634615	0.11316426	0.034730536
C8 (1707, 1711, _)	0.52460629	2.12837194		0	0	0	4.61295052	0.22340286	0.25455486		0	0	0	0.090906093
C9(1603, 1601, 1601)	0	0	0.66451601		0	0	0	0	0	0	0	0	0	0.079319948
C4(1547, 1543, 1539)	0	0	2.49035609	0.70959155		0	0	0	0	0	0	0	0	0.527263458
C5(1444, 1447, 1443)	0	0	0.36775795	0.14644648		0	0	0	0	0	0	0	0	0.099468884
C6(1199, 1197, 1197)	0	0	0	0	0	0	0	0	0	0	0	0	0	0.054605543

Table 2: A comparison of the distribution of carbon clusters produced in several studies.

4.3 Our Results

Our apparatus after 40 minutes of deposition measured the following spectrum shown in figure 4.3. Using the information in Table 1, the peaks have been identified. Every IR active carbon cluster up to C_{12} is clearly present, and many have signal from multiple vibrational modes.

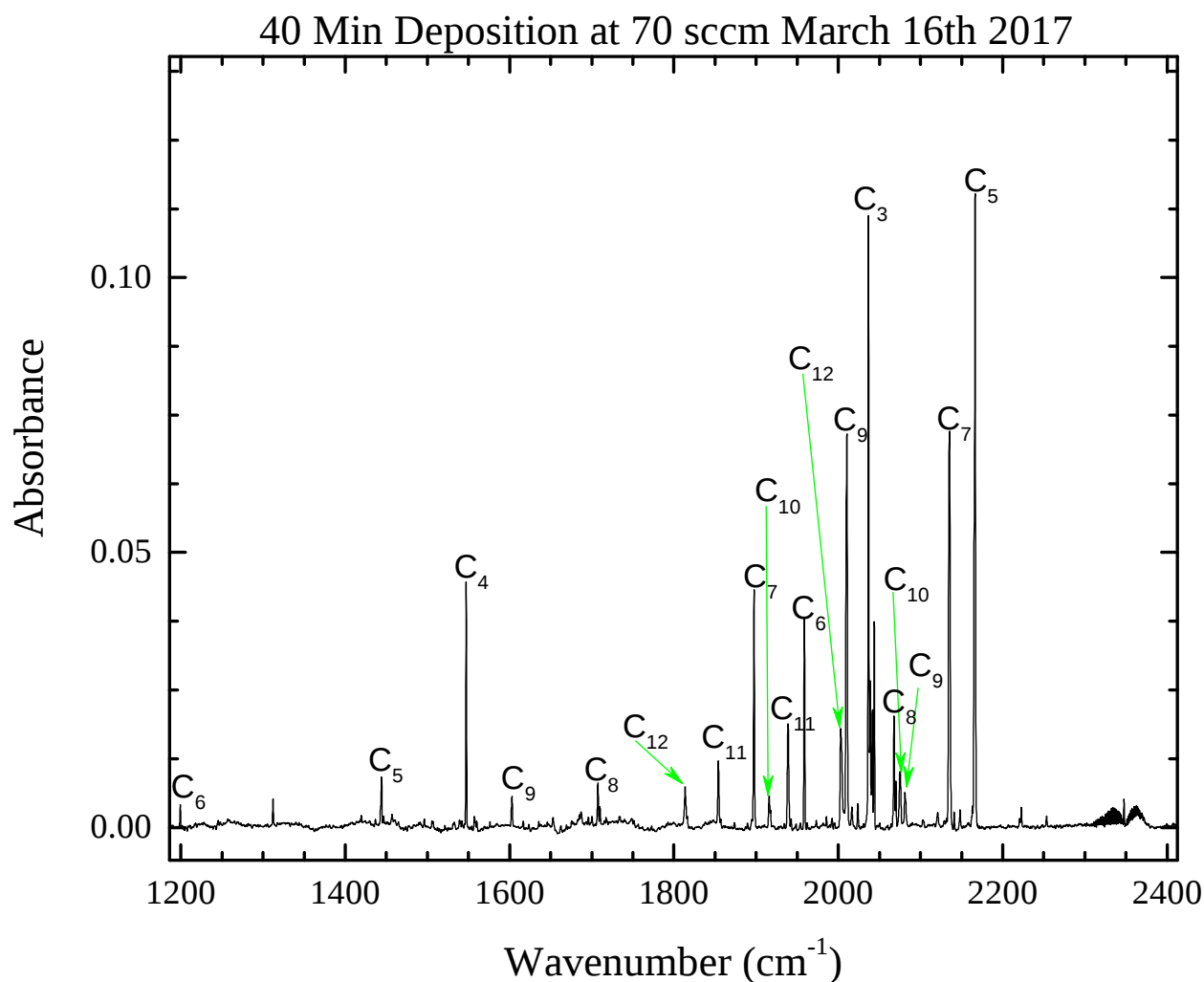


Fig. 4.3: An example spectrum from our apparatus with its peaks identified according to Table 1.

From Table 2, it's clear that this managerie of peaks is far from common. Most experiments detect around ten clearly identifiable peaks whereas our apparatus has yielded twenty. Our standard deposition time is 30 minutes and the signal to noise ratio is excellent, typically around 25,000-50,000 (i.e. $>10^4$), for sets of scans that take the spectrometer ~ 45 seconds at 1 cm^{-1} resolution. This is a remarkably large signal for such a brief deposition time. Some experiments with different sources of carbon deposit for hours in order to achieve acceptable SN ratios.^{5,7}

Table 2 also suggests that our distribution of carbon clusters more closely resembles the post-annealing spectra of experiments rather than pre-annealing. For instance, the presence of C_{12} is a common feature only in the post annealing spectra. This similarity suggests that the carbon clusters in our system are aggregating. These reactions may be taking place in the crystal itself if it is not being properly cooled to 5K, or the clusters could be reacting directly after ablation while they are in a hot, dense cloud.

The CBGB has proven to be an efficient apparatus for creating a bright source of carbon clusters. Moving forward we will be able to perform our own annealing studies, and then to move on to other experiments with the CBGB and apply these same techniques to other molecules, such as vanadium oxide.

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