Communicating Research to the General Public

At the March 5, 2010 UW-Madison Chemistry Department Colloquium, the director of the Wisconsin Initiative for Science Literacy (WISL) encouraged all Ph.D. chemistry candidates to include a chapter in their Ph.D. thesis communicating their research to non-specialists. The goal is to explain the candidate's scholarly research and its significance to a wider audience that includes family members, friends, civic groups, newspaper reporters, state legislators, and members of the U.S. Congress.

Ten Ph.D. degree recipients have successfully completed their theses and included such a chapter, less than a year after the program was first announced; each was awarded $500.

WISL will continue to encourage Ph.D. chemistry students to share the joy of their discoveries with non-specialists and also will assist in the public dissemination of these scholarly contributions. WISL is now seeking funding for additional awards.

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COMPUTATIONAL AND MATRIX-ISOLATION SPECTROSCOPY STUDIES

OF CYANOCYCLOBUTADIENES

by

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CHAPTER 6

Matrix Isolation and Computational Studies of Cyanocyclobutadienes:

For Those Who Do Not Speak Chemistry as Their First, Second, or Even Third Language

Introduction

I am writing this chapter for, and dedicating it to, all of the people in my life that read the title of my thesis and immediately say, "Huh?" Since a majority of those who care about how the last five years of my life have been spent are likely in this situation, I hope that this chapter makes it all a bit more understandable.

Matrix Isolation: When most people look up at the night sky, they typically think, wow, how beautiful. Even most chemists might initially think the same thing. However, there are a few of us, with connections to the field of astrochemistry, who have other thoughts pop into our heads. What kind of chemical reactions are going on up there in the interstellar medium (ISM, the vast space that exists between the stars), where the temperature can be as cold as 100 K (-280 °F)? Or what reactions are occurring on Titan (the largest moon of Saturn), where the conditions are very similar to those that existed on primitive Earth? And finally, how might we go about studying these potential reactions in the laboratory here on Earth?

Answers to the first two questions are vast, and scientists are continually adding to the lists. I will discuss some of the kinds of reactions we are interested in below. By answering the last question—how can we study these reactions in the lab—I will define the

first part of my title—Matrix Isolation. Because the ISM and atmosphere of Titan are environments vastly different than those here on Earth, we must somehow simulate those conditions. Matrix isolation is a laboratory technique in which we can produce molecules at very low temperatures, 10 K (-440 °F), very low pressures, 10^{-7} Torr, and keep them isolated from one another by placing them in a matrix of unreactive gas such as argon (Ar) or nitrogen (N_2), Figure 6.1.
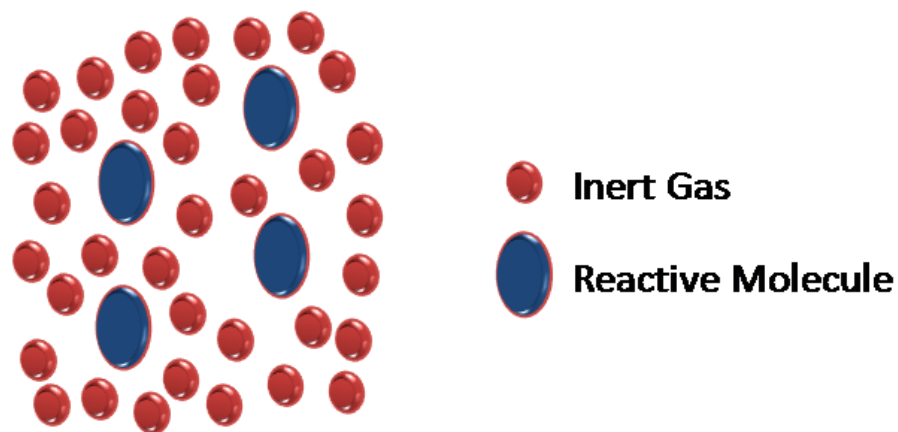
Figure 6.1. Representation of matrix isolation showing reactive molecules isolated from one another by an unreactive/inert gas (Ar or N_2).

All of this occurs on a very small window on a much larger equipment setup as shown in Figure 6.2. The full setup contains pumps to reduce the pressure, a refrigeration system and temperature controller to keep it cold, a manifold which allows us to control the argon and nitrogen, and the window upon which the chemistry is actually done. We call the entire system a "cart."
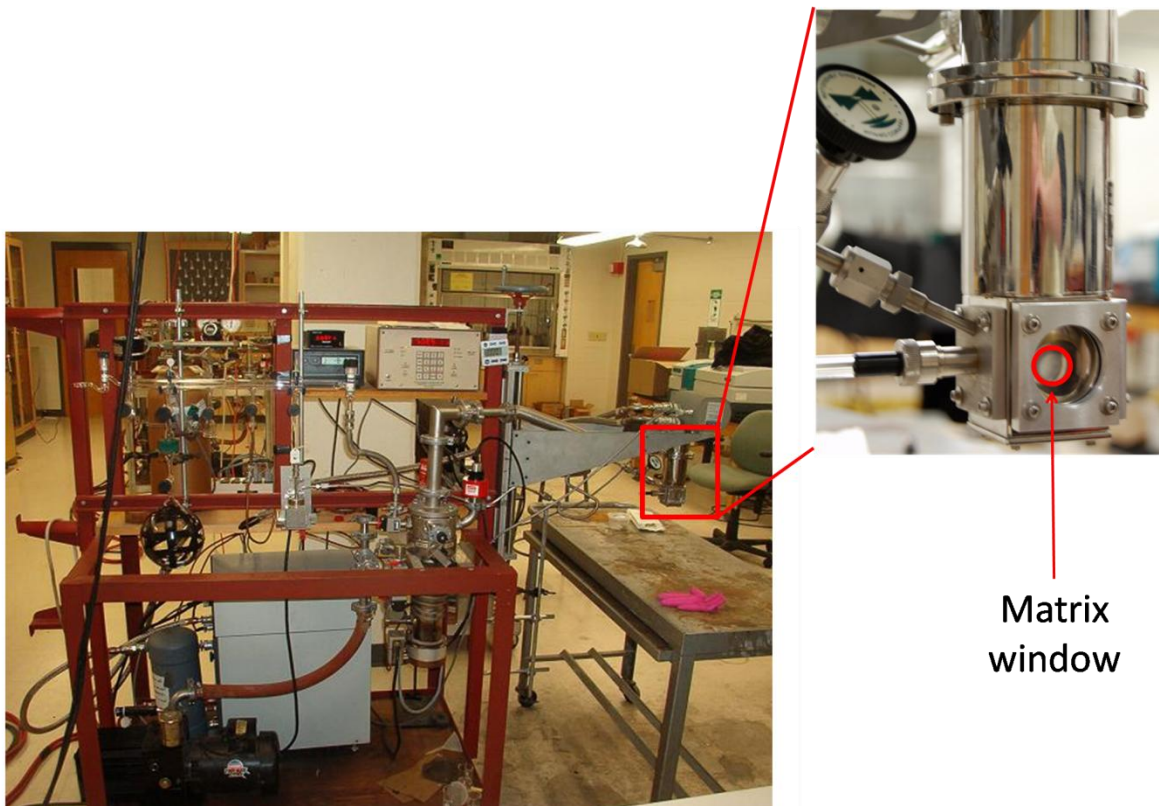
Matrix
window

Figure 6.2. The cart setup has components that allow for low pressure and temperature, and control of gasses. The expansion shows the matrix window where the sample and inert gas are deposited and the chemistry occurs.

The cart is on wheels, which allows us to place the window in instruments such as an IR spectrometer and an UV/vis spectrometer, both of which will be discussed later.

Although it is great that this system at least partially simulates that of the ISM and Titan's atmosphere, it is more widely used to isolate what would otherwise be highly reactive molecules. Many molecules that are interesting to chemists are too reactive to simply make at room temperature on the laboratory bench top. However, by cooling the environment down, the molecules cannot undergo thermal reactions (reactions in which heat energy is needed)—you can't cook an egg in a cold pan. The isolation in a matrix keeps the molecules

from touching each other, and therefore keeps them from reacting with each other—if you put your kids in separate rooms, they're not going to fight.
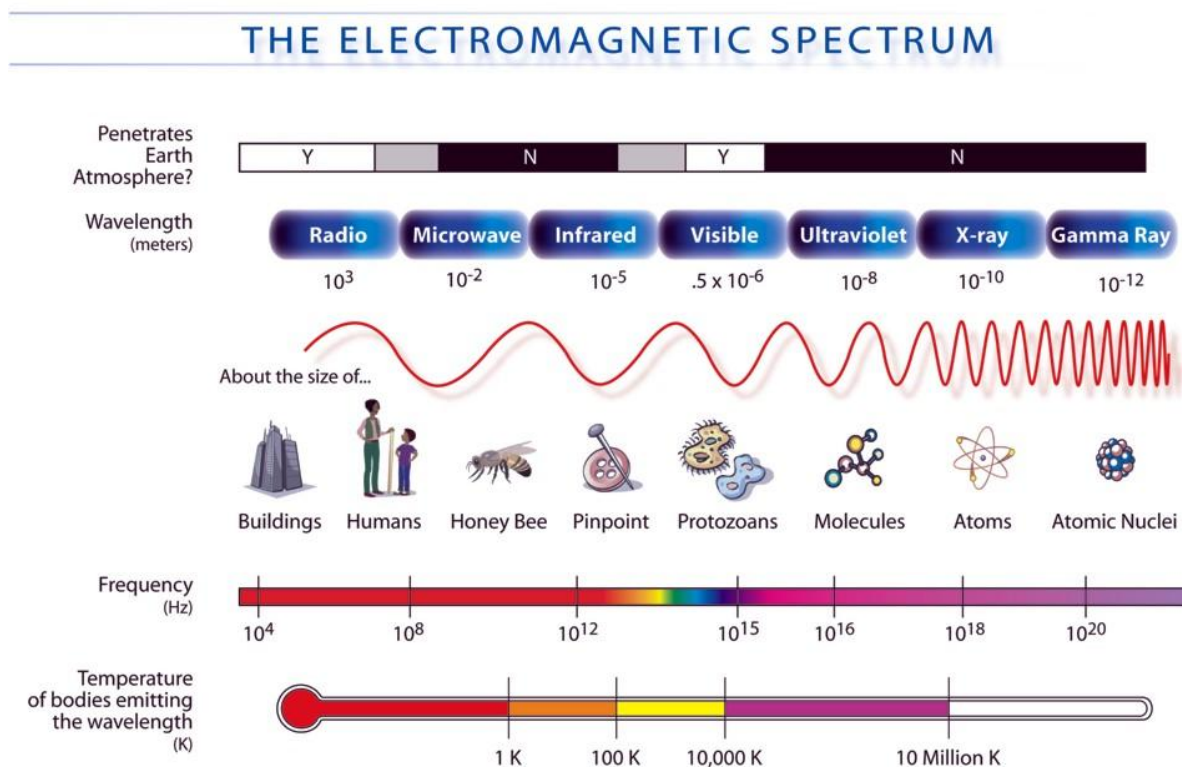
With our molecules isolated in an environment where they cannot react, you might be wondering how the molecules do anything interesting and worth observing. By shining light onto the matrix window, the molecules can undergo photochemistry. Photochemistry is any chemical transformation induced by light energy. Some molecules are able to absorb light. This light is a form of energy that the molecule can then use to undergo some type of transformation. It is these transformations in which we are interested.

In order to get these reactive molecules onto the cart window, we need to synthesize a more stable precursor—a molecule that, once on the matrix and then exposed to light, will react to give the molecules we are interested in. Once the precursor has been made (or if you are lucky, purchased), it is deposited onto the cart window. This is done by vaporizing the precursor, which is typically a solid or a liquid, by heating it. Sometimes, it requires first cooling the sample, and then slowly warming to a temperature that is still lower than room temperature. Again, this is highly dependent on the molecule (specifically its volatility).

Once the precursor is on the matrix, we irradiate (shine light on) the window with a lamp. We can control what wavelength of light is used with a filter. The filter will remove all light below a certain wavelength. As the wavelength of the light gets smaller, the amount of energy it has increases. We therefore start with longer wavelengths of light (red, orange, yellow) so that it doesn't fully destroy our molecules right away. We then progressively step

down through the spectrum (blue, purple) and even out of visible light into the ultra violet region.

We are able to monitor the reactions by IR (Infra Red) and UV/vis (Ultraviolet/visible) spectroscopy. Spectroscopy is a general term for methods of detection that use various portions of the electromagnetic spectrum, Figure 6.3.

THE ELECTROMAGNETIC SPECTRUM

Penetrates Earth Atmosphere?	Y		N		Y		N	

Wavelength (meters)

Radio	Microwave	Infrared	Visible	Ultraviolet	X-ray	Gamma Ray
10^3	10^{-2}	10^{-5}	$.5 \times 10^{-6}$	10^{-8}	10^{-10}	10^{-12}

About the size of...

Buildings	Humans	Honey Bee	Pinpoint	Protozoans	Molecules	Atoms	Atomic Nuclei

Frequency (Hz)

10^4	10^8	10^{12}	10^{15}	10^{16}	10^{18}	10^{20}

Temperature of bodies emitting the wavelength (K)

1 K	100 K	10,000 K	10 Million K

Figure 6.3. The electromagnetic spectrum broken down into the different regions by wavelength. The infrared and ultraviolet/visible regions were used to detect molecules in our experiments. Adapted from NASA (my.larc.nasa.gov/electromag.html).

Electromagnetic radiation can be broken down based on its wavelength. Each region produces a specific amount of energy and can be used for different applications. The light that we see has wavelengths of approximately 0.5 x 10^{-6} meters, the size of protozoa. The waves we use to cook food (microwaves) are about the size of a honey bee. As scientists, we take advantage of several regions of the spectrum. In our lab, we make particular use of the Infra Red (IR) and UltraViolet/visible (UV/vis) regions.

The energy in the infra red section of the electromagnetic spectrum causes a molecule to vibrate. IR spectroscopy monitors these vibrations. Every molecule has a unique way of stretching and bending. Figure 6.4 depicts some of these modes for a molecule such as water.
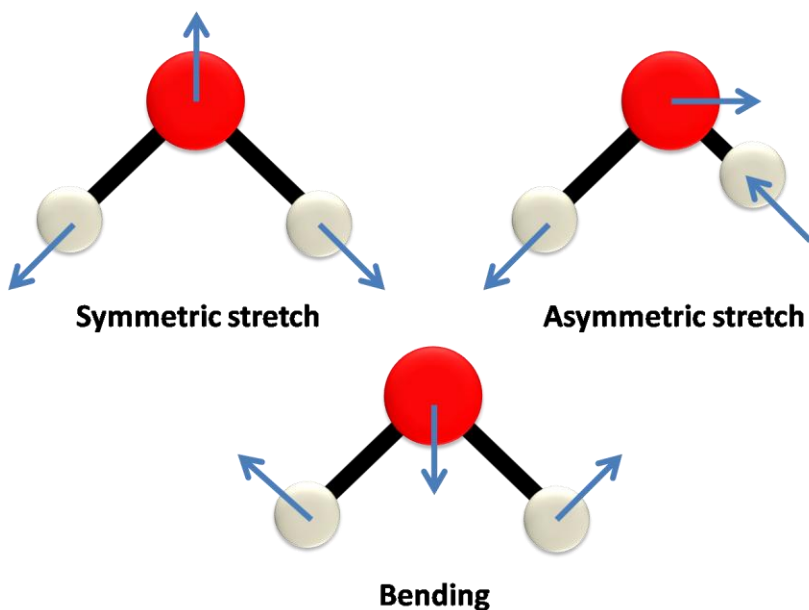

Figure 6.4. Modes of vibration for a molecule such as water.

Each motion occurs at a certain energy or frequency. The IR spectrometer will provide energy to the molecule. Any energy that is absorbed causes specific stretches and bends to occur. The spectrometer then monitors what wavelengths are absorbed by the molecule, and which just simply pass through. The output of this process is a spectrum—a graph showing peaks at the frequencies at which energy was absorbed, indicating which vibrations occurred. Because every molecule has a unique way of bending and stretching, every molecule has a unique IR spectrum. These unique spectra can then be compared to spectra we compute. We typically have a reasonable idea of what kind of reaction should be occurring on the matrix. We then can compute geometries and IR spectra for the products that we expect to see. These IR spectra are compared to those obtained from the matrix. If they match, then we know what reaction has occurred.

For easier comparison, look at subtraction IR spectra, Figure 6.5. We will take a spectrum of the sample before shining light on it (red), another after irradiation (blue), and then subtract the two from each other (purple). What the subtraction does is makes any peaks that were present in the first spectrum but not the second (peaks from any molecules that have reacted/disappeared) go down. Any molecules that were not in the first spectrum but are in the second (peaks from any products produced) go up. This then tells us what molecules reacted to give what products.
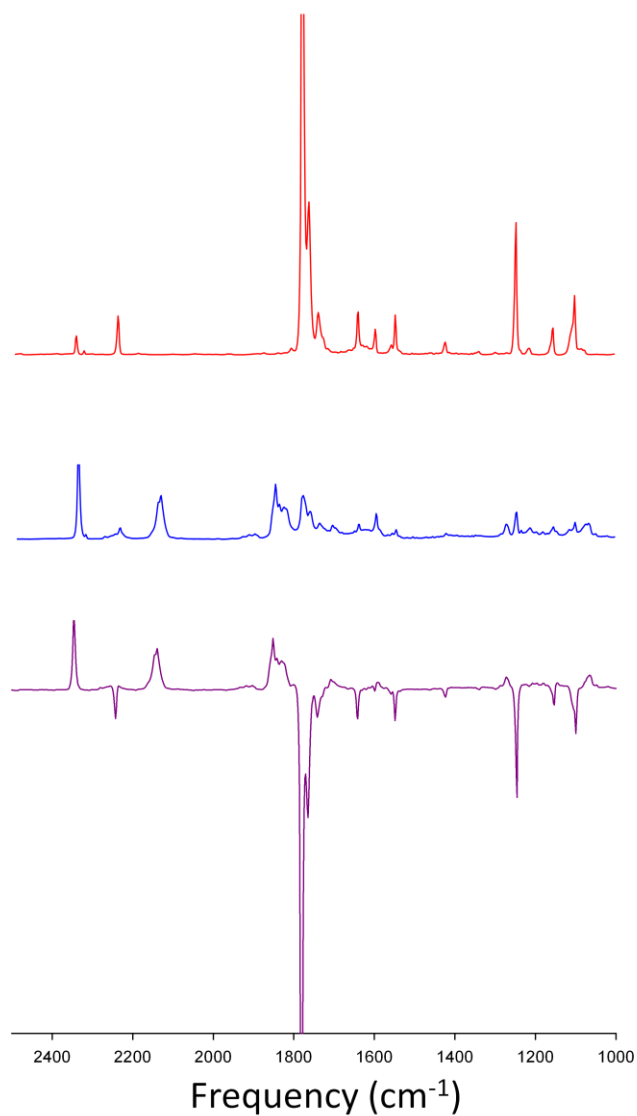
Figure 6.5. Red: IR spectrum taken before irradiation. Blue: IR spectrum taken after irradiation. Purple: IR subtraction spectrum showing reactants (peaks going up) and products (peaks going down).

Energy in the ultraviolet and visible section of the electromagnetic spectrum will cause molecules to change electronic states. This is a bit more difficult to describe, but essentially, what is being detected is what wavelengths of energy cause electrons in the

molecule to become excited (increase in energy). Again, this is assessed by providing the molecule with energy from the UV/vis portion of the electromagnetic spectrum and monitoring what wavelengths are absorbed (cause electrons to be excited), and which simply pass through. These spectra cannot be computed as easily as the IR spectra can, and therefore typically only tell us whether a change has occurred. Figure 6.6 shows two spectra, one before irradiation and one after. The spectrum has clearly changed, and therefore we know a reaction has occurred, but unfortunately we typically don't know what reaction has occurred.
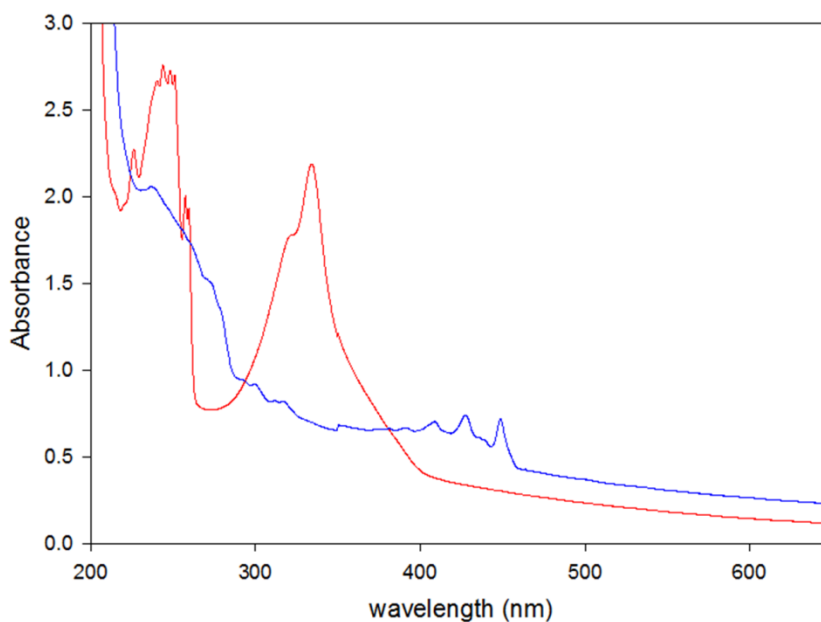
Figure 6.6. Red: UV/vis spectrum before irradiation. Blue: UV/vis spectrum after irradiation.

Computational Studies: Now moving on to the second portion of my title—Computational Studies. I briefly mentioned in the previous section one way we use computational chemistry, but I would like to give you the bigger picture. Computational chemistry is a great tool chemists use to study a wide variety of topics. For our purposes, we take any structure we want, whether it is a known compound or not, and use quantum mechanics (a way of describing energy at the atomic level) to determine what its optimized (lowest energy) geometry (structure) is. As I mentioned earlier, we can compute what the IR spectrum should look like. If we compute several molecules, we can then determine how the energies of the molecules compare to each other. These relative energies tell us which molecule would be most likely to exist—lower energy molecules are more stable, and more likely to exist. We can also determine how much energy would be required to cause a reaction to occur by computing a transition state between two molecules. A transition state is the geometry of a molecule at the highest energy point required along the path of change.

Cyanocyclobutadienes: While the first two components of my title might not have been familiar to a non-chemist, one could probably have at least made a guess to their general meaning. "Cyanocyclobutadienes," however, probably really brings out the "huh" factor. This is the structure of cyclobutadiene:
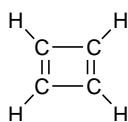
It is a four membered ring of carbons, each with a single bond to a hydrogen atom. To make it a cyanocyclobutadiene, one (or more) of the hydrogens are replaced with cyano (-C≡N) groups:
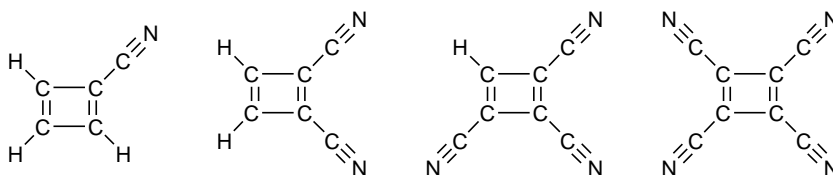
Cyclobutadienes are interesting molecules for a number of reasons. To start, the rectangular, four-membered ring is highly strained. Typically, the bond angle around a carbon-carbon double bond (C=C) is 120°. In the ring, it is only 90°. This ring strain adds energy to the molecule and makes it unstable.
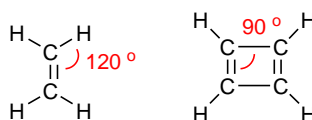
Imagine taking a metal, circular ring and compressing it into an oval shape. It takes energy to force the circle into an oval, and you feel the ring pushing back out against your hands.

Another interesting aspect of cyclobutadienes has to do with a topic called aromaticity. Aromaticity is a characteristic of cyclic molecules that have alternating single and double bonds. Rings that have three, five, seven ((4n + 2)/2 for any integral value of n) double bonds are considered aromatic.

benzene   napthalene   anthracene
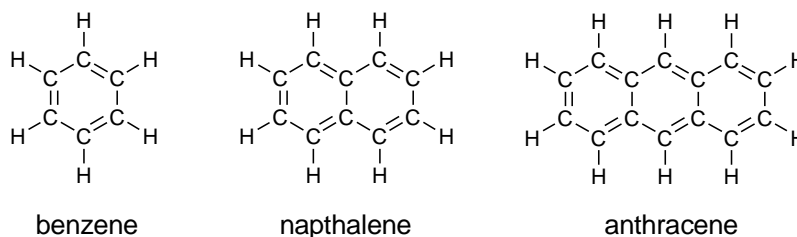
These molecules are highly stable. You might recognize the connection between aromatic and aroma—aromatic molecules are known to have strong scents. Napthalene is the primary compound in moth balls. I am sure you are familiar with the very characteristic smell of moth balls!

Molecules containing two, four, and six double bonds are antiaromatic. These molecules are unstable, and typically distort from a symmetric cyclic structure to reduce their energy. This is why cyclobutadienes are rectangular rather than square.
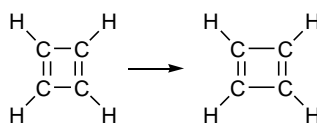
A number of cyclobutadienes have been made and studied using matrix isolation. We became interested in cyanocyclobutadienes because there is a possibility they may be present in the ISM. Cyanoacetylene is a known ISM molecule. If two of these were to combine, they could form dicyanocyclobutadiene.
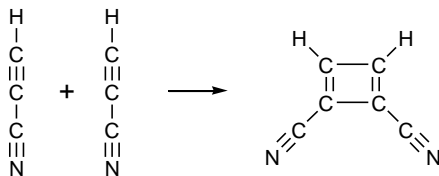
By studying cyanocyclobutadienes here in a laboratory, we can collect data that could then be used to possibly identify them in the ISM or in the atmosphere of Titan.

Results and Discussion

Computational Studies: Initially the goal of this project was to study cyanocyclobutadienes computationally to see if the cyano groups would make the ring more stable (lower in energy) or less stable (higher in energy) than the unsubstituted cyclobutadiene that had already been produced. It turns out that the cyano groups do make the ring a little more stable. This gave us hope that we could produce them in a matrix.

Matrix Isolation: We attempted to make several different cyanocyclobutadienes using several different precursors. Tetracyanocyclobutadiene was the first one attempted. The precursor used was diazotetracyanocyclopentadiene (**1**), Scheme 6.1. Diazo compounds are molecules that have a carbon-nitrogen ($C=N_2$) bond that is easily broken when the molecule is irradiated because it forms a very stable molecule of nitrogen (N_2). The other product is a carbene—in this reaction the carbene is molecule **2**. A carbene is a molecule that has a carbon atom with only two bonds and a pair of electrons that are not bonded to anything else. Typically, a carbon atom has four bonds. The carbene is very reactive and will react with any oxygen we might introduce into the matrix to give molecule **3**. This molecule can then further react when irradiated by forming a new ring, **4** (a pyrone), and then contract to form a bicyclic ring **5**. This ring can then lose a molecule of carbon dioxide (CO_2) to make tetracyanocyclobutadiene (**6**).

Scheme 6.1
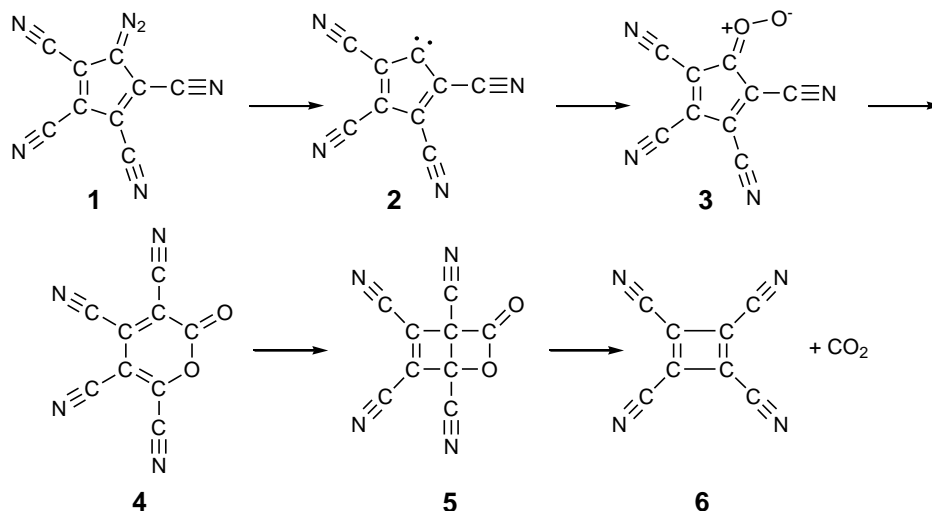
This reaction pathway has worked for producing cyclobutadiene without the cyano groups. We were unable to complete this reaction because we were never able to prove we could produce carbene **2**. It turns out that the diazo compound **1** is not very volatile. For that reason, we could not get very much sample to deposit on the cart window. Therefore, we could not follow the photochemical reaction using IR spectroscopy. We could, however, tell that reactions were occurring by UV/vis spectroscopy. UV/vis spectroscopy is more sensitive, and could follow the chemical changes that were occurring. However, as discussed earlier, the structures of the compounds in the matrix cannot be identified by UV/vis spectra.

The next attempt was to make monocyanocyclobutadiene. To do this, we followed a similar pathway. This time we started with the pyrone ring with one cyano group, **7**. The compound can be purchased, so it was an easy place to start. It was expected to go through the same pathway, Scheme 6.2, to give the monocyanocyclobutadiene (**9**).

Scheme 6.2
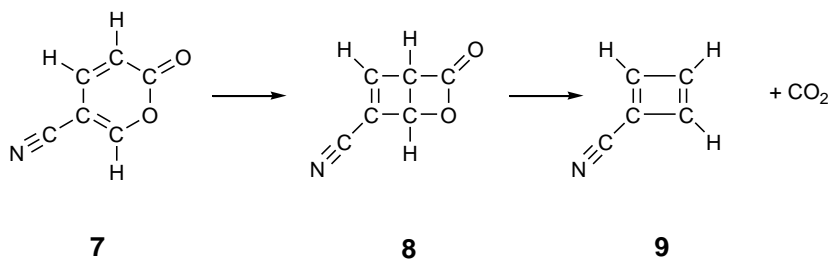
This reaction was successfully followed using IR spectroscopy. Figure 6.7 shows a portion of the IR subtraction spectrum showing the conversion of pyrone **7** to the bicycle **8**, and also the comparison to the computed IR spectra for each molecule.

Identification is made by comparing peak height and spacing for the computed spectra with the experimental spectrum. This is not an easy task, and it is not always obvious. It is a bit of a puzzle. But if you look closely, you might be able to see a similar pattern between the reactant computed spectrum (blue) and the peaks growing in on the experimental spectrum (peaks coming up in black spectrum). The computed product spectrum (red) has a similar pattern to the peaks going away on the experimental spectrum (peaks going down in black spectrum).

The conversion of the bicycle **8** to monocyanocyclobutadiene (**9**) was observed in the same way; however, only a small amount of **9** was produced. It is also reactive in the light used to produce it. Therefore, it is difficult to detect.
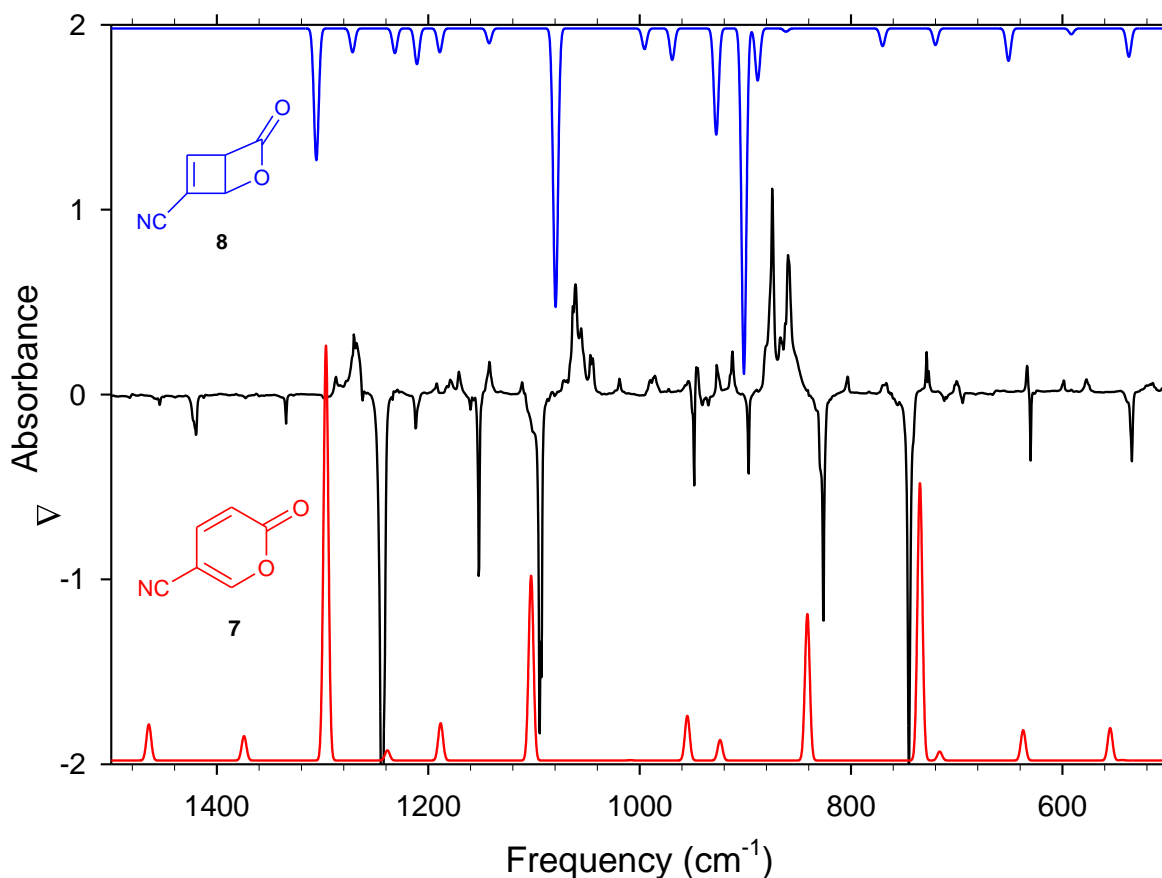
Figure 6.7 Blue: Computed IR spectrum for the bicycle product **8**. Black: IR subtraction spectrum obtained after irradiation of pyrone **7** at 299 nm for 2 hours showing the pyrone going away (down) and the bicycle growing in (up). Red: Computed IR spectrum for pyrone**7**.

Summary

Matrix isolation is a great technique used to make highly reactive molecules that cannot be produced under ordinary conditions in the laboratory. It simulates some of the key characteristics of the ISM and the atmosphere of Titan—low temperature, low pressure, molecules isolated from one another. In combination with IR and UV/vis spectroscopy, it

allows us to photochemically produce molecules such as cyanocyclobutadienes. Although the production of tetracyanocyclobutadiene was hindered by the non-volatile precursor, monocyanocyclobutadiene was isolated and studied. Computational chemistry allowed for identification of these molecules by computing the IR spectra and comparing them to the experimentally obtained spectra. It additionally provided initial support for possibility of producing cyanocyclobutadienes by showing they are lower in energy than the unsubstituted cyclobutadienes.

This summary is a very abbreviated version of my work from the last few years. I hope that you have been able to understand at least some of it. I have to say, writing this was more difficult than I anticipated. As scientists, we get pulled into our own little worlds. We are surrounded by others in the same field, and we rarely think about trying to explain what it is we do to others who are not familiar with the field. I admit to doing this myself, but I have been able to pass on some of my experience to you by writing this.