

VIBRATIONAL MOTION IN THIOPHOSGENE AND RELATED STUDIES

BY

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THESIS

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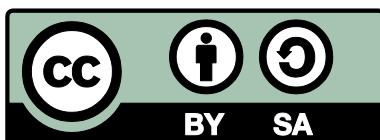
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Abstract

Over 300 second excited state to ground state vibrational transitions have been located, measured and assigned by dispersed fluorescence spectroscopy. The energies of these transitions were also fit with a spectroscopic effective Hamiltonian. These spectra show high activity in the ν_1 and ν_4 modes which is expected due to their known high Frank-Condon activity. However, predicted activity in other modes, particularly ν_2 and ν_6 was not observed, quite likely due to the poor resolution of the higher energy spectrum. This made low-lying lines difficult to assign, thus hindering assignments of progressions in the higher region of this spectra. A higher resolution spectrum is required. A torsional potential energy surface was also constructed for the 2-fluoroethanol molecule, in an attempt to make theoretical predictions and corroborate known experimental work on the molecule. This surface includes zero-point energy (ZPE) corrections, to see if it would lower the torsional barrier significantly. It did not. A computer program used to predict potential couplings in a tier model of IVR is also presented.



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Bless this tiny alley

Acknowledgements

I'd like to take this chance to speak from the heart.

There was a time, a time I can only conjure when lost in the deep recesses of my mind with my eyes closed and a piercing soundscape flying at me from vibrating boxes equidistant from me and the pain of emotion wafting up and down my rib cage trying to lift my head off my body, when I felt something. While stuck in a moment, one might say. I'm quite sure there was nothing in particular that brought about this feeling, it just floated through me, stopping to visit on its way to the coasts no doubt. How very thoughtful.

A funny thing about the flatland. You can erect as many windbreakers as you want, but you'll just be circumvented, like standing in front of a giant trembling with fear only to watch him deftly sidestep you on his way to somewhere he thinks he needs to be, which is the real reason why he's here. Sometimes I feel like I am stuck in the crossfire of a battle between Mr. Atlantic and Herr Pacific. They like to throw wind at each other and wrap them in clouds.

This feeling was different. It wasn't low blood sugar. It wasn't a reaction to a foreign chemical substance, not that I'm a xenophobe. I quite like indoles of the tryptamine family, to be honest.

If a class of compounds could be a diaspora, I suppose they would be the diaspora of the dead. It wasn't from anything at all though, really. I remember not feeling physically attached to the ground, even though I reasoned to myself that I was - because, I mean, my feet were on the ground. I remember feeling completely separate from all else, while simultaneously being tethered by invisible, vibrating strings to everything else in the universe. It's a strange dichotomy, and I'm grateful I could watch it unfurl, quite like a reporter at the edge of life, taking notes for the local Sunday Mail. While I was initially struck by the power of the feeling and the smell of Death's halitosis, I grew steadily euphoric.

Time was of no consequence, it appeared to just pop out of the air, an infinitely stretched out line that just kept going on forever and in front of me. But it was only apparent when I stopped to look for it, and tried to focus my eyes on a spot instead of trying to take in the scene with no struggle. Not that I was struggling, it's just that my mind was still moving pretty nimbly. Everything that comes with Time seemed to do the same thing, too. Purpose became contextual, like the speedy movement of ant antennae on an unmoving ant body. Ambition looked like Desire on rollerblades with a stupid grin on his face. All movements reduced to limited superpositions of these fundamental feelings. It all just seemed kinda boring. I mean, I was euphoric - I didn't really give a shit. But I took notes anyway, I think I am quite good at writing about things I don't *really* care about.

Somewhere in the distance though, I could see some Man bludgeoning a family to death. He seemed very calm, very composed, and knew exactly what he was doing. Not like read-it-in-a-book-and-memorized-and-thus-know knowing, his hands just moved with fluidity of intent and

clarity of purpose. He was simultaneously delivering an entertaining lecture to two young boys who stood watching, trembling with fear but trying to stay still and look awestruck, as if that's what the Man wanted or something. I couldn't really make out words very well, they were of no consequence either. I could feel their character however, and that's all that seemed to matter. I assume he was talking about what life *ought* to be about or something. Ideology of some sort I'm sure, the kind little boys start daydreaming to when you start talking about it. I do remember some of the words though –

“... blab la bla... (other unintelligible gibberish)... *NATION*... ..
.FAMILY FIRST... .. *plan for our future, boys*... .. *prophecy*...
institutional structure...”

Whatever – I'm pretty sure I just heard what I wanted to hear anyway. I don't care for ideology very much, but I'm pretty sure that all 'life-changing' social theories that ended up in mass genocide began as inspiring, small-brained ideas sold to the Proletariat. That's when I left that domain, much to my chagrin. I mean, it was just starting to get funny.

Then there was nothing. Just a brief, momentary flashing of light somewhere in the distance. A splotch of color in it every now and again. The frequency of event occurrences was decaying to zero quite quickly. I guess my synapses were taking their own sweet time to catch up with the rest of me. And then I remember blackness.

And that's when *She* popped out, like the sexy protagonist of the play.

Of course she was *gorgeous*. I mean, its not like she was tied to an earthly confine. She floated from my periphery toward me before eventually enveloping me. She had no physical form. But she had a face. I guess my Fusiform Gyrus was still working. I remember a feeling getting stronger in proportion to her movement towards me. Love, I guess. It definitely had that fleeting transience to it.

... That's when my memory fails me. I've never been the same though, and I'd like to thank her for that. I wish I got her phone number, though.

Before I proceed to do the whole thanking bit, I'd like to include a passage a friend of mine wrote late at night after heavy disembodiment, I suppose stuck in limbo between night and the imminent sunrise.

“Consider the refinement of a thought. If we spoke to the university as the university speaks to us, it would be a voice wrapped in fear, culminated by its doubt, shallow as the sands stretching off a coast that exists in memory but never actually existed. Consider the realms that we have never inhabited but have spoken of, as if we understand them, as if their existence was obvious and justifies our words but these realms exist in our words and nowhere else. Consider science. The epoch. The word. Consider Determinism, its sisyphian task, its need to prove unarguably that particles are not waves. Consider this. What are the fluids? What are the flows? If the moon

spoke to us would it be in tides? Is that language? It speaks to the core of the person. We all imagine that eternal consummation upon the ebb of the consciousness. We all imagine the moonlight embracing our lovers skin in silver abandon. But can that exist? Someday it can. But for now we bear something. Some weight. And it is too much. In the daylight it is a concept but at night it flows out of the glasses we hold, it flows laminar out of our cigarettes. They follow us to our imbibing as if following us will make them understand. They shudder and conceptualize. But the true nature of the thing is not in this speech. The true nature of the thing has never been contained to the objects which are met with frameworks and analyses. We are some other thing. Rewired by trauma, reiterated by psilocybin, reinvoked by the music. We have travelled in cars. We always will choose cars for the spatial. The temporal is reserved for the indoor-outdoor debate, the temporal is reserved for these albums. And we traverse, in a way that will never be understood. But we understood it, briefly, certainly, with absolute intention.”

I’d like to begin by thanking my parents for kicking off this whole chain of events.

My father, for being the most steadfast, resolute, sanyasin of a man through it all.

My mother, for being afflicted with an insanity of perception that could make me laugh while simultaneously cringing in the fetal position, contemplating a myriad of ways to kill myself and everyone on the damn planet. I get my creativity from her.

I’d like to thank my sister for sibling rivalry, and the spectrum of emotions we shared as only brother and sister can.

I'd like to thank every teacher I ever had that made me forget about what I was daydreaming about to catch what was being said.

Martin Gruebele deserves the most thanks for this work. I was an undergraduate somewhere deep in the heart of Texas, and I read a lot of books and kept switching my major every few weeks. I ended up in junior year picking the one that I had the most credits in and could lead to a degree and a graduate school, because I heard that's easier than getting a job and the whole 'trying to live in a foreign country that you weren't born in without wage slavery? You fool' bit. I heard you needed to do research to get into grad school, so I picked the lab with nothing but computers so I could surf the internet when I was bored, a nice view, and 20 paces from a cool, large patio where I dutifully took hundreds of cigarette breaks and enjoyed the occasional spliff. I only had one gift – I could ace any standardized test you put in front of me. I guess that and good grades you didn't work for will get you into grad school. I was excited at first. I always wanted to be in a place with a pretty campus and nice buildings and an awesome library where I had access to all the knowledge in the world with just a few keystrokes. Rubbing shoulders with intelligent people at coffeeshops and bars. Listening to smart people talk with intent. Smart people from all disciplines, in highly ranked academic departments. I mean, my parents were impressed, and they were even fronting me money for my flight there. I am convinced Martin Gruebele is the smartest man I've ever met and talked to from across a table or seated on a couch. I wanted desperately to just be like him. I'm more interested in me these days though, but I will always revere you, Martin.

I'd like to thank Praveen Chowdary for explaining every single experimental and theoretical detail, no idea excluded, no stone unturned, while I stared intently and nodded whilst

daydreaming. I'm sorry I'm kinda pissing away all that time you put into me. I'm thankful for it though, and always will be. Dan Weidinger too.

Dan Weidenger, for being funny and smart and never minding engaging me on my silly whims and thoughts and for being a great listener.

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Tarun Kumar, for being my first partner in the crime of true friendship. What town do you want to meet in next?

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Heath Timmons, for falling into this category when he isn't chasing after something or ruminating about love that can't exist. And for his magnitude and immediacy of true feeling, draped in pretty words.

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My current neighbors Robert Rhinehart, Dan Duitscher and Adam Bullock.

Rebecca Greenlee, I would like it very much if we exchanged letters about things we write like Rainer Maria Rilke did with unnamed strangers. Please continue to share your lovely thoughts with me.

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Joe Muggli. Enough said, when I'm gonna see you again?

Kai Goodman. You're a good man.

Tim Wotherspoon and Liz Jackson, for showing me, even in the midst of all this transience and fleeting desire, that the truest love is also the simplest.

Spencer Corning. Now there's some honesty that's direly needed.

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To SmoroniusMonk, for many fun times watching you interrogate the Other through your enormously large pinholes. And for being my favorite and only Feline.

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Lisa Zangerl, for moments, and Hajji Hollow.

Lola McQueen, for coming to me at a time when my need for love was only outmatched by my vicious detachment.

Every woman I've ever loved, and every person who's sat down in front of me, looked me in the eye, and said something honest.

And of course, YOU, if your name isn't in here, and you got this far. My apologies, I'm about to miss this Thesis Deposit Deadline any second now.

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Chapter 1

Introduction

“In other words, out of the expected chaotic motion in the vibrational and rotational phase space we could see ordered and coherent motion despite the presence of numerous vibrational degrees of freedom. This point was theoretically appreciated by only a few scientists.”¹

Intramolecular Vibrational Redistribution (IVR), in short, is the mechanism which underpins how vibrational energy that is initially localized in one vibrational mode is redistributed among other vibrational modes in a molecule. IVR is a phenomenon that was identified over 50 years ago, but the exact mechanism by which it occurs continue to perplex scientists today. It is a field of study that involves experimental interrogation into spatial and temporal resolutions where chemistry at a fundamental level occurs. It has spawned innumerable experiments and theoretical constructs in an attempt to delineate its mysterious ubiquity in all molecules.

In the 1930's, a Transition State Theory by Wigner and Eyring was being developed to understand how molecules are activated in chemical reactions. They, as was naturally assumed at the time, stated that no barrier recrossing could occur in this process, when picturing trajectories on energy surfaces. Rice, Ramsperger, Kassel and Marcus^{2,3} published a prediction of kinetic rates of chemical reactions because they understood that an entropy barrier arises from the improbability of concentrating the vibrational energy in a few degrees of freedom prior to

reaction. The RRKM theory that was spawned as a result is now an accepted part of textbooks everywhere and is still used to this day in literature to predict reaction rates. However, their theory rests on the assumption that energy flow is instantaneous (facile or ergodic). We know today though, that IVR as a theory rests entirely on the understanding that this mechanism of energy transfer in small molecules, and even in large molecules upto energies of 6000 cm^{-1} , is NOT instantaneous, and can most certainly lead to barrier recrossings.

IVR is crucial in determining the rates and mode specificity of chemical reactions. Understanding how IVR works is crucial in understanding if the rate of a chemical reaction can be accurately described by statistical theories or whether a more dynamical treatment is necessary. Molecular vibration has always been treated theoretically using a network of non-linear oscillators. Low energy modes are generally treated with uncoupled harmonic oscillators, while higher energy is usually treated using coupled harmonic oscillators. However, when multiple dimensions are required, as are in most real molecules, the dynamics are nontrivial. One need only to go as far as the Fermi-Pasta-Ulam⁴ problem of the 1950's to acknowledge this. Their theories showed that energy flow couldn't occur when linear springs were used, but when non-linear springs were used, energy flow was certainly observed, but it certainly wasn't ergodic. In IVR today, nonlinear mode-mode resonances are absolutely crucial in any theoretical model. IVR is like energy transport on the resonance super-highway – it is all about expressways, by-lanes, dead ends, bifurcations and irrational quantum transport.

It was once pointed out to me that the viewpoint on IVR today is reminiscent of the 1890's when Henri Poincare was studying perturbations of conditionally periodic motions⁵. Birkhoff said, in 1927,

“At a time when no physical theory can be properly termed fundamental – the known theories appear to be merely more or less fundamental in certain directions – it may be asserted with confidence that ordinary differential equations in the real domain, and particularly equations of dynamical origin, will continue to hold a position of highest importance.”⁶

So when is energy transfer not ergodic, and why? Work by prior scientists, and work done in this lab, point to certain facts. Many have argued that in large molecules, where statistical nature of energy flow is assumed, the density of states in phase space allows it to be treated as a continuum, allowing direct application of Fermi’s Golden Rule⁷. It is generally thus assumed that in molecules with over 5-10 atoms, vibrational energy flow is largely ergodic. The IVR rate of the initially excited state then simply given by the rms coupling $\langle V^2 \rangle$ and the density of states ρ as per the Golden Rule:

$$\Gamma = \frac{2\pi}{\hbar} \langle V^2 \rangle \rho$$

This however, assumes that the coupling matrix elements are strong, and statistically independent, and it was assumptions like these that led to the development of ergodic models such as the Gaussian Orthogonal Ensemble (GOE)¹⁰.

A variety of studies though, seem to indicate that in many situations, the rate of IVR does not scale evenly with the density of states^{8,9}. Also, even though the density of states is an easily obtained value, accurate coupling matrix elements $\langle V^2 \rangle$ depend on accurate knowledge of the potential energy surface and one must also discount the effects of intermediate resonant states, large amplitude motions etc.

Theory is constantly improving, however. Wolynes, Gruebele and others have produced more accurate predictions using an approach known as Local Random Matrix Theory⁹ (LRMT), for instance. Using appropriate scaling laws for intramolecular vibrational couplings especially helps. The Hamiltonians in this method has the standard model of normal mode harmonic oscillators with anharmonic couplings. Visualizing IVR with this theory brings out certain characteristics ignored by prior models. For one, it is clear that certain paths through phase space are more facile than others. Such paths usually follow local resonances, such that quanta from one mode gets evenly distributed amongst other modes such that total mode energy is roughly conserved. In a state space basis, other interesting observations can be made – for instance, modes that lie toward the interior of state space, ‘interior states’ if you will, that have excitation in many modes and have many connections to other states via non-linear couplings have many possible paths for energy to flow as opposed to ‘edge states’ with few couplings. As a result of this picture, the determining factor now becomes a ‘local’ density of states $\rho_{\text{loc}}(\Delta E)$, which is a function of the energy change during flow. This is explained in great detail in prior work.¹¹

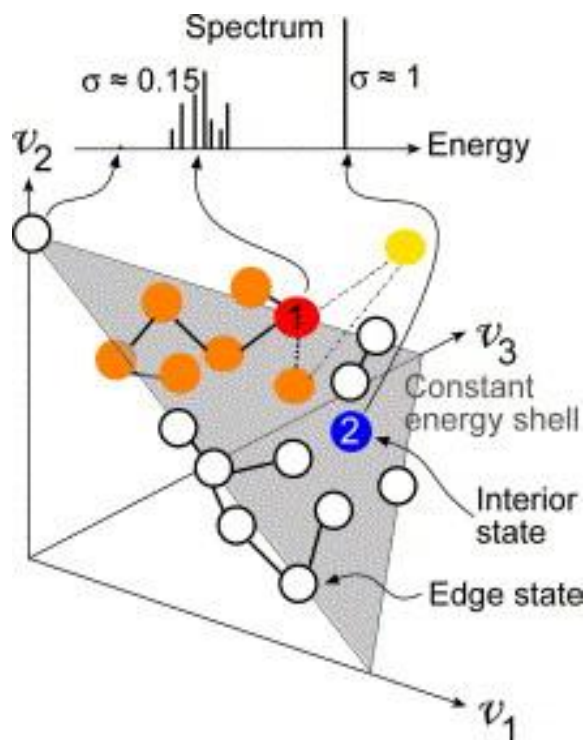


Fig 1-1 Three mode state space model showing bright/dark quantum states as lattice points¹²

This work is split up into two parts – experimental and theoretical. In the experimental chapter, I discuss the experimental setup used to procure fluorescence excitation spectra and dispersed fluorescence measurements in detail. This is followed by a section devoted to the results of the data acquisition, and is accompanied by images of the respective spectra. The data processing methodology is then described. The next section is devoted to data analysis, and lists out all the assigned peaks and the modes excited. A spectroscopic Hamiltonian is also described and fit to the data to bind theory to experiment. Lastly, the implications of these results are considered.

The theoretical chapter focuses on one particular project I undertook during my tenure here as a graduate student. It centers around the construction of a potential energy surface for the

small molecule 2-Fluoroethanol. After a brief introduction to the general steps required to construct such a surface, the motivations for this study are discussed, and followed by surface construction methodology, the surface itself, and a brief discussion on what conclusions can be abstracted as a result.

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Chapter 2

Fluorescence Experiments

“The atoms become like a moth, seeking out the region of higher laser intensity.”

- Dr. Steven Chu

2.1 Introduction

2.1.1 Thiophosgene

This chapter is devoted to fluorescence experiments on thiophosgene (SCCl_2) performed in our lab by me under the gracious auspices of Dr. Martin Gruebele. Thiophosgene is one of the most extensively studied small molecules, with collections of its spectroscopy and photochemical/physical properties readily available in literature¹⁻⁴. One of the reasons it is such an excellent candidate for study is because it fluoresces from both the first and second excited singlet states, in direct violation of Kasha's rule⁵. This allows for convenient dispersed fluorescence, and opens up possibilities of experiments in which wavepackets can be formed and fluorescence detected from two independent electronic states. Moreover, thiophosgene has only four atoms, and possesses no hydrogens, and is hence excellent for studying purely skeletal vibrational energy flow. Also, because of its small size, it is far more convenient to use in theoretical computations whose processing time scale exponentially with the number of atoms.

The normal mode vibrations of thiophosgene are depicted in Table 2-1, and the fundamental frequencies (as calculated from averaging data over many series of spectra collected in this lab) are listed in Table 2-1. The most active vibrational modes are the ν_1 (or Q_1 , CS symmetric stretching) and ν_4 (or Q_4 , out of plane bending) modes, as these result in the largest equilibrium geometry changes for the molecules. Indeed, thiophosgene is quite special because fluorescence can occur all the way up from the dissociation region to the ground state via these two highly Frank-Condon active modes.

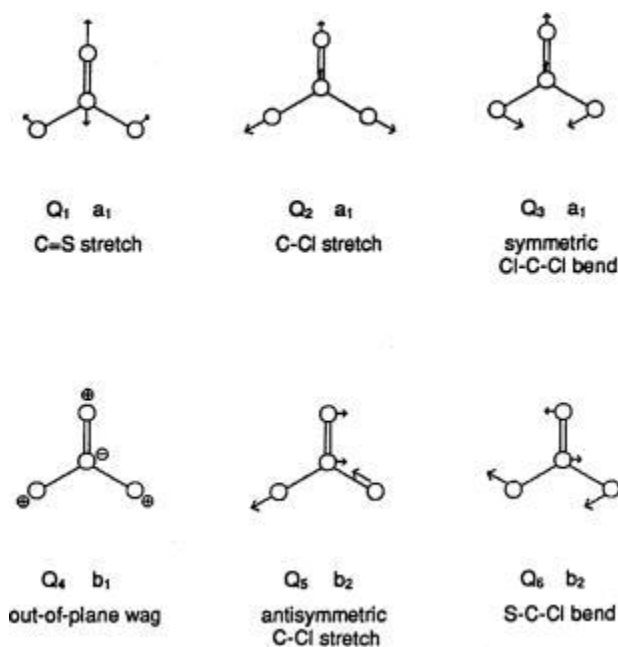


Fig 2-1 Vibrational Modes of thiophosgene in the ground state

Table 2-1 Normal Mode frequencies of thiophosgene in the ground state

Normal mode	Fundamental Frequency
ν_1	1155.9 cm ⁻¹
ν_2	514.06 cm ⁻¹
ν_3	295.46 cm ⁻¹
ν_4	476.27 cm ⁻¹
ν_5	821.79 cm ⁻¹
ν_6	301.22 cm ⁻¹

2.1.2 Fluorescence Experiments

The general scheme for the fluorescence experiments is as follows. Excitation spectra were initially gathered by scanning the exciting laser while it interacts with the thiophosgene molecular beam to find absorption bands worthy of interrogating. Once an unstudied band that promises insight was found, dispersed fluorescence studies were undertaken. This was done by setting the exciting laser energy at the peak of the absorption band, and channeling the fluorescence into a monochromator to understand its spectral decomposition. By analyzing this data, we are able to understand what energy levels are accessed after the initially excited ‘bright’ state begins to fluoresce, and a wealth of other spectroscopic information, some of which is outlined in this chapter.

2.2 Instrumentation

2.2.1 Lasers and Beam Generation

The initial 532.075 nm laser pulse is produced by a 20 Hz, frequency-doubled Continuum Surelite I-20 Nd:YAG laser providing 60 mJ/pulse. This pulse is used to pump a high resolution Continuum ND6000 dye laser. The dye laser is equipped with a 2400 groove/mm grating, which can be substituted with an 1800 groove/mm grating depending on necessary application.



Fig 2-2 Continuum Surelite I-20 Nd:YAG laser

The grating has a high tenability in most of the visible range (420 – 740 nm) with upto 0.08 cm^{-1} resolution at 560 nm. For all the experiments described in this chapter, the dye used was Fluorescein 548. This dye was found to produce a very strong output pulse (~60-100 mJ)

over the entire range of interest (540-550 nm undoubled) and did not quench easily, thus allowing continuous run time without having to replace the dye often.



Fig 2-3 Continuum ND6000 dye laser w/Fluorescein 548

The dye laser output pulse is run through a 39 mm KDP crystal which doubled the frequency of the dye pulse. The doubled pulse was optimized and kept from fluctuating left to right with the use of the Inrad Autotracker III. The output pulse, after alignment through the autotracker was fixed, is dispersed via a Pellin-Broca prism.

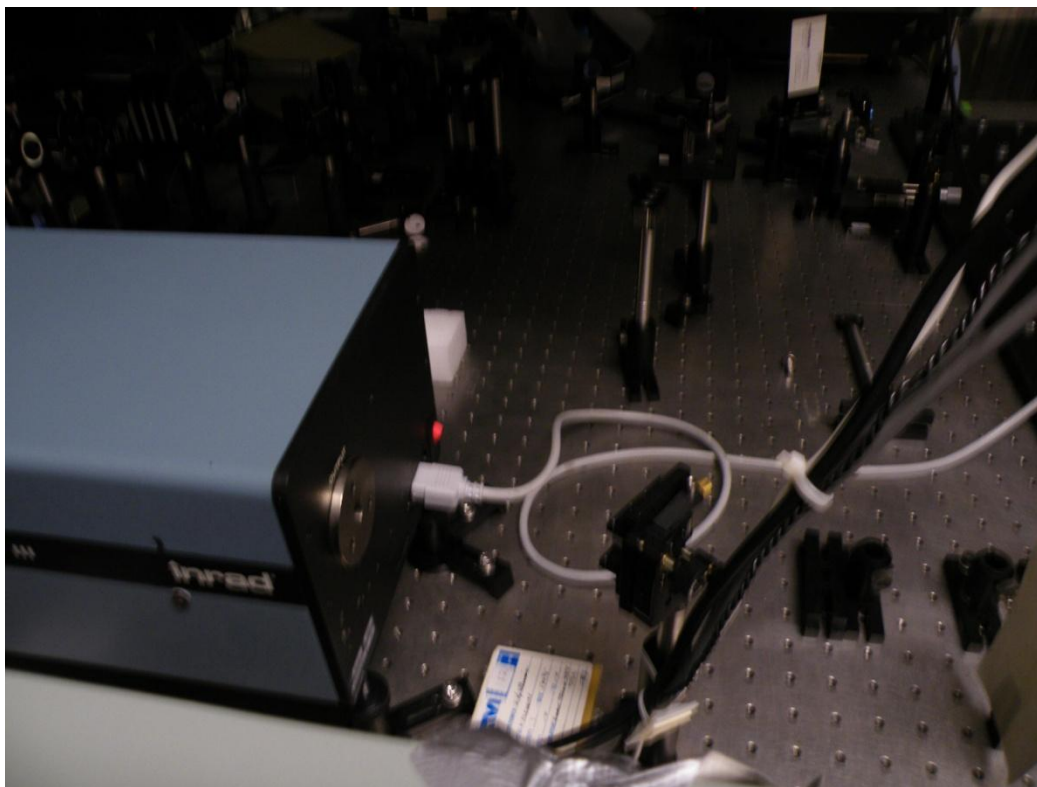


Fig 2-4 Output port of INRAD Autotracker III w/ Pellin-Broca prism

A Pellin-Broca prism displaces different frequencies of light by different amounts. This allows maximum spatial separation of the doubled pulse from the remaining dye output that makes its way through the autotracker. This pulse is then focused by a 40 cm UV lens through the front window of the molecular beam chamber, which is discussed in the next section. The shot to shot pulse fluctuation was monitored via a photodiode that was monitored externally.

2.2.2 Molecular Beam Vacuum Chamber

The beam is focused into the cavity of an 8-inch by diameter cylindrical vacuum chamber. The chamber is built out of stainless steel and its inner surface is evenly covered with

a black PTFE coating which minimizes corrosion on the surface and reduces the possibility of scattered light contributing to the fluorescence signal.

There are 4 ports fitted to the chamber. An entry port and exit port along the line of the laser beam, and a sample introduction port and fitting for attachment to an optional mass spectrometer perpendicular to the line of the exciting beam. The entry and exit ports are fronted by a 3 mm aperture in which fused silica lenses are fit. The entry port lens is normal to the incoming beam to allow maximum throughput while the exit lens is cut at Brewster's angle to prevent reflections, thus minimizing scatter. At the bottom of the chamber, mutually perpendicular to the two directions mentioned above, there is a polished curved mirror which enables direction of lost fluorescence towards the top flange of the chamber. The top flange of the chamber contains a port which is fitted with a finely threaded window in which is mounted a 25 mm diameter, 100 mm focal length fused silica lens which enables collimation of the fluorescence into the PMT or monochromator, which is discussed later. The fine threading allows for fine adjustments to the lens position, ensuring maximum signal level is achieved.

Vacuum is achieved in the chamber by a combination of two vacuum sources – a Leybold turbo mechanical pump is applied to evacuate the chamber upto a pressure of 5-9 millitorr. To evacuate the chamber to the very low pressures required for our experiments, a Varian VHS-6 diffusion pump is fitted to the bottom of the chamber via an 8-inch electro-pneumatic gate valve and cryo-baffle. The diffusion pump enables us to reach pressures of upto 0.5 microtorr at a pumping speed of ~ 2400 L/s air. The diffusion pump is heated by a heating element and cooled by a water-water heat exchanger at 23°C. The Leybold is connected to the chamber via a separate valve which allows the initial evacuation. The exhaust of the diffusion

pump is also connected to this line to allow evacuation of the hot gas that is produced during its operation.

The pressure in this line and the chamber are monitored by Granville Phillips Convector gauges that have a sensitivity of upto 1 microtorr. Monitoring of the pressure in the chamber once the gate valve is open to the diffusion pump is done by an iridium filament ion gauge. An external digital vacuum gauge controller allows the reading of the pressures monitored by the two convector gauges and the ion gauge. The entire system (diffusion pump, gate valve, pulsed valve) is protected by an homemade interlock switchbox that automatically shuts off the vacuum system in a safe manner if the pressures are outside of safe, standard operating ranges. In addition, the diffusion pump is also fitted with a thermostat which shuts down the heating element if the pump overheats.

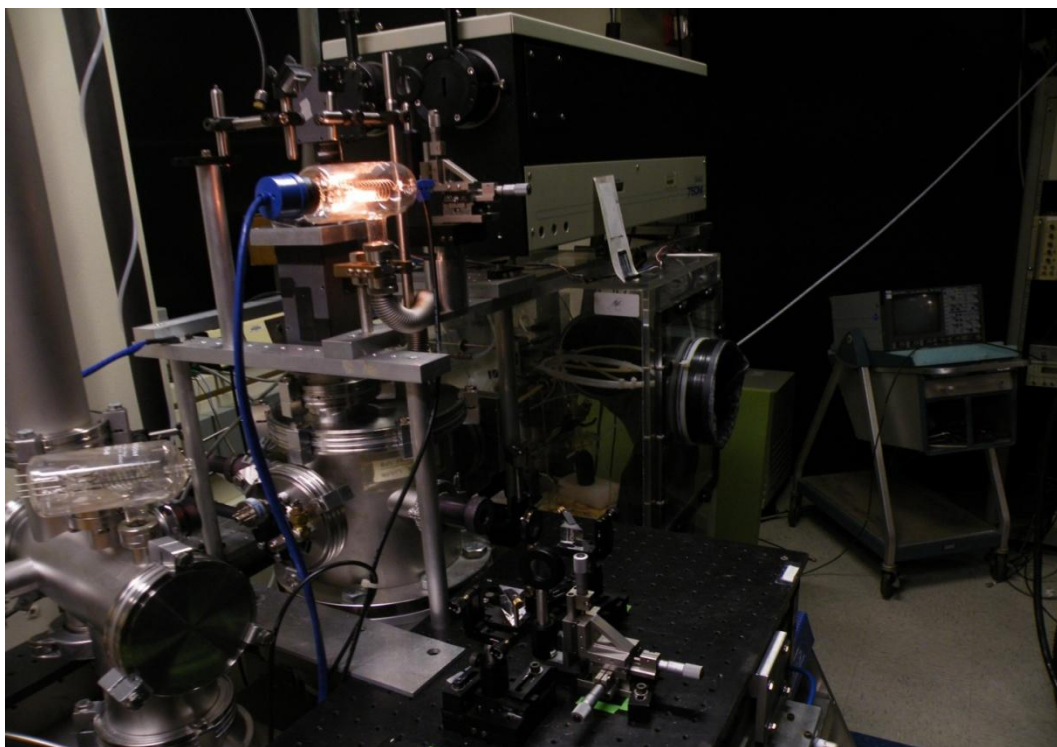


Fig 2-5 Molecular beam chamber, vacuum system, sample delivery and monochromator

2.2.3 Sample Delivery System

The thiophosgene is delivered to the chamber via a homebuilt sample handling system. A very crude schematic is shown in Fig 2-5. The entire sample handling system is contained in a transparent acrylic glovebox fitted with thick neoprene gloves. This prevents the accidental leakage of toxic thiophosgene into the laboratory or adjacent laboratories via air ducts. Stainless steel tubing is coupled into and out of the glovebox through rubber and neoprene grommets.

97% Thiophosgene samples obtained from Aldrich were used as the sample in our experiments. The sample container consists of a 100 ml brown glass bottle fitted with a modified cap with two PTFE tubes running and out of it. The modified cap also contains a stop cock to prevent vaporization of the sample when not in use. A stainless steel insert is machined and fitted with Kalrez compound 4079 o-ring seals which resist swelling upon contact with corrosive gases. The insert contains two holes through which stainless steel tubes pass and are epoxied in place. Helium is the carrier gas of choice and can be fed into the system through two channels – one that bypasses the sample container before it meets the sample line again as it is pulsed through a specially designed nozzle, and one line that goes to the sample holder and bubbles through the solution. A needle valve was placed on this line so as to control the bubbling rate. The typical concentration of SCCl_2 in the helium stream heading into the chamber is ~1-2%.

The SCCl_2 -seeded helium needs to then be converted into a fine spray in the chamber. This is achieved by the use of a piezoelectric pulsed valve adapted from the design of Proch and Trickle. The valve was constructed to replace the older solenoid valve in order to generate shorter gas pulses (200 μs) with lower duty cycles, higher molecule densities and more stable

operation. The valve and high-voltage driver were constructed following schematics donated to the group by H. Floyd Davis. The valve body is made of stainless steel and coated with a 0.001 inch PTFE coating to minimize corrosion. The nozzle aperture is 0.5 mm. The piezo disk was obtained from Polytec Physik Instrumente (P/N P-286.23). It translates horizontally a distance of 100 μm . It was liberally coated with fluorinated grease to resist corrosion and ensure smooth travel. The valve is sealed via a combination of Viton O-rings and one Kalrez compound 4079 O-ring.

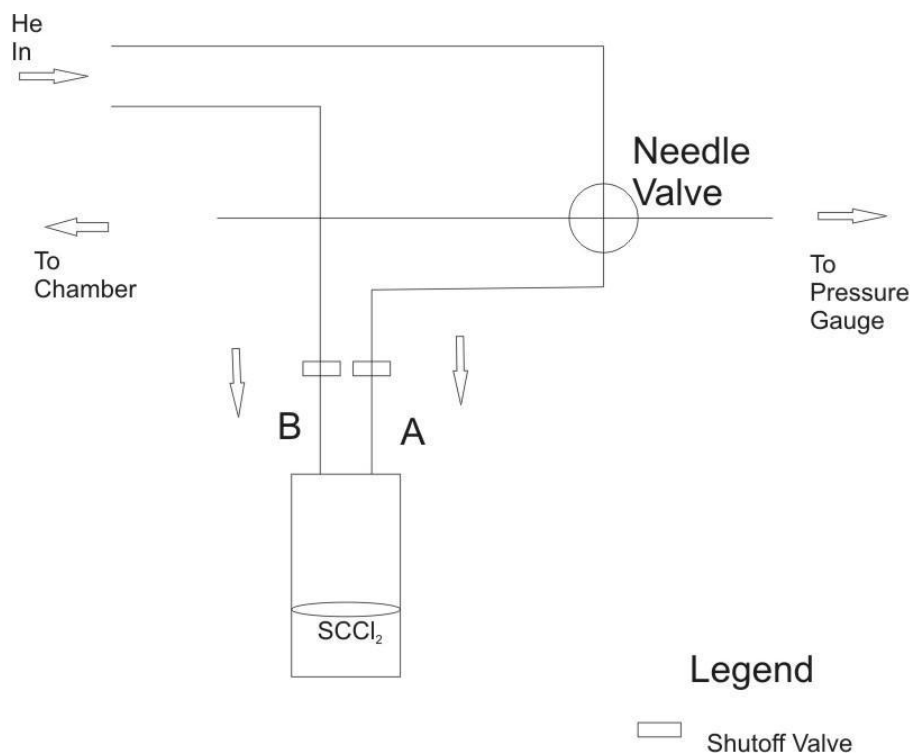


Fig 2-6 Thiophosgene Sample Handling System

The piezo disk is driven by negative polarity HV pulses (0 to -1000V) and triggered externally by the timing control unit, which is described in a later section. The HV driver comprises three circuits: a pulsing circuit that triggers and gates the valve at the correct times, a group of three low-voltage power supplies which provide power for the pulsing circuit and a high-voltage power supply which provides the voltage to translate the piezo disk. Potentiostats were also installed to enable adjustability of output voltage and pulsewidth.

The valve is mounted to a homemade XYZ translation stage via a 2-inch by diameter threaded cylinder assembly. This allows fine adjustment of the nozzle position in the chamber to ensure that the excitation laser pulse can overlap with a high density segment of the fine sample spray. The translation stage is mounted external to the chamber to allow this fine adjustment without having to evacuate the chamber.

Studies of SCCl_2 excitation hot band contours performed by Dr. Bob Bigwood in this group place the upper limit on the vibrational temperature 10 mm from the nozzle at 145 K. His analysis of rotation contours places the rotational temperature at 5-12 K.

2.2.4 Monochromator

A SPEX 750M scanning monochromator is used for all dispersed fluorescence experiments. This monochromator features an f/6 aperture, GPIB interface, and a single 110 x 110 mm 1800 groove/mm holographic grating. This grating allows a high resolution of 0.0067 nm resolution through adjustable 2 μm slits that are present at the entry and exit ports. The exit port is fitted with a side-on Hamamatsu multialkali photocathode PMT (model R928). This photomultiplier tube has a 185-900 nm spectral range and a 2.2 ns anode rise time. It is driven by a Hamamatsu regulated HV power supply (model HC123-01). They are contained within a

black-anodized aluminum box, and connected to an adjustable knob to control the voltage with a sensitivity of ~ 10 V (range 0-1 kV).

The fluorescence signal from the chamber is collimated into the monochromator through the entry slit via a 25 mm by diameter, 100 mm EFL fused silica lens mounted on an XYZ translation stage approximately 10 cm from the slit. Two aluminum-coated mirrors are used to steer the signal up and sideways from the chamber on to this lens and into the monochromator. During dispersed fluorescence experiments, slits were generally between 30 – 250 μm depending on how the signal was optimized. A special longpass filter was applied when collecting dispersed fluorescence above 435 nm. This filter enables the filtering out of interference from the 280+ nm light (especially the excitation fundamental) that can appear at around 560 nm as a second-order diffraction signal. The SPEX 750 M is easily calibrated periodically using the known spectral lines from a Hg(Ar) lamp.

The GPIB interface allows the entire assembly to be controlled via computer using a homemade control program made using *LabWindows*. Vacuum correction is also applied by the control program. Dispersed fluorescence line intensities are normalized based on the spectral response of the monochromator and PMT, and is outlined in the data processing section.

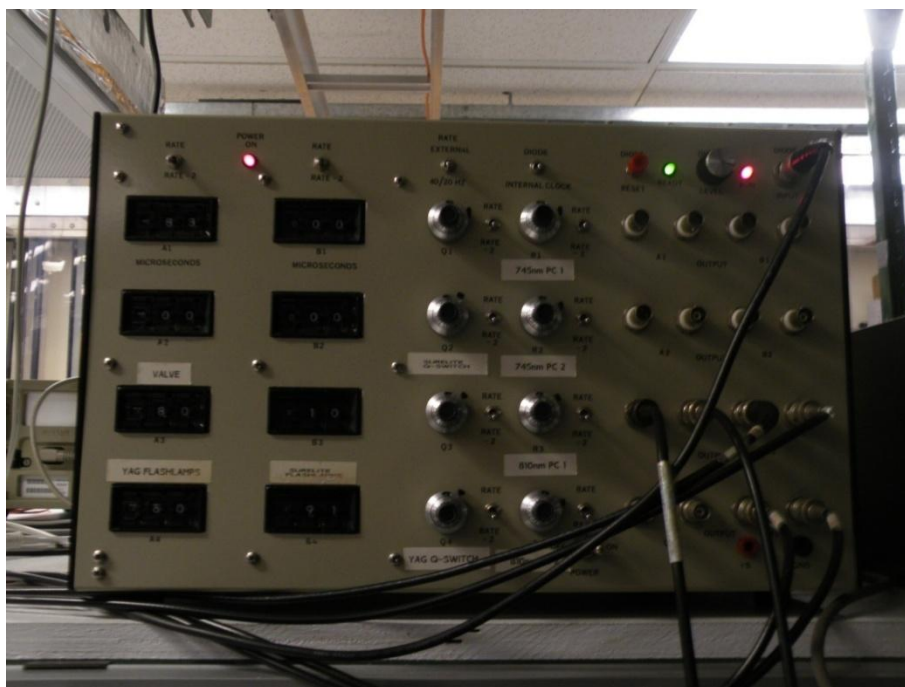


Fig 2-7 Timing Box

2.2.5 Timing Box

A timing control unit as described by Bigwood is used to control timing and triggering for experiments. This unit provides variable delays for the $10\ \mu\text{s}$ 5 V negative pulses needed to trigger the Nd:YAG flashlamp, Q-switch, and pulsed valve voltage driver. The Q-switch trigger is also used to trigger the boxcar integrator and oscilloscope.

2.2.6 Signal Averaging

A Stanford Research Systems SR250 Boxcar integrator is used for final signal processing and data collection. It allows for fast signal averaging and variable gates can be programmed to adjust the temporal width and position of the signal collection. Gates were generally set to begin approximately 10 ns after the beginning of the fluorescence decay in order to filter scatter from the excitation fundamental. The gates were set to be upto 120-200 ns long, depending on the

fluorescence lifetimes of the states being accessed. Signals were generally averaged over somewhere between 30-100 shots depending on the magnitude of the signal-to-noise ratio. Signal-to-noise ratio is in turn determined by the power of the exciting laser beam, intensity of the fluorescence and fluorescence quantum yield arising from the state being accessed, fluorescence wavelengths and monochromator slit width. The signal-to-noise ratio varied widely with differing experiments, and was often a prohibitive factor when it came to data acquisition.

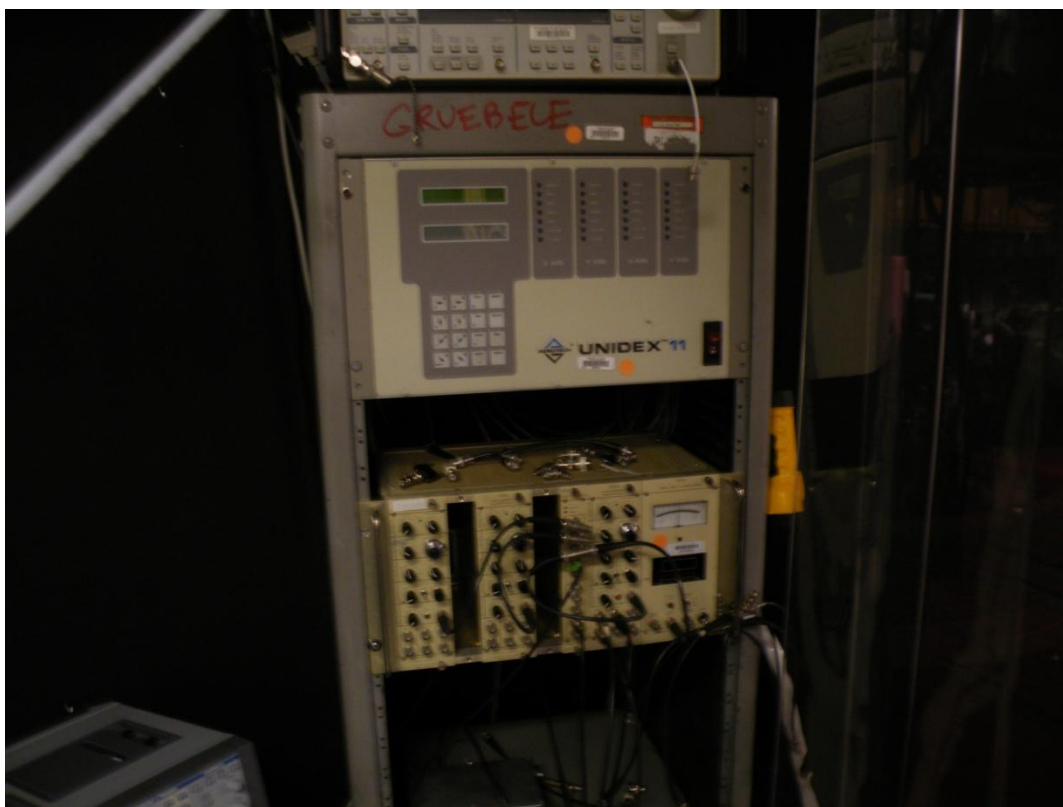


Fig 2-8 Boxcar Integrator (bottom) with UNIDEX translation stage controller (top)

2.3 Spectra and Raw Data

2.3.1 Excitation Spectra

Excitation spectra was gathered in a region between $35,400 - 36,700 \text{ cm}^{-1}$ to extend the work of prior members in this group^{6,7}. There are many absorption bands in this yet-unstudied region, and two were picked (bands centered at $36,036 \text{ cm}^{-1}$ and $36,667 \text{ cm}^{-1}$), to further interrogate for dispersed fluorescence to see the nature of the absorption, fluorescence lifetime, states accessed, etc. Fig 2-9 shows a region of the spectra including the $36,036 \text{ cm}^{-1}$ band. This band has a much higher absorption than the upstream $36,667 \text{ cm}^{-1}$ band.

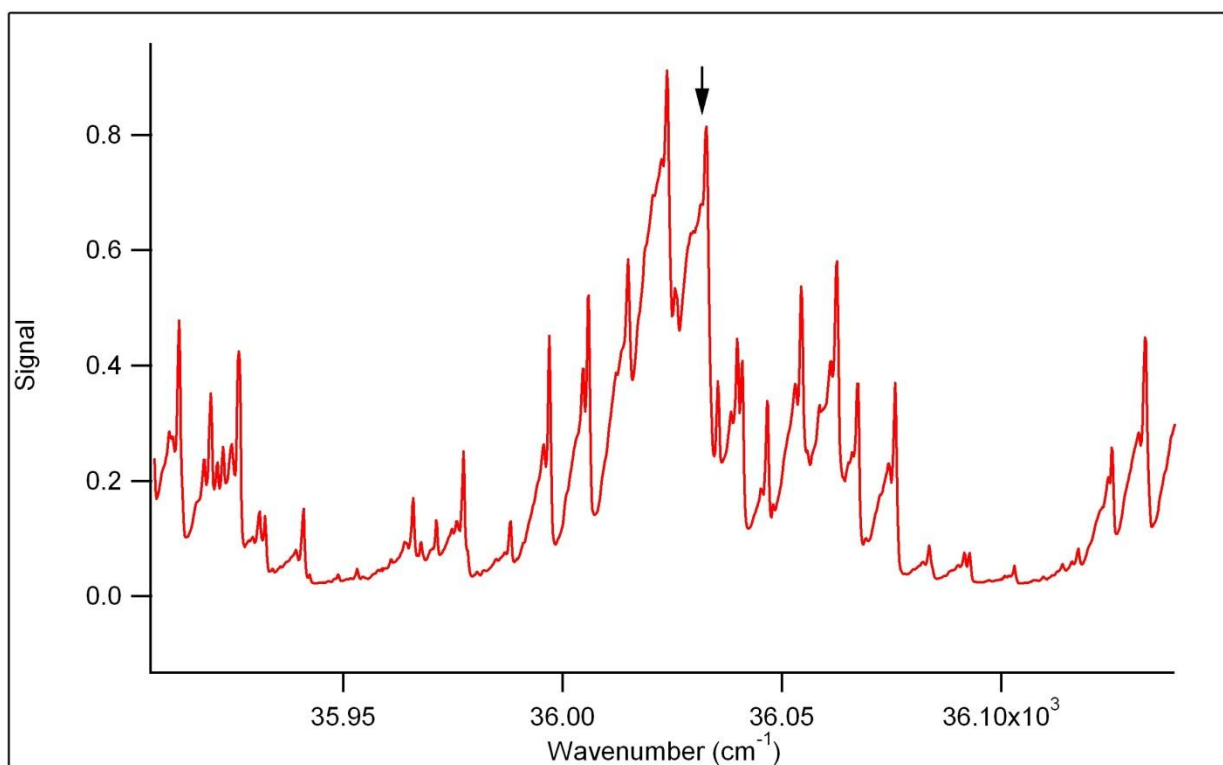


Fig 2-9 Fluorescence excitation spectra showing a peak used for dispersed fluorescence

2.3.2 Dispersed Fluorescence Spectra

After identifying the estimated location of the center of the absorption bands by repeating the excitation scan around the peaks and fitting Gaussians to find the peak centers, dispersed fluorescence measurements were collected for the two bands. The resulting spectra are depicted in Figs 2-10 and 2-11.

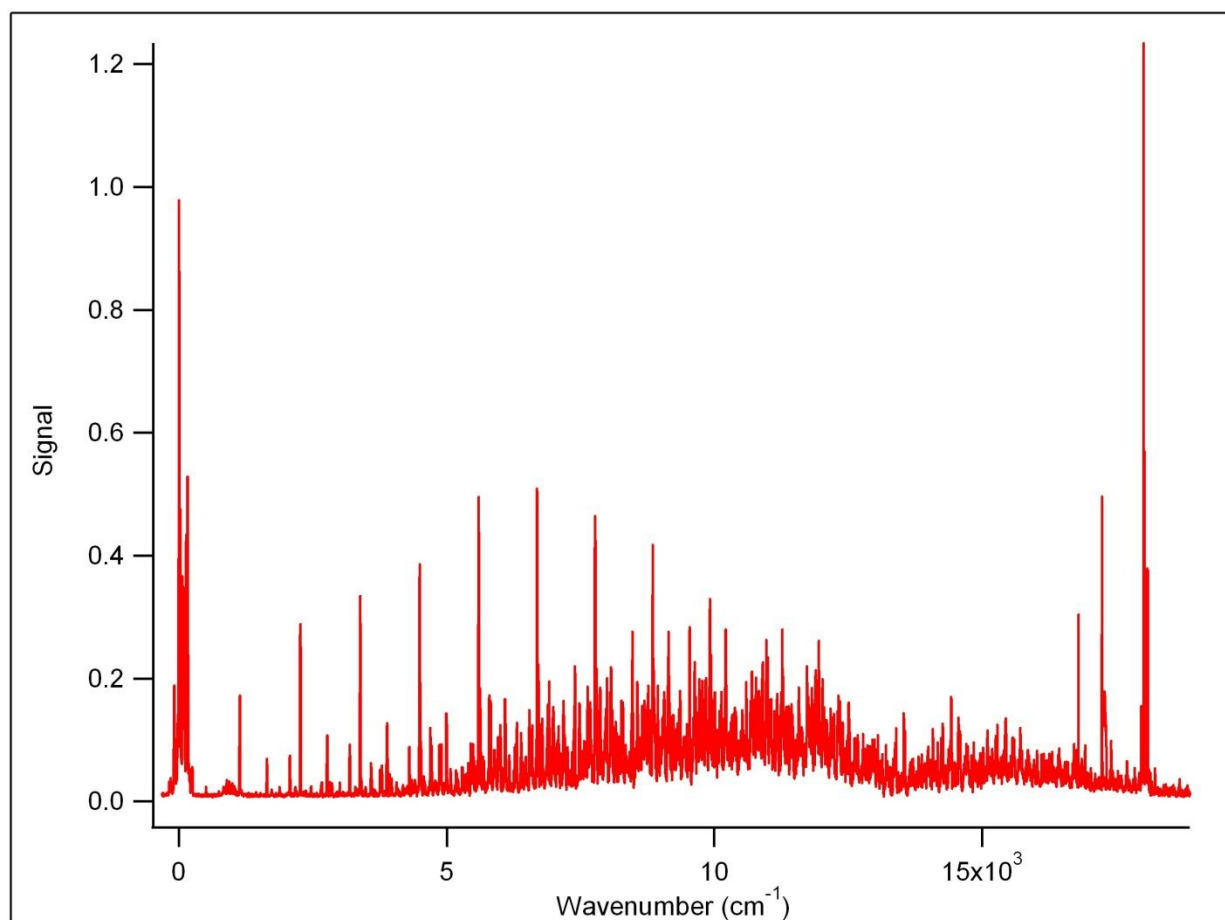


Fig 2-10 Dispersed Fluorescence Spectra for 36036 cm⁻¹ band

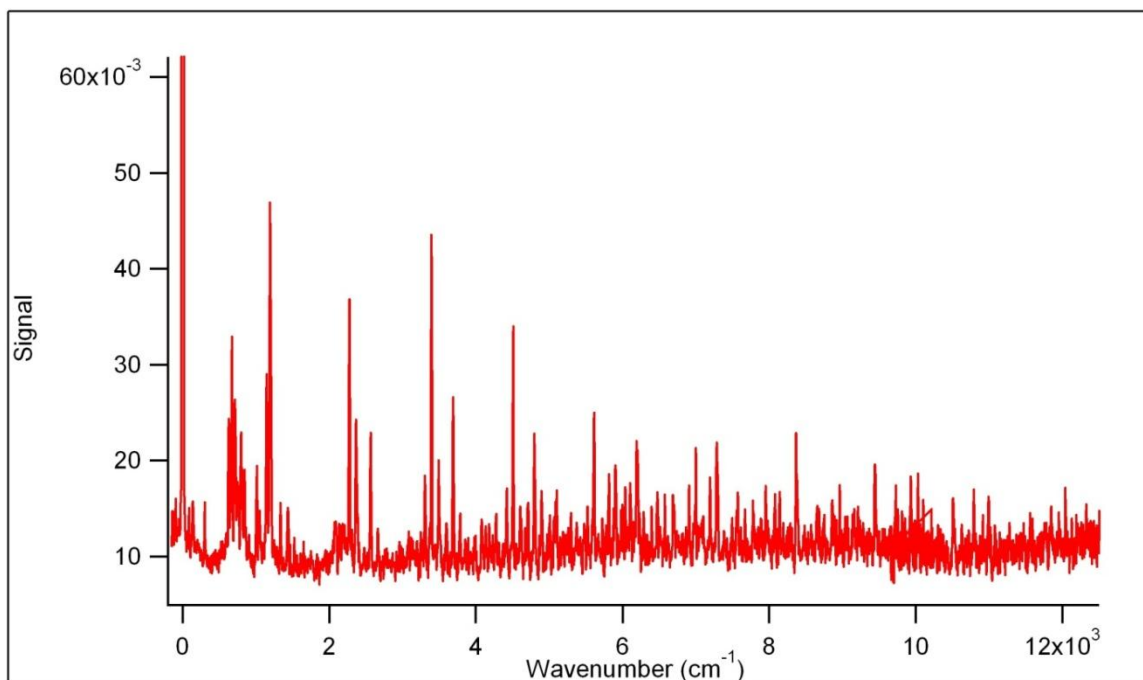


Fig 2-11 Dispersed Fluorescence Spectra for 36667 cm^{-1} band

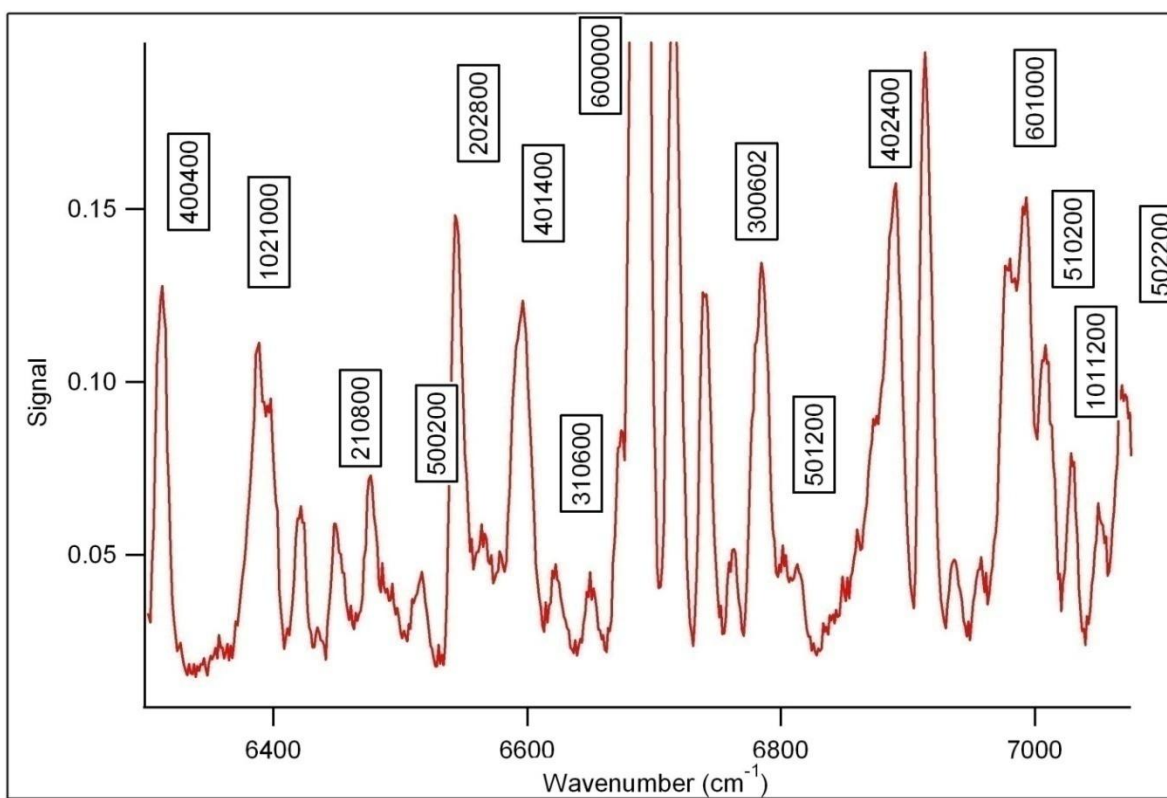


Fig 2-12 Sample region of Dispersed Fluorescence Spectra for 36036 cm^{-1} band, showing some assignments

2.4 Data Processing Methodology

The raw dispersed fluorescence data collected with the monochromator was first checked for correct calibration by locating the positions of three lines – the excitation wavelength, the dye laser fundamental (before doubling), and the second harmonic Nd:YAG line. In the above experiments, the excitation wavelength was at ~ 272.5 and 277.5 nm, the dye laser fundamental was at ~ 545 and 555 nm and the Nd:YAG line is always at 532.075 nm. For all peak positions, Gaussian line shapes were fit to them to determine the peak centers. If these lines appear to be miscalibrated, then the entire spectra was linearly scaled to preserve the positions of these three lines in the following way: first the entire spectra is shifted to ensure that the Nd:YAG center is at 532.075 nm. If the excitation wavelength and the second harmonic are then not in the expected locations, then the spectra is linearly (keeping the Nd:YAG line fixed) scaled until they are in close proximity to their assumed locations. Gaussian lineshapes are then fitted to all other peaks appearing in the spectra and their peak centers thus located.

The next step is to scale the intensities of the peaks against fluctuations in laser power and the spectrometer system response to a black body source, which was recorded by previous members of the group⁶. Since signal intensity is directly related to the power of the excitation beam, the intensities of the peaks are scaled against the data taken from the photodiode mounted close to chamber window that monitors laser power. The spectral response was found by dividing the measured spectrum of a black body source (a 75 W tungsten filament halogen bulb driven by 80 VDC) by its integrated radiant sensitivity. The response was then fit with a sum of three Gaussians and the signal-to-noise ratio is corrected, as outlined by Dr. Brent Stephen Strickler⁶.

After these corrections are applied, and all peak intensities and positions corrected, the spectra is converted into a simplified stick spectra with each stick position representing the Gaussian peak centers and the stick height representing scaled intensity.

2.5 Spectral Line Assignment and other Results

The resulting lines for the two dispersed fluorescence experiments are listed in Tables 2-2 and 2-3. To aid the assignment process, a prediction program (Appendix A) constructed in this group was used to estimate theoretical line positions. The prediction program is based on an effective Hamiltonian designed specifically for thiophosgene. The prediction program was constructed from assignments for known transitions based on experimental data that have been obtained by prior members of the group. The spectroscopic Hamiltonian has the following form:

$$H_{vib} = \sum_i \omega_i \left(v_i + \frac{1}{2} \right) + \sum_{ij} \chi_{ij} \left(v_i + \frac{1}{2} \right) \left(v_j + \frac{1}{2} \right) + \chi_{114} \left(v_1 + \frac{1}{2} \right)^2 \left(v_4 + \frac{1}{2} \right) + \chi_{144} \left(v_1 + \frac{1}{2} \right) \left(v_4 + \frac{1}{2} \right)^2$$

This Hamiltonian includes two cubic terms χ_{114} and χ_{144} as there are a number of v_1/v_4 combination bands that occur in the higher energy regions of the spectra. There is a Fermi resonance between v_5 ($\sim 818 \text{ cm}^{-1}$) and v_2+v_6 ($\sim 831 \text{ cm}^{-1}$). This resonance is not treated in the fit.

Both these data exist at a very high-energy region of the spectra, and this area of the spectra is largely unstudied. The primary purpose of undertaking this study was to shed light on

this dark corner of the molecule. On analyzing the spectra, certain patterns come to light. The ν_1/ν_4 progressions continue to be the most pronounced, as expected. However, certain theoretical predictions have not been corroborated by this set of data. For instance, the $2\nu_3$ - $2\nu_6$ resonance is known to be one of the important ones for this molecule. They are however, highly under-sampled in these two data sets. The presence of low-lying overtones of these two modes, or even seeing certain transitions forbidden in the ‘bright’ area of the B state would certainly yield some light as to what could be going on in this strange area of the spectra.

Part of the reason why this data is quite inconclusive is that many of the lines that are as yet unassigned (and not included here) happen to lie in the region where IVR is likely to be strong. The dispersed fluorescence data from the 36667 cm^{-1} band, which is expected to show the ‘interesting’ transitions, are quite inconclusive. Part of the reasons why the assignments were so difficult is because the progressions in this region were very weak, and appear to be missing lines that are likely lost in the poor signal-to-noise ratio in the low energy region of the spectra. And without a properly assigned set of low-lying progressions, it is hard to assign the ones higher to them. I am optimistic however, that with sustained experimental tweaking, that this can be rectified, and a higher-resolution spectra obtained.

The extension of this study is important in other regards as well. Taylor and Jung, as well as Sibert⁸, have created Hamiltonians based on the current data. Their theoretical treatment makes specific predictions about which mode combinations break down and where. A new high resolution spectra would allow us to directly test these predictions, and further our understanding of the subtle dynamics. At the very least, there will be new questions to answer. After all, if our predictions don’t get better, then we certainly don’t understand, and we might as well buy a new drawing board if the old one doesn’t hold the picture straight.

Table 2-2 Assignments and effective Hamiltonian predictions for Dispersed Fluorescence of the 36036 cm⁻¹ band of thiophosgene

Observed	Predicted	Obs-Pred	Intensity	v1	v2	v3	v4	v5	v6
0.021194	0	0.021194	0.97837	0	0	0	0	0	0
505.1334	508.51	-3.37656	0.023788	0	1	0	0	0	0
832.6974	833.78	-1.08259	0.02375	0	1	0	0	0	1
939.8952	942.6	-2.7048	0.032337	0	0	0	2	0	0
1136.929	1137.4	-0.47135	0.1719	1	0	0	0	0	0
1641.771	1644.4	-2.62878	0.0688	1	1	0	0	0	0
1879.518	1883.8	-4.28168	0.0233	0	0	0	4	0	0
2070.337	2072.4	-2.06294	0.074313	1	0	0	2	0	0
2173.245	2178.6	-5.35456	0.023275	0	0	1	4	0	0
2267.346	2266	1.345921	0.28828	2	0	0	0	0	0
2465.91	2471.7	-5.78962	0.024075	0	0	2	4	0	0
2652.267	2658.4	-6.13268	0.025	1	0	2	2	0	0
2666.825	2670.51	-3.68539	0.030725	0	0	2	2	1	1
2767.82	2771.5	-3.67996	0.10705	2	1	0	0	0	0
2819.41	2823.5	-4.08978	0.031275	0	0	0	6	0	0
3004.387	3007.6	-3.21348	0.030462	1	0	0	4	0	0
3190.117	3194.4	-4.28251	0.092038	2	0	0	2	0	0
3292.903	3299.4	-6.49705	0.023487	1	0	1	4	0	0

Table 2-2
(continued)

3383.991	3390.6	-6.60943	0.33455	3	0	0	0	0	0
3485.571	3486.1	-0.52898	0.023062	2	0	1	2	0	0
3586.943	3590.8	-3.85686	0.062575	1	0	2	4	0	0
3758.732	3762.9	-4.16829	0.051438	0	0	0	8	0	0
3886.284	3892.9	-6.61603	0.1272	3	1	0	0	0	0
3934.063	3939.2	-5.13717	0.04405	1	0	0	6	0	0
3969.086	3975.2	-6.11404	0.037163	3	0	2	0	0	0
4061.463	4057.8	3.663335	0.031038	0	0	1	8	0	0
4111.775	4119.9	-8.125	0.018012	2	0	0	4	0	0
4180.976	4186.5	-5.52422	0.026425	2	2	0	2	0	0
4225.866	4232.1	-6.2336	0.02	1	0	1	6	0	0
4302.012	4307.9	-5.88792	0.088725	3	0	0	2	0	0
4344.259	4349.8	-5.54147	0.03515	0	0	2	8	0	0
4387.193	4390.5	-3.30749	0.0285	3	2	0	0	0	0
4407.468	4411.4	-3.93184	0.0352	2	0	1	4	0	0
4495.461	4501.5	-6.03914	0.3857	4	0	0	0	0	0
4517.978	4525	-7.02247	0.097338	1	0	2	6	0	0
4572.104	4581.2	-9.09578	0.0405	1	0	0	6	0	2
4594.019	4596.8	-2.78132	0.031638	3	0	1	2	0	0

Table 2-2
(continued)

4695.395	4698	-2.6052	0.11959	2	0	2	4	0	0
4716.257	4704.7	11.55744	0.090562	0	0	0	10	0	0
4762.487	4766	-3.51273	0.030138	2	0	0	4	0	2
4785.502	4791	-5.49754	0.033925	4	0	1	0	0	0
4809.068	4806.3	2.767708	0.030862	3	1	0	2	0	0
4863.56	4871.5	-7.93986	0.091662	1	0	0	8	0	0
4996.033	4998.2	-2.16726	0.14306	4	1	0	0	0	0
5075.533	5084.6	-9.0666	0.05265	4	0	2	0	0	0
5190.371	5193	-2.62938	0.04585	0	1	0	10	0	0
5214.279	5223.8	-9.52098	0.03555	3	0	0	4	0	0
5291.161	5294.7	-3.5393	0.055475	3	2	0	2	0	0
5351.508	5362	-10.4921	0.043413	1	1	0	8	0	0
5401.976	5410.3	-8.3239	0.062125	4	0	0	2	0	0
5495.81	5515.2	-19.3901	0.093212	3	0	1	4	0	0
5527.797	5538	-10.2034	0.046575	2	1	0	6	0	0
5597.581	5604.1	-6.51879	0.49544	5	0	0	0	0	0
5622.526	5629.1	-6.57391	0.18362	2	0	2	6	0	0
5682.044	5682.8	-0.75616	0.072676	2	0	0	6	0	2
5797.1	5797.5	-0.39992	0.17274	3	0	2	4	0	0

Table 2-2
(continued)

5898.695	5892.4	6.294761	0.083571	5	0	1	0	0	0
5913.01	5907.1	5.910421	0.067667	4	1	0	2	0	0
5961.113	5968.9	-7.78705	0.10475	2	0	0	8	0	0
5983.124	5984.7	-1.57621	0.074989	4	0	2	2	0	0
6092.519	6098.4	-5.8812	0.16638	5	1	0	0	0	0
6132.378	6141.2	-8.822	0.035955	3	0	0	6	0	0
6171.063	6178.5	-7.43671	0.074717	5	0	2	0	0	0
6253.714	6260.7	-6.98637	0.075012	2	0	1	8	0	0
6311.589	6318.1	-6.51104	0.12764	4	0	0	4	0	0
6387.94	6376	11.94006	0.11129	1	0	2	10	0	0
6447.744	6458	-10.2563	0.059021	2	1	0	8	0	0
6516.269	6503.1	13.169	0.045031	5	0	0	2	0	0
6544.424	6552.7	-8.27599	0.14816	2	0	2	8	0	0
6595.211	6608.4	-13.1895	0.12342	4	0	1	4	0	0
6622.179	6632.5	-10.3206	0.047249	3	1	0	6	0	0
6688.956	6697.5	-8.5435	0.50882	6	0	0	0	0	0
6784.244	6775.7	8.54442	0.13438	3	0	0	6	0	2
6801.658	6792.2	9.458348	0.052721	5	0	1	2	0	0
6812.659	6810.8	1.859429	0.047249	4	1	0	4	0	0

Table 2-2
(continued)

6888.673	6888.5	0.173168	0.15743	4	0	2	4	0	0
6956.952	6952.5	4.451721	0.049243	4	0	0	4	0	2
6991.772	6984.8	6.97151	0.15337	6	0	1	0	0	0
7007.678	7000.2	7.478269	0.11053	5	1	0	2	0	0
7050.011	7057.2	-7.18853	0.064923	3	0	0	8	0	0
7070.462	7076.3	-5.83809	0.098979	5	0	2	2	0	0
7181.346	7191.6	-10.2536	0.16349	6	1	0	0	0	0
7218.203	7227.6	-9.39705	0.08271	4	0	0	6	0	0
7258.108	7268.9	-10.7923	0.088212	6	0	2	0	0	0
7302.684	7301.6	1.08357	0.050918	4	2	0	4	0	0
7342.027	7347.8	-5.77328	0.079599	3	0	1	8	0	0
7366.5	7373.3	-6.79986	0.098054	2	1	0	10	0	0
7395.764	7403.2	-7.43579	0.22002	5	0	0	4	0	0
7684.278	7692.8	-8.52154	0.16105	5	0	1	4	0	0
7707.212	7717	-9.78806	0.0766	4	1	0	6	0	0
7772.92	7781.7	-8.77985	0.4641	7	0	0	0	0	0
7977.433	7977.5	-0.06662	0.15105	5	0	2	4	0	0
8263.603	8272.3	-8.69657	0.16386	7	1	0	0	0	0
8470.457	8478.4	-7.94287	0.27633	6	0	0	4	0	0

Table 2-2
(continued)

8764.721	8766.4	-1.67926	0.18777	6	0	1	4	0	0
8781.421	8791.4	-9.97912	0.14912	5	1	0	6	0	0
8848.166	8855.9	-7.73436	0.41718	8	0	0	0	0	0
9058.529	9053	5.528889	0.1777	6	0	2	4	0	0
9337.409	9344.8	-7.39059	0.15001	8	1	0	0	0	0
9536.743	9544.3	-7.55677	0.28311	7	0	0	4	0	0
9828.217	9831	-2.78259	0.19686	7	0	1	4	0	0
9847.481	9856.2	-8.71875	0.20027	6	1	0	6	0	0
9915.194	9921.9	-6.70591	0.32927	9	0	0	0	0	0
10109.54	10118.1	-8.55858	0.14168	7	0	2	4	0	0
10401.72	10408.4	-6.67632	0.14586	9	1	0	0	0	0
10594.83	10601.5	-6.66849	0.19408	8	0	0	4	0	0
10893.21	10890.1	3.107776	0.2005	8	0	1	4	0	0
10904.95	10912.7	-7.75018	0.22595	7	1	0	6	0	0
10969.46	10978.8	-9.33832	0.26287	10	0	0	0	0	0
11458.1	11464.7	-6.59528	0.14135	10	1	0	0	0	0
11952.43	11959.7	-7.26914	0.26099	8	1	0	6	0	0
12017.18	12023.4	-6.22196	0.19908	11	0	0	0	0	0
12991.28	12995.2	-3.92266	0.10045	9	1	0	6	0	0

Table 2-2
(continued)

13052.12	13056.8	-4.68477	0.10788	12	0	0	0	0	0
14018.46	14023.7	-5.24087	0.054059	10	1	0	6	0	0

Table 2-3 Assignments and effective Hamiltonian predictions for Dispersed Fluorescence of the 36667 cm⁻¹ band of thiophosgene

Observed	Predicted	Obs-Pred	Intensity	v1	v2	v3	v4	v5	v6
292.0154	294.8	-2.78458	0.92882	0	0	1	0	0	0
587.4845	587.85	-0.36552	0.57871	0	0	2	0	0	0
619.7296	620	-0.27037	1.7505	0	0	1	0	0	1
1092.912	1092.91	0.002383	0.48584	0	1	2	0	0	0
1136.507	1137.45	-0.94309	2.2284	1	0	0	0	0	0
1185.911	1184.28	1.630884	4.0184	0	1	0	0	0	2
1235.178	1237.42	-2.24236	0.48959	0	0	1	2	0	0
1426.291	1431.29	-4.99928	0.8317	1	0	1	0	0	0
1457.054	1459.68	-2.62559	0.45076	1	0	0	0	0	1
1514.839	1514.92	-0.08116	0.5209	0	3	0	0	0	0
1549.024	1554.97	-5.946	0.35227	0	0	3	0	0	2
2060.163	2072.4	-12.2367	0.6817	1	0	0	2	0	0

Table 2-3
(continued)

2170.797	2178.6	-7.80302	0.6667	0	0	1	4	0	0
2265.943	2266	-0.05684	3.0084	2	0	0	0	0	0
2356.918	2366.3	-9.38195	1.7509	1	0	1	2	0	0
2468.588	2471.7	-3.11161	0.41301	0	0	2	4	0	0
2555.821	2558.9	-3.07936	1.6167	2	0	1	0	0	0
2654.756	2658.4	-3.644	0.63976	1	0	2	2	0	0
3297.415	3299.9	-2.48483	1.1684	1	0	1	4	0	0
3386.344	3385.7	0.64447	3.6809	3	0	0	0	0	0
3492.304	3486.1	6.203834	1.3284	2	0	1	2	0	0
3588.295	3592.1	-3.80475	0.6709	1	0	2	4	0	0
3680.47	3677.7	2.769657	2.0336	3	0	1	0	0	0
3778.297	3777.2	1.096506	0.78838	2	0	2	2	0	0
3885.861	3889.7	-3.83897	0.5184	3	1	0	0	0	0
3987.6	3996.3	-8.69961	0.5409	2	0	0	2	1	0
4174.43	4181.06	-6.63	0.6634	3	0	0	0	1	0
4412.154	4412	0.153993	1.0375	2	0	1	4	0	0
4499.8	4496.6	3.199591	2.7259	4	0	0	0	0	0
4593.862	4596.8	-2.93838	0.8467	3	0	1	2	0	0
4700.456	4703.2	-2.74387	0.90884	2	0	2	4	0	0

Table 2-3
(continued)

4790.201	4787.6	2.601124	1.6075	4	0	1	0	0	0
4889.643	4887	2.642586	1.0075	3	0	2	2	0	0
4996.589	4999	-2.41061	0.7567	4	1	0	0	0	0
5093.354	5100.1	-6.74602	1.0178	3	0	0	2	1	0
5287.876	5300.6	-12.7239	0.7792	3	2	0	2	0	0
5514.495	5514.7	-0.20524	0.8492	3	0	1	4	0	0
5602.53	5598.6	3.930434	1.8455	5	0	0	0	0	0
5805.897	5805	0.897434	1.1834	3	0	2	4	0	0
5894.568	5888.6	5.967942	1.3051	5	0	1	0	0	0
5988.659	5987.7	0.958814	0.88332	4	0	2	2	0	0
6099.279	6099.4	-0.12082	1.0917	5	1	0	0	0	0
6183.673	6194.9	-11.2269	1.5689	4	0	0	2	1	0
6388.601	6400.1	-11.4991	0.8442	4	2	0	2	0	0
6605.524	6608.2	-2.67612	0.5384	4	0	1	4	0	0
6681.667	6691.7	-10.0329	0.9675	6	0	0	0	0	0
6899.387	6897.5	1.886604	1.0778	4	0	2	4	0	0
6992.459	6980.8	11.65934	1.4367	6	0	1	0	0	0
7184.692	7191	-6.30837	1.1493	6	1	0	0	0	0
7276.337	7280.5	-4.16332	1.5191	5	0	0	2	1	0

Table 2-3
(continued)

7486.386	7490.5	-4.11385	0.7267	5	2	0	2	0	0
7689.258	7692.3	-3.04244	0.5117	5	0	1	4	0	0
7768.784	7775.9	-7.11645	0.8883	7	0	0	0	0	0
8067.614	8064.1	3.514222	0.9775	7	0	1	0	0	0
8357.603	8357.1	0.503195	1.6134	6	0	0	2	1	0
8845.743	8851.2	-5.45693	0.8784	8	0	0	0	0	0

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Chapter 3

Torsional Potential Energy Surface of 2-Fluoroethanol

*“it is almost platitudinous to say that a chemist who does not understand conformational analysis does not understand organic chemistry. Even the area of physical chemistry related to molecular structure and physical properties has fallen heavily under the sway of conformational concepts.”*¹

3.1 Introduction

Generating a potential energy surface (PES) has long been a method used in spectroscopy to predict molecular vibrational spectra and the structural and dynamics information that can be derived from it: conformational energetics, vibrational frequencies, energy barriers and transition states etc. From the standpoint of understanding energy flow, a full potential energy surface allows one to be able to predict with accuracy how energy is funneled in the molecule in question. There are computational methods by which such molecular spectra can be evaluated from a full molecular potential energy surface². However, only approximate PESs are available, and that too, usually for small molecules as we are limited by our current computational speed and level of theory. The exact determination of potential energy functions for large-amplitude molecular motion, as hindered by barriers of various types, remains a vexing problem for both

theory and experiment. To understand the salient features of molecular spectra though, one need not be able to generate an exact surface, and important insights can yet be gained. Our group has a strong history of pursuing these lines of thought, and serve as a great starting point^{3,4}.

Ab-initio methods have long been the best computational tool theorists can arm themselves with when it comes to such questions. However, ab-initio harmonic vibrational frequencies ($\tilde{\nu}$) are typically larger than the fundamentals ($\tilde{\nu}$) observed experimentally⁵. The main reason for this incongruity is the neglect of anharmonicity in the theoretical treatment. Other sources for this inconsistency include the incomplete incorporation of electron correlation and the use of finite basis sets. Thus, for example, Hartree-Fock (HF) theory tends to overestimate vibrational frequencies because of improper dissociation behavior, a shortcoming that can be partially compensated for by the explicit inclusion of electron correlation. Pople, et al. estimated the harmonic vibrational oversight of 38 molecules calculated at HF/3-21G. They found that the mean calculated/experimental ratio of vibrational frequencies to be about 1.123 or roughly 12%⁶. The overestimation of ab initio harmonic vibrational frequencies is, however, found to be relatively uniform, and as a result generic frequency scaling factors are often applied. Good overall agreement between the scaled theoretical harmonic frequencies and the anharmonic experimental frequencies can then usually be obtained.

2-fluoroethanol, depicted in Fig 3-1, is an excellent test candidate to perform such a study. It is a small molecule, with extensive spectral information available in the literature. It is small enough to be computationally handled, and much information about dynamics, especially involving torsional modes, can be gleaned.

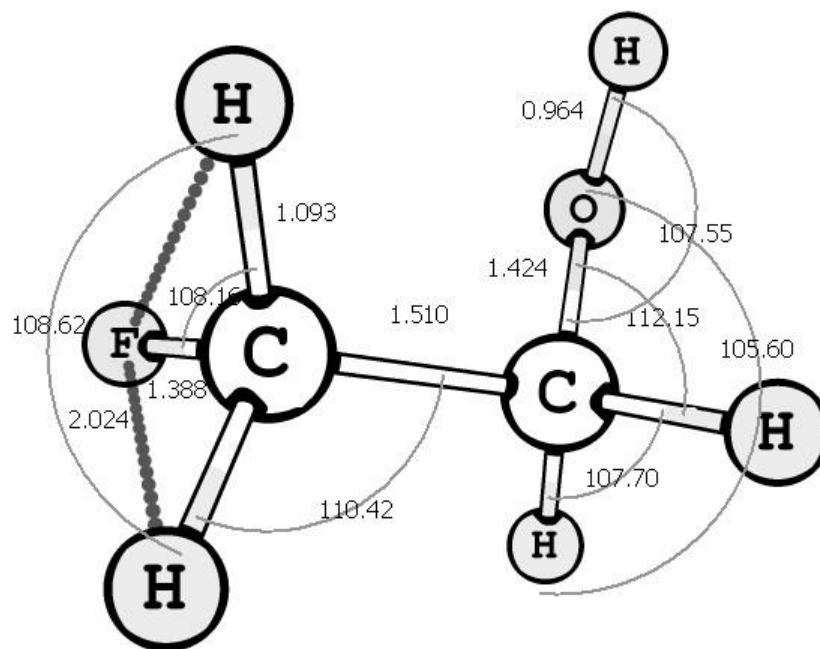


Fig 3-1 2-fluoroethanol w/structural parameters

Brooks Pate and friends have done a few studies⁷⁻⁹ on IVR lifetimes and conformational isomerization in this molecule which serve as motivation for this undertaking. They have high-resolution spectra of a highly vibrationally mixed quantum state and rates of conformational isomerization, rotational spectra of single molecular eigenstates, plenty of information about the asymmetric $\text{-CH}_2\text{F}$ stretching mode, to name a few. They also have strong theoretical models that incorporate tiers to study energy redistribution. It is my sincere hope that this study, when completed, will accompany their work well in the literature.

3.2 Surface Construction Methodology

The torsional surface is constructed by calculating conformational energies of the molecule as considered in an 18 x 10 grid. The grid is created by rotating the molecule along two dihedral angles that delineate the two major torsions (across the central C-C bond and across the C-O bond of the alcohol moiety), while keeping all other bond lengths and angles fixed at their known equilibrium values (rigid rotor). The points were considered in 20° increments of these two dihedral angles, while preserving the symmetry features of the molecule. The basic molecular geometries were created using SPARTAN '96. The Z-matrix of each molecular geometry was then found, and this was used as the basis to create the input Z-matrices of all the other grid points.

Once the grid was set up this way, the conformational energies of the geometries described by these Z-matrices were determined by feeding the input into the computational chemistry package GAUSSIAN '03, available on the supercomputer cluster for use at the Department of Chemistry, here at the University of Illinois at Urbana-Champaign. Frequencies and conformational energies were all determined at the MP2 level of theory, using the 6-31G** basis set.

The resulting grid points were fitted to a 3-D surface using the Thin Plate Spline (TPS) smoothing regimen. This was done by taking the energies from GAUSSIAN and having them re-gridded in an XYZ Matrix. The data analysis/scientific graphing package ORIGIN 8 proved extremely useful, especially with the worksheet-to-matrix conversion tool, which automated the XYZ gridding. The TPS smoothing was then applied, and the surface shown in Fig 3- resulted.

The next step was to determine all stationary points on the surface (saddle points, maxima and minima). During the generation of the surface, the TPS XYZ grid had extended the grid from 18 x 10 to 32 x 30. In this new grid, the stationary points could be found with greater accuracy. Simple quadratures were then applied to data points neighboring the location of the yet-to-be-determined saddle points to estimate their ‘true’ location. Once all the locations of all the stationary points were thus estimated, the Z-matrices of those geometries were recreated and then once again, fed into GUASSIAN. This time, an optimization and frequency protocol was applied at the same level of theory (MP2/6-31G**) whilst allowing the entire model to relax, thus enabling finding the stationary points to the best accuracy. The presence of negative frequencies in the resulting output confirms the presence of a stationary point. All minima are known to have no negative frequencies. Transition states have exactly one negative frequency.

3.3 Results and Discussion

The prepared torsional potential energy surface is shown in Fig 3-5. A cursory glance over the surface shows the expected undulating pattern with evenly spaced hills and valleys associated with barriers to rotation in between stable equilibrium states. The global minima structure is shown in Fig 3-2. It is a staggered conformation, with the O-H-F interaction clearly stabilizing the structure. An example of a local minima (Fig 3-3) and a transition state (Fig 3-4) are also shown.

Another noteworthy observation to make here is the effect of the zero point correction on the surface. Although not particularly noticeable in the 3-D representation, the contour plot

highlights the difference. In particular, the width of the energy contours associated with the stable equilibrium structures (blue valleys) appear to contract while the contours around the transition states (orange hilltops) appear to widen. This is directly attributable to zero point activity.

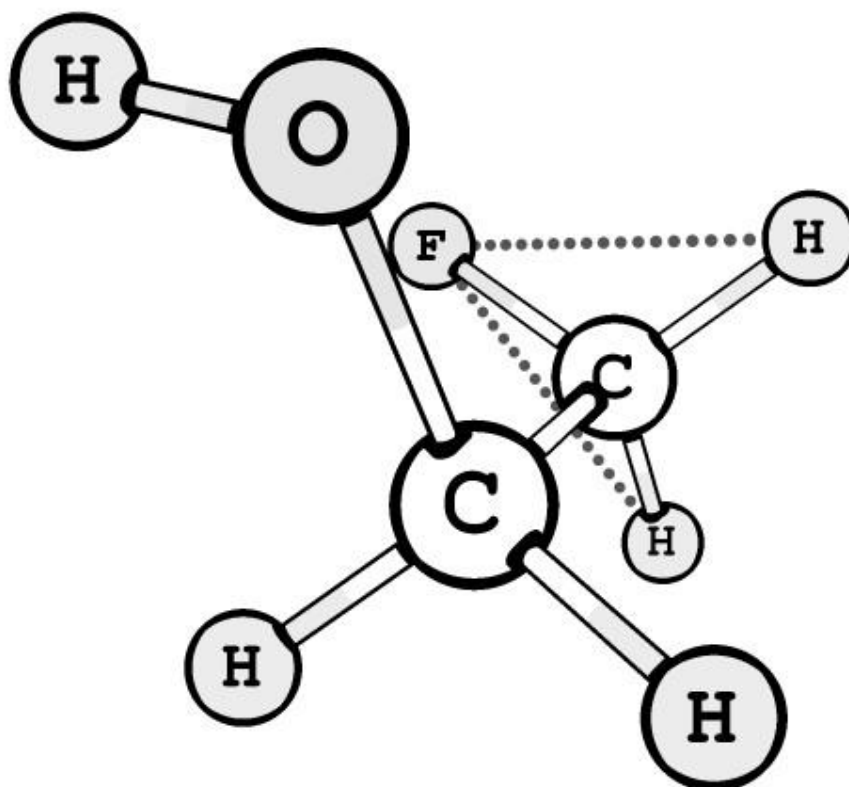


Fig 3-2 Global minima

In this particular study, zero point activity isn't enough to greatly alter the torsional barrier to free rotation. However, this effect can definitely not be ignored for larger molecules possessing, say hundreds of thousands of these modes. In a protein for instance, conformational dynamics can definitely cause enough energy flow to overcome small barriers, and torsional barriers are the lowest and easiest to overcome. Neglecting zero point contributions while

constructing a surface for such a molecule will thus definitely propagate the error over the interactions of hundreds of modes, leading to completely incorrect conformational entropies and as a result, conformations as well. It is thus imperative that we continue studies of this nature, especially with molecules possessing numerous adjacent torsional modes so that we can get a much better qualitative picture of the global combinatorial effect and come up with more accurate conformations.

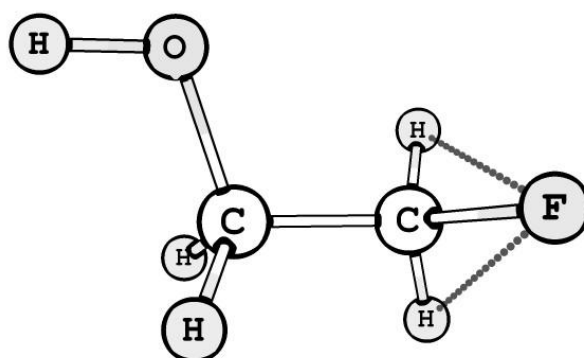


Fig 3-3 One of the local minima of 2-Fluoroethanol

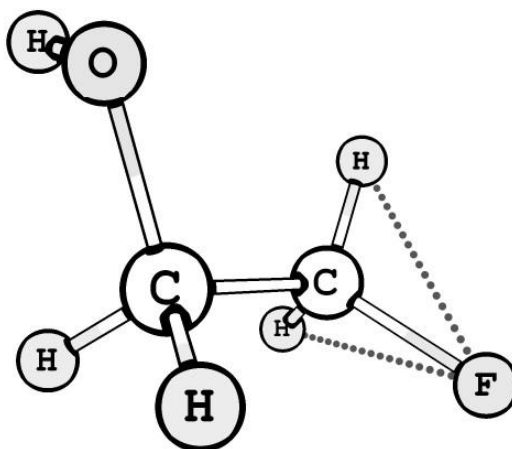


Fig 3-4 One of the transition states of 2-fluoroethanol

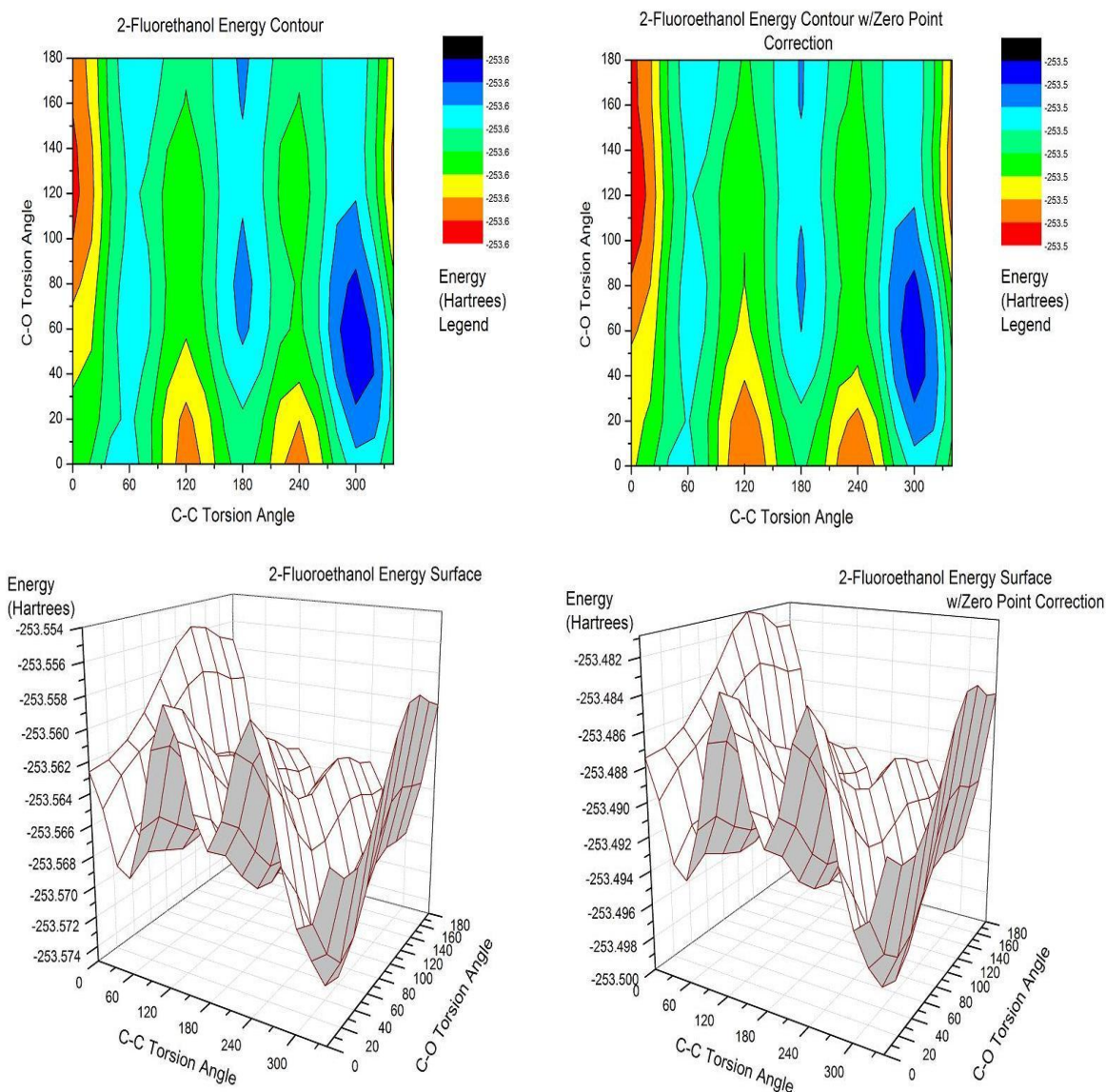


Fig 3-5 2-fluoroethanol energy landscape

Such a surface also serves as the basis for computing vibrational wavefunctions to analyze the rates of conformational interconversion. In a new generation of experiments^{10, 11} (e.g. Zwier, Rizzo), such conformers are frozen out and selectively populated by multiple laser pulse sequences, allowing different conformers to be isolated in complex spectra.

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Appendix A

Codes

A.1 sccl2lev2005.f

This program was developed by earlier members of the group and is used to predict assignments if fed dispersed fluorescence energies. It can also be used to predict the energy if given assignment as input.

```

c    Finds frequencies in SCCL2 to match SEP or IR spectra
c    Using Brent's 2004 constants
      implicit none
      real*8 el,eu,we(0:2,6),chi(0:2,6,6),e4(0:10),e0,efind,unc,
      le1(0:10),chi2(0:2,6,6,6),energ
      integer v(6),flag,i1,estate,vl(6),vu(6),vmax(0:2,6),
      lv1,v2,v3,v4,v5,v6,vu1,vu2,vu3,vu4,vu5,vu6,maxsum,i,j,
      2vsum,v0(6)
c Hardwired X state constant
      we(0,1)=1155.9
      we(0,2)=514.06
      we(0,3)=295.46
      we(0,4)=476.27
      we(0,5)=821.79
      we(0,6)=301.22
      chi(0,1,1)=-4.51
      chi(0,1,2)=-1.56
      chi(0,1,3)=-0.78
      chi(0,1,4)=-3.93
      chi(0,1,5)=-7.75
      chi(0,1,6)=-2.97
      chi(0,2,2)=-2.68
      chi(0,2,4)=-2.01
      chi(0,3,3)=-1.02
      chi(0,4,4)=-0.22
      chi(0,4,6)=-1.94
      chi(0,6,6)=12.61
      chi2(0,1,1,4)=-0.042

```



```

        chi2(0,1,4,4)=-0.020
c Or read them in from data file
        do i=1,6
            read(4,*) we(0,i)
            do j=i,6
                read(4,*) chi(0,i,j)
            enddo
        enddo
        read(4,*) chi2(0,1,1,1)
        read(4,*) chi2(0,1,1,4)
        read(4,*) chi2(0,1,4,4)
        read(4,*) chi2(0,4,4,4)

c This needs to be the zero point term difference between states "0" and
"1"
        e0=34277
c Hardwired constants for the B state
        we(1,1)=505
        we(1,2)=470
        we(1,3)=213
        we(1,5)=818
        we(1,6)=249
        e1(0)=0
        e1(1)=506
        e1(2)=992
        e1(3)=1466
        e4(0)=0
        e4(1)=0.007
        e4(2)=341
        e4(3)=341.5
        e4(4)=628
        e4(5)=645
        e4(6)=828
c For zero point energy calculation
        v0(:)=0
c Upper cutoff on v quantum numbers
        vmax(0,1)=7
        vmax(0,2)=3
        vmax(0,3)=3
        vmax(0,4)=10
        vmax(0,5)=2
        vmax(0,6)=2
        vmax(1,1)=3
        vmax(1,2)=1
        vmax(1,3)=1
        vmax(1,4)=4
        vmax(1,5)=1
        vmax(1,6)=1

c
        write(6,*) 'Single level (0), transition (1), find (2), or'
        write(6,*) 'emission find? (3)'
c
        flag=2
        read(5,*) flag
        if(flag.eq.0) then

```

```

write(6,*) 'Enter state, v1,v2,v3,v4,v5,v6:'
read(5,*) estate,(v(i1), i1=1,6)
el = energ(v,we,chi,chi2,6,0)-energ(v0,we,chi,chi2,6,0)
write(6,20) estate,(v(i1),i1=1,6),el
20  format(7i3,f10.1)
else if(flag.eq.1) then
write(6,*) 'Enter lower E. state, v1,v2,v3,v4,v5,v6:'
read(5,*) estate,(v1(i1), i1=1,6)
el = energ(v1,we,chi,chi2,6,0)-energ(v0,we,chi,chi2,6,0)
write(6,*) 'Enter upper E. state, v1,v2,v3,v4,v5,v6:'
read(5,*) estate,(vu(i1), i1=1,6)
eu = energ(vu,we,chi,chi2,6,0)-energ(v0,we,chi,chi2,6,0)
write(6,20) estate,(v1(i1),i1=1,6),el
write(6,20) estate,(vu(i1),i1=1,6),eu
write(6,30) eu-el
30  format('Transition at: ', f10.1,10x,i4)
else if (flag.eq.2) then
write(6,*) 'Upper estate, E and +/- range, max nonzero modes:'
read(5,*) estate,efind,unc,maxsum

c  Uncomment to scan through two states
c      do 100 v1=0,vmax(0,1)
c      do 100 v2=0,vmax(0,2)
c      do 100 v3=0,vmax(0,3)
c      do 100 v4=0,vmax(0,4)
c      do 100 v5=0,vmax(0,5)
c      do 100 v6=0,vmax(0,6)
c  Comment to scan through two states
v1=0
v2=0
v3=0
v4=0
v5=0
v6=0
do 100 vu1=0,vmax(estate,1)
do 100 vu2=0,vmax(estate,2)
do 100 vu3=0,vmax(estate,3)
c Note: ,2 needs to be removed to obtain full density of states
do 100 vu4=0,vmax(estate,4),2
do 100 vu5=0,vmax(estate,5)
do 100 vu6=0,vmax(estate,6)
vsum=0
if(v1.ne.0) vsum=vsum+1
if(v2.ne.0) vsum=vsum+1
if(v3.ne.0) vsum=vsum+1
if(v4.ne.0) vsum=vsum+1
if(v5.ne.0) vsum=vsum+1
if(v6.ne.0) vsum=vsum+1
if(vu1.ne.0) vsum=vsum+1
if(vu2.ne.0) vsum=vsum+1
if(vu3.ne.0) vsum=vsum+1
if(vu4.ne.0) vsum=vsum+1
if(vu5.ne.0) vsum=vsum+1
if(vu6.ne.0) vsum=vsum+1

```

c Note: second condition needs to be removed to obtain full density of states

```

      if(vsum .le. maxsum .and. mod(vu6+vu5,2) == 0) then
        vl(1)=v1
        vl(2)=v2
        vl(3)=v3
        vl(4)=v4
        vl(5)=v5
        vl(6)=v6
        el = energ(vl,we,chi,chi2,6,0)-energ(v0,we,chi,chi2,6,0)
        vu(1)=vu1
        vu(2)=vu2
        vu(3)=vu3
        vu(4)=vu4
        vu(5)=vu5
        vu(6)=vu6
        eu = energ(vu,we,chi,chi2,6,estate)-
1          energ(v0,we,chi,chi2,6,estate)
        if(abs(eu-el-efind).lt.unc) then
          write(6,fmt='(6i3,f10.2)') (vu(i1),i1=1,6),eu-el
        endif
      endif
100    continue
    else if(flag.eq.3) then
      write(6,*) 'Upper E, trans. E, uncertainty, max. v sum:'
      read(5,*) eu,efind,unc,maxsum
      do 110 v1=0,vmax(0,1)
      do 110 v2=0,vmax(0,2)
      do 110 v3=0,vmax(0,3)
      do 110 v4=0,vmax(0,4)
      do 110 v5=0,vmax(0,5)
      do 110 v6=0,vmax(0,6)
        vsum=0
        if(v1.ne.0) vsum=vsum+1
        if(v2.ne.0) vsum=vsum+1
        if(v3.ne.0) vsum=vsum+1
        if(v4.ne.0) vsum=vsum+1
        if(v5.ne.0) vsum=vsum+1
        if(v6.ne.0) vsum=vsum+1
        if(vsum.le.maxsum) then
          vl(1)=v1
          vl(2)=v2
          vl(3)=v3
          vl(4)=v4
          vl(5)=v5
          vl(6)=v6
          el = energ(vl,we,chi,chi2,6,0)-energ(v0,we,chi,chi2,6,0)
          if(dabs(eu-el-efind).lt.unc) then
            write(6,*) 'Possible match at:'
            write(6,fmt='(6i3,f10.2)') (vu(i1),i1=1,6),eu-el
          endif
        endif
110    continue
      endif
    endif
  endif

```

```

end

real*8 function energ(v,we,chi,chi2,modnum,state)
implicit none
integer modnum,modim
parameter (modim=6)
integer v(modim),i,j,state
real*8 we(0:2,modim),chi(0:2,modim,modim),
1chi2(0:2,modim,modim,modim)

c
  energ=0
  do i=1,modnum
    energ=energ+we(state,i)*(dfloat(v(i))+0.5d0)
    do j=i,modnum
      energ=energ+chi(state,i,j)*(dfloat(v(i))+0.5d0)*
1      (dfloat(v(j))+0.5d0)
    enddo
  enddo
  energ=energ+chi2(state,1,1,1)*(dfloat(v(1))+0.5d0)*
1  (dfloat(v(1))+0.5d0)*(dfloat(v(1))+0.5d0)

  energ=energ+chi2(state,1,1,4)*(dfloat(v(1))+0.5d0)*
1  (dfloat(v(1))+0.5d0)*(dfloat(v(4))+0.5d0)

  energ=energ+chi2(state,1,4,4)*(dfloat(v(1))+0.5d0)*
1  (dfloat(v(4))+0.5d0)*(dfloat(v(4))+0.5d0)

  energ=energ+chi2(state,4,4,4)*(dfloat(v(4))+0.5d0)*
1  (dfloat(v(4))+0.5d0)*(dfloat(v(4))+0.5d0)
  if( v(1) == 5 .and. v(4) == 8 .and. v(2)+v(3)+v(5)+v(6) == 0)
1 then
  endif
  return
end

```

A.2 fethfind.f90

This program was developed by me and is used to predict potential coupling constants for approximate factorization of molecular potential surfaces. Aside from predicting which couplings are relevant and can participate in IVR in interior states, the program is also expanded to a tier model with relevant couplings serving as new initial states. This program calculates upto the 2nd Tier from the initial bright state (bright state – 1st tier – 2nd tier).

```

program tiers
  implicit none
  integer :: i,j,k,z,tiernum,u=1,v=1,o
  real::c1,c2
  real, dimension(19):: w,om
  integer, dimension(19) :: a,y
  integer, dimension(19) :: b,x
  integer, dimension(1000,19)::h
  integer, dimension(3,1000,1000,19)::tier

  print>('Enter state')"

read(*,'(i1,i1,i1,i1,i1,i1,i1,i1,i1,i1,i1,i1,i1,i1,i1,i1,i1,i1,i1)') &
  x(1:19)
  y(1:19)=x(1:19)

  write(2,*)'Tier 1'
  write(2,*)'Input State:'
  write(2,*)x(1:19)
  write(2,*)

  do i=1,19
    read(1,*) w(i)
    !write(3,*) w(i)
    om(i)=w(i)
  enddo

10  do j=1,19
    a(j)=3
    !!write(2,*) a(1:19)
    b(1:19)=a(1:19)
    call potconstant3(c1)
    call state3(b,y,h,j,z,c1,c2,om)
    !!write (2,*)
    a(j)=0
  enddo

```

```

do k=1,19
  do j=1,19
    a(k)=2
    if(j.ne.k) then
      a(j)=1
      !!write(2,*) a(1:19)
      b(1:19)=a(1:19)
      call potconstant3(c1)
      call state21(b,y,h,k,j,z,c1,c2,om)
      !!write (2,*)
    endif
    a(k)=0
    a(j)=0
  enddo
enddo

do i=1,19
  do j=i+1,19
    do k=j+1,19
      if(i.ne.j) then
        if(j.ne.k) then
          if(i.ne.k) then
            a(i)=1; a(j)=1; a(k)=1
            !!write(2,*) a(1:19)
            b(1:19)=a(1:19)
            call potconstant3(c1)
            call state111(b,y,h,i,j,k,z,c1,c2,om)
            !!write (2,*)
          endif
          a(i)=0; a(j)=0; a(k)=0
        endif
      endif
    enddo
  enddo
enddo

do j=1,19
  a(j)=4
  !!write(2,*) a(1:19)
  b(1:19)=a(1:19)
  call potconstant4(c1)
  call state4(b,y,h,j,z,c1,c2,om)
  !!write (2,*)
  a(j)=0
enddo

do k=1,19
  do j=1,19
    a(k)=3
    if(j.ne.k) then
      a(j)=1

```

```

!!write(2,*) a(1:19)
b(1:19)=a(1:19)
call potconstant4(c1)
call state31(b,y,h,k,j,z,c1,c2,om)
!!write (2,*)
endif
a(k)=0
a(j)=0
enddo
enddo

do k=1,19
do j=k+1,19
a(k)=2
if(j.ne.k) then
a(j)=2
!!write(2,*) a(1:19)
b(1:19)=a(1:19)
call potconstant4(c1)
call state22(b,y,h,k,j,z,c1,c2,om)
!!write (2,*)
endif
a(k)=0
a(j)=0
enddo
enddo

do i=1,19
do j=1,19
do k=j+1,19
if(i.ne.j) then
if(j.ne.k) then
if(i.ne.k) then
a(i)=2; a(j)=1; a(k)=1
!!write(2,*) a(1:19)
b(1:19)=a(1:19)
call potconstant4(c1)
call state211(b,y,h,i,j,k,z,c1,c2,om)
!!write (2,*)
endif
endif
a(i)=0; a(j)=0; a(k)=0
endif
endif
enddo
enddo
enddo

do i=1,z
write(2,*)h(i,1:19)
enddo
write(2,*)

```

```

tier(u,v,1:z,1:19)=h(1:z,1:19)
if (u.gt.1) then
v=v+1
goto 20
else
o=z
v=1
end if

write(2,*) 'Tier2'
u=2
20 do while (v.le.o)
write(2,*) 'Input State',v
write(2,*) tier(1,1,v,1:19)
write(2,*)
y(1:19)=tier(1,1,v,1:19)
z=0
goto 10
end do

end program tiers

subroutine state3(c,d,r,n,t,v1,v2,omega)
implicit none

integer::n,t
integer, dimension(19)::c,d
integer, dimension(1000,19)::r
real, dimension(19)::omega
real::v1,v2,mat
c(1:19)=c(1:19)+d(1:19)
!!write(2,*) 'States'
mat=(( (d(n)+1) * (d(n)+2) * (d(n)+3) ) **0.5)
v2=(v1/ (3*omega(n))) * ((omega(n)) **1.5) *mat
!!write(2,*) c(1:19)
!!write(2,*) 'Cutoff value'
!!write(2,*) v2
if(v2.gt.(0.05)) then
!write(2,*) c(1:19)
!write(2,*) v2
t=t+1; !write(2,*) t
r(t,1:19)=c(1:19); call check(c,r,t)
end if
c(n)=c(n)-2
mat=(( (d(n)+1) **0.5)
v2=(v1/omega(n)) * ((omega(n)) **1.5) *mat
!!write(2,*) c(1:19)
!!write(2,*) 'Cutoff value'
!!write(2,*) v2
if(v2.gt.(0.05)) then
!write(2,*) c(1:19)
!write(2,*) v2
t=t+1; !write(2,*) t

```



```

r(t,1:19)=c(1:19); call check(c,r,t)
end if
c(n)=c(n)-2
if (c(n).ge.0) then
mat=((d(n))**0.5)
v2=(v1/omega(n))*((omega(n))**1.5)*mat
!!write(2,*)mat
!!write(2,*)c(1:19)
!!write(2,*)'Cutoff value'
!!write(2,*)v2
if(v2.gt.(0.05)) then
!write(2,*)c(1:19)
!write(2,*)v2
t=t+1; !write(2,*)t
r(t,1:19)=c(1:19); call check(c,r,t)
end if
end if
c(n)=c(n)-2
if (c(n).ge.0) then
mat=((d(n))*(d(n)-1)*(d(n)-2))**0.5)
v2=(v1/(3*omega(n)))*((omega(n))**1.5)*mat
!!write(2,*)mat
!!write(2,*)c(1:19)
!!write(2,*)'Cutoff value'
!!write(2,*)v2
if(v2.gt.(0.05)) then
!write(2,*)c(1:19)
!write(2,*)v2
t=t+1; !write(2,*)t
r(t,1:19)=c(1:19); call check(c,r,t)
end if
end if
end subroutine state3

subroutine potconstant3(v1)

implicit none
real::v1
v1=(3050./(270.**3))
!!write(2,*)v1

end subroutine potconstant3

subroutine potconstant4(v1)

implicit none
real::v1
v1=(3050./270.**4)
!!write(2,*)v1

end subroutine potconstant4

subroutine state21(c,d,r,m,n,t,v1,v2,omega)

```

```

implicit none
integer::m,n,t
real::v1,v2,mat2,mat1
real, dimension(19)::omega
integer, dimension(19)::c,d
integer, dimension(1000,19)::r

c(1:19)=c(1:19)+d(1:19)
!!write(2,*) 'States'
mat2=(( (d(m)+1)*(d(m)+2))**0.5)
mat1=(( (d(n)+1)*0.5)
v2=(v1/((2*omega(m))+(omega(n))))*omega(m)*(omega(n)**0.5)*mat2*mat1
!!write(2,*)c(1:19)
!!write(2,*) 'Cutoff value'
!!write(2,*)v2
if(v2.gt.(0.05)) then
!write(2,*)c(1:19)
!write(2,*)v2
t=t+1; !write(2,*)t
r(t,1:19)=c(1:19); call check(c,r,t)
end if
c(m)=c(m)-2
mat1=(( (d(n)+1)*0.5)
v2=(v1/omega(n))*omega(m)*(omega(n)**0.5)*mat1
!!write(2,*)c(1:19)
!!write(2,*) 'Cutoff value'
!!write(2,*)v2
if(v2.gt.(0.05)) then
!write(2,*)c(1:19)
!write(2,*)v2
t=t+1; !write(2,*)t
r(t,1:19)=c(1:19); call check(c,r,t)
end if
c(m)=c(m)-2
mat2=(( (d(m))*(d(m)-1))**0.5)
mat1=(( (d(n)+1)*0.5)
if (c(m).ge.0) then
v2=(v1/(abs((-
2*omega(m))+omega(n))))*(omega(n)**0.5)*omega(m)*mat2*mat1
!!write(2,*)c(1:19)
!!write(2,*) 'Cutoff value'
!!write(2,*)v2
if(v2.gt.(0.05)) then
!write(2,*)c(1:19)
!write(2,*)v2
t=t+1; !write(2,*)t
r(t,1:19)=c(1:19); call check(c,r,t)
end if
end if
c(n)=c(n)-2
if (c(n).ge.0) then
if (c(m).ge.0) then
mat2=(( (d(m))*(d(m)-1))**0.5)
mat1=(( (d(n))*0.5)

```

```

v2=(v1/((2*omega(m))+omega(n)))*(omega(n)**0.5)*omega(m)*mat2*mat1
!!write(2,*)c(1:19)
!!write(2,*)'Cutoff value'
!!write(2,*)v2
if(v2.gt.(0.05)) then
!write(2,*)c(1:19)
!write(2,*)v2
  t=t+1; !write(2,*)t
  r(t,1:19)=c(1:19); call check(c,r,t)
end if
end if
end if
c(m)=c(m)+2
if (c(n).ge.0) then
mat1=((d(n))*0.5)
v2=(v1/omega(n))*(omega(n)**0.5)*omega(m)*mat1
!!write(2,*)c(1:19)
!!write(2,*)'Cutoff value'
!!write(2,*)v2
if(v2.gt.(0.05)) then
!write(2,*)c(1:19)
!write(2,*)v2
  t=t+1; !write(2,*)t
  r(t,1:19)=c(1:19); call check(c,r,t)
end if
end if
c(m)=c(m)+2
if (c(n).ge.0) then
mat2=((d(m)+1)*(d(m)+2)**0.5)
mat1=((d(n))*0.5)
v2=(v1/(abs((2*omega(m))-
omega(n))))*(omega(n)**0.5)*omega(m)*mat2*mat1
!!write(2,*)c(1:19)
!!write(2,*)'Cutoff value'
!!write(2,*)v2
if(v2.gt.(0.05)) then
!write(2,*)c(1:19)
!write(2,*)v2
  t=t+1; !write(2,*)t
  r(t,1:19)=c(1:19); call check(c,r,t)
end if
end if

end subroutine state21

subroutine state111(c,d,r,m,n,q,t,v1,v2,omega)

implicit none
integer, dimension(19)::c,d
integer, dimension(1000,19)::r
integer::m,n,q,t
real::v1,v2,mat
real, dimension(19)::omega

```

```

c(1:19)=c(1:19)+d(1:19)
!!write(2,*) 'States'
mat=((d(m)+1)**0.5)*((d(n)+1)**0.5)*((d(q)+1)**0.5)

v2=(v1/(omega(m)+omega(n)+omega(q)))*(omega(m)**0.5)*(omega(n)**0.5)&
*(omega(q)**0.5)*mat
!!write(2,*)c(1:19)
!!write(2,*) 'Cutoff value'
!!write(2,*)v2
if(v2.gt.(0.05)) then
!write(2,*)c(1:19)
!write(2,*)v2
t=t+1; !write(2,*)t
r(t,1:19)=c(1:19); call check(c,r,t)
end if
c(q)=c(q)-2
if (c(q).ge.0) then
mat=((d(m)+1)**0.5)*((d(n)+1)**0.5)*((d(q))**0.5)
v2=(v1/(abs(omega(m)+omega(n)-omega(q))))*(omega(m)**0.5)&
*(omega(n)**0.5)*(omega(q)**0.5)*mat
!!write(2,*)c(1:19)
!!write(2,*) 'Cutoff value'
!!write(2,*)v2
if(v2.gt.(0.05)) then
!write(2,*)c(1:19)
!write(2,*)v2
t=t+1; !write(2,*)t
r(t,1:19)=c(1:19); call check(c,r,t)
end if
end if
c(q)=c(q)+2
c(n)=c(n)-2
if (c(n).ge.0) then
mat=((d(m)+1)**0.5)*((d(n))**0.5)*((d(q)+1)**0.5)
v2=(v1/(abs(omega(m)-omega(n)+omega(q))))*(omega(m)**0.5)&
*(omega(n)**0.5)*(omega(q)**0.5)*mat
!!write(2,*)c(1:19)
!!write(2,*) 'Cutoff value'
!!write(2,*)v2
if(v2.gt.(0.05)) then
!write(2,*)c(1:19)
!write(2,*)v2
t=t+1; !write(2,*)t
r(t,1:19)=c(1:19); call check(c,r,t)
end if
end if
c(q)=c(q)-2
if (c(n).ge.0) then
if (c(q).ge.0) then
mat=((d(m)+1)**0.5)*((d(n))**0.5)*((d(q))**0.5)
v2=(v1/(abs(omega(m)-omega(n)-omega(q))))*(omega(m)**0.5)&
*(omega(n)**0.5)*(omega(q)**0.5)*mat
!!write(2,*)c(1:19)
!!write(2,*) 'Cutoff value'

```

```

!!write(2,*)v2
if(v2.gt.(0.05)) then
!write(2,*)c(1:19)
!write(2,*)v2
  t=t+1; !write(2,*)t
  r(t,1:19)=c(1:19); call check(c,r,t)
end if
end if
end if
c(m)=c(m)-2
if (c(n).ge.0) then
if (c(q).ge.0) then
if (c(m).ge.0) then
mat=((d(m))**0.5)*((d(n))**0.5)*((d(q))**0.5)

v2=(v1/(omega(m)+omega(n)+omega(q)))*(omega(n)**0.5)*(omega(m)**0.5)&
*(omega(q)**0.5)*mat
!!write(2,*)c(1:19)
!!write(2,*)'Cutoff value'
!!write(2,*)v2
if(v2.gt.(0.05)) then
!write(2,*)c(1:19)
!write(2,*)v2
  t=t+1; !write(2,*)t
  r(t,1:19)=c(1:19); call check(c,r,t)
end if
end if
end if
end if
c(n)=c(n)+2
if (c(m).ge.0) then
if (c(q).ge.0) then
mat=((d(m))**0.5)*((d(n)+1)**0.5)*((d(q))**0.5)
v2=(v1/(abs(omega(n)-omega(m)-omega(q))))*(omega(n)**0.5)&
*(omega(m)**0.5)*(omega(q)**0.5)*mat
!!write(2,*)c(1:19)
!!write(2,*)'Cutoff value'
!!write(2,*)v2
if(v2.gt.(0.05)) then
!write(2,*)c(1:19)
!write(2,*)v2
  t=t+1; !write(2,*)t
  r(t,1:19)=c(1:19); call check(c,r,t)
end if
end if
end if
c(n)=c(n)-2
c(q)=c(q)+2
if (c(n).ge.0) then
if (c(m).ge.0) then
mat=((d(m))**0.5)*((d(n))**0.5)*((d(q)+1)**0.5)
v2=(v1/(abs(omega(q)-omega(m)-omega(n))))*(omega(n)**0.5)&
*(omega(m)**0.5)*(omega(q)**0.5)*mat
!!write(2,*)c(1:19)

```

```

!!write(2,*) 'Cutoff value'
!!write(2,*) v2
if(v2.gt.(0.05)) then
!write(2,*) c(1:19)
!write(2,*) v2
  t=t+1; !write(2,*) t
  r(t,1:19)=c(1:19); call check(c,r,t)
end if
end if
end if
c(n)=c(n)+2
if (c(m).ge.0) then
mat=((d(m))**0.5)*((d(n)+1)**0.5)*((d(q)+1)**0.5)
v2=(v1/(abs(omega(q)+omega(n)-omega(m))))*(omega(m)**0.5)&
*(omega(n)**0.5)*(omega(q)**0.5)*mat
!!write(2,*) c(1:19)
!!write(2,*) 'Cutoff value'
!!write(2,*) v2
if(v2.gt.(0.05)) then
!write(2,*) c(1:19)
!write(2,*) v2
  t=t+1; !write(2,*) t
  r(t,1:19)=c(1:19); call check(c,r,t)
end if
end if

end subroutine state111

subroutine state4(c,d,r,n,t,v1,v2,omega)

implicit none
integer, dimension(19)::c,d
integer, dimension(1000,19)::r
integer::n,t
real::v1,v2,mat
real, dimension(19)::omega

c(1:19)=c(1:19)+d(1:19)
!!write(2,*) 'States'
mat=((d(n)+1)**0.5)*((d(n)+2)**0.5)*((d(n)+3)**0.5)*((d(n)+4)**0.5)
v2=(v1/(4*omega(n)))*((omega(n))**2)*mat
!!write(2,*) c(1:19)
!!write(2,*) 'Cutoff value'
!!write(2,*) v2
if(v2.gt.(0.05)) then
!write(2,*) c(1:19)
!write(2,*) v2
  t=t+1; !write(2,*) t
  r(t,1:19)=c(1:19); call check(c,r,t)
end if
c(n)=c(n)-2
mat=((d(n)+1)**0.5)*((d(n)+2)**0.5)
v2=(v1/(2*omega(n)))*((omega(n))**2)*mat
!!write(2,*) c(1:19)

```

```

!!write(2,*) 'Cutoff value'
!!write(2,*) v2
if(v2.gt.(0.05)) then
!write(2,*) c(1:19)
!write(2,*) v2
t=t+1; !write(2,*) t
r(t,1:19)=c(1:19); call check(c,r,t)
end if
c(n)=c(n)-2
v2=0.0
!!write(2,*) c(1:19)
!!write(2,*) 'Cutoff value'
!!write(2,*) v2
if(v2.gt.(0.05)) then
!write(2,*) c(1:19)
!write(2,*) v2
t=t+1; !write(2,*) t
r(t,1:19)=c(1:19); call check(c,r,t)
end if
c(n)=c(n)-2
if (c(n).ge.0) then
mat=((d(n))**0.5)*((d(n)-1)**0.5)
v2=(v1/(2*omega(n)))*((omega(n))**1.5)*mat
!!write(2,*) c(1:19)
!!write(2,*) 'Cutoff value'
!!write(2,*) v2
if(v2.gt.(0.05)) then
!write(2,*) c(1:19)
!write(2,*) v2
t=t+1; !write(2,*) t
r(t,1:19)=c(1:19); call check(c,r,t)
end if
end if
c(n)=c(n)-2
if (c(n).ge.0) then
mat=((d(n))**0.5)*((d(n)-1)**0.5)*((d(n)-2)**0.5)*((d(n)-3)**0.5)
v2=(v1/(4*omega(n)))*((omega(n))**1.5)*mat
!!write(2,*) c(1:19)
!!write(2,*) 'Cutoff value'
!!write(2,*) v2
if(v2.gt.(0.05)) then
!write(2,*) c(1:19)
!write(2,*) v2
t=t+1; !write(2,*) t
r(t,1:19)=c(1:19); call check(c,r,t)
end if
end if

end subroutine state4

subroutine state31(c,d,r,n,m,t,v1,v2,omega)

implicit none
integer::n,m,t

```

```

integer, dimension(19)::c,d
integer, dimension(1000,19)::r
real::v1,v2,mat1,mat3
real, dimension(19)::omega

c(1:19)=c(1:19)+d(1:19)
mat3=((d(n)+1)**0.5)*((d(n)+2)**0.5)*((d(n)+3)**0.5)
mat1=((d(m)+1)**0.5)
v2=(v1/((3*omega(n))+(omega(m))))*(omega(m)**0.5)*(omega(n)**1.5)&
*mat3*mat1
!!write(2,*)'States'
!!write(2,*)c(1:19)
!!write(2,*)'Cutoff value'
!!write(2,*)v2
if(v2.gt.(0.05)) then
!write(2,*)c(1:19)
!write(2,*)v2
t=t+1; !write(2,*)t
r(t,1:19)=c(1:19); call check(c,r,t)
end if
c(n)=c(n)-2
mat3=((d(n)+1)**0.5)
mat1=((d(m)+1)**0.5)

v2=(v1/((omega(n))+(omega(m))))*(omega(m)**0.5)*(omega(n)**1.5)*mat3*mat1
!!write(2,*)c(1:19)
!!write(2,*)'Cutoff value'
!!write(2,*)v2
if(v2.gt.(0.05)) then
!write(2,*)c(1:19)
!write(2,*)v2
t=t+1; !write(2,*)t
r(t,1:19)=c(1:19); call check(c,r,t)
end if
c(n)=c(n)-2
if (c(n).ge.0) then
mat3=((d(n))**0.5)
mat1=((d(m)+1)**0.5)
v2=(v1/(abs((-
omega(n))+omega(m))))*(omega(n)**1.5)*(omega(m)**0.5)&
*mat3*mat1
!!write(2,*)c(1:19)
!!write(2,*)'Cutoff value'
!!write(2,*)v2
if(v2.gt.(0.05)) then
!write(2,*)c(1:19)
!write(2,*)v2
t=t+1; !write(2,*)t
r(t,1:19)=c(1:19); call check(c,r,t)
end if
end if
c(n)=c(n)-2
if (c(n).ge.0) then
mat3=((d(n))**0.5)*((d(n)-1)**0.5)*((d(n)-2)**0.5)

```



```

mat1=((d(m)+1)**0.5)
v2=(v1/(abs((-
3*omega(n))+omega(m))))*((omega(n))**1.5)*(omega(m)**0.5)&
*mat3*mat1
!!write(2,*)c(1:19)
!!write(2,*)'Cutoff value'
!!write(2,*)v2
if(v2.gt.(0.05)) then
!write(2,*)c(1:19)
!write(2,*)v2
t=t+1; !write(2,*)t
r(t,1:19)=c(1:19); call check(c,r,t)
end if
end if
c(m)=c(m)-2
if (c(n).ge.0) then
if (c(m).ge.0) then
mat3=((d(n))**0.5)*((d(n)-1)**0.5)*((d(n)-2)**0.5)
mat1=((d(m))**0.5)
v2=(v1/((3*omega(n))+omega(m)))*((omega(n))**1.5)*(omega(m)**0.5)&
*mat3*mat1
!!write(2,*)c(1:19)
!!write(2,*)'Cutoff value'
!!write(2,*)v2
if(v2.gt.(0.05)) then
!write(2,*)c(1:19)
!write(2,*)v2
t=t+1; !write(2,*)t
r(t,1:19)=c(1:19); call check(c,r,t)
end if
end if
end if
c(n)=c(n)+2
if (c(n).ge.0) then
if (c(m).ge.0) then
mat3=((d(n))**0.5)
mat1=((d(m))**0.5)
v2=(v1/(omega(m)+omega(n)))*((omega(n))**1.5)*(omega(m)**0.5)&
*mat3*mat1
!!write(2,*)c(1:19)
!!write(2,*)'Cutoff value'
!!write(2,*)v2
if(v2.gt.(0.05)) then
!write(2,*)c(1:19)
!write(2,*)v2
t=t+1; !write(2,*)t
r(t,1:19)=c(1:19); call check(c,r,t)
end if
end if
end if
c(n)=c(n)+2
if (c(m).ge.0) then
mat3=((d(n)+1)**0.5)
mat1=((d(m))**0.5)

```

```

v2=(v1/(abs(omega(n)-omega(m))))*(omega(n)**1.5)*(omega(m)**0.5)&
*mat3*mat1
!!write(2,*)c(1:19)
!!write(2,*)'Cutoff value'
!!write(2,*)v2
if(v2.gt.(0.05)) then
!write(2,*)c(1:19)
!write(2,*)v2
t=t+1; !write(2,*)t
r(t,1:19)=c(1:19); call check(c,r,t)
end if
end if
c(n)=c(n)+2
if (c(m).ge.0) then
mat3=((d(n)+1)**0.5)*((d(n)+2)**0.5)*((d(n)+3)**0.5)
mat1=((d(m))**0.5)
v2=(v1/(abs((3*omega(n))-
omega(m))))*(omega(n)**1.5)*(omega(m)**0.5)&
*mat3*mat1
!!write(2,*)c(1:19)
!!write(2,*)'Cutoff value'
!!write(2,*)v2
if(v2.gt.(0.05)) then
!write(2,*)c(1:19)
!write(2,*)v2
t=t+1; !write(2,*)t
r(t,1:19)=c(1:19); call check(c,r,t)
end if
end if

end subroutine state31

subroutine state22(c,d,r,n,m,t,v1,v2,omega)

implicit none
integer::n,m,t
integer, dimension(19)::c,d
integer, dimension(1000,19)::r
real::v1,v2,mata,matb
real, dimension(19)::omega

c(1:19)=c(1:19)+d(1:19)
mata=((d(n)+1)*(d(n)+2))**0.5)
matb=((d(m)+1)*(d(m)+2))**0.5)
v2=(v1/((2*omega(n))+(2*omega(m))))*omega(m)*omega(n)*mata*matb
!!write(2,*)'States'
!!write(2,*)c(1:19)
!!write(2,*)'Cutoff value'
!!write(2,*)v2
if(v2.gt.(0.05)) then
!write(2,*)c(1:19)
!write(2,*)v2
t=t+1; !write(2,*)t
r(t,1:19)=c(1:19); call check(c,r,t)

```

```

end if
c(n)=c(n)-2
matb=(( (d(m)+1)*(d(m)+2))**0.5)
v2=(v1/(2*omega(m)))*omega(m)*omega(n)*matb
!!write(2,*)c(1:19)
!!write(2,*)'Cutoff value'
!!write(2,*)v2
if(v2.gt.(0.05)) then
!write(2,*)c(1:19)
!write(2,*)v2
t=t+1; !write(2,*)t
r(t,1:19)=c(1:19); call check(c,r,t)
end if
c(n)=c(n)-2
if(c(n).ge.0)then
mata=(( (d(n))*(d(n)-1))**0.5)
matb=(( (d(m)+1)*(d(m)+2))**0.5)
v2=(v1/(abs((-
2*omega(m))+(2*omega(n)))))*omega(m)*omega(n)*mata*matb
!!write(2,*)c(1:19)
!!write(2,*)'Cutoff value'
!!write(2,*)v2
if(v2.gt.(0.05)) then
!write(2,*)c(1:19)
!write(2,*)v2
t=t+1; !write(2,*)t
r(t,1:19)=c(1:19); call check(c,r,t)
end if
end if
c(m)=c(m)-2
if (c(n).ge.0) then
mata=(( (d(n))*(d(n)-1))**0.5)
v2=(v1/(2*omega(n)))*omega(n)*omega(m)*mata
!!write(2,*)c(1:19)
!!write(2,*)'Cutoff value'
!!write(2,*)v2
if(v2.gt.(0.05)) then
!write(2,*)c(1:19)
!write(2,*)v2
t=t+1; !write(2,*)t
r(t,1:19)=c(1:19); call check(c,r,t)
end if
end if
c(n)=c(n)+2
v2=0.0
!!write(2,*)c(1:19)
!!write(2,*)'Cutoff value'
!!write(2,*)v2
if(v2.gt.(0.05)) then
!write(2,*)c(1:19)
!write(2,*)v2
t=t+1; !write(2,*)t
r(t,1:19)=c(1:19); call check(c,r,t)
end if

```

```

c(n)=c(n)+2
mata=((d(n)+1)*(d(n)+2))**0.5)
v2=(v1/(2*omega(n)))*omega(n)*omega(m)*mata
!!write(2,*)c(1:19)
!!write(2,*)'Cutoff value'
!!write(2,*)v2
if(v2.gt.(0.05)) then
!write(2,*)c(1:19)
!write(2,*)v2
t=t+1; !write(2,*)t
r(t,1:19)=c(1:19); call check(c,r,t)
end if
c(m)=c(m)-2
if (c(m).ge.0) then
mata=((d(n)+1)*(d(n)+2))**0.5)
matb=((d(m))*(d(m)-1))**0.5)
v2=(v1/(abs((2*omega(n))+(-
2*omega(m)))))*omega(n)*omega(m)*mata*matb
!!write(2,*)c(1:19)
!!write(2,*)'Cutoff value'
!!write(2,*)v2
if(v2.gt.(0.05)) then
!write(2,*)c(1:19)
!write(2,*)v2
t=t+1; !write(2,*)t
r(t,1:19)=c(1:19); call check(c,r,t)
end if
end if
c(n)=c(n)-2
if (c(m).ge.0) then
matb=((d(m))*(d(m)-1))**0.5)
v2=(v1/(2*omega(m)))*omega(m)*omega(n)*matb
!!write(2,*)c(1:19)
!!write(2,*)'Cutoff value'
!!write(2,*)v2
if(v2.gt.(0.05)) then
!write(2,*)c(1:19)
!write(2,*)v2
t=t+1; !write(2,*)t
r(t,1:19)=c(1:19); call check(c,r,t)
end if
end if
c(n)=c(n)-2
if (c(n).ge.0) then
if (c(m).ge.0) then
mata=((d(n))*(d(n)-1))**0.5)
matb=((d(m))*(d(m)-1))**0.5)
v2=(v1/((2*omega(n))+(2*omega(m))))*omega(m)*omega(n)*mata*matb
!!write(2,*)c(1:19)
!!write(2,*)'Cutoff value'
!!write(2,*)v2
if(v2.gt.(0.05)) then
!write(2,*)c(1:19)
!write(2,*)v2

```

```

        t=t+1; !write(2,*)t
        r(t,1:19)=c(1:19); call check(c,r,t)
    end if
end if
end if

end subroutine state22

subroutine state211(c,d,r,m,n,q,t,v1,v2,omega)

    implicit none
    integer, dimension(19)::c,d
    integer::m,n,q,t
    real::v1,v2,mat2,mata,matb
    real, dimension(19)::omega
    integer, dimension(1000,19)::r

    c(1:19)=c(1:19)+d(1:19)
    mat2=(( (d(m)+1)*(d(m)+2))**0.5)
    mata=((d(n)+1)**0.5)
    matb=((d(q)+1)**0.5)
    v2=(v1/((2*omega(m))+omega(n)+omega(q)))*omega(m)*(omega(n)**0.5)&
    *(omega(q)**0.5)*mat2*mata*matb
    !!write(2,*)'States'
    !!write(2,*)c(1:19)
    !!write(2,*)'Cutoff value'
    !!write(2,*)v2
    if(v2.gt.(0.05)) then
        !write(2,*)c(1:19)
        !write(2,*)v2
        t=t+1; !write(2,*)t
        r(t,1:19)=c(1:19); call check(c,r,t)
    end if
    c(m)=c(m)-2
    mata=((d(n)+1)**0.5)
    matb=((d(q)+1)**0.5)
    v2=(v1/(omega(n)+omega(q)))*((omega(n))**0.5)*((omega(q))**0.5)&
    *omega(m)*mata*matb
    !!write(2,*)c(1:19)
    !!write(2,*)'Cutoff value'
    !!write(2,*)v2
    if(v2.gt.(0.05)) then
        !write(2,*)c(1:19)
        !write(2,*)v2
        t=t+1; !write(2,*)t
        r(t,1:19)=c(1:19); call check(c,r,t)
    end if
    c(m)=c(m)-2
    if (c(m).ge.0) then
        mat2=(( (d(m))*(d(m)-1))**0.5)
        mata=((d(n)+1)**0.5)
        matb=((d(q)+1)**0.5)
        v2=(v1/(abs((-2*omega(m))+omega(n)+omega(q)))*omega(n)**0.5)&
        *(omega(q)**0.5)*omega(m)*mat2*mata*matb

```

```

!!write(2,*)c(1:19)
!!write(2,*)'Cutoff value'
!!write(2,*)v2
if(v2.gt.(0.05)) then
!write(2,*)c(1:19)
!write(2,*)v2
  t=t+1; !write(2,*)t
  r(t,1:19)=c(1:19); call check(c,r,t)
end if
end if
c(n)=c(n)-2
if (c(n).ge.0) then
  if(c(m).ge.0) then
mat2=(( (d(m)) * (d(m)-1)) **0.5)
mata=(( (d(n)) **0.5)
matb=(( (d(q)+1) **0.5)
v2=(v1/ (abs((-2*omega(m))-omega(n)+omega(q)))) * (omega(n) **0.5) &
* (omega(q) **0.5) * omega(m) * mat2 * mata * matb
!!write(2,*)c(1:19)
!!write(2,*)'Cutoff value'
!!write(2,*)v2
if(v2.gt.(0.05)) then
!write(2,*)c(1:19)
!write(2,*)v2
  t=t+1; !write(2,*)t
  r(t,1:19)=c(1:19); call check(c,r,t)
end if
end if
end if
c(m)=c(m)+2
if (c(n).ge.0) then
mata=(( (d(n)) **0.5)
matb=(( (d(q)+1) **0.5)
v2=(v1/ (abs(-omega(n)+omega(q)))) * (omega(n) **1.5) * (omega(q) **0.5) &
* omega(m) * mata * matb
!!write(2,*)c(1:19)
!!write(2,*)'Cutoff value'
!!write(2,*)v2
if(v2.gt.(0.05)) then
!write(2,*)c(1:19)
!write(2,*)v2
  t=t+1; !write(2,*)t
  r(t,1:19)=c(1:19); call check(c,r,t)
end if
end if
c(m)=c(m)+2
if (c(n).ge.0) then
mat2=(( (d(m)+1) * (d(m)+2)) **0.5)
mata=(( (d(n)) **0.5)
matb=(( (d(q)+1) **0.5)
v2=(v1/ (abs((2*omega(m))-omega(n)+omega(q)))) * (omega(n) **0.5) &
* (omega(q) **0.5) * omega(m) * mat2 * mata * matb
!!write(2,*)c(1:19)
!!write(2,*)'Cutoff value'

```

```

!!write(2,*)v2
if(v2.gt.(0.05)) then
!write(2,*)c(1:19)
!write(2,*)v2
  t=t+1; !write(2,*)t
  r(t,1:19)=c(1:19); call check(c,r,t)
end if
end if
c(n)=c(n)+2
c(q)=c(q)-2
if (c(q).ge.0) then
mat2=(( (d(m)+1)*(d(m)+2))**0.5)
mata=(( (d(n)+1)**0.5)
matb=(( (d(q))**0.5)
v2=(v1/(abs((2*omega(m))+omega(n)-omega(q))))*(omega(n)**0.5)&
*(omega(q)**0.5)*omega(m)*mat2*mata*matb
!!write(2,*)c(1:19)
!!write(2,*)'Cutoff value'
!!write(2,*)v2
if(v2.gt.(0.05)) then
!write(2,*)c(1:19)
!write(2,*)v2
  t=t+1; !write(2,*)t
  r(t,1:19)=c(1:19); call check(c,r,t)
end if
end if
c(m)=c(m)-2
if (c(q).ge.0) then
mata=(( (d(n)+1)**0.5)
matb=(( (d(q))**0.5)
v2=(v1/(abs(omega(n)-omega(q))))*(omega(n)**0.5)*(omega(q)**0.5)&
*omega(m)*mata*matb
!!write(2,*)c(1:19)
!!write(2,*)'Cutoff value'
!!write(2,*)v2
if(v2.gt.(0.05)) then
!write(2,*)c(1:19)
!write(2,*)v2
  t=t+1; !write(2,*)t
  r(t,1:19)=c(1:19); call check(c,r,t)
end if
end if
c(m)=c(m)-2
if (c(q).ge.0) then
if(c(m).ge.0) then
mat2=(( (d(m))*(d(m)-1))**0.5)
mata=(( (d(n)+1)**0.5)
matb=(( (d(q))**0.5)
v2=(v1/(abs((-2*omega(m))+omega(n)-
omega(q))))*(omega(m)*(omega(n)**0.5)&
*(omega(q)**0.5)*mat2*mata*matb
!!write(2,*)c(1:19)
!!write(2,*)'Cutoff value'
!!write(2,*)v2

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```

    if(v2.gt.(0.05)) then
!write(2,*)c(1:19)
!write(2,*)v2
    t=t+1; !write(2,*)t
    r(t,1:19)=c(1:19); call check(c,r,t)
end if
end if
end if
c(n)=c(n)-2
if (c(n).ge.0) then
if (c(m).ge.0) then
if(c(q).ge.0) then
mat2=(( (d(m)) * (d(m)-1)) **0.5)
mata=(( (d(n)) **0.5)
matb=(( (d(q)) **0.5)
v2=(v1/ ((2*omega(m))+omega(n)+omega(q))) * (omega(n) **0.5) &
*omega(m) * (omega(q) **0.5) *mat2*mata*matb
!!write(2,*)c(1:19)
!!write(2,*) 'Cutoff value'
!!write(2,*)v2
if(v2.gt.(0.05)) then
!write(2,*)c(1:19)
!write(2,*)v2
    t=t+1; !write(2,*)t
    r(t,1:19)=c(1:19); call check(c,r,t)
end if
end if
end if
end if
c(m)=c(m)+2
if (c(n).ge.0) then
if(c(q).ge.0) then
mata=(( (d(n)) **0.5)
matb=(( (d(q)) **0.5)
v2=(v1/ (omega(q)+omega(n))) * (omega(n) **0.5) * (omega(q) **0.5) &
*omega(m) *mata*matb
!!write(2,*)c(1:19)
!!write(2,*) 'Cutoff value'
!!write(2,*)v2
if(v2.gt.(0.05)) then
!write(2,*)c(1:19)
!write(2,*)v2
    t=t+1; !write(2,*)t
    r(t,1:19)=c(1:19); call check(c,r,t)
end if
end if
end if
c(m)=c(m)+2
if (c(n).ge.0) then
if(c(q).ge.0) then
mat2=(( (d(m)+1) * (d(m)+2)) **0.5)
mata=(( (d(n)) **0.5)
matb=(( (d(q)) **0.5)
v2=(v1/ (abs((2*omega(m))-omega(n)-omega(q)))) * (omega(n) **0.5) &

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```

      *omega(m)*(omega(q)**0.5)*mat2*mata*matb
      !!write(2,*)c(1:19)
      !!write(2,*)'Cutoff value'
      !!write(2,*)v2
      if(v2.gt.(0.05)) then
!write(2,*)c(1:19)
!write(2,*)v2
      t=t+1; !write(2,*)t
      r(t,1:19)=c(1:19); call check(c,r,t)
      end if
    end if
  end if

end subroutine state211

subroutine check(cc,s,u)

implicit none
integer::u,i,j,n,m
integer, dimension(1000,19)::s
integer, dimension(19)::cc
m=0
do i=1,u-1
  n=0
  do j=1,19
    if(s(u,j).eq.s(i,j)) then
      n=n+1
    end if
  end do
  if(n.eq.19) then
    m=m
  else
    m=m+1
  end if
end do
if (m.lt.(u-1)) then
  u=u-1
end if

end subroutine check

```