Computational Investigation of Stellar Cooling, Noble Gas Nucleation, and Organic Molecular Spectra

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Abstract

Since the advent and optimization of the Hartree-Fock method, quantum chemistry has been utilized to investigate systems operating on timeframes and environments traditionally unavailable to bench-top chemistry. As computational methods have grown more robust and less time consuming, quantum chemistry has been utilized to investigate a range of fields, including the steadily growing discipline of computational astrochemistry. Through the lens of computational astrochemistry, chemistry that occurred billions of years ago can be explored with equal clarity to that which is currently happening in the cosmos. The work presented throughout this thesis is a series of investigations into different timeframes of the universe: 1) a study on novel cooling mechanisms of the earliest stars to ever form following the calamity of the big bang; 2) a look into the solvation of a ubiquitous molecule in noble gas atoms; and 3) an investigation of the anharmonic vibrational frequencies of a molecule that has promise to be a fundamental building block of amino acids in the ISM.
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Chapter 1

The History of Quantum Mechanics

If one was pressed with naming the most influential scientific discovery in history, they would have dozens of correct answers from which to choose depending upon their audience. From Democritus’s ancient musings on atomos to Einstein’s revered theory of relativity, humanity’s understanding of the natural world has been overturned countless times with each somersault opening doors to new technology. In the last century, however, few revelations have had the academic or technological weight than the introduction of the world to quantum mechanics.

1.1 Blackbody Emitters and the Dawn of Quantum Mechanics

The key to understanding quantum mechanics manifested in what was previously thought to be an unassuming phenomena, black body radiation. A black body is a hypothetical object that absorbs and emits electromagnetic radiation at all frequencies. Physicists Lord Rayleigh and James Jean modelled an ideal black body at thermal equilibrium utilizing the well accepted equipartition theorem, which states that all harmonic oscillating modes at thermal equilibrium have an average energy of $\frac{1}{2}kT$, where $k$ is the Boltzmann constant [1].
The resulting Rayleigh-Jeans Law is successful when modeling black body radiation at long wavelengths, but proposed energies quickly balloon as frequency increases.

These drastic inaccuracies spawned due to an artifact of classical electromagnetism where the number of electromagnetic modes in a three dimensional cavity is proportional to the square of the frequency. Therefore, as frequency steadily increased, the number of modes skyrocketed as well, and each additional mode brought with it an equipartition of energy to add to the system [2]. This resulted in the Rayleigh-Jean law proposing infinite energy as wavelengths approached zero. This was obviously a nonsensical solution and required physicists to turn their attention to another possible solution to the problem, which up until that time was also considered nonsense.

Five years prior to the presentation of the Rayleigh-Jean law, Max Planck reverse engineered a mathematical law that perfectly plotted the intensity distribution of a black body emitter at all wavelengths [3]. This proposal was initially rejected due to the strange assumptions and implications it made regarding the nature of electromagnetic radiation energy, with it implying that electromagnetic radiation existed in discrete packets of energy rather than the continuum that classical physics assumed. The challenge to this proposition was intense, but a curious phenomenon regarding metal and light would prove Planck right and win Albert Einstein a Nobel Prize in the meantime.

The photoelectric effect had been garnering increasing interest over the decades preceding Einstein’s musings on the topic, but the observed behavior was seemingly contradictory to classical electromagnetism. When light was shone on a freshly cut and clean metal surface, the emission of electrons from its surface could be observed [4]. Curiously though, the emission of electrons was not reliant on intensity like one would expect to follow from Maxwell’s wave theory of light, but rather the wavelength or, equivalently, frequency of incident light. Relating this strange behavior to Maxwell’s previous assertion regarding the quantization of electromagnetic energy, Einstein hypothesized that light existed and transferred energy in the form of discrete quanta, which we now know as photons [5]. Einstein went on to assert
that the energy of these quanta was equal to the frequency of light multiplied by a certain 
constant \( (h) \), one that we now know as Planck’s constant, and can be seen below in Equation 
1.1.

\[
E = h\nu
\] 

With the introduction of the photoelectric effect and the quantization of energy, the 
classical school of thought was turned upside down. In the years following Einstein and 
Planck’s discoveries, the comforting, predictable continua that were commonplace in the 
large scale world of classical physics would be found to be incompetent in explaining the 
atomic and subatomic world. In their place probabilities, uncertainty, and mind bending 
logic would rein.

1.1.1 Schrodinger, Heisenberg, and the Introduction of Uncer-
tainty

Einstein’s particle definition of light was met with much scrutiny, but this particle def-
definition was quickly discovered to not be mutually exclusive with the wave definition that 
classical physicists knew so well. In 1923, de Broglie theorized that the motion of electrons 
may be characterized by wave behavior [6], with the wavelength of an electron with mass \( m \), 
speed \( v \), and momentum \( p \) represented below in Equation 1.2.

\[
\lambda = \frac{h}{mv} = \frac{h}{p}
\] 

This strange, counter-intuitive notion was supported four years later when reflected electrons 
were shown to produce diffraction patterns. Furthermore, this duality was abstracted to 
include photons, hydrogen molecules, and any other particle for which \( \lambda \) is greater than the 
spatial extent of the object.

Within a year of the experimental validation of the wave-particle duality of light and 
matter, Werner Heisenberg had discovered a troubling limitation that it wrought among
observation on the molecular scale. The uncertainty principle states that as a quantum system is observed, like the previously mentioned electron diffraction experiment, there is an inherent uncertainty in determining the position and momentum of such a system. More specifically, the more precisely a particle’s position is known, the less accurately its momentum can be known and vice versa [1]. This uncertainty can be approximated as seen below in Equation 1.3, with uncertainty of position represented by $\Delta x$, the uncertainty in momentum represented by $\Delta p$, and $h$ represents Planck’s constant:

$$\Delta x \Delta p \approx h \quad (1.3)$$

This uncertainty is a manifestation of observation itself inciting a change on the system, therefore the more precisely one aspect of a system is observed, the more other aspects of the system are clouded by uncertainty. However, there is a point in which no more knowledge can be gained about a certain aspect of a system, even by sacrificing knowledge about all other aspects.

Despite the uncertainty inherent in observing a quantum system, meaningful data may still be uncovered while making some simplifications. For example, the wave function, $\psi$, of the system can be reasonably assumed to be unchanging with respect to time, therefore making it time-independent. By making this assumption, one of the most powerful tools in quantum chemistry presents itself: the time-independent Schrödinger equation as seen below in Equation 1.4.

$$-\frac{\hbar^2}{2m} \frac{d^2 \psi}{dx^2} + V\psi = E\psi \quad (1.4)$$

This equation yields one of the most important things a chemist can know about a system, quantum or otherwise, its energy.

By knowing the energy of a quantum system, we are given a way to interpret concepts ranging from bond stability to likelihood of excitation and are given stepping stones to calculating secondary data for all kinds of quantum systems. The trouble for physicists of
the late 1920s was the notorious difficulty of solving the Schrödinger equation for a system as simple as the hydrogen atom. In fact, the equation is impossible to solve for a system with more electrons. It would take great innovations in technology and creative solutions in mathematics to bring about the dawn of computational chemistry, but it would come none the less.

1.2 The History of Computational Chemistry

1.2.1 The creation and optimization of the Hartree-Fock Method

Note: This section was written utilizing Levine’s Quantum Chemistry [1] alongside Szabo and Ostlund’s Modern Quantum Chemistry [2] as reference material.

Prior to 1926, many physicists and chemists were attempting to formulate mathematical methods to solve for the energy of multi-electron atoms, but these trials made corrections to classical solutions of quantum systems and left much to be desired. However, the inception of the time independent Schrödinger equation opened the door for physicist Douglas Hartree to approach the problem with a fresh methodology.

Hartree began his process by formulating a guess wave function for a spatial orbital, $\Phi$, comprised of a number, $n$, of $s_i$ functions of the radial distance, $r$, multiplied by a spherical harmonic as seen below in equation 1.5:

$$\Phi_0 = s_1(r_1, \theta_1, \phi_1)s_2(r_2, \theta_2, \phi_2)...s_n(r_n, \theta_n, \phi_n)$$  

(1.5)

Next, the Hartree method makes a critical assumption that streamlines the calculation of the electron potential drastically. Rather than treating all of the electrons in the system simultaneously, the Hartree method considers all of the potentials imposed on the $i$th electron individually, sums them, and corrects them in order to calculate the potential function for electron $i$, $V_i(r_i, \theta_i, \phi_i)$. To do so, the point charges from the other electrons, $Q_j$ are considered
as continuous charge distribution fields with charge densities $\rho_j$. For example, below is the process for creating the potential function for electron one.

First, to find the potential between electron one and electron two, $V_{12}$, the charge of electron two, $Q_2$, is instituted as a continuous field with a charge density of $\rho_2$. Equation 1.6 below is used to sum the charge densities for all infinitesimal volume elements $dv$ in the radial space $r_{12}$.

$$V_{12} = \frac{Q_1}{4\pi\epsilon_0} \int \frac{\rho_2}{r_{12}^2} \, dv_2$$  \hspace{1cm} (1.6)

As $Q_1 = Q_2 = -e$, and $\rho_2 = -e|s_2|^2$ where $|s_2|$ is the probability density of electron 2, Equation 1.6 can be simplified to the form of Equation 1.7 below.

$$V_{12} = \frac{e^2}{4\pi\epsilon_0} \int \frac{|s_2|^2}{r_{12}^2} \, dv_2$$  \hspace{1cm} (1.7)

This process is then repeated for all other electrons in the system, and all $n$ potential terms are summed. Furthermore, this summation is then corrected by taking into account the interaction with electron one and the nucleus, resulting in $V_1(r_1, \theta_1, \phi_1)$. These two steps can be seen below in Equations 1.8 and 1.9 respectively.

$$V_{12} + V_{12} + \ldots V_{1n} = \sum_{j=2}^{n} \frac{e^2}{4\pi\epsilon_0} \int \frac{|s_2|^2}{r_{1j}^2} \, dv_2$$  \hspace{1cm} (1.8)

$$V_1(r_1, \theta_1, \phi_1) = \sum_{j=2}^{n} \frac{e^2}{4\pi\epsilon_0} \int \frac{|s_2|^2}{r_{1j}^2} \, dv_2 - \frac{Ze^2}{4\pi r_0}$$  \hspace{1cm} (1.9)

Next, the Hartree method makes another critical assumption, that the potential function can be sufficiently modeled solely as a function of $r$. Therefore, $V_1(r_1, \theta_1, \phi_1)$ is converted to $V_1(r_1)$. This potential as a function of $r_1$ is then used as the potential energy in a one-electron Schrödinger equation as seen below in Equation 1.10. At this point in the Hartree method, we have solved for an approximation of the orbital energy, $\epsilon_1$, but at this point it
is still highly inaccurate and unrefined.

\[ \left[ -\frac{\hbar^2}{2m_e} \nabla^2 + V_1(r_1) \right] t_1(1) = \epsilon_1 t_1(1) \quad (1.10) \]

Solving for \( t(1) \) in Equation 1.10 provides an improved orbital of electron one. This process is repeated for all other electrons in the system until there are improved orbitals for all \( n \) electrons. Then, using the improved orbitals obtained in the first iteration, the process is repeated again for all electrons, thus obtaining even more optimized orbitals. This process is repeated continuously until there is next to no change between iterations or, in other words, until a self consistency is obtained.

In order to find the total energy of the system, it is tempting to sum all the orbital energies, but this process would actually count all repulsions between electron pairs twice thus increasing the expected energy. For this reason, the Coulombic integral notation, \( J \) is introduced to account for this double-counting of repulsion integrals as seen below in Equation 1.11.

\[ E = \sum_{i}^{n} \epsilon_i - \sum_{j>i}^{n} J_{ij} \quad (1.11) \]

Despite the intense rigor that Hartree put into his methodology, there was a critical oversight in his method. In 1930, Hartree’s peers Slater and Fock recognized that, although the Hartree method partially accounted for the Pauli exclusion principle by not allowing more than one electron in the trial spatial orbitals, it did not fully account for spin or the antisymmetric nature of electron wave functions.

In order to solve this error, it was recognized that Slater determinants could be utilized to represent the trial wave functions as spin orbitals rather than the trial spatial orbitals like those in Equation 1.5. Aside from this correction, the SCF method remains largely untouched with the Schrödinger equation keeping the same form as Equation 1.10 from earlier. However, in this more-refined Hartree-Fock method, Equation 1.10 can be expressed as Equation 1.12 below, with \( u_i \) representing the spin orbital for the \( i \)th electron, and \( \hat{F} \) representing the newly
introduced Fock operator which serves as the Hartree-Fock equivalent to the Hamiltonian.

\[ \hat{F} u_i = \epsilon_i u_i \]  \hspace{1cm} (1.12)

Like the Hartree method, the Hartree-Fock method continues to optimize orbital wave functions until self consistency is achieved. At this point, the energy of the system can be determined; however, another consideration must be made regarding the antisymmetric nature of electron wave functions. Where the Hartree method corrected solely for Coulombic interactions when summing the orbital energies, the Hartree-Fock approach considers the effect that spin has on exchange interactions and introduces exchange integrals, \( K_{ij} \), as well. This inclusion can be seen below in Equation 1.13.

\[ E = \sum_{i}^{n} \epsilon_i - \sum_{j>i}^{n} J_{ij} K_{ij} \]  \hspace{1cm} (1.13)

This initial form of the Hartree-Fock process was solved utilizing numerical methods, as was sufficient if not painstaking. However, by the 1950s, it was becoming readily apparent that the arduous process of completing the Hartree-Fock process by hand using numerical methods could be completed much faster with less opportunity for error if it was instead solved using computers. The primary issue is that the notation utilized with the traditional Hartree-Fock method did not lend itself well to computational methods, where matrices were the primary language of computation. In steps Roothaan, who proposed the representation of Hartree-Fock spin orbitals as the linear combination of atomic orbitals, \( \chi_i \), with expansion coefficients, \( b_i \), that would be solved for using the SCF method. This representation can be seen below in Equation 1.14 where \( f \) is a trial orbital under this new formulation.

\[ f = \sum_{i} b_i \chi_i \]  \hspace{1cm} (1.14)

This substitution is known as the Roothaan expansion procedure and allows for the us-
age of matrix algebra to solve the Hartree-Fock process. With this reimagining of orbital representation, Roothaan introduced his eponymous equations to the Hartree-Fock process. Although the intricacies of their behavior are outside of the scope of this introduction, the Roothaan equations can be written succinctly as one equation, the single matrix equation as seen below in Equation 1.15.

\[ FC = SC\epsilon \]  

\[ (1.15) \]

\( F \) in Equation 1.15 is the Fock matrix, \( S \) is the overlap matrix of the atomic orbital basis functions, \( C \) is the expansion coefficient matrix, and, of course, \( \epsilon \) is the orbital energy.

By using the single matrix equation in place of the Hartree-Fock equation from earlier, Equation 1.12, the Hartree Fock SCF method that Roothaan helped create in the 1950s is largely the same as the method we know and utilize today. Although it is not perfect, this method has opened doors to understand quantum systems on a level of efficiency that would have likely surprised Schrödinger when he proposed his equations decades earlier. Not only has the Hartree-Fock method utilizing the Roothaan equations shown itself to be incredibly efficient and effective at generating an upper bound approximation to the energy of quantum systems, but it has also been steadily improved by introducing what are known as post-Hartree-Fock corrections.

### 1.2.2 Coupled Cluster Theory

*Note: This section was written referencing Daniel Crawford’s chapter An Introduction to Coupled Cluster Theory for Computational Chemists which is featured in Reviews in Computational Chemistry [7].*

Despite the revolutionary nature of the Hartree-Fock method and its ability to produce good upper bound approximations of energies, it still has its shortcomings stemming from its assumptions and simplifications. Due to these assumptions, the Hartree-Fock method is inherently limited as it averages out electron correlation energies rather than computing
them exactly. The difference in energy between the Hartree-Fock Energy, $E_0$, and the true non-relativistic energy of the system, $\mathcal{E}_0$, is known as the correlation energy and can be seen below in Equation 1.16.

$$E_{corr} = \mathcal{E}_0 - E_0$$ (1.16)

There are multiple ways to approach electron correlation, with two famous and prominent methods being configuration interaction (CI) and Moller-Plesset (MP) perturbation theory. Despite these methods’ ingenuity and practicality, they are not directly relevant to the following work. For that reason and the sake of brevity, only the most relevant post Hartree-Fock correction will be considered: coupled cluster theory. To showcase the methodology of coupled cluster (CC) theory, a four electron system will be utilized throughout the remainder of this explanation.

The CC method starts where the Hartree-Fock method finishes, by creating a wavefunction comprised of SCF optimized molecular orbitals. In the case of the four electron system, this can be represented as a four-by-four Slater determinant with each column representing a different HF SCF optimized atomic orbital, with $\phi$ representing the one electron functions for each SCF optimized atomic orbital. Due to the inherent clunkiness in this representation, representing the wavefunction using the Dirac-notation ket shorthand is optimal, in which only the diagonal terms of the Slater determinant are considered and the normalization constant is implied as seen below in Equation 1.17.

$$\Phi_0 = |\phi_i(x_1)\phi_j(x_2)\phi_k(x_3)\phi_l(x_4)\rangle$$ (1.17)

Once the wavefunction notation is ironed out, CC can begin calculating electron correlation. First, the CC method considers the existence of “virtual” or unoccupied orbitals which arise as a consequence of the SCF process. An electron can be excited from a familiar occupied orbital, for example $u_i$, to a virtual orbital, $u_a$. The CC method then considers the behavior of two correlated electrons as they are excited from their occupied orbitals to virtual orbitals.
by use of the cluster function, \( f \) as seen below in Equation 1.18:

\[
f_{ij}(x_m, x_n) = \sum_{a>b} t_{ij}^{ab} \phi_a(x_m) \phi_b(x_n)
\]  

(1.18)

The utility of the cluster function, \( f \), is that it accounts for all unique correlations of electrons, represented by arbitrary electrons \( x_m \) and \( x_n \), in the selected occupied orbitals, in this case \( u_i \) and \( u_j \), by inserting the cluster coefficient \( t_{ij}^{ab} \). The value of \( t_{ij}^{ab} \) is solved for via the electronic Schrödinger equation. By inserting this cluster function into the trial function \( \Phi_0 \), a more accurate electron wavefunction can be produced that now accounts for correlation between any two electrons in orbitals \( u_i \) and \( u_j \). The resulting wavefunction can be seen below in Equation 1.19

\[
\Psi = |[\phi_i(x_1)\phi_j(x_2) + f_{ij}(x_1, x_2)]\phi_k(x_3)\phi_l(x_4)\rangle
\]  

(1.19)

The beauty of the cluster function is that it can be used to correlate the behavior of any two electrons in any two occupied orbitals. For example, if one wanted to correlate electrons in orbitals \( u_k \) and \( u_l \) rather than the previous example of orbitals \( u_i \) and \( u_j \), the semi-improved electron wavefunction would appear as Equation 1.20 below.

\[
\Psi = |\phi_i(x_1)\phi_j(x_2)[\phi_k(x_3)\phi_l(x_4) + f_{ij}(x_3, x_4)]\rangle
\]  

(1.20)

However, rather than only considering the electron configuration of electrons in two orbitals at a time, one can instead consider all possible pairwise combination of correlation interactions for a four electron system. The resulting electron wavefunction is seen below in Equation 1.21. The variation in the signs for terms is a result of the antisymmetric principle of electron orbitals.

\[
\Psi = |\phi_i\phi_j\phi_k\phi_l\rangle + |f_{ij}\phi_k\phi_l\rangle - |f_{ik}\phi_j\phi_l\rangle + |f_{il}\phi_j\phi_k\rangle + |\phi_i f_{jk} \phi_l\rangle
\]

(1.21)
Furthermore, cluster operators describing one and three orbital interactions, for example $f_i$ and $f_{jkl}$ respectively, can be introduced to increase accuracy even further. However, as the electronic Hamiltonian only considers pairwise interactions at most, three orbital interactions can be ignored which simplifies notation significantly. Therefore, a wavefunction that accounts for all one and two orbital correlations is sufficient for most cases, and can be written for a four electron system that accounts for single, double, triple, and quadruple excitations.

To define such a system using the notation introduced in Equation 1.21 would be extremely taxing and difficult to read. To make this easier to read, second quantization must be preformed on the system to the establish the “exponential Ansatz” form of the wave equation. This process begins by defining the creation and annihilation operators. These operators act as their names imply, where the creation operator, $a^\dagger$, acting on a vacuum state results in the creation of an electron in a new orbital as seen below in Equation 1.22.

$$a^\dagger_a |\rangle = |\phi_a\rangle$$

(1.22)

As expected, the annihilation operator, $a$, acts as the opposite of the creation operator and results in the removal of an orbital and electron as seen below in equation 1.23.

$$a_a |\phi_a\rangle = |\rangle$$

(1.23)

Using these second quantization operators, the single and double cluster operators can be defined easily. These operators serve to annihilate the occupied orbital that an electron occupies and create a new electron to take its place in a virtual orbital. For example, we can see a single-orbital cluster operator promote an electron from orbital $u_i$ to orbital $u_a$ in Equation 1.24, and we can see a double-cluster orbital operator that promotes electrons
from orbitals \( u_i \) and \( u_j \) to orbitals \( u_a \) and \( u_b \), respectively, in Equation 1.25.

\[
\hat{t}_i = \sum_a t^a_i a_a^\dagger a_i \quad (1.24)
\]

\[
\hat{t}_{ij} = \sum_{a>b} t_{ij}^{ab} a_a^\dagger a_b^\dagger a_i a_j \quad (1.25)
\]

By using these operators, elements of the pairwise expansion of the four electron system can be represented more succinctly as seen below in Equation 1.26.

\[
|f_{ij} f_k \phi_l \rangle = \hat{t}_{ij} \hat{t}_k |\phi_0 \rangle \quad (1.26)
\]

By making this simplification to all terms, the electron wavefunction can be written as a summation of all \( \hat{t}_i \) and \( \hat{t}_{ij} \) operators, with \( i \) and \( j \) representing arbitrary orbital labels. With this in mind, we can simplify the wavefunction even further by introducing the orbital cluster operators as seen below.

\[
\hat{T}_1 = \sum_i \hat{t}_i \quad (1.27)
\]

\[
\hat{T}_2 = \frac{1}{2} \sum_{ij} \hat{t}_{ij} \quad (1.28)
\]

Considering that the \( \hat{t}_i \) and \( \hat{t}_{ij} \) operators always contain an even number of the second quantization operators, they will always commute. Therefore, so will their sums, \( \hat{T}_1 \) and \( \hat{T}_2 \). Therefore, the electron wavefunction can be written as an exponential expansion of \( \hat{T}_1 \) and \( \hat{T}_2 \), thus allowing us to generate the aforementioned exponential ansatz as seen below with \( \Psi \) representing the electron wavefunction, and \( \Phi_0 \) representing the normalized ground-state Hartree-Fock wave function of the system.

\[
\Psi = e^{\hat{T}_1 + \hat{T}_2} \Phi_0 = e^{\hat{T}} \Phi_0 \quad (1.29)
\]

As alluded to earlier, \( \hat{T} \) does not have to be confined to contain single excitations and double
excitations, but can include triple, quadruple, and even up to \( n \)-touple excitations as well. In fact, the naming of the CC method that is being used is determined by the limitations put upon the \( \hat{T} \). For example: if the cluster operator accounts solely for single excitations the method is referred to as CCS, if \( \hat{T} \) accounts for singles and doubles the method is CCSD, and so on.

The goal of the CC method is to calculate the coefficients \( t_{ia}, t_{ij}, t_{ijk}, \text{ etc.} \) for all \( i, j, k, \ldots \) and all \( a, b, c, \ldots \) found within \( \hat{T} \). Once these coefficients are known, we have effectively solved for the exact nonrelativistic ground-state electron wave function, \( \Psi \), from Equation 1.29 as desired. In doing so, the total correlation energy introduced at the beginning of this section can be found. As expected, the computational demand for the CC method increases as more excitations are considered. For this reason, CCSDT is too computationally expensive to be feasible despite its higher accuracy in accounting for electron correlation. To reconcile the desirable accuracy of the CCSDT method with the computational efficiency of the CCSD method the CCSD(T), read as “coupled cluster singles, doubles and perturbative triples”, method was created. The CCSD(T) method manages to bridge the gap between the CCSD and CCSDT methods by first running a traditional CCSD calculation to find \( \Psi \) and then running a single, disconnected triples calculation afterwards as a perturbative extension to the CCSD result. The resulting method is extremely useful for accounting for correlation accurately and computationally cheaply in small to medium systems, and has even become known as the “Gold-Standard” method of computational chemistry [8].

1.3 The Application of Computational Chemistry in Astrochemistry

Hartree-Fock, coupled cluster, and numerous other computational methodologies have found a home in chemistry serving purposes ranging from determining reaction mechanisms to optimizing molecular geometries. In this way, computational chemistry has a solid foun-
dation in providing reference data for experimentalists, but computational chemistry serves as more than just reference: it can also investigate systems that are often off-limits to the laboratory.

One such environment is the interstellar medium (ISM). The cold, seemingly empty, expanse between stars may not be the first place that one would expect chemistry to happen, but it is now known to be teeming with activity. Furthermore, the chemistry that takes place in the ISM is frequently unlike any known on earth, leading to the formation of strange molecules that seem to break traditional chemistry logic. These molecules have long enough lifetimes to be detected by spectroscopic means, however, as unstable tautomers are able to exist in the ISM so long as they are not imparted enough energy to transition to more stable species [9].

Furthermore, computational astrochemistry is not confined to any particular timeframe, meaning that quantum chemists can model molecules in environments ranging from the most primordial to the modern universe. Through the lens of computational astrochemistry, the earliest chemistry to happen in the universe can be investigated in order gain a sense for the trajectory that lead the formation of reality as it is today. Similarly, one can explore the chemistry of complex organic molecules that are now known to be ubiquitous throughout the modern ISM in order to gain a deeper understanding to how amino acids and other building blocks of life form deep in space for instance. In tackling such fundamental questions about the nature of the universe itself, much can be learned in the expansion of the planetary sciences as well as the search for a non-terrestrial origin for life.

The work presented throughout the rest of this thesis is a series of investigations into different timeframes of the universe: 1) a study on novel cooling mechanisms of the earliest stars to ever form following the calamity of the big bang; 2) a look into the solvation of a ubiquitous molecule in noble gas atoms; and 3) an investigation of the anharmonic vibrational frequencies of a molecule that has promise to be a fundamental building block of amino acids in the ISM.
Chapter 2

Investigation of Novel Cooling Mechanisms for Pop III Stars

2.1 Introduction

The universe observed today is almost unrecognizable to that which the first stars, known as population III (Pop III), inhabited. The metal (elements heavier than Helium) enrichment of the universe, which is attributed to nuclear fusion reactions in the interiors of stars and supernovae [10–13], was yet to occur. Therefore, these fledgling stars were comprised solely of hydrogen, helium, and trace amounts of lithium. This difference in environment does not only manifest in the composition of Pop III stars but also leads to them having very unique physical properties when compared to modern, metal-rich stars.

Theory is yet to agree on whether the first cosmological objects in the universe to form were globular clusters, supermassive black holes, or stars [14, 15]. Furthermore, Pop III stars may have formed as small stars with masses as low as 0.5 solar masses ($M_\odot$) or as large stars with masses in the tens of solar masses [16, 17]. Despite this uncertainty, the general consensus in the field is that most primordial metal-free stars most likely grew to be very large in comparison to modern metal-rich standards [18]. This conclusion is supported by
a series of thermodynamic simulations outside of the scope of this discussion, as well as the simple fact that all remote, metal-scarce stars found in the inter-galactic medium today are of very high masses and volumes when compared to their metal-rich counterparts [19].

The mysteries of Pop III stars do not end at their size, but also encompass their primary mechanism for cooling. The cooling mechanisms of Population I and II stars, those more richly comprised of metals than Pop III stars, are well understood and fall generally under two categories: metal-line cooling, and dust-induced fragmentation. Metal-line cooling occurs when metal atoms in the star are excited by collisions and then radiate off this gained energy. This process is especially productive in stars of low density, as high density systems can lead to excess collisions that interfere with the metal ions before they are allowed to radiatively relax back to the ground state [20]. Dust-induced fragmentation occurs when the dust surrounding the star in a cloud-like formation absorbs and re-radiates the energy produced by the star, dampening the total energy of the system [20]. Note that following the astronomer notation, dust is primarily comprised of silicon-based materials.

Although these cooling methods are nice and tidy interpretations for the cooling of Pop I and II stars, they do not cleanly fit to observations or simulations of Pop III stars. The cooling of Pop III stars could be flippantly attributed to the trace amounts of lithium doing the majority of the work for cooling, but recent work has shown that traditional metal-line cooling cannot account for the complete energy dissipation for Pop III stars [16]. The same work does show, however, that the dust-fragmentation cooling mechanism supports the cooling behavior seen in Pop III stars, and this conclusion is also supported by numerical calculations [21]. Despite the promise of the dust-fragmentation method, it has shortcomings as well. Pop III stars have been shown to be incredibly inefficient in producing dust, thus making dust-fragmentation cooling less probable [22]. Furthermore, dust-fragmentation cooling would be even less likely in first generation Pop III stars containing almost exclusively hydrogen and helium, with negligible amounts of lithium.

Considering all these uncertainties, the information surrounding most aspects of Pop III
stars, especially their cooling mechanism, are murky and lacking agreement. Also, traditional cooling methods, although possibly present to varying degrees, are likely not sufficient to fully explain the means to which Pop III stars can sustain such large masses and volumes while maintaining reasonable temperatures. For this reason, a novel mechanism for the cooling of Pop III stars would greatly increase the understanding of how the first stars in the universe formed, grew, died, and formed the universe that we know today.

One possible mechanism has the molecules helium hydride (HeH) and triatomic hydrogen (H\textsubscript{3}), shown in Figure 2.1, dissipate energy through cascades of transitions in highly-excited states. This mechanism shares clear similarities to that of the metal-line cooling mechanism. However, rather than taking advantage of atomic orbital transitions, this mechanism relies upon the transition of the third electron between various excited molecular orbital \textit{Rydberg states}. These Rydberg states are diffuse, unoccupied molecular orbitals that approximate the behavior of hydrogen orbitals.

HeH\textsuperscript{+} and H\textsubscript{3}\textsuperscript{+} are known to be present in the ISM [23, 24], and hydrogen and helium are the nearly exclusive components of first generation Pop III stars. The only possible limitations upon the feasibility of this novel mechanism are the electronic transitions that HeH and H\textsubscript{3} undergo when excited.

Figure 2.1: From left to right: Optimized structures of HeH and H\textsubscript{3}.

\section{2.2 Computational Details}

Geometry optimizations and reference wavefunction calculations for HeH\textsuperscript{+} and H\textsubscript{3}\textsuperscript{+} are completed at the CCSD(T) level of theory utilizing the t-aug-cc-pVTZ basis set within the
quantum chemistry calculation suite Molpro [25]. This is done so that the state-to-state transitions can be considered as the movement of the third, diffuse electron moving around the \(\text{HeH}^+\) and \(\text{H}_3^+\) species.

To investigate the Rydberg molecular orbitals of these two molecules, equation-of-motion coupled clusters singles and doubles (EOM-CCSD) [26] is utilized to find the energies of all the excited state molecular orbitals simultaneously. Then, the iterative, approximate triples EOM-CC3 method [27] produces the energies of all the excited state molecular orbitals individually, as well as a slightly higher level of theory. The differences in these values are then taken, to determine the energies of state-to-state transitions. These excited state computations are all completed within the quantum chemistry suite Psi4 [28] utilizing the t-aug-cc-pVTZ basis set, which has been shown to be sufficient for excited states [29].

In doing so, both \(\text{HeH}\) and \(\text{H}_3\) are specified to contain nine \(2\text{A}_1\) states, six \(2\text{A}_2\) states, nine \(2\text{B}_1\) states, and nine \(2\text{B}_2\) states. Also, the Abelian \(C_{2v}\) irreducible representation is used for \(\text{HeH}\) rather than its true irreducible representation of \(C_{\infty v}\).

AN attempt has been made to visually identify the Rydberg orbitals of the two molecules so that the state-to-state transitions could be more denitively defined, but these attempts were unsuccessful for reasons further discussed in the Discussion Section.
2.3 Results

2.3.1 Discussion of Tabulated Results

Table 2.1: Excited State Transition Data for HeH

<table>
<thead>
<tr>
<th>Transition Label</th>
<th>EOM-CCSD</th>
<th>EOM-CC3</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>E (eV)</td>
<td>E(cm$^{-1}$)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$2^2B_1 \leftarrow 2^2A_1$</td>
<td>0.750191</td>
<td>6050.69</td>
</tr>
<tr>
<td>$2^2B_2 \leftarrow 2^2A_1$</td>
<td>0.750191</td>
<td>6050.69</td>
</tr>
<tr>
<td>$6^2A_1 \leftarrow 3^2A_1$</td>
<td>0.746245</td>
<td>6018.87</td>
</tr>
<tr>
<td>$3^2A_1 \leftarrow 2^2A_1$</td>
<td>0.675577</td>
<td>5448.89</td>
</tr>
<tr>
<td>$6^2A_1 \leftarrow 2^2B_1$</td>
<td>0.671631</td>
<td>5417.07</td>
</tr>
<tr>
<td>$5^2A_1 \leftarrow 2^2B_1$</td>
<td>0.443165</td>
<td>3574.36</td>
</tr>
<tr>
<td>$2^2A_2 \leftarrow 3^2B_1$</td>
<td>0.421804</td>
<td>3402.07</td>
</tr>
<tr>
<td>$3^2B_2 \leftarrow 3^2A_1$</td>
<td>0.133962</td>
<td>1080.47</td>
</tr>
<tr>
<td>$4^2A_1 \leftarrow 3^2A_1$</td>
<td>0.122288</td>
<td>986.32</td>
</tr>
<tr>
<td>$1^2A_2 \leftarrow 2^2B_1$</td>
<td>0.086451</td>
<td>697.27</td>
</tr>
<tr>
<td>$2^2B_2 \leftarrow 3^2A_1$</td>
<td>0.074641</td>
<td>602.02</td>
</tr>
<tr>
<td>$2^2A_2 \leftarrow 3^2A_1$</td>
<td>0.070722</td>
<td>570.41</td>
</tr>
<tr>
<td>$3^2B_2 \leftarrow 2^2B_2$</td>
<td>0.059321</td>
<td>478.45</td>
</tr>
</tbody>
</table>

Table 2.2: Excited State Transition Data for H$_3$

<table>
<thead>
<tr>
<th>Transition Label</th>
<th>EOM-CCSD</th>
<th>EOM-CC3</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>E (eV)</td>
<td>E(cm$^{-1}$)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$8^2A_1 \leftarrow 3^2A_1$</td>
<td>0.813321</td>
<td>6559.87</td>
</tr>
<tr>
<td>$4^2A_2 \leftarrow 5^2B_2$</td>
<td>0.801294</td>
<td>6462.87</td>
</tr>
<tr>
<td>$4^2B_1 \leftarrow 2^2B_1$</td>
<td>0.800341</td>
<td>6455.19</td>
</tr>
<tr>
<td>$2^2A_2 \leftarrow 2^2B_1$</td>
<td>0.800015</td>
<td>6452.55</td>
</tr>
<tr>
<td>$8^2A_1 \leftarrow 1^2A_2$</td>
<td>0.724615</td>
<td>5845.05</td>
</tr>
<tr>
<td>$4^2B_1 \leftarrow 4^2A_1$</td>
<td>0.788722</td>
<td>6361.47</td>
</tr>
<tr>
<td>$4^2B_2 \leftarrow 4^2A_1$</td>
<td>0.519084</td>
<td>4186.70</td>
</tr>
<tr>
<td>$6^2A_1 \leftarrow 4^2A_1$</td>
<td>0.518839</td>
<td>4184.72</td>
</tr>
<tr>
<td>$4^2B_2 \leftarrow 3^2B_2$</td>
<td>0.518676</td>
<td>4183.40</td>
</tr>
<tr>
<td>$6^2A_1 \leftarrow 3^2B_2$</td>
<td>0.518431</td>
<td>4181.43</td>
</tr>
<tr>
<td>$5^2A_1 \leftarrow 2^2A_1$</td>
<td>0.513560</td>
<td>4142.14</td>
</tr>
<tr>
<td>$5^2A_1 \leftarrow 2^2B_2$</td>
<td>0.512799</td>
<td>4136.00</td>
</tr>
<tr>
<td>$7^2A_1 \leftarrow 6^2A_1$</td>
<td>0.158615</td>
<td>1279.32</td>
</tr>
</tbody>
</table>

The ground state term symbol was determined to be $1^2A_1$ for HeH and H$_3$. Tables 2.1 and 2.2 showcase selected Rydberg excited state transitions for the HeH and H$_3$ molecules,
respectively. These transitions are selected as they are some of the lowest energy transitions for which both the EOM-CCSD and EOM-CC3 calculations both converged, and are likely the most valuable for application in astronomical detection.

The EOM-CCSD and EOM-CC3 energies for these state-to-state transitions are presented alongside Einstein A coefficients and oscillator strengths, which are both calculated at the EOM-CCSD level. The Einstein A coefficient for a given transition is indicative of the likelihood of the transition taking place with larger values showcasing a higher likelihood for transition. Note that some transitions have an Einstein A coefficient of zero, which suggests a forbidden transition. The oscillator strengths, \( f \), reported for a transition are indicative of the intensity of the transition, with larger \( f \) values indicating more intense transitions. For this reason, the oscillator strength of a transition can be likened to the absorption coefficient \( \epsilon \) from Beer’s law, the cornerstone relation of spectroscopy. Of the transitions listed here, many have Einstein A coefficient greater than \( 1 \times 10^5 \), and Oscillator strengths greater than 0.01, thus indicating that these transitions are feasible and intense enough for detection.

As seen in rows one and two of Table 2.1, the transitions 2\(^2\)\(B_1 \leftarrow 2\(^2\)A_1\) and 2\(^2\)\(B_2 \leftarrow 2\(^2\)A_1\) are equivalent at 6554.32 cm\(^{-1}\). This is because the energies of 2\(^2\)\(B_1\) and 2\(^2\)\(B_2\) states with equivalent coefficients, in this case 2\(^2\)\(B_1\) and 2\(^2\)\(B_2\), have equivalent energies for HeH. This degeneracy is due to HeH being represented C\(_{2v}\) when it is actually C\(_{\infty v}\), and the 2\(^2\)\(B_1\) and 2\(^2\)\(B_2\) modes from the C\(_{2v}\) representation are equivalent within the \( \pi \) mode of C\(_{\infty v}\). However, H\(_3\) clearly lacks linearity, so its 2\(^2\)\(B_1\) and 2\(^2\)\(B_2\) states are not degenerate, as seen by transitions 4\(^2\)\(B_1 \leftarrow 4\(^2\)A_1\) and 4\(^2\)\(B_2 \leftarrow 4\(^2\)A_1\) in Table 2.2 having nonequivalent energies.

### 2.3.2 Further Description of State-to-State Transitions

This work initially sought to further define the state-to-state transitions showcased in Tables 2.1 and 2.2 by associating them with specific orbital-to-orbital transitions. To do so, the state-to-state transitions are first described utilizing generic orbital representations. Next, these generic orbitals are translated visually by plotting them in the software Avogadro.
and assigning hydrogen-atom-like quantum numbers $n$ and $l$ to each orbital.

For example, consider a hypothetical $3^2 B_2 \leftarrow 2^2 A_1$ transition in which the $2^2 A_1$ state is primarily comprised of what is assigned to be the $3a_1$ orbital and the $3^2 B_2$ state is primarily comprised of the $4b_2$ orbital. These two orbitals are then visualized in Avogadro [30] and are identified to be the $3s$ and $4d$ orbitals, respectively. This translation would be completed as:

$$3^2 B_2 \leftarrow 2^2 A_1$$

$$3a_1 \rightarrow 4b_2$$

$$3s \rightarrow 4d$$

However, the LCAO-MO procedure from SCF that is further employed within EOM-CCSD is insufficient to provide an accurate visual interpretation for the diffuse nature of Rydberg orbitals, as this process would often result in impossible transitions being described with positive energy changes. For example, one such misattributed transition is the $3^2 A_1 \leftarrow 2^2 A_1$ transition in HeH, which was described using this method to be a $3s \rightarrow 2s$ transition with an energy of 0.058045 H. This description is obviously incorrect and is far from being alone. In fact, the majority of transitions present in HeH and H$_3$ are described with impossible hydrogen-atom-like transitions when utilizing this method. For this reason, the LCAO-MO method utilized in SCF needs more refinement before such precise assignment can be accomplished while utilizing basis sets as diffuse as t-aug-cc-pVTZ as was done in this case.

### 2.4 Conclusions

Despite the inability to further describe the state-to-state transitions of HeH and H$_3$, the orbital transition energies showcased in Tables 2.1 and 2.2 are a promising starting point for providing a novel mechanism for the cooling of Pop III stars that resembles traditional metal-cooling mechanisms. Tables 2.1 and 2.2 showcase excited state-to-state transitions that occupy promising energy ranges and have large Einstein $A$ coefficients and large oscillator
strengths. This signifies that the excited state transitions of HeH and H$_3$ are not only likely, but they occur in energy ranges necessary for detection and have high enough intensity to be detected easily in follow-up laboratory work.

In order to investigate the feasibility of these orbital transitions astronomically, attention needs to be directed towards modern Pop III stars with extremely low metal concentrations, like SDSSJ1029151+172927 [16]. Although these modern Pop III stars are not as metal poor as the first Pop III stars that formed in the universe, they still have the possibility of showcasing these transitions in high concentrations. By investigating modern Pop III stars through the lens of this novel cooling mechanism, light may begin to seep into the inky mystery surrounding the first stars in the universe.
Chapter 3

The Solvation effects of Neon on HeH$^+$

Note: This Chapter was previously published as


3.1 Introduction

Chemists have long had conflicts about how noble gases fit into the puzzle of the study of matter. Noble gases are often labeled as nothing more than ornaments to adorn the rightmost edge of the periodic table and placeholders for the completion of the various orbital shells. They are lauded for their inertness, but their chemistry is far from dull [31–37]. In fact, helium, the lightest noble gas and along with hydrogen, was actually the first element to engage in chemistry in the early universe. After the age of electron-ion recombination, helium atoms bonded with protons that were yet to undergo recombination themselves [38, 39]. This association is fundamental to the eventual formation of the H$_3^+$ ion, a molecule that acts as a “hydrogen factory” for the subsequent gas-phase formation of small molecules that then seeded the chemical universe [40, 41]. Without this reaction between He and H$^+$, the steps
to form \( H^+ \) would not have been able to outpace the rapid expansion of the universe, and everything chemical we know would never have come to pass. This reasoning places \( \text{HeH}^+ \) at the root of all chemistry, and information collected from further studies of this molecule can transform the way that the early universe is understood.

Studies of this molecule have only been encouraged by the recent discovery of \( \text{HeH}^+ \) in the NGC 7027 nebula by Güsten et al. [23]. While this region for observation is not the edge of the universe where primordial \( \text{HeH}^+ \) would be detected (and has yet to be) [42], its presence provides a natural environment where this molecule’s chemistry can be directly observed [43]. This molecule can be examined here on Earth and actually has been since its first observation in 1925 [44]. However, the high reactivity of \( \text{HeH}^+ \) prevents traditional approaches to exploring its chemistry from being readily applied. A recent cryogenic ion storage ring experiment by Novotný et al. [45] investigates recombination rates for different electronic states of \( \text{HeH}^+ \) which provides new estimates for its likely higher primordial abundance. However, the large, expensive equipment used in experiments like this one is not easily accessible and hinders the study of this and related noble gas molecules.

An alternative approach to the study of transient molecules such as noble gas species is matrix isolation spectroscopy. Matrix isolation avoids setbacks attributed to the difficulties of studying both gas-phase and transient molecules via the entrapment of the species in question within a solid [46, 47]. The lightweight noble gases (He, Ne, and Ar), when sufficiently cooled, are often used for this purpose due to the spectroscopic clarity that they provide and their typical lack of reactivity with the species to be observed. Despite these precautions, \( \text{HeH}^+ \) is so reactive that the proton will, at best, likely be shared among the solvating host atoms, as well [48, 49]. This is due to the exceedingly low proton affinity of helium. Hence, at best, matrix isolation experiments will only produce proton-bound complexes of helium either with other helium atoms or the matrix gas, likely neon or argon. Proton-bound complexes of \( \text{HeH}^+ \) with other noble gases have been studied extensively recently [50–53] even solvated within other helium atoms [54, 55], but how \( \text{HeH}^+ \) behaves when solvated in more than one
non-helium noble gas atom has yet to be seen [52, 56]. Knowledge of such behavior would help to understand what the limits are to the stability of this first molecule in the universe.

The HeHHe\(^+\), HeHNe\(^+\), and NeHNe\(^+\) noble gas, proton-bound molecules have similar bond strengths, force/spring constants, and bonding behavior. For instance, the He–H and Ne–H force constants change by less than 5\% between HeHHe\(^+\) and HeHNe\(^+\) [52]. The inclusion of argon changes the bonding environments notably. The larger and more polarizable argon atom preferentially binds to the proton leaving the He or Ne atom weakly bound in a van der Waals-type complex for ArHHe\(^+\) and ArHNe\(^+\) [51, 52]. Clearly, inclusion of one neon atom with HeH\(^+\) does not do this [52], but can two or more? He and Ne are among the five most abundant elements in the universe [57] making associations of these atoms possible in various astronomical environments. Furthermore, such mixed species could play a role in other proton-bound complexes with molecules that also have “ideal gas” properties like CO or N\(_2\) [58–62].

Proton-bound complexes are characterized by their exceptionally bright infrared features for the motion of the central proton between the two exterior ligands. Most of the charge is moving with the proton while most often single-digits percentages of the mass are moving at the same time. This produces extreme intensities with the infrared, with the anharmonic frequency of the proton shuttling motion occurring at 1453.6 cm\(^{-1}\) for NeHeH\(^+\) [52]. The frequencies will shift based on the bonding character of the proton-bound complex [50–52, 58] and the presence of any potential distant ligands, but the large peak is indicative of a proton-bound complex making them relatively easy to detect in the infrared even if they are somewhat metastable.

As a result, the present study examines the structures, binding energies, and vibrational frequency shifts of the Ne\(_x\)H\(^+\) (x = 1–5), Ne\(_x\)HeH\(^+\) (x = 1–4), and Ne\(_4\)He\(_2\)H\(^+\) proton-bound families. While Ne matrix isolation of HeH\(^+\) is almost certainly impossible, this quantum chemical study will provide insights into how HeH\(^+\) would behave in a Ne matrix or with Ne tagging. Quantum chemistry is flexible enough and, with current methods, accurate
enough to provide insights into such systems where stand-alone experiments are exceedingly challenging. While NeH\(^+\) will likely not be observed in astrophysical regions due to an unfavorable potential energy surface (PES) [63, 64], the role that neon atoms could play in the degradation of HeH\(^+\) in regions like NGC 7027 where it is known to exist will be explored here. Furthermore, the manner in which neon atoms likely usurp the strongest bonding positions of the helium atoms in such proton-bound complexes will be provided. These insights may provide laboratory scientists with more data such that, at least, proton-bound complexes of HeHNe\(^+\) could be observed in matrix isolation potentially increasing the natural inventory of noble gas molecules.

3.2 Computational Details

Initial geometry optimizations of molecular formulas Ne\(_x\)H\(^+\) \((x = 1 - 5)\), Ne\(_x\)HeH\(^+\) \((x = 1 - 4)\), and Ne\(_x\)He\(_2\)H\(^+\) utilize restricted Hartree-Fock reference wave functions and coupled cluster singles, doubles, and perturbative triples (CCSD(T)) along with the aug-cc-pVTZ basis set within the MOLPRO 2015.1 quantum chemistry program [7, 25, 65–70]. Basis set superposition error (BSSE) was not considered as previous work with noble gas atoms has shown that BSSE is unlikely to be large enough to affect conclusions.[71] Following these, harmonic vibrational frequency calculations are carried out to determine the zero-point vibrational energy of the optimized molecule. The frequency calculations also confirm that the molecule in question is a minimum on its potential energy surface. Additionally, MP2/6-31+G(d) computations within Gaussian09 provide the intensities for the double-harmonic vibrational frequencies [72–74] shown to be in good agreement with higher-level, anharmonic intensities for NNHNN\(^+\) [60]. Sequential binding energies (BEs) for Ne\(_x\)H\(^+\) (neon) and Ne\(_x\)HeH\(^+\) (mixed neon and helium) are calculated using the following formulae:

\[
\text{BE(He)} = E(\text{Ne}_x\text{HeH}^+) - E(\text{Ne}_xH^+) - E(\text{He})
\] (3.1)
and

\[
BE(\text{Ne}) = E(\text{Ne}_x\text{HeH}^+) - E(\text{Ne}_{x-1}\text{HeH}^+) - E(\text{Ne}).
\] (3.2)

The distant helium binding energy is found by allowing the Ne$_{x-1}$HeH$^+$ structure to optimize freely. The binding energy of the close helium atom is determined by constraining the geometrical parameters to those of the minimum save for the He–H bond length. The same procedure is employed for the neon energies as well. In the previously-examined, proton-bound, noble gas complexes, the binding energy drops notably when $n \geq 7$ implying a filled first solvation/complexation shell after six atoms surround the proton [50, 54]. Hence, this study will not move beyond this limit of six atoms in addition to the proton. The BEs are reported as negative showing that the bound complexes are more favorable than the lone atoms. At each optimized geometry the harmonic vibrational frequencies are computed, and the resulting zero-point vibrational energies are added to the electronic energies for the reported, relative and binding energy values.

A relaxed PES scan is also performed for the lowest-energy constitutional isomers of Ne$_x$HeH$^+$ $(x = 1 - 4)$ and Ne$_4$He$_2$H$^+$. The HeH$^+$ bond length is fixed for each point in the scan, and the rest of the molecule is allowed to optimize. Each new computation changes the HeH$^+$ bond distance by a length of 0.05 Bohr. The ground-state electronic energies of these optimized geometries are collected and plotted as a function of the HeH$^+$ bond length in order to provide a meaningful interpretation of each PES.

### 3.3 Results & Discussion

#### 3.3.1 NeHeH$^+$

Table 3.1 provides the binding energy and structural parameters for NeHeH$^+$. Previously, this molecule was called HeHNe$^+$, but it will be referred to from here on as NeHeH$^+$ in order to remain consistent with the present Ne$_x$HeH$^+$ family nomenclature where $x = 1$ in
Table 3.1: Optimized properties of NeHeH+

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>close Neon BE (kcal/mol)</td>
<td>17.11</td>
</tr>
<tr>
<td>close Helium BE (kcal/mol)</td>
<td>10.23</td>
</tr>
<tr>
<td>$\omega_1$ (cm$^{-1}$)</td>
<td>1641.3</td>
</tr>
<tr>
<td>$\nu_1$ (cm$^{-1}$)</td>
<td>1453.6(^a)</td>
</tr>
<tr>
<td>scale</td>
<td>0.8856</td>
</tr>
<tr>
<td>$f_1$ (km/mol)</td>
<td>2617</td>
</tr>
<tr>
<td>H-Ne Bond Length (Å)</td>
<td>1.111</td>
</tr>
<tr>
<td>H-He Bond Length (Å)</td>
<td>0.953</td>
</tr>
</tbody>
</table>

\(^a\)Ref. [52].

this case. The Ne BE is within 3.0 kcal/mol and He BE within 0.5 kcal/mol of previous CCSD(T)/aug-cc-pV5Z benchmarks [52]. The destabilization effect that neon atoms have on the He binding energy is seen through the change in the binding energy of the close He as the number of neons in the Ne\(_x\)HeH\(^+\) species increases. This is the difference in the close He BE of the species in question and that of the \(x = 1\) species. This value is given in subsequent tables as $\Delta$ close He BE.

The bond lengths of NeHeH\(^+\) are within 0.02 Å of even higher-level theory where complete basis set extrapolations, core electron correlation, and scalar relativity (CcCR) are included [52]. The present 1641.3 cm$^{-1}$ harmonic frequency in Table 3.1 is around 70 cm$^{-1}$ higher than the CcCR value at 1569.8 cm$^{-1}$. The CcCR anharmonic value from the same, previous study is 1453.6 cm$^{-1}$, and CcCR has been shown to produce anharmonic vibrational frequencies regularly within 5 cm$^{-1}$ and often within 1 cm$^{-1}$ of gas phase experiment [51, 75-84]. While there is some discrepancy between the present CCSD(T)/aug-cc-pVTZ results and those from earlier work, on the whole, the present computations demonstrate solid performance. Such higher-level computations are not feasible for the higher \(x\) values in this Ne\(_x\)HeH\(^+\) family implying that CCSD(T)/aug-cc-pVTZ should be adequate for analysis of the larger complexes in this family. Likely, this value of 1463.6 cm$^{-1}$ is higher than the actual, physical value since previous CcCR values for He\(_2\)H\(^+\) and Ar\(_2\)H\(^+\) have been higher than their corresponding experimental frequencies [50-52, 55]. However, the shifts brought about by higher numbers of neon atoms should remain physically relevant.
Figure 3.1: The He–H dissociation PES for NeHeH\(^+\) with the minimum energy structure shown.

Figure 3.1 shows the PES scan for elongating the He–H bond length; clear Morse behavior is present. The larger, bright green atom is the Ne while the smaller, light blue one is He. The He is well-bound if only at 10.23 kcal/mol. Clearly from Table 3.1 the Ne is around 50\% more tightly bound, but the helium atom will not spontaneously leave the system as clearly shown in Figure 3.1. In either case, the bright proton shuttle frequency (\(\omega_1\)) is well below the He BE implying that it will be visible if this molecule could form.

The brightest vibrational frequency, noted as \(\omega_1\) or \(\nu_1\) depending upon whether reported as harmonic or anharmonic, respectively, will be the most important observable for this study. The full set of harmonic vibrational frequencies for this and the other molecules in this study are given in the supplemental information (SI). From Table 3.1, the \(f_1\) intensity is 2617 km/mol; the notable antisymmetric stretch in water at this same level of theory is \(\sim 70\) km/mol for comparison. This anti-symmetric stretching frequency has such a tremendous intensity resulting from nearly all of the charge but very little of the mass moving as the proton shuttles between the two heavier atoms. The shift in \(\omega_1\) between higher \(x\) values or isomers of a given \(x\) level will be scaled in order to provide a good estimate for how the vibrational frequency will change upon isomerization or addition of further Ne atoms. The
ratio of $\nu_1/\omega_1$ for NeHeH$^+$, as given in Table 3.1, is 0.8856, and the raw shift in the harmonic frequencies relative to the $x = 1$ species $[\Delta(\omega_1)]$ will be multiplied by this value creating $\Delta(\nu_1)$. The resulting shift $[\Delta(\nu_1)]$ will be added to the 1453.6 cm$^{-1}$ CcCR anharmonic frequency [52] in order to provide an estimate for the new complex’s anharmonic vibrational frequency. For Ne$_2$H$^+$, the CCSD(T)/aug-cc-pVTZ harmonic frequency is 1616.2 cm$^{-1}$, and the anharmonic CcCR value is 1436.6 cm$^{-1}$ [51]. The ratio for the NeHNe$^+$ moiety will then be 0.8889. Hence, this $\Delta(\nu_1)$ will be the applied to $\nu_1$ for NeHeH$^+$ or Ne$_2$H$^+$ depending upon the isomer in question. These shifts will clearly show the progression of neon coordination around the central proton and allow for any potential experimental corroboration.

### 3.3.2 Ne$_2$HeH$^+$

![Figure 3.2: The He−H dissociation PES for the two isomers of Ne$_2$HeH$^+$: Structure a. in blue and b. in red.](image)

In moving on to $x = 2$ for the Ne$_2$HeH$^+$ family, Ne$_2$HeH$^+$ in this case, there are two isomers. The one with the helium atom more closely bonded to the proton is listed as structure a. The one with the Ne−H−Ne moiety and the helium atom noncovalently bonded (with the helium BE of 1.20 kcal/mol) is structure b. in Figure 3.2. Structure b. is the lowest-
energy isomer by 4.48 kcal/mol from Table 3.2, and this is given visually in Figure 3.2. Once the He–H bond length surpasses 1.3 Å in structure a., the PES takes on the form of structure b. with the bond angles changing. There is a near minimum on the red, structure b. He–H PES nearly at the minimum for the blue structure b. in Figure 3.2, but the triligated proton-bound complex is ultimately not favored. The optimized parameters of the two structures are given in Table 3.2 showing clear noncovalent interactions in the long bond lengths of one Ne atom in structure a. and the He atom in structure b.

Table 3.2: Optimized properties of Ne₂HeH+

<table>
<thead>
<tr>
<th></th>
<th>Structure a.</th>
<th>Structure b.</th>
</tr>
</thead>
<tbody>
<tr>
<td>ΔE (kcal/mol)</td>
<td>4.48</td>
<td>0.00</td>
</tr>
<tr>
<td>distant Ne BE (kcal/mol)</td>
<td>1.35</td>
<td>5.84</td>
</tr>
<tr>
<td>distant He BE (kcal/mol)</td>
<td>–</td>
<td>0.57</td>
</tr>
<tr>
<td>close Ne BE (kcal/mol)</td>
<td>16.69</td>
<td>15.25</td>
</tr>
<tr>
<td>close He BE (kcal/mol)</td>
<td>9.84</td>
<td>–</td>
</tr>
<tr>
<td>Δ close He BE (kcal/mol)</td>
<td>-0.39</td>
<td>–</td>
</tr>
<tr>
<td>ω₁ (cm⁻¹)</td>
<td>1620.3</td>
<td>1607.8</td>
</tr>
<tr>
<td>Δ(ω₁) (cm⁻¹)</td>
<td>-21.0</td>
<td>-33.5</td>
</tr>
<tr>
<td>Δ(ν₁) (cm⁻¹)</td>
<td>-18.7</td>
<td>-29.7</td>
</tr>
<tr>
<td>f₁ (km/mol)</td>
<td>2199</td>
<td>2468</td>
</tr>
<tr>
<td>H-He Bond Length (Å)</td>
<td>0.900</td>
<td>2.200</td>
</tr>
<tr>
<td>H-Ne₁ Bond Length (Å)</td>
<td>1.144</td>
<td>1.140</td>
</tr>
<tr>
<td>H-Ne₂ Bond Length (Å)</td>
<td>2.347</td>
<td>1.141</td>
</tr>
</tbody>
</table>

Even in structure a. where the Ne–H–He moiety is maintained, the helium is somewhat less well bonded in the presence of the second neon atom. As seen by Δ close He BE in Table 3.2 the close helium BE drops relative to NeHeH⁺ by a mere 0.39 kcal/mol to 9.84 kcal/mol. However, the distant neon BE in structure b. is also much less than in NeHeH⁺ implying that the noble gas atoms are perturbing one another and competing with one another. Additionally, this behavior was also shown with ArHHe⁺ and ArHNe⁺ [51, 52], but, presently, this is not influenced by the stronger Ar–H bond. Hence, the weakening of the He–H and Ne–H bonds in these proton-bound complexes appears to arise more from more competition for interactions with the proton than from the type of atom producing the competition.
Regardless, each of these structures will have a unique $\nu_1$ allowing for characterization. The $\Delta(\omega_1)$ for structure a. relative to NeHeH$^+$ actually is negative at $-21.0^{-1}$ since the additional neon atom increases the harmonic frequency. This puts $\Delta(\nu_1)$ at $-18.7$ cm$^{-1}$ and the likely $\nu_1$ at $1434.9$ cm$^{-1}$. For structure b. inclusion of the helium atom expectedly lowers the harmonic frequency to $1607.8$ cm$^{-1}$ producing the $\Delta(\omega_1)$ of $-33.5$ cm$^{-1}$ and $\Delta(\nu_1)$ of $-29.7$ cm$^{-1}$. Consequently, the signature antisymmetric stretch of Ne$_2$HeH$^+$ will be $-29.7$ cm$^{-1}$ lower in frequency than the Ne$_2$H$^+$ at close to $1420.1$ cm$^{-1}$.

3.3.3 Ne$_3$HeH$^+$ & Ne$_4$HeH$^+$

![Figure 3.3: The He–H dissociation PES for the two isomers of Ne$_3$HeH$^+$: Structure a. in blue and c. in red.](image)

The Ne$_3$HeH$^+$ PES in Figure 3.3 is quite similar to that for Ne$_2$HeH$^+$ in Figure 3.2. The blue line leading to the minimum structure (structure c.) has its minimum with the Ne–H–Ne moiety. This blue line, again, has a near-minimum above the red line’s minimum (structure a.) where the proton-bound complex has a Ne–H–He moiety. The red line is allowed to continue in this plot to give a third stationary point on the PES in structure b. However, structure b. is actually not a true minimum as it gives an imaginary frequency in
an a” mode. The breaking of the symmetry allows the molecule to rearrange into structure c. Consequently, removing the imaginary portion of the red He–H PES produces a plot nearly identical to that from Ne$_2$HeH$^+$ in Figure 3.2. Hence, more global behavior for HeH$^+$ solvated in neon atoms in the Ne$_x$HeH$^+$ family appears to be surfacing even for $x = 3$.

Table 3.3: Optimized properties of Ne$_3$HeH$^+$

<table>
<thead>
<tr>
<th></th>
<th>Structure a.</th>
<th>Structure c.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta E$ (kcal/mol)</td>
<td>4.29</td>
<td>0.00</td>
</tr>
<tr>
<td>distant Ne BE (kcal/mol)</td>
<td>1.47</td>
<td>1.27</td>
</tr>
<tr>
<td>distant He BE (kcal/mol)</td>
<td>–</td>
<td>0.62</td>
</tr>
<tr>
<td>close Ne BE (kcal/mol)</td>
<td>16.29</td>
<td>14.95</td>
</tr>
<tr>
<td>close He BE (kcal/mol)</td>
<td>9.24</td>
<td>–</td>
</tr>
<tr>
<td>$\Delta$ close HE BE (kcal/mol)</td>
<td>-0.99</td>
<td>–</td>
</tr>
<tr>
<td>$\omega_1$ (cm$^{-1}$)</td>
<td>1588.4</td>
<td>1588.2</td>
</tr>
<tr>
<td>$\Delta(\omega_1)$ (cm$^{-1}$)</td>
<td>-52.9</td>
<td>-53.1</td>
</tr>
<tr>
<td>$\Delta(\nu_1)$ (cm$^{-1}$)</td>
<td>-46.8</td>
<td>-47.2</td>
</tr>
<tr>
<td>$f_1$ (km/mol)</td>
<td>2103</td>
<td>2371</td>
</tr>
<tr>
<td>H-He Bond Length (Å)</td>
<td>0.979</td>
<td>2.434</td>
</tr>
<tr>
<td>H-Ne$_{1/2}$ Bond Length (Å)</td>
<td>2.334</td>
<td>1.141</td>
</tr>
<tr>
<td>H-Ne$_3$ Bond Length (Å)</td>
<td>1.103</td>
<td>2.439</td>
</tr>
</tbody>
</table>

The addition of the neon atom will lower the $\nu_1$ frequency notably compared to the lone NeHeH$^+$ molecule; $\Delta(\nu_1)$ is -46.8 cm$^{-1}$. Expectedly, the bright frequency will red-shift as more neon atoms are added. This is borne out in structure c. where a neon atom is now part of the noncovalent shell along with the helium atom. However, this shift in Ne$_2$H$^+$ is not nearly as great compared to that from NeHeH$^+$. Furthermore, the addition of the neon atom further destabilizes the He–H bond, leading to a decrease in -0.99 kcal/mol for the close He BE from NeHeH.
Figure 3.4: The He–H dissociation PES for the two isomers of Ne₄HeH⁺: Structure a. in blue and b. in red.

Figure 3.4 highlights the same behavior for Ne₄HeH⁺ as is shown for Ne₂HeH⁺ and Ne₃HeH⁺. The additional neon atom is too far removed from the proton for there to be any notable, qualitative effect in the PES. This is further corroborated by the structural, BE, and vibrational frequency data in Table 3.4. The BEs and frequencies show a minimal decrease for Ne₄HeH⁺ relative to Ne₃HeH⁺ implying a notable level of convergence. This is further confirmed in Figure 3.5 which shows that as more neutrons are added to the NeₓHeH⁺ species the harmonic frequencies begin to converge. While Ne₇HeH⁺ will likely have a marked drop in Ne BE compared to the 𝑥 = 6 complex from previous work [50, 54], the Ne atoms are bound to this proton more strongly than argon (≈ 2.2 kcal/mol) and helium (≈ 1.0 kcal/mol) in proton-bound complexes and clusters containing only one type of noble gas atom.
Table 3.4: Optimized properties of Ne₄HeH⁺

<table>
<thead>
<tr>
<th></th>
<th>Structure a.</th>
<th>Structure b.</th>
</tr>
</thead>
<tbody>
<tr>
<td>ΔE (kcal/mol)</td>
<td>4.25</td>
<td>0.00</td>
</tr>
<tr>
<td>distant Ne BE (kcal/mol)</td>
<td>1.42</td>
<td>1.38</td>
</tr>
<tr>
<td>distant He BE (kcal/mol)</td>
<td>–</td>
<td>2.90</td>
</tr>
<tr>
<td>close Ne BE (kcal/mol)</td>
<td>16.12</td>
<td>14.92</td>
</tr>
<tr>
<td>close He BE (kcal/mol)</td>
<td>8.83</td>
<td>–</td>
</tr>
<tr>
<td>Δ close He BE (kcal/mol)</td>
<td>1.39</td>
<td>–</td>
</tr>
<tr>
<td>ω₁ (cm⁻¹)</td>
<td>1578.9</td>
<td>1581.2</td>
</tr>
<tr>
<td>Δ(ω₁) (cm⁻¹)</td>
<td>-62.4</td>
<td>-60.1</td>
</tr>
<tr>
<td>Δ(ν₁) (cm⁻¹)</td>
<td>-55.3</td>
<td>-53.4</td>
</tr>
<tr>
<td>f₁ (km/mol)</td>
<td>2019</td>
<td>2286</td>
</tr>
<tr>
<td>H-He Bond Length (Å)</td>
<td>0.953</td>
<td>2.328</td>
</tr>
<tr>
<td>H-Ne₁ Bond Length (Å)</td>
<td>1.117</td>
<td>1.142</td>
</tr>
<tr>
<td>H-Ne₂ Bond Length (Å)</td>
<td>2.331</td>
<td>1.141</td>
</tr>
<tr>
<td>H-Ne₃/₄ Bond Length (Å)</td>
<td>3.384</td>
<td>2.478</td>
</tr>
</tbody>
</table>

Figure 3.5: The change in harmonic frequencies as the number of neons in the NeₓHeH⁺ species increases.

The harmonic vibrational frequency for Ne₄HeH⁺ structure a. in Table 3.4 appears to settle around 1578.9 cm⁻¹ putting the estimated anharmonic value at 1398.3 cm⁻¹. For the structure with the Ne–H–Ne moiety (structure b.), the anharmonic frequency appears to converge to close to 1581.2 cm⁻¹ harmonically and 1400.2 cm⁻¹ anharmonically. However,
the barrier to isomerization is less than 3.0 kcal/mol (1050 cm\(^{-1}\)) making observation of
the bright, antisymmetric \(\nu_1\) difficult for He–H–Ne bearing structure a. While Feshbach
resonances or other means of observing the vibrational frequency above the PES barrier may
be possible to observe this frequency, the fact that the He–H bond distance changes means
that helium atom will likely reposition itself into structure c. before the vibrational signature
of structure a. could be observed. Another possible phenomenon further limiting the lifetime
of these species is the tunneling of neon atoms from one potential surface to another but is
beyond the scope of the current work and will be left for future work.

3.3.4 \(\text{Ne}_4\text{He}_2\text{H}^+\)

![Figure 3.6: The He–H dissociation PES for the two isomers of \(\text{Ne}_4\text{He}_2\text{H}^+\): Structure a. in red and b. in blue.](image)

Introduction of a second helium atom into the \(\text{Ne}_4\text{HeH}^+\) structure was hoped to stabilize
the He–H bonds. Instead, the same behavior seen in the single helium clusters is present.
The short He–H bonds produce a minimum structure in structure a. from Figure 3.6, but
this is not the global minimum. The long He–H bonds with the helium atoms noncovalently
interacting with the proton are preferred in structure b. In either case, only one helium
atom bond length was varied in the scan, but the other mirrored it in the relaxed nature of this procedure even with symmetry reduced from $D_{2h}$ to $C_{2v}$. A third isomer is also possible with the helium atoms adjacent to one another. However, the distant complexes for structure b. and the perpendicular He isomer (structure c.) are degenerate for the precision of the utilized CCSD(T)/aug-cc-pVTZ level of theory. Furthermore, the perpendicular He isomer actually reports an imaginary frequency of less than 15 cm$^{-1}$ correlating with a bend that would put the helium atoms opposite one another creating structure b.

Table 3.5: Optimized properties of Ne$_4$He$_2$H$^+$

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta E$ (kcal/mol)</td>
<td>8.74</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>distant He BE (kcal/mol)</td>
<td>–</td>
<td>0.53</td>
<td>0.57</td>
</tr>
<tr>
<td>distant Ne BE (kcal/mol)</td>
<td>1.57</td>
<td>1.26</td>
<td>1.37</td>
</tr>
<tr>
<td>close He BE (kcal/mol)</td>
<td>13.69</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>close Ne BE (kcal/mol)</td>
<td>–</td>
<td>14.43</td>
<td>14.45</td>
</tr>
<tr>
<td>$\omega_1$ (km/mol)</td>
<td>1644.0</td>
<td>1581.5</td>
<td>1584.2</td>
</tr>
<tr>
<td>$f_1$ (km/mol)</td>
<td>1735</td>
<td>2234</td>
<td>2234</td>
</tr>
<tr>
<td>H-He Bond Length (Å)</td>
<td>0.947</td>
<td>2.350</td>
<td>2.357</td>
</tr>
<tr>
<td>H-Ne$_1$ Bond Length (Å)</td>
<td>2.278</td>
<td>1.142</td>
<td>1.142</td>
</tr>
<tr>
<td>H-Ne$_2$ Bond Length (Å)</td>
<td>2.278</td>
<td>2.477</td>
<td>2.479</td>
</tr>
</tbody>
</table>

The vibrational frequencies of structure b. in Table 3.5 are in line with those from Ne$_4$HeH$^+$ implying that the additional noble gas atom in the shell does not greatly perturb the system. The frequency for structure a. is notably different from the corresponding isomer in Ne$_4$HeH$^+$, but structure a. for Ne$_4$He$_2$H$^+$ has helium atoms opposite one another raising the vibrational frequency above that for Ne$_4$HeH$^+$ where a helium and neon are opposite one another about the proton. In structure b. where the neon atoms are opposite one another, $\omega_1$ is nearly identical to that for Ne$_4$HeH$^+$ further implying convergence of the first solvation shell.
3.4 Conclusions

HeH $^+$ cannot be stabilized in a shell of neon atoms. At best, it can produce the NeHeH$^+$ proton-bound complex, a molecule of its own interest, but not the first molecule in the universe, HeH$^+$. As more neon atoms are added to the complex, they assume the position of the two closest atoms to the proton creating a proton-bound complex with noncovalently interacting atoms around it. This includes any helium atoms present along with any additional neon atoms. The helium atom can exhibit relatively strongly bound to the central proton, but incident energies on the order of 2.5 kcal/mol will readily push the He–H bond to a point where it breaks replacing the helium with neon. The bright vibrational frequency found in proton-bound complexes begins to converge to 1580 cm$^{-1}$ harmonically and likely close to 1398 cm$^{-1}$ anharmonically as more neon atoms are added putting the experimental solvated frequency closer to 1350 cm$^{-1}$ due to considerations from CcCR and experimental frequencies for this motion in He$_2$He$^+$ [52, 55]. Hence, the presence of the helium atom is almost completely unfelt. Again, mixed NeHeH$^+$ may yet be observed opening the door for potential observation of OCHHe$^+$ and N$_2$HHe$^+$, but once a third ligand is added, the helium will be retained in the system as a distant ligand at best. Most likely it will simply evaporate from the complex.

This behavior further showcases that HeH$^+$ is a rare molecule. Even solvated in the next-least reactive atom, neon, HeH$^+$ will dissociate the system with the slightest provocation. HeH$^+$ can only be studied in the gas phase (or theoretically), and even its proton-bound dimer, He$_2$H$^+$, will easily break apart upon exposure to any other atoms, again, even neon. Consequently, the early universe and the shells of supernova remnants are almost certainly the only places where HeH$^+$ and any of its derivatives are likely to be found in nature.
Chapter 4

Anharmonic Vibrational Frequencies for the Detection of Ethynol in Space

Note: This Chapter was previously published as


4.1 Introduction

Structural isomers of complex organic molecules (COMs) are telling of the chemical and physical traits of interstellar environments and are useful testers of molecular cloud chemical models [85]. Therefore, the ability to accurately recognize the abundance of COM building blocks in interstellar environments is critical for the prediction of interstellar chemical pathways. Two promising reactants to form larger COMs are ethynol [86], also known as hydroxyactylene, and ketene, both members of the C$_2$H$_2$O isomer family. Ketene has a carbon=carbon double bond as well as a carbon=oxygen double bond. Ethynol has a carbon—carbon triple bond and an accompanying hydroxyl group. Previous ab initio computations have shown ethynol to lie 150.9 kJ/mol above the more stable ketene [87].
third \( \text{C}_2\text{H}_2\text{O} \) isomer, oxirene, is suspected to be a possible intermediate structure facilitating some isomerization between the more stable structures of ethynol and ketene [85]. Visual representation of these three molecules can be seen in Fig. 4.1. Of these three molecules, only ketene and its ketenyl radical have been observed in the interstellar medium (ISM) with the former first detected toward Sgr B2 [88]. However, the downhill pathway for the formation of ethynol from the same starting materials as ketene implies that it should have non-negligible abundance.

Figure 4.1: From left to right: ethynol, oxirene, and ketene

Previous work by Turner et al. (2020) explored ice phase experiments and quantum chemical reaction schemes at the coupled cluster singles, doubles, and perturbative triples [CCSD(T)] level beginning with dicarbon monoxide in the presence of free hydrogen and found barrier free pathways producing both ketene and ethynol. The ketenyl radical is an intermediate along this pathway. A full visualization of this reaction pathway can be seen in Figure 5 of [85]. The addition of hydrogen to the carbon of the ketenyl radical is strongly preferred and leads to the formation of ketene. The addition of hydrogen to the oxygen of the radical is feasible, however extremely disfavored, and leads to the formation of ethynol. This barrier free pathway was then tested experimentally and resulted in the first identification of ethynol in interstellar ice analogs [85]. Preceding work before this has also experimentally shown the reversible conversion of ketene into ethynol via photolysis in an argon matrix [89]. However, energy must be put into the system for this conversion to take place. Regardless, considering these reaction pathways and that ketene and the ketenyl radical have been previously observed in the ISM, ethynol is likely present in detectable quantities as even tautomers that are less stable than HCCOH compared to their global
minima are known to persist in the ISM if their barriers to rearrangement are high enough [9]. Before it can be detected, however, the anharmonic vibrational frequencies and/or rotational spectroscopic data for ethynol must be produced in order to provide the necessary reference data for comparison to any subsequent experiments or observations. This is the primary objective of the current work.

The current approach to obtaining high level, theoretical vibrational frequencies is via a fourth order Taylor series expansion to the internuclear potential with composite CCSD(T) energies making considerations for complete basis set extrapolation, core electron correlation, and scalar relativity.[75–77]. The rigor of this method makes it very attractive, with it producing vibrational frequencies within 1.0 cm$^{-1}$ of gas phase experimental values in many cases. [51, 75–84]. However, its high computational cost makes this method less viable as molecules become larger and more complex. For this reason, a less complete but less computationally demanding method utilizing explicit correlation with a triple–zeta basis set is used as a point of comparison [90–93], as it typically provides vibrational frequencies to within 7.0 cm$^{-1}$ of gas phase experimental values. The rotational constants, on the other hand, still require the more expensive composite approach in order to provide high-accuracy values [91–93].

Both of the aforementioned methods are utilized within the current work to produce accurate vibrational frequencies for ethynol. By using the high level anharmonic vibrational frequencies proposed in the current work, the search for interstellar ethynol may continue with more clarity in the regions in which ketene has been previously detected such as Sgr B2 [88]; Orion KL [94]; and TMC-1 [95].

### 4.2 Computational Details

Optimized geometries, dipole moments, and harmonic frequencies are computed using the MOLPRO 2015.1 software package [25] with canonical CCSD(T) and CCSD(T) within
the F12 explicitly correlated construction (CCSD(T)-F12b) [7, 66, 67, 96]. As mentioned above, anharmonic frequencies are produced by a fourth-order Taylor series expansion of the internuclear portion of the Watson A-Reduced Hamiltonian referred to as a quartic force field (QFF). Two QFFs are utilized. The CCSD(T)-F12/cc-pVTZ-F12 version [96–99] will be referred to as the F12-TZ QFF. The second QFF is the composite approach mentioned previously. This methodology is defined as the CcCR QFF since it includes complete basis set extrapolation (“C”) using a three-point formula from aug-cc-pVTZ, aug-cc-pVQZ, and aug-cc-pV5Z [100]; core electron correlation (“cC”) using the Martin-Taylor (MT) core correlating basis set [101]; and scalar relativity (“R”) using Douglas-Kroll scalar relativity [102, 103]. Recent results show that the F12-TZ QFF produces comparable anharmonic data to the CcCR QFF but with significantly lower computational costs [92].

For both QFFs, an optimized reference geometry is required. For the F12-TZ QFF, this optimization is carried out at the CCSD(T)-F12/cc-pVTZ level. For the CcCR QFF, structural optimizations are determined at the CCSD(T) level using the aug-cc-pV5Z basis set [aug-cc-pvzx, 68, 104] as well as the MT core correlating basis set [101]. The difference in the bond lengths and angles between the CCSD(T)/MT with and without the core correction is then added to the respective variables within the optimized CCSD(T)/aug-cc-PV5Z geometry in order to correct for core correlation.

From the previously discussed reference geometries, displacements of 0.005 Å for bond lengths, 0.005 radians for bond angles, and 0.005 unitless displacements of LINX/LINY coordinates [78], which are necessary for the near-prolate structure of ethynol, are used to generate a QFF of 3161 points using the following coordinate system:
\begin{align}
S_1 &= H - C \quad (4.1) \\
S_2 &= C - C \quad (4.2) \\
S_3 &= C - O \quad (4.3) \\
S_4 &= O - H \quad (4.4) \\
S_5 &= \text{LINX}(H - C - C) \quad (4.5) \\
S_6 &= \angle(C - C - O) \quad (4.6) \\
S_7 &= \angle(C - O - H) \quad (4.7) \\
S_8 &= \text{LINY}(H - C - C - O) \quad (4.8) \\
S_9 &= \tau(C - C - O - H) \quad (4.9)
\end{align}

From this coordinate system, single point energies are computed for the composite method using the definition described above. The F12-TZ method only relies on CCSD(T)-
F12/cc-pVTZ-F12. Once the single point energies are computed for both of the QFFs, they are fit using a least squares procedure with a sum of squared residuals less than $3 \times 10^{-16}$ a.u.$^2$ for both CcCR and F12-TZ. Next, the force constants’ simple internal coordinates are converted into Cartesian coordinates using the INTDER program [105]. These Cartesian coordinates are then fed into the SPECTRO program [106] in which rotational, rovibrational, and vibrational perturbation theory at second order (VPT2) [107–109] are used to obtain the fundamental vibrational frequencies and spectroscopic constants.

Combinations of $\nu_5$ and $\nu_3$, $\nu_6$ and $\nu_5$, and $\nu_7$ and $\nu_5$ are considered as type 1 Fermi resonances. Combinations of $\nu_5$, $\nu_3$, and $\nu_2$ are treated as type 2 Fermi resonances as well as combinations of $\nu_5$, $\nu_4$, and $\nu_3$. Finally, Coriolis resonances are included, with the combinations of $\nu_7$ and $\nu_6$, $\nu_9$ and $\nu_7$, and $\nu_9$ and $\nu_8$ all resulting in A-type Coriolis resonances.
### 4.3 Results and Discussion

Table 4.1: Structural Data and Rotational Constants for HCCOH

<table>
<thead>
<tr>
<th></th>
<th>Previous MP2/6–31+G∗∗</th>
<th>F12-TZ</th>
<th>CcCR</th>
</tr>
</thead>
<tbody>
<tr>
<td>r(H–C) Å</td>
<td>1.067</td>
<td>1.04922</td>
<td>1.05946</td>
</tr>
<tr>
<td>r(C–C) Å</td>
<td>1.213</td>
<td>1.20637</td>
<td>1.20103</td>
</tr>
<tr>
<td>r(C–O) Å</td>
<td>1.327</td>
<td>1.31690</td>
<td>1.31213</td>
</tr>
<tr>
<td>r(O–H) Å</td>
<td>0.966</td>
<td>0.97184</td>
<td>0.96082</td>
</tr>
<tr>
<td>θ(H–C–C)</td>
<td>180.1</td>
<td>180.000</td>
<td>180.000</td>
</tr>
<tr>
<td>θ(C–C–O)</td>
<td>177.5</td>
<td>179.561</td>
<td>176.737</td>
</tr>
<tr>
<td>θ(C–O–H)</td>
<td>108.2</td>
<td>109.280</td>
<td>109.320</td>
</tr>
<tr>
<td>A_e cm⁻¹</td>
<td>23.55629</td>
<td>22.37505</td>
<td>22.48597</td>
</tr>
<tr>
<td>B_e cm⁻¹</td>
<td>0.32282</td>
<td>0.32360</td>
<td>0.32521</td>
</tr>
<tr>
<td>C_e cm⁻¹</td>
<td>0.31772</td>
<td>0.31898</td>
<td>0.32058</td>
</tr>
<tr>
<td>A_0 cm⁻¹</td>
<td>22.447957</td>
<td>22.56464</td>
<td></td>
</tr>
<tr>
<td>B_0 cm⁻¹</td>
<td>0.322853</td>
<td>0.32445</td>
<td></td>
</tr>
<tr>
<td>C_0 cm⁻¹</td>
<td>0.317992</td>
<td>0.31946</td>
<td></td>
</tr>
<tr>
<td>A_1 cm⁻¹</td>
<td>21.472817</td>
<td>21.57986</td>
<td></td>
</tr>
<tr>
<td>B_1 cm⁻¹</td>
<td>0.322732</td>
<td>0.32433</td>
<td></td>
</tr>
<tr>
<td>C_1 cm⁻¹</td>
<td>0.317600</td>
<td>0.31917</td>
<td></td>
</tr>
<tr>
<td>A_2 cm⁻¹</td>
<td>22.444530</td>
<td>22.56071</td>
<td></td>
</tr>
<tr>
<td>B_2 cm⁻¹</td>
<td>0.322004</td>
<td>0.32361</td>
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</tr>
<tr>
<td>C_2 cm⁻¹</td>
<td>0.317068</td>
<td>0.31864</td>
<td></td>
</tr>
<tr>
<td>A_3 cm⁻¹</td>
<td>22.420548</td>
<td>22.53609</td>
<td></td>
</tr>
<tr>
<td>B_3 cm⁻¹</td>
<td>0.320953</td>
<td>0.32256</td>
<td></td>
</tr>
<tr>
<td>C_3 cm⁻¹</td>
<td>0.316046</td>
<td>0.31763</td>
<td></td>
</tr>
<tr>
<td>A_4 cm⁻¹</td>
<td>23.735437</td>
<td>23.87603</td>
<td></td>
</tr>
<tr>
<td>B_4 cm⁻¹</td>
<td>0.323091</td>
<td>0.32469</td>
<td></td>
</tr>
<tr>
<td>C_4 cm⁻¹</td>
<td>0.317748</td>
<td>0.31932</td>
<td></td>
</tr>
<tr>
<td>A_5 cm⁻¹</td>
<td>22.407782</td>
<td>22.52530</td>
<td></td>
</tr>
<tr>
<td>B_5 cm⁻¹</td>
<td>0.321515</td>
<td>0.32311</td>
<td></td>
</tr>
<tr>
<td>C_5 cm⁻¹</td>
<td>0.316463</td>
<td>0.31803</td>
<td></td>
</tr>
<tr>
<td>A_6 cm⁻¹</td>
<td>23.363518</td>
<td>23.36010</td>
<td></td>
</tr>
<tr>
<td>B_6 cm⁻¹</td>
<td>0.323311</td>
<td>0.32492</td>
<td></td>
</tr>
<tr>
<td>C_6 cm⁻¹</td>
<td>0.317961</td>
<td>0.31954</td>
<td></td>
</tr>
<tr>
<td>A_7 cm⁻¹</td>
<td>22.381920</td>
<td>22.50984</td>
<td></td>
</tr>
<tr>
<td>B_7 cm⁻¹</td>
<td>0.323065</td>
<td>0.32467</td>
<td></td>
</tr>
<tr>
<td>C_7 cm⁻¹</td>
<td>0.318537</td>
<td>0.32011</td>
<td></td>
</tr>
<tr>
<td>A_8 cm⁻¹</td>
<td>21.323761</td>
<td>21.54286</td>
<td></td>
</tr>
<tr>
<td>B_8 cm⁻¹</td>
<td>0.323349</td>
<td>0.32492</td>
<td></td>
</tr>
<tr>
<td>C_8 cm⁻¹</td>
<td>0.318951</td>
<td>0.32049</td>
<td></td>
</tr>
<tr>
<td>A_9 cm⁻¹</td>
<td>22.627112</td>
<td>22.74742</td>
<td></td>
</tr>
<tr>
<td>B_9 cm⁻¹</td>
<td>0.324165</td>
<td>0.32574</td>
<td></td>
</tr>
<tr>
<td>C_9 cm⁻¹</td>
<td>0.318473</td>
<td>0.32002</td>
<td></td>
</tr>
</tbody>
</table>

*aVibrationally-excited rotational constants are provided in the same order as vibrational frequencies. Structural parameters provided at the MP2/6–31+G∗∗ level are equilibrium values, while those provided for F12-TZ and CcCR are zero-point corrected.

Ref. [9]
Table 4.2: Quartic and Sextic Spectroscopic Constants

<table>
<thead>
<tr>
<th></th>
<th>Previous MP2/6−31G**</th>
<th>F12-TZ</th>
<th>CcCR</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\Delta_J) kHz</td>
<td>3.3</td>
<td>3.2167</td>
<td>3.2373</td>
</tr>
<tr>
<td>(\Delta_K) MHz</td>
<td>250</td>
<td>253.08</td>
<td>259.35</td>
</tr>
<tr>
<td>(\Delta_{JK}) kHz</td>
<td>560</td>
<td>622.16</td>
<td>617.68</td>
</tr>
<tr>
<td>(\delta_J) Hz</td>
<td>41.641</td>
<td>42.022</td>
<td></td>
</tr>
<tr>
<td>(\delta_K) kHz</td>
<td>275.98</td>
<td>274.60</td>
<td></td>
</tr>
<tr>
<td>(\Phi_J) mHz</td>
<td>-314.76</td>
<td>-297.27</td>
<td></td>
</tr>
<tr>
<td>(\Phi_K) kHz</td>
<td>145.02</td>
<td>152.58</td>
<td></td>
</tr>
<tr>
<td>(\Phi_{JK}) Hz</td>
<td>3.4790</td>
<td>3.2803</td>
<td></td>
</tr>
<tr>
<td>(\phi_J) Hz</td>
<td>275.98</td>
<td>274.60</td>
<td></td>
</tr>
<tr>
<td>(\phi_K) kHz</td>
<td>68.713</td>
<td>66.530</td>
<td></td>
</tr>
<tr>
<td>(\mu_X) D</td>
<td>1.50</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(\mu_Z) D</td>
<td>-0.51</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(\mu) D</td>
<td>1.58</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\[9\].

Table 4.3: Description of Vibrational Modes

<table>
<thead>
<tr>
<th>(\nu_i)</th>
<th>Symmetry</th>
<th>Exp. [110]</th>
<th>Previous Harmonic [85]</th>
<th>Harmonic [110]</th>
<th>Fundamental</th>
<th>Harmonic [110]</th>
<th>Fundamental</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\nu_1)</td>
<td>a'</td>
<td>3501.3</td>
<td>3798.2</td>
<td>3819.7 (138)</td>
<td>3628.4</td>
<td>3828.1</td>
<td>3635.2</td>
</tr>
<tr>
<td>(\nu_2)</td>
<td>a'</td>
<td>3339.6</td>
<td>3474.0</td>
<td>3478.9 (93)</td>
<td>3347.8</td>
<td>3482.9</td>
<td>3354.7</td>
</tr>
<tr>
<td>(\nu_3)</td>
<td>a'</td>
<td>2198.3</td>
<td>2230.4</td>
<td>2243.3 (139)</td>
<td>2203.3</td>
<td>2251.5</td>
<td>2212.8</td>
</tr>
<tr>
<td>(\nu_4)</td>
<td>a'</td>
<td>1232.1</td>
<td>1270.2</td>
<td>1272.6 (85)</td>
<td>1235.9</td>
<td>1273.9</td>
<td>1236.1</td>
</tr>
<tr>
<td>(\nu_5)</td>
<td>a'</td>
<td>1072.1</td>
<td>1062.0</td>
<td>1069.5 (85)</td>
<td>1052.8</td>
<td>1074.0</td>
<td>1058.7</td>
</tr>
<tr>
<td>(\nu_6)</td>
<td>a'</td>
<td>610.3</td>
<td>622.7 (47)</td>
<td>629.2</td>
<td>631.3</td>
<td>639.1</td>
<td></td>
</tr>
<tr>
<td>(\nu_7)</td>
<td>a&quot;</td>
<td>527.3</td>
<td>537.8 (54)</td>
<td>548.4</td>
<td>544.4</td>
<td>558.0</td>
<td></td>
</tr>
<tr>
<td>(\nu_8)</td>
<td>a&quot;</td>
<td>378.4</td>
<td>401.6 (4)</td>
<td>417.1</td>
<td>416.6</td>
<td>432.3</td>
<td></td>
</tr>
<tr>
<td>(\nu_9)</td>
<td>a'</td>
<td>355.0</td>
<td>368.3 (10)</td>
<td>386.1</td>
<td>377.8</td>
<td>393.5</td>
<td></td>
</tr>
</tbody>
</table>

*Argon Matrix Experimental Data \[110\].
\[85\]CCSD(T)/aug-cc-pVTZ harmonics \[85\].

*Double Harmonic MP2/6-31+G* intensities (km/mol) in parenthesis.
4.3.1 Structure and Rotational Spectroscopic constants

The optimized structures at both the F12-TZ and CcCR levels are given in Table 4.1. The optimized bond lengths computed at both levels of theory agree to within 0.02 Å when compared to one another and previous computations at the MP2/6-31+G** level of theory [9]. The quartic and sextic A-reduced Hamiltonian spectroscopic constants of ethynol are given in Table 4.2 alongside dipole moments. Ethynol’s vibrationally-excited rotational constants are provided in Table 4.1 in the same order as the fundamental vibrational frequencies. Due to ethynol’s considerable dipole moment of 1.58 D, as shown in Table 4.2, its rotational transitions should be easily observable via rovibrational spectroscopy.

A useful point of comparison for ethynol’s equilibrium rotational constants would be with those of acetonitrile. Acetonitrile is a prolate molecule that compares nicely to ethynol’s near-prolate structure and has a nearly equivalent molecular weight to that of ethynol. As seen in Table 4.1, ethynol has CcCR $B_0$ and $C_0$ values of 0.32445 cm$^{-1}$ and 0.31946 cm$^{-1}$ respectively. Previous work has shown CcCR rotational constants to be accurate within $6.67 \times 10^{-4}$ cm$^{-1}$ of experimental values for closed shell molecules [111]. Acetonitrile has equivalent $B_0$ and $C_0$ values of 0.30684 cm$^{-1}$ [112]. As expected, ethynol has $B_0$ and $C_0$ values higher than those of acetonitrile due to its near-prolate, as opposed to fully prolate, nature. These similarities will make acetonitrile a useful sign-post for the observation of ethynol in the ISM, but, because acetonitrile has a larger dipole moment (3.92 D), observed rotational modes of ethynol will have considerably lower intensity than those of acetonitrile.

4.3.2 Vibrational Frequencies

Vibrational frequencies for ethynol are given at the F12-TZ and CcCR levels of theory alongside experimental values in Table 4.4. F12-TZ and CcCR anharmonic frequencies compare well to each other, with a mean absolute error of less than 8 cm$^{-1}$ between the two methods. Although gas phase experimental data are currently unavailable for ethynol, argon matrix experimental data [110] correlates in expected fashion with theoretical values.
presented in this work. Of the nine vibrational frequencies present in ethynol, only the five most intense have experimental data. The others are too weak to be observed. This is corroborated by MP2 intensities presented alongside F12-TZ harmonic frequencies in Table 4.4, which are seen to drastically drop off after \( \nu_5 \).

Of ethynol’s vibrational frequencies, \( \nu_1 \), \( \nu_2 \), and \( \nu_3 \) have the three brightest intensities. These modes are described in Table 4.4 using the coordinate system established in the Computational Details section and are attributed to the O–H, C–H, and C–C stretching modes, respectively. Comparison of ethynol’s anharmonic frequencies to known values of similar structures in the gas phase may be useful in aiding the vibrational assignment of ethynol in the ISM. The CcCR \( \nu_3 \), corresponding to the C–C stretching mode, occurs at 2212.8 cm\(^{-1}\) or 4.519 \( \mu \)m and is the brightest vibrational mode present in ethynol, making it a critical resource for the future assignment of ethynol in the ISM. The C–N triple bond stretch present in acetonitrile, a molecule of, again, similar structure and weight to ethynol that is known to be present in the ISM [113], is observed at 2267 cm\(^{-1}\) or 4.411 \( \mu \)m in gas phase experiment [114]. The reported CcCR frequency for \( \nu_3 \) is redshifted 0.108 \( \mu \)m from the experimental acetonitrile C–N stretch. This redshifting is to be expected as ethynol is a slightly more massive system.

With only a slightly lower intensity than \( \nu_3 \), the CcCR \( \nu_1 \) is observed at 3635.2 cm\(^{-1}\) or 2.751 \( \mu \)m. As \( \nu_1 \) is attributed to the O–H stretch of ethynol, a reasonable mode to compare as an analog is the O–H stretch present in methanol, which is well known in the ISM [115]. This methanol stretching mode is observed in gas phase experiment at 3681 cm\(^{-1}\) [114] or 2.717 \( \mu \)m. When \( \nu_1 \) to this stretching mode in methanol, the CcCR \( \nu_1 \) exhibits a redshift of 0.034 \( \mu \)m away from methanol’s stretching mode.

Of the three brightest vibrational frequencies present in ethynol, \( \nu_2 \), observed at 3354.7 cm\(^{-1}\) or 2.980 \( \mu \)m, is considerably dimmer than \( \nu_1 \) and \( \nu_3 \) but still has potential to serve as a useful indicator in future detection. As \( \nu_2 \) is attributed to the C–H stretching mode of ethynol, a practical mode for comparison would be that of the C–H stretching mode of the
ethynyl radical, which has also been previously observed in the ISM [116]. This gas phase stretching mode is observed at 3298.85 cm\(^{-1}\) or 3.031 \(\mu\)m [117]. Similar to \(\nu_1\) and \(\nu_3\), \(\nu_2\) is shifted by 0.051 \(\mu\)m when compared to the C–H stretch present in the ethynyl radical.

Positive anharmonicities are present for \(\nu_6 - \nu_9\) in Table 4.4. These positive anharmonicities range from 6.5 cm\(^{-1}\) to 17.8 cm\(^{-1}\) when examining \(\nu_6\) and \(\nu_9\), respectively. This behavior in the anharmonicities arises due to the nearly linear nature of the H–C–C–O backbone present in ethynol and has been documented previously in molecules of similar near-prolate construction [78, 118, 119].

The high intensity stretching modes \(\nu_1 - \nu_5\) are observed in the region of previously identified peaks [120]. However, the \(\nu_1 - \nu_5\) frequencies occur in regions not typically attributed to polycyclic aromatic hydrocarbons or dust, thus making these regions less well confined in terms of potential molecular provenance. Although far from conclusive, ethynol’s distinct vibrational peaks combined with their high intensity show promise for IR spectroscopy identifying the molecule in the ISM. Additionally, its notable dipole moment is encouraging for rotational observation, thus providing even more avenues of detection.

4.4 Conclusions

Considering that ethynol has already been shown to form in interstellar ice analogs and that the related ketene molecule [85] is known to be present in the ISM, the high level vibrational and rotational data provided here may lead to the detection of ethynol in various astrophysical regions, especially those where ketene and its dehydrogenated radical are known to exist. Detection of ethynol through rotational spectroscopy is possible due to its 1.58 D dipole moment, but it may be shrouded by lines associated with acetonitrile. Even so, detection is also feasible via mid-IR spectroscopy due to the bright nature of vibrational frequencies \(\nu_1 - \nu_3\), leading to multiple spectral regions for detection. Once ethynol has been detected in the ISM, investigation of relative populations of ethynol compared to ketene within certain regions will increase understanding of the recently proposed mechanism by
Turner et al. (2020). This knowledge may then further augment models exploring COM formation in the ISM and help the collective understanding of how small molecules like ethynol and ketene relate to the molecular origins of life in the ISM.
Chapter 5

Conclusions

Humanity’s understanding of the natural world has been turned on its head time and time again in the last century with the conceptualization of the quantization of energy, the introduction of uncertainty, the advent of computational chemistry, and countless other advancements. With each somersault, the problems that humanity can solve get larger and more fundamental. We now face questions prodding the very foundation of the universe and the stars that comprised it in its earliest stages, the trajectory that these stars set our reality down, and how that trajectory has lead us look for an origin of life deep within the cold confines of space.

Even more remarkably, topics as far reaching as these can be explored with precision that was considered impossible decades ago without stepping foot in the experimental laboratory, let alone the icy reaches of the ISM itself. Through the lens of quantum chemistry, phenomena that would generally be too short-lived and unstable to observe in a terrestrial laboratory can be explored with excruciating detail, lending knowledge to otherwise unreachable systems. That being said, experimental astrochemistry has grown into an incredibly strong field in the recent decades and can mimic many phenomena also explored by computational astrochemistry. This alliance between theory and experiment has allowed for a recent explosion in the field and has lead to an unprecedented increase in accountability and accuracy in astrochemistry.
As seen from the work herein, astrochemistry, both computational and experimental, is a field spanning numerous methodologies and even more topics. There are few other fields in which one can jump from exploring the atmospheric chemistry of Titan to pondering the inner workings of stars light years away, shifting methods entirely with each new topic. For this reason, computational astrochemistry is a phenomenal field to explore as an undergraduate researcher. During my time spent as a member of the Astrochemistry Research Group here at the University of Mississippi, I have had the opportunity to rigorously pursue topics of my chemistry and mathematics education simultaneously, an opportunity that I would have been hard-pressed to find elsewhere on campus.
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