Computational Infrared Spectroscopy of HNO Beyond the Double Harmonic Approximation

Harkiran Kaur Dhah
University of Tennessee

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Robert Hinde, Major Professor

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Dixie L. Thompson

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Computational Infrared Spectroscopy of HNO Beyond the Double Harmonic Approximation

A Dissertation Presented for the
Doctor of Philosophy Degree
The University of Tennessee, Knoxville

Harkiran Kaur Dhah
December 2018
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To my parents, Mohinder and Ravinder, you taught me at an early age the importance of education. It was with your love, encouragement, and understanding that I was able to pursue my doctoral degree and reach this point in my life. I love you with all of my heart and I can never thank you enough for all that you have done for me.

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Abstract

This work explores, for the first time, the calculation of HNO molar absorptivities using methods that go beyond the double harmonic approximation. Accurate molar absorptivities of HNO are essential for the kinetic interpretation of recent experiments that studied tunneling-mediated chemistry of H + NO reactions at low temperatures. This work will show that the double harmonic approximation for computing molar absorptivities is not sufficient to obtain accurate molar absorptivities for HNO. Since the only published molar absorptivities for HNO are computed using the double harmonic approximation, they cannot be used to interpret the experimental data.

First, we compute the molar absorptivity values using the double harmonic approximation with several combinations of basis sets and theories. With the double harmonic approximation, we also calculate the vibrational frequency shifts with isotopic substitutions of the individual atoms within the HNO molecule. After comparing double harmonic results to experimental results, we consider extensions to this approximation. By including anharmonic effects, we first consider electrical anharmonicity alone, and then consider the combination of electrical and mechanical anharmonicity. With the inclusion of both forms of anharmonicity, the molar absorptivity values change greatly from the double harmonic molar absorptivity values. Lastly effects of mechanical coupling are investigated. Results from this investigation encourage future work that
would include mechanical coupling, and also consider electrical coupling, in accurate calculations of HNO molar absorptivities.

This work will show that large basis sets are required for the theoretical calculation of the molar absorptivities of HNO, and that the double harmonic approximation is unreliable for this molecule. In particular, the NH stretching mode is very anharmonic. The computed isotopic shifts in the vibrational frequencies of HNO are found to be very sensitive to the way in which electron-electron correlation is treated. This indicates that very high level electron correlation models may be important for accurate theoretical studies of HNO. Finally, the extension beyond the double harmonic approximation and treatment with anharmonic effects are proven to be extremely valuable in describing the true mechanical and electrical properties of HNO.
Table of Contents

Chapter 1  Introduction ............................................................................................. 1
  1.1  Importance of Nitrosyl Hydride .................................................................. 2
  1.2  Experimental Background ......................................................................... 4
  1.3  Theoretical Background ............................................................................ 7
  1.4  Overview of Work ...................................................................................... 8

Chapter 2  Double Harmonic Approximation .......................................................... 10
  2.1  Introduction ............................................................................................... 11
    2.1.1  Optimization ................................................................................. 12
    2.1.2  Basis Sets and Theory ................................................................. 13
  2.2  Molar Absorptivity and the Double Harmonic Approximation ................. 14
  2.3  Mass-weighted Hessian Matrix and Dimensionless Normal Mode
    Displacements .............................................................................................. 16
    2.3.1  Cartesian Coordinates ..................................................................... 16
    2.3.2  Internal Coordinates ....................................................................... 19
  2.4  Isotopic Effect ........................................................................................... 19
  2.5  Potential Energy Functions ....................................................................... 20
  2.6  Dipole Moment Vectors ............................................................................. 20
Chapter 3 Double Harmonic Results ................................................................. 23

3.1 Optimization and Harmonic Frequencies ................................................. 24

3.2 Isotopic Substitution Effect ................................................................. 28

3.3 Internal Coordinates ........................................................................ 33

3.4 Double Harmonic Potential Energy Functions ...................................... 35

3.5 Double Harmonic Dipole Moment Functions ........................................... 39

Chapter 4 Anharmonicity and Coupling ......................................................... 46

4.1 Introduction ....................................................................................... 47

   4.1.1 Complete Potential Energy .......................................................... 47

   4.1.2 Complete Dipole Moment ............................................................. 48

4.2 Anharmonicity ................................................................................... 49

   4.2.1 Electrical Anharmonicity ............................................................... 50

   4.2.2 Electrical and Mechanical Anharmonicity ..................................... 52

4.3 Coupling ......................................................................................... 60

Chapter 5 Conclusions and Future Work ...................................................... 66

5.1 Importance of Work ........................................................................ 67

5.2 Double Harmonic Results ................................................................. 67

5.3 Anharmonic Effects ........................................................................ 68

5.4 Conclusions .................................................................................... 69
List of Tables

Table 1.1.1. Listing of all four possible products from the reaction of a hydrogen radical with a NO radical, and literature values of exothermicity from formation of products and the activation energy for each product. ................................................................. 3

Table 3.1.1. HNO optimization results for each basis set and theory. Optimal parameters listed are NH bond length (Å), NO bond length (Å), bond angle (in degrees), and optimal energy (Hartrees). .................................................. 25

Table 3.1.2. Harmonic frequency (cm⁻¹) results for each normal mode using each basis set and theory. These results are from Hessian entries of second derivatives with respect to Cartesian coordinates of the atoms. .................................................. 27

Table 3.2.1. Harmonic frequency (cm⁻¹) results for each normal mode using each basis set and theory for the HNO molecule with the ¹⁵N isotopic substitution. These results are from Hessian entries of second derivatives with respect to Cartesian coordinates of the atoms. Values in parenthesis are the frequency shifts from the ¹H¹⁴N¹⁶O molecule using the same basis set and theory. ............................................. 29

Table 3.2.2. Harmonic frequency (cm⁻¹) results for each normal mode using each basis set and theory for the HNO molecule with the ¹⁸O isotopic substitution. These results are from Hessian entries of second derivatives with respect to Cartesian coordinates of the atoms. Values in parenthesis are the frequency shifts from the ¹H¹⁴N¹⁶O molecule using the same basis set and theory. ............................................. 31

Table 3.2.3. Harmonic frequency (cm⁻¹) results for each normal mode using each basis set and theory for the HNO molecule with the ²H isotopic substitution. These results are from Hessian entries of second derivatives with respect to Cartesian coordinates of the atoms. Values in parenthesis are the frequency shifts from the ¹H¹⁴N¹⁶O molecule using the same basis set and theory. ............................................. 32

Table 3.3.1. Harmonic frequency (cm⁻¹) results for each normal mode considering internal coordinates, using aug-cc-pVQZ and CCSD(T) for the HNO molecule without isotopic substitution, and for the molecule with the ²H isotopic substitution, with the ¹⁵N...
isotopic substitution, and with the $^{18}$O isotopic substitution. These results are from Hessian entries of second derivatives with respect to internal coordinates of the atoms. Values in parenthesis are the frequency shifts from the same isotopes using aug-cc-pVQZ and CCSD(T) with considering Cartesian coordinates.

Table 4.2.1. This table lists, for each mode, the contributions from each harmonic wavefunction in the linear combination of harmonic wavefunctions to form the anharmonic wavefunctions. The harmonic frequencies required for these calculations came from the internal coordinate Hessian matrix. *Ab initio* results came from aug-cc-pVQZ and CCSD(T).

Table 4.2.2. This table lists, for the q1 mode, the integral of the anharmonic wavefunctions with the x- and y-components of the dipole moment operator, multiplied by the products of $b_i$ and $c_j$. The harmonic frequencies required for these calculations came from the internal coordinate Hessian matrix. *Ab initio* results came from aug-cc-pVQZ and CCSD(T).

Table 4.2.3. Anharmonic frequency (cm$^{-1}$) of each mode, considering mechanical and electrical anharmonicity with different amounts of maximum vibrational states for the harmonic wavefunctions. *Ab initio* results came from aug-cc-pVQZ and CCSD(T).

Table 4.2.4. Anharmonic frequency (cm$^{-1}$) of each mode, considering mechanical and electrical anharmonicity. Values in parenthesis is the difference of the anharmonic frequency from the harmonic frequency for the $v=0$ to $v=1$ transition. Experimental frequencies are listed for comparison. The harmonic frequencies required for these calculations came from the internal coordinate Hessian matrix. *Ab initio* results came from aug-cc-pVQZ and CCSD(T).

Table 4.2.5. Molar Absorptivity (km/mol) of each mode. The anharmonic calculations specify maximum vibrational state of harmonic wavefunctions that were considered.

Table 4.2.4. Molar absorptivity ratios, which are equal to the relative integrated intensities from an infrared spectrum.
List of Figures

Figure 3.4.1. Aug-cc-pVQZ, CCSD(T) \textit{ab initio} potential energies vs. \(q_1\) mode for the \(q_1\) mode resultant from internal coordinate Hessian matrix. The sixth order polynomial fit is an expansion to the double harmonic potential energy function. .......................................................... 36

Figure 3.4.2. Aug-cc-pVQZ, CCSD(T) \textit{ab initio} potential energies vs. \(q_2\) mode for the \(q_2\) mode resultant from internal coordinate Hessian matrix. The sixth order polynomial fit is an expansion to the double harmonic potential energy function. .......................................................... 37

Figure 3.4.3. Aug-cc-pVQZ, CCSD(T) \textit{ab initio} potential energies vs. \(q_3\) mode for the \(q_3\) mode resultant from internal coordinate Hessian matrix. The sixth order polynomial fit is an expansion to the double harmonic potential energy function. .......................................................... 38

Figure 3.5.1. Aug-cc-pVQZ, CCSD(T) \textit{ab initio} \(x\)-component of dipole moment vs. \(q_1\) mode for the \(q_1\) mode resultant from internal coordinate Hessian matrix. The fifth order polynomial fit is an expansion to the double harmonic dipole moment function. ............................................... 40

Figure 3.5.2. Aug-cc-pVQZ, CCSD(T) \textit{ab initio} \(x\)-component of dipole moment vs. \(q_2\) mode for the \(q_2\) mode resultant from internal coordinate Hessian matrix. The fifth order polynomial fit is an expansion to the double harmonic dipole moment function. ............................................... 41

Figure 3.5.3. Aug-cc-pVQZ, CCSD(T) \textit{ab initio} \(x\)-component of dipole moment vs. \(q_3\) mode for the \(q_3\) mode resultant from internal coordinate Hessian matrix. The fifth order polynomial fit is an expansion to the double harmonic dipole moment function. ............................................... 42

Figure 3.5.4. Aug-cc-pVQZ, CCSD(T) \textit{ab initio} \(y\)-component of dipole moment vs. \(q_1\) mode for the \(q_1\) mode resultant from internal coordinate Hessian matrix. The fifth order polynomial fit is an expansion to the double harmonic dipole moment function. ............................................... 43

Figure 3.5.5. Aug-cc-pVQZ, CCSD(T) \textit{ab initio} \(y\)-component of dipole moment vs. \(q_2\) mode for the \(q_2\) mode resultant from internal coordinate Hessian matrix. The fifth order polynomial fit is an expansion to the double harmonic dipole moment function. ............................................... 44

Figure 3.5.6. Aug-cc-pVQZ, CCSD(T) \textit{ab initio} \(y\)-component of dipole moment vs. \(q_3\) mode for the \(q_3\) mode resultant from internal coordinate
Hessian matrix. The fifth order polynomial fit is an expansion to the double harmonic dipole moment function. .................................................. 45

Figure 4.3.1. Potential energies contour plot of q1 vs. q2. Left graph: Full potential energy curve from the contributions of q1 and q2. Each line is 0.003 Ha apart. The higher red character of a line indicates a lower energy, and the higher blue character of a line indicates a higher energy. Spacing between lines is 0.003 Ha. Right graph: Coupling contributions alone to the potential energy. The higher red character of a line indicates a lowering of the energy, and the higher blue character indicates a raising of the energy. Spacing between lines is 0.0003 Ha. Energies are resultant from ab initio calculations with aug-cc-pVTZ, MP2... ................................................................. 62

Figure 4.3.2. Potential energies in a contour plot of q1 vs. q3. Left graph: Full potential energy curve from the contributions of q1 and q3. Each line is 0.003 Ha apart. The higher red character of a line indicates a lower energy, and the higher blue character of a line indicates a higher energy. Spacing between lines is 0.003 Ha. Right graph: Coupling contributions alone to the potential energy. The higher red character of a line indicates a lowering of the energy, and the higher blue character indicates a raising of the energy. Spacing between lines is 0.0003 Ha. Energies are resultant from ab initio calculations with aug-cc-pVTZ, MP2. .......................................................................................... 63

Figure 4.3.3. Potential energies in a contour plot of q2 vs. q3. Left graph: Full potential energy curve from the contributions of q2 and q3. Each line is 0.003 Ha apart. The higher red character of a line indicates a lower energy, and the higher blue character of a line indicates a higher energy. Spacing between lines is 0.003 Ha. Right graph: Coupling contributions alone to the potential energy. The higher red character of a line indicates a lowering of the energy, and the higher blue character indicates a raising of the energy. Spacing between lines is 0.0003 Ha. Energies are resultant from ab initio calculations with aug-cc-pVTZ, MP2. .......................................................................................... 64
Chapter 1

Introduction
1.1 Importance of Nitrosyl Hydride

The nitrosyl hydride molecule, HNO, was first experimentally observed in 1958 (Dalby 1958). This molecule over the past century has been studied experimentally and theoretically due to its involvement in several areas. The breakdown of stratospheric ozone has been suggested to involve HNO as an intermediate (Patrick and Golden 1984). In 1977, HNO was first reported to be detected from interstellar emissions, which was important to the astrochemical community as it confirmed the first detection of the NO bond in interstellar molecules (Ulich, Hollis et al. 1977). HNO has also been expected to have an application towards heart failure treatment (Miranda, Katori et al. 2005). Ongoing research of this molecule continues.

HNO molecules can be produced from reactions of hydrogen radicals with NO molecules. As shown in Table 1.1.1 (Bozkaya, Turney et al. 2012), these reactants can result in four possible products, which are $^1\text{HNO}$, $^3\text{HNO}$, $^1\text{NOH}$, and $^3\text{NOH}$. All of these product formations are exothermic, so the resultant molecule formed is lower in energy than that of the hydrogen radical and NO molecule from which they were produced. As seen from this table, all of the products but $^1\text{HNO}$ have a classical energy barrier that must be overcome by the reactants before the products can be formed. To surpass this barrier, the reactants must have enough kinetic energy, and this energy increases with the temperature of the environment. The distribution of kinetic energies at a specific temperature is described by the Maxwell-Boltzmann distribution.
Table 1.1.1. Listing of all four possible products from the reaction of a hydrogen radical with a NO radical, and literature values of exothermicity from formation of products and the activation energy for each product. (Bozkaya, Turney et al. 2012)

<table>
<thead>
<tr>
<th>Product</th>
<th>Exothermicity (kcal/mol)</th>
<th>Activation Energy (kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^1\text{HNO}$</td>
<td>47.48</td>
<td>None</td>
</tr>
<tr>
<td>$^3\text{HNO}$</td>
<td>29.03</td>
<td>3.38</td>
</tr>
<tr>
<td>$^1\text{NOH}$</td>
<td>5.25</td>
<td>2.63</td>
</tr>
<tr>
<td>$^3\text{NOH}$</td>
<td>21.3</td>
<td>12.37</td>
</tr>
</tbody>
</table>
1.2 Experimental Background

David Anderson from the University of Wyoming Department of Chemistry studies low temperature reaction kinetics. Reactions between hydrogen atoms and several co-reagents are being studied within a para-hydrogen matrix at extremely low temperatures between 1 and 5 Kelvin. By studying the several hydrogen atom reactions that occur with these co-reagents at such low temperatures, Anderson aims to gain an understanding of the reaction rate and mechanism through which these reactions take place. Spectroscopic analysis aids in understanding these reactions (Ruzi and Anderson 2015).

Para-hydrogen molecules have a rotational state of $j = 0$ at ground state, whereas the rotational state of ortho-hydrogen molecules is $j = 1$ at ground state. The rotational quantum number, $j$, is determined from the nuclear spin. The antisymmetric para nuclear spin state is composed of the two hydrogen atoms in the H$_2$ molecule with opposite spins, resulting in $j$ of 0, 2, 4, and other even state numbers. The symmetric ortho nuclear spin state is composed of the two hydrogen atoms in the H$_2$ molecule with the same spins, resulting in $j$ of 1, 3, and other odd state numbers. A para-hydrogen molecule with $j$ of 0 is the lowest in energy, and hence is the most stable hydrogen spin state. Nuclear spin state conversions between ortho and para are forbidden except in the presence of a substance that can act as a converter. Anderson utilizes matrix isolation of para-hydrogen complexes at low temperatures.

Anderson has been studying the kinetics of low temperature reactions, particularly at 1.8 and 4.3 K, of nitric oxide (NO) radical dopants in a predominately
para-hydrogen crystal matrix after a portion of the crystal is irradiated with ultraviolet light. The NO radicals that were struck with this light then dissociate into N and O atoms. Each of these atoms react with their neighboring hydrogen molecules to produce, as one of the products, a hydrogen atom.

An ortho-para converter is used to insure 99.97% of the hydrogen gas molecules are in the para-hydrogen state. The NO-doped solid para-hydrogen crystal is prepared by codeposition of both NO and para-hydrogen gas onto a BaF$_2$ substrate. Ultraviolet light is passed through the doped crystal at a wavelength of 193 nm, producing the nitrogen and oxygen atoms that then react with H$_2$ molecules to produce hydrogen atoms. The hydrogen atoms then diffuse through the crystal. Electron Spin Resonance (ESR) spectroscopy studies have concluded that this hydrogen atom diffusion occurs in solid para-hydrogen through reactive tunneling (Kumada, Sakakibara et al. 2002, Kumada 2003). Quantum tunneling refers to reactions that occur by passing through a potential energy barrier. This type of reaction neglects the requirement of having or supplying enough energy to overcome the potential energy barrier. The hydrogen atom diffusion through the para-hydrogen matrix involves an exchange reaction between the para-hydrogen molecules and the hydrogen atoms.

\[ \text{H} + \text{H}_2 \rightarrow \text{H}_2 + \text{H} \]

The energy barrier between the reactants and products in the above reaction is \(~10\text{ kcal mol}^{-1}\) (Ruzi and Anderson 2015). At Anderson’s experimental temperature of 4.3 K, integration of the tail of the Maxwell-Boltzmann distribution shows that less than 1
hydrogen atom out of $10^{250}$ atoms will have 10 kcal mol$^{-1}$ of kinetic energy (Benderskii, Goldanskii et al. 1993), therefore the reaction must occur through tunneling.

Anderson studies the bimolecular reactions that occur with the hydrogen atoms and the NO dopants. Completing these studies at low temperatures allows immobilization of certain species, thus preventing reactions from taking place between these species and others within the matrix, or reactions between the same species. Once a hydrogen radical is in proximity to a NO dopant, a reaction occurs. As expected from Table 1.1.1, HNO is a product. Although this reaction also takes place at the same low temperatures, this reaction occurs without tunneling, as this is a barrierless exothermic reaction.

\[ \text{H} + \text{NO} \rightarrow \text{HNO} \]

Surprisingly, the other product that is formed is $^3\text{NOH}$. Due to the high energetic barrier to produce $^3\text{NOH}$ and the low temperatures at which Anderson performs his experiments, the production of $^3\text{NOH}$ occurs through tunneling.

A fourier transform infrared (FTIR) spectrometer records spectra at the onset of irradiation and at subsequent times for a period of up to 5 hours. The three peaks in the $^1\text{HNO}$ spectra represent the NH stretch, NO stretch, and molecular bend vibrations. The FTIR peak intensities are shown to increase over time following photolysis, indicating a growth in the amount of $^1\text{HNO}$ and $^3\text{NOH}$ produced since the initial production of the nitrogen and oxygen atoms. If the peak intensities can be converted to concentrations, then Anderson’s group can follow the growth rate of the $^1\text{HNO}$ and $^3\text{NOH}$ products.
during the experiment. An accurate growth rate is required for kinetic analysis of this reaction.

1.3 Theoretical Background

Once the doped para-hydrogen crystal is irradiated, HNO production is initiated. To calculate the kinetics of the HNO production, accurate absorption coefficients are needed that represent the absorbance per unit concentration for this molecule. The pattern of growth of HNO over time using previously calculated absorption coefficients indicates a first-order reaction (Lee 1993). The exact concentration of HNO can be calculated from any of the HNO FTIR peaks by considering the integrated absorption coefficients (ε) and the absorbances (A) of the peaks, where 

\[
A = \log_{10} \left( \frac{I_0}{I} \right), \quad \text{where } I_0 \text{ is the light intensity initially striking the crystal and } I \text{ is the light intensity remaining after passing through the crystal.}
\]

\[
V_0 \text{ has a set value of } 23.16 \text{ cm}^3 \text{ mol}^{-1} \text{ which represents the molar volume of the solidified para-hydrogen at the temperature of liquid helium, and } l \text{ is the path length the infrared light travels through the crystal.}
\]

\[
[HNO] = 2.303 \int \log_{10} \left( \frac{I_0}{I} \right) \frac{d\theta}{\varepsilon l} V_0 (10^6)
\]

The only previously published integrated absorption coefficients available prior to this work were reported in 1993 by T.J. Lee (Lee 1993), using a computational approximation called the double harmonic approximation and using a comparatively small basis set as to those easily available today. A basis set is a set of basis functions to be used to model the electronic wave function of an atom. The specific basis set used by Lee was the triple-zeta double polarized (TZ2P) basis set. The double harmonic
approximation treats potential energy functions as second-order polynomials to describe each vibrational motion. Additionally, the double harmonic approximation also treats dipole moment functions as first-order polynomials to describe each vibrational motion. These simplifications greatly simplify the work required to obtain molar absorptivity values.

When Anderson’s group uses these absorption coefficients, the resultant HNO concentration determined from the NH stretch vibration differs from that calculated from the molecular bend vibration by a factor of two. This means that the HNO concentrations produced in Anderson’s experiments are still too uncertain to allow a kinetic analysis of the reaction. This large disagreement of the HNO concentration makes it essential to explore absorption coefficients computed with larger basis sets and with calculations that are beyond the double harmonic approximation.

1.4 Overview of Work

The following chapters will detail our work to obtain more accurate absorption coefficients than those currently available. All of this work was completed through \textit{ab initio} calculations and through code written in Maple. All of the calculations in this dissertation were for singlet HNO.

In chapter 2 we will detail our work testing the double harmonic approximation, which was completed through \textit{ab initio} calculations with use of modern basis sets, as well as with different levels of theories. Chapter 3 will include results of the double harmonic approximation and analysis of these results. Harmonic frequencies were
obtained for the HNO molecule, along with harmonic frequencies following substitution of different isotopes of the atoms within the molecule for analysis of the kinetic isotope effect. Using these vibrational frequencies and further \textit{ab initio} work, we obtained harmonic potential energy functions and dipole moment functions to describe each vibrational motion. This allowed us to compute the double harmonic molar absorptivity of each vibrational motion. The measurement by which our values were determined accurate was by comparison to experimental work by Anderson.

In chapter 4 we will detail our work for extending potential energy functions and dipole moment functions beyond the double harmonic approximation to see the effects of including anharmonicity to compute molar absorptivities. After this we will consider including coupling between different vibrational motions to see the effect of more than one vibrational mode influencing the molecule at one time.

Chapter 5 includes details of how to further extend this work. Lastly, a summary of the importance of this work and the results of this work will be provided.
Chapter 2

Double Harmonic Approximation
2.1 Introduction

Prior calculations of molar absorptivity for the vibrational motions of HNO have treated the molecule using only the double harmonic approximation (Lee 1993). This approximation is frequently used to avoid extra computational cost, but for certain molecules the vibrational behavior requires an extension to the double harmonic approximation to describe more accurately behaviors such as the potential energy change and dipole moment change with each vibrational motion, which in turn has an effect on the molar absorptivity. The double harmonic approximation assumes non-coupling of vibrational modes; that is that each vibration has an independent effect on the molecule. The number of vibrational modes for a nonlinear molecule is \((3N-6)\), where \(N\) represents the total number of atoms within the molecule. For the nonlinear HNO molecule there are a total of three vibrational modes, labeled \(q_1, q_2, q_3\), in order of decreasing frequency. Each vibrational mode is described by the collective displacements of the H, N, and O atoms. Three geometric parameters are affected by these normal modes, which are the NH bond length, NO bond length, and the HNO bond angle.

The potential energy function of the molecule is dependent on each of the normal modes. In the double harmonic approximation, each potential energy function is assumed to be symmetric and quadratic in the minimum vicinity of the potential energy. The dipole moment function of the molecule is also dependent on each of the normal modes, and in the double harmonic approximation each dipole moment function is assumed to be a linear function of the normal mode coordinates. As will be discussed in
section 2.2, the molar absorptivity computed within the double harmonic approximation requires components from accurate potential energy functions and dipole moment functions. The calculations for the optimization of HNO, as well as for potential energies and dipole moments of the HNO structures, will be completed through *ab initio* molecular orbital theory calculations. The *ab initio* optimization adjusts the geometrical parameters, such as bond lengths and bond angle, calculating the potential energy after each adjustment, and repeats this process though several iterations until a minimal energy is found.

**2.1.1 Optimization**

To compute the optimized geometry of HNO and the potential energy of this optimal geometry, which corresponds to the minimal energy along the potential energy curve, an optimized *ab initio* calculation was completed. Geometric optimization of HNO is simplified by treating this 2-dimensional molecule in the (x, y) plane. Past work by Bozkaya studied the energetics of HNO and its isomer, NOH, and the kinetics of the HNO ↔ NOH isomerization (Bozkaya, Turney et al. 2012). Our work initialized the placement of each atom in the HNO structure by using Bozkaya’s computed geometry, although we used a different basis set than used by Bozkaya, and we converted this geometry to coordinates of each of the H and O atoms while placing the N atom at the origin and the NO bond along the x-axis. Optimization of this initial geometry yielded optimal bond lengths, bond angle, and potential energy.
2.1.2 Basis Sets and Theory

In order to test the dependence of our optimization and the work that followed the optimization on the basis set, two basis sets were used. Our work employed augmented correlation-consistent polarized valence basis sets, specifically aug-cc-pVTZ and aug-cc-pVQZ. The basis set for each atom is made up of a number of Gaussian functions and when implemented for each atom in our molecule, it provides a close approximation to the molecular orbitals. Increasing from triple zeta to quadruple zeta raises the number of basis functions significantly, and this large increase of basis functions results in a considerable increase in computational cost. Augmentation of these basis sets adds diffuse functions to more accurately describe the outer regions of the atoms, which is necessary for the correct description of weak bonds, such as the NH bond in the HNO molecule, as well as for correct calculations of certain properties such as dipole moment.

Several computational theories were used in our calculations, specifically Hartree-Fock (HF), second-order Møller-Plesset theory (MP2), and coupled-cluster theories, including CCSD and CCSD(T). The Hartree-Fock theory treats the electrons of an orbital in an average manner and neglects instantaneous interactions between electrons in other orbitals known as electron-electron correlation. This neglect of electron correlation enables the Hartree-Fock method to conserve computational cost, and this method is correct to the first order of energies. Møller-Plesset includes an approximate treatment of electron correlation using perturbation theory, and MP2 is correct to the second order in the perturbation. Coupled-cluster models excitation of
electrons into virtual orbitals using the cluster operator, and includes increasing amounts of electron correlation. CCSD treats single and double excitations, and CCSD(T) includes, in addition, a non-iterative treatment of triple excitations, which reduces computational cost significantly compared to the CCSDT method. The mean absolute error of standard dipole moment calculations of relatively small molecules was found to be 0.16 D with Hartree Fock, 0.048 D with MP2, 0.025 D with CCSD, and less than 0.01 D with CCSD(T) (Bak, Gauss et al. 2000). A similar pattern is observed for the mean absolute error of bond lengths and bond angles of relatively small molecules that contain atoms from the second row of the period table (Coriani, Marchesan et al. 2005).

2.2 Molar Absorptivity and the Double Harmonic Approximation

The formula for calculating the molar absorptivity ($A$) of a specific vibrational mode considers both its vibrational frequency ($v$) and the absorption intensity ($G_{ji}$), where $i$ and $j$ represent the initial and final vibrational levels, respectively (Cohen, et al. 2008).

$$A = \frac{G_{ji}v}{16.60540}$$

$G_{ji}$ is a function of the transition dipole moment ($M_{ji}$). The transition dipole moment, squared, is made up of a sum over the Cartesian components of the integral of the dipole moment operator $\mu_p(q)$, squared, over vibrational levels $i$ and $j$.

$$G_{ji} = \frac{8\pi^3}{3hc_0(4\pi\varepsilon_0)} |M_{ji}|^2 = 41.6238 |M_{ji}|^2$$
The double harmonic approximation assumes equal spacing between each energy level and limits transitions to between the ground state, \( i = 0 \), and the first excited energy level, \( j = 1 \).

The dipole moment functions for each normal mode are polynomial functions of the normal mode. These polynomial functions essentially form a Taylor expansion of the dipole moment function for each Cartesian component.

\[
\mu_\rho(q) = \mu_\rho(q)_{q=0} + \frac{q}{1!} \left( \frac{\partial \mu_\rho(q)}{\partial q} \right)_{q=0} + \frac{q^2}{2!} \left( \frac{\partial^2 \mu_\rho(q)}{\partial q^2} \right)_{q=0} + \cdots + \frac{q^n}{n!} \left( \frac{\partial^n \mu_\rho(q)}{\partial q^n} \right)_{q=0}
\]

One of the restrictions of the double harmonic approximation is that this Taylor expansion is truncated at \( n=1 \). The transition dipole moment thereby becomes a summation of integrals of linear dipole moment functions for each Cartesian component, with \( i \) and \( j \) of 0 and 1, respectively.

\[
|M_{ji}|^2 = \sum_\rho \left| \left( \begin{array}{c} 0 \\ \mu_\rho(q)_{q=0} + \frac{q}{1!} \left( \frac{\partial \mu_\rho(q)}{\partial q} \right)_{q=0} \\ 1 \end{array} \right) \right|^2
\]

\[
|M_{ji}|^2 = \left| \begin{array}{c} 0 \\ \mu_x(q)_{q=0} + \frac{q}{1!} \left( \frac{\partial \mu_x(q)}{\partial q} \right)_{q=0} \\ 1 \end{array} \right|^2 + \left| \begin{array}{c} 0 \\ \mu_y(q)_{q=0} + \frac{q}{1!} \left( \frac{\partial \mu_y(q)}{\partial q} \right)_{q=0} \\ 1 \end{array} \right|^2
\]

\[
+ \left| \begin{array}{c} 0 \\ \mu_z(q)_{q=0} + \frac{q}{1!} \left( \frac{\partial \mu_z(q)}{\partial q} \right)_{q=0} \\ 1 \end{array} \right|^2
\]
2.3 Mass-weighted Hessian Matrix and Dimensionless Normal Mode Displacements

To find the harmonic frequencies of each normal mode, the Hessian matrix will need to be formed and diagonalized. The individual entries for the Hessian matrix will consist of second derivatives of the energies of the structure with respect to the Cartesian coordinates of one or two atoms. We estimated these derivatives as described below using a finite difference approach that required adjustments along the Cartesian coordinates of each atom, and attempted to conserve computational cost by considering adjustments along internal coordinates in place of Cartesian coordinates.

2.3.1 Cartesian Coordinates

The harmonic vibrational frequencies are found through diagonalization of a mass-weighted Hessian matrix. The Hessian matrix \( D \) is composed of second-order partial derivatives of the molecular potential energy surface with respect to one or two Cartesian coordinates of the atoms. For the HNO molecule, the Hessian matrix is a 9x9 square matrix. Laying the 2-dimensional HNO molecule along the xy-plane eliminates the translational motion along the z-axis and rotational motions of both the x-axis and y-axis. Considering only terms with x and y components reduces the matrix size to 6x6. The numbering 1-3 represent each of the three atoms in the HNO molecule.
The Hessian matrix is converted into a mass-weighted Hessian matrix ($D'$) with use of the diagonal mass-weighting matrix ($M^{1/2}$).

$$D' = M^{-1/2}DM^{-1/2}$$

Diagonalization of the mass-weighted matrix produces multiple eigenvalues ($\lambda$). Three of these eigenvalues are essentially zero, which come from the translational motion along the x-axis, the translational motion along the y-axis, and the rotational motion around the z-axis. The three non-zero eigenvalues represent the vibrational motion for each of the three normal modes. This follows the (3N-6) rule for number of vibrational modes in a non-linear molecule, such as HNO. These eigenvalues can be converted to vibrational frequency ($h\omega$) by a direct relation to the eigenvalue.

$$\omega = \sqrt{\lambda}$$

Also produced by the diagonalization of $D'$ are dimensionless normalized eigenvectors, one for each normal mode. These eigenvectors are converted to Cartesian displacement coordinates through a product of multiple matrices,

$$M^{-1/2}QW^{-1}$$
Where $Q$ is the matrix of the normalized eigenvectors, and $W$ is the diagonal matrix of $\sqrt{\omega_1/h}$.

The partial second derivatives of the Hessian matrix were approximated with the finite central difference method. For the diagonal Hessian entries, the coordinate of interest is adjusted from its optimized geometry by a small amount ($h$), which represents a “finite difference”, in both the positive and negative directions and the energies for these new geometries are obtained and then inputted into the following formula to calculate the partial second derivative with respect to one coordinate.

$$\frac{\partial^2 U}{\partial x_1^2} = \frac{U(x_1 + h) - 2U(x_1) + U(x_1 - h)}{h^2}$$

For the off-diagonal Hessian entries, a similar approach is used but considering adjustments of two different coordinates by this finite difference.

$$\frac{\partial^2 U}{\partial x_1 \partial y_2} = \frac{U \left( \frac{x_1 + h}{y_2 + h} \right) - U \left( \frac{x_1 + h}{y_2 - h} \right) - U \left( \frac{x_1 - h}{y_2 + h} \right) + U \left( \frac{x_1 - h}{y_2 - h} \right)}{4h^2}$$

This central difference method is exact for a purely quadratic energy surface.

Although the 6x6 Hessian matrix contains 36 entries, the upper triangle of the matrix can be duplicated to make the lower triangle, which is a benefit of a symmetric matrix, such as the Hessian matrix when computing for the HNO molecule. This can be seen by noticing the finite difference formula is the same for $\frac{\partial^2 U}{\partial x_1 \partial y_2}$ as for $\frac{\partial^2 U}{\partial y_2 \partial x_1}$. 

18
2.3.2 Internal Coordinates

The Hessian matrix entries of HNO consists of second derivatives of potential energy with respect to the 21 unique combinations of the six x- and y-Cartesian coordinates of individual atoms. To reduce computational cost, we computed the Hessian matrix with each entry consisting of second derivatives of potential energy with respect to the 6 combinations of the three internal coordinates. The three internal coordinates that describe the geometry of the HNO molecule are HN bond length, NO bond length, and the cosine of the bond angle. This essentially reduces our need of 72 \textit{ab initio} calculations to 18 \textit{ab initio} calculations for the Hessian matrix with this internal coordinate method.

2.4 Isotopic Effect

The quantitative displacement of each atom for a normal mode is described by the eigenvector of that normal mode. In experimental spectroscopy, when two vibrational frequencies are nearly equal to each other, it is possible that there will be strong coupling of the corresponding normal modes. Replacing one of the H, N, or O atoms with the next largest isotopes of $^2$H, $^{15}$N, or $^{18}$O will shift certain vibrational frequencies and could decouple the normal modes that previously had nearby frequencies. $^2$H substitution will have the largest effect in vibrational frequency shifts due to the large increase in reduced mass of the atoms involved in a vibration. Currently Anderson et al is experimenting with the $^{15}$N isotope in HNO to determine the kinetic distinction between the $^{14}$N and $^{15}$N isotopomers. Performing isotopic substitution will
aid in Anderson’s analysis of experimental spectroscopic data, as well as possibly confirm our vibrational normal mode assignments.

Each electronic energy is independent of the atomic masses of each atom. Therefore the isotopic effects yielding new harmonic frequencies, eigenvalues, and eigenvectors for selected isotopes can be studied without requiring new energetic calculations. Instead, the energetic calculations performed earlier for the Hessian matrix were used, and the only adjustment was altering the isotopic masses in creating the mass-weighted Hessian matrix ($D'$) from the Hessian matrix.

### 2.5 Potential Energy Functions

The potential surface is important for the molar absorptivity calculations in providing the energy levels, the frequency, and force constants along each normal mode. The double harmonic approximation limits the potential energy as a function of each normal mode coordinate $q$ to be a second-order function.

$$V(q) = V_{q=0} + \text{constant} \times q^2$$

### 2.6 Dipole Moment Vectors

The other crucial component to calculating the molar absorptivity for each normal mode is the transition dipole moment which is comprised of dipole moment functions along each Cartesian direction. To find the dipole functions, the molecule was stretched and compressed along each normal mode. For each normal mode, the eigenvectors, once converted to Cartesian displacement coordinates, describe the amount of
displacement along each Cartesian coordinate that is attributed to the stretching or compression of that normal mode.

The molecule is initially at the optimized geometry. For each normal mode analysis, varying magnitudes of the normal mode are applied to the geometry by multiplying the unitless normal mode displacement with the eigenvector associated with a particular normal mode, and the initially optimized geometry is adjusted with this amount. *Ab initio* calculations at this new geometry provide the potential energy as well as dipole moment of this new configuration. This process is repeated along multiple amounts of the normal mode, including fractions of the normal mode. The resulting dipole moments are plotted against the normal mode.

With lower levels of theories in the *ab initio* calculations, such as MP2 and CCSD, a command can be directly inserted into the input file to retrieve the dipole moment of the new geometry in the output file. Higher levels of theory, like CCSD(T), however, require a different approach for the dipole moment. The new geometry must be placed in a uniform electric field oriented along the x- or y-axis, and these electric fields influence the potential energy of the molecule. The strength of the electric field is varied. The potential energy at each field strength is plotted against the strength of electric field (EF), and the negative first derivative of the potential energy with respect to the electric field at the field strength of zero gives the dipole moment vector of $\rho$, where $\rho = x$ or $y$.

$$
\bar{\mu}_\rho = - \left[ \frac{\partial V}{\partial E_{F\rho}} \right]_{EF=0}
$$
The dipole moments for a normal mode are then fit to a polynomial equation and the coefficient leading the linear term is proportional to the first derivative of the dipole moment with respect to the normal mode. This derivative is inserted into the double harmonic approximation of the transition dipole moment, which then, along with the harmonic frequency found previously from the Hessian matrix, gives the double harmonic molar absorptivity value for that specific normal mode. Anderson’s experimental results are not directly comparable to our molar absorptivity values, but instead to a ratio of each pair of molar absorptivities. Hence, after having retrieved the theoretical molar absorptivity for each normal mode, such a ratio was created and compared to Anderson’s results.
Chapter 3

Double Harmonic Results
3.1 Optimization and Harmonic Frequencies

The normal modes and vibrational frequencies of the HNO molecule were calculated through the double harmonic approximation and compared to those of T.J. Lee. However, Lee’s data used a smaller basis set than the basis sets we considered (Lee 1993). The results that will be shown in this chapter and the next chapter will indicate that the double harmonic approximation breaks down for the HNO molecule.

The molecule was optimized using the aug-cc-pVTZ or aug-cc-pVQZ basis sets, with either the Hartree Fock, MP2, CCSD, or CCSD(T) levels of theory. The bond lengths and bond angle which yielded the minimal potential energy for each basis set and theory combination are detailed in Table 3.1.1. One clear pattern from the optimization results is that increasing the basis set with each theory results in a small change in the bond lengths and bond angle to yield the optimal energy. As basis set is increased, the decrease in optimal energy from Hartree-Fock to the electron-electron correlation considering methods (MP2, CCSD, CCSD(T)) is greater than the differences in energy between the electron correlation methods, which demonstrates the importance of including electron correlation in the ab initio calculations. Within each basis set, the minimal energy decreases when considering Hartree Fock to MP2 to CCSD to CCSD(T), thus showing consistency across the theories.

After obtaining the optimal bond lengths and bond angle and placing the atoms on a xy-plane, as described in Chapter 2, the x- and y- coordinates of each atom were displaced by a small value of $h = 0.01$ Å. As expected, each adjustment of a coordinate resulted in a new and higher energy than the energy for the optimized geometry. The
Table 3.1.1. HNO optimization results for each basis set and theory. Optimal parameters listed are NH bond length (Å), NO bond length (Å), bond angle (in degrees), and optimal energy (Hartrees).

<table>
<thead>
<tr>
<th>Basis Set</th>
<th>Theory</th>
<th>$R_{\text{NH}}$ (Å)</th>
<th>$R_{\text{NO}}$ (Å)</th>
<th>bond angle (°)</th>
<th>Energy (Ha)</th>
</tr>
</thead>
<tbody>
<tr>
<td>aug-cc-pVTZ</td>
<td>HF</td>
<td>1.03034</td>
<td>1.16610</td>
<td>109.38</td>
<td>-129.84295114</td>
</tr>
<tr>
<td></td>
<td>MP2</td>
<td>1.05068</td>
<td>1.22167</td>
<td>107.65</td>
<td>-130.28424878</td>
</tr>
<tr>
<td></td>
<td>CCSD</td>
<td>1.05173</td>
<td>1.20371</td>
<td>108.25</td>
<td>-130.28878822</td>
</tr>
<tr>
<td></td>
<td>CCSD(T)</td>
<td>1.05527</td>
<td>1.21518</td>
<td>107.98</td>
<td>-130.30975046</td>
</tr>
<tr>
<td>aug-cc-pVQZ</td>
<td>HF</td>
<td>1.02986</td>
<td>1.16468</td>
<td>109.40</td>
<td>-129.85158882</td>
</tr>
<tr>
<td></td>
<td>MP2</td>
<td>1.04924</td>
<td>1.21773</td>
<td>107.77</td>
<td>-130.31997667</td>
</tr>
<tr>
<td></td>
<td>CCSD</td>
<td>1.04979</td>
<td>1.19972</td>
<td>108.35</td>
<td>-130.32035738</td>
</tr>
<tr>
<td></td>
<td>CCSD(T)</td>
<td>1.05331</td>
<td>1.21104</td>
<td>108.10</td>
<td>-130.34262935</td>
</tr>
</tbody>
</table>
central difference method used these energies to formulate an approximation for the second derivatives of the potential energy of HNO with respect to the x- and y-coordinates of each atom. The diagonalization of the 6 x 6 Hessian matrix yielded six eigenvalues, three of which were zero, specifically for the x-translational mode, y-translational mode, and the z-rotational mode. The three non-zero eigenvalues were for the three vibrational modes, which is consistent with the (3N-6) rule. The vibrational eigenvalues were converted to the three harmonic vibrational frequencies. Table 3.1.2 shows the harmonic frequencies obtained from each basis set and computational theory. The first labeled frequency, \( \omega_1 \), is the highest in wavenumbers and the third labeled frequency, \( \omega_3 \), is the lowest, and this notation will be consistent throughout this document.

Just as with the results of optimization, Table 3.1.2 shows that for the vibrational frequencies there is more disagreement between levels of theory than between basis sets. For both basis sets, as theory increases from Hartree Fock, which does not take into account the electron-electron correlation, to MP2, all of the vibrations display a distinctly large decrease of several hundred wavenumbers in harmonic frequency. This large decrease in frequency from Hartree-Fock to MP2 resulted in more agreement to experimental frequencies (Ruzzi and Anderson 2015). This demonstrates the importance of including electron correlation to correctly describe each vibrational behavior.

\( \omega_2 \) and \( \omega_3 \) exhibit an increase of just below 100 cm\(^{-1}\) as the theory changes from MP2 to CCSD. The CCSD(T) frequency values for \( \omega_2 \) and \( \omega_3 \) are between the MP2 and CCSD values. Similar to the lower vibrational frequencies, \( \omega_1 \) shows a decrease as
Table 3.1.2. Harmonic frequency (cm\(^{-1}\)) results for each normal mode using each basis set and theory. These results are from Hessian entries of second derivatives with respect to Cartesian coordinates of the atoms.

<table>
<thead>
<tr>
<th>Basis Set</th>
<th>Theory</th>
<th>(\omega_1)</th>
<th>(\omega_2)</th>
<th>(\omega_3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>aug-cc-pVTZ</td>
<td>HF</td>
<td>3307.3</td>
<td>1934.9</td>
<td>1706.2</td>
</tr>
<tr>
<td></td>
<td>MP2</td>
<td>3031.1</td>
<td>1577.7</td>
<td>1475.8</td>
</tr>
<tr>
<td></td>
<td>CCSD</td>
<td>3003.6</td>
<td>1662.0</td>
<td>1582.7</td>
</tr>
<tr>
<td></td>
<td>CCSD(T)</td>
<td>2950.4</td>
<td>1593.4</td>
<td>1535.7</td>
</tr>
<tr>
<td>aug-cc-pVQZ</td>
<td>HF</td>
<td>3307.1</td>
<td>1939.0</td>
<td>1708.3</td>
</tr>
<tr>
<td></td>
<td>MP2</td>
<td>3037.9</td>
<td>1583.8</td>
<td>1490.2</td>
</tr>
<tr>
<td></td>
<td>CCSD</td>
<td>3018.7</td>
<td>1677.4</td>
<td>1586.8</td>
</tr>
<tr>
<td></td>
<td>CCSD(T)</td>
<td>2964.6</td>
<td>1602.1</td>
<td>1544.2</td>
</tr>
</tbody>
</table>
theory is adjusted from MP2 to CCSD, but with a smaller shift in wavenumbers of less than 30 cm$^{-1}$. Unlike with $\omega_2$ and $\omega_3$, the frequency of $\omega_1$ continues to decrease when coupled-cluster theory considers a perturbative treatment of triple excitations.

The eigenvectors that were calculated for each mode from the diagonalization of the mass-weighted Hessian matrix described the displacement of each atom along the x- and y-directions. To get a general depiction of which vibration was described by which normal mode, multiples of each normal mode were applied by positive and negative magnitudes and the resulting changes in the NH bond length, NO bond length, and the HNO bond angle were noticed. The q1 mode almost entirely described the NH bond length. The q2 and q3 modes, however, had a great influence on both the NO bond length and the HNO bond angle.

### 3.2 Isotope Substitution Effect

The vibrational frequencies with isotopic substitution of $^{15}$N with differing basis sets and theories are listed in Table 3.2.1. All three vibrational modes were expected to be affected by the $^{15}$N substitution, as nitrogen is the central atom of the triatomic molecule and has contribution to the NH stretch, NO stretch, and HNO bend. As expected, Table 3.2.1 shows this trend. Although $\omega_1$ experiences an almost constant decrease with the $^{15}$N substitution, the other modes experience an inconsistent shift depending on computational theory applied. At times $\omega_2$ experiences a larger decrease while $\omega_3$ experiences a lower decrease, and at other times $\omega_2$ experiences a lower decrease while $\omega_3$ experiences a larger decrease. Due to this inconsistent behavior of
Table 3.2.1. Harmonic frequency (cm\(^{-1}\)) results for each normal mode using each basis set and theory for the HNO molecule with the \(^{15}\)N isotopic substitution. These results are from Hessian entries of second derivatives with respect to Cartesian coordinates of the atoms. Values in parenthesis are the frequency shifts from the \(^{1}\)H\(^{14}\)N\(^{16}\)O molecule using the same basis set and theory.

<table>
<thead>
<tr>
<th>Basis Set</th>
<th>Theory</th>
<th>(\omega_1)</th>
<th>(\omega_2)</th>
<th>(\omega_3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>aug-cc-pVTZ</td>
<td>HF</td>
<td>3300.2 (-7.1)</td>
<td>1901.2 (-33.7)</td>
<td>1700.2 (-6.0)</td>
</tr>
<tr>
<td></td>
<td>MP2</td>
<td>3024.3 (-6.8)</td>
<td>1572.7 (-5.1)</td>
<td>1450.0 (-25.8)</td>
</tr>
<tr>
<td></td>
<td>CCSD</td>
<td>2997.0 (-6.6)</td>
<td>1640.2 (-21.8)</td>
<td>1570.5 (-12.1)</td>
</tr>
<tr>
<td></td>
<td>CCSD(T)</td>
<td>2943.9 (-6.5)</td>
<td>1584.4 (-9.0)</td>
<td>1512.5 (-23.1)</td>
</tr>
<tr>
<td>aug-cc-pVQZ</td>
<td>HF</td>
<td>3300.0 (-7.1)</td>
<td>1905.2 (-33.8)</td>
<td>1702.3 (-6.0)</td>
</tr>
<tr>
<td></td>
<td>MP2</td>
<td>3031.1 (-6.8)</td>
<td>1578.2 (-5.6)</td>
<td>1464.6 (-25.6)</td>
</tr>
<tr>
<td></td>
<td>CCSD</td>
<td>3012.1 (-6.5)</td>
<td>1653.7 (-23.8)</td>
<td>1576.3 (-10.6)</td>
</tr>
<tr>
<td></td>
<td>CCSD(T)</td>
<td>2958.1 (-6.5)</td>
<td>1589.9 (-12.2)</td>
<td>1523.8 (-20.3)</td>
</tr>
</tbody>
</table>
these shifts in frequency between $\omega_2$ and $\omega_3$, it is may be beneficial to include a higher level theory until consistency is found. After including a full treatment of triple excitations, as in CCSDT, if frequencies are found to agree between CCSD(T) and CCSDT, this can assure us that CCSD(T) level of theory is sufficient.

The vibrational frequencies with isotopic substitution of $^{18}$O are listed in Table 3.2.2. As stated previously, the NH stretch was most largely attributed to arise from the q1 mode, while q2 and q3 were both found to a great contribution to both the NO stretch and the HNO bend. As the NO stretch and HNO bend both involve oxygen directly, the $^{18}$O substitution was predicted to have the greatest influence on the q2 and q3 modes. This expected behavior is shown in Table 3.2.2, however the magnitude of shifts are inconsistent, as was noted earlier with the nitrogen substitution.

The resulting frequencies from the $^2$H substitution in the HNO molecule are shown in Table 3.2.3. Hydrogen is major component in both the HN stretch and the HNO bend. Since the HN stretch is most affected by the q1 mode, the vibrational frequency of the q1 mode is expected to be largely altered by the $^2$H substitution. The HNO bend, however, was shown to be largely affected by both the q2 and q3 modes. As seen in Table 3.2.3, the highest frequency is now nearly 800 cm$^{-1}$ lower than highest frequency of the non-isotopically substituted molecule, and the lowest frequency is now nearly 300-400 cm$^{-1}$ lower than the lowest frequency of the non-isotopically substituted molecule. It is not clear which of the q2 and q3 modes from the non-isotopically substituted molecule resulted in the lowest frequency with the $^2$H substitution. If identification of the modes is an interest in the future, the HNO molecule should be
Table 3.2.2. Harmonic frequency (cm\(^{-1}\)) results for each normal mode using each basis set and theory for the HNO molecule with the \(^{18}\)O isotopic substitution. These results are from Hessian entries of second derivatives with respect to Cartesian coordinates of the atoms. Values in parenthesis are the frequency shifts from the \(^{1}\)H\(^{14}\)N\(^{16}\)O molecule using the same basis set and theory.

<table>
<thead>
<tr>
<th>Basis Set</th>
<th>Theory</th>
<th>(\omega_1)</th>
<th>(\omega_2)</th>
<th>(\omega_3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>aug-cc-pVTZ</td>
<td>HF</td>
<td>3307.1 (-0.2)</td>
<td>1883.2 (-51.7)</td>
<td>1701.4 (-4.8)</td>
</tr>
<tr>
<td></td>
<td>MP2</td>
<td>3030.9 (-0.2)</td>
<td>1563.2 (-14.5)</td>
<td>1445.7 (-30.0)</td>
</tr>
<tr>
<td></td>
<td>CCSD</td>
<td>3003.3 (-0.3)</td>
<td>1619.0 (-43)</td>
<td>1577.0 (-5.6)</td>
</tr>
<tr>
<td></td>
<td>CCSD(T)</td>
<td>2950.1 (-0.3)</td>
<td>1571.5 (-21.9)</td>
<td>1511.5 (-24.2)</td>
</tr>
<tr>
<td>aug-cc-pVQZ</td>
<td>HF</td>
<td>3306.9 (-0.2)</td>
<td>1887.2 (-51.8)</td>
<td>1703.4 (-4.8)</td>
</tr>
<tr>
<td></td>
<td>MP2</td>
<td>3037.7 (-0.2)</td>
<td>1568.0 (-15.8)</td>
<td>1461.0 (-29.2)</td>
</tr>
<tr>
<td></td>
<td>CCSD</td>
<td>3018.4 (-0.3)</td>
<td>1632.6 (-44.8)</td>
<td>1582.5 (-4.4)</td>
</tr>
<tr>
<td></td>
<td>CCSD(T)</td>
<td>2964.3 (-0.3)</td>
<td>1574.1 (-28)</td>
<td>1525.5 (-18.7)</td>
</tr>
</tbody>
</table>
Table 3.2.3. Harmonic frequency (cm\(^{-1}\)) results for each normal mode using each basis set and theory for the HNO molecule with the \(^2\)H isotopic substitution. These results are from Hessian entries of second derivatives with respect to Cartesian coordinates of the atoms. Values in parenthesis are the frequency shifts from the \(^1\)H\(^{14}\)N\(^{16}\)O molecule using the same basis set and theory.

<table>
<thead>
<tr>
<th>Basis Set</th>
<th>Theory</th>
<th>(\omega_1)</th>
<th>(\omega_2)</th>
<th>(\omega_3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>aug-cc-pVTZ</td>
<td>HF</td>
<td>2416.6 (-890.5)</td>
<td>1934.2 (-0.7)</td>
<td>1289.9 (-416.2)</td>
</tr>
<tr>
<td></td>
<td>MP2</td>
<td>2217.4 (-813.7)</td>
<td>1498.4 (-79.4)</td>
<td>1169.7 (-306.1)</td>
</tr>
<tr>
<td></td>
<td>CCSD</td>
<td>2196.4 (-807.2)</td>
<td>1653.5 (-8.5)</td>
<td>1198.7 (-394.0)</td>
</tr>
<tr>
<td></td>
<td>CCSD(T)</td>
<td>2158.1 (-792.3)</td>
<td>1563.1 (-30.3)</td>
<td>1178.4 (-357.3)</td>
</tr>
<tr>
<td>aug-cc-pVQZ</td>
<td>HF</td>
<td>2416.6 (-890.5)</td>
<td>1938.3 (-0.6)</td>
<td>1291.6 (-416.7)</td>
</tr>
<tr>
<td></td>
<td>MP2</td>
<td>2222.3 (-815.6)</td>
<td>1514.4 (-69.4)</td>
<td>1173.4 (-316.8)</td>
</tr>
<tr>
<td></td>
<td>CCSD</td>
<td>2207.1 (-811.6)</td>
<td>1670.7 (-6.8)</td>
<td>1201.4 (-385.4)</td>
</tr>
<tr>
<td></td>
<td>CCSD(T)</td>
<td>2168.4 (-796.3)</td>
<td>1580.3 (-21.8)</td>
<td>1179.4 (-364.8)</td>
</tr>
</tbody>
</table>
studied with several small incremental hydrogen mass changes until reaching the $^2$H mass. Then, the observation of the smaller frequency shifts with each mass adjustment will help understand the frequency behavior each mode experiences.

3.3 Internal Coordinates

Changing the entries of the Hessian matrix from second derivatives of the potential energy with respect to two Cartesian coordinates to matrix entries expressed in terms of derivatives with respect to the internal coordinates reduces the computational time substantially, as there are far more deviations to consider when considering the six Cartesian coordinates than when considering only three internal coordinates. The three internal coordinates were the NH bond length, NO bond length, and cosine of the molecular angle. Table 3.3.1 lists the frequencies of the HNO molecule and the frequencies of the molecule’s isotopic substitutions. The largest disagreement from the Hessian resultant frequencies calculated using internal coordinates compared to using Cartesian coordinates is less than 3.0 cm$^{-1}$. This indicates a good agreement of frequencies between internal and Cartesian coordinates, as much larger differences in frequencies were noticed earlier when studying the effect of basis sets and computational theories with Cartesian coordinates alone. The agreement of frequencies from using internal coordinates compared to using Cartesian coordinates for the Hessian calculation, along with the benefit of four times reduction of computational cost, motivates us to consider future work with the Hessian matrix to be from computations of geometries adjusted along internal coordinates in place of Cartesian coordinates.
Table 3.3.1. Harmonic frequency (cm$^{-1}$) results for each normal mode considering internal coordinates, using aug-cc-pVQZ and CCSD(T) for the HNO molecule without isotopic substitution, and for the molecule with the $^2$H isotopic substitution, with the $^{15}$N isotopic substitution, and with the $^{18}$O isotopic substitution. These results are from Hessian entries of second derivatives with respect to internal coordinates of the atoms. Values in parenthesis are the frequency shifts from the same isotopes using aug-cc-pVQZ and CCSD(T) with considering Cartesian coordinates.

<table>
<thead>
<tr>
<th></th>
<th>$\omega_1$</th>
<th>$\omega_2$</th>
<th>$\omega_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^1$H$^{14}$N$^{16}$O</td>
<td>2963.0 (-1.6)</td>
<td>1600.2 (-1.9)</td>
<td>1542.2 (-2.0)</td>
</tr>
<tr>
<td>$^2$H$^{14}$N$^{16}$O</td>
<td>2167.4 (-1.0)</td>
<td>1579.7 (-0.6)</td>
<td>1176.7 (-2.7)</td>
</tr>
<tr>
<td>$^1$H$^{15}$N$^{16}$O</td>
<td>2956.5 (-1.6)</td>
<td>1587.6 (-2.3)</td>
<td>1522.4 (-1.4)</td>
</tr>
<tr>
<td>$^1$H$^{14}$N$^{18}$O</td>
<td>2962.8 (-1.6)</td>
<td>1571.2 (-2.9)</td>
<td>1524.5 (-1.0)</td>
</tr>
</tbody>
</table>
3.4 Double Harmonic Potential Energy Functions

It is assumed in the double harmonic approximation that potential energies that are functions of normal modes can be sufficiently described by a quadratic function. The coefficient leading the normal mode is the harmonic force constant. Manipulation of the harmonic frequency that was retrieved from diagonalization of the Hessian matrix yields the harmonic force constant. The optimal energy and force constant of each normal mode would create the quadratic potential energy function of each normal mode.

Figures 3.4.1, 3.4.2, and 3.4.3 show data points for \textit{ab initio} potential energies resulting from the geometrical changes from the HNO optimal geometry by normal modes 1, 2, and 3, respectively. As described above, to model the double harmonic potential energy certain parameters are already set, specifically the optimal energy and the harmonic force constant. For each figure, the line in red is a best fit sixth-power polynomial function that best describes the trend set by the collection of the individual potential energies. To see the quantitative influence of the higher polynomials in describing the trend of the collective potential energies, the sixth-power potential energy expression is given in each figure.

Figure 3.4.1 shows the potential energy behavior for the q1 mode, and this mode, as described earlier, predominately describes the HN bond vibration. By visual inspection alone it can be seen that the behavior of the energies would not be explained well by a symmetric quadratic function. This indicates that the next several orders beyond the second order are important to accurately describe the potential energy function.
Figure 3.4.1. Aug-cc-pVQZ, CCSD(T) ab initio potential energies vs. q1 mode for the q1 mode resultant from internal coordinate Hessian matrix. The sixth order polynomial fit is an expansion to the double harmonic potential energy function.
Figure 3.4.2. Aug-cc-pVQZ, CCSD(T) \textit{ab initio} potential energies vs. q2 mode for the q2 mode resultant from internal coordinate Hessian matrix. The sixth order polynomial fit is an expansion to the double harmonic potential energy function.
Figure 3.4.3. Aug-cc-pVQZ, CCSD(T) ab initio potential energies vs. q3 mode for the q3 mode resultant from internal coordinate Hessian matrix. The sixth order polynomial fit is an expansion to the double harmonic potential energy function.
The quantitative contributions of higher orders are not as significant in the potential energy functions which describe the q2 and q3 modes, given in Figures 3.4.2 and 3.4.3, respectively. However it is apparent from a visual inspection of both of the potential energy behaviors relative to their normal modes that terms beyond the second order are necessary to correctly describe the functions.

### 3.5 Double Harmonic Dipole Moment Functions

The transition dipole moment is made up x- and y-components of the dipole moment functions of normal modes. The double harmonic approximation assumes a linear function to adequately describe the behavior of these dipole moments.

The x-component of the dipole moments with geometrical changes of q1, q2, and q3 modes are displayed in Figures 3.5.1, 3.5.2, and 3.5.3, respectively. The red line is a fifth-power function best fit to the *ab initio* data of the x-component dipole moments. It is both visually and quantitatively clear that the x-component dipole moments for the q1 and q3 modes, especially, have a great contribution from the higher powers.

The y-component of the dipole moments with geometrical changes of q1, q2, and q3 modes, displayed in Figures 3.5.4, 3.5.5, and 3.5.6, respectively, give a similar trend as that described for the x-component dipole moment, except the y-component dipole moment for q2 shows an especially stronger non-linear behavior than for the x-component dipole moment for q2.
Figure 3.5.1. Aug-cc-pVQZ, CCSD(T) \textit{ab initio} x-component of dipole moment vs. q1 mode for the q1 mode resultant from internal coordinate Hessian matrix. The fifth order polynomial fit is an expansion to the double harmonic dipole moment function.
Figure 3.5.2. Aug-cc-pVQZ, CCSD(T) \textit{ab initio} x-component of dipole moment vs. q2 mode for the q2 mode resultant from internal coordinate Hessian matrix. The fifth order polynomial fit is an expansion to the double harmonic dipole moment function.
Figure 3.5.3. Aug-cc-pVQZ, CCSD(T) \textit{ab initio} x-component of dipole moment vs. q3 mode for the q3 mode resultant from internal coordinate Hessian matrix. The fifth order polynomial fit is an expansion to the double harmonic dipole moment function.
Figure 3.5.4. Aug-cc-pVQZ, CCSD(T) *ab initio* y-component of dipole moment vs. q1 mode for the q1 mode resultant from internal coordinate Hessian matrix. The fifth order polynomial fit is an expansion to the double harmonic dipole moment function.
Figure 3.5.5. Aug-cc-pVQZ, CCSD(T) ab initio y-component of dipole moment vs. q2 mode for the q2 mode resultant from internal coordinate Hessian matrix. The fifth order polynomial fit is an expansion to the double harmonic dipole moment function.
Figure 3.5.6. Aug-cc-pVQZ, CCSD(T) ab initio y-component of dipole moment vs. q3 mode for the q3 mode resultant from internal coordinate Hessian matrix. The fifth order polynomial fit is an expansion to the double harmonic dipole moment function.
Chapter 4

Anharmonicity and Coupling
4.1 Introduction

The potential energy and dipole moment behaviors of each normal mode were graphically shown in Chapter 3 to not be described sufficiently well by the double harmonic approximation. This chapter explores expanding the potential energy function beyond a quadratic function and the dipole moment function beyond a linear function, and including these expanded functions in the determination of the transition dipole moment. The inclusion of these expanded functions is known as considering effects of both mechanical and electrical anharmonicity. Mechanical anharmonicity is the potential energy anharmonicity, and electrical anharmonicity is the dipole moment anharmonicity. This chapter will also look into coupling of normal modes.

4.1.1 Complete Potential Energy

The true potential energy of the HNO molecule is a system of contributions from all three vibrational normal modes. The double harmonic approximation has a very simple potential energy equation. Below, $V_{opt}$ represents the minimal energy found at the optimal geometry, where $q_1 = q_2 = q_3 = 0$.

$$V_{DHA}(q_1 q_2 q_3) = V_{opt} + \frac{\hbar \omega_1}{2} q_1^2 + \frac{\hbar \omega_2}{2} q_2^2 + \frac{\hbar \omega_3}{2} q_3^2$$

The harmonic frequencies were found from diagonalizing the Hessian matrix. The computational cost to formulate this equation is near equivalent to the sum of the cost of individual ab initio calculations required to formulate the Hessian matrix. As mentioned earlier, computing the Hessian matrix with internal coordinates reduces the computational cost by 75% when compared to Cartesian coordinates. The Cartesian
coordinates require 72 \textit{ab initio} calculations, whereas using internal coordinates requires only 18 \textit{ab initio} calculations.

The full potential energy, however, is composed of terms higher than quadratic for each individual mode. Including mechanical anharmonic contributions from each normal mode extends the potential energy equation to include individual mode contributions beyond the second power.

\[ V_{DHA+ANHARM}(q_1q_2q_3) = V_{DHA}(q_1q_2q_3) + k_{111}q_1^3 + k_{222}q_2^3 + k_{333}q_3^3 + k_{1111}q_1^4 + \cdots \]

Here, the coefficients leading the individual normal modes represent the powers to which the normal mode was applied. For example, \( k_{111} \) represents the coefficient leading the \( q_1 \) mode to the third power.

The full potential energy equation also includes an additional important concept that is ignored in the double harmonic approximation, which is the coupling between normal modes. The mechanical coupling of two or more modes will affect the potential energy of the molecule, with differing effects that depend on the modes that are coupled. Generally, modes are more likely to couple the closer the vibrational frequencies of the modes are to one another.

\[ V_{DHA+ANHARM+COUPLING}(q_1q_2q_3) \]

\[ = V_{DHA+ANHARM}(q_1q_2q_3) + k_{112}q_1^2q_2 + k_{122}q_1q_2^2 + k_{113}q_1^2q_3 + k_{133}q_1q_3^2 + k_{223}q_2^2q_3 + k_{233}q_2q_3^2 + k_{1112}q_1^2q_2^2 + \cdots \]
4.1.2 Complete Dipole Moment

The dipole function for each Cartesian component, \( \rho \), assumed by the double harmonic approximation is limited to a first power.

\[
\mu_{DHA,\rho}(q_1q_2q_3) = \mu_{opt} + c_1q_1 + c_2q_2 + c_3q_3
\]

Moving beyond this approximation and including electrical anharmonicity leads to the individual normal modes contributing higher powers to the dipole function.

\[
\mu_{DHA+ANHARM,\rho}(q_1q_2q_3) = \mu_{DHA,\rho}(q_1q_2q_3) + c_{11}q_1^2 + c_{22}q_2^2 + c_{33}q_3^2 + c_{111}q_1^3 + \cdots
\]

And finally, including electrical coupling between the normal modes gives the full dipole function for each Cartesian component, \( \rho \).

\[
\mu_{DHA+ANHARM+COUPLING,\rho}(q_1q_2q_3) = \mu_{DHA+ANHARM,\rho}(q_1q_2q_3) + c_{12}q_1q_2 + c_{13}q_1q_3 + c_{23}q_2q_3 + c_{112}q_1^2q_2 + \cdots
\]

4.2 Anharmonicity

The anharmonic wavefunction (\( \psi_{anhar} \)) for each vibrational level consists of a linear combination of harmonic oscillator wavefunctions (\( \phi_{har} \)) at vibrational states \( \nu=0 \) through \( \nu=n \). Due to Anderson’s kinetic infrared studies specializing specifically in the \( i=0 \) to \( j=1 \) transitions, we only considered the anharmonic wavefunctions for the \( \nu=0 \) and \( \nu=1 \) vibrational states.

\[
\psi_{anhar,\nu=0}(q) = b_0\phi_{har,\nu=0}(q) + b_1\phi_{har,\nu=1}(q) + \cdots + b_n\phi_{har,\nu=n}(q)
\]

\[
\psi_{anhar,\nu=1}(q) = c_0\phi_{har,\nu=0}(q) + c_1\phi_{har,\nu=1}(q) + \cdots + c_n\phi_{har,\nu=n}(q)
\]
The $b$ coefficients represent the contributions of each harmonic oscillator vibrational level function needed for defining the anharmonic wavefunction at $v=0$, and the $c$ coefficients represent the same but for defining the anharmonic wavefunction at $v=1$. The sum of the coefficients squared is equal to one, and the value of each coefficient squared represents the weighted contribution from each harmonic wavefunction towards the anharmonic wavefunction.

For the following anharmonic work, we used expanded potential energy functions to the sixth power. Lower polynomial expansions were also tested but each next higher expansion resulted in a more accurate fit to the \textit{ab initio} results. The sixth order functions’ mean absolute deviation values were $9.8 \times 10^{-4}$ Ha for $q_1$, $9.0 \times 10^{-6}$ Ha for $q_2$, and $2.7 \times 10^{-5}$ Ha for $q_3$. As with the harmonic potential energy functions in Chapters 2 and 3, the optimal energy and Hessian-derived harmonic frequency converted to the second order force constant were used to make up the harmonic portion of the potential energy function of each mode. The expanded dipole moment functions we used were to the fifth power. As mentioned previously, we considered harmonic wavefunctions of the ground vibrational state and up to and including the third harmonic vibrational state.

\subsection*{4.2.1 Electrical Anharmonicity}

We first considered contributions from electrical anharmonicity alone. Since mechanical anharmonicity was not yet considered, only the harmonic wavefunction at the vibrational state of the anharmonic wavefunction will contribute to the anharmonic wavefunction. That is for $\psi_{\text{anhar}_v=0}(q)$, only $\phi_{\text{harm}_v=0}(q)$ will contribute, and similarly for $\psi_{\text{anhar}_v=1}(q)$, only $\phi_{\text{harm}_v=1}(q)$ will contribute. Therefore $b_0$ and $c_1$ will have full
weight on the $\psi_{anharm,v=0}(q)$ and $\psi_{anharm,v=1}(q)$ anharmonic wavefunctions, respectively. Since the potential is still harmonic, a harmonic Hamiltonian is computed.

With considering electrical anharmonicity, the dipole moment function can be treated as a Taylor expansion.

$$\mu_\rho(q) = \mu_\rho(q)_{q=0} + \frac{q}{1!} \frac{\partial \mu_\rho(q)}{\partial q} \Bigg|_{q=0} + \frac{q^2}{2!} \frac{\partial^2 \mu_\rho(q)}{\partial q^2} \Bigg|_{q=0} + \cdots + \frac{q^n}{n!} \frac{\partial^n \mu_\rho(q)}{\partial q^n} \Bigg|_{q=0}$$

Now the transition dipole moment becomes more intricate than earlier with the double harmonic approximation. Assuming that we allow both the x and y dipole moment functions to include up to nth order contributions, and considering harmonic contributions up to the vibrational state of 3, the transition moment squared becomes the following.

$$|M_{ji}|^2 = \sum_\rho \sum_{i=0}^{3} \sum_{j=0}^{3} b_i \ast c_j \ast \left[ (\mu_\rho)_{q=0} \langle i|j \rangle + \frac{(\partial \mu_\rho)}{1!} \frac{\partial q}{\partial q} q=0 \langle i|q|j \rangle + \cdots + \frac{(\partial^n \mu_\rho)}{n!} \frac{\partial q^n}{\partial q^n} q=0 \langle i|q^n|j \rangle \right]^2$$

The integrals up to $\langle i|q^n|j \rangle$ were simplified by defining the $q$ operator using ladder operators. Using raising and lowering operators resulted in each integral becoming a constant multiplied by a much simpler integral of the form $\langle i|m \rangle$ where m represented some additive of j.
Since these harmonic wavefunctions are orthonormal to each other, the integrals result in a value of 1 or 0 using Kronecker delta. The molar absorptivities of each normal mode were calculated using this transition dipole moment, along with the harmonic frequency.

### 4.2.2 Electrical and Mechanical Anharmonicity

Next we included both electrical and mechanical anharmonicity. The combinations of the harmonic components of the Hamiltonian matrix with the anharmonic components gave us the anharmonic vibrational state eigenvalues and the corresponding eigenvector. The eigenvector corresponding to the lowest energy eigenvalue gave us the contribution of each harmonic wavefunction for the ground state v=0 anharmonic wavefunction. Similarly, the eigenvector corresponding to the second lowest eigenvalue gave us the contribution of each harmonic wavefunction for the v=1 anharmonic wavefunction. As described earlier, the linear combination of these coefficients multiplied by the corresponding harmonic wavefunction gave us the anharmonic wavefunction for the particular vibrational level.
Table 4.2.1 lists the resultant b and c eigenvectors for each normal mode when considering contributions from the ground vibrational state (v=0) up to and including the third excited vibrational state of v=3. As seen for each mode, the anharmonic wavefunction for the ground vibrational state has the largest coefficient coming from the v=0 harmonic vibrational state, which indicates the v=0 harmonic wavefunction has the most contribution to the ground state anharmonic wavefunction. There is a considerable contribution from each of the excited harmonic wavefunctions as well, with the largest of these from the v=1 harmonic wavefunction. The highest contribution from the v=1 harmonic wavefunction towards the anharmonic ground state wavefunction comes from the q1 mode.

The anharmonic wavefunction for the first excited vibrational state is mostly made up of the v=1 vibrational state harmonic wavefunction. The largest contribution from other harmonic wavefunctions comes from the q1 mode. The largest anharmonic effects for both v=0 and v=1 anharmonic wavefunctions come from the q1 normal mode. Table 4.2.2 shows the $b_i^*c_j$ multiplied by the corresponding integral that contributes to $|M_{ji}|^2$. As expected $b_0^*c_1$ has the largest contribution towards the transition moment for the anharmonic wavefunctions, but several anharmonic transitions given by other $b_i^*c_j$ combinations make large contributions of approximately 10% that of $b_0^*c_1$.

See Appendix 1 for the Maple code that calculated the eigenvectors for the v=0 and v=1 anharmonic wavefunction, and Appendix 2 for the Maple code that used the calculated eigenvectors and the calculated v=0 to v=1 anharmonic vibrational frequency to calculate the square of the transition dipole function.
Table 4.2.1. This table lists, for each mode, the contributions from each harmonic wavefunction in the linear combination of harmonic wavefunctions to form the anharmonic wavefunctions. The harmonic frequencies required for these calculations came from the internal coordinate Hessian matrix. *Ab initio* results came from aug-cc-pVQZ and CCSD(T).

<table>
<thead>
<tr>
<th>Anharmonic vibrational state</th>
<th>Harmonic vibrational state</th>
<th>q1</th>
<th>q2</th>
<th>q3</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>0.9913</td>
<td>0.9988</td>
<td>0.9999</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>0.1264</td>
<td>0.0470</td>
<td>-0.0158</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>0.0147</td>
<td>0.0026</td>
<td>0.0001</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>0.0335</td>
<td>0.0127</td>
<td>-0.0042</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Anharmonic vibrational state</th>
<th>Harmonic vibrational state</th>
<th>q1</th>
<th>q2</th>
<th>q3</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>-0.1255</td>
<td>-0.0471</td>
<td>0.0158</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>0.9323</td>
<td>0.9902</td>
<td>0.9989</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>0.3355</td>
<td>0.1313</td>
<td>-0.0443</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>0.0492</td>
<td>0.0090</td>
<td>0.0007</td>
</tr>
</tbody>
</table>
Table 4.2.2. This table lists, for the q1 mode, the integral of the anharmonic wavefunctions with the x- and y-components of the dipole moment operator, multiplied by the products of $b_i$ and $c_j$. The harmonic frequencies required for these calculations came from the internal coordinate Hessian matrix. *Ab initio* results came from aug-cc-pVQZ and CCSD(T).

<table>
<thead>
<tr>
<th>cj</th>
<th>bi</th>
<th>0</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td></td>
<td>-6.10E-04</td>
<td>-4.21E-04</td>
<td>-1.26E-05</td>
<td>1.14E-06</td>
<td>x</td>
</tr>
<tr>
<td></td>
<td></td>
<td>8.61E-04</td>
<td>6.17E-04</td>
<td>1.78E-05</td>
<td>-3.00E-07</td>
<td>y</td>
</tr>
<tr>
<td>1</td>
<td></td>
<td>2.46E-02</td>
<td>1.71E-03</td>
<td>5.10E-04</td>
<td>3.60E-04</td>
<td>x</td>
</tr>
<tr>
<td></td>
<td></td>
<td>-3.59E-02</td>
<td>-2.41E-03</td>
<td>-7.54E-04</td>
<td>-5.06E-04</td>
<td>y</td>
</tr>
<tr>
<td>2</td>
<td></td>
<td>2.27E-03</td>
<td>1.57E-03</td>
<td>1.18E-04</td>
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<td></td>
<td>-3.19E-03</td>
<td>-2.33E-03</td>
<td>-1.66E-04</td>
<td>-7.53E-04</td>
<td>y</td>
</tr>
<tr>
<td>3</td>
<td></td>
<td>-1.33E-05</td>
<td>7.17E-05</td>
<td>3.25E-05</td>
<td>5.41E-05</td>
<td>x</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3.48E-06</td>
<td>-1.01E-04</td>
<td>-4.86E-05</td>
<td>-7.60E-05</td>
<td>y</td>
</tr>
</tbody>
</table>
To test the maximum vibrational state for the linear combinations of harmonic wavefunctions, we varied the maximum vibrational state for each mode. The ν=0 to ν=1 anharmonic vibrational frequencies are listed in Table 4.2.3. Modes q2 and q3 were shown to converge using a maximum vibrational state of 5. Mode q1 was still changing at this vibrational state. We continued increased the maximum vibrational state for q1 until reaching maximum of ν=9, by which point the frequency had changed from the ν=8 by only 0.32 cm⁻¹. For all of the normal modes, the anharmonic ν=0 to ν=1 frequencies with the above maximum vibrational states are lower than the harmonic frequencies, as shown in Table 4.2.4. The biggest shift in frequency is from q1 with a decrease of 176.5 cm⁻¹, whereas the smallest decrease of less than 1 cm⁻¹ is from the q3 mode.

Our calculated molar absorptivities, considering double harmonic approximation and differing amounts of anharmonicities, are given in Table 4.2.5. This table also includes, for comparison, the molar absorptivities of Lee which considered the double harmonic approximation with the TZ2P basis set (Lee 1993). Our double harmonic molar absorptivities differ greatly from Lee’s double harmonic values, which must be mostly due to the difference in basis sets. This large difference shows the importance of performing calculations with our much larger aug-cc-pVQZ basis set compared to Lee’s TZ2P basis set. Considering the electrical anharmonicity alone gives only a slightly different molar absorptivity than with our use of the double harmonic approximation, as the difference in molar absorptivity values are only around ±1 km/mol. The molar absorptivity from considering both mechanical and electrical anharmonicity resulted in the largest difference for q1 and q2 modes compared to our double harmonic
Table 4.2.3. Anharmonic frequency (cm$^{-1}$) of each mode, considering mechanical and electrical anharmonicity with different amounts of maximum vibrational states for the harmonic wavefunctions. *Ab initio* results came from aug-cc-pVQZ and CCSD(T).

<table>
<thead>
<tr>
<th>Maximum v</th>
<th>$\nu_1$</th>
<th>$\nu_2$</th>
<th>$\nu_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3253.28</td>
<td>1616.91</td>
<td>1544.78</td>
</tr>
<tr>
<td>2</td>
<td>2861.98</td>
<td>1588.99</td>
<td>1541.75</td>
</tr>
<tr>
<td>3</td>
<td>2857.90</td>
<td>1589.51</td>
<td>1541.83</td>
</tr>
<tr>
<td>4</td>
<td>2814.82</td>
<td>1586.36</td>
<td>1541.52</td>
</tr>
<tr>
<td>5</td>
<td>2793.66</td>
<td>1586.14</td>
<td>1541.51</td>
</tr>
<tr>
<td>6</td>
<td></td>
<td></td>
<td>2790.60</td>
</tr>
<tr>
<td>7</td>
<td>2788.15</td>
<td></td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>2786.86</td>
<td></td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>2786.54</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table 4.2.4. Anharmonic frequency (cm\(^{-1}\)) of each mode, considering mechanical and electrical anharmonicity. Values in parenthesis is the difference of the anharmonic frequency from the harmonic frequency for the v=0 to v=1 transition. Experimental frequencies are listed for comparison. The harmonic frequencies required for these calculations came from the internal coordinate Hessian matrix. \textit{Ab initio} results came from aug-cc-pVQZ and CCSD(T).

<table>
<thead>
<tr>
<th>Mechanical and Electrical Anharmonicity (q1: vmax=9; q2,q3: vmax=5)</th>
<th>q1</th>
<th>q2</th>
<th>q3</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\Delta) from Harmonic Potential</td>
<td>2786.5</td>
<td>1586.1</td>
<td>1541.5</td>
</tr>
<tr>
<td>Experiment (Ruzi and Anderson 2015)</td>
<td>2694.5</td>
<td>1563.3</td>
<td>1500.9</td>
</tr>
<tr>
<td>Experiment (Johns, McKellar et al. 1983)</td>
<td>2684.0</td>
<td>1565.4</td>
<td>1500.8</td>
</tr>
<tr>
<td>Experiment (Jacox and Milligan 1973)</td>
<td>2717.0</td>
<td>1563.5</td>
<td>1505.0</td>
</tr>
</tbody>
</table>
Table 4.2.5. Molar Absorptivity (km/mol) of each mode. The anharmonic calculations specify maximum vibrational state of harmonic wavefunctions that were considered.

<table>
<thead>
<tr>
<th></th>
<th>q1</th>
<th>q2</th>
<th>q3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lee</td>
<td>126</td>
<td>43</td>
<td>17</td>
</tr>
<tr>
<td>Double Harmonic</td>
<td>107.46</td>
<td>59.69</td>
<td>4.32</td>
</tr>
<tr>
<td>Electrical Anharmonicity (q1,q2,q3: vmax=3)</td>
<td>106.39</td>
<td>60.54</td>
<td>5.02</td>
</tr>
<tr>
<td>Mechanical &amp; Electrical Anharmonicity (q1,q2,q3: vmax=3)</td>
<td>136.39</td>
<td>58.54</td>
<td>4.73</td>
</tr>
<tr>
<td>Mechanical &amp; Electrical Anharmonicity (q1: vmax=9; q2,q3: vmax=5)</td>
<td>137.69</td>
<td>58.44</td>
<td>4.73</td>
</tr>
</tbody>
</table>
calculations. This large change in molar absorptivity values demonstrates the importance of including anharmonic effects for the vibrational analysis of the HNO molecule. Including larger harmonic vibrational states had a small but still important impact on all three modes, where the most impacted mode was mode 1.

Anderson measures the ratios of the integrated intensities of the observed vibrational infrared peaks, which are equal to the ratio of the vibrational molar absorptivities. Table 4.2.6 lists theoretical ratios from the molar absorptivities of mode 2 to mode 1 and of mode 3 to mode 1 from the molar absorptivities listed in Table 4.2.5, and also lists Anderson’s experimental ratios for comparison (Anderson 2014). Our work has resulted in ratios much closer to Anderson’s experimental work. Our anharmonic molar absorptivity ratios still are in need of improvement, which highlights the importance to consider coupling of normal modes.

4.3 Coupling

This chapter so far has discussed and explored the effects on frequency, eigenvectors, potential energy functions and dipole moment functions, and molar absorptivities with inclusion of anharmonic effects. The last topic we will briefly consider is the coupling of two or more normal modes. We explored the coupling between two modes. Figures 4.3.1, 4.3.2, and 4.3.3 show contour plots consisting of MP2, aug-cc-pVTZ potential energies of q1 with q2 coupling, q1 with q3 coupling, and q2 with q3 coupling, respectively. For this analysis only mechanical coupling was considered, and in the future electrical coupling will also need to be investigated for the HNO molecule. For each point on the potential energy graphs, the optimal HNO geometry was altered
Table 4.2.6. Molar absorptivity ratios, which are equal to the relative integrated intensities from an infrared spectrum.

<table>
<thead>
<tr>
<th></th>
<th>$v_2/v_1$</th>
<th>$v_3/v_1$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lee</td>
<td>0.341</td>
<td>0.134</td>
</tr>
<tr>
<td>Double Harmonic</td>
<td>0.555</td>
<td>0.040</td>
</tr>
<tr>
<td>Electrical Anharmonicity ($q_1,q_2,q_3$: $v_{max}=3$)</td>
<td>0.569</td>
<td>0.047</td>
</tr>
<tr>
<td>Mechanical &amp; Electrical Anharmonicity ($q_1,q_2,q_3$: $v_{max}=3$)</td>
<td>0.429</td>
<td>0.035</td>
</tr>
<tr>
<td>Mechanical &amp; Electrical Anharmonicity ($q_1$: $v_{max}=9$; $q_2,q_3$: $v_{max}=5$)</td>
<td>0.424</td>
<td>0.034</td>
</tr>
<tr>
<td>Anderson - Experimental</td>
<td>0.694</td>
<td>0.018</td>
</tr>
</tbody>
</table>
Figure 4.3.1. Potential energies contour plot of q1 vs. q2. *Left graph:* Full potential energy curve from the contributions of q1 and q2. Each line is 0.003 Ha apart. The higher red character of a line indicates a lower energy, and the higher blue character of a line indicates a higher energy. Spacing between lines is 0.003 Ha. *Right graph:* Coupling contributions alone to the potential energy. The higher red character of a line indicates a lowering of the energy, and the higher blue character indicates a raising of the energy. Spacing between lines is 0.0003 Ha. Energies are resultant from *ab initio* calculations with aug-cc-pVTZ, MP2.
Figure 4.3.2. Potential energies contour plot of $q_1$ vs. $q_3$. *Left graph:* Full potential energy curve from the contributions of $q_1$ and $q_3$. Each line is 0.003 Ha apart. The higher red character of a line indicates a lower energy, and the higher blue character of a line indicates a higher energy. Spacing between lines is 0.003 Ha. *Right graph:* Coupling contributions alone to the potential energy. The higher red character of a line indicates a lowering of the energy, and the higher blue character indicates a raising of the energy. Spacing between lines is 0.003 Ha. Energies are resultant from *ab initio* calculations with aug-cc-pVTZ, MP2.
Figure 4.3.3. Potential energies contour plot of q2 vs. q3. Left graph: Full potential energy curve from the contributions of q2 and q3. Each line is 0.003 Ha apart. The higher red character of a line indicates a lower energy, and the higher blue character of a line indicates a higher energy. Spacing between lines is 0.0003 Ha. Right graph: Coupling contributions alone to the potential energy. The higher red character of a line indicates a lowering of the energy, and the higher blue character indicates a raising of the energy. Spacing between lines is 0.0003 Ha. Energies are resultant from ab initio calculations with aug-cc-pVTZ, MP2.
by displacements along both normal modes before computing the potential energy of the new geometry.

The left graph in each of these figures show the behavior of the true potential energy, which has contributions from the harmonic quadratic force constant, the anharmonic effects, and possible coupling effects. These figures considered up to the fourth power of anharmonic and coupling contributions. The graph on the right subtracts the harmonic and anharmonic contributions, and any remaining effects to the potential energy are from the coupling contributions. The higher red character of a line indicates the coupling contributes a lowering of the potential energy, and the higher blue character of a line indicates the coupling contributes a raising of the energy. It is clear from these graphs that coupling is occurring from each combination of two normal modes. Future work can include a similar analysis to study the coupling between all three normal modes. Future work can also study the coupling at higher powers, as well as at different basis sets and theories. Including coupling contributions results in understanding more of the true behavior of these normal modes and should lead to more agreement between the theoretical molar absorptivity ratios and Anderson’s experimental ratios.
Chapter 5

Conclusions and Future Work
5.1 Importance of Work

For Anderson to correctly understand the results of his experimental work with the *para*-hydrogen matrix doped with NO radicals and the reactions through which HNO molecules and NOH molecules are formed, accurate molar absorptivities for each HNO vibration are needed. Currently the only available HNO molar absorptivities were calculated using a small basis set and assumed the double harmonic approximation. Anderson’s use of those previously computed molar absorptivities along with the peak intensities in his infrared spectra gives vastly large disagreements of the HNO concentration depending on whether he uses the HN stretching mode or the bending mode to calculate concentrations. This called our attention to explore how to improve the molar absorptivities.

5.2 Double Harmonic Results

Chapters 2 and 3 tested the double harmonic approximation with aug-cc-pVTZ and aug-cc-pVQZ basis sets and the Hartree Fock, MP2, CCSD, and CCSD(T) theories, and our results were compared to each other, as well as to previous results by Lee which were obtained from *ab initio* calculations using the smaller TZ2P basis set with the CCSD(T) theory (Lee 1993). The Hessian matrix was first calculated with respect to Cartesian coordinates. The diagonalization of this matrix provided the harmonic frequencies and eigenvectors to describe each normal mode. It was discovered that the q1 mode was most attributing to the stretch of the NH bond, while the q2 and q3 modes both had large effects on the NO bond stretch and the HNO bond
angle bend. Due to the close proximity of the frequencies of the q2 and q3 modes, coupling of these normal modes may be seen in spectroscopic data.

Isotopic substitution in computing the mass-weighted Hessian matrix gave us insight to the frequency shift of each normal mode when the $^2\text{H}$, $^{15}\text{N}$, or $^{18}\text{O}$ isotopes are substituted into the molecule. The largest shift in frequencies, as expected due to the mass percentage increase of the isotope, was in substituting $^2\text{H}$ for $^1\text{H}$. The $^{14}\text{N}$ to $^{15}\text{N}$ isotopic substitution was especially important to test due to both of these nitrogen isotopes being included in Anderson’s experiments.

To reduce computational cost, we investigated completing the Hessian matrix through calculations with respect to internal coordinates. The Hessian matrix results proved to have minimal differences between the internal coordinate technique and the Cartesian coordinate technique. Future Hessian calculations for the HNO molecule are, therefore, recommended to be completed through the internal coordinate technique.

Lastly, the behavior of the ab initio potential energies and dipole moments indicated the breakdown of the double harmonic approximation with the HNO molecule.

### 5.3 Anharmonic Effects

Mechanical and electrical anharmonicities were considered by expansion of the potential energy functions and dipole moment functions, respectively. The largest shift in the molar absorptivity when including anharmonicities was for the q1 mode. Molar absorptivity ratios with including anharmonic effects agreed much more to Anderson’s experimental results than the ratios from Lee’s work. This proves the importance of
including larger basis sets and anharmonic effects in future work with the HNO molecule.

5.4 Conclusions

This work has shown that the TZ2P basis set that was used for previous molar absorptivity calculations does not consider enough basis functions to compute an accurate HNO molar absorptivity. In addition, even with the inclusion of larger basis sets, the double harmonic approximation is shown to break down for HNO.

With the inclusion of both mechanical and electrical anharmonicity effects, it was shown that there is an especially large anharmonicity in the q1 mode that describes the NH stretch, while the other modes are less anharmonic. As a result, we found that the amount of mode q1 harmonic functions required to describe the anharmonic wavefunction and energy levels of q1 must be substantially higher than the amount of harmonic wavefunctions for q2 and q3.

The theoretical isotopic substitutions of the atoms within HNO have shown the q2 and q3 shifts in frequencies to be very sensitive to the level of electron-electron correlation within the theory. Consideration of higher electron correlated theories should provide a convergence of the frequencies of each mode.

The contour plots have provided graphical evidence of coupling between the three modes. This coupling work was completed with aug-cc-pVTZ, MP2 energies. Similar work with aug-cc-pVQZ and CCSD(T) will provide a better understanding of the coupling between the modes within HNO.
5.5 Future Work

In addition to the earlier expressed importance of calculating Hessian matrices through internal coordinates in future work with HNO, it is also extremely important to consider coupling of normal modes in future work. The inclusion of coupling along with anharmonic effects will improve the molar absorptivities of the normal modes and the ratios of these molar absorptivities to be compared to experimental ratios.
References


Appendices
Appendix 1
# APPENDIX 1

# Maple worksheet to fit potential energies to a 6th order polynomial.
# This worksheet then uses the force constants from the potential energy functions (not considering coupling force constants) in Hamiltonian matrix to calculate the anharmonic eigenvalues, the anharmonic \( \nu=0 \rightarrow \nu=1 \) frequency from these eigenvalues, and eigenvector of each harmonic oscillator wavefunction that make up each overall anharmonic wavefunction.

# Each time this is run, we will need to provide:
# - the maximum vibrational levels we're considering for each normal mode (n1max, n2max, n3max)
# - the data file for xpts (amount of normal modes applied) and ypts for each mode (potential energies at those applied normal modes)
# - the Hessian frequencies for each mode (v1_freq, v2_freq, v3_freq)

# restart Maple to clear the memory
restart,

# Load linear algebra package
with(linalg);

[BlockDiagonal, GramSchmidt, JordanBlock, LUDecom, QRAccomp, Wronskian, addcol, addrow, ad, adjoint, angle, augment, backsol, band, basis, bezout, blockmatrix, charmat, charpoly, cholesky, col, coldim, colspace, colspan, companion, concat, cond, copyinto, crossprod, curl, definite, deicols, devrows, det, diag, diverge, dotprod, eigenvals, eigenvalues, eigenvectors, eigenvectors, enermatrix, equal, exp, exponential, extend, ffgausselim, fibonacci, forwards, frobenius, gausselim, gaussjord, genesys, genmatrix, grad, hadamard, hermite, hessian, hilbert, htranspose, ihermite, indexfunc, innerprod, iatbasis, inverse, ismith, issimilar, iszero, jacobian, jordan, kernel, laplacian, leastsqrs, linsolve, mataad, matrix, minor, minpoly, mulcol, mulrow, multiply, norm, normalize, nullspace, orthog, permanent, pivot, potential, randmatrix, randvector, rank, ratform, row, rowdim, rowspace, rowspan, rref, scalarmul, singularvals, smith, stackmatrix, submatrix, subvector, sumbasis, swapcol, swaprow, svd, toepz, trace, transpose, vandermonde, vecpotent, vectdim, vector, wronskian]

# load the fitting package
with(stats); with(plots); with(PolynomialTools);

[anova, describe, fit, importdata, random, statevalf, stats, transform]

[animate, animate3d, animatecurve, arrow, changecoords, complexplot, complexplot3d, conformal, conformal3d, contourplot, contourplot3d, coordsplot, coordsplot3d, densityplot, display, dualaxisplot, fieldplot, fieldplot3d, gradplot, gradplot3d, implicitplot, implicitplot3d, inequal, interactive, interactiveparams, intersectplot, listcontplot, listcontplot3d, listdensityplot, listplot, listplot3d, loglogplot, logplot, matrixplot, multile, odeplot, pareto, plotcompare, pointplot, pointplot3d, polarplot, polygonplot, polygonplot3d, polyhedralplot, supported, polyhedralplot, root locus, semilogplot, setcolors, setoptions, setoptions3d, shadebetween, spacecurve, sparsesmatrixplot, surfdata, textplot, textplot3d, tubeplot]
\begin{verbatim}
[AnnihilatingPolynomial, CoefficientList, CoefficientVector, FromCoefficientList, FromCoefficientVector, GcdFreeBasis, GreatestFactorialFactorization, Homogenize, Hurwitz, IsHomogeneous, IsSelfReciprocal, MinimalPolynomial, PDEToPolynomial, PolynomialToPDE, ShiftEquivalent, ShiftlessDecomposition, Shorten, Shorter, Sort, Split, Splits, SquareFreePart, Translate]

# Parameters to set. n1, n2, n3 represents the vibrational energy levels for each mode.
# Set maximum n1 (n1max), maximum n2 (n2max), maximum n3 (n3max).
# n1max := 3; n2max := 0, n3max := 0

n1max := 3
n2max := 0
n3max := 0

n1 := [seq(seq(seq(n1, n1 = 0..n1max), n2 = 0..n2max), n3 = 0..n3max)]
n1 := [0, 1, 2, 3]

n2 := [seq(seq(seq(n2, n1 = 0..n1max), n2 = 0..n2max), n3 = 0..n3max)]
n2 := [0, 0, 0, 0]

n3 := [seq(seq(seq(n3, n1 = 0..n1max), n2 = 0..n2max), n3 = 0..n3max)]
n3 := [0, 0, 0, 0]

# number of points (nops) here represents the size of each side of the matrix
n1size := nops(n1); n2size := nops(n2); n3size := nops(n3);
n1size := 4
n2size := 4
n3size := 4

# these are the x values; x=normal mode
xpts :=
  readdata("C:/Users/Kirano/Documents/Research/TheoriesAndBasisSets/ccsd(t)
/aug-cc-pvqz/InternalCoordinates/q1/V−vs−q/q−range.txt", 1)
xpts := [−5.0, −4.5, −4.0, −3.5, −3.0, −2.5, −2.0, −1.5, −1.0, −0.5, 0., 0.5, 1.0, 1.5, 2.0,
2.5, 3.0, 3.5, 4.0, 4.5, 5.0]
nops(xpts);
21

Digits := 13

# these are the y values; y=Potential Energy
ypts_y1 :=
\end{verbatim}
readdata("C:/Users/Kirano/Documents/Research/TheoriesAndBasisSets/ccsd(t)/aug-cc-pvqz/InternalCoordinates/q1/V→vs−q/PotE.txt", 1)

\[ \text{ypts}_v1 := \{ -130.2684311470, -130.2809089089, -130.2927740085, -130.3037478566, \]
\[ -130.3136076294, -130.3221863270, -130.3293656603, -130.3350629274, \]
\[ -130.3392144984, -130.3417597355, -130.3426293322, -130.3417410978, \]
\[ -130.339041430, -130.3343301564, -130.3276487796, -130.3189235390, \]
\[ -130.3081652155, -130.2954403905, -130.2808734052, -130.2646393655, \]
\[ -130.2469443680 \]  

\[ \text{ypts}_v2 := \]
\[ \text{readdata("C:/Users/Kirano/Documents/Research/TheoriesAndBasisSets/ccsd(t)/aug-cc-
\text{pvqz/InternalCoordinates/q2/V→vs−q/PotE.txt", 1)} \]
\[ \text{ypts}_v2 := \{ -130.2016968454, -130.2331479762, -130.2597169002, -130.2818188423, \]
\[ -130.2998528166, -130.3142007879, -130.3252257596, -130.3332704432, \]
\[ -130.3386563754, -130.3416833821, -130.3426293322, -130.3417501428, \]
\[ -130.3392800269, -130.3354319790, -130.3303985020, -130.3243525800, \]
\[ -130.3174489357, -130.3098256174, -130.3016059945, -130.2929012902, \]
\[ -130.2838138394 \]  

\[ \text{ypts}_v3 := \]
\[ \text{readdata("C:/Users/Kirano/Documents/Research/TheoriesAndBasisSets/ccsd(t)/aug-cc-
\text{pvqz/InternalCoordinates/q3/V→vs−q/PotE.txt", 1)} \]
\[ \text{ypts}_v3 := \{ -129.5172460596, -129.790319620, -129.9784445791, -130.1078961035, \]
\[ -130.1963467288, -130.2558932730, -130.2949542699, -130.3194728555, \]
\[ -130.3336931811, -130.3406729555, -130.3426293322, -130.3411763569, \]
\[ -130.3374899417, -130.3324235075, -130.3265900330, -130.3204216919, \]
\[ -130.3142147896, -130.3081647185, -130.3023935636, -130.2969718387, \]
\[ -130.2919352895 \]  

# "a" value can be set to the minimum value of the energy (all modes should have the same min E), a.k.
a, the optimum energy (OptE), which is the energy at \(x=0\).

\[ \text{min(ypts}_v1); \text{min(ypts}_v2); \text{min(ypts}_v3) \]
\[ -130.3426293322 \]
\[ -130.3426293322 \]
\[ -130.3426293322 \]  

\[ \text{OptE} := \text{min(ypts}_v1); \]
\[ \text{OptE} := -130.3426293322 \]  

\[ \text{nops(ypts}_v1); \text{nops(ypts}_v2); \text{nops(ypts}_v3) \]
\[ 21 \]
\[ 21 \]
\[ 21 \]  

# In atomic units: \(\hbar = [1 \text{ Ha \cdot a.u.time}] = \text{constant}; \text{Eigenvalue} = \lambda = \left[\text{a.u.time}^{-2}\right] = \text{freq}^2\); 

\[ \text{in atomic units, freq = \left[\text{a.u.time}^{-1}\right]} \]  

\[ \hbar := 1 \]
\[ h := 1 \] (17)

# Give the frequencies (in cm⁻¹) of the three modes
\[ v1 \_freq := 1542.18025 \; ; \; v2 \_freq := 1600.228641 \; ; \; v3 \_freq := 2963.03259 \]
\[ v1 \_freq := 1542.18025 \]
\[ v2 \_freq := 1600.228641 \]
\[ v3 \_freq := 2963.03259 \] (18)

\[ w1 := \left( \frac{v1 \_freq}{219474.63} \right) \]
\[ w1 := 0.007026690283063 \] (19)

\[ w2 := \left( \frac{v2 \_freq}{219474.63} \right) \]
\[ w2 := 0.007291178214994 \] (20)

\[ w3 := \left( \frac{v3 \_freq}{219474.63} \right) \]
\[ w3 := 0.01350056992920 \] (21)

# Define the results of the integral \[ \langle v1 \mid q^n \rangle_v2 \_n \], where \( q \) is defined using ladder operators. \( q_0 \) is \[ \langle v1 \mid q^n \rangle_v2 \_n \], \( q_1 \) is \[ \langle v1 \mid q_1^n \rangle_v2 \_n \], ... Define \( q_0, q_1, q_2, q_3, q_4 \).
\[ q_0 := (n1, n2) \rightarrow \text{if } n1 = n2 \text{ then } 1 \text{ else } 0 \text{ fi} \]
\[ q_0 := (n1, n2) \rightarrow \text{if } n1 = n2 \text{ then } 1 \text{ else } 0 \text{ end if} \] (22)

\[ q_1 := (n1, n2) \rightarrow \text{if } n1 < 0 \text{ then } 0 \text{ elif } n2 < 0 \text{ then } 0 \text{ elif } |n1 - n2| = 1 \text{ then } \sqrt{\frac{\max(n1, n2)}{2}} \text{ else } 0 \text{ fi} \]
\[ q_1 := (n1, n2) \rightarrow \text{if } n1 < 0 \text{ then } 0 \text{ elif } n2 < 0 \text{ then } 0 \text{ elif } |n1 - n2| = 1 \text{ then } \sqrt{\frac{\max(n1, n2)}{2}} \text{ else } 0 \text{ end if} \] (23)

\[ q_2 := (n1, n2) \rightarrow \text{add}(q1(n1, i) \cdot q1(i, n2), i = n2 - 1 \cdot n2 + 1) \]
\[ q_2 := (n1, n2) \rightarrow \text{add}(q1(n1, i) \cdot q1(i, n2), i = n2 - 1 \cdot n2 + 1) \] (24)

\[ q_3 := (n1, n2) \rightarrow \text{add}(q2(n1, i) \cdot q1(i, n2), i = n2 - 1 \cdot n2 + 1) \]
\[ q_3 := (n1, n2) \rightarrow \text{add}(q2(n1, i) \cdot q1(i, n2), i = n2 - 1 \cdot n2 + 1) \] (25)

\[ q_4 := (n1, n2) \rightarrow \text{add}(q3(n1, i) \cdot q1(i, n2), i = n2 - 1 \cdot n2 + 1) \]
\[ q_4 := (n1, n2) \rightarrow \text{add}(q3(n1, i) \cdot q1(i, n2), i = n2 - 1 \cdot n2 + 1) \] (26)

\[ q_5 := (n1, n2) \rightarrow \text{add}(q4(n1, i) \cdot q1(i, n2), i = n2 - 1 \cdot n2 + 1) \]
\[ q_5 := (n1, n2) \rightarrow \text{add}(q4(n1, i) \cdot q1(i, n2), i = n2 - 1 \cdot n2 + 1) \] (27)
\[ q_6 := (n_1, n_2) \rightarrow add(q_5(n_1, i) \cdot q_1(i, n_2), i = n_2 - 1 \ldots n_2 + 1) \]
\[ q_6 := (n_1, n_2) \rightarrow add(q_5(n_1, i) \cdot q_1(i, n_2), i = n_2 - 1 \ldots n_2 + 1) \] (28)

# Quadratic force constant is equal to \( \frac{hbar^2 \sqrt{\text{eigval}}}{2} \), where each eigenvalue is equal to \( \left( \frac{\text{freq}}{219474.63} \right)^2 \), and 219474.63 converts to Ha from cm\(^{-1}\).

\[ \nu_1 = \text{OptE} + \left( \frac{hbar \cdot \nu_1 \cdot \text{freq}}{2} \right) \cdot \frac{1}{219474.63} \cdot x^2 + c \cdot x^3 + d \cdot x^4 + e \cdot x^5 + f \cdot x^6 \]
\[ \nu_1 = -130.3426293322 + 0.003513345141532 \cdot x^2 + c \cdot x^3 + d \cdot x^4 + e \cdot x^5 + f \cdot x^6 \] (29)

# recalculate the fit
\[ \nu_1 = \text{rhs(\text{fit(leastsquare}[[x, y], y = \nu_1\_\text{Eqn}]]([xpts, ypts_\nu1]))} \]
\[ \nu_1 = -130.3426293322 + 0.003513345141532 \cdot x^2 + 0.0001072187911663 \cdot x^3 \\
+ 4.089828590046 \cdot 10^{-6} \cdot x^4 - 8.60988690258 \cdot 10^{-7} \cdot x^5 - 3.505288048860 \cdot 10^{-7} \cdot x^6 \] (30)

printf("OptE, linear coefficient (should be zero), b, c, d, e, f are:\nconst_\nu1 := 
CoefficientList(\nu_1\_\text{Func}, x)"");
OptE, linear coefficient (should be zero), b, c, d, e, f are:
const_\nu1 := [-130.3426293322, 0, 0.003513345141532, 0.0001072187911663, 4.089828590046 \cdot 10^{-6}, -8.60988690258 \cdot 10^{-7}, -3.505288048860 \cdot 10^{-7}] \) (31)

const_\nu1 := -130.3426293322 \) (32)
const_\nu1 := 0 \) (33)
const_\nu1 := 0.003513345141532 \) (34)
const_\nu1 := 0.0001072187911663 \) (35)
const_\nu1 := 4.089828590046 \cdot 10^{-6} \) (36)
const_\nu1 := -8.60988690258 \cdot 10^{-7} \) (37)
const_\nu1 := -3.505288048860 \cdot 10^{-7} \) (38)

# Calculate the deviations between the actual energies and the predicted ones
# AND isolate the Maximum Absolute Deviation
\[ \nu_1 = \text{subs}(\text{xpts}_\nu1[i], \nu_1 = 1 \ldots \text{nops}(\text{xpts})) \]; \text{max}(|\text{seq}(\text{subs}(\%[i]), i)\|)
\]
\begin{align*}
\text{v1}_\text{dev} &= [-2.8149 \times 10^{-6}, -9.6464 \times 10^{-6}, 0.0000109213, 0.0000184310, 0.0000115430, \\
& \quad 1.6302 \times 10^{-6}, -2.5135 \times 10^{-6}, -8.6 \times 10^{-6}, 4.1072 \times 10^{-6}, 4.3857 \times 10^{-6}, 0, -3.7274 \times 10^{-6}, \\
& \quad 1.7470 \times 10^{-6}, 0.0000221118, 0.0000539698, 0.0000819928, 0.0000825827, 0.0000363007, \\
& \quad -0.0000491754, -0.0001031944, 0.0000604467] \\
& \quad 0.0001031944
\end{align*}

# Calculate the Mean Absolute Deviation
\begin{align*}
\text{add}(\text{abs}([\text{v1}_\text{dev}[i]], i = 1 .. \text{\texttt{nops(xpts})])) \\
\text{nops(xpts)} \\
& = 0.00002672621428571
\end{align*}

# Calculate the Root Mean Square Deviation
\begin{align*}
\text{sqrt}\left( \frac{\text{\texttt{sum}}(\text{abs}([\text{v1}_\text{dev}[i]], i = 1 .. \text{\texttt{nops(xpts})]))^2}{\text{nops(xpts)}} \right) \\
& = 0.0000412532532481
\end{align*}

\begin{align*}
v2_\text{Eqn} := \text{OptE} + \left( \frac{\text{hbar} \cdot \text{v2_freq}}{2} \cdot \frac{1}{219474.63} \right) \cdot x^2 + c \cdot x^3 + d \cdot x^4 + e \cdot x^5 + fx^6 \\
v2_\text{Eqn} := -130.3426293322 + 0.003645589107497 x^2 + c x^3 + d x^4 + e x^5 + fx^6
\end{align*}

# recalculate the fit
\begin{align*}
v2_\text{Func} := \text{rhs}(\text{fit[leastsquare}[x, y, y = v2_\text{Eqn}]]([\text{xpts}, \text{ypts}_v2])); \\
v2_\text{Func} := -130.3426293322 + 0.003645589107497 x^2 - 0.00003246477232452 x^3 \\
& + 0.00001465079109528 x^4 - 1.547178080177 \times 10^{-7} x^5 - 2.713685859482 \times 10^{-8} x^6
\end{align*}

\begin{verbatim}
printf("OptE, linear coefficient (should be zero), b, c, d, e, f are:");
const \text{v2} :=
\text{CoefficientList(v2_\text{Func}, x)}
\text{OptE, linear coefficient (should be zero), b, c, d, e, f are:}
\text{const \text{v2} := } [-130.3426293322, 0, 0.003645589107497, -0.00003246477232452, \\
0.00001465079109528, -1.547178080177 \times 10^{-7}, -2.713685859482 \times 10^{-8}] \\
const \text{v2}_1 \\
& = -130.3426293322
const \text{v2}_2 \\
& = 0
const \text{v2}_3 \\
& = 0.003645589107497
const \text{v2}_4 \\
& = -0.00003246477232452
\end{verbatim}

82
const\_v2\_5 \quad 0.00001465079109528

const\_v2\_6 \quad -1.547178080177 \times 10^{-7}

const\_v2\_7 \quad -2.713685859482 \times 10^{-8}

# Calculate the deviations between the actual energies and the predicted ones
# AND isolate the Maximum Absolute Deviation

\texttt{v2\_dev := [seq(ypts[v2[i]] - subs(x = xpts[i], v2\_Func), i = 1..nops(xpts))]; max(seq(|abs(%[i])|, i = 1..nops(xpts))):}


\texttt{-9.7888 \times 10^{-6}, -0.0000135925, -0.0000144080, -0.0000120584, -6.9483 \times 10^{-5}, 0,}

\texttt{7.4626 \times 10^{-6}, 0.0000138949, 0.0000177782, 0.0000179307, 0.0000138789, 6.2481 \times 10^{-6},}

\texttt{-2.8695 \times 10^{-6}, -9.6526 \times 10^{-6}, -8.5176 \times 10^{-6}, 7.4927 \times 10^{-6}]

\quad 0.0000179307

# Calculate the Mean Absolute Deviation

\texttt{\frac{\text{add}(\text{abs}(v2\_dev[i]), i = 1..nops(xpts))}{\text{nops}(xpts)}}

\quad 9.039095238095 \times 10^{-6}

# Calculate the Root Mean Square Deviation

\texttt{\sqrt{\left(\frac{\text{sum}(\text{abs}(v2\_dev[i]), i = 1..nops(xpts))}{\text{nops}(xpts)}\right)^2}}

\quad 0.00001022543070636

# recalculate the fit

\texttt{v3\_Eqn := OptE + \left(\frac{hbar\cdot\nu_3}{2\cdot219474.63}\right) \cdot \frac{1}{2} \cdot x^2 + c \cdot x^3 + d \cdot x^4 + e \cdot x^5 + f \cdot x^6}

\texttt{v3\_Eqn := -130.3426293322 + 0.006750284964599 \cdot x^2 + c \cdot x^3 + d \cdot x^4 + e \cdot x^5 + f \cdot x^6}

\texttt{\textcolor{red}{\textbf{OptE}}, linear coefficient (should be zero), b, c, d, e, f are:}}
\[ const\_v3 \equiv [ -130.3426293322, 0, 0.006750284964599, -0.001591041803368, 0.0002594445982952, -0.0005986640415720, 6.830689208016 \times 10^{-6}] \]  
(57)

\[ const\_v3_1 \]

\[ const\_v3_2 \]

\[ const\_v3_3 \]

\[ const\_v3_4 \]

\[ const\_v3_5 \]

\[ const\_v3_6 \]

\[ const\_v3_7 \]

\[ -130.3426293322 \]  
(58)

\[ 0 \]  
(59)

\[ 0.006750284964599 \]  
(60)

\[ -0.001591041803368 \]  
(61)

\[ 0.0002594445982952 \]  
(62)

\[ -0.0005986640415720 \]  
(63)

\[ 6.830689208016 \times 10^{-6} \]  
(64)

# Calculate the deviations between the actual energies and the predicted ones
# AND isolate the Maximum Absolute Deviation

\[ v3\_dev \equiv [ \text{seq}(ypts\_v3[i] \rightarrow \text{subs}(x = xpts[i], v3\_Func), i = 1..\text{nops}(xpts)); \text{max}(%[i]), i = 1..\text{nops}(xpts)) ]; \]

\[ v3\_dev \equiv [ 0.0017810173, -0.0029468805, -0.0013459998, 0.0008938364, 0.0020297889, 0.0020382182, 0.0014415854, 0.0007527148, 0.0002686826, 0.0000517325, 0, -0.0000501669, -0.0002262616, -0.0005491840, -0.0009060591, -0.0010774873, -0.0008269421, -0.0000570280, 0.0009647623, 0.0013093176, -0.0009827358, 0.0029468805 ] \]  
(65)

# Calculate the Mean Absolute Deviation

\[ \frac{\text{add}(\text{abs}(v3\_dev[i]), i = 1..\text{nops}(xpts))}{\text{nops}(xpts)} \]

\[ 0.0009762095761905 \]  
(66)

# Calculate the Root Mean Square Deviation

\[ \sqrt{\frac{\text{sum}(v3\_dev[i]^2, i = 1..\text{nops}(xpts))}{\text{nops}(xpts)}} \]

\[ 0.001236276039002 \]  
(67)

# Non-coupling anharmonic force constants. Ex: k300 is the 3rd order force constant for mode 1, k030 is
\[ k300 := \text{const}_v l_4 \quad \text{with} \quad k300 := 0.0001072187911663 \] (68)

\[ k400 := \text{const}_v l_5 \quad \text{with} \quad k400 := 4.089828590046 \times 10^{-6} \] (69)

\[ k500 := \text{const}_v l_6 \quad \text{with} \quad k500 := -8.609888690258 \times 10^{-7} \] (70)

\[ k600 := \text{const}_v l_7 \quad \text{with} \quad k600 := -3.505288048860 \times 10^{-7} \] (71)

\[ k030 := \text{const}_v l_4 \quad \text{with} \quad k030 := -0.003246477232452 \] (72)

\[ k040 := \text{const}_v l_5 \quad \text{with} \quad k040 := 0.0001465079109528 \] (73)

\[ k050 := \text{const}_v l_6 \quad \text{with} \quad k050 := -1.547178080177 \times 10^{-7} \] (74)

\[ k060 := \text{const}_v l_7 \quad \text{with} \quad k060 := -2.713685859482 \times 10^{-8} \] (75)

\[ k003 := \text{const}_v l_4 \quad \text{with} \quad k003 := -0.00159104180368 \] (76)

\[ k004 := \text{const}_v l_5 \quad \text{with} \quad k004 := 0.0002594445982952 \] (77)

\[ k005 := \text{const}_v l_6 \quad \text{with} \quad k005 := -0.00005986640415720 \] (78)

\[ k006 := \text{const}_v l_7 \quad \text{with} \quad k006 := 6.830689208016 \times 10^{-6} \] (79)

# Define the harmonic component of the Hamiltonian matrix

\[
\text{h\_harm} := \text{matrix}(4, 4, [\text{seq}(\text{seq}(q0(n1[i], n1[j]) \cdot q0(n2[i], n2[j]) \cdot q0(n3[i], n3[j]) \cdot (w1 \cdot (n1[i] + 0.5) + w2 \cdot (n2[i] + 0.5) + w3 \cdot (n3[i] + 0.5)) \cdot (j \in 1..4), i \in 1..4)])
\]

\[
\text{h\_harm} :=
\begin{bmatrix}
0.01390921921363 & 0. & 0. & 0. \\
0. & 0.02093590949669 & 0. & 0. \\
0. & 0. & 0.02796259977976 & 0. \\
0. & 0. & 0. & 0.03498929006282
\end{bmatrix}
\] (80)

# Define the anharmonic contributions from mode 1 alone

\[
\text{h\_q1} := \text{matrix}(4, 4, [\text{seq}(\text{seq}(q0(n2[i], n2[j]) \cdot q0(n3[i], n3[j]) \cdot (q3(n1[i], n1[j])) \cdot k300])
\]

85
\[ + q^4(n_1[i], n_1[j]) \cdot k_{400} + q^5(n_1[i], n_1[j]) \cdot k_{500} + q^6(n_1[i], n_1[j]) \cdot k_{600}, j = 1..4, i = 1..4) \]

\[ h_{q1} := \begin{bmatrix}
0.4102993373 \cdot 10^{-6}, & 0.0000789973924530 \cdot \sqrt{2}, & 4.163018357585 \cdot 10^{-6} \sqrt{2}, & 0.00002578246170530 \cdot \sqrt{2}, & 0.0000789973924530 \cdot \sqrt{2}, & 0.0000107361664854, & 0.0003119702487224, & 5.623880910991 \cdot 10^{-5} \sqrt{6}, & 4.163018357585 \cdot 10^{-6} \sqrt{2}, & 0.0003119702487224, & 0.0002344479102392, & 0.0002310180373045 \cdot \sqrt{6}, & 0.00002578246170530 \cdot \sqrt{2}, & 5.623880910991 \cdot 10^{-5} \sqrt{6}, & 0.0002310180373045 \cdot \sqrt{6}, & 0.00003527807098620 \end{bmatrix} \]

# Define the anharmonic contributions from mode 2 alone

\[ h_{q2} := \text{matrix}(4, 4, [ \text{seq}(\text{seq}(q^0(n_1[i], n_1[j]) \cdot q^0(n_3[i], n_3[j]) \cdot (q^3(n_2[i], n_2[j]) \cdot k_{030} + q^4(n_2[i], n_2[j]) \cdot k_{040} + q^5(n_2[i], n_2[j]) \cdot k_{050} + q^6(n_2[i], n_2[j]) \cdot k_{060}), j = 1..4), i = 1..4) \]); \]

\[ h_{q2} := \begin{bmatrix}
0.00001093721171159, & 0., & 0., & 0., \\
0.00001093721171159, & 0., & 0., & 0., \\
0.00001093721171159, & 0., & 0., & 0., \\
0.00001093721171159, & 0., & 0., & 0., \\
\end{bmatrix} \]

# Define the anharmonic contributions from mode 3 alone

\[ h_{q3} := \text{matrix}(4, 4, [ \text{seq}(\text{seq}(q^0(n_1[i], n_1[j]) \cdot q^0(n_2[i], n_2[j]) \cdot (q^3(n_3[i], n_3[j]) \cdot k_{003} + q^4(n_3[i], n_3[j]) \cdot k_{004} + q^5(n_3[i], n_3[j]) \cdot k_{005} + q^6(n_3[i], n_3[j]) \cdot k_{006}), j = 1..4), i = 1..4) \]); \]

\[ h_{q3} := \begin{bmatrix}
0.002073909909864, & 0., & 0., & 0., \\
0.002073909909864, & 0., & 0., & 0., \\
0.002073909909864, & 0., & 0., & 0., \\
0.002073909909864, & 0., & 0., & 0., \\
\end{bmatrix} \]

# Eigenvalues
\[ \text{eigenvalues}(h_{\text{harm}}); \]

\[ 0.0139092192136300, 0.0209359094966900, 0.0279625997797600, 0.0349892906282000 \]

# Eigenvalues of the anharmonic vibrational states
\[ \text{eigval} := \text{eigenvalues}(h_{\text{harm}} + h_{q1} + h_{q2} + h_{q3}); \]

\[ \text{eigval} := 0.0141278182943811, 0.0211529248120400, 0.0281728715983544, 0.0352885858175147 \]

# Calculate the ANharmonic frequency for the normal mode that included excited states.
\[ v_{\text{anharm\_freq}} := (eigval[2] - eigval[1]) \cdot 219474.63 \]
\[ v_{\text{anharm\_freq}} := 1541.83265367378 \tag{86} \]

# Eigenvectors for each eigenvalue

# For a harmonic wavefunction, each eigenvalue should have total population in one vibrational state. Reconfirm using command below.
\[ \text{vex\_harm} := \text{eigenvectors(h\_harm)} \]
\[ \text{vex\_harm} := \begin{bmatrix} 0.03498929006282, 1, \begin{bmatrix} 0 & 0 & 0 \\ 1 & 0 & 0 \end{bmatrix} \end{bmatrix}, 0.01390921921363, 1, \]
\[ \begin{bmatrix} 0.02093590949669, 1, \begin{bmatrix} 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \end{bmatrix}, 0.02796259977976, 1, \]
\[ \begin{bmatrix} 0.02093590949669, 1, \begin{bmatrix} 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \end{bmatrix}, 0.02796259977976, 1, \]
\[ \begin{bmatrix} 0.02093590949669, 1, \begin{bmatrix} 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \end{bmatrix}, 0.02796259977976, 1, \]
\[ \begin{bmatrix} 0.02093590949669, 1, \begin{bmatrix} 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \end{bmatrix}, 0.02796259977976, 1, \]
\[ \begin{bmatrix} 0.02093590949669, 1, \begin{bmatrix} 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \end{bmatrix}, 0.02796259977976, 1, \]
\[ \begin{bmatrix} 0.02093590949669, 1, \begin{bmatrix} 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \end{bmatrix}, 0.02796259977976, 1, \]

# For an anharmonic wavefunction, each eigenvalue has population in all vibrational states, but has an overwhelming population in the vibrational state describing the eigenvalue.
\[ \text{vex\_anharm} := \text{eigenvectors(h\_harm + h\_g1 + h\_g2 + h\_g3)} \]
\[ \text{vex\_anharm} := \begin{bmatrix} 0.02817287159839, 1, \]
\[ \begin{bmatrix} -0.0002616512585637, -0.04417870346862, -0.9958318137024, 0.07979456445536 \end{bmatrix}, 0.02115292481207, 1, \]
\[ \begin{bmatrix} 0.01582213462534, 0.9988943860429, -0.04426256023948, 0.0007009639895876 \end{bmatrix}, 0.01412781829437, 1, \]
\[ \begin{bmatrix} 0.9998658167623, -0.01583004563139, 0.0001020009946264, -0.004212804580395 \end{bmatrix}, 0.03528858581751, 1, \]
\[ \begin{bmatrix} 0.004235571484453, 0.002767191495755, 0.07974844308818, 0.9968021811827 \end{bmatrix} \]
\[ \begin{bmatrix} 0.004235571484453, 0.002767191495755, 0.07974844308818, 0.9968021811827 \end{bmatrix} \]

#-----------------------------------END-----------------------------------
Appendix 2
# APPENDIX 2

# Maple worksheet that uses the 5th order dipole moment function for each vector to calculate transition
dipole moments of each normal mode using the overall HARMONIC wavefunction for each mode,
that was determined in the "Hamiltonian-Anharmonic-NoCoupling" Maple Sheet.

# Must provide correct:
# -eigenvectors that were found in "Hamiltonian-Anharmonic-NoCoupling" Maple Sheet.
# -the ANHARMONIC vibrational frequencies (in cm⁻¹) for each mode, which were calculated from the
energy difference from the ground state to the first excited state in "Hamiltonian-Anharmonic-
NoCoupling" Maple Sheet.
# -the maximum vibrational state for each mode (n1max for mode 1, n2max for mode 2, n3max for mode
3). Since we are not looking at coupling, only one nmax should have an excited maximum
vibrational state, while the others have nmax of zero.

# When looking at multiple vibrational states of a certain mode while the others stay at ground state,
expect the other Molar Adsorptivity from the other modes to be essentially zero. A recalculation
must be completed using this code by changing which mode has excited states for the Transition
Dipole Moment of that normal mode, and the Molar Absorptivity of that normal mode.

# -----------------------------------------------

# restart Maple to clear the memory
restart;

# Load linear algebra package
with(linalg);

{ BlockDiagonal, GramSchmidt, JordanBlock, LUdecomp, QRdecomp, Wronskian, addcol,
  addrow, adj, adjoint, angle, augment, backsub, band, basis, bezout, blockmatrix, charmat,
  charpoly, cholesky, col, coldim, colspace, colspan, companion, concat, cond, copyinto,
  crossprod, curl, definite, delcols, delrows, det, diag, diverge, dotprod, eigenvals, eigenvalues,
  eigenvectors, eigenvecs, entermatrix, equal, exponential, extend, ffgausselim, fibonacci,
  forwardsub, frobenius, gausselim, gaussjord, geneqns, gennmatrix, grad, hadamard, hermite,
  hessian, hilbert, htransp, ihermite, indexfunc, innerprod, intbasis, inverse, ismth,
  issimilar, iszero, jacobian, jordan, kernel, laplacian, leastsqs, linsolve, matadd, matrix,
  minor, minpoly, mulcol, mulrow, multiply, norm, normalize, nullspace, orthog, permanent,
  pivot, potential, randmatrix, randvector, rank, ratform, row, rowdim, rowspace, rowspan,
  rref, scalarmul, singularvals, smith, stackmatrix, submatrix, subvector, svdsbasis, swapcol,
  swaprow, sylvestre, toeplitz, trace, transpose, vandermonde, vecpoten, vecdim, vector,
  wronskian }
plotcompare, pointplot, pointplot3d, polarplot, polygonplot, polygonplot3d, polyhedra_supported, polyhedraplot, rootlocus, semilogplot, setcolors, setoptions, setoptions3d, shadebetween, spacecurve, sparsematrixplot, surftdata, textplot, textplot3d, tubeplot]
[AnnihilatingPolynomial, CoefficientList, CoefficientVector, FromCoefficientList, FromCoefficientVector, GcdFreeBasis, GreatestFactorialFactorization, Homogenize, Hurwitz, IsHomogeneous, IsSelfReciprocal, MinimalPolynomial, PDEToPolynomial, PolynomialToPDE, ShiftEquivalent, ShiftlessDecomposition, Shorten, Shorter, Sort, Split, Splits, SquareFreePart, Translate]

# Parameters to set. n1, n2, n3 represents the vibrational energy levels for each mode.
# Set maximum n1 (n1max), maximum n2 (n2max), maximum n3 (n3max).
n1max := 3; n2max := 0; n3max := 0

n1max := 3
n2max := 0
n3max := 0

n1 := [seq(seq(seq(n1, n1 = 0..n1max), n2 = 0..n2max), n3 = 0..n3max)]
n1 := [0, 1, 2, 3]

n2 := [seq(seq(seq(n2, n1 = 0..n1max), n2 = 0..n2max), n3 = 0..n3max)]
n2 := [0, 0, 0, 0]

n3 := [seq(seq(seq(n3, n1 = 0..n1max), n2 = 0..n2max), n3 = 0..n3max)]
n3 := [0, 0, 0, 0]

# number of points (nops) here represents the size of each side of the matrix
n1size := nops(n1); n2size := nops(n2); n3size := nops(n3);
n1size := 4
n2size := 4
n3size := 4

#size := nops([[]])
size := n1size

size := 4

# Define the results of the integral <v1|q^n|v2>, where q is defined using ladder operators.
# q0 is <v1|q^0|v2>, q1 is <v1|q^1|v2>, ... Define q0, q1, q2, q3, q4.
q0 := (n1, n2) → if n1 = n2 then 1 else 0 fi
q0 := (n1, n2) → if n1 = n2 then 1 else 0 end if

90
\[ q_1 := (n_1, n_2) \rightarrow \text{if } n_1 < 0 \text{ then } 0 \text{ endif } \text{ elif } n_2 < 0 \text{ then } 0 \text{ endif } \text{ abs}(n_1 - n_2) = 1 \text{ then } \sqrt{\frac{\max(n_1, n_2)}{2}} \]

\[ q_1 := (n_1, n_2) \rightarrow \text{if } n_1 < 0 \text{ then } 0 \text{ endif } \text{ elif } n_2 < 0 \text{ then } 0 \text{ endif } \text{ abs}(n_1 - n_2) = 1 \text{ then } \sqrt{\frac{\max(n_1, n_2)}{2}} \]

\[ q_2 := (n_1, n_2) \rightarrow \text{add}(q_1(n_1, i) \cdot q_1(i, n_2), i = n_2 - 1 .. n_2 + 1) \]

\[ q_2 := (n_1, n_2) \rightarrow \text{add}(q_1(n_1, i) \cdot q_1(i, n_2), i = n_2 - 1 .. n_2 + 1) \]

\[ q_3 := (n_1, n_2) \rightarrow \text{add}(q_3(n_1, i) \cdot q_1(i, n_2), i = n_2 - 1 .. n_2 + 1) \]

\[ q_3 := (n_1, n_2) \rightarrow \text{add}(q_3(n_1, i) \cdot q_1(i, n_2), i = n_2 - 1 .. n_2 + 1) \]

\[ q_4 := (n_1, n_2) \rightarrow \text{add}(q_4(n_1, i) \cdot q_1(i, n_2), i = n_2 - 1 .. n_2 + 1) \]

\[ q_4 := (n_1, n_2) \rightarrow \text{add}(q_4(n_1, i) \cdot q_1(i, n_2), i = n_2 - 1 .. n_2 + 1) \]

\[ q_5 := (n_1, n_2) \rightarrow \text{add}(q_5(n_1, i) \cdot q_1(i, n_2), i = n_2 - 1 .. n_2 + 1) \]

\[ q_5 := (n_1, n_2) \rightarrow \text{add}(q_5(n_1, i) \cdot q_1(i, n_2), i = n_2 - 1 .. n_2 + 1) \]

\[ q_6 := (n_1, n_2) \rightarrow \text{add}(q_6(n_1, i) \cdot q_1(i, n_2), i = n_2 - 1 .. n_2 + 1) \]

\[ q_6 := (n_1, n_2) \rightarrow \text{add}(q_6(n_1, i) \cdot q_1(i, n_2), i = n_2 - 1 .. n_2 + 1) \]

# List the dipole moments x and y vectors for each mode.

# these are the x values; x=normal mode

xpts :=

\text{readdata}("C:/Users/Kirano/Documents/Research/TheoriesAndBasisSets/ccsd(t)
 aug-cc-pvqz/InternalCoordinates/q1/DM=vs=q/q-range.txt", 1)

xpts := [-5.0, -4.5, -4.0, -3.5, -3.0, -2.5, -2.0, -1.5, -1.0, -0.5, 0.0, 0.5, 1.0, 1.5, 2.0, 2.5, 3.0, 3.5, 4.0, 4.5, 5.0]

nops(xpts); 21

#Digits:=13

# these are the y values; y=Dipole Vector

ypts_DMX y1 :=

\text{readdata}("C:/Users/Kirano/Documents/Research/TheoriesAndBasisSets/ccsd(t)/aug-cc-
 pvqz/InternalCoordinates/q1/DM=vs=q/DMX.txt", 1)

ypts_DMX y1 := [-0.2245000000, -0.2464500000, -0.2662500000, -0.2841250000, -0.3002250000, -0.3146000000, -0.3272500000, -0.3380750000, -0.3470000000, -0.3536750000, -0.3577250000, -0.3585000000, -0.3552250000, -0.3467500000, -0.3316000000, -0.3079250000, -0.2733250000, -0.2251250000, -0.1604750000,
\[ -0.0770250000, 0.0261000000 \]

\[ \text{yptrs}_\text{DM} y_1 := \text{readdata}(" C:/Users/Kirano/Documents/Research/TheoriesAndBasisSets/ccsd(t)/aug-cc-pvqz/InternalCoordinates/q1/DM-\text{vs}=q/DMy.txt", 1) \]

\[ \text{yptrs}_\text{DM} y_1 := [0.5387750000, 0.5433250000, 0.5487000000, 0.5344000000, 0.5600000000, 0.5649500000, 0.5687750000, 0.5709000000, 0.5707500000, 0.5675500000, 0.5606250000, 0.5491250000, 0.5321250000, 0.5086000000, 0.4775000000, 0.4376000000, 0.3877500000, 0.3268750000, 0.2543750000, 0.1707000000, 0.0778250000] \]

\[ \text{yptrs}_\text{DM} x_2 := \text{readdata}(" C:/Users/Kirano/Documents/Research/TheoriesAndBasisSets/ccsd(t)/aug-cc-pvqz/InternalCoordinates/q2/DM-\text{vs}=q/DMx.txt", 1) \]

\[ \text{yptrs}_\text{DM} x_2 := [0.0849750000, 0.0254000000, -0.0298500000, -0.0811000000, -0.1287750000, -0.1732000000, -0.2147500000, -0.2537250000, -0.2904000000, -0.3250000000, -0.3577250000, -0.3887250000, -0.4181500000, -0.4461750000, -0.4729000000, -0.4984250000, -0.5229000000, -0.5464500000, -0.5692000000, -0.5913000000, -0.6128750000] \]

\[ \text{yptrs}_\text{DM} y_2 := \text{readdata}(" C:/Users/Kirano/Documents/Research/TheoriesAndBasisSets/ccsd(t)/aug-cc-pvqz/InternalCoordinates/q2/DM-\text{vs}=q/DMy.txt", 1) \]

\[ \text{yptrs}_\text{DM} y_2 := [0.2415250000, 0.3049750000, 0.3572250000, 0.4005500000, 0.4366500000, 0.4669500000, 0.4924500000, 0.5140500000, 0.5323000000, 0.5477000000, 0.5606250000, 0.5713250000, 0.5800250000, 0.5869000000, 0.5921000000, 0.5956500000, 0.5976750000, 0.5982250000, 0.5973750000, 0.5951500000, 0.5915500000] \]

\[ \text{yptrs}_\text{DM} x_3 := \text{readdata}(" C:/Users/Kirano/Documents/Research/TheoriesAndBasisSets/ccsd(t)/aug-cc-pvqz/InternalCoordinates/q3/DM-\text{vs}=q/DMx.txt", 1) \]

\[ \text{yptrs}_\text{DM} x_3 := [-0.3196250000, -0.3396750000, -0.3569000000, -0.3711000000, -0.3820000000, -0.3892500000, -0.3924250000, -0.3911500000, -0.3851000000, -0.3740000000, -0.3577250000, -0.3362750000, -0.3099750000, -0.2793750000, -0.2452500000, -0.2087750000, -0.1710750000, -0.1335250000, -0.0972500000, -0.0633250000, -0.0325750000] \]

\[ \text{yptrs}_\text{DM} y_3 := \text{readdata}(" C:/Users/Kirano/Documents/Research/TheoriesAndBasisSets/ccsd(t)/aug-cc-pvqz/InternalCoordinates/q3/DM-\text{vs}=q/DMy.txt", 1) \]

\[ \text{yptrs}_\text{DM} y_3 := [0.5566250000, 0.5741500000, 0.5888500000, 0.6007000000, 0.6094250000, 0.6145000000, 0.6152750000, 0.6109750000, 0.6009000000, 0.5842750000, 0.5666250000, 0.5296500000, 0.4914500000, 0.4466250000, 0.3962000000, 0.3416750000, 0.2848500000, 0.2277250000, 0.1721500000, 0.1198500000, 0.0721250000] \]

# Identify x and y dipole moment when q=0
# The x-dipole moment at q=0 will be the same for all modes, and the y-dipole moment at q=0 will be the same for all modes.
\[
\begin{align*}
x_{DM\_no\_q} &:= \text{ypts\_DMx\_vl} \left[ \frac{nops(\text{xpts}) + 1}{2} \right] \\
x_{DM\_no\_q} &:= -0.3577250000 \tag{24} \\
y_{DM\_no\_q} &:= \text{ypts\_DMy\_vl} \left[ \frac{nops(\text{xpts}) + 1}{2} \right] \\
y_{DM\_no\_q} &:= 0.5606250000 \tag{25}
\end{align*}
\]

# Give the ANHARMONIC frequencies (in cm\(^{-1}\)) of the three modes
\[
\begin{align*}
v1\_anhnarm\_freq &:= 1541.83265367378 \ ; v2\_anhnarm\_freq := 1589.51100047163 \ ; v3\_anhnarm\_freq := 2857.89762078017 \\
v1\_anhnarm\_freq &:= 1541.83265367378 \\
v2\_anhnarm\_freq &:= 1589.51100047163 \\
v3\_anhnarm\_freq &:= 2857.89762078017 \tag{26}
\end{align*}
\]

\[
\begin{align*}
v1\_xDM\_Eqn &:= x_{DM\_no\_q} + b \cdot x + c \cdot x^2 + d \cdot x^3 + e \cdot x^4 + f \cdot x^5 \\
v1\_xDM\_Eqn &:= f x^5 + e x^4 + d x^3 + c x^2 + b x - 0.3577250000 \tag{27}
\end{align*}
\]

# Recalculate the fit
\[
\begin{align*}
v1\_xDM\_Func &:= \text{rhs}(\text{fit}([\text{least}],[x, y] = v1\_xDM\_Eqn)([\text{xpts}, \text{xpts\_DMx\_vl}])); \\
v1\_xDM\_Func &:= 6.353149572 \times 10^{-6} x^5 + 0.0001527055762 x^4 + 0.001065994493 x^3 \\
&+ 0.006548132126 x^2 - 0.00549786374 x - 0.3577250000 \tag{28}
\end{align*}
\]

\[
\begin{align*}
\text{printf}("x_{DM\_no\_q}, b, c, d, e, f \ arc;"); \ \colon \ \text{const\_v1\_xDM} := \text{CoefficientList}(v1\_xDM\_Func, x) \\
x_{DM\_no\_q}, b, c, d, e, f \ \text{are:} \\
\text{const\_v1\_xDM} &:= [ -0.3577250000, -0.00549786374, 0.006548132126, 0.001065994493, \\
&0.0001527055762, 6.353149572 \times 10^{-6}] \tag{29}
\end{align*}
\]

\[
\begin{align*}
k\_v1\_x\_g0 &:= \text{const\_v1\_xDM1} \\
k\_v1\_x\_g0 &:= -0.3577250000 \tag{30} \\
k\_v1\_x\_g1 &:= \text{const\_v1\_xDM2} \\
k\_v1\_x\_g1 &:= -0.00549786374 \tag{31} \\
k\_v1\_x\_g2 &:= \text{const\_v1\_xDM3} \\
k\_v1\_x\_g2 &:= 0.006548132126 \tag{32} \\
k\_v1\_x\_g3 &:= \text{const\_v1\_xDM4} \\
k\_v1\_x\_g3 &:= 0.001065994493 \tag{33} \\
k\_v1\_x\_g4 &:= \text{const\_v1\_xDM5} \\
k\_v1\_x\_g4 &:= 0.0001527055762 \tag{34} \\
k\_v1\_x\_g5 &:= \text{const\_v1\_xDM6}
\end{align*}
\]

93
\[ k_{v1 \_ y \_ g5} := 6.353149572 \times 10^{-6} \] (35)

\[
v1 \_ yDM\_ Eqn := yDM\_ no \_ q + b \cdot x + c \cdot x^2 + d \cdot x^3 + e \cdot x^4 + f \cdot x^5
v1 \_ yDM\_ Eqn := f x^5 + e x^4 + d x^3 + c x^2 + b x + 0.5606250000
\] (36)

# recalculate the fit
\[
v1 \_ yDM\_ Func := rhs( fit[ leastsquare[ [x, y], y = v1 \_ yDM\_ Eqn ] ]( [xpts, ypts\_ DMy \_ v1] ));
v1 \_ yDM\_ Func := 5.728256497 \times 10^{-6} x^5 - 0.00002737681533 x^4 - 0.001278042438 x^3
- 0.009447662847 x^2 - 0.01777263229 x + 0.5606250000
\] (37)

\[
printf("yDM\_ no \_ q, b, c, d, e, f are:") : const\_ v1 \_ yDM := CoefficientList( v1 \_ yDM\_ Func, x)
yDM\_ no \_ q, b, c, d, e, f are:
const\_ v1 \_ yDM := [ 0.5606250000, -0.01777263229, -0.009447662847, -0.001278042438, -0.00002737681533, 5.728256497 \times 10^{-6} ]
\] (38)

\[ k_{v1 \_ y \_ q0} := const\_ v1 \_ yDM_1 \]
\[ k_{v1 \_ y \_ q1} := const\_ v1 \_ yDM_2 \]
\[ k_{v1 \_ y \_ q2} := const\_ v1 \_ yDM_3 \]
\[ k_{v1 \_ y \_ q3} := const\_ v1 \_ yDM_4 \]
\[ k_{v1 \_ y \_ q4} := const\_ v1 \_ yDM_5 \]
\[ k_{v1 \_ y \_ q5} := const\_ v1 \_ yDM_6 \]
\[ k_{v1 \_ y \_ q0} := 0.5606250000 \] (39)
\[ k_{v1 \_ y \_ q1} := -0.01777263229 \] (40)
\[ k_{v1 \_ y \_ q2} := -0.009447662847 \] (41)
\[ k_{v1 \_ y \_ q3} := -0.001278042438 \] (42)
\[ k_{v1 \_ y \_ q4} := -0.00002737681533 \] (43)
\[ k_{v1 \_ y \_ q5} := 5.728256497 \times 10^{-6} \] (44)

# recalculate the fit
\[
v2 \_ xDM\_ Eqn := xDM\_ no \_ q + b \cdot x + c \cdot x^2 + d \cdot x^3 + e \cdot x^4 + f \cdot x^5
v2 \_ xDM\_ Eqn := f x^5 + e x^4 + d x^3 + c x^2 + b x - 0.3577250000
\] (45)

# recalculate the fit
\[
v2 \_ xDM\_ Func := rhs( fit[ leastsquare[ [x, y], y = v2 \_ xDM\_ Eqn ] ]( [xpts, ypts\_ DMx \_ v2] ));
v2 \_ xDM\_ Func := -1.102557915 \times 10^{-6} x^5 + 0.00001292633055 x^4 - 0.00002182779573 x^3
+ 0.003429057780 x^2 - 0.06364249220 x - 0.3577250000
\] (46)

\[
printf("xDM\_ no \_ q, b, c, d, e, f are:") : const\_ v2 \_ xDM := CoefficientList( v2 \_ xDM\_ Func, x)
xDM\_ no \_ q, b, c, d, e, f are:
const\_ v2 \_ xDM := [ -0.3577250000, -0.06364249220, 0.003429057780, -0.00002182779573, 94]
\[ k_{v2\_x\_q0} \equiv \text{const\_v2\_xDM}_1 \quad k_{v2\_x\_q0} \equiv -0.3577250000 \]  
\[ k_{v2\_x\_q1} \equiv \text{const\_v2\_xDM}_2 \quad k_{v2\_x\_q1} \equiv -0.06364249220 \]  
\[ k_{v2\_x\_q2} \equiv \text{const\_v2\_xDM}_3 \quad k_{v2\_x\_q2} \equiv 0.003429057780 \]  
\[ k_{v2\_x\_q3} \equiv \text{const\_v2\_xDM}_4 \quad k_{v2\_x\_q3} \equiv -0.0002182779573 \]  
\[ k_{v2\_x\_q4} \equiv \text{const\_v2\_xDM}_5 \quad k_{v2\_x\_q4} \equiv 0.00001292633055 \]  
\[ k_{v2\_x\_q5} \equiv \text{const\_v2\_xDM}_6 \quad k_{v2\_x\_q5} \equiv -1.102557915 \times 10^{-6} \]

# recalculated the fit  
\[ v_{2\_yDM\_Eqn} := y\_DM\_no\_q + b \cdot x + c \cdot x^2 + d \cdot x^3 + e \cdot x^4 + f \cdot x^5 \]  
\[ v_{2\_yDM\_Eqn} := f x^5 + e x^4 + d x^3 + c x^2 + b x + 0.5606250000 \]

# recalculate the fit  
\[ v_{2\_yDM\_Func} := \text{rhs}(\text{fit}[[\text{leastsquare}[[x, y], y = v_{2\_yDM\_Eqn}]]])[[\text{xpts}, \text{ypnts\_DMy\_v2}})); \]  
\[ v_{2\_yDM\_Func} := 6.026897780 \times 10^{-6} x^5 - 0.00005854774208 x^4 + 0.0003058144811 x^3 \]  
\[ - 0.004288476042 x^2 + 0.02358596791 x + 0.5606250000 \]

printf("yDM\_no\_q, b, c, d, e, f are:") : const\_v2\_yDM := CoefficientList(v2\_yDM\_Func, x)  
\[ y\_DM\_no\_q, b, c, d, e, f are: \]
\[ \text{const\_v2\_yDM} := [0.5606250000, 0.02358596791, -0.004288476042, 0.0003058144811, \]
\[ -0.00005854774208, 6.026897780 \times 10^{-6}] \]

\[ k_{v2\_y\_q0} \equiv \text{const\_v2\_yDM}_1 \quad k_{v2\_y\_q0} \equiv 0.5606250000 \]  
\[ k_{v2\_y\_q1} \equiv \text{const\_v2\_yDM}_2 \quad k_{v2\_y\_q1} \equiv 0.02358596791 \]  
\[ k_{v2\_y\_q2} \equiv \text{const\_v2\_yDM}_3 \quad k_{v2\_y\_q2} \equiv -0.004288476042 \]  
\[ k_{v2\_y\_q3} \equiv \text{const\_v2\_yDM}_4 \quad k_{v2\_y\_q3} \equiv 0.0003058144811 \]  
\[ k_{v2\_y\_q4} \equiv \text{const\_v2\_yDM}_5 \quad k_{v2\_y\_q4} \equiv -0.00005854774208 \]  
\[ k_{v2\_y\_q5} \equiv \text{const\_v2\_yDM}_6 \quad k_{v2\_y\_q5} \equiv 6.026897780 \times 10^{-6} \]
\[ v_3^*_{\text{DM}_E} := x_{\text{DM}_{\text{no g}}} + b \cdot x + c \cdot x^2 + d \cdot x^3 + e \cdot x^4 + f \cdot x^5 \]
\[ v_3^*_{\text{DM}_E} := f \cdot x^5 + e \cdot x^4 + d \cdot x^3 + c \cdot x^2 + b \cdot x - 0.3577250000 \]  

# recalculate the fit
\[ v_3^*_{\text{DM}_F} := \text{rks}\left(\text{fit}\left[\text{leastsquare}\left[\left[\text{x}, \text{y} = v_3^*_{\text{DM}_E}\right]\right]\left[\left[\text{xpts}, \text{ypts}\_\text{DMx}\_v3\right]\right]\right]\right); \]
\[ v_3^*_{\text{DM}_F} := -2.988556797 \cdot 10^{-6} \cdot x^5 - 0.0001093197246 \cdot x^4 - 0.0002993556753 \cdot x^3 + 0.009966323469 \cdot x^2 + 0.03803436445 \cdot x - 0.3577250000 \]  

\[ \text{printf}\left("\text{yDM}_{\text{no g}}, b, c, d, e, f \text{ are:}\right) : \text{const}_v3^*_{\text{DM}} := \text{CoefficientList}\left(\text{v3^*_{DM}_F}, x\right) \]
\[ \text{const}_v3^*_{\text{DM}} := \left[-0.3577250000, 0.03803436445, 0.009966323469, -0.0002993556753, -0.0001093197246, -2.988556797 \cdot 10^{-6}\right] \]  

\[ k_{v3^*_{x, q0}} := \text{const}_v3^*_{\text{DM}_1} \]
\[ k_{v3^*_{x, q0}} := -0.3577250000 \]  

\[ k_{v3^*_{x, q1}} := \text{const}_v3^*_{\text{DM}_2} \]
\[ k_{v3^*_{x, q1}} := 0.03803436445 \]  

\[ k_{v3^*_{x, q2}} := \text{const}_v3^*_{\text{DM}_3} \]
\[ k_{v3^*_{x, q2}} := 0.009966323469 \]  

\[ k_{v3^*_{x, q3}} := \text{const}_v3^*_{\text{DM}_4} \]
\[ k_{v3^*_{x, q3}} := -0.0002993556753 \]  

\[ k_{v3^*_{x, q4}} := \text{const}_v3^*_{\text{DM}_5} \]
\[ k_{v3^*_{x, q4}} := -0.0001093197246 \]  

\[ k_{v3^*_{x, q5}} := \text{const}_v3^*_{\text{DM}_6} \]
\[ k_{v3^*_{x, q5}} := -2.988556797 \cdot 10^{-6} \]  

# recalculate the fit
\[ v_3^*_{\text{DM}_E} := y_{\text{DM}_{\text{no g}}} + b \cdot x + c \cdot x^2 + d \cdot x^3 + e \cdot x^4 + f \cdot x^5 \]
\[ v_3^*_{\text{DM}_E} := f \cdot x^5 + e \cdot x^4 + d \cdot x^3 + c \cdot x^2 + b \cdot x + 0.5606250000 \]  

\[ \text{printf}\left("\text{yDM}_{\text{no g}}, b, c, d, e, f \text{ are:}\right) : \text{const}_v3^*_{\text{DM}} := \text{CoefficientList}\left(\text{v3^*_{DM}_E}, x\right) \]
\[ \text{const}_v3^*_{\text{DM}} := \left[0.5606250000, -0.05506493094, -0.01409266917, 0.00003630441029, 0.0001718271804, 9.199317679 \cdot 10^{-6}\right] \]
\[ k_{v3\_y\_q0} \equiv \text{const}\_v3\_yDM_1 \]
\[ k_{v3\_y\_q0} = 0.5606250000 \]  
(75)

\[ k_{v3\_y\_q1} \equiv \text{const}\_v3\_yDM_2 \]
\[ k_{v3\_y\_q1} = -0.05506493094 \]  
(76)

\[ k_{v3\_y\_q2} \equiv \text{const}\_v3\_yDM_3 \]
\[ k_{v3\_y\_q2} = -0.01409266917 \]  
(77)

\[ k_{v3\_y\_q3} \equiv \text{const}\_v3\_yDM_4 \]
\[ k_{v3\_y\_q3} = 0.00003630441029 \]  
(78)

\[ k_{v3\_y\_q4} \equiv \text{const}\_v3\_yDM_5 \]
\[ k_{v3\_y\_q4} = 0.0001718271804 \]  
(79)

\[ k_{v3\_y\_q5} \equiv \text{const}\_v3\_yDM_6 \]
\[ k_{v3\_y\_q5} = 9.199317679 \times 10^{-6} \]  
(80)

# List all of the eigenvectors from lowest Energy level (lowest eigenvalue) <-list "Eigvect\_v0\_mode1"
# The mode that each eigenvector describes will be in title --> ex. eigenvectors that describe lowest energy level for normal mode 1 is titled "Eigvect\_v0\_mode1"

# For mode 1:

\[ \text{Eigvect\_state0\_v1} := \begin{bmatrix} 0.9998658167623 & -0.01583004563139 & 0.0001020009946264 & -0.004212804580395 \end{bmatrix} \]
\[ \text{Eigvect\_state0\_v1} \equiv \text{Matrix} (\text{Eigvect\_state0\_v1}) \]  
(81)

\[ \text{Eigvect\_state0\_v1} := \begin{bmatrix} 0.9998658167623, -0.01583004563139, 0.0001020009946264, \\
-0.004212804580395 \end{bmatrix} \]

\[ \text{Eigvect\_state1\_v1} := (0.01582213462534, 0.9988943860429, -0.04426256023948, \]
\[ 0.0007009639895876) ; \text{Eigvect\_state1\_v1} \equiv \text{Matrix} (\text{Eigvect\_state1\_v1}) \]

\[ \text{Eigvect\_state1\_v1} = \begin{bmatrix} 0.01582213462534 \end{bmatrix} \]
\[ 0.9988943860429 \]
\[ -0.04426256023948 \]
\[ 0.0007009639895876 \]  
(82)

# For mode 2

\[ \text{Eigvect\_state0\_v2} := \begin{bmatrix} 0.9988101763001 & 0.04700728260698 & 0.00257087188967 & 0.01272563367080 \end{bmatrix} \]
\[ \text{Eigvect\_state0\_v2} \equiv \text{Matrix} (\text{Eigvect\_state0\_v2}) \]
\[ \text{Eigvec}_\text{state0}_v^2 := \begin{bmatrix} 0.9988101763001 & 0.04700728260698 & 0.002570087188967 & 0.01272563367080 \end{bmatrix} \]  
\[ \text{Eigvec}_\text{state1}_v^2 := (-0.04705385068098, 0.9901803313392, 0.1313304274160, 0.009009184159322) \]  
\[ \text{Eigvec}_\text{state1}_v^2 := \begin{bmatrix} -0.04705385068098 \\ 0.9901803313392 \\ 0.1313304274160 \\ 0.009009184159322 \end{bmatrix} \]  
\[ \text{Eigvec}_\text{state1}_v^2 := \text{Matrix}(\text{Eigvec}_\text{state1}_v^2) \]

# For mode 3

\[ \text{Eigvec}_\text{state0}_v^3 := \begin{bmatrix} 0.9913061684432 & 0.1263834757661 & 0.01473639167681 & 0.03349830174750 \end{bmatrix} ; \]  
\[ \text{Eigvec}_\text{state0}_v^3 := \text{Matrix}(\text{Eigvec}_\text{state0}_v^3) \]

\[ \text{Eigvec}_\text{state0}_v^3 := \begin{bmatrix} 0.9913061684432 & 0.1263834757661 & 0.01473639167681 & 0.03349830174750 \end{bmatrix} \]  
\[ \text{Eigvec}_\text{state3}_v^3 := (-0.1255163020413, 0.9323459414381, 0.3354943228465, 0.04919616595636) \]  
\[ \text{Eigvec}_\text{state3}_v^3 := \text{Matrix}(\text{Eigvec}_\text{state3}_v^3) \]

\[ \text{Eigvec}_\text{state1}_v^3 := \begin{bmatrix} -0.1255163020413 \\ 0.9323459414381 \\ 0.3354943228465 \\ 0.04919616595636 \end{bmatrix} \]  
\[ \text{Eigvec}_\text{state1}_v^3 := \text{Matrix}(\text{Eigvec}_\text{state1}_v^3) \]

#------------------------------------------

\[ \text{mat0} := \text{matrix}(\text{size}, \text{size}, \text{seq}(\text{seq}(q0^n1[r], n1[c]), q0^n2[r], n2[c]), q0^n3[r], n3[c]), c = 1..\text{size}, r = 1..\text{size}) \]  
\[ \text{mat0} := \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{bmatrix} \]  
\[ \text{mat0} := \text{Matrix}(\text{mat0}) \]

\[ \text{mat1} := \text{matrix}(\text{size}, \text{size}, \text{seq}(\text{seq}(q1^n1[r], n1[c]), q0^n2[r], n2[c]), q0^n3[r], n3[c]), c = 1..\text{size}, r = 1..\text{size}) \]  
\[ \text{mat1} := \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{bmatrix} \]  
\[ \text{mat1} := \text{Matrix}(\text{mat1}) \]
\[
\text{mat1} := \begin{bmatrix}
0 & \frac{\sqrt{2}}{2} & 0 & 0 \\
\frac{\sqrt{2}}{2} & 0 & 1 & 0 \\
0 & 1 & 0 & \frac{\sqrt{6}}{2} \\
0 & 0 & \frac{\sqrt{6}}{2} & 0
\end{bmatrix}
\]

(88)

\[\# 2 \rightarrow = q_1^0 q_2^1 q_3^0\]

\[
\text{mat2} := \text{matrix}(\text{size}, \text{size}, \text{[seq(seq(q0(n1[r], n1[c]) \cdot q1(n2[r], n2[c]) \cdot q0(n3[r], n3[c]), c = 1 ..\text{size}), r = 1 ..\text{size})]})
\]

(89)

\[
\text{mat2} := \begin{bmatrix}
0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0
\end{bmatrix}
\]

\[\# 3 \rightarrow = q_1^0 q_2^0 q_3^1\]

\[
\text{mat3} := \text{matrix}(\text{size}, \text{size}, \text{[seq(seq(q0(n1[r], n1[c]) \cdot q0(n2[r], n2[c]) \cdot q1(n3[r], n3[c]), c = 1 ..\text{size}), r = 1 ..\text{size})]})
\]

(90)

\[
\text{mat3} := \begin{bmatrix}
0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0
\end{bmatrix}
\]

\[\# 11 \rightarrow = q_1^2 q_2^0 q_3^0\]

\[
\text{mat11} := \text{matrix}(\text{size}, \text{size}, \text{[seq(seq(q2(n1[r], n1[c]) \cdot q0(n2[r], n2[c]) \cdot q0(n3[r], n3[c]), c = 1 ..\text{size}), r = 1 ..\text{size})]})
\]

(91)

\[
\text{mat11} := \begin{bmatrix}
\frac{1}{2} & 0 & \frac{\sqrt{2}}{2} & 0 \\
0 & \frac{3}{2} & 0 & \frac{\sqrt{6}}{2} \\
\frac{\sqrt{2}}{2} & 0 & \frac{5}{2} & 0 \\
0 & \frac{\sqrt{6}}{2} & 0 & \frac{7}{2}
\end{bmatrix}
\]

\[\# 22 \rightarrow = q_1^0 q_2^2 q_3^0\]
\[ \text{mat22} := \text{matrix}(\text{size, size}, \{ \text{seq(seq(q0(n1[r], n1[c])), q2(n2[r], n2[c]), q0(n3[r], n3[c]), c = 1 \ldots \text{size}), r = 1 \ldots \text{size} } \}) \]

\[ \text{mat22} := \begin{bmatrix}
\frac{1}{2} & 0 & 0 & 0 \\
0 & \frac{1}{2} & 0 & 0 \\
0 & 0 & \frac{1}{2} & 0 \\
0 & 0 & 0 & \frac{1}{2}
\end{bmatrix} \quad (92) \]

\[ \text{mat33} := \text{matrix}(\text{size, size}, \{ \text{seq(seq(q0(n1[r], n1[c])), q2(n2[r], n2[c]), q2(n3[r], n3[c]), c = 1 \ldots \text{size}), r = 1 \ldots \text{size} } \}) \]

\[ \text{mat33} := \begin{bmatrix}
\frac{1}{2} & 0 & 0 & 0 \\
0 & \frac{1}{2} & 0 & 0 \\
0 & 0 & \frac{1}{2} & 0 \\
0 & 0 & 0 & \frac{1}{2}
\end{bmatrix} \quad (93) \]

\[ \text{mat111} := \text{matrix}(\text{size, size}, \{ \text{seq(seq(q3(n1[r], n1[c])), q0(n2[r], n2[c]), q0(n3[r], n3[c]), c = 1 \ldots \text{size}), r = 1 \ldots \text{size} } \}) \]

\[ \text{mat111} := \begin{bmatrix}
0 & \frac{3 \sqrt{2}}{4} & 0 & \frac{\sqrt{2} \sqrt{6}}{4} \\
\frac{3 \sqrt{2}}{4} & 0 & 3 & 0 \\
0 & 3 & 0 & \frac{9 \sqrt{6}}{4} \\
\frac{\sqrt{2} \sqrt{6}}{4} & 0 & \frac{9 \sqrt{6}}{4} & 0
\end{bmatrix} \quad (94) \]

\[ \text{mat222} := \text{matrix}(\text{size, size}, \{ \text{seq(seq(q0(n1[r], n1[c])), q3(n2[r], n2[c]), q0(n3[r], n3[c]), c = 1 \ldots \text{size}), r = 1 \ldots \text{size} } \}) \]
mat222 := 
\[
\begin{bmatrix}
0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 
\end{bmatrix}
\]  (95)

mat333 := matrix(size, size, [seq(q0(n1[r], n1[c]) \cdot q0(n2[r], n2[c]) \cdot q3(n3[r], n3[c]), c = 1 .. size), r = 1 .. size])

mat333 := 
\[
\begin{bmatrix}
0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 
\end{bmatrix}
\]  (96)

mat111 := matrix(size, size, [seq(seq(q4(n1[r], n1[c]) \cdot q0(n2[r], n2[c]) \cdot q0(n3[r], n3[c]), c = 1 .. size), r = 1 .. size])

mat111 := 
\[
\begin{bmatrix}
\frac{3}{4} & 0 & \frac{3\sqrt{2}}{2} & 0 \\
0 & \frac{15}{4} & 0 & \frac{5\sqrt{6}}{2} \\
\frac{3\sqrt{2}}{2} & 0 & \frac{39}{4} & 0 \\
0 & \frac{5\sqrt{6}}{2} & 0 & \frac{75}{4} 
\end{bmatrix}
\]  (97)

mat222 := matrix(size, size, [seq(seq(q0(n1[r], n1[c]) \cdot q4(n2[r], n2[c]) \cdot q0(n3[r], n3[c]), c = 1 .. size), r = 1 .. size])

mat222 := 
\[
\begin{bmatrix}
\frac{3}{4} & 0 & 0 & 0 \\
0 & \frac{3}{4} & 0 & 0 \\
0 & 0 & \frac{3}{4} & 0 \\
0 & 0 & 0 & \frac{3}{4} 
\end{bmatrix}
\]  (98)

mat333 := matrix(size, size, [seq(seq(q0(n1[r], n1[c]) \cdot q0(n2[r], n2[c]) \cdot q4(n3[r], n3[c]), c = 1 .. size), r = 1 .. size])

mat333 := 
\[
\begin{bmatrix}
\frac{3}{4} & 0 & 0 & 0 \\
0 & \frac{3}{4} & 0 & 0 \\
0 & 0 & \frac{3}{4} & 0 \\
0 & 0 & 0 & \frac{3}{4} 
\end{bmatrix}
\]  (99)
$\begin{pmatrix}
\frac{3}{4} & 0 & 0 & 0 \\
0 & \frac{3}{4} & 0 & 0 \\
0 & 0 & \frac{3}{4} & 0 \\
0 & 0 & 0 & \frac{3}{4}
\end{pmatrix}$

\text{mat3333 := (99)}

\# 11111 -> $= q^1 q^2 q^3$
\text{mat11111 := matrix(size, size, [seq(seq(q5(n1[r], n1[c]) \cdot q0(n2[r], n2[c]) \cdot q0(n3[r], n3[c]), c = 1 ..size), r = 1 ..size)])}

$\begin{pmatrix}
0 & 15 \sqrt{2} & 0 & 5 \sqrt{2} \sqrt{6} \\
15 \sqrt{2} & 0 & 45 & 45 \sqrt{2} \\
0 & 45 & 0 & 95 \sqrt{6} \\
5 \sqrt{2} \sqrt{6} & 0 & 95 \sqrt{6} & 0
\end{pmatrix}$

\text{mat11111 := (100)}

\# 22222 -> $= q^1 q^2 q^3$
\text{mat22222 := matrix(size, size, [seq(seq(q0(n1[r], n1[c]) \cdot q5(n2[r], n2[c]) \cdot q0(n3[r], n3[c]), c = 1 ..size), r = 1 ..size)])}

$\begin{pmatrix}
0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0
\end{pmatrix}$

\text{mat22222 := (101)}

\# 33333 -> $= q^1 q^2 q^3$
\text{mat33333 := matrix(size, size, [seq(seq(q0(n1[r], n1[c]) \cdot q0(n2[r], n2[c]) \cdot q5(n3[r], n3[c]), c = 1 ..size), r = 1 ..size)])}

$\begin{pmatrix}
0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0
\end{pmatrix}$

\text{mat33333 := (102)}

### Calculating transition dipole moment of $q1$

102
Calculating the x-vector transition dipole moment:

\[ mat_{\text{sum}}_{vl} \cdot x := \text{evalm}(k_{vl} \cdot x \cdot q_{0} \cdot \text{mat0} + k_{vl} \cdot x \cdot q_{1} \cdot \text{mat1} + k_{vl} \cdot x \cdot q_{2} \cdot \text{mat2} + k_{vl} \cdot x \cdot q_{3} \cdot \text{mat3}) + k_{vl} \cdot x \cdot q_{4} \cdot \text{mat4} + k_{vl} \cdot x \cdot q_{5} \cdot \text{mat5}) \]

\[ mat_{\text{sum}}_{vl} \cdot x := [[-0.3543364007, -0.00193752162 \sqrt{2}, 0.005303124427 \sqrt{2},
0.002744400602 \sqrt{2} \sqrt{6}],
[-0.00193752162 \sqrt{2}, -0.3473301559, -0.002928409962, 0.003655830004 \sqrt{6}],
[0.003503124427 \sqrt{2}, -0.002928409962, -0.398657903, -0.0002750019268 \sqrt{6}],
[0.002744400602 \sqrt{2} \sqrt{6}, 0.003655830004 \sqrt{6}, -0.0002750019268 \sqrt{6},
-0.3319433080]] \]

Up to the n-th derivative of dipole function at q=0 (here labeled "k_{vl} \cdot x \cdot q_{0}" for the zeroth derivative, "k_{vl} \cdot x \cdot q_{1}" for the first derivative, etc.) multiplied with the integral of \( \phi_{\text{harm}}(\text{harm}, \nu = i) \) \( q \)

\[ \phi_{\text{harm}}(\text{harm}, \nu = j). \]

\[ \text{dipintegral}_{vl} \cdot x := \text{evalf} \left( \text{evalm}(\text{mat}_{\text{sum}}_{vl} \cdot x) \right) \]

\[ \text{dipintegral}_{vl} \cdot x := [[-0.3543364007, -0.002740074361, 0.004954166074, 0.0009506882558],
-0.002740074361, -0.3473301559, -0.002928409962, 0.008954918097,
0.004954166074, -0.002928409962, -0.398657903, -0.0006736143990,
0.0009506882558, 0.008954918097, -0.0006736143990, -0.3319433080]] \]

Make a matrix of the product of the eigenvectors of the lowest energy and the next lowest energy

\[ \text{coefficient}_{vl} := \text{Eigvec}_{\text{state1}} \cdot \text{Eigvec}_{\text{state0}} \cdot \text{vl} \]

\[ \text{coefficient}_{vl} := [[0.0158200115600886, -0.000250465113105128, 1.61387346889748 \times 10^{-6}, -0.000066665555612212587],
[0.998760351160060, -0.158125437119984, 0.000101888220930103, -0.00420814684485238],
[-0.0442566209458382, 0.00070678348353117, -4.51482516913791 \times 10^{-6}, 0.000186469516516891],
[0.000700869931969966, -0.0000110962919411329, 7.14990241352247 \times 10^{-8}, -2.95302430602659 \times 10^{-6}]] \]

Integral of anharmonic wave functions with dipole vector operator multiplied by its product of
eigenvectors, summed.

This gives the contribution from the x-dipole vector towards the transition dipole moment.

\[ x_{\text{TDM}}_{vl} := \text{add}(\text{dipintegral}_{vl} \cdot x[i,j] \cdot \text{coefficient}_{vl}[i,j], j = 1..4), i = 1..4) \]

\[ x_{\text{TDM}}_{vl} := -0.00310525020779377 \]

Calculating the y-vector transition dipole moment:

\[ mat_{\text{sum}}_{vl} \cdot y := \text{evalm}(k_{vl} \cdot y \cdot q_{0} \cdot \text{mat0} + k_{vl} \cdot y \cdot q_{1} \cdot \text{mat1} + k_{vl} \cdot y \cdot q_{2} \cdot \text{mat2} + k_{vl} \cdot y \cdot q_{3} \cdot \text{mat3}) \]
\[ \cdot \text{mat111} + k_{v1yq4} \cdot \text{mat111} + k_{v1yq5} \cdot \text{mat111} \]

\[ \text{mat\_sum\_v1\_y} := \left[ \begin{array}{c}
0.5558806360, -0.00098340107493 \sqrt{2} , -0.0004764896647 \sqrt{2} , \\
-0.0003123502889 \sqrt{2} , \\
-0.00098340107493 \sqrt{2} , 0.5463508426 , -0.02154231671 , -0.0004792273462 \sqrt{6} , \\
-0.004764896647 \sqrt{2} , -0.02154231671 , 0.5367389190 , -0.0116938858 \sqrt{6} , \\
-0.0003123502889 \sqrt{2} , -0.004792273462 \sqrt{6} , -0.0116938858 \sqrt{6} , \\
0.5270448647
\end{array} \right] \]

# Up to the n-th derivative of dipole function at q=0 (here labeled "k_{v1yq0}" for the zeroth derivative, 
"k_{v1yq1}" for the first derivative, etc.) multiplied with the integral of \( (\varphi_\text{(harm, v = i)})^n \)

\[ \text{dipintegral\_v1\_y} := \text{eval}(\text{evalm(mat\_sum\_v1\_y)}) \]

\[ \text{dipintegral\_v1\_y} := \left[ \begin{array}{c}
0.5558806360, -0.01390752819 , -0.006738581460 , -0.001082013140 \\
-0.01390752819 , 0.5463508426 , -0.02154231671 , -0.0117862469 \\
-0.006738581460 , -0.02154231671 , 0.5367389190 , -0.02864406013 \\
-0.001082013140 , -0.0117862469 , -0.02864406013 , 0.5270448647
\end{array} \right] \]

# Make a matrix of the product of the eigenvectors of the lowest energy and the next lowest energy

\[ \text{coeffprod\_v1} := \text{Eigvec\_state1\_v1} \cdot \text{Eigvec\_state0\_v1} \]

\[ \text{coeffprod\_v1} := \left[ \begin{array}{c}
0.0158200115600886 , -0.000250465113105128, \\
1.61387346889748 \cdot 10^{-6} , -0.0000666555612212587, \\
0.998760351160060 , -0.0158125437119984 , 0.00010188822093103, \\
-0.00420814684485238 , \\
-0.0442566290453832 , 0.00070067834835317 , -4.51482516913791 \cdot 10^{-6}, \\
0.0001864651561891, \\
0.00070086993196966 , -0.0000110962919411329, 7.14990241352247 \cdot 10^{-8}, \\
-2.95302430602659 \cdot 10^{-6}
\end{array} \right] \]

# Integral of anharmonic wave functions with dipole vector operator multiplied by its product

# This gives the contribution from the y-dipole vector towards the transition dipole moment.

\[ \text{y\_TDM\_v1} := \text{add}(\text{add}(\text{dipintegral\_v1\_y[i,j] \cdot coeffprod\_v1[i,j], j = 1 .. 4}, i = 1 .. 4)) \]

\[ \text{y\_TDM\_v1} := -0.0134115171217542 \]

#### Calculate the TOTAL transition dipole moment SQUARED

\[ \text{Tot\_TDM\_v1\_sqr} := (x\_TDM\_v1)^2 + (y\_TDM\_v1)^2 \]

\[ \text{Tot\_TDM\_v1\_sqr} := 0.000189511370360109 \]

# Plug the squared total transition dipole moment into molar absorptivity equation to get the Molar

# Absorptivity of v1
# Use the harmonic frequency of q1

\[
\text{MolAbs}_v1 := \frac{41.6238 \cdot (\text{Tot TDM}_v1.\text{sqr} \cdot (2.541765)^2) \cdot v1 \cdot \text{anharm_freq}}{16.6054} \\
\text{MolAbs}_v1 := 4.73190139569590
\]  \hfill (112)

### Calculating transition dipole moment of q2

#### Calculating the x-vector transition dipole moment:

\[
\text{mat_sum}_v2_\cdot x := \text{evalm}(k_{v2_\cdot x \cdot q0} \cdot \text{mat0} + k_{v2_\cdot x \cdot q1} \cdot \text{mat2} + k_{v2_\cdot x \cdot q2} \cdot \text{mat22} + k_{v2_\cdot x \cdot q3} \cdot \text{mat222} + k_{v2_\cdot x \cdot q4} \cdot \text{mat2222} + k_{v2_\cdot x \cdot q5} \cdot \text{mat22222})
\]

\[
\begin{bmatrix}
-0.3560007764 & 0. & 0. & 0. \\
0. & -0.3560007764 & 0. & 0. \\
0. & 0. & -0.3560007764 & 0. \\
0. & 0. & 0. & -0.3560007764 \\
\end{bmatrix}
\]  \hfill (113)

#### Up to the n-th derivative of dipole function at q=0 (here labeled "k_{v2_\cdot x \cdot q0}" for the zeroth derivative, "k_{v2_\cdot x \cdot q1}" for the first derivative, etc.) multiplied with the integral of \(\varphi_c(harm, v = i) \mid q^n \varphi_c(harm, v = j)\).

\[
\text{dipintegral}_v2_\cdot x := \text{evalf}(\text{evalm}(\text{mat_sum}_v2_\cdot x))
\]

\[
\begin{bmatrix}
-0.3560007764 & 0. & 0. & 0. \\
0. & -0.3560007764 & 0. & 0. \\
0. & 0. & -0.3560007764 & 0. \\
0. & 0. & 0. & -0.3560007764 \\
\end{bmatrix}
\]  \hfill (114)

#### Make a matrix of the product of the eigenvectors of the lowest energy and the next lowest energy

\[
\text{coeffprod}_v2 := \text{Eigvect_state1}_v2 \cdot \text{Eigvect_state0}_v2
\]

\[
\text{coeffprod}_v2 := \begin{bmatrix}
-0.02499987848942682, & -0.00221187365670747, \\
-0.0012093249826753, & -0.00059879006656675, \\
0.98900291313798, & 0.0465456866671349, & 0.00254484978434198, \\
0.012600621646540, \\
0.131174176360942, & 0.00617348651643939, & 0.000337530649023422, \\
0.00167126290912561, \\
0.00899846481849247, & 0.000423497265835577, & 0.00002315438879017, \\
0.000114647577284306 \\
\end{bmatrix}
\]  \hfill (115)

#### Integral of anharmonic wave functions with dipole vector operator multiplied by its product of eigenvectors, summed.

This gives the contribution from the x-dipole vector towards the transition dipole moment.

\[
x_{\text{TDM}}_v2 := \text{add}(\text{add}(\text{dipintegral}_v2_\cdot x[i, j] \cdot \text{coeffprod}_v2[i, j], j = 1..4), i = 1..4)
\]
\[ x_{\text{TDM}_v 2} := 2.93924078327047 \times 10^{-13} \]  

\[ \# \text{----- Calculating the } y = \text{vector transition dipole moment}: \]

\[ \text{mat}_\text{sum}_\text{v2}_y := \text{eval}(k_{y q0} \cdot \text{mat0} + k_{y q1} \cdot \text{mat2} + k_{y q2} \cdot \text{mat22} + k_{y q3} \cdot \text{mat222} + k_{y q4} \cdot \text{mat2222} + k_{y q5} \cdot \text{mat22222}) \]

\[
\begin{bmatrix}
0.5584368512 & 0. & 0. & 0. \\
0. & 0.5584368512 & 0. & 0. \\
0. & 0. & 0.5584368512 & 0. \\
0. & 0. & 0. & 0.5584368512 \\
\end{bmatrix}\]

\[ \text{mat}_\text{sum}_\text{v2}_y := \]

\[ \# \text{ Up to the } n \text{-th derivative of dipole function at } q=0 \text{ (here labeled } k_{y q0} \text{ for the zeroth derivative, } k_{y q1} \text{ for the first derivative, etc.) multiplied with the integral of } |q^{n}\varphi(h_{\text{v=1}})| q \]

\[\text{dipintegral}_\text{v2}_y := \text{evalf}(\text{eval}(\text{mat}_\text{sum}_\text{v2}_y)) \]

\[
\begin{bmatrix}
0.5584368512 & 0. & 0. & 0. \\
0. & 0.5584368512 & 0. & 0. \\
0. & 0. & 0.5584368512 & 0. \\
0. & 0. & 0. & 0.5584368512 \\
\end{bmatrix}\]

\[ \# \text{ Make a matrix of the product of the eigenvectors of the lowest energy and the next lowest energy} \]

\[ \text{coeffprod}_\text{v2} := \text{Eigvec}_\text{state1}_\text{v2} \cdot \text{Eigvec}_\text{state0}_\text{v2} \]

\[ \text{coeffprod}_\text{v2} := [ [ -0.0469978648942682, -0.00221187365670747, \\
-0.00120932498826753, -0.000598790066566675 ], \\
[ 0.989002191313798, 0.04654568666671349, 0.0025484978434198, \\
0.0126006721646540 ], \\
[ 0.131714167360942, 0.00617348651643939, 0.000337530649023422, \\
0.00167126290912561 ], \\
[ 0.00899846481849247, 0.000423497265835577, 0.0000231543887909179, \\
0.000114647577284306 ] ] \]

\[ \# \text{Integral of anharmonic wave functions with dipole vector operator multiplied by its product of} \]

\[ \# \text{ This gives the contribution from the } y \text{-dipole vector towards the transition dipole moment.} \]

\[ y_{\text{TDM}_v 2} := \text{add}(\text{add}(\text{dipintegral}_\text{v2}_y[i, j] \cdot \text{coeffprod}_\text{v2}[i, j], j=1..4), i=1..4) \]

\[ y_{\text{TDM}_v 2} := -4.61055672806854 \times 10^{-13} \]

\[ \# \text{ Calculate the TOTAL transition dipole moment SQUARED} \]

\[ \text{Tot}_{\text{TDM}_v 2}_\text{sqr} := (x_{\text{TDM}_v 2})^2 + (y_{\text{TDM}_v 2})^2 \]

\[ \text{Tot}_{\text{TDM}_v 2}_\text{sqr} := 2.98963697247785 \times 10^{-25} \]

\[ \# \text{ Plug the squared total transition dipole moment into molar absorptivity equation to get the Molar} \]
Absorptivity of q2
# Use the harmonic frequency of q2

\[
MolAbs_{\nu 2} := 41.6238 \cdot \left( \frac{\text{Tot TD}_M \cdot \nu_2 \cdot \text{sqr} \cdot (2.541765)^2}{16.6054} \right) \cdot \nu_2 \cdot \text{anhar} \cdot \text{freq}
\]
\[
MolAbs_{\nu 2} := 7.69564753580083 \times 10^{-21}
\]

#---------------------------------------------------------------

##### Calculating transition dipole moment of q3

#---- Calculating the \(\nu\)-vector transition dipole moment:

\[
\text{mat\_sum\_v3\_x} := \text{eval}(k_{v3\_x\_1}\cdot\text{mat}0 + k_{v3\_x\_1}\cdot\text{mat}3 + k_{v3\_x\_1}\cdot\text{mat}33 + k_{v3\_x\_1}\cdot\text{mat}333 + k_{v3\_x\_1}\cdot\text{mat}3333 + k_{v3\_x\_1}\cdot\text{mat}33333)
\]
\[
\begin{bmatrix}
-0.3528238281 & 0. & 0. & 0. \\
0. & -0.3528238281 & 0. & 0. \\
0. & 0. & -0.3528238281 & 0. \\
0. & 0. & 0. & -0.3528238281 \\
\end{bmatrix}
\]

# Up to the \(n\)-th derivative of dipole function at \(q=0\) (here labeled "k\_v3\_x\_1\(q0\)" for the zeroth derivative, "k\_v3\_x\_1\(q1\)" for the first derivative, etc.) multiplied with the integral of \(|\varphi(\text{harm}, \nu = i)\|^n|\)

\[
\text{dipintegral\_v3\_x} := \text{evalf}(\text{eval}(\text{mat\_sum\_v3\_x}))
\]

\[
\begin{bmatrix}
-0.3528238281 & 0. & 0. & 0. \\
0. & -0.3528238281 & 0. & 0. \\
0. & 0. & -0.3528238281 & 0. \\
0. & 0. & 0. & -0.3528238281 \\
\end{bmatrix}
\]

# Make a matrix of the product of the eigenvectors of the lowest energy and the next lowest energy

\[
\text{coefficient\_v3} := \text{Eigvec\_state1\_v3} \cdot \text{Eigvec\_state0\_v3}
\]

\[
\text{coefficient\_v3} := \left[ \begin{bmatrix}
-0.124425084453720, & -0.0158631865172871, & -0.00184965738870538, & -0.0042045829600982 \\
0.924240282870571, & 0.117833120695364, & 0.0137394169713160, & 0.031232056793504 \\
0.3325775915410, & 0.0424009382611348, & 0.00494397574681217, & 0.0112384900612852 \\
0.048764627762950, & 0.00621758244793066, & 0.000724973970530267, & 0.00164798801202623
\end{bmatrix} \right]
\]

# Integral of anharmonic wave functions with dipole vector operator multiplied by its product of
eigenvectors, summed.
# This gives the contribution from the \(\nu\)-dipole vector towards the transition dipole moment.

\[
\text{x\_TDM\_v3} := \text{add}(\text{add}(\text{dipintegral\_v3\_x[i,j]} \cdot \text{coefficient\_v3[i,j]}, j = 1..4), i = 1..4)
\]
\[ x_{	ext{TD}M_{v3}} := -1.69965712511211 \times 10^{-13} \]  

### Calculating the \( y \)-vector transition dipole moment:

\[
\text{mat}_{\text{sum}_{v3} y} := \text{evalm}(k_{v3 \cdot y \cdot q0} \cdot \text{mat0} + k_{v3 \cdot y \cdot q1} \cdot \text{mat3} + k_{v3 \cdot y \cdot q2} \cdot \text{mat33} + k_{v3 \cdot y \cdot q3} \cdot \text{mat333} + k_{v3 \cdot y \cdot q4} \cdot \text{mat3333} + k_{v3 \cdot y \cdot q5} \cdot \text{mat33333})
\]

\[
\text{mat}_{\text{sum}_{v3} y} := \begin{bmatrix}
0.5537075358 & 0. & 0. & 0. \\
0. & 0.5537075358 & 0. & 0. \\
0. & 0. & 0.5537075358 & 0. \\
0. & 0. & 0. & 0.5537075358 \\
\end{bmatrix}
\]

\[
\text{dipintegral}_{v3 y} := \text{evalf}(\text{evalm}(\text{mat}_{\text{sum}_{y} y}))
\]

\[
\text{dipintegral}_{v3 y} := \begin{bmatrix}
0.5537075358 & 0. & 0. & 0. \\
0. & 0.5537075358 & 0. & 0. \\
0. & 0. & 0.5537075358 & 0. \\
0. & 0. & 0. & 0.5537075358 \\
\end{bmatrix}
\]

### Make a matrix of the product of the eigenvectors of the lowest energy and the next lowest energy

\[
\text{coeffprod}_{v3} := \text{Eigvec}_0 \cdot \text{Eigvec}_{v3}
\]

\[
\text{coeffprod}_{v3} := \begin{bmatrix}
-0.124425084453720, -0.0158631865172871, -0.00184965738870538, \\
-0.0042045829600982, \\
0.924240282870571, 0.117833120695364, 0.0137394149713160, 0.0312320056793504, \\
0.332577591715410, 0.0424009386211348, 0.00494397574681217, \\
0.0112384900612852, \\
0.0487684627762950, 0.00621758244793066, 0.000724973970530267, \\
0.0016479801202623 \\
\end{bmatrix}
\]

### Integral of anharmonic wave functions with dipole vector operator multiplied by its product of eigenvectors, summed.

### This gives the contribution from the \( y \)-dipole vector towards the transition dipole moment.

\[ y_{\text{TDM}_{v3}} := \text{add}(\text{add}(\text{dipintegral}_{v3 y[i, j]} \cdot \text{coeffprod}_{v3[i, j]}; j = 1..4), i = 1..4) \]

\[ y_{\text{TDM}_{v3}} := 2.66735526895101 \times 10^{-13} \]

### Calculate the TOTAL transition dipole moment SQUARED

\[ \text{Tot}_{\text{TDM}_{v3 \text{sqr}}} := (x_{\text{TDM}_{v3}})^2 + (y_{\text{TDM}_{v3}})^2 \]

\[ \text{Tot}_{\text{TDM}_{v3 \text{sqr}}} := 1.00036184737451 \times 10^{-25} \]

### Plug the squared total transition dipole moment into molar absorptivity equation to get the Molar Absorptivity of \( q3 \)

### Use the harmonic frequency of \( q3 \)
\[
\text{MolAbs}_v^3 := \frac{41.6238 \cdot (\text{Tot_TDM}_v^3 \cdot \text{sqr} \cdot (2.541765)^2) \cdot \text{v3_anharm_freq}}{16.6054}
\]

\[
\text{MolAbs}_v^3 := 4.62985043703483 \times 10^{-21}
\]  

(132)
Vita

Harkiran Kaur Dhah was born in Fresno, California to Mohinder and Ravinder Dhah in 1987. She attended Central High School and upon graduating in 2005 attended California State University of Fresno to graduate in 2011 with a bachelor of science in chemistry, a bachelor of science in biomedical physics, and a minor in computer science. While at California State University of Fresno she conducted research in organic synthesis under the mentorship of Dr. Santanu Maitra. In Fall of 2012 she began attendance at University of Tennessee, Knoxville to pursue her Doctorate of Philosophy in Physical Chemistry under the mentorship of Dr. Robert J. Hinde. Harkiran will graduate in Summer of 2018 with hopes to pursue an academic career in teaching.