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

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Spectroscopy and vibrational dynamics of Methoxy and D-Methoxy radicals

by

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Chapter 6

Thesis summary for non-specialists: Interpreting the vibrational dance in CH_3O and CD_3O using spectroscopy

This chapter is submitted as part of the Wisconsin Initiative for Science Literacy

In this chapter, I outline the fundamental science research undertaken as part of this thesis, as well as its potential application to society. I have tried to provide a cursory glance into the kind of questions asked in my research field, and how we can go about answering them. I have stated some of the results and hope that the reader perceives some of the excitement that drives my research. I have not avoided usage of technical words from this chapter; they are important to appreciate the results. But I have tried to explain them using examples that we can relate to in our daily lives, I hope that the reader will learn to appreciate the thought process behind tackling such research questions.

To understand and control reactions is a chemist's dream. Past few decades has seen a phenomenal growth in laser technology, allowing design of better experiments that can literally 'track' the formation of products in a reaction. Understanding vibrations is critical to understanding reaction mechanisms, because often, thermal energy may not be enough to make a reaction happen; energy put in a particular molecular vibration will! The research in this thesis aims to study the vibrations of methoxy (CH_3O) family of molecules. These molecules are important to the society because they form part of a family of reaction intermediates called alkoxy radicals. Radicals are short-lived species formed in intermediate step(s) of many reactions and alkoxy radicals are known to be intermediates in a plethora of atmospheric and combustion reactions. Because they are so short-lived (of the order of μs or so) they are hard to isolate and characterise experimentally. Theory therefore can play a complimentary role in understanding properties of these reactive species. The study of methoxy vibrations brings up fundamental research questions on its own, and traveling the road towards answering them is a rewarding journey by itself. The stimulating part of development of our theory is in identifying many special properties of methoxy, and learning to use them to build a predictive model of its vibrational spectroscopy. In the rest of the chapter, we hope that we have provided a flavour of the challenges we faced in the journey of the research in this thesis.

6.1 Introduction

6.1.1 As is Newton's equation to a ball, so is Schrödinger's equation to an atom

Werner Heisenberg, a German physicist (who along with Erwin Schrödinger laid the foundations of Quantum theory) said:

> *"It is not surprising that our language should be incapable of describing the processes occurring within the atoms, for, as has been remarked, it was invented to describe the experiences of daily life, and these consists only of processes involving exceedingly large numbers of atoms. Furthermore, it is very difficult to modify our language so that it will be able to describe these atomic processes, for words can only describe things of which we can form mental pictures, and this ability, too, is a result of daily experience. Fortunately, mathematics is not subject to this limitation, and it has been possible to invent a mathematical scheme the quantum theory which seems entirely adequate for the treatment of atomic processes."*

Quantum theory provides us the mathematical tools we need to understand the microscopic world of atoms and molecules. Molecules are nothing but groups of atoms 'glued' together via bonds. Like a macroscopic object such as a ball, molecules can translate and rotate as a whole. The bonds behave like springs and the atoms forming the bond vibrate about their equilibrium positions. The difference between a molecule and a macroscopic object, however, is that the latter can have any amount of translational, rotational or vibrational energy; the former has only certain allowed values. Quantum mechanics is the physical theory explaining the existence of these allowed ‘energy levels’ in molecules. The total energy of a molecule is said to be ‘quantised’. To obtain these energy levels, or specific energy values, we use the Schrödinger’s equation. For a ball, solution of Newton’s equation of motion tells us where the ball will be at any point of time in future given its initial position and velocity; we obtain the so-called ‘trajectory’ of the ball in space. By solving the Schrödinger’s equation, we obtain energy ‘eigenfunctions’ that will contain all the spatial and time information about the molecule or atom. When we substitute these eigenfunctions back into the Schroödinger equation, we obtain energy ’eigenvalues’. We will use the word ‘state’ and ‘eigenfunction’ interchangeably in the rest of the chapter.

Any object possesses a certain amount of energy, and can be broken down into kinetic and potential energy. For an object such as a ball, Newton’s equation tells us how to calculate the potential (V) and kinetic (T) energy knowing the position and velocity of the ball. The total energy of the molecule is the energy ‘eigenvalue’ obtained by solving Eqn. 6.1. H is called the Hamiltonian, E is called the energy eigenvalue and Ψ is called the energy eigenfunction. An atom is formed of a nucleus and electrons. The bonds in molecules are formed by electrons. Electronic energy is also ‘quantised’ and so is the ‘spin’ associated with each electron. The spin is a completely quantum-mechanical property, but is often explained in a way similar to how an electron behaves like a spinning top. For purposes of understanding this thesis work however, it is sufficient for us to know that there exists a quantity such as spin ‘S’, and it has a value of ‘1/2’. Every atom of molecule has a certain value of total spin (written as 2S+1) associated with it. The energy eigenfunction(Ψ), in general, is a function of nuclear and electronic spatial coordinates, spin and time (in time-dependent Schrödinger equation); the energy eigenvalue (E) is a number denoting the total molecular energy.

$$H\Psi = E\Psi \tag{6.1}$$

$$H = H_{el} + H_{nucl} \tag{6.2}$$

$$H_{el}\Psi_{el}(R) = E_{el}(R)\Psi_{el}(R) \tag{6.3}$$

In language of quantum theory, in order to solve the Schrödinger equation, the first step is to write down the Hamiltonian. Without going much into the Quantum theory jargon, we only need to know that the Hamiltonian contains mathematical expressions such as derivatives (similar to Newton's equation, which contains second order derivatives with respect to time) written using a set of postulates. As it turns out, the full molecular Schrödinger equation is too complex to solve, and the heartening fact is that we can make some very good approximations to make our life easier. One of the simplest approximations is to assume that the electronic, vibrational and rotational motions do not 'talk' to each other. Simply put, when the molecule is vibrating, it is not rotating. The electrons being ~ 2000 times lighter than a proton move much faster and hence only 'see' a static arrangement of nuclei in the molecule. This is the Born-Oppenheimer approximation. Mathematically speaking, we write the Hamiltonian as a sum of 2 quantities- electronic and nuclear (Eqn. 6.2). This works remarkably for a large set of molecules. A typical starting point to calculate molecular energy levels is to solve the electronic Schrödinger equation (Eqn. 6.3) first at fixed nuclear geometry or arrangement of nuclei and repeat this for many more geometries. E_{el} gives us the electronic energy of the molecule for some nuclear configuration, consisting of bond lengths and bond angles, R. Repeating the solution process for different R's gives us the molecular potential energy surface (PES). The set of eigenfunctions $\{\Psi_{el}\}$ represents different electronic states and each electronic state is associated with a different PES.

6.1.2 Breakdown of Born-Oppenheimer approximation: Nuclei 'move' faster than we think!

As it happens with approximations in any theory, there are limits where they will break down. This is true for CH_3O and CD_3O radicals. In Eqn. 6.3, the eigenfunction associated with the lowest energy eigenvalue is called 'ground electronic state' and is often well-separated from the higher electronic states. Every so often, it happens that two PES come close to each other. When this happens, the electronic states associated with the 2 surfaces start 'talking' to each other. This interaction, which we have conveniently assumed to be non-existent in the Born-Oppenheimer picture has to be accounted for. In other words, electrons do not 'see' a static picture of the nuclei anymore, they can 'see' nuclei 'move'! The electronic and nuclear motion have to be solved together now, since the electrons do not necessarily adjust as instantaneously to changes in nuclear coordinates as we expect.

The meeting of PES have far reaching implications in understanding events as common as vision. Many chemical reactions take place faster or slower often due to interaction of two different PES, and it is only recently that laser technology has progressed significantly to probe reactions at the molecular level.

The breakdown of Born-Oppenheimer approximation in the ground electronic state is common in what are called 'open-shell' molecules. In many possible ways of classifying molecules, a common way is to arrange all the electrons in molecular orbitals (orbital denotes electronic energy level) and ask whether there are unpaired electrons. Each orbital can accommodate two paired electrons, one with a spin 'up' (1/2 denoted as up arrow) and other with spin 'down' (-1/2 denoted as down arrow). In methoxy, it so happens that there is one unpaired electron, and hence is an open-shell molecule. If all electrons are paired up, the molecules are classified as 'closed-shell' molecules.

Fig. 6.1 is a 3-D plot of PES of methoxy as a function of motion of CO bond around the z-axis. The point marked as C_{3v} denotes the intersection of two potential energy surfaces. The electronic states of upper and lower surfaces have the same energy and are said to be 'degenerate'. If two states have the same energy, then we have a double degeneracy. In molecular theory, the letter 'E' (meaning double degeneracy; German, entartet) is used as a label for such states. The double degeneracy can be clearly understood by examining the possible arrangement of electrons in the molecule. In Fig. 6.2 we show the outermost atomic orbitals of oxygen atom. Methoxy has 17 electrons in total. Among the valence electrons of oxygen in the 2p orbitals, one is a lone pair, one of the 2 unpaired electrons pairs up with an unpaired electron from carbon to form C-O bond (denoted by red arrow paired with black arrow). From the figure, it is clear that there are two energetically equivalent configurations possible for the ground electronic state. This is the reason we use the label 'E'.

Figure 6.1: 2-D PES of methoxy. The nuclear motion involves rotation of CO bond around the z-axis.

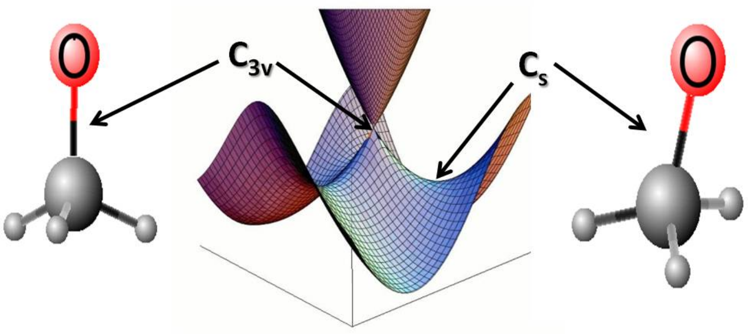
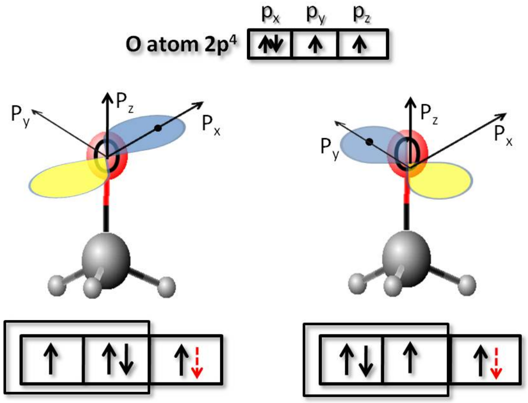


Figure 6.2: Orbital degeneracy in ground state of methoxy.



We will return to the PES of methoxy, once we have more background in understanding symmetry. For now, we know that methoxy has an orbitally degenerate ground electronic state. The interaction of 2 electronic states is one of many types and all of them together are termed as vibronic interactions; in this thesis, we are interested in understanding 'Jahn-Teller' type of interactions. Although the Born-Oppenheimer approximation involves separation of electronic from nuclear motion, and nuclear motion involves vibrational and rotational motion, we choose to first build a theory to study electronic and vibrational motions only. To make the problem tractable, we choose a molecular Hamiltonian with zero rotational energy or a non-rotating molecule.

Another important interaction in methoxy is the spin-orbit interaction, involving the interaction of spin and orbital motion of electron. Loosely speaking, the orbital motion of electrons around the nuclei can be compared with motion of planets around the sun. The spin-orbit interaction involves interaction between the spin of the electron with its orbital motion.The two effects (Jahn-Teller and spin-orbit) together profoundly affect the forces within the molecule and we will soon see just by how much.

Spectroscopy provides the tools we require to probe the molecular structure experimentally. It involves shining light on molecules, and 'watching' the atoms dance in reaction to the incident light. The energy level structure depends not only on the molecule, but also whether it is electronic, vibrational or rotational motion. For example, UV-Visible spectroscopy is a tool to probe the electronic energy level structure, Infrared (IR) spectroscopy probes the vibrational levels and microwave, the rotational levels. We will provide more background on spectroscopy to understand the results in this thesis.

6.1.3 Aims of this thesis

We have studied two types of spectra. One involves the ground electronic state (denoted as $\Psi_{el}^{gs}(R)$ from Eqn. (6.3)) and excited state denoted as $\Psi_{el}^{es}(R)$. There are many fancy techniques available to map energy levels in the two electronic states. There are many experimental techniques that can study these two electronic states by shining infrared or uv-visible light. We will not go into the details of these fancy techniques here, since we are making a theoretical attempt to model the spectra. The methods in these fancy techniques only differ in detail in method of obtaining the energy level information. The ultimate goal is map out the energy level spacings in the two electronic states. Our aim is to reproduce these two types of spectra theoretically and interpret them in terms of the effect of Jahn-Teller and spin-orbit interactions on the spectra.

Studying isotopologues of a molecule (measuring spectrum of molecules by replacing various atoms of the molecule with its isotopes) is an extremely useful way to determine molecular structure. The skeleton (bonding pattern) of the molecule remains the same, but we get more information about the effect of the isotope on the molecular properties, such as the differeces in nature of vibrational dances in the molecule. CH_3O and CD_3O have the same type of vibrations and an analysis of their spectroscopy can provide complimentary and supplementary understanding of their vibrations. Hence we have investigated the spectroscopy of both CH_3O and CD_3O in this thesis.

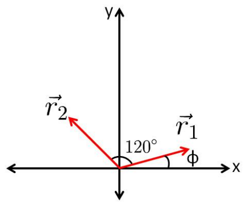
6.2 Theoretical Background

6.2.1 Symmetry in molecules: A theorists' aid in interpreting experiments

A knowledge of group theory is usually necessary to grasp and appreciate the elegance of theoretical foundations of spectroscopy. However, we use only basic aspects of group theory in our models that can be explained using simple examples as follows. We assume that the reader has a basic knowledge of vectors and matrices.

Nature exploits symmetry in countless number of ways; in both living and non-living forms. Flowers are common symmetrical objects, with petals arranged in ways ranging from triangular symmetry (each petal is 120° with respect to the other) to circular symmetry. Molecules can take symmetrical shapes too, depending on the types of atoms present. To understand how we use symmetry in our theory, we talk about 'transformation' of various quantities such as potential energy, molecular dipole moment etc under the influence of rotations. To understand what the word 'transformation' means, we direct the reader to Figs. 6.3 and 6.4. In Fig. 6.3, we rotate a vector $\vec{r}_1$ by 120° giving rise to a new vector $\vec{r}_2$. This is a 3-fold rotation of $\vec{r}_1$ and is denoted as $\mathrm{C}_3\vec{r}_1$. In the 2-D plane used, the vectors can be written in terms of x, y components as

Figure 6.3: $2\pi/3$ rotation of a vector in a 2-D plane.



$$\begin{aligned} \vec{r}_1 &= x\hat{i} + y\hat{j} \qquad (6.4) \\ C_3\vec{r}_1 = \vec{r}_2 &= \begin{pmatrix} \cos(2\pi/3) & -\sin(2\pi/3) \\ \sin(2\pi/3) & \cos(2\pi/3) \end{pmatrix} \vec{r}_1 \qquad (6.5) \end{aligned}$$

When it comes to understanding rotations, a clever mathematical trick is to recast a given position vector (for e.g., $\vec{r}_1$) as a complex number 'z'. The 2-D plane is now formed by real and imaginary axes along x and y respectively. The x component is along the real axis and y component is along the imaginary axis. In the complex representation of a vector, the polar or trigonometric form is particularly useful, as we will see in a moment. Equation 6.6 also uses the Euler formula relating the exponential function to the trigonometric functions (introduced in 18th century by Leonhard Euler)

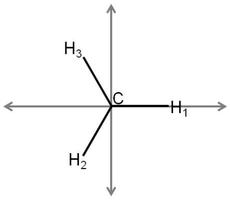
$$\begin{aligned} z &= x + iy \\ z &= r_1(\cos\phi + i\sin\phi) = r_1 e^{i\phi}. \qquad (6.6) \end{aligned}$$

A position vector has magnitude and direction. The rotation of a vector in a 2-D plane involves multiplication of a 2×2 matrix as shown in Eqn. 6.5. The rotation matrix *itself* is replaced by another complex number, $z' = e^{i2\pi/3}$. This is because, z' represents a unit vector rotated from the x-axis by 120° (The determinant of the 2×2 matrix is 1, and is the magnitude of the complex number z'). So just by changing our notation to that of a complex polar representation, the rotation of a vector is just multiplication by another complex number. So we rewrite Eqn. 6.5 as

$$\begin{aligned} C_3\vec{r}_1 &= e^{i2\pi/3}\vec{r}_1 \\ &= e^{i2\pi/3} r_1 e^{i\phi} = r_1 e^{i(\phi+2\pi/3)} = \vec{r}_2 \end{aligned} \tag{6.7}$$

It is now obvious that if we wish to carry out an clockwise rotation of the vector $\vec{r}_1$ we multiply by $e^{-i2\pi/3}$. Such is the elegance of the complex representation and we exploit this in building our model Hamiltonian and Dipole moment operators.

Figure 6.4: Top-down view of methoxy along CO bond (z-axis).



In methoxy, the 3-fold symmetry is apparent when we view the molecule along the CO bond at the 3 H in Fig. 6.4. The 3 H transform into each other on 120° rotation. Hence the potential energy of the molecule has to be the same under 3-fold rotation. In an equation form, we write this as

$$C_3V = V \tag{6.8}$$

This is true of the Hamiltonian as well.

The geometry shown in the left of Fig. 6.1 has an axis of symmetry (3-fold axis, also called C_3 axis) along the z-axis (vertical axis) involving a 120° rotation. As the CO bond tilts away from the C_3 axis, the electronic energies of the 2 states are different and we obtain a 3-fold symmetric surface as shown. This makes sense, because looking down the CO axis on the left geometry, the 3 H are equivalent and so the potential has to be 3-fold symmetric. The picture is a classic example of how Jahn-Teller interaction brings about a symmetry breaking process.

The dipole moment is another quantity like the Hamiltonian that is crucial for understanding the spectroscopy of molecules. There are two types of dipole moment - Permanent and Transition dipole moment. Dipole moment basically refers to the asymmetric distribution of positive and negative charges on a molecule. If we take the example of a diatomic molecule like H_2, due to a symmetric charge distribution of positive (charge due to nucleus) and negative (charge due to number of electrons) charges, the dipole moment is zero. On the other hand, a molecule like HCl, there is more negative charge on Cl than on H; hence the molecule is 'polar' and possesses a dipole moment with a '+' charge towards H and '-' charge towards Cl end. Methoxy is also a polar molecule and possesses a dipole moment. We care about dipole momemt, because they help us write down 'rules' that determine molecular transitions when light is shone on a sample. We state these rules in a later section. To understand the spectroscopy of the ground electronic state, we care about the permanent dipole moment. To do the same of the excited state ($\tilde{A}^2A_1$) we care about the transition dipole moment. The word 'transition' in the latter type of dipole moment really means transition between two electronic states, since in all kinds of molecular spectroscopy, there is always transition between two states. But for sake of clarity in distinguishing the two types of spectroscopy in methoxy, we will use the traditional language as I have stated. When the molecule makes a transition from one electronic state to another, its charge distribution changes (as we can imagine if we an electron is removed from CO bond and 'placed' in an orbital perpendicular to the CO bond) and this is characterised by the transition dipole moment.

The dipole moment is a vector quantity and has components μ_x, μ_y and μ_z. Each transforms in its own way under C$_3$ operation. In the same frame of reference as we used in Fig. 6.4 (the z-axis is pointing towards us out of the plane of the paper), let us look at the transformation of the dipole moment vector.

$$\vec{\mu} = \mu_x\hat{\imath} + \mu_y\hat{\jmath} + \mu_z\hat{k} \tag{6.9}$$

$$C_3\mu_x = -\frac{1}{2}\mu_x + \frac{\sqrt{3}}{2}\mu_y \tag{6.10}$$

$$C_3\mu_y = -\frac{\sqrt{3}}{2}\mu_x - \frac{1}{2}\mu_y \tag{6.11}$$

$$C_3\mu_z = \mu_z \tag{6.12}$$

However if we switch to a complex plane picture, we see that the following holds true:

$$\mu_{\pm} = \mu_x + i\mu_y \tag{6.13}$$

$$C_3\mu_{\pm} = e^{\pm i2\pi/3}\mu_{\pm}. \tag{6.14}$$

This is a fundamental symmetry property of the molecule and whether we talk of electronic or vibrational or rotational degrees of freedom, the different mathematical quantities such as H, μ and wavefunctions have well-defined transformation properties under 3-fold rotation. For studying rotational energy level structure, we also have to take into account reflection symmetry, but we will not discuss that at the moment, since we are only interested in building a vibronic model. The key message from this subsection is the exploitation of 3-fold symmetry and complex representation to build our theoretical model.

6.2.2 Spectroscopy: A tool to 'watch' atoms dance

All types of spectroscopies are based on interaction of light belonging to some region of the electromagnetic spectrum with molecules and the experiment involves obtaining a plot of the response of the absorbance or transmittance of light as a function of wavelength or frequency. A molecule's spectrum is its signature, and contains hidden information about the static and dynamic molecular structural properties. Spectroscopy is a qualitative and quantitative tool to detect, identify and quantify chemical species. It is common practice to detect organic compounds using infrared spectroscopy, because a vibrational spectrum of a molecule has peaks corresponding to different types of bonds present in the molecule (for e.g., CH, CO, OH, NH bonds etc), and hence is a unique reflection of the molecular structure. Arnold Sommerfeld, yet another German Physicist (who pioneered many developments in quantum physics) said:

"Quantum theory is the mysterious organ on which Nature plays her music of the spectra, and according to the rhythm of which she regulates the structure of the atoms and nuclei."

This succinctly tells us how interweaved the theories of spectroscopy and quantum are. In order to appreciate this, we look at the central concept of ‘resonance’.

In macroscopic systems such as pendulums, or systems that oscillate, if they are driven at their natural or ‘resonant’ frequency, they absorb more energy and tend to execute large amplitude oscillations. Other examples of such mechanical resonances are bridges and buildings, and musical instruments (acoustic resonance). A plot of amplitude versus excitation frequency will have a peak centered at the resonant frequency and the peak is called a spectral line. In quantum mechanical systems such as atoms and molecules, a resonance is coupling of light (formed of particles or packets of energy called photons, of a particular frequency ν) and two atomic or molecular 'energy' states that differ by an energy corresponding to the same frequency (ΔE). In other words,

$$\Delta E = h\nu. \tag{6.15}$$

In language of spectroscopy, a particular pair of states in resonance with incident photon is said to bring about a ‘transition’ of the molecule or atom from lower to upper energy level. Each peak in a spectrum might consist of overlapping transitions with contributions from pairs of rotational, vibrational and/or electronic states. Relatively speaking, the electronic energy levels are the farthest apart, followed by vibrational levels and then by rotational levels. In molecular spectroscopy theory, a particular rotational transition is called a spectral line (lowest frequency among the 3), a rovibrational transition is called a band (which consists of a series of rotational lines) and a rovibronic transition is called a band system (which consists of a series of bands and rotational lines within each band). In this thesis, we care only about vibronic transitions or band positions and intensities of these bands in a given band system.

As mentioned in introduction, we are interested in mapping out the vibronic level structure of the ground and excited electronic states Ψ_{el}^{gs} and Ψ_{el}^{es}. In the language of spectroscopy of polyatomic molecules, the former is denoted as $\tilde{X}$ and the latter as $\tilde{A}$. The $\tilde{X}$ PES, as we saw in Fig. 6.2 has 'E' symmetry. The symmetry label for Ψ_{el}^{es} used is A_1, because in this electronic state, only one electronic arrangement in the molecular orbitals is possible. This is because, roughly speaking, one of the two electrons forming the CO bond is promoted to the orbital with the odd electron (refer Fig. 6.2). As a result, the double degeneracy is lost, and the electronic state is non-degenerate. The symbol A_1 comes from group theory and the details of its origin is not relevant here. It is merely a label for our purposes. We have seen that methoxy has one unpaired electron, and so has $2S + 1 = 2$ denoted in the superscript. This is true of the $\tilde{X}$ and $\tilde{A}$ electronic states. We therefore have the following labels for the 2 electronic states of interest - $\tilde{X}^2E$ and $\tilde{A}^2A_1$.

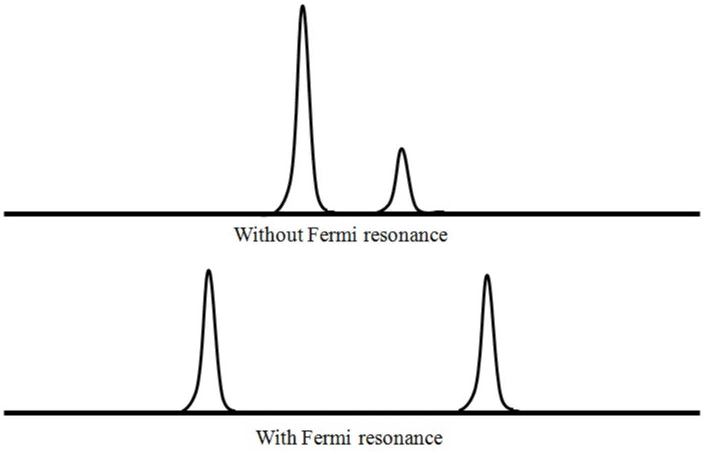
A well-known method of characterisation of methoxy radical is its electronic absorption spectrum, also called LIF excitation spectrum. This spectrum involves the UV-Visible portion of the electromagnetic spectrum, and involves excitation of the molecule from $\tilde{X}^2E$ state to $\tilde{A}^2A_1$. Extensive experimental studies have been carried out to characterise the radical using infrared spectroscopy as well, and we explain the challenges of such an attempt in the results section.

6.2.3 Vibrational resonances

Before we move on to the results, we need to understand a second type of resonance important to vibrational spectroscopy - Fermi resonance. In general, there are two types of vibrations in molecules - stretching and bending vibrations. The vibrational states are labeled using vibrational quantum numbers $v = 0, 1, 2 \ldots$. A transition involving $v = 0$ and $v = 1$ pair of states is called a fundamental transition, and $v = 0$ and $v > 1$ pairs of states are called overtones. A transition involving two independent vibrations are called combination bands.

Every so often, it so happens that a pair of vibrational states belonging to one normal mode has the same or nearly the same energy as another pair of vibrational states from a different normal mode. For example in water, it so happens that a pair of 'stretch' vibrational states accidentally have the same or nearly the same energy as that of a pair of 'bend' vibrational states. Fermi resonance in this case therefore involves nearly perfect match of energies of the OH stretch fundamental and H_2O bend overtone states. A second condition also needs to be satisfied, which is more technical; we are merely concerned with the consequence of such a phenomenon and shall not go into details here. The consequence of such a resonance is the 2 peaks in the actual spectrum do not appear at the expected positions, they appear farther apart than expected, and the 2 peaks have intensities different from that predicted without including the interaction. This is shown schematically in Fig. 6.5. As seen in the figure, the weaker peak grows *at the expense of* the stronger peak. Such a sharing of intensities among the two sets of vibrational states is common in polyatomic vibrational spectra.

Figure 6.5: Effect of Fermi resonance interaction on vibrational spectrum.



There exists other kinds of interactions in vibrational spectroscopy, which couple vibrational states not necessarily in resonance. These also contribute to various features in the molecular spectrum.

6.2.4 Normal mode representation of vibrations

Given that we have the experimental spectra, and the theoretical tools to calculate spectra, the interpretation of the different peaks and intensities is commonly carried out in ′′normal mode representation′ of vibrations. We talked about describing molecular vibrations in terms of extensions and compressions of internal coordinates such as bond lengths and bond angles. In reality, the molecule is executing some complicated motion involving all kinds of vibrations. How do we build simple physical pictures of such motions and analyse the spectra? It so happens, that by doing certain mathematical tricks (transformation) of internal coordinates to 'normal coordinates' complex concerted motions of atoms in the molecule can be described (mostly) in terms of displacement of the molecule along 'normal coordinates'. Here is a short example of how a theorist's' life becomes simpler by such a transformation.

The example below has been adopted from book on vibrations by Wilson, Decius and Cross.[5] For a single spring that executes simple harmonic oscillations about an equilibrium value, the potential and kinetic energy of the spring is given by

$$\begin{aligned} V &= \frac{1}{2}F(x-x_e)^2 = \frac{1}{2}F(\Delta x)^2 \\ T &= \frac{1}{2}m(\dot{\Delta x})^2 \quad \text{where} \\ \dot{\Delta x} &= \frac{d(\Delta x)}{dt}. \end{aligned} \tag{6.16}$$

For a system of two coupled harmonic oscillators as shown in Fig. 6.6 (with two point masses m_1,m_2 and weightless springs allowed to move along x direction only), the potential energy is given by

$$
\begin{aligned}
r_1 &= x_1 - x_{1,e} \\
r_2 &= x_2 - x_{2,e} \\
V &= \frac{1}{2}F_1 r_1^2 + \frac{1}{2}F_2 r_2^2 + F_{12}(r_2 - r_1)^2 && (6.17) \\
T &= \frac{1}{2}m_1(\dot{r_1})^2 + \frac{1}{2}m_2(\dot{r_2})^2 \text{where} && (6.18) \\
\dot{r_1} &= \frac{dr_1}{dt} \quad \text{and} \quad \dot{r_2} = \frac{dr_2}{dt}. && (6.19)
\end{aligned}
$$

Figure 6.6: System of 2 coupled harmonic oscillators.

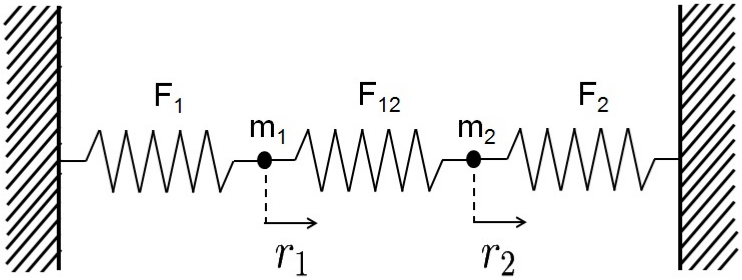
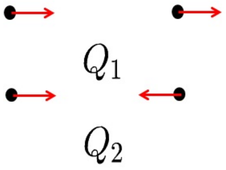


Figure 6.7: Normal modes of 2 coupled harmonic oscillators.



For sake of simplicity, let us assume $m_1 = m_2 = m$ and $F_1 = F_2 = F$. Solutions to Newton's equations of motion will give us the displacements of the 2 masses as a function of time. The solutions are called 'normal modes'. The 2 normal modes are shown in Fig. 6.7. The Hamiltonian is given by $H = T + V$. In terms of displacement coordinates, the form of H is not a simple function of two variables and has a 'mixed' term, involving both variables. In other words, it is not in a variable-separable form. Without going into the details of the route to get the solutions, we note that by introducing 'normal coordinates' Q_1 and Q_2 defined as

$$\begin{aligned} r_1' &= \sqrt{m} r_1 \quad r_2' = \sqrt{m} r_2 \\ Q_1 &= \frac{1}{\sqrt{2}}(r_1' + r_2') \qquad (6.20) \\ Q_2 &= \frac{1}{\sqrt{2}}(r_1' - r_2'), \qquad (6.21) \end{aligned}$$

the Hamiltonian becomes

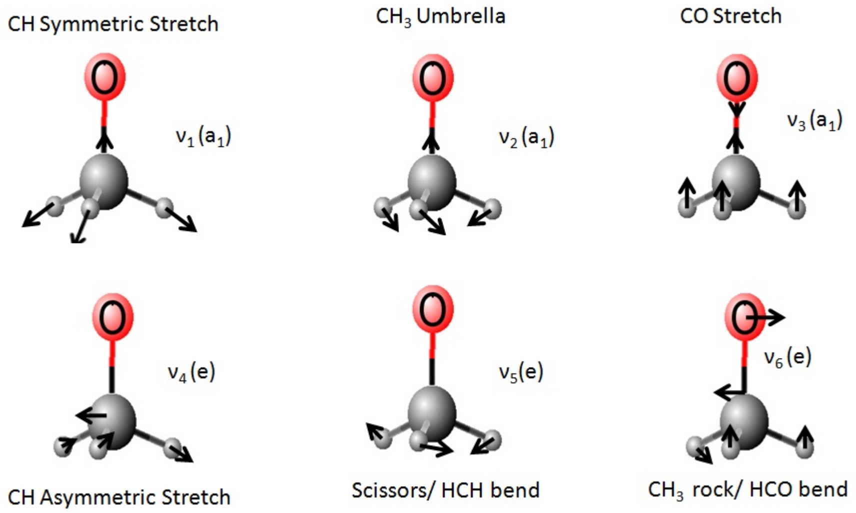
$$H = \frac{1}{2}\dot{Q_1}^2 + \frac{1}{2}\dot{Q_2}^2 + \lambda_1 Q_1^2 + \lambda_2 Q_2^2, \qquad (6.22)$$

now a variable separable form. The pictures of the normal modes, when extended to molecules, are built on very similar ideas. The vibrations in molecules are coupled to each other. The normal modes of a molecule are good descriptions of the vibrations as long as we approximate the vibrations to be simple harmonic oscillators.

A molecule has 3N coordinates (or degrees of freedom), N being the number of atoms. Out of these, 3 degrees of freedom involve translation of the molecule as a whole. A linear molecule has 2 rotational degrees of freedom and non-linear molecule has 3. That leaves us with 3N-5 vibrational degrees of freedom for linear molecules and 3N-6 for non-linear molecules. Methoxy has 9 vibrational degrees of freedom. Figure 6.8

shows the normal modes in methoxy, where 3 are non-degenerate (labeled as a_1, with same meaning as electronic state label A_1, meaning non-degenerate) and 3 are doubly degenerate (labeled as e, named so because two vibrations of that type have the same frequency).

Figure 6.8: Normal modes of CH_3O.[3]



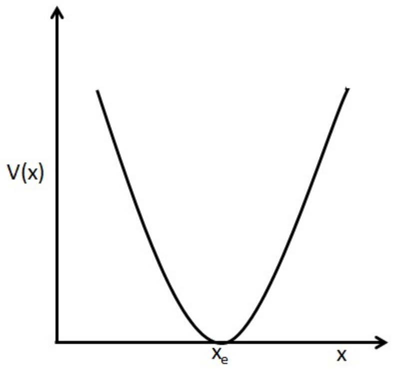
Normal modes are useful, because they are best of two worlds - we can build a physical picture of each normal mode ‘mostly’ in terms of displacement along internal coordinates, and they include simultaneous displacement of all atoms, a model much more closer to reality than modeling one stretching or bending vibration. This is evident in Fig. 6.8. We will be using normal mode representation to interpret the methoxy spectra, and test how good such a description is.

6.2.5 Anharmonicity: Bond-breaking and more

A simplistic picture of bonds in a molecule is to assume that they behave like harmonic oscillators. Any spring, in the absence of a restoring force will have a resting position and when we elongate the spring, the restoring force allows the spring to excecute oscillatory motion about the resting position. If we trace the potential energy of the spring for various displacements from equilibrium, we get a parabola corresponding to Eqn. 6.23 and shown in Fig. 6.9.

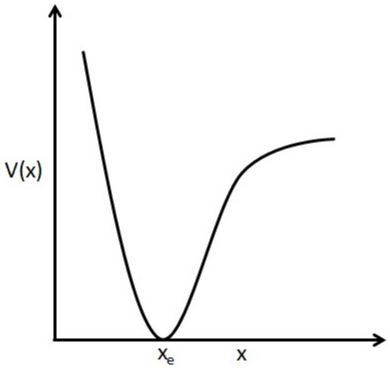
$$V = \frac{1}{2}k(x - x_e)^2 \tag{6.23}$$

Figure 6.9: A simple harmonic oscillator



A bond behaves in a similar way, but only at low energies. As we put more energy into a bond, their oscillations are 'anharmonic'. This is because real bonds break and cause dissociation of molecules. A more realistic potential to describe a bond, therefore cannot just have a quadratic term as shown in Eqn. 6.23, but also needs to include higher order terms such as third order, fourth order etc. A more realistic potential of the bond energy is shown in Fig. 6.10. Hence bonds are anharmonic oscillators. Another type of anharmonicity is between two types of vibrations. We saw how two oscillators can be coupled to each other through a potential energy term involving displacements of both the oscillators and couples the two equations of motion. Coupling between vibrations in molecules happens in the same way and in methoxy potential, we have such terms that couple different normal modes to each other. These terms are also termed as anharmonic terms.

Figure 6.10: Anharmonic oscillator



6.2.6 Selection rules: 'Permission' for molecules to get excited!

A selection rule tells us whether a transition of the molecule from one quantum state (Ψ_i) to another (Ψ_f) is allowed. Theoretically this is written in terms of an integral, for which we need 3 quantities - the initial and final energy states (Ψ_i and Ψ_f) and the dipole moment function. Mathematically, (without worrying about other details in the equation below such as $d\tau$ or $\pm\infty$ momemtarily), this is stated as the following integral being non-zero.

$$\int_{-\infty}^{\infty} \Psi_i \mu \Psi_f d\tau \neq 0 \tag{6.24}$$

The dipole moment operator is in general a function of nuclear and electronic co-ordinates. In this thesis, we have determined the functional form of the 3 components of the dipole, μ_z, μ_+ and μ_- as a function of nuclear coordinates $\{Q\}$. In our model, we are looking at transitions of methoxy among vibronic states. These states are labeled by the vibronic quantum number, ℓ. Without going into details, it suffices to say that there are 3 possible sets of ℓ states, labeled as 0,1 or 2. We have derived the following selection rules for the 3 components of the dipole moment operator.

$$\begin{aligned} &\mu_z && \Delta\ell = 0 \\ &\mu_+ && \Delta\ell = +1 \\ &\mu_- && \Delta\ell = -1 \end{aligned} \tag{6.25}$$

Table 6.1 lists the initial and final state possibilities using the above selection rules. We have decomposed the infrared and electronic spectra into these 3 types of transitions. We will refer to the selection rules corresponding to $\mu_\pm$ as perpendicular selection rules and that of μ_z as parallel selection rule.

Table 6.1: Selection rules for transitions among different ℓ states.

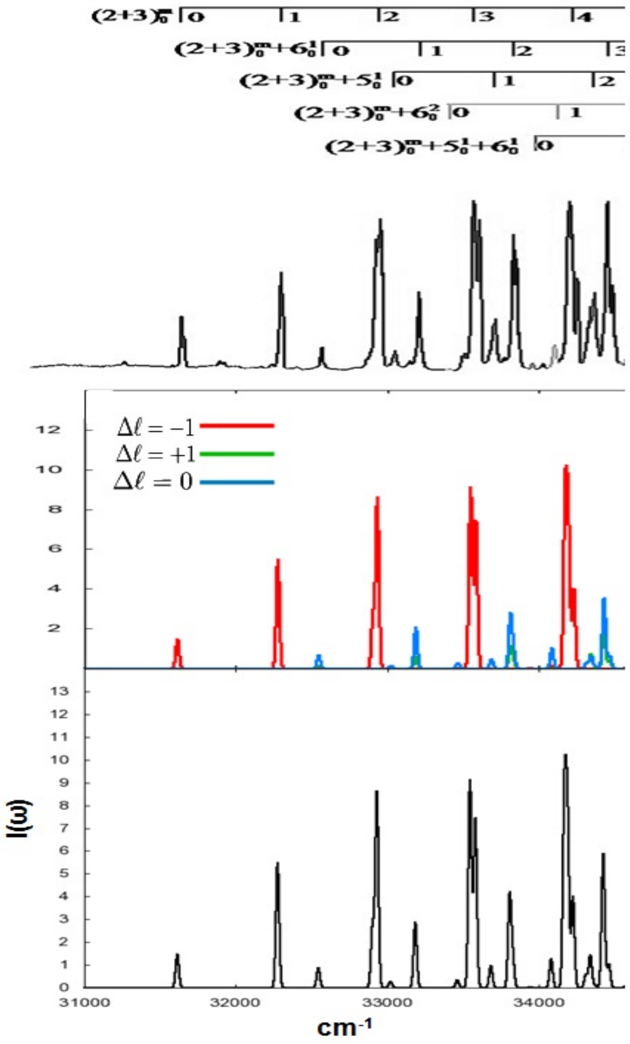
ℓ	μ_+	μ_-	μ_z
1	2	0	1
2	0	1	2
0	1	2	0

Now that we have a flavour for some of the concepts that goes into developing a theory of vibrations in methoxy, it will suffice to know that we ultimately calculate a 'model' energy level structure of the vibronic states in the $\tilde{X}^2E$ and $\tilde{A}^2A_1$. We then calculate the 2 types of spectra and compare it to experiment. This is shown in the next section, along with some of the key challenges we have faced in interpreting these spectra.

6.3 Results

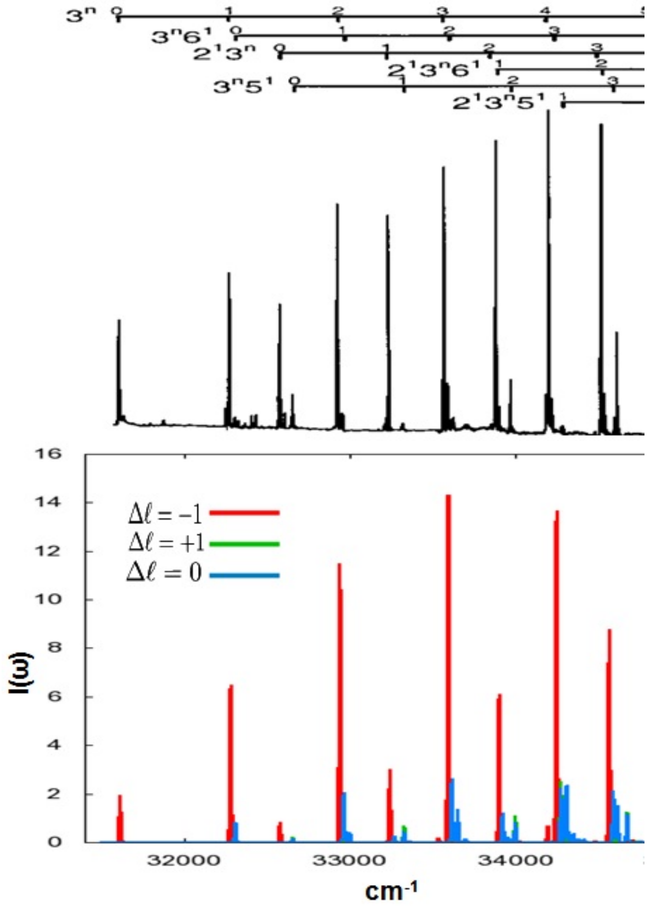
As explained in Sec. 6.2.2, the electronic excitation of methoxy radical from $\tilde{X}^2E$ to $\tilde{A}^2A_1$ involves removing an electron from the CO bond. Hence the CO bond becomes weaker, or longer. Also there is less bond-bond repulsion between CO and CH bonds and causes increased planarity of the CH_3 group. In the experimental spectrum, such a change in electronic arrangement causes significant excitation along the CO stretch and CH_3 group vibrations. Figure 6.11 shows the lower energy portion of the electronic spectrum. The spectrum is labeled in terms of 'progressions' or peaks corresponding to different levels of excitation of CO stretch vibration, namely $v = 0 - 1$, $v = 0 - 2$, $v = 0 - 3$ etc. Typically experiments are carried out at very low temperatures ($< 25K$), and all the molecules in

Figure 6.11: LIF excitation spectra of CH_3O: (a) Experiment[2,4] (reproduced with permission) (b) and (c) Theory



the sample are assumed in their ground states, i.e., $v = 0$ (subscript in the figure denotes initial vibrational state in $\tilde{X}^2E$); the superscript in the figure denotes the final vibrational state (in $\tilde{A}^2A_1$) to which the molecule is excited to. The CO stretch vibration is labeled by normal mode number 3.

Figure 6.12: LIF excitation spectra of CD_3O: (a) Experiment[1] (reproduced with permission) (b) Theory



A key difference between the experimental CH_3O and CD_3O spectra is the presence of doublet features in CH_3O spectrum. This is due to a strong Fermi resonance interaction between CO stretch and CH_3 umbrella vibrations. It so happens that, $\nu_2 \approx 2\nu_3$ and causes the transitions to vibrational levels of normal mode 2 to become more intense 'at the expense of' intensity of mode 3 (recall background information on Fermi resonance). We have captured the doublet features very well in our simulated spectrum.

It also happens that the electronic excitation spectrum of methoxy has new features that is otherwise not allowed in a spectrum of a closed shell species. These are peaks labeled with modes 5,6 in the figures. They appear due to the presence of Jahn-Teller effect in the molecule. By including vibronic coupling in our model, we predict these features correctly in the calculated spectrum.

In Figs. 6.11 and 6.12, resolution of the spectrum into 3 types of transition is shown in panel (b). Panel (c) in former shows the theoretical spectrum with the 3 component's contributions summed and added together. Overall, we can see that there is very good agreement between theory and experiment. In a more detailed analysis (chapter 4), we have examined the relative intensities between the peaks more closely. We believe that the differences between theory and experiment as far as the relative intensity is concerned, is possibly due to poor estimate of the molecular dipole moment using electronic structure theory methods. Our theory captures the features of both CH_3O and CD_3O spectra very well, and we have perfect agreement in terms of peak positions.

$$H = H_{HO} + \delta W \tag{6.26}$$

We have examined (chapters 2 and 3) in detail the vibronic level structure of the $\tilde{X}^2E$ state. Equation 6.26 separates the Hamiltonian into a harmonic part and anharmonic parts. The harmonic part includes vibronic coupling up to second order. The correlation diagrams show the evolution of the energy eigenvalues as a function of the parameter δ that slowly increases the amount of anharmonic coupling from 0 to 1. Figures 6.13 and

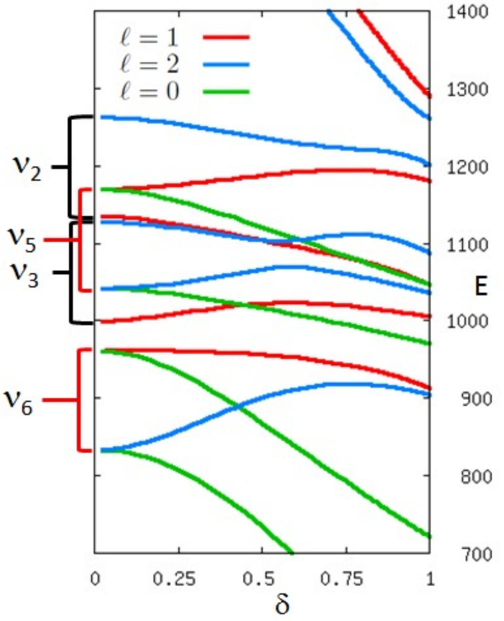


Figure 6.13: Correlation diagram for CD_3O as a function of δ.

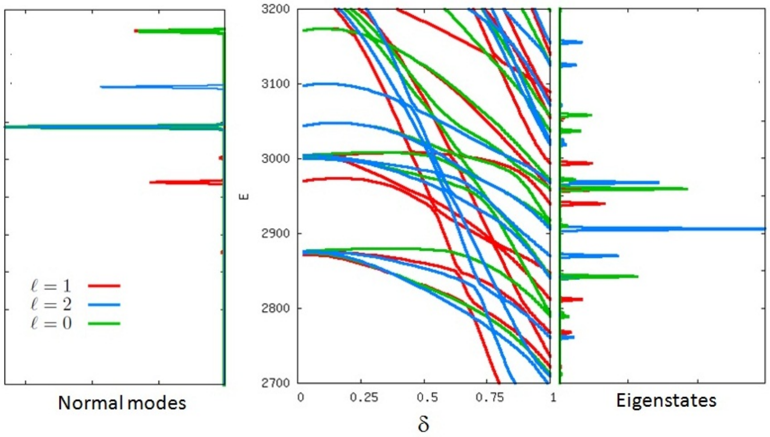


Figure 6.14: Correlation diagram in CH stretch region of CH_3O.

6.14 illustrate how the normal modes of CH_3O and CD_3O mix with each other as we include more and more anharmonic terms in the Hamiltonian. The IR spectrum incorporates the full Hamiltonian ($\delta = 1$) and an attempt to assign the spectrum, i.e., label the peaks using normal mode quantum numbers is futile. The ground state spectroscopy and dynamics of CH_3O and CD_3O is therefore very complex, and such analysis shows why this family of radicals still continues to pose challenges for theorists and experimentalists alike.

6.4 Concluding remarks

Many mysteries in the spectroscopy of CH_3O and CD_3O still remain, and one could ask, what happens when we replace only 1 or 2 H by D? The radicals CH_2DO and CHD_2O have also been studied experimentally, and a theoretical analysis will likely help us understand some of the congestion in the spectra of the symmetric analogs better. It could also be useful to examine other members of the CX_3Y family, to understand the effect of vibronic and anharmonic interactions better on the positions and intensities of the peaks in both infrared and electronic spectra.

In this thesis, we have deepened the understanding of $\tilde{X}^2E$ and $\tilde{A}^2A_1$ vibronic levels and transitions. A detailed examination of the Hamiltonian and dipole moment operators' role in spectroscopy of methoxy has helped uncover the molecular forces responsible the complex spectroscopy. We believe that a systematic theoretical approach like ours will provide insights into vibrational spectroscopy of similar systems and serve as a stepping stone to build models to understand their reaction dynamics.

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