THE THEORETICAL STUDY OF TORSION – VIBRATIONAL DYNAMICS IN METHANOL
AND THE IMPROVEMENT OF CW-CRDS EXPERIMENTAL APPARATUS

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ABSTRACT

Research using both theory and experimental avenues is integral to understanding intramolecular vibrational redistribution energy (IVR). Earlier experimental results\(^1\) indicated that the large amplitude internal rotation coordinate in methanol accelerates IVR especially when coupled to other small-amplitude vibrations. Theoretical methods such as \textit{ab initio} calculations, adiabatic approximation and full-dimensional models are used to understand how the coupling of the torsional motion to small-amplitude vibrations influences IVR.

Experimentally observed spectra of the \(3\nu_1 - 6\nu_1\) OH stretch overtone region\(^2\)\(^-\)\(^4\) show that the stretch of the \textit{anti} CH bond and the torsional motion around the CO bond are coupled to the OH stretch. In this work, we performed \textit{ab initio} calculations on the \((\text{CH}_3\text{OH} \rightarrow \text{CH}_2\text{O} + 2\text{H})\) reactive channel that takes both static and dynamic correlation effects into account. Our calculations show that a partial double bond between the C-O is formed early in the reaction coordinate. This partial double bond leads to an increase of the torsional barrier height that explains the experimental observations.

A four-dimensional model developed by Wang and Perry\(^5\) was used to compare the approximate adiabatic separation of the torsion and the CH stretches in methanol\(^6\) to an exact solution of the same Hamiltonian. The adiabatic approximation accounts for the correct energy level splittings at low torsional energies including the inverted torsional tunneling splittings, but does not account for the correct 2-fold and 4-fold systematic near degeneracies at high torsional excitation. However, the adiabatic approximation was able to show the origin of the strong IVR coupling and the scaling of the IVR coupling matrix elements.
Finally, a high-resolution experimental apparatus was developed to record the spectrum spanning the range of the polyad $v_{\text{CH}}=2$ region. This experimental spectrum will be used to test and challenge the findings of both Perry’s$^7$ and Halonen-Hännien’s$^8$ theoretical models.
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Finally, I dedicate this dissertation to my family especially my parents, Clifford and Ingrid George who never doubted my abilities as well as my grandparents, Ena and Percival Clasp who instilled in me the value of education. A special thanks for my fiancée Deshaun Kimbrough who is always there for me.
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CHAPTER I
INTRODUCTION

1.1 Motivation for Studying Methanol

Methanol is one of the simplest molecules that possess a large amplitude internal coordinate. This coordinate is the internal rotation around the C-O bond with a three-fold symmetric potential, where the potential minima are separated by 373.5421 cm\textsuperscript{-1} barriers. This large amplitude torsional motion, when coupled to other small-amplitude vibrations can accelerate intramolecular vibrational redistribution of energy (IVR). Research using both theory and experiment on methanol and other related molecules offers the opportunity to study the torsion-vibrational dynamics and how they impact IVR. The approximate adiabatic separation of the large amplitude motion from the other small amplitude vibrations offers an attractive simplification of the problem. In this dissertation, the usefulness of such an adiabatic separation will be tested. It will be shown that this theoretical approach reveals the origin of the strong IVR couplings and the scaling of the coupling matrix elements in torsional molecules. The impact of a potentially reactive channel (CH\textsubscript{3}OH→CH\textsubscript{2}O+2H) on IVR in methanol will also be examined by means of \textit{ab initio} calculations. Finally, a high-resolution spectroscopy experiment has been designed to test some of these theoretical concepts.

1.2 Models of IVR

The study of energy flow within polyatomic molecules requires understanding the process of IVR. According to the Rice-Ramsperger-Kassel-Marcus theory (RRKM)\textsuperscript{11,12} of unimolecular reactions, IVR is assumed to randomize the energy among all vibrational degrees of
freedom on a timescale faster than the formation or breakage of a chemical bond. When all the vibrational energy is localized in a bond, the bond may break and lead to the formation of products. If the chemical reaction rate is faster than the rate of redistribution of vibrational energy into other modes, bond-selective chemistry can occur. Therefore, identifying possible sources of bond-selective chemistry relies on an accurate description of the IVR rate as well as finding ways to beat the IVR clock.

Another mechanical model of unimolecular reactions is the Slater theory, which is based on the normal mode harmonic approximation. According to Slater’s theory, the vibrational motions are uncoupled, therefore there is no free exchange of energy among the oscillators and instead the energy is trapped within the normal modes. Bond breakage or bond formation occurs when the normal modes are coming in phase so that the energy becomes concentrated in a single bond causing the bond to erupt. This is starkly different from the RRKM theory, which is based on the existence of rapid IVR and energy flowing freely among the vibration modes. Because Slater’s theory did not accurately predict the correct rate constants in certain chemical reactions, for example the dissociation of hydrogen peroxide and the decomposition of cyclobutane, it was later abandoned. Nevertheless his work contributed to the development of the theories of unimolecular reactions.

1.2.1 Golden Rule Formula

In frequency domain spectra, the IVR process is illustrated in Fig. 1.1. A single zeroth-order rovibrational state is considered as the bright state, which carries all the oscillator strength from the ground vibrational state and is coupled to the bath states, which consist mainly of overtones and combinations of low energy vibrations. When the vibrational density of states exceeds the threshold of 5 to 30 states per cm, the anharmonic coupling terms can cause the dark states to mix with the bright state, borrowing some intensity from the bright state. The result is a set of molecular eigenstates, which appear in the spectrum with various intensities.
Fig 1.1 Illustration of the Intramolecular Vibrational Redistribution Energy. This figure shows the standard interpretation of IVR in frequency domain. The bright state is a single rotational state in an excited anharmonic normal-mode vibrational state that is assumed to carry all of the oscillator strength in this energy region. The bright state is coupled to the near resonant bath states through higher-order terms in the rovibrational Hamiltonian. This coupling results in molecular eigenstates that mix the character of zeroth-order rovibrational states in which is recorded in the spectrum in a distribution of intensities.
This description of the IVR process in the frequency domain spectra is shown to be consistent with earlier experiments by Freed and others\textsuperscript{19,20}, which revealed that the rate of IVR of polyatomic molecule is based on Fermi’s Golden Rule Formula derived from time-dependent first order perturbation theory:

\[ k_{IVR} = \frac{2\pi}{\hbar} \rho_{tot} V_{rms}^2 \]  

(1.1)

where \( k_{IVR} \) is the IVR rate, \( \rho_{tot} \) is the total density of vibrational states at the bright state energy and the \( V_{rms} \) term is an average over individual \( V_{0i} \), where \( V_{0i} \) is the coupling from the bright state \( |0\rangle \) to a manifold of dark states \( |i\rangle \). The survival probability \( P(t) \) of the bright state coupled to the manifold of dark states is then expressed in the following equation:

\[ P(t) = e^{-k_{IVR} t} \]  

(1.2)

where \( t \) is the time.

In the golden rule model, it is assumed that the total density of states is directly proportional to the rate of IVR. However, frequency resolved experiments of the lifetimes indicate that the total density of states and the IVR rate are largely uncorrelated. In table 1 we present data for the lifetimes of the acetylenic C-H stretch and the densities of states for a series of molecules of the form (CY\textsubscript{3})\textsubscript{3}X=C=CH. For all the molecules in this table, the origin of the frequency band and the vibrational potentials are similar. Therefore, the initially excited vibrational motion is similar and the data may be compared to one another. Clearly for the molecules in this table, the density of states are not the primary factor effecting the IVR rate. Nonetheless, the density of states plays a role in initiating IVR but once the IVR is initiated the density of states is no longer significant in vibrational dynamics\textsuperscript{21}.

Experimental results indicate that strong couplings via nonresonant vibrational states often determine the IVR rate rather than the density of states. As we will discuss in detail in Sec. 1.2, these vibrational states are coupled through the low order coupling terms in the potential.
energy surface resulting in large anharmonic coupling matrix elements that dominate the average-squared coupling out of the bright state$^{13}$. To understand these coupling effects tier models have been developed.

Table 1. Experimental IVR lifetimes and densities of state for the acetylenic C-H stretch molecules for the form (CY$_3$)$_3$XCCH

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Level of excitation</th>
<th>Density of State (cm)$^b$</th>
<th>Lifetime (ps)</th>
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<tbody>
<tr>
<td>(CH$_3$)$_3$CCCH</td>
<td>v=1</td>
<td>4.9×10$^2$</td>
<td>200</td>
<td>$^{22}$</td>
</tr>
<tr>
<td></td>
<td>v=2</td>
<td>6.2×10$^5$</td>
<td>110</td>
<td>$^{22}$</td>
</tr>
<tr>
<td>(CD$_3$)$_3$CCCH</td>
<td>v=1</td>
<td>2.8×10$^3$</td>
<td>40</td>
<td>$^{23}$</td>
</tr>
<tr>
<td></td>
<td>v=2</td>
<td>7.6×10$^6$</td>
<td>&lt;40$^c$</td>
<td>$^{23}$</td>
</tr>
<tr>
<td>(CH$_3$)$_3$SiCCH</td>
<td>v=1</td>
<td>1.0×10$^4$</td>
<td>2000</td>
<td>$^{22}$</td>
</tr>
<tr>
<td></td>
<td>v=2</td>
<td>2.9×10$^7$</td>
<td>830</td>
<td>$^{22}$</td>
</tr>
<tr>
<td>(CD$_3$)$_3$SiCCH</td>
<td>v=1</td>
<td>1.0×10$^5$</td>
<td>4000</td>
<td>$^{23}$</td>
</tr>
<tr>
<td></td>
<td>v=2</td>
<td>6.0×10$^8$</td>
<td>140</td>
<td>$^{23}$</td>
</tr>
<tr>
<td>(CH$_3$)$_3$SnCCH</td>
<td>v=1</td>
<td>1.0×10$^6$</td>
<td>6000</td>
<td>$^{22}$</td>
</tr>
<tr>
<td></td>
<td>v=2</td>
<td>1.0×10$^9$</td>
<td>&gt;1000$^d$</td>
<td>e</td>
</tr>
<tr>
<td>(CF$_3$)$_3$CCCH</td>
<td>v=1</td>
<td>4.2×10$^6$</td>
<td>60</td>
<td>$^{24}$</td>
</tr>
<tr>
<td></td>
<td>v=2</td>
<td>1.0×10$^{11}$</td>
<td>&lt;40$^c$</td>
<td>$^{24}$</td>
</tr>
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</table>

$^a$This table is taken from Ref. 12

$^b$ The state densities (state/cm$^{-1}$) are for vibrational bath states of A$_1$ symmetry, which can couple via anharmonic interactions.

$^c$Upper bound to the lifetime. The overtone absorption was unobservable, despite observation of the fundamental.

$^d$Lower limit to the lifetime. The Q branch structure was too sharp to obtain an estimate of the Lorentzian wing. Other inhomogeneity (either isotopes, torsional, or K structure) was also present.

$^e$ERTh Kerstel, KK Lehmann, TF Mentel, BH Pate, and G Scoles, unpublished results.

1.2.2 Tier Models of IVR

Stuchebrukhov and Marcus$^{25}$ presented a tier model, a widely used approach that gives detailed information of the flow of IVR. In the Stuchebrukhov and Marcus$^{25}$ tier model, IVR proceeds through the low order coupling terms of the doorway states, where the doorway states constitute the first tier and are then coupled to a larger set of states that form the second tier. The second tier in turn are coupled to another tier and so on. The low order coupling term consists of cubic and quartic coupling order, where the cubic coupling order is defined as the creation plus
destruction ladder operators to the cubic power \[ (a_i^+ + a_i)^3 \] and quartic are to the fourth power \[ (a_i^+ + a_i)^4 \]. For example, a cubic term also called a Fermi interaction occurs when a state including one quantum of the high frequency vibrational mode \( \nu_i \) is close in energy to an overtone state \( 2\nu_i \) or combination state \( \nu_i + \nu_i \) which contain two quanta of lower-frequency vibrational modes. Expanding the ladder operators the cubic coupling term is obtained as:

\[
\langle \nu_r, \nu_s, \nu_t | H_{\text{Fermi}} | \nu_r - 1, \nu_s + 1, \nu_t + 1 \rangle
= f_{rst} \left[ \frac{\nu_r(\nu_r + 1)(\nu_t + 1)}{8} \right]^{1/2}
\]

where \( f_{rst} \) is defined as the anharmonic force constant. The quartic terms arise from the Darling-Dennison resonances, which occur between pairs of states, where the energy levels of the states have a 2:2 ratio. The coupling matrix elements are defined by expanding the quartic term in the following form

\[
\langle \nu_r, \nu_s | H_{\text{D-D}} | \nu_r - 2, \nu_s + 2 \rangle
= \frac{1}{4} K_{rst} \left[ \nu_r(\nu_r - 1)(\nu_s + 1)(\nu_s + 2) \right]^{1/2}
\]

where \( K_{rst} \) are the Darling-Dennison resonance constants.

### 1.2.3 Scaling of the IVR coupling matrix elements

According to the scaling model by Pearman, Gruebele et al., the scaling of the coupling matrix elements is represented by the cubic terms relative to the higher order coupling terms, since the higher coupling terms decrease exponentially. This scaling behavior is expressed in the following form:

\[
V_{kl} \sim a^n
\]

where \( a \) is the scaling parameter and \( n \) is the coupling matrix order defined as \( \sum |\nu_i - \nu_j| \), the difference between the vibrational quantum numbers. In rigid molecules, the \( a \) parameter is
within the range of 0.05-0.2, whereas in molecules with large amplitude motion the $a$ parameter increases to 0.5. The value of torsional scaling parameter indicates that the high order coupling terms play a more vital role in the torsional molecules in comparisons with rigid molecules, since in rigid molecule, the coupling strength falls off one order of magnitude for each higher order coupling terms. The scaling behavior, which mandates sequential couplings through quantum number space rather than direct high order couplings in torsional molecules, indicates that the number of states participating in IVR increases at a slower rate in comparison to an exponential decay. In experimental findings, the survival probability does not follow an exponential decay in the Golden rule theory, instead it follows a power law. For instance, time-resolved fluorescence experiments used to monitor IVR in fluorine and cyclohexylaniline indicates the presence of power law behavior. Also, multiple timescales are reported for the $v_1$=5 OH stretch overtone of methanol, which was fitted to a power law decay as well as other experimental work reported power law decays for the benzene molecules and small molecules such as CH$_2$I$_2$ by Crim and coworkers.

1.3 Theories of Molecular Vibrations

The normal mode and local mode theories are two most widely used is described in the following sections.

1.3.1. The Normal Mode Theory

The normal mode$^{29-31}$ theory is a traditional description of vibrational motions, which is based on the classical harmonic approximation. According to the harmonic approximation, all vibrational modes move in phase and are orthogonal to each other. In a nonlinear polyatomic molecule, the Taylor series expansion of the potential energy about the equilibrium geometry may be written as

$$V = V_0 + \left( \frac{\partial V}{\partial S_i} \right)_0 S_i + \sum_i \frac{1}{2} \left( \frac{\partial^2 V}{\partial S_i \partial S_k} \right)_0 S_i S_k + \frac{1}{3} \sum_{ijk} \left( \frac{\partial^3 V}{\partial S_i \partial S_j \partial S_k} \right)_0 S_i S_j S_k + .... \quad (1.6)$$
where $S_j$ are 3N-6 uncoupled symmetry-adapted internal coordinates, 

\[ \left( \frac{\partial V}{\partial S_j} \right) = 0 \]

is the condition for being the equilibrium state and $V_0=0$ by convention. In the harmonic approximation, terms higher than second order are neglected so that

\[ V = \sum_{i<k} \frac{1}{2} \left( \frac{\partial^2 V}{\partial S_i \partial S_k} \right) S_i S_k = \frac{1}{2} \sum_{i<k} f_{ik} S_i S_k \]  \hspace{1cm} (1.7)

where $f_{ik} = \left( \frac{\partial^2 V}{\partial S_i \partial S_k} \right)$ are elements of the $f$-matrix, $S_i$ coordinates are given by

\[ S_n = \sum_i B_{ni} \xi_i \]  \hspace{1cm} (1.8)

where the coefficients $B_{ni}$ are derived from the geometry of the molecule, and the variables $\xi_i$ are the Cartesian displacement coordinates of each atom within a molecule. The harmonic normal mode approach is suitable at low energies where the ratio of inter-bond coupling to bond-anharmonicity is relatively large. At higher energies, the anharmonic terms such as the cubic and quartic coupling terms (low order coupling terms) must be added to the potential to account for bond dissociation.

1.3.2 The Local Mode Picture

Another description of vibrational motion of a molecule is the local mode picture\textsuperscript{29,30,32} based on vibrational modes localized in individual bonds. This localization of the vibrational energy is the main difference from normal mode theory, where the vibrational energy is distributed over all internal coordinates. The potential function for a local vibration may be approximated as a Morse potential.\textsuperscript{33}

\[ V = D_e \left[ 1 - \exp(-a\delta r) \right]^2 \]  \hspace{1cm} (1.9)

where $D_e$ is the bond dissociation energy, $a$ controls the width of the potential, and $\delta r$ is the difference between the equilibrium distance and the distance between atoms. The corresponding energy levels $E_n$ are given by
\[ E_n / hc = \sum_i \omega_i (n_i + \frac{1}{2}) + \sum_i \omega x_i (n_i + \frac{1}{2})^2 \]  \hspace{1cm} (1.10)

where \( h \) and \( c \) is the Planck constant and speed of light, \( \omega_i \) and \( \omega x_i \) are harmonic frequency and anharmonicity respectively and \( n_i \) is the number of quanta of excitation of the \( i \)th bond oscillator.

At low vibrational energy, the harmonic approximation was able to describe the molecular vibrations accurately. However, earlier work by Siebrand and co-workers\(^{34}\) and by Henry\(^{35}\) has shown that the normal mode model is not adequate for highly excited vibrational states. The normal mode model is especially inappropriate for treating molecules with large amplitude vibration, because this vibration contains anharmonic terms from the potential energy. These bond anharmonic terms become larger at higher excited states and dominate the energy difference between distinct normal mode states (inter-bond coupling). Therefore, the local mode treatment is a more suitable model for treating highly excited vibrational states.

1.3.3 Local Mode Treatment of the Torsion-Vibrational problem

In methanol, Wang and Perry’s\(^5\) experimental work indicates that the two asymmetric stretches (\( \nu_2 \) and \( \nu_9 \)), the ground torsional tunneling splittings are inverted with E level 3.26 cm\(^{-1}\) below the \( A_1 \) mode for \( \nu_2 \), while \( \nu_9 \) the E level is 5.48 cm\(^{-1}\) below the \( A_2 \) mode. In the symmetric stretch, \( \nu_3 \) the torsional tunneling splittings are normal according to the one dimensional Hamiltonian which leads to the A level below the E level. Because of the inversion property, Wang and Perry\(^{36}\) developed a local model treatment to account for the inversion property present in the two asymmetric stretches. In their model, a local mode treatment is chosen because it uses fewer parameters than the normal mode representation.

1.3.3.1 Local CH stretches and the Local Local Hamiltonian

The vibrational Hamiltonian \( H_{vib} \) applied to methanol molecule includes the local C-H stretches and a local-local coupling Hamiltonian.

\[ H_{vib} = H_{str} + H_{l-l} \]  \hspace{1cm} (1.11)
This Hamiltonian is based on the local mode treatment described by Child and Halonen\textsuperscript{37} and explicitly derived in Wang and Perry's internal coordinate model\textsuperscript{5}. The term $H_{\text{str}}$, describing the stretching of the methyl CH bonds are expanded in a Fourier series in the torsional angle ($\gamma$).

$$H_{\text{str}} = H_{\text{str}}^{(0)} + H_{\text{str}}^{(1)} + H_{\text{str}}^{(2)} + ....... \quad (1.12)$$

The Zeroth-order terms are given by

$$H_{\text{str}}^{(0)}(\gamma) = \omega \left( \nu_1 + \frac{1}{2} + \nu_2 + \frac{1}{2} + \nu_3 + \frac{1}{2} \right), \quad (1.13)$$

where $\omega$ represents the three uncoupled local modes with the C-H frequency value of 2934.0 cm\textsuperscript{-1} and $\nu_i$ denote quantum numbers. The first order term $H_{\text{str}}^{(1)}$ describes the torsion-vibration coupling.

$$H_{\text{str}}^{(1)}(\gamma) = \mu^{(1)} \left( a_i^+ a_i + a_i a_i^+ \right) \cos(\alpha) + \left( a_i^+ a_i + a_i a_i^+ \right) \cos(\alpha - \frac{2\pi}{3})$$

$$+ \left( a_i^+ a_i + a_i a_i^+ \right) \cos(\alpha + \frac{2\pi}{3}) \quad (1.14)$$

where $\mu^{(1)}$ is the coupling parameter and has the value of 19.35 cm\textsuperscript{-1}. The operators $a_i^+$ and $a_i$ describes the creation and destruction of quanta in the three C-H stretches respectively, where the operator subscripts ($i=1,2,3$) label the three CH bonds. In Eq. (1.14), the torsion angle $\gamma$ appears in the form $\cos(\alpha - \phi)$ with $\phi = 0, 2\pi/3, -2\pi/3$ for $i=1,2,3$ respectively. The phase $\phi$ results from the requirement that $H_{\text{str}}^{(1)}$ transform as $A_1$ in the $G_6$, which is isomorphic to $C_{3v}$ molecular symmetry group (Fig 1.2). The higher order terms in Eq. 1.12 and 1.15 are neglected because the higher order terms are indistinguishable in the fundamental spectra from the first order coupling term. The local-local coupling Hamiltonian formalism is also expanded in term of the torsional angle.

$$H_{l-i} = H_{l-i}^{(0)} + H_{l-i}^{(1)} + H_{l-i}^{(2)} + ....... \quad (1.15)$$

The Zeroth-order term has the form
Fig 1.2 Diagram of the Torsional and phase angles of methanol

Fig (a) shows the torsional angle around the C-O bond, Fig (b) shows the Newman projection where the torsional angle is the angle of the O-H rotated from its anti position with respect to the CH$_1$ methyl group.
Fig 1.3 Torsion potential and torsional energies for a 3-fold symmetric case. The $v_{12}$ and $m$ are nominal labels for the torsional quantum numbers. $v_{12}$ is used in intermediate to high barrier limits, where it represents the harmonic behavior. The $m$ quantum number is used in low barrier case where $m$ represents the free internal rotor behavior.
\[ H_{\text{tot}}^{(0)} = \lambda^{(0)} \left( a_1^* a_2 + a_4 a_5^* + a_1^* a_3 + a_4 a_3^* + a_2^* a_3 + a_2 a_3^* \right), \]  
where \( \lambda \) is the local-local coupling parameter approximated at the value of \(-42.2 \text{ cm}^{-1} \). The first and higher order local-local coupling terms are all set to zero.

1.3.3.2 Torsional part

The internal rotation about the C-O bond has a small potential barrier height of \( 373.5421 \text{ cm}^{-1} \) \(^9,^{10} \) for the ground state (Fig 1.3). The torsional Hamiltonian written for a free internal rotor is given by

\[ H_{\text{tors}}^{(0)} = FJ^2 + \frac{V_3}{2}(1 - \cos 3\alpha) + \frac{V_6}{2}(1 - \cos 6\alpha) + \ldots. \]  
where \( F \) is the inertial constant, \( J_\alpha \) is the internal rotation angular momentum operator, \( V_3 \) and \( V_6 \) are the potential Fourier constants. The torsional part is included in the total Hamiltonian to obtain the torsional-vibrational energies.

\[ H_{\text{tot}} = H_{\text{vib}} + H_{\text{tors}} \]  

1.4 The Adiabatic Approximation

The adiabatic approach is used for reducing the dimensionality of complex problems by separating the fast degrees of freedom from the slow degrees of freedom. The most famous example is the Born-Oppenheimer approximation\(^ {38} \), which involves the separation of the electronic and nuclear motions. Another example is the work of Fehrensen and co-workers\(^ {39} \) who used the adiabatic approximation to treat the 12 vibrational degrees of freedom in methanol. In this case, the large amplitude torsional coordinate or the reaction channel is adiabatically separated from the other 11 small amplitude vibrations. The inverted torsional tunneling structure (see Chapter III) was treated by including a geometric phase factor into the reaction path Hamiltonian to solve the effects of a conical intersection present at the linear C-OH geometry. The adiabatic approximation derivation will be based on the Born-Oppenheimer approximation.
1.4.1 Zeroth Order Adiabatic Approximation

The zeroth-order adiabatic approximation\textsuperscript{40,41} is derived from the time-independent Schrödinger equation

\[ H\Psi = E\Psi. \] (1.19)

The electronic wavefunction is solved at each nuclear geometry and the resulting electronic energies become the effective potential that governs the motion of the nuclei. Hence the solutions of the Schrodinger’s equation are written as the product of the electronic wavefunction \( \psi_i(q;Q) \) and the nuclear wavefunction, \( \chi_n(Q) \).

\[ \Psi(q,Q) = \psi_i^0(q;Q)\chi_n(Q) \] (1.20)

where \( q \) and \( Q \) are the electronic and nuclear coordinates respectively. The electronic wavefunctions are found as the solutions to

\[ \hat{H}_i^0\psi_i^0(q;Q) = E_i^0(Q)\psi_i^0(q;Q). \] (1.21)

where \( \hat{H}_i^0 \) is the electronic Hamiltonian and \( E_i^0(Q) \) is the electronic energy of the \( i \)th electronic state at nuclear geometry \( Q \). The zeroth-order nuclear wavefunctions are then obtained by solving

\[ (E_e^0(Q) + \hat{T}_n - E_i^{(0)})\chi_n(Q) = 0, \] (1.22)

where \( \hat{T}_n \) is the nuclear kinetic operator and \( E_i^{(0)} \) is the zeroth-order total energy. In this approximation, any coupling of the nuclear and electronic motions are neglected, although the first order corrections may easily be applied.

1.4.2. First Order Corrections to the Crude Adiabatic Approximation

The first order corrections\textsuperscript{42} to the crude adiabatic approximation are obtained from the neglected terms, \( \left( \frac{\partial^2 \psi_i}{\partial Q^2} \right) \) and \( \left( \frac{\partial \psi_i}{\partial Q} \right) \left( \frac{\partial \chi_n}{\partial Q} \right) \). The first order corrections\textsuperscript{42} are given by

\[ E^{(1)} = \left\langle \psi_i \right| \hat{T}_n \left| \psi_i \right\rangle \] (1.23)
where $\hat{T}_n^2 = \partial^2 / \partial Q^2$ is the square of the nuclei kinetic operator. The cross terms,

$$(\partial \psi_i / \partial Q)(\partial \chi_n / \partial Q)$$

are not included since they are negligible.

1.4.3 Breakdown of the Adiabatic Approximation

The adiabatic approximation works well when the electronic states are well spaced and the energy gap ($\Delta \varepsilon_{12}$) exceeds $10^4 \text{ cm}^{-1}$. Below this value when $\Delta \varepsilon_{12} \approx 10^3 \text{ cm}^{-1}$, the adiabatic approximation begins to break down and phenomena such as radiationless transitions occurred. The off diagonal terms responsible for occurrence of radiationless transitions is explain by the proximity effect concept. However, in strong coupling, where $\Delta \varepsilon_{12} \leq 10^2 \text{ cm}^{-1}$, off-diagonal terms diverge and the electronic states are degenerate or near degenerate forming a conical intersection.

1.4.3.1 Conical Intersections

Conical intersections are singular points in nuclear coordinate space where electronic states are degenerate or near degenerate. Two potential energy curves form a double cone when they intersect. The occurrence of degeneracy at the intersection point is a result of the non-crossing rule by von Neumann and Wigner, which states “that the rule of seam of conical intersection may have dimension of $N^{\text{int}} - 2$ for same-symmetry intersections where $N^{\text{int}}$ is the number of internal degrees of freedom. Equivalently, two internal coordinates must be varied to find an intersection.” Therefore, conical intersections are prevalent phenomena, that may affect a great many photochemical and chemical reaction involving excited electronic states.

1.4.3.2 Geometric Phase

The presence of the conical intersection may be felt at the ground electronic state as the result of a geometric phase. Geometric phase is a phase difference in the wavefunction that is accumulated when the wavefunction is evaluated along a closed path. An indicator of the presence of a geometric phase is the inversion of the energy levels caused by the change of sign from +1 to -1 of the electronic wave function in so-called Jahn-Teller (JT) systems. The
geometric phase in a JT system is illustrated by the experimental results discussed by Ham’s paper. The experimental data for defects of crystals revealed an unusual ordering of energy levels, which is attributed to the sign change due to the geometric phase.

A geometric phase results in a multi-valued and non-continuous electronic wavefunction. There are three approaches used in alleviating this problem. One approach is to transform the adiabatic basis to a diabatic basis. The second approach is to multiply the multi-valued electronic wavefunction by a phase factor, which yields a single-valued, continuous, and real nuclear wavefunction. This is a more common antidote to this problem because of its simplicity and convenience. The third approach is implementing double-valued boundary conditions for the electronic wavefunction instead of the second method above, which employs single-valued boundary conditions with a phase factor. Kupperman et. al. used a double valued boundary condition method to calculate the differential cross sections of the reaction

\[ \text{H}+\text{D}_2(\nu=0,j=0) \rightarrow \text{HD}(\nu=0,j=4) + \text{D} \text{ at } E_{\text{tot}}=1.481\text{eV}. \]

This value is within the experimental value, showing that the double valued boundary condition approach is valuable in treating the geometric phase effect. All three approaches treat the geometric phase effects, but which is most useful depends on the molecular system.

1.5 Ab initio Calculations

Fehrensen and others have used \textit{ab initio} calculations to understand the torsion-vibrational dynamics of methanol. They mapped out the potential energy surface of the torsion-vibration coordinates as well as the coupling between the anti-CH and OH stretch coordinates. Correlation effects, both static and dynamic play an important role in molecular dynamics. Hence, it is important to choose appropriate basis sets and levels of approximation in \textit{ab initio} calculations. For our work on methanol, we experimented with different choices as described in Chapter II.
1.6 Organization of this Dissertation

The remainder of this dissertation is organized as follows: Chapter II describes the *ab initio* calculations of the impact of the potentially reactive channel (CH$_3$OH→CH$_2$O+2H) on the vibrational dynamics of methanol. The application of the adiabatic approximation to the three CH stretches and the torsional motion is presented in Chapter III. This chapter has been published in the Journal of Chemical Physics. Chapter IV describes a new experimental setup that will allow us to investigate the $v_{\text{CH}}$=2 region of methanol in detail. Finally, Chapter V is a summary of the results of this dissertation.
CHAPTER II

AB INITIO CALCULATIONS ON THE IMPACT OF A POTENTIALLY REACTIVE PATHWAY ON VIBRATIONAL COUPLINGS IN METHANOL

Experimental studies on IVR of highly vibrational excited molecules are integral to understanding how chemical reactions occur. These experimental results reveal the importance of a large amplitude motion, which is known to increase the flow of vibrational energy depending on its coupling to the other small-amplitude vibrational modes\(^1\). According to the RRKM theory, IVR is responsible for the energy flow within the molecule leading to a statistical distribution of reaction products. Whereas in the RRKM theory\(^{11,12}\), the assumption of fast IVR is used to construct a theory of unimolecular reactions, in this present work, knowledge of a potentially reactive channel is used to derive an understanding of the IVR coupling mechanisms. Our investigation of a potentially reactive pathway focuses on leading to the formation of formaldehyde dissociation channel (\(\text{CH}_3\text{OH} \rightarrow \text{CH}_2\text{O} + 2\text{H}\)). It explains the experimental observations of the coupling between the \textit{anti} CH bond and the OH bond in methanol and links it to the coupling of the large torsional amplitude motion to the OH stretch vibration. In this chapter, a brief introduction of the experimental observations detail the coupling between the small-amplitude vibrations and the large amplitude motion. The third section introduces the theoretical methods used in this work and addresses the treatment of electron correlation effects. Finally, a discussion of the results obtained from the \textit{ab initio} calculations and their connection to the experimental observations is presented in section 2.4.
Fig 2.1 (a) Single resonance experiment diagram of IRLAPS, where the arrows indicate the excitation from the fundamental to the $2v_1-5v_1$ OH overtone (b) Double resonance experiment diagram of IRLAPS where the first arrow indicates the excitation of a specific rotational quantum number $J$ of the fundamental band. The second arrow indicates the excitation from the $v_1-6v_1$ overtone region. This figure is taken from Ref 2. Fig 1 and pg. 8411
2.1 Experimental Observations

The experimental observations of the coupling between the torsional motion and the small amplitude vibrations are discussed in the following sections.

2.1.1 An Experimental Observation of the Coupling between the \textit{anti-CH} bond and the OH bond

Rizzo et al\cite{2}. used infrared assisted photofragment spectroscopy (IRLAPS) in a single resonance experiment to measure the vibrational OH overtone excitation spectrum of methanol. In the single resonance experiment (Fig 2.1a) jet-cooled methanol molecules are excited from ground vibrational state to OH vibrational overtones levels 2-5 using a pulsed dye laser or Raman shifted dye laser. Then a pulse from a transverse excited atmospheric (TEA) CO$_2$ laser, after a delay of about 100 ns, selectively pumps the vibrationally excited molecules to an energy above the dissociation limit of the CO bond. About 600 ns later, a UV laser detects the OH fragments by means of laser-induced fluorescence (LIF). The vibrational OH overtone excitation spectrum is obtained by scanning the frequency of the pulsed dye laser, with the frequency of the TEA CO$_2$, while the LIF probe is kept fixed. Rizzo et al, found a 50 cm$^{-1}$ splitting of the OH overtone signal.

In the 5\nu$_1$ region of the spectrum, where \nu$_1$ is the OH stretch (see Fig 2.2a), the two peaks in the spectrum occur representing the interaction of 4\nu$_1$+\nu$_2$ with 5\nu$_1$, where \nu$_2$ is the asymmetric CH stretch. The IVR coupling matrix element of 23.5 cm$^{-1}$ arise from the 50 cm$^{-1}$ splitting between the 5\nu$_1$ and 4\nu$_1$+\nu$_2$ vibrations. Since the \nu$_2$ CH stretch has the greatest amplitude on the CH bond anti to the OH, therefore the IVR coupling matrix element gives the value of the interaction between the OH and \textit{anti} CH bond.

\textit{Ab initio} calculations by Halonen\cite{56} accounted for these experimental results. In Halonen’s calculations, a curvilinear internal coordinate representation was able to reproduce and provide an explanation for the 50 cm$^{-1}$ splitting found between the 5\nu$_1$ and the 4\nu$_1$+\nu$_2$ features of the spectrum. In Halonen’s earlier work\cite{56}, a harmonic potential energy term is responsible for the
Fig 2.2 IR frequency resolved signal of 5ν₁ region of the OH overtone spectrum. This figure is taken from Ref. 2, Fig 2 pg. 8412. In a) represents the 7ν₁ spectrum where the 5ν₁/4ν₁+ν₂ vibrational states are not observed. In panel b) represents the 6ν₁ region where a small interaction between the 5ν₁+ν₂ is observed. In panel c) the 50 cm⁻¹ splitting between the 5ν₁/4ν₁+ν₂ is detected. Panel d) represents the 4ν₁ region where a small interaction between the 3ν₁+ν₂ is observed. The dashed line indicate the increase of the interaction from 4ν₁ to 5ν₁ region and reduction of the interaction in the 6ν₁ region.
50 cm\(^{-1}\) splitting, however it has been suggested by Mills\(^{37}\) that the quartic Darling-Dennison\(^{27}\) term in a normal mode coordinate contributes to the 50 cm\(^{-1}\) splitting. Therefore, Halonen\(^{56}\) applied a unitary transformation method by converting the curvilinear internal coordinates of these calculations to normal mode representation. The normal mode representation produced the matrix element of 28.3 cm\(^{-1}\) and a splitting of 56.6 cm\(^{-1}\) if the two zeroth-order interacting states (5\(\nu_1\) and the 4\(\nu_1+\nu_2\)) are degenerate. The 56.6 cm\(^{-1}\) splitting is close to the experimental value, thus validating that the quartic Darling-Dennison\(^{27}\) term is responsible for the splittings. Also, Halonen\(^{56}\) computed the interaction coupling strength parameters in the curvilinear internal coordinate model for the two non-unique CH and for the unique (anti) CH bond. The coupling strength parameter (Eq. 2.7 of Ref 57) of the non-unique CH is 3.3 cm\(^{-1}\), which give rise to a 21 cm\(^{-1}\) splitting. On the other hand the unique CH (anti) coupling strength parameter is 12.1 cm\(^{-1}\), which give rise to a 54 cm\(^{-1}\) splitting, therefore accounting for the experimental findings that the anti CH bond is coupled to the OH bond.

In Quack and Willeke’s\(^{54}\) MP2 ab initio theory, they calculated the potential energy surface of methanol isotopomer CD\(_2\)HOH and the coupling matrix element between the OH and the CH stretch. In their results, the coupling matrix element was calculated from the absorption spectrum of the potential energy surface as 26.5 cm\(^{-1}\), which is close to Halonen’s\(^{56}\) work. Therefore this calculations agrees with Halonen that the 50 cm\(^{-1}\) splitting orginate from the coupling between the anti CH bond and the OH bond.

2.1.2 An Experimental Observation of the Dependence the Torsional Barrier on the OH Stretch Vibrational Excitation

The second experimental observation relevant to this work (Fig 2.3) is obtained from the rotationally resolved spectrum of the 3\(\nu_1\)-6\(\nu_1\) OH stretching overtones using the IRLAPS double resonance technique\(^{58}\) (Fig 2.1b). The double resonance version is similar to the single resonance version but with the exception that a jet cooled methanol molecule is excited in the fundamental
band of the OH stretch with specific rotation quantum numbers. Subsequently after 80 ns, a visible pulse from Neodymium Yttrium Aluminum Garnet (ND:YAG) pumped dye laser excites the bond further to overtone levels from 3 to 6. In Fig 2.3 we present experimental data for the relationship between OH stretch excitation and torsional motion. The top panel shows the torsional splittings as a function of the excitation level $\nu_1$ of the OH stretch. The data show a decrease of the tunneling splitting with increasing $\nu_1$ excitation level. The central panel shows the inertial constant, $F$, as a function of $\nu_1$. The data indicate that the moment of inertia about the CO axis decreases as the excitation level increases. The bottom panel shows the torsional barrier height $V_3$ as a function of $\nu_1$, which is seen to increase with increasing excitation level. The experimental values in Fig 2.3 were fitted to theoretical calculations using the OH and HOOH radicals as models, these fits are indicated by the solid and dashed lines respectively.

According to the results presented in the bottom panel of Fig 2.3 the torsional barrier increases from a value of 373.5421 cm$^{-1}$ in the vibrational ground state to more than 600 cm$^{-1}$ when the OH stretch is excited with six quanta$^{58}$. Further studies$^4$ reported the OH stretch overtones $2\nu_1$ and $3\nu_1$ and the torsional combinations, $2\nu_1+\nu_{12}$, $2\nu_1+2\nu_{12}$, $3\nu_1+\nu_{12}$ and $3\nu_1+2\nu_{12}$, where $\nu_{12}$ represents torsional vibration. The studies indicate that for each quantum of OH stretch excitation, the torsional barrier height increases by $40.9\pm1.9$ cm$^{-1}$. In addition, the central panel of Fig 2.3 shows that the moment of inertia constant ($F$) decreases in a linear fashion by $0.89\pm0.02$ cm$^{-1}$ per quantum of OH stretch excitation. The decrease in the torsional tunneling splittings in Fig 2.3 arises both from the change in the torsional inertial constant from the increase in the torsional barrier. These two effects increase the difficulty of the quantum mechanical tunneling through the barrier, hence reducing the torsional tunneling splittings as the OH bond is extended. Together these effects account for the decrease of the torsional tunneling splittings from 9.1 cm$^{-1}$ in the ground state to 1.6 cm$^{-1}$ at $\nu_1=6$ shown in the top panel of Fig 2.3. These findings clearly show that the torsional motion is coupled to the OH stretch.
Fig 2.3 Relationship between the OH stretch excitation ($v_1$) and torsional motion$^{58}$. This figure is taken from Ref. 53, Fig 5, pg. 11364. The points, open and solid are experimental data. The solid line is a calculation based on the OH radical as a model, while the dashed line is a similar calculation using HOOH as the model.
To address these experimental findings, Halonen and coworkers\textsuperscript{59} extended the \textit{ab initio} calculations mentioned in section 2.1.1 by including the torsional terms in their Hamiltonian. In their calculations, the moment of inertia constant was found to decrease as the OH stretching energy increases similar to the experimental data in Fig 2.3. The OH inertial constant is proportional to the average of the inverse square of the OH bond length. The moment of inertia of the methyl group also contributes, but it gives a small contribution because it is heavier than the OH group. The inertial constant effect together with the increase of the effective torsional barrier height at high OH stretching states is responsible for the changes of the tunneling splittings.

The Fehrensen \textit{et al.}\textsuperscript{39} \textit{ab initio} calculations of the 12 vibrational degrees of freedom of methanol further supports the analysis of the IRLAPS spectra\textsuperscript{2}. In their results, the torsional barrier height increases with OH excitation and they indicate that the effective torsional barrier height and the torsional inertial constant both contribute, where the effective torsional barrier height with the largest contribution towards the reduction of the tunneling splittings.

The relationship between the torsional barrier height and the OH excitation is not based on steric behavior, because the extension of the OH bond should decrease the steric hindrance, causing the effective torsional barrier height to decrease. Instead, the effect is primarily electronic in nature\textsuperscript{4}. For the hydrogen peroxide molecule, Carpenter and others\textsuperscript{60-62} proposed that the increase of the torsional barrier height with OH vibrational excitation stems from an increase of the charge-transfer interaction. This charge-transfer interaction occurs between the nonbonding orbital of the donor lone pair electrons on the oxygen atom (n\textsubscript{O}\textsuperscript{*}) and the acceptor antibonding orbital of the OH bond (\sigma\textsubscript{OH}\textsuperscript{*}) as the OH bond is elongated. Kuhn et al.,\textsuperscript{63} applied a six-dimensional analytical potential calculation to the hydrogen peroxide molecule. These results further substantiated the work of Carpenter \textit{et al.}\textsuperscript{60-62} and determined that changes in the hybridization of the \textit{s} and \textit{p} character of the bonding orbitals effect the torsional barrier height.
Additional support for the concept that the vibrationally induced changes in the torsional barrier are electronic in nature comes from three sources. First, \textit{Ab initio} calculations by Go and Perry\textsuperscript{64} (Fig. 2.4) indicated that the excitation of the OH stretch induces the shortening of the CO bond. Second, experimental findings\textsuperscript{2,3,58,65} such as a change of dipole moment along the CO axis leading to $a$-type (parallel) character in the OH stretch overtones. Third, MP2 level calculations of the plot of p-like character of hybrid $\sigma_{\text{OH}}$ as the OH bond is extended (Fig 2.5a) is related to the enhancement of the hyperconjugation energy between the $n_{\text{OH}} \rightarrow \sigma_{\text{OH}}^*$ (Fig 2.5b) as a function of the OH bond length. Hyperconjugation energy\textsuperscript{66} represents the electron transfer between bonding (donate electrons (or lone pairs)) and antibonding orbitals (accept electrons). This enhancement is an indicator that the acceptor ability itself increased, therefore the occupied molecular orbital energy ($\epsilon_{\text{OH}}$) is lowered facilitated the formation of the partial $\pi$-like double bond character at the CO bond. This shows that the lowering of the occupied molecular orbital energy is attributed to the increase of the overlap between the nonbonding oxygen lone pairs and the vicinal $\sigma_{\text{OH}}^*$ similar to the results reported by Carpenter and others\textsuperscript{60,61} for the hydrogen peroxide molecule. Therefore corroborating that the relationship between the torsional barrier height and the OH excitation is electronic in nature.

2.2 Influence of a Potentially Reactive Channel

In this section, a connection is proposed between a potentially reactive channel and the two experimental observations, that is, the 50 cm$^{-1}$ splitting in the $5\nu_1$ region and the increase of torsional barrier height with OH excitation. The potentially reactive channel is

$$\text{CH}_3\text{OH} \rightarrow \text{CH}_2=\text{O} + 2\text{H}. \quad (2.1)$$

Although this is by no means the lowest energy fragmentation channel, even modest progress along this reaction coordinate induces changes that can account for the two observations. When both the OH and \textit{anti} CH bond is extended, the CO bond develops some double bond character, lowering the electronic energy relative to independent stretches of the two bonds.
Fig 2.4 CO bond shortening and $V_3$ barrier height vs the OH bond distances. The vertical dotted line corresponds to the equilibrium geometry. This figure is taken from Ref. 4 Fig. 6 pg. 98.
In figure a) the % of p character of the $\sigma_{\text{OH}}$ orbital in methanol is plotted vs. the different R(Å) bond lengths. In figure b) the hyperconjugation energy of the $\eta_{\text{OH}} \rightarrow \sigma_{\text{OH}}^*$ is plotted vs. the different OH bond lengths for methanol. In figure a) and b) the calculations, the MP2-6-311+G(3df,2p) method and basis set were used to obtain the results. In c) and d) figures are calculated using HF-6-311+G(d) of hydrogen peroxide. Panels c) and d) are taken from Ref. 58 fig. 6 and 7.
1) The lowering of the energy relative to the independent stretches implies that these two coordinates, the \textit{anti} CH bond and the OH bond are coupled.

2) The formation of partial double bond character (1\%) of the CO bond as the OH bond is extended increases the torsional barrier height.

Therefore, the formaldehyde channel accounts for the coupling between the OH and \textit{anti} CH bond (Experimental observation 1 in section 2.1). The formation of the partial double bond character in the CO bond is an indicator of the coupling of the torsional motion with the OH excitation (Experimental observation 2 in section 2.2). Therefore, the formaldehyde potentially reactive channel provides insight into the origin of both experimental observations (1 and 2).

In the limit of complete reaction, Hess’s Law can be used to calculate the $\Delta(\Delta H^\circ)$ (depth of the product valley). The depth of valley is the measure of the coupling between the \textit{anti} CH bond and the OH bond can be obtained as the non-additivity of the energy changes incurred when the two bonds are stretched. This non-additivity is most easily appreciated in the limit of complete reaction. The energy required to dissociate the OH bond is

$$\text{CH}_3\text{OH} \rightarrow \text{CH}_3\text{O}^* + \text{H}^* \quad \Delta H_3^0 = 435\text{kJ/mol},$$

(2.2)

while the energy required to dissociate a CH bond is

$$\text{CH}_3\text{OH} \rightarrow \cdot\text{CH}_2\text{OH} + \text{H}^* \quad \Delta H_2^0 = 408\text{kJ/mol}.$$  

(2.3)

The sum of these energies can be compared to the energy required to dissociate both hydrogens,

$$\text{CH}_3\text{OH} \rightarrow \text{CH}_2\text{O} + 2\text{H}^* \quad \Delta H_1^0 = 521\text{kJ/mol}.$$  

(2.4)

Because of the formation of the C=O bond in formaldehyde, the energy required to dissociate both bonds is much less than the sum of the independent (CH and OH) dissociation energies.

$$\Delta(\Delta H^0) = \Delta H_1^0 - \left(\Delta H_2^0 + \Delta H_3^0\right) = -321\text{kJ/mol}.$$  

(2.5)

For convenience we will refer to this non-additivity, $\Delta(\Delta H^0)$ as the “depth of valley of the product valley” for the formaldehyde channel (Eq. 2.5). We will show in the following sections
that the effects of the product valley extends well down into the bound region of the potential and
gives rise to coupling (i.e non-addictivity) between the OH and anti CH stretches.

In earlier work by Quack and Willeke\textsuperscript{54}, second order Möller-Plesset perturbation theory
is used to produce the potential energy surface for the CD\textsubscript{3}H-OH molecule. In their work, a five
dimensional potential energy surface is produced and a two dimensional cut through that surface
is shown in Fig. 2.6. When \( q_1 \) the (OH stretching mode) is extended from -2 to -8 Å, and \( q_2 \) the
(CH stretching mode) is fixed at the equilibrium geometry at 0 Å bond extension, the energy
increases toward the energy of CH\textsubscript{3}O•+H•. Likewise, when \( q_1 \) is fixed (OH stretching mode) at
equilibrium geometry at 0 Å bond extension and \( q_2 \) is extended from -2 to -8 Å the energy
increases toward that of •CH\textsubscript{2}OH +H•. When both coordinates \( q_1 \) and \( q_2 \) are extended \( \approx 0.7 \) Å the
system progresses toward the formaldehyde channel, CH\textsubscript{2}=O +2H•. Although the results of
interest are contained in that calculation, the authors did not analyze their data in terms of the
coupling between these two vibrational modes in terms of the formaldehyde reactive channel.

Other theoretical calculations\textsuperscript{54,67,68} and experimental results\textsuperscript{69} indicate that the two radicals
hydroxymethyl (CH\textsubscript{2}OH•) and methoxy (CH\textsubscript{3}O•) play an important role in the formation of
formaldehyde from the decomposition of methanol. In Muckerman and Hua-Gen\textsuperscript{68} \textit{ab initio}
calculations using the complete-active-space self consistent field (CASSCF) and multireference
configuration theory produced a potential energy surface of methanol. In their findings, the
formaldehyde channel is formed from a direct mechanism from the methoxy radical similiar to
Lin and coworkers\textsuperscript{69} experimental results. In this work, a potentially reactive channel (Eq. 2.1)
will be shown to affect the bound region of methanol and result in the IVR coupling involving the
CH, OH and torsional degrees of freedom.

2.3 \textit{Ab initio} Methods and basis sets

In dealing with bond breakage and bond formation especially mapping out a potential
ergy surface, one must choose an \textit{ab initio} method that will properly account for both static and
Fig 2.6 Two-dimensional cut coordinate potential energy surface of isotopic methanol molecule. $q_1$ represents the OH stretching coordinate and $q_2$ is the CH stretching coordinate. This graph is a cut near the minimum of the five dimensional coordinates mentioned above in text. The negative values correspond to positive extensions of the OH and CH stretching coordinate. This figure is taken from Ref. Fig. 55. Pg.11961
dynamic correlation effects as well as one must choose a method that is practical within the limit of time and memory. Also, the electronic energy should be variational, meaning that the electronic energy should be an upper bound to the exact solution of the Schrödinger’s equation. Hartree-Fock self-consistent field theory fit these requirements, but with the exception of neglecting correlation effects associated with bond formation as well as correlation effects at the equilibrium structure\textsuperscript{70}.

2.3.1 Dynamic Electronic Correlation Effects

It is well known that restricted Hartree-Fock self-consistent field theory fails to treat correlation effects of a pair of electrons with opposing spins. In examining the Hartree-Fock self-consistent method, which is based on a single determinate matrix that represent the spatial and spin orbital of a molecule, the electronic Hamiltonian of the helium atom is expressed below to describe the correlation effects

\[
H = \frac{1}{2} \nabla_i^2 \frac{1}{2} \nabla_j^2 - \frac{2}{r_i} - \frac{2}{r_j} + \frac{1}{r_{ij}}. \tag{2.6}
\]

The first and second terms are the kinetic energy operators of electrons one and two, while the third and fourth terms are the electron-nuclear attraction and the last term is the inverse distance between the two electrons also called the Coulomb operator. In Hartree-Fock theory, the Coulomb operator is calculated by taking the average potential field experienced by the ith electrons in the company of other electrons. According to the exact wavefunction of the Schrödinger equation, when \( r_{ij} \) approaches zero of the electronic wavefunction a cusp shape is formed (Fig. 2.6). This cusp shape illustrates that the exact solution has a Coulomb hole at \( r_{ij} = 0 \). In the Hartree-Fock equation this behavior is not replicated when the two electrons approach each other, and instead the shape of the graph is a parabola\textsuperscript{71} (Fig. 2.7) This implies that restricted
$r_{12}$ is distance between electron one and electron two

Fig. 2.7 Interelectronic cusp$^{71}$. The graph is electronic wavefunction vs the $r$, is the distance between two electrons. This figure is taken from Ref. 71 Fig. 3. pg. 7
Hartree-Fock theory overestimates the electron repulsion energy. Since Hartree-Fock method is variational, the correlation energy is negative and defined in the following equation:

\[ E_{\text{corr}} = E_{\text{exact}} - E_{\text{HF}} \]  

(2.7)

There are two types of correlation effects, radial and angular, which are neglected by the Hartree-Fock theory, when \( r_{12} \) approaches zero. Radial correlation effect is described as the energy of repulsion between two electrons that causes one electron to be farther away from the nucleus, where the second electron is closer to the nucleus. On the other hand, angular correlation effect is described as the energy of repulsion between two electrons that causes one electron to be located at the right of the nucleus, while the second electron tends to migrate to the left of the nucleus. These two types of correlation effects are often referred as dynamic correlation effects and occur at short-range distances. The neglect of these two types within the Hartree-Fock method leads to about 1eV unaccounted for in each doubly occupied orbital \(^{31}\).

Möller-Plesset perturbation and coupled cluster theory are two of the most widely used method that treats dynamic correlation effects. In the case of Möller-Plesset perturbation method, where the derivation is taken from Szabo and Ostlund\(^ {32}\) “Modern Quantum Chemistry: Introduction To Advanced electronic structure theory”, the full Hamiltonian is partition into two Hermitian parts \( H_0 \) and \( \hat{V} \). \( H_0 \) consists of the kinetic energy operator and the nuclear-electron attraction, while \( \hat{V} \) is the Coulomb operator, which is the perturbation part

\[ H = H_0 + \lambda \hat{V}. \]  

(2.8)

The wavefunction and the energy are expanded in terms according to the perturbation factor \( \lambda \) in a Maclaurin series to yield the following equations:

\[ |\psi_i\rangle = |\psi_i^{(0)}\rangle + \lambda |\psi_i^{(1)}\rangle + \lambda^2 |\psi_i^{(2)}\rangle + \ldots \]  

\[ E_i = E_i^{(0)} + \lambda E_i^{(1)} + \lambda^2 E_i^{(2)} + \ldots \]  

(2.9)

Where Eq. (2.8) is substituted into Eq. (2.9) to yield the full solutions
\[(H_0 + \lambda V)(\psi_i^{(0)} + \lambda \psi_i^{(1)} + \ldots) = \left( E_i^{(0)} + \lambda E_i^{(1)} + \ldots \right)(\psi_i^{(0)} + \lambda \psi_i^{(1)} + \ldots). \tag{2.10}\]

Rearranging Eq. (2.10) by equating like terms with each other, the following derivations are produced for the zeroth to second order, where \(|\psi_i^{(0)}\rangle = |\psi\rangle\) is used to compact the following equations

\[
H_0 |\psi\rangle = E_i^{(0)} |\psi\rangle \quad n=0 \tag{2.11}
\]
\[
H_0 |\psi_i^{(1)}\rangle + V |\psi\rangle = E_i^{(0)} |\psi_i^{(1)}\rangle + E_i^{(1)} |\psi\rangle \quad n=1 \tag{2.12}
\]
\[
H_0 |\psi_i^{(2)}\rangle + V |\psi_i^{(1)}\rangle = E_i^{(0)} |\psi_i^{(2)}\rangle + E_i^{(1)} |\psi_i^{(1)}\rangle + E_i^{(2)} |\psi\rangle \quad n=2. \tag{2.13}
\]

Multiplying each of these equations by \(\langle i |\) and equating coefficients of \(\lambda^{(i)}\), the solutions of each order are expressed below:

\[
H_0 |\psi\rangle = E_i^{(0)} |\psi\rangle \quad n=0 \tag{2.14}
\]
\[
H_0 |\psi_i^{(1)}\rangle + V |\psi\rangle = E_i^{(0)} |\psi_i^{(1)}\rangle + E_i^{(1)} |\psi\rangle \quad n=1 \tag{2.15}
\]
\[
H_0 |\psi_i^{(2)}\rangle + V |\psi_i^{(1)}\rangle = E_i^{(0)} |\psi_i^{(2)}\rangle + E_i^{(1)} |\psi_i^{(1)}\rangle + E_i^{(2)} |\psi\rangle \quad n=2. \tag{2.16}
\]

Using the orthogonality relationship \(\langle i |\psi_i^{(0)}\rangle = 0\), the following \(n^{th}\)-order energy is given by

\[
E_i^{(0)} = \langle i |H_0|\psi\rangle \tag{2.17}
\]
\[
E_i^{(1)} = \langle i |V|\psi\rangle \tag{2.18}
\]
\[
E_i^{(2)} = \langle i |V|\psi_i^{(1)}\rangle. \tag{2.19}
\]

The solutions of the \(n^{th}\) order perturbation energy are obtained by solving the wavefunction \(\Psi_n^{(n-1)}\) first. Since the full Hamiltonian consists of the Hermitian zeroth order Hamiltonian \(H_0\), which are a set of non-degenerate solutions that are orthogonal and formed a complete set. If the zeroth-order wavefunction, \(\Psi^{(0)}\) is a solution, then any vector orthogonal to this zeroth-order can be expressed as linear combinations of all the other solutions to the eigenvalue equation. For example, the second order energies are obtained from first expanding the first order
wavefunction, which gives the first order solutions. The first order solutions are equal to the energy of the Hartree Fock method, since the Möller-Plesset second order perturbation is the correction to the Hartree Fock theory

$$\Psi_{i}^{(0)} = \sum_{a, b, r, s} C_{iabrs}^{(1)} \Psi_{ab}^{r}.$$ (2.20)

$\Psi_{ab}^{r}$ is the excited wavefunction in which electrons have been excited from $\chi_a, \chi_b$ spin orbitals to virtual orbitals $\chi_r$ and $\chi_s$. $C_{iabrs}^{(1)}$ is the coefficients, which are determined by the following equation

$$C_{iabrs}^{(1)} = \langle \Psi_{ab}^{r} | \Psi_{i}^{(0)} \rangle = \sum_{a, b, r, s} \frac{\langle \Psi_{ab}^{r} | \Psi_{i}^{(0)} \rangle}{\epsilon_a + \epsilon_b - \epsilon_r - \epsilon_s}. $$ (2.21)

Inserting Eq (2.21) into Eq. (2.20) into the expression Eq. (2.19), then the second order energy equation becomes

$$E^{(2)} = \sum_{a, b, r, s} \frac{\langle \Psi_{0}^{(0)} | \frac{1}{r_{12}} | \Psi_{ab}^{r} \rangle^2}{\epsilon_a + \epsilon_b - \epsilon_r - \epsilon_s}. $$ (2.22)

In the numerator, $\Psi_{0}^{(0)}$ is the ground state wavefunction, $\Psi_{ab}^{r}$ is the double excited wavefunction, the $\frac{1}{r_{12}}$ term is defined above, and $\epsilon_n$ is the energy of electronic orbital. According to Brillouin's theorem, the single excited wavefunction does not interact directly with the ground state, therefore it is neglected in calculating the second order energies.

The second order Möller-Plesset perturbation method is sufficient in reaching convergence of small molecules since second order includes the dynamics correlation effects into the Hartree Fock. In most computer programs e.g. Gaussian, the Möller Plesset perturbation method is limited to the fourth-order because increasing it to higher orders than fourth-order introduces unnecessary demands for computational power. Nonetheless, Möller-Plesset perturbation theory is known to diverge when molecules exhibit small HOMO-LUMO energy.
gaps or circumstances in which degeneracies/near-degeneracies occur in electronic states.

The coupled cluster singles and doubles (CCSD) and coupled cluster singles, doubles with the corrected triples (CCSD(T)), (corrected triples are CCSD(T) not regular CCSDT explained below) uses a different approach than the Möller-Plesset perturbation theory mentioned above. In coupled cluster theory, where the derivation below is taken from the Crawford and Schaefer III review on coupled cluster theory, the wavefunction is expressed in an exponential form instead of a partition form in the Möller-Plesset perturbation theory. Also, the coupled cluster theory focuses on the electron correlation from the motions of any pair of electrons, whereas, Möller-Plesset perturbation theory, the perturbation parameter ($\lambda$) part is not a small value and may overestimate the correlation of paired electrons.

For example, a reference four-particle Hartree-Fock wavefunction defined below in shorthand notation, is used to derive the couple cluster theory,

$$\Psi_0^{HF} = \left\{ \chi_i(x_i)\chi_j(x_j)\chi_k(x_k)\chi_l(x_l) \right\}$$

(2.23)

where $\chi_i$, $\chi_j$, $\chi_k$, and $\chi_l$ are the one–electron functions, where one-electron functions (discussed in section 2.3.3) of the four electrons $i, j, k, l$ and $x_1, x_2, x_3, x_4$ are the position vectors of the four electrons including spin. In this shorthand notation of the reference wavefunction is a Dirac notation containing all diagonal elements within a Slater determinant of the wavefunction, which includes the normalization factor and the anti-symmetric property of the wavefunction. The correlation effects are included between the electrons $i$ and $j$, as well as the correlation between $k$ and $l$ with all possible pairwise combinations, using either one-particle or two-particle cluster functions. The two-particle cluster function is defined as

$$f_{ij}(x_m,x_n) = \sum_{a>b} f_{ab}(x_m)\chi_a(x_m)\chi_b(x_n),$$

(2.24)
where \( f_{ij} \) correlates a unique pair of electrons indicated by the notation \( a>b \), the double summation means that it includes the entire set of all one-electron functions. The \( t_{ij}^{ab} \) variable represents the cluster coefficients, and \( \chi_a, \chi_b \) are the one-electron functions within the occupied orbitals of \( i \) and \( j \). The two-particle cluster function is inserted into the reference electronic wavefunction, modifying the Hartree-Fock wavefunction in Eq. (2.23) to give the total electronic wavefunction.

\[
\Psi = |\chi_i \chi_j \chi_k \chi_l \rangle + |f_{ij} \chi_i \chi_k \rangle - |f_{ik} \chi_i \chi_l \rangle + |f_{il} \chi_i \chi_k \rangle + |f_{ij} \chi_j \chi_k \rangle - |f_{ik} \chi_j \chi_l \rangle + |f_{il} \chi_j \chi_k \rangle.
\]

In Eq. (2.26) all cluster of one and two particles are included into the wavefunction

\[
\Psi = |\chi_i \chi_j \chi_k \chi_l \rangle + |f_{ij} \chi_i \chi_k \chi_l \rangle + |f_{ik} \chi_i \chi_j \chi_l \rangle + |f_{il} \chi_i \chi_j \chi_k \rangle + |f_{ij} \chi_j \chi_k \chi_l \rangle - |f_{ik} \chi_j \chi_k \chi_l \rangle + |f_{il} \chi_j \chi_k \chi_l \rangle + |f_{ij} \chi_i \chi_j \chi_k \rangle - |f_{ik} \chi_i \chi_j \chi_l \rangle + |f_{il} \chi_i \chi_j \chi_k \rangle - |f_{ij} \chi_i \chi_k \chi_l \rangle - |f_{ik} \chi_i \chi_j \chi_l \rangle + |f_{il} \chi_i \chi_j \chi_k \rangle + |f_{ij} \chi_j \chi_k \chi_l \rangle - |f_{ik} \chi_j \chi_k \chi_l \rangle + |f_{il} \chi_j \chi_k \chi_l \rangle - |f_{ij} \chi_i \chi_j \chi_k \rangle - |f_{ik} \chi_i \chi_j \chi_l \rangle + |f_{il} \chi_i \chi_j \chi_k \rangle - |f_{ij} \chi_i \chi_k \chi_l \rangle - |f_{ik} \chi_i \chi_j \chi_l \rangle + |f_{il} \chi_i \chi_j \chi_k \rangle.
\]

This equation can be expanded to \( N \)-electron systems but it becomes more complicated, which lead to occurrences of inaccuracies in calculating the total wavefunction. This can be avoided by using the second quantized operators, \( a^\dagger \) and \( a \); the former operator is the annihilation operator while the latter is the creation operator. The creation operator, when it acts on a Slater determinant adds another column (orbital) and one more row (electron) to form a new determinant on the right hand side.

\[
a_i^\dagger |\chi_i \chi_j \ldots \chi_s \rangle = |\chi_i \chi_j \ldots \chi_s \chi_i \rangle
\]

The annihilation operator, when applied to the Slater determinant, a column (orbital) and a row (electron) is removed to form a new determinant.

\[
a_i |\chi_i \chi_j \ldots \chi_s \rangle = |\chi_i \chi_j \ldots \chi_s \rangle
\]
The creation operators can only act on the virtual orbital because the creation operator acting on a true vacuum state (a state containing no electrons or orbitals), produces a new column and a row, while the annihilation operator acting on this vacuum state gives a zero result. Thus, the annihilation operator can only act on the occupied orbital. To obtain the \( n \)-particle cluster functions (\( \hat{T} \)) in second quantized form, the one cluster function, also known as single excitations, first is defined as shown below. The operator \( a_i \) deletes the one electron orbital \( \chi_i \) (occupied orbitals) from the determinant and \( a^+ \) adds the orbital \( \chi_a \) (virtual orbitals) functions which take the place of \( \chi_i \).

\[
\hat{T}_1 = \sum_i t_i = \sum_{ia} t_{ia}^a a_i^+. \tag{2.29}
\]

Similarly, the two-particle function, also known as the double excitations where the operation \( a \) deletesthe orbital \( \chi_i \) and \( \chi_j \) (occupied orbitals) from the determinant and the \( a^+ \) operator adds the orbitals \( \chi_a \) and \( \chi_b \) (virtual orbitals) to take the place of the deleted orbitals.

\[
\hat{T}_2 = \frac{1}{2} \sum_{ij} \hat{t}_{ij} = \frac{1}{4} \sum_{ijab} t_{ij}^{ab} a_i^+ a_j^+ a_i a_j. \tag{2.30}
\]

The \( n \)-cluster functions is defined as

\[
\hat{T}_n = \left( \frac{1}{n!} \right)^2 \sum_{ij...ab} t_{ij...ab}^{ab...} a_i^+ a_j^+ a_i a_j. \tag{2.31}
\]

Then Eq. (2.31) is inserted into the total wavefunction to form the following expression

\[
\Psi = \left( 1 + \hat{T}_1 + \frac{1}{2!} \hat{T}^2 + \frac{1}{3!} \hat{T}^3 + \ldots \right) \chi_o. \tag{2.32}
\]

Since the right-side of the wavefunction resembles the Maclaurin power series of the exponential form, Eq.(2.32) is truncated to the following expression for the couple cluster singles and doubles (CCSD)

\[
\Psi = \exp(\hat{T}_1 + \hat{T}_2) \chi_{(0)} = \exp(\hat{T}) \chi_{(0)} \tag{2.33}
\]

Eq. (2.33) is inserted into the full electronic Schrodinger equation given by
\[ \hat{H}\Psi = E\Psi, \] (2.34)

and multiplied at the left side by the reference wavefunction to yield the CCSD energy

\[ \langle \chi_{(0)}|\hat{H}\hat{e}^f|\chi_{(0)}\rangle = E\langle \chi_{(0)}|\hat{e}^f|\chi_{(0)}\rangle = E. \] (2.35)

The coupled cluster singles, doubles with the corrected triples (CCSD(T))\(^77\) does not contain the full CCSDT\(^77\) approach in which the triplet excitation is derived from \( \hat{T} = \hat{T}_1 + \hat{T}_2 + \hat{T}_3 \) cluster operator, where \( \hat{T}_3 \) is given by

\[ \hat{T}_3 = \frac{1}{6} \sum_{ijk} t_{ijk} = \frac{1}{36} \sum_{ijkabc} t_{ijk} a_i^+ a_j^+ a_k^+ a_l a_j a_k. \] (2.36)

The cost of computing the triples excitation directly is equal to \( N^8 \), \( N \) is the number of electrons. The alternative approach is to implement the triples excitation using the Möller-Plesset perturbation theory\(^72\). In this approach the CCSDT Hamiltonian is instead similarity-transformed to the fourth-order Möller-Plesset perturbation method (MP4)\(^77\).

\[ \hat{H}_{\text{CCSDT}} = \exp(-\hat{T}_1 - \hat{T}_2 - \hat{T}_3)\hat{H}_N \exp(\hat{T}_1 + \hat{T}_2 + \hat{T}_3) \] (2.37)

Since the singles and doubles excitation are already computed from the CCSD method the corrected CCSD(T)\(^71\) is calculated from the fourth-order Möller-Plesset perturbation method\(^72\).

\[ E_{\text{CCSD+T\,(4)}} = E_{\text{CCSD}} + E_T^{\,(4)} \] (2.38)

This correction greatly reduces the computation cost\(^79\) from \( N^8 \) to \( N^7 \).

2.3.2 Balancing of Static-Dynamic Correlation Effects

The Möller-Plesset perturbation theory\(^72\) and coupled cluster theory\(^77\) methods are both adequate in treating dynamic correlation effects. However, both methods rely on the reference wavefunction (Hartree-Fock wavefunction) as a starting point to compute its respective energies. A consequence of using the reference Hartree-Fock wavefunction with molecules that exhibit bond dissociation/formation is that it yields overestimation/underestimation of bond lengths. Second, the Hartree-Fock wavefunction fails for molecules that have quasi-degenerate electronic
states localized at either long-range inter-nuclear distances or molecules that have multiple resonance structures at the equilibrium geometry\(^{32}\) such as the ozone molecule. The occurrence of quasi degeneracies of the electronic states at the long-internuclear distances is called static correlation effects. The reason for the breakdown of the Hartree-Fock wavefunction\(^{71}\) when dealing with bond dissociation is that the electron repulsion is based on a mean average between the two electrons. Thus, it cannot account for the localization of the electrons on different atoms. According to Hartree-Fock theory\(^{72}\), the electrons are required to occupy the same spatial orbital, the outcome of this is that the electrons have equal probability of being on either on atom A or atom B. Therefore, the wavefunction contains equal amount of covalent and ionic terms instead of a varying amount dependent on the molecule in question. For example, for the \(\text{H}_2 \rightarrow 2\text{H}\) dissociation reaction,\(^{71}\) the restricted Hartree-Fock wavefunction for the ground state of \(\text{H}_2\) molecule is

\[
\Psi_x = \hat{A} \sigma_g^a(1) \sigma_g^b(2), \tag{2.39}
\]

where \(\sigma_g = Z_{\sigma_g}(\chi_A + \chi_B)\) the bonding orbital with \(\chi_A\) is a \(s\)-orbital centered on hydrogen A and \(\chi_B\) is a \(s\)-orbital centered on hydrogen B to give the paired electrons according to molecular orbital theory; \(Z_{\sigma_g}\) is the normalization constant. At long-range distances \(\chi_A = 1s_A\) and \(Z_{\sigma_g} \approx \frac{1}{\sqrt{2}}\) and the Hartree-Fock wavefunction for hydrogen atoms is given as

\[
\Psi_x \approx \frac{1}{2} \hat{A}(1s_A^\alpha 1s_B^\beta + 1s_B^\alpha 1s_A^\beta + 1s_A^\alpha 1s_A^\beta + 1s_B^\beta 1s_B^\alpha), \tag{2.40}
\]

which clearly indicates equal amounts of covalent \((1s_A 1s_B, 1s_B 1s_A)\) and ionic terms \((1s_A 1s_A, 1s_B 1s_B)\). The wavefunction with the correct symmetry for the singlet hydrogen atoms is

\[
\Psi_f = \frac{1}{2} [1s_A^\alpha 1s_B^\beta - 1s_A^\beta 1s_B^\alpha + 1s_A^\alpha 1s_A^\beta - 1s_B^\beta 1s_B^\alpha]. \tag{2.41}
\]
Eq. (2.41) is obtained through a multi-determinate wavefunction by using the anti-bonding orbital of H₂ or virtual excited state of H₂ and taking a linear combination of Eq. (2.39) and Eq. (2.40).

The coefficients are varied, cₓ or cₑ in Eq. (2.42) to correct the Hartree-Fock wavefunction

\[ \Psi_f = \frac{1}{2} \hat{A}(1sᵢ^α1sᵣ^β + 1sᵣ^α1sᵢ^β - 1sᵣ^α1sᵣ^β - 1sᵢ^α1sᵢ^β) \]

or

\[ \Psi_f = cₓ\Psiₓ + cₑ\Psiₑ. \]

Eq. (2.42) is considered as a multi-determinate wavefunction or configuration interaction (CI) wavefunction\(^{71}\). The CI wavefunction\(^{71}\) treats both static and dynamic correlation effects by the use of virtual or antibonding orbitals to obtain the correct wavefunction. However, the number of different determinants in a molecular systems is based on the following binomial formula

\[ \binom{2K}{N} = \frac{(2K)!}{N!(2K-N)!} \]

where N represents the number of electrons and 2K, K is the number of spin orbitals\(^{72}\), therefore, in larger molecules the different combinations of determinants increases with the size of the molecule. For example in a small molecule such as H₂, N=2 and 2K spin orbitals is equal to 2 \times N = 2 \times 2 = 4. The number of Slater determinant combinations of hydrogen molecule are \( \binom{4}{2} = \frac{4!}{2!2!} = 6 \). In a larger molecule such as, methanol, N=18 electrons and 2K=36.

The number of Slater determinant combinations of the methanol molecule are

\[ \binom{36}{18} = \binom{36}{18!18!} \approx 9,075,135,300 \text{(See Appendix B). Even though the full CI theory gives the correct Schrödinger solution of the molecule, unfortunately, it is impossible with the computational power and memory available today to calculate the energy for moderately small to large size molecules. Therefore, other methods\(^{72}\) such as: single doubles configuration interaction (SDCI), double configuration interaction (DCI), and multi-configuration self-consistent field theory (MCSCF)/Complete active space self-consistent field theory (CASSCF) have been developed to } \]
truncates the number of combinations of Slater determinant \( \frac{2K}{N} \). In this section, the concentration is on the application of the MCSCF/CASSCF because the SDCI and DCI have serious deficiencies in computing energies for molecules with small HOMO and LUMO energy gap and they lack the size extensive property\(^72\).

The MCSCF theory, also called CASSCF theory,\(^80\) unlike the Möller-Plesset perturbation method\(^72\) and coupled cluster theory,\(^77\) is based on the variational principle to determine the multi-configurational wavefunction. It is derived from first expanding the electronic wavefunction, using the configuration state functions (CSF) basis instead of the Slater determinate basis.

\[
\Psi = \sum_k \chi_k a_k
\]  

where \( a_k \) is the mixing coefficient of the configuration \( \chi_k \), and \( \chi_k \) is the CSF, which are linear combinations of Slater determinants over a set of molecular or atomic orbitals. The set of molecular orbitals are expanding in terms of a set of atomic-basis functions given below.

\[
\phi_i = \sum_j c_{ij} \phi_j
\]

The molecular orbitals must be orthonormal and the mixing coefficients must be orthogonal to obtain the optimum form of orbitals and mixing coefficients.

\[
\sum_k a_k^2 = 1, \quad \langle \chi_k | \chi_j \rangle = \delta_{ij}
\]

Therefore, MCSCF/CASSCF\(^80\) uses the variational method to optimize both the \( a_k \) mixing coefficient and the molecular orbital expansion coefficient \( c_{ij} \) to obtain accurate bond dissociation energies and geometry of the molecule.

The CASSCF method\(^71,80,81\) truncates the \( \frac{2K}{N} \) Slater determinants by using the spin symmetry of the electron spin. According to Delbrück’s theorem\(^71,82\), the electron spin
eigenfunctions $\alpha$ (spin up) and $\beta$ (spin down) must be eigenfunctions of the spin electron spin operators $\hat{S}_z$ and $\hat{S}^2$. Therefore the Slater determinants are combined into functions that are eigenfunction of the spin electron operators, which are called configuration state functions basis (CSFs). The Slater determinants $\begin{pmatrix} 2K \\ N \end{pmatrix}$ are condensed into the CSFs basis using the Weyl-Robinson formula\textsuperscript{80,83}

$$CSFs = \frac{2S + 1}{n + 1} \frac{n + 1}{(n + 1)(N/2 - S)!} \binom{n + 1}{N/2 + S + 1}$$  \hspace{1cm} (2.47)

where $S$ is the total spin, $n$ is the active orbitals and $N$ active electrons. For methanol, which has 18 electrons and 18 orbitals with a total spin of 0 for the singlet ground state, the size of the full CI expansion with CSFs as a basis will reduce from 9,075,135,300 (see above) for the number of Slater determinants, to 40,831,076 basis functions using Eq. 2.47 (See Appendix A). These configuration state functions are further reduced to comprise the active space of the molecule, which includes the electrons that are specifically undergoing substantial changes in a chemical reaction\textsuperscript{80}. The inactive electrons are those electrons that are just spectators in the chemical reaction and usually consist of the core electrons and/or doubly occupied electrons\textsuperscript{80}.

Once the active space is determined, the next step is to locate the starting orbitals. The right choice of starting orbitals can lead to quicker and accurate results of the CASSCF\textsuperscript{80,81} calculations. Pulay and others\textsuperscript{84} recommended that the unrestricted Hartree-Fock method in the natural bond orbital (NBO) basis is the optimum choice in determining the starting orbitals. The reason is that the NBO\textsuperscript{85} introduced by Löwdin\textsuperscript{86} is closer to the Lewis-structure of the molecule.

According to Löwdin,\textsuperscript{86} the natural orbital (NO) basis is derived from the one-density matrix. This one-particle density matrix gives the probability of finding an electron in a space-spin volume element $dx_1$ located in the position $x_1$ independent of the location of the other electrons. The one particle density matrix is written in the following form.

\hspace{1cm} (2.48)
\[ \rho(x_1,x_i') = N \int dx_2...dx_N \chi(x_1,...,x_N)\chi^*(x_1',...x_N) \]

The NO is simply the eigen-orbitals (\(\phi_i\)) of the one-particle density matrix with its corresponding eigenvalues as the occupation numbers (\(\gamma_i\)).

\[ \rho(x_1,x_i')\phi_i = \gamma_i\phi_i \] (2.49)

This NO is similar to the NBO\(^{85}\) with the exception that the NO mentioned above are eigenvectors of the full one-electron density whereas the NBO\(^{85}\) basis correspond to localized eigenvectors of both one and two center blocks of the density matrix. This one center block describes the 1-center core, and nonbonding pairs (lone pairs), while the two center blocks depict the bonding (Lewis orbitals) and anti-bonding orbitals (non-Lewis orbitals). The full set of bonding and anti-bonding (denoted by *) orbitals span the space of the occupied molecular orbitals\(^{60,85}\). The procedure\(^{60,85}\) of the NBO\(^{85}\) is as follows:

\[ \text{AO} \rightarrow \text{NAO} \rightarrow \text{NHO} \rightarrow \text{NBO} \]

The atomic orbitals are optimized to obtain an orthonormal set of atomic orbitals (NAO), which is analogous to the NO, then it is unitarily transformed to orthonormal hybrid orbitals (NHO) and finally to NBO\(^{85}\) with maximum occupancy as determined by one electron density matrix.

In a perfect Lewis structure the occupation of the bonding orbitals is paired giving an occupation number \(\approx 2\). Any fractional occupation number of an orbital is an indicator of the triplet instability of the Hartree-Fock wavefunction. This triplet instability is a red flag that there are multiple solutions of the Hartree-Fock wavefunction; hence a multiple-determinate wavefunction is needed to obtain the correct eigenfunction of the molecule\(^{80,84,87}\).

Although, the CASSCF method\(^{80,81}\) is adequate in treating the static correlation associating with dissociation/bond-formation process of molecules, it does not take into effect the dynamic correlation effects. Dynamic correlation effects are excluded because they neglect any correlation effects associating with the inner core valence orbitals. These inner core valence orbitals are doubly occupied but are not excited to the external or virtual orbitals to include the
dynamic correlation effects.\textsuperscript{79,80} The dynamic correlation effects are included in the multi-reference configuration interaction (MRCI)\textsuperscript{71,80} or multi-reference perturbation theory (MR-PT/CASPT2)\textsuperscript{71}.

The CASPT2 method\textsuperscript{71} and the MRCI\textsuperscript{71,88} both use the CASSCF \textsuperscript{71} wavefunction as the reference wavefunction; however, MRCI\textsuperscript{71,88} is considered as a more accurate method in dealing with the dissociation of small molecules and moderately large molecules than CASPT2. The reason is that MRCI\textsuperscript{71,88} is based on the variational principle, therefore the energy of the system is not higher than the exact solution as in CASPT2\textsuperscript{71}. In the CASPT2\textsuperscript{71} method, which is based on a perturbation method, tends to overestimate the energy of the molecules because of the large value of the perturbation parameter (similar to that used in the Möller-Plesset perturbation method). However, CASPT2 has developed into a well-established method in treating molecules where CASSCF\textsuperscript{71} calculations are possible.

The electronic wavefunction used in the MRCI\textsuperscript{71,88} method implemented in the Molpro\textsuperscript{89} program is composed of the first order corrected wavefunction in Eq. 2.50 and the zeroth-order wavefunction, which is the CASSCF/reference wavefunction.

\begin{equation}
\Psi_{\text{Total}} = \Psi_{\text{REF}} + \Psi_{\text{MRCI}}
\end{equation}

where $\Psi_{\text{REF}}$ is from Eq. (2.43). The first order corrected wavefunction consists of the internal $\psi_I$, singly external $\psi_S^a$, and doubly $\psi_P^{ab}$ external configurations.

\begin{equation}
\Psi_{\text{MRCI}} = \sum_I c^I \psi_I^I + \sum_S \sum_a C^S_a \psi_S^a + \sum_P \sum_{ab} C^P_{ab} \psi_P^{ab}
\end{equation}

In the first term, the internal configurations are referred to as the valence orbitals, in which the reference wavefunction (CASSCF) is a subset of these configurations. The $a,b$ are the external orbitals not occupied in the reference wavefunction (CASSCF), $S$ and $P$ are the internal $N-1$ and $N-2$ electron hole states. According to externally contracted scheme developed by Siegbahn\textsuperscript{90}, the single and double external configurations are contracted as:
\[ \psi_S = \sum_a \alpha^S_a \psi^a_S \]  
(2.52)

\[ \psi_P = \sum_{ab} \alpha^P_{ab} \psi^{ab}_P \]  
(2.53)

A major disadvantage of this contraction scheme is that the contraction coefficient \((\alpha)\) may be zero because of Brillouin’s theorem,\(^{72}\) leading to errors calculating the energy of the molecule. An alternative scheme is to apply pair excitation operators to the reference wavefunction as a whole, which generates linear combinations of the doubly external configurations and therefore are internally contracted. The single and internal configurations are uncontracted in order to simplified the orthogonalization process\(^{76}\). In Molpro,\(^{89}\) the calculations are done by using the same active space mentioned above for the four methanol structures, since MRCI\(^{88}\) uses the CASSCF\(^{71,80,81}\) as a reference wavefunction. The result is recorded and compared to the results from CASPT2\(^{71}\) calculation.

2.3.3 Basis set Effects

The above methods indicate the various procedures in solving the Schrödinger’s equation (Eq. 2.29); however, the basis set functions\(^{70,76,91,92}\) serves as a mathematical description of the atomic orbitals of the constituent atoms. These basis set functions\(^{70,76,91,92}\), \(\phi\) are taken as linear combinations to give the molecular orbital, \(\chi\) for each \(\alpha\) and \(\beta\) spin orbital. The molecular orbitals are then substituted into the various methods mentioned above to obtain the electronic energy

\[ \chi^{\alpha}_i = \sum_{\mu} N c^{\alpha}_{\mu} \phi_{\mu} \]  
(2.54)

\[ \chi^{\beta}_i = \sum_{\mu} N c^{\beta}_{\mu} \phi_{\mu}, \]  
(2.55)

where \(N\) represents the nuclear-centered basis functions, \(\mu = 1,2, \ldots, N\) and \(c^{\alpha,\beta}_{\mu}\) is the expansion coefficients. The basis set functions are themselves, linear combination of Gaussian functions,
which forms the atomic orbitals. The Gaussian functions in Cartesian coordinates are defined as

$$\chi_{kmn} = N x^k y^m z^n \exp(-\zeta r_b^2),$$

(2.56)

where $N$ is the normalization constant, $k,m,n$ are referred as nonnegative integers that add up to the angular momentum of the orbital quantum number $L=k+m+n=0$ for $s$ orbital, 1 for $p$ orbital… $\zeta$ is the orbital exponent, $x_b, y_b, z_b$ are cartesian coordinates with the orgin at nucleus b, and $r_b$ is the distance from the origin b. In Molpro package either spherical or Cartesian coordinates are used, whereas in the Gaussian 03 the basis set functions are in the Cartesian coordinates. To maintain consistency between the two packages, the results are calculated using Cartesian coordinates. Gaussian functions are used because they are efficient in calculating one (the first term in first bracket and first term in second bracket in Eq. 2.7) and two electron properties (the last term in Eq. 2.7) of a molecule. However, its drawback at small values of $r_b$ where the origin is at the nucleus b, it does not give the cusp shape, therefore the atomic orbitals are not accurately depicted. Using several more linear combinations of Gaussian functions can alleviate this problem, particularly the core orbitals. Even though, increasing the amount of Gaussian functions will effect the computational time, nevertheless employing a contraction scheme will greatly reduce the computational cost and not affect the accuracy of the calculation.

The contracted basis set function is defined as

$$\phi = N \sum_i\chi_i t_i,$$

(2.57)

where $N$ is normalization constant, $\chi_i$ is the primitive functions (uncontracted basis set functions) and $t_i$ are a set of fixed contraction coefficients. Even though using the above contraction scheme will solve the problem of obtaining the accurate shape of the core orbitals, additional type of functions in the valence orbitals are nonetheless needed to account for the anisotropic and polar properties of molecules.
In the case of anisotropic properties\textsuperscript{70} adding more single sets of p-and/or d-type functions will allow more flexibility of the size of the basis functions. This is used to accommodate for the differences in the valence orbitals from one molecule to the next. For example\textsuperscript{70}, the acetylene molecule is oriented along the x-axis, to adequately describe the $\sigma$ bond on the carbon; additional $p_x$ functions are used to adjust the radial components to produce a highly contracted function. The reason for the highly contracted function of the $\sigma$ bond in acetylene is that there must be space to accommodate the $2\pi$ bonds together with the $\sigma$ bond to form the triple bond. Whereas, the methane and ethane molecule, additional functions are not needed since they are all single bonds and no allowance is needed for the orientation of the $\sigma$ bond\textsuperscript{70}.

In polar molecules\textsuperscript{70}, the charges of the electrons are displaced non-uniformly away from the atomic centers. Therefore, inclusion of higher angular momentum quantum number functions (d-type functions on heavy atoms and p-type functions on hydrogen) is used to displace the center of the basis functions. For example\textsuperscript{70}, mixing $p_x$-type functions into the s-function of a hydrogen atom in a polar molecule for instance water, will shift the center of the basis function along the x-axis and away from the hydrogen nucleus\textsuperscript{70}. Another type of function is diffuse functions. These functions are usually applied to excited molecules, anions and molecules with diffuse lone pairs or to anti-bonding orbitals particularly when the electronic density is more spread out. The diffuse functions consist of a mixture of s and p-type Gaussian functions to account for the significant electronic density that is further away from the centers. The effect of added diffuse functions is known to yield accurate results in calculating electron affinities, proton affinities, inversion barriers and internal rotors\textsuperscript{70}.

The different combinations of Gaussian functions comprise a basis set\textsuperscript{70,91,92}. The basis set\textsuperscript{70,91,92} depending on the molecule can contain a combination of polarization, contraction and diffuse functions. In this calculation, the basis set\textsuperscript{70,91,92} employed for the four structures are a combination of polarization and diffuse functions to accurately depict the atomic orbitals of the
dissociation of hydrogen bonds from the methanol four structures. The following nomenclature of
the basis set used in this calculations are:

6-311+G(2d,p). This basis set also called valence triple zeta + polarization plus diffuse basis set
is usually used in correlated functions and it has 78 contracted Gaussian basis functions. The
contraction scheme is (12s,6p,2d/[5s,4p,2d], where the first set is the primitive functions
(12s,6p,2d) correspond to an additional of six Gaussian type functions (GTFs) to each inner-shell
atomic orbital of carbon and oxygen and three additional GTF to each valence orbital of the
carbon and oxygen atoms. The 2d represents the set of two polarization functions on both carbon
and oxygen. The second set [5s,4p,2d] represents the contraction Gaussian type functions (CGTF)
determine by the excited states . The hydrogen atom contraction scheme is (6s,2p)/[4s,2p]
where the first set correspond to additional of six GTF for inner-shell and two polarization
functions on the hydrogen . The + sign indicates diffuse functions on all atoms. The (2d,p)
represents another set of polarization functions with the two 5-component d functions on the
oxygen and carbon atoms with $\alpha=1.252$ and 0.313 for the carbon and $\alpha=2.584$ and 0.646 for the
oxygen. The hydrogen $\alpha=0.75$ and 1.50 for p-type in the Gaussian 03 package.63

6-311+G(3df,2p). This basis set is similar to the one above with a total of 114 contracted
Gaussian basis functions with the exception of three 5-component d functions on the oxygen and
carbon atoms with $\alpha=0.5165,0.626,2.504$ for the carbon atom, and $\alpha=0.323,1.292$, and 5.168 for the
oxygen atom. The f function $\alpha=0.80$ for carbon and 1.40 for oxygen. The two p functions $\alpha$
on the hydrogen atoms are 1.50 and 0.375 in the Gaussian 03 package.63

cc-pVDZ, cc-pVTZ, aug-cc-pVDZ, aug-cc-pVTZ. These basis sets developed by Dunning and
coworkers are designed for post-HF methods that include electron correlation such as coupled
cluster and configuration interaction methods (See Appendix F for exponents). The first two basis
sets stand for correlation consistent polarized valence double zeta and correlation consistent
polarized valence triple zeta set. The correlation consistent basis sets consist of groups of GTF
functions that give the similar amount of correlation energy. In the \textbf{cc-pVDZ}, there is 48 contracted basis functions. For first row atoms (carbon and oxygen in this calculation), the basis set contraction scheme is $(9s,4p,1d)/[3s,2p,1d]$\textsuperscript{94}. The $(1s,1p)$ within the $[3s,2p,1d]$ contracted set lowers the correlation energy as the same amount as the $(1d)$ set. The other functions $(2s1p)$ lower the correlation energy at smaller amounts\textsuperscript{95}. The hydrogen molecule the contraction scheme is $(4s,1p)/[2s,1p]$. Whereas, \textbf{cc-pVTZ}, there is 116 contracted basis functions. For first row atoms (carbon and oxygen in this calculation), the contraction scheme is $(10s,5p,2d,1f)/[4s,3p,2d,1f]$, in which the $(2s,2p), (2d)$ within the $[4s,3p,2d,1f]$ basis set lowers the correlation energy as the same amount as the $(1f)$ set. The other functions $(1s1p)$ lower the correlation energy at smaller amounts\textsuperscript{94,95}. The hydrogen atom contraction scheme is $(5s,2p,1d)/[3s,2p,1d]$\textsuperscript{94}. The \textbf{aug-cc-VDZ} and \textbf{aug-ccVTZ} includes augmenting sets with contraction scheme for the first row elements (carbon and oxygen) are $(10s,5p,2d)/[4s,3p,2d]$ and $(11s,6p,3d,2f)/[5s,4p,3d,2f]$ and hydrogen is $(5s,2p)/[3s,2p]$ and $(6s,3p,2d)/[4s,3p,2d]$ respectively, which are additional diffuse non-polarization functions on the hydrogen bonding species\textsuperscript{76,94}. There are 82 contracted basis functions for the \textbf{aug-cc-VDZ}, whereas there are 184 basis functions for \textbf{aug-ccVTZ}.

2.4 Discussion of Results

In the following section, the results of the MP2 level calculations are discussed for methanol. The subsequent sections, the results of the advanced \textit{ab initio} calculations for methanol and other molecules, ethane and hydrogen peroxide is recorded and discussed.

2.4.1 The Impact of the Potentially Reactive Pathway

\textit{Ab initio} calculations of a reduced dimensional potential energy surface of methanol, produced at the MP2 level is shown in Fig 2.8a. The coordinates of this two dimensional surface are the OH bond length ($r_1$) and the anti CH bond length ($r_2$). These two coordinates were varied in 0.1 Å intervals from 0.6 - 1.8 Å for each point on the surface, the two coordinates, $r_1$ and $r_2$ kept fixed while all the other 10 coordinates were optimized. These are called partially optimized
calculations (POPT). The 2-D potential energy surface (Fig 2.8) results are similar to those of Quack and Willeke\textsuperscript{54} (Fig. 2.6). The onset of the product valley leading to CH$_2$O + 2H• lowers the potential energy when both the OH bond ($r_1$) and the anti CH bond ($r_2$) are extended (upper right corner of Fig. 2.8a).

The impact of the product valley is most easily appreciated in a plot of the non-additive part of the surface (Fig. 2.8b). The additive part is defined as

$$V_{\text{additive}}(r_1, r_2) = V(r_1; r_2_{\text{equil}}) + V(r_2; r_1_{\text{equil}}) - V_{\text{equil}}$$

(2.58)

The $V(r_1; r_2_{\text{equil}})$ term is the potential as $r_2$ is varied and $r_1$ is held fixed at the equilibrium anti CH bond length. The $V(r_2; r_1_{\text{equil}})$ term is the potential as $r_2$ is varied and $r_1$ is held fixed at the equilibrium OH bond length. The $V_{\text{equil}}$ term is the potential energy at the equilibrium bond lengths of both the OH and anti CH bond. The non-additive part ($V_{\text{non-additive}}$) is obtained by subtraction of the additive part from the calculated surface Fig 2.8a,

$$V_{\text{non-additive}} = V(r_1, r_2) - V_{\text{additive}}$$

(2.59)

The non-additive part becomes large and negative (upper right hand corner of Fig. 2.8b) when both the OH bond and the anti CH bond are extended.

The potential energy surface reveals the linkage of the formadehyde dissociation channel in Eq. 2.4 to the coupling between the torsional motion and the small amplitude vibrations in the following ways:

1) The changes in the partially optimized geometries as the OH and anti CH bonds are extended show the onset of the formaldehyde channel and give insight into the coupling of these degrees of freedom to other vibrational modes.

2) An approximate expression for the coupling of the anti CH and OH coordinates is obtained by fitting the non-additive potential energy surface.
Fig 2.8 Two dimensional potential energy surface MP2-6-311+G(2d,p)

a) The energy surface calculation of the $r_{\text{OH}}$ ($r_1$) and $r_{\text{CH}}$ ($r_2$) coordinates
b) The non-additive part of the energy surface a)

i), ii), iii), and iv) indicate four points on the potential energy surface, where i) is the equilibrium geometry, ii) has $r_1$ extended by 0.7 Å, iii) has the $r_2$ extended by 0.7 Å and iv) has the both $r_1$ and $r_2$ extended by 0.7 Å.

The arrow indicates the direction toward the formaldehyde reactive channel.
3) The torsional barrier heights found for the partially optimized geometry structures indicate the coupling between the torsional motion and the OH bond extension.

The geometric structures of the four reference points (Fig 2.8) on the potential energy surface are shown in Fig 2.9. The $r_{CO}$ bond length and $\theta_{OCH}$ angle are the main focus because the $r_{CO}$ bond length indicates the percentage of partial double bond character according to Pauling rules (Eq. 2.60).

$$r = r_{\text{equil}} - 0.26 \ln n$$

(2.60)

where, $r$ is the bond length, $r_{\text{equil}}$ is the equilibrium bond length, and $n$ is bond order. Second, the $\theta_{OCH}$ angle is related to the approach to the planar geometry of formaldehyde, where $\theta_{OCH}$ becomes 121.9°. The extension of the $r_1$ by 0.7 Å (structure (ii)) induces ~0.005 Å decrease of the $r_{CO}$ bond length, where according to Eq. 2.60 reflects an increase of partial double bond order of 0.5% and the $\theta_{OCH}$ angle widened by about 1° towards the formaldehyde planar geometry. These slight changes of the $r_{CO}$ and $\theta_{OCH}$ show that for the $r_1$ bond extended by 0.7 Å, the molecule progresses slightly towards the potentially reactive channel. In the case of extension of the $r_2$ bond, the $r_{CO}$ bond length is shortened from 1.4280 Å to 1.3889 Å, which produces ~4% of partial double bond character (Eq. 2.60), meanwhile, the $\theta_{OCH}$ angle changes by 3.4 ° towards the planar geometry of formaldehyde. The effects of extension of the $r_2$ bond length are greater than extension of $r_1$ because the lone pairs on the oxygen bond to the carbon when the methyl hydrogen is abstracted, whereas when $r_1$ is extended this is not chemically possible. However, when both bonds are broken, the $r_{CO}$ bond length is further reduced to 1.3562 Å, with a partial double bond character of 6.4% and the $\theta_{OCH}$ goes about halfway toward the planar geometry limit of formadehyde. These dramatic changes indicate that when both the $r_1$ and $r_2$ bonds are extended, large changes occur in the $r_{CO}$ bond length and $\theta_{OCH}$ angle. Therefore the OH and the anti CH
Fig 2.9. Partially optimized geometries of four points reference on the potential energy surface using \textit{MP2-6-311+G(2d,p)}. The coordinates highlighted in bold face with asteriks are kept fixed.
bonds are coupled. The shortening of $r_{\text{CO}}$, with increased double-bond character indicates that the torsional barrier height is coupled to the OH bond.

The coupling between the \textit{anti} CH bond and the OH bond is revealed by an approximate fit of the non-additive part of the 2-D potential energy surface. The fitted expression is given by a fourth order polynomial

$$V_{\text{non-additive}}(r_1, r_2) = C_{11} r_1 r_2 + C_{21} r_1^2 r_2 + C_{12} r_1 r_2^2 + C_{22} r_1^2 r_2^2 + C_{13} r_1^3 r_2 + C_{31} r_1^3 r_2.$$  \hspace{1cm} (2.61)

The $C_{ij}$ are the coefficients that give a measure of the coupling between the two coordinates $r_1$ and $r_2$ and the power indices are the coupling order of $r_1$ and $r_2$. In Quack and Willeke’s work, the matrix element coupling $5\nu_1$ with $4\nu_1+\nu_2$ in CHD$_2$OH is obtained from the effective Hamiltonian

$$\hat{H}_{5,0;4,1} = C_{31} \frac{3}{2} \left( \frac{5\nu_1}{2} \right)^{1/2} \left( \frac{\nu_2 + 1}{2} \right)^{1/2} + C_{13} \frac{3}{2} \left( \frac{\nu_2 + 1}{2} \right)^{1/2} \left( \frac{4\nu_1}{2} \right)^{1/2}.$$  \hspace{1cm} (2.62)

for coupling between the $5\nu_1$ and $4\nu_1+\nu_2$ vibrational states, $\nu_1=5$ and $\nu_2=0$. Eq. 2.62 then becomes

$$W = \hat{H}_{5,0;4,1} = 8.38 \times C_{31} + 1.677 \times C_{13}.$$  \hspace{1cm} (2.63)

In their work, the $C_{31}$ and $C_{13}$ values are in dimensionless coordinates 3.70 and -1.79 cm$^{-1}$ respectively as obtained from a fourth order polynomial fit of the CHD$_2$OH potential energy surface. The values were inserted into Eq. 2.63, which gives a matrix element of 34.0 cm$^{-1}$. This value is 30% higher than experimental coupling matrix element for CH$_3$OH in section 2.1. In our calculation, the $C_{31}$ and $C_{13}$ values are -986.6 and -2952 cm$^{-1}$ (Appendix H), where the coupling element is converted from dimensionless units to angstroms to give the scaling factor of 0.00430 Å for the $r_1^3 r_2$ term and 0.005 Å for the $r_2^3 r_1$ term in Eq. 2.61. Inserting these two scaling factors and the coupling coefficients ($C_{ij}$) into Eq. 2.63 the coupling matrix element is -19.581 cm$^{-1}$. The coupling matrix element is qualitative in agreement with Quack and Willekes calculation, and with the experimental value (23.5 cm$^{-1}$). The present 2-D potential energy surface is partially
optimized but the interactions from the gauche CH stretches are not taken into account, whereas Quack and Willeke’s calculation, the potential energy surface is a 2-D cut from a 5-D potential energy surface which includes these interactions.

The torsional barrier heights of the four reference points on the potential energy surface are obtained by subtracting the global minimum and maximum energy values calculated at MP2-6-311+G(2d,p). Further analysis of the torsional barrier potential (Eq. 2.63) is obtained by calculated data points fitted to the Fourier series in the torsional angles (0° to 180° torsional angles in 10° intervals).

\[ V(\gamma) = \sum_{n=1}^{6} \frac{V_n}{2}(1 - \cos n\gamma) \]  

(2.63)

Here V is the torsional potential, \( \gamma \) is the torsional angle, and \( V_n \) are the potential constants. The results are tabulated in table 2 along with the torsional barrier height.

When the OH bond (structure (ii)) is extended by 0.7 Å, the barrier height increases ~ 2.6 times the ground torsional potential. This is in agreement with experimental observation in section 2.2 which indicates that for 6 quanta of OH excitation the torsional barrier height increases ~ 2 times the ground torsional potential.

In the case of stretching the anti CH bond (structure (iii)) by 0.7 Å, the barrier height increased 5 times the equilibrium structure. The torsional potential minimum changes from the anti-staggered position to the nearly gauche position when the anti CH bond is extended. The highest torsional barrier found when one CH bond is extended is consistent with the double bond character (3.4%). However, the \( V_3 \) term the torsional barrier is comparable to the equilibrium torsional barrier height.

In structure (iv), when both the OH and anti CH bond are extended by 0.7 Å, the barrier height increases to 7 times the equilibrium torsional barrier height. This barrier height increase is reflected in the changes in the geometry, where the double partial bond character increases to
Table 2. Torsional Barrier heights of Four reference points on potential energy surface

<table>
<thead>
<tr>
<th>Fourier Terms</th>
<th>Energy/cm(^{-1})</th>
<th>Energy/cm(^{-1})</th>
<th>Energy/cm(^{-1})</th>
<th>Energy/cm(^{-1})</th>
<th>Four Terms/cm(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>V(_0)</td>
<td>741.50</td>
<td>1975.70</td>
<td>-1402.30</td>
<td>3327.40</td>
<td>---------</td>
</tr>
<tr>
<td>V(_1)</td>
<td>-8.47</td>
<td>-30.87</td>
<td>1070.10</td>
<td>-424.16</td>
<td>---------</td>
</tr>
<tr>
<td>V(_2)</td>
<td>-7.12</td>
<td>-41.00</td>
<td>-1510.10</td>
<td>-1302.80</td>
<td>---------</td>
</tr>
<tr>
<td>V(_3)</td>
<td>368.10</td>
<td>984.73</td>
<td>350.90</td>
<td>1244.00</td>
<td>373.5421</td>
</tr>
<tr>
<td>V(_4)</td>
<td>9.43</td>
<td>43.67</td>
<td>-29.94</td>
<td>9.96</td>
<td>---------</td>
</tr>
<tr>
<td>V(_5)</td>
<td>5.64</td>
<td>27.85</td>
<td>-17.66</td>
<td>2.75</td>
<td>---------</td>
</tr>
<tr>
<td>V(_6)</td>
<td>-3.48</td>
<td>-21.25</td>
<td>-4.70</td>
<td>-31.16</td>
<td>-0.8</td>
</tr>
<tr>
<td>Barrier height</td>
<td>371.00</td>
<td>986.00</td>
<td>2025.00</td>
<td>2441.00</td>
<td>---------</td>
</tr>
<tr>
<td>Global Minimum</td>
<td>0°</td>
<td>0°</td>
<td>70°</td>
<td>70°</td>
<td></td>
</tr>
<tr>
<td>Global Maximum</td>
<td>180°</td>
<td>180°</td>
<td>180°</td>
<td>180°</td>
<td></td>
</tr>
<tr>
<td>Partial double bond character (%)</td>
<td>----</td>
<td>0.5</td>
<td>3.4</td>
<td>6.4</td>
<td></td>
</tr>
</tbody>
</table>

a- Reference \(^9\)

Reflected in the changes in the geometry, where the double partial bond character increases to 6.4%. This is also observed with the V\(_3\) term of structure (iv), where it increases 4× the equilibrium V\(_3\) term, even though the fitting potential did not account for the changes in the global minimum. Therefore, the V\(_3\) and the barrier height of structure (iv) clearly indicates that the torsional barrier height accounts for the coupling between the torsional motion and other small amplitude vibrations.

Examination of ethylene can give insight into the impact of double bond character on the torsional potential. Clearly in ethylene, the double bond character between the C=C is 100%.

When the C=C bond is twisted, the internal rotation barrier\(^{97}\) height is 20,920 cm\(^{-1}\). This twisting of the C=C bond raises the energy and reduces it to a single bond character\(^{98}\) at the top of torsional barrier. Therefore the torsional barrier height is comparable to the energy of a π bond.

When both anti CH bond and OH bond are extended, the energy of the π bond at 6.4% partial double bond character is approximately 1339 cm\(^{-1}\). This value is comparative to the V\(_3\) term, but approximately 2× smaller than the barrier height in Table 3. This further corroborate that the torsional barrier height is correlated with the double bond character in the C=O bond in methanol.
The results obtained at the MP2-6-311+G (2d,p) level show that the dissociative formaldehyde channel is linked to the coupling between the large amplitude torsional motion and the other small amplitude vibrations. Evidence to support the validity of the MP2 calculations comes from previous calculations at this level, which accurately calculate the 12 harmonic vibration frequencies, particularly the torsional barrier height of methanol. However, to test the findings of the MP2 results, the depth of the product valley was calculated with advanced \textit{ab initio} levels out at the following four partially optimized geometries (four reference points on potential energy surface Fig 2.8):

i. The global equilibrium structure of methanol.

ii. Methanol with the O-H bond extended by 0.7 Å and the anti CH bond constrained to its equilibrium value=0.9647 Å

iii. Methanol with the \textit{anti} CH bond extended by 0.7 Å and the OH bond constrained to its equilibrium value=1.0929 Å

iv. Methanol with both the \textit{anti} CH bond and OH bond extended by 0.7 Å.

\[ E_{\text{Depth}} = E_{(iv)} + E_{(i)} - E_{(ii)} - E_{(iii)} \] (2.64)

The depth of the product valley of the partially reacted geometry (iv) is then estimated as

\[ E_{\text{Depth}} = E_{(iv)} + E_{(i)} - E_{(ii)} - E_{(iii)} \] (2.64)
The $E_{\text{Depth}}$ is calculated at the MP2-6-311+G(2d,p) level and at higher basis set of (3df,2p) to include more Gaussian basis functions is recorded in Table 3. This value will be compared to the advanced ab initio calculations in section 2.4.2.

Table 3. Calculations of Depth of Valley using Möller-Plesset Perturbation theory

<table>
<thead>
<tr>
<th></th>
<th>MP2-6-311+G(2D,P)</th>
<th>MP2-6-311+G(3DF,2P)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>EQUIL</strong></td>
<td>-115.5102284</td>
<td>-115.5586527</td>
</tr>
<tr>
<td><strong>R-OH a</strong></td>
<td>-115.3830235</td>
<td>-115.4297635</td>
</tr>
<tr>
<td><strong>R-CH b</strong></td>
<td>-115.4075648</td>
<td>-115.4556549</td>
</tr>
<tr>
<td><strong>BOTH c</strong></td>
<td>-115.2879128</td>
<td>-115.334916</td>
</tr>
</tbody>
</table>

<p>| | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>EQUIL</strong></td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td><strong>R-OH a</strong></td>
<td>27921.47555</td>
<td>28291.1794</td>
</tr>
<tr>
<td><strong>R-CH b</strong></td>
<td>22534.6602</td>
<td>22608.0171</td>
</tr>
<tr>
<td><strong>BOTH c</strong></td>
<td>48798.2742</td>
<td>49110.20565</td>
</tr>
<tr>
<td><strong>DEPTH OF VALLEY</strong></td>
<td>-1657.86155</td>
<td>-1788.99085</td>
</tr>
</tbody>
</table>

*a-OH bond is extended at 0.7Å  
b—the anti CH bond is extended at 0.7 Å  
c—both the OH bond and the anti CH bond is extended at 0.7 Å  
The first four structures is in Hartree units, the last four structures is in cm$^{-1}$

2.4.2 Calculations of Advanced Dynamic Electronic Correlation Effects

The results of the depth of valley calculated in the coupled cluster theory are recorded in Table 4. The results in Table 4 indicate the same trend as in the MP level but the depth of valley decreases to ~14% in the coupled cluster theory. The higher value of $E_{\text{Depth}}$ in the MP2 level is attributed to the overestimation of the correlation effects in Möller-Plesset perturbation theory, since the energy values tend to be much higher than the true value (Eq. 2.10).

A comparison between the CCSD and the CCSD (T) within the same correlation consistent basis set, the depth of valley decrease ~15%-19%. The inclusion of the corrected triplet excited states (Eq. 2.38) to the calculation of the four methanol structures lowers the correlation energy, therefore affecting the depth of valley. The triplet excited states (Eq. 2.38) are known to be lower in energy than the singlet excited states because Hartree-Fock theory, which is the reference wavefunction takes into account the correlation effects of electrons with parallel
Table 4. Calculations of Depth of Valley using Coupled Cluster Theory

<table>
<thead>
<tr>
<th>Table 4.</th>
<th>CCSD-cc-pVDZ</th>
<th>CCSD(T)-cc-pVDZ</th>
<th>CCSD-cc-pVTZ</th>
<th>CCSD(T)-cc-pVTZ</th>
</tr>
</thead>
<tbody>
<tr>
<td>EQUIL</td>
<td>-115.4174484</td>
<td>-115.4253655</td>
<td>-115.5657312</td>
<td>-115.5807715</td>
</tr>
<tr>
<td>R-OH a</td>
<td>-115.29616</td>
<td>-115.3092117</td>
<td>-115.4380944</td>
<td>-115.4592555</td>
</tr>
<tr>
<td>R-CH b</td>
<td>-115.3214266</td>
<td>-115.3319596</td>
<td>-115.4677812</td>
<td>-115.4857673</td>
</tr>
<tr>
<td>BOTH c</td>
<td>-115.2096841</td>
<td>-115.2275522</td>
<td>-115.3495482</td>
<td>-115.3753593</td>
</tr>
<tr>
<td>EQUIL</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>R-OH a</td>
<td>26622.8038</td>
<td>25495.7591</td>
<td>28016.2776</td>
<td>2667.262</td>
</tr>
<tr>
<td>R-CH b</td>
<td>21076.7851</td>
<td>20502.5905</td>
<td>21500.025</td>
<td>20853.4219</td>
</tr>
<tr>
<td>BOTH c</td>
<td>45604.2638</td>
<td>43420.01935</td>
<td>47452.1685</td>
<td>45087.9779</td>
</tr>
<tr>
<td>DEPTH OF</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>VALLEY</td>
<td>-2095.32505</td>
<td>-2578.3348</td>
<td>-2064.1341</td>
<td>-2438.206</td>
</tr>
</tbody>
</table>

a-OH bond is extended at 0.7 Å
b—the anti CH bond is extended at 0.7 Å
c- both the OH bond and the anti CH bond is extended at 0.7 Å
The first four structures is in Hartree units, the last four structures is in cm$^{-1}$

spin in the coulomb operator. This trend is observed in the last two columns where both methods differ by addition of triple excitation states in the calculation.

The 2-D dimensional potential energy surface diagram in Fig 2.11 was calculated using the CCSD-pVDZ level. The $C_{13}$ and $C_{31}$ terms obtained from fitting the non-additive part (Eq. 2.59) are -3288 cm$^{-1}$ and -4254 cm$^{-1}$ which gives rise to -21.8 cm$^{-1}$ coupling matrix element. The coupling matrix element increases by 10% in the coupled cluster calculation because the shape of the potential energy surface changes. These changes in the section where the extension of the $r_1$ bond by ~0.7 Å at small bond lengths of $r_2$ is smaller than in the MP2 level, therefore this effect lowers the $C_{31}$, hence small changes are revealed in the coupling matrix element.

In the coupled cluster with corrected triples, the $C_{13}$ and $C_{31}$ terms are -2634 cm$^{-1}$ and -2862 cm$^{-1}$ respectively (Appendix H1), where the coupling matrix element is -26.0 cm$^{-1}$. This value is qualitively in agreement with Quack and Willekes calculation where they fitted the CHD$_2$OH potential energy surface to sixth order polynomial. The reason for the increase of the coupling matrix element is attributed to the inclusion of the triples states.
Fig 2.11 Two dimensional potential energy surface $CCSD-cc-pVDZ$

a) The non-additive potential energy surface
b) The 2D potential energy surface of OH vs the CH bonds.
2.4.3 Calculations of Static and Dynamic Electronic Correlation Effects

The results of CASSCF, MRCI, and CASPT2 calculations using (10,10) active space, which represents 10 active electrons with 10 active orbitals with 8 inactive electrons, are recorded in Table No. 5, 6 and 7. The 10 orbitals are the valence in the equilibrium structure indicated by the first part in the equation below, while the other three structures consist of the second part in Eq (2.65)

\[(5\sigma,5\sigma^*) \rightarrow (2\sigma,2\sigma^*,\pi,\pi^*,2s,2s^*).\]  

(2.65)

The reason for the choice for (10,10) as the active space is based on Kuhn and others\(^63\) work on hydrogen peroxide, which indicates the hybridization of the bonding orbitals \(s\) and \(p\) changes when the OH bond is elongated. This trend is exemplified in methanol (Appendix C), where the natural bond analysis reveals that the hybridization of the \(s\) and \(p\) changes from small amounts when the \(anti\) CH bond or OH bond is elongated to larger amounts when both the OH and \(anti\) C-H bond are extended. The CSFs basis for the four structures using the Weyl-Robinson’s formula\(^80,83\) is 19404 for singlet state (see Appendix A). The active space consists of the starting orbitals in Appendix E. Table E.1.

In Table 5, the CASSCF energy calculations are \(~0.22-0.31\) a.m.u lower than either the MRCI or CASPT2 calculations. This indicates that the dynamics contribution in the static/dynamics method, MRCI and CASPT2 is \(~85-93\%\). Therefore, even though the MP2 is a low level method, nonetheless recovered 70\% of the dynamic correlation effects. Therefore the dynamic correlation effects are dominant in the formadehyde dissociation channel.

Nonetheless, the depth of valley computed at the CASSCF level follows the trend of the coupled cluster calculations, where the values are within \(~2000\) cm\(^{-1}\), even though the static correlation contributions are \(~8-15\%). The only difference in the CASSCF results is that the depth of valley based on \(cc-pVDZ\) basis set is \(~1400\) cm\(^{-1}\) lower than any of the CASSCF higher-
Table 5. Calculations of the Depth of Valley using CASSCF Theory

<table>
<thead>
<tr>
<th></th>
<th>CASSCF-cc-pVDZ</th>
<th>CASSCF-cc-pVTZ</th>
<th>CASSCF-aug-pVDZ</th>
<th>CASSCF-aug-pVTZ</th>
</tr>
</thead>
<tbody>
<tr>
<td>EQUIL</td>
<td>-115.1412472</td>
<td>-115.2086047</td>
<td>-115.1800918</td>
<td>-115.2127403</td>
</tr>
<tr>
<td>R-OH(^a)</td>
<td>-115.0285644</td>
<td>-115.0956068</td>
<td>-115.0678325</td>
<td>-115.0990678</td>
</tr>
<tr>
<td>R-CH(^b)</td>
<td>-115.0250877</td>
<td>-115.1215125</td>
<td>-115.0933593</td>
<td>-115.1259246</td>
</tr>
<tr>
<td>BOTH(^c)</td>
<td>-114.9280919</td>
<td>-115.0181529</td>
<td>-114.9906558</td>
<td>-115.0216826</td>
</tr>
<tr>
<td>EQUIL</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>R-OH(^a)</td>
<td>24733.86801</td>
<td>24803.0588</td>
<td>24640.92074</td>
<td>24951.12473</td>
</tr>
<tr>
<td>R-CH(^b)</td>
<td>25497.00064</td>
<td>19116.74866</td>
<td>19037.79034</td>
<td>19056.05493</td>
</tr>
<tr>
<td>BOTH(^c)</td>
<td>46787.59274</td>
<td>41804.17229</td>
<td>41581.20639</td>
<td>41937.17173</td>
</tr>
<tr>
<td>DEPTH OF VALLEY</td>
<td>-3443.28091</td>
<td>-2115.63516</td>
<td>-2097.50468</td>
<td>-2070.00792</td>
</tr>
</tbody>
</table>

\(a\)-OH bond is extended at 0.7Å
\(b\)—the anti CH bond is extended at 0.7 Å
\(c\)- both the OH bond and the anti CH bond is extended at 0.7 Å
The first four structures is in Hartree units, the last four structures is in cm\(^{-1}\)

Table 6. Calculations of the Depth of Valley of MRCI Theory

<table>
<thead>
<tr>
<th></th>
<th>MRCI-cc-pVDZ</th>
<th>MRCI-cc-pVTZ</th>
<th>MRCI-aug-pVDZ</th>
<th>MRCI-aug-pVTZ</th>
</tr>
</thead>
<tbody>
<tr>
<td>EQUIL</td>
<td>-115.396186</td>
<td>-115.5262527</td>
<td>-115.4396492</td>
<td>-115.5210898</td>
</tr>
<tr>
<td>R-OH(^a)</td>
<td>-115.2831614</td>
<td>-115.4058271</td>
<td>-115.3237045</td>
<td>-115.4088924</td>
</tr>
<tr>
<td>R-CH(^b)</td>
<td>-115.2535584</td>
<td>-115.4313403</td>
<td>-115.3503472</td>
<td>-115.4284445</td>
</tr>
<tr>
<td>BOTH(^c)</td>
<td>-115.2002733</td>
<td>-115.3216836</td>
<td>-115.2437368</td>
<td>-115.3222728</td>
</tr>
<tr>
<td>EQUIL</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>R-OH(^a)</td>
<td>24808.90189</td>
<td>26433.4192</td>
<td>25449.88141</td>
<td>24627.34027</td>
</tr>
<tr>
<td>R-CH(^b)</td>
<td>31306.74942</td>
<td>20833.28716</td>
<td>19601.79339</td>
<td>20335.54677</td>
</tr>
<tr>
<td>BOTH(^c)</td>
<td>43002.83546</td>
<td>44902.92623</td>
<td>43002.78277</td>
<td>43640.34028</td>
</tr>
<tr>
<td>DEPTH OF VALLEY</td>
<td>-13112.81586</td>
<td>-2363.78013</td>
<td>-2048.89202</td>
<td>-1322.54677</td>
</tr>
</tbody>
</table>

\(a\)-OH bond is extended at 0.7Å
\(b\)—the anti CH bond is extended at 0.7 Å
\(c\)- both the OH bond and the anti CH bond is extended at 0.7 Å
The first four structures is in Hartree units, the last four structures is in cm\(^{-1}\)
Table 7. Calculations of the Depth of Valley at CASPT2 Theory

<table>
<thead>
<tr>
<th></th>
<th>CASPT2-cc-pVDZ</th>
<th>CASPT2-cc-pVTZ</th>
<th>CASPT2-aug-pVDZ</th>
<th>CASPT-aug-pVTZ</th>
</tr>
</thead>
<tbody>
<tr>
<td>EQUIL</td>
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<td>-115.5188147</td>
<td>-115.4275246</td>
<td>-115.5198787</td>
</tr>
<tr>
<td>R-OH&lt;sup&gt;a&lt;/sup&gt;</td>
<td>-115.2726507</td>
<td>-115.400768</td>
<td>-115.3134295</td>
<td>-115.4086781</td>
</tr>
<tr>
<td>R-CH&lt;sup&gt;b&lt;/sup&gt;</td>
<td>-115.2512644</td>
<td>-115.4255677</td>
<td>-115.3395389</td>
<td>-115.4317756</td>
</tr>
<tr>
<td>BOTH&lt;sup&gt;c&lt;/sup&gt;</td>
<td>-115.196103</td>
<td>-115.3190924</td>
<td>-115.2360602</td>
<td>-115.3305052</td>
</tr>
</tbody>
</table>

|               | 0              | 0              | 0               | 0              |
| R-OH<sup>a</sup> | 24838.02735    | 25911.24406    | 25043.87664     | 24408.53828    |
| R-CH<sup>b</sup> | 29532.3202     | 20467.72089    | 19312.86554     | 19338.63923    |
| BOTH<sup>c</sup> | 41640.2453     | 43839.04265    | 42026.44897     | 41567.48983    |
| DEPTH OF VALLEY | -12730.10225   | -2539.92230    | -2330.29321     | -2179.68768    |

<sup>a</sup>-OH bond is extended at 0.7Å  
<sup>b</sup>-the anti CH bond is extended at 0.7 Å  
<sup>c</sup>-both the OH bond and the anti CH bond is extended at 0.7 Å  
The first four structures is in Hartree units, the last four structures is in cm<sup>-1</sup>

level basis set or the couple cluster calculations. The reason is that it needs additional polarized Gaussian functions to treat the static correlation effects.

The 2-D potential energy surface and non-additive part of the 2-D surface in the CASSCF level is recorded in the Appendix H. The C<sub>13</sub> and C<sub>31</sub> terms are -6538 cm<sup>-1</sup> and -2549 cm<sup>-1</sup> respectively, which gives a coupling matrix element of -41 cm<sup>-1</sup>. This value is ~40% higher than the coupled cluster and MP2 level calculations. The high value of the coupling matrix element in the CASSCF calculations is attributed to the static contributions, which affects the potential energy surface. The static contribution changes the onset of negativity of the non-additive part at ~1.1 Å in the r<sub>i</sub> coordinate instead of ~1.2-1.3 Å in the dynamic calculations, which increases the C<sub>13</sub> term, therefore increasing the coupling matrix element.
In Table 6, the MRCI calculations were first obtained by partially optimizing the four structures using the CASSCF method (reference wavefunction), then CASSCF energy is used to calculate the MRCI by single point calculations to minimize computation time and memory. In the results, the \textit{cc-pVDZ} basis set depth of valley is 9500 cm\(^{-1}\) lower than the CASSCF method, even though the dynamic contributions are within 90-95%. Therefore more Gaussian functions are needed to treat static correlation effects, which can adversely affect the calculated depth of valley in the MRCI calculations. However, the depth of valley calculations follows the trend of the coupled cluster and CASSCF calculations. The only difference is that the last column of Table 6, the depth of valley is \(~1000\) cm\(^{-1}\) below the \textit{CASPT2} level of the basis set \textit{aug-cc-pVTZ} basis set. The reason for the low level of the MRCI calculation is contributed from the fact that the \textit{CASPT2} structure is partially optimized, while the MRCI is a single point calculation.

In the \textit{CASPT2} level calculations shown in Table 7, the results are similar to the MRCI calculations with the exception of the high basis set. Therefore, using either the perturbation method in \textit{CASPT2} or the variational method in MRCI clearly shows that the short distance correlation effects are dominant in the potentially reactive channel. Therefore, the MP2 level with high basis set results are thus validated and can be used to illustrate the relationship between torsional-vibrational dynamics and a potentially reactive channel in methanol and other related molecules.

In summary, the results of the depth of valley and the reduced potential energy surface of methanol using the MP2 low level show that the coupling between the torsional motion and CH/OH stretches are a link to the formaldehyde potentially reactive channel. This link is reflected by the changes of the geometry when \textit{anti} CH and OH bond are extended. Second, the fitting of the non-additive part by a polynomial gives the coupling matrix element that is qualitively in agreement with experimental value\(^2\) and Quack and Willekes\(^54\) calculations. Therefore the formaldehyde dissociation channel is due to the coupling between the CH and OH stretches.
Finally, the torsional relationship of the four reference points on the potential surface reveals the coupling between the torsional motion and other small amplitude vibrations.

In the advanced \textit{ab initio} calculations, the coupled cluster calculations of the depth of valley and the reduced potential energy surface of methanol, the results are in qualitative agreement with the MP2 findings. The static/dynamics further corroborate the findings in both coupled cluster and MP2 levels and show that the corrections for the dynamics correlations are much larger than the static correlation effects. Therefore, the MP2 level calculations is used to show the relationship between the potentially reactive channel and coupling between the torsional and small-amplitude motions, which is applied to other molecules such as ethane and hydrogen peroxide.

2.4.4 Generalization to Other Molecules

To show that this trend of torsional-vibrational dynamics is observed in the bound region of a potentially reactive channel in other molecules such as ethane and hydrogen peroxide, the depth of valley is calculated at the MP2 level and compared to methanol.

Methanol is related to ethane and hydrogen peroxide in the following ways:

1) Methanol, ethane, and hydrogen peroxide all have large amplitude torsional motion. The torsional barrier height ranges from intermediate in the methanol and hydrogen peroxide of the \textit{trans} geometry case to the high barrier limit of ethane and the \textit{cis} geometry of hydrogen peroxide. The \textit{trans}-barrier of hydrogen peroxide\cite{100} is 361 cm$^{-1}$. The ethane molecule\cite{101} has a three-fold torsional barrier height around the C-C bond\cite{102} at 1008 cm$^{-1}$, while the \textit{cis}-barrier\cite{103} of hydrogen peroxide is 2460 cm$^{-1}$.

2) The three molecules have a similar structural motif indicated below:
where the X=X produces a partial double bond when a pair of \textit{anti} X-H bonds are extended. This is exemplified below where the potentially reactive channel for both molecules are given by

\[
\text{H}_2\text{O}_2 \rightarrow \text{O}=\text{O} + 2\text{H} \cdot \quad \Delta H^0 = 569 \text{ kJ/mol}
\]

\[
\text{C}_2\text{H}_6 \rightarrow \text{H}_2\text{C}=\text{CH}_2 + 2\text{H} \cdot \quad \Delta H^0 = 570 \text{ kJ/mol}
\]

The depth of valley results in Table 8 of the two molecules follow the trend of methanol,

Table 8. Calculations of Depth of Valley of ethane, methanol and hydrogen peroxide. \textit{MP2-6-311+G(2d,p)}

<table>
<thead>
<tr>
<th>Table 8</th>
<th>ETHANE</th>
<th>METHANOL</th>
<th>H$_2$O$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>\text{EQUIL}</td>
<td>-79.586304</td>
<td>-115.510228</td>
<td>-151.319177</td>
</tr>
<tr>
<td>R-\text{XH}^a</td>
<td>-79.486682</td>
<td>-115.383024</td>
<td>-151.201040</td>
</tr>
<tr>
<td>R-\text{XH}^b</td>
<td>-79.486681</td>
<td>-115.407565</td>
<td>-151.201040</td>
</tr>
<tr>
<td>\text{BOTH}^c</td>
<td>-79.393182</td>
<td>-115.287913</td>
<td>-151.094108</td>
</tr>
<tr>
<td>\text{EQUIL}</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.0000</td>
</tr>
<tr>
<td>R-\text{XH}^a</td>
<td>21867.0290</td>
<td>27921.4756</td>
<td>25931.0057</td>
</tr>
<tr>
<td>R-\text{XH}^b</td>
<td>21867.2924</td>
<td>22534.6602</td>
<td>25931.0057</td>
</tr>
<tr>
<td>\text{BOTH}^c</td>
<td>42390.1912</td>
<td>48798.2742</td>
<td>49402.5797</td>
</tr>
<tr>
<td>\text{DEPTH OF VALLEY}</td>
<td>-1344.1302</td>
<td>-1657.8616</td>
<td>-2459.4317</td>
</tr>
</tbody>
</table>

where X is either carbon or oxygen atom depending on the molecule
\textit{a}-\text{XH} bond is extended at 0.7Å
\textit{b}—\text{the anti XH bond is extended at 0.7 Å}
\textit{c}—both the \text{XH} bond and the \text{anti XH} bond is extended at 0.7 Å

The first four structures is in Hartree units, the last four structures is in cm$^{-1}$

where the non-additive part produces a negative value when both bonds are extended. This clearly indicates that one X-H bond is coupled to the \textit{anti} X-H across the X-X torsional bond.

Second, the torsional barrier heights calculated for the four reference points at \textit{MP2-6-311+G(2d,p)} (Tables 9 and 10) for hydrogen peroxide (trans barrier) and ethane results follow
Table 9 Torsional barrier heights of hydrogen peroxide for four reference geometries

<table>
<thead>
<tr>
<th>Calculated</th>
<th>Torsional Barriers</th>
<th>One O-H bond is extended by 0.7 Å</th>
<th>Both bonds are extended By 0.7 Å</th>
<th>Expta</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fourier Terms</td>
<td>Energy/cm⁻¹</td>
<td>Energy/cm⁻¹</td>
<td>Energy/cm⁻¹</td>
<td>Energy/cm⁻¹</td>
</tr>
<tr>
<td>V₀</td>
<td>5110.00</td>
<td>3440.00</td>
<td>4431.40</td>
<td>------</td>
</tr>
<tr>
<td>V₁</td>
<td>-2474.50</td>
<td>-1400.00</td>
<td>-1023.70</td>
<td>------</td>
</tr>
<tr>
<td>V₂</td>
<td>1384.00</td>
<td>2718.80</td>
<td>6025.00</td>
<td>------</td>
</tr>
<tr>
<td>V₃</td>
<td>-71.77</td>
<td>-290.66</td>
<td>-1077.30</td>
<td>------</td>
</tr>
<tr>
<td>V₄</td>
<td>-31.47</td>
<td>3.44</td>
<td>-189.59</td>
<td>------</td>
</tr>
<tr>
<td>V₅</td>
<td>-9.54</td>
<td>-42.21</td>
<td>-145.22</td>
<td>------</td>
</tr>
<tr>
<td>V₆</td>
<td>-2.04</td>
<td>12.82</td>
<td>105.41</td>
<td>------</td>
</tr>
<tr>
<td>cis Barrier height</td>
<td>2555.87</td>
<td>3570.83</td>
<td>7030.00</td>
<td>2460a</td>
</tr>
<tr>
<td>trans Barrier height</td>
<td>369</td>
<td>1850</td>
<td>4800a</td>
<td>361a</td>
</tr>
<tr>
<td>Minimum/cis and trans</td>
<td>120°</td>
<td>90°</td>
<td>90°</td>
<td>111.8°</td>
</tr>
<tr>
<td>Maximum</td>
<td>180°</td>
<td>180°</td>
<td>180°</td>
<td>180°</td>
</tr>
<tr>
<td>% of Partial O-O double bond character</td>
<td>0.00</td>
<td>4.55</td>
<td>15.69a</td>
<td></td>
</tr>
</tbody>
</table>

a-expressed in cm⁻¹ Reference 63

the trend of the torsional barrier heights of the four reference points in methanol. When both X-Y bonds are extended (iv) the torsional barrier height is more than 2x the torsional barrier when only onone X-H bond is extended ((ii) and (iii)). For instance, in the hydrogen peroxide case, the trans torsional barrier height increases to 5x the torsional barrier height equilibrium structure (i) when one of the OH bond is extended ((ii) and (iii)) and increases to 13x when both OH bonds are extended. Another example is in ethane where the torsional barrier height increases only slightly when the C-H bond is extended ((ii) and (iii)) to but increased by 2.3x the equilibrium structure (i) torsional barrier height when both CH bonds are extended. When both bonds are extended for ethane and hydrogen peroxide, partial double bond character is found and values are
Table 10. Torsional barrier heights of ethane four reference geometries

<table>
<thead>
<tr>
<th>Calculated</th>
<th>Equilibrium</th>
<th>One C-H bond is extended by 0.7 Å</th>
<th>Both bonds are extended by 0.7 Å</th>
<th>Expta</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fourier Terms</td>
<td>Energy/cm⁻¹</td>
<td>Energy/cm⁻¹</td>
<td>Energy/cm⁻¹</td>
<td>Fourier Terms/</td>
</tr>
<tr>
<td>V₀</td>
<td>2023.60</td>
<td>2133.40</td>
<td>4782.40</td>
<td>-----------</td>
</tr>
<tr>
<td>V₁</td>
<td>-1.02</td>
<td>-3.24</td>
<td>-1274.10</td>
<td>-----------</td>
</tr>
<tr>
<td>V₂</td>
<td>3.66</td>
<td>-17.40</td>
<td>831.93</td>
<td>-----------</td>
</tr>
<tr>
<td>V₃</td>
<td>1011.60</td>
<td>1072.80</td>
<td>1203.60</td>
<td>1010.0</td>
</tr>
<tr>
<td>V₄</td>
<td>-2.69</td>
<td>12.74</td>
<td>-21.51</td>
<td>-----------</td>
</tr>
<tr>
<td>V₅</td>
<td>0.92</td>
<td>9.19</td>
<td>90.39</td>
<td>-----------</td>
</tr>
<tr>
<td>V₆</td>
<td>28.63</td>
<td>31.32</td>
<td>31.18</td>
<td>10.0</td>
</tr>
<tr>
<td>Barrier height</td>
<td>1012.84</td>
<td>1066.00</td>
<td>2390.20</td>
<td>1008.0</td>
</tr>
<tr>
<td>Minimum</td>
<td>0°</td>
<td>0°</td>
<td>90°</td>
<td>0°</td>
</tr>
<tr>
<td>Maximum</td>
<td>180°</td>
<td>180°</td>
<td>180°</td>
<td>180°</td>
</tr>
<tr>
<td>% of Partial C-C double bond character a</td>
<td>0.00</td>
<td>1.00</td>
<td>6.43</td>
<td></td>
</tr>
</tbody>
</table>

a-expressed in cm⁻¹ Reference¹⁰¹-¹⁰⁴

given in tables 9 and 10. Therefore, the potentially reactive channels reveal the correlation between the torsional barrier height and the small-amplitude vibrations, similar to that found for methanol.

Even though the torsional behavior of ethane is similar to the behaviors of hydrogen peroxide and methanol; the torsional effects are larger in the hydrogen peroxide case. This observation is linked to the increase of the hyperconjugation energy of the three molecules in the same order ethane, methanol, and hydrogen peroxide as the increase of the depth of valley. In the ethane molecule, the hyperconjugation energy plays a major role in the origin of the torsional barrier. According to Goodman and Hongbin Gu et. al¹⁰⁵, they indicate that hyperconjugation energy, in which the $\sigma_{\text{CH}}$ donates to the $\sigma_{\text{CH}}^*$ increases due to the overlap between these two orbitals and gives rise to the torsional barrier of ethane molecule. Carpenters et. al¹⁰⁶,¹⁰⁷ attributed the hyperconjugation between $n_o$ and $\sigma_{\text{OH}}^*$ orbital as the origin of the torsional barrier in hydrogen peroxide and it is also observed in the methanol molecule between $n_o$ and $\sigma_{\text{CH}}^*$. 70
Therefore the hyperconjugation effects are linked to the coupling between the torsional motion and small-amplitude motion.

These three molecules, hydrogen peroxide, methanol and ethane differ in geometry structure and elemental composition, nevertheless all three molecules have a potentially reactive channel that gives rise to a torsion-vibrational coupling mechanism. The potentially reactive channel extends all the way into the bound region of the molecule, therefore indicating a relationship between the potentially reactive channel and IVR coupling mechanism.
3.1 Experimental Background of the coupling between the CH stretches (\(v_2\), \(v_9\) and \(v_3\)) and the Torsion motion

In methanol, two experiments have provided evidence of coupling between the torsional and the high frequency vibrations\(^2\)\(^4\)\(^106\)-\(^108\). The first experiment, the \(2v_1-5v_1\) OH stretch overtone structure, was detected by a single version infrared laser assisted photofragment spectroscopy technique (IRLAPS) described in chapter II. In Rizzo et al.\(^2\) findings, the \(5v_1\) spectrum consisted of a 50 cm\(^{-1}\) splitting between the bright state \(5v_1\) and \(4v_1+v_2\) dark state (\(v_2\) is asymmetric CH stretch vibration) (Fig 2.2)\(^2\), this implied that the OH stretch is coupled to the CH stretch vibrations. Further studies, on the \(5v_1\) spectrum on the deuterated methanol molecules, CH\(_2\)DOH, CHD\(_2\)OH, and CD\(_3\)OH substantiated these findings\(^2\). Later, Boyarkin \textit{et al.} investigated the OH stretch overtones \(2v_1\) and \(3v_1\) with torsional combinations, \(2v_1+v_1+2v_1\), \(2v_1+2v_1\), \(3v_1+v_1\), and \(3v_1+2v_1\) using the IRLAPS technique\(^4\). The experimental results indicated that for each quantum of OH stretch excitation presented in Chapter 2 (Fig 2.3), the torsional barrier (\(V_3\)) increases by 40.9\(\pm\)1.9 cm\(^{-1}\) and the torsional inertial constant (\(F\)) decreases by 0.89\(\pm\)0.02 cm\(^{-1}\). This is accounted for by the decrease of the torsional splitting from 9.1 cm\(^{-1}\) in the ground state to 1.6 cm\(^{-1}\).

Figure 3.1 Multiscale dynamics of the $5\nu_1$ OH overtone stretching mode with $4\nu_1 + 2\nu_2$. The diagram at the left is the spectrum of the $5\nu_1$ OH stretching mode with $4\nu_1 + 2\nu_2$ with the corresponding graph of the probability of the lifetime at the right of the diagram. The sequence of the graphs, a) The initial decay represents the fastest timescale of 100fs, b) the second graph is the tertiary timescale of $\sim$10ps c) the third probability is the secondary timescale of $\sim$1ps.
at $v_1=6$ in the OH stretch overtones of methanol\cite{1}. Experimental results indicated that there is a strong coupling between the torsional vibrations and the OH stretch.

Further examination of the OH overtone structure ($2v_1-8v_1$) using the double version IRLAPS technique discussed in Chapter II revealed a wide range of IVR timescales\cite{2} (Fig. 3.1). The three distinct timescales recorded in the OH overtone spectrum were: the fastest timescale (Fig 3.1a) indicated by the large splitting between the OH stretch and a combination with the asymmetric CH stretch ($5v_1 \leftrightarrow 4v_1+v_2$ and $6v_1 \leftrightarrow 5v_1+v_2$) corresponds to an initial decay of $P(t)$ of 100 fs and the first recurrence with a period of 700 fs represents oscillation between the two vibrations. Another fast timescale analogous to the OH stretch in combination with the asymmetric C-H stretch is the combination of the OH stretch overtone with the COH bend combination $7v_1 \leftrightarrow 6v_1+2v_6$ at 240 fs recurrence time. The second timescale (Fig 3.1c) corresponds to $\sim$1 ps estimated from the width of a group of unidentified dark states coupled one of the $5v_1$ with $4v_1+v_2$ mixed states (highlighted in Fig 3.1c). The tertiary timescale (Fig 3.1b) at $\sim$10 ps is located at the line widths of the individual features\cite{3,108}. The multiple timescales mentioned above are indicators of resonance low-order coupling terms from the torsional motion\cite{3,28,108}.

The second experimental results is a combination of two spectra (Fig. 3.2), one spectrum recorded from 2977 cm\textsuperscript{-1} to 3027 cm\textsuperscript{-1} from this group used direct absorption technique\cite{106} and another from NIST in the range of 2965 cm\textsuperscript{-1} to 3027 cm\textsuperscript{-1} used molecular beam technique\cite{107}. Assignments of both spectra yielded the following results for the three CH stretches ($v_9$ $v_2$ $v_3$). The two asymmetric CH stretches ($v_9$ and $v_2$), ground torsional tunneling splittings are inverted with the E level which is 3.26 cm\textsuperscript{-1} below the $A_1(G_6$ permutation group theory) level for $v_2$ and the E level is 5.48 cm\textsuperscript{-1} below the $A_2$ level in $v_9$ ($G_6$ permutation group theory). Whereas, the $v_3$ torsional tunneling splitting are considered normal according to the one dimensional Hamiltonian
Figure 3.2 Experimental results of the inversion property of the $\nu_9$, and $\nu_2$ asymmetric stretches, the $E$ below the $A$, $\nu_3$ is the symmetric stretch behaving normal with $A$ below $E^5$. This figure is taken from Ref. 5. Fig. 1 pg. 10796
which leads to the A level below the E level\textsuperscript{107}. The permutation inversion group theory is used in the methanol case instead of the C\textsubscript{s} (A\textsuperscript{'}, A\textsuperscript{`}) rigid point group because of the large amplitude motion, and tunneling between the three torsional minimum of the methanol molecule. Other experiments later confirmed that this inversion property is present in other vibrational bands such as: the $\nu_7$ CH$_3$ rocking mode\textsuperscript{39,109} and the $\nu_{11}$ out-of-plane CH$_3$\textsuperscript{30,110} rocking mode in methanol. Theoretical predictions of the inversion property in the following vibrational modes: $\nu_4$ and $\nu_{10}$ CH bend\textsuperscript{39,99}, which demonstrate that the inversion property is not an artifact but is observed in cases where torsional tunneling is present.

3.2 Theoretical Motivation of the coupling between the three CH stretches ($\nu_2$, $\nu_9$, $\nu_3$) and the Torsional motion

These experimental findings, particularly the inverted torsional structures have stimulated a variety of theoretical and computational approaches. The internal coordinate Hamiltonian of Wang and Perry\textsuperscript{5} invoked the lowest order coupling between the three C-H stretch fundamentals ($\nu_3$, $\nu_2$, $\nu_6$) and torsion. That model recognized that the stretching force constant of each CH bond is depends on the torsional angle, which interchanges the identities of the CH bonds from anti to gauche conformations. This is a consequence of the coupling between the CH stretches and torsional motion. This is depicted in the Newman projection of methanol\textsuperscript{5} (Fig. 3.3.) A C-H bond 1 is trans to the O-H 4 and therefore has a different stretching force constant from the gauche C-H bonds 2 and 3. The $\nu_2$ C-H stretch which has the greatest amplitude on the trans C-H is about 41.8\textsuperscript{cm}$^{-1}$ higher in frequency than the $\nu_9$ C-H stretch which by symmetry has no amplitude on the interchanging of the identities of trans to gauche as proceeds from a trans C-H. The $\nu_2$ and $\nu_9$ normal modes are both asymmetric C-H stretches and they are degenerate if the C-O-H bond was linear. The rapid torsional tunneling is responsible for the a$\Rightarrow$b$\Rightarrow$c. This fully coupled four-dimensional model was able to reproduce the torsional and vibrational splitting patterns of the CH fundamentals (Fig. 3.4.) Abouti Temsamani et al.\textsuperscript{111} extended the internal coordinate approach to
Fig. 3.3 Newman Projections of the three torsional minima of methanol\textsuperscript{5}.
This figure is taken from Ref. 5 Fig. 2 pg. 10796
include rotation-vibration-torsion coupling and the role of Coriolis coupling by examining the three CH$_3$ bending vibrations, ($\nu_4$ asymmetric bending, $\nu_5$ symmetric bending, and $\nu_{11}$ out-of-plane rocking). Hougen$^{112}$ showed that the inverted torsional splittings could be understood by the coupling between the one-dimensional torsional models to the small amplitude vibrations of A$_1$ or E symmetry in the G$_6$ molecular group$^{113}$.

Fehrensen et al.$^{39}$ implemented a reaction path Hamiltonian based on \textit{ab initio} data to adiabatically separate the reaction coordinate (large-amplitude torsional motion) from the other eleven small-amplitude vibrations. Like other authors,$^{56,114}$ they found that the adiabatic approach was successful in treating the torsional tunneling splitting of the OH overtones, but they were also able to account for the inverted torsional tunneling splitting. In the adiabatic approximation, the inverted torsional tunneling splittings of the CH stretches arise from the accumulation of a geometric phase of -1 by the torsional wavefunctions upon a $2\pi$ internal rotation. This approach provides a conceptual unity with the treatment of conical intersections in electronic spectroscopy and gives a general basis for predicting the occurrence of inverted torsional structure.

Others such as Miani \textit{et al.}$^{115}$ and Castillo-Chara and Silbert$^{116}$ have carried out full dimensional calculations of methanol vibrational level structure. Miani \textit{et al.}$^{115}$ used second order perturbation theory to obtain the fundamental frequencies. Castillo-Chara and Silbert$^{116}$ extended the \textit{ab initio} potential energy surface of Miani’s \textit{et al.}$^{115}$ to include full torsional symmetry and obtain the correct tunneling splittings. They incorporated Van Vleck perturbation theory to decouple the small-amplitude vibrations and then found the torsion-vibration eigenstates variationally. In a later paper, Sibert and Castillo-Chara$^{117}$ extended their approach with higher level \textit{ab initio} calculations and obtained better agreement with their experiment. By artificially varying the torsional mass, they obtained correlation diagrams in which avoided crossings revealed pronounced torsion-vibration mixing. Gruebele, Wolynes and coworkers$^{118}$ developed a local matrix theory used in calculating hydrogen peroxide and methanol flow rates and an
analytical expression for the degree of vibrational mixing. In their calculations, they have corroborated that multiple timescales mentioned above in the CH/OH stretch in methanol corresponded to a power law behavior.\textsuperscript{119}

The power law as discussed in Chapter I arises from the scaling behavior of the IVR coupling matrix elements\textsuperscript{119,120}, where, in relatively rigid molecules, anharmonic coupling matrix elements decrease by roughly one order of magnitude for each higher coupling order\textsuperscript{121}. Pearman and Gruebele\textsuperscript{121} found that the coupling to a large-amplitude torsional vibration scales more gently, decreasing in some cases only by a factor of 2 or 3 for each coupling order. Therefore, they concluded that the presence of a large amplitude motion especially when the torsional energies are comparable to the torsional barrier in methanol greatly increases the number of locally coupled states through the high-order coupling terms, thereby accelerating IVR.

3.3 Computational Methodology

The computational method of the 4-Dimensional model and the Adiabatic approximation are expressed in the following sections.

3.3.1 Four-Dimensional Model of the Three CH stretches ($\nu_3$, $\nu_9$, $\nu_2$) coupled to the Torsional motion.

The 4-Dimensional model Hamiltonian developed by Wang and Perry\textsuperscript{5} to treat the torsion plus the three CH stretches in methanol is an internal coordinate vibration-torsion Hamiltonian discuss in Chapter I. This Hamiltonian consists of the sum of the three independent CH stretches, the local-local coupling term, torsional potential and the torsional kinetic operator.

$$\hat{H}_{\text{vib-tors}} = \hat{H}_{\text{str}} + \hat{H}_{l-l} + V_{\text{pot}}(\gamma) + \hat{H}_{\text{tor}}$$  \hspace{1cm} (3.1)

The basis functions is the product of the harmonic oscillator on each local CH stretch $|\nu_j\rangle$ and a free internal basis $|m\rangle$ for the torsional motion:

$$|\nu_1\nu_2\nu_3\rangle = |\nu_1\rangle|\nu_2\rangle|\nu_3\rangle|m\rangle = |\nu_1\rangle|\nu_2\rangle|\nu_3\rangle(2\pi)^{-1/2}e^{-im\gamma}$$  \hspace{1cm} (3.2)
Fig. 3.4 Comparison between the 4-Dimensional model and Experimental Results
To address the three CH stretch fundamentals and the torsional states built on them, we apply the restriction $\nu_1+\nu_2+\nu_3=1$ which gives only 3 vibrational basis states, $\{|\nu_1\nu_2\nu_3\rangle\} = \{100\}, \{010\}, \{001\}$. The local C-H stretches are expanded in a Fourier series, retaining the two lowest terms.

$$\hat{H}_{str} = \hat{H}_{str}^{(0)} + \hat{H}_{str}^{(1)} + \ldots .$$ (3.3)

The first term is the zeroth order contribution written in the well-known harmonic oscillator equation, the $\omega$ parameter at 2934 cm$^{-1}$, and $\nu$ is the corresponding quantum number.

$$\hat{H}_{str}^{(0)} = \omega (\nu_1 + \frac{1}{2} + \nu_2 + \frac{1}{2} + \nu_3 + \frac{1}{2})$$ (3.4)

The second term includes the coupling between the stretch and the torsion with the $\mu$ parameter at the estimated value of 19.35 cm$^{-1}$. In Ref (5) the contribution of the coupling term in Eq. (10) to the zero point energy was mistakenly neglected. The consequence is that the coefficients of $\mu$ in Eq. (25) of that reference should be 1 rather than 3/2 and Eq. (22) should also be corrected accordingly. The published calculations and conclusions remain valid except that the reported values of $\mu$ should all be multiplied by 3/2.

$$\hat{H}_{str}^{(1)} = \mu^{(1)} \left[ (a_1^* a_1 + a_1 a_1^*) \cos(\gamma) + (a_2^* a_2 + a_2 a_2^*) \cos(\gamma - \frac{2\pi}{3}) \right]$$ (3.5)

The lowest term in the Fourier expansion of the local-local term are maintained as indicated in Wang and Perry’s^5 with the local-local parameter at the estimated value of -42.2 cm$^{-1}$.

$$\hat{H}_{l-l} = \lambda (a_1^* a_1 + a_1 a_1^* + a_2^* a_2 + a_2 a_2^* + a_3^* a_3 + a_3 a_3^*)$$ (3.6)

The internal rotation potential which are included in the three C-H stretches Hamiltonian consists of Fourier components held at the ground state values of $V_3=373.54$ cm$^{-1}$ and $V_6=0.80$ cm$^{-1}$.

$$V_{pot}(\gamma) = \frac{V_3}{2} (1 - \cos 3\gamma) + \frac{V_6}{2} (1 - \cos 6\gamma)$$ (3.7)
The kinetic portion of the torsional Hamiltonian consist of the inertial force constant and the torsional momentum \( \hat{p}_\gamma^2 \) indicated below:

\[
\hat{H}_{\text{tors}} = F \hat{p}_\gamma^2
\]  

(3.8)

3.3.2 Zeroth-order Adiabatic Approximation: Separation of the Three CH Stretches \((\nu_3, \nu_9, \nu_2)\) from the Torsional motion

The vibration-torsion Hamiltonian of methanol can be written as the sum of two parts

\[
\hat{H} = \hat{H}_{\text{vib}} + F \hat{p}_\gamma^2
\]

(3.9)

where \( F \hat{p}_\gamma^2 = F \partial^2 / \partial \gamma^2 \) is the operator for the torsional kinetic and \( \hat{H}_{\text{vib}} \) contains the full potential energy and the kinetic operator for the other vibrations. In this chapter, the other vibrational modes are specifically the C-H vibration, \( \nu_2, \nu_3 \) and \( \nu_9 \). The torsional kinetic energy is simplified by taking the inertial parameter \( F \) to be a constant that is fixed at ground state value of 27.65 cm\(^{-1}\).

In the crude adiabatic approximation, the solutions of

\[
\hat{H}\Psi = E\Psi
\]

(3.10)

are written as product wavefunctions.

\[
\Psi = \psi_i(\hat{r};\gamma) \phi_{i,n}(\gamma)
\]

(3.11)

where the \( \psi_i(\hat{r};\gamma) \) are the solutions of the vibrational problem

\[
\hat{H}_{\text{vib}} \psi_i(\hat{r};\gamma) = E_{\text{vib},i}(\gamma) \psi_i(\hat{r};\gamma)
\]

(3.12)

In the Zeroth-order (crude) approximation, we ignore the parametric dependence of the \( \psi_i(\hat{r};\gamma) \) on the torsional angle \( \gamma \) when solving for the torsional wavefunctions in the effective potential \( E_{\text{vib},i}(\gamma) \) (Appendix K) is obtained from the solution of the vibrational problem. The Zeroth-order torsional wavefunctions \( \phi_{i,n}^0(\gamma) \) are then obtained by solving

\[
\left( E_{\text{vib},i}(\gamma) + F \hat{p}_\gamma^2 - E_{i,n}^{(0)} \right) \phi_{i,n}^0(\gamma) = 0.
\]

(3.13)
The torsional solutions have two indices \( i \) and \( n \) because of the effective potential \( E_{\text{vib},i}(\gamma) \) is different in each vibrational state \( i \). Below, a better approximation will be obtained by including the vibrationally diagonal correction that results from the parametric dependence of the \( \psi_i(\vec{r};\gamma) \) on \( \gamma \).

3.3.3 Adiabatic Limit with Geometric Phase Treatment of the Torsional motion

The full solution is derived by first expanding the total eigenfunctions into a complete set combinations of the vibration-torsion wavefunction.

\[
\Psi = \sum_{i,n} c_{i,n} \psi_i(\vec{r};\gamma) \phi_{i,n}(\gamma)
\]  

(3.14)

The vibrational basis function \( \psi_i(\vec{r};\gamma) \) defined by Eq. (3.12) and the torsional basis function \( \phi_{i,n}(\gamma) \) defined below. After Eq. (3.14) is substituted into Eq. (3.10), the result was multiplied by \( \psi^*_i(\vec{r};\gamma) \) and integrated over the vibrational coordinates \( \vec{r} \) to obtain

\[
\sum_{n} \left\{ \sum_{i} c_{i,n} F \left[ \sum_{i} A_{i,i}(\gamma) A_{i,i}(\gamma) \right] + 2 A_{i,i}(\gamma) \hat{p} \phi_{i,n}(\gamma) \right\} + c_{i,n} \left[ F \hat{p}^2 + E_{\text{vib},i}(\gamma) - E \right] \phi_{i,n} = 0
\]

(3.15)

where the vector potential \( A_{i,i}(\gamma) \) is given by

\[
A_{i,i}(\gamma) = \int \psi^*_i(\vec{r};\gamma) \hat{p} \psi_i(\vec{r};\gamma) d\vec{r}
\]

(3.16)

In Eq. (3.15) we take the term with \( n=n \) and \( i=i \) and set it to zero.

\[
\left[ F \left( \sum_{i} A_{i,i}(\gamma) A_{i,i}(\gamma) \right) + 2 FA_{i,i}(\gamma) \hat{p} + F \hat{p}^2 + E_{\text{vib},i}(\gamma) - E \right] \phi_{i,n} = 0
\]

(3.17)

The torsional functions that satisfied Eq. (3.17) constituted the adiabatic limit. Eq. (3.13) and (3.17) defined the adiabatic basis functions that is used in Eq. (3.15) and Eq. (3.16). When Eq. (3.16) is multiplied on the left by \( \phi^*_{i,n}(\gamma) \) and integrated over \( \gamma \), we obtain the usual secular equations for the fully coupled solutions. That use of Eq. 3.17 means that all terms the secular equations with \( i=i \), but \( n\neq n \) are zero.
As was pointed out by Fehrensen et al.\textsuperscript{39}, and earlier in the section 3.2 some of the vibrational fundamentals (including \( v_2 \) and \( v_9 \)) correlate to degenerate E-type vibrations in the \( C_3v \) geometry, which, in this adiabatic approximation, results in the accumulation of a geometric phase of -1 as \( \gamma \) is varied from 0 to \( 2\pi \). The vibrational functions \( \psi_j(\bar{r};\gamma) \) are chosen to be real, which causes the vibrational diagonal parts of the vector potential to vanish,

\[
A_{ij}(\gamma) = 0.
\]  

When Eq. (3.12) is solved at each \( \gamma \) and the solutions are required to vary smoothly as a function of \( \gamma \), we find that for \( v_2 \) and \( v_9 \), \( \psi_j(\bar{r};\gamma) \) changes sign when \( \gamma \Rightarrow \gamma + 2\pi \) (Appendix K). To ensure that the total adiabatic wavefunction Eq. (3.13) is periodic on \( 2\pi \), the torsional part of the wavefunction must also change sign when \( \gamma \Rightarrow \gamma + 2\pi \). As a practical matter the two asymmetric stretches (\( v_2, v_9 \)) are handled using double-value boundary condition. Eq. (3.19) and (3.20) below represents a description of the basis set function and the corresponding even and odd integer rotor states, for the two asymmetric stretches (\( v_9 \) and \( v_2 \)). Eq. (3.21) and Eq. (3.22) are single-value boundary condition for the symmetric CH stretch (\( v_3 \)).

\[
|v_1, v_2, v_3, m\rangle = |v_1\rangle |v_2\rangle |v_3\rangle |m\rangle = (4\pi)^{\frac{1}{2}} e^{im\gamma} |v_1\rangle |v_2\rangle |v_3\rangle
\]  

(3.19)

\[
|m\rangle = 0, \pm \frac{1}{2}, \pm 1 + \ldots .
\]  

(3.20)

\[
|v_1, v_2, v_3, m\rangle = |v_1\rangle |v_2\rangle |v_3\rangle |m\rangle = (2\pi)^{\frac{1}{2}} e^{im\gamma} |v_1\rangle |v_2\rangle |v_3\rangle
\]  

(3.21)

\[
|m\rangle = \pm 1, \pm 3 + \ldots .
\]  

(3.22)

3.3.4 Transformation Method: Conversion of the Rotor basis set To The First-order Adiabatic basis set

The free rotor basis set in Wang and Perry’s\textsuperscript{5} paper was transformed into the adiabatic basis set by using the unitary transformation method. In this method, the free rotor basis set Hamiltonian is diagonalized in the Matlab program, where a 81x81 matrix is produced. The
basis set was further expanded to a maximum of 126 functions where a $154 \times 154$ matrix is obtained. The results were compatible and consistent demonstrating a convergence of the calculation.

This matrix contains the diagonal terms corresponding to the adiabatic limit of the vibration-torsion manifold and the off-diagonal terms are considered the IVR coupling matrix elements derived from the neglected cross terms illustrated above. The unitary transformation method expressed in the equation below, with the $H_{AB}^{LM}$ as the Hamiltonian in the adiabatic basis set, where the transformation $Q$, gives the adiabatic basis in terms of the local mode free rotor basis, is obtained from the solution Eq. (3.13) and Eq. (3.17).

$$H_{AB}^{LM} = QH_{LM}^{FR}Q^{-1}$$

Since, the geometric phase of the $\nu_2$ and $\nu_9$ vibration required that the vibrational $(\psi_{i}(\vec{r};\gamma))$ and torsional $(\phi_{i,n}(\gamma))$ parts of the adiabatic basis functions are each antisymmetric on a $2\pi$ internal rotation. Accordingly, in the free rotor basis, each of $\psi_{i}(\vec{r};\gamma)$ and $\phi_{i,n}(\gamma)$ are expressed in terms of half-integer values of $m$. However, the products $\psi_{i}(\vec{r};\gamma)\phi_{i,n}(\gamma)$ are symmetric on $2\pi$ and can be expressed in terms of integer values of $m$. Therefore, the matrices in Eq. (3.23) reference only integer values of $m$ and have dimension $3(2m_{\text{max}}+1) \times 3(2m_{\text{max}}+1)$. The elements of $H_{AB}^{LM}$ are noted as $H_{i,n,i,n}^{AB} = H_{kl}^{AB}$.

3.4 Discussion and Conclusions

The results from the adiabatic approximation calculations and the conclusions are summarized in section 3.4.1 and 3.4.2.

3.4.1 Comparison of Adiabatic Approximation and Exact Results from the 4-Dimensional Model Hamiltonian

Fig 3.5 compares the energy levels obtained under the adiabatic approximation with those from the fully coupled model calculation. In agreement with the results of Fehrensen et al\textsuperscript{39}, we find that the adiabatic approximation yields the correct ordering of the torsional levels for the
three CH stretch fundamentals, \(v_3, v_2\) and \(v_9\). The adiabatic tunneling splittings are reasonable except the splitting for \(v_2\) asymmetric stretch of the ground torsional state is too large (9.5 cm\(^{-1}\) as compared to 2.75 cm\(^{-1}\)). The quality of the adiabatic approximation deteriorated when torsional excitation was added to the CH fundamentals. One quantum of torsional excitation \((v_{12}=1)\) correspond to states near the top of the torsional barrier, and \(v_{12}=2\) is well above the barrier. At \(v_{12}=1\) there are substantial energy shifts and the ordering of some levels is changed. At \(v_{12}=2\), the exact model calculation yield four nearly degenerate states \((A_1+A_2+2E)\), and the pattern of two-fold and four-fold near-degeneracies persist at higher torsional excitation. This pattern is not found in the adiabatic calculations. The correspondence between the adiabatic and fully coupled states is summarized in Table No 11.

<table>
<thead>
<tr>
<th>(v_{12})</th>
<th>(v_3)</th>
<th>(v_9)</th>
<th>(v_2)</th>
<th>(v_3)</th>
<th>(v_9)</th>
<th>(v_2)</th>
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<td>0</td>
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<td>0</td>
<td>0.5</td>
<td>0.5</td>
</tr>
<tr>
<td>0</td>
<td>E</td>
<td>A(_2)</td>
<td>A(_1)</td>
<td>1</td>
<td>1.5</td>
<td>1.5</td>
</tr>
<tr>
<td>1</td>
<td>E</td>
<td>A(_1)</td>
<td>A(_2)</td>
<td>2</td>
<td>1.5</td>
<td>1.5</td>
</tr>
<tr>
<td>1</td>
<td>A(_2)</td>
<td>E</td>
<td>E</td>
<td>3</td>
<td>2.5</td>
<td>2.5</td>
</tr>
<tr>
<td>2</td>
<td>A(_1)</td>
<td>E</td>
<td>E</td>
<td>3</td>
<td>3.5</td>
<td>3.5</td>
</tr>
<tr>
<td>2</td>
<td>E</td>
<td>A(_2)</td>
<td>A(_1)</td>
<td>4</td>
<td>4.5</td>
<td>4.5</td>
</tr>
<tr>
<td>3</td>
<td>E</td>
<td>A(_1)</td>
<td>A(_2)</td>
<td>5</td>
<td>4.5</td>
<td>4.5</td>
</tr>
<tr>
<td>3</td>
<td>A(_2)</td>
<td>E</td>
<td>E</td>
<td>6</td>
<td>5.5</td>
<td>5.5</td>
</tr>
<tr>
<td>4</td>
<td>A(_1)</td>
<td>E</td>
<td>E</td>
<td>6</td>
<td>6.5</td>
<td>6.5</td>
</tr>
<tr>
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<td>E</td>
<td>A(_2)</td>
<td>A(_1)</td>
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<td>7.5</td>
<td>7.5</td>
</tr>
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<td>A(_1)</td>
<td>A(_2)</td>
<td>8</td>
<td>7.5</td>
<td>7.5</td>
</tr>
<tr>
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<td>A(_2)</td>
<td>E</td>
<td>E</td>
<td>9</td>
<td>8.5</td>
<td>8.5</td>
</tr>
<tr>
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<td>E</td>
<td>E</td>
<td>9</td>
<td>9.5</td>
<td>9.5</td>
</tr>
<tr>
<td>6</td>
<td>E</td>
<td>A(_2)</td>
<td>A(_1)</td>
<td>10</td>
<td>10.5</td>
<td>10.5</td>
</tr>
</tbody>
</table>

\(^a\)The adiabatic basis states may be labeled by \(\{i=v_3, v_2, v_9; \Gamma=A_1, A_2, E; v_{12}\}\) or alternatively by \(\{i, \Gamma, m^*\}\) where \(m=m^*\) is the free internal rotor function making the largest contribution.

\(^b\)The fully coupled eigenfunctions may also be labeled by either scheme. Here, \((m^*)\) means \(m=m^*\) contributes <75% to the eigenfunction; \([m^*]\) means 75%-90%, and otherwise >90%.

At high energy, \(v_2\) and \(v_9\) states with the same \(m^*\) converge, that is, \(\{v_2, v_9\} \rightarrow v_E\).
The pattern of energy levels in the adiabatic limit is similar to zeroth-order adiabatic calculations but shifted to higher energy (Fig. 3.5). Since the diagonal elements of the vector potential converge to zero, $A_{ij} = 0^{51}$ the correction to the zeroth-order adiabatic torsional energies Eq. (3.16) needed to reach the adiabatic limit Eq. (3.18) comes from the positive-definite term,

$$ F\left( \sum_i A_{i,i}(\gamma)A_{i,i}^\ast \right) = F \int \psi_i^\ast (\tilde{r};\gamma) \hat{p}^2 \psi_i (\tilde{r};\gamma) d\tilde{r} \geq 0. \quad (3.24) $$

As shown in Fig. 3.5, these corrections do not change qualitatively the pattern of the energy levels.

In the adiabatic limit, all of the vibrationally diagonal corrections to the torsional structure have been included. Therefore, the failings of the adiabatic approximation result from the mixing of the adiabatic basis functions. The mixing of methanol vibrations has been depicted graphically by both Wang and Perry$^5$ and Sibert and Castillo-Chara$^{117}$ as avoided crossings in correlation diagrams. In Figs 3.6, 3.7 and 3.8, the calculation is repeated for a wide range of $\lambda$, local-local coupling parameter. In Wang and Perry$^5$ 4-Dimensional model calculation of the $\lambda$ parameter calculations the torsion inversion is maintained similar to the crude adiabatic approximation and the adiabatic limit. However, the only difference between the crude adiabatic and Wang and Perry’s$^5$ model is that in the Wang and Perry’s$^5$ model (Fig 3.6) there are avoided crossings at the $\nu_2$ with the $\nu_3$ and the $\nu_3 + \nu_{12}$ with the $\nu_2$. In the crude adiabatic approximation and adiabatic limit (Fig 3.7) these avoided crossings do not exist. These findings confirmed that IVR is a non-adiabatic effect. Another difference is located in the Wang and Perry’s$^5$ model the graph of the $\lambda$ calculations are continuous at $\lambda=0$ cm$^{-1}$ value, whereas, in the adiabatic limit (Fig. 3.8) a singularity occurs at this value. This singularity arise from the neglected terms in the crude adiabatic approximation that is included in the adiabatic limit $\partial \psi / \partial \gamma$ is unable to treat the interaction of the torsion-vibration when it is totally isolated. This is visible from examining the
Figure 3.5 Calculated Torsion-Vibration energy levels in the Crude adiabatic approximation, the adiabatic limit and for a coupled fully solution of the model Hamiltonian. The doubly degenerate levels have E symmetry in $G_6$ and the single degenerate levels are $A_1$ and $A_2$ with the levels $A_2$ represented by #. Correlation lines between three stacks of levels of the same symmetry and the same or similar vibration character. This figure is taken from Ref. 56 Fig.1 pg. 104313-4
following symmetry element in Table 7., the $\nu_9 (A_2)$ is heavily mixed with the $\nu_3+\nu_{12}$ and the $\nu_2+\nu_{12}$ vibrations, the mixing criterion is recorded as of 0.14 and 0.17 respectively with mixing order of 0.3. This indicates that the adiabatic limit is unable to treat the torsion and three CH stretches because of the high amount of coupling between these modes.

In the Born-Oppenheimer case, (the electronic/vibration problem) the nodal spacing of the electronic wavefunction, which is considered the fast coordinate, is on the order of a bond length (≈100 pm), while the nodal spacing of the vibrational wavefunction, the slow coordinate, is of ~10 pm or less. Whereas, in the torsion-vibration problem the reverse is observed, the small-amplitude vibrations (fast coordinate) is ~10 pm or less and the torsion (slow coordinate) is of a bond length ~100 pm. This indicates that the non-adiabatic coupling is stronger in the torsion/vibration problem in comparison to the electronic/vibration problem. This same effect can also be appreciated by considering the reduced masses involved. In the BOA, the non-adiabatic effects scale $(m/M)^{1/4}$ where $m$ is the reduced mass for the fast degree of freedom (electronic motion) and $M$ is the reduced mass for the slow degree of freedom (nuclear motion)\textsuperscript{38,122}. For the BOA, we have then $(m/M)^{1/4} \approx 0.1$. However, in methanol, both the vibrations and the torsion are motions of hydrogen atoms; therefore, $(m/M)^{1/4} \approx 1$. The only reason that the vibrations are fast and the torsion is slow is the softness of the torsional potential. Accordingly, we can expect the non-adiabatic coupling to be stronger (relative to spacings in the spectrum of the slow degree of freedom) in this vibration-torsion problem than in a typical electronic-vibration. Therefore, the fully coupled 4-Dimensional model is more adequate in dealing with the torsion/vibration problem than an adiabatic approximation.

In figure 3.9, 3.10 and 3.11 the calculation was repeated for various values of $\mu$, the stretch-torsion coupling parameter. In the crude adiabatic approximation and adiabatic limit (Fig 3.12 and 3.13) the inversion patterns of the $\nu_9$ and $\nu_2$ is maintained similarly to the 4-dimensional
Figure 3.6 Fully coupled Torsion-vibration energies calculation of the $\lambda$ parameter (3.25)
Figure 3.7 Zeroth order Torsion-vibration energy calculations of the \( \lambda \) parameter
Figure 3.8 Adiabatic Limit of Torsion-vibration energy calculation of the $\lambda$ parameter
Figure 3.9 Full 4-Dimensional Torsion-vibration energies calculations of the \( \mu \) parameter
Figure 3.10 Zeroth order Torsion-vibration energies calculations of the $\mu$ parameter
Figure 3.11 Adiabatic limit Torsion-vibration energies calculations of the $\mu$ parameter
case. This indicates that an inclusion of double-valued boundary condition in the adiabatic approximation is adequate in treating the inversion property of the $\nu_9$ and $\nu_2$. However at $\mu=0$ cm$^{-1}$ term, the avoided crossings in the 4-dimensional case is become actual crossings in both the zeroth-order and the adiabatic limits. The crossings of the same symmetry E states of $\nu_9$ and $\nu_2$ point indicates the degeneracy and severe mixing of the E states in $\nu_9$ and $\nu_2$ vibrational modes. This is further explained below.

Pearman and Grubele$^{28}$ incorporated a mixing criterion to determine the extent of mixing between two states.

\[ L_{kl} = 1 + \left( \frac{\Delta E_{kl}}{V_{kl}} \right)^2 \]  

(3.25)

where $\Delta E_{kl}$ is the energy difference between two basis states, $\chi_k$ and $\chi_l$, and $V_{kl}$ is the matrix element coupling them. In the limit of the weak mixing, $L_{kl} = V_{kl} / \Delta E_{kl} \ll 1$, but when two basis states are strongly coupled at an avoided crossings $L_{kl} = 1$. In a two-level, $L_{kl}$ approximates, for both limits, the mixing ratio of the two basis states. That is, $L_{kl} = |c_l / c_k|$ where mixed state is

$\Psi = c_k \chi_k + c_l \chi_l$ and $|c_l| \leq |c_k|$. In a many-level system, provides a convenient means of identifying pairs of basis states that are either weakly or strongly mixed. The sum

$N_k = \sum_l L_{kl}$ provides a measure of the extent that $\chi_k$ is mixed with other basis functions.

Table 12 provided a summary of the extent of mixing of the adiabatic basis for the CH fundamentals and some of the torsional combination states built on them. The tabulated values of $L_{kl}$ are derived from the matrix elements and energy differences in $H^{AB}$ in the transformation method. Where the sum $N_k \ll 1$, the adiabatic basis state is a good approximation to the eigenstates of the model Hamiltonian. The data show that $N_k < 0.5$ for most of the CH stretch.
<table>
<thead>
<tr>
<th>Symmetry</th>
<th>Reference Vibration $\chi_k$</th>
<th>Coupled Vibrations $\chi_l$</th>
<th>Matrix Element $V_{kl}$ / cm$^{-1}$</th>
<th>Mixing Criterion $L_{kl}$</th>
<th>$1N_k = \sum_i L_{kl}$</th>
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<td>$v_3$</td>
<td>$v_9 + v_{12}$</td>
<td>16</td>
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<td>0.1</td>
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<td>$v_9$</td>
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<td>0.13</td>
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</tr>
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<td>0.2</td>
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<td>E</td>
<td>$v_9 + 2v_{12}$</td>
<td>$v_3 + 3v_{12}$</td>
<td>127</td>
<td>0.94</td>
<td>1.1</td>
</tr>
<tr>
<td>A$_1$</td>
<td>$v_2 + v_{12}$</td>
<td>$v_9 + 3v_{12}$</td>
<td>127</td>
<td>0.94</td>
<td>1.1</td>
</tr>
</tbody>
</table>

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fundamentals and for the torsional combination \( \nu_3 + \nu_{12} \). Generally, the mixing is more severe for the asymmetric CH stretches \( \nu_2 \) and \( \nu_9 \) than for \( \nu_3 \) and increases with torsional excitation. In table 12 there are several cases that approach the limit of strong mixing, \( L_{kl} \approx 1 \). Among the strongest mixings is the coupling of the E components of \( \nu_2 + n \nu_{12} \) and \( \nu_9 + n \nu_{12} \), \( n=1,2 \). The corresponding A components cannot mix because they have different symmetries (A\(_1\), A\(_2\)); however, the pairs \( \nu_2 + n \nu_{12} \) and \( \nu_9 + (n \pm 1) \nu_{12} \) do have the symmetry (A\(_1\) or A\(_2\)) and are strongly mixed.

The mixing between the \( \nu_2 \) and \( \nu_9 \) stacks yields, at high torsional energy, eigenstates that are approximately product functions of a free internal rotor (doubly degenerate) with an E-type symmetric-rotor asymmetric CH stretch (“\( \nu_E \)” , also double degenerate). This accounts for the pattern of near 4-fold degeneracies found from the coupled calculation at high torsional energies. Thus the asymmetric CH stretches undergo a change of character from two distinct vibrations (A and A\(''\) in C\(_s\) or A\(_1\) and A\(_2\) in G\(_6\)) in the torsional ground state to an E-type degenerate vibration at high torsional energy.

Jon Hougen\(^{112} \) has pointed out that, in 3-fold internal rotor molecules, one has to pick the symmetry of the normal mode vibrations. In rigid molecules point group symmetry applies, and the symmetries of the normal modes are completely specified by the usual procedure. However, in the presence of large amplitude motion there is no fixed reference geometry, and permutation-inversion group theory must be used. The choice in G\(_6\) for the two asymmetric CH stretch normal modes of methanol is between an \( \{A_1, A_2\} \) pair of vibrations and a degenerate E vibration. While either choice is theoretically valid, the former is more descriptive of the eigenstates at low torsional energy and the latter at higher energy.

The symmetric CH stretch \( \nu_3 \) does not undergo a dramatic change in character upon torsional excitation, but it does change more subtly. When the torsional angle is fixed at \( \gamma=0 \), the three methyl CH bonds are equivalent. The bond anti to the OH bond has a slightly larger force constant than the other two, which means that the adiabatic \( \nu_3 \) basis states do not have equal

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amplitude on the three CH bonds. At high torsional energy where the motion is effectively free internal rotation, the amplitudes on the three bonds become approximately equal. The result is that the \( \nu_3 \) stack mixes with the \( \nu_6 \) and \( \nu_2 \) stacks and the mixing increases with torsional excitation.

The adiabatic basis is defined as above is just one basis. Is there a better product basis? One could use a symmetric rotor \( A_1+E \) basis for the CH stretches by proceeding as above by setting the torsion-vibration coupling \( \mu \) to zero when solving Eq. 3.4. Such a basis is also adiabatic and would be attractive at high torsional energy, but it would be poor for the torsional ground states. The central issue is the transition from one kind of motion to another over the range \( \nu_{12}=0-2 \), which means that an adiabatic basis designed for either limit will not work well through the transition.

3.4.2 Non-adiabatic effects Associating with the Adiabatic Approximation: IVR

Most of the non-adiabatic coupling matrix elements mix the torsional and vibrational characters of the wave functions and therefore result in IVR. The matrix \( H^{AB} \), which contains many IVR matrix elements \( H_{kl}^{AB} \), allows us to examine how they scale with coupling order.

In the application of their scaling model to small internal rotor molecules (hydrogen peroxide and methanol), Pearman and Gruebele\textsuperscript{28} found that the IVR coupling matrix elements scale as:

\[
V_{kl} \sim a^n
\]

(3.26)

where \( a \) is the scaling parameter and \( n \) is the coupling order between states \( k \) and \( l \) defined below. For rigid molecules, the small value of \( a \) [0.05-0.2\textsuperscript{42 and 58}] which implies that the dominance of low-order IVR coupling pathways because the coupling strength falls by about an order of magnitude for each higher coupling order. However, molecules that contain a large amplitude motion the scaling parameter is as large as 0.5, this indicates that higher order couplings is dominant in torsional molecules.
The coupling order between the adiabatic basis states \( k \) and \( l \) may be defined as

\[
\nu = |v_{2k} - v_{2l}| + |v_{3k} - v_{3l}| + |v_{9k} - v_{9l}| + |v_{12k} - v_{12l}| = 2 + |v_{12k} - v_{12l}|
\]

(3.27)

where the \( v \)'s are quantum numbers of the different modes in a pair of coupled states. Since the nonzero off-diagonal elements \( H_{kl}^{AB} \) all represent the exchange of one quantum of one CH stretch vibration for one quantum of another, the simplification in the second line of Eq. (3.27) is obtained. For \( \nu=2 \), the coupled states have the same number of torsional quanta, and the coupling represents only a rehybridization of the energy among the CH stretches. However, for \( \nu \geq 3 \), one or more torsional quanta are exchanged between the coupled vibrations, and the coupling represents IVR.

For states well above the torsional barrier, the torsional angular momentum \( m \) is a better quantum number than the torsional vibrational quantum number \( v_{12} \), so an alternative definition of coupling order may be used:

\[
\nu = |v_{2k} - v_{2l}| + |v_{3k} - v_{3l}| + |v_{9k} - v_{9l}| + |m_k^* - m_l^*| = 2 + |m_k^* - m_l^*|
\]

(3.28)

Here \( m^* \) indicates the free rotor function making the largest contribution to a given adiabatic torsional function. In the present situation, where there are states both below and above the barrier, both \( m^* \) and \( v_{12} \) are nominal labels for the adiabatic basis states, and the correspondence between them is given by Table 11. Note that for the higher torsional states, \( m^* = \frac{3}{2} v_{12} \), which means that the apparent coupling order derived from Eq. (3.28) is larger (\( \nu_m > \nu \)). For the adiabatic torsional functions built on the \( v_2 \) and \( v_9 \) vibrations, \( m \) takes on half-integer values, implying that Eq. (3.28) gives both integer and half-integer coupling orders.

The scaling of the average IVR coupling matrix elements with \( \nu \geq 3 \) is shown in Fig. 3.12. The scaling parameter \( a \) is obtained by a fit to the equation

\[
\log_{10}(H_{kl}^{AB}) = \nu \log_{10} a + C
\]

(3.29)
where the bar indicates an average over all off-diagonal elements of a given order \( n \), involving basis states up to a maximum value of \( \nu_{12} \) and \( C \) is a constant. Fig. 3.12 shows that the scaling relationship Eq. (3.29) is followed and that the scaling constant \( a_\nu = 0.3 \) depends on slightly on the range of \( \nu_{12} \) included in the average. When the matrix elements \( H_{kl}^{AB} \) are resorted according to Eq. (3.28), averaged, and plotted, a similar plot to Fig 3.12 results, except that the scatter about the fitted lines is greater and the fitted scaling constant is \( a_\nu = 0.44-0.51 \). By either definition the scaling parameter is larger than for rigid molecules and is within the range found by Pearman and Gruebele’s\(^{28} \) for torsional molecules. Whereas Pearman and Gruebele’s\(^{28} \) employed \textit{ab initio} calculation and an approximate full-dimensional model, the present result is derived from a simple four-dimensional model that provides the opportunity to examine the origins of the scaling behavior based on the physics contained in that model. The model Hamiltonian contains only a single torsion-vibration coupling, the term \( \mu \) in Eq. (3.10). Without that term, the torsional vibrational degrees of freedom would be rigorously separable, and there would be no IVR exchanging energy between the torsion and the CH stretches. In the free internal rotor basis, the \( \mu \) term couples basis states with \( \Delta m=\pm 1 \). If we allow a transformation from the local mode basis to normal mode basis, then the \( \mu \) term is second order in the CH stretches. The overall coupling is then third order in a product basis, this single third order term gives rise to the plethora of IVR coupling matrix elements summarized in Fig 3.12.

\[
\phi_k = \sum_m b_{km} e^{im\gamma}
\]  

(3.30)

Since the torsional parts of the adiabatic basis functions are linear combinations of the free rotor states. Therefore, it is the scaling of the coefficient \( b_{km} \) that determines scaling properties of the IVR coupling matrix elements. In Fig 3.13 the log plots of the coefficients take the form of an inverted \( v \) with the apex at the nominal. For the high torsional state in the \( \nu_2 \) manifold, the fall off is in a linear fashion. The slope of this is -0.4, which gives a scaling parameter \( a_\nu = 0.4 \) for \( |b_{km}| \).
Figure 3.12 Anharmonic coupling terms vs Coupling order

\[ \ln(|H_{AB}|) \text{ cm}^{-1} \]

\[ \text{Coupling Order (} n_\nu) \]

\[ \text{Coupling Order (} n_\nu) \]

\[ m_{1-13} : a = 0.472 \]
\[ m_{1-25.5} : a = 0.481 \]
\[ m_{1-28.5} : a = 0.482 \]
\[ m_{1-32.5} : a = 0.462 \]
While the plot for $m=0.5$ is not linear, the extent of the fall-off for $|m-m'|=12$ is similar but 5 order of magnitude, implying a similar effective value for the scaling parameter. A plot of the 1-butyne torsional coefficients illustrate similar behavior, thereby confirming that the torsional coefficients is responsible for the scaling properties. However, lack of experimental data on the CH stretches for the 1-butyne prevented further research of the scaling of IVR coupling matrix elements. We reiterate that the scaling properties of IVR coupling matrix elements arise from the nature of the adiabatic torsional functions, and not from the specifics of the torsion-vibration interaction included in the Hamiltonian.

At high excitation, the torsion becomes nearly free internal rotation and Pearman and Gruebele found that in the “rotational limit”, the scaling parameter becomes much smaller ($\alpha=0.015$). In this adiabatic approximation, the scaling parameter is maintained at the corresponding value indicated above, with only slight decrease in its value when the state space is increased. For example, the data of Fig. 3.12 and Fig 3.13 included many free internal rotor states about more than 10 times the torsional.

In conclusion, the adiabatic approximation applied to the three CH stretches and the torsion vibrations is adequate in replicating the inverted torsional structure of the two asymmetric stretches ($\nu_2$ and $\nu_9$), however, it fails to account for the correct level spacings which is important in elucidating the IVR pathways. In addition, it was unable to reproduce the correct energy patterns of the 2-fold and 4-fold near degeneracies at high excited torsional states, nevertheless it was useful in verifying that free internal rotation is a new type of motion.
Figure 3.13 Graph above is the scaling relationship of the ground torsional state of methanol, the graph below is the scaling relationship of the ground torsional state of 1-butyne.
CHAPTER IV
CAVITY RINGDOWN TECHNIQUE USING OPO LASER

4.1 Overview of Experimental Objectives

This section entails the experimental purpose and the previous theoretical and experimental work pertaining to the polyad region $v_{\text{CH}}=2$.

4.1.1 Experimental Purpose

The polyad region $v_{\text{CH}}=2$, where $v_{\text{CH}}=2$ is the binary combination of the $v_2, v_9$, and $v_3$ CH stretches of methanol, spans a range of 400 cm$^{-1}$ from 5600 cm$^{-1}$ to 6000 cm$^{-1}$ (Fig. 4.1$^{124,125}$). This region is particularly important because it is the transition region between the normal and local mode behaviors$^{124}$. In the normal mode limit at low energy, the inter-bond coupling between the bonds is dominant, causing the normal modes to be linear combinations of the local vibrations on each CH bond$^{29,126}$. Conversely, in the local mode limit, energy is localized within one bond$^{29,126}$. Within this region, Halonen and Hänninen’s$^8$ theoretical calculations provided evidence of Fermi$^{26}$ and Darling-Dennison resonances$^{27}$, whereas Perry’s$^7$ calculations reveal how the torsion-vibrational coupling affects the normal to local mode transition. These two calculations will be tested and challenged by the assignment of the experimental spectrum of this region.

There are four criteria for recording an analyzable spectrum of the $v_{\text{CH}}=2$ region:

1) Sub-Doppler frequency resolution is required in order to resolve discrete transitions.

2) The experimental technique must be highly sensitive to detect weak combination and overtone bands and weakly perturbing levels.

3) The methanol molecules must be jet-cooled for spectral simplification.
4) The laser tuning range should span the wavelengths of the $v_{\text{CH}}=2$ region.

In Fig (4.1) an IRLAPS$^{124}$ spectrum of the $2v_{\text{CH}}$ region of methanol is recorded with the positions of Hänninen and Halonen’s$^8$ calculated vibrational eigenstates taken from Perry’s Grant proposal (DE-FG02-90ER14151)$^{125}$.

4.1.2 Previous Experimental and Theoretical work on the Polyad $v_{\text{CH}}=2$

The experimental spectrum of the $v_{\text{CH}}=2$ region was recorded using the IRLAPS technique applied to jet-cooled methanol$^{124}$. The features of the spectrum are more complicated than either the CH fundamental ($v_{\text{CH}}=1$)$^5,36$ or $v_{\text{CH}}=3$ and higher overtone levels$^{124}$. The fundamental CH stretch region has been assigned at high resolution$^5,36$, where the local-local coupling in the three normal vibrations is shown to be dominant over the bond anharmonicity. At $v_{\text{CH}}=3$ or higher levels$^{124}$, a single band is observed for each of the two CH bond types (gauche, and anti to the OH bond) as expected for the local mode limit. The bond dipole model in which the local modes of the two types, gauche and anti to the OH bond, carry all the oscillator strength further supports this. Accordingly, the $v_{\text{CH}}=2$ region is the transition region between the normal and local mode behaviors.

Theoretical work by Halonen and Hännienen$^8$ of the $v_{\text{CH}}=2$ region in methanol uses a normal mode description. In their normal mode calculations, they included, quartic Darling-Dennison$^{37}$ interactions between the O-H and the C-H stretches because the coupling appears
prominently as the 50 cm\(^{-1}\) splitting between the 5\(\nu_1\) and 4\(\nu_1+\nu_2\) states. In addition, the Fermi\(^{26}\) anharmonic coupling terms between the higher C-H stretches and lower frequency H-C-H and C-O-H bends. These two interactions were able to successfully account for their experimental spectra of methanol. Meanwhile, Perry\(^7\) has extended Wang and Perry’s 4-dimensional model\(^{5,36}\) to include the CH bond anharmonicity term (\(\omega x\)) and the torsion-stretch coupling anharmonicity term (\(\mu x\)) in a local mode treatment. Those calculated results (Fig 4.2) predict the torsional tunneling splittings in the \(v_{\text{CH}}=2\) polyad. For example, the torsional tunneling splittings for 2\(\nu_9\) and 2\(\nu_2\) are predicted to be inverted and 2\(\nu_3\) to be normal, but the magnitudes of the splittings are different from the fundamentals. At higher CH stretch excitation, the torsional tunneling splittings are quenched indicating the arrival of the local mode limit. This indicates that the torsional motion which is anharmonic in nature is strongly coupled to the CH stretches.

These two theoretical models by Hänninen, Halonen\(^8\) and Perry\(^7\) are complementary in assigning the \(v_{\text{CH}}=2\) region. Hänninen and Halonen’s\(^8\) Hamiltonian can be used to assign the bending combinations as well as the stretch-bend interactions. Although, Hänninen and Halonen’s\(^8\) model excluded the torsional motion in their calculations, Perry’s\(^7\) calculation in conjunction with cavity ringdown spectroscopy (CRDS) can potentially yield the band origin and the torsional tunneling splitting of each assigned band.

Cavity ringdown spectroscopy (CRDS) together with a planar supersonic expansion\(^{127}\) is suitable for recording an analyzable spectrum of the \(v_{\text{CH}}=2\) region. First, the CRDS sensitivity is within the range\(^{128}\) of 10\(^{-10}\)-10\(^{-12}\) cm\(^{-1}\) whereas typical absorption technique the sensitivity is 10\(^{-4}\) cm\(^{-1}\). Second, a planar supersonic expansion allows for spectral simplification since the molecules are jet cooled to 1-15K. In addition, a continuous wave with CRDS method (CW-CRDS) will further enhance the sensitivity and resolution because a single axial and transverse mode is excited, thus eliminating mode beating as a source of error. Finally, the new continuous wave
Fig 4.2 The A-E torsional tunneling splittings
laser (Linos PPLN OPO model 4500 OS) source has a narrower bandwidth; hence more light can be coupled to the cavity.

4.2 Fundamentals of Cavity Ringdown Spectroscopy (CRDS)

The following sections give a brief history of the cavity ringdown method and the description of this highly sensitive technique (CRDS).

4.2.1 History of Cavity Ringdown Spectroscopy (CRDS)

Initially the cavity ringdown technique was developed in the 1980’s to measure the reflectivity of highly reflective mirror surfaces for different applications\textsuperscript{128,129}. The first cavity ringdown apparatus was known as the cavity attenuated phase shift (CAPS) method\textsuperscript{130}. With this method, the input laser was modulated from a continuous laser source with an electro-optical birefringent method. Then the decay time according to the equation below was obtained from the measured phase shift of the output beam exiting the cavity consisting of two highly reflective mirrors.

\[
\tan \alpha = 4\pi f \tau \tag{4.1}
\]

where \( f \) is the modulation frequency and \( \tau = n \ell / 2 ln/c \) is the decay ringdown time and \( \alpha \) is the ratio between the input and output signal from a two channel lock-in amplifier. The ringdown time corresponds to the time required to complete a number of passes (\( n \)) within an optical resonator of length \( \ell \). The number of passes for a two mirror cavity with reflectivity \( R_1 \) and \( R_2 \) is written below:

\[
n = \frac{R_1R_2}{2(1 - R_1R_2)} \tag{4.2}
\]

substituting Eq. (4.2) into Eq. (4.1) yields

\[
\tan \alpha = \frac{4\pi f (R_1R_2)}{c(1 - R_1R_2)} \tag{4.3}
\]
By generating a plot of $\tan \alpha$ vs. $l$ for different resonator lengths or various modulation frequencies one can determine the reflectivity of the mirrors. For the purpose of obtaining the molecular absorption of a molecule, this technique can be used by inserting $(1-A)^2$ into two places in Eq (4.3), where $A$ is the fractional absorption of the light per pass.

$$\tan \alpha = \frac{4 \pi l f [R_1 R_2 (1 - A)^2]}{c \left[ 1 - R_1 R_2 (1 - A)^2 \right]}$$ \hspace{1cm} (4.4)$$

The uncertainty in the measurement of the phase shift reduces the sensitivity of this method. The phase shift angle introduced uncertainties on the order of $5\text{-}10^\circ$. This results from the phase fluctuations that arise from the coupling between the longitudinal modes of the laser and the resonator modes.

Anderson and others\textsuperscript{131} improved the CAPS technique by measuring the intensity decay time, instead of the relative phase shift between the input and output signals. In their experimental setup, a continuous laser source is used to inject light into the cavity. Once this laser light begins to enter into the cavity, the energy within the cavity begins to build up. When the intensity within the cavity reaches a chosen threshold, then the input light is switched off by a Pockel cell. The detector located at the output mirror monitors the intensity decay and this intensity decay, also referred to as the “ringdown” is subsequently recorded on an oscilloscope. This decay has exponential form.

$$I(t) = I_0 e^{-t/\tau}$$ \hspace{1cm} (4.5)$$

where $\tau$ is the ringdown time, $I$ is the intensity after time $t$, $I_0$ is the initial intensity. The ringdown time is related to the mirror reflectivity

$$\tau = \frac{l}{c} \left( \frac{\sqrt{\mathcal{R}}}{1 - \sqrt{\mathcal{R}}} \right)$$ \hspace{1cm} (4.6)$$

where $l$ is the mirror separation, $c$ is the speed of light, and $\mathcal{R} = R_1 R_2 = R_i^2$ is the product of reflectivities of the cavity mirrors.
The approach of Anderson et al.\textsuperscript{131} is a great improvement of sensitivity from the CAPS method because the measured quantities are the cavity length and decay time. However it was incapable of continuous scanning the laser frequency, since adjustments of the switching threshold was required for each wavelength. O’Keefe and Deacon\textsuperscript{132} introduced pulsed laser source which eliminated fast optical switches. This changes the experimental setup by the use of a photomultiplier tube and an oscilloscope to detect the decay, then the digitized signal is sent to the computer for analysis.

In this pulsed laser approach, the derivation of the cavity ringdown expression is simpler, since the amount of light exiting the cavity is directly proportional to the cavity transmission \((T)\) and the intensity \(I\) of the trapped pulse. The time derivative of the output pulse is

\[
\frac{dI}{dt} = -\frac{ITc}{2l}.
\]  
(4.7)

The solution to this equation is

\[
I = I_0 e^{-\frac{Trc}{2l}}.
\]  
(4.8)

This expression can be rearranged to yield the total round trip loss \((\Gamma)\)

\[
\Gamma = 1 - e^{-2l/c\tau}, \text{ where } \frac{2l}{c\tau} \ll 1
\]  
(4.9)

Subsequently a plot of cavity loss versus wavelength one can determine the transmission curve for the two mirrors or the absorption spectrum of an absorbing species.

Many scientific researchers\textsuperscript{128,133} have used this technique in kinetics studies and detection of trace species in the gas phase. However, the sensitivity of the pulsed laser source is limited by multi-mode excitation and broad bandwidth, therefore Lehmann\textsuperscript{13} proposed the use of a CW laser source instead of a pulsed laser because of the narrower bandwidth and the operation on a single-mode TEM\(_{00}\). Later on, Romanini et al.\textsuperscript{134} used a CW laser source with an acousto-optic modulator (AOM), where the AOM acts as a switch. When the AOM is switched on, it allows only the deflected beam into the cavity until sufficient buildup of light, and then it is
switched off to allow the ringdown time to begin and data collection is initiated. The technology of CW laser sources has improved since this experiment making this type of technique practical and popular.

4.2.2 Cavity Ringdown Spectroscopy (CRDS)

The CRDS method involves an optical cavity composed of two mirrors. When light is mode-matched into the cavity, the light is reflected back and forth within the cavity. With each reflection, the intensity decreases exponentially as the energy is absorbed and leaked out of the cavity. This ringdown time measurement is subsequently used to plot the absorption coefficient as a function of the laser frequency to produce the absorption spectrum of the methanol sample. The derivation of the ringdown time is based on Zalicki and Zare’s paper, where the pulsed laser description is used because the CRDS concept is easier to grasp.

The measurement of the intensity of light $S(t)$ is transmitted through the exit mirror of the cavity as a function of time is directly related to the time dependence of the light intensity $I(t)$ within the cavity. The intensity of the signal $S(t)$ is given by the following equation:

$$S(t) = TI(t)$$

(4.10)

where $T$ is the mirror transmittivity. The intensity $I(t)$ decreases according to the equation below for a round-trip period $t_r$ (i.e. the time for the light to complete the full round trip in the cavity), where $t_0$ is the initial time.

$$I(t_0 + t_r) = R^2 I(t_0)$$

(4.11)

$R$ is the mirror reflectivity. Then the output signal $S(t_0 + nt_r)$ after $n$ round trips at initial time $t$ has the following measured form.

$$S(t_0 + nt_r) = R^{2n}S(t_0) = \exp[2n \ln(R)]S(t_0)$$

(4.12)

At high reflectivity of the mirror where $R=R_1=R_2$ is close to one, $\ln(R)$ is approximately $-(1-R)$ and Eq. 4.12 becomes

$$S(t_0 + nt_r) = R^{2n}S(t_0) = \exp[-2n(1-R)]S(t_0)$$

(4.13)
\[ S(t_0 + nt_r) = \exp[-2n(1 - R)]S(t_0) \]

The total round-trip loss coefficient for the empty cavity is

\[ L_0 = 2(1 - R). \tag{4.14} \]

Substituted Eq. 4.14 into Eq. 4.13 yields the following equation:

\[ S(t_0 + nt_r) = \exp(-nL_0)S(t_0) \tag{4.15} \]

since the empty cavity loss is equal to the equation below

\[ L_0 = \frac{t_r}{\tau_0} \tag{4.16} \]

where \( t_r = 2l/c \) is the transit time for the roundtrip and \( \tau_0 \) is ringdown time of the empty cavity.

The number of roundtrips after time \( t = nt_r \), therefore Eq. 4.15 is reduced to the following form by using Eq. 4.16 and the above equation.

\[ S(t_0 + t) = \exp\left(-\frac{t}{\tau}\right)S(t_0) \tag{4.17} \]

When the cavity is filled with an absorbing medium that obeys the Beer’s Lambert Law\textsuperscript{128,135}, an additional loss is introduced on each round trip. This loss is given by the sample absorbance \( 2\alpha l_s \), where \( \alpha \) is the frequency-dependent absorption coefficient of the sample having a path-length \( l_s \) inside the cavity or length of the cavity. The round trip loss coefficient for the cavity is

\[ L = 2[(1 - R) + \alpha l_s] \tag{4.18} \]

The CRDS spectrum of absorbance is given as the difference of the cavity loss coefficients

\[ \alpha l_s = \frac{1}{2(L - L_0)} \tag{4.19} \]

Expressing these two loss coefficients by means of the ringdown time \( \tau = t_r/L \) and \( \tau_0 = t_r/L_0 \) (\( \tau_0 \) is not to be confused with the initial time), then the absorption of the molecular species is given by

\[ \alpha l_s = \frac{1}{2L_0(\Delta \tau / \tau)} = (1 - R)(\Delta \tau / \tau) \tag{4.20} \]
where \((\Delta \tau / \tau)\) is the actual measurement from the CRDS method.

The error measurement or performance of the technique is expressed by the following equation.

\[
\delta \alpha = \frac{(1 - R)}{l_s} \delta (\Delta \tau / \tau)
\]  \hspace{1cm} (4.21)

Previous work in this lab calculated the sensitivity using the total cavity length \(l = 98\) cm instead of the actual sample length \(l_s = 2\) cm. Thus the reported values of \(\delta \alpha\) are 49 times smaller than they would have been had the actual sample length was used in the calculation.

4.2.3 Features of the Previous CW-CRDS Experimental Setup

In the previous setup by Shucheng, Kay and Perry, a CW-CRDS apparatus was constructed using a 1.5 µm external cavity diode laser with a 2 cm pulsed slit jet and a mode matched near-confocal geometry of the cavity. According to Eq. 4.21, the performance of the previous setup CRDS technique depends on the uncertainty of the measured ringdown (\(\tau\)). In the previous setup by Shucheng and others, the uncertainty ringdown time \((\Delta \tau / \tau)\) is \(10^{-3}\) and the experimental spectrum of the combination band \(\nu_1 + \nu_3\) of methanol was recorded and assigned.

The contributing factors for the high precision of the measured ringdown time \((\tau)\) were:

1) High reflectivity of the mirrors at 99.985%.

2) The external cavity diode laser was a continuous laser source, which produced a single axial and transverse mode at a narrow bandwidth, hence eliminated mode beating as a source of error.

3) Near-confocal geometry together with mode-matching optics was implemented to shift unwanted modes from the TEM\(_{00}\) modes; therefore only pure TEM\(_{00}\) modes were recorded.

4) A planar-pulsed slit jet\(^{127}\) was used to obtain a longer absorption path-length and narrower Doppler line width; therefore the spectral lines were frequency resolved.
5) A linear fitting algorithm was employed where the log of each decay curve was fitted to a linear equation to obtain $\tau$.

4.2.4 Limitations of the Previous CW-CRDS Experimental Setup

The previous experimental setup was close to current state of the art, however there were some limitations in the performance for the present purpose of recording the $v_{CH}=2$ region. First, the external cavity diode laser tuning range was 6657.75 cm$^{-1}$-6325.11 cm$^{-1}$, which does not coincide to the $v_{CH}=2$ region. One approach is to purchase another external cavity diode laser from New Focus, but the overwhelming drawback is the low output power. The low output power would limit the spectral brightness defined as power per unit frequency interval, thus reducing the amount of light entering the cavity. The low output power effects the uncertainty measurement because it introduces more shot noise into the experiment, where shot noise is defined as the statistical noise arising from the arrivals of individual photons the detector. Second, the linear fit of the log of the ringdown ($\tau$) was fast enough for real time data collection, but provided a less precise determination of $\tau$ than a non-linear fit to an exponential function. Finally, the frequency fluctuations (8 kHz) of the external cavity diode laser limited the effective data collection rate to ~5 Hz (ringdowns/second).

4.3 Design of an Improved CW-CRDS Apparatus

The first improvement was the reflectivity of the cavity mirrors. The Los Gatos Instruments produced the cavity mirrors with higher reflectivity at 99.995%. Because $(1-R)$ is three times less, the uncertainty measurement of the experiment is expected to decrease from $1.5 \times 10^{-9}$ cm$^{-1}$ to $5.0 \times 10^{-10}$ cm$^{-1}$. Secondly, a periodically poled lithium niobate (PPLN) optical parametric oscillator (OPO) laser was purchased since it has a broad tuning range from 1.4-4 $\mu$m with the exception of the degeneracy occurring at 2.1 $\mu$m and extremely narrow bandwidth (~50 kHz), the effect allows for more light coupling into the ringdown cavity. Third, the pulsed slit jet is replaced by CW slit jet to increase the ringdown repetition rate (5 Hz⇒100 Hz), which yields
better signal averaging and faster data collection. Finally, a new fitting algorithm is used to determine a more precise ringdown time and to increase the speed of the data processing.

4.3.1 Cavity Mirrors

Based on Eq. 4.16, the ringdown time of 66.69 µs (within an empty cavity) is calculated using the reflectivity of 99.995%. The ringdown time is 3x slower than the previous setup (22 µs) because of the increased mirror reflectivity. Consequently, the expected sensitivity will increase by a factor of 3 (Eq. 4.21), and, in addition, the shot noise will be reduced by a factor of the $\sqrt{3}$ because of the increase in the total number of photons detected per ringdown if the initial detector intensity ($S(t_0)$) remains the same.

4.3.2 Continuous Wave Laser source PPLN-OPO

The PPLN-OPO continuous laser source offers a narrower bandwidth than the external cavity diode laser. Since the bandwidth is narrower (50kHz compared to 8MHz), more light can be coupled to the cavity. Secondly, the PPLN-OPO produces ~50% more output power than the external cavity diode laser. These two features increase the spectral brightness, which determines the number of photons coupled into the cavity. In the previous setup, the measured sensitivity without signal averaging was $1.7 \times 10^{-9}$ cm$^{-1}$, which was close to the shot noise limit. However, in this present setup the spectral brightness is higher thus the shot noise is smaller, and sensitivity increases.

One major drawback of this PPLN-OPO laser is that it is sensitive to the nearby vibrations from the vacuum system and other external vibrations. There are three features installed in the new system to alleviate this problem. First the legs, which support the optic table were replaced with isolators to absorb external vibrations. Second, the vacuum system was isolated from the optic table to minimized migration of vibrations. Finally, bellows/vibration dampers were installed between the turbopump and the vacuum chamber to reduce vibrations.
Also, the turbo pump is one with magnetic bearings, which minimizes the vibrations from the rotation of the turbine.

The OPO model consists of a diode Nd:YAG (Innolight Mephisto 1200) pump laser at fixed frequency of 1064 nm at 1 W power. The Nd: YAG laser is used as a pump source produces two new beams, the signal and idler beam when it is incident on the MgO-doped periodically poled lithium niobate (PPLN) non-linear medium. The lithium niobate is doped by MgO to reduce any optical damage of the crystal. The lithium niobate is periodically poled to achieve quasi-phase matching and the wavelengths are tuned in mode-hop steps of OPO-cavity free spectral range (~460 MHz) by either angle-tuning the intracavity etalon and by scanning the temperature of the PPLN crystal. The etalon within the OPO-cavity angle-tuned by applying voltage to a galvanometer.

In this present setup, the idler beam (2.28-4.67 µm, ~100 mW) from OPO model Linos OS 4500 laser is aligned through a Faraday rotator and split into two fractions, one directed into a 150 MHz marker etalon (Burleigh CFT100P) and the other into a 7.5 GHz spectral analyzer (Burleigh FCL975). These two etalons are diagnostic tools for relative frequency calibration. The signal beam at the frequency tuning range of 1.38-2.00 µm with ~50 mW of power is aligned through a second Faraday rotator (Optics For Research IO-05-1650/1770-VLP) and then through an acoustic-optical modulator (AOM Isomet 1205C-1). The first order diffracted beam (37%) from the AOM is mode-matched into the near-confocal ringdown cavity (98.98 cm) by two lens and a pinhole, whilst the undiffracted beam is aligned into a wavemeter.

4.3.3 CW slit jet nozzle

The CW slit jet nozzle (Part No. 8,9,10 Appendix K) is employed instead of previously used pulsed slit jet because it allows a higher repetition rate of cavity ringdown events. In the pulsed slit jet, the repetition rate of cavity ringdown time is limited by the repetition rate of the pulsed jet and the mass throughput, (or mass flow rate) of the vacuum system. In the previous
setup, the pulsed slit jet nozzle with a duty cycle of 3% has a calculated throughput at 0.8 Torr·l/s. Using the same duty cycle with the CW slit jet, the throughput is calculated at 26.6 Torr·l/s. Since the throughput is 33 times more than the pulsed slit jet making the operation of a continuous slit jet possible. With the jet on all the time, the data collection rate may be increased from 5 Hz in the previous experiment to 100 Hz or more.

In the present setup, a turbomolecular pump (Part 3 Appendix L) replaced the diffusion pumps because the turbomolecular pumps operate at higher throughput, therefore a new cavity ringdown apparatus was designed to accommodate the geometry specifications of the turbomolecular pump. The design of the CW-CRDS is as follows: A new stand (Part No.1 Appendix L) was constructed to uphold the cavity ringdown apparatus with a turbomount (Part No. 2 Appendix L). The turbomount securely holds the turbomolecular pump to the floor. The cavity consists of four ISO nipples (Part No.5 Appendix L) forming the arms of the cavity and a six way cross (Part No.4 Appendix L) as the vacuum chamber, where the ISO nipples were chosen for easier assembly. Buffer gases such as N₂ or methane (reference gas) are introduced into a nipple (Part No.12 Appendix L) of each arm to prevent any contamination or dust buildup on the cavity mirrors. Within the cavity, a cavity tubing (Part No.6 Appendix L) is designed to avoid any interference occurring between the laser beam and the background molecules in the chamber. Third, two optic mounts (Part No.14 Appendix L) are attached to each of the cavity mirror mounts pieces and held by rods to ensure the optical axis is maintained. Three invar rods are 48” long each were placed within the optic mount to absorb any thermal fluctuations occurring within the vacuum system, while thermal compensators (Part No.15 Appendix L) are used as fine adjustments to null out the thermal expansion of the ringdown cavity. Finally, one of the cavity mirror mounts (Part No.13 Appendix L) contain the piezoceramic was modified from the original drawings by Jeff Kay in the previous setup. The new piezomount (Part No.13 Appendix L) is designed with feedthroughs for better electrical insulation of piezo voltage signal.
Disc spring washers together with a piezoclamp provide applied force for better performance of the piezoceramic.

4.3.4. Fitting Algorithm

Another improvement is using the Halmer-Basum-Hering-Mürtz (HBHM)\textsuperscript{137} method instead of the linear fitting algorithm. The HBHM\textsuperscript{137} method is based on the fact that an integration of an exponential function is an exponential function, where the observed ringdown decay (Eq. 4.24)

\[ Y(t) = Y_0 \exp\left(\frac{-t}{\tau}\right) + b \]  

be found by its own integral and fitted to a linearized equation below:

\[ Y(X,t) = A + BX + Ct. \]  

In eq. (4.2.5), A, B and C are parameters in a linear fit. \( t \) is time, one of the independent variables; \( X \) is the other independent variable constructed as the integral of \( Y(t) \) from \( t=0 \) to \( t \). That integral is conveniently approximated using eq. (4.26).

\[ \int_0^t Y(t) + Y(t + \Delta t) \frac{\Delta t}{2} \]  

where \( \Delta t \) is the time between adjacent points on the digitized ringdown decay. The physical significance of A and C don’t really matter because all we need is the ringdown time, \( \tau = \frac{1}{B} \).

A comparison between the HBHM method\textsuperscript{137} and the non-linear Levenberg-Marquardt (LM)\textsuperscript{138} fit indicated that the HBHM method\textsuperscript{137} was 700 times faster than the LM\textsuperscript{138}. Therefore, the HBHM method\textsuperscript{137} allows the ringdowns to be processed more quickly and the data collection rate and signal averaging to be increased.

The LM\textsuperscript{138} method is an iterative technique that minimizes the total square error between the data points and the fitted functions\textsuperscript{138}. This method is considered a combination between the Gauss-Newton method and the steepest descent method. Since the LM\textsuperscript{138} method depends on the
initial guess of the function, thus the amount of time for convergence is unpredictable. In the HBHM method\textsuperscript{137}, it does not depend on an initial guess because it is non-iterative, therefore it is faster than the LM\textsuperscript{138} method.

However, the linear fit together were not compared to the HBHM method\textsuperscript{137} in this paper. Therefore, Slyvestre Twagirayezu, a graduate student in Perry’s group fitted a consistent data points to the linear, exponential (LM) and HBHM method mention above and obtained the standard derivation for evaluation. In the linear fit, where the log of the \( \tau \) is fitted to an linear equation written below:

\[
\ln y(t) = a + bt
\]

The exponential method is fitted \( \tau \) and the number of data points to the following equation.

\[
y(t) = A \times \exp\left(-\frac{t}{\tau}\right) + B.
\]

Table 14. Comparison of different Fitting Algorithms

<table>
<thead>
<tr>
<th></th>
<th>Average\textsuperscript{a}</th>
<th>STD %\textsuperscript{a}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ringdown Time</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Exponential fit (LM)</td>
<td>19.99</td>
<td>0.35</td>
</tr>
<tr>
<td>Linear fit</td>
<td>18.82</td>
<td>0.54</td>
</tr>
<tr>
<td>HBHM method</td>
<td>20.00</td>
<td>0.25</td>
</tr>
</tbody>
</table>

\textsuperscript{a}-obtained from Sylvestre Twagirayezu

The linear fit STD\%, where STD represents the standard derivation, or the mean value of the spread of data points is \(~2\times\) higher than the other methods. The linear fitting converges at \(~50\) data points but at higher data points it diverges, because the log function becomes indeterminate when it approaches smaller difference in the ringdown time values. The HBHM method\textsuperscript{137} is 1.4\times more precise than the exponential function even though there is a 0.05\% difference of the average ringdown time between these two methods. The reason is that exponential method depends on the initial guess of the amplitude and the baseline, which effects the STD \%, whereas the HBHM
method\textsuperscript{137} this is not necessary only the integration of the exponential function $X$ and $B$ is relevant.

4.4 Testing and Outlook

The above experimental setup was tested and the results were recorded to ensure no flaws were present in the design. First, the PPLN-OPO signal beam was fitted to the Gaussian beam, where the beam waist were maintained at 2 mm and the angle of divergence at $\sim 0.0042$ radian indicating the stability of the laser. Second, the alignment of the idler beam into the 150MHz and the 7.5 GHz etalons were manual scanned to check for mode-hopping properties, where Lou Delgiumberto is responsible for designing a computer program to control the laser using the 150MHz and 7.5 GHz. Third, the PPLN-OPO laser power was recorded at each optic piece within the optical layout of both the signal and idler beam to check for misalignment. Finally, the vacuum system pressure was recorded at each assembly piece to check for leakage of gas.

The power was recorded for both signal and idler beam in Table 14. The results indicated there are minimum losses therefore there is no indication of misalignment of both signal and idler beams (The experimental setup is in Appendix L).

<table>
<thead>
<tr>
<th>Optic Piece</th>
<th>Power/mV</th>
<th>Optic Piece</th>
<th>Power/mV</th>
</tr>
</thead>
<tbody>
<tr>
<td>M1</td>
<td>40</td>
<td>BS3</td>
<td>17</td>
</tr>
<tr>
<td>M2</td>
<td>25</td>
<td>M8</td>
<td>15</td>
</tr>
<tr>
<td>output F.R</td>
<td>15</td>
<td>M11</td>
<td>10</td>
</tr>
<tr>
<td>M3</td>
<td>10</td>
<td>M9</td>
<td>2-4</td>
</tr>
<tr>
<td>Trans/B1</td>
<td>4</td>
<td>M10</td>
<td>2-4</td>
</tr>
<tr>
<td>Refl/B1</td>
<td>5</td>
<td>M15</td>
<td>2-4</td>
</tr>
<tr>
<td>M4</td>
<td>5</td>
<td>M16</td>
<td>1-2</td>
</tr>
<tr>
<td>Refl/B2</td>
<td>2</td>
<td>M17</td>
<td>1-2</td>
</tr>
<tr>
<td>Trans/B2</td>
<td>1</td>
<td>M14</td>
<td>0/He-Ne</td>
</tr>
<tr>
<td>M5</td>
<td></td>
<td>M13</td>
<td>0/He-Ne</td>
</tr>
</tbody>
</table>

Trans means transmitted beam, Refl is reflected beam, and the power was recorded by the pyroelectric detector where $1mV=1mW$
Fig. 4.4 Signal Beam Optical Layout

Fig. 4.4 Idler Beam Optical Layout
The vacuum system pressure of the CW-CRDS apparatus was documented in table 15. There are minimum leaks but the CW-CRDS apparatus can operate at the experimental pressure of $10^{-4}$ Torr. The results in Table 14 and 15 indicate that the CW-CRDS is designed with minimum flaws.

<table>
<thead>
<tr>
<th>Vacuum Part</th>
<th>Pressure/Torr</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vacuum chamber w/o arms</td>
<td>$1 \times 10^{-7}$-$2 \times 10^{-6}$</td>
</tr>
<tr>
<td>Vacuum chamber w/ arms</td>
<td>$1 \times 10^{-7}$-$4 \times 10^{-6}$</td>
</tr>
<tr>
<td>Vacuum chamber w/arms and mirror mounts</td>
<td>$1 \times 10^{-7}$-$4 \times 10^{-6}$</td>
</tr>
<tr>
<td>Vacuum chamber w/</td>
<td>$2 \times 10^{-6}$-$7 \times 10^{-6}$</td>
</tr>
<tr>
<td>CW-Slit jet</td>
<td></td>
</tr>
</tbody>
</table>

and capable of recording the spectrum of the $v_{\text{CH}}=2$ region. Further test of the laser system and data acquisition will be done by Lou Deligemberto’s computer program using the Labview interface. Finally, Sylvester Twaigirayezu is designing the HBHM fitting algorithm of the CW-CRDS apparatus.
CHAPTER V
SUMMARY

Theoretical models and calculations such as \textit{ab initio} calculations and a simple model, adiabatic approximation is useful in providing an understanding of the torsion-vibrational dynamics in methanol and other related molecules. Two qualitative conclusions about the nature of intramolecular vibrational redistribution (IVR) have been obtained. First, it was shown that a potentially reactive pathway in which a new bond is formed can give rise to the IVR coupling in the bound region. Second, the adiabatic approximation reveals the origin of the scaling properties of IVR coupling matrix elements in torsional molecules.

Suggestions for future work:

(i) The 2-D potential energy surface of methanol could be calculated using the CASPT2 and MRCI level and compared to the 2-D CASSCF potential energy surface to further validate the connection between the potentially reactive pathway and the IVR coupling mechanism.

(ii) The adiabatic approximation can be transformed into the time-dependent Hamiltonian, where a wave packet is formed to follow the trajectories of the high torsional levels. The results will be able to give the projection of the changes of the motion at high torsional states.

(iii) The bending modes should also be considered together with the stretches to understand the stretch-bend interactions. Therefore, this experimental setup can be used to record the OH stretch and C-OH bending mode ($\nu_1 + \nu_6$) combination.
(iv) band spanning 1800 nm-2000 nm range, but the degeneracy gap of the OPO laser system occurs at 2.000 nm spanning the range of 653 cm$^1$. This is reaching the edge of the laser operation so it would be difficult but possible to obtain the combination band.
REFERENCES


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a. d. a. d. b. t. M. S. C. F. Basis sets were obtained from the Extensible Computational Chemistry Environment Basis sets Database, Environmental and Molecular Sciences Laboratory which is part of the Pacific Northwest Laboratory, P.O. Box 999, Richland, Washington 99352, USA, and funded by the U.S. Department of Energy. The Pacific Northwest Laboratory is a multi-program laboratory operated by Battelle Memorial Institute for the U.S. Department of Energy under contract DE-AC06-76RLO 1830.


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APPENDIX A

CALCULATION OF NUMBER OF CONFIGURATION STATE FUNCTIONS (CSF) AND SLATER DETERMINANT

The number of Slater determinants are calculated based on the following equation

\[
\frac{(2K)!}{N!(2K-N)!}.
\]

Using the binomial formula, \( \binom{n}{k} = \frac{n!}{k!(n-k)!} \) one can obtain the number of Slater determinants for methanol molecule, where \( 2K \) is spin orbitals and \( N \) is the number of electrons for methanol case of \( N=18 \) electrons, the number of spin orbitals =36.

The Weyl-Robinson’s Formula is used to calculate the number of CSF functions in a multiconfiguration calculation of the methanol molecule.

\[
CSFs = \frac{2S+1}{n+1} \binom{n+1}{N/2-S} \binom{n+1}{N/2+S+1}
\]

\( S=\text{total spin}=0 \) for singlet state, \( n \) is the active orbitals, \( N \) active electrons. In methanol \( N \) is 18 electrons with 18 orbitals. The formula is rewritten in the following form:

\[
CSFs = \frac{1}{19} \binom{19}{8} \binom{19}{10}
\]

Using the binomial formula the above equation is

\[
CSFs = \frac{1}{19} \left( \frac{19!}{9!11!} \right) \left( \frac{19!}{10!9!} \right) = 40,831,076
\]

Using the formula of 10 active electrons with 10 active orbitals the CSFs is further reduce to

\[
CSFs = \frac{1}{11} \left( \frac{11!}{5!6!} \right) = \frac{1}{11} \left( \frac{11!}{5!6!} \right) = 19,404
\]
APPENDIX B

NATURAL BOND ORBITALS ANALYSIS FOR METHANOL

The calculations of the four reference geometries were performed using \textit{MP2-6-311+G(2d,p)} using NBO as a keyword in the input file.

Table B.1 Natural Bond Orbitals analysis of Equilibrium Structure

<table>
<thead>
<tr>
<th>NBO</th>
<th>occupancy</th>
<th>%s</th>
<th>%p</th>
<th>Hybridization</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\sigma_{CH}$</td>
<td>1.998</td>
<td>74.26</td>
<td>25.74</td>
<td>$sp^3$</td>
</tr>
<tr>
<td>$\sigma_{CH}$</td>
<td>1.998</td>
<td>74.26</td>
<td>25.74</td>
<td>$sp^3$</td>
</tr>
<tr>
<td>$\sigma_{CH/anti-CH}$</td>
<td>1.994</td>
<td>74.04</td>
<td>25.96</td>
<td>$sp^3$</td>
</tr>
<tr>
<td>$\sigma_{CO}$</td>
<td>1.998</td>
<td>76.94</td>
<td>23.06</td>
<td>$sp^3$</td>
</tr>
<tr>
<td>$\sigma_{OH}$</td>
<td>1.994</td>
<td>77.68</td>
<td>22.32</td>
<td>$sp^3$</td>
</tr>
<tr>
<td>$n_O$</td>
<td>1.975</td>
<td>100</td>
<td>0.00</td>
<td>Nonbonding</td>
</tr>
<tr>
<td>$n_O$</td>
<td>1.988</td>
<td>52.7</td>
<td>47.30</td>
<td>Nonbonding/sp$^3$</td>
</tr>
<tr>
<td>$\sigma_{CH^*}$</td>
<td>0.000</td>
<td>74.26</td>
<td>25.74</td>
<td>$sp^3$</td>
</tr>
<tr>
<td>$\sigma_{CH^*}$</td>
<td>0.015</td>
<td>74.26</td>
<td>25.74</td>
<td>$sp^3$</td>
</tr>
<tr>
<td>$\sigma_{CH^*/anti-CH}$</td>
<td>0.010</td>
<td>74.04</td>
<td>25.96</td>
<td>$sp^3$</td>
</tr>
<tr>
<td>$\sigma_{CO^*}$</td>
<td>0.001</td>
<td>76.94</td>
<td>23.06</td>
<td>$sp^3$</td>
</tr>
<tr>
<td>$\sigma_{OH^*}$</td>
<td>0.006</td>
<td>77.68</td>
<td>22.32</td>
<td>$sp^3$</td>
</tr>
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</table>
### Table B.2 Natural Bond Orbitals analysis of R-OH extended for methanol

<table>
<thead>
<tr>
<th>NBO</th>
<th>occupancy</th>
<th>%s</th>
<th>%p</th>
<th>Hybridization</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\sigma_{\text{CH}}$</td>
<td>1.9967</td>
<td>25.36</td>
<td>74.64</td>
<td>$sp^3$</td>
</tr>
<tr>
<td>$\sigma_{\text{CH}}$</td>
<td>1.9967</td>
<td>25.36</td>
<td>74.36</td>
<td>$sp^3$</td>
</tr>
<tr>
<td>$\sigma_{\text{CH}/\text{anti-CH}}$</td>
<td>1.9742</td>
<td>25.76</td>
<td>74.24</td>
<td>$sp^3$</td>
</tr>
<tr>
<td>$\sigma_{\text{CO}}$</td>
<td>1.9830</td>
<td>24.06</td>
<td>75.94</td>
<td>$sp^3$</td>
</tr>
<tr>
<td>$\sigma_{\text{OH}}$</td>
<td>1.9763</td>
<td>2.65</td>
<td>97.35</td>
<td>$p$-orbital</td>
</tr>
<tr>
<td>$n_O$</td>
<td>1.9938</td>
<td>68.50</td>
<td>31.50</td>
<td>$Nonbonding/sp^1$</td>
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<td>$n_O$</td>
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<td>100.00</td>
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<td>$\sigma_{\text{CH}}^*$</td>
<td>0.0178</td>
<td>25.36</td>
<td>74.64</td>
<td>$sp^3$</td>
</tr>
<tr>
<td>$\sigma_{\text{CH}}^*$</td>
<td>0.0178</td>
<td>25.36</td>
<td>74.64</td>
<td>$sp^3$</td>
</tr>
<tr>
<td>$\sigma_{\text{CH}/\text{anti-CH}}^*$</td>
<td>0.0174</td>
<td>25.76</td>
<td>74.24</td>
<td>$sp^3$</td>
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<tr>
<td>$\sigma_{\text{CO}}^*$</td>
<td>0.0014</td>
<td>24.06</td>
<td>75.94</td>
<td>$sp^3$</td>
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<tr>
<td>$\sigma_{\text{OH}}^*$</td>
<td>0.0273</td>
<td>2.65</td>
<td>97.35</td>
<td>$p$-orbital</td>
</tr>
</tbody>
</table>

### Table B.3 Natural Bond Orbitals analysis of R-CH extended for methanol

<table>
<thead>
<tr>
<th>NBO</th>
<th>occupancy</th>
<th>%s</th>
<th>%p</th>
<th>Hybridization</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\sigma_{\text{CH}}$</td>
<td>1.9951</td>
<td>28.98</td>
<td>71.02</td>
<td>$sp^3$</td>
</tr>
<tr>
<td>$\sigma_{\text{CH}}$</td>
<td>1.9951</td>
<td>28.98</td>
<td>71.02</td>
<td>$sp^3$</td>
</tr>
<tr>
<td>$\sigma_{\text{CH}/\text{anti-CH}}$</td>
<td>1.9870</td>
<td>16.48</td>
<td>83.52</td>
<td>$sp^3$</td>
</tr>
<tr>
<td>$\sigma_{\text{CO}}$</td>
<td>1.9966</td>
<td>26.08</td>
<td>73.92</td>
<td>$sp^3$</td>
</tr>
<tr>
<td>$\sigma_{\text{OH}}$</td>
<td>1.9774</td>
<td>19.02</td>
<td>80.98</td>
<td>$sp^1$</td>
</tr>
<tr>
<td>$n_O$</td>
<td>1.9836</td>
<td>50.87</td>
<td>49.13</td>
<td>$Nonbonding/sp^1$</td>
</tr>
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<td>$n_O$</td>
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<td>100.00</td>
<td>$Nonbonding$</td>
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<td>71.02</td>
<td>$sp^3$</td>
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<tr>
<td>$\sigma_{\text{CH}}^*$</td>
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<td>71.02</td>
<td>$sp^3$</td>
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<td>16.48</td>
<td>83.52</td>
<td>$sp^3$</td>
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<td>$\sigma_{\text{CO}}^*$</td>
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B.4 Natural Bond Orbitals analysis of Both R-CH and R-OH extended for methanol

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APPENDIX C

CONTOUR PICTURES OF THE MOLECULAR ORBITALS OF
THE EQUILIBRIUM STRUCTURE OF METHANOL

The orbital diagrams does not consist of the 1s orbitals of oxygen and carbon since the 1s orbitals are not part of the valence space. Also, the orange part of each orbital represent minimum electron density while the green part represent maximum electron density. Methanol is a C\textsubscript{s} point group with A\textsuperscript{'} symmetry element, which is symmetrical in the z axis and A\textsuperscript{\texttextit{\textprime}} symmetry element, which is asymmetrical in the z axis. The calculations were performed using MP2-6-311+G(2d,p) and molden package was used to visualize the orbitals.

Symmetry element 3A\textsuperscript{'} bonding orbital
Symmetry element 4A' antibonding orbital

Symmetry Element 5A' bonding orbital
Symmetry Element 6A" non-bonding orbital

Symmetry element of 7A' bonding orbitals
Symmetry element of $8A'$ anti-bonding orbitals

Symmetry elements $9A''$ non-bonding orbital (HOMO)
Symmetry element 10A’ anti-bonding orbital (LUMO) orbital - energy gap is 0.6002 a.m.u

Symmetry element 11 A’ virtual orbital
Symmetry element 12A” of virtual orbital

Symmetry element of 13A’ of virtual orbital
Symmetry element 14A’ of virtual orbital

Symmetry element of 15A’ of virtual orbital
APPENDIX D

MOLECULAR COEFFICIENTS OF THE EQUILIBRIUM STRUCTURE FOR METHANOL

The calculations were performed using $MP2\cdot6-311+G(2d,p)$

D.1 Molecular coefficients of the R-OH atom and R-CH hydrogen atoms

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<td>0.1404</td>
<td>3A'</td>
<td>2S</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2PX</td>
<td></td>
<td></td>
<td>2PX</td>
</tr>
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<td></td>
<td>2PY</td>
<td></td>
<td></td>
<td>2PY</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2PZ</td>
<td></td>
<td></td>
<td>2PZ</td>
</tr>
<tr>
<td>0.1101</td>
<td>4A'</td>
<td>2S</td>
<td>0.0391</td>
<td>4A'</td>
<td>2S</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2PX</td>
<td></td>
<td></td>
<td>2PX</td>
</tr>
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<td></td>
<td>2PY</td>
<td></td>
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<td>2PY</td>
</tr>
<tr>
<td></td>
<td></td>
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<td></td>
<td></td>
<td>2PZ</td>
</tr>
<tr>
<td>0.0642</td>
<td>5A'</td>
<td>2S</td>
<td>0.1442</td>
<td>5A'</td>
<td>2S</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2PX</td>
<td></td>
<td></td>
<td>2PX</td>
</tr>
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<td>2PY</td>
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</tr>
<tr>
<td></td>
<td></td>
<td>2PZ</td>
<td></td>
<td></td>
<td>2PZ</td>
</tr>
<tr>
<td>0.1114</td>
<td>6A''</td>
<td>2S</td>
<td>0.0847</td>
<td>6A''</td>
<td>2S</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2PX</td>
<td></td>
<td></td>
<td>2PX</td>
</tr>
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<td>2PZ</td>
</tr>
<tr>
<td>0.1195</td>
<td>7A'</td>
<td>2S</td>
<td>0.1072</td>
<td>7A'</td>
<td>2S</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2PX</td>
<td></td>
<td></td>
<td>2PX</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2PY</td>
<td></td>
<td></td>
<td>2PY</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2PZ</td>
<td></td>
<td></td>
<td>2PZ</td>
</tr>
<tr>
<td>0.0687</td>
<td>8A'</td>
<td>2S</td>
<td>0.2772</td>
<td>8A'</td>
<td>2S</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2PX</td>
<td></td>
<td></td>
<td>2PX</td>
</tr>
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<td></td>
<td></td>
<td>2PY</td>
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<td>2PZ</td>
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<td>9A''</td>
<td>2S</td>
<td>0.0092</td>
<td>9A''</td>
<td>2S</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2PX</td>
<td></td>
<td></td>
<td>2PX</td>
</tr>
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<td>2PY</td>
<td></td>
<td></td>
<td>2PY</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2PZ</td>
<td></td>
<td></td>
<td>2PZ</td>
</tr>
<tr>
<td>0.0245</td>
<td>10A'</td>
<td>2S</td>
<td>0.0176</td>
<td>10A'</td>
<td>2S</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2PX</td>
<td></td>
<td></td>
<td>2PX</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2PY</td>
<td></td>
<td></td>
<td>2PY</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2PZ</td>
<td></td>
<td></td>
<td>2PZ</td>
</tr>
</tbody>
</table>
D3. Cont’d The probability coefficients of carbon and oxygen in each symmetry element of 
$C_3$ point group

<table>
<thead>
<tr>
<th>$\sum_{i} c_{iu}^2$</th>
<th>Symmetry/Carbon</th>
<th>Orbitals</th>
<th>$\sum_{i} c_{iu}^2$</th>
<th>Symmetry/Oxygen</th>
<th>Orbitals</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.02268 11A'</td>
<td>2S</td>
<td>2PX 2PY 2PZ</td>
<td>0.17936 11A'</td>
<td>2S</td>
<td>2PX 2PY 2PZ</td>
</tr>
<tr>
<td>0.00000 12A&quot;</td>
<td>2S</td>
<td>2PX 2PY 2PZ</td>
<td>0.00000 12A&quot;</td>
<td>2S</td>
<td>2PX 2PY 2PZ</td>
</tr>
<tr>
<td>0.07040 13A'</td>
<td>2S</td>
<td>2PX 2PY 2PZ</td>
<td>0.00432 13A'</td>
<td>2S</td>
<td>2PX 2PY 2PZ</td>
</tr>
<tr>
<td>0.04550 14A'</td>
<td>2S</td>
<td>2PX 2PY 2PZ</td>
<td>0.08432 14A'</td>
<td>2S</td>
<td>2PX 2PY 2PZ</td>
</tr>
<tr>
<td>0.00151 15A'</td>
<td>2S</td>
<td>2PX 2PY 2PZ</td>
<td>0.01284 15A'</td>
<td>2S</td>
<td>2PX 2PY 2PZ</td>
</tr>
</tbody>
</table>
APPENDIX E

NATURAL ORBITAL BOND ORDER OF METHANOL STRUCTURES

In accordance with Pulay and others\(^4\), the starting orbitals are chosen based on the criteria that any fractional occupations numbers between the values of 0.02 and 1.98 are considered part of the active space, whereas occupation numbers >1.98 are doubly occupied and <0.02 are unfilled orbitals, these are usually consist of the inactive space. In the table 2 above, the following orbitals in the b), c) and d) structures clearly indicated the triplet instability of the Hartree-Fock wavefunction within the three structures b), c), and d). This calculations were performed using MP2-6-311+G(2d,p).

Table E1. Natural Orbital bond order of Methanol Structures

<table>
<thead>
<tr>
<th></th>
<th>(a)</th>
<th>(b) R-CH extended</th>
<th>(C) R-OH extended</th>
<th>(d) Both Extended</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Symmetry</strong></td>
<td>7A’ σ\text{CH}/anti</td>
<td>7A’ σ\text{CH}/anti</td>
<td>7A’ σ\text{CH}/anti</td>
<td>7A’ σ\text{CH}/anti</td>
</tr>
<tr>
<td><strong>Occupation</strong></td>
<td>1.994</td>
<td>1.987</td>
<td>1.9742</td>
<td>1.9424</td>
</tr>
<tr>
<td><strong>Symmetry</strong></td>
<td>13A’ σ\text{CH}*/anti</td>
<td>13A’ σ\text{CH}*/anti</td>
<td>13A’ σ\text{CH}*/anti</td>
<td>13A’ σ\text{CH}*/anti</td>
</tr>
<tr>
<td><strong>Occupation</strong></td>
<td>0.01</td>
<td>0.3276</td>
<td>0.0174</td>
<td>0.0643</td>
</tr>
<tr>
<td><strong>Symmetry</strong></td>
<td>3A’ σ\text{CO}/anti</td>
<td>...</td>
<td>...</td>
<td>3A’ σ\text{CO}/anti</td>
</tr>
<tr>
<td><strong>Occupation</strong></td>
<td>1.998</td>
<td>...</td>
<td>...</td>
<td>1.998</td>
</tr>
<tr>
<td><strong>Symmetry</strong></td>
<td>10A’ σ\text{CO}*/anti</td>
<td>...</td>
<td>...</td>
<td>10A’ σ\text{CO}*/anti</td>
</tr>
<tr>
<td><strong>Occupation</strong></td>
<td>0.001</td>
<td>...</td>
<td>...</td>
<td>0.0398</td>
</tr>
<tr>
<td><strong>Symmetry</strong></td>
<td>5A’ σ\text{OH}/anti</td>
<td>5A’ σ\text{OH}/anti</td>
<td>5A’ σ\text{OH}/anti</td>
<td>5A’ σ\text{OH}/anti</td>
</tr>
<tr>
<td><strong>Occupation</strong></td>
<td>1.994</td>
<td>1.9774</td>
<td>1.9763</td>
<td>1.9357</td>
</tr>
<tr>
<td><strong>Symmetry</strong></td>
<td>11A’ σ\text{OH}*/anti</td>
<td>11A’ σ\text{OH}*/anti</td>
<td>11A’ σ\text{OH}*/anti</td>
<td>11A’ σ\text{OH}*/anti</td>
</tr>
<tr>
<td><strong>Occupation</strong></td>
<td>0.006</td>
<td>0.0072</td>
<td>0.0273</td>
<td>0.0525</td>
</tr>
<tr>
<td><strong>Symmetry</strong></td>
<td>9A’n_\text{O}</td>
<td>9A’n_\text{O}</td>
<td>9A’n_\text{O}</td>
<td>9A’n_\text{O}</td>
</tr>
<tr>
<td><strong>Occupation</strong></td>
<td>1.988</td>
<td>1.972</td>
<td>1.9716</td>
<td>1.9726</td>
</tr>
</tbody>
</table>
APPENDIX F

CORRELATION CONSISTENT BASIS SET EXponents

The exponents of the basis set are given by using the GFinput or GFprint or Gen keyword in the route section of the Gaussian input file.

F1. The exponents of the correlation consistent basis sets in the Gaussian 'O3 program

<table>
<thead>
<tr>
<th>Gaussian '03</th>
<th>Contraction Scheme</th>
</tr>
</thead>
<tbody>
<tr>
<td>cc-pVDZ</td>
<td>3S((\zeta))</td>
</tr>
<tr>
<td>CARBON</td>
<td>0.1596</td>
</tr>
<tr>
<td>OXYGEN</td>
<td>0.3023</td>
</tr>
<tr>
<td>HYDROGEN</td>
<td>2S((\zeta))</td>
</tr>
<tr>
<td></td>
<td>0.1220</td>
</tr>
<tr>
<td>cc-pVTZ</td>
<td>4S((\zeta))</td>
</tr>
<tr>
<td>CARBON</td>
<td>0.1285</td>
</tr>
<tr>
<td>CARBON</td>
<td>0.2384</td>
</tr>
<tr>
<td>HYDROGEN</td>
<td>3S((\zeta))</td>
</tr>
<tr>
<td></td>
<td>0.1027</td>
</tr>
</tbody>
</table>

The exponents of the Molpro package is given in the basis set library of the user’s manual or the following website: [http://www.emsl.pnl.gov/forms/basisform.html](http://www.emsl.pnl.gov/forms/basisform.html)
APPENDIX G

EXAMPLE OF AN INPUT OF THE MCSCF CALCULATION ON MOLRPO

***ch3ohequil
roh=3.151925392, rco=2.73065184, ahco=105.93547563, rch2=2.06154682, rch=2.094808338,
acoh=108.09064819, ahco2=111.62097560, da=61.66525187, dc=180
geometry={Z;
  C;
  O, C, rco;
  H1, O, roh, C, acoh;
  H2, C, rch, O, ahco, H1, dc;
  H3, C, rch2, O, ahco2, H1, da;
  H4, C, rch2, O, ahco2, H1, -da}
cartesian
basis=avdz

{hf;occ,7,2;wf,18,1,0}

{multi;closed,4;occ,11,3;wf,18,1,0}

optg;inactive,roh,rch
APPENDIX H

POTENTIAL ENERGY SURFACES OF ADVANCED AB INITIO CALCULATIONS

a) 2-D potential energy surface of CCSD(T)-pVDZ level b) non-additive part of a)

a) 2-D potential energy surface of CASSCF-aug-pVDZ level b) non-additive part of a)
Table H.1 Coefficients obtained from fitting the potential energy surface

<table>
<thead>
<tr>
<th></th>
<th>MP2 level</th>
<th>CCSD-pVDZ</th>
<th>CCSD(T)-pVDZ</th>
<th>CASSCF-aug-pVDZ</th>
<th>Expt$^d$</th>
<th>Calculated$^d$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_{11}$</td>
<td>-1458</td>
<td>-1013</td>
<td>-844.8</td>
<td>-2006</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$C_{21}$</td>
<td>908.5</td>
<td>1284</td>
<td>-1644</td>
<td>-3750</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$C_{12}$</td>
<td>-2428</td>
<td>-2502</td>
<td>-39.41</td>
<td>1896</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$C_{22}$</td>
<td>575.3</td>
<td>2494</td>
<td>-892.3</td>
<td>-434.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$C_{13}$</td>
<td>-2952</td>
<td>-3288</td>
<td>-2634</td>
<td>-6583</td>
<td>-1.79</td>
<td></td>
</tr>
<tr>
<td>$C_{31}$</td>
<td>-986.6</td>
<td>-4254</td>
<td>-2862</td>
<td>-2549</td>
<td>3.70</td>
<td></td>
</tr>
</tbody>
</table>

**Coupling Matrix element**

- $C_{11}$: -19.6
- $C_{21}$: -21.8
- $C_{12}$: -26.0
- $C_{22}$: -41.4
- $C_{31}$: 23.5
- Calculated: 26.5

Units are in cm$^{-1}$

- **a**-Reference 2
- **b**-Reference 54
- **c**- The potential energy surface from b is fitted by a fourth order polynomial
- **d**-The potential energy surface from b is fitted by a sixth order polynomial
APPENDIX I

FILENAMES AND THEIR LOCATION IN PERRY'S COMPUTER

OF THE AB INITIO CALCULATIONS

Gaussian '98

Computer Names

Metis/Europa

DESKTOP

MAIN FILENAME

G98

H₂O₂

BACKUP

CONTOUR

ETHANE

NEWDATA

THERMO

TIGHT

opt.com
opt.log
eclhXX.com
eclhXX.log
eclhtestXX.com
eclhtestXX.log
mapXX.com
mapXX.log
eclethXX.com
eclethXX.log
ethXX.com
ethXX.log
opt.com
opt.log
XXrchi5.com/X
Xrchi5.log
bothXX.com/bo
thXX.log
XXroh.com
XXroh.log
2EQUIL

ccdpot.com/ccdpot.log
cpot.com/ccpot.log
cctt.com/cctt.log
fre.com/fre.log
fre2.com/fre2.log
freq.com/freq.log
tigXX.com/tigXX.log
troXX.com/troXX.log

cXX.com/cXX.log
etXX.com/etXX.log
davidXX.com/davidXX.log
equiXX.com/equiXX.log
uXX.com/uXX.log
DESCRIPTION OF FILENAMES AND DIRECTORIES

In the Directory H$_2$O$_2$, the following filenames contained the results of the depth of valley calculations of the hydrogen peroxide.

opt.com/opt.log- The optimized equilibrium structure at $MP2-6-311+G(3df,2p)$.

elchXX.com/elchXX.log- XX represents 01-03 series is the partial optimized of all four structures in the $MP2-6-311+G(2D,2P)$ first calculated on Jupiter computer.

eclhtestXX.com/eclhtestXX.log-XX represents 01-06 is the partial optimization of all four structures with the torsional dihedral angle constrained at different values.

The directory Backup all the files within the 6 directories is saved.

The Contour Directory the following filenames contained the results of the potential energy surface at $CCSD-pVDZ$ level. The XX represents 00-13 files.

The directory Ethane consists of the results of the depth of valley calculations of the Ethane molecule.

eclethXX.com/eclethXX.log-The XX represents 00-04 where the first file is an optimization of eclipsed equilibrium structure at $MP2-6-311+G(3df,2p)$, the subsequent files are partial optimization of the four structures at $MP2-6-311+G(2d,2p)$ of the eclipsed structure.

ethXX.com/ethXX.log- The XX represents 00-03 and it contains the results of partial optimization of the four structure using $MP2-6-311+G(2d,2p)$ of the staggered conformation.

opt.com/opt.log- the optimized structure of the staggered equilibrium structure at $MP2-6-311+G(3df,2p)$.

The subdirectory 2EQUIL is under Newdata directory. This subdirectory contains the higher-level calculations.
APPENDIX I CONT’D
DESCRIPTION OF FILENAMES AND DIRECTORIES CONT’D

ccpot.com/ccpot.log- the four structures partially optimized at CCSD-pVDZ level.

cctt.com/cctt.log- are the results of the partially optimization of the four structures at the CCSD-pVTZ level.

fre.com/fre.log, fre2.com/fre2.log and freq.com/freq.log are Raman frequencies of the
equilibrium geometry from MP2-6-311+G(2d) to MP2-6-311+G(2d,2p).

tigXX.com/tigXX.log-XX is 00 series where the four structures are partially optimized at the
CCSD(T)-cc-pVDZ.

troXX.com/troXX.log-XX is 00-03 series, where the four structures are partially optimized at the
CCSD(T)-pVTZ.

The directory THERMO consists of file that pertains to calculations of the bond energies
of the methoxyl, hydroxylmethyl radicals and the formadehyde molecule.

XXrch5.com/XXrch5.log, XXroh.com/XXroh.log and XXboth.com/XXboth.log- XX represents
01-03 are files that each contained the bond energy of hydroxylmethyl, methoxyl and
formadehyde molecule. The first XX are their respective equilbrium geometries optimized at
MP2-6-311+G(3df,2p). The 02 files are error in convergence and 03 are recalculation of 02 files.

The directory TIGHT is single point energy calculation of 2EQUIL.

ccXX.com/cc.XX.log- XX represents 00-03 series. The files are single point calculation at
CCSD-pVDZ level.

cXX.cm/cXX.log- XX represents 00-03 series. The files are single point calculation at
CCSD(T)-pVDZ level.
APPENDIX I CONT’D

DESCRIPTION OF FILENAMES AND DIRECTORIES CONT’D

davidXX.com/davidXX.log - XX represents 00-03 series. The files consist of partially optimization of the four structures but using the keyword add-redundant instead of opt=z-matrix is used to request the calculations be done in redundant internal coordinates instead of non-redundant internal coordinates.

equiXX.com/equiXX.log-are similar to davidXX.com/davidXX.log but the torsional angle is constrained, both files MP2-6-311+G(2d,2p) levels are used.

uXX.com/uXX.log-is single point calculations of the four structures but with unrestricted MP2-6-311+G(2d,2p).

The results are recorded and saved in energy3-98 and energy3xreal excel files in g98 directory.

The igor file ccsd.pxp file contained all the potential energy graphs while nbo.pxp is where the natural bond analysis graph on the desktop of both computers.

Molpro 2002.6 (Higher Level Calculations) Filenames

CASSCF directory contained the calculations of the depth of valley for the CASSCF calculations.

XX correspond to the 00-02 series.

optimcarXX.com/optimcarXX.log -is the optimized calculations of the four structures using the cc-pVDZ basis set.

testcarXX.com/testcarXX.log -is the partially optimized calculations of the four structures using the cc-pVTZ basis set.
APPENDIX I CONT’D

MOLPRO 2002.6 (HIGHER LEVEL CALCULATIONS) FILENAMES CONT’D

augcarXX.com/augcarXX.log -is the partially optimized calculations of the four structures using the aug-cc-pVDZ basis set.

augcartvzXX.com/augcarvtz.XX.log -is the partially optimized calculations of the four structures using the aug-cc-pVTZ basis set.

The directory energypoint contained the MRCI and the CASPT2 calculations.

XX-correspond to the series 00-03.

The mrci prefix is the MRCI calculations, while rst prefix is the CASPT2 calculations.

mrciXX.com/mrciXX.log and rsXX.com/rsXX.log-is the partially optimized calculations of the four structures using the cc-pVDZ basis set.

mrcivtzXX.com/mrcivtzXX.log and rstvtzXX.com/rstvtzXX.log-is the partially optimized calculations of the four structures using the cc-pVTZ basis set.

mrciavdzXX.com/mrciavdzXX.log and rstavdzXX.com/rstavdzXX.log- is the partially optimized calculations of the four structures using the aug-cc-pVDZ basis set.

mrciavtzXX.com/mrciavtzXX.log and rstavtzXX.com/rstavtzXX.log- is the partially optimized calculations of the four structures using the aug-cc-pVTZ basis set.
The excel file energyG-03 contained all the results of the calculation above.
Results of this calculation is recorded in energy3-G03.xls excel file
APPENDIX J

SOFTWARE DOCUMENTATION OF THE ADIABATIC APPROXIMATION

The main directory is matlabwork saved on the Desktop of both Europa and Metis. The following is the list of the programs and the authors.

1. BOhelp.m

David S.Perry; Matlab 6.1 version; This program give the list of all the programs used in the adiabatic approximation calculation of the three CH stretches($\nu_3$, $\nu_9$ and $\nu_2$) as fast coordinate and torsion as the slow coordinate.

Files implemented for the Zeroth (Crude) Adiabatic Approximation

2. vibs2.m;torsv2.m

David S.Perry; Originally written by David S. Perry and Xiaoliang Wang; Maple package; Matlab 6.1 version; This program calculates the vibrations at one torsional angle, while torsv2 calculates the effective torsional potentials and vibrational eigenvector as a function of torsional angle.

3. cur_torsv2.m

Trocia Clasp; Matlab 6.1 version; curve fitting using linear least squares fit from the output of torsv2 file to obtain the $v_0$, $v_3$ and $v_6$ terms of the torsional potential fourier series (Eq. 3.7).

4. torsham.m

Trocia Clasp; Matlab 6.1 version; Originally written by David S. Perry and Xiaoliang Wang; Maple package; This file produces the Hamiltonian matrix for a three-fold potential (Eq. 3.8).
5. **pot_torsv3.m**

    Trocia Clasp; Matlab 6.1 version; This program calculates the torsional levels from the effective potential obtained the output of cur_torsv2.m which is entered as input in torsham.m file.

6. **BO_vects.m**

    David S. Perry; Matlab 6.1 version; This program returns the Zeroth order eigenvectors and calls the same routines as BO_vibs.

7. **mmth.m**

    David S. Perry; Matlab 6.1 version; produces a matrix to convert torsional eigenvectors to wavefunctions in angle space.

8. **BO_plot.m**

    David S. Perry; Matlab 6.1 version; plots the torsional probability function.

9. **phase.m**

    David S. Perry; Matlab 6.1 version; aligns the vibrational eigenvector phases to fix phase jumps.

**Files implemented for the First-Order Correction to the Adiabatic Approximation**

**torsv2.m, vibs2.m, cur_torsv2.m pot_torsv3.m and torsham.m** are used with their respective functions expressed above.

1. **vibsfit.m**

    David S. Perry; Matlab 6.1 version; fits the three CH vibrational wavefunctions from the output of torsv2.m into a Fourier series the result is given in a 3-Dimensional matrix.

2. **adiabatcorr.m**

    Trocia Clasp; Matlab 6.1 version; calculates the Fourier terms from vibsfit.m of the adiabatic correction.

3. **adiabat_pot.m**
Trocia Clasp; Matlab 6.1 version; applies the adiabatic corrections to the output of cur_torsv2 to obtain a better effective torsional potential.

**Files implemented for finding the torsional adiabatic energies and wavefunctions and transformation to the adiabatic basis (Eq. 3.17 and Eq. 3.23).**

torsv2.m, vibs2.m, vibsfit.m and pot_torsv3.m are used with their respective functions expressed above.

1. adiabat23.m
   Trocia Clasp; Matlab 6.1 version; calculates the squared vector potential (Eq. 3.16)

2. adiabat_pot12.m
   Trocia Clasp; Matlab 6.1 version; Forms the adiabatic effective potential “ad1” from the zeroth-order effective potential “a” and the vector potential “Ae2”.

3. BO3.m
   Trocia Clasp; Matlab 6.1 version; calculates the torsional energies and eigenfunctions using integer or half-integer angular momenta as necessary for each of the three normal modes.

4. llop2.m
   Trocia Clasp; Matlab 6.1 version; calculates the transformation matrix “QQQ” that transforms the free-rotor/local mode basis into the adiabatic basis.

5. coupling.m
   Trocia Clasp; Matlab 6.1 version; calculates the coupling matrices and torsional energies in the adiabatic basis,

**Files implemented of David S. Perry and Xialang Wang’s Hamiltonian**

1. wangham.m
   David S. Perry and Xialang Wang; Matlab 6.1 version; sets up the free internal rotor basis Hamiltonian.

2. diagblock.m
David S. Perry and Xialang Wang; Matlab 6.1 version; sets up the diagonal block.

3. **lamblock.m**

David S. Perry and Xialang Wang; Matlab 6.1 version; sets up the lambda block.

**Files implemented for the torsional levels of Butyne**

1. **Butyntorsv.m**

Trocia Clasp; Matlab 6.1 version; calculates the torsional levels from the effective potentials contained in “a”.

2. **Butysham.m**

Trocia Clasp; Matlab 6.1 version; produces the torsional Hamiltonian matrix for a 3-fold torsional problems.

3. **Info.m**

Trocia Clasp; Matlab 6.1 version; is the input file for the Butyntorsv.m and Butysham.m

**Visual Basis Files implemented for analysis of data in \( \lambda \) plots.**

1. **Module 1-SubRealExamples**

Trocia Clasp; Microsoft Excel Visual Basis; retrieves and organized the \( \lambda \) values.

2. **Module (2-5 and 7-8)-Nu9E, Nu9A, Nu3A, Nu3E, Nu2A, Nu2E**

Trocia Clasp; Microsoft Excel Visual Basis; organized the \( \lambda \) values.

3. **Module 6-Copyit**

Trocia Clasp; Microsoft Excel Visual Basis; copy the values to a new worksheet.

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function hlp=BOhelp

% The following is a list of the m-files used in the Adiabatic Approximation
% and the relationships among them.
% Files for the implementation of the 0th-order Born-Oppenheimer calculation
% * BO * calculates the torsional manifolds for the 3 CH vibrations
% in the Born-Oppenheimer limit; it calls:
% * torsv2 * calc effective torsional potentials and vibrational eigenvector
% as a function of torsional angle.
% * vibs2 * calculates vibrations at one torsional angle
% * cur_torsv2 * curve fits to get V0, V3, and V6 terms => "a"
% * pot_torsv3 * calculates the torsional levels
% * torsham * sets up the torsional Hamiltonian matrix
% * BO_vects * returns the BO eigenvectors and calls the same routines as BO-vibs
% * mmth * produces a matrix to convert torsional eigenvectors to wavefunctions in angle space
% * BO_plot * plots the torsional probability function
% * phase * aligns the vibrational eigenvector phases to fix phase jumps
% Files for implementation of 1st-order correction to the BO approximation
% * torsv2 * calc effective torsional potentials and vibrational eigenvector
% as a function of torsional angle.
% * vibs2 * calculates vibrations at one torsional angle
% * cur_torsv2 * curve fits to get V0, V3, and V6 terms => "a"
% * vibsfit * fits vib eigenvectors to a Fourier series in the torsional angle => "c"
% * phase * aligns the vibrational eigenvector phases to fix phase jumps
% * adiabatcorr * calculates the Fourier terms of the adiabatic correction => "ve1"
% * adiabat_pot * applies adiabatic corrections to the output of * cur_torsv2 * to
% obtain a better effective torsional potential => "ad"
% * pot_torsv3 * calculates the torsional levels. Use "ad" as input.
% * torsham * sets up the torsional Hamiltonian matrix
% Files for finding the torsionally adiabatic energies and wavefunctions
% (solution to Eq. E-9) and
% transformation to adiabatic basis (Eq G-1)
% * torsv2 * calc effective torsional potentials and vibrational eigenvector
% as a function of torsional angle.
% * vibs2 * calculates vibrations at one torsional angle
% based on Wang's parameters
% * vibsfit * fits vib eigenvectors to a Fourier series in the torsional angle => "c"
% "c" contains the coefficients "f_ski" in Eq G-4.
% * phase * aligns the vibrational eigenvector phases to fix phase jumps
% * adiabat23 * calculates the squared vector potential (Eq E-7)
% "c" -> "Ae2"
% (* adiabat12 * Calculates the plain vector potential (eq E-6a)
% "c" -> "Ae1"; not actually used)
% * adiabat_pot12" * Forms the adiabatic effective potential "ad1" from the
% zeroth order effective potential "a" and the vector potential "Ae2".
% * BO3 * calculates the torsional energies and eigenfunctions
% using integer or half integer angular momenta as necessary
% for each of the three normal modes l=1,2,3.
% "ad1" -> "BO_vibs" gives "b" in Eq G-5.
% * pot_torsv3 * calculates the adiabatic energies and
% wavefunctions (Eq E-9),
% Treats only half-integer OR integer angular momenta
% * torsham * sets up the torsional Hamiltonian matrix
% * llop2 * calculates the transformation matrix "QQQ" that transforms the
% free-rotor/local-mode basis into the adiabatic basis
% * Files for implementation of Wang's Hamiltonian
% * wangham * sets up Wang's Hamiltonian matrix
% * diagblock * sets up the diagonal block
% * lamblock * sets up the lambda blocks
% Wang's parameters mu=12.9340
% lbda= -42.2450
% w=2933.95
% v=373.5421
% v1= -0.80
% F =27.65388
hlp= ' Type "help BOhelp" to get a list of m-files';

function [vibfv]=vibs2(v,v1,w,lbda,mu,gam)
%VIBS Calculate CH frequencies, vibf, and wavefunctions, vibv,
% as a function of the torsional angle, gam.
% SYNTAX: vibfv=vibs2(w,lbda,mu,gam)
% Wang Eq 22.
% gam is torsional angle in degrees; internally gamr is in radians
gamr=gam*pi/180;
r=v/2-v/2*cos(3*gamr)+v1/2-v1/2*cos(6*gamr);
l=[w,0,0;0,0,0;0,v1,0];
ll=[0,lbda,lbda;lbda,0,lbda;lbda,lbda,0];
M=[3*mu*cos(gamr),0,0,3*mu*cos(gamr-2*pi/3),0,0,3*mu*cos(gamr+2*pi/3)];
H=l+ll+M;
[vibv,EE]=eig(H);
vibf1=diag(EE);
vibf=vibf1+r;
v=[vibf';vibv];
vibfv=sortrows(v');

vibs2.m Cont'd
torsv2.m

function [th,vib]=torsv2(th0,thinc,thf,v,v1,w,lbda,mu)
%TORSV  Use function VIBS2 to calculate eff torsional potentials
% for angles 'th0' to 'thf' in steps 'thinc'
% Concatenate results into the 3-D array 'vib'
% List of torarional angles is given in the column vector 'th'.
n=0;
for t=th0:thinc:thf
  if n==0
    th=t;
    [vib]=vibs2(v,v1,w,lbda,mu,t);
  else
    th=[th;t];
    [vibfv]=vibs2(v,v1,w,lbda,mu,t');
    vib=cat(3,vib,vibfv);
  end
  n=n+1;
end

cur_torsv2.m

function [a]=cur_torsv2(th,vib)
% Cur_fitting of vib to get V0, V3, and V6 terms
% using a linear least squares fit
% On output, "a" contains

y=squeeze(vib(:,1,:));  % y is a matrix with 3 columns,
                        % each column being a set of frequencies to be fit.
P=randn(72,1);        % produces a random matrix
P=repmat(1,[72,1]);  % replaces the random matrix with one's
T=0.5-0.5*cos(3*th*pi/180);  % this is equation for the V3 torsional energy
M=0.5-0.5*cos(6*th*pi/180);  % This is equation for the V6 torsional energy
X=[P T M];          % vector of X
[a]=X'y;            % Non-linear polynomial equations solutions to torsional potential

torsham.m

function [H]=torsham(vn,F, mmax)
% TORSHAM produces the hamiltonian matrix for a 3-fold torsional problem
% vn is a vector with V0, V3, and V6
% F is the torsional inertial constant
% mmax is maximum value of the free internal rotor quantum number, m
% The dimension of H is 2*mmax+1 by 2*mmax+1

for i=1:2*mmax+1 % initialize rows

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for j=1:2*mmax+1 %initialize columns
    m=-mmax+j-1;
    if i==j
        H(i,j)=m^2*F+vn(1)+vn(2)/2+vn(3)/2;
    elseif i==j+3 | i==j-3
        H(i,j)=-vn(2)/4;
    elseif i==j+6 | i==j-6
        H(i,j)=-vn(3)/4;
    else
        H(i,j)=0;
    end
end
end

pot_torsv3.m

function [BOvibs]=pot_torsv3(a,f,mmax)
%pot_torsv3 calculates the torsional levels
%          from the effective potentials contained in "a"
%          "f" is the torsional inertial constant in cm-1
%          If mmax is integer then 2pi boundary conidions are used
%                 (geometric phase = 0)
%          If mmax is a half-integer then 4pi boundary conidions
%                 are used (geometric phase = 1)

for n=1:3
    vn=a(:,n);
    [H]=torsham(vn,f,mmax); % set up the first hamiltonian matrix
    [D,Tor]=eig(H);       % find the eigenvalues and vectors
    Time=diag(Tor);
    Time2=[Time',D];
    Time3=sortrows(Time2');
    % sort in descending order
    if n==1
        [BOvibs]=Time3;
    else
        BOvibs=cat(3,BOvibs,Time3);
    end
end

pot_torsv3.m Cont’d

[BOvibs]=Time3;
else
    BOvibs=cat(3,BOvibs,Time3);
end
BO_vects.m

function [symvibs, antivibs]=BO_vects(v,f,w,lbda,mu,mmax)
% BO_vects calculates the lowest torsional eigenvectors for the 3 CH vibrations
% in the Born-Oppenheimer limit
% v is the V3 potential term
% f is the torsional inertial constant
% w the local vibrational frequency
% lbda is the local-local coupling
% mu is the torsion-vibration coupling as per Wang's paper
% mmax is the maximum value of m in the internal rotor basis
% BO_vects on output has 3 columns, one each for the torsional
% manifolds of nu3, nu9, and nu2, with nu9 and nu2 calculated
% based on 4 pi boundary conditions and half-integer free
% rotor basis functions.

th0=0;
thinc=10;
thf=360;
[th,vib]=torsv2(th0,thinc,thf,v,w,lbda,mu);
[a]=eur_torsv2(th,vib)
m=fix(mmax);
[symvibs]=pot_torsv3(a,f,m); % 2 pi boundary conditions
mp=m+0.5;
[asymvibs]=pot_torsv3(a,f,mp); % 4 pi boundary conditions
symvects=symvibs(1:9,:,:);
antivects=asymvibs(1:9,:,:);

mmth.m

function mth=mmth(mmax,thinc)
% function MMTH produces a rectangular matrix mth that will transform
% the wavefunction mvec in the m basis (-mmax<=m<=mmax)
% to the the to a wavefunction in the torsional angle in increments thine (degrees)

mmth.m Cont’d

inc=thinc*pi/180;
k=1;
norm=1/sqrt(2*pi)
for k=0:inc:2*pi % rows are torsional angles
    for j=1:2*mmax+1 % columns are m's
        m=-mmax+j-1;
        mth(kk,j)=norm*exp(i*m*k);
    end
    kk=kk+1;
end
**phase.m**

```matlab
function vv=phase(vv)
%PHASE adjusts the phases of the eigenvectors given in the rows of "vv"
% so that there are no arbitrary phase jumps on progressing from
% one row to the next.
% (Note that the first column of "vv" contains the eigenvalues and
% and the corresponding eigenvectors follow in the same row.)
max=size(vv,1);
nswitch=0;
for t=2:max
   if ( abs(vv(t,2)-vv(t-1,2))>0.2 | abs(vv(t,3)-vv(t-1,3))>0.2 | abs(vv(t,4)-vv(t-1,4))>0.2 )
      vv(t,2:4)=-vv(t,2:4);
      nswitch=nswitch+1;
   end
end
```

**adiabt_pot.m**

```matlab
function ad=adiabt_pot(a,ve1)
%ADIABT_POT applies the adiabatic corrections "c" to the effective torsional
% potential in "a"
b(1,:)=2*sum(ve1(1:end,:))
s=size(ve1);
ss=s(1);
st=(ss+1)/2;
b(2,:)=-2*(ve1(st+6,:)+ve1(st-6,:));
b(3,:)=-2*(ve1(st+12,:)+ve1(st-12,:));
ad=real(a+b);
```

**adiabatcorr.m**

```matlab
function ve1=adiabatcorr(c,f)
%ADIABATCORR calculates the Fourier terms of the adiabatic correction
% to the approximate separation of torsion form the CH vibrations
% ve1 will contain the Fourier components of the correction for each CH
% vibration as given in "c" and obtained from "vibsfit".
% f is the torsional inertial constant
% for n=1:3
   ff=c(:,2:end,n);
   gg=ff';
   hh=ff*gg
   hha=size(hh);
   hhn=hha(1);  % total number of m values including half intergers
   mmax=(hn-1)/4;
   lmax=mmax;
   for l=-lmax:0.5:lmax  % l labels the Fourier terms
```
ll=2*(lmax+l)+1; % ll is the index that corresponds to l
ve1(ll,n)=0;
for m=-mmax:0.5:mmax % m labels a Fourier component of the CH wavefunction
    mm=2*(mmax+m)+1; % mm is the index the corresponds to m
    ml=m-l;
    mll=2*(mmax+ml)+1;
    if (mll>=1) & (mll<=hhn);
        ve1(ll,n)=ve1(ll,n)+f*m^2*hh(mm,mll);
    end
end
end

vibsfit.m

function [c,th2]=vibsfit(th,vib)
%VIBSFIT fits the CH vibrational wavefunctions in vib to a Fourier series
% and the result is given in the 3-D matrix c.
% th2 is the list of torsional angles. When th has range 0 to 2-pi,
% then th2 has range 0 to 4-pi.
% vv1, vv2, and vv3 contain the eigenvalues and eigenvectors for each
% of the 3 CH stretches from lowest to highest frequency.
vv3=[squeeze(vib(3,:,:))';squeeze(vib(3,:,1:end))'];
vv2=[squeeze(vib(2,:,:))';squeeze(vib(2,:,1:end))'];
vv1=[squeeze(vib(1,:,:))';squeeze(vib(1,:,1:end))'];
th2=[th;th(1:end)+360];

vibsfit.m

vv1=phase(vv1);
vv2=phase(vv2);
vv3=phase(vv3);
d=size(vv1);
dd=d(1);
mmax=13;
n=4*mmax+1;
X=ones(dd,n);
for m=-mmax:0.5:mmax;
    k=2*mmax+1+2*m;
    X(:,k)=exp(-m*i*th2*pi/180);
end
X;
vv1;
[c1]=X\vv1; % linear polynomial equations solutions to torsional potential
vv2;
[c2]=X\vv2;
vv3;
[c3]=X\vv3;
c=cat(3,c1,c2,c3);
adiabt23.m

function Ae2=adiabt23(c,f)
%This function calculates the square of the geometric potential
%c is the fourier components from vibsfit

for n=1:3
    for p=1:3
        ff=c(:,2:end,n);
        ffp=c(:,2:end,p);
        gg=ffp';
        hh=ff*gg;
        hhn=size(hh);
        mmax=(hhn-1)/4;
        lmax=mmax;
        for l=-lmax:0.5:lmax
            ll=2*(lmax+l)+1;
            Ae2(ll,n,p)=0;
            for m=-mmax:0.5:mmax
                mm=2*(mmax+m)+1;
                ml=m-l;
                mll=2*(mmax+ml)+1;
                if (mll>=1) & (mll<=hnn)
                    Ae2(ll,n,p)=Ae2(ll,n,p)+m^2*(hh(mm,mll))^2;
                end
            end
        end
    end
end

adiabat23.m

adiabat_pot12.m

function ad1=adiabt_pot12(a,Ae2)
%ADIABT_POT appiles the adiabatic corrections "c" to the effective torsional potential in "a"
%b1(1,:)=2*sum(Ae2(1:end,:))
s=size(Ae2);
s1=s(1);
s2=(s1+1)/2;
b1(2,:)=-2*(Ae2(st+6,:)+Ae2(st-6,:));
b1(3,:)=-2*(Ae2(st+12,:)+Ae2(st-12,:));
b2=real(b1);
b3=b2(1,:)+b2(4,:)+b2(7,:);
b4=b2(2,:)+b2(5,:)+b2(8,:);
b5=b2(3,:)+b2(6,:)+b2(9,:);
b0=[b3,b4,b5];
ad1=a+b0;
function QQQnew=llop2(c,BO_vibs3,qlim)

% llop2 calculate the transformation matrix from the free-rotor/local-mode
% basis (q,k) to the adiabatic basis (n,i)

ppn=BO_vibs3; % Fourier comonents of the adiabatic torsional wavefunctions
ff=c(:,2:end,:); % Fourier components of the vibrational wavefunctions

ppna=size(ppn);
mlim=0.5*ppna(1) % total number of m values including half intergers

ca=size(c)
slim=0.25*(ca(1)-1) % number od s values: -s to +s
sslim=4*slim+1; % 4*slim+1

qna=2*qlim+1; % number of q values: -q to +q

for i=1:3; % i goes from 1 to 3 - Labels nu3, nu9, and nu2
    for n=1:ppna(1); % n goes from 1 to 55 - Labels adiabatic torsional functions
        in=(i-1)*ppna(1) + n;
        for k=1:3 % Labels the 3 local CH bonds
            for q=qlim:qlim % Labels ang momentum components of the local-CH - free-rotor basis functions
                kq=(k-1)*qna+qlim+1+q; %14
                QQQ(in,kq)=0;
                for m=-mlim:0.5:mlim % Labels ang momentum of free-rotor basis
                    s=q-m;
                    mm=2*mlim+1+2*m;
                    ss=2*slim+1+2*s;
                    if (ss>=1) & (ss<=sslim)
                        ppnt=ppn(n,mm,i);
                        fft=ff(ss,k,i);
                        QQQ(in,kq)=QQQ(in,kq)+ppnt*fft;
                    end
                end
            end
        end
    end
end
end
coupling.m

function [hbnew,couptm]=coupling(QQQ,H1)
%This function calculates the coupling matrices and torsional energies in
%the adiabatic basis limit.

QQQnew=conj(QQQ);
hbnew=QQQnew*H1*QQQnew';
[P,hbp]=eig(hbnew);
Cou=diag(hbp);
coupt=[Cou';P];
couptm=sortrows(coupt');

wangham.m

function H1=wangham(vn,F,mu,lbda,phi,mmax)
% wangham sets up Wang's Hamiltonian matrix according to his Eq 22, 23, and 24
% vn is a vector with the V0, V3 and V6 torsional potential terms
% V0 is the same as omega used by Wang
% f is the torsional inertial constant
% mu is the torsion-vibration coupling
% phi is the phase angle for the particular block
% lbda is the local-local coupling parameter

phi1=0;
h11=diagblock(vn,F,mu,phi1,mmax);
phi2=-2*pi/3;
h22=diagblock(vn,F,mu,phi2,mmax);
phi3=2*pi/3;
h33=diagblock(vn,F,mu,phi3,mmax);
ho=lamblock(lbda,mmax);
h1=[h11 ho ho];
h2=[ho h22 ho];
h3=[ho ho h33];
H1=cat(1,h1,h2,h3);
function H1=diagblock(vn,F,mu,phi,mmax)
% Calculate a diagonal block accoring to Wang eq 25
% vn is a vector with the V0, V3 and V6 torsional potential terms
% V0 is the same as omega used by Wang
% f is the torsional inertial constant
% mu is the torsion-vibration coupling
% phi is the phase angle fopr the particular block

for k=1:2*mmax+1 % initialize rows
    for j=1:2*mmax+1 %initialize columns
        m=-mmax+j-1;
        if k==j
            H1(k,j)=m^2*F+vn(1)+vn(2)/2+vn(3)/2;
        elseif k==j+1
            H1(k,j)=1.5*mu*exp(-i*phi);
        elseif k==j-1
            H1(k,j)=1.5*mu*exp(+i*phi);
        elseif k==j+3 | k==j-3
            H1(k,j)=-vn(2)/4;
        elseif k==j+6 | k==j-6
            H1(k,j)=-vn(3)/4;
        else
            H1(k,j)=0;
        end
    end
end

function H1=lamblock(lbda,mmax)
% Calculate an off-diagonal block accoring to Wang eq 24

for k=1:2*mmax+1 % initialize rows
    for j=1:2*mmax+1 %initialize columns
        m=-mmax+j-1;
        if k==j
            H1(k,j)=lbda;
        else
            H1(k,j)=0;
        end
    end
end
butyneHlp.m

function ButyneHlp=info()
% Butysham calculates the torsional eigenfunctions
% 1-Butyne Torsional eigenfunctions is used to
% illustrate the similar scaling properties as Methanol

%**************************F=5.8433cm^{-1}
%************************** V3=1089.9cm^{-1}
% ****************************************Vn= is not entered because it is for any CH-stretches
% ****************************************V6= is not known but could be added later

Butysham.m

function [BH]=Butysham(vn,F, mmax)

% TORSHAM produces the hamiltonian matrix for a 3-fold torsional problem
% vn is a vector with V0, V3, and V6
% F is the torsional inertial constant
% mmax is maximum value of the free internal rotor quantum number, m
% The dimension of H is 2*mmax+1 by 2*mmax+1

for i=1:2*mmax+1 % initialize rows
    for j=1:2*mmax+1 % initialize columns
        m=-mmax+j-1;
        if i==j
            BH(i,j)=m^2*F+vn(1)+vn(2)/2+vn(3)/2;
        elseif i==j+3 | i==j-3
            BH(i,j)=-vn(2)/4;
        elseif i==j+6 | i==j-6
            BH(i,j)=-vn(3)/4;
        else
            BH(i,j)=0;
        end
    end
end
[vibv,EE]=eig(BH);
vibf1=diag(EE);
v=[vibf1';vibv];
vibfv=sortrows(v);
function [BHvibs]=Butyntorsv(vn,F, mmax,BH)
%Buynetorsv calculates the torsional levels
% from the effective potentials contained in "a"
% "f" is the torsional inertial constant in cm^{-1}

[BH]=Butysham(vn,F, mmax)
[vib,EE]=eig(BH);
vibf1=diag(EE);
v=[vibf1';vibv];
BHvibs=sortrows(v');

Public Sub Real Example

Public Sub RealExample()

' This program is set up to retrieve the values of nu3A-E,nu9A-E,nu2A-E
' in a large matrix 27*1083 with lambda values ranging from -16:0.1:20

Dim ws As Worksheet
Dim newsheet As Object
Set newsheet = Worksheets.Add
For Each ws In ActiveWorkbook.Worksheets
    NU_3A 'Retrieve data for Nu3A
    NU_3E 'Retrieve data for Nu3E
    NU_9A 'Retrieve data for Nu9A
    NU_9E 'Retrieve data for Nu9E
    NU_2A 'Retrieve data for Nu2A
    NU_2E 'Retrieve data for Nu2E
    Next
End Sub
Public Sub NU_9E

Public Sub NU_9E()

For n = 1 To 63

Cells(3, 2 + ((n - 1) * 3)).Copy

Cells(n, 64).PasteSpecial Transpose:=True

Next

End Sub

Public Sub NU_3A

Public Sub NU_3A()

For n = 1 To 63

Cells(1, 1 + ((n - 1) * 3)).Copy

Cells(n, 64).PasteSpecial Transpose:=True

Next

End Sub

Public Sub NU_9A

Public Sub NU_9A()

For n = 1 To 63

Cells(1, 2 + ((n - 1) * 3)).Copy

Cells(n, 64).PasteSpecial Transpose:=True

Next

End Sub
Public Sub NU_3E

Public Sub NU_3E()

For n = 1 To 63

Cells(2, 1 + ((n - 1) * 3)).Copy

Cells(n, 64).PasteSpecial Transpose:=True

Next

End Sub

Public Sub CopyIt

Public Sub CopyIt()

' This macro will only work if your sheet names are numeric

' Example: the sheet for the first day is 1

' Count how many sheets are in this workbook

LastSheet = ActiveWorkbook.Sheets.Count

' What is the name of the last sheet?

LastName = ActiveWorkbook.Sheets(LastSheet).Name

' Add one to the last name to get the new name

NewName = LastName + 1

' Make a Copy of the last sheet

ActiveWorkbook.Sheets(LastSheet).Copy after:=Worksheets(LastName)

'Rename the sheet for today

NewLast = LastSheet + 1

ActiveWorkbook.Sheets(NewLast).Name = NewName

End Sub
Public Sub NU_2A

Public Sub NU_2A()
For n = 1 To 63
Cells(3, 3 + ((n - 1) * 3)).Copy
Cells(n, 64).PasteSpecial Transpose:=True
Next
End Sub

Public Sub NU_2E

Public Sub NU_2E()
For n = 1 To 63
Cells(1, 3 + ((n - 1) * 3)).Copy
Cells(n, 64).PasteSpecial Transpose:=True
Next
End Sub
APPENDIX K

ADIABATIC APPROXIMATION GRAPHS OF EFFECTIVE POTENTIALS

AND GEOMETRIC PHASE

![Graph showing Adiabatic Approximation of Effective Potentials and Geometric Phase](image)
A plot of wavefunction of the $\nu_2$ vs the torsional angle. The 1,2,3 correspond to the CH bond position 1,2,3. This graph illustrates the geometric phase.
APPENDIX L

AUTOCAD DIAGRAMS OF CAVITY RINGDOWN APPARATUS

ASSEMBLY DIAGRAM OF CW-CRDS APPARATUS
The main directory EXPERIMENT saved on the Desktop of Metis and Europa contained the autocad drawings under the subdirectory CR06Drawings. Ricardo Campos-Ramos designed all the components of the Cavity Ringdown instrument except for one of the two cavity mirror mount (Piezomount) and the turbomount designed by Trocia Clasp. Jeff Kay designed the second cavity mirror mount (Not shown in this experimental setup).

1. **Vacuum stand** - The vacuum stand supports the vacuum chamber, turbomolecular pump, and the vibrator isolator.

2. **Turbomount** - This piece is securely attached to the floor to prevent movement of the turbomolecular pump.

3. **Mag W 2200 C turbomolecular pump and vibrator isolator** - designed and purchase by Leybolds vacuum.

4. **Six-way cross** - This item is the main chamber of the CW-CRDS apparatus.

5. **Arms of the cavity** - This item consists of NW 100 nipples for easier assembly and adjustment of length.

6. **Cavity tubing** - This piece is designed to prevent any interference effects.

7. **Flange #1** - This piece supports the CW-slit jet nozzle and the nozzle manipulation stage.

   Flange #2 (Not shown in assembly picture) - designed to accommodate an ionization gauge, leak valve of the chamber, and thermocouple gauge. The vacuum chamber consists of another Flange #3 (Not shown in assembly picture), which is used for checking the alignment of deflected laser beam.

8. **Nozzle manipulation stage** - this changes the x-y direction of the CW slit jet Nozzle for better signal reception. It contains three pieces, the lid, x-y assembly and the nozzle holder.

9. **Venting tube holder** - this item is the inlet for the sample gas (methanol) and argon the carrier gas.
(10) **CW slit jet nozzle**- purpose is to produce a jet nozzle for passage of the sample methanol and argon the carrier gas.

(11) **NW100 Centering Ring**- The centering ring is an attachment to the Invar rod mount plate, bellows, and piezomount.

(12) **NW100 Flange**- The NW100 flange is an attachment from the NW100 centering ring to the cavity arms. It also contains the 1/16” npt inlet, which allows the passage of nitrogen gas to the piezomount to keep the cavity ringdown mirrors clean.

(13) **Piezomount**- This piece contained the cavity ringdown mirrors and electrical components for the operation of the piezo.

(14) **Invar Rod mounting plate**- This attachment supports the invar rod in place and maintains the optical axis of the arms.

(15) **Thermal Compensator**- This is a sliding holder fitted for the invar rod. The purpose is to accommodate small changes occurring within the vacuum system.
The Vacuum Stand

CW CRDLAS PROJECT

MATERIAL: Angle (L-1/2x-1/2x3/16)
STAINLESS STEEL 304 (brush finished)
Hole diameter: 0.43" (for all)
SCALE: 3" = 1" UNIT INCHES
By: Ricardo Campos Ramos
11/07/05
File: documents/layout 11
The Vacuum Stand Cont’d

FRAME TOP VIEW

CW CRDLAS PROJECT

MATERIAL: Angle (1–1/2x–1/2x3/16)
STAINLESS STEEL 304(brush finished)
Hole diameter: 0.43” (for all) BOLTS: M10x1.5x30
SCALE: 3”=1” UNIT: INCHES
By: Ricardo Campos Ramos
11/07/05
File: documents/layout 11
Vacuum stand Cont’d

CW CRDLAS PROJECT

MATERIAL: Angle (1–1/2x1/2x3/16)
STAINLESS STEEL 304 (brush finished)
SCALE: 3” = 1’ UNIT: INCHES
By: Ricardo Campos Ramos
11/07/05
FILE: documents/layout11

FRAME
TOP VIEW
TOP VIEW
ASSEMBLED WITH PUMP FLANGE BOLT CIRCLE

The four holes in the A, B, C stainless steel pieces are to mate with 4 holes 90 degrees apart in a ISO-NW200 flange.

Ø10.2400"

CW CRDLAS PROJECT
MATERIAL: Angle (1-1/2x-1/2x3/16)
STAINLESS STEEL 304 (brush finished)
Hole diameter: 0.43" (for all)
SCALE: 3"=1' UNIT: INCHES
By: Ricardo Campos Ramos
11/07/05
File: layout 11
Vacuum stand Cont’d

**FRAME SIDE VIEW**

**CW CRDLAS PROJECT**

**MATERIAL:**
STAINLESS STEEL 304 (brush finished)

**SCALE:** 3” = 1” Unit: inches

By: Ricardo Campos Ramos
10/06/05

File: layout 11

Flat sides for adjustment with wrench

2.5000"

5.0000"

30.4500"

29.5000"
CW CRDLA PROJECT

BY: Trocia Clasp
Material: Steel, welded for strength
Tube wall Thickness: (1/4–1/2)"
Flanges may have center holes to make welding easier.
The thickness of flanges and of the tube may be adjusted to match convenient stock sizes.
The top surface of the small flange must be machined flat to mate with a turbopump, but the bottom surface is not critical.
Six-way cross

SIX WAY CROSS
4 way cross w 2 additional NW 100 (VF-6800-SF)
UNITs: inches
SCALE: 3”=1’
Material: SS 304

PROJECT CW CRDLA
By: Ricardo Campos Ramos
FILE: documents/layout04a
October 28, 2005

QUOTE: Q011669 Huntington(10/25/05)
Arms of the Cavity

NIPPLES (ISO–NW100)
Material: SS 304
Scale: 1:2 Units: inches
Quantity: One of each.

CW CRDLA PROJECT
By Ricardo Campos Ramos
File: my documents/layout14a
04/15/06
Cavity Tubing

CAVITY TUBING HOLDER
Material: ALUMINUM
Scale: 1:1 Unit: Inches
02 pieces

o-ring:
ID=1.0
OD=1-3/8
w=3/16

CAVITY TUBING
Material: ALUMINUM
Scale: 1:1 Unit: Inches
02 pieces

CW CRDLA PROJECT
By: Ricardo Campos Ramos
File: layout19
02/23/06
Flange #1, #2

O-RING 2-231
(ID: 2–5/8, OD: 2–7/8, width: 1/8)

FLANGE # 1
(ISO-NW200)
Material: SS 304
Scale: 1:2 Units: inches
Quantity: 1

CROSS SECTION

CW CRDLA PROJECT
By Ricardo Campos Ramos
File: my documents/layout14
11/14/05
FLANGE # 2 (ISO–NW200)
2 NW16 AND 2 NW40 NIPPLES
Material: SS 304
Scale: 1:2 Units: inches

FRONT VIEW

CROSS SECTION

CW CRDLA PROJECT
By Ricardo Campos Ramos
File: my documents/layout12
11/14/05
Nozzle manipulation stage

![Diagram of nozzle manipulation stage with dimensions and notes.]

**NOZZLE MANIPULATION STAGE**
- Material: Aluminum-2024 (duralumin)
- Quantity: 1
- Scale: 1:1 Unit: Inches

CW CRDLAS PROJECT
Nozzle manipulation stage Cont’d

FRONT VIEW

X-Y ASSEMBLY
Material: Aluminum
Scale: 1:1 Unit: Inches
Quantity: 01

CW CRDLAS PROJECT
By: Ricardo Campos Ramos
12/07/05 File: documents/layout13
Nozzle manipulation stage Cont’d

VENTING TUBE
Material: SUS-304
Scale: 1:1 Units: Inches
Quantity: 01

SLIDER
Material: Teflon
Scale: 1:1 Units: Inches
Quantity: 8 (4A and 4B)

SLEEVE FOR NOZZLE VENTING TUBE
Material: Teflon
Scale: 1:1 Unit: Inches
Quantity: 01

CW CRDLAS PROJECT
By: Ricardo Campos Ramos
12/07/05 File: documents/layout13
Nozzle manipulation stage Cont’d

FRONT VIEW

SIDE VIEW

LID
Material: Aluminum
Scale: 1:1 Unit: Inches
Quantity: 01

CW CRDLAS PROJECT
By: Ricardo Campos Ramos
12/06/05 File: documents/layout13
Venting tube holder

VENTING TUBE HOLDER
Material: SUS-304
Quantity: 1
Scale: 1:1 Unit: Inches

CW CRDLAS PROJECT
By: Ricardo Campos Ramos
11/22/05 File: documents/layout13
CW slit jet nozzle

**CW SLIT JET NOZZLE**
Material: Aluminum Scale: 1:2
Units: inches Quantity: 1

**CW CRDLA PROJECT**
By Ricardo Campos Ramos
File: my documents/layout16
01/23/06
**CW slit jet nozzle**

**RAZOR BLADE**
Cut and make holes in two single-edge razor blades.

Scale: 1:2 Units: inches

**CW CRDLA PROJECT**
By Ricardo Campos Ramos
File: my documents/layout16
01/23/06
CW slit jet nozzle

SLIT NOZZLE BODY
Material: SS 304
Scale: 1:2 Units: inches
Quantity: 1

CW CRDLA PROJECT
By Ricardo Campos Ramos
File: my documents/layout16
01/23/06
CW slit jet nozzle

CROSS SECTION B

CW SLIT JET NOZZLE
Material: Aluminum Scale: 1:2
Units: inches Quantity: 1

CW CRDLA PROJECT
By Ricardo Campos Ramos
File: my documents/layout16
01/23/06
CW slit jet nozzle

CROSS SECTION A

CROSS SECTION B,C

CW SLIT JET NOZZLE
Material: Aluminum Scale: 1:2
Units: inches Quantity: 1

CW CRDLA PROJECT
By Ricardo Campos Ramos
File: my documents/layout16
01/23/06
NW100 Centering Ring

Material: Stainless steel
Scale: 1:1 Unit: Inches
02 pieces

NW100 CENTERING RING

Material: Stainless steel
Scale: 1:1 Unit: Inches
02 pieces

CW CRDLA PROJECT

By: Ricardo Campos Ramos
File: layout19
02/07/06
NW100 Flange

MOUNTING FLANGE
(ISO--NW100)
Material: SS 304
Scale: 1:2 Units: inches
Quantity: 2

CW CRDLA PROJECT
By Ricardo Campos Ramos
File: my documents/layout14a
04/18/06
Piezomount

SIDEVIEW OF PIEZO ASSEMBLY

Piezo Clamp

Washers OD: 1-3/16", ID: 7/8"
Thickness: 1/64"
Quantity: 2

Disc Spring Washer: OD: 1.159"
ID: 901"
Thickness: .040" deflection distance

Cavity

Mirror

Clamp

Ceramic Piezo

Gap Between

Optic Mount drawing
J. Kay

Top Teflon Holder

Bottom Teflon Holder

0.597"
Piezomount

FRONT VIEW OF PIEZO MOUNT

BACK VIEW OF PIEZO MOUNT

SIDE VIEW OF PIEZO MOUNT

A - DR four clearance holes fitted for 8-32 Socket screw
B - DR four tapped holes fitted for 8-32 Socket screw
Material: stainless steel
Quantity: 2
Units: inches
Scale: 1" = 1"
Piezomount

SIDEVIEW OF PIEZO CLAMP

TOP VIEW OF PIEZO CLAMP

Groove for 2-128 O-ring
INVAR ROD MOUNTING PLATE

Material: Aluminum
Scale: 1:2 Units: inches
Quantity: 2

CW CRDLA PROJECT
By Ricardo Campos Ramos
File: my documents/layout14a
04/19/06
Thermal Compensator

Holes Tapped for #8–32 set screw

0.874”

6.000”

0.510”

(0.210” (Sliding fits on Invar Rod 0.5”)

0.520” Cross Section A (90 degrees apart)

0.625” Cross Section B (90 degrees apart)

THERMAL COMPENSATOR

Material: Aluminum (Anodized black)

PIECES #1

Scale: 1:2 Units: inches

Quantity: 3

CW CRDLA PROJECT

By Ricardo Campos Ramos

File: my documents/layout20

04/19/06