

PHOTOLUMINESCENT ORGANIC MOLECULES FROM THE
PERSPECTIVE OF DENSITY FUNCTIONAL THEORY

by

Richard Douglas Massaro
A Dissertation
Submitted to the
Graduate Faculty
of
George Mason University
in Partial fulfillment of
The Requirements for the Degree
of
Doctor of Philosophy
Computational Sciences and Informatics

Committee:

Estela Blaisten

Dr. Estela Blaisten-Barojas, Dissertation Director

D. Papacon

Dr. Dimitrios Papaconstantopoulos, Committee Member

Howard Sheng

Dr. Howard Sheng, Committee Member

J. Cebal

Dr. Juan Cebal, Committee Member

Michael Summers

Dr. Michael Summers, School Director

R. Diecchio

Dr. Richard Diecchio, Associate Dean for Academic and
Student Affairs, College of Science

Vikas Chandhoke

Dr. Vikas Chandhoke, Dean, College of Science

Date: April 29, 2011

Spring Semester 2011
George Mason University
Fairfax, VA

Photoluminescent Organic Molecules from the Perspective of Density Functional Theory

A dissertation submitted in partial fulfillment of the requirements for the degree of
Doctor of Philosophy at George Mason University

By

Richard Douglas Massaro

Master of Arts

Boston University, 2004

Bachelor of Science

James Madison University, 2001

Director: Dr. Estela Blaisten-Barojas, Professor
School of Physics, Astronomy, and Computational Sciences

Spring Semester 2011
George Mason University
Fairfax, VA

Copyright © 2011 by Richard Douglas Massaro
All Rights Reserved

Dedication

I dedicate this dissertation to my family from whom I have received endless love, support, and understanding.

Acknowledgments

I would like to thank my advisor, Professor Estela Blaisten-Barojas, for her invaluable guidance and patience throughout my education at George Mason University. She painstakingly took the time to review all of my work and happily offered her insight and knowledge at every step along the way. Simply put, this dissertation would not have been possible without her help.

I would also like to thank my committee members, Dr. Dimitrios Papaconstantopoulos, Dr. Howard Sheng, and Dr. Juan Cebral. They took the time to review my manuscripts and supplied me with excellent recommendations.

I am grateful to the U.S. Army Corps of Engineers and U.S. Department of the Army for financial support of my education. I would like to thank Dr. John Anderson and Dr. Clint Smith for their guidance and providing me with the motivation to pursue the research presented in this dissertation.

Finally, I would like to thank my family for their unending source of love and understanding. To my parents, who have always been there to support me and provide much needed confidence boosts, and to my wife, Maggie, for her love, patience, and understanding - even while seven months pregnant with our first baby.

Table of Contents

	Page
List of Tables	vii
List of Figures	ix
Abstract	xi
1 Introduction	1
1.1 Methyl Salicylate	2
1.2 Dipicolinic Acid	6
2 Methods	8
2.1 Ab Initio Methods	8
2.1.1 Hartree-Fock Method	9
2.1.2 Configuration Interaction (CI) and CI-Singles (CIS)	11
2.2 Density Functional Methods	12
2.2.1 Density Functional Theory (DFT)	12
2.2.2 Time-Dependent Density Functional Theory (TDDFT)	16
2.3 Structural Optimization	20
2.4 Vibrational Analysis	21
2.4.1 Free Energy	23
2.5 Chemical Reaction Paths	24
3 Methyl Salicylate	26
3.1 Introduction	26
3.2 Structural Isomers and Energetics	27
3.3 Vibrational Analysis	33
3.4 Free Energy	40
3.5 Gas Phase Reaction Paths	41
3.6 Conclusion	42
4 Methyl Salicylate Excited States	44
4.1 Introduction	44
4.2 Excitation	44
4.3 Optimized Excited State Structures	45

4.4	Excited State Vibrational Analysis	59
4.5	Calculated Photoluminescence	60
4.6	ESIPT physical representation	62
4.7	Results	64
4.8	Conclusion	70
5	Dipicolinic Acid	73
5.1	Introduction	73
5.2	Structural Isomers and Energetics	73
5.3	Vibrational Analysis	80
5.4	Gas Phase Reaction Paths	85
5.5	Dimers	87
5.6	2-Dimensional and 3-Dimensional Structures	92
5.7	Band Structure	97
5.8	Conclusion	104
6	Computational Tools and Implementation	106
6.1	Computing Platforms	106
6.2	Software	106
6.3	Scripts and Pseudocode	108
7	Concluding Remarks	111
A	Script for job submission to ERDC HPC	114
B	Pseudo-code for calculating Franck-Condon factors	115
C	List of publications	117
	Bibliography	143

List of Tables

Table	Page
3.1 Geometry of methyl salicylate in the ground state.	30
3.2 Total electronic energy, zero point energy (ϵ_0), dipole moment, binding energy (BE), electron affinity (E.A.), ionization potential (I.P.), and HOMO/LUMO gap of each MS isomer.	31
3.3 Rotational constants for the six gas phase isomers of MS calculated with B3PW91/6-311++G	33
3.4 Calculated vibrational spectra of ¹ ketoB and ¹ ketoA isomers	36
3.5 Vibrational frequencies of the five MS isomers.	37
4.1 TDDFT calculated vertical excitations of MS in gas phase. ΔE is energy (in eV) above each isomer ground state, λ is the wavelength (in nm) of transition from ground to excited states, and f is the oscillator strength ($\times 10^{-2}$). . . .	47
4.2 Geometry of the first excited singlet of the ketoB isomer calculated with B3PW91/6-311++G(3d,3p)	48
4.3 Geometry of the first excited singlet of the enol isomer calculated with B3PW91/6-311++G(3d,3p)	49
4.4 Comparison of key structural differences in ground and first excited singlet state isomers of MS computed at the B3PW91/6-311++G(3d,3p) level. . .	50
4.5 TDDFT calculated excited state emissions of MS isomers in gas phase. ΔE is energy (in eV) above isomer ground state, λ is the wavelength (in nm) of transition, and f is the oscillator strength.	51
4.6 Summary of the vibrational calculations for the excited states of ¹ ketoB and ¹ enol using B3PW91 with different basis sets.	59
5.1 Bond lengths (in Å) of DPA isomers optimized with B3LYP/6-31G(d) . . .	76
5.2 Angles (in deg) of DPA isomers optimized with B3LYP/6-31G(d)	76

5.3	Electronic states, total electronic energies, zero point energies (ϵ_0), binding energies (BE), and dipole moments of the DPA isomers. The electron affinities (EA), ionization potentials (IP), and HOMO-LUMO gap (Δ) are also reported. Total electronic energies E are relative to the $^1\text{DPA1}$ ground state energy of -17.018746 keV.	77
5.4	Mulliken charges of DPA isomers calculated with B3LYP/6-31G(d)	77
5.5	Calculated Vibrational Spectra of DPA Ground State Isomer and Comparison with Experiments	83
5.6	Calculated Vibrational Spectra of DPA Isomers	84
5.7	Electronic states, total electronic energies, zero point energies (ϵ_0), dimer formation energies ($E_{\text{formation}}$), electron affinities (EA), ionization potentials (IP), and HOMO-LUMO gap (Δ) of DPA dimers. Total electronic energies E are relative to the $^1\text{2DPA1}$ ground state energy of -34.038310 keV. . . .	89
5.8	Summary of 2-D and 3-D DPA structures optimized at the B3LYP/6-31G(d) level. Total electronic energies E for the 2-D and 3-D structures are relative to the DPA4 case.	93

List of Figures

Figure	Page
3.1 Geometries of the six MS isomers	29
3.2 Plot of sum squared error vs. vibrational scaling factor for ketoB and ketoA MS isomers	34
3.3 IR spectra of MS	38
3.4 Free energy vs. temperature of the MS isomers	41
3.5 IRC reaction path of ketoB to ketoA	42
4.1 Structure of three stable MS isomers in their singlet excited states optimized at the B3PW91/6-311++G(3d,3p) level.	46
4.2 Occupied and unoccupied molecular orbital levels of ground and excited state ketoB and enol.	52
4.3 Excited and ground state energy levels at varying OH bond distances. At each point, MS was structurally optimized with a frozen O15-H12 length. .	54
4.4 (A) Variation of the O9-O15 distance with O9-H12 length in the excited states of ketoB and enol. At each point, MS was structurally optimized with a frozen O15-H12 length. (B) Mulliken atomic charges of O9, O15, and H12 at varying R_c	56
4.5 Contour plot of the excited state potential energy surface with changing O9- O15 and O15-H12 bonds. Each contour line represents a difference of 0.001 eV.	57
4.6 Surface plot of the excited state potential energy surface showing variation with O9-H12 distance and with C13-O15 distance. The minimum energy ESIPT path is shown as a black line on the surface.	58
4.7 Calculated gas phase MS fluorescence spectra at 300 K	65
4.8 Experimental liquid MS spectra at 300 K	67
4.9 Calculated MS fluorescence spectra at temperatures of 77, 173, 201, 231, 258, and 273 K.	68
4.10 Law and Shoham's experimental spectra with temperature dependence. . .	69
5.1 Six isomers of gas phase DPA optimized at the B3LYP/6-31G(d) level. . . .	75

5.2	Calculated Fukui functions for DPA isomers.	79
5.3	Calculated infrared spectra of the six isomers of DPA at the B3LYP/6-31G(d) level.	82
5.4	IRC reaction pathways between the DPA monomers.	86
5.5	Dimers of DPA optimized at the B3LYP/6-31G(d) level.	88
5.6	Calculated infrared spectra of the five dimers of DPA at the B3LYP/6-31G(d) level.	90
5.7	Occupied and unoccupied molecular orbital levels calculated for DPA isomers.	91
5.8	Optimized 2-D sheet of DPA4	94
5.9	Optimized 2-D sheet of DPA5	95
5.10	Optimized 2-D sheet of DPA6	96
5.11	Band structure of DPA4 crystal calculated along symmetry lines Δ , C, Σ , D.	98
5.12	Band structure of DPA4 crystal calculated along symmetry lines Λ , A, Σ , G.	99
5.13	Band structure of DPA5 crystal calculated along symmetry lines Δ , C, Σ , D.	100
5.14	Band structure of DPA5 crystal calculated along symmetry lines Λ , A, Σ , G.	101
5.15	Band structure of DPA6 crystal calculated along symmetry lines Δ , C, Σ , D.	102
5.16	Band structure of DPA6 crystal calculated along symmetry lines Λ , A, Σ , G.	103
6.1	Flow chart of the calculations needed to model photoluminescence using Gaussian and the Franck-Condon factor code.	110

Abstract

PHOTOLUMINESCENT ORGANIC MOLECULES FROM THE PERSPECTIVE OF DENSITY FUNCTIONAL THEORY

Richard Douglas Massaro, PhD

George Mason University, 2011

Dissertation Director: Dr. Estela Blaisten-Barojas

I have studied the electronic structure, vibrational modes, and photophysics of methyl salicylate (MS) isomers in detail using density functional theory (DFT) and its time-dependent (TDDFT) companion. I have confirmed that six isomers are stable in their ground states with the ketoB isomer being the global minimum structure. I have performed free energy calculations which show that other isomers may be energetically favorable at higher temperatures. The calculated vibrational modes of ketoB match well with experimental infrared spectra.

Using TDDFT, I have confirmed that the ketoB isomer undergoes an energetically favorable excited-state intermolecular proton transfer (ESIPT) to an enol isomer. I found that the ESIPT has a small potential energy barrier when the proton transitions from the ketoB to the enol structure and a ten times larger barrier to accomplish a reverse ESIPT from enol to ketoB. The barrier asymmetry is responsible for the temperature dependent suppression of the far-blue fluorescence. I modeled the emission spectra for gas phase MS using Franck-Condon factors based on the calculated 0-0 transition and vibrational modes for the ground and excited states. The calculated spectra match well to gas phase experimental spectra.

Finally, I performed detailed DFT studies on dipicolinic acid (DPA) and determined its

stable structures, energetics, and vibrational modes. My calculations predict the existence of six stable isomers of gas phase DPA in the ground state. Three of these isomers are nearly energetically degenerate. I calculated several transition state reaction paths between these isomers. I performed similar calculations on five dimerized formations. By using periodic boundary conditions (PBC) on three dimerized DPA arrays containing hydrogen-bonding DPA monomers, I was able to predict three different crystal structures. I report the band structures of the resulting DPA crystals for the first time. All of them are insulators.

Chapter 1: Introduction

Photoluminescence is the process in which a material undergoes an energy transition from an excited state to its ground or lower excited state by the emission of a photon. The excited state is typically populated through photon absorption. Fluorescence and phosphorescence are two forms of photoluminescence. In fluorescence, an atom or molecule will absorb a high energy photon (typically at UV wavelengths), dissipate some energy away as heat or vibrations, and then emit a lower energy photon. The entire fluorescence process is very fast and occurs on the order of a few nanoseconds or less. In phosphorescence, the process can take many orders of magnitude longer. A photon is absorbed in the same way as the fluorescence process but, instead of a rapid emission of a longer wavelength photon, a more complicated mechanism of intersystem crossing takes place. Intersystem crossing is the transition from one spin state, or multiplicity, to another one. Intersystem crossings typically occur between singlet and triplet states. As applied to phosphorescence, the absorbed photon energy is contained in the triplet state and the subsequent long-lived emission is a “forbidden transition” from the triplet back to the ground state. This energy transition is said to be “forbidden” because quantum selection rules do not allow electric dipole mediated transitions. However, multipole transitions are still allowed to occur; albeit at slower rates. The slow rate of multipole transitions is the reason for the long lifetime of phosphorescence. The characterization of photoluminescence can also be described as “steady-state” or “lifetime”. Steady-state photoluminescence refers to the wavelength dependent spectrum while lifetime refers to the actual temporal decay of the photoluminescence due to repopulation of the ground state from the excited state.

Photoluminescence is very useful in remote sensing applications. Within a given environment, one can utilize photoluminescence to identify materials, detect changes, and tag constituents among other potential uses. Two photoluminescent molecules used in these

sensing applications are methyl salicylate and dipicolinic acid. There have been many experiments carried out on these two molecules to determine the characteristics of their photoluminescence. However, computational studies on their electronic structure and photoluminescence mechanisms have been sparse or inconclusive. This dissertation investigates these two molecules using computational chemistry to elucidate their photoluminescence mechanisms as well as their ground and excited state electronic structures, vibrational modes, and isomerization reaction pathways.

1.1 Methyl Salicylate

Methyl salicylate (MS), $C_8H_8O_3$, is a semivolatile, organic compound well-known for its signaling properties in nature[1, 2]. MS is released into the atmosphere by certain plants when under stress or when being attacked and is used as an additive to enhance aroma in many commercial products. MS is also used in small amounts in foods to add a wintergreen taste, which gives rise to its alternative name of oil of wintergreen. MS is photoluminescent and is known to have two emission peaks. The dual emission has been studied for possible applications as markers. MS is considered to be a surrogate to study certain biological and chemical threats[3]. More recently, MS is being used in Förster resonance energy transfer (FRET) systems and as the fluorescence component in optical bar code systems[3, 4].

Weller[5–7] was the first to propose that methyl salicylate undergoes a dual fluorescence by means of an excited state intermolecular proton transfer (ESIPT). In particular, he noticed two emission peaks: one in the near-UV (360nm) and one in the blue (440nm). Weller suggested the existence of a dual potential well in the excited state. The hypothesis is that one isomer gives rise to the near-UV fluorescence while the other form yields the blue fluorescence. Later studies countered Weller’s suggestion and proposed that the longer wavelength emission peaks in aromatic o-hydroxycarboxyl acids and compounds are the result of transitions to higher vibrational sublevels of the ground state while the simultaneous presence of two emissions is dependent on large differences in the well depth energies of the

ground and excited states ($E_1 \geq 2E_0$)[8].

On the basis of gas phase, solution, and supersonic jets, several authors have since proposed that two different rotamers ketoA and ketoB of methyl salicylate exist in equilibrium[9–12] and that MS has open forms of the ketoA and ketoB rotamers[13,14]. Both ketoA and ketoB structures contain an internal hydrogen bond, which is absent in the open forms. The most recent theories suggest that the short wavelength fluorescence of MS is due to the ketoA rotamer while the long wavelength fluorescence is due to the ketoB rotamer undergoing an ESIPT to the enol isomer[15–20].

Within this dissertation, I have adopted Law and Shoham’s[9] nomenclature for the previously known structural isomers: ketoB, ketoA, ketoB_{open}, ketoA_{open}, and enol.

The observations of Smith and Kaufmann[21] support the idea of a proton-transferred structure (enol) giving rise to the blue emission. Measurements of the blue fluorescence risetime indicate a proton transfer rate greater than 10^{11} s^{-1} . The transfer rate reportedly did not change even as the temperature was lowered to 4K and a deuteron was used to replace the proton. A fluorescence lifetime of 280ps for MS in methylcyclohexane was observed at room temperature. The measurements performed at a range of lower and higher temperatures yielded lifetimes that were longer and shorter, respectively. The steady state fluorescence intensity of the blue emission was found to decrease (by a factor of 6) with decreasing temperature (between 253 to 333K) while the near-UV fluorescence remained steady. The excitation spectra of MS measured at 340 and 450nm are slightly different and may suggest different ground state species giving rise to the two different emissions. As temperature is shown to have little effect on the 340nm emission, the ground state equilibrium between the two isomers must have a very small difference in enthalpy. This suggests that the two ground state isomers are both hydrogen bonded. Smith and Kaufmann dismissed the possibility of rapid deactivation at room temperature being due to OH vibrations since the energy of deactivation is much less than the vibrational frequency of an OH bond. Alternatively, they suggest that intramolecular rotational motion may play a part in the deactivation. These authors also state that the proton transfer mechanism

may decrease the singlet-triplet energy gap in the enol form and could therefore result in enhanced intersystem crossing.

Goodman and Brus noted an absence of the near-UV emission of MS in a solid Ne host at -25°C and only observed the blue (440nm) emission[22]. They also observed only one lifetime (12 ± 2 ns) and no change in the emission spectra when using a 60% deuterated MS sample. Goodman and Brus concluded that no hydrogen motion double potential well exists. Klopffer and Naundorf[23] and Kosower and Dodiuk[24] suggested the near-UV emission in solvents is due to MS forms where external hydrogen bonds are present on the phenolic and carboxylic oxygens while the blue emission is due to the internally hydrogen bonded species.

Klöpffer and Kaufmann made observations of MS in the vapor phase and came to the conclusion that the near-UV emission was due to MS with open hydrogen bonds while the blue emission was due to the closed form[14]. They estimated a ring opening energy of 15 kJ/mol. The observations of Acuna et al. attribute the blue emission to the “closed form” (ketoB) undergoing a proton tautomerization in the excited state[11, 13]. The near-UV emission has been suggested [14, 23] to arise from the existence of “open forms” in solution or in gas phase. In solution, the intramolecular hydrogen bond is broken through competitive binding with the solvent molecules. In gas phase, a modest increase in temperature would allow for an increase in the population of the open form. The existence of the open form, however, is not supported by experimental observations of MS and a number of similar molecules [8, 13, 17, 25]. Acuna et al suggest that a rotamer (ketoA) is responsible for the near-UV emission, especially when MS is within hydrogen bonding solvents. They suggest a breakdown of the ketoB hydrogen bond due to solvent molecules while the ketoA form will stabilize. Their findings of the near-UV to blue emission intensity ratio of MS in alcohols is consistent with the theory of a ground state equilibrium between ketoB and ketoA.

Catalan and Diaz, more recently, observed a possible triplet-singlet transition in the enol form of MS through a heavy atom perturbation technique. Using a 300nm excitation, they did not observe the UV emission but did observe 440nm (blue) and 560nm (green)

emissions. They attribute the blue emission to a singlet-singlet fluorescence and attribute the green emission to a triplet-singlet phosphorescence that is induced through heavy atom perturbation. The phosphorescence was determined to have a lifetime of 1.4 ± 0.25 ms.

A general picture of MS in the ground state is that the two rotamers, ketoA and ketoB, exist in equilibrium. The short wavelength fluorescence is thought to be due to excitation and emission of the ketoA rotamer. Meanwhile, the longer wavelength fluorescence is thought to have a more complicated fluorescence (or possibly phosphorescence) mechanism. Law and Shoham postulated that the excited ketoB form undergoes a tautomerization to an excited enol form. The excited enol form then emits fluorescence when it transitions back to the keto ground state. During this process, they report that there is also a radiationless decay process which involves the proton transfer. Catalan and Diaz went a step further in determining the mechanism for the long wavelength fluorescence and found two long wavelength peaks. They postulated that the ground state ketoB form absorbs a photon to elevate the molecule to an excited singlet state. It then undergoes a proton transfer to a singlet state of the enol form. Through intersystem crossing from the Franck-Condon state excited by the primary absorption to the ketoB excited singlet, there is a formation of a lower triplet state. Subsequently, there is a transition from that triplet to the ground singlet of the enol form. This triplet-singlet transition emits a long wavelength photon ($\approx 450\text{nm}$). The singlet-singlet transition of the enol form yields a lower wavelength photon ($\approx 340\text{nm}$). While there have been computational studies of MS excited states using CASSCF and AIMD[26], investigation of the optimized excited state structures and transitions have not been performed with Time-Dependent Density Functional Theory.

I have thoroughly investigated the ground and excited states of several MS isomers and describe the methodologies used. In upcoming chapters, I compare the computational results with established experimental findings. Finally, a theory for the equilibrium isomeric ratio and excited state photoluminescence mechanisms is put forth. These investigations are contained in Chapters 3 and 4.

1.2 Dipicolinic Acid

Powell[27,28] was the first to discover the fact that dipicolinic acid (DPA, 2,6-pyridinedicarboxylic acid, $C_5H_3N(COOH)_2$) is excreted by most or all species of germinating bacterial spores. Since that discovery, it has been used as an indicator for bacterial sporulation. In fact, DPA is thought to make up at least 10% of the bacterial cell's dry weight[29]. DPA's presence within the spore medium is primarily found as a calcium chelated form, calcium dipicolinate (CaDPA). It is thought that bacterial spore germination is induced by DPA and CaDPA and it has been theorized that the germination process is enhanced by the presence of DPA compounds[30]. Up to 50% of the solids excreted by spores are thought to be compounds of DPA.

DPA is thought to protect bacterial spores because of its ability to strongly absorb ultraviolet light. DPA is well-known to be a molecule with high chelation. While calcium and sodium bound to DPA are more often to be found in nature, there have also been studies to design optical reporters based on lanthanide elements[31–33] and molecularly imprinted polymer surfaces[34]. CaDPA also retains the characteristic of having a strong UV absorption.

Experiments performed on wet paste and dry crystal forms of DPA and CaDPA have shown interesting effects on their fluorescence intensities[35]. The drying of DPA crystals showed an increase in the observed fluorescence as well as a broader emission peak. UV-exposed samples exhibited dramatic increases in fluorescence[36]. It has been theorized that a photochemical reaction takes place to form new molecular species or isomers in those UV-irradiated samples[37]. Experiments have illustrated the vibrational spectra, one-dimensional supramolecular structure[38], and crystallography of anhydrous DPA[39].

Computational investigations of DPA and CaDPA have been relatively sparse. Complete active space multiconfiguration self-consistent field (MCSCF) calculations have determined ground and excited state geometries and vibrational frequencies for one isomer of gas phase DPA and its anion[40]. DFT and TDDFT studies performed on DPA and its dianion

showed an acceptable agreement between the calculated IR, Raman, NMR, and measured photoabsorption spectra[41]. The study by Xie et al reports that the lowest singlet state for DPA is dipole-forbidden and the first dipole-allowed transition is the second singlet excitation. This study also ruled out a direct singlet-triplet excitation process. To my knowledge, there is no literature which reports a thorough computational investigation of all DPA isomers along with their proposed liquid phase and crystalline structures.

In this dissertation, I have calculated the energetics and vibrational modes of DPA gas phase isomers, dimers, and crystal structures. The results of these investigations are contained in Chapter 5. I compare the results to experiment and previous computational investigations for monomers, dimers, and crystals. The band structures of the theorized crystalline forms of DPA will be calculated for the first time.

Chapter 2: Methods

Computational chemistry methods have shown to be capable of producing accurate calculations of atomic and molecular physical properties. These physical properties include geometric structure, ionization and dissociation energies, electronic charge distribution, dipole and quadrupole moments, vibrational frequencies, and, perhaps most important to this research, excited state transitions. However, in order to explain the excited state energy transfer mechanisms of a molecule, one needs to have a thorough description of the molecule’s ground state isomers, vibrational frequencies, and other important physical properties. Computational chemistry methods vary widely and each method has specific advantages and disadvantages. This chapter describes a number of these methods.

2.1 Ab Initio Methods

The term *ab initio* means “from the beginning” and computational chemistry methods of this type do not use any empirical data. Ab initio methods work purely with theoretical concepts from quantum mechanics. In studying molecules using ab initio methods, one begins with writing the molecular Hamiltonian for the system of interest,

$$\hat{H} = -\frac{\hbar^2}{2} \sum_{\mu} \frac{1}{m_{\mu}} \nabla_{\alpha}^2 - \frac{\hbar^2}{2m_e} \sum_i^n \nabla_i^2 + \sum_{\mu}^N \sum_{\nu > \alpha}^N \frac{Z_{\mu} Z_{\nu} e^2}{r_{\mu\nu}} + \sum_{\mu}^N \sum_i^n \frac{Z_{\mu} e^2}{r_{i\mu}} + \sum_j \sum_{i > j} \frac{e^2}{r_{ij}} \quad (2.1)$$

where μ ’s are indices for the N nuclei, i and j are indices for the n electrons, Z ’s are the nuclear charge, e the electron charge, m_e the electron mass, and r is the distance between different particles. The Born-Oppenheimer approximation is made whereby the nuclei of the atoms are considered fixed. Using this approximation and writing (2.1) in atomic units

($e^2 = \hbar = m = 1$, with energies in Hartrees and distances in Bohr),

$$\hat{H} = -\frac{1}{2} \sum_i^N \nabla_i^2 - \sum_{\mu}^N \sum_i^n \frac{Z_{\mu}}{r_{i\mu}} + \sum_j \sum_{i>j} \frac{1}{r_{ij}} \quad (2.2)$$

The nuclear repulsion term, the third term on the right in (2.1), is an additive constant since the nuclei are fixed. The goal is to construct the molecular wavefunction ψ and solve the Schrödinger equation,

$$\hat{H}\psi = E\psi \quad (2.3)$$

In many instances the form of ψ includes variable parameters so that one can minimize E ,

$$E = \frac{\int \psi^* \hat{H} \psi d\tau}{\int \psi^* \psi d\tau} \quad (2.4)$$

with respect to those parameters. This energy depends parametrically on the fixed positions of the nuclei.

2.1.1 Hartree-Fock Method

The Hartree-Fock (HF) method assumes that the N-body wavefunction of a system can be represented by a single Slater determinant,

$$\Psi(\mathbf{r}_1, \dots, \mathbf{r}_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_1(\mathbf{r}_1) & \dots & \phi_N(\mathbf{r}_1) \\ \vdots & \ddots & \vdots \\ \phi_1(\mathbf{r}_N) & \dots & \phi_N(\mathbf{r}_N) \end{vmatrix} \quad (2.5)$$

Using a Slater determinant assures an antisymmetrized wavefunction, and therefore adherence to the Pauli exclusion principle. The molecular orbitals (MOs) ϕ_i that make up Ψ in (2.5) need to be chosen. One can approximate the MOs as a linear combination of

atomic orbitals (LCAO),

$$\phi_i = \sum_{s=1}^b c_{si} \chi_s \quad (2.6)$$

where the χ_s represent the atomic orbitals and c_{si} are constants that are to be determined. One can now employ the variation method to arrive at an equation which relates the Hamiltonian in (2.2) and the choice of a single determinantal wavefunction,

$$\hat{F} \phi_i = \epsilon_i \phi_i \quad (2.7)$$

These equations are the Hartree-Fock equations with $\hat{F}$ being the Fock operator,

$$\hat{F}(1) = -\frac{1}{2} \nabla_1^2 - \sum_{\mu}^N \frac{Z_{\mu}}{r_{\mu 1}} + \sum_{j=1}^n \left(2\hat{J}_j - \hat{K}_j \right) \quad (2.8)$$

Here, $\hat{J}$ and $\hat{K}$ are the coulomb and exchange operators, respectively. They arise due to the electronic repulsion term in the Hamiltonian. The coulomb operator comes from charge cloud repulsions while the exchange operator comes about from electron exchange symmetry consideration.

The Fock operator (in particular, the coulomb and exchange operators) in (2.8) is a function of the MOs ϕ_i . Since both the Fock operator and the MOs need to be determined, an iterative approach is applied for solving the HF equations. An initial guess of the MOs is supplied which in turn leads to an expression for $\hat{F}$. The Fock operator is then used to solve for a new set of MOs, which again leads to a new expression for the Fock operator. The process is continued until there is no significant difference between the last two iterations. This type of calculation for the MOs and $\hat{F}$ is said to be self-consistent since the ϕ_i 's produced by $\hat{F}$ are the same as the ϕ_i 's that produce the coulomb and exchange fields in $\hat{F}$. It is commonly known as a self-consistent field (SCF) method.

However, this is not the complete picture for the true energy of a physical system. Mathematically, the use of a single determinant in the HF method does not completely explain the nature of the wavefunction. The HF energy is always higher in value than the true energy defined by the molecular Hamiltonian. Physically, electrons tend to stay out of each other's way and their movement is said to be correlated. The energy related to this correlated electron motion is called the correlation energy. The HF method is incapable of calculating the correlation energy; therefore other methods need to be implemented in order to obtain a more accurate energy value. Thus, the correlation energy is all due to the contribution of electrons beyond the HF, single determinant approach.

2.1.2 Configuration Interaction (CI) and CI-Singles (CIS)

In the HF method, one assumes the molecular wavefunction is a single Slater determinant. The next logical choice is to allow the wavefunction to be a linear combination of determinants,

$$\psi = c_1 D_1 + c_2 D_2 + \dots \quad (2.9)$$

where D_i 's stand for determinants with different orbital occupation schemes. One can then minimize the energy as a function of linear mixing coefficients c_i .

Excited state configurations are actually formed as a residue of performing LCAO-MO-SCF calculations in order to find the ground state. These excited state configurations are referred to as virtual orbitals. For instance, in performing a calculation on H_2 the CI method will converge on the $1\sigma^2$ configuration (the ground state). However, the virtual MOs of H_2 will also be produced if a large enough AO basis set is provided. One can mix the determinantal functions, which include the virtual MOs, using (2.9). So, for example, a $1\sigma_g 2\sigma_u$ configuration can be obtained by promoting an electron from the ground state MO to a virtual MO. These are referred to as CI-singles (CIS) because there is a singly-excited electron. One can also perform doubly-excited, triply-excited, etc calculations. A limitless number of configurations can be mixed.

CI can provide information about excited states. However, its consideration of spin states is not complete in that it does not yield pure spin states for closed-shell systems. The spin orbitals involved in CI have been variationally determined for the *ground state*. Therefore, virtual orbital occupation is more like ionization rather than excitation. CI is also not appropriate for excitations into degenerate spin orbitals.

2.2 Density Functional Methods

2.2.1 Density Functional Theory (DFT)

Hohenberg and Kohn (1964) showed that for molecules with a non-degenerate ground state, the ground state molecular energy, wavefunction, and all other molecular electronic properties can be determined as a function of the ground state electron probability density $\rho_0(\mathbf{x}, \mathbf{y}, \mathbf{z})$. They essentially reduced a function of $3n$ coordinates (where n is the number of electrons) to a function having only 3 spatial coordinates. Hohenberg and Kohn were able to show that there is a unique value for ρ_0 that produces the ground state energy E_0 . Furthermore, it was shown that there is a unique external potential, v_{ext} , that gives rise to ρ_0 . v_{ext} is the middle term of the Hamiltonian in (2.2) and is considered external because it is a field generated by particles (the nuclei) not included in the group of electrons. The energy can be separated into its components,

$$E_0 = T[\rho_0] + V_{Ne}[\rho_0] + V_{ee}[\rho_0] \quad (2.10)$$

where T is kinetic energy contribution, V_{Ne} is the nuclear-electron attraction energy, and V_{ee} is the electron repulsion. In order to evaluate the kinetic energy term, one must differentiate a wavefunction.

Kohn and Sham (1965) therefore proposed to express the electronic density in terms of one-electron orbitals, ϕ_i . Using this framework, one can calculate kinetic energies similar to those found in HF theory and the electron density can be written as,

$$\rho = \sum_{i=1}^n |\phi_i|^2 \quad (2.11)$$

The ϕ_i are known as Kohn-Sham (KS) orbitals and are constructed numerically or from a basis set of Slater or Gaussian functions. One can write an expression for the DFT energy as

$$E_{DFT}[\rho] = T[\rho] + V_{Ne}[\rho] + J[\rho] + E_{XC}[\rho] \quad (2.12)$$

where the exchange-correlation functional E_{XC} is the difference between the exact kinetic energy and the exchange energy of electron-electron repulsion plus correlation contributions. Since the KS orbitals are eigenfunctions of a Hamiltonian that is almost identical to the Fock operator in HF theory, one can use a SCF method to converge on values for the KS orbitals and the electron density. In practice, a guess for the electron density is made, the KS eigenvalue equations are solved for the orbitals, and a new electron density is formed.

A problem arises in that the exact form of E_{XC} is unknown. Two common methods have been implemented within DFT to account for E_{XC} : the local density approximation (LDA) and the generalized gradient approximation (GGA). Hohenberg and Kohn showed that if ρ changes slowly with position then E_{XC} can be written,

$$E_{XC}^{LDA}[\rho] = \int \rho(\mathbf{r}) \epsilon_{XC}(\rho) d\mathbf{r} \quad (2.13)$$

where ϵ_{XC} is the exchange plus correlation energy per electron in a homogeneous electron gas of density ρ . The exchange correlation potential v_{XC} is the functional derivative of E_{XC}

$$\nu_{XC}^{LDA} = \frac{\partial E_{XC}^{LDA}}{\partial \rho} = \epsilon_{XC}(\rho(\mathbf{r})) + \rho(\mathbf{r}) \frac{\partial \epsilon_{XC}}{\partial \rho} \quad (2.14)$$

Kohn and Sham suggested (2.13) as an approximation to E_{XC} in (2.12). They also suggested (2.14) as an approximation to v_{XC} in the energy eigenvalue problem incorporating the KS orbitals,

$$\left[-\frac{1}{2}\nabla_1^2 - \sum_{\mu} \frac{Z_{\mu}}{r_{\mu 1}} + \int \frac{\rho(\mathbf{r}_2)}{r_{12}} d\mathbf{r}_2 + \nu_{XC}(1) \right] \phi_1^{KS}(1) = \epsilon_i^{KS} \phi_i^{KS}(1) \quad (2.15)$$

One can show that ϵ_{XC} is the sum of exchange and correlation energies,

$$\epsilon_{XC}(\rho) = \epsilon_X(\rho) + \epsilon_C(\rho) \quad (2.16)$$

and,

$$\epsilon_X(\rho) = -\frac{3}{4} \left(\frac{3}{\pi} \right)^{1/3} (\rho(\mathbf{r}))^{1/3} \quad (2.17)$$

The correlation part ϵ_C has been calculated by Vosko, Wilk, and Nusair[42] and is a complicated function of ρ . The exchange energy within LDA can then be written,

$$E_X^{LDA} \equiv \int \rho \epsilon_X d\mathbf{r} = -\frac{3}{4} \left(\frac{3}{\pi} \right)^{1/3} \int [\rho(\mathbf{r})]^{4/3} d\mathbf{r} \quad (2.18)$$

One evaluates E_X within a closed-shell molecule by replacing the HF orbitals by the KS orbitals in the exchange integral,

$$E_X \equiv -\frac{1}{4} \sum_{i=1}^n \sum_{j=1}^n \left\langle \phi_i^{KS}(1) \phi_j^{KS}(2) \left| \frac{1}{r_{12}} \right| \phi_j^{KS}(1) \phi_i^{KS}(2) \right\rangle \quad (2.19)$$

and evaluating (2.19) with the expression for E_X in (2.18). In order to find E_C one must obtain an accurate solution for the energy from the uniform electron gas Schrödinger equation for a particular density ρ . One combines that result with the calculated KS energies to

obtain E_C for a particular ρ . The process is repeated many times for many different density values to arrive at E_C as a function of ρ .

One can go beyond the LDA and suppose that the energies are not only a function of ρ but also a function of its derivative. The GGA attempts to correct for the variation of electron density with position by including gradients of the density,

$$E_{XC}^{GGA}[\rho^\alpha, \rho^\beta] = \int f(\rho^\alpha(\mathbf{r}), \rho^\beta(\mathbf{r}), \nabla\rho^\alpha(\mathbf{r}), \nabla\rho^\beta(\mathbf{r}))d\mathbf{r} = E_X^{GGA} + E_C^{GGA} \quad (2.20)$$

where α and β stand for different spin orbitals, and f is a function of the spin densities and their gradients. E_X^{GGA} and E_C^{GGA} are modeled separately and commonly include empirical parameters.

Hybrid functionals used within DFT mix the KS orbital-substituted HF E_X formula with gradient-corrected E_X and E_C formulas. In my work, I used B3PW91 and B3LYP. B3PW91 is Becke's 3-parameter functional[43] combined with Perdew and Wang's 1991 gradient-corrected correlation functional[44–48],

$$E_{XC}^{B3PW91} = (1 - a_0 - a_X)E_X^{LSDA} + a_0E_X^{exact} + a_XE_X^{B88} + (1 - a_C)E_C^{VWN} + a_CE_C^{PW91} \quad (2.21)$$

B3LYP is Becke's 3-parameter functional combined with the Lee-Yang-Parr (LYP) gradient-corrected correlation functional[49, 50],

$$E_{XC}^{B3LYP} = (1 - a_0 - a_X)E_X^{LSDA} + a_0E_X^{exact} + a_XE_X^{B88} + (1 - a_C)E_C^{VWN} + a_CE_C^{LYP} \quad (2.22)$$

where E_X^{B88} is Becke's 1988 exchange functional, E_C^{VWN} is the correlation functional from Vosko, Wilk, and Nusair, and a_0 , a_X , and a_C are fitting parameters. Overall, hybrid functionals tend to demonstrate the best performance due to their flexibility. Gradient-corrected and hybrid functionals give good equilibrium geometries, vibrational frequencies, dipole moments, and accurate molecular atomization energies. The major advantage for using DFT

is the computational cost savings over pure ab initio methods. DFT has been proven to provide excellent ground state energies and works well for large molecules. However, the choice of functional is not always completely clear and, more importantly, excited state calculations are not possible with the theory just presented.

2.2.2 Time-Dependent Density Functional Theory (TDDFT)

Time Dependent Density Functional Theory (TDDFT) states that there is a unique mapping between the time-dependent external potential of a system and the time-dependent electron density[51]. The application of TDDFT to organic molecules[52] and coumarins[53] have been highly successful in calculating ground to first excited state transition energies. In my study, I used linear response, non-equilibrium TDDFT as implemented in the Gaussian 09[54] software package.

The Hohenberg-Kohn-Sham theory discussed earlier is restricted to a time-independent (TI) treatment of DFT. A number of researchers have worked on generalizing DFT to the time-dependent (TD) case. Essentially, the goal was to demonstrate a one-to-one correspondence between time-dependent one-body densities $\rho(\mathbf{r},t)$ and time-dependent one-body potentials $v_{ext}(\mathbf{r},t)$ for a given initial state. Runge and Gross proved this concept in 1984[51]. The theory depends upon an external potential, an initial interacting wavefunction Ψ_0 , the initial Kohn-Sham wavefunction Φ_0^{KS} , and an exchange-correlation potential $v_{XC}(\mathbf{r},t)$ which is a functional of the entire history of the density $\rho(\mathbf{r},t)$.

Consider an n electron system described by the time-dependent Schrödinger equation,

$$\hat{H}\Psi(t) = i\frac{\partial}{\partial t}\Psi(t) \tag{2.23}$$

where Ψ_0 must be given since it is a first-order differential equation in time. The molecular Hamiltonian is the same as (2.2) except that now the middle term is considered to be a one-body external potential,

$$\hat{V}_{ext} = \sum_n^{i=1} v_{ext}(\mathbf{r}_i, t) \quad (2.24)$$

where $v_{ext}(\mathbf{r}, t)$ differs from problem to problem. For instance, a hydrogenic atom with a nuclear charge Z within an alternating electric field of strength E oriented along the z -axis with a frequency ω will have

$$v_{ext}(\mathbf{r}_i, t) = -\frac{Z}{r} + (E \cdot z) \cos(\omega t) \quad (2.25)$$

One may think of the system within a TD field that is “switched on” at time t_0 .

The goal is to obtain TD expectation values as functionals of the TD charge density. Runge and Gross showed[51] that the TD charge density, ρ , determines the wave function up to a TD phase factor,

$$\Psi(t) = e^{-i\phi(t)} \Psi[\rho, \Psi_0](t) \quad (2.26)$$

Specifically, they showed that $v_{ext}(\mathbf{r}, t)$ is determined by ρ up to a spatially constant TD function $c(t)$ as long as ρ derives from a system with an initial state Ψ_0 and $v_{ext}(\mathbf{r}, t)$ can be represented as an electric potential with a normalizable charge distribution and has a time dependence which can be written as a Taylor series expansion around $t = t_0$. The variational principle from the time-independent case can be modified in the TD case involving the action,

$$A = \int_{t_0}^{t_1} \left\langle \Psi(t) \left| i \frac{\partial}{\partial t} - \hat{H}(t) \right| \Psi(t) \right\rangle dt \quad (2.27)$$

The true TD density is one which makes the action stationary,

$$0 = \frac{\partial A}{\partial \rho(\mathbf{r}, t)} = \int_{t_o}^{t_1} \left\langle \frac{\partial \Psi(t')}{\partial \rho(\mathbf{r}, t)} \left| i \frac{\partial}{\partial t'} - \hat{H}(t') \right| \Psi(t') \right\rangle dt' + c.c. \quad (2.28)$$

and the effect of the phase factor yields,

$$A = \int_{t_o}^{t_1} \left\langle \Psi[\rho](t) \left| i \frac{\partial}{\partial t} - \hat{H}(t) \right| \Psi[\rho](t) \right\rangle dt + \phi(t_1) - \phi(t_0) = A[\rho] + const \quad (2.29)$$

so that the TD density determines the action up to an additive constant. In using the variational theorem in (2.28) the constant turns out to be immaterial. The action functional can be re-written as,

$$A[\rho] = B[\rho] - \int_{t_o}^{t_1} \int v_{ext}(\mathbf{r}, t) \rho(\mathbf{r}, t) d\mathbf{r} dt \quad (2.30)$$

where the functional B is independent of the external potential v_{ext} . A TD Kohn-Sham equation can be derived in a similar way as to the time independent case. One needs to assume there exists a potential $v_{eff}(\mathbf{r}, t)$ in an independent system whose orbitals ψ_i yield the same charge density ρ for the interacting system,

$$\rho(\mathbf{r}, t) = \sum_i f_i |\psi_i(\mathbf{r}, t)|^2 \quad (2.31)$$

where the f_i are orbital occupation numbers. Assuming v_{eff} exists, the functional B is written,

$$B[\rho] = \sum_i f_i \int_{t_o}^{t_1} \left\langle \psi_i(t) \left| i \frac{\partial}{\partial t} - \frac{1}{2} \nabla^2 \right| \psi_i(t) \right\rangle dt - \frac{1}{2} \int_{t_o}^{t_1} \int \int \frac{\rho(\mathbf{r}_1, t) \rho(\mathbf{r}_2, t)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2 dt - A_{XC}[\rho] \quad (2.32)$$

where A_{XC} is the exchange-correlation action functional and is similar to the exchange-correlation functional in the TI case. The TD Kohn-Sham equations are found if one minimizes the action functional subject to the condition for v_{eff} ,

$$\left[-\frac{1}{2}\nabla^2 + v_{eff}(\mathbf{r}, t) \right] \psi_i(\mathbf{r}, t) = i \frac{\partial}{\partial t} \psi_i(\mathbf{r}, t) \quad (2.33)$$

where,

$$v_{eff}(\mathbf{r}, t) = v(\mathbf{r}, t) + \int \frac{\rho(\mathbf{r}', t)}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + v_{XC}(\mathbf{r}, t) \quad (2.34)$$

and,

$$v_{XC}(\mathbf{r}, t) = \frac{\partial A_{XC}[\rho]}{\partial \rho(\mathbf{r}, t)} \quad (2.35)$$

The solution of the TD Kohn-Sham equations is an initial value problem. One supplies an initial state and propagates the initial state through time. The Kohn-Sham equations are solved at small increments in time using a time-dependent exchange correlation functional. The DFT MO's used are Slater determinants of KS orbitals. These are ultimately what describe the electron excitations. In most cases, the adiabatic local density approximation is made which allows one to use existing exchange-correlation functionals from ground state DFT. This approximation is valid for small temporal dependence and locally close to equilibrium.

TDDFT is not a simple extension of ground-state DFT. Instead it uses the philosophy of DFT to explain driven systems that can be described by the time-dependent Schrödinger equation. As mentioned before, ground-state DFT provided no accurate way of calculating excited state energies. With TDDFT however, one can get an accurate zeroth-order approximation to the spectroscopic excitation energies while not expending an inordinate amount of computational resources.

2.3 Structural Optimization

The geometrical optimization of molecular structures is a very important aspect of computational chemistry. A very practical and often used structural optimization routine is the Berny algorithm[55–58]. It begins by choosing an initial geometry. Initial geometries are typically obtained through molecular mechanics or Monte Carlo approaches. One may also choose to fix certain intermolecular bonds or angles. At this point, a coordinate system is chosen. Nonredundant internal coordinates and cartesian coordinates can be used as coordinate systems. Research has shown that the use of redundant internal coordinates is the best approach[55, 56, 59].

The initial Hessian used is either taken from a previous computation or an empirical estimate that is diagonal in the redundant internal coordinate space[60, 61]. The Hessian is updated iteratively using the Broyden, Fletcher, Goldfarb, Shanno (BFGS) formula[62–64]. The modification typically uses a valence force field taken from the original Schlegel update procedure[60] in addition to energies and first derivatives calculated along the optimization pathway. In most cases, the Hessian matrix only needs to be calculated explicitly at the beginning of the optimization and is updated throughout. In some rare cases, the Hessian changes considerably between optimization steps and the entire Hessian needs to be recomputed at each step.

A linear search is performed between the last step point and a previous point with the lowest energy. A polynomial fit is applied to the energy surface and a minimum is sought using that polynomial fit in a range between the best and most recent steps. If all polynomial fits fail and the most recent step is not the best, then a step corresponding to the midpoint of the most recent and best points is taken. A quadratic step is then taken using the second derivatives or their approximations. The quadratic step uses the Rational Function Optimization (RFO) approach[65, 66] which behaves better than the Newton-Raphson method. If the Newton-Raphson method is used, the step size is updated using the Fletcher method[64, 67]. Components of the step vector which correspond to frozen variables are set to zero or projected out. If the quadratic step exceeds a given trust radius,

or maximum allowed step size, then the step is reduced to that trust radius and a minimum of the quadratic function on the sphere having that trust radius is determined[68]. Finally, the algorithm ends by testing for convergence in the maximum force component, root-mean square force, maximum step component, and root-mean-square-step.

In summary, the Berny algorithm for structural optimization is performed by (1) choosing an initial geometry, (2) choosing a coordinate system, (3) estimating the initial Hessian, (4) updating the Hessian, (5) stepping in the search direction, and then repeating (4) and (5) until a minimum has been found.

2.4 Vibrational Analysis

Optimized structures require the use of vibrational analysis to confirm the existence of a minimum, transition state, or higher order saddle point on the molecule’s potential energy surface[69]. Many other physical properties can then be calculated from the vibrational analysis results. The vibrational analysis must be calculated with the same level of theory as was used for the structural optimization.

To perform the vibrational analysis, one begins with the Hessian matrix (H_{CART}) which is a matrix of the force constants. H_{CART} is the second derivative of the potential energy (U) with respect to the atoms’ displacements away from their equilibrium positions in cartesian coordinates,

$$H_{CARTij} = \left(\frac{\partial^2 U}{\partial r_i \partial r_j} \right)_0 \quad (2.36)$$

H_{CART} is a $3N \times 3N$ matrix where N is number of atoms. r_i and r_j are the displacements of the atoms in cartesian coordinates $(\Delta x_1, \Delta y_1, \Delta z_1, \dots, \Delta x_N, \Delta y_N, \Delta z_N)$ away from their

equilibrium (0 subscript) so that

$$H_{CARTij} = \begin{vmatrix} \frac{\partial^2 U}{\partial^2 \Delta x_1} & \frac{\partial^2 U}{\partial \Delta x_1 \partial \Delta y_1} & \cdots & \frac{\partial^2 U}{\partial^2 \Delta z_N} \\ \frac{\partial^2 U}{\partial \Delta y_1 \partial \Delta x_1} & \frac{\partial^2 U}{\partial^2 \Delta y_1} & \cdots & \frac{\partial^2 U}{\partial \Delta y_1 \partial \Delta z_N} \\ \vdots & \vdots & \ddots & \vdots \\ \frac{\partial^2 U}{\partial \Delta z_N \partial \Delta x_1} & \frac{\partial^2 U}{\partial \Delta y_1 \partial \Delta z_N} & \cdots & \frac{\partial^2 U}{\partial^2 \Delta z_N} \end{vmatrix} \quad (2.37)$$

H_{CART} may be slightly different from the Hessian used in the geometry optimization if the optimization used an approximate Hessian throughout the calculation.

Typically, the matrix is then mass-weighted so that

$$H_{MWCij} = \frac{H_{CARTij}}{\sqrt{m_i m_j}} = \left(\frac{\partial^2 U}{\partial q_i \partial q_j} \right)_0 \quad (2.38)$$

where $q_i = \sqrt{m_i} r_i$ are the mass-weighted coordinates (MWC). Next, a unitary transformation matrix ($\mathbf{D}$) is formed to generate coordinates in the rotating and translating frame. H_{MWC} is then transformed to internal coordinates (INT) by

$$H_{INT} = \mathbf{D}^\dagger H_{MWC} \mathbf{D} \quad (2.39)$$

so that H_{INT} is now an $N_{vib} \times N_{vib}$ matrix with matrix elements in internal coordinates where the rotation and translation of the molecule has been separated out (so that $N_{vib} = 3N - 6$, or $3N - 5$ for linear molecules). If H_{INT} is diagonalized, then there are N_{vib} eigenvectors which compose a transformation matrix $\mathbf{L}$ so that

$$\mathbf{L}^\dagger H_{INT} \mathbf{L} = \mathbf{\Lambda} \quad (2.40)$$

where $\mathbf{\Lambda}$ is a diagonal matrix with eigenvalues $\lambda_i = 4\pi^2 \nu_i^2$. The vibrational frequencies are

then simply solved for and their units are changed to wavenumbers by

$$\tilde{\nu}_i = \sqrt{\frac{\lambda_i}{4\pi^2 c^2}} \quad (2.41)$$

Imaginary frequencies are reported as negative eigenvalues of Λ . A molecule having no imaginary frequencies represents a minimum on the potential energy surface. A structure with one imaginary frequency represents a saddle, or transition state while structures with more than one imaginary frequency represent higher order saddle points. Additionally, the eigenvectors of atomic displacements for each vibrational mode are obtained after transforming them back to cartesian coordinates.

2.4.1 Free Energy

The Helmholtz free energy of a molecular system is a very important physical quantity. It is a measure of the amount of potential energy available for work within a system at constant volume and temperature, as described in the canonical ensemble[70]. One can derive the Helmholtz free energy (A) of a closed system within the canonical ensemble and harmonic approximation using the partition function[71],

$$Q = \prod_{i=1}^{3N-6} \left[\frac{e^{-h\nu_i/2kT}}{1 - e^{-h\nu_i/kT}} \right] e^{-E_0/kT} \quad (2.42)$$

where N is the number of atoms in the system, ν_i is the frequency of the i^{th} vibrational mode, k is Boltzmann's constant, T is the temperature, and E_0 is the electronic energy of the ground state. Taking the natural logarithm of Q one obtains,

$$\ln(Q) = \frac{-E_0}{kT} + \sum_{i=1}^{3N-6} \left[\frac{-h\nu_i}{2kT} - \ln \left[1 - e^{-h\nu_i/kT} \right] \right] \quad (2.43)$$

One readily can calculate the Helmholtz free energy of a system at a given temperature T using,

$$A = -kT \ln(Q) \quad (2.44)$$

From there, the internal energy is

$$E = kT^2 \left(\frac{\partial \ln(Q)}{\partial T} \right)_{N,V} \quad (2.45)$$

and the specific heat is

$$C_v = \left(\frac{\partial E}{\partial T} \right)_{N,V} \quad (2.46)$$

Using the 2nd Law of Thermodynamics, one can also write the entropy (S) of the system as

$$S = \frac{(E - A)}{T} \quad (2.47)$$

and calculate its value within the harmonic approximation using equations (2.44) and (2.45).

2.5 Chemical Reaction Paths

Molecular transition states are very useful because they provide valuable information on reactions between two states, typically a reactant and a product. A transition state is a saddle point on the potential energy surface between two minima.

One method for determining transition structures is the Synchronous-Transit Quasi-Newton (STQN) method[57,58]. Using redundant internal coordinates, the STQN method implements a quadratic synchronous transit approach to get close to the quadratic region of the transition state. As the quadratic region becomes close, it then uses a quasi-Newton or eigenvector-following algorithm to complete the transition state structural optimization. The STQN method efficiently converges on a transition structure when provided with an

empirical estimate of the Hessian and given the correct reactant and product structures. The STQN method also allows one to input a guess for the transition structure.

Once a transition state has been optimized using the STQN method, a vibrational analysis of the saddle point is needed. An n^{th} order saddle point will have n imaginary frequencies. A first order saddle point is needed to confirm a transition structure. The displacements of the imaginary frequency mode will also tend to lead in the direction of the reactant and product. After the transition structure is confirmed through vibrational analysis, one can further characterize the transition state and the reaction pathway using an intrinsic reaction coordinate (IRC) calculation[72, 73].

The IRC calculation requires initial force constants. The force constants are often taken from the vibrational analysis performed on the saddle point. From the transition state geometry, one defines a forward and reverse pathway towards the product and reactant structures, respectively. In many cases it is useful to define the pathway along a phase of the transition vector, such as an internal coordinate (bond or angle). The reaction path is followed using the Hessian-based Predictor-Corrector (HPC) integrator[73]. The HPC algorithm uses a Hessian-based local quadratic approximation as the prediction step component. It then uses a modified Bulirsch-Stoer integrator as a correction[74]. The energies and gradients are calculated along each point of the reaction path. The reaction path is followed in both the forward and reverse directions until the product and reactant minima have been reached. Thus, a complete reaction path is calculated along a given phase vector and the likelihood of a transition can be deduced through analysis of the energies along the path.

Chapter 3: Methyl Salicylate

Energetics and vibrational analysis study of six isomers of methyl salicylate (MS) in their singlet ground state and first excited triple state is put forward in this chapter at the density functional theory level and large basis sets. The ketoB isomer is the lowest energy isomer, followed by its rotamer ketoA. For both ketoB and ketoA, their enolized tautomers are found to be stable as well as their open forms that lack the internal hydrogen bond. The calculated vibrational spectra are in excellent agreement with IR experiments of methyl salicylate in the vapor phase. It is demonstrated that solvent effects have a weak influence on the stability of these isomers. The ionization reaction from ketoB to ketoA isomers shows a high barrier of 0.67 eV ensuring that thermal and chemical equilibria yield systems containing mostly the ketoB isomer at normal conditions.

3.1 Introduction

Methyl salicylate (methyl 2-hydroxybenzoate, 2-HOC₆H₄COOCH₃) is a naturally occurring organic ester and is a product of many plant species. MS is often found in wintergreens, hence its common name “oil of wintergreen”. In 1843, MS was isolated from oil of wintergreen for the first time[75]. MS may be produced commercially by distilling twigs from the plant species *Betula lenta* and *Gaultheria procumbens* but can now be synthetically produced by esterifying salicylic acid with methanol. Due to its signaling properties in plants[2] and its similar volatility to sarin (chemical warfare agents), MS has been thoroughly studied in experiments.

Despite the experimental interest on MS, theoretical calculations are very scarce. A recent density functional calculation demonstrates that both ketoA and ketoB are indeed stable isomers of MS[76]. Measurements of the IR spectra and a Hartree-Fock frequency

calculation for ketoA were reported in Ref. [77]. The work described in this chapter focuses on computing the structure, energetics, and vibrational analysis of six stable isomers, ketoA, ketoB, ketoA_{open}, ketoB_{open}, enol, and enolized ketoA (ekA), in their singlet and triplet states. Results from these calculations are important for supporting empirical predictions on the phase equilibria between isomers. This chapter is organized as follows. The second section on energetics describes the methodology used and presents the results of the geometry optimization, energy calculations, and other physical properties of the six isomers in their lowest singlet and triplet states. The following two sections provide the vibrational analysis of the six isomers, including a comparison with experimental IR spectra when available, and calculations of the free energies. The next section gives a discussion of the isomerization reaction from ketoB to ketoA, the transition state structure and potential energy along the reaction coordinate. This work is concluded in the last section.

3.2 Structural Isomers and Energetics

All-electron density functional theory (DFT) and the hybrid Becke-Perdew-Wang 1991 (B3PW91) approach were used throughout this study, which includes local and nonlocal correlation functionals[43, 57, 58]. Calculations of the MS isomers were obtained using the Gaussian 03 package[78] and a triple- ζ basis set with s, p, d polarization functions and extra diffuse d-functions (6-311++G)[79, 80]. A multitude of molecular structures from an unrestricted Monte Carlo and small basis sets simulation were used as initial conditions for the structural optimization. These molecular structures were subsequently minimized using the Berny optimization algorithm with redundant internal coordinates[58] described in Chapter 2. The vibrational frequencies were calculated to ensure for the presence of a minimum. The convention throughout this dissertation for designating a singlet or triplet state will be a superscript (1 or 3) preceding the isomer name.

The geometries of ketoA, ketoB, ketoA_{open}, ketoB_{open}, enol, and ekA isomers of MS were identified as stable in both the singlet and triplet states. Although there has been

experimental hints on the existence of the first five isomers, the ekA form has not been predicted experimentally yet. The ground state of all isomers are singlet states. The optimized singlet geometries of the six different isomers are shown in Figure 3.1. Carbon atoms are gray, oxygen atoms are red, and hydrogen atoms are white. The atoms are all numbered so that may be easily identified later. The MS coloring and numbering scheme stays consistent throughout this dissertation.

Table 3.1 provides the detailed geometric parameters of ketoB in its singlet state, which is the most stable isomer. The molecular symmetry of all isomers is low since they belong to the C_1 point group in either their singlet or triplet states. The singlet states of all isomers have planar geometries (excluding the hydrogens in the CH_3 group), whereas the triplet states are nonplanar geometries. Both the $^3\text{ketoA}_{open}$ and $^3\text{ketoB}_{open}$ forms are notably nonplanar, with the carbonyl group bending above the benzene ring plane and the phenol oxygen bending below the ring plane. The $^3\text{enol}$ structure is nonplanar with the hydrogen from the OH radical attached to the phenol oxygen and popping above the ring plane. The ^3ekA form has the $COOCH_3$ group rotated quite noticeably out of the ring plane with the H12 atom sticking out at an angle almost normal to the ring plane.

The total energies of the different isomers in their lowest singlet and triplet states are compiled in Table 3.2. The $^1\text{ketoB}$ geometry was determined to have the lowest total energy of -14.562 keV. This finding is in agreement with a previous DFT calculation with smaller basis set[76]. Therefore, the $^1\text{ketoB}$ isomer is the global minimum structure and all energies reported in Table 3.2 are relative to the energy of this isomer. The $^1\text{ketoA}$ isomer is the next lowest energy at 0.082 eV above the $^1\text{ketoB}$. This result was checked against an all-electron ab initio MP2 (same basis set) calculation that yields 0.128 eV as the difference in energy between the two optimized rotamer structures. In supersonic jet experiments at various temperatures, an estimate of 0.11 eV was reported for the energy difference between $^1\text{ketoB}$ and $^1\text{ketoA}$ rotamers[10]. Although the DFT result is about 25% lower than the experiment and the MP2 result 16% higher than experiment, it is believed that thermal excitation of the vibrations in these two rotamers during the experiment accounts for such

Table 3.1: Geometry of methyl salicylate in the ground state.

bond	distance (Å)	bond	angle (deg)	dihedral bond	angle (deg)
C ₁ -C ₂	1.385	(2,1,6)	119.5	(6,1,2,3)	0.0
C ₁ -C ₆	1.404	(2,1,7)	120.2	(6,1,2,8)	-180.0
C ₁ -H ₇	1.082	(6,1,7)	120.3	(7,1,2,3)	180.0
C ₂ -C ₃	1.408	(1,2,3)	120.8	(7,1,2,8)	0.0
C ₂ -H ₈	1.081	(1,2,8)	120.9	(2,1,6,5)	0.0
C ₃ -C ₄	1.416	(3,2,8)	118.4	(2,1,6,11)	180.0
C ₃ -C ₁₃	1.456	(2,3,4)	119.1	(7,1,6,5)	-180.0
C ₄ -C ₅	1.399	(2,3,13)	121.8	(7,1,6,11)	0.0
C ₄ -O ₉	1.366	(4,3,13)	119.0	(1,2,3,4)	0.0
C ₅ -C ₆	1.386	(3,4,5)	119.8	(1,2,3,13)	-180.0
C ₅ -H ₁₀	1.081	(3,4,9)	122.8	(8,2,3,4)	180.0
C ₆ -H ₁₁	1.083	(5,4,9)	117.5	(8,2,3,13)	0.0
O ₉ -H ₁₂	0.991	(4,5,6)	120.0	(2,3,4,5)	0.0
C ₁₃ -O ₁₄	1.359	(4,5,10)	118.1	(2,3,4,9)	180.0
C ₁₃ -O ₁₅	1.254	(6,5,10)	121.9	(13,3,4,5)	180.0
O ₁₄ -C ₁₆	1.463	(1,6,5)	120.8	(13,3,4,9)	0.0
C ₁₆ -H ₁₇	1.085	(1,6,11)	119.8	(2,3,13,14)	0.0
C ₁₆ -H ₁₈	1.089	(5,6,11)	119.4	(2,3,13,15)	-180.0
C ₁₆ -H ₁₉	1.089	(4,9,12)	110.0	(4,3,13,14)	-180.0
		(3,13,14)	114.8	(4,3,13,15)	0.0
		(3,13,15)	124.0	(3,4,5,6)	0.0
		(14,13,15)	121.2	(3,4,5,10)	-180.0
		(13,14,16)	117.1	(9,4,5,6)	-180.0
		(14,16,17)	104.6	(9,4,5,10)	0.0
		(14,16,18)	110.1	(3,4,9,12)	0.0
		(14,16,19)	110.1	(5,4,9,12)	180.0
		(17,16,18)	111.1	(4,5,6,1)	0.0
		(17,16,19)	111.1	(4,5,6,11)	-180.0
		(18,16,19)	109.6	(10,5,6,1)	180.0
				(10,5,6,11)	0.0
				(3,13,14,16)	180.0
				(15,13,14,16)	0.0
				(13,14,16,17)	-180.0
				(13,14,16,18)	60.5
				(13,14,16,19)	-60.5

Table 3.2: Total electronic energy, zero point energy (ϵ_0), dipole moment, binding energy (BE), electron affinity (E.A.), ionization potential (I.P.), and HOMO/LUMO gap of each MS isomer. Total energies E are relative to the $^1\text{ketoB}$ ground state energy of -14.561723 keV.

isomer	state	E (eV)	ϵ_0 (eV)	BE (eV)	dipole (D)	E.A. (eV)	I.P. (eV)	Δ (eV)
ketoB	^1A	0	4.027	88.640	3.1	0.440	8.452	4.712
	^3A	3.117	3.887	85.528	1.4			2.356
ketoA	^1A	0.082	4.026	88.559	0.8	0.369	8.478	4.787
	^3A	3.240	3.904	85.404	3.0			2.349
$\text{ketoA}_{\text{open}}$	^1A	0.566	4.001	88.075	3.4	0.149	8.604	5.135
	^3A	3.825	3.879	84.820	4.2			2.568
$\text{ketoB}_{\text{open}}$	^1A	0.573	4.004	88.068	2.9	0.149	8.588	5.122
	^3A	3.829	3.879	84.817	3.3			2.559
enol	^1A	0.765	3.997	87.877	4.3	0.763	7.740	3.748
	^3A	2.861	3.917	85.783	2.7			2.848
ekA	^1A	1.926	3.983	86.714	5.7	1.038	7.341	3.553
	^3A	3.536	3.896	85.109	3.6			2.750

discrepancy. The $^1\text{ketoA}$ rotamer is theorized to coexist in equilibrium with $^1\text{ketoB}$ [6,10,11]. However, an energy barrier between these two isomers may not allow chemical equilibrium to occur at room or medium-to-high temperatures, as discussed in a later section. Both open-form isomers have considerably higher energy structures about 0.57 eV above $^1\text{ketoB}$. The geometry of the $^1\text{enol}$ is similar to the $^1\text{ketoB}$ due to the proton transfer from the carbonyl to the phenol groups and this isomer is 0.764 eV above the $^1\text{ketoB}$. Previous DFT studies using smaller basis sets were unable to find the singlet enol optimized structure[76]. The ekA is new to the literature and is the highest energy of all six isomers.

First excited triplet states of the six isomers are reported in Table 3.2. These triplet states are the lowest excited state for each isomer. Although the DFT approach used in this paper ensures that the reported triplet states are indeed the lowest of all triplets, the approach is inadequate for calculation of other excited states as will be shown in the following chapter. It is interesting to note that in the lowest triplet states, the energy ordering of the six isomers is altered when compared to the ordering in the ground state.

The $^3\text{enol}$ isomer is the lowest, followed by the $^3\text{ketoB}$ and $^3\text{ketoA}$. Table 3.2 provides values of the zero point energy ϵ_0 for both singlets and triplets of the six MS isomers showing that this quantity does not change much across the different isomers. The binding energies are defined as $BE = E_{MS} - E_{atomic}$, where E_{atomic} is the sum of energies of atoms at infinity. As expected, the isomer with the highest binding energy is $^1\text{ketoB}$. The isomer with the lowest binding energy is $^3\text{ketoBopen}$. The electron affinities (E.A.) and ionization potentials (I.P.) of the isomers are also reported. The E.A. and I.P. are calculated as the energy differences between the optimized state of the neutral and optimized state of the anion or cation, respectively. The E.A. and I.P. are only physically relevant for the singlet states. The highest E.A. belongs to ^1ekA while the lowest belongs to the open forms. The enolized structures have considerably lower I.P. than the keto forms.

In addition, calculated dipole moments of the MS isomers are reported in Table 3.2, showing that the $^1\text{ketoA}$ is the least polar of all isomers. Results of the $^1\text{ketoB}$ and $^1\text{ketoA}$ dipole moments are in agreement with the 3.1 and 0.8 D ab initio values obtained at the MP2 level. The hydrogen bond lengths in ketoB, ketoA, and enol are 1.75, 1.73, and 1.51 Å, respectively. These bond lengths compare well with the MP2 values of 1.75 Å(ketoB) and 1.78 Å(ketoA). Rotational constants for the six isomers are similar and are shown in Table 3.3. At the MP2 level, the rotational constants are 2.15870, 0.83002, and 0.60179 GHz for ketoB and 2.24933, 0.82818, and 0.607639 GHz for ketoA. Rotational constants for the most stable isomer ketoB are in agreement with experimental measurements[76].

In the liquid phase, solvent effects may induce structural shifts in the solute molecular constituents. Therefore, properties such as the binding energy, dipole moments, and quadrupole moments will change. A mixture of ketoB and ketoA in the liquid phase was considered and the polarized continuum model (PCM)[81] was used to calculate molecular properties of the solute. Considering one $^1\text{ketoB}$ molecule in an MS solvent with relative dielectric constant, $\epsilon = 9.0$ (ketoB value[82]), the solvent destabilizes $^1\text{ketoB}$ by 0.085 eV, zero-point energy decreases 0.005 eV to 4.022 eV, and the dipole moment increases to 3.9 D from 3.1 D. The total energy for $^1\text{ketoA}$ increased 0.062 eV, the zero-point energy decreased

Table 3.3: Rotational constants for the six gas phase isomers of MS calculated with B3PW91/6-311++G

Isomer	A (GHz)	B (GHz)	C (GHz)
ketoB	2.14358	0.82490	0.59792
ketoA	2.24913	0.82585	0.60637
ketoB _{open}	2.09378	0.82141	0.59216
ketoA _{open}	2.22137	0.81777	0.59998
enol	2.21092	0.82402	0.60258
ekA	2.23019	0.81010	0.59755

0.004 eV to 4.022 eV, the dipole moment changed from 0.8 to 0.9 D.

3.3 Vibrational Analysis

The calculated vibrational spectra of ketoB and ketoA in the singlet electronic states are reported in Table 3 and compared to IR experimental results in the gas phase[77, 83]. Reported frequencies are the calculated frequencies scaled by a factor of 0.97. The scaling factor was chosen as it produced the minimum sum squared error between the the most prominent frequencies with IR intensity higher than 50 km/mol are compared to experimental data in [83]. A plot of the sum squared error versus scaling factor is shown in Figure 3.2 for the ketoB and ketoA isomers. Additionally, this table contains the calculated intensity of the different lines and their summarized assignment. The scaled vibrational spectra for the other four isomers in their singlet electronic states and for all six isomers in the triplet states are reported in Table 4.

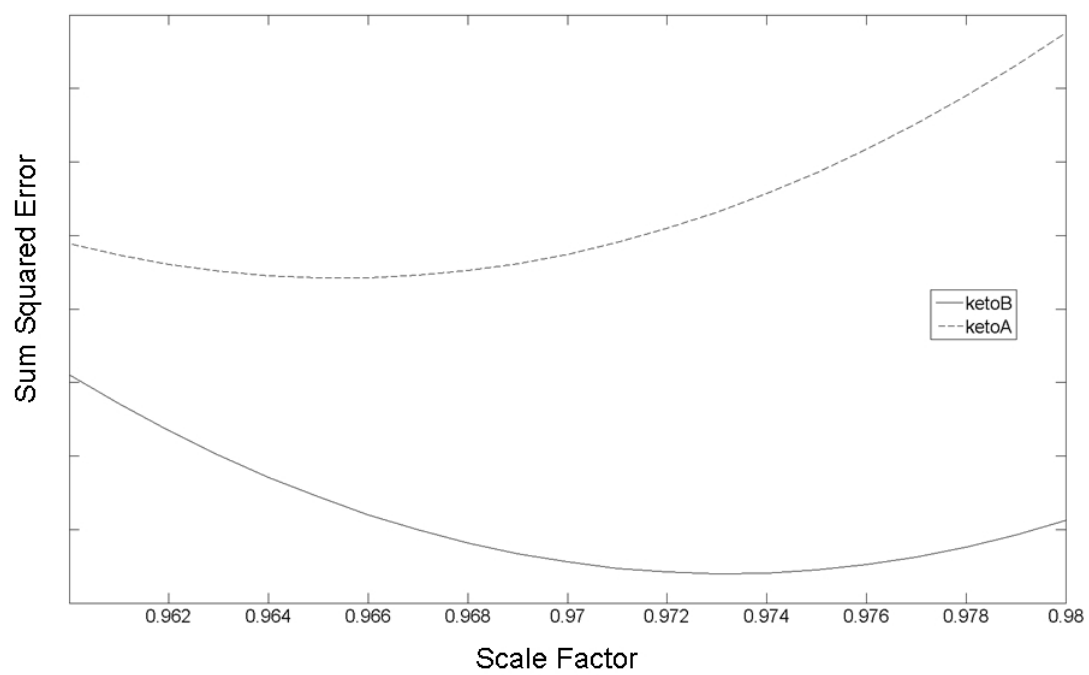


Figure 3.2: Plot of sum squared error vs. vibrational scaling factor for ketoB (solid line) and ketoA (dashed line) MS isomers.

In the high frequency range, a modestly intense absorption line in the experiment is seen at about 3200 cm^{-1} [83]. This absorption is likely due to the OH stretch in the phenol. From the calculations, both $^1\text{ketoB}$ and $^1\text{ketoA}$ isomers have strong IR intensities due to the contribution of the OH stretching to the normal mode vibrations at 3262 and 3387 cm^{-1} , respectively. The calculated OH stretch for $^1\text{enol}$ is the second most intense feature of its vibrational spectrum and is located at a significantly red-shifted 2978 cm^{-1} . The calculated OH stretching of $^1\text{ketoA}_{open}$ and $^1\text{ketoB}_{open}$ isomers are located at 3615 cm^{-1} and their IR-active intensity is weak. In the triplet state of $^3\text{ketoA}$ the OH stretching appears in two modes at 2979 and 2993 cm^{-1} while in $^3\text{ketoB}$ it appears in only one mode at 2424 cm^{-1} , both cases displaying a dramatic red shift. However, the OH stretching in the $^3\text{ketoA}_{open}$ and $^3\text{ketoB}_{open}$ is shifted by only a few wavenumbers to 3590 and 3589 cm^{-1} . The $^3\text{enol}$ isomer was calculated to have a strong OH stretching at 3004 cm^{-1} . The ^1ekA and ^3ekA have OH stretching modes shifted to the blue at 3644 and 3622 cm^{-1} , respectively. The experimental less intense lines at $2850\text{-}3100\text{ cm}^{-1}$ are due to CH stretches and CH₃ symmetric and asymmetric stretches.

One of the two strongest absorption lines in [83] is at 1698 cm^{-1} (Table 3). This intense line is almost always seen in carboxylic acid derivatives[84,85]. In aromatic esters, the rule of three bands (RTB)[84] places the C=O stretching line within $1715\text{-}1730\text{ cm}^{-1}$. Our calculation shows a strong C=O stretching vibration at 1647 cm^{-1} (1686 cm^{-1} without scaling) for $^1\text{ketoB}$ and at 1655 cm^{-1} (1694 cm^{-1} without scaling) for $^1\text{ketoA}$. The $^1\text{ketoB}_{open}$ C=O stretch is also in the vicinity at 1656 cm^{-1} and for $^1\text{ketoA}_{open}$, $^1\text{enol}$, ^1ekA the calculated line lies considerably lower at 1625 , 1638 , 1646 cm^{-1} , respectively. The other strong line reported in [83] is at 1310 cm^{-1} . Again from the RTB, the C-C-O stretch of aromatic esters is in the $1250\text{-}1310\text{ cm}^{-1}$ range. The calculated C-C-O stretching mode is located at 1308 cm^{-1} in $^1\text{ketoB}$ and at 1269 cm^{-1} in $^1\text{ketoA}$. In the open forms $^1\text{ketoB}_{open}$, $^1\text{ketoA}_{open}$ and in $^1\text{enol}$, ^1ekA this mode appears at 1245 , 1316 , 1334 , and 1357 cm^{-1} , respectively. The third vibration frequency from RTB for aromatic esters is the O-C-C stretch, which

Table 3.4: Calculated vibrational spectra of ¹ketoB and ¹ketoA isomers and comparison with experiments. Ref [77] is taken from Table 2, columns 2-4.

¹ ketoB ν (cm ⁻¹)	Intensity	Assignment	¹ ketoA ν (cm ⁻¹)	Intensity	Ref [83] (cm ⁻¹)	Ref [77] (cm ⁻¹)	Experiment Ref [77] (cm ⁻¹)	Ref [77] (cm ⁻¹)
3262	244	ν O-H	3387	305	3262	3188		
3151	8	ν_s ring C-H	3147	10				
3145	7	ν_a ring C-H	3140	11				
3126	14	ν_a ring C-H	3125	8				
3115	11	ν_a CH ₃	3114	9		3010		
3108	6	ν_a ring C-H	3109	6	3078	2954	3081	2977
3080	17	ν_a CH ₃	3086	14		2920	2964	2931
2988	32	ν_s CH ₃	2992	31	2966	2850	2854	2874
1647	200	ν C=O, ν ring C-C, ρ Ph H	1655	234	1698	1682	1683	1647
1593	136	ν C=O, ν ring C-C	1633	248	1618	1616	1620	
1579	30	ν C=O, ρ Ph H	1587	32		1586	1590	1562
1490	70	ρ ring C-H	1494	17	1482			1509
1487	28	σ CH ₃	1488	6				
1473	14	τ CH ₃	1484	122				
1463	10	ρ ring H	1472	15				
1444	78	ω CH ₃	1442	14	1450	1488	1472	1449
1385	135	ρ Ph H	1386	17	1410	1442	1437	
1357	40	ν ring C-C	1343	23				1350
1308	273	ν C-Me O, ρ ring H	1269	320	1310	1339	1337	1277
1253	50	ν C-Ph O, ρ ring H	1247	32	1254	1307		
1222	291	ρ Ph H	1214	90	1214	1255	1255	
1179	38	σ ring H	1178	10		1218	1203	
1174	79	τ CH ₃	1168	38	1166	1159	1162	
1139	27	σ ring H	1137	1		1137	1143	
1136	1	τ CH ₃	1116	64				
1091	81	ν O-Me	1077	162	1094	1092	1068	
1034	15	ω ring CH	1035	59		1034	1039	
992	0	ω ring CH	997	1				
981	2	ω ring CH	985	2				
941	8	ν O-Me	934	14		965	965	
874	0	ω ring CH	876	0				
835	20	ring breath, ν C-Ph O	844	2	854	850	858	874
786	28	ω ring CH	790	30	754	802	814	
784	1	σ C(=O)-O	765	20				
748	8	ω C-C/C-H/O-H	751	35		760		
728	208	ω OH	693	104	706	702		735
680	2	ω ring	662	80				
671	12	ring breath	661	6		667	671	
563	4	ring breath	556	8			566	
529	7	ω ring	531	5	530	563	517	523
507	12	ρ O ₉ H ₁₂ -O ₁₅	528	4		511		
437	0	ω out-of-plane	441	0				
431	5	ρ in-plane	387	8			442	432
342	19	ρ O ₉ H ₁₂ -O ₁₅	351	3			346	345
323	8	ρ in-plane	312	12				
259	2	ω full molecule	256	1			267	219
174	3	ω full molecule	183	2			190	
166	2	ρ CH ₃	176	2				
128	2	τ CH ₃	108	0				
86	1	τ CH ₃	85	0				
74	0	τ CH ₃	62	6				

ν , stretching; ω , wagging; ρ , rocking; τ , twisting; σ , scissoring; Ph, phenyl; Me, methyl.
Subscripts : a, asymmetric; s, symmetric.

Table 3.5: Vibrational frequencies of the five MS isomers.

¹ ketoA _{open} (cm ⁻¹)	¹ ketoB _{open} (cm ⁻¹)	¹ enol (cm ⁻¹)	¹ ekA (cm ⁻¹)	³ ketoB (cm ⁻¹)	³ ketoA (cm ⁻¹)	³ ketoA _{open} (cm ⁻¹)	³ ketoB _{open} (cm ⁻¹)	³ enol (cm ⁻¹)	³ ekA (cm ⁻¹)
3615	3615	3142	3644	3158	3157	3590	3589	3149	3622
3145	3163	3136	3135	3151	3145	3147	3154	3143	3140
3129	3131	3123	3125	3132	3131	3141	3145	3127	3125
3113	3113	3119	3122	3106	3107	3108	3107	3106	3115
3110	3105	3098	3094	3103	3101	3102	3098	3106	3108
3087	3089	3090	3085	3064	3075	3079	3080	3070	3101
3070	3068	2995	3046	2978	2993	3059	3058	3004	3068
2982	2981	2978	2991	2424	2979	2975	2974	2981	2973
1625	1656	1638	1646	1592	1550	1556	1550	1570	1536
1621	1619	1571	1595	1542	1536	1507	1518	1504	1527
1590	1600	1543	1540	1508	1506	1489	1492	1491	1490
1511	1512	1524	1508	1489	1493	1472	1471	1489	1482
1486	1490	1485	1482	1470	1472	1470	1465	1473	1478
1471	1472	1474	1477	1455	1471	1445	1447	1459	1448
1460	1455	1464	1466	1441	1437	1431	1431	1445	1410
1439	1441	1446	1448	1425	1427	1390	1394	1420	1381
1359	1357	1386	1396	1376	1407	1381	1381	1385	1350
1316	1313	1357	1357	1337	1332	1312	1293	1370	1270
1293	1269	1334	1281	1288	1291	1276	1282	1266	1250
1243	1245	1254	1239	1265	1272	1207	1209	1243	1213
1185	1185	1202	1184	1198	1173	1167	1168	1213	1171
1181	1174	1173	1173	1169	1161	1156	1161	1166	1170
1169	1168	1163	1152	1149	1149	1132	1135	1146	1126
1133	1137	1142	1126	1131	1137	1101	1104	1129	1096
1124	1121	1132	1114	1121	1109	1087	1086	1081	1085
1086	1067	1100	1053	1076	1057	1063	1061	1068	1036
1048	1050	1008	1005	1012	967	973	963	1002	1014
1010	999	998	1000	956	942	923	932	953	960
974	971	981	948	949	910	909	912	931	924
938	944	924	910	937	898	842	852	890	914
860	861	855	848	892	849	814	790	829	855
844	828	838	842	808	819	774	773	819	833
795	799	770	761	804	808	736	736	811	758
777	774	746	746	741	714	684	683	735	694
757	759	738	711	681	667	642	640	715	683
673	667	723	655	594	600	609	613	617	603
662	667	674	617	587	598	560	554	605	557
558	564	629	547	549	528	527	515	545	529
536	537	554	538	511	519	470	480	535	505
527	499	544	512	505	516	450	443	483	459
453	448	521	461	423	393	391	401	447	383
372	391	451	401	408	371	381	390	408	350
338	353	417	387	355	358	334	335	345	323
295	329	370	341	321	352	312	307	328	313
292	292	316	301	314	298	270	262	319	267
247	256	243	224	222	221	180	183	226	200
168	170	174	161	151	182	152	147	164	181
156	164	158	139	141	119	128	139	148	124
110	111	119	112	101	100	111	107	119	102
94	94	86	65	85	77	78	66	98	64
26	24	81	60	75	57	49	58	59	41

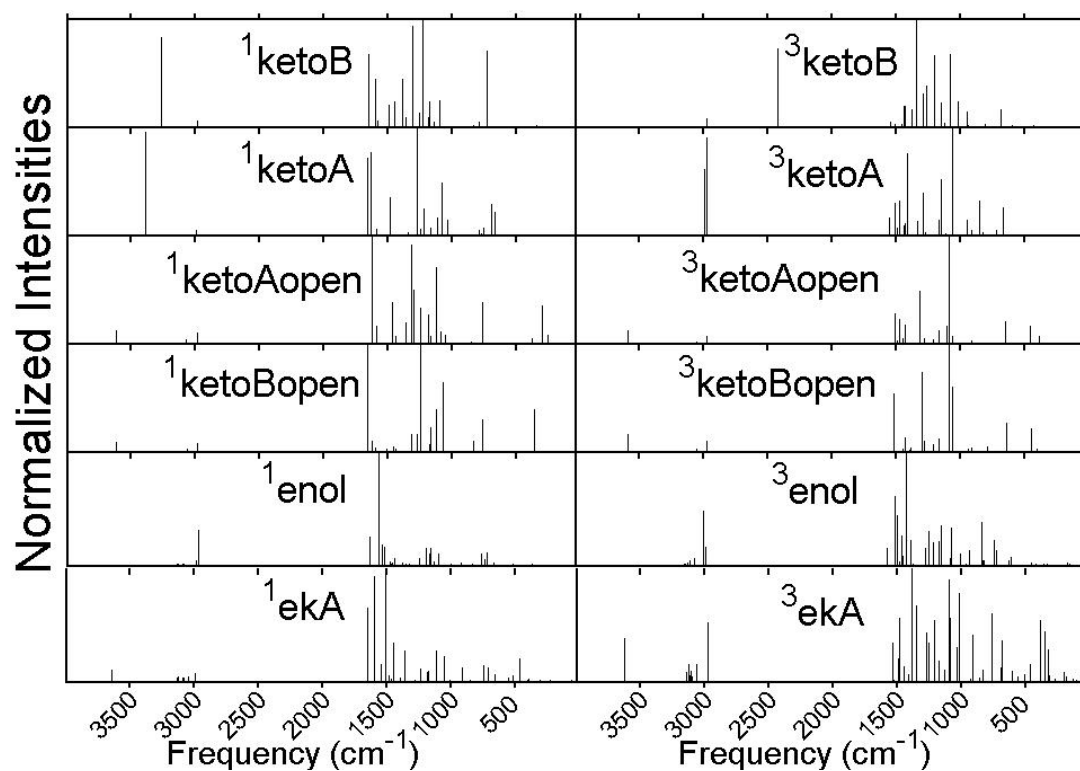


Figure 3.3: IR active spectra of the six MS isomers in the ground state and first excited triplet state.

typically falls in the 1000-1130 cm^{-1} range. Experimental work locates this O-C-C stretch absorption line at 1094[77,83] which coincides well with the calculations at 1091 cm^{-1} for $^1\text{ketoB}$ and a rather intense line at 1077 cm^{-1} for $^1\text{ketoA}$. The calculated O-C-C stretching mode in $^1\text{ketoB}_{open}$ is very strong at 1067 cm^{-1} , in $^1\text{ketoA}_{open}$ is intense at 1124 cm^{-1} , and appears rather intense in $^1\text{enol}$ at 1100 cm^{-1} and ^1ekA at 1053 cm^{-1} , respectively. This O-C-C stretch is strong in both $^3\text{ketoB}$ at 1076 cm^{-1} and $^3\text{ketoA}$ at 1057 cm^{-1} . All four isomers $^3\text{ketoB}_{open}$ and $^3\text{ketoA}_{open}$, $^3\text{enol}$ and ^3ekA show the O-C-C stretch as their most intense lines at 1086, 1087, 1068, and 1085 cm^{-1} , respectively. All three RTB calculated lines agree very well with the experimental values listed in Table 3.

In $^1\text{ketoB}$, the umbrella mode is located at 1444 cm^{-1} and the in-plane OH bend at 1385 cm^{-1} . Two prominent experimental absorption lines[83] are located at approximately 754 and 705 cm^{-1} . Since MS has an ortho-substituted benzene ring, then the first line is due to out-of-plane CH motion while the latter is due to aromatic ring bending vibrations. The calculated out-of-plane CH bending vibrations for the different isomers have the following wavenumbers: $^1\text{ketoB}$ at 786 cm^{-1} , $^1\text{ketoA}$ at 790 cm^{-1} , $^1\text{ketoA}_{open}$ at 757 cm^{-1} , $^1\text{ketoB}_{open}$ at 759 cm^{-1} , $^1\text{enol}$ at 770 cm^{-1} , ^1ekA at 746 cm^{-1} , $^3\text{ketoA}$ at 808 and 667 cm^{-1} , $^3\text{ketoB}$ at 808 and 681 cm^{-1} , $^3\text{ketoA}_{open}$ at 774 and 642 cm^{-1} , $^3\text{ketoB}_{open}$ at 773 and 640 cm^{-1} , $^3\text{enol}$ at 735 cm^{-1} , and ^3ekA at 758 cm^{-1} . Except for $^3\text{enol}$ and ^3ekA , isomers in the triplet states show a CH out-of-plane motions into two different modes because only some of the CH bonds participate in one mode while the rest move in the other mode.

The calculated aromatic ring bending vibrations appear at the following wavenumbers: $^1\text{ketoA}$ at 662 cm^{-1} , $^1\text{ketoB}$ at 680 cm^{-1} , $^1\text{ketoA}_{open}$ at 673 cm^{-1} , $^1\text{ketoB}_{open}$ at 667 cm^{-1} , $^1\text{enol}$ at 674 cm^{-1} , ^1ekA at 655 cm^{-1} , $^3\text{ketoA}$ at 600 cm^{-1} , $^3\text{ketoB}$ at 594 cm^{-1} , $^3\text{ketoA}_{open}$ at 609 cm^{-1} , $^3\text{ketoB}_{open}$ at 613 cm^{-1} , $^3\text{enol}$ at 617 cm^{-1} , and ^3ekA at 683 cm^{-1} .

3.4 Free Energy

With the calculated normal-mode frequencies, a harmonic analysis of several thermodynamic functions is feasible within the canonical ensemble[86]. For example, the free-energy, internal energy, and vibrational specific heat were calculated for all six isomers as a function of temperature. By inspecting the temperature dependence of the Helmholtz free energy of each MS isomer in their singlet and triplet states, it is estimated that these structures will not undergo thermal isomerization up to temperatures of about 2000 K (Figure 3.4). More so, at temperatures above 2000 K, the $^1\text{ketoA}$ isomer becomes more stable than $^1\text{ketoB}$ and a crossing of the free energy curves occurs[87]. At even higher temperatures the $^1\text{ketoA}_{open}$ is the most stable isomer. The harmonic approximation of the thermodynamic functions is very accurate at lower energies. However, it is believed that as a first estimate, the high temperature results provide a qualitative description of a given process. Therefore, the findings are indicative that at $T = 300$ K thermal fluctuations would not be responsible for an isomer structural transition. On the basis of this fact, extra energy of about 0.3 eV is needed to isomerize ketoB into ketoA, and chemical equilibrium would strongly favor a high relative concentration of about 100% ketoB versus ketoA. This result is consistent with previously proposed chemical equilibrium in which MS vapor at room temperature is mainly ketoB and only 1/70 of its concentration is ketoA[10].

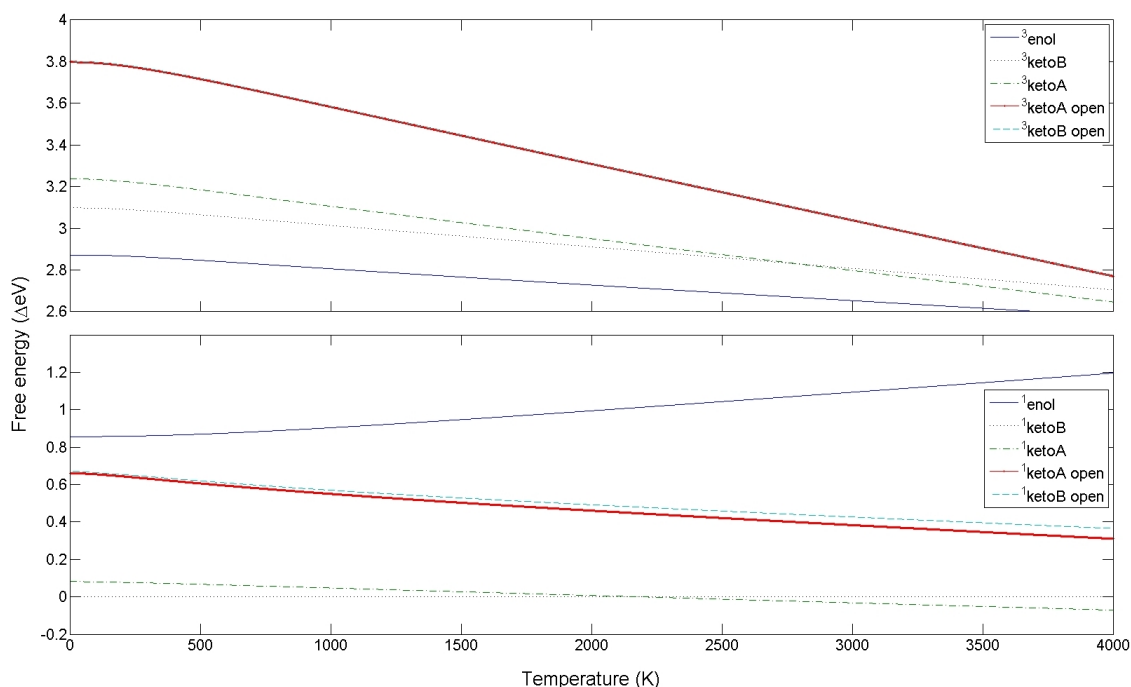


Figure 3.4: Free energy vs. temperature of the MS isomers.

3.5 Gas Phase Reaction Paths

On the basis of the harmonic estimate of the isomer transition, the isomerization reaction of ketoB to ketoA at the DFT level of calculation was investigated. A transition state was found at 0.67 eV above the ketoB energy, which has the lowest positive and one negative frequencies at $+85$ and -125 cm^{-1} . The transition state geometry was discovered with the synchronous transit-guided quasi-Newton method[57,58] and letting all bond lengths and angles relax. This structure has the COOCH_3 group rotated $\pm 90^\circ$ with respect to the ring plane and away from its position in the ketoB structure. For comparison, the transition state geometry was recalculated at the MP2 level and the energy difference with respect to the MP2 optimized structure of ketoB yields 0.71 eV. Adding the solvent effect with PCM reduces the transition barrier to 0.5 eV. Next, the transition state geometry and the computed force constants were used as input for calculating the MS energy along the

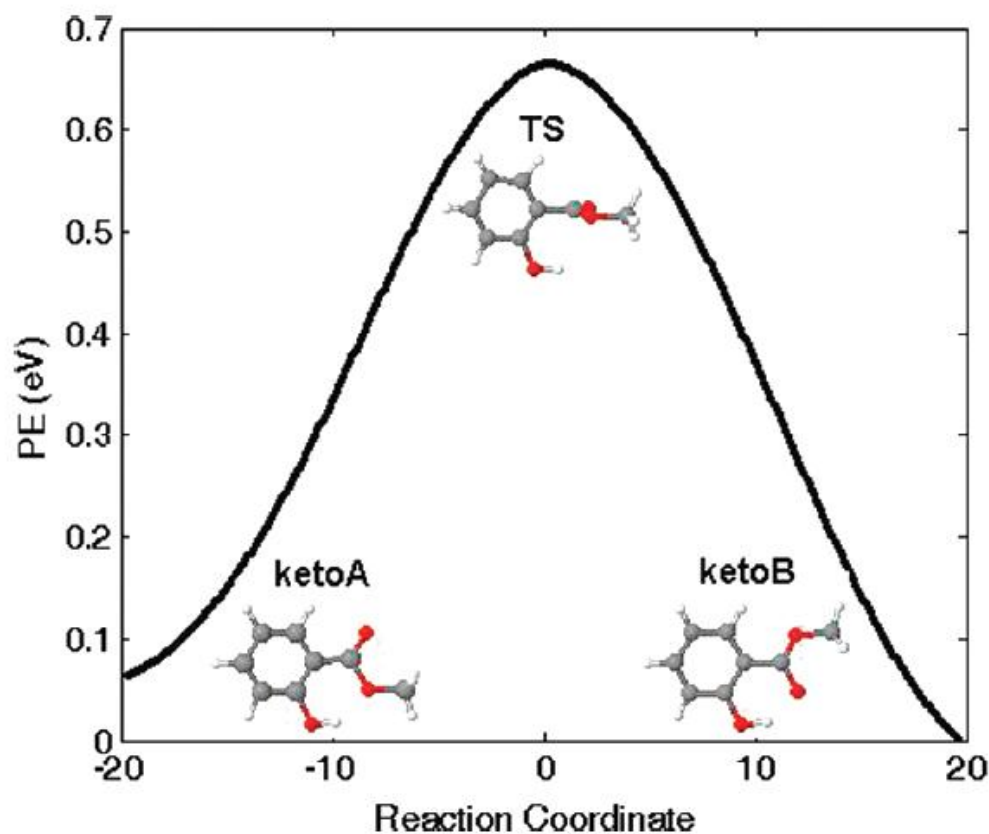


Figure 3.5: IRC isomerization reaction path following the O14-C13-C3-C2 dihedral angle changes.

intrinsic reaction coordinate path (IRC)[87] shown in Figure 3.5. The IRC path was followed by relaxing the mass-weighted internal coordinates of atoms 14, 13, 3, 2 (Figure 3.1) that participate in the pertinent dihedral angle, which changes from 0° (ketoB) to 180° (ketoA) along the reaction.

3.6 Conclusion

The full energetics and vibrational analysis study of six isomers of MS are presented in this chapter. It is predicted that at the BPW91/6-311++G level of calculation all six isomers in their ground state are singlets. A full report of structures and energies of both the ground state and first excited triplet state is part of this chapter. The ketoB isomer is

the global minimum followed in energy by its rotamer ketoA. The calculations for ketoB and ketoA confirms an earlier DFT study with smaller basis sets[76]. The structure and energy of the open forms of the ketoB and ketoA isomers, the isomer with ring-inserted carbonyl radical (enol), and the enolized ketoA are new to the literature. The full calculated vibrational spectra of these six isomers in their ground state and first triplet state are also reported. The calculated vibrational lines of ¹ketoB correspond quite well to the peaks of the experimental spectrum[77,83]. Specifically, the calculated lines corresponding to the OH and CH stretching vibrations in the 3000-3500 cm⁻¹ region correlate well with the experiments. The match of C=O stretching vibrations near 1700 cm⁻¹ is less well-defined. However, the C-C-O and O-C-C calculated stretching vibrations lie close to the experimental bands. One intense line calculated at approximately 727 cm⁻¹ is due to the aromatic ring bending vibration and might be correlated to either of the observed lines at 754 or at 705 cm⁻¹.

The isomerization reaction between the rotamers ketoB and ketoA was followed in detail showing the existence of an energy barrier of 0.67 eV. Estimates of the liquid phase of MS, by assuming each molecule in a solvent of all the others, depletes the isomerization barrier by 0.17 eV. The high value of this barrier to the internal rotation of the -COOCH₃ group is indicative that at room temperature the isomerization reaction is unlikely to occur. However, since the reverse isomerization energy (ketoA to ketoB) barrier of 0.59 eV is almost as high, then it is likely that any ketoA species that are present in a sample will remain ketoA at room temperature.

The MS ground state results presented in this chapter are significant because they provide a starting point for excited state electronic structure and photoluminescence calculations. One needs to have thoroughly investigated the ground state energetics and various geometrical conformations prior to studying a molecule's excited state. More importantly, the energetics and vibrational analysis results will be used as inputs for the excited state calculations presented in the next chapter.

Chapter 4: Methyl Salicylate Excited States

4.1 Introduction

The photophysics of methyl salicylate (MS) isomers studied in Chapter 3 is studied in this chapter using Time-Dependent Density Functional Theory[51] and large basis sets[43, 45, 48, 88, 89]. The singlet and triplet excited state energies were calculated and compared to ground state energies. The newly calculated photochemical pathway involving excited state intermolecular proton transfer (ESIPT) is shown to agree well with the dual fluorescence obtained from experiments[9, 10, 18]. Temperature effects on the fluorescence mechanisms are also presented. It is suggested that many forward and reverse ESIPT traverse a barrier in the excited state which gives rise to the temperature-dependent dual fluorescence seen in experiments. Finally, a barrier-less back proton transfer repopulates the ground state of methyl salicylate after photoemission occurs.

4.2 Excitation

Time Dependent Density Functional Theory (TDDFT) states that there is a unique mapping between the time-dependent external potential of a system and the time-dependent electron density[51]. The application of TDDFT to organic molecules[52] and coumarins[53] have been highly successful in calculating transition energies from ground to first excited state. In the study presented in this chapter, linear response, non-equilibrium TDDFT calculated with the Gaussian 09[54] software package is used.

In previous and present calculations, three MS isomers (ketoB, enol, and ketoA)[90] in their gas phase were optimized at the B3PW91/6-31++G, B3PW91/6-311++G, B3PW91/6-311++G(d), B3PW91/6-31+G(3d,3p), and B3PW91/6-311++G(3d,3p) levels of theory to

determine the ground state structures, force constants, and wavefunctions. A variety of basis sets were used in order to investigate the dependence on the size of split-valence basis sets, polarization functions, and diffuse functions. 6-31++G is a double- ζ basis set with two extra diffuse d-functions. 6-311++G is a triple- ζ basis set. The (d) option adds a d function for first and second row atoms while the (3d,3p) option adds 3 sets of d functions on heavy atoms and 3 sets of p functions on hydrogens. The energies and oscillator strengths of the six lowest singlet and triplet excited states were calculated. The oscillator strengths of the triplet states are all zero because they are spin forbidden transitions. The results from the larger basis set calculations are shown in Table 4.1.

4.3 Optimized Excited State Structures

The wavefunction of the first excited singlet state along with the same structure and force constants were then used as inputs for a TDDFT geometry optimization at the same levels of theory. The TDDFT optimization used analytical gradients to determine the equilibrated geometries of the first excited singlet states. Figure 4.1 shows the optimized structures from the B3PW91/6-311++G(3d,3p) calculations. A frequency calculation was then performed on each of the stable geometries to confirm that each was a local minimum on its potential energy surface. Successful optimization was achieved for the ketoB, ketoA, enol, and ketoA_{open} structures. The ketoB_{open} and ekA structures did not converge to stable excited state geometries. Tables 4.2 and 4.3 give the optimized geometries of ketoB and enol in their excited singlet states calculated at the B3PW91/6-311++G(3d,3p) level, respectively.

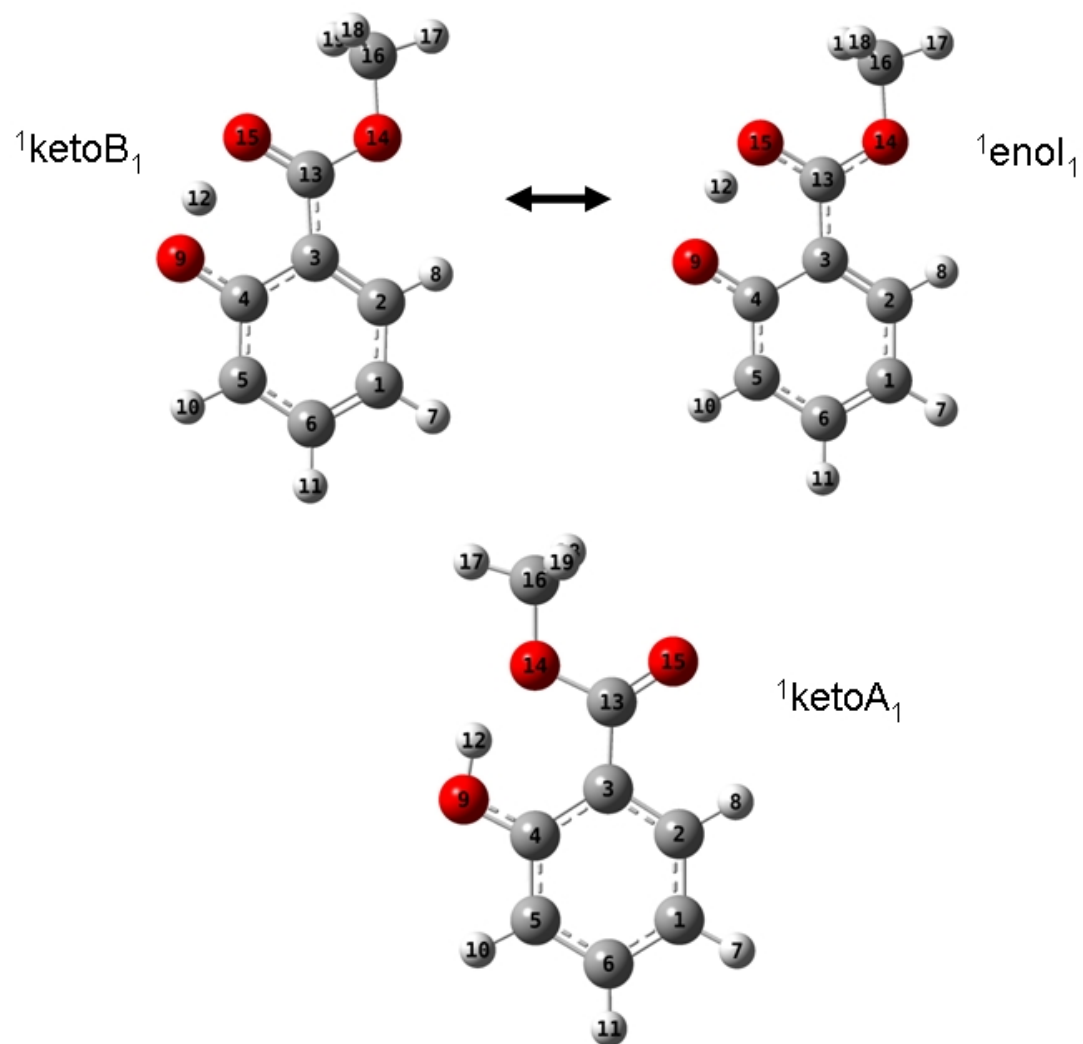


Figure 4.1: Structure of three stable MS isomers in their singlet excited states optimized at the B3PW91/6-311++G(3d,3p) level.

Table 4.1: TDDFT calculated vertical excitations of MS in gas phase. ΔE is energy (in eV) above each isomer ground state, λ is the wavelength (in nm) of transition from ground to excited states, and f is the oscillator strength ($\times 10^{-2}$).

	6-311++G				6-311+G(d)				6-31+G(3d,3p)			
	State	ΔE	λ	f	State	ΔE	λ	f	State	ΔE	λ	f
ketoB	³ A	3.26	381	0	³ A	3.30	376	0	³ A	3.26	380	0
	³ A	3.53	351	0	³ A	3.54	350	0	³ A	3.52	352	0
	¹ A	4.15	299	9.4	¹ A	4.24	292	9.4	¹ A	4.20	295	9.2
	³ A	4.34	285	0	³ A	4.30	288	0	³ A	4.27	290	0
	³ A	4.52	274	0	³ A	4.79	259	0	³ A	4.76	260	0
	¹ A	4.90	253	0	¹ A	5.17	240	0	¹ A	5.14	241	0
ketoA	³ A	3.30	375	0	³ A	3.37	368	0	³ A	3.35	370	0
	³ A	3.54	350	0	³ A	3.55	349	0	³ A	3.53	351	0
	¹ A	4.23	293	8.7	³ A	4.32	287	0	³ A	4.29	289	0
	³ A	4.34	285	0	¹ A	4.33	286	8.4	¹ A	4.31	288	8.0
	³ A	4.49	276	0	³ A	4.76	261	0	³ A	4.71	263	0
	¹ A	4.94	251	0.0	¹ A	5.18	240	0.0	¹ A	5.13	242	0.0
ketoB _{open}	³ A	3.42	363	0	³ A	3.44	360	0	³ A	3.42	362	0
	³ A	3.80	327	0	³ A	3.74	332	0	³ A	3.70	335	0
	³ A	3.98	311	0	³ A	4.28	290	0	³ A	4.27	291	0
	³ A	4.42	281	0	³ A	4.37	284	0	³ A	4.34	286	0
	¹ A	4.42	281	0.0	¹ A	4.54	273	9.0	¹ A	4.51	275	8.6
	¹ A	4.52	275	9.2	¹ A	4.69	265	0.0	¹ A	4.67	265	0.0
ketoA _{open}	³ A	3.42	363	0	³ A	3.45	360	0	³ A	3.43	361	0
	³ A	3.81	326	0	³ A	3.75	330	0	³ A	3.72	334	0
	³ A	4.26	291	0	³ A	4.37	284	0	³ A	4.34	286	0
	³ A	4.40	282	0	³ A	4.55	272	0	³ A	4.52	274	0
	¹ A	4.52	274	8.6	¹ A	4.56	272	8.3	¹ A	4.53	274	7.9
	¹ A	4.67	266	0.0	¹ A	4.93	252	0.0	¹ A	4.90	253	0.0
enol	³ A	1.57	790	0	³ A	2.23	555	0	³ A	2.27	546	0
	¹ A	2.96	419	11.6	³ A	3.45	359	0	³ A	3.44	360	0
	³ A	2.97	417	0	¹ A	3.48	356	13.1	¹ A	3.49	356	12.5
	¹ A	3.20	387	0	³ A	3.65	340	0	³ A	3.69	336	0
	³ A	3.22	385	0	¹ A	3.88	319	0	¹ A	3.91	317	0
	³ A	3.91	317	0	³ A	4.13	300	0	³ A	4.11	302	0
ekA	³ A	1.69	734	0	³ A	1.83	674	0	³ A	1.83	676	0
	³ A	2.38	521	0	³ A	2.65	468	0	³ A	2.63	471	0
	¹ A	2.70	458	0.1	¹ A	2.93	423	0.3	¹ A	2.92	424	0
	¹ A	3.42	363	17.8	¹ A	3.43	361	17.0	¹ A	3.39	366	16.4
	³ A	3.45	360	0	³ A	3.48	356	0	³ A	3.46	358	0
	³ A	3.97	312	0	³ A	4.03	307	0	³ A	4.02	308	0

Table 4.2: Geometry of the first excited singlet of the ketoB isomer calculated with B3PW91/6-311++G(3d,3p)

	distance		angle	dihedral	angle
bond	(Å)	bond	(deg)	bond	(deg)
C ₁ -C ₂	1.435	(2,1,6)	121.6	(6,1,2,3)	0.0
C ₁ -C ₆	1.379	(2,1,7)	118.2	(6,1,2,8)	0.0
C ₁ -H ₇	1.083	(6,1,7)	120.2	(7,1,2,3)	0.0
C ₂ -C ₃	1.382	(1,2,3)	121.5	(7,1,2,8)	0.0
C ₂ -H ₈	1.082	(1,2,8)	119.1	(2,1,6,5)	0.0
C ₃ -C ₄	1.446	(3,2,8)	119.4	(2,1,6,11)	0.0
C ₃ -C ₁₃	1.442	(2,3,4)	116.6	(7,1,6,5)	0.0
C ₄ -C ₅	1.405	(2,3,13)	126.0	(7,1,6,11)	0.0
C ₄ -O ₉	1.308	(4,3,13)	117.4	(1,2,3,4)	0.0
C ₅ -C ₆	1.413	(3,4,5)	121.5	(1,2,3,13)	0.0
C ₅ -H ₁₀	1.082	(3,4,9)	118.0	(8,2,3,4)	0.0
C ₆ -H ₁₁	1.081	(5,4,9)	120.5	(8,2,3,13)	0.0
O ₉ -H ₁₂	1.097	(4,5,6)	120.6	(2,3,4,5)	0.0
C ₁₃ -O ₁₄	1.346	(4,5,10)	117.7	(2,3,4,9)	0.0
C ₁₃ -O ₁₅	1.275	(6,5,10)	121.8	(13,3,4,5)	0.0
O ₁₄ -C ₁₆	1.424	(1,6,5)	118.2	(13,3,4,9)	0.0
C ₁₆ -H ₁₇	1.087	(1,6,11)	121.2	(2,3,13,14)	0.0
C ₁₆ -H ₁₈	1.091	(5,6,11)	120.6	(2,3,13,15)	0.0
C ₁₆ -H ₁₉	1.091	(4,9,12)	104.2	(4,3,13,14)	0.0
		(3,13,14)	115.9	(4,3,13,15)	0.0
		(3,13,15)	122.5	(3,4,5,6)	0.0
		(14,13,15)	121.5	(3,4,5,10)	0.0
		(13,14,16)	115.9	(9,4,5,6)	0.0
		(14,16,17)	105.7	(9,4,5,10)	0.0
		(14,16,18)	110.9	(3,4,9,12)	0.0
		(14,16,19)	110.9	(5,4,9,12)	0.0
		(17,16,18)	110.3	(4,5,6,1)	0.0
		(17,16,19)	110.3	(4,5,6,11)	0.0
		(18,16,19)	108.9	(10,5,6,1)	0.0
				(10,5,6,11)	0.0
				(3,13,14,16)	0.0
				(15,13,14,16)	0.0
				(13,14,16,17)	0.0
				(13,14,16,18)	60.5
				(13,14,16,19)	-60.5

Table 4.3: Geometry of the first excited singlet of the enol isomer calculated with B3PW91/6-311++G(3d,3p)

bond	distance (Å)	bond	angle (deg)	dihedral bond	angle (deg)
C ₁ -C ₂	1.438	(2,1,6)	120.2	(6,1,2,3)	0.0
C ₁ -C ₆	1.370	(2,1,7)	118.8	(6,1,2,8)	0.0
C ₁ -H ₇	1.082	(6,1,7)	121.0	(7,1,2,3)	0.0
C ₂ -C ₃	1.376	(1,2,3)	121.7	(7,1,2,8)	0.0
C ₂ -H ₈	1.083	(1,2,8)	118.9	(2,1,6,5)	0.0
C ₃ -C ₄	1.449	(3,2,8)	119.4	(2,1,6,11)	0.0
C ₃ -C ₁₃	1.442	(2,3,4)	118.6	(7,1,6,5)	0.0
C ₄ -C ₅	1.409	(2,3,13)	123.9	(7,1,6,11)	0.0
C ₄ -O ₉	1.287	(4,3,13)	117.5	(1,2,3,4)	0.0
C ₅ -C ₆	1.419	(3,4,5)	118.7	(1,2,3,13)	0.0
C ₅ -H ₁₀	1.083	(3,4,9)	119.1	(8,2,3,4)	0.0
C ₆ -H ₁₁	1.082	(5,4,9)	122.2	(8,2,3,13)	0.0
O ₉ -H ₁₂	1.427	(4,5,6)	121.7	(2,3,4,5)	0.0
C ₁₃ -O ₁₄	1.329	(4,5,10)	117.2	(2,3,4,9)	0.0
C ₁₃ -O ₁₅	1.305	(6,5,10)	121.1	(13,3,4,5)	0.0
O ₁₄ -C ₁₆	1.428	(1,6,5)	119.1	(13,3,4,9)	0.0
C ₁₆ -H ₁₇	1.086	(1,6,11)	120.9	(2,3,13,14)	0.0
C ₁₆ -H ₁₈	1.090	(5,6,11)	120.0	(2,3,13,15)	0.0
C ₁₆ -H ₁₉	1.090	(4,9,12)	102.3	(4,3,13,14)	0.0
		(3,13,14)	118.7	(4,3,13,15)	0.0
		(3,13,15)	122.2	(3,4,5,6)	0.0
		(14,13,15)	119.1	(3,4,5,10)	0.0
		(13,14,16)	117.2	(9,4,5,6)	0.0
		(14,16,17)	105.5	(9,4,5,10)	0.0
		(14,16,18)	110.7	(3,4,9,12)	0.0
		(14,16,19)	110.7	(5,4,9,12)	0.0
		(17,16,18)	110.3	(4,5,6,1)	0.0
		(17,16,19)	110.3	(4,5,6,11)	0.0
		(18,16,19)	109.3	(10,5,6,1)	0.0
				(10,5,6,11)	0.0
				(3,13,14,16)	0.0
				(15,13,14,16)	0.0
				(13,14,16,17)	0.0
				(13,14,16,18)	60.7
				(13,14,16,19)	-60.7

Table 4.4 lists several key structural differences between the optimized excited states. The change in the O9-H12 distances are most notable for ketoB and enol. A ground-to-excited state increase of 0.12 Å is calculated for ketoB while the enol distance decreases by only 0.02 Å. The O9-O15 distance is interesting as well. The ketoB O9-O15 distance decreases by 0.16 Å going from ground to excited state while the enol O9-O15 distance increases by 0.05 Å. The ketoB and enol excited state O9-O15 distances are nearly equal. The oxygens involved in the ESIPT actually appear to move towards each other in the excited state to facilitate the transfer of the hydrogen. The O9-H12 bonds for ketoA and ketoA_{open} are similar and are considerably shorter than ketoB and enol. The same is true for the C13-O15 double bond lengths.

Table 4.4: Comparison of key structural differences in ground and first excited singlet state isomers of MS computed at the B3PW91/6-311++G(3d,3p) level.

Coordinate	ketoB		ketoA		enol		ketoA _{open}	
	Ground	Excited	Ground	Excited	Ground	Excited	Ground	Excited
R(O ₉ H ₁₂)	0.98	1.10	0.97	1.00	1.45	1.43	0.96	0.97
R(O ₉ O ₁₅)	2.58	2.42	-	-	2.39	2.44	-	-
R(C ₁₃ O ₁₅)	1.22	1.27	1.20	1.23	1.29	1.31	1.21	1.23
A(C ₄ O ₉ H ₁₂)	106.8	104.2	108.2	107.1	100.2	102.3	108.5	109.5

The $v = 0$ to $v = 0$ (or 0-0) transition energies for photo-emission of ketoB, ketoA, enol, and ketoA_{open} first excited singlet states calculated with several different basis sets are shown in Table 4.5. Here, v identifies the vibrational quantum number associated to the normal modes. Their associated emission wavelengths and oscillator strengths are also reported. The calculated ketoB emissions cover a fairly wide range of energies. The basis sets without extra polarization functions (6-31++G and 6-311++G) predict 0-0 emission wavelengths at 359 and 357 nm, respectively. The 6-311++G(d) basis set predicts a considerably shorter emission wavelength of 338 nm while the 6-31+G(3d,3p) predicts a longer emission wavelength of 410 nm. It is important to note, however, that the 6-31+G(3d,3p) excited state ketoB optimization converged on an enol structure (O9-H12 > O15-H12). The

Table 4.5: TDDFT calculated excited state emissions of MS isomers in gas phase. ΔE is energy (in eV) above isomer ground state, λ is the wavelength (in nm) of transition, and f is the oscillator strength.

Basis set	Isomer	State	ΔE (eV)	λ (nm)	f ($\times 10^{-2}$)
6-31++G	ketoB	1A	3.45	359	8.7
	ketoA	1A	3.72	333	8.2
	enol	1A	2.93	423	9.2
	ketoA _{open}	1A	4.16	298	9.0
6-311++G	ketoB	1A	3.48	357	8.7
	ketoA	1A	3.73	332	8.2
	enol	1A	2.87	432	9.3
	ketoA _{open}	1A	4.16	298	8.9
6-311++G(d)	ketoB	1A	3.67	338	9.0
	ketoA	1A	3.87	321	8.3
	enol	1A	2.87	433	9.7
	ketoA _{open}	1A	4.19	296	8.9
6-31+G(3d,3p)	ketoB	1A	3.03	410	9.0
	ketoA	1A	3.73	332	8.2
	enol	1A	3.03	410	9.0
	ketoA _{open}	1A	4.16	298	8.9
6-311++G(3d,3p)	ketoB	1A	3.52	352	8.9
	ketoA	1A	3.85	322	8.0
	enol	1A	2.99	414	9.1
	ketoA _{open}	1A	4.17	297	8.5

largest basis set used, 6-311++G(3d,3p), predicts a ketoB 0-0 emission of 352 nm. The calculated enol 0-0 emission ranged from 410 to 433 nm. The enol 6-31+G(3d,3p) structure was optimized to the same minimum as the ketoB optimization minimum, hence the identical values in Table 4.5 for that basis set. The calculations on ketoA and ketoA_{open} resulted in much shorter emission wavelengths: 321-332 nm for ketoA and 296-298 nm for ketoA_{open}. Because these are outside the range of laser excitation used experimentally, no analysis was done on these two isomers.

The molecular orbital energy levels of ground and first excited singlet state ketoB and enol are shown in Figure 4.2. The orbital energy level at $E = 0$ eV is the highest occupied molecular orbital (HOMO). The next highest energy level is the lowest unoccupied molecular

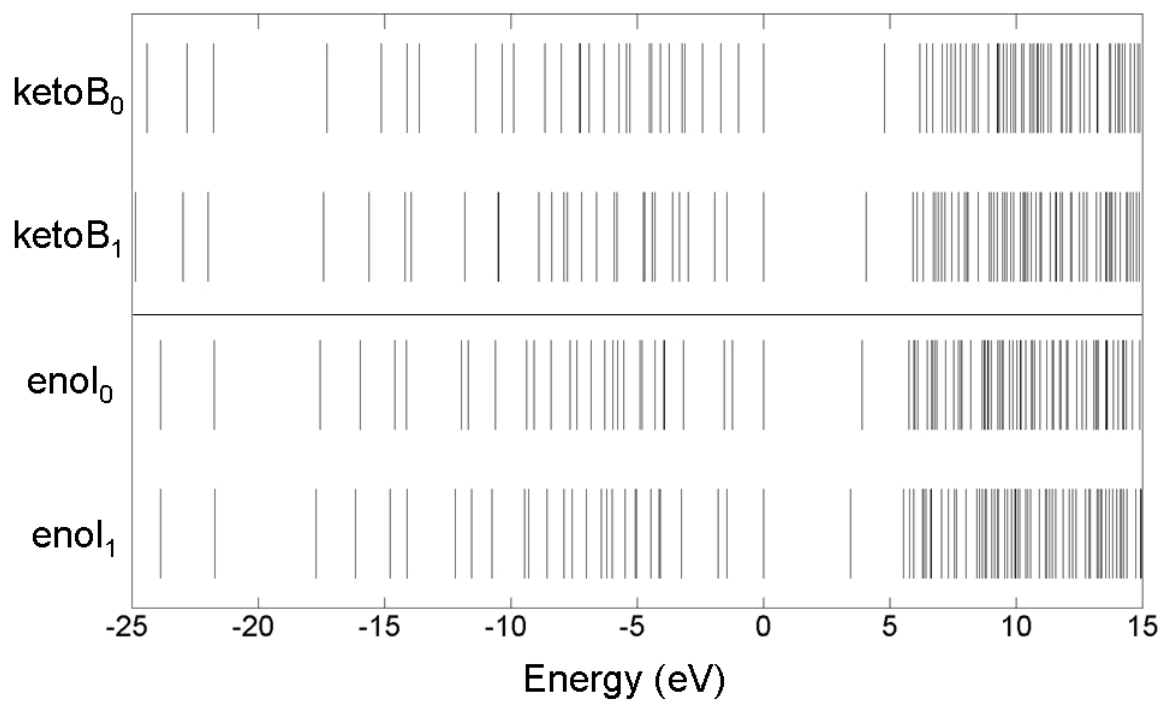


Figure 4.2: Occupied and unoccupied molecular orbital levels of ground (“0” subscript) and first excited singlet state (“1” subscript) ketoB and enol.

orbital (LUMO). The ketoB ground state HOMO-LUMO gap is 4.804 eV and 4.061 eV for its excited state. The enol ground state HOMO-LUMO gap is 3.906 eV and 3.453 eV for its excited state. The higher energy HOMO-LUMO gap of ketoB and the lower energy HOMO-LUMO gap of enol lend evidence to excited state populations of ketoB and enol that give rise to the dual fluorescence.

An excited state energy pathway involving an ESIPT between ketoB and enol has been theorized by previous MS research[5,9,19]. In order to model the ESIPT energy pathway, structural optimizations and electronic energies were calculated with TDDFT at several points between the $^1\text{ketoB}$ and $^1\text{enol}$ states. To perform these calculations, the O15-H12 bond length was constrained to a set length at several points between the two minima. All other bond lengths and angles were left unconstrained. The energies are plotted against R_c , which is defined as $R_c = \text{O9H12-O15H12}$. The results calculated with the B3PW91/6-311++G(3d,3p) level of theory are shown in Figure 4.3. The higher energy line in the upper half of Figure 4.3 shows the ESIPT energy pathway from ketoB (left) to enol (right). Notably, there is an energy maximum (or barrier) between the two minima. This is thus a cut of the electronic energy along the minimum energy ESIPT reaction path. The energy from ketoB to the top of the barrier will be referred to as the forward ESIPT energy (E_{fd}) and the energy from enol to the top of the barrier will be referred to as the reverse ESIPT energy (E_{rev}).

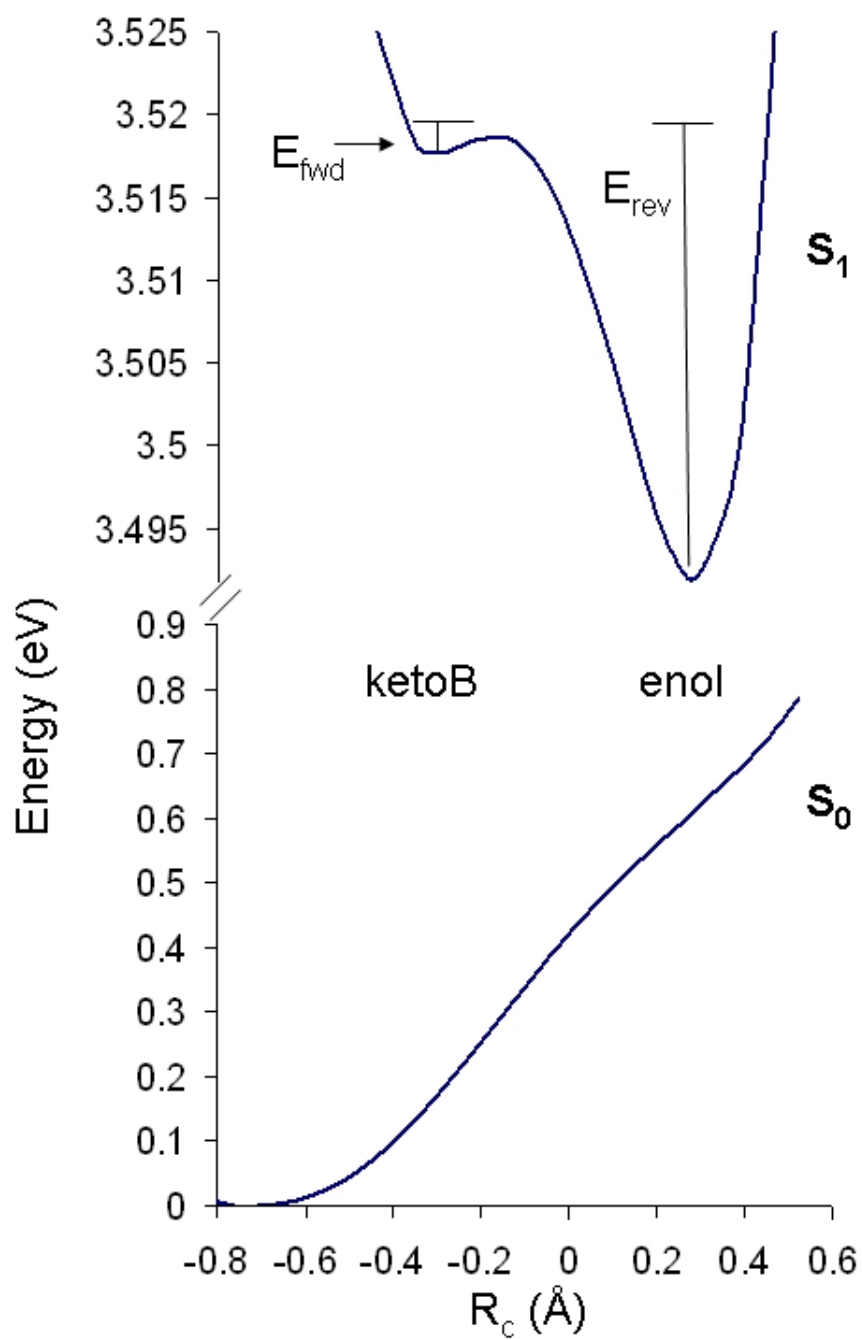


Figure 4.3: Excited and ground state energy levels at varying OH bond distances. At each point, MS was structurally optimized with a frozen O15-H12 length.

In addition, ground state calculations were performed in the same manner. The O15-H12 bond length was constrained to a set length at several points between the ketoB and enol ground states. All other bond lengths and angles were left unconstrained. The results calculated again with the B3PW91/6-311++G(3d,3p) level of theory are shown in the lower half of Figure 4.3. The ground state calculations give insight into the back proton transfer (BPT) mechanism. In particular, there is a steep energy gradient from the enol ground state to the ketoB ground state. Also, there is no energy barrier separating the ketoB and enol ground states. The enol ground state appears to be an unstable state, yet vibrational analysis confirms the existence of a stable structure with no imaginary frequencies. Interestingly, all but one (O15-H12=1.15 Å) of the ground state calculations along the BPT surface had all positive vibrational frequencies. The calculated OH stretching mode decreased to 1702 cm⁻¹ in the middle of the BPT, a change of nearly 1300 cm⁻¹.

The two excited state minima are clearly defined in three out of the four basis sets used. In those three cases, there is a significant energy barrier delineating the two minima. It is theorized that this energy barrier plays a crucial role in the dual fluorescence mechanism of MS. It is also interesting to note the variation in the O9-O15 distance as the O9-H12 distance is changing. This variation is shown in Figure 4.4 (A). A minimum in the O9-O15 distance is reached when the proton is approximately 1.2 Å from O9. Also interesting is the variation of the Mulliken atomic charges for the oxygens and hydrogen involved in the ESIPT. The redistribution of charge carries the hydrogen away from the oxygen. At the center of the ESIPT path, the hydrogen has lost 80% of its electron, thus closely resembling a proton. The ESIPT reaction path along the potential energy surface can be more clearly seen in Figures 4.5 and 4.6. In both Figures 4.5 and 4.6, a series of Morse potentials was used along the minimum energy ESIPT path to model the potential energy. Figure 4.5 shows the potential energy variation as a function of O9-H12 and O15-H12 bond lengths. Figure 4.6 shows the potential energy surface as a function of O9-H12 and C13-O15 bond lengths. The spline-fitted minimum energy ESIPT path is designated as the black line along the surface.

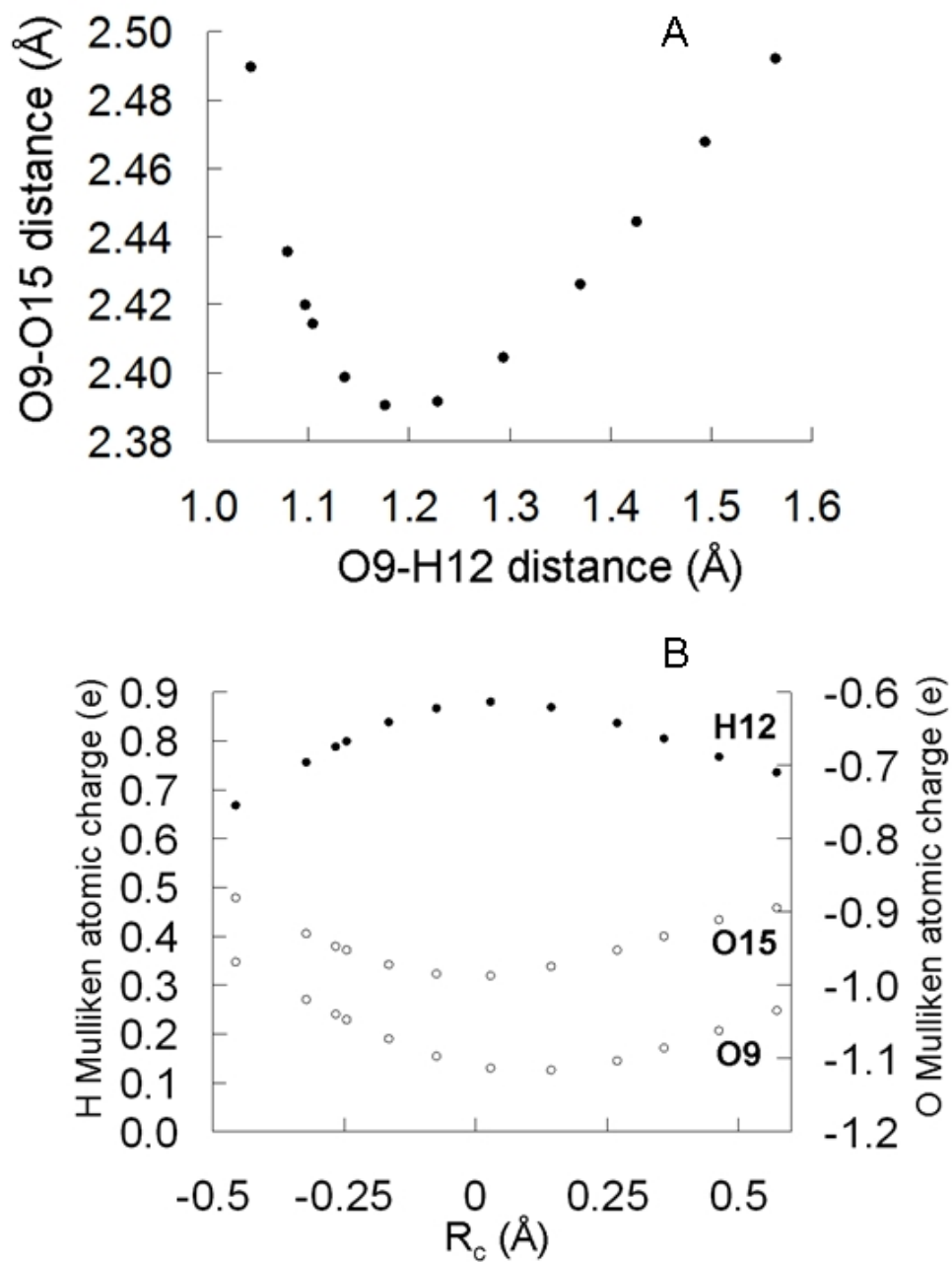


Figure 4.4: (A) Variation of the O9-O15 distance with O9-H12 length in the excited states of ketoB and enol. At each point, MS was structurally optimized with a frozen O15-H12 length. (B) Mulliken atomic charges of O9, O15, and H12 at varying R_c .

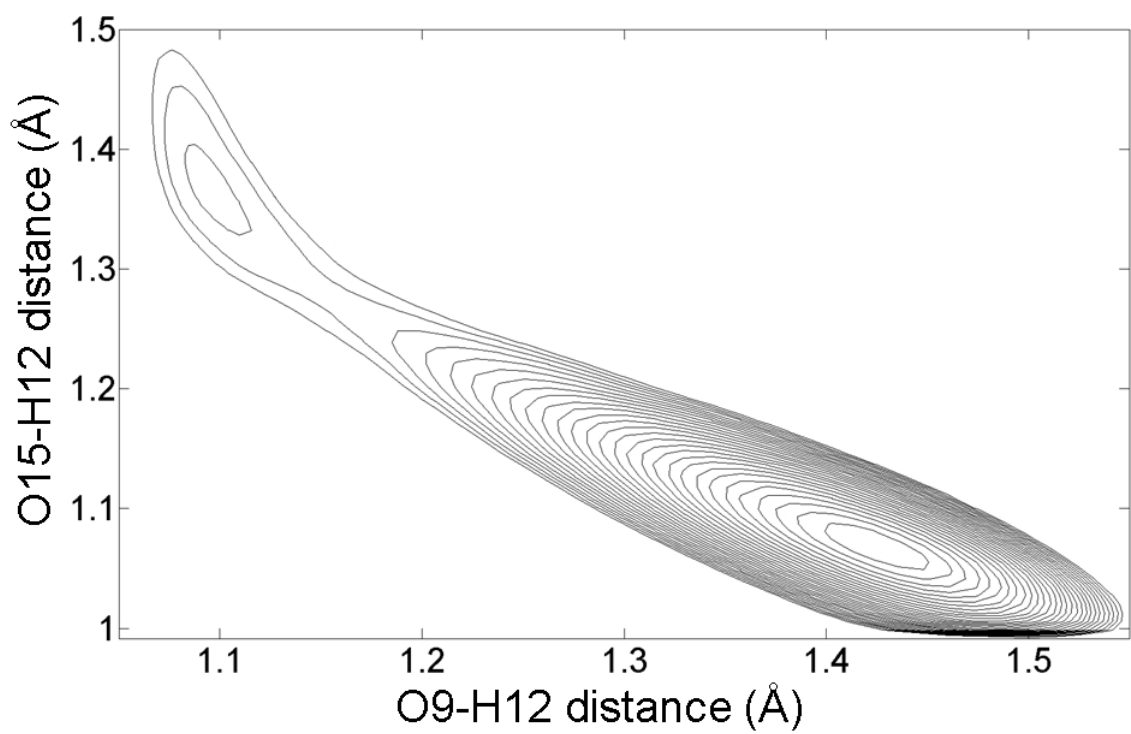


Figure 4.5: Contour plot of the excited state potential energy surface with changing O9-O15 and O15-H12 bonds. Each contour line represents a difference of 0.001 eV.

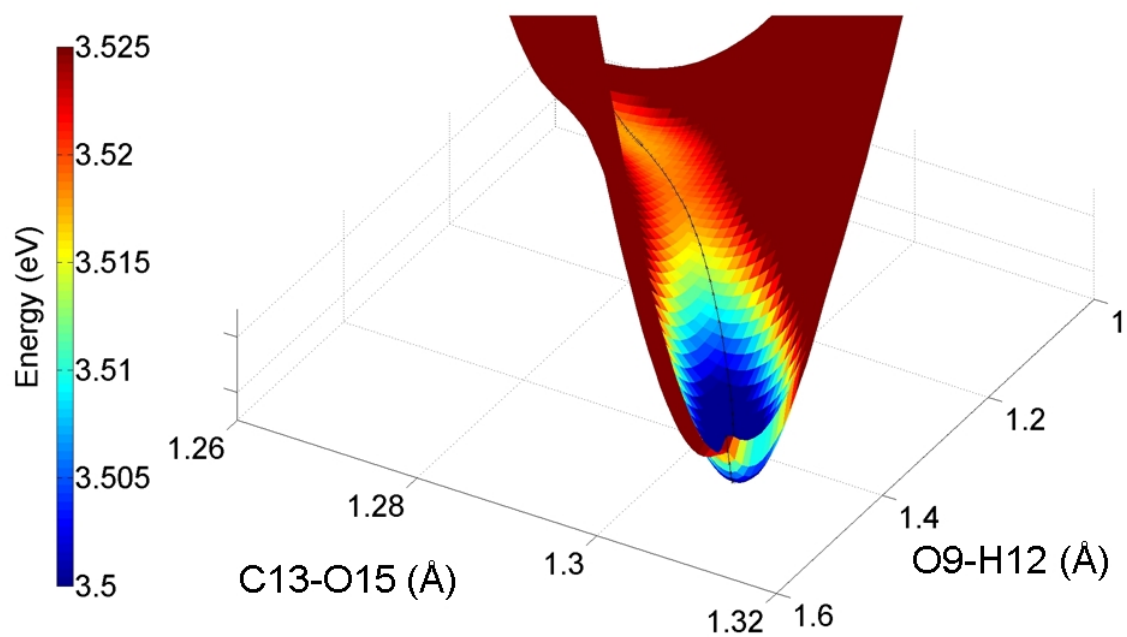


Figure 4.6: Surface plot of the excited state potential energy surface showing variation with O9-H12 distance and with C13-O15 distance. The minimum energy ESIPT path is shown as a black line on the surface.

4.4 Excited State Vibrational Analysis

The vibrational analysis associated to the first excited state was calculated for $^1\text{ketoB}$ and $^1\text{enol}$ using five different basis sets at the B3PW91 level: 6-31++G, 6-311++G, 6-311++G(d), 6-31+G(3d,3p), and 6-311++G(3d,3p). The results varied among the five basis sets, particularly concerning the existence of imaginary frequencies. This is shown in Table 4.6. The entry “all +” in Table 4.6 means that a stable excited state structure was confirmed with all positive (no imaginary) normal mode frequencies. The “one -” entry means that one of the normal mode frequencies was negative (imaginary). This signifies an unstable, saddle point structure.

Table 4.6: Summary of the vibrational calculations for the excited states of $^1\text{ketoB}$ and $^1\text{enol}$ using B3PW91 with different basis sets.

isomer	Basis set				
	6-31++G	6-311++G	6-311++G(d)	6-31+G(3d,3p)	6-311++G(3d,3p)
$^1\text{ketoB}$	all +	all +	all +	N.A.	all +
$^1\text{enol}$	one -	one -	one -	all +	all +

For both of the calculations not using polarization functions (6-31++G and 6-311++G) and the calculation using a d polarization function on heavy atoms (6-311++G(d)), the $^1\text{enol}$ excited state was calculated to have one imaginary frequency. For the 6-31+G(3d,3p) calculation, the $^1\text{ketoB}$ excited state had optimized into the $^1\text{enol}$ form. No stable excited state was found for the $^1\text{ketoB}$ form, hence the entry of “N.A.” in Table 4.6. In essence, there was only one stable, optimized structure in the excited state found with the 6-31+G(3d,3p) basis set. All vibrational frequencies were determined to be positive for the $^1\text{enol}$ form. Finally, both $^1\text{ketoB}$ and $^1\text{enol}$ forms were found to be stable, optimized structures with the 6-311++G(3d,3p) basis set. Therefore, it seems to accurately calculate both stable excited states, one needs to use at least a triple- ζ basis set with three sets of d functions on heavy atoms and 3 sets of p functions on hydrogens.

4.5 Calculated Photoluminescence

It has been shown that an ESIPT takes place in less than 10 ps and given that the photoluminescence lifetime of MS is greater than 1 ns[21], one can assume that the lifetime of MS is long compared to excited state nuclear motions. Therefore, nuclear vibrational motions should be considered when modeling the photoluminescence spectrum of MS.

The intensity of a given transition is proportional to the square of the transition moment integral[91]

$$\mathbf{M}_{e,v} = \int \psi_{e',v'}^* \boldsymbol{\mu} \psi_{e'',v''} d\tau \quad (4.1)$$

where $\psi_{e,v} = \psi_e \psi_v$ because of the Born-Oppenheimer approximation. The dipole moment operator can also be broken into its electronic and nuclear components

$$\boldsymbol{\mu} = \boldsymbol{\mu}_e + \boldsymbol{\mu}_N \quad (4.2)$$

so that the transition moment integral becomes

$$\mathbf{M}_{e,v} = \int \psi_{e'}^* \boldsymbol{\mu}_e \psi_{e''} d\tau \int \psi_{v'}^* \boldsymbol{\mu}_e \psi_{v''} d\tau + \int \psi_{e'}^* \boldsymbol{\mu}_N \psi_{e''} d\tau \int \psi_{v'}^* \boldsymbol{\mu}_N \psi_{v''} d\tau \quad (4.3)$$

The second term on the right is zero because the electronic wavefunctions are orthogonal and $\boldsymbol{\mu}_N$ will come out of the integral because of the Born-Oppenheimer approximation. If one lets

$$\mathbf{R}_e = \int \psi_{e'}^* \boldsymbol{\mu}_e \psi_{e''} d\tau_{el} \quad (4.4)$$

then the transition dipole moment becomes

$$\mathbf{M}_{e,v} = \mathbf{R}_e \boldsymbol{\mu}_e \int \psi_{v'}^* \psi_{v''} dr \quad (4.5)$$

The intensity (I) of the transition is proportional to the square of the transition moment integral so that

$$I_{e'v'e''v''} \propto |\mathbf{R}_e|^2 \mu_e^2 FC_{v'v''} \quad (4.6)$$

where $FC_{v'v''} = |\langle v' | v'' \rangle|^2$ is known as the Franck-Condon vibrational overlap factor[92].

The electronic parts of the Franck-Condon (FC) approximation ($\mathbf{R}_e$ and μ_e) have already been calculated using TDDFT. The electronic 0-0 transitions along with their oscillator strengths were reported in Table 4.5. The transition dipole moment for a given transition $n \rightarrow m$ is defined by

$$\mathbf{d}_{nm} = \int \Psi_n^* \hat{\mathbf{d}} \Psi_m d^3r \quad (4.7)$$

where $\hat{\mathbf{d}}$ is the dipole moment operator and given by

$$\hat{\mathbf{d}} = e \left(\sum_{i=1}^{N_e} x_i, \sum_{i=1}^{N_e} y_i, \sum_{i=1}^{N_e} z_i \right) \quad (4.8)$$

Here, N_e in the summations above is the total number of electrons in the system and (x_i, y_i, z_i) are the electrons' displacements. The x,y,z transition dipole components and the total transition dipole moment are outputs of a TDDFT calculation.

The FC factors are the square of the nuclear overlap terms between ground and excited state vibrational modes,

$$FC_{j',j} = \left[\int_{-\infty}^{\infty} \psi_n^*(x_{j'}) \psi_m(x_j) d\tau \right]^2 \quad (4.9)$$

where m and n are the vibrational quantum numbers and j and j' are the vibrational modes of the ground and excited states, respectively.

If one assumes that the vibrational motions for each mode can be modeled as a quantum harmonic oscillator[70] then

$$\psi_m(x_j) = \frac{1}{\sqrt{2^m m!}} \left(\frac{\alpha}{\pi}\right)^{1/4} e^{-\frac{\alpha x^2}{2}} H_m(\sqrt{\alpha} x_j) \quad (4.10)$$

where H_m is a Hermite polynomial. The x 's are the displacements from equilibrium for the m^{th} level of the vibrational mode.

The individual emission lines are then broadened using a Lorentzian function,

$$L(\nu) = \frac{1}{\pi} \left[\frac{\gamma}{(\nu - \nu_0)^2 + \gamma^2} \right] \quad (4.11)$$

where ν_0 is the center of the transition line. A broadening factor γ of 500cm^{-1} was used. The $L(\nu)$'s are summed together and the resulting spectrum is normalized according to the ratio described in the following paragraphs.

4.6 ESIPT physical representation

A physical picture of the ESIPT mixing is explained here. We assume that molecules in the total system, N_0 , are in thermal equilibrium so that Boltzmann statistics may apply. It is theorized that excited state mixing occurs through ESIPT such that a portion of the molecules is still ketoB and the other part has transitioned to enol. After many ESIPT back-and-forth oscillations between the two minima (Figure 4.3), the ratio of the two populations can be described by Boltzmann's equilibrium condition. In the calculation of the fluorescence spectra, the ketoB and enol spectral contributions are multiplied by their respective population ratios. The population probability of the excited singlet state of $^1\text{ketoB}$ is

$$f_{\text{ketoB}} = \frac{N_0 e^{-E_{rev}/kT}}{Z} \quad (4.12)$$

and the population probability of the excited singlet state of $^1\text{enol}_1$ is

$$f_{enol} = \frac{N_0 e^{-E_{fwd}/kT}}{Z} \quad (4.13)$$

where Z is a normalization factor so that the sum of Eqns. 4.13 and 4.14 is 1.

A plausible, more dynamic model for the ESIPT could also be put forward. For a bulk collection of excited state MS molecules, we theorize a type of population diffusion between the two relevant excited state minima to explain the temperature dependence on the photoluminescence spectrum. We assume that the timescale for diffusion is on the tens to hundreds of femtoseconds (10-500 fs) scale. This is because the harmonic oscillations occur in the 50-3000 cm^{-1} range. The photoluminescence lifetime of MS has been measured at 1.1 ± 0.2 ns [11] and, depending on temperature, between 0.1 and 8.3 ns [21]. These lifetimes are 4+ orders of magnitude greater than the oscillation timescale. Therefore, one can also assume that many oscillations take place during the excited state lifetime of MS.

Consider a collection, N_0 , of MS molecules where at time $t < t_0 = 0$, all of the molecules are assumed to be completely composed of the $^1\text{ketoB}$ in its ground state at a given temperature, T . At time $t = 0$, it is assumed that all of the molecules are promoted to the first excited singlet state of $^1\text{ketoB}$. This is reasonable because the timescale for photoexcitation ($\approx 10^{-18}\text{s}$) is much faster than the proposed oscillation timescale. If one also assumes a single exponential decay of the excited state population, then at time $t_1 = t_0 + \Delta t$ where $\Delta t = 10$ fs, the total population of excited state molecules has been reduced to $N(t_1) = N_0 e^{-t_1/\tau}$ where τ is the photoluminescence lifetime of MS. However, a fraction of the $^1\text{ketoB}$ population in the excited state will have overcome the “forward” ESIPT energy barrier (E_{fwd}) to populate the $^1\text{enol}$ excited state. Therefore, some of the fluorescence will have originated from $^1\text{ketoB}$ and some will have originated from $^1\text{enol}$.

At the next timestep, t_2 , there will of course be a smaller population of excited state MS molecules than at t_1 . However, the excited state population diffusion will continue for those molecules. Some of the $^1\text{enol}$ excited state population will have overcome the higher,

“reverse” ESIPT energy barrier (E_{rev}) to repopulate the $^1\text{ketoB}$ excited state. Likewise, some of the $^1\text{ketoB}$ excited state population remaining from the last timestep will now overcome the E_{fwd} barrier to populate the $^1\text{enol}$ excited state. This type of excited state diffusion or oscillation will continue for as long as there are molecules in the excited state, or many times the fluorescence lifetime.

4.7 Results

The results for the calculated fluorescence of MS are presented in this section. The summed fluorescence spectrum for gas phase MS at 300K is shown in Figure 4.7. The summed spectrum is the sum of the individual Lorentzian functions in Eqn. 4.11 over all ν . The line spectrum of the individual vibronic transitions is displayed in Figure 4.7. Each individual stick represents a vibronic transition with an intensity calculated using Eqn. 4.6. The blue represent ketoB while the green represent enol. The lighter the shade of blue and green, the higher the vibronic level of the transition. The individual vibronic transitions are normalized to the population probability (f_{ketoB} or f_{enol}) for the corresponding isomer.

For comparison to the calculated spectra, liquid MS emission spectrum was taken with a Horiba Jobin Yvon fluorescence spectrometer. The sample was spectral grade ($> 99\%$) liquid MS from Sigma Aldrich. An excitation wavelength of 330 nm, 0.5 second integration time, and 4 nm slit widths at 1 nm increments were used. The steady-state emission spectrum is shown in Figure 4.8 (A). The dual fluorescence is clearly apparent here: the shorter wavelength peak located at 373 nm and the longer wavelength peak located at 441 nm.

Time-correlated single-photon counting (TCSPC) lifetime measurements were also taken of the same MS sample using a Horiba time domain spectrofluorometer. A diode laser centered at 327 nm was used as the excitation source. LUDOX was used to calibrate the lifetime measurements. The lifetime plots are shown in Figure 4.8 (B). Analysis of the 441 nm emission yielded a lifetime of 1.18 ± 0.1 ns at 327 nm excitation. Analysis of the 373

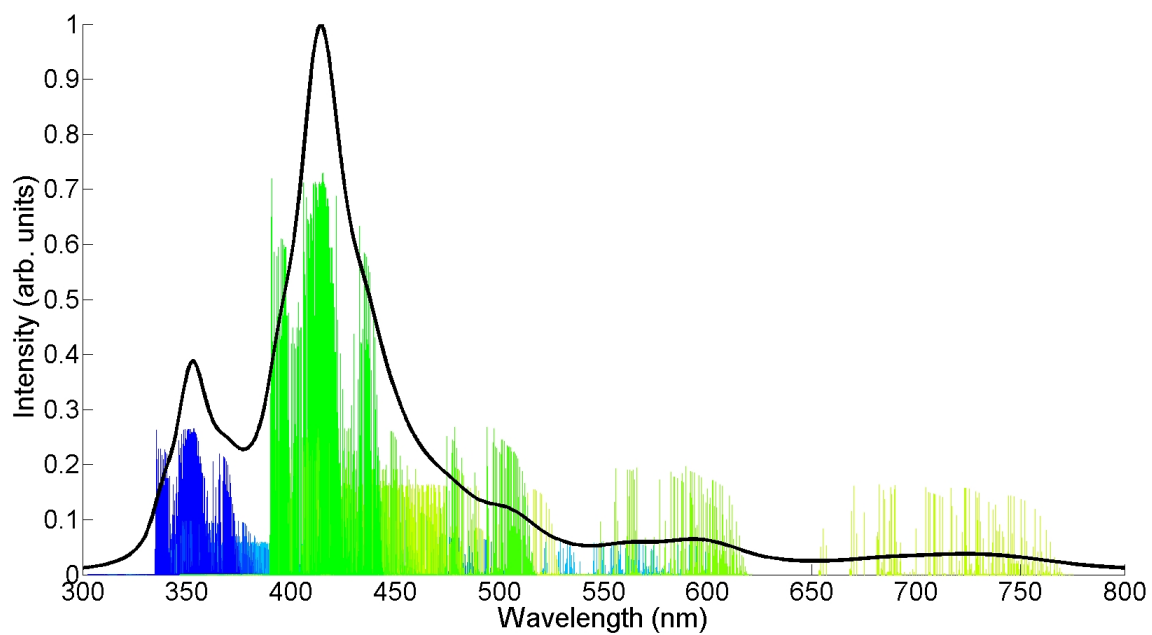


Figure 4.7: Calculated gas phase MS fluorescence spectra at 300 K. Line spectra represent ketoB (blue) and enol (green) vibronic transitions. The line spectra are normalized to their corresponding isomer's population probability. Lighter shades of blue and green signify higher vibronic level transitions.

nm emission yielded a lifetime of 0.95 ± 0.1 ns at 327 nm excitation. These lifetimes are in generally good agreement with previous experiments[11,21].

The room temperature ($T = 300\text{K}$) calculated (Figure 4.7) and experimental spectra (Figure 4.8 (A)) are in quite good agreement. The shape of the peaks match well. However, there is a distinct blue-shift in the calculated spectrum from the experimental spectrum. The peak centers of the calculated spectrum are approximately 94 % of the experimental spectrum. This is actually in better agreement than some previous TDDFT results[93,94]. Part of the blue-shift may very well be due to solvent effects as the calculations were performed on gas phase MS and the experiments were performed on pure liquid MS. The intensity ratios of the two peaks in the calculated and experimental results are in fairly good agreement. The short wavelength peak in the calculated result achieves a maximum intensity of 0.38 (in arbitrary units) while the short wavelength peak in the experimental result reaches 0.23 (in arbitrary units). At longer wavelengths ($\lambda > 450$ nm), the calculated and experimental spectra both fall off at approximately the same rate. The calculations do predict higher mode vibronic transitions at the wavelengths but the intensities are very small and thus contribute very little to the total spectrum. The experimental spectrum does show residual fluorescence at these long wavelengths which may be due to those vibronic transitions.

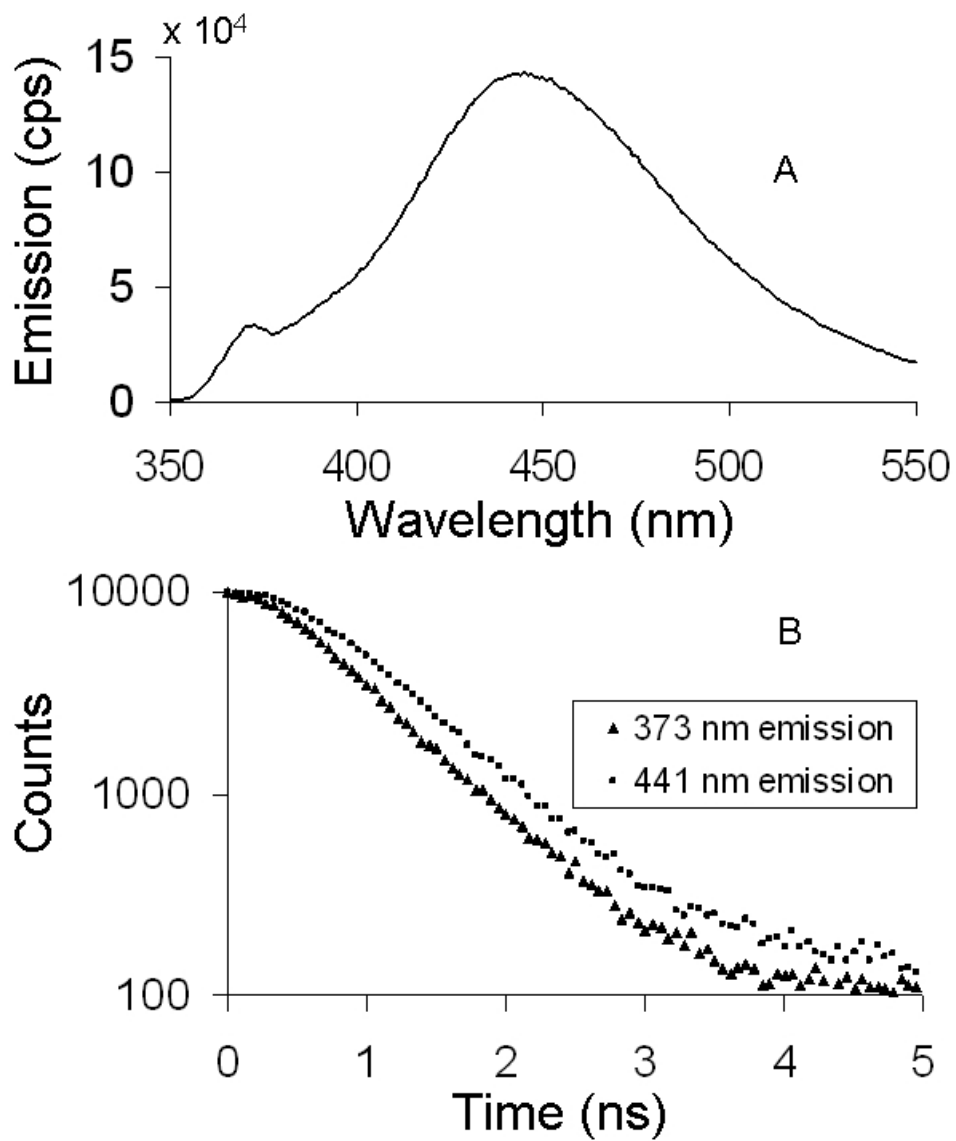


Figure 4.8: (A) Experimental liquid MS fluorescence spectrum at 300 K. (B) Experimental fluorescence lifetimes ($\lambda_{ex} = 327$ nm) of the two spectral peaks (373 and 441 nm) from (A).

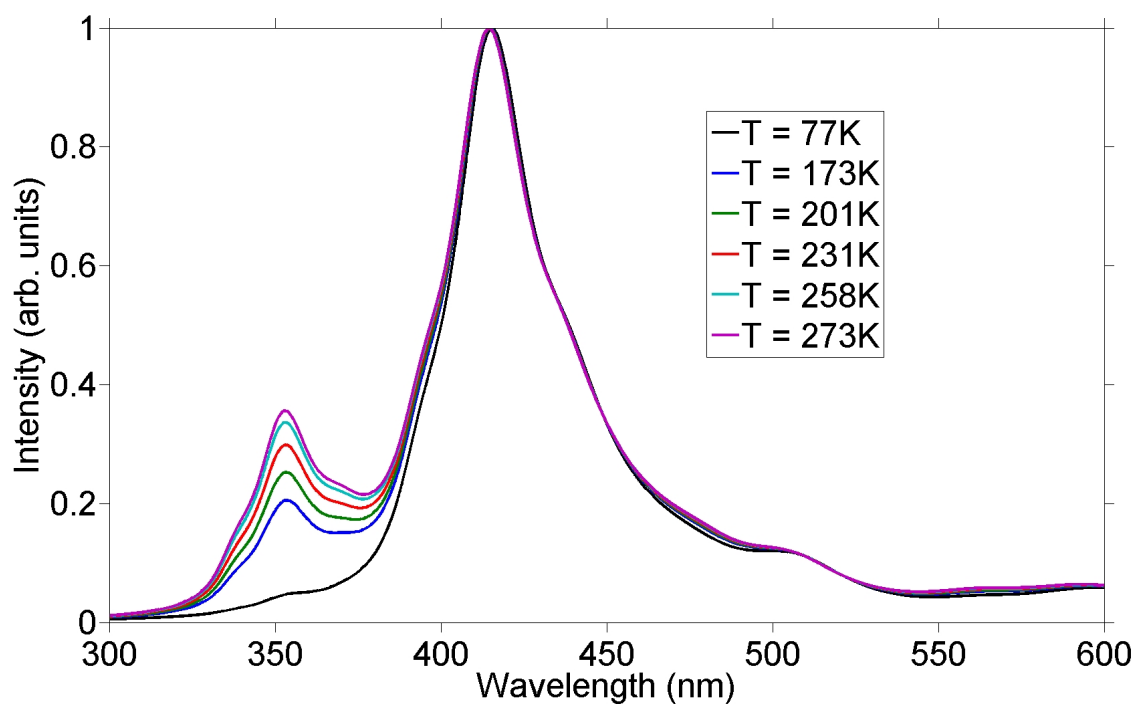


Figure 4.9: Calculated MS fluorescence spectra at temperatures of 77, 173, 201, 231, 258, and 273 K.

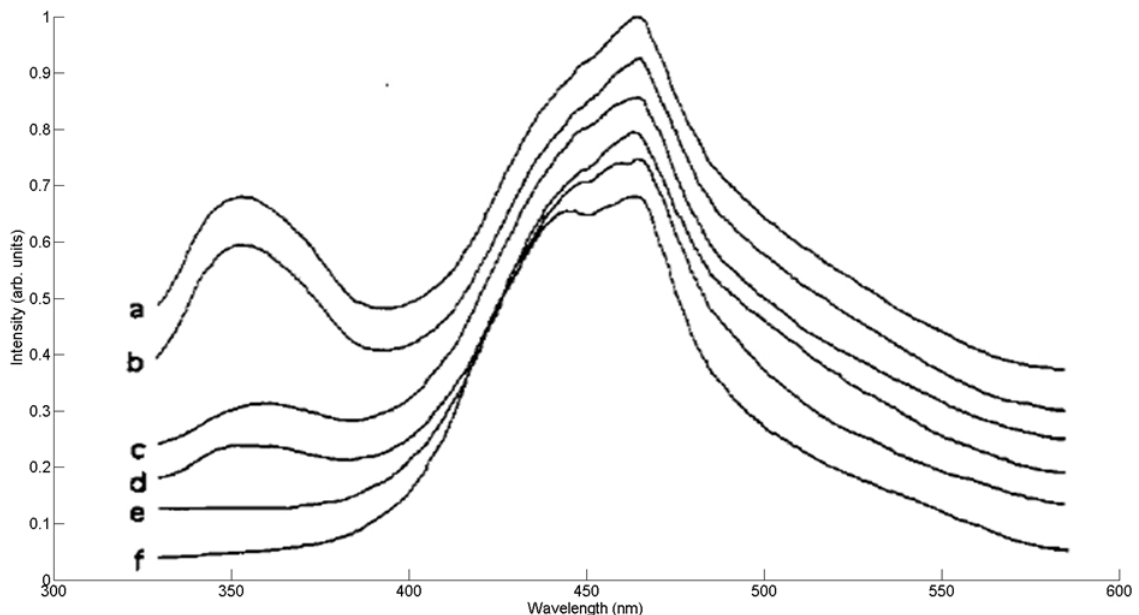


Figure 4.10: Variable-temperature emission spectra of MS in ethanol at (a) 273, (b) 258, (c) 231, (d) 201, (e) 173, and (f) 77 K from [9].

Calculated fluorescence spectra for varying temperatures ($T = 77, 173, 201, 231, 258$, and 273 K) are shown in Figure 4.9. Notice that, with the chosen parameters, the short wavelength peak does not appear above the background until $T > 100$ K. The temperatures used in Figure 4.9 were chosen to compare with experimental temperature dependence effects seen in Figure 4.10 [9]. The spectra in Figure 4.9 are with liquid MS in ethanol. The experimental short wavelength fluorescence peak in Figure 4.10 does not rise above the background until approximately $T > 175$ K. It is clear, however, that the calculated spectra in Figure 4.9 do demonstrate a temperature dependence very similar to that of the experimental spectra in Figure 4.10. The short wavelength peak to long wavelength peak ratios for the calculated spectra in Figure 4.9 are 0.05, 0.2, 0.24, 0.29, 0.33, and 0.35 for $T = 77, 173, 201, 231, 258$, and 273 K, respectively. Meanwhile, the short wavelength peak to long wavelength peak ratios for the experimental spectra in Figure 4.10 are 0.06, 0.18, 0.30, 0.36, 0.66, and 0.68 for $T = 77, 173, 201, 231, 258$, and 273 K, respectively. The ratios

are very similar at low temperatures ($T < 231$ K), however they are drastically different at the higher temperatures. This discrepancy could be due to a number of factors. First, one reason may be because the experimental spectra in Figure 4.10 were taken with a liquid solution of MS in ethanol. Hydrogen binding to solvent molecules could alter the energetics of the ESIPT. Second, the discrepancy between the intensities of the short wavelength peaks may be due to temperature effects that are unaccounted for in the calculations or the excited state potential energy surface may be more complicated. Lastly, the experimental results may have been limited by detection capabilities since they were taken nearly two decades prior to the time of this dissertation.

4.8 Conclusion

A thorough computational investigation into the excited state of MS using DFT and TDDFT methods has been presented. To the author’s best estimation, the dual fluorescence of MS arises from the presence of two potential wells in the excited state separated by a small energy barrier due to a hydrogen displacement between the hydroxyl and carbonyl oxygens. Previous computational studies[18], as well as calculations within this study, suggest that the rotamer (ketoA) does not have a substantial effect on the total photoluminescence. Instead, the ketoB and enol forms are the dominant players. Phosphorescence from the first triplet states of ketoB and enol is not ruled out. However, the large computed oscillator strengths of the singlet-singlet transitions suggest that the contribution due to phosphorescence would be minimal. Additionally, the lifetime experiments measured lifetimes in the range of 1 ns and there is no indication of long lifetime MS photoluminescence in the literature. A temperature dependent fluorescence effect is also theorized due to excited state oscillations between the two potential wells.

The overall shape of the calculated spectra match very well with laboratory measurements of liquid MS (Figures 4.8 and 4.10). There is a considerable blue shift (≈ 20 nm) in the gas phase calculated spectra from the liquid MS experimental spectra. The blue shift is approximately the amount that is typically seen due to liquid phase effects[95]. The relative

intensity peaks of the short and long wavelength fluorescence match relatively well with the temperature dependent results from [9] reproduced in Figure 4.10.

A complete picture of the process is theorized as follows: Initially, the population of MS is almost totally composed of the ketoB ground state. A negligible amount of ketoA in the ground state may exist, but the barrier for ketoB to ketoA isomerization (0.67 eV) is far too high for a substantial amount of ketoA to form at normal conditions ($T \approx 300\text{K}$, $\rho \approx 1 \text{ atm}$). A photo-excitation occurs with a wavelength of approximately 300 nm. This excitation creates an excited state population (N_0) which is all $^1\text{ketoB}_1$ immediately after the excitation. Next, random oscillations occur between the $^1\text{ketoB}_1$ and $^1\text{enol}_1$ states which are highly dependent upon the temperature of the system. The total population in the excited state is thus now split into two species, $N_0 = N_{\text{ketoB}_1} + N_{\text{enol}_1}$ before decaying to the ground state. A greater temperature will allow more molecules to cross the barrier from the ketoB to the enol excited state wells and vice versa. However, the energy barrier from enol to ketoB is greater. Therefore, there will eventually be a bias of excited state population wanting to remain in the excited state of the enol form. The number of crossings not only depends upon the system temperature but also on the excited state harmonic vibrations and the excited state lifetime. Experiments have shown a temperature-dependence effect in the measured lifetime[21]. In particular, the temperature and fluorescence lifetime have been measured to be inversely proportional: a greater temperature will result in a shorter fluorescence lifetime. The diffusion argument just described may explain some of these observations. At lower temperature, more of the excited state MS population will be “stuck” in the ketoB energy well for a longer amount of time. And, since ketoB was calculated as having a smaller oscillator strength, then the lifetime from the lower temperature population will be longer because of the inverse relation between fluorescence lifetime and transition oscillator strength[96]. Conversely, at higher temperatures a large population of molecules will have crossed over to the enol energy well in a shorter amount of time. The higher enol oscillator strength will result in more photo-emission and hence a shorter lifetime.

Any re-population of enol in the ground state created from enol photo-emission will be

short-lived due to a back proton transfer along a steep, barrier-less potential energy surface to the ketoB ground state. It is expected that the back proton transfer occurs on a timescale of less than 1 ps.

Chapter 5: Dipicolinic Acid

5.1 Introduction

Dipicolinic acid (DPA, 2,6-pyridinedicarboxylic acid, $C_5H_3N(COOH)_2$) was first identified in 1936 as a viscous matter in Natto, a Japanese food made with steamed soybeans and fermented with *Bacillus natto*[97]. It was not until 1953 that DPA was first recognized to be a by-product of bacterial spore germination[27,28]. Since then, DPA has been investigated as a potential indicator of bacterial spore formation and germination using a wide range of detection techniques[31,33–35].

Density Functional Theory (DFT) calculations were performed on six isomers of DPA in the gas phase and all six isomers are predicted as stable. The structures of the isomers were optimized at the B3LYP/6-31G(d) level. The electronic states, energies, dipole moments, electron affinities, and ionization potentials for these six isomers are reported. Additionally, DFT calculations of planar dimer formations of those isomers were run at the B3LYP/6-31G(d) level. 1-D, 2-D, and 3-D periodic boundary conditions were employed on three of the dimer formations to form crystalline DPA. Structural optimizations were performed on the 1-D and 2-D cases. The optimized 2-D structures were then layered to form a 3-D crystal. Band structures of those crystals were then calculated along the lines of high symmetry.

5.2 Structural Isomers and Energetics

All-electron Density Functional Theory (DFT) calculations were performed on six isomers of DPA in the gas phase. The calculations were done within the Becke’s Three Parameter Hybrid Functional together with the correlation functional of Lee, Yang, and Parr (B3LYP) and a double- ζ basis set with an extra d polarization function (6-31G(d)). Structural

optimization of the isomers were performed with the Berny algorithm using redundant internal coordinates[55–58] as described in Chapter 2. All calculations were performed with the Gaussian 09 package[54]. The optimized singlet structures of the isomers are shown in Figure 5.1. Carbon atoms are colored gray, oxygen atoms are red, nitrogen atoms are blue, and hydrogen atoms are white. In order to easily reference the atoms of DPA, they have been numbered in a consistent scheme. DPA2, DPA4, and DPA6 have C_{2v} point group symmetry while DPA1, DPA3, and DPA5 have C_s symmetry. Triplet states were calculated for the isomers and it was determined that none of the DPA isomers are stable in the triplet state. Vibrational frequencies were calculated to confirm that minima were obtained.

Previous studies of DPA have focused on the DPA4, DPA5, and DPA6 isomers as these are hydrogen-bonding monomer structures. DPA1, DPA2, and DPA3 are newly predicted isomers in the gas phase. Several other structures were also found but were determined to be unstable when vibrational analysis was performed. Initial guesses for their optimization were formed by rotating key dihedral angles, such as the N1-C2-C7-O8 and C2-C7-O9-H16 dihedrals. The calculated bond lengths of all six isomers are shown in Table 5.1 while the calculated angles are shown in Table 5.2. Also, the calculated Mulliken atomic charges for the six isomers are reported in Table 5.4.

The electronic states, energies, dipole moments, electron affinities, and ionization potentials for these six isomers are given in Table 5.3. DPA1 is the global minimum structure taking into account that its total electronic energy plus the zero point energy is the lowest of the six predicted structures. Two isomers, DPA2 and DPA3, lie in almost degenerate states above the DPA1 structure at 0.046 and 0.050 eV, respectively. Isomers DPA4, DPA5 and DPA6 lie higher up above DPA1 at 0.144, 0.215, and 0.296 eV, respectively. The DPA1 isomer has previously been proposed by Carmona[38] as the unique structure for DPA. The DPA2 isomer is the structure proposed in Ref. [98] and determined by Tellez et al[39] to be the main component in solid supramolecular structures. The structure of the DPA3 isomer was reported in previous calculations[40] and identified experimentally in Raman measurements[99]. It is thus important to point out that three additional stable isomers

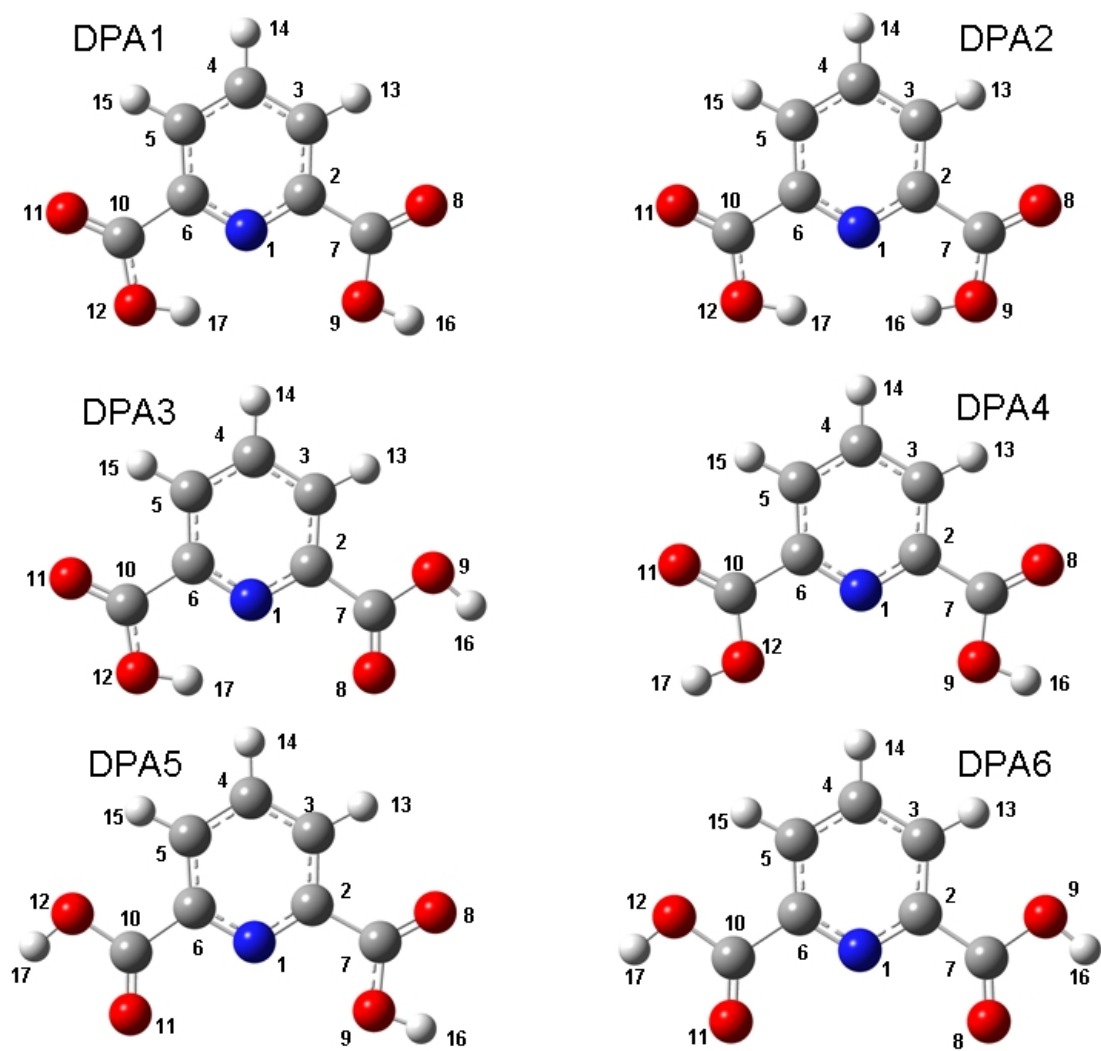


Figure 5.1: Six isomers of gas phase DPA optimized at the B3LYP/6-31G(d) level.

Table 5.1: Bond lengths (in Å) of DPA isomers optimized with B3LYP/6-31G(d)

Bond length	DPA1	DPA2	DPA3	DPA4	DPA5	DPA6
N1-C2	1.338	1.342	1.339	1.337	1.337	1.336
C2-C3	1.399	1.396	1.400	1.401	1.402	1.403
C3-C4	1.394	1.393	1.396	1.392	1.394	1.392
C4-C5	1.393	1.393	1.392	1.392	1.391	1.392
C6-N1	1.337	1.342	1.336	1.337	1.334	1.336
C7-C2	1.500	1.510	1.503	1.502	1.505	1.505
C7-O8	1.214	1.208	1.208	1.216	1.207	1.206
C7-O9	1.347	1.343	1.357	1.345	1.361	1.362
C6-C10	1.511	1.510	1.512	1.502	1.502	1.505
C10-O11	1.210	1.208	1.210	1.216	1.216	1.206
C10-O12	1.341	1.343	1.340	1.345	1.344	1.362
C3-H13	1.084	1.084	1.083	1.084	1.083	1.083
C4-H14	1.086	1.086	1.086	1.086	1.086	1.086
C5-H15	1.084	1.084	1.084	1.084	1.084	1.083
O8-H16	0.976	0.978	0.975	0.976	0.975	0.975
O9-H17	0.984	0.978	0.984	0.976	0.976	0.975

Table 5.2: Angles (in deg) of DPA isomers optimized with B3LYP/6-31G(d)

Angle	DPA1	DPA2	DPA3	DPA4	DPA5	DPA6
N1-C2-C3	122.69	122.91	122.38	123.60	123.24	123.29
C2-C3-C4	118.63	118.49	118.65	118.38	118.45	118.31
C3-C4-C5	119.00	118.98	119.13	118.68	118.80	118.90
C6-N1-C2	118.18	118.21	118.47	117.37	117.65	117.91
C7-C2-N1	118.82	117.41	115.26	118.66	115.31	115.37
O8-C7-C2	123.26	122.46	125.04	123.13	125.64	125.68
O9-C7-C2	113.28	114.72	111.74	113.63	111.59	111.56
C10-C6-N1	115.69	117.41	115.64	118.66	118.67	115.37
O11-C10-C6	122.79	122.46	122.67	123.13	123.04	125.68
O12-C10-C6	113.77	114.72	113.81	113.63	113.61	111.56
H13-C3-C2	119.13	118.85	119.98	119.23	120.13	120.20
H14-C4-C3	120.38	120.51	120.24	120.66	120.52	120.55
H15-C5-C4	122.75	122.66	122.82	122.39	122.44	121.49
H16-O9-C7	105.78	107.35	106.00	105.56	105.64	105.61
H17-O12-C10	106.70	107.35	106.89	105.56	105.66	105.61

Table 5.3: Electronic states, total electronic energies, zero point energies (ϵ_0), binding energies (BE), and dipole moments of the DPA isomers. The electron affinities (EA), ionization potentials (IP), and HOMO-LUMO gap (Δ) are also reported. Total electronic energies E are relative to the $^1\text{DPA1}$ ground state energy of -17.018746 keV.

isomer	state	E (eV)	ϵ_0 (eV)	BE (eV)	dipole (D)	EA (eV)	IP (eV)	Δ (eV)
DPA1	^1A	0	3.236	113.890	3.378, 1.809, 0	0.770	9.482	5.220
DPA2	$^1\text{A}_1$	0.046	3.233	113.843	0, 2.599, 0	0.816	9.706	5.409
DPA3	^1A	0.050	3.234	113.840	4.864, 3.949, 0	0.631	9.495	5.191
DPA4	$^1\text{A}_1$	0.144	3.228	113.746	0, 0.679, 0	0.286	9.021	5.383
DPA5	^1A	0.215	3.223	113.674	1.401, 2.893, 0	0.282	9.070	5.437
DPA6	$^1\text{A}_1$	0.296	3.218	113.594	0, 5.190, 0	0.280	9.149	5.599

Table 5.4: Mulliken charges of DPA isomers calculated with B3LYP/6-31G(d)

Atom	DPA1	DPA2	DPA3	DPA4	DPA5	DPA6
N1	-0.591	-0.663	-0.578	-0.503	-0.491	-0.479
C2	0.245	0.250	0.232	0.231	0.217	0.218
C3	-0.141	-0.140	-0.145	-0.136	-0.139	-0.138
C4	-0.107	-0.103	-0.105	-0.111	-0.109	-0.107
C5	-0.139	-0.140	-0.138	-0.136	-0.135	-0.138
C6	0.249	0.250	0.251	0.231	0.233	0.218
C7	0.560	0.589	0.562	0.555	0.559	0.560
O8	-0.462	-0.447	-0.442	-0.471	-0.437	-0.433
O9	-0.559	-0.574	-0.581	-0.548	-0.587	-0.587
C10	0.586	0.589	0.587	0.555	0.556	0.560
O11	-0.457	-0.447	-0.458	-0.471	-0.471	-0.433
O12	-0.582	-0.574	-0.581	-0.548	-0.545	-0.587
H13	0.187	0.195	0.183	0.183	0.179	0.179
H14	0.167	0.173	0.166	0.160	0.159	0.158
H15	0.190	0.195	0.190	0.183	0.183	0.179
H16	0.419	0.424	0.420	0.414	0.416	0.416
H17	0.437	0.424	0.440	0.414	0.414	0.416

put forward in this dissertation are new to the literature. The ionization potential of the three most stable isomers is larger than the remaining three. Additionally, DPA1, DPA2 and DPA3 have significantly larger electron affinities, making them more reactive than the others. Of all isomers, DP3 is the most polar compound out of the six studied structures.

A Mulliken analysis of the wave function yields to charges on the different atoms which are very similar across the six isomers as shown in Table 5.4. The Fukui function

$$f(\mathbf{r}) = \left(\frac{\partial \rho(\mathbf{r})}{\partial N} \right) \quad (5.1)$$

is the differential change in electron density (ρ) due to an infinitesimal change in the number of electrons (N) at a fixed molecular geometry[100–102]. The Fukui function has discontinuities at integer N when evaluated from above ($f^+(\mathbf{r})$) and below ($f^-(\mathbf{r})$) which signify either nucleophilic or electrophilic attack, respectively. One can use one-sided derivatives to evaluate $f^+(\mathbf{r})$ and $f^-(\mathbf{r})$ so that

$$f_N^+(\mathbf{r}) = \rho_{N+1}(\mathbf{r}) - \rho_N(\mathbf{r}) \quad (5.2)$$

and

$$f_N^-(\mathbf{r}) = \rho_N(\mathbf{r}) - \rho_{N-1}(\mathbf{r}) \quad (5.3)$$

where ρ_N is the SCF electron density for the neutral molecule. ρ_{N+1} and ρ_{N-1} are the SCF electron densities for the anion and cation, respectively, at the neutral molecule's geometry. The reactivity indicator for radical attack is defined by

$$f^0(\mathbf{r}) = \frac{1}{2} (f^+(\mathbf{r}) + f^-(\mathbf{r})) \quad (5.4)$$

The Fukui functions (f^+ , f^- , and f^0) have been calculated for the six isomers of DPA and are shown in Figure 5.2. All three Fukui functions for each isomer have been represented

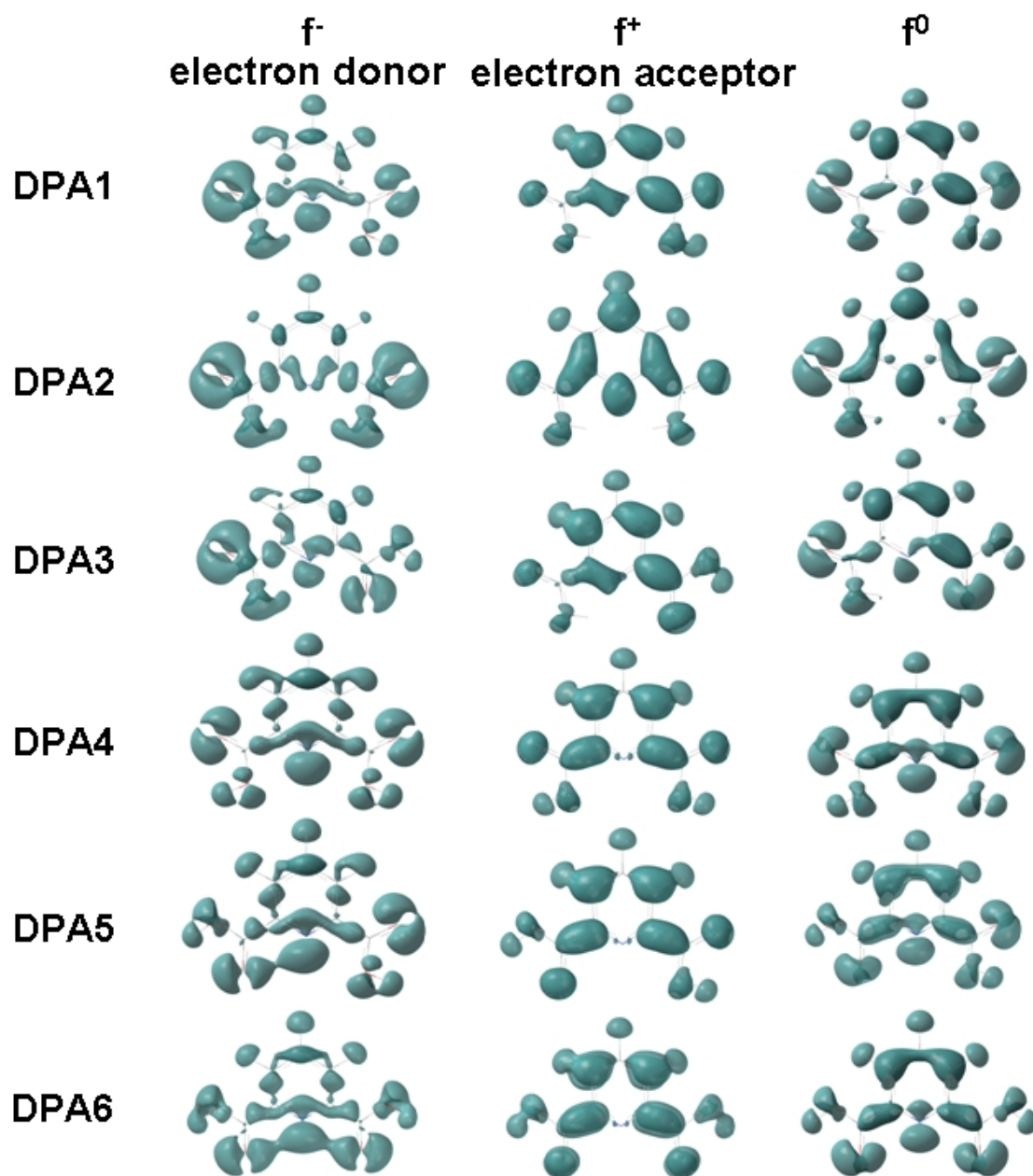


Figure 5.2: Calculated Fukui functions, [left] electron acceptor (f^-), [center] electron donor (f^+), and [right] indicator for radical attack (f^0) for DPA isomers at the B3LYP/6-31G(d) level. An isovalue of ± 0.002 was used to create the positive (blue-green) isosurfaces. The negative isosurface is small and therefore is not pictured.

as an isosurface with isovalues of ± 0.002 . Positive values are represented by the blue-green surface. The negative isosurface is not pictured because it is small and is not physically relevant.

It can be seen that DPA4 has the largest f^- value at the nitrogen (N1) site. The other isomers have similarly large f^- values at the nitrogen site except for DPA2. All of the isomers show a large f^- value at the carboxyl oxygens (O8 and O11). Calcium is an element that usually binds to DPA by electrophilic substitution with two hydrogens forming a Ca-DPA new compound. Thus, the binding site for a calcium atom to DPA is likely to occur near the nitrogen or carboxylic oxygens.

The f^+ Fukui function is much less pronounced for all of the DPA isomers. This is expected because DPA is known to be an electron acceptor and not an electron donor. However, the sites most prone to nucleophilic attack were calculated to be above and below the pyridine ring carbon atoms. The carboxyl oxygens were also calculated to be susceptible to nucleophilic attack. Additionally, the nitrogen atom has an unusually high f^+ value for DPA2.

Inspection of the f^0 Fukui function shows that it is similar to f^- . Sites susceptible to radical attack are the nitrogen atom and carboxyl oxygens for DPA1, DPA2, and DPA6. DPA3 only has high f^0 at the O11 site. DPA4 has high f^0 only at the nitrogen and DPA5 has high f^0 at the nitrogen and moderately high f^0 at the O11 site.

5.3 Vibrational Analysis

The vibrational spectra of all six monomers were calculated and are shown in Figure 5.2. The heights of the line spectra in Figure 5.2 are normalized to the peak intensity for each isomer. The vibrational frequencies are unscaled.

All of the isomers have prominent OH stretching modes in the high frequency range ($> 3500\text{ cm}^{-1}$). The two OH stretching modes for DPA1 (3692 and 3530 cm^{-1}) and DPA3 (3699 and 3524 cm^{-1}) are clearly split while the other isomers' OH stretching modes are

almost exactly overlapping. The OH stretching modes of DPA4, DPA5, and DPA6 are also blue-shifted from those of DPA1, 2, and 3.

The very intense C=O stretching mode is seen in all of the monomers between 1816 and 1868 cm^{-1} . It can be seen that there is a slight splitting of the C=O stretching modes in DPA1 and DPA5. The 1863 cm^{-1} line in DPA1 is due to the C10-O11 stretching mode and the 1825 cm^{-1} line is due to the C7-O8 stretching mode. Meanwhile in DPA5, the 1855 cm^{-1} line is due to the C7-O8 stretching mode and the 1818 cm^{-1} line is due to the C10-O11 stretching mode.

The most intense line calculated in DPA1, DPA2, and DPA3 is the OH scissoring mode between 1400 and 1440 cm^{-1} . In all three of these modes, H17 is swung towards N1. For the DPA2 OH scissoring mode, both H16 and H17 have the same swinging motion inwards to N1. Those same OH scissoring modes exist for DPA4, DPA5, and DPA6 but their motion brings the hydrogen closer to the carboxyl oxygen and results in a lower intensity line.

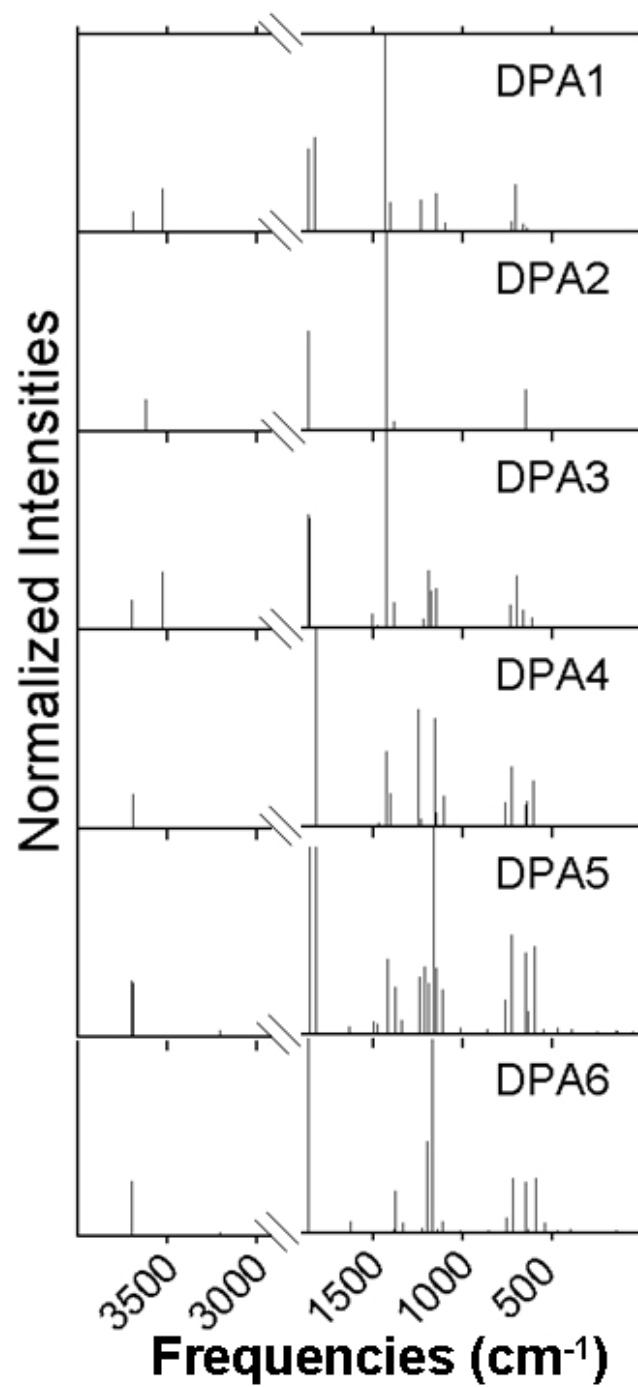


Figure 5.3: Calculated infrared spectra of the six isomers of DPA at the B3LYP/6-31G(d) level.

Table 5.5: Calculated Vibrational Spectra of DPA Ground State Isomer and Comparison with Experiments

DPA1			Experiment[38]	
ν (cm ⁻¹)	intensity	assignment	IR	Raman
3692	81	ν OH	3115	3113
3530	145	ν OH	3102	3105
3246	0	ν_s C-H		3070
3243	1	ν_a C-H	3070	
3212	7	ν_a C-H	2800	2650
1863	253	ν C=O	1710	1646
1825	287	ν C=O	1700	1640
1644	2	ν ring C-C	1576	1580
1630	3	ν ring C-C, C-N	1571	1577
1508	7	ρ CH	1470	1475
1469	15	ν C-N	1468	1447
1437	572	σ OH	1422	1439
1405	108	σ OH	1387	1423
1355	16	ν ring C-C, C-N	1341	1332
1277	14	σ OH, ν C-C	1308	1304
1236	114	σ OH	1275	1279
1185	8	σ CH	1260	1262
1165	10	ν C-O	1178	1183
1152	132	ν C-O	1151	1156
1102	50	σ CH	1082	1090
1028	0	ω CH	998	
1023	10	ring breath	987	998
974	0	ω CH	937	987
898	11	ν C-C, ρ ring	890	895
862	13	ω CH	855	855
796	22	τ full molecule	751	802
767	5	ω CH	705	762
742	2	ring breath, σ C(=O)-O	692	752
731	55	ω OH	668	698
709	156	ω C-C/O-H	647	647
663	48	ρ in-plane	592	630
645	37	ring breath	583	619
625	32	ω OH	530	
576	3	ρ in-plane	519	495
478	2	ρ in-plane	421	491
467	11	ω ring	365	437
437	0	ρ out-of-plane	330	396
384	4	ρ in-plane	226	298
359	2	ring breath	218	209
259	20	ρ in-plane	208	192
176	2	τ ring	199	135
155	1	ρ out-of-plane	107	121
131	5	σ full molecule	89	85
82	4	τ C-COOH	79	72
55	3	τ C-COOH		28

ν , stretching; ω , wagging; ρ , rocking; τ , twisting; σ , scissoring; Ph , phenyl
Subscripts : a , asymmetric; s , symmetric.

Table 5.6: Calculated Vibrational Spectra of DPA Isomers

DPA2 ν (cm ⁻¹)	DPA3 ν (cm ⁻¹)	DPA4 ν (cm ⁻¹)	DPA5 ν (cm ⁻¹)	DPA6 ν (cm ⁻¹)
3633	3699	3690	3701	3700
3617	3524	3690	3693	3700
3248	3250	3244	3248	3249
3247	3244	3242	3243	3248
3215	3211	3209	3209	3208
1868	1862	1820	1855	1862
1861	1851	1816	1818	1853
1647	1641	1637	1635	1635
1626	1632	1631	1631	1629
1504	1503	1502	1497	1490
1464	1475	1472	1475	1478
1427	1426	1429	1418	1383
1382	1387	1403	1380	1378
1343	1351	1343	1339	1335
1295	1276	1250	1245	1229
1229	1218	1233	1216	1212
1187	1195	1185	1193	1197
1168	1177	1159	1164	1170
1155	1150	1148	1147	1145
1103	1108	1108	1114	1117
1031	1025	1027	1024	1020
1024	1022	1016	1015	1013
975	965	977	969	960
897	890	890	882	873
859	858	867	863	860
779	794	808	806	804
764	767	765	762	760
750	740	732	728	724
690	736	732	727	721
671	703	659	651	650
653	662	651	649	642
648	642	642	640	637
611	614	612	600	592
579	567	563	555	545
486	486	464	470	476
474	464	460	457	455
440	437	432	432	432
377	389	389	393	399
357	350	357	350	342
247	261	253	255	258
177	173	171	167	163
163	152	150	148	147
143	132	134	136	139
76	83	56	52	43
57	48	48	38	33

The DPA4, DPA5, and DPA6 C-O stretching and CH scissoring modes between 1100 and 1170 cm^{-1} were calculated to be very intense. These same modes are present in DPA1, DPA2, and DPA3 but were calculated to be far less intense. The most prominent feature for DPA1, DPA2, and DPA3 below 1000 cm^{-1} is the C-C and OH wagging mode. This mode was calculated at approximately 700 cm^{-1} . Meanwhile, for DPA4, DPA5, and DPA6, several moderately intense lines were calculated between 600 and 800 cm^{-1} . These lines are due to the OH wagging mode (590 to 615 cm^{-1}), in-plane rocking mode (645 to 655 cm^{-1}), out-of-plane rocking mode (700 to 735 cm^{-1}), and CH wagging mode (750 to 770 cm^{-1}). The only moderately intense lines for DPA1, DPA2, and DPA3 below 1000 cm^{-1} belong to the C-C and OH wagging modes between 670 and 740 cm^{-1} .

5.4 Gas Phase Reaction Paths

Transition states were found between the isomers using the synchronous transit-guided quasi-Newton method[57,58] (see Chapter 2). Transition state structures were confirmed through vibrational analysis. All of the transition structures were determined to be near the midpoint ($\pm 90^\circ$) geometry of complete dihedral angle rotations: DPA1 $\rightarrow$ DPA2 (2,7,9,16) dihedral, DPA1 $\rightarrow$ DPA3 (1,2,7,8) dihedral, DPA1 $\rightarrow$ DPA4 (6,10,12,17) dihedral, DPA4 $\rightarrow$ DPA5 (1,2,7,8) dihedral, and DPA5 $\rightarrow$ DPA6 (5,6,10,11) dihedral. Those transition states were then used to determine the reaction pathway between the two isomers using intrinsic reaction coordinates (IRC). The IRC transition vectors were chosen to be the dihedral angles differentiating the two isomers. The energy paths for the three DPA1 isomerization reactions (DPA1 $\rightarrow$ DPA2, DPA1 $\rightarrow$ DPA3, DPA1 $\rightarrow$ DPA4) are shown in Figure 5.4 (A). The energy path for the DPA4 $\rightarrow$ DPA5 isomerization reaction is shown in Figure 5.4 (B) and the energy path for the DPA5 $\rightarrow$ DPA6 isomerization reaction is shown in Figure 5.4 (C).

Transition states were found between the isomers using the QST3 method[58,103]. Those transition states were then used to determine the reaction pathway between the two isomers

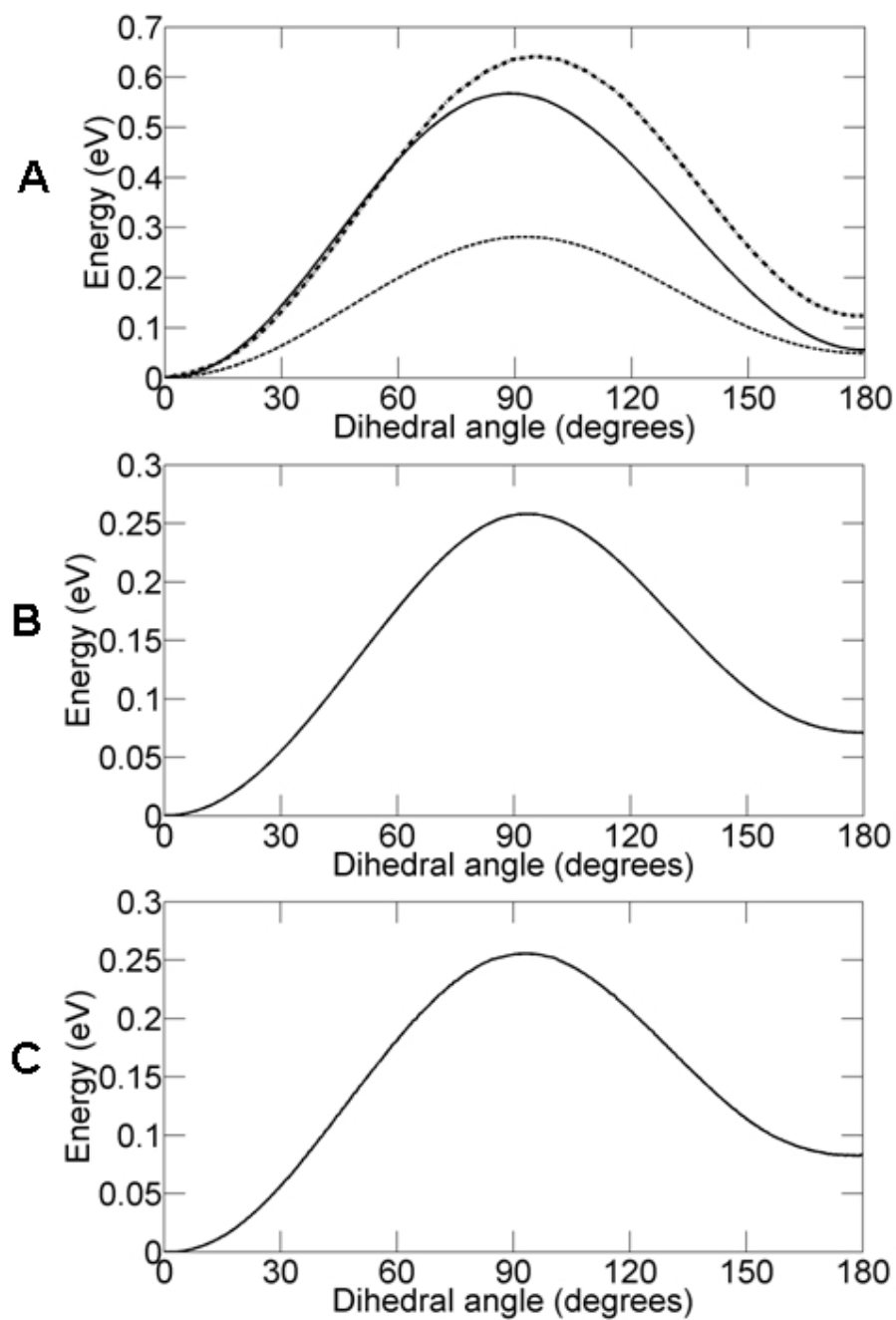


Figure 5.4: (A) Reaction energy pathways for three different isomerization reactions: DPA1 to DPA2 [solid line], DPA1 to DPA3 [small dots], DPA1 to DPA4 [large dots]. (B) Reaction energy pathway for DPA4 to DPA5. (C) Reaction energy pathway for DPA5 to DPA6. Energies in (A), (B), and (C) are relative to the DPA1, DPA4, and DPA5 minima, respectively.

using intrinsic reaction coordinates (IRC)[73]. The IRC transition vectors were chosen to be the dihedral angles differentiating the two isomers.

5.5 Dimers

DFT calculations of planar dimer formations of DPA isomers were run at the B3LYP/6-31G(d) level. The optimized dimer structures are shown in Figure 5.5. All of the dimers are hydrogen bonded in a dual OH-O bond within the COOH group. It is possible to mix and match several of the monomer structures to form other dimers but that was not included in this work.

Noticeably, dimers of DPA2 are absent because there is no possible OH-O configuration between two DPA2 monomers. The electronic states, energies, dipole moments, electron affinities, ionization potentials for these five dimers are shown in Table 5.7. All five dimers have C_{2h} symmetry. The DPA1 dimer configuration (2DPA1) was determined to be the ground state of the five dimers investigated. This is consistent with the monomer findings. The calculated zero point energies are all quite similar with the 2DPA1 structure having the lowest. The electric dipole moments are all zero as would be expected from dimer configurations with inversion symmetry. The 2DPA1 and 2DPA3 structures have the highest electron affinities while those of 2DPA4, 2DPA5, and 2DPA6 are approximately 0.45 eV less. Similarly, the 2DPA1 and 2DPA3 structures have the highest ionization potentials. This pattern is consistent with the monomer findings.

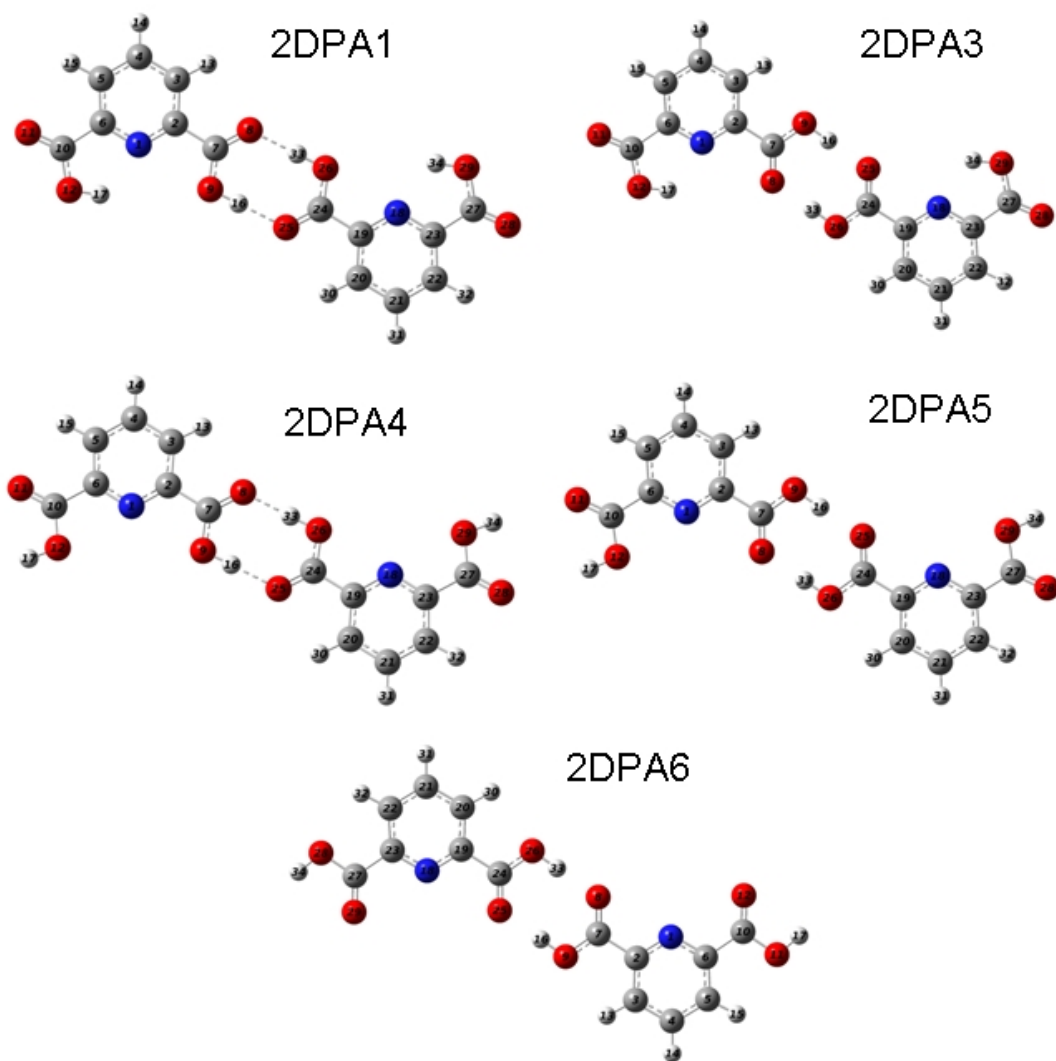


Figure 5.5: Dimers of DPA optimized at the B3LYP/6-31G(d) level.

Table 5.7: Electronic states, total electronic energies, zero point energies (ϵ_0), dimer formation energies ($E_{formation}$), electron affinities (EA), ionization potentials (IP), and HOMO-LUMO gap (Δ) of DPA dimers. Total electronic energies E are relative to the 12DPA1 ground state energy of -34.038310 keV.

dimer	state	E (eV)	ϵ_0 (eV)	$E_{formation}$ (eV)	EA (eV)	IP (eV)	Δ (eV)
2DPA1	1A_1	0	6.514	-0.818	1.264	8.928	5.089
2DPA3	1A_1	0.042	6.510	-0.875	1.255	8.917	5.084
2DPA4	1A_1	0.292	6.498	-0.814	0.813	8.553	5.353
2DPA5	1A_1	0.351	6.492	-0.898	0.804	8.580	5.388
2DPA6	1A_1	0.501	6.482	-0.908	0.775	8.695	5.551

Vibrational frequencies were calculated to confirm that the structures were minima. The calculated vibrational IR spectra for the dimers are shown in Figure 5.6. As is typical for dimerized carboxylic acids[84], the OH stretching modes between 3200 and 3250 cm^{-1} dominates all five of the spectra. The other vibrational lines are similar to those of the monomers, except perhaps for the notable splitting of the intense C=O stretching mode between 1775 and 1865 cm^{-1} . This splitting is due to the coordinated C=O stretching vibrations among the four C=O bonds in the dimer formation.

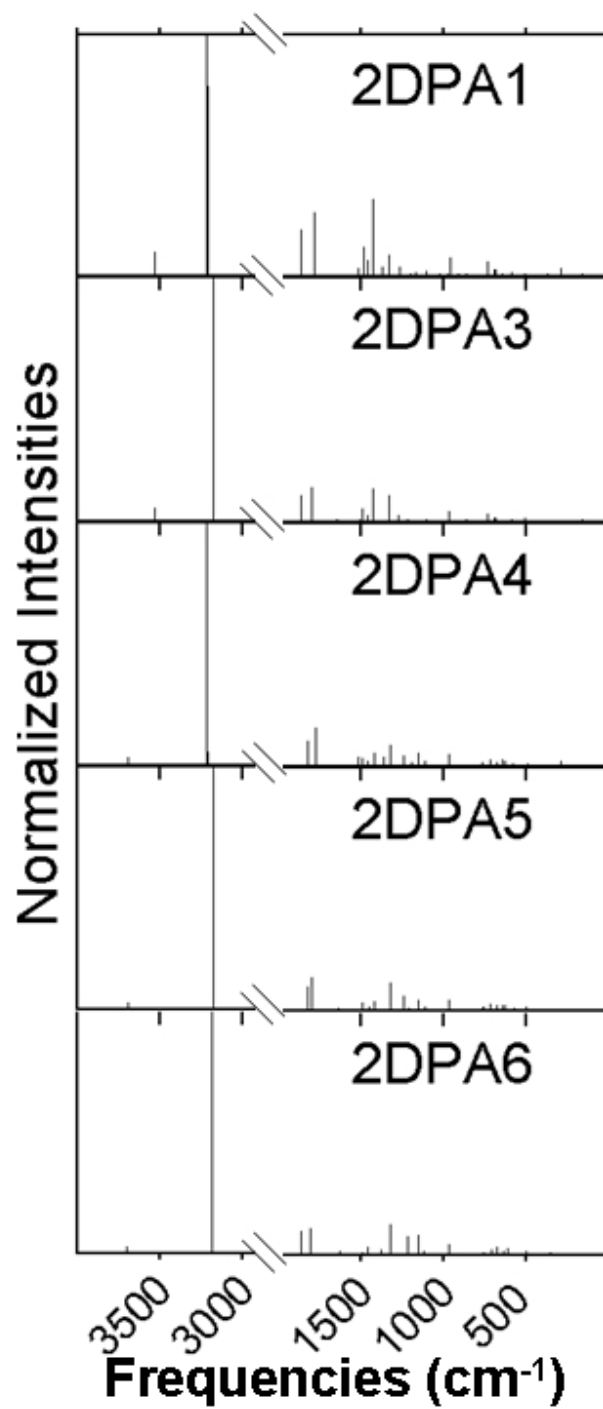


Figure 5.6: Calculated infrared spectra of the five dimers of DPA at the B3LYP/6-31G(d) level.

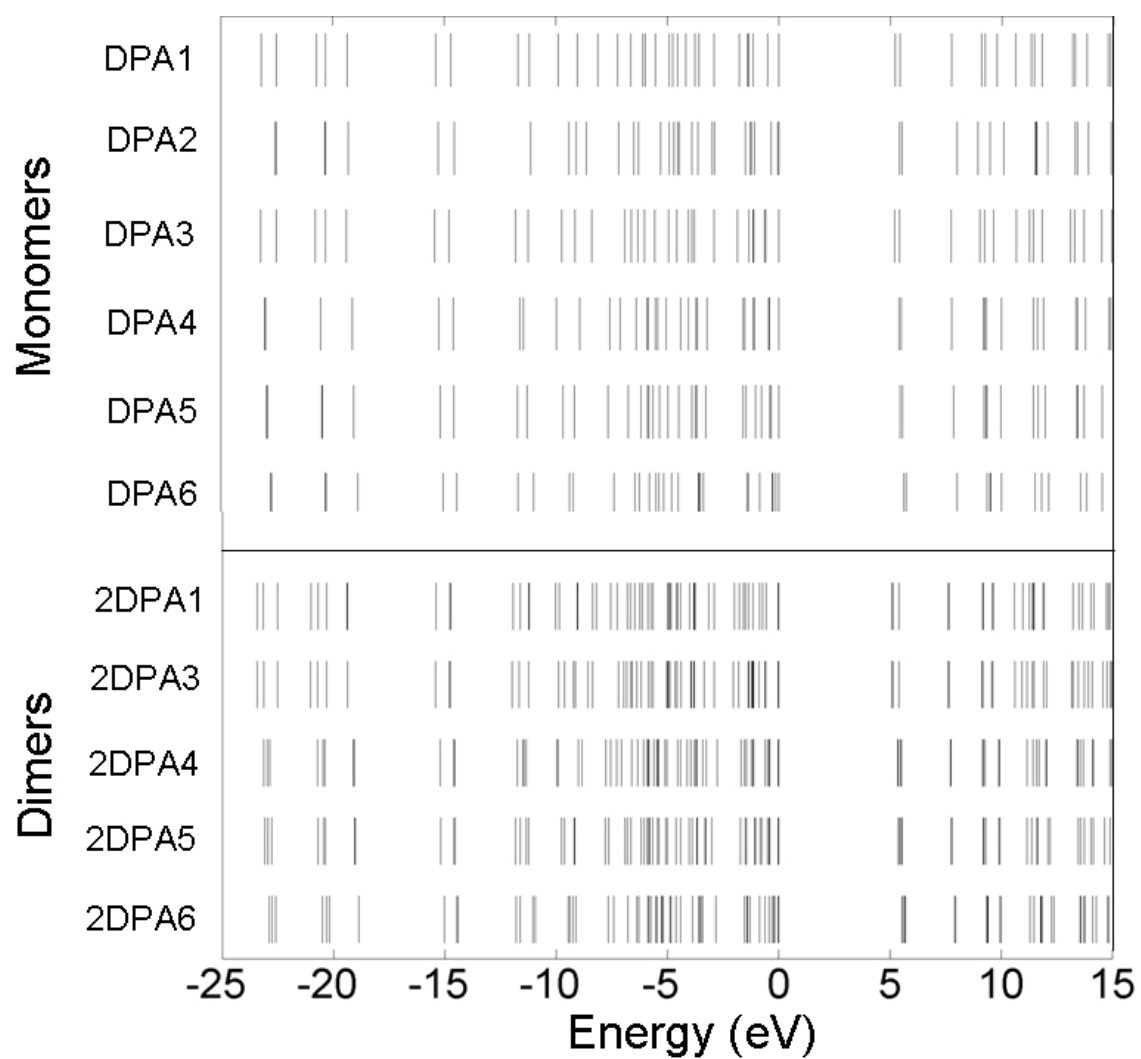


Figure 5.7: Occupied and unoccupied molecular orbital levels calculated for DPA isomers.

The molecular orbital energy levels of the DPA monomers and dimers are shown in Figure 5.7. The orbital energy level at $E = 0$ eV is the highest occupied molecular orbital (HOMO). The smallest of the monomer HOMO-LUMO gaps (5.191 eV) is found in DPA3 while the largest HOMO-LUMO gap (5.599 eV) is found in DPA6. The HOMO-LUMO gaps of the dimer formations are only slightly smaller: 5.084 eV for 2DPA3 and 5.551 eV for 2DPA6. The distribution of each isomer’s monomer and dimer orbital energy levels are quite similar.

5.6 2-Dimensional and 3-Dimensional Structures

Several of the dimer structures, 2DPA4, 2DPA5, and 2DPA6 in particular, lend themselves to be extended in a linear chain. One-dimensional chains of 2DPA4, 2DPA5, and 2DPA6 were optimized at the B3LYP/6-31G(d) level while using periodic boundary conditions (PBC). The initial guess for the unit cell length (i.e., a chain of two monomers) of 16.167 Å was taken from experimental crystallographic data[39]. The chain of 2DPA4 was determined to have the lowest total energy of the three. The 2DPA5 and 2DPA6 chains have energies of 0.060 and 0.156 eV, respectively, above the 2DPA4 chain. Optimized unit cell lengths of 16.497, 16.318, and 16.257 Å were calculated for the 2DPA4, 2DPA5, and 2DPA6 chains, respectively.

The optimized 1-D structures and x-dimension translation vectors were then used as the initial guesses for a two-dimensional calculation for 2DPA4, 2DPA5, and 2DPA6 with PBC. The initial guess for the y-dimension unit cell length of 5.571 Å was taken from experimental results[39]. The 2-D structures were optimized at the B3LYP/6-31G(d) level. Energies of these optimized sheets were nearly degenerate with the 2DPA4 sheet having the lowest total energy. The 2DPA5 and 2DPA6 sheets had total energies of 0.022 and 0.041 eV above that of the 2DPA4 sheet, respectively. The 2-D optimization results agree with previous experiments[39] and show that chains of DPA arrange themselves in rows within a planar sheet. However, the calculations predict larger unit cell lengths along the

Table 5.8: Summary of 2-D and 3-D DPA structures optimized at the B3LYP/6-31G(d) level. Total electronic energies E for the 2-D and 3-D structures are relative to the DPA4 case.

Structure	E (eV)	2-D		3-D	
		a (Å)	b (Å)	E (eV)	c (Å)
DPA4	0	16.398	6.754	0	3.77
DPA5	0.022	16.376	6.690	0.022	3.77
DPA6	0.041	16.378	6.611	0.042	3.77

xy-plane. The optimized lattice constants were calculated to be (16.398, 6.754), (16.376, 6.690), and (16.378, 6.611) Å for the 2DPA4, 2DPA5, and 2DPA6 2-D sheets, respectively. For comparison, single crystals of DPA were measured to have (16.167, 5.571) Å [39] and (14.034, 13.205) Å [104]. It should be noted that in Ref. [104] the authors claim that the monomeric structure has a hydrogen bound to the nitrogen. Such a structure was not found in these results. The results here agree reasonably well with those reported in Ref. [39]. The energies and optimized unit cell lengths are summarized in Table 5.8. Optimized unit cells and predicted 2x2 supercells of the two-dimensional sheets of 2DPA4, 2DPA5, and 2DPA6 are shown in Figures 5.8, 5.9, and 5.10, respectively.

Single point energies of the three-dimensional crystal structures of 2DPA4, 2DPA5, and 2DPA6 were calculated by stacking the optimized 2-D sheets on top of each other and separated by the lattice parameter, $c = 3.77$ Å, from experiments[39]. The energy separation of the three structures was nearly identical to the 2-D case. The 2DPA5 and 2DPA6 crystal structures had total energies of 0.022 and 0.042 eV , respectively, above that of the 2DPA4 crystal.

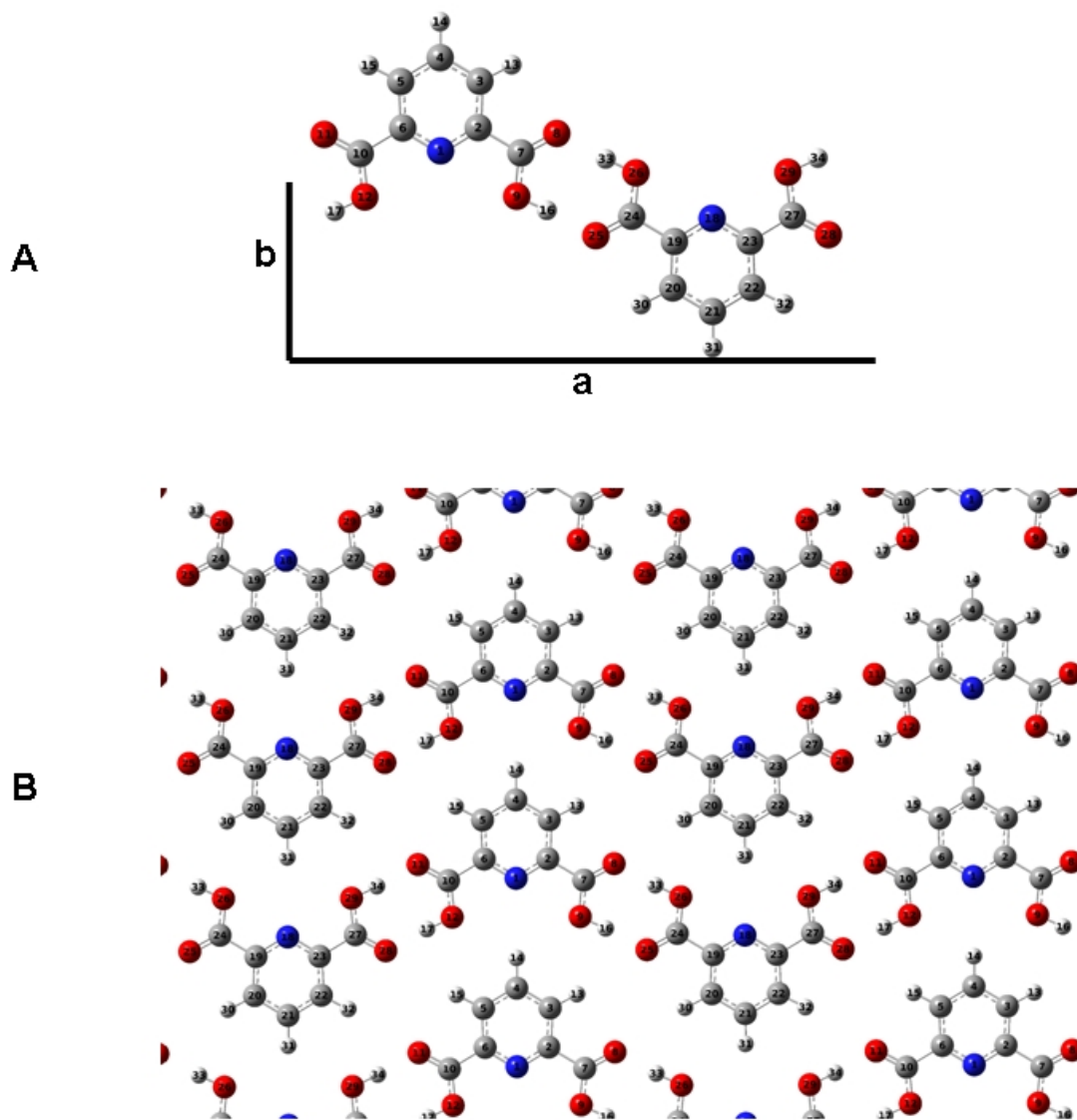


Figure 5.8: (A) Optimized 2-D unit cell of DPA4 with PBC lattice constants of $a = 16.398$ Å and $b = 6.754$ Å and (B) a 2x2 supercell.

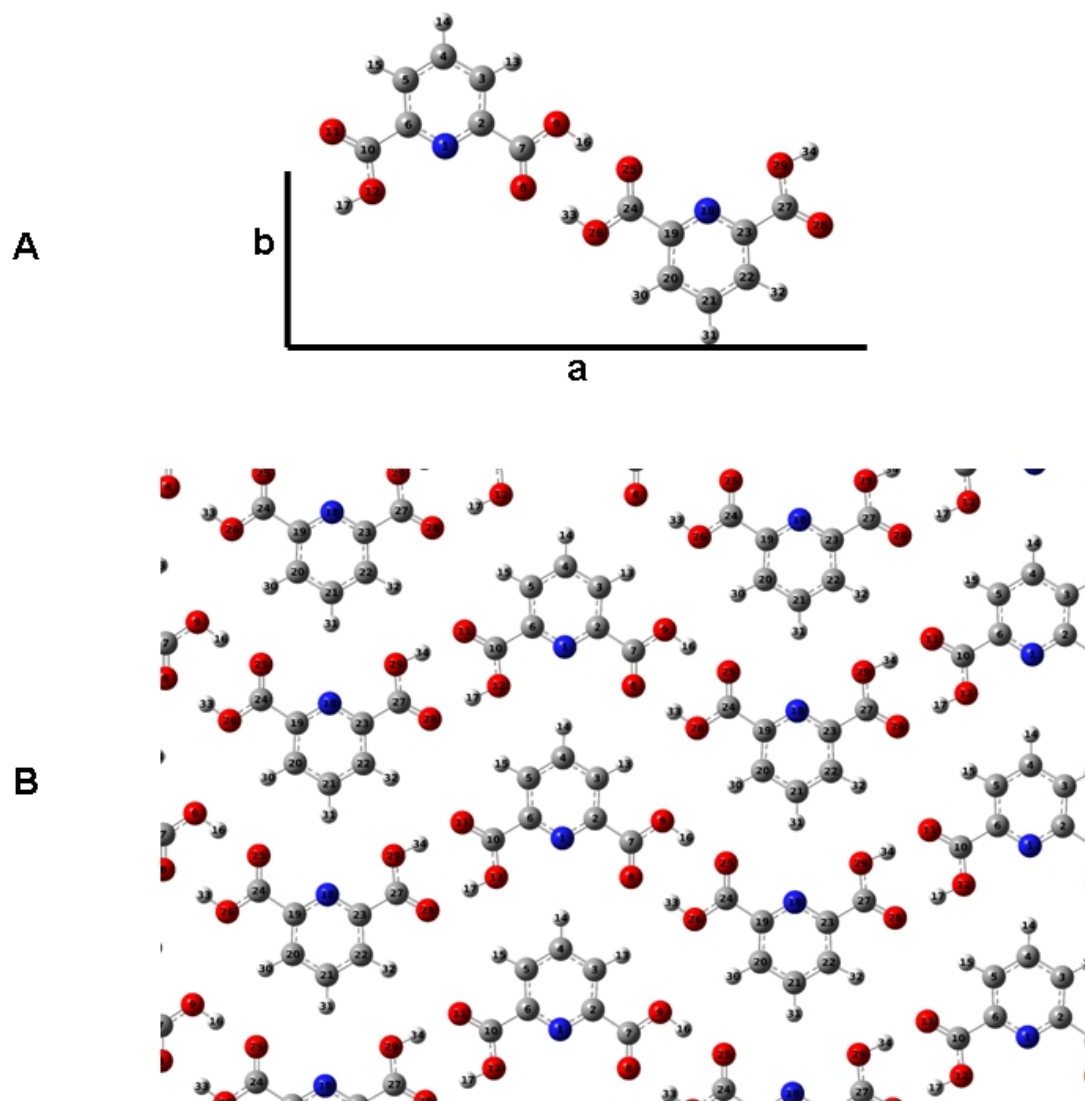


Figure 5.9: (A) Optimized 2-D unit cell of DPA5 with PBC lattice constants of $a = 16.376$ Å and $b = 6.690$ Å and (B) a 2x2 supercell.

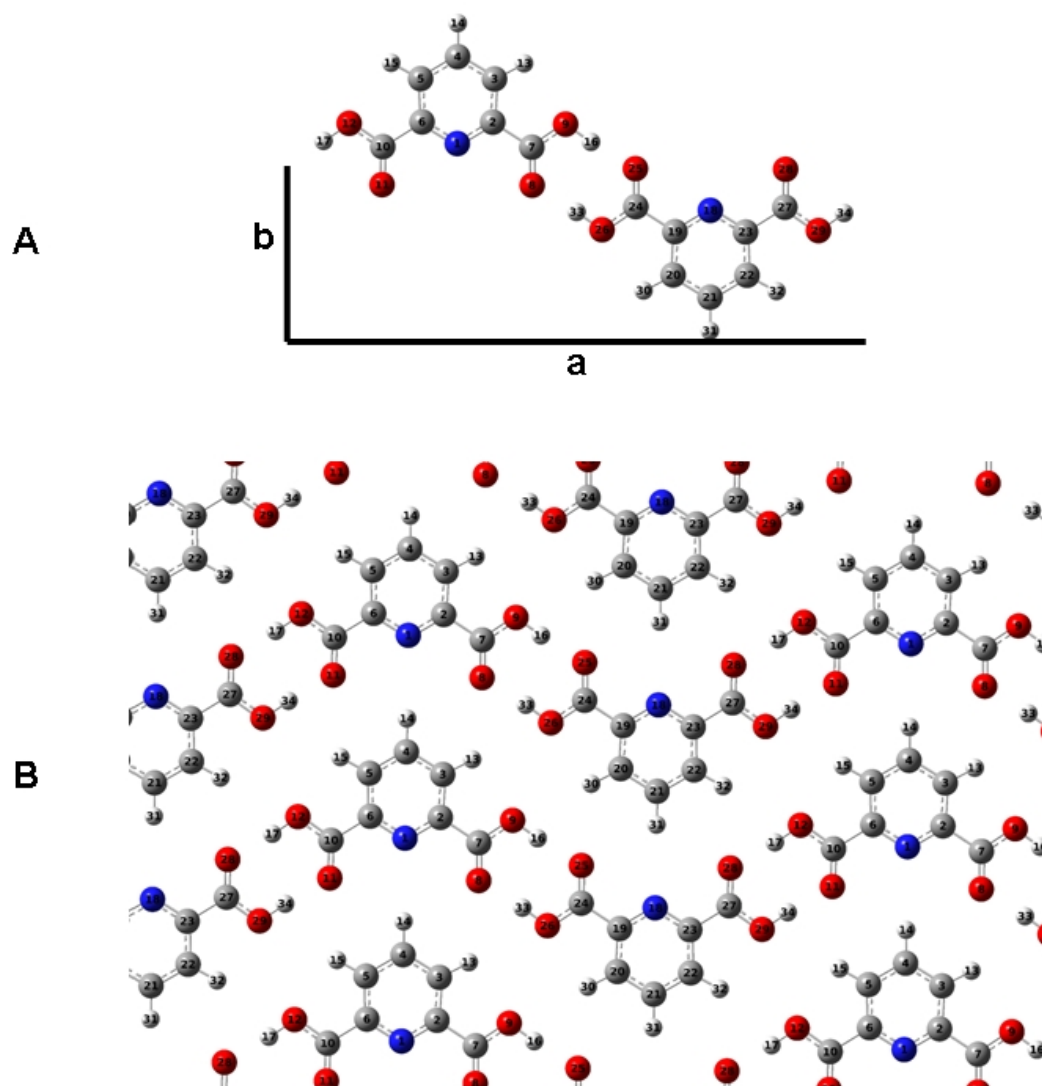


Figure 5.10: (A) Optimized 2-D unit cell of DPA6 with PBC lattice constants of $a = 16.378$ Å and $b = 6.611$ Å and (B) a 2x2 supercell.

5.7 Band Structure

The band structures of the three different crystalline forms were calculated and are plotted along important symmetry lines of the Brillouin zone for a simple orthorhombic Bravais lattice[105]. Ten occupied and ten unoccupied orbital electronic energy levels are plotted along the edges and two faces of one-eighth of the irreducible Brillouin zone. Energies are referred to the Fermi energy (E_F) level of the DPA crystal. The Fermi energies were calculated for each DPA crystal by solving a self-consistent equation described in Ref. [106]. It equates the number of electrons (N) to the sum of electron occupation probabilities (Fermi functions) of eigenstates composing the bands,

$$N = \sum_{\alpha=1}^{n_{band}} \sum_{k=1}^{n_k} \frac{2}{1 + e^{\frac{E_{\alpha,k} - E_F}{k_B T}}} \quad (5.5)$$

where $n_{band} = 10$ is the number of occupied bands, $n_k = 2884$ is the number of k-points in each band, k_B is Boltzmann's constant, $T = 300K$, and $N = 2n_k n_{band}$. Accuracies of better than 0.001 eV were achieved in the determination of E_F .

The energy bands were plotted relative to the E_F for each crystal so that the Fermi level lies at $E = 0$ eV in Figures 5.11 through 5.16. The DPA4 crystal has a calculated indirect band gap of 4.844 eV and a direct band gap of 5.019 eV. The DPA5 crystal has a calculated indirect band gap of 4.847 eV and a direct band gap of 5.079 eV. The DPA6 crystal has a calculated indirect band gap of 4.847 eV and a direct band gap of 5.154 eV. The indirect band gaps of crystalline DPA structures are between 0.5 and 0.7 eV less than their associated dimer formation HOMO-LUMO gaps from Figure 5.7.

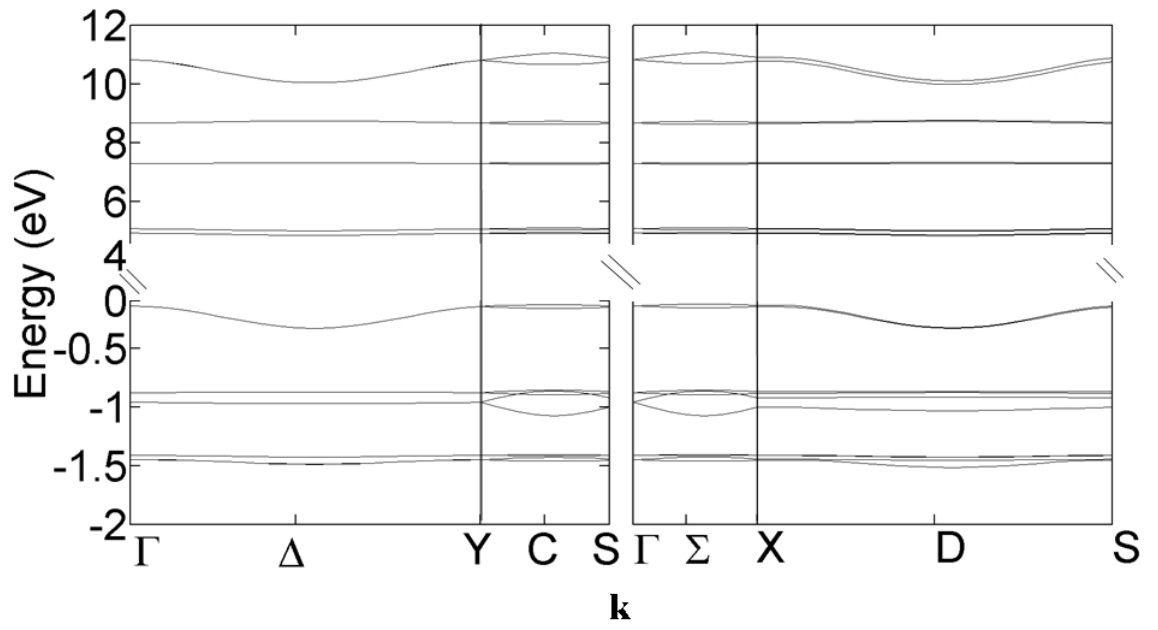


Figure 5.11: Band structure of DPA4 crystal calculated along symmetry lines Δ , C, Σ , D.

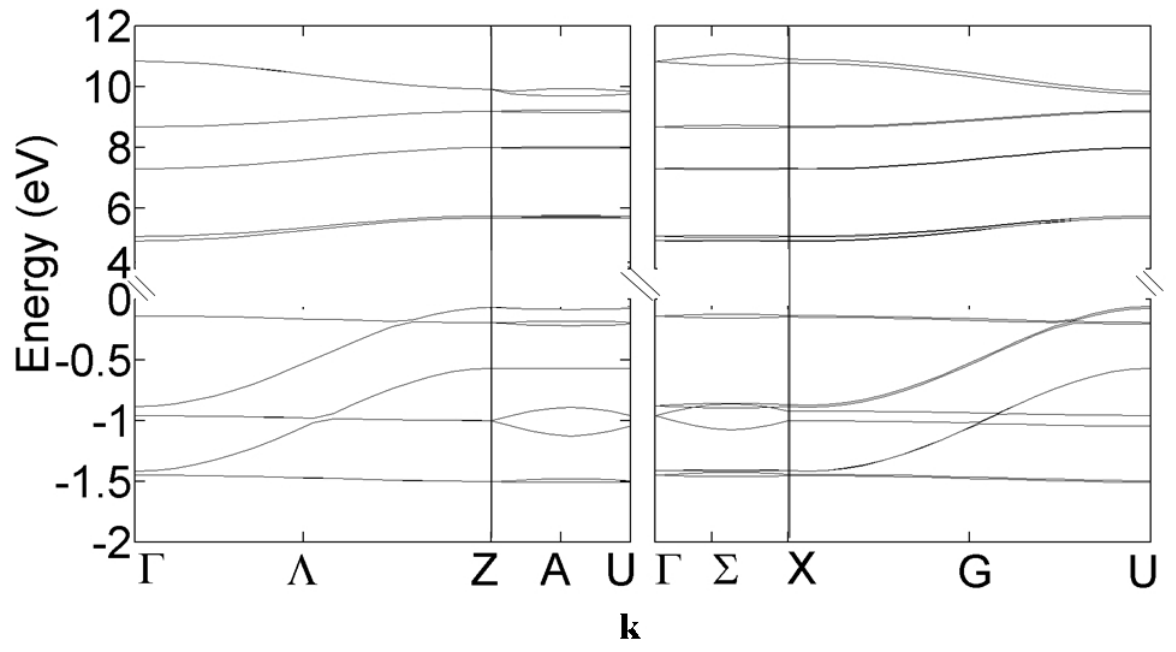


Figure 5.12: Band structure of DPA4 crystal calculated along symmetry lines Λ , A , Σ , G .

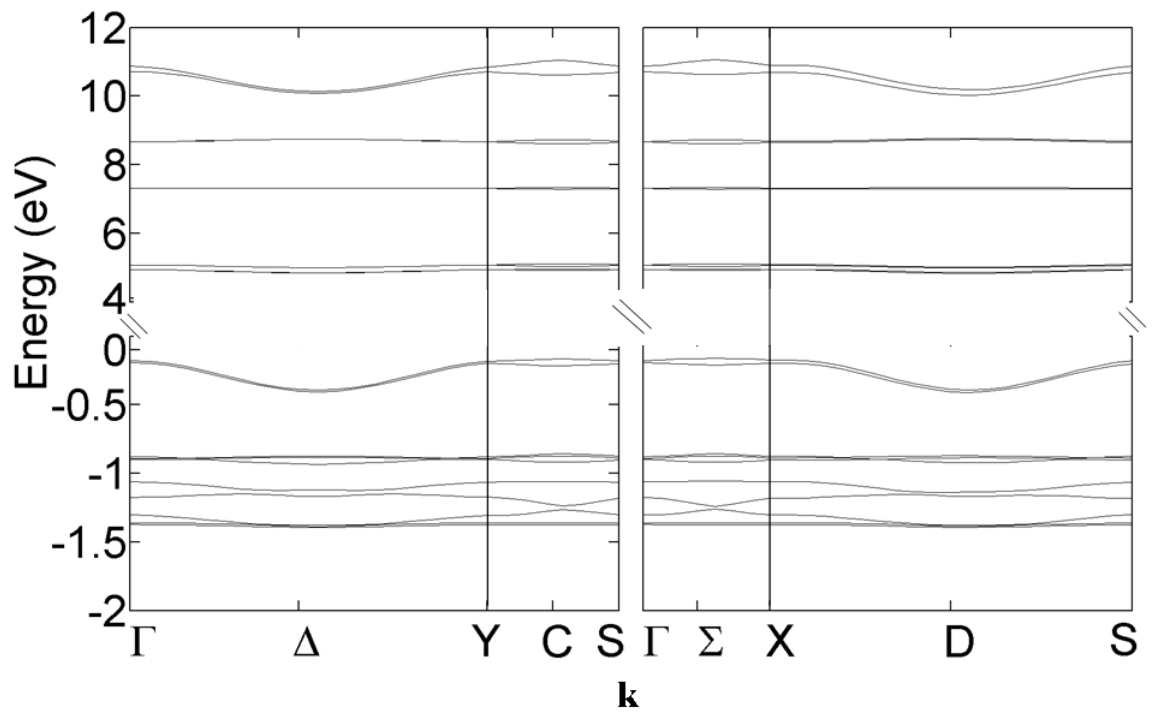


Figure 5.13: Band structure of DPA5 crystal calculated along symmetry lines Δ , C, Σ , D.

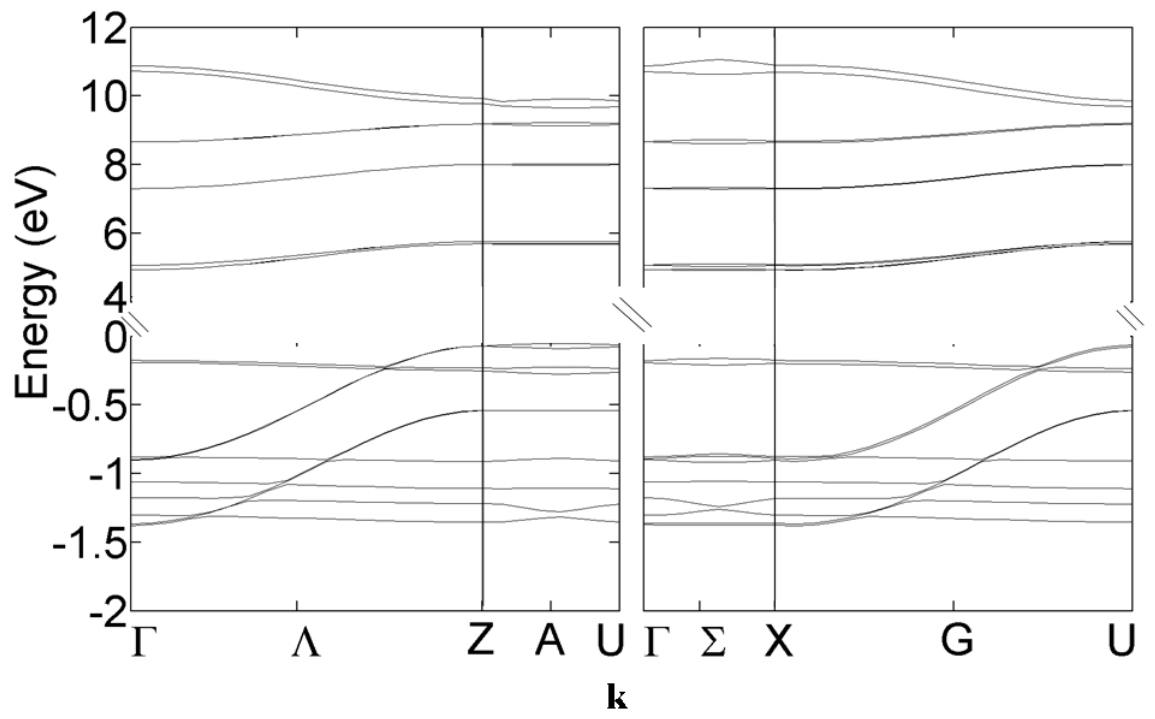


Figure 5.14: Band structure of DPA5 crystal calculated along symmetry lines Λ , A, Σ , G.

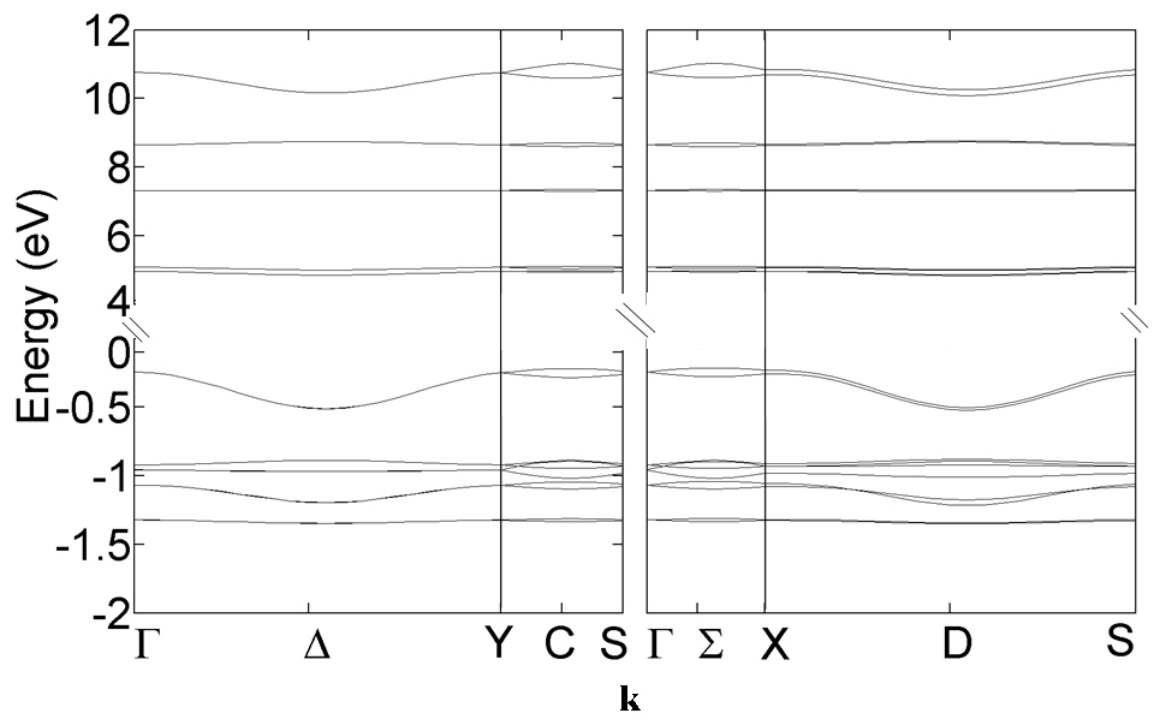


Figure 5.15: Band structure of DPA6 crystal calculated along symmetry lines Δ , C, Σ , D.

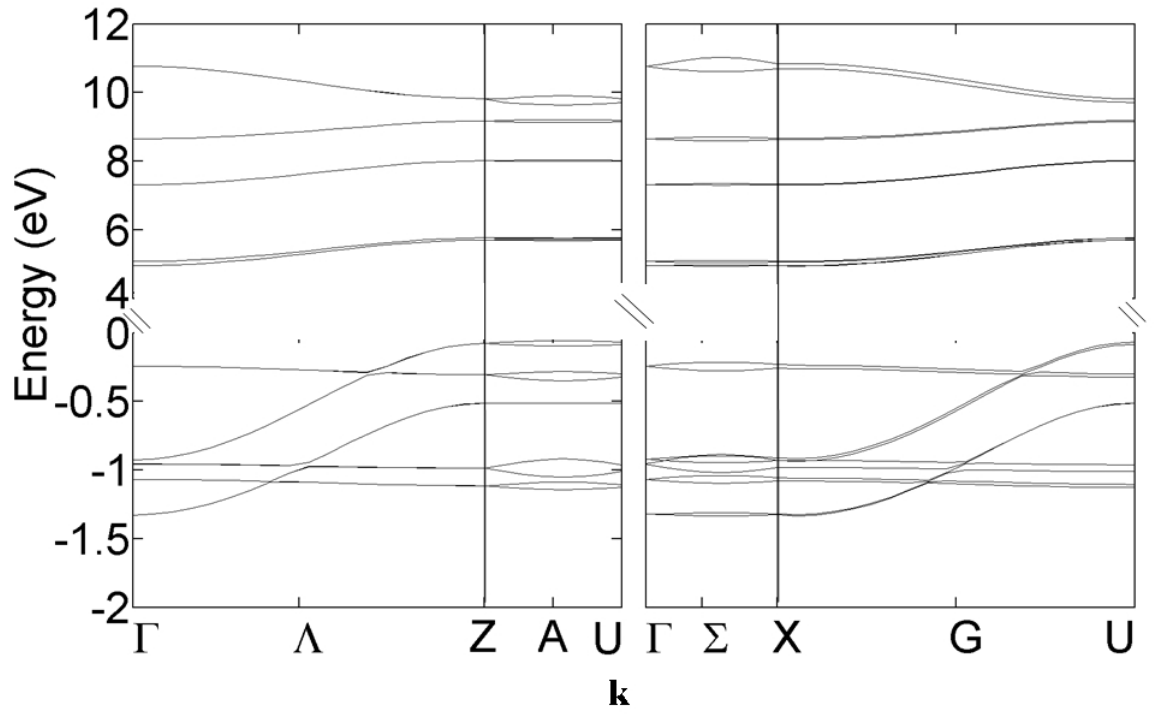


Figure 5.16: Band structure of DPA6 crystal calculated along symmetry lines Λ , A , Σ , G .

5.8 Conclusion

The structures, energetics, and vibrational analysis of gas phase monomers and dimers of DPA have been presented using the B3LYP/6-31G(d) level of calculation. All structures were determined to exist only in singlet states as there was no stable triplet state. In the gas phase, it is predicted that the majority of DPA has the structure of DPA1. Populations of DPA2 and DPA3 may also exist in the gas phase as those two structures were calculated to have an almost degenerate energy level of <0.05 eV above the DPA1 structure. The Fukui functions indicating regions of electrophilic, nucleophilic, and radical attack were calculated for all six isomers. The carboxylic oxygen sites of all the isomers were indicated to regions of high electrophilic attack. Meanwhile, the nitrogen sites of all isomers except DPA2 were indicated to be regions of high electrophilic attack. Regions of radical attack were similar to that of the electron acceptor regions, although with lower reactivity indicators. The calculations support the evidence that DPA monomers will most likely bind to calcium at the nitrogen and carboxylic oxygen sites. It is predicted that water molecules will bind to the nitrogen, carbon, or carboxylic oxygen atoms at an orientation normal to the pyridine ring plane.

Transition states between five possible isomeric reactions were found. The energy barriers of those isomerization reactions were calculated. The highest energy barrier of 0.63 eV exists for the DPA1 $\rightarrow$ DPA4 reaction. The lowest energy barrier of 0.17 eV exists for the DPA6 $\rightarrow$ DPA5 reaction.

Clear differences exist in the vibrational spectra of the crystal-forming monomers of DPA (4, 5, and 6) and the lower energy monomers (1, 2, and 3). The latter are predicted to only exist in vapor and liquid phases. A most evident difference is the greater IR intensity of the O-H scissoring mode between 1420 and 1440 cm^{-1} for the 1, 2, and 3 forms. Meanwhile, the C-H scissoring modes between 1160 and 1200 cm^{-1} are much more intense for the crystal-forming monomers than for the 1, 2, and 3 forms. Interestingly, the less symmetric monomers (DPA1, DPA3, and DPA5 appear to have double IR lines between 1820 and 1870

cm^{-1} which correspond to the C=O bond stretching. The decrease in the O-H vibrational stretching bands as the phase proceeds from vapor to liquid to solid [99,107] is seen in the vibrational spectra of the monomers and dimers. The difference in O-H stretching modes between monomer and dimer formations is 400 to 500 cm^{-1} .

Linear, one-dimensional chains and two-dimensional sheets of DPA4, DPA5, and DPA6 were optimized using periodic boundary conditions. The translation vectors were optimized for both 1-D and 2-D cases. It was determined that the DPA4 isomer forms the lowest energy periodic chains and sheets. However, both the DPA5 and DPA6 2-D sheets lie very close in energy (0.022 and 0.041 eV, respectively) above the 2-D DPA4 sheet. As a chelating agent, DPA has been reported to have a structure resembling DPA4, DPA5, and DPA6. Using the lattice parameter ($c = 3.77 \text{ \AA}$) taken from experimental results, single point calculations of three-dimensional crystal structures suggest that DPA4 is the preferred form of solid DPA. This agrees with experimental findings [99].

Regardless of the preferred form, DPA in its crystalline phase acts as an insulator with a minimum direct band gap around 5 eV. An optimized 3-D crystal structure may very well involve sheets of DPA arranged at different orientation angles, not directly on top of each other. It should be noted that a calculation of two stacked chains of DPA resulted in a stable structure with approximately a 45 degree angle of orientation between the two chain directions. However, three-dimensional optimization with PBC calculations proved to be too computationally intensive for the resources available.

Chapter 6: Computational Tools and Implementation

6.1 Computing Platforms

A number of computational resources were used to complete this dissertation. Several systems from the US Army Corps of Engineers (USACE) Engineering Research and Development Center (ERDC) Major Shared Resource Center (MSRC) were used. “Sapphire” was a Cray XT3 with 4128 64-bit 2.6 GHz Opteron single (later upgraded to dual) cores with 2 GB of memory per processor. “Sapphire” was decommissioned on February 4, 2011. “Jade” is a Cray XT4 with 76 64-bit 2.8 GHz dual-core service nodes, 2,146 64-bit 2.1 GHz quad-core compute nodes and 8 GB of dedicated memory per node. “Diamond” is an SGI Altix ICE with 1,920 compute nodes with each containing two 64-bit 2.8 GHz quad core Nehalem processors and 24 GB of dedicated memory. “Garnet” is a Cray XE6 with 1264 compute nodes with each containing two eight-core 2.4 GHz processors sharing 32 GB of memory. Gaussian 03 and, later, Gaussian 09 was used on these systems.

Early computations with Gaussian 03 were performed on GMU’s College of Science (COS) computer cluster. The COS cluster was composed of 20 computers each with dual Intel Pentium(R)4 3.80 GHz processors. I also accessed the Altix SGI at the Pittsburgh Supercomputing Center named “Pople” through the Teragrid allocation CHE100033.

6.2 Software

DFT calculations were performed with Gaussian 03 and Gaussian 09. Gaussian 09 was readily available on the ERDC MSRC systems as soon as the package was released. Gaussian 03 and 09 are comprehensive computational chemistry software packages that calculate the electronic structure of atomic and molecular systems up to hundreds or thousands of

atoms. The Gaussian software is able to calculate the optimized structures, vibrational frequencies, chemical reaction paths, and many other physical properties which may not be experimentally feasible to obtain. The Gaussian package includes the implementation of many computational chemistry techniques and methods including Hartree-Fock, Density Functional Theory, coupled cluster, and configuration interaction among others. Most importantly for this research, this package contains implementation of Time-Dependent Density Functional Theory (TDDFT) to calculate excited state properties. Beginning with Gaussian 09, TDDFT structural optimizations and vibrational frequency calculations were made possible. These are only available for the first excited state of the system of interest. Several of the most often used keywords within Gaussian 03 and 09 were OPT, FREQ, TD, GEOM, GUESS, and PBC.

OPT will perform a structural minimization on the molecular system. OPT will iteratively search for a potential energy minimum by updating its trial step size while following the energy gradient. It will also search for transition states and higher order saddle points. The Berny algorithm was used for all structural minimizations in this work. The MODREDUNDANT option allows the user to specify extra geometrical constraints or variables.

FREQ performs vibrational frequency calculations on a given geometry. Typically, the structure will have been minimized using the OPT routine prior to the FREQ calculation. FREQ computes the mass-weighted coordinates of the Hessian matrix and then computes the eigenvalues of that matrix. The roots of the eigenvalues are the fundamental frequencies of the molecular system[69]. If all the fundamental frequencies are positive, then a potential energy minimum has been found. If one or more of the frequencies are negative, then the structure is a transition state or higher order saddle point. The “OPT FREQ” combination will work for ground states but need to be separated into two separate jobs for excited states when using Gaussian 09.

The TD keyword requests an excited state calculation using time-dependent DFT. The NStates option will calculate N excited state energy levels. Singlet and triplet states will be

calculated with the 50-50 option. For excited state structural optimizations and frequency calculations, the Root=1 option was used to choose the first excited singlet state. The Read option was also used to read in the initial wavefunction guess from the checkpoint file.

The GEOM keyword allows the user to read the molecular structure from a saved checkpoint file. This option was used extensively when performing TDDFT calculations using the optimized ground and excited state structures. The MODREDUNDANT option was also used to freeze and activate key internal coordinates, such as the O15-H12 bond length in MS calculations. The GUESS keyword was used to read in the wavefunction from the saved checkpoint file.

PBC requests a periodic boundary condition calculation. The actual PBC keyword does not need to be specified, only the translation vectors of the 1-D, 2-D, or 3-D lattice need to be included in the geometry specification. Gaussian will then replicate the specified unit cell in the directions specified by the translation vectors. PBC was used for DPA 1-D, 2-D, and 3-D lattice calculations. The IOp(5/98=1) and IOp(5/103=10) options were also used. IOp(5/98=1) requests to save eigenvalues and orbitals at all k-points while IOp(5/103=10) requests the printing of 10 occupied and 10 virtual orbital electron levels.

6.3 Scripts and Pseudocode

The ERDC-HPC implements the Portable Batch System (PBS) which is a system for submitting batch job scripts. A sample script used to run jobs on the ERDC-HPC is shown in Appendix A. One specifies the number of CPU's, the project name, queue type, and required wall time within the PBS script.

The photoluminescence calculation described in Chapter 4 necessitates full computational implementation. A flow chart is provided in Figure 6.1. This calculation begins with the calculation of the ground state energy and vibrational spectrum of the isomer being investigated (top of Figure 6.1). If a stable structure is confirmed, then TDDFT vertical excitations are calculated. The first excited singlet state (Root=1) is then used to optimize

(relax) the excited state geometry of the isomer. It is often that the excited state optimization does not converge on the first try and small displacements in the atomic configuration need to be made. If an excited state optimization does converge, then TDDFT vibrational analysis is performed on that structure. A stable excited state structure is confirmed if there are no imaginary frequencies listed among the normal modes.

The photoluminescence calculation was written with MATLAB and uses several inputs from the DFT and TDDFT calculations: the calculated 0-0 emission energies, vibrational frequencies of the ground and excited states, normal mode eigenvectors of the ground and excited states, transition dipole moments, temperature, line broadening factor, and maximum vibrational energy level to consider.

The ketoB and enol components to the photoluminescence spectrum are calculated in the same manner. As can be seen in Appendix B, there are four nested for-loops: a loop over the ground state normal modes, a loop over the excited state normal modes, a loop over the excited vibrational levels, and a loop over the ground state vibrational levels. The “g-factors” of the approximated harmonic oscillation are calculated which describe the maximum displacement of the atoms associated to the given normal mode. Next the Franck-Condon overlap factors are calculated, centered on the transition wavelength, Lorentzian-broadened, and added to the complete spectrum. The temperature-dependent ESIP energy barrier is then calculated and the Boltzmann factor of crossing the barrier is applied to the ketoB and enol spectral components. Finally, the entire calculated spectrum is summed and normalized.

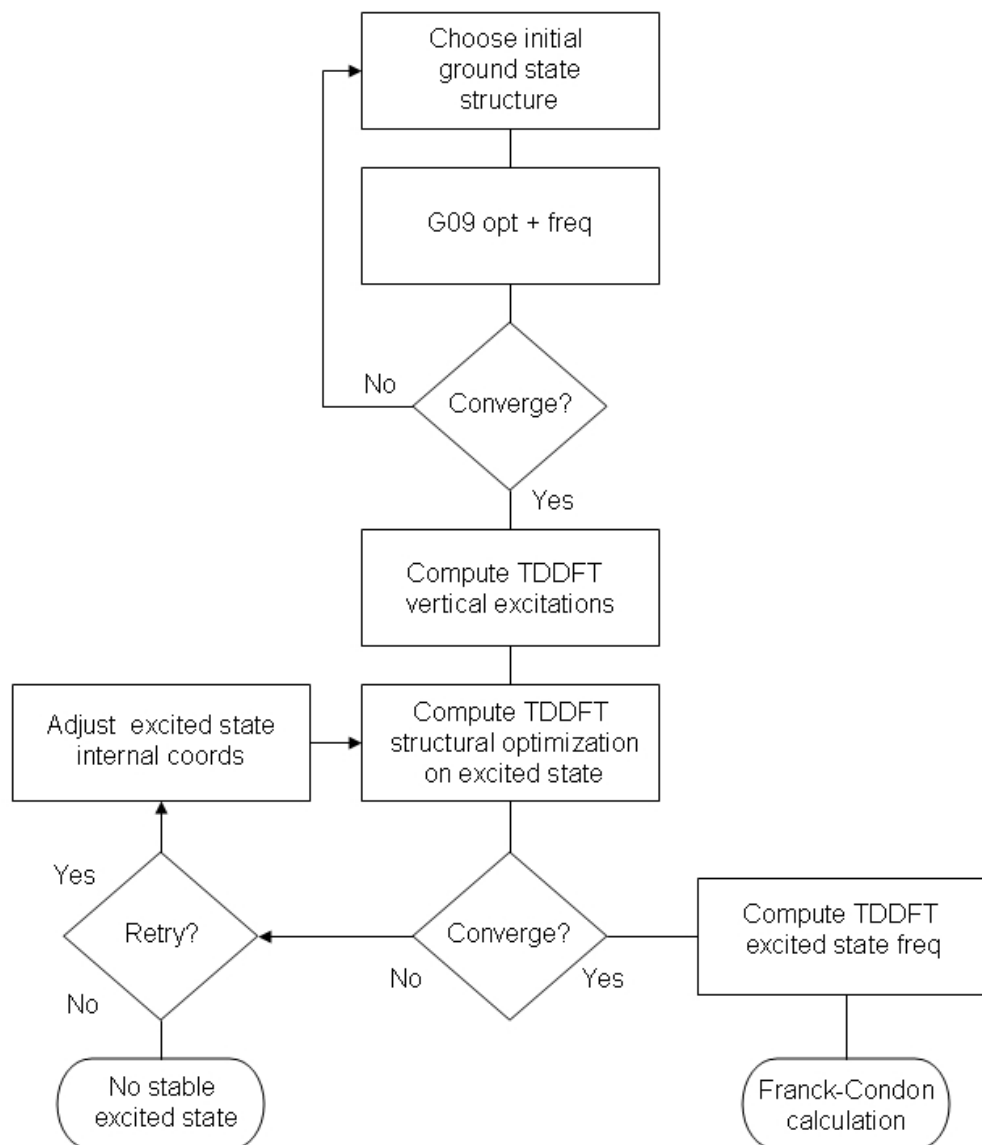


Figure 6.1: Flow chart of the calculations needed to model photoluminescence using Gaussian and the Franck-Condon factor code.

Chapter 7: Concluding Remarks

Methyl salicylate (MS) isomers were investigated using hybrid Density Functional Theory (DFT) and Time-Dependent DFT (TDDFT). Six isomer configurations (ketoB, ketoA, ketoB_{open}, ketoA_{open}, enol, and ekA) were determined to be stable in both the ground singlet and first excited triplet state. The ground state energies and vibrational spectra were investigated in detail. The ¹ketoB structure was determined to be the global minimum structure with its rotamer ¹ketoA located only 0.08 eV higher in total electronic energy. However, a transition state between the two rotamers was found to be 0.67 eV higher than the ¹ketoB energy. Thus, an isomeric reaction between the two states is unlikely at normal conditions and the vast majority of MS is therefore thought to be composed of the ¹ketoB structure. The ground state of a proton-transferred structure, ¹enol, was confirmed for the first time using computational techniques. The vibrational spectra of ¹ketoB was shown to match very well with experimental IR spectra. Dipole moments, quadrupole moments, rotational constants, and free energies of the isomers were also calculated. At high temperatures, the free energy calculations suggest that ¹ketoA and other isomers may be the energetically preferred structures.

With the ground state structures identified, TDDFT calculations were performed with several basis sets to determine the vertical excitation energies of the isomers. The vertical excitation energy of ¹ketoB to the first excited singlet matched the experimental absorption spectrum center line. Excited state geometry optimizations were then used to find the relaxed first excited singlet state structures of ¹ketoB₁, ¹ketoA₁, and ¹enol₁. The optimized excited state structures provided the 0-0 transition emission energy. Excited state frequency calculations were also performed to validate the existence of a minimum structure and to calculate the vibrational spectra. The excited state and ground state vibrational frequencies

were used to calculate Franck-Condon overlap factors and the resulting emission spectrum of MS. An excited state barrier between $^1\text{ketoB}_1$ and $^1\text{enol}_1$ was calculated for the first time. A small energy barrier was determined for the forward ($^1\text{ketoB}_1 \rightarrow ^1\text{enol}_1$) excited state intramolecular proton transfer (ESIPT) but a much larger energy barrier was determined for the reverse ESIPT ($^1\text{enol}_1 \rightarrow ^1\text{ketoB}_1$). Using Boltzmann statistics, it was determined that this energy barrier is critical to the temperature-dependent dual fluorescence of MS. After photo-emission occurs from the enol form, there is a rapid, barrier-less, back proton transfer that repopulates the $^1\text{ketoB}_0$ state.

Dipicolinic acid (DPA) was investigated thoroughly using hybrid DFT methods. Six gas phase isomers (DPA1, DPA2, DPA3, DPA4, DPA5, and DPA6) were determined to be stable configurations. Vibrational analysis confirmed these structures as stable minima. The DPA1 structure was found to be the lowest in energy but DPA2 and DPA3 were found to be nearly degenerate in energy with DPA1. Dimer configurations of five of these isomers were then calculated. The 2DPA1 structure was determined to be lowest in energy with 2DPA3 only 0.038 eV above 2DPA1. Energies of formation were also calculated for the dimers. All of the dimers were calculated to have almost no dipole moments. Three of the isomers lend themselves to be formed into periodic structures: DPA4, DPA5, and DPA6. Linear chains and two-dimensional sheets of these structures were optimized using periodic boundary conditions. Cell lengths and repeating structures were optimized. Finally, three-dimensional, periodic crystalline structures were formed by stacking the 2-D planes and using a unit cell length from experiment. Energies and band structures for the three different crystals were calculated. From these results, it was determined that DPA4 is the likely monomer structure in crystalline DPA while occasional intermolecular proton transfers causes DPA5 and DPA6 to form within the crystal sporadically.

From the computational perspective, it was demonstrated that DFT can accurately predict ground state structures, energies, and infrared spectra of organic molecules. Excited state energies and photoluminescence spectra can also be accurately modeled using TDDFT and a novel Franck-Condon vibrational overlap calculation presented in Chapter 4. In

order to account for temperature dependencies in the spectra, it has also been shown that the excited state potential energy pathway separating isomers of a molecule suspected of undergoing an ESIPT should be studied in detail so that Boltzmann statistics can be applied. Chemical reactivity of organic molecules can be modeled using electron density calculations. Band structures of organic crystals can also be predicted using DFT and periodic boundary conditions. The DFT and TDDFT calculations would not have been possible without the computational resources provided by the ERDC HPC. In particular, the large basis set excited state vibrational frequency calculations took several weeks to complete even with the state-of-the-art computer resources at the ERDC HPC. In summary, it has been shown that the electronic structure and key physical characteristics of two important photoluminescent organic molecules can be modeled accurately and confidently using DFT and TDDFT calculations.

The studies presented in this dissertation required extensive calculations using high performance and supercomputing resources. The research, software development, and computer tools resulted in three publications which are attached in Appendix C.

Appendix A: Script for job submission to ERDC HPC

```
#!/bin/csh
### Declare a project
#PBS -A ERDCA23616P33
### Declare a jobname
#PBS -N kA1
### Request n processors
#PBS -l ncpus=0
### Limit request to x:00:00 hours of wallclock time
#PBS -l walltime=168:00:00
### Submit job to standard queue
#PBS -q standard
### Send standard output (stdout) and error (stderr) to the same file
#PBS -j oe

cd $ PBS_O_WORKDIR

setenv g09root /usr/local/applic/gaussian/g09.B01
setenv GAUSS_SCRDIR $ PBS_O_WORKDIR
source $ g09root/g09/bsd/g09.login

g09 kA1freq.com
```

Appendix B: Pseudo-code for calculating Franck-Condon factors

Declare constants: temperature, line broadening factor, maximum vibrational levels to consider for ground and excited states.

Read in ground state energies, frequencies, and normal mode eigenvectors.

Read in excited state energies, transition dipole moments, frequencies, and normal mode eigenvectors.

If necessary, transform ground state coordinate system to match excited state coordinate system.

Check orthogonality of normal modes.

Loop over ketoB ground state modes

 Loop over ketoB excited state modes

 Loop over ketoB excited state vibrational levels

 Calculate ketoB g-factors for harmonic oscillation.

 Loop over ketoB ground state vibrational levels

 Calculate ketoB coordinate overlap (dQ)

 Calculate ketoB Franck-Condon overlap integral (FCI)

 Calculate ketoB transition wavelength

 Broaden ketoB transition line and add to spectrum sum

 End

 End

End

End


```

Loop over enol ground state modes
  Loop over enol excited state modes
    Loop over enol excited state vibrational levels
      Calculate enol g-factors for harmonic oscillation.
      Loop over enol ground state vibrational levels
        Calculate enol coordinate overlap (dQ)
        Calculate enol Franck-Condon overlap integral (FCI)
        Calculate enol transition wavelength
        Broaden enol transition line and add to spectrum sum
      End
    End
  End
End
Spline-fit excited state potential energy surface.
Determine forward and reverse ESIPT energy barriers.
Apply ESIPT factors to ketoB and enol spectra.
Sum and normalize.

```

Appendix C: List of publications

Energetics and Vibrational Analysis of Methyl Salicylate Isomers

Richard D. Massaro, Yafei Dai, and Estela Blaisten-Barojas*

Computational Materials Science Center and Department of Computational and Data Sciences, George Mason University, Fairfax, Virginia 22030

Received: June 23, 2009; Revised Manuscript Received: August 11, 2009

Energetics and vibrational analysis study of six isomers of methyl salicylate in their singlet ground state and first excited triplet state is put forward in this work at the density functional theory level and large basis sets. The ketoB isomer is the lowest energy isomer, followed by its rotamer ketoA. For both ketoB and ketoA their enolized tautomers are found to be stable as well as their open forms that lack the internal hydrogen bond. The calculated vibrational spectra are in excellent agreement with IR experiments of methyl salicylate in the vapor phase. It is demonstrated that solvent effects have a weak influence on the stability of these isomers. The ionization reaction from ketoB to ketoA shows a high barrier of 0.67 eV ensuring that thermal and chemical equilibria yield systems containing mostly the ketoB isomer at normal conditions.

Introduction

Methyl salicylate (MS), $C_8H_8O_3$, is a semivolatile compound well-known for its signaling properties in nature.^{1,2} MS is released into the atmosphere by certain plants when under stress or when being attacked and is used as an additive to enhance aroma in many commercial products. MS is also used in small amounts in foods to add a wintergreen taste, which gives rise to its alternative name of oil of wintergreen. MS is photoluminescent and is considered to be a surrogate to study certain biological and chemical threats.³

More recently, MS is being used in Forster's resonance energy transfer (FRET) systems and as the fluorescence component in optical bar code systems.^{3,4} MS has an interesting dual fluorescence with peaks at 340 and 450 nm. Weller first proposed that the dual fluorescence is due to an excited state intermolecular proton transfer (ESIPT).⁵ On the basis of gas phase, solution, and supersonic jets, several authors have since proposed that two different rotamers ketoA and ketoB of methyl salicylate exist in equilibrium^{6–9} and that MS has open forms of the ketoA and ketoB rotamers.^{10,11} Both ketoA and ketoB structures contain an internal hydrogen bond, which is absent in the open forms. The most recent theories suggest that the short wavelength fluorescence of MS is due to the ketoA form while the long wavelength fluorescence is due to the ketoB form undergoing an ESIPT to the enol form.^{12–17}

Despite the experimental interest on MS, theoretical calculations are very scarce. A recent density functional calculation demonstrates that both ketoA and ketoB are indeed stable isomers of MS.¹⁸ Measurements of the IR spectra and a Hartree–Fock frequency calculation for ketoA were reported in ref 19. The work in this paper focuses on computing the structure, energetics, and vibrational analysis of six stable isomers, ketoA, ketoB, ketoA_{open}, ketoB_{open}, enol, and “enolized” ketoA (ekA), in their singlet and triplet states. Results from these calculations are important for supporting empirical predictions on the phase equilibria between isomers. This paper is organized as follows. The second section on energetics describes the methodology used and presents the results of the geometry optimization, energy calculations, and other physical properties

of the six isomers in their lowest singlet and triplet states. The following section provides the vibrational analysis of the six isomers, including a comparison with experimental IR spectra when available. The next section gives a discussion of the isomerization reaction from ketoB to ketoA, the transition state structure and potential energy along the reaction coordinate. This work is concluded in the last section.

Energetics of Methyl Salicylate

All-electron density functional theory (DFT) and the hybrid Becke–Perdew–Wang 1991 (B3PW91) approach were used throughout this study, which includes local and nonlocal correlation functionals.^{20–22} Calculations of the MS isomers were obtained using the Gaussian 03 package²³ and a triple- ζ basis set with s, p, d polarization functions and extra diffuse d-functions (6-311++G).^{24,25} A multitude of molecular structures from an unrestricted Monte Carlo and small basis sets simulation were used as initial conditions for the structural optimization. These molecular structures were subsequently minimized using the Berny optimization algorithm with redundant internal coordinates.²⁶ The vibrational frequencies were calculated to ensure for the presence of a minimum. The convention in this paper for designating a singlet or triplet state will be a superscript (1 or 3) preceding the isomer name.

The geometries of ketoA, ketoB, ketoA_{open}, ketoB_{open}, enol, and ekA isomers of MS were identified as stable in both the singlet and triplet states. Although there has been experimental hints on the existence of the first five isomers, the ekA form has not been predicted experimentally yet. The ground state of all isomers are singlet states. The optimized singlet geometries of the six different isomers are shown in Figure 1. Table 1 provides the detailed geometric parameters of ketoB in its singlet state, which is the most stable isomer. Geometries of all other isomers are provided as Supporting Information to this paper. The molecular symmetry of all isomers is low since they belong to the C_1 point group in either their singlet or triplet states. The singlet states of all isomers have planar geometries (excluding the hydrogens in the CH_3 group), whereas the triplet states are nonplanar geometries. Both the ³ketoA_{open} and ³ketoB_{open} forms are notably nonplanar, with the carbonyl group bending above the benzene ring plane and the phenol oxygen bending below

* Corresponding author. E-mail: blaisten@gmu.edu.

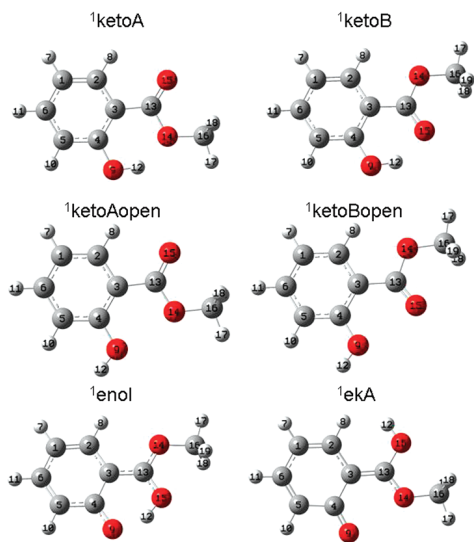


Figure 1. Geometries of the six MS isomers.

TABLE 1: Geometry of ¹ketoB Ground State

bond	distance (Å)	bond	angle (deg)	dihedral bond	angle (deg)
C ₁ –C ₂	1.385	(2,1,6)	119.5	(6,1,2,3)	0.0
C ₁ –C ₆	1.404	(2,1,7)	120.2	(6,1,2,8)	–180.0
C ₁ –H ₇	1.082	(6,1,7)	120.3	(7,1,2,3)	180.0
C ₂ –C ₃	1.408	(1,2,3)	120.8	(7,1,2,8)	0.0
C ₂ –H ₈	1.081	(1,2,8)	120.9	(2,1,6,5)	0.0
C ₃ –C ₄	1.416	(3,2,8)	118.4	(2,1,6,11)	180.0
C ₃ –C ₁₃	1.456	(2,3,4)	119.1	(7,1,6,5)	–180.0
C ₄ –C ₅	1.399	(2,3,13)	121.8	(7,1,6,11)	0.0
C ₄ –O ₉	1.366	(4,3,13)	119.0	(1,2,3,4)	0.0
C ₅ –C ₆	1.386	(3,4,5)	119.8	(1,2,3,13)	–180.0
C ₅ –H ₁₀	1.081	(3,4,9)	122.8	(8,2,3,4)	180.0
C ₆ –H ₁₁	1.083	(5,4,9)	117.5	(8,2,3,13)	0.0
O ₉ –H ₁₂	0.991	(4,5,6)	120.0	(2,3,4,5)	0.0
C ₁₃ –O ₁₄	1.359	(4,5,10)	118.1	(2,3,4,9)	180.0
C ₁₃ –O ₁₅	1.254	(6,5,10)	121.9	(13,3,4,5)	180.0
O ₁₄ –C ₁₆	1.463	(1,6,5)	120.8	(13,3,4,9)	0.0
C ₁₆ –H ₁₇	1.085	(1,6,11)	119.8	(2,3,13,14)	0.0
C ₁₆ –H ₁₈	1.089	(5,6,11)	119.4	(2,3,13,15)	–180.0
C ₁₆ –H ₁₉	1.089	(4,9,12)	110.0	(4,3,13,14)	–180.0
		(3,13,14)	114.8	(4,3,13,15)	0.0
		(3,13,15)	124.0	(3,4,5,6)	0.0
		(14,13,15)	121.2	(3,4,5,10)	–180.0
		(13,14,16)	117.1	(9,4,5,6)	–180.0
		(14,16,17)	104.6	(9,4,5,10)	0.0
		(14,16,18)	110.1	(3,4,9,12)	0.0
		(14,16,19)	110.1	(5,4,9,12)	180.0
		(17,16,18)	111.1	(4,5,6,1)	0.0
		(17,16,19)	111.1	(4,5,6,11)	–180.0
		(18,16,19)	109.6	(10,5,6,1)	180.0
				(10,5,6,11)	0.0
				(3,13,14,16)	180.0
				(15,13,14,16)	0.0
				(13,14,16,17)	–180.0
				(13,14,16,18)	60.5
				(13,14,16,19)	–60.5

the ring plane. The ³enol structure is nonplanar with the hydrogen from the OH radical attached to the phenol oxygen and popping above the ring plane. The ³ekA form has the COOCH₃ group rotated quite noticeably out of the ring plane with the H₁₂ atom sticking out at an angle almost normal to the ring plane.

The total energies of the different isomers in their lowest singlet and triplet states are compiled in Table 2. The ¹ketoB geometry was determined to have the lowest total energy of

–14.562 keV. This finding is in agreement with a previous DFT calculation with smaller basis set.¹⁸ Therefore, the ¹ketoB isomer is the global minimum structure and all energies reported in Table 2 are relative to the energy of this isomer. The ¹ketoA isomer is the next lowest energy at 0.082 eV above the ¹ketoB. This result was checked against an all-electron ab initio MP2 (same basis set) calculation that yields 0.128 eV as the difference in energy between the two optimized rotamer structures. In supersonic jet experiments at various temperatures an estimate of 0.11 eV was reported for the energy difference between ¹ketoB and ¹ketoA rotamers.⁷ Although our DFT result is about 25% lower than the experiment and the MP2 result 16% higher than experiment, we believe that thermal excitation of the vibrations in these two rotamers during the experiment accounts for such discrepancy. The ¹ketoA rotamer is theorized to coexist in equilibrium with ¹ketoB.^{6,8,7} However, an energy barrier between these two isomers may not allow chemical equilibrium to occur at room or medium-to-high temperatures, as discussed in a later section. Both open-form isomers have considerably higher energy structures about 0.57 eV above ¹ketoB. The geometry of the ¹enol is similar to the ¹ketoB due to the proton transfer from the carbonyl to the phenol groups and this isomer is 0.764 eV above the ¹ketoB. Previous DFT studies using smaller basis sets were unable to find the singlet enol optimized structure.¹⁸ The ekA is new to the literature and is the highest energy of all six isomers.

First excited triplet states of the six isomers are reported in Table 2. These triplet states may or may not be the lowest excited state for each isomer. Although the DFT approach used in this paper ensures that the reported triplet states are indeed the lowest of all triplets, the approach is inadequate for calculation of other excited states. It is interesting to note that in the lowest triplet states, the energy ordering of the six isomers is altered when compared to the ordering in the ground state. The ³enol isomer is the lowest, followed by the ³ketoB and ³ketoA. Table 2 provides values of the zero point energy ϵ_0 for both singlets and triplets of the six MS isomers showing that this quantity does not change much across the different isomers.

In addition, calculated dipole and quadrupole moments of the MS isomers are reported in Table 2, showing that the ¹ketoA is the least polar of all isomers. Our results of the ¹ketoB and ¹ketoA dipole moments are in agreement with the 3.1 and 0.8 D ab initio values obtained at the MP2 level. The hydrogen bond lengths in ketoB, ketoA, and enol are 1.75, 1.73, and 1.51 Å, respectively. These bond lengths compare well with the MP2 values of 1.75 Å (ketoB) and 1.78 Å (ketoA). Rotational constants for the six isomers are similar. For the singlet states these constants in GHz are 2.14358, 0.82490, 0.59792 (2.15870, 0.83002, 0.60179 with MP2) for ketoB, and 2.24913, 0.82585, 0.60637 (2.24933, 0.82818, 0.607639 with MP2) for ketoA. For the other isomers rotational constants in GHz are 2.09378, 0.82141, 0.59216 (ketoB_{open}), 2.22137, 0.81777, 0.59998 (ketoA_{open}), 2.21092, 0.82402, 0.60258 (enol), and 2.23019, 0.81010, 0.59755 (ekA). Rotational constants for the most stable isomer ketoB are in agreement with experimental measurements.¹⁸

In the liquid phase, solvent effects may induce structural shifts in the solute molecular constituents. Therefore, properties such as the binding energy, dipole moments, and quadrupole moments will change. We considered a mixture of ketoB and ketoA in the liquid phase and used the polarized continuum model (PCM)²⁸ to calculate molecular properties of the solute. Considering one ¹ketoB molecule in an MS solvent with relative dielectric constant, $\epsilon = 9.0$ (ketoB value²⁹), the solvent

TABLE 2: Total Electronic Energy, Zero Point Energy (ϵ_0), Dipole and Quadrupole of the MS Isomers^a

isomer	state	singlet				triplet				
		E (eV)	ϵ_0 (eV)	dipole (D)	quadrupole (D/Å)	state	E (eV)	ϵ_0 (eV)	dipole (D)	quadrupole (D/Å)
ketoB	¹ A	0	4.027	3.1	49, 68, 67, 1, 0, 0	³ A	3.117	3.887	1.4	50, 70, 67, -9, 0, 0
ketoA	¹ A	0.082	4.026	0.8	47, 71, 67, 7, 0, 0	³ A	3.240	3.904	3.0	52, 66, 67, -0, 0, 0
ketoA _{open}	¹ A	0.566	4.001	3.4	50, 61, 67, 1, 0, 0	³ A	3.825	3.879	4.2	53, 59, 67, -3, -1, 2
ketoB _{open}	¹ A	0.573	4.004	2.9	48, 62, 67, 10, 0, 0	³ A	3.829	3.879	3.3	50, 60, 68, 9, 1, 2
enol	¹ A	0.765	3.997	4.3	46, 71, 67, 0, 0, 0	³ A	2.861	3.917	2.7	50, 67, 67, -0, 0, 0
ekA	¹ A	1.926	3.983	5.7	47, 67, 67, -0, -1, -0	³ A	3.536	3.896	3.6	50, 66, 66, -2, -3, -4

^a Total energies E are relative to the ¹ketoB ground state energy of -14.561723 keV.

destabilizes ¹ketoB by 0.085 eV, zero-point energy decreases 0.005–4.022 eV, the dipole moment increases to 3.9 D from 3.1 D, and the quadrupole changes very little to 47, 68, 67, 0, 0, 0 D/Å. The total energy for ¹ketoA increased 0.062 eV, the zero-point energy decreased only 0.004 to 4.022 eV, the dipole moment changed from 0.8 to 0.9 D, and the quadrupole also showed little change to 44, 72, 67, -9, 0, 0 D/Å.

Vibrational Analysis

The calculated vibrational spectra of ketoB and ketoA in the singlet electronic states are reported in Table 3 and compared to IR experimental results in the gas phase.^{19,30} Reported frequencies are the calculated frequencies scaled by a factor of 0.977, which gives the smallest error when the most prominent frequencies with IR intensity higher than 50 are compared to experimental data in ref 30. Additionally, this table contains the calculated intensity of the different lines and their summarized assignment. The scaled vibrational spectra for the other four isomers in their singlet electronic states and for all six isomers in the triplet states are reported in Table 4.

In the high frequency range, a modestly intense absorption line in the experiment is seen at about 3200 cm⁻¹.³⁰ This absorption is likely due to the OH stretch in the phenol. From our calculations, both ¹ketoB and ¹ketoA isomers have strong IR intensities due to the contribution of the OH stretching to the normal mode vibrations at 3262 and 3387 cm⁻¹, respectively. The calculated OH stretch for ¹enol is the second most intense feature of its vibrational spectrum and is located at a significantly red-shifted 2978 cm⁻¹. The calculated OH stretching of ¹ketoA_{open} and ¹ketoB_{open} isomers are located at 3615 cm⁻¹ and their IR-active intensity is weak. In the triplet state of ³ketoA the OH stretching appears in two modes at 2979 and 2993 cm⁻¹ while in ³ketoB it appears in only one mode at 2424 cm⁻¹, both cases displaying a dramatic red shift. However, the OH stretching in the ³ketoA_{open} and ³ketoB_{open} is shifted by only a few wavenumbers to 3590 and 3589 cm⁻¹. The ³enol isomer was calculated to have a strong OH stretching at 3004 cm⁻¹. The ¹ekA and ³ekA have OH stretching modes shifted to the blue at 3644 and 3622 cm⁻¹, respectively. The experimental less intense lines at 2850–3100 cm⁻¹ are due to CH stretches and CH₃ symmetric and asymmetric stretches.

One of the two strongest absorption lines in ref 30 is at 1698 cm⁻¹ (Table 3). This intense line is almost always seen in carboxylic acid derivatives.^{31,32} In aromatic esters, the rule of three bands (RTB)³¹ places the C=O stretching line within 1715–1730 cm⁻¹. Our calculation shows a strong C=O stretching vibration at 1647 cm⁻¹ (1686 cm⁻¹ without scaling) for ¹ketoB and at 1655 cm⁻¹ (1694 cm⁻¹ without scaling) for ¹ketoA. The ¹ketoB_{open} C=O stretch is also in the vicinity at 1656 cm⁻¹ and for ¹ketoA_{open}, ¹enol, ¹ekA the calculated line lies considerably lower at 1625, 1638, 1646 cm⁻¹, respectively. The other strong line reported in ref 30 is at 1310 cm⁻¹. Again

from the RTB, the C–C–O stretch of aromatic esters is in the 1250–1310 cm⁻¹ range. The calculated C–C–O stretching mode is located at 1308 cm⁻¹ in ¹ketoB and at 1269 cm⁻¹ in ¹ketoA. In the open forms ¹ketoB_{open}, ¹ketoA_{open} and in ¹enol, ¹ekA this mode appears at 1245, 1316, 1334, and 1357 cm⁻¹, respectively. The third vibration frequency from RTB for aromatic esters is the O–C–C stretch, which typically falls in the 1000–1130 cm⁻¹ range. Experimental work locates this O–C–C stretch absorption line at 1094,^{30,19} which coincides well with our calculations at 1091 cm⁻¹ for ¹ketoB and a rather intense line at 1077 cm⁻¹ for ¹ketoA. The calculated O–C–C stretching mode in ¹ketoB_{open} is very strong at 1067 cm⁻¹, in ¹ketoA_{open} is intense at 1124 cm⁻¹, and appears rather intense in ¹enol at 1100 cm⁻¹ and ¹ekA at 1053 cm⁻¹, respectively. This O–C–C stretch is strong in both ³ketoB at 1076 cm⁻¹ and ³ketoA at 1057 cm⁻¹. All four isomers ³ketoB_{open} and ³ketoA_{open}, ³enol and ³ekA show the O–C–C stretch as their most intense lines at 1086, 1087, 1068, and 1085 cm⁻¹, respectively. All three RTB calculated lines agree very well with the experimental values listed in Table 3.

In ¹ketoB, the umbrella mode is located at 1444 cm⁻¹ and the in-plane OH bend at 1385 cm⁻¹. Two prominent experimental absorption lines³⁰ are located at approximately 754 and 705 cm⁻¹. Since MS has an ortho-substituted benzene ring, then the first line is due to out-of-plane CH motion while the latter is due to aromatic ring bending vibrations. The calculated out-of-plane CH bending vibrations for the different isomers have the following wavenumbers: ¹ketoB at 786 cm⁻¹, ¹ketoA at 790 cm⁻¹, ¹ketoA_{open} at 757 cm⁻¹, ¹ketoB_{open} at 759 cm⁻¹, ¹enol at 770 cm⁻¹, ¹ekA at 746 cm⁻¹, ³ketoA at 808 and 667 cm⁻¹, ³ketoB at 808 and 681 cm⁻¹, ³ketoA_{open} at 774 and 642 cm⁻¹, ³ketoB_{open} at 773 and 640 cm⁻¹, ³enol at 735 cm⁻¹, and ³ekA at 758 cm⁻¹. Except for ³enol and ³ekA, isomers in the triplet states show a CH out-of-plane motions into two different modes because only some of the CH bonds participate in one mode while the rest move in the other mode.

The calculated aromatic ring bending vibrations appear at the following wavenumbers: ¹ketoA at 662 cm⁻¹, ¹ketoB at 680 cm⁻¹, ¹ketoA_{open} at 673 cm⁻¹, ¹ketoB_{open} at 667 cm⁻¹, ¹enol at 674 cm⁻¹, ¹ekA at 655 cm⁻¹, ³ketoA at 600 cm⁻¹, ³ketoB at 594 cm⁻¹, ³ketoA_{open} at 609 cm⁻¹, ³ketoB_{open} at 613 cm⁻¹, ³enol at 617 cm⁻¹, and ³ekA at 683 cm⁻¹.

ketoB to ketoA Isomerization Reaction

With the calculated normal-mode frequencies, a harmonic analysis of several thermodynamic functions is feasible within the canonical ensemble.³³ For example, the free-energy, internal energy, and vibrational specific heat were calculated for all six isomers as a function of temperature. By inspecting the temperature dependence of the Helmholtz free energy of each MS isomer in their singlet and triplet states, we estimate that these structures will not undergo thermal isomerization up to

TABLE 3: Calculated Vibrational Spectra of ¹ketoB and ¹ketoA Isomers and Comparison with Experiments in Ref 30 and Table 2 of Ref 19^a

¹ ketoB			¹ ketoA		experiment			
ν (cm ⁻¹)	intensity	assignment	ν (cm ⁻¹)	intensity	ref 30 (cm ⁻¹)	ref 19 (cm ⁻¹)	ref 19 (cm ⁻¹)	ref 19 (cm ⁻¹)
3262	244	ν O–H	3387	305	3262	3188		
3151	8	ν_s ring C–H	3147	10				
3145	7	ν_a ring C–H	3140	11				
3126	14	ν_a ring C–H	3125	8				
3115	11	ν_a CH ₃	3114	9		3010		
3108	6	ν_a ring C–H	3109	6	3078	2954	3081	2977
3080	17	ν_a CH ₃	3086	14		2920	2964	2931
2988	32	ν_s CH ₃	2992	31	2966	2850	2854	2874
1647	200	ν C=O, ν ring C–C, ρ Ph H	1655	234	1698	1682	1683	1647
1593	136	ν C=O, ν ring C–C	1633	248	1618	1616	1620	
1579	30	ν C=O, ρ Ph H	1587	32		1586	1590	1562
1490	70	ρ ring C–H	1494	17	1482			1509
1487	28	σ CH ₃	1488	6				
1473	14	τ CH ₃	1484	122				
1463	10	ρ ring H	1472	15				
1444	78	ω CH ₃	1442	14	1450	1488	1472	1449
1385	135	ρ Ph H	1386	17	1410	1442	1437	
1357	40	ν ring C–C	1343	23				1350
1308	273	ν C–CH ₃ O, ρ ring H	1269	320	1310	1339	1337	1277
1253	50	ν C–Ph O, ρ ring H	1247	32	1254	1307		
1222	291	ρ Ph H	1214	90	1214	1255	1255	
1179	38	σ ring H	1178	10		1218	1203	
1174	79	τ CH ₃	1168	38	1166	1159	1162	
1139	27	σ ring H	1137	1		1137	1143	
1136	1	τ CH ₃	1116	64				
1091	81	ν O CH ₃	1077	162	1094	1092	1068	
1034	15	ω ring CH	1035	59		1034	1039	
992	0	ω ring CH	997	1				
981	2	ω ring CH	985	2				
941	8	ν O CH ₃	934	14		965	965	
874	0	ω ring CH	876	0				
835	20	ring breath, ν C–Ph O	844	2	854	850	858	874
786	28	ω ring CH	790	30	754	802	814	
784	1	σ C(=O)–O	765	20				
748	8	ω C–C/C–H/O–H	751	35		760		
728	208	ω OH	693	104	706	702		735
680	2	ω ring	662	80				
671	12	ring breath	661	6		667	671	
563	4	ring breath	556	8			566	
529	7	ω ring	531	5	530	563	517	523
507	12	ρ O ₉ H ₁₂ –O ₁₅	528	4		511		
437	0	ω out-of-plane	441	0				
431	5	ρ in-plane	387	8			442	432
342	19	ρ O ₉ H ₁₂ –O ₁₅	351	3			346	345
323	8	ρ in-plane	312	12				
259	2	ω full molecule	256	1			267	219
174	3	ω full molecule	183	2			190	
166	2	ρ CH ₃	176	2				
128	2	τ CH ₃	108	0				
86	1	τ CH ₃	85	0				
74	0	τ CH ₃	62	6				

^a Symbols: ν , stretching; ω , wagging; ρ , rocking; τ , twisting; σ , scissoring; Ph, phenyl; s symmetric; a, asymmetric. Calculated frequencies are scaled by a 0.977 factor.

temperatures of about 2000 K. More so, at temperatures above 2000 K, the ¹ketoA isomer becomes more stable than ¹ketoB and a crossing of the free energy curves occurs.³⁴ At even higher temperatures the ¹ketoA_{open} is the most stable isomer. The harmonic approximation of the thermodynamic functions is very accurate at lower energies. However, we believe that as a first estimate, the high temperature results provide a qualitative description of a given process. Therefore, our findings are indicative that at $T = 300$ K thermal fluctuations would not be responsible for an isomer structural transition. On the basis of this fact, extra energy of about 0.3 eV is needed to isomerize ketoB into ketoA, and chemical equilibrium would strongly

favor a high relative concentration of about 100% ketoB versus ketoA. This result is consistent with previously proposed chemical equilibrium in which MS vapor at room temperature is mainly ketoB and only 1/70 of its concentration is ketoA.⁷

On the basis of the harmonic estimate of the isomer transition, we additionally investigated the isomerization reaction of ketoB $\rightarrow$ ketoA at the DFT level of calculation. A transition state was found at 0.67 eV above the ketoB energy, which has the lowest positive and one negative frequencies at +85 and -125 cm⁻¹. The transition state geometry was discovered with the synchronous transit-guided quasi-Newton method^{26,27} letting relax all bond lengths and angles. This structure has the COOCH₃ group

TABLE 4: Vibrational Frequencies of ¹ketoB_{open}, ¹ketoA_{open}, ¹enol, and ¹ekA and of All Six Isomers in Their Triplet Electronic States^a

¹ ketoA _{open} (cm ⁻¹)	¹ ketoB _{open} (cm ⁻¹)	¹ enol (cm ⁻¹)	¹ ekA (cm ⁻¹)	³ ketoB (cm ⁻¹)	³ ketoA (cm ⁻¹)	³ ketoA _{open} (cm ⁻¹)	³ ketoB _{open} (cm ⁻¹)	³ enol (cm ⁻¹)	³ ekA (cm ⁻¹)
3615	3615	3142	3644	3158	3157	3590	3589	3149	3622
3145	3163	3136	3135	3151	3145	3147	3154	3143	3140
3129	3131	3123	3125	3132	3131	3141	3145	3127	3125
3113	3113	3119	3122	3106	3107	3108	3107	3106	3115
3110	3105	3098	3094	3103	3101	3102	3098	3106	3108
3087	3089	3090	3085	3064	3075	3079	3080	3070	3101
3070	3068	2995	3046	2978	2993	3059	3058	3004	3068
2982	2981	2978	2991	2424	2979	2975	2974	2981	2973
1625	1656	1638	1646	1592	1550	1556	1550	1570	1536
1621	1619	1571	1595	1542	1536	1507	1518	1504	1527
1590	1600	1543	1540	1508	1506	1489	1492	1491	1490
1511	1512	1524	1508	1489	1493	1472	1471	1489	1482
1486	1490	1485	1482	1470	1472	1470	1465	1473	1478
1471	1472	1474	1477	1455	1471	1445	1447	1459	1448
1460	1455	1464	1466	1441	1437	1431	1431	1445	1410
1439	1441	1446	1448	1425	1427	1390	1394	1420	1381
1359	1357	1386	1396	1376	1407	1381	1381	1385	1350
1316	1313	1357	1357	1337	1332	1312	1293	1370	1270
1293	1269	1334	1281	1288	1291	1276	1282	1266	1250
1243	1245	1254	1239	1265	1272	1207	1209	1243	1213
1185	1185	1202	1184	1198	1173	1167	1168	1213	1171
1181	1174	1173	1173	1169	1161	1156	1161	1166	1170
1169	1168	1163	1152	1149	1149	1132	1135	1146	1126
1133	1137	1142	1126	1131	1137	1101	1104	1129	1096
1124	1121	1132	1114	1121	1109	1087	1086	1081	1085
1086	1067	1100	1053	1076	1057	1063	1061	1068	1036
1048	1050	1008	1005	1012	967	973	963	1002	1014
1010	999	998	1000	956	942	923	932	953	960
974	971	981	948	949	910	909	912	931	924
938	944	924	910	937	898	842	852	890	914
860	861	855	848	892	849	814	790	829	855
844	828	838	842	808	819	774	773	819	833
795	799	770	761	804	808	736	736	811	758
777	774	746	746	741	714	684	683	735	694
757	759	738	711	681	667	642	640	715	683
673	667	723	655	594	600	609	613	617	603
662	667	674	617	587	598	560	554	605	557
558	564	629	547	549	528	527	515	545	529
536	537	554	538	511	519	470	480	535	505
527	499	544	512	505	516	450	443	483	459
453	448	521	461	423	393	391	401	447	383
372	391	451	401	408	371	381	390	408	350
338	353	417	387	355	358	334	335	345	323
295	329	370	341	321	352	312	307	328	313
292	292	316	301	314	298	270	262	319	267
247	256	243	224	222	221	180	183	226	200
168	170	174	161	151	182	152	147	164	181
156	164	158	139	141	119	128	139	148	124
110	111	119	112	101	100	111	107	119	102
94	94	86	65	85	77	78	66	98	64
26	24	81	60	75	57	49	58	59	41

^a Reported frequencies are scaled by a 0.977 factor.

rotated $\pm 90^\circ$ with respect to the ring plane and away from its position in the ketoB structure. For comparison, the transition state geometry was recalculated at the MP2 level and the energy difference with respect to the MP2 optimized structure of ketoB yields 0.71 eV. Adding the solvent effect with PCM reduces the transition barrier to 0.5 eV. Next, the transition state geometry and the computed force constants were used as input for calculating the MS energy along the intrinsic reaction coordinate path (IRC)³⁵ shown in Figure 3. The IRC path was followed by relaxing the mass-weighted internal coordinates of atoms 14, 13, 3, 2 (Figure 1) that participate in the pertinent dihedral angle, which changes from 0° (ketoB) to 180° (ketoA) along the reaction.

Conclusion

The full energetics and vibrational analysis study of six isomers of MS is presented in this paper. We predict that at the BPW91/6-311++G level of calculation all six isomers in their ground state are singlets and report structures and energies of both the ground state and first excited triplet state. The ketoB isomer is the global minimum followed in energy by its rotamer ketoA. Our calculation for ketoB and ketoA confirms an earlier DFT study with smaller basis sets.¹⁸ The structure and energy of the open forms of the ketoB and ketoA isomers, the tautomer with ring-inserted carbonyl radical (enol), and the enolized ketoA are new to the literature. We also provide the full

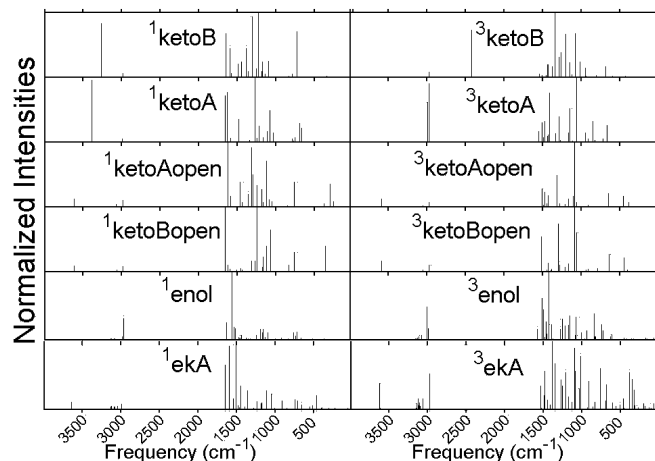


Figure 2. IR active spectra of the six MS isomers in the ground state and first excited triplet state.

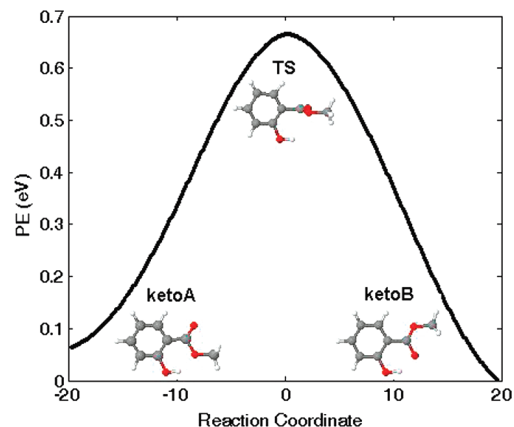


Figure 3. IRC isomerization reaction path following the O14–C13–C3–C2 dihedral angle changes.

calculated vibrational spectra of these six isomers in their ground state and first triplet state. The calculated vibrational lines of ¹ketoB correspond quite well to the peaks of the experimental spectrum.^{30,19} Specifically, the calculated lines corresponding to the OH and CH stretching vibrations in the 3000–3500 cm^{−1} region correlate well with the experiments. The match of C=O stretching vibrations near 1700 cm^{−1} is less well-defined. However, the C–C–O and O–C–C calculated stretching vibrations lie close to the experimental bands. One intense line calculated at approximately 727 cm^{−1} is due to the aromatic ring bending vibration and might be correlated to either of the observed lines at 754 or at 705 cm^{−1}.

The isomerization reaction between the rotamers ketoB and ketoA was followed in detail, showing the existence of an energy barrier of 0.67 eV. Estimates of the liquid phase of MS by assuming each molecule in a solvent of all the others depletes the isomerization barrier by 0.17 eV. The high value of this barrier to the internal rotation of the –COOCH₃ group is indicative that at room temperature the isomerization reaction is unlikely to occur. However, since the reverse isomerization energy (ketoA to ketoB) barrier of 0.59 eV is almost as high, then it is likely that any ketoA species that are present in a sample will remain ketoA at room temperature.

Acknowledgment. We acknowledge the National Science Foundation grant CHE-0626111 for partial support and the TERAGRID grant PHY050026T for the computer time allocation.

Supporting Information Available: Table of atomic parameters for the geometry of six isomers. This material is available free of charge via the Internet at <http://pubs.acs.org>.

References and Notes

- (1) Canosa-Mas, C. E.; Duffy, J. M.; King, M. D.; Thompson, K. C.; Wayne, R. P. *Atmos. Environ.* **2002**, *36*, 2201–2205.
- (2) Shulaev, V.; Silverman, P.; Raskin, I. *Nature* **1997**, *385*, 718–721.
- (3) Smith, C.; Anderson, J.; Tatineni, B.; Tepper, G. Optical Barcode recognition of methyl salicylate (MES) for environmental monitoring using fluorescence resonance energy transfer (FRET) on thin films. *Proc. SPIE—Int. Soc. Opt. Eng.* **2006**, *6378*, 637811–1–5.
- (4) Smith, C.; Anderson, J. E.; Massaro, R. D.; Tatineni, B.; Kam, K. C.; Tepper, G. C. *Appl. Spectrosc.* **2008**, *62*, 604–610.
- (5) Weller, A. Z. *Elektrochem.* **1956**, *60*, 1144–1147.
- (6) Law, K.; Shoham, J. *J. Phys. Chem.* **1994**, *98*, 3114–3120.
- (7) Helmbrook, L.; Kenny, J. E.; Kohler, B. E.; Scott, G. W. *J. Phys. Chem.* **1983**, *87*, 280–289.
- (8) Acuña, A. U.; Catalan, J.; Toriblo, F. *J. Phys. Chem.* **1981**, *85*, 241–245.
- (9) Lopez-Delgado, R.; Sylvain, L. *J. Phys. Chem.* **1981**, *85*, 763–768.
- (10) Acuña, A. U.; et al. *J. Phys. Chem.* **1980**, *84*, 629–631.
- (11) Klöpffer, W.; Kaufmann, G. *J. Lumin.* **1979**, *20*, 283–289.
- (12) Sanchez-Cabezudo, M.; De Paz, J. L. G.; Catalan, J.; Amat-Guerri, F. *J. Mol. Struct.* **1985**, *131*, 277–289.
- (13) Orton, E.; Morgan, M. A.; Pimentel, G. C. *J. Phys. Chem.* **1990**, *94*, 7936–7943.
- (14) Catalan, J.; Diaz, C. *J. Phys. Chem. A* **1998**, *102*, 323–328.
- (15) Catalan, J.; Palomar, J.; de Paz, J. L. G. *J. Phys. Chem.* **1997**, *101*, 7914–7921.
- (16) Herek, J. L.; Pedersen, S.; Bañares, L.; Zewail, A. H. *J. Chem. Phys.* **1992**, *97*, 9046–9061.
- (17) Felker, P. M.; Lambert, W. R.; Zewail, A. H. *J. Chem. Phys.* **1982**, *77*, 1603–1605.
- (18) Melandri, S.; et al. *J. Phys. Chem. A* **2007**, *111*, 9076–9079.
- (19) Varghese, H. T.; et al. *Spectrochim. Acta A* **2007**, *66*, 959–963.
- (20) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648–5652.
- (21) Perdew, J. P.; Chevary, J. A.; Vosko, S. H. *Phys. Rev. B* **1992**, *46*, 6671–6687.
- (22) Perdew, J. P.; Burke, K.; Wang, Y. *Phys. Rev. B* **1996**, *54*, 16533–16539.
- (23) Frisch, M. J.; et al. *Gaussian 03*, revisions B.04 and E.01; Gaussian Inc.: Wallingford, CT, 2004.
- (24) Ditchfield, R.; Hehre, W. J.; Pople, J. A. *J. Chem. Phys.* **1971**, *54*, 724–728.
- (25) Krishnan, R.; Binkley, J. S.; Seeger, R.; Pople, J. A. *J. Chem. Phys.* **1980**, *72*, 650–654.
- (26) Peng, C.; Ayala, P. Y.; Schlegel, H. B.; Frisch, M. J. *J. Comput. Chem.* **1996**, *17*, 49–56.
- (27) Peng, C.; Schlegel, H. B. *Isr. J. Chem.* **1994**, *33*, 449–455.
- (28) Tomasi, J.; Cancès, E. *J. Mol. Struct. (THEOCHEM)* **1999**, *464*, 211–226.
- (29) *Lange's Handbook of Chemistry*, 14th ed.; Dean, J. A., Ed.; McGraw-Hill: New York, 1992; p 5.
- (30) *NIST Chemistry WebBook*; Linstrom P. J., Mallard, W. G., Eds.; NIST Standard Reference Database 69; National Institute of Standards and Technology: Gaithersburg MD; <http://webbook.nist.gov>.
- (31) Smith, B. C. *Infrared Spectral Interpretation: A Systematic Approach*; CRC: Boca Raton, FL, 1999.
- (32) Roeges, N. P. G. *A Guide to the Complete Interpretation of Infrared Spectra of Organic Structures*; Wiley: New York, 1994.
- (33) Mirick, J.; Chien, C. H.; Blaisten-Barojas, E. *Phys. Rev. A* **2001**, *63*, 023202.
- (34) Wang, G. M.; Blaisten-Barojas, E.; Roitberg, A. E.; Martin, T. P. *J. Chem. Phys.* **2001**, *115*, 3640–3646.
- (35) Gonzalez, C.; Schlegel, H. B. *J. Phys. Chem.* **1990**, *94*, 5523–5527.

JP905887M

Theoretical Investigation of the Photophysics of Methyl Salicylate Isomers

Richard D. Massaro and Estela Blaisten-Barojas*

*Computational Materials Science Center and
School of Physics, Astronomy, & Computational Sciences, George Mason University, Fairfax, Virginia 22030*

Abstract

The photophysics of methyl salicylate isomers has been studied using time-dependent density functional theory and large basis sets. First singlet and triplet excited states energies, structure, and vibrational analysis were calculated for the ketoB, enol, and ketoA isomers. It is demonstrated that the photochemical pathway involving excited state intermolecular proton transfer (ESIPT) from the ketoB to the enol tautomer agrees well with the dual fluorescence at 330 nm (from ketoB) and 440 nm (from enol) obtained from experiments. Our calculation confirms the existence of a double minimum in the excited state pathway along the O-H-O coordinate corresponding to two preferred energy regions: (1) the hydrogen belongs to the OH moiety and the structure of methyl salicylate is ketoB, (2) the hydrogen flips to the closest carboxyl entailing electronic rearrangement and tautomerization to the enol structure. This double well in the excited state is highly asymmetric. It is also demonstrated that the rotamer ketoA is not stable in an excited state close to the desired emission wavelength. This observation eliminates the conjecture that fluorescence at 330 nm originates from the ketoA rotamer. The Frank Condon vibrational overlap is calculated and accounts for the broadening of the two bands. It is suggested that forward and backward ESIPT through the barrier separating the two minima is temperature-dependent and affects the intensity of the fluorescence as seen in experiments. When the enol fluoresces and returns to its ground state, a barrier-less back proton transfer repopulates the ground state of methyl salicylate ketoB. New experimental results for pure MS in the liquid state are reported and theoretical results compared to them.

Keywords: methyl salicylate, excited state, TDDFT, photoluminescence * *Corresponding author:* Email: blaisten@gmu.edu, Fax: (703) 993-9300

1. Introduction

Excited state intermolecular proton transfer (ESIPT) is relevant in laser physics and in several applications including among others hard-scintillation counters{1}, triplet quenchers{2}, and polymer photostabilizers{3}. ESIPT has potential for use as an optical probe for biomolecules{4} and could be the central mechanism in naturally occurring fluorescent proteins{5}. Methyl salicylate (MS), $C_8H_8O_3$, is a large molecule exhibiting hydrogen transfer in the excited state. In this prototypical system, the structure is ketonic before the transfer and enolic after the transfer. Fifty years ago Weller{6, 7, 8} proposed that MS undergoes a dual fluorescence by means of ESIPT. He measured two emission peaks of MS in solution, one in the near-UV (360 nm) and one in the blue (440 nm). Weller suggested the existence of a double potential well along a reaction coordinate in the excited state such that one MS isomer gives rise to the near-UV fluorescence while the other MS form yields the blue fluorescence. Since then, a voluminous literature has discussed MS dual fluorescence {9, 10, 11, 12, 13, 14, 15, 16}. In particular the idea of the double-well has been controversial based on experiments of MS in different media (matrices, beams, liquid, solvents). Also along the way, the different isomers of MS have received

different names. Recently, we have reported the ground state structures and energetics of six MS isomers calculated within a hybrid density functional theory (DFT) approach{17}. Notably, we have predicted that the enol form is stable in the ground state, ketoB is the most stable isomer followed in energy by the rotamer ketoA. We also established that ketoB $\rightarrow$ ketoA isomerization is not a thermally induced reaction in the gas phase and demonstrated that ketoB and enol isomers do not exist as an equilibrium mixture in the ground state. In our previous publication we adopted Law and Shoham's{18} nomenclature of the structural isomers, same that will be used throughout this paper.

An accepted picture of MS in the ground state is that the two rotamers, ketoB and ketoA, exist in equilibrium. Based on experimental indirect observations, the near-UV fluorescence (330 nm) is thought to be due to excitation and emission of the ketoA rotamer. Meanwhile, the emission in the blue wavelength (440 nm) is thought to have a more complicated fluorescence (or possibly phosphorescence) mechanism. One postulate says that the excited ketoB isomer undergoes a tautomerization to an excited enol form {19, 18}. The excited enol isomer then emits fluorescence when it transitions back to the enol ground state, followed by a nonradiative back-hydrogen-transfer into the ketoB ground state. A different postulate{20} indicates that ketoB in its ground state absorbs a photon to elevate the molecule to an excited singlet state. KetoB then undergoes a proton transfer to a singlet state of the enol and through intersystem crossing a lower triplet state of the enol is accessed. Subsequently, there is a transition from that triplet to the ground singlet of the enol

form. This triplet-singlet transition emits a blue wavelength photon (≈ 450 nm) while the singlet-singlet transition of the enol form emits in the near-UV (≈ 340 nm).

While there have been computational studies of ESIPT in small molecules[21] comparing methods such as CIS, CASSCF and CASPT2, and DFT for several molecules[22, 23, 24], only one study of MS excited states within AIMD-CASPT2 and 6-31G* basis sets[25] exists in the literature. Investigation of the optimized excited state structures and transitions have not been performed with time-dependent density functional theory (TDDFT). This approach has gained popularity and has been demonstrated to be appropriate for the study of excited states in the Frank-Condon region[26]. In the adiabatic approximation, the best TDDFT results are obtained with the Becke three-parameter[27] and the Lee-Yang-Parr (B3LYP) correlation functional [28]. This hybrid approach includes exact exchange (Hartree Fock) and functional representation of the correlation energy. TDDFT states that there is a unique mapping between the time-dependent external potential of a system and the time-dependent electron density[29]. Application of TDDFT to organic molecules[30] and coumarins[31] have been highly successful in calculating ground to first excited state transition energies.

In this article, Sec. II, we present the TDDFT structural and energetics results of MS obtained for the ketoB, ketoA, and enol isomers in their singlet and triplet excited states. Additionally, the photophysical mechanism of ESIPT that emerges from our calculations is presented. Sec. III includes determination of the Frank-Condon contributions of overlapping vibrational states. A comparison of theory versus experimental results and temperature effects are the subject of Sec. IV. Experimental fluorescence measurements of pure MS in its liquid state are given in Sec. V. A summary of our predictions in Sec. VI concludes this work.

2. Structural characteristics of MS isomers in excited states

Non-equilibrium TDDFT, as implemented within the Gaussian 09 software package[32], was used throughout this work. Three MS isomers (ketoB, enol, and ketoA)[17] in their gas phase were optimized within the hybrid B3PW91 scheme and basis sets 6-31++G, 6-311++G, 6-311++G(d), 6-31+G(3d,3p), and 6-311++G(3d,3p) to determine the ground state structures, force constants, and wave functions. These structures were then used as input to vertical excitation TDDFT calculations at the same level of theory. The energies and oscillator strengths of the lowest singlet and lowest triplet excited states were calculated. Oscillator strengths of the triplet-to-singlet transitions are all zero because of the spin forbidden transitions. In this paper we report results with the largest basis set 6-311++G(3d,3p). Values for the smaller basis sets are reported elsewhere[33].

Subsequently, all excited states structures were relaxed and a geometry optimization at the same level of theory (TDDFT-B3PW91) was accomplished. The optimization employs analytical gradients to determine the equilibrium geometries of

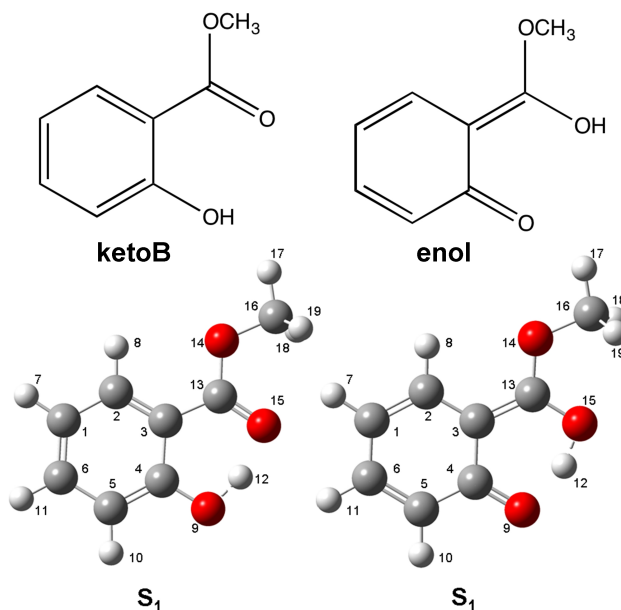


Figure 1: Optimized geometry of MS isomers ketoB and enol in the excited state S_1 . The number scheme to recognize the different atoms is provided.

Table 1: Energetics of MS isomers. S_0 is ground state energy referred to ketoB, ΔE_{frozen} is energy difference between S_0 and excited state in frozen configuration, $\Delta E_{relaxed}$ is energy difference between S_0 and excited state relaxed configurations at their minimum, $E_{Stokes} = \Delta E_{frozen} - \Delta E_{relaxed}$.

Isomer	Singlet States				Triplet States		
	S_0 (eV)	ΔE_{frozen} (eV)	$\Delta E_{relaxed}$ (eV)	E_{Stokes} (eV)	ΔE_{frozen} (eV)	$\Delta E_{relaxed}$ (eV)	E_{Stokes} (eV)
ketoB	0	4.214	3.518	0.697	3.275	3.094	0.182
ketoA	0.178	4.500	3.862	0.638	3.544	3.354	0.190
enol	0.729	4.225	3.492	0.733	3.014	2.934	0.080

Table 2: Geometry of ketoB and enol planar isomers at minima in the excited state S_1

ketoB				enol			
bond	(Å)	angle	(deg)	bond	(Å)	angle	(deg)
C1-C2	1.435	(2,1,6)	121.6	C1-C2	1.438	(2,1,6)	120.2
C1-C6	1.379	(2,1,7)	118.2	C1-C6	1.370	(2,1,7)	118.8
C1-H7	1.083	(6,1,7)	120.2	C1-H7	1.082	(6,1,7)	121.0
C2-C3	1.382	(1,2,3)	121.5	C2-C3	1.376	(1,2,3)	121.7
C2-H8	1.082	(1,2,8)	119.1	C2-H8	1.083	(1,2,8)	118.9
C3-C4	1.446	(3,2,8)	119.4	C3-C4	1.449	(3,2,8)	119.4
C3-C13	1.442	(2,3,4)	116.6	C3-C13	1.442	(2,3,4)	118.6
C4-C5	1.405	(2,3,13)	126.0	C4-C5	1.409	(2,3,13)	123.9
C4-O9	1.308	(4,3,13)	117.4	C4-O9	1.287	(4,3,13)	117.5
C5-C6	1.413	(3,4,5)	121.5	C5-C6	1.419	(3,4,5)	118.7
C5-H10	1.082	(3,4,9)	118.0	C5-H10	1.083	(3,4,9)	119.1
C6-H11	1.081	(5,4,9)	120.5	C6-H11	1.082	(5,4,9)	122.2
O9-H12	1.097	(4,5,6)	120.6	O9-H12	1.427	(4,5,6)	121.7
C13-O14	1.346	(4,5,10)	117.7	C13-O14	1.329	(4,5,10)	117.2
C13-O15	1.275	(6,5,10)	121.8	C13-O15	1.305	(6,5,10)	121.1
O14-C16	1.424	(1,6,5)	118.2	O14-C16	1.428	(1,6,5)	119.1
C16-H17	1.087	(1,6,11)	121.2	C16-H17	1.086	(1,6,11)	120.9
C16-H18	1.091	(5,6,11)	120.6	C16-H18	1.090	(5,6,11)	120.0
C16-H19	1.091	(4,9,12)	104.2	C16-H19	1.090	(4,9,12)	102.3
		(3,13,14)	115.9			(3,13,14)	118.7
		(3,13,15)	122.5			(3,13,15)	122.2
		(14,13,15)	121.5			(14,13,15)	119.1
		(13,14,16)	115.9			(13,14,16)	117.2
		(14,16,17)	105.7			(14,16,17)	105.5
		(14,16,18)	110.9			(14,16,18)	110.7
		(14,16,19)	110.9			(14,16,19)	110.7
		(17,16,18)	110.3			(17,16,18)	110.3
		(17,16,19)	110.3			(17,16,19)	110.3
		(18,16,19)	108.9			(18,16,19)	109.3

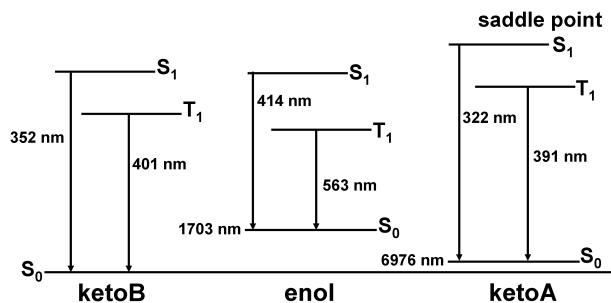


Figure 2: Schematics of the ground and excited states of MS isomers ketoB, enol, and ketoA. S stands for singlet states and T for triplet states.

molecules in their first excited singlet state. A frequency calculation was then performed on each of the excited state geometries to confirm that the stable geometries were minima on the corresponding excited state energy surface. Successful optimization was achieved for ketoB and enol. The ketoA, ketoB_{open}, ketoA_{open}, and ekA structures did not converge to stable excited state geometries. In particular, ketoA corresponds to a saddle point. The convention for designating singlet states is S_0 , S_1 and for triplet states T_1 preceded by the isomer name. Figure 1 shows the optimized structures of ketoB and enol in the excited singlet state S_1 calculated within the largest basis set approach, 6-311++G(3d,3p). Pertinent energy differences are summarized in Table 1. A pictorial illustration of the various electronic states where MS is stable is given in Fig. 2. For completeness, this figure includes the S_1 saddle of ketoA.

Because a true minimum exists in the S_1 state for both tautomers ketoB and enol, we followed a cut in the energy surfaces of the S_1 excited states along the O-H-O coordinate involving oxygen O9 in the ketoB structure, the traveling hydrogen H12, and oxygen O15 in the enol structure. To perform these calculations, the O15-H12 bond length was frozen at several points between the two minima while all other bond lengths and angles were allowed to be optimized. Additionally the same strategy was followed in the ground state and all coordinates were allowed to be optimized except for the frozen distances along the O-H-O pathway. The TDDFT B3PW91/6-311++G(3d,3p) results are shown in Fig. 3. The ESIPT path is clearly seen. When MS is excited to S_1 in the ketoB structure, the molecule relaxes to a shallow minimum. A small energy $E_{fwd} = 0.0025$ eV is enough to leave that well and fall into the basin of the enol, $E_{rev} = 0.125$ eV. When MS molecules in ketoB structure are elevated to their S_1 state, some can emit from the ketoB S_1 with fluorescence at 352 nm and others can tautomerize to the enol S_1 state and emit at 414 nm as depicted in Fig. 2. The asymmetry between the two minima in the S_1 state is clearly shown in the contour plot of Fig. 4A. Additionally, the ESIPT path is quite visible as shown in Fig. 4B where the O-H-O coordinate is plotted against changes in the carbon-oxygen bond length, C13-O15, which transitions from double bond in the ketoB structure into single bond in the enol structure. In fact, the tautomerization involves a re-adjustment of many bonds and angles in the MS molecule. Quantitative values of bonds and angles corre-

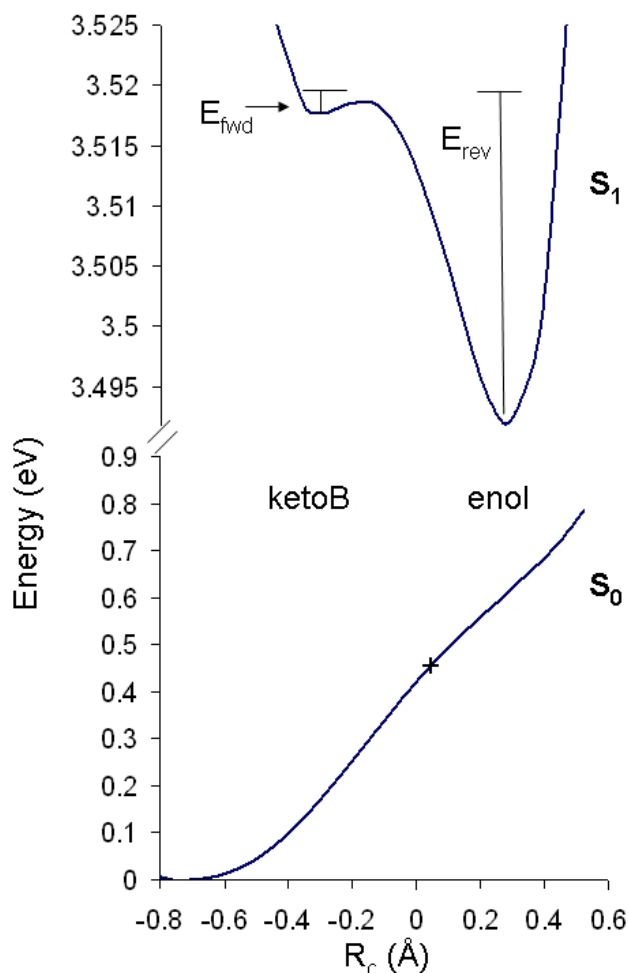


Figure 3: Excited state variation of the O9-O15 distance with O9-H12 bond length. At each point, MS was structurally optimized with a frozen O5-H12 bond length.

sponding to the MS geometry in the two minima are given in Table 2. Summarizing, the two S_1 minima are clearly defined in three out of the four basis sets used in this study. There is a significant energy barrier delineating the two minima (Fig. 4). We believe this energy barrier plays a crucial role in the dual fluorescence mechanism of MS. It is also interesting to note the variation in the O9-O15 distance along the ESIPT as the O9-H12 distance is changing. This variation is shown in Figure 5A. A minimum in the O9-O15 distance is reached when the proton is approximately 1.2 Å away from O9. Also interesting is to follow the changes in the charges of the two oxygens and the hydrogen along the ESIPT pathway. This is shown in Fig. 5B where the charges on atoms calculated from the Mulliken analysis of the wave function are depicted. It is clear that the redistribution of charge carries the hydrogen away from the oxygen and in the center of the path the hydrogen has lost 80% of its electron resembling a proton very closely. The additional S_0 optimizations performed along the ground state back proton transfer (GSBPT) mechanism are also interesting and shown in

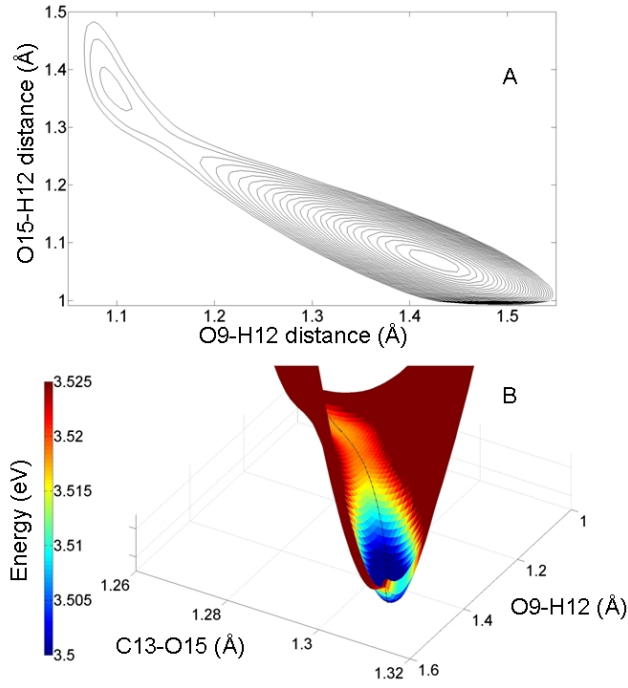


Figure 4: Contour plot (A) and 3D representation (B) of the dramatically asymmetric double minimum in S_1 of MS isomers showing the shallow minimum of the ketoB and the deeper minimum of the enol.

Fig. 3. The GSBPT proceeds without a barrier such that the enol structure transitions back to the ketoB structure. Interestingly, along the GSBPT pathway all geometries yielded positive vibrational frequencies except for one in which O15-H12=1.15 Å. This point is depicted with a cross in the path shown in Fig. 3. The calculated OH stretching vibrational mode decreased to 1702 cm^{-1} in the middle of the GSBPT, a change of nearly 1300 cm^{-1} .

3. Frank-Condon vibrational overlap factors in the dual fluorescence of MS

In the calculation of the fluorescence spectrum, we considered the Franck-Condon (FC) vibrational overlap factors. The FC factors are the square of the nuclear overlap terms between vibrational states $\psi(n, x_j)$ in S_0 and vibrational states $\psi^*(m', x_{j'})$ in S_1 associated to vibrational modes j and j' :

$$FC_{j',j}^{m',n} = \left[\int_{-\infty}^{\infty} \psi^*(m', x_{j'}) \psi(n, x_j) d\tau \right]^2 \quad (1)$$

where n, m are quantum numbers identifying the different vibrational states and x 's are the displacements from equilibrium of the vibrational modes in appropriate units. We have calculated the FC for the 51 normal modes of MS ketoB between its S_0 and S_1 electronic states assuming that the vibrational states for each normal mode are modeled as states of a quantum harmonic oscillator. For the S_0 , n could take values 0, 1, 2, 3, while for S_1 only m' equal to 0 and 1 were considered. This gives a

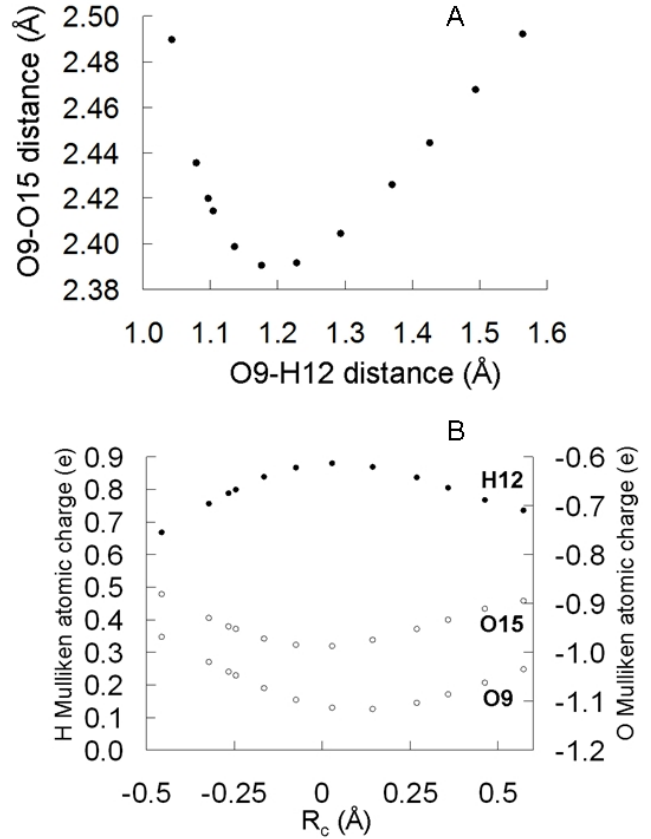


Figure 5: Properties along the ESIPIT pathway in the S_1 excited state: (A) distance between the two oxygens O9-O17, (B) Mulliken atomic charges.

total of 20,808 FC overlap factors that were calculated. Additionally, the FC series calculated from $m' = 1$ was multiplied by $\exp(-\epsilon_{j'}^{m'}/(k_B T))$, with $\epsilon_{j'}^{m'}$ being the harmonic energy of mode j' in state m' , k_B the Boltzmann constant, and $T = 300$ K. These factors are plotted in Fig. 6A as blue lines placed at each transition energy and with height equal to the FC value. Dark blue identifies the series starting at $m' = 0$ and light blue indicates the transitions from $m' = 1$. Clearly seen is that these FC contributions bundle around the fluorescence line 0-0 at 352 nm. In a similar manner, the normal modes of MS enol between S_0 and S_1 electronic states were calculated considering the same accessible vibrational states as for ketoB. These lines are shown in Fig. 6B colored blue and light-blue depending if the series started from $m' = 0$ or 1, respectively. Once again, very clearly it is seen that the highest density of these vibrational overlaps is around the 0-0 fluorescence at 414 nm. For visual clarity in Fig. 6, once all the FC were calculated, then all lines were normalized to the value of the highest FC overlap.

4. Temperature effects on the fluorescence

For a bulk collection of excited state MS molecules, we theorize a type of population diffusive exchange between the two relevant excited state minima to explain the temperature depen-

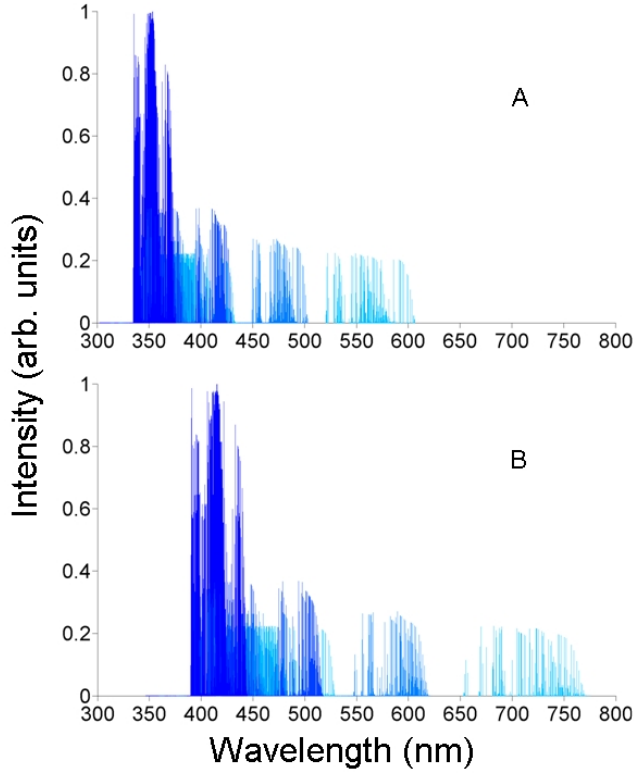


Figure 6: Calculated individual vibronic transitions from ketoB (A) and enol (B) first excited state. The intensity of the transitions is normalized to the maximum intensity.

dence on the photoluminescence spectrum. We assume that the timescale for transitioning between the two minima in S_1 (Fig. 4) is on the tens to hundreds of femtoseconds (10-500 fs) scale. This is because the vibrational oscillations occur in the 50-3000 cm^{-1} range. The photoluminescence lifetime of MS has been measured at 1.1 ± 0.2 ns [14], at 12.0 ± 0.5 ns [12], and by us in the same nanosecond range as described in Sec. V. These lifetimes are at least two orders of magnitude greater than the vibrational periods of oscillation. Therefore, one can also assume that many oscillations take place during the excited state lifetime of MS. During that time there is opportunity for MS in the S_1 state to “forward” ESIPT from the continuously populated ketoB minimum to the enol well. When that happens, the population fraction that has transitioned to the enol S_1 is hot and may account for “reverse” ESIPT repopulating the ketoB. After many oscillation periods, the emission ratio from the two populations can be described as a steady state process in which the emission from ketoB S_1 is

$$f_{\text{ketoB}} = \frac{e^{-E_{\text{rev}}/k_B T}}{Q} \quad (2)$$

and the emission from enol S_1 is

$$f_{\text{enol}} = \frac{e^{-E_{\text{fwd}}/k_B T}}{Q} \quad (3)$$

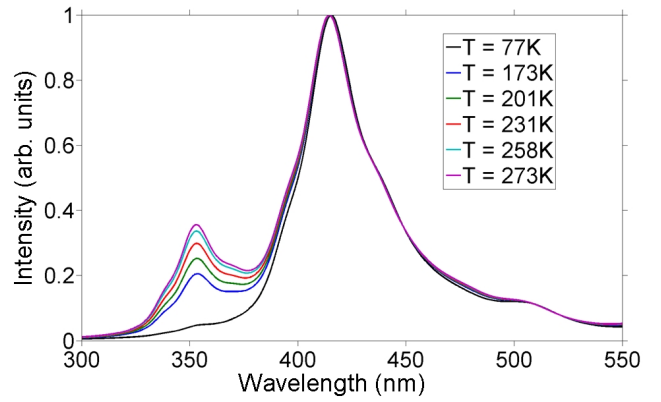


Figure 7: Calculated MS fluorescence spectra at temperatures of 77, 173, 201, 231, 258, and 273 K.

where Q is a normalization factor. We assume that the total population of MS molecules in the excited state, N_0 , has reached this steady state and that local thermal equilibrium may apply. Thus, in the calculation of the fluorescence spectra, we scaled the ketoB and the enol FC contributions by their respective emission ratios given in Eqs. 2-3. Additionally, individual emission lines in Fig. 6 are broadened by a Lorentzian function centered at the transition line and with a broadening factor of 500 cm^{-1} . The Lorentzians are summed together and the resulting spectrum is normalized to the value of the highest peak at each temperature. Fig. 7 shows the summed result for six temperatures. This dual fluorescence is very much in agreement with experiments [18, 19] and reproduces well the observations of the disappearance of the fluorescence at the shorter wavelengths as temperature is decreased. The complete picture of the process that emerges from our calculations is as follows: Initially, the population of MS is almost totally composed of the ketoB S_0 ground state. A negligible amount of ketoA S_0 may exist, but the isomerization barrier for ketoB to ketoA S_0 (0.67 eV) is far too high for a substantial amount of ketoA S_0 to form at normal conditions ($T \approx 300\text{K}$, $\rho \approx 1$ atm). A photo-excitation occurs with a wavelength of approximately 300 nm. This excitation creates an excited state population (N_0) which is all ketoB S_1 immediately after the excitation. Next, mutual repopulation occurs between the ketoB S_1 and enol S_1 states which is highly dependent upon the temperature of the system. The total population in S_1 is thus split into two, $N_0 = N_{\text{ketoB}} + N_{\text{enol}}$. A greater temperature favors forward/reverse ESIPT from ketoB S_1 to enol S_1 and backwards. However, the energy barrier from enol S_1 to ketoB S_1 is greater, eventually producing a bias favoring excited state population to remain in the enol S_1 well (see Fig. 3). Lower temperatures increase the bias, and eventually eliminate the possibility of reverse ESIPT.

5. Experimental

For comparison to the calculated spectra, liquid MS emission spectrum was taken with a Horiba Jobin Yvon fluorescence spectrometer. The sample was spectral grade (> 99%)

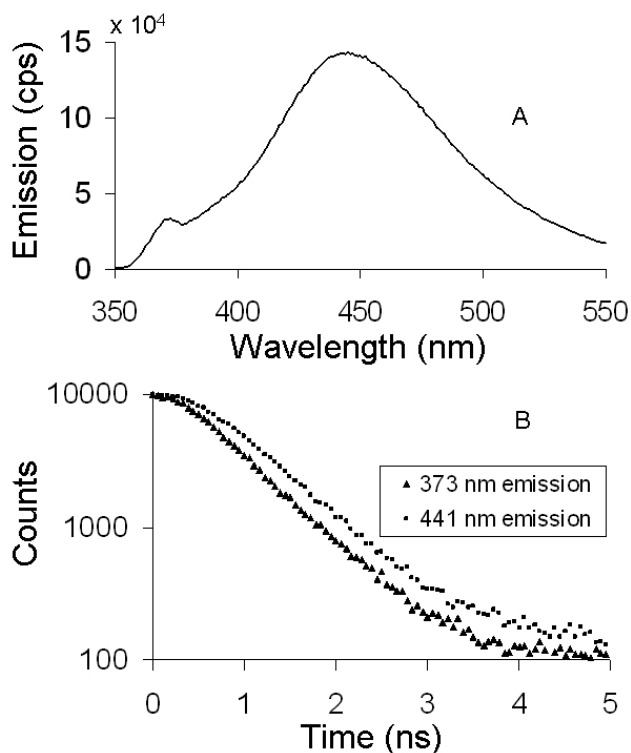


Figure 8: Pure liquid MS fluorescence experiment: (A) emission spectrum at 300 K with $\lambda_{ex} = 327$ nm excitation, (B) fluorescence lifetimes of the two spectral peaks (373 and 441 nm) from (A).

liquid MS from Sigma Aldrich. An excitation wavelength of 330 nm, 0.5 second integration time, and 4 nm slit widths at 1 nm increments were used. The steady-state emission spectrum is shown in Fig. 8. The dual fluorescence is clearly apparent here: the shorter wavelength peak located at 373 nm and the longer wavelength peak located at 441 nm.

Time-correlated single-photon counting (TCSPC) lifetime measurements were also taken of the same MS sample using a Horiba time domain spectrofluorometer. A diode laser centered at 327 nm was used as the excitation source. LUDOX was used to calibrate the lifetime measurements. The lifetime plots are shown in Fig. 8B. Analysis of the 441 nm emission yielded a lifetime of 1.18 ± 0.1 ns at 327 nm excitation. Analysis of the 373 nm emission yielded a lifetime of 0.95 ± 0.1 ns at 327 nm excitation. These lifetimes are in generally good agreement with previous experiments[14, 12]. The agreement between our calculations and experimental results is remarkable (Fig. 7 and Fig. 8). In particular, the ratio of intensities of the two prominent peaks is very well reproduced. The experiment also confirms that the dual fluorescence occurs in between 340-550 nm.

6. Conclusion

We have presented a thorough computational investigation of the excited state of MS using DFT and TDDFT methods. In

our best estimation, the dual fluorescence of MS arises from the presence of two potential wells in the excited state separated by a small energy barrier due to a hydrogen displacement between the hydroxyl and carbonyl oxygens that entails significant electronic rearrangement. Previous computational studies, as well as calculations within this study, suggest that the rotamer (ketoA) does not have a substantial effect on the total photoluminescence. Instead, the ketoB and enol isomers are the dominant players. Phosphorescence from the first triplet states of ketoB and enol is not ruled out. However, the large computed oscillator strengths of the singlet-singlet transitions suggest that the contribution due to phosphorescence would be minimal. Additionally, experiments have measured lifetimes in the range of nanoseconds (this work and [14, 12]). There is no indication of long lifetime MS photoluminescence in the literature and we have not observed it.

We also predict a temperature dependent fluorescence due to excited state forward and reverse ESIPT during which the excited molecules visit the two possible minima in the excited state (Fig. 4). However, the energy barrier from enol to ketoB is greater than the barrier from ketoB to enol. Therefore, there is eventually a slight bias of excited state population wanting to remain in the excited state of the enol isomer. The forward/reverse ESIPT depends upon the system temperature and the excited state lifetime. Experiments have shown a temperature-dependence effect in the measured lifetime[12]. In particular, a greater temperature will result in a shorter fluorescence lifetime. Our argument on the population of the excited state and the forward/reverse ESIPT explains these observations. At low temperature, more of the excited state MS population is "stuck" in the enol energy well for a longer amount of time. Since ketoB S_1 has a relatively small oscillator strength, then the lifetime will be longer because of the inverse relation between fluorescence lifetime and transition oscillator strength[34]. Conversely, at higher temperatures a large population of hot molecules crosses over to the ketoB energy well. The higher enol oscillator strength results in more photo-emission and hence a shorter lifetime.

Any population of enol returning to S_0 created from the photo-emission process will be short-lived due to a back proton transfer along a ground state steep, barrierless potential energy surface to ketoB S_0 (Fig. 3). We expect that this process in the ground state occurs on a timescale of less than 1 ps. Accompanying the excitation-fluorescence process there is an important electronic reorganization creating a carbon single-double bond pattern that favors tautomerization in the excited state and relaxes in the ground state to its original pattern through a back proton transfer.

Acknowledgments

This work was partially supported under the National Science Foundation grant CHE-0626111. We acknowledge the Teragrid allocation award CHE100033 and the USACE ERDC MSRC for the extensive software and computational resources.

References

- [1] P.-T. Chou and M. L. Martinez, *Radiat. Phys. Chem.* 41, 373 (1993).
- [2] R. M. Tarkka, X. Zhang, and S. A. Jenekhe, *J. Am. Chem. Soc.* 118, 9438 (1996).
- [3] O. G. Piringir and A. L. B. (eds), *Plastic Packaging* (Wiley-VCH, Weinheim, 2008).
- [4] W.-H. Chen, Y. Xing, and Y. Pang, *Org. Lett.* 13, 1362 (2011).
- [5] R. Y. Tsien, *Ann. Rev. Biochem.* 67, 509 (1998).
- [6] A. Weller, *Naturwissenschaften* 42, 175 (1955).
- [7] A. Weller, *Zeitschrift für Elektrochemie* 60, 1144 (1956).
- [8] A. Weller, *Prog. React. Kinet.* 1, 188 (1961).
- [9] B. Zadorozhnyi and I. Ishchenko, *Opt. Spectrosc.* 19, 306 (1965).
- [10] W. Klöpffer and G. Naundorf, *J. Lumin.* 8, 457 (1974).
- [11] E. Kosower and H. Dodiuk, *J. Lumin.* 11, 249 (1975).
- [12] K. Smith and K. Kaufmann, *J. Phys. Chem.* 82, 2286 (1978).
- [13] W. Klöpffer and G. Kaufmann, *J. Lumin.* 20, 283 (1979).
- [14] A. U. Acuña, F. Amat-Guerri, J. Catalan, and F. Gonzalez-Tablas, *J. Phys. Chem.* 84, 629 (1980).
- [15] A. Acuña, J. Catalan, and F. Toriblo, *J. Phys. Chem.* 85, 241 (1981).
- [16] J. Catalan and A. Macias, *J. Mol. Struct.* 38, 209 (1977).
- [17] R. D. Massaro, Y. Dai, and E. Blaisten-Barojas, *J. Phys. Chem. A* 113, 10385 (2009).
- [18] K. Law and J. Shoham, *J. Phys. Chem.* 98, 3114 (1994).
- [19] J. L. Herek, S. Pedersen, L. Bañares, and A. H. Zewail, *J. Chem. Phys.* 97, 9046 (1992).
- [20] J. Catalan and C. Diaz, *J. Phys. Chem. A* 102, 323 (1998).
- [21] S. Scheiner, *J. Phys. Chem. A* 104, 5898 (2000).
- [22] P. G. Yi, Y. H. Liang, and C. Z. Cao, *Chem. Phys.* 315, 297 (2005).
- [23] R. B. Singh, S. Mahanta, S. Karl, and N. Guchhait, *Chem. Phys.* 331, 373 (2007).
- [24] A. Cembran and J. Gao, *Theor. Chem. Acc.* 118, 211 (2007).
- [25] J. Coe, B. Levine, and T. Martinez, *J. Phys. Chem. A* 111, 11302 (2007).
- [26] F. Furche and R. Ahlrichs, *J. Chem. Phys.* 117, 7433 (2002).
- [27] A. D. Becke, *J. Chem. Phys.* 98, 5648 (1993).
- [28] R. Bauernschmitt and R. Ahlrichs, *Chem. Phys. Lett.* 256, 454 (1996).
- [29] E. Runge and E. Gross, *Phys. Rev. Lett.* 52, 997 (1984).
- [30] C. J. Jamorski and M. E. Casida, *J. Phys. Chem. B* 108, 7132 (2004).
- [31] K. A. Nguyen, P. N. Day, and R. Pachter, *J. Chem. Phys.* 126, 094303 (2007).
- [32] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, et al. (2009), Gaussian Inc., Wallingford, CT.
- [33] R. D. Massaro, doctoral dissertation, George Mason University, Chap. 4 (2011).
- [34] A. Siegman, *Lasers* (University Science Books, Sausalito, CA, 1986).

Density Functional Theory Study of Dipicolinic Acid Isomers and Crystalline Polytypes

Richard D. Massaro and Estela Blaisten-Barojas*

Computational Materials Science Center and School of Physics, Astronomy, & Computational Sciences, George Mason University, Fairfax, Virginia 22030, USA

Abstract

Six isomers of dipicolinic acid (DPA) in the gas phase are predicted based on a detailed density functional theory study. Energetics include the binding energy, ionization potential and electron affinity. Dipole moments; rotational constants, atomic charges, and Fukui functions are also calculated. Several isomerization reactions are shown as possible, with calculated reaction path and transition barriers in the range 0.3 to 0.6 eV. Prediction of five DPA dimers and three crystalline DPA polytypes are also reported. Vibrational analysis for monomers and dimers is calculated and compared to existing experimental results. The electronic band structure of three crystalline polytypes shows that DPA crystals are insulators. The three stable polytypes display distinct hydrogen-bonding formations that originate sheets of DPA molecules that are further stacked to form layered crystals that are energetically nearly degenerate.

Keywords: dipicolinic acid, vibrational spectrum, density functional theory, DPA crystal

* *Corresponding author:* Email: blaisten@gmu.edu, Fax: (703) 993-9300

1. I. Introduction

Powell{1, 2} was the first to discover the fact that dipicolinic acid (DPA, 2,6-pyridinedicarboxylic acid, $C_5H_3N(COOH)_2$) is excreted by most or all species of germinating bacterial spores. DPA is thought to protect bacterial spores because of its ability to strongly absorb ultraviolet light. DPA is well-known to be a molecule with high chelation. The Ca^{2+} chelate of DPA is a major constituent of the dormant spore core, accounting for approximately 10% of total spore dry weight {3, 4}. Indeed, DPA's presence within the spore medium is primarily found as a calcium chelated form, calcium dipicolinate (CaDPA), which induces and enhances bacterial spore germination {5}. Up to 50% of the solids excreted by the spores and up to 15% of the total dry weight of each spore are thought to be CaDPA. Additionally, CaDPA retains the characteristic of having a strong UV absorption, as does pristine DPA. While calcium and sodium bound to DPA are more often to be found in nature, there have also been studies to design optical reporters based on lanthanide elements{6, 7, 8} and molecularly imprinted polymer surfaces{9}.

Experiments performed on wet paste and dry crystal forms of DPA and CaDPA have shown interesting effects on their fluorescence intensities{10}. The drying of DPA crystals showed an increase in the observed fluorescence as well as a broader emission peak. UV-exposed samples exhibited dramatic increases in fluorescence{11}. It has been theorized that a photochemical reaction takes place to form new molecular species or isomers in those UV-irradiated samples{12}. Experiments have illustrated

the vibrational spectra, supramolecular structure of the crystal unit cell {13}, and crystallography of anhydrous DPA{14, 15}.

Computational investigations of DPA and CaDPA have been relatively sparse. Early calculations with small basis sets have suggested that CO_2 groups are oriented perpendicular to the ring plane{16}. Complete active space multi-configuration self-consistent field (MCSCF) calculations have determined ground and excited state geometries and vibrational frequencies for one isomer of gas phase DPA and its anion{17}. DFT and TDDFT studies performed on DPA and its dianion showed an acceptable agreement between the calculated IR, Raman, NMR, and photoabsorption spectra as compared with experimental values{18}. The latter study reports that the lowest excited singlet state for DPA is dipole-forbidden and the first dipole-allowed transition is the excitation to the second singlet state. This study also rules out a direct singlet-triplet excitation process. To the authors' knowledge, there is no literature which reports a thorough computational investigation of all DPA isomers along with their proposed liquid phase and crystalline structures.

In this article we put forward a thorough density functional theory calculation to predict several stable gas phase isomers, their dimers, and crystalline polytypes. Section 2 gives an overview of the structure, energetics, vibrational analyses and isomerization pathways of six DPA isomers. Section 3 gives a description of the possible dimers that can be formed from the predicted monomers through a tandem of hydrogen bonds. Structure, energetics and vibrational analyses are included in this section for the predicted dimers. Section 4 contains a description of three optimized crystalline polytypes of DPA, which are formed by stacking sheets of molecules arranged in parallel chains. The electronic band structure of these predicted crystals is calculated, indicating that these crystals are insulators. Concluding remarks in Section 5 close this article. An Appendix contains detailed structural information, IR spectra, and the molecular orbital distribution of the gas phase DPA iso-

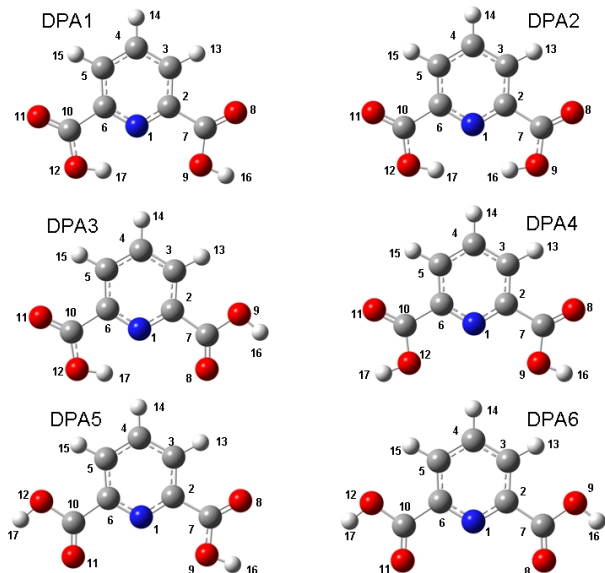


Figure 1: Optimized structure of the six DPA isomers in the gas phase.

mers presented in section 3.

2. II. DPA isomers

All-electron density functional theory (DFT) calculations of DPA in the gas phase are performed within Becke’s 3-parameter hybrid functional approach with Lee-Yang-Parr’s[19] correlation functional (B3LYP) and a double- ζ basis set augmented with d polarization function (6-31G(d)). Structural optimizations of DPA isomers are performed with the Bery algorithm using redundant internal coordinates[20]. All calculations were carried out with the Gaussian 09 package[21]. Optimized structures of the DPA predicted isomers are shown in Figure 1. Detailed bond lengths and angles of these geometries are reported in the appendix, Tables 5 and 6.

The electronic ground state of all of these isomers are singlets. Furthermore, it is determined that none of the DPA isomers is stable in triplet electronic states. Calculation of vibrational frequencies associated to all states confirm that stable structures correspond to minima of the electronic energy surface. DPA2, DPA4 and DPA6 have C_{2v} symmetry while the other three isomers are C_s . Electronic state energies (E), zero point energies (ϵ), binding energies (BE), dipole moments, ionization potentials (IP), adiabatic electronic affinities (EA), and HOMO-LUMO gaps (Δ) for the six predicted isomers are summarized in Table 1. The binding energy is defined as $BE = |E_{DPA} - E_{atomic}|$, where E_{atomic} is the sum of the individual atoms energies. The IP and EA are calculated as differences between the optimized state of the neutral and the optimized state of the cation or anion, respectively.

DPA1 is the global minimum structure taking into account that its total electronic energy plus the zero point energy is the lowest of the six predicted structures. Two isomers, DPA2 and

Table 2: Atomic charges of DPA isomers calculated from the Mulliken analysis.

Atom	DPA1	DPA2	DPA3	DPA4	DPA5	DPA6
N1	-0.591	-0.663	-0.578	-0.503	-0.491	-0.479
C2	0.245	0.250	0.232	0.231	0.217	0.218
C3	-0.141	-0.140	-0.145	-0.136	-0.139	-0.138
C4	-0.107	-0.103	-0.105	-0.111	-0.109	-0.107
C5	-0.139	-0.140	-0.138	-0.136	-0.135	-0.138
C6	0.249	0.250	0.251	0.231	0.233	0.218
C7	0.560	0.589	0.562	0.555	0.559	0.560
O8	-0.462	-0.447	-0.442	-0.471	-0.437	-0.433
O9	-0.559	-0.574	-0.581	-0.548	-0.587	-0.587
C10	0.586	0.589	0.587	0.555	0.556	0.560
O11	-0.457	-0.447	-0.458	-0.471	-0.471	-0.433
O12	-0.582	-0.574	-0.581	-0.548	-0.545	-0.587
H13	0.187	0.195	0.183	0.183	0.179	0.179
H14	0.167	0.173	0.166	0.160	0.159	0.158
H15	0.190	0.195	0.190	0.183	0.183	0.179
H16	0.419	0.424	0.420	0.414	0.416	0.416
H17	0.437	0.424	0.440	0.414	0.414	0.416

DPA3, lie in almost degenerate states above the DPA1 structure at 0.046 and 0.050 eV, respectively. Isomers DPA4, DPA5 and DPA6 lie higher up above DPA1 at 0.144, 0.215, and 0.296 eV, respectively. The DPA6 isomer has previously been proposed by Carmona[13] as the unique structure for DPA. The DPA5 isomer is the structure proposed in Ref. [22] and determined by Tellez et al[14] to be the main component in DPA supramolecular arrays. The structure of the DPA4 isomer was reported in previous calculations[17] and identified experimentally in Raman measurements[23]. It is thus important to point out that three additional stable isomers, put forward in this paper, are new to the literature. The ionization potential of the three most stable isomers is larger than the reminding three. Additionally, DPA1, DPA2 and DPA3 have significantly larger electron affinities, making them more reactive than the others. The HOMO-LUMO gap is quite large in all six isomers. The spectrum of one-electron Khon-Sham molecular orbital levels for the monomeric isomers is given in the Appendix, Figure 9. It is interesting to note that the more symmetric monomers show degeneracies in the valence and virtual states that disappear in the less symmetric isomers. Of all isomers, DPA3 is the most polar compound out of the six studied structures. A Mulliken analysis of the wave function yields charges on the different atoms which are very similar across the six isomers as shown in Table 2. The Fukui function[24] $f(\mathbf{r}) = \partial\rho(\mathbf{r})/\partial N$ is evaluated from right or left to avoid the discontinuity at integer N yielding the electron acceptor function f^+ (derivative taken from the right)

$$f^+(\mathbf{r}) = \rho_{N+1}(\mathbf{r}) - \rho_N(\mathbf{r}) \quad (1)$$

and the electron donor function f^- (derivative taken from the left)

$$f^-(\mathbf{r}) = \rho_N(\mathbf{r}) - \rho_{N-1}(\mathbf{r}) \quad (2)$$

Table 1: Electronic states, total electronic energies, zero point energies (ϵ_0), binding energies (BE), and dipole moments of the DPA isomers. The electron affinities (EA), ionization potentials (IP), and HOMO-LUMO gap (Δ) are also reported. Total electronic energies E are relative to the $^1\text{DPA1}$ ground state energy of -17.018746 keV.

isomer	state	E (eV)	ϵ_0 (eV)	BE (eV)	dipole (D)	EA (eV)	IP (eV)	Δ (eV)
DPA1	^1A	0	3.236	113.890	3.378, 1.809, 0	0.770	9.482	5.220
DPA2	$^1\text{A}_1$	0.046	3.233	113.843	0, 2.599, 0	0.816	9.706	5.409
DPA3	^1A	0.050	3.234	113.840	4.864, 3.949, 0	0.631	9.495	5.191
DPA4	$^1\text{A}_1$	0.144	3.228	113.746	0, 0.679, 0	0.286	9.021	5.383
DPA5	^1A	0.215	3.223	113.674	1.401, 2.893, 0	0.282	9.070	5.437
DPA6	$^1\text{A}_1$	0.296	3.218	113.594	0, 5.190, 0	0.280	9.149	5.599

where $\rho_N(\mathbf{r})$ is the electron density of a system with N electrons [25]. These functions are useful for predicting the nucleophilic and electrophilic reactivity of compounds. The reactivity indicator for radical attack is defined by

$$f^0(\mathbf{r}) = \frac{1}{2} (f^+(\mathbf{r}) + f^-(\mathbf{r})) \quad (3)$$

The Fukui functions f^- and f^0 for DPA are shown in Figure 2. Calcium is an element that usually binds to DPA as a cation by electrophilic substitution with two hydrogens leaving the molecule and a new compound, CaDPA , being formed. Thus, DPA is an electron donor molecule. We see in Fig. 2 that DPA4 has the largest f^- value at the nitrogen site. The other isomers have similarly large f^- values at the nitrogen site except for DPA2. All of the isomers show a large f^- value at the carboxyl oxygens (8 and 11 in the figure). The binding site for a calcium atom to DPA is likely to occur near the nitrogen or carboxylic oxygens.

Inspection of the f^0 Fukui function shows that it is similar to f^- . Sites susceptible to radical attack are the nitrogen atom and carboxyl oxygens for DPA1, DPA2, and DPA6 while DPA3 only has high f^0 at the carboxyl oxygen # 11 site. DPA4 has high f^0 only at the nitrogen and DPA5 has high f^0 at the nitrogen and moderately high f^0 at the oxygen # 11 site.

The calculated vibrational spectra of all six monomers are shown in Figure 3, where peak heights are normalized to the peak of maximum intensity for each isomer. Assignment of the normal modes of vibration in DPA1 is given in Table 3 and compared with experiment [13]. Frequencies for the other five isomers are reported in the appendix Table 7. It is interesting to note that DPA1 through DPA3 have similar spectra, and these are quite different than the spectra of the other three isomers. All isomers have prominent OH stretching modes in the high frequency range ($> 3500 \text{ cm}^{-1}$). The two OH stretching modes for DPA1 (3692 and 3530 cm^{-1}) and DPA3 (3699 and 3524 cm^{-1}) are clearly split while the other isomers' OH stretching modes are almost exactly overlapping. The OH stretching modes of DPA4, DPA5, and DPA6 are also blue-shifted from those of DPA1, 2, and 3. The quite intense C=O stretching mode is seen in all of the monomers between 1816 and 1868 cm^{-1} . A slight splitting of the C=O stretching modes in DPA1 and DPA5 is also noticeable. The 1863 cm^{-1} line in DPA1 is due to the C10-O11 stretching mode and the 1825 cm^{-1} line is

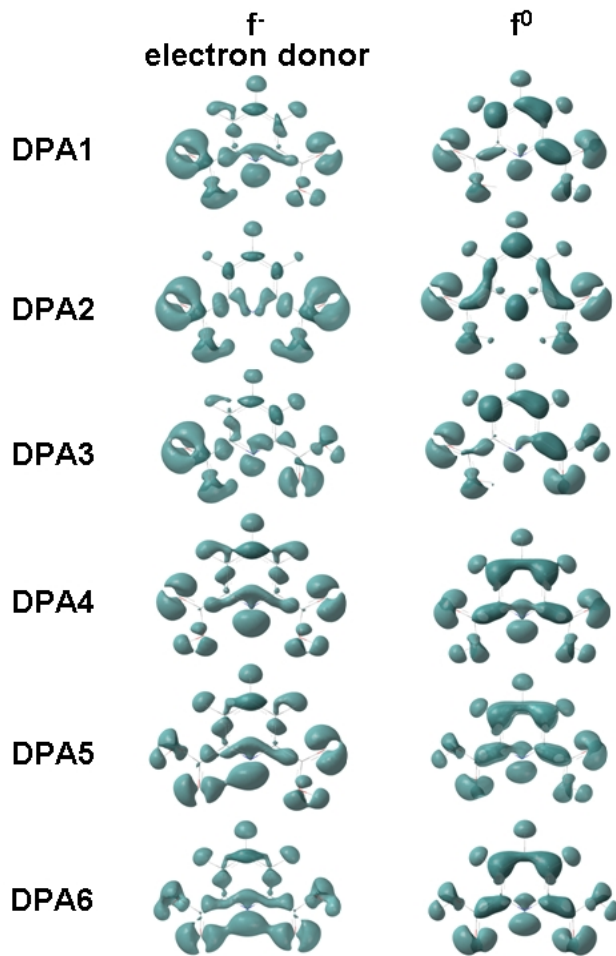


Figure 2: Fukui functions, f^- (electron donor) and f^0 (radical attack) of DPA isomers. A value of 0.002 was used to create the positive iso-surfaces.

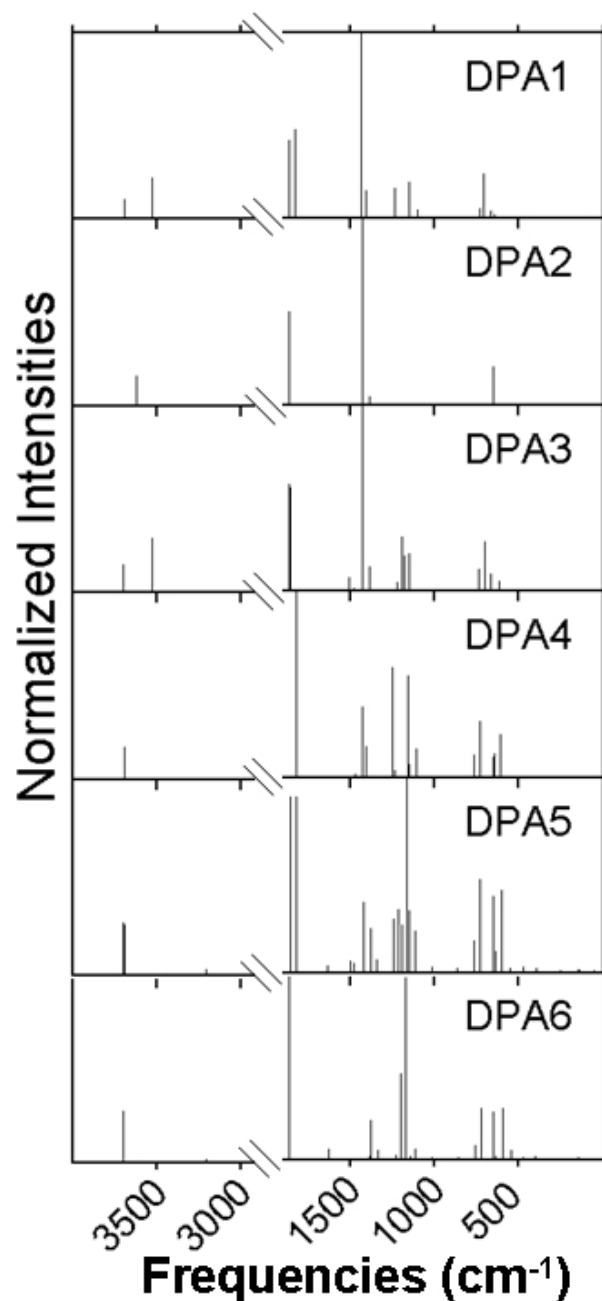


Figure 3: Calculated infrared spectra of the six gas phase isomers of DPA.

due to the C7-O8 stretching mode. Meanwhile in DPA5, the 1855 cm^{-1} line is due to the C7-O8 stretching mode and the 1818 cm^{-1} line is due to the C10-O11 stretching mode.

The most intense mode in DPA1, DPA2, and DPA3 is the OH scissoring mode located at 1400 and 1440 cm^{-1} . In all three of these modes; H17 is swung towards the nitrogen. For the DPA2 OH scissoring mode, both H16 and H17 have the same swinging motion inwards to N1. Those same OH scissoring modes exist for DPA4, DPA5, and DPA6 but their motion brings the

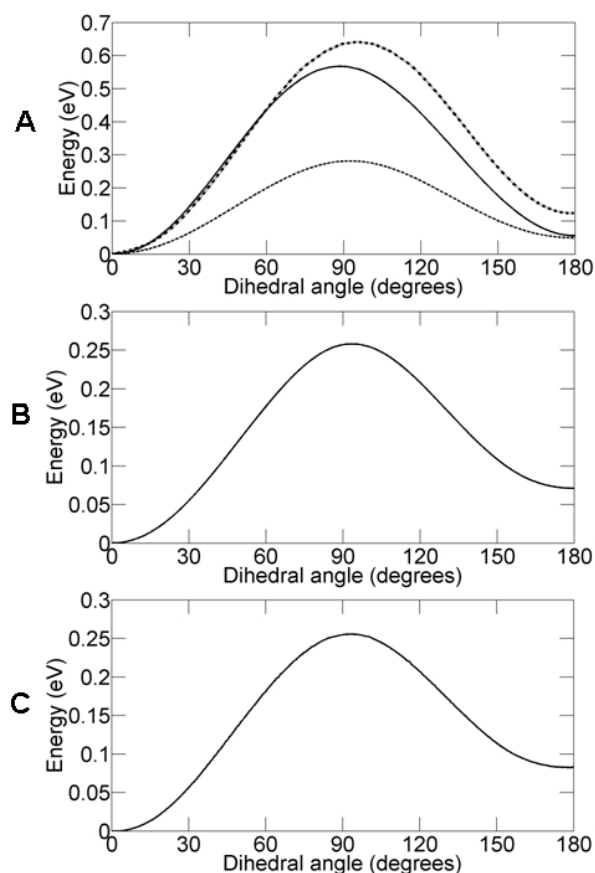


Figure 4: Energy pathways for five different reactions: (a) DPA1 to DPA2 [solid], DPA1 to DPA3 [small dots], DPA1 to DPA4 [large dots]; (b) DPA4 to DPA5; (c) DPA5 to DPA6. The energies in (a), (b), and (c) are relative to the DPA1, DPA4, and DPA5 minima, respectively.

hydrogen closer to the carboxyl oxygen and results in a lower intensity line. The DPA4, DPA5, and DPA6 C-O stretching and CH scissoring modes between 1100 and 1170 cm^{-1} are very intense. These same modes are present in DPA1, DPA2, and DPA3 but are less intense. The most prominent feature for DPA1, DPA2, and DPA3 below 1000 cm^{-1} is the C-C and OH wagging mode. This mode appears at approximately 700 cm^{-1} . Meanwhile, for DPA4, DPA5, and DPA6, several moderately intense lines lie between 600 and 800 cm^{-1} . These lines are due to the OH wagging mode (590 to 615 cm^{-1}), the in-plane rocking mode (645 to 655 cm^{-1}), the out-of-plane rocking mode (700 to 735 cm^{-1}), and the CH wagging mode (750 to 770 cm^{-1}). The only moderately intense lines for DPA1, DPA2, and DPA3 below 1000 cm^{-1} belong to the C-C and OH wagging modes between 670 and 740 cm^{-1} .

The rotational constants of all six isomers are quite similar. These rotational constants in GHz are 1.76967 , 0.64388 , and 0.47210 for DPA1, 1.77310 , 0.64430 , 0.47258 for DPA2, 1.80582 , 0.63269 , 0.46853 for DPA3, 1.79468 , 0.62793 , 0.46517 for DPA4, 1.83484 , 0.61616 , 0.46126 for DPA5, and 1.87671 , 0.60428 , 0.45710 for DPA6.

Several isomerization reaction coordinates are predicted and

Table 3: Calculated vibrational spectrum of the DPA isomer with lowest energy and comparison with experiments.

DPA1			Experiment{13}	
ν (cm ⁻¹)	intensity	assignment	IR	Raman
3692	81	ν OH	3115	3113
3530	145	ν OH	3102	3105
3246	0	ν_s C-H		3070
3243	1	ν_a C-H	3070	
3212	7	ν_a C-H	2800	2650
1863	253	ν C=O	1710	1646
1825	287	ν C=O	1700	1640
1644	2	ν ring C-C	1576	1580
1630	3	ν ring C-C, C-N	1571	1577
1508	7	ρ CH	1470	1475
1469	15	ν C-N	1468	1447
1437	572	σ OH	1422	1439
1405	108	σ OH	1387	1423
1355	16	ν ring C-C, C-N	1341	1332
1277	14	σ OH, ν C-C	1308	1304
1236	114	σ OH	1275	1279
1185	8	σ CH	1260	1262
1165	10	ν C-O	1178	1183
1152	132	ν C-O	1151	1156
1102	50	σ CH	1082	1090
1028	0	ω CH	998	
1023	10	ring breath	987	998
974	0	ω CH	937	987
898	11	ν C-C, ρ ring	890	895
862	13	ω CH	855	855
796	22	τ full molecule	751	802
767	5	ω CH	705	762
742	2	ring breath, σ C(=O)-O	692	752
731	55	ω OH	668	698
709	156	ω C-C/O-H	647	647
663	48	ρ in-plane	592	630
645	37	ring breath	583	619
625	32	ω OH	530	
576	3	ρ in-plane	519	495
478	2	ρ in-plane	421	491
467	11	ω ring	365	437
437	0	ρ out-of-plane	330	396
384	4	ρ in-plane	226	298
359	2	ring breath	218	209
259	20	ρ in-plane	208	192
176	2	τ ring	199	135
155	1	ρ out-of-plane	107	121
131	5	σ full molecule	89	85
82	4	τ C-COOH	79	72
55	3	τ C-COOH		28

ν , stretching; ω , wagging; ρ , rocking; τ , twisting;
 σ , scissoring; Ph, phenyl. Subscripts: a , asymmetric; s , symmetric.

the transition state in each reaction is identified using the synchronous transit-guided quasi-Newton method[26, 27]. The energy paths for the five isomerization reactions are shown in Figure 4. Reaction pathways are calculated along the intrinsic reaction coordinates (IRC). The structure of the compound at the transition state is confirmed through vibrational analysis by displaying one imaginary frequency. All of the transition structures are near the midpoint ($\pm 90^\circ$) geometry of complete dihedral angle rotations: DPA1 $\rightarrow$ DPA2 (2,7, 9, 16) dihedral; DPA1 $\rightarrow$ DPA3 (1,2,7,8) dihedral, DPA1 $\rightarrow$ DPA4 (6,10,12,17) dihedral; DPA4 $\rightarrow$ DPA5 (1,2,7,8) dihedral; and DPA5 $\rightarrow$ DPA6 (5,6,10,11) dihedral. Thus; the IRC transition vectors chosen are the dihedral angles differentiating the two isomers. As seen in Figure 4, the barriers for these reactions are quite high. The most favorable to isomerize DPA1 into DPA3 costs about 0.28 eV. Isomerization of DPA1 into DPA2 or DPA4 requires twice as much energy (0.57 and 0.64 eV, respectively). It is interesting to note that the isomerization from DPA4 to DPA5 and DPA5 to DPA6 is possible when a barrier of 0.26 eV is surmounted.

3. III. DPA Dimers

A number of DPA dimers are plausible to be predicted when two molecules bind by means of two hydrogen bonds. We study here several possibilities within the same DFT level of calculation. Five stable and optimized dimer structures are shown in Figure 5. All structures have C_{2h} symmetry. The notation adopted for identifying these dimers is 2DPAn, $n = 1, 3-6$. These dimers of two DPA molecules bind through two inter-molecular hydrogen bonds (O–H–O) joining the COOH groups. Dimers of DPA2 are absent because there is no possible O–H–O bonds between two DPA2 monomers. The electronic states, energies, zero point energy, formation energies, ionization potential, electronic affinity, and HOMO-LUMO gap for these five dimers are reported in Table 4. The DPA1 dimer (2DPA1) is the lowest in energy of the five dimers investigated. In Table 4, the energy of each dimer is referred to the energy of the 2DPA1. As for the monomers, the zero point energies are very comparable for the five isomers. The formation energy $E_{\text{formation}} = 2E_{\text{monomer}} - E_{\text{dimer}}$ is lowest for 2DPA4, which also has the lowest IP. For a balance of energies, 2DPA4 is then quite effective for forming supramolecular structures such as chains linked through pairs of O–H–O bonds. Additionally, this isomer is the central unit for forming the crystal. We note that despite the fact that 2DPA1 is the lowest in energy, this dimer and 2DPA3 may only exist in the gas or liquid phases since there are no paths for forming inter-molecular hydrogen bonds. Electron affinities and HOMO-LUMO gap are quite comparable for the five dimers. Also notable is the expected shrinkage of the HOMO-LUMO gap in the dimers when compared to gaps in the monomers (Table 1). It is possible to mix and match different DPA isomers to form other dimers but such speculation is not part of this work.

All five DPA dimers are non-polar with zero dipole moments. Calculation of the vibrational frequencies confirms that the structures reported in Fig. 5 are minima. The calculated

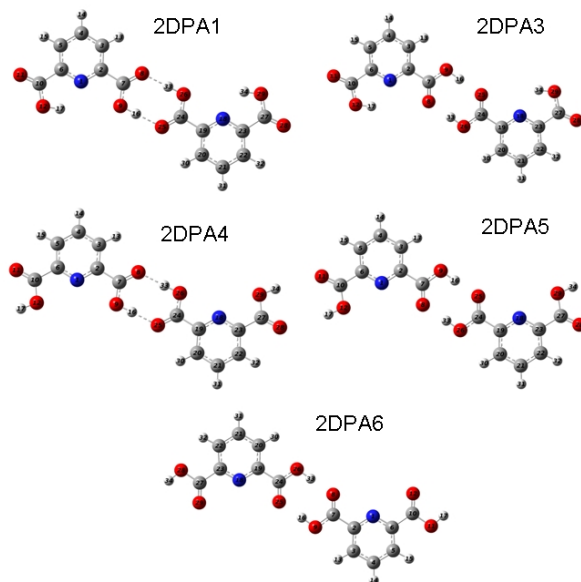


Figure 5: Structure of optimized dimers of DPA showing the tandem of hydrogen bonds required for forming them.

vibrational IR spectra for the DPA dimers are shown in Figure 6. The OH stretching mode at frequencies 3100 and 3200 cm^{-1} is quite dominant and overshadows the spectrum in all five dimers. It has been pointed out [23, 28] that the O–H vibrational stretching bands are blue shifted as DPA changes phase from vapor $\rightarrow$ liquid $\rightarrow$ solid. A blue shift of the O–H stretching modes from 400 to 500 cm^{-1} is already present when comparing the monomer to the dimer spectra.

By stacking two 2DPA4 dimers and optimizing the geometry of the supramolecular arrangement, we find that the two dimers tend to form a fan-looking structure in which the initially parallel planes organize themselves at a 45° angle.

4. IV. DPA crystalline polytypes

Several of the DPA dimer structures lend themselves to be extended in linear chains by adding more monomers. Using the same DFT level of calculation plus periodic boundary conditions (PBC), one-dimensional chains of DPA4, DPA5, and DPA6 are optimized and found to be stable. The initial guess of 16.167 Å for the lattice parameter (i.e., two monomers long) was taken from experimental crystallographic data[14] of DPA crystals. The chain of DPA4 has the lowest total energy of the three. The DPA5 and DPA6 chains have energies of 0.060 and 0.156 eV above the DPA4 chain, respectively. The optimized lattice parameters have lengths of 16.497, 16.318, and 16.257 Å for DPA4, DPA5, and DPA6 chains, respectively. These values are slightly expanded (at most 2%) with respect to the experimental observation in the crystal.

These optimized 1-D chains and X-direction translation vectors are then used as the initial guesses for a two-dimensional

Table 4: Electronic states, total electronic energies, zero point energies (ϵ_0), dimer formation energies ($E_{formation}$), electron affinities (EA), ionization potentials (IP), and HOMO-LUMO gap (Δ) of DPA dimers. Total electronic energies E are relative to the 2DPA1 ground state energy of -34.038310 keV.

dimer	state	E (eV)	ϵ_0 (eV)	$E_{formation}$ (eV)	EA (eV)	IP (eV)	Δ (eV)
2DPA1	1A_1	0	6.514	0.818	1.264	8.928	5.089
2DPA3	1A_1	0.042	6.510	0.875	1.255	8.917	5.084
2DPA4	1A_1	0.292	6.498	0.814	0.813	8.553	5.353
2DPA5	1A_1	0.351	6.492	0.898	0.804	8.580	5.388
2DPA6	1A_1	0.501	6.482	0.908	0.775	8.695	5.551

calculation of DPA4, DPA5, and DPA6. The initial guess for the lattice constant in the y-direction is 5.571 Å, again taken from experiments[14] of crystalline DPA. The energies of the optimized sheets are nearly degenerate with the 2DPA4 sheet having the lowest total energy. The DPA5 and DPA6 sheets have total energies of 0.022 and 0.041 eV above that of the DPA4 sheet, respectively. The 2-D optimization results agree with the crystal structure of previous experiments[14] and show that chains of DPA arrange themselves in rows within a plane as illustrated in Fig. 7. However, the calculation predicts larger unit cell lengths along the XY-plane than experiment. The optimized lattice constants are (16.398, 6.754), (16.376, 6.690), and (16.378, 6.611) Å for the DPA4, DPA5, and DPA6 2-D sheets, respectively. Finally, single point calculation of three-dimensional crystal structures of DPA4, DPA5, and DPA6 are calculated by stacking the optimized 2-D sheets on top of each other with an inter-plane distance $c = 3.77$ Å. The c lattice constant is again taken from experiments[14]. The energy ordering of the three structures is nearly identical to the 2-D case, with DPA5 and DPA6 crystal structures having total energies of 0.022 and 0.042 eV above that of the DPA4 crystal, respectively.

These DPA layered crystals are orthorhombic. The band structures of the three crystalline forms are then plotted along characteristic symmetry lines of the irreducible Brillouin zone[29] and shown in Fig. 8 for the DPA4 crystal. Nine occupied and nine unoccupied bands are plotted along the edges and two faces of one eighth of the irreducible Brillouin zone. All energies in Fig. 8 are referred to the Fermi energy level of the DPA crystal, which is computed by solving self-consistently the expression equating the number of electrons (N) to the sum of electron occupation probabilities (Fermi functions) of states composing the bands [30],

$$N = \sum_{\alpha=1}^{n_{band}} \sum_{k=1}^{n_k} \frac{2}{1 + e^{\frac{E_{\alpha k} - E_F}{k_B T}}} \quad (4)$$

where $n_{band} = 20$ is the number of bands, $n_k = 144$ is the number of k-points in each band, k_B is Boltzmann's constant, and $T = 300K$. Accuracies better than 0.001 eV were achieved in the determination of E_F . The calculated Fermi energy of the DPA4 crystal is -7.534 eV. As expected, this crystal is an insulator with indirect band gap of 4.84 eV and direct band gap of 5.02 eV. The DPA5 crystal has a Fermi energy of -7.679 eV, indirect band gap of 4.85 eV and direct band gap of 5.08 eV.

The Fermi energy of the DPA6 crystal is -7.770 eV and has an indirect band gap of 4.85 eV and a direct band gap of 5.15 eV.

5. V. Conclusion

The structures, energetics, and vibrational analyses of gas phase monomers and dimers of DPA have been calculated within the DFT B3LYP/6-31G(d) computational modeling frame. All structures were determined to exist only in singlet states as there was no stable triplet state. In the gas phase we predict that DPA1 is the most abundant isomer. Populations of DPA2 and DPA3 may also exist in the gas phase as those two isomers have almost degenerate ground states at ≈ 0.05 eV above the DPA1 structure. Ionization potentials of all these isomers are high and the HOMO-LUMO energy gap is substantial of about 5 eV. Transition states between five possible isomeric reactions were found plausible at high temperatures, demonstrating that the DPA1 $\rightarrow$ DPA3 and DPA4 $\rightarrow$ DPA5 reactions are energetically most favorable with a barriers of about 0.25 eV. The least favorable isomerization reaction is DPA1 $\rightarrow$ DPA4 with a barrier of 0.6 eV. Experiments of DPA in the gas phase are long overdue, and we expect that our predictions may lead to future experiments.

Clear differences exist between the vibrational spectra of the crystal-forming monomers of DPA (4, 5, and 6) and the lower energy monomers (1, 2, and 3) which we theorize to only exist in vapor and liquid phases. The most evident difference is the much larger IR intensity of the O-H scissoring modes at 1420 and 1440 cm^{-1} for the 1, 2, and 3 isomers. Another important difference appears for the C-H scissoring modes at 1160 and 1200 cm^{-1} which are more intense for the crystal-forming monomers than for the 1, 2, and 3 forms. We predict that only DPA4, DPA5 and DPA6 can aggregate in supramolecular linear chains. When these chains are laid parallel lengthwise on a plane, we have demonstrated that planar sheets are stable, well bound 2-D structures.

The crystal forming DPA4, DPA5, and DPA6 originate three crystal polytypes, all three being lattices formed by stacking DPA sheets. These three crystals are basically degenerate in energy. Their orthorhombic crystal structure is quite similar and all three polytypes are insulators. DPA5 and DPA6 crystals have been mentioned in the literature [14, 13]. The three now confirmed crystal structures of DPA4, DPA5 and DPA6 deserve future experimental study. During the first step of germination spore-specific, DPA is released[31]. DPA polytypes may react

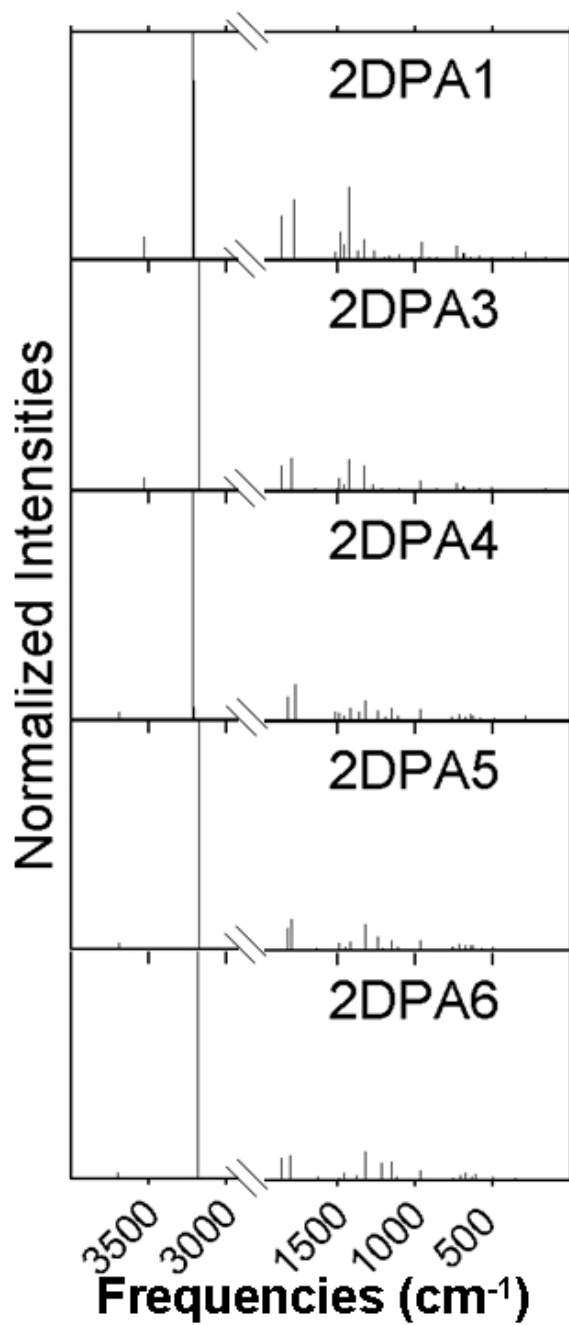


Figure 6: Calculated infrared spectra of the five dimers of DPA in the gas phase.

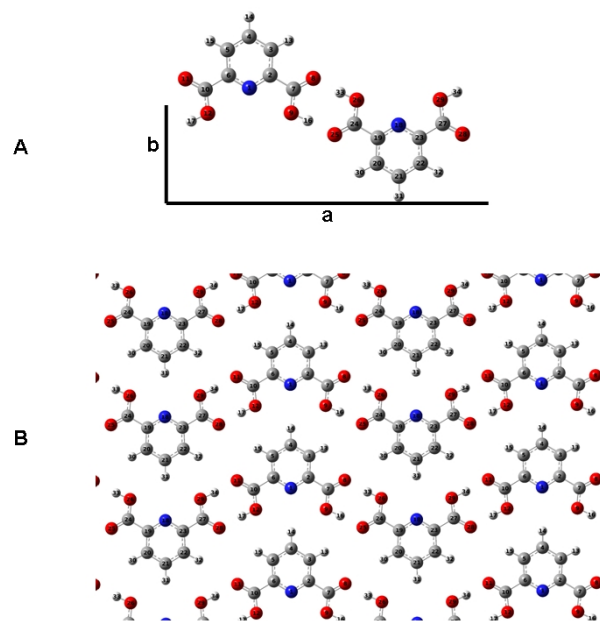


Figure 7: Sheet formation of DPA4 in two dimensions showing the arrangement of parallel chains in the plane. (a) Optimized unit cell with lattice constants of $a = 16.398 \text{ Å}$ and $b = 6.754 \text{ Å}$; (b) a 2×2 supercell.

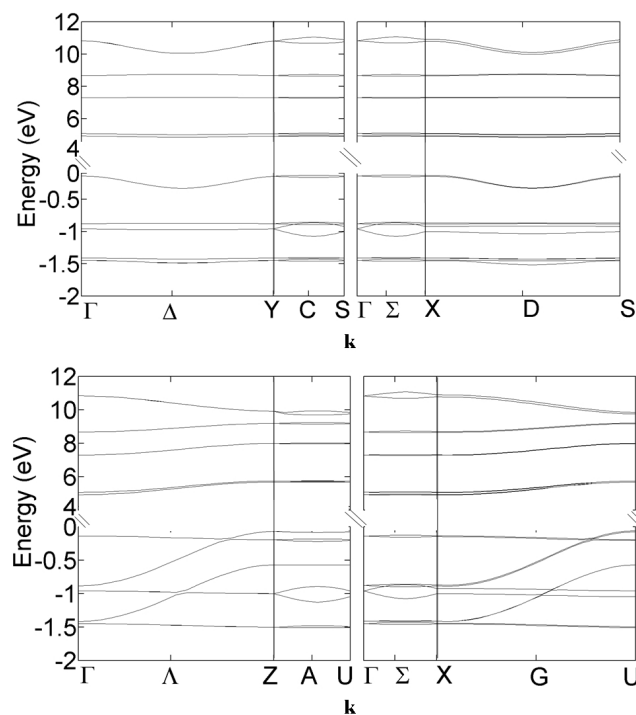


Figure 8: Band structure of the orthorhombic DPA4 crystal calculated along symmetry lines Δ , C, Σ , D (top) and symmetry lines Δ , A, Σ , G (bottom).

differently with rare earths to form distinctive fluorescent complexes. Speculating that different markers may be devised with these three crystals, our predictions may help tailoring DPA for measuring the specificity of germinated spores.

Acknowledgments

This work was partially supported under the National Science Foundation grant CHE-0626111. We acknowledge the Teragrid allocation award CHE100033 and the USACE ERDC MSRC for the extensive software and computational resources.

Appendix

Bond lengths and angles pertaining to the geometry of the six DPA isomers are given in Tables 5 and 6. There are small structural variations between the six structures. The main difference between them is the location of the hydrogens numbered 16 and 17 (see Figure 1). The spectra of one-electron molecular orbital levels are plotted in Figure 9 for all six isomers in the gas phase. This figure illustrates differences of the density of states between the six isomers. Table 7 contains the IR vibrational spectra of isomers DPA2.

References

- [1] J. Powell, R. Strange, Biochemical changes occurring during the germination of bacterial spores, *Biochem. J.* 54 (1953) 205–209.
- [2] J. Powell, Isolation of dipicolinic acid from spores of *Bacillus megatherium*, *Biochem. J.* 54 (1953) 210–211.
- [3] W. G. Murrell, The biochemistry of the bacterial endospore, *Advances in Microbial Physiology* 1 (1967) 133–251.
- [4] T. A. Slieman, W. L. Nicholson, Role of dipicolinic acid in survival of *Bacillus subtilis* spores exposed to artificial and solar UV radiation, *Appl. Environ. Microbiol.* 67 (2001) 1274–1279.
- [5] S. Matys, J. Raff, U. Soltmann, S. Selenska-Pobell, H. Btcher, W. Pompe, Calcium dipicolinate induced germination of *Bacillus* spores embedded in thin silica layers: Novel perspectives for the usage of biocers, *Chem. Mater.* 16 (2004) 5549–5551.
- [6] D. Rosen, C. Sharpless, L. McGown, Bacterial spore detection and determination by use of terbium dipicolinate photoluminescence, *Anal. Chem.* 69 (1997) 1082–1085.
- [7] P. M. Pellegrino, J. Nicholas F. Fell, D. L. Rosen, J. B. Gillespie, Bacterial endospore detection using terbium dipicolinate photoluminescence in the presence of chemical and biological materials, *Anal. Chem.* 70 (1998) 1755–1760.
- [8] A. A. Hindle, E. A. H. Hall, Dipicolinic acid (dpa) assay revisited and appraised for spore detection, *Analyst* 124 (1999) 1599–1604.
- [9] J. Anderson, J. Nelson, C. Reynolds, D. Ringelberg, G. Tepper, D. Pestov, Steady-state and frequency-domain lifetime measurements of an activated molecular imprinted polymer imprinted to dipicolinic acid, *J. of Fluor.* 14 (2005) 269–274.
- [10] S. Sarasanandarajah, J. Kunnil, B. Bronk, L. Reinisch, Two-dimensional multiwavelength fluorescence spectra of dipicolinic acid and calcium dipicolinate, *Appl. Opt.* 44 (2005) 1182–1187.
- [11] R. Nudelman, N. Feay, M. Hirsch, S. Efrima, B. Bronk, Fluorescence of dipicolinic acid as a possible component of the observed UV emission spectra of bacterial spores, in: *SPIE Conference on Air Monitoring and Detection of Chemical and Biological Agents*, volume 3533, Boston, MA, pp. 190–195.
- [12] R. Nudelman, B. Bronk, S. Efrima, Fluorescence emission derived from dipicolinic acid, its sodium, and its calcium salts, *Appl. Spectrosc.* 54 (2000) 445–449.
- [13] P. Carmona, Vibrational spectra and structure of crystalline dipicolinic acid and calcium dipicolinate trihydrate, *Spectrochim. Acta* 36A (1980) 705–712.
- [14] V. Téllez, B. Gaytán, S. Bernés, E. Vergara, The supramolecular structure of pyridine-2,6-dicarboxylic acid, *Acta. Cryst. C* 58 (2002) o228–o230.
- [15] M. Grossel, A. Dwyer, M. Hursthouse, J. Orton, Polymorphism in pyridine-2,6-dicarboxylic acid: Competition between “robust” synthons, *Cryst. Eng. Comm.* 8 (2006) 123–128.
- [16] K. Edgecombe, D. Weaver, J. V.H. Smith, Electronic structure analysis of compounds of interest in drug design: mono- and dicarboxylated pyridines, *Can. J. Chem.* 72 (1994) 1388–1403.
- [17] H. Hameka, J. O. Jensen, L. J. Jensen, C. N. Merrow, C. P. Vlahacos, Theoretical studies of the fluorescence of dipicolinic acid and its anion, *J. Mol. Struct. (Theochem)* 365 (1996) 131–141.
- [18] J. Xie, V. S. Jr., R. Allen, Spectroscopic properties of dipicolinic acid and its dianion, *Chem. Phys.* 322 (2006) 254–268.
- [19] C. Lee, W. Yang, R. Parr, Theory, *Phys. Rev. B* 37 (1988).
- [20] C. Peng, P. Y. Ayala, H. B. Schlegel, M. J. Frisch, Using redundant internal coordinates to optimize equilibrium geometries and transition states, *J. Comp. Chem.* 49 (1996) 49–56.
- [21] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, J. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, Gaussian 09 Revision A.1 (2009), Gaussian Inc., Wallingford, CT.
- [22] F. Takusagawa, K. Hirotsu, A. Shimada, The crystal structure of dipicolinic acid monohydrate, *Bull. Chem. Soc. Japan* 46 (1973) 2020–2027.
- [23] A. Kolomenskii, H. Schuessler, Raman spectra of dipicolinic acid in crystalline and liquid environments, *Spectrochim. Acta, Part A* 61 (2005) 647–651.
- [24] P. W. Ayers, W. Yang, L. J. Bartolotti, Fukui function, in: *Chemical Reactivity Theory: A Density Functional View*, CRC Press, Boca Raton, 2009, pp. 255–267.
- [25] K. Fukui, Role of frontier orbitals in chemical reactions, *Science* 217 (1982) 747–784.
- [26] C. Peng, P. Ayala, H. Schlegel, M. Frisch, Using redundant internal coordinates to optimize equilibrium geometries and transition states, *J. Comp. Chem.* 17 (1996) 49–56.
- [27] C. Peng, H. Schlegel, Combining synchronous transit and quasi-newton methods to find transition states, *Isr. J. Chem.* 33 (1993) 449–454.
- [28] F. Dollish, W. Fateley, F. Bentley, *Characteristic Raman Frequencies of Organic Compounds*, Wiley, New York, 1974.
- [29] T. Grandke, L. Ley, Angular-resolved UV photoemission and the band structure of *ges*, *Phys. Rev. B* 16 (1977) 832–842.
- [30] Y. Dai, S. Chowdhury, E. Blaisten-Barojas, Density functional theory study of the structure and energetics of negatively charged oligopyrroles, *Int. J. of Quantum Chem.* 111 (2011) in press.
- [31] P. Setlow, Spore germination, *Curr. Opin. in Microbiol.* 6 (2003) 550–556.

Appendix A. Appendix

Table A.5: Bond lengths (in Å) of six optimized structures of DPA isomers.

Bond length	DPA1	DPA2	DPA3	DPA4	DPA5	DPA6
N1-C2	1.338	1.342	1.339	1.337	1.337	1.336
C2-C3	1.399	1.396	1.400	1.401	1.402	1.403
C3-C4	1.394	1.393	1.396	1.392	1.394	1.392
C4-C5	1.393	1.393	1.392	1.392	1.391	1.392
C6-N1	1.337	1.342	1.336	1.337	1.334	1.336
C7-C2	1.500	1.510	1.503	1.502	1.505	1.505
C7-O8	1.214	1.208	1.208	1.216	1.207	1.206
C7-O9	1.347	1.343	1.357	1.345	1.361	1.362
C6-C10	1.511	1.510	1.512	1.502	1.502	1.505
C10-O11	1.210	1.208	1.210	1.216	1.216	1.206
C10-O12	1.341	1.343	1.340	1.345	1.344	1.362
C3-H13	1.084	1.084	1.083	1.084	1.083	1.083
C4-H14	1.086	1.086	1.086	1.086	1.086	1.086
C5-H15	1.084	1.084	1.084	1.084	1.084	1.083
O8-H16	0.976	0.978	0.975	0.976	0.975	0.975
O9-H17	0.984	0.978	0.984	0.976	0.976	0.975

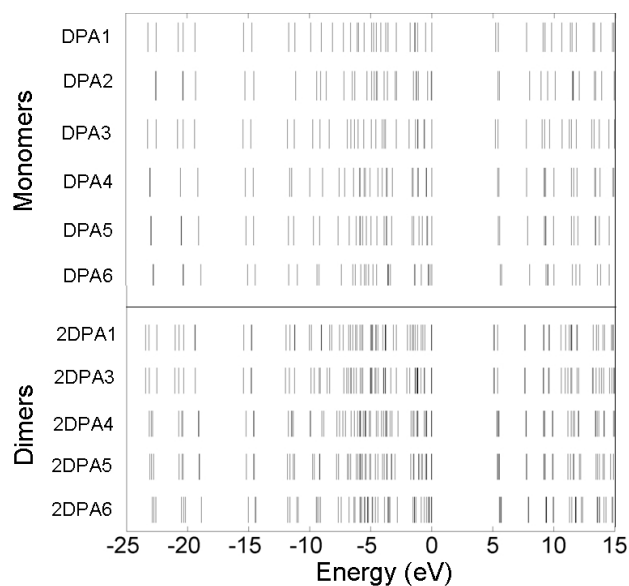


Figure A.9: Spectrum of occupied and virtual molecular orbital levels for DPA isomers. Energies are relative to the HOMO.

Table A.6: Angles (in deg) six optimized optimized structure of DPA isomers.

Angle	DPA1	DPA2	DPA3	DPA4	DPA5	DPA6
N1-C2-C3	122.69	122.91	122.38	123.60	123.24	123.29
C2-C3-C4	118.63	118.49	118.65	118.38	118.45	118.31
C3-C4-C5	119.00	118.98	119.13	118.68	118.80	118.90
C6-N1-C2	118.18	118.21	118.47	117.37	117.65	117.91
C7-C2-N1	118.82	117.41	115.26	118.66	115.31	115.37
O8-C7-C2	123.26	122.46	125.04	123.13	125.64	125.68
O9-C7-C2	113.28	114.72	111.74	113.63	111.59	111.56
C10-C6-N1	115.69	117.41	115.64	118.66	118.67	115.37
O11-C10-C6	122.79	122.46	122.67	123.13	123.04	125.68
O12-C10-C6	113.77	114.72	113.81	113.63	113.61	111.56
H13-C3-C2	119.13	118.85	119.98	119.23	120.13	120.20
H14-C4-C3	120.38	120.51	120.24	120.66	120.52	120.55
H15-C5-C4	122.75	122.66	122.82	122.39	122.44	121.49
H16-O9-C7	105.78	107.35	106.00	105.56	105.64	105.61
H17-O12-C10	106.70	107.35	106.89	105.56	105.66	105.61

Table A.7: Calculated vibrational spectra of DPA2, DPA3, DPA4, DPA5 and DPA6 isomers.

DPA2 ν (cm ⁻¹)	DPA3 ν (cm ⁻¹)	DPA4 ν (cm ⁻¹)	DPA5 ν (cm ⁻¹)	DPA6 ν (cm ⁻¹)
3633	3699	3690	3701	3700
3617	3524	3690	3693	3700
3248	3250	3244	3248	3249
3247	3244	3242	3243	3248
3215	3211	3209	3209	3208
1868	1862	1820	1855	1862
1861	1851	1816	1818	1853
1647	1641	1637	1635	1635
1626	1632	1631	1631	1629
1504	1503	1502	1497	1490
1464	1475	1472	1475	1478
1427	1426	1429	1418	1383
1382	1387	1403	1380	1378
1343	1351	1343	1339	1335
1295	1276	1250	1245	1229
1229	1218	1233	1216	1212
1187	1195	1185	1193	1197
1168	1177	1159	1164	1170
1155	1150	1148	1147	1145
1103	1108	1108	1114	1117
1031	1025	1027	1024	1020
1024	1022	1016	1015	1013
975	965	977	969	960
897	890	890	882	873
859	858	867	863	860
779	794	808	806	804
764	767	765	762	760
750	740	732	728	724
690	736	732	727	721
671	703	659	651	650
653	662	651	649	642
648	642	642	640	637
611	614	612	600	592
579	567	563	555	545
486	486	464	470	476
474	464	460	457	455
440	437	432	432	432
377	389	389	393	399
357	350	357	350	342
247	261	253	255	258
177	173	171	167	163
163	152	150	148	147
143	132	134	136	139
76	83	56	52	43
57	48	48	38	33

Bibliography

Bibliography

- [1] C. Canosa-Mas, J. Duffy, M. King, K. Thompson, and R. Wayne, "The atmospheric chemistry of methyl salicylate reactions with atomic chlorine and with ozone," *Atmos. Environ.*, vol. 36, pp. 2201–2205, 2002.
- [2] V. Shulaev, P. Silverman, and I. Raskin, "Airborne signalling by methyl salicylate in plant pathogen resistance," *Nature*, vol. 385, pp. 718–721, 1997.
- [3] C. Smith, J. Anderson, B. Tatineni, and G. Tepper, "Optical bar code recognition of methyl salicylate (mes) for environmental monitoring using fluorescence resonance energy transfer (fret) on thin films," in *Proc. SPIE 6378 Chemical and Biological Sensors for Industrial and Environmental Monitoring II*, vol. 637811, 2006.
- [4] C. Smith, J. Anderson, R. Massaro, B. Tatineni, K. Kam, and G. Tepper, "Fluorescence resonance energy transfer based mcm-edta-tb³⁺-mes sensor," *Applied Spectroscopy*, vol. 62, pp. 604–610, 2008.
- [5] A. Weller, "ber die fluoreszenz der salizylsüre und verwandter verbindunge," *Naturwissenschaften*, vol. 42, no. 7, pp. 175–176, 1955.
- [6] ———, "Inermolekularer protonenbergang im angeregten zustand," *Zeitschrift fr Elektrochemie*, vol. 60, p. 1144, 1956.
- [7] ———, "Fast reactions of excited molecules," *Progress in Reaction Kinetics*, vol. 1, p. 188, 1961.
- [8] B. Zadorozhnyi and I. Ishchenko, "Hydrogen bond energies and shifts of the stretching vibration bands of c=o groups," *Optics and Spectroscopy*, vol. 19, p. 306, 1965.
- [9] K. Law and J. Shoham, "Photoinduced proton transfers in methyl salicylate and methyl 2-hydroxy-3-naphthoate," *J. Phys. Chem.*, vol. 98, pp. 3114–3120, 1994.
- [10] L. Helmbrook, J. Kenny, B. Kohler, and G. Scott, "Lowest excited singlet state of hydrogen-bonded methyl salicylate," *J. Phys. Chem.*, vol. 87, pp. 280–289, 1983.
- [11] A. Acuna, J. Catalan, and F. Toriblo, "Photon energy relaxatlon and thermal effects on gas-phase electronically excited methyl salicylate," *J. Phys. Chem.*, vol. 85, pp. 241–245, 1981.
- [12] R. Lopez-Delgado and S. Lazare, "Fluorescence properties of methyl salicylate in vapor, liquid, and solution," *J. Phys. Chem.*, vol. 85, pp. 763–768, 1981.

- [13] A. Acuna and et al., “Dual fluorescence and ground state equilibria in methyl salicylate, methyl 3-chlorosalicylate, and methyl 3-tert-butylsalicylate,” *J. Phys. Chem.*, vol. 84, pp. 629–631, 1980.
- [14] W. Klöpffer and G. Kaufmann, “Absorption and fluorescence spectra of methyl salicylate in the vapor phase,” *J. Lumin.*, vol. 20, pp. 283–289, 1979.
- [15] M. Sanchez-Cabezudo, J. D. Paz, J. Catalan, and F. Amat-Guerri, “Photoinduced intramolecular proton transfer in methyl salicylates: a theoretical study with spectroscopic support,” *J. Mol. Struct.*, vol. 131, pp. 277–289, 1985.
- [16] E. Orton, M. Morgan, and G. Pimentel, “Photorotamerization of methyl salicylate and related compounds in cryogenic matrices,” *J. Phys. Chem.*, vol. 94, pp. 7936–7943, 1990.
- [17] J. Catalan and A. Macias, “Dipole moment, isomerization, and intramolecular hydrogen bond in some benzene derivatives (computations),” *J. Mol. Struct.*, vol. 38, pp. 209–220, 1977.
- [18] J. Catalan and C. Diaz, “Induction of triplet-state emission of the transient proton-transfer keto form of methyl salicylate by heavy-atom perturbation,” *J. Phys. Chem. A*, vol. 102, pp. 323–328, 1998.
- [19] J. L. Herek, S. Pedersen, L. Bañares, and A. H. Zewail, “Femtosecond real-time probing of reactions. ix. hydrogen-atom transfer,” *J. Chem. Phys.*, vol. 97, pp. 9046–9061, 1992.
- [20] P. Felker, W. Lambert, and A. Zewail, “Picosecond excitation of jet-cooled hydrogen-bonded systems: Dispersed fluorescence and time-resolved studies of methyl salicylate,” *J. Phys. Chem.*, vol. 77, pp. 1603–1605, 1982.
- [21] K. Smith and K. Kaufmann, “Picosecond studies of intramolecular proton transfer,” *J. Phys. Chem.*, vol. 82, pp. 2286–2291, 1978.
- [22] J. Goodman and L. Brus, “Proton transfer and tautomerism in an excited state of methyl salicylate,” *J. Am. Chem. Soc.*, vol. 100, pp. 7472–7474, 1978.
- [23] W. Klöpffer and G. Naundorf, “On the fluorescence of methyl salicylate in hydrogen bonding solvents,” *J. Lumin.*, vol. 8, pp. 457–461, 1974.
- [24] E. Kosower and H. Dodiuk, “Multiple fluorescences iii. methyl 2,6-dihydroxybenzoate and methyl salicylate,” *J. Lumin.*, vol. 11, pp. 249–254, 1975.
- [25] E. Canadell, J. Catalan, and J. Fernandez-Alonso, “Theoretical study of the intramolecular hydrogen bonding in benzene derivatives,” *Advances in Molecular Relaxation and Interaction Processes*, vol. 12, p. 265, 1978.
- [26] J. Coe, B. Levine, and T. Martinez, “Ab initio molecular dynamics of excited-state intramolecular proton transfer using multireference perturbation theory,” *J. Phys. Chem. A*, vol. 111, pp. 11 302–11 310, 2007.

- [27] J. Powell and R. Strange, "Biochemical changes occurring during the germination of bacterial spores," *Biochem. J.*, vol. 54, pp. 205–209, 1953.
- [28] J. Powell, "Isolation of dipicolinic acid from spores of bacillus megatherium," *Biochem. J.*, vol. 54, pp. 210–211, 1953.
- [29] G. Gould and A. Hurst, *The Bacterial Spore*. London: Academic Press, 1969.
- [30] S. Matys and et al., "Calcium dipicolinate induced germination of bacillus spores embedded in thin silica layers: Novel perspectives for the usage of biocers," *Chemistry of Materials*, vol. 16, pp. 5549–5551, 2004.
- [31] D. Rosen, C. Sharpless, and L. McGown, "Bacterial spore detection and determination by use of terbium dipicolinate photoluminescence," *Anal. Chem.*, vol. 69, pp. 1082–1085, 1997.
- [32] P. M. Pellegrino, J. a. D. L. R. Nicholas F. Fell, and J. B. Gillespie, "Bacterial endospore detection using terbium dipicolinate photoluminescence in the presence of chemical and biological materials," *Anal. Chem.*, vol. 70, pp. 1755–1760, 1998.
- [33] A. A. Hindle and E. A. H. Hall, "Dipicolinic acid (dpa) assay revisited and appraised for spore detection," *Analyst*, vol. 124, pp. 1599–1604, 1999.
- [34] J. Anderson, J. Nelson, C. Reynolds, D. Ringelberg, G. Tepper, and D. Pestov, "Steady-state and frequency-domain lifetime measurements of an activated molecular imprinted polymer imprinted to dipicolinic acid," *J. of Fluor.*, vol. 14, pp. 269–274, 2005.
- [35] S. Sarasanandarajah, J. Kunnil, B. Bronk, and L. Reinisch, "Two-dimensional multi-wavelength fluorescence spectra of dipicolinic acid and calcium dipicolinate," *Applied Optics*, vol. 44, pp. 1182–1187, 2005.
- [36] R. Nudelman, N. Feay, M. Hirsch, S. Efrima, and B. Bronk, "Fluorescence of dipicolinic acid as a possible component of the observed uv emission spectra of bacterial spores," in *SPIE Conference on Air Monitoring and Detection of Chemical and Biological Agents*, vol. 3533, Boston, MA, 1998, pp. 190–195.
- [37] R. Nudelman, B. Bronk, and S. Efrima, "Fluorescence emission derived from dipicolinic acid, its sodium, and its calcium salts," *Applied Spectroscopy*, vol. 54, pp. 445–449, 2000.
- [38] P. Carmona, "Vibrational spectra and structure of crystalline dipicolinic acid and calcium dipicolinate trihydrate," *Spectrochimica Acta*, vol. 36A, pp. 705–712, 1980.
- [39] V. Téllez, B. Gaytán, S. Bernés, and E. Vergara, "The supramolecular structure of pyridine-2,6-dicarboxylic acid," *Acta. Cryst.*, vol. C58, pp. o228–o230, 2002.
- [40] H. Hamelka and et al., "Theoretical studies of the fluorescence of dipicolinic acid and its anion," *Journal of Molecular Structure (Theochem)*, vol. 365, pp. 131–141, 1996.
- [41] J. Xie, V. S. Jr., and R. Allen, "Spectroscopic properties of dipicolinic acid and its dianion," *Chemical Physics*, vol. 322, pp. 254–268, 2006.

- [42] S. Vosko, L. Wilk, and M. Nusair, “Accurate spin-dependent electron liquid correlation energies for local spin density calculations: a critical analysis,” *Canadian Journal of Physics*, vol. 58, pp. 1200–1211, 1980.
- [43] A. D. Becke, “Density-functional thermochemistry. iii. the role of exact exchange,” *J. Chem. Phys.*, vol. 98, pp. 5648–5652, 1993.
- [44] J. Perdew, *Electronic Structure of Solids '91*. Berlin: Akademie Berlin, 1991, ch. 11.
- [45] J. Perdew, J. Chevary, and S. Vosko, “Atoms, molecules, solids, and surfaces: Applications of the generalized gradient approximation for exchange and correlation,” *Phys. Rev. B*, vol. 46, p. 6671, 1992.
- [46] J. P. Perdew, J. A. Chevary, S. H. Vosko, K. A. Jackson, M. R. Pederson, D. J. Singh, and C. Fiolhais, “Erratum: Atoms, molecules, solids, and surfaces - applications of the generalized gradient approximation for exchange and correlation,” *Phys. Rev. B*, vol. 48, p. 4978, 1993.
- [47] J. Perdew, K. Burke, and Y. Wang, “Generalized gradient approximation for the exchange-correlation hole of a many-electron system,” *Phys. Rev. B*, vol. 54, pp. 16 533–16 539, 1996.
- [48] K. Burke, J. P. Perdew, and Y. Wang, *Electronic Density Functional Theory: Recent Progress and New Directions*. Plenum, 1998.
- [49] C. Lee, W. Yang, and R. Parr, “Development of the colle-salvetti correlation-energy formula into a functional of the electron density,” *Phys. Rev. B*, vol. 37, pp. 785–789, 1988.
- [50] B. Miehlich, A. Savin, H. Stoll, and H. Preuss, “Results obtained with the correlation-energy density functionals of becke and lee, yang and parr,” *Chem. Phys. Lett.*, vol. 157, pp. 200–206, 1989.
- [51] E. Runge and E. Gross, “Density-functional theory for time-dependent systems,” *Phys. Rev. Lett.*, vol. 52, pp. 997–1000, 1984.
- [52] C. J. Jamorski and M. E. Casida, “Time-dependent density-functional theory investigation of the fluorescence behavior as a function of alkyl chain size for the 4-(n,n-dimethylamino)benzonitrile-like donor-acceptor systems 4-(n,n-diethylamino)benzonitrile and 4-(n,n-diisopropylamino)benzonitrile,” *J. Phys. Chem. B*, vol. 108, pp. 7132–7141, 2004.
- [53] K. A. Nguyen, P. N. Day, and R. Pachter, “Effects of solvation on one- and two-photon spectra of coumarin derivatives: A time-dependent density functional theory study,” *The Journal of Chemical Physics*, vol. 126, p. 094303, 2007.
- [54] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta,

- F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, . Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, "Gaussian 09 Revision A.1," gaussian Inc. Wallingford CT 2009.
- [55] P. Pulay, G. Fogarasi, F. Pang, and J. E. Boggs, "Systematic ab initio gradient calculation of molecular geometries, force constants, and dipole moment derivatives," *J. Am. Chem. Soc.*, vol. 101, pp. 2550–2560, 1979.
 - [56] P. Pulay and G. Fogarasi, "Geometry optimization in redundant internal coordinates," *J. Chem. Phys.*, vol. 96, pp. 2856–2860, 1992.
 - [57] C. Peng and H. Schlegel, "Combining synchronous transit and quasi-newton methods to find transition states," *Isr. J. Chem.*, vol. 33, pp. 449–454, 1993.
 - [58] C. Peng, P. Ayala, H. Schlegel, and M. Frisch, "Using redundant internal coordinates to optimize equilibrium geometries and transition states," *J. Comp. Chem.*, vol. 17, pp. 49–56, 1996.
 - [59] G. Fogarasi, X. Zhou, P. W. Taylor, and P. Pulay, "The calculation of ab initio molecular geometries: Efficient optimization by natural internal coordinates and empirical correction by offset forces," *J. Am. Chem. Soc.*, vol. 114, pp. 8191–8201, 1992.
 - [60] H. B. Schlegel, "Estimating the hessian for gradient-type geometry optimizations," *Theor. Chim. Acta*, vol. 66, pp. 333–340, 1984.
 - [61] T. H. Fischer and J. Almlof, "General methods for geometry and wave function optimization," *J. Phys. Chem.*, vol. 96, pp. 9768–9774, 1992.
 - [62] E. Wilson, J. Decius, and P. Cross, *Molecular Vibrations*. New York: McGraw-Hill, 1955.
 - [63] M. Powell, "Recent advances in unconstrained optimization," *Mathematical Programming*, vol. 1, pp. 26–57, 1971.
 - [64] J. M. Bofill, "Updated hessian matrix and the restricted step method for locating transition structures," *J. Comp. Chem.*, vol. 15, pp. 1–11, 1994.
 - [65] J. Simons, P. Jorgensen, H. Taylor, and J. Ozment, "Walking on potential energy surfaces," *J. Phys. Chem.*, vol. 87, pp. 2745–2753, 1983.
 - [66] J. Baker, "An algorithm for geometry optimization without analytical gradients," *J. Comp. Chem.*, vol. 8, pp. 563–574, 1987.
 - [67] R. Fletcher, *Practical Methods of Optimization*. New York: Wiley, 1980.
 - [68] J. Golab, D. Yeager, and P. Jorgensen, "Proper characterization of mc scf stationary-points," *Chem. Phys.*, vol. 78, pp. 175–199, 1983.

- [69] J. W. Ochterski, *Vibrational Analysis in Gaussian*, help@gaussian.com, 1999.
- [70] I. N. Levine, *Physical Chemistry*. New York: McGraw Hill, 1978.
- [71] L. Landau and E. Lifshitz, *Statistical Physics, 3rd Edition Part 1*. Oxford: Butterworth-Heinemann, 1996.
- [72] K. Fukui, "The path of chemical-reactions," *Acc. Chem. Res.*, vol. 14, pp. 363–368, 1981.
- [73] H. Hratchian and H. Schlegel, *Theory and Applications of Computational Chemistry: The First 40 Years*. Amsterdam: Elsevier, 2005, pp. 195–249.
- [74] E. Hairer, S. P. Norsett, and G. Wanner, *Solving ordinary differential equations I: Nonstiff problems*. Berlin: Springer-Verlag, 1993.
- [75] W. Sneader, *Drug Discovery: A History*. West Sussex, England: John Wiley & Sons, Ltd, 2005.
- [76] S. Melandri, B. M. Giuliano, A. Maris, L. B. Favero, P. Ottaviani, B. Velino, and W. Caminati, "Methylsalicylate: A rotational spectroscopy study," *J. Phys. Chem. A*, vol. 111, pp. 9076–9079, 2007.
- [77] H. T. Varghese, C. Y. Panicker, D. Philip, J. R. Mannektla, and S. Inamdar, "Ir, raman and sers studies of methyl salicylate," *Spectrochimica Acta Part A*, vol. 66, pp. 959–963, 2007.
- [78] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople, "Gaussian 03, Revision C.02," Gaussian, Inc., Wallingford, CT, 2004.
- [79] R. Ditchfield, W. Hehre, and J. Pople, "Self-consistent molecular-orbital methods. ix. an extended gaussian-type basis for molecular-orbital studies of organic molecules," *J. Chem. Phys.*, vol. 54, pp. 724–728, 1971.
- [80] R. Krishnan, J. Binkley, R. Seeger, and J. Pople, "Self-consistent molecular orbital methods. xx. a basis set for correlated wave functions," *J. Chem. Phys.*, vol. 72, pp. 650–654, 1980.

- [81] J. Tomasi, B. Mennucci, and E. Cancès, “The ief version of the pcm solvation method: an overview of a new method addressed to study molecular solutes at the qm ab initio level,” *Journal of Molecular Structure (Theochem)*, vol. 464, pp. 211–226, 1999.
- [82] J. Dean, *Lange’s Handbook of Chemistry*. New York: McGraw-Hill, 1992.
- [83] P. Linstrom and W. Mallard, *NIST Chemistry WebBook*, NIST Standard Reference Database <http://webbook.nist.gov>, 1999.
- [84] B. Smith, *Infrared Spectral Interpretation: A Systematic Approach*. Boca Raton, FL: CRC Press, 1999.
- [85] N. Roeges, *A Guide to the Complete Interpretation of Infrared Spectra of Organic Structures*. New York: Wiley, 1994.
- [86] J. W. Mirick, C.-H. Chien, and E. Blaisten-Barojas, “Electronic structure of calcium clusters,” *Phys. Rev. A*, vol. 63, p. 023202, 2001.
- [87] C. Gonzalez and H. B. Schlegel, “Reaction path following in mass-weighted internal coordinates,” *J. Phys. Chem.*, vol. 94, pp. 5523–5527, 1990.
- [88] A. McLean and G. Chandler, “Contracted gaussian-basis sets for molecular calculations. 1. 2nd row atoms, $z=11-18$,” *J. Chem. Phys.*, vol. 72, pp. 5639–5648, 1980.
- [89] K. Raghavachari, J. S. Binkley, R. Seeger, and J. A. Pople, “Self-consistent molecular orbital methods. 20. basis set for correlated wave-functions,” *J. Chem. Phys.*, vol. 72, pp. 650–654, 1980.
- [90] R. D. Massaro, Y. Dai, and E. Blaisten-Barojas, “Energetics and vibrational analysis of methyl salicylate isomers,” *J. Phys. Chem. A*, vol. 113, pp. 10 385–10 390, 2009.
- [91] P. F. Bernath, *Spectra of Atoms and Molecules*. New York: Oxford University Press, 1995.
- [92] E. Condon and G. Shortley, *The Theory of Atomic Spectra*. Cambridge: Cambridge University Press, 1935.
- [93] Y. Shigemitsu, K. Komiya, N. Mizuyama, and Y. Tominaga, “Td-dft investigation on the electronic spectra of novel n-methylmaleimides linked with indolizine ring system,” *Journal of Molecular Structure*, vol. 855, pp. 92–101, 2008.
- [94] D. Jacquemin, E. A. Perpète, G. Scalmani, M. J. Frisch, X. Assfeld, I. Ciofini, and C. Adamo, “Time-dependent density functional theory investigation of the absorption, fluorescence, and phosphorescence spectra of solvated coumarins,” *The Journal of Chemical Physics*, vol. 125, p. 164324, 2006.
- [95] G. Scalmani, M. J. Frisch, B. Mennucci, J. Tomasi, R. Cammi, and V. Barone, “Geometries and properties of excited states in the gas phase and in solution: Theory and application of a time-dependent density functional theory polarizable continuum model,” *J. Chem. Phys.*, vol. 124, p. 094107, 2006.
- [96] A. Siegman, *Lasers*. Sausalito, CA: University Science Books, 1986.

- [97] S. Udo, "Studies on the constituents of "natto", the fermented soybeans. part i," *J. Agr. Chem. Soc. Japan*, vol. 12, pp. 386–394, 1936.
- [98] F. Takusagawa, K. Hirotsu, and A. Shimada, "The crystal structure of dipicolinic acid monohydrate," *Bull. Chem. Soc. Japan*, vol. 46, pp. 2020–2027, 1973.
- [99] A. Kolomenskii and H. Schuessler, "Raman spectra of dipicolinic acid in crystalline and liquid environments," *Spectrochimica Acta Part A*, vol. 61, pp. 647–651, 2005.
- [100] P. W. Ayers, W. Yang, and L. J. Bartolotti, "Fukui function," in *Chemical Reactivity Theory: A Density Functional View*. Boca Raton: CRC Press, 2009, ch. 18, pp. 255–267.
- [101] K. Fukui, *Theory of Orientation and Stereoselection*. Berlin: Springer, 1973.
- [102] ———, "Role of frontier orbitals in chemical reactions," *Science*, vol. 217, pp. 747–784, 1982.
- [103] H. B. Schlegel, "Optimization of equilibrium geometries and transition structures," *J. Comp. Chem.*, vol. 3, pp. 214–218, 1982.
- [104] M. Grossel, A. Dwyer, M. Hursthouse, and J. Orton, "Polymorphism in pyridine-2,6-dicarboxylic acid:competition between "robust" synthons," *CrystEngComm*, vol. 8, pp. 123–128, 2006.
- [105] T. Grandke and L. Ley, "Angular-resolved uv photoemission and the band structure of ges," *Physical Review B*, vol. 16, pp. 832–842, 1977.
- [106] Y. Dai, S. Chowdhury, and E. Blaisten-Barojas, "Density functional theory study of the structure and energetics of negatively charged oligopyrroles," *International Journal of Quantum Chemistry*, vol. 29 Jun 2010, pp. 1–11, 2010.
- [107] F. Dollish, W. Fateley, and F. Bentley, *Characteristic Raman Frequencies of Organic Compounds*. New York: Wiley, 1974.

Curriculum Vitae

Richard D. Massaro received his Bachelor of Science degree in Physics from James Madison University in 2001. In 2004, he graduated from Boston University with a Master of Arts in Astronomy. He began working for the United States Army Corps of Engineers in 2004 as a Physical Scientist. In 2005, he enrolled in the Computational Science and Informatics Ph.D. program at George Mason University. In 2008, he was advanced to Ph.D. candidacy.

His relevant publications include:

Richard D. Massaro, Yafei Dai, and Estela Blaisten-Barojas, “*Energetics and Vibrational Analysis of Methyl Salicylate Isomers*”, J. Phys. Chem. A, 113, 10385-10390, 2009.

Richard D. Massaro and Estela Blaisten-Barojas, “*Density Functional Theory Study of Dipicolinic Acid Isomers and Crystalline Polytypes*”, Comp. and Theor. Chem. [submitted], 2011.

Richard D. Massaro and Estela Blaisten-Barojas, “*Theoretical Investigation of the Photo-physics of Methyl Salicylate Isomers*”, J. Chem. Phys. [submitted], 2011.

Presentations at scientific conferences include:

Richard D. Massaro and Clint Smith, “*Density Functional Theory Studies of Methyl Salicylate*”, U.S. Army Corps of Engineers Research and Development Conference, Nov 17-19, 2009.