

**VIBRATIONAL SPECTRUM, AB INITIO CALCULATIONS,  
CONFORMATIONAL STABILITIES AND ASSIGNMENT OF  
FUNDAMENTALS OF SMALL FLEXIBLE MOLECULES**

A Dissertation Presented

by

ARTHUR JAMES LAPLANTE

Submitted to the Graduate School of the  
University of Massachusetts Amherst in partial fulfillment  
of the requirements for the degree of

DOCTOR OF PHILOSOPHY

MAY 2010

Department of Chemistry

UMI Number: 3409616

All rights reserved

INFORMATION TO ALL USERS

The quality of this reproduction is dependent upon the quality of the copy submitted.

In the unlikely event that the author did not send a complete manuscript and there are missing pages, these will be noted. Also, if material had to be removed, a note will indicate the deletion.

UMI<sup>®</sup>

Dissertation Publishing

UMI 3409616

Copyright 2010 by ProQuest LLC.

All rights reserved. This edition of the work is protected against unauthorized copying under Title 17, United States Code.

ProQuest<sup>®</sup>

ProQuest LLC  
789 East Eisenhower Parkway  
P.O. Box 1346  
Ann Arbor, MI 48106-1346

PREVIEW

© Copyright by Arthur James LaPlante 2010  
All Rights Reserved

**VIBRATIONAL SPECTRUM, AB INITIO CALCULATIONS,  
CONFORMATIONAL STABILITIES AND ASSIGNMENT OF  
FUNDAMENTALS OF SMALL FLEXIBLE MOLECULES**

A Dissertation Presented

by

Arthur James LaPlante

Approved as to style and content by:

---

Professor Howard D. Stidham, Chair

---

Professor Ricardo Metz, Member

---

Professor Edward Voigtman, Jr., Member

---

Professor Danny Schnell, Member

---

Craig T. Martin, Department Head  
Department of Chemistry

## **ACKNOWLEDGMENTS**

To Professor Howard D. Stidham without his patients this document would not have been possible and yes I did use the spell check.

PREVIEW

## **ABSTRACT**

### **VIBRATIONAL SPECTRUM, AB INITIO CALCULATIONS, CONFORMATIONAL STABILITIES AND ASSIGNMENT OF FUNDAMENTALS OF SMALL FLEXIBLE MOLECULES**

MAY 2010

Arthur James LaPlante, A.S., Central New England Collage

B.S., Worcester State College

M.S., University of Massachusetts Amherst

Ph.D., University of Massachusetts Amherst

Directed By: Professor Howard D. Stidham

Ab initio calculations were utilized to demonstrate the theory behind molecular properties and were correlated to actual spectroscopic results in the infrared and Raman. Symmetrical aspects of small flexible molecules were examined to determine how symmetry coordinates mix in the potential energy distribution and whether these are infrared and Raman active.

The difficulty is the spectroscopic landscape of the spectrum gets extremely complicated even in very small carbon chain dihalides. The example of 1,4-dichlorobutane is provided. The work here will provide a solid reference for future research as we have found in previous work that 1,2-dibromopropane, a sensitive compound, has in previous publications shown what looks to be degradation. Three other publications are in preparation allyldichlorosilane, n-butylgermane and n-butylsilane of which the two finial compounds have conformers with the same symmetry.

Instrumentation has been updated to be continually maintained and upgraded to be viable and competitive. Times for crystallizations of spectroscopic compounds for the IR and Raman cold cells can exceed 50-60 hours of continuous annealing. Modification and development of equipment allowed a level of automation and a much more precise temperature control at lower temperatures that would not have been possible before.

PREVIEW

## TABLE OF CONTENTS

	Page
ACKNOWLEDGMENTS .....	iv
ABSTRACT .....	v
LIST OF TABLES .....	ix
LIST OF FIGURES .....	xii
 CHAPTER	
1. INTRODUCTION .....	1
1.1 Introduction .....	1
1.2 Motivation .....	2
1.3 Background .....	3
1.4 References .....	14
 2. VIBRATIONAL SPECTRUM, AB INITIO CALCULATIONS, CONFORMATIONAL STABILITIES AND ASSIGNMENT OF FUNDAMENTALS OF THE C <sub>1</sub> CONFORMER OF 1,4-DICHLOROBUTANE.18	 18
2.1 Abstract .....	18
2.2 Introduction .....	19
2.3 Experimental .....	20
2.4 Calculations .....	21
2.5 Results and Discussion .....	21
2.6 Conclusion .....	29
2.7 References: .....	61
 3. VIBRATIONAL SPECTRUM, AB INITIO CALCULATIONS, CONFORMATIONAL STABILITIES AND ASSIGNMENT OF FUNDAMENTALS OF 1,2-DIBROMOPROPANE .....	 63
3.1 Abstract .....	63
3.2 Introduction .....	64
3.3 Experimental .....	65
3.4 Calculations .....	66
3.5 Results and Discussion .....	67
3.5.1 Calculations .....	67
3.5.2 Infrared and Raman .....	69
3.5.3 Assignments .....	69
3.5.4 Ab initio Comparison .....	71



3.5.5	Temperature Dependence of the Raman Spectrum .....	73
3.6	Conclusion .....	74
3.7	References.....	112
4.	VIBRATIONAL SPECTRUM, AB INITIO CALCULATIONS, CONFORMATIONAL STABILITIES AND ASSIGNMENTS OF THE FUNDAMENTALS OF THE C <sub>s</sub> CONFORMER OF N-BUTYLGERMANE. .	114
4.1	Abstract.....	114
4.2	Introduction.....	114
4.2	Experimental.....	115
4.3	Calculations .....	117
4.4	Results and Discussion .....	119
4.5	References.....	140
5.	VIBRATIONAL SPECTRUM, AB INITIO CALCULATIONS, CONFORMATIONAL STABILITIES AND ASSIGNMENTS OF THE FUNDAMENTALS OF THE C <sub>s</sub> CONFORMER OF N-BUTYLSILANE.....	141
5.1	Abstract.....	141
5.2	Introduction.....	141
5.3	Experimental.....	142
5.4	Calculations .....	142
5.5	Results and Discussion .....	143
5.6	Conclusion .....	145
5.7	References.....	183
6.	INSTRUMENTATION .....	184
7.	CONCLUSION.....	190
	BIBLIOGRAPHY .....	191

## LIST OF TABLES

Table	Page
1.1 Sum of conformations in small chain dihalide alkanes. ....	10
1.2 Point groups with corresponding symmetry species associated to 1,4-dichlorobutane .....	11
1.3 Conformational studies of n-Alkanes ( $C_nH_{2n+2}$ ). ....	12
1.4 Conformations of various halo-alkanes with some reference to the conformer found in the crystal. ....	13
2.1 The 27 configurations and 10 conformers of 1,4-dichlorobutane. ....	31
2.2 Observed infrared and Raman wavenumbers for 1,4-dichlorobutane. Assignments given in the last column refer to the annealed crystal, except for two bands that appear to be unique to the $C_{2h}$ conformer .....	32
2.3 Density functional calculated energies of optimized geometries of the nine stable or metastable conformers at various levels of the theory. Energies are given as $-(E + 1077)$ hartree, and were obtained by specifying "tight" on the command line of the program. ....	38
2.4 Restricted Hartree-Fock calculated energies with second order Moeller-Ploessett electron correlation of optimized geometries of the nine stable or metastable conformers at various levels of the theory. Energies are given as $-(E + 1076)$ hartree, and were obtained by specifying "tight" on the command line of the program. ....	39
2.5 Calculated relative energies in $cm^{-1}$ of the 9 metastable conformers of 1,4-dichlorobutane. ....	40
2.6 Relative abundances at room temperature calculated from ab initio energies in Table 3, expressed as mole fractions, assuming only the nine conformers displayed are present in the liquid. ....	41
2.7 Geometries of nine stable conformers of 1,4-dichlorobutane using the B3LYP/6-311+g(2d,2p) density functional. Distances are in Angstroms, angles in degrees and rotational constants in gigaHertz. ....	42
2.8 Dipole moments in Debye and relative energies in $cm^{-1}$ of the conformers according to B3LYP density functional calculations. ....	45

2.9	Symmetry coordinates for the GaG'/C <sub>i</sub> conformer. The same coordinates were used for the other eight conformers. The torsion angle variable $\tau$ refers to the central C-C bond. The torsion angle variables $\tau_1$ and $\tau_2$ refer to variations in chloromethyl group torsion angles. These coordinates correspond approximately to the frequencies in descending order, though mechanical interactions in conformers of other symmetry modify the order somewhat. The symmetry species of the C <sub>2h</sub> conformer is given in parentheses, and that of the C <sub>i</sub> conformer in the associated comment. ....	46
2.10	Calculated relative energies in cm <sup>-1</sup> of the 9 metastable conformers of 1,4-dichlorobutane. ....	48
3.1	Calculated relative energies in cm <sup>-1</sup> of the three optimized metastable conformers at various levels of theory for Restricted Hartree-Fock, second order Moeller-Ploessett electron correlation and density functional theory .....	76
3.2	Density functional calculated energies for optimized geometries of the three metastable conformers of 1,2-dibromopropane at various levels of theory. ....	77
3.3	Calculated relative energies in cm <sup>-1</sup> for the three conformers of 1,2-dibromopropane. ....	78
3.4	Observed infrared and Raman wavenumbers for 1,2-dibromopropane. ....	79
3.5	Optimized geometries, rotational constants, dipole moments, and energies for 1,2-dibromopropane at B3LYP/6-311++G(3DF,2PD). ....	90
3.6	Symmetry coordinates for 1,2-dibromopropane. ....	92
3.7a	Observed and calculated frequencies (cm <sup>-1</sup> ) and potential energy distribution for the A conformer of 1,2-dibromopropane. ....	94
3.7b	Observed and calculated frequencies (cm <sup>-1</sup> ) and potential energy distribution for the G conformer of 1,2-dibromopropane. ....	97
3.7c	Observed and calculated frequencies (cm <sup>-1</sup> ) and potential energy distribution for the G' conformer of 1,2-dibromopropane. ....	99
4.1	B3LYP energies in hartrees for the conformers of n-butylgermane. Relative energies in cm <sup>-1</sup> are shown below the mantissas. ....	122

4.2	Geometries of the five conformers of n-butylgermane using the B3LYP/6-311++g(2d,2p) density functional calculation. Distances are in Angstroms, angles in degrees and rotational constants in gigaHertz. ....	123
4.3	Observed infrared and Raman wavenumbers for n-butylgermane. Assignments given in the last column refer to the annealed crystal, and are thus for the aa conformer. ....	125
4.4	Local symmetry coordinates for the aa conformer of n-butylgermane. The same set of coordinates was used for all five conformers. In the approximate mode descriptions, ip = in plane and op = out of plane. The carbon atoms involved are denoted in parentheses. ....	130
4.5	Observed and calculated fundamentals ( $\text{cm}^{-1}$ ) and potential energy distribution (PED) for the aa conformer of n-butylgermane. ....	132
5.1	B3LYP/6-3 energies for the conformers of n-butylsilane in hartree and the difference from the aa conformer in $\text{cm}^{-1}$ . ....	146
5.2	Energies, mol-fractions and molecular volume calculations (keyword: SCRF) at B3LYP/6-311++g(2d,2p) for n-butylsilane. ....	148
5.3	Preliminary assignment of normal modes of vibration, observed and calculated frequencies ( $\text{cm}^{-1}$ ) and potential energy distribution for the aa conformer of n-butylsilane. ....	149
5.4	Observed infrared and Raman wavenumbers for n-butylsilane. ....	155
5.5	Local symmetry coordinates for the aa conformer of n-butylsilane. The same set of coordinates was used for all five conformers. In the approximate mode descriptions, ip = in plane and op = out of plane. The carbon atoms involved are denoted in parentheses. ....	173

## LIST OF FIGURES

Figures	Page
2.1	Conformers of 1,4-dichlorobutane.....51
2.2	Raman spectrum of 1,4-dichlorobutane. A, liquid. B, amorphous solid at 77 K. C, annealed polycrystalline solid at 77 K.....52
2.3	Mid-infrared spectrum of 1,4-dichlorobutane. A, vapor. B, liquid. C, amorphous solid near 77K. D, annealed polycrystalline solid near 77K.....53
2.4	Raman spectrum of the CH stretching region of 1,4-dichlorobutane. Upper trace, liquid at room temperature. Lower trace, annealed crystal at liquid nitrogen temperature.....54
2.5	Infrared spectrum of the CH stretching region of 1,4-dichlorobutane. A, gas at room temperature. B, liquid at room temperature. C, annealed polycrystalline mat at liquid nitrogen temperature.....55
2.6	Low frequency Raman spectrum of liquid 1,4-dichlorobutane. A, experiment. Calculated: B, composite. C, C <sub>i</sub> . D, C <sub>2</sub> . E, C <sub>2h</sub> . F, C <sub>1</sub> . G, C <sub>2a</sub> . H, C <sub>1a</sub> . I, C <sub>2b</sub> . J, C <sub>1b</sub> . K, C <sub>1c</sub> .....56
2.7	Low frequency infrared spectrum of liquid 1,4-dichlorobutane. A, experiment. Calculated: B, composite. C, C <sub>i</sub> . D, C <sub>2</sub> . E, C <sub>2h</sub> . F, C <sub>1</sub> . G, C <sub>2a</sub> . H, C <sub>1a</sub> . I, C <sub>2b</sub> . J, C <sub>1b</sub> . K, C <sub>1c</sub> .....57
2.8	Far infrared spectrum of 1,4-dichlorobutane. A. gas. B. liquid. C. Amorphous solid. D. Annealed crystal. ....58
2.9	Internal coordinates for the C <sub>2h</sub> conformer. Similar internal coordinates were used for each of the other eight conformers. ....59
2.10	Temperature dependence of the Raman spectrum of liquid 1,4-dichlorobutane from 200 to 1000 cm <sup>-1</sup> . Temperatures: A, 25 C. B, 0 C. C, -10 C. D, -20 C. E, -30 C. F, -35 C. G, -41 C. H, -45 C. I, -50 C. J, -56 C. K, -60 C. L, -67 C.....60
3.1	Three torsional potential energy scans of 1,2-dihalopropane one level of theory at RHF/3-21G* (...) and two at B3LYP/6-311+G(d,p) (____) with the second(.) using SDD on the halide in the ab initio calculations: (A) Fluoro, (B) Cloro, (C) Bromo, (D) Iodo. ....101

3.2	Raman spectrum of 1,2-dibromopropane: (A) liquid, (B) amorphous solid near 77 K and (C) annealed polycrystalline solid near 77 K. ....	102
3.3	Mid Infrared of 1,2-dibromopropane: (A) gas, (B) liquid, (C) amorphous solid near 77 K and (D) annealed polycrystalline solid near 77 K.....	103
3.4	Raman spectrum of the CH stretching region of 1,2-dibromopropane: (A) liquid, (B) amorphous solid near 77 K and (C) annealed polycrystalline solid near 77 K. ....	104
3.5	Mid-infrared of CH stretching region of 1,2-dibromopropane: (A) gas, (B) liquid, (C) amorphous solid near 77 K and (D) annealed polycrystalline solid near 77 K. ....	105
3.6	Low-frequency Raman spectrum of liquid 1,2-dibromopropane: (A) experimental; calculated: (B) composite, (C) A, (D) G and (E) G' .....	106
3.7	Low-frequency infrared spectrum of 1,2-dibromopropane: (A) experimental; calculated: (B) composite, (C) A, (D) G and (E) G' .....	107
3.8	Far-infrared of 1,2-dibromopropane: (A) gas, (B) liquid, (C) amorphous solid, (D) annealed. ....	108
3.9	Internal coordinates for 1,2-dibromopropane. ....	109
3.10	A Raman temperature dependence study of the CCC bend for conformers G', A, G at 464, 404 and 360 cm <sup>-1</sup> respectively, absolute temperatures were (A) 300.2, (B) 293.15, (C) 278.2, (D) 263.2, (E) 248.1, (F) 233.2, (I) 218.2. The spectra were normalized using the peak for the G conformer. ....	110
3.11	Graph of the logarithm of ratio of peak height for Raman bands at 361G / 464 G'(x), 464G' / 405A (o) and 464G' / 405A (+) of liquid 1,2-dibromopropane vs. reciprocal absolute temperature. From the slope $\Delta H(\text{cm}^{-1})$ is 327 +/- 12, 236 +/- 11 and -91 +/- 20 between conformers AG, AG' and GG', respectively. ....	111
4.1	Symmetry coordinates for n-butylgermane, germane (IV). ....	136
4.2	Raman spectrum of n-butylgermane: A, aa simulation. B, -160 <sup>0</sup> C. ....	137
4.3	Raman spectrum of n-butylgermane: Upper trace, RT liquid. Lower trace -160 <sup>0</sup> C. ....	138

4.4	Infrared spectrum of n-butylgermane: Upper trace, amorphous. Lower traces, annealed polycrystalline solid. ....	139
5.1	Symmetry coordinates for n-butylsilane, silane (IV).....	175
5.2	Mid infrared spectrum of gas phase of n-butylsilane. ....	176
5.3	Infrared spectrum for the hydrogen stretching region of gas phase n-butylsilane. ....	177
5.4	Infrared spectrum of the gas, liquid and poly-crystalline solid of n-butylsilane. ....	178
5.5	Infrared spectrum of the hydrogen stretching region of gas, liquid and poly-crystalline sold of n-butylsilane. ....	179
5.6	Raman spectrum of the 3 Si-H stretches of n-butylsilane ....	180
5.7	Raman spectrum of low frequency and lattice for n-butylsilane listed top down: liquid (Rt), liquid (-130C), amorphous and poly crystalline solid.....	181
5.8	Raman spectrum of C-H stretching region for n-butylsilane listed top down: room temperature liquid, amorphous and annealed solid.. ....	182
6.1	LN2 dispenser and temperature controller smaller unit for use with the Raman cold cell.....	187
6.2	LN2 dispenser and temperature controller larger unit.....	188
6.3	Modified Raman cold cell.....	189

# CHAPTER 1

## INTRODUCTION

### 1.1 Introduction

The current work compiles spectroscopic evidence from the Raman and infrared of fundamental molecular vibrations for five small flexible molecules. First two compounds 1,4-dichlorobutane  $\text{CH}_2\text{Cl}(\text{CH}_2)_2\text{CH}_2\text{Cl}$  [1] and 1,2-dibromopropane  $\text{CH}_2\text{BrCHBrCH}_3$  [2] have been published. The experimental work for n-butylsilane  $\text{CH}_3(\text{CH}_2)_3\text{SiH}_3$  and n-butylgermane  $\text{CH}_3(\text{CH}_2)_3\text{SiH}_3$  have been completed and is in process. There is a possibility that n-butylgermane degrades over time and may have a contaminate in the final spectra. Allyldichlorosilane  $\text{CH}_2\text{CHCH}_2\text{SiCl}_2\text{H}$  is in process and will be completed after I have graduated, preliminary work not shown. The experimental results for the gas, liquid, amorphous solid and semi-polycrystalline solid are compared with ab initio calculations. The optimized energy calculated for each conformer is used to determine the mole fraction, no intermolecular interactions are taken in consideration in the initial ab initio calculations thus it is similar to the gas phase where the molecules are far apart and collisions infrequent. Computed vibrational frequencies help to identify the fundamental normal modes of molecular vibration. In these nonlinear molecules there are  $3n-6$  bands for each conformer, for  $n$  atoms. The potential energy distribution for each available conformation gives a more complete view of the motion of the atoms. This information is important for many aspects of chemistry and physics providing reference data to demonstrate molecular properties that are experimentally determined and reliable [3].



## 1.2 Motivation

These studies provide a data base of structural information for multiple conformations of pure compounds, and include bond distances, angles, torsions, normal modes of vibrations and mole fractions of the conformers in gas and liquid phases. This author will not speculate how this information will be used but will offer areas in which the conformational aspects are expected to be important.

Specific uses for structural information have been found in the petrochemical industry in catalytic cracking and conversion of small n-alkanes to gasoline in zeolites. In the coordination of the substrate there is a need to understand the selectivity of the structures involved and characterize the interaction at the active site for better control of the reaction, increasing yield and assisting design of the new selective catalysts. For every reaction there is specific orientation at the site of interaction. Unfortunately conformation reactions involve transition states that are of low concentration with short time spans of existence, making analysis difficult[4]. Similar information will be needed to develop solid surface catalysis to move to a hydrogen based economy. Presently there is a move to a more rational design strategy as Norskov and Christensen [5] state several resources for hydrogen production such as natural gas, biorenewables and biomass fermentation. One illustration used highlights a multiple step process demonstrating the liberation of 4 hydrogen atoms from methanol. By modeling the potential energy barriers of the competing reactions the intermediates can be identified for a more intuitive design of a catalyst [5]. Reinhart Hoffmann [6] reviewed “conformational design in nature” in an attempt to mimic nature’s natural evolution for flexible molecules to have a preferred conformation with beneficial activity. Reinhart stated, “Conformation is the mediator

between structure and function,” and continued by suggesting a larger data base of J coupling constants from NMR spectroscopy, first published for natural products by Murata, [7-9] would help understand the inherent preferences of the compounds for these conformations. Currently a database for polychlorinated arrays [10] and other template systems is available [11-13].

### **1.3 Background**

These studies address the problem of rotational isomerism in dihalide alkanes and mono-substituted heavier main group IV atoms. Rotational isomerism arises from the hindered rotation about a single bond that produces differences in the potential energy from the change in spatial orientation of atoms. The stabilities of the conformations that depend on this orientation are mostly due to steric interference giving rise to various electrostatics [14]. In the purified compounds used, the connectivity of atoms is all the same but this internal rotation produces many configurations. Some are degenerate either by being identical or by being enantiomers. For example, a dihalodecane has 9 carbon-carbon bonds with hindered rotation, producing 19,683 possible configurations. When the degeneracies are considered, one third plus one are mathematically possible leading to 6,562 different conformers. Each of these conformers has 90 degrees of vibrational freedom for a sum total of 590,580 frequencies that might contribute to the vibrational spectrum. The spectroscopic landscape becomes more complex with each additional rotation, as summarized in Table 1.1. Because of this complexity a complete analysis is only possible for small systems.

The composition of conformers changes with the phase of the compound. In the liquid the molecules can have dipole interactions and multiple conformations produce a composite spectrum that can be difficult to interpret. We have shown that the volume occupied by a conformer can affect the electrostatic interaction between proximal conformers by reducing the distance between them [2]. The temperature dependence of the conformations can be used to calculate the change in enthalpy between conformations given in ref [2]. Other thermodynamic studies on the conformational equilibrium for the effect of solvents are in [15], temperature and pressure[16] have been done but is out of the scope of this thesis.

In the crystal, crystal field forces rigorously exclude all but one conformer. To achieve this in a cold cell, the vapor is sprayed on a surface cooled to liquid nitrogen temperature producing an amorphous solid. Annealing produces a semi-polycrystalline form from the frozen solid. Annealing consists in warming the solid to just below the melting point, but without melting the sample, then chilling it. The warming increases the molecular mobility allowing the higher energy states to convert to a low energy state in the crystal, and chilling encourages the low energy conformer to nucleate. These cold-cell experiments provide a single conformation for spectroscopic analysis, substantially simplifying the landscape of the infrared and Raman spectrum. The results are often comparable with the lowest energy state calculated by ab initio methods, and are thus used to decipher the high temperature spectroscopic landscape by providing the fundamental modes of vibration for one conformation.

Infrared and Raman spectroscopy are complementary. Bands are often found that have low intensity in one of these, but high intensity in the other, even in the absence of

symmetry. These experimental results can then be used to measure the vibrational bands. Ab initio calculations are compared to the spectroscopic results in an attempt to identify the fundamental modes of vibration. The simulations have no intermolecular interactive components and refer to molecules in the gas phase. The calculated energies are higher than what is found experimentally due to anharmonicities and approximations, but are normally in the correct order.

Over the decades advances in computer technology has continually increased the level of theory and complexity of molecules that can be investigated. This is especially the case for calculations that can be done at high levels of theory for larger atoms like germanium and bromine, where there are many more electrons to consider. Fortunately not all conformations contribute to the actual spectrum. The difference in energies obtained from the ab initio calculations can provide a population for each conformation. Those of the lowest energies should have the highest mole fraction, though this may be modified by the statistical weight, or degeneracy, of each conformer.

Group theory is applied to define the symmetry coordinates for the normal coordinate calculation, providing a potential energy distribution. Only certain symmetries are allowed depending on the geometry of the molecule, as shown in Table 1.2. Only symmetry coordinates of the same symmetry species will mix producing the normal modes of vibration as found in the normal coordinate calculations. Transformation from one conformation to another due to free rotation about the carbons conserves the symmetry coordinates of that molecule.

Butane is the smallest hydrocarbon molecule that possesses rotational isomerism. When the methyl end groups are rotated 120 degrees, each hydrogen is replaced with a

hydrogen, producing a conformer indistinguishable from the original. With the rotation of the central bond in butane the methyl groups swing into the gauche position (G). Reverse rotation produces the mirror image of the gauche configuration, for two vibrationally different conformers, called anti (trans) and gauche. In mono halogen alkanes replacement of one hydrogen in propane will produce the anti and gauche conformers. For the dihalogenethane replacement of one hydrogen on each methyl group will produce anti and gauche conformers. When the halogens are different the reverse rotation gauche' (G') will mirror the gauche state. A listing of possible conformations of short chain alkanes are given in Table 1.3.

A limited compilation of previous publications on 1-halogenalkanes and 1,n-dihalogenalkanes is listed in Table 1.4. Where published the possible conformers is given with the molecular formula the sub halide category gives references of gas-phase electron diffraction, infrared, Raman and other investigations of internal rotation. Signaled out conformers in the sub halide heading are low energy states found in the solid phase. Some works are very though but earlier works there were limitations and may not have resolver all of the internal rotations. In the 1974 publication [17] of n-pentyl and n-hexyl fluoride by Crowder because of the large amount of possible conformers the normal coordinate calculations were done for only two conformers T and G and were designated as such.

Elimination of one halogen from dihalogenalkanes reduces the number of internal rotations by one due to the three hydrogens on the methyl. The conformations of 1,n-dihalogenalkane are equivalent by increasing one methyl group to the 1-halogenalkane shown in Table 1.4. Resulting 1-halogenalkanes have no symmetry. This will

complicate the spectrum by allowing a mixing of all symmetry coordinates. Equilivalent conformational structures for these 1-halogenalkanes increases the number of atoms by 3 for the ab initio calculations. These complexities are apparent by the larger amount of publication on equivalent dihalogenalkanes and the gaps may indicate areas of future research.

In vibrational exploration of 1,4-dichlorobutane the practical limit was met in comparing theory to experiment. The conformational and vibrational distribution is covered in chapter 3 of this thesis and ref [1]. Assignment of all vibrational bands for each conformer was not possible. Of the nine conformers possible, only the GaG' conformer with  $C_i$  symmetry was found in the crystal and had all of its frequencies identified. Two bands of the all trans (AaA) configuration were identified in the low frequency region at  $229\text{ cm}^{-1}$  (the ClCC bend) and  $416\text{ cm}^{-1}$  (the CCC bend). In the liquid there are  $9 \times 36$  possible frequencies, for 324 vibrational bands. Many overlap, leaving the contribution of various bands in question. The all trans conformer has  $C_{2h}$  symmetry. This is the highest symmetry possible in this molecule and is significantly different from the rest. All the carbons and chlorines are in the anti position, and the two bending modes are shifted away from those conformers with gauche contributions.

One of the objectives of researching the conformational aspect of internal rotation of these small flexible molecules is to determine the lowest energy or most stable conformation in the solid. Matsuura compiled a series on 1,n-dihalogenalkanes  $n=3-6$  conformational stabilities of the crystalline solid results were all trans for  $n=3$  iodo,  $n=5$  bromo,  $n=6$  chloro and the fluoro compound at  $n=6$  still prefers a non-trans conformation [18]. In the dihalogenethane the preference is for the heavier atoms to be trans,

the furthest position from the other halide reducing steric interference while the difluoroethane preference is gauche [19]. With the addition of one carbon for 1,3-dihalogenpropane the gauche predominates the halogens as the stable state in the crystal shown in Table 1,4.

The work of n-butylgermane was undertaken with the collaboration of Gamil A Guigis from the Department of Chemistry, College of Charleston in Charleston, SC. Professor Guigis synthesized the compound on his own and is not part of this report. He also implemented a study of the rotational aspects of the compound via microwave spectroscopy that will be published in the same works. All experiments, frequencies and normal coordinate calculations are complete and the analysis is near completion and the paper is in the process, included in chapter 4.

An analog of n-butylgermane is n-butylsilane and upon finding it was available was purchased to continue with this series of substituted alkanes. All experiments are completed, frequencies and normal coordinate calculations but the infrared cold cell experiment could be done at a lower concentration to clarify the one area of peaks that are saturated. More analysis on the assignment of the vibrational modes needs to be done and the paper is in process. Compiled work will be in chapter 5.

The analog of n-butylsilane and n-butylgermane is pentane. Pentane and hexane would be the next logical step in researching these molecules of 4 and five conformers. Each has the same number of atom, internal rotations and conformations. Due to symmetry one of pentane's conformers is degenerate leaving four and only one of the five conformers of the analogs has a plane of symmetry in the all trans conformation. The heavier type IV valence atoms have the same tetrahedral structure but the end of the

molecules center of gravity shifts toward that end. The hydrogens on the silane and germane are shifted down in the range of 2163 and 2070  $\text{cm}^{-1}$  respectively. In the annealed crystal the all trans conformer is found. There are three individual IV-H peaks and are split showing two or more molecules per unit cell also indicating their environments are not equivalent as the two gauche hydrogens would expected to be in the all trans conformation.

The study of allyldichlorosilane  $\text{CH}_2\text{CHCH}_2\text{SiCl}_2\text{H}$  is another synthesized compound from the Guigis lab. The temperature dependence and the infrared and Raman amorphous solid are complete. The normal coordinate calculations and the Raman crystal are near completion. This work will be finish by someone other than myself, preliminary work is not shown.

Some of the challenges of this work has been the extended times needed to crystallize the compound and keep the sample frozen around the clock. Additionally with the newer samples start to anneal at temperatures below  $-170^\circ\text{C}$ , close to the temperature of liquid nitrogen ( $\text{LN}_2$ ). To adapted to the difficulties a Dewar was modified to dispense  $\text{LN}_2$  automatically for both the infrared and Raman cold cells and is defined in Chapter 6. The infrared cold cell needed modification to mount into the new IR the Vertex 70. Instead of a temporary stand for the cold cell and separately blocking off the sample compartment to constant the purged air to eliminate water and  $\text{CO}_2$ , a semi-permanent 2 axis adjustable stand was mounted to a Vertex 70 base in a plexiglass purge chamber. The purge chamber and stand can be clipped in seconds to what would normally taken part of an afternoon. The purge chamber can also include dessicant and sealed for storage to protect the CeI salt windows that are sensitive to moisture.