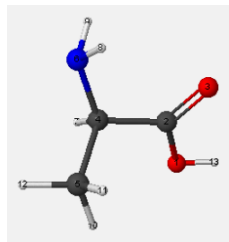


*Geometry optimizations of the conformers of alanine  
using different electronic structure techniques.*

Elizabeth Prettner

Advisor: G. G. Hoffman



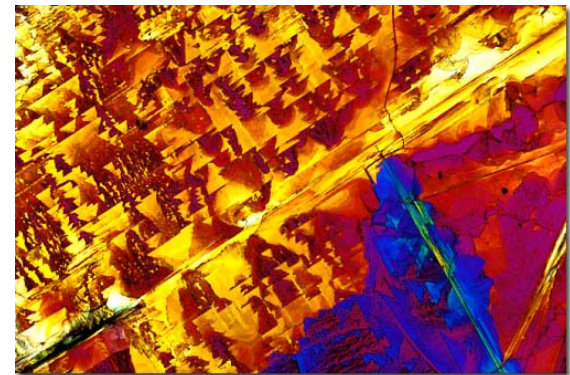


# Abstract

Alanine, like many molecular compounds, exists as a mixture of conformational structures. A full understanding of the properties of this substance requires an accurate description of this mixture. Calculations in the literature indicate that there are ten relatively stable conformers for alanine. Those calculations were performed at the HF/6-31+G(d,p) and MP2/6-31+G(d,p) level of theory. This study attempts to go beyond those calculations by using a larger basis set and by including DFT calculations to the set. The conformer structures were optimized at the HF/6-311++G(d,p), MP2/6-311++G(d,p), and B3PW91/6-311++G(d,p) levels of theory. Contrary to the previous calculations, differences were found in the relative energy orderings of the conformers for the different calculation methods. This casts a cloud on the validity of the calculations and begs further study. MP2 calculations are typically viewed as an improvement on HF and DFT calculations are often viewed as of comparable quality to MP2. However, it is difficult to assess which calculation (if any!) is accurate for this system. This provides a springboard for further work.

# Introduction

- Alanine is a non-essential amino acid found in all living creatures used as a building block for proteins
- On average, alanine is found as a building block in approximately 9% of proteins per mole sample
- Like all molecules, alanine exists as a mixture of conformations, with some conformations more stable than others



Microscopy image of Alanine  
(National High Magnet Field Research Laboratory)



## Introduction (continued)

- The stability of these conformations may be determined via Gibbs Free Energy
- The initial conformations were retrieved from a literature source and used as an initial starting point for the calculations
- The most stable conformations (and the Gibbs Free Energy values) may be generated using Electronic Structure Calculations, specifically HF, MP2, and DFT approximations.



# Method

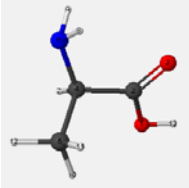
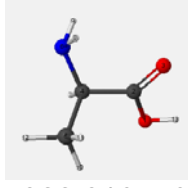
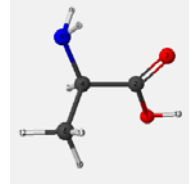
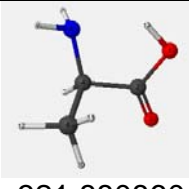
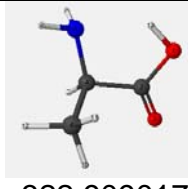
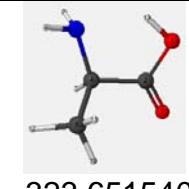
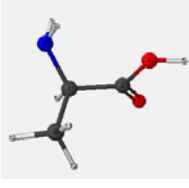
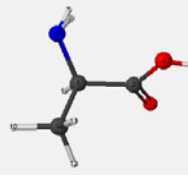
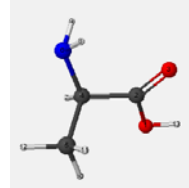
- All calculations used the 6-311++G(d,p) basis set. Three levels of theory were used:
  - **Hartree-Fock (HF)**: a solid, first-order approximation. This is the fastest method.
  - **Second-order Møller-Plesset (MP2)**: a higher-order, more accurate approximation that improves the HF results, but requires more computation.
  - **Density Functional Theory (DFT)**: an alternate approximation that tends to agree with MP2, but can require less computational effort.
- Calculations were performed using the *Gaussian* suite of programs.

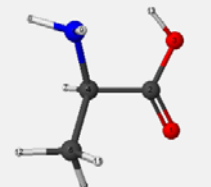
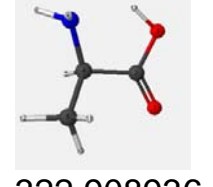
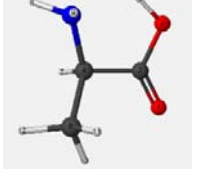
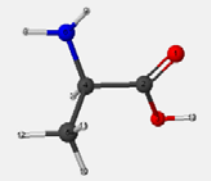
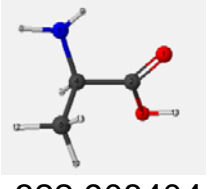
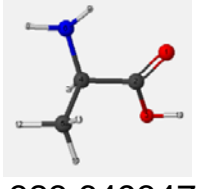
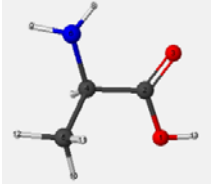
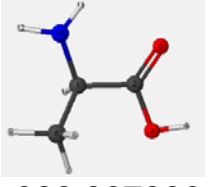
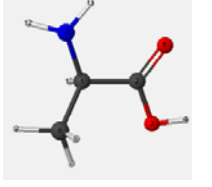
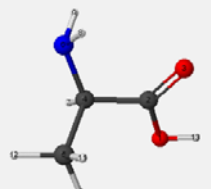
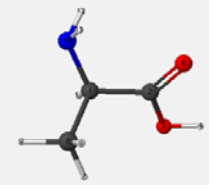
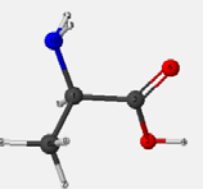


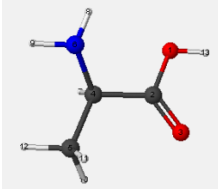
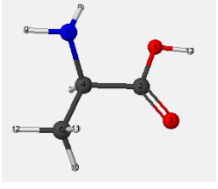
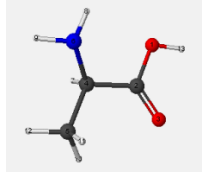
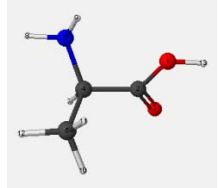
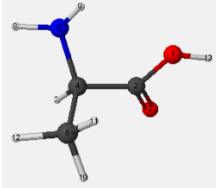
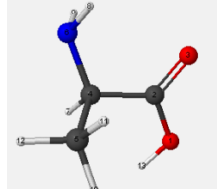
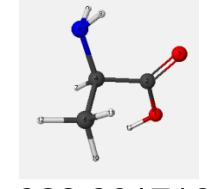
# Objective

- The experiment delved into the reliability of these approximations.
  - Is the HF level of theory sufficient? If not, do the MP2 and DFT results agree? If not, which is superior?
- The experiment is to provide a stepping stone for further research into the accuracy of the calculation methods

# Comparison of Total Gibbs Free Energy

Alanine Conformation	Hartree-Fock (Hartree)	Moller-Plesset 2 (Hartree)	Density Functional Theory (Hartree)
1	 -321.885674	 -322.910570	 -323.651601
2	 -321.880860	 -322.909017	 -323.651540
3			

4	 -321.880878	 -322.908936	
5	 -321.883181	 -322.908404	 -323.649347
6	 -321.882981	 -322.907960	 -323.648880
7	 -321.885674		

8	 -321.882617	 -322.907550	
9	 -321.882173	 -322.907190	
10	 -321.875261	 -322.901716	

\*data from First Principles Study of the Conformers of Alanine and its IR Spectrum, Pamela N. Ostroski

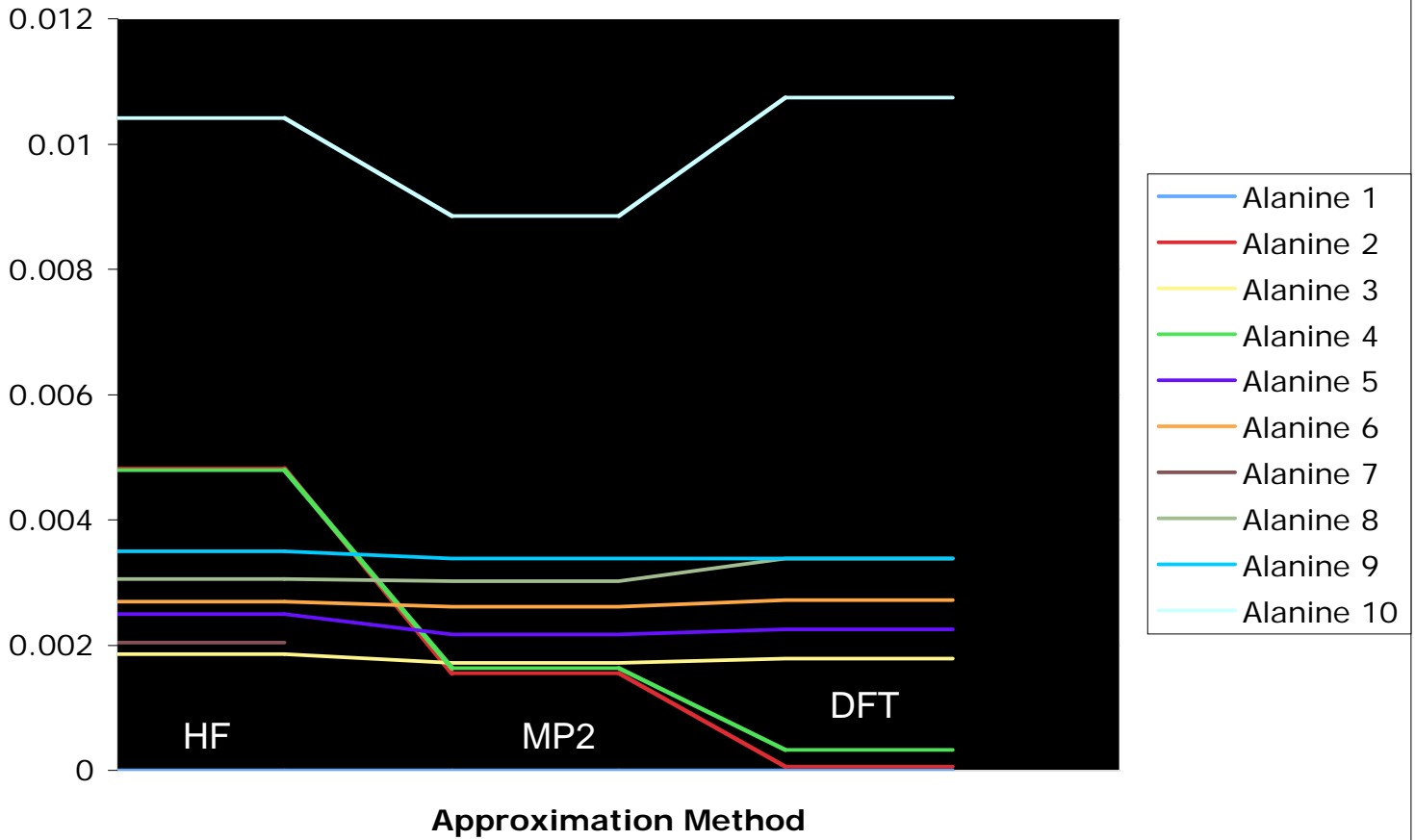
\*\*data obtained using 6-311+G(d,p) basis set

# Comparative Energy Levels

Alanine Conformation	Hartree-Fock	Moller-Plesset 2	Density Functional Theory
1	0	0	0
2	0.004814	0.001553	0.000061
3	*0.001853	0.00171	*0.001782
4	0.004796	0.001634	0.000327
5	0.002493	0.002166	0.002254
6	0.002693	0.00261	0.002721
7	*0.002041		
8	0.003057	0.00302	0.003384
9	0.003501	0.00338	*0.003383
10	0.010413	0.008854	*0.010745

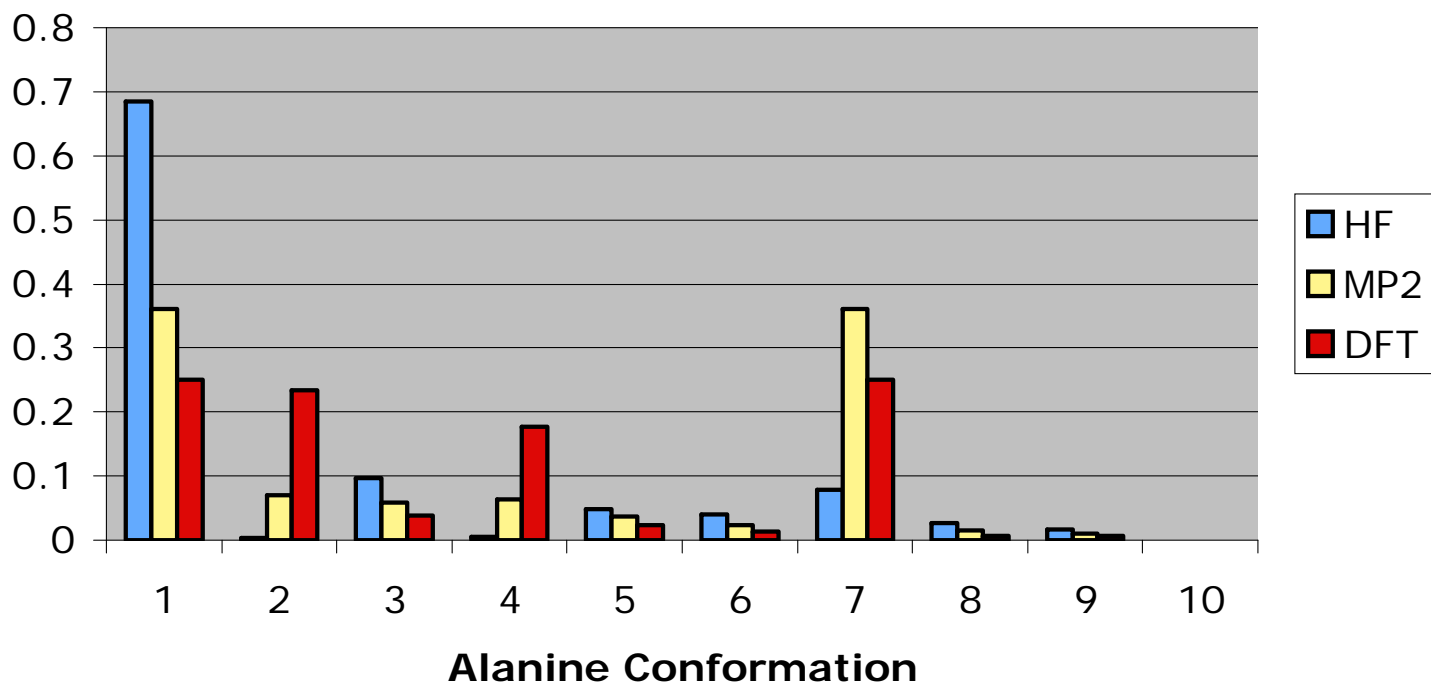
\*data from First Principles Study of the Conformers of Alanine and its IR Spectrum, Pamela N. Ostroski

## Comparative Energy Levels Between HF, MP2, and DFT Approximations



# Relative Abundance Chart

**Comparison of Relative Abundance Values for HF, MP2, and DFT**





# Conclusions

- The calculation methods do not agree in terms of the order of the stability of the conformations, specifically conformations 2, 4, and 7 disagree not only with the literature value, but between calculation methods as well.
- This provides evidence that the calculation methods used (HF, MP2, and DFT) are not all accurate for the molecule alanine.



## Conclusions (contd)

- Therefore, further research must be conducted to determine the validity of the approximations and to determine if one (or any) of the approximation methods are the most appropriate to use for the molecule alanine
- Conformations 2 and 4 both possess a hydroxide pointing towards the nitrogen atom, which could indicate weaknesses in the program for handling calculations of molecules with this particular feature.



# Further Research Possibilities

- Using the computed relative abundances of the ten conformations, an experimental IR Spectrum can be predicted for each method. These can be compared with the experimental spectrum.
- A comparison of the theoretical and experimental IR spectra should lead to a conclusion of the most accurate approximation method for alanine and similar molecules



# References

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