

**Rotational Spectroscopy and Observational Astronomy of  
Prebiotic Molecules**

Thesis by  
Susanna Leigh Widicus Weaver

In Partial Fulfillment of the Requirements  
for the Degree of  
Doctor of Philosophy



California Institute of Technology  
Pasadena, California

2005

(Defended May 2, 2005)

© 2005

Susanna Leigh Widicus Weaver

All Rights Reserved

# Acknowledgements

I owe my gratitude to so many people for their guidance, assistance, friendship, and moral support during the completion of my graduate work. My time at Caltech has been an incredible experience, and I will always remember the wonderful people that I have met in the last few years.

Thank you to Geoff Blake, my advisor, for showing all of us with his daily example that a person can indeed still have fun while being a scientist. Yet for all of the fun, you have also taught me how to look at all sides of an issue and how to find answers for myself, even when there might not be an answer to find. As a first-year student in your class I would have never guessed just how well I would know those numbers that I am supposed to keep in the back of my head! Also, thank you for teaching me when to be cautious and when to cut my losses, and especially how to make this choice effectively at 3 A.M. at an altitude of 14,000 feet. Thank you for opening the doors to the field of astrochemistry—I knew when I came to Caltech that I wanted to combine the fields of chemistry and astronomy, and with your help I have now carved out my own niche in this exciting, emerging field. Most notably, though, thank you for understanding that there are things that are equally, if not more, important than research, and always encouraging me to lead a balanced life.

I would like to thank my committee members Jack Beauchamp, Pat Collier, and Doug Rees for keeping me on my toes as well as understanding the struggles I faced as I attempted

to master two fields.

Thank you to the past and current members of the Blake group. To those who have accompanied me on this incredible journey of the Yellow Submarine—Suzanne Bisschop, Garrett Bittner, Rogier Braakman, Dan Holland, Vadym Kapinus, Matt Kelley, Brian Meehan, and Mike Morton—I am so glad to have had you all as office and lab mates, and I want to thank you for your help and support in getting the Great Yellow Beast up and running. To my SURF students Katie Dyl and Maryam Ali, it was a pleasure to help you get started in your scientific careers; thank you for all of your help and hard work. As for the astronomy side of the group, I would like to thank Adwin Boogert, Suzanne Bisschop, and Rogier Braakman for being great backup observers on those long, long nights atop Mauna Kea, and Karin Oberg for just being a great person. I would especially like to thank Jackie Kessler-Silacci for the many long hours of pouring over equations and observational spectra and her extreme patience as I learned a new field. But I would most notably like to thank Karin, Suzanne, and Jackie for being not only great group members but also true and wonderful friends.

To the JPL Spectroscopy Group, thank you for sharing your wealth of knowledge about rotational spectroscopy. I would especially like to thank Brian Drouin, without whom most of the laboratory portion of this thesis would be nonexistent. Thank you for your patience and understanding as you taught me everything I know about fitting spectra.

I owe extreme thanks to Tryggvi Emilsson for all of his help in transferring the massive collection of everything Flygare into new hands. You have not only taught me how to effectively rebuild and use this amazing instrument, but you have also taught me the finer points of applying everyday things to scientific problems.

I would like to offer a special word of thanks to the Caltech Chemistry and GPS staff.

Dian Buchness, without you we would all be lost. To the guys in the machine shop, especially Mike Roy, I promise that I am done bringing you impossibly difficult things to build! Thank you for being so skilled at taking my ideas and turning them into real, fully-functional pieces of equipment. To Tom Dunn, thank you for working your magic with many pieces of very old equipment and for the scavenger hunts through cabinets, closets, labs, and hallways hunting for just the right components. I owe a special thanks to Catherine May for not only keeping us all running in the BI, but also for many much-needed pep talks along the way. And thank you Leticia Calderon for keeping track of all of us (and all of our equipment) in the Blake Group. I thank all of you for your help throughout the years, as I would not have been able to complete this work without you.

Thank you to the Okumura and Wennberg groups for your advice and encouragement. I have learned quite a lot about infrared spectroscopy and atmospheric chemistry at our group meetings, and I hope that you have likewise learned a bit about rotational spectroscopy and astrochemistry from me. Also, thanks to Chip Kent and Mike Feldmann from the Goddard group for the great collaboration on the two *ab initio* studies that are included in their theses rather than mine.

Thank you to the many astronomers who have offered their help and advice throughout this work. This includes the CSO, OVRO, and GBT staff and the Caltech Submillimeter group. I owe special thanks to Frank Rice and Chip Sumner for the long hours, hard work, and most importantly the incredible receiver for the survey project. I would also like to thank the hot core astronomers Sheng-Yuan Liu, Tony Remijan, Doug Friedel, Lew Snyder, and Mike Hollis for their advice and support.

I owe my neverending gratitude to those teachers from my earlier schooling who inspired me to become the scientist that I am today. There are too many great professors from Illinois

Wesleyan University to be able to name them all here, so I will simply say thank you to all of you. I would especially like to thank my undergraduate advisor, Wendy Wolbach, who taught me the skills necessary to be an excellent chemist and supported me in every choice along the way. In addition to the wonderful influence of my college professors, I would like to thank my high school chemistry teacher, Don Wayman, who first introduced me to chemistry, and most importantly to cosmochemistry.

Thank you to my wonderful friends, both at Caltech and afar. To Jill Bose-Deakins, Rebecca Connor, Amanda Sisk, and Rachel Niemer, thanks for being the best bridesmaids a bride could ask for! I would also like to thank Andy Waltman, who worked so hard to leave Jeremy and me alone in so many different places. In addition to Jill, Rebecca, Amanda, and Rachel, I would like to thank Brian Sisk, Andrew Udit, Jolene Fernandes, and Lauren Webb for being such a great bunch of friends. Thank you to the HUMRingers, Gary, Bryan, and the rest of my family-away-from-home at Holliston for always offering loving support. To all of my other close friends at Caltech who are too great in number to name, it has been a great ride, and I cannot think of a better bunch of folks to work and play with. Also, although we were not close friends, I would like to mention our friend and colleague Ben Edelson—you were an inspiration to all of us, and we will miss you greatly.

I would like to especially thank my parents, Paul and Sue Widicus, for all of their love and support. You have always taught me to reach for the highest point possible, no matter how far out of reach that point might seem. You encouraged me to pursue my dreams despite the fact that it took me so far away from my family and friends. Whether it be stargazing with a new telescope on a snowy Christmas evening or memorizing the periodic table, you have always supported me in everything I have done, and I would not be who I am today without that help. Thank you, and I love you.

Last, but certainly not least, I would like to thank my husband Jeremy, who promised to love, laugh with, cry with, and grow with me. Thank you for always holding true to your word. I promise to always hold true to mine. This journey would have been so very different without you by my side. I will forever be thankful that they cancelled that lunch on the first day of orientation! I am so excited about beginning the next chapter in our life together. Thank you for putting up with me while we have both been writing our theses. And thank you for being such a wonderful husband. I love you.

# Abstract

It is now widely believed that prebiotic molecules were delivered to the early Earth by planetesimals and their associated interplanetary dust particles. Yet the formation pathways for these molecules are not clear. Amino acids and sugars have been found in carbonaceous chondrites, but only much simpler species have been detected in the interstellar medium (ISM). Prebiotic organics could have formed in the ISM and been directly incorporated into planetesimals, or simpler species could have formed in the ISM and then been incorporated into planetesimals, undergone further processing, and been delivered to Earth. Limits on interstellar chemistry must therefore be established through observational astronomy before potential prebiotic formation pathways can be assessed. These observations require laboratory spectroscopic investigation of the species of interest.

This thesis is an interdisciplinary study involving laboratory rotational spectroscopy and astronomical observations of several key prebiotic molecules. The laboratory work has focused on obtaining the rotational spectra of the simplest three-carbon ketose sugar, 1,3-dihydroxyacetone, and its structural isomers methyl glycolate and dimethyl carbonate, as well as aminoethanol, the predicted interstellar precursor to alanine. The pure rotational spectral analysis of the low-lying torsional states of the simplest  $\alpha$ -hydroxy aldehyde, glycolaldehyde, has also been completed. The original Balle-Flygare Fourier transform microwave spectrometer was used to obtain the microwave spectra, while both the Jet

Propulsion Laboratory and Caltech direct absorption flow cell spectrometers were used for additional direct absorption millimeter and submillimeter studies.

The results of these laboratory experiments were used to guide observational searches with the Caltech Submillimeter Observatory, the Owens Valley Millimeter Array, and the Green Bank Telescope toward the hot core sources Sgr B2(N-LMH), Orion Hot Core/Compact Ridge, and W51 e1/e2. Evidence has been found for the presence of dihydroxyacetone and methyl glycolate in Sgr B2(N-LMH).

These results have important implications for interstellar grain surface chemistry, and proposed additions to grain surface chemical models are also discussed. Reactions involving surface radicals and molecules containing carbonyl groups can efficiently compete with the simple grain surface reactions included in previous models. Such aldehyde abstraction reactions should be considered as pathways to complex carbonyl-containing species on interstellar grain surfaces.

# Contents

<b>Acknowledgements</b>	<b>iii</b>
<b>Abstract</b>	<b>viii</b>
<b>1 Introduction</b>	<b>1</b>
1.1 Prebiotic Interstellar Chemistry . . . . .	1
1.2 Grain Surface and Hot Core Chemistry . . . . .	2
1.3 Thesis Overview . . . . .	4
<b>2 Experimental Laboratory Methods</b>	<b>7</b>
2.1 Introduction . . . . .	7
2.2 Spectroscopic Techniques . . . . .	8
2.2.1 Pulsed Fourier Transform Microwave Spectroscopy . . . . .	8
2.2.2 Direct Absorption Flow Cell Spectroscopy . . . . .	11
<b>3 Observational Astronomy</b>	<b>14</b>
3.1 Observational Requirements for Interstellar Detections . . . . .	14
3.2 Observatories . . . . .	16
3.3 Column Density Calculations . . . . .	17
3.3.1 Rotation Diagrams . . . . .	17

3.3.2	Integrated Intensities . . . . .	18
3.3.3	Line Strengths . . . . .	19
3.3.4	Molecular Partition Functions . . . . .	20
<b>4</b>	<b>1,3-Dihydroxyacetone</b>	<b>21</b>
4.1	Introduction . . . . .	21
4.2	<i>Ab Initio</i> Studies . . . . .	22
4.3	Spectroscopic Studies . . . . .	24
4.3.1	Experimental . . . . .	24
4.3.2	FT-Microwave Studies . . . . .	24
4.3.3	Direct Absorption Millimeter and Submillimeter Studies . . . . .	25
4.3.4	Data Analysis . . . . .	27
4.3.5	Discussion . . . . .	30
4.4	Observational Studies . . . . .	31
4.4.1	CSO Observations . . . . .	31
4.4.1.1	Observations . . . . .	31
4.4.1.2	Results . . . . .	33
4.4.2	OVRO Observations . . . . .	37
4.4.2.1	Observations . . . . .	37
4.4.2.2	Results . . . . .	39
4.4.3	GBT Observations . . . . .	39
4.4.3.1	Observations . . . . .	39
4.4.3.2	Results . . . . .	40
4.4.4	Discussion . . . . .	42

<b>5 Dimethyl Carbonate &amp; Methyl Glycolate</b>	<b>46</b>
5.1 Introduction . . . . .	46
5.2 Spectroscopic Studies . . . . .	48
5.2.1 Experimental . . . . .	48
5.2.2 FT-Microwave Studies . . . . .	48
5.2.3 Direct Absorption Millimeter and Submillimeter Studies . . . . .	51
5.2.4 Data Analysis . . . . .	51
5.2.4.1 Dimethyl Carbonate . . . . .	54
5.2.4.2 Methyl Glycolate . . . . .	56
5.2.5 Discussion . . . . .	57
5.3 Observational Studies . . . . .	60
<b>6 Glycolaldehyde</b>	<b>66</b>
6.1 Introduction . . . . .	66
6.2 Spectroscopic Studies . . . . .	68
6.2.1 Experimental . . . . .	68
6.2.2 Data Analysis . . . . .	69
6.2.3 Discussion . . . . .	71
<b>7 Aminoethanol</b>	<b>75</b>
7.1 Introduction . . . . .	75
7.2 Spectroscopic Studies . . . . .	77
7.2.1 Experimental . . . . .	77
7.2.2 Data Analysis . . . . .	77
7.2.3 Discussion . . . . .	79

7.3 Observational Studies . . . . .	81
7.3.1 CSO Observations . . . . .	82
7.3.1.1 Observations . . . . .	82
7.3.1.2 Results . . . . .	82
7.3.2 OVRO Observations . . . . .	84
7.3.2.1 Observations . . . . .	84
7.3.2.2 Results . . . . .	85
7.3.3 Discussion . . . . .	86
<b>8 Conclusions and Implications for Interstellar Chemistry</b>	<b>87</b>
8.1 Laboratory Rotational Spectroscopy . . . . .	87
8.2 Observational Astronomy . . . . .	89
8.3 Implications for Interstellar Chemistry . . . . .	90
8.3.1 Proposed Grain Surface Chemical Network . . . . .	94
8.3.2 Determination of the Rate Constants . . . . .	100
8.3.3 Discussion . . . . .	101
8.4 Future Work . . . . .	106
<b>A Flygare Operation</b>	<b>108</b>
A.1 Instrumentation . . . . .	108
A.1.1 Instrument Control System . . . . .	109
A.1.2 Gas Handling and Sample Delivery . . . . .	113
A.1.3 Valve Assemblies . . . . .	115
A.1.4 Heated Sample Holder . . . . .	116
A.2 Spectrometer Startup Procedure . . . . .	117

<b>B Flow Cell Operation</b>	<b>130</b>
B.1 Instrumentation . . . . .	130
B.2 Spectrometer Startup Procedure . . . . .	130
B.3 Spectrometer Parameters . . . . .	132
B.4 Spectrometer Alignment Procedure . . . . .	134
B.5 Spectral Acquisition Procedure . . . . .	136
B.6 Sample Pressure and Temperature Regulation . . . . .	137
B.7 Spectral File Format . . . . .	139
<b>C Spectral Assignment</b>	<b>140</b>
C.1 The CALPGM Suite . . . . .	140
C.2 The Submillimeter Analysis Program . . . . .	142
<b>D Geometry Optimizations of the C<sub>2</sub>H<sub>4</sub>O<sub>2</sub> &amp; C<sub>3</sub>H<sub>6</sub>O<sub>3</sub> Structural Isomers</b>	<b>147</b>
D.1 Introduction . . . . .	147
D.2 Z-Matrices . . . . .	151
<b>E 1,3-Dihydroxyacetone Spectral Analysis</b>	<b>157</b>
E.1 1,3-Dihydroxyacetone .int File . . . . .	157
E.2 1,3-Dihydroxyacetone .par File . . . . .	158
E.3 1,3-Dihydroxyacetone .lin File . . . . .	159
<b>F Dimethyl Carbonate Spectral Analysis</b>	<b>204</b>
F.1 Dimethyl Carbonate .int File . . . . .	204
F.2 Dimethyl Carbonate .par File . . . . .	205
F.3 Dimethyl Carbonate .lin File . . . . .	206

<b>G Methyl Glycolate Spectral Analysis</b>	<b>212</b>
G.1 Methyl Glycolate .int File . . . . .	212
G.2 Methyl Glycolate .par File . . . . .	213
G.3 Methyl Glycolate .lin File . . . . .	215
<b>H Glycolaldehyde Spectral Analysis</b>	<b>263</b>
H.1 Glycolaldehyde .int File . . . . .	263
H.2 Glycolaldehyde .par File . . . . .	264
H.3 Glycolaldehyde .lin File . . . . .	265
<b>I Aminoethanol Spectral Analysis</b>	<b>325</b>
I.1 Aminoethanol .int File . . . . .	325
I.2 Aminoethanol .par File . . . . .	326
I.3 Aminoethanol .lin File . . . . .	328
<b>Bibliography</b>	<b>367</b>

# List of Figures

1.1	Schematic diagram of a hot core, adapted from [1]. The indicated size scale is that appropriate for a hot core surrounding a high mass protostar. ‘Hot corinos’ have also been detected around low mass protostars and have similar temperature profiles but are much less massive and smaller in size [2]. . . . .	3
2.1	Schematic diagram of an FTMW instrument. . . . .	9
2.2	Schematic diagram of the Caltech Direct Absorption Flow Cell Spectrometer. . . . .	11
4.1	Structures of the two lowest energy dihydroxyacetone conformers: a. doubly hydrogen bonded conformer (ground state); b. singly hydrogen bonded conformer. . . . .	24
4.2	Single-shot dihydroxyacetone spectra from the FT-microwave experiments. . . . .	25
4.3	The flow cell dihydroxyacetone spectrum from 112 to 120 GHz. . . . .	26
4.4	Possible dihydroxyacetone transitions observed toward Sgr B2(N-LMH) with the least-squares Gaussian fits to each line. Spectra are from the CSO 500 MHz AOS, and a linear baseline subtraction of the continuum has been performed. The vertical dotted line indicates $v_{lsr} = 64$ km/s. The positions of additional dihydroxyacetone lines relative to 64 km/s are indicated in spectrum (b). . . . .	34
4.5	The rotation diagram for dihydroxyacetone toward SgrB2(N-LMH). The labels correspond to the panels of Figure 4.4. . . . .	36

4.6	The simulated spectrum of dihydroxyacetone lines at 220 K compared to an observed Sgr B2(N-LMH) spectrum. The structure of dihydroxyacetone is shown in the inset. . . . .	37
5.1	Ground state structures for a. dimethyl carbonate and b. methyl glycolate. .	47
5.2	FTMW Doppler-doublet spectra of the dimethyl carbonate $1_{0,0} \rightarrow 0_{0,0}$ quartet. The frequencies are in units of MHz. . . . .	49
5.3	A FTMW Doppler-doublet spectrum of dimethyl carbonate for which manual de-Dopplerization was performed for line frequency determination. . . . .	50
5.4	The room temperature methyl glycolate spectrum from 103 to 111 GHz. . . . .	52
5.5	The simulated spectrum of methyl glycolate at 200 K (red) compared to a Sgr B2(N-LMH) 3 mm survey spectrum. The vertical lines correspond to line center positions, with red representing methyl glycolate lines and blue representing formic acid lines. Formic acid is the only identified species with lines in this window; all other emission features are unidentified. . . . .	62
5.6	A map of the possible methyl glycolate emission feature at 89815 MHz in Sgr B2(N-LMH). . . . .	65
6.1	The room temperature glycolaldehyde spectrum from 101 to 122.5 GHz. . . . .	69
7.1	The ground state structure of 2-aminoethanol. . . . .	76
7.2	The room temperature aminoethanol spectrum from 97 to 120 GHz. . . . .	78
8.1	The simplest chemical model of grain surface reactions driven by single-atom addition to CO [3]. . . . .	92

8.2	Initial results from a deep broadband line survey of the Orion Compact Ridge. The temperature and frequency calibrations are preliminary, but the RMS level is $\sim$ 20 mK. . . . .	107
A.1	A schematic diagram of the FTMW mixing manifold. . . . .	114
A.2	A schematic diagram of the FTMW heated nozzle. . . . .	117
D.1	The relative energies of the $\text{C}_2\text{H}_4\text{O}_2$ (top panel) and $\text{C}_3\text{H}_6\text{O}_3$ (bottom panel) structural isomers. . . . .	150

# List of Tables

3.1	A summary of the observatories used in these studies. . . . .	17
4.1	Spectral parameters predicted for dihydroxyacetone from quantum mechanical calculations using B3LYP DFT. . . . .	24
4.2	Spectral parameters determined for dihydroxyacetone. . . . .	29
4.3	A summary of dihydroxyacetone emission lines from Sgr B2(N-LMH). . . . .	32
4.4	Dihydroxyacetone column density upper limits in Orion and W51 from CSO observations. . . . .	38
4.5	Dihydroxyacetone column density upper limits in Sgr B2(N-LMH) from OVRO observations. . . . .	40
4.6	Dihydroxyacetone column density upper limits in Sgr B2(N-LMH) from GBT observations. . . . .	41
5.1	The frequencies (in MHz) of dimethyl carbonate lines observed in the FTMW experiments. . . . .	50
5.2	Spectral parameters determined for dimethyl carbonate. . . . .	56
5.3	Spectral parameters determined for methyl glycolate. . . . .	58
5.4	Dimethyl carbonate and methyl glycolate molecular partition function values at various temperatures. . . . .	60

5.5	Methyl glycolate column density in Sgr B2(N-LMH) determined from lines observed in the 3 mm line survey [4]. . . . .	64
6.1	Spectral parameters determined for the ground and first three excited vibrational states of glycolaldehyde. . . . .	72
6.2	Glycolaldehyde molecular partition function values at various temperatures. .	73
7.1	Spectral parameters determined for the ground and fundamental vibrational states of aminoethanol. . . . .	80
7.2	Spectral parameters determined for overtone and combination vibrational states of aminoethanol. . . . .	81
7.3	Aminoethanol column density upper limits in Orion, W51, and Sgr B2 from CSO observations. . . . .	83
7.4	Aminoethanol column density upper limits in Orion and W51 from OVRO observations. . . . .	85
8.1	Photolysis pathways and rates for major grain mantle components in dense interstellar clouds at $A_v=6$ . . . . .	95
8.2	Reactions of CO with surface radicals. . . . .	96
8.3	Radical-radical reactions between photolysis products and secondary radicals.	97
8.4	Aldehyde proton abstraction reactions. . . . .	98
8.5	Aldehyde radical recombination reactions. . . . .	99
8.6	Diffusion barriers and rates for reactive surface species. . . . .	102
8.7	Observed and calculated abundance ratios for the products of HCO+radical combination reactions relative to formaldehyde at 50 K. The observed column densities are those determined for Sgr B2(N-LMH). . . . .	104

B.1	Caltech Direct Absorption Flow Cell Spectrometer Instrumentation . . . . .	131
B.2	Optimized parameters for flow cell experiments. . . . .	137
D.1	The 2C structural isomer parameters determined by Gaussian 98 MP2 6-311G++(d,p) geometry optimizations. . . . .	148
D.2	The 3C structural isomer parameters determined by Gaussian 98 MP2 6-311G++(d,p) geometry optimizations. . . . .	149
D.3	trans-Acetic Acid Z-Matrix. . . . .	151
D.4	cis-Acetic Acid Z-Matrix. . . . .	151
D.5	Methyl Formate Z-Matrix. . . . .	152
D.6	Glycolaldehyde Z-Matrix. . . . .	152
D.7	Methylene Glycol Monoformate Z-Matrix. . . . .	152
D.8	Lactic Acid Z-Matrix. . . . .	153
D.9	Dimethyl Carbonate Z-Matrix. . . . .	153
D.10	Methyl Glycolate Z-Matrix. . . . .	154
D.11	Methoxy Acetic Acid Z-Matrix. . . . .	154
D.12	Glycol Monoformate Z-Matrix. . . . .	155
D.13	1,3-Dihydroxyacetone Z-Matrix. . . . .	155
D.14	Glyceraldehyde Z-Matrix. . . . .	156
D.15	Trioxane Z-Matrix. . . . .	156