

CURRENT RESEARCH

Since 2014, I have been extremely fortunate to hold a Jansky Postdoctoral Fellowship with the National Radio Astronomy Observatory. This fellowship provides me with complete autonomy to direct my own research, the freedom to choose my collaborators, and the resources to carry out a robust program of interdisciplinary inquiry. While my undergraduate and graduate research experiences were highly-focused in developing expertise in narrowly-defined techniques and research areas, I have taken the opportunities provided by my fellowship to explore a far broader range of research areas and techniques in laboratory spectroscopy and observational astronomy. I firmly believe that having hands-on experience in such a diverse array of projects provides me with the broad perspective necessary to both identify new avenues for interdisciplinary work and to open entirely new lines of inquiry in my own research. Below, I briefly highlight a selection of the projects I have worked on in the past two years, and a number of lines of current study.

Investigations of Interstellar Molecular Chirality

In the culmination of more than four years of work, I and my colleague Brandon Carroll reported this summer in *Science* on the interstellar detection of propylene oxide, the first chiral molecule discovered outside our solar system, using radio-astronomical observations [1], a discovery which generated significant press coverage¹. The genesis of biological homochirality, the exclusive use of a single enantiomer of many biomolecules (such as exclusively *L* amino acids), is one of the greatest mysteries in the origins of life [2]. While studies of meteorites have shown that Earth may have been seeded with an initial enantiomeric excess (e.e.) of many biomolecules [3], there is no consensus as to the mechanism by which this e.e. was generated in the primordial cloud [4,5]. Our discovery now provides a laboratory with which to test these hypotheses, if we can determine whether an e.e. exists in the Sagittarius B2(North) molecular cloud in which we found propylene oxide.

We are fortunate that we observed propylene oxide in absorption, and that modern radio telescopes can distinguish left and right circularly polarized light, making a circular dichroism (CD)² measurement theoretically possible. Yet, despite being routine in the IR-VIS-UV, CD has only been studied theoretically in the radio regime [6], somewhat fortuitously using propylene oxide as one of two primary examples of best-case-scenarios. Brandon and I are now actively exploring methods with which we might measure CD of propylene oxide in the laboratory, and consulting with experts both in laboratory polarization-sensitive spectroscopy and full-polarization astronomical observations to form collaborative teams going forward.

TeraHertz Time-Domain Spectroscopy

My graduate work focused on the development of a THz Time-Domain (THz-TDS) spectrometer, and its application to interstellar ice analogs [7-9], and I have maintained a collaboration with Prof. Blake to expand the use of the THz-TDS spectrometer to other areas of study. In November 2015, I returned to Caltech and spent several weeks collecting data on matrix-isolated water in argon.

¹In perhaps a sign of the times, the largest exposure came as the story was a trending topic on Facebook.

²CD distinguishes enantiomers via the (very small) preferential absorption of one handedness of polarized light over another by a given enantiomer.

Unlike in the infrared, which is largely sensitive to intramolecular signals, the THz is exquisitely-sensitive to intermolecular forces. My initial findings are that the signals from the isolated water are extraordinarily sensitive to the cluster size and internal energy of that water, and my analysis is ongoing as I learn more about matrix-isolated spectroscopy. I am also actively helping to remotely guide a pair of graduate students in their study of deuterium exchange between mixtures of H_2O and D_2O ices, and the effects of crystal structure and layering in this exchange.

Microwave Spectroscopy and Technique Development

As there are no laboratory facilities at the NRAO Headquarters, I sought out a collaboration with Dr. Michael McCarthy at Harvard-CfA to broaden my experimental horizons to include microwave spectroscopy techniques. The first project I assisted with as I was learning the ropes was a laboratory study of C_3H^+ [10], a molecule which was first detected in the interstellar medium before ever being seen on Earth [11], and which I had previously studied extensively from an observational perspective [12-14]. This was the first time I was part of a project that truly spanned from observational astronomy to laboratory spectroscopy, and it has shown me the powerful insights that can come when experts reach across their disciplines.

Since then, I have participated in a number of additional studies of astrochemical (the $[\text{H}, \text{N}, \text{C}, \text{S}]$ isomeric family [15]) and atmospheric (the *cis*- and *trans*-HOCO radicals [16]) interest, as well as the development of automated spectral analysis tools in the microwave (AMDOR spectroscopy [17]). I am currently working on my first foray into laser-ablation microwave spectroscopy with the study of the GeO and GeS molecules, and a study of the electron donor-acceptor bonding in the ethanol- CO_2 dimer, which is thought to be a key interaction in the ability of ethanol-doped supercritical CO_2 to dissolve polar solutes such as caffeine.

Observational Astronomy

I have taken advantage of the on-site expertise at the NRAO in the use of the state-of-the-art ALMA array to develop my skills in radio interferometry. Last year, I successfully proposed for observations targeting the elusive hydroxylamine (NH_2OH) molecule toward a pair of promising interstellar sources, NGC 6334I and G+0.693-0.027. I have been hunting for and constraining NH_2OH chemistry for some time [18][19]. My initial analysis of the results shows a continuing (and astonishing) lack of NH_2OH , which will establish the most rigorous constraints on its chemistry yet. As I discuss later, the observational data reveal an astonishingly rich chemistry and contain a wealth of information far beyond the non-detection of NH_2OH , which I am anxious to explore.

I am also working to expand my endeavors beyond the molecular clouds and star-forming regions I have thus far exclusively studied. This observing cycle I proposed for, and had approved, observations targeting C_3H^+ in a protoplanetary disk (HD 163296), a nascent solar system. My previous work with C_3H^+ has shown it to be extraordinarily dependent on the presence of enhanced UV-radiation fields to drive its production, and thus is an excellent tracer of such enhancement. These observations, which are forthcoming, will aim to use C_3H^+ to map the distribution and intensity of UV-radiation from the newborn star as the radiation propagates through the protoplanetary disk.

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GETTING AWAY FROM ONE-POT SYNTHESSES: HETEROGENEITY IN MOLECULAR EVOLUTION REVEALED WITH ALMA

For decades, the evolution of complex molecules in the interstellar medium (ISM) has been treated as a cosmic-scale one-pot synthesis: all molecules seen in a single observation were assumed to be available to react with each other. With the advent of the Atacama Large Millimeter/submillimeter Array (ALMA), we now have the sensitivity to observe low-abundance, complex molecules at high spatial resolution. Figure 1 shows observations of acetic acid (CH_3COOH) and methyl formate (CH_3OCHO) in NGC 6334I. These molecules are *structural isomers* of one another: they possess identical atomic compositions, but are bonded differently. Yet, the observations clearly show resolved differences in their spatial distributions. The chemistry driving the presence (or lack thereof) of these two molecular cousins is clearly different, and as these and a select few other previous observations 1,2 are now revealing, it is highly-unphysical to ignore this spatial differentiation when considering chemical evolution in sources like this. To illustrate the impact of this chemical differentiation in a broader astrophysical context, overlaid and outlined in red circles on Figure 1 are Hubble images of newborn stars with protoplanetary disks taken toward the Orion Molecule Cloud. It is clear that the location of star-formation within a chemically-differentiated region like NGC 6334I will have a significant effect on its initial molecular inventory. As this differentiation is almost certainly driven by underlying physical conditions, these differences are also likely indicators that critical factors such as radiation environment, density, temperature, and pressure will affect the nascent solar systems, resulting in the variety of protoplanetary disk systems we observe today. *Understanding why and how the distinct spatial distributions of complex organic molecules like methyl formate and acetic acid arose will therefore provide invaluable insight into the varying physical and chemical conditions into which solar systems are born, and help us to understand why they have evolved as they have.*

Here, I outline a combined laboratory and observational program to understand the molecular inventories, and spatial distributions thereof, in star-forming regions at various stages of evolution.

Observational Astronomy

The full 2 GHz bandwidth window extracted toward the northern source in Figure 1 is shown in Figure 2. There is little to no true continuum baseline in this survey; the spectra are essentially line-confusion limited. Preliminary analysis of the dataset indicate a wealth of complex organic molecules, particularly oxygen-bearing species. Yet, while these data can provide a partial molecular inventory, and offer tantalizing hints at an unprecedented degree of chemical differentiation, the narrow spectral coverage means that only a handful of transitions of any given molecule, covering a very narrow range in upper state energies, are accessible. As a result, it is not possible to constrain the excitation conditions, and by extension the abundances, of these molecules needed to make any quantitative assessments, or to interface with astrochemical models. *To truly understand the distribution, excitation, and abundances of complex molecules in star-forming regions, multi-band observations with ALMA will be required.*

I will propose ALMA Cycle 5 spectral scan observations of NGC 6334I in Bands 3, 6, and 7, leveraging my preliminary results. Spectra will be extracted from the chemically-differentiated regions identified in my current observations, and column densities and abundances will be determined using well-established methods 6. I will also propose identical ALMA Cycle 5 observations toward a second extraordinarily chemically-rich massive star-forming region, G31.41+0.31 7. As Figure

[1] shows, my preliminary results indicate that while the spatial differentiation is resolvable with the 1'' synthesized beam used for these observations, there is finer-scale structure to be seen.¹ Given the intensity of the complex molecular features seen in Figure [2], the small decrease in surface brightness sensitivity by moving to a more extended configuration will not result in a loss of detectability, and thus I will propose to observe these sources at 0.3'' resolution.

I will propose to observe the entirety of Band 3 (84 – 116 GHz), the lower half of Band 6 (211 – 244 GHz), and a smaller portion of Band 7 (330 – 347 GHz) in spectral scan mode, with an achievable RMS of 10 mJy in Bands 3 & 6 and 100 mJy in Band 7. This particular spectral setup provides an optimal balance between spectral coverage and sensitivity, and will allow tracing the excitation conditions of not only the individual complex molecules, but of the bulk gas through observations of CO, ¹³CO, C¹⁸O, and C¹⁷O in each Band. The total time required using the Cycle 4 specifications is ~5.5 hours per source.

As the observations toward NGC 6334I and G31.41+0.31 will likely not be delivered until the second year of the Fellowship, I will use archival ALMA observations of Orion KL, Sgr B2(N), and IRAS 16293, all of which have physical and chemical conditions distinct from those of NGC 6334I and G31.41+0.31, to begin my study. Even in the case that the proposed ALMA observations are unsuccessful, these archival observations will produce significant results on their own.

Using these observations, I will seek to answer three simple questions: (1) are methyl formate and acetic acid (and their isomer glycolaldehyde) spatially distinct in every star-forming region when observed at high enough spatial resolution? (2) do other molecules, especially precursor molecules like methanol (CH₃OH) and formic acid (HCOOH), share the same distribution, or have differing relative abundance ratios between methyl formate and acetic acid peaks? and (3) is there a notable difference in the physical conditions between methyl formate and acetic acid peaks, especially density and excitation temperature, as probed not just by the molecules themselves, but by other reliable tracers?

The observations obtained as part of this project will contain a wealth of valuable information far beyond the initial focus of the work. These data should not and will not languish unused. I will ensure the maximum value possible is obtained from the existing data, and any future observations obtained. I am currently a co-PI of the Prebiotic Interstellar Molecular Survey (PRIMOS) project, whose goal is to provide fully-reduced, science-ready spectral line surveys of interesting regions to the community. I strongly believe that the public-availability of reduced data, especially information-rich products such as line surveys, is critical to the future of astronomy. I will work with the creators of the Open Supernova Catalog (OSC) to create a system that will allow all end users to contribute their reduced line survey data to the PRIMOS project in a way that is efficient and indexable, with flexible meta-data functionality. The OSC infrastructure allows for user submissions, and massively-interconnected meta-data functionality, allowing searches by source name, frequency coverage, telescope, detected molecules, and much more. Indeed, this source of large-scale indexing of data on individual line surveys will certainly lead to interesting scientific insights that will rely on the large-number statistics provided by this sort of detailed archive.

Finally, in the long-term, I intend to use these projects as a bridge to conduct complementary observations of regions of both active star-formation and those regions containing protoplanetary

¹Indeed, recent, unrelated observations of the source at sub-arcsecond resolution reveal a far more complicated spatial structure [C. Brogan, private communication].

disks, with ALMA, SOFIA, and the James Webb Space Telescope. The JWST and SOFIA will provide a complementary set of observations, specifically on the dust and molecular ice present in these regions. I believe that the results will show that the gas-phase chemical differentiation we are now seeing with ALMA will have counterparts in the infrared observations of physical and chemical conditions probed by these continuum and condensed-phase ice observations.

Laboratory Spectroscopy

Full characterization of the molecular line surveys that will result from this work will require both the identification of new molecular species, and the assignment of lines due to isotopologues and vibrationally-excited states of known molecules. Indeed, while the identification of new molecules is highly desirable for constraining models and adding to the known interstellar inventory, lines from isotopologues and vibrationally-excited species are thought to account for a vast majority of the remaining unidentified features in current line surveys [8].

For decades, astrochemists have undertaken targeted laboratory searches for species of astrophysical interest, aiming to provide rotational frequencies for astronomical detection [9]. On the other hand, astronomers have led the field by long-ago abandoning targeted searches in favor of broadband, unbiased surveys of well-chosen sources [10,11]. Unidentified features are flagged for study, often awaiting laboratory measurements, but occasionally producing new molecular assignments ahead of terrestrial work [12-14]. I will leverage my membership in the rotational spectroscopy group of Dr. Michael McCarthy at the Harvard-CfA to bring the best of unbiased molecular astronomy to the laboratory through cutting-edge advancements in the field of automated microwave spectroscopy and complex mixture analysis. I will select astrophysically-relevant precursor mixtures (e.g., CH_3OH and HCOOH), dissociate them into their constituent functional groups using a supersonic expansion electrical discharge source, and study the resulting complex mixture.

As an example, I have recently used a novel set of techniques developed by the McCarthy group, Microwave Spectral Taxonomy (MST) [15] and Automated Microwave Double Resonance (AMDOR) spectroscopy [18], which allow for the rapid collection and analysis of broadband, unbiased molecular line surveys in the laboratory, on a discharge combination of CS_2 with HC_4H . Analysis of these spectra is still in progress, however I have already identified and definitively assigned two new vibrationally excited states of C_2S and five of C_3S . Some years ago, the same chemical system was investigated in the mm-wavelength regime in the McCarthy laboratory, but many of the transitions seen could not be assigned due to a lack of complementary cm-wave data to anchor the predictions. Using the results of the MST/AMDOR measurement, I have now been able to definitively identify and assign the new C_2S and C_3S transitions in this wavelength range. These results constrain the predictions, and now provide reliable data for comparison with astronomical observations, particularly a spectral line survey of IRC+10216 (ALMA Project #2013.1.00432.S).

I will use MST/AMDOR spectroscopy to explore astrochemically-relevant reaction mixtures in an unbiased way to both identify new molecular species and to catalog previously un-observed isotopologues and vibrationally-excited states. My initial target will be mixtures which produce methyl formate and/or acetic acid in measurable abundance, starting with CH_3OH and HCOOH , which are thought to be the principle precursor molecules [19]. When new species and states are found, I will then leverage those predictions to identify and fit higher-frequency transitions in an upgraded mm-wave flow cell spectrometer that is available in the McCarthy laboratory.

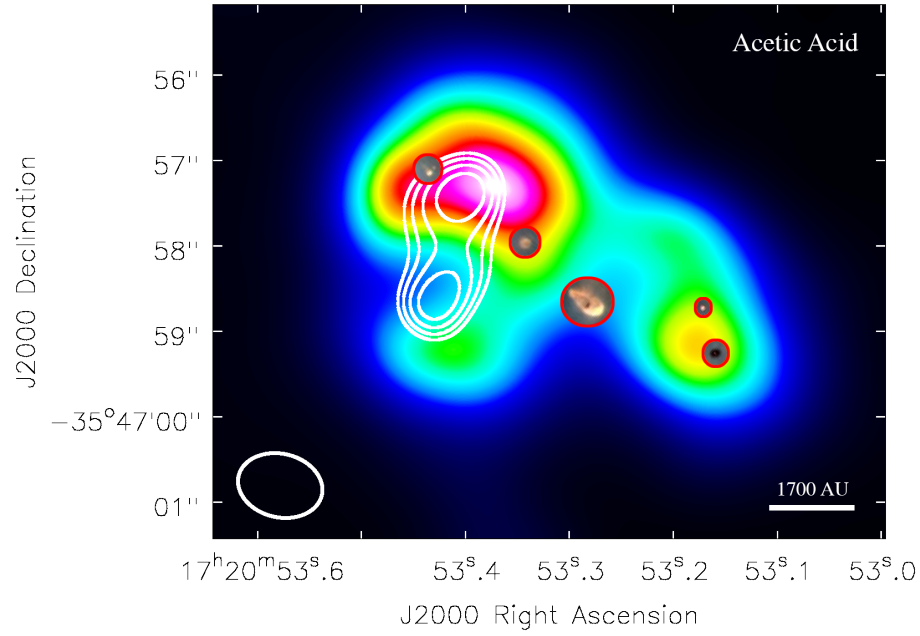


Figure 1: ALMA observations of methyl formate (color) and acetic acid (white contour) in NGC 6334I. Overlaid (\sim to scale, red outline) are young stars with protoplanetary disks as seen by Hubble in a different source (Orion). Data taken as part of ALMA Project 2015.1.0050.S., PI: B. McGuire. Hubble Credit: C.R. O'Dell/Rice University; NASA.

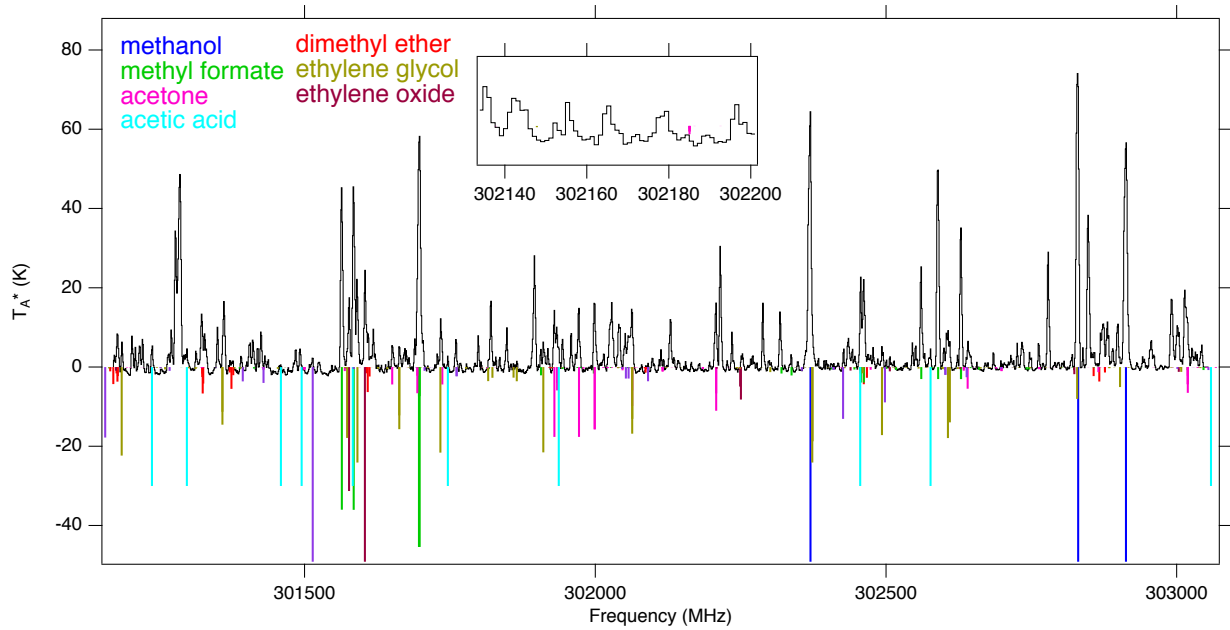


Figure 2: Spectral scan of one hot core within NGC 6334I from Project 2015.1.00150.S., PI: B. McGuire. A selection of complex, oxygen-bearing species are labeled. Inset shows detail.

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