Chapter 1

Introduction

1.1 Prebiotic Interstellar Chemistry

It is now widely believed that molecules that could have played a central role in the development of biological systems were delivered to the early Earth by planetesimals and their associated interplanetary dust particles [5]. Yet the degree of complexity reached by prebiotic organic chemistry before the formation of planetesimals and its impact on the evolution of planetary surfaces remains a mystery. Nearly 140 molecules, mostly organic, have been discovered in the interstellar medium (ISM), principally toward so-called hot molecular cores where the radiation and/or shocks from newly formed stars evaporates grain mantles and drives a complex gas-grain chemistry [3]. Approximately 50 of these compounds have been seen in the comae of comets, and many biologically-related monomers, including amino acids and sugars, have also been detected in carbonaceous chondrites [6–8].

The chemical processes leading to the formation of these prebiotic molecules are not fully understood. Aqueous alteration of simple organic species within the meteorite parent body is a viable explanation for the existence of the more complex species. The large enrichment of deuterium in the carbonaceous components of chondrites is not explainable by known or plausible solar system processes, however, and suggests an interstellar origin for the species present therein, or at least their immediate precursors [3, 9].

There are two possible mechanisms for the formation of these molecules, the first being that a variety of prebiotic species were formed before our planetary system was assembled, integrated into planetesimals, and introduced to the Earth through interplanetary dust and comet or meteorite impacts. Alternatively, the planetesimals could have formed from interstellar dust grains whose mantles contained much simpler organic species. More complex prebiotic chemistry could then follow in the parent body, with the products ultimately being delivered to the early Earth through impact.

1.2 Grain Surface and Hot Core Chemistry

Interstellar grain surfaces are processed by charged particles, UV radiation, and radiative heating, and laboratory studies have shown that various combinations of these processes produce a highly complex mixture of organic species with molecular weights into the hundreds of atomic mass units (amu, see [10, 11]). Early chemical models considered complex molecule formation on grains [12], but current theoretical models of grain surface chemistry concentrate largely on the precursors to the more complex compounds, such as simple alcohols and aminoalcohols [3]. Many potential grain surface reaction pathways are eliminated by the conditions imposed on these models, greatly simplifying the possible products of grain synthesis and eliminating the possibility for much larger organics to form on the grain surfaces. Gas phase theoretical models of the chemistry in hot protostellar cores involving the products of grain surface reactions are therefore required to explain the formation of substantially larger organics under interstellar conditions.

A hot core is a region of dust and gas around a newly formed star where the temperature is sufficient to thermally evaporate grain mantles but low enough that organics remain stable in the gas phase. The temperature of a hot core is typically ∼100–300 K. A schematic diagram of a hot core is shown in Figure 1.1.

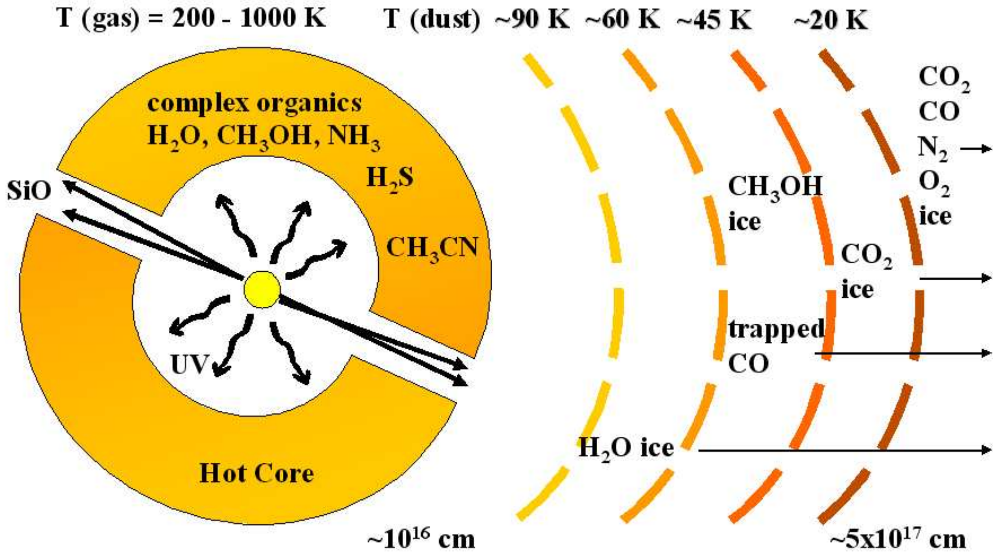

Figure 1.1: Schematic diagram of a hot core, adapted from [1]. The indicated size scale is that appropriate for a hot core surrounding a high mass protostar. ‘Hot corinos’ have also been detected around low mass protostars and have similar temperature profiles but are much less massive and smaller in size [2].

Current models assume that species such as alcohols and aminoalcohols undergo gas phase reactions in hot cores to form more complex prebiotic species. It has recently been shown, however, that gas phase pathways are insufficient for the production of organics such as ethanol (CH_3CH_2OH) and methyl formate (CH_3OCHO) [13, 14]. Recent observations have also reopened the possibility for complex molecule formation on grains. Glycolaldehyde, ($CHOCH_2OH$), the simplest two-carbon (2C) α-hydroxy aldehyde, has recently been detected toward the galactic center Sagittarius B2(N) molecular cloud complex [15]. The glycolaldehyde emission is spatially extended by $\geq 60''$ around the Sgr B2(N-LMH) hot core [16], a conclusion reinforced by the low excitation temperature of the centimeter-wave transitions recently detected with the Green Bank Telescope (GBT, [17]). While the more compact emission gives a rotational temperature of $\sim$50 K, the extended emission lines yield a rotational temperature of $\sim$8 K, indicating that glycolaldehyde is likely sub-thermally excited after liberation from grain surfaces. Similar properties are exhibited by ethanol and acetaldehyde (CH_3CH_2OH & CH_3CHO, [18, 19]). Glycolaldehyde is closely related to polyhydroxylated aldehydes, or aldoses (sugars), which are produced biologically via glycolysis and used in the production of ATP. The presence of a species so closely related to aldoses could potentially link grain surface pathways to prebiotic interstellar chemistry.

The sugars and other polyhydroxylated organic species observed in meteorites are present in similar concentrations to amino acids, indicating that these species might form from similar processes. The most likely route to amino acids in the ISM is gas phase ion-molecule reactions. This possible link between hot core gas phase chemistry and the formation of α-hydroxy compounds stands in stark contrast to the grain surface production indicated by the glycolaldehyde observations, but it should be stressed that neither the formation of glycolaldehyde nor any other sugar-related species can be explained by existing grain surface or gas phase hot core chemical models. Detailed laboratory and observational investigations of both predicted grain surface precursors and more complex prebiotic species are clearly required before interstellar prebiotic chemistry can be understood.

1.3 Thesis Overview

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 three-carbon (3C) ketose sugar, 1,3-dihydroxyacetone ($CO(CH_2OH)_2$), and its structural isomers methyl glycolate (CH_3OCOCH_2OH) and dimethyl carbonate ($CH_3OCOOCH_3$). The pure rotational spectral analysis of glycolaldehyde's low-lying torsional states has also been completed. Additional laboratory studies involved the simple grain surface species aminoethanol ($NH_2CH_2CH_2OH$), the predicted precursor to the amino acid alanine. The original Fabry-Perot cavity pulsed Fourier transform microwave (FTMW) spectrometer, or Balle-Flygare instrument, was used to obtain the microwave spectra, while both the Jet Propulsion Laboratory (JPL) 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 (CSO), the Owens Valley Millimeter Array (OVRO), and the Green Bank Telescope (GBT). A combination of microwave, millimeter, and submillimeter spectral line searches and spatial imaging has been conducted. The Sgr B2(N-LMH) high mass hot core was the primary target for these observations, as it is found to have among the highest column densities of large organics ever detected. Other high mass hot cores targeted in these studies include the Orion Hot Core/Compact Ridge and W51 e1/e2.

These spectroscopic and observational studies have led to a revised theory for the formation of complex molecules on grains. The importance of reactions involving surface radicals and molecules containing carbonyl groups has been demonstrated, and suggestions for the adaptation of grain surface chemical models have been developed.

The techniques used for the laboratory and observational studies are outlined in Chapters 2 and 3, respectively. Detailed information on the FTMW instrument is given in Appendix A, while details on the Caltech Direct Absorption Flow Cell Spectrometer are given in Appendix B. The spectroscopic and observational results for each molecule are presented in Chapters 4–7. An overview of the programs used for spectral fitting is given in Appendix C, while the files used for fitting the spectrum of each molecule are presented in Appendices E–I. The implications of the results of these studies for interstellar grain surface chemistry will be discussed in Chapter 8.

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