Complex Molecules and the GBT: Is Isomerism the Key?

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Abstract. Interstellar aldehydes have been called the "sugars of space" ever since the discoveries of formaldehyde (H_2CO) in 1969 and acetaldehyde (CH_3CHO) in 1973. At present, more than 135 interstellar molecular species have been identified. Excluding diatomic species, 30% of all interstellar molecules have isomeric counterparts. The newest instrument in the interstellar molecule search arsenal is the Green Bank Telescope (GBT), which is credited with the discovery of the large aldehydes propenal (CH_2CHCHO) and propanal (CH_3CH_2CHO). In addition, the GBT has been used to observe interstellar glycolaldehyde (CH_2OHCHO), the simplest possible aldehyde sugar, and interstellar ethylene glycol ($HOCH_2CH_2OH$), the sugar alcohol of glycolaldehyde. These new GBT observations that suggest a universal prebiotic chemistry are presented and discussed. While there is no consensus regarding how large complex interstellar molecules are formed, it may be that the first step in the polymerization of interstellar formaldehyde (H_2CO) with its isomer trans hydroxy methylene (t-HCOH) is responsible for the formation of interstellar glycolaldehyde. We discuss this polymerization mechanism that can result in the generation of more complex sugars. We assess the likelihood of interstellar trans hydroxy methylene and suggest a search strategy for it using the GBT.

Keywords. ISM: abundances — ISM: clouds — ISM: individual (Sagittarius B2(N-LMH)) — ISM: molecules — radio lines: ISM

1. Introduction

The giant molecular cloud complex Sgr B2 near the center of our Galaxy is undoubtedly the preeminent source for the study of large complex interstellar molecules. The Sgr B2 complex is a star-forming region containing compact hot molecular cores of arcsecond dimensions, molecular maser emitting regions, and ultracompact continuum sources surrounded by larger-scale continuum features as well as molecular material extended on the order of arcminutes. In addition, small-scale and large-scale shock phenomenon characterize the complex. In particular, the hot molecular core known as the Large Molecule Heimat (LMH) has for the last ten years been the first source searched to detect and identify new large interstellar molecules since many of the large organic species have been previously found confined to its ∼5″ diameter. For example, Figure 1 is a VLA image of the ethyl cyanide (CH_3CH_2CN), a well-documented LMH molecule.

These results are consistent with conventional wisdom persisting for decades that the interesting complex molecules would be found and studied with high-resolution arrays able to couple to more compact molecular sources. In fact, this view was a driver in the design of future mm-wave arrays. In 2001 the picture radically changed for one large interstellar molecule. Having recently identified glycolaldehyde (CH_2OHCHO) with the NRAO 12-meter telescope (Hollis, Lovas, & Jewell 2000), an attempt was made to map one of the same mm-wave transitions with the BIMA Array (Hollis *et al.* 2001). The interferometer was unable to recover the flux measured by the single antenna, thereby indicating that glycolaldehyde toward the LMH has to be extended on a scale of at least
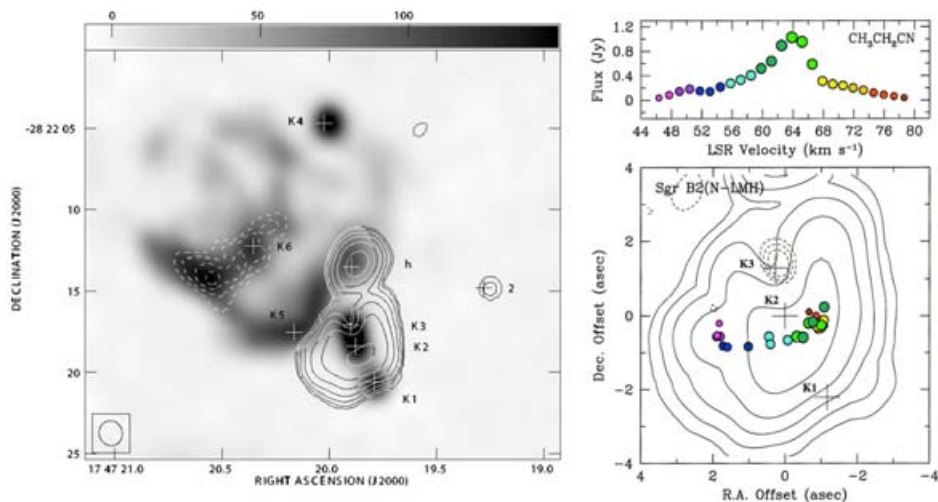
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Figure 1. VLA images of the 5_{15}–4_{14} transition of ethyl cyanide (Hollis *et al.* 2003). *Left:* Contours of the integrated intensity Sgr B2(N-LMH) overlaid on a grey-scale image of 43.5 GHz continuum emission. *Right:* LSR velocity structure of the LMH. Centroid emission from each velocity channel shows a spatio-velocity gradient consistent with a rotating molecular disk seen approximately edge-on. This plot is color-coded in Hollis *et al.* (2003).

an arcminute. Subsequently, acetaldehyde (CH_3CHO) was imaged with the GMRT (see Figure 2), showing that another large aldehyde has a widespread spatial distribution of several arcminutes toward Sgr B2 (Chengalur & Kanekar 2003).

The Green Bank Telescope (GBT) may well be the ideal instrument for capitalizing on the spectral identification of both compact and spatially extended complex interstellar molecules toward Sgr B2. For example, the half-power beamwidth of the GBT is $740''/\nu$(GHz). The GBT beam size will nearly match that of the LMH when observing in the vicinity 70–100 GHz, a spectral region characterized by a large number of rotational transitions of hot core molecules. Conversely, at lower frequencies <50 GHz, the GBT samples the colder gas of spatially extended molecules such as the low temperature transitions of the larger aldehydes. It is chiefly in this latter context that our experiences with the GBT as a cold molecular gas telescope will be discussed.

2. Recent Spectral Line Observations with the GBT

With a collecting area of 7854 m^2 and a mass of 7.6 million kg, the GBT is the largest and heaviest movable structure on land in the world. For spectral line searches at Ku- (12–15.4 GHz) and K-bands (18–22.5 GHz) discussed here, we define a "track" as 6 hrs, the amount of time that the GBT is able to continuously track Sgr B2 for elevations above 10º. The GBT was pointed at the Sgr B2(N-LMH) position which is coincident with the K2 ultracompact continuum source. The spectrometer is typically configured into four 200 MHz bands in two polarizations which yield a spectral resolution of 24.4 kHz. A scan consisted of observing OFF the source 60′ east for two minutes followed by observing ON the source for two minutes. These short scans were performed to minimize spectra baseline fluctuations. Figure 3 shows two raw spectral bandpasses representing the accumulation of scans for one track at Ku- and K-bands. In the presence of continuum emission, the instrumental slopes in a bandpass can be quite significant but can be reliably
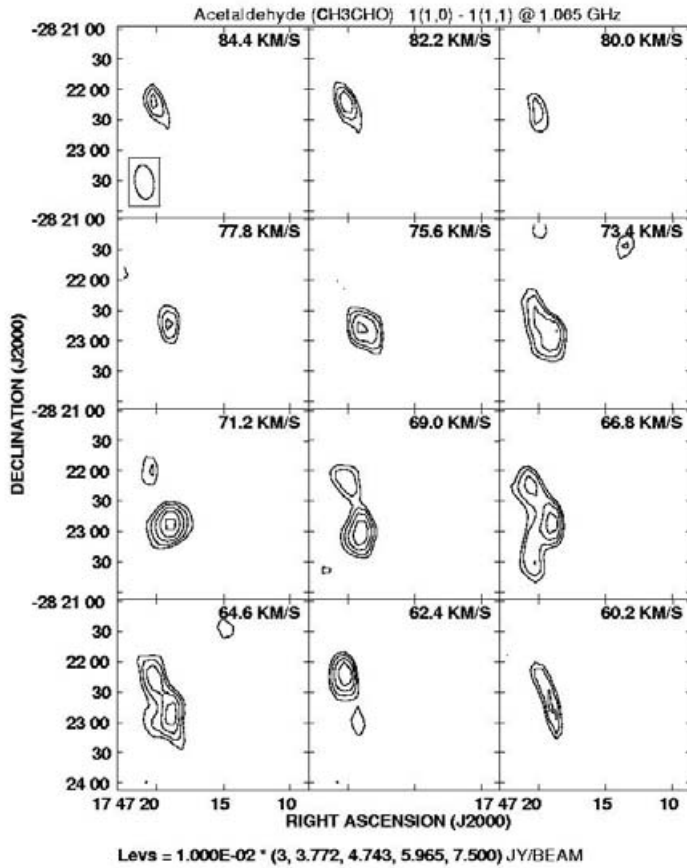
Figure 2. GMRT velocity channel contour images of the 1_{10}–1_{11} transition of acetaldehyde toward Sgr B2 (courtesy of J.N. Chengalur and N. Kanekar).

removed with a median filtering technique (G. Langston 2005, in preparation), taking care not to distort spectral line shapes. As can be seen, recombination lines are the dominant spectral features at the Ku- and K-bands and molecular spectral lines are few when compared to the mm-wave range.

2.1. *The Inverse P Cygni Profile of N-15 Ammonia*

The 6_5–6_5 transition of N-15 ammonia (^{15}NH$_3$) in Figure 4 is heretofore an unpublished GBT spectrum displaying a classic inverse P Cygni profile which is representative of other transitions of this molecule toward Sgr B2(N). The 6_5–6_5 transition of ^{15}NH$_3$ has a lower energy level 450 K above ground, indicative of hot molecular gas. We interpret the inverse P Cygni spectra of ^{15}NH$_3$ transitions as critical evidence for the collapse of the molecular cloud in proximity to the LMH. As Figure 4 shows, the absorption is clearly red-shifted relative to the LMH systemic velocity of +64 km s^{-1}, whereas the blue-shifted gas is seen entirely in emission. The spectra show that the absorbed gas on the near side of the continuum source and the emission gas on far side are both moving toward the continuum source. Moreover, the molecular ring has a characteristic LSR systemic velocity of +64 km s^{-1} as well, indicating that the collapse is probably towards the molecular ring (see Figure 1). Thus, the simplest interpretation of the ^{15}NH$_3$
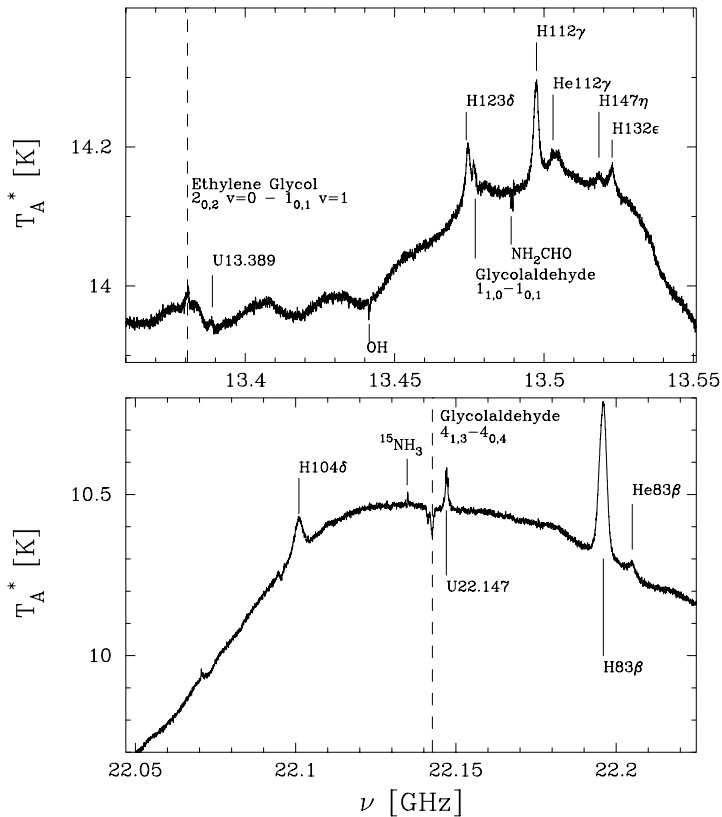
Figure 3. Typical raw GBT spectral bandpasses at Ku- and K-bands.

observations is that the ambient molecular cloud is in free-fall toward the molecular ring which contains a number of continuum sources. Observations of the normal isotope of NH_3 at high temperature have previously been interpreted as evidence for shock-heated gas toward Sgr B2(N) as would be expected for a collapsing molecular cloud (*e.g.*, Ceccarelli *et al.* 2002; Flower *et al.* 1995). On the other hand, our GBT observations of the normal isotopic form of ammonia did not show inverse P Cygni profiles, but, rather, were dominated by two simple emission features at LSR velocities of $+64$ and $+82 \, \mathrm{km \, s^{-1}}$. These strong components at $+82$ and $+64 \, \mathrm{km \, s^{-1}}$ are associated with star-forming cores that may have been triggered by collision between two molecular clouds with these systemic velocities as suggested by Mehringer & Menten (1997).

2.2. *Glycolaldehyde and Ethylene Glycol*

Glycolaldehyde (CH_2OHCHO), the simplest possible aldehyde sugar, was detected with the GBT toward Sgr B2(N) by means of the $1_{10}-1_{01}$, $2_{11}-2_{02}$, $3_{12}-3_{03}$, and $4_{13}-4_{04}$ rotational transitions at 13.48, 15.18, 17.98, and 22.14 GHz, respectively (see Figure 5, and Hollis *et al.* 2004a). An analysis of these four rotational transitions yields a glycolaldehyde state temperature of $\sim$8 K. Previously reported emission line detections of glycolaldehyde with the NRAO 12-m telescope at mm-wavelengths (71 GHz to 103 GHz) are characterized by a state temperature of $\sim$50 K. By comparison, the GBT detections are surprisingly strong and seen in emission at 13.48 GHz, emission and absorption at 15.18 GHz, and absorption at 17.98 GHz and 22.14 GHz. The GBT detects glycolaldehyde absorption primarily at an LSR velocity of $+64 \, \mathrm{km \, s^{-1}}$ with a possible weaker component
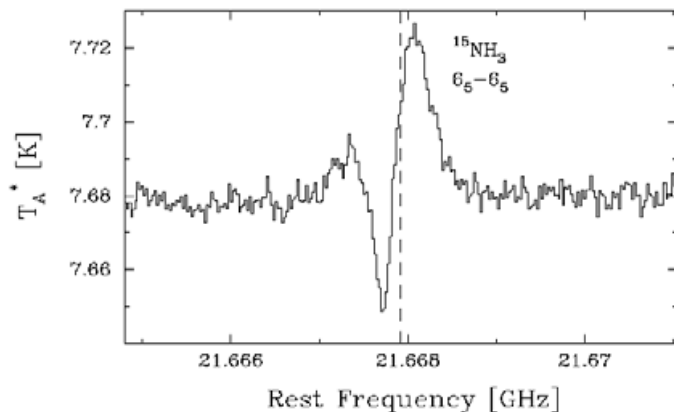
Figure 4. The inverse P Cygni profile of Nitrogen-15 ammonia observed with the GBT. The dashed line indicates an LSR velocity of +64 km s^{-1}.

at +82 km s^{-1}; any emission components detected are centered near +73 km s^{-1}. On the other hand, glycolaldehyde emission observed with the NRAO 12-m telescope (Hollis, Lovas, & Jewell 2000) is found to have an LSR velocity of $\sim$+71 km s^{-1} (see Hollis *et al.* 2002). Emission components with LSR velocities of +71 or +73 km s^{-1} suggest the emission comes from a cool extended cloud that surrounds the two star forming cores characterized by LSR velocities of +64 and +82 km s^{-1}. For the +64 km s^{-1} LSR velocity component, we believe that the hot ammonia is in proximity to the colder glycolaldehyde, suggesting that the $^{15}NH_3$ molecule characterizes the infall shock front while the glycolaldehyde represents much older, colder, post-shock gas.

Figure 6 shows two heretofore unpublished GBT spectra of ethylene glycol (HOCH$_2$CH$_2$OH), the reduced sugar alcohol of glycolaldehyde. Since both glycolaldehyde and ethylene glycol are easily seen with the GBT in a spectral region that is not dominated by molecular emission, it suggests that these two molecules are spatially and chemically related. This suggests that successive hydrogen addition could account for production of ethylene glycol from glycolaldehyde on the surface of interstellar grains:

$$CH_2OHCHO \xrightarrow{2H} HOCH_2CH_2OH \qquad (2.1)$$
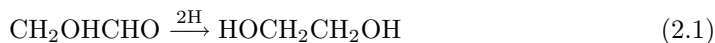
2.3. *Propynal, Propenal, and Propanal*

As a consequence that hydrogen addition appears important in creating successively larger interstellar molecules, we used the GBT to search for the molecular aldehyde hydrogen-addition sequence of propynal (HC$_2$CHO), propenal (CH$_2$CHCHO), and propanal (CH$_3$CH$_2$CHO) shown here:

$$HC_2CHO \xrightarrow{2H} CH_2CHCHO \xrightarrow{2H} CH_3CH_2CHO \qquad (2.2)$$

Propynal had previously been identified as an interstellar molecule (Irvine *et al.* 1988; Turner 1991), and the GBT detected this species, as well as the new interstellar aldehydes propenal shown in Figure 7 and propanal shown in Figure 8. It is noteworthy that the line intensities of the propynal, propenal, and propanal sequence decrease. Each propanal spectrum in Figure 8 represents the accumulation of 2 full tracks. LSR velocity components for propenal and propanal are similar to those of glycolaldehyde.
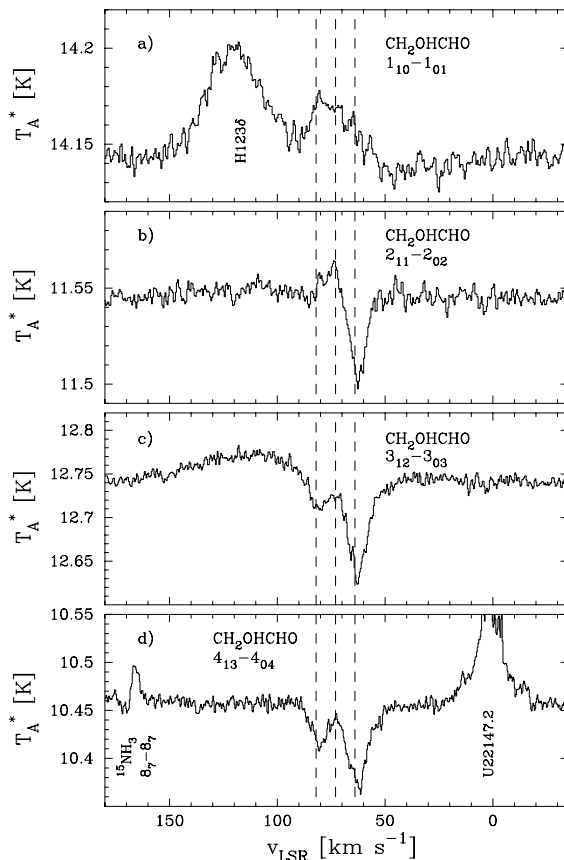
Figure 5. Glycoladehyde GBT spectra (Hollis *et al.* 2004a). Fiducial LSR velocities are +82, +73, and +64 $km\,s^{-1}$ in this and following figures.

3. Implications of Complex Interstellar Molecules

Although the chemistry on Earth and in interstellar clouds is much different, the results can be very similar. For example, laboratory experiments in aqueous solution that start with mixtures of methane (CH_4), ammonia (NH_3), and molecular hydrogen (H_2) have been able to synthesize amino acids (Strecker synthesis). These experiments purport to simulate conditions of the early Earth and result in substantial quantities of hydrogen cyanide (HCN) and a number of aldehydes in the initial stage and the concentration of these intermediate products fall off as the experiment proceeds. Our GBT experiments confirm the presence of aldehydes that may be associated with a similar process in interstellar clouds. It could be that prebiotic chemistry—the formation of the molecular building blocks essential to life—occurs in an interstellar cloud long before the collapse to form a new solar system with planets. Since many of the interstellar molecules discovered to date are the same kinds detected in laboratory experiments specifically designed to synthesize prebiotic molecules, this suggests a universal prebiotic chemistry. Moreover, there appears to be a high degree of isomerism among interstellar molecules. Of all interstellar molecules that could have isomers (*i.e.*, molecules containing 3 or more atoms), 30% have isomeric counterparts. Additionally, it appears that isomerism may favor the more complex species. For example, of the nine interstellar molecules comprised of 8 atoms, acetic acid (CH_3COOH), methyl formate (CH_3OCHO), and glycolaldehyde
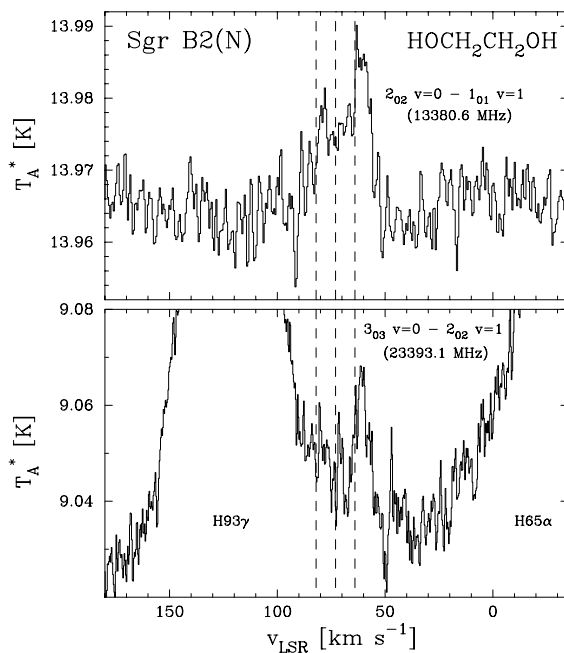
Figure 6. Ethylene glycol GBT spectra.

(CH$_2$OHCHO) are isomers, and hexapentaenylidene (H$_2$C$_6$) and triacetylene (HC$_6$H) are isomers. Thus, the role of isomerism seems to be an important clue in the study of complex interstellar molecules.

4. Formaldehyde Polymerization May Explain Sugars

The discoveries of interstellar formaldehyde (H$_2$CO) in 1969 (Snyder *et al.* 1969) and interstellar glycolaldehyde(CH$_2$OHCHO) in 2000 (Hollis, Lovas, & Jewell 2000) suggest that the polymerization of two formaldehyde molecules may produce glycolaldehyde. However, the exact details as to how the polymerization occurs has not been amenable to experimental verification. For example, it has been long thought that prebiotic synthesis of sugars on the early Earth occurs via the so-called formose reaction which is an aqueous-catalyzed polymerization of formaldehyde. The formose reaction itself is shrouded in some mystery as to exactly how the bond-breaking/bond-making proceeds to produce a molecule of glycolaldehyde from two formaldehyde molecules. One theoretical possibility is that hydroxy methylene (HCOH—a formaldehyde isomer of unusual reactivity) is first formed, which can more readily combine with formaldehyde to produce glycolaldehyde. In such a scenario hydroxy methylene would be an intermediate product that would be difficult if not impossible to observe in the laboratory. The first step in the polymerization reaction is depicted in Figure 9.

The formation of glycolaldehyde in Figure 9 occurs because the highly reactive trans hydroxy methylene divalent carbon adds to the formaldehyde carbon which causes the formaldehyde oxygen to accept the trans hydroxy methylene hydrogen and the double C=O bond characteristic of glycolaldehyde is created. This reaction is essentially instantaneous. Trans hydroxy methylene can produce 3-carbon glyceraldehyde by adding to glycolaldehyde; similarly, more complex sugars can be synthesized. Strong experimental evidence for this polymerization mechanism was provided by Flanagan, Ahmed, &
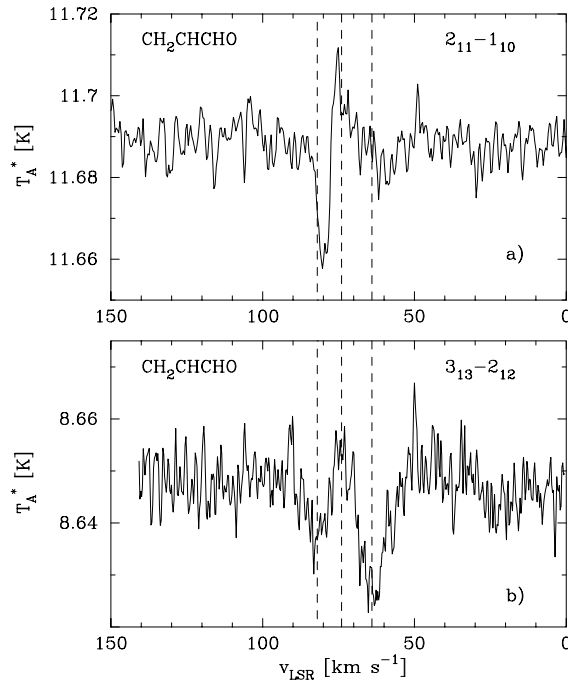
Figure 7. Propenal GBT spectra (Hollis *et al.* 2004b).

Shevlin (1992) in a laboratory study in which condensation of atomic carbon with water at 77 K generated a mixture of aldehyde sugars that included glycolaldehyde as a principal product. It is noteworthy that this experiment was conducted under conditions that are somewhat similar to those that exist in hot cores of interstellar clouds.
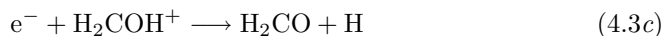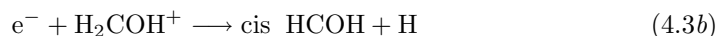
We next explore the likelihood that interstellar hydroxy methylene exists. For that we must consider the interstellar chemistry that produces formaldehyde itself. The production of interstellar formaldehyde is widely accepted to be produced primarily in the gas phase by the following reaction:

$$O + CH_3 \longrightarrow H_2CO + H \tag{4.1}$$

Succeeding reactions proceed by classic ion-molecule chemistry. Gas-phase formaldehyde is depleted to protonated formaldehyde, a known interstellar molecule, by the following reaction:

$$H_3^+ + H_2CO \longrightarrow H_2COH^+ + H_2 \tag{4.2}$$
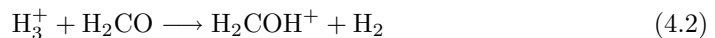
This gas-phase protonated formaldehyde combines with an electron to again form formaldehyde and two conformers of hydroxy methylene (Hoffmann & Schaefer 1981):

$$e^- + H_2COH^+ \longrightarrow trans\ HCOH + H \tag{4.3a}$$

$$e^- + H_2COH^+ \longrightarrow cis\ HCOH + H \tag{4.3b}$$

$$e^- + H_2COH^+ \longrightarrow H_2CO + H \tag{4.3c}$$

The branching ratios in equations (4.3) are not known. The dissociative recombination of the interstellar molecule H_2COH^+ is considered very important in interstellar
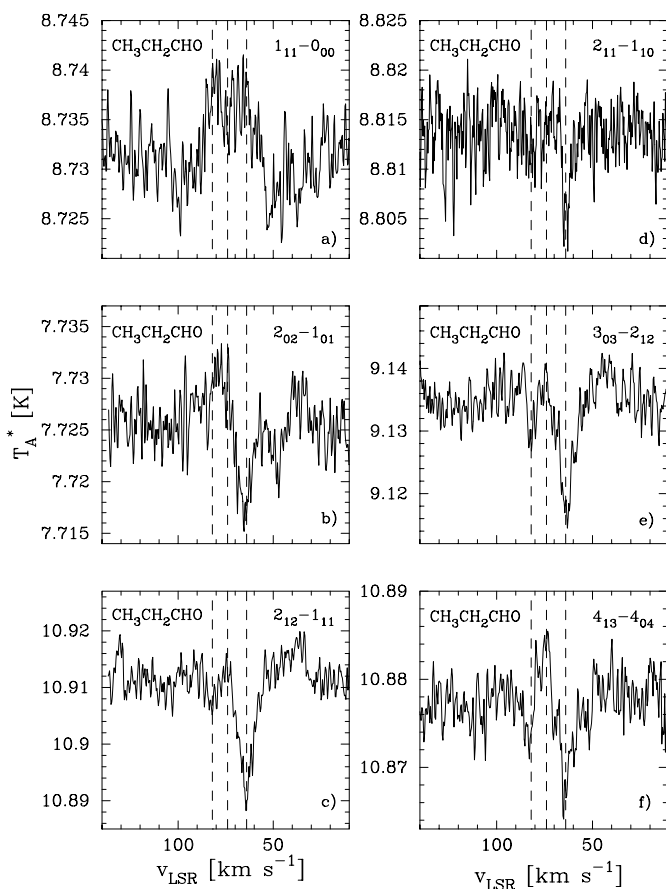
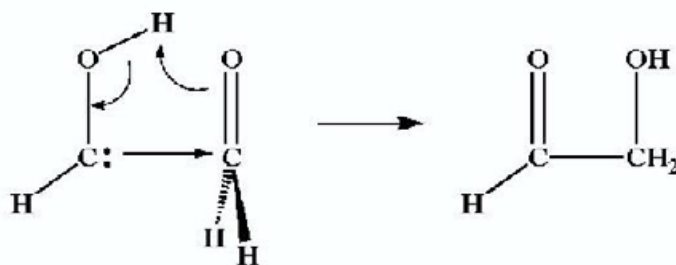**Figure 8.** Propanal GBT spectra (Hollis *et al.* 2004b).

Figure 9. The first step in formaldehyde polymerization. Trans hydroxy methylene combining with formaldehyde to form glycolaldehyde.

clouds and hydroxy methylene (HCOH) should be a relatively stable and long- lived molecule under interstellar cloud conditions (Hoffmann & Schaefer 1981). Trans HCOH lies $\sim$5 kcal mole^{-1} (2516 K) below cis HCOH with a substantial isomerization barrier of $\sim$30 kcal mole^{-1} (15,098 K) to the formation of formaldehyde. Thus, it is evident that the likely form of interstellar hydroxy methylene would favor trans HCOH.

Ab initio quantum chemical models may be able to determine the molecular structure of hydroxy methylene with sufficient precision such that an accurate rotational spectrum

can be calculated. An interstellar search could then be mounted for this important isomer of formaldehyde by searching for low energy transitions that occur in the K-band range. Such transitions would have the least frequency uncertainty and likely be detectable since low energy transitions of both formaldehyde and glycolaldehyde are readily detected by the GBT. If interstellar trans HCOH were found, it would provide strong evidence for the mechanism by which glycolaldehyde is formed and that the synthesis of more complex sugars similarly occurs.

Acknowledgements

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Discussion

HERBST: Could you discuss the current state of knowledge of the reaction t-HCOH + $H_2CO \rightarrow$ glycolaldehyde?

HOLLIS: The formation of glycolaldehyde occurs because the highly reactive t-HCOH divalent carbon adds to the H_2CO carbon. The reaction is fully discussed in Flanagan *et al.* (1992; *J. Am. Chem. Soc.* 114, 3892) along with experimental results that verify the reaction occurs in low temperature conditions.

IRVINE: How accurately can the lowest rotational transitions of t-HCOH be calculated *ab initio*?

HOLLIS: The lowest transition frequency is the difference between the rotational constants B and C. The uncertainty on $(B - C)$ is ~ 50 MHz.

BOTTA: Under what conditions did the polymerization reaction in the laboratory had been carried out (solution, temperature)?

HOLLIS: These are condensation experiments of atomic carbon and deuterated water at 77 K. The solid is later warmed and analyzed for sugar content.