# GREEN BANK TELESCOPE DETECTION OF NEW INTERSTELLAR ALDEHYDES: PROPENAL AND PROPANAL

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# ABSTRACT

The new interstellar molecules propenal (CH<sub>2</sub>CHCHO) and propanal (CH<sub>3</sub>CH<sub>2</sub>CHO) have been detected largely in absorption toward the star-forming region Sagittarius B2(N) by means of rotational transitions observed with the 100 m Green Bank Telescope (GBT) operating in the range from 18 GHz ( $\lambda \sim 1.7$  cm) to 26 GHz ( $\lambda \sim$ 1.2 cm). The GBT was also used to observe the previously reported interstellar aldehyde propynal (HC<sub>2</sub>CHO) in Sagittarius B2(N), which is a known source of large molecules presumably formed on interstellar grains. The presence of these three interstellar aldehydes toward Sagittarius B2(N) strongly suggests that simple hydrogen addition on interstellar grains accounts for successively larger molecular species: from propynal to propenal and from propenal to propanal. Energy sources within Sagittarius B2(N) likely permit the hydrogen addition reactions on grain surfaces to proceed. This work demonstrates that successive hydrogen addition is probably an important chemistry route in the formation of a number of complex interstellar molecules. We also searched for but did not detect the three-carbon sugar glyceraldehyde (CH<sub>2</sub>OHCHOHCHO).

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

## 1. INTRODUCTION

The large molecules found to date in interstellar clouds suggest a grain chemistry that favors aldehyde production. Consistent with this, we (Hollis et al. 2000) successfully detected interstellar glycolaldehyde (CH<sub>2</sub>OHCHO) and suggested that it might result from the polymerization of two formaldehyde molecules (H<sub>2</sub>CO) analogous to the early stage of the sugar synthesis (formose) reaction studied in the laboratory by investigators of prebiotic chemistry. Additionally, laboratory experiments have shown that subjecting interstellar ice analogs at ~16 K to ionizing radiation dosages that simulate interstellar cloud ages (Moore et al. 2001) results in solid-phase hydrogen addition reactions (Hudson & Moore 1999). The combination of the prevalence of interstellar aldehydes and the likelihood of subsequent hydrogen addition reactions with aldehydes prompted a successful search for interstellar ethylene glycol (HOCH<sub>2</sub>CH<sub>2</sub>OH) by Hollis et al. (2002). The detection of interstellar ethylene glycol, which differs in constituent atoms from glycolaldehyde by two hydrogen atoms, suggested that ethylene glycol is the product of two successive low-temperature hydrogen addition reactions with glycolaldehyde on grain surfaces or in grain ice mantles. As a consequence of these successes, we were motivated to search for the more complex sugar glyceraldehyde (CH<sub>2</sub>OHCHOHCHO), which may result from the polymerization of three formaldehyde molecules. Additionally, we searched for simpler aldehydes, specifically propenal (CH<sub>2</sub>CHCHO) and propanal (CH<sub>3</sub>CH<sub>2</sub>CHO), which could be the result of simple hydrogen addition reactions with the known interstellar aldehyde propynal (HC<sub>2</sub>CHO; Irvine et al. 1988; Turner 1991).

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#### 2. OBSERVATIONS AND RESULTS

Observations of propynal, propenal, and propanal and attempts to detect glyceraldehyde were made in 2004 February 25-April 17 with the NRAO<sup>6</sup> 100 m Robert C. Byrd Green Bank Telescope (GBT). Table 1 lists the rotational transitions of the molecules sought. The transition quantum numbers, types, calculated rest frequencies, lower level energies  $(E_i)$ , and line strengths (S) are listed in the first five columns. The GBT K-band receiver is divided into two frequency ranges with separate feed/amplifier sets covering 18-22.4 and 22-26.5 GHz. The GBT spectrometer was configured in its eight intermediatefrequency (IF), 200 MHz, three-level mode, which allows observing four 200 MHz frequency bands simultaneously in two polarizations through the use of offset oscillators in the IF. This mode affords 24.4 kHz channel separation. Antenna temperatures are on the  $T_{A}^{*}$  scale (Ulich & Haas 1976) with estimated 20% uncertainties. GBT half-power beamwidths can be approximated by  $\theta_B = 720''/\nu$  (GHz). Observations ranged between 18 and 26 GHz, corresponding to  $\theta_B \sim 40''$  and  $\theta_B \sim 28''$ , respectively. The Sgr B2(N-LMH) J2000 pointing position employed was  $\alpha = 17^{h}47^{m}19^{s}8$ ,  $\delta = -28^{\circ}22'17''$ , and a local standard of rest (LSR) source velocity  $(v_{LSR})$  of +64 km s<sup>-1</sup> was assumed. Data were taken in the OFF-ON position-switching mode, with the OFF position 60' east in azimuth with respect to the ON-source position. A single scan consisted of 2 minutes in the OFF-source position followed by 2 minutes in the ON-source position. Automatically updated dynamic pointing and focusing corrections were employed based on real-time temperature measurements of the structure input to a thermal model of the GBT; zero points were adjusted typically every 2 hr or less using the calibrators 1626-298 and/or 1733-130. The two polarization outputs from the spectrometer were averaged in the final data reduction process to improve the signal-to-noise ratio.

Observations of propynal, propenal, and propanal are summarized in Table 1, in which columns (6), (7), and (8) give measured intensities at LSR velocities of +82, +74, and +64

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 TABLE 1

 Summary of Spectral Line Observations toward Sgr B2(N-LMH)

TRANSITION		<b>FREQUENCY</b> <sup>a</sup>	E.		$\Delta T_A^* ({ m mK})^{ m b}$		
$J'_{\kappa-\kappa+} - J''_{\kappa-\kappa+}$	Type	(MHz)	$(cm^{-1})$	S	+82	+74	+64
(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)
		Propynal	(HC <sub>2</sub> CHC	<b>)</b> )°			
2 <sub>02</sub> -1 <sub>01</sub>	а	18650.308(4)	0.31	2.000	-3(1)	11(1)	-14(1)
		Propenal (	CH <sub>2</sub> CHCH	IO) <sup>d</sup>			
2 <sub>11</sub> -1 <sub>10</sub>	а	18221.164(2)	1.74	1.500	-29(2)	14(2)	
$3_{13} - 2_{12}$	а	26079.449(1)	2.30	2.667	-9(1)		-19(1)
		Propanal (C	CH <sub>3</sub> CH <sub>2</sub> CH	IO) <sup>e,f</sup>			
1 <sub>11</sub> -0 <sub>00</sub>	b	21268.611(9)	0.00	1.000		6(1)	
$2_{02} - 1_{01}$	а	20875.059(7)	0.35	1.995		5(1)	-7(1)
2 <sub>12</sub> -1 <sub>11</sub>	а	19690.426(7)	0.71	1.500	-4(1)		-18(1)
$2_{11} - 1_{10}$	а	22279.346(7)	0.75	1.500			-8(1)
$3_{03} - 2_{12} \dots \dots$	b	21451.572(8)	1.37	1.284	-3(1)		-16(1)
4 <sub>13</sub> -4 <sub>04</sub>	b	19182.445(10)	3.45	3.383	-5(1)	6(1)	-9(1)
		Glyceraldehyde (	CH <sub>2</sub> OHCH	ЮНСНО	) <sup>g</sup>		
2 <sub>21</sub> -1 <sub>11</sub>	с	19193.051(2)	0.26	1.500		<5	
$2_{20} - 1_{10}$	с	18845.484(2)	0.28	1.597		<5	
$3_{12} - 2_{02} \dots \dots$	с	19623.303(2)	0.52	1.934		<5	
$4_{13} - 3_{03} \dots \dots$	с	25656.520(1)	1.03	2.254		<10	
6 <sub>51</sub> -6 <sub>43</sub>	с	25724.488(3)	5.18	1.560		<10	
7 <sub>53</sub> -7 <sub>43</sub>	с	25655.113(3)	6.40	2.181		<10	
8 <sub>53</sub> -8 <sub>45</sub>	с	25612.418(3)	7.79	2.732		<15	
$13_{56} - 13_{4,10} \dots$	с	25618.963(8)	17.40	4.550		<10	

<sup>a</sup> Uncertainties in parentheses refer to the least significant digit and are 2  $\sigma$  values (Taylor & Kuvatt 1994).

<sup>b</sup> Uncertainties are 1  $\sigma$  values, and limits are 5  $\sigma$ .

<sup>c</sup> Propynal:  $\mu_a = 2.359(18)$  D, and  $\mu_b = 1.468(22)$  D (Brown & Godfrey 1984).

<sup>d</sup> Propenal:  $\mu_a = 3.052(4)$  D, and  $\mu_b = 0.630(1)$  D (Blom et al. 1984).

<sup>e</sup> Propanal:  $\mu_a = 1.71(4)$  D, and  $\mu_b = 1.85(4)$  D (Butcher & Wilson 1964).

 $^{f}$  A-state frequencies; the *E*-state is approximately frequency-coincident and cannot be resolved in a dense cloud.

<sup>g</sup> Glyceraldehyde:  $\mu_a = 0.459(3) \text{ D}, \mu_b = 0.36(4) \text{ D}, \text{ and } \mu_c = 2.068(8) \text{ D}$  (Lovas et al. 2003).

km s<sup>-1</sup>, respectively; in the case of glyceraldehyde, where no lines were detected, 5  $\sigma$  noise limits on the spectra are given. Spectra for all lines detected are shown in Figures 1–3. Propynal in Figure 1 shows the prototypical aldehyde spectrum with a strong absorption component at an LSR velocity of +64



FIG. 1.—Propynal (HC<sub>2</sub>CHO) spectrum toward Sgr B2(N-LMH) at 24.4 kHz channel spacing. Transition quantum numbers are shown in the upper right. The spectrum was processed with a median filter to remove instrumental slopes in the bandpass (G. Langston 2004, in preparation). The abscissa is the radial velocity with respect to the LSR calculated for the rest frequency of the transition shown (see Table 1) at an assumed source velocity of 64 km s<sup>-1</sup>. Dashed lines show LSR velocities at 64, 74, and 82 km s<sup>-1</sup>. The continuum level of the source is shown as a component of the temperature scale.

km s<sup>-1</sup>, a weaker absorption component at +82 km s<sup>-1</sup>, and a self-absorbed emission component at  $+74 \text{ km s}^{-1}$ . Propenal spectra in Figure 2 and propanal spectra in Figure 3 do not show all of the aforementioned velocity features that are presumably due to differences in the competing effects of emission and absorption for any given transition. While propanal data in Figure 3 have a large noise component, Figure 3a clearly shows an emission feature at  $+74 \text{ km s}^{-1}$  that has a suggestion of self-absorption, and Figures 3b-3f clearly show the stronger absorption component at  $+64 \text{ km s}^{-1}$ . Moreover, the figures also show that line-to-continuum ratios of the absorption features associated with propynal, propenal, and propanal indicate apparent optical depths of much less than 1. Table 1 and the figures show that the lowest energy level transitions observed for each molecule tend to result in emission (e.g., the  $2_{02}-1_{01}$ transition of propynal and the  $1_{11}-0_{00}$  transition of propanal) or, at least, some emission (the  $2_{11}-1_{10}$  transition of propenal). Higher energy level transitions tend toward absorption. This suggests a very low temperature regime (a few kelvins), in which the low energy levels are more populated, giving rise to the case in which emission dominates absorption. This complication, the likely variance in excitation temperatures among transitions, and the fact that the distribution function over all energy levels is not known preclude reliable number density estimates.

Other molecular probes toward Sgr B2(N-LMH) show that the LSR velocities seen here in propynal, propenal, and propanal are typical and that aldehydes in particular are widespread and would fill the GBT beam. For example, a recent Giant Metrewave



FIG. 2.—Propenal (CH<sub>2</sub>CHCHO) spectra toward Sgr B2(N-LMH) at 24.4 kHz channel spacing. The Fig. 1 caption applies. Panel a is the low energy level transition observed, and panel b is the higher energy level transition observed (see Table 1).

Radio Telescope image and spectrum of the  $1_{10}$ - $1_{11}$  transition of acetaldehyde (CH<sub>3</sub>CHO) at 1065 MHz show emission on a scale of at least an arcminute toward Sgr B2(N-LMH); that emission is characterized by two LSR velocity components near +64 and  $+82 \text{ km s}^{-1}$  (see Fig. 1 of Chengalur & Kanekar 2003). Moreover, the spatial scale of glycolaldehyde emission has been shown to be on the order of an arcminute (Hollis et al. 2001), and its LSR velocity is on the order of  $+72 \text{ km s}^{-1}$  (Hollis et al. 2002). While most large molecules seen in emission toward the hotcore source Sgr B2(N-LMH) have characteristic LSR velocities near  $+64 \text{ km s}^{-1}$ , recent Very Large Array (VLA) velocity images of the hot-core source molecule ethyl cyanide ( $CH_2CH_2CN$ ) also show another source  $\sim 5''$  north of the hot core with a characteristic LSR velocity of  $+72 \text{ km s}^{-1}$  (see Fig. 1 of Hollis et al. 2003); unfortunately, the VLA data did not extend far enough in velocity space to image a potential +82 km s<sup>-1</sup> source.

The observational evidence for interstellar propanal consists of the six transitions shown in Figure 3, and its identification is secure. By comparison, propenal has only three likely transitions in the 18-26 GHz range accessible to the GBT. We have observed two, but the third one  $(2_{02}-1_{01})$  is unfortunately frequency-coincident with H102 $\gamma$ . Observing only two transitions would ordinarily be considered a tentative detection of an interstellar molecule. However, the observational evidence for propenal is most likely sufficient because of the following arguments: (1) Line confusion is less likely in the K-band range since most molecular transitions of interstellar molecules have peak emission in the millimeter-wave region of the spectrum because of typical dense cloud temperatures of 50-100 K. In fact, most large interstellar molecules are associated with dense cloud hot cores. (2) A few large molecules such as the aldehydes are spatially widespread and have their strongest tran-



FIG. 3.—Propanal (CH<sub>3</sub>CH<sub>2</sub>CHO) spectra toward Sgr B2(N-LMH) at 24.4 kHz channel spacing. The Fig. 1 caption applies. Panels a-f are ordered from the lowest energy level transition to the highest energy level transition observed (see Table 1).

sitions at low temperatures characteristic of the colder gas sampled by the GBT at K band. The two propenal lines as well as the propanal lines are largely in absorption, indicating that the GBT is sampling the much colder, extended, and rarefied foreground gas in the vicinity of Sgr B2(N-LMH). (3) Since successive hydrogen addition is the simplest formation mechanism that could account for propenal, then the two lines that we attribute to propenal are securely identified because both the parent molecule, propynal, and the daughter molecule, propanal, are securely identified as interstellar molecules in the same source. We note that Dickens et al. (2001) previously reported the possible detection of propenal at millimeter wavelengths, but the assignment is unlikely because the more likely a-type transitions they attempted to observe (e.g.,  $10_{09}-9_{09}$  and  $11_{0.11}$ -10<sub>0.10</sub>) were missing (W. M. Irvine 2004, private communication). The a-type propenal lines reported here are the most favorable low-energy transitions accessible to the GBT. However, additional confirming transitions are problematical since the rotational constants of propenal yield few transitions whose energy levels would be populated at low temperatures.

### 3. DISCUSSION

Most complex molecules seen in the direction of Sgr B2(N-LMH) are shown by interferometry to be largely confined to the Large Molecule Heimat (LMH) region, which is a hot-core source of  $\sim 5''$  diameter; such molecules include methyl formate, acetic acid, ethyl cyanide, acetone, formic acid, vinyl cyanide, and methyl cyanide. However, the ease with which aldehydes

(e.g., formaldehyde, formamide, acetaldehyde, glycolaldehyde, propynal, propenal, and propanal) are detected with single-dish telescopes or large synthesized beam interferometers indicates that these molecules have significant spatial scales on the order of arcminutes. Since Sgr B2 is known to have large-scale shocks (see Chengalur & Kanekar 2003 and references therein), it is likely that the energy source necessary for endothermic reactions to occur on the surfaces or within the mantles of grains are provided by such shocks, and these shocks could also account for the release into the gas phase and the widespread distribution of the more common molecules whose formation is aided by this process. Certainly one of the simplest processes in building larger molecular species is successive hydrogen addition to extant grain surface or grain mantle molecules, and this is borne out by laboratory experiments with interstellar ice analogs (e.g., Hudson & Moore 1999). The detection of interstellar propynal, propenal, and propanal in the same source strongly implies the following hydrogen addition formation sequence:

$$HC_2CHO + 2H \rightarrow CH_2CHCHO + 2H \rightarrow CH_3CH_2CHO.$$

Aldehydes have been called the "sugars of space" ever since the discovery of interstellar formaldehyde by Snyder et al. (1969). This title took on greater significance with the detection of the simplest sugar glycolaldehyde (Hollis et al. 2000). These authors suggested that formaldehyde polymerization on interstellar grains may be responsible for the formation of glycolaldehyde and more complex sugars—an interstellar variant of the so-called formose reaction that has been extensively studied in the laboratory with regard to prebiotic chemistry (Larralde et al. 1995). In the initial stages of the formaldehyde polymerization, glycolaldehyde is produced, and rapidly thereafter glyceraldehyde, the next more complex sugar (see Walker 1975, p. 217). Our difficulty in attempting to detect glyceraldehyde (see Table 1 limits) suggests that, if interstellar glyceraldehyde exists, it is much more spatially extended such that our telescope beam may not couple efficiently to the source complex or, alternatively, a less efficient process than the formose reaction produces it. Based on our simpler aldehyde observations that are most easily explained by hydrogen addition, we suggest that the interstellar ice analog experiments with glycolaldehyde that facilitate carbon, oxygen, and hydrogen addition reactions may eventually be able to produce glyceraldehyde.

In summary, we have detected two new interstellar molecules, propenal and propanal, largely in absorption toward the star-forming region of Sgr B2(N). We also found propynal, a previously reported molecule, in the same region. These findings strongly indicate that two successive hydrogen additions on interstellar grains produce propenal from propynal; similarly, two successive hydrogen additions produce propanal from propenal. This result is supported by laboratory experiments that indicate low-temperature solid-phase hydrogen additions are responsible for the production of more complex molecules from simpler species. We searched for the three-carbon sugar glyceraldehyde and were not successful. As a result, we conclude that an efficient formaldehyde polymerization chemistry is not the likely production mechanism for either glycolaldehyde or glyceraldehyde.

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