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INTERSTELLAR GLYCOLALDEHYDE: THE FIRST SUGAR

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ABSTRACT

Interstellar glycolaldehyde (CH_2OHCHO) has been detected in emission toward the Galactic center source Sagittarius B2(N) by means of millimeter-wave rotational transitions. Glycolaldehyde is an important biomarker since it is structurally the simplest member of the monosaccharide sugars that heretofore have gone undetected in interstellar clouds. There is no consensus as to how any such large complex molecules are formed in the interstellar clouds. It may be that the typical environment of dense interstellar clouds is favorable to glycolaldehyde synthesis by means of the polymerization of formaldehyde (H_2CO) molecules either on grain surfaces or in the gas phase. Alternatively, we speculate that glycolaldehyde and other complex molecules may undergo assembly from functional molecular groups on grain surfaces. Utilizing common chemical precursors, a chance process could account for the high degree of isomerism observed in complex interstellar molecules (e.g., methyl formate, acetic acid, and glycolaldehyde). This work suggests that the phenomenon of isomerism be investigated further as a means of potentially constraining interstellar chemistry routes for those individual sources where the condition of good source-beam coupling can be achieved.

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

1. INTRODUCTION

Simple monosaccharide sugars are carbohydrates or, more specifically, compounds of carbon and water, with the following empirical chemical expression:

$$(C + H_2O)_n = C_nH_{2n}O_n, \quad (1)$$

where $n \geq 2$ is the number of carbon or oxygen atoms present. For example, a two-carbon sugar (i.e., $C_2H_4O_2$) is referred to as diose, and similarly, a three-carbon sugar is triose, a four-carbon sugar is tetrose, etc. Furthermore, these monosaccharides or monomer subunits can be connected to form polysaccharide chains. Ribose (i.e., $C_5H_{10}O_5$—a pentose class sugar monomer), along with phosphates and nucleic bases, are the building blocks of nucleic acids, which are the carriers of the genetic code.

Aldehyde sugars or aldoses are hydroxyaldehydes, and glycolaldehyde is the simplest possible hydroxyaldehyde. Therefore, glycolaldehyde is the simplest possible sugar (Marstokk & Møllendal 1973) and has an alternative name of diose, a two-carbon monosacchahride whose structural formula is CH_2OHCHO. There is no theoretical formation mechanism for either gas-phase chemistry or grain-surface reactions that accounts for interstellar glycolaldehyde. The generally accepted prebiotic synthesis of sugars on the early Earth is thought to occur via the formose reaction, which is an aqueous-catalyzed polymerization of formaldehyde, H_2CO (Larralde, Robsertson, & Miller 1995). In the initial stage of the formose reaction, glycolaldehyde is produced, and this glycolaldehyde itself subsequently becomes autocatalytic:

$$2H_2CO \rightarrow CH_2OHCHO. \quad (2)$$

The initial catalyzing agent in equation (2) can be a base, clay, or radiation. While the formose reaction has been questioned with regard to conditions that were likely extant on the prebiotic Earth (e.g., Shapiro 1988), it may well be that the typical environment of an interstellar cloud is favorable to sugar synthesis by this means since interstellar formaldehyde is ubiquitous. For example, interstellar clouds have grain surfaces, externally impinging UV radiation, abundant gas-phase formaldehyde that is readily polymerizable, and presumably grain-surface formaldehyde—such conditions may be favorable to an interstellar analog of the formose reaction in equation (2). Thus, due to the potential biological importance of finding any sugar molecule in interstellar clouds, we were motivated to conduct a search for glycolaldehyde whose gas-phase emission spectrum is relatively simple in comparison with all other monosaccharides.

2. OBSERVATIONS AND RESULTS

The observations were made in 2000 May 25–31 with the NRAO[1] 12 m telescope. Table 1 lists the six strongest *b*-type transitions of the lowest energy conformer of glycolaldehyde in the 3 mm range that were used in this search. These transitions were calculated from a fit of the transitions measured by Marstokk & Møllendal (1970). The transition quantum numbers, the transition rest frequency with 2 σ uncertainty, the energy of the upper level (E_u), and the transition strength (S) are listed in the first four columns. Our search concentrated on the *b*-type, *R*-branch spectrum of glycolaldehyde since it is expected to be strong because $\mu_b = 2.33$ D while $\mu_a = 0.26$ D (Marstokk &

[1] The National Radio Astronomy Observatory is a facility of the National Science Foundation, operated under cooperative agreement by Associated Universities, Inc.

TABLE 1

SUMMARY OF GLYCOLALDEHYDE OBSERVATIONS TOWARD SGR B2(N)[a]

Transition J'_{k-k+}–J''_{k-k+} (1)	Frequency[b] (MHz) (2)	E_u (cm^{-1}) (3)	S (4)	T_R^{*} [b,c] (mK) (5)	ΔV [b,d] (km s^{-1}) (6)	$N_T \times 10^{-15}$ [b,e] (cm^{-2}) (7)
7_{07}–6_{16}	71542.7(9)	10.3	5.2	34(5)	22.3(33)	1.3(4)
8_{17}–7_{26}	75347.3(5)	14.9	2.8	15(4)	40.0(30)	1.9(8)
8_{08}–7_{17}	82471.2(14)	13.1	6.3	45(6)	24.3(28)	1.4(3)
9_{09}–8_{18}	93053.3(21)	16.2	7.3	40(5)	[f]	...
$10_{0,10}$–9_{19}	103392.0(30)	19.7	8.4	[g]	[f]	...
10_{19}–9_{28}	103667.4(16)	22.2	4.8	25(5)	29.0(24)	1.0(3)

[a] Observed using the J2000 pointing position of the Large Molecule Heimat (Mehringer et al. 1997), $\alpha = 17^h47^m19\overset{s}{.}8$, $\delta = -28°22'17''$, and assumed at $V_{lsr} = 62.5$ km s^{-1} (see Fig. 1 caption).

[b] Uncertainties in parentheses refer to the least significant digit and are 2 σ values for col. (2) and 1 σ estimates for cols. (5), (6), and (7).

[c] Temperature-to-flux conversion factors are 31.9, 32.2, 32.6, 33.4, 34.2, and 34.3 Jy K^{-1} for the corresponding increasing frequencies in col. (2).

[d] FWHM estimates of weaker intensity lines are more difficult to determine, but the full width at zero intensity values for all clean lines detected are consistent with ~40 km s^{-1}.

[e] NRAO 12 m abundance values derived from eq. (3) using $T_{ROT} = 200$ K (see text). These values must be multiplied by ~20 to compare with other Sgr B2(N) molecules observed with the OVRO array (see text).

[f] Blended lines (see Fig. 1).

[g] No discernible peak (see Fig. 1).

Møllendal 1973) and because *R*-branch transitions have larger statistical line strengths than the *Q*- or *P*-branch transitions for a given rotational state. The receiver used dual-channel SIS mixers, operating in a single-sideband mode. The image sideband was rejected at a level of 20 dB by tuning the mixer backshorts. The Millimeter AutoCorrelator (MAC) spectrometer was used in the 600 MHz bandwidth mode. The channel spacing was 195 kHz, and the effective frequency resolution was 391 kHz owing to internal Hanning weighting. The two receiver polarization intermediate frequencies were connected to separate signal inputs of the MAC spectrometer. The two polarization outputs from the MAC were subsequently averaged in the final data reduction process to improve the signal-to-noise ratio.

Calibration by the chopper method was used, and the resultant data are on the T_R^* scale (Kutner & Ulich 1981). This scale includes corrections for atmospheric extinction and telescope spillover losses, but not for error-beam losses or the forward beam coupling to the source. At 71, 75, 82, 93, and 103 GHz, the half-power beamwidths were ~87″, ~84″, ~77″, ~68″, and ~61″, respectively. Data were taken in the position-switching mode, with the reference position 30′ west in azimuth. Pointing was monitored by continuum measurements of Uranus and quasars, including 3C 279, 3C 273, 0420−014, and NRAO 530.

Table 1 summarizes our search results for glycolaldehyde transitions toward Sagittarius B2(N), and sample spectra for all six glycolaldehyde transitions detected are shown in Figure 1. Four transitions (i.e., 7_{07}–6_{16}, 8_{17}–7_{26}, 8_{08}–7_{17}, and 10_{19}–9_{28}) appear to be clear of any significant line contamination from other species. Moreover, the 9_{09}–8_{18} transition is blended with, but distinguishable from, a stronger vinyl cyanide line. While the $10_{0,10}$–9_{19} transition is heavily blended with comparable-strength line(s) of methyl formate and/or vinyl cyanide, we show a comparison spectrum of OMC-1 suggesting that the Sgr B2(N) spectrum has excess emission at the expected rest frequency for this glycolaldehyde transition.

The glycolaldehyde column densities in Table 1 were calculated from the following expression that employs cgs units and assumes optically thin, LTE conditions:

$$N_T = \frac{T_R^* \Delta V}{(8\pi^3/3k)\,\nu S\mu^2} \quad \frac{Q_{ROT} e^{E_u/kT_{ROT}}}{1 - [(e^{h\nu/kT_{ROT}} - 1)/(e^{h\nu/kT_{bg}} - 1)]}, \quad (3)$$

where N_T is the total projected column density averaged over the 12 m beam (col. [7]), T_R^* is the observed peak line temperature (col. [5]), ΔV is the observed FWHM line width (col. [6]), the molecular rotational temperature $T_{ROT} = 200$ K (e.g., Mehringer et al. 1997 and discussion in Miao & Snyder 1997), $Q_{ROT} = 6.9T_{ROT}^{1.5}$ is the rotational partition function (see Gordy & Cook 1984, p. 58, for a more detailed formulation), ν is the transition frequency (col. [2]), E_u is the upper rotational energy level (col. [3]), S is the transition line strength (col. [4]), the electric dipole moment is $\mu = 2.33$ D (Marstokk & Møllendal 1973), and $T_{bg} \geq 2.7$ K is the continuum background temperature.

3. DISCUSSION

Glycolaldehyde (CH_2OHCHO) is an isomer of both methyl formate ($HCOOCH_3$) and acetic acid (CH_3COOH); structural diagrams for all three isomers are shown in Figure 2. These $C_2H_4O_2$ molecules are the first isomer triplet detected in interstellar clouds. Unlike glycolaldehyde, which has only been detected in Sgr B2(N), and acetic acid, which has only been reported in Sgr B2(N) and W51, interstellar methyl formate is ubiquitous. Methyl formate is composed of a central oxygen atom (i.e., an ether group) that bonds with a methyl group and an aldehyde group; glycolaldehyde is composed of a central methylene group that bonds with a hydroxyl group and an aldehyde group; and acetic acid is composed of a central carbonyl group that bonds with a methyl group and a hydroxyl group. We expect that the interstellar abundances of glycolaldehyde and acetic acid would be much less than methyl formate since structural configurations of complex interstellar molecules seem to show a preference for C-O-C (e.g., methyl formate) rather than C-C-O (e.g., acetic acid and gylcolaldehyde) backbones (see Mehringer et al. 1997).

It is somewhat problematic to compare the Sgr B2(N) abundances of the $C_2H_4O_2$ isomer triplet since acetic acid was detected with the Berkeley-Illinois-Maryland Association and Owens Valley Radio Observatory (OVRO) arrays with beam sizes of ~10.″8 × 7.″1 and ~11.″5 × 4.″4, respectively, and since glycolaldehyde was detected with the NRAO 12 m telescope. Comparison of methyl formate spectra taken with the NRAO 12 m antenna telescope system with those extracted from OVRO interferometric observations suggest that a Sgr B2(N) abundance derived from the NRAO 12 m antenna data using equation (3) and a $T_{ROT} \sim 200$ K must be scaled by a factor of ~20 to achieve the same abundance derived from the OVRO array data; this factor compensates for beam dilution and any extended source component beyond the Sgr B2(N) concentration. From such an analysis, specifically for Sgr B2(N), as would be observed by the OVRO array, we obtain a methyl formate abundance of ~1.9×10^{17} cm^{-2} and a prediction of a glycolaldehyde abundance of ~2.8×10^{16} cm^{-2}, while Mehringer et al. (1997) obtained an acetic acid abundance of ~7.3×10^{15} cm^{-2}. Hence, the Sgr B2(N) relative abundances of (acetic acid) : (glycolaldehyde) : (methyl formate) ~ 1 : 4 : 26, which is consistent with the observed preference for C-O-C backbone structures in complex interstellar molecules.

The mechanism by which a molecule is made plays the

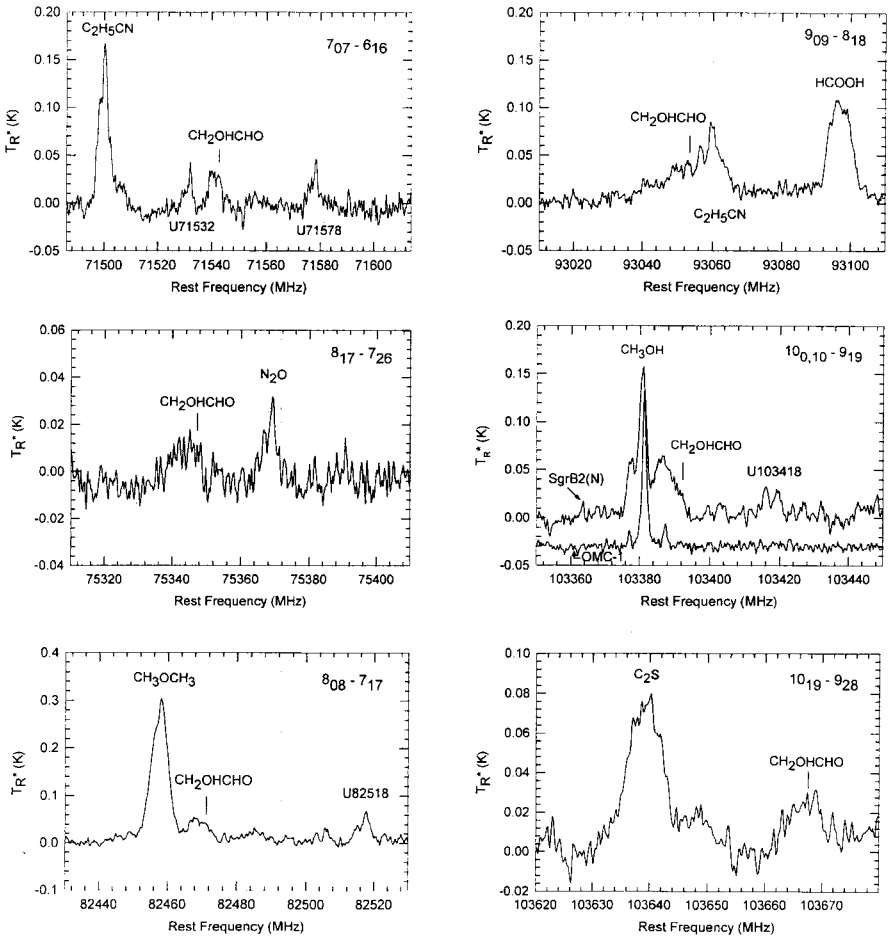

FIG. 1.—Glycolaldehyde (CH_2OHCHO) spectra toward Sgr B2(N) at 195 kHz channel spacing. Transition quantum numbers are shown for glycolaldehyde in the upper right-hand corner of each panel. The rest-frequency axes reflect the assumed V_{lsr} of 62.5 km s^{-1} for this source. The glycolaldehyde rest-frequency fiducials in all panels are consistently offset from line centers toward higher frequencies (equivalently, lower velocities); this is consistent with rest-frequency uncertainties (see Table 1) but may also be due, in part, to the uncertainty in the assumed source velocity since Mehringer et al. (1997) obtain 64 km s^{-1} for acetic acid and Miao et al. (1995) obtain 63.7 km s^{-1} for methyl formate. Note that the $10_{0,10}$–9_{19} transition is heavily blended (see text) and that an offset OMC-1 spectrum, whose CH_3OH peak has been normalized to the same peak in Sgr B2(N), is provided for comparison.

largest role in determining its abundance. At present, there is no consensus regarding how any large complex interstellar molecule is formed. For example, there are at least two plausible but different scenarios for the formation of methyl formate. Suppose the simple species formic acid and methanol reside on the grain surface. The subsequent surface reaction of formic acid and methanol (a condensation or neutralization reaction) would form methyl formate preferentially because the acidic hydrogen on formic acid would preferentially condense with the OH on methanol to form water. This does not happen in the gas phase because the reaction barrier is too high. This formation scenario does happen in solution, and it may happen on a grain surface. Alternatively, methanol and formaldehyde are the precursors for the formation of methyl formate through gas-phase reactions in hot cores (Caselli, Hasegawa, & Herbst 1993). Similarly, the polymerization of formaldehyde on a grain surface or, alternatively, through gas-phase reactions could lead to glycolaldehyde as indicated in equation (2) above. A gas-phase formation mechanism has been proposed for interstellar acetic acid (Huntress & Mitchell 1979). However, toward Sgr B2(N), acetic acid is inferred to be cospatial with other complex species likely to be formed on grains suggesting that grain-surface chemistry must also play a significant role in acetic acid formation as well (Mehringer et al. 1997). It may be that isomerism may hold clues as to how large complex molecules are formed, and we will consider that potential subsequently.

There are nine interstellar molecular isomer pairs in addition to the $C_2H_4O_2$ isomer triplet discussed here. Since interstellar isomerism is common, it suggests that molecular formation routes for isomeric species may have common precursors. Since most large complex interstellar molecules are suspected to originate on the surface of interstellar grains, it may be that the molecular groups that comprise a complex molecule are first formed on the grains. From these structural group building blocks, we speculate that molecular assembly may be able to occur on grain surfaces. Each such surface group would be subject, at the least, to the following scenarios: (1) the group could undergo hydrogenation, (2) the group could react with gaseous species that impinge on the grains, or (3) the group could diffuse over the grain surface and react with another surface group under favorable conditions such as a thermal

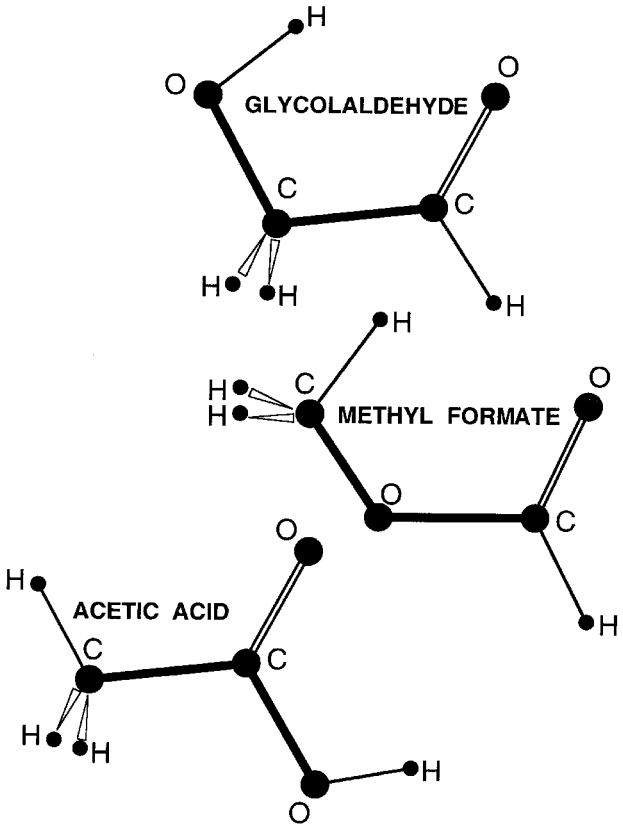

FIG. 2.—Interstellar isomer geometry of $C_2H_4O_2$. All atoms lie in the plane of the paper, except those hydrogen atoms in the methyl groups or in the methylene group that show perspective triangles indicating relative positions in and out of the plane of the paper.

transient, the reduction of H atom surface reactions, or the reduction of H atom surface abundance. Subsequently, stable heavy molecular species could be formed by combinations and permutations of the above scenarios. If this grain chemistry scheme does occur, it is likely that isomers would be formed and that observations would point to the precursor functional molecular groups on the grains from which all such species originate. As regards the $C_2H_4O_2$ isomers considered in this work, it could be that the more abundant and ubiquitous methyl formate enjoys some preferential chemical affinity on the gains and is therefore a more "successful" molecule from a molecular assembly point of view.

In summary, we have detected interstellar glycolaldehyde in emission toward the Galactic center source Sgr B2(N) by means of millimeter-wave rotational transitions. From an astrobiology viewpoint, the detection of interstellar glycolaldehyde is a significant milestone since it is structurally the simplest possible member of the monosaccharide sugars and the first sugar reported in interstellar clouds. While we have presented several possible formation routes for the production of the isomer triplet composed of glycolaldehyde, methyl formate, and acetic acid, there is no consensus as to how these large complex species are formed in the interstellar medium. However, we suggest that the detection and abundance determinations of isometric forms (like methyl formate, acetic acid, and glycolaldehyde) may be able to provide clues to the different chemical routes involved in their formation by observing the isometric differentiation.

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