

INTERSTELLAR ANTIFREEZE: ETHYLENE GLYCOL

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ABSTRACT

Interstellar ethylene glycol ($\text{HOCH}_2\text{CH}_2\text{OH}$) has been detected in emission toward the Galactic center source Sagittarius B2(N-LMH) by means of several millimeter-wave rotational torsional transitions of its lowest energy conformer. The types and kinds of molecules found to date in interstellar clouds suggest a chemistry that favors aldehydes and their corresponding reduced alcohols—e.g., formaldehyde (H_2CO)/methanol (CH_3OH), acetaldehyde (CH_3CHO)/ethanol ($\text{CH}_3\text{CH}_2\text{OH}$). Similarly, ethylene glycol is the reduced alcohol of glycolaldehyde (CH_2OHCHO), which has also been detected toward Sgr B2(N-LMH). While there is no consensus as to how any such large complex molecules are formed in the interstellar clouds, atomic hydrogen (H) and carbon monoxide (CO) could form formaldehyde on grain surfaces, but such surface chemistry beyond that point is uncertain. However, laboratory experiments have shown that the gas-phase reaction of atomic hydrogen (H) and solid-phase CO at 10–20 K can produce formaldehyde and methanol and that alcohols and other complex molecules can be synthesized from cometary ice analogs when subject to ionizing radiation at 15 K. Thus, the presence of aldehyde/reduced alcohol pairs in interstellar clouds implies that such molecules are a product of a low-temperature chemistry on grain surfaces or in grain ice mantles. This work suggests that aldehydes and their corresponding reduced alcohols provide unique observational constraints on the formation of complex interstellar molecules.

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

1. INTRODUCTION

Ethylene glycol ($\text{HOCH}_2\text{CH}_2\text{OH}$), an alcohol commonly used as antifreeze in automobile coolant systems, is a key organic species associated with prebiotic sugar synthesis. Ethylene glycol is the sugar alcohol of glycolaldehyde (CH_2OHCHO), the simplest possible aldehyde sugar (Marstokk & Møllendal 1973), which has been detected by Hollis, Lovas, & Jewell (2000) toward Sagittarius B2(N-LMH). On the parent bodies of carbonaceous meteorites, the formose reaction is a potential prebiotic pathway to gradually synthesize hydroxylated compounds and sugars of increasing carbon number (Cooper et al. 2001). In this reaction, formaldehyde reacts with itself in aqueous solution, and glycolaldehyde is the primary condensation product that can be reduced by hydrogenation to ethylene glycol (e.g., see Walker 1975). There are variations of this scenario. For example, a photochemical formose reaction can produce ethylene glycol and other alcohols as major products (e.g., see Irie 1989). Most recently, Charnley (2001) has suggested the likelihood that both ethylene glycol and glycolaldehyde would result from molecular synthesis on interstellar grain surfaces. Moreover, ethylene glycol has been identified in both the Murchison and Murray meteorites as the most abundant of the sugar-related alcohols found in such objects (Cooper et al. 2001).

Ethylene glycol is a triple rotor molecule. Torsions around the two CO bonds and the CC bond produce 10 different spatial arrangements (conformers) of ethylene glycol (see Fig. 1 of

Christen et al. 2001). Two of the conformers can establish internal hydrogen bonds that have a locking effect on the CC bond, thus lowering their energy relative to the other conformers. The conformer of lowest energy is designated the *g'*Ga form whose structure is represented as both a “sawhorse” and a Newman projection in Figure 1. The *g'*Ga structure of ethylene glycol gives rise to a microwave spectrum due to torsion of both hydroxyl groups. The strongest transitions are *a*-type and involve rovibration energy level changes. Such transitions occur for changes from a rotational level in the $v = 1$ state to a rotational level in the $v = 0$ state or vice versa, i.e., across the tunneling splitting of ~ 7 GHz. The spectrum for ethylene glycol was first successfully assigned in the laboratory by Christen et al. (1995); that work and subsequent unpublished improvements to it provide the basis for our astronomical identification of several *a*-type lines of ethylene glycol.

2. OBSERVATIONS AND RESULTS

The observations were made in 2000 May 25–31 with the NRAO² 12 m telescope. Table 1 lists the five strongest *a*-type transitions of the lowest energy conformer of ethylene glycol that we fortuitously found while searching for glycolaldehyde (Hollis et al. 2000). These ethylene glycol transition frequencies and molecular parameters were calculated from a fit of transitions measured in the laboratory by Christen et al. (1995) and

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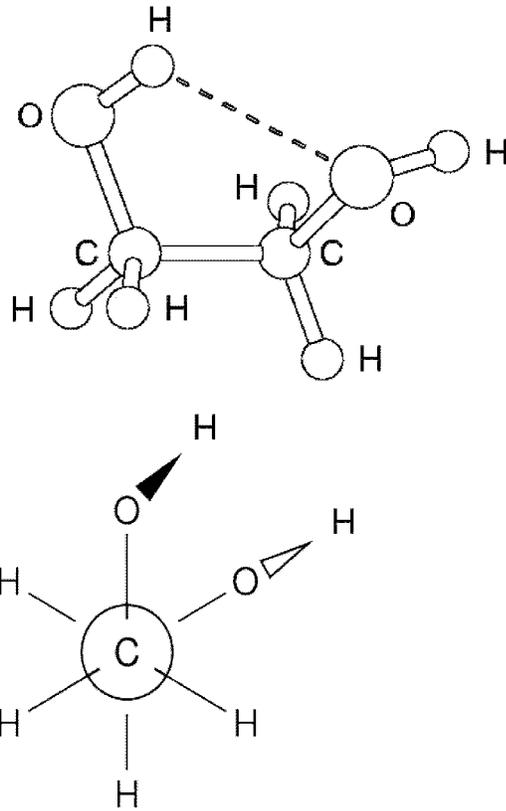


FIG. 1.—Sawhorse diagram and Newman projection of the $g'Ga$ conformer of ethylene glycol. In this lowest energy conformer of ethylene glycol, the capital letter G specifies the rotation around the CC bond in which the OH groups adopt the *Gauche* orientation with respect to each other. The lower case letters a and g' specify the rotation around the two CO bonds. For additional details on the structural nomenclature, see Christen et al. (1995, 2001). The dashed line in the sawhorse diagram depicts the internal hydrogen bond. The Newman projection is looking along the CC bond from left to right in the sawhorse diagram. The Newman projection hydrogen bonds on the O -atoms appear as perspective triangles, with each H -atom farther away than its corresponding O -atom. The filled and open triangles indicate the closer and more distant O -atom, respectively.

D. Christen & H. Muller (2002, unpublished). The transition quantum numbers, the calculated transition frequency, the energy of the upper level (E_u), and the product of the coupled dipole moments times the transition strength ($\mu^2 S$) are listed in the first four columns of Table 1. Immediately following a calculated or measured value in this work, parentheses contain an estimate of 1σ uncertainty in the least-significant digit. For

all transitions of ethylene glycol, coupled contributions from all three dipole moments occur. Dipole moments were measured by Christen et al. (1995), who obtained $\mu_a = 2.080(3)$ D, $\mu_b = 0.936(7)$ D, and $\mu_c = -0.47(1)$ D in the preferred Fit III of that work.

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^* temperature scale (Kutner & Ulich 1981). This scale includes corrections for atmospheric extinction and rear and forward telescope spillover losses but not error beam losses nor forward beam coupling to the source. At 75 and 93 GHz, the half-power beamwidths were $\sim 84''$ and $\sim 68''$, respectively, and at these frequencies the conversion factor from T_R^* to janskys is $32.8(30)$ Jy K^{-1} . The Sgr B2(N-LMH) J2000 pointing position used was $\alpha = 17^h 47^m 19^s.8$ and $\delta = -28^\circ 22' 17''$, and an LSR source velocity of 62.5 km s^{-1} was assumed. 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 ethylene glycol detection results toward Sgr B2(N-LMH) in terms of T_R^* intensities (col. [5]) and FWHM intensity line widths (col. [6]). Additionally, LSR velocity estimates (col. [7]) are provided for transitions showing no apparent line contamination, which is discussed later in this section. Spectra corresponding to Table 1 data are shown in Figure 2. Reflecting the assumed 62.5 km s^{-1} LSR source velocity, rest-frequency fiducials in Figure 2 fall on the high-frequency side of the highest emission peak in the observed lines. This consistent offset in each spectrum amounts to ~ 8 km s^{-1} , indicating that the LSR velocity for ethylene glycol is ~ 71 km s^{-1} . Turner & Apponi (2001) maintain that NRAO 12 m observations toward Sgr B2(N) show that dimethyl ether and methyl formate have an LSR velocity of ~ 64 km s^{-1} typical of the Large Molecule Heimat (LMH) core source, whereas vinyl alcohol and glycolaldehyde have an LSR velocity of ~ 71 km s^{-1} typical of the surrounding ambient cloud.

Note that in Table 1, the $8_{36}, (v=0) - 7_{35}, (v=1)$ and the $8_{44}, (v=0) - 7_{43}, (v=1)$ transitions are frequency-coincident,

TABLE 1
SUMMARY OF ETHYLENE GLYCOL OBSERVATIONS TOWARD SGR B2(N-LMH)

TRANSITION $J'_{K-K+}, v' - J''_{K-K+}, v''$ (1)	FREQUENCY (MHz) (2)	E_u (cm^{-1}) (3)	$\mu^2 S$ (D^2) (4)	T_R^* (mK) (5)	ΔV (km s^{-1}) (6)	V_{LSR} (km s^{-1}) (7)	OBS. RI (8)	T_{ROT}			
								50 K LTE RI (9)	200 K LTE RI (10)	50 K $N_T \times 10^{-14}$ (cm^{-2}) (11)	200 K $N_T \times 10^{-14}$ (cm^{-2}) (12)
$8_{45}, (v=0) - 7_{44}, (v=1)$	75151.4(4)	17.675	24.454	46(4)	34(3)	...	2.00	0.58	0.70	<14.5	<77.8
$8_{36}, (v=0) - 7_{35}, (v=1)$	75186.1(4)	15.286	28.822	33(4)	24(3)	71.1(16)	1.43	1.31	1.52	3.3(11)	17.9(62)
$8_{44}, (v=0) - 7_{43}, (v=1)$	75186.1(4)	17.676	24.439								
$7_{07}, (v=1) - 6_{06}, (v=0)$	75299.9(4)	9.400	33.300	23(4)	25(3)	70.7(16)	1.00	1.00	1.00	3.1(9)	19.8(58)
$9_{19}, (v=1) - 8_{18}, (v=0)$	92975.9(4)	14.919	43.735	38(4)	40(3)	...	1.65	1.38	1.56	<5.9	<33.5

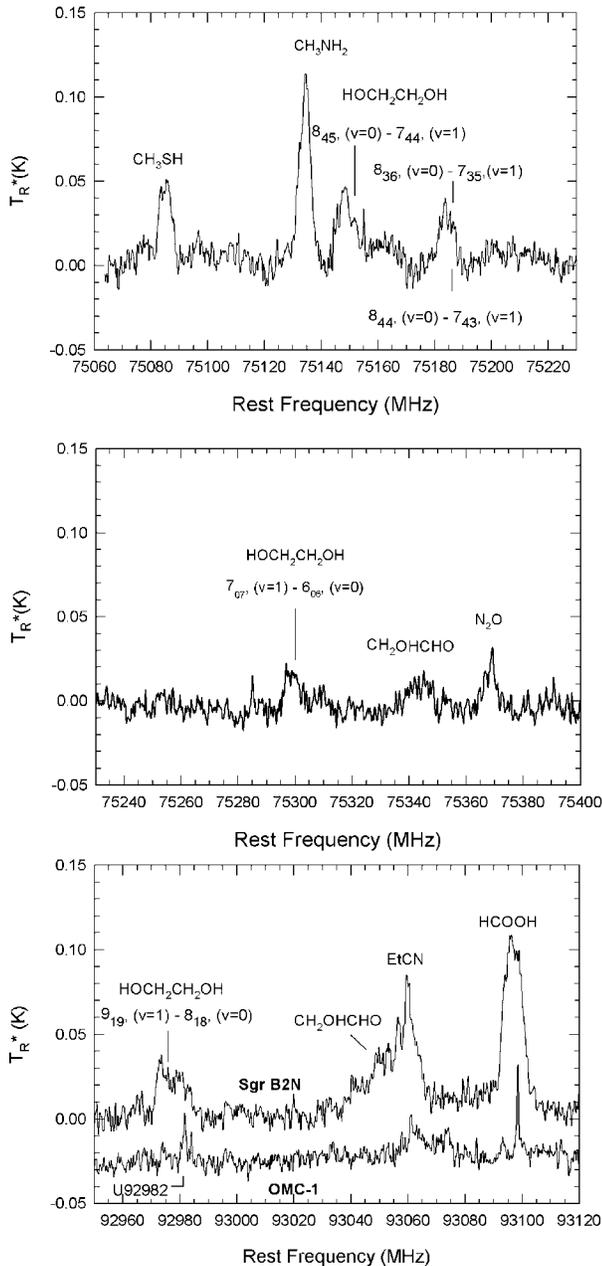


FIG. 2.—Ethylene glycol ($\text{HOCH}_2\text{CH}_2\text{OH}$) spectra toward Sgr B2 (N-LMH) at 195 kHz channel spacing. Transition quantum numbers are also shown. The rest-frequency axes reflect an assumed 62.5 km s^{-1} LSR source velocity. Note that the $9_{19}, (v=1)$ – $8_{18}, (v=0)$ transition is likely blended with U92982, which is shown in the offset OMC-1 spectrum that is provided for comparison. U92982 may be the 3_{03} – 2_{02} transition of HDCS (see § 2).

and these two transitions and the $7_{07}, (v=1)$ – $6_{06}, (v=0)$ transition are apparently clear of any line contamination from other molecular species as shown in Figure 2. Table 1 columns (8), (9), and (10) are the observed intensities, predicted 50 K LTE intensities, and predicted 200 K LTE intensities, respectively, relative to the $7_{07}, (v=1)$ – $6_{06}, (v=0)$ transition; therefore, in the column headings, RI denotes relative intensity. In calculating ethylene glycol LTE intensities, we have adopted a T_{ROT} of 200 K (Mehring et al. 1997; Miao & Snyder 1997) appropriate for the $\sim 5''$ diameter LMH core source and a T_{ROT} of 50 K more appropriate for the surrounding ambient

cloud. The latter temperature is based on a rotational diagram for glycolaldehyde. Column (8) shows that the $8_{45}, (v=0)$ – $7_{44}, (v=1)$ transition is anomalously strong by a factor of ~ 3 in comparison with the predicted LTE values in columns (9) and (10). It is likely that the $8_{45}, (v=0)$ – $7_{44}, (v=1)$ line is contaminated by an unknown molecular species that would account for the suggestive structure on the high-frequency shoulder of the line complex that has a 34 km s^{-1} line width as compared with the uncontaminated line widths of $\sim 24 \text{ km s}^{-1}$ as shown in column (6) of Table 1. Clearly, the $9_{19}, (v=1)$ – $8_{18}, (v=0)$ transition is also contaminated by another line on its high-frequency side because of its larger 40 km s^{-1} line width. The contaminating line in Sgr B2(N-LMH) may be U92982, which is present in the OMC-1 comparison spectrum shown in the bottom panel of Figure 2. U92982 may be the 3_{03} – 2_{02} transition of HDCS that has a rest frequency of 92981.592 MHz and was observed in TMC-1 by Minowa et al. (1997). However, these authors also inspected spectral line data of other sources, including Orion KL and Sgr B2, and could not definitively identify HDCS.

The ethylene glycol total column densities in Table 1 were calculated from the following expression, which employs cgs units and assumes optically thin LTE conditions:

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

where N_T , the total column density averaged over the NRAO 12 m beam, is given in columns (11) or (12) for a rotational temperature (T_{ROT}) of either 50 or 200 K, respectively; T_R^* is the observed peak line temperature (col. [5]); ΔV is the observed FWHM line width (col. [6]); $Q_{\text{ROT}} = 16.94T_{\text{ROT}}^{1.5}$ is the rotational partition function (e.g., Gordy & Cook 1984, p. 58); ν is the transition frequency (col. [2]); E_u is the upper rotational energy level (col. [3]); $\mu^2 S$ is the product of the coupled dipole moment squared times the transition line strength (col. [4]); and $T_B \geq 2.7 \text{ K}$ is the continuum background temperature. For the frequency-coincident $8_{36}, (v=0)$ – $7_{35}, (v=1)$ and $8_{44}, (v=0)$ – $7_{43}, (v=1)$ transitions, the ~ 18 and $\sim 15 \text{ mJy}$ intensities, respectively, were separated by assuming LTE, and the total column densities that resulted were therefore the same for both transitions. The total column densities for the $8_{45}, (v=0)$ – $7_{44}, (v=1)$ and the $9_{19}, (v=1)$ – $8_{18}, (v=0)$ transitions must be considered upper limits due to line contamination as discussed previously.

3. DISCUSSION

The types and kinds of molecules found to date in interstellar clouds suggest a chemistry that favors aldehydes and their corresponding reduced alcohols (e.g., formaldehyde/methanol, acetaldehyde/ethanol, and glycolaldehyde/ethylene glycol). There is no consensus as to how any such large complex molecules are formed in the interstellar clouds. However, Hiraoka et al. (1994) have shown in laboratory experiments that the formation of formaldehyde and methanol are possible from reactions of gas-phase atomic hydrogen (H) with solid-phase carbon monoxide (CO) at 10–20 K. Additionally, Moore & Hudson (1998) were successful in synthesizing alcohols and other complex molecules found in interstellar clouds by subjecting cometary ice analogs to ionizing radiation at $\sim 15 \text{ K}$, and they concluded that solid-phase H- and OH-addition reactions can contribute to many of the molecules observed in comets and interstellar objects. Thus, the presence of aldehyde/

reduced alcohol pairs in interstellar clouds suggests that such molecules are a product of a low-temperature chemistry on grain surfaces or in grain ice mantles.

The detection and identification of interstellar ethylene glycol is fortuitous since the objective of the original experiment was to detect interstellar glycolaldehyde that was identified (Hollis et al. 2000) toward Sgr B2(N-LMH). Since the glycolaldehyde experiment was purely a spectral detection with a single antenna, no spatial information was obtained. However, Hollis et al. (2000) assumed that glycolaldehyde, like its isomers methyl formate and acetic acid, would be confined to the $\sim 5''$ diameter of the LMH core source. Observing the strongest known glycolaldehyde transition with the Berkeley-Illinois-Maryland Association (BIMA) array, Hollis et al. (2001) indeed produced a map of glycolaldehyde showing a weak concentration of emission confined to the LMH core source. However, since the BIMA array was not able to recover the flux measured by the NRAO 12 m telescope, modeling showed that the bulk of the glycolaldehyde emission is coming from the less dense cloud extremities in the vicinity of the LMH core source and that this more extended source has a spatial scale of $\geq 60''$. Such a result was surprising because heretofore large complex molecules were assumed to be confined to small, compact hot cores. If aldehyde/reduced alcohol pairs represent a series of organic compounds that result from a common synthesis pathway, then ethylene glycol may well have a spatial distribution similar to glycolaldehyde toward Sgr B2(N-LMH). The similar ~ 71 km s $^{-1}$ LSR velocities and ~ 24 km s $^{-1}$ line widths argue that glycolaldehyde and ethylene glycol share the same emitting volume in the Sgr B2(N) cloud. Assuming the two molecules are copatial, then the ratio of ethylene glycol total column density [$3.2(10) \times 10^{14}$ cm $^{-2}$] to that of glycolaldehyde [$2.5(6) \times 10^{14}$ cm $^{-2}$] yields a range of ~ 0.7 to ~ 2.2 for the abundance ratio of ethylene glycol to glycolaldehyde.

The Murchison and Murray meteorite studies show that sugar-related compounds such as ethylene glycol have survived while no aldehyde sugars have yet been detected (Cooper et al. 2001). It may be that glycolaldehyde is more easily destroyed in hot, compact molecular cores than its reduced alcohol ethylene glycol because glycolaldehyde may undergo a formose-type reaction

with formaldehyde to form larger, more fragile sugars (e.g., Walker 1975). Thus, unlike glycolaldehyde, ethylene glycol may have a significant component confined to the LMH core source that can be detected with an interferometer. In the analogous case of the formaldehyde/methanol pair, methanol is seen to be more abundant in hot cores than formaldehyde.

The foregoing demonstrates that a combination of single-antenna and interferometric data is required for determining the spatial distribution of a new complex molecular species in proximity to a molecular core. Ultimately, it will be important to conduct studies of aldehyde/reduced alcohol pairs toward the same pointing position with sensitivity on all spatial scales so that good coupling to the emission source(s) is achieved. This will provide excellent observational criteria for various chemistry scenarios and, in the case of sugar/sugar alcohols like glycolaldehyde/ethylene glycol, investigating prebiotic sugar synthesis and searching for correlation with meteorite chemistry.

In summary, we have detected interstellar ethylene glycol in emission toward the Galactic center source Sgr B2(N-LMH) by means of several millimeter-wave rotational torsional transitions of its lowest energy conformer. Ethylene glycol is the reduced alcohol of glycolaldehyde that has also been detected toward Sgr B2(N-LMH). Aldehyde/reduced alcohol pairs are apparently common in interstellar clouds, suggesting a common formation pathway (Charnley 2001). Laboratory studies suggest that these pairs can be synthesized by low-temperature solid-phase H-addition reactions with, for example, CO on grain surfaces or ice mantles.

We appreciate the advice of S. Charnley, who suggested that the search for interstellar ethylene glycol would likely be successful. We thank D. Christen and H. Muller for providing laboratory data in advance of publication that allowed us to improve ethylene glycol frequency predictions. We thank an anonymous referee for helpful comments. J. M. H. received support from NASA RTOP 344-02-03-01. F. J. L. received support from the Laboratory of Astronomical Imaging at the University of Illinois and from NSF AST 99-81363.

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