ALMA Detection of Interstellar Methoxymethanol (CH$_3$OCH$_2$OH)

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Abstract

We report the detection of interstellar methoxymethanol (CH$_3$OCH$_2$OH) in Atacama Large Millimeter/submillimeter Array (ALMA) Bands 6 and 7 toward the MM1 core in the high-mass star-forming region NGC 6334I at $\sim$0.01–1$''$ spatial resolution. A column density of $4(2) \times 10^{18}$ cm$^{-2}$ at $T_e = 200$ K is derived toward MM1, $\sim$34 times less abundant than methanol (CH$_3$OH), and significantly higher than predicted by astrochemical models. Probable formation and destruction pathways are discussed, primarily through the reaction of the CH$_3$OH photodissociation products, the methoxy (CH$_3$O) and hydroxymethyl (CH$_2$OH) radicals. Finally, we comment on the implications of these mechanisms on gas-phase versus grain-surface routes operative in the region, and the possibility of electron-induced dissociation of CH$_3$OH rather than photodissociation.

Key words: astrochemistry – ISM: individual objects (NGC 6334I) – ISM: molecules

Supporting material: machine-readable table

1. Introduction

Given its high abundance in the interstellar medium (ISM), the photodissociation of methanol (CH$_3$OH)—producing the methyl (CH$_3$), hydroxymethyl (CH$_2$OH) and methoxy radicals (CH$_3$O)—is one of the most dominant sources of reactive organic species driving interstellar chemical evolution. The branching ratio for these reactions,

$$\text{CH}_3\text{OH} + h\nu \rightarrow \text{CH}_3 + \text{OH}, \quad (1)$$

$$\text{CH}_3\text{OH} + h\nu \rightarrow \text{CH}_2\text{OH} + \text{H}, \quad (2)$$

$$\text{CH}_3\text{OH} + h\nu \rightarrow \text{CH}_2\text{O} + \text{H}, \quad (3)$$

is a topic of considerable interest, both in the laboratory and in astrochemical models (Laas et al. 2011). These ratios are difficult to experimentally constrain, however, given that CH$_3$OH and CH$_2$OH are indistinguishable by mass spectroscopic techniques, and gas-phase production rates are low enough that direct detection by rotational spectroscopy is challenging (Laas et al. 2013). There is also a question of the relative importance of these branching ratios in gas-phase versus grain-surface chemistry (Laas et al. 2011). The observation of interstellar species that are likely to be products of one or more of these radicals, and insight into its formation in either the gas or solid phase (or both), is highly desirable.

One such target is methoxymethanol (CH$_3$OCH$_2$OH), which is thought to form primarily through the direct reaction of CH$_3$O with CH$_2$OH in the solid phase (Garrod et al. 2008):

$$\text{CH}_3\text{O} + \text{CH}_2\text{OH} \rightarrow \text{CH}_3\text{OCH}_2\text{OH} \quad (4)$$

Although CH$_3$O has been detected in the ISM (Cernicharo et al. 2012), CH$_2$OH has proven elusive, making it difficult to accurately incorporate into chemical models. If CH$_3$OCH$_2$OH does form through Reaction (4), and the rate can be reliably measured in the laboratory, observation of the species in the ISM would therefore provide quantitative insight into the presence of CH$_2$OH, even without its direct detection. The observation of CH$_3$OCH$_2$OH would provide much-needed constraints on the branching ratios for Reactions (1)–(3), if CH$_3$OCH$_2$OH can be determined to have a grain-surface formation pathway.

Here, we present the first interstellar detection of CH$_3$OCH$_2$OH using Atacama Large Millimeter/submillimeter Array (ALMA) data in Bands 6 and 7 toward NGC 6334I, a massive protocluster (Hunter et al. 2006) currently forming numerous massive stars and harboring two distinct regions of hot core line emission (MM1 and MM2; Zernickel et al. 2012; Brogan et al. 2016) at a distance of 1.3 kpc (Reid et al. 2014). The observations are detailed in Section 2 and the spectroscopy in Section 3. In Section 4, the results are presented and analyzed, and in Section 5, the formation and destruction chemistry for CH$_3$OCH$_2$OH is explored in the context of the detection.

2. Observations

We present detections of the CH$_3$OCH$_2$OH molecule in four ALMA data sets. The salient observing and imaging parameters are presented in Table 1. The Cycle 3 data (observed in 2016) were calibrated by the ALMA Cycle 4 pipeline (CASA 4.7.2) as described in Hunter et al. (2017), and the Cycle 4 data (observed in 2017) were calibrated by the ALMA Cycle 5 pipeline (CASA 5.1.1). For each data set, the (relatively) line-free continuum channels were carefully selected and used to...
construct an initial continuum image model that was then used to iteratively self-calibrate the data. The same channels were also used to subtract the continuum emission in the $uv$-plane before the spectral cubes were imaged. The data presented here have been corrected for primary beam attenuation.

### 3. Spectroscopy

The rotational spectra of two conformers of CH$_2$OCH$_2$OH were recently published by Motiyenko et al. (2018) between 150 and 450 GHz. The detection of the lower energy conformer, Conformer I, is reported here. The dipole moment components determined in that study at the MP2/aug-cc-pVTZ level of theory and basis set were $\mu_d = 0.22$ D, $\mu_p = 0.08$ D, $\mu_e = 0.13$ D. A careful analysis of the relative intensities of A- and C-type lines in the laboratory spectrum, by a subset of the authors, showed that better agreement with corresponding relative intensities in the calculated spectrum was obtained by scaling the value of $\mu_d$ to 0.11 D. We have therefore adopted this value for this work. The overall rms deviation of the fit was reported to be 40 kHz, corresponding to ~0.04 km s$^{-1}$ at these frequencies.

### 4. Results and Analysis

Figure 1 shows the detections of CH$_2$OCH$_2$OH in the 0''2 Band 7 data (black) toward MM1 convolved to the spectral resolution of the observations and with a 2.4 km s$^{-1}$ line width (red). The position chosen for analysis (J2000 17:20:53.373, -35:46:58.14) lies ~400 au west of the brightest continuum peak, denoted MM1b by Brogan et al. (2016). The spectra were converted from a Jy/beam to K intensity scale in each spectral window using the beam sizes listed in Table 1. Also shown is a total simulation in green of the major contributors to the line density in these portions of the spectrum: methyl cyanide (CH$_3$CN) v$_8$ = 0.1, CH$_3$OH v$_1$ = 0.1, methyl formate (CH$_3$OCHO) v$_2$ = 0.1, ethanol (CH$_3$CH$_2$OH), g'Ga-ethylene glycol (g'Ga-(CH$_2$OH)$_2$), and g'Gg-(CH$_2$OH)$_2$, the latter of which has only recently been detected for the first time in the ISM (Jørgensen et al. 2016). Emission from many of the lines of these species is optically thick, and a correction was applied using the formalisms of Goldsmith & Langer (1999) and Turner (1991).

This Band 7 data contained the largest number of unblended features, and so was chosen for a preliminary excitation and column density analysis. Given the rms noise of the observations, the somewhat significant uncertainty introduced by the continuum subtraction due to the lack of line-free channels, and the extremely large spectral dynamic range, only features at least 10$\sigma$ above the rms, and not substantially blended with another spectral feature, were considered significant enough to be claimed as a detected line.

The underlying substructure of the methyl rotor-split transitions results in challenging, non-Gaussian line profiles that make it difficult to extract physically meaningful quantitative results from a rotation diagram analysis. Instead, the convolved spectra were simulated using a single-excitation model following the formalism established in Hollis et al. (2004):

$$N_T \approx \frac{Q_{rot}E_u/T_e}{8\pi^3/3k} \sqrt{\frac{1}{2\ln(2)} \frac{\Delta T_T \Delta V}{\eta_{bg}}} \times \frac{1}{1 - e^{\nu/\Delta T_T \Delta V - 1}} \left(\frac{e^{\nu/\Delta T_T \Delta V} - 1}{e^{\nu/\Delta T_T} - 1}\right)$$

where $N_T$ is the column density (cm$^{-2}$), $E_u$ is the upper state energy (K), $\Delta T_T \Delta V$ is integrated line intensity (K cm s$^{-1}$), $T_e$ is the excitation temperature (K), $T_{bg}$ is the background continuum temperature (~53 K at 287 GHz and ~66 K at 344 GHz), $\nu$ is the transition frequency (Hz), S is the intrinsic line strength, $\mu$ is the transition dipole moment (Debye$^2$), and $\eta_{bg}$ is the beam efficiency (assumed to be unity for these interferometric observations). The rotational partition function, $Q_{rot}$, is calculated explicitly by direct summation of states ($Q_{rot}[300 \text{K}] = 81794$); the vibrational partition function correction, $Q_{vib}$, was obtained from quantum chemical calculations ($Q_{vib}[300 \text{K}] = 5.33$; see Appendix B). We assume that the

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### Table 1

Summary of ALMA Observing Parameters

| Parameter                  | 249 GHz | 287 GHz | 303 GHz | 344 GHz |
|---------------------------|---------|---------|---------|---------|
| Observation Date (s)      | 2017 Aug 18, 19 | 2016 Jul 18, 2016 Aug 02 | 2016 Jan 17 | 2016 Jul 17, 2016 Aug 02 |
| Cycle: Configuration (s)  | 4: C40-7 | 3: C36-4, C36-5 | 3: C36-6 | 3: C36-4, C36-5 |
| Project Code              | 2016.1.00383.S | 2015.A.00022.T | 2015.1.0150.S | 2015.A.00022.T |
| Phase Center (J2000 R.A., decl.) | 17:20:53.30, −35:47:00.0 | 17:20:53.36, −35:47:00.0 | 17:20:53.35, −35:47:01.5 | 17:20:53.36, −35:47:00.0 |
| Band                       | Band 6 | Band 7 | Band 7 | Band 7 |
| Time on Source (minutes)   | 37, 37 | 26, 26 | 27 | 27, 27 |
| Number of Antennas         | 42, 42 | 40, 39 | 40 | 38, 37 |
| FWHM Primary Beam (″)      | 23 | 20 | 19 | 17 |
| SPW Center Frequencies (GHz) | 239.69, 241.16, 257.09, 258.29 | 280.1, 282.0, 292.1, 294.0 | 301.20, 302.00, 303.72 | 337.1, 339.0, 349.1, 351.0 |
| Bandwidth per SPW (GHz)    | 4 × 0.9375 | 4 × 1.875 | 1.875, 1.875, 0.46875 | 4 × 1.875 |
| Correlated Channel width (MHz) | 0.244, 0.488, 0.244, 0.244 | 0.977 | 0.488 | 0.977 |
| Bandpass Calibrator        | J1924–2914 | J1924–2914, J1517–2422 | J1924–2914 | J1924–2914 |
| Gain Calibrator            | J1733–3722 | J1717–3342 | J1717–3342 | J1717–3342 |
| Flux Calibrator            | J1733–1304, J1617–5848 | J1733–1304 | J1733–1304 | J1733–1304 |
| Angular Resolution (″ × ″ (P.A.)) | 0.11 × 0.08 (+76) | 0.25 × 0.19 (−82) | 0.87 × 0.64 (+74) | 0.22 × 0.17 (−76) |
| Spectral Resolution (km s$^{-1}$) | 0.6 | 1.1 | 1.0 | 1.1 |
| rms Per Channel (mJy beam$^{-1}$ (K))$^a$ | 1.1 (2.5) | 2.0 (0.62) | 20.0 (0.48) | 3.3 (0.91) |

Note.

$^a$ The rms noise per channel varies significantly depending on whether bright emission is present in a particular channel; these estimated noise levels are the average of several channels and several off-source locations in channels with moderate line emission present.
Figure 1. Band 7 spectrum of NGC 6334I extracted toward the MM1 core at 0"0.2 resolution in black and adjusted to a $v_{lsr} = -7$ km s$^{-1}$. Single-excitation-temperature model spectra of CH$_3$OCH$_2$OH at $T_{ex} = 200$ K, $\Delta V = 2.4$ km s$^{-1}$, and $N_P = 4(2) \times 10^{18}$ cm$^{-2}$ are overlaid in red. In green, are simulations of the species that are major contributors to the line density in these windows (see Section 4). Transitions of CH$_3$OCH$_2$OH that are largely unblended (and have distinguishable line shapes) are marked with blue asterisks.
source fills the beam. The excitation temperature was fixed to 200 K, and the column density was varied to minimize the rms intensity error for unblended transitions. A few of the strongest lines are marginally affected by optical depth, and a correction was applied using the formalisms of Goldsmith & Langer (1999) and Turner (1991). The final derived value is \( N_T = 4(2) \times 10^{18} \) cm\(^{-2} \) at \( T_{ex} = 200 \) K. The ~60% uncertainty in the column density is taken as a contribution of 30% resulting from the fit to the unblended transitions, and an estimated 50% from the assumed excitation temperature, added in quadrature.

Further unblended transitions were identified in the 0″1 Band 6 and 1″ Band 7 data sets toward MM1 (Figure 2). The simulated profiles of CH\(_3\)OCH\(_2\)OH in the Band 6 data were made using the same values of \( N_p \), \( T_{ex} \), and \( \Delta V \) as the 0″2 Band 7 data, and with \( T_{bg} \) values appropriate for the data (~32 K). Because these profiles show remarkably good agreement even at twice the spatial resolution, this is likely indicating that the two observations are probing the same gas and that the distribution is at least mostly resolved. The 1″ Band 7 data required a column density a factor of two lower, and substantially more optically thin, in agreement with a larger beam which did not resolve the substructure seen in the higher-resolution observations. In total, more than two dozen largely unblended transitions were identified in the data sets for which a distinguishable line-shape contribution was seen in the spectrum matching the predicted shape at the correct frequency. As noted earlier, the intensity match is not always precise, due to the uncertainty in the excitation temperature.

4.1. Spatial Distributions

The line density in the region is such that it is challenging to select transitions that are not blended from which spatial distributions can be inferred. Figure 3 shows integrated intensity images of three unblended CH\(_3\)OCH\(_2\)OH transitions (panels (a)–(c)), as well as images of a single unblended transition each of \( ^a\)Gg-(CH\(_2\)O)\(_2 \), CH\(_3\)CN, and \(^{13}\)CH\(_3\)OH \( v_t = 1 \). The CH\(_3\)OCH\(_2\)OH transitions show nearly identical spatial distributions to each other, as expected, and markedly different distributions from \( ^g\)Gg-(CH\(_2\)O)\(_2 \), which is significantly more compact, as well as CH\(_3\)CN which, especially in MM2, shows an anti-correlated distribution. Notably, the distribution of CH\(_3\)OCH\(_2\)OH appears to be similar to, but slightly more compact than, that of \(^{13}\)CH\(_3\)OH \( v_t = 1 \). The ring-like appearance of the molecular emission toward MM1 is due to the high dust continuum opacity (>1) and brightness temperature of the 1 mm dust continuum emission toward the dust peaks (>100 K; Brogan et al. 2016). Toward the continuum peaks, the high dust opacity attenuates the line emission from the backside of the region, and the high background continuum brightness temperature compared to the line excitation temperature of the transitions shown here (of the order of 100–200 K) leads to weaker line emission (lower excitation lines are seen in absorption against the continuum peaks). To mitigate these effects, the spectra were extracted and analyzed at a position offset from the continuum peak.

4.2. Chemical Modeling

CH\(_3\)OCH\(_2\)OH was included in the three-phase chemical kinetics model MAGICKAL of Garrod (2013). In an initial effort to explore the ability of the model to reproduce the observed abundance, we modified the model with the back-diffusion correction of Willis & Garrod (2017) and used a network based on...
that of Belloche et al. (2017), in which CH$_3$OCH$_2$OH is produced via Reaction (4). The network also contains likely gas-phase and grain-surface destruction mechanisms for CH$_3$OCH$_2$OH.

The chemical modeling was performed using the two-stage approach described in Garrod (2013). Phase 1 is a cold collapse to a maximum density of 2 $\times$ 10$^8$ cm$^{-3}$ and a dust-grain temperature of 8 K. This is followed by a warm up from 8 to 400 K, simulating the “ignition” of a hot core. Three different warm-up timescales have been used, as the choice of timescale has been previously shown to have significant effects on the chemistry (Garrod 2013). The fastest timescale reaches a temperature of 200 K at $5 \times 10^4$ years, and 400 K at $7.12 \times 10^4$ years. The slowest timescale reaches these milestones at 10$^6$ years and $1.43 \times 10^6$ years; the intermediate timescale takes $2 \times 10^5$ years and $2.85 \times 10^5$ years.

The results of the model are shown graphically in Figure 4. The fast warm-up timescale produces the highest abundance of CH$_3$OCH$_2$OH, with a maximum fractional abundance of $\sim$10$^{-12}$ with respect to total hydrogen, which is well maintained to a temperature of 400 K. The abundance of CH$_3$OH in the same model approaches $10^{-5}$, corresponding to CH$_3$OCH$_2$OH:CH$_3$OH of $\sim$10$^{-7}$. The observed ratio of CH$_3$OCH$_2$OH:CH$_3$OH is estimated to be 1:34 (see Appendix C). The intermediate timescale shows very similar results, while the slowest timescale produces a very low gas-phase abundance of CH$_3$OCH$_2$OH, peaking at $\sim$10$^{-17}$. This is due to the increased efficiency of grain-surface destruction mechanisms in the slow warm-up timescale.

5. Discussion

Most complex organic molecules (COMs), particularly (partially) saturated species, are thought to have efficient formation pathways in the solid phase on the surface of dust grains (Garrod et al. 2008). In star-forming regions like NGC 6334I, the gradual warm up of these grains can then thermally desorb the product molecules into the gas phase, where they are detected by radio observations (Garrod 2013). For instance, the successive hydrogenation of CO on grains is likely the major formation route for methanol (Watanabe & Kouchi 2002; Fuchs et al. 2009). Yet, other studies have shown that some (partially) saturated COMs, such as methyl formate and formamide (NH$_2$CHO), might have significant, if perhaps not dominant, gas-phase formation pathways (Neill et al. 2012; Codella et al. 2017). It is worthwhile, then, to consider the potential operative pathways, both in the gas and solid phase, for the formation of CH$_3$OCH$_2$OH.

5.1. Radical–Radical Recombination

As noted by Motiyenko et al. (2018), the most obvious astrochemically relevant formation mechanism is the association
Figure 4. Abundance profiles of CH$_3$OCH$_2$OH for three warm-up timescales. Gas-phase abundance is displayed as a solid curve, while grain-surface abundance is shown as a dotted curve. Panel (a) shows the abundance profile for the longest warm-up timescale; panels (b) and (c) show the abundance profile for the intermediate and fast warm-up timescales, respectively.

of the CH$_3$O and CH$_2$OH radicals, which can occur on grains or in the gas. In the gas phase, an association reaction occurs via an intermediate complex, which re-dissociates into reactants unless it can relax sufficiently rapidly. In the low-density ISM, the relaxation mechanism is radiative, typically via emission from vibrational levels above the energy of reactants to levels below this energy and therefore stable. For ion–neutral systems such as

\[ \text{CH}_3^+ + \text{H}_2 \rightarrow \text{CH}_3^+ + h\nu, \]

experiments in ion traps and other low-density devices have been performed and show a wide range of reaction rate coefficients, depending upon the depth of the complex potential well (which helps to determine the lifetime of the complex against dissociation), the size of the reactants, and the temperature (Gerlich & Horning 1992). The experiments have also been supplemented by statistical calculations (e.g., Herbst 1985).

Both approaches show that a large complex well depth (a few eV), large reactants (more than 4–5 atoms), and low temperatures (<100 K) are needed for the radiative rate coefficient to approach the collisional rate coefficient and make these reactions feasible. Without these constraints, much smaller rate coefficients are obtained.

For neutral–neutral systems, very few reactions have been studied in the laboratory. Some theoretical rate coefficients have been obtained via statistical theories (Vuitton et al. 2011); these indicate indirectly that the association of the CH$_3$O and CH$_2$OH radicals might have a large rate coefficient at temperatures under 100 K, although it is also likely that the low gas-phase abundances of the reactants would render the process inefficient even with a large rate coefficient. Thus, if the radicals CH$_3$O and CH$_2$OH are more abundant on grains than in the gas for large ranges of temperature, the solid-phase association should be the more important. On the other hand, in their gas-grain modeling of the formation of CH$_3$OHCH$_3$ in cold clouds, Balucani et al. (2015) found the dominant process to be the gas-phase radiative association between CH$_3$ and CH$_3$O, assuming that it occurred at the collisional rate.

5.2. O(^4_D) Insertion Reactions

Another possible formation route involves the insertion of O(^4_D) into one of the C-H bonds of CH$_3$OCH$_3$ (Hays & Widicus Weaver 2013). Electronically excited species like O(^4_D) can form in cosmic-ray-irradiated dust-grain ice mantles, where they quickly react with a neighboring species or are quenched by the solid (Shingledecker et al. 2017; Shingledecker & Herbst 2018). Indeed, Bergner et al. (2017) recently found evidence that an analogous reaction,

\[ \text{O}[^4\text{D}] + \text{CH}_4 \rightarrow \text{CH}_3\text{O}, \]

could occur efficiently in interstellar ices. It is possible that such excited species could also react in the gas phase in the ISM; however, it is perhaps more likely that the excited species will emit a photon and radiatively relax before encountering a collisional reaction partner in the gas phase.

5.3. Photodissociation versus Cosmic Rays

As mentioned in Section 1, both CH$_3$O and CH$_2$OH can be formed from the dissociation of methanol. In the ISM, the two main drivers of dissociation are photons and cosmic rays. As recently noted by Shingledecker & Herbst (2018), the products of photochemistry and radiative chemistry are often similar, but not necessarily identical, due to differences in the underlying microscopic interactions that drive such processes. The distinction between photochemistry and radiation chemistry is potentially important for CH$_3$OCH$_2$OH, as was noted by Boamah et al. (2014) and Sullivan et al. (2016). In the experiments described in those works, CH$_3$OCH$_2$OH was detected after the exposure of condensed methanol to low-energy (<20 eV) electrons, which are characteristic of the secondary electrons produced in interstellar ices due to cosmic-ray bombardment (Shingledecker et al. 2017). In photodissociation experiments, however, CH$_3$OCH$_2$OH was not detected as a product of UV-irradiated methanol ice, which Sullivan et al. (2016) indicate might make CH$_3$OCH$_2$OH a good tracer of cosmic-ray-induced chemistry in the ISM.

5.4. Grain-surface Hydrogenation

Yet another potential formation pathway is through hydrogenation of precursor species on grain surfaces, such as

\[ \text{CH}_3\text{O} + \text{CH}_2\text{O} \rightarrow \text{CH}_3\text{OCH}_2\text{OH} \]

or

\[ \text{CH}_3\text{OCHO} \rightarrow \text{CH}_3\text{OCH}_2\text{OH}. \]

Successive hydrogenation reactions have been proposed as the formation mechanism for a number of (partially) saturated species, including CH$_3$OH (Woon 2002) and NH$_2$OH (Fedoseev et al. 2016), among numerous others (Linnartz et al. 2015), although recent work has suggested this may not
be efficient for substituted aldehydes (Jonas et al. 2017). A more in-depth analysis of the potential of these types of reactions to both form CH$_3$OCH$_2$OH and suggest other potential products is warranted.

5.5. Comparison to Models

As discussed in Section 4.2, current models using only Reaction (4) are significantly underproducing CH$_3$OCH$_2$OH. While the derived abundance of CH$_3$OH in our observations has a high degree of uncertainty, it is clear that the current models do not properly treat CH$_3$OCH$_2$OH formation, destruction, or both. Yet, as shown in Figure 3, the CH$_3$OCH$_2$OH distribution is remarkably similar to that of CH$_3$OH and different from other COMs. While not definitive, this is highly suggestive of a closely tied chemistry between these two species that would favor Reaction (4).

6. Conclusions

We have reported the detection of methoxymethanol CH$_3$OCH$_2$OH for the first time in the ISM using ALMA Band 6 and 7 observations toward the massive Galactic protocluster NGC 6334I. More than two dozen unblended transitions above 100 km s$^{-1}$ were identified. These transitions show identical spatial distributions, distinct from other complex species, and well matched to that of CH$_3$OH, a likely precursor. Current treatments for the grain-surface formation of CH$_3$OCH$_2$OH from CH$_3$O and CH$_2$OH significantly underproduce CH$_3$OCH$_2$OH, likely indicating other unconsidered formation pathways exist. Further, as has recently been suggested, cosmic-ray-induced chemistry may play a substantial role, making CH$_3$OCH$_2$OH a potentially powerful tracer of this process.

This Letter makes use of the following ALMA data: ADS/JAO. ALMA-##2015.A.00022.T, ADS/JAO.ALMA-##2015.1.00150.S, and ADS/JAO.ALMA-##2016.1.00383.S. ALMA is a partnership of ESO (representing its member states), NSF (USA) and NINS (Japan), together with NRC (Canada) and NSC and ASIAA (Taiwan) and KASI (Republic of Korea), in cooperation with the Republic of Chile. The Joint ALMA Observatory is operated by ESO, AUI/NAOJ and NAOJ. The National Radio Astronomy Observatory is a facility of the National Science Foundation operated under cooperative agreement by Associated Universities, Inc. E.H. thanks the National Science Foundation for support of his astrochemistry program. A.M.B. is a Grote Reber Fellow, and support for this work was provided by the NSF through the Grote Reber Fellowship Program administered by Associated Universities, Inc./National Radio Astronomy Observatory. Support for B.A.M. was provided by NASA through Hubble Fellowship grant HST-HF2-51396, awarded by the Space Telescope Science Institute, which is operated by the Association of Universities for Research in Astronomy, Inc., for NASA, under contract NAS5-26555. This work was supported in part by the Programme National “Physique et Chimie du Milieu Interstellaire” (PCMI) of CNRS/INSU with INC/INP co-funded by CEA and CNES.

Appendix A

Observed Line Parameters

Table 2 provides pertinent line parameters for CH$_3$OCH$_2$OH and other molecules discussed here.

Table 2

Pertinent Line Parameters of Selected Observed CH$_3$OCH$_2$OH, g$^0$Gg-(CH$_3$OH)$_2$, CH$_3$CN, and $^{13}$CH$_3$OH $v_1$ = 1 Transitions

| Quantum Numbers | Frequency (MHz) | $S_{\mu^2}$ (Debye$^2$) | $E_j$ (K) |
|-----------------|----------------|------------------------|----------|
| CH$_3$OCH$_2$OH | $^{2}7_{12,15}$ - $^{2}6_{12,14}$ E | 281024.6590 | 1.05 | 271.81 |
|                 | $^{2}7_{12,16}$ - $^{2}6_{12,15}$ A | 281026.0480 | 1.05 | 271.81 |
|                 | $^{2}7_{12,15}$ - $^{2}6_{12,14}$ A | 281026.0480 | 1.05 | 271.81 |
|                 | $^{2}7_{12,16}$ - $^{2}6_{12,15}$ E | 281027.8190 | 1.05 | 271.81 |
| g$^0$Gg-(CH$_3$OH)$_2$ | $^{2}8_{15,13}$ - $^{2}8_{14,14}$ $v_1$ = 1 | 292703.3917 | 199.61 | 307.44 |
|                 | $^{2}8_{15,14}$ - $^{2}8_{14,14}$ $v_1$ = 1 | 292703.3917 | 155.24 | 307.44 |
| CH$_3$CN | $^{16}$s - $^{15}$s | 294.02549 | 274.21 | 469.79 |
|                 | $^{13}$CH$_3$OH $v_1$ = 1 | 282383.0330 | 3.64 | 465 |

Note. Only a sample of the CH$_3$OCH$_2$OH transitions is shown here; the full table of all transitions within the range of these observations is available as a machine-readable table.

Appendix B

CH$_3$OCH$_2$OH Vibrational Partition Function

The vibrational correction to the partition function for CH$_3$OCH$_2$OH was calculated according to Equation (10):

$$Q(T)_{\text{vib}} = \prod_{i=1}^{3N-6} \frac{1}{1 - e^{-\Delta E_i/KT}}$$

(10)

To obtain the vibrational energy levels for CH$_3$OCH$_2$OH, a geometry optimization and frequency analysis was performed using Gaussian 09 (Frisch et al. 2009) at the B3LYP/6-311 +G(d, p) level of theory and basis set. The five lowest energy levels contribute $>0.1\%$ correction to the partition function at 200 K and have energies of 139, 188, 360, 396, and 584 cm$^{-1}$. The total correction at 200 K is 2.49.

Appendix C

CH$_3$OH Column Density

To compare with the column density of CH$_3$OCH$_2$OH, a column density estimate of CH$_3$OH was required. In the 0$^{0}\!$2 Band 7 data, nearly every CH$_3$OH transition is optically thick, as is nearly every transition of $^{13}$CH$_3$OH. The lines of $^{13}$CH$_3$OH $v_1$ = 1 are, however, largely optically thin (see Figure 5). We assume that the $v_1$ = 0 and $v_1$ = 1 states of $^{13}$CH$_3$OH are described by a single excitation temperature, and we calculate a total column density of $^{13}$CH$_3$OH using the $6_{13} - 5_{33}$ transition at 282,383 MHz, which appears to be the least blended optically thin line. A background temperature of $T_B = 53$ K was used, and an excitation temperature of $T_{ex} = 150$ K, based on the background temperature and the brightness temperature of the optically thick $^{13}$CH$_3$OH lines. The partition function included contributions from both $v_1$ = 0 and $v_1$ = 1. A line width of 2.8 km s$^{-1}$ was fit to the lines. The resulting column density was $N_{\text{v1}} = 1.95 \times 10^{18}$ cm$^{-2}$. A CH$_3$OH column density of $N_f = 1.4 \times 10^{22}$ cm$^{-2}$ was then inferred by scaling by a $^{12}$C/$^{13}$C ratio of 68 (Milam et al. 2005). Given the uncertainties involved and assumptions made, this value should be viewed as an estimate and as a lower limit.
Figure 5. Simulation of $^{13}$CH$_3$OH $v_T = 1$ in red over observations of MM1 in black with $N_T = 1.95 \times 10^{18}$ cm$^{-2}$, $T_{ex} = 150$ K, and $\Delta V = 2.8$ km s$^{-1}$.

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