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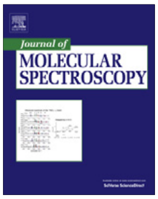

The pure rotational spectrum of glycolaldehyde isotopologues observed in natural abundance

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ABSTRACT

The pure rotational spectrum of glycolaldehyde has been recorded from 6.5–20 GHz and 25–40 GHz in two pulsed-jet chirped pulse Fourier transform microwave spectrometers. The high phase stability of the spectrometers enables deep signal integration, allowing transitions from the ^{13}C-substituted, ^{18}O-substituted, and deuterium-substituted isotopologues to be observed in natural abundance. Transitions from $HCOCH_2{}^{18}OH$ are reported for the first time. Additional transitions from the ^{13}C-substituted, deuterium-substituted, and $HC^{18}OCH_2OH$ isotopologues, as well as previously unobserved weak lines from the main isotopologue, have been observed. Transitions from all isotopologues are used with previously reported transitions to refine the spectroscopic parameters for each isotopologue. A Kraitchman analysis was performed using the experimental rotational constants to determine the molecular structure of glycolaldehyde.

1. Introduction

Glycolaldehyde ($HCOCH_2OH$) is the simplest α-hydroxy aldehyde, and as a sugar-related species is important in prebiotic chemical pathways. Glycolaldehyde is one of a set of complex organic molecules (COMs) detected in the interstellar medium (ISM), and is one of the few members of the $C_nH_{2n}O_n$ family to be detected thus far. Given its importance as a prebiotic molecule and the level of its chemical complexity compared to other COMs, detection of glycolaldehyde in an astronomical source and determination of its physical properties can provide important insight into the complex chemistry of the source. Glycolaldehyde has been detected in three interstellar sources, Sgr B2(N) [1–3], G31.41+0.31 [4], and IRAS 16293-2422 [5], and tentatively detected in G24.78+0.08 [6], through observations of its pure rotational spectral lines at microwave, millimeter, and submillimeter wavelengths. New submillimeter observatories such as the Atacama Large Millimeter Array (ALMA), the Stratospheric Observatory for Infrared Astronomy (SOFIA), and the Herschel Space Observatory (HSO) are providing observations with unprecedented spectral sensitivity and spatial resolution. The increased sensitivity of these instruments over existing ground-based observatories will enable the detection of glycoladehyde and other COMs in many additional sources. Indeed, the recent detection of glycolaldehyde lines in IRAS 16293-2422 was from an ALMA science verification dataset [5].

Reported isotopic ratios for $^{13}C/^{12}C$, $^{18}O/^{16}O$, and D/H in interstellar environments vary significantly from the standard terrestrial abundances, and depend both on the isotope and location within the galaxy. The Galactic $^{13}C/^{12}C$ ratio ranges from 0.01 to 0.05 [7], and has been reported to be as high as 0.09 in some sources [8]. The $^{18}O/^{16}O$ ratio has been reported to be as low as 0.002 in the local ISM, and as high as 0.004 in the Galactic center [7]. The Galactic D/H ratio is 1.7×10^{-5} [7], though isotopic fractionation effects can raise the observed D/H ratio for many molecules by several orders of magnitude, as evidenced by the detection of ND_3 [9] in cold clouds. Given these abundances, it is expected that as more sensitive observatories such as ALMA come online, the isotopologues of glycolaldehyde may be observable toward some Galactic sources, particularly in the Galactic Center. Accurate transition frequencies for the various isotopic species of glycolaldehyde are therefore necessary to eliminate confusion between unassigned spectral features arising from known interstellar species and spectral features arising from truly unidentified species. Additionally, isotopic fractionation is strongly dependent on physical conditions present during formation, and determination of isotopic fractionation in glycolaldehyde may provide insight into the formation pathways for interstellar glycoladehyde.

The rotational spectrum of glycolaldehyde has been well-studied. The main glycolaldehyde isotopologue has been characterized

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to 1.2 THz [10–14]. The three singly-deuterated species have been studied from 12.3 to 26 GHz with $J_{max} = 33$ [10], and from 150 to 630 GHz with $J_{max} = 67$ [15]. The two ^{13}C isotopologues have been studied in the 12.3–26 GHz frequency range with $J_{max} = 8$ and $J_{max} = 14$ [11]. Spectral assignments for the two ^{13}C isotopologues from 150 to 945 GHz were also recently reported [17]. Additionally, $HC^{18}OCH_2OH$ has been studied from 12.4 to 36.3 GHz with $J_{max} = 15$ [11]. $HCOCH_2{}^{18}OH$ was not included in the previous microwave studies due to difficulties in isotopically-enriching the hydroxyl oxygen, and therefore has no reported microwave spectra. Sensitivity limitations with previous microwave spectral techniques led to only a handful of lines being measured at lower frequencies for each of these glycolaldehyde isotopic variants. These microwave measurements underpin the spectral predictions for higher frequency transitions that are applicable to new observational studies. It is therefore important to revisit these measurements with new high-sensitivity microwave spectrometers so that the spectral fits can be refined by inclusion of additional line assignments.

Here we report the laboratory rotational spectroscopic studies of the various glycolaldehyde isotopologues observed in natural abundance using pulsed-jet chirped pulse Fourier transform microwave spectrometers operating in the ranges of 6.5–20 GHz and 25–40 GHz. These measurements refine the previously reported measurements by offering higher spectral resolution, and improve upon the previous datasets with the inclusion of more transitions for each isotopologue. The experimental details, data analysis methods, and refined molecular parameters are presented below.

2. Experimental

Glycolaldehyde spectra were acquired at the University of Virginia, using two chirped-pulse Fourier transform microwave (CP-FTMW) spectrometers operating in the frequency ranges of 6.5–20 GHz and 25–40 GHz. The spectra are shown in Figs. 1–4. The 6.5–20 GHz spectrum was acquired using a CP-FTMW spectrometer that was previously described [18], and the 25–40 GHz spectrum was acquired using a newly-developed K_a band CP-FTMW spectrometer that has been recently described [19]. In both cases, a sample of 99% pure solid glycolaldehyde from Sigma–Aldrich was used without further purification or alteration. For both experiments, the sample was placed in a sample holder and gently heated to a temperature of 45 °C to produce sufficient gas-phase sample. Neon gas flowed over the solid sample, and the gas mixture was delivered to two pulsed valves (1 mm nozzle diameter, General Valve Series 9) at a backing pressure of $\sim$1 atm. A total of 450 000 and 1 100 000 individual free induction decays (FIDs) were acquired for the low-frequency and high-frequency bands, respectively. A total of 10 FIDs were acquired on each valve cycle. The FID lengths were 20 μs and 10 μs in the low-frequency and high-frequency bands, respectively. These FIDs were averaged and converted to frequency spectra by taking a fast Fourier transform (FFT), and a Kaiser-Bessel window was applied. The resultant spectra given in Figs. 1–4 are magnitude spectra. The FWHM linewidths are on the order of 130 kHz in the low-frequency band and 200 kHz in the high-frequency band.

The strongest transition observed in the 6.5–20 GHz spectrum was the $1_{1,0}$–$1_{0,1}$ transition for $HCOCH_2OH$, with a signal strength

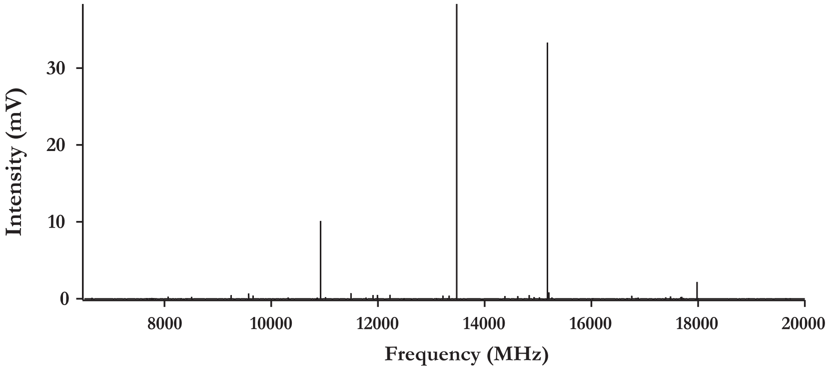

Fig. 1. Spectrum of glycolaldehyde from 6.5 to 20 GHz.

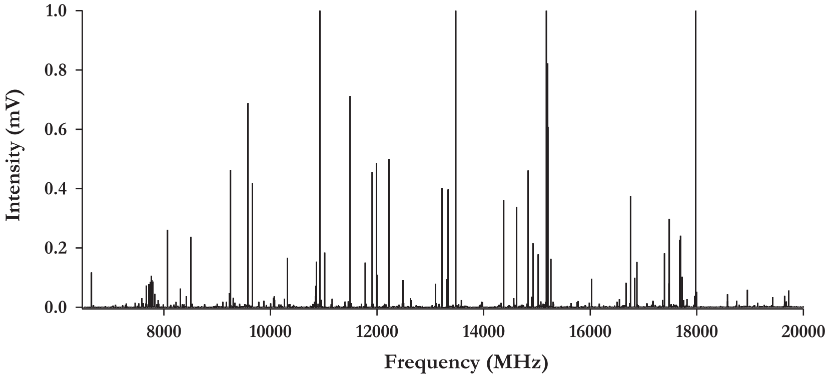

Fig. 2. Spectrum of glycolaldehyde from 6.5 to 20 GHz, showing spectral detail.