Laboratory Measurement of Millimeter-wave Transitions of $^{13}$CH$_2$DOH for Astronomical Use

Yuki Ohno$^{1,2}$, Takahiro Oyama$^{1}$, Akemi Tamanai$^{1}$, Shaoshan Zeng$^{1}$, Yoshimasa Watanabe$^{1,3}$, Riouhei Nakatani$^{1}$, Takeshi Sakai$^{1}$, and Nami Sakai$^{1}$

$^1$RIKEN Cluster for Pioneering Research, 2-1 Hirosawa, Wako-shi, Saitama 351-0198, Japan; takahiro.oyama@riken.jp
$^2$Department of Chemistry, Faculty of Science Division I, Tokyo University of Science, 1-3 Kagurazaka, Shinjuku-ku, Tokyo 162-8601, Japan
$^3$Materials Science and Engineering, College of Engineering, Shibaura Institute of Technology, 3-7-5 Toyosu, Koto-ku, Tokyo 135-8548, Japan

Abstract

Methanol (CH$_3$OH) is an abundant interstellar species and is known to be an important precursor of various interstellar complex organic molecules. Among the methanol isotopologues, CH$_3$DOH is one of the most abundant isotopologues and it is often used to study the deuterium fractionation of CH$_3$OH in interstellar medium. However, the emission lines of CH$_2$DOH can sometimes be optically thick, making the derivation of its abundance unreliable. Therefore, observations of its presumably optically thin $^{13}$C substituted species, $^{13}$CH$_2$DOH, are essential to overcome this issue. In this study, the rotational transitions of $^{13}$CH$_2$DOH have been measured in the millimeter-wave region from 216 GHz to 264 GHz with an emission-type millimeter- and submillimeter-wave spectrometer by using a deuterium and $^{13}$C enriched sample. The frequency accuracy of measured $^{13}$CH$_2$DOH is less than a few kHz, and the relative line intensity error is less than 10% in most of the frequency range by taking advantage of the wide simultaneous frequency-coverage of the emission-type spectrometer. These results offer a good opportunity to detect $^{13}$CH$_2$DOH in space, which will allow us to study the deuterium fractionation of CH$_3$OH in various sources through accurate determination of the CH$_2$DOH abundance.

Unified Astronomy Thesaurus concepts: Molecular spectroscopy (2095); Line positions (2085); Line intensities (2084); Astrochemistry (75)

1. Introduction

Methanol (CH$_3$OH) is known as a crucial molecule in the formation process of interstellar complex organic molecules (e.g., Garrod & Herbst 2006; Herbst & van Dishoeck 2009; Caselli & Ceccarelli 2012). Among the methanol isotopologues, CH$_2$DOH is one of the most abundant species in interstellar clouds and it is commonly used to study the deuterium fractionation in CH$_3$OH (e.g., Tielens & Whittet 1997; Watanabe & Kouchi 2002; Jørgensen et al. 2018). Although the cosmic abundance of deuterium is as low as D/H $\sim$ 10$^{-5}$ (Linsky 1998), deuteron fractionation up to several tens of percent has been reported for CH$_2$DOH (e.g., Parise et al. 2004). As CH$_3$OH, CH$_2$DOH is thought to be produced via surface reactions on icy grain mantles, successive addition of hydrogen/deuterium atoms to CO (Watanabe & Kouchi 2002; Rimola et al. 2014; Soma et al. 2015). According to the grain chemistry models (e.g., Charnley et al. 1997; Osamura et al. 2004), the statistical value of the CH$_2$DOH/CH$_3$OD ratio should be 3. However, the observed ratios in star-forming regions such as hot corinos differ from this statistical value (e.g., Ospina-Zamudio et al. 2019; Parise et al. 2004; Drozdovskaya et al. 2021). Nagaoka et al. (2005, 2007) proposed that substitution reactions on the methyl group by a deuterium atom are more efficient and can result in the higher D/H ratio observed for CH$_2$DOH. However, the combination of a compact source and possibly high optical depth of observed lines could obviously confound attempts to determine accurate D/H ratios. An accurate abundance of CH$_2$DOH and a D/H ratio of CH$_3$OH would have novel information on deuterium fractionation history along star formation.

The accurate evaluation of the deuterium fractionation of CH$_3$OH is challenging mainly due to the high optical depths of the observing lines. Not only the normal species lines but the CH$_2$DOH lines are often affected by this problem because of their high abundances. Although observations of the $^{13}$C substituted species, $^{13}$CH$_2$DOH, can overcome this difficulty, its frequency data of the torsion–rotation transition are not available. Since $^{13}$CH$_2$DOH as well as CH$_2$DOH is a floppy molecule and has an internal rotation of a partially deuterated methyl group, it is not straightforward to estimate accurate transition frequencies and line intensities empirically or theoretically. In the present study, torsion–rotation transitions of $^{13}$CH$_2$DOH are measured experimentally for the first time in the millimeter-wave region (216–264 GHz). This will benefit future astronomical studies as it covers nearly the entire receiver band (Band 6) that is most frequently used in the Atacama Large Millimeter/submillimeter Array (ALMA). The emission-type millimeter- and submillimeter-wave spectrometer, Spectrometer Using superconductor MIxer REceiver (SUMIRE), used in this study (Watanabe et al. 2021) enables us to determine the transition frequencies and the line intensities (Section 2). In this study, effective molecular constants of $^{13}$CH$_2$DOH are derived by using the common program distributed by JPL (SPFIT; Pickett 1991). This program is what was actually used in the analysis of CH$_2$DOH by Pearson et al. (2012). The results are summarized in Section 3.
2. Experiment

Details of the spectrometer used in this study are reported by Watanabe et al. (2021), and hence only points that are specific to the present measurement are described below. The gas cell (diameter: 10 cm, length: 200 cm) is evacuated to $2 \times 10^{-4}$ Pa using turbo molecular pump (Pfeiffer HiCube 80 Classic). The sample gas of $^{13}$CH$_2$DOH (ISOTEC: 98 atom% D and 99 atom% $^{13}$C) is introduced into the gas cell. The pressure of the gas for all the measurements are kept within the range of $0.51 \pm 0.05$ Pa and the cell temperature is kept to be $296 \pm 1$ K (room temperature). The thermal emission of the sample gas is measured against a background of the blackbody radiation at the liquid nitrogen temperature (77 K) by using the two-sideband superconductor heterodyne-mixer receiver (Watanabe et al. 2021). The backend is a bank of the eXtended Fast Fourier Transform Spectrometers (XFFTS; Klein et al. 2006, 2012). The bandwidth and frequency resolution of the

![Figure 1. Spectrum of $^{13}$CH$_2$DOH measured by using SUMIRE. The solid and dashed lines show the measured spectrum and the result of Gaussian fitting, respectively.](image1)

![Figure 2. Assignments of the $b$-type Q branch of $^{13}$CH$_2$DOH. The numbers in the top panel are the $J$ values. The top panel shows the spectrum taken by SUMIRE. The bottom panel shows the frequencies and the relative intensities obtained by the calculation using the optimized molecular constants as shown in Table 3.](image2)
| $e\_0$ | $Q$ branch | $e\_1$ | $Q$ branch |
|---|---|---|---|
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| $J'$ | $K_a'$ | $K_c'$ | $J''$ | $K_a''$ | $K_c''$ | Obs. Frequency (MHz) | $1\sigma$ Error | Calc. Frequency (MHz) | $1\sigma$ Error | Obs. -- Calc. | Obs. Intensity | $1\sigma$ Error | Calc. Intensity | $1\sigma$ Error | Obs. FWHM (MHz) | $1\sigma$ Error | $E_{\text{upper}}$ (cm$^{-2}$) |
|-----|------|------|------|------|------|-----------------|-------------|-----------------|-------------|--------------|--------------|-------------|--------------|-------------|----------------|-------------|----------------|
| 11  | 2    | 10   | 11  | 1    | 11   | 244178.911     | 0.002       | 244178.831     | 0.008       | 1.96         | 0.013        | 2.4          | 0.600        | 0.005       | 114.7         |             |
| 12  | 2    | 11   | 12  | 1    | 12   | 250304.251     | 0.002       | 250304.386     | 0.013       | 2.23         | 0.015        | 2.4          | 0.608        | 0.005       | 132.2         |             |
| 13  | 2    | 12   | 13  | 1    | 13   | 256981.608     | 0.002       | 256981.580     | 0.028       | 2.39         | 0.015        | 2.4          | 0.632        | 0.005       | 151.1         |             |

Table 1 (Continued)
Table 1

| $J'$ | $K_a'$ | $K_c'$ | $J''$ | $K_a''$ | $K_c''$ | Obs. Frequency (MHz) | $1\sigma$ Error | Calc. Frequency (MHz) | Obs. -- Calc. | Obs. Intensity ($^b$) | $1\sigma$ Error ($^b$) | Calc. Intensity ($^b$) | Obs. FWHM (MHz) | $1\sigma$ Error | $E_{\text{upper}}$ (cm$^{-2}$) |
|------|--------|--------|-------|--------|--------|-----------------------|----------------|-----------------------|-------------|---------------------|----------------|-------------------|----------------|----------------|----------------|
| 24   | 2      | 22     | 24    | 1      | 23     | 223508.261            | 0.003          | 223508.266            | −0.005      | 1.51                | 0.014          | 3.3               | 0.552          | 0.006          | 460.3          |
| 25   | 2      | 23     | 25    | 1      | 24     | 225559.571            | 0.002          | 225559.563            | −0.008      | 1.40                | 0.013          | 3.0               | 0.568          | 0.006          | 499.6          |
| 26   | 2      | 24     | 26    | 1      | 25     | 228462.095            | 0.002          | 228462.080            | −0.016      | 1.17                | 0.011          | 2.7               | 0.553          | 0.006          | 537.6          |
| 27   | 2      | 25     | 27    | 1      | 26     | 232335.006            | 0.003          | 232335.000            | −0.036      | 1.11                | 0.013          | 2.5               | 0.559          | 0.008          | 577.1          |
| 28   | 2      | 26     | 28    | 1      | 27     | 236930.452            | 0.004          | 236930.465            | −0.013      | 0.98                | 0.014          | 2.3               | 0.584          | 0.010          | 618.1          |
| 29   | 2      | 27     | 29    | 1      | 28     | 242582.290            | 0.003          | 242582.297            | −0.007      | 0.78                | 0.009          | 2.0               | 0.559          | 0.009          | 660.5          |
| 30   | 2      | 28     | 30    | 1      | 29     | 249215.118            | 0.004          | 249215.095            | 0.023       | 0.68                | 0.009          | 1.8               | 0.601          | 0.010          | 704.3          |
| 31   | 2      | 29     | 31    | 1      | 30     | 256843.533            | 0.005          | 256843.541            | −0.008      | 0.54                | 0.009          | 1.6               | 0.601          | 0.012          | 749.6          |

Notes.

$^a$ Weights of the least-squares fitting are set to zero.

$^b$ Out of the observable frequency region.

$^c$ The values of measured intensities are equally divided into the two lines.

$^d$ Blended lines.

$^e$ This line may be blended with an unassigned line because its line intensity is quite different from other $K$ structure lines of the $J = 6-5$ transition.

$^f$ Peak intensity obtained from the Gaussian fit.

$^g$ Error of the Gaussian fit. It does not include the calibration error of 10%.

$^h$ Dipole moments of CH$_2$DOH are used for the calculation.
XFFTS are 2.5 GHz and 88.5 kHz, respectively. A 10 MHz reference signal generated by a rubidium atomic clock with the aid of the coordinated universal time provided via GPS is used to ensure the absolute frequency accuracy of $2 \times 10^{-12}$ or better. The overlap of the frequency ranges of the spectrometers is set to be 0.3 GHz. Both ends (0.2 GHz) of the bandwidth for each spectrometer are excluded from analysis because these band edges are badly affected by the cutoff character of the bandpass filters. To cover the frequency range from 216 GHz to 264 GHz, we observed the spectrum at the six frequency setups with the local oscillator frequencies of 224, 228, 232, 248, 252, and 256 GHz. At each frequency setup, a 5 minute integration was carried out 10 times, resulting in the total integration time of 50 minutes. rms noise is typically 16–20 mK. Intensity calibration was carried out by the chopper wheel method with the liquid nitrogen temperature load at 77 K and the room temperature load at 296 ± 1 K (Ulich & Haas 1976). The calibration error of the intensity measurement is estimated to be 10% including the absolute error of the gas pressure measurement (Watanabe et al. 2021). It should be noted that the relative line intensities are as accurate as 1.4% among the 10 spectra of the 5 minute integration each at the same local frequency setup. The column density of the gas in the cell at the conditions of 0.51 ± 0.05 Pa and 296 ± 1 K is calculated to be $(2.50 \pm 0.26) \times 10^{16}$ cm$^{-2}$ on the assumption of the ideal gas.

3. Results and Discussion

More than 970 lines are detected in the 216–264 GHz frequency region. A typical line shape of $^{13}$CH$_2$DOH is shown in Figure 1. The line shape is mainly the result of Doppler effect, which can be approximately reproduced by the Gaussian function. Although the Lorentzian profile due to the collisional effect is found in the skirt of strong lines, its contribution to the line shape is almost negligible. The contribution to the line integrated intensity is less than 10%. In the present study, the Gaussian fitting is therefore used to determine the transition frequency, intensity, and line width of each line. An FWHM line width of each line is about 0.6 MHz. The measurement error of the frequency is a few kHz for the lines with intensities higher than $3\sigma$ of the baseline noise.

CH$_3$OH has the A and E torsional substates. Monodeuteration of the methyl group lifts the degeneracy of the E state; the A and E states mix with each other resulting in the $e_0$, $e_1$, and $o_1$ states (Richard Quade & $\&$ Suenram 1980). The $e_1$ and $o_1$ states lay about 8 and 13 cm$^{-1}$ above the $e_0$ state, respectively (Pearson et al. 2012). Complicated interactions occur between these states. For example, strong perturbation, so-called avoided crossing, drastically changes the line positions and its intensities for certain levels (Pearson et al. 2012). For CH$_2$DOH, torsion–rotation transitions were reported (e.g., Pearson et al. 2012 and Coudert et al. 2014), and their frequencies are listed in the JPL rest frequency catalog (Pickett et al. 1998). Since the energy structure of $^{13}$CH$_2$DOH should be similar to that of CH$_2$DOH, the same empirical internal axis method as reported by Pearson et al. (2012) for CH$_2$DOH was also employed in this study. The line assignments and the analysis of $^{13}$CH$_2$DOH were carried out by utilizing the SPCAT and SPFIT programs (Pickett 1991; Drouin 2017), which are often used in the JPL catalog. Apart from the local level crossings mentioned above, the substitution effect of $^{13}$C on the molecular constants in methanol is relatively small. For example, the centrifugal distortion constants of $^{13}$CH$_2$OH are reported to be very similar to those of CH$_3$OH (see Table 1 in Walsh et al. 2000), although the analysis method is different from the present study. Hence, the line positions of $^{13}$CH$_2$DOH were predicted by using the molecular constants of CH$_2$DOH, where the only rotational constants were modified with the scaling factors to take the isotope effect of the $^{13}$C atom into account. The scaling factors were estimated to be 1.00381, 0.979243, and 0.964541 for $A-(B+C)/2$, (B+C)/2, and (B−C)/4, respectively, based on the quantum chemical calculation using the hybrid exchange-correlation functional using the coulomb-attenuating method CAM-B3LYP (Yanai et al. 2004) with the correlation-consistent valence triple zeta basis set (Dunning 1989; Kendall et al. 1992). The quantum chemical calculations were carried out using the GAUSSIAN 16 package (Frisch et al. 2016).

The torsion–rotation transitions of $^{13}$CH$_2$DOH are classified into two types: (1) transitions within the same torsional substate and (2) transitions between the different substates. Comparing the observed spectrum to the predicted one, distinctive a-type $\tilde{R}$ and b-type $\tilde{Q}$ branches for type (1) were identified. The assignments of the $\tilde{Q}$-branch lines for three torsional substates, $e_0$, $e_1$, and $o_1$, are shown in Figure 2. In total, 115 lines were assigned for the three torsional substates as listed in Table 1.5

In the least-squares analysis to derive the molecular constants, some rotational and centrifugal distortion constants are optimized, while the other constants are fixed to the corresponding values of CH$_3$DOH. The optimized constants are listed in Tables 2 and 3. Since the identified lines are limited to the transitions within the same torsional substate, only a portion of the constants could be adjusted. Hence, the determined molecular constants are regarded as “effective

---

Table 2  
Optimized Molecular Constants and the Label in SPFIT

| Diagonal Term$^a$ | $e_0$ | $e_1$ | $o_1$ |
|-------------------|-------|-------|-------|
| $A-(B+C)/2$ | 10000000101 | 11000000102 | 11000000112 |
| $(B+C)/2$ | 100 | 111 | 122 |
| $(B+C)/2c$ | 10000000111 | 10000000112 | 10000000122 |
| $(B+C)/2c^2$ | 20000000122 |
| $(B−C)/4$ | 40000 | 40011 | 40022 |
| $(B−C)/4c$ | 1000040000 | 1000040001 | 1000040002 |
| $(B−C)/4c^2$ | 2000040000 | 2000040001 | 2000040002 |
| $D_{0r}$ | 610000 | 610011 | 610022 |
| $D_{0r}$ | 200 | 211 | 222 |
| $D_{0r}$ | 1100 | 1111 | 1122 |
| $H_{e1}$ | 1200 | 1211 | 1222 |
| $H_{e1}$ | 2100 | 2111 | 2122 |
| Off-diagonal Term$^b$ | $e_0$/$e_1$ | $e_0$/$o_1$ | $e_1$/$o_1$ |
| $[(B+C)/2]x$ | 1000000101 | 1100000102 | 1100000112 |
| $(B+C)/2x^2$ | 2000000102 | 1200000102 | 1200000112 |
| $(B−C)/4x$ | 1000040001 | 1000040002 | 1000040012 |
| $(B−C)/4x^2$ | 2000040002 | 2000040003 | 2000040004 |
| $[D_{0r}]x$ | 1000610001 | 1100610002 | 1100610002 |
| $D_{0r}$ | … | … | 410012 |
| $D_{0r}$ | … | … | 210012 |

Notes.

$^a$ The c indicates Fourier series in cos(2πρK).

$^b$ The x indicates Fourier series in cos(2πρK) for $e_0$/$e_1$ or sin(2πρK) for $e_0$/$o_1$ and $e_1$/$o_1$.

---

5 Remaining unassigned lines are available upon request.
values.” Although most of the determined molecular constants of $^{13}$CH$_2$DOH are close to those of CH$_2$DOH, some of them give significantly different values. For example, $[(B+C)/4]x$ in $e_i/o_i$ is 0.38(31) and $-20.232(48)$ for $^{13}$CH$_2$DOH and CH$_2$DOH, respectively. This inconsistency would originate from the limited number of the optimized molecular constants. The measured transition frequencies are reasonably fitted by the molecular constants in Table 3 with the rms of the residual of 147 kHz. The line assignment is therefore secure. The rms of the residuals is larger than the frequency measurement error, which could also originate from the limited number of the optimized molecular constants. Note that the transitions reported to display avoided crossing for CH$_2$DOH ($K_a = 2$ and 1 at $J = 5$ for $e_0$ and $e_1$, respectively; Pearson et al. 2012) are dropped from the fit for $^{13}$CH$_2$DOH. Further analysis with the transitions between different substates is required for full optimization, which will be done in future studies. The frequency range, 216–264 GHz, would cover the frequencies of such inter-substate transition lines. However, frequencies of such inter-substate transitions largely depend on the molecular constants fixed in the fitting and have large uncertainties, which makes their assignments difficult. To solve this issue, more spectral line data for a wider frequency range are required as in the case of studies reported for CH$_2$DOH (4–1628 GHz; Pearson et al. 2012).

In this experiment, absolute intensities have been measured. The intensities for the $a$-type transitions agree well with their theoretical values except for perturbed lines. The difference is within about 20%. On the other hand, it shows large differences for the $b$-type transitions as shown in Figure 2. For the CH$_2$DOH lines, extreme caution was made for the intensities of $b$-type and $c$-type transitions by Pearson et al. (2012) and the JPL rest frequency catalog (Pickett et al. 1998). This situation is also seen in $^{13}$CH$_2$DOH. Direct measurements of the transition intensities would therefore help the theoretical study on the energy level structure of the asymmetric-top asymmetric-frame molecules such as CH$_2$DOH.

The intensities of the $a$-type transitions are consistent with the calculated ones by considering the $\sim$10% error in calibration and the <10% in effect of the Lorentzian skirt. We therefore derived the column density of the gas cell by the rotation diagram, using only the $a$-type transitions as shown in Figure 3. The derived column density is $(2.70 \pm 0.04) \times 10^{16}$ cm$^{-2}$ at 296 K. The error denotes the fitting error. It is consistent with that calculated from the pressure of the gas cell (see Section 2). Note that the partition function of $^{13}$CH$_2$DOH was set to 15172, which is the value listed for CH$_2$DOH in the JPL catalog (Pickett et al. 1998), since it cannot be calculated from the limited range of identified transitions. The isotopic effect for the partition function is estimated to be only a few percent.

The rotational spectrum of CH$_2$DOH was measured in the laboratory in the 1980s and was detected in interstellar mediums (Richard Quade & Suenram 1980; Jacq et al. 1993). Since then, CH$_2$DOH has widely been observed in various astronomical objects (e.g., Parise et al. 2006), where the column densities were reported to be about $10^{13}$–$10^{15}$ cm$^{-2}$. In the recent observations at a high spatial resolution, the column densities as high as $10^{17}$–$10^{18}$ cm$^{-2}$ have been reported toward several low-mass protostars (e.g., IRAS16293-2422, Manigand et al. 2020; H212, Bianchi et al. 2017; B1-c, van Gelder et al. 2020). Under the assumption of $^{12}$C/$^{13}$C $\sim$ 70 (Milam et al. 2005, at the galactocentric distance of 8.3 kpc), the column density of $^{13}$CH$_2$DOH is estimated to be higher than $10^{15}$ cm$^{-2}$. This is sufficient for the detection with the sensitive radio telescopes such as ALMA. Since the error of the transition frequencies measured in this study is typically a few kHz, which corresponds to $\sim$0.005 km s$^{-1}$ in velocity at the

---

**Table 3**

Comparison of Molecular Constants for $^{13}$CH$_2$DOH and CH$_2$DOH in MHz

|   | $^{13}$CH$_2$DOH | CH$_2$DOH | $^{13}$CH$_2$DOH | CH$_2$DOH | $^{13}$CH$_2$DOH | CH$_2$DOH |
|---|---|---|---|---|---|---|
| A $-(B+C)/2$ | 81535.94(67) | 81193.93(33) | 80579.23(17) | 80214.1(4) | 80368.89(20) | 80015.9(23) |
| (B+C)/2 | 21917.47(31) | 22367.214(48) | 21874.95(19) | 22326.894(36) | 21878.28(36) | 22320.218(25) |
| $[(B+C)/2]c$ | $-8.31(14)$ | $-7.799(49)$ | $4.33(19)$ | $3.422(34)$ | $-17.10(37)$ | $-8.307(33)$ |
| $[(B+C)/2]d$ | ... | ... | ... | ... | $-1.647(52)$ | $-1.625(41)$ |
| (B–C)/4 | 326.87(32) | 340.304(63) | 179.54(18) | 180.564(33) | 179.23(25) | 167.804(43) |
| (B–C)/4$e$ | 15.06(36) | 11.4066(66) | 75.05(24) | 88.235(81) | 4.29(32) | 25.259(37) |
| (B–C)/4$f$ | $-3.928(79)$ | $-3.707(26)$ | $-5.392(78)$ | $-9.888(37)$ | $6.27(69)$ | $2.949(31)$ |
| $D_{ab}$ | 1103.83(14) | 720.18(78) | $-968.64(33)$ | $-866.2(11)$ | $-1033.13(33)$ | $-865.7(11)$ |
| $-D_{J}$ | $-0.04768(26)$ | $-0.04467(62)$ | $-0.04787(23)$ | $-0.066187(57)$ | $-0.05154(32)$ | $-0.05287(47)$ |
| $-D_{JK}$ | $-0.9973(31)$ | $-0.9362(21)$ | $0.267(61)$ | $-0.024(12)$ | $-2.10(15)$ | $1.73(15)$ |
| $H_{KK}$ | $0.000585(39)$ | $0.005027(67)$ | $0.000467(25)$ | $0.001951(63)$ | $0.000575(35)$ | $0.0010232(55)$ |
| $H_{KJ}$ | $0.02533(79)$ | $0.029(11)$ | $-0.0771(20)$ | $-0.06484(65)$ | $0.0185(64)$ | $-0.13144(24)$ |

|   | $e_i/o_i$ | $e_i/o_i$ | $e_i/o_i$ | $e_i/o_i$ |
|---|---|---|---|---|
| $[(B+C)/2]x$ | 29.11(12) | 24.186(18) | $-20.56(17)$ | $-22.861(45)$ |
| $[(B+C)/2]x^2$ | 0.0813(13) | 0.01354(36) | $-0.024(11)$ | $0.5306(62)$ |
| $[(B–C)/4]x$ | $-89.108(20)$ | $-95.1097(275)$ | $57.53(25)$ | $72.08(10)$ |
| $[(B–C)/4]x^2$ | 23.39(10) | 15.49(21) | $-10.76(12)$ | $-19.044(28)$ |
| $[D_{ab}]x$ | 203.26(82) | 259.83(33) | $-322.7(27)$ | $-309.2(51)$ |
| $D_{ab}$ | ... | ... | ... | ... |
| $D_{ab}$ | ... | ... | ... | ... |

**Note.**

$^a$ Pearson et al. (2012).
corresponding frequency, the measured frequencies can directly be used for astronomical observation. The detection of $^{13}$CH$_2$DOH would give an opportunity to evaluate reliable abundances of CH$_2$DOH and improve the deuterium fractionation studies of CH$_3$OH.

We thank the anonymous reviewers for invaluable comments. We are grateful to Satoshi Yamamoto for extensive help, suggestions, and discussions. We are also grateful to Takashi Kojima and NAOJ staff for great help with maintaining the SIS receiver installed on the SUMIRE. This study is supported by a Grant-in-Aid from the Ministry of Education, Culture, Sports, Science, and Technology of Japan (18H05222, 20H05845, 20H05844), and a pioneering project in RIKEN (Evolution of Matter in the Universe). This study used distributed software, SPCAT and SPFIT, provided at Jet Propulsion Laboratory in NASA (Pickett 1991).

ORCID iDs
Yuki Ohno https://orcid.org/0000-0002-5674-6624
Takahiro Oyama https://orcid.org/0000-0002-7391-7951
Akemi Tamanai https://orcid.org/0000-0002-5430-1170
Shaoshan Zeng https://orcid.org/0000-0003-3721-374X
Yoshimasa Watanabe https://orcid.org/0000-0002-9668-3592
Riouhei Nakatani https://orcid.org/0000-0002-1803-0203
Takeshi Sakai https://orcid.org/0000-0003-4521-7492
Nami Sakai https://orcid.org/0000-0002-3297-4497

References
Bianchi, E., Codella, C., Ceccarelli, C., et al. 2017, A&A, 606, L7
Caselli, P., & Ceccarelli, C. 2012, A&ARv, 20, 56
Charnley, S. B., Tielens, A. G. G. M., & Rodgers, S. D. 1997, ApJL, 482, L203

Figure 3. Rotational diagram for the $a$-type transitions of $^{13}$CH$_2$DOH. The solid line indicates the fitting result where the rotational temperature is fixed to room temperature as 296 K. The $6_{43} – 5_{33}$ line for $e_0$, the $6_{42} – 5_{31}$ and $6_{43} – 5_{42}$ lines for $e_1$, and the $6_{06} – 5_{05}$ line for $o_1$ are omitted in this plot because these are suspected of blending with unassigned lines.