

## Deuterated methanol toward NGC 7538-IRS1<sup>★</sup>

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### ABSTRACT

We investigate the deuteration of methanol towards the high-mass star-forming region NGC 7538-IRS1. We carried out a multi-transition study of CH<sub>3</sub>OH, <sup>13</sup>CH<sub>3</sub>OH, and the deuterated flavors, CH<sub>2</sub>DOH and CH<sub>3</sub>OD, between 1.0 and 1.4 mm with the IRAM-30 m antenna. In total, 34 <sup>13</sup>CH<sub>3</sub>OH, 13 CH<sub>2</sub>DOH lines and 20 CH<sub>3</sub>OD lines spanning a wide range of upper-state energies ( $E_{\text{up}}$ ) were detected. From the detected transitions, we estimate that the measured D/H does not exceed 1%, with a measured CH<sub>2</sub>DOH/CH<sub>3</sub>OH and CH<sub>3</sub>OD/CH<sub>3</sub>OH of about  $(32 \pm 8) \times 10^{-4}$  and  $(10 \pm 4) \times 10^{-4}$ , respectively. This finding is consistent with the hypothesis of a short-timescale formation during the pre-stellar phase. We find a relative abundance CH<sub>2</sub>DOH/CH<sub>3</sub>OD ratio of  $3.2 \pm 1.5$ . This result is consistent with a statistical deuteration. We cannot exclude H/D exchanges between water and methanol if water deuteration is of the order 0.1%, as suggested by recent *Herschel* observations.

**Key words.** ISM: molecules – ISM: abundances – radio lines: ISM – astrochemistry – ISM: individual objects: NGC 7538

### 1. Introduction

Observational studies of deuterated molecules are powerful ways to probe the chemical and physical evolution of star-forming regions. Indeed, many of the organic species that are abundant constituents of molecular clouds are synthesized in the cold prestellar phase (see Caselli & Ceccarelli 2012, for a review). At low temperatures, the difference in zero-point energy between deuterated molecules and their hydrogenated counterparts (about 1000 K for methanol and its singly deuterated flavors, Nandi et al. 2019) makes it possible for deuterated species to be formed with significantly higher relative abundances than the elemental D/H ratio ( $\sim 10^{-5}$ , see e.g., Ceccarelli et al. 2007, 2014; Caselli & Ceccarelli 2012). These enhanced abundance ratios can be preserved as the protostar heats the gas to temperatures large enough ( $\geq 100$  K) to evaporate the ice mantles. Thus, studies of molecular D/H ratios can provide strong insight into the physical history of star-forming regions along with information on the chemical routes through which the molecular content is formed. Deuterium fractionation in low-mass star-forming regions has been the subject of significant study (e.g., see Roberts et al. 2002; Parise et al. 2006; Ratajczak et al. 2011; Jørgensen et al. 2018). These sources have shown remarkably high enhancements of deuterated molecules, including even doubly and triply deuterated species (e.g., ND<sub>3</sub>, CD<sub>3</sub>OH), which in some cases occur at abundances 12–13 orders of magnitude higher than elemental abundance would suggest (Lis et al. 2002; Parise et al. 2002, 2004). Regarding high-mass star-forming

regions, only a few observations of deuterated molecules have been performed so far (e.g., Jacq et al. 1993; Ratajczak et al. 2011; Peng et al. 2012; Neill et al. 2013a,b), the best studied high-mass source of deuterated molecules being the Orion KL nebula. Low levels of fractionation are typically observed, consistent with molecular formation at higher temperatures; alternatively, warm gas-phase chemistry could alter the D/H ratio in high-mass regions during the post-evaporative phase. Interestingly enough, from chemical modeling using experimental kinetic data, Faure et al. (2015a) suggested that the D/H ratio measured in Orion-KL might not be representative of the original mantles due to deuterium exchanges between water and methanol in interstellar ices during the warm-up phase. The study of the abundance ratio of the deuterated isotopologs of methanol (CH<sub>3</sub>OD/CH<sub>2</sub>DOH) could give access to the initial deuteration of water ices before the warm-up phase sets in. Nonetheless, taking into account the limited number of observations of deuterated species in high-mass star-forming regions, the extent to which the D/H ratios observed toward Orion KL are representative of high-mass source chemistry is uncertain. Bøgelund et al. (2018) recently reported low deuteration levels of methanol towards the HMSFR NGC6334 I, with typical values in the range of 0.01–1% for both CH<sub>2</sub>DOH and CH<sub>3</sub>OD. Large uncertainties on the column densities of a factor of 4–10 depending on the species remain however, which prevent any robust conclusions on the CH<sub>2</sub>DOH/CH<sub>3</sub>OD ratio and the initial ice composition. Further observations of a sample of high-mass sources are thus required for comparison between sources and for improving our understanding of the chemistry that creates organic molecules with significant deuterium fractionation (in particular, the roles of grain-surface and gas-phase reactions).

<sup>★</sup> This paper is dedicated to the memory of our dear colleague, Dr. Li-Hong Xu, who recently passed away.

In this study, we investigate the D/H ratio for methanol ( $\text{CH}_3\text{OH}$ ,  $\text{CH}_2\text{DOH}$ , and  $\text{CH}_3\text{OD}$ ) towards the high-mass star-forming region NGC 7538-IRS1 ( $L = 1.3 \times 10^5 L_\odot$ ,  $d = 2.8$  kpc,  $M \sim 30 M_\odot$ , see Bisschop et al. 2007; Beuther et al. 2012), which is known to harbor high abundances of organic molecules, including methanol (e.g., Bisschop et al. 2007; Wirström et al. 2011). Results are given in Sect. 3 and discussed in Sect. 4.

## 2. Observations and data reduction

The data were acquired with the IRAM 30 m telescope on 2013 December 5, 6, and 10 towards NGC 7538-IRS1 with a single pointing ( $\alpha_{J2000} = 23^{\text{h}}13^{\text{m}}45^{\text{s}}.5$ ,  $\delta_{J2000} = +61^\circ28'12''.0$ ). The  $v_{\text{LSR}}$  was  $-57 \text{ km s}^{-1}$ . The observations were taken in position-switching mode, using a reference for the OFF position at  $[-600'', 0'']$ . The EMIR receiver at 1 mm was used in connection with the Fourier transform spectrometer (FTS) as backend, providing a spectral resolution of 195 kHz. The spectral resolution was subsequently degraded to 780 KHz, which corresponds to about  $1 \text{ km s}^{-1}$ , in order to improve the signal-to-noise ratio (S/N) of the data. The following frequency ranges were covered: 212.6–220.4 GHz, 228.3–236.0 GHz, 243.5–251.3 GHz, 251.5–259.3 GHz, 259.3–267.0 GHz, and 267.2–274.9 GHz. The half-power beam sizes are  $10''$  and  $12''$  for observations at 250 and 212 GHz, respectively.

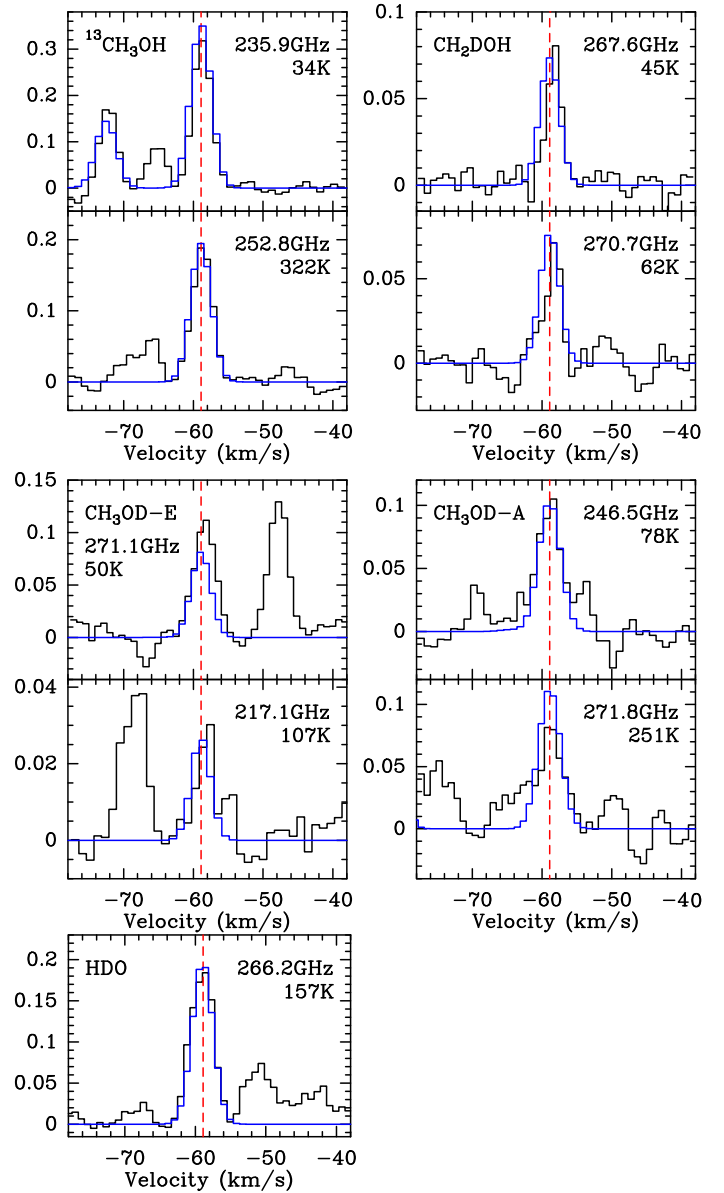
The data were reduced using the CLASS90 package from the GILDAS software<sup>1</sup>. The spectra are reported in this study in main beam temperature units,  $T_{\text{MB}}$ , given by  $T_{\text{MB}} = \frac{\eta_f}{\eta_{\text{MB}}} \times T_{\text{A}}^*$ , where  $T_{\text{A}}^*$  is the antenna temperature,  $\eta_f$  the forward efficiency ( $\eta_f = 94, 92$  and  $87$  at 210, 230 and 274 GHz, respectively), and  $\eta_{\text{MB}}$  the main beam efficiency ( $\eta_{\text{MB}} = 63, 59, 49$  at 210, 230 and 274 GHz, respectively<sup>2</sup>). Finally, the data presented some spurs along with standing waves, which have been removed during the data reduction. In this paper, we focus on methanol and its deuterated flavors.

The spectroscopic parameters of the targeted lines are given in Appendix A (see Tables A.1–A.4). More specifically, we used the spectroscopic data parameters<sup>3</sup> from Xu & Hougen (1995a,b), Xu & Lovas (1997), Xu et al. (2008), and Müller et al. (2004) for  $\text{CH}_3\text{OH}$ . The parameters for  $\text{CH}_2\text{DOH}$  come from Pearson et al. (2012) and those for  $^{13}\text{CH}_3\text{OH}$  are from Xu & Lovas (1997), Xu et al. (1996, 2008, 2014). Regarding  $\text{CH}_3\text{OD}$ , we used the same unpublished data as Neill et al. (2013b) used for analyzing the HIFI/Herschel observations of Orion-KL. Nonetheless, the  $\text{CH}_3\text{OD}$  partition functions we use in the present study (see also, Walsh et al. 2000) are given in Appendix B. Finally, collisional rates are assumed to be identical to those of  $\text{CH}_3\text{OH}$  and taken from Rabli & Flower (2010). This point is addressed in more detail in Sect. 3.3

## 3. Results and analysis

### 3.1. Detected lines

We detect several bright lines covering a wide range of upper energy levels: 34  $^{13}\text{CH}_3\text{OH}$  lines with  $E_{\text{up}}$  spanning from 23 to 397 K; 13  $\text{CH}_2\text{DOH}$  lines with  $E_{\text{up}}$  spanning from 25 to



**Fig. 1.** Montage of detected transitions of methanol  $^{13}\text{C}$  isotopolog and deuterated forms along with that of the detected HDO line. Intensities are expressed in units of  $T_{\text{mb}}$ . Our LTE modeling is displayed in blue. The red dashed line marks the peak velocity of methanol transitions  $v_{\text{LSR}} = -58.9 \text{ km s}^{-1}$ .

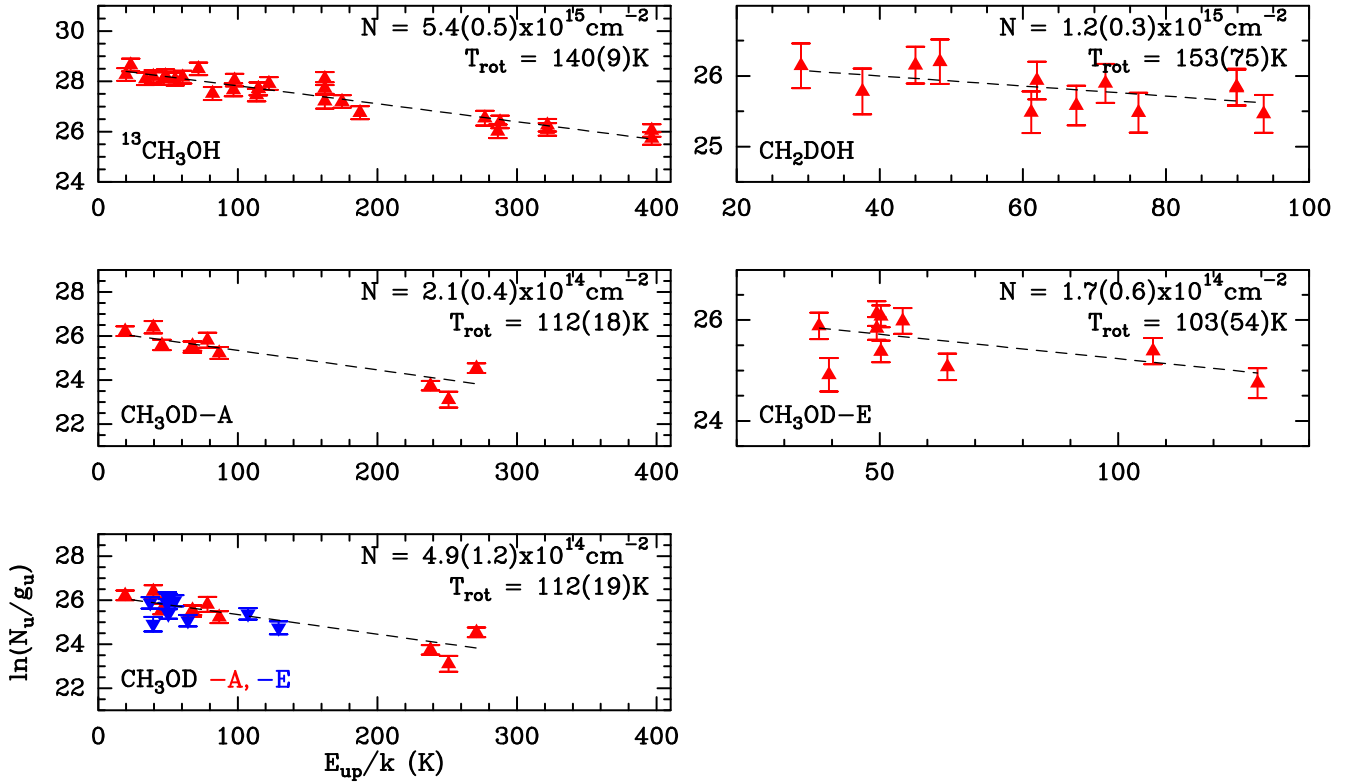
94 K; and 20  $\text{CH}_3\text{OD}$  lines (10 lines for both A- and E-forms) with  $E_{\text{up}}$  spanning from 19 to 271 K. The observational line parameters of the clearly detected transitions are summarized in Tables A.1–A.4.

The lines profiles are well fitted by a single Gaussian profile with a little scatter on the fitted full width at half maximum (mean  $\Delta v = 3.4 \pm 0.7 \text{ km s}^{-1}$ ) and the peak intensity velocity (mean  $v_{\text{LSR}} = 58.6 \pm 0.6 \text{ km s}^{-1}$ ). We note that the scatter on the peak velocity lies within 1 element of spectral resolution ( $1 \text{ km s}^{-1}$ ), which makes us confident as to the line assignments. In addition, if we take into account the pointing uncertainties (typically  $1''$ – $2''$ ), the observed scatter in emission velocity peak is consistent with the large velocity gradient observed within the source by Beuther et al. (2012, and their Fig. 8). Figure 1 shows a montage of two detected transitions probing different excitation energies of  $^{13}\text{CH}_3\text{OH}$ ,  $\text{CH}_2\text{DOH}$ , and  $\text{CH}_3\text{OD}$  (A and E) along

<sup>1</sup> <http://www.iram.fr/IRAMFR/GILDAS/>

<sup>2</sup> See <http://www.iram.es/IRAMES/mainWiki/Iram30mEfficiencies>

<sup>3</sup> The spectroscopic data parameters are available at the Cologne Database for Molecular Spectroscopy catalog (CDMS; Müller et al. 2005) and/or at the JPL catalog (Pickett et al. 1998).



**Fig. 2.** Population diagram analysis of the  $^{13}\text{C}$ -methanol and the deuterated forms. A size of  $3.8''$  was adopted for the emitting region. In the analysis we separate the methanol E-form from the A-form. However, as shown in the bottom left panel, their respective SLEDs are consistent with one another. Finally, please note that the  $y$ -range varies from plot to plot.

with our local thermodynamical equilibrium (LTE) modeling. In addition, Fig. 1 also displays the spectrum of the  $2_{2,0}-3_{1,3}$  transition of deuterated water which is also detected in our survey. Finally, Figs. C.1–C.3 display a montage of all the detected transitions associated with the  $^{13}\text{CH}_3\text{OH}$ ,  $\text{CH}_2\text{DOH}$ , and  $\text{CH}_3\text{OD}$  species along with our LTE modeling.

### 3.2. Local thermodynamical equilibrium analysis

The physical properties (excitation temperature, column densities) of the methanol species were obtained from a population diagram analysis of their spectral line energy distributions (SLEDs). In the present study, we assume a source size of  $3.8''$ , corresponding to the ice evaporation region (see Bisschop et al. 2007). The derived column densities are therefore determined and given for a source size of  $3.8''$ . We estimate the line opacities, under LTE conditions following Goldsmith & Langer (1999). We conclude that the  $^{13}\text{CH}_3\text{OH}$ ,  $\text{CH}_2\text{DOH}$ , and  $\text{CH}_3\text{OD}$  emissions are optically thin with  $\tau \leq 0.03$ . We note that most of the transitions associated with the main methanol isotopolog are optically thick with  $\tau(\text{CH}_3\text{OH}) \geq 1$ . As a consequence, we cannot determine the excitation temperature and column density of the  $^{12}\text{CH}_3\text{OH}$  with sufficiently accurate precision. We therefore exclude the analysis of the  $^{12}\text{CH}_3\text{OH}$  for the present study. The resulting physical properties are summarised in Table 1.

Figure 2 shows the population diagrams that are all well fitted by a single rotational temperature. More specifically, the population diagram analysis of  $^{13}\text{CH}_3\text{OH}$  yields  $N(^{13}\text{CH}_3\text{OH}) = (5.4 \pm 0.5) \times 10^{15} \text{ cm}^{-2}$  and  $T_{\text{rot}} = 140 \pm 9 \text{ K}$ . Assuming a  $^{12}\text{C}/^{13}\text{C}$  elemental abundance ratio of 70 for the local ISM (Wilson 1999), we determine the methanol column density  $N(\text{CH}_3\text{OH}) = (3.8 \pm 0.4) \times 10^{17} \text{ cm}^{-2}$ . Regarding

**Table 1.** Physical properties of methanol isotopologs: rotational temperature and column density.

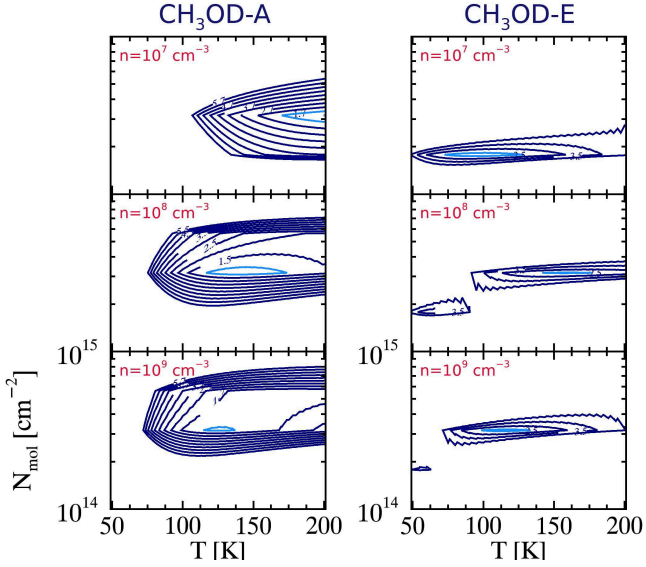
Species	$T_{\text{rot}}$ (K)	$N$ ( $10^{14} \text{ cm}^{-2}$ )
$^{13}\text{CH}_3\text{OH}$	$140 \pm 9$	$54 \pm 5$
$\text{CH}_2\text{DOH}$	$153 \pm 75$	$12 \pm 3$
$\text{CH}_3\text{OD-E}$	$103 \pm 54$	$1.7 \pm 0.6$
$\text{CH}_3\text{OD-A}$	$112 \pm 18$	$2.1 \pm 0.4$

**Notes.** A source size of  $3.8''$  was adopted.

$\text{CH}_2\text{DOH}$ , we estimate a rotational temperature similar to that of  $^{13}\text{C}$  methanol,  $T_{\text{rot}} = 153 \pm 75 \text{ K}$ , and a column density  $N(\text{CH}_2\text{DOH})$  of  $(1.2 \pm 0.3) \times 10^{15} \text{ cm}^{-2}$ . For  $\text{CH}_3\text{OD}$  we derive a lower rotational temperature of  $T_{\text{rot}} = 103 \pm 54 \text{ K}$  ( $112 \pm 18 \text{ K}$ ) for both the E- and A-forms. Nonetheless, within the error bars, the derived rotational temperatures for the deuterated methanol flavors are in agreement with that of the  $^{13}\text{C}$  isotopolog. The derived column densities of both E- and  $\text{CH}_3\text{OD-A}$  are comparable with  $N(\text{CH}_3\text{OD-E}) = (1.7 \pm 0.6) \times 10^{14} \text{ cm}^{-2}$  and  $N(\text{CH}_3\text{OD-A}) = (2.1 \pm 0.4) \times 10^{14} \text{ cm}^{-2}$ , which results in a total  $\text{CH}_3\text{OD}$  column density,  $N(\text{CH}_3\text{OD})$ , of  $(3.8 \pm 1.0) \times 10^{14} \text{ cm}^{-2}$ . We note that the computed total  $\text{CH}_3\text{OD}$  column density is commensurate within the error bars to that found if we treat both substates (E- and A-) simultaneously (see Fig. 2).

### 3.3. Nonlocal thermodynamic equilibrium analysis

The present section aims to verify whether the apparent LTE distribution of the  $\text{CH}_3\text{OD}$  targeted transitions is consistent



**Fig. 3.** CH<sub>3</sub>OD-A (left column) and CH<sub>3</sub>OD-E (right column)  $\chi^2$  distributions as computed with RADEX for  $n = 10^7$ ,  $10^8$  and  $10^9$  cm<sup>-3</sup>. The minimum  $\chi^2$  is displayed in cyan.

with nonLTE conditions along with the derived densities and temperatures.

For this purpose we combined the (unpublished) spectroscopic data of CH<sub>3</sub>OD (energy levels and radiative rates) with the collisional rate coefficients computed by Rabli & Flower (2010) for the rotational excitation of CH<sub>3</sub>OH by H<sub>2</sub>. We assumed that the -OH H/D substitution has a negligible impact on the scattering dynamics (the change in reduced mass is only 0.2%). The coupled statistical equilibrium–radiative transfer equations were then solved using the RADEX code (van der Tak et al. 2007).

Assuming a source size of 3.8'' and a line width of 4 km s<sup>-1</sup>, we ran a grid of models for the following gas densities  $n = 10^7$ ,  $10^8$ , and  $10^9$  cm<sup>-3</sup> with the kinetic temperature varying from 20 to 200 K and the CH<sub>3</sub>OD column density lying between  $1 \times 10^{10}$  and  $1 \times 10^{19}$  cm<sup>-2</sup>. We then compared the observed and modeled LGV CH<sub>3</sub>OD-A and CH<sub>3</sub>OD-E integrated fluxes by the mean of the  $\chi^2$ . The computed results and minimized  $\chi^2$  distributions are shown in Fig. 3.

There is no common solution for both E- and A-species with a density of  $10^7$  cm<sup>-3</sup>. A common region of minimum  $\chi^2$  in the parameter space (N,T) is found for a density in the range  $10^8$ – $10^9$  cm<sup>-3</sup>. The latter is commensurate with the one derived by Beuther et al. (2012) from PdBI observations as well as that derived by Bisschop et al. (2007) from James Clerk Maxwell Telescope (JCMT) observations. Our best fits are obtained for a CH<sub>3</sub>OD column density of about  $\approx 3 \times 10^{14}$  cm<sup>-2</sup> and a temperature of 100–150 K, both consistent with our LTE analysis.

## 4. Discussion

### 4.1. D/H in methanol

As can be seen in Table 2, the fractionation degree of singly deuterated methanol is low in NGC 7538-IRS1, with relative abundance values of 0.1% (taking into account the statistical ratio for the -CH<sub>3</sub> functional group). Such values are similar to those reported towards other HMSRs like Orion KL. Thanks to the numerous detected lines for both CH<sub>2</sub>DOH and CH<sub>3</sub>OD,

**Table 2.** Deuteration ratios measured towards NGC 7538-IRS1.

Species	Ratios
CH <sub>2</sub> DOH/CH <sub>3</sub> OH	$(3.2 \pm 0.8) \times 10^{-3}$
CH <sub>3</sub> OD/CH <sub>3</sub> OH	$(1.0 \pm 0.4) \times 10^{-3}$
CH <sub>2</sub> DOH/CH <sub>3</sub> OD	$3.2 \pm 1.5$

the relative abundance between the two deuterated flavors is determined with good accuracy, and is found to be equal to  $3.2 \pm 1.5$ .

### 4.2. Water and HDO

Water does not exhibit the same level of fractionation as methanol in low-mass star-forming regions, with a HDO/H<sub>2</sub>O lying in the range 0.01–0.07 (Liu et al. 2011; Parise et al. 2005, 2006; Ratajczak et al. 2011; Coutens et al. 2012; Faure et al. 2015a). However, in Orion-KL water and methanol seem to be fractionated to a similar extent (Neill et al. 2013b). This is likely the result of recent desorption from ice mantles (see further details on thermal H/D exchanges between water and methanol during the warm-up phase in Faure et al. 2015a).

Although only the HDO (2<sub>2,0</sub>–3<sub>1,3</sub>) transition is detected in our data, as shown in Fig. 1, we can roughly estimate the D/H ratio for water combining our result with that of different studies. Indeed, combining the observed HDO integrated flux ( $\sim 0.8 \pm 0.1$  K km s<sup>-1</sup>) with the ones measured by Jacq et al. (1990) for the (3<sub>1,2</sub>–2<sub>2,1</sub>) and (2<sub>1,1</sub>–2<sub>1,2</sub>) transitions and assuming a source size of 3.8'', we derived a HDO column density of about  $1.6 \times 10^{15}$  cm<sup>-2</sup> and a rotational temperature of  $\sim 130$  K.

From recent *Herschel*/HIFI observations of water in NGC 7538-IRS1, Herpin et al. (2017) derived a water abundance,  $\chi_{(\text{H}_2\text{O})}$ , of  $8 \times 10^{-6}$ . Assuming a  $n_{\text{H}_2}$  of about  $10^8$  cm<sup>-3</sup> (see Sect. 3.3), we estimate a HDO/H<sub>2</sub>O ratio lying in the range  $10^{-4}$ – $10^{-3}$  according to the source size taken into account (see also van der Tak et al. 2006).

Incidentally, we note that Herpin et al. (2017) also derived a H<sub>2</sub>O abundance of  $5 \times 10^{-5}$  for the very inner part of the hot core, as probed by a THz line observed with SOFIA.

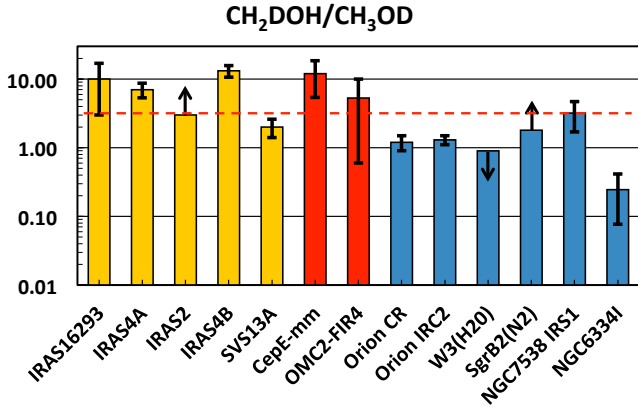
These findings show that the water emission source size provides strong constraints on the deuteration ratio. Therefore, further interferometric observations of water and its isotopologs are clearly needed to investigate water fractionation in this source in more detail.

### 4.3. Comparison with other sources

Figure 4 reports the relative CH<sub>2</sub>DOH/CH<sub>3</sub>OD abundance ratio measured towards a large sample of star-forming regions, from low- to high-mass, ordered from left to right by increasing source luminosity. It is immediately apparent that there is a variation between the sources of two orders of magnitude. More specifically, in low-mass star-forming regions, methanol deuteration strongly favors the methyl group (CH<sub>2</sub>DOH) by far more than the statistical factor (3), whereas in high-mass the opposite trend is observed.

### 4.4. Modeling

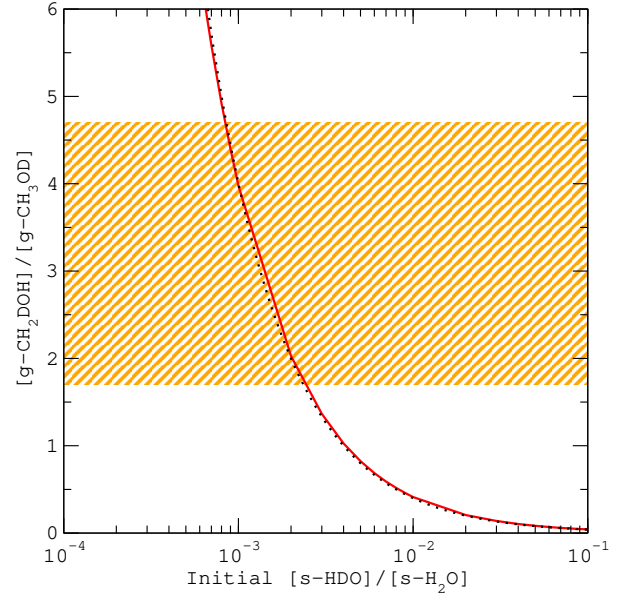
The value of the abundance ratio CH<sub>2</sub>DOH/CH<sub>3</sub>OD toward NGC 7538-IRS1 is  $3.2 \pm 1.5$ , in good agreement with the value



**Fig. 4.** CH<sub>2</sub>DOH/CH<sub>3</sub>OD ratios observed towards low- (yellow), intermediate- (red), and high-mass (blue) star-forming regions: IRAS 16293-2422 (Parise et al. 2002; Jørgensen et al. 2018), IRAS 4A, IRAS 2, IRAS 4B (Parise et al. 2006), SVS13A (Bianchi et al. 2017), CepE-mm (Ratajczak et al. 2011), OMC2-FIR4 (Ratajczak et al. 2011), Orion CR (Neill et al. 2013b), Orion Irc2, W3(H<sub>2</sub>O), SgrB2(N<sub>2</sub>) (Belloche et al. 2016), NGC 7538-IRS1 (this work; blue and white stripes), and NGC 6334I (Bøgelund et al. 2018). We note that values derived by Parise et al. (2006) and Ratajczak et al. (2011) were divided by a factor of 2 and 1.5, respectively, due to a spectroscopic issue (see Belloche et al. 2016). The dashed red line shows the statistical factor CH<sub>2</sub>DOH/CH<sub>3</sub>OD = 3.

of three predicted by grain chemistry models (e.g., Charnley et al. 1997; Osamura et al. 2004). In these models, the deuterium fractionation of methanol proceeds in the ice during the early cold prestellar phase through the statistical addition of H and D atoms to CO molecules and the ratio s-CH<sub>2</sub>DOH/s-CH<sub>3</sub>OD is equal to the statistical value of three. More recent and sophisticated models also predict a ratio close to three (e.g., Bøgelund et al. 2018). These models however neglect processes occurring in the subsequent warm-up phase. In particular, Faure et al. (2015a) have shown that the s-CH<sub>2</sub>DOH/s-CH<sub>3</sub>OD ratio can change during this phase as a result of H/D exchanges between the hydroxyl (-OH) functional groups of methanol and water (see details in Faure et al. 2015b). This scenario was successful in explaining both the high value (>3) of the CH<sub>2</sub>DOH/CH<sub>3</sub>OD abundance ratio towards the low-mass protostar IRAS 16293-2422 and the low-value (<3) measured towards Orion (see Fig. 4).

We adapted the model of Faure et al. (2015a) to the conditions of NGC 7538-IRS1. First, the density was taken as  $n_{\text{H}} = 2 \times 10^8 \text{ cm}^{-3}$  and the (equal) gas and dust temperatures as  $T = 100 \text{ K}$ . The methanol abundance (by number) relative to water is 4% (Öberg et al. 2011; Boogert et al. 2015) and the mean water abundance is  $5 \times 10^{-5} n_{\text{H}}$ . The accreting D/H ratio is inferred from the observed CH<sub>2</sub>DOH/CH<sub>3</sub>OH ratio (see Table 2) as  $\alpha_{\text{m}} = 1.1 \times 10^{-3}$ , assuming that the initial (statistical) deuteration of CH<sub>2</sub>DOH in the ice is conserved during the hot core phase. The post-evaporative gas-phase chemistry is also entirely neglected (full details can be found in Faure et al. 2015a). The results of the model are plotted in Fig. 5: it is found that the observed CH<sub>2</sub>DOH/CH<sub>3</sub>OD ratio of  $3.2 \pm 1.5$  can be reproduced for a solid s-HDO/s-H<sub>2</sub>O ratio in the range  $\sim 8 \times 10^{-4} - 2 \times 10^{-3}$ . Therefore, while the CH<sub>2</sub>DOH/CH<sub>3</sub>OD ratio of  $3.2 \pm 1.5$  is consistent with a statistical deuteration, the occurrence of H/D exchanges cannot be excluded. In particular, it should be noted that H/D exchanges can explain the range of values depicted in Fig. 4, that is CH<sub>2</sub>DOH/CH<sub>3</sub>OD ratios in the range



**Fig. 5.** Gas-phase abundance ratio of the deuterated isotopologs, CH<sub>2</sub>DOH/CH<sub>3</sub>OD, as function of the initial (cold) water ice deuteration. The dotted line corresponds to the analytic solution CH<sub>2</sub>DOH/CH<sub>3</sub>OD = 0.004/(HDO/H<sub>2</sub>O), see Faure et al. (2015a) for details. The ratio observed toward NGC 7538-IRS1 is represented by the orange hatched zone.

$\sim 0.1 - 10$ . To our knowledge, this is currently the only mechanism able to explain the nonstatistical deuteration of methanol in both low- and high-mass protostars.

## 5. Conclusions

To summarize, we investigated the deuteration of methanol in the high-mass star-forming regions NGC 7538-IRS1 using IRAM-30m observations. Our study shows that the fractionation degree of deuterated methanol is low in this source. From the numerous ( $\geq 10$ ) detected lines, we estimate a CH<sub>2</sub>DOH/CH<sub>3</sub>OD relative abundance ratio of  $3.2 \pm 1.5$ . Although our findings are commensurate with statistical deuteration at the icy surface of grain mantles, we cannot exclude H/D exchanges between water and methanol at the present time. Further observations of water and HDO are required to address this point.

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## Appendix A: Spectroscopic and observational line parameters

Tables A.1–A.4 list the spectroscopic and observational line

parameters for the observed CH<sub>3</sub>OH-A, CH<sub>3</sub>OH-E, <sup>13</sup>CH<sub>3</sub>OH, CH<sub>2</sub>DOH, CH<sub>3</sub>OD-A and CH<sub>3</sub>OD-E transitions.

**Table A.1.** Methanol.

Species	Frequency (MHz)	Quantum numbers	$E_{\text{up}}$ (K)	$A_{\text{ul}}$ ( $10^{-5} \text{ s}^{-1}$ )	Flux ( $\text{K km s}^{-1}$ )	$V_{\text{lsr}}$ ( $\text{km s}^{-1}$ )	$\Delta V$ ( $\text{km s}^{-1}$ )	$T_{\text{peak}}$ (mK)
CH <sub>3</sub> OH-E	213 159.150	20 <sub>-4,0</sub> – 19 <sub>-5,0</sub>	567.0	1.6	1.6 (0.3)	–59.0 (0.0)	4.0 (0.1)	374 (9)
	213 377.528	13 <sub>6,0</sub> – 14 <sub>5,0</sub>	382.0	1.1	1.4 (0.3)	–59.0 (0.0)	3.5 (0.1)	368 (7)
	213 427.061	1 <sub>1,0</sub> – 0 <sub>0,0</sub>	15.5	3.4	4.4 (0.9)	–58.8 (0.0)	3.5 (0.0)	1173 (18)
	217 886.504	20 <sub>1,0</sub> – 20 <sub>0,0</sub>	500.5	3.4	1.8 (0.4)	–59.2 (0.0)	3.7 (0.0)	439 (5)
	218 440.063	4 <sub>2,0</sub> – 3 <sub>1,0</sub>	37.6	4.7	10.0 (2.0)	–58.1 (0.0)	5.3 (0.1)	1776 (12)
	219 983.675	25 <sub>3,0</sub> – 24 <sub>4,0</sub>	794.3	2.0	0.4 (0.1)	–59.0 (0.1)	3.1 (0.3)	130 (13)
	219 993.658	23 <sub>5,0</sub> – 22 <sub>6,0</sub>	768.0	1.7	0.6 (0.1)	–58.9 (0.1)	3.8 (0.2)	143 (8)
	220 078.561	8 <sub>0,0</sub> – 7 <sub>1,0</sub>	88.7	2.5	2.9 (0.6)	–58.7 (0.0)	4.1 (0.1)	677 (7)
	229 589.056	15 <sub>4,0</sub> – 16 <sub>3,0</sub>	366.5	2.1	2.2 (0.4)	–59.1 (0.0)	3.1 (0.1)	651 (14)
	229 758.756	8 <sub>-1,0</sub> – 7 <sub>0,0</sub>	81.2	4.2	5.0 (1.0)	–58.3 (0.0)	4.2 (0.0)	1124 (11)
	230 027.047	3 <sub>-2,0</sub> – 4 <sub>-1,0</sub>	31.9	1.5	3.0 (0.6)	–58.6 (0.0)	4.2 (0.1)	658 (14)
	230 368.763	22 <sub>4,0</sub> – 21 <sub>5,0</sub>	674.8	2.1	1.1 (0.2)	–59.0 (0.2)	3.9 (0.5)	274 (62)
	232 624.811	15 <sub>6,1</sub> – 15 <sub>7,1</sub>	861.9	0.7	0.3 (0.1)	–58.8 (0.1)	3.3 (0.3)	74 (6)
	232 645.103	8 <sub>6,1</sub> – 8 <sub>7,1</sub>	667.7	0.9	0.4 (0.1)	–58.8 (0.2)	4.1 (0.4)	84 (7)
	232 847.103	9 <sub>6,1</sub> – 9 <sub>7,1</sub>	688.6	1.0	0.5 (0.1)	–59.0 (0.1)	4.2 (0.3)	106 (6)
	232 945.797	10 <sub>-3,0</sub> – 11 <sub>-2,0</sub>	182.5	2.1	3.8 (0.8)	–59.0 (0.0)	3.6 (0.1)	999 (15)
	233 011.878	10 <sub>6,1</sub> – 10 <sub>7,1</sub>	711.7	1.1	0.3 (0.1)	–58.7 (0.2)	3.3 (0.4)	87 (9)
	233 121.162	11 <sub>6,1</sub> – 11 <sub>7,1</sub>	737.1	1.1	0.5 (0.1)	–59.2 (0.2)	4.2 (0.5)	113 (10)
	233 155.874	12 <sub>6,1</sub> – 12 <sub>7,1</sub>	764.9	1.0	0.3 (0.1)	–59.0 (0.3)	4.0 (0.8)	68 (10)
	234 698.519	5 <sub>-4,0</sub> – 6 <sub>-3,0</sub>	114.8	0.6	1.8 (0.4)	–59.0 (0.0)	3.3 (0.0)	527 (6)
	244 337.983	9 <sub>1,1</sub> – 8 <sub>0,1</sub>	387.7	4.0	1.5 (0.3)	–59.4 (0.1)	4.4 (0.1)	329 (9)
	245 094.503	18 <sub>-6,1</sub> – 17 <sub>-7,1</sub>	881.0	2.1	0.2 (0.0)	–58.6 (0.2)	3.0 (0.4)	67 (7)
	247 161.950	16 <sub>2,0</sub> – 15 <sub>3,0</sub>	330.2	2.6	1.9 (0.4)	–59.3 (0.0)	3.5 (0.1)	518 (12)
	247 840.050	12 <sub>-2,1</sub> – 13 <sub>-3,1</sub>	537.2	6.3	1.7 (0.3)	–58.9 (0.0)	3.7 (0.1)	434 (8)
	247 968.119	23 <sub>1,0</sub> – 23 <sub>0,0</sub>	653.5	4.4	1.0 (0.2)	–59.0 (0.0)	4.1 (0.1)	228 (5)
	248 854.996	15 <sub>-1,1</sub> – 16 <sub>-2,1</sub>	683.3	1.3	0.4 (0.1)	–58.7 (0.1)	3.6 (0.2)	107 (5)
	249 004.019	10 <sub>7,1</sub> – 9 <sub>6,1</sub>	700.5	3.6	0.5 (0.1)	–58.7 (0.1)	3.9 (0.2)	114 (6)
	249 192.836	16 <sub>-3,0</sub> – 15 <sub>-4,0</sub>	370.4	2.5	1.6 (0.3)	–59.0 (0.0)	4.0 (0.1)	376 (6)
	250 970.042	17 <sub>3,1</sub> – 18 <sub>4,1</sub>	763.1	7.7	1.0 (0.2)	–59.0 (0.1)	3.7 (0.1)	250 (7)
	254 015.377	2 <sub>0,0</sub> – 1 <sub>-1,0</sub>	12.2	1.9	3.1 (0.6)	–58.9 (0.3)	4.1 (0.3)	704 (104)
	254 419.419	11 <sub>5,0</sub> – 12 <sub>4,0</sub>	281.3	1.8	1.8 (0.4)	–58.7 (0.0)	3.2 (0.1)	536 (9)
	259 581.398	24 <sub>1,0</sub> – 24 <sub>0,0</sub>	709.1	4.9	0.7 (0.1)	–59.0 (0.1)	3.4 (0.2)	191 (8)
	261 061.320	21 <sub>-4,0</sub> – 20 <sub>-5,0</sub>	615.7	3.0	1.0 (0.2)	–58.8 (0.1)	2.9 (0.3)	327 (29)
	261 704.409	12 <sub>6,0</sub> – 13 <sub>5,0</sub>	351.9	1.8	1.1 (0.2)	–59.2 (0.1)	3.4 (0.2)	301 (19)
	261 805.675	2 <sub>1,0</sub> – 1 <sub>0,0</sub>	20.1	5.6	5.3 (1.1)	–58.2 (0.0)	4.4 (0.1)	1132 (15)
	264 732.426	13 <sub>2,1</sub> – 12 <sub>3,1</sub>	602.6	0.5	0.2 (0.1)	–58.6 (0.2)	3.0 (0.4)	75 (10)
	265 289.562	6 <sub>1,0</sub> – 5 <sub>2,0</sub>	61.9	2.6	1.5 (0.3)	–59.0 (0.0)	2.9 (0.2)	497 (40)
	266 838.148	5 <sub>2,0</sub> – 4 <sub>1,0</sub>	49.2	7.7	3.9 (0.8)	–57.9 (0.0)	3.5 (0.1)	1052 (24)
	267 887.317	24 <sub>5,0</sub> – 23 <sub>6,0</sub>	823.6	3.2	0.5 (0.1)	–59.1 (0.2)	3.5 (0.4)	127 (13)
	268 743.954	9 <sub>-5,0</sub> – 10 <sub>-4,0</sub>	220.5	1.8	1.8 (0.4)	–59.2 (0.1)	3.8 (0.2)	449 (23)
	271 222.675	26 <sub>3,0</sub> – 25 <sub>4,0</sub>	854.6	3.8	0.7 (0.1)	–58.7 (0.2)	4.3 (0.4)	154 (11)
	271 933.603	25 <sub>1,0</sub> – 25 <sub>0,0</sub>	767.0	5.5	0.9 (0.2)	–59.0 (0.1)	3.6 (0.3)	230 (18)
	274 022.001	24 <sub>-7,0</sub> – 25 <sub>-6,0</sub>	947.6	3.1	0.2 (0.1)	–58.9 (0.2)	3.8 (0.5)	60 (6)

Table A.2. Methanol.

Species	Frequency (MHz)	Quantum numbers	$E_{\text{up}}$ (K)	$A_{\text{ul}}$ ( $10^{-5} \text{ s}^{-1}$ )	Flux (K km s $^{-1}$ )	$V_{\text{lsr}}$ (km s $^{-1}$ )	$\Delta V$ (km s $^{-1}$ )	$T_{\text{peak}}$ (mK)
CH <sub>3</sub> OH-A	215 302.206	6 <sub>1,+1</sub> - 7 <sub>2,+1</sub>	373.8	4.2	2.4 (0.5)	-59.1 (0.0)	3.6 (0.1)	637 (8)
	217 299.205	6 <sub>1,-1</sub> - 7 <sub>2,-1</sub>	373.9	4.3	1.8 (0.4)	-59.0 (0.0)	3.1 (0.1)	530 (23)
	231 281.110	10 <sub>2,-0</sub> - 9 <sub>3,-0</sub>	165.3	1.8	1.7 (0.3)	-59.0 (0.0)	3.5 (0.1)	460 (18)
	232 418.521	10 <sub>2,+0</sub> - 9 <sub>3,+0</sub>	165.4	1.9	1.6 (0.3)	-58.9 (0.0)	3.0 (0.1)	518 (16)
	232 783.446	18 <sub>3,+0</sub> - 17 <sub>4,+0</sub>	446.5	2.2	2.4 (0.5)	-59.2 (0.0)	3.8 (0.1)	589 (7)
	233 795.666	18 <sub>3,-0</sub> - 17 <sub>4,-0</sub>	446.6	2.2	2.4 (0.5)	-59.2 (0.0)	3.6 (0.0)	617 (7)
	234 683.370	4 <sub>2,-0</sub> - 5 <sub>1,-0</sub>	60.9	1.8	3.7 (0.7)	-58.9 (0.0)	3.6 (0.0)	955 (9)
	243 915.788	5 <sub>1,-0</sub> - 4 <sub>1,-0</sub>	49.7	6.0	6.1 (1.2)	-58.0 (0.0)	4.2 (0.0)	1345 (9)
	246 873.301	19 <sub>3,-0</sub> - 19 <sub>2,+0</sub>	490.7	8.0	1.5 (0.3)	-59.2 (0.0)	3.3 (0.1)	442 (9)
	247 228.587	4 <sub>2,+0</sub> - 5 <sub>1,+0</sub>	60.9	2.2	3.5 (0.7)	-59.0 (0.0)	3.7 (0.1)	876 (14)
	247 610.918	18 <sub>3,-0</sub> - 18 <sub>2,+0</sub>	446.6	8.1	1.5 (0.3)	-59.2 (0.0)	3.3 (0.1)	437 (9)
	248 282.424	17 <sub>3,-0</sub> - 17 <sub>2,+0</sub>	404.8	8.1	1.7 (0.3)	-59.2 (0.0)	3.6 (0.1)	444 (6)
	248 885.468	16 <sub>3,-0</sub> - 16 <sub>2,+0</sub>	365.4	8.2	1.8 (0.4)	-59.2 (0.0)	3.4 (0.1)	482 (9)
	249 419.924	15 <sub>3,-0</sub> - 15 <sub>2,+0</sub>	328.3	8.2	1.8 (0.4)	-59.2 (0.0)	3.5 (0.1)	479 (11)
	249 443.301	7 <sub>4,-0</sub> - 8 <sub>3,-0</sub>	145.3	1.5	1.6 (0.3)	-59.1 (0.0)	4.0 (0.1)	375 (8)
	249 451.842	7 <sub>4,+0</sub> - 8 <sub>3,+0</sub>	145.3	1.5	1.5 (0.3)	-59.1 (0.0)	3.9 (0.1)	372 (8)
	249 887.467	14 <sub>3,-0</sub> - 14 <sub>2,+0</sub>	293.5	8.2	1.5 (0.3)	-59.2 (0.0)	3.1 (0.1)	443 (14)
	250 291.181	13 <sub>3,-0</sub> - 13 <sub>2,+0</sub>	261.0	8.2	2.0 (0.4)	-59.1 (0.0)	3.6 (0.1)	526 (8)
	250 506.853	11 <sub>0,+0</sub> - 10 <sub>1,+0</sub>	153.1	4.2	2.6 (0.5)	-58.6 (0.0)	4.5 (0.1)	535 (7)
	250 635.200	12 <sub>3,-0</sub> - 12 <sub>2,+0</sub>	230.8	8.2	2.3 (0.5)	-59.3 (0.0)	3.7 (0.1)	590 (8)
	250 924.398	11 <sub>3,-0</sub> - 11 <sub>2,+0</sub>	203.0	8.2	2.5 (0.5)	-59.2 (0.0)	3.5 (0.0)	673 (5)
	251 164.108	10 <sub>3,-0</sub> - 10 <sub>2,+0</sub>	177.5	8.2	2.7 (0.5)	-59.1 (0.0)	3.5 (0.1)	711 (12)
	251 517.309	8 <sub>3,-0</sub> - 8 <sub>2,+0</sub>	133.4	7.9	3.1 (0.6)	-59.0 (0.0)	3.5 (0.1)	835 (10)
	251 641.787	7 <sub>3,-0</sub> - 7 <sub>2,+0</sub>	114.8	7.7	3.2 (0.6)	-59.0 (0.0)	3.8 (0.1)	797 (9)
	251 738.437	6 <sub>3,-0</sub> - 6 <sub>2,+0</sub>	98.5	7.4	3.4 (0.7)	-58.8 (0.0)	4.0 (0.0)	800 (8)
	251 811.956	5 <sub>3,-0</sub> - 5 <sub>2,+0</sub>	84.6	7.0	3.6 (0.7)	-58.8 (0.0)	4.3 (0.1)	790 (17)
	251 866.524	4 <sub>3,-0</sub> - 4 <sub>2,+0</sub>	73.0	6.1	3.1 (0.6)	-58.6 (0.0)	4.1 (0.1)	717 (8)
	251 890.886	5 <sub>3,+0</sub> - 5 <sub>2,-0</sub>	84.6	7.0	3.3 (0.7)	-58.5 (0.0)	3.8 (0.1)	818 (8)
	251 895.728	6 <sub>3,+0</sub> - 6 <sub>2,-0</sub>	98.5	7.5	3.4 (0.7)	-58.6 (0.0)	3.8 (0.1)	817 (7)
	251 900.452	4 <sub>3,+0</sub> - 4 <sub>2,-0</sub>	73.0	6.1	3.4 (0.7)	-58.5 (0.0)	4.0 (0.1)	781 (9)
	251 905.729	3 <sub>3,-0</sub> - 3 <sub>2,+0</sub>	63.7	4.4	3.4 (0.7)	-58.7 (0.0)	4.2 (0.1)	629 (8)
	251 917.065	3 <sub>3,+0</sub> - 3 <sub>2,-0</sub>	63.7	4.4	3.0 (0.6)	-58.8 (0.0)	4.1 (0.1)	683 (9)
	251 923.701	7 <sub>3,+0</sub> - 7 <sub>2,-0</sub>	114.8	7.8	3.2 (0.7)	-58.8 (0.0)	3.8 (0.0)	793 (6)
	251 984.837	8 <sub>3,+0</sub> - 8 <sub>2,-0</sub>	133.4	8.0	3.1 (0.6)	-59.0 (0.0)	3.7 (0.1)	780 (10)
	252 090.409	9 <sub>3,+0</sub> - 9 <sub>2,-0</sub>	154.2	8.1	3.2 (0.6)	-59.0 (0.0)	3.7 (0.1)	799 (9)
	252 252.849	10 <sub>3,+0</sub> - 10 <sub>2,-0</sub>	177.5	8.3	2.9 (0.6)	-59.1 (0.0)	3.6 (0.0)	749 (8)
	252 485.675	11 <sub>3,+0</sub> - 11 <sub>2,-0</sub>	203.0	8.4	2.7 (0.5)	-59.1 (0.0)	3.6 (0.0)	708 (8)
	252 803.388	12 <sub>3,+0</sub> - 12 <sub>2,-0</sub>	230.8	8.4	2.5 (0.5)	-59.2 (0.0)	3.5 (0.1)	677 (9)
	253 221.376	13 <sub>3,+0</sub> - 13 <sub>2,-0</sub>	261.0	8.5	2.4 (0.5)	-59.2 (0.0)	3.4 (0.1)	660 (9)
	253 755.809	14 <sub>3,+0</sub> - 14 <sub>2,-0</sub>	293.5	8.6	2.5 (0.5)	-59.2 (0.0)	3.4 (0.1)	694 (11)
	254 423.520	15 <sub>3,+0</sub> - 15 <sub>2,-0</sub>	328.3	8.7	2.6 (0.5)	-59.2 (0.0)	3.7 (0.1)	674 (10)
	255 241.888	16 <sub>3,+0</sub> - 16 <sub>2,-0</sub>	365.4	8.8	2.2 (0.4)	-59.2 (0.0)	3.3 (0.1)	615 (8)
	256 228.714	17 <sub>3,+0</sub> - 17 <sub>2,-0</sub>	404.8	9.0	1.9 (0.4)	-59.3 (0.0)	3.3 (0.1)	545 (10)
	257 402.086	18 <sub>3,+0</sub> - 18 <sub>2,-0</sub>	446.5	9.1	2.8 (0.6)	-59.9 (0.0)	4.3 (0.1)	613 (14)
	258 780.248	19 <sub>3,+0</sub> - 19 <sub>2,-0</sub>	490.6	9.3	2.1 (0.4)	-59.4 (0.0)	3.9 (0.1)	502 (11)
	263 793.875	5 <sub>1,+1</sub> - 6 <sub>2,+1</sub>	360.0	8.2	2.7 (0.5)	-58.5 (0.1)	4.5 (0.1)	566 (13)
	265 224.426	5 <sub>1,-1</sub> - 6 <sub>2,-1</sub>	360.0	8.3	2.2 (0.4)	-59.0 (0.0)	3.6 (0.1)	569 (9)
	267 406.071	17 <sub>1,+0</sub> - 16 <sub>2,+0</sub>	366.3	4.2	5.3 (1.1)	-56.9 (0.1)	7.3 (0.2)	681 (9)
	260 381.463	20 <sub>3,+0</sub> - 20 <sub>2,-0</sub>	536.9	9.4	2.3 (0.5)	-59.8 (0.1)	4.8 (0.1)	438 (11)
	246 074.605	20 <sub>3,-0</sub> - 20 <sub>2,+0</sub>	537.0	8.0	1.7 (0.3)	-59.5 (0.0)	3.7 (0.1)	417 (10)
	229 939.095	19 <sub>5,-0</sub> - 20 <sub>4,-0</sub>	578.6	2.1	1.3 (0.3)	-59.0 (0.1)	3.9 (0.2)	315 (12)
	229 864.121	19 <sub>5,+0</sub> - 20 <sub>4,+0</sub>	578.6	2.1	1.4 (0.3)	-58.8 (0.1)	4.8 (0.2)	281 (9)
	262 223.872	21 <sub>3,+0</sub> - 21 <sub>2,-0</sub>	585.6	9.7	1.3 (0.3)	-59.3 (0.0)	3.5 (0.1)	350 (10)
	245 223.019	21 <sub>3,-0</sub> - 21 <sub>2,+0</sub>	585.7	7.9	1.9 (0.4)	-58.6 (0.2)	4.3 (0.2)	408 (13)
	264 325.354	22 <sub>3,+0</sub> - 22 <sub>2,-0</sub>	636.6	9.9	1.5 (0.3)	-59.3 (0.1)	4.3 (0.2)	325 (14)
	244 330.372	22 <sub>3,-0</sub> - 22 <sub>2,+0</sub>	636.8	7.8	1.5 (0.3)	-59.3 (0.0)	3.9 (0.1)	362 (8)
	271 562.485	17 <sub>2,+1</sub> - 16 <sub>1,+1</sub>	652.6	6.5	1.4 (0.3)	-59.2 (0.1)	4.4 (0.2)	307 (12)
	259 273.686	17 <sub>2,-1</sub> - 16 <sub>1,-1</sub>	652.7	5.6	1.1 (0.2)	-59.0 (0.0)	3.8 (0.1)	270 (6)
	266 703.383	23 <sub>3,+0</sub> - 23 <sub>2,-0</sub>	689.9	10.2	1.0 (0.2)	-59.3 (0.0)	3.2 (0.1)	306 (7)
	266 872.190	14 <sub>6,+1</sub> - 15 <sub>5,+1</sub>	711.0	3.1	0.9 (0.2)	-59.0 (0.1)	3.6 (0.2)	234 (10)
	269 374.884	24 <sub>3,+0</sub> - 24 <sub>2,-0</sub>	745.5	10.5	1.2 (0.3)	-59.2 (0.1)	3.7 (0.3)	310 (21)
	217 642.677	15 <sub>6,-1</sub> - 16 <sub>5,-1</sub>	745.6	1.9	1.1 (0.2)	-58.8 (0.1)	4.4 (0.1)	234 (7)
	272 356.098	25 <sub>3,+0</sub> - 25 <sub>2,-0</sub>	803.4	10.9	1.2 (0.2)	-59.2 (0.0)	3.6 (0.2)	308 (8)
	233 916.950	13 <sub>3,-2</sub> - 14 <sub>4,-2</sub>	868.5	1.4	0.4 (0.1)	-58.7 (0.1)	3.6 (0.2)	115 (4)
	233 917.018	13 <sub>3,+2</sub> - 14 <sub>4,+2</sub>	868.5	1.4	0.4 (0.1)	-58.7 (0.1)	3.5 (0.3)	111 (7)
	268 345.816	20 <sub>4,-1</sub> - 21 <sub>5,-1</sub>	967.6	5.3	0.8 (0.2)	-58.9 (0.1)	4.1 (0.3)	189 (14)
	268 346.226	20 <sub>4,+1</sub> - 21 <sub>5,+1</sub>	967.6	5.3	0.8 (0.2)	-58.5 (0.2)	4.1 (0.4)	189 (14)

Table A.3.  $^{13}\text{C}$  methanol.

Species	Frequency (MHz)	Quantum numbers	$E_{\text{up}}$ (K)	$A_{\text{ul}}$ ( $10^{-5} \text{ s}^{-1}$ )	Flux (K km s $^{-1}$ )	$V_{\text{lsr}}$ (km s $^{-1}$ )	$\Delta V$ (km s $^{-1}$ )	$T_{\text{peak}}$ (mK)
$^{13}\text{CH}_3\text{OH}$	212 775.66	$1_{1,0,0} - 0_{0,0,0}$	23.3	3.3	296 (60)	-58.8 (0.1)	2.7 (0.2)	104 (8)
	215 707.92	$8_{4,5,-0} - 9_{3,6,-0}$	162.3	1.1	134 (33)	-58.7 (0.3)	2.5 (0.7)	51 (12)
	215 722.48	$8_{4,4,+0} - 9_{3,7,+0}$	162.3	1.1	222 (45)	-58.9 (0.1)	3.3 (0.2)	63 (2)
	216 370.39	$10_{2,9,-0} - 9_{3,6,-0}$	162.4	1.5	540 (113)	-59.5 (0.2)	4.9 (0.5)	103 (8)
	234 011.58	$5_{1,5,+0} - 4_{1,4,+0}$	48.3	5.3	1093 (220)	-58.8 (0.0)	3.5 (0.2)	290 (12)
	235 881.17	$5_{0,5,0} - 4_{0,4,0}$	47.1	5.6	1044 (209)	-58.8 (0.0)	3.2 (0.1)	307 (7)
	235 938.22	$5_{-1,5,0} - 4_{-1,4,0}$	39.6	5.4	1092 (221)	-58.8 (0.1)	3.2 (0.2)	318 (18)
	235 960.37	$5_{0,5,+0} - 4_{0,4,+0}$	34.0	5.6	1032 (207)	-58.7 (0.0)	3.1 (0.0)	316 (4)
	235 971.07	$5_{4,2,-0} - 4_{4,1,-0}$	114.8	2.0	498 (103)	-58.6 (0.1)	2.7 (0.3)	176 (19)
	235 971.07	$5_{4,1,+0} - 4_{4,0,+0}$	114.8	2.0	502 (101)	-58.6 (0.0)	2.7 (0.1)	175 (6)
	235 978.62	$5_{-4,2,0} - 4_{-4,1,0}$	122.3	2.0	307 (64)	-58.9 (0.2)	2.6 (0.6)	110 (19)
	235 997.23	$5_{3,3,+0} - 4_{3,2,+0}$	84.0	3.6	1772 (360)	-57.9 (0.1)	4.6 (0.3)	360 (17)
	235 997.23	$5_{3,2,-0} - 4_{3,1,-0}$	84.0	3.6	1771 (360)	-57.9 (0.1)	4.6 (0.3)	360 (18)
	236 008.39	$5_{2,4,-0} - 4_{2,3,-0}$	71.8	4.8	1390 (287)	-57.6 (0.2)	5.1 (0.5)	258 (19)
	236 006.10	$5_{3,2,0} - 4_{3,1,0}$	81.9	3.6	1459 (299)	-60.6 (0.2)	5.4 (0.5)	253 (15)
	236 016.55	$5_{-3,3,0} - 4_{-3,2,0}$	96.9	3.6	428 (90)	-58.7 (0.1)	2.5 (0.4)	162 (20)
	236 041.40	$5_{1,4,0} - 4_{1,3,0}$	55.0	5.5	1002 (202)	-58.7 (0.0)	3.5 (0.1)	267 (8)
	236 049.52	$5_{2,3,+0} - 4_{2,2,+0}$	71.8	4.8	1300 (260)	-58.5 (0.0)	3.7 (0.1)	332 (5)
	236 062.00	$5_{-2,4,0} - 4_{-2,3,0}$	60.0	4.7	1971 (397)	-59.3 (0.1)	4.3 (0.1)	432 (13)
	236 062.85	$5_{2,3,0} - 4_{2,2,0}$	56.3	4.7	1973 (397)	-58.2 (0.1)	4.3 (0.2)	431 (18)
	248 654.97	$10_{-3,8,0} - 11_{-2,10,0}$	187.5	2.6	234 (48)	-58.4 (0.1)	2.4 (0.2)	91 (7)
	250 125.69	$5_{3,2,0} - 6_{2,4,0}$	81.9	1.6	164 (34)	-58.5 (0.1)	2.8 (0.3)	54 (5)
	250 784.61	$2_{0,2,0} - 1_{-1,1,0}$	19.9	1.8	179 (37)	-58.7 (0.1)	2.8 (0.3)	61 (6)
	254 321.72	$4_{2,2,+0} - 5_{1,5,+0}$	60.5	2.3	365 (74)	-58.6 (0.1)	3.1 (0.2)	112 (6)
	254 509.36	$10_{3,7,-0} - 10_{2,8,+0}$	174.6	8.5	1190 (239)	-58.7 (0.0)	3.3 (0.1)	340 (10)
	254 959.40	$7_{3,4,-0} - 7_{2,5,+0}$	113.5	8.1	1042 (209)	-58.8 (0.0)	3.1 (0.1)	314 (9)
	255 050.97	$6_{3,3,-0} - 6_{2,4,+0}$	97.6	7.8	1569 (315)	-58.6 (0.1)	3.9 (0.1)	383 (12)
	251 796.08	$17_{3,14,-0} - 17_{2,15,+0}$	396.5	8.6	465 (94)	-58.6 (0.1)	3.3 (0.1)	131 (5)
	259 036.49	$17_{3,15,+0} - 17_{2,16,-0}$	396.5	9.1	667 (135)	-57.8 (0.1)	4.1 (0.2)	152 (6)
	252 870.23	$15_{3,12,-0} - 15_{2,13,+0}$	321.8	8.7	697 (140)	-58.7 (0.0)	3.4 (0.1)	191 (3)
	257 421.79	$15_{3,13,+0} - 15_{2,14,-0}$	321.8	9.0	607 (122)	-58.5 (0.0)	3.3 (0.1)	175 (5)
	256 826.57	$14_{3,12,+0} - 14_{2,13,-0}$	287.8	8.9	758 (153)	-58.7 (0.1)	3.2 (0.2)	221 (9)
	273 962.69	$11_{5,7,0} - 12_{4,8,0}$	286.2	2.2	103 (24)	-58.7 (0.2)	1.8 (0.5)	52 (14)
	269 530.49	$15_{-1,15,0} - 14_{-2,13,0}$	277.0	3.1	324 (81)	-58.0 (0.3)	2.8 (0.8)	107 (25)

**Table A.4.** Deuterated methanol.

Species	Frequency (MHz)	Quantum numbers	$E_{\text{up}}$ (K)	$A_{\text{ul}}$ ( $10^{-5} \text{ s}^{-1}$ )	Flux ( $\text{K km s}^{-1}$ )	$V_{\text{lsr}}$ ( $\text{km s}^{-1}$ )	$\Delta V$ ( $\text{km s}^{-1}$ )	$T_{\text{peak}}$ (mK)	
CH <sub>2</sub> DOH	234 471.03	8 <sub>2,6,0</sub> – 8 <sub>1,7,0</sub>	93.7	8.4	171 (38)	–57.5 (0.2)	2.8 (0.4)	57 (6)	
	255 647.82	3 <sub>2,2,0</sub> – 3 <sub>1,3,0</sub>	29.0	6.3	101 (28)	–57.9 (0.3)	2.3 (0.8)	41 (11)	
	256 731.55	4 <sub>1,4,0</sub> – 3 <sub>0,3,0</sub>	25.2	6.9	126 (31)	–58.2 (0.3)	3.4 (0.7)	35 (6)	
	258 337.11	4 <sub>2,3,0</sub> – 4 <sub>1,4,0</sub>	37.6	7.0	101 (29)	–58.8 (0.3)	2.9 (0.7)	33 (7)	
	264 017.72	6 <sub>1,6,0</sub> – 5 <sub>1,5,0</sub>	48.4	5.8	182 (51)	–58.2 (0.3)	2.5 (0.6)	68 (14)	
	265 509.20	6 <sub>1,6,2</sub> – 5 <sub>1,5,2</sub>	67.5	7.5	126 (30)	–58.0 (0.2)	2.5 (0.5)	48 (7)	
	265 682.51	6 <sub>2,5,0</sub> – 6 <sub>1,6,0</sub>	61.2	8.2	126 (32)	–58.1 (0.2)	3.0 (0.6)	40 (7)	
	267 634.61	6 <sub>0,6,0</sub> – 5 <sub>0,5,0</sub>	45.0	6.3	187 (40)	–58.2 (0.1)	2.3 (0.2)	77 (6)	
	267 731.74	6 <sub>2,5,1</sub> – 5 <sub>2,4,1</sub>	71.6	7.1	163 (38)	–57.9 (0.1)	2.4 (0.4)	64 (8)	
	267 741.09	6 <sub>3,4,1</sub> – 5 <sub>3,3,1</sub>	89.9	5.9	258 (54)	–58.6 (0.1)	3.2 (0.3)	76 (5)	
	267 742.05	6 <sub>3,3,1</sub> – 5 <sub>3,2,1</sub>	89.9	5.9	261 (55)	–57.5 (0.1)	3.3 (0.3)	76 (5)	
	270 299.93	7 <sub>2,6,0</sub> – 7 <sub>1,7,0</sub>	76.2	8.8	117(31)	–57.8 (0.1)	2.6 (0.3)	43 (4)	
	270 734.57	6 <sub>1,5,1</sub> – 5 <sub>1,4,1</sub>	62.0	7.8	187 (41)	–58.3 (0.1)	2.5 (0.3)	69 (7)	
CH <sub>3</sub> OD-E	217 132.73	9 <sub>1,8,0</sub> – 8 <sub>2,6,0</sub>	107.32	1.7	115 (28)	–58.0 (0.3)	4.2 (0.9)	26 (5)	
	245 143.16	5 <sub>–1,5,0</sub> – 4 <sub>0,4,0</sub>	37.27	5.9	212 (54)	–58.6 (0.3)	3.8 (0.7)	53 (12)	
	252 624.31	6 <sub>0,6,0</sub> – 5 <sub>–1,5,0</sub>	49.39	5.0	207 (47)	–57.6 (0.1)	2.8 (0.3)	70 (10)	
	264 576.81	10 <sub>1,9,0</sub> – 9 <sub>2,7,0</sub>	129.23	3.0	115 (31)	–59.0 (0.3)	3.4 (1.0)	31 (8)	
	269 844.66	4 <sub>–2,3,0</sub> – 4 <sub>–1,4,0</sub>	39.36	11.1	156 (46)	–58.9 (0.3)	1.9 (0.4)	75 (18)	
	270 581.30	5 <sub>–2,4,0</sub> – 5 <sub>–1,5,0</sub>	50.25	11.6	310 (65)	–58.6 (0.1)	3.2 (0.3)	90 (8)	
	271 079.19	6 <sub>–1,6,0</sub> – 5 <sub>–1,5,0</sub>	50.27	7.5	416 (88)	–58.4 (0.1)	3.6 (0.3)	109 (12)	
	271 417.31	6 <sub>0,6,0</sub> – 5 <sub>0,5,0</sub>	49.39	6.1	332 (73)	–57.9 (0.3)	3.9 (0.8)	80 (12)	
	272 328.66	6 <sub>2,4,0</sub> – 5 <sub>2,3,0</sub>	64.21	6.9	187 (48)	–58.3 (0.2)	3.0 (0.5)	58 (13)	
	272 922.56	6 <sub>1,5,0</sub> – 5 <sub>1,4,0</sub>	54.83	7.7	435 (101)	–57.5 (0.3)	3.8 (0.6)	108 (20)	
	CH <sub>3</sub> OD-A	218 156.16	14 <sub>1,13,0</sub> – 14 <sub>0,14,0</sub>	237.96	9.1	259 (54)	–57.5 (0.4)	3.1 (0.7)	79 (6)
		230 105.09	5 <sub>1,4,0</sub> – 4 <sub>1,3,0</sub>	39.53	4.4	286 (77)	–58.2 (0.3)	2.8 (0.6)	94 (21)
232 077.53		15 <sub>1,14,0</sub> – 15 <sub>0,15,0</sub>	270.96	10.5	740 (150)	–56.9 (0.2)	3.9 (0.4)	180 (8)	
246 522.69		8 <sub>0,8,0</sub> – 7 <sub>1,7,0</sub>	78.24	8.6	596 (127)	–58.9 (0.7)	6.3 (2.2)	89 (13)	
265 235.75		3 <sub>1,3,0</sub> – 2 <sub>0,2,0</sub>	19.26	13.2	310 (66)	–58.4 (0.1)	3.1 (0.3)	94 (10)	
271 704.94		6 <sub>0,6,0</sub> – 5 <sub>0,5,0</sub>	45.67	7.6	244 (72)	–58.8 (0.2)	2.8 (0.4)	81 (24)	
271 843.69		14 <sub>2,12,0</sub> – 14 <sub>1,13,0</sub>	251	16.5	247 (62)	–58.5 (0.4)	3.4 (0.8)	69 (15)	
272 004.50		6 <sub>2,5,0</sub> – 5 <sub>2,4,0</sub>	67.49	6.9	295 (67)	–58.1 (0.3)	3.3 (0.7)	83 (13)	
272 138.36		6 <sub>3,3,0</sub> – 5 <sub>3,2,0</sub>	86.73	6.0	254 (60)	–57.8 (0.3)	3.9 (0.9)	61 (13)	
272 417.25		6 <sub>2,4,0</sub> – 5 <sub>2,3,0</sub>	67.53	7.0	323 (72)	–58.0 (0.9)	4.6 (0.9)	66 (11)	

**Appendix B: Partition function of CH<sub>3</sub>OD**

Table B.1 gives the respective CH<sub>3</sub>OD-A and CH<sub>3</sub>OD-E rotation partition functions we use in the present study.

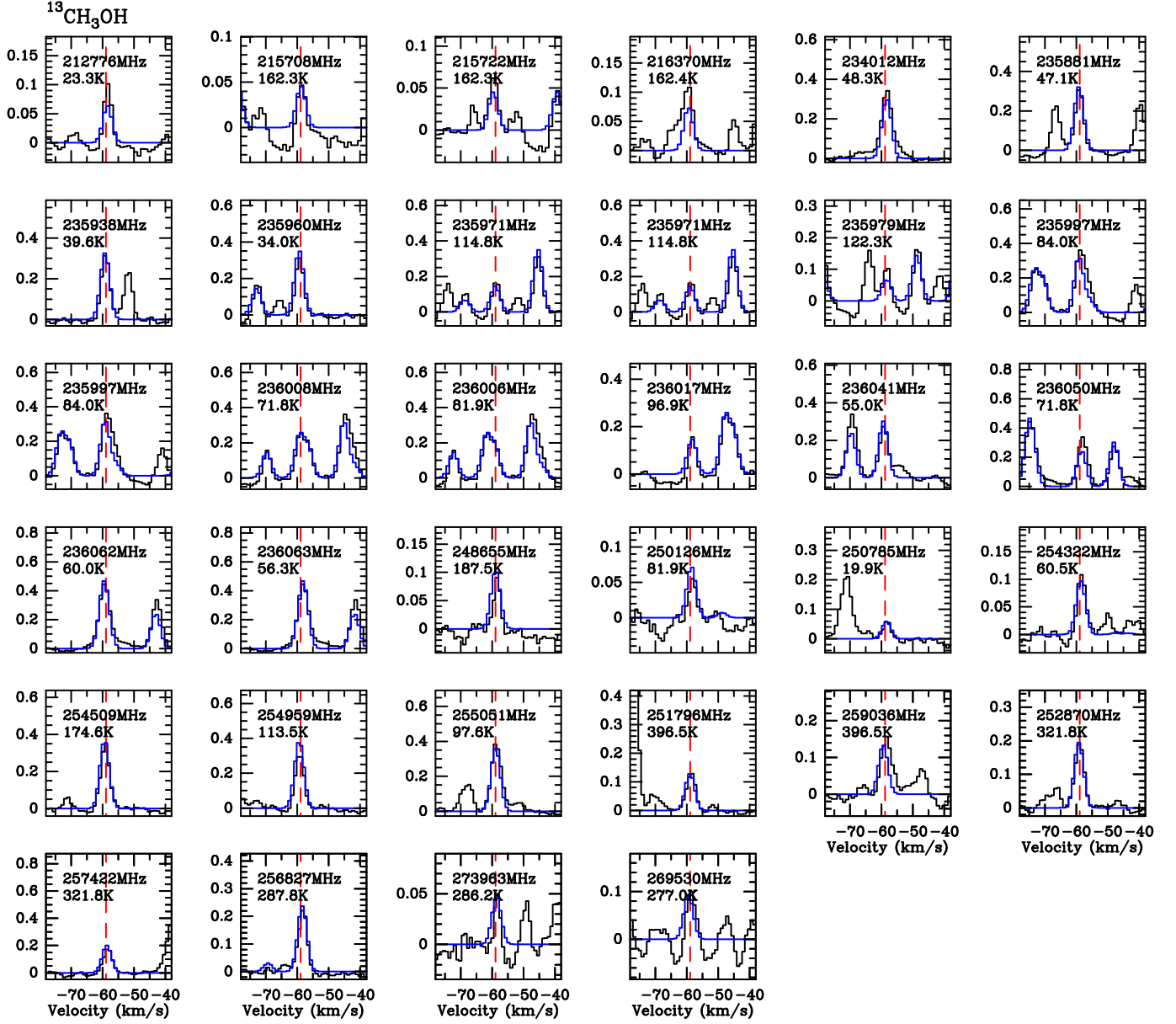
**Table B.1.** Rotational partition function for CH<sub>3</sub>OD.

CH <sub>3</sub> OD-A		CH <sub>3</sub> OD-E	
$T$ (K)	Q	$T$ (K)	Q
9.375	18.1	9.375	15.5
18.75	52.3	18.75	50.8
37.5	153.5	37.5	153.2
75	458.6	75	458.6
150	1537.5	150	1537.1
225	3319.7	225	3316.7
300	5739.8	300	5727.9

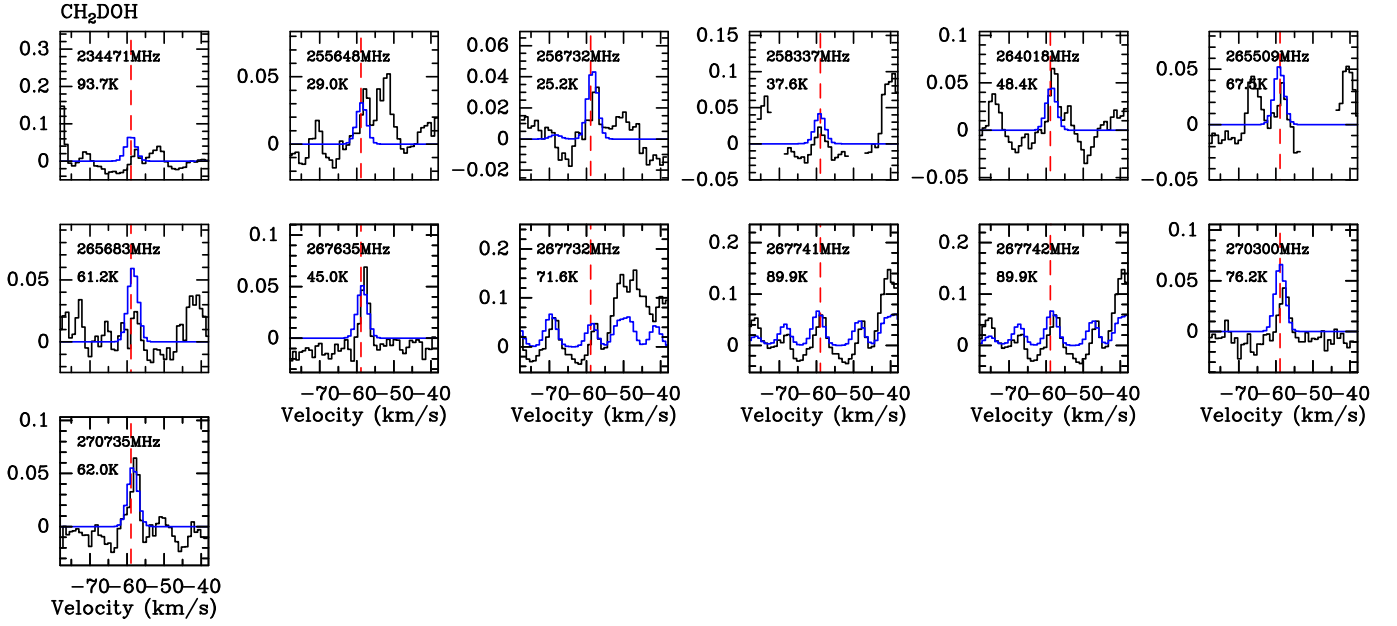
**Appendix C: IRAM-30m observations overlaid with our LTE modeling for  $^{13}\text{CH}_3\text{OH}$ ,  $\text{CH}_3\text{OD-A}$  and  $\text{CH}_3\text{OD-E}$**

Figures C.1–C.3 show a montage of the detected  $^{13}\text{CH}_3\text{OH}$ ,

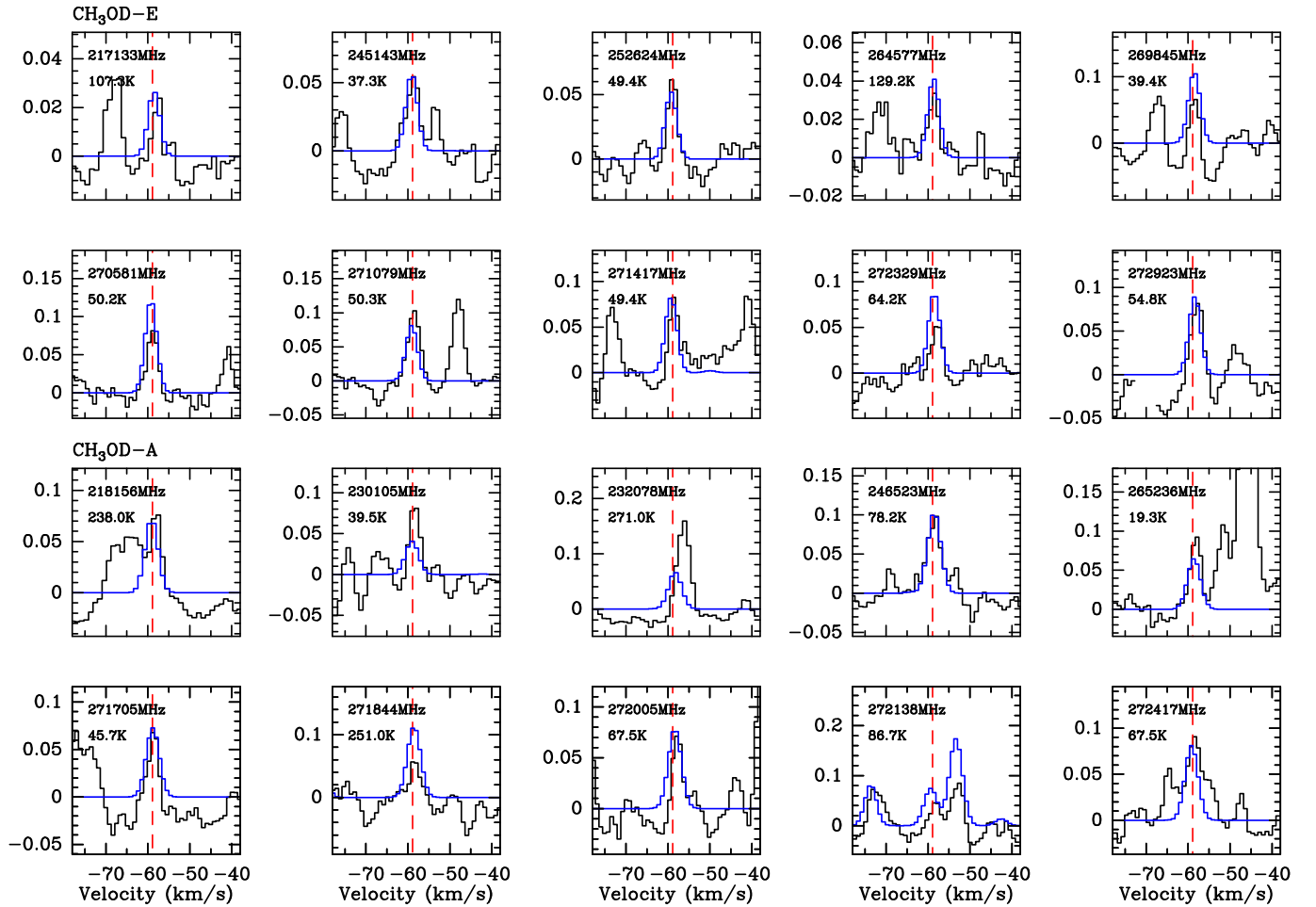
$\text{CH}_2\text{DOH}$ ,  $\text{CH}_3\text{OD-A}$  and  $\text{CH}_3\text{OD-E}$  transitions (see Tables A.3 and A.4 for the observational line parameters) along with our LTE modeling.



**Fig. C.1.** Montage of detected transitions associated with the methanol  $^{13}\text{C}$  isotopolog towards NGC 7538-IRS1. Our LTE modeling is displayed in blue. Intensities are expressed in units of  $T_{\text{mb}}$ . The red dashed line marks the ambient cloud velocity  $v_{\text{LSR}} = -58.9 \text{ km s}^{-1}$ .



**Fig. C.2.** Montage of detected transitions associated with the deuterated CH<sub>2</sub>DOH methanol towards NGC 7538-IRS1. Our LTE modeling is displayed in blue. Intensities are expressed in units of  $T_{mb}$ . The red dashed line marks the ambient cloud velocity  $v_{LSR} = -58.9 \text{ km s}^{-1}$ .



**Fig. C.3.** Montage of detected transitions associated with the CH<sub>3</sub>OD, -A and -E forms towards NGC 7538-IRS1. Our LTE modeling is displayed in blue. Intensities are expressed in units of  $T_{mb}$ . The red dashed line marks the ambient cloud velocity  $v_{LSR} = -58.9 \text{ km s}^{-1}$ .