Deuteration and evolution in the massive star formation process: the role of surface chemistry

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Received date; accepted date

ABSTRACT

Context. An ever growing number of observational and theoretical evidence suggests that the deuterated fraction (column density ratio between a species containing D and its hydrogenated counterpart, \( D_{\text{frac}} \)) is an evolutionary indicator both in the low- and the high-mass star formation process. However, the role of surface chemistry in these studies has not been quantified from an observational point of view.

Aims. Because many abundant species, like NH\(_2\), H\(_2\)CO and CH\(_3\)OH, are actively produced on ice mantles of dust grains during the early cold phases, their \( D_{\text{frac}} \) is expected to evolve differently from that of species formed only (or predominantly) in the gas, like N\(_2\)H\(^+\), HCN, HCN and their deuterated isotopologues. The differences are expected to be relevant especially after the protostellar birth, in which the temperature rises up causing the evaporation of ice mantles.

Methods. In order to compare how the deuterated fractions of species formed only in the gas and partially or uniquely on grain surfaces evolve with time, we observed rotational transitions of CH\(_3\)OH, \(^{13}\)CH\(_3\)OH, CH\(_3\)DOH, CH\(_3\)OD at 3 and 1.3 mm, and of NH\(_2\) at 2.8 mm with the IRAM-30m telescope, and the inversion transitions (1,1) and (2,2) of NH\(_3\) with the GBT. We observed \( \text{D}_{\text{frac}}(\text{NH}_2) \) in most of the cores already observed by Fontani et al. (2011, 2014) in N\(_2\)H\(^+\), N\(_2\)D\(^+\), HNC, DNC.

Results. NH\(_2\)D is detected in all but two cores, regardless of the evolutionary stage. \( D_{\text{frac}}(\text{NH}_2) \) is on average above 0.1, and does not change significantly from the earliest to the most evolved phases, although the highest average value is found in the protostellar phase (∼ 0.3). Few lines of CH\(_3\)DOH and CH\(_3\)OD are clearly detected, and only towards protostellar cores or externally heated starless cores. In quiescent starless cores, we have found only one doubtful detection of CH\(_3\)DOH.

Conclusions. This work clearly confirms an expected different evolutionary trend of the species formed exclusively in the gas (N\(_2\)D\(^+\) and N\(_2\)H\(^+\)) and those formed partially (NH\(_2\)D and NH\(_3\)) or totally (CH\(_3\)DOH and CH\(_3\)OH) on grain mantles. The study also reinforces the idea that \( \text{D}_{\text{frac}}(\text{N}_2\text{H}^+) \) is the best tracer of massive starless cores, while high values of \( \text{D}_{\text{frac}}(\text{CH}_3\text{OH}) \) seem rather good tracers of the early protostellar phases, at which the evaporation/sputtering of the grain mantles is most efficient.

Key words. Stars: formation – ISM: clouds – ISM: molecules – Radio lines: ISM

1. Introduction

Theory and observations suggest that the abundance of deuterated molecules in dense star-forming cores is related to the core evolution. The formation of deuterated molecules is favoured by the combination of low temperatures (\( T \leq 20 \text{ K} \)) and high-densities (\( n \geq 10^6 \text{ cm}^{-3} \)), which on one hand boosts the depletion of CO and other neutrals, and on the other hand makes the relative abundance between a species containing D and its hydrogenated counterpart (the so-called deuterated fraction, \( D_{\text{frac}} \)) higher by 3-4 orders of magnitude with respect to the [D/H] interstellar abundance (\( \sim 10^{-5} \)), e.g. Oliveira et al. (2003), due to the endothermicity of their backward reactions (see e.g. Millar et al. 1989, Gerlich et al. 2002). After protostellar birth, the young stellar object formed at the core centre heats up its surrounding material, and the temperature enhancement favours the progressive destruction of deuterated species and, consequently, makes \( D_{\text{frac}} \) decrease (see e.g. Caselli et al. 2002). Observations of low-mass star-forming cores have confirmed this theoretical scenario: both the column density ratio \( D_{\text{frac}}(\text{N}_2\text{H}^+) \) and the column density of ortho-H\(_2\)D\(^+\), the parent species of most of the deuterated molecules formed in the gas (e.g. DCO\(^+\), N\(_2\)D\(^+\), DNC), increase in starless cores close to the onset of gravitational collapse, and then, after the formation of the protostar, decrease as the core evolves (Crapsi et al. 2005, Emprechtinger et al. 2009, Caselli et al. 2008). Growing observational evidence suggests that high values of \( D_{\text{frac}} \) are typical also in high-mass star-forming cores (e.g. Fontani et al. 2006, Pillai et al. 2007, Miettinen et al. 2011), and that \( D_{\text{frac}} \) of some species could be an evolutionary indicator also in the intermediate- and high-mass regime (e.g. Busquet et al. 2010, Fontani et al. 2011, Sakai et al. 2012).
To investigate the relation between $D_{\text{frac}}$ and core evolution in the high-mass regime in a systematic way, our team started a survey of deuterated molecules in about 30 dense cores carefully selected and almost equally divided among the three evolutionary phases in which we can roughly divide observationally the high-mass star formation process (see e.g. Beuther et al. 2007 and Tan et al. 2014): high-mass starless cores (HMSCs), high-mass protostellar objects (HMPOs) and ultracompact HII regions (UC HII). In brief, the targets were selected as follows: the HMSCs had to be dense molecular cores not associated with indicators of star formation; the HMPOs had to show outflows, and/or infrared sources, and/or faint ($S_{6cm} < 1$ mJy) radio continuum emission; the UCHII had to be associated with stronger ($S_{6cm} \geq 1$ mJy) radio continuum. In selecting the sources, we rejected cores blended with nearby cores to avoid confusion and make the emission of the targeted core dominant.

In the first study, we (Fontani et al. 2011 hereafter paperI) presented the results obtained from spectroscopic observations of millimeter rotational transitions of $N_2^+$ and $N_2^+$ obtained with the IRAM-30m telescope, where we showed that $D_{\text{frac}}$(N$_2^+$) is $\approx 0.26$ in HMSCs, and drops by about an order of magnitude in the HMPO and UC HII stages. These results are consistent with the fact that deuteration of $N_2^+$ starts from the reaction $H_2D^+ + N_2 \rightarrow N_2D^+ + H_2$, efficient only at temperatures $\leq 20$ K (Gerlich et al. 2002). In a following study, focused on DNC/HNC, Fontani et al. (2014 paperII) showed that $D_{\text{frac}}$(HNC) also decreases from the pre- to the proto-stellar phase, but much more moderately, indicating that the ratio $N_2D^+$-to-$N_2^+$ is more appropriate to identify massive starless cores. This is consistent with the prediction that DNC can also easily form when the gas gets warmer, because the route to deuteration $N_2^+$ via the relation $T_\lambda = T_{\text{MB}}(B_{\text{eff}} / F_{\text{ch}})$, the spectra were obtained with the Fast Fourier Transform Spectrometers (FTS), providing a broad band of $\approx 8$ GHz simultaneously at 3 and 1.3 mm (see Table 2 for details). All calibrated spectra were analyzed using the GILDAS software developed at the IRAM and the Observatoire de Grenoble. The rest frequencies used for the line identification have been taken from the Cologne Molecular Database for Spectroscopy (CDMS, http://www.astro.uni-koeln.de/cdms, Müller et al. 2001, 2005).

2.2. IRAM-30m observations

Run-1: towards all sources in Table 1 observations of the ortho- and parah-NH$_2$D($J_{1,1} - l_{0,0}$) line were obtained simultaneously to the $N_2D^+$ and $N_2^+$ observations described in paperI. Table 2 lists the main observational parameters. We refer to Sect. 2 of paperI for any other technical detail related to these observations.

Run-2: we performed CH$_3$OH and CH$_3$DOH observations towards all sources observed in paperI from the 6th to the 9th of February, 2013. We observed simultaneously two bands at 3 and 1.3 mm, covering some important rotational transitions of CH$_3$OH, $^{13}$CH$_3$OH and CH$_3$DOH. Table 2 presents the observed spectral windows and some main technical observational parameters. The atmospheric conditions were very stable during the whole observing period, with precipitable water vapour usually below $\approx 2$ mm. The observations were made in wobbler-switching mode. Pointing was checked almost every hour on nearby quasars or bright HII regions. The data were calibrated with the chopper wheel technique (see Kutner & Ulich 1981), with a calibration uncertainty of $\approx 20\%$. The spectra were obtained in antenna temperature units, $T_A^*$, and then converted to main beam brightness temperature, $T_{\text{MB}}$, via the relation $T_A^* = T_{\text{MB}}(B_{\text{eff}} / F_{\text{ch}})$. The spectra were obtained with the Fast Fourier Transform Spectrometers (FTS), providing a broad band of $\approx 8$ GHz simultaneously at 3 and 1.3 mm (see Table 2 for details). All calibrated spectra were analyzed using the GILDAS software developed at the IRAM and the Observatoire de Grenoble. The rest frequencies used for the line identification have been taken from the Cologne Molecular Database for Spectroscopy (CDMS, http://www.astro.uni-koeln.de/cdms, Müller et al. 2001, 2005).

2.3. GBT observations

The ammonia (1,1) and (2,2) inversion transitions (rest frequencies $23.6944955$ and $23.7226363$ GHz, respectively) were observed with the 100 m Robert C. Byrd Green Bank Telescope (GBT) during the 13th and 21st March and the 4th and 21th April 2013. The GBT spectrometer backend was configured to simultaneously observe the two transitions in separate spectral windows, using bands of 50 MHz and spectral resolution of 12.2070 kHz, corresponding to 0.154 km s$^{-1}$ for both lines. The main observational parameters are listed in Table 2. The data were taken using in-band frequency switching with a throw of $7.5$ MHz. The beam FWHM was approximately $32''$. The pointing was checked at hourly intervals on a nearby quasar, with corrections approximately $2''-3''$. Flux calibration was performed on 3C123 and NGC7027. The absolute flux accuracy is $10\%-20\%$. Data re-

1 The GILDAS software is available at http://www.iram.fr/IRAMFR/GILDAS
2 The National Radio Astronomy Observatory is a facility of the National Science Foundation operated under cooperative agreement by Associated Universities, Inc.
Table 1. List of the observed sources. Col. 4 shows the velocity at which we centred the spectra, corresponding to the systemic velocity. More information (e.g. source distances, bolometric luminosities of the associated star forming regions, reference papers) are given in Table 1 of paper I.

| source                  | RA(J2000)  | Dec(J2000) | \(V_{\text{LSR}}\) |
|-------------------------|------------|------------|---------------------|
|                         | hr m s     | \(\circ \) | \(\text{km s}^{-1}\) |
| HMSP                    |            |            |                     |
| I00117–MM2              | 00:14:26.3 | +64:28:28   | −36.3               |
| AFG1542–EC \(^{a}\)    | 05:30:48.7 | +33:47:53   | −3.9                |
| 05358–mm3 \(^{a}\)     | 05:39:12.5 | +35:45:55   | −17.6               |
| G034–G2(MM2)            | 18:56:50.0 | +01:23:08   | +43.6               |
| G034–F2(MM7)            | 18:53:19.1 | +01:26:53   | +57.7               |
| G034–F1(MM8)            | 18:53:16.5 | +01:26:10   | +57.7               |
| G028–C1(MM9)            | 18:42:46.9 | −04:04:08   | +78.3               |
| G028–C3(MM11) \(^{a}\) | 18:42:44   | −04:01:54   | +78.3               |
| I20293–WC               | 20:31:10.7 | +40:03:28   | +6.3                |
| I22134–G \(^{a}\)      | 22:15:10.5 | +58:48:59   | −18.3               |
| I22134–B                | 22:15:05.8 | +58:48:59   | −18.3               |
|                        |            |            |                     |
| HMPO                    |            |            |                     |
| I00117–MM1              | 00:14:26.1 | +64:28:44   | −36.3               |
| I04579–VLA1             | 05:01:39.9 | +47:07:21   | −17.0               |
| AFG1542–MM2             | 05:30:48.0 | +33:47:54   | −3.9                |
| 05358–mm1               | 05:39:13.1 | +35:45:51   | −17.6               |
| 18089–1732              | 18:11:51.4 | −17:31:28   | +32.7               |
| 18517+0437              | 18:54:14.2 | +04:41:41   | +43.7               |
| G175–core               | 20:21:44.0 | +37:26:38   | +0.2                |
| I20293–MM1              | 20:31:12.8 | +40:03:23   | +6.3                |
| I21307                  | 21:32:30.6 | +51:02:16   | −46.7               |
| I23385                  | 23:40:54.5 | +61:10:28   | −50.5               |
| UC Hii                  |            |            |                     |
| G5.89–0.39              | 18:00:30.5 | −24:04:01   | +9.0                |
| I19035–VLA1             | 19:06:01.5 | +06:46:35   | +32.4               |
| I9410+2336              | 19:43:11.4 | +23:44:06   | +22.4               |
| ON1                     | 20:10:09.1 | +31:31:36   | +12.0               |
| I22134–L1A1             | 22:15:09.2 | +58:49:08   | −18.3               |
| 230333+5951             | 23:05:24.6 | +60:08:09   | −53.0               |
| NGC7538–IRS9            | 23:14:01.8 | +61:27:20   | −57.0               |

**Notes.** \(^{a}\) Source not included in paper I, selected from Butler & Tan (2009). See also Butler et al. (2014). \(^{w}\) "warm" (\(T \geq 20\) K) HMSPs externally heated (see paper I).

**production and calibrations** were done using the GBTIDL package, and subsequently converted to CLASS format.

3. Results and derivation of physical parameters

3.1. \(NH_3\) and \(NH_2D\)

3.1.1. Detection summary and parameters derived directly from the fits

\(NH_3\): the \(NH_3(1,1)\) and (2,2) inversion lines have been detected with excellent signal-to-noise ratio in all sources observed. The spectra of all HMSPs, HMPOs and UC Hii are shown in Figs. [A–1][A–2] and [A–3], respectively, of Appendix-A. Both transitions consist of 18 hyperfine components, grouped in 5 lines: the main one at the center of the spectrum, and four satellites symmetrically placed in frequency with respect to the main one (see Ho & Townes 1983 for details). The spectra have been fit considering this hyperfine structure when the satellites are detected. When they are not, we adopted a simplified approach in which we fitted the main line with a Gaussian curve. This simplified method was used for 8 of the (2,2) spectra observed, in which the satellites have not been detected. The fit procedure has given good results (with very low residuals, see Figs. [A–1][A–2] and [A–3] using both methods. The simplified approach in principle tends to overestimate the intrinsic line width, as the main line is in reality a blending of several hyperfine components. To quantify this, we have taken a (2,2) spectrum with hyperfine structure nicely fit (one spectrum per evolutionary group), applied the simplified method and compared the derived line width with that obtained from the accurate method (the hyperfine fit method). From this comparison, we quantify an overestimate of at most the 10% of the true intrinsic line width. Nevertheless, because the column density in this approach is derived from the integral of the line (see Sects. 3.1.2 and 3.1.3), this overestimation does not influence the calculation of neither the column density nor the deuterated fraction.

The line parameters derived from these fit procedures are listed in Tables [3][3][3] and [3]. The accurate method has given a well-constrained value of the optical depth of the main component of the (1,1) line \((\tau_{m}(1,1) / \Delta \tau_{m}(1,1) \geq 3)\) for all objects except for I04579–VLA1, for which the line is optically thin. The average \(\tau_{m}(1,1) \sim 1\), with no significant differences between the three evolutionary groups, while \(\tau_{m}(2,2)\) is usually smaller than 1. The average line widths of the (1,1) lines are \(\sim 1.7, \sim 2.3\), and \(\sim 2.6\) km s\(^{-1}\) for the HMSP, HMPO and UC Hii groups (standard deviation 0.5, 0.6 and 0.7 km s\(^{-1}\), respectively), and tend to increase with evolution, as expected (Sánchez-Monge et al. 2013).

\(NH_2D\): the \(ortho-NH_2D(1_{1,1} - 0_{0,0})\) line has been detected in all sources observed except in two HMPOs (I04579–VLA1 and I21307). The detection rate is \(\sim 92\%\). The \(para-NH_2D(1_{1,1} - 0_{0,0})\) line has been detected in 13 out of 26 sources observed (detection rate of 50%). The spectra of both lines are shown in Figs. [A–4] and [A–5]. In this work we will use the \(ortho-NH_2D(1_{1,1} - 0_{0,0})\) line to derive the physical parameters of our interest because of its higher detection rate and signal-to-noise ratio. The line of the \(para\)-species will be used to test whether the \(ortho/para\)-ratio assumed to derive the total column density in Sect. 3.1.3 is correct. Like ammonia, the \(NH_2D\) lines have been fit taking into account their hyperfine structure driven by the quadrupole moment of the Deuterium and Nitrogen nuclei (see Olberg et al. 1985 for details).

In general, the procedure has provided good fits to the spectra, except a few cases in which deviations from the LTE (symmetric) pattern are seen (e.g. G028–C1, I20293–WC, I20293–MM1, 230333+5951, see Fig. [A–4]). To check if (and how) our simplified LTE approach gives results different from those of a non-LTE analysis, we have run the non-LTE radiative transfer code RADEX (Van der Tak et al. 2007) in order to reproduce the measured line ratios of the two lines (\(ortho-NH_2D\) and \(para-NH_2D\)). The molecular data were taken from the LAMDA database (Schöier et al. 2005) using the collisional rate coefficients with \(H_2\) of Daniel et al. (2014). We built grids of models with kinetic temperatures in the range \(8 - 25\) K, \(H_2\) volume densities in the range \(10^8 - 10^{10}\) cm\(^{-3}\), and total column densities of \(10^{12} - 10^{15}\) cm\(^{-2}\). We assumed line widths of 1.5 km s\(^{-1}\) and an \(ortho/para\)-ratio of 3. The "best estimate" of the col-

\(^{3}\) GBTIDL is an interactive package for reduction and analysis of spectral line data taken with the GBT. See http://www.gbtsnrao.edu

\(^{4}\) http://www.sron.nl/vdtak/radex
Table 2. Observed transitions and technical parameters

| Molecular line | Line rest frequency (GHz) | HPBW (″) | $\Delta v$ (km s$^{-1}$) | $T_{\text{sys}}$ (K) | $\eta_{\text{MB}}$ |
|----------------|---------------------------|----------|--------------------------|-------------------|---------------|
| ortho-NH$_2$D$(1_{11} - 1_{01})$ | 85.9263 | ~ 28 | 0.136 | ~ 85 − 120 | 0.85 |
| para-NH$_2$D$(1_{11} - 1_{01})$ | 110.1536 | ~ 22 | 0.106 | ~ 95 − 125 | 0.83 |
| CH$_3$OH(3mm-band) | 89.11 − 96.89 | 27$^b$ | ~ 0.62$^a$ | ~ 100 − 120 | 0.84 |
| CH$_3$OH(1mm-band) | 216.0 − 223.78$^v$ | 11$^b$ | ~ 0.26$^a$ | ~ 200 − 300 | 0.66 |
| **IRAM-30m Telescope** | | | | | |
| NH$_3$ (1,1) | 23.6945 | ~ 32 | ~ 0.15 | ~ 50 − 100 | ~ 0.81 |
| NH$_3$ (2,2) | 23.7226 | ~ 32 | ~ 0.15 | ~ 50 − 100 | ~ 0.81 |
| **Green Bank Telescope** | | | | | |
| **Notes.** (a) Total spectral window covered by the FTS correlator. Please see Tables B-1 and B-2 to see the transitions detected in it. (b) Telescope HPBW at the central frequency of the spectral window. (c) Maximum spectral resolution obtained with FTS.

Table 3. Derived line parameters of NH$_3$ (1,1). All lines have been fit taking into account the hyperfine structure as explained in Sect. 3.1.2. Cols. 2–5 report the output parameters of the fitting procedure ($A \times \tau_m = f[I_r(T_{\text{ex}}) - J_r(T_{\text{BG}})]$, where $f$ is the filling factor, assumed to be unity, $J_r(T_{\text{ex}})$ and $J_r(T_{\text{BG}})$ are the equivalent Rayleigh-Jeans excitation and background temperatures, respectively, and $\tau_m$ is the opacity of the main group of hyperfine components; $V_{\text{peak}} = \text{peak velocity}; \Delta v = \text{full width at half maximum corrected for hyperfine splitting}; \tau_m = \text{opacity of the main group of hyperfine components}$ for the (1,1) line, and Col. 6 lists the excitation temperature of the transition derived as explained in Sect. 3.1.2. The uncertainties obtained from either the fitting procedure (parameters in Cols. 2 – 5) or from the propagation of errors (Col. 6) are in parentheses.

| Source | $A \times \tau_m (1,1)$ (km s$^{-1}$) | $V_{\text{peak}} (1,1)$ (km s$^{-1}$) | $\Delta v (1,1)$ (km s$^{-1}$) | $\tau_m (1,1)$ | $T_{\text{ex1,1}}$ (K) |
|--------|---------------------------------|-----------------------------|-----------------------------|-----------------|------------------|
| **HMSCs** | | | | | |
| I00117–MM2 | 1.83(0.06) | −36.16(0.01) | 1.71(0.03) | 0.71(0.09) | 15(4) |
| AFG15412–EC | 3.69(0.03) | −2.936(0.004) | 2.44(0.01) | 0.77(0.02) | 7.4(0.2) |
| 05358–mm3 | 5.32(0.01) | −16.258(0.004) | 1.989(0.005) | 0.85(0.01) | 8.86(0.07) |
| G034–G2 | 3.68(0.04) | 41.854(0.007) | 2.25(0.01) | 1.52(0.04) | 5.0(1.1) |
| G028–C1 | 2.69(0.01) | 79.810(0.007) | 2.30(0.01) | 2.50(0.07) | 3.67(0.05) |
| G028–C3 | 2.89(0.08) | 80.858(0.007) | 1.15(0.02) | 1.91(0.1) | 4.1(0.2) |
| I20293–WC | 5.46(0.02) | 6.419(0.004) | 2.080(0.006) | 1.31(0.01) | 6.76(0.07) |
| I21214–G | 2.41(0.07) | −18.643(0.006) | 1.33(0.02) | 0.40(0.07) | 9(2) |
| I21214–B | 1.72(0.08) | −18.800(0.01) | 1.15(0.03) | 0.60(0.1) | 5.4(0.9) |
| **HMPOs** | | | | | |
| I00117–MM1 | 1.59(0.03) | −36.320(0.01) | 1.59(0.04) | 0.13(0.03) | 5.2(0.6) |
| I04579–VL1A | 1.72(0.01) | −16.73(0.03) | 1.73(0.07) | 0.1$^c$ | 1.7$^c$ |
| AFG15412–MM1 | 3.5240(0.001) | −3.072(0.002) | 2.644(0.007) | 0.75(0.01) | 7.28(0.01) |
| 05358–mm1 | 4.636(0.003) | −16.318(0.003) | 2.064(0.001) | 0.80(0.01) | 8.39(0.02) |
| 18089–1732$^b$ | 8.3010(0.006) | 33.02(0.01) | 3.241(0.004) | 2.53(0.01) | 5.0(1.1) |
| 18517+0437 | 1.76(0.03) | 43.908(0.009) | 2.52(0.03) | 0.43(0.04) | 6.7(0.7) |
| G75–core | 2.99(0.04) | 0.067(0.009) | 3.42(0.02) | 0.50(0.03) | 8.6(0.6) |
| I20293–MM1 | 8.40(0.04) | 6.058(0.003) | 1.739(0.004) | 1.15(0.02) | 9.9(0.2) |
| I21307 | 0.61(0.05) | −46.57(0.01) | 1.9(0.1) | 0.8(0.2) | 3.4(0.5) |
| I23385$^d$ | 0.84(0.03) | −50.21(0.03) | 2.09(0.08) | 0.15(0.05) | 8(5) |
| **UC Huts** | | | | | |
| G5.89–0.39 | 5.63(0.02) | 8.70(0.01) | 3.745(0.002) | 0.65(0.01) | 11.2(0.1) |
| I19035–VL1A | 1.90(0.03) | 32.56(0.01) | 3.64(0.03) | 1.08(0.05) | 4.4(0.2) |
| 19410+2336 | 12.054(0.005) | 22.458(0.001) | 1.389(0.001) | 1.05(0.01) | 14.12(0.02) |
| ON1 | 13.25(0.02) | 10.985(0.001) | 2.886(0.005) | 1.58(0.01) | 10.98(0.02) |
| 23035+5951 | 4.96(0.07) | −53.444(0.006) | 1.95(0.02) | 0.98(0.04) | 7.7(0.4) |
| NGC7538–IRS9 | 3.94(0.04) | −57.31(0.01) | 2.17(0.03) | 1.00(0.01) | 6.54(0.08) |

Notes. (a) Integrated area of the main group of hyperfine components, in K km s$^{-1}$; (b) Peak intensity of the main group of hyperfine components, in K; (c) The spectrum shows two velocity components (Fig. [2]). Only the fit to the stronger component is shown; (d) The spectrum shows two velocity components (Fig. [3]). Fontani et al. (2004) also found these two components in C$^{18}$O and attributed the one centred at ~ −50 km s$^{-1}$ to the HMPO. Only the fit to this component is shown; (e) derived from the hyperfine fit procedure; (f) an average value of 6.5 K, computed from the HMPOs with well-constrained opacity, is assumed.
Table 4. Same as Table 3 for the NH$_3$ (2,2) transitions. For the sources with 'HFS' in Col. 2, the line hyperfine structure has been fit and the same output parameters in Cols. 2–6 of Table 3 are given in Cols. 3, 5, 6, 7, 9. For the sources with 'G' in Col. 2, the satellites of the (2,2) line are undetected, so that the main group of hyperfine components has been fit with a single Gaussian. For these objects, we give integrated area (in K km s$^{-1}$, Col. 4) and peak intensity (in K, Col. 8) of this Gaussian, respectively. For the sources marked with a 'T' in Col. 2, we clearly detect the satellites in the (2,2) transition, and performed a good fit to the hyperfine structure, but the line is optically thin. Hence, in Col. 8 we also give the peak temperature of the main group of hyperfine components, which is the parameter used to derive the NH$_3$ total column density in this case (see Sect. 3.1.2). The uncertainties of all parameters are in parentheses.

| Source            | HFS   | T (K) | –53.69 (0.02) | 1.90 (0.2) | 0.42 (0.03) | 1.4 (0.6), 2.5 (1.3) and 2.4 (1) km s$^{-1}$, respectively. All line parameters are listed in Table 3. | 3.1.2. NH$_3$ rotation temperature and total column density | From the NH$_3$(1,1) and (2,2) line parameters, we have obtained rotation temperatures, $T_{\text{rot}}$, adopting two methods: for the nine sources having $T_{\text{rot}}$, adopting two methods: for the nine sources having $T_{\text{rot}}$, we derived first the excitation temperature of the (1,1) and (2,2) lines ($T_{\text{ex},1,1}$ and $T_{\text{ex},2,2}$, respectively) independently using Eq. A.2 of Busquet et al. (2009), and, from these, the column densities of the two levels, $N_{1,1}$ and $N_{2,2}$, from the relations given in Anglada et al. (1998). Note that, although Eq. A.2 in Busquet et al. (2009) is derived for the (1,1) line, it is valid also for the (2,2) line given. |
Then, the rotation temperature has been derived from the relation:

\[ T_{\text{rot}} = -\frac{41.5}{\ln[(3/5)(N(2,2)/N(1,1))]} \]  

(1)

For sources with an optically thin (2,2) line, or with \( \tau_{2,2} \) not determined because the satellites are undetected, \( T_{\text{ex,2,2}} \) is assumed to be equal to \( T_{\text{ex,1,1}} \). This hypothesis is justified by the good agreement between the two excitation temperatures in the sources in which they can both be measured (see Sect. 4.2).

Under this assumption, we have applied eq. A.4 in Busquet et al. (2009), which utilises the peak intensity of the main hyperfine component of the (2,2) line.

In both methods, the total \( \text{NH}_3 \) column density, \( N(\text{NH}_3) \), has been calculated from Eq. A.6 in Busquet et al. (2009). Both \( T_{\text{rot}} \) and \( N(\text{NH}_3) \) are listed in Table 7. Rotation temperatures range from 11.7 to 29 K, and on average they are \( \sim 17, \sim 22 \) and \( \sim 22 \) K for HMSCs, HMPOs and UC H\( \alpha \)s, respectively (standard deviations are 2.6, 3.5 and 4 K, respectively). Separately, quiescent and "warm" HMSCs have mean temperatures of 16 and 20 K (standard deviations of 2.6 and 1.2 K, respectively), which confirms the higher gas temperature in the "warm" cores. Total \( \text{NH}_3 \) column densities range from \( 5.6 \times 10^{13} \) to \( 3.6 \times 10^{15} \) cm\(^{-2} \), and the average values are \( 9.4 \times 10^{14}, 9.3 \times 10^{14} \) and \( 1.6 \times 10^{15} \) cm\(^{-2} \) in the HMSC, HMPO and UC H\( \alpha \) groups, respectively. We have assumed a unity filling factor because available VLA interferometer ammonia maps of some of the targets show that the ammonia emission is extended and fills most of the GBT beam. Nevertheless, we stress that the emission from the target cores is clearly dominant with respect to that of nearby condensations (see Sanchez-Monge et al. 2013).
3.1.3. NH$_2$D total column density

The NH$_2$D column densities have been computed from the line parameters of the ortho-NH$_2$D line following Eq. (1) in Busquet et al. (2010), which assumes the same $T_{\text{ex}}$ for all the hyperfine components. $T_{\text{ex}}$ was computed as described in Sect. 3.1.2 for sources with opacity of the main component well-constrained. For the others, we have assumed $T_{\text{ex}} = 7.5$ K, which is the average value derived from the sources with well-constrained opacity, and obtained the column density from Eq. (A4) of Caselli et al. (2002b), valid for optically thin lines.

Again, we have assumed a unity filling factor because there are few high angular resolution observations of this line towards the targets from which the emitting region of NH$_2$D can be determined. This assumption is critical, as the ortho-NH$_2$D line has a critical density of $\sim 10^6$ cm$^{-3}$, higher than that of the inversion transitions of NH$_3$ ($\sim 10^3$–$10^4$ cm$^{-3}$). However, while by neglecting the beam dilution the absolute values of the column densities can be certainly affected, the evolutionary trend of the column density ratio should not be affected by this assumption because the beam dilution is expected to be almost constant, and thus it should introduce only a systematic correction (see also paper I). Also, observations at high angular resolution towards massive star forming regions (Busquet et al. 2010, Pillai et al. 2011) indicate that the emission of NH$_2$D can be as extended as that of NH$_3$, despite the different critical density. For example, the emitting region of NH$_2$D($1_1^1 - 1_0^1$) and NH$_3$ (1,1) in I20293–WC and I20293–MM1, both included in our survey, is approximately the same (Busquet et al. 2010). $N$(NH$_2$D) is listed in Table 7.

3.2. Methanol and deuterated methanol lines

In this work we focus the attention on the deuterated fraction of CH$_3$OH, and on the physical quantities relevant to derive it (i.e. temperature and total column density). Therefore, in what follows we will present the approach adopted to identify the lines from which $D_{\text{frac}}$(CH$_3$OH) will be derived (Sect. 3.2.1), the method to compute rotation temperature and total column density from the line parameters (Sect. 3.2.2), and the deuterated fraction in the sources detected in CH$_2$DOH (Sect. 4.4).

3.2.1. Lines detected and fit procedure

Multiple CH$_3$OH lines are detected in the observed spectral windows (Col. 1 of Table 2) towards all sources, while $^{13}$CH$_3$OH lines are clearly detected in four HMSCs, seven HMPOs and six UC H ii regions. CH$_2$DOH lines are detected only towards 6 objects: three HMSCs and three HMPOs, and two out of the three HMSCs are "warm" cores (see Sect. 2). Moreover, in two HMPOs (AFGL5142–MM and 18089–1732), the CH$_3$OD ($5_1^1 - 4_1^1$A++) line at 1.3 mm has been detected, although in 18089–1732 this could be blended with emission of (CH$_2$OH)$_2$. Tables 5–7 and 8–9 give the line parameters obtained from Gaussian fits to the lines detected at the 3$\sigma$ level and not probably blended with other transitions.

The detection of the deuterated lines has been double-checked by comparing observed and synthetic spectra. For this purpose, the observed spectra were smoothed to 1.0 km s$^{-1}$ at 1 mm and to 2.5 km s$^{-1}$ at 3 mm, to improve the signal-to-noise ratio. The CH$_2$DOH synthetic spectra were computed assuming LTE and optically thin emission as in Palau et al. (2011), and using the molecular data from the Jet Propulsion Laboratory (Pickett et al. 1998). To build the synthetic spectra, we adopted a line width of 1.5 km s$^{-1}$ at 1 mm and 2.5 km s$^{-1}$ at 3 mm, and used the rotational temperature listed in Table 8 derived from CH$_3$OH. Examples of the synthetic spectra of CH$_2$DOH overlaid on the observed spectra are shown in Fig. 1. The figure shows that several transitions are (marginally) detected at 1 mm in each of the four cases shown.

![Fig. 1. Example of spectra observed at 1 mm with the CH$_2$DOH synthetic spectra (red line) used for the identification of the deuterated methanol lines superimposed on them.](image-url)
3.2.2. Derivation of molecular column densities and rotation temperatures

From the line parameters in Tables B-1 and B-2, we derived rotation temperature ($T_{\text{rot}}$) and total column densities, $N$, of CH$_3$OH, $^{13}$CH$_3$OH and CH$_2$DOH from the rotation diagram method. As an example, in Fig. 2 we show the rotation diagrams obtained for 18089–1732. We will include all rotation diagrams in an Appendix on-line. The method has been applied when the number of transitions detected was sufficient to built a "reliable" rotation diagram; for example, we rejected the results obtained from this method for sources in which rotation diagrams provide meaningless negative temperatures, or for objects in which few lines associated with large uncertainties and/or similar energy of the upper levels have been detected. Specifically, for CH$_2$DOH the rotation diagram method has given acceptable results only for two sources, AFGL5142–MM and 18089–1732. However, because in AFGL5142–MM we have only two lines, and in 18089–1732 the fit results are not very accurate (bottom panel in Fig. 2), the column densities have been derived also from Eq. (A4) of Caselli et al. (2002b), taking the strongest line detected and assuming the gas temperature equal to $T_{\text{rot}}$ derived from CH$_3$OH.

For $^{13}$CH$_3$OH, we have assumed that all transitions are optically thin; for CH$_3$OH, we have first derived a rough estimate of the opacity by comparing two identical lines (specifically, we compared the 2($-$1,$2$) − $1$($-$1,$1$) and the 2(0,$2$) − 1(0,$1$) transitions) of CH$_3$OH and $^{13}$CH$_3$OH, and assumed an LTE abundance ratio of $[^{12}\text{C}]/[^{13}\text{C}]=77$ (Wilson & Rood 1994). From this check, we have derived low opacities (values smaller than 1) in all sources, so that we have decided to compute $N$ and $T_{\text{rot}}$ assuming optically thin conditions too. As for NH$_3$ and NH$_2$D, the source sizes of CH$_3$OH and CH$_2$DOH are unknown, but they are expected to be smaller than the beam size and to have a comparable extent, based on observations at high angular resolution in Orion (Peng et al. 2012). Therefore, to take into account the beam dilution, the column densities in the rotation diagrams have been corrected by assuming the same source sizes as in paper I, namely 6.5, 4.1 and 5.5$''$ for HMSCs, HMPOs, and UC H$_{\text{II}}$s, assuming that methanol and its deuterated forms trace approximately the same material. This is a reasonable general assumption also from a theoretical point of view if deuterated methanol is formed from methanol through H–D substitution reactions on dust grains. In principle, CH$_2$DOH could be formed following other pathways, but the H–D substitution reaction on solid ices remains the most efficient one (Nagaoka et al. 2005). Moreover, due to the lack of direct measurements in the cores, assuming a different source size for methanol and their deuterated forms would be an arbitrary choice not supported by observations.

For the deuterated species for which only one line is detected, and for sources in which $N$($^{13}$CH$_3$OH) cannot be derived from rotation diagrams, we derived $N$ using Eq. (A4) of Caselli et al. (2002b) from one transition only assuming optically thin conditions and adopting as excitation temperature the rotation temperature derived from CH$_3$OH, available in all sources. The partition functions of all species have been calculated from the approximated expressions valid for asymmetric rotors provided, e.g., in Ratajczak et al. (2011); see also Parise (2004). The results of this analysis are presented in Table 8.

Fig. 2. Rotation diagrams obtained for 18089–1732 from lines of CH$_3$OH, $^{13}$CH$_3$OH and CH$_2$DOH (from top to bottom). Derived rotation temperatures and total column densities are shown in the top-right corner of each panel.
Table 6. Integrated area of the ortho- and para-lines (Cols. 1 and 2, respectively), and their ratio (Col. 3). Note that the integrated area of the ortho-line is equal to the integrated area of the best-fit Gaussian (Table 5) within the errors.

| Source              | Integrated area $\langle T_{mb} \rangle$ [K km s$^{-1}$] | $\int T_{mb}[\rho]$ [K km s$^{-1}$] | Ratio $\langle T_{mb} \rangle / \int T_{mb}[\rho]$ |
|---------------------|---------------------------------------------------------|------------------------------------|-------------------------------------------------|
| NGC7538–IR5          | 0.19(0.01)                                              | 0.15(0.01)                         | 1.23(0.09)                                      |
| G034–F1 (MM8)        | 0.23(0.02)                                              | 0.20(0.01)                         | 1.15(0.09)                                      |
| G034–F2 (MM7)        | 0.32(0.03)                                              | 0.29(0.02)                         | 1.12(0.09)                                      |
| G034–C1 (MM9)        | 0.29(0.02)                                              | 0.26(0.02)                         | 1.15(0.09)                                      |
| I00117–MM1           | 0.28(0.02)                                              | 0.25(0.02)                         | 1.12(0.09)                                      |
| I04759–VLA1          | 0.31(0.03)                                              | 0.28(0.02)                         | 1.11(0.09)                                      |
| 05358–mm1            | 0.51(0.04)                                              | 0.46(0.03)                         | 1.11(0.09)                                      |
| 18089–1732           | 2.33(0.06)                                              | 2.03(0.05)                         | 1.15(0.09)                                      |
| 18517+0437           | 0.50(0.02)                                              | 0.45(0.02)                         | 1.11(0.09)                                      |
| G5.89–0.39           | 0.29(0.02)                                              | 0.26(0.02)                         | 1.11(0.09)                                      |
| UC Hn                | 0.19(0.02)                                              | 0.16(0.02)                         | 1.18(0.09)                                      |
| I00117–MM1           | 0.38(0.03)                                              | 0.35(0.03)                         | 1.11(0.09)                                      |
| I04759–VLA1          | 0.31(0.03)                                              | 0.28(0.02)                         | 1.11(0.09)                                      |
| 05358–mm1            | 0.51(0.04)                                              | 0.46(0.03)                         | 1.11(0.09)                                      |
| 18089–1732           | 2.33(0.06)                                              | 2.03(0.05)                         | 1.15(0.09)                                      |
| 18517+0437           | 0.50(0.02)                                              | 0.45(0.02)                         | 1.11(0.09)                                      |
| G5.89–0.39           | 0.29(0.02)                                              | 0.26(0.02)                         | 1.11(0.09)                                      |
| UC Hn                | 0.19(0.02)                                              | 0.16(0.02)                         | 1.18(0.09)                                      |

4. Discussion

4.1. The ortho-/para- ratio of NH$_2$D

The total column density of NH$_2$D has been derived from lines of ortho-NH$_2$D taking into account the statistical o/p ratio (3:1). In the sources detected also in the para-NH$_2$D line at ~ 110 GHz (see Fig. A5), we have verified if the assumption is correct: first, we have fit the hyperfine structure of the para-NH$_2$D line, and found that all detected lines are optically thin. Because most of the ortho-NH$_2$D lines detected are either optically thin or have $r \leq 1$, we have decided to compare the integrated areas of the two transitions under the channels with signal. These are reported in Table 6. As we can see, the ratio $\int T_{mb}[\rho] / \int T_{mb}[\rho]$ is consistent with 3 within the errors in most of the sources: the mean value is 2.6, with standard deviation 0.6, hence consistent with three.

Shah & Wootten (2001) have found similar results in a sample of protostellar cores, in which they compare the integrated intensity of the same two transitions, and derived a mean value of the o/p ratio of 3.2 (with a larger standard deviation of ~ 1.3). Comparable values have been also found by Pillai et al. (2007) in infrared dark clouds and by Tiné et al. (2008) in the two dark molecular clouds L134-N and TMC1.

4.2. On the NH$_3$ and NH$_2$D excitation temperatures

The excitation temperatures of the three lines examined in the previous sections have very similar mean values: 7.8, 8.2 and 7.5 K for NH$_3$(1,1), NH$_3$(2,2) and ortho-NH$_2$D, respectively. The NH$_3$(1,1) and (2,2) lines are also well correlated (see upper panel of Fig. 3), while the excitation temperatures of the ortho-NH$_2$D line and that of NH$_3$(1,1) are not correlated due to the different dispersion around the average values: in fact, $T_{ex}$ of NH$_3$(1,1) spans a range from ~ 3.5 K to 15 K, while $T_{ex}$ of the ortho-NH$_2$D lines is distributed tightly around the average value. This may indicate either that ortho-NH$_2$D is in sub-thermal conditions, as it was suggested by the asymmetric pattern of the hyperfine structure observed in some spectra (see Sect. 3.1.1), or to the fact that we are neglecting the correction for beam dilution. The former hypothesis seems plausible for the ortho-NH$_2$D line, which has a high critical density (~ 10$^6$ cm$^{-3}$). About the possible different beam dilution: as stated in Sect. 3.1.3 in the few cores in which both NH$_3$ (1,1) and ortho-NH$_2$D(1–1, 1–0), has been mapped at high angular resolution, the emissions have comparable extension, despite the different critical densities. Therefore, sub-thermal conditions of the ortho-NH$_2$D lines seem the most likely explanation to the different excitation temperatures.

4.3. Deuterated fraction of NH$_3$

By dividing $N$(NH$_2$D) by $N$(NH$_3$) we have computed $D_{frac}$(NH$_3$). The three parameters are given in Table 7. The average values of $D_{frac}$(NH$_3$) for HMSCs, HMPo at UC Hns, are 0.26 (0.23 if one excludes the "warm" HMSCs, see Sect. 2), 0.34 and 0.21 respectively. These values are consistent with those obtained by Pillai et al. (2007) in a sample of infrared-dark clouds, for which, however, the evolutionary stage of the embedded sources was not determined. The mean $D_{frac}$(NH$_3$) is thus maximum at the HMPO stage, although the large dispersion of the data does not allow to find a statistical difference between the three groups. This is apparent in Fig. 4, where we compare the total column densities of NH$_2$D and NH$_3$; the plot shows that the three groups are not clearly separated. Kolmogorov-Smirnov tests applied to the data confirm that the difference is not statistically significant. If one compares Fig. 4 with the same plot made in paper I for N$_2$H$^+$, we note clearly that, unlike $D_{frac}$(N$_2$H$^+$), $D_{frac}$(NH$_3$) does not decrease with core evolution. Thus, it is not a tracing of pre–protostellar or young protostellar objects, because it keeps above 0.1 even in the evolved stage of UC Hn region. Moreover, because for both N$_2$H$^+$ and NH$_3$ the deuteration in the gas-phase is linked to H$_2$D$^+$, our results would confirm that the formation of NH$_2$D is largely influenced by surface chemistry.

Furthermore, $D_{frac}$(NH$_3$) does not show any clear anti-correlation with typical indicators of evolution. This is suggested by Figs. 5 and 6 where we plot $D_{frac}$(NH$_3$) against the gas temperature and the line widths of the (1,1) transition, both known to increase with time (e.g., Sánchez-Monge et al. 2013): by applying statistical tests, we even find that $D_{frac}$(NH$_3$) could be slightly correlated with both the ammonia rotation temperature (Pearson’s linear correlation coefficient $\rho$ ~ 0.2) and line widths (Pearson’s linear correlation coefficient $\rho$ ~ 0.4). On the contrary, $D_{frac}$(N$_2$H$^+$) is anti-correlated with both parameters, as shown in Fig. 2 of paper I. We stress, however, that the $p$-value (measure of the probability of chance correlation) is 0.12 for $D_{frac}$(NH$_3$) vs $T_{ex}$, and 0.22 for $D_{frac}$(NH$_3$) vs $\Delta v$(1,1). Therefore, because typically the significance level under which
4.4. Deuterated fraction of methanol

In the six objects detected in CH$_2$DOH, we have computed $D_{\text{frac}}$(CH$_2$OH)=$N$(CH$_2$DOH)/$N$(CH$_2$OH). The results are listed in the last column of Table 8. The average $D_{\text{frac}}$(CH$_3$OH) in the three HMPOs detected is ~0.04 if one uses $N$(CH$_2$DOH) derived from rotation diagrams, ~0.01 if we use the simplified approach from one line only (see Sect. 3.2.2). In the two “warm” HMSCs is ~0.0025. G034–G2 is the unique quiescent HMSC detected in CH$_2$DOH, and in this core $D_{\text{frac}}$(CH$_3$OH) is ~0.015. For the cores undetected in CH$_2$DOH, the large majority of the targets observed, we have estimated upper limits of $D_{\text{frac}}$(CH$_3$OH) in this way: we have computed the $3\sigma$ level in the spectrum of the $(2_0-1_0)_{e0}$ line, which is the transition with the smallest energy of the upper level ($E_u$ ~ 6.5 K) at 3 mm, and estimated the upper limit to the integrated area from the relation $\int T_{\text{mb}}\,\text{d}v = 3\sigma / \Delta v$, valid for a Gaussian line having peak temperature = $3\sigma$. We have assumed $\Delta v=1$ km s$^{-1}$, which is the average value of the detected CH$_3$DOH lines both in the HMSCs and the HMPOs (see Table 8), then, the upper limit on the CH$_3$DOH column density has been computed using the same equations as for the detected sources. We have followed the same method to compute the upper limits on the $^{13}$CH$_3$OH lines, using this time the $(2_0-1_0)$ line.

The case of the HMSC G034–G2 is quite peculiar, because it is the only quiescent starless core detected in CH$_2$DOH (in one line only), and its $D_{\text{frac}}$(CH$_3$OH) exceeds 0.01, while the upper limits found in the other quiescent HMSCs are lower. Its detection is thus quite doubtful. We have checked for possible contamination from other species by running synthetic spectra (see Sect. 3.2.1) of molecules that possess transitions at a similar frequency, and concluded that indeed contributions from lines of CH$_3$OH, and HCCCH$_2$OH are possible. Therefore, this detection remains doubtful.

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Table 7. Rotation temperatures, total column densities of NH$_3$ and NH$_3$D, and ammonia deuterated fraction derived as explained in Sect. 5.4

| Source       | $T_{\text{ex}}$ (K) | $N_{\text{NH}_3}$ ($\times 10^{10}$ cm$^{-2}$) | $N_{\text{NH}_2D}$ ($\times 10^{10}$ cm$^{-2}$) | $D_{\text{frac}}$(NH$_3$) |
|--------------|---------------------|---------------------------------------------|---------------------------------------------|--------------------------|
| HMSCs        |                     |                                             |                                             |                          |
| I00117-MM2   | 17.9(0.6)           | 4.220(0.06)                                 | 2.62(0.05)                                 | 0.62(0.02)               |
| AFG1512-EC   | 20(1)               | 10.39(0.03)                                 | 4.31(0.07)                                 | 0.41(0.01)               |
| 05358-mm3    | 21(0.3)             | 9.27(0.02)                                  | 4.62(0.07)                                 | 0.49(0.008)              |
| G034-G2      | 15.2(0.4)           | 12.12(0.04)                                 | 2.40(0.02)                                 | 0.19(0.002)              |
| G034-F2      |                      |                                              |                                             |                          |
| G034-F1      |                      |                                              |                                             |                          |
| G028-C1      | 17.7(0.3)           | 20.70(0.02)                                 | 0.47(0.03)                                 | 0.02(0.002)              |
| G028-C3      | 11.7(0.4)           | 8.29(0.04)                                  | 0.07(0.02)                                 | 0.009(0.004)             |
| I20293-WC    | 19.4(0.4)           | 3.5(0.2)                                    | 0.78(0.02)                                 | 0.519(0.002)             |
| I22134-G     | 18.2(0.4)           | 2.98(0.06)                                  | 0.12(0.03)                                 | 0.014(0.005)             |
| I22134-B     | 14.9(0.5)           | 2.76(0.06)                                  | 0.16(0.01)                                 | 0.057(0.005)             |
| HMPOs        |                     |                                             |                                             |                          |
| I00117-MM1   | 16.4(0.7)           | 2.05(0.05)                                  | 0.24(0.04)                                 | 0.12(0.02)               |
| B04579-VLA1  | 20(2)               | 0.56(0.03)                                  | 0.06                                        | 0.12(0.02)               |
| AFG1512-MM   | 21.5(0.5)           | 10.65(0.02)                                 | 5.50(0.08)                                 | 0.516(0.008)             |
| 05358-mm1    | 21.6(0.3)           | 8.53(0.03)                                  | 4.62(0.07)                                 | 0.49(0.008)              |
| 18089-1732   | 28.1                | 35.55(0.02)                                 | 9.16(0.01)                                 | 0.255(0.003)             |
| 18517+0437   | 22(1)               | 5.32(0.05)                                  | 7.30(0.01)                                 | 0.14(0.001)              |
| G034-G2      | 26(9.6)             | 8.94(0.07)                                  | 0.19(0.04)                                 | 0.02(0.005)              |
| I20293-MM1   | 17(1)               | 15.82(0.03)                                 | 3.07(0.02)                                 | 0.19(0.002)              |
| I22134-G     | 20(1)               | 2.99(0.05)                                  | 0.05                                        | 0.02(0.005)              |
| I22385       | 23(1)               | 2.53(0.05)                                  | 0.09(0.03)                                 | 0.04(0.01)               |
| UC HMCs      |                     |                                             |                                             |                          |
| G5 89-00.39  | 29.0(0.3)           | 17.06(0.03)                                 | 12.0(0.5)                                  | 0.71(0.03)               |
| I19035-VLA1  | 24(1)               | 12.67(0.05)                                 | 0.40(0.04)                                 | 0.031(0.003)             |
| 1941+2336    | 18.7(0.2)           | 13.47(0.03)                                 | 2.20(0.03)                                 | 0.165(0.002)             |
| ON1          | 21.4(0.7)           | 36.58(0.03)                                 | 4.75(0.08)                                 | 0.125(0.002)             |
| I22134-VLA1  |                      |                                              |                                             |                          |
| G034-G2      | 23(1)               | 2.53(0.05)                                  | 0.09(0.03)                                 | 0.04(0.01)               |

Notes. (a) Not observed.
Although the number of detections is low, and the results are affected by the faintness of the CH$_3$DOH lines, these findings suggest that high values of $D_{\text{frac}}$(CH$_3$OH) tend to be associated with "warm" HMSCs and HMPOs rather than with the very young (quiescent HMSCs) or evolved (UC HUs), although the remarkable value derived in G034–G2 (if confirmed) suggests that the story could not be so simple. Parise et al. (2006) measured values of $D_{\text{frac}}$(CH$_3$OH) higher than ours by at least an order of magnitude in a sample of low-mass protostellar cores. Nevertheless, due to the smaller linear resolution of their observations (most of their cores are in Perseus, at a distance of ~ 200 pc), their measurements should be less affected than ours by non-deuterated gas along the line of sight. Moreover, our $D_{\text{frac}}$(CH$_3$OH) are consistent with the upper limits found by Loinard et al. (2003) in high-mass protostellar objects (where, however, they observed D$_2$CO and derived [D$_2$CO] / [H$_2$CO] < 0.5%), as well as with observations of deuterated methanol in the intermediate-mass protostar NGC1279-FIRS2 (Fuente et al. 2014) and in Orion BN/KL (Peng et al. 2012).

4.5. Deuteration and core evolution: the role of surface chemistry

In Fig. 7 we report the mean values of $D_{\text{frac}}$ obtained in HMSCs, HMPOs and UC HUs for the four molecular species investigated so far towards our source sample: N$_2$H$^+$ (paperI), HNC (paperII), NH$_3$ and CH$_3$OH (this work). We show separately the values derived for quiescent HMSCs and "warm" HMSCs to underline the effect of nearby star formation. We also include the mean values (with standard deviation) of the ammonia rotation temperatures derived in this work to highlight possible (anti-)correlation between $D_{\text{frac}}$ and gas temperature. Inspection of Fig. 7 leads to these immediate results: (i) only $D_{\text{frac}}$(N$_2$H$^+$) shows a net decrease from the HMSC stage to the HMPO stage, associated to a temperature enhancement; (ii) $D_{\text{frac}}$(NH$_3$) remains nearly constant in all stages; (iii) $D_{\text{frac}}$(CH$_3$OH) is maximum in the HMPO stage, although this result must be interpreted carefully due to the low number of detections and the caveats on the methods to derive $D_{\text{frac}}$ (see Sects. 3.2 and 3.3); (iv) the behaviour of $D_{\text{frac}}$(HNC) is something in between that of $D_{\text{frac}}$(N$_2$H$^+$) and that of $D_{\text{frac}}$(NH$_3$), because its maximum value is found in the HMSC phase, like $D_{\text{frac}}$(N$_2$H$^+$), but the statistically significant decrease when going to the HMPO stage is not seen. In paperII we have already discussed this difference, and attributed it to a slower process of destruction of DNC into the warm gas with respect to N$_2$D$^+$. As stated in Sect. 1 $D_{\text{frac}}$(N$_2$H$^+$) and $D_{\text{frac}}$(CH$_3$OH) should represent the two "extreme" situations under which deuteration can occur: in the gas only and on grain mantles only, respectively. In the classical framework, both ammonia and methanol (and their deuterated isotopologues) are produced efficiently on grain mantles during the pre–stellar phase through hydrogenation of N and CO, respectively. Specifically, hydrogenation of CO forms sequentially formaldehyde first and then methanol: thus, as time proceeds, the formation of methanol and their deuterated isotopologues is boosted, until the energy released by the nascent protostellar object in the form of radiation increases the temperature of its environment, causing the evaporation of the grain mantles and the release of these molecules into the gas. As the temperature increases and the protostar evolves towards the UC Hn region phase, the deuterated species are expected to be gradually destroyed due to the higher efficiency of the backward endothermic reactions (see Caselli & Ceccarelli 2012 for a review). The trends shown in Fig. 7 are consistent with this classic framework, and show clearly that high deuterated fractions of ammonia cannot be used as evolutionary indicator of a high-mass star forming core. On the other hand, $D_{\text{frac}}$(CH$_3$OH) may be potentially a tracer of the very early stages of the protostellar evolution, at which the evaporation/sputtering of the grain mantles is most efficient. Our results, however, suffers from a too low statistics, and needs to be reinforced by other observations of deuterated methanol at higher sensitivity.

Chemical models of low-mass star-forming cores predict how the abundance of several deuterated species varies during the evolution, including the amount formed on ices during the early cold phase (e.g. Taquet et al. 2012, Aikawa et al. 2012). Aikawa et al. (2012) show that the relative abundance ratios [NH$_2$D]/[NH$_3$] and [CH$_3$DOH]/[CH$_3$OH] in the ices during the pre–stellar phase are both in between 0.01 and 0.1. These values are consistent with $D_{\text{frac}}$(CH$_3$OH) measured in this work, and confirm that methanol and its deuterated forms are products of the evaporation of grain mantles. On the other hand, $D_{\text{frac}}$(NH$_3$) measured in our work (≥ 0.1) is larger than the values predicted on ices by Aikawa et al. (2012), suggesting that the emission we see must include a contribution from material formed through gas-phase reactions. Awad et al. (2014) modeled the deuteron chemistry of star-forming cores using both gas-phase and grain-surface reactions, but focus on the protostellar phase, when the evaporation of the icy mantles of dust grains is maximum. The model that best reproduces a HMPO predicts $D_{\text{frac}}$(NH$_3$) ~ 10$^{-3}$–10$^{-2}$ and $D_{\text{frac}}$(CH$_3$OH) ≤ 4 × 10$^{-3}$, both smaller than our observed values. However, the abundance of deuterated species strongly depends on the density of the gas: lower-density cores have lower abundances of deuterated species, due to a smaller degree of CO depletion. Therefore, larger core densities could be able to reproduce the larger deuterated fractions that we measure.

In any case, the huge dispersion of the data do not allow us to derive firmer quantitative conclusions, and push us to interpret any comparison with chemical models with caution. Moreover, the chemical models of Taquet et al. (2012) and Aikawa et al. (2012) neglect the spin states of the deuterated species, which can significantly influence the deuteration fractionation depending on the ortho-to-para H$_2$ ratio (Flower et al. 2006). Nevertheless, the clear different trend between $D_{\text{frac}}$(NH$_3$) and $D_{\text{frac}}$(N$_2$H$^+$) indicates undoubtedly that gas-phase chemistry cannot play a dominant role in the production of NH$_3$D.

5. Summary and conclusions

The deuterated fraction of species that can be formed on dust grains (in part, like NH$_3$, or uniquely, like CH$_3$OH) has been investigated towards a sample of dense cores harbouring different evolutionary stages of the high-mass star formation process. As expected, the deuterated fraction of these species and those of molecules totally or predominantly formed in the gas, like N$_2$H$^+$ and HNC, evolve differently with time and with temperature: $D_{\text{frac}}$(NH$_3$) does not show statistically significant changes with evolution, unlike $D_{\text{frac}}$(N$_2$H$^+$) and $D_{\text{frac}}$(HNC), which decrease (especially $D_{\text{frac}}$(N$_2$H$^+$)) when temperature increases. Few lines of CH$_3$DOH and CH$_3$OD are clearly detected, and only towards protostellar cores or externally heated starless cores. Only one line of CH$_3$DOH could have been detected in a quiescent starless core, but the detection is doubtful. No lines of deuterated methanol species are detected in UC Hn regions. This work clearly supports the scenario in which the contribution of surface chemistry to the formation of deuterated forms of ammonia
The evaporation seems suitable to trace the earliest protostellar phases, but this result needs to be supported by further, higher sensitivity excellent starting point for higher angular resolution studies to molecules are formed with different mechanisms, do we expect different distributions of the emission too? Unless when specified different, only lines with very close upper energies are detected, and the rotation diagram provides a meaningless negative $T_{\text{rot}}$. Therefore, the column density has been derived from the transition (5$\rightarrow$3) assuming the temperatures obtained from CH$_3$OH.

| source               | $T_{\text{rot}}$ (K) | $N$(CH$_3$OH) ($\times 10^{13}$)cm$^{-2}$ | $T_{\text{rot}}$ (K) | $N$(1$^{13}$CH$_3$OH) ($\times 10^{13}$)cm$^{-2}$ | $T_{\text{rot}}$ (K) | $N$(CH$_2$DOH) ($\times 10^{14}$)cm$^{-2}$ | $D_{\text{rot}}$(CH$_3$OH) |
|---------------------|----------------------|------------------------------------------|----------------------|-----------------------------------------------|----------------------|------------------------------------------|-------------------------|
| HHMSC               |                      |                                          |                      |                                               |                      |                                          |                         |
| I00117–MM2          | 19.0                 | 1.80                                     | ≤ 0.3                | ≤ 0.03                                        | ≤ 0.01               | ≤ 0.007                                   |                         |
| AFGL5142–EC         | 41.5                 | 61.5                                     | 14.1                 | 5.27                                          | 0.11$^a$             | 0.002(0.001)                             |                         |
| 05358–mm3           | 26.1                 | 24.9                                     | 5.1                  | 1.53                                          | 0.08                 | 0.003(0.001)                             |                         |
| G034–G2(MM2)        | 6.0                  | 1.75                                     | –$^a$                | 0.09$^a$                                      | 0.03                 | 0.015(0.07)                              |                         |
| G034–F2(MM7)        | 5.7                  | 0.95                                     | ≤ 0.15               | ≤ 0.007                                       | ≤ 0.007              |                                        |                         |
| G034–F1(MM8)        | 17.5                 | 2.24                                     | ≤ 0.3                | ≤ 0.01                                        | ≤ 0.006              |                                        |                         |
| G028–C1(MM9)        | 14.2                 | 2.69                                     | 6.8                  | 0.71                                          | ≤ 0.01               | ≤ 0.004                                   |                         |
| I20293–WC           | 24.4                 | 3.44                                     | ≤ 0.5                | ≤ 0.02                                        | ≤ 0.005              |                                        |                         |
| I22134–G            | 18.1                 | 2.87                                     | ≤ 0.3                | ≤ 0.01                                        | ≤ 0.004              |                                        |                         |
| I22134–B            | 7.8                  | 0.35                                     | ≤ 0.2                | ≤ 0.007                                       | ≤ 0.02               |                                        |                         |
| HMPO                |                      |                                          |                      |                                               |                      |                                          |                         |
| I00117–MM1          | 27.7                 | 1.22                                     | ≤ 0.6                | ≤ 0.02                                        | ≤ 0.02               |                                        |                         |
| AFGL5142–MM        | 112.6                | 262.7                                    | 7.9                  | 5.81                                          | 10.4                 | 19.0$^b$;2.1$^c$                         | 0.07(0.03)$^b$; 0.008(0.004)$^c$ |
| 05358–mm1           | 84.0                 | 125.1                                    | –$^a$                | 6.1$^a$                                       | ≤ 0.13               | ≤ 0.001                                  |                         |
| 18089–1732          | 158.6                | 318.1                                    | 153.0                | 64.2                                          | 56                   | 14.0$^b$;4.0$^c$                         | 0.04(0.02)$^b$; 0.01(0.01)$^c$ |
| 18517+0437          | 137.6                | 209.2                                    | 44.5                 | 25.6                                          | ≤ 0.2                | ≤ 0.001                                  |                         |
| G57–core            | 108.5                | 150.6                                    | 4.2$^a$              | 0.55                                          | ≤ 0.005              |                                        |                         |
| I20293–MM1          | 35.1                 | 27.5                                     | –$^a$                | 0.9$^a$                                       | ≤ 0.04               | ≤ 0.001                                  |                         |
| I21307              | 29.4                 | 6.54                                     | ≤ 0.5                | ≤ 0.03                                        | ≤ 0.004              |                                        |                         |
| I23385              | 25.3                 | 18.0                                     | –$^a$                | 0.3$^a$                                       | ≤ 0.02               | ≤ 0.01                                  |                         |
| UC Hn               |                      |                                          |                      |                                               |                      |                                          |                         |
| G5.89–0.39          | 64.1                 | 128.1                                    | 37.9                 | 14.0                                          | ≤ 0.14               | ≤ 0.001                                  |                         |
| I19035–VLA1         | 30.7                 | 16.4                                     | 28.6                 | 4.80                                          | ≤ 0.03               | ≤ 0.002                                  |                         |
| 19410+2336          | 31.1                 | 20.2                                     | 20.8                 | 5.79                                          | ≤ 0.03               | ≤ 0.001                                  |                         |
| ON1                 | 31.3                 | 32.4                                     | 25.5                 | 8.98                                          | ≤ 0.02               | ≤ 0.00007                                |                         |
| I22134–VLA1         | 19.4                 | 1.64                                     | ≤ 0.3                | ≤ 0.02                                        | ≤ 0.009              |                                        |                         |
| 23033+5951          | 24.2                 | 12.0                                     | 37.4                 | 8.33                                          | ≤ 0.02               | ≤ 0.002                                  |                         |
| NGC7538–IRS9        | 28.7                 | 17.6                                     | 0.5$^a$              | ≤ 0.02                                        | ≤ 0.001              |                                        |                         |

Notes. $^a$ Only lines with very close upper energies are detected, and the rotation diagram provides a meaningless negative $T_{\text{rot}}$. Therefore, the column density has been derived from the transition (2$_{0,2}$ – 1$_{1,1}$)++ assuming LTE conditions and $T_{\text{rot}}$ from methanol; $^b$ derived from rotation diagrams; $^c$ derived from the transition (5$_{2,3}$ – 4$_{1,4}$)11 assuming LTE conditions and $T_{\text{rot}}$ from methanol.

Acknowledgments. FF and AP are grateful to the IRAM-30m staff for their help in the observations at the IRAM-30m telescope. GB is grateful to Amanda Kepley for her help during the GBT observations, and to Jeff Magnum for providing the procedures to convert the GBT spectra from GBTIDL to CLASS format. AP acknowledges the financial support from UNAM, and CONACyT, México. GB is supported by the Spanish MICINN grant AYA2008–06189–C03–01 (co-funded with FEDER funds) and by the Italian Space Agency (ASI) fellowship under contract number I/005/07/01. PC acknowledges the financial support of the European Research Council (ERC; project PALs 320620). AS-M is supported by the Deutsche Forschungsgemeinschaft (DFG) through the collaborative research grant SFB 956 “Conditions and Impact of Star Formation”, project area A6. The research leading to these results has received funding from the European Commission Seventh Framework Programme (FP/2007-2013) under grant agreement N 28393 (RadioNet3).

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Fig. 4. Comparison between the total column density of NH$_2$D, N(NH$_2$D), and NH$_3$, N(NH$_3$). Blue symbols correspond to HMSCs (triangles: warm cores, see Sect. 2); green squares show HMPOs (open squares are upper limits); black pentagons correspond to UC H II regions. In most cases, the errorbars are barely visible because comparable to (or smaller than) the size of the symbol. The straight lines represent the loci of $D_{\text{frac}}$(NH$_3$) = 0.01 and 0.1.

Fig. 5. $D_{\text{frac}}$(NH$_3$) against the ammonia rotation temperature. The symbols have the same meaning as in Fig. 4. No clear (anti-)correlation is found between the two parameters. In some cases, the errorbars are barely visible because comparable to (or smaller than) the size of the symbol.

Fig. 6. $D_{\text{frac}}$(NH$_3$) against the NH$_3$ (1,1) line width. The symbols have the same meaning as in Fig. 4. No clear (anti-)correlation is found between the two parameters, like in Fig. 5. The errorbars are barely visible because comparable to (or smaller than) the size of the symbol.
Fig. 7. Panels one to four, from top: comparison between the mean deuterated fractions (black dots) of N$_2$H$^+$ (first panel, paper I), HNC (second panel, paper II) NH$_3$ and CH$_3$OH (third and fourth panels, this work). The mean values have been computed for each evolutionary group. Quiescent HMSCs (HMSC-q) and warm HMSCs (HMSC-w) have been treated separately. The errorbars indicate the standard deviation. The grey arrows represent mean upper limits for those evolutionary groups in which no sources have been detected. The red dot in the fourth panel represents the doubtful CH$_2$DOH detection in G034-G2 (see Sect. 4.4), while the square indicates the mean D$_{\text{frac}}$ of HMPOs when N(CH$_3$DOH) is derived from rotation diagrams for AFGL5142-MM and 18089–732.

Bottom panel: mean rotation temperatures (filled diamonds) derived from ammonia in the four groups (see Table 7).

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Appendix A: $\text{NH}_3$ and $\text{NH}_2\text{D}$ spectra
Fig. A-1. GBT spectra of NH$_3$(1,1) and (2,2) obtained towards the sources classified as HMCSs. For each spectrum, the x-axis represents a velocity interval of ±35 km s$^{-1}$ from the systemic velocity listed in Table 1. The y-axis shows the intensity scale in main beam brightness temperature units. In each spectrum, the red curve indicates the best fit either obtained by fitting the hyperfine structure, when possible, or with a single Gaussian (see Sect. 3.1).
Fig. A-2. Same as Fig. A-1 for the sources classified as HMPOs. Note that for the spectra of I23385 and 18089–1732, a fit with two velocity components has been performed.
Fig. A-3. Same as Fig. A-1 for the sources classified as UC H
cs.
Fig. A-4. IRAM-30m spectra of ortho-NH$_2$D(1$_1$-1$_0$) obtained towards all sources observed. We show the HMSCs in the left column, the HMPOs in the central column, and the UC H$	extsc{ii}$s in the right column, from top to bottom in the same order as they appear in Table I. For each spectrum, the x-axis represents a velocity interval of ±20 km s$^{-1}$ from the systemic velocity listed in Table I. The y-axis shows the intensity scale in main beam brightness temperature units. In each spectrum, the red curve indicates the best fit either obtained by fitting the hyperfine structure, when possible, or with a single Gaussian (see Sect. V.1).
Fig. A-5. Same as Fig. A-4 for para-NH$_2$D(1,1 – 0,0). Note that two sources (18517+0437 and I19035–VLA1) have not been observed. In each spectrum, the red curve indicates the best fit (see Sect. 3.1).
Appendix B: Tables
Table B-1. Transitions of CH$_3$OH, $^{13}$CH$_3$OH, CH$_3$DOH and CH$_2$OD detected at 3 mm, and line parameters derived from Gaussian fits: line integrated intensity ($\overline{I}_{\text{mb}}(\nu_0)$), full width at half maximum ($\Delta V$) and main beam temperature at line peak ($T_{\text{mb}}$).

| freq MHz | transition | $\overline{I}_{\text{mb}}(\nu_0)$ K km s$^{-1}$ | $\Delta V$ km s$^{-1}$ | $T_{\text{mb}}$ K |
|----------|------------|-----------------------------------------------|------------------------|----------------|
| 94405.16 | $^{13}$CH$_3$OH 2(1,2)–1(1,1) | 0.014(0.004) | 1.1(0.4) | 0.012 |
| 95169.46 | CH$_3$OH 8(0,8)–7(1,7)++ | 0.031(0.006) | 2.4(0.5) | 0.012 |
| 96739.36 | CH$_3$OH 2(1,2)–1(1,1) | 0.35(0.02) | 0.7(0.2) | 0.45131 |
| 96741.38 | CH$_3$OH 2(0,2)–1(0,1)++ | 0.48(0.02) | 0.7(0.2) | 0.62447 |
| 96744.55 | CH$_3$OH 2(0,2)–1(0,1) | 0.06(0.02) | 0.6(0.2) | 0.09 |
| 96755.51 | CH$_3$OH 2(1,1)–1(1,0) | 0.02(0.01) | 0.7(0.3) | 0.02 |
| 95169.46 | CH$_3$OH 2(0,2)–1(0,1) | 0.06(0.02) | 0.6(0.2) | 0.09 |
| 96755.51 | CH$_3$OH 2(1,1)–1(1,0) | 0.02(0.01) | 0.7(0.3) | 0.02 |

| freq MHz | transition | $\overline{I}_{\text{mb}}(\nu_0)$ K km s$^{-1}$ | $\Delta V$ km s$^{-1}$ | $T_{\text{mb}}$ K |
|----------|------------|-----------------------------------------------|------------------------|----------------|
| 95169.46 | CH$_3$OH 8(0,8)–7(1,7)++ | 0.039(0.005) | 0.9(0.1) | 0.04 |
| 95169.46 | CH$_3$OH 8(0,8)–7(1,7)++ | 0.033(0.015) | 1.8(0.6) | 0.017 |
| 96739.36 | CH$_3$OH 2(1,2)–1(1,1) | 0.94(0.04) | 1.1(0.4) | 0.84 |
| 96741.38 | CH$_3$OH 2(0,2)–1(0,1)++ | 1.12(0.04) | 1.0(0.4) | 1.03 |
| 96744.55 | CH$_3$OH 2(0,2)–1(0,1) | 0.32(0.04) | 2.9(0.4) | 0.1 |
| 96755.51 | CH$_3$OH 2(1,1)–1(1,0) | 0.02(0.008) | 0.9(0.4) | 0.02 |

| freq MHz | transition | $\overline{I}_{\text{mb}}(\nu_0)$ K km s$^{-1}$ | $\Delta V$ km s$^{-1}$ | $T_{\text{mb}}$ K |
|----------|------------|-----------------------------------------------|------------------------|----------------|
| 95169.46 | CH$_3$OH 8(0,8)–7(1,7)++ | 0.25(0.05) | 0.94(0.03) | 0.2 |
| 95169.46 | CH$_3$OH 8(0,8)–7(1,7)++ | 0.06(0.02) | 2.3(0.9) | 0.023 |
| 96739.36 | CH$_3$OH 2(1,2)–1(1,1)++ | 0.84(0.03) | 1.6(0.4) | 0.48 |
| freq (MHz) | transition | \( T_{\text{MB}0} \) (K km s\(^{-1}\)) | \( \Delta V \) (km s\(^{-1}\)) | \( T_{\text{PA}} \) (K) |
|-----------|------------|-------------------------------|------------------|-----------------
| 96741.38  | CH\(_2\)OH (2,0)–(1,1)++ | 0.73 (0.03) | 1.0 (0.4) | 0.66 |
| 96744.55  | CH\(_2\)OH (2,0)–(1,1) | 0.14 (0.03) | 1.4 (0.4) | 0.09 |
| 96755.51  | CH\(_2\)OH (1,1)–(1,0) | 0.05 (0.03) | 1.6 (0.4) | 0.03 |

**Table B-1.** continued.
| freq MHz | transition      | $T_{	ext{MBde}}$ K km s$^{-1}$ | $\Delta V$ km s$^{-1}$ | $T_{p}$ K |
|---------|-----------------|---------------------------------|------------------------|----------|
| 94405.16 | $^{13}$CH$_{3}$OH 2(1,2)–1(1,1) | 0.055(0.004) | 1.4(0.4) | 0.04 |
| 94407.13 | $^{13}$CH$_{3}$OH 2(0,2)–1(0,1)++ | 0.066(0.004) | 1.1(0.4) | 0.06 |
| 94411.02 | $^{13}$CH$_{3}$OH 2(0,2)–1(0,1) | 0.017(0.004) | 1.0(0.4) | 0.015 |
| 94514.76 | CH$_{3}$OH 8(3,5)–9(2,7) | 0.139(0.004) | 2.0(0.4) | 0.06 |
| 95169.46 | CH$_{3}$OH 8(0,8)–7(1,7)++ | 0.649(0.003) | 0.82(0.006) | 0.74 |
| 95914.31 | CH$_{3}$OH 8(0,2)–1(0,1)++ | 0.468(0.004) | 1.8(0.1) | 0.32 |
| 96739.36 | CH$_{3}$OH 2(1,2)–1(1,1)++ | 1.93(0.09) | 1.2(0.4) | 1.5 |
| 96741.38 | CH$_{3}$OH 2(0,2)–1(0,1) | 2.79(0.09) | 1.2(0.4) | 2.12 |
| 96744.55 | CH$_{3}$OH 2(0,2)–1(0,1) | 0.85(0.09) | 1.2(0.4) | 0.64 |
| 96755.51 | CH$_{3}$OH 2(1,1)–1(1,0) | 0.46(0.09) | 1.4(0.4) | 0.31 |

**G75–HCHII**

| freq MHz | transition      | $T_{	ext{MBde}}$ K km s$^{-1}$ | $\Delta V$ km s$^{-1}$ | $T_{p}$ K |
|---------|-----------------|---------------------------------|------------------------|----------|
| 89505.78 | CH$_{3}$OH 8(–4,5)–9(–3,7) | 0.1(0.1) | 0.9(0.8) | 0.06 |
| 94405.16 | $^{13}$CH$_{3}$OH 2(1,2)–1(1,1) | 0.033(0.009) | 1.6(0.5) | 0.02 |
| 94407.13 | $^{13}$CH$_{3}$OH 2(0,2)–1(0,1)++ | 0.025(0.008) | 1.0(0.3) | 0.024 |
| 94514.76 | CH$_{3}$OH 8(3,5)–9(2,7) | 0.074(0.005) | 1.4(0.1) | 0.06 |
| 95169.46 | CH$_{3}$OH 8(0,8)–7(1,7)++ | 0.934(0.006) | 1.98(0.02) | 0.44 |
| 95914.31 | CH$_{3}$OH 2(1,2)–1(1,1)++ | 0.37(0.06) | 1.4(0.25) | 0.26 |
| 96739.36 | CH$_{3}$OH 2(1,2)–1(1,1)++ | 1.13(0.06) | 1.5(0.4) | 0.70 |
| 96741.38 | CH$_{3}$OH 2(0,2)–1(0,1)++ | 2.00(0.06) | 1.7(0.4) | 1.07 |
| 96744.55 | CH$_{3}$OH 2(0,2)–1(0,1) | 0.81(0.06) | 1.8(0.4) | 0.42 |
| 96755.51 | CH$_{3}$OH 2(1,1)–1(1,0) | 0.34(0.06) | 1.3(0.4) | 0.24 |

**L2029–MMI**

| freq MHz | transition      | $T_{	ext{MBde}}$ K km s$^{-1}$ | $\Delta V$ km s$^{-1}$ | $T_{p}$ K |
|---------|-----------------|---------------------------------|------------------------|----------|
| 95169.46 | CH$_{3}$OH 8(0,8)–7(1,7)++ | 0.20(0.004) | 0.64(0.02) | 0.5 |
| 95914.31 | CH$_{3}$OH 2(1,2)–1(1,1)++ | 0.03(0.01) | 1.2(0.6) | 0.02 |
| 96739.36 | CH$_{3}$OH 2(1,2)–1(1,1)++ | 0.22(0.004) | 0.84(0.02) | 0.25 |
| 96741.38 | CH$_{3}$OH 2(0,2)–1(0,1)++ | 0.32(0.004) | 0.86(0.02) | 0.35 |
| 96746.55 | CH$_{3}$OH 2(0,2)–1(0,1) | 0.08(0.005) | 0.97(0.06) | 0.08 |
| 96755.51 | CH$_{3}$OH 2(1,1)–1(1,0) | 0.026(0.004) | 0.9(0.2) | 0.03 |

**G5.89–0.39**

| freq MHz | transition      | $T_{	ext{MBde}}$ K km s$^{-1}$ | $\Delta V$ km s$^{-1}$ | $T_{p}$ K |
|---------|-----------------|---------------------------------|------------------------|----------|
| 94405.16 | $^{13}$CH$_{3}$OH 2(1,2)–1(1,1) | 0.015(0.004) | 0.9(0.2) | 0.016 |
| 94407.13 | $^{13}$CH$_{3}$OH 2(0,2)–1(0,1)++ | 0.013(0.004) | 0.9(0.3) | 0.013 |
| 95169.46 | CH$_{3}$OH 8(0,8)–7(1,7)++ | 0.464(0.005) | 1.15(0.02) | 0.38 |
| 95914.31 | CH$_{3}$OH 2(1,2)–1(1,1)++ | 0.11(0.02) | 1.25(0.3) | 0.08 |
| 96739.36 | CH$_{3}$OH 2(1,2)–1(1,1)++ | 0.77(0.04) | 1.3(0.4) | 0.57 |
| 96741.38 | CH$_{3}$OH 2(0,2)–1(0,1)++ | 1.13(0.04) | 1.3(0.4) | 0.8 |
| 96744.55 | CH$_{3}$OH 2(0,2)–1(0,1) | 0.33(0.04) | 1.8(0.4) | 0.2 |
| 96755.51 | CH$_{3}$OH 2(1,1)–1(1,0) | 0.08(0.04) | 0.75(0.4) | 0.1 |

**UC Hii**

| freq MHz | transition      | $T_{	ext{MBde}}$ K km s$^{-1}$ | $\Delta V$ km s$^{-1}$ | $T_{p}$ K |
|---------|-----------------|---------------------------------|------------------------|----------|
| 19035–VL1A

| freq MHz | transition      | $T_{	ext{MBde}}$ K km s$^{-1}$ | $\Delta V$ km s$^{-1}$ | $T_{p}$ K |
|---------|-----------------|---------------------------------|------------------------|----------|
| 94407.13 | $^{13}$CH$_{3}$OH 2(0,2)–1(0,1)++ | 0.032(0.005) | 1.2(0.2) | 0.024 |
| 94411.02 | CH$_{3}$OH 2(0,2)–1(0,1) | 0.008(0.003) | 0.4(0.0) | 0.02 |
| 94420.45 | CH$_{3}$OH 2(1,1)–1(1,0) | 0.014(0.006) | 2.0(0.8) | 0.007 |
| 95414.76 | CH$_{3}$OH 8(3,5)–9(2,7) | 0.033(0.009) | 4(1) | 0.008 |
| 95169.46 | CH$_{3}$OH 8(0,8)–7(1,7)++ | 0.147(0.007) | 1.9(0.1) | 0.07 |
| freq MHz | transition | \( J_{\text{MB}de} \) K km s\(^{-1} \) | \( \Delta V \) km s\(^{-1} \) | \( T_{\text{mb}} \) K |
|----------|------------|-------------------|-------------------|-------------------|
| 95914.31 | CH\(_2\)OH 2(1,2)–1(1,1)++ | 0.12(0.02) | 1.7(0.4) | 0.065 |
| 96739.36 | CH\(_2\)OH 2(–1,2)–1(–1,1) | 0.98(0.045) | 1.5(0.4) | 0.62 |
| 96741.38 | CH\(_2\)OH 2(0,2)–1(0,1)++ | 1.70(0.045) | 1.8(0.4) | 0.89 |
| 96744.55 | CH\(_2\)OH 2(0,2)–1(0,1) | 0.52(0.045) | 2.1(0.4) | 0.23 |
| 96755.51 | CH\(_2\)OH 2(1,1)–1(1,0) | 0.17(0.045) | 1.9(0.4) | 0.08 |
| 94405.16 | \({}^{13}\)CH\(_2\)OH 2(–1,2)–1(–1,1) | 0.026(0.004) | 0.9(0.2) | 0.03 |
| 94407.13 | \({}^{13}\)CH\(_2\)OH 2(0,2)–1(0,1)++ | 0.044(0.004) | 1.0(0.1) | 0.04 |
| 94541.76 | CH\(_2\)OH 8(3,5)–9(2,7) | 0.028(0.005) | 1.6(0.4) | 0.016 |
| 95169.46 | CH\(_2\)OH 8(0,8)–7(1,7)++ | 1.014(0.004) | 0.641(0.003) | 1.49 |
| 95914.31 | CH\(_2\)OH 2(1,2)–1(1,1)++ | 0.24(0.05) | 1.0(0.3) | 0.22 |
| 96739.36 | CH\(_2\)OH 2(–1,2)–1(–1,1) | 1.56(0.08) | 1.0(0.4) | 1.51 |
| 96741.38 | CH\(_2\)OH 2(0,2)–1(0,1)++ | 2.32(0.08) | 1.0(0.4) | 2.16 |
| 96744.55 | CH\(_2\)OH 2(0,2)–1(0,1) | 0.61(0.08) | 1.0(0.4) | 0.57 |
| 96755.51 | CH\(_2\)OH 2(1,1)–1(1,0) | 0.21(0.08) | 0.8(0.4) | 0.27 |

**ON1**

| freq MHz | transition | \( J_{\text{MB}de} \) K km s\(^{-1} \) | \( \Delta V \) km s\(^{-1} \) | \( T_{\text{mb}} \) K |
|----------|------------|-------------------|-------------------|-------------------|
| 95169.46 | CH\(_2\)OH 8(0,8)–7(1,7)++ | 0.014(0.005) | 2.3(0.8) | 0.006 |
| 95914.31 | CH\(_2\)OH 2(1,2)–1(1,1)++ | 0.010(0.004) | 0.9(0.5) | 0.011 |
| 96739.36 | CH\(_2\)OH 2(–1,2)–1(–1,1) | 0.23(0.01) | 0.9(0.4) | 0.25 |
| 96741.38 | CH\(_2\)OH 2(0,2)–1(0,1)++ | 0.30(0.01) | 0.744(0.4) | 0.38 |
| 96744.55 | CH\(_2\)OH 2(0,2)–1(0,1) | 0.06(0.01) | 0.7(0.4) | 0.085 |
| 96755.51 | CH\(_2\)OH 2(1,1)–1(1,0) | 0.01(0.01) | 0.5(0.4) | 0.026 |

**2303+35951**

| freq MHz | transition | \( J_{\text{MB}de} \) K km s\(^{-1} \) | \( \Delta V \) km s\(^{-1} \) | \( T_{\text{mb}} \) K |
|----------|------------|-------------------|-------------------|-------------------|
| 94405.16 | \({}^{13}\)CH\(_2\)OH 2(–1,2)–1(–1,1) | 0.022(0.005) | 1.2(0.3) | 0.017 |
| 94407.13 | \({}^{13}\)CH\(_2\)OH 2(0,2)–1(0,1)++ | 0.034(0.004) | 1.2(0.3) | 0.026 |
| 95169.46 | CH\(_2\)OH 8(0,8)–7(1,7)++ | 0.634(0.003) | 0.647(0.004) | 0.92 |
| 95914.31 | CH\(_2\)OH 2(1,2)–1(1,1)++ | 0.09(0.03) | 1.1(0.5) | 0.07 |
| 96739.36 | CH\(_2\)OH 2(–1,2)–1(–1,1) | 1.59(0.07) | 1.1(0.4) | 1.33 |
| 96741.38 | CH\(_2\)OH 2(0,2)–1(0,1)++ | 1.94(0.07) | 1.0(0.4) | 1.75 |
| 96744.55 | CH\(_2\)OH 2(0,2)–1(0,1) | 0.32(0.07) | 1.0(0.4) | 0.31 |
| 96755.51 | CH\(_2\)OH 2(1,1)–1(1,0) | 0.1(0.2) | 1.1(0.9) | 0.09 |

**NGC7538–IRS9**

| freq MHz | transition | \( J_{\text{MB}de} \) K km s\(^{-1} \) | \( \Delta V \) km s\(^{-1} \) | \( T_{\text{mb}} \) K |
|----------|------------|-------------------|-------------------|-------------------|
| 94405.16 | \({}^{13}\)CH\(_2\)OH 2(–1,2)–1(–1,1) | 0.020(0.004) | 1.1(0.3) | 0.02 |
| 94407.13 | \({}^{13}\)CH\(_2\)OH 2(0,2)–1(0,1)++ | 0.019(0.004) | 0.7(0.2) | 0.03 |
| 95169.46 | CH\(_2\)OH 8(0,8)–7(1,7)++ | 0.94(0.003) | 0.73(0.002) | 1.17 |
| 95914.31 | CH\(_2\)OH 2(1,2)–1(1,1)++ | 0.15(0.03) | 1.1(0.2) | 0.13 |
| 96739.36 | CH\(_2\)OH 2(–1,2)–1(–1,1) | 0.95(0.05) | 1.2(0.4) | 0.77 |
| 96741.38 | CH\(_2\)OH 2(0,2)–1(0,1)++ | 1.67(0.05) | 1.5(0.4) | 1.06 |
| 96744.55 | CH\(_2\)OH 2(0,2)–1(0,1) | 0.46(0.05) | 1.6(0.4) | 0.28 |
| 96755.51 | CH\(_2\)OH 2(1,1)–1(1,0) | 0.17(0.05) | 1.4(0.4) | 0.11 |
### Table B-2.

Same as Table B-1 for the transitions detected at 1 mm.

| freq MHz | transition | $\int T_{MB}$ K km s$^{-1}$ | $\Delta V$ km s$^{-1}$ | $T_{pk}$ K |
|----------|------------|----------------------------|------------------------|-------------|
| HMSCs    |            |                            |                        |             |
| I00117–MM12 |          |                            |                        |             |
| 218440.05 | CH$_3$OH 4(2,2)–3(1,2) | 0.29(0.03) | 1.9(0.2) | 0.14 |
| APolS142–EC |          |                            |                        |             |
| 218440.05 | CH$_3$OH 4(2,2)–3(1,2) | 10.1(0.4) | 2.9(0.1) | 3.23 |
| 220078.5 | CH$_3$OH 8(0,8)–7(1,6) | 2(1) | 3.7(0.9) | 0.59 |
| 223071.3 | CH$_3$DOH 5(2,3)–4(1,4)e1 | 0.02(0.01) | 0.4(0.8) | 0.06 |
| 223107.3 | CH$_3$DOH 5(0,5)–4(0,4)e01 | 0.03(0.02) | 0.6(0.3) | 0.04 |
| 223153.7 | CH$_3$DOH 5(3,2)–4(3,1)e0 | 0.06(0.03) | 2.1(0.7) | 0.03 |
| 223315.4 | CH$_3$DOH 5(2,3)–4(2,2)e1 | 0.05(0.02) | 2.0(0.7) | 0.024* |
| 223422.3 | CH$_3$DOH 5(2,4)–4(2,3)e0 | 0.09(0.02) | 2.6(0.6) | 0.032* |
| 05358–mm1 |          |                            |                        |             |
| 218440.05 | CH$_3$OH 4(2,2)–3(1,2) | 0.29(0.03) | 2.2(0.5) | 0.29 |
| 220078.49 | CH$_3$OH 8(0,8)–7(1,6) | 10.1(0.4) | 2.9(0.1) | 3.23 |
| G034–G2 |          |                            |                        |             |
| 218440.05 | CH$_3$OH 4(2,2)–3(1,2) | 0.11(0.02) | 2.4(0.6) | 0.045 |
| G034–F2 |          |                            |                        |             |
| 218440.05 | CH$_3$OH 4(2,2)–3(1,2) | 0.10(0.02) | 2.1(0.01) | 0.043 |
| G034–F1 |          |                            |                        |             |
| 218440.05 | CH$_3$OH 4(2,2)–3(1,2) | 0.09(0.01) | 1.188(0.001) | 0.074 |
| G028–C1 |          |                            |                        |             |
| 218440.05 | CH$_3$OH 4(2,2)–3(1,2) | 0.08(0.01) | 2.0(0.7) | 0.24 |
| G22134–G |          |                            |                        |             |
| 218440.05 | CH$_3$OH 4(2,2)–3(1,2) | 0.23(0.02) | 1.1(0.1) | 0.20 |
| 218440.05 | CH$_3$OH 4(2,2)–3(1,2) | 0.08(0.02) | 2.1(0.7) | 0.03 |
| HMPs     |            |                            |                        |             |
| I00117–MM1 |          |                            |                        |             |
| 218440.05 | CH$_3$OH 4(2,2)–3(1,2) | 0.19(0.02) | 1.9(0.3) | 0.10 |
| APoLS142–MM |          |                            |                        |             |
| 218440.05 | CH$_3$OH 4(2,2)–3(1,2) | 0.59(0.06) | 5.8(0.7) | 0.09 |
| 219983.99 | CH$_3$OH 25(3,22)–24(4,20) | 0.10(0.09) | 2.7(0.6) | 0.037 |
| 220078.49 | CH$_3$OH 8(0,8)–7(1,6) | 2(1) | 3(1) | 0.6 |
| 223071.3 | CH$_3$DOH 5(2,3)–4(1,4)e1 | 0.05(0.02) | 2.0(0.7) | 0.034* |
| 223308.57 | CH$_3$OD 5(1,5)–4(1,4)eA++ | 0.08(0.02) | 1.4(0.4) | 0.05a* |
| 05358–mm1 |          |                            |                        |             |
| 218440.05 | CH$_3$OH 4(2,2)–3(1,2) | 0.29(0.07) | 3.3(0.4) | 0.26 |
| 220078.5 | CH$_3$OH 8(0,8)–7(1,6) | 1.0(0.4) | 3(1) | 0.33 |
| 18089–1732 |          |                            |                        |             |
| 218440.05 | CH$_3$OH 4(2,2)–3(1,2) | 0.4(0.6) | 2.5(0.2) | 1.75 |
| 18517+0437 |          |                            |                        |             |
| 218440.05 | CH$_3$OH 4(2,2)–3(1,2) | 2.3(0.2) | 3.6(0.3) | 0.59 |
| 218440.05 | CH$_3$OH 4(2,2)–3(1,2) | 5.8(0.3) | 2.7(0.2) | 2.0 |
| 219983.99 | CH$_3$OH 25(3,22)–24(4,20) | 0.14(0.09) | 3.8(0.8) | 0.034 |

* Additional transitions detected at 1 mm.
| freq MHz | transition | $\int T_{MB} dv$ K km s$^{-1}$ | $\Delta V$ km s$^{-1}$ | $T_{pk}$ K |
|----------|------------|-------------------------------|---------------------|--------|
| 219993.94 | CH$_3$OH 2$_3$(5,19)$-$2$_3$(6,17) | 0.13(0.09) | 3.3(0.5) | 0.038 |
| 220078.49 | CH$_3$OH 8$_2$(0,8)$-$7$_2$(1,6) | 2.1(0.7) | 3.9(0.9) | 0.52 |
| 221285.24 | $^{13}$CH$_3$OH 8$_{-1}$(1,8)$-$7$_{-1}$(0,7) | 0.39(0.03) | 3.8(0.3) | 0.095 |
| 216945.60 | CH$_3$OH 5$_1$(1,4)$-$4$_2$(2,2) | 2.3(0.2) | 3.1(0.2) | 0.09 |
| 217399.54 | CH$_3$OH 10$_{(2,8)}$–9$_{(3,7)}$A++ | 0.57(0.06) | 2.7(0.4) | 0.20 |
| 217886.39 | CH$_3$OH 20$_{(1,19)}$–20$_{(0,20)}$ | 0.45(0.06) | 3.0(0.5) | 0.14 |
| 220078.49 | CH$_3$OH 8$_2$(0,8)$-$7$_2$(1,6) | 2.2(0.8) | 3.1(0.9) | 0.66 |
| 223107.3 | CH$_3$OH 5$_{(0,5)}$–4$_{(0,4)}$ | 0.07(0.03) | 2.2(0.9) | 0.03 |
| 223422.3 | CH$_3$OH 5$_{(2,4)}$–4$_{(2,3)}$e0 | 0.04(0.02) | 0.8(0.3) | 0.05 |
| 216945.60 | CH$_3$OH 5$_1$(1,4)$-$4$_2$(2,2) | 0.18(0.06) | 2.9(0.9) | 0.06 |
| 220078.49 | CH$_3$OH 8$_2$(0,8)$-$7$_2$(1,6) | 0.4(0.2) | 5.4(0.9) | 0.06 |
| 223107.3 | CH$_3$OH 5$_1$(1,4)$-$4$_2$(2,2) | 0.10(0.02) | 1.9(0.4) | 0.05 |
| 220078.49 | CH$_3$OH 8$_2$(0,8)$-$7$_2$(1,6) | 0.1(0.2) | 2.5(0.9) | 0.07 |
| 22410 + 2336 | CH$_3$OH 5$_1$(1,4)$-$4$_2$(2,2) | 0.55(0.04) | 3.3(0.3) | 0.16 |
| 220078.49 | CH$_3$OH 8$_2$(0,8)$-$7$_2$(1,6) | 0.6(0.4) | 3.8(0.9) | 0.14 |
| 221285.24 | CH$_3$OH 5$_{1}$(1,4)$-$4$_{2}$(2,2) | 1.0(0.1) | 3.6(0.5) | 0.25 |
| 220078.49 | CH$_3$OH 8$_{2}$(0,8)$-$7$_{2}$(1,6) | 1.1(0.6) | 4.2(0.9) | 0.25 |
| 221285.24 | $^{13}$CH$_3$OH 8$_{1}$(1,8)$-$7$_{1}$(0,7) | 0.12(0.02) | 3.4(0.6) | 0.033 |
| 22410 + 2336 | CH$_3$OH 5$_{1}$(1,4)$-$4$_{2}$(2,2) | 1.0(0.1) | 3.6(0.5) | 0.25 |
| 220078.49 | CH$_3$OH 8$_{2}$(0,8)$-$7$_{2}$(1,6) | 0.3(0.3) | 4.7(0.9) | 0.06 |
| 220078.49 | CH$_3$OH 5$_{1}$(1,4)$-$4$_{2}$(2,2) | 0.23(0.03) | 1.4(0.2) | 0.16 |
| 220078.49 | CH$_3$OH 8$_{2}$(0,8)$-$7$_{2}$(1,6) | 0.03(0.05) | 1.1(0.7) | 0.03 |
| 22033–UCHII | CH$_3$OH 5$_{1}$(1,4)$-$4$_{2}$(2,2) | 0.21(0.04) | 2.9(0.7) | 0.07 |
| 220078.49 | CH$_3$OH 8$_{2}$(0,8)$-$7$_{2}$(1,6) | 0.5(0.3) | 3.3(0.9) | 0.15 |

*a tentative detection in between 2 and 3σ rms; 
*b partially blended with (CH$_3$OH)$_2$ (ethylene-glycol).